NICKEL, PALLADIUM AND PLATINUM; ANNUAL SURVEY COVERING THE YEAR 1978*

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CONTENTS

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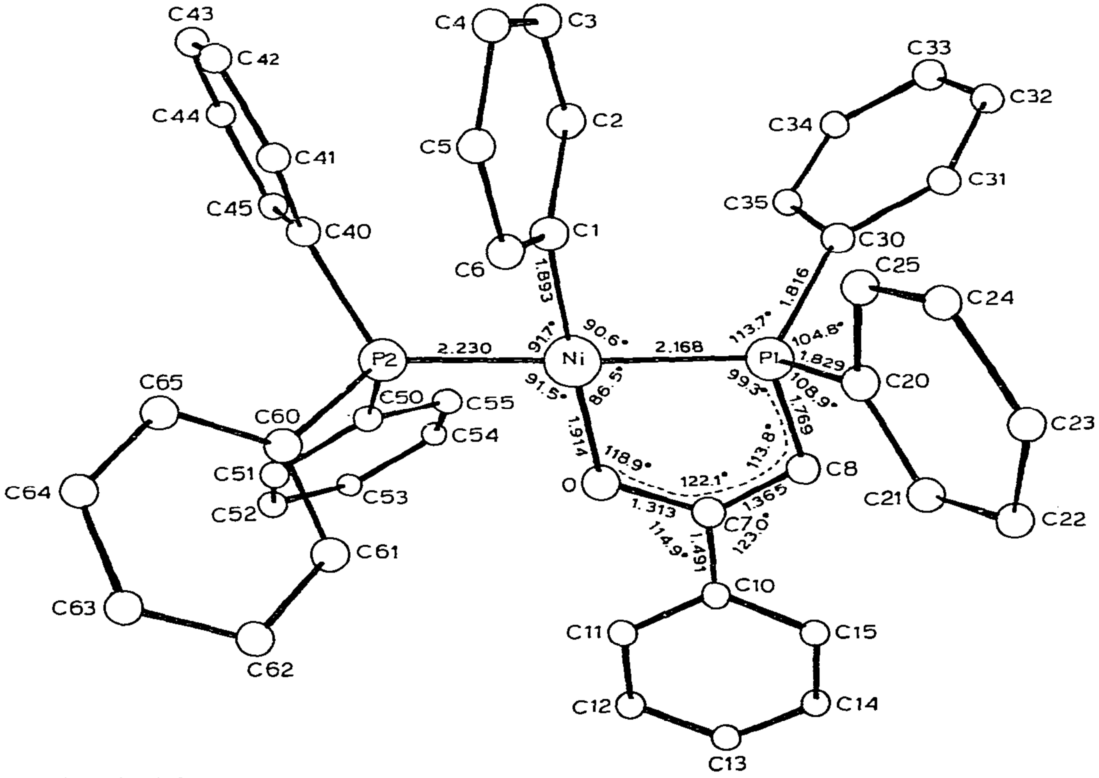
*Nickel, palladium and platinum. Annual Survey covering the year 1977, see J. Organometal. Chem., Vol. 167 (1977) p. 265-359.

ABBREVIATIONS

dppm	bis-1,2-(diphenylphosphino)methane	OAc	acetate
dppe	bis-1-2-(diphenylphosphino)ethane	acac	acetylacetonate
dppp	bis-1,2-(diphenylphosphino)propane	NBD	norbornadiene
dppb	bis-1,2-(diphenylphosphino)butane	1,5-COD	1,5-cyclooctadiene
py	pyridine	cp	cyclopentadienyl
bipy	2,2'-bipyridyl	THF	tetrahydrofuran
phen	1,10-phenanthroline		

I. Metal-carbon σ complexes

A phenyl nickel complex Ni(Ph)(OC(Ph)CHPPh$_2$)(PPh$_3$) has been prepared from Ni(COD)$_2$, Ph$_3$P=CHCOPh and triphenylphosphine. The structure (1) has been solved [1]



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(1)

- The crystal and molecular structures of cis-p-tolylbis(triethylphosphine)platinum(II) and cis-chloroperfluorophenylbis(triethylphosphine)platinum(II) have been solved [2]. No significant difference is found in the Pt-C bond lengths which are 2.05(3) and 2.08(2)Å, respectively. The kinetics of displacement of X^- from the complexes trans-$Ni(PEt_3)_2(C_6H_2Me_3\text{-}2,4,6)X$ by various nucleophiles Y^- (X = Cl, Br, I, N_3, NO_2; Y = Cl, Br, I, NO_2, SCN, N_3) at 25° in ethanol suggest a mechanism involving competitive associative and solvolytic pathways. Comparisons to other studies are made [3]. Cationic aryl complexes $[PtAr(COD)(PMe_2Ph)]BF_4$ (2) have been prepared

$$[PtCl(COD)PMe_2Ph]BF_4 + SnArMe_3 \rightarrow [PtAr(COD)PMe_2Ph]BF_4 + SnClMe_3$$

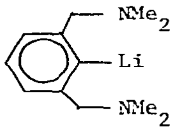
(2)

from $SnArMe_3$ (Ar = 2-thienyl, 2-benzo[b]thienyl or 2-benzo[b]furyl). No reaction takes place when R = Ph. The COD ligand can be replaced by ligands such as PMe_2Ph, dppe or $4\text{-}Me_2Npy$ [4]. Treatment of $Ni(acac)_2$ with $AlPh_3.Et_2O$ in the presence of PR_3 (R = Et, Ph, Cy) gives complexes $NiPh(acac)(PR_3)_n$ (3) [5]. The kinetics of the elimination of PhCN in the reaction of $NiPh(CN)(PEt_3)_2$ with $P(OEt)_3$ show that

$$Ni(acac)_2 + AlPh_3 + nPR_3 \rightarrow NiPh(acac)(PR_3)_n + \text{"}AlPh_2acac\text{"}$$

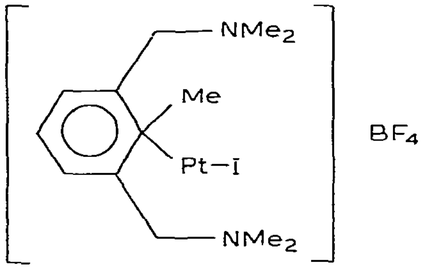
(3)

the elimination mainly takes place by intramolecular decomposition of $NiPh(CN)[P(OEt)_3]_2$ formed in initial substitution steps. A minor contribution to PhCN formation comes from the 5-coordinate species $NiPh(CN)PEt_3[P(OEt)_3]_2$ [6]. The phosphorus ligand exchange of trans-$M(o\text{-}MeC_6H_4)X(PPh_3)_2$($M$ = Ni, Pd, Pt; X = Br, I) has been investigated by ^{31}P NMR spectroscopy. On addition of tertiary phosphine ligands PPh_3 is readily displaced, and in chlorobenzene solvent the displacement follows the sequence $PPhMe_2 \simeq PPh_2Me \gg P(p\text{-}C_6H_4OMe)_3 > P(p\text{-}C_6H_4Me)_3 > P(p\text{-}C_6H_4F)_3 \simeq P(p\text{-}C_6H_4Cl)_3 \ggg P(o\text{-}C_6H_4OMe)_3 \simeq P(o\text{-}C_6H_4Me)_3$. For phosphite ligands the order is $P(OMe)_3 > P(OEt)_3 > P(O\text{-}i\text{-}Pr)_3 \gg P(OPh)_3$. Steric factors are considered to predominate over electronic factors [7]. A series of phenylplatinum(II) and phenylpalladium(II) complexes have been prepared from (4). The structure of one of these



(4)

compounds (5) has been solved. A series of reactions and transformations involving



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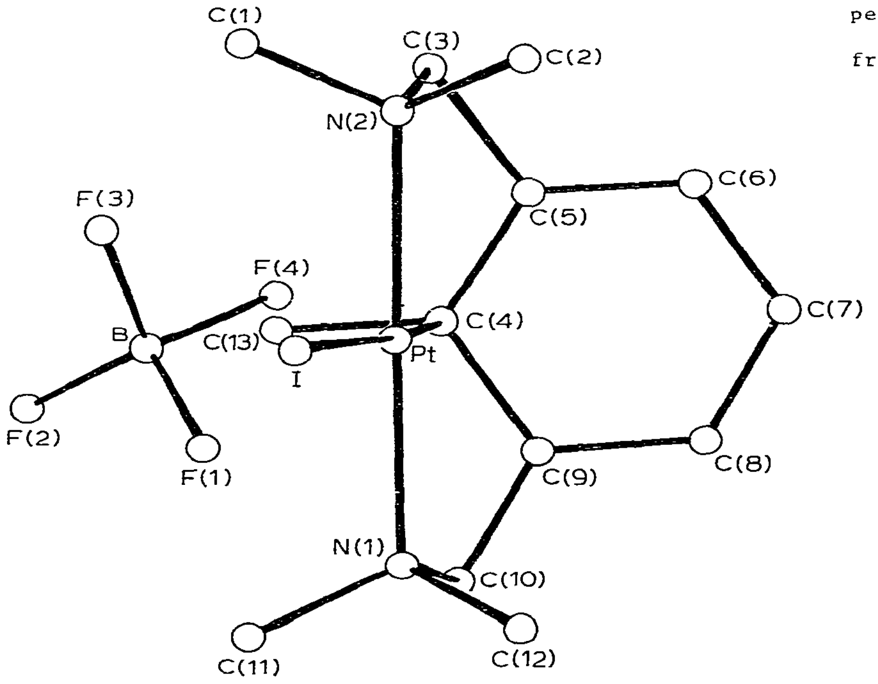

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(5)

these compounds is given [8]. The thermal decomposition of NiPh(CN)(PCy$_3$)$_2$ in decalin gives only minor amounts of PhCN [9]. Reaction with P(OEt)$_3$ gives PhCN quantitatively. The mechanism involves a bimolecular attack of P(OEt)$_3$ at the metal center before reductive elimination of PhCN. Anodic oxidation of NiR(Ar)(PEt$_3$)$_2$ (R = aryl or methyl) leads to the coupling products Ar-R and/or to radical formation [10]. The reductive coupling of organometals has been induced by oxidation with IrCl$_6^{2-}$ and other oxidants. Thus, NiEt$_2$(bipy) gives n-butane, and the aryl complex will give biaryls [11]. Similarly, a series of monoarylnickel(II) complexes *trans*-NiX(Ar)(PEt$_3$)$_2$ (X = Br, Cl, I, NCS, NO$_2$, NCO) give arylphosphoniums (6). Detection

$$\textit{trans}\text{-NiBr(Ar)(PEt}_3)_2 \;+\; 2\text{IrCl}_6^{2-} \;\rightarrow\; \text{NiBr(PEt}_3)^+ \;+\; \text{ArPEt}_3^+ \;+\; 2\text{IrCl}_6^{3-}$$

(6)

of metastable paramagnetic intermediates is also reported. The voltammetric behavior of *cis*-Pt(YC$_6$H$_4$)$_2$(PEt$_3$)$_2$ in MeCN has been studied by cyclic voltammetry and controlled potential coulometry. The oxidation potential increases linearly with increasing electron-withdrawing ability of the Y substituent in the aryl ligand [12]. Plots have been made of the potential against the Hammett σ value. A kinetic study of the electrophilic proton cleavage of one Pt-C σ bond in complexes *cis*-Pt(YC$_6$H$_4$)$_2$(PEt$_3$)$_2$ (Y = *p*-NMe$_2$, *p*-Me, *p*-OMe, H, *M*-OMe, *p*-F, *p*-Cl, *M*-F, *o*-Me, *o*-Et, *M*-CF$_3$) shows the rate to increase with electron-releasing substituents. A mechanism good LFER is found on plotting log k_{rel} vs the Hammett σ parameter Y. A mechanism is proposed involving rate-determining direct attack of the proton on the Pt-C bond with release of YC$_6$H$_5$ in a three-center transition state [13].

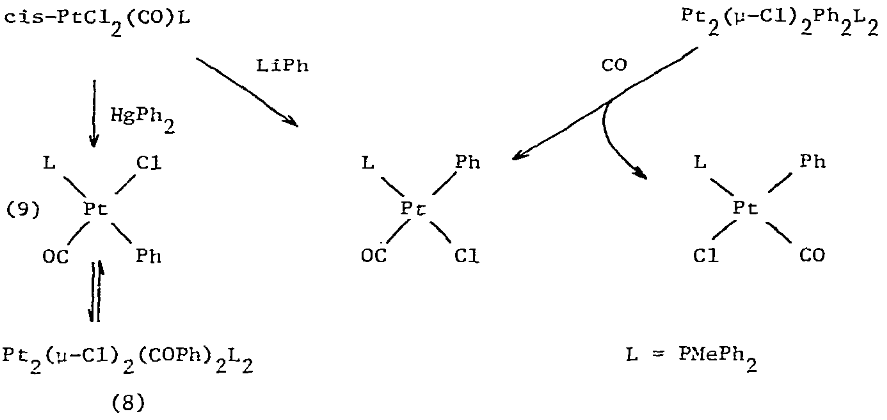
Carbon monoxide readily inserts into the Ni-Ph bond in NiPh(acac)(PR$_3$)$_n$ to give benzoylnickel complexes (7) [14]. Reacting complexes (7) with MeI and alcohols give

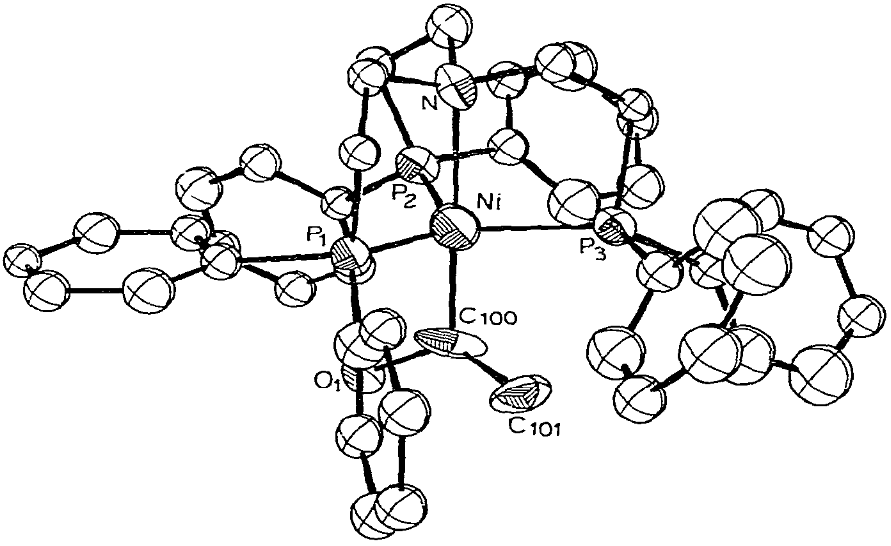
$$\text{NiPh(acac)(PR}_3)_n \;+\; \text{CO} \;\rightarrow\; \text{PhCONi(acac)PR}_3$$

(7)

$n = 1$, R = Ph, Cy. $n = 2$, R = Et.

acetophenone and benzoates, respectively. The dynamic behavior of the acac ligand is studied and the activation parameters for acac exchange are given. The equilibration of chloride bridged acyl complexes $Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2$ (8) with one isomer of $Pt\text{-}ClR(CO)PMePh_2$ (9) in solution is dependent on R [15]. Insertion of CO into the Ni–R bond of $[NiR(L)]BPh_4$ (R = Me, Et, benzyl; L = tris(2-diphenylarsinoethyl)amine or tris(2-diphenylphosphinoethyl)arsine) gives $[Ni(COR)L]BPh_4$ [16]. The structure of the phosphine complex (10) has been solved. Cationic palladium





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acyl complexes (11) have been prepared from $Pd(PMe_3)_4$ [17]. Anions $[PtCl_2R(CO)]^-$ (R = Me, Et, n-Pr, i-Pr, n-Bu, Ph) have been prepared by reacting $Pt_2Cl_4(CO)_2$ with HgR_2. The ^1H, ^{13}C and ^1H-$\{^{195}Pt\}$ INDOR spectra are discussed [18]. Aroylnickel(II) complexes trans-$Ni(C_6Cl_5)(COC_6H_4X$-p$)(PPhMe_2)_2$ (X = NMe_2, OMe, Me) have been prepared

$$Pd(PMe_3)_4 \xrightarrow{RI} \underline{\text{trans}}\text{-}Pd(R)I(PMe_3)_2 \xrightarrow[NaBPh_4]{CO,\ PMe_3} [Pd(COR)(PMe_3)_3]BPh_4$$

(11)

from CO and the arylnickel compound [19]. Methylation with methyl fluorosulfonate occurs at the aryl oxygen atom and the aryl(methoxy)carbene nickel complexes are formed. The rates of carbonylation of a series of $PtI(aryl)(PPh_3)_2$ complexes have been measured [20]. The data are interpreted in terms of a 5-coordinate carbonyl intermediate which forms the acyl complex by two paths, a migratory route and a dissociative one. The former is much more sensitive to electronic effects in the migrating group than the latter. CO insertion is not rate limiting.

Thermally stable alkyl(imido)nickel(II) complexes (12) have been prepared from reacting dialkylnickel(II) complexes with succinimide and phthalimide [21]. In

$$NiEt_2(bipy) \ + \ HN(CO)_2(CH_2)_2 \ \rightarrow \ NiEt(N(CO)_2(CH_2)_2bipy \ + \ C_2H_6$$

(12)

the isomerization of complexes $PtRX(PEt_3)_2$ it is emphasized that the solvolysis step is not rate determining for the isomerization. These authors also point out that this is contrary to the work of Louw [22].

Optically active germyl-lithium compounds can be used to prepare transition metal complexes such as (13) which contain a bonded optically active germyl ligand [23].

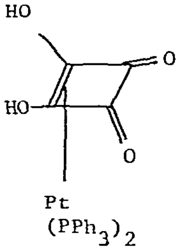
$$PtHCl(PR^4_3)_2 \ + \ R^1R^2R^3Ge^*H \ \rightarrow \ PtCl(Ge^*R^1R^2R^3)(PR^4_3)_2 \ + \ H_2$$

(13)

R^1 = Et or Me; R^2 = Ph; R^3 = α-naphthyl

Unsymmetrical dialkylbis(triphenylphosphine)platinum(II) complexes $PtR^1R^2(PPh_3)_2$ have been prepared by treating the complex $PtR^1X(PPh_3)_2$ with R^2MgX or R^2Li [24]. T compound $NiEt_2$(bipy) reacts with CO_2 to give diethyl ketone and nickel propionate [The ketone is considered formed through an intramolecular rearrangement in an intermediate NiEt(OCOEt)bipy compound.

The reaction of squaric acid with Pt(0) complexes gives a series of complexes. With $Pt(PPh_3)_4$ the salt $[PtH(PPh_3)_3][HC_4O_4]$ is formed. From $Pt(C_2H_4)(PPh_3)_2$ the complex (14) is obtained. Heating this compound gives the ring-opened complex (15) [26]. New complexes $PtMe_2X(GeR_nX_{3-n})$(L-L) (X = Cl, R = Me, n = 1,2,3; X = Cl, R = Ph, n = 2,3; X = Br, R = Me, Ph, n = 3) (L-L = bipyridine,1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) have been prepared from GeR_nX_{4-n}



(14)

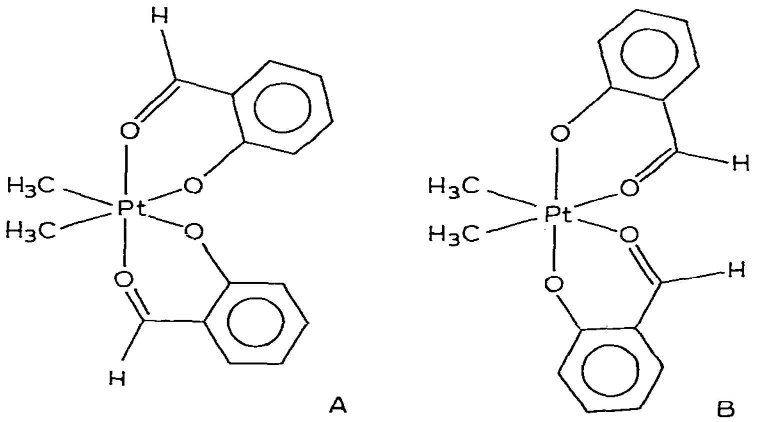
(15)

and $PtMe_2$(L-L) [27]. Solution stabilities are compared. The monomeric complex PtMe(OH)dppe has been obtained by heating $[PtMe(MeOH)dppe]^+$ with NaOH [28]. Anatic can be used to prepare complexes $PtMe(CH_2COMe)$dppe and $PtMe(CH_2CN)$dppe. The complexes have been used to assign trans influences to ligands such as $C(CN)_3$, C(COMe) and CF_3.

Binuclear complexes $PtMe_2X(HgX)(L\text{-}L)$ ($X = Cl, Br, I, O_2CMe, O_2CCF_3$) are obtained from $PtMe_2(L\text{-}L)$ and HgX_2 in equimolar amounts [29]. Treating $PtMe_2(bipy)$ with 4 moles of $Hg(O_2CCF_3)_2$ gives the compound $Pt_4Me_3(O_2CCF_3)(HgO_2CCF_3)(bipy)_4$. Other similar synthetic reactions are described. Complexes $\pi\text{-}cpNiMe(P(OR)_3)$ ($R = Me, Ph$) (16) are obtained in good yield from $\pi\text{-}cpNiCl(P(OR)_3)$ and MeLi [30]. The Ni-Me bond is cleaved by HCl, CCl_4 or I_2 to form the halo complexes.

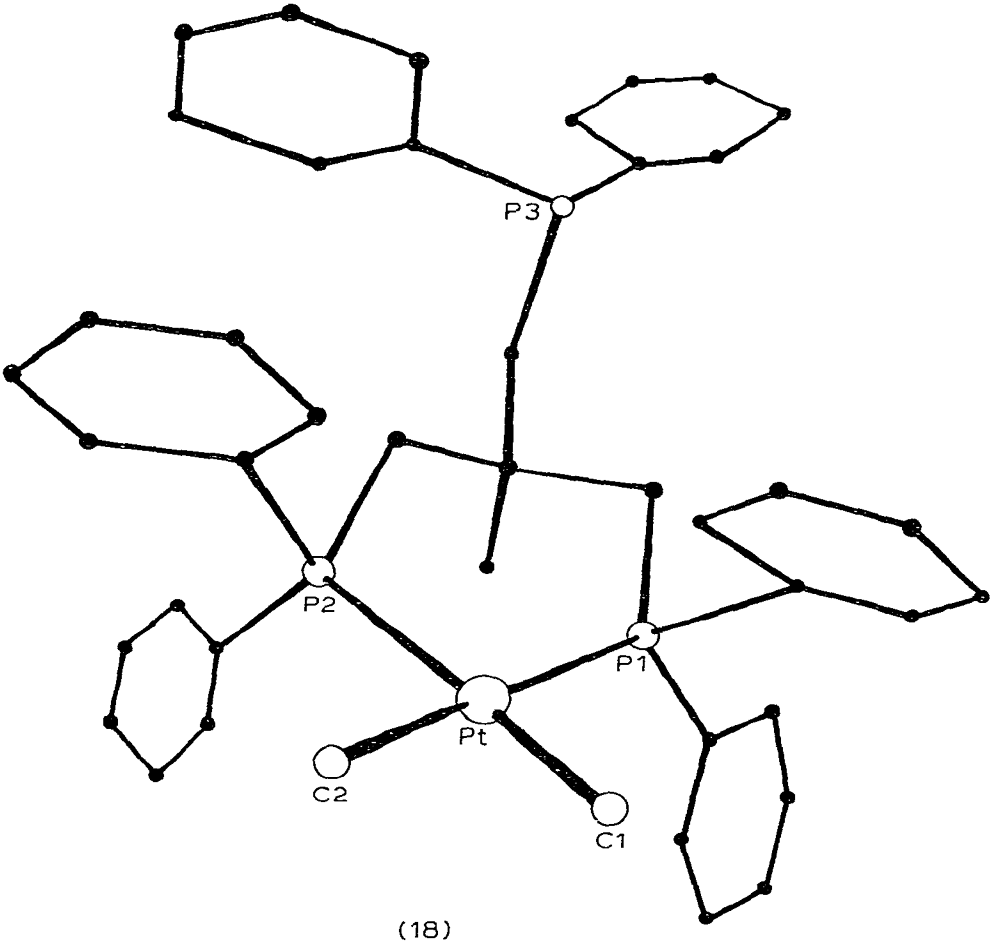
$$\pi\text{-cpNiCl(P(OR)}_3) + \text{MeLi} \rightarrow \underset{(16)}{\pi\text{-cpNiMe(P(OR)}_3)} + \text{LiCl}$$

Two geometric isomers of $PtMe_2(sal)_2$(A and B) (17) have been prepared and identified by ^1H NMR spectroscopy [31]. Isomer B reacts with C_5D_5N to produce species containing unidentate sal in solution, while isomer A tends to lose sal with formation of hydroxo compounds. $(\underline{n}\text{-}Bu_4N)_2PtCl_6$ reacts with MeLi/LiI to give a solution containing Li_2PtMe_6 [32]. Solid $(\underline{n}\text{-}Bu_4N)_2PtMe_6$ is stable under nitrogen at room temperature, but ether solutions of $PtMe_6^{2-}$ decompose in the absence of MeLi. A single crystal study of $PtMe_2$(1,1,1-tris(diphenylphosphinomethyl)ethane) (18) shows a square planar platinum with the triphosphine functioning as a bidentate ligand [33]. Adducts of type $PtXMe_3L$ ($X = Cl, Br, I$; $L = MeSCH_2CH_2SMe$) show pyramidal inversion at individual sulfur atoms, whereas the compounds $(PtXMe_3)_2L^1$



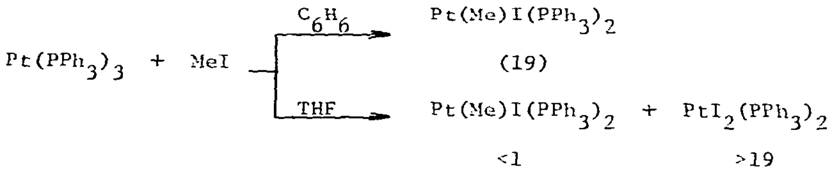
(17)

(X = Cl, Br, I; L^1 = $MeSCH_2SMe$) show both ring inversion and synchronous inversion about both sulfur atoms [34]. The reaction between $PtMe_3(H_2O)_3^+$ and sodium glycinat gives a series of glycinato complexes $PtMe_3(gly)(H_2O)$, $[PtMe_3gly]_2$, $[PtMe_3(gly)_2]^-$ and $[PtMe_3(gly)_3]^{2-}$. Intramolecular exchange reactions have been studied [35].



(18)

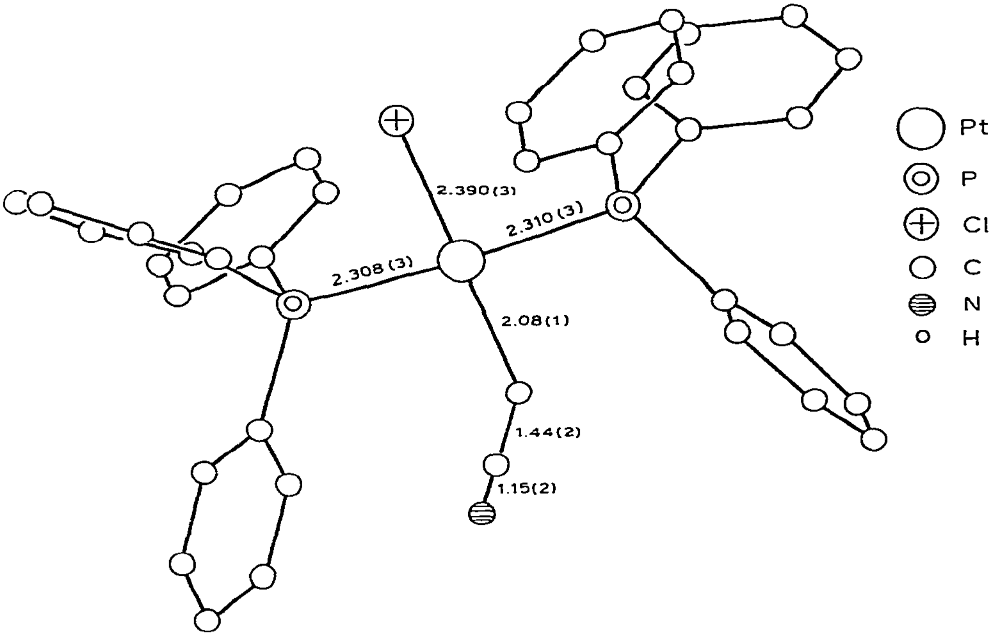
Nickel(I) complexes of N,N^1-ethylenebis(salicylideneiminato) are formed electrochemically and reacted with alkyl bromides and iodides. The product is the nickel(complex and an alkyl radical [36]. Methyl-palladium and platinum complexes containing pentaborane have been prepared [37]. ^1H, ^{11}B, ^{31}P and ^{195}Pt NMR for comple such as $PtMe(B_5H_8)(PMe_2Ph)_2$ are reported and discussed. Photoelectron spectra have been measured for a series of methyl(tertiaryphosphine)platinum(II) complexes [38]. The data are in the opposite order from that anticipated for electronic effects in the substituted phosphines, and it is concluded that steric effects are dominant in the oxidative addition reaction. Emphasis is laid on solvent effects in oxidative addition reactions. Thus, the addition of MeI to $Pt(PPh_3)_3$, with elimination of $[PPh_3Me]I$, leads to $PtMeI(PPh_3)_2$ (19) as sole product in benzene solvent, but in THF the predominant product is $PtI_2(PPh_3)_2$ (20) [39]. In a communication the isomerization, exchange, and ring-closure of glycinate complexes of cis-dimethylplatinum(IV) are described [40].



(20)

In the reaction of alkylplatinum(II) compounds $PtMe_2L_2$ with electrophiles such as Me_3PbCl, MeHgCl or $PbMe_4$, the mechansim is dependent on both the electrophile and on L [41].

The molecular structures of trans-$PtCl(CH_2CN)(PPh_3)_2$ (21) and trans-$PtH(CH_2CN)(PPh_3)_2$ (22) show Pt-C distances of 2.08(1) and 2.15(1), respectively; the longer distance in the latter being due to the greater trans influence of the hydride ligand [42].



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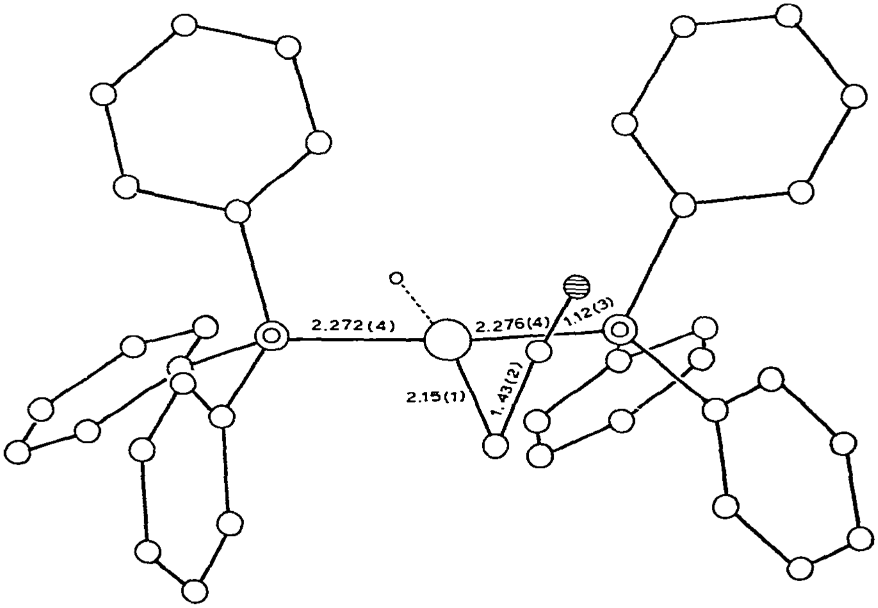

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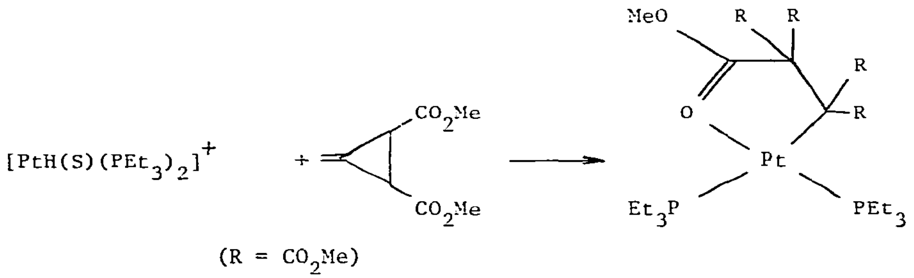
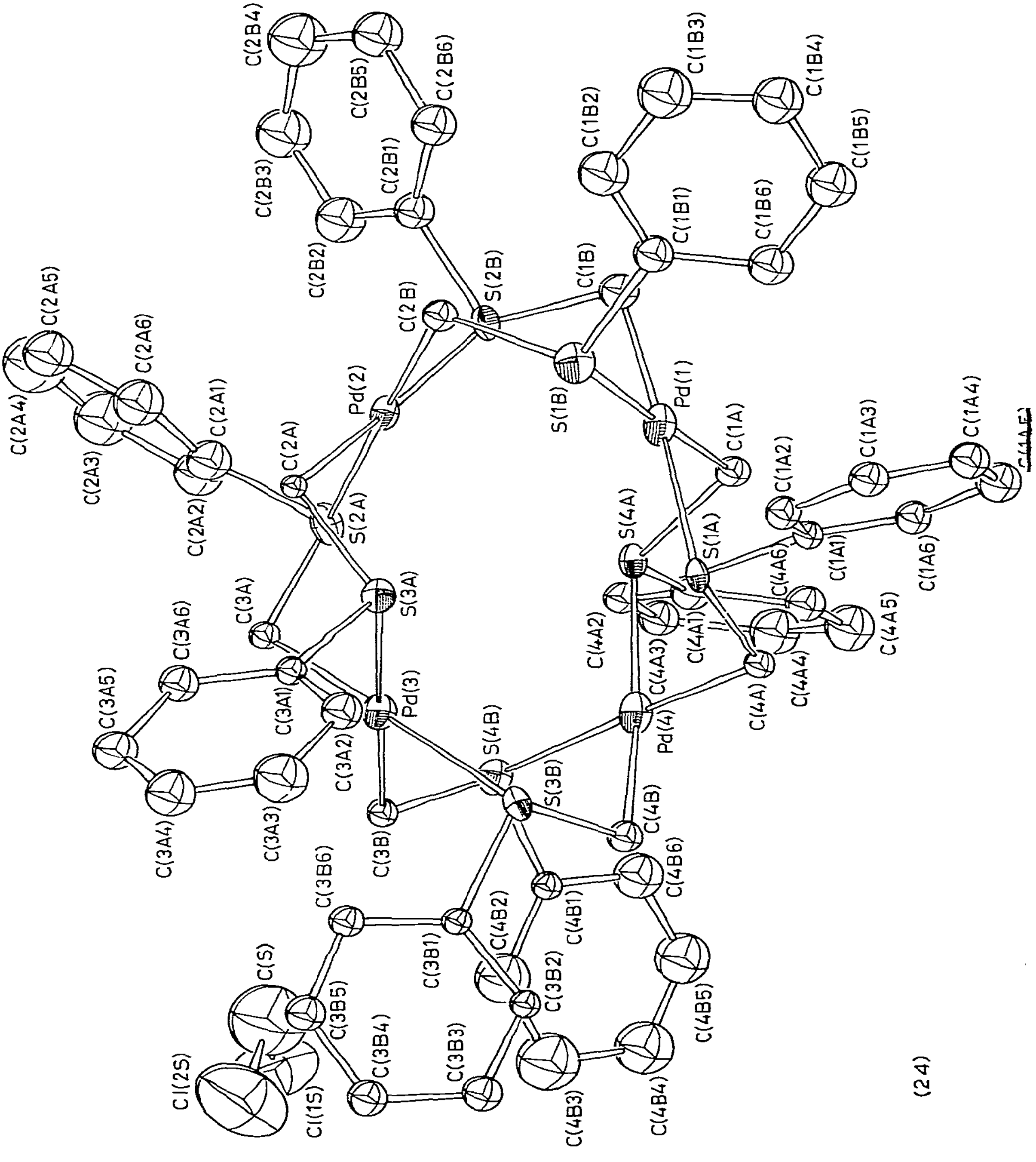
The absolute configurations of the products of oxidative addition of optically active benzyl-α-d chloride and bromide to $Pd(PEt_3)_3$ have been determined by carbonylation and cleavage to the methyl esters. Possible pathways for racemization are discussed [43]. The platinum(II) hydrides trans-$[PtH(S)(PEt_3)_2]PF_6$ and trans-$PtHX(PEt_3)_2$ (X = Cl, NO_3) react with the dimethyl ester of Feist's acid stereospecifically with cleavage of the 1,2 bond of the cyclopropane ring and formation of the but-3-enyl complexes (23) [44]. In some cases the but-2-enyl complex is formed, and 3 to 2 isomerization is discussed.

In matrix isolation studies it has been found that nickel clusters will cleave pentane at very low temperatures with retention of organic fragments to produce thermally stable catalytically active "organometallic" powders. Alkyl and carbenoid nickel binding is proposed [45].



(23)

Organopalladium intermediates have been prepared in situ from C-5 mercurated uridine or 2^1-deoxyiridine and Li_2PdCl_4 in methanol. These compounds react with olefins to produce nucleosides substituted at C-5 by carbon chains [46]. Deuteration studies suggest a palladium facilitated hydride shift. A mechanism involving alkylpalladium intermediate is proposed. A stable palladium complex $[Pd(CH_2SPh)_2]_4$ has been obtained from $PdCl_2(PhCN)_2$ and $LiCH_2SPh$ [47]. The structure (24) shows a tetramer with palladiums at the corners of a distorted rectangle and two averaged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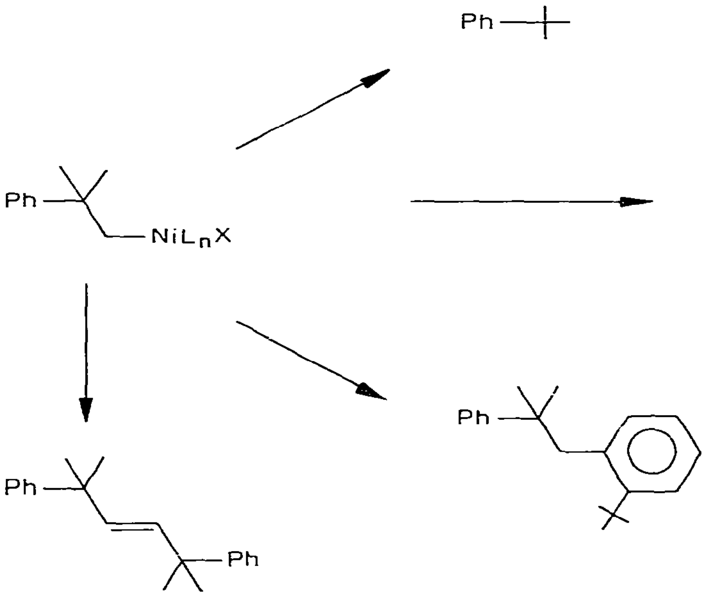
C(S)
C(3B5)
C(3B2)
C(4B5)
C(3B4)
C(3B3)
Cl(2S)
Cl(1S)
C(4B3)
C(4B4)

(24)

Pd . . . Pd distances of 4.051 and 3.304Å. The CH_2SPh groups bridge four palladium atoms. Neophylnickel complexes (25) are formed from neophylmagnesium chloride and nickel chloride in the presence of ligands such as phosphines or bipyridyl [48]. Decomposition gives t-butylbenzene and both saturated and unsaturated dimers.



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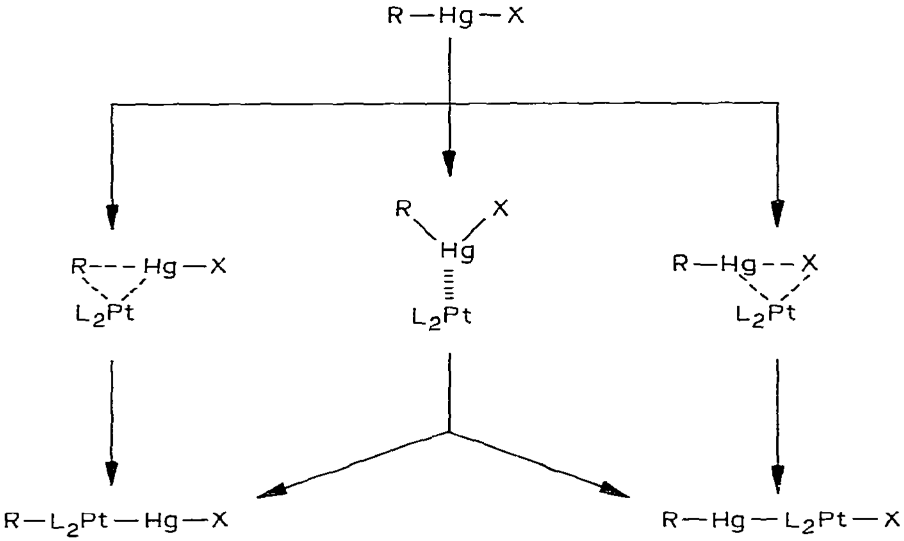
Solutions claimed to contain $Ni(C_6F_5)_2$ are obtained from anhydrous $NiBr_2$ and C_6F_5MgBr in THF. Addition of L (L = PEt_3, PBu_3, PPh_3, $AsPh_3$, $SbPh_3$, $OPPh_3$, $OAsPh_3$, p-dioxane) gives $Ni(C_6F_5)_2L_2$ [49]. The complex $Ni(C_6F_5)_2$(p-dioxane)$_2$ has been used as a precursor to prepare a wide range of compounds $Ni(C_6F_5)_2L_2$ [50]. Using ^1H and ^{31}F NMR parameters for cis-PtX_2L_2 and $[PtXL_3]^+$ complexes where L is $P(C_6F_5)Me_2$, it is concluded that electron-withdrawal has only a limited effect on metal-ligand bonding, and that the trans influence of Me and CF_3 are closely similar [51]. The complex trans-$Pt(C_6F_5)_2py_2$ has been prepared from $TlO_2CC_6F_5$ [52]. Single crystal structural work show that the complex $CF_3HgPt(CF_3(PPh_3)_2$ has the cis configuration and that the Hg-Pt bond length is 2.569(2)Å [53]. Crucible effects have been noted in the reactions of Ni and Pd with benzyl chloride [54]. The reaction between $Pt(PPh_3)_3$ and diastereoisomeric L-menthyl esters of α-bromomercuriphenylacetic acid or related HgR_2 compounds has been studied [55]. It is suggested that organomercur undergo $Pt(PPh_3)_2$ insertion into both the Hg-Br and Hg-C bonds, the latter being a stereoselective process. Insertion into the Hg-C bond proceeds with retention. The possible mechanisms are shown below (26). The oxidative addition of diorganoditellurides to $Pd(PPh_3)_4$ has been observed [56]. Dimeric compounds (27) containin both bridging and terminal TeR groups are formed.



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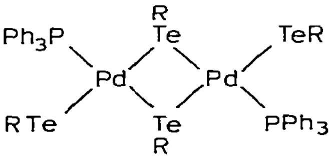
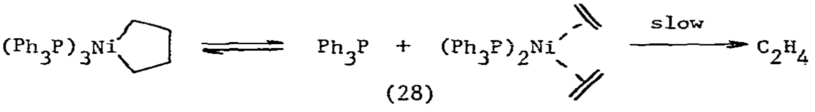
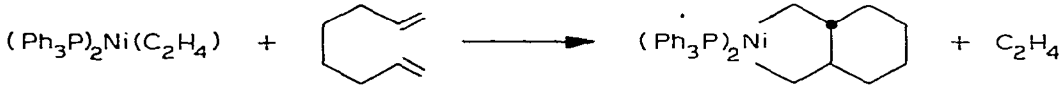


(27)

In a study of the catalysis of olefin reactions, a deuterium labelling experimen has shown that there is an equilibrium between metallacyclopentanes and bis(olefin) metal complexes (28) [57]. In a following paper these authors describe the



preparation of seven phosphine nickelmetallacyclopentanes from 1,4-dilithiobutane and the appropriate complex $NiCl_2L_2$. Analysis of the thermal decomposition of these compounds to give ethylene, cyclobutane and butenes is presented [58]. The work has been extended to use complexes $NiCH_2CH_2CH_2CH_2(PPh_3)_3$ to catalytically dimerize ethylene to butane [59]. Details of temperature and pressure are given, and work with acrylonitrile is described. Further work shows that C-C cleavage leading to metathesis is also involved in the process, and it is stressed that C-C cleavage can occur on a single metal center and does not require multimetallic centers [60]. The cis and trans isomers of 2-nickelahydrindane have been prepared. The more stable trans isomer (29) is obtained from 1,7-octadiene and tris(triphenylphosphine)nickelacyclopentane. The cis isomer (30) is obtained from $NiCl_2(PPh_3)_2$



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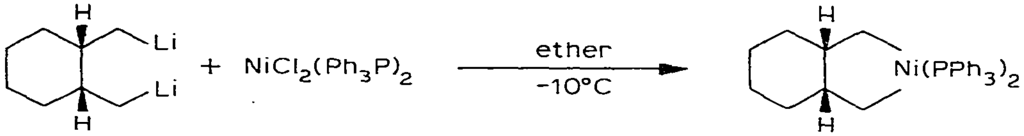

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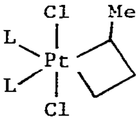
and cis-1,2-dilithiomethylcyclohexane [61]. Cis-trans isomerization occurs under the influence of light or added triphenylphosphine.

The reaction of arylcyclopropanes with either $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$ or $[PtCl_2(CH_2CH_2CH_2)]_4$ to give $[PtCl_2(CHArCH_2CH_2)]_4$ and ethylene or cyclopropane, respectively, are first order in each reactant [62]. The order of reactivity is X = EtO >> Me > H for $4\text{-}XC_6H_4C_3H_5$ compounds. The photolysis of $I_2PtCH_2CH_2CH_2CH_2(PMe_2Ph)_2$ gives ethylene and butene-1; the latter being proposed to arise from a five coordinate intermediate [63]. The formation of propene from the photolysis of $Cl_2PtCH_2CH_2CH_2(phen)$ is considered to involve direct hydrogen transfer of a hydrogen atom between neighboring CH_2 groups in the ring. The platinacyclobutane complexes $PtCl_2L_2(C_3H_5Me)$ (L = py, CD_3CN, THF) exist as a mixture of isomers containing $PtCH_2CHMeCH_2$ (31) or $PtCHMeCH_2CH_2$ (32) groups in rapid equilibrium [64].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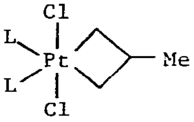
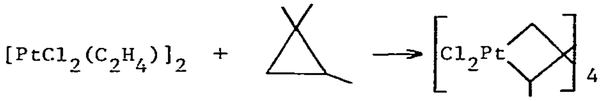
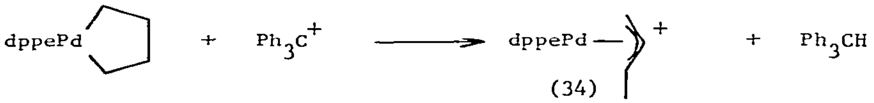

(32)

The ratio of the mixture is dependent on the ligand L. The cyclopropylplatinum complex cis-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$ has been prepared from cis-$PtCl_2(PMe_2Ph)_2$ and cyclopropyllithium. The compound adds MeI, forms the dibromo compound with allyl bromide, and reacts with HCl to give trans-$Pt(CHCH_2CH_2)Cl(PMe_2Ph)_2$. The products of thermal decomposition are reported [65]. The complex dichloro-2,3,3-trimethyl-1-platinacyclobutane (33) has been prepared by the reaction of Zeise's dimer with 1,1,2-trimethylcyclopropane [66]. The reaction with pyridine and thermal isomerization is reported and discussed. Mono-, di-, and tri-alkyl- substituted cyclopropanes react with Pt complexes to form platinacyclobutanes. The products result



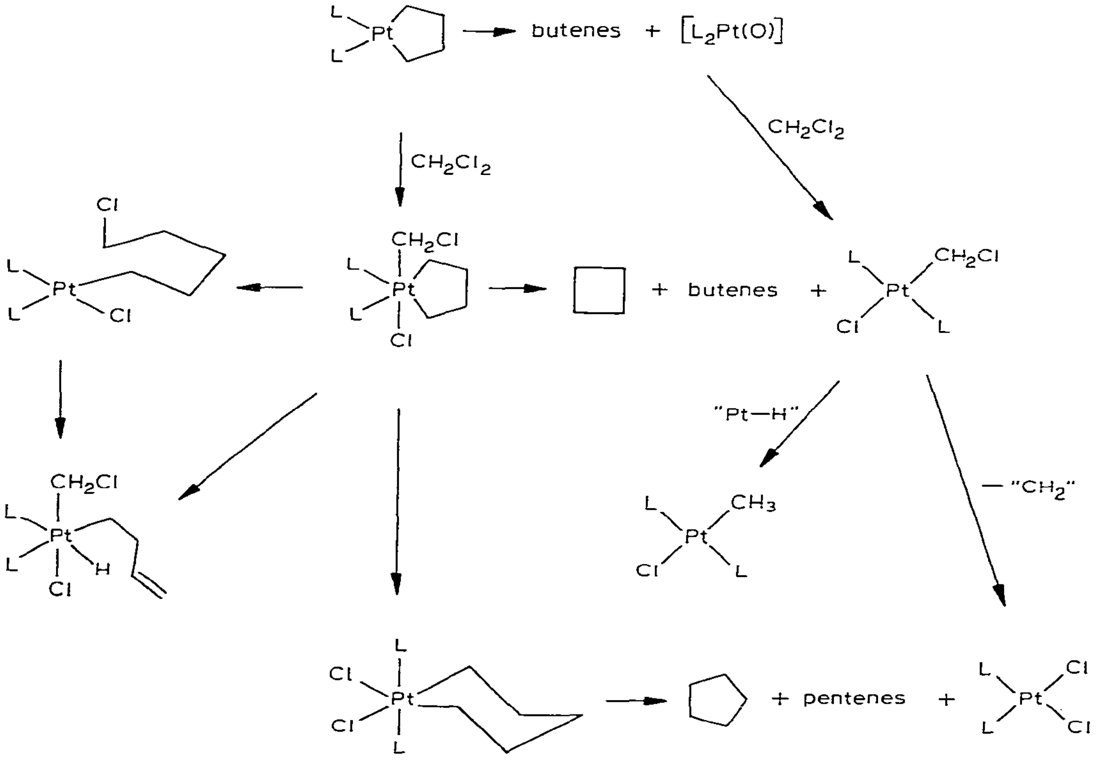
(33)

from insertion of Pt into the least-substituted C-C bond of the cyclopropane ring [67]. α,α^1-bipyridyl-5-nickela-3,3,7,7-tetramethyl-trans-tricyclo[4.1.0.0] heptan undergoes reductive elimination on treatment with maleic anhydride, tetracyanoethy or triphenyl phosphite to give 3,3,6,6-tetramethyl-trans-tricyclo[3.1.0.0] hexane. With triphenyl phosphite bi(2,2-dimethylcyclopropyl) and 1-(2,2-dimethylcyclopropy 3-methylbutadiene-1,3 are also formed. Evidence is presented for the intermediacy of metallacyclopentanes in transition metal catalyzed [2π + 2π] cycloadditions [68 The reactions of the palladacyclopentane complex $PdCH_2CH_2CH_2CH_2(dppe)$ with Br_2, HCl, L, CO, SO_2 and Ph_3C^+ have been studied [69]. The latter reagent converts the compound into the methallyl compound (34). The thermal decomposition of platinacy alkanes $L_2Pt(CH_2)_nCHR$ (L = n-Bu_3P, Et_3P; L_2 = $Me_2PCH_2CH_2PMe_2$, bipy; R = H, n = 3,4; R = Me, n = 3) in CH_2Cl_2 or CH_2Br_2 give cycloalkanes and alkenes from the metallacycle,



(34)

and homologous cycloalkanes and alkenes formed by incorporation of a solvent derived methylene group [70]. A series of possible reactions are outlined in the scheme shown below. Activated cyclopropanes react with $Pt(C_2H_4)(PPh_3)_2$ by cleavage of



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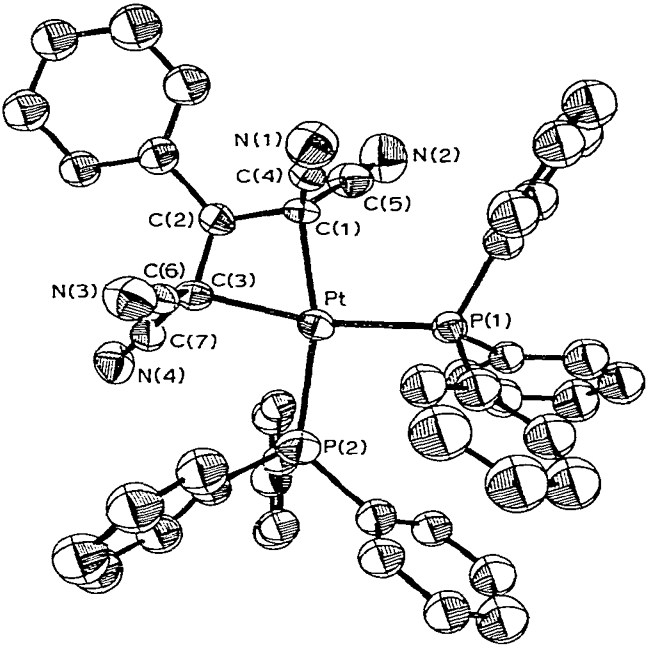
the C–C bond having the most cyano groups in substitution [71]. Crystal structures of $Pt[C_3H(Ph)(CN)_4](PPh_3)_2$ (35) and $Pt[C_3H(Ph)(CN)_3CO_2Et](PPh_3)_2 \times CHCl_3 (x \simeq 0.8)$ (3



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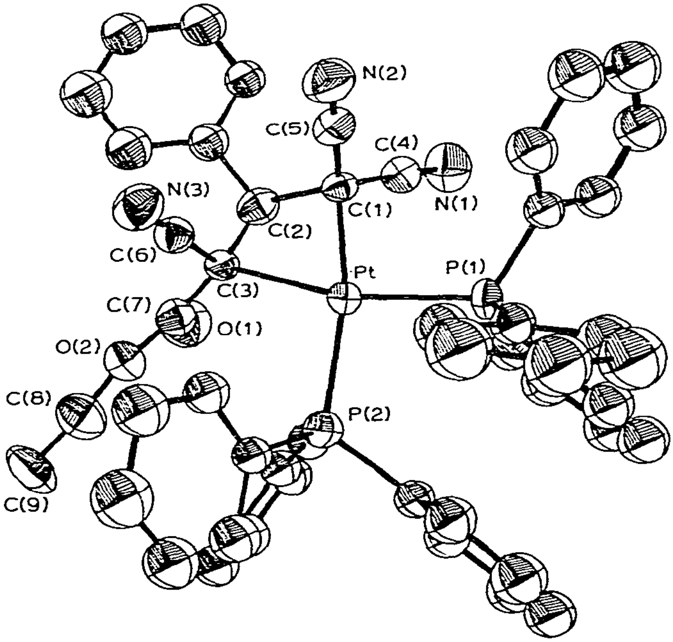

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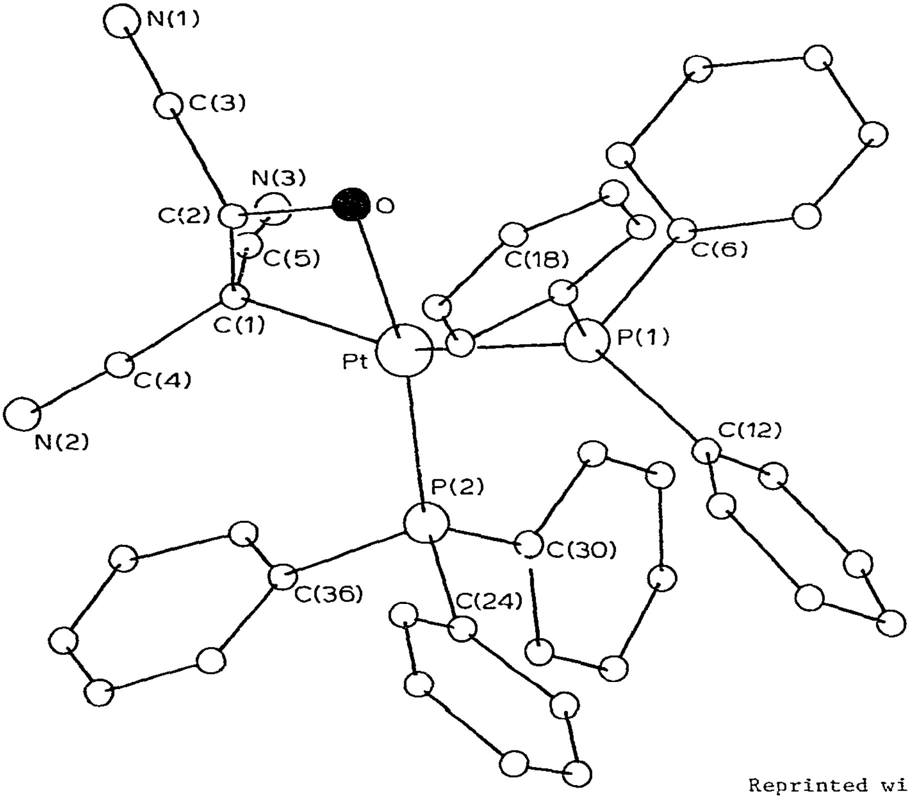
have been solved. Complexes of platinum(II) containing the 4-membered ring Pt-C-C-N have been prepared by the aminoplatination of olefins [72]. Both the neutral complexes $Pt(CH_2CHRNMe_2)Cl(L)$ (R = H, alkyl; L = PPh_3, DMSO) and the cationic complexes $[Pt(CH_2CHRNMe_2)(PPh_3)(L^1)]BF_4$ (R = H, Me; L^1 = MeCN, PhCN, $NHMe_2$, py, DMSO, PPh_3, CO) have been formed. Treating $Pt(C_2H_4)(PPh_3)_2$ with 2,2,3-tricyano-oxacyclo propane gives 3,3,4-tricyano-2,2-bis(triphenylphosphine)-1-oxa-2-platinacyclobutane (37) [73]. The compound results from insertion of platinum into the C-O bond. The



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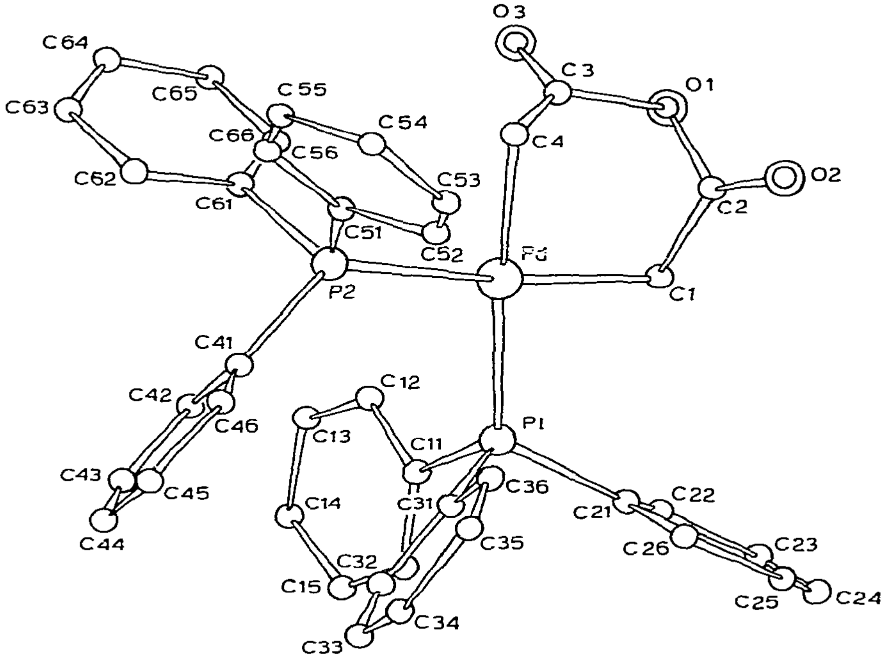
molecular structure of oxydi(carboxymethyl)bis(triphenylphosphine)palladium(II) (38)



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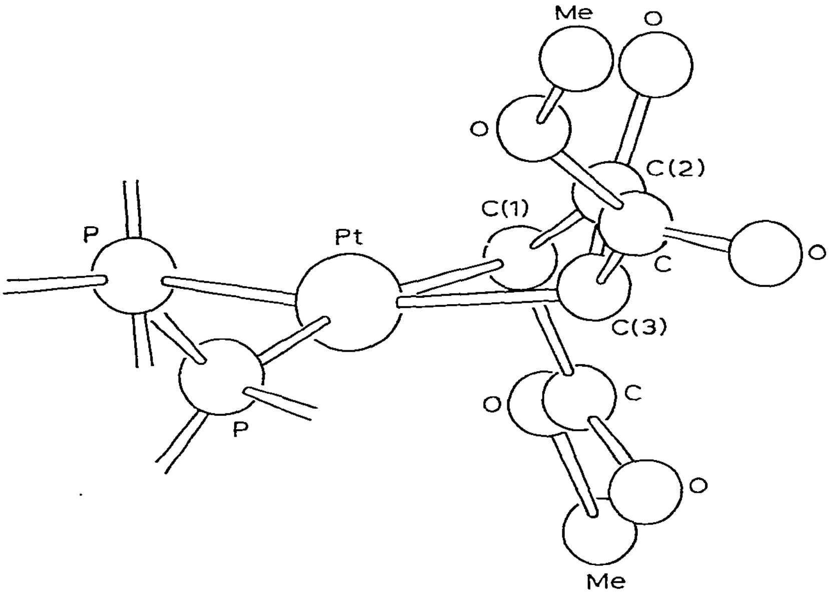
has palladium chelated by an acetic anhydride to form a 6-membered ring with Pd–C of 2.141(13) and 2.124(11) Å [74]. Dimethyl-3-oxoglutarate reacts with ML_4 (M = Pd, L = PPh_3; M = Pt, L = PPh_3, $PMePh_2$, PMe_2Ph) to give the metallacyclo butan-3-one complexes. The structure of one of these complexes $Pt(CH(CO_2Me)COCH(CO_2Me))(PPh_3)_2$ (39) is shown [75].



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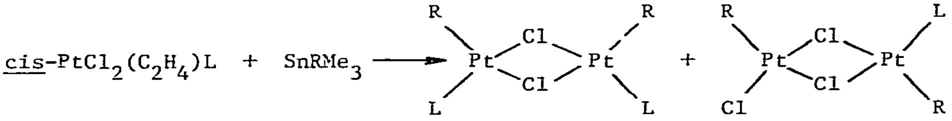
$PdCl_2(PhCN)_2$ reacts with acacH to give $[PdCl(acac\text{-}O,O^1)]_2$. An alkyl complex of Pd is reported which exhibits the keto-enol tautomerism of the terminal C-bonded acac [76]. The terminal proton on this ligand has been removed by base and bonded to a second metal [77].

The compounds $Pd(CO_2Me)(OAc)(PPh_3)_2$ (40) and $Pd(CO_2Me)_2(PPh_3)_2$ (41) have been isolated and characterized in an investigation of the behavior of phosphinepalladium(I complexes in MeOH/CO [78]. The compound trans-$PdCl(CO_2Me)(PPh_3)_2$ has been prepared

$$Pd(OAc)_2(PPh_3)_2 \xrightarrow[-AcOH]{CO,\ MeOH} \underset{(40)}{Pd(OAc)(CO_2Me)(PPh_3)_2} \xrightarrow[-AcOH]{CO,\ MeOH} \underset{(41)}{Pd(CO_2Me)_2(PPh_3)_2}$$

from $PdCl_2$ and $AcOHgCO_2Me$ and PPh_3 in methanol. The crystal structure has been solved [79]. The cleavage of Si-C bonds in tetraalkyl- and trialkylsilanes by chloro complexes of Pt(IV) and Pd(II) has been observed [80]. The complex $Ni(CH_2SiMe_3)_2(bipy)$ has been obtained from $Ni(acac)_2$ and either $(Me_3SiCH_2)_3Al$ or $(Me_3SiCH_2)_2AlOEt$ [81].

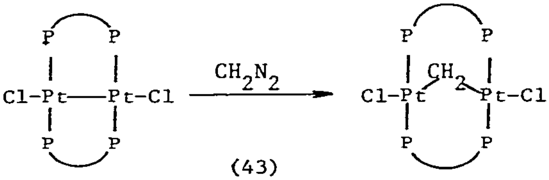
The complexes cis-$PtCl_2(C_2H_4)L$ react with $SnRMe_3$ (R = aryl) (1 mol) to give chloro bridged compounds $[PtClRL]_2$ (42) [82]. Mononuclear compounds are obtained



(42)

on treating with MeCN, t-Bu_2S, py, n-BuH_2N, $AsPh_3$, PEt_3, n-Bu_3P, PPh_3, $P(OPh)_3$. The compound $SnRMe_3$ is also used to produce benzoyl complexes from the carbonyl platinum compounds.

The first diplatinum compounds containing a bridging CH_2 group are reported [83]. The compound $Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2$ (43) has been prepared from $Pt_2Cl_2(\mu\text{-}dppm)_2$



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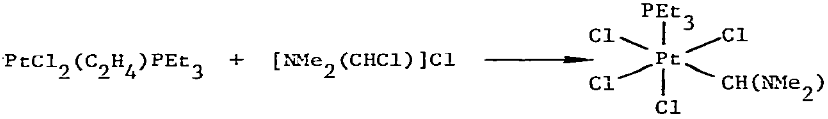
II. Metal carbenes and ylides

(Chloromethylene)dimethylammonium chloride $[NMe_2(CHCl)]Cl$ is a convenient source of secondary carbene metal complexes $M\{CH(NMe_2)\}L_n$. Using this reagent with cis-$PtCl_2(C_2H_4)(PEt_3)$ or $[PtCl_2(C_2H_4)]_2$, the carbene complex (44) has been prepared [84]. Carbene complexes of nickel (45) have been prepared from $Ni(NO)(PPh_3)_2Cl$ and



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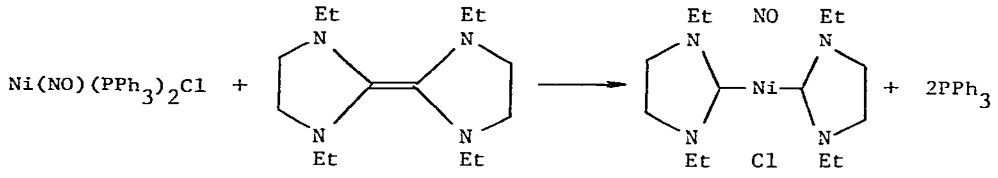
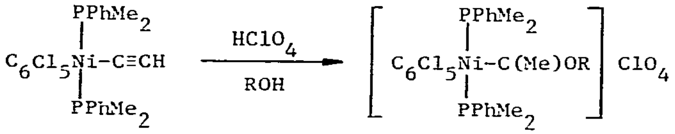


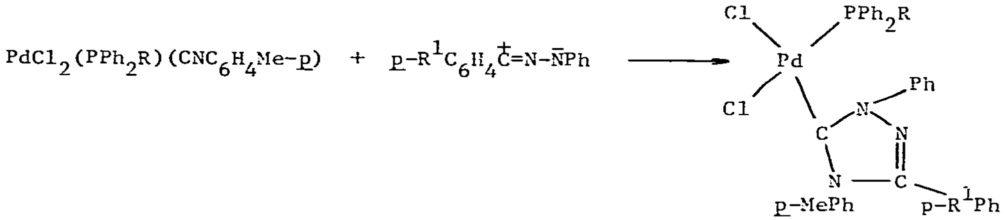
(45)

$(CH_2NEt)_2C{=}C(CH_2NEt)_2$ [85]. Treatment of the halogen bridged dimer $Pt_2X_4L_2$ (L = PMe_2Ph, PEt_3; X = Cl, Br, I) with monosubstituted acetylenes RC≡CH (R = Ph, Me, Et) and alcohols R^1OH (R^1 = Me, Et, n-Pr) yields carbene complexes cis-$PtX_2L\{C(OR^1)CH_2R\}$. The structure of cis-$PtCl_2(PMe_2Ph)\{C(OEt)CH_2Ph\}$ has been solved [86]. Similarly treatment of trans-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CH$ with alcohols yields carbene complexes trans-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OR^1)Me\}]ClO_4$ (46) [87]. Cyclic carbene



(46)

complexes (47) have been obtained by reacting nitrilimines with cis-$[PdCl_2(PPh_2R)(CNC_6H_4Me\text{-}p)]$ (R = Ph, Et) [88]. An imidazolindinylidene palladium(II) complex (48)



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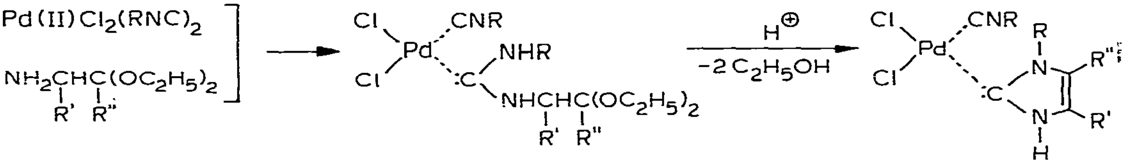
has been obtained by the intramolecular cyclization of a diaminocarbene palladium intermediate [89]. The compounds have been prepared from both cyclohexyl and



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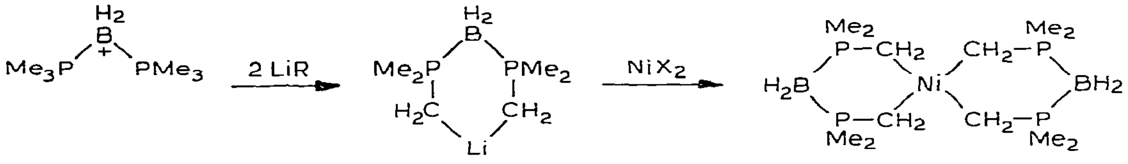
t-butyl isocyanide. The structure of trans-chloro(3-hydroxypropyl-N,N-dimethylamino carbene)bis(dimethylphenylphosphine) platinum(II) hexafluorophosphate shows the carbene ligand lying close to perpendicular to the plane of the platinum coordinatio The Pt-C(carbene) distance is 1.978(12)Å and the C(carbene)-N distance is 1.293(16) Å [90]. The complex trans-$[PtCl\{C(OMe)CH_2C_5H_4Fecp\}(PMe_2Ph)_2]PF_6$ has been prepared from trans-PtCl(ethynylferrocene)$(PMe_2Ph)_2$ and HPF_6 in methanol [91]. The complexes are viewed as a stabilized carbonium ion. Traces of (μ_3-benzylidine)(tris(π-cp) nickel) have been identified from the reaction of cp_2Ni with trans-bromotetracarbony (phenylcarbyne)chromium [92]. The major product is $(cpNi)_2PhC\equiv CPh$. Carbenoid decomposition of ethyl diazoacetate in the presence of various palladium complexes as catalysts is kinetically dependent on the nature of the halide ions [93].

Boratobis(trimethylphosphonium)bromide reacts with two equivalents of butyllithi to give the ylide anion. Reaction with nickel halides gives the chelate complexes (49) in good yield. The structure of (49) has been solved [94]. Polyspirocyclic dimers $[R_2P(CH_2)_2Pd\text{-}\mu\mu^1\text{-}[R_2P(CH_2)_2]_2\text{-}Pd(CH_2)_2PR_2]$ (50) (R_2 = $(CH_3)_2$, $-(CH_2)_4-$, $-(CH_2)_5-$) have been prepared [95]. New palladium allyl ylide complexes $[(\eta^3\text{-}R^1_3PCH CR^2CHR^3)_2Pd_2X_2]Y_2$ (R^1 = Et, Ph; R^2 = H, Me; R^3= H, Me; X = Cl, Br; Y = PF_6, BF_6, CF_3SO_3) have been prepared from $(\eta^3R^1_3PCHCR^2CHR^3)PdX_2$ and the silver salt of Y [96]. The phosphonium allyl ylide is coordinated as a η^3-ligand. Nitrilylides react with cis-$PdCl_2(PPh_2Et)$(p-CNC_6H_4Me) and triethylamine to give cyclic carbene palladium(II complexes cis-$PdCl_2(PPh_2Et)\{$(p-$CNC_6H_4Me)C($p-$RC_6H_4)=NCH($p-$NO_2C_6H_4)\}$ [97]. The ^{13}C chemical shifts, the ^{13}C-^{31}P coupling constants, and some one-bond ^{13}C-^{1}H coupling constants have been measured for some phosphonium, arsonium, sulfonium and pyridini keto-stabilized salts, and ylides of their palladium(II) complexes [98].



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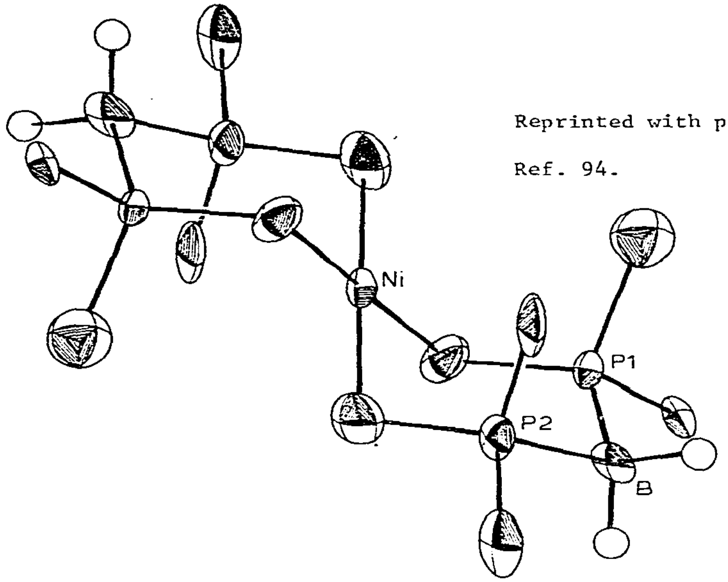

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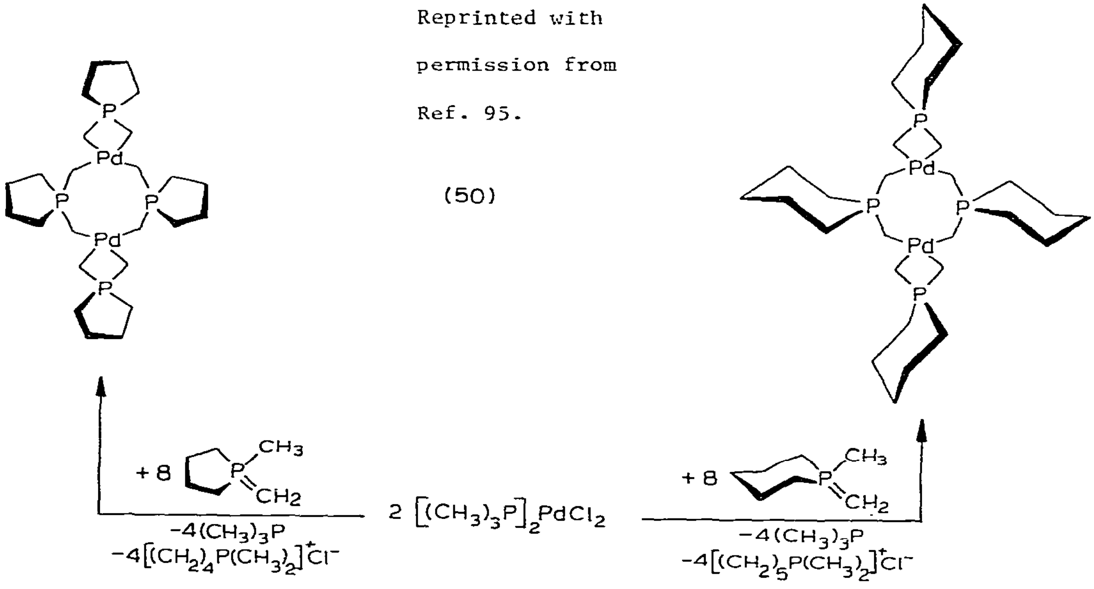

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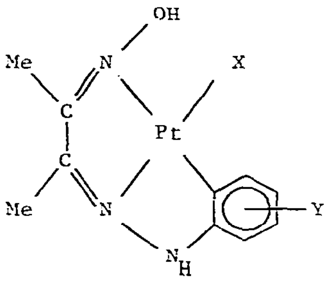
(50)

III. Internal metalation reactions

Palladation with $PdCl_2$ of substituted azobenzenes shows that this compound behav as an electrophilic reagent [99]. Metallation of the 2- and 4- substituted azobenzenes $XC_6H_4N{=}NPh$ may give products metallated in either ring. Using $XC_6H_4N{=}NC_6F$ the C_6F_5 group is not metallated. Electron donating substituents activate the ring towards electrophilic attack by $PdCl_2$. Palladium(II) complexes of biacetylmonoxime arylhydrazones (HL, aryl=phenyl, o-, m-, p-tolyl, p-chloro- and p-nitrophenyl) and biacetylmonoxime N^1-methyl-phenylhydrazone (HL^1) have been isolated (51) [100]. Under basic conditions deprotonation occurs at the oxime group of HL^1. The azobenz nickel complex (52) can be reduced to PhN=NPh, and reaction with $Hg(OAc)_2$ followed by iodine gives $o\text{-}IC_6H_4N{=}NC_6H_4I\text{-}o$ [101]. Metallation of o-hydroxydiarylazo compoun with Pd(II) or Pt(II) gives compounds containing a metal-carbon bond [102]. The compounds will insert CO, leading to the reductive elimination of heterocyclic products. When benzo[h] quinoline is added to $[Pd(dmp)Cl]_2$ (dmp = 2-dimethylamino methyl)phenyl-N) followed by $AgClO_4$, the complex $[Pd(dmp)(benzo[h]quinoline)H_2O]ClO_4$ (53) is formed [103]. The structure has been confirmed by X-ray crystallography. In the following paper the dynamic behavior of this compound is described [104].



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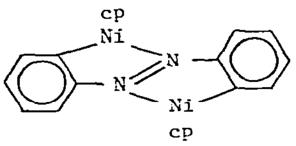

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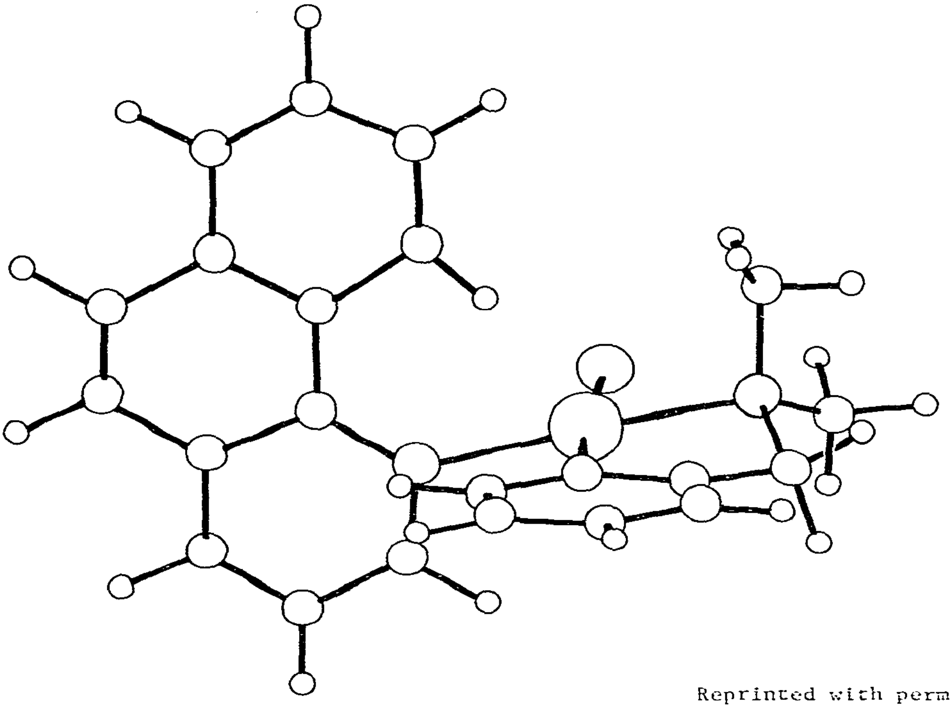

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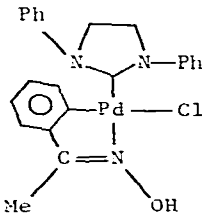
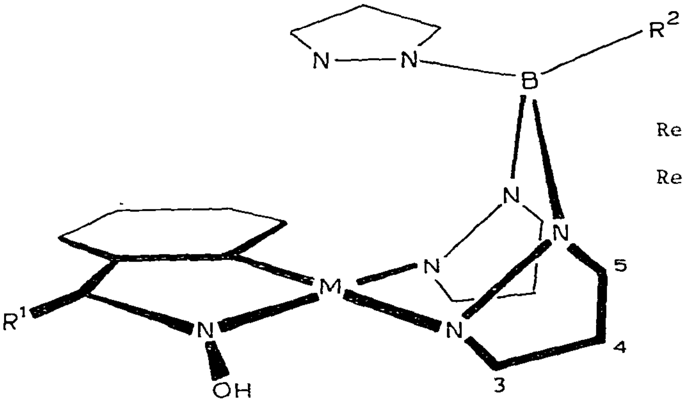
(53)

Cyclometallation of 2-aryl-4,5-dimethyl-1,2,3-triazoles occurs with Pd(II) [105]. The dimers can be cleaved with pyridine and PBu$_3$. The corresponding bromo and iodo analogs have been prepared by metathetical replacement. The reaction of the oxime of isopropyl phenyl ketone with Na$_2$PdCl$_4$/NaOAc gives Pd$_3$(ON=C-*i*-PrPh)$_6$. Pinacolone oxime carbopalladates regiospecipically on the *t*-Bu group, and the dimethylhydrazone carbopalladates only on the methyl group [106]. New carbene complexes (54) have



(54)

been prepared which also contain a cyclometallated aryl group [107]. Stereochemistries and reactivities are discussed. New (acetophenone oximato, 2-C,N)- and (benzophenone oximato, 2-C,N) palladium(II) complexes (55) containing poly(1-pyrazolyl)borato ligands or poly(1-pyrazolyl)methane have been prepared. For the BPz$_4$ complexes the tumbling motion of this ligand averages all four pyrazolyl groups to give spectroscopic equivalence above 65°C, and is frozen at *ca* -9°C [108]. The proposed geometric arrangement is shown. The hydrazone derived from 2-acetylpyridin and *p*-tolylhydrazine acts as an anionic terdentate ligand involving a Pd-C bond in the complex (56) [109]. Cyclopalladation will also occur with acetylthiophene acetylhydrazone to give complex (57) [110]. 8-Methylquinoline reacts with Pd(OAc)$_2$ give palladation at the 8-methyl group [111]. Evidence is presented for metallation occurring when the ligand plane and the coordination plane are coincident. An



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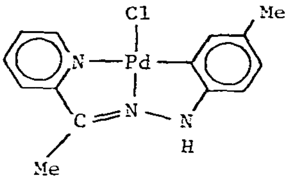

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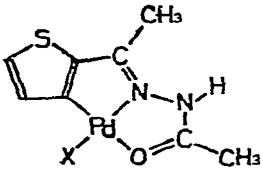

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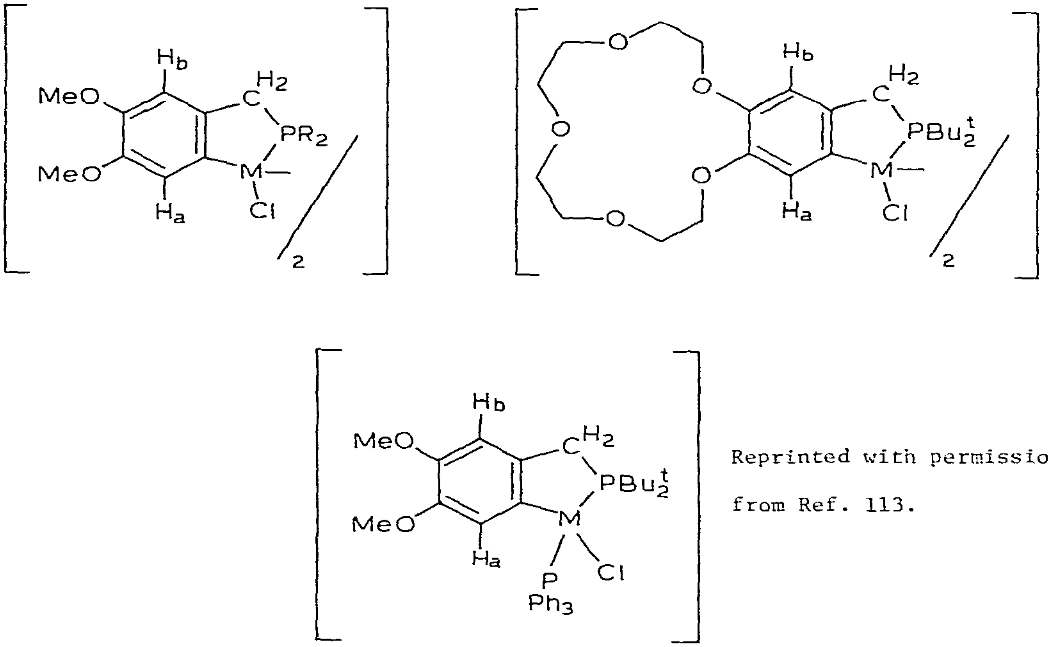
(57)

o-metallated carbene ligand complex $[Pt\{C(NHPhMe)(NHPhMe)\}dppe]ClO_4$ has been prepared and characterized [112]. A number of metallated ether and crown ether substituted phenyl complexes have been prepared (58) [113]. Examples are shown where R = *t*-Bu and M = Pd. Similar results have been reported with tertiary dimethoxyphenylphosphines [114]. O-metallation has not been successful with palladium. O-metallation



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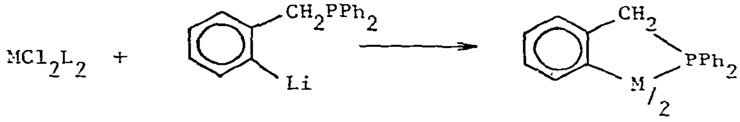
(58)

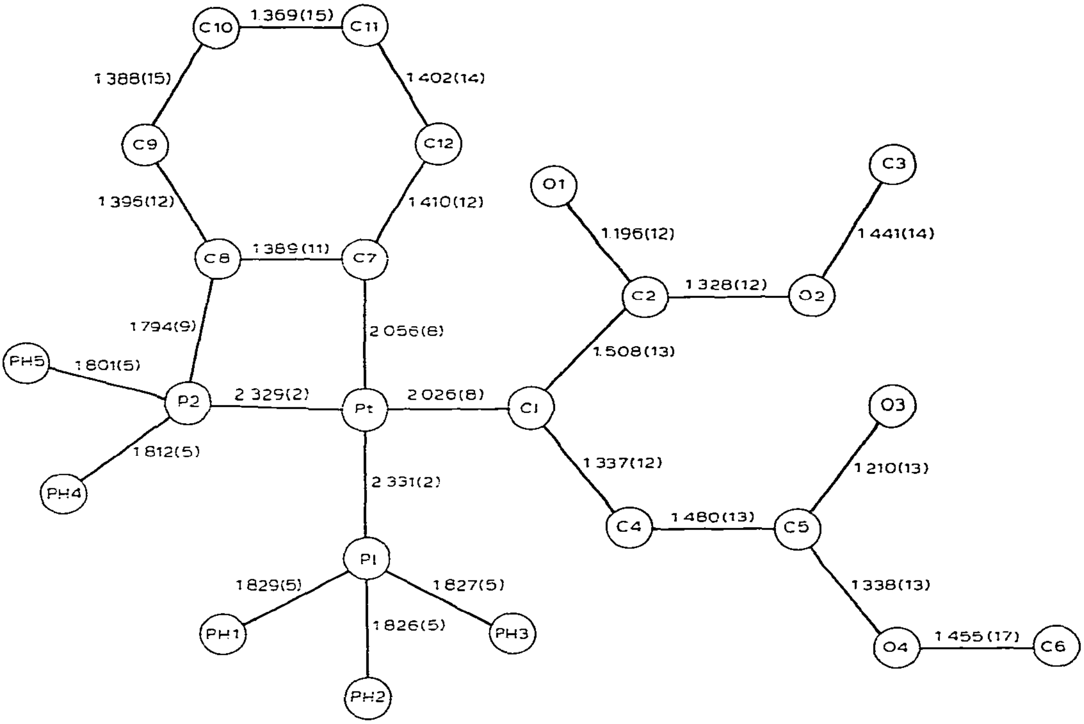
is favored by a polar solvent, but in xylene the platinum complex $Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2$ is formed from $PtCl_2(NCPh)_2$ and $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$. When $NiCl_2(TMEDA)$, $PdCl_2(SEt_2)_2$, or $PtCl_2(SEt_2)_2$ is treated with (o-lithiobenzyl)diphenyl phosphine, the cyclometallated compounds (59) are obtained [115]. The Pd and Pt



(59)

compounds appear as cis-trans isomers. The structure of $Ph_3P(Ph_2P(C_6H_4))Pt$-*cis*-

($CO_2MeC{=}CHCO_2Me$) (60) shows the two phosphorus mutually cis. The σ-bonded vinyl



(60)

has cis stereochemistry [116]. The vinyl group in trans-$PtBr_4[2-(CH_2{=}CH)py]PEt_3$ undergoes oxidation/metallation in damp solvents to give $PtBr_3[2-(CH_2CO)py]PEt_3$ [117]. In the preparation of $[PtP\text{-}t\text{-}Bu_2C(Me)_2CH_2Cl]_2$ and $[PdP\text{-}t\text{-}Bu_2C(Me)_2CH_2Cl]_2$ a marked solvent dependence has been noted [118]. There has also been a report in the organic literature of the reactions of cyclometallated palladium compounds [119]. Treating o-palladation products of (dimethylaminoethyl)ferrocene and 2-pyridylferrocene with olefins under mild conditions leads to 1,2-disubstituted ferrocene derivatives [120].

IV. Metal carbonyls and thiocarbonyls

The interaction of the diatomic ligands N_2 and CO with nickel has been investigated through ab initio LCAO-MO-SCF calculations for the systems NiN_2 and NiCO [121]

The sequence of electronic states is largely determined by the σ-acceptor and π-donor character at the level of the metal. Isocarbonyl coordination NiOC appears energetically unfavorable, and comparatively much more so than isocyanide coordination MNC. In contrast to the recently reported strong oscillation in the formation rate of $Ni(CO)_4$ in an external field, no field dependence of the reaction rate has been found in fields up to 7 Tesla [122]. In the mass spectrum of $Ni(CO)_4$, the ratio of the intensities $Ni(CO)_3^+/Ni(CO)_4^+$ decreases with increasing pressure, with increasing CO pressure, and decreasing temperature [123]. The ratio of the intensities $Ni(CO)_2^+/Ni(CO)_3^+$ is independent of the reaction conditions. The first stage of thermal decomposition of $Ni(CO)_4$ is the formation of $Ni(CO)_3$ and its aggregation into a binuclear subcarbonyl $Ni_2(CO)_z$ ($z \geq 2$).

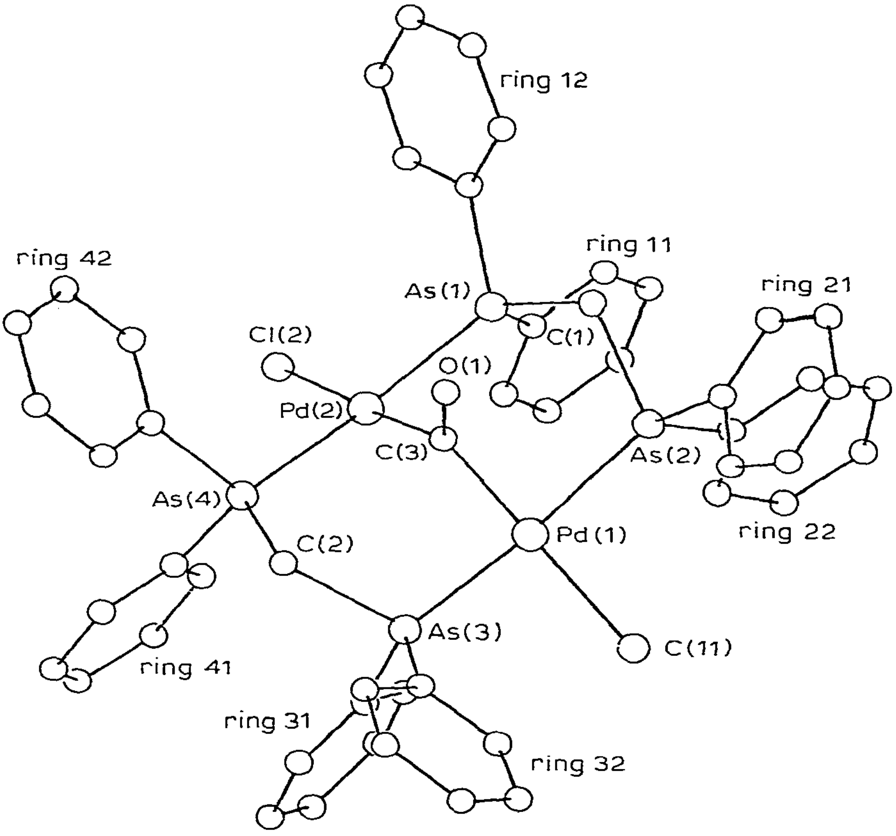
When $Ni(CO)_4$ is treated with a rhodium(I) olefin complex in DMF, complete decarbonylation occurs with the formation of a rhodium(I) carbonyl [124]. Complexes have been obtained from the reaction of cyclo-$(RB\ CH{=}CH)_2$ with nickel carbonyl [125]. Nickel carbonyl has been used as a reducing agent in diene dimerization catalysis [126]. High substrate conversion has been found for butadiene using the complexes $Fe(NO)_2X$ (X = Cl, Br. I), $Co(NO)_2X$ (X = Cl, Br, I), $Fe(NO)_2Cl$, and π-C_3H_5NiBr in the presence of $Ni(CO)_4$. The authors suggest the formation of a bimetallic catalyst. Iodine azide reacts with nickel carbonyl to give nickel azide (61) and nickel iodide [127]. The negative ion mass spectrum of the complex $[cpNi(CO)]_2$ and others has been measured [128].

$$2Ni(CO)_4 + 2IN_3 \longrightarrow \underset{(61)}{Ni(N_3)_2} + NiI_2 + 8CO$$

The compound $[(CF_3)_2PO]_2O$ reacts with $Ni(CO)_4$ to give $[(CF_3)_2PO]_2O.Ni(CO)_3$ [129]. A new synthetic procedure to $Ni(CO)_2(PPh_3)_2$ (62) has been described. The method involves treating $NiBr_2(PPh_3)_2$ with a 10-fold excess of $Fe(CO)_5$ at room temperature

$$NiBr_2(PPh_3)_2 + Fe(CO)_5 + 2PPh_3 \rightarrow \underset{(62)}{Ni(CO)_2(PPh_3)_2} + Fe(CO)_2(PPh_3)_2Br_2 + CO$$

and atmospheric pressure in the presence of triphenylphosphine [130]. Yields are of the order of 90%. The reactions of Pd(CO)X (X = Cl, Br) with dppm and its arseni analog (dpam) have been studied [131]. With dppm the product is $[PdX(dppm)]_2$, but with dpam the product is $[PdX(dpam)]_2CO$ (63). The compound $[PdCl(dpam)]_2CO.3C_6H_{14}$



(63)

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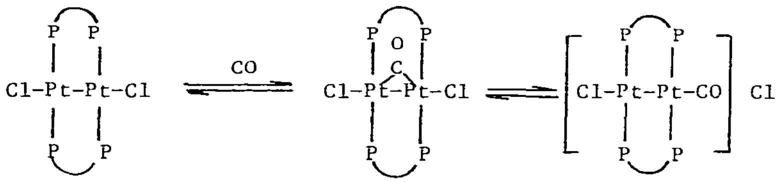
has two trans-arsenic atoms and a bridging carbonyl. There is no twist about the Pd-Pd axis so the Pd_2As_4 unit is planar. The Pd-Pd distance, 3.274(8) Å, is too long for metal-metal bonding, so it is assumed that spin pairing occurs through the carbonyl bridge. Treating a solution of $Pd(OAc)_2$ in HOAc with CO gives Pd(OAc)CO.0 HOAc. Crystallography shows the compound to be a tetranuclear cluster. Drying over KOH gives Pd(OAc)CO [132]. Force constants for planar complexes $[MX_3CO]^-$

(MX = PdCl, PdBr, PtCl, PtBr and PtI) have been calculated using a modified valence force field [133]. The stretching force constants to Pd are lower than to Pt. The difference is more marked for the MC bonds than for the MX bonds showing the much weaker π-donor ability of 4d orbitals of Pd(II) than 5d orbitals of Pt(II). The anions $[PdX_5(CO)]^-$ (X = Cl, Br) have been identified in solution. The CO stretching frequency of $[PtCl_5(CO)]^-$, 2184 cm^{-1}, is the highest reported for a metal carbonyl complex in solution [134].

Carbon monoxide reacts at room temperature with surface species obtained by heptene-1 chemisorption on an evaporated Ni film to produce a species which from ir evidence is an acyl species [135].

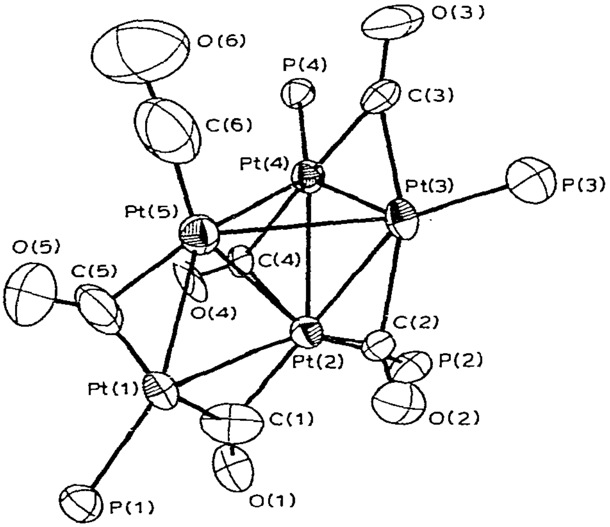
The complex $Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2$ (64) has been prepared from CO and $Pt_2Cl_2(\mu\text{-dppm})_2$, and also from $[NPr_4]_2[Pt_2Cl_4(CO)_2]$ with dppm. In polar solvents the compound isomerizes to $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ (65). The ir, Raman, ^1H and ^{31}P nmr



(64) (65)

spectra of these complexes are discussed [136]. Addition of carbon monoxide to $Pd_2(dppm)_2X_2$ and $Pt_2(dppm)X_2$ (X = Br, I, N_3, NCO, SCN, NO_2) results in insertion into the metal-metal bond to form $Pd_2(dppm)(\mu\text{-CO})X_2$ (X = Cl, Br, I, N_3, NCO, SCN) and $Pt_2(dppm)_2(\mu\text{-CO})X_2$ (X = Cl, I). The CO can be removed by heating the solids under vacuum or refluxing CH_2Cl_2 solutions [137]. The compound $[PdCl(dpam)]_2CO$ (63) has been challenged [138]. These authors suggest the structure can be more realistically interpreted as a dimetallated formaldehyde derivative. It is concluded that bridging CO ligands are capable of two distinct bonding modes; one with a M-C-M angle of 80-85° and $\nu(CO)$ of 1850 cm^{-1}, and the latter with a M-C-M angle of 120° and $\nu(CO)$ of 1700 cm^{-1}. The latter is visualized as two discrete σ bonds and is compared to an organic ketone. The tetranuclear cluster from $Pd(OAc)_2$ and CO has been confirmed crystallographically [139]. Treating <u>cis</u>-$PtCl_2(PPh_3)_2$ with $NaMn(CO)_5$

gives a homopentametallic cluster $Pt_5(CO)(\mu_2\text{-}CO)_5(PPh_3)_4$ (66) which crystallizes with 3 molecules of toluene. The structure of the compound has been solved [140]. The structure of the first platinum-cobalt heteropentametallic cluster compound $Pt_3Co_2(CO)_4(\mu_2\text{-}CO)_5(PEt_3)_2$ (67) shows a slightly distorted trigonal bipyramid structure. The compound was prepared from the reaction between cis-$PtCl_2(PEt_3)_2$ and



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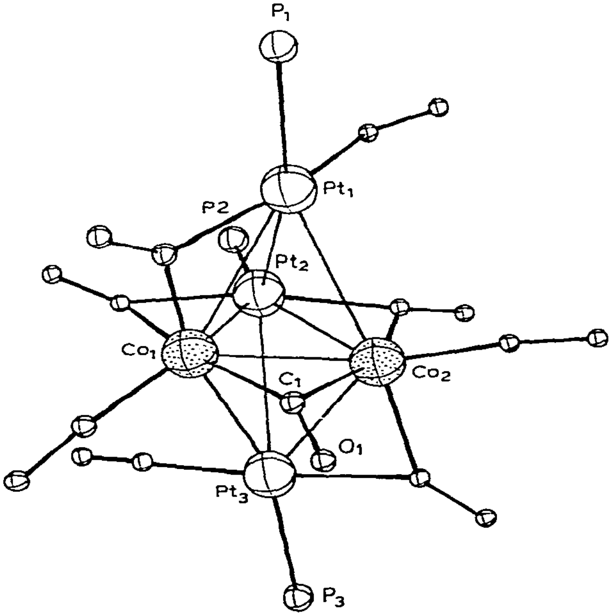

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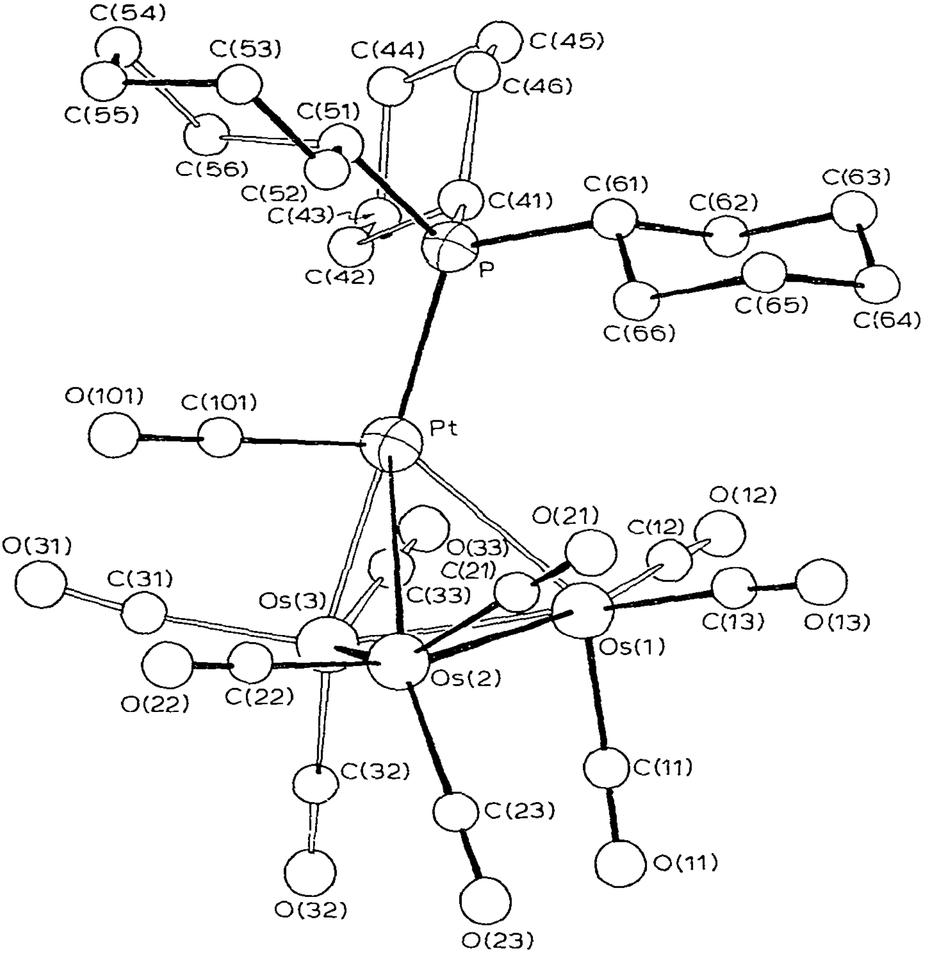
(67)

NaCo(CO)$_4$ [141]. The syntheses and structures of Os$_3$Pt(μ-H)$_2$(CO)$_{10}$(PCy$_3$) (68) and Os$_2$Pt$_2$(μ-H)$_2$(CO)(PPh$_3$)$_2$ (69) have been reported [142]. The cluster [Rh$_5$Pt(CO)$_{15}$]$^-$ (70)



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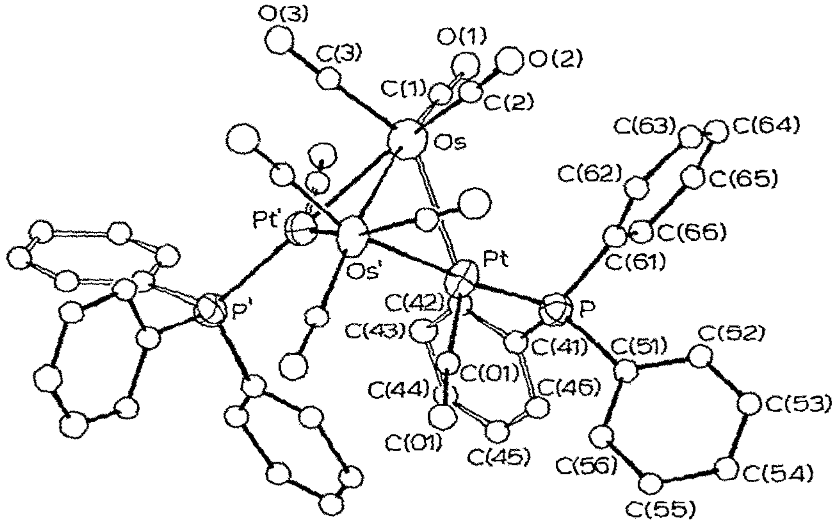

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has been prepared both from $[Pt_{12}(CO)_{24}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$, and from $RhCl_3$, $PtCl_6{}^{2-}$ and CO in base [143]. The structure of (70) is shown.

$$5RhCl_3 + PtCl_6^{2-} + 20\ OH^- + 25CO \rightarrow \underset{(70)}{[Rh_5Pt(CO)_{15}]^-} + 10CO_2 + 21Cl^- + 10H_2O$$

Treating trans-$PdCl_2(PEt_3)_2$ with π-$cpMo(CO)_3^-$ leads to the formation of $Pd_2Mo_2(\pi\text{-}cp)_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PEt_3)_2$ (71) [144]. The structure is shown with the four metal atoms forming a planar triangulated frame with a center of symmetry in the middle of the Pd-Pd bond.

An ab initio molecular orbital method has been used to calculate the interaction between Ar matrix isolated NiF_2 with CO. The electronic structure of $NiF_2(CO)$ has been calculated. The presence of the dipositive nickel atom induces a polarization of the charges leading to a strengthening of the bond. This is consistent with the experimental observation of a 70 cm^{-1} shift of $\nu(CO)$ toward higher wavenumbers [145]

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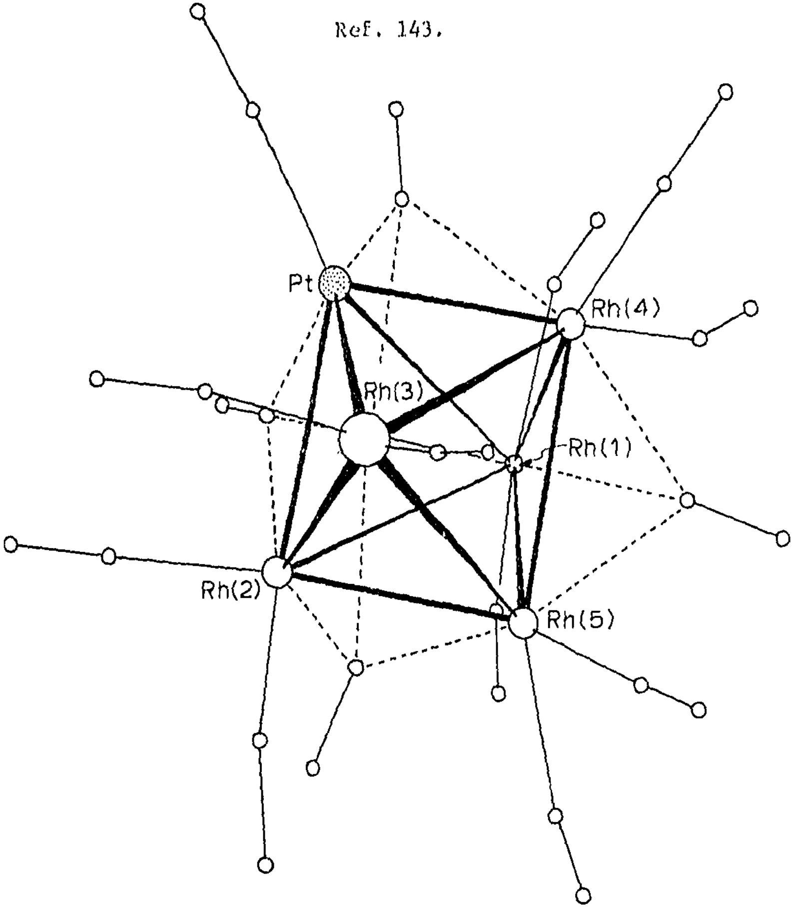

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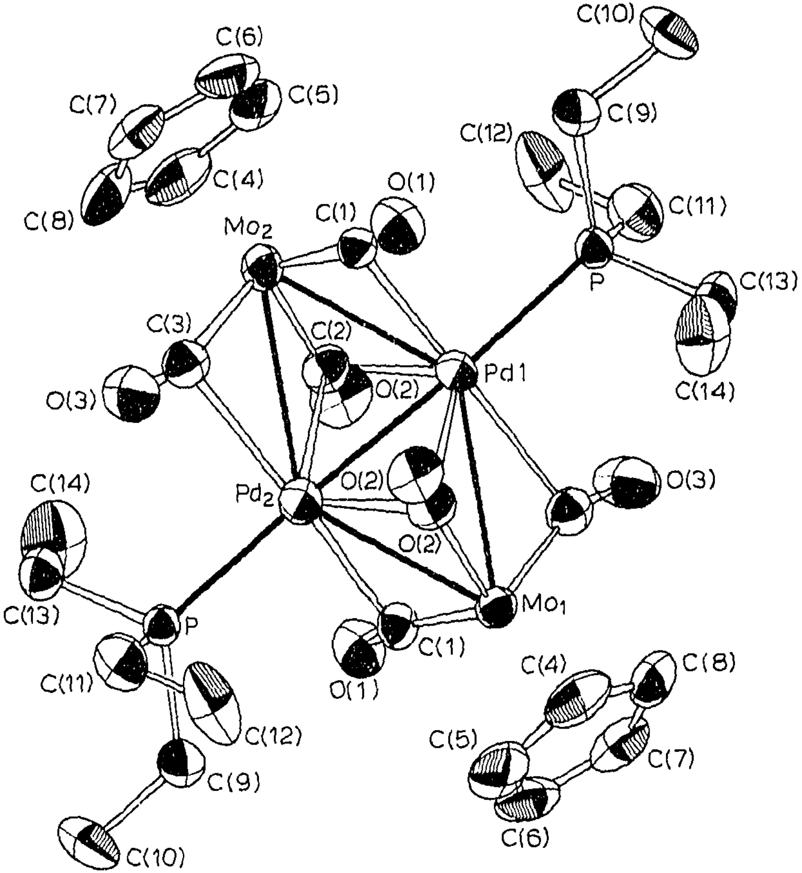


(71)

V. Metal olefins and vinyls

A review on platinum olefin complexes has been published in the Russian literatu [146]. Treating ethylene saturated solutions of $Pt(COD)_2$ with tertiary phosphines or $AsPh_3$ gives complexes $Pt(C_2H_4)_2L$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, PCy_3, $AsPh_3$) (72). The compound $Pt(C_2H_4)_2PCy_3$ reacts with C_2F_4 to give $Pt(C_2H_4)(C_2F_4)PCy_3$.

$$Pt(COD)_2 + 2C_2H_4 + L \rightarrow Pt(C_2H_4)_2L + 2COD \tag{72}$$

Activation energies for olefin rotation fall in the range 10-13 kcal/mol [147]. Reacting $Pt(COD)_2$ with allene or butadiene-1,3 gives (η-COD)(2,3-dimethylenebutane-1,4-diyl)platinum and (η-COD)(1,4-*trans*-divinylbutane-1,4-diyl)platinum. The compound reacts with 2 mol equivalents of PMe_3 to give $\overline{Pt\{CH}(CH{=}CH_2)CH_2CH_2\overline{CH}(CH{=}CH_2)\}(PMe_3)_2$. The structures of these two compounds, along with a variety of other reactions, are described [148].

Condensation of nickel atoms with alkyl, fluoro, or chloro-olefins in the 10-77 K range gives π-complexes $Ni(olefin)_n$ (n = 1-3) [149]. Values for λ(max) are reported for the compounds. The transition (in the UV) is only slightly sensitive to the substituent(s) on the coordinated olefin, but highly sensitive to the number of coordinated olefins. Generalized valence bond and configuration interaction calculations have been carried out on $Ni(C_2H_4)$ and $Ni_2(C_2H_4)$. The ethylene is only weakl perturbed with the CH bonds being bent only 2° out of the ethylene molecular plane [150]. Similar results are published by one of these authors elsewhere [151]. Co-condensation of palladium and ethylene at 15 K leads to the formation of $Pd(C_2H_4)$, $Pd(C_2H_4)_2$ and $Pd(C_2H_4)_3$. The spectroscopy is discussed, and again the relevance to adsorption of ethylene on a metal surface is considered [152].

In the ^1H NMR spectrum of $PtCl(\eta^2$-cyanoethylene)(acac) the 3 ligand protons appea to be equivalent. ^{13}C NMR and IR studies indicate the metal-ligand bonding is of the conventional π-type [153].

The electronic structure of NiC_2H_4 and $Ni_2C_2H_4$ species have been investigated theoretically by other workers. The Chatt-Dewar-Duncanson model is supported. The excited electronic states of $Ni(\pi\text{-}C_2H_4)$ show that low-lying $4s\rightarrow\pi^*$ and $3d\rightarrow\pi^*$ (M→L) charge transfer transitions are predicted [154]. The spectral behavior of Ni(COD)(bipy) complexes with heteroolefins and polar olefins (L) shows a variance on ligand parameters [155]. Thermochromic effects on the systems NiL(bipy) + L are discussed and thermodynamic data determined. Reacting $Ni(COD)_2$ with α,β-unsaturated esters in the presence of tertiary phosphines gives a series of complexes $Ni(PR_3)_nL$ (L = methyl acrylate or methyl cinnamate; n = 2, L = PPh_3, $PEtPh_2$, PMe_2Ph, PEt_3; n = 1, PCy_3). The reactions of Ni(ethylmethacrylate)$(PPh_3)_2$ and Ni(ethylmethacrylate)PCy_3 with vinyl acetate at room temperature cause cleavage of the C-O bond in vinyl acetate to give ethylene and nickel acetate [156].

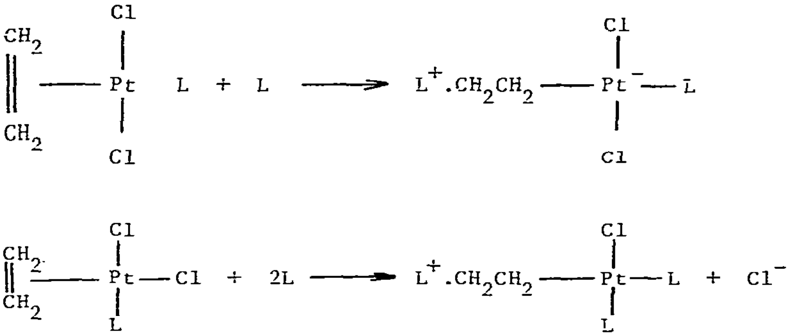
Treating $Ni(C_2H_4)_3$ with HCl at -78°C gives $Ni(C_2H_4)_2.HCl$ which decomposes at -50°C first to $Ni(H)Cl(C_2H_4)_2$ and then C_2H_4, C_2H_6, NiCl and NiCl(butyl). The latter decomposes at -30°C to NiCl, butane and butene-1, which isomerizes to butene-2 [157].

The vibrational spectra of C-C and M-C bonds have been studied for $[PtCl_3(C_2H_4)]^-$ [158]. The hydrolysis of $PtCl_4^{2-}$ proceeds faster in the presence of $[PtCl_3(C_2H_4)]^-$.

$$[PtCl_4]^{2-} + H_2O \rightarrow [PtCl_3(OH_2)]^- + Cl^-$$

The actual catalyst is $PtCl_2(C_2H_4)OH_2$ [159]. For the reaction of olefins with $PtCl_4^{2-}$ a series of rate constants and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values have been obtained. There is a small decrease in the rate constant as substituents are added to the olefin. Ionic strength effects in the reaction medium have also been measured [160]. A new salt, $[Ph_4P][PtCl_3$(S,S-trans-butene-2[1,3-^{3}H])] undergoes racemization and ligand isotopic exchange in acetone containing a large excess of trans-butene-2. The rates and activation parameters have been measured [161].

Complexes cis-$PtCl_2(\pi\text{-}C_2H_4)L$ (L = 3,5-dimethylpyridine or $H_2NCHMePh$) react in solution with two molecules of L, undergoing substitution of the chlorine trans to ethylene and nucleophilic attack on the π-bonded ethylene to yield cis-$[Pt[\sigma\text{-}C_2H_4(L)]ClL_2]Cl$ (73) [162]. Addition of a large excess of trans-butene-2 to a solution of



$$\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\|}} - \overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{Pt}}}\ \mathrm{L} + \mathrm{L} \longrightarrow \mathrm{L^+.CH_2CH_2} - \overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{Pt^-}}} - \mathrm{L}$$

$$\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\|}} - \overset{\mathrm{Cl}}{\underset{\mathrm{L}}{\mathrm{Pt}}} - \mathrm{Cl} + 2\mathrm{L} \longrightarrow \mathrm{L^+.CH_2CH_2} - \overset{\mathrm{Cl}}{\underset{\mathrm{L}}{\mathrm{Pt}}} - \mathrm{L} + \mathrm{Cl^-}$$

(73)

cis- or *trans*-(N,ethylene)[PtCl(L-am)(C_2H_4)] (L-am is 9 kinds of L-aminocarboxylate gives first an increase, then a decrease, in CD strength in the region =26500 cm^{-1} Kinetic analysis of this CD curve shows that the first fast increase in CD reflects the greater rate of substitution of the prochiral olefins for ethylene in S-configuration than that in R-configuration, and the second step seems to involve the exchai of coordinated *trans*-butene-2, catalyzed by ethylene produced in the first step [16 Bridge cleavage of chloro-bridged amine dimers of Pt(II) by olefins leads to complexes *cis*-$PtCl_2$(amine)(olefin) (74) [164]. Using nitrogen containing unsaturated

$$Pt_2Cl_4(\text{amine})_2 + \text{olefin} \rightarrow 2\textit{cis}\text{-}PtCl_2(\text{amine})(\text{olefin})$$

(74)

ligands, e.g. allylamine, the nitrogen coordinates preferentially to the double bond Irradiation of complexes $PtCl_2$(amine)(olefin) leads to the reverse of the previous reaction and re-formation of the chloro-bridged dimer [165]. The ^1H NMR spectrum of $PtCl_2(C_2H_4)(C_5D_5N)$ has been obtained by decoupling of the spin coupling to deuterium for samples dissolved in thermotropic liquid crystals [166]. The dipolar couplings give the relative positions of the protons and platinum. The equilibrium structures have the pyridine ring inclined at an angle to the $PtCl_2$ plane, with rapid reorientation between the symmetry-related forms.

The reaction between $Pt(C_2H_4)(PPh_3)_2$ and a wide range of compounds SnR_3X, $SnArMe_3$, SnR_2X_2 and SnX_4 has been studied. The insertion of Pt into the Sn-R, Sn-Ar or Sn-X bond occurs depending on the nature of the tin substrate [167]. The compounds Sn_2Ph_6 and Pb_2Ph_6 give products cis-$PtPh(M_2Ph_5)(PPh_3)_2$ (M = Sn, Pb) (75).

$$Pt(C_2H_4)(PPh_3)_2 + M_2Ph_6 \rightarrow PtPh(M_2Ph_5)(PPh_3)_2 + C_2H_4$$

(75)

One or both chloride ligands in $PdCl_2(COD)$ can be selectively replaced by aryl groups by treating the complex with aryltrimethylstannanes. Preparative and spectral details are included, and the method is advantageous over the use of aryllithiums or aryl Grignard reagents [168].

The complexes M(diene.OMe)(L-L)Y (76) (M = Pd(II); diene = 1,5-COD, endo-dicyclopentadiene; L-L = bipy, phen; Y = PF_6; diene = dicyclopentadiene; L-L = dppe, Y = PF_6; diene = COD, L-L = en, Y = Cl; diene = NBD, L-L = bipy, phen, Y = Cl. M = Pt(II), diene = COD, L-L = bipy, phen, Y = PF_6) have been prepared [169].

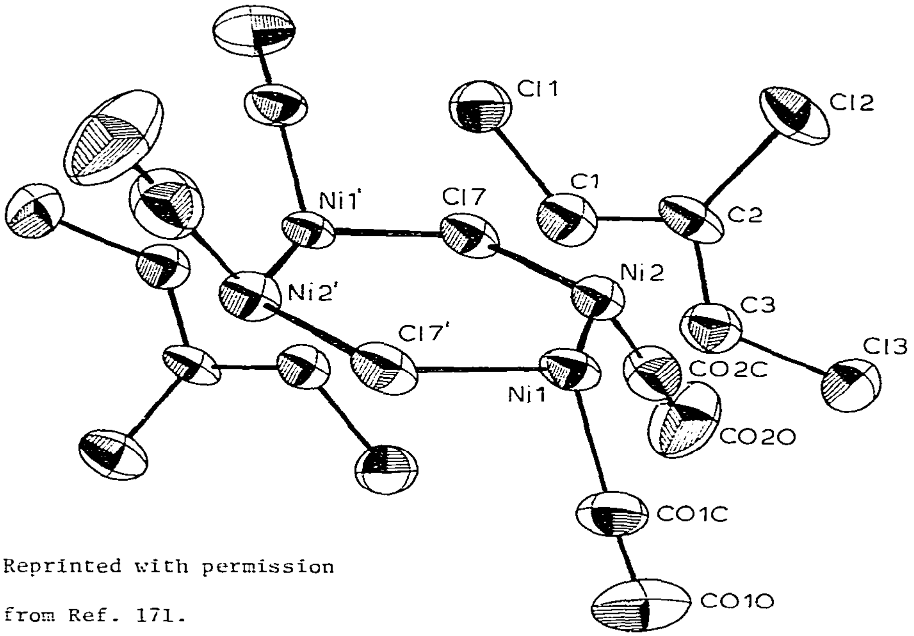
$$\begin{tikzcd}
M(diene)Cl_2 \arrow[r, "Ag^+", "MeOH"'] & {[M(diene)(MeOH)_2]^{2+}} \arrow[r, "L\text{-}L"] \arrow[d, shift left, "MeOH"'] & {[M(diene)L\text{-}L]^{2+}} \arrow[d, "MeOH"] \\
 & {[M(diene.OMe)(MeOH)_2]^{+}} \arrow[u, shift left] & {[M(diene.OMe)L\text{-}L]^{+}}
\end{tikzcd}$$

(76)

Pyrazolato bridged binuclear complexes palladium and platinum $(C_8H_{12}X)_2M_2(\mu\text{-}pz_2)$ (X = OMe or pyrazolato) have been obtained from treating $MCl_2(COD)_2$ (M = Pd, Pt) with a 1-monosubstituted pyrazole and sodium hydroxide in methanol. The infrared and ^1H NMR spectra of the complexes are presented and discussed [170]. Nickel carbonyl reacts with tetrachlorocyclopropene to give $[Ni(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ (77) [171]. The compound has a planar 6-membered Ni_4Cl_2 ring. Within the ring, Cl atoms bridge nonbonded pairs of Ni atoms, while ring-opened trichloropropenyl ligands bridge bonded pairs of Ni atoms. The dihedral angles between the Ni_4Cl_2 plane and the C_3Cl_3 planes are 85 and 86°.

$Ni(CO)_4 + C_3Cl_4 \rightarrow [Ni(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$

(77)



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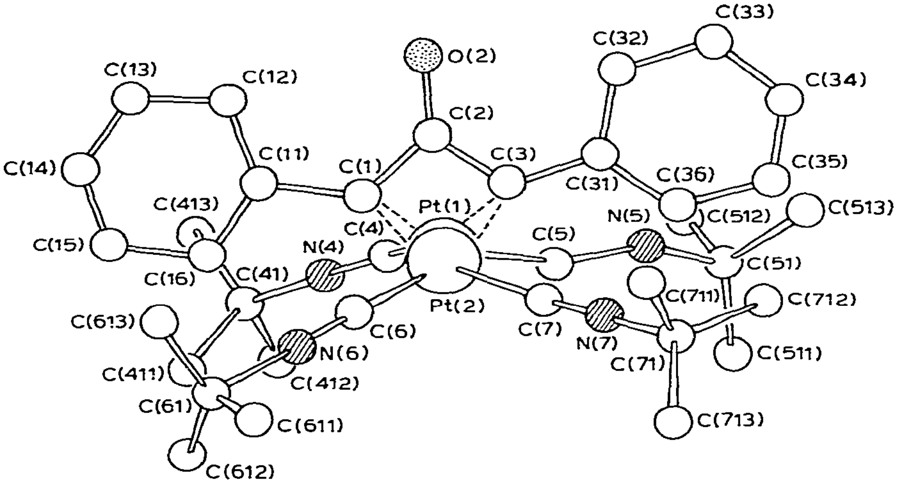
(77)

Treating $PdCl_2(C_2H_4)_2$ in water/CH_3CN at -20°C to -25°C in the presence of CO(3 a gives β-propiolactone. The stereochemistry of the hydroxypalladation step is determined by using bis(cis-1,2-dideuteroethylene)$PdCl_2$, which yields trans-2,3-dideuter β-propiolactone. Since CO insertion into a Pd-C σ bond proceeds with retention of configuration then hydroxypalladation must proceed with trans stereochemistry [172] Allylanilines have been prepared by treating π-allylnickel halides with 2-bromoanilines. These were cyclized to 2-methylindoles by treatment with $PdCl_2$ under bo stoichiometric and catalytic conditions [173].

Palladium(II) and platinum(II) porphyrin complexes are efficient photosensitizer for stilbene isomerization. The results suggest the intermediacy of a sensitizer-acceptor cage-encounter complex which may have different preferred geometry and altered nonradiative decay properties compared to the free stilbene [174].

Reaction of $Pt_3(t\text{-}BuNC)_6$ with diphenylcyclopropenone gives the complex $[Pt_2(\mu\text{-}(PhC)_2CO)(t\text{-}BuNC)_4]$ (78). The molecule shows ring opening at the carbon-carbon double bond of the cyclopropenone, the resulting C_3 fragment symmetrically bridging the two platinum atoms. An analogous complex has been obtained with $(COD)_2$ replacing (*t*-BuNC)$_4$ [175].



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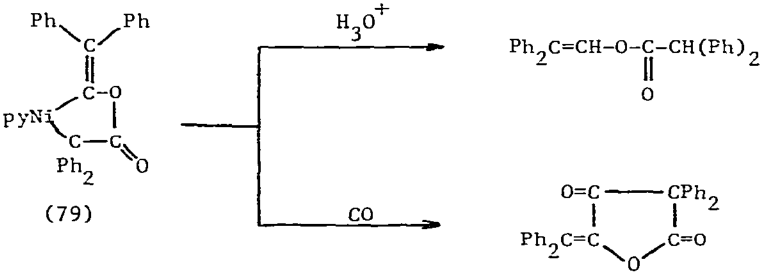
Treating $Ni(COD)_2$ with $Ph_2C{=}C{=}O$ and pyridine gives $Ni(Ph_2CCO)_2py$ (79) [176].

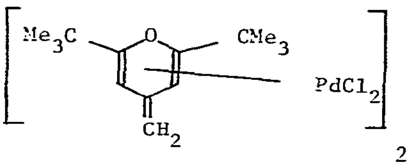


(79)

Organic coupling products are obtained on protonation or treatment with CO. The complex $(PPh_3)_2Ni(Ph_2C{=}C{=}O)$ has been prepared from $Ph_2C{=}C{=}O$ and a variety of triphenylphosphine nickel(0) complexes [177]. In toluene solution decarbonylation of the ketene occurs and $Ni(CO)(PPh_3)_3$ is formed via a proposed diphenylcarbene intermediate. The zerovalent diisopropyldibenzylideneacetone complexes of Pd and Pt have been prepared. The metal atoms in the dimer are π-bonded to the olefin. The ^1H NMR spectra show the aryl groups to be rotating at 25°C but to be frozen out on the

NMR time scale at low temperatures [178]. ^{1}H NMR studies have been carried out on the deuterated dibenzylideneacetone complexes Pd$_2$[(C$_6$D$_5$CH=CH)$_2$CO]$_3$, Pd$_2$[(C$_6$D$_5$CD=CH)$_2$CO]$_3$ and Pd[(C$_6$D$_5$CH=CD)$_2$CO]$_3$. The three triply bridging ligands are all in the s-cis, trans conformation [179].

Treating 2,6-di-t-butyl-4-methylpyrylium perchlorate with PdCl$_2$ gives the complex (80) [180]. A similar complex is obtainable from 2-methyl-4,6-diphenylpyrylium perchlorate. The crystal structures of PtCl(o-Me$_2$NC$_6$H$_4$CH=CH$_2$)(OC$_6$F$_5$) (81) and PtCl(o-Me$_2$NC$_6$H$_4$CH=CH$_2$)(SC$_6$F$_5$) (82) have the olefin π-bonded to platinum, cis to the chloride ligand [181]. The structure of methyl[hydrotris(1-pyrazolyl)borato]tetra



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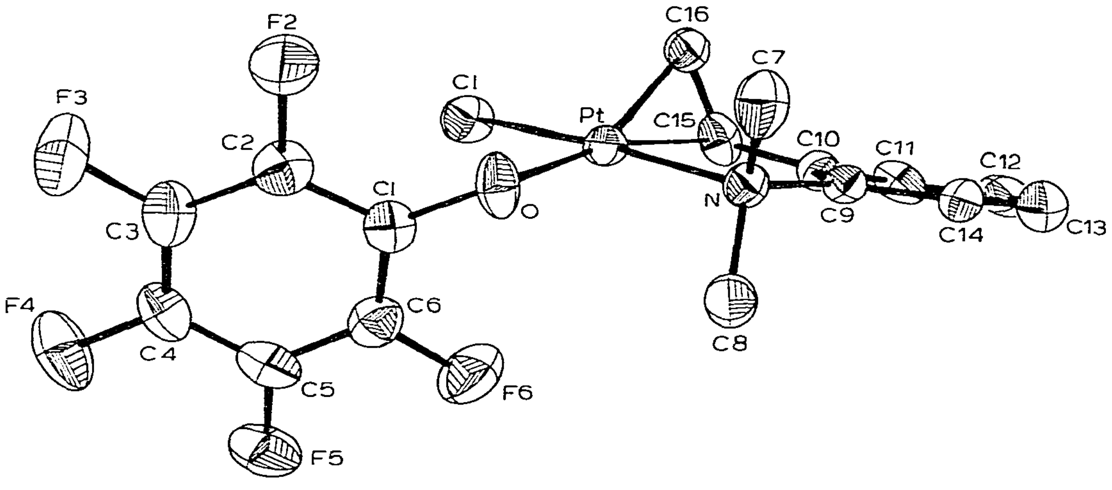

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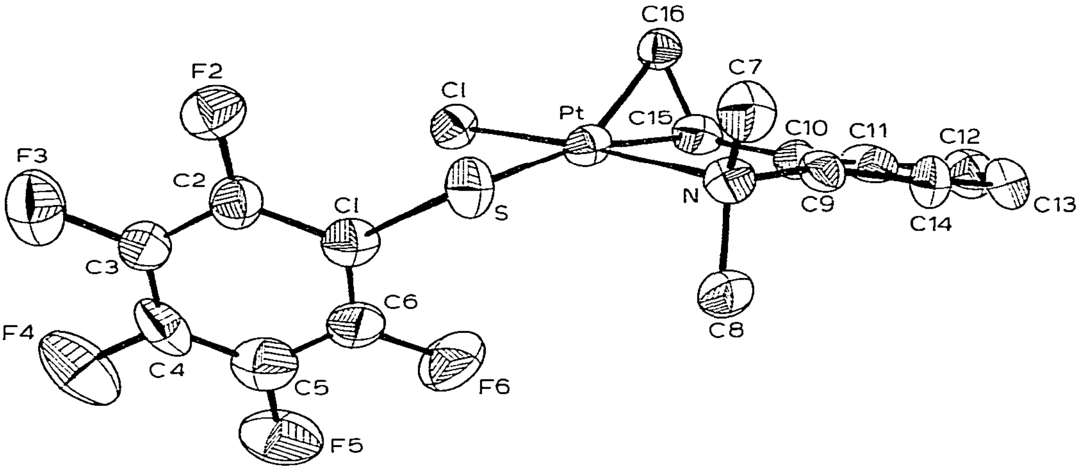
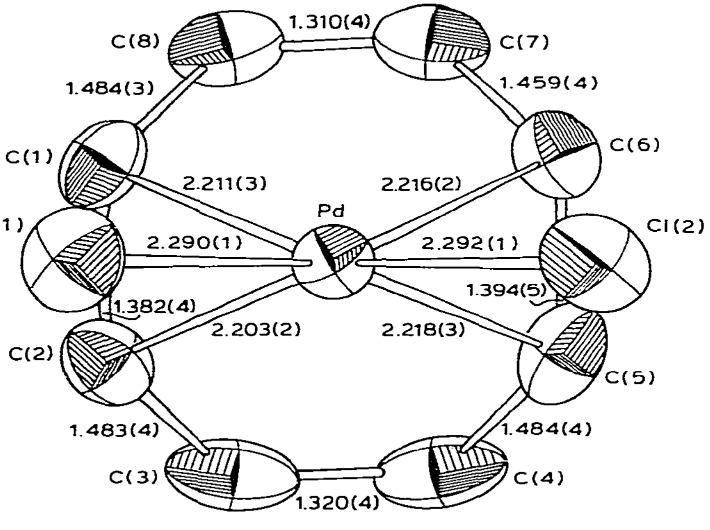


(82)

fluoroethyleneplatinum shows the C_2F_4 symmetrically bonded. There is a close non-bonded interaction between a methyl-H atom and two of the F atoms of the C_2F_4 ligand [182].

The structure of [PdCl$_2$(1-2:5-6-η-cyclooctatetraene)] (83) is a monomer with the two Cl atoms and the centers of the 1-2 and 5-6 double bonds of the cyclooctatetraene ligand lying in a plane [183]. This is shown in the figure looking down the bisector of the Cl-Pd-Cl angle. A similar structure of di-μ-chloro-bis[4,6-η-(1-chlorocyclo



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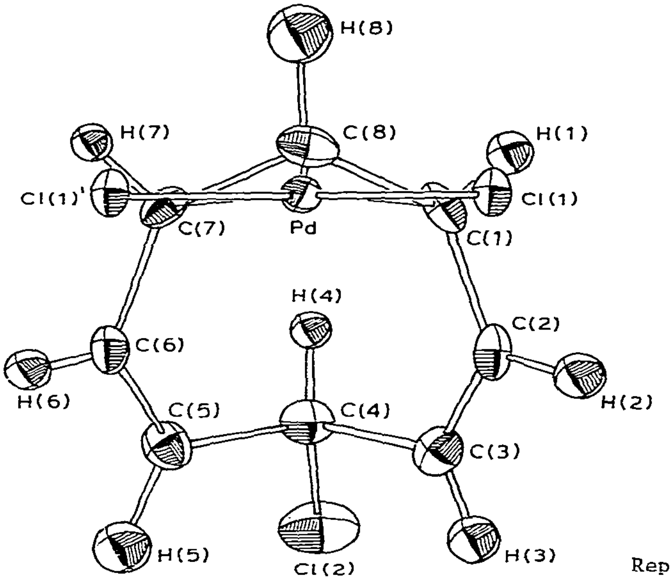
octatrienyl)]dipalladium(II) (84) shows allylic type π bonds to a boat-shaped



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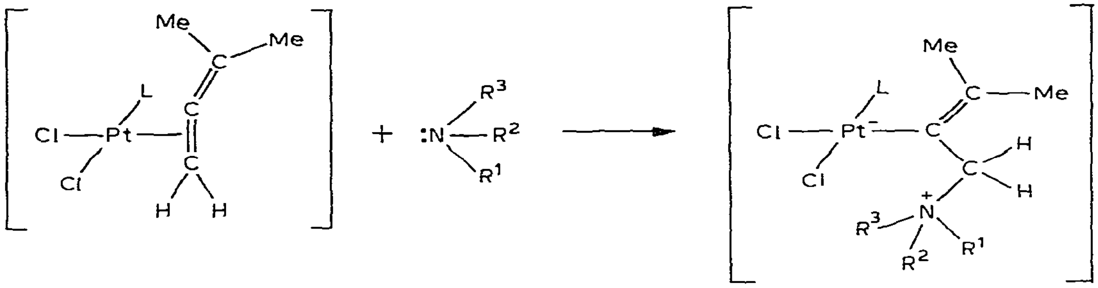
cyclooctatetraene molecule which has undergone addition of a Cl atom <u>trans</u> to the allylic type bond [184]. Coordination of the olefin-like molecule t-BuN=C=NBu-t in $PdCl_2$(t-BuN=C=NBu-t)$_2$ shows the ligand to be N-bonded to the metal [185]. The double bond of ethyl vinyl ether is coordinated in the complex $[Et_4N][PtCl_3(CH_2{=}CH{-}OEt)]$ [186]. The mid-point of the double bond is 0.19 Å off the plane determined by $PtCl_3$. The C atom of the double bond bearing the ether O atom is 0.08 Å further from Pt than the unsubstituted C atom, and there is no significant interaction of th ether oxygen with Pt in the solid state.

Some new platinum(II) complexes cis-$[PtCl_2(Me_2C{=}C{=}CH_2)L]$ (L = PPh_3, $AsPh_3$, $H_2NC_6H_4Me$-p or DMSO) have been isolated. Reaction with aliphatic and aromatic amine gives zwitterionic alkenyl derivatives cis-$[PtCl_2(Me_2C{=}CCH_2NR^1R^2R^3)L]$ (85) [187]. Single crystal structural data show the σ-bonded alkenyl group perpendicular to the coordination plane. The η^3-allylnickel bromide dimer reacts with NO to form a 3-oximinopropene complex $Ni(CH_2{=}CHCH{=}NOH)Br(NO)$ [188]. The oxime is weakly bound and



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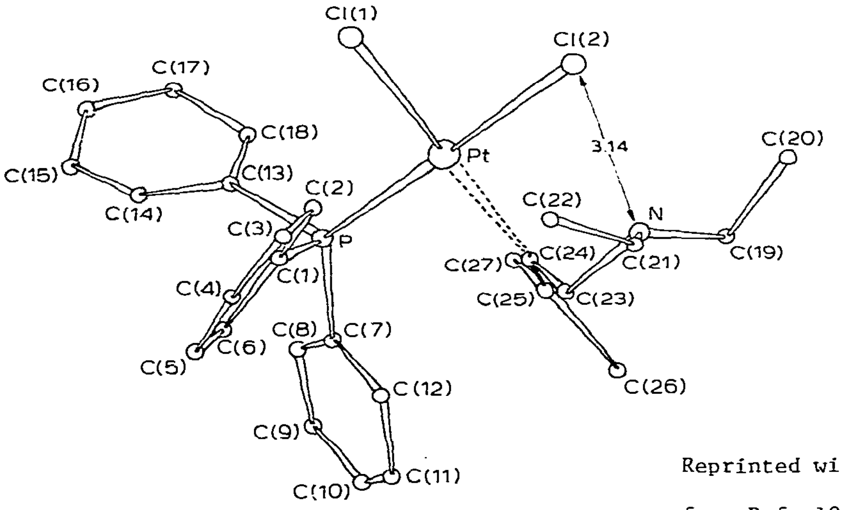

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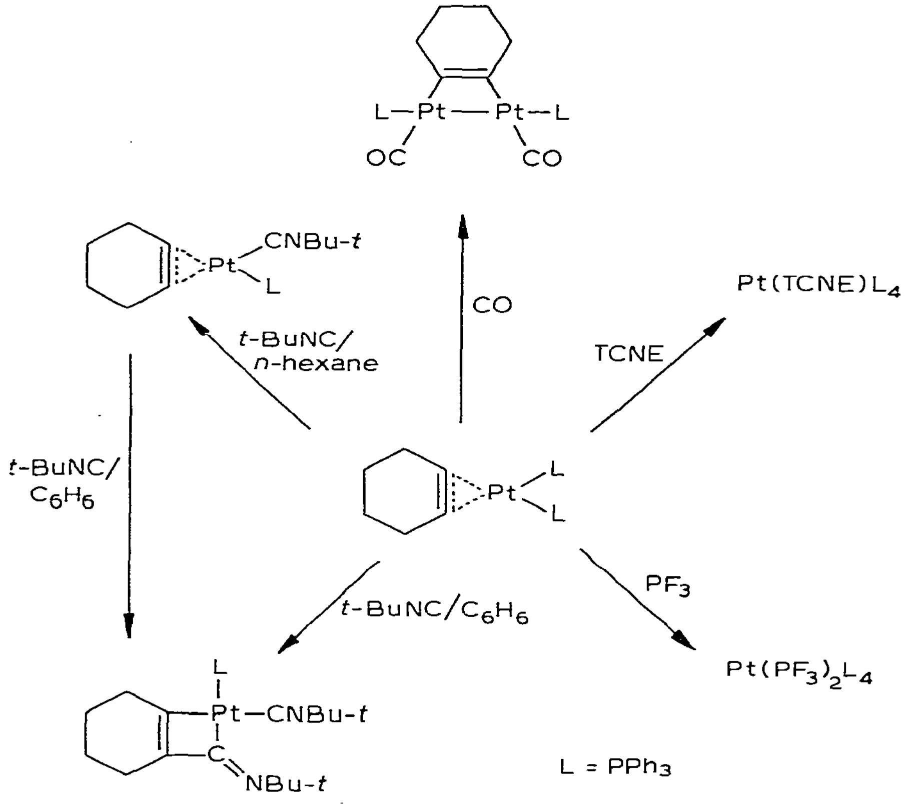
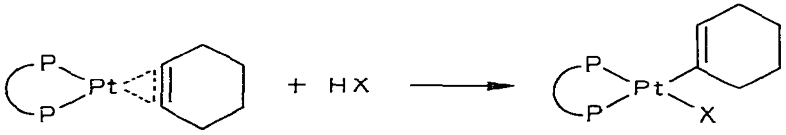
is displaced with triphenylphosphine. The series of vinylsilane platinum(0) complexes of formulae $[(Ph_3P)_2PtCH_2{=}CHSi(Me)_n(OEt)_{3-n}]$ (n = 0,1,2,3) have been prepared. The complex $(Ph_3P)_2Pt(CH_2{=}CHCMe_3)$ has also been synthesized and decomposes in solution much more readily than its silicon analog [189]. Detailed calculations have been published on the interaction of ethylene and acetylene with the nickel atom. Calculated Ni-C and C-C distances are given and tentatively compared with structural data [190].

VI. Metal Acetylenes and Acetylides

A molecular orbital theory combining two-body atomic repulsion and one-electron molecular orbital delocalization energies has been used to examine catalytic reactions adsorption site is preferred on the surface. The results are compared for the complexes $Ni_2(COD)_2(RC{\equiv}CR)$ and $cp_2Ni_2(RC{\equiv}CR)$ [191]. A full paper has been published on the syntheses and reactions of Pt(0) complexes of cyclic acetylenes. A series of reactions are shown below, and treating the complex $Pt(C_6H_8)(dppe)$ with weak protonic acids yields the vinyl compounds (86) [192]. The acetylene cluster





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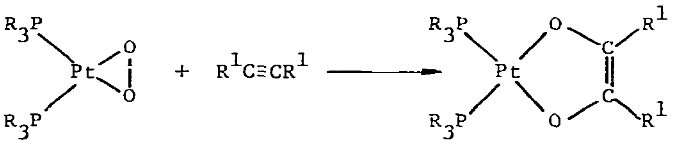
compounds $Ni_2(COD)_2(RC{\equiv}CR)$ (87) (X = OMe, OH, OC_6H_4Me-p, SPh, NHCOR, CHRCN, CH_2NO_2, CH_2COR) react with H_2 and H_2 plus $RC{\equiv}CR$ respectively, to form stoichiometrically and catalytically the cis-alkene. The coordinately saturated complex $cp_2Ni_2(PhC{\equiv}CPh)$ does not react with H_2. Acetylene ligand lability for the former compound is due to a monomer-dimer equilibrium [193]. Nickel or palladium atoms dispersed in excess

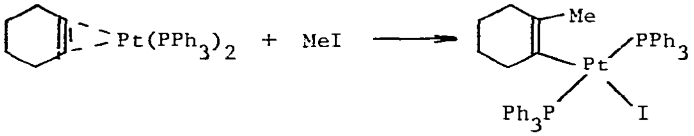
$$\underset{(87)}{Ni_2(COD)_2(RC{\equiv}CR)} + RC{\equiv}CR \rightleftharpoons 2Ni(COD)(RC{\equiv}CR)$$

hexafluorobutyne-2 when treated with CO at low temperature yield $M(CO)_2(CF_3C{\equiv}CCF_3)$. On warming, these compounds spontaneously form clusters $Ni_4(CO)_4(CF_3C{\equiv}CCF_3)$ and $Pd_4(CO)_4(CF_3C{\equiv}CCF_3)_3$ [194]. The oxygen complexes $PtO_2(PR_3)_2$ (PR = PCy_3, $P(i\text{-}Pr)_3$, $P(t\text{-}Bu)_2(n\text{-}Bu)$, $P(t\text{-}Bu)_2Me$, PPh_3) react with hexafluorobutyne-2 and acetylenedicarboxylate to give complex (88) [195]. The structural proof is based on ^{31}P NMR



(88)

evidence. Ab initio calculations have also been made on the complex $(\pi\text{-}cpNi)_2CH{\equiv}CH$ [196]. The reaction between $(Ph_3P)_2Pt$(hexyne-3) and MeI gives $PtIMe(PPh_3)_2$ and $PtI_2(PPh_3)_2$. In contrast the strained cyclic alkyne complexes $Pt(C_6H_8)(PPh_3)_2$, $Pt(C_7H_{10})(PPh_3)_2$, $Pt(C_6H_8)$dppe and $Pt(C_7H_{10})$dppe react with MeI to give mainly 2-methylcycloalkenyl platinum(II) complexes such as $PtI(C_6H_8Me)(PPh_3)_2$ (89) [197].



(89)

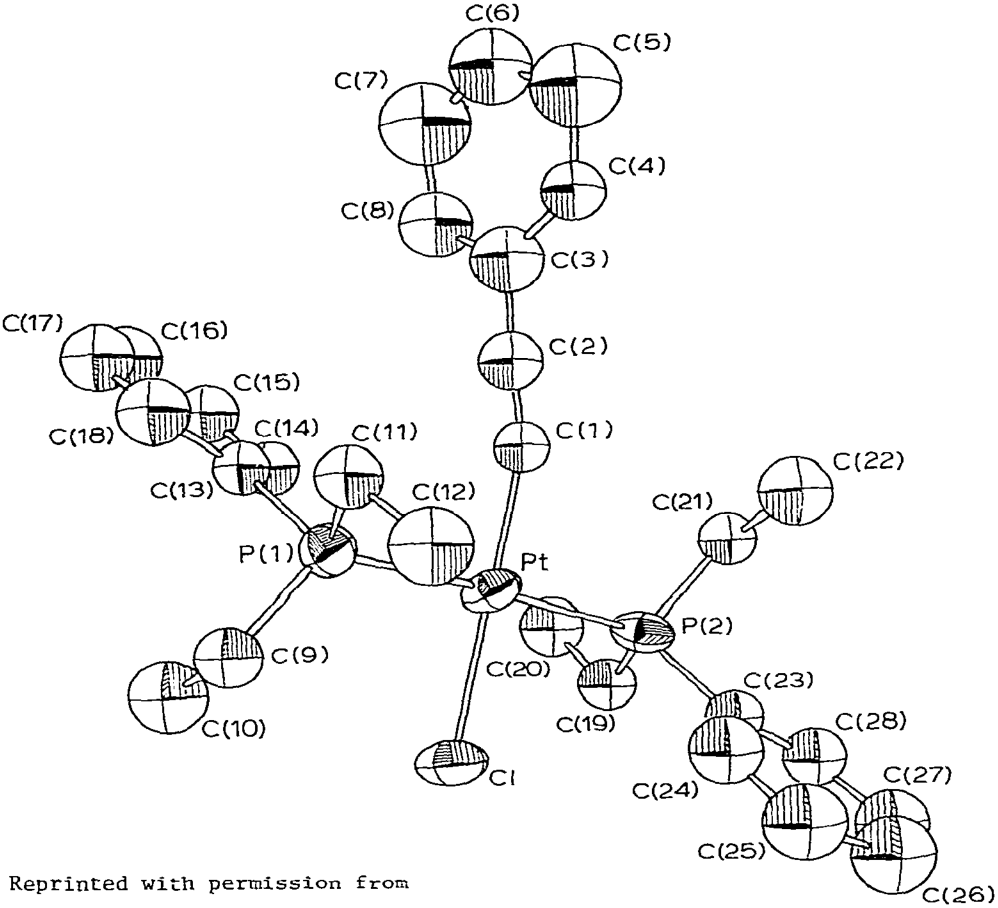
Iodine reacts similarly. 1,4-Diphenylbutadiyne-1,3 reacts with $Pt(C_2H_4)L_2$ (L = PPh_3, PPh_2Me) to give successively, mono- and di-platinum compounds $Pt(PhC_4Ph)L_2$ and

Pt$_2$(PhC$_4$Ph)L$_4$. In the diplatinum compounds both acetylenes are η^2-bonded to Pt atom Treating Pt$_3$(*t*-BuNC)$_6$ with 1,4-diphenylbutadiyne-1,3 and hexadiyne-2,4 gives diplatinum compounds having diplatinacyclobutene rings [198]. A polymer [trans, trans-Pt(PBu$_3$)$_2$-C≡C-C≡C-Pd(PBu$_3$)$_2$-C≡C-C≡C]$_{n/2}$ has been prepared from *trans*-Pt(C≡C-C≡CH)$_2$(PBu$_3$)$_2$ and *trans*-PdCl$_2$(PBu$_3$)$_2$ [199]. Stable alkynyl complexes K$_2$[M(C≡CR)$_4$] (M = Ni Pd, Pt; R = CH$_2$C(Ph)$_2$CN, CH$_2$C(Me)$_2$CN) have been prepared. Assignments of ν(M-C) has been attempted and differential thermal analysis data is given [200]. Complexes *cis*-[Pd(C≡CR)$_2$dppe] (90) and [*cis*-Pd(C≡CC$_6$H$_4$C≡CH-*o*)Cl(dppe)] (91) have been prepared

$$\textit{cis}\text{-PdCl}_2(\text{dppe}) + 2\text{MC}{\equiv}\text{CR} \rightarrow \textit{cis}\text{-Pd(C}{\equiv}\text{CR)}_2(\text{dppe}) + 2\text{MCl}$$
$$(\text{M} = \text{Li, Na; R} = \text{H, Ph, Me}) \qquad (90)$$

$$\textit{cis}\text{-PdCl}_2(\text{dppe}) + \text{HC}{\equiv}\text{CC}_6\text{H}_4\text{C}{\equiv}\text{CH-}\textit{o} + \text{NH}_3 \rightarrow \textit{cis}\text{-Pd(C}{\equiv}\text{CC}_6\text{H}_4\text{C}{\equiv}\text{CH-}\textit{o})\text{Cl(dppe)}$$
$$+ \text{NH}_4\text{Cl} \qquad (91)$$

Treatment with excess KC≡CR gives K$_2$[Pd(C≡CR)$_4$]. The compounds can be reduced to the Pd(O) complexes K$_2$[Pd(C≡CR)$_2$] [201]. Hydrazine reduction of *cis*-PtCl$_2$(PPh$_3$)$_2$ in the presence of PhC≡CCl gives Pt(PhC≡CCl)(PPh$_3$)$_2$. Similar reactions with PhC≡CX (X = Br, I) give PtX(C≡CPh)(PPh$_3$)$_2$. Treating [Pt(*trans*-PhHC=CHPh)(PPh$_3$)$_2$] with PhC≡CX (X = Cl, Br, I) gives *cis*-PtX(C≡CPh)(PPh$_3$)$_2$, which isomerizes to the trans complex in benzene. Other similar reactions are described and discussed [202]. The structure of *trans*-PtCl(C≡CPh)(PEt$_2$Ph)$_2$ (92) shows a non-linear phenylethynyl group. The Pt-C distance is 1.98(2) Å [203]. Details of selective syntheses have been reported for the preparation of acetylide complexes Pt(C≡CR^1)$_2$(PR$_3$)$_2$ (R^1 = H, CH=CH$_2$, C≡CH, Ph, *p*-C$_6$H$_4$C≡C; R = Et, *n*-Bu) [204]. Nickel acetylide complexes Ni(C≡CR^1)$_2$(PPh$_3$)$_2$ (R^1 = EtOCH$_2$, BuOCH$_2$, PhOCH$_2$, *o*-ClC$_6$H$_4$OCH$_2$, (HO)MeCH, (HO)Me$_2$C, 1-hydroxycyclohexyl, Ac, Ph; R = Bu, Cy) have been obtained from NiX$_2$(PR$_3$)$_2$ and NaC≡CR^1 in liquid ammonia [205]. XPS Photoelectron spectra have been measured for some nickel acetylide compounds. The respective values for the Ni 2p 3/2 bridging energies for the complexes Ni(C≡CPh)(NCS(PPh$_3$)$_2$, Ni(C≡CPh)$_2$(PPh$_3$)$_2$, and Ni(C≡CPh)$_2$(PBu$_3$)$_2$ are 854.0, 854.9, and 855.0 eV respectively [206]. Treating αω-dodecatriene diyl nickel with dimethyl acetylenedicarboxylate at 0°C yields the 12- and 14-member ring products. Similarly treatment of a bis(π-allyl) nickel complex, from α, ω-



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(92)

dodecatrienyldiylnickel and allene, with dimethyl acetylenedicarboxyalte gives dimethyl 14-methylenecyclohexadeca-1,4,8,12-tetraene-1,2-dicarboxylate [207]. In the presence of nickel complexes, triisobutylaluminum and 1-bromo-1-hexyne react to give predominantly 2-methyl-4-nonyne. Nickel acetylide complexes such as (93) are proposed

$$\underset{(93)}{L_nNiBr(C\equiv CR^1)} + AlR_3 \rightarrow L_nNiR_2 \rightarrow L_nNi + R\text{-}R + R_2AlC\equiv CR^1$$

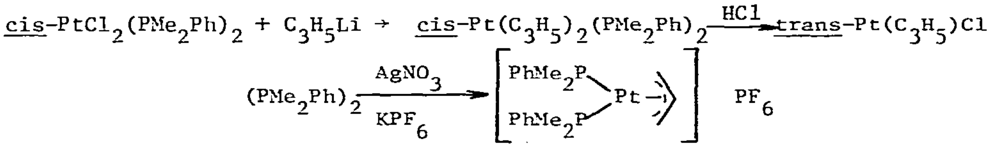
to be involved in the reaction [208]. Similarly $NiCl_2(PPh_3)_2$ has been used as a catalyst for the addition of Grignard reagents to acetylenes [209].

Condensation of $(\pi\text{-cp})_2Ni_2(HC\equiv CMe)$ with $Fe_3(CO)_{12}$ gives $Fe_2(CO)_7(\pi\text{-cp})Ni(CEt)$

and $Fe_2(CO)_6(\pi\text{-cp})Ni(C{\equiv}CMe)$, based on a Fe_2Ni core. Intramolecular and intermolecul hydrogen shifts account respectively for the reduction of the triple bond and the dehydrogenation of the alkyne. Structures are proposed based on IR, ^{1}H NMR, and mass spectral evidence [210].

VII. Metal allyls

Treating cis-$PtCl_2(PMe_2Ph)_2$ with cyclopropyllithium gives cis-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$. Reaction with HCl gives trans-$Pt(CHCH_2CH_2)Cl(PMe_2Ph)_2$, which with $AgNO_3$ and KPF_6 gives the 1-3-π-allyl platinum complex $[Pt(\pi\text{-}C_3H_5)(PMe_2Ph)_2]PF_6$ (94) [211].



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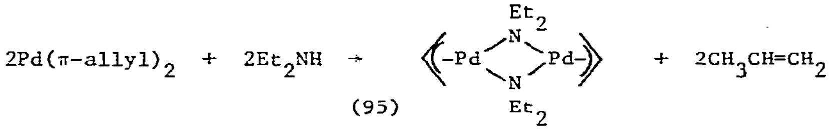
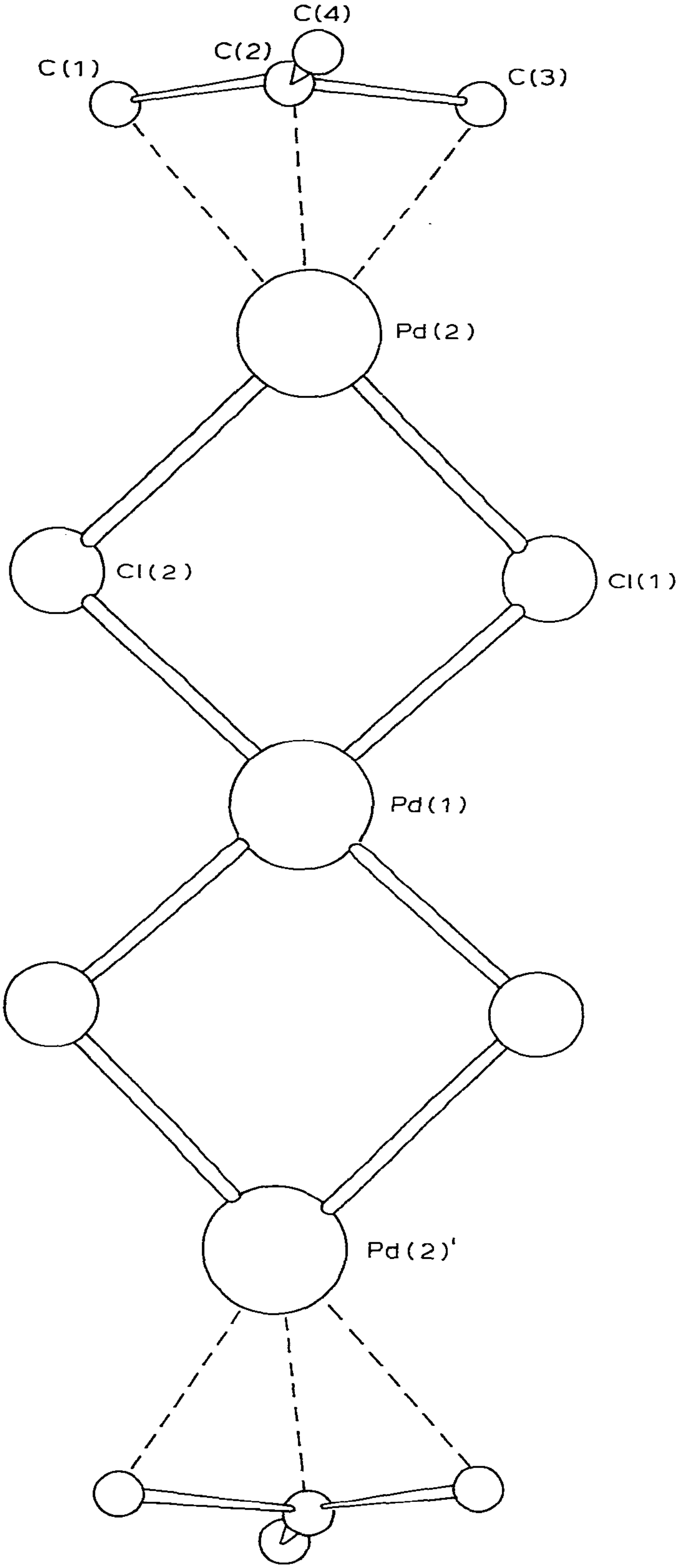
Allyl complexes $\{[C_3H_3(COR)(COR^1)]PdCl\}_2$ and $[C_3H_3(COR)(COR^1)]Pd(acac)$ (R = Ph; R^1 = Ph, p-BrC_6H_4, p-ClC_6H_4, p-ClC_6H_4) have been isolated [212]. Similar allylpalladium complexes have been prepared where R = R^1 = $C_5H_4Mn(CO)_3$ by refluxing the manganese substituted oxonium compound with $PdCl_2$ in the presence of Na_2CO_3 [213]. The allylic palladium complex (95) has been obtained by reacting $Pd(\pi\text{-allyl})_2$ with Et_2NH. The analogous methyl compound has been synthesized by an analogous procedure [214]. Gel filtration and the tlc methods have been used to show that $[\pi\text{-allylPdCl}]_2$ is indeed dimeric in solution [215].



(95)

The structure of $Pd_3(2\text{-methylallyl})_2Cl_4$ (96) shows a rippled near planar arrangement of $PdCl_2PdCl_2Pd$ with the terminal Pd atoms being π-bonded to the 2-methylallyl ligand [216]. In an article dealing with sulfur containing complexes the compounds $[PdL(1,4\text{-dithian})]PF_6$ (L = π-2-methylallyl and π-1-phenylallyl) have been synthesized

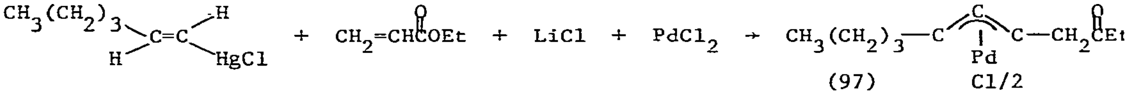


(96)

[217]. A similar complex $[Pd(\pi\text{-}2\text{-}MeC_3H_4)(tetramethylthiophen)_2]PF_6$ has also been prepared by this group [218].

A general procedure to prepare π-allylpalladium(II) complexes from simple and complex olefins has been developed using cupric chloride to prevent reduction of the palladium to the element. A wide range of allyl complexes has been prepared and synthetic details of the method described [219]. In the following paper these authors describe the use of phosphines and phosphites for enhancing the allylic alkylation of alkyl substituted π-allylpalladium complexes [220]. The nature of the nucleophile for attack at the π-allyl is discussed, and also these authors apply the project to prenylation [221]. In the final paper of the series, organopalladium chemistry is used for a stereocontrolled approach to steroid side chain in the parti synthesis of 5α-cholestanone [222].

Vinylmercuric chlorides react with $PdCl_2$, LiCl and alkenes in THF to give π-allyl palladium compounds (97). The method is regiospecifically useful and the stereochemistry of the compounds is determined by NMR. The mechanism is presumed to involve addition of a vinylpalladium compound to the alkene, followed by a Pd hydride rearrangement to the π-allylpalladium complex [223]. The reaction of quinones with π-allyl nickel bromide proceeds through unstable allylquinol intermediates. These compounds have been isolated and characterized, and their rearrangements studied [224]. When (S)-(-)-trans-chloro(η^1-α-deuteriobenzyl)bis(triethylphosphine)palladiun (II) is treated with $NaBPh_4$ the product is [(S)-(+)-(η^3-α-deuteriobenzyl)bis(triethylphosphine)palladium(II)]tetraphenylborate (98) [225]. Regeneration of the η^1 complex with Cl^- proceeds with 94% net retention of configuration. The preparatic of π-allylnickel complexes has been reported from the reaction between $NiCl_2$ and $Al(CH_2CHMe_2)_3$ in the presence of dienes [226]. It is suggested that the primary mechanism of interaction of $Ni(\pi\text{-methallyl})_2$ and $TiCl_4$ is the ligand transfer to



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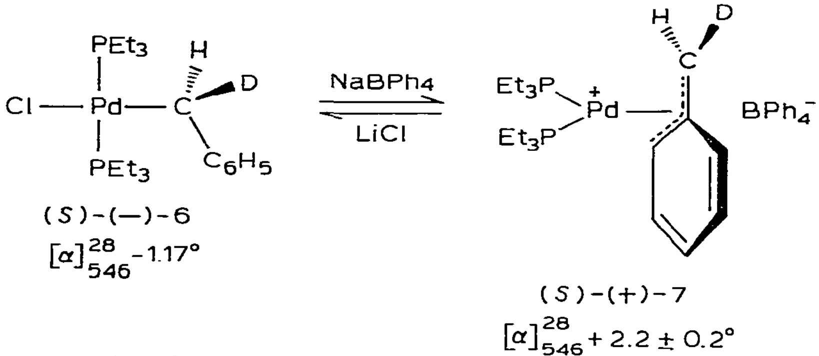

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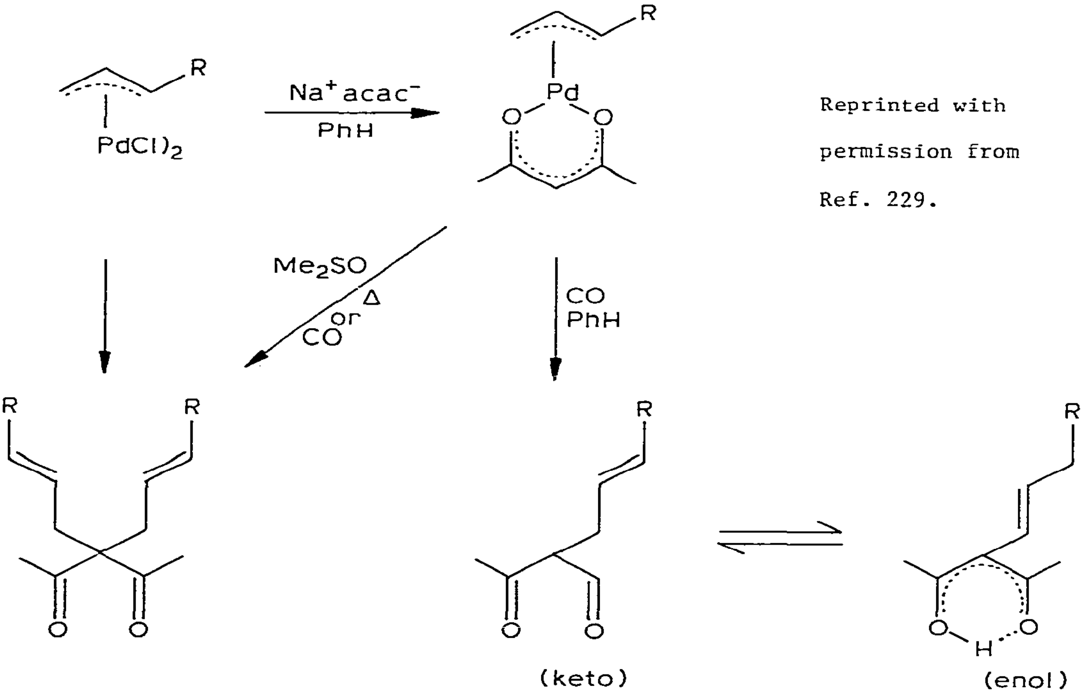
(98)

Ti with reduction to β-$TiCl_3$ *and the formation of a product which can initiate the* polymerization of isoprene [227].

The chloride in $[Pd(\pi\text{-allyl})Cl]_2$ (allyl = allyl, 2-methylallyl, 1,3-dimethylallyl) can be displaced with silver ion and the simultaneous addition of substituted quino-



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(99)

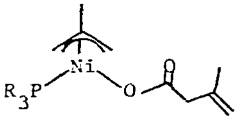
lines (L) gives the complexes $[Pd(\pi\text{-allyl})L_2]ClO_4$ [228]. The dynamic exchange process in these compounds is studied by NMR techniques. Reactions of π-allylpalladium compounds with Na(acac), sodium malononitrile, and sodium ethylacetoacetat give diallyl substitution products (99) [229]. The structure of the π-allylic palladium(II) complex dihapto-3,5-dimethylpyrazolido-π-allylpalladium dimer has been solved [230]. The structure of $[Pt(C_3H_5)(PCy_3)_2]PF_6$ shows the π-allyl group occupy two discrete orientations within the coordination sphere in the solid state [231].

^1H and ^{31}P NMR spectroscopy shows that $Pt\text{-}Cl(\eta^1\text{-allyl})(PPh_3)MeNC$ undergoes extensive $\eta^1 \rightarrow \eta^3$ allyl conversion at room temperature through PPh_3, Cl and MeNC ligand displacements [232]. At lower temperatures this conversion only involves chloride displacement. A similar type study has been made for the compound $PtCl(\eta^1\text{-allyl})(PPh_3)(2,6\text{-}Me_2C_6H_3NC)$ [233].

In the presence of phosphines $Ni(\pi\text{-methylallyl})_2$ reacts with CO_2 to give carboxylato complexes (100). A further π-allylnickel complex reacts with CO_2 to give the

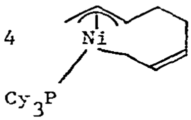
$$Ni(\pi\text{-methylallyl})_2 + PR_3 + CO_2 \rightarrow$$

(R = Me, Cy)



(100)

dimer (101), which on heating rearranges to the tetrameric nickelalactone (102) [234

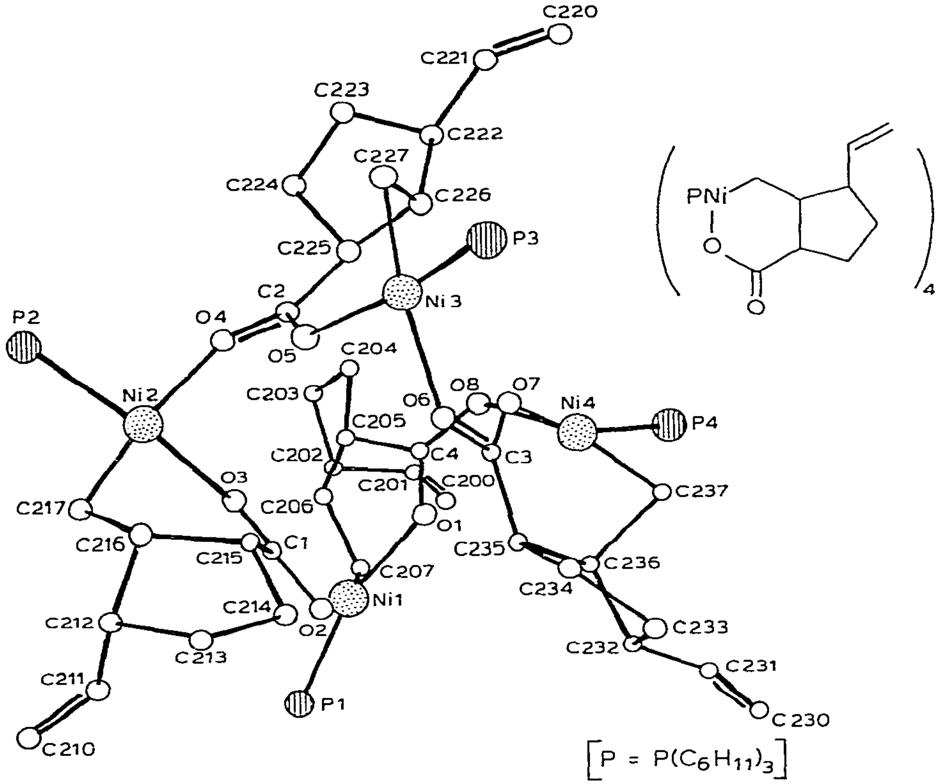
4 

$$+ 4CO_2 \rightarrow 2[(Cy_3P)NiC_8H_{12}CO_2]_2 \rightarrow (102)$$

(101)

Allylpalladium(II) complexes have been used in the anti-Markownikoff 1,2-hydrosulphonylation of 1,3-dienes [235]. The formation of Pd metal and propene from the reaction of π-allylpalladium(II) complexes in THF with H_2 is discussed in terms of the fluxionality of the allyl group and the stability of a proposed Pd-H intermediat The reaction of allylpalladium(II) complexes with H_2 and allene results in catalytic selective hydrogenation to propene [236].

In the formation of the 4α-6α-η-PdCl complex from 2,2-dimethylcholest-4-en-3-one,



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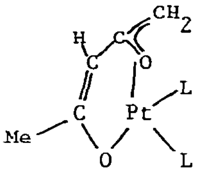
the initial π-complexation appears to be rate limiting [237]. The compound $PdCl_2(PhCN)_2$ reacts with [6β-^{2}H] cholest-4-ene to give the α-4-6-η and β-4-6-η PdCl derivatives with respective specific syn 6-H, or 6-^{2}H elimination [238].

When the compound $Pt(acac)_2$ is treated with a phosphine L (L = PPh_3, $PMePh_2$, PMe_2Ph), new complexes $Pt(C_5H_6O_2)L_2$ (103) are formed [239]. On the basis of spectral data these complexes are shown to have a π-oxoallyl type of bonding. An allylic



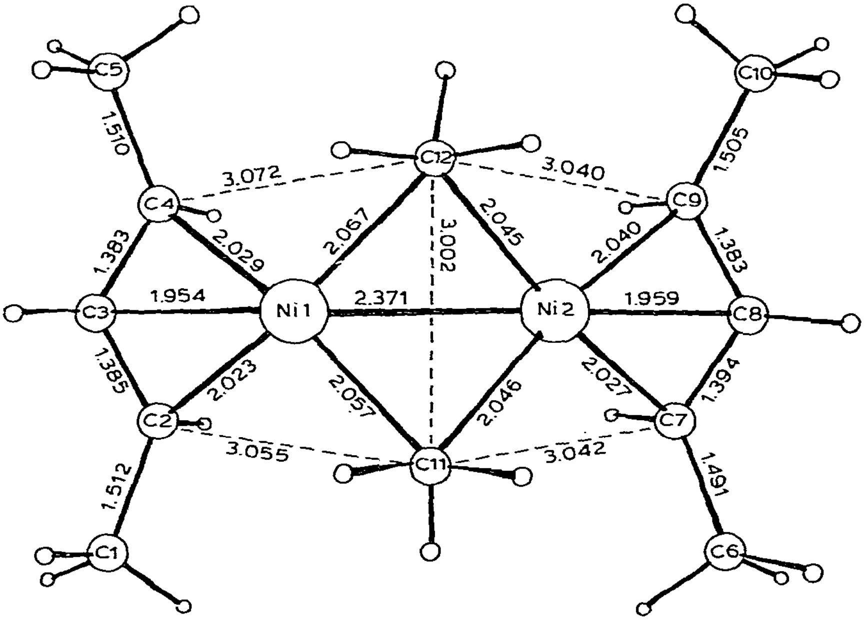
(103)

intermediate is proposed in the catalysis by $Pt(PPh_3)_2$ of the conversion of some allyl enol ethers into C-allylated compounds [240]. Phenylhydrazones react catalytically with allyl acetates to give azo compounds (104). The complexes used in the reaction are NiL_4 ($L = PPh_3$, $P(OCHMe_2)_3$) [241].

$$PhNH\text{-}N{=}CRR^1 + H_2C{=}CH\text{-}CH_2OAc \xrightarrow{NiL_4} PhN{=}N\text{-}C(R)(R^1)CH_2\text{-}CH{=}CH_2 + CH_3CO_2H$$

(104)

The structure of bis(-μ-methyl-1,3-dimethyl-h^3-allylnickel) (105) has two square planar nickels, each carrying a h^3-C_5H_9 group linked by two methyl bridges. The molecule is folded about the center leading to a close Ni-Ni distance of 2.371 Å. The electronic structure of the complex has been analyzed by MO methods. The structure also shows that the bridging methyl groups form slightly unsymmetrical two



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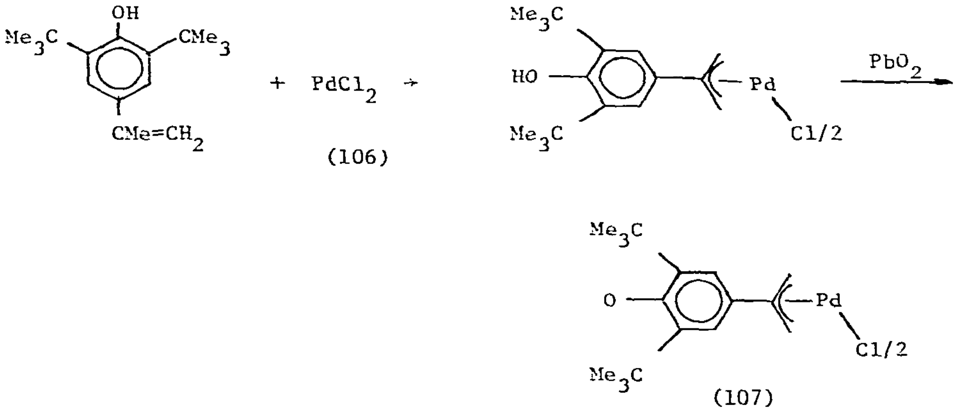
electron-three center bonding systems [242]. Allyl compounds of palladium have been synthesized with m- and p-fluorophenyl groups in the 1- and 2- positions of the allyl group. From the shielding of the fluoro group, the electron density distribution within the allyl group is discussed [243].

Inelastic neutron scattering spectra ($\leq$ 800 cm^{-1}) of $[\pi\text{-}C_3H_5NiBr]_2$, $[\pi\text{-}C_3H_5PdCl]_2$ and $M(\pi\text{-}C_3H_5)_2$ (M = Ni, Pd) have been obtained and compared with optical data to assign the low frequency vibrations [244]. In agreement with previous data the force constants for the metal-allyl bond have the same value for Ni and Pd compounds. In a similar study using infrared and Raman spectroscopy the metal-allyl force constant increases in the series $Ni \lesssim Pd < Pt$ [245].

Catalysts containing aluminum halides, PPh_3, and π-allyl-, π-pentenyl- or π-crotylnickel halides are active in olefin dimerization or oligomerization. From EPR data it is concluded that the catalytic species contain Ni(I) [246]. The allyl compound (106) can be oxidized by PbO_2 to give the new compound (107) [247].



(106)

(107)

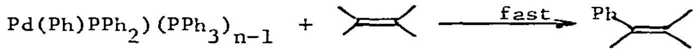
VIII. Complexes formed by Insertion Reactions

The reaction of $NiR_2(bipy)$ and NiR(X)bipy (R = Me, Et; X = imido, OCOMe) with CH_2Cl_2 or CH_2I_2 gives RCH_2CH_2R, RCH_2R, RMe and $R(-H)=CH_2$, in addition to R-R, RH and R(-H) [248]. Insertion of a carbene ($:CH_2$) into the Ni-R bond is believed to occur in the reaction pathway. Work has been published on the influence of the organophosphine on the palladium catalyzed reaction of 4-bromophenol with methyl acrylate [249]. Equally good results can be obtained with an aryl iodide in the absence of phosphine. A mechanism is proposed involving olefin insertion into the Pd-phenyl bond. A mechanistic study has been made of the arylation of olefins by PPh_3 in the presence of Pd(II) compounds. The kinetic scheme is represented by the following sequence [250].

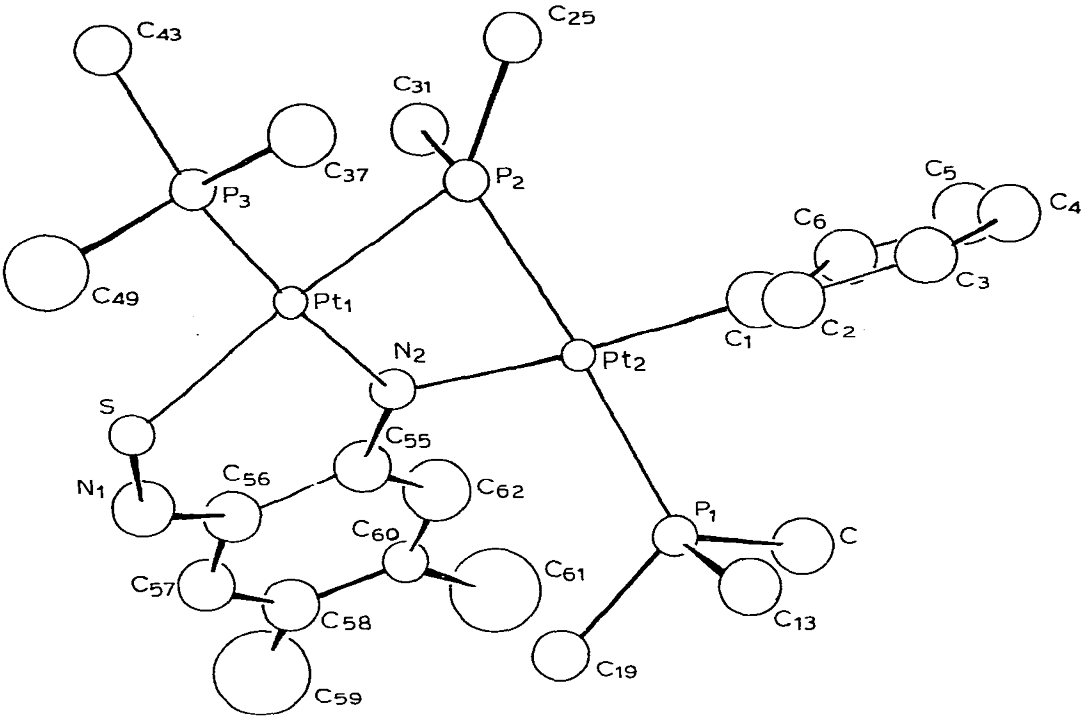
$$Pd(OAc)_2(PPh_3)_2 \overset{K}{\rightleftharpoons} Pd(OAc)_2(PPh_3) + PPh_3$$

$$Pd(OAc)_2(PPh_3) \xrightarrow{k_1} Pd(PPh_3)_n^0$$

$$Pd(PPh_3)_n^0 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pd(Ph)PPh_2(PPh_3)_{n-1}$$

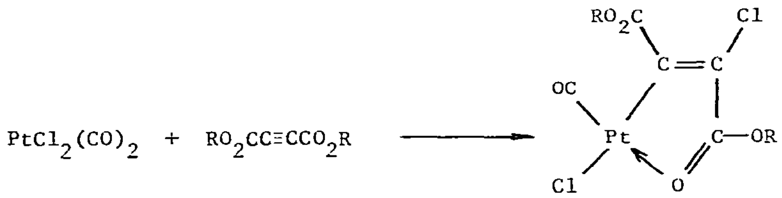


The nickel(I) complex $Ni(teta)^+$ (teta = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) reacts with alkyl bromides to form an unstable alkylnickel complex. In the presence of an olefin such as acrylonitrile, insertion occurs and the C-C coupled organic product is liberated [251]. The compounds trans-$PdH(NO_3)(PCy_3)_2$ and trans-$[PdH(MeCN)(PCy_3)_2]PF_6$ insert acetylenes to give the alkenyl complex. It is shown that cis addition occurs and that the hydridic hydrogen adds to the acetylenic carbon containing the electron-withdrawing group [252]. The reaction of $Pt(C_2H_4)(PPh_3)_2$ with 5,6-dimethyl-2,1,3-benzothiadiazole gives $[Pt_2S\{N(6-\mu-N-4,5-Me_2C_6H_2)\}(\mu-PPh_2)(PPh_3)Ph$ (108). The structure shows that one of the Pt atoms is inserted into one of the N=S bonds [253]. A possible mechanism for the formation of (108) is presented. The reaction of the vinyl complexes $Pt(CO)Cl(RO_2CC{=}C(Cl)CO_2R)$ and $[$cis-$Pt(CO)Cl_2(RO_2CC{=}C(Cl)CO_2R)]^-$ (R = Me, Et) with primary and secondary alcohols gives specific alcoholysis at the α-alkoxy group [254]. These starting compounds (109) have been synthesized by treating $PtCl_2(CO)_2$ with $RO_2CC{\equiv}CCO_2R$, which inserts into one of the Pt-Cl bonds [255]. A study has



(108)

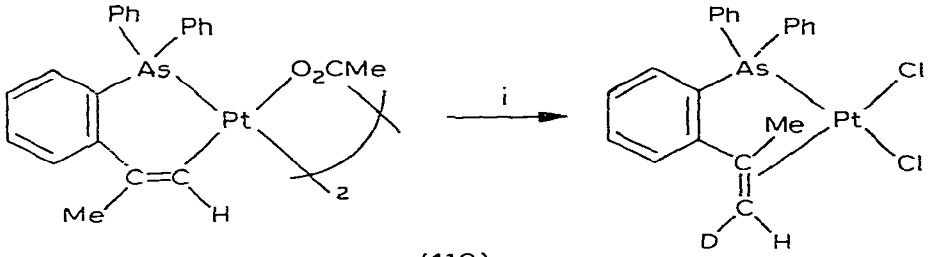
been made on the insertion of butyne-2 into a metal-carbon bond in a cyclobutenylpalladium complexes. Structures are proposed for the products and their relation to the $PdCl_2$ induced cyclotrimerization of acetylenes is discussed [256].



(R = Me, Et)

(109)

The o-isopropenylphenyl(diphenyl)arsine(L) compounds $PtCl_2(L)$ and $[Pt(acac)L]BF_4$ react with metal acetates to give $[AsPh_2C_6H_4\text{-}\underline{o}\text{-}C(Me){=}CH\text{-}Pt(O_2CMe)]_2$ (110) and $AsPh_2C_6H_4\text{-}\underline{o}\text{-}C({=}CH_2)CH_2Pt(acac)$ (111). The former is shown from X-ray structural work to have the deprotonated olefin bonded to Pt as a σ-vinyl group, and in the latter the ligand is bonded as a σ-allylic group [257]. Insertion-like reactions



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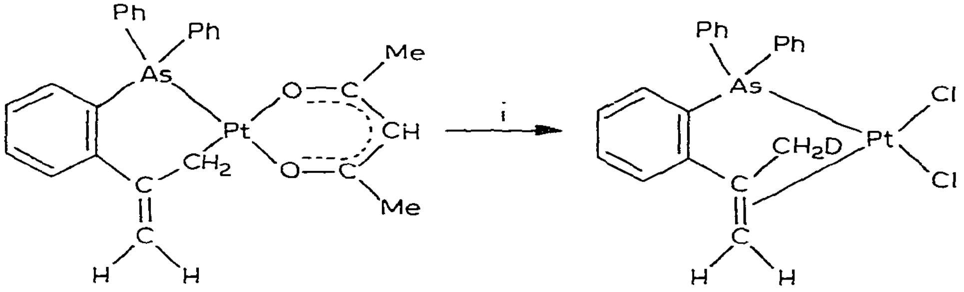

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occur with DCl. Chloro(trans-3-oxo-3-phenyl-1-propenyl)bis(triphenylphosphine) palladium(II) and chloro(3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) have been prepared from $Pd(PPh_3)_4$ and linear or cyclic 2-chlorovinyl ketones [258].

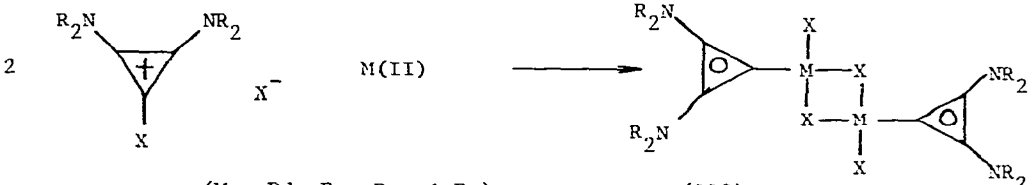
A tetrakis(methoxycarbonyl)cyclohexadiene annelation of norbornene, cyclopentene, and cyclohexene with two molecules of dimethyl acetylenedicarboxylate is catalyzed by an equimolar mixture of triphenylphosphine and an oligomeric palladiacyclopentadiene complex $[Pd(C_4(CO_2Me)_4)]_n$. Treatment with 2,6-lutidine gives $[Pd(C_4(CO_2Me)_4)$ 2,6-lutidine$]_2$. The structure of this complex has been solved [259].

Associative and dissociative processes have been examined theoretically for the insertion of ethylene into a Pt-H bond. There is no easy insertion pathway from a five coordinate intermediate, nor is there a facile reaction by a direct route from a four coordinate complex with ethylene and hydride mutually trans. The calculations indicate that the reaction is best achieved by a sequence of associative and, preferably, dissociative steps [260]. In a broad study of organometallic migration reactions, reference is briefly made to some organometallic compounds of Ni and Pt [261].

The C-bonded imine, *trans*-$Pd[C(Me){=}N(\textit{p}\text{-tolyl})]Cl(PEt_3)_2$ reacts with $MeO_2CC{\equiv}CCO_2Me$ to give two compounds, each having a substituted pyrrole derivative as ligand. The reaction proceeds by the N-H fragment of the enamine form adding across the triple bond of the acetylene to give an intermediate which undergoes ring closure with methanol elimination [262].

IX. Delocalized carbocyclic systems. Metal carboranes

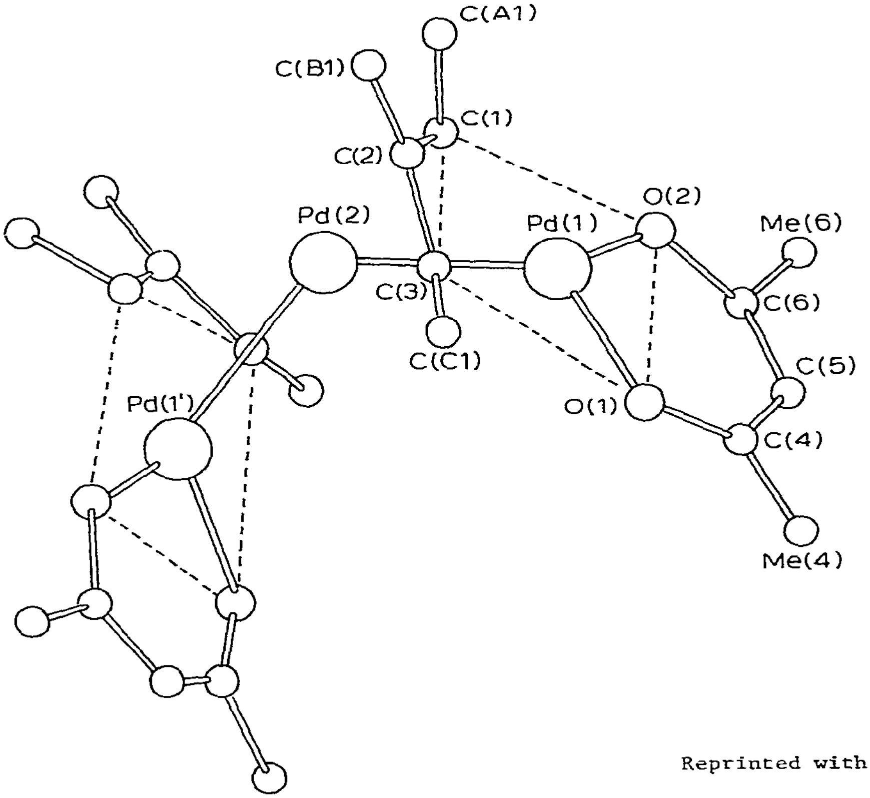
Neutral and cationic diaminocyclopropenylidene complexes of Pd(II) and Pt(II), *trans*-X_2-μ-$X_2M_2(C_3(NR_2)_2)_2$ (112), *cis*-$R_3PX_2M(C_3(NR_2)_2)$, and [*trans*-$(R_3P)_2XMC_3(NR_2)_2$]ClO_4 have been prepared [263]. Stereochemistry of the peripheral dialkylamino groups



(M = Pd, Pt; R = *i*-Pr)

(112)

is briefly discussed on the basis of IR and ^{13}C NMR spectroscopy. This work on similar complexes is continued in a further article [264]. Treating $Pd_2(PhCH{=}CHCOCH{=}CHPh)(CHCl_3)$ with $[C_3Ph(\textit{p}\text{-}MeOC_6H_4)_2]Br$ followed by reaction with Tlacac gives $Pd_3\{C_3Ph(\textit{p}\text{-}MeOC_6H_4)_2\}_2(acac)_2$ (113). The compound is composed predominantly (67%) of enantiomers of one isomer which arises from the addition of the $C_3R^1R^2_2$ group to Pd by ring opening the CR^2-CR^2 bond. This palladium is also O,O^1-bonded to acac, and two such units are linked by the second Pd atom [265]. Cyclopropenylium palladium complexes $[PdCl_2(C_3R_2)]_2$ (R = *t*-Bu, N(*i*-Pr)$_2$) have been prepared from 2,3-R_2-1,1-dichlorocyclopropene and Pd black. The complexes will undergo Pd-C cleavage with reagents such as $SbCl_5$ or H_2SO_4 [266].



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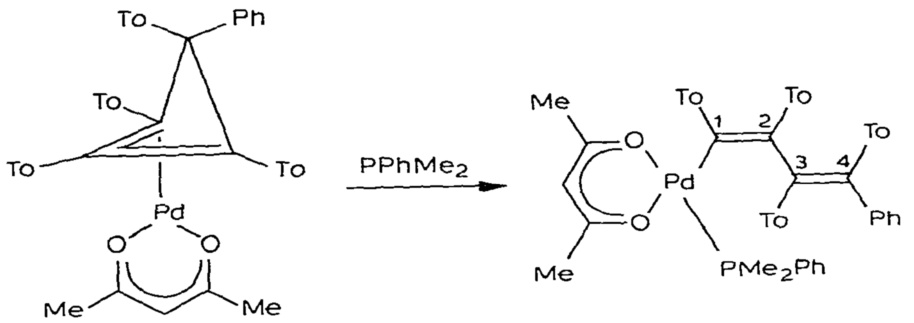
Treating tetramethylcyclobutadienenickel dichloride with sodium in the presence o bipy gives tetramethylcyclobutadienenickelbis(2,2^1-bipyridine) (114) [267]. Fused

$$[(Me_4C_4)NiCl_2]_2 \;+\; 4Na \xrightarrow{bipy} 2[(Me_4C_4)]Ni(bipy) \;+\; 4NaCl$$

(114)

ring organic compounds are formed on treating (114) with CO, CH_2=CHCN, PhC≡CPh. Arylation (with $NaBPh_4$) of $[PdCl_2(C_4$p-tol$_4)]_2$ gives the 1-3-η-cyclobutenyl complex $[Pd(C_4$p-tol$_4$Ph)Cl$]_2$ with the phenyl group entering endo to the metal. On reaction of $[Pd(C_4$p-tol$_4$Ph)X] (X = acac, S_2CNR_2) with ligands such as $PPhMe_2$, ring opening occurs to form the σ-butadienyl complexes $Pd(C_4$p-tol$_4$Ph)X($PPhMe_2$) (115) where the 1-3-η-cyclobutenyl ligand has opened stereospecifically in the conrotary manner [268 The complex Pd(η^3-C_4p-tol$_4$Ph)(S_2CN-i-Pr_2) undergoes spontaneous ring opening to give two complexes Pd(1:3,4-η-C_4p-tolPh)(S_2CN-i-Pr_2) (116) which differ as a disorder in the p-methyl groups of the phenyls. The structures of (116) and (117) have been solved [269]. Similar ring opening reactions have been found in the conversion of



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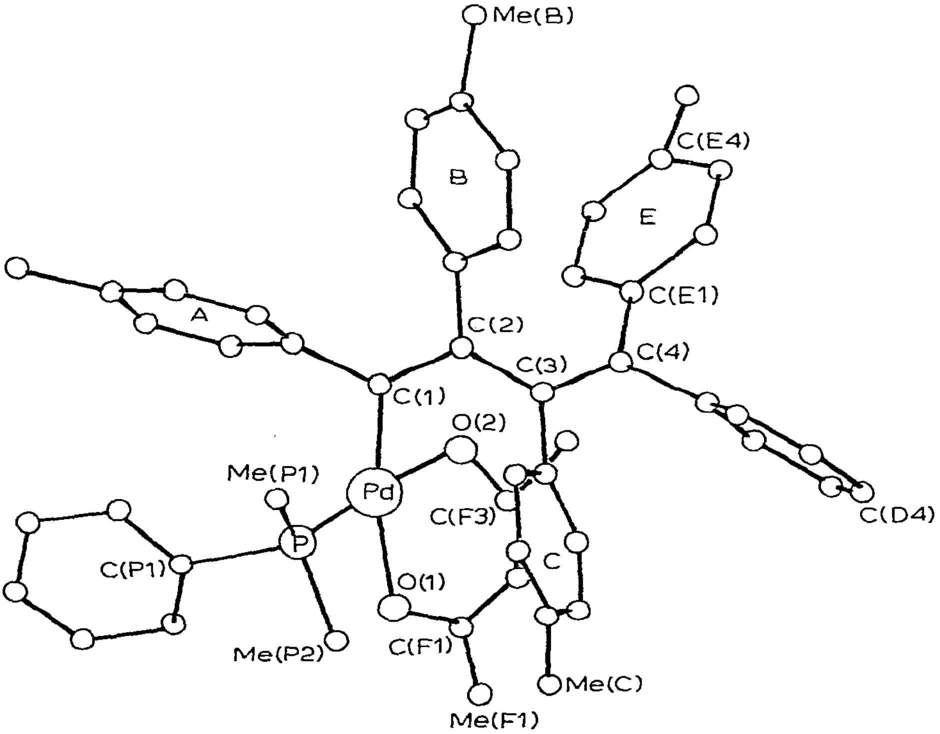

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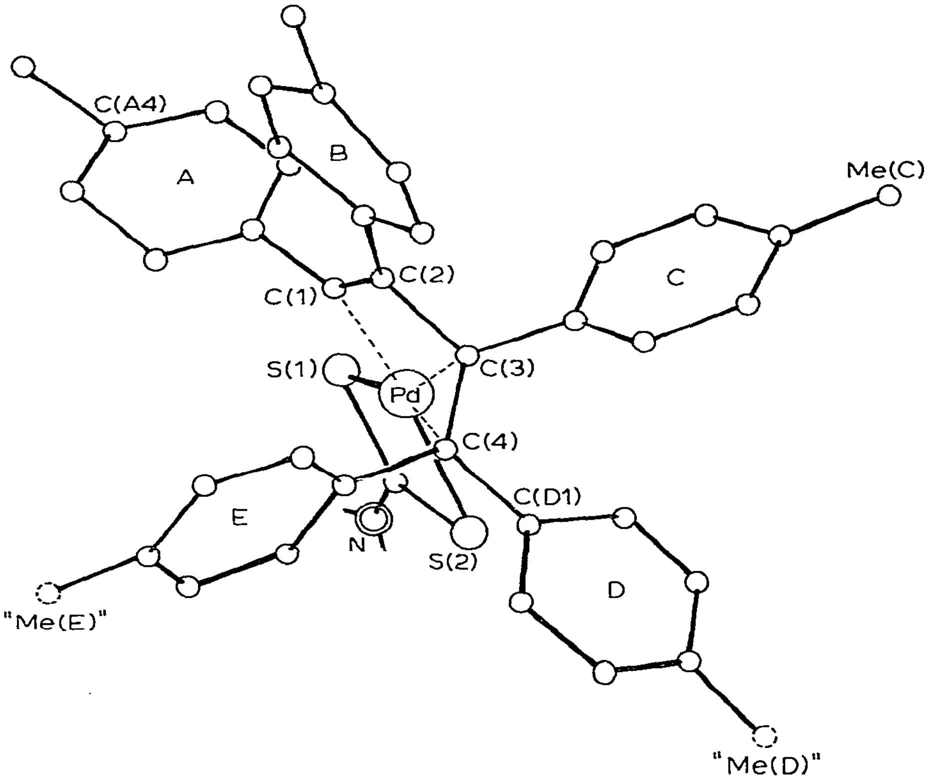

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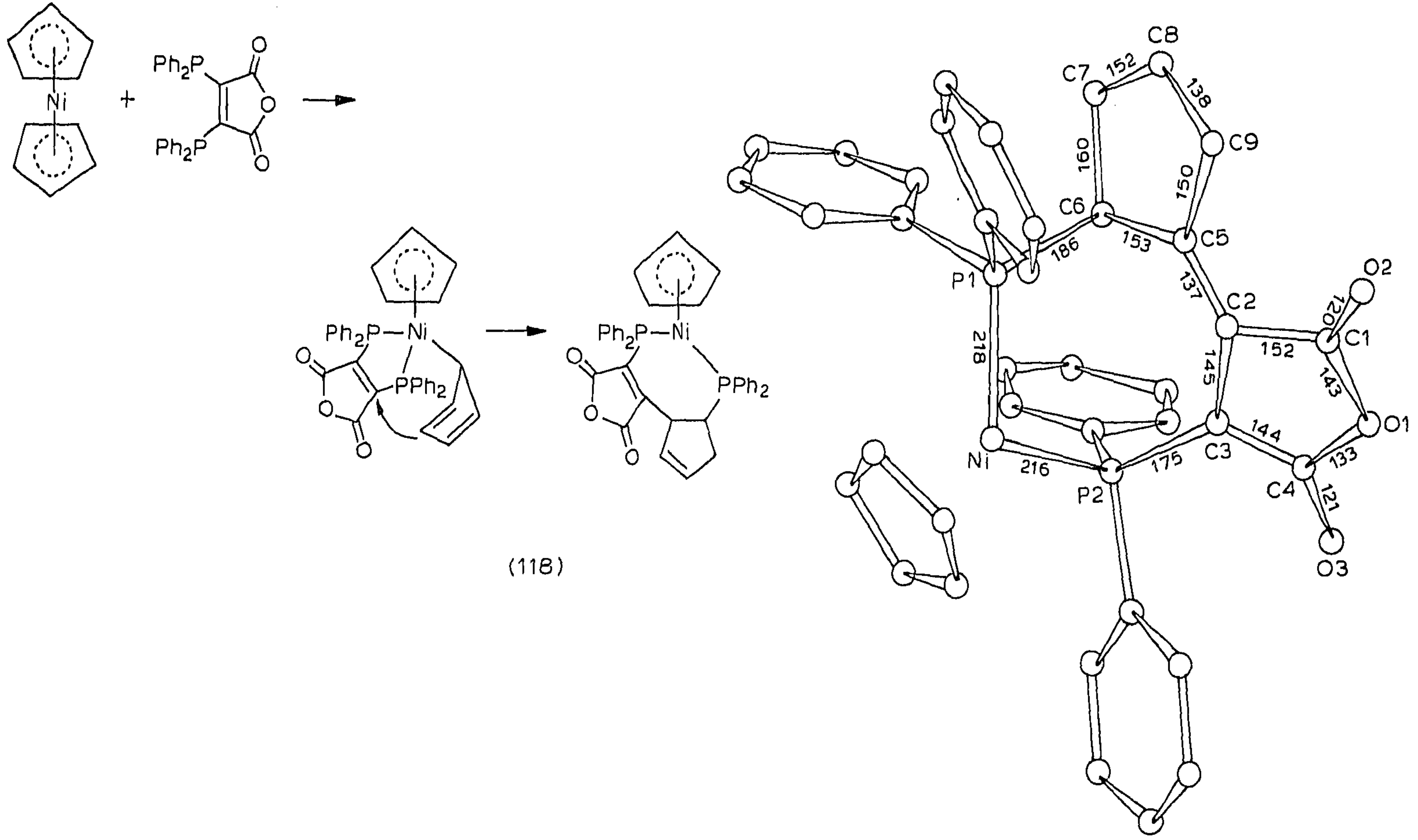
η^3-endo-alkoxytetraphenylcyclobutenylpalladium chloride dimer to cis-1-trans-3-tetraphenyl-4-alkoxybutadien-1-yl complexes [270].

INDO-SCF calculations on π-cp-π-cyclopropenylnickel indicate a formal d^{10} electrc configuration for Ni. Electron loss should occur first from the occupied closely grouped set of predominantly d orbitals, and then from a cp orbital. The behavior of the π-cyclopropenyl ligand is discussed using the calculated charge distributions [271]. IDNO-SCF calculations have also been carried out for Ni(π-cyclobutadiene)$_2$. Bonding is mainly through mixing of the π-ligand $e_{(g)}$ level and the Ni $3d_{xz}$ $3d_{yz}$ orbitals [272].

Nickelocene reacts with bis(diphenylphosphino)maleic anhydride to give a product (118) resulting from insertion of the cp ligand into a P-C bond of the bis(phosphine ligand [273]. The structure of (118) has been confirmed crystallographically.



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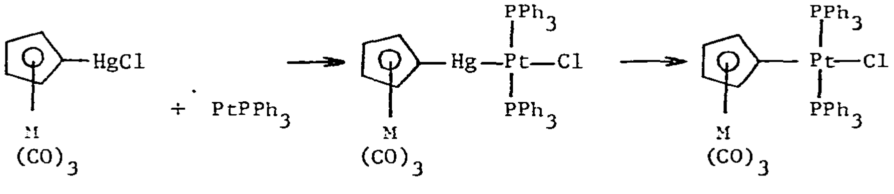
Ref. 273.

Nickelocene reacts with hexachlorocyclopentadiene to give 1,2,3,4,5-pentachloro-5-(2,4-cyclopentadienyl)-1,3-cyclopentadiene, which isomerizes to 1,2,3,4-tetrachloro-5-(4-chloro-2-cyclopentenylidene)-1,3-cyclopentadiene on addition of trifluoroacetic acid [274].

Complexes $[PtXR_1R_2R_3]_4$ ($R_1 = R_2 = Me$, $R_3 = C(O)Me$, Et; $R_1 = R_2 = Et$, $R_3 = Me$, C(O)Me; $R_1 = Me$, $R_2 = Et$, $R_3 = C(O)Me$ with X = Cl, I) on treatment with Tlcp give (π-cp)$PtR_1R_2R_3$. Conformational isomerization about the Pt-acetyl bond has been detected by IR spectroscopy. Treatment with HCl, $HgCl_2$ or I_2 leads to the formation of $[PtMe_2RX]_4$ rather than cleavage of a Pt-Me or Pt-C(O)Me bond. The complexes have a piano stool chiral structure and they have been investigated by ^1H and ^{13}C NMR spectroscopy. The spectra are very sharp and it is concluded that the isomers inter convert rapidly on the NMR time scale. Three possible isomers exist using the different orientations of the acetyl group about the piano stool. For the ethyl complex no β-elimination to hydride is observed [275].

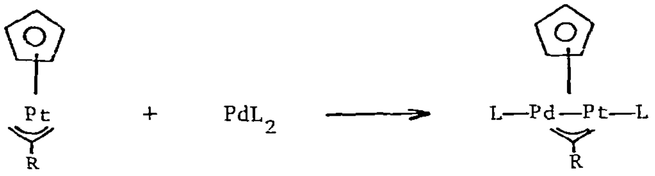
A detailed study has been made of the sequential alkylation of (π-cp)Ni^+ by MeBr in the gas phase by ICR spectroscopy. An activated complex is proposed involving transfer of Br to the nickel and $CH_3(CD_3)$ to the ring [276].

When compound (119) is treated with $Pt(PPh_3)_3$ in toluene at -20°C the product is a complex (120). Upon warming to 20°C the complex changes to (121) [277].



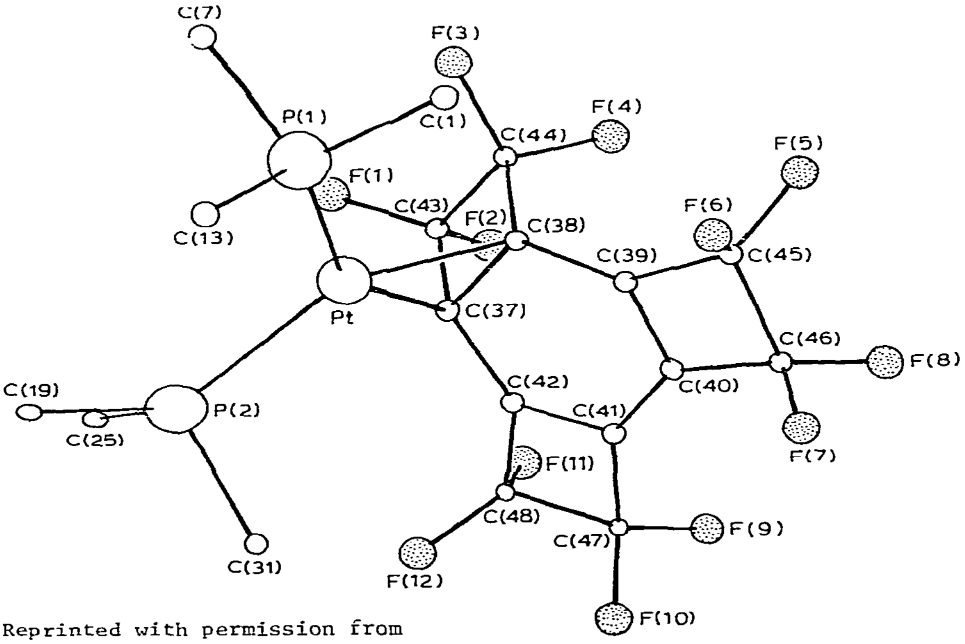
(119) (120) (121)

The salt π-cpNi$[OP(OMe)_2]_2^-$ will form O,O^1 complexes with Ni, Tl, Al and VO. ^1H NMR of the diamagnetic complexes, and magnetic data for the paramagnetic ones, are given [278]. Treating $cpPt(2\text{-}RC_3H_4)$ (R = H, Me) with PdL_2 (L = $P(i\text{-}Pr)_3$, PCy_3) in a 1:1 ratio gives the binuclear complexes (μ-cp)(μ-2-RC_3H_4)$PdPtL_2$ (122). Based on the ^1H, ^{13}C and ^{31}P NMR spectra the compounds have a heterometallic Pd-Pt bond [279]. Thermolysis of cpPd(allyl) gives Pd and a complex mixture of organic products [280].



(122)

The compound C_6F_5NiBr is an intermediate in the synthesis of $(C_6F_5)_2Ni(\pi\text{-toluene})$ from Ni vapor. The π-bonded toluene is labile and can be exchanged with other arene ligands at room temperature. In toluene solution at 25°C and at 100 atm pressure of H_2, the complex catalytically converts toluene to methylcyclohexane [281]. Benzene, benzene-d_6, and fluorobenzene react with nickel atoms to give π-complexes. The IR spectra are shown and discussed in detail [282]. Bis(triphenylphosphine)(perfluoro-1,2,3,4,5,6-triethanobenzene)platinum (123) has a trigonal planar structure about Pt with the $C_{12}F_{12}$ bonded via a double bond of the benzene ring. Bond lengths around the $C_{12}F_{12}$ benzene ring alternate, with the exception of the bond coordinated to Pt which is also long [283]. When $Pt(C_2H_4)(PPh_3)_2$ is treated with compound (124)



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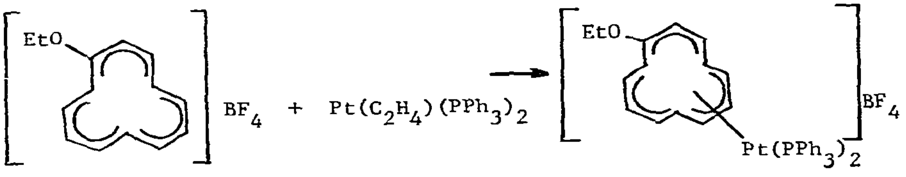
(123)

the complex 4-6-η-1-ethoxyphenalenylbis(triphenylphosphine)platinum tetrafluorobora (125) is obtained. The structure of the product complex has been confirmed crystallographically [284].



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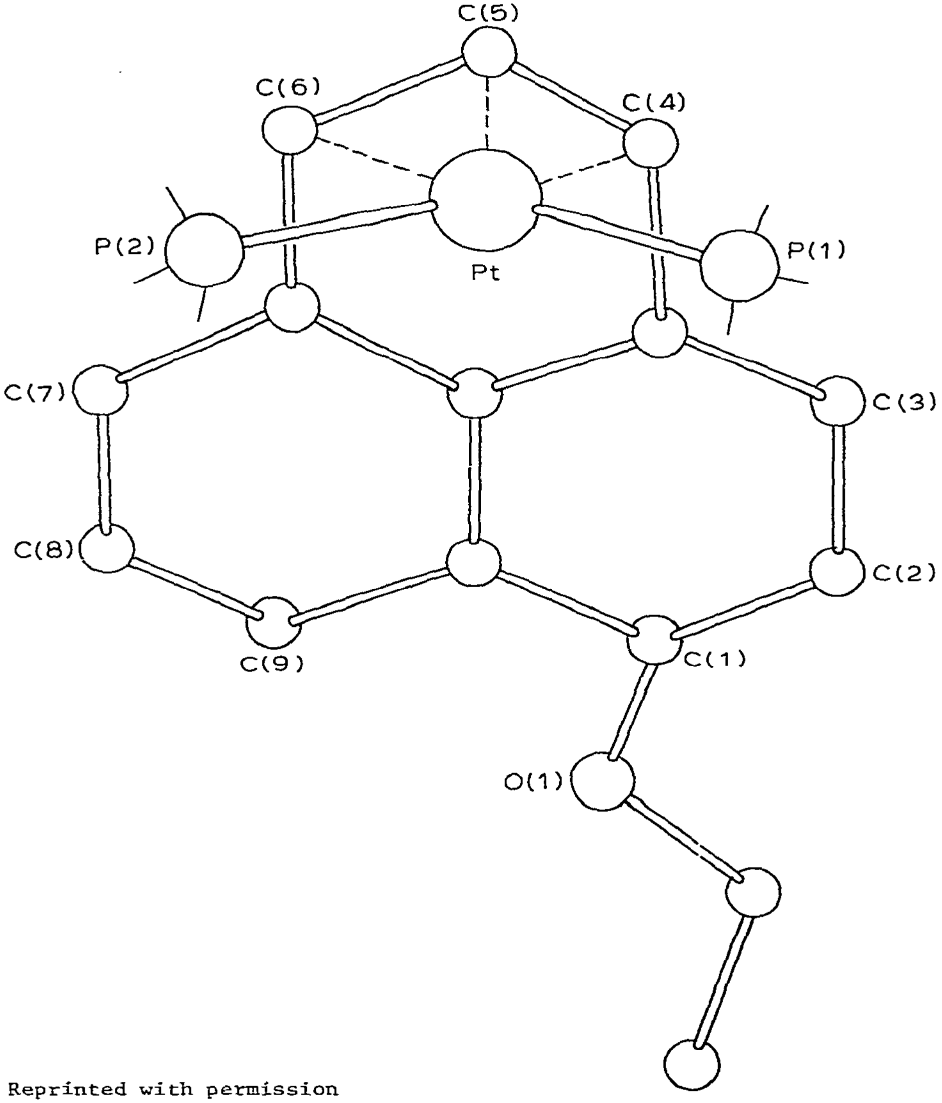

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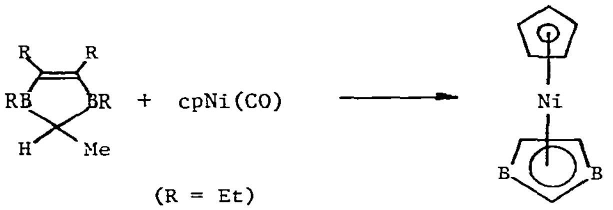
(125)

Metallacyclobutenyl complexes have been obtained from the addition of triarylcyclopropenium salts to zerovalent Pd and Pt compounds. A wide range of compounds is described. The complexes are mainly multimetallic and have either π-cp or acac in the other coordination positions. The complexes exhibit dynamic behavior and some $\Delta G^{\ddagger}$ values are given [285].

The structure of a substituted 1,3-diborolene nickel complex has been reported [286]. The synthesis is effected by treating the 1,3-diborolene with cpNi(CO) to give the complex (126) [287].



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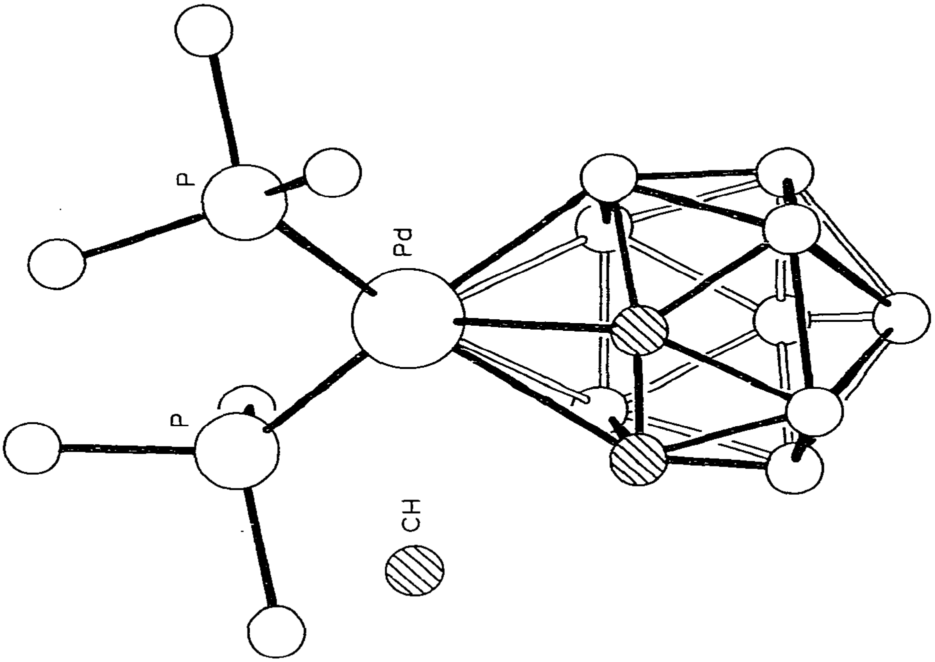
The dicarbollide π-complexes of Ni, Cs[$(1,2\text{-}B_9C_2H_{11})_2$Ni], $(1,2\text{-}B_9C_2H_{11})_2$Ni and $(1,7\text{-}B_9C_2H_{11})_2$Ni have been studied by X-ray photoelectron spectroscopy. Binding energies are given [288]. The reaction of $Nicp_2$ with nido-$(B_{11}H_{13})^{2-}$, $(B_{10}H_{13})^-$ or $(B_9H_{12})^-$ in the presence of a catalytic amount of Na/Hg amalgam gives closo-(cpNi) $B_{11}H_{11}^-$, nido-(cpNi)$B_{10}H_{12}^-$ and the isomeric closo-1- and 2-(cpNi)$B_9H_9^-$ anions respectively. Polyhedral expansion occurs through B-B oxidative addition. The reaction between the compounds and chlorine is described [289]. The molecular structures of 3-[$C_2H_4(NMe_2)_2$]3,1,2-$PdC_2B_9H_{11}$ (127) and 3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$ (128) have been determined by X-ray crystallography. The former compound (127) adopts a "slipped" configuration whereas the latter one (128) is much more symmetrical [290]. Reaction of $Pt(PEt_3)_2$ with nido-2,3-$C_2B_4H_8$ or nido-2,3-Me_2-2,3-$C_2B_4H_6$ gives respectively nido-$\mu_{4,5}$-[trans-$Pt(PEt_3)_2H$]-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$ (129) and nido-$\mu_{4,5}$-[trans-$Pt(PEt_3)_2$ H]-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$. These compounds give closo-platinacarbaboranes with adjacent and non-adjacent carbon atoms respectively [291]. Treating $Pt(PPh_3)_4$ with 4-CB_8H_{14} gives 9-nido-bis(triphenylphosphine)-6-carbodecarborane platinum, 9-$Pt(PPh_3)_2$-6-CB_8H_{12} [292]. The crystal structure has been solved. The structure of 3,3-bis (triethylphosphine)-1,2-dicarba-3-platinadodecacarborane (130) has been solved.



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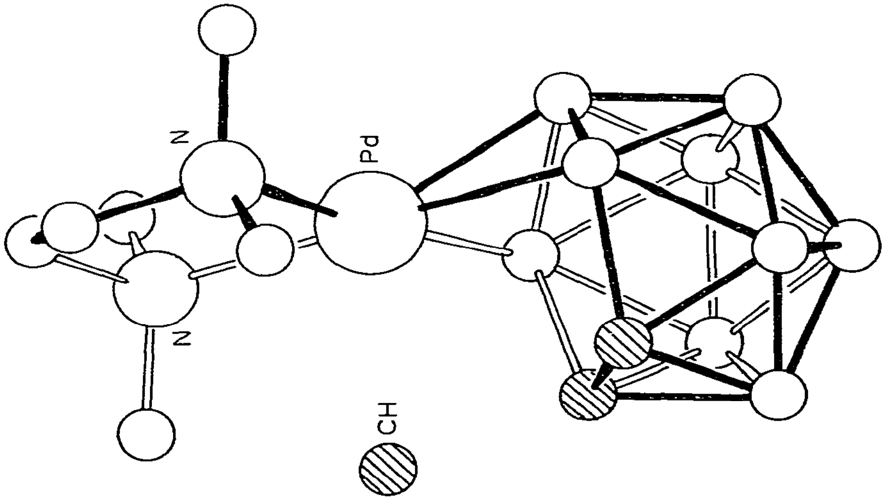
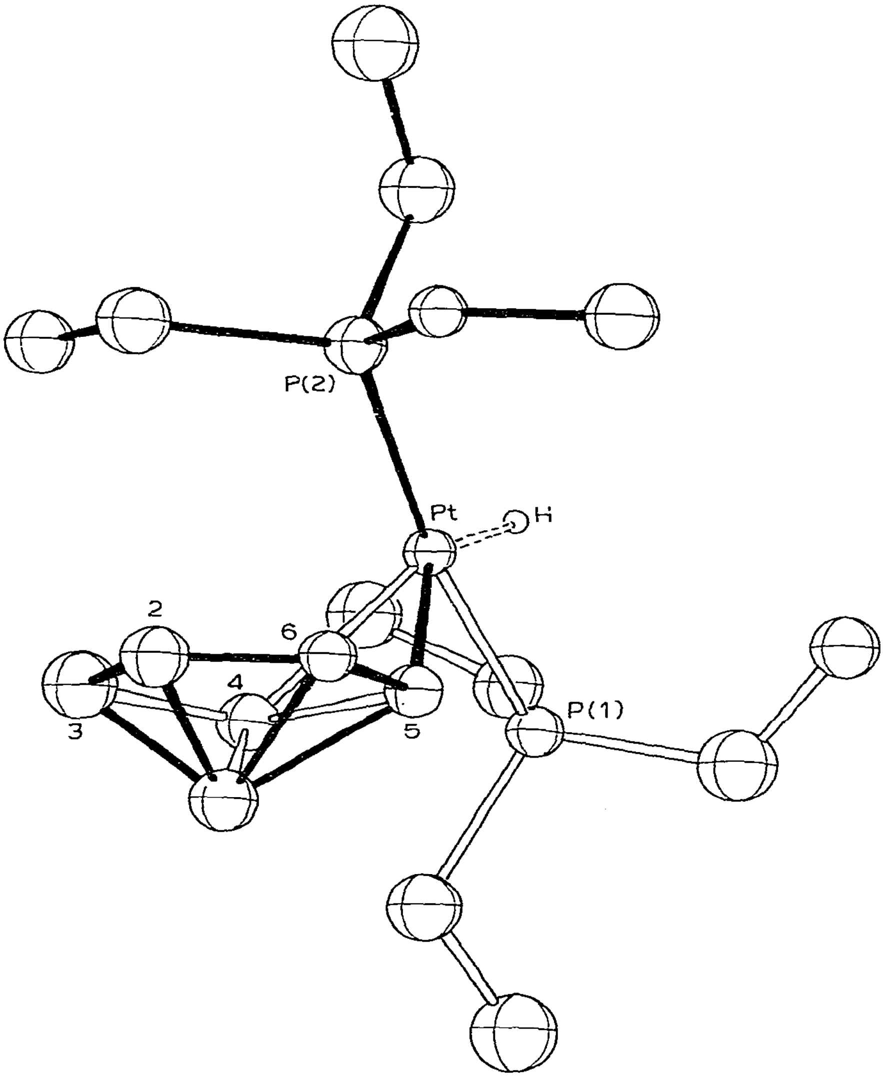


(127)

Molecular orbital calculations based on the extended Hückel approximation account for the "slip" and "fold" distortion observed in this and other carbametallaboranes [293].



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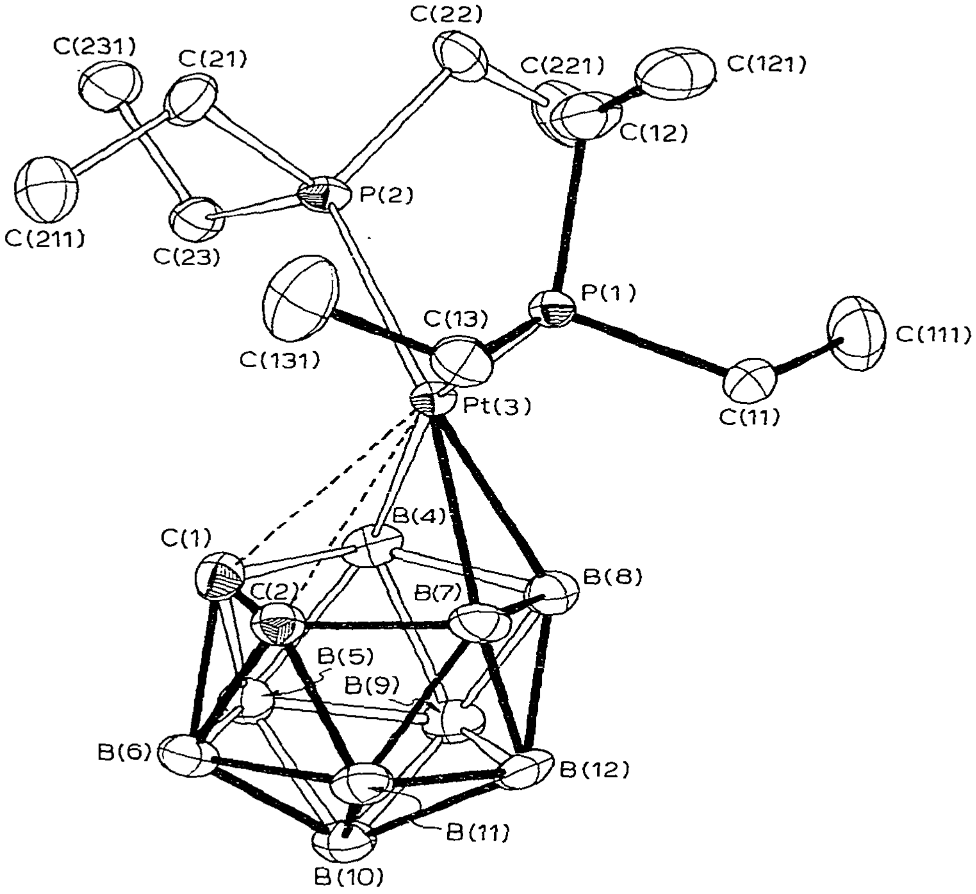

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X. Metal hydrides

An article has been written discussing the reactivity patterns in the formation of platinum hydrides by protonation reactions [294]. The complexes $[\{PtX(PEt_3)_2\}_2PH_2]Y$ (X = H, Y = Cl, Br; X = Y = Cl, Br) have been prepared and the structures of two isomers determined by ^{31}P NMR spectroscopy. The compounds are linked by single PH_2 bridges. This bridging PH_2 group is relatively stable, and it has a greater trans influence than PEt_3 in the complexes [295]. Complexes $PtH(EH)(PEt_3)_2$ and $Pt(EH)_2(PEt_3)_2$ (E = S, Se) have been prepared. Oxidative addition to trans-$PtHX(PEt_3)_2$ (X = Cl, Br, I, SH, SeH, CN) gives 6-coordinate Pt(IV) dihydrides. Addition of HY (Y = Cl, I) to trans-$PtH(SH)(PEt_3)_2$ gives Pt(IV) dihydrides which decompose to $Pt(EH)_2(PEt_3)_2$ (E = S, Se) [296]. The complexes $PtH_2X(CN)(PEt_3)_2$ (X = Cl, Br, I) (131) have been identified by ^1H and ^{31}P NMR spectroscopy at -80°C as the initial products from the reaction of trans-$PtH(CN)(PEt_3)_2$ and HX. Similarly $[PtH(PEt_3)_3]^+$ and HCl give $[PtH_2Cl(PEt_3)_3]^+$ [297]. In the equilibrium of trans-$PtHI(PEt_3)_2$ with

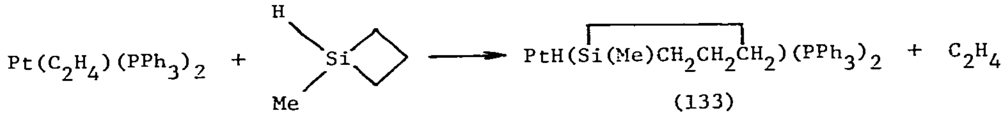
$$PtH(CN)(PEt_3)_2 \;+\; HX \xrightarrow{-90^\circ C} \underset{(131)}{PtH_2X(CN)(PEt_3)_2} \xrightarrow{0^\circ C} PtX(CN)(PEt_3)_2 \;+\; H_2$$

additional phosphine L (L = $PMe_{3-n}H_n$(n=0-3) or PEt_3) the temperature dependent ^1H and ^{31}P NMR spectra show the cation $[PtH(PEt_3)_2L]^+$ at -90°C. These cations (except PH_3) have been isolated as tetraphenylborate salts [298]. Well resolved spectra of the 5-coordinate complex $[PtH(PEt_3)L_3]^+$ are given. These authors have also investigated the reaction between $PtH_2(PCy_3)_2$ and MH_3X (M = Si, X= H, Cl, SiH_3; M = Ge, X = H) to give trans-$PtHY(PCy_3)_2$ (Y = MH_2X). The structure of trans-$PtH(SiH_3)(PCy_3)_2$ has been solved [299]. The crystal structure of trans-$[PtH(PCy_3)_2(PPh_3)]PF_6$ shows a very small angle of 155.2° for the P-Pt-P angle between the PCy_3 ligands [300]. The complex $PtH[Ph_2P(C_6H_4SO_3)](PPh_3)_2$ (132) has been prepared from trans-$PtHCl(PPh_3)_2$ and the sodium salt of diphenylphosphinobenzene-m-sulfonate [301]. The complex $PtH(SnMe_3)_3(dppm)$ has been prepared from $PtMe_2(dppm)$ and $SnMe_3H$ [302].

$$\text{trans-}PtHCl(PPh_3)_2 \;+\; Ph_2P(C_6H_4SO_3Na) \;\rightarrow\; \underset{(132)}{PtH[Ph_2P(C_6H_4SO_3)](PPh_3)_2} \;+\; NaCl$$

Plots of J(PtH) and τ(PtH) against σ_p have been made for complexes trans-PtH(1,3-diaryltriazenido)$(PPh_3)_2$. Good linear plots are obtained for Me, H, F and Cl in the para position of the triazenido ligand [303].

Several cis-hydridoalkylbis(tertiary phosphine)platinum(II) compounds have been synthesized and their decomposition to alkanes studied [304]. Rate data are supplied for the initial rate-determining intramolecular reductive elimination of alkanes. The qualitative sequence of decreasing reactivity for R in compounds $PtH(R)(PPh_3)_2$ is R=Ph>Et>Me>$CH_2CH{=}CH_2$. Considerations about the oxidative addition of alkanes to low-valent platinum metal complexes are discussed. Treating $Pt(C_2H_4)(PPh_3)_2$ with silacyclobutane gives a hydride complex (133). The compound is unstable to decomposition [305]. The complexes trans-$PtH[(CH_2)_nCN]L_2$ (L = 1,3; L_2 = $2PPh_3$, $Ph_2PCH{=}CHPPh_2$) (134) undergo reductive elimination induced by ligands CO, PhC≡CPh, PEt_3,



(133)

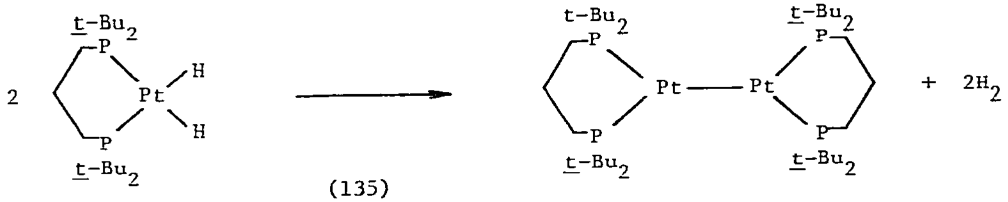
$PPhMe_2$, cis-$Ph_2PCH{=}CHPPh_2$, giving the Pt(0) complex [306]. The hydride $PtH(NO_3)L_2$

$$\text{trans-}PtH[(CH_2)_nCN]L_2 + 2CO \rightarrow Pt(CO)_2L_2 + CH_3(CH_2)_{n-1}CN$$

(134)

reacts with methylenecyclopropane to give π-methylallyl platinum complexes. The mechanism has been studied using $PtD(NO_3)L_2$ [307]. The reaction of platinum hydrid with Feist's acid gives a range of reactivity. Reactions are described involving cleavage of a cyclopropyl bond, addition of Pt-H across the exocyclic double bond o the methylenecyclopropane derivative, and reductive elimination of the Pt-H hydroge as a proton [308].

The ^{31}P NMR spectra of $PtH[OPPh_2][QOPPh_2]PMePh_2$ (Q = H, BF_2) are compared. The trans influence of the hydride can be seen in the ^{31}P chemical shift data, and the boron quadrupole partially broadens the spectrum of the BF_2 capped product [309]. series of diphosphinedichloroplatinum(II) complexes with bulky phosphine substituen react with Na/Hg to give the corresponding dihydride complexes (135). Electron-poo



(135)

olefins will irreversibly displace H_2. The complexes can be thermally decomposed to Pt dimers with loss of H_2 [310]. Complexes *trans*-PtH_2L_2 (L = PCy_3, P-*i*-Pr_3, P-n-Bu-*t*-Bu_2 and PMe-*t*-Bu_2) (136) have been prepared by reacting the peroxycarbonato complexes with $NaBH_4$. A similar reaction with the dioxygen complexes gives the products less readily. All the complexes insert highly activated acetylenes to yield *trans*-hydridovinyl complexes [311]. The hydrides *trans*-PtHX(P-*t*-$Bu_3)_2$ (X = Cl, Br, I, CF_3CO_2) and *trans*-PtH_2(P-*t*-$Bu_3)_2$ with bulky substituents will readily undergo facile intramolecular metallation [312]. From the reaction of *trans*-$PtH(NO_3)(PEt_3)_2$ with $NaBPh_4$ a complex $[PhPt(PEt_3)_2(\mu\text{-}H)Pt(PEt_3)_2H]BPh_4$ has been isolated. The structure is confirmed by single crystal X-ray crystallography, and the hydride region by ^1H NMR spectroscopy [313]. Bridged hydride complexes $[Pt(\mu\text{-}H)(SiR_3)(PCy_3)]_2$ have been prepared from $Pt(C_2H_4)_2PCy_3$ and SiR_3H (SiR_3 = $SiCl_3$, $SiClMe_2$, $SiMe_2Ph$, $SiMe_2(CH_2Ph)$, $SiMe_2Et$, $SiEt_3$, $Si(OEt)_3$). The structure of $[Pt(\mu\text{-}H)(SiEt_3)(PCy_3)]_2$ has been solved [314]. A similar germanium compound has been prepared. Additional discussion of these platinum hydrides is given elsewhere [315]. A series of binuclear hydrides of platinum containing terminal and bridging hydrides have been prepared from $PtCl_2$(dppm) and $NaBH_4$. Reactions involving CCl_4 and HCl to produce compounds such as complex (137) are described [316]. In a related paper the ^{31}P NMR spectra of these compounds are discussed and data given for $J(^{31}P\text{-}^{31}P)$ and $J(^{31}P\text{-}^{31}Pt)$ [317].

$$\underline{trans}\text{-}PtCl_2L_2 \rightarrow PtL_2 \rightarrow PtL_2O_2 \xrightarrow{CO_2} PtL_2CO_4 \xrightarrow{NaBH_4} PtH_2L_2$$

(136)

$$PtCl_2(dppm) + NaBH_4 \rightarrow [Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+ \xrightarrow{HCl} [Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$$

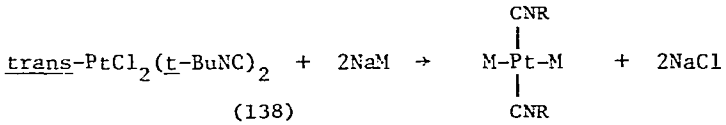
(137)

The structure of *trans*-$NiH(BH_4)(PCy_3)_2$ has an angle P-Ni-P of 155.4(7)° [318]. A palladium hydride intermediate has been suggested in the palladium catalyzed amine exchange reaction. These authors propose the insertion of Pd(0) into the carbon-hydrogen bond [319].

XI. Metal isocyanides

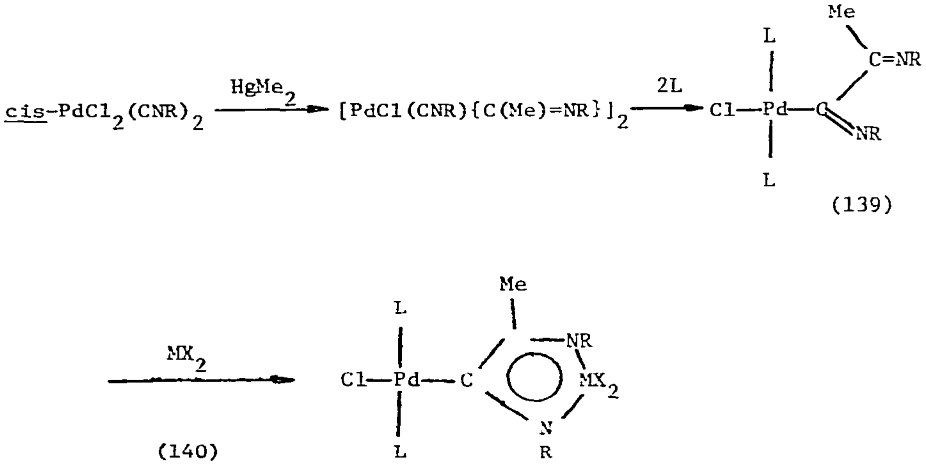
An article from a symposium talk on isocyanide, carbene and related chemistry of Pd(II) and Pt(II) has been published. Subjects covered include formimidoyl and carbene complexes, *o*-metallation of carbenes, enamine-ketimine tautomerism of the Pd-C(Me)=NR group, and the palladium(II) hydride insertion reaction. The complex and reactions are derived from isocyanides [320].

Nickel vapor in a methyl isocyanide argon matrix at 20-45K gives Ni(CNMe), linear and angular $Ni(CNMe)_2$, planar and pyramidal $Ni(CNMe)_3$, and planar and tetrahedral $Ni(CNMe)_4$, the force constants being determined from the IR spectrum. CO is a stronger π-acceptor than MeNC [321]. The vibrational spectra (4,000-30 cm^{-1}) for $[Pd(CNMe)_4](PF_6)_2$ and $[Pd_2(CNMe)_6](PF_6)_2$ have been measured and assigned. From a Raman study of the Pd_2 compound the fluxionality, bond polarizability, and bond orde of the Pd(I)-Pd(I) bond were estimated [322]. Linear dimetalloplatinum complexes $M-PtL_2-M$ ($M = Co(CO)_4$, $Co(CO)_3PPh_3$, $Fe(CO)_3NO$, $Mn(CO)_5$, π-$cpMo(CO)_3$, π-$cpW(CO)_3$; L = *t*-BuNC, CyNC (138) have been prepared from *trans*-$PtCl_2$(*t*-BuNC)$_2$ and NaM. Infrared data in the CN and CO regions are given [323]. When $K_2[Pt(SCN)_4]$ reacts with cycloh isocyanide the complex *trans*-$Pt(CNCy)_2(SCN)_2$ is formed. The complex undergoes isomerization at 130°C to the *cis* isomer [324]. 1,2-bis(arylimino)propylpalladium complexes *trans*-$PdX\{C(NR)CMe(NR)\}L_2$ (X = Cl, Br; R = C_6H_4OMe-*p*-or Cy; L = PPh_3, $PMePh_2$ (139) and *cis*-$[PdCl\{C(NC_6H_4OMe\text{-}p)CMe(NC_6H_4OMe\text{-}p)\}dppe]$, obtained from isocyanides, react with anhydrous metal halides MX_2 (M = Fe, Co, Ni, Cu, Zn) to give chelate complexes (140) [325]. Another paper has been published by this group using this same concept [326].



$$\textit{trans}\text{-PtCl}_2(t\text{-BuNC})_2 + 2\text{NaM} \rightarrow \text{M-}\overset{\text{CNR}}{\underset{\text{CNR}}{\text{Pt}}}\text{-M} + 2\text{NaCl}$$

(138)



(139)

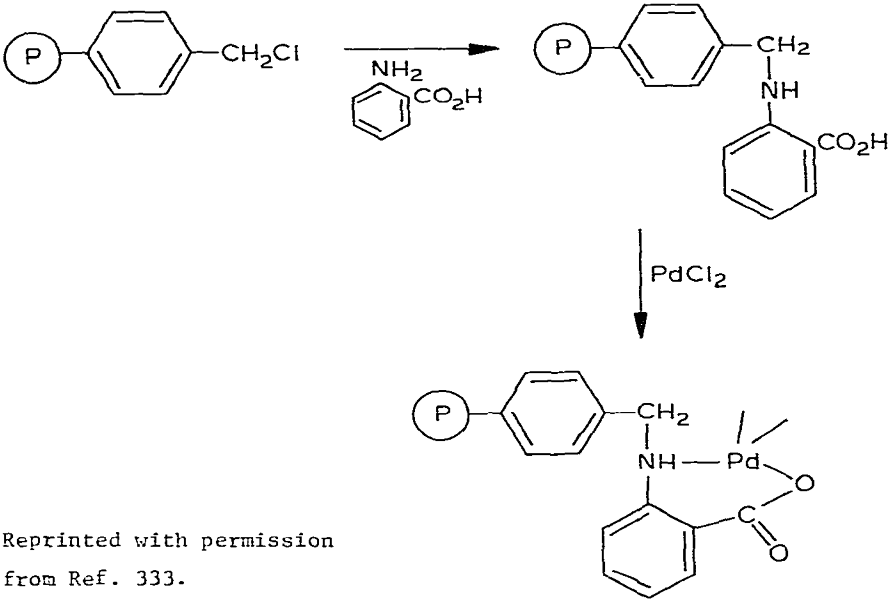
(140)

Vibrational and multinuclear magnetic resonance spectroscopy has been studied for methyl isocyanide complexes of Pd(II), Pt(II) and Pt(IV). The ^{1}H NMR spectra show coupling to ^{14}N, and ^{14}N chemical shifts have been determined from ^{1}H-{^{14}N} INDOR experiments. For the Pt compounds the ^{195}Pt chemical shifts have been measured [327]. ^{13}C NMR chemical shifts have been measured for trans-$[PtX(CNR)(PEt_3)_2]^+$ (X = Cl, Br; R = Me, t-Bu, Cy, $4\text{-}C_6H_4R^1$ (R^1 = H, Me, OMe, Cl, NO_2) or $2,6\text{-}C_6H_3Cl_2$); cis-$PtCl_2(CNR)(PEt_3)$; cis-$PtCl_2(CNCy)_2$; cis-$PdCl_2(4\text{-}MeOC_6H_4NC)PEt_3$. Values $^{1}J(Pt\text{-}C)$ have been obtained and a correlation of chemical shifts of $4\text{-}R^1C_6H_4NC$ ligands with the σ_p^+ substituent constant for R^1 presented [328]. The ^{14}N NMR of t-butyl isocyanide complexes of palladium have been measured and discussed [329].

XII. Catalytic reactions involving complexes

A short review of 37 references has been published which includes references on reactions of acetylenes catalyzed by metal complexes, and the reactions between Ni or Pd complexes, and a benzene ring [330]. A silica-gel supported Pd(0) compound provides enhanced selectivity because of steric steering. This steric steering of the nucleophile has been used for allylic alkylation [331]. Palladium and nickel complexes have been used to catalyze reactions of active methylene and carbonyl compounds with myrcene. The mixtures contain tri-n-butylphosphine. The reactions are considered to involve π-allylic intermediates [332].

A polymer bound catalyst (141) has been used for the hydrogenation of nitrobenzene and benzonitrile. From benzonitrile at 100°C, a 2:1 ratio of N-benzylbenzamidine and α-(benzylideneamino)toluene are obtained. Hydrogenation of nitrobenzene at 80°C for 3.5 h under a pressure of 1000 lb in^{-2} results in a 97% conversion into aniline [333]. The selective catalytic hydrogenation of COD to cyclooctene with $PdCl_2(PPh_3)_2$



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(141)

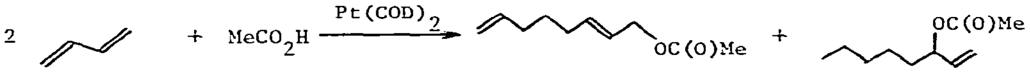
does not require $SnCl_2$ and the reactivity is similar to that of the corresponding heterogeneous Pd(II) polymer catalyst. The π-allylic intermediate PdCl(π-cycloocten PPh_3 has been isolated from the hydrogenation solution and is a much more active catalyst than $PdCl_2(PPh_3)_2$. The catalysts are poisoned by excess triphenylphosphine but unaffected by chloride ion. With both H_2 and HCl present the hydrogenation is faster than with pure H_2 [334]. Other results on the catalytic activity of polymer bound Pd(0) complexes have been published [335]. Hydrogenation of $PhCH{=}C(NHCOR)CO_2R$ (R = Ph, R^1 = H; R = Me, R^1 = H, Me, $HOCH_2CH_2$, Me_2CH, $PhCH_2$) in the presence of palladium(II) complexes of the styrene-(s)-phenylalanine maleimide copolymer shows a degree of selectivity dependent on the steric bulk and polarizability of the substituents RCONH and R^1O_2C on the prochiral carbon [336]. In an autocatalysis study the kinetics of the reaction of H with the acetate bridged dimer $[Pd(OAc)_2PPh_3]_2$ has been studied manometrically [337]. A polymer bonded palladium(II) chloride complex with phosphinated polystyrene catalyzes the hydrogenation of alkenes and alkynes, and particularly the selective hydrogenation of dienes to monoenes [338]. The catalytic activity decreases in the order: conjugated dienes > nonconjugated dienes > terminal olefins > internal olefins. A mechanism is based on kinetic studies. A very active hydrogenation catalyst has been prepared from $Pd(\pi\text{-allyl})_2$ and vitreous materials containing surface OH groups, followed by reduction with LiH. Kinetic activity and rate constant data are presented and discussed [339]. It has been concluded that the yield of cis-2-pentene from 1-pentene $CHD{=}CD(CH_2)_2CH_3$ is a measure of steric crowding at a catalyst site. Both homogeneous and supported nickel and platinum catalysts have been used, and the kinetics of isomerization measured [340]. A mechanistic study of the catalyzed olefin isomerization by $NiX(PPh_3)_3$, a low nickel (II) hydride (142) is responsible for the catalytic activity and is apparently produced from a nickel(I) compound. This conclusion is based on mass spectral analysis

$$2Ni(I) + \text{olefin} \rightleftharpoons \underset{(142)}{Ni(II)\text{hydride}} + Ni(II)\text{allyl}$$

of the isomerization products of 1-butene-3,3-d_2, and the similarity of the catalytic and chemical activity of hydrido species produced from $Ni(PPh_3)_4$ and HX at -78°C [341]. Allylic rearrangements have also been reported catalyzed by mixtures of $PtCl_2(PPh_3)_2$ and $SnCl_2$ [342]. The complex $NiCl_2(PPh_3)_2$ has been used for the catalytic dimerization of isoprene [343]. Palladium complexes have similarly been used for the catalytic dimerization of butadiene [344].

Among other materials, the compound $Ni(COD)_2$ mixed with $\mu\mu^1$-dichlorotetranitrosyldiiron has been used for the cyclodimerization of butadiene to 4-vinylcyclohexene. A mechanism involving olefin, then coupled vinyl complexes, is proposed [345]. The dimerization of 1,2,4-pentatriene on a Pd(O)/triisopropylphosphine catalyst at 35°C gives four 6-membered ring dimers. Intermediates of the π-allylic type are suggested leading to the formation of the organic products [346].

The $Pt(COD)_2$ catalyzed reaction of butadiene with secondary amines (morpholine, piperidine, diethylamine and dimethylamine) gives octa-2,7-dienylamines. Addition of PPh_3 has little effect. The complex $Pt(COD)_2$ catalyzes the addition of acetic acid to butadiene to give octa-2,7-dienyl acetate (143) and 1-vinylhex-5-enyl acetat (144) in the ratio of 4:1. A mixture of $Pt(COD)_2$ and PPh_3 catalyzes the addition of



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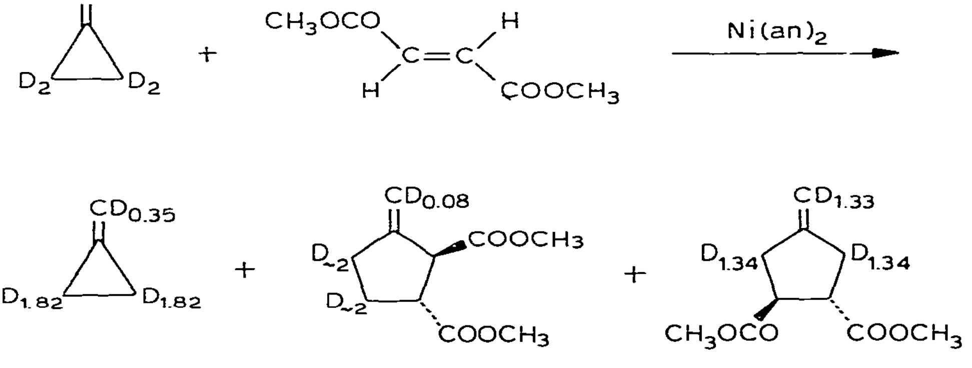
acetaldehyde to butadiene to give 2-methyl-3,6-divinyltetrahydropyran. Mechanisms involving allylic intermediates are discussed [347]. The dimerization-alkylation of butadiene to 1-methoxy-3,7-octadiene and 3-methoxy-1,7-octadiene has been studied with both $Pd(PPh_3)_4$ and resin-bound Pd(0) catalysts. Limiting rates are achieved on increasing the concentration of the homogeneous catalyst, but this problem is not encountered with the larger loading on resin-bound materials [348]. Butadiene oligomerization has also been studied on polymer anchored palladium acetate [349]. The cyclodimerization of butadiene to 1,5-cyclooctadiene proceeds selectively in the presence of $Ni[P(OC_6H_4R)_3]$ (R = 2-Ph, $2\text{-}SiMe_3$) catalysts. Yields are lower when R=H, and least selective when catalysts from $P(OC_6H_3Me_2\text{-}2,6)_3$ are used [350].

The reaction of 2,2,3,3-tetradeuteriomethylenecyclopropane and dimethyl fumarate has been carried out in the presence of $Ni(an)_2$ (an = acrylonitrile). The data (145 strongly suggest that a trimethylenemethane-nickel(0) complex of type (146) is responsible for the formation of these adducts [351].



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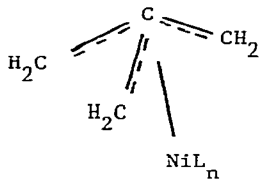
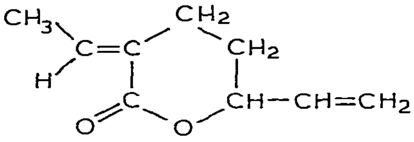


(L = olefin)

(146)

The complexes trans-$PtCl_2(C_2H_4)(Et_2NH)$ and $PtCl_2CH_2CH_2NHEt_2(Et_2NH)$ promote the conversion of acrylonitrile into propionitrile and 1,4-dicyanobutadiene [352]. The kinetics of oxidative dimerization of styrene to 1,4-diphenylbutadiene in the presence of palladium acetate in acetic acid and acetate show the most reactive species to be $Pd_3(OAc)_6$. This compound does not form detectable complexes with styrene. The complex $Na_2Pd_2(OAc)_6$ is the next most reactive and the reaction involves intermediate π-complex formation. The monomer $Na_2Pd(OAc)_4$ is unreactive. The role of π-complexes in the reaction mechanism is discussed, especially the rate determining α-vinyl complex formation [353]. Bis(diazadiene)nickel(0) complexes have been used for the catalytic tetramerization of alkynes [354]. Butadiene polymerization has been carried out with supported π-allyl complexes of nickel [355]. The reaction of styrene and butadiene occurs in the presence of a 3-component catalyst consisting of a palladium salt, a Lewis acid, and a tertiary phosphine. The reaction mainly gives the straight-chain codimer 1-phenyl-1,4-hexadiene. The proposed mechanism involves the addition of butadiene to a palladium hydride [356]. The complex $[NiH(dppe)_2]OCOCF_3$ has been used as a homogeneous catalyst for the oligomerization of hexyne-3 [357]. These authors have also reported the oligomerization of hexyne-3 by nickel(0) compounds under a CO_2 atmosphere [358]. Non chelating tertiary phosphine complexes of Pd(0) in the absence of or in apolar solvents are effective catalysts for the telomerization reaction of butadiene and CO_2. The products are the 6-membered lactone (147) and the octadienyl esters of 2-ethylidenehept-6-en-5-olide (148) [359]. In a similar study in polar aprotic solvents, CO_2 and butadiene give 2-ethylidene-5-hepten-4-olide, together with the formation of butadiene dimers. A possible mechanism is discussed involving π- and σ-allyls [360].

The polymerization of butadiene in the presence of a π-crotylnickel chloride-sulfuryl chloride catalyst is first order with respect to the monomer and, at low



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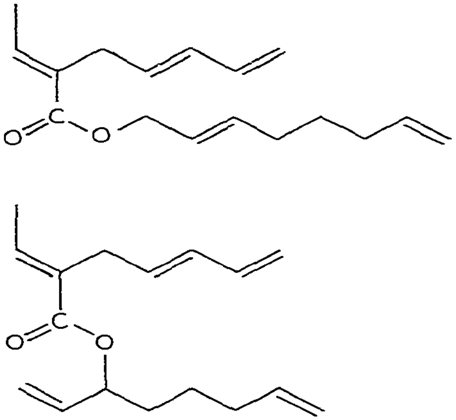

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(148)

catalyst concentrations, second order with respect to the catalyst. At high catalyst concentrations it becomes zero order in the reaction [361]. Propionaldehyde has been dimerized by nickel(O) complexes [362]. A sequence of ligand insertions is proposed in the polymerization of isocyanides by complexes of nickel(II). The mechanism is related to the kinetic data and to reactivities of coordinated isocyanides [363]. One turn of the polymer helix contains approximately four repeating units. The entropy of activation for the reaction is low and it is unknown how the chain terminates [363]. In the following paper these authors present a rule which predicts the screw sense of the polymers. Data from ten chiral isocyanides have been used to develop these ideas [364]. The complex $NiEt_2$(bipy) has been used for the catalyzed polymerization of aldehydes [365].

Palladium(O) complexes have been used as catalysts for the allylic alkylation of olefins [366]. Palladium allyls have been reacted with vitreous materials to place palladium on a support for use as a hydrogenation catalyst [367]. The complex $Ni(COD)_2$ has been used in the cyclodimerization of 1,12-dibromo-2,10-dodecadien The reaction is carried out at 20°C and the yield is in the vicinity of 20%. The reaction is used as a replacement for $Ni(CO)_4$ [368].

The reduction of aryl bromides, catalyzed by $Pd(PPh_3)_4$, works better with sodium formate than with sodium methoxide. The reaction conditions for the formation of ArH (149) involve a temperature of 100°C in DMF solvent [369]. The reaction has been

$$\text{Ar-Br} + HCO_2Na \xrightarrow{Pd(PPh_3)_4} \text{ArH}$$

(149)

carried out at high conversion on a series of 10 aryl bromides. The arylation of styrene (150) by Grignard reagents has been carried out in the presence of stoichiometric or catalytic amounts of $PdCl_2$ [370]. Palladium complexes have also been used

$$\text{PhMgBr} + \text{PhCH=CH}_2 \rightarrow \text{PhCH=CHPh} + \text{HBr} \qquad (150)$$

for aryl coupling [371] and the complex $Pd(PPh_3)_4$ used to catalyze the reaction of aryl halides with methoxide ion [372]. Zerovalent palladium complexes have also been used as catalysts for the conversion of aryl halides to aryl sulfides (151) [373]. Similarly the complexes have been used to catalyze the reaction of toluene

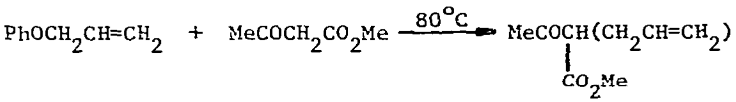
$$\text{PhX} + \text{RS}^- \rightarrow \text{PhSR} + \text{X}^- \qquad (151)$$

with sulfuryl chloride to give substituted benzyl chlorides (152) [374]. In a similar

$$XC_6H_4CH_3 + SO_2Cl_2 \rightarrow XC_6H_4CH_2Cl \qquad (152)$$

type of reaction nickel complexes have been used as catalysts for the synthesis of vinyl bromides by halogen substitution on a vinylic position [375].

Palladium complexes have been used in a new synthetic method for aromatic type medium and large membered lactones. The method is based on intramolecular alkylation of ω-haloalkyl 2-phenylthiomethylbenzoate, and is applied to the synthesis of (±)-lasiodiplodin [376]. Palladium is involved in the synthesis of one of the reactants, 8-chloro-6-octen-2-ol. The allylation of β-diketone, β-ketoesters, and methine active hydrogen compounds by allyl phenyl ethers or allyl esters with palladium phosphine catalysts has been studied (153). The use of DIOP gives up to 10% e.e. [377]. A mechanism has been proposed which involves carbanion attack at a palladium allyl complex. Asymmetric hydroformylation has been carried out with chiral platinum complexes [378].



$$PhOCH_2CH{=}CH_2 + MeCOCH_2CO_2Me \xrightarrow{80^\circ C} \underset{\displaystyle CO_2Me}{MeCOCH}(CH_2CH{=}CH_2) \qquad (153)$$

Telomerization of butadiene with $RSO_2CH_2CO_2Me$ (R = Ph, tolyl) using a catalyst containing $Pd[CH(CO_2Me)_2]_2$:PPh_3:$AlEt_3$:CF_3CO_2H in proportions 1:3:4:10 gives 90-95% $RSO_2CHR^1CO_2Me$[$R^1{=}CH_2CH{=}CH(CH_2)_3CH{=}CH_2$-trans] and $RSO_2CR^1_2CO_2Me$. Transformations of these organic compounds into other products are described [379]. A terminal conjugated diene system is obtained by the palladium catalyzed elimination reactions of allylic acetates and phenyl ethers (154). The catalyst is composed of palladium

(154)

(R = Ph, CH_3CO)

acetate and triphenylphosphine [380]. π-Allylic complexes of nickel, palladium and platinum have been used to catalyze the telomerization of butadiene with Et_2NH to form $C_{12}H_{19}NEt_2$ and $C_8H_{13}NEt_2$. The reaction is accelerated by the addition of triphenylphosphine [381]. The dimethylamination of duroquinone, $Ni(duroquinone)_2$, and $Ni(duroquinone)(COD)_2$ with Me_2NH or $(Me_2N)_2CH_2$ gives 51% 2,3-dimethyl-5,6-bis[(dimethylamino)methyl]hydroquinone. No 2,5-dimethyl-3,6-bis[(dimethylamino)methyl] hydroquinone is obtained [382].

Zerovalent phosphine complexes of palladium have been used as catalysts for the synthesis of conjugated dienes from the reaction of bromo- and cp_2ClZr substituted vinyl compounds [383]. Similarly the palladium complexes have been used in the reaction of tin substituted allyls with α-chloroketones. The reaction is used for the synthesis of epoxides [384]. Linear, fatty type, carboxylic acid esters have been obtained by regioselective 1-alkene carbonylation. The reaction is catalyzed b dispersions of ligand-stabilized Pd(II) chlorides in quaternary Group VB salts of trichlorostannate. The dependence of alkene and catalyst composition is described. Also the techniques are described for multiple recycling and regeneration of the catalyst [385].

Chiral dibenzophospholes have been used as ligands to Pd for the catalyzed hydroesterification of α-methylstyrene. The optical purity of the product is reported for a series of optically active chelating phosphines and the relative effectiveness of the ligands to induce enantiomeric excess compared [386].

The addition of cyanogen to acetylacetone is catalyzed by $Ni(acac)_2$ under ambient conditions. A complex $Ni(acac)_2.2(C_2N_2)$ has been isolated from the reaction mixture. It is proposed that cyanogen has inserted into the methino C-H bond. If the reaction is carried out in the presence of an excess of acetylacetone and cyanogen, cyanation occurs [387]. A mixture of $Ni(acac)_2$ and $AlMe_3$ has been used to catalyze the addition of Grignard reagents to silylacetylenes (155) [388]. The method has been used

$$RC{\equiv}CSiMe_3 \;+\; MeMgBr \;\rightarrow\; R(Me)C{=}C(SiMe_3)MgBr \qquad (155)$$

in the synthesis of tetrasubstituted alkenes. The hydrosilylation of isoprene catalyzed by a palladium complex using chlorohydrosilanes proceeds by 1,4- addition to give Z-2-methylbuten-2-yl-silanes. The reaction is highly regioselective and stereoselective. The complex used is a mixture composed of $PdCl_2(PhCN)_2$ and triphenylphosphine [389]. A new synthesis of alk-1-en-4-ynes (156) is described which is

$$R^1CH{=}CHCH_2OCOR \;+\; R^2C{\equiv}CH \;\rightarrow\; R^1CH{=}CHCH_2C{\equiv}CR^2 \;+\; RCO_2H \qquad (156)$$

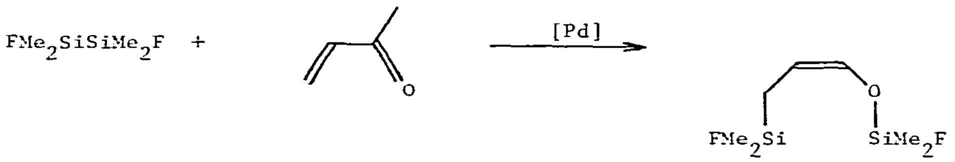
catalyzed by Ni(0) complexes. The complex has PPh_3, PBu_3, $P(OEt)_3$, COD as stabilizing ligands. The reaction proceeds under mild conditions and yields are given for a range of substituents R, R^1 and R^2 [390].

The complex $PdCl_2(py)_2$ has been used as a catalyst for the carbonylation of p-nitrotoluene [391]. A second similar paper has been published by these authors [392]. Attachment of palladium to quinone polymers gives a catalyst which can be used for the oxidation of ethylene to acetaldehyde [393].

Palladium(II) salts supported on Amberlyst have been used as catalysts for ester interchange reactions involving vinylacetate and vinylpropionate. Results are also given for the oxidative esterification of ethylene at 110°C to vinyl acetate and aldehyde [394]. Methylchlorodisilanes such as 1,2-dimethyl-1,1,2,2-tetrachlorodisilane, 1,1,2-trimethyl-1,2,2-trichlorodisilane and 1,1,2,2-tetramethyl-1,2-dichlor disilane are cleaved by HCl in the presence of $Pd(PPh_3)_4$ to give methylchlorohydisilanes (157) in good yield [395]. The reactivity order follows the sequence $Me_2SiCl_4 > Me_3Si_2Cl_3 > Me_4Si_2Cl_2$. Compounds such as $PdCl_2(PPh_3)_2$ and $NiCl_2(PPh_3)_2$

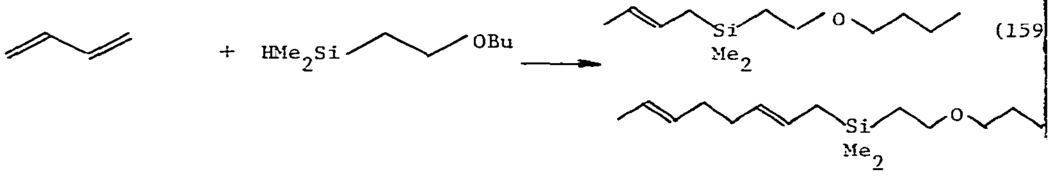
$$Cl_2MeSiSiMeCl_2 + HCl \xrightarrow{Pd(O)} \underset{50\%}{MeSiHCl_2} + \underset{50\%}{MeSiCl_3} \qquad (157)$$

do not give the symmetrical cleavage. In the presence of palladium complexes such as $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$, fluorinated disilanes add to 1,3-dienes, methyl vinyl ketone, and p-benzoquinone, to give mainly 1,4-addition products such as (158) [396]



(158)

The catalytic mixture of $Ni(acac)_2$, AlR_3 and PPh_3 has been used for dimethylsilane hydrosilylation. The interaction proceeds through only a single Si-H bond. The addition is reported to CH_2=CHCN, CH_2=CHCO$_2$Me, CH_2=C(Me)OCOMe, CH_2=CHOBu, CH_2=CHOCOM CH_2=C(Me)CO$_2$Me. Repeated reactions of dienes leads to coupled products (159) [397].

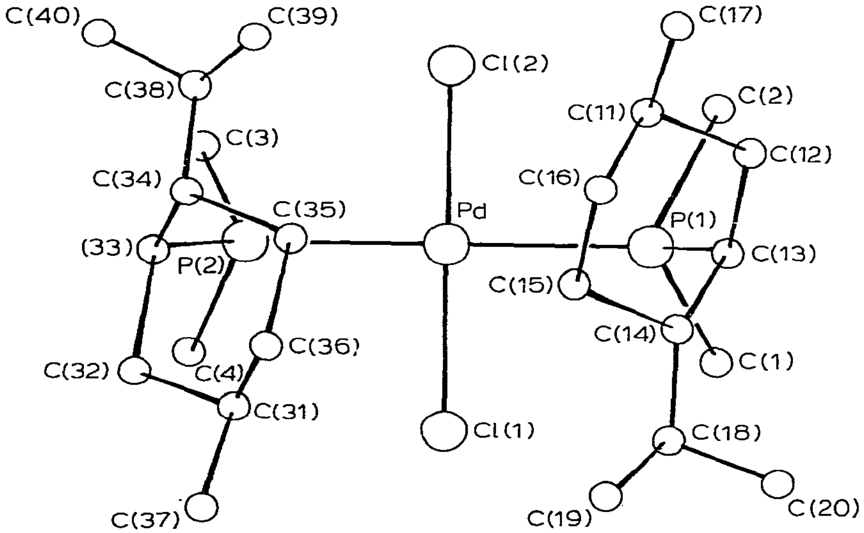


(159

Allylmethylsilanes (160) can be prepared from methylchlorodisilanes and allylic hali using $Pd(PPh_3)_4$ as catalyst. Concentration/time profiles are plotted and details of competitive reactions are given [398].

$$\underset{}{Me_3SiSiMe_3} + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{(160)}{CH_2{=}CHCH_2SiMe_3} + Me_3SiCl$$

The molecular structures of two asymmetric olefin hydrogenation catalysts, $PdCl_2\{(Me_2\underline{neo}Men)P\}_2$ (161) and $PdCl_2\{(Me_2Men)P\}_2$ (162) have been solved [399]. The neomenthyl groups in (161) are located on the same side of the coordination



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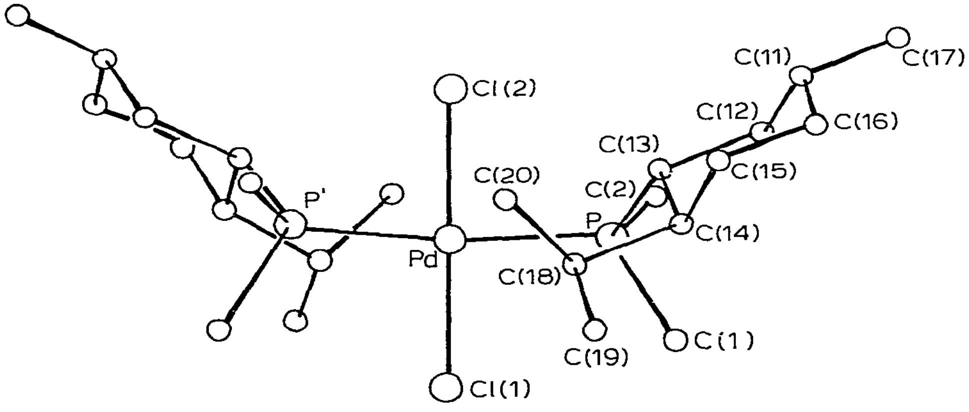
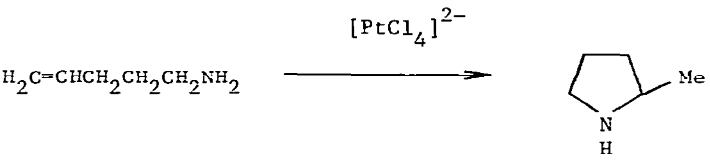


(162)

plane but the menthyl groups in (162) are located on either side of the coordinatio plane.

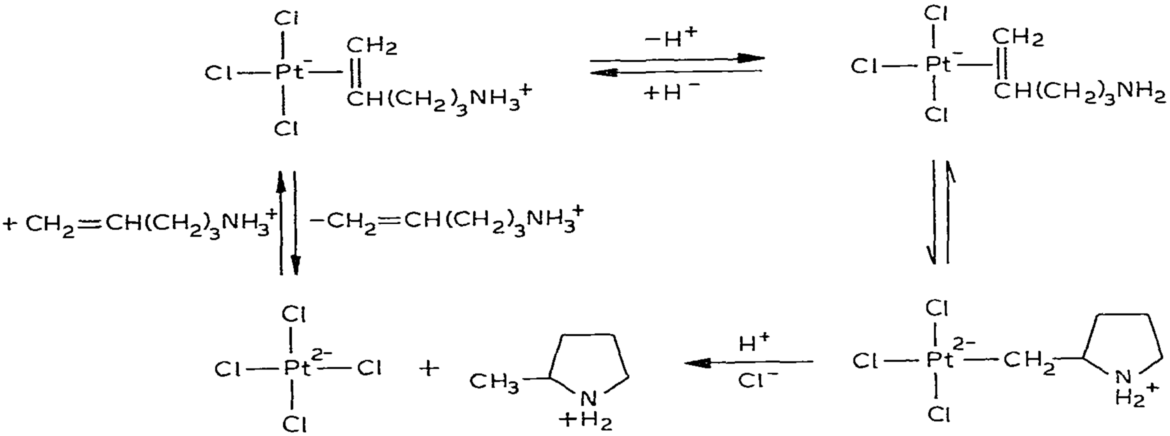
The complex Ni$(PPh_3)_n$ has been used as a catalyst for alkaloid synthesis [400]. Complexes Pt$(PEt_3)_3$ and Pt$[P(i\text{-}Pr)_3]_3$ have been used in the water gas shift reactio The reaction is carried out in acetone solvent between temperatures of 100^o and 150^o and turnover numbers up to 345 found. A possible mechanism is presented involving hydride, formate, carbonyl and hydroxy complexes in the cycle [401]. A platinum chloride-tin chloride homogeneous catalyst has been also used for the water gas shif reaction. Large excess of $SnCl_2$ inhibits the reaction, and no catalysis occurs in the absence of either strong protic acid or a chloride source. The complex ions $[PtCl(CO)(SnCl_3)_2]^-$ and $[PtCl_2(CO)SnCl_3]^-$ have been identified and isolated from the reacting mixture [402].

The complex $PdCl_2(MeCN)_2$ in conjunction with $AgBF_4$ will catalyze the cyclization of a isoquinuclidine to the racemic ibogamine [403]. Olefinic amines of type $CH_2{=}CH(CH_2)_nNHR$ cyclize in acidic solution at 60°C in the presence of $PtCl_4^{2-}$. The reaction is catalytic because the $PtCl_4^{2-}$ is regenerated. An example is shown (163) where n=3 [404]. The mechanism of the cyclization is shown leading to the protonate amine (164). The Pd(II) catalyzed asymmetric cyclization of 2-(but-2-enyl)phenol to optically active 2,3-dihydro-2-vinylbenzofuran (165) in 12% optical yield occurs in



(163)

the presence of a catalytic amount of (−)-β-pinene. A π-allylic palladium intermediate is suggested [405]. Palladium acetate has again been used by these authors in a further article on this reaction [406]. Complexes of nickel(0) have been used to catalyze the cyclization of (166) to (167) [407]. The intermediate arylnickel(II



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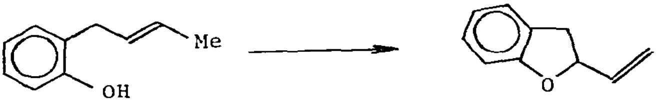

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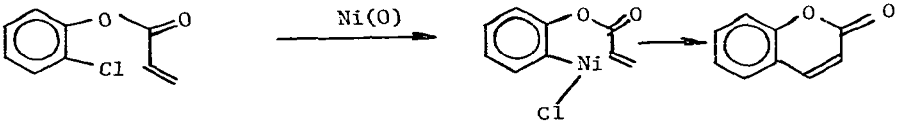

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(167)

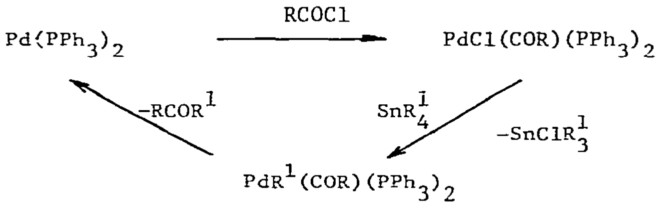
compound is proposed. The complex $NiCl_2(PPh_3)_2$ has been used as a catalyst for the addition of dichloromethane to olefins [408].

Homogeneous solutions of naphthalene and a platinum metal chloro complex in D_2O and CH_3CO_2D cause deuteration of the naphthalene. The found sequence of catalyst efficiency is in the sequence $Na_2PtCl_4.4H_2O >> Na_2IrCl_6.6H_2O > Na_2OsCl_6.6H_2O >> RhCl_3.3H_2O > RuCl_3.3H_2O > Na_2PdCl_4.4H_2O$ [409].

Organotin compounds undergo a palladium catalyzed coupling reaction with acid halides to give ketones (168). The reaction is general both for the organotin compound and the acid chloride [410]. The reaction proceeds through the scheme shown

$$\mathrm{RCOCl} + \mathrm{SnR^1_4} \rightarrow \mathrm{RCOR^1} + \mathrm{SnClR^1_3} \qquad (168)$$

and the yields are high for a good range of substituents. Zerovalent Ni or Pd phosphine complexes have been used in cross-coupling reactions, and applications to the



Scheme

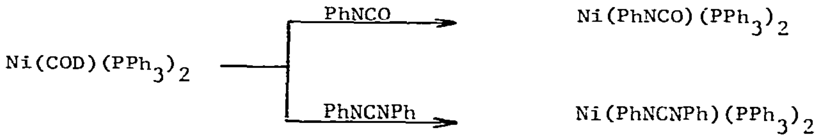
stereo- and regioselective synthesis of trisubstituted olefins made. The catalytic activity is promoted by zinc salts. The reactions involve the interaction of the alkenylaluminum or -zirconium compounds with alkenyl, aryl or alkynyl halides [411]. A solution of $\mathrm{Ni(acac)_2}$ in the presence of an aluminum reducing agent has been used as a catalyst for the conjugate addition of organoaluminum acetylides to α,β-enones. Optimal yields are obtained in the presence of excess dialkylaluminum acetylide [41

XIII. Complexes and reactions of general interest

A review has been published in the Japanese literature on the chemistry of zerovalent complexes of Ni, Pd and Pt [413]. Complexes of type $\mathrm{M_xNi(EPh_3)_x(THF)_y}$ are formed from $\mathrm{Ni(COD)_2}$ and $\mathrm{MEPh_3}$ (M = Li, Na, K; E = Si, Ge, Sn) in THF. With $\mathrm{GePh_3^-}$ and $\mathrm{SnPh_3^-}$, x = 4; but with $\mathrm{SiPh_3^-}$, x = 2 or 3. Treating $\mathrm{Ni(COD)_2}$ with $\mathrm{LiPbPh_3}$ gives $\mathrm{Li_2Ni(COD)Ph_2(THF)_5}$ and $\mathrm{Ph_3PbPbPh_3}$. The ^{1}H and ^{29}Si NMR spectra, and the Mössbauer spectra are compared with those of $\mathrm{MEPh_3}$ [414].

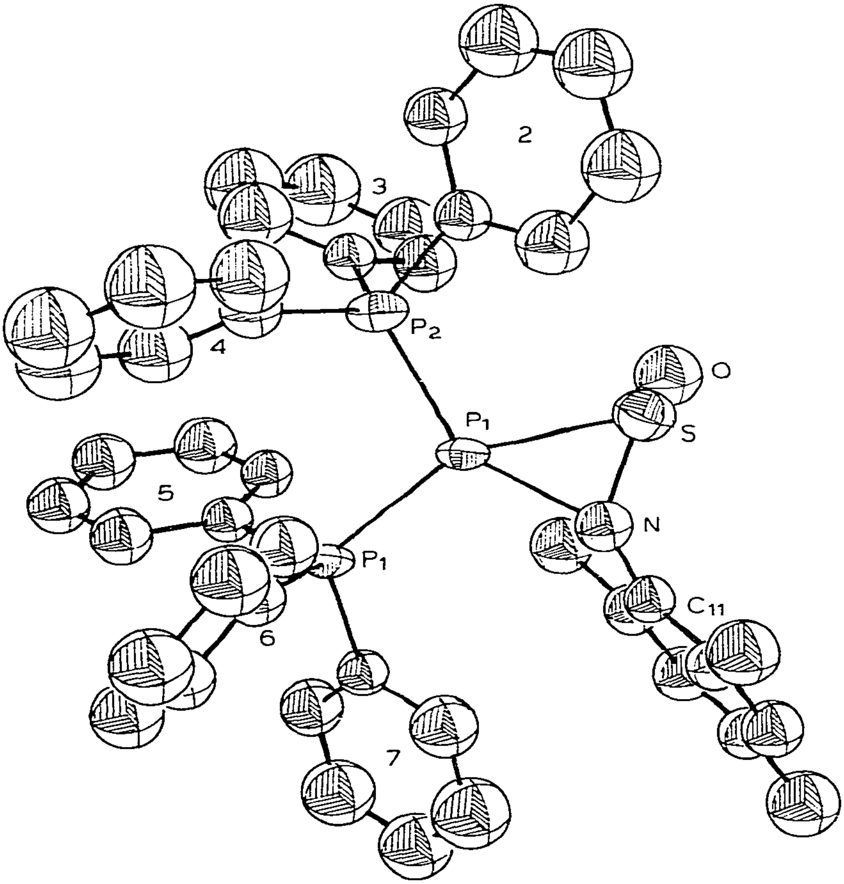
Modern size-exclusion chromatography has been used for the separation and identification of low-valent complexes of Ni and Fe. The compounds contain either phosphi or phosphite ligands [415].

The compound $\mathrm{Ni(COD)(PPh_3)_2}$ reacts with isocyanate or diphenylcarbodiimide to giv 1:1 complexes (169) [416]. Infrared data are presented and discussed and the structures are shown as side-on bonded. On dissolving the compound Ni(PhNCO)(PPh$_3$)$_2$ in



(169)

toluene, conversion to Ni(CO)(PPh$_3$)$_3$ occurs. The crystal structure of Pt(PPh$_3$)$_2$ (2,4,6-mesitylN=S=O) (170) shows a side-on coordination via the N=S group to Pt(0), with the mesityl group in the <u>cis</u> configuration with respect to S=O. The same structure is found in solution [417]. Re-investigation of the unstable compounds



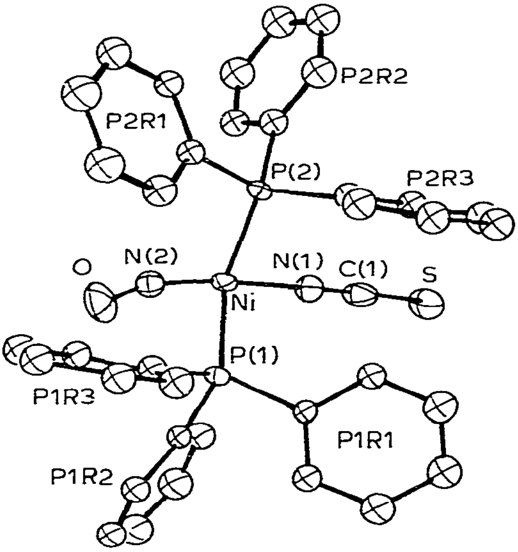
(170)

$Pt(PPh_3)_2(RNSNR)$ [418], for which N-coordination has been proposed, show from ^{31}P and ^{195}Pt NMR spectra that the compound $Pt(PPh_3)_2(Ph^{15}NS^{15}NPh)$ has the sulfurdiimine side-on coordinated via one N=S bond [417].

The synthesis and spectroscopic properties of mixed trihalophosphine complexes of Ni(O) and Pt(II) have been described. Typical compounds are $Ni(PCl_3)_3PF_3$, $Ni(PCl_3)_2(PF_3)_2$, $Ni(PBr_3)_3PF_3$, $Ni(PBr_3)_2(PF_3)_2$, $Ni(PBr_3)(PF_3)_3$ [419]. An electrochemical procedure has been published for the preparation of $Ni(P(\underline{o}\text{-tolyl})_3)_3$. The two step procedure involves the preparation of a very pure nickel(II) solution by anodic oxidation of metallic Ni, followed by cathodic reduction of this solution on mercury in the presence of excess phosphite [420].

The ^{19}F chemical shifts for m- and p-fluorophenylphosphines incorporated in a range of Group VIII complexes have been measured. The data are used to obtain values of the σ_I and σ_R^o parameters used to correlate the electron withdrawing and donating parameters of aromatic compounds. It is concluded that the donor or acceptor properties of a metal ion containing moiety are determined more by the nature of the ligands present than by the formal oxidation state of the metal ion [421].

Intramolecular rearrangements of square planar β-diketonate complexes of Pd(II)



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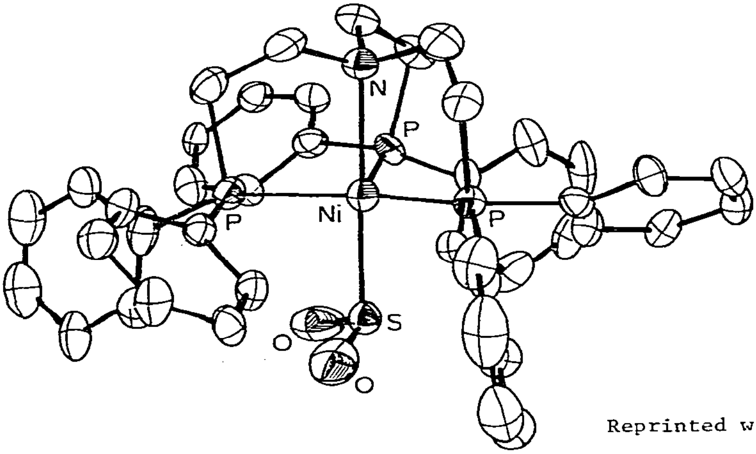
and Pt(II) occur by a dissociative mechanism [422]. The systems studied involve π-allyls and other delocalized organopalladium complexes as well as platinum-olefin compounds.

The structure of $Ni(NCS)NO(PPh_3)_2$ (171) has pseudotetrahedral geometry about the Ni atom. The nonlinear Ni-N-O angle is 161.5(5)°, and the two Ni-P distances are significantly different [423]. Treating $[NiBr(np_3)]BPh_4$ (np_3 = tris(2-(diphenylphosphino)ethyl)amine with SO_2 in the presence of $NaBH_4$ gives the complex $Ni(np_3)SO_2$ (172) [424]. The nickel is pentacoordinate with the SO_2 group (Ni-S is 2.336(3) Å) bonded in a bent mode. The poly(tertiary phosphine) ligands bis(2-diphenylphosphinoethyl)-n-propylamine, bis(2-diphenylphosphinoethyl)phenylphosphine and N,N-bis(2-diphenylphosphinoethyl)2^1-diethylaminoethylamine form stable thiol complexes of nickel (II). The structure of the complex (173) formed with the latter ligand has the nickel coordinated by one N and two P atoms, and also by the sulfur atom [425]. A similar nickel complex has been prepared with a tridentate ligand except now there is a sole Ph_3Sn ligand coordinated to the nickel atom [426].



(172)

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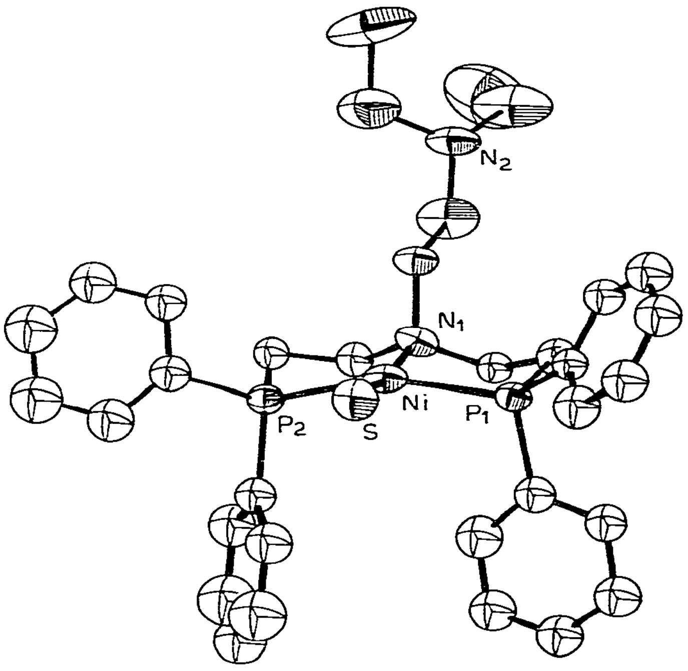
The compound $Ni(SeH)_2(dppe)$ (174) can be prepared by treating $NiCl_2(dppe)$ with two moles of NaSeH. This red-brown compound is air-stable, and evolution of H_2Se is only observed above 100°C. Bands in the infrared spectrum at 249 and 209 cm^{-1} are assigned to ν(Ni-Se) [427]. Substituted phosphines have been used to prepare nickel(I) complexes [428].



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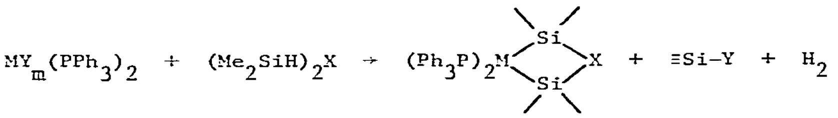
$$\mathrm{NiCl_2(dppe)} + \mathrm{2NaSeH} \rightarrow \mathrm{Ni(SeH)_2dppe} + \mathrm{2NaCl}$$

(174)

A low temperature matrix isolation study has been made of the interaction between PH_3 and zerovalent Cu, Ni and Cr. A band at 1004 cm^{-1} is assigned to $Ni(PH_3)_4$ [429].

The new metallocylces $Pd(Si_2Me_4O)(PPh_3)_2$, $Pd(Si_2Me_4CH_2)(PPh_3)_2$ and $Pt(Si_2Me_4CH_2)(PPh_3)_2$ have been prepared. The new complexes act as catalysts for the disproportionation of tetramethyldisiloxane into dimethylsilane and linear polysiloxanes. A general method of preparation for the compounds is shown below (175) [430].



(X = O, CH_2)

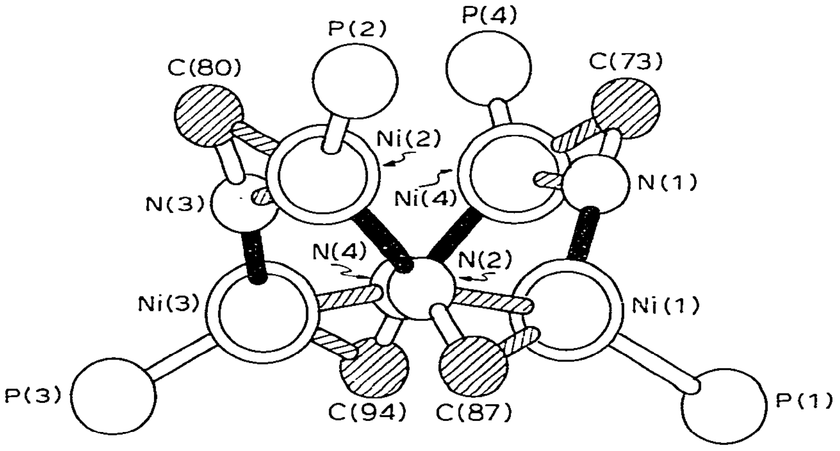
(175)

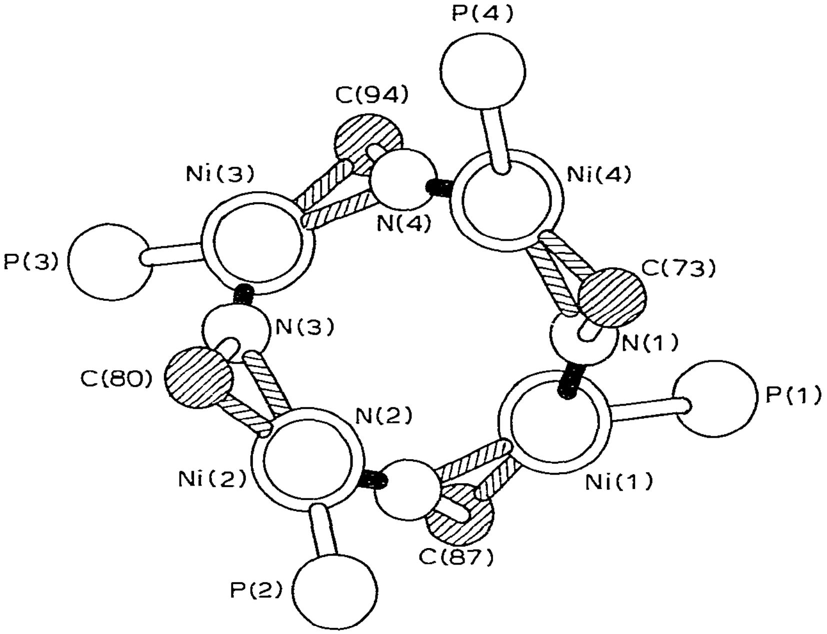
Compounds $MNi(PPh_3)_3(EPh_3)(THF)_x$ (E = Ge, Sn, Pb) and $M_3Ni(PPh_3)(EPh_3)_3(THF)_x$

(E = Ge, Sn) are formed from $Ni(C_2H_4)(PPh_3)_2$ and $MEPh_3$ (M = Na, Li). ^1H NMR and ^{119}Sn Mössbauer spectra are reported and discussed [431]. A range of metalate(0) compounds have been prepared with $SnCl_3^-$ as ligand. Thus thermal substitution reactions of $Ni(CO)_4$, $Pd(PF_3)_4$ and $Pt(PF_3)_4$ give $[M(SnCl_3)_4]^{4-}$ (M = Ni, Pd, Pt) (176) [432]. The preparation and chemistry of the clathrate compound $[PhCN.PPh_3.Ni]_4.2C_7H_8$ are described. The crystal structure shows that each Ni atom of the tetramer is linked by σ-bonds to a P and N atom, and by π-bonds to the N≡C group of another benzonitrile molecule. The coordination of the nickel atoms is roughly trigonal and the Ni and N atoms form an 8-membered ring with a boat conformation (177). Four

$$
\begin{aligned}
Ni(CO)_4 &+ 4SnCl_3^- \rightarrow [Ni(SnCl_3)_4]^{4-} + 4CO \\
Pd(PF_3)_4 &+ 4SnCl_3^- \rightarrow [Pd(SnCl_3)_4]^{4-} + 4PF_3 \\
Pt(PF_3)_4 &+ 4SnCl_3^- \rightarrow [Pt(SnCl_3)_4]^{4-} + 4PF_3
\end{aligned}
$$

(176)





(177)

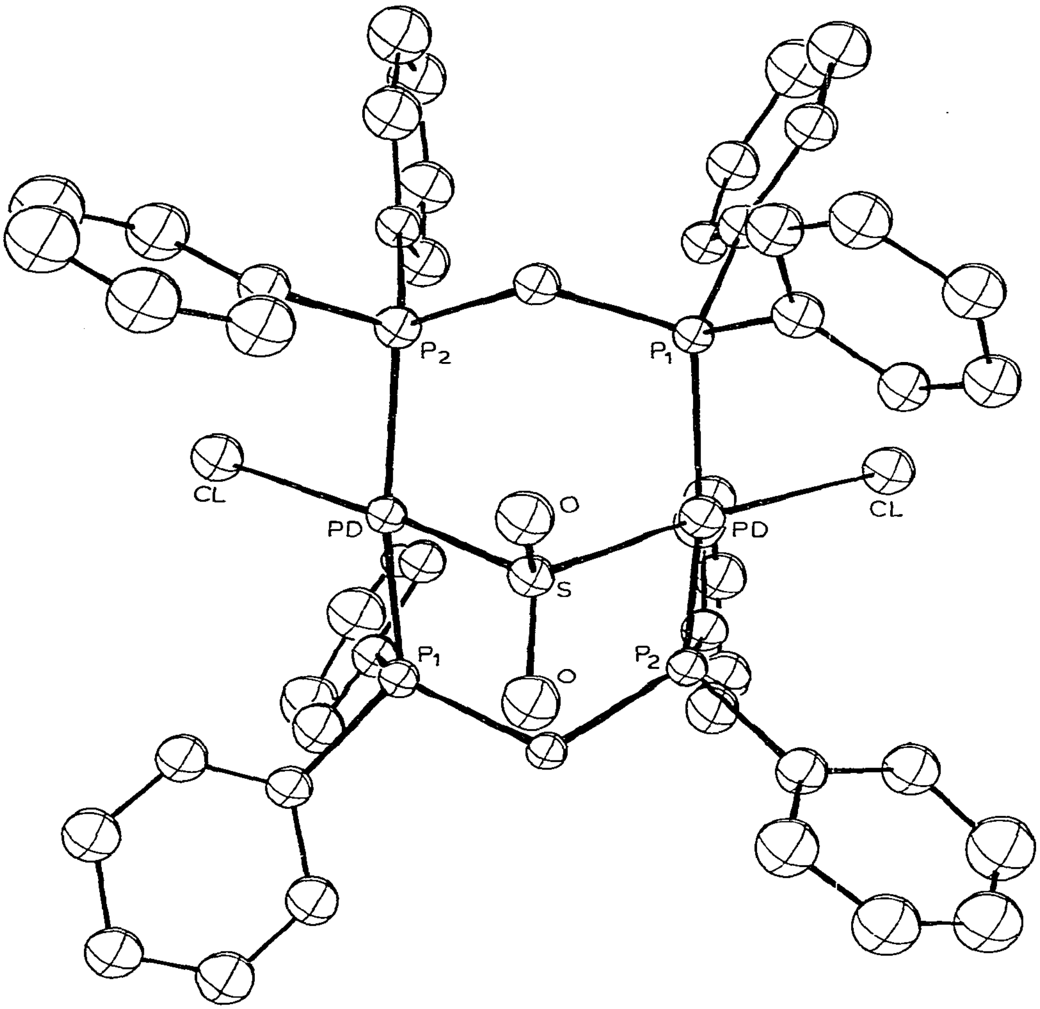
solvent molecules, 2 toluene, n-hexane, and COD are present per asymmetric unit in the unit cell [433].

The Pt(0) dimer $[Pt_2(\mu\text{-dppm})_3]$ has been used for the catalytic reduction of NO and O_2 by CO under ambient conditions (178) [434]. Addition of SO_2 to $PdX_2(dppm)_2$

$$\begin{aligned} O_2 + 2CO &\xrightarrow{Pt_2(\mu\text{-dppm})_3} 2CO_2 \\ 2NO + CO &\xrightarrow{Pt_2(\mu\text{-dppm})_3} N_2O + CO_2 \end{aligned} \qquad (178)$$

(X = Cl, Br), $Pt_2Cl_2(dppm)_2$ or $Pd_2Cl_2(Ph_2AsCH_2AsPh_2)_2$ gives 1:1 adducts. The crysta structure of $Pd_2(\mu\text{-}SO_2)Cl_2(dppm)_2$ (179) shows two approximately planar palladium

$$Pd_2Cl_2(dppm)_2 + SO_2 \rightleftharpoons \underset{(179)}{Pd_2(\mu\text{-}SO_2)Cl_2(dppm)_2}$$



(179)

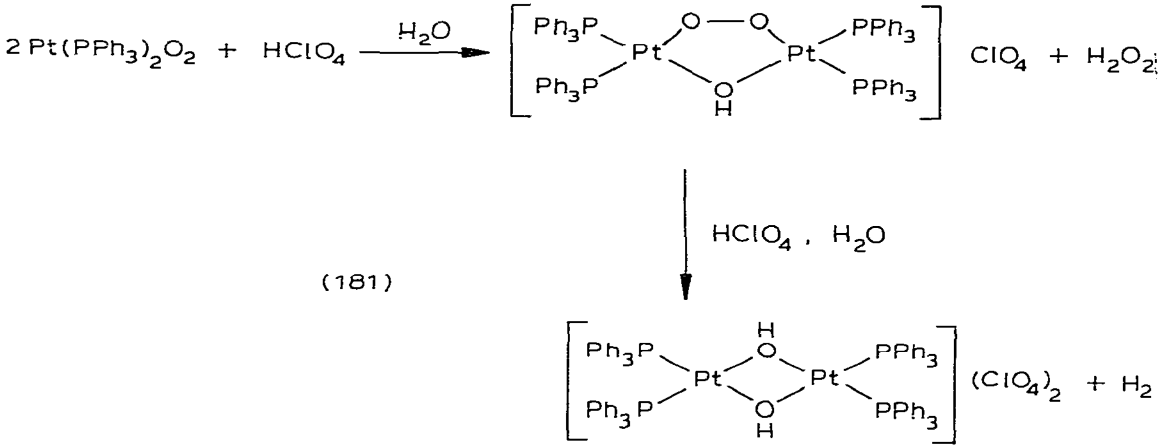
centers having a bridging SO_2 molecule [435].

The compound $cp_2Mo_2(CO)_4$ has a reactive Mo≡Mo triple bond. The formation of the complex in refluxing xylene occurs by odd-electron intermediates from homolysis of the Mo-Mo bond in $cp_2Mo_2(CO)_6$. The reactions of the compound with PPh_3, $P(OMe)_3$, Me_2S_2, CN^-, I_2, HCl, $HgPh_2$, $C_2(CN)_4$ are described. Cluster compounds such as $[\mu-(PPh_3)_2Pt]cp_2Mo_2(CO)_4$ (180) have been prepared from $Pt(PPh_3)_4$ [436].

$$2cp_2Mo_2(CO)_4 + Pt(PPh_3)_4 \rightarrow \underset{(180)}{cp(CO)_2Mo{=}Mo(CO)_2cp[\mu-Pt(PPh_3)_2]} + \underset{(PPh_3)_2}{cp_2Mo_2(CO)_4}$$

The hydrolysis of $Pt(PPh_3)_2O_2$ with non-coordinating acids gives $[Pt_2(O_2)(OH)(PPh_3)_4]X$ (X = ClO_4, PF_6, BF_4, NO_3) (181), and then $[Pt_2(OH)_2(PPh_3)_4]X_2$ with stepwise loss of H_2O_2. The structure of (181) has been confirmed by X-ray crystallography [437].

The interaction of two d^{10} centers in a recently prepared P_2PtPtP_2 dimer has been calculated. An admixture of metal s and p functions into M.O.'s primarily composed of d functions converts, in part, bonding and antibonding interactions into more bonding and nonbonding ones [438]. Details of the calculation are given.



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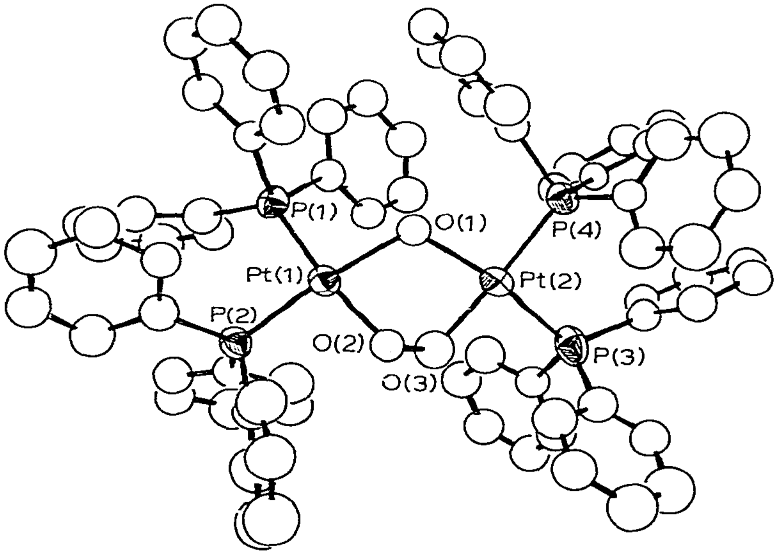

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The asymmetric chelating ligand (R,R)-diop forms a mononuclear Pt(0) complex which exhibits conformational isomerism observable by ^{31}P NMR. There is considerable selectivity in ligand bridging favoring the optically active bis(diop) complex over its meso diastereomer in solution [439].

REFERENCES

1 W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, Angew. Chem. Int. Ed. Engl., 17(1978)466.

2 N. Bresciani-Pahor, N. Plazzotta, L. Randaccio, G. Bruno, V. Ricevuto, R. Romeo and U. Belluco, Inorg. Chim. Acta, 31(1978)171.

3 M. Cusumano and V. Ricevuto, J. Chem. Soc., Dalton Trans., (1978)1682.

4 C. Eaborn, K. J. Odell and A. Pidcock, J. Organometal. Chem., 146(1978)17.

5 K. Mauryama, T. Ito and A. Yamamoto, J. Organometal. Chem., 155(1978)359.

6 G. Favero, A. Morvillo and A. Turco, J. Organometal. Chem., 162(1978)99.

7 Y. Nakamura, K. Maruya and T. Mizoroki, Nippon Kagaku Kaishi, (1978)1486; Chem. Abstr., 90(1979)71324c.

8 G. Van Koten, K. Timmer, J. G. Noltes and A. L. Spek, J. Chem. Soc., Chem. Commun., (1978)250.

9 G. Favero, M. Gaddi, A. Morvillo and A. Turco, J. Organometal. Chem., 149(1978)395.

10 M. Almemark and B. Akermark, J. Chem. Soc., Chem. Commun., (1978)66.

11 T. T. Tsou and J. K. Kochi, J. Am. Chem. Soc., 100(1978)1634.

12 R. Seeber, G. A. Mazzocchin, D. Minniti, R. Romeo, P. Uguagliati and U. Belluco, J. Organometal. Chem., 157(1978)69.

13 R. Romeo, D. Minniti, S. Lanza, P. Uguagliati and U. Belluco, Inorg. Chem., 17(1978)2813.

14 K. Maruyama, T. Ito and A. Yamamoto, J. Organometal. Chem., 157(1978)463.

15 G. K. Anderson and R. J. Cross, J. Chem. Soc., Chem. Commun., (1978)819.

16 P. Stoppioni, P. Dapporto and L. Sacconi, Inorg. Chem., 17(1978)718.

17 H. Werner and W. Bertleff, J. Chem. Res(S), (1978)201.

18 J. Browning, P. L. Goggin, R. J. Goodfellow, N. W. Hurst, L. G. Mallinson and M. Murray, J. Chem. Soc., Dalton Trans., (1978)872.

19 M. Wada, N. Asada and K. Oguro, Inorg. Chem., 17(1978)2353.

20 N. Sugita, J. Minkiewiecz and R. F. Heck, Inorg. Chem., 17(1978)2809.

21 T. Kohara, T. Yamamoto and A. Yamamoto, J. Organometal. Chem., 154(1978)C37.

22 R. Romeo, Inorg. Chem. 17(1978)2040.

23 E. Colomer and R. J. P. Corriu, J. Chem. Soc., Chem. Commun., (1978)435.

24 S. Komiya, A. Yamamoto and T. Yamamoto, Chem. Lett., (1978)1273.

25 T. Yamamoto and A. Yamamoto, Chem. Lett., (1978)615.

26 W. Beck, F. Goetzfried and M. W. Chen, Chem. Ber., 111(1978)3719.

27 J. Kuyper, Inorg. Chem., 17(1978)77.

28 T. G. Appleton and M. A. Bennett, Inorg. Chem., 17(1978)738.

29 J. Kuyper, Inorg. Chem., 17(1978)1458.

30 N. Kuhn and H. Werner, Synth. React. Inorg. Met.-Org. Chem., 8(1978)249.

31 J. R. Halland, G. A. Swirle, J. Organometal. Chem., 161(1978)121.

32 C. S. Creaser and J. A. Creighton, J. Organometal. Chem. 157(1978)243.

33 R. M. Kirchner, R. G. Little, K. D. Tau and D. W. Meek, J. Organometal. Chem., 149(1978)C15.

34 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell and V. Sik, J. Organometal. Chem 145(1978)C18.

35 T. G. Appleton, J. R. Hall and L. Lambert, Inorg. Chim. Acta, 29(1978)89.

36 C. Gosden, K. P. Healy and D. Pletcher, J. Chem. Soc., Dalton Trans., (1978)97

37 N. N. Greenwood, J. D. Kennedy and J. Staves, J. Chem. Soc., Dalton Trans., (1978)1146.

38 J. Behan, R. A. W. Johnstone and R. J. Puddephatt, J. Chem. Soc., Chem. Commun (1978)444.

39 M. J. S. Gynane, M. F. Lappert, S. J. Miles and P. P. Power, J. Chem. Soc., Ch Commun., (1978)192.

40 N. H. Agnew, T. G. Appleton and J. R. Hall, Inorg. Chim. Acta, 30(1978)L343.

41 J. K. Jawad and R. J. Puddephatt, Inorg. Chim. Acta, 31(1978)L391.

42 R. Ros, R. A. Michelin, U. Belluco, G. Zanotti, A. DelPra and G. Bombieri, Inorg. Chim. Acta, 29(1978)L187.

43 Y. Becker and J. K. Stille, J. Am. Chem. Soc., 100(1978)838.

44 T. G. Attig, Inorg. Chem., 17(1978)3097.

45 S. C. Davis and K. J. Klabunde, J. Am. Chem. Soc., 100(1978)5973.

46 D. E. Bergstrom and M. K. Ogawa, J. Am. Chem. Soc., 100(1978)8106.

47 K. Miki, G. Yoshida, Y. Kai, N. Yasuoka and N. Kasai, J. Organometal. Chem., 149(1978)195.

48 B. Akermark and A. Ljungqvist, J. Organometal. Chem., 149(1978)97.

49 A. Arcas and P. Royo, Inorg. Chim. Acta, 30(1978)205.

50 A. Arcas and P. Royo, Inorg. Chim. Acta, 31(1978)97.

51 L. Manojlovic-Muir, K. W. Muir, T. Solomun, D. W. Meed and J. L. Peterson, J. Organometal. Chem. 146(1978)C26.

52 G. B. Deacon, S. J. Faulks and I. L. Grayson, Transition Met. Chem. (Weinheim Ger.), 3(1978)317; Chem. Abstr., 90(1979)6521a.

53 L. G. Kuz'mina, Yu. T. Struchkov. V. V. Bashilov, V. I. Sokolov and O. A. Reuto Izv. Akad. Nauk SSSR, Ser. Khim, (1978)621; Chem. Abstr., 89(1978)43730t.

54 K. J. Klabunde, T. Groshens, H. F. Efner and M. Kramer, J. Organometal. Chem., 157(1978)91.

55 O. A. Reutov, V. I. Sokolov, G. Z. Suleimanov and V. V. Bashilov, J. Organometal. Chem., 160(1978)7.

56 L-Y. Chia and W. R. McWhinnie, J. Organometal. Chem., 148(1978)165.

57 R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100(1978)1300.

58 R. H. Grubbs, A. Miyashita, M. Liu and P. Burk, J. Am. Chem. Soc., 100(1978)2418.

59 R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100(1978)7416.

60 R. G. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100(1978)7418.

61 R. H. Grubbs and A. Miyashita, J. Organometal. Chem., 161(1978)371.

62 R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser and C. F. H. Tipper, J. Organometal. Chem., 150(1978)295.

63 D. C. L. Perkins, R. J. Puddephatt and C. F. H. Tipper, J. Organometal. Chem., 154(1978)C16.

64 R. J. Al-Essa, R. J. Puddephatt, C. F. H. Tipper and P. J. Thompson, J. Organometal. Chem., 157(1978)C40.

65 R. L. Phillips and R. J. Puddephatt, J. Chem. Soc., Dalton Trans., (1978)1732.

66 B. M. Cushman and D. B. Brown, J. Organometal. Chem., 152(1978)C42.

67 B. M. Cushman, S. E. Earnest and D. B. Brown, J. Organometal. Chem., 159(1978)431.

68 P. Binger and M . J. Doyle, J. Organometal. Chem., 162(1978)195.

69 P. Diversi, G. Ingrosso and A. Lucherini, J. Chem. Soc., Chem. Commun., (1978)735.

70 G. B. Young and G. M. Whitesides, J. Am. Chem. Soc., 100(1978)5808.

71 J. Rajaram and J. A. Ibers, J. Am. Chem. Soc., 100(1978)829.

72 A. de Renzi, A. Panunzi and A. Vitagliano, Gazz. Chim. Ital., 108(1978)45.

73 M. Lenarda, N. B. Pahor, M. Calligaris, M. Graziani and L. Randaccio, J. Chem. Soc., Dalton Trans., (1978)279.

74 Y. Zenitani, H. Tokunan, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jap., 51(1978)1730.

75 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, M. D. Schilling and D. R. Russell, J. Chem. Soc., Chem. Commun., (1978)744.

76 Z. Kanda, Y. Nakamura and S. Kawaguchi, Inorg. Chem., 17(1978)910.

77 N. Yanase, Y. Nakamura and S. Kawaguchi, Inorg. Chem., 17(1978)2874.

78 F. Rivetti and U. Romano, J. Organometal. Chem., 154(1978)323.

79 L. N. Zhir-Lebed, L. G. Kuz'mina, Yu. T. Struchkov, O. N. Temkin and V. A. Golodov, Koord. Khim., 4(1978)1046; Chem. Abstr., 89(1978)109929y.

80 I. S. Akhrem, N. M. Chistovalova, S. M. Airapetyan, E. I. Mysov and M. E. Vol'pin, Izv. Nauk SSSR, Ser. Khim., (1978)1126; Chem. Abstr., 89(1978)109684q.

81 G. Sonnek and E. Dinjus, Z. Anorg. Allg. Chem., 441(1978)58.

82 C. Eaborn, K. J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1978)1288.

83 M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt and K. R. Seddon, J. Chem. Soc., Chem. Commun., (1978)749.

84 A. J. Hartshorn, M. F. Lappert and K. Turner, J. Chem. Soc., Dalton, Trans., (1978)348.

85 M. F. Lappert and P. L. Pye, J. Chem. Soc., Dalton Trans., (1978)837.

86 G. K. Anderson, R. J. Cross, L. Manojlovic-Muir, K. W. Muir and R. A. Wiles, Inorg. Chim. Acta, 29(1978)L193.

87 K. Oguro, M. Wada and R. Okawara, J. Organometal. Chem., 159(1978)417.

88 K. Hiraki, Y. Fuchita and S. Morinaga, Chem. Lett., (1978)1.

89 Y. Ito, T. Hirao, K. Tsubata and T. Saegusa, Tet. Lett., (1978)1535.

90 R. F. Stepaniak and N. C. Payne, Can. J. Chem., 56(1978)1602.

91 M. H. Chisholm and R. K. Potkul, Synth. React. Inorg. Metal-Org. Chem., 8(1978)65.

92 E. O. Fischer and A. Daweritz, Chem. Ber., 111(1978)3525.

93 A. Nakamura, T. Koyama and S. Otsuka, Bull. Chem. Soc. Jap., 51(1978)593.

94 H. Schmidbaur, G. Muller, U. Schubert and O. Orama, Angew. Chem. Int. Ed. Engl., 17(1978)126.

95 H. Schmidbaur and H. P. Scherm, Chem. Ber., 111(1978)797.

96 M-F. Hirai, M. Miyasaka, K. Itoh and Y. Ishii, J. Organometal. Chem., 160(1978)25.

97 K. Hiraki and Y. Fuchita, Chem. Lett., (1978)841.

98 G. Fronza, P. Bravo and C. Ticozzi, J. Organometal. Chem., 157(1978)299.

99 M. I. Bruce, B. L. Goodall and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1978)687.

100 M. Nonoyama, J. Organometal. Chem., 154(1978)169.

101 T. I. Voevodskaya, I. V. Barinov and Yu. A. Ustynyuk, Vestn. Mosk. Univ., Ser. 2: Khim., 19(1978)453; Chem. Abstr., 90(1978)23231y.

102 E. Steiner, F. A. L'Eplattenier, Helv. Chim. Acta., 61(1978)2264.

103 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and L. New, J. Chem. Soc., Dalton Trans., (1978)1490.

104 A. J. Deeming and I. P. Rothwell, J. Chem. Soc., Dalton Trans., (1978)1497.

105 M. Nonoyama and C. Hayata, Transition Met. Chem. (Weinheim Ger) 3(1978)366; Chem. Abstr., 90(1979)121781x.

106 A. G. Constable, W. S. McDonald, L. C. Sawkins and B. L. Shaw, J. Chem. Soc., Chem. Commun., (1978)1061.

107 K. Hiraki, M. Onishi, K. Sewaki and K. Sugino, Bull. Chem. Soc. Jap., 51(1978)2548.

108 M. Onishi, K. Sugimura and K. Hiraki, Bull. Chem. Soc. Jap., 51(1978)3209.

109 M. Nonoyama, Inorg. Chim. Acta, 28(1978)L163.

110 M. Nonoyama, Inorg. Nucl. Chem. Lett., 14(1978)337.

111 A. J. Deeming and I. P. Rothwell, J. Chem. Soc., Chem. Commun., (1978)344.

112 D. F. Christian, D. A. Clarke, H. C. Clark, D. H. Farrar and N. C. Payne, Canad. J. Chem., 56(1978)2516.

113 E. M. Hyde, B. L. Shaw and I. Shepherd, J. Chem. Soc., Dalton Trans., (1978)1696.

114 H. D. Empsall, P. M. Heys and B. L. Shaw, J. Chem. Soc., Dalton Trans., (1978)257.

115 H. P. Abicht and K. Issleib, J. Organometal. Chem., 149(1978)209.

116 N. C. Rice and J. D. Oliver, J. Organometal. Chem. 145(1978)121.

117 B. T. Heaton and K. J. Timmins, J. Organometal. Chem., 152(1978)125.

118 H. C. Clark, A. B. Goel, R. G. Goel, S. Goel and W. O. Ogini, Inorg. Chim. Acta, 31(1978)L441.

119 S. Murahashi, Y. Tamba, M. Yamamura and N. Yoshimura, J. Org. Chem., 43(1978)4099.

120 T. Izumi, K. Endo, O. Saito, I. Shimizu, M. Maemura and A. Kasahara, Bull. Chem. Soc. Jap., 51(1978)663.

121 H. Veillard, Nouv. J. Chem., 2(1978)215.

122 P. De Groot and K. Dransfeld, Z. Anorg. Allg. Chem., 446(1978)39.

123 A. Ya. Kipnis and Z. P. Fedorova, Kinet. Katal., 19(1978)848; Chem. Abstr., 89(1978)172870n.

124 Yu. S. Varshavskii, V. A. Kormer, E. D. Shestakova, N. V. Kiseleva, T. G. Cherkasova, N. A. Buzina and L. S. Bresler, Koord. Khim. 4(1978)947; Chem. Abstr., 89(1978)109920p.

125 G. E. Herberich and B. Hessner, J. Organometal. Chem., 161(1978)C36.

126 I. Tkatchenko, J. Mol. Catal., 4(1978)163.

127 K. Dehnicke and R. Duebgen, Z. Anorg. Allg. Chem., 444(1978)61.

128 M. R. Blake, J. L. Garnett, I. K. Gregor and S. B. Wild, Org. Mass Spectrom, 13(1978)20.

129 A. B. Burg, Inorg. Chem., 17(1978)2322.

130 A. N. Nesmeyanov, L. S. Isaeva and L. N. Morozova, Inorg. Chim. Acta, 29(1978)L210.

131 R. Colton, M. J. McCormick and C. D. Pannan, Aust. J. Chem., 31(1978)1425.

132 T. A. Stromnova, L. G. Kuz'mina, M. N. Vargaftik, G. Ya. Mazo, Yu. T. Struchkov and I. I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)720; Chem. Abstr., 88(1978)202347w.

133 P. L. Goggin, M. G. Norton and J. Mink, Inorg. Chim. Acta, 26(1978)125.

134 C. Crocker, P. L. Goggin and R. J. Goodfellow, J. Chem. Soc., Chem. Commun., (1978)1056.

135 R. Queau and R. Poilblanc, J. Chem. Soc., Chem. Commun., (1978)617.

136 M. P. Brown, R. J. Puddephatt, N. Rashidi and K. R. Seddon, J. Chem. Soc., Dalton Trans., (1978)1540.

137 L. S. Benner and A. L. Balch, J. Am. Chem. Soc., 100(1978)6099.

138 S. D. Robinson, Inorg. Chim. Acta, 27(1978)L108.

139 I. I. Moiseev, T. A. Stromnova, M. N. Vargaftig, G. J. Mazo, L. G. Kuz'mina and Y. T. Struchkov, J. Chem. Soc., Chem. Commun., (1978)27.

140 J-P. Barbier, R. Bender, P. Braunstein, J. Fischer and L. Ricard, J. Chem. Res.(S), (1978)230.

141 J-P. Barbier, P. Braunstein, J. Fischer and L. Ricard, Inorg. Chim. Acta, 31(1978)L361.

142 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1978)260.

143 A. Fumagalli, S. Martinengo, P. Chini, A. Albinati, S. Bruckner and B. T. Heaton, J. Chem. Soc., Chem. Commun., (1978)195.

144 R. Bender, P. Braunstein, Y. Dusausoy and J. Protas, Angew. Chemie. Int. Ed. Engl., 17(1978)596.

145 S. Besnainou and J. L. Whitten, J. Am. Chem. Soc., 100(1978)3692.

146 P. I. Starosel'skii and Yu. I. Solv'ev, Koord. Khim., 4(1978)1123; Chem. Abstr., 89(1978)163617h.

147 N. C. Harrison, M. Murray, J. L. Spencer and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1978)1337.

148 G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1978)1839.

149 G. A. Ozin and W. J. Power, Inorg. Chem., 17(1978)2836.

150 G. A. Ozin, W. J. Power, T. H. Upton and W. A. Goddard, J. Am. Chem. Soc., 100(1978)4750.

151 G. A. Ozin and W. J. Power, Ber. Bunsenges. Phys. Chem., 82(1978)93.

152 G. A. Ozin and W. J. Power, Ber. Bunsenges. Phys. Chem., 82(1978)105.

153 I. M. Al-Najjar and M. Green, Transition Met. Chem. (Weinheim Ger), 3(1978)142; Chem. Abstr., 89(1978)120312n.

154 H. Basch, M. D. Newton and J. W. Moskowitz, J. Chem. Phys., 69(1978)584.

155 E. Dinjus, H. Langbein and D. Walther, J. Organometal. Chem., 152(1978)229.

156 J. Ishizu, T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Jap., 51(1978)2646.

157 N. V. Petrushanskaya, A. I. Kurapova, N. M. Rodionova, T. B. Fedotova and V. Sh. Fel'dblyum, Zh. Obshch. Khim., 48(1978)2270; Chem. Abstr., 90(1979)72335u.

158 M. Bigorgne, J. Organometal. Chem., 160(1978)345.

159 M. Green and M. G. Swanwick, J. Chem. Soc., Dalton Trans., (1978)158.

160 M. Green and C. J. Wilson, J. Chem. Res. (S), (1978)175.

161 Y. Terai and K. Saito, Bull. Chem. Soc. Jap., 51(1978)503.

162 G. Natile, J. Chem. Soc., Chem. Commun., (1978)654.

163 Y. Terai, H. Kido, K. Kashiwabara and K. Saito, Bull. Chem. Soc. Jap., 51(1978)3245.

164 P. Courtot, R. Rumin, A. Peron and J. P. Girault, J. Organometal. Chem., 145(1978)343.

165 P. Courtot, R. Rumin and A. Peron, J. Organometal. Chem., 144(1978)357.

166 J. W. Emsley and J. Evans, J. Chem. Soc., Dalton Trans., (1978)1355.

167 G. Butler, C. Eaborn and A. Pidcock, J. Organometal. Chem., 144(1978)C23.

168 C. Eaborn, K. J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1978)357.

169 R. Pietropaolo, F. Cusmano, E. Rotondo and A. Spadaro, J. Organometal. Chem., 155(1978)117.

170 F. Bonati and H. C. Clark, Canad. J. Chem., 56(1978)2513.

171 P. D. Frisch, R. G. Posey and G. P. Khare, Inorg. Chem., 17(1978)402.

172 J. K. Stille and R. Divakaruni, J. Am. Chem. Soc., 100(1978)1303.

173 L. S. Hegedus, G. F. Allen, J. J. Bozell and E. L. Waterman, J. Am. Chem. Soc., 100(1978)5800.

174 J. A. Mercer-Smith and D. G. Whitten, J. Am. Chem. Soc., 100(1978)2620.

175 W. E. Carroll, M. Green, J. A. K. Howard, M. Pfeffer and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1978)1472.

176 H. Hoberg and J. Korff, J. Organometal. Chem., 152(1978)C39.

177 H. Hoberg and J. Korff, J. Organometal. Chem., 152(1978)255.

178 A. Keasey, B. E. Mann, A. Yates and P. M. Maitlis, J. Organometal. Chem., 152(1978)117.

179 H. Kawazura, H. Tanaka, K. Yamada, T. Takahashi and Y. Ishii, Bull. Chem. Soc. Jap., 51(1978)3466.

180 L. Yu. Ukhin and E. P. Onokolova, Dokl. Akad. Nauk SSSR 241(1978)858; Chem. Abstr., 89(1978)197699b.

181 M. K. Cooper, N. J. Hair and D. W. Yaniuk, J. Organometal. Chem., 150(1978)157.

182 N. C. Rice and J. D. Oliver, Acta Crystallogr., B34(1978)3748.

183 N. C. Baenziger, C. V. Goebel, T. Berg and J. R. Doyle, Acta Crystallogr., B34(1978)1340.

184 N. C. Baenziger, C. V. Goebel, B. A. Foster and J. R. Doyle, Acta Crystallogr., B34(1978)1681.

185 R. A. Anderson and F. W. B. Einstein, Acta Crystallogr., B34(1978)271.

186 R. C. Elder and F. Pesa, Acta Crystallogr., B34(1978)268.

187 A. De Renzi, B. Di Blasio, A. Panunzi, C. Pedone and A. Vitagliano, J. Chem. Soc., Dalton Trans., (1978)1392.

188 R. A. Clement, U. Klabunde and G. W. Parshall, J. Mol. Catal., 4(1978)87.

189 J. W. Fitch, K. C. Chan and J. A. Froelich, J. Organometal. Chem., 160(1978)477.

190 T. H. Upton and W. A. Goddard, J. Am. Chem. Soc., 100(1978)321.

191 A. B. Anderson, J. Am. Chem. Soc., 100(1978)1153.

192 M. A. Bennett and T. Yoshida, J. Am. Chem. Soc., 100(1978)1750.

193 E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day and A. B. Anderson, J. Am. Chem. Soc., 100(1978)2090.

194 K. J. Klabunde, T. Groshens, M. Brezinski and W. Kennelly, J. Am. Chem. Soc., 100(1978)4437.

195 H. C. Clark, A. B. Goel and C. S. Wong, J. Am. Chem. Soc., 100(1978)6241.

196 M. Benard, J. Am. Chem. Soc., 100(1978)7740.

197 T. G. Appleton, M. A. Bennett, A. Singh and T. Yoshida, J. Organometal. Chem., 154(1978)369.

198 J. B. B. Heyns and F. G. A. Stone, J. Organometal. Chem., 160(1978)337.

199 K. Sonogashira, S. Kataoka, S. Takahashi and N. Hagihara, J. Organometal. Chem., 160(1978)319.

200 M. C. Barral, R. Jimenez, E. Royer, V. Moreno and A. Santos, Inorg. Chim. Acta, 31(1978)165.

201 R. Nast, H-P Müller and V. Pank, Chem. Ber., 111(1978)1627.

202 J. Burgess, M. E. Howden, R. D. W. Kemmitt and N. S. Sridhara, J. Chem. Soc., Dalton Trans., (1978)1577.

203 C. J. Cardin, D. J. Cardin, M. F. Lappert and K. W. Muir, J. Chem. Soc., Dalton Trans., (1978)46.

204 K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Hagihara, J. Organometal. Chem., 145(1978)101.

205 A. I. Borisova, L. P. Safronova, A. S. Medevedeva and N. S. Vyazankin, Zh. Obshch. Khim., 48(1978)2040; Chem. Abstr., 90(1979)6517d.

206 A. Furlani, G. Polzonetti, M. V. Russo and G. Mattogno, Inorg. Chim. Acta, 26(1978)L39.

207 R. Baker, P. C. Bevan, R. C. Cookson, A. H. Copeland and A. D. Gribble, J. Chem. Soc., Perkin Trans., 1(1978)480.

208 G. Giacomelli and L. Lardicci, Tet Letts, (1978)2831.

209 J. Duboudin and B. Jousseaume, J. Organometal. Chem., 162(1978)209.

210 V. Raverdino, S. Aime, L. Milone and E. Sapa, Inorg. Chim. Acta, 30(1978)9.

211 R. L. Phillips and R. J. Puddephatt, J. Chem. Soc., Dalton Trans., (1978)1732.

212 Yu. L. Ukhin, Zh. I. Orlova, V. I. Il'in, A. I. Pyshchev and G. N. Dorofeenko, Koord. Khim., 4(1978)772; Chem. Abstr., 89(1978)109911m.

213 L. Yu. Ukhin, V. V. Krasnikov and G. N. Dorofeenko, Koord. Khim., 4(1978)455; Chem. Abstr., 89(1978)24512g.

214 A. M. Lazutkin and V. M. Mastikhin, Zh. Obshch. Khim., 48(1978)474; Chem. Abstr., 88(1978)191039n.

215 M. A. Kononova and E. F. Kozlovskaya, Vestn. Leningr. Univ. Fiz. Khim., (1978)74; Chem. Abstr., 88(1978)198688p.

216 P. M. Bailey, E. A. Kelley and P. M. Maitlis, J. Organometal. Chem., 144(1978)C52.

217 M. J. H. Russell, C. White, A. Yates and P. M. Maitlis, J. Chem. Soc., Dalton Trans., (1978)849.

218 M. J. H. Russell, C. White, A. Yates and P. M. Maitlis, J. Chem. Soc., Dalton Trans., (1978)857.

219 B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton and T. J. Dietsche, J. Am. Chem. Soc., 100(1978)3407.

220 B. M. Trost, L. Weber, P. E. Strege, T. J. Fullerton and T. J. Dietsche, J. Am. Chem. Soc., 100(1978)3416.

221 B. M. Trost, L. Weber, P. Strege, T. J. Fullerton and T. J. Dietsche, J. Am. Chem. Soc., 100(1978)3426.

222 B. M. Trost and T. R. Verhoeven, J. Am. Chem. Soc., 100(1978)3435.

223 R. C. Larock and M. A. Mitchell, J. Am. Chem. Soc., 100(1978)180.

224 L. S. Hegedus and B. R. Evans, J. Am. Chem. Soc., 100(1978)3461.

225 Y. Becker and J. K. Stille, J. Am. Chem. Soc., 100(1978)845.

226 A. I. Yashin, E. I. Tinyakova, Yu. V. Bryantseva, K. G. Miesserov, V. Mahdi and B. A. Dolgoplosk, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)1608; Chem. Abstr., 89(1978)129693v.

227 V. A. Vasiliev, T. I. Sokoryanskaya and V. A. Kormer, J. Polym. Sci., Polym. Chem. Ed., 16(1978)2159; Chem. Abstr., 89(1978)198074f.

228 A. J. Deeming and I. P. Rothwell, Inorg. Chim. Acta, 31(1978)271.

229 W. R. Jackson and J. U. Strauss, Aust. J. Chem., 31(1978)1073.

230 G. W. Henslee and J. D. Oliver, J. Cryst. Mol. Struct., 7(1978)137.

231 J. D. Smith and J. D. Oliver, Inorg. Chem., 17(1978)2585.

232 G. Carturan, A. Scrivanti, U. Belluco and F. Morandini, Inorg. Chim. Acta, 26(1978)1.

233 G. Carturan, A. Scrivanti, U. Belluco and F. Morandini, Inorg. Chim. Acta, 27(1978)37.

234 P. W. Jolly, S. Stobbe, G. Wilke, R. Goddard, C. Krüger, J. C. Sekutowski and Y. H. Tsay, Angew Chem. Int. Ed. Engl., 17(1978)124.

235 Y. Tamaru, M. Kagotani and Z-i. Yoshida, J. Chem. Soc., Chem. Commun., (1978)367.

236 G. Carturan and G. Strukul, J. Organometal. Chem., 157(1978)475.

237 K. Henderson and F. J. McQuillin, J. Chem. Soc., Chem. Commun., (1978)15.

238 I. J. Harvie and F. J. McQuillin, J. Chem. Soc., Chem. Commun., (1978)747.

239 T. Ito and A. Yamamoto, J. Organometal. Chem., 161(1978)61.

240 G. Balavoine, G. Bram and F. Guibe, Nouv. J. Chem., 2(1978)207.

241 U. Bersellini, G. P. Chiusoli and G. Salerno, Angew. Chemie. Int. Ed. Engl., 17(1978)353.

242 C. Krueger, J. C. Sekutowski, H. Berke and R. Hoffmann, Z. Natuforsch. B: Anorg. Chem., Org. Chem., 33B(1978)1110.

243 S. P. Gubin, A. Z. Rubezhov and L. I. Voronchikina, J. Organometal. Chem., 149(1978)123.

244 J. Howard and T. C. Waddington, J. Chem. Soc., Faraday Trans. 2, 74(1978)879.

245 T. B. Chenskaya, L. A. Leites and V. T. Aleksanyan, J. Organometal. Chem., 148(1978)85.

246 N. A. Borisova, G. P. Karpacheva, E. A. Mushina and B. A. Krentsel, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)2131; Chem. Abstr., 90(1979)5522q.

247 E. R. Milaeva, A. Z. Rubezhov, A. I. Prokof'ev and O. Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)1231; Chem. Abstr., 89(1978)109913p.

248 T. Yamamoto, J. Chem. Soc., Chem. Commun., (1978)1003.

249 C. B. Ziegler and R. F. Heck, J. Org. Chem., 43(1978)2941.

250 A. D. Ryabov and A. K. Yatsimirsky, J. Mol. Catal., 4(1978)449.

251 K. P. Healy and D. Pletcher, J. Organometal. Chem., 161(1978)109.

252 H. C. Clark and C. R. Milne, J. Organometal. Chem., 161(1978)51.

253 R. Meij, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers and A. R. Overbeek, J. Organometal. Chem., 155(1978)123.

254 F. Canziani, A. Albinati, L. Garlaschelli and M. C. Malatesta, J. Organometal. Chem., 146(1978)197.

255 F. Canziani, L. Garlaschelli and M. C. Malatesta, J. Organometal. Chem., 146(1978)179.

256 S. H. Taylor, B. E. Mann and P. M. Maitlis, J. Organometal. Chem., 145(1978)255.

257 M. K. Cooper, P. J. Guerney, H. J. Goodwin and M. McPartlin, J. Chem. Soc., Chem. Commun., (1978)861.

258 M. Onishi, H. Yamamoto and K. Hiraki, Bull. Chem. Soc. Jap., 51(1978)1856.

259 L. D. Brown, K. Itoh, H. Suzuki, K. Hirai and J. A. Ibers, J. Am. Chem. Soc., 100(1978)8232.

260 D. L. Thorn and R. Hoffmann, J. Am. Chem. Soc., 100(1978)2079.

261 H. Berke and R. Hoffmann, J. Am. Chem. Soc., 100(1978)7224.

262 H. C. Clark, C. R. C. Milne and N. C. Payne, J. Am. Chem. Soc., 100(1978)1164.

263 H. Konishi, S. Matsumoto, Y. Kamitori, H. Ogoshi and Z-i. Yoshida, Chem. Lett., (1978)241.

264 Z. Yoshida, Y. Kamitori, Chem. Lett., (1978)1341.

265 P. M. Bailey, A. Keasey and P. M. Maitlis, J. Chem. Soc., Dalton Trans., (1978)1825.

266 R. Weiss and C. Priesner, Angew. Chem. Int. Ed. Engl., 17(1978)457.

267 U. Griebsch and H. Hoberg, Angew. Chemie. Int. Ed. Engl., 17(1978)950.

268 S. H. Taylor and P. M. Maitlis, J. Am. Chem. Soc., 100(1978)4700.

269 P. M. Bailey, S. H. Taylor and P. M. Maitlis, J. Am. Chem. Soc., 100(1978)4711.

270 T. R. Jack, C. J. May and J. Powell, J. Am. Chem. Soc., 100(1978)5057.

271 D. W. Clack and K. D. Warren, J. Organometal. Chem., 149(1978)401.

272 D. W. Clack and K. D. Warren. J. Organometal. Chem., 161(1978)C55.

273 W. Bensmann and D. Fenske, Angew. Chemie. Int. Ed. Engl., 17(1978)462.

274 C. Moberg, Acta Chem. Scand., Ser. B, B32(1978)149.

275 A. Shaver, Canad. J. Chem., 56(1978)2281.

276 R. R. Corderman and J. L. Beauchamp, Inorg. Chem., 17(1978)68.

277 O. A. Reutov, G. Z. Suleimanov, I. A. Amiraslanov, V. V. Bashilov and V. I. Sokolov, Zh. Org. Khim., 14(1978)1802; Chem. Abstr., 89(1978)215538e.

278 H. Werner and T. N. Khac, Inorg. Chim. Acta, 30(1978)L347.

279 H. Werner and A. Kuehn, Z. Natu forsch., B: Anorg. Chem. Org. Chem., 33B(1978)1360.

280 K. G. Shal'nova, O. F. Rachkova, I. A. Teplova, G. A. Razuvaev and G. A. Abakumov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)2422; Chem. Abstr., 90(1979) 55084n.

281 K. J. Klabunde, B. B. Anderson, M. Bader and L. J. Radonovich, J. Am. Chem. Soc., 100(1978)1313.

282 H. F. Efner, D. E. Tevault, W. B. Fox and R. R. Smardzewski, J. Organometal. Chem., 146(1978)45.

283 R. E. Cobbledick and F. W. B. Einstein, Acta Crystallogr., B34(1978)1849.

284 A. Keasey, P. M. Bailey and P. M. Maitlis, J. Chem. Soc., Chem. Commun., (1978)142.

285 A. Keasey and P. M. Maitlis, J. Chem. Soc., Dalton Trans., (1978)1830.

286 W. Siebert, M. Bochmann, J. Edwin, C. Krüger and Y-H. Tsay, Z. Natuforschung, 33b(1978)1410.

287 W. Siebert, J. Edwin and M. Bochmann, Angew. Chemie. Int. Ed. Engl., 90(1978)868.

288 L. N. Mazalov, V. V. Volkov, S. Ya. Dvurechesnskaya and L. Nasonova, Russ. J. Inorg. Chem., 23(1978)1023.

289 R. N. Leyden, B. P. Sullivan, R. T. Baker and M. F. Hawthorne, J. Am. Chem. Soc., 100(1978)3758.

290 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, J. Chem. Soc., Chem. Commun., (1978)322.

291 G. K. Barker, M. Green, T. P. Onak, F. G. A. Stone, C. B. Ungermann and A. J. Welch, J. Chem. Soc., Chem. Commun., (1978)169.

292 G. A. Kukina, I. A. Zakharova, M. A. Porai-Koshits, B. Stibr, V. S. Sergienko, K. Base and J. Dolansky, Izv. Akad. Nauk SSSR Ser. Khim., (1978)1228; Chem. Abstr., 89(1978)109637.

293 D. M. P. Mingos, M. I. Forsyth and A. J. Welch, J. Chem. Soc., Dalton Trans., (1978)1363.

294 D. M. Roundhill, Adv. Chem. Ser., 167(1978)160.

295 E. A. V. Ebsworth, B. J. L. Henner and F. J. S. Reed, J. Chem. Soc., Dalton Trans., (1978)272.

296 I. M. Blacklaws, E. A. V. Ebsworth, D. W. H. Rankin and H. E. Robertson, J. Chem. Soc., Dalton Trans., (1978)753.

297 I. M. Blacklaws, L. C. Brown, E. A. V. Ebsworth and F. J. S. Reed, J. Chem. Soc., Dalton Trans., (1978)877.

298 E. A. V. Ebsworth, J. M. Edward, F. J. S. Reed and J. D. Whitelock, J. Chem. Soc., Dalton Trans., (1978)1161.

299 E. A. V. Ebsworth, V. M. Marganian, F. J. S. Reed and R. O. Gould, J. Chem. Soc., Dalton Trans., (1978)1167.

300 H. C. Clark, M. J. Dymarski and J. D. Oliver, J. Organometal. Chem. 154(1978)C40.

301 A. F. Borowski, D. J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chem., 2(1978)137.

302 F. Glockling and P. J. M. L. Ssebuwufu, Inorg. Chim. Acta, 31(1978)105.

303 L. Toniolo and G. Cavinato, Inorg. Chim. Acta, 26(1978)L5.

304 L. Abis, A. Sen and J. Halpern, J. Am. Chem. Soc., 100(1978)2915.

305 C. S. Cundy and M. F. Lappert, J. Organometal. Chem., 144(1978)317.

306 R. Ros, R. A. Michelin, R. Bataillard and R. Roulet, J. Organometal. Chem., 161(1978)75.

307 R. L. Phillips and R. J. Puddephatt, J. Chem. Soc., Dalton Trans., (1978)1736.

308 T. G. Attig, J. Organometal. Chem., 145(1978)C13.

309 R. P. Sperline, W. B. Beaulieu and D. M. Roundhill, Inorg. Chem. 17(1978)2032.

310 T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers and S. Otsuka, J. Am. Chem. Soc., 100(1978)2063.

311 H. C. Clark, A. B. Goel and C. S. Wong, J. Organometal. Chem., 152(1978)C45.

312 H. C. Clark, A. B. Goel, R. G. Goel and W. O. Ogini, J. Organometal. Chem., 157(1978)C16.

313 G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura and L. Zambonelli, Angew. Chemie. Int. Ed. Engl., 17(1978)778.

314 M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, J. Chem. Soc., Dalton Trans., (1978)801.

315 M. Ciriano, M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, F. G. A. Stone and C. A. Tsipsis, Adv. Chem. Ser., 167(1978)111.

316 M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, J. Chem. Soc., Dalton Trans., (1978)516.

317 M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt and K. R. Seddon. J. Organometal. Chem., 161(1978)C46.

318 T. Saito, M. Nakajima, A. Kobayashi and Y. Sasaki, J. Chem. Soc., Dalton Trans., (1978)482.

319 S-I Murahashi, T. Hirano and T. Yano, J. Am. Chem. Soc., 100(1978)348.

320 H. C. Clark, Pure Appl. Chem., 50(1978)43.

321 T. S. Kurtikyan and V. T. Alekoanyan, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)1526; Chem. Abstr., 89(1978)179085u.

322 E. Garciafigueroa and C. Sourisseau, Nouv. J. Chem., 2(1978)593.

323 J-P. Barbier and P. Braunstein, J. Chem. Res. (S), (1978)412.

324 Yu. N. Kukushkin, L. V. Vrublevskaya, T. S. Isachkina and S. I. Bakhireva, Russ. J. Inorg. Chem., 23(1978)1357.

325 B. Crociani, M. Nicolini and R. L. Richards, J. Chem. Soc., Dalton Trans., (1978)1478.

326 B. Crociani and R. L. Richards, J. Organometal. Chem., 154(1978)65.

327 J. Browning, P. L. Goggin and R. J. Goodfellow, J. Chem. Res. (S), (1978)328.

328 B. Crociani and R. L. Richards, J. Organometal. Chem., 144(1978)85.

329 Y. Yamamoto and J. Uwaza, Chem. Lett., (1978)1213.

330 R. Oda, Kagaku(Kyoto), 33(1978)462; Chem. Abstr., 89(1978)145948n.

331 B. M. Trost and E. Keinan, J. Am. Chem. Soc., 100(1978)7779.

332 R. Baker and R. J. Popplestone, Tet. Letts., (1978)3575.

333 N. L. Holy, J. Chem. Soc., Chem. Commun., (1978)1074.

334 Y. Fujii and J. C. Bailer, J. Catal., 55(1978)146.

335 M. Terasawa, K. Kaneda, T. Imanaka and S. Teranishi, J. Organometal. Chem., 162(1978)403.

336 V. K. Latov, V. M. Belikov, T. A. Belyaeva and A. I. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)660; Chem. Abstr., 89(1978)110304x.

337 A. S. Berenblyum, A. G. Knizhnik, S. L. Mund and I. I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)2711; Chem. Abstr., 90(1979)93115n.

338 M. Terasawa, K. Kaneda, T. Imanaka and S. Teranishi, J. Catal., 51(1978)406.

339 G. Carturan and V. Gottardi, J. Mol. Catal., 4(1978)349.

340 D. McMunn, R. B. Moyes and P. B. Wells, J. Catal., 52(1978)472.

341 M. J. D'Aniello and E. K. Barefield, J. Am. Chem. Soc., 100(1978)1474.

342 Y. Ichinohe, H. Sakamaki and N. Kameda, Chem. Lett., (1978)835.

343 I. Mochida, K. Kitagawa, H. Fijitsu and K. Takeshitia, J. Catal., 54(1978)175.

344 Y. Tamaru, M. Kagotani, R. Suzuki and Z-i. Yoshida, Chem. Lett., (1978)1329.

345 D. Huchette, B. Thery and F. Petit, J. Mol. Catal., 4(1978)433.

346 H. Siegel, H. Hopf, A. Germer and P. Binger, Chem. Ber., 111(1978)3112.

347 M. Green, G. Scholes and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1978)309.

348 C. U. Pittman and Q. Ng, J. Organometal. Chem., 153(1978)85.

349 C. U. Pittman, Jr. and S. E. Jacobson, J. Mol. Catal., 3(1978)293.

350 P. Svoboda and J. Hetflejs, Chem. Prum., 28(1978)27; Chem. Abstr., 89(1978)59382s.

351 R. Noyori, M. Yamakawa and H. Takaya, Tet. Letts., (1978)4823.

352 D. J. Milner and R. Whelan, J. Organometal. Chem., 152(1978)193.

353 A. K. Yatsimirsky, A. D. Ryabov and I. V. Berezin, J. Mol. Catal., 4(1978)151.

354 H. Tom Dieck, M. Svoboda and J. Kopf, Z. Natuforschung, 33b(1978)1381.

355 F. Dawans and D. Morel, J. Mol. Catal., 3(1978)403.

356 T. Ito and Y. Takami, Bull. Chem. Soc. Jap., 51(1978)1220.

357 Y. Inoue, Y. Itoh and H. Hashimoto, Chem. Lett., (1978)911.

358 Y. Inoue, Y. Itoh and H. Hashimoto, Chem. Lett., (1978)633.

359 A. Musco, C. Perego and V. Tartiari, Inorg. Chim. Acta, 28(1978)L147.

360 Y. Inoue, Y. Sasaki and H. Hashimoto, Bull. Chem. Soc. Jap., 51(1978)2375.

361 E. S. Novikova, O. P. Parengo and V. M. Frolov, Kinet. Katal., 19(1978)268; Chem. Abstr., 88(1978)153090w.

362 D. Walther and E. Dinjus, Z. Anorg. Allg. Chem., 440(1978)22.

363 R. J. M. Nolte, J. W. Zwikker, J. Reedijk and W. Drenth, J. Mol. Catal., 4(1978)423.

364 A. J. M. van Beijnen, R. J. M. Nolte, J. W. Zwikker and W. Drenth, J. Mol. Catal., 4(1978)427.

365 T. Yamamoto, S. Kanagaya, and A. Yamamoto, J. Polym. Sci., Polym. Lett. Ed., 16(1978)7.

366 L. S. Hegedus, T. Hayashi and W. H. Darlington, J. Am. Chem. Scoc., 100(1978)7747.

367 G. Cocco, G. Fagherazzi, G. Carturan and V. Gottardi, J. Chem. Soc., Chem. Commun., (1978)979.

368 P. J. M. Reijnders, J. F. Blankert and H. M. Back, Recl. Trav. Chim. Pays-Bas., 97(1978)30.

369 P. Helquist, Tett. Lett., (1978)1913.

370 N-C Luong-Thi and H. Riviere, J. Chem. Soc., Chem. Commun., (1978)918.

371 A. O. King, E. Negishi, F. J. Villiani and A. Silveira, J. Org. Chem., 43(1978) 358.

372 A. Zask and P. Helquist, J. Org. Chem., 43(1978)1619.

373 M. Kosugi, T. Shimizu and T. Migita, Chem. Lett., (1978)13.

374 H. Matsumoto, T. Nakano, M. Kato and Y. Nagai, Chem. Lett., (1978)223.

375 K. Takagi, N. Hayama and S. Inokawa, Chem. Lett., (1978)1435.

376 T. Takahashi, K. Kasuga and J. Tsuji, Tet. Lett., (1978)4917.

377 J. C. Fiaud, A. H. de Gournay, M. Larcheveque and H. B. Kagan, J. Organometal. Chem., 154(1978)175.

378 Y. Kawabata, T. M. Suzuki and I. Ogata, Chem. Lett., (1978)361.

379 R. V. Kunakova, G. A. Tolstikov, V. M. Dzhinulev, F. V. Sharipova and D. L. Sazikova, Izv. Akad. Nauk SSR, Ser. Khim., (1978)931; Chem. Abstr., 89(1978) 42352j.

380 J. Tsuji, T. Yamakawa, M. Kaito and T. Mandai, Tet. Lett., (1978)2075.

381 A. M. Lazutkin, V. M. Mastikhin and A. I. Lazutkina, Kinet. Katal., 19(1978) 1061; Chem. Abstr., 89(1978)179451k.

382 A. N. Nesmeyanov, L. S. Isaeva and T. A. Peganova, Dokl. Akad. Nauk SSSR 240(1978)352; Chem. Abstr., 89(1978)108448d.

383 N. Okukado, D. E. Van Horn, W. L. Klima and E-I. Negishi, Tet. Lett., (1978)1027.

384 M. Kosugi, H. Arai, A. Yoshino and T. Migita, Chem. Lett., (1978)795.

385 J. F. Knifton, J. Am. Oil Chem. Soc., 55(1978)496; Chem. Abstr., 89(1978)129033c.

386 T. Hayashi, M. Tanaka and I. Ogata, Tet. Letts., (1978)3925.

387 B. Corain, J. Organometal. Chem., 157(1978)C19.

388 B. B. Snider, M. Karras and R. S. E. Conn, J. Am. Chem. Soc., 100(1978)4624.

389 I. Ojima and M. Kumagi, J. Organometal. Chem., 157(1978)359.

390 M. Catellani, G. P. Chiusoli, G. Salerno and F. Dallatomasina, J. Organometal. Chem., 146(1978)C19.

391 H. Tietz, K. Unverferth, D. Sagasser and K. Schwetlick, Z. Chem., 18(1978)141.

392 H. Tietz, K. Unverferth and K. Schwetlick, Z. Chem., 18(1978)217.

393 H. Arai and M. Yashiro, J. Mol. Catal., 3(1978)427.

394 N. P. Allen, F. O. Bamiro, R. P. Burns, J. Dwyer and C. A. McAuliffe, Inorg. Chim. Acta, 28(1978)231.

395 H. Matsumoto, T. Motegi, M. Hasegawa and Y. Nagai, Bull. Chem. Soc. Jap., 51(1978)1913.

396 K. Tamao, S. Okazaki and M. Kumada, J. Organometal. Chem., 146(1978)87.

397 I. M. Salimgareeva, V. V. Kaverin and V. P. Jurjev, J. Organometal. Chem., 148(1978)23.

398 H. Matsumoto, T. Yako, S. Nagashima, T. Motegi and Y. Nagai, J. Organometal. Chem., 148(1978)97.

399 K. Kan, K. Miki, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jap., 51(1978)733.

400 M. Mori and Y. Ban, Heterocycles, 9(1978)391.

401 T. Yoshida, Y. Ueda and S. Otsuka, J. Am. Chem. Soc., 100(1978)3941.

402 C-H. Cheng and R. Eisenberg, J. Am. Chem. Soc., 100(1978)5968.

403 B. M. Trost, S. A. Godleski and J. P. Genet, J. Am. Chem. Soc., 100(1978)3930.

404 J. Ambuehl, P. S. Pregosin, L. M. Venanzi, G. Ughetto and L. Zambonelli, J. Organometal. Chem., 160(1978)329.

405 T. Hosokawa, S. Miyagi, S-I. Murahashi and A. Sonoda, J. Chem. Soc., Chem. Commun., (1978)687.

406 T. Hosokawa, S. Miyagi, S. Murahashi and A. Sonoda, J. Org. Chem., 43(1978)2752.

407 D. R. Fahey and J. E. Mahan, J. Mol. Catal., 3(1978)447.

408 Y. Inoue, S. Ohno and H. Hashimoto, Chem. Lett., (1978)367.

409 M. Preece and S. D. Robinson, Inorg. Chim. Acta, 29(1978)L199.

410 D. Milstein and J. K. Stille, J. Am. Chem. Soc., 100(1978)3636.

411 E-I. Negishi, N. Okukado, A. O. King, D. E. Van Horn and B. I. Spiegel, J. Am. Chem. Soc., 100(1978)2254.

412 R. T. Hansen, D. B. Carr and J. Schwartz, J. Am. Chem. Soc., 100(1978)2244.

413 T. Yoshida, Kagaku No Ryoiki, 32(1978)434; Chem. Abstr., 89(1978)156649s.

414 V. E. Uhlig, B. Hipler and P. Muller, Z. Anorg. Allg. Chem., 440(1978)11.

415 P. E. Antle and C. A. Tolman, J. Organometal. Chem., 159(1978)C5.

416 H. Hoberg and J. Korff, J. Organometal. Chem., 150(1978)C20.

417 R. Meij, D. J. Stufkens, K. Vrieze, E. Roosendal and H. Schenk, J. Organometal. Chem., 155(1978)323.

418 R. Meij, D. J. Stufkens and K. Vrieze, J. Organometal. Chem., 144(1978)239.

419 D. S. Rycroft, D. W. A. Sharp and J. G. Wright, Inorg. Nucl. Chem. Lett., 14(1978)451.

420 B. Corain, G. Bontempelli, L. de Nardo, G-A. Mazzocchin, Inorg. Chim. Acta, 26(1978)37.

421 W. J. Louch and D. R. Eaton, Inorg. Chim. Acta, 30(1978)215.

422 C. J. May and J. Powell, Inorg. Chim. Acta, 26(1978)L21.

423 K. J. Haller and J. H. Enemark, Inorg. Chem., 17(1978)3552.

424 C. Mealli, A. Orlandini, L. Sacconi and P. Stoppioni, Inorg. Chem., 17(1978)3020.

425 M. Di Vaira, S. Midollini and L. Sacconi, Inorg. Chem., 17(1978)816.

426 S. Midollini, A. Orlandini and L. Sacconi, J. Organometal. Chem., 162(1978)109.

427 M. Schmidt and G. G. Hoffmann, Angew. Chemie. Int. Ed. Engl., 17(1978)598.

428 D. G. Holah, A. N. Hughes, B. C. Hui and C-T. Kan, Canad. J. Chem., 56(1978)2552.

429 G. A. Bowmaker, Aust. J. Chem., 31(1978)2549.

430 M. D. Curtis and J. Greene, J. Am. Chem. Soc., 100(1978)6362.

431 Von E. Uhlig, B. Hipler and P. Muller, Z. Anorg. Allg. Chem., 447(1978)18.

432 T. Kruck, W. Thielmann and C. Sauer, Z. Natuf., 33b(1978)1291.

433 I. W. Bassi, C. Benedicenti, M. Calcaterra, R. Intrito, G. Rucci and C. Santini, J. Organometal. Chem., 144(1978)225.

434 C-K. Chin, M. S. Sennett, P. J. Wier and L. Vaska, Inorg. Chim. Acta, 31(1978)L443.

435 L. S. Benner, M. M. Olmstead, H. Hope and A. L. Balch, J. Organometal. Chem., 153(1978)C31.

436 D. M. Curtis and R. J. Klinger, J. Organometal. Chem., 161(1978)23.

437 S. Bhadivi, P. R. Raithby, C. I. Zuccaro, M. B. Hursthouse, L. Casella and R. Ugo, J. Chem. Soc., Chem. Commun., (1978)991.

438 A. Dedieu and R. Hoffmann, J. Am. Chem. Soc., 100(1978)2074.

439 J. M. Brown and P. A. Chaloner, J. Am. Chem. Soc., 100(1978)4307.