

NICKEL, PALLADIUM AND PLATINUM

ANNUAL SURVEY COVERING THE YEAR 1975

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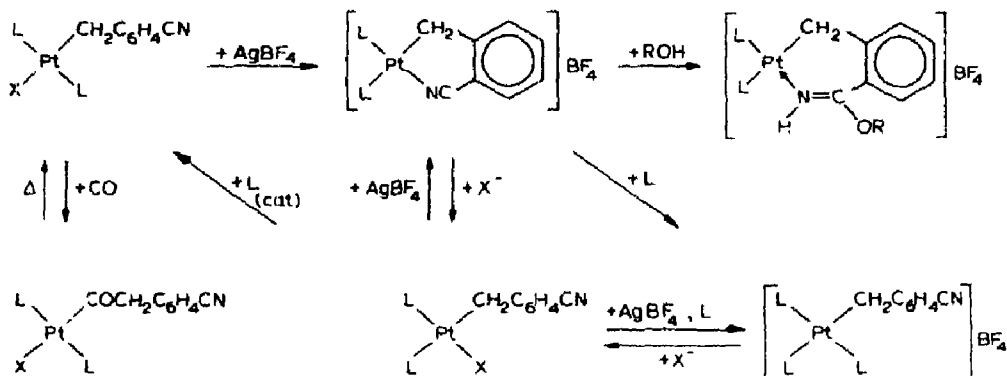
ABBREVIATIONS

DPM	bis-1,2(diphenylphosphino)methane		
DPE	bis-1,2(diphenylphosphino)ethane		
DPP	bis-1,2(diphenylphosphino)propane		
DPB	bis-1,2(diphenylphosphino)butane		
en	ethylenediamine	acac	acetylacetonate
pn	propylenediamine	THF	tetrahydrofuran
bipy	2,2'-bipyridyl	1,5-COD	1,5-cyclooctadiene
phen	1,10-phenanthroline	pz	1,2-pyrazine
py	pyridine		

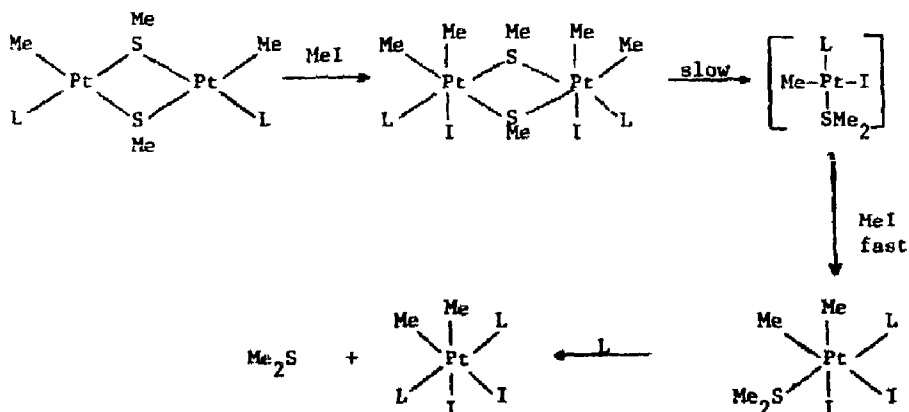
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I. Metal-carbon σ complexes

A number of metal alkyls have been prepared by oxidative addition. Treating $PtL_4(PPh_3, AsPh_3)$ with $o\text{-XCH}_2C_6H_4CN$ ($X = Cl, Br$) yields trans- $PtX(CH_2C_6H_4CN)L_2$ [1]. Ligands L can be displaced by bidentate phosphorus ligands, and facile insertion of CO into the Pt-C bond occurs. The trans

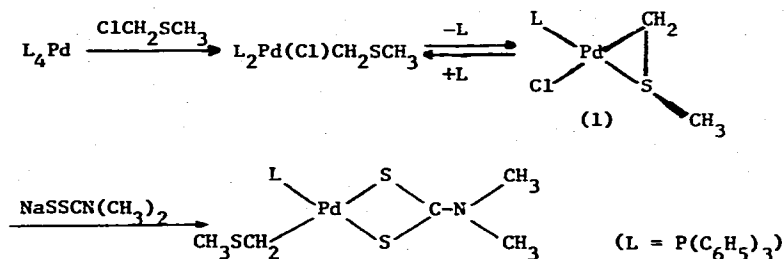


complex is thermodynamically the stable isomer but cis-trans isomerization by free L occurs in CH_2Cl_2 solvent. Similarly the oxidative addition of $XRCN$ ($X = Cl, Br$; $R = (CH_2)_n$, $n = 1, 2, 3$) to PtL_4 ($L = PPh_3, PMePh_2, AsPh_3$) yields cis- and/or trans- $PtX(RCN)L_2$ [2]. The reaction of MeI with $(SMe)PhL_2$ ($L = PMe_2Ph$) gives $PtI(Ph)SMe_2(L)$ [3]. Similarly $[Pt(SMe)MeL]_2$ gives $PtMe_2I_2(L)SMe_2$. Isolation of $[Pt(SMe)Me_2I(L)]_2$ verifies that alkylation occurs on the platinum center. Arylnickel(II) compounds have been prepared by the oxidative addition of RC_6H_4X ($R = H, m$ or p -Me, $-Cl, -CN$, and OPh , p -OMe, $-COMe$, and $COPh$, and m - CO_2Me ; $X = Cl, Br, I$) to



$Ni(PPh_3)_2$. A linear correlation of rates against Hammett's σ is found with $\sigma > 0.23$ for electron withdrawing substituents [4]. Benzylnickel(II)

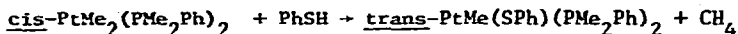
complexes have been prepared by the oxidative addition of benzyl halides to $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ [5]. Trimethylstannane displaces alkane from $\text{PtR}_2(\text{DPM})$ ($\text{R} = \text{Me}, \text{Et}$) to give $\text{PtH}(\text{SnMe}_3)_2(\text{DPM})$, which reversibly dissociates SnMe_3H to give $\text{Pt}(\text{SnMe}_3)_2(\text{DPM})$. The following compounds are also described: $\text{Pt}(\text{MMe}_3)\text{Me}(\text{DPM})$ ($\text{M} = \text{Si}, \text{Ge}$); $\text{Pt}(\text{PbPh}_3)_2(\text{DPM})$; $\text{PtHCl}(\text{SnMe}_3)_2(\text{DPM})$; $\text{PtCl}(\text{SnMe}_3)(\text{DPM})$ [6]. A compound $\text{PdCl}(\text{CH}_2\text{SMe})(\text{PPh}_3)$ (1) has been prepared from $\text{Pd}(\text{PPh}_3)_4$ and MeSCH_2Cl , where the MeSCH_2 group acts as a chelate ligand [7]. Preliminary X-ray structural data suggests the molecule to be square planar about the platinum, and the ^1H nmr spectrum shows magnetically equivalent methylene protons at -30°C because of inversion through the sulfur atom. Alkoxallyl complexes of $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$, trans- $\text{MCl}(\text{COCO}_2\text{R})\text{L}_2$ ($\text{R} = \text{Me}, \text{Et}$; $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PEt}_3$) have been prepared by



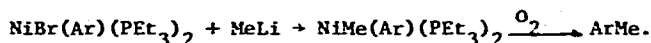
oxidative addition reactions of ML_4 with ClCOCO_2R . In solution the s-trans and s-cis conformers are postulated to exist [8]. The compounds are decomposed by Cl_2 to PtCl_2L_2 , and transesterification with $\text{EtOH}|\text{EtO}^-$ gives $\text{PtCl}(\text{COCO}_2\text{Et})(\text{PPh}_3)_2$ from the methyl derivative. The palladium analogs undergo decarbonylation in solution to form carboxylato complexes $\text{PdCl}(\text{CO}_2\text{R})\text{L}_2$. Reaction of $\text{Ni}(\text{DPP})_2$ and $\text{Ni}(\text{DPB})_2$ with acyl halides RCOX ($\text{R} = \text{Ph}, \text{Et}$; $\text{X} = \text{Cl}, \text{Br}$) gives haloacylnickel(II) compounds [9]. $\text{NiBr}(\text{Ph})\text{DPB}$ is carbonylated to the acyl with CO . Acyl platinum complexes trans- $\text{PtCl}(\text{COR})(\text{PPh}_3)_2$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{OMe-p}, \text{C}_6\text{H}_4\text{Cl-p}, \text{CH}=\text{CH}_2, \text{CH}=\text{CHMe}, \text{CMe}=\text{CH}_2, \text{CH}=\text{CHPh}$) have been prepared from $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and RCOCl [10]. The sulphonato complexes trans- $\text{PtCl}(\text{SO}_2\text{R})(\text{PPh}_3)_2$ ($\text{R} = \text{Me}, \text{Ph}$) have been obtained by a similar route from RSO_2Cl . The complex trans- $[\text{PtCl}(\text{COCH}=\text{CHPh-trans})(\text{PPh}_3)_2]$ undergoes thermal decarbonylation to trans- $[\text{PtCl}(\text{CH}=\text{CHPh-trans})(\text{PPh}_3)_2]$. Values for $\nu_{\text{Pt-Cl}}$ indicate a medium trans influence for the SO_2R group. The in situ generation of $\text{Ni}(0)$ has been used for aryl coupling [11]. Complexes of $\text{Pd}(\text{IV})$, $\text{PdCl}_2(\text{C}_6\text{F}_5)_2(\text{L-L})$ ($\text{L-L} = \text{en}, \text{bipy}, \text{phen}, \text{pn}$), have been claimed from the chlorination of $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{L-L})$ [12].

A wide range of alkyls have been obtained by metathetical replacement

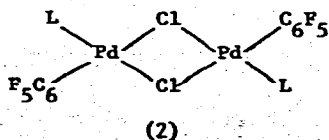
reactions. Benzenethiol reacts with cis-PtMe₂L₂ (L = PMe₃, PMe₂Ph, PPh₂, PPh₃) to give CH₄ and trans-PtMe(SPh)L₂ or trans-Pt(SPh)₂L₂. Observation



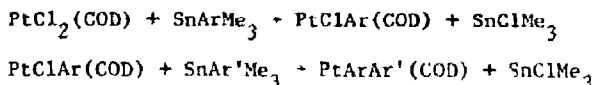
of a signal for Bu^tMeNO in the presence of Bu^tNO has been presented as evidence for a contribution from a radical chain pathway [13]. These authors have also carried out a similar study on the cleavage of methyl-platinum(II) bands by halide. A series showing the gradation of methylating power for several methylmetal complexes has been developed [14]. Complexes (o-XC₆H₄CH₂)₂Ni(PR₃)₂ (X = F, Cl, Br, Me; R = Et, Bu) have been prepared by treating the corresponding nickel chlorides with the appropriate Grignard reagent [15]. The cross coupling of bromobenzene and o-bromotoluene with MeLi and MeMgBr has been studied. Intermediate methyl-arylnickel(II) complexes have been prepared and interestingly the reductive elimination of alkylated aryl is accelerated by oxygen and by aryl bromides



[16]. A procedure to prepare PtIME₃ in yields of 80%, has been reported [17]. The Grignard or lithio method, followed by anion replacement, has been used to prepare complexes MX(C₆Cl₅)(PPh₃)₂ (M = Pd, X = Cl, Br, I, NCO, NCS, N₃; M = Ni, X = NCS, NCO, N₃) [18]. This method was extended to prepare complexes NiX(C₆Cl₅)(DPE) (X = Cl, Br, I, NCS, NCO, N₃, CN, NO₂) [19]. The halide can be replaced in these complexes by 3,5-lutidine to yield the cationic compounds [Ni(C₆Cl₅)L_{3-n}(3,5-lut)_n]ClO₄ (L = PMe₂Ph, PPh₂; n = 1, 2, 3) [20]. Haloarylnickel bipyridyl complexes have been prepared from Et₂Ni(bipy) and aryl halides for aryls:- phenyl, o-tolyl, m-tolyl, p-tolyl or o-chlorophenyl and X = I, Br, Cl. The reaction has been followed in the visible region of the electronic spectrum [21]. In combination with Lewis acids such as AlEtCl₂ and AlEt₂Cl the complexes show higher catalytic activity for propylene dimerization than do NiCl₂(bipy) and NiEt₂(bipy). A reexamination of the reaction between compounds PdCl₂L₂ (L = PPh₃, PPh₂Me, AsPh₃) and TlBr(C₆F₅)₂ yields binuclear compounds (2) mixed with mononuclear compounds [22]. Addition of further ligand L converts the dimers into monomers PdCl(C₆F₅)L₂. Complexes of tetrachlorophenyl have been prepared by treating PdCl(π-C₃H₅)PPh₃, PdCl(π-C₃H₅)py

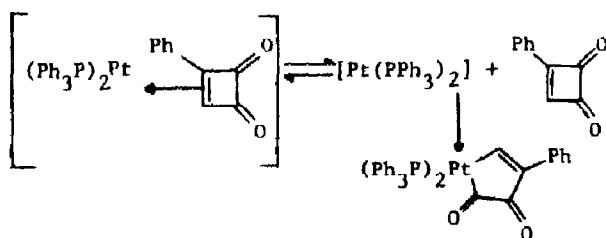


and $\text{PtCl}(\pi\text{-C}_3\text{H}_5)\text{PPh}_3$ with $(2,3,5,6\text{-}^o\text{HCl}_4)_3\text{Ti}$, when the halide is replaced by C_6HCl_4 [23]. The compound trans- $\text{PtI}(\text{CF}_3)(\text{PEt}_3)_2$ is obtained by treating cis- $\text{PtMe}_2(\text{PEt}_3)_2$ with CF_3I for 48 hr at 25°C [24]. ^{19}F nmr data is reported. Aryltrimethyltin reagents have been used to prepare aryl-platinum(II) complexes under mild conditions [25]. The reactivity of

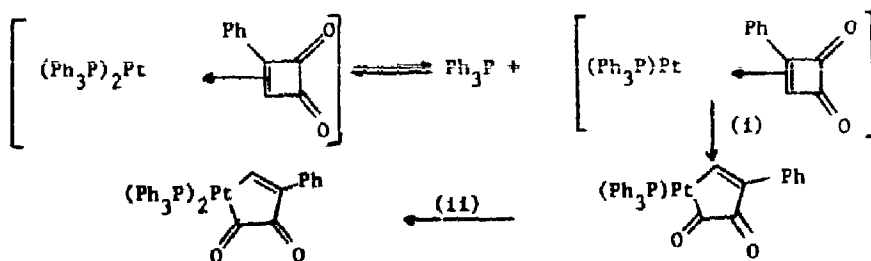


Group IV compounds appears to decrease in the sequence $\text{Pb} > \text{Sn} > \text{Ge} > \text{Si}$. Phenyl (acetylacetonato) nickel(II) complexes $\text{NiPh}(\text{acac})\text{L}$ ($\text{L} = \text{PCy}_3, \text{PPh}_3$) and $\text{NiPh}(\text{acac})(\text{PEt}_3)_2$ have been prepared from $\text{Ni}(\text{acac})_2$ and $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ in the presence of a slight excess of phosphine at -20°C under an atmosphere of N_2 [26].

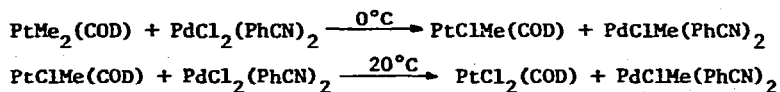
A number of ring opening and alkyl transfer reactions have been reported. Kinetics for the ring opening of benzocyclobutene-1,2-dione, 3-phenylcyclobutene-1,2-dione, 4-methoxy-3-phenylcyclobutene-1,2-dione, and 3,4-dimethoxycyclobutene-1,2-dione with the zerovalent platinum complexes $\text{Pt}(\text{trans-PhCH=CHPh})(\text{PPh}_3)_2$ and $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ show the reaction follows first order kinetics in platinum complex and zero order in dione. Thus the rate-determining step is dissociation of stilbene or diphenylacetylene. Interestingly for the ring opening isomerization step the activation entropy in CHCl_3 is zero, but in benzene it is markedly positive. Two schemes are presented to explain this latter effect, with scheme I being preferred [27]. Homonuclear methyl transfer between



SCHEME 1

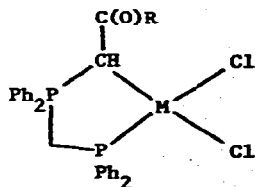
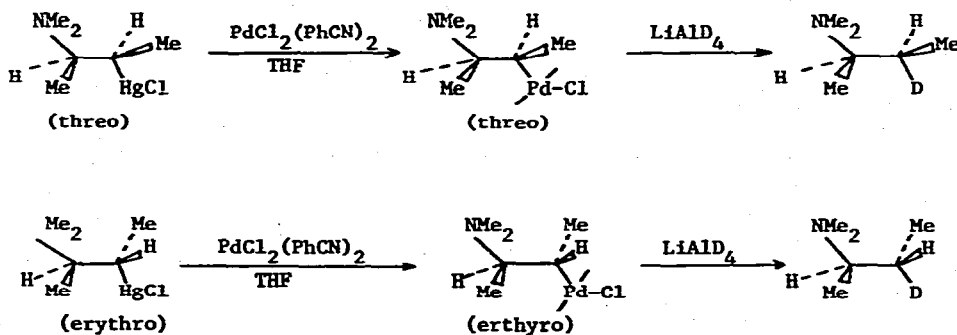
SCHEME 2 (1), $-\text{PPh}_3$; (11), $+\text{PPh}_3$

and heteronuclear methyl transfer between platinum and palladium is facile [28]. Reaction of cis-PtMe₂(PMe₂Ph)₂ and cis-Pt(NO₃)₂(PMe₂Ph)₂ yields cis-PtMe(NO₃)(PMe₂Ph)₂ which undergoes subsequent slow isomerization to



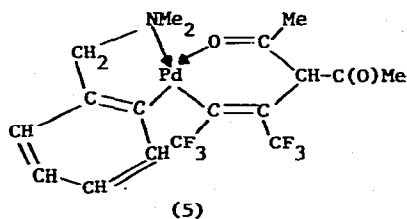
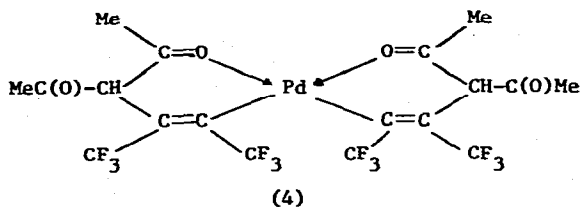
the more stable trans isomer [29]. Alkyl transfer from threo- and erythro-MeCH(NMe₂)CH(HgCl)Me to palladium(II) proceeds with retention of configuration. Degradation of threo- and erythro-MeCH(NMe₂)CH(Me)PdCl(PhCN)₂ to the free amine can be effected with LiAlD₄ [30].

A number of vinyl and ylide compounds have been reported. Complexes of the chloro-Pd(II) and Pt(II) with ligands Ph₂P(CH₂)₂⁺P(Ph₂)⁻CHC(O)R (n = 1, R = Ph; n = 2, R = Me, OMe) have been prepared (3) [31]. The crystal structures of two addition products of hexafluorobut-2-yne with palladium(II) β-diketonate rings: cis-bis[1,2-bis(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl-O, C¹] palladium(II) and ab-[1,2-bis(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl-O, C¹]-cd-(2-(dimethylamino)methyl]

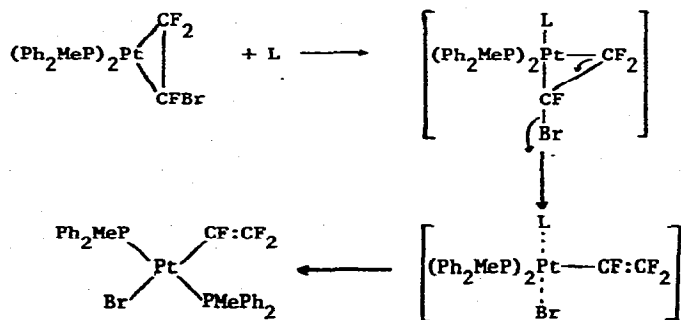


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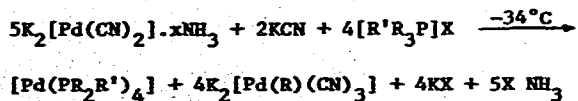
phenyl-C¹,N palladium(II) (4) (5) are reported [32]. A study of the vinyl rearrangement of $\text{Pt}(\text{C}_2\text{F}_3\text{Br})(\text{PMePh}_2)_2$ and $\text{Pt}(\text{C}_2\text{F}_3\text{Br})(\text{PPh}_3)_2$ indicates intermediacy of a pentacoordinate species. The reaction is favored by



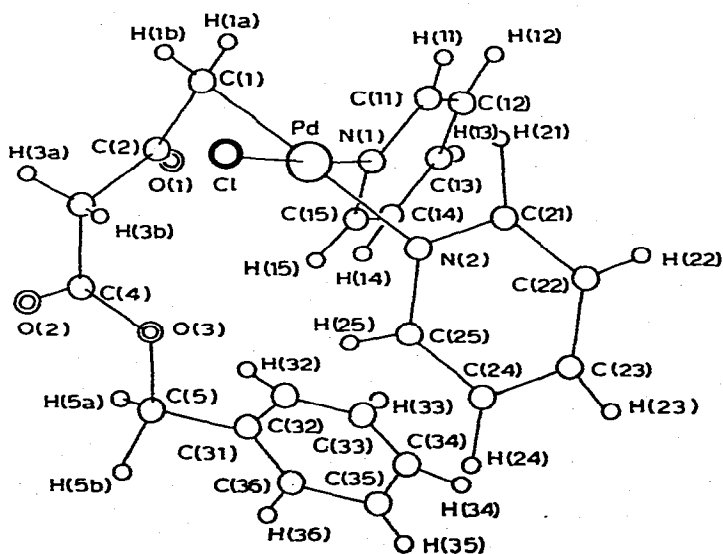
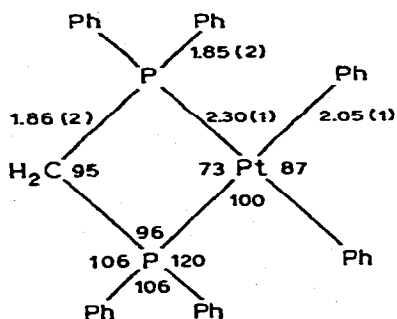
coordinating solvents. The reaction has been used to prepare complexes $\text{PtX}(\text{CF}=\text{CF}_2)(\text{PMePh}_2)_2$ and $\text{PtX}(\text{CF}=\text{CF}_2)(\text{PPh}_3)_2$ ($\text{X} = \text{SCN}, \text{NO}_2, \text{NO}_3, \text{OAc}$) [33].



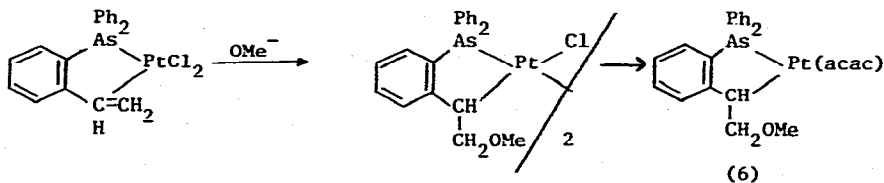
Anionic phenylpalladium(II) complexes are formed when compounds of type $[\text{R}'\text{R}_3\text{P}]_2[\text{Pd}(\text{CN})_2]$ are allowed to warm above -40°C [34]. Infrared spectra are reported and discussed. Complexes $\text{Li}_2[\text{Ni}(\text{C}_2\text{Ph})_4] \cdot 4\text{THF}$,



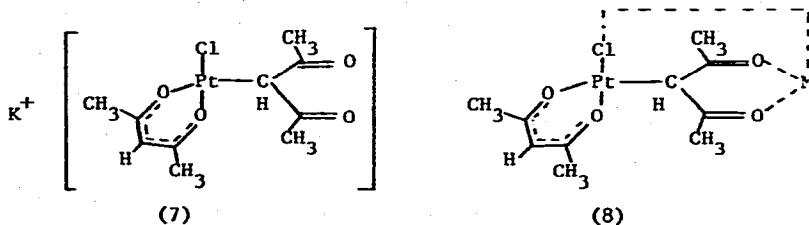
$\text{Li}_2[\text{NiPh}_4] \cdot 4\text{THF}$, and $\text{Li}_2[\text{NiMe}_4] \cdot 2\text{THF}$ are obtained by treating $\text{Ni}(\text{dpi})_2$ (dpi^- = anion of 1,3-bis(2-pyridoylimino)isoindole) with LiC_2Ph , LiPh , or LiMe at -78°C [35]. The crystal structure of $\text{Pt}(\text{Ph})_2(\text{DPM})$ shows internal ring angles at Pt and P which are approximately 15° less than the unconstrained P-Pt-P and Pt-P-C angles [36]. The angles are normal and it is suggested that the unusually low Pt-P coupling constant is a consequence of the distortion of these valence angles in the 4-membered ring.



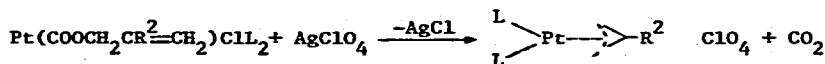
A series of metal alkyls having keto groups have been reported. The crystal structure of $\text{PdCl}(\text{CH}_2\text{COCH}_2\text{COOCH}_2\text{Ph})(\text{py})_2$ has a square planar geometry about Pd. The benzylacetoacetate is coordinated by the terminal carbon atom. The acetoacetate moiety in the benzylacetoacetate ligand is bent perpendicular to the coordination plane, and the terminal benzyl group is again bent with its phenyl ring approximately parallel to the coordination plane [37]. Compound (6) has been obtained by the route shown [38]. A coupling constant of 113 Hz between ^{195}Pt and the methine proton, in



addition to the observation of a temperature dependence of the methylene protons, is presented as evidence for the formation of the 5-membered ring. A detailed analysis of the infrared spectra of complexes (7) and (8) ($M = \text{VO}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Pd}$ for $n = 2$ and $M = \text{Fe}$ for $n = 3$) has been performed [39]. Assignments have been assisted by using isotopic metal substitution. The C O groups retain the keto character even after coordination of the second metal. For the allyloxycarbonyl- and N-allylcarbamoyleplatinum(II)

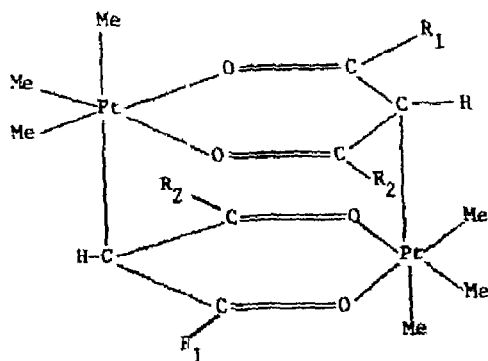
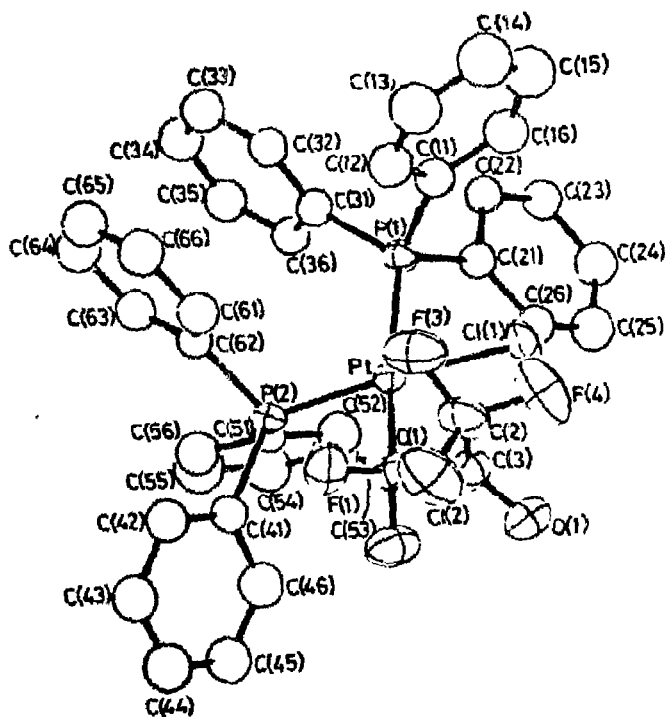


complexes $\text{Pt}(\text{COXCHR}^1\text{CR}^2=\text{CHR}^3)\text{ClL}_2$ ($X = \text{O}, \text{NH}$; $R^1, R^2, R^3 = \text{H}, \text{Me}$; $L = \text{PPh}_2\text{Me}, \text{PPh}_3$) there is no significant interaction between platinum and the C=C bond [40]. The compounds undergo quite facile decarboxylation upon treatment with an equimolar amount of AgClO_4 .



Possible mechanistic pathways are discussed. The crystal structure of $\text{PtCl}(\text{CF}_2\text{COCF}_2\text{Cl})(\text{PPh}_3)_2$ shows a very long Pt-P bond trans to $-\text{CF}_2\text{COCF}_2\text{Cl}$ [41]. An ^1H nmr study of the trimethylplatinum(IV) compound (7) shows that kinetically rigid dimers are present in solution. The 1:1 adducts with py

and bipy have been prepared [42]. A quantitative analysis, however, of the ^1H nmr of the compound (7) ($\text{R} = \text{Me}$) has shown that exchange of the acetylacetonate ligand is first order and proceeds predominantly by dimer

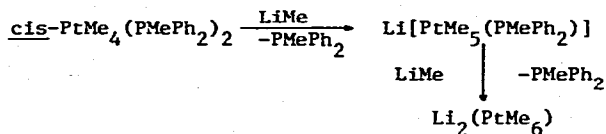
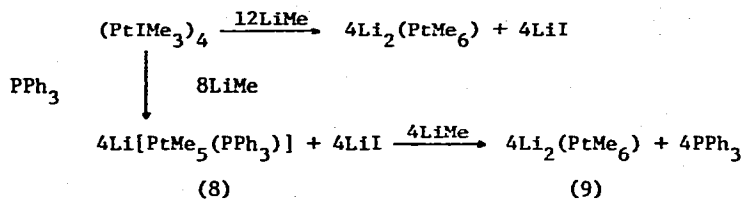


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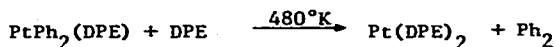
($\text{R}^1 = \text{R}^2 = \text{Pr}^n$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{OEt}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{OMe}$; $\text{R}^1 = \text{R}^2 = \text{OEt}$;
 $\text{R}^1 = \text{R}^2 = \text{OMe}$)

dissociation into two separated pentacoordinated species. The activation energy is $61.5 \pm 0.8 \text{ kJ mol}^{-1}$ [43]. The anionic complexes pentamethyl (8) and hexamethyl (9) platinate(IV) have been prepared from $(\text{PtIME}_3)_4$ and cis-

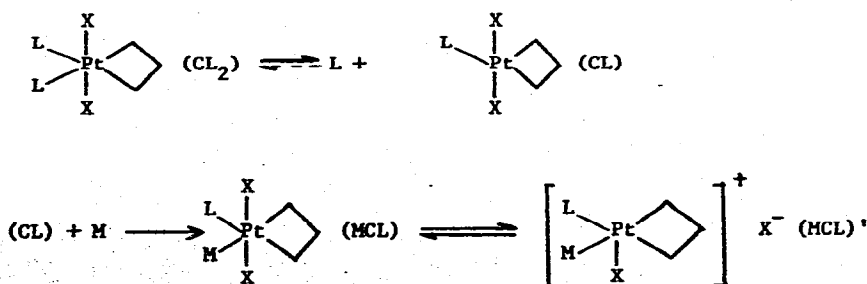
$\text{PtMe}_4(\text{PMePh}_2)_2$ with methyl lithium [44]. The infrared and ^1H nmr spectra of a series of complexes $\text{PtMe}_3(\text{o-OC}_6\text{H}_4\text{CH=NR})\text{X}$ with $\text{X} = \text{lutidine, PPh}_3$, and $\text{R} = \text{H, Me, Pr}^i, \text{CH}_2\text{Ph, Ph}$ have been studied [45].

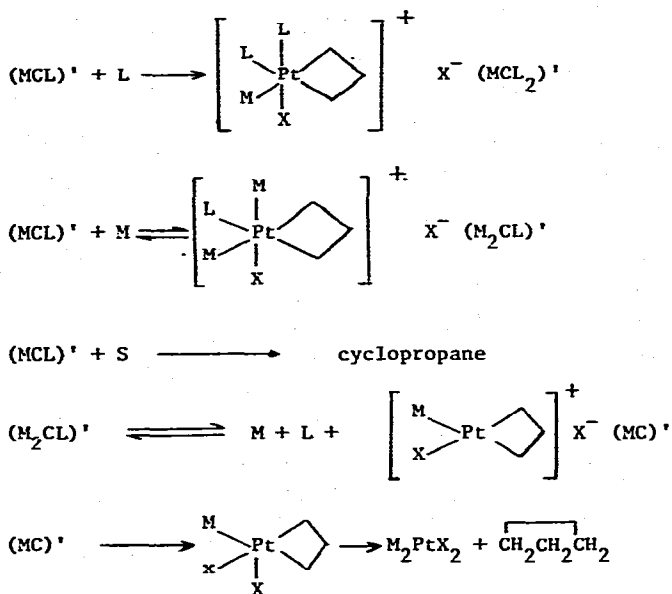


Thermal decomposition of complexes $\pi\text{-cpNi}(\text{PPh}_3)\text{R}$ ($\text{R} = \text{Me, Et, Pr}^i, \text{Pr}^n, \text{Bu}^n, \text{Bu}^s, \text{PhCH}_2, \text{Me}_3\text{SiCH}_2$) has been studied by ^1H nmr spectroscopy in aromatic solvents [46]. For compounds having a β -hydrogen, decomposition occurs by a β -elimination reaction. The order of stability is $\text{Me}_3\text{SiCH}_2 > \text{PhCH}_2 > \text{Me} > \text{Et} \sim \text{Bu}^n > \text{Pr}^n > \text{Bu}^s \sim \text{Bu}^i$. Radical pathways are not involved. The pyrolysis of diarylplatinum complexes is facilitated by the presence of added ligands because of the promotion of the reductive elimination reaction [47]. A study has been made of the displacement of

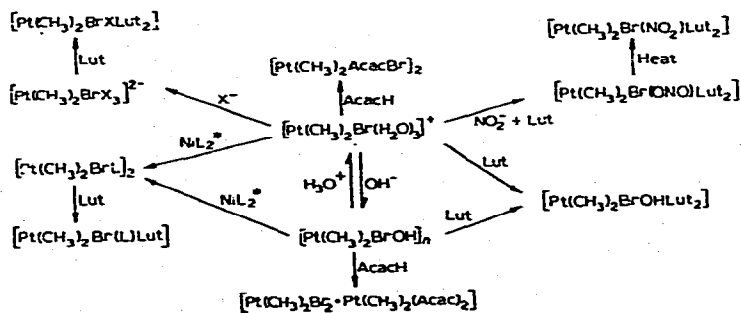


the cyclopropane moiety from $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ ($\text{X} = \text{Cl, Br; L} = \text{THF, py, en}$). Depending on the new ligand reacting with the system, either L or cyclopropane is preferentially displaced. Rate law plots for the evolution of cyclopropane are given. A speculative mechanistic scheme is suggested [48].





Further work has been carried out to deduce factors involved in the cis-trans isomerization of square planar complexes $\text{PtBr}(\text{Ar}')(\text{PET}_3)_2$ ($\text{Ar}' = \text{Ph}, \text{p-MeC}_6\text{H}_4, \text{p-EtC}_6\text{H}_4, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2, \text{p-MeC}_6\text{H}_4, \text{p-FC}_6\text{H}_4$). Comparison is made with the rates for halide substitution by MeOH [49]. Treating $[\text{PtBr}_2\text{Me}_2]_n$ with aqueous Ag^+ in acid solution yields $[\text{PtBrMe}_2(\text{H}_2\text{O})_3]^+$, which converts to $[\text{PtBr}(\text{OH})\text{Me}_2]_n$ upon neutralization. These compounds undergo a variety of reactions with halides, lutidine, and nickel complexes of salicylaldiminate or β -thiodiketonates [50]. The enthalpies of the



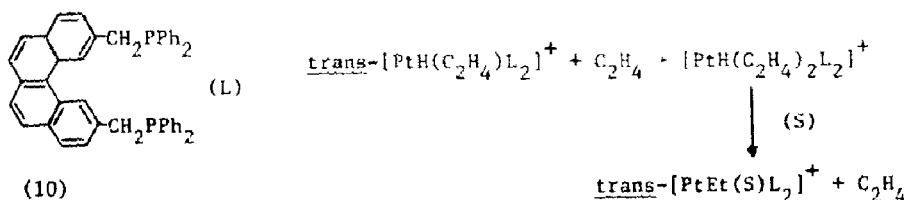
*L = Sal-N-R or thio- β -diketonate

SCHEME 1

reaction of a series of Group V donors with $[\text{PtMe}(\text{THF})\text{P}_2]\text{PF}_6$ ($\text{P} = \text{PMe}_2\text{Ph}$) shows a good correlation with the cone angle L [51]. The range of enthalpies from 27.8 to 0.5 for $\sim\text{H}$ in Kcal mol^{-1} are reported corresponding to a change in cone angle of 107° to 190° [$\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ to $\text{P}(\text{O}-\text{C}_6\text{H}_3(\text{Me}_2))_3$]. Alkyl- and aryl-(bipy)Pt(II) complexes have been prepared by treating the appropriate 1,5-COD compounds with 2,2'-bipyridine. Analogous $\text{PtMe}_2(\text{phen})$ complexes have been prepared [52]. The electronic spectra in the charge-transfer region are considered to be suggestive of π -bonding in the Pt-Ph bond. A systematic study has been made of the ^{13}C nmr spectra of three series of the π -bonded 1,5-COD complexes of platinum, $\text{PtMeR}(\text{COD})$, $[\text{PtMeL}(\text{COD})]\text{PF}_6$ and $\text{PtRR}'(\text{COD})$ where R and R' are anionic, and L is a neutral ligand. Linear correlations of $^1\text{J}_{\text{PtC}}(\text{CH}_3)$ vs $^1\text{J}_{\text{PtC}}(\text{COD})$ and $^2\text{J}_{\text{PtAsC}}$ vs $^1\text{J}_{\text{PtC}}(\text{COD})$ are presented [53]. ^{13}C nmr spectroscopy has also been used to determine the position of deuterium incorporation into alkanes and tertiary phosphine platinum(II) complexes [54].

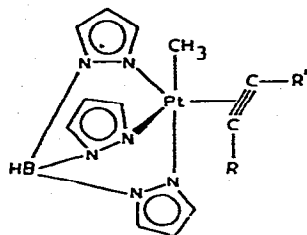
II. Metal complexes formed by insertion and related reactions

An interesting report of the insertion of ethylene into a Pt-H bond has been published [55]. The hydroplatinum(II) complex contains a bidentate ligand (10) which spans the trans positions, and cannot become a cis chelate. The observation of facile insertion of ethylene to form an ethylplatinum(II) complex shows that ethylene insertion occurs even in cases when the hydro and olefin ligands cannot adopt mutually cis-orientations in a square-planar complex. For complexes $\text{trans}-[\text{PtH}(\text{PET}_3)_2]\text{PF}_6$ ($\text{L} = \text{acetone, CO, PET}_3, \text{AsPh}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3$) and $\text{trans}-\text{PtHX}(\text{PET}_3)_2$ ($\text{X} =$



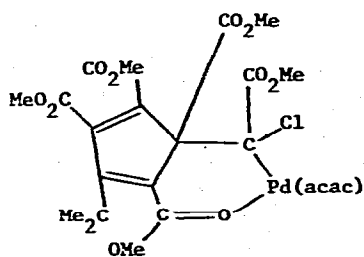
$\text{Cl}, \text{NO}_3, \text{NO}_2, \text{CN}$) the facility to insertion of olefins and acetylenes follows the order: $\text{L} = \text{acetone} >> \text{CO} > \text{AsPh}_3 > \text{P}(\text{OPh})_3, \text{PET}_3$; and $\text{X} = \text{NO}_3 > \text{Cl} > \text{NO}_2, \text{CN}$. $\text{PhC}\equiv\text{CMe}$ inserts more readily than C_2H_4 [56]. In a study of the insertion of $\text{R}_1\text{C}\equiv\text{CR}_2$ ($\text{R}_1 = \text{Me}, \text{R}_2 = \text{Ph}, \text{CO}_2\text{Me}$; $\text{R}_1 = \text{Ph}, \text{R}_2 = \text{Ph}, \text{CF}_3$; $\text{R}_1 = \text{CO}_2\text{Me}, \text{R}_2 = \text{CO}_2\text{Me}$) into $\text{PtHX}(\text{PET}_3)_2$ ($\text{X} = \text{NO}_3, \text{Cl}, \text{acetone}, \text{MeOH}$) the π -alkenyl group has been shown to be cis about Pt and H. The formation of a cis geometry about Pt is not always observed but is favored by (i) electron withdrawing substituents on the acetylene (ii) a coordinating solvent for cationic complexes and a non-planar solvent for neutral complexes

(iii) the presence of a more strongly coordinating anion X [57]. Complexes $\text{PtMe}(\text{R}_2\text{Bpz}_2)\text{L}$ ($\text{R} = \text{Et}, \text{Ph}$; $\text{L} = \text{tert. phosphine, isocyanide}$) form stable acetylene complexes with $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CMe}$ (11). With $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ the methylvinyl compounds are obtained [58]. In a continuing



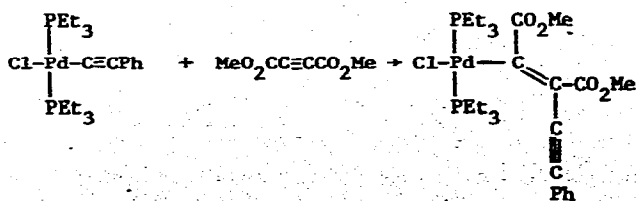
(11)

study of the reactions of dimethyl acetylenedicarboxylate with palladium(II) chloride the structure of {[chloro(methoxycarbonyl)(1,2,3,4,5-pentamethoxycarbonylcyclopenta-2,4-dienyl)-2-MeOCO]methyl}(acetylacetonate)Pd(II) has been reported (12) [59]. This compound is formed from the chloro-bridged dimer, and products obtained from treating this dimer with PPh_3 , CN^- , Br^- , HCl are also described. The insertion of dimethyl acetylenedicarboxylate

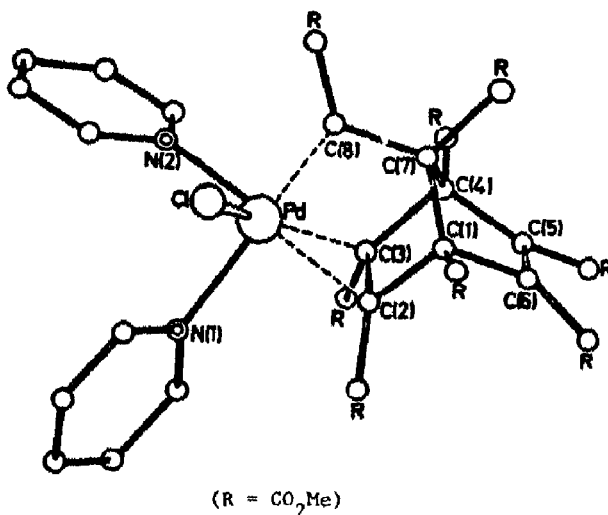


(12)

into the Pd-C bond of trans- $\text{PdCl}(\text{C}\equiv\text{CPh})(\text{PEt}_3)_2$ yields trans- $\text{PdCl}[\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{C}\equiv\text{CPh}](\text{PEt}_3)_2$ (13) [60]. Treating PdCl_2 with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ in MeOH

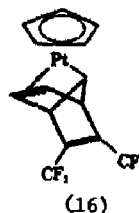
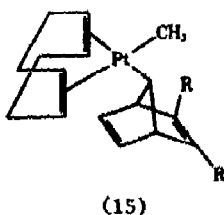


yields $\{\text{PdCl}[\text{HC}_8(\text{CO}_2\text{Me})_8]\}_2$ which gives $\text{PdClpy}_2[\text{HC}_8(\text{CO}_2\text{Me})_8]$ (14) with pyridine. A single crystal structure of (14) shows it to be a 5-coordinate Pd(II) complex [61]. $\text{Ni}(\text{allyl})_2$ effects the stereospecific *cis*-diallyla-



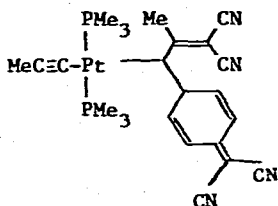
tion of $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}=\text{CMe}$ in 30-50% yield. The formation of 1,4- d_2 alkadiene from the deuterolytic workup leads the authors to postulate a nickelole intermediate [62].

Diels-Alder reactions of $\text{PtMe}(\eta^1\text{-C}_5\text{H}_5)\text{COD}$ and $\text{Pt}(\eta^1\text{-C}_5\text{H}_5)_2\text{COD}$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ yields adducts (15) and (16). A single crystal structure of compound (15) has been solved [63]. Addition of C_4F_6 to the ring on the side opposite the Pt atom substituent is presented as implication that there



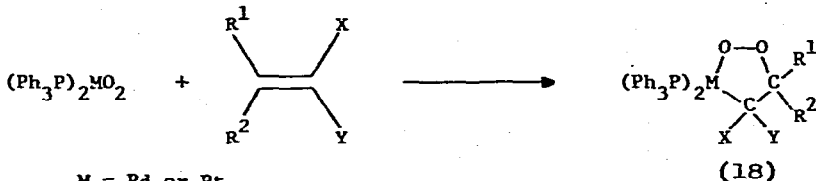
is no metal participation via a template or activation mechanism and no precoordination of the attacking C_4F_6 molecule. A crystal structure of the adduct (17) of 7,7,8,8-tetracyanoquinodimethane (TCNQ) to *trans*- $\text{Pt}(\text{CECMe})_2(\text{PMe}_3)_2$ shows that part of the TCNQ is bonded to the α -carbon,

and the other part to the β -carbon of the propynyl ligand [64]. Electro-

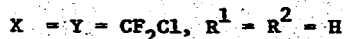
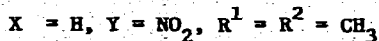
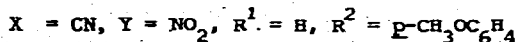
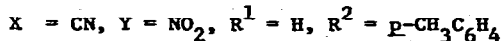
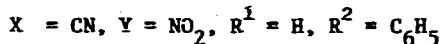
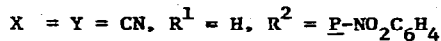
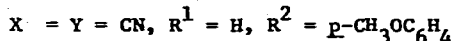
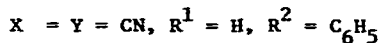
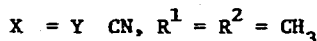
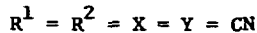


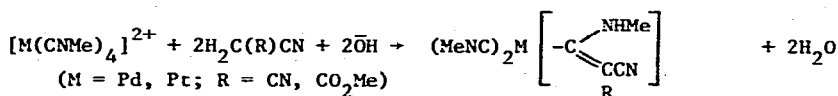
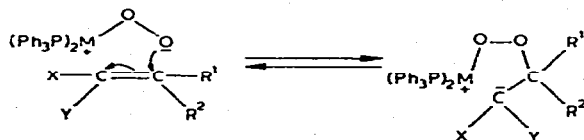
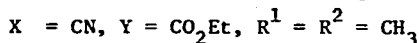
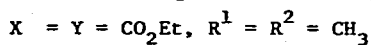
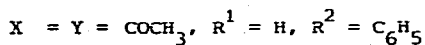
(17)

philic olefins such as 1,1-dicyano-olefins add to complexes $MO_2(PPh_3)_2$ ($M = Pd, Pt$) [65]. 1H nmr evidence is presented for the structures of the compounds (18). The Pt compounds undergo facile decomposition only at temperatures of $100^\circ C$ or higher, whereas the corresponding Pd complexes tended to be unstable at room temperature. The complexes are cleaved with CF_3CO_2H . An ionic type mechanism is proposed for the formation of these compounds. The preparation of σ -monohapto-vinyl complexes of type $M-C(NHMe)=CR^2R^3(L)_n$ from the addition of active methylene groups to isocyanides has been reported [66]. The insertion of $CyNC$ into the Pd-N bond of complexes (19) gives a new compound (20) [67]. Azido bridged

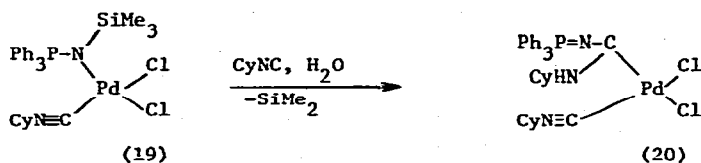


$M = Pd \text{ or } Pt$





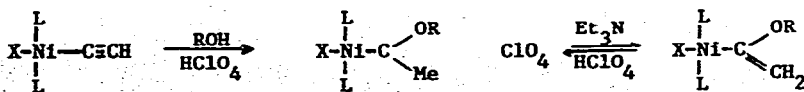
complexes $[\text{MN}_3(\text{dieneOMe})_2]$ (M = Pd, Pt) react with CO to form the cyanato-bridged compounds, and with CS₂, CF₃CN and SCNPh by 1,3-cycloaddition to form thiazotriazolate or tetrazolate groups as bridges [68]. Acylpalladium(II)



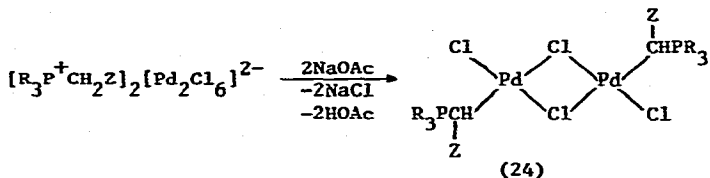
complexes have been formed by insertion of CO into the σ -alkyl compounds obtained from nucleophilic attack of Et₂NH on the Pd(II) chloride complexes of C₂H₄, C₃H₆ and 1-C₄H₈ [69]. A similar approach has led to isolation of acylpalladium(II) complexes from carbonylation of the products of attack by NH₃, PhCH₂NH₂ and phthalimide on PdCl₂(COD) [70]. A study of the carbomethoxylation of σ -bonded mercurials in the presence of stoichiometric amounts of Li₂PdCl₄ and CO proceeds with predominant retention of configuration at carbon [71]. This leads the authors to the conclusion that exchange of Pd for Hg occurs with predominant retentions.

III. Metal carbene complexes

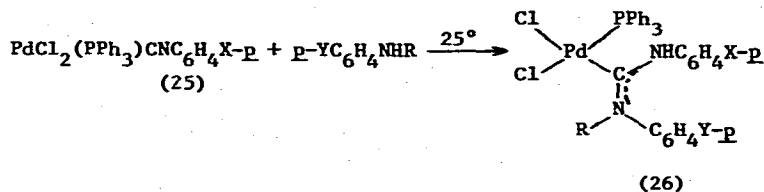
Cationic carbenes of nickel(II) (22) have been prepared by treating the nickel acetylide (21) with ROH in the presence of an equivalent amount of perchloric acid [72]. Subsequent addition of base yields a further



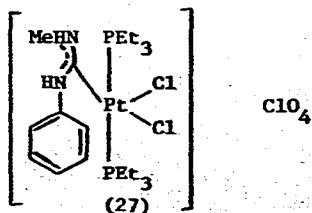
stable nickel carbene complex (23). Carbene complexes of palladium(II) (24) were obtained in good yield by treating $[\text{R}_3\text{P}^+\text{CH}_2\text{Z}]_2[\text{Pd}_2\text{Cl}_6]^{2-}$ ($\text{R}_3\text{P} = \text{Ph}_3\text{P}$, $\text{Z} = \text{COMe}$, CO_2Et , CONH_2 , CN ; $\text{R}_3\text{P} = \text{PMe}_2\text{Ph}$, $\text{Z} = \text{COPh}$) with sodium acetate [73]. The crystal structure of cis-dichlorobis[methyl-



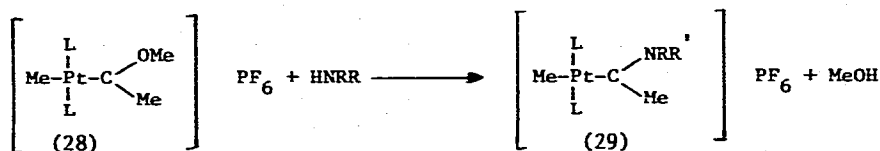
amino(methoxy)carbene]Pd(II) shows expected angles about the carbene carbons [74]. Complexes of type $\text{MCl}_2(\text{ylid})_2$ were isolated from treating PdCl_2 or PtCl_2 in refluxing CH_3CN with an ylid of the type $\text{R}_3\text{ZCR}''$ ($\text{Z} = \text{P}$, $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$, $\text{R}'' = \text{COPh}$, COMe , CO_2Et , CO_2Me , CN ; $\text{R}' = \text{Me}$, $\text{R}'' = \text{COPh}$, CO_2Et ; $\text{R}' = \text{COPh}$, $\text{R}'' = \text{COPh}$; $\text{R} = \text{Bu}^n$, $\text{R}' = \text{H}$, $\text{R}'' = \text{COPh}$; $\text{Z} = \text{As}$, $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$, $\text{R}'' = \text{COPh}$, CO_2Me), $\text{Me}_2\text{SCHCOPh}$, and $\text{C}_5\text{H}_5\text{NCHOPh}$. The ^1H nmr of the methine proton in the complex is downfield shifted relative to free ylid [75]. Kinetics of the addition of secondary aromatic amines $p\text{-YC}_6\text{H}_4\text{NHR}$ ($\text{Y} = \text{MeO}$, Me , H ; $\text{R} = \text{Me}$, Et) with compound (25) to yield carbenes (26) leads to the proposal of a stepwise mechanism involving direct nucleophilic attack of the entering amine on the isocyanide carbon, followed by proton transfers to yield the final carbene complexes [76]. A single crystal



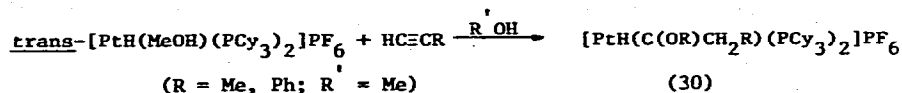
structure of (27) shows values of 2.034(11) and 1.973(11) for Pt-C(Ph) and Pt-C(carbenoid) [77]. A series of heterocyclic carbene and carbanion complexes of Pt(II) containing C(2)-bonded oxazolines, oxazoles, pyrrolines,



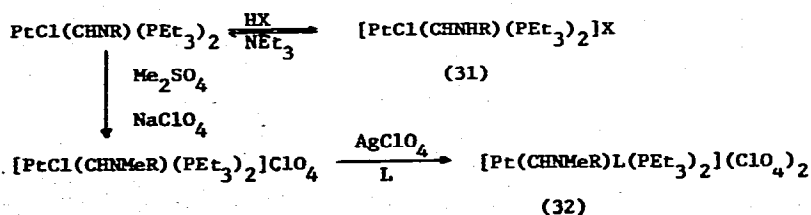
pyrroles, and imidazoles have been prepared in high yield by treating $[\text{PtCl}(\text{CNCH}_2\text{CO}_2\text{Et})(\text{PPh}_3)]\text{BF}_4$ with the respective 1,3-dipolarophiles [78]. A ^{13}C nmr study of carbene complexes $\text{trans}-[\text{PtMe}(\text{CNHMeC}_6\text{H}_4\text{X-p})]\text{PF}_6$ has deduced from comparisons of the σ^+ substituent constants for X, with the carbene ^{13}C shieldings, that both σ and π interactions occur between the carbene and the aromatic ring. The phenyl rings adopt cis orientations with respect to the carbene methyl groups. Coupling constant and chemical shift data are reported [79]. These authors have done a similar study of complexes $[\text{PtR}(\text{carbene})\text{L}_2]\text{PF}_6$ ($\text{R} = \text{Me}, \text{Cl}, \text{I}$; $\text{L} = \text{AsMe}_3, \text{PMe}_2\text{Ph}$; carbene is a range of substituted N and O heteroatom carbenes) [80]. Stereochemical implications are discussed, and it is noted that for J_{PtCNC} the coupling of a cis methyl to Pt is greater than that of a trans methyl. The aminolysis of a series of methyl Pt(II) alkoxy-carbene complexes has been described [81]. The general reaction converts compounds of type (28) into those of (29). The reaction is extended to carbene complexes of cyclic



ethers. Treating the hydro complex, $\text{trans}-[\text{PtH}(\text{MeOH})(\text{PCy}_3)_2]\text{PF}_6$, with terminal acetylenes yields hydromethoxycarbene complexes (30) rather than vinylic derivatives [82]. Platinum carbene complexes have also been



prepared by this research group by protonation (31) or alkylation (32) at nitrogen of a product arising from insertion of an isocyanide into a Pt-H bond. Infrared and ^1H nmr data of these cationic secondary carbene complexes are reported [83]. In a study of the thermolysis of complexes

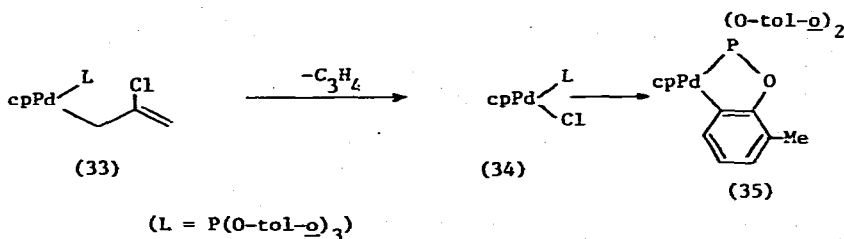


ML_2 (dialkylcarbene) ($\text{M} = \text{Ni}, \text{Pd}$; $\text{L} = \text{Bu}^t\text{NC}, \text{PPh}_3$; dialkylcarbene = 9-diazafluorene,

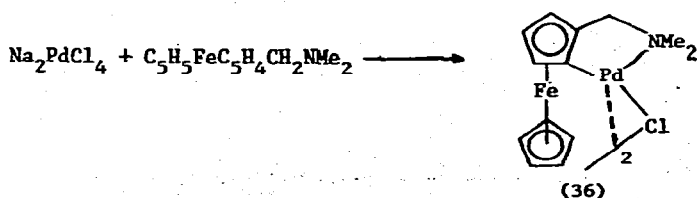
diphenyldiazomethane) a fluorenylidene complex is obtained [84]. A series of carbene complexes $[PtCl[C(SR)Y]L_2]X$ ($R = Me, Et; Y = OMe, SEt, NMe_2; L = PPh_3, PMePh_2; X = BF_4, CF_3SO_3^-$) have been prepared by alkylation at sulfur of the thio esters $PtCl[C(S)OMe]L_2$ or $PtCl[C(S)SEt]L_2$, or thio-carbamyl complex $PtCl[C(S)NMe_2]L_2$, with $[Et_3O]BF_4$ or $MeOSO_2F$. Compounds $[PtCl[C(SR)NMe_2](PPh_3)_2]X$ ($R = PhCH_2, CH_2=CHCH_2, MeHg, H; X = BF_4$) have been prepared by treating the thiocarbonyl with the appropriate halide, or CF_3SO_3H for the latter [85].

IV. Internal metallation reactions

Carbonylation of a series of *o*-palladation products from azobenzene, benzaldazine, acetophenone dimethylhydrazone, 1-methyl-1-phenylhydrazones, and tertiary benzylamines has been used to prepare a range of heterocyclic organic compounds [86]. Metallation of tri-*o*-tolyl phosphite occurs with compound (33) via an elimination of alkene. The resulting halo complex (34) undergoes *o*-metallation of the phosphite by HCl elimination to yield compound (35) [87]. A single crystal structure of a complex $Pt(TP)(TP-H)X$

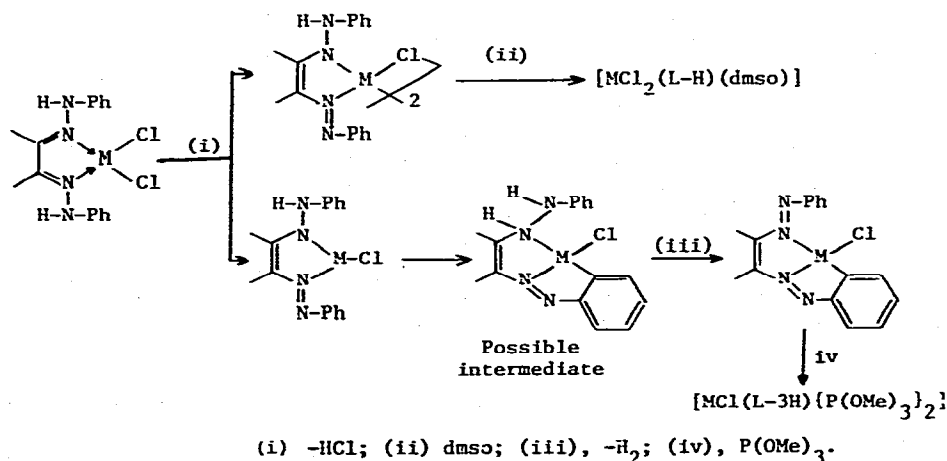


(X = Br, I.; TP = 2-(2'-thienyl)pyridine) shows the platinum coordinated to two pyridyl nitrogens mutually trans to each other, a thienyl carbon, and an iodide [88]. The sulfur atom in the thiophene ring is not coordinated. The ferrocenyl derivative $C_5H_5FeC_5H_4CH_2NMe_2$ reacts with Na_2PdCl_4 and sodium acetate to give the internally metallated binuclear species (36) [89]. The

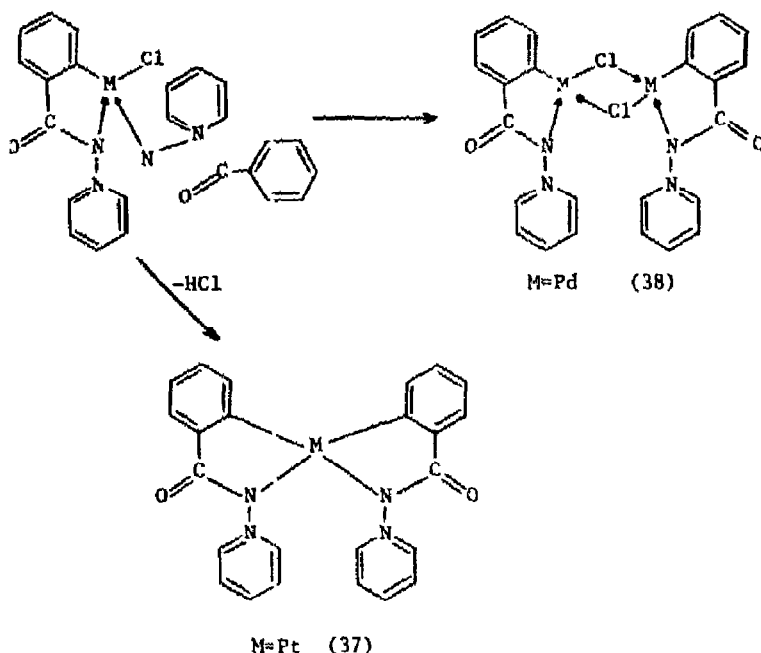


dimer can be cleaved with acac, PMe_2Ph , $AsMe_2Ph$, $P(OMe)_3$, PPh_3 . Compounds di-*o*-(2-azoaryl)Pd(II) can be obtained in good yield by treating

$\text{Pd}_2(\text{dibenzylideneacetone})_3$ with the corresponding mercury compound [90]. A series of σ -metallated compounds have been obtained from Li_2PdCl_4 and dimethyl yellow, 4,4'-azobis(N,N-dimethylaniline), azoxybenzene, and 4,4'-azoxyanisole [91]. The dimer from 4,4'-azoxyanisole can be cleaved by Tlcp. New 6-membered ring compounds have been isolated from the palladation of N-aryl-amidine and amides. These dimers can be cleaved with NaCp, allylMgCl, Tlacac, $\text{LiN}(\text{R}^1)\text{C}(\text{R}^2)=\text{NR}^1$ [92]. A study has been made of the internal metallation reactions of Pd(II) and Pt(II) with osazones. The transformation studied are shown. Anomalous features found for the metallation of osazones are discussed [93]. Treatment of halo complexes of Pd(II) and Pt(II) with ylides $\text{PhCONC}_5\text{H}_5$ gives metallated betaines [94]. The mechanism is considered to involve initial coordination of the ylide



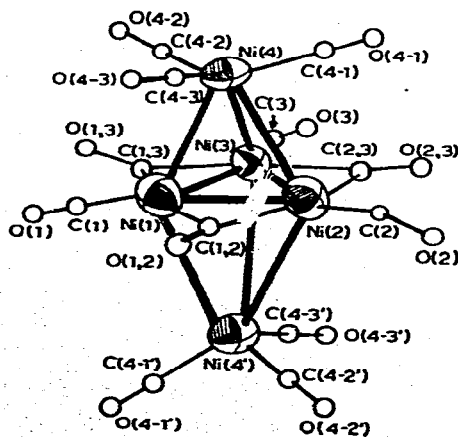
followed by intramolecular electrophilic attack by the metal. Monomers (37) are formed with Pt and dimers (38) are obtained with Pd. Complexes $\text{trans-PdCl}_2\text{L}_2$ [$\text{L} = \text{P}^t\text{Bu}(\text{benzyl})_2$, $\text{P}^t\text{Bu}_2(\text{benzyl})$] only undergo internal metallation with difficulty [95], with the former ligand being the most difficult. Since the analogous compounds $\text{P}^t\text{Bu}_2(\text{o-tolyl})$ and $\text{P}^t\text{Bu}(\text{o-tolyl})_2$ undergo metallation under mild conditions to form an analogous 5-membered ring, steric rather than electronic differences are considered to be responsible for the failure of the former ligands to undergo facile metallation.



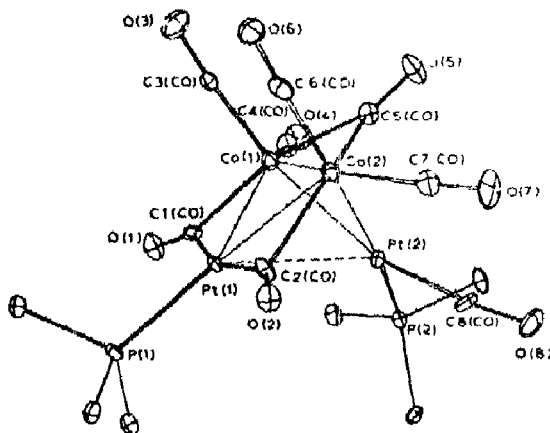
V Metal carbonyls and thiocarbonyls

Compound π -cpM(CO)₃Sb(Me)₂Ni(CO)₃ has been prepared by treating Ni(CO)₄ with π -cpM(CO)₃SbMe₂ (M = Cr, Mo, W) [96]. Infrared and mass spectral data are tabulated. A series of tricarbonyl(organophosphine)nickel(0) compounds have been prepared by substitution reactions on the tetracarbonyl [97]. The phosphines used are P(CMe₃)₃, P(CMe₃)₂EMe₃, P(CMe₃)(EMe₃)₂, P(EMe₃)₃ (E = Si, Ge, Sn). Tabulated infrared data, along with the band assignment given. The ¹³C nmr spectra have been obtained for a series of L_nNi(CO)_{4-n} derivatives (n = 0-3) where L = PR₃, PPh₂Y, PPhY₂, P(OR')₃ and PCl₃ (R = Me, Et, Bu, Ph; R' = Me, Et, Prⁱ, Ph; Y = Cl, Me, OMe, OPh) [98]. The data is tabulated and the ¹³C nmr chemical shifts plotted against the infrared stretching force constant for the carbonyl, and also plotted against Kibachnik's σ . Good correlations are found in each case. Both the sequential replacement of carbonyl by phosphine ligands, and the change of Y in the ligand, has an additive effect on the carbonyl chemical shift. The ¹³C nmr data for chemical shifts of the carbonyl group in platinum carbonyls has been reported [99]. For the series trans-[PtX(CO)₂L₂]BF₄ (X = H, C₆H₄Cl, CH₂Ph, NCS, NO₃, Br, Cl, I; L = PEt₃, PPh₃, AsEt₃), cis-PtCl₂(CO)(AsEt₃)₂, and [Hpy][PtCl₃(CO)] the chemical shifts and coupling constants are reported. The chemical shift decreases with increasing charge on the complex, but shows little sensitivity to the nature of the cis ligands. For ligands X of high trans influence, the values for $J(^{195}\text{Pt}-^{13}\text{C})$ fall in the range of 960-990 Hz, but for ligands of low trans influence, the values range between 1658-1817 Hz. A series of

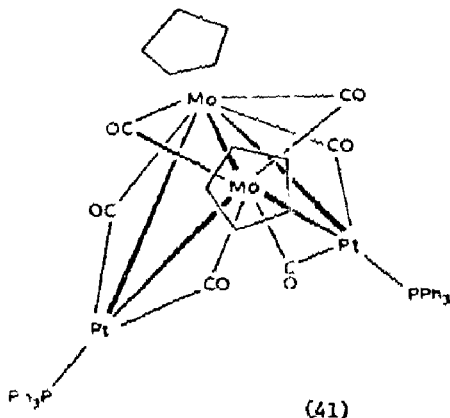
cyanocarbonylpalladium(0) complexes, $R[\text{Pd}(\text{CN})(\text{CO})]$ ($R = \text{PPh}_4, \text{PMePh}_3$), $\text{Ba}[\text{Pd}(\text{CN})(\text{CO})]_2$ have been isolated by treating $\text{K}_2[\text{Pd}(\text{CN})_2]$ with CO in liquid NH_3 and precipitating the complex with the appropriate cation. Values of ν_{CO} in the range 1780–1790 cm^{-1} are found [100]. The structure of the anion in $[\text{NPr}_4^{\text{n}}]_2[\text{Pt}_2\text{Cl}_2(\text{CO})_2]$ consists of two slightly distorted square planar $[\text{PtCl}_2(\text{CO})]^-$ entities linked by an unbridged Pt-Pt bond, giving a dihedral angle of 60° [101]. The carbonyl groups occupy the transoid sites on the adjacent metal atoms. The Pt-Pt distance of 2.584(2) Å has a strong trans influence on the Pt-Cl bond lengths. A study of the chemistry of hydrazine derivatives of platinum has been made, and a number of species are suggested to arise from the carbonylation reactions [102]. The following are proposed to be formed in the carbonylation of $[\text{PtN}_2\text{H}(\text{PPh}_3)_2]_2[\text{BF}_4]_2$: $[\text{PtN}_2\text{H}(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$, $[\text{PtH}(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$, $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$, $\text{Pt}_3(\text{CO})_3(\text{PPh}_3)_4$. Infrared and Raman spectra for compounds trans- PtCl_2XY ($X = \text{C}_2\text{H}_4, \text{CO}$; $Y = \text{-R-py}$; $R = \text{NH}_2, \text{Me}, \text{Et}, \text{CH}_2\text{OH}, \text{H}, \text{Cl}, \text{Br}, \text{CO}_2\text{Et}, \text{CO}_2\text{H}, \text{COMe}, \text{CN}$) have been studied [103]. Variation of R has little effect on $\nu(\text{C}=\text{C})$, and only a small influence on $\nu(\text{C}=\text{O})$. The values of $\nu(\text{C}=\text{O})$ for a series of complexes $\text{PdCl}_2(\text{CO})\text{L}$ ($\text{L} = \text{thiolan}, \text{Pr}_2\text{S}, (\text{PhCH}_2)_2\text{SO}, \text{Et}_2\text{SO}, \text{Me}_2\text{SO}, \text{Me}_2\text{S}, \text{Et}_2\text{S}$) have been reported [104]. Correlations with $\nu(\text{Pd}-\text{C})$ and values of $\nu(\text{S}=\text{O})$ are discussed. A trigonal bipyramidal metal cluster $[\text{Ni}_5(\text{CO})_9(\mu_2-\text{CO})_3]^{2-}$ (39) has been investigated by X-ray crystallography [105]. The structure (39) can be described as a trigonal cluster of transition metal atoms in which a planar $\text{Ni}_3(\text{CO})_3(\mu_2-\text{CO})_3$ fragment is symmetrically capped by Ni-Ni interactions to two identical apical $\text{Ni}(\text{CO})_3$ groups. New cluster compounds $(\text{CO})_5\text{Co}_2(\text{CO})_2\text{Pt}_2(\text{CO})(\text{PPh}_3)_2$ (40), $(\pi\text{-cp})_2(\text{CO})_2\text{Mo}_2(\text{CO})_4\text{Pt}_2(\text{PPh}_3)_2$ (41), and $\text{Pt}_3(\text{CO})_2(\text{PPh}_3)_4$ (42) have been obtained by treating $\text{PtCl}_2(\text{PPh}_3)_2$ with $\text{Na}[\text{Co}(\text{CO})_4]$ or



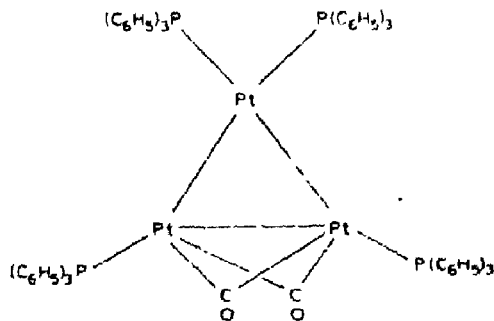
$\text{Ni}[(\pi\text{-cp})\text{Mo}(\text{CO})_3]$. The structures are based on infrared spectroscopy, with substantiating preliminary X-ray results for (40) and (41) [106]. The X-ray structure of compound (40) has also been published separately [107]. The reactivity of cationic thiocarbonyls of platinum to nucleo-



(40)

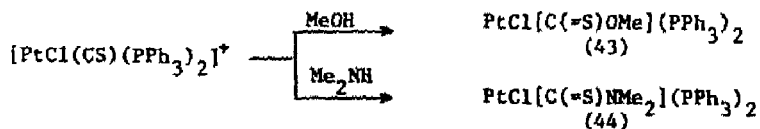


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(42)

philes has been used to prepare compounds (43) and (44). When a solution

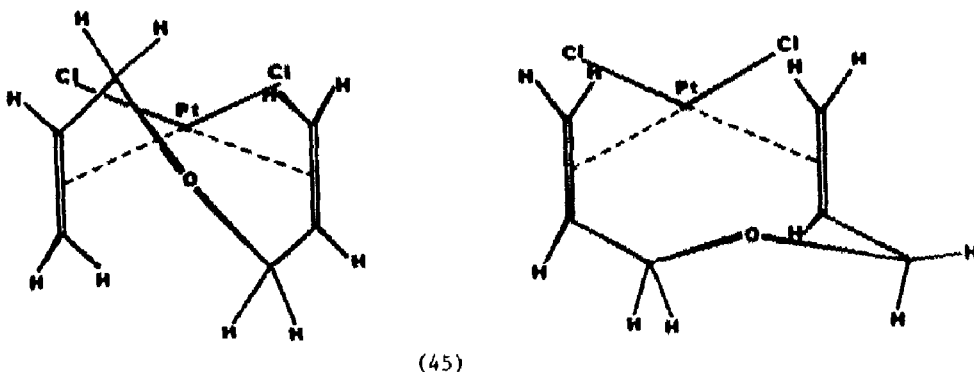
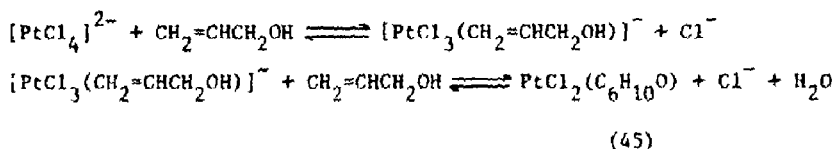


of $[\text{PtCl}(\text{CS})(\text{PPh}_3)_2]\text{BF}_4$ in CH_2Cl_2 -hexane is allowed to stand in air at 25°

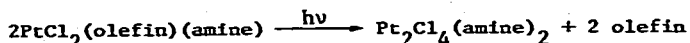
for 1-2 days, the compound $[\text{PtCl}(\text{PPh}_3)_2(\text{CS}_2)\text{Pt}(\text{PPh}_3)_2]\text{BF}_4$ precipitates. An X-ray study shows the compound to be a metallodithiocarboxylate complex [108].

VI. Metal olefins

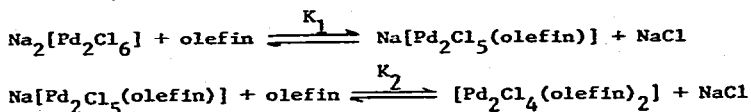
Treatment of K_2PtCl_4 with 2-propenol, 2-butenol, and 3-buten-2-ol yields initially the complex $[\text{PtCl}_3(\text{olefin})]^-$, followed by a rearrangement to *cis*- $\text{PtCl}_2(\text{diolefin})$ [109]. The resulting olefinic ether complex (45) is considered to arise from the series of reactions:



Compounds $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{N-N})$ have been prepared by reaction of Zeise's salt with a series of chelating nitrogen ligands. These pentacoordinate compounds lose ethylene [110]. Zeise's salt reacts with $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ to yield compounds $\text{K}[\text{PtCl}_3(\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2)]$ and $[\text{PtCl}_2(\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2)]_2$ [111]. A report has been published that C_2H_4 reacts with PtCl_2 to give $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, which converts to $\text{H}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ with HCl [112]. Halo-olefin Pt(II) compounds have been obtained from $[\text{PtCl}_4]^{2-}$ and EtOH [113]. Alkylallyl ethers undergo ether abstraction to form π -olefin complexes $[\text{C}_n\text{H}_{2n}\text{PdCl}_2]_2$ and π -complexes $[\text{C}_n\text{H}_{2n-1}\text{PdCl}]_2$ with PdCl_2 [114]. Two diastereomers form on complexation of the chiral olefin to Pt(II) in *trans*- $\text{PtCl}_2(\text{py})[\text{R}(\text{Me})^*\text{CH}=\text{CH}=\text{CH}_2]$ [115]. The proportion of each diastereomer in solution is dependent on the bulkiness of the R group; the configurational assignments were made using ^1H nmr and CD spectroscopy. Polarography and thermodynamic stability of *cis*- $[\text{PtCl}(\text{C}_2\text{H}_4)(\text{NH}_3)_2]^+$ has been studied. Photochemical elimination of olefin from $\text{PtCl}_2(\text{olefin})(\text{amine})$ is facilitated



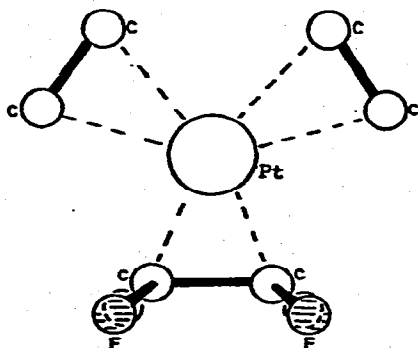
by increasing the substitution on the olefin [117]. Compounds cis- $\text{PtCl}_2(\text{C}_2\text{H}_4)\text{L}$ (L = py, *p*-anisidine, PPh_3 , PEt_3) have been obtained by cleavage of the resulting dimers by ethylene. Replacement of trans-butene-2 in trans(N,olefin)-chloro-L-prolinato-trans-butene-2 platinum(II) shows a second order rate constant with $\Delta H^\ddagger = 10 \text{ K cal mol}^{-1}$ and $\Delta S^\ddagger = -25$ to $-46 \text{ cal mol}^{-1} \text{ K}^{-1}$ [118]. The steric interaction between the olefin nucleophile and the coordinated ligands is a very important factor in determining ease of substitution. Stability constants K_1 and K_2 below have



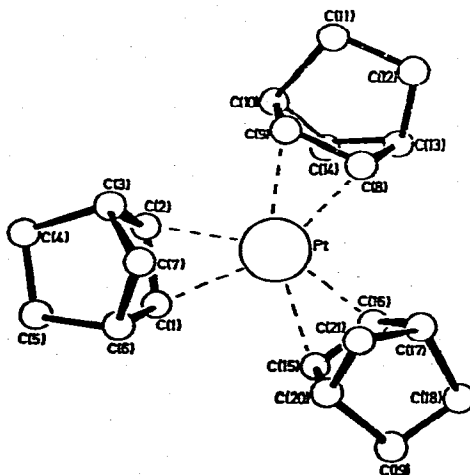
been measured in acetic acid, and are found to be independent of chain length of hydrocarbon (C_5 - C_9) [119]. A similar study with $\text{Pd}(\text{OAc})_2$ has found that again only two complexes are found, $\text{Na}[\text{Pd}_2(\text{OAc})_5(\text{olefin})]$ and $\text{Na}[\text{Pd}(\text{OAc})_3(\text{olefin})]$. These authors find the data inconsistent with the formation of $\text{Pd}_2(\text{OAc})_4(\text{olefin})_2$ [120]. The rate of exchange of vinyl propionate with acetic acid solvent to give vinyl acetate is catalyzed by $\text{Pd}(\text{OAc})_2$ and reaches a maximum when $[\text{NaOAc}]$ is 0.2 M. Rate laws are discussed, and acetoxypalladium is considered to be nonstereospecific [121]. A kinetic study is reported of the catalysis by $\text{PdCl}_2(\text{PhCN})_2$ of the oxidation of octene-1 by *p*-benzoquinone [122]. ^1H nmr data on complexes $\text{PtCl}_2(\text{C}_2\text{H}_4)\text{L}$ (L = substituted pyridine) has been presented and used to demonstrate halogen, olefin and/or L exchange [123]. Irradiation of trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)$ (isoquinoline) with UV light causes isomerization to its cis isomer [124]. Ring opening of a haloalkylpalladium(II) complex by HCl has been used to synthesize a haloalkylfuran compound [125]. Complexes $\text{Pt}_2\text{Cl}_4(\text{alkene})_2$ (alkene = 3,3-dimethylbutene-1, 3,3-dimethylpentene-1, 3,3-dimethylhexene-1) have been prepared and the ^1H nmr of these asymmetric compounds discussed [126]. Alkene exchange is preceded by dissociation of monomers. Electronic absorption spectra of trans- PtCl_2XY (X = C_2H_4 , CO; Y = 4-R-py) show two UV bands which are sensitive to R [127]. One band is a ligand $\pi\text{-}\pi^*$ transition, and the second is a CT transition between Pt and py. ^{13}C nmr spectra are reported for compounds $\text{Ni}[\text{P}(\text{O}-\text{o-tol})_3]_2(\text{olefin})$ (olefin = C_2H_4 , acrylonitrile, fumaronitrile, methyl acrylate, dimethyl maleate, maleic anhydride) [128]. A rough correlation between $\delta(\text{C})$, τ and other measures of back-bonding such as $\nu(\text{C-C})$ and $d(\text{C-C})$ exists, although exceptions were noted. Values of $^1\text{J}(\text{C-H})$ of ethylene complexes are all near to 160 Hz. A detailed spectroscopic study of Zeise's salt again identifies the CC stretching ($\nu_{\text{C-C}}$) mode of coordinated ethylene at

1243 cm^{-1} . The local electronic state of coordinated ethylene is regarded as the core of a doubly excited radical anion of the free species, or as a near-radical-cation [129]. Correlation of ^1H , ^{13}C nmr, vibrational spectra, and extended Hückel treatment, leads to the conclusion that the coordination bonding of ethylene to Pt(II) is dominated by the σ donation from ethylene to platinum, and the bond strength between C_2H_4 and Pt(II) increases with decreasing trans influence of L, the trans ligand [130]. Calculation of approximate force-fields for ethylene-Pt bonding show that many of the normal modes are derived from more than one type of internal coordinate, and hence vibrational wavenumbers are of limited application to discussions of bonding [131]. The compound $\text{Ni}(\text{acrylonitrile})_2$ has been used to prepare a number of organic compounds resulting from trapping a reactive intermediate from a catalyzed ring opening of quadricyclane. The species was trapped by electron poor olefins [132]. Complexes of triphenylphosphine stabilized Ni(0) with aldehydes and ketones as π -acceptor ligands have been reported [133].

Crystal structure data has been reported for $\text{Pt}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)_2$ (46) and $\text{Pt}(\text{C}_7\text{H}_{10})_3$ (47) (C_7H_{10} = bicyclo[2.2.1]heptene) [134]. In addition to the preparative procedures for these compounds, the authors also report the isolation of $\text{Pd}(\text{C}_7\text{H}_{10})_3$, $\text{Pd}(1,5\text{-COD})_2$, $\text{Pd}(\text{C}_2\text{H}_4)_3$ or 4, $\text{M}(\text{C}_2\text{H}_4)_2\text{L}$ ($\text{M} = \text{Pd}$, $\text{L} = \text{PCy}_3$; $\text{M} = \text{Pt}$, $\text{L} = \text{PMe}_3$, PCy_3). The crystal structure of $\text{Pt}(\Delta^{1,4}\text{-bicyclo[2.2.0]hexene})(\text{PPh}_3)_2$ (48) shows a long distance for the

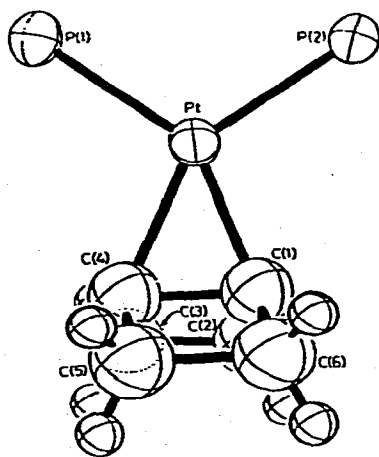


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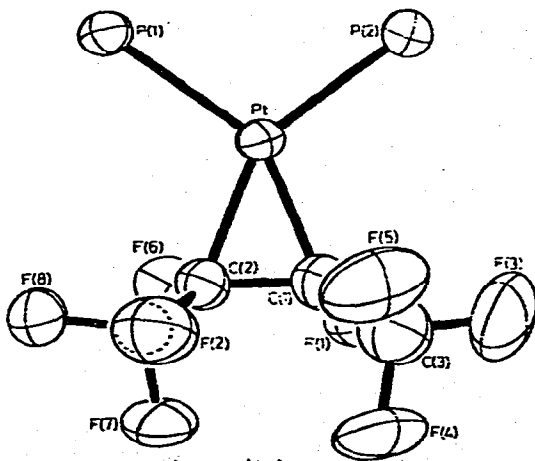
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CC bond of the coordinated olefin (1.52 Å), and a dihedral angle of 3.2° between the PtP₂ and PtC₂ planes [135]. The crystal structure of a complex



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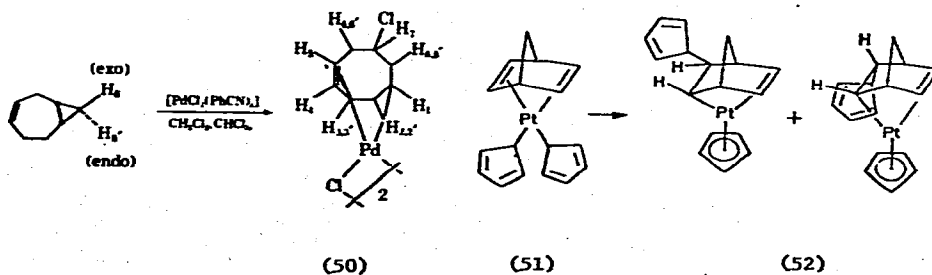
Pt(C₄F₈)(PPh₃)₂ (C₄F₈ = Octafluoro-trans-butene-2) (49), previously reported by this author, shows unusually long C-F bonds [136]. The dihedral angle between the PtP₂ and PtC₂ planes is 10.8°, and considerations of bonding

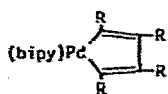


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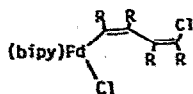
leads the authors to question whether the Dewar-Chatt-Duncanson model is appropriate. The structure of $\text{Pt}(\text{C}_2\text{F}_4)(\text{AsPh}_3)_2$ shows a distance of 1.45 Å for CC [137]. A neutron diffraction study of Zeise's salt show the hydrogens of ethylene bent away from the Pt atom [138]. The lengthening of the C-C bond is less than in metal complexes of C_2F_4 and $\text{C}_2(\text{CN})_4$.

A series of complexes $\text{Ni}(\text{TCNE})(\text{CNR})_3$ have been reported where the magnetic equivalence of the isocyanides is considered to be likely due to a free rotation of TCNE, rather than to a dissociative exchange mechanism [139]. Compounds $\text{Pd}(1,5\text{-COD})_2$ and $\text{Pt}(\text{bicyclo}[2.2.1]\text{heptene})_3$ have been obtained on the gram scale by treating the olefins with Pd atoms at low temperature [140]. A report has appeared of the failure to repeat the published rearrangement of 4-vinylcyclohexene to 1,5-cyclooctadiene with $\text{PdCl}_2(\text{PhCN})_2$ [141]. The product is identified as the π,π -complex of 4-vinylcyclohexene. Rearrangements of cis, cis-1,3-; cis, trans-1,3-; and 1,4-cyclooctadienes has been found to be solvent dependent [142]. The synthesis of compounds $[\text{MCl}_2(\text{diene})]_n$ ($\text{M} = \text{Pd}, \text{Pt}$, diene = cis, cis-cyclonona-1,5-diene) is reported [143]. Unusual compounds result from treating $\text{Ni}(1,5\text{-COD})_2$ or $\text{Ni}(\text{trans,trans,trans-1,5,9-cyclododecatriene})(\text{CDT})$ with lithium in the presence of N,N',N',N'-tetramethylethylenediamine [144]. The stoichiometry of the product from the latter reaction corresponds to $[(\text{CDT})\text{Ni}(\text{Li}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2))]_2$. Possible structures are presented. The compound di- μ -chloro-(1.4.5- η -7-chlorocyclooctenyl) dipalladium (50) has been prepared by treating $\text{PdCl}_2(\text{PhCN})_2$ with cis-bicyclo[5.1.0]oct-3-ene [145]. Complex (50) slowly rearranges to a π -allylic compound. The complex $\text{Pt}(\sigma\text{-cp})_2(\text{C}_7\text{H}_8)$ (51) is reported. The $\sigma\text{-cp}$ rings are fluxional with a low activation energy, and in solution the complex rearranges slowly to a further $\sigma\text{-}\pi$ one (52) having a $\pi\text{-cp}$ ring coordinated to platinum and a further cyclopentadienyl group attached to the dienyl ligand [146]. Compounds (53) (54) and (55) have been prepared by treating the palladiacyclopentadiene compound $\text{Pd}(\text{C}_4\text{R}_4)(\text{bipy})$ ($\text{R} =$

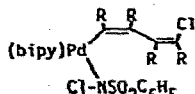




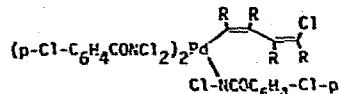
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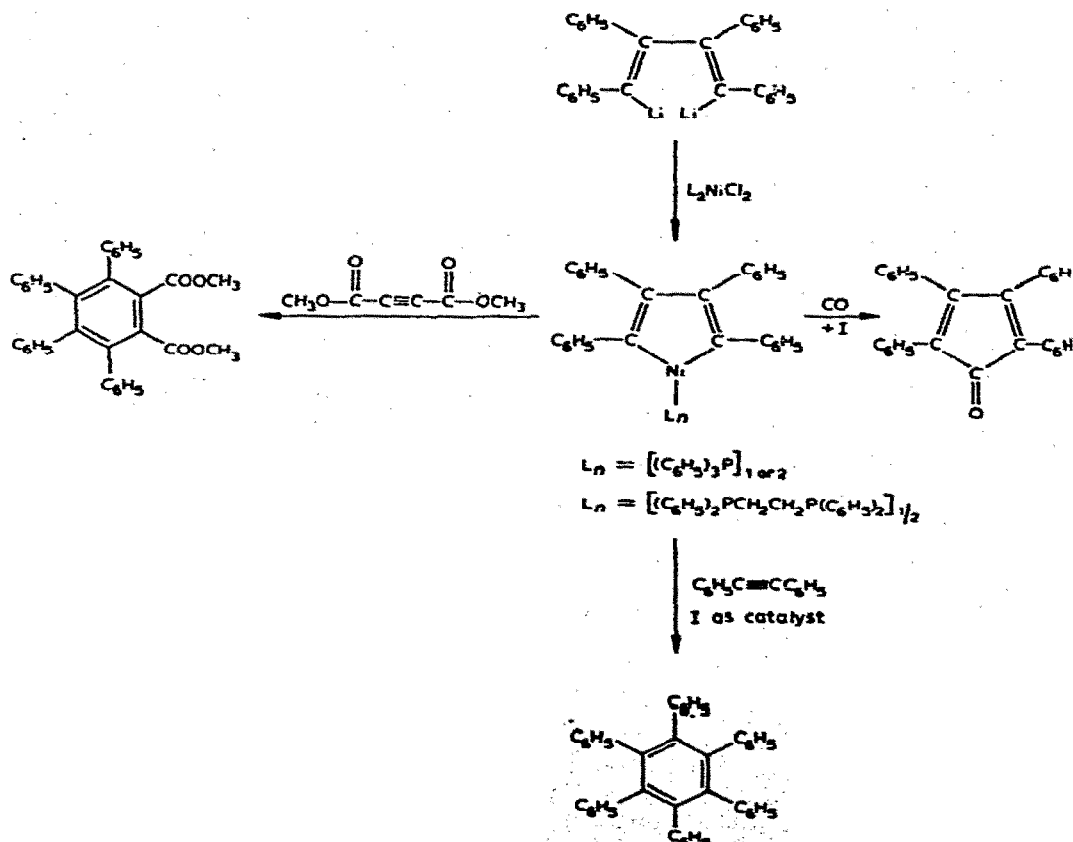
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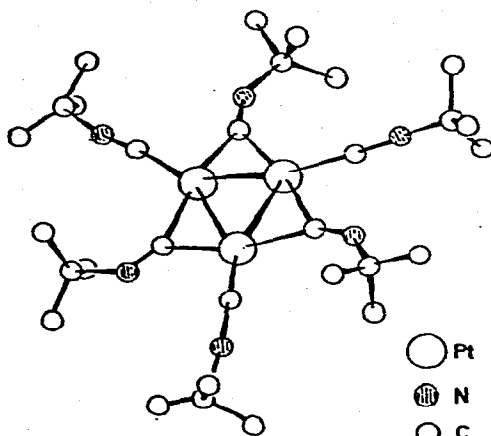
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with the appropriate *N,N*-dichloroamine and amide [147]. A nickelole complex (56) has been prepared from $\text{NiCl}_2(\text{PPh}_3)_2$ and the dilithio derivative [148]. The compound gives a substituted benzene when treated with dimethyl acetylenedicarboxylate or diphenylacetylene, and tetraphenylcyclopentadienone on treatment with CO. Reaction of $\text{C}_6(\text{CF}_3)_6$ with triangulo- $\text{Pt}_3(\text{Bu}^t\text{NC})_6$ or $\text{Pt}(\text{PhCH}=\text{CHPh})(\text{PMe}_3)_2$ gives the metallocyclohepta-cis,cis,cis-trienes $\text{Pt}(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3))\text{L}_2$. The

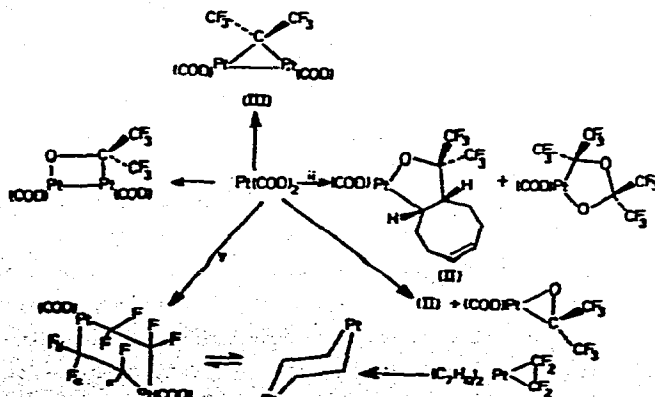


complex with $L = \text{Bu}^t\text{NC}$ has been structurally investigated by X-ray crystallography [149]. Treatment of $\text{Pt}(1,5\text{-COD})_2$ with Bu^tNC yields $\text{Pt}_3(\text{Bu}^t\text{NC})_6$ (57) [150], and with PCy_3 or C_2H_4 , $\text{Pt}(\text{PCy}_3)_2$ and $\text{Pt}(\text{C}_2\text{H}_4)_3$ respectively. In similar work with $\text{Pt}(0)$ compounds, treating $\text{Pt}(\text{PCy}_3)_2$

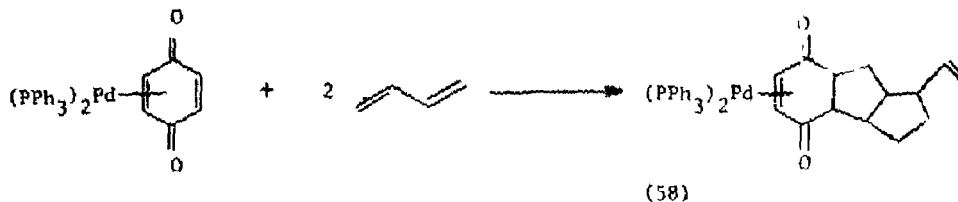


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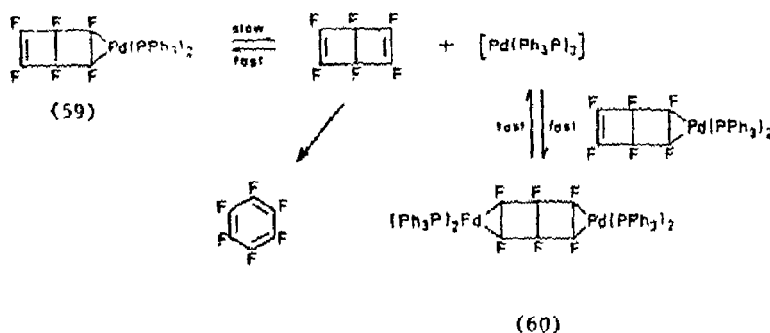
with H_2 the compound $\text{PtH}_2(\text{PCy}_3)_2$ is obtained. A series of compounds are formed when $\text{Pt}(\text{COD})_2$ is treated with hexafluoroacetone and tetrafluoroethylene [151]. The molecular structure of $\text{Pt}_2\{\text{C}(\text{CF}_3)_2\text{O}\}(\text{COD})_2$ shows two platinum atoms, 2.585 Å apart, with one bonded to the carbon atom of hexafluoroacetone, Pt-C 2.08 Å, and one bonded to the oxygen atom, Pt-O = 1.96 Å. When $\text{Pd}(\text{p-benzoquinone})(\text{PPh}_3)_2$ is treated with two moles of



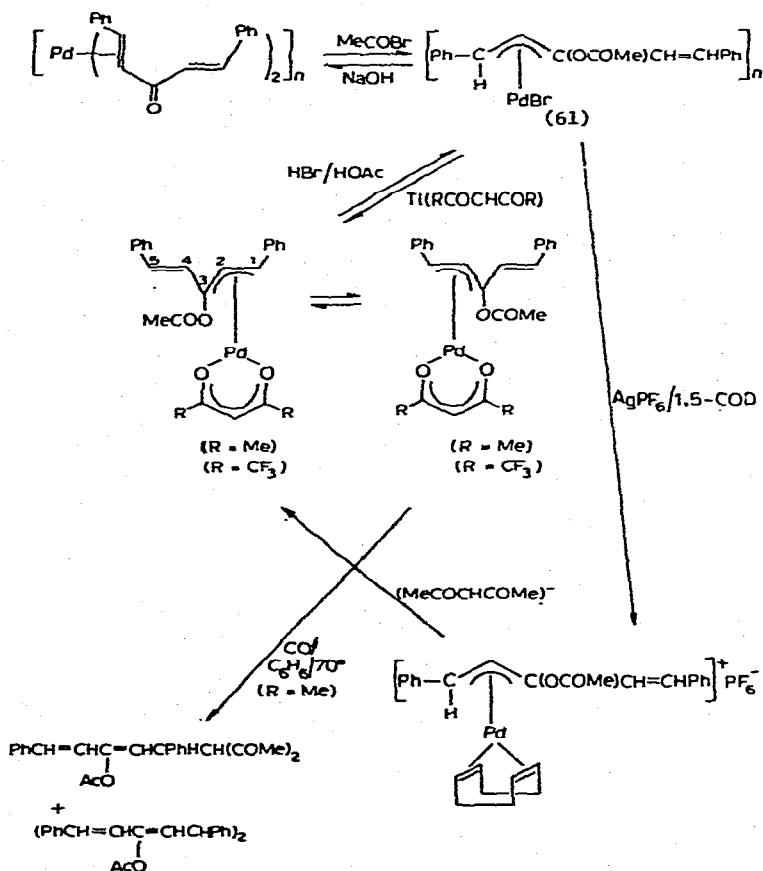
butadiene a new compound (58) is obtained [152]. For complexes $\text{Pd}(\text{p-benzoquinone})\text{L}_2$ [$\text{L} = \text{PBU}^n_3$, $\text{P}(\text{OC}_6\text{H}_4\text{Me-p})_3$, PPh_3 , $\text{P}(\text{C}_6\text{H}_4\text{Cl-p})_3$, $\text{P}(\text{OPh})_3$] the ^1H chemical shifts and $\nu(\text{C}=\text{O})$ of the benzoquinone correlate with the



basicity of the phosphorus ligand [153]. The structure of a duroquinone-like complex: dicarbonyl(1,4-difluoro-2,3,5,6-tetramethyl-1,4-dihoracyclohexa-1,5-dienyl)nickel(0), has been solved [154]. When $\text{M}(\text{PPh}_3)_4$ ($\text{M} = \text{Pd}, \text{Pt}$) is treated with hexafluorobicyclo[2.2.0]hex-2,5-diene, both monomer (59) and dimer (60) complexes of these metals are obtained [155]. The ^{19}F nmr spectra of these compounds are presented and discussed. Complexes $\text{Pt}(\text{un})(\text{PPh}_3)_2$ (un = methylenecyclopropane, trans-2,3-dimethoxy-



carbonylmethylenecyclopropane, cis-2,3-dimethoxycarbonylmethylenecyclopropane) and trans- $[\text{PtCl}_2(\text{un})\text{py}]$ (un = cis or trans-2,3-dimethoxycarbonylmethylenecyclopropane) have been prepared. The η^2 -bonded methylenecyclopropane ligands are inert toward heat and UV radiation [156]. Comprehensive ^1H and ^{13}C nmr data is given. Crystal structures of 1,2-dimethyl- and 3-methyl-cyclopropenebis(triphenylphosphine) $\text{Pt}(0)$ show the cyclopropene ring remains intact upon coordination, with a C-C distance of 1.50 Å between the coordinated carbon atoms of the ring [157]. Hydroxy-palladation of 1,5-cyclooctadiene gives a trans product, indicating that oxypalladation proceeds exclusively with attack by the nucleophile (water) from outside the coordination sphere of palladium [158]. Kinetics of methanolysis on a C=C bond of $\text{PdCl}_2(\text{norbornadiene})$ shows a complicated mechanism [159]. Acetyl bromide reacts with $\text{Pd}(\text{dba})_n$ to yield an insoluble

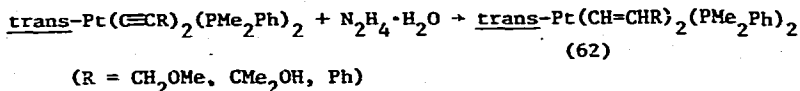


polymer (61) which can be cleaved to prepare the fluxional *S*-diketonates [160]. Enthalpy measurements show relative Pt-olefin bond strengths: $\text{trans-1,2-Ph}_2\text{C}_2\text{H}_2 > \text{cis-1,2-Ph}_2\text{C}_2\text{H}_2 > \text{PhHC}_2\text{H}_2$ [161].

VII. Metal acetylenes

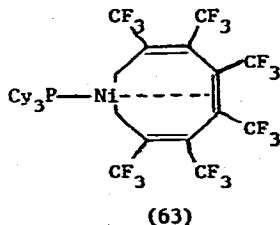
Complexes $\text{Pt}(\text{ArC}\equiv\text{CAr}')(\text{PPh}_3)_2$ ($\text{Ar} = \text{Ar}' = \text{Ph}$, $\text{Ar} = \text{Ph}$, $\text{Ar}' = 2\text{-py}$; $\text{Ar} = \text{Ar}' = 2\text{-py}$; $\text{Ar} = \text{Ar}' = 2\text{-(6-Me-py)}$), with the acetylenic triple bond coordinated to Pt, have been prepared [162]. A second metal e.g. Co, Pd will coordinate to the compounds through the chelating pyridyl nitrogens. The X-ray structure of $(\text{PPh}_3)_2\text{Pt}[\text{C}_2(2\text{-py})_2](\text{CoCl}_2)$ has been solved showing a tetrahedral coordination about Co(II). Complexes $\text{trans-Pt}[\text{C}\equiv\text{CR}_1\text{R}_2(\text{OR})_3]_2$ (PMe_2Ph)₂ ($\text{R}_1 = \text{R}_2 = \text{H}$, Me: $\text{CR}_1\text{R}_2 = \text{cyclohexylidene}$; $\text{R}_3 = \text{H}$, Me, Ph), $\text{trans-Pt}(\text{C}\equiv\text{CCH}_2\text{CH}_2\text{OH})_2(\text{PMe}_2\text{Ph})_2$, $\text{trans-Pt}(\text{p-tolylacetylidene})_2(\text{PMe}_2\text{Ph})_2$, $\text{trans-PtX}(\text{p-tolylacetylidene})(\text{PMe}_2\text{Ph})_2$ have been prepared using the sodium-

tertiary hydroxy compounds dehydrate to ene-yne compounds with $\text{Ac}_2\text{O}/\text{pyridine}$. Analogous compounds with primary hydroxyl groups do not dehydrate but give acetates. ^{13}C nmr data is given, and the use of $\text{Eu}(\text{fod})_3$ is discussed to analyze the ^1H nmr spectrum of $\text{trans-Pt}(\text{C}\equiv\text{CCH}_2\text{CH}_2\text{OH})_2(\text{PMe}_2\text{Ph})_2$. Subsequently these workers found that these acetylides could be reduced by hydrazine hydrate to dialkylplatinum(II) compounds (62) [164]. Reactions with HCl and details of the ^1H , ^{13}C , ^{31}P nmr spectra are discussed.



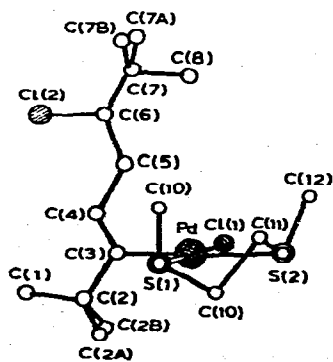
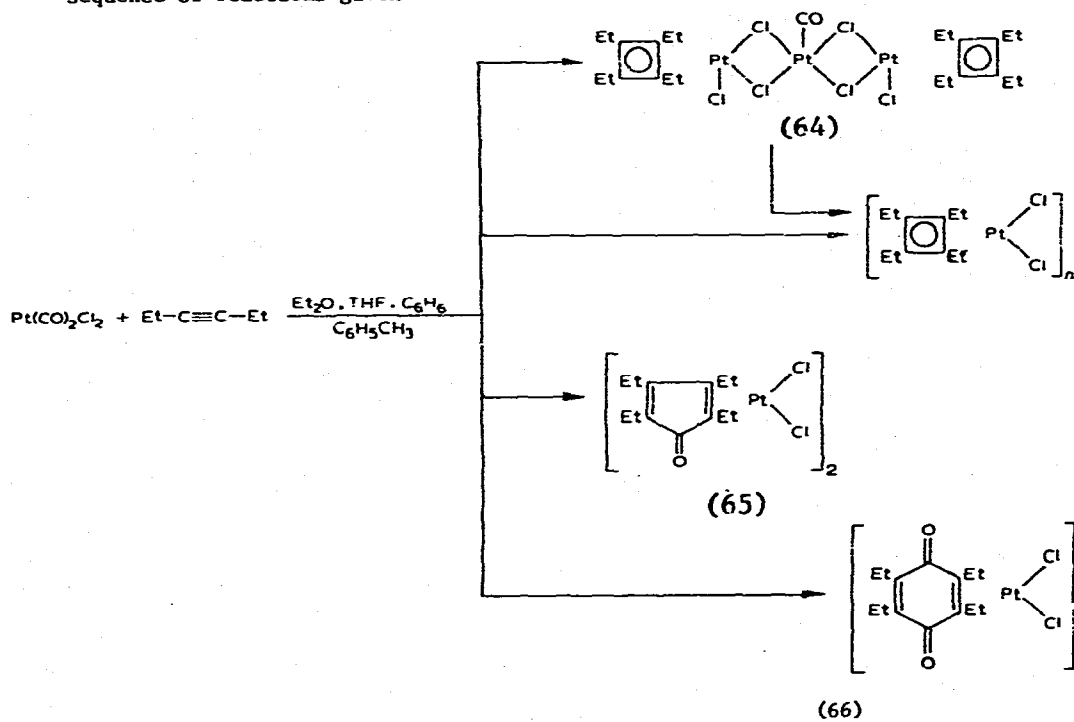
Oxidative addition of $\text{RC}\equiv\text{CH}$ (R = Ph, Bu, Me_3C , $\text{CH}_2=\text{CMe}$) to $\text{Pd}(\text{PPh}_3)_4$ gives compounds $\text{PdH}(\text{C}\equiv\text{CR})(\text{PPh}_3)_2$ in 55-90% yield [165]. Alkali metal acetylides in liquid ammonia or methylamine react with $\text{cis-PtCl}_2(\text{DPE})$ to give monomers $\text{cis-Pt}(\text{C}\equiv\text{CR})_2(\text{DPE})$ where R = H, Me, Ph [166]. Use of excess acetylide leads to polymers $[\text{K}_2\text{Pt}(\text{C}\equiv\text{CR})_4(\text{DPE})]_n$. Use of the dianion from α -diethynylbenzene yields $\text{cis-}[\text{Pt}(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4(\text{DPE})]_n$. Compounds $\text{trans-Pd}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})_2(\text{PBu}_3)_2$ give polymer on treatment with $\text{CuCl}-\text{O}_2$ [167].

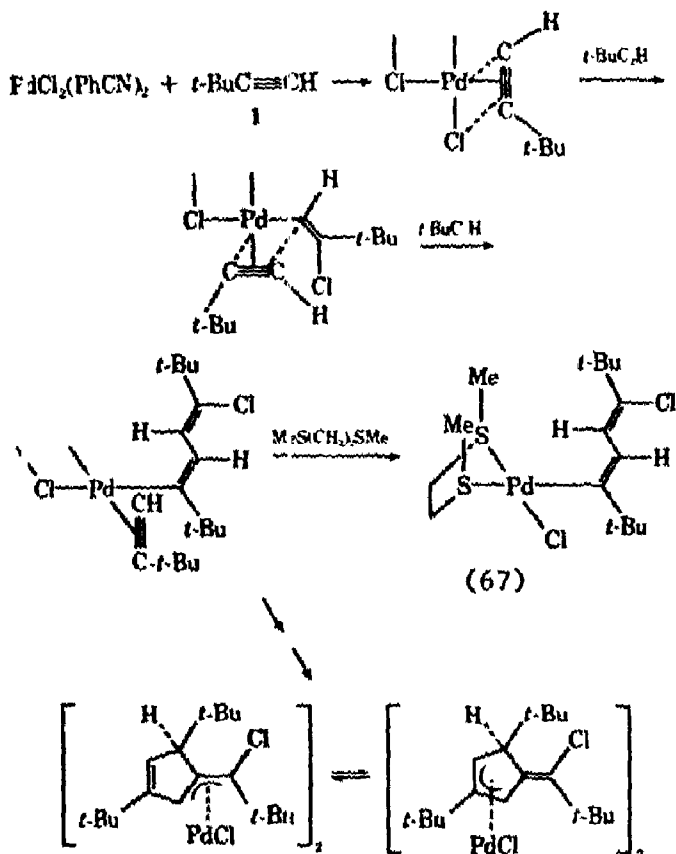
A number of articles have appeared describing cyclization reactions of acetylenes. A complex $\text{Ni}(\text{CF}_3\text{C}\equiv\text{CCF}_3)_3\text{PCy}_3$ (63) results from treating $\text{trans-}[\text{NiH}(\text{PCy}_3)_2\text{L}]\text{BF}_4$ (L = Me-py, MeCN) with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ [168]. A cyclic ring structure is proposed. Twelve and fourteen-membered ring organic compounds



have been prepared from α,ω -dodecatrienediynickel and dimethyl acetylenedicarboxylate [169]. Complexation of $\text{Me}_3\text{CC}\equiv\text{CCMe}_2\text{OH}$ with $\text{PdCl}_2(\text{PPh}_3)_2$ gives a π -olefin complex which cyclizes to give a further complex with a furan ring π -bonded to palladium(II) [170]. In a study of the products arising from $\text{Me}_3\text{CC}\equiv\text{CH}$ and SiF_2 , further cycloaddition occurs in the presence of $\text{Ni}(\text{CO})_4$; an oxidative addition of the Si-Si bond to Ni(0) is proposed [171]. Treating $\text{PtCl}_2(\text{CO})_2$ with hexyne-3 leads to complexes of substituted cyclobutadienes (64), cyclopentenones (65), and cyclohexenediones (66) [172]. Spectral data is presented, but the authors refrain

of $\text{Bu}^t\text{C}\equiv\text{CH}$, the first step occurs with *cis*-chloropalladation of the acetylene [173]. The structure of compound (67) has been solved and a sequence of reactions given.

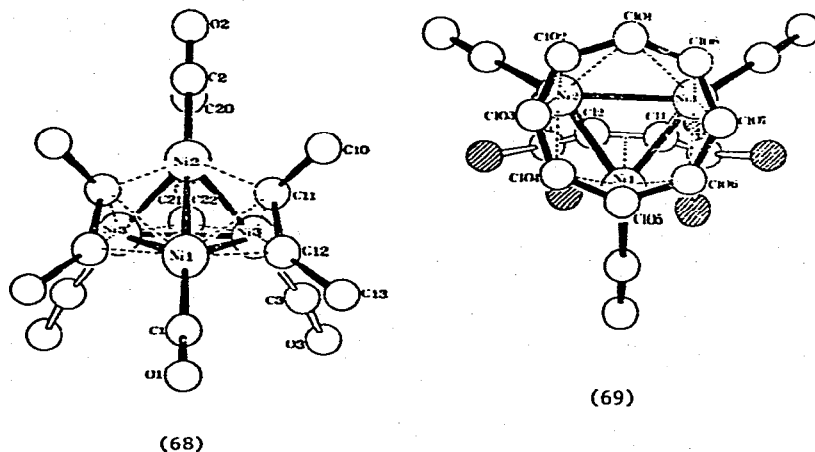




A number of other crystal structures of alkyne complexes have been reported. The complex $\text{Pt}(\text{MeC}\equiv\text{CPh})(\text{PPh}_3)_2$ shows an expected deviation of 10° from linearity for the coordinated acetylene. The carbon-carbon bond length of the coordinated acetylene is 1.277(25) Å [174]. These authors also report the structure of $\text{PtMe}(\text{Et}_2\text{B}(\text{pz})_2)(\text{MeC}\equiv\text{CPh})$ [175]. Assuming a single coordination position of the acetylene the platinum coordination geometry is square planar. The acetylene substituents are cis-bent away from the acetylene; $1.7(1.0)^\circ$ for the Me and $21.2(9)^\circ$ for the phenyl. The carbon-carbon triple bond length is 1.227(10) Å. The structures of $\text{Pt}(\text{C}_6\text{H}_8)(\text{PPh}_3)_2$ and $\text{Pt}(\text{C}_7\text{H}_{10})(\text{PPh}_3)_2$ ($\text{C}_6\text{H}_8 = \text{cyclohexyne}$; $\text{C}_7\text{H}_{10} = \text{cycloheptyne}$) show dihedral angles of $4.4(3)^\circ$ and $7.9(3)^\circ$, acetylenic carbon-carbon distances 1.297(8) Å and 1.283(5) Å respectively [176]. The crystal structures of $\text{Ni}_4(\text{CO})_4(\text{CF}_3\text{C}_2\text{CF}_3)_3$ (68) and $\text{Ni}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)(\text{C}_8\text{H}_8)$ (69) show the compounds to be clusters [177]. The cyclooctatetraene ring in (6) is unusual in being planar.

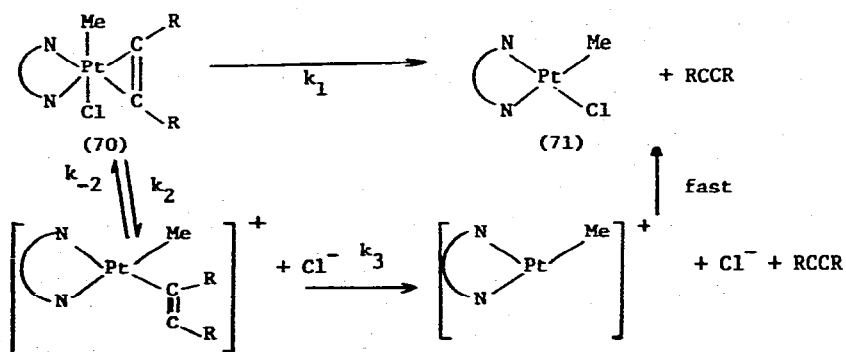
Energetics of reactions involving acetylenes and compounds of this triad have attracted some attention. A mechanism has been presented for

the decomposition of $\text{PtClMe}(\text{bipy})(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})$ (70) to $\text{PtClMe}(\text{bipy})$ (71) with loss of $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ [178]. The rate is first order but strongly



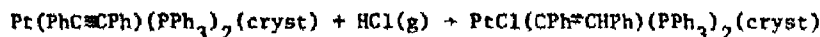
solvent dependent. The data is rationalized in the following scheme for which $k_1 = 0.0122 \text{ min}^{-1}$, $k_2 = 0.179 \text{ min}^{-1}$ and $k_{-2}/k_3 = 1.65 \times 10^4 \text{ l mol}^{-1}$. The enthalpy ΔH_{298} of the reaction of PhC_2Ph with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ is

SCHEME (NN = 2,2'-bipyridyl, R = CO_2Me)

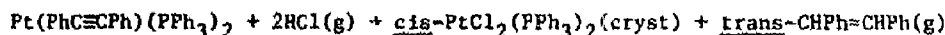


$-82 \pm 2 \text{ kJ mol}^{-1}$ [179]. Ethylene is gas phase and other reagents crystalline. The enthalpies of reactions between HCl and $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$

have been measured, and used to set up a table of bond dissociation energies Pt-X (X = Cl, PhC≡CPh, C(Ph)=CHPh, Ph) [180]. In mass spectrometry complexes Ni₂Cp₂(RC₂R') decompose by loss of alkyne, loss of



$$\Delta H = -90.2 \pm 6 \text{ kJ mol}^{-1}$$

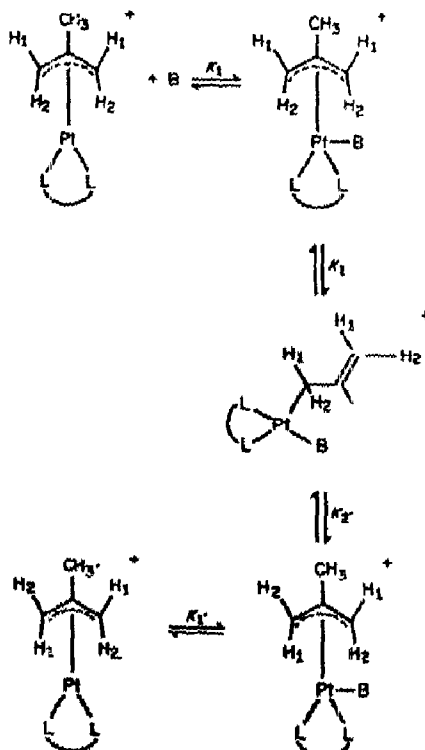


$$\Delta H = -139.0 \pm 16 \text{ kJ mol}^{-1}$$

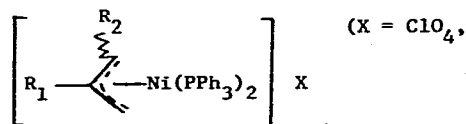
cyclopentadiene, loss of cpNi fragment, or fragmentation of R groups [181].

V II. Metal Allyls

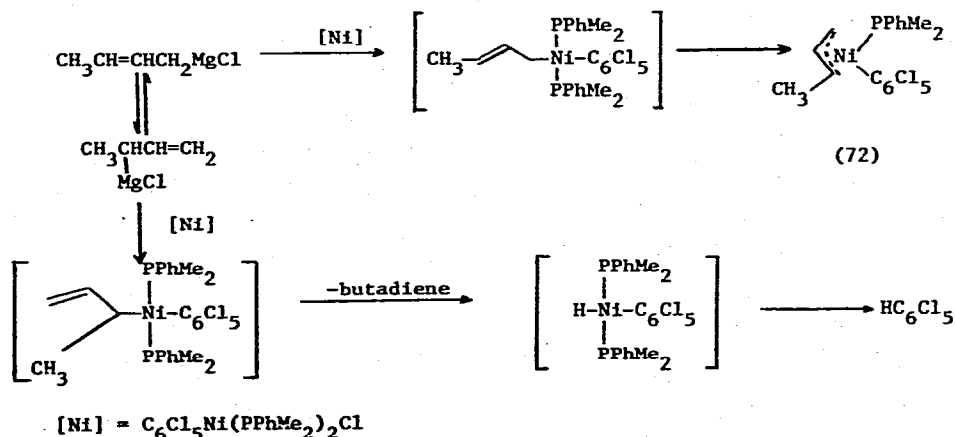
A series of η^3 -allylic complexes of palladium have been prepared by the addition of PdH[Ph₇ECH₂CH₂EPh₂]⁺ (E = P, As) to 1,3-dienes, cycloocta-1,5-diene, cyclohepta-1,3,5-triene and cyclododeca-1,5,9-triene [182]. Heating M(dibenzylideneacetone)_n (M = Pd, n = 2; M = Pt, n = 3) with PPh₃CCl gives an insoluble compound [MCl(CPh₃)₃]_n which converts into M(acac)(CPh₃) upon treatment with Tl(acac). ¹H and ¹³C nmr is used to study fluxionality about the triphenylmethyl ligand [183]. The ¹H nmr spectrum of [η³-C₃H₅Pt(PCy₃)₂]PF₆ shows a "static" η³-allyl structure at



room temperature. Non-equivalence of the syn protons is observed at room temperature. This magnetic non-equivalence is ascribed to the restricted rotation of the PCy_3 groups about the Pt-P bond [184]. A series of compounds $\text{Pt}(2\text{-Me allyl})(\text{L-L})$ have been prepared. Bases which are good nucleophiles to Pt(II) give stable 1:1 adducts, which are dynamic in solution at room temperature, and apparently have a η^1 -allylic structure at low temperature [185]. The proposed mechanism is outlined in the scheme. The insertion reaction of trans $[\text{PtMe}(\pi\text{-allene})(\text{PMe}_2\text{Ph})_2]\text{X}$ ($\text{X} = \text{BF}_4, \text{PF}_6, \text{SbF}_6$) to cis $[\text{Pt}(\pi\text{-2-Meallyl})(\text{PMe}_2\text{Ph})_2]\text{X}$ is first order in initial complex, and shows a relative anion dependence on ΔH^\ddagger of $\text{SbF}_6^- \sim \text{BF}_4^- > \text{PF}_6^-$. Reactions of $\text{I}^-, \text{NO}_3^-, \text{py}, \text{CO}, \text{PPh}_3$ are described, and general reaction schemes discussed [186]. Stable π -allylnickel complexes (72) have been prepared which are structurally rigid even in the presence of phosphines and phosphites [187]. Air stable complexes

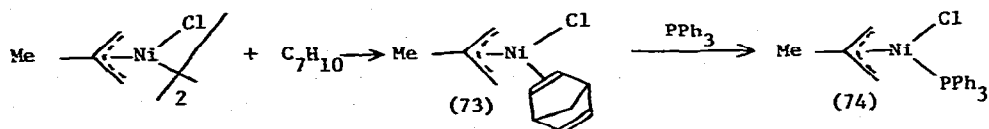


($\text{R}_1 = \text{H}, \text{Me}, \text{Ph}; \text{R}_2 = \text{H}, \text{Me}$) are obtained in high yield by treating

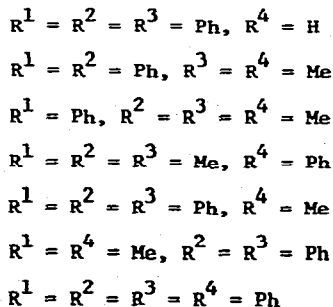
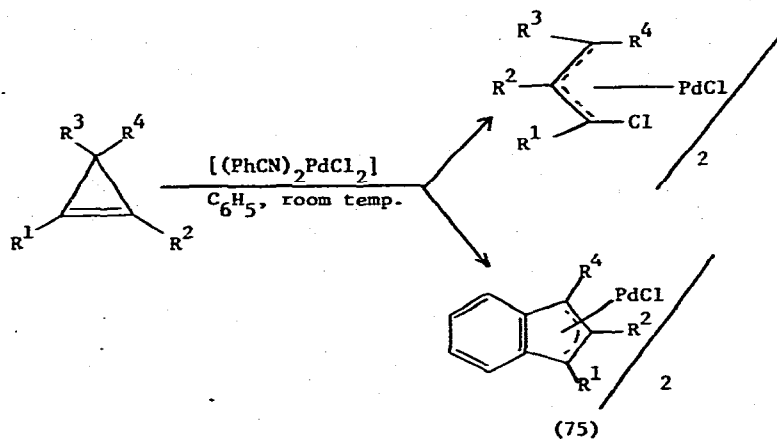


$\text{Ni}(\text{CO})_4$ with salts $[\text{R}_2\text{CH}=\text{CR}_1\text{CH}_2\text{OP}(\text{NMe}_2)_3]\text{X}$ followed by addition of PPh_3 [188]. A high yield synthesis of π -allylnickel complexes has been reported using nickel halides and conjugated dienes in the presence of metallic zinc [189]. Treating chloronickel(2-methylallyl) dimer with norbornene yields a complex (73) which can be converted to the chlorotriphenylphosphine-

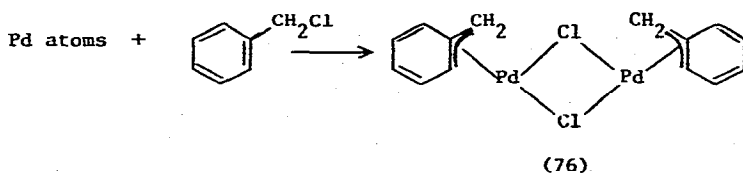
nickel(2-methylallyl) derivative (74) with PPh_3 [190]. Treatment of $\text{PdCl}_2(\text{PhCN})_2$ with substituted cyclopropenes leads to the formation of



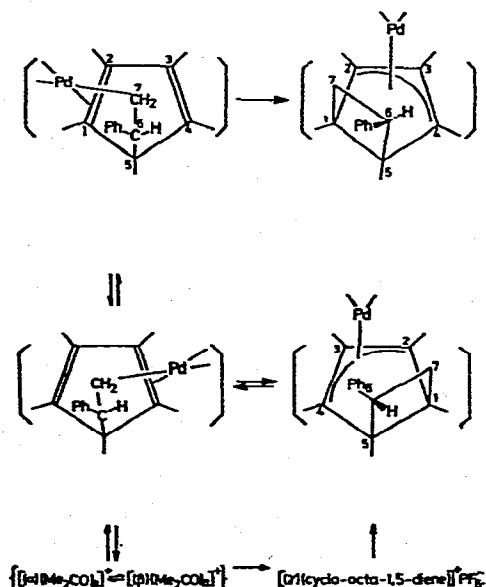
indenyl complexes (75) in addition to open-chain π -allyl complexes [191]. Compounds of type $[\text{Pd}(1\text{-}3\text{-}\eta\text{-allyl})(p\text{-RC}_6\text{H}_4\text{N}=\text{CH}=\text{NC}_6\text{H}_4\text{R-p})]_2$ ($\text{R} = \text{H}, \text{Cl}$,



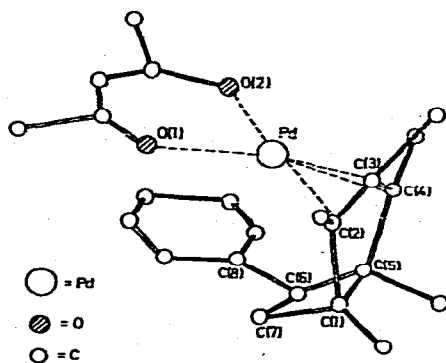
Me) are formed by treating $[\text{Pd}(1\text{-}3\text{-}\eta\text{-allyl})\text{Cl}]_2$ with $\text{Li}(\text{N},\text{N}'\text{-diarylformamido})$ [192]. Two conformers exist. At $80\text{-}100^\circ$ one conformer undergoes an intramolecular process bringing the allyl group to equivalence, and a mechanism involving inversion of the $\text{C}_2\text{N}_4\text{Pd}_2$ ring via a chair conformation is proposed. Additional structural work has been done on these triazendo allylic systems [193]. Chlorobenzylpalladium(II) dimer (76) has been



obtained in good yield by treating Pd atoms with benzyl chloride in a low temperature matrix [194]. The use of metal atoms is discussed in a series of articles in *Angewandte Chemie*, one of which [195] discusses applications to the synthesis of nickel allyls. The distribution of organic products from treating bis- π -allylnickel complexes, derived from isoprene and allene, with active methylene compounds, amines, and aldehydes, has shown the first two groups attack at the π -allyl site, whilst aldehydes attack at the σ -allyl group of the nickel complexes [196]. The σ, η -complex (77) undergoes spontaneous reversible ring closure to give the endo-phenyl allylic complex (78) in addition to an irreversible ring closure to the most stable exo-phenyl allylic isomer (79). The crystal structure of the

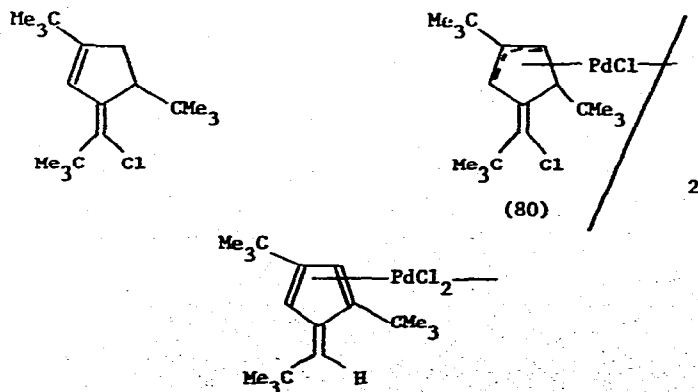


acetylacetonate derivative of (78) is reported [197]. A quantitative measure of the ability of a coordinated carboxylate to stabilize intermediates by chelation has been obtained from a variable temperature nmr study of $(\pi\text{-2-methylallyl})\text{Pd}(\text{O}_2\text{CR})(\text{PMe}_2\text{Ph})$ [$\text{R} = \text{Me}, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3, \text{CF}_3, \text{CMe}_3, \text{CPh}_3, \text{CH}_2\text{Ph}$] [198]. The order of increasing $\Delta G^\ddagger_{\text{T}_c}$ ($\text{R} = \text{Me} <$



(78)

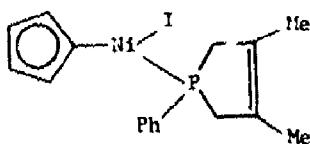
$\text{CH}_2\text{Ph} < \text{CH}_2\text{Cl} < \text{CF}_3$) for 3,4-allylic proton exchange is in agreement with a decreasing ability of the carboxylate ligand to stabilize the carboxylate as a chelate. Complexes $\text{NiI}(\text{C}_3\text{H}_5)\text{L}$ ($\text{L} = \text{PPh}_3, \text{SBu}_2$) have been prepared from $[\text{NiI}(\text{C}_3\text{H}_5)]_2$ and L ; THF, 1,4-dioxane, and Et_2O do not react [199]. Treating π -crotylnickel halides with alkyl and allyl iodides gives attack mainly at the CH_2 group to form 2-alkenes and 1,5-alkadienes [200]. The thermal decomposition of $[\text{PdBr}(\text{C}_3\text{H}_5)]_2$ gives allyl bromide, benzene, diallyl, PdBr_2 , and Pd ; while $[\text{PdI}(\text{C}_3\text{H}_5)]_2$ gives benzene, diallyl, PdI_2 , and Pd [201]. Complexation of 1,2-dihydrofulvene with Na_2PdCl_4 gives (80),



which gives (81) on treatment with HCl. Complex (80) can also be prepared by treating $\text{PdCl}_2(\text{PhCN})_2$ with $\text{Me}_3\text{C}\equiv\text{CH}$ [202]. Treating $\text{Ni}(1,5\text{-COD})_2$ with allyl chloride and RNC ($\text{R} = \text{Me}, \text{Et}, \text{Bu}^t$) gives $\text{NiCl}(\text{CNR})(\pi\text{-C}_3\text{H}_5)$ [203]. The regiospecific oxidation of steroidal π -allylic palladium compounds with 3-chlorobenzoic acid is described [204]. Steric effects of this reaction are considered [205]. The charge transfer transition of bridging halide to palladium is a characteristic band, and is found at 227 nm and 245 nm respectively for the Cl and Br complexes $[\text{PdX}(\text{C}_3\text{H}_5)]_2$ [206]. The crystal structure of di- μ -trifluoroacetato-bis[2-(methylallyl-3-norbornyl)Ni(II)] has been solved [207]. Compounds $(+)\text{-}\pi\text{-RNiX}$ and $(-)\text{-}\pi\text{-NiBr}$ ($\text{R} = \text{pinenyl}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) have been prepared from $(-)\text{-}(1\text{S},5\text{S})\text{-}\beta\text{-pinene}$ and $(+)\text{-}(1\text{R},5\text{R})\text{-}\alpha\text{-pinene}$ respectively by a photochemical oxidation reaction with PX_3 and reaction with $\text{Ni}(1,5\text{-COD})_2$. The compounds $(+)\text{-}(\pi\text{-R})_2\text{Ni}$ (82) and $(-)\text{-}(\pi\text{-R})_2\text{Ni}$ have been prepared from $(+)\text{-}$ and $(-)\text{-}\pi\text{-RNiBr}$ respectively with allyl MgBr, with disproportionation of the intermediate π -allyl- π -pinene nickel compound [208]. The authors report the crystal structure of (82).

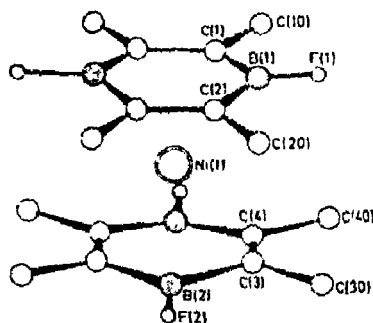
IX. Delocalized carbocyclic systems

Trifluoroacetic acid protonates nickelocene to give $[\text{C}_5\text{H}_5\text{NiC}_5\text{H}_6]^+$. Deuteration experiments are used to show that electrophilic attack occurs at one of the ring ligands rather than at the metal, leading to the entering proton occupying an *exo*-methylene position [209]. The single crystal structure of a ring opened tetraphenylcyclobutenyl palladium complex has been reported. Mechanistic pathways are discussed [210]. A reduction-complexation reaction between nickelocene and phosphine sulfides leads to complexes of type (83) [211]. 1,4-Difluoro-2,3,5,6-tetramethyl-



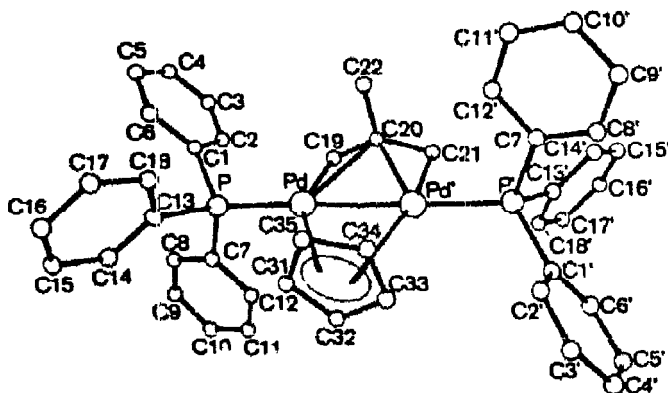
(83)

-1,4-diboracyclohexa-2,5-diene displaces CO from $\text{Ni}(\text{CO})_4$ to give compounds $(\text{C}_4\text{Me}_4\text{B}_2\text{F}_2)\text{Ni}(\text{CO})_2$ and $(\text{C}_4\text{Me}_4\text{B}_2\text{F}_2)_2\text{Ni}$ (84). A single crystal study of compound (84) shows it to have a sandwich structure with idealized D_{2d} symmetry. The molecular structure and spectroscopic properties of the complexes closely resemble those of the isoelectronic complexes of duroquinone [212]. An electron diffraction study of epNiNO shows a linear Ni-N-O arrangement with distances of 2.128(5) and 1.58(1) Å respectively



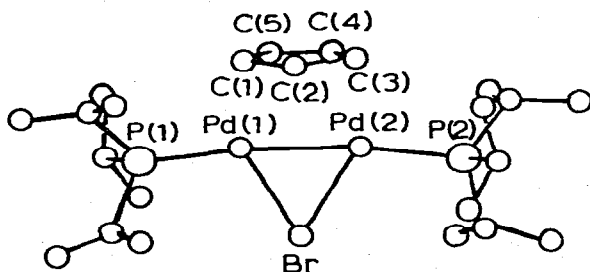
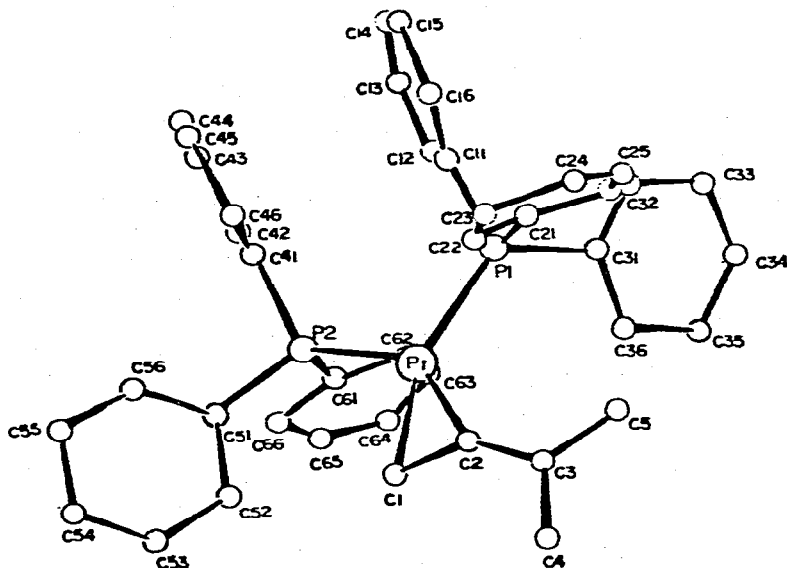
(84)

for the Ni-C and Ni-N distances [213]. Reaction of (2-methylallyl)cyclopentadienylpalladium and PR_3 (R = OMe, OPh, Ph) in exactly stoichiometric amounts leads to a dimer $\text{cpPd}_2(\text{C}_4\text{H}_7)(\text{PR}_3)_2$ (85) [214]. The crystal structure of (84) shows it to have both the 2-methylallyl and cyclopentadienyl ligands in bridging positions. The crystal structure of 1,1-dimethylallene bis(triphenylphosphine)platinum shows that the olefin with



(85)

no adjacent methyl groups is coordinated to platinum [215]. Treating $\text{cpPdBr}(\text{PPr}_3^1)$ with M_2 in THF gives a compound $\mu\text{-cp-}\mu\text{-M}_2\text{Pd}_2(\text{PPr}_3^1)_2$, where the crystal structure shows the palladiums bridged by Br and a cyclopentadienyl ring with unequal C-C bonds [216]. Use of the shift reagent



$\text{Eu}(\text{fod})_3$ has been used to provide evidence for preferred conformations and rotational barriers for complexes $\text{cpFeCOCN}(\text{PPh}_2\text{Me})$, $\text{cpFeCOCN}(\text{PPhMe}_2)$, and $\text{cpNiCN}(\text{PPh}_3)$. For the nickel compound the phenyl multiplet remains sharp to -65°C . Effects of $\text{Eu}(\text{fod})_3$ on the aromatic protons is reported [217]. ^{119}Sn Mossbauer spectra are reported for eleven Sn-Ni complexes of type $\text{Cl}_x\text{Sn}[\text{NiLcp}]_{4-x}$ ($\text{L} = \text{CO}, \text{PPh}_3$; $x = 2, 3$) and $\text{Cl}_3\text{SnNiL}_2\text{cpS}$ ($\text{S} = \text{solvent molecule}$). For compounds with an Sn-Ni bond, $\text{cpNi}(\text{PPh}_3)$ is the best donor and the Sn-Ni bond has the highest s-character. $\text{CpNi}(\text{CO})$ is a slightly poorer donor and the Sn-Ni bond has smaller s-character. [218].

X. Metal hydrides

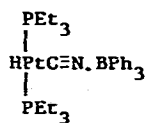
A series of complexes $\text{trans-PtH}(\text{PEt}_3)_2\text{CN}\cdot\text{L}$ have been prepared. The tabulated data for $^1\text{J}(\text{Pt-H})$ can be used as a measure of the relative acceptor strengths of the Lewis acids (L). Coordination of the cyanide to

(87) have been prepared which are the first examples of linkage isomerism

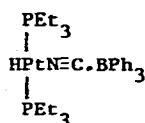
Table. $^1J(\text{Pt-H})$ for Lewis and (L) adducts of $\text{trans-PtH}(\text{PEt}_3)_2\text{CN}$

L	$^1J(\text{Pt-H})(\text{H}_2)$
AlCl_3	860
$\text{B}(\text{p-tolyl})_3$	854
$\text{B}(\text{naphthyl})_3$	851
$\text{B}(\text{o-tolyl})_3$	851
BEt_3	844
CoCl_2	843
$\text{B}(\text{CH}_2\text{Ph})_3$	842
ZnCl_2	832
$\text{B}(\text{OPh})_3$	820
AlMe_3	816

of the cyanide ligand in a platinum(II) compound, where both isomers have been isolated and isolated and characterized [220]. Treating $\text{Pt}(\text{PPh}_3)_3$

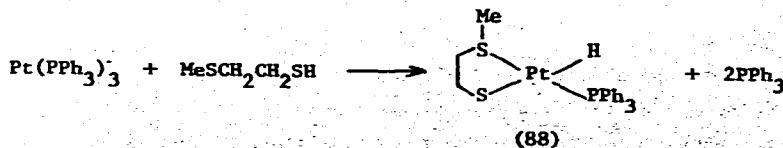


(86)

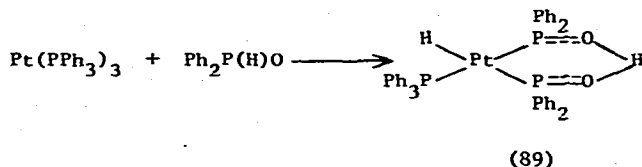


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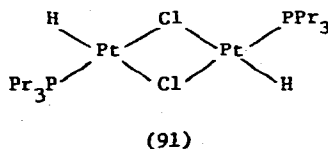
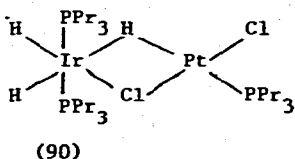
with anhydrous HCl or HBr gives $\text{cis-PtX}_2(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$) and hydrogen. With the Pd analogue the reaction proceeds further, since the $\text{trans-PdCl}_2(\text{PPh}_3)_2$ formed itself reacts with liquid HCl to give $[\text{Ph}_3\text{PH}]_2[\text{Pd}_2\text{Cl}_6]$ [221]. These authors also report their results from the reaction between $\text{Pt}(\text{PPh}_3)_3$ and H_2SO_4 , $\text{CF}_3\text{CO}_2\text{H}$. The oxidative addition of $\text{MeSCH}_2\text{CH}_2\text{SH}$ to $\text{Pt}(\text{PPh}_3)_3$ yields (88) [222]. The hydride $\text{PtH}(\text{SEt})(\text{PPh}_3)_2$ has been identified in solution from treating $\text{Pt}(\text{PPh}_3)_3$ with EtSH. The platinum



hydride (89) is obtained by treating $\text{Pt}(\text{PPh}_3)_3$ with diphenylphosphine oxide [223]. $\text{Ni}(\text{acac})_2$ reacts with ethylaluminum bromide and triphenylphosphine



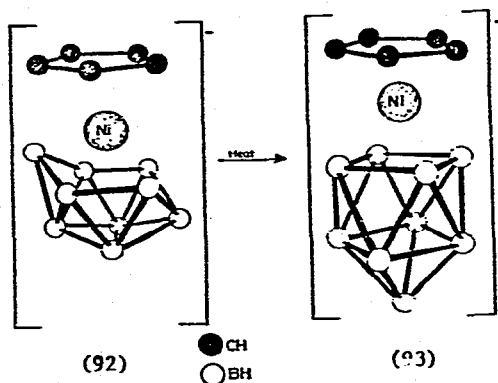
to give $\text{NiHBr}(\text{PPh}_3)_2$ [224]. Hydrolysis of the fluoroplatinum(II) complexes $[\text{PtFL}_3]^+$ ($\text{L} = \text{PPh}_3, \text{PEt}_3, \text{PMe}_2\text{Ph}$) yields hydroxy-bridged complexes $[\text{Pt}_2(\text{OH})_2\text{L}_4]^{2+}$ which react with excess phosphine to give $[\text{PtHL}_3]^+$. Reaction of $\text{Pt}(\text{PPh}_3)_3$ with excess anhydrous HF gives $[\text{PtF}(\text{PPh}_3)_3][\text{H}_n\text{F}_{n+1}]$ ($n \sim 2-3$) [225]. The compound $\text{PtH}[\text{Si}(\text{p-FC}_6\text{H}_4)_3](\text{PMe}_2\text{Ph})_2$ has been obtained in low yield by treating $\text{Pt}(\text{CO}_3)(\text{PMe}_2\text{Ph})_2$ with the $\text{SiH}(\text{p-FC}_6\text{H}_4)_3$ [226]. Similarly the compound cis.trans.cis- $\text{PtH}_2(\text{SnR}_3)_2(\text{PMe}_2\text{Ph})_2$ ($\text{R} = \text{Ph}, \text{PhCH}_2, \text{o-}, \text{m-}, \text{p-MeC}_6\text{H}_4$) can be prepared by treating $\text{Pt}(\text{CO}_3)(\text{PMe}_2\text{Ph})_2$ with R_3SnH [227]. Treating $[\text{Pt}(\pi\text{-allyl})(\text{PCy}_3)_2]\text{PF}_6$ with sodium methoxide leads to trans- $\text{PtH}_2(\text{PCy}_3)_2$ [228]. These authors' data agrees with the previous data of Shaw for this compound, and not with that of Kudo. An X-ray crystal structure shows a short Pt-P distance and a trans arrangement for the phosphines. Hydrido transfer from IrH_5L_2 to $\text{Pt}_2\text{Cl}_4\text{L}_2$ or $\text{Pd}_2\text{Cl}_4\text{L}_2$ ($\text{L} = \text{PPr}_3$) proceeds via a hydrido bridged intermediate (90). This compound slowly disproportionates to give a platinum hydride which is tentatively



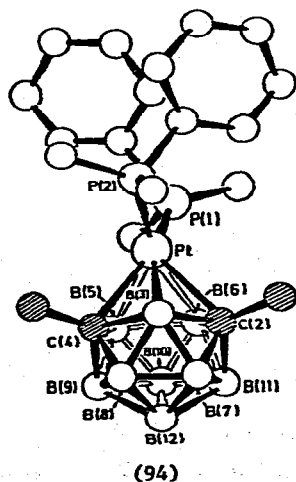
assigned structure (91) [229]. Semi-empirical SCF-MO calculations on trans- $\text{PtHX}(\text{PH}_3)_2$ ($\text{X} = \text{halogen}, \text{CN}$) show a high electron density (ca. 1.25 e) on the H ligand, which decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I} > \text{CN}$ [230].

XI. Metal carboranes

When $\text{Ni}(\text{cp})_2$ is treated with $\text{B}_9\text{H}_{12}^-$ and sodium amalgam a complex $[\text{cp-2-Ni}(\text{B}_9\text{H}_9)]^-$ (92) is formed, which can be converted to $[\text{cp-1-Ni}(\text{B}_9\text{H}_9)]^-$ (93) by thermal isomerization [231]. A report has appeared of the first icosahedral metalloborane species derived from the hypothetical $\text{B}_{11}\text{H}_{11}^{4-}$ and $\text{B}_{10}\text{H}_{10}^{6-}$ ions. The compounds are $\text{cpNi}(\text{B}_{11}\text{H}_{11})$ and $(\text{cpNi})_2\text{B}_{10}\text{H}_{10}$ [232].



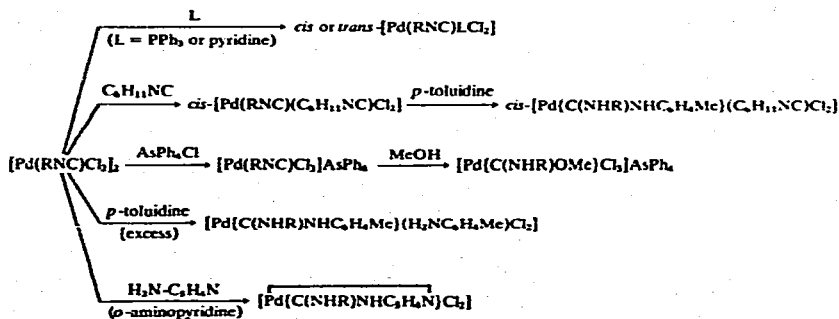
Reaction of $\text{Pt}(\text{PEt}_3)_3$, $\text{Pt}(\text{PMe}_3)_2$ (*trans*-stilbene), $\text{Pt}(\text{PMe}_2\text{Ph})_4$, $\text{Ni}(1,5\text{-COD})_2$, $\text{Ni}(\text{PEt}_3)_2(1,5\text{-COD})$, $\text{Pd}(\text{CNBu}^t)_2$ with *closo*-2,3-Me₂-2,3-C₂B₉H₉ gives the *closo*-metallocarboranes 1,1-L₂-2,4-Me₂-1,2,4-MC₂B₉H₉ (M = Pt, L = PEt₃, PMe₃, PMe₂Ph; M = Ni, L₂ = 1,5-COD, L = PEt₃; M = Pd, L = Bu^tNC). The complex (94) from $\text{Pt}(\text{PMe}_2\text{Ph})_4$ has been investigated by X-ray crystallography [233]. These authors also report the reaction of $\text{Ni}(\text{COD})(\text{Bu}^t\text{NC})_2$, $\text{Pd}(\text{Bu}^t\text{NC})_2$ and $\text{Pt}(\text{PEt}_3)_2$ (*trans*-stilbene) with [*closo*-CB₁₀H₁₁]⁻ and *closo*-2-NMe₃-2-CB₁₀H₁₀ to give the *closo*-metallocarboranes [1,1-L₂-1,2-MCB₁₀H₁₁]⁻ and 1,1-L₂-2-NMe₃-1,2-MCB₁₀H₁₀ (M = Ni, Pd; L = Bu^tNC; M = Pt, L = PEt₃).



A single crystal structure of the Pd complex is given [234]. Reaction of Ni(1,5-COD)(PEt₃)₂ with 5,9-Me₂-5,9-C₂B₇H₁₁ gives Ni(C₂B₇H₉Me₂)(PEt₃)₂. Analogous reactions between C₂B₇H₁₁Me₂ and Ni(1,5-COD)(PMe₃)₂, Pt(PEt₃)₂ (stilbene), Pt(PMe₃)₂(stilbene), Pt(PPh₃)₂(stilbene) gives respectively Ni(C₂B₇H₉Me₂)(PMe₃)₂, Pt(C₂B₇H₉Me₂)(PEt₃)₂, Pt(C₂B₇H₉Me₂)(PMe₃)₂, Pt(C₂B₇H₁₁)(PEt₃)₂. A structure of [6,6-(PEt₃)₂-5,9-Me₂-6,5,9-NiC₂B₇H₉] shows the metal bonded to a B₂C system in a 1,2,3-η bonding mode [235]. Reaction of *closo*-2,4-C₂B₅H₇ with Pt(PEt₃)₂(styrene) gives *closo*-2,3{PEt₃}₂-1,2,3,6-CPt₂CB₅H₇. Reacting Pt(1,5-COD)(PMe₃)₂ with 1,6-C₂B₈H₁₀ gives *nido*-η(4,8)-(PMe₃)₂Pt]-8,8-(PMe₃)₂]-7,8,10-CPtCB₈H₁₀, which on treatment with activated charcoal gives *nido*-8,8-(PMe₃)₂]-7,8,10-CPtCB₈H₁₀. X-ray structures of all three compounds are given [236].

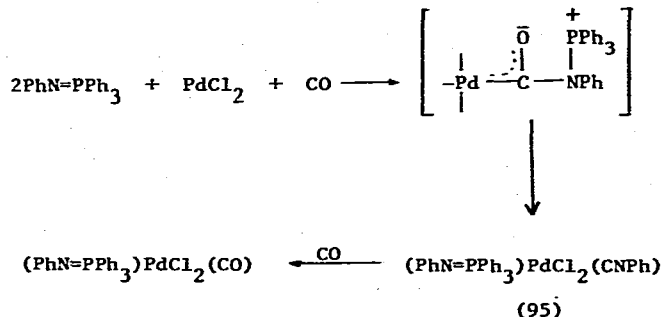
XII. Metal isocyanides

Binuclear complexes [PdCl₂(CNR)]₂ (R = Ph, *p*-MeC₆H₄) have been prepared from PdCl₂(CNR)₂ and PdCl₂(MeCN)₂. Treating the dimers with donor ligands causes bridge splitting. Carbenes result from treating the trichloro complex with methanol [237]. A similar chemistry with platinum isocyanides has been used to prepare PtCl₄(CNR)₂, PtCl₄(CNR)(PMe₂Ph), [PtCl₃(CNR)(PMe₂Ph)]⁺, [PtCl₂(CNR)₂(PMe₂Ph)]²⁺ (R = Me, Bu^t, Cy, *p*-tolyl). The Pt(IV) complexes are obtained by addition of Cl₂ to the Pt(II) compounds. Complexes PtCl₂(CN)₂(CNR)₂ and [PtCl₂(CN)(CNR)(PMe₂Ph)]⁺ (R = Bu^t) are also reported [238]. An interesting fluorescent compound [Pt(CNPh)₂][Pt(CN)₄] has been reported along with the [Ni(CN)₄]²⁻ derivative [239]. Treating Pt(C₂H₄)(PPh₃)₂ with Bu^tCN gives Pt(CNBu^t)₂(PPh₃)₂.

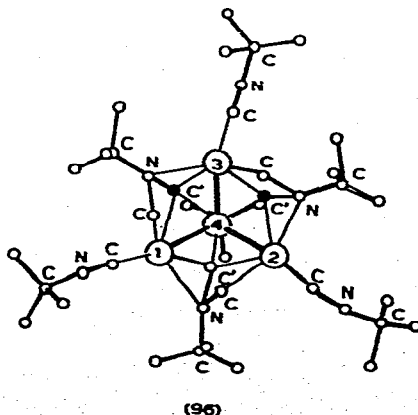


Evidence is presented for analogous compounds with RNC (R = Prⁱ, Cy, *p*-MeOC₂H₅, *p*-ClC₂H₅). These compounds add I₂, MeI, CF₃I, SnClPh₃. Treating

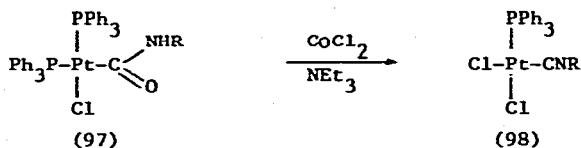
$\text{Pt}(\text{C}_2\text{F}_4)(\text{AsPh}_3)_2$ with RNC ($\text{R} = \text{Bu}^t, \text{Pr}^i$) gives $\text{Pt}(\text{CNR})_2(\text{C}_2\text{F}_4)$. The compound $\text{PtI}_2(\text{CNMe})_2$ is obtained from $\text{Pt}(\text{CN})_2(\text{PPh}_3)_2$ and MeI [240]. Careful synthetic work leads to compounds $[\text{Pt}(\text{CNR})_2(\text{CNR}')_2][\text{Pt}(\text{CN})_4]$ and $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]$ [241]. The compound $[\text{Ni}(\text{S}_2\text{CNR}_2)_3]^+$ ($\text{R} = \text{Et}, \text{Bu}^n$) reacts with CNR' ($\text{R}' = \text{Bu}^t, p\text{-ClC}_6\text{H}_4$) to give $[\text{Ni}(\text{CNR}')_2(\text{S}_2\text{CNR}_2)]^+$ [242]. The reaction of CO and triphenyl(phenylimino)phosphorane in the presence of PdCl_2 gives a phenyl isocyanide palladium(II) complex (95). In the presence of a large excess of CO , complex (95) is converted into a carbonylpalladium(II) compound [243]. A dark red cluster compound



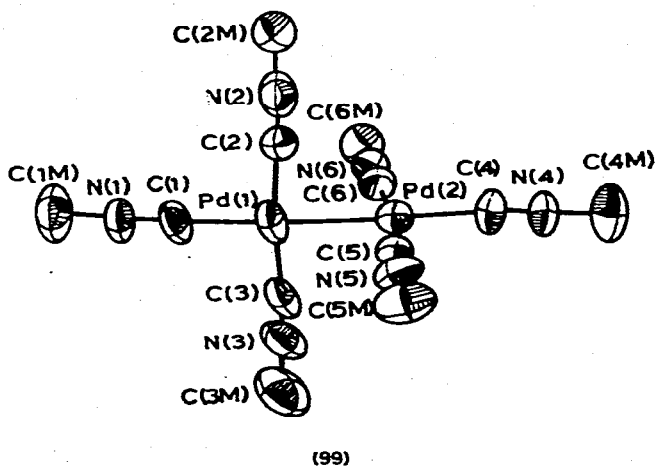
$\text{Ni}_4(\text{CNBu}^t)_7$ has been prepared from $\text{Ni}(1,5\text{-COD})_2$ and Bu^tNC . The ^1H nmr spectrum shows stereochemical nonrigidity by a two-step process, the lower energy step being one involving the bridging ligands. The structure of (96) has been solved [244]. Acyl chlorides or phosgene have been used



to convert the carbonyl compound (97) into the isocyanide compound (98) [245]. Electronic absorption and MCD spectra of $M(\text{CNR})_4^{2+}$ ($M = \text{Pt}$, $R = \text{Me}$, Et ; $M = \text{Pd}$, $R = \text{Et}$) shows intense $M \rightarrow L$ charge-transfer transitions in the visible or UV region. Spectral assignments and d orbital participation



in bonding are discussed [246]. The compound $[\text{Pd}_2(\text{CNMe})_6](\text{PF}_6)_2$ (99) results from treating Na_2PdCl_4 with MeNC . The ^1H nmr spectrum is temperature dependent. The crystal structure shows a Pd-Pd distance of

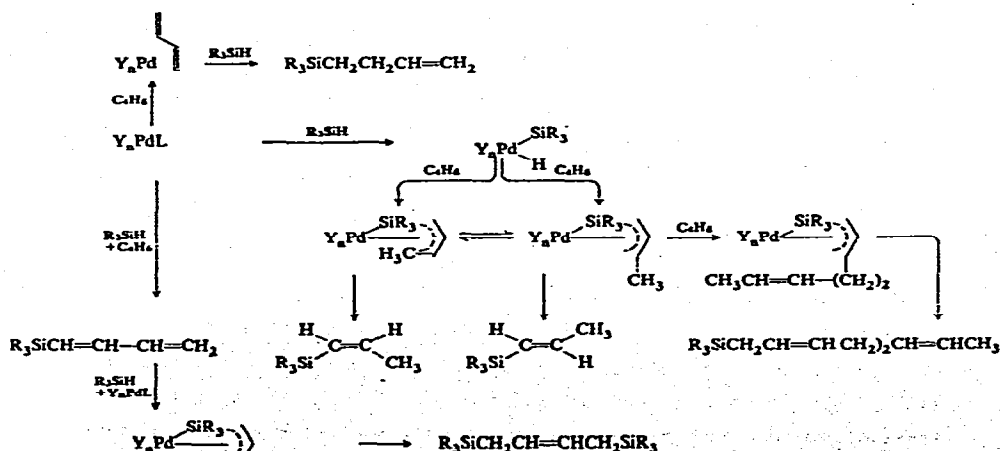


2.531 Å, which is the shortest recorded distance for this bond [247]. The structure of $\text{Ni}(\text{O}_2)(\text{CNBu}^\dagger)_2$ shows a value of 1.45(1) Å for the O-O distance. The angle about the N of $\text{Bu}^\dagger\text{NC}$ is 172(1)° [248].

XIII. Catalytic reactions involving complexes

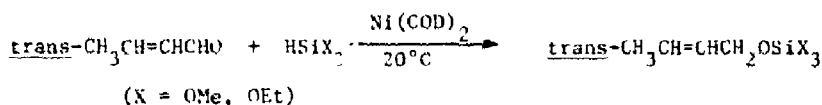
Diphenylphosphino-functionalized polystyrenes coordinated with PdCl_2 or PtCl_2 have been used for the homogeneous hydrogenation of monoalkenes [249]. A mixture of $\text{Pt}(\text{acac})_2$ and pyridine has been used for the conversion of nitrobenzene to aniline in 90% yield [250]. The complex $\text{PtH}(\text{SnCl}_3)\text{CO}(\text{PPh}_3)_2$ has been prepared, and used for the hydroformylation of

greater than 95% yield [251]. The structure of the complex is uncertain, and it is reported to be relatively unstable. Homogeneous Na_2PtCl_4 , and heterogeneous Pt, catalyze the exchange in D_2O of naphthalene, anthracene, and pyrene. Naphthalene yields initially β -orientation with $\beta\text{-D}_4$ being the final product. Only with the heterogeneous Pt does prolonged exchange give naphthalene- D_3 . Intermediates of the π -bonded type are suggested to be involved with both types of catalyst [252]. A similar comparative study has been made by these same authors with diphenyl, *m*- and *p*-terphenyl [253]. This latter work is also published in communication form [254]. Alkenes $\text{RC}(\text{Me}_2)\text{CH}=\text{CH}_2$ ($\text{R} = \text{Et}, \text{Pr}, \text{Bu}$) undergo H-D exchange with a $\text{D}_2\text{O}/\text{CH}_3\text{CO}_2\text{D}$ solvent containing HClO_4 and a homogeneous Pt(II) catalyst. Incorporation of deuterium into the alkyl part of the alkene occurs exclusively at C(5). Exchange of the olefinic hydrogens is also observed, and is considered to be an acid-catalyzed reaction [255]. Complexes $\text{Pt}_2\text{Cl}_4\text{L}_2$ ($\text{L} = \text{PPr}_3, \text{PEu}_3, \text{PBu}^t\text{Pr}_2, \text{FBu}^t_2\text{Pr}, \text{PPrPh}_2, \text{PPr}_2\text{Ph}, \text{PBu}^t\text{Ph}_2$) undergo a regiospecific H-D exchange in $\text{D}_2\text{O}/\text{CH}_3\text{CO}_2\text{D}$ to give complexes with deuterium in the alkyl groups of the tertiary phosphine, however with PBu^tPh deuterium is incorporated in the aryl group. Steric factors are considered to be dominant, and in internal metallation of Pt, the ease of ring formation decreases in the order: 5-membered > 6-membered > 4-membered [256]. The reaction of Me_3SiH with butadiene catalyzed by PdCl_2L_2 ($\text{L} = \text{PhCN}, \text{CyNC}, \text{Bu}^t\text{NC}, \text{PPh}_3$), $\text{PdClL}(\text{PPh}_3)$ ($\text{L} = \text{CyNC}, \text{Bu}^t\text{NC}$), and $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ has been reinvestigated. In addition to 1-trimethylsilyl-2,6-octadiene, the following compounds are also formed: 4-trimethylsilyl-1-butene, 1-trimethylsilyl-*trans*-2-butene, 1-trimethylsilyl-1,3-butadiene, 1,4-bis(trimethylsilyl)-2-butene. The analogous reaction with Me_3SiD has been carried out. A mechanism involving π -allyls is suggested [257]. The major products from

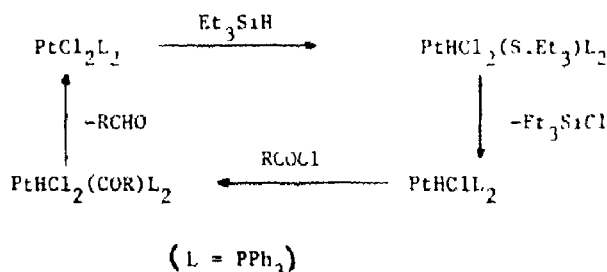


the hydrosilylation of butadiene with Cl_3SiH are 1-trichlorosilyl-cis-2-butene and 1-trichlorosilyl-trans-2-butene. The catalysts used are of type NiX_2L_2 ($\text{X} = \text{F}, \text{Cl}, \text{I}, \text{NO}_3, \text{MeC}(\sim\text{O})=\text{CHC}(\text{O})\text{Me}, \text{MeCH}(\text{OH})\text{COO}$; $\text{L} = \text{PPh}_3, \text{PBu}_3^{\text{H}}, \text{PCy}_3, \text{P}(\text{OPh})_3, \text{AsPh}_3$; $\text{L}_2 = \text{DPE}$). Similar allylnickel intermediates are postulated [258]. Hydrosilylation of $\text{HOCH}_2\text{CH}_2\text{CH}=\text{C}=\text{CH}_2$ with Et_3SiH in the presence of H_2PtCl_6 gives $\text{HOCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{SiEt}_3$. Similar catalyzed additions are reported [259]. The system $\text{Ni}(\text{acac})_2\text{-Et}_3\text{Al}$ catalyzes the addition to Me_3SiH to butadiene to give cis-trimethylsilyl-2-butene [260]. Again further uses are described.

Acetylenes add HSiCl_3 or HSiCl_2Me to give silyl-olefins. The reaction is catalyzed by $\text{NiEt}_2(\text{bipy})$, and double silylation occurs [261]. A variety of zerovalent nickel compounds catalyze the addition of silanes to the carbonyl group of crotonaldehyde. Addition across the carbon-carbon double bond does not occur [262]. Aryl halides $\text{XC}_6\text{H}_4\text{COCl}$ ($\text{X} = \text{H}, \text{p-Me}, \text{o-MeO}, \text{p-MeO}, \text{p-Cl}, \text{p-Br}, \text{p-NO}_2$) are converted into aldehydes $\text{XC}_6\text{H}_4\text{CHO}$ by treat-



ment with Et_3SiH at 120°C in the presence of cis- $\text{PtCl}_2(\text{PPh}_3)_2$. The proposed scheme involves an initial oxidative addition [263]. A product



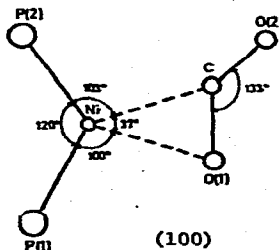
distribution is reported for the catalyzed isomerization of homocubane. Compounds used are $\text{PtCl}_2, \text{PdCl}_2(\text{PhCN})_2, \text{PdCl}_2(\text{PPh}_3)_2, \text{PdI}_2(\text{PPh}_3)_2$ [264]. These authors also report a similar study on the catalyzed 1,8-bishomocubane rearrangement [265].

Polyatyrene-divinylbenzene resin-anchored $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ has been used selectively to oligomerize butadiene to either 4-vinylcyclohexene or 1,5-COD. Anchored $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ catalyzes the hydrogenation of 1,5-COD to cyclooctene [266]. The catalytic system $\text{NiBr}_2(\text{PPh}_3)_2$ mixed with NaBH_4 gives a 95% yield of one specific linear product (E,E)-1,3,6-octatriene [267]. The chloro analog gives only 81% yield. The polymer bound analog

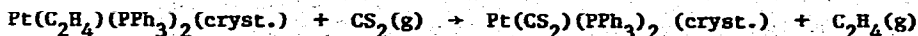
of the bromo compound gives 91% of the product. Further work on anchored and free $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ shows that butadiene can be cyclooligomerized to 4-vinylcyclohexene, 1,5-cyclooctadiene and (E,E,E)-1,5,9-cyclododecatriene [268]. This work has been extended to a multistep process when these three dienes are hydrogenated to alkane on the same polymer anchored catalyst used for their synthesis from butadiene [269]. The complex $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ catalyzes the cycloaddition of norbornadiene to a dimeric pseudo-norbornene. The catalyst then further is involved with the addition of this product to a third molecule of norbornadiene to give a trimeric addition product [270]. Isomerization of complexes NiX_2L_2 is likely facilitated by ligands L which possess π -acceptor properties. This facility of isomerization between tetrahedral and square geometries is discussed in relation to the catalytic activity of these and similar compounds [271].

XIV. Complexes and reactions of general interest

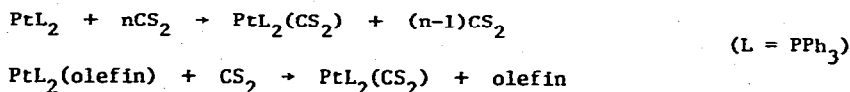
The reduction of $\text{NiX}_2(\text{PCy}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$) with sodium yields $[\text{NiX}(\text{PCy}_3)_2]_2$ or $\text{Ni}(\text{PCy}_3)_3$. Similarly NiX_2L_2 ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{PEt}_3, \text{PBu}_3^{\text{n}}, \text{PEt}_2\text{Ph}$) to compounds NiL_4 are obtained. These compounds react with N_2 to give $\text{Ni}(\text{N}_2)\text{L}_3$. Electronic absorption spectra are presented and discussed for these compounds [272]. Treating $\text{Ni}(\text{PCy}_3)_3$ or $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ with CO_2 gives $\text{Ni}(\text{CO})_2(\text{PCy}_3)_2$ (100). The infrared spectrum shows bands at 1740(vs), 1698(vs) and 1150(s) cm^{-1} , which are assigned to vibrations of the coordinated CO_2 . The single crystal structure of compound (100) is



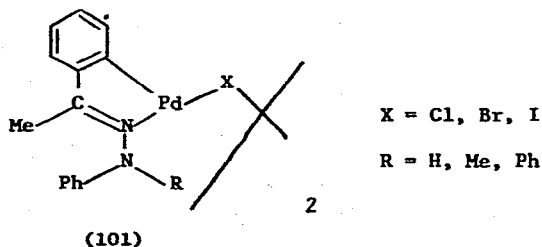
shown [273]. A series of complexes PdL_n ($n = 2, 3, 4$) have been prepared. Ligands L cover a wide range of phosphines, the lower coordination number being favored by the more bulky phosphine ligand (e.g. $\text{PBu}_2^{\text{t}}\text{Ph}$). Dissociation equilibria has been studied by ^{13}C nmr spectroscopy [274]. The crystal structure of $\text{Pt}(\text{PCy}_3)_2$ shows a bond angle of 160.5° for PtP [275].



disulfide has a ΔH of $-44.0 \pm 2.2 \text{ kJ mol}^{-1}$. The bond dissociation energy $D(\text{Pt-CS}_2)$ is slightly greater than $D(\text{Pt-C}_2\text{H}_4)$ [276]. Enthalpies have been measured for the reactions:

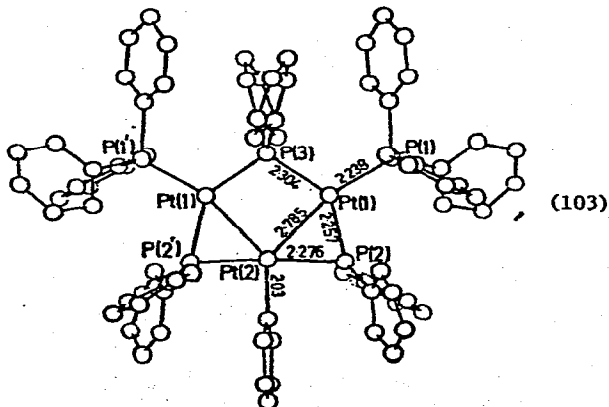
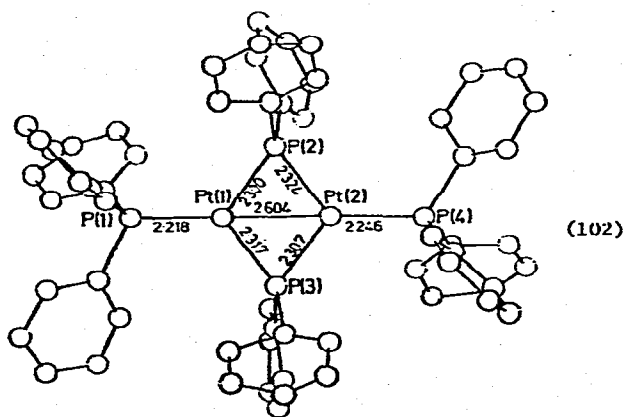


This data, when combined with previous work, shows the relative strengths of the Pt-olefin bonds decreases in the order trans-1,2-diphenylethylene > cis-1,2-diphenylethylene > phenylethylene > ethylene [277]. Treating cis- $\text{MCl}_2(\text{Ph}_2\text{C}=\text{CCF}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) with HCl yields trans- $\text{PdCl}_2(\text{Ph}_2\text{PCH}=\text{C}(\text{Cl})\text{CF}_3)_2$ and cis- $\text{PtCl}_2(\text{Ph}_2\text{PCH}=\text{C}(\text{Cl})\text{CF}_3)_2$ by trans addition to the triple bonds. The structure of the palladium compounds confirms the stereochemistry about the double bond [278]. Treating $\text{Pt}(\text{HC}\equiv\text{CPh})(\text{PPh}_3)_2$ with $p\text{-FC}_6\text{H}_4\text{N}_2\text{BF}_4$ gives $\text{Pt}(\text{C}\equiv\text{CPh})(\text{HNNC}_6\text{H}_4\text{Fp})(\text{PPh}_3)_2$. The crystal structure of the product shows it to have a trans configuration about the $\text{N}=\text{N}$ bond [279]. A series of π -bonded diazene complexes of nickel have been prepared [280]. The compound $\text{Ni}(\text{PhN}=\text{NPh})[\text{P}(p\text{-tolyl})_3]_2$ exhibits photochromism. The compound obtained from bis(*p*-methylbenzoyl)diazene with nickel(0) exhibits fluxionality. The structure of $\text{PdCl}_2(\text{azobenzene})_2$ shows a $\text{N}-\text{N}$ distance of 1.238(9) Å. Steric crowding within the molecule leads to a twisting of the phenyl rings [281]. When ketoximes are heated at 60°C in the presence of $\text{Pd}(\text{PPh}_3)_4$ and molecular oxygen, a Beckman fragmentation of the ketoxime occurs to give a nitrile and an aldehyde [282]. When the cyclopalladated dimer of acetophenone hydrazone (101) is treated with py , PR_3 ($\text{R} = \text{alkyl}, \text{aryl}$), AsPh_3 , SbPh_3 , the monomers are formed. In the presence of excess phosphine a second molecule coordinates in place of the nitrogen. With ethylenediamine an ionic complex is formed, and with DPE a dimer is obtained with the DPE



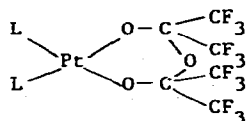
molecule bridging two palladiums [283]. The compounds NiL_2 and $\text{NiL}(\text{PPh}_3)_2$ have been obtained by treating $\text{Ni}(1,5\text{-COD})_2$ or $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ with $\text{N,N}'\text{-bis}(p\text{-methylphenyl})\text{ethylenediamine}(\text{L})$. Similarly $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$

reacts with PhCH=NPh to give $\text{Ni}(\text{PhCH=NPh})(\text{PPh}_3)_2$ [284]. The compounds of $\text{Ni}(0)$, $\text{Li}[\text{NiPPh}_2]_2\text{THF}$, $\text{Li}_2[\text{Ni}(\text{SiPh}_3)_2]_5\cdot 5\text{THF}$, and $\text{Li}_3[\text{Ni}(\text{SiPh}_3)_3]\cdot 5\text{THF}$ are reported [285]. The binuclear $\text{Pt}_2(\text{PPh}_2)_2(\text{PPh}_3)_2$ (102) and trinuclear $\text{Pt}_3(\text{PPh}_2)_3\text{Ph}(\text{PPh}_3)_2$ (103) cluster compounds have been obtained by refluxing $\text{Pt}(\text{PPh}_3)_4$ in benzene for several days under a N_2 or Ar atmosphere. The verification of the structure comes from an X-ray study [286]. Paramagnetic species have been observed on treating compounds NiL_4 ($\text{L} = \text{PEt}_3, \text{PPh}_3$; $\text{L-L} = \text{DPE}$) with electron acceptors such as tetracyanoethylene. The initial transient paramagnetic species are not observed [287]. The compounds $\text{PdX}(\text{Bu}_2\text{NO})\text{L}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{P}(\text{OPh})_3$) have been prepared. The nitroxide is "side-on" bonded and



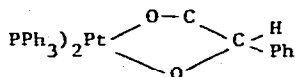
the ^1H nmr and infrared data for the compounds is reported [288]. The crystal structures of compounds (104) and (105) have been solved. The compounds are prepared by treating compounds $\text{Pt}_2\text{N}(\text{R})\text{N}=\text{NN}(\text{R})\text{L}_2$ ($\text{R} = \text{Ph}, \text{p-}$

small amounts of hydrate $(CF_3)_2C(OH)_2$ [289]. The liquid phase oxidation of



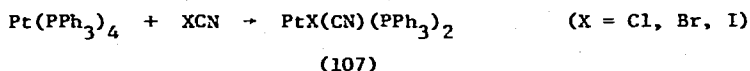
L = PPh_3 (104), $PMePh_2$ (105)

benzaldehyde is catalyzed by $PdO_2(PPh_3)_2$, $Pd(PPh_3)_4$, $PtO_2(PPh_3)_2$. The products are benzoic acid and perbenzoic acid. The latter compound resembles triphenylphosphine in markedly retarding the reaction [290]. An intermediate of type (106) is considered to be a possible intermediate, but work by us [291] on the oxidation of ketones by these complexes

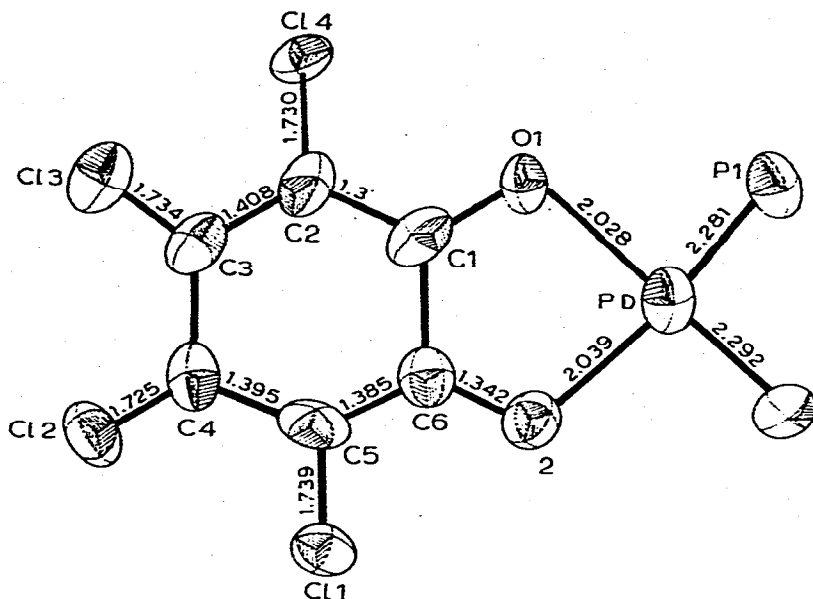


(106)

concludes that a free-radical chain mechanism is operative. Low frequency vibrations have been observed for $Ni(N_2)_n$, $Pd(N_2)_m$ and $Pt(N_2)_m$ ($n = 1-4$ and $m = 1-3$), and are assigned to metal-nitrogen stretching modes. The compound $Pt(N_2)_2$ has a value of ν_{NN} at 2197.6 cm^{-1} , and for the asymmetric Pt-N stretch at 360 cm^{-1} [292]. Condensation of Ni, Pd and Pt atoms with O_2 , N_2 , Ar mixtures at $6-10^\circ K$ gives compounds $M(O_2)_x(N_2)_y$. The assignments of the vibrational spectra are made with the assistance of isotopic labelling [293]. "End-on" bonded nitrogen and "side-on" bonded oxygen are observed. Mixed halocyno complexes (107) have been prepared by the



oxidative addition of cyanogen halides to $Pt(PPh_3)_4$ [294]. Metathetical replacement of X by N_3 , NCO, NCS, CNO leads to the corresponding pseudo-halide compounds. Infrared data is reported. Under suitable conditions halogens (X) (Cl_2 , Br_2 , I_2) add to $Pt(PPh_3)_4$ to give trans- $PtX_2(PPh_3)_2$ [295]. The conditions are such that subsequent isomerization of the compounds to the cis isomer does not occur. This can be done by using excess halogen which reacts with any free triphenylphosphine. The complex bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) is a white powder which is stable to air. An analysis of the ^{19}F nmr spectrum of the complex has concluded that two isomers exist [296]. A crystal structure of $Pd(O_2C_6Cl_4)(PPh_3)_2$ (108) shows the quinone chelated to the metal through



(108)

oxygen donors. Bonding parameters within the quinone ligand are consistent with a hydroquinone electronic structure [297]. A unified molecular orbital treatment of pentacoordination in transition metal compounds has appeared which is of general interest to any workers in transition metal organometallics [298].

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