

NICKEL, PALLADIUM AND PLATINUM ANNUAL SURVEY COVERING THE YEAR 1976

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ABBREVIATIONS

dpm	bis-1,2-(diphenylphosphino)methane
dpe	bis-1,2-(diphenylphosphino)ethane
dae	bis-1,2-(diphenylarsino)ethane
dpp	bis-1,2-(diphenylphosphino)propane
dpb	bis-1,2-(diphenylphosphino)butane
bipy	2,2'-bipyridyl
phen	1,10-phenanthroline
py	pyridine
Me	methyl

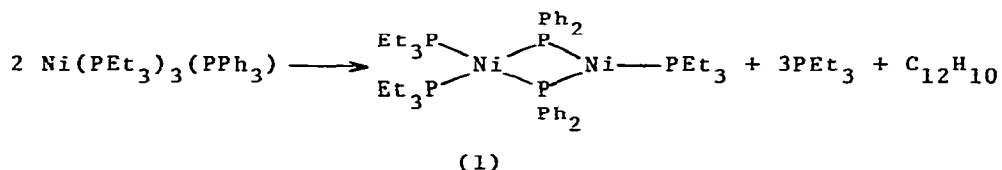
Nickel, palladium and platinum, Annual Survey covering the year 1975, see J. Organometal. Chem., 126 (1977) 431-499.

ABBREVIATIONS (cont.)

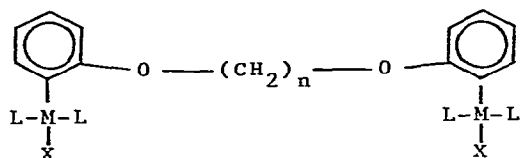
Et	ethyl
Ph	phenyl
Lut	lutidine
H Sal	salicylaldehyde
HAcacNCH ₃	4-methyliminopent-3-en-2-one
Sbzae	3-mercapto-1-phenyl-2-buten-1-one
acac	acetylacetonate
THF	tetrahydrofuran
1,5-COD	1,5-cyclooctadiene
p2	1,2-pyrazine
cp	cyclopentadienyl
im	imidazole

I. Metal-carbon σ complexes

Coordinately unsaturated complexes of Ni(0), Pd(0) and Pt(0) oxidatively add triphenylphosphine. When Ni(PET₃)₃(PPh₃) is heated, complex (1) is formed, along with biphenyl and triethylphosphine [1]. Similarly one of the products of the reaction of C₆F₅PPh₂



with Pd(PET₃)₃ is trans-Pd(C₆F₅)(PPh₂)(PET₃)₂. Treating trans-NiBr₂L₂ (L = PET₂Ph, PET₃) with LiC₆H₄O[CH₂]_nOC₆H₄Li (Li₂X) gives a compound NiL₂X containing a trans-bonded bidentate chelate 11-membered ring. With platinum(II) the compounds formed are binuclear species of type (2). The dibromo complexes [(Bu^tMe₂P)₂BrPt(C₆H₄O[CH₂]_nOC₆H₄)PtBr(PMe₂Bu^t)₂] react with NaBH₄ with replacement of the bromide by hydride. Palladium complexes of type [(Et₃P)₂XPd(C₆H₄O[CH₂]₄OC₆H₄)PdX(PET₃)₂] (X = Cl, Br) have also been reported. ¹H and ³¹P nmr data are given [2]. X-ray crystal structures have been solved for complexes [(p-YC₆H₄CH=CH₂)PtCl₂(p-Xpy) for (i) Y = NMe₂, X = Me; (ii) Y = H,

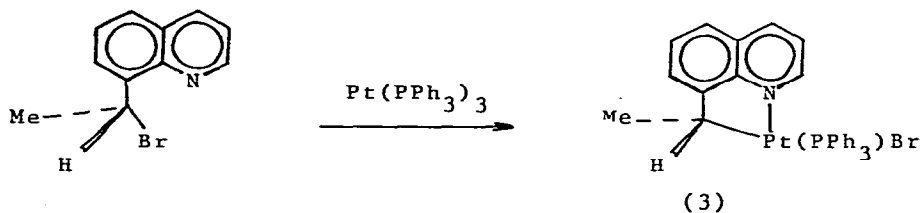


(2)

X = Me; (iii) Y = NO₂, X = Cl. The platinum-ethylene distances correlate with $J(^{195}\text{Pt}-^{13}\text{C})$ when both are plotted against σ_p^+ , a measure of the electron-donating ability of Y [3]. A study has been made of the pyrolysis of diarylbis(phosphine) platinum(II) complexes [4]. The compounds studied in the gas phase are PtR_2L_2 and $\text{PtR}_2(\text{L-L})$, where R = Me, C₆H₄Me-p; L = PPh₃ or P(C₆H₄Me-p)₃; L-L = dpe, dpm. The primary decomposition step is reductive elimination to form R₂. Secondary decompositions give non-stoichiometric amounts of biaryl and arene. A mechanism involving bridging diphenylphosphido groups is postulated, and intermediates similar to the compounds obtained in ref [1] are suggested. In a following paper the pyrolysis is studied in the presence of excess phosphine ligand [5]. This change in conditions has the effect of promoting the reductive elimination of biaryl from cis-PtR₂L₂ (R = aryl) complexes, and suppressing secondary decomposition modes.

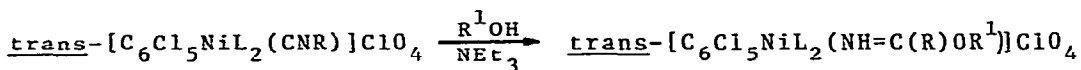
The rates of the uncatalyzed cis-trans isomerization of complexes cis-Pt(PEt₃)₂RBr (R = Ph, C₆H₄Me-p, C₆H₄Me-o, C₆H₄Et-o, 2,4,6-C₆H₂Me₃) have been measured in methanol and compared with the rates of bromide replacement in methanol [6]. The isomeric equilibrium is well over in the trans form. o-Substitution in the phenyl ring little affects isomerization rates but dramatically reduces the rate of attack by MeOH. The authors conclude an associative mode of activation for solvolysis with isomerization proceeding via a dissociative asynchronous mechanism. In this reaction the rate-determining step is one involving Pt-X cleavage. Rates and activation parameters are presented.

The complex (3) has been formed by the oxidative addition of optically active 8-(α -bromoethyl)quinoline to Pt(PPh₃)₃ [7]. The complex has opposite sign to that of the initial quinoline, and



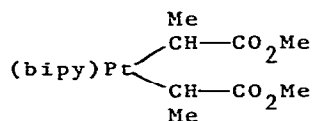
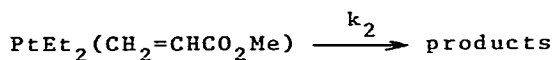
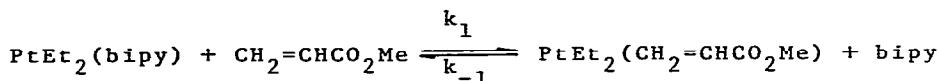
(3)

from considerations of relative polarizabilities about the chiral center it is concluded that the addition occurs with inversion of configuration. A series of cationic pentachlorophenylnickel(II) complexes trans-[C₆Cl₅NiL₂(CNR)]ClO₄ (L = PPhMe₂, PPh₂Me; R = Me, CH₂Ph, Ph) have been prepared from the neutral chloride, and then treated with alcohols in Et₃N to give imidate complexes (4) [8].



(4)

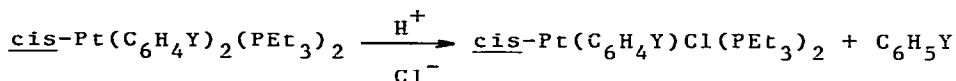
Infrared and ¹H nmr spectral data is reported. Bridged thiolato complexes cis-[Pt₂X₂(PMe₂Ph)₂(μ-SMe)₂] (X = Cl, I, Me, Ph) and cis-[Pt₂X₂(PMe₂Ph)₂(μ-SEt)₂] (X = Cl, Me) undergo a fluxional process involving inversion at the sulfurs. Treating the complexes with MeI gives oxidative addition-reductive elimination sequences leading to monomeric organoplatinum complexes. ¹H nmr data is reported [9]. The complex PdCl(C₆H₄Me-o)(phen) has been prepared from Pd[(PhCH=CH)₂CO]₂ and Hg(C₆H₄Me-o)Cl. Treating Pt(PPh₃)₃ with Hg(C₆F₅)₂ gives Pt(C₆F₅)(HgC₆F₅)(PPh₃)₂, which is converted to Pt(C₆F₅)(O₂CCF₃)(PPh₃)₂ with CF₃CO₂H [10]. Complexes Pd(Cl)R (R = Ph, C₆H₄Me-p, C₆H₄OMe-p, C₆H₄NO₂-m) prepared from Li₂PdCl₄ and RHgCl, react with N,N-dimethylallylamine to give [Pd(Cl)CH₂CHRCH₂NMe₂]₂. These complexes react with pyridine to give Pd(Cl)(py)CH₂CHRCH₂NMe₂ [11]. Methyl acrylate reacts with PtEt₂(bipy) to give ethylene and Pt{CH(OMe)(CO₂Me)}₂(bipy) [12]. The reaction is first order in both methyl acrylate and platinum complex, and is strongly retarded by excess bipy. A mechanism is proposed involving initial displacement of bipy from platinum by methyl acrylate, followed by β-elimination of ethylene from the ethylplatinum groups, insertion of methyl acrylate into the resulting Pt-H bonds, and re-coordination of bipy. The complex is proposed to have the structure (5). Continuing mechanistic studies on electrophilic attack on Pt-C bonds has been extended to complexes cis-Pt(C₆H₄Y)₂(PEt₃)₂. Kinetics have been reported for the formation of (7) from (6) [13]. The mechanism shown is one which accommodates the experimental findings. Correlation between the ¹³C nmr spectra of complexes trans-PtX(C₆H₅)(PEt₃)₂ has been made with sets of both Taft and Swain-Lupton substituent parameters. The results show reasonable correlation to use these parameters to describe the effects of substituents bonded to platinum. An anomalous behavior of substituents I and Br is found, and



(5)

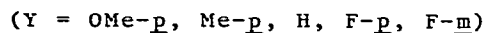
evidence is presented supporting significant π interactions between platinum and an aryl ligand [14]. From a study of X-ray photoelectron spectroscopy of aryl-nickel complexes it is concluded that π -bonding between nickel and the aryl is of little importance. Binding energies for Ni2p_{3/2}, Cl2p and P2s for the compounds NiCl(aryl)(PPh₃)₂ are reported, and as expected show little change on varying the substituent groups on the aryl [15]. Arylnickel complexes have also been used as reagents for the synthesis of indoles [16].

Reaction of the methylnickel compounds trans-NiXMeL₂ and Ni(acac)MeL (X = Cl, Br, I, CH₃CO₂; L = PMe₃) with CO yields compounds trans-NiX(COMe)L₂ and Ni(acac)(COMe)L. The reaction can be reversed by adding Ni(PMe₃)₄, which is itself converted to Ni(CO)(PMe₃)₃. The rate of decarbonylation increases in the order acac < CH₃CO₂ < Cl < Br < I. Strong protonic acids liberate CO and CH₄ but no acetaldehyde [17]. In the following paper is re-



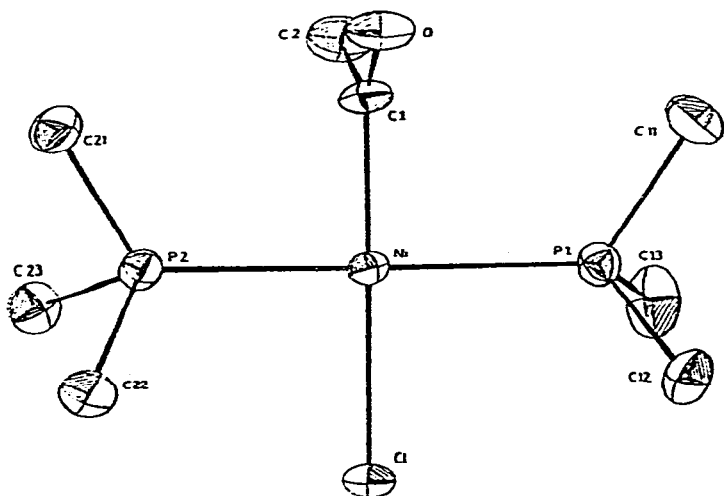
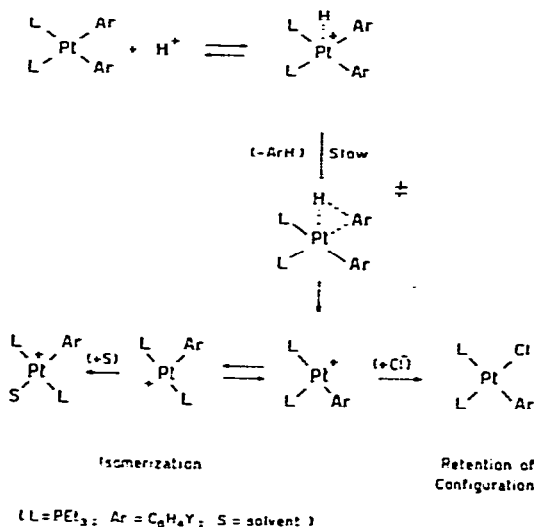
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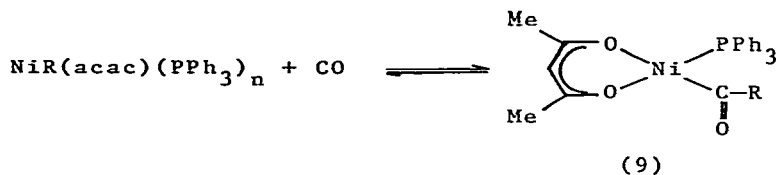


ported the crystal structure of the complex NiCl(COMe)L₂ (8) [18]. Comment is made on the C-Me bond length being unusually long. The dialkynickel complexes NiR₂L₂ (R = Me, Et, Pr; L = PEt₃; L₂ = bipy, dpe) react with CO to give ketones, diketones, and aldehydes. The nature of the product depends on the alkyl group and reaction temperature [19]. The dialkylpalladium complex PdMe₂L₂ (L = PEt₃, PPh₂) reacts with CO₂ to give complexes PdMe(CO₂)L₂ [20]. Evidence is largely based on ¹H nmr and infrared spectroscopy, and

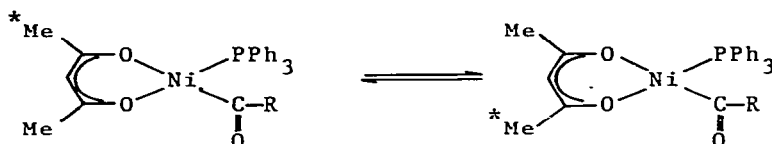
the finding that H_2SO_4 releases quantitative amounts of CH_4 and CO_2 from the complex. In non-polar solvents MeI adds to $\text{Ni}(\text{PMe}_3)_4$ to give the compound $\text{NiI}_2(\text{PMe}_3)_3$, whereas in polar solvents the cation $[\text{NiMe}(\text{PMe}_3)_4]^+$ is formed [21]. Convenient high yield syntheses of $\text{Ni}(\text{PMe}_3)_4$, $\text{Ni}(\text{CO})(\text{PMe}_3)_3$, and $\text{Ni}(\text{CO})_2(\text{PMe}_3)_2$ are described. New stable complexes $\text{NiX}(\text{C}_6\text{Cl}_5)(\text{dpe})$ ($\text{X} = \text{NO}_2$, CH_3CO_2 , $\text{C}_6\text{Cl}_5\text{O}$) and $[\text{NiL}(\text{C}_6\text{Cl}_5)\text{dpe}]\text{ClO}_4$ ($\text{L} = \text{py}$, im , 3,5- Me_2 pyrazole, α -, β -, γ -picoline) have been prepared from $\text{Ni}(\text{ClO}_4)(\text{C}_6\text{Cl}_5)\text{dpe}$. Spectral properties are reported. Treating $\text{NiCl}_2(\text{bipy})$ with $\text{C}_6\text{Cl}_5\text{MgCl}$



gives $\text{NiCl}(\text{C}_6\text{Cl}_5)(\text{bipy})$ [22]. When $\text{NiR}(\text{acac})(\text{PPh}_3)_n$ ($\text{R} = \text{Et}$, $n = 1$; $\text{R} = \text{Me}$, $n = 2$) is treated with CO the acyl complexes (9) are obtained. These complexes show a tendency to decarboxylate at room

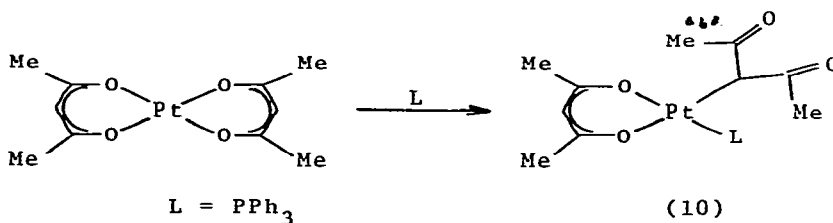


temperature and undergo disproportionation. A variable temperature ^1H nmr study reveals that the acac ligand in these acyl complexes exchanges according to the equilibrium shown. Rate data is presented [23]. In a further study on the dynamic behavior of

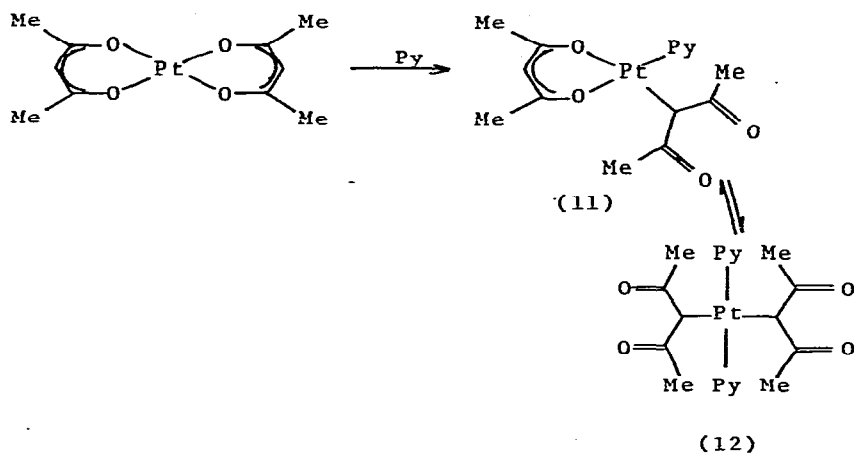


complexes of this type, the complexes $\text{NiR}(\text{acac})(\text{PPh}_3)_n$ have been investigated [24]. The exchange process is accelerated by added triphenylphosphine and the ^{31}P nmr spectrum shows replacement of this ligand by pyridine in that solvent. The activation energy for acac interchange is 10 kcal/mol. Interestingly, upon standing in solution the complex $\text{Ni}(\text{CH}_2\text{CD}_3)\text{acac}(\text{PPh}_3)$ undergoes H-D scrambling.

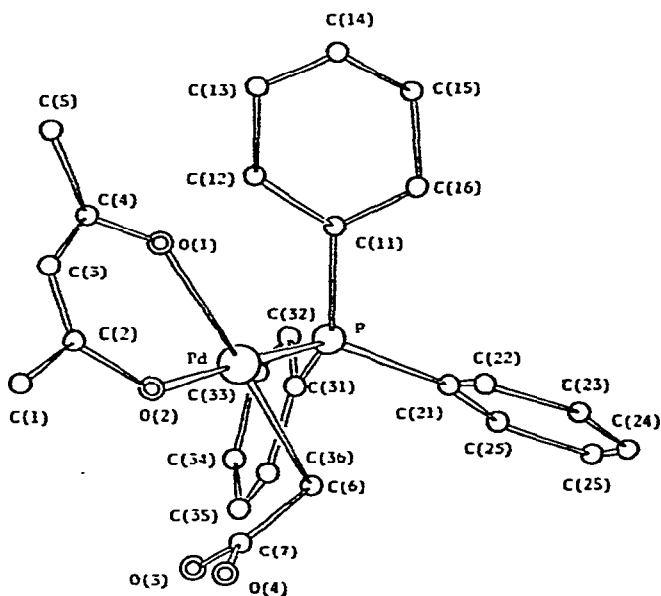
Addition of tertiary phosphines to $[\text{Pt}(\text{acac})_2]$, which is O-bonded, causes rearrangement of one of the ligands to a C-bonded tautomer (10) [25]. In the following paper a similar type of



effect is noted with pyridine. From heating the solutions both compounds (11) and (12) can be isolated [26]. A single crystal

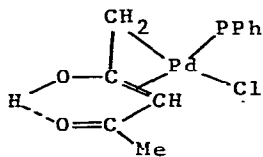


structure of the compound $\text{Pd}(\text{CH}_2\text{CO}_2\text{H})(\text{acac})\text{PPh}_3$ has been solved down to an R value of 0.032. The molecule forms a dimer through an inter-molecular hydrogen bond between acetic acid moieties [27].



Treating Na_2PdCl_4 with ethyl acetoacetate in aqueous alkali yields a compound which on treatment with pyridine gives $\text{Pd}(\text{l-ethoxycarbonylacetonato-C}^1)_2\text{py}_2$. The C-bonding of ethyl acetoacetate to Pd has been verified by ^1H nmr and infrared spectroscopy, and by single crystal structure analysis [28]. A method for the introduction

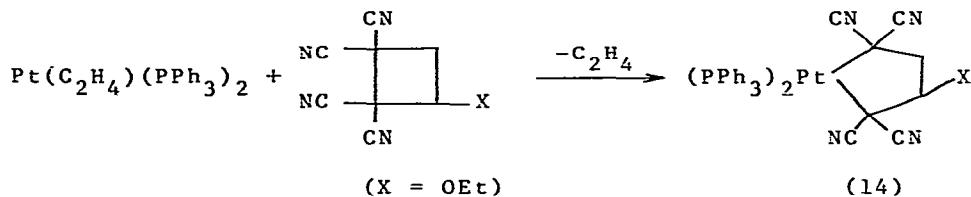
of carbon chains at the C-5 position of pyrimidine nucleosides using palladium compounds has been reported [29]. An unusual coordination for compound (13), obtained by treating $\text{PdCl}_2(\text{PhCN})_2$ with acacH followed by triphenylphosphine, has been proposed. The



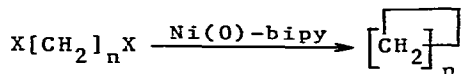
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basis for the structural claim is the ^1H nmr and infrared spectral data [30].

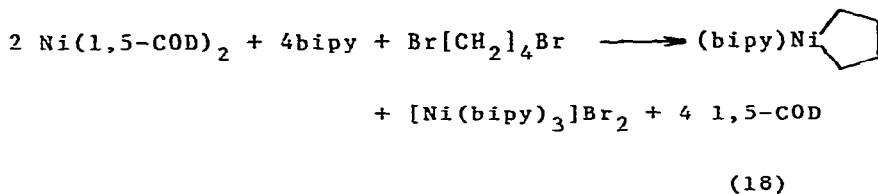
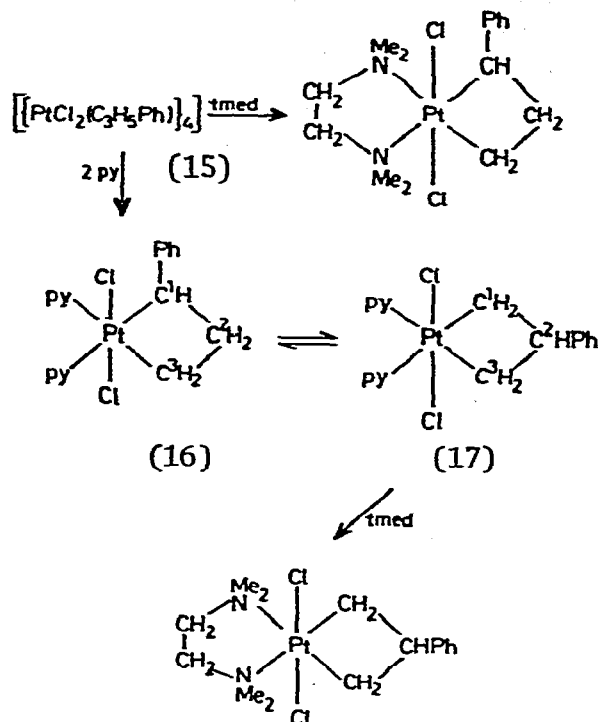
The compound $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ reacts with 1,1,2,2-tetracyano-3-ethoxycyclobutane and 1,1,2,2-tetracyano-3-(*p*-methoxyphenyl)cyclobutane to give platinum cyclopentane complexes [31]. A single crystal of the former complex (14) shows that the platinum has inserted into a C-C bond. An isomerization reaction of the platinum metallocyclobutane complexes $\text{Pt}(\text{CHPhCH}_2\text{CH}_2)\text{Cl}_2\text{py}_2$ and



$\text{Pt}(\text{CH}_2\text{CHPhCH}_2)\text{Cl}_2\text{py}_2$ is described, and the relevance of the observations to olefin metathesis noted [32]. Thus compound (15) isomerizes to give (16) and (17) in a 1:2.3 ratio in 45 min at 50° . The use of bipyridyl nickel (0) compounds for the synthesis of cycloalkanes has been reported [33]. These authors have also isolated compound (18) as a dark green crystalline solid, which liberates cyclobutane on treatment with strong π -acceptor ligands. The crystal structure of $\text{PtI}_2(\text{CH}_2)_4(\text{PMe}_2\text{Ph})_2$ (19) shows a Pt-carbon

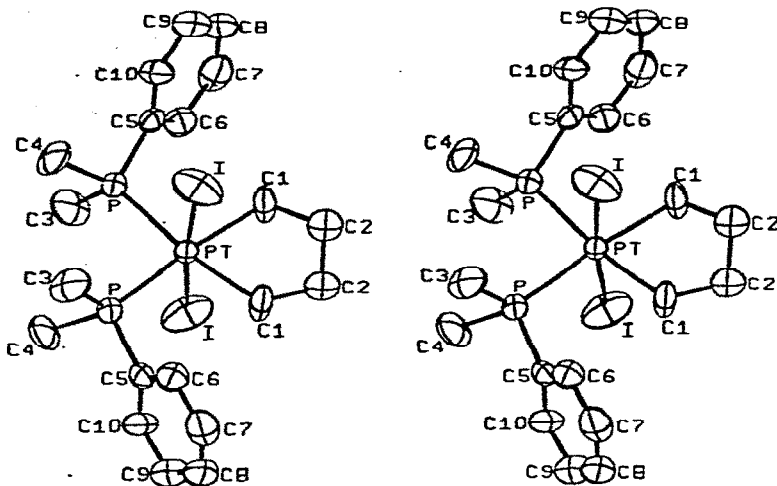


distance of 2.15(1) Å [34]. Methylated cyclopropanes react with chloroplatinic acid in acetic anhydride to give diacylation and

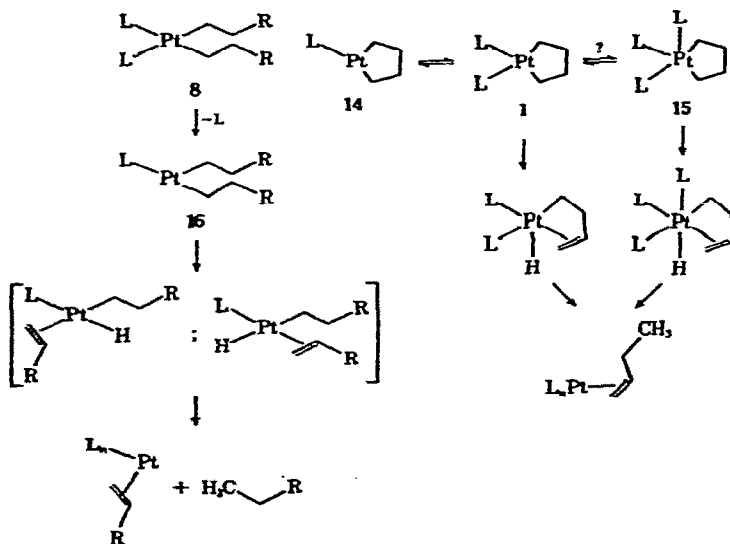


pyrylium ion formation [35]. The thermal decomposition of the metallocyclic compounds $\text{Pt}(\text{CH}_2)_4(\text{PPh}_3)_2$, $\text{Pt}(\text{CH}_2)_5(\text{PPh}_3)_2$, and $\text{Pt}(\text{CH}_2)_6(\text{PPh}_3)_2$ shows considerable retardation over the straight chain homologues. These authors suggest the higher stability of the heterocyclic compounds is a reflection of the failure of the relatively rigid 5- and 6-membered rings to permit the PtCCH dihedral angle to assume the preferred orientation for β -elimination and hydride formation. Product distributions are presented and the mechanism proposed is the one shown below [36].

Multiple-resonance methods have been used to determine the signs and magnitudes of $^3J(^{31}\text{P}\dots^1\text{H})$ and $^3J(^{31}\text{P}\dots^{19}\text{F})$ in methyl and trifluoromethyl complexes of Pt(II) and Pt(IV). Values for $^3J(^{31}\text{P}\dots^1\text{H})$ are most negative when the coupling path is trans than when it is cis, but the converse is true for



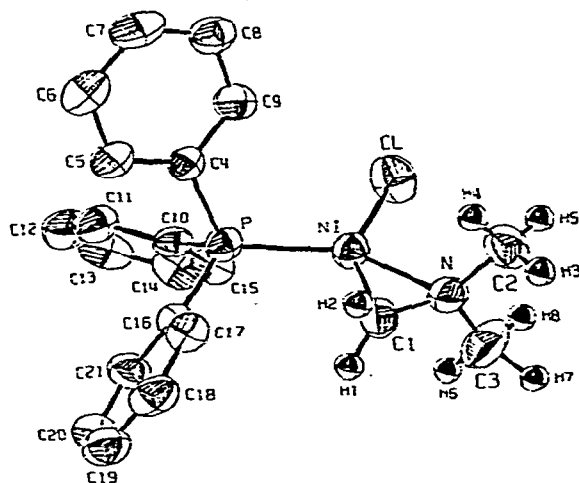
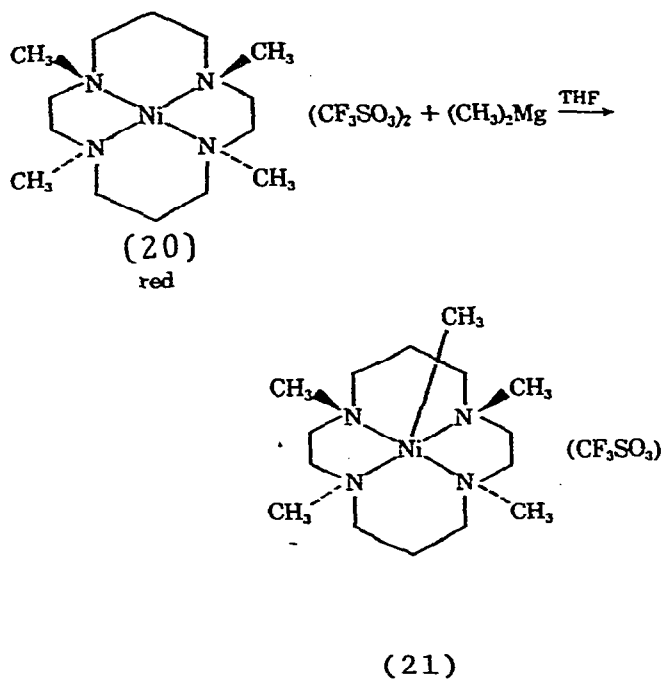
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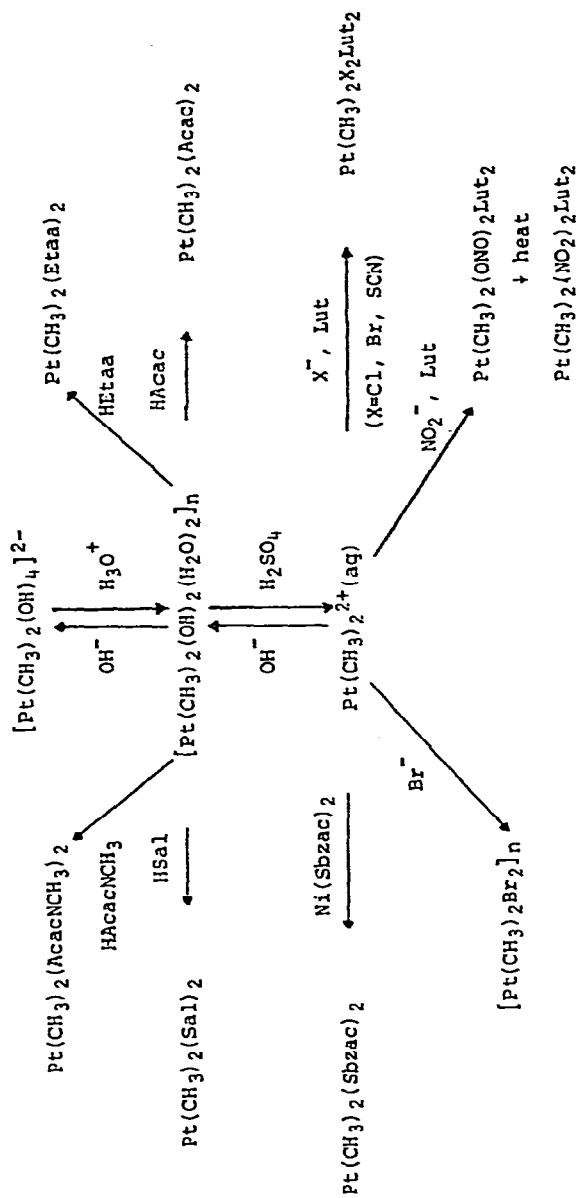
$^3J(^{31}\text{P} \dots ^{19}\text{F})$ [37]. Data and correlations of ^{195}Pt chemical shifts for 78 platinum complexes (most having Pt-C bonds) have been tabulated [38]. A pentacoordinate methyl nickel complex (21) has been prepared by alkylation of the macrocyclic nickel precursor (20) with dimethylmagnesium [39]. Aerobic incubation of micromolar

levels of K_2PtCl_6 and methylcobalamin at pH 2.0 results in complete demethylation of the cobalt compound to aquocobalamin without the accumulation of any corrinoid intermediates [40].

A series of cyanomethyl complexes of Pd(II) and Pt(II) have been isolated and characterized by 1H nmr and infrared spectro-

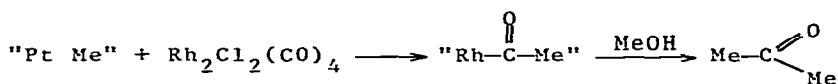


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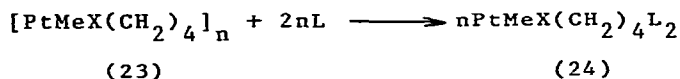


scopy. The range of complexes of type $\text{MX}(\text{CH}_2\text{CN})(\text{PPh}_3)_2$ are for $\text{X} = \text{N}_3, \text{NCO}, \text{NO}_2, \text{N}(\text{CO})_2\text{C}_6\text{H}_4, \text{NO}_3, \text{CH}_3\text{CO}_2, \text{Br}, \text{I}$ [41]. In a further article the ^1H nmr spectra of complexes cis- $\text{Pt}(\text{CH}_2\text{CN})(\text{SCH}_2\text{Ph})(\text{PPh}_3)_2$, trans- $\text{Pt}(\text{CH}_2\text{CN})(\text{SCH}_2\text{Ph})(\text{PPh}_3)_2$, and $\text{Pt}(\text{CH}_2\text{CN})(\text{SCH}_2\text{Ph})(\text{PH}_2\text{PCH}=\text{CHPPh}_2)$ are discussed, and methods outlined for determining stereochemistries of these cyanomethyl complexes [42]. The complex $\text{Ni}(\text{CH}_2\text{NMe}_2)\text{Cl}(\text{PPh}_3)_2$ (22) has been prepared by treating nickel(0) compounds with iminium salts [43]. A single crystal structure shows that the complex is a trigonally coordinated molecule with the iminium cation π -bonded to the nickel.

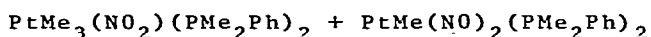
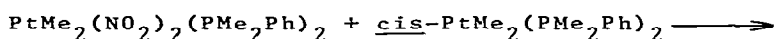
When $[\text{PtBr}_2\text{Me}_2]_n$ is treated with hot NaOH , a solution containing the anion $[\text{PtMe}_2(\text{OH})_4]^{2-}$ is formed. Upon acidification a white precipitate of $\text{PtMe}_2(\text{OH})_2(\text{H}_2\text{O})_2$ is formed. The substitution chemistry of this compound is shown here [44]. The symmetrization reaction between cis- $\text{PtMe}_2(\text{PMe}_2\text{Ph})_2$ and cis- $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$ to give cis- $\text{PtClMe}(\text{PMe}_2\text{Ph})_2$ has been found to be catalyzed by $\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PMe}_2\text{Ph})_2$ [45]. It is proposed that the catalyst is initially methylated by cis- $\text{PtMe}_2(\text{PMe}_2\text{Ph})_2$ to give cis- $\text{Pt}_2\text{Me}_2(\mu\text{-Cl})_2(\text{PMe}_2\text{Ph})_2$. A more detailed study has been made of the alkyl transfer reaction. The propyl group appears to be unique among



functional groups R studied in being the only one to undergo appreciable isomerization. Suggested pathways are presented [46]. An ^1H and ^{13}C nmr study over a range of temperatures for the system $\text{NiR}_2(\text{bipy})$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}$), and the system $\text{NiR}_2(\text{bipy})$ -alkene, has been made [47]. The formation constant K for $\text{NiEt}_2(\text{bipy})(\text{alkene})$, and the thermodynamic parameters ΔG° , ΔH° , and ΔS° have been measured. The chemical shift changes and the thermodynamic data suggests strong coordination with alkenes which are stronger π -acceptors. When $\text{PtMeCl}(1,5\text{-COD})$ is treated with dpe or dpp , the monomeric complexes $\text{PtMeCl}(\text{dpe})$ and $\text{PtMeCl}(\text{dpp})$ are formed. With the ligand dpm a low yield of the compound $\text{PtMeCl}(\text{dpm})$ is obtained. Similar procedures have been used to prepare $\text{PtMe}_2(\text{dpe})$ and $\text{PtMe}_2(\text{dpp})$, and the effects of phosphine on the oxidative addition of I_2 or MeI is discussed [48]. The platinum(IV) complexes $[\text{PtMeX}(\text{CH}_2)_4]_n$ ($\text{X} = \text{Br}, \text{I}$) (23) have been prepared by addition of MeBr or MeI to $\text{Pt}(\text{CH}_2)_4(1,5\text{-COD})$. Cleavage with $\text{L} = \text{bipy}, \text{PMe}_2\text{Ph}, \text{dpe}$ gives monomers (24) [49].



The chemistry of NO and NO₂ with methylplatinum(II) complexes has been investigated [50]. With PtMe₂(PMe₂Ph)₂ the reaction with NO first gives cis-cis-cis-PtMe₂(NO)₂(PMe₂Ph)₂, which then isomerizes to the cis-cis-trans isomer. The final products are trans-PtMe(NO₂)(PMe₂Ph)₂ and fac-PtMe₃(NO₂)(PMe₂Ph)₂, formed by reaction of cis-PtMe₂(PMe₂Ph)₂ with PtMe₂(NO₂)₂(PMe₂Ph)₂. On treating cis-PtMe₂(PMe₂Ph)₂ + 4NO \longrightarrow PtMe₂(NO₂)₂(PMe₂Ph)₂ + N₂

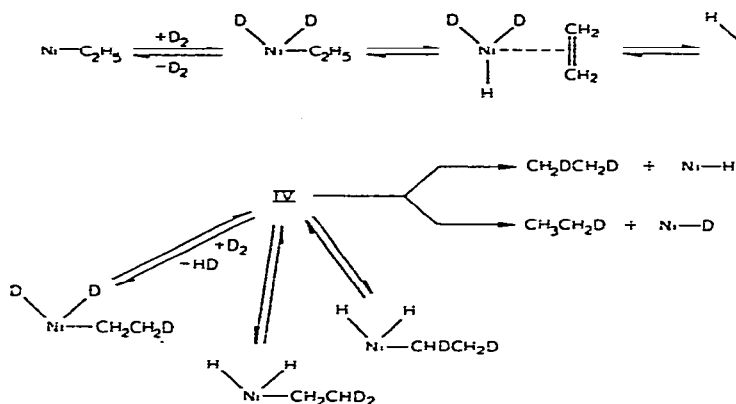


cis-PtMe₂(PMe₂Ph)₂ with NO₂ the product is cis-cis-trans-PtMe₂(NO₃)₂(PMe₂Ph)₂. The complex trans-PtHI(PMe₂Ph)₂ reacts with NO to give cis-PtI(NO₂)(PMe₂Ph)₂ which is also formed from cis-Pt(NO₂)₂(PMe₂Ph)₂ and PtI₂(PMe₂Ph)₂. Triorganotin chlorides add to Pt(0) with Sn-C rather than Sn-Cl bond cleavage. Products of type cis-PtR(SnR₂¹X)(PPh₃)₂ (R = Ph, R₂¹X = Ph₂Cl, MePhCl, Me₂Cl, BrPh₂, Ph₂I, Ph₂OH, Ph₂ONO₂, Ph₃) are formed from Pt(C₂H₄)(PPh₃)₂ and SnPhR₂¹X [51]. The known complex cis-PtPh(GePh₂OH)(PET₃)₂ can be formed by insertion of Pt(PET₃)₂ into a Ge-Ph bond. A series of mononuclear methoxy complexes MR(OMe)(PPh₃)₂ (M = Pd, Pt, R = aryl or alkenyl) have been prepared by treating the corresponding chlorides with NaOMe. The complexes will hydrolyze to the hydroxy complexes. Stabilities of the compounds are discussed [52]. Treating benzylpalladium(II) or platinum(II) compounds with m-chloroperbenzoic acid yields the compound m-ClC₆H₄CO₂CH₂Ph [53].

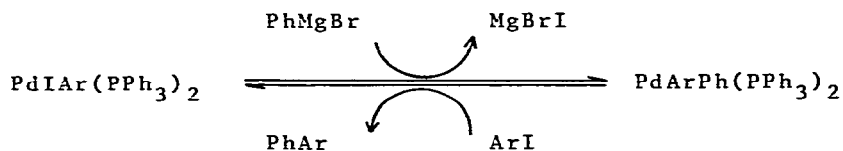
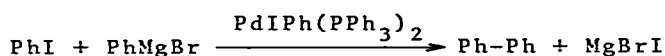
When the compounds NiMe₂(bipy) and NiEt₂(bipy) are reacted with D₂ the former complex gives CH₃D and CH₄, and the latter complex gives C₂D₆, C₂HD₅, C₂H₂D₄, C₂H₃D₃ and C₂H₄D₂, in addition to C₂H₅D and C₂H₆. A mechanism involving oxidative addition, β-elimination, and hydrido-deuterido exchange is postulated [54]. Interestingly H atoms in the 4- and 6-positions of the bipyridyl ligand also undergo exchange with D₂. Phenylselenol, diphenylphosphine, and diphenylarsine cleave the Me-Pt bond in Pt(II) compounds, but N-bromosuccinimide and 2-nitrophenylsulfenyl chloride oxidize the complexes without Pt-Me cleavage to methylplatinum(IV)

complexes [55].

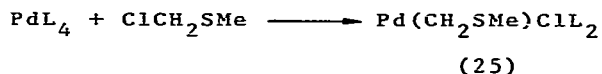
The new complexes $\text{Pt}(\text{C}_6\text{F}_5)_2\text{dpe}$ and *cis* and *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{L} = \text{PBu}_3, \text{AsPh}_3$) are described along with their oxidative addition products of Cl_2 and Br_2 [56]. The palladium catalyzed cross-coupling of aryl halides with Grignard reagents yields a variety of biaryls and alkylbenzenes [57]. A kinetic study of the reaction of $\text{PtPh}_2(\text{bipy})$ with MeI to give $\text{PtPh}_2(\text{I})\text{Me}(\text{bipy})$ follows the rate law: $\text{rate} = k_2[\text{PtPh}_2(\text{bipy})][\text{MeI}]$. The rate is enhanced in solvents of increasing polarity [58]. Oxidative addition of



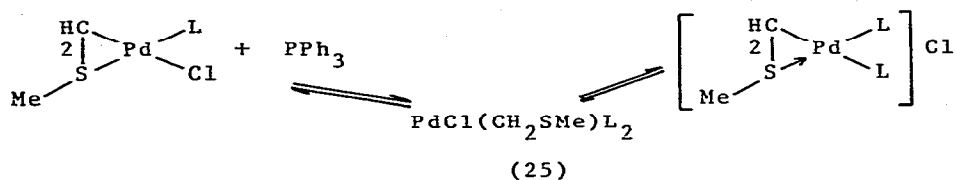
MeSCH_2Cl to PdL_4 ($\text{L} = \text{PPh}_3, \text{PMePh}_2$) gives a complex $\text{Pd}(\text{MeSCH}_2)\text{ClL}_2$



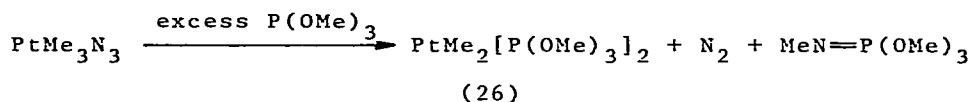
which dissociates in solution [59]. In the thermal decomposition of the compounds $\text{PtX}(\text{C}_3\text{H}_6)\text{L-L}$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L-L} = \text{bipy}, \text{phen}$) the



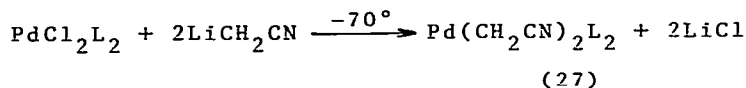
products are cyclopropane, and the reaction is first order in



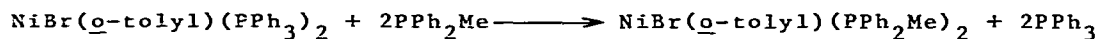
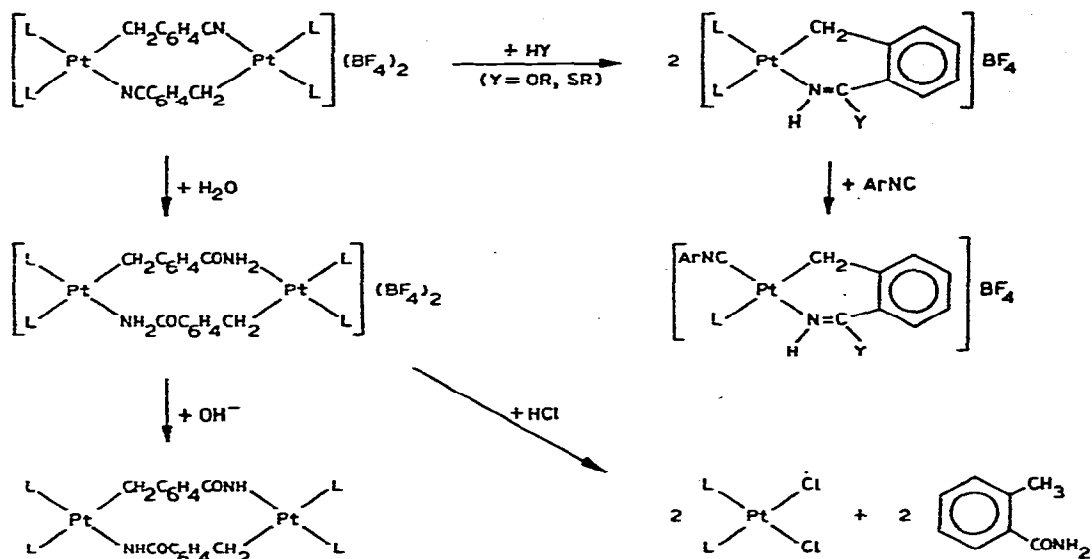
platinum complex [60]. The complexes $\text{PtMePh}_2\text{I}(\text{L-L})$ ($\text{L-L} = \text{bipy}$, phen) can be prepared by the oxidative addition of MeI to complexes $\text{PtMe}_2(\text{L-L})$. These stable compounds can be used for metathetical replacement of I by Cl , Br , CN , SCN , CNO , N_3 [61]. The complex cis- $\text{PtMe}_2[\text{P}(\text{OMe})_3]_2$ (26) can be prepared by treating $[\text{PtMe}_3\text{N}_3]_4$ with $\text{P}(\text{OMe})_3$ [62]. Nucleophilic addition of alcohols, thiols and



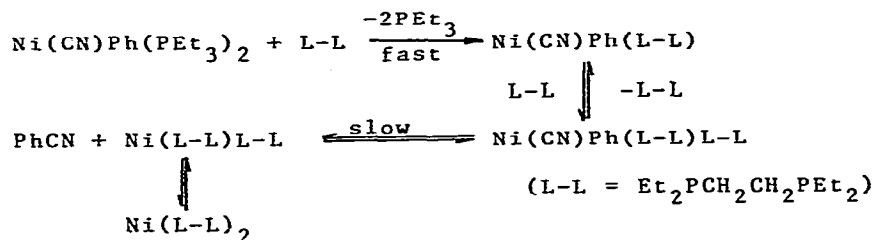
water to the coordinated CN group of cis- $[\text{Pt}(\text{o-CH}_2\text{C}_6\text{H}_4\text{CN})(\text{PPh}_3)_2]_2(\text{BF}_4)_2$ gives stable N -bonded imino-ether, iminothioether and amide complexes [63]. In further work these authors have extended this study to amines when stable amidine complexes are formed [64]. Similar starting compounds $\text{Pd}(\text{CH}_2\text{CN})_2\text{L}_2$ ($\text{L} = \text{PPh}_3$, $\text{Bu}_3^{\text{n}}\text{P}$; $\text{L}_2 = \text{dpe}$, bipy) (27) have been prepared from lithium cyanomethanide and PdCl_2L_2 [65].



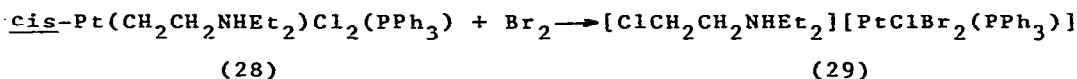
Neutral and cationic pentafluorophenylpalladium(II) complexes, $\text{PdX}(\text{C}_6\text{F}_5)(\text{AsPh}_3)_2$ ($\text{X} = \text{Br}$, I , CN , SCN , CNO , CH_3CO_2 , NO_3 , ClO_4) and $[\text{Pd}(\text{C}_6\text{F}_5)\text{L}(\text{AsPh}_3)_2](\text{ClO}_4)$ ($\text{L} = \text{py}$, PET_3 , PPh_3 , SbPh_3 , OPPh_3) and $[\text{Pd}(\text{C}_6\text{F}_5)\text{L}_3](\text{ClO}_4)$ ($\text{L} = \text{AsPh}_3$, py , PET_3 , PPh_3) have been reported [66]. Similarly a series of new complexes $\text{PdX}(\text{C}_6\text{Cl}_5)(\text{PET}_3)_2$ ($\text{X} = \text{Cl}$, I , NCS , NCO , N_3 , NO_2 , CN , OC_6Cl_5 , ClO_4) and $[\text{Pd}(\text{C}_6\text{Cl}_5)\text{L}(\text{PET}_3)_2]\text{ClO}_4$ ($\text{L} = \text{py}$, $\alpha\text{-pic}$, $\beta\text{-pic}$, $\gamma\text{-pic}$) have been prepared from $\text{PdBr}(\text{C}_6\text{Cl}_5)(\text{PET}_3)_2$ [67]. In a ^{31}P nmr study of exchange reactions of $\text{NiBr}(\text{o-tolyl})(\text{PPh}_3)_2$ with tertiary phosphines it has been concluded that the ligand exchange equilibria are dominated by steric factors [68]. Mechanistic studies on the reaction

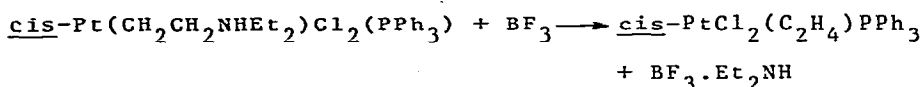
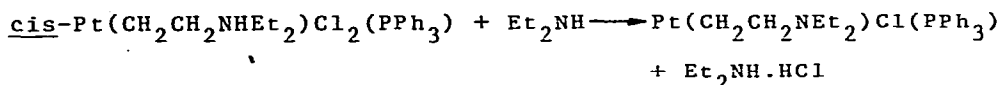


of the complex $\text{Ni}(\text{CN})\text{Ph}(\text{PEt}_3)_2$ with $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$, leading to reductive elimination of PhCN , indicates the rate-determining elimination step is preceded by substitution of PEt_3 by $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ [69]. A five-coordinate intermediate is proposed. The complex $\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{NHEt}_2)\text{PPh}_3$ (28) reacts in a manner depending on the reagent. One pathway (with X_2 , CNBr , CO) involves $\text{Pt}-\text{C}$ bond attack, a second one involves reactivity at the nitrogen (bases),

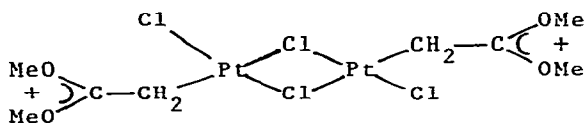


and the reaction with acids and electrophiles forms a platinum-olefin complex [70]. The crystal structure of (29) is also reported.





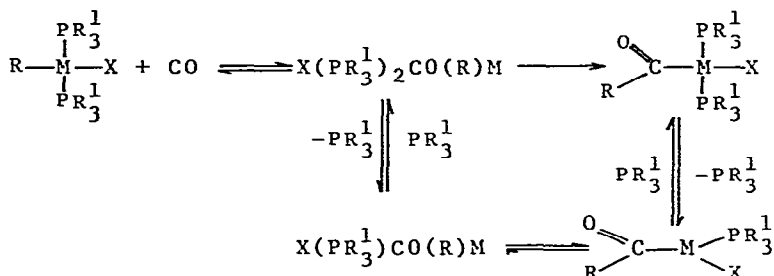
A crystal structure of the compound (30) has been solved and interpreted in terms of zwitterionic type compound [71].



(30)

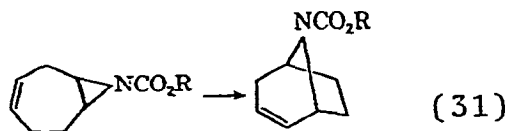
II. Metal complexes formed by insertion and related reactions

Carbonylation of a wide variety of complexes $\text{MX}(\text{R})\text{ER}_3^1$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{E} = \text{P}, \text{As}, \text{Sb}$; $\text{R} = \text{Ph}, \text{Et}, \text{Cy}, \text{OPh}$, etc.) shows pseudo first-order kinetics. Triarylphosphine ligands with electron donating substituents produced stepwise reactions, and the data is explained in terms of the mechanism shown below [72]. N-Carboxynortropidine (31) can be obtained by rearrangement of

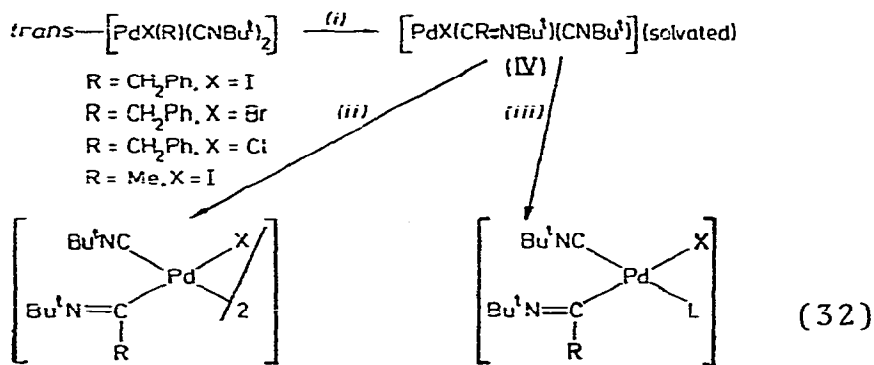


N-carbomethoxy-8-azabicyclo [5.1.0] oct-3-ene in the presence of $\text{PdCl}_2(\text{PhCN})_2$ [73]. The complex $\eta^5\text{-CpNi}(\text{PBu}_3)\text{CH}(\text{CN})_2$ readily inserts ethyl or phenyl-isothiocyanate to give compounds $\eta^5\text{-CpNi}(\text{PBu}_3)\text{SC}(\text{NRH})=\text{C}(\text{CN})_2$ [74]. With compounds RNCS , complexes of type $\eta^5\text{-CpNi}(\text{PPh}_3)\text{SC}[\text{NEtH}]=\text{C}(\text{CN})_2$ or $\eta^5\text{-CpNi}(\text{PPh}_3)\text{SC}(=\text{NPh})\text{CH}(\text{CN})_2$ are obtained. Treatment with PBu_3 gives ionic complexes. Reaction of trans- $\text{PdX}(\text{R}^1)(\text{CNBu}^t)_2$ ($\text{R} = \text{Me}, \text{PhCH}_2$) in the presence of

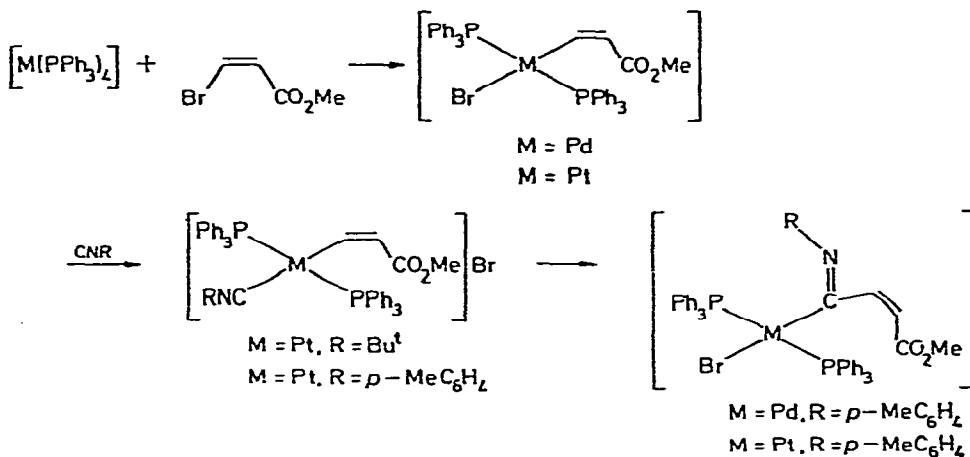
a nucleophile L gives the mono-insertion product



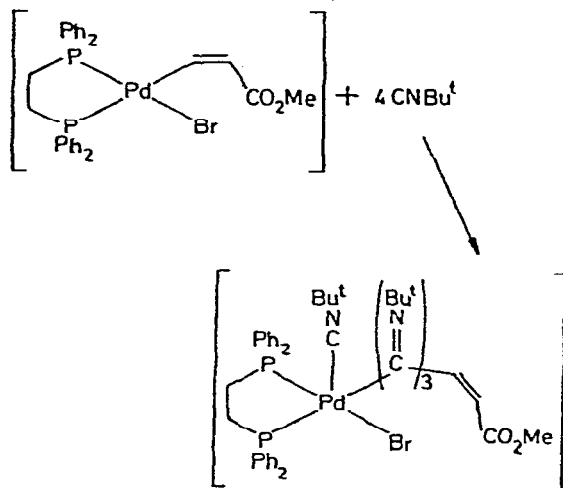
a, R = CH₂CH₃
b, R = CH₃



(i), solvent, slow; (ii), fast; (iii), L, fast

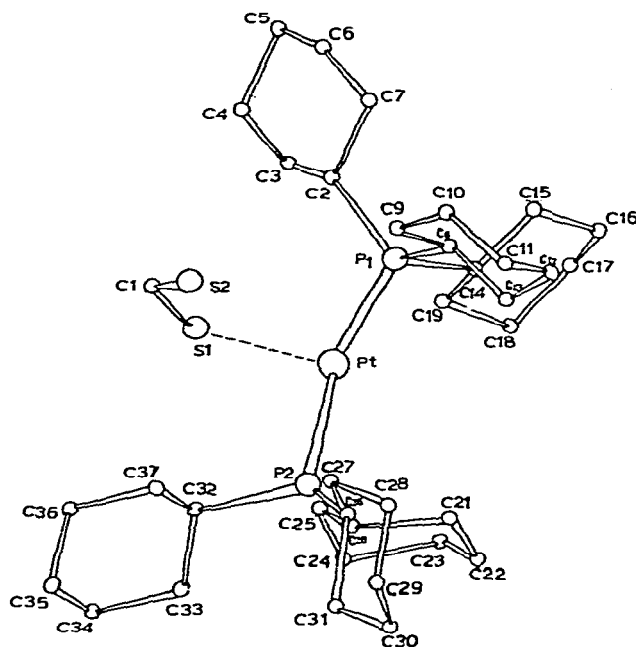


$\text{PdX}(\text{CR}^1=\text{NBu}^t)(\text{CNBu}^t)\text{L}$ (32). The authors have also studied intramolecular insertion reactions and given a rationalization of these insertion reactions [75]. Finally these authors present examples



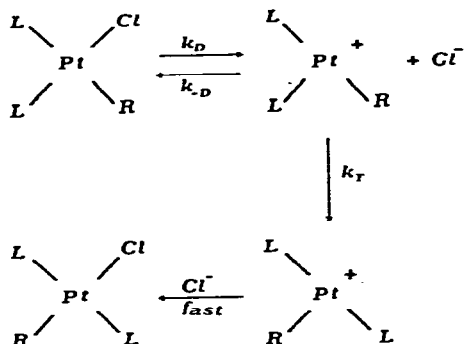
(33)

of multiple insertions of the isocyanide ligand (33). Carbon disulfide has been found to insert into the Pt-H bond of trans-PtH₂(PCy₃)₂ to give trans-PtH(S₂CH)(PCy₃)₂ (34). A single crystal structure of (34) shows it to have the sulfur group bonded as a monodentate thioformate anion [76]. The cis-trans isomerization

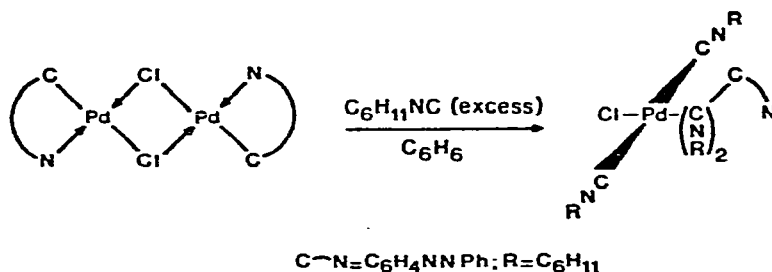


(34)

of cis-PtMe(Cl)(PEt₃)₂ is considered to proceed by a dissociative asynchronous mechanism [77]. Rate data is presented and is discussed in terms of a three-coordinate intermediate being involved



in ethylene insertion into the platinum-hydrogen bond. Treating nickelocene with 1-chloro-2-butene and with 3-chloro-1-butene gives mixtures of 1-methyl-2-propenyl-, trans-2-butenyl-, and cis-2-butenyl-cyclopentadienes [78]. A scheme involving allyls and insertion reactions is suggested. When the complex [PdCl(C₆H₄N=NPh)]₂ is treated with CyNC the insertion product PdCl(CNCy)₂{(C=NCy)₂C₆H₄NNPh} (35) is formed [79]. In the presence of the complex PdCl₂(PhCN)₂, diarylacetylenes are coupled with alkenes to give chloro(syn-1-chloro-anti-1-aryl-syn-3-

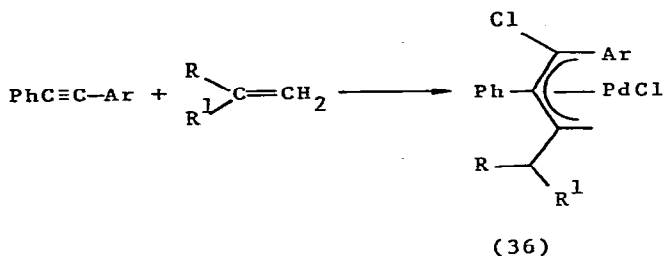


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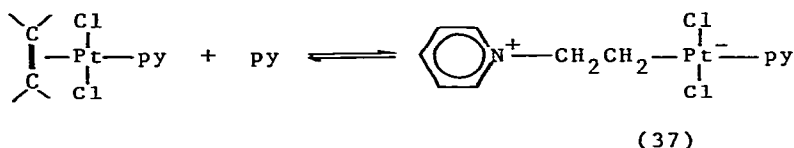
alkyl) π -allylpalladium compounds (36) [80]. ¹H nmr data is presented which is used for structure assignment.

III. Metal carbene and ylide complexes

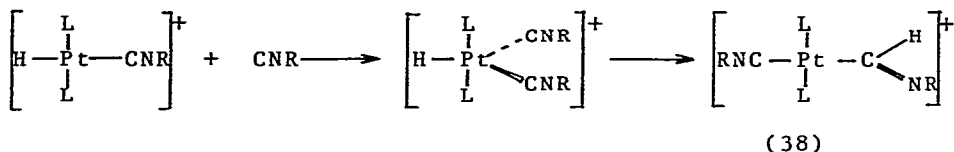
When the compound trans-PtCl₂(cis-ethylene-d₂)py is treated with excess pyridine at -15° reversible formation of the C-bonded



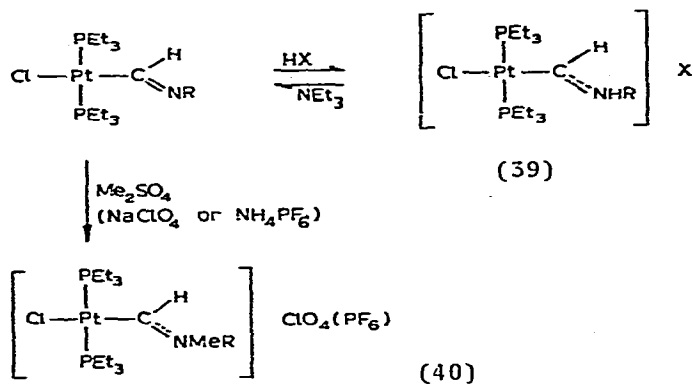
zwitterion (37) occurs. On release of the olefin to finally give PtCl_2py_2 , no isomerization of the olefin occurs [81]. Complexes of general formula $\text{PdCl}_2(\text{ylide})_2$ are formed in high yield on treating alkylphosphoranes ($\text{XY}_2\text{P}=\text{CHCOR}$), arsonanes ($\text{Ph}_3\text{As}=\text{CHCOR}$) and



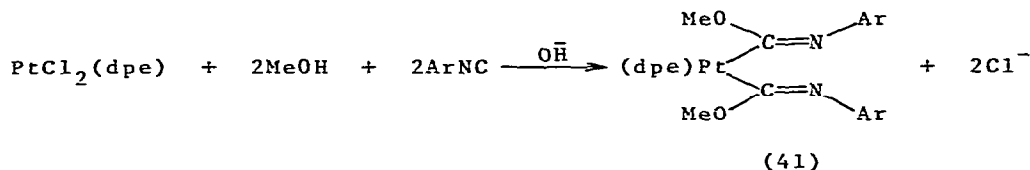
pyridinium ylides ($\text{C}_5\text{H}_5\text{N}^+ - \text{C}^- \text{HCOR}$) with $\text{PdCl}(\text{PhCN})_2$ [82]. Cross exchange between different series of ligands has been observed. The complexes trans- $[\text{PtH}(\text{CNR})\text{L}_2]\text{Cl}$ ($\text{R} = \text{p-tolyl}$; $\text{L} = \text{PEt}_3, \text{PMe}_2\text{Ph}$) undergo insertion of isocyanide into the Pt-H bond to give formimidoyl complexes (38) [83]. ^1H nmr studies of equilibria between syn and anti isomers is reported. In a further study of these



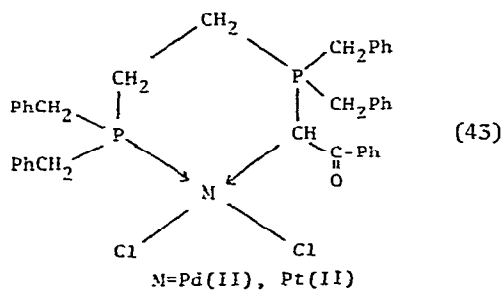
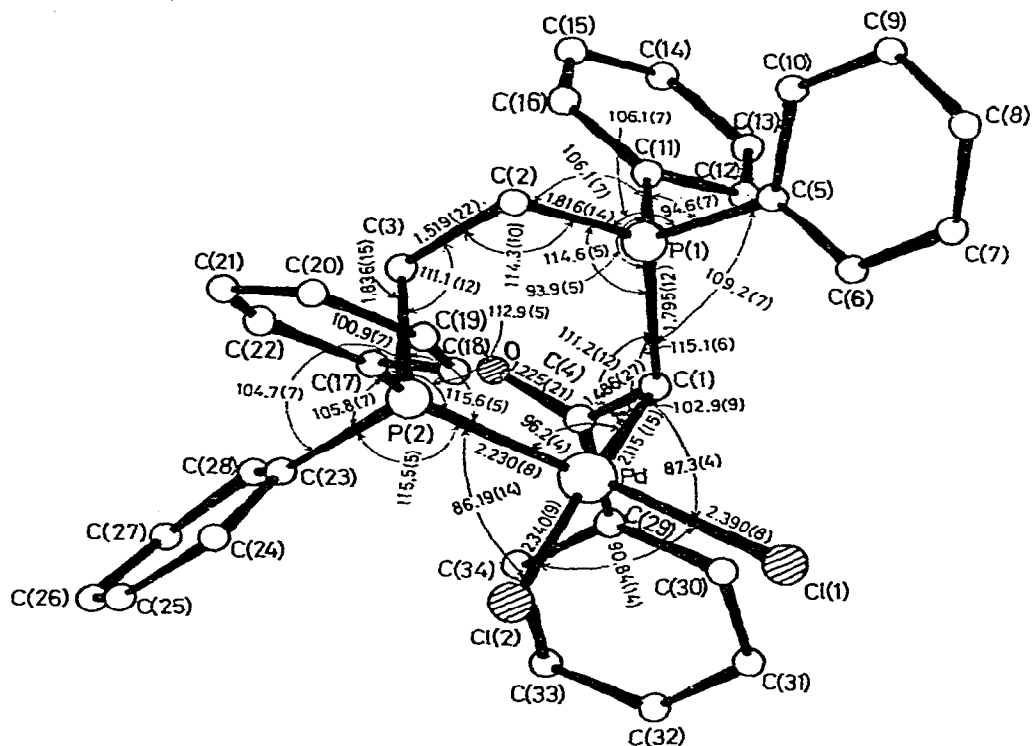
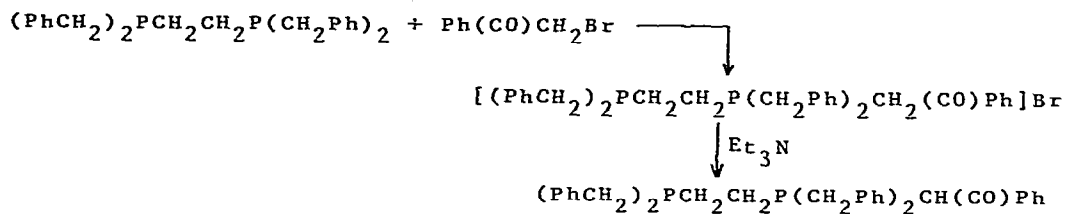
isocyanide systems, it has been found that protonation of (38) leads to the formation of a cationic secondary carbene product (39), and alkylation with methyl sulfate gives (40) [84]. Further ^1H nmr studies are reported and the reactions with p-toluidine studied. In an X-ray photoelectron study of carbenoid complexes of Pd(II) and Pt(II) it has been concluded from considerations of the $\text{Pt}4f_{7/2}$ and $\text{Pd}3d_{5/2}$ binding energies that carbenes are better donors than is MeNC . Correspondingly the Cls binding energy of the carbenoid ligand is less positively charged than the C atoms of the coordi-



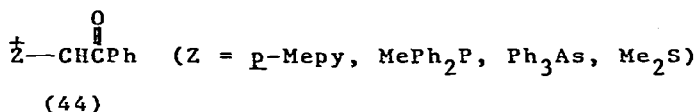
nated MeNC [85]. Complexes of a vinyl carbene-type ligand attached to platinum will bond to a second metal ion. These complexes contain a (methoxy)(N-arylamino) methyl ligand, and are found by treating an aryl isocyanide in alcoholic base solution with the metal ion. Treating an aryl isocyanide in methanol with $\text{PtCl}_2(\text{dpe})$ gives a complex (41). This complex will bind a second metal such as Co, Rh, Cd, Hg in the bidentate N-chelate ligand position [86]. A single crystal structure of the complex dichloro (benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane)-palladium (42) has been solved. The shift in $\nu(\text{CO})$ has previously



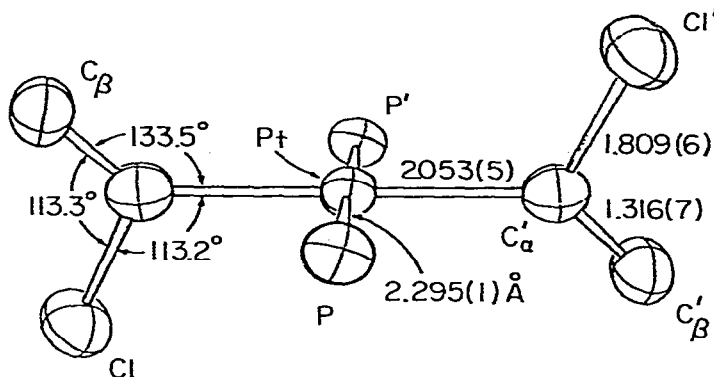
been used to identify coordination of the ylide carbon [87]. In a later article [88] these authors have prepared a range of complexes of this ylide ligand with a range of halides and pseudohalides, and with different substituents on the ylide ligand. The palladium and platinum complexes of a similar ylide have been reported (43) [89]. The ylide is prepared as shown along with the structure of the complexes (43). Cationic ylides of formula $[\text{MCl}(\text{Y})\text{L}]\text{BPh}_4$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{Y} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{Ph}_2\text{CH}$, $\text{C}(\text{O})\text{Ph}(n=1, 2)$; $\text{L} = 4\text{-Mepy}$, 3,5-dimethylpyrazole, PPh_3 , PCy_3 , PMePh_2 , $\text{P}(\text{OMe})_3$, AsPh_3 , SbPh_3) have been prepared. Complexes $[\text{MY}_2(4\text{-Mepy})_2]\text{BPh}_4$ ($\text{M} = \text{Pd}, \text{Pt}$) are also characterized [90]. In their final article of the year, these workers prepared the keto-stabilized mono-ylide complexes of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{Ph}_2\text{CHC}(\text{O})\text{R}$ ($\text{R} = \text{Ph}$; $n = 1, 2$; $\text{R} = \text{Ph}, \text{Me}, \text{OMe}$) with palladium(II) and platinum(II) [91]. A series of palladium(II) and



platinum(II) complexes of phenacylides have been reported [92]. These compounds are derived from the ligand (44) with a range of

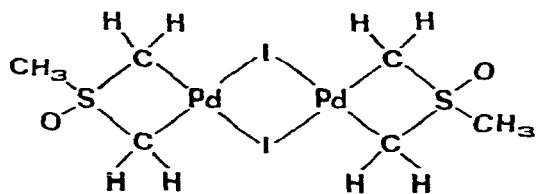
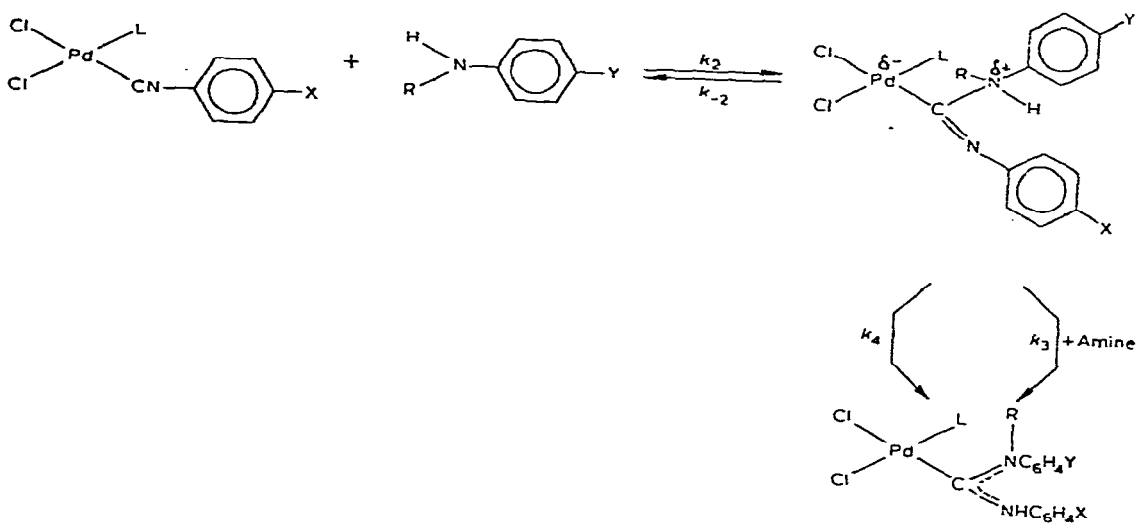
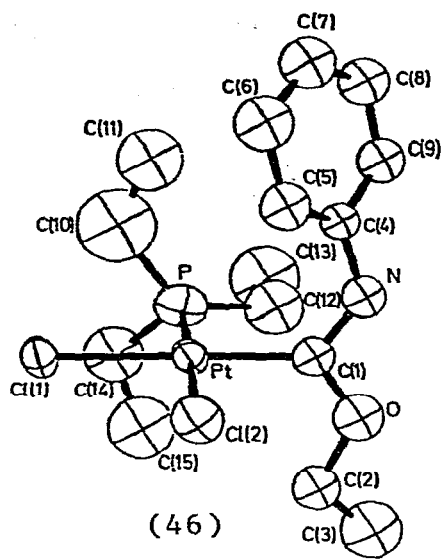


substituents. The reactions of Cl_2 with the complexes cis- $\text{PtCl}_2\{\text{C}(\text{NHR}^1)(\text{NHR}^2)\}\text{PEt}_3$, cis- $\text{PtCl}_2\{\text{C}(\text{OR}^3)(\text{NHR}^2)\}\text{PR}_3^4$ and trans- $[\text{PtCl}\{\text{C}(\text{NHR}^1)(\text{NHR}^2)\}(\text{PEt}_3)_2]\text{ClO}_4$ shows that when $\text{R}^1=\text{R}^2=\text{Me}$, the platinum(IV)-carbene complexes $\text{PtCl}_4\{\text{C}(\text{NHMe})_2\}\text{PEt}_3$ and $[\text{PtCl}_3\{\text{C}(\text{NHMe})_2\}(\text{PEt}_3)_2]\text{ClO}_4$ result, but when $\text{R}^1 = \text{Me}, \text{Et}$, and $\text{R}^2 = \text{Ph}$, o- ClC_6H_4 or p- ClC_6H_4 , o-metallation of the phenyl group occurs giving the complexes $\text{PtCl}_3\{\text{C}(\text{OR}^3)(\text{NHC}_6\text{H}_3\text{Cl-p})\}\text{PR}_3^4$, $[\text{PtCl}_2\{\text{C}(\text{NHR}^1)(\text{NHC}_6\text{H}_3\text{Cl-p})\}(\text{PEt}_3)_2]\text{ClO}_4$ and $\text{PtCl}_2\{\text{C}(\text{NHMe})(\text{NHC}_6\text{H}_3\text{Cl-o})\}(\text{PEt}_3)_2]\text{ClO}_4$ [93]. Spectral data assignment is given. The structure of trans- $\text{Pt}(\text{CCl}=\text{CH}_2)_2(\text{PMe}_2\text{Ph})_2$ (45) shows a long C-Cl bond. On dissolving the complex in methanol the complex trans- $[\text{Pt}(\text{CCl}=\text{CH}_2)(\text{C}(\text{OMe})(\text{Me}))(\text{PMe}_2\text{Ph})_2]\text{Cl}$ is formed [94]. The crystal



(45)

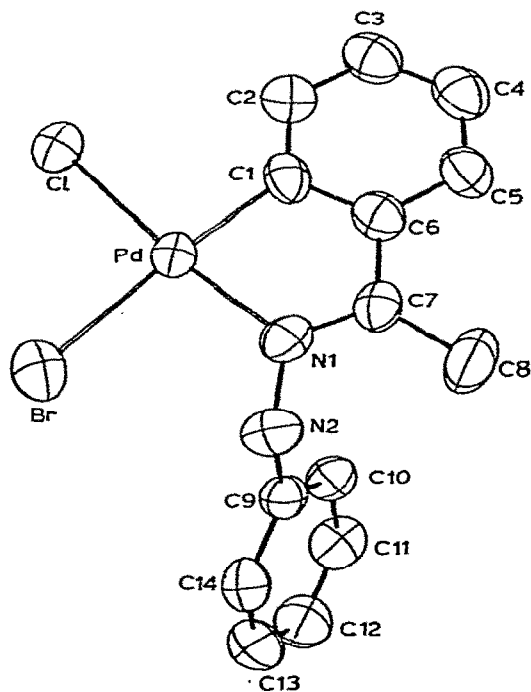
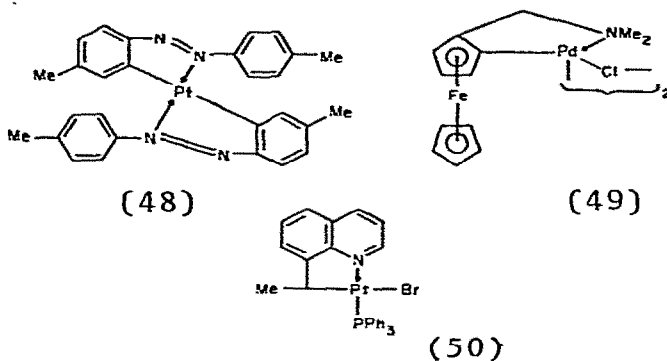
structure of the platinum(II) carbenoid complex cis- $\text{PtCl}_2\{\text{C}(\text{OEt})\text{NHPh}\}\text{PEt}_3$ (46) shows one of the shortest Pt-C (carbenoid) distances (1.96 Å) known [95]. Complexes of the ylides $\text{Z}-\text{CH}(\text{CO})\text{Ph}$ ($\text{Z} = \text{Ph}_2\text{MeP}^\ddagger, \text{Ph}_3\text{P}^\ddagger, \text{Ph}_3\text{As}^\ddagger, \text{Me}_2\text{S}^\ddagger$) with $\text{PdCl}(\text{Bu}_2\text{NO})$ have been prepared [96]. The kinetics of carbene formation from cis- $\text{PdCl}_2(\text{CNR})\text{PPh}_3$ ($\text{R} = \text{p-NO}_2\text{C}_6\text{H}_4, \text{p-ClC}_6\text{H}_4, \text{o-MeC}_6\text{H}_4, \text{o, o}^1\text{-Me}_2\text{C}_6\text{H}_3$) shows a stepwise mechanism via an intermediate formed by nucleophilic attack by amine on the isocyanide carbon. Steric strain in



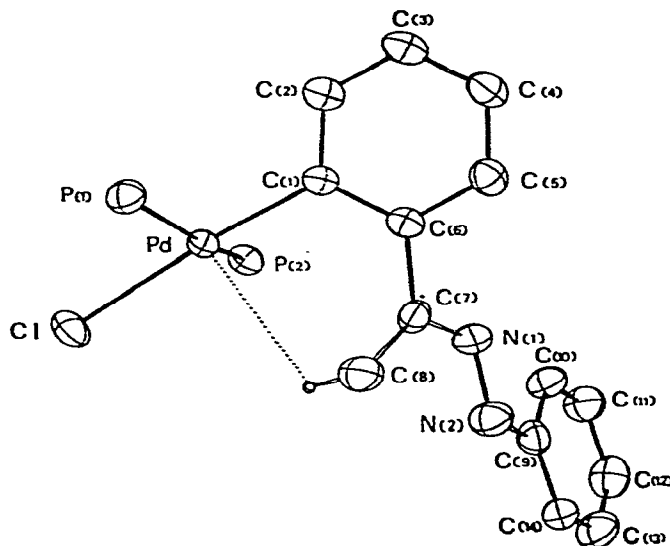
the intermediate caused by *o*-substitution decreases the rate [97].
 A complex $[\text{PdI}(\text{MeSO}(\text{CH}_2)_2)]_2$ (47) with a new methylsulfoxonium dimethylide chelate has been reported [98].

IV. Internal metallation reactions

High yield syntheses are reported for complexes (48-50) [99].

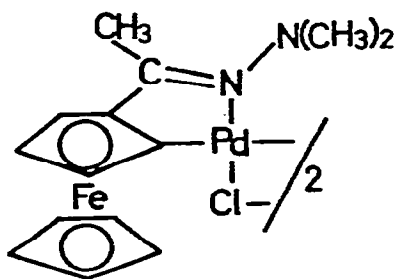


o-Metallated complexes of phenyl and *p*-tolyl(1,2-pyrazoles) are reported, where chelation is attained to Pd(II) or Pt(II) by coordination of the carbon in the aryl, and the nitrogen in the

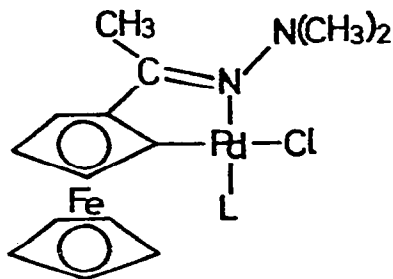


(52)

pyrazine [100]. The crystal structures of chlorobromo(N-(phenylamino)- α -methylbenzylideneimino-2-C,N)bis(triethylphosphine)palladium(II) (52) have been solved. In the latter compound the nitrogen is uncoordinated [101]. Treating acetylferrocene N,N-dimethylhydrazone with Li_2PdCl_4 gives the dimer (53), which can be cleaved by L (L = 4-Mepy, PPh_3) to give the complex (54) [102].

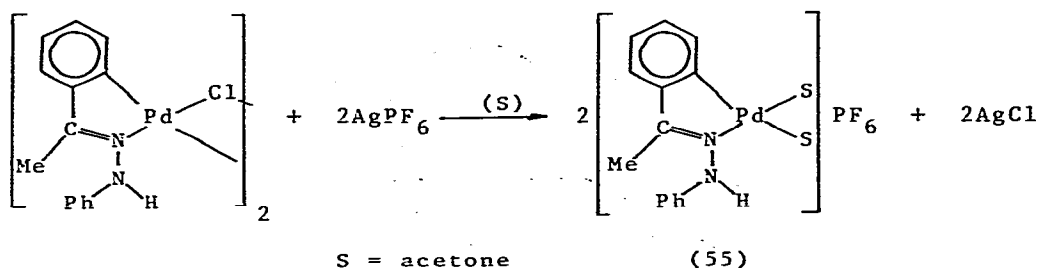


(53)



(54)

A crystal structure of trans- μ -dichloro-bis(phenylazophenyl-2C,N¹)-diplatinum(II) has been solved [103]. Complexes containing an o-metallated phenylazo group have been converted into solvated cations (55) using silver fluorophosphate in acetone [104]. The



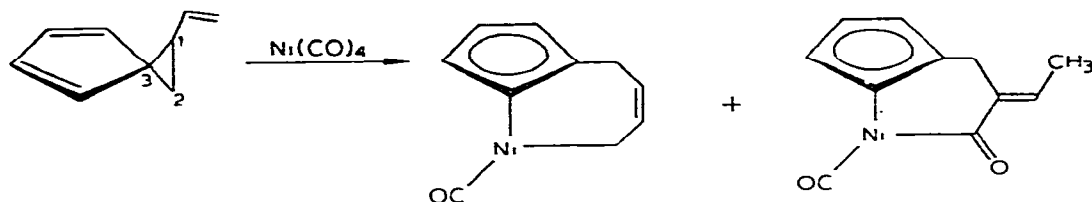
diazadiene, glyoxalbis(diisopropylmethylimine) forms a complex with nickel bromide, which reacts with o-tolylmagnesium bromide to undergo metallation with a methyl group in the γ -position [105]. The compound $\text{PdClL}(\text{o-PhNHN}=\text{CMeC}_6\text{H}_4)$ can be used to prepare new bimetallic compounds. The metal-metal bond is trans to the Pd-C σ bond. Complexes with $\text{Mn}(\text{CO})_5^-$ and $\text{cpFe}(\text{CO})_2^-$ have been prepared in solution [106]. Treating trans- $\text{PdCl}_2(\text{NH}_2\text{X})_2$ (X = NPhR or PhCH_2 ; R = Ph, Me, H) with acetophenone gives the cyclopalladated dimer $[\text{PdCl}(\text{C}_6\text{H}_4\text{CMe}=\text{NX})]_2$ with the acetophenone ring o-metallated [107].

V. Metal carbonyls and thiocarbonyls.

A theory combining extended Hückel one-electron orbital energies with atom-atom repulsive energies on structure and energy levels are calculated for $\text{Ni}(\text{CO})_4$ [108]. A detailed calculation on NiCO has been made with GVB and GVB-C1 wave functions. This leads to a qualitative description in which the Ni atom is neutral with a $4s^1 3d^9$ atomic configuration. The $d\pi$ pairs on the Ni are slightly involved in back-bonding to CO. Excited state levels and vibrational energies are given [109]. An INDO molecular-orbital method developed for use with 3d orbitals has been applied to $\text{Ni}(\text{CO})_4$. The Koopmans theorem values for ionization potentials agree with photoelectron spectroscopy data [110]. Values of ionization potentials and electron affinities within the nickel triad have been discussed in terms of stabilization of the zerovalent state for these elements [111].

On chemisorbed nickel it has been possible to observe the oxygen exchange reaction between H_2^{18}O and carbon monoxide [112]. When $\text{Ni}(\text{CO})_4$, mixed with various phosphines and AlCl_3 , is used in a suitable solvent the mixture is an active catalyst for propylene

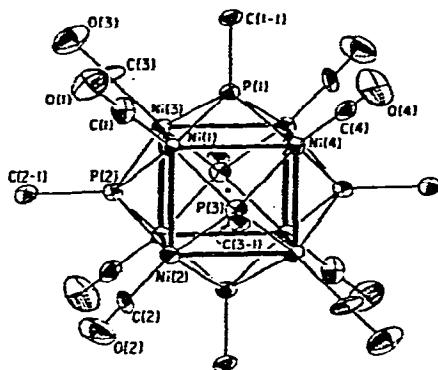
dimerization [113]. The mass spectra and appearance potentials for the major singly charged ions from $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$, and mixtures of the two, have been presented [114]. The mean M-C bond dissociation energy for $\text{Ni}(\text{CO})_4$ is $156.5 \text{ kJmole}^{-1}$. Nickel carbonyl has been used to cleave a cyclopropane ring in 1-vinylspiro [2.4]hepta-4,6-diene to give a mixture of compounds [115]. Nickel



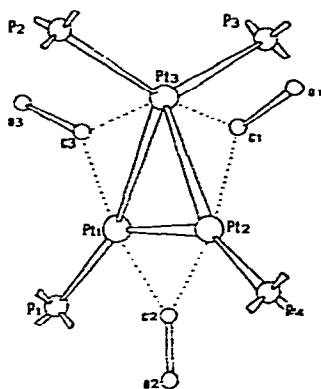
carbonyl has also been used in an organic oxidation reaction [116].

Nickel cluster carbonyls of ≤ 3 Ni atoms are formed by condensing at low temperatures monatomic Ni vapor with CO [117]. Supported platinum aggregates have been prepared by pyrolysis of Pt_{15} - Pt_6 carbonyl clusters in highly dispersed form in SiO_2 and $\gamma\text{-Al}_2\text{O}_3$. The infrared spectrum shows bands due to carbonyls in the 2000 cm^{-1} region [118]. Reduction of $\text{Ni}(\text{CO})_4$ leads to the isolation of the anions $[\text{Ni}_5(\text{CO})_{12}]^{2-}$ and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$. The anions are air sensitive and readily interconvert. The structure of $[\text{Ni}_5(\text{CO})_{12}]^{2-}$ shows 3 edge bridging carbonyls about the trigonal plane, and 9 terminal carbonyls with three on each axial nickel. For the anion $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ the nickels are arranged in a trigonal-antiprismatic geometry generated by two staggered $\text{Ni}_3(\text{CO})_3(\mu\text{-CO})_3$ triangular units [119]. In the following article these authors report isolation of the cherry red $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ ion, both by redox condensation of $\text{Ni}(\text{CO})_4$ and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$, and by oxidation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ with nickel(II) chloride [120]. The structure consists of three triangular $\text{Ni}_3(\text{CO})_3(\mu\text{-CO})_3$ units stacked along the ternary axes. These authors also report a series of new dianions $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = \sim 10, 6, 5, 4, 3, 2, 1$) by reducing $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or $\text{PtCl}_2(\text{CO})_2$ under CO (25°/1 atm) in the presence of base [121]. Infrared spectra and structural features are discussed. Treating the compound $[\text{NMe}_4]_2[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2$ with PhPCl_2 leads to the cluster compound $\text{Ni}_8(\text{CO})_8(\mu_4\text{-PPh})_6$ (56) [122]. The structure shows a cube of nickel atoms with each square face symmetrically capped by a phenylphosphido ligand and with the carbonyls terminal. A cluster compound $\text{Pt}_3(\text{CO})_3(\text{PCy}_3)_4$ (57) has been prepared by treating trans- $\text{PtH}_2(\text{PCy}_3)_2$ with CO at atmospheric pressure [123]. A

single crystal structure shows edge bridging carbonyls. Cluster carbonyls have been obtained by treating both monomeric and cluster triphenylphosphine platinum compounds with CO. Compounds



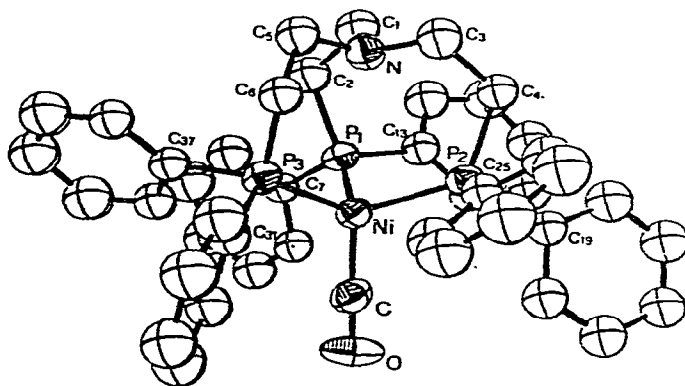
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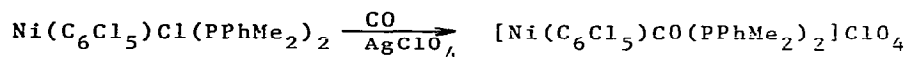
obtained are $\text{Pt}_4(\text{CO})_5(\text{PPh}_3)_3$, $\text{Pt}_3(\text{CO})_3(\text{PPh}_3)_4$, and a material claimed to be either $\text{Pt}_5(\text{CO})_5(\text{PPh}_3)_4$ or $\text{Pt}_6(\text{CO})_5(\text{PPh}_3)_5$ [124]. A series of complexes of the tripod ligand tris(2-diphenylarsinoethyl)amine with nickel have been isolated. Of interest to the organometallic chemist are cationic complexes containing a single carbonyl or phenyl group [125]. A similar carbonyl nickel complex (58) has been prepared with tris(2-diphenylphosphinoethyl)amine [126]. An X-ray structural analysis of the phenyl compound shows it to have a trigonal bipyramidal structure with the phenyl group

σ -bonded in the axial position. Bimetallic nickel carbonyls $[\text{Ni}(\text{CO})_3]_2\text{PR}_2$ have been obtained by carbonylation of the product of treating $\text{Ni}(1,5\text{-COD})_2$ with LiPR_2 and ethylene [127]. Among a



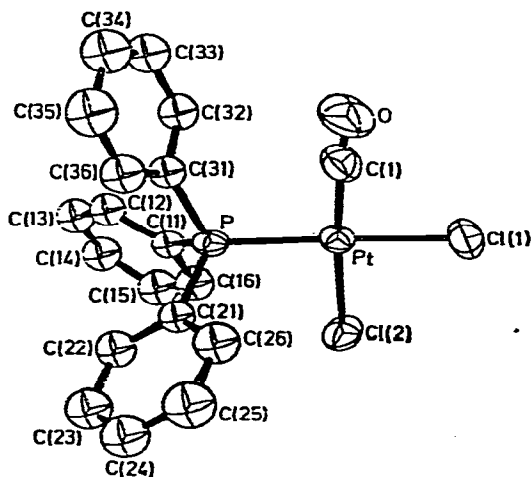
(58)

series of similar carbonyl complexes there is a report on the compounds $(\text{CO})_3\text{NiPMe}_2\text{PMe}_2\text{Ni}(\text{CO})_3$ and $(\text{CO})_2\text{Ni}[\text{PMe}_2\text{PMe}_2]_2(\text{Cr}(\text{CO})_5)_2$, where the phosphorus ligands are bridging [128]. The crystal structure of $\text{Ni}(\text{CO})_3(\text{PBU}_3^t)$ has been solved [129]. The chemistry of the phosphido complex $\text{cpFe}(\text{CO})_2[\text{P}(\text{CF}_3)_2]$ has been studied which will form a tricarbonylnickel complex $\text{cpFe}(\text{CO})_2[\text{P}(\text{CF}_3)_2]\text{Ni}(\text{CO})_3$ by coordination to the metals by a bridging phosphide [130]. A cationic complex $[\text{Ni}(\text{C}_6\text{Cl}_5)\text{CO}(\text{PPhMe}_2)_2]\text{ClO}_4$ has been prepared from trans- $\text{Ni}(\text{C}_6\text{Cl}_5)\text{Cl}(\text{PPhMe}_2)_2$. Treatment with ROH gives $[\text{Ni}(\text{C}_6\text{Cl}_5)(\text{COOR})(\text{PPhMe}_2)_2]\text{ClO}_4$ [131]. A crystal structure of the



compound cis- $\text{PtCl}_2(\text{CO})\text{PPh}_3$ (59) indicates that CO exerts an extremely small trans influence on chloride [132]. The possibility of a weak cis influence of a carbonyl group is suggested. Complexes $\text{Ni}(\text{CO})(\text{dpb})_2$ have been prepared where one of the ligands is monodentate. Treatment with $\text{P}(\text{OR})_3$ gives $\text{Ni}(\text{CO})(\text{dpb})[\text{P}(\text{OR})_3]$. Other reactions of the complex are described [133].

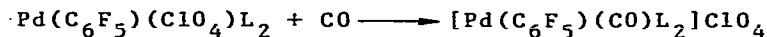
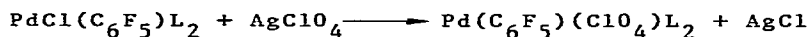
Carbon monoxide has been used to catalyze the isomerization of cis- $\text{PtCl}_2(\text{PBU}_3^n)_2$ to trans- $\text{PtCl}_2(\text{PBU}_3^n)_2$ [134]. There is a report on a tungsten-nickel carbonyl complex having a methylstibine bridge [135]. Organogermyl- and organostannyphosphine complexes of $\text{Ni}(\text{CO})_3$



(59)

have been prepared by substitution reactions of $\text{Ni}(\text{CO})_4$ [136]. The vibrational spectra in the carbonyl region, and both the ^1H and ^{31}P nmr spectra are discussed. Triphenylphosphite reacts with the complex $\text{Ni}(\text{CO})(\text{dpb})_2$ in dichloromethane with quantitative displacement of one dpb molecule. Interestingly the rate is accelerated by the presence of protonic acids, and these authors suggest the intermediacy of a labile hydrido nickel complex [137]. A second report has appeared on the structure of the anion $[\text{PtCl}_3(\text{CO})]^-$ [138]. The crystal structure of $\text{PtMe}(\text{CO})[\text{HB}(\text{pz})_3]$ shows a square planar geometry with only two of the three pyrazolyl groups coordinated to platinum. The Pt-C(methyl) and Pt-C(carbonyl) distances are 2.070(12) and 1.798(16) Å, respectively [139].

The carbonylation of complexes $\text{Pd}(\text{C}_6\text{F}_5)(\text{C}_{10}\text{O}_4)\text{L}_2$ (where $\text{L} = \text{PR}_3$ or L_2 is bipy or phen) gives compounds $[\text{Pd}(\text{C}_6\text{F}_5)\text{COL}_2]\text{C}_{10}\text{O}_4$ [140].

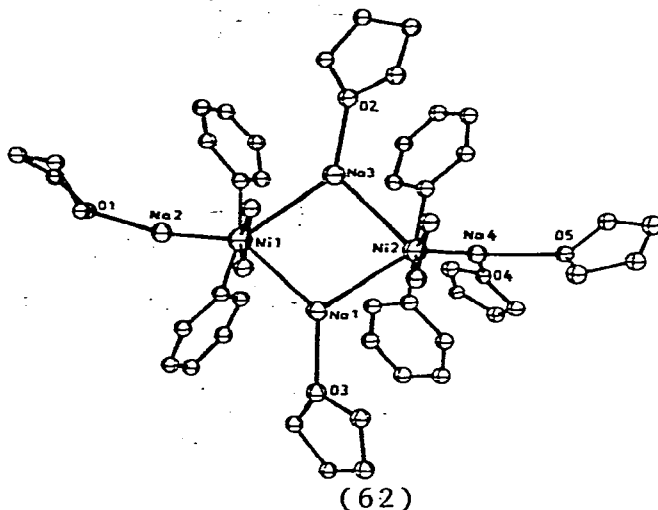


When $\text{PtCl}_2(\text{PPh}_3)_2$ is treated with CO in the presence of an amine the compound $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$ is formed [141]. Secondary amines under these conditions yield the dicarbonyl complexes $\text{Pt}(\text{CONR}_2)_2(\text{PPh}_3)_2$, and α -amino esters give carbonyl complexes $\text{MCl}[\text{CONHCHR}^1\text{CO}_2\text{R}](\text{PPh}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{R} = \text{Me}, \text{Et}$; $\text{R}^1 = \text{H}, \text{Me}$).

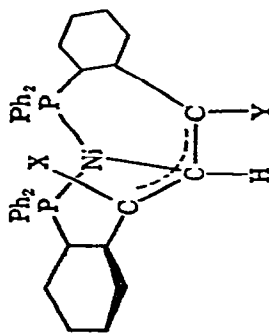
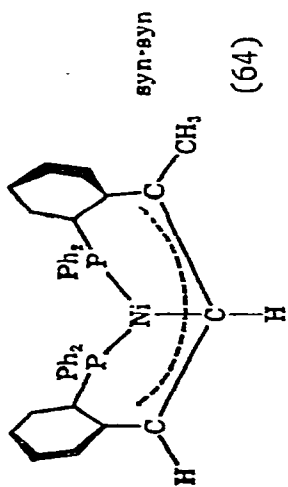
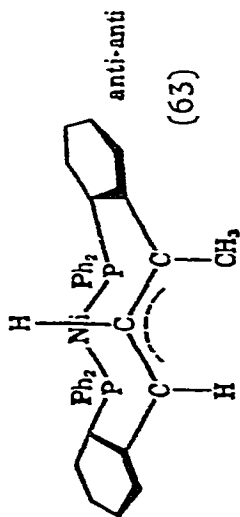
A published review on carbonyl complexes includes those of palladium and platinum [142].

VI. Metal olefin complexes.

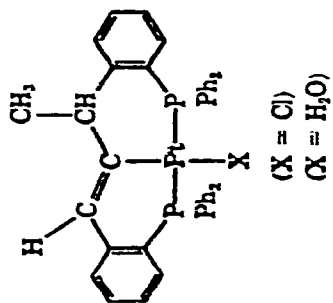
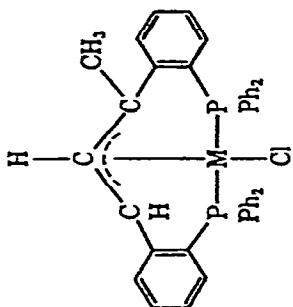
When all-*trans*-1,5,9-cyclododecatrienickel (0) is treated with a mixture of NaPh/LiPh and ethylene in diethyl ether two compounds (60) and (61) are formed [143]. These complexes have the stoichiometries $(\text{NaPh})_2\text{NiC}_2\text{H}_4(\text{Et}_2\text{O})_2$ (60) and $(\text{LiPh})_2\text{Ni}(\text{C}_2\text{H}_4)\text{Et}_2\text{O}$ (61). In the following paper the crystal structure of a similar compound $[\text{Ph}_2\text{NiC}_2\text{H}_4]_2\text{Na}_4(\text{THF})_5$ is reported (62) [144]. The red



compound is composed of two $\text{Ph}_2\text{NiC}_2\text{H}_4$ units and four $\text{Na}(\text{THF})_x$ ($x = 1, 2$) groups. A similar type of ethylene nickel complex anion $[\text{R-Ni}(\text{C}_2\text{H}_4)_2]^-$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) has been prepared by treating $\text{Ni}(\text{1,5-COD})_2$ with ethylene and alkylolithiums [145]. The crystal structure shows a trigonal planar geometry about the nickel atom. Ethylene chemisorbed on silica-supported Pd and Pt catalysts indicates coexistence of π -bonded species with σ -bonded $\text{M-CH}_2\text{CH}_2\text{-M}$ types. Evidence from infrared spectroscopy is presented [146]. The cocondensation of Ni atoms with C_2H_4 and $\text{C}_2\text{H}_4/\text{Ar}$ matrices of 15K is a direct route to complexes $\text{Ni}(\text{C}_2\text{H}_4)_n$ ($n = 1, 2, 3$) [147]. The infrared active $\nu(\text{C}=\text{C})$ stretching modes for all three complexes are assigned as are the respective $\text{Ni} \rightarrow \text{C}_2\text{H}_4$ charge transfer transitions in the uv. Experiments in solid C_2H_4 show that both $\text{Ni}(\text{C}_2\text{H}_4)_3$ and $\text{Ni}(\text{C}_2\text{H}_4)_2$ form on decomposition at 15K, but $\text{Ni}(\text{C}_2\text{H}_4)_2$, rather than $\text{Ni}(\text{C}_2\text{H}_4)_3$, is the favored complex on warming in the 20-60K range.

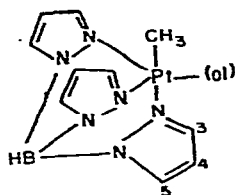


X = H, Y = CH₃ anti-syn
X = CH₃, Y = H syn-anti



Relevance to catalysis is discussed. Detailed synthesis of compounds $\text{Pd}(\text{C}_2\text{H}_4)(\text{PR}_3)_2$ ($\text{R} = \text{Ph}, \text{Cy}, \text{o-MeC}_6\text{H}_4\text{O}$) from $\text{Pd}(\text{acac})_2$, ethylene, and the appropriate phosphorus ligand have been published [148]. When Zeise's salt is treated with hydrazones, complexes of formulae trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{hydrazone})$ result [149]. Relative conformations are discussed. Further coordination chemistry of vinylphosphines has been reported. 1,3-Bis[(o-diphenylphosphino)phenyl]-trans-1-butene reacts with dichloro complexes of Ni(II), Pd(II), Pt(II). For Ni(II) a 1:1 isomeric mixture of (63) and (64) is formed. For Pd(II) complex (65) is formed, and a crystal structure is reported. For platinum treating $\text{PtCl}_2(\text{PhCN})$ with the ligand gives a complex (66) whereas treating $\text{PtClMe}(1,5\text{-COD})$ with the ligand gives (67) [150]. Enantioselective π -coordination of styrene has been investigated by ^1H nmr and cd spectroscopy for Pt(II) complexes of L-alanine in trans or cis-(N, olefin) form. Equilibration studies are reported for addition of free styrene [151]. Crotyl platinum(II) complexes $\text{PtCl}(\text{CH}_2\text{CH}=\text{CHMe})(\text{PPh}_3)_2$ and $\text{PtClL}(\text{CH}_2\text{CH}=\text{CHMe})(\text{AsPh}_3)_2$ have been prepared by addition of the compounds $\text{CH}_2=\text{CHCHMeCl}$ or trans- $\text{MeCH}=\text{CHCH}_2\text{Cl}$ to PtL_4 ($\text{L} = \text{PPh}_3, \text{AsPh}_3$) [152]. In benzene solution the σ -allylic form is the dominant species, but in chloroform the complex has the ionic π -allylic structure. The crystal structure of trichloro-(π -cis-pent-3-enylammonium)platinum(II) shows that the cis-pentenylammonium cation, coordinated through its double bond, has lost its pure cis configuration [153]. Complexes of di- and tri-peptides with Zeise's salt are reported [154]. An infrared study of the compound $\text{PtCl}_3(\text{H}_2\text{C}=\text{CHCH}_2\text{NH}_3^+)$, which has the ligand coordinated through the double bond, shows $\nu(\text{C}=\text{C})$ at 1349 or 1416 cm^{-1} . The band near 415 cm^{-1} is assigned to the stretching frequency for $\nu(\text{Pt-alkene})$ [155]. The coupling constants between alkyl protons and ^{195}Pt in $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{R}^1\text{R}^2\text{C}=\text{N.NR}^3\text{R}^4)$ is higher when the alkyl group is cis to the metal, with respect to the azomethine double bond, than when it is trans to it. Chemical shifts and coupling constants are reported for a series of these hydrazone compounds [156]. Infrared, Raman, and ^{13}C nmr spectroscopy on complexes trans- $\text{PtCl}_2(\text{olefin})\text{py}$ is related to bonding properties. A series of olefins with electron-withdrawing groups have been compared to ethylene and propylene. Infrared data shows that acrylates are the most strongly coordinated, and the ^{13}C data is correlated within the Chatt-Dewar-Duncanson model. The π -energy levels of some of the olefins has been measured by photoelectron spectroscopy [157]. Similar work is also reported from these same laboratories on complexes trans-

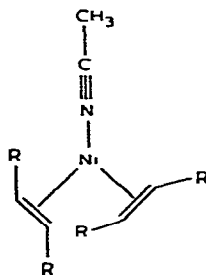
$\text{PtCl}_2(\text{C}_2\text{H}_4)\text{L}$. The ^{13}C nmr shift of ethylene varies linearly with the bond character of ethylene and correlates well with the total $\text{Pt}-\text{C}_2\text{H}_4$ bond strength. A correlation of $\delta^{13}\text{C}$ (ppm) with $\nu(\text{C}=\text{C})$ and $\delta(\text{CH})$ is shown [158]. ^{13}C Nuclear magnetic resonance spectra for complexes $\text{PtMe}[\text{HB}(\text{pz})_3](\text{olefin})$ (68) again show a relation to $\text{M} \rightarrow \text{olefin} \pi$ back-bonding [159]. A similar study has also been



(68)

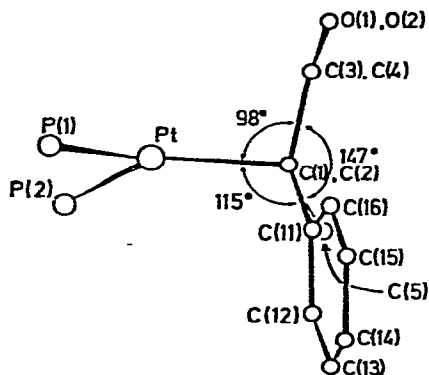
carried out with complexes $\text{PtCl}(\text{NH}_3)_2(\text{olefin})$ (olefin = $\text{pYC}_6\text{H}_4\text{C}=\text{CH}_2$, $\text{RCH}=\text{CH}_2$, $\text{RHC}=\text{CHR}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{X}$). The data is in agreement with donation from olefin- π to platinum- σ being the predominant component of the olefin-metal bond [160]. In a study of the signs and magnitudes of $^{195}\text{Pt}-^{13}\text{C}$ coupling constants in olefin and carbonyl complexes it has been found that $^1\text{J}(\text{Pt}-\text{C})$ is positive in $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, but in $\text{Pt}(\text{II})$ -cyclooctadiene complexes both positive and negative signs are found. The greater magnitude of $^1\text{J}(\text{Pt}-\text{C})$ in $[\text{PtCl}_3(\text{CO})]^-$ is related to the s orbital coefficients of Pt and C [161].

A new preparation of $\text{Ni}(1,5\text{-COD})_2$ using finely divided manganese as reducing agent has been described. In addition these authors give procedures for $\text{Ni}(\text{maleate})_2(\text{MeCN})$ and $\text{Ni}(\text{fumarate})_2(\text{MeCN})$ (69) complexes [162]. The decomposition of $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{bipy})$ to $\text{PtCl}_2(\text{bipy})$ proceeds with different mechanisms depending on the solvent used. In $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ a single step mechanism operates, but in



(69)

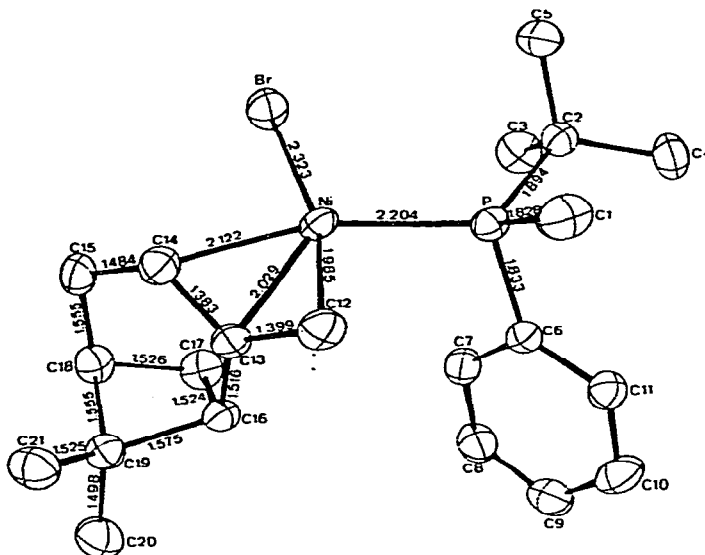
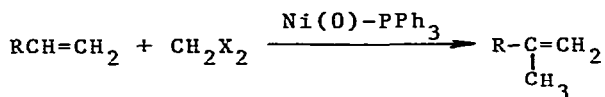
num(0) (72) shows the ligand coordinated via its double bond [168]. A crystal structure of $\text{PtCl}_2(\text{C}_2\text{H}_4)[\text{Me}(\text{H})\text{N}=\text{N}=\text{C}(\text{Me})\cdot\text{C}(\text{Me})=\text{N}(\text{H})\text{Me}]$



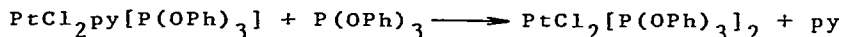
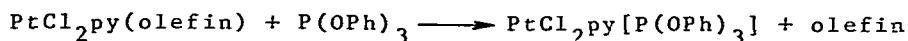
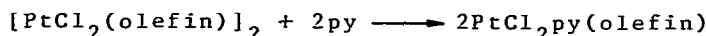
(72)

has also been reported [169]. Treating complexes $\text{Pd}(\text{dba})(\text{bipy})$ with PPh_3 in 1:1 and 1:2 molar ratios gives $\text{Pd}_2(\text{dba})(\text{PPh}_3)_2$ and $\text{Pd}_2(\text{dba})_3(\text{PPh}_3)_3$. The product from $\text{P}(\text{O}Ph)_3$ is $\text{Pd}_2(\text{dba})_2[\text{P}(\text{O}Ph)_3]_3$ (dba is dibenzylideneacetone) [170]. The structures of the complexes trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{Me}_2\text{C}=\text{N}-\text{NMePh})$ and trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{MeHC}=\text{N}-\text{NMe}_2)$ have been reported [171]. The hydrazone molecule coordinates through the imine nitrogen. From the numbering system given it appears that C-C bond distances in the ethylene molecule of 1.33(5) and 1.71(9) Å are obtained, which seems unusual. The crystal structure of the platinum-olefin complex $\text{PtCl}_2(\text{PhCH}=\text{CH}_2)[\text{Me}(\text{O})\text{S}(\text{C}_6\text{H}_4\text{Me})_3]$ has also been reported. The double bond of the olefin (1.360(11) Å) is at an angle of 77.6(6)° to the coordination plane [172]. The structure and absolute configuration of [(S)-tert-butylmethylphenylphosphine][(+)-(1R,5R)-3-2-10- η -pinenyl]nickel bromide (73) shows the pinene coordinated in exo position via a non-symmetric π -allyl group. The absolute configuration has been determined with a high degree of certainty [173].

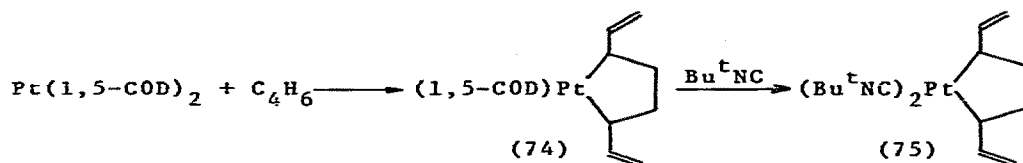
An alkenyl cross-coupling reaction of alkenylalanes with alkyl halides is catalyzed by nickel or palladium [174]. Detailed syntheses of platinum vinyl compounds have been reported [175]. Zerovalent nickel complexes of bipy or triphenylphosphine have been used in the reaction of ethylene with methylene dihalides to give propene. Similarly isobutene has been obtained with propene [176]. Calorimetric results are reported for the following reactions. The



(73)

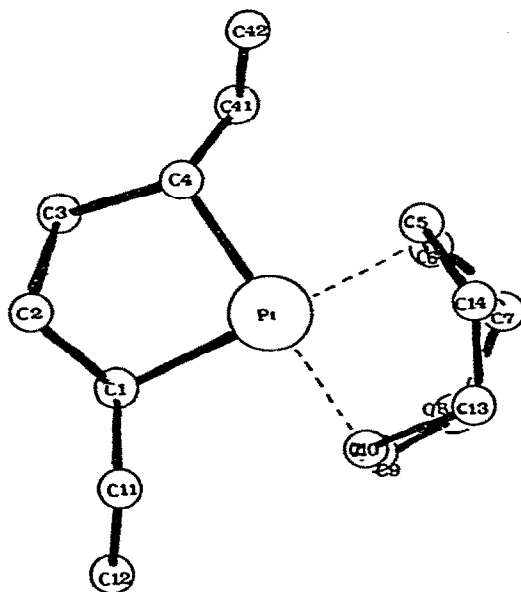


relative displacement energies follow the sequence $\text{P}(\text{OPh})_3 \gg \text{C}_2\text{H}_4 > \text{cyclooctene} > \text{cis-butene} > \text{styrene} > \text{cyclopentene} > \text{nitrostyrene} > \text{cyclohexene}$. The ordering of olefin interaction depends on the metal: for Pd(II), $\text{C}_8 > \text{C}_7 > \text{C}_6 > \text{C}_5$; for Pt(II), $\text{C}_8 > \text{C}_7 > \text{C}_5 > \text{C}_6$; and for Ni(0), $\text{C}_8 > \text{C}_5 > \text{C}_7 > \text{C}_6$ [177]. Treating $\text{Pt}(1,5\text{-cyclooctadiene})_2$ with butadiene leads to a 2,5-divinylplatinacyclopentane complex having in addition a coordinated 1,5-cyclooctadiene. The crystal structure of this complex (74) has been solved in addition to that of complex (75) formed by addition of Bu^tNC [178]. When trans- and cis-2,3-dimethoxycarbonylmethylene-cyclopropanes react with $\text{PdCl}_2(\text{MeCN})_2$ the products are isomeric ring



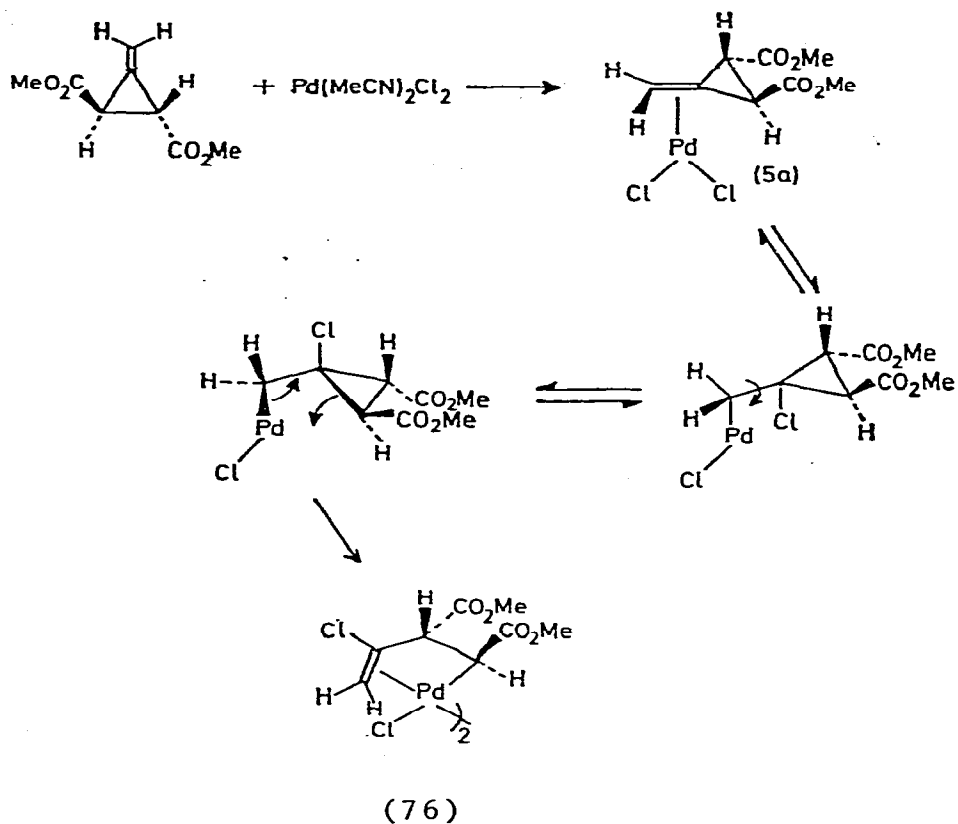
opened η^3 -[3-chloro-1,2-bis(methoxycarbonyl)but-3-enyl]palladium(II) complexes (76) [179]. A wide range of substituent nmr data on these compounds is compiled and mechanistics are discussed. In the following paper the crystal structure of one of these complexes, $\text{PdClpy}_2\{\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{CO}_2\text{Me})\text{C}(\text{Cl})=\text{CH}_2\}$ is presented [180].

A study of the replacement of styrene by pentene-1 in complexes trans- $\text{PtCl}_2(\text{olefin})\text{L}$ (L = substituted aniline) has been studied by stopped-flow methods [181]. The rates of olefin substitution decreases as a function of the *p*-substituent on the aniline in the order $\text{Cl} > \text{H} > \text{Me} > \text{OMe}$. Chloro-bridged complexes $[\text{M}_2\text{Cl}_2(\text{diolefin})_2](\text{BF}_4)_2$ have been prepared by treating

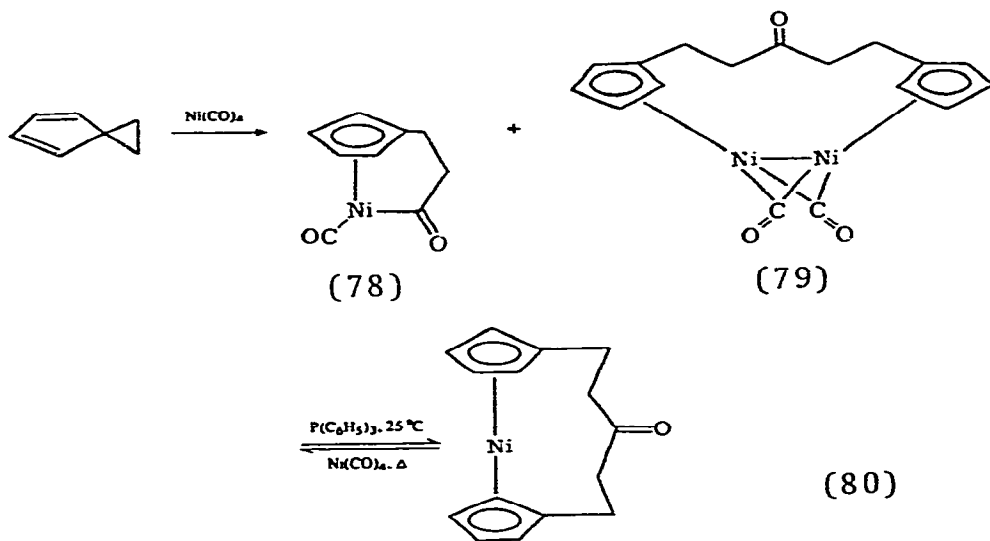
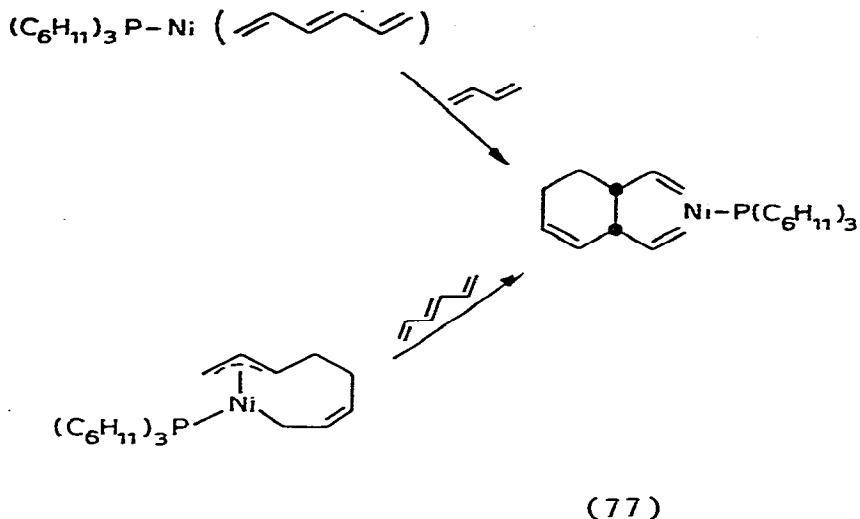


(74)

$\text{MCl}_2(\text{diolefin})$ (M = Pd, Pt) with $[\text{Et}_3\text{O}][\text{BF}_4]$ [182]. The diolefins used are 1,5-COD and norborna-2,5-diene. The palladium complex forms 5,6- η -cyclooct-5-enyl complexes with MeOH, MeCO_2H or H_2O . When PPh_3 is added one obtains $[\text{Pd}_2\text{Cl}_2(\text{PPh}_3)_4][\text{BF}_4]_2$ and $[\text{PtCl}(1,5-$

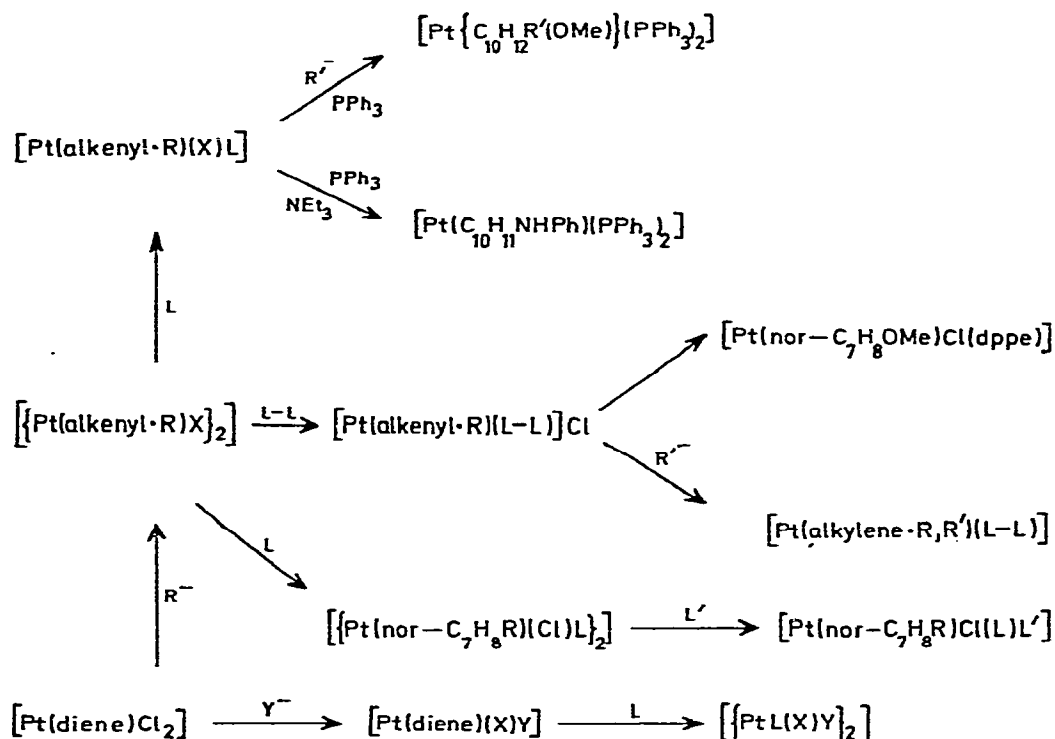


$\text{COD}(\text{PP})_3][\text{BF}_4]$. Butadiene reacts with hexatriene nickel phosphine compounds to give divinylcyclohexene nickel complexes (77). The complex obtained from 2,4,6-octadiene is similar and has been confirmed crystallographically [183]. The crystal structure of $[\text{Ni}(\text{COT})]_2$ (COT = cyclooctatetraene) shows a sandwich type molecule with both metal atoms between the COT rings. Each nickel forms π -allyl type bonds to three carbons of each COT ring [184]. A series of dichloro-platinum adducts of methyl-substituted cyclopropanes and olefins have been prepared which in acid anhydride solvents result in β,γ -unsaturated carbonyl complexes [185]. A mechanism is proposed involving electrophilic attack on the cyclopropane or olefin. The reaction of $\text{Ni}(\text{CO})_4$ with spiro[2.4]hepta-4,6-diene results in C-C bond cleavage and insertion of CO to form the complex (78). A further complex (79) can be isolated, and treatment of (79) with triphenylphosphine gives (80) [186]. The carbonylation of octadienylnickel and bis- π -allylnickel complexes to give ketones is reported [187]. A study of the fluxionality of η^3 -cyclohepta-2,4-dienylpalladium shows that a 1,3-shift mechanism

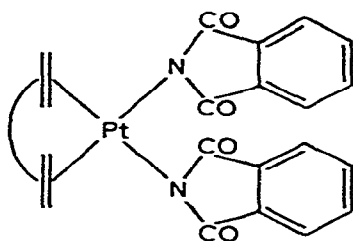


is operative. A relation between ΔG^\ddagger and the trans effectiveness of L in $Pd(C_7H_9)L_2$ or $[Pd(C_7H_9)L_2]PF_6$ has been found [188]. The reactions of $PtCl_2(diene)$ with nucleophiles OPr^- , NH_2Ph , SPh^- and SCN^- are reported. Attack can occur at the diene or at the metal, with the latter being most likely with the S-nucleophiles. A scheme of reactions is shown with Y^- being a nucleophile and L being a neutral ligand such as PPh_3 . A wide range of compounds is

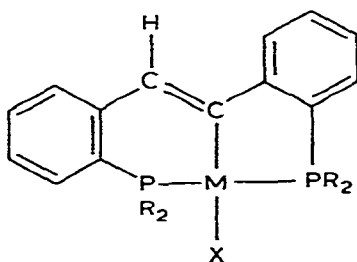
reported [189]. The conversion of dienes to allylic ethers via allylpalladium compounds is reported. The solvent system is water or aqueous acetone and some of the intermediates have been isolated [190]. The organic products arising from the methanolysis of $\text{PdCl}_2(1,5\text{-COD})$ in the presence of base have been identified [191]. Complexes $\text{PdCl}_2(\text{diene})$ react with maleimide or phthalimide to give compounds $\text{Pt}(\text{imidate})_2(\text{diene})$ (diene = 1,5-COD, dicyclopentadiene and norbornadiene) (81) [192]. The compound $\text{PdCl}_2(1,5\text{-COD})$ has been used to prepare a series of sulfur-chelate palladium compounds [193]. Complexes $\text{Ni}(\text{bipy})(\text{PR}_3)_2$ have been prepared from



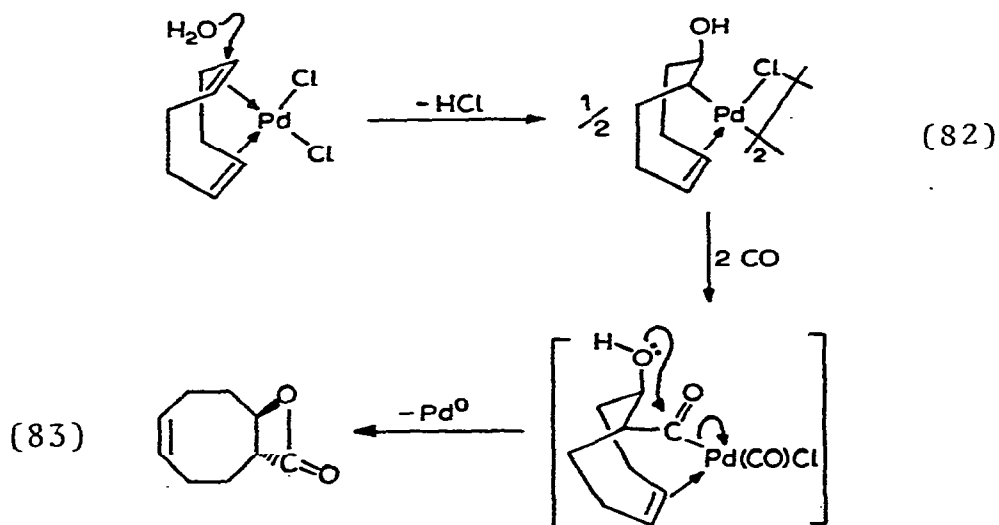
bipy and $\text{Ni}(1,5\text{-COD})(\text{bipy})$, or from $\text{NiEt}_2(\text{bipy})$ and PR_3 [194]. Stilbene ligands $\text{o-R}_2\text{PC}_6\text{H}_4\text{CH=CHC}_6\text{H}_4\text{PR}_2\text{o}$ react with halide complexes of $\text{Ni}(\text{II})$, $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ with loss of HCl and the formation of chelate σ -vinyls of formula $\text{MX}(\text{o-R}_2\text{PC}_6\text{H}_4\text{C=CHC}_6\text{H}_4\text{PR}_2\text{o})$. Analogous methyl derivatives $\text{PtMe}(\text{o-R}_2\text{PC}_6\text{H}_4\text{C=CHC}_6\text{H}_4\text{PR}_2\text{o})$ are obtained from $\text{PtMe}_2(1,5\text{-COD})$. The ^1H nmr spectra of compounds with $\text{R} = \text{o-tolyl}$ show temperature dependence because of interconversion of enantiomers caused by restricted rotation about the M-P and M-C bonds [195]. When $\text{PdCl}_2(1,5\text{-COD})$ is treated with aqueous sodium carbonate



(81)

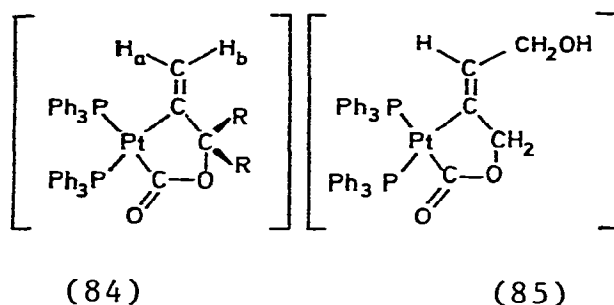


a σ -bonded hydroxypalladium enyl complex (82) is formed. Carbonylation to give lactone (83) shows that hydroxypalladation occurs stereospecifically trans [196].

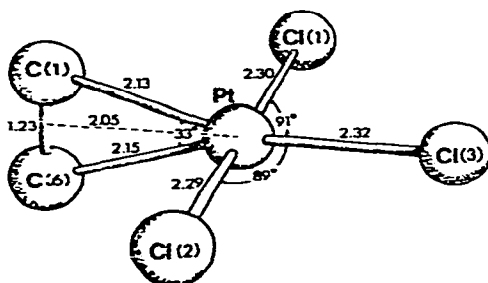


VII. Metal acetylene complexes

Thermochemical data has been published on the bonding of acetylenes to platinum [197]. New complexes of the type $\text{Pt}[\text{R}^1\text{C}\equiv\text{CCR}^2\text{R}^3(\text{OH})](\text{PPh}_3)_2$ ($\text{R} = \text{H}, \text{Ph}$ or CH_2OH) have been prepared and the ^1H and ^{31}P nmr spectra are discussed. Significant second-order character in the ^1H nmr patterns of the methine proton is noted [198]. Upon carbonylation of the above complexes with $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{Me}$; and $\text{R}^1 = \text{CH}_2\text{OH}$; $\text{R}^1 = \text{R}^2 = \text{H}$; the cyclic compounds (84) and (85) are formed, the crystal structure work having been previously surveyed in this article [166]. The crystal structure of

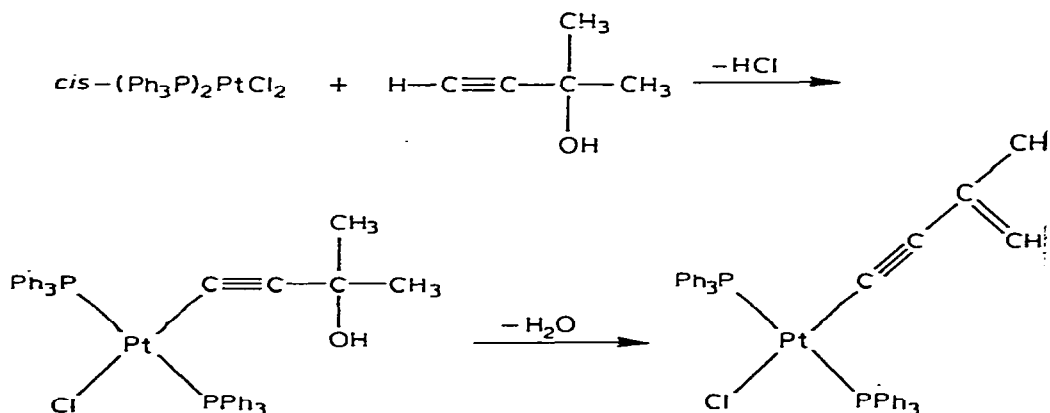
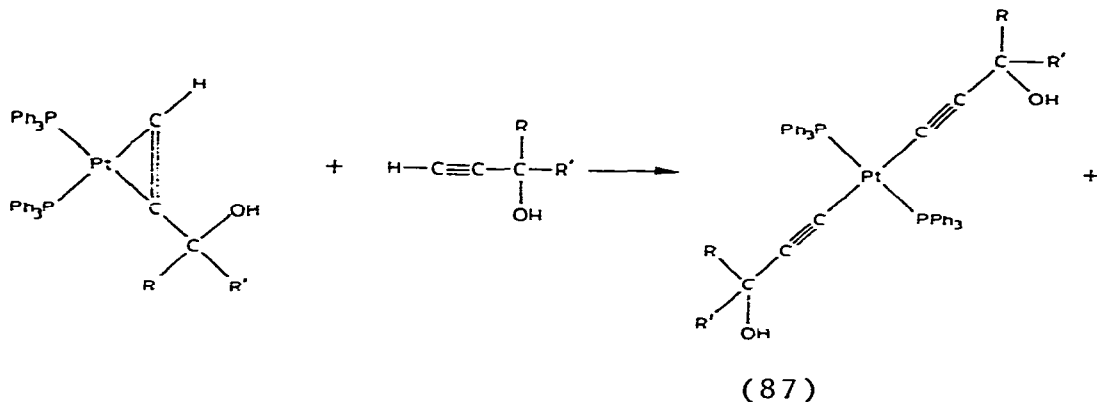


$\text{Pt}(1\text{-ethynylcyclohexanol})(\text{PPh}_3)_2$ shows two independent molecules in the asymmetric unit which are isomers having the acetylene equatorially bonded to the cyclohexane in one molecule and axially bonded in the other [199]. The acetylene group is symmetrically bonded to platinum and adopts the *cis*-*bent* configuration. The crystal structure of $\text{K}\{\text{PtCl}_3[\text{EtMeC}(\text{OH})\text{C}\equiv\text{C}(\text{OH})\text{MeEt}]\}$ (86) shows the acetylenic bond perpendicular to the plane of platinum coordination. The higher trans influence of the acetylene as compared to chloride

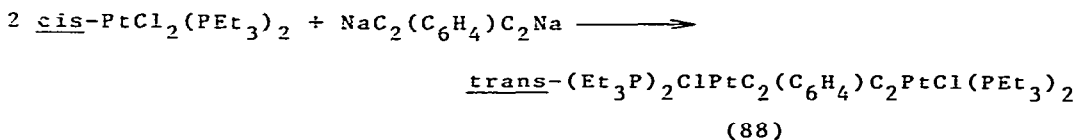


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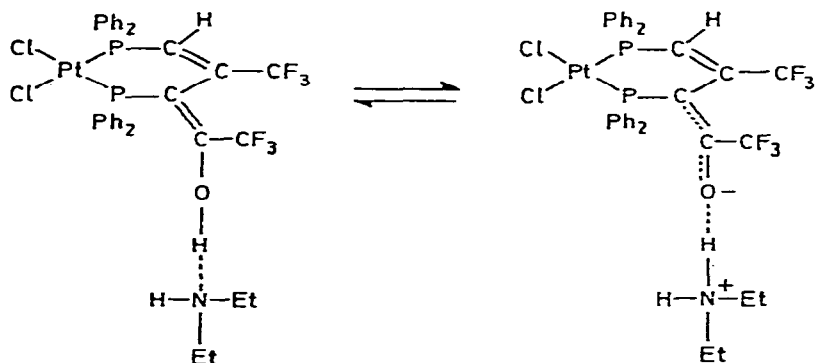
is exhibited in the Pt-Cl bond distances [200]. When complexes $\text{Pt}(\text{HC}\equiv\text{CR})(\text{PPh}_3)_2$ [$\text{R} = \text{CMe}_2\text{OH}, \text{CMeEtOH}, \text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$] are treated with α -hydroxyacetylenes the product is $\text{Pt}(\text{HC}\equiv\text{CR})_2(\text{PPh}_3)_2$ (87). By contrast when α -hydroxyacetylenes are reacted with cis- $\text{PtCl}_2(\text{PPh}_3)_2$ the products are chloroacetylide or chloroeneyne compounds [201]. The compound $\text{PdCl}_2(\text{PhCN})_2$ reacts with o-substituted



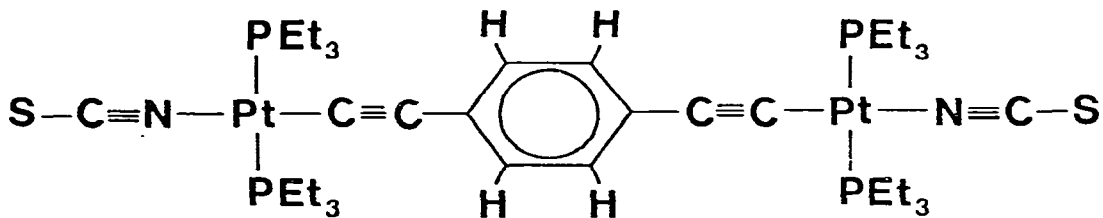
diphenylacetylenes to give cyclobutadiene complexes and higher oligomers [202]. A binuclear planar complex trans- $(\text{Et}_3)_2\text{ClPt}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{PtCl}(\text{PEt}_3)_2$ (88) has been prepared from cis- $\text{PtCl}_2(\text{PEt}_3)_2$



and the disodium salt of *p*-diethynylphenylene [203]. The crystal structure of $(\text{cpNi})_2\text{CH}\equiv\text{CH}$ at room and 77°K shows a short Ni-Ni separation. The acetylene is *cis*-bent with a C-C distance of 1.341(6) Å [204]. Base promoted coupling of phosphinoacetylenes in the complex *cis*- $\text{PtCl}_2(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2$ leads to compounds *cis*- $\text{PtCl}_2[\text{Ph}_2\text{PCH}=\text{C}(\text{CF}_3)\text{C}(\text{PPh}_2)=\text{C}(\text{OH})\text{CF}_3]\cdot\text{L}$ (L = Et_2NH , Et_3N , Me_3N , Pr_3N) [205]. The crystal structure of the complex with L = Et_2NH

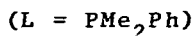
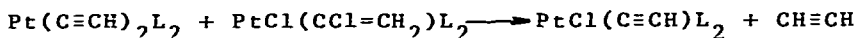
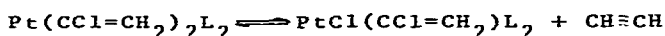
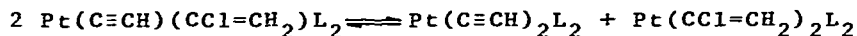
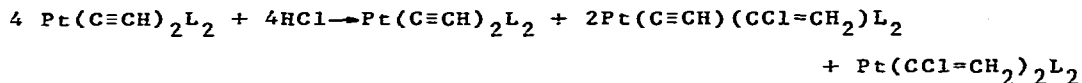


has been solved. Treating $[\text{Nicp}(\text{SCF}_3)]_2$, Nicp_2 , $\text{Nicp}[\text{cp}(\text{CF}_3\text{C}_2\text{CF}_3)]$, $\text{Nicp}[\text{cp}(\text{C}_2\text{F}_3\text{Cl})]$, and $[(\text{Nicp})_2(\text{CF}_3\text{C}_2\text{CF}_3)]$ with $\text{CF}_3\text{C}_2\text{CF}_3$ gives the new compounds $\text{Nicp}[(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{H}]$, $\text{Ni}_3\text{cp}_2(\text{CF}_3\text{C}_2\text{CF}_3)_3$, $\text{Ni}_2\text{cp}_2(\text{CF}_3\text{C}_2\text{CF}_3)_3$, $\text{Nicp}_2(\text{CF}_3\text{C}_2\text{CF}_3)_3$, $\text{Nicp}[\text{cp}(\text{CF}_3\text{C}_2\text{CF}_3)_2]$, $[\text{Nicp}(\text{CF}_3\text{C}_2\text{CF}_3)]_4$, and $(\text{CF}_3\text{C}_2\text{CF}_3)_2[\text{cp}(\text{C}_2\text{F}_3\text{Cl})]$ [206, 207]. Structures, reaction schemes, infrared and nmr data, in addition to preparative details are given. The crystal structure of the compound $[\text{Pt}(\text{NCS})(\text{PEt}_3)_2]_2\text{-p-C}_6\text{H}_4(\text{C}\equiv\text{C})_2$ shows two parallel planes of

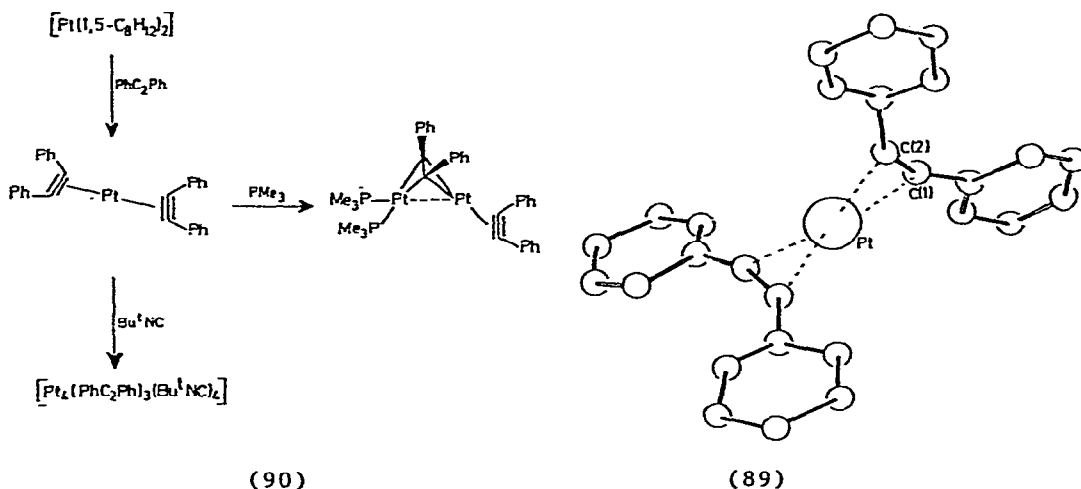


The crystal structure of the compound $(\mu_2(\eta^2)\text{-PhC}\equiv\text{CPh})[\text{Ni}(1,5\text{-COD})]_2$ shows each nickel atom π -bonded to the two double bonds of a single 1,5-COD ligand, and bonded to the bridging diphenylacetylene ligand through a μ -type bond [209]. The addition of HCl to *trans*- $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PMe}_2\text{Ph})_2$ leads to a sequence of Pt(II) promoted addition-elimination reactions [210]. Cuprous acetylides have been used to

prepare bis(acetylide) platinum(II) complexes from $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)$.

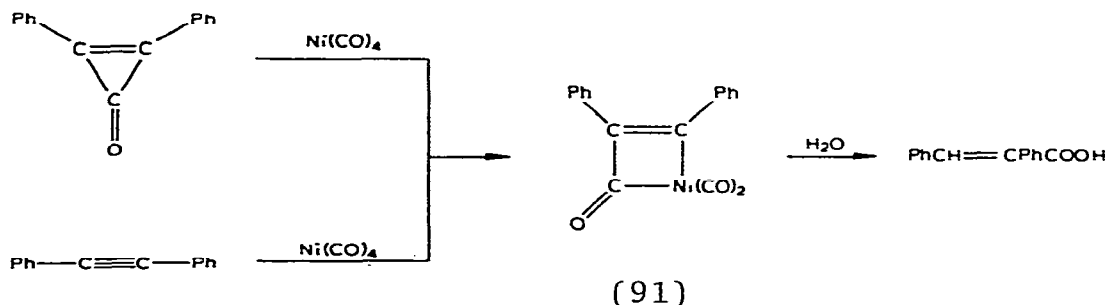


The acetylene $\text{HC}_2\text{C}_6\text{F}_5$ reacts with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ to give $\text{Pt}(\eta^2\text{-HC}_2\text{C}_6\text{F}_5)(\text{PPh}_3)_2$, but with $\text{Pt}(\text{PR}_3)_4$ ($\text{R} = \text{Ph}, \text{Et}$) to give complexes trans- $\text{Pt}(\text{HC}_6\text{F}_5)(\text{PR}_3)_2$ [211]. The compound $\text{Pt}(1,5\text{-COD})_2$ reacts with C_2Ph_2 to give $\text{Pt}(\text{PhC}_2\text{Ph})_2$ (89). This complex gives $\text{Pt}_4(\text{PhC}_2\text{Ph})_3(\text{Bu}^t\text{NC})_4$ (90) on treating with Bu^tNC . Crystal structures of compounds (89) and (90) are presented [212].

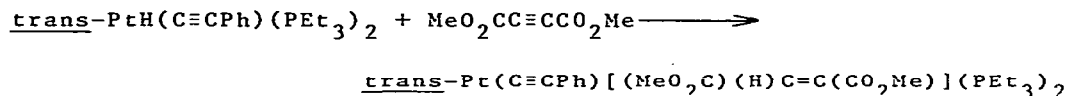


A review article has been published on the palladium induced oligomerization of acetylenes [213]. Dihydropentalenes have been prepared by treating phenyl- or *p*-chlorophenyl-acetylene with $[\text{PdCl}(\text{MeSCH}_2\text{CH}_2\text{SMe})(\text{Bu}^t\text{C}=\text{CHCH}=\text{CBu}^t\text{Cl})]$ [214]. These materials are isostructural with the compound $\text{Ph}_4\text{C}_8\text{H}_4$ obtained from phenylacetylene and PdCl_2 . A structure of this tetramer, along with the dihydropentalene obtained from phenylacetylene by the first reaction,

are published. The linear polymerization of 2-methylbut-3-yn-2-ol is reported [215]. Tetrasubstituted cyclopentenones have been prepared in 25-70% yields from dialkyl- or diacylacetylenes and Ni(CO)_4 [216]. Cyclopentene-1,2-diones have been prepared by treating Ni(CO)_4 with diphenylcyclopropenone and ketenes. The reaction is considered to go via a nickelacyclobutene complex (91), which can be formed from nickel carbonyl and diphenylacetylene [217]. The structure of $\text{Ni(ethylfumarate)}_2(\text{MeCN})$ shows a slightly distorted



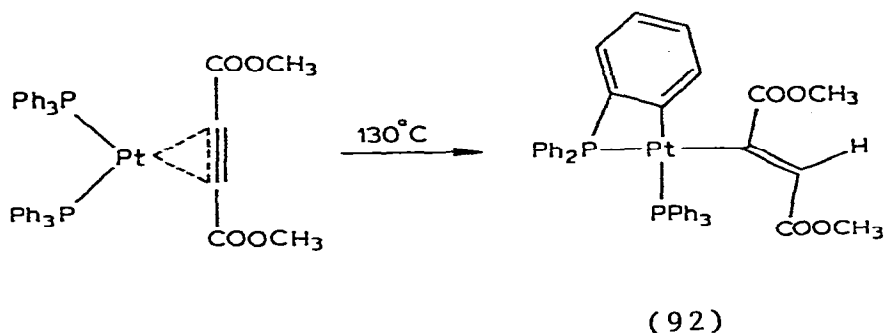
trigonal symmetry for the four C atoms of the $-\text{C}=\text{CH}-$ groups and the N atom of acetonitrile [218]. The torsion angles around the $-\text{CH}=\text{CH}-$ groups are significantly different from 180° . The four asymmetric carbon atoms of a molecule have the same absolute configuration with SSSS and RRRR molecules present in the unit cell. The complex trans- $\text{M}(\text{C}\equiv\text{CPh})[(\text{MeO}_2\text{C})(\text{H})\text{C}=\text{C}(\text{CO}_2\text{Me})](\text{PEt}_3)_2$ has been prepared from trans- $\text{MH}(\text{C}\equiv\text{CPh})(\text{PEt}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) and dimethyl acetylenedicarboxylate. The results are tentatively interpreted as supportive



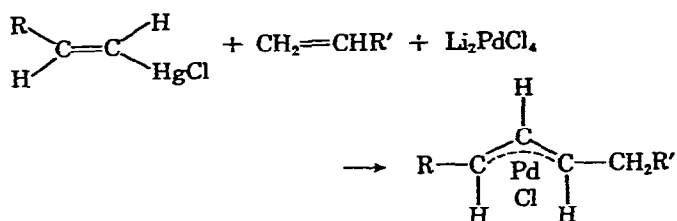
of alkenylalkynyl intermediates in the polymerizations of terminal acetylenes [219]. When a toluene solution of $\text{Pt}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})(\text{PPh}_3)_2$ is heated at 130° the ortho metallated complex (92) is formed [220].

VIII. Metal allyls

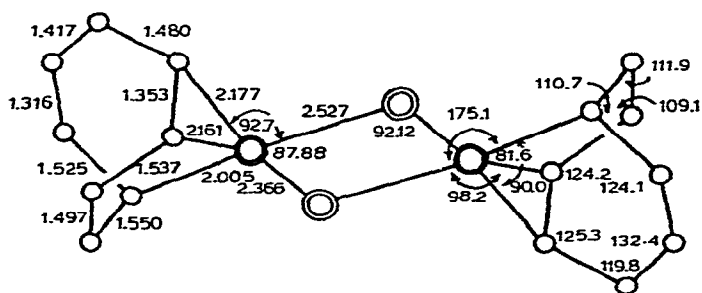
A new route to allyl palladium complexes is to treat Li_2PdCl_4 with a mixture of an alkene and a vinyl mercury compound [221]. A



wide range of allyls has been obtained in high yield using this



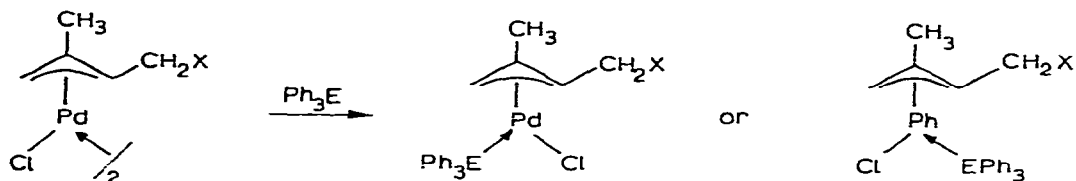
method, either with substituents such as esters, cyanides, or alkyls, or with the simplest olefin ethylene. The crystal structure of the dimeric complex $[\text{PdCl}(\text{C}_8\text{H}_{11})]_2$ (93) derived from 1,5-COD is shown to have a σ -allyl structure [222]. A series of σ -allyl



(93)

complexes $[\text{Pt}(\sigma\text{-allyl})\text{Cl}(\text{CNR})_2]$ ($\text{R} = \text{Me}, \text{Cy}, p\text{-ClC}_6\text{H}_4, 2,6\text{-Me}_2\text{C}_6\text{H}_3$) have been prepared by treating the π -allyl complex $\text{Pt}(\eta^3\text{-allyl})\text{Cl}(\text{CNR})$ with the appropriate isocyanide [223]. The crystal structure data on the MeNC structure is presented. A list of ^{13}C nmr data for allylpalladium chloride dimers has been published and

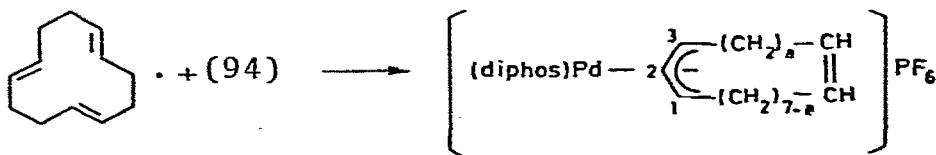
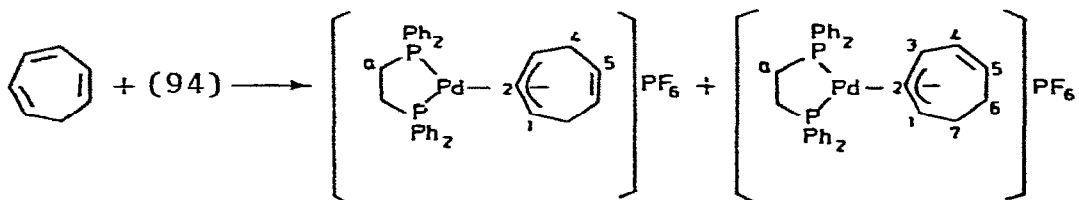
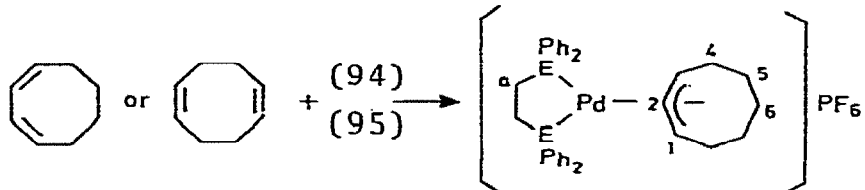
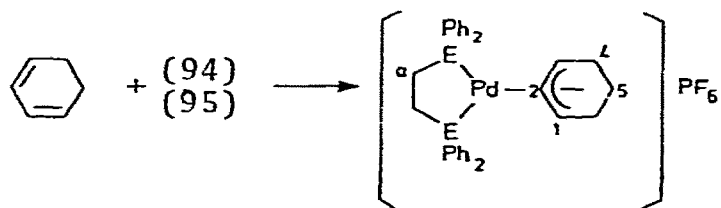
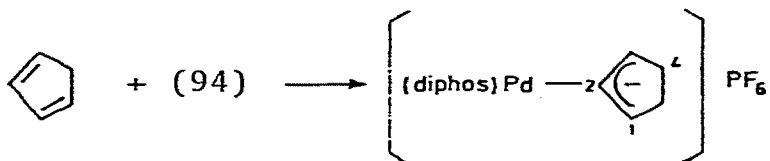
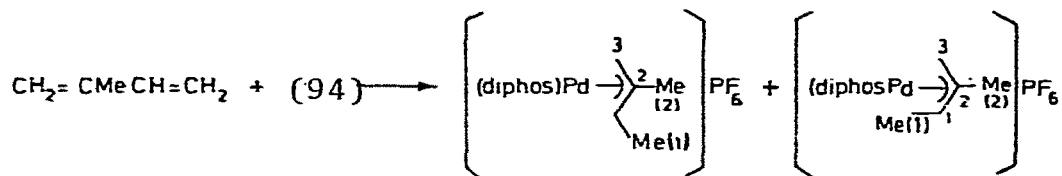
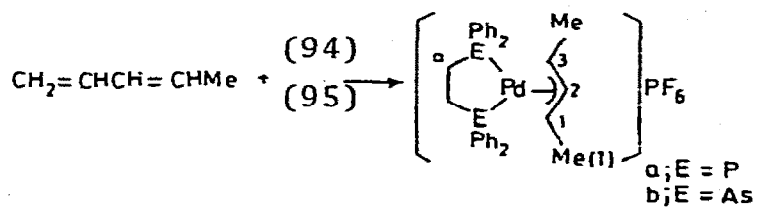
the upfield shift of the resonances of the allyl ligands noted [224]. The reaction of butadiene and phenylhydrazones in the presence of Ni and Pd complexes yields a series of azo compounds. A mechanism is presented involving allylic intermediates [225]. The chloro bridges in di-*μ*-chloro-4-methoxy- and di-*μ*-chloro-4-acetoxy-2-methyl-but-2-enylchloro-palladium are split by EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) [226]. These allylic complexes are readily decomposed to



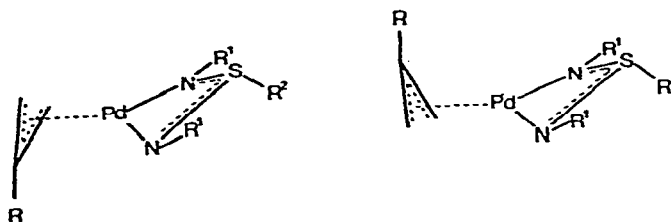
isoprene by HCl. Complexes of type $[\text{PdHL}_2]^+$ ($\text{L} = \text{dpe}$ (94) dae (95)) are generated in situ and reacted with a wide range of dienes to give complexes $\text{Pd}[(\text{allyl})\text{L}_2]\text{PF}_6$ [227]. Equilibrium studies on complexes $\text{Pt}(\text{allyl})\text{ClL}_2$ (allyl = $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}=\text{CHMe}$, $\text{CH}_2\text{CMe}=\text{CH}_2$; $\text{L} = \text{PPh}_3$, AsPh_3) have been reported [228].

The He(I) photoelectron spectra of bis(π -methallyl)Ni, bis(π -crotyl)Ni, and bis(π -1,3-dimethylallyl)Ni are related to bis(π -allyl)Ni. An assignment for $\text{Ni}(\text{allyl})_2$ is given which differs from previous work and brings the agreement with Koopmans type calculations closer [229]. The vibrational spectra and force constants for $[\pi\text{-C}_5\text{H}_9\text{NiCl}]_2$, $[\pi\text{-C}_5\text{H}_9\text{NiI}]_2$, $[\pi\text{-C}_3\text{H}_5\text{NiCl}]_2$, and $[\pi\text{-C}_3\text{H}_5\text{NiI}]_2$ have been reported. The nickel-carbon force constants of the pentenyl complexes are greater than those of the allyl complexes, but the reverse is true for the nickel-halogen force constants [230]. A complete vibrational assignment has been made for $[(\text{ClC}_3\text{H}_4)\text{PdCl}]_2$ which indicates a weakening of the Pd-C bond as compared with that in $[\text{C}_3\text{H}_5\text{PdCl}]_2$ [231].

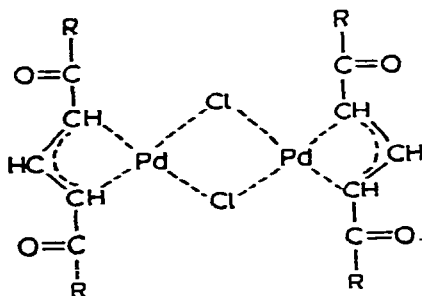
Treating $[\text{PdCl}(\text{CH}_2\text{CH}=\text{CH}_2)]_2$ with CdEt_2 in toluene at -15° for 30 min. gives 0.25 mole ethane, 0.13 mole butane, 0.48 mole propene, 0.46 mole ethylene, 0.07 mole diallyl, and small quantities of benzene and hydrogen, together with Cd, CdCl_2 and Pd [232]. The dimerization of allene at $20\text{--}180^\circ$ over π -allylnickel bromide/ Al_2O_3 gives 1,3-bis(methylene)cyclobutane. A 4-membered cyclic activated complex is postulated as an intermediate [233]. The complexes $(\eta^3\text{-RC}_3\text{H}_4)\text{Pd}[\text{R}^1\text{NS}(\text{R}^2)\text{NR}^1]$ ($\text{R} = \text{H}, \text{Me}$; $\text{R}^1 = \text{aryl}$; $\text{R}^2 = \text{Me}, \text{Bu}^t$) have been prepared by the reaction of $[(\eta^3\text{-RC}_3\text{H}_4)\text{PdCl}]_2$ with $\text{Li}[\text{R}^1\text{NS}(\text{R}^2)\text{NR}^1]$. Two isomers are produced



differing in allyl group orientation. Compounds $[(\eta^3\text{-RC}_3\text{H}_4)\text{Pd}(\text{R}^3\text{N}_3\text{R}^3)]_2$ and $[(\eta^3\text{-RC}_3\text{H}_4)\text{Pd}(\text{R}^3\text{NC}(\text{R}^4)\text{NR}^3)]_2$ ($\text{R} = \text{H}, \text{Me}$; $\text{R}^3 = \text{Me}, \text{aryl}$; $\text{R}^4 = \text{H}, \text{Me}$) are also reported. Possible isomers of the S compounds are shown [234]. A series of σ - and π -allyls

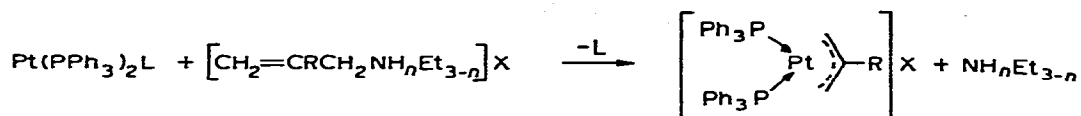


from 1- and 2-trialkylsilyl-3-chloropropene-1 have been isolated with Pd, and an in situ silylallyl Grignard reagent has been used to prepare the Ni complexes [235]. When vinyl- and allylsilanes are reacted with $\text{Pt}_2\text{Cl}_2(\text{C}_2\text{H}_4)_2$ a rapid coordination step is followed by cleavage of the activated Si-C bond [236]. 2,6-Disubstituted pyrylium salts react with PdCl_2 in a ring opening reaction to give a π -allyl complex (96) [237]. The crystal structure of this compound ($\text{R} = \text{Bu}^t$) verifies the structure of the compound, and the

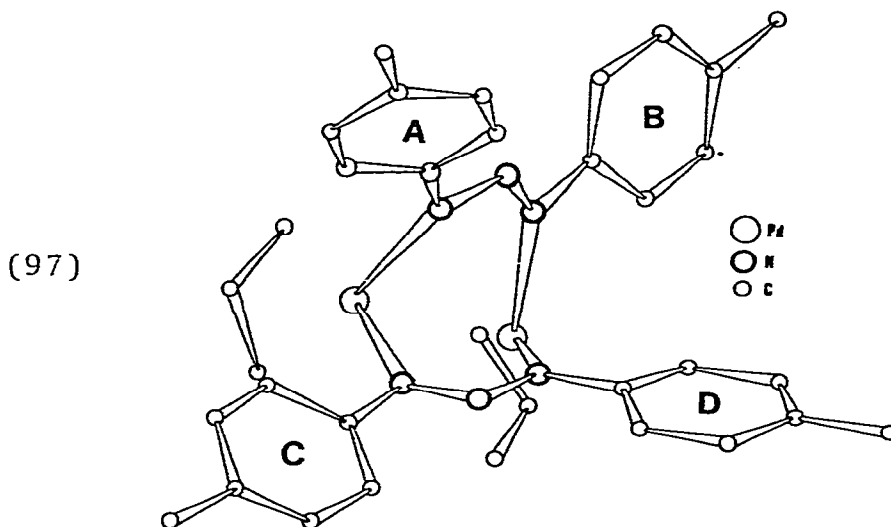


(96)

reaction is proposed to proceed via protonation and hydrolysis of the pyrylium ring. The π -allyl complexes $[\text{Pt}(\pi\text{-C}_3\text{H}_4\text{R})(\text{PPh}_3)_2]\text{X}$ are formed from $\text{PtL}(\text{PPh}_3)_2$ ($\text{L} = \text{PPh}_3, \text{C}_2\text{H}_4$), along with compounds $[(\text{CH}_2=\text{CRCH}_2)\text{NH}_n\text{Et}_{3-n}]\text{X}$ ($\text{R} = \text{H}, n = 0, 1$; $\text{R} = \text{Me}, n = 0$; $\text{X} = \text{ClO}_4, \text{BPh}_4$) [238]. The compounds $[(1,3\text{-}\eta\text{-C}_3\text{H}_4)\text{Pd}(\text{p-MeC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{Me-p})]_2$ (97) shows two stereochemically equivalent allyls with the carbons pointing out. The rigid triazenido groups cause a close Pd-Pd separation of 2.86 Å [239].



(L = PPh₃, C₂H₄; R = H, Me; n = 0, 1; X = ClO₄, BPh₄)



IX. Delocalized carbocyclic systems.

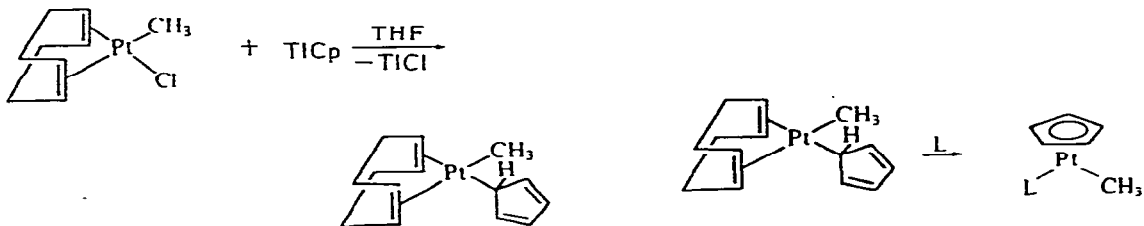
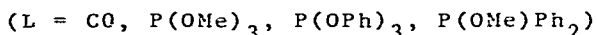
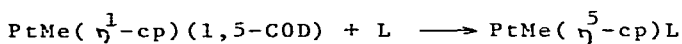
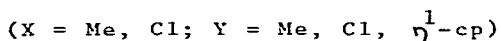
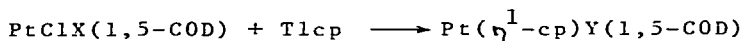
The reaction of nickel atoms and styrene at -196°C gives, after work-up at -40°C and recrystallization at -80°C from toluene, red-brown crystals of $\text{Ni}(\text{styrene})_3$. This compound reacts with bipy at -30°C to give $\text{Ni}(\text{styrene})(\text{bipy})$ [240]. Supported nickel cluster catalysts for olefin hydrogenation and the 'oxo' reaction, have been prepared by pyrolysis of compounds cp_2Ni , $\text{cp}_2\text{Ni}_2(\text{CO})_2$, and $\text{cp}_3\text{Ni}_3(\text{CO})_2$ [241]. The Raman and infrared spectra of nickelocene shows that the cp ring tilt vibration $\nu_{16}(e_{1g})$ is very low and close to 200 cm^{-1} . This vibration is associated with an $a_{1g}(\text{metal})$ -cp stretching mode. The spectra of ferrocene and nickelocene are analyzed in some detail, with the bands in the latter compound generally coming at lower energy [242]. The heat capacity curves for ferrocene and nickelocene have been determined, the latter in the 130-300 K range. A high order transition in nickelocene is suggested by the deviation from a normal variation in the range 170-240 K [243]. The data from about forty X-ray powder diagrams in the temperature range 5-295 K for nickelocene also show an order-disorder transition in the 170-240 K range. This is analyzed as

being due to the existence of domains and frontier zones, and the reorganization of the molecular packing, in the order phase. The Nipc_2 molecule is likely eclipsed (D_{5h}) in the ordered phase [244]. Nickelocene in ion cyclotron resonance spectroscopy experiments has been shown to be a very strong base in the gas phase. In equilibrium proton-transfer reactions with Et_2NH the proton affinity is 218.9 ± 1.0 kcal/mol, as compared to a value of 201 ± 1 kcal/mol for NH_3 [245]. The anion $[\text{Nipc}_2]^-$ has a long lifetime and is quite unreactive. Rate constants for the reactions of the primary fragment ions at 70 eV are given. In a further article these workers have compiled a list of binding energies and proton affinities to cpNi^+ . The ligand binding energies to cpNi^+ follow the sequence: $\text{Me}_3\text{P} > \text{PH}_3$, $\text{Me}_2\text{O} > \text{MeOH} > \text{H}_2\text{O}$, $\text{Me}_2\text{S} > \text{MeSH} > \text{H}_2\text{S}$, and is also larger when the methyl substitution on carbon α to the base site is increased:

$\text{Me}_3\text{COH} > \text{Me}_2\text{CHOH} > \text{EtOH} > \text{MeOH}$, $\text{Et}_2\text{O} > \text{Me}_2\text{O}$, $\text{MeCN} > \text{HCN}$. Finally the sequence:

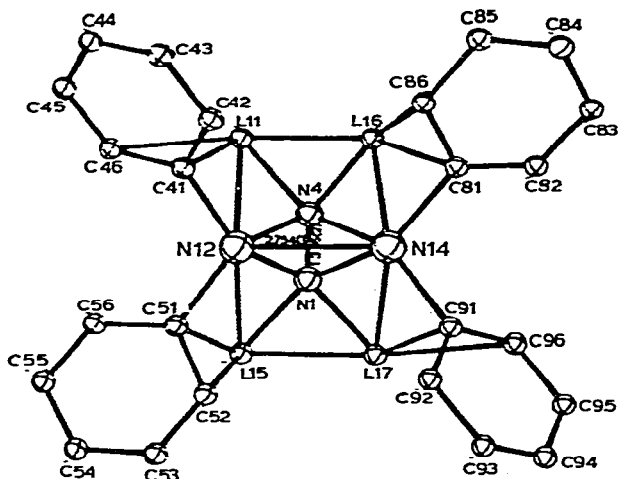
$\text{Me}_3\text{P} > \text{Me}_3\text{N}$, $\text{Me}_2\text{S} > \text{Me}_2\text{O}$ is noted [246].

A series of cyclopentadienyl platinum(II) complexes containing a range of other organometallic ligands have been prepared as outlined below [247]. Diels-Alder adducts of $\text{CF}_3\text{C}\equiv\text{CCF}_3$ or maleic anhydride to the η^1 -ring are reported. ^1H and ^{13}C nmr data are presented for some cp complexes. The crystal structure of the



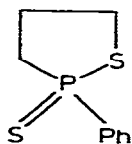
unusual complex $[\text{Ph}(\text{Na.OEt}_2)_2(\text{Ph}_2\text{Ni})_2\text{N}_2\text{NaLi}_6(\text{OEt})_4.\text{OEt}_2]_2$ (98) shows a pseudocenter of symmetry between two $(\text{Ph}_2\text{Ni})_2\text{N}_2$ units in which the N_2 ligands bridge 'side-on' to nickel atoms of a $(\text{Ph}_2\text{Ni})_2$ system. The two $(\text{Ph}_2\text{Ni})_2$ units are linked by two sodium atoms and two

$\text{Li}_6(\text{Et})_4\text{OEt}_2$ aggregates [248]. Thiophosphinates will reductively complex to nickelocene to give 1,2-oxaphospholane complexes (100)

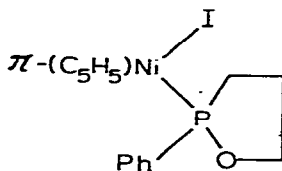


(98)

[249]. Thus when nickelocene is treated with phenyl-2-thio-2-oxaphospholane-1,2 (99) in the presence of methyl- or allyl iodide, complex (100) is obtained. These authors have carried out a similar chemistry to prepare complexes $\text{cpNiI}(\text{L})$ from a phosphine sulfide ($\text{L}=\text{S}$) [250]. Alkylcyclopentadienyl palladium complexes $\text{cpPdR}^1(\text{PR}_3)$ ($\text{R} = \text{Ph}$; $\text{R}^1 = \text{Me}, \text{Bu}^n, \text{Ph}$. $\text{R} = \text{Pr}^i$; $\text{R}^1 = \text{Ph}$) have been prepared from $\text{cpPdBr}(\text{PR}_3)$ and R^1MgBr at -78° [251]. The complexes insert SO_2 to give $\text{cpPd-S}(\text{O}_2)\text{R}(\text{PR}_3)$. A series of cyclopentadienyl palladium complexes $\text{cpPd}(\text{CH}_2\text{R})(\text{PPh}_3)$ and $\text{cpPd}(\text{CH}_2\text{SMe})$ have been prepared from the corresponding chloro complexes and



(99)

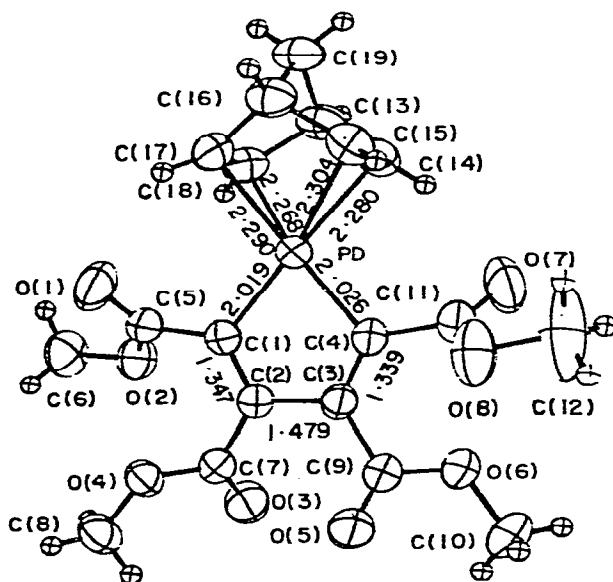


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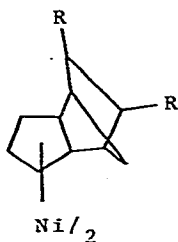
TiIcp [252]. In further investigation of reactions of cyclopentadienyl compounds, the decarbonylation of aldehydes has been studied by ion cyclotron resonance methods [253]. These authors suggest that decarbonylation reactions effected by NiIcp^+ are specific for

aldehydes, require significant stability for RCO^+ , and involve a final intermediate from which competitive elimination of CO and RH occurs.

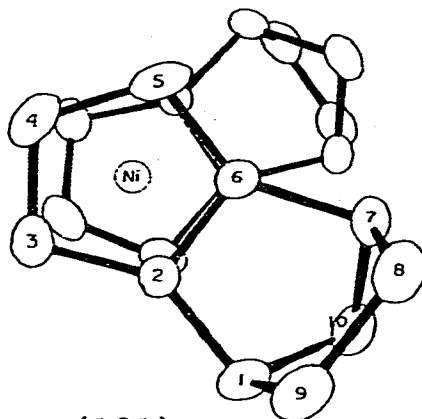
From the photolytic reaction of $\text{Pd}(\text{C}_3\text{H}_5)\text{cp}$ and hexafluorobutyne-2 the dinuclear complex $\text{Pd}_2\text{C}_4(\text{CF}_3)_4(\text{C}_3\text{H}_5)\text{cp}$ is formed. This contrasts with the reactions of the Fe and Mo systems [254]. Tetrakis(methoxycarbonyl)palladiacyclopentadiene $\text{Pd}[\text{C}_4(\text{CO}_2\text{Me})_4]$ (norbornadiene) has been prepared by treating $\text{Pd}[\text{C}_4(\text{CO}_2\text{Me})_4]$ with norbornadiene. The structure of this metallocycle shows evidence of electron transfer from norbornadiene to the electron-withdrawing



metallocyclic ring. The parent oligomer $\text{Pd}[\text{C}_4(\text{CO}_2\text{Me})_4]$ is an effective catalyst for the cyclocotrimerization of two dimethylacetylenedicarboxylate molecules with norbornadiene to give 1,2,3,4-tetrakis(methoxycarbonyl)benzene [255]. An angular dependence of hydrogen magnetic resonance contact shifts in substituted nickelocenes has been noted, and the crystal structure of bis(η^5 -isodicyclopentadienyl)Ni (101) solved [256]. The crystal structure of $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_2$ supports the recent suggestion that the methylene H atoms of the $\text{Ni}[\text{Et}_2\text{B}(\text{pz})_2]$ complex do not act as apical ligands [257]. Fluxional pyrazolyl groups in the complexes $\text{PdB}(\text{pz})_4\text{L}$ ($\text{L} = \text{N,N}$ -dimethylbenzylamine, *o*-phenylpyridine, azobenzene) and $\text{Pd}[\text{HB}(\text{pz})_3]\text{L}$ ($\text{L} = \text{benzo}(\text{h})\text{quinoline-2-C,N}$) are reported [258]. The fluxionality is suggested to be due to a tumbling process involving

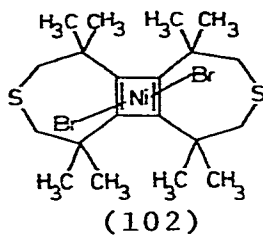


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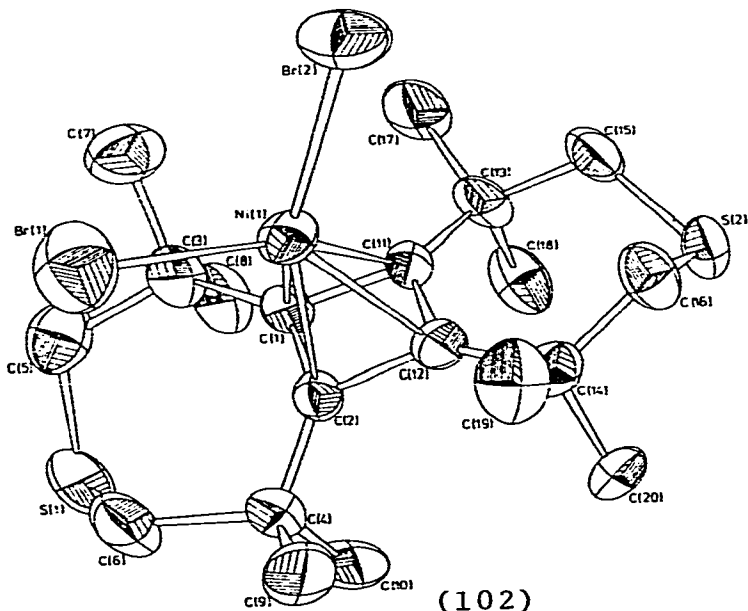


(101)

the coordinated and uncoordinated nitrogens. The crystal structure of $[(\text{Me}_2\text{N})_3\text{C}_3]_2\text{Pt}_2\text{Cl}_6$ has been solved and single crystal spectral data presented in detail [259]. The crystal structure of the cyclobutadiene nickel complex (102) shows coordination of the nickel to two bromides and the cyclobutadiene ring [260]. An unusual nickel

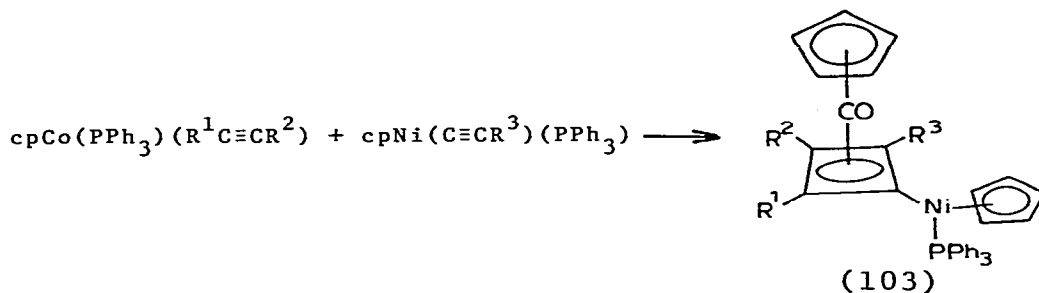


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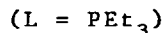
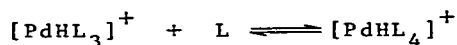
complex (103) has been prepared by treating $\text{cpNi}(\text{C}\equiv\text{CR}^3)(\text{PPh}_3)$ with $\text{cpCo}(\text{PPh}_3)(\text{R}^1\text{C}\equiv\text{CR}^2)$. The R groups used are phenyls and methyl



esters [261]. Alkali borinates $\text{M}[\text{C}_5\text{H}_5\text{B-R}]$, where boron is a ring hetero-atom, will coordinate to platinum to form complexes $\text{PtMe}_3(\text{C}_5\text{H}_5\text{B-R})$ [262]. The ^1H and ^{13}C nmr spectra of nickelocene and a series of alkyl substituted derivatives have been reported [263].

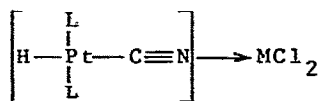
X. Metal hydrides.

Two papers have been published on the mechanism of ligand association in solution of complexes $[\text{MHL}_3]\text{X}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) [264,265]. The methods used are to measure the noise decoupled ^{31}P nmr spectra of the compounds over a range of temperatures, and to use a computed permutational line shape analysis to investigate the exchange. The situation is covered where both intramolecular and intermolecular bond breaking processes are simultaneously involved. Thus for the equilibrium shown below there is the added component to the problem that HPdL_3^+ is planar and rigid, whereas $[\text{PdHL}_4]^+$ is

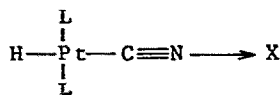


fluxional. The conclusions reached in the second paper are that comparison of ligand dissociation k_{-1} from $[\text{MHL}_4]^+$ as compared to

intramolecular rearrangement k_m leads to the observations in $[\text{MHL}_4^+]$: $k_{-1} \gg k_m(\text{Pt})$; $k_{-1} \sim 10^2 k_m(\text{Pd})$; $k_{-1} \ll k_m(\text{Ni})$. In each case it is considered that the two species involved are of planar (C_{2v}) and distorted trigonal bipyramidal (C_{3v}) geometries. The complexes ML_4 ($M = \text{Pd}, \text{Pt}$; $L = \text{PEt}_3$), prepared from the dichlorides with potassium metal in THF, protonate to $[\text{MHL}_3]^+$ with ethanol [266]. The salts $[\text{NiHL}_4^+]$ ($L^1 = \text{PMe}_3, \text{PMe}_2\text{Ph}$) were obtained using $\text{Ni}(1,5\text{-COD})_2$ and L^1 in ethanol. A range of Lewis acids give stable adducts with trans- $\text{PtH}(\text{CN})(\text{PEt}_3)_2$. The ^1H nmr spectra in the high field region of these complexes (104,105) are compared. As the



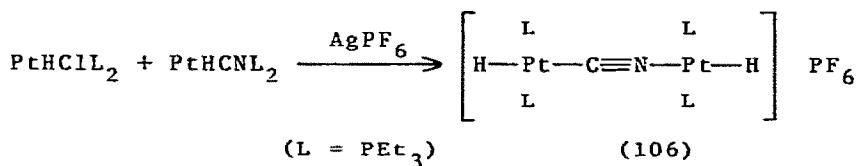
(104)



(105)

(L = PEt_3 ; M = Zn, Co, Ni)

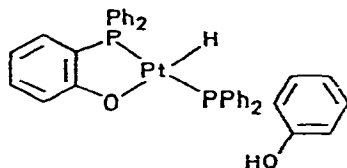
acidity of X increases the σ -donor power of CN^- will correspondingly decrease. Thus as the σ bond strength of CN^- decreases there will be an increase in the Pt 6s character of the Pt-H bond. From the value of $^1\text{J}(\text{Pt}-\text{H})$ the acid strength decreases in the order: $\text{AlCl}_3 > \text{BAr}_3 > \text{BR}_3 \sim \text{CoCl}_2 > \text{PtHL}_2^+ (106) > \text{AlAr}_3 > \text{ZnCl}_2 > \text{B}(\text{OAr})_3 > \text{AlR}_3 > \text{AlR}_2(\text{OR})$. The Pt compound in this list (106) is prepared by treating PtHClL_2 and trans- PtHCNL_2 with AgPF_6 [267]. Pentacoordinate nickel hydrides, $\text{NiH}(\text{CN})\text{L}_3$ ($L = \text{PEt}_3$) have been prepared by adding HCN to NiL_4 . A line shape analysis of the ^1H nmr spectrum indicates the phosphine exchanges by a dissociative process [268].



The compound $\text{HS}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{SMe}$ oxidatively adds to $\text{Pt}(\text{PPh}_3)_3$ to

give $\text{PtH}[\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{SMe}](\text{PPh}_3)$ which has the terminal thioether group uncoordinated [269].

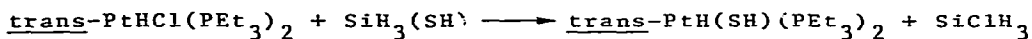
The first cis-dihydride platinum(II) compound has been reported. This complex $\text{PtH}_2(\text{Bu}_2^t\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}_2^t)$ is obtained in very high yield by reduction of $\text{PtCl}_2(\text{Bu}_2^t\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}_2^t)$ with NaBH_4 in ethanol. The monohydride $\text{PtHCl}(\text{Bu}_2^t\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}_2^t)$ is also reported. ^1H , ^{31}P nmr, and infrared data is given [270]. A similar phosphine ligand has been prepared with the methylenes in a meta- rather than an ortho-position. This ligand undergoes metallation very readily, and Ni, Pd, and Pt hydrides have been prepared where the phosphines span the trans positions [271]. When K_2PtCl_4 is treated with $\text{PPh}_2(\text{C}_6\text{H}_4\text{OH-}o\text{)}(\text{L})$ an intermediate PtCl_2L_2 is formed, which readily loses HCl to give cis- $\text{Pt}(\text{OC}_6\text{H}_4\text{PPh}_2)_2$. With NaBH_4



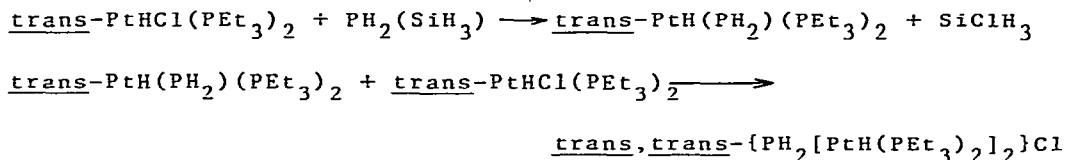
(107)

the hydride complex (107) is formed [272]. A group of hydrido-platinum(II) complexes $\text{PtH}(\text{YCN})(\text{PPh}_3)_2$ [$\text{Y} = (\text{CH}_2)_n$ ($n=1-3$); $o\text{-CH}_2\text{C}_6\text{H}_4$.] have been prepared. Carbon disulfide inserts into the hydride [273]. The effect on the ^1H nmr spectra of complexes trans- $\text{PtH}(\text{NCS})(\text{PBu}_3^n)_2$ and trans- $\text{PtH}(\text{NCS})(\text{AsBu}_3^n)_2$ from using a wide range of solvents has been investigated [274].

Platinum hydrides have been reacted with a variety of silanes and germanes. The products are silyl- and germyl-platinum complexes formed via unstable Pt(IV) intermediates. The interesting compound trans- $\text{PtH}(\text{SH})(\text{PEt}_3)_2$ is obtained from trans- $\text{PtHCl}(\text{PEt}_3)_2$ and $\text{SiH}_3(\text{SH})$ [275]. ^1H nmr data for this compound is given. In the



following paper the products arising from reacting $\text{PtHCl}(\text{PEt}_3)_2$ with silyl-amines and phosphines are published [276]. A very interesting compound $\text{trans,trans-}\{\text{PH}_2[\text{PtH}(\text{PEt}_3)_2]_2\}^+$ is reported from

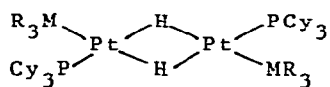


$\text{PtHCl}(\text{PEt}_3)_2$ and $\text{PH}_2(\text{SiH}_3)$. The palladium hydride $\text{PdH}(\text{NO}_3)(\text{PCy}_3)_2$ reacts with L (pyridines, pz, im.) to give complexes $[\text{PdH}(\text{L})(\text{PCy}_3)_2]^+$ [277]. ^1H nmr and infrared data is given. A series of hydrides $\text{PtHX}(\text{PBz}_3)_2$ (Bz = benzyl) and $[\text{PtH}(\text{L})(\text{PBz}_3)_2]\text{Y}$ (X = NO_3 , Cl, Br, I; L = NH_3 , PPh_3 , AsPh_3 , SbPh_3 ; Y = BPh_4 , ClO_4) have been prepared by treating the complex $\text{trans-PtH}_2(\text{PBz}_3)_2$ with HX, and then subsequently with L and NaY [278]. These authors also report similar analogues with PCy_3 [279].

When $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PCy}_3)_2$ is reacted with H_2 or R_3MH the hydride bridged compounds $[\text{PtH}(\mu\text{-H})(\text{PCy}_3)]_2$ (108) and $[\text{PtMR}_3(\mu\text{-H})(\text{PCy}_3)]_2$ (109) are formed [280]. The structure of the triethylsilyl complex shows a Pt-Pt distance of 2.692(3) Å. A series of platinum hydrides $\text{trans-}[\text{PtHL}(\text{PPh}_3)_2]\text{ClO}_4$ have been prepared where L is an allylic amine [281]. The complexes can eliminate amine to give π -allylic cationic Pt(II) compounds. Fluxionality for complexes $\text{trans-PtH}(\text{ArNNNAr})(\text{PPh}_3)_2$ is considered to occur via a pseudo penta-coordinated intermediate having both nitrogen atoms σ -facing the metal through two lone pairs. The structural parameters for the compound with Ar = p-tolyl are presented [282]. This crystal has been prepared using hydrazine or borohydride as reducing agents [284]. Calculations have been carried out on the molecule $\text{PtHCl}(\text{PH}_3)_2$ [285], and the compound $[\text{N,N}^1\text{-ethylenebis(salicylaldehyde)Pd}]^{2+}$ is discussed in terms of hydrogenase model [286].

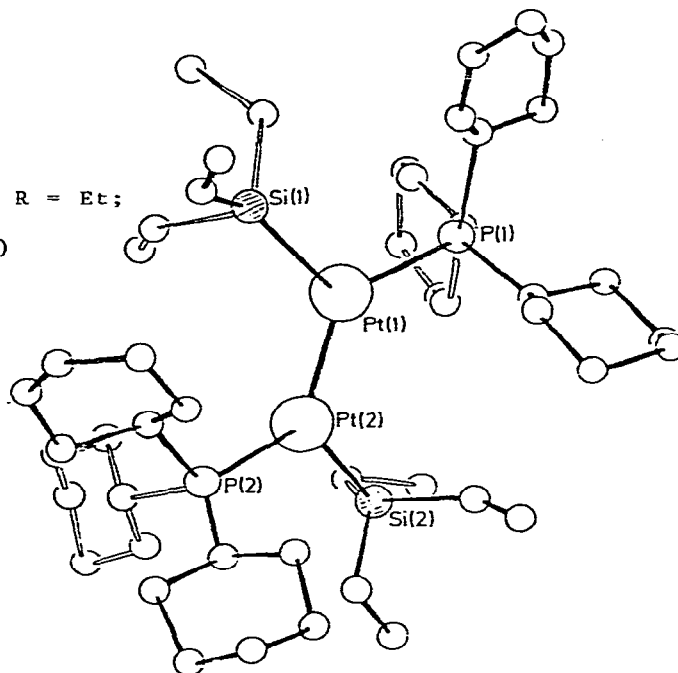
XI. Metal carboranes.

In a comparison of the ligand field strengths of NiCp_2 and $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})^{2-}$ the carborane ligand shows a weaker field. Four parameter ligand field theory is used to assign the bands, and the spin-orbit coupling constants and relativistic nephelauxetic parameters are estimated [287]. When the compound $\text{closo-3,3-}(\text{PPh}_3)_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}$ is heated in benzene the hydrido compound closo-

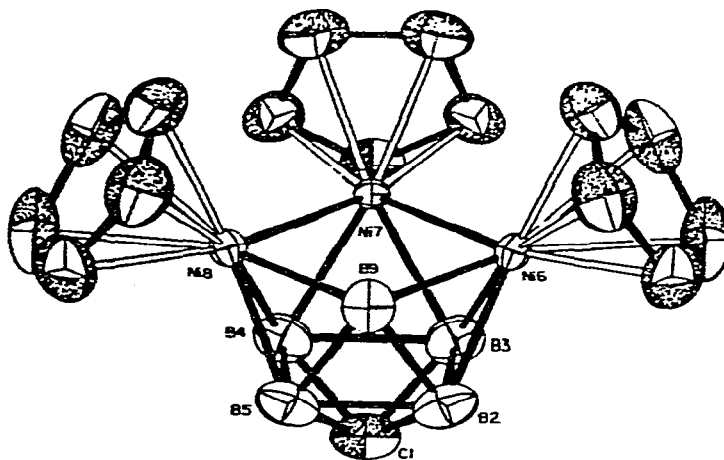


$R_3M = H$ (108); $M = Si, R = Et$;

$M = Ge, R = Me$ (109)

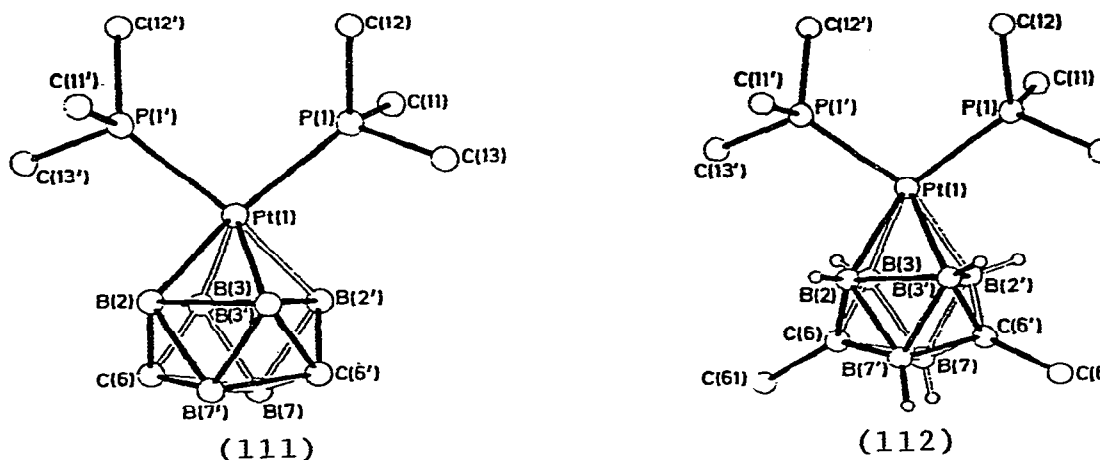


$3,8-(PPh_3)_2-3-H-3,1,2-NiC_2B_9H_{10}$ is formed quantitatively [288]. The hydride is identified by $\nu(Ni-H)$ at 1984 cm^{-1} and a resonance at $\tau 28.4$ ($J_{PH} = 89.0$; $J_{PH}^1 = 7.5\text{ Hz}$). A crystal structure of nido-(cpNi) $_3CB_5H_6$ (110), formed from $Nicp_2$ and Na/THF , shows the molecule to consist of a nine-vertex "opened" polyhedron [289]. This communication has been followed up and complexes (cpNi) $_3CB_5H_5R$ ($R = H, Me$) have been isolated in several isomeric forms. The compounds are formulated as mixed-valence systems with



(110)

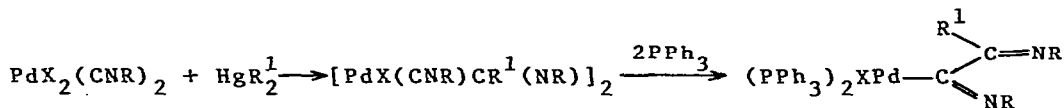
substantial mixed-valence charge transfer [290]. Complexes $ML(PPh_3)_2$ ($L = o$ -carborane dianion) have been prepared by treating $MCl_2(PPh_3)_2$ ($M = Pd, Pt$) with Li_2L [291]. Ligand displacement reactions have been used to convert $Pd(B_{10}H_{12})(PPh_3)_2$ into $[Pd(CN)_2(B_{10}H_{12})]^{2-}$, $[Pd[C_2S_2(CN)_2](PPh_3)_2]^{2-}$, and $Pd(phen)(B_{10}H_{12})$. This 1,10-phenanthroline complex can be reduced with butyllithium to $[Pd(B_{10}H_{11})]_2(phen)$ [292]. The crystal structures of closo-carbaplatinaoctaboranes 6,8-dimethyl-1,1-bis(trimethylphosphine) (111) and 1,1-bis(trimethylphosphine)-6,8-dicarba-1-platinaoctaborane (112) have been solved but not refined [293]. A series of complexes $PtH(\sigma\text{-carb.})L_2$ (carb = 2-R-1,2- or 7-R-1, 7- $B_{10}C_2H_{10}^-$



with $R = H, Me, Ph$; $L = PEt_3, PPh_3, PMePh_2, PMe_2Ph$) have been prepared by treating the chloroplatinum(II) compound with the lithium salt of the carborane [294]. Interestingly both the complexes with the carborane *cis* or *trans* to hydride have been isolated.

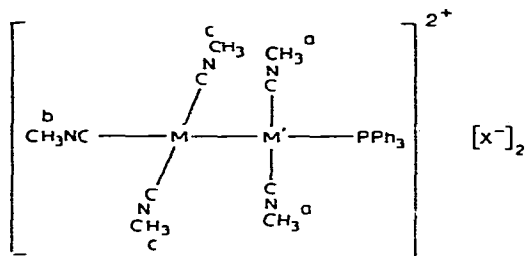
XII. Metal isocyanides.

Complexes trans- $PdX\{C(=NR)C(R^1)=NR\}(PPh_3)_2$ ($X = Cl, I$) are formed by treating the compounds cis- $PdCl_2(CNR)_2$ ($R = Ph, p\text{-MeC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4$) with HgR_2^1 ($R^1 = Me, Ph$), followed by addition of PPh_3 [295]. Spectroscopic data is presented for this range of complexes.

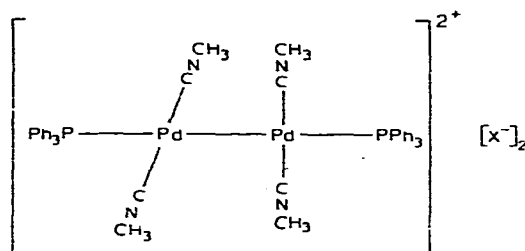


Compounds $[PdX(CNR)_2]_n$ and $[Pd_2(CNR)_6]Y_2$ ($X = Cl, Br$; $Y = Cl, Br, PF_6$; $R = Bu^L, Me$) are reported. Complexes of the former type are

obtained by treating $\text{Pd}(\text{dibenzylideneacetone})_3$ with $\text{PdCl}_2(\text{PhCN})_2$ and RNC . Addition of excess MeNC to $[\text{PdX}(\text{CNMe})_2]_n$ gives $[\text{Pd}_2(\text{CNMe})_6]\text{X}_2$. This dimer is considered to have a Pd-Pd bond, and to have orthogonal coordination planes about the palladium [295]. In a report on the chemistry of the cation $[\text{M}_2(\text{CNMe})_6]^{2+}$ it has been found that triphenylphosphine substitutes in an axial position. This pattern emerges for both the monosubstituted (113) and disubstituted product (114). The palladium complex is fluxional which

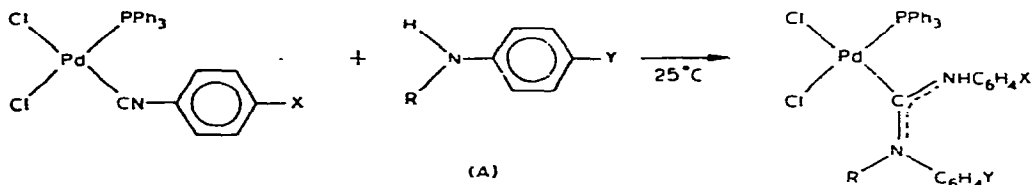


(113)



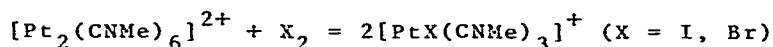
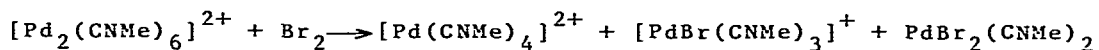
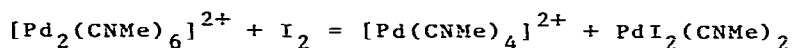
(114)

is considered to be a consequence of rotation about the Pd-Pd bond succeeding the attainment of tetrahedral geometry about palladium [297]. In a study of the reaction of the isocyanide compound *cis*- $\text{PdCl}_2(\text{CN-}p\text{-C}_6\text{H}_4\text{Cl})(\text{PPh}_3)$ with *N*-methylaniline to give the carbene derivative *cis*- $\text{PdCl}_2\{\text{C}(\text{NH-}p\text{-C}_6\text{H}_4\text{Cl})\text{NMePh}\}(\text{PPh}_3)$, it is concluded that H-bond formation with the solvent shows the rate of reaction. The nucleophilic attack of amine on the $\text{C}\equiv\text{N}$ carbon atom of the coordinated isocyanide is favored by low steric requirements and a high π -acceptor ability for L. Activation parameters are given [298]. In a further paper on the chemistry of isocyanide complexes

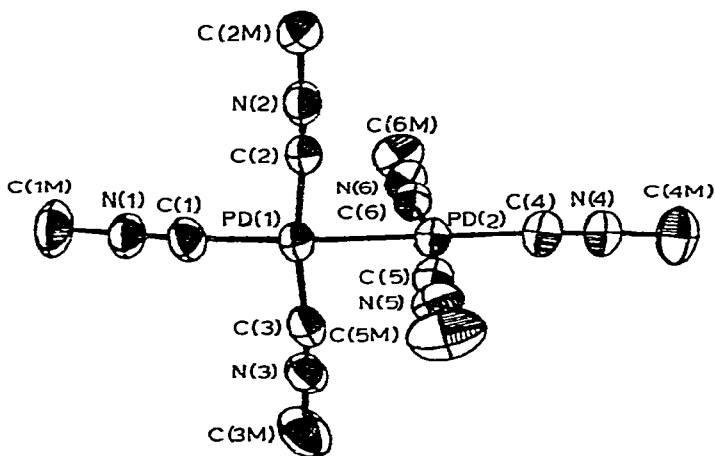


($\text{X} = \text{MeO}, \text{Me}, \text{H}, \text{Cl}, \text{NO}_2$; $\text{Y} = \text{MeO}, \text{Me}, \text{H}, \text{Cl}$; $\text{R} = \text{H}, \text{Me}, \text{Et}$)

with HgMe_2 and PPh_3 the initial product will function as a chelate ligand to a first row transition metal ion [299]. A more detailed account has been given of the syntheses of $[\text{Pd}_2(\text{CNMe})_6][\text{PF}_6]_2$ and $[\text{Pt}_2(\text{CNMe})_6]\text{X}_2$ ($\text{X} = \text{PF}_6, \text{BF}_4$) [300]. These compounds, which are formally Pd(I) and Pt(I), show little tendency to disproportionate, and the M-M bonds are quite resistant to homolytic cleavage. The cleavage reactions of halogens do occur, however, and are shown in the equations below:



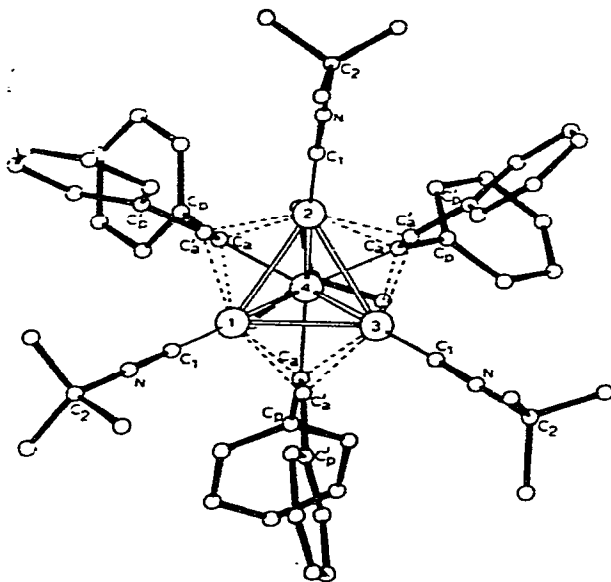
The molecular structure of $[\text{Pd}_2(\text{CNMe})_6](\text{PF}_6)_2 \cdot \frac{1}{2}\text{Me}_2\text{CO}$ shows a Pd-Pd distance of 2.5310(9) Å which is the shortest Pd-Pd distance recorded. The Pd-axial bonds to carbon are significantly longer than the equatorial ones [301]. The compound $[\text{Pd}(\text{CNMe})_4](\text{TCNQ})_4 \cdot 2\text{MeCN}$ has



been synthesized and the structure solved. Semiconductor behavior is found for the triclinic material, but there is no interaction between the anions and cations [302]. The electronic structure of $[\text{Pt}(\text{CNMe})_4](\text{PF}_6)_2$ shows 9 bands in the electronic spectrum. Assignments are presented and a state diagram is shown [303]. The complexes $[\text{Pt}(\text{CNR})_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{CNR})_2(\text{CNR}^1)_2][\text{PtCl}_4]$ have been

synthesized with a range of R groups [304].

The crystal structure of $\text{Ni}_4(\text{CNCMe}_3)_4[\mu_3(\eta^2)\text{-PhC}\equiv\text{CPh}]_3$ shows a slightly compressed nickel tetrahedron with a terminal isocyanide bonded to each metal atom. The diphenylacetylene ligand is bonded to one of the three trimetallic faces [305]. A structure of $\text{PtMe}[\text{HB}(\text{pz})_3](\text{CNMe}_3)$ shows the isocyanide linearly coordinated at



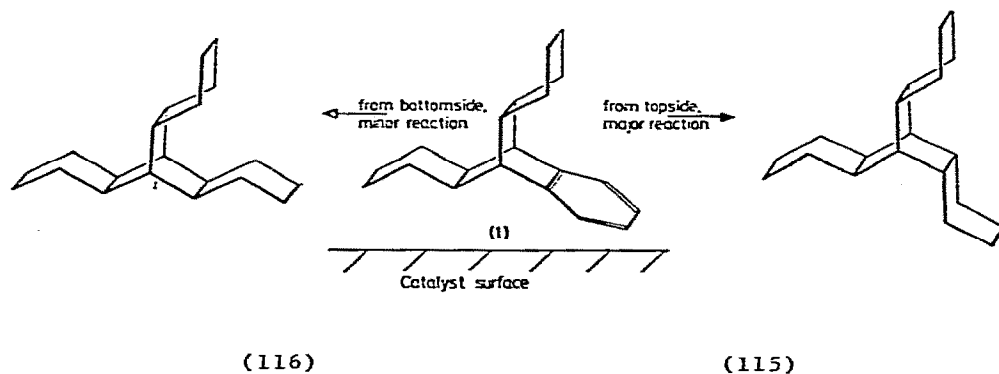
a distance of $1.86(2) \text{ \AA}$ for Pt-C [306]. A series of isocyanide nitroso complexes $\text{M}(\text{ArNO})(\text{CNBu}^t)_2$ [$\text{M} = \text{Ni}$; $\text{Ar} = \text{p-XC}_6\text{H}_4$ ($\text{X} = \text{NMe}_2$, OMe , Me , H , Cl , Br), $3,4\text{-Cl}_2\text{C}_6\text{H}_3$; $\text{M} = \text{Pd}$; $\text{Ar} = \text{p-ClC}_6\text{H}_4$] have been reported. A good correlation exists between the $\text{N}\equiv\text{C}$ stretching frequencies (A^1 and A^{11} modes) and the Hammett σ constant (σ_p) of the para substituent. Consistently a linear correlation is found between $\Delta\tau$ of the metal protons and the cis stretch-stretch interaction $\Delta\nu(\text{N}\equiv\text{C})$. The reaction of PhNO with CNBu^t to give Bu^tNCO , $\text{PhN}=\text{N}(\text{O})\text{Ph}$, and $\text{PhN}=\text{C}=\text{NBu}^t$ can be carried out catalytically [307].

Calculations are reported on molecules $\text{Ni}(\text{O}_2)(\text{CNH})_2$ [308] and $\text{Ni}(\text{HC}\equiv\text{CH})(\text{CNH})_2$ [309].

XIII. Catalytic reactions involving complexes.

In a comparative study of the hydrogenation of acetone to isopropanol the complex $\text{PtCl}_2(\text{PPh}_3)_2$ is effective, $\text{Pt}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$ is less effective, and isopropanol is not obtained with the compounds $\text{MCl}_2(\text{PPh}_3)_2$ ($\text{M} = \text{Ni}$, Pd). Somewhat surprisingly $\text{CF}_3\text{CO}_2\text{H}$ is the best solvent [310]. Butyraldehyde and ben-

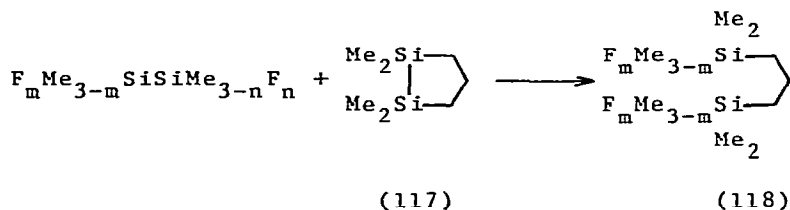
zaldehyde are hydrogenated to the alkyl trifluoroacetates; cyclohexanone is converted to the ether, and acetophenone and benzophenone to the hydrocarbons. Treating $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ with PPh_3 , and reducing with NaBH_4 in air, gives an active catalyst for the hydrogenation of hexene-1, cyclohexene, benzaldehyde and nitrobenzene [311]. Active catalysts for the hydrogenation of aromatic compounds have been prepared from $\text{Ni}(\text{acac})_2$ and LiAlH_4 or NaBH_4 [312]. The temperatures used for the catalytic work are in the 150-200° range, and the catalyst has been used to hydrogenate toluene, xylene, and naphthalene to saturation. An interesting report considers the stereochemical consequences in product distribution for hydrogenation occurring on platinum by attack of chemisorbed hydrogen on chemisorbed aromatic, or by gas-phase attack by hydrogen



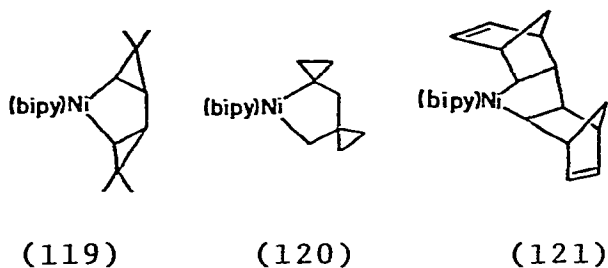
on chemisorbed aromatic. The ratio of compounds (115):(116) is 10:1 indicating predominance of the Rideal mechanism of topside attack [313]. A polymer-palladium complex, prepared from PdCl_2 and styrene-divinylbenzene copolymer with iminodiacetic acid groups, catalyzes the selective hydrogenation of conjugated dienes to monoenes at 30°C under an atmosphere hydrogen pressure [314]. The stereochemistry of the Pd-catalyzed exchange of deuterium with the allylic hydrogens in cholest-8(14)-en-3 β -ol shows only one allylic methylene group participates. This is considered to be in disagreement with previous mechanistic concepts. The isomerization of cholest-7-en-3 β -ol is catalyzed by $\text{PdCl}_2(\text{PhCN})_2$ but not by $\text{RhH}(\text{PPh}_4)_4$ [315]. Complexes $\text{PtCl}_2(\text{PPh}_3)_2\text{-X}$ ($\text{X} = \text{SnCl}_2, \text{GeCl}_2, \text{SnCl}_4, \text{PbCl}_2, \text{SiCl}_4, \text{SbCl}_3$) catalyze the hydroformylation of olefins to aldehydes. Conditions of temperature and pressure are given for the conversion to linear straight-chain aldehyde with high selectivity [316]. A mechanistic catalytic cycle is presented.

The complex $\text{NiCl}_2[(\text{R})-(\text{PhCH}_2)\text{Me}(\text{Ph})\text{P}]_2$ is a good catalyst precursor for the asymmetric hydrosilylation of 1,1-disubstituted

prochiral olefins with SiMeCl_2H [317]. The highest optical yield of 20.9% was obtained with 1-methylstyrene. The addition products were obtained in much lower optical yields with chiral platinum(II) complexes. The details of the synthesis and use of these chiral platinum(II) complexes as asymmetric hydrosilylation catalysts is described in an earlier article by these authors [318]. An interesting disilane metathesis occurs between fluorinated disilanes and 5-membered ring silanes (117) at 100° in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ as catalyst to give a mixed fluoro-cyclic silane (118) [319]. The complex $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$ is reported to catalyze the

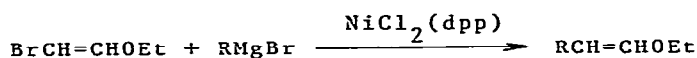


hydrosilylation of ketones PhCOR with SiMeCl_2H [320]. PdCl_2 , $\text{Pd}(\text{PPh}_3)_4$, and $\text{Pd}(\text{OAc})_2$ have been anchored to diphenylphosphinated styrene-divinylbenzene resins and the resulting materials used as catalysts for the oligomerization of butadiene [321]. The product distribution is unchanged from comparable homogeneous catalysts using the same phosphine:palladium ratio. In view of the effectiveness of $\text{Ni}(0)$ to catalyze $[2\pi + 2\pi]$ cycloaddition of strained-ring olefins to cyclobutane derivatives, an attempt to isolate possible intermediates is of interest. The complexes (119–121) have been



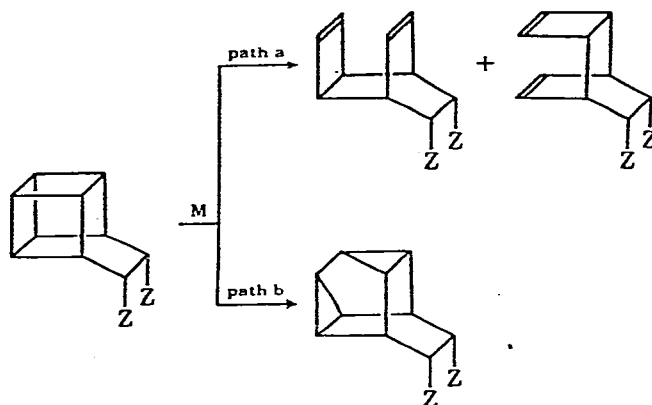
isolated as air-sensitive dark green crystals by treating $\text{Ni}(1,5\text{-COD})(\text{bipy})$ with 1,1-dimethylcyclopropene, methylenecyclopropane, and norbornadiene respectively [322]. The complex $\text{NiCl}_2(\text{dpp})$ is useful for the coupling reaction of β -bromovinyl ethers with

Grignard reagents to form the corresponding alkylated and arylated vinyl ethers in high yield [323].



Reduction of $\text{PdCl}_2(\text{PPh}_3)_2$ with NaOPr in the presence of cis- and/or trans- $\text{CH}_2=\text{CHCH}=\text{CHMe}$, or isoprene, gives complexes $\text{Pd}(\text{diene})(\text{PPh}_3)_2$. These compounds catalyze the dimerization of dienes to give conjugated linear dimers in high yield with negligible concomitant trimerization [324]. The complexes $\text{Ni}(\text{PPh}_3)_4$, $\text{Ni}[\text{P}(\text{OEt})_3]_4$, $\text{NiCl}_2(\text{PPh}_3)_2$, or $\text{NiCl}(\text{PPh}_3)_3$ and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyze propene dimerization. The addition of acids enhances catalytic activity [325]. The complex $[\text{Pt}(\text{MeCN})_4](\text{BF}_4)_2$, prepared from $\text{PtCl}_2(\text{MeCN})_2$ and AgBF_4 in acetonitrile solution, can be used as a catalyst for the dimerization of branched olefinic monomers at room temperature in nitromethane as solvent [326]. The oligomerization of propene has been effected by catalysts formed by reacting $\text{Ni}(\text{C}_3\text{H}_5)_2$ with the hydroxide groups of silica gel, and complexation with the different Lewis acids TiCl_4 , AlCl_3 , AlBr_3 and $\text{R}_n\text{AlCl}_{3-n}$ ($\text{R} = \text{Me}, \text{Et}; n = 1, 1.5, 2, 3$) [327]. The temperature and preferred Lewis acid has been optimized. In a similar manner a complex has been formed from nickel(II) chloride and ethylaluminum dichloride which can be used as a catalyst for butadiene polymerization [328].

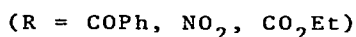
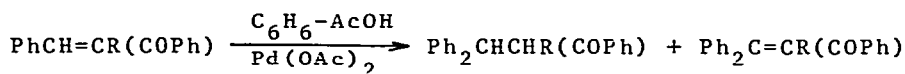
Skeletal isomerization of cis-9,10-dicarbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane with $\text{Ni}(0)$ complexes gives exo- and endo-cis-9,10-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7-dienes, and only a small amount of cis-9,10-dicarbomethoxypentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane. Using $\text{Ni}(1,5\text{-COD})_2$ or $\text{Ni}(\text{acrylonitrile})_2$ alone is ineffective for the transformation, but the use of additional electron-deficient olefins or PPh_3 causes the transformation to proceed smoothly [329]. A molecular orbital approach to the mechanistic is discussed. Nickel complexes such as $\text{Ni}(\text{PPh}_3)_4$ have been used for stereoselective alkenyl-aryl coupling between trans-alkenylalanes and aryl bromides or iodides [330]. In a stereochemical study of the reaction of CO with cis- and trans-2-butene it has been concluded that the exclusive pathway involves stereospecific methoxypalladation [331]. In the subsequent paper, the synthetic utility of this reaction has been explored [332].



Aryl, benzyl, vinyl, and heterocyclic halides RX, can be converted to the acids RCO_2H by adding the RX along with a small amount of PPh_3 to a mixture of $\text{PdCl}_2(\text{PPh}_3)_2$, NaOH , and $\text{Bu}_4^{\text{n}}\text{NI}$ under a CO atmosphere [333]. Benzaldehyde has been obtained in good yield by

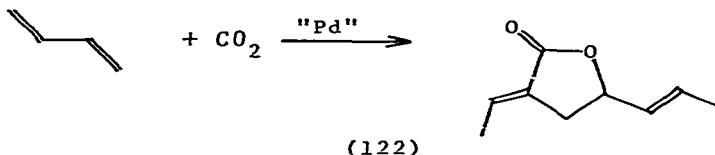


the formylation of PhI with CO and H_2 in the presence of $\text{PdCl}_2/\text{pyridine}$ as catalyst [334]. Kinetic data is presented which is interpreted in favor of a mechanism involving formyl- and benzoyl-palladium(II) intermediates. These authors have also made a kinetic study of the formation of methyl cyclohexanecarboxylate by the carbonylation of cyclohexene in methanol using a $\text{PdCl}_2/\text{PPh}_3$ catalyst [335]. The rate is first-order in cyclohexene and is not affected by changing the mole ratio of $\text{PdCl}_2:\text{PPh}_3$ from 3 to 8. A mixture of $\text{Pd}(\text{OAc})_2$ and acetic acid in benzene is an effective catalyst for the addition of benzene to $\text{PhCH}=\text{CR}(\text{COPh})$. The reaction formally



involves addition of benzene across a C=C double bond [336]. Ethyl 3-phenylpropionate can be prepared by the carbonylation of styrene with CO and ethanol, using complexes $\text{Pd}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$ ($n = 3, 4, 5$) as catalysts [337].

Nickel (0) complexes promote cleavage of C-O bonds in phenyl carboxylates and alkenyl acetates to give nickel carbonyls and nickel phenoxide. A mixture of $\text{Ni}(1,5\text{-COD})_2$ and a phosphine is quite effective [338]. Asymmetric induction in the hydrocarboxylation of olefins has been studied using a (-)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane/ PdCl_2 catalyst [339]. The catalytic addition of CO_2 to butadiene in the presence of phosphine palladium complexes gives, in addition to butadiene oligomers, a small amount of 2-ethylidenehept-5-ene-4-olide (122) [340].



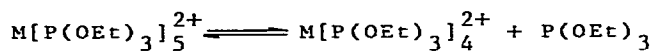
Formic acid has been catalytically synthesized from CO_2 and H_2 using complexes $\text{Pd}(\text{dpe})_2$, $\text{Pd}(\text{PPh}_3)_4$, and $\text{Ni}(\text{dpe})_2$ as catalysts in the presence of an amine. Catalytic quantities of water increase the yield of formic acid considerably [341].

An aqueous solution of palladium salts will oxidize benzene-1,4-diol to benzoquinone. The first stage of the reaction involves the conjugate base of a Pd(II) aquo ion and leads to formation of an isolable palladium(0)-benzoquinone intermediate. This intermediate slowly decomposes in the second stage. Chloride ion inhibits the reaction [34]. In the oxidation of olefins by $\text{Na}_2\text{Pd}_2(\text{OAc})_6$ in acetic acid the rate of oxidation of 3,3-dimethyl-1-butene is slower than ethylene [343]. The rate is decreased upon increasing the olefin concentration. Rate and equilibrium constants have been measured, and an important feature of the mechanism is the requirement of a vacant coordination site on Pd(II), before Pd(II) hydride elimination can occur from the acetoxypalladation intermediate. A palladium catalyzed oxidation of α -allyl and α -3-butenyl ketones has been used to prepare 1,4- and 1,5-diketones [344].

XIV. Complexes and reactions of general interest

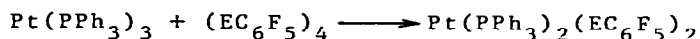
In addition to the work on hydrides described earlier, the

du Pont group have measured free energies of activation (ΔG^\ddagger) for the equilibrium:



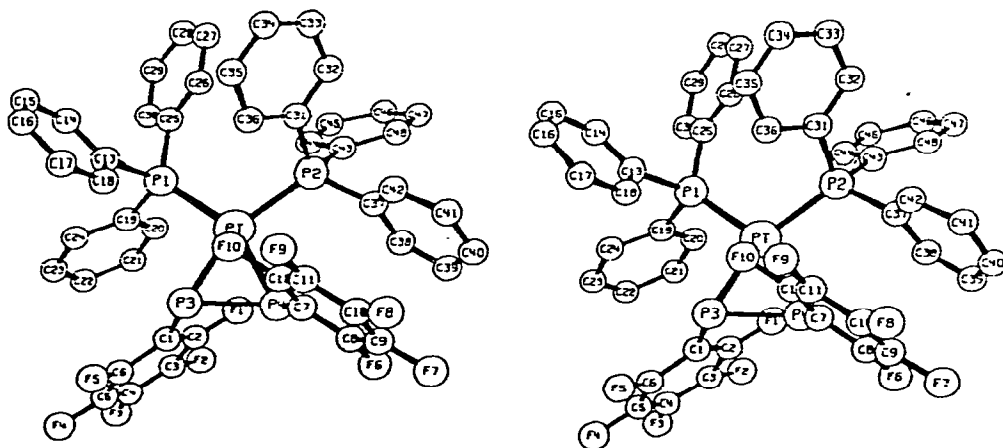
(M = Ni, Pd, Pt)

The planar association-trigonal bipyramidal reaction coordinate appears to involve tetragonal pyramidal intermediates or transition states, implying that the axial ligands in the trigonal bipyramid do not remain collinear with the metal throughout the reaction [345]. The method of probing the system is by use of ^{31}P nmr spectroscopy. Calculations have been carried out on the molecule $\text{Ni}(\text{PF}_3)_4$ [346], and electron diffraction work on $\text{Pt}(\text{PF}_3)_4$ concludes the structure to be tetrahedral with a Pt-P distance of 2.229(5) Å [347]. The PF_3 groups freely rotate. An X-ray structure of $\text{Pd}(\text{PPh}_3)_4 \cdot 0.5\text{C}_6\text{H}_6$ shows a tetrahedral geometry with 4 equal Pd-P bonds of length 2.443(5) Å [348]. The platinum complexes $\text{Pt}(\text{PPh}_3)_2(\text{PC}_6\text{F}_5)_2$ and $\text{Pt}(\text{PPh}_3)_2(\text{AsC}_6\text{F}_5)_2$ have been prepared from $\text{Pt}(\text{PPh}_3)_3$ with $(\text{PC}_6\text{F}_5)_4$ and $(\text{AsC}_6\text{F}_5)_4$ respectively [349]. A crystal structure of the phosphorus derivative shows a distorted square

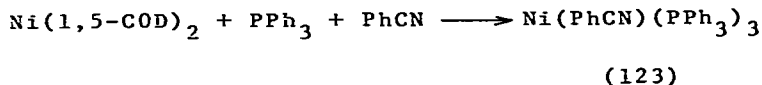


E = P, As

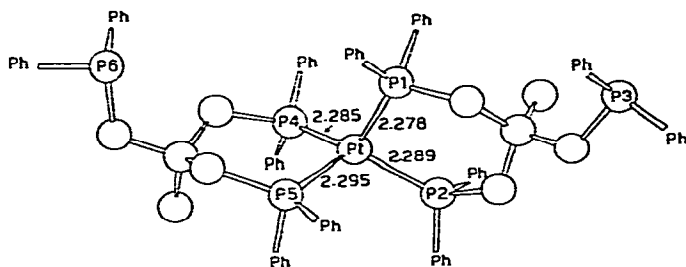
planar geometry about platinum and a dihedral angle between the two



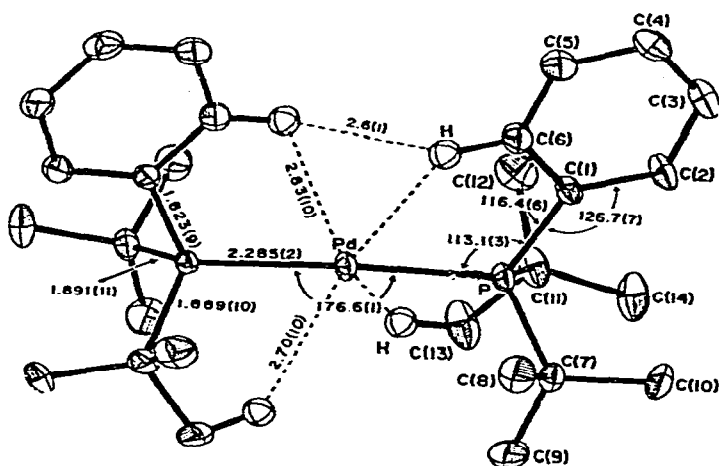
PtP₂ planes of 20.4° [349]. Treating PPh₃ with Ni(1,5-COD)₂ in a ratio of 3:1, followed by addition of PhCN, gives Ni(PhCN)(PPh₃)₃ (123). The structure of (123) shows a pseudo-tetrahedral geometry



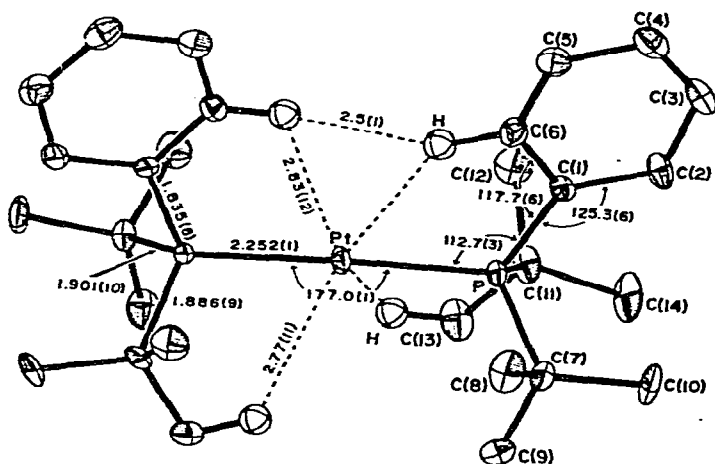
about Ni. The PhCN is coordinated through N. For PPh₃, three P-C bonds take up nearly eclipsed conformations while the other six are in nearly staggered positions [350]. Linear complexes PdL₂ (L = PBu₃^t, PPhBu₂^t (124), PCy₃) have been prepared from Pdcp(C₃H₅), and analogous compounds PtL₂ (L = PBu₃^t, PPhBu₂^t (125), PCy₃, PPr₃ⁱ) from trans-PtCl₂L₂ and Pt(1,5-COD)₂. Crystal structures for (124) and (125) show a slightly bent linear coordination 176.6(1)° (124), 177.0(1)° (125). The M-P distances are 2.285(2) Å (124) and 2.252(1) Å (125), and there is no indication for the formation of ML₃ with PPhBu₂^t [351]. The isolation and characterization of a series of triarylstibine complexes of Ni(0), Pd(0) and Pt(0) is reported [352]. An X-ray structure of Pt(triphos)₃ (triphos = MeC(CH₂PPh₂)₃) shows the molecule to be electron precise



because one phosphorus containing arm of each triphos is bent away from platinum and is not coordinated [353]. Sulfur dioxide and carbon disulfide adducts of Ni[1,1,1-tris(diphenylphosphinomethyl)ethane] have been prepared, and an X-ray structure of the SO₂ compound (126) shows the molecule bonded through sulfur with a Ni-S bond length of 2.013(3) Å [354]. A structure of a further SO₂



(124)

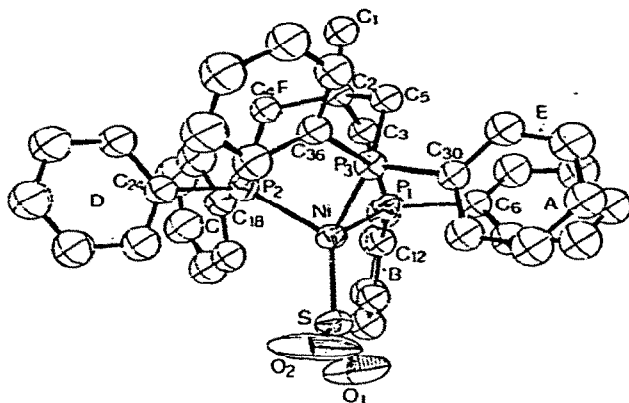


(125)

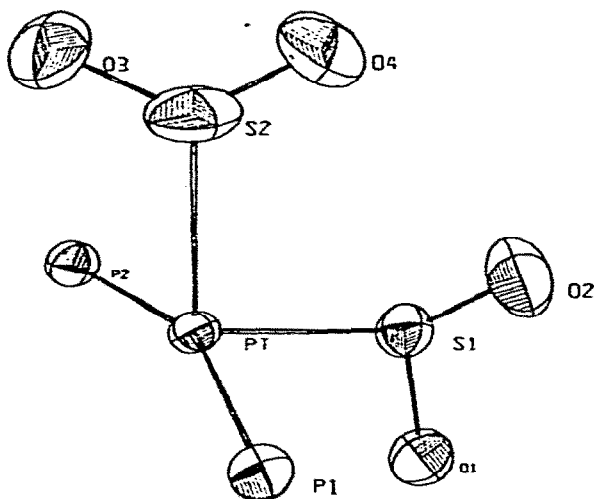
adduct, $\text{Pt}(\text{SO}_2)_2(\text{PPh}_3)_2$ (127) shows a severely distorted tetrahedral geometry about platinum with P-Pt-P and S-Pt-S angles of $158.58(6)^\circ$ and $106.33(8)^\circ$ respectively [355]. In a further paper these workers have published the structure of $\text{Pt}(\text{SO}_2)(\text{PPh}_3)_3 \cdot 0.7\text{SO}_2$ (128) which again shows the S-bonded sulfur dioxide molecule [356].

In a calorimetric study of $\text{Ni}(1,5\text{-COD})_2$ with PR_3 and $\text{Bu}^{\text{t}}\text{NC}$,

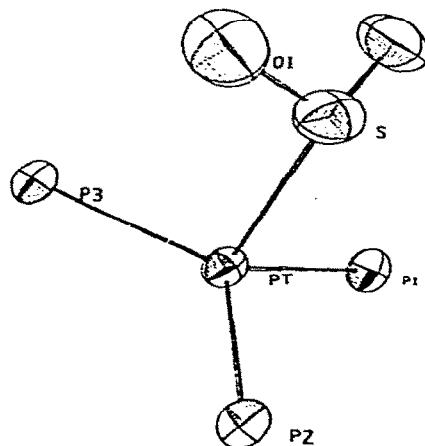
the extent of reaction and mean Ni-P bond strength decreases with increasing ligand size. This data is tabulated with the cone



(126)



(127)

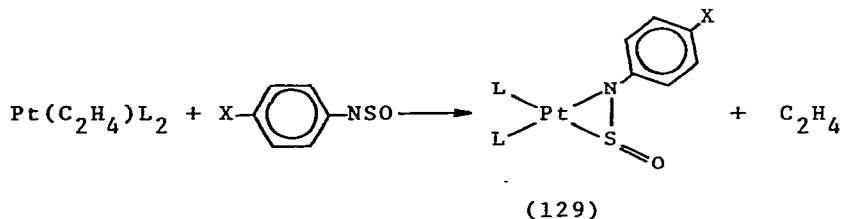


(128)

angle values of the ligands in order to estimate steric strain energies in NiL_4 complexes [357]. Two articles have appeared on the oxidative addition to Pd(0) complexes [358,359]. From work with optically active benzyl chloride it has been concluded that

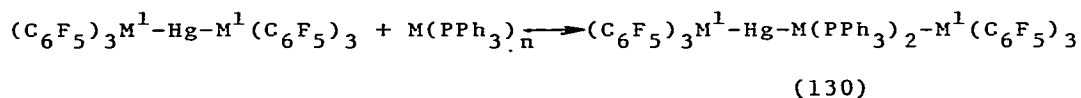
the addition proceeds with inversion at carbon. In the second paper the course of reaction leading to organic products is determined by the stability of the alkylpalladium intermediate. Instability can lead to β -elimination or to a free radical decomposition leading to coupling products.

In a re-investigation of the reaction of N-sulfinylanilines with $\text{Pt}(\text{PPh}_3)_2^0$ and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, the former compound yields $\text{Pt}(\text{SO}_4)(\text{PPh}_3)_2$ as the only isolable product. These authors do, however, report 1:1 adduct formation (129) between *p*-substituted N-sulfinylanilines and $\text{Pt}(\text{PPh}_3)_2$ [360]. The first stage of the



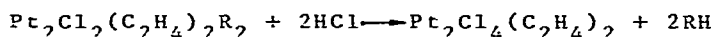
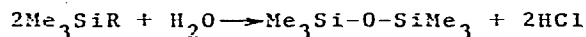
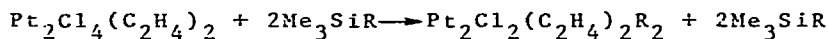
(L = PPh_3 ; X = H, Me, NO_2)

reaction between organomercurials and complexes of $\text{Pt}(0)$ yield organoplatinum mercury compounds. These compounds have been found to be quite stable when perfluorinated groups, or steric hindrance in the vicinity of the metal-metal bond, is present [361]. The species $\text{Pt}(\text{PPh}_3)_2$ and $\text{Pd}(\text{PPh}_3)_2$ will insert into the Hg-Ge or Hg-Sn bond in the compounds $(\text{C}_6\text{F}_5)_3\text{M}-\text{Hg}-\text{R}$ (M = Ge, Sn; R = Et, $\text{Ge}(\text{C}_6\text{F}_5)_3$, $\text{Sn}(\text{C}_6\text{F}_5)_3$) to give the tetrametallic chain compounds (130) [362]. Complexes *cis*- or *trans*- $[\text{PtX}(\text{R}-\text{N}=\text{S}=\text{N}-\text{R})\text{L}_2](\text{ClO}_4)$ (X = Cl;

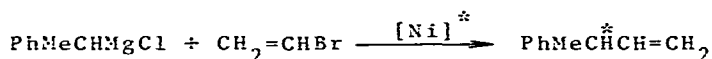


(M = Pt, $\text{M}^1 = \text{Ge}$; M = Pd, $\text{M}^1 = \text{Ge}$; M = Pt, $\text{M}^1 = \text{Sn}$)

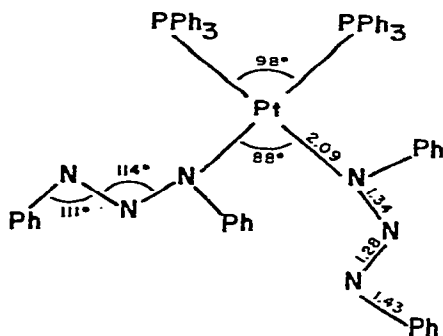
L = Et_2S , AsMe_2Ph , PMe_2Ph ; R = Me, Bu^t . X = Me; L = PMe_2Ph ; R = Me) have been prepared. The intramolecular and intermolecular conversions between isomers in solution is reported [363]. Complexes $\text{Pt}_2\text{Cl}_4(\text{olefin})_2$ react with alkyl- and aryl-silanes with cleavage of the silicon-carbon bond [364].



Among a set of data on ^{13}C nmr of transition metal carbonyls is reported the spectra of $[\text{cpNi}(\text{CO})]_2$. Chemical shift data for terminal and bridging carbonyls over a range of temperatures is reported [365]. Chiral (aminoalkylferrocenyl) phosphines have been used as ligands for nickel complexes which will catalyze asymmetrical Grignard cross-coupling to form an optically active hydrocarbon



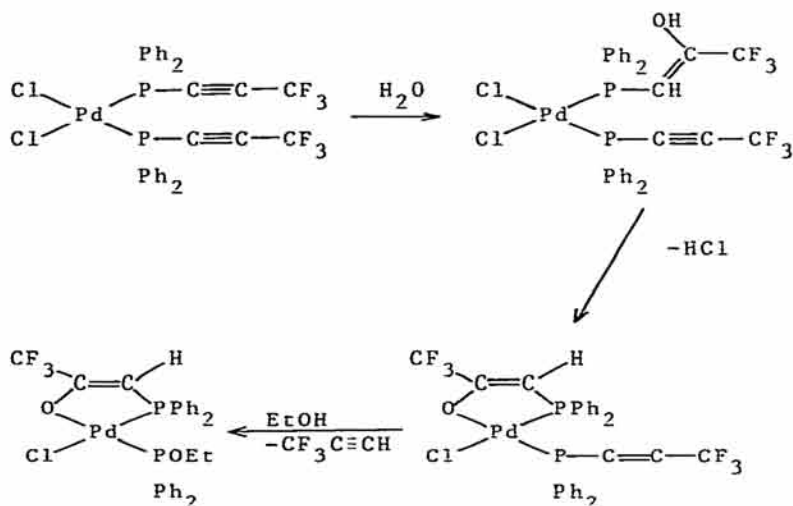
[366]. The first example of a monodentate mode of bonding for the 1,3-diphenyltriazenido ligand is found in the complex cis-Pt(PhNNNPh)(PPh₃)₂ (131) [367]. An interesting compound Ni(toluene) has been



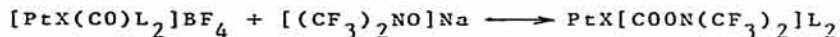
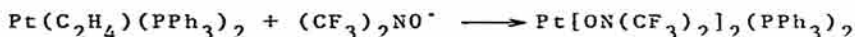
(131)

prepared from nickel atoms and toluene. The complex is considered to be a π -complex and can be used to prepare $\text{Ni}[\text{P}(\text{OEt})_3]_4$ [368]. The controlled hydrolysis of cis-PdCl₂(Ph₂PC≡CCF₃)₂ leads to the complex PdCl[Ph₂PCH(CF₃)O][Ph₂P(OEt)] (132), which has been verified by an X-ray structure [369]. A series of tricyanomethanide complexes Pd[NCC(CN)₂]₂L₂ (L = PPh₃, AsPh₃; L₂ = dpe) have been prepared from Ag[C(CN)₃] [370]. When PtCl₂(PhCN)₂ is

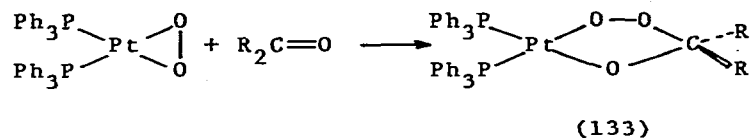
reacted with $\text{Me}_3\text{C}\cdot\text{CH}_2\text{PBU}_2^t$ the compound $[\text{PtCl}(\text{PBU}_2^t\text{CH}_2\text{CMe}_2\text{CH}_2)]_2$ is formed. A crystal structure shows that σ -metallation on the neo-pentyl group has occurred [371]. Transition metal complexes of bis(trifluoromethyl)nitroxide, including one of Pt(II), have been prepared from Pt(0) and Pt(II) precursors [372]. A nickel(I) (d^9) intermediate has been identified by epr on irradiation of $\text{NiCl}(\text{NO})(\text{dpe})$ with O_2 . The final product is $\text{NiCl}(\text{NO}_2)(\text{dpe})$ [373]. A kinetic study on the addition of ketones to the compound $\text{PtO}_2(\text{PPh}_3)_2$ to yield cyclic ozonide products (133) has been interpreted in favor of a dual mechanism. The faster pathway is one



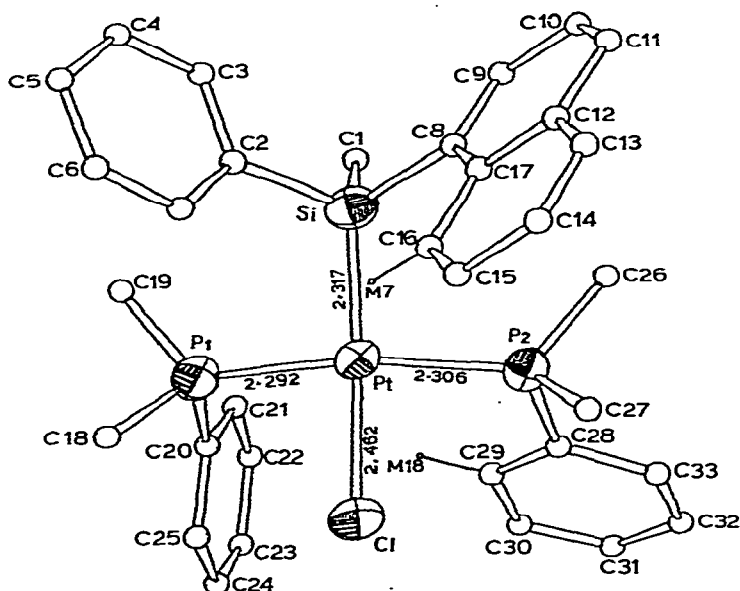
which is first order in each reactant, and is considered to involve coordination of the ketone prior to insertion. The slower path is



less well understood, but is independent of ketone in the transition state [374]. The compound $\text{Pt}(\text{NO}_2)_2(\text{PPh}_3)_2$ has been prepared from $\text{Pt}(\text{PPh}_3)_4$ and NOBF_4 [375]. A complex $\text{Pt}(\text{SiPh}_2)_3\text{SiPh}_2$, with



platinum incorporated into a silicon ring, has been prepared from $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and $\text{Si}_4\text{H}_2\text{Ph}_8$ [376]. The crystal structure and absolute configuration of the complex (+)-*trans*- $\text{PtCl}[\text{SiMe}(\text{l-C}_{10}\text{H}_7)\text{Ph}](\text{PMe}_2\text{Ph})_2$ shows the (S) absolute configuration which corresponds to that of its precursor (R)(+)- $\text{Me}(\text{l-C}_{10}\text{H}_7)\text{PhSiH}$ [377]. The crystal



structure of $\text{PtCl}[\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}](\text{PMe}_2\text{Ph})_2$ shows a Pt-Si bond length of 2.292 Å [378]. The reaction of $\text{Ni}(\text{C}_2\text{H}_4)_2(\text{PPr}_3^i)$ with BF_3 at -78° gives a compound $\text{Ni}(\text{BF}_3)_3(\text{PPr}_3^i)$, which on warming to room temperature gives $\text{Ni}(\text{BF}_3)(\text{PPr}_3^i)$ [379].

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