NICKEL, PALLADIUM AND PLATINUM

ANNUAL SURVEY COVERING THE YEAR 1974

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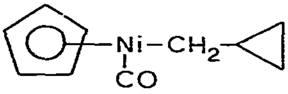
NOTE: This article on organometallic derivatives of Ni, Pd and Pt and their reactions, is only comprehensive if read in conjunction with the survey for 1974 appearing in this journal entitled "Transition Metals in Organic Synthesis", by L. Hegedus. Duplications in these two surveys have been minimised (see Vol.103 (1975) 421-474).

ABBREVIATIONS

Ac = acyl
acac = acetylacetonate
aq = aqueous
bipy = 2,2 -bipyridyl
COD = 1,5 -cyclooctadiene
COT = cyclooctatetraene
Cp = cyclopentadienyl
dba = dibenzylidene acetone
DIARS = 1,2 -bis(methylphenylarsino)ethane
dma = dimethyl acetylenedicarboxylate
DMF = dimethylformamide
DPB = bis-1,2-(diphenylphosphino)butane
DPE = bis-1,2-(diphenylphosphino)ethane
DPM = bis-1,2(diphenylphosphino)methane
en = ethylenediamine
Hfaca = hexafluoroacetyl acetone
NBD = norbornadiene
phen = *ortho*-phenanthroline
py = pyridine
RT = room temperature
sal=N-R = N-organosalicylaldimines
THF = tetrahydrofuran
TMMP = trimethylenephosphorane

I Metal-carbon σ-complexes

A review on stable homoleptic metal alkyls, containing references to Cu, Ni and Pd complexes has appeared [1]. The structural determination of $Ni(Et)(acac)PPh_3$ has shown the compound to have a normal stereochemical configuration (Ni-C 1.97Å). The single sharp resonance observed for the ethyl protons has been attributed from ^{13}C NMR measurements, to accidental proton equality and not scrambling [2]. New cyclopentadienyliron alkyl carbonyls and nickel alkyls have been prepared [e.g. $CpNiR(PPh_3)$, $R=CF_3, CF_2CF_3, CF(CF_3)_2$] and evidence obtained, from ^1H and ^{19}F NMR data, for restricted rotations about the metal-alkyl bond [3]. NMR studies showed the existence of the $[NiMe(PMe_3)_4]^+$ cation in solutions of $NiMe(PMe_3)_3X$ ($X=Cl, Br, I, SCN, O_2PMe_2$) and PMe_3. The cation was fluxional and computer simulation of the NiMe PMR gave an activation energy of 11.6 kcal/mole for the intramolecular pseudorotation [4]. $CpNi(CH_2SPh)PPh_3$ is formed from $LiCH_2SPh$ and the corresponding halide and tended to eliminate CH_2 to give the metal thiophenolates [5]. The carbonyl-π-cyclopentadienylnickel anion reacted with but-3-enyl chloride and cyclopropylmethyl bromide in THF at 75° to give cis- and trans-(η^2-but-2-enyl)-π-cyclopentadienylnickel and (1) respectively. Photolysis of (1) effected insertion of the carbonyl group into the cyclopropylmethyl ring [6]. Ni and Pd atoms have been employed as synthetic reagents for the formation of a series of bis(methylphosphine) organonickel and palladium complexes [7]. Two kinetically distinct steps in the mechanism of methyl transfer from methylcobalamin to Pd(II) have been identified. The initially established equilibrium involves a relatively rapid complexation between $PdCl_4^{2-}$ and the benzimazole nitrogen of the cobalamin, followed by a slower methyl transfer to palladium [8].



(1)

Trimethylplatinum azide has been prepared [9] and characterised crystallographically. The cubane structure consists of $[PtMe_3N_3]_4$ molecules in which each α-nitrogen of the azide groups links three platinum atoms [10]. A number of acac complexes of dimethylplatinum (IV) have been synthesised [11]. R_2Mg(R=Me,Ph) were found to be as active as organolithium compounds in preparing PtR_2L_2 complexes (L = mono- or L_2 = bidentate tertiary phosphines) [12]. The tetramer $[Me_3PtI]_4$ or $CpPtMe_3$ and potassium trispyrazolylborate or tetrakispyrazolylborate gave $Me_3Pt(C_3H_3N_2)_nBR$ (R=H, n=3; R=O, n=4) respectively. Potassium bispyrazolylborate and $[Me_3PtI]_4$ produced $Me_3Pt(C_3H_3N_2)BH_2$ which contains a novel B-H-Pt bridge, as characterised by an IR band at 2039 cm^{-1} [13]. Compounds of the type $PtMeL_2I$ were prepared by olefin displacement from PtMe(NBD)I (L_2 = COD, $Me_2N(CH_2)_2NMe_2$; L = 3,5-lutidene, $PhCH_2NH_2$). Oxidative additions to some of these products with I_2 and MeI gave mono- and dimethylplatinum(IV) compounds [14]. Neutral and cationic cyanoalkyls of Pt(II) have been characterised [15,16], e.g. cis- and trans- $[PtCl(CH_2CN)(PPh_3)_2]$ were formed from $Pt(PPh_3)_4$ and $ClCH_2CN$ in acetone and benzene respectively [16]. In some cases [15] coordination of the CN group promoted cis-trans isomerisations, as well as addition reactions of alcohols to give imino ethers. Insertion reactions with CO were also observed.

A number of studies on the mechanistic aspects of oxidative additions to palladium and platinum compounds have been reported [17-24]. The crystal structure of trans-bromo(trans-styryl)bis-(triphenylphosphine)platinum(II) indicated that the oxidative addition reaction of trans-β-bromostyrene to $Pt(PPh_3)_4$ is stereospecific [17]. With sec-alkyl and benzyl halides and $Pt(PPh_3)_4$, only PtX_2L_2 products were obtained. A mechanism was proposed and the importance of some new five-coordinate PtX_2L_3 complexes in the mechanism of phosphino catalysed isomerisations of square planar PtX_2L_2 compounds discussed [18]. The formation of $MBr_2(PEt_3)_2$ from $M(PEt_3)_3$ (M=Pd,Pt) and reactive alkyl halides occurred too rapidly for a radical chain process and with some additions a one electron process, as a component of the oxidative addition reaction, has been inferred from CIDNP enhancements in ^{1}H NMR spectra of the reaction mixtures [19]. In other alkyl halide reactions with M(PEt$_3$)$_3$ the evidence points to a radical chain process as the major pathway in the addition reaction. Part of this evidence was; (i) neopentyl bromide and Pt(PEt$_3$)$_3$ in toluene produced, as well as the expected product, <u>trans</u>- [Pt(CH$_2$C$_6$H$_5$)Br(PEt$_3$)$_2$]; (ii) radical scavengers reduce the reaction rate by a factor of $5-10^3$. (iii) optically active addenda molecules produce optically inactive species [20]. Similar studies of additions of S(+)-PhCHDCl to Pd(PPh$_3$)$_4$ [21], and of S(−)-α-phenethyl bromide to Pd(CO)(PPh$_3$)$_3$ [22] showed, by a series of carbonylation and/or degradation steps, that a stereospecific inversion at the asymmetric carbon atom centre occurred on complex formation. Kinetic behaviour observed for the reactions of MeI with Pt(PPh$_3$)$_n$ (n = 2,3) was consistent with scheme 1.

$$\begin{aligned}
&\mathrm{PtL_3} \overset{K}{\rightleftharpoons} \mathrm{PtL_2} + \mathrm{L}\\
&\mathrm{PtL_3} + \mathrm{MeI} \xrightarrow{k_1} \mathrm{PtMeIL_2} + \mathrm{L}\\
&\mathrm{PtL_2} + \mathrm{MeI} \xrightarrow{k_2} trans\text{-}\mathrm{PtMeIL_2}
\end{aligned}$$

(Scheme 1)

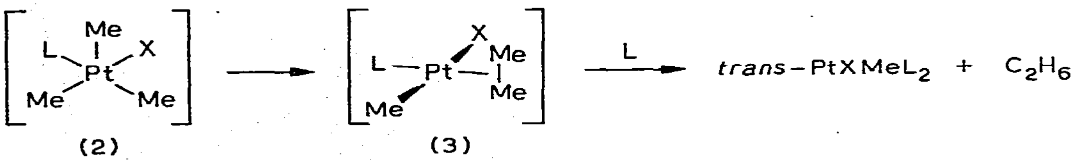
A polar transition state was inferred from rate increases in polar solvents [23]. The stereochemistry of the reactions of MeI and CF$_3$I with <u>cis</u>-PtR$_2$L$_2$ (R=Ph, Me; L=CNC$_6$H$_4$Me, AsMe$_3$, PMe$_2$Ph) were dependent upon R and L, and stereochemical rearrangements were facilitated by cation formation. In several instances reductive eliminations to Pt(II) compounds occurred. Kinetic data for MeI additions to <u>cis</u>-[PtMe$_2$(CNC$_6$H$_4$Me)$_2$] were given, and the stereochemistry of the Pt(IV) complexes formed from I$_2$, MeI and CF$_3$I and <u>trans</u>-[PtRI(PMe$_2$Ph)$_2$] (R = Ph, Me) were discussed [24].

A series of spectroscopic studies on platinum alkyl complexes have appeared [25-36]. Far IR and Raman measurements on PtR^{1}R$_2$XL$_2$ (R = Me,

CD_3; R^1 = Me, CD_3, CF_3, MeCO, $PhCH_2$, CH_2= CH-CH_2; X = Cl, Br, I; L = phosphine, arsine) have led to an unambiguous assignment of ν(Pt-X) [25]. The $^{129}Ie^2qQ$ values from the ^{129}I Mössbauer spectra of neutral and cationic compounds of type *trans*-[Pt $^{129}IXL_2$] (X = Me, CF_3, I; L = PMe_2Ph) and *trans*-[Pt $^{129}IL^1L_2]^+$ (L^1 = $P(OMe)_3$, $P(OMe)_2Ph$, PPh_3, $AsPh_3$, EtNC, *p*-$MeOC_6H_4NC$) were shown to be very sensitive to *trans*-ligand influence and a *trans*-influence series for these ligands was established [26]. Various factors affecting fragmentation paths and ion abundances have been identified in a mass spectroscopic study on PtR_2L_2 (R = alkyl, aryl; L = PR_3; L_2 = chelating diphosphine). Rearrangement processes occur in which organic groups are transferred to and from phosphorus and platinum and a mechanism is proposed whereby polyphenyl ions are formed [27]. Pt 4f bond energies have been calculated from the X-ray photoelectron spectra of L_2PtXY (L = PPh_3, $SbPh_3$; X = Y = halogen, H, Me, $C(CN)_3$, NCO, SCN, $(NC)_2C = C(CN)_2$, N_3, CN). Lower Pt 4f bond energies were observed for stibine complexes compared with phosphine compounds [28]. ^1H-$\{^{31}P\}$ and ^1H- $\{^{195}Pt\}$ INDOR spectra have been recorded for $PtMe_3(acac)PPh_3$. The stereochemical dependence of the absolute signs of $^3J_{P,H}$ for the Pt-Methyl protons was determined [29]. The ^1H, ^{13}C and ^{195}Pt NMR spectral parameters of the cyclopropane complexes $PtX_2(C_3H_6)L_2$ (X = Cl, Br; L = py, 4-Mepy; L_2=en) suggest the presence of the ring $\mathrm{P}\overline{\mathrm{t}}\rfloor$ in these compounds [30]. A comparison of the ^{13}C shieldings and ^{13}C-^{195}Pt coupling constants of a series of *trans*-Pt aryl and alkyl complexes was presented. A bonding model in which σ-rather than π-interactions are dominant in the phenyl-platinum bond was suggested [31]. Four papers on ^{13}C NMR spectra of platinum-methyl complexes have appeared and differences between the NMR *cis*- and *trans*-influences discussed [32-35]. It is of interest to note that in recent correspondence the validity of many papers rationalising ^{13}C chemical shifts for carbon atoms bound to transition metals has been convincingly questioned [36].

Silicon-nickel [37] and -platinum [38] complexes have been prepared from corresponding metal-alkyls and silicon hydrides. Compounds characterised were $Ni(bipy)(SiX_3)_2$ (X_3 = Cl_3, $MeCl_2$), $CpNi(SiCl_3)PPh_3$, $PtH(SiR_3)(PMe_2Ph)_2$ (R = Ph, p-FC_6H_4) and cis-$[Pt(SiR_3)_2(PMe_2Ph)_2]$ (R_3 = $MePh_2$, Ph_2H), and some of these compounds were found to be active catalysts for hydrosilylation of olefins [37]. Relevant parameters from the X-ray structure of $Pt(CH_2SiMe_3)Cl(PMe_2Ph)_2$ were Pt-C 2.08 Å, Pt-Cl 2.42 Å and Pt-P 2.29 Å [39]. Benzenethiol reacts with methylplatinum(II) compounds to cleave the metal-C bond by a free radical chain mechanism [40]. In inert solvents CF_3HgX (X = O_2CCF_3, Cl) and cis-$[PtMe_2(PPh_3)_2]$ give CF_3HgMe and cis- $[PtClMe(PPh_3)_2]$ [41].

The products from the thermal decomposition of $[PtMe_3(acac)]_2$ have been characterised [42]. Ethane, ethylbenzene and CD_3COMe were the primary components from heating $PtR_2R^1X(PMe_2Ph)_2$ (X = halogen; R = Me; R^1 = benzyl, allyl; R = CD_3, R^1 = acetyl; R = Et, R^1 = Me). For X = Br, R = Me, R^1 = CH_2-$CH = CH_2$ the decomposition apparently occurs via a free radical mechanism, and for X = I, R^1 = Me, R = Et the initial step was the β-elimination of C_2H_4 [43]. The reductive elimination of ethane from fac-$[PtXMe_3L_2]$ (X = Cl, Br; L = PMe_2Ph; X = I, L = PMe_3, PMe_2Ph, $PMePh_2$) has been studied kinetically, and the mechanism was inferred to proceed via an intramolecular reductive elimination process involving a five coordinate intermediate formed by ligand dissociation. Further evidence for the five-coordinate intermediate came from the scrambling of methyl and $[^2H_3]$ methyl groups in $[PtMe(CD_3)IL_2]$ (L = PMe_2Ph, $AsMe_2Ph$) and $Pt(CD_3)_2MeX(PMe_2Ph)$ (X = Cl, Br, I). The pathway, involving the intermediates (2) and (3) is favoured by (i)



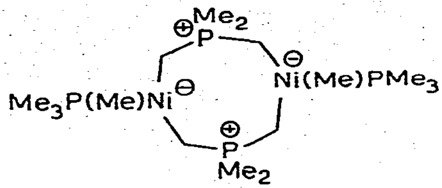
reduction in metal electron density from initial ligand dissociation and (ii) stabilisation of the intermediate because of a preferred coordination number [44]. The first estimated Pt–C bond strength for the cyclopropyl-platinum products $PtX_2C_3H_6$ and $PtX_2(C_3H_6)L_2$ (X = Cl, Br; L = py, 4-Mepy; L_2 = bipy, en) calculated from differential scanning calorimetry and thermo-gravimetric analysis is reported [45].

Oxidative additions of fluorohalobenzenes and benzonitriles with the zerovalent compounds $M(PEt_3)_4$ (M = Ni, Pd, Pt) and $Ni(DPB)_2$ gave the σ-aryl complexes $MXRL_2$ (M = Ni, Pd, Pt, X = Cl, Br, I, CN, F, R = C_6H_4F, L = PEt_3 [46]; M = Ni, X = CN, R = Ph, L_2 = DPB [47]). Reaction of the bromo derivatives with PhMgBr and with MeLi provided a route to <u>trans</u>-$M(R)(C_6H_4F)(PEt_3)_2$ (R = Ph, Me) [46]. The electronic interaction between nickel containing groups and the aromatic ring in <u>p</u>-$CNC_6H_4NiX(PR_3)_2$ and <u>p</u>-$MeCOC_6H_4NiX(PR_3)_2$ (R = Ph, C_6H_{11}, Et; X = Cl, Br, N_3, CNO, SCN) was studied by IR [48]. When nickel core electron binding energies in <u>trans</u>-$[NiXY(PEt_3)_2]$ (X = Y = alkyl, alkenyl, alkynyl, aryl, halide) are compared with calculated nickel charges, Ni–aryl π-bonding is concluded to be unimportant [49].

A new series of reactive intermediates of formula ArPdX, RPdX and RCOPdX were formed by inserting Pd atoms into aryl, alkyl and acyl carbon bonds at low temperatures. The stability of the species was a function of R and these intermediates could be trapped with ligands to form the corresponding species $PdRXL_2$ [50]. Bis(pentafluorophenyl)palladium(II) complexes with monodentate and bidentate nitrogen-donor ligands have been prepared [51]. Protonation of $Pd(Ph)Br(PPh_3)_2$ with HBr in dioxane to give benzene has been reported to be first order in HBr. A mechanism involving attack on a solvolysed intermediate formed by PPh_3 dissociation was invoked [52].

Bond lengths of Pt-C(CO) 1.97 Å, Pt-C(phenyl) 2.06 Å and Pt-P(mean) 2.30 Å were obtained from the X-ray structural determination of $[Pt(CO)(\textit{p}\text{-}ClC_6H_4)(PEt_3)_2]PF_6$ [53]. A novel reaction between RHgX (R = *p*-tolyl, $(\textit{p}\text{-}MeOC_6H_5)_2C = CH$, MeO_2CCH_2, X = Br, Cl) and $Pt(PPh_3)_n$ (n = 3,4) was a useful route to $PtRX(PPh_3)_2$ [54]. Other routes to pentafluorophenylpalladium and platinum complexes were (i) metathetical replacements of Cl in $[PdCl(C_6F_5)(PPh_3)_2]$ with X (X = Br, I, NO_3, CN, AcO, SCN, ClO_4) [55]; (ii) displacement of ClO_4 in $M(C_6F_5)L_2(ClO_4)$ (M = Pd, L = PPh_3 [56]; M = Pt, L = PEt_3 [57]) by L^1(L^1 = PPh_3, PEt_3 $AsPh_3$, PBu_3, py, H_2O, CO, $OPPh_3$, $SPPh_3$, $HNPr_2$) [56,57] and (iii) oxidative additions of Cl_2,Br_2,I_2 and $BrTl(C_6F_5)_2$ to Pt(II) compounds [58]. In a study of the rates of reversible reactions between *trans*-$[PtCl(\textit{o}\text{-}tolyl)(PEt_3)_2]$ and various substituted pyridines in methanol the strong rate dependence of the incoming group arises because of competition between the incoming pyridine and leaving chloride ion for a solvolysed intermediate [59]. The rate of displacement of chloride ion in the complexes *cis*- and *trans*- $[PtRCl(PEt_3)_2]$ (R = Ph, *o*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$) by CN^- decreases as steric hindrance in the complex increases and inferences were drawn as to the configuration of the transition state. Spontaneous isomerisation of *cis* to the *trans*-isomer in methanol was observed [60].

The reactions of the ylide $Me_3P = CH_2$ with $NiMe_2(PMe_3)_2$ and $NiMeCl(PMe_3)_2$ produced the molecular ylide $[Me_2\bar{N}i][(CH_2\overset{+}{P}Me_3)PMe_3]$, and the ionic ylide $[Me(Me_3P)\bar{N}i(CH_2\overset{+}{P}Me_3)_2]Cl$ containing three covalent Ni-C δ bonds stabilised by the proximity of the ylide onium centre. With an excess of $Me_3P{=}CH_2$, the ionic ylide is converted to (4). The isoelectronic dimethylphosphinate (5) was also prepared [61]. Corresponding reactions [62] of $Me_3P = CH_2$ with $NiCl_2(PMe_3)_2$ gave 2 isomeric forms, one a cage-like structure containing four equivalent $Me_2P(CH_2)_2$ bridges between two Ni atoms, and the other a tricyclic molecule which was solved crystallo-



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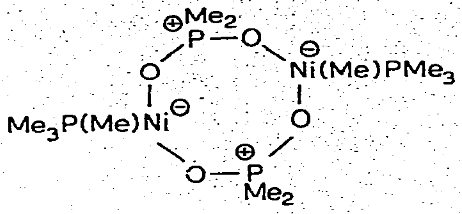
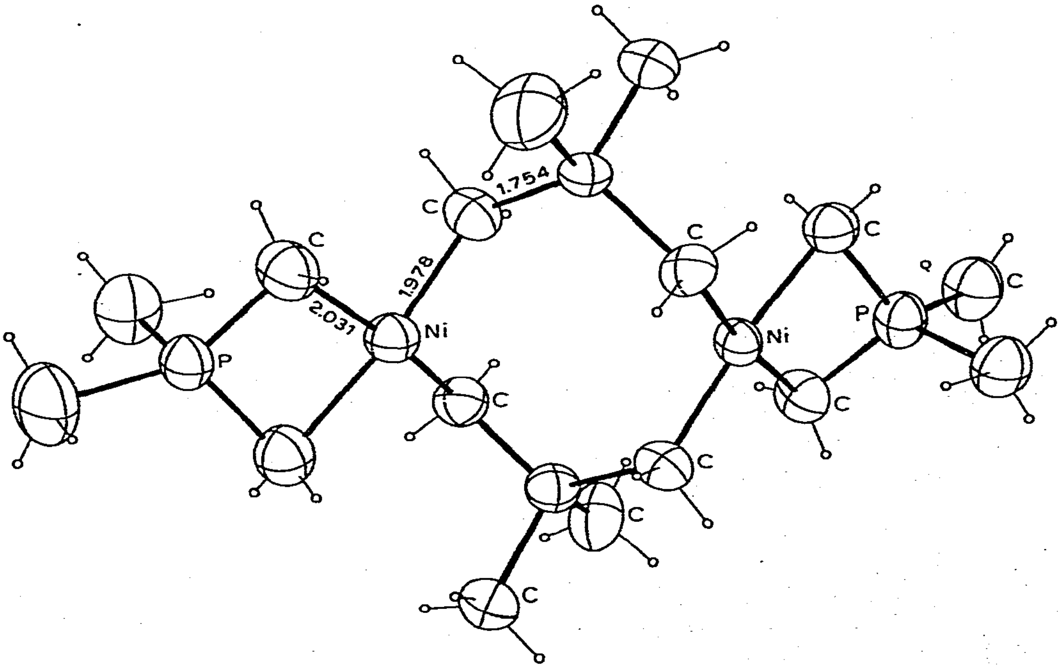


(5)

graphically (6) [63]. Keto stabilised sulphonium ylides displace styrene and PhCN from palladium complexes to give stable 2:1 ylide-$PdCl_2$ compounds. An epimeric equilibrium between _trans_ square-planar structures in solution was described, and a 1:1 ylide-PdI_2 product from $Me_2S = CH_2$ was reported [64]. Methylphenylsulphonium _p_-chlorophenacylide (= Sy) additions to _cis_-$[PtX_2(SR_2)_2]$ (X = Cl, Br, I; R = Me, Et) gave (7), which exists as the _cis_- and _trans_-isomer in solution. ^1H NMR evidence indicated restricted rotation about the Pt-S bond of coordinated dimethyl sulphide [65].



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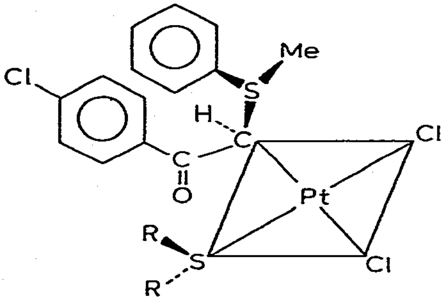
II Metal complexes formed by insertion and related reactions

Some insertion reactions into metal-alkyl bonds with isocyanides [66-69], carbon monoxide [70-71], diphenylketene [72] and acetylenes [73] are reported and a review on insertion reactions involving platinum complexes has appeared [74]. Palladium [66] and platinum [67] iminoalkyl complexes have been prepared and the structure of $PtI\{C(Me)=NC_6H_4Cl\}(PEt_3)_2$ has been resolved [67]. New compounds isolated were trans-$[PdL_2X\{C(R) = NR^1\}]$ ($R = Me$, Ph, o-tolyl; $R^1 = C_6H_{11}$, Me_3C, $PhCH_2$, Ph; $X = Br$, I; $L = PPh_3$, PMe_2Ph, PMe_3, $P(n\text{-}C_4H_9)_3$, $PPh_2(C_6H_{11})$) and with $PMePh_2$ the bridged species (8) was formed. Doubly inserted products obtained were trans-$[PdL_2I\{(C = NC_6H_{11})_2Me\}]$ ($L = PPh_3$, $PMePh_2$, PMe_2Ph, PMe_3) and triple insertions gave $Pd(PMePh_2)I\{(C = NC_6H_{11})_3Me\}$, of structure (9) [66]. The reaction of (10) with varying amounts of RNC ($R = C_6H_{11}$, Me) gave the compounds (11) and (12), and the insertion product (14) was formed from (13) and $C_6H_{11}NC$ [68,69]. The complexes $Pt_4(CO)_5L_4$ [$L = PPh_3$, $PPh_2(o\text{-}MeC_6H_4)$, $PPh(o\text{-}MeC_6H_4)_2$],



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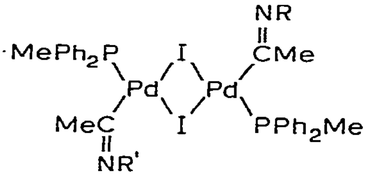

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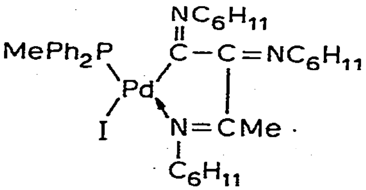

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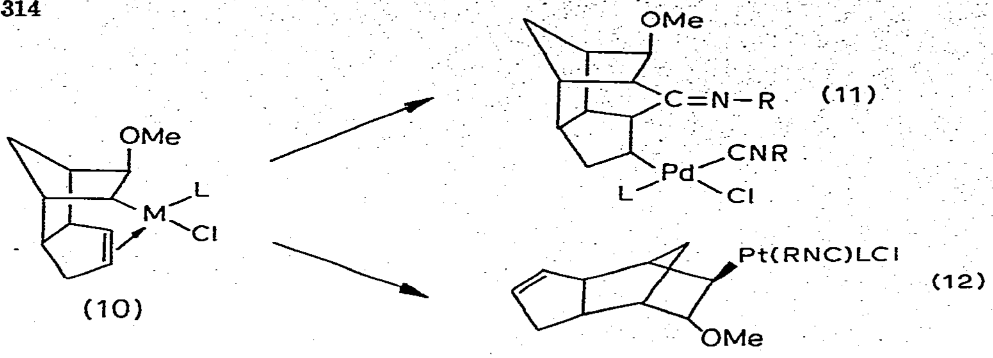

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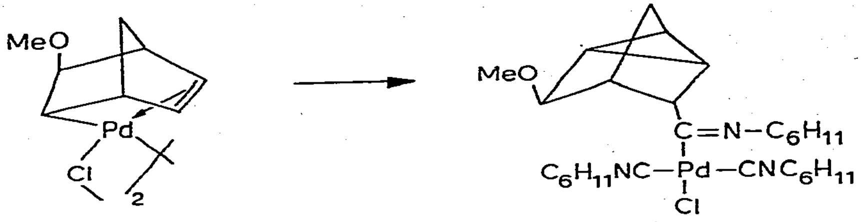
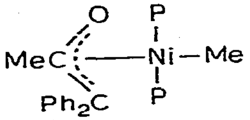


(13) (14)

prepared from a one step reduction of $PdCl_2$, add MeI to give Pt(Me)I(CO)L and which further react with L^1 to form Pt(COMe) inserted products. A balance of steric and electronic effects determined whether substitution or insertion occurred [70]. A kinetic study of the reaction $PtMeI(CO)PPh_3 + L^1 \longrightarrow Pt(COMe)I(PPh_3)L^1$ for L^1 = $AsPh_3$, As(p-$MeC_6H_4)_3$, AsMe(o- $MeC_6H_4)_2$ and $SbPh_3$ showed that the first and largely rate controlling step involves neither L^1 nor solvent and was thought to involve the intermediate [Pt(COMe) $IPPh_3$] [71]. Treatment of $NiMe_2(PMe_2Ph)_2$ with diphenylketene gave (15) [72]. The new olefin complexes [PtMe(olefin)DIARS]PF_6 (olefin=C_2H_4, C_3H_6) do not insert whereas [PtMe(acetone)L_2]PF_6 (L_2 = DIARS, DPE) and $PtMeL_2NO_3$ react smoothly at 25° with the acetylenes RC ≡ CR (R = CF_3, CO_2Me) to give the corresponding vinylic derivatives $Pt\{RC = CRMe\}XL_2]^{n+}$ (X = NO_3, n = 0; X = acetone, n = 1). The results are consistent with electronic effects of olefin and acetylene controlling the insertion reaction [73]. The complex formed from <u>trans</u>-[$PtMeXL_2$] (X = Cl, Br, I; L = PMe_2Ph) and RC ≡ CCO_2Me using a radical initiator (for R = CO_2Me) or by HCl addition (for R = CO_2Me, Ph, Me, H) is now shown to be the β-chlorovinylplatinum complex *trans*-[PtXL$_2${C(CO$_2$Me)=CR^{1}R}] (R^1 = Cl) and not the complex (R^1 = Me) initially postulated [75]. Enthalpies for the thermal decarbonylation of PtCl(RCO)(PPh$_3$)$_2$ (R = phenyl or substituted phenyl) were measured by differential scanning calorimetry and a value for the Pt–benzoyl bond dissociation energy of ~180 Kj mole^{-1} obtained. A Pt–C π-bond dissociation energy of 273 Kj mole $^{-1}$ was calculated for bis(dibenzylideneacetone)palladium (0) [76]. The reactivity of alkyl-transition metals towards alkenes and alkynes falls in the sequence NiEt$_2$(bipy) >PtMe$_2$(bipy) >PtMeCl (bipy) > PdMeCl(bipy), which is also the order of decreasing energy of the filled metal d-orbital [77].

Metal-alkyl bonds have been formed from metal-olefins by alkoxide or amination reactions. Thus [CpNi diene]BF$_4$ (diene = NBD, COD) and OMe$^-$ gave CpNi(C$_7$H$_8$OMe) and CpNi(C$_8$H$_{12}$OMe) [78] and similar reactions produced (16) and (17) (M = Pt, R = OMe) with OMe$^-$ [79] and (17) (M = Pd, R = NHCH$_2$Ph) and (18) with PhCH$_2$NH$_2$ [80]. Abstraction of methanol from the nickel COD complex gave CpNiC$_8$H$_{11}$, possessing a cyclic π-allylic ligand [78], and bridge-splitting reactions on (16) gave monomeric products [79]. The complex obtained from the interaction of Et$_3$N with CODPtCl$_2$, and postulated to be a π-allylic-platinum(II) compound, has been shown to be the first Pt σ-allyl complex (19) by X-ray analysis [81].



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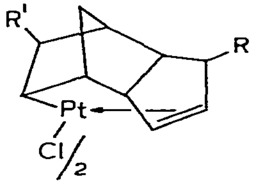

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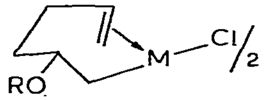

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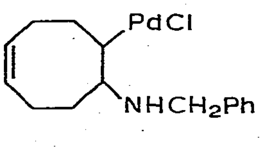

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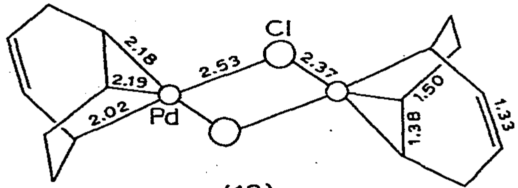
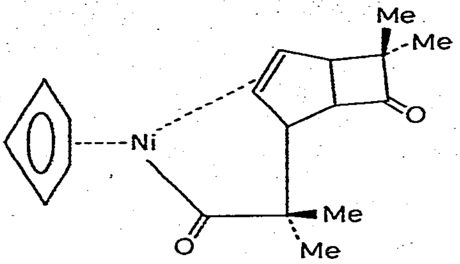


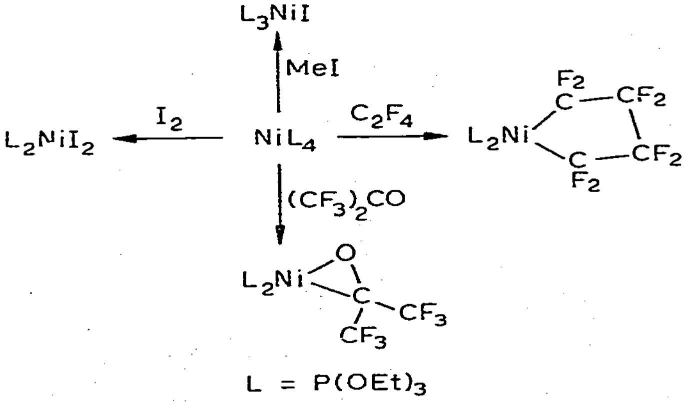
(19)

Cp_2Ni and dimethylketene have produced a complex which was initially inferred to contain a 4-membered lactone ring π-bonded to Ni and which has now been shown by X-ray analysis to be (20) [82].



(20)

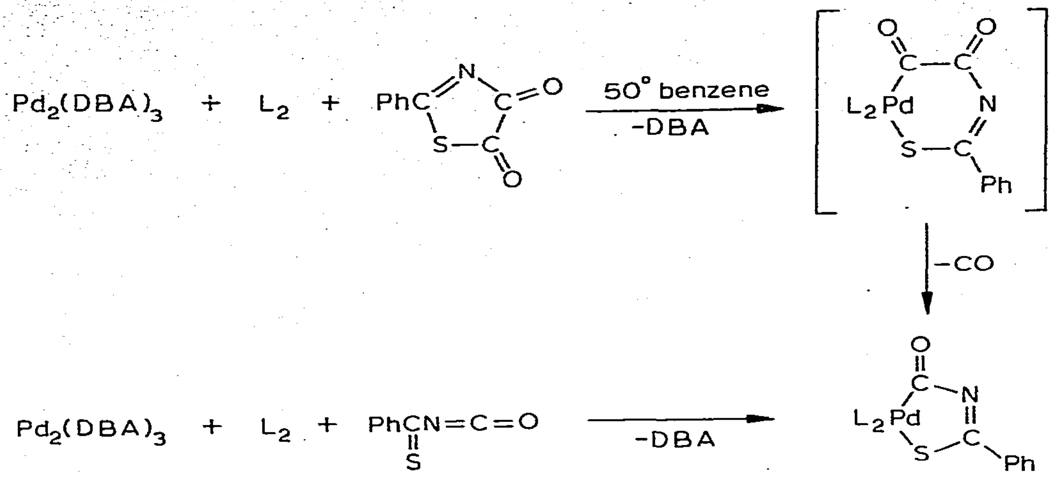
Some reactions of the new complex $Ni[P(OEt)_3]_4$ have given metallocenes (scheme 2) [83]. Treatment of $Pd_2(dba)_3$ with bipy and benzoyl isocyanate produced (21), and similar reactions with 2-phenylthiazoline-4,5-dione and L_2 (L_2 = bipy, phen) gave (22) via scheme 3 [84]. Tetracyanocyclopropane



L = P(OEt)₃

(Scheme 2)

gave (23) on reacting with ML_n (M = Pd, Pt; n = 3,4) [85], which was characterised structurally [86]. With Pt(trans-stilbene)L_2 as a precursor, reactions of hexafluorobut-2-yne have given (24) (M = Ni, L = $P(OMe)_3$,



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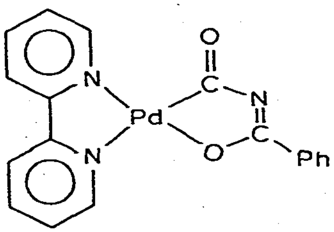
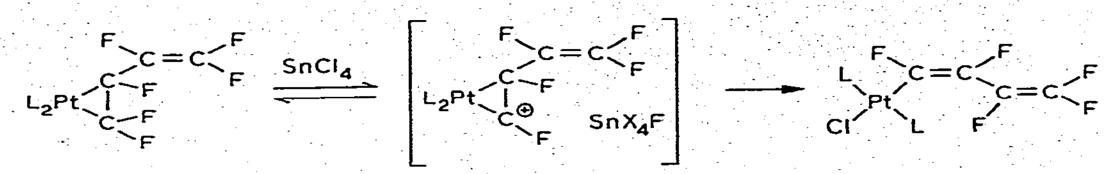
(Scheme 3)



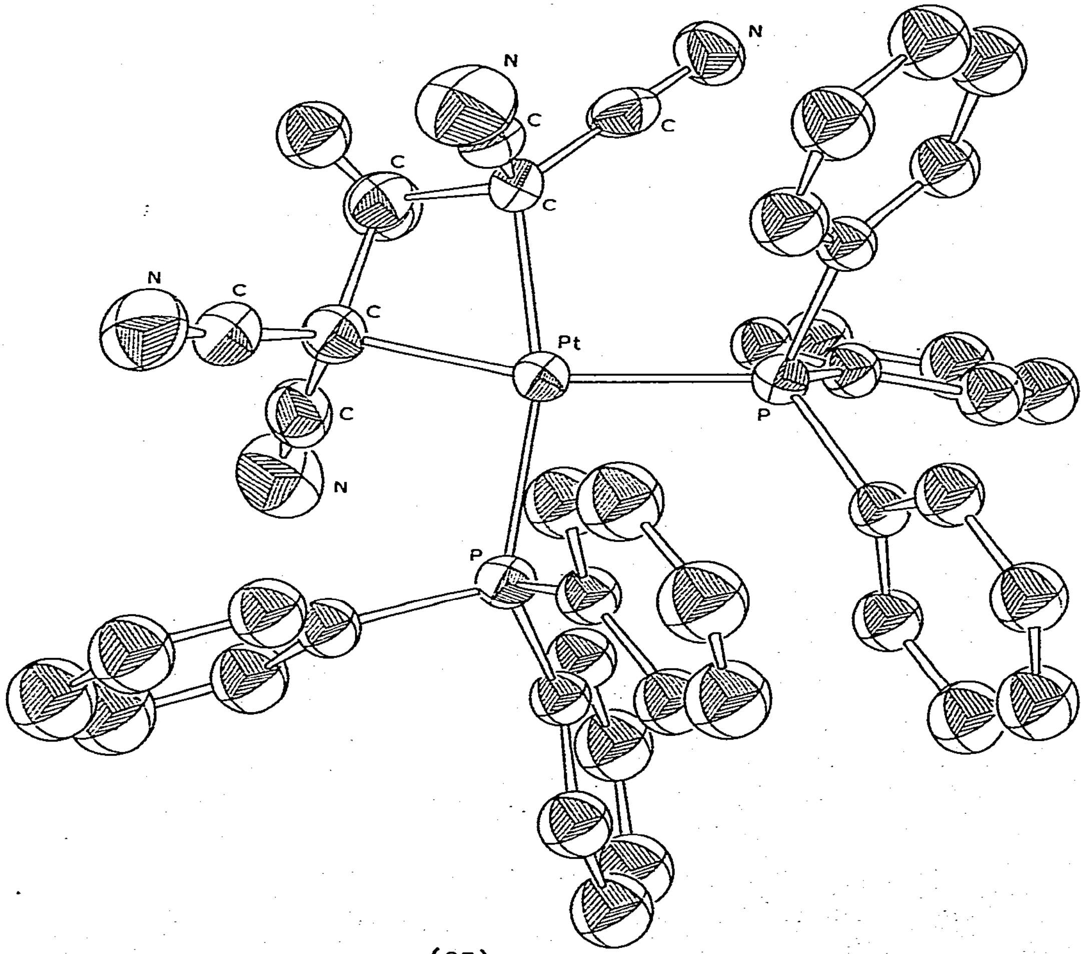
(21)

$AsMe_2Ph$; M = Pt, L = PEt_3), confirmed by structural analysis on the platinum compound [87], whilst $Pt(CF_2CF\text{-}CF{=}CF_2)L_2$ (L = PPh_3, $AsPh_3$) is formed with hexafluorobuta-1,3-diene [88]. In the latter reaction, a small percentage of $Pt(CF_2CF{=}CFCF_2)(AsPh_3)_2$ was characterised from the yield by X-ray analysis, and $Pt(CF_2CF\text{-}CF{=}CF_2)L_2$ underwent exchange with $SnCl_4$ to give a single isomer of a vinyl-Pt(II) species (scheme 4) [88]. Further reactions of (24) (M = Ni, L = $P(OMe)_3$, $AsMe_2Ph$) with $CF_3C \equiv CCF_3$ gave (25) [87]. Cleavage of (26) by Pt(trans-stilbene)$(PPh_3)_2$ produced (27), a crystallographic determination of which was reported. The ring



(Scheme 4)

opening of the cyclobutadieneone was facilitated by electron withdrawing groups, as the complexes characterised as (28) (M = Pd; R = Me, H; L = PPh_3; M = Pt, R = Me, H; L = PPh_3, $AsPh_3$), do not undergo ring cleavage [89]. Oxida-



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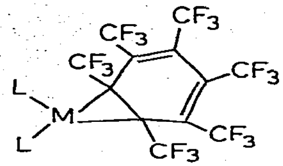

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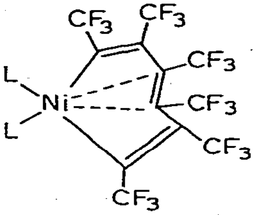

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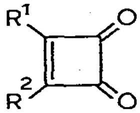

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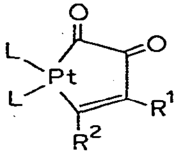

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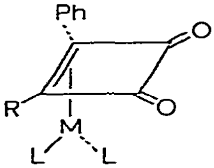
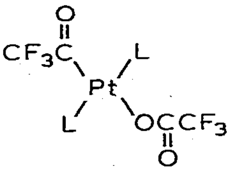


(28)

tive additions of perfluorocarboxylic acid anhydrides and perfluorosuccinic anhydride to $Pt(C_2H_4)(PPh_3)_2$ and $Pt(PPh_3)_3$ produce (29) and (30) [90]. Metallooxacyclobutane complexes $Pt[C_2(CN)_4O]L_2$ (L = PPh_3, $P(p\text{-}MeC_6H_4)_3$, $AsPh_3$) have been synthesised from $C_2(CN)_4O$ and PtL_4. The structure (31) for L = $AsPh_3$ has been completed and relevant parameters reported were Pt-As (mean) 2.37 Å, Pt-C 2.10 Å and Pt-O 2.05 Å [91]. Insertion of platinum into the C-S bond in (32) gave (33) [92]. Reactions of $MMeI(PPh_3)_2$ or $MCl(CH_2COR)(PPh_3)_2$ (M=Pd, Pt) with $NaCH(CN)_2$ in MeOH produced the complexes (34), (35) (R = Me, Ph) and $PdCl\{CH(CN)_2\}(PPh_3)_2$ [93]. The compound (36) was synthesised by oxidative addition of 1-(chloromethyl) naphthalene to Pt(*trans*-stilbene)$(PPh_3)_2$, followed by treatment with MeLi and heating the Pt-Me product in toluene [94]. A series of palladium and



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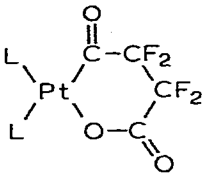

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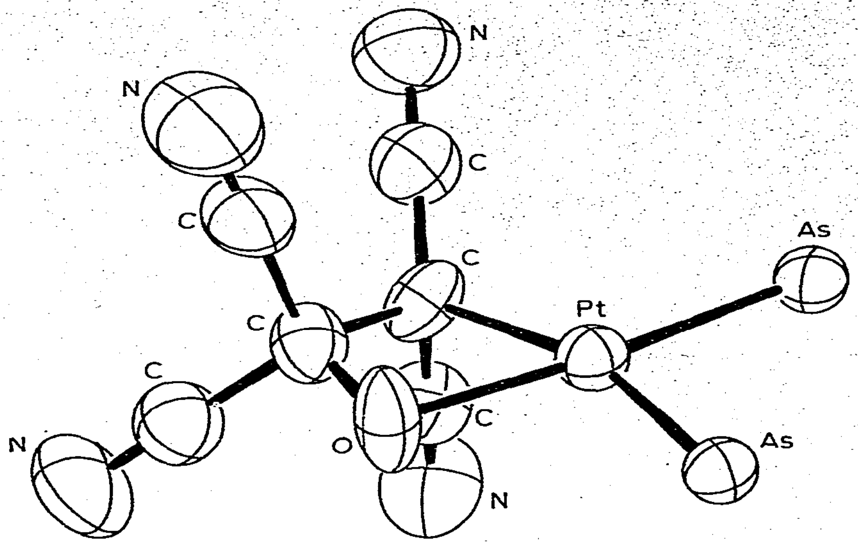

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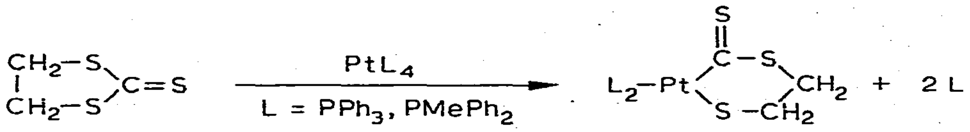

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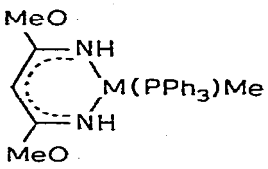

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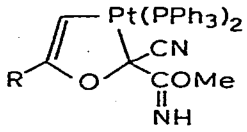

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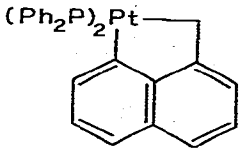
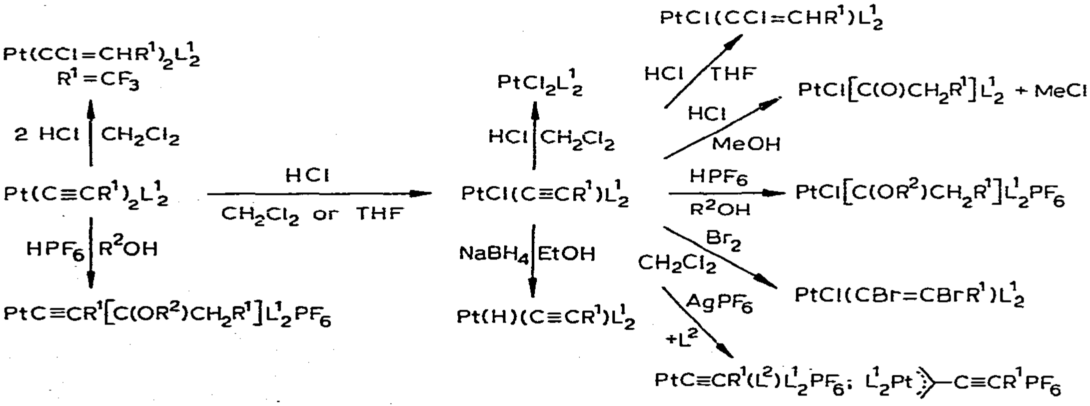


(36)

platinum vinyls have been prepared by metal(0) insertions into a C-Cl bond in chlorovinyl substrates. Complexes characterised were $[MX\{C(Z)=C(Y)R\}L_2]$ (M= Pd, Pt; X = Y = Z = R = Cl; M = Pd, Pt, X = Z = Y = Cl, R = H; M = Pd, Pt; X = Cl, Z = R = H; for L = PPh_3, $PMePh_2$ [95] M = Pd, X = Cl Z = Y = H, R = CN, $CONH_2$, CO_2H, CO_2Me, M = Pd, X = Br, Z = Y = H, R = CN for L = PPh_3 [96]). In some cases additions of HCl cause fission of the M-C bond with the exception of $PtCl\{C(Cl)=CHCl\}(PMePh_2)_2$ in which olefin isomerisation occurs [95]. Aryl iodides or iodinated polystyrene add to $Pt(PPh_3)_4$ to give trans-square planar Pt-C inserted products [97].

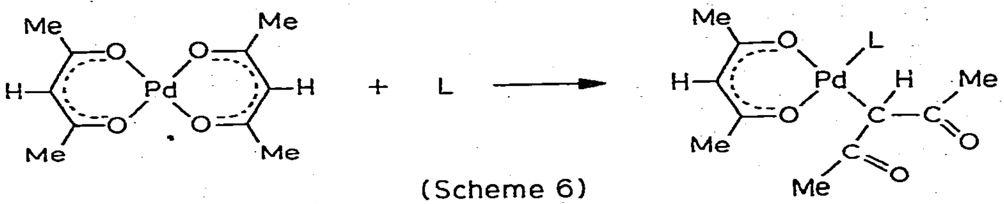
Bond lengths in electroneutral monomeric chloroplatinum(II) complexes containing carbon-donor ligands indicate that there is a correlation between the extent of Pt-C multiple bonding and the length of the Pt-Cl (trans to C) bond. A qualitative model is suggested to account for the trans-influence of both σ-donor and π-acceptor ligands on Pt-Cl bonds [98]. The reactions of trans-$[Pt(C{\equiv}CMe)_2(PMe_2Ph)_2]$ and trans-$[PtCl(C{\equiv}CMe)(PMe_2Ph)_2]$ with protic acids is shown to be dependent on X,R and solvent (scheme 5) and evidence



R^1 = Me; R^2 = Me, Et, Pr^n, Pr^i, L^1 = PMe_2Ph; L^2 = 2-oxacyclopentylidene, CO, py, MeCN and allene

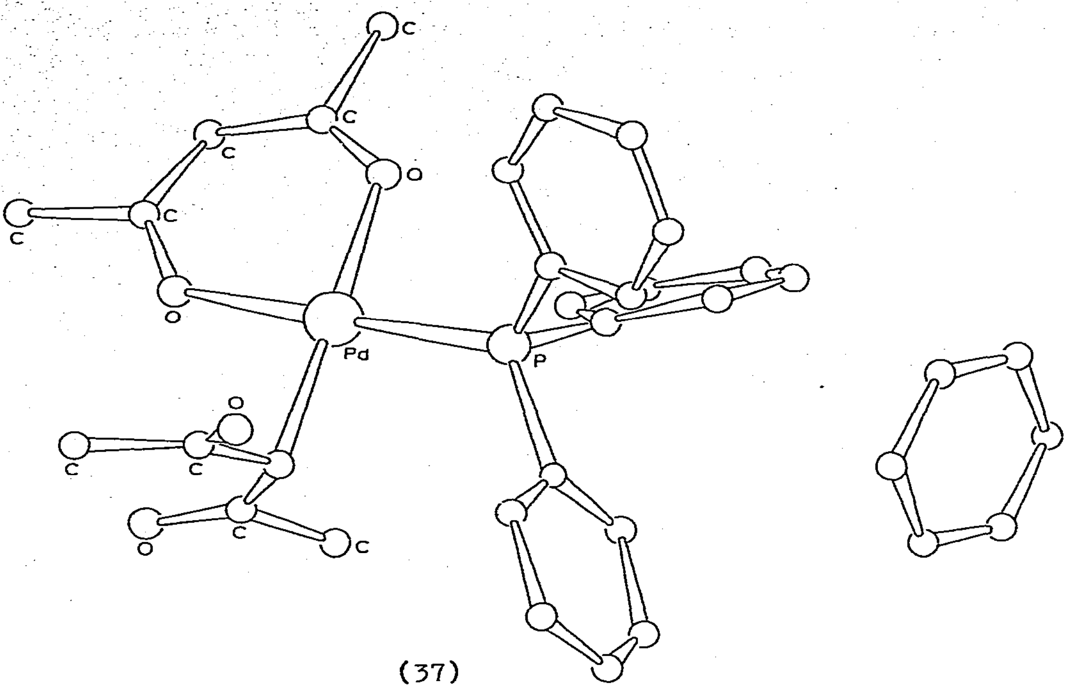
(Scheme 5)

for a Pt-stabilised carbonium ion is reported [99]. A review on the activation of CS_2 by transition metal complexes has appeared [100]. The oxidative addition of $MeNO_2$ to $Pt(PPh_3)_4$ in polar solvents (H_2O-EtOH-PhH) is a convenient and safe method for the preparation of <u>trans</u>-$[Pt(CNO)_2(PPh_3)_2]$ [101]. In the presence of Me_2CO or Ph_2CO, these fulminato complexes rearrange to the isomeric isocyanato compounds [102] and reaction with organic thiocarbonyls (e.g. CS_2, Ph_2CS) gave $Pt(NCS)_2(PPh_3)_2$. Safe preparations of <u>trans</u>-$[Pt(CNO)_2L_2]$ (L = $PBuPh_2$, PBu_2Ph, PBu_3, $SbPh_3$) from the corresponding chloro derivatives by metathetical replacement with (Ph_4As) CNO were described [102]. Additions of Me_2CHNO_2 or $EtNO_2$ to $Pt(PPh_3)_4$ in benzene gave $Pt(NO_2)_2(PPh_3)_3$ and $(H_2C = NOH)_3HCl$ formed <u>trans</u>-$[PtCl(CN)(PPh_3)_2]$ [101]. One of the chelating acac ligands in $Pd(acac)_2$ is transformed into a Pd-C bonded group by neutral ligands L (L = PPh_3, py, $NHEt_2$, $NH(Me)CH_2Ph$) [103] (scheme 6). The molecular structure of $Pd(acac)_2(PPh_3)$.



(Scheme 6)

C_6H_6 (37) has been determined and bond lengths of Pd-O 2.05 Å, Pd-C 2.11 Å and Pd-P 2.26 Å were observed [104]. Assignment of the stereochemistry of the products $PtXY(PPh_3)_2$ for Y = X = Cl, O, CH_2; X = Cl, Y = H, COPh, CO_2Me from IR and Raman bands in the region 160 - 200 cm^{-1} has been made from characteristic Pt(II)-P stretching modes. Two bands were observed in the region 195 - 170 cm^{-1} for <u>cis</u>-complexes and one in the region of 165 - 175 cm^{-1} for <u>trans</u>. For all complexes examined the band at 550 ± 5 cm^{-1} in the Raman is very strong for <u>cis</u> and weak for <u>trans</u> complexes [105].



(37)

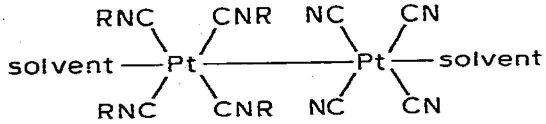
III Metal cyanides

A review on cyanide complexes of metals including compounds of Ni, Pd and Pt has been published [106]. The crystal structures of two salts containing the anion $[Ni(CN)_5]^{3-}$ have been determined at -80° and -10°. Both contain the $[Ni(CN)_5]^{3-}$ moiety in a regular square pyramid in which the apical Ni-C(N) bond is considerably longer than basal Ni-C(N)'s, and this constitutes evidence of stereochemical rigidity of the square pyramid, as crystal packing forces differ substantially from one salt to another. The structure of $[Ni(CN)_5]^{3-}$ in the $Cr(en)_3$ salt is trigonal bipyramidal, suggesting that though thermodynamic stability of the two forms only differs by 1-2 Kcals/mole, the energy barrier to interconversion must be much higher [107]. The crystal structure of a biphenyl clathrate $Ni(NH_3)_2 \cdot Ni(CN)_4 \cdot 2C_{12}H_{10}$ has shown the host lattice to have a layer structure of two dimensional networks of $[Ni(NH_3)_2Ni(CN)_4]_\infty$ and the guest biphenyl molecules are accommodated between the inorganic layers with their longest axis perpendicular to the layers [108]. Mixing of $NiL_2(NCS)_2$ (L = thiourea) with KCN and Me_2CO has given $Ni(CN)_2L_2$ $2Me_2CO$ [109]. The complexes $M(CN)_4^{2-}$, and $M(C^{15}N)_4^{2-}$ (M = Ni, Pd, Pt) have been synthesised, and from IR and Raman studies, many of the vibrational frequencies have been determined, and force constants for a general quadratic force field have been estimated. The results indicate that the Pt-C σ bond and the Pt-CN π-bond are both stronger than for the other metals [110]. The spectral properties of $Ni(CN)_2(PMe_3)_3$ and $Ni(CN)_2(PMe_3)_2$ have been considered in the light of the unusual temperature dependence of ligand field spectra of other Ni(II), Pd(II) and Pt(II) complexes [111]. A new semiquantitative SCF LCAO MO calculation scheme was applied to $Ni(CO)_4$, $Ni(CN)_4^{2-}$, $Cr(CO)_6$ and Cp_2Fe. Comparison was made with current ab initio calculations [112]. Spectral changes observed with the change of pressure on the ion $[Ni(CN)_5]^{3-}$ indicate that a change of geometry from trigonal bipyramidal to square pyramidal takes place [113]. Temperature dependent ^1H NMR spectra of $Ni(CN)_2(PMe_3)_2$ and $NiX_2(PMe_3)_3$ (X = CN, Br) have been recorded and the existence of a cis-trans equilibrium for the former has been observed [114]. On radiolysis in aq. solution, $Ni(CN)_4^{2-}$ is reduced to $Ni_2(CN)_6^{4-}$ by the radical ion CO_2^-. A mechanism is proposed [115]. The reaction of $Ni(CN)_4^{2-}$ with NH_2OH has been studied [116]. The rate of dissociation of cyanoglycylglycinamidonickelate(II) is 38,000 times slower than that of the corresponding aquonickelate [117]. A kinetic study of the replacement of the triglycinate ion in $NiH_{-2}GGG$ (GGG = triglycinate ion and two protons are ionised from the peptide nitrogen) by CN^- is reported [118]. Ammonia, diamines and glycinate ions greatly accelerate the rate of decomposition of $Ni(CN)_4^{2-}$ in the presence of iodine as a scavenger for CN^- [119]. The rate controlling step for the exchange in $Ni(CN)_2L_3$ is $Ni(CN)_2L_3 \xrightleftharpoons{k_1} Ni(CN)_2L_2 + L$, as determined from NMR studies for

$L = P(OEt)_3$, $P(OEt)Ph_2$, $P(OEt)_2Ph$ and PMe_2Ph. With the system $NiX_2(PMe_2Ph)_3$ ($X = Cl, Br, CN$), the exchange rates are ordered as $CN < Br < Cl$ [120]. The ionisation constants K_1 and K_2 of $NiH_2(CN)_4$, determined in aq. solution by electrometry at 25 – 50°, obeyed the relationship $pk_1 = 11,419.90/T - 69.65 + 0.1219T$ and $pk_2 = 5777.98/T - 32.74 + 0.0669T$. The thermodynamic values for the ionisation were also given [121]. The report on the crystal structure of $Cd[Pd(CN)_6]$ gave values of Pd-C 2.07 Å, Cd-N 2.27 Å, C-N 1.11 Å for the relevant bond lengths. The molecular structure consists of an uninterupted cubic Pd-C-N-Cd framework [122]. The atomic parameters, bond distances and bond angles of the $Na_2Pd(CN)_4.3H_2O$ triclinic lattice have been refined. Average atomic distances were Pd-C 1.99 Å, C-N 1.45 Å and Na-N 2.51 Å [123]. Complexes of formula $PdX_2(SbR_3)$ and $Pd_2X_4(SbR_3)_2$ have been characterised for R = o-,m- and p-tolyl and X = Cl, Br, I, NO_2, CN, and SCN [124]. A reinvestigation of the crystal structure of $K_2[Pt(CN)_6]$ has been undertaken [125]. A single crystal neutron diffraction structure of $K_2[Pt(CN)_4]Br_{0.3}\ 3H_2O$ has shown its non-centrosymmetric nature [126]. The valence bond X-ray photoelectron spectra of $K_2[Pt(CN)_4].3H_2O$, $K_2[Pt(CN)_4]Cl_{0.3}.XH_2O$ and $K_2[Pt(CN)_4Cl_2].3H_2O$ imply that the binding energy of the highest occupied MO (HOMO) in $K_2[Pt(CN)_4].3H_2O$ is greater than in $K_2[Pt(CN)_4]\ Cl_{0.3}.XH_2O$. A band-like character for the HOMO of the latter with finite electron density at the Fermi level is consistent with this observation [126]. The SCF X_α SW method was used to calculate the ground state electronic structure of the $Pt(CN)_4^{2-}$ ion as well as excitation energies for transitions to various singlet and triplet excited states. The results are in good agreement with experimental optical and photoemission data but indicate a different order of d-orbital energy levels ($d_{x^2-y^2} \gg d_{zy} > d_{xz,yz} \gg d_{z^2}$) than was assumed in previous work. [128]. The double salts $[Pt(CNR)_4][Pt(CN)_4]$ ($R = Me, Et, t-C_4H_9$) exhibit low energy electronic absorption bands at 22.25, 22.30 kK for R = Me, Et respectively (in KBr) and at 17.70 kK for R = t-Bu (in nujol mull), which are responsible for the intense colours of the solids. These are ascribed to metal-ligand charge transfers which have been red-shifted by Davydov interactions between anion and cation in the solid lattice. In solution the appearance of a band at 30 kK (absent in the spectra of either ion alone) and the failure of Beer's Law for the solution spectra were interpreted in terms of the equilibrium,

$$Pt(CNR)_4^{2+} + Pt(CN)_4^{2-} \xrightleftharpoons{k} [Pt(CNR)_4 \ldots\ldots Pt(CN)_4]^0$$

in which significant perturbations of the spectroscopically important energy levels of the two complexes give rise to 30 kK absorption. The most plausible direction for significant perturbation in the planar complex would be along the line perpendicular to the molecular plane as in (38)

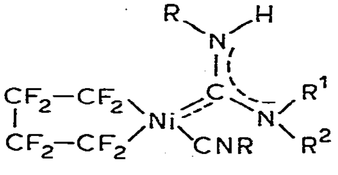


(38)

[129]. Single crystal rotation spectra were obtained for the ^{13}C resonance in $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ and the ^{13}C chemical shift tensor was calculated [130]. The reaction of $Pt(NH_3)_4^{2+}$ with CN^- proceeds by a second order reaction with pH dependence analogous to the pH dependence of the free CN^- ion concentration. Second order rate constants were determined and the rate equation for the reaction of trans-$Pt(NH_3)_2(CN)_2$ with CN^- is given [131]. The oxidative addition reaction of ICN to $[Pt(CN)_4]^{2-}$ is second order with a rate law of $k[CN^-][Pt(CN)_4^{2-}][ICN]$. A mechanism is discussed [132].

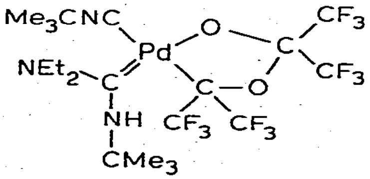
IV Metal carbenes

Of the carbenoids $M(CO)_{x-1}C(NMe_2)OTi(NMe_2)_3$ (M = Mo, W, x = 6; M = Fe, x = 5; M = Ni, x = 4) formed by interaction of $Ti(NMe_2)_4$ with $M(CO)_x$ only the Mo, W and Fe complexes were stable enough to be isolated [133]. Reactions between $[\overline{NiCF_2CF_2CF_2C}F_2(CNR)_2]$ (R = Bu^t, Pr^i) and Me_2NH, Et_2NH, Bu^tNH_2, pyrrolidene, and morpholine gave $[\overline{NiCF_2CF_2CF_2C}F_2(CNR)\{C(NHR)NR^1_2\}]$ for which a typical structure (39) is proposed. Analogous reactions

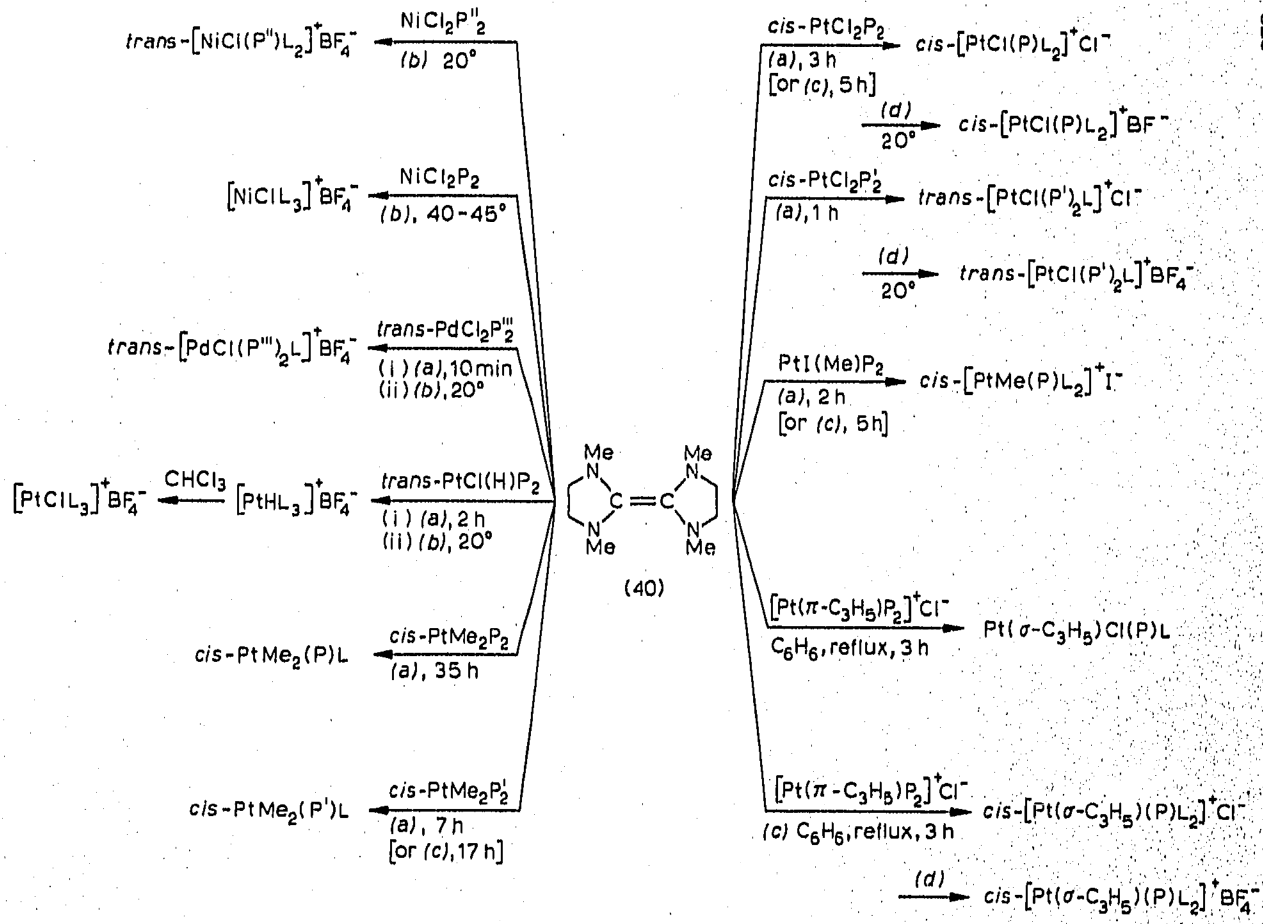


(39)

with $[\overline{MC(CF_3)_2OC(CF_3)_2O}(CNR)_2]$ (M = Ni, Pd, Pt; R = Bu^t, Pr^i), $[\overline{PdC(CF_3)_2{=}C(CF_3)C(CF_3){=}C}(CF_3)(CNBu^t)_2]$ and $[\overline{PdC(CF_3)_2{-}C}(CN)_2(CNBu^t)_2]$ formed corresponding monocarbene complexes [134]. A series of Ni,Pd and Pt mono-, di- and tri-carbenes were characterised by displacement of neutral and anionic ligands with the electron-rich olefin (40) (scheme 7) [135]. Oxidative addition of $[Cl\overline{CN(Me)CHC(Me)S}]BF_4$ to $Ni(PPh_3)_4$, PdL_4(L = PPh_3, $PMePh_2$), $Pt(PMePh_2)_4$ and $Pt(stilbene)(PEt_3)_2$ produced the cationic carbenes $\{MX[\overline{CN(Me)CHC(Me)S}]L_2\}^+$ (M = Ni, X = Cl, L = PPh_3; M = Pd, X = I, L = PPh_3; M = Pd, X = Cl, L = PPh_3, $PMePh_2$; M = Pt, X = Cl, L = PEt_3, $PMePh_2$). $Pt(stilbene)(PEt_3)_2$ and 2-chloro-5-methyl-1,3-thiazole formed $[PtCl\{\overline{C = NCH = C(Me)S}\}(PEt_3)_2]$ which further reacted with HBF_4 to give $[PtCl\{\overline{CNHCHC(Me)S}\}(PEt_3)_2]BF_4$ [136]. The crystal structure of $[Pd\overline{\{C(NEt_2)(NHCMe_3)\}(CNCMe_3)\{OC(CF_3)_2O}C(CF_3)_2\}]$ (41) has been completed [137]. The



(41)

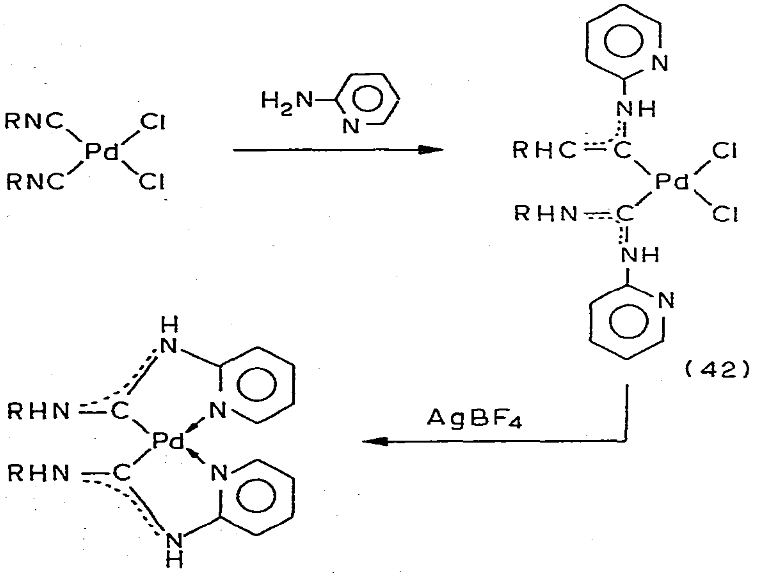


P = PPh$_3$, P' = PPhMe$_2$, P'' = PPhEt$_2$, P''' = PEt$_3$

Reaction conditions: (a) PhMe, reflux, (b) Me$_2$CO, NaBF$_4$, (c) excess of olefin
(d) H$_2$O, NaBF$_4$, 20°

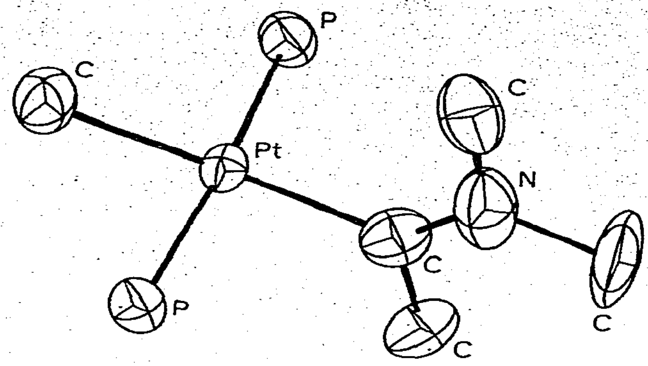
(Scheme 7)

assignment of carbene configurations in a known series of Pd(II) and Pt(II) complexes in solution has been made by measurements of ^{195}Pt couplings with carbene heteroatom substituents i.e. ^3J(PtCNH) for *trans* groups is much greater than for *cis* [138]. Infrared bands mainly associated with $\nu(M\text{-}X_2)$ stretching modes (M = Pd, Pt; X = Cl, Br, P) were identified in the spectra of 35 carbene complexes. Based on these results and on ^1J (^{31}P-^{195}Pt), the *trans*-influence of the carbene ligands was assessed [139]. The series *cis*-[Pd(RNC)LCl$_2$] (R = Ph, *p*-MeC$_6$H$_4$,*p*-MeOC$_6$H$_4$,*p*-O$_2$NC$_6$H$_4$; L = PhNC, *p*-MeC$_6$H$_4$NC, PPh$_3$) reacted with bifunctional amines (e.g. en, *o*-phenylenediamine, ethanolamine, 2-aminopy, allylamine) to form (42). Ligand chelate formation occurs on further treatment with AgBF$_4$. Bis(carbene) derivatives *cis*-[Pd{C(NHR)NHY}$_2$Cl$_2$] (R = Ph, *p*-MeC$_6$H$_4$; YNH = 2-aminopy), which undergo chelation on reaction with NaClO$_4$ and deprotonation with KOH, were reported (scheme 8) [140].



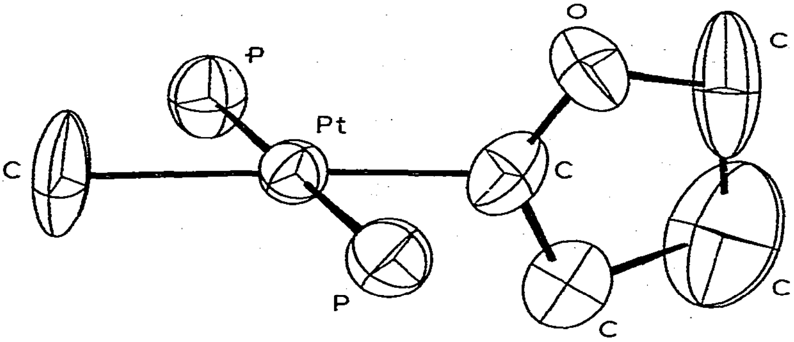
(Scheme 8)

Structural determinations of three Pt-carbenes have been completed; *trans*-[PtMe{MeCN(Me)$_2$}(PMe$_2$Ph)$_2$]PF$_6$ (43), with Pt-P(mean) 2.29 Å, Pt-C(methyl)



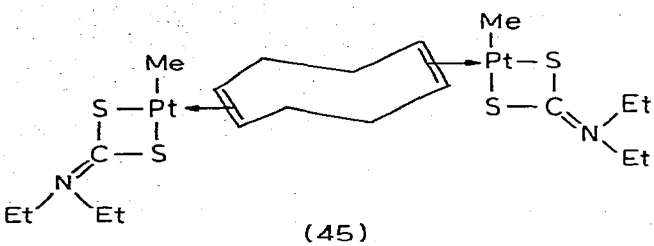
(43)

2.15 Å and Pt-C(carbene) 2.08 Å [141]; *trans*-[methyl-2-oxacyclopentylidene)-bis(dimethylphenylphosphine)platinum(II) hexafluorophosphate (44), with



(44)

Pt-P 2.31 Å, Pt-C(methyl) 2.08 Å and Pt-C(carbene) 2.00 Å [142] and *trans*- and *cis*- $[PtCl_2\{\overline{CNPh(CH_2)_2N}Ph\}(PEt_3)]$, with Pt-C 2.02 Å (trans), 2.01 (cis) suggestive of a Pt-C bond order of 1 [143]. The solvolysed complex $[PtMe(COD)(solvent)]PF_6$, prepared from [PtMe(COD)Cl] and $AgPF_6$, forms $[PtMe(RNC)_3]PF_6$ (R = Et, *p*-tolyl) with RNC. Further reaction with sodium benzenethiolate gave *cis*-$[PtMe(SC_6H_6)(CNC_6H_4Me)_2]$, with dialkylamines gave *trans*-$[PtMe(CNC_6H_4Me)\{C(NR_2)(NHC_6H_4Me)\}_2]PF_6$, with C_6F_5CN in methanol gave the iminoether complex $[PtMe(COD)\{NH = C(OMe)C_6F_5\}]PF_6$ and with NaS_2CNEt_2 gave (45) [144]. Treating $PtCl_2(PPh_3)_2$ with $4\text{-}MeC_6H_4NC$ in ROH-KOH gave

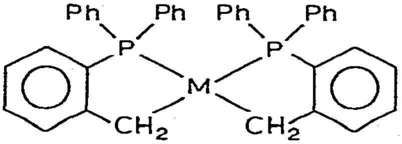


(45)

$Pt\{C(NC_6H_4Me)OR\}_2(MeC_6H_4NC)PPh_3$ (R = Me,Et) whereas cis-$[PtCl_2(C_6H_{11}NC)_2]$ and $C_6H_{11}NC$ in methanol with 1,8-bis(dimethylamino)naphthalene formed $[PtCl\{C(=NC_6H_{11})(OMe)\}\{C(OMe)(NHC_6H_{11})\}(C_6H_{11}NC)]$ [145]. The platinum vinyls trans-$[PtCl\{CCl=C(H)R^1\}(PMe_2Ph)_2]$ (R^1=Me, Ph) give the alkoxycarbenes trans-$[PtCl\{C(OR)CH_2R^1\}(PMe_2Ph)_2]^+$ with ROH (R = Me, Et, Pr^n) [146]. A review on advances in the chemistry of isocyanide ligands has appeared [147].

V Internal metallation reactions

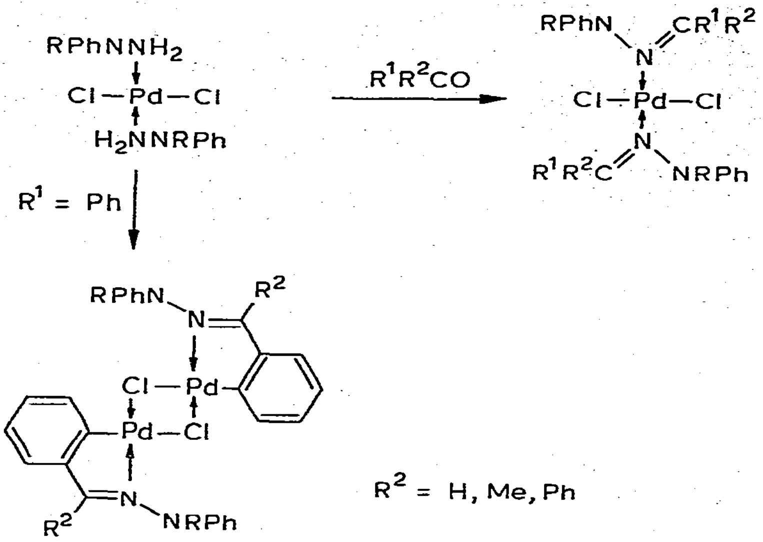
2-(Diphenylphosphino)benzylpotassium and Ni(II), Pd(II) and Pt(II) salts formed (46) which was shown to have the cis-configuration from NMR



(46)

[148]. Cyclometallations with azobenzene derivatives have been obtained by various routes. Bis(2-phenylazo)phenylmercury with Cp_2Ni and $MCl_2(PR_3)_2$ gave $Cp\overline{NiC_6H_4N{=}N}C_6H_5$ and $\overline{Pt\{C_6H_4N{=}N}C_6H_5\}(Cl)PR_3$ respectively [149].

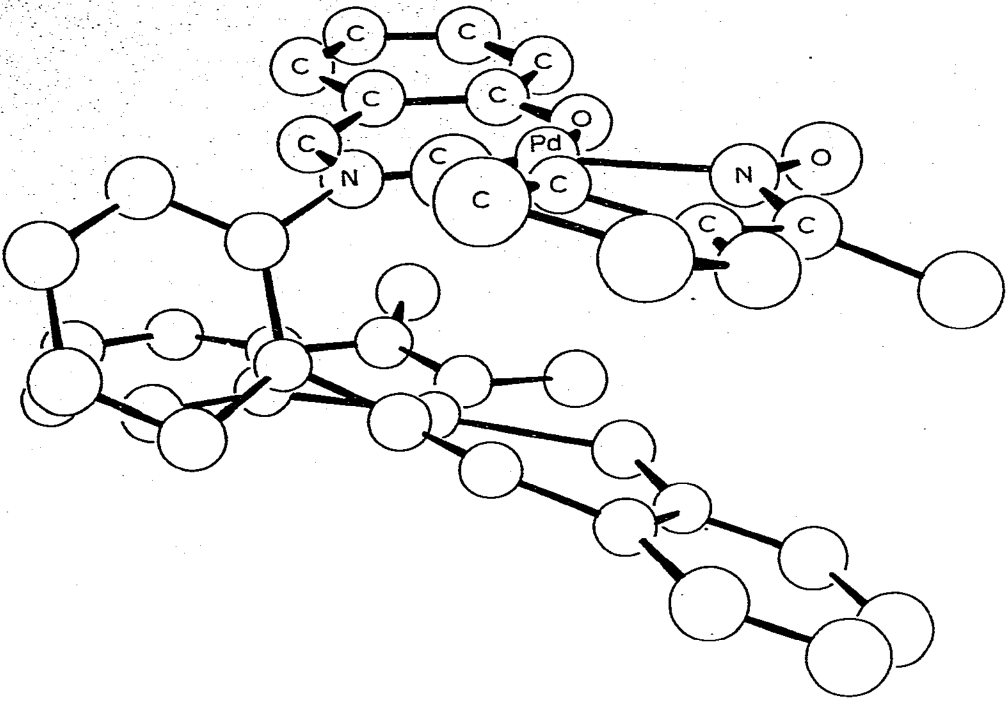
Pentafluoroazobenzene and $PdCl_2$ have produced $[\overline{Pd\{C_6H_4N{=}N}C_6F_5\}Cl]_2$ [150], and condensation of hydrazine-Pd complexes with carbonyl compounds of formula R^1R^2CO ($R^1 = R^2 = H$, Me, Et; $R^1 = Ph$, $R^2 = H$, Me) gave hydrazone complexes, or when $R^1 = Ph$, cyclopalladated complexes (scheme 9) [151].



(47)

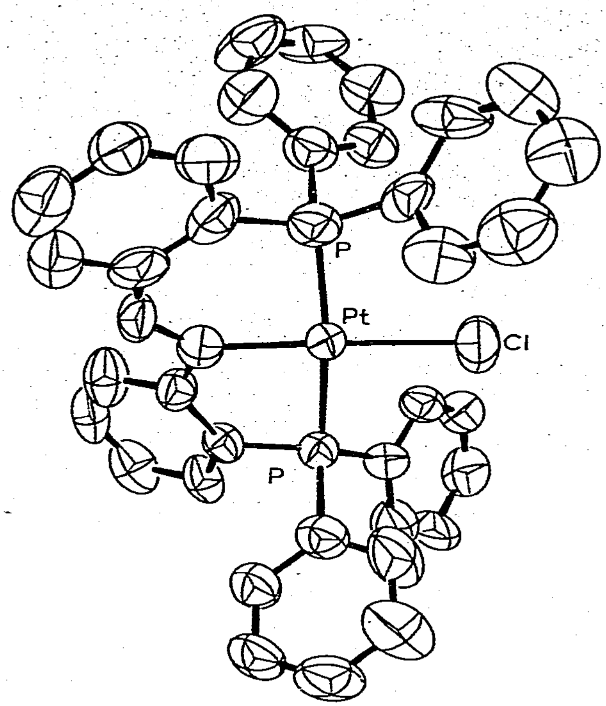
(Scheme 9)

The dipalladium product (47) ($R = H$, $R^2 = Me$) was cleaved by R^3_4NX ($R^3 = Et$, Bu; $X = Cl$, Br, I) to give $R^3_4N[\overline{Pd\{C_6H_4C(Me){=}N}NHPh\}X_2]$ [152], and the py adduct $[\overline{Pd\{C_6H_4C(Me){=}N}NHPh\}Xpy]$ ($X = Cl$) formed the bimetallic species, for $X = Co(CO)_4$, $CpMo(CO)_3$, $Mn(CO)_5$ and $CpFe(CO)_2$, with NaX [153]. The variations in the ^1H NMR of $Pt(C_6H_4N{=}NC_6H_5)Cl(PMePh_2)_2$ indicated an intramolecular substitution (S_Ni) involving $\overline{Pt(C_6H_4N{=}N}C_6H_5)Cl(PMePh_2)$ which undergoes S_N2 reactions with free and coordinated $PMePh_2$ [154]. The crystal structures of μ-N,N^1-*o*-phenylenebis(salicylideneiminato) bis(acetophenoneoxime-2,C,N)palladium(II) (48) [155] and Δ-$[\overline{PtCl\{\underline{o}\text{-}(C_6H_5)_2PC_6H_4C}{=}CHC_6H_4P(C_6H_5)_2\text{-}\underline{o}\}]$ (49) have been determined. For the latter, the novel tridentate ligand

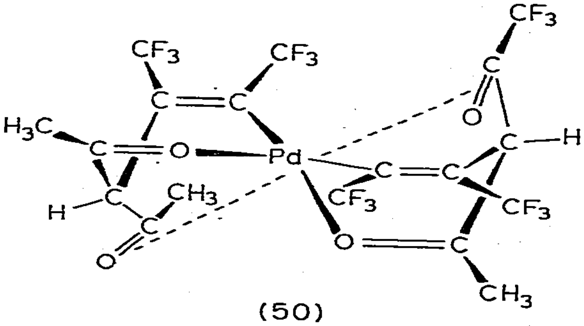


(48)

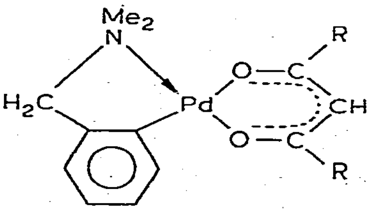
is bound to platinum with two P's <u>trans</u>. Relevant bond lengths are Pt-Cl 2.38 Å, Pt-P(mean) 2.28 Å, Pt-C 2.02 Å and C=C 1.34 Å [156]. Treating [Pd(acac)$_2$] with $F_3CC{\equiv}CCF_3$ gave the compound (50) which was resolved crystallographically. Similarly (51) (R=Me, CMe$_3$) with $CF_3C{\equiv}CCF_3$ produced (52) [157]. (N,N-dimethylbenzylamine-2C,N)palladium(II) and -platinum(II) β-diketonates have been synthesised [158]. A preliminary report of reactions of $[Cp\overset{+}{N}\overset{-}{N}COPh]Li$ with salts of Pd, Pt, Rh and Ir, to give internally metallated products e.g. $[Pd(L\text{-}H)ClL^1]$ (L-H=CpNNCO-$\underline{o}$-C_6H_4), has appeared [159]. The complexes $MX_2\{EMe_2(1\text{-naphthyl})\}_2$ (M=Pd, Pt; X = Cl, I, Me; E = P, As) have been synthesised. No internal metallations with Pd occurred at all and with Pt only for X = Me or in the presence of NaOAc were metallated products obtained (in the 8-(peri) position of the naphthyl ring) [160]. The Pt(II) halide compounds PtX_2L_2, with the new ligands L[L =PPh$_2$-


P
Pt
Cl
P

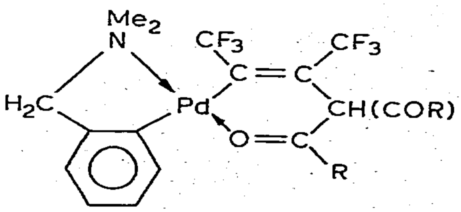
(49)


CF3
CF3
CF3
C
O
C
C
H3C
C
O
Pd
C
H
C
C
C
H
CH3
CF3
CF3
C
O
O
C
CH3

(50)

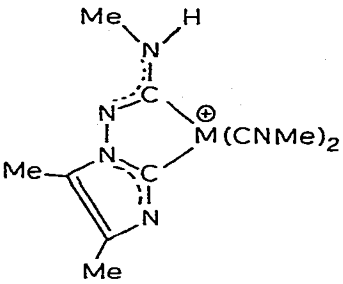

Me2
N
R
O
C
H2C
Pd
CH
O
C
R

(51)


Me2
N
CF3
CF3
C
C
H2C
Pd
CH(COR)
O
C
R

(52)

(2-MeOC_6H_4), $PBu^tMe(2\text{-MeOC}_6H_4)$, $PBu^t(2\text{-MeOC}_6H_4)_2$, $PPh_2(2\text{-EtOC}_6H_4)$, PMe_2-(2-MeOC_6H_4)], formed *o*-metallated products on heating in polar solvents [161]. New chelating ligands were obtained from reactions of amidines and 2-aminopyridine with $Pt(CNMe)_4^{2+}$. Biacetyldihydrazone reacted with $M(CNMe)_4^{2+}$ (M = Pd, Pt) to produce (53), and 2,6-diaminopyridine gave (54) [162].



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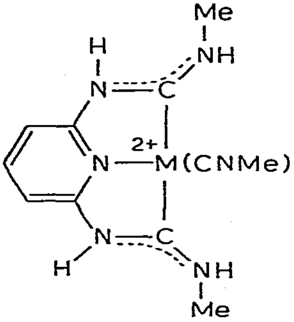
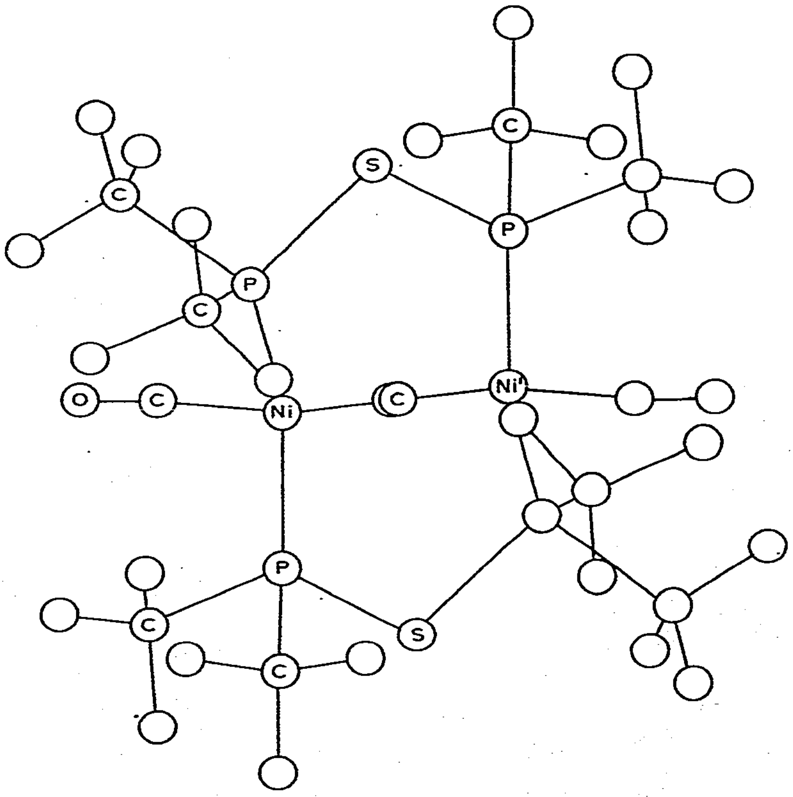


(54)

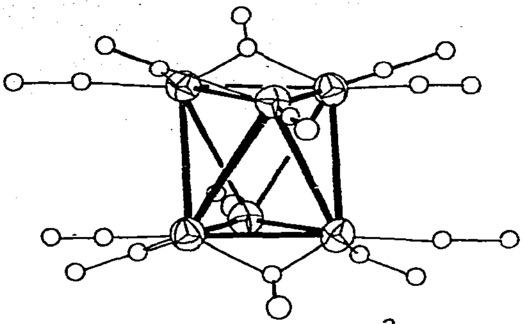
VI Metal carbonyls

A review on ^{13}C NMR spectra of metal carbonyls has been published [163]. Components of the ^{13}C shielding tensor σ for CO, $Ni(CO)_4$ and $Fe(CO)_5$ were separated into diamagnetic and paramagnetic parts and the paramagnetic part of the perpendicular component of the chemical shift σp was mainly responsible for the large isotropic shift between free and coordinated CO [164]. The preparation of $NiL_x(CO)_{4-x}$ (x = 1,2) with constrained arsenic and silyl ligands together with NMR and IR data is reported [165]. The HeI photoelectron spectra of the isoelectronic series $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$ and $Ni(CO)_4$ were observed and interpreted by *ab initio* SCF MO calculations [166]. A normal coordinate analysis of $Fe(CO)_4^{2-}$, $Co(CO)_4^-$ and $Ni(CO)_4$ was carried out using Wilson's F-G matrix and the general valence potential function[167]. The ν(CO) and their shifts in the new complexes $NiL(CO)_3$ ($L = EPh_3$, $(4\text{-XC}_6H_4)_3E$, $(3\text{-XC}_6H_4)_3E$; X = Cl, F; E = P, As, Sb) were discussed in terms of the σ-bonding involved [168]. A new route to Ni(0) carbonyls via the reductive elimination of a Ni-disulphide is reported. Treatment of $NiCl_2L_2$ ($L_2 = (PPh_3)_2$, $(PMePh_2)_2$, DPE, $Ph_2PCH{=}CHPPh_2$) with MeSNa and CO in ethanol gave $NiL_2(CO)_2$ [169]. Similarly $NiL_2(SeCONEt_2)_2$ and CO produced $NiL_2(CO)_2$ and $(SeCONEt_2)$ [170]. New derivatives of nickel carbonyl prepared were $[Ni(CO)_3L]^{n-}$(L = $\{Me_3M\}_3Sb$[M = C, Si, Ge, Sn], n = 0 [171]; triphenylcyclotriphosphane, n = 0 [172]; $Ph_2PCH_2R\{R$ = polystyrene residue$\}$, n = 0 [173, 174] and $GeCl_3$, n = 1 [175]) and $[Ni(CO)_2L_2]^{n-}$ (L = $GeCl_3$, n = 2 [175]; 2,3-bis(diphenylphosphino)maleic anhydride) [176]. The polystyrene metal carbonyl complexes were found to be effective hydroformylating agents for alkenes [173, 174]. Nickel carbonyl structures resolved were (i) $Ni(CO)_2(PPh_3)_2$ [177], (ii) $Ni_2\{(CF_3)_2PSP(CF_3)_2\}_2(CO)_3$ (55)



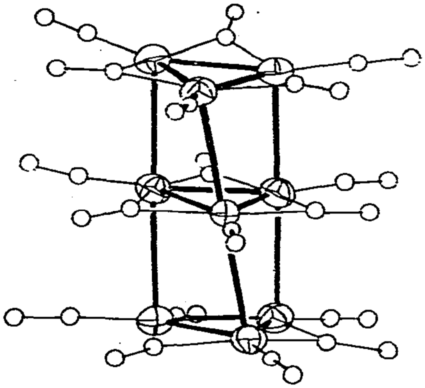
(55)

with a Ni-Ni interaction of 2.58 Å [176], (iii) $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$ (56) in which the nickel structure is a trigonal antiprism [179] in contrast to the Pt analogue (57) which is trigonal prismatic [180]. The carbonyl dianions of general formula $[M_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ (n = 2,3,4,5) represent new types of metal cluster geometries formally derived by tinker-toy construction from a basic $M_3(CO)_3(\mu_2\text{-}CO)_3$ building block. They were prepared by reduction of some suitable metal carbonyl with varying amounts of alkali metals or methanolic NaOH in the presence of CO [180]. $Cp_3Ni_3(CO)_2$ forms a 1:1 adduct with BF_3 at -78° in which the Lewis acid is bonded to a carbonyl oxygen atom [181]. Photodisappearance spectra were obtained for 10 transition metal carbonyl anions, and the ion disappearance mechanism is inferred to be photodissociation [182]. The salt $(NR_4)_2$ $[Pd_2X_4(CO)_2]$ (X = Cl, Br) was isolated from mixtures containing K_2PdCl_4, HX and CO. A bridging carbonyl structure is postulated (58) [183]. A kinetic study of the oxidative decomposition of palladium carbonyl chloride has been completed and a mechanism for the reaction proposed [184]. The reactions of $Pd(CO)(PPh_3)_3$ with RN_3 in dry benzene gave the urea derivatives [Pd(RNCONR)



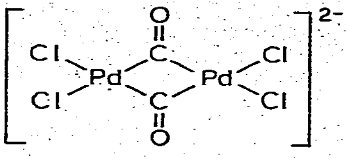
$[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$

(56)



$[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_3^{2-}$

(57)



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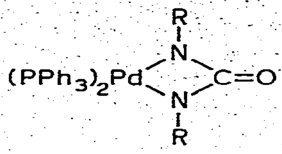
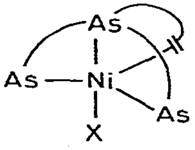


(59)

$(PPh_3)_2]$ (59) (R = p-$MeC_6H_4SO_2$). Corresponding complexes were synthesised from oxidative additions of N,N'-ditoluene-p-sulphonyl urea to $M(PPh)_4$ (M = Pt), or from toluene-p-sulphonyl isocyanate (M = Pd, Pt). In protic solvents e.g. $R^1OH(R^1$ = Me, Et, $Pr^n)$, RN_3 and $Pt(PPh_3)_n(CO)_{4-n}$ gave trans-$[Pt(PPh_3)_2(CO_2R^1)_2]$ for n = 2 and $Pt(PPh_3)_2N_3(-N(R)COOR^1)$ for n = 3 [185]. The crystal structures of the platinum carbonyl compounds cis-$[PtCl_2(CO)PPh_3]$ [186], $(Et_4N)[PtH_2(CO)Br_3]$ [187] and the mixed metal clusters $PtFe_2(CO)_9(PPh_3)$ [188] and $FePt_2(CO)_5[P(OPh)_3]_3$ [189] have been elucidated. trans-$[PtCl(CO)L_2]$ (L = $AsEtPh_2$, $AsPrPh_2$) has been prepared from $PtCl_2L_2$ and CO [190]. The first stage in the substitution of $[Pt(CO)Cl_3]^-$ with bipy is a reaction of $[Pt(CO)Cl_3]^-$ with $[bipy\ H]^+$ to give $[Ptbipy(CO)Cl]^+$. The second stage is a slow replacement of CO by Cl [191]. Equilibrium constants K_{eq} for the reaction (R_4N) $[PtCl_2(CO)X]$ + 4-Zpy $\longrightarrow$ R_4NX + $PtCl_2(CO)(4\text{-}Zpy)$ (X = Cl, Br, I, Z = COMe, CO_2Me, H, Et, Me, CMe_3) were determined in $CHCl_3$. As expected, the more electron releasing Z results in larger K_{eq} [192]. SCl_2 and $Pt(CO)_2(PPh_3)_2$ gave $Pt(CO)Cl_2(PPh_3)$ [193], whereas the reaction of cis-MX_2L_2 with CO, MeOH and NEt_3 produced trans-$[MX(CO_2Me)L_2]$ (M = Pd, X = Cl, L = PPh_3, PMe_2Ph; M = Pd, X = Br, L = PPh_3; M = Pt, X = Cl, L = PPh_3, $PMePh_2$, PMe_2Ph) [194]. The crystal structure of $Pt(CO_2Et)_2(PPh_3)_2$ has shown the complex to have a trans-configuration [195]. The rate limiting step in the oxidation of CO to CO_2 has been calculated from charge distribution, bond populations and kinetic data for the series $[PtH_2(CO)X_3]^-$ (X = Cl, Br, I) by MO LCAO methods [196].

VII Metal olefins

The structure of the two olefin-nickel complexes, $(Me_2C = CMe_2)Ni(C_6H_{11})_2P$ $CH_2CH_2P(C_6H_{11})_2$ [197] and bis-(tri-p-tolylphosphine)(trans-stilbene)nickel(0) [198] have been completed. Mean bond lengths observed were Ni-C 1.98 Å, Ni-P 2.16 Å and C = C 1.42 Å for the former [197] and Ni-C 2.02 Å, Ni-P 2.18 Å and C = C 1.47 Å for the latter structure [198]. Coordinatively unsaturated Ni(0) complexes of formula $Ni(tbp)_n$ (n = 2,3), $Ni(tbp)_2L$ and $[(tbp)_2Ni(\mu\text{-}COD)Ni(tbp)_2]$ (L = monoolefin, tbp = tri[(+)-bornan-2-yl]phosphite have been prepared. Further reaction with the COD-bridged dimer produced the stable compounds $[NiCl(tbp)R^1]$ (R^1 = R, COR; R = aryl) and asymmetric induction occurred in forming $Ni(CH_2 = CHCO_2CH_2CF_3)(tbp)_2$ [199]. Simple NiX_2 (X = Cl, Br) salts form stable bonds with the olefin in bis(3-dimethylarsinopropyl)-3-butenylarsine, e.g. (60) [200]. The preparation and properties of $QNiL_2$ complexes [$L = P(OC_6H_4Me\text{-}\underline{o})_3$, Q = maleic anhydride, acrylonitrile, styrene, propylene, COD and $F_2C = CF_2$] are described. With $F_2C = CF_2$ only (61) was isolated from solution [201].



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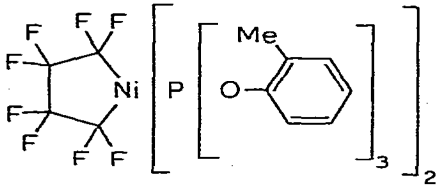
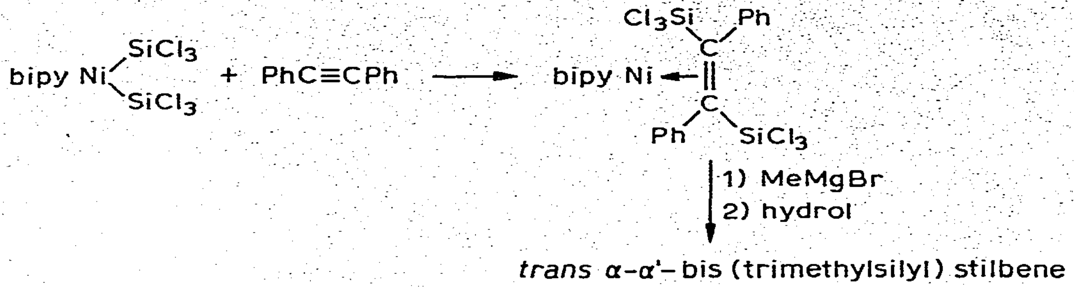


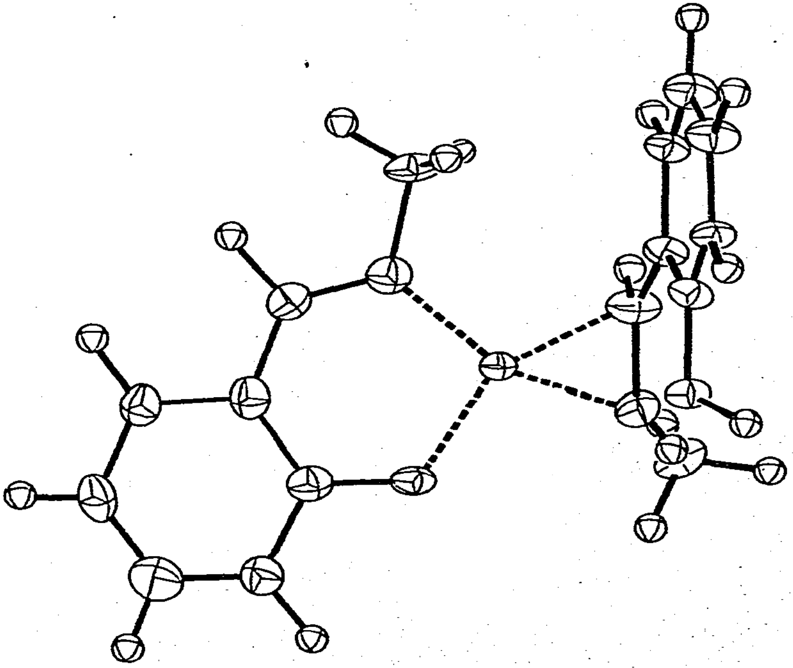
(61)

Acetylenes with $Ni(SiCl_3)_2bipy$ gave a mixture of cis- and trans- silyl-olefins (scheme 9a). The cis-trans ratio decreased in the order PhC≡CMe>PhC≡CH> PhC≡CPh and with PhC≡CH the cis-trans ratio decreased as PhH>Et_2O>THF [202]. Treatment of $Ni(COD)_2$ with N-alkylsalicylaldimines, ($\underline{o}\text{-}HOC_6H_4CH{=}NR$) gave the new zero-valent compounds $Ni(\underline{o}\text{-}HOC_6H_4CH{=}NR)_2$. A 3-dimensional X-ray



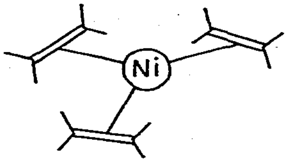
(Scheme 9a)

analysis has shown that the complex is best formulated as a Ni(0) azomethine containing the Schiff base anion salicylaldiminato and the protonated species, salicylaldiminium (62) [203]. Corresponding additions of $Ph_2C{=}NR$ (R = Et_2B, Me_3Si) to $PdCl_2(PhCN)_2$ gave the air sensitive $PdCl_2(Ph_2C{=}NR)_2$ in which the ketimine is CN bonded [204]. M.O. calculations were carried out for allyl and ethylene π-complexes of Cu, Fe, Ni, Ag, Cu^+, Fe^+, Ni^+ and Ag^+ [205].



(62)

A theoretical study of M(ethylene)$_n$ (n = 2-4, M = Ni; n = 6, M = Cr) also had implications for the corresponding allyls. Symmetry arguments supported by semiempirical MO calculations were used in the analysis. For n = 3, a planar structure (63) is prefered to (64) as a consequence of symbiotic effects of σ- and π-bonding. For n = 2, either (65) or (66) are valid. For n = 4 the quasidodecahedral structure (67) has the lowest energy. In all systems the discrimination between various geometries rests on the symmetry-specific back-bonding of the ethylene π^*-levels. Using analogous symmetry properties of a π-allyl ligand, qualitative theories of the geometries of Ni(allyl)$_n$ systems can be set up predicting significant rotational barriers for (allyl)$_2$M (M = Ni, Pd) and quasitrigonal prismatic upright structures for (allyl)$_3$M (M = Co, Rh) [206]. Equilibrium constants have been determined for the reaction of 38 olefins with Ni[P(O-*o*-tolyl)$_3$]$_3$ and the stabilising and destabilising effects of electron withdrawing and releasing groups noted.



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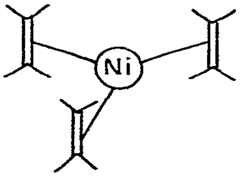

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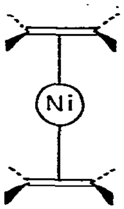

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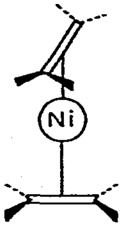

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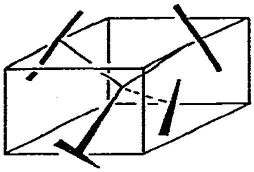
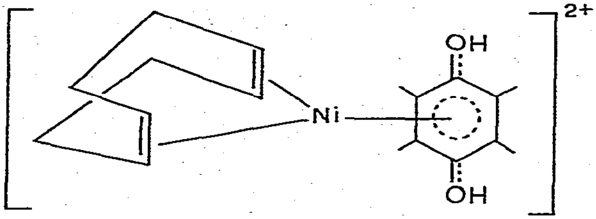


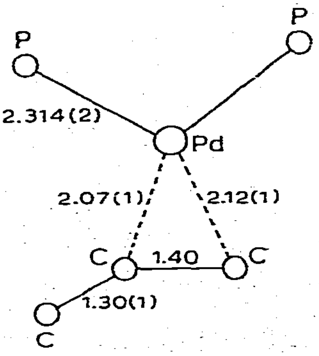
(67)

An estimate of Ni-olefin bond strengths has been made and the results were discussed in terms of energy level separations of highest occupied and lowest unoccupied molecular orbitals of nickel and the free olefin [207]. Absolute rate coefficients have been determined for redox reactions of organic halides with $Ni(methylmethacrylate)\{P(OPh)_3\}_2$ [208]. Low temperature protonation of Ni(COD)(duroquinone) with HSO_3F gave the stable cation (68) [209].



(68)

The molecular structure of $Pd(allene)(PPh_3)_2$ (69) has been determined from 3-dimensional X-ray diffraction data. One allene bond is coordinated to Pd, the allene ligand is no longer linear ($C-\hat{C}-C$ 148.3°) and relevant parameters defined were Pd-C 2.07 Å, C=C (coord.) 1.40 Å and C=C (uncoord.) 1.30 Å [210]. A series of papers on the structure [211], preparation [212, 213] and properties [213, 214] of palladium dibenzylideneacetone complexes has appeared. $Pd_2(dba)_3$ (70) reactions with neutral donor ligands,



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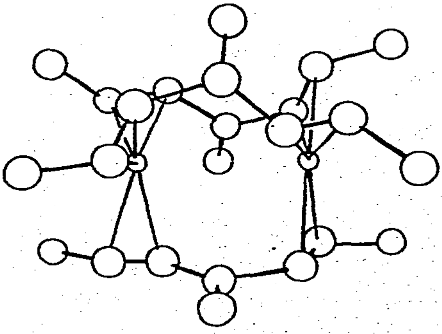
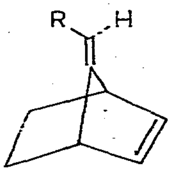
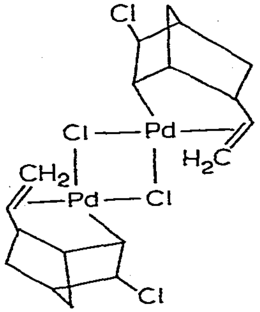


(70)

olefins, and acetylenes were similar to those of Pd(dba)$_2$ [212-214]. A comparison, of the stability of complexes of isomeric hexenes with PdCl$_2$ and Ag$^+$ based on retention data from gas chromatography, was made [215]. The dicationic olefins [ML(MeCN)$_2$](PF$_6$)$_2$ (L = COD, NBD) and [CODPdL$_2$](PF$_6$)$_2$ (L$_2$ = bipy, DPE) have been synthesised [216]. With unsaturated tertiary phosphines and arsines internal metal olefin complexes of the type MLX$_2$(M = Pd, X = Cl, I; M = Pt, X = Cl, Br, I, CNS, L = tris(but-3-enyl)arsine [217]; M = Pd, Pt, X = Cl, Br, I, L = Ph$_n$P(CH$_2$CH$_2$CH=CH$_2$)$_{3-n}$ (n = 0-2) [218] were formed. ^{1}H NMR evidence for these compounds suggested rapid olefin intramolecular exchange. Halogen complexes of Pd, Pt and Rh with 1,5-hexadiene [219] and oligomeric Pd-π-complexes with norbornadiene [220] have been synthesised. Additions of Pd-Cl across a double bond in 5-vinyl-2-norbornene [221] and (71) [222] gave (72) and (73) respectively. The mechanism, postulated to occur via an ionic or bimolecular path, is discussed [222]. Substituted norbornenylpalladium salts react with neutral donor ligands to yield nortricyclenylpalladium complexes, and with mono and 1,3-dienes, to give olefin products which are in equilibrium with the starting material. The role of steric and electronic factors are discussed. Reactions with 1,2-dienes generate π-allylic products above 0° [223] (scheme 10). Using a modified CNDO MO method, the electronic structures



(71)



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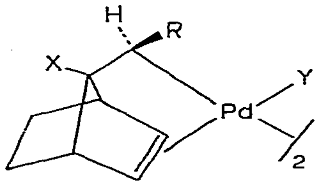

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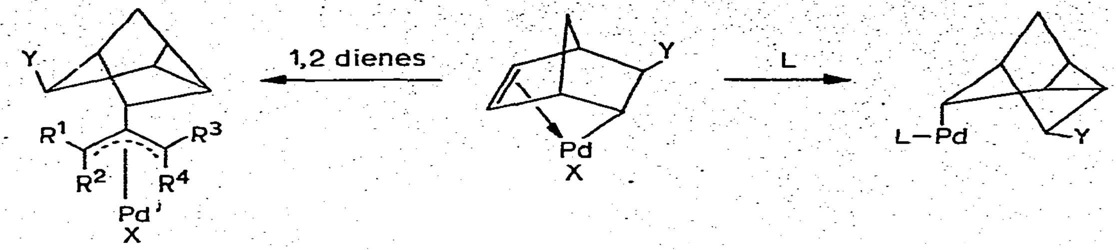
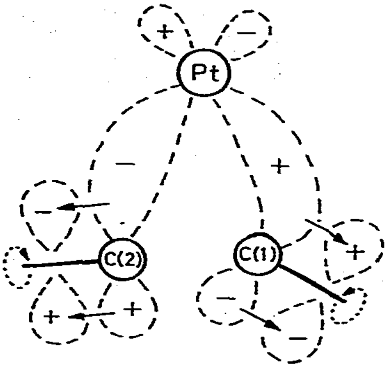


L = neutral ligand, X = Hfacac, Y = OAc or OMe
R groups either H or methyls in various orders

(Scheme 10)

of Pd(II) and Hg(II)-ethylene complexes have been studied, and related to OH^- attack on the ethylene in the Wacker process [224]. A kinetic study of the solution phase decomposition of hexamethyldewarbenzene-Pd(II) chloride has shown that the form of the rate law (e.g. first order v.s. autocatalytic) and observed rate constants depend on sample history [225]. The true catalyst complex in the $PdCl_2L_2$ isomerisation of 1-pentene is said to be either a monobridged dimeric π-complex or the monomers $PdCl_2$(olefin)(base) or $PdCl_2(olefin)_2$ [226]. The kinetics of oxidation of olefins by $PdCl_4^{2-}$, Cl^- and H_3O^+ are described by a two-term equation containing a quadratic term in $[PdCl_4^{2-}]$. A one-term rate law is only applicable at low Pd(II) concentrations [227]. The following reactions have been characterised by NMR, IR and UV spectra and microcalorimetry; $[PdCl_2(olefin)]_2 + 2py \longrightarrow 2[PdCl_2(olefin)py]$ and $[PdCl_2(olefin)py] + py \longrightarrow [PdCl_2py_2] + olefin$ [228].

The crystal structures of di-μ-chlorodichlorobis(cyclopentene)dipalladium (II) (and the corresponding cycloheptene complex) [229]; $Pt\{(C_6H_4NO_2)CH = CH(C_6H_4NO_2)\}(PPh_3)_2$ [230] and cis-dichloro[(R)-α-methylbenzylamine][(S)-1,2,2-trimethylpropyl-(R)-vinyl ether]platinum(II) (75) [231] are reported. In the Pt(0) complex the substituents on the olefin were perpendicular to the Pt–C_2 plane as this allows maximum substituent π-orbital overlap with occupied metal d-orbitals and olefin π^*-orbitals (e.g. 74). Because of this orientation the substituents are bent back from the metal to minimise hydrogen non-bonded contacts and the substituents must be powerful electron withdrawing groups for the energy gained in achieving the perpendicular orientation to be sufficient to cause this asymmetric olefin geometry [230].



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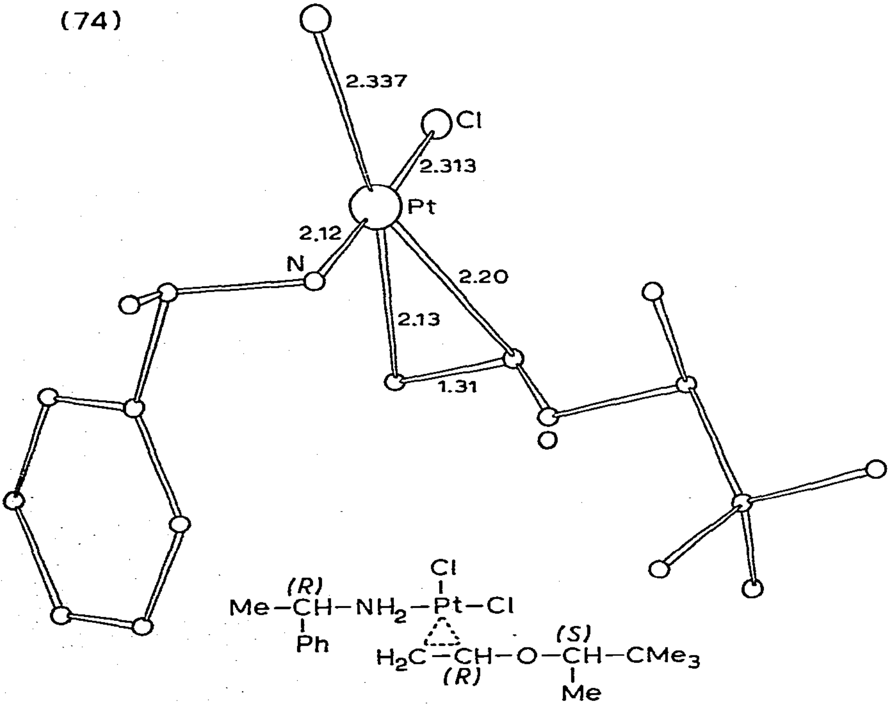
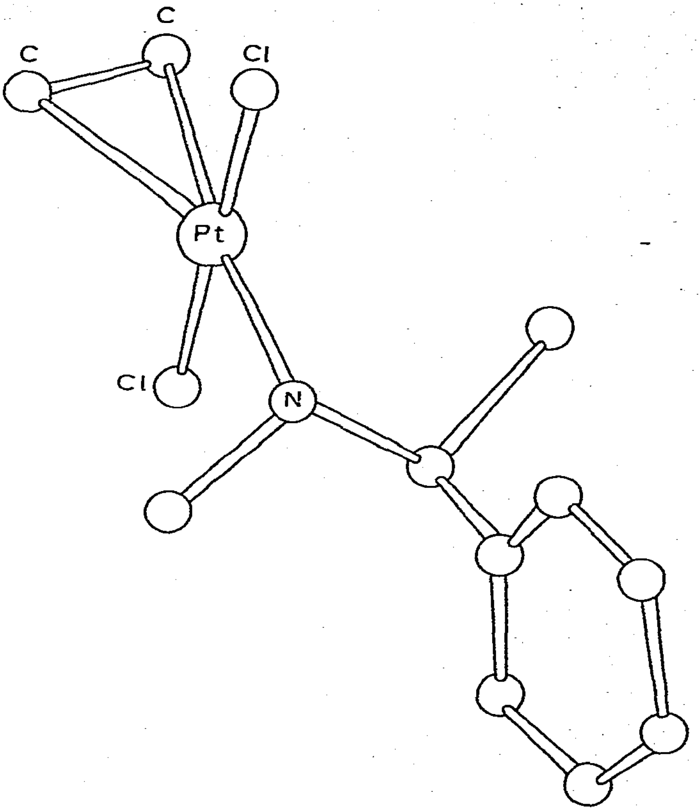


(75)

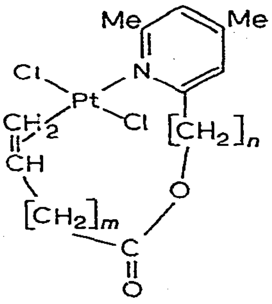
In the Pt(II) compound [231] the absolute configuration at the chiral centre formed by complexation of the vinyl group is R and gave indications of the conformations of the amine and olefin ligands. Evidence that coordination of the amine ligand in trans-dichloro[(S)-N-methyl-α-methylbenzylamine]ethyleneplatinum(II) (76) occurs in a highly stereoselective manner



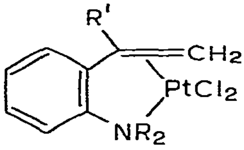
(76)

was obtained from an X-ray structural analysis of the product [232]. Stabilisation of a series of five-coordinate Pt-olefin and allene complexes by $HB(pz)_3$ has been observed. With some olefins two isomers were observed in the ^{1}HNMR the spectra, which coalesced at higher temperatures. In $Pt(COMe)[HB(pz)_3]$, the pyrazolylborate ligand is fluxional [233]. [Pt(PhHC=

$CHC(O)CH{=}CHPh)_2$] forms $Pt(PhHC{=}CHC(O)CH{=}CHPh)L_3$ (L = PPh_3, $PMePh_2$, PEt_3, $AsPh_3$, $AsEt_3$) with L in which only one double bond in the olefin is coordinated to Pt. Further reactions of the tertiary ligand substituted product with L^1 (L^1 = C_2Cl_4, C_2F_4, $CF_3C{\equiv}CCF_3$, $(CF_3)_2CO$, CS_2) gave PtL^1L_2 [234]. Olefin-platinum products characterised from alkenylpyridines were (77), in which trans-bidentate bonding occurs [235] and $[PtX(PEt_3)_2\,L][PtX_3(PEt_3)]$ (L = 2-allylpy, 2-(1-methallyl)py) [236], in which NMR evidence suggested a mono-bidentate allylpy equilibrium in solution. With alkenyl-aniline the Pt compounds (78) were synthesised [237]. Certain NMR characteristics of the trans-$[PtCl_2(olefin)L]$

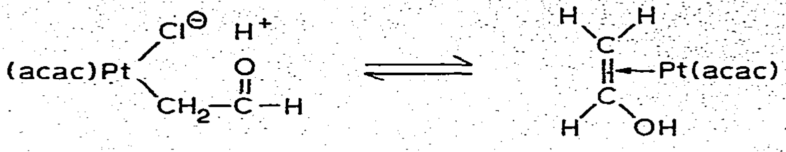


m = 1, n = 3
m = 2, n = 3
m = 4, n = 3
m = 8, n = 3
(77)

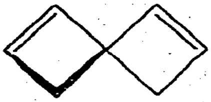


R, R' = H,H; H,Me; Me,H; Me,Me
(78)

(L = isoquinoline, py) have been attributed to adventitious free ligand contaminations [238]. The platinum allene products $PtR(PPh_3)_2$($R{=}CH_2{=}C{=}CH_2$, $CF_3CH{=}C{=}CH_2$) abstract sulphur from R^1NCS(R^1 = Ph, Me) to give $[Pt(S_2C{=}NR^1)(PPh_3)_2]$ [239]. The vinyl alcohol complex chloro(acac)(π-ethenol)platinum(II) was prepared from either the hydrolysis of the analogous π-vinyl trimethylsilyl ether complex or by the reaction of $PtCl(C_2H_4)acac$ with MeCHO in the presence of aq. base. The NMR of this compound indicated a rapid equilibrium between the π-complex and its conjugate base (a σ-bonded β-oxoethyl product) is occuring [240] (scheme 11). Both enantiomers of (79) were resolved

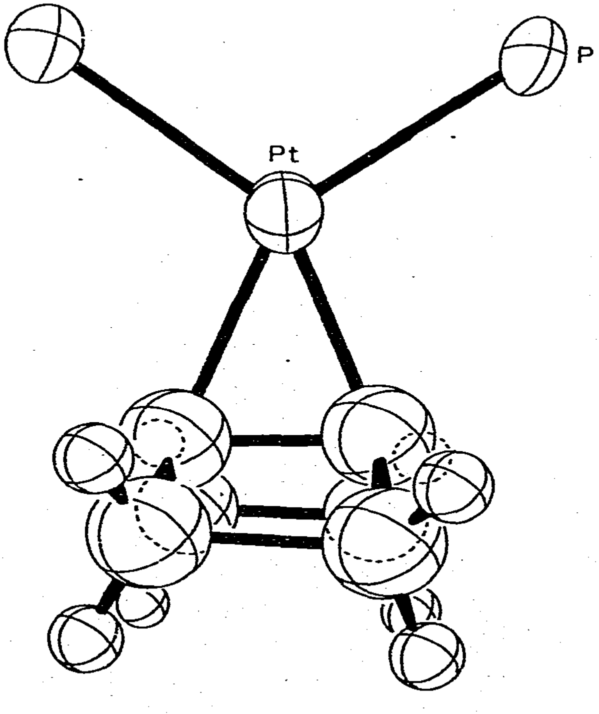


(Scheme 11)



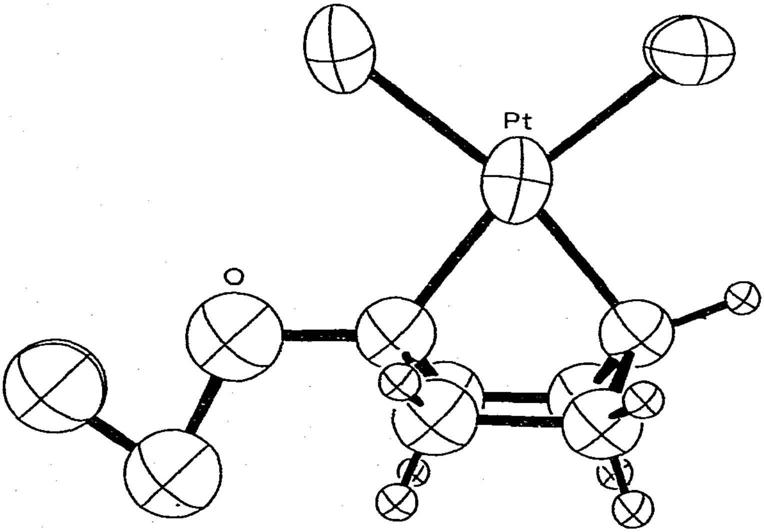
(79)

by separation of their diastereomeric platinum(II) complexes containing optically active amines [241]. The displacement of ethylene from [Pt(C_2H_4)(PPh_3)$_2$] by $\Delta^{1,4}$-bicyclo[2.2.0] hexene gave the platinum [2.2.1] propellane (80) which was resolved crystallographically. (80) further reacted with

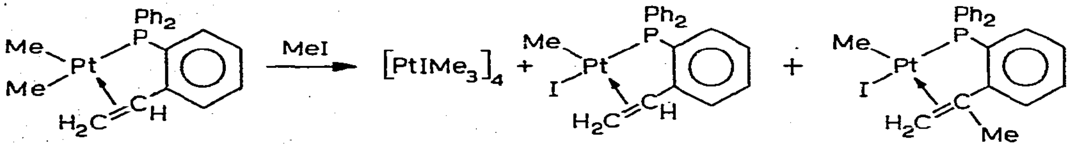


(80)

EtOH to form (81) by cleaving the central C-C bond [242]. Attempts to prepare Pt(IV) olefin complexes by oxidative addition of MeI to (82) gave instead three Pt(II) products, one of which was obtained by a methyl insertion at the internal olefin carbon atom (scheme 12) [232]. When Pt(II)-olefin compounds, e.g. *cis*-[$PtCl_2(C_2H_4)(PEt_2Ph)$] are treated with methoxide ions three reactions occur, namely nucleophilic attack on the coordinated olefin by MeO^- and decomposition of the resulting methoxy complex to HCHO, and displacement of the olefin resulting in the formation of [$PtCl_2(PEtPh_2)$]$_2$. The relative importance of these three reactions depends upon the precise experimental conditions used [244]. The energy barrier to olefin rotation



(81)



(82)

(Scheme 12)

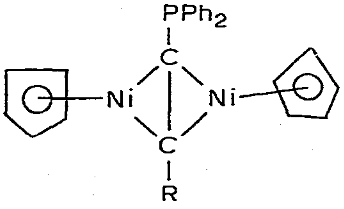
in cis-[$PtCl_2L$(olefin)] and PtCl(acac)(olefin) (L = tertiary phosphine or arsine) has been measured. ΔG_c is dependent upon the bulk and electronegativity of substituents on the olefin and the symmetry of the olefin. Orientations of the olefin in the ground state, as deduced from Pt-^{1}H coupling constants,are strongly influenced by steric factors [245].

Reasonably accurate geometrical information has been elucidated from NMR spectra of Pt-olefins in trans-[$PtCl_2(C_2H_4)$py] in liquid crystals, and parameters related to the geometry in solution have been obtained with reasonable precision [246]. The stability of trans-[$PtCl_2(C_2H_4)$py] with respect to various solvents and nucleophiles, was studied by NMR [247], and the instability constants for trans-[$PtCl_2(C_2H_4)NH_3$], $[Pt(C_2H_4)(NH_3)_3]^{2+}$ and $[Pt(NH_3)_3PPh_3]^{2+}$ were determined by potentiometric titration with HCl or $HClO_4$ in acetone solution [248]. An enthalpy of -155.8 kJ/mole was obtained from solution calorimetry for the reaction $Pt(C_2H_4)(PPh_3)_2$(cryst) + $(NC)_2C{=}C(CN)_2$(gas) $\rightarrow$ $Pt(NC)_2C{=}C(CN)_2(PPh_3)_2$(cryst) + C_2H_4(gas) [249]. With a twin-type calorimeter, the enthalpy changes of reactions of aq. KCN solutions with Zeise's salts were measured, and from these measurements an order of strength of Pt-olefin bonding of $C_3H_6 \geqslant C_2H_4 \geqslant 1\text{-}C_6H_{12} \geqslant 1\text{-}C_4H_8 \geqslant 1\text{-}C_5H_{10}$ was obtained [250]. SCF Xα-scattered wave method was used to calculate the electronic structure of Zeise's anion and from which the σ-component of the bonding appears much more important than the π-contribution [251]. The trans-effect in Pt(II) products, some containing olefins, was studied by a self-consistent MO method based on the complete-neglect-of-differential-overlap approach [252]. The mechanism of substitution reactions by bidentate ligands in Pt(II) complexes with N-,O- and S-donor ligands, amino acids, olefins and acetylenes has been reviewed [253]. Olefin substitution in trans- [$PtCl_2$(olefin)py] by free olefin or py was markedly slowed down by the presence of ortho-substituents on py [254]. The reaction of $[Pt(C_2H_4)Cl_3]^-$ with D,L-alanine (L) to give [$Pt(C_2H_4)$LCl] proceeds stepwise.

At pH 3.2–4.0, one stage is observed involving a bimolecular reaction of both $[Pt(C_2H_4)Cl_3]^-$ and the aquo species trans-$[Pt(C_2H_4)Cl_2(H_2O)]$, producing trans-$[Pt(C_2H_4)L\ Cl_2]^-$ in which L is bonded to Pt through the N-atom. The second fast reaction is the closure of the chelate ring [255].

VIII Metal acetylene complexes

A review on the reactions of diynes with transition metal complexes has appeared [256]. A series of complexes has been stabilised with phosphinoacetylenes. Thus treatment of $[CpNiCO]_2$ with $RC{\equiv}CPPh_2$ ($R{=}CMe_3$, Ph) gave (83) which for $R{=}CMe_3$ produced (84) from $PdCl_2(PhCN)_2$. The carbonyl compounds $Ni(CO)_2(Ph_2PC{\equiv}CR)_2$ and $Ni(CO)_3\{(CpNi)_2(Ph_2PC{\equiv}CPh)\}$ are described as well as complexes in which the P of the acetylene is quaternised [257]. X-ray structures of $Ni_2(CO)_2(Ph_2PC{\equiv}CCMe_3)_2$ (85) [258], $[Pd(Ph_2PC{\equiv}CCF_3)(PPh_3)]_2$ (86) [259] and di-μ-thiocyanatobis[hydrogen-bis(diphenylphosphinato)] dipalladium(II) (87) [260] were reported, and the complex stability was attributed, in the nickel case, to strong Ni–C interactions (e.g. C≡C 1.28° Å and Ni–C 2.02 Å). The preparation of $[M(Ph_2PC{\equiv}CCF_3)_2]_2$ (M=Pd, Pt) and $[Pt(Ph_2PC{\equiv}C\ CF_3)(PPh_3)]_2$ was also reported [259]. The magnitudes of spectral shift in the IR spectra of Ni, Pd and Pt complexes with BuC≡CH and $ClCH_2C{\equiv}CH$ at – 180° varied in the order Ni<Pd<Pt [261]. The nickel alkynes $Cp_2Ni_2RC_2R^1$ ($R{=}H$, $R^1{=}Me$, $R{=}Me$, $R^1{=}Ph$, $R{=}R^1{=}CO_2Me$) were prepared and the sub-



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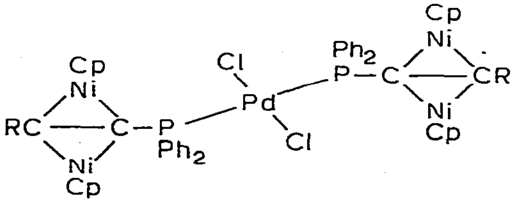

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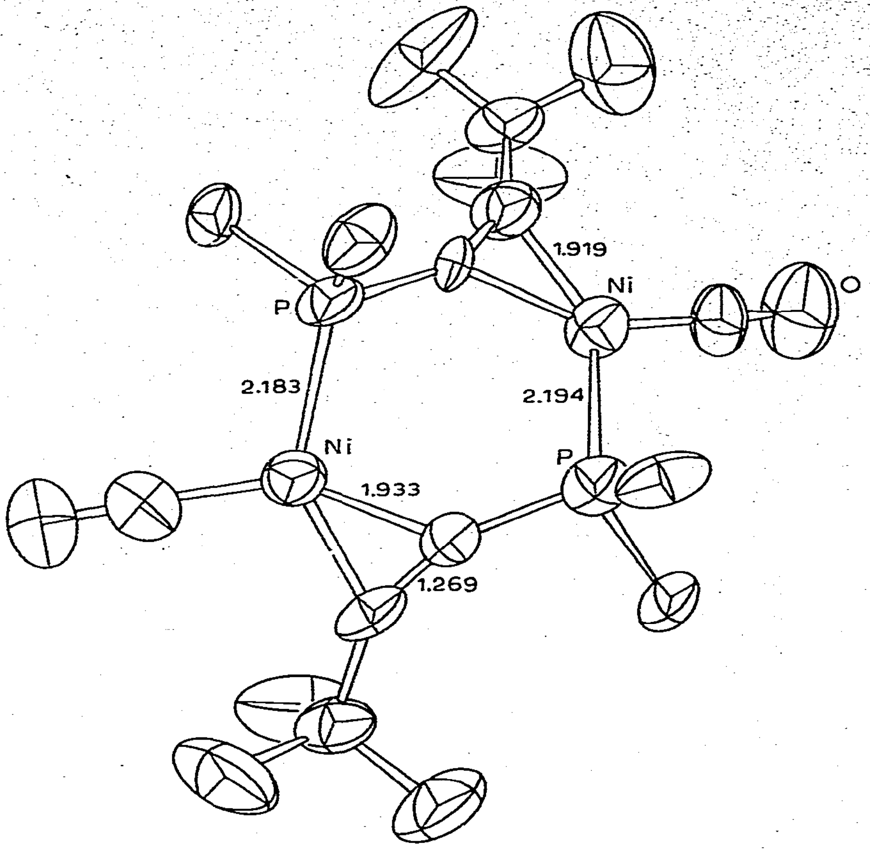
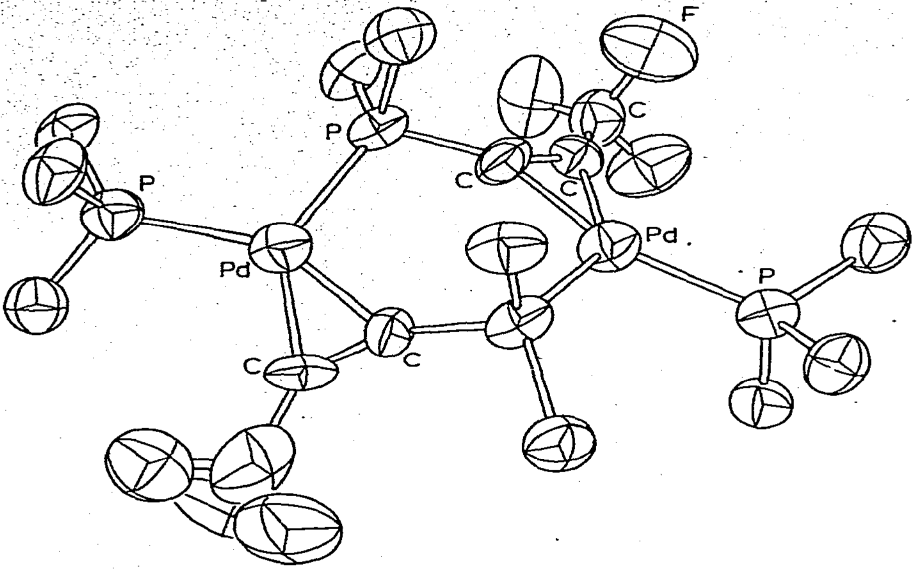


(85)

stituent effects in alkyne displacement was investigated. Spectroscopic properties and the nature of the bond between Ni and acetylene was discussed [262]. A re-examination of the kinetics of reaction between PhC≡CPh and $Cp_2Ni_2(CO)_2$ showed that a second order mechanism was significant at high ligand concentrations, whereas at low concentrations a two stage mechanism is operative [263]. The bonding in the acetylene compound $Pd\{C_2(CO_2Me)_2\}(PPh_3)_2$, solved structurally, was discussed in comparison with other known compounds. Mean parameters observed were Pd-C 2.06 Å, C≡C 1.28 Å and Pd-P 2.32 Å [264]. $Pd(PPh_3)_n$ (n = 3,4) and $(R_3P)_2Pd(C_2H_4)$ with RC≡CH gave $Pd(C{\equiv}CR)_2(PR_3)_2$



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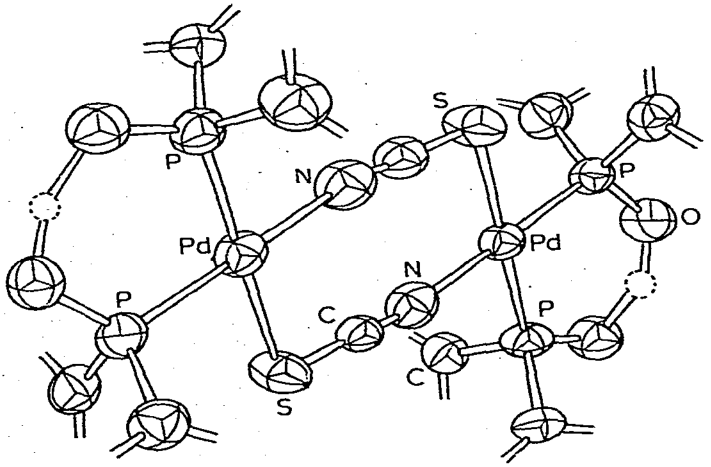
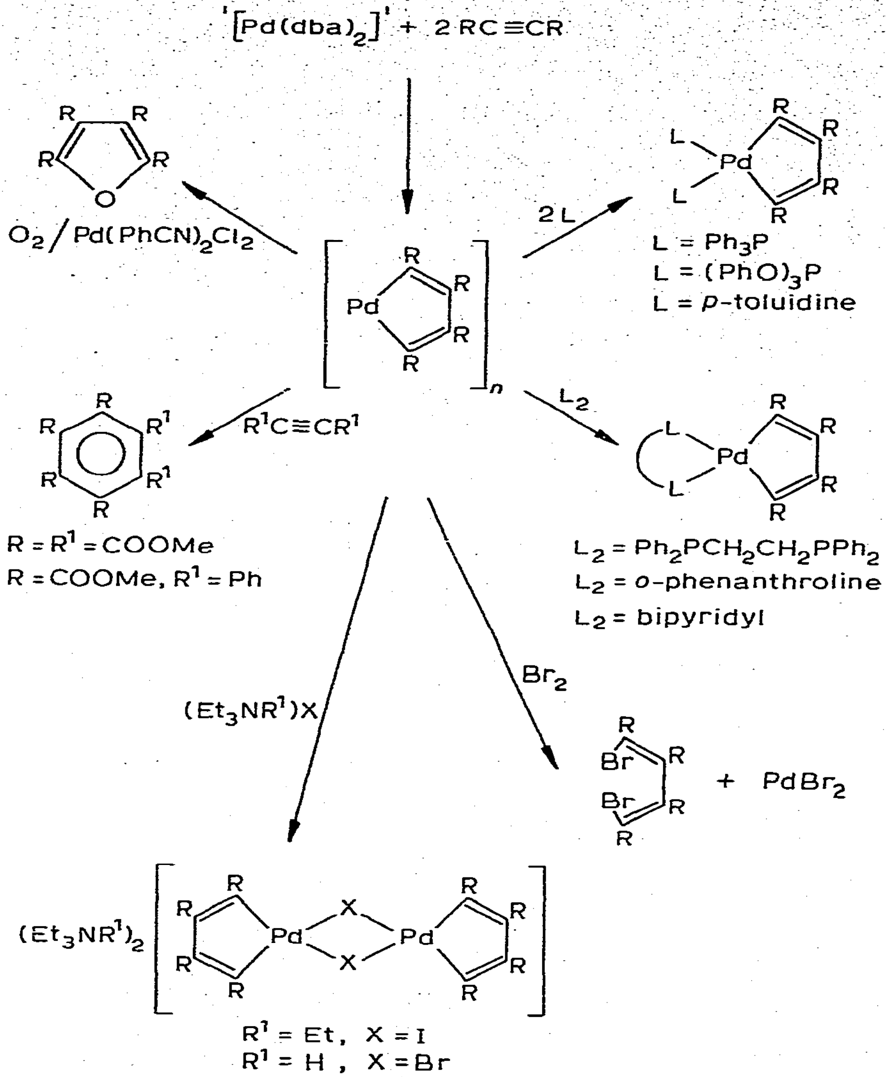


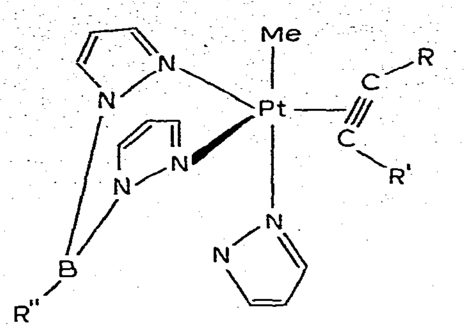
(87)

(R_3 = Me_2Ph, Ph_3) [265]. The formation of the palladacyclopentadienes $[Pd(C_4R_4)]_n$ from $MeCO_2C{\equiv}CCO_2Me$ and $Pd(dba)_2$ and their subsequent reactions have been studied [266] (scheme 13). The preparation of a series of five-coordinate Pt-Me-acetylenes (88) stabilised by the tridentate poly(pyrazolyl)



(Scheme 13)

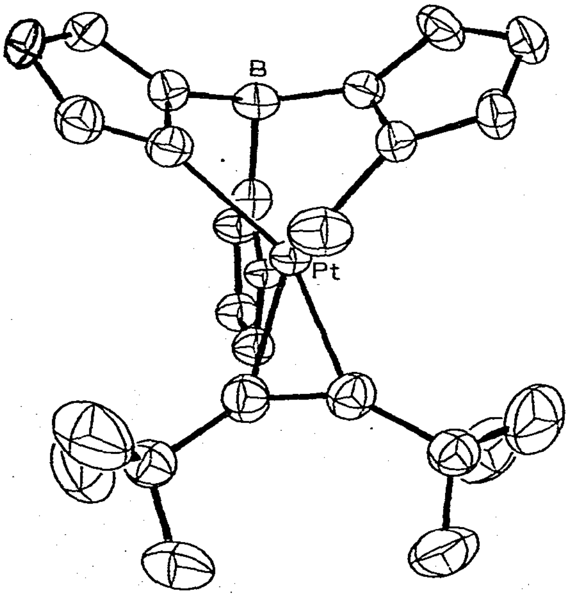
borate ligand [267] and the X-ray structure of $PtMe(CF_3C{\equiv}CCF_3)[HB(pz)_3]$ (89) [268] are reported. Parameters observed in the structural refinement of $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ were C≡C 1.26 Å; Pt-C 2.02 Å and Pt-P 2.28 Å [269]. Treatment of 2-pyridyl acetylenes with $Pt(PPh_3)_n$ (n = 2,4) gave $Pt(RC{\equiv}CR^1)PPh_3$



R'' = pyrazolyl, R = R^1 = CF_3, C_6H_5, CO_2CH_3
R'' = H, R = R' = CF_3, CO_2CH_3, Ph,
R = Me, R' = Ph, CO_2CH_3
R = Ph, R' = CO_2CH_3
R = H, R' = CO_2CH_3, $COCH_3$, CF_3

(88)

(R=R^1=2-pyridyl, R=Ph, R^1=2-pyridyl, R=R^1=6-Mepyridyl) which further reacted with anhydrous $CoCl_2$ (for R=R^1=2-pyridyl) to form (90) [270].



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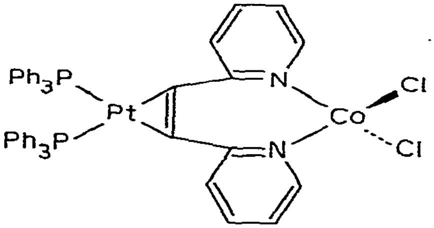


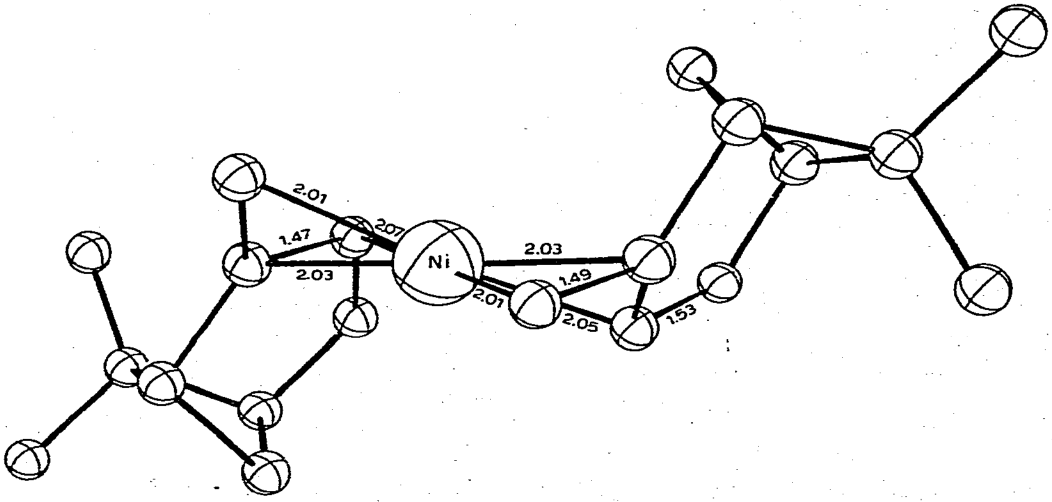
(90)

The low frequency IR spectra of the series $Pt(HC{\equiv}CR)(PPh_3)_2$ ($R=Ph$, $CH_2{=}CMe$, CH_2OH etc) were measured in the range 600-300 cm^{-1} and Pt-P and Pt-C stretching frequencies were assigned [271].

IX Metal allyls

Approaches to the synthesis of pentalene via metal complexes, including nickel allyls, have been surveyed [272]. Several spectroscopic characteristics of the structure and of the nature of internal bonds in allyl groups (e.g. $C_3H_5^+$, C_3H_5 and $C_3H_5^-$) are compared and clearly deduced from IR and Raman spectra of some organometallic compounds [273].

The X-ray crystallographic determinations of (+)-bis(π-pinenyl)nickel (91) [274], di-μ-acetatobis[(2-methylallyl-3-norbornyl)nickel(II)] orthorhombic [275] and monoclinic [276] form, acetonitrilebromo[1,3-η-(carbomethoxy-2-methylallyl)]nickel [277], [π-cyclohexanylnickelbis(triphenylphosphine)] trichlorozincate (92) [278] and the two complexes with σ-and π-nickel-carbon



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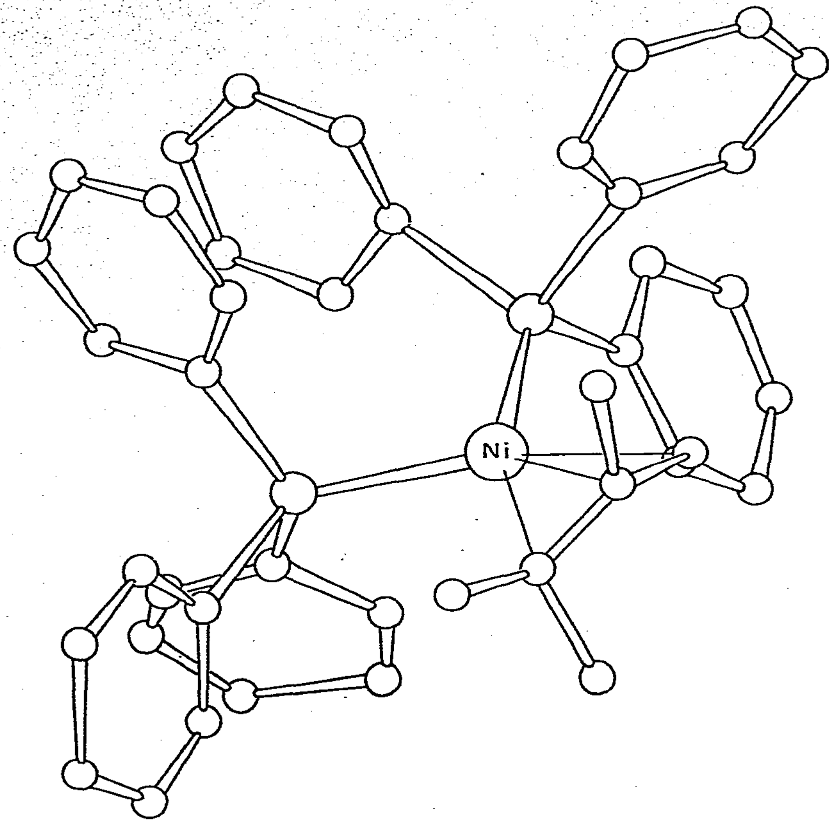
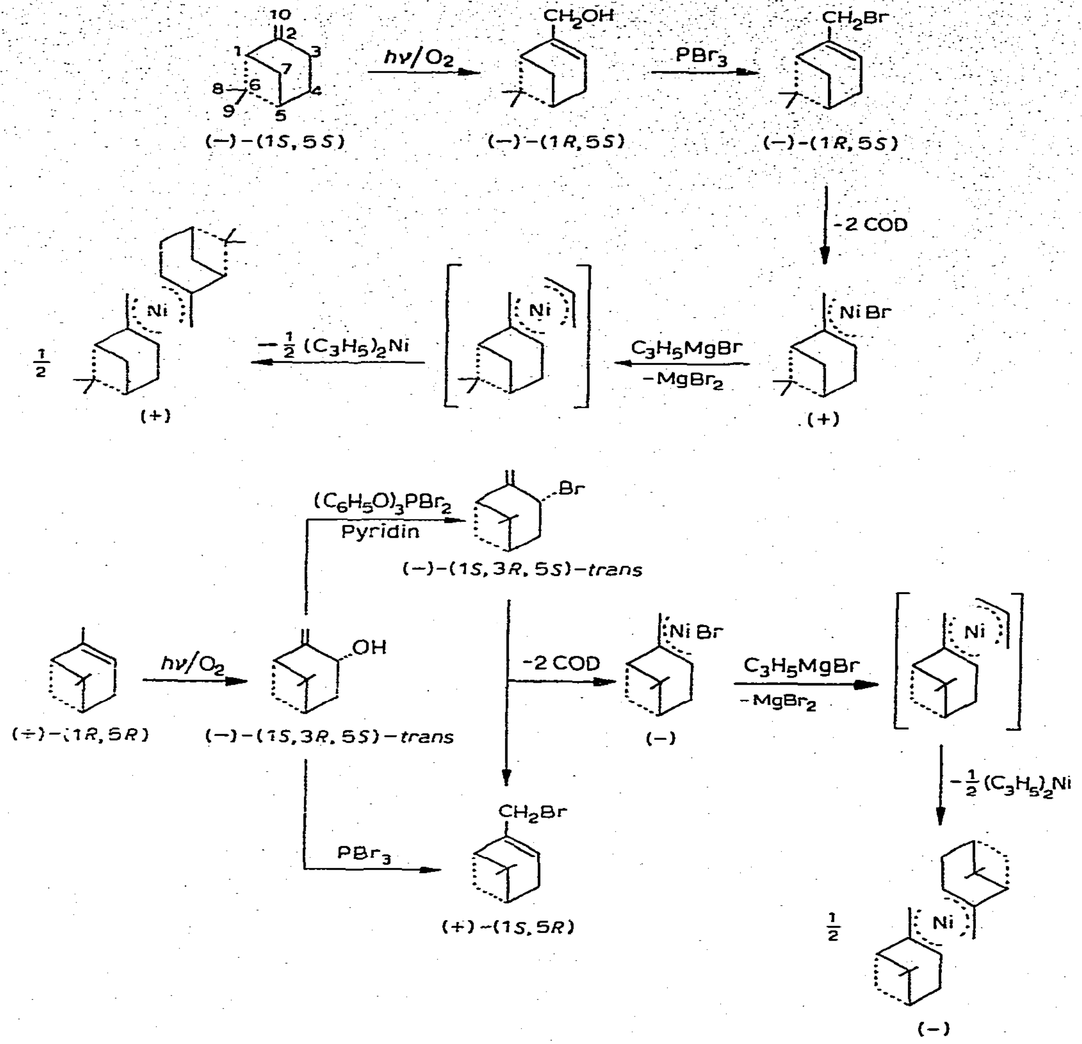


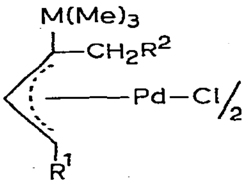
(92)

bonds, (π-pentenyl)(diisopropylphenylphosphine)methylnickel(II) and (π-pentenyl)dimenthylmethylphosphine)methylnickel(II) [279] have been completed. The absolute configuration of the π-pentenyldimenthylmethylphosphine product was R [279]. The preparations of (−) and (+)-π-pentylnickel halides and (−)-bis(π-pinenyl)nickel have appeared [274] (scheme 14). The IR spectra of $Ni(C_3H_5)_2$, $Ni_2(C_3H_5)_2X_2$(X=Cl, Br, I) [280] and $(RMO_2CR^1)_2$ (R=π-allyl, M=Ni, Pd, R^1=Me, CD_3, CF_3) [281] and the Raman and/or IR of $Ni(C_3H_5)_2$, $[C_3H_5PdCl]_2$, $C_3H_5Mn(CO)_4$ and $(C_3H_5)_2Fe(CO)_2$ [282] were recorded and correlated with structure. Results have been presented of a $^{13}C-\{^1H\}$ NMR study of π-allyl complexes of Ni, Pd and Pt and of π-diene and π-trienenickel compounds [283].



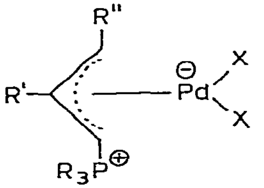
(Scheme 14)

The ^{13}C NMR spectra of some π-indenyl products of Cr, Fe, Co and Ni that have been measured allow a distinction to be made of h^6, h^5 and h^3 structures. In particular the structure of bis(h^3-indenyl)nickel was determined and an improved synthesis proposed [284]. The force fields of $[\pi\text{-}C_3H_5PdCl]_2$ and its nickel analogue were calculated from available X-ray data and the force constants for the individual bonds were tabulated by a modified least squares method of value selection. Vibrational spectra were also recorded [285]. The photolysis of h^3-allylnickel complexes in solution was studied [286]. The reaction of $[(\pi\text{-}C_3H_5)NiCl]_2$ with chloranil in toluene gave 1:1 adducts followed by loss of the allyl ligand, forming mainly trans-1,3-pentadienes [287]. R_2Ni (R=π-allyl, π-crotyl) and HCl form $NiCl_2$ and the corresponding olefins [288]. μ-N,N^1-ethylenebis(salicylaldiminato)bis[2-methylallylpalladium(II)] has been resolved crystallographically [289]. Several new monomeric π-allyl Pd(II)Sal=N-R complexes and binuclear Schiff base complexes have been synthesised and shown by NMR to exist in isomeric forms. From studies on their dynamic stereochemistry and on competing monomolecular-bimolecular equilibria, a mechanism for end to end exchange of the π-allyl group is proposed. 1,3-diene insertion reactions were also studied [290]. Novel π-allyls have been characterised from vinylsilanes (93) [291] and allylphosphonium ylide (94) [292]. The action of Na_2PdCl_4 on tricyclic



$R^1 = R^2 = H, Me$; M = Si, Ge

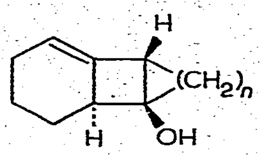
(93)



X = Cl, Br; R' = H, Me;
R'' = H, Me; $R_3 = Ph_3, PhMe_2$

(94)

alcohols (95) (n = 4,5,6) with a methylenecyclobutane group gave π-allylic species of formula (96) with rearrangement of the backbone. The corresponding acetates allow the isolation of complexes without rearrangement [293]. Cycloocta-1,3-dienepalladium(II) dichloride, an intermediate in the synthesis of (97) is formed from an initial nucleophilic substitution of MeOH on the diene followed by an acid catalysed elimination of MeOH. With 1-methyl-1,3-cyclooctadiene it was shown that solvent substitutions takes place by



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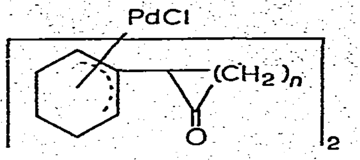

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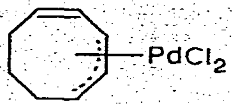
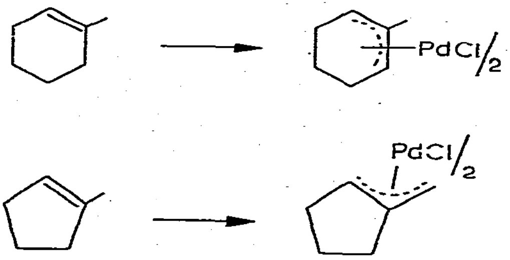


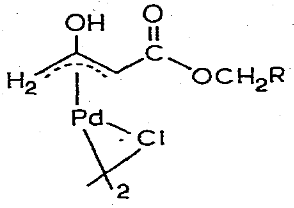
(97)

an S_n2' process [294]. Additions of cycloalkenes and alkylidenecycloalkanes to an active palladium solution, formed as a mixture of $PdCl_2$, NaCl, NaOAc and $CuCl_2$ in AcOH at 90-95° and then cooled to 60°, have produced a series of π-allylpalladium complexes regiospecifically [295] (scheme 15). Complex



(Scheme 15)

formation in aq. solutions of π-allylpalladium bromide was studied at pH 2-14 and 0-1.0M Br^- and a series of neutral, cationic and anionic π-allyl species identified [296]. A kinetic study of the reaction between $PdCl_4^{2-}$ and isoprene is interpreted in terms of the formation of two π-complexes between Pd(II) and isoprene, one having a monoolefin-Pd linkage and the other a diolefin chelate structure. Nucleophilic attack of MeOH on these intermediates gives methoxy π-allyl compounds [297]. Exchange reaction kinetics of $[(\pi\text{-}C_3H_5)PdCl]_2$ with butadiene, chloroprene, isoprene and styrene were determined by NMR and a mechanism was discussed [298]. ^{19}F NMR spectra of $RC_5H_4C_6H_4F$-m or- p (R = Li, Na, Tl, BrMg, C_3H_5Pd, CpFe) were determined in THF, MeCN or CCl_4 and the data used to estimate the ionicity of the Tl-Cp bond($\geqslant$ 40-50%) [299]. The ^{1}H NMR of diastereoisomeric (π-allyl)(N-α-phenylethylsalicylaldiminato)palladium showed that the phenyl ring caused an anisotropic shielding effect on the substituents of the allyl moiety cis to the nitrogen atom of the chelate. The stereochemistry of the allyl ligand was correlated with that of the Schiff base and the chemical shifts [300]. The allyl (98) reacted with py or its derivatives to give

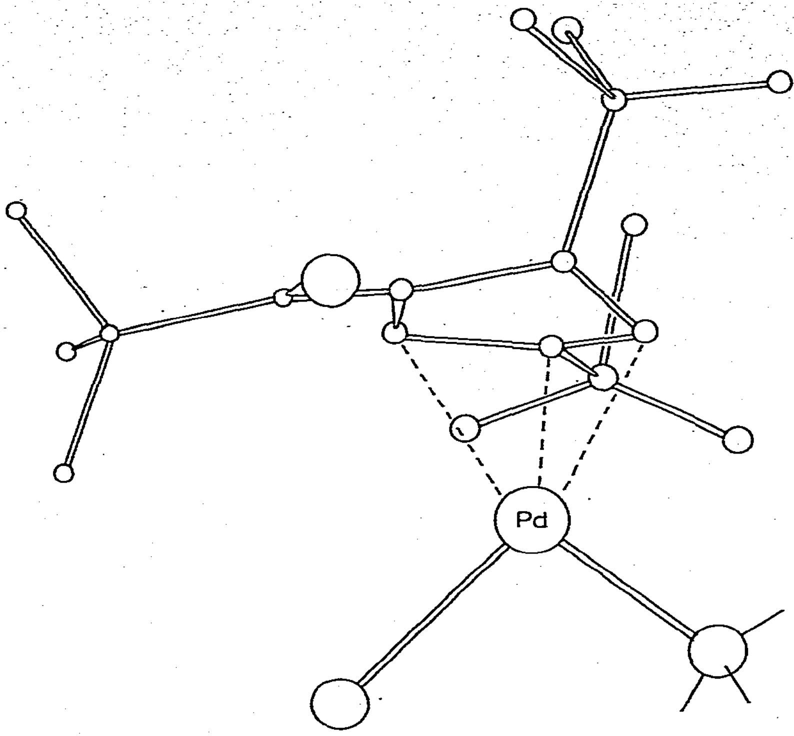


R = Me, Ph

(98)

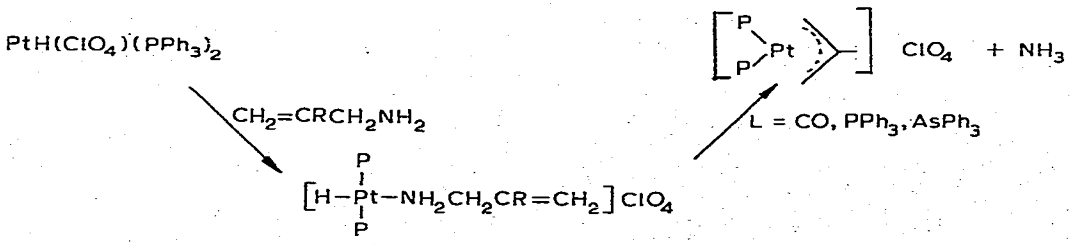
terminal bonded Pd-C products of formula $PdCl(CH_2COCH_2CO_2CH_2R)L_2$ (L = py, 2-Mepy, 4-Mepy, 2,6-Me_2py) [301]. Allyl iodide gave a 2:1 mixture of $[(\pi\text{-allyl})PdI]_2$ and $[(\pi\text{-crotyl})PdI]_2$, together with $CH_2 = CHCH_2Cl$, $CH_2 = CHCHClMe$ and $ClCH_2CH = CHMe$, on mixing with $[(\pi\text{-crotyl})PdCl]_2$ [302]. The oxidation of π-allylpalladium chloride with a range of oxidising agents has been studied [303]. The quantitative preparation of π-allylpalladium complexes from Pd(II) salts was obtained rapidly when a stream of ethylene was passed through an aq. solution of Na_2PdCl_4 and the allylic chloride. The first stage in the reaction is the formation of an olefin-Pd species [304].

The structure of chloro-[4-(chloro-tert-butyl)methylene-2,5-di-tert-butyl-1,3-η-cyclopent-2-enyl]triphenylphosphinepalladium (99) has been resolved. The complex, formed as a t-butylacetylenetrimer, exists in interconverting exocyclic and endocyclic η^3-allylic forms from ^{1}H and ^{13}C NMR evidence [305]. Treatment of trans-$[PtH(PPh_3)_2ClO_4]$ with $CH_2{=}CHCH_2X$ (X=Cl, Br) and allyl alcohol gave $[PtX(C_3H_6)(PPh_3)_2]ClO_4$ (X = Cl, Br) and $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]ClO_4$

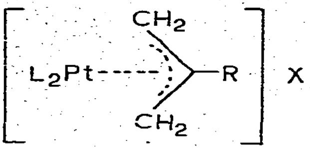


(99)

respectively [306]. Cationic platinum hydrides and allylamine or 2-methylallylamine have given π-allylplatinum(II) species [307] (scheme 16). The allyloxycarbonyl products $Pt(CO_2CH_2CR{=}CH_2)ClL_2$ (R = H, Me; L = PPh_3, $PMePh_2$) decarboxylate to the corresponding complexes (100) (X = Cl, ClO_4). The importance of olefin coordination to platinum in the transition state is suggested [308].



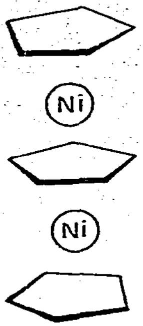
(Scheme 16)



(100)

X Delocalised carbocyclic systems

The chemistry of nickelocene has been reviewed [309], together with the chemical bonding in sandwich-type compounds [310]. Wideline NMR spectra of a number of solid metallocenes including some of Ni were recorded, and the second moments of the linewidths calculated. These calculations were consistent with essentially free rotation about the principle molecular symmetry axis, which is indicative of very low ring rotation barriers [311]. The UV photoelectron spectra of Cp_2M (M=V, Cr, Mn, Co, Ni) and their 1,1'-di-Me derivatives were observed and the metal 3d ionisation structure was discussed in terms of ligand field theory [312]. Principal species in the mass spectra of Cp_2M are Cp_2M^+, M^+ and fragment ions CpM^+(M=V, Cr, Fe, Ni). The dissociation energy for Ni was calculated as 69 kcal/mole [313]. The He 1 photoelectron spectra of CpNiNO and (π-C_5H_4Me)NiNO were recorded. Ab initio SCF MO calculations using Koopmans' theories did not give a satisfactory interpretation of the spectra since orbital relaxation accompanying ionisation from the metal 3d MO's was larger than that from the ligand valence orbitals. Expectation values of the second monent operator for occupied MO's of the ground state of CpNiNO were calculated to obtain a semiquantitative relationship between the spatial extent of an MO and the relaxation energy [314]. NMR studies were used to demonstrate the formation of the cation $[CpNiC_5H_6]^+$ in solutions of Cp_2Ni in HF. Additions of gaseous BF_3 to the cation gave the ionic compound $[CpNi]BF_4$, which was shown to be an intermediate in the formation of the cationic triple-decker sandwich complex $[Cp_3Ni_2]^+$, through reactions with Cp_2Ni [315]. An X-ray analysis of $[Cp_3Ni_2]BF_4$ (101) has been completed [316]. Other cyclopenta-



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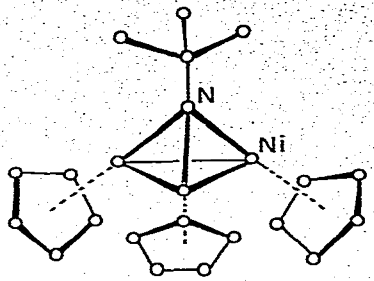
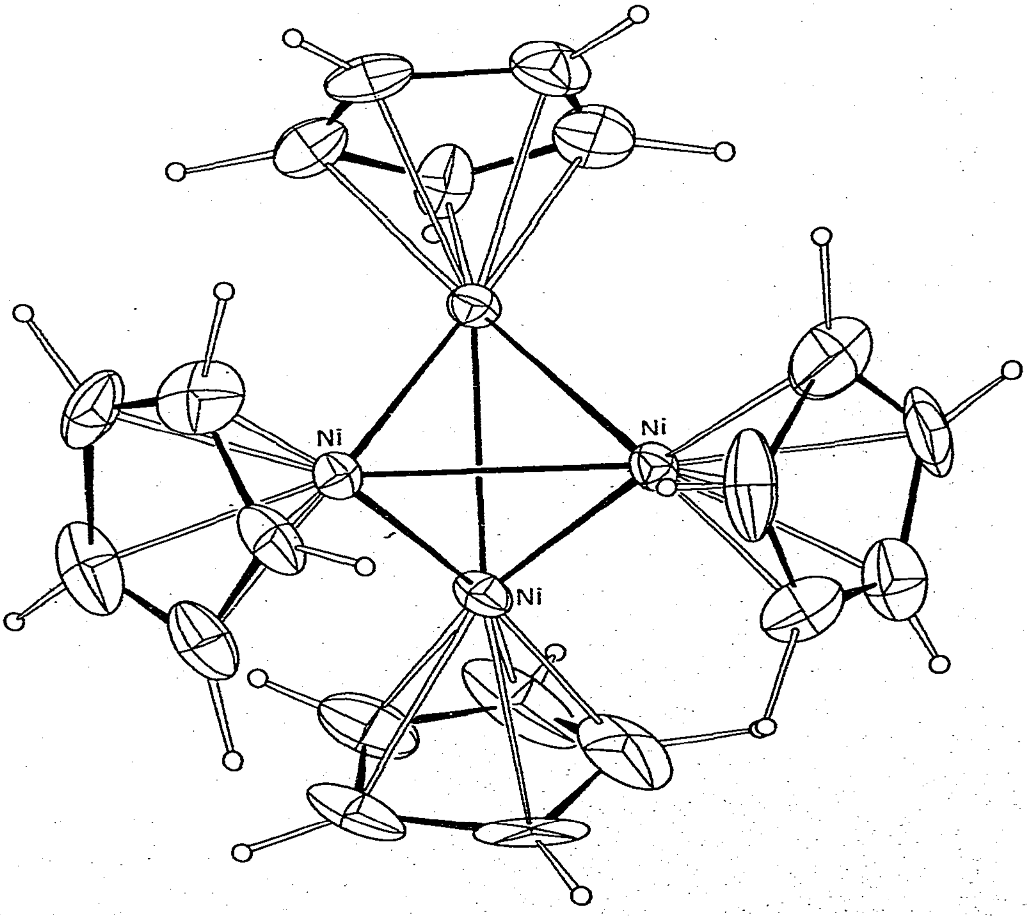


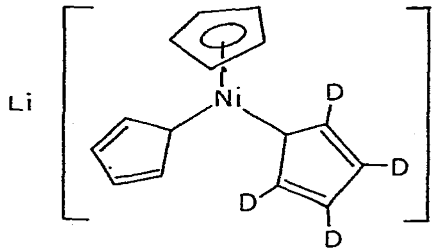
(102)

dienyl structures reported were $(Me_3C)_3N[CpNi]_3$ (102) [317] and $Cp_4Ni_4H_3$ (103), which contains a pseudotetrahedral Ni_4 cluster. Each Ni atom is



(103)

bonded to a planar Cp ring and hydrogen atoms bridge the nickel at three of the four faces of the tetrahedron [318]. Studies on the exchange reactions of Cp_2Ni with (i) LiC_5D_5, (ii) the tetramethylethylene diamine adduct of LiC_5D_5 and (iii) Cp_2Mn in THF, have appeared. With LiC_5D_5 alone, the observed rate law has first and second order terms and this was accounted for by k_1 referring to a $k_{obs} = k_o[LiCp]_{tot}[Cp_2Ni]_{tot}+k_1[LiCp]^2_{tot}[Cp_2Ni]_{tot}$ reaction of a $[LiCp]_2$ with CpNi. k_o refers to the LiCp + Cp_2Ni reaction. With tetramethylethylenediamine-LiC_5D_5 the reaction is first order, presumably due to no $[LiCp]_2$ species forming. The intermediate structure (104) is proposed, and an associative mechanism for (iii) was also inferred [319]. Substitution reactions of Cp_2Ni have produced the new products $CpNi[P(OR)_3]_nX$ (X = Cl, Br, I, n = 1,2) in CCl_4 [320], $CpNi(PRBu_2)_2$ (R = Ph, p-tolyl) which gave $CpNi(PPhBu_2)_2Cl$ with HCl, NiL_4 (L = PBu_3, $PBuPh_2$) [321] and (105) from bis(trifluoromethyl)diazomethane at -5° over a period of days



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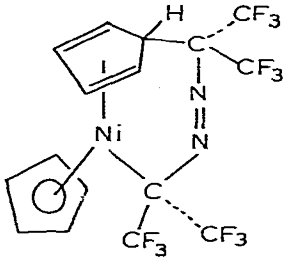
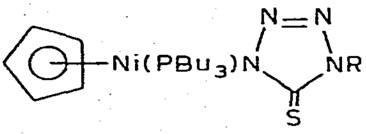


(105)

[322]. The N-bonded tetrazoline-5-thione organonickel compounds [CpNi $(N_4CSR)PBu_3]$ (106) (R = Ph, Me, Et) were prepared from $CpNi(PBu_3)N_3$ and RNCS [323]. Similar reactions with the salt $[CpNi(PBu_3)_2]Cl$ and $CS(S)X^-$ in aq.

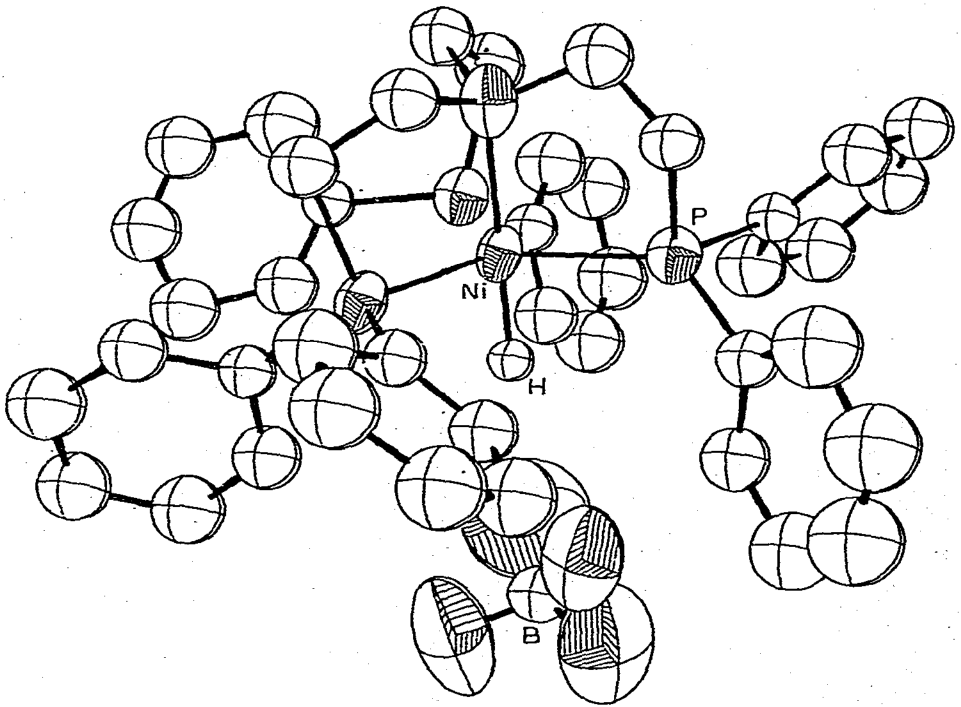


(106)

solution gave $CpNi(PBu_3)SC(S)X$ (X=OR, R, NRH), which was also formed from $CpNi(PBu_3)SH$ and RNCS. Treatment of $CpNi(PBu_3)SEt$ or $[CpNi(PBu_3)S(CH_2)_n]_2$ (n = 1-3) with PhNCS gave $CpNi(PBu_3)[SC(NPh)SEt]$ and $[CpNi(PBu_3)\{SC(NPh)S(CH_2)_n\}]_2$ respectively, and additions of RNCO to $CpNi(PBu_3)SH$ produced $CpNi(PBu_3)SC(O)NHR$ [324]. Eleven complexes of benzene and hexafluorobenzene with Ti, V, Cr, Mn, Fe, Co, Ni and Cu were prepared and their thermal stabilities determined [325].

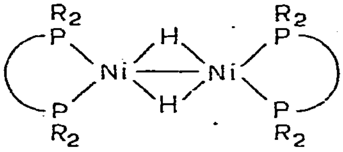
XI Metal hydrides

Addition of gaseous HCl to $Ni\{P(OCH_2)_3CR\}_4$ (R = Me) gave $[NiH\{P(OCH_2)_3CMe\}_4]HCl_2$ and with HX (X = BF_4, PF_6) formed $[NiH\{P(OCH_2)_3CMe\}]_4$ X. When R = n-C_6H_{13} protonations with HSO_3F and CF_3COOH gave $[NiH\{P(OCH_2)_3$



(107)

$CC_6H_{13}\}]X$ ($X = SO_3F$, CF_3COO) [326]. Non-stoichiometric hydrides of formula $[NiH_xL]BF_4$ [$L = N(CH_2CH_2PPh_2)_3$] were obtained from $Ni(BF_4)_2$ and L in the presence or absence of $NaBH_4$. Hydrogen-rich compounds were prepared from [NiL] and HBF_4, and the X-ray analysis of $[NiH_{0.5}L]BF_4$ (107) shows one crystallographic type of cation but because of the hydride ligand deficiency some of these cations are trigonal bipyramidal, with N and H in axial positions, and the rest are trigonal pyramidal [327]. A study of the reactions of MCl_2(M = Co, Ni, Cu, Pd, Pt) with $NaBH_4$ and $NaBH_3CN$ in the presence of tertiary phosphines showed that the complexes obtained varied enormously using different conditions. The products ML_n, MBL_n, $MHBL_n$ (L = phosphine, $B = BH_4$, BH_3CN, $n = 2$-4) and $PtH(CN)L_2$ were characterised from solution [328]. Treatment of $NiH(NO_3)(PCy_3)_2$ (Cy = cyclohexyl) with L in the presence of $NaBH_4$ was reported to give $[NiHL(PCy_3)_2]BPh_4$ (L = py, pyrazole, imidazole) [329]. The complexes, $Ni\{R_2P(CH_2)_nPR_2\}_2C_6H_6$ ($n = 2,3$), formed from $NiCl_2\{R_2P(CH_2)_nPR_2\}$ (R = cyclohexyl) and Li powder in benzene, activated hydrogen forming (108) [330]. The $^{31}P\{^1H\}$ and hydride region



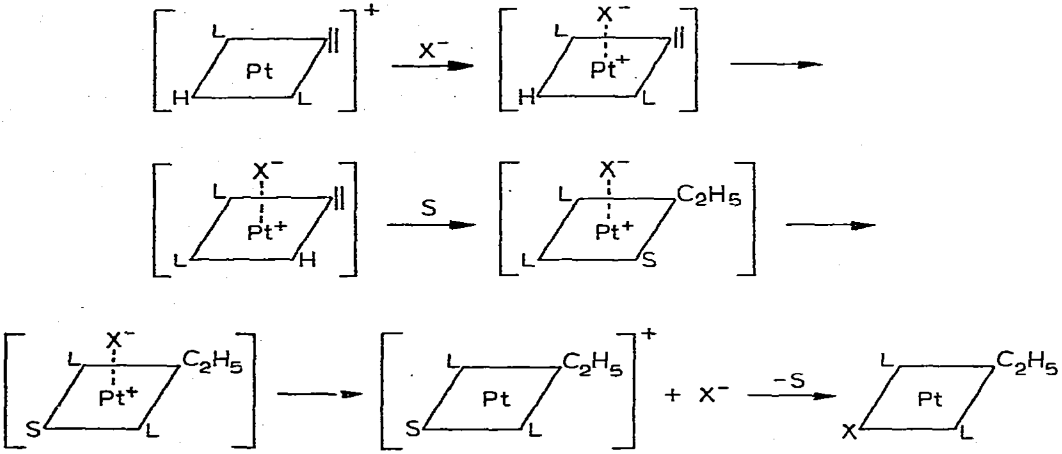
(108)

^1H NMR spectra for the complexes $[MHL_3]X$(M = Ni, Pd, Pt; $L = PEt_3$; $X = BPh_4$) were studied as a function of temperature and free ligand concentration. The spectral behaviour was found to be a result of an exchange process between 4 - and 5 - coordinate species. For M = Pt one ligand remains unique throughout the exchange process indicating that the 5-coordinate intermediate does not, on average, undergo intramolecular rearrangement before dissociation of an equatorial ligand takes place. For M = Pd the rate of intramolecular exchange is less than the rate of dissociation but both processes contribute to the line shape effects. For M = Ni the intramolecular exchange process is faster than ligand dissociation and there is some evidence for intramolecular exchange in $NiH(PEt_3)_3^+$ in the absence of added ligand [331].

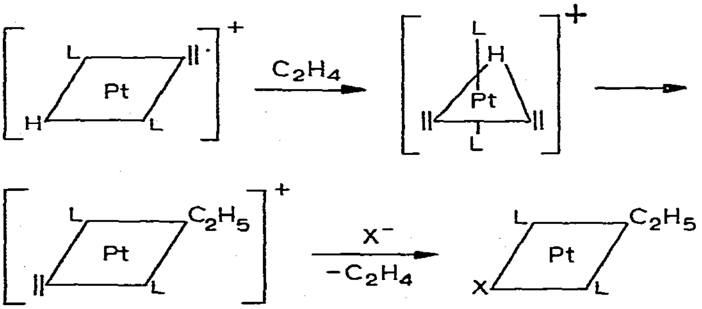
Hydride complexes of Group VIII (e.g. $PdH_2[P(C_6H_{11})_3]_2$) promote C–O bond cleavage in vinyl or allyl carboxylates, liberating ethylene or propylene and forming the metal-carboxylates [332]. The hydrides trans-$[PtH_2L_2']$ and $[PtH(P-C)L]$ have been prepared from trans-$[PtHClL_2]$ and cis-$[PtCl_2L_2]$ with $NaBH_4$ in EtOH for L' = PBu^tMe_2, PBu^tEt_2 $PBu^tBu^n_2$, $PBu^t(CH_2Ph)_2$, $PBu^t_2CH_2Ph$ and $P(cyclohexyl)_3$, and with L = PBu^t(o-tolyl)$_2$, PBu^t_2(o-tolyl) and $PBu^t(CH_2Ph)_2$ for the internally metallated hydrides [333]. Oxidative additions of areneselenols to PtL_4 gave $PtH(SeR)L_2$(R=Ph, p-MeC_6H_4; L = PPh_3, $PMePh_2$) which further reacted to form $Pt(SeR)_2L_2$ [334]. New hydrides were obtained by solvolysis of $Pt(ROPPh_2)_4$. Characterised products were $[PtH(OPPh_2)(HOPPh_2)(ROPPh_2)]$ (R = Bu^n, Pr^i, H) [335]. One of the sets of hydride ^1H NMR patterns for the isothiocyanato-thiocyanato mixture in trans-$[PtH(SCN)(PEt_3)_2]$ is broad due to ^{14}N quadrupole relaxations [336]. Analysis of the spin system for the cations $[PtH(PEt_3)_3]^+$, $[PtH(PEt_3)_2PPh_3]^+$ and $[PtH(PPh_3)_3]^+$ as AB_2X and AB_2MX (A = B = ^{31}P; M = ^{195}Pt, X = ^1H) has shown that different side and centre band multiplets for the hydride resonance are to be expected in any general case of A_nB_mX (A_nB_mMX in these systems) and are only similar when $|\delta_{AB}| \gg \frac{1}{2}|J_{AM}-J_{BM}|$. In the case where $|\delta_{AB}| \simeq \frac{1}{2}||J_{AX}-J_{BX}|-J_{AB}||$ it is not possible to neglect the effect on the X-spectrum of remote active nucleii which are coupled to A or B. Thus tertiary phosphine effects from remote alkyl or aryl hydrogen atoms cannot be neglected [337]. Kinetic studies of the reversible insertion into the Pt-H bond with ethylene, in the system trans-$[PtH(acetone)(PEt_3)_2]^+$ [338,339] and methyl acrylate in $PtH(NO_3)(PEt_3)_2$ [340] are reported. With ethylene, under pseudo first order conditions in C_2H_4 the rate law was:

$$-d[\mathrm{Pt\text{-}H]}/_{dt} = k_{obs}\,[\mathrm{PtHydride}], \text{ with } k_{obs} = \frac{k^1[C_2H_4]}{(1+K[C_2H_4])}$$

over a 20 fold variation in $[C_2H_4]$ [338]. Either of two mechanisms proposed (scheme 17 a,b) [338,339], however could account for the kinetic

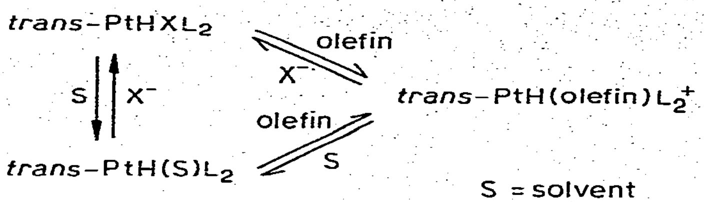


(Scheme 17a)



(Scheme 17 b)

results obtained, though all schemes proposed [338-340] invoke the cation *trans*-$[\mathrm{PtH(olefin)L_2}]^+$ (scheme 18). Treatment of $\mathrm{PtHCl(PR_3)_2}$ (R = Ph, Et)



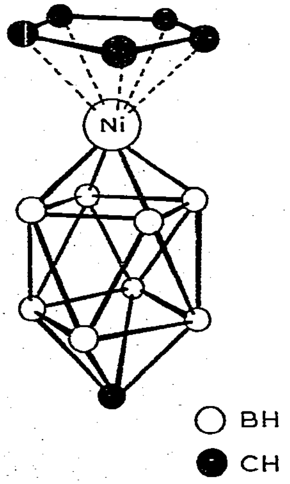
S = solvent

(Scheme 18)

with 1,3-diaryltriazenes formed $PtCl(ArNNNAr)(PR_3)_2$ [341], and trans-$[PtH(ClO_4)(PPh_3)_2]$ with HNRR' (R = R' = H, R = H, R' = Me, R = R' = Me) gave $[Pt(NRR')(PPh_3)_2]ClO_4$ [342].

XII Metal carboranes

The reaction of $NaC_2B_4H_7$ with $NiCl_2(DPE)$ gave $(\pi\text{-}2,3\text{-}C_2B_4H_6)NiDPE$ and when $NiBr_2$, NaCp, HCl and air are mixed, $(\pi\text{-}C_2B_5H_7)Ni_2Cp_2$ is formed [343]. A novel Ni(IV) carborane was isolated in small yield during the synthesis of $CpNi(IV)(\eta\text{-}7\text{-}B_{10}H_{11})$, and was formulated as (109) from ^{11}B NMR and mass spectral data [344]. The abstraction of NMe_3 and bridging protons from $B_{10}H_{12}C[NMe_3]$ with sodium in THF, followed by NaCp and $NiBr_2(MeOC_2H_4OMe)_2$ additions and oxidation gave $CpNi^{IV}(\eta\text{-}7\text{-}CB_{10}H_{11})$ [345]. Direct insertion of transition metals (e.g. $Ni(C_2H_4)(PPh_3)_2$) into $C_2B_4H_6$ produced (110) [346].



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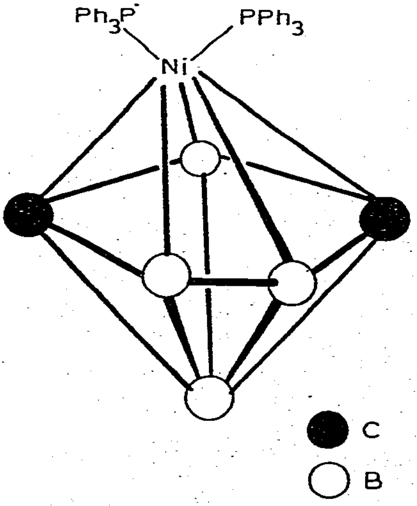

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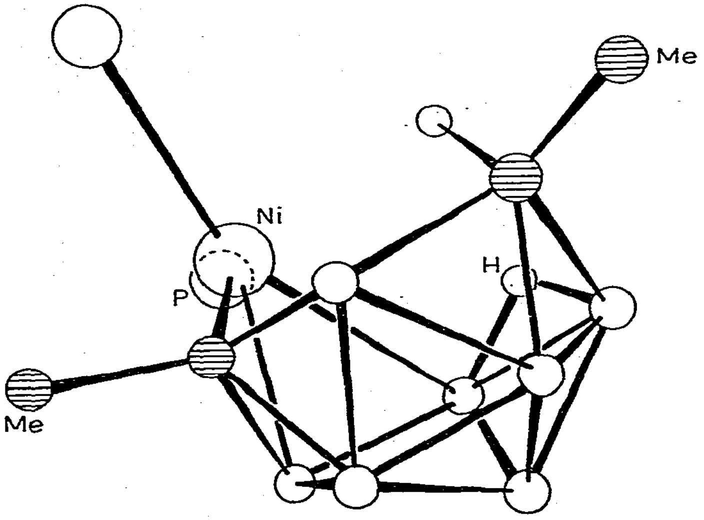
The arachno-carborane 1,3-$Me_2B_7C_2H_{11}$ and $Ni(PR_3)_4$ (R = Me, Et) or [Pt(stilbene)$(PR_3)_2$] (R = Me, Et, Ph) gave the corresponding $M(B_7C_2H_9Me_2)(PR_3)_2$. (M = Ni, Pt). $Pt(B_7C_2H_{11})(PEt_3)_2$ was also prepared. X-ray characterisation of the nickel complex (R = Et) (111) showed it to be the first example of an η-carbadiboraallyl species [347]. The rearrangement and oxidation of $(\pi\text{-}C_{10}H_{10}C_2RR^1)_2M^{n-}$ (M = Co, Fe, Ni) has been studied. The nido complex structure is oxidised by $CuCl_2$ to the closo-carbaborane $B_{10}H_{10}C_2RR^1$, and readily undergoes polyhedral rearrangement into isomeric compounds [348]. A new synthetic route to π-(3)-1,2-dicarbollylplatinum(II) complexes of formula $Pt(\pi\text{-}(3)\text{-}1,2\text{-}C_2B_9H_9R^1R^2)(PR_3)_2$ (R = Et, n-C_3H_7, Ph, R^1 = H, Me, R^2 = Me, Ph) has been described [349], and the structure of closo-[$Me_2C_2B_9H_9$ Pt$(PMe_2Ph)_2$] (112) was determined [350]. The preparation and structure of nido-[$Me_2C_2B_7H_7$ Pt$(PEt_3)_2$] (113) was also reported [350]. The X-ray structure of [Pt(2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)[P(n-propyl)$_3$]$_2$ (114) shows the carborane to be σ-bonded to the Pt atom together with one of the carbon atoms of the n-propyl group on a



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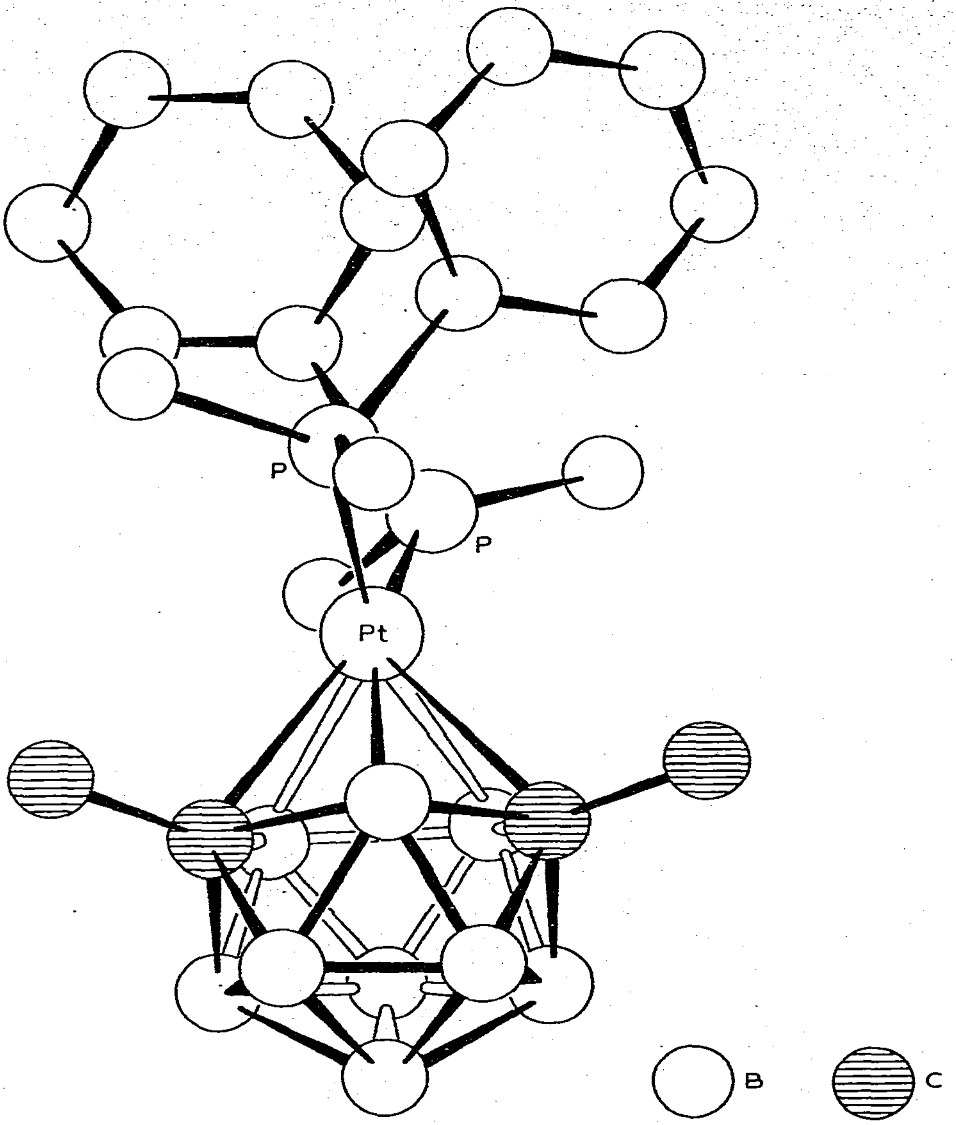
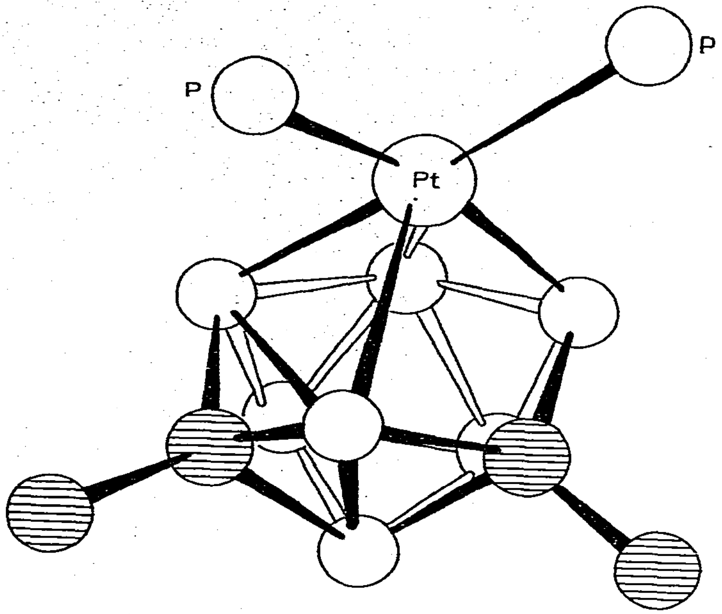


(112)

phosphine ligand [351]. The reaction of *closo*-1,6-R_2-1,6-$C_2B_6H_6$ with Pt(stilbene)L_2 (L = PEt_3, PMe_3) gave two products characterised as *closo*-1,1-Me_3P-6,8-Me_2-1,6,8-$PtC_2B_6H_6$ (115), containing a boron analogue of a

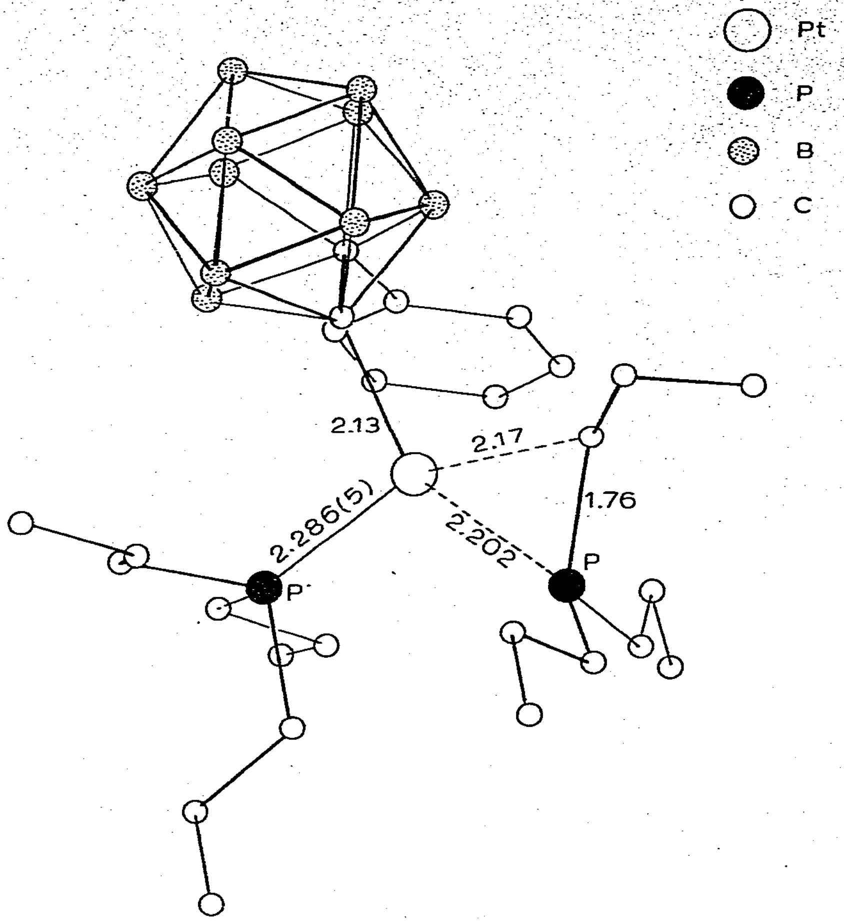


(113)

coordinated cyclobutadiene and <u>nido</u>-[$C_2B_6H_6Me_2Pt(PEt_3)_2$] (116) [352]. Six lithium carboranes gave crystalline <u>cis</u>- or <u>trans</u>-Pt(II) hydrido-dicarba-<u>closo</u>-dodecarborane with $PtHCl(PEt_3)_2$ [353]. Hexaborane formed <u>trans</u>-[$Pt(C_6H_{10})_2Cl_2$] in which the borane is bound via a 3-centre, 2-electron bond with Pt in the 4,5 bridging position [354].

XIII Hydrosilylation and germylation reactions

Addition of $Me_3SiCH{=}CH_2$ to $PdCl_2(PhCN)_2$ gave bis[h^3-1-(trimethylsilyl)-1-methylallyl]-μ-dichlorodipalladium(II). The germanium analogue was also characterised, as were other silyl allyls [355]. $Pt(C_2H_4)L_2$ (L = PPh_3) produced a variety of the organosilylhydrides, $PtH(SiR_3)L_2$, with R_3SiH. The compounds [$Pt(SiR_3)L_2$] (R_3 = Cl_3, Me_2Cl, $MeCl_2$; L = PPh_3, $PMePh_2$) were also characterised [356]. Evidence has been presented for the formation of M–C σ-bonds in the metal-catalysed cleavage of Si–C linkages [357–359].



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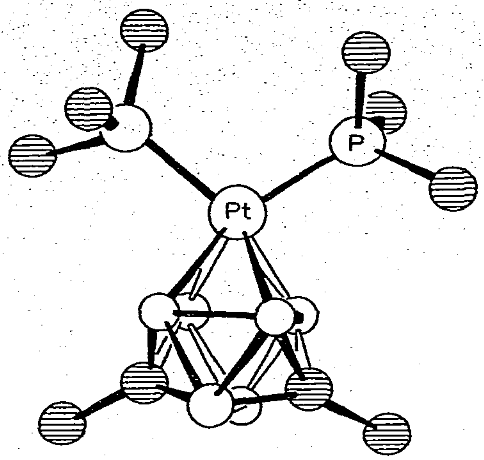
The substitution and reduction mechanism of organosilanes by Grignard reagents catalysed by nickel complexes is said to involve formation of nickel(0) species which subsequently oxidatively add silanes. Reduction then takes place by direct attack of a nickel hydride formed on the alkoxysilane [360]. A series of papers on the metal-catalysed hydrosilylation of olefins and acetylenes has appeared [361-369]. Selective hydrosilylation of terminal monoolefins or conjugated diolefins by Pd complexes [361-362] and by the polymer (117) (M = Ni, Pd, Pt, Rh) [363] have been observed, and the kinetics of the reaction of $PhCH=CH_2$ with $MeSiHCl_2$ in the presence of platinum compounds reported



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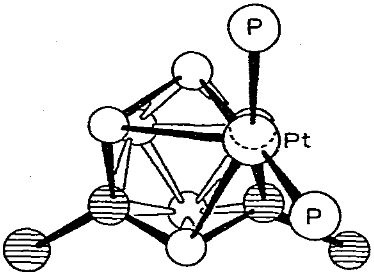

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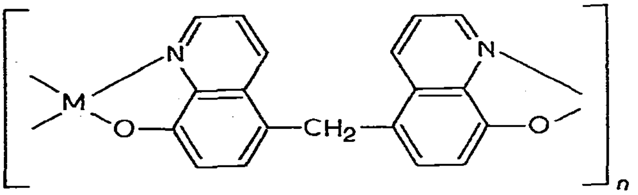
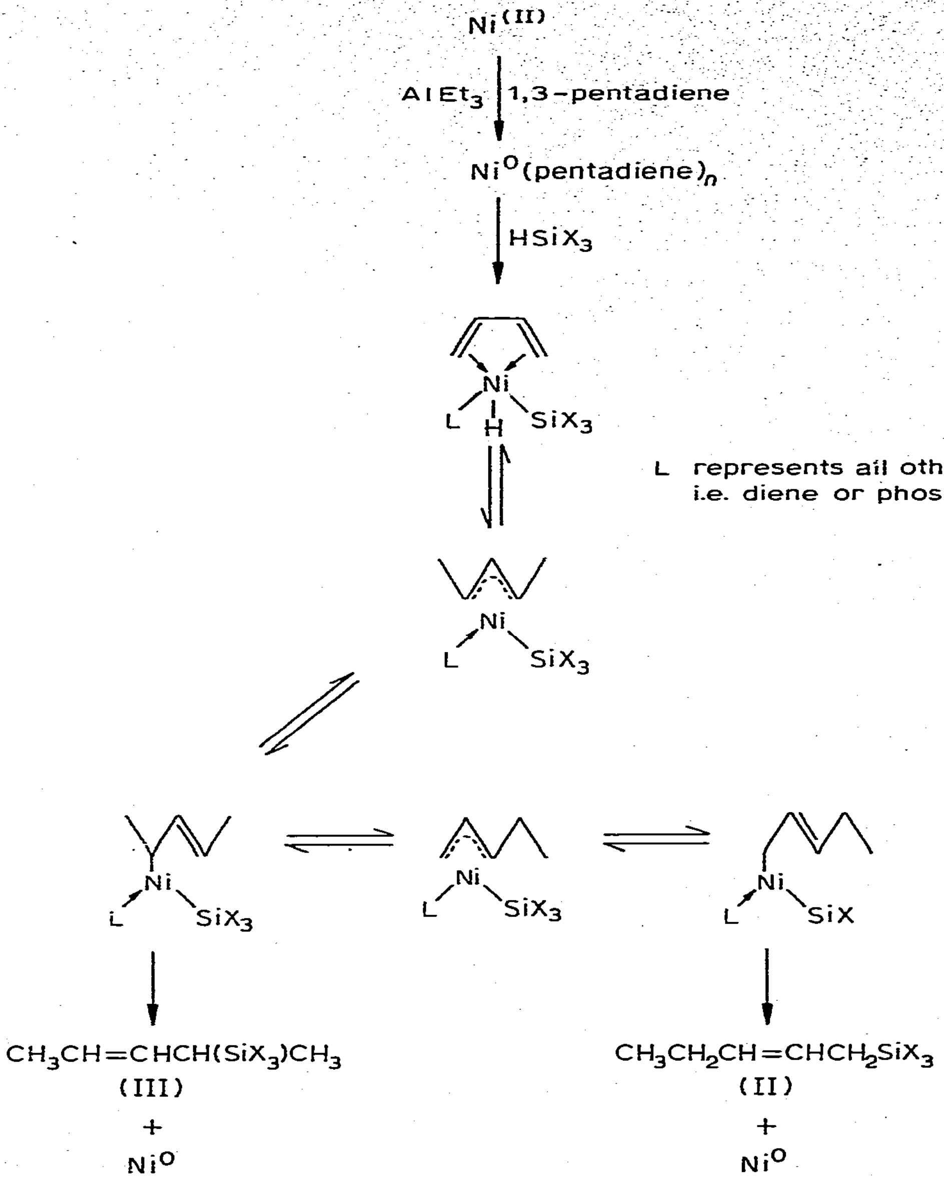
▤ = C



(117)

[364,365]. The effective nature of H_2PtCl_6 as a catalyst in the addition of silanes to 1-hexyne is dependent upon storage [366]. Ziegler-type systems e.g. $M(acac)_n$-$AlEt_3$ (M = Ni, Co, Fe) catalyse the hydrosilylation of 1,3-dienes or terminal acetylenes. With isoprene or 1,3-pentadiene the 1,4-adducts $MeCH{=}CMeCH_2SiX_3$ or $MeCH_2CH{=}CHCH_2SiX_3$ (X=OEt, Et, OMe) are the major products, and nickel salts e.g. $NiCl_2$ or $Ni(acac)_2$, provide the best catalysts. A chain reaction mechanism is proposed (scheme 19). Terminal acetylenes RC≡CH yield the products in which linear dimerisation accompanies hydrosilylation. The head-to-tail adduct $H_2C{=}CRCR{=}CHSiX_3$ predominates over the isomer $RCH{=}CHCR{=}CHSiX_3$, and hydrosilylation was favoured by electronegative



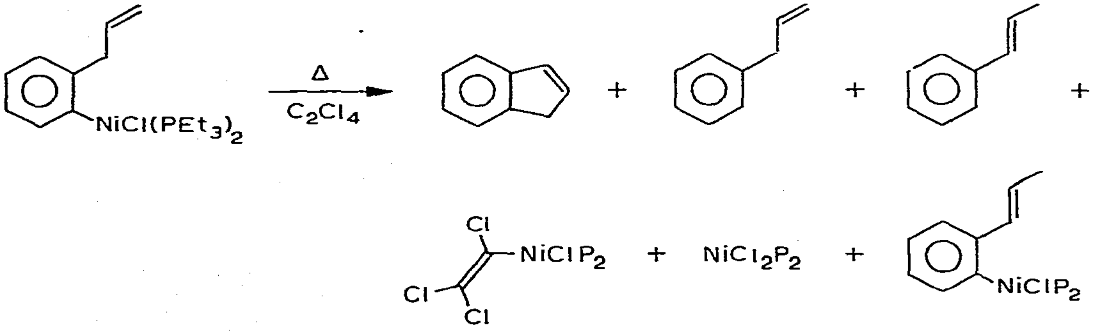
L represents all other ligands i.e. diene or phosphine

(Scheme 19)

substituents X at Si[367]. Platinum catalysed addition of dichlorosilane to acetylenes proceeded in a stereospecific *cis* fashion yielding *trans* adducts [368]. The products RR^{1}SiHCHMeCN (R = R^1 = Ph, R = Me, R^1 = Ph) were obtained from RR^1SiH_2 and CH_2=CHCN with H_2PtCl_6 [369]. The hydrosilylation of carbodiimides proceeded at higher temperatures in the presence of catalytic amounts of $PdCl_2$ to afford N-silylformamidines [370]. Treating ketones and Et_3SiH with $PdCl_2$ gave Et_2SiOR for a large range of R's [371]. The effect of n upon the ease of ring formation from $[CH_2{=}CH(CH_2)_nSi\,Me_2H]$ (n= 0-6) and H_2PtCl_6 as catalyst was studied [372]. An optically active digermane is obtained from the reaction of $PhCH_2MgCl$ (activated by a nickel(II) complex) with (α-neopentyl)PhMeGeH. It was proposed that a GeMgX species was formed, and its activation by Ni(II) allowed cleavage of the Ge–H bond with retention of configuration [373].

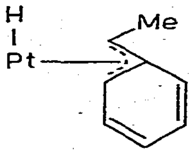
XIV Catalytic reactions involving Ni, Pd, Pt

EPR studies on nickel Ziegler-type catalytic systems has provided evidence for nickel(I) [374-376] bridged [374-375] species. The thermolysis of (118) in C_2Cl_4 and PhH has been studied and a number of products were characterised (scheme 20) [377]. The large multiple ^1H - ^2H exchange factor observed in the Pd(II) catalysed reaction of cyclobutane with D_2 is attributed to a Pt-alkane or cycloalkane complex intermediate. Ph_4C_4 is cleaved by Pt(II) to trans-stilbene whilst norbornadiene shows preferential exo-exchange [378]. Monomer insertion at the Ni-C σ-bond, rather than



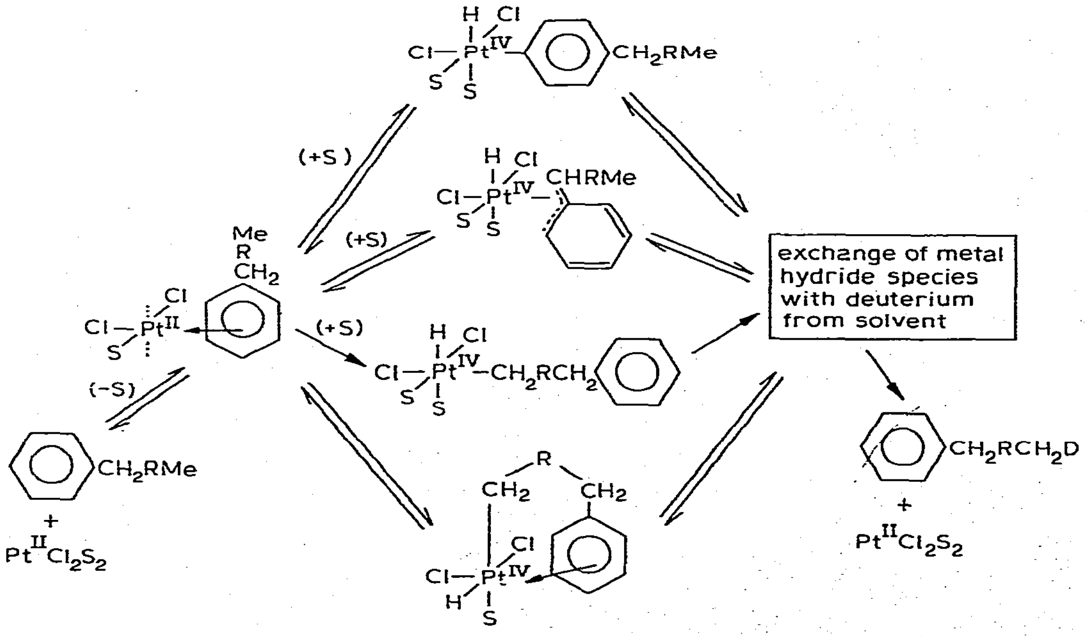
(Scheme 20)

hydrogen transfer, was proposed as the rate determining factor in the isotopic exchange obtained when perdeuteropropylene was dimerised with a nondeuterated olefin by allylnickel bromide–$TiCl_4$ mixtures [379]. The intermediate platinum allyl (119) accounts for the D_2 exchange noted in short chain alkyl-



(119)

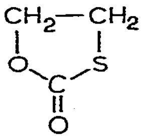
benzenes [380]. An overall mechanism to explain the D_2O exchanges with alkylbenzenes has been given [381] (scheme 21). Known data on the oxidation of C_2H_4 to AcH by quinone in the presence of $PdCl_2$ and $PdCl_2$-$LiClO_4$ were discussed in terms of the ionic strength of catalyst compounds [382]. Two types of catalyst were used in the oxidation of cyclohexene to cyclohexene



(Scheme 21)

oxide and 2-cyclohexen-1-ol. The epoxidation catalysts were Mo complexes and the autoxidation catalysts were transition metal phosphines or acetylacetonates [383]. With $MoO_5[(Me_2N)_3PO]H_2O$ and $M(acac)_2$ (M = Ni, Pd), a different product distribution in the cyclohexene autoxidation to that obtained with the Mo compound alone, was obtained [384].

The carbonylation of PhI with CO and $PdCl_2$ has been investigated kinetically. Rate equations were derived and intermediates involving MeO- and MeOCO-Pd species were suggested [385]. 2-Mercaptoethanol undergoes carbonylation in py in the presence of O_2 and $Ni(CO)_3$ py to form (120) [386]. The reactions of cycloheptacyclopropenone gave (121) and diphenylcyclopropenone (122) on reacting with $Ni(CO)_4$ [387]. The insertion reactions of CO with olefins, catalysed by metal carbonyls, to give the corresponding carboxylates have been examined [388-390]. With cyclic olefins and methallyl or crotyl chloride, CO insertions to produce ketones and carboxylates were facile when the olefin contained a strained double bond or contained a second or third double bond capable of chelating the Ni atom [388]. The factors effecting the formation of isomers and byproducts of a desired compound, formed by these reactions, were studied [389].



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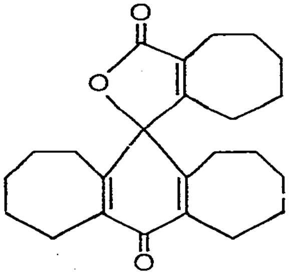

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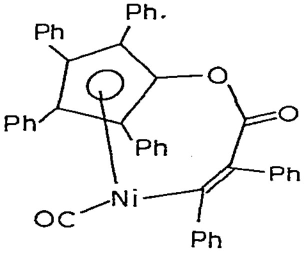
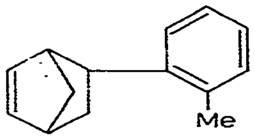


(122)

The complex $PtCl_2(H_2O)[P(C_6F_5)_3]$ was found to be an active hydrogenation catalyst for sulpholene, alkenes and alkadienes [391-393]. Heating 1-methylcyclohexanol with H_2 in the presence of $PtCl_2(PPh_3)_2$ and CF_3COOH gave 86% of methylcyclohexane [394]. The reduction of $PhNO_2$ and phenyl substituted products with $NaBH_4$ using $K_2Ni(CN)_4$ as catalyst gave PhN(O)=NPh, PhN=NPh and PhNHNHPh [395]. Catalysts used for the homogeneous hydrogenation of olefins and acetylenes, usually with H_2, have been (i) $Pd\{P(OPh)_3\}_4$ for C_2H_2 and C_2H_4 [396] (ii) $K_4Ni_2(CN)_6$ for the 3,4 double bond in 6-methyl-3,5-heptadien-2-ol [397], (iii) $PdCl_2(Me_2SO)_2/NaBH_4$ for $CH_2{=}CHCH_2NH_2$ [398] and for acetylenes [399] (iv) $Ni(acac)_2/R_3Al$ ($R_3{=}Et_3$, Et_2OPh, $Et(OPh)_2$) for *cis-trans-trans*-1,5,9-cyclododecatriene [400].

Investigations into the homogeneous oligomerisation of monoenes have shown the effective nature as catalysts of $NiHCl[P(Me_2CH)_3]_2$ [401], $Ni(C_2H_4)[P(Me_2CH)_3]_2$ [402], $Ni[P(OPh)_3]_4$ [403] and $Ni(acac)_2$ [404], all in the presence of Lewis acids. Mixtures of nickel δ-hydroxyquinolinate with di-9-fluorenylphenylphosphine cyclooligomerised *trans*-piperylene [405]. Norbornadienes, together with Ni or Pd complexes and amine in the presence or absence of protic acids, gave (123) and (124) respectively. With [Pd(maleic anhydride)$(PPh_3)_2$] the sole product produced under the above conditions was (125) [406]. The oligomerisation of butadiene with atoms of Ti, V, Cr, Mn, Fe, Co and Ni and the cocatalyst $[Et_2AlCl]_2$ has been studied [407]. The efficiency of butadiene oligomerisation with $MHX(PR_3)_2$ (M=Ni, Pd) depends upon both the nature of X and the solvent. The cationic hydrides



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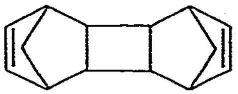

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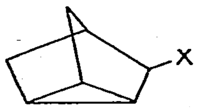
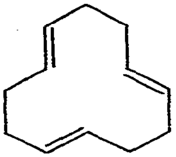


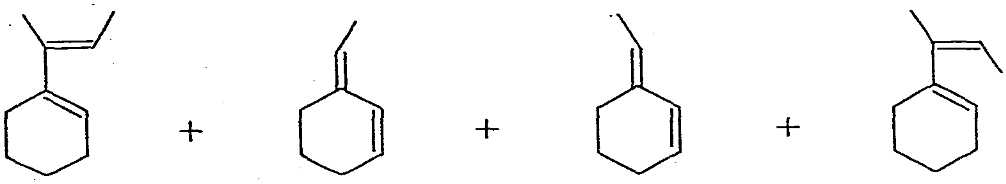
(125)

[PdH(PR$_3$)DPE]PF$_6$ (R = cyclohexyl, Pr^i) were characterised in this study [408]. Catalyst systems containing Ni(acac)$_2$ and a heterocycle were found to effect nearly quantitative conversions of butadiene into trans-1-trans-5- trans-9-, cis-1- trans-5- trans-9-, and cis-1- cis-5- trans-9-cyclododecatriene [409]. The compound (126) was the major product of



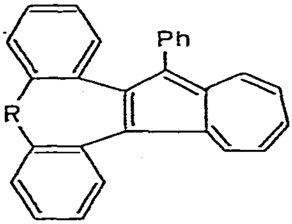
(126)

reactions of butadiene with aluminum alkyls and (δ-quinolyloxy)nickel [410], whereas Pd products and organic acids dimerise butadiene to 1,3,7-octatriene [411]. Octatrienes or dodecatetraenes were the major products, depending upon reaction conditions, of butadiene oligomerisations with Ni(acac)$_2$PR$_3$ (R = NMe$_2$, Bu, Ph), BuLi and R^{1}R^{2}NH$_2$ (R^1=Et, Ph, R^2 = Me, Et, piperidine, morpholine) [412]. Telomerisation of butadiene occurs in methanol with Ziegler-Natta type systems [413] or Ni and Pd salts-phosphine mixtures [414] giving methoxybutenes, methoxyoctadienes and 1,3,7-octatriene. Diallylplatinum halides and (π-C$_3$H$_5$)$_2$M (M = Ni, Pd, Pt) catalyse the telomerisation of butadiene with diethylamine to give Et$_2$N-(C$_4$H$_6$)$_n$-H (n = 3, 50%; n = 4,40%) [415]. An increase in catalytic activity and selectivity were observed when amines were introduced into isoprene dimerisation reactions catalysed



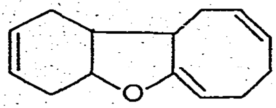
(Scheme 22)

by $NiCl_2(PPh_3)_2$-$NaBH_4$. The yield of linear dimers was ~ 60% with n-propylamine and only 3% with t-butylamine [416]. With nickel naphthenate and isoprene magnesium, using phosphites as donors, cyclic dimeric isoprene products were obtained [417]. The compounds in scheme 22 were formed from 4-vinylcyclohexene and ethylene with $NiCl_2(PBu_3)_2$ and $AlEt_3$ or Et_2AlBr [418]. In codimerisation of ethylene or propylene with styrene by the 3-component catalyst, Pd complex, Lewis acid and $P(OR)_3$, a mechanism involving the formation of a catalytically active Pd-H species was proposed [419]. Linear pentenes constituted $\leqslant$ 77% of the C_5 fraction obtained from codimerising ethylene and propylene with $Ni(acac)_2$ and $(Me_2CH)_2AlCl$. Introducing tertiary phosphines and phosphites into the system increased the content of methylenebutenes to $\leqslant$ 92% of the total yield [420]. A catalytic amount of water enhanced the conversion of butadiene and ethylene to hexa- and pentadienes with $Ni(aryl)X(PPh_3)_2$ (X=halide) and BF_3 [421]. This latter catalyst system effected the selective conversion of styrene and ethylene to 3-phenyl-1-butene [422]. A series of nickel catalysts was used to transform various acetylenes into linear dimers [423 ,424], aromatic trimers [425,426], and cyclooctatetraenes [427,428]. The reaction of o-$PhC{\equiv}CC_6H_4SiMe_2C_6H_4C{\equiv}CPh$-o with $PdCl_2$ gave (127) (R = $SiMe_2$) [429],



(127)

and $(2\text{-}PhC{\equiv}CC_6H_4)_2SO$ with $PdCl_2(PhCN)_2$ produced (127) (R = SO) [430]. 2-Vinylfuran and methylsorbate gave (128) [431] and a mixture of (129) and (130) [432] with butadiene respectively, using $Ni(acac)_2$, PPh_3 and Et_3Al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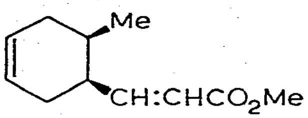

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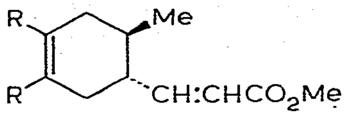

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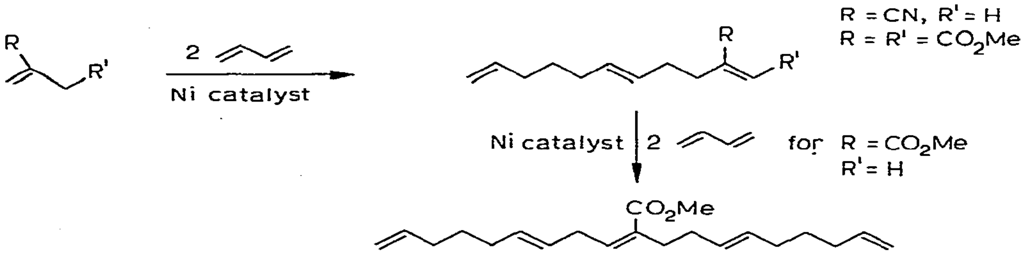
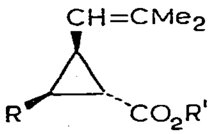
as catalysts. Cycloalkadienes and ethylene with Ni complexes formed vinylcycloalkenes [433]. Products characterised from the reactions of acrylic acid derivatives with butadiene are given in scheme 23 [434].



(Scheme 23)

3,3-Dimethylcyclopropene reacted with *trans*-$RCH{=}CHCO_2R^1$ ($R = CO_2R^1$), *cis*-$MeO_2CCH{=}CHCO_2R^1$ and $CH_2{=}CHCO_2R^1$ in the presence of $Ni(COD)_2$ to give 50–75% (131) (R^1=Me, Et, Bu, $R = CO_2R^1$), 94% (132) ($R = CO_2R^1$; R^1 = Me) and 50% (132) (R = H, R^1 = Me) along with 50% (133) respectively [435].



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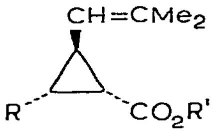

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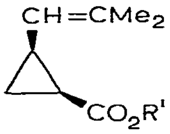

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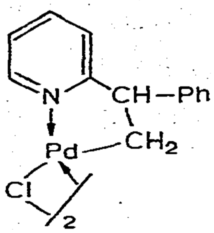
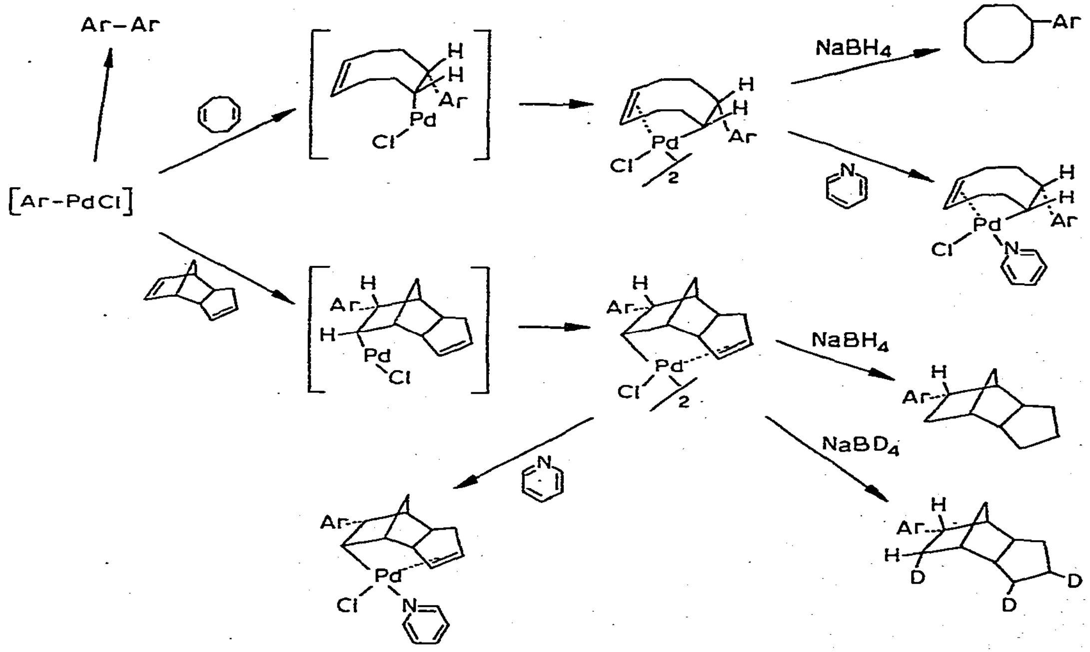
Alkylation reactions with organoderivatives of copper and nickel have been reviewed [436]. Grignard reagents, activated by Ni(II) complexes, activate Ge–H bonds to alkyl or aryl substitution reactions [437]. The



(134)

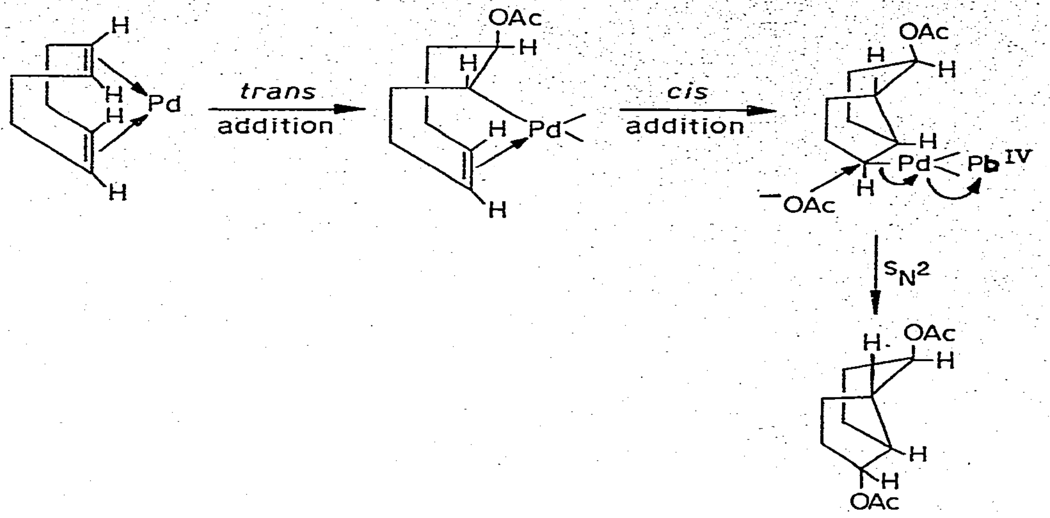
complex di-μ-chloro-bis[2-phenyl-2-(α-pyridyl)ethyl]dipalladium(II) (134) was isolated from a reaction mixture containing Li_2PdCl_4, 2-vinylpy and PhHgCl, and characterised crystallographically [438]. [ArPdCl] reactions with COD and *endo*-dicyclopentadiene have been studied (scheme 24) [439]. Treatment of a series of norbornenes [440] and 1,2-dihydronaphthalene [441] with [PhPdCl] effected PhPd addition across the olefinic bonds.



Ar = phenyl, *p*-tolyl, *p*-anisyl

(Scheme 24)

The effect of steric influence of the o-alkyl substituents of styrene on the aromatic substitution reactions has been investigated [442]. The vinyl esters $R^2CH(R^1NH)COOCH{=}CH_2$ were prepared by an exchange reaction with vinyl acetate using Na_2PdCl_4 as catalyst [443]. Palladium acetate and PPh_3 catalyse the coupling of aryl and vinyl halides with olefins in which the vinylic hydrogen of the olefin is replaced by the organic group of the halide e.g. $Me_2C{=}CHBr + CH_2{=}CHCO_2Me \longrightarrow Me_2C{=}CH{-}CH{=}CHCO_2Me$ [444]. $NiX_2(PR_3)_2$ complexes exhibit high activity for selective cross-coupling reactions of Grignard reagents with aromatic and olefinic halides [445]. Treating 1:1 BuMgBr with $H_2C{=}CHCH_2Cl$ in the presence of nearly equal amounts of Ni-phosphine complexes gave 56-61% octane and 40-59% 1,5-hexadiene, which is in marked contrast to 70% propylene and 71% butenes obtained with metal chlorides [446]. Amine complexes of Pd(II) effect a predominantly meta-directing acetoxylation with potassium peroxydisulphate in glacial AcOH [447]. Addition of olefins to a Pd-sulphone produced Pd metal and the corresponding oxidised product e.g. $[CODPdCl(CH_2SO_2Ph)]+R^1CH{=}CR^2R^3 \longrightarrow PhSO_2CH_2CR^1{=}CR^2R^3+Pd(0) + HCl$ [448]. The structure of the product di-endo-2,6-diacetoxy-cis-bicyclo[3.3.0]octane, obtained from reactions of COD, $PdCl_2$, $Pb(OAc)_4$ and AcOH, was elucidated crystallographically. A mechanism for the reaction was proposed [449] (scheme 25). The reactions of isobutene, methylenecyclopentane, methylene cyclohexane and methylene cycloheptane with $Pd(OAc)_2$ were studied in AcOH at 30-80°. Two types of oxidation were identified, acetoxylation to allylic acetates (methylene cycloheptane) and oxidative coupling to dimers (isobutene and methylenecyclohexane). A mechanistic study indicated that the former was produced by thermal decomposition of the initially formed π-allylic complex. The latter process was presumed to proceed via an insertion of the olefin into the Pd-C bond in the acetoxypalladate adduct followed by the elimination of AcOH and $Pd(OAc)_2$[450]. The stereochemistry of

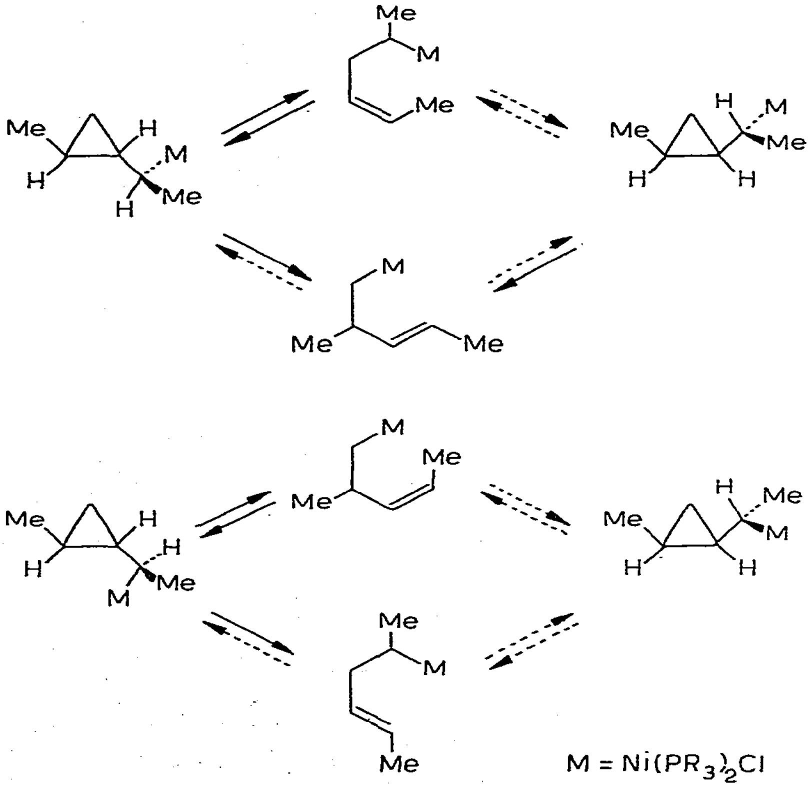


(Scheme 25)

nucleophilic attack on olefins coordinated to Pd(II) and Pt(II) by OH^- proceeds, where possible, by prior coordination to the metal [451]. The hitherto unknown E,Z-$PhCH{=}C(CO_2H)C(CO_2H){=}CHPh$ and the Z,Z-isomer were prepared in 92% yield by the oxidative coupling of trans-$PhCH{=}C(CO_2H)HgCl$ with Li_2PdCl_4-$CuCl_2$ [452]. $Pd(PPh_3)_4$ was found to be the best catalyst for the stereoselective conversion of bis(propenyl)mercury into 2,4-hexadienes [453]. Addition of Me_3Al and $LiAlMe_4$ to ketones [454,455] and nitriles [456] occurs readily using $Ni(acac)_2$ as catalyst. The mechanism was suggested to proceed via an oxidative addition of Me_3Al to a zerovalent Ni(0) species. The formation of cinnamonitrile from acetylenes and $Ni_2(CN)_2(DPB)_3$ is presumed to proceed via a cyanovinyl intermediate which gives the required product on protonation [457]. m-$MeC_6H_4NiCl(PPh_3)_2$ and p-$RC_6H_4NiCl[(p\text{-}R^1C_6H_4)_3P]_2$ ($R = Me, Cl, R^1 = H; R = H, R^1 = Me$) decompose quantitatively in toluene at 90° to give three different diaryls. To explain this, an aryl transfer from phosphine to Ni is proposed to occur via a binuclear Cl-bridged Ni(I) complex [458]. The mechanism of the Ni-catalysed synthesis of phosphonium salts from aryl halides and PPh_3

is reported. The formation of phosphonium salts occurs by the oxidative addition reaction of $Ni(PPh_3)_3$ with the aryl halides and reaction of the coordinated aryl groups with PPh_3 e.g. $Ni(PPh_3)_3 + ArX \longrightarrow NiAr(X)(PPh_3)_2 + PPh_3 \longrightarrow ArPPh_2X + Ni(PPh_3)_2 \xrightarrow{PPh_3} Ni(PPh_3)_3$ [459].

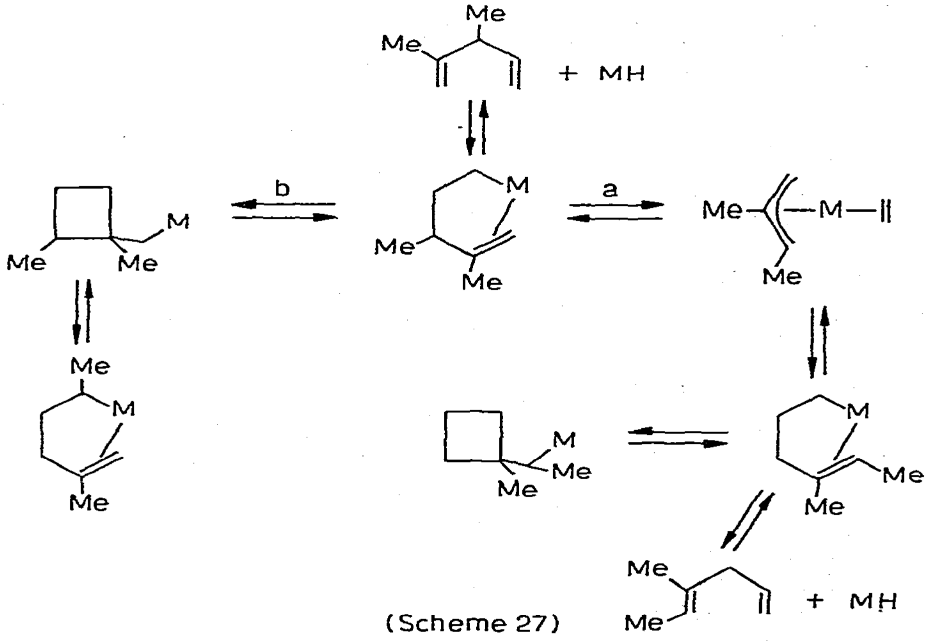
Two types of skeletal rearrangements of 1,4-dienes occur with $NiX_2(PR_3)_2$ and $(Me_2CHCH_2)_2AlCl$, namely (i) that in which the isoprenoid C skeleton is generated, as exemplified by the 1,4-pentadiene isomerisation to 2-methyl-1,3-butadiene and (ii) a rearrangement exemplified by the 3-methyl-1,4-pentadiene conversion to 1,4-hexadiene. The competing reaction in each case is the positional isomerisation of the terminal double bonds in the 1,4-diene reactant to afford conjugated diene products



M = $Ni(PR_3)_2Cl$

(Scheme 26)

of the same C skeleton. Investigations into these reactions are reported [460-463], and mechanisms for routes (i) and (ii) have been investigated [462-463]. For (i) the results were interpreted in terms of the intervention of cyclopropylcarbinylnickel derivatives (scheme 26) and the stereochemistry of each intermediate was discussed [462]. For (ii) a diene rearrangement mechanism is proposed which involves a C-Ni β-elimination reaction of an alkenylnickel intermediate and in which route (a) is favoured in scheme 27 [463]. The rate law for the $PdCl_2(PhCN)_2$ catalysed isomerisation of quadricyclane was second order [464].

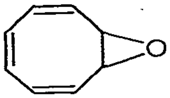


(Scheme 27)

The activity of the complexes $PdX_2(nitrile)_2$ in the isomerisations of olefins decreases in the order PhCN>MeCN for X = Cl, Br. The ratio of cis-2-olefin to trans-2-olefin decreased in the order Cl>Br>I [465]. Double bond migration in CH_2=CHCHMeEt catalysed by $Ni\{P(OEt)_2Ph\}_4$ and $4\text{-}MeC_6H_4SO_3H$ gave 99% of a 2:3 mixture of cis- and trans-MeCH=CMeEt [466].

Alcohols in the presence of π-palladium chlorides isomerised 1-heptene selectively to trans-products [467]. The preferential formation of trans-pent-2-ene from pent-1-ene and cis-pent-2-ene in non-protic solvents with $PdCl_2(PhCN)_2$ or $Fe_3(CO)_{12}$ was attributed to an intramolecular hydrogen transfer mechanism [468].

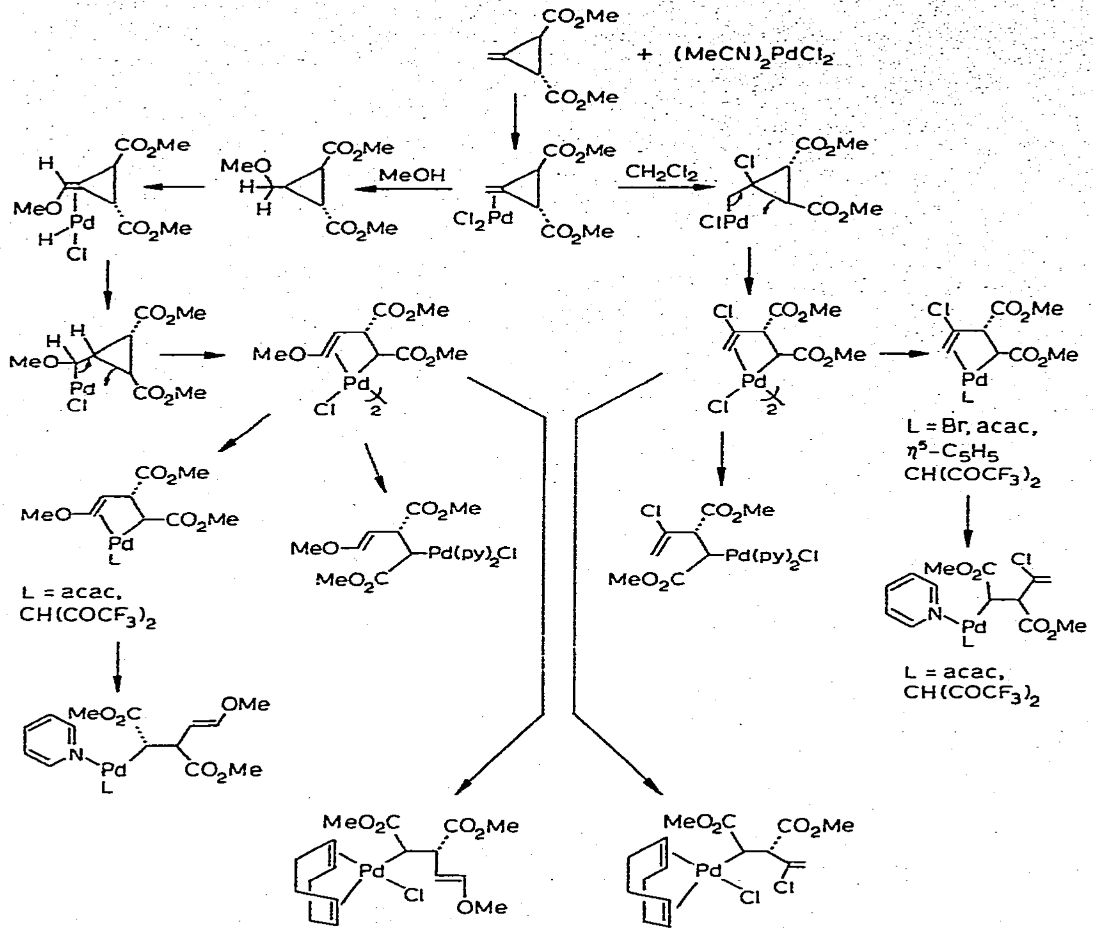
Carbonium ion formation in the $PdCl_2$-$CuCl_2$ promoted rearrangements of bicyclic olefins occurs less in the $CuCl_2$-catalysed reaction [469]. trans-Stilbene oxide is converted by Pd and Pt complexes to small amounts of $PhCOCH_2Ph$, Ph_2CH_2 and cis-stilbene oxide [470]. The rearrangements



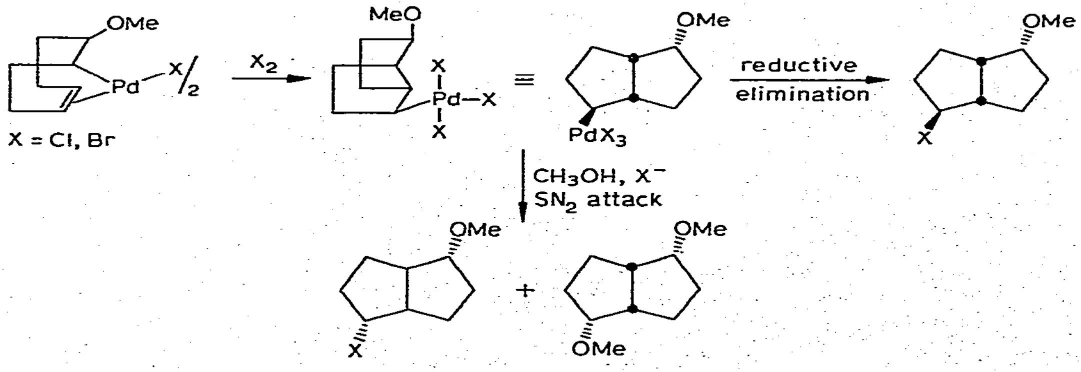
(135)

of (135) to aldehydes was carried out in the presence of complexes of Cu, Ag, Pd and Pt. The cycloheptatrienealdehyde formed was stabilised by copper salts [471]. $Me_2C{=}CH(CH_2)_2CHMeCH{=}CH_2$ with $PdCl_2$ and $CuCl_2$ in DMF, or $PdCl_2$ in aq. acetone, formed $Me_2C{=}CH(CH_2)_2$-CHMeCOMe, α-terpineol and bis[chloro(2,4-η-2,6-dimethyloct-2-ene)palladium(II)] [472]. The reaction of cis- and trans-isomers of Feist's acid dimethylester with a series of metal olefin compounds has been studied. A series of ring opened species was obtained from reactions of $PdCl_2(MeCN)_2$ and $[Pd(C_2H_4)L_2]$ [473] (scheme 28). Halogenation of some enyl Pd(II) complexes proceeded with predominant retention of configuration at the carbon bearing Pd but with overall inversion of configuration in the presence of halide ion. The results were interpreted in terms of an oxidative addition-reductive elimination mechanism [474] (scheme 29).

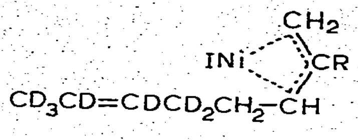
The addition of h^3-perdeuterocrotylnickel iodide to 2-methyl-and 2-isopropyl-1,3-butadiene gave the anti-isomer (136) (R = Me, Me_2CH) as the



(Scheme 28)



(Scheme 29)



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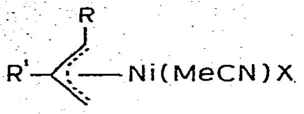
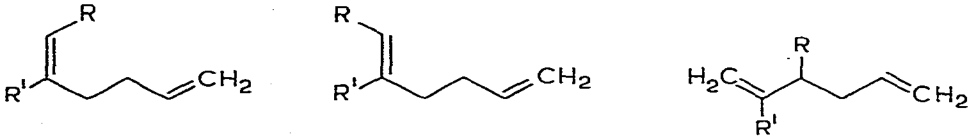


R = R' = H, X = Br, I;
R = CO_2Me, R' = H, Me, X = Br

(137)

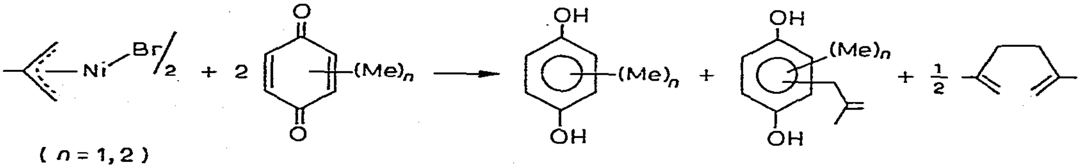
product of kinetic control. Subsequent rearrangement to the syn-isomer and to the h^1-complex occurred [475]. The allylnickel complex (137) coupled with CH_2=$CHCH_2Br$ or MeO_2CCH=$CHCH_2Br$ to give the products in scheme 30. The synthesis of geranyl acetate and methylfarnesoates via allylnickel



R = R' = H, X = Br, iodo; R = CO_2Me, R' = H, Me, X = Br

(Scheme 30)

species was also reported [476]. When the reaction of stoichiometry given in scheme 31 is run under conditions for maximum yields, all the

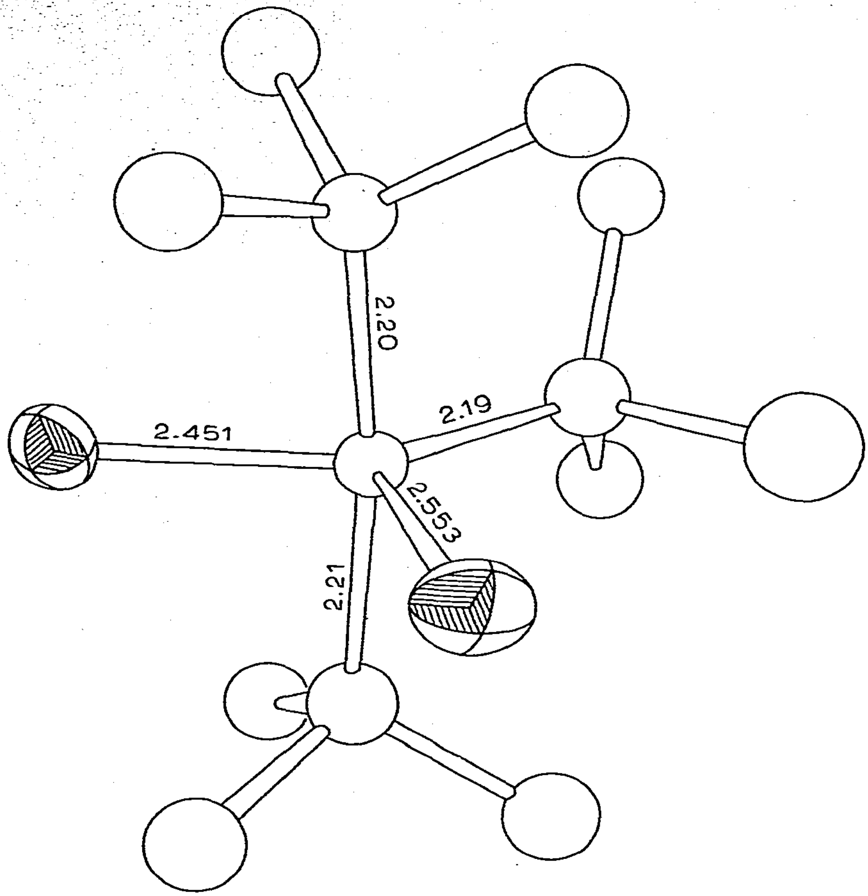


(Scheme 31)

quinones are obtained in their reduced state. The site of alkylation corresponds to the noncarbonyl ring site of highest spin density, indicating that electron transfer processes are involved prior to coordination to the nickel of what would be a reduced quinone species [477]. The activity of π-allylpalladium halides in exchange reactions with dienes decreases in the order $ClCH$=$CHCH_2$>CH_2=$CHCH_2$>$MeCH$=$CHCH_2$>CH_2=$CMeCH_2$ for the complex, decreases in the order butadiene>isoprene>chloroprene>CH_2=CMeCMe=CH_2 for the diene, and increases in the order Me_2SO>$PhNO_2$>$CHCl_3$>PhH for the solvent [478]. The different products obtained in the allyl bromide-crotyl chloride reaction with Grignards and π-allyls of Ni, Co and Fe were attributed to increased lability for exchange of the π-crotyl metal compounds [479]. π-Allyl intermediates are proposed in the nickel catalysed amination of 1,3-dienes and the different reactivities observed were discussed on the basis of the stabilities of the π-allyl complexes [480].

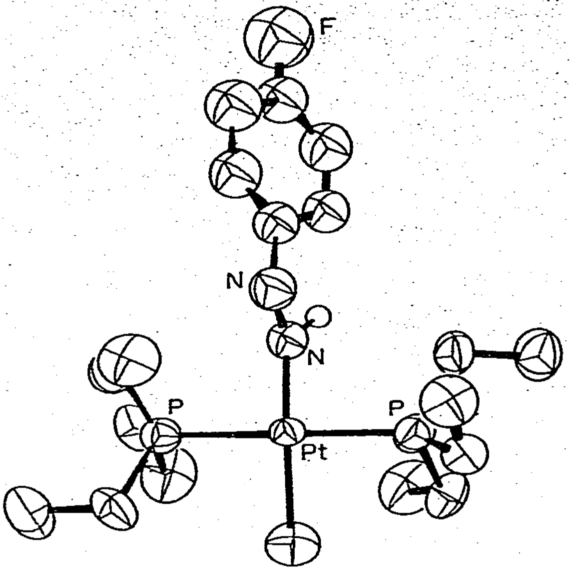
XV Complexes and reactions of general interest

The molecular structures of Ni, Pd and Pt complexes by X-ray diffraction have been reviewed [481]. Some crystal structures of general interest that have appeared this year are; (i) MX_2L_2 (X = Cl, L = $Ph_2PCH_2CH_2P(CF_3)_2$, M = cis-Pd [482]; X = S-bonded SCN, L = $P(OPh)_3$, M = trans-Pd [483]; X = I, L = $P(C_6H_{11})_3$, M = trans-Pt [484]; X = Cl, L = PPh_3, M = cis-Pt, in which distinct solvent adducts occurred and $PtCl(CCl_3)(PPh_3)_2$ was reformulated as $[PtCl_2(PPh_3)_2]$ $(solvent)_x$ [485]; X_2=(NCS)(SCN), L = P-bonded $Ph_2PC{\equiv}CR$ ($R{=}Bu^t$), M = cis-Pt, prepared from MeCN solutions of X=NCS at 0°, together with other R = Et, Ph, Pr^i products [486]; X = Cl, ML_2 = (–)-2,3,-o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butanenickel(II) [487]), (ii) $PdBr_2L_3$ (L = 2-phenylisophosphindoline, orange racemate form and optically resolved red form in which Pd-Br is 2.92 (red) Å and 3.02 (orange) Å and the differences are attributed to differences in molecular environment [488]; L = 5-alkyl-5H-dibenzophosphole, alkyl = methyl, ethyl [489]) (iii) $NiBr_2(PMe_3)_3$ (138) [490] (iv) trans-chlorobis(triethylphosphine)-(p-fluorophenyldiazene)platinum(II) perchlorate (139), formed by protonation of a Pt-aryldiazonium complex [491] (v) $NiIL_3$ (L_3 = 1,1,1-tris-(diphenylphosphinomethyl)ethane), confirming the monovalent nature of the nickel



(138)

[492], (vi) $(Et_4N)_2$ $[Pt_2(NO)_2Cl_6]$, (140) with the Pt atoms in square planar, and octahedral environments, respectively, bridged by Cl atoms and an NO group (N–O{bridging} 1.27 Å, N–O {terminal} 1.05 Å) [493] (vii) PdL_2 (L = $P(C_6H_{11})_3$, $(Me_3C)_2PhP$) (141) [494], together with their preparations and the formation of $PdO_2\{PPh(CMe_3)_2\}_2$ [495]. A series of fluorine exchange reactions in $Ni(PF_3)_4$ with $(Me_3Si)_2NNa$, $HNRR^1$ (R = H or C_{1-5} alkyl, R^1 = C_{1-5} alkyl) and RONa (R=Et, Pr) have been reported [496-498]. Complexes synthesised during the year were (142) [499], $MXYLL^1$ (M = Pd, Pt, $L=L^1=PPh_3$, XY = $(ZC_6H_4R)_2$ R = O,S, Z = NH_2, NO_2, H [500, 501]; M = Pd, Pt, LL^1 = $Ph_2Sb(CH_2)_3SbPh_2$,



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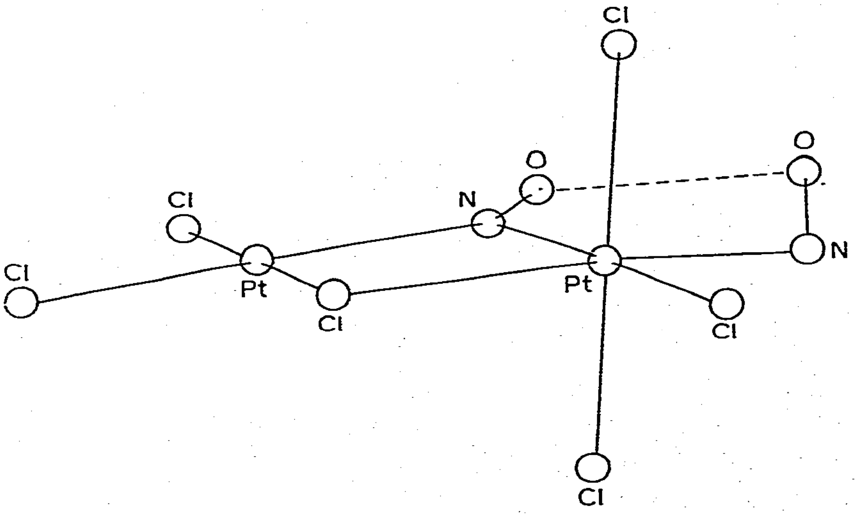
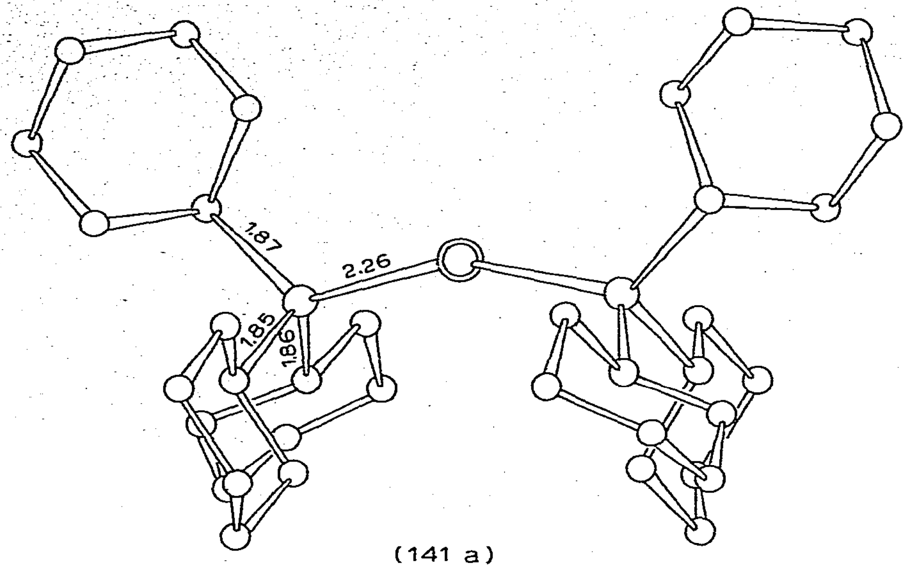
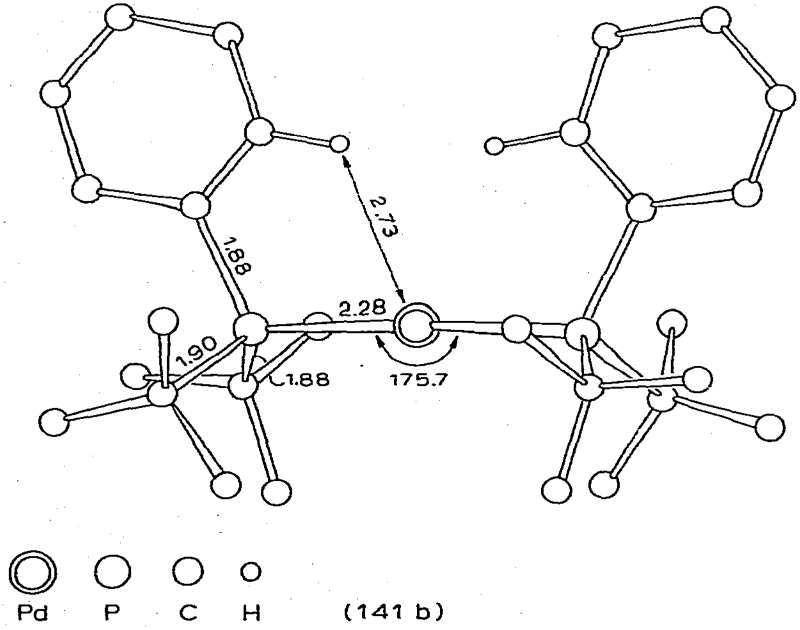


(140)

X=Y=anionic ligand [502]; M=Pd, X=Y=Cl, L=L^1=PPhRR^1 {R=R^1=Me, Et, Pr; R = Me R^1 = Et} [503]; M = Pd, X=Y=L=L^1 = NCNR{R = H, Ph}; M = Pd, X=Y=NHCN, L = L^1 = PPh$_3$; [504] M = Pt, X=Y=Cl, L = N(R)=NZR^1 {Z = CH, N, R = R^1 = aryl, alkyl, L^1 =

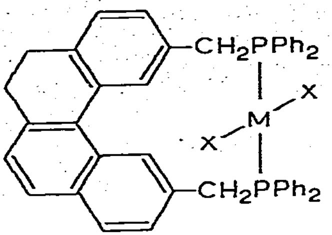


(141 a)



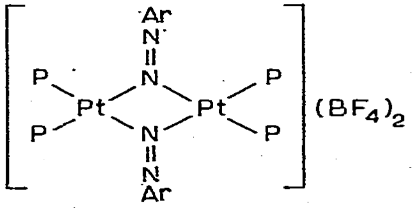
(141 b)

C_2H_4, $AsEt_3$, PEt_3} [505]; $N(CMe_3){=}SNCMe_3$ [506]; M = Pd, Pt, X=Y=Cl, $L{=}L^1{=}P(OR)Ph_2$; M = Pt, X=Y=Br, $L{=}L^1{=}P(OR)_2Ph$(R=Me, Et) [507]; M = Pd, Pt,



(142)

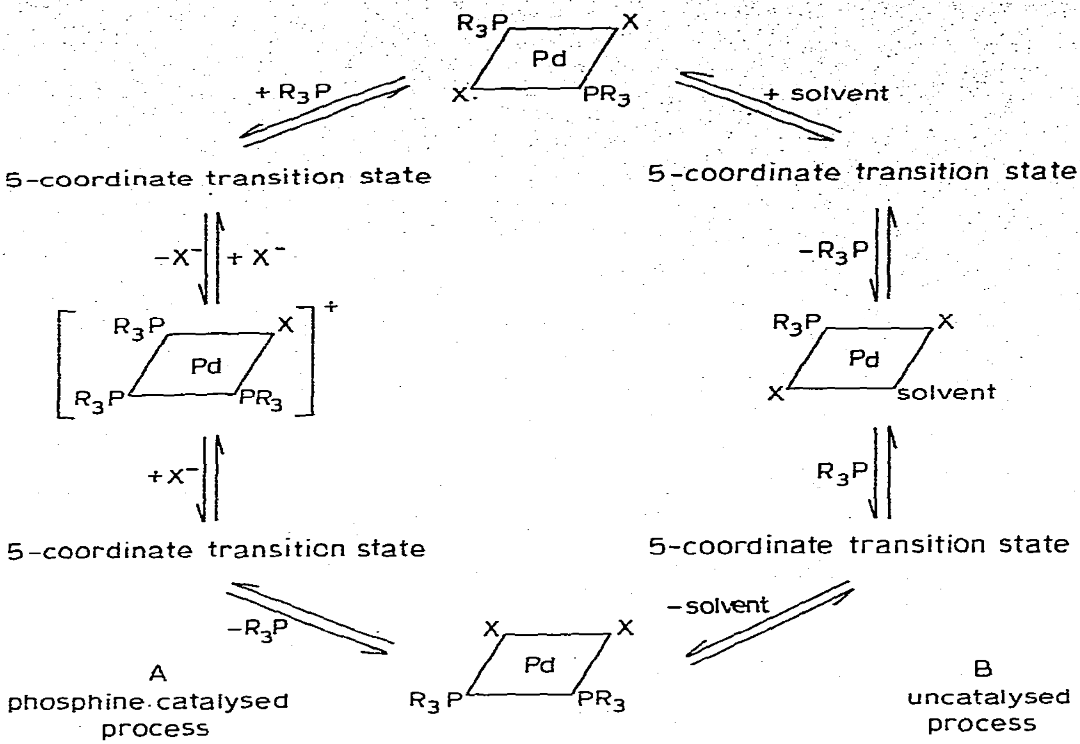
Rh, X=Y=halide, LL^1=*o*-phenylenebis(diphenylarsine), (*o*-diphenylarsinophenyl) diphenylphosphine [508]; M=Pd, Pt, $L=L^1= PR_3$ (R=Et, Ph), $X=Y=SO_2(OMe)$; $X=CO_2Me$, $Y=SO_2(OMe)$, $L=L^1=PPh_3$; $X=Y=S_2CO$, $L=L^1=PPh_3$ [509]); a range of *trans*- and *cis*-$[PtX(SCF_3)(PEt_3)_2]$ compounds in which a definate correlation exists between *cis*- and *trans* influences of the ionic ligand X when long range NMR coupling constants ($^3J_{PtF}$) are used to measure these effects [510]; $NiI_2(AsMe_3)_3$ [511], and five-coordinate complexes of Fe(II), Co(II) and Ni(II), in general, were reviewed [512]; [NiIL]I ($L = PhP\overline{CB_{10}H_{10}C}PPh_2$) [513]; stereospecific syntheses of $[PtClL(PEt_3)_2]^+$ and *cis*-$[PtClX(PEt_3)_2]$ for a range of X and L were developed [514]; $[MCl\{P(OR)_3\}_3]^+$ and $[M\{P(OR)_n Ph_{3-n}\}_4]^+$ (n = 1,2; R = Me, Et) [515,516]; $[DPEPtCl]_2$ from $[Pt(HgSiMe_3)_2(SiMe_3)_2DPE]$ [517]; the species $PdPtCl_4(PBu_3)_2$ was inferred from ^{31}P NMR



(143)

measurements on mixtures of $Pt_2Cl_4(PBu_3)_2$ and $Pd_2Cl_4(PBu_3)_2$ [518]; $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{2+}$; $[NiCl\{oC_6H_4(PMe_2)_2\}]^+$, and a series including $[NiCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{n+}$ (n = 3,4) [519]; (143) [520], $[Cp_2Fe]PdCl_3$ and $[CpFeC_6H_4CH{=}CH_2PdCl_2]_2$ [521]; *trans*-$[Mpy_2\{Co(CO)_3L\}_2]$, M = Pd, Pt [522];

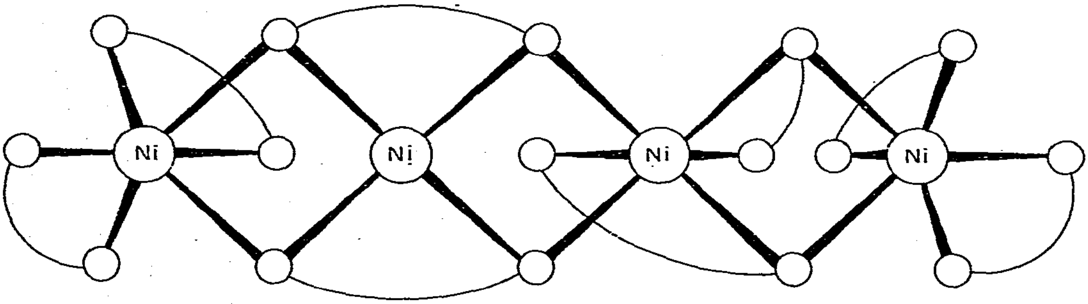
$[Ph_2XCH_2]_2PtCo_2(CO)_7$ (X = P, As) [523]; *trans*-$M^1L_2[Mn(CO)_5]_2$ (M^1 = Pd, Pt, L = py, 3-Mepy, 4-Mepy, 4-Mepy) with linear Mn-M^1-Mn bonds [524]; *trans*-$[Pt(N_2Ar)(PEt_3)_2L]^+$ ($N_2Ar = N_2C_6H_4F$-*m* or *p*, L = NH_3, py, PEt_3, EtNC) and the corresponding aryldiimides and arylhydrazines from protonation reactions and reduction reactions respectively [525]. The S-bonded $\rightarrow$ N-bonded isomerisation in complexes *cis*-$[Pt(SCN)_2L_2]$ (L = PPh_3, $AsPh_3$) have been studied [526]. A series of investigations into the intermediates formed in *cis*-*trans*-isomerisations of square-planar palladium and platinum complexes has appeared [527-530]. Equilibrium thermodynamics for the *cis*-*trans*-isomerisation of $Pd(N_3)_2\{P(CH_2C_6H_5)_{3-n}Ph_n\}_2$ (n = 1,2) have been obtained. With the N_3^- ion in $Pd(N_3)_2\{P(CH_2C_6H_5)_3\}_2$ the complex is so sterically hindered that only the *trans*-isomer exists [527]. Isomerisation energetics (*cis*-*trans* and linkage) and mechanisms for the palladium(II) phosphine complex containing trifluoromethyltetrazoles have been studied by ^1H and ^{19}F NMR. A unified mechanism for isomerisations of square-planar complexes was proposed and discussed in terms of orbital symmetry selection rules [528] (scheme 32). *cis*-$[PtCl_2(PEt_3)_2]$ isomerised to the *trans*-isomer in the presence of PPh_3 with no phosphine mixing, and $[PtCl(PEt_3)_3]^+$ did not react with Cl^-, which was said to be evidence for a mechanism involving a five-coordinate intermediate rather than one involving a consecutive displacement step [529]. ^1H NMR data on these catalysed isomerisations suggested that no unique mechanism is in operation but rather 3 different and separate pathways whose importance is a function of, and varies with, metal, solvent, ligand catalyst used and anion [530]. Helium I photoelectron spectra of $M(PF_3)_4$ (M = Ni, Pd, Pt) were measured and from ionisation potential data the evidence pointed to strongest bonding with Pt. Charge shifts from σ-to π-bonding cancel each other in these molecules [531]. Vibrational spectra of $[M_2X_6]^{2-}$ (M=Pd, Pt, X = Cl, Br, I) [532], $[MX_4]^{2-}$ (M = Pd, X = Cl; M = Pt, X = Cl, Br) [533], *cis*- and *trans*-MX_2L_2 (M = Ni, Pd; X = Cl, Br, I; L = ter-



(Scheme 32)

tiary phosphine) [534] and $NiL(CO)_3$ were recorded and relative assignments for ligand stretching frequencies made [535]. The synthesis, reactivity and ^{19}F NMR of the dimers $[M_2(SCF_3)_2(PR_3)_4]X_2$ (M = Pd, Pt, R = Et, Ph; $X = BF_4$, ClO_4) is reported. Monomeric products, from bridge-splitting reactions were obtained [536]. Vibrational spectra and NMR parameters of the Pt(IV) complexes $[PtX_4L_2]$ and $[PtX_5L]^-$ (X = Cl, Br, I; L = NMe_3, PMe_3, $AsMe_3$, SMe_2) were measured [537,538]. The signs of the $^2J_{P-P}$ couplings have been determined for a series of Pd and Pt alkylphosphite or phosphine compounds [539]. ^{19}F NMR spectra have been recorded for 15 different *m*-and *p*-fluorobenzenediazo complexes and the evidence points to ArN_2 being a poorer π-acceptor than NO^+ [540]. $^{1}H-\{^{195}Pt\}$ heteronuclear double resonance is shown to be valuable for identification of species present in

Pt(II) compounds. ^{195}Pt chemical shifts were explained in terms of variations in electronic excitation energies for ligands of approximately the same size. Bulky ligand atoms however produce large shifts to high field which tend to dominate [541]. Physical studies on NiL_4 have been completed. Electronic factors strongly influence the rate of dissociation, and phosphines dissociate more rapidly than phosphites. Steric effects are largely responsible for variations in equilibrium constants [542]. The series of complexes $[ML_5]^{n+}$ (M = Ni, Pd, Pt; n = 2; L = phosphite) have been synthesised [543] and their fluxional behaviour in solution studied [544]. Detailed line shape analysis and rearrangement barriers were reported [544]. A review on transition metal dinitrogen complexes, their synthesis, properties and significance, has appeared [545]. The dinitrogen adducts MN_2L_n (M = Co, Ni, Fe; L = triarylphosphine, -arsine, -stibine, n = 2,3 [546]; M = Ni, L = PEt_3 n = 3 [547]) have been synthesised by reduction of the corresponding acac complexes or by direct reaction with the metal(0) species, respectively. The reaction of $[Ni(acac)_2]_3$ with CS_2 gave $[Ni(acac)_2]_4$ (144) [548]. M.O. calculations were carried out to obtain a complete and non-empirical description of the M-O_2 and M-P bondings in metal-dioxygen compounds [549,550].



(144)

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