Nickel, Palladium and Platinum

Annual Survey covering the Year 1973.

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Contents

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ABBREVIATIONS

Bipy = 2,2'-bipyridyl
Acac = acetylacetone
DPE = 1,2-bis(diphenylphosphino)ethane
Phen = o-phenanthroline
Py = Pyridine
DIARS = 1,2-bis(methylphenylarsino)ethane
mad = dimethylacetylene dicarboxylate
THF = tetrahydrofuran
en = ethylenediamine
fum = fumaronitrile
man = maleic anhydride
Cp = cyclopentadienyl
DMF = dimethylformamide
COT = cyclooctatetraene
COD = 1,5-cyclooctadiene
Tcne = tetracyanoethylene
HFacac = hexafluoroacetylacetone
DMSO = dimethylsulphoxide
EDTA = ethylenediamine tetra acetic acid
Lut = 3,5-dimethylpyridine
$HB(pz)_3$ = polypyrazolylborate

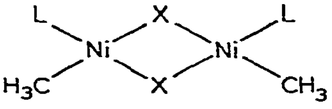
I Metal-carbon σ-complexes.

The crystal structure of $[(Ph_3P)_2Ni\{C(CF_3)_2O\}]$ has been determined. Ni, C and O form a three membered ring, with bond parameters of Ni-C = 1·89 Å, Ni-O = 1·87 Å and C-O = 1·32 Å being observed [1]. The complex $[C_6H_{11}P(CH)CH_3Ni(CO)_3]$ contains a ylide ligand bonded via the secondary carbon atom. No Ni-P interactions were observed and the Ni-C parameter of 2·10 Å was reported [2].

Electron spectroscopy for chemical analysis (ESCA) data have been presented and discussed for 46 nickel compounds including alkyl- and aryl-derivatives. The binding energies were discussed in terms of molecular bonding and structure [3]. The formation of alkoxycarbonyl-, acyl- and alkyl-nickel(II) and palladium(II) complexes by oxidative addition reactions has been described and the thermal decompositions of these species studied [4]. The kinetics of the cleavage of Ni-R bonds of $[NiR_2Bipy]$ (R =Me or Et) in the presence of organoaluminium compounds have shown the reactions to be first order with respect to the concentrations of the alkyl-nickel compounds [5]. Attempts have been made to prepare nickel-benzyl complexes by the reactions of nickel halides, tertiary phosphine nickel halide complexes, $[Ni(COD)_2]$ or $[Ni(PPh_3)_4]$ with various benzylating agents. Although the intermediacy of unstable benzyl complexes was proposed, none could be isolated [6].

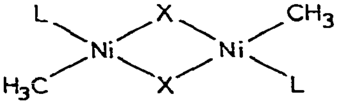
The complexes $[RNi(Acac)(PPh_3)_2]$ (R = Me,Et), made from R_2Al OEt, $[Ni(Acac)_2]$ and PPh_3 exhibited fluxional ^1H NMR behavior [7]. The IR spectra of $[RNiX]_2$ (R = alkyl, X = Br; R = butenyl, X = Cl; R = 2-pentenyl, X = Cl,I) have been interpreted [8].

A series of dimeric methylnickel complexes of type $[NiMe(PMe_3)X]_2$ (X = NH_2,*p*-NHC_6H_4Me,F,OH,OMe,OEt,$OSiMe_3$,OPh,OC_6H_4Me- *p* ,O_2CH,O_2CMe or Cl) has been prepared [9,10]. The positions of the equilibria of *cis* (1) and *trans* (2) isomers were shown by low temperature ^1H NMR studies. Mixed bridge complexes of type $[NiMe(PMe_3)]_2XY$ (X = OMe, Y = OH, OEt,OPh; X = NMe_2, Y = OMe,F,Cl; X = F,Y = OMe, Cl; X = OMe, Y = Cl) only occur in the *cis*-configuration. The new methylnickel complexes $[NiMe_2(PMe_2Ph)_3]$ and $[NiMe(OPh)(PMe_2Ph)_2]$ have been reported [11]. The reactions of carbon monoxide with *trans*-$[NiMe(PMe_3)_2X]$(X = Cl,Br or I) gave quantitative yields of the corresponding acetyl complexes, which showed only a limited tendency to decarbonylate [12].



(1)

L=PMe

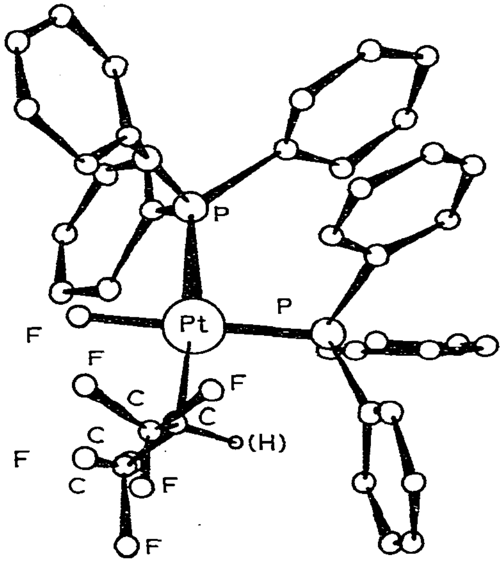


(2)

A systematic ^{13}C NMR study of three series of *trans*-methylplatinum(II) complexes $[PtMe(AsMe_3)_2L]\ PF_6$,$[PtMe(PMe_2Ph)_2L]\ PF_6$ and $[PtMe(PMe_2Ph)_2X]$ (L = neutral ligand; X = anionic ligand) has been made [13]. ^{13}C shieldings and $J(^{13}C-^{195}Pt)$ were reported and compared with data obtained from ^1H

NMR spectra. The data support the rehybridization concept of the NMR *trans* influence. NMR data for the complexes *trans*- $[PtRX(PMe_2Ph)_2]$ and *trans*-$[PtR(PMe_2Ph)_2L]^+$ (R = $-\underset{CF_3}{C}=C{<}^{H}_{OMe}$, L = neutral ligand, X = anionic ligand) showed a linear correlation between both $^3J(Pt{-}C{-}CF_3)$ and $^3J(Pt{-}C{=}C{-}H)$ and $^2J(Pt{-}Me)$ for the corresponding methylplatinum complexes. These results were explained in terms of platinum hybridization in the Pt-C bond dominating the coupling constant [14].

The crystal structure of the complex *cis*-$[PtF\{CH(CF_3)_2\}(PPh_3)_2]$ (3) has been determined. The platinum atom is in a square planar configuration and the Pt-P distance, *trans* to F, of 2.218 Å is significantly shorter than Pt-P *trans* to $CH(CF_3)_2$ (2.310 Å). The Pt-F distance is 2.03 Å [15].

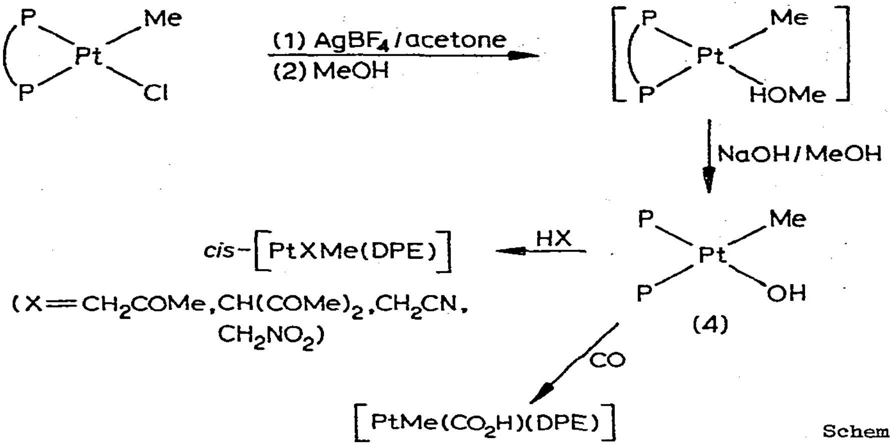


(3)

The preparations of the first benzoyl complexes of palladium $[PdX(COPh)(PPh_3)_2]$ (X = Cl or Br) have been reported from the reaction of $[Pd(PPh_3)_4]$ with the appropriate benzoyl halide. The analogous complexes [PdCl(COPh)L] (L= DPE or Phen) were obtained by ligand exchange [16]. Alkyl and aryl migration from CO to Pt has been found to occur on abstraction of chloride ion with $AgPF_6$ from $[PtCl(RCO)(PPh_3)_2]$ (R = Me, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$ or *p*-$O_2NC_6H_4$) with the formation of

$[PtR(CO)(PPh_3)_2]$ [17]. If the reaction was carried out in acetonitrile, then migration of R was not observed and the complexes $[Pt(RCO)(PPh_3)_2(MeCN)]^+$ were isolated.

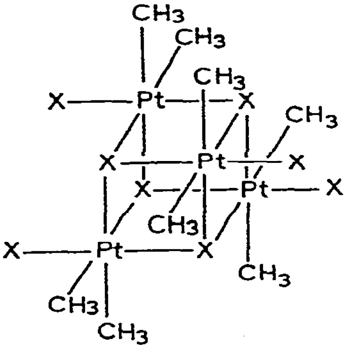
The platinum(II) hydroxo-complex (4) has been prepared and some reactions reported (Scheme1); the similarity of the chemistries of



Scheme 1

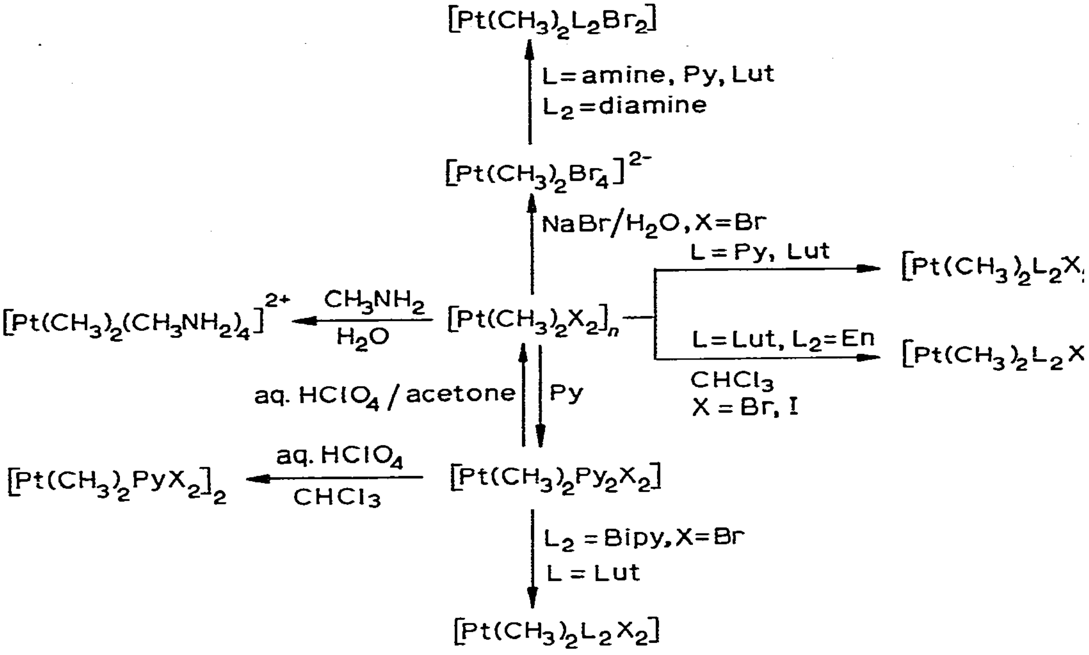
the platinum(II) hydroxo-complex and hydroxo-derivatives of vitamin B12 analogues was noted [18].

The IR spectra in the region 4000-60 cm^{-1} have been recorded for the compounds $[PtMe_2X_2]_n$(X = Cl, Br or I). The spectra are consistent with structure (5) for these compounds which has both bridging and terminal halogens [19]. The reactions of $[PtMe_2X_2]_n$ with neutral and uninegative



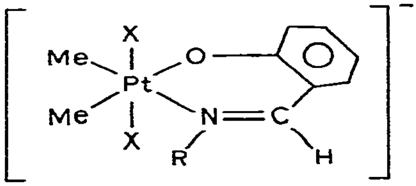
(5)

ligands have been studied (Scheme 2) [19], and also with bidentate N-organosalicylaldimines [20]. The latter ligands afforded anionic dimethylplatinum(IV) Schiff-base chelate complexes of type $[PtMe_2X_2(Sal{=}N{-}R)]^-$ (6) which were isolated as salts of large cations [20].



scheme 2

IR and ^1H NMR data were reported for the complexes $[PtMe_2X_2L_2]$ (L=monodentate or L_2 = bidentate ligand) [19,20]. An improved synthesis for complexes $[PtR_2(COD)]$ has been developed and reactions of these species with halogens, HCl, neutral donor ligands, MeI and CF_3I studied (Scheme 3) [21]. ^1H NMR data and the mechanisms of some of the reactions were discussed. From this, and previous studies, several generalizations



(6)

have emerged concerning methyl- and trifluoromethylplatinum complexes:

a) both Me and CF_3 have a high _trans_-influence,

b) there is a high Pt(6s) orbital contribution in the Pt-C bond,

c) the trifluoromethyl derivatives are much more thermally stable than the methyl analogs,

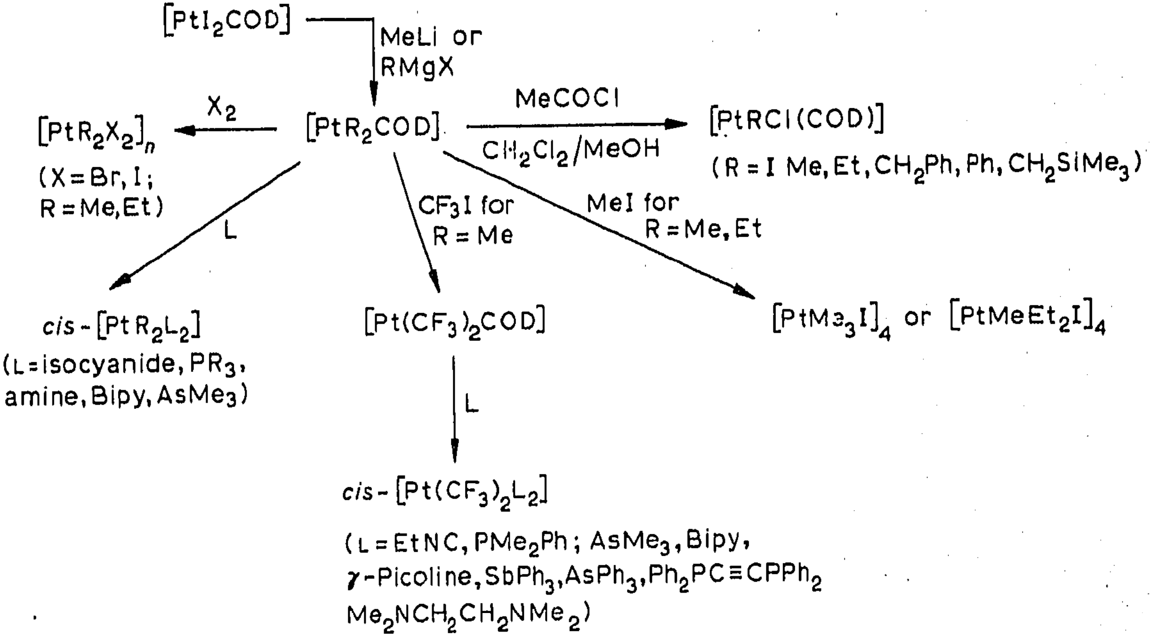
d) Pt-CF_3 complexes are much less nucleophilic than Pt-Me complexes,

e) the Pt-R bond is very covalent and there appears to be no significant π-back bonding from Pt to either CF_3 or CH_3.

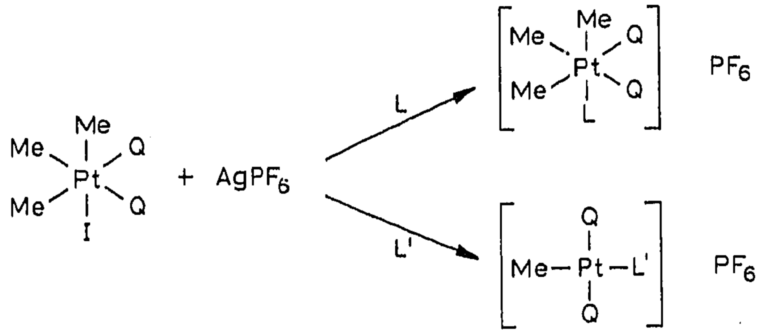
An analysis of the ^1H NMR spectrum of the platinum-bonded methyl group of _cis_-$[PtMe_2(PMe_3)_2]$ has shown that it is of the $[AR_3X_9]_2$ spin type [22] not $[AX_3]_2$ as has been previously proposed. It was also suggested that in the analysis of the spectra for the analogous complexes _cis_-$[PtMe_2L_2]$ (L=PPh_3 or PMe_2Ph), all the phenyl protons must be considered. In another study, the absolute signs of ^3J(P-H) couplings in three methylplatinum(II) complexes have been determined [23].

A series of iodo methylplatinum complexes, $[PtMe_3I]_4$, $[PtMe_3I]_2$, $[Pt_2Me_5I_3]$, $[PtMe_2I_2]$ and $[PtMeI_3]$ has been obtained by the reaction of $(NH_4)_2PtCl_6$ with MeMgI. The thermal stability of the iodo methylplatinums decreases as the methyl groups are replaced by iodine [24]. Trimethylplatinum(IV) cations of type _fac_-$[PtMe_3Q_2L]^+$ (7) (Q = PMe_2Ph,Py or _p_-$CNC_6H_4CH_3$) have been prepared; in some cases however, reductive elimination of ethane occurs (Scheme 4) [25]. IR, Raman and ^1H NMR data were discussed. From reactions of Pt^{IV}-CD_3 complexes, it appeared that the CD_3-Pt bond is more resistant to cleavage than the CH_3-Pt bond [25]. An X-ray structural determination has been carried out on the complex $[PtMe_3$(_rac_-diars)I] (8) [26]. Trimethylplatinum(IV) compounds of type $[PtMe_3L]_2$(L = β-diketone,thio-β-diketone and β-iminoketone) have been prepared and from the ^1H NMR and IR spectra, it was suggested that the β-iminoketones bridge via the γ-carbon atom, as is found for the β-diketone complexes, whereas the thio-β-diketones bridge via sulphur atoms [27].

Carboranyl and _neo_-carboranyl platinum(II) complexes containing a $B_{10}C_2H_{10}R^-$ (R=Me or Ph) ligand bound to platinum by a metal-carbon σ-bond have been prepared (Scheme 5) [28]. The preparation and structure of the complex $[Ni(PPh_3)_2C_2B_{10}H_{10}]$ (9) has been reported [29]. This


[PtI2COD]
MeLi or RMgX
[PtR2COD]
X2
[PtR2X2]n
(X=Br,I; R=Me,Et)
MeCOCl
CH2Cl2/MeOH
[PtRCl(COD)]
(R = I Me, Et, CH2Ph, Ph, CH2SiMe3)
L
cis-[PtR2L2]
(L=isocyanide, PR3, amine, Bipy, AsMe3)
CF3I for R = Me
[Pt(CF3)2COD]
MeI for R = Me, Et
[PtMe3I]4 or [PtMeEt2I]4
L
cis-[Pt(CF3)2L2]
(L = EtNC, PMe2Ph; AsMe3, Bipy, γ-Picoline, SbPh3, AsPh3, Ph2PC≡CPPh2 Me2NCH2CH2NMe2)

(scheme 3)

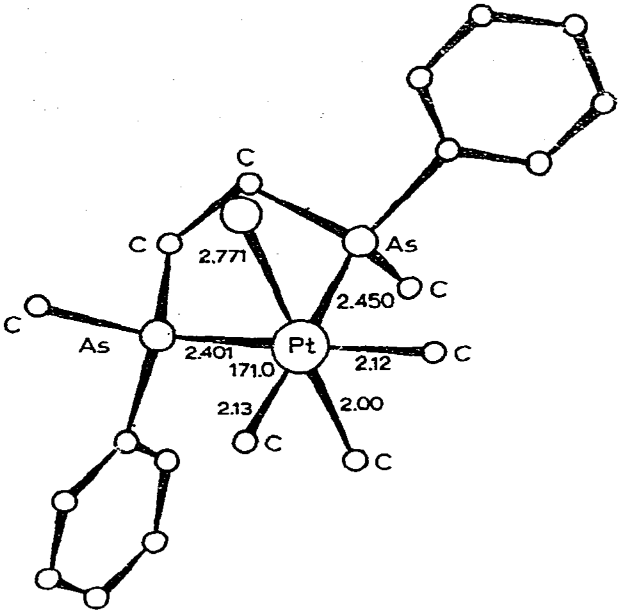


(7)

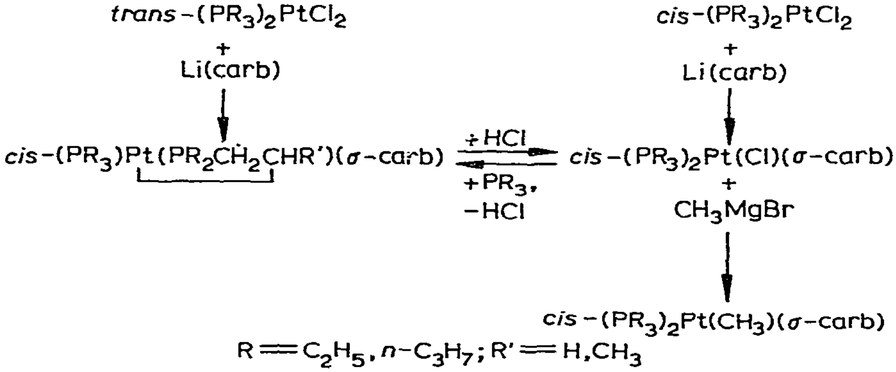
(L = Py, PMe$_2$Ph, P(OMe)$_3$, CNC$_6$H$_4$Me, CNC$_6$H$_4$OMe, CNMe, CNEt, SbMe$_3$)

(L' = Me$_2$CO, MeOH, NCCH=CH$_2$, NCC$_6$H$_4$OMe, SbPh$_3$, PPh$_3$, AsPh$_3$, CO, HC≡CCH$_2$CH$_2$OH)

(scheme 4)



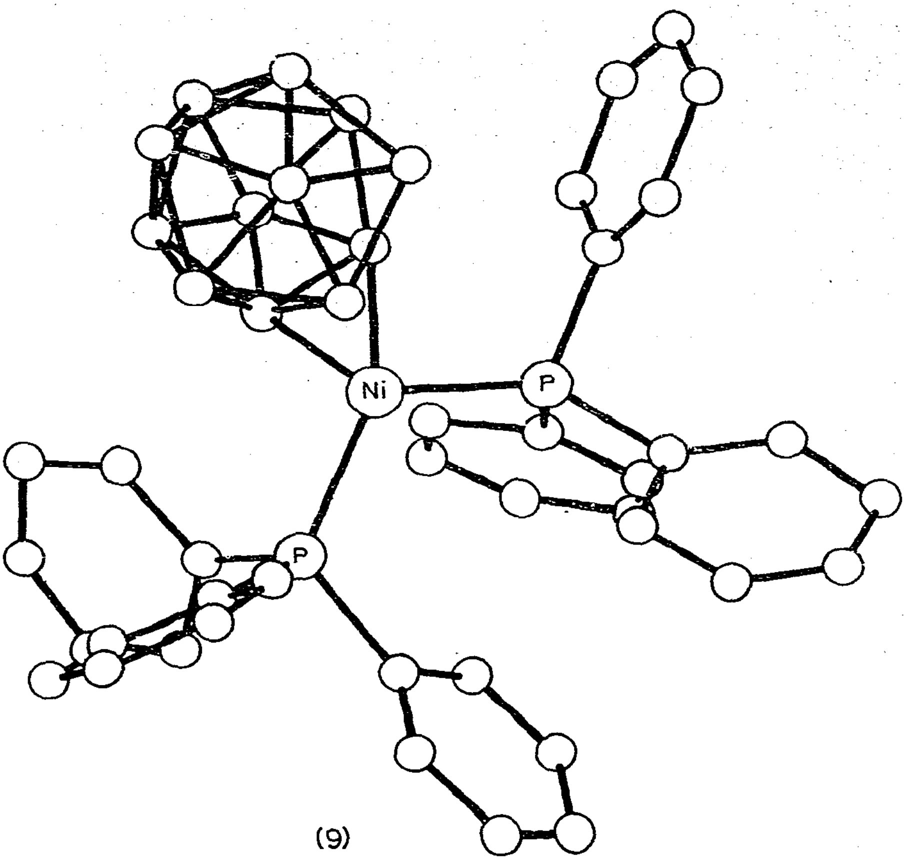
(8)



(scheme 5)

complex contains a chelating o-carboranyl group bonded to nickel by two metal-carbon σ bonds (Ni-C = 2.00 and 1.91Å).

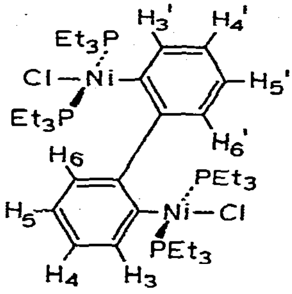
The preparation of the complexes [Ni(o-chlorobenzyl)$_2$L$_2$] (L = PEt$_3$ or P(Bu^n)$_3$) has been reported [30]. The ^{1}H NMR spectrum of the arylnickel(II) complex (10) showed a downfield shift for the protons



(9)

H_6 and H_6' (relative to biphenyl) which was attributed to the short distances of these protons to the nickel atoms; (10) being in a sterically-fixed conformation [31]. The crystal structure of the complex $[Ni(PMePh_2)_2(\sigma\text{-}C_6F_5)Br]$ (11) has been determined. Comparison is made with structures of other pentafluorophenylnickel(II) complexes and it is evident that the Ni-C σ-bond is significantly affected by the ligand *trans* to it (Ni-C in this study is 1.880 Å) [32].

Oxidative additions of chloroacetonitrile [33], $HN = C{=}C(CN)_2$ [34] or $C(CN)_4$ [34] to $[M(PPh_3)_4]$ (M = Pd [33], Pt [34]) gave the complexes $[PdCl(CH_2CN)(PPh_3)_2]$, *trans*-$[PtH\{C(CN)_3\}(PPh_3)_2]$ and *trans*-$[Pt(CN)\{C(CN)_3\}(PPh_3)_2]$ respectively. Ligand exchange reactions of the palladium complex gave the products $[PdX(CH_2CN)L]$ (X = Cl, for; L = DPE, DIARS, PHEN, $Ph_2PCH = CHPPh_2$) [33]. $[MX\{C(CN)_3\}L_2]$ (L = $PR_3\{R = Ph, Bu\}$,



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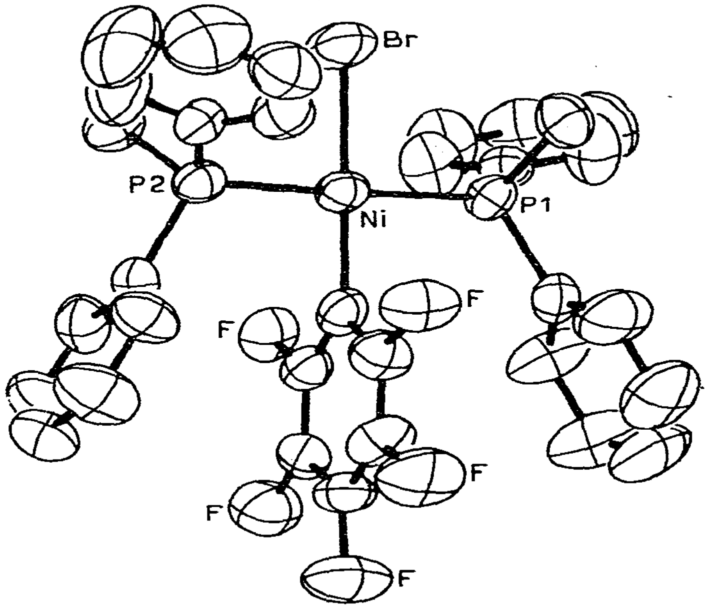

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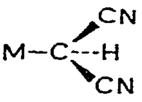
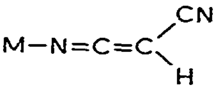


$\mathrm{M{-}C(H)(CN)_2}$

(12)



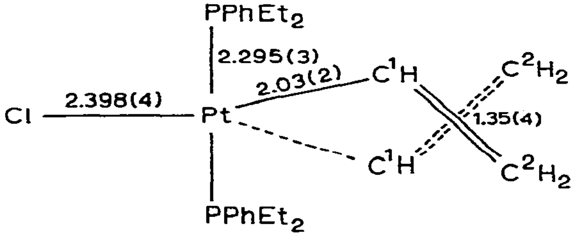
$\mathrm{M{-}N{=}C{=}C(CN)H}$

(13)

AsPh$_3$; M = Pd, Pt; X = Cl, Br, C(CN)$_3$) compounds have been isolated from the reactions of corresponding halo complexes and K[C(CN)$_3$] [34].

Dicyanomethyl complexes have been prepared by the reaction of noble metal halide complexes with sodium dicyanomethanide, whereas the palladium and platinum complexes reported appear to contain the bonding mode (12), the rhodium and iridium complexes are envisaged as (13) [35].

Trialkyltin compounds R'_3SnR (R' = Me or Et; R = $CH{=}CH_2$, $CF{=}CF_2$ or $C{\equiv}CPh$) were found to react by oxidative addition to Pt(0), or ligand exchange with Pt(II) complexes giving trans-$[PtXRL_2]$ (X = Cl or SnR'_3 ; L = PPh_3 or PEt_2Ph) [36,37]. Some reactions of the new complexes were discussed. An X-ray analysis on two such compounds (X = Cl; R = $CH{=}CH_2$ (14) or $C{\equiv}CPh$ (15)) indicated that the trans-influence of R has only a low sensitivity to hybridisation at carbon with $sp^3 > sp > sp^2$ [37].



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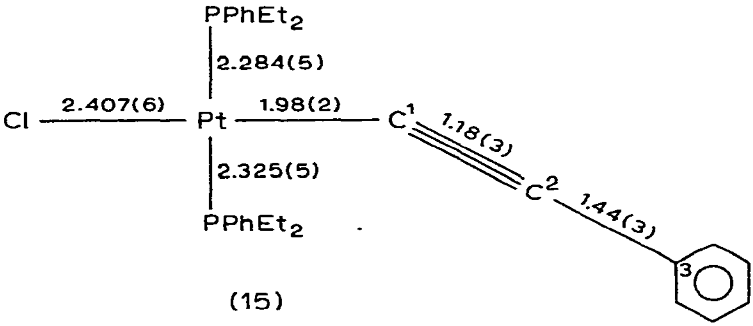
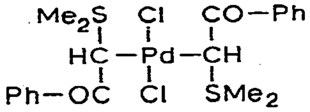


(15)

The reaction of $[PdCl_2(PhCN)_2]$ with (p-XC_6H_4 $COCHSMe_2$, X = H, Me, or MeO) produced crystalline solids of formulation $[(p\text{-}XC_6H_4COCHSMe_2)_2PdCl_2)]$ (16) which preliminary X-ray data showed to have a trans-planar structure with the ylidic ligands bound through the anionic carbon [38]. The X-ray structural determination of $[Pd_2Cl_2(CSNMe_2)_2\{P(OMe)_3\}_2]$ (17) [39] has shown that the $CSNMe_2$ ligand bridges two Pd atoms via the carbon and sulphur



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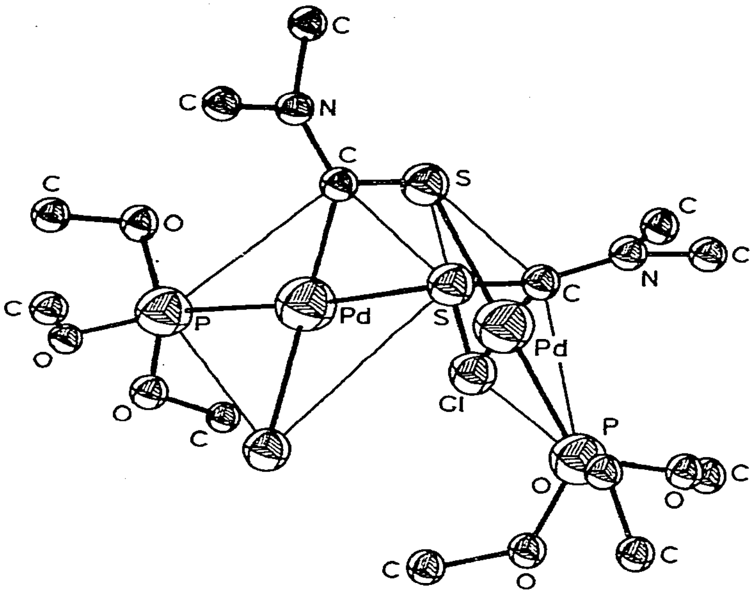
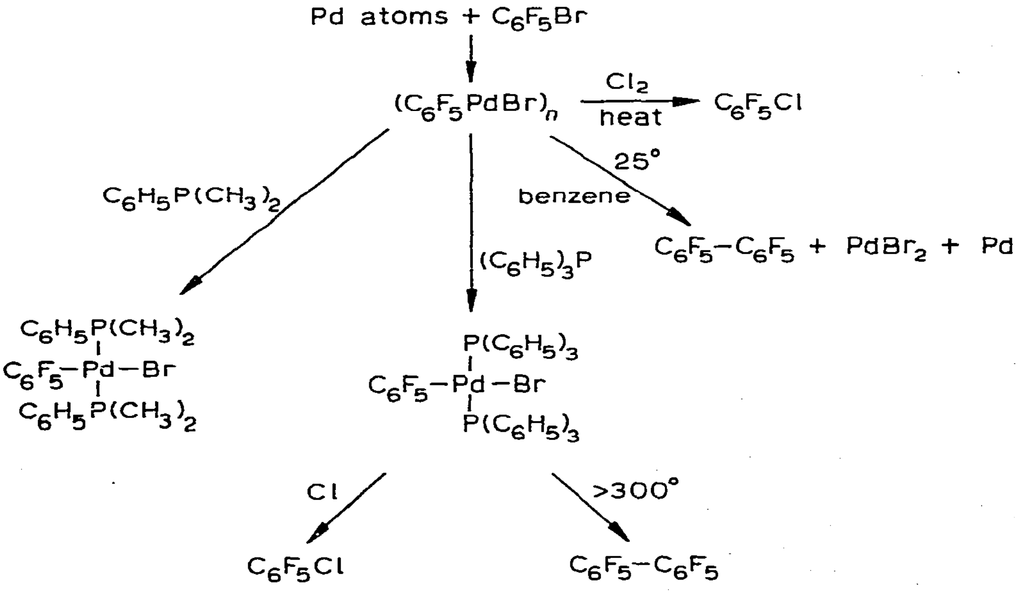


(17)

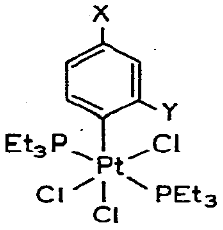
atoms. D_{4h} symmetry of the fulminate complexes $[M(CNO)_4]^{2-}$ (M = Ni, Pd, Pt) has been inferred from Raman and IR spectroscopy [40]. The complex $[(Ph_3P)_2PtCl_2]$ has been found to cleave carbon-carbon bonds in reactions with Tl(I) salts of nitroacetone, 2-nitroacetophenone, and 1-nitrobutan-2-one, the fragments then coordinating to Pt(II) as fulminato and carboxylato groups [41]. The complexes characterised from these reactions were $[(Ph_3P)_2PtCl(CNO)]$, $[(Ph_3P)_2Pt(OCOR)(CNO)]$, and $[(Ph_3P)_2PtCl(OCOR)]$ (R = Me, Et, or Ph). Treatment of $[Pt(Ph_3P)_4]$ with 2-nitroacetophenone led to the formation of $[(Ph_3P)_2Pt(OCOPh)(CNO)]$ and $[(Ph_3P)_2Pt(CNO)_2]$. Infra red spectra indicated the isomerization of coordinated fulminate ligand in $[PtCl(CNO)(PPh_3)_2]$ to the isocyanate product [41]. A preliminary communication [42] has reported an X-ray diffraction study of $H_2[PtCl_2(C{\equiv}CCMe_3)(OCHMe_2)]$ which confirmed the original formulation.

Free radicals have been trapped, using Bu^tNO, and identified by ESR in the reactions of alkenes with diakylplatinum(II) complexes [43] and in the oxidative addition of alkyl halides to Pt(0) complexes [44]. It was suggested that many reactions of transition-metal alkyls involve radical rather than molecular reaction paths [43]. The isotope content of the ethane formed by pyrolysis of $[PtMe_3I(PMe_2Ph)_2]$ and its deuterated analogs has been examined [45]. It was concluded that this reductive elimination reaction is an intramolecular process. Nickel(II) compounds were formed when certain radicals (trityl, 1,1,3,3-tetraphenylalkyl, 1,2,3,4,5,-pentaphenyl-2,4-cyclopentadienyl,2,4,6-tri-tert.butylphenoxyl, 4-cyano-2,6-di-tert.butylphenoxyl or di(p-anisyl) nitrogen oxide) were trapped by nickel(0), which was either generated in situ or used as an olefin complex. The catalytic activity of some of the new products and the mechanism of cleavage of the alkyl group from nickel were discussed [46]. Palladium atoms have been found to insert into the C-Br bond of C_6F_5Br to yield a polymeric species $[C_6F_5PdBr]_n$; some reactions of this species were reported (Scheme 6). Nickel atoms gave the analogous compound $[C_6F_5NiBr]_n$ [47].



(scheme 6)

Homolytic cleavage of the Ni-C σ bond, formed by the reaction of $[Ni(COD)_2]$ with styrene in the presence of a series of organic acids, gave free radicals, resulting in the polymerisation of styrene [48]. The mechanism of this reaction was discussed. The stereochemical course of the oxidative addition of <u>cis</u> or <u>trans</u> β-bromostyrene to $[NiL_4]$ (L = PPh_3 or PEt_3) has been studied and complexes $[Ni(CH{=}CHPh)L_2Br]$ were obtained with retention of configuration [49]. Protonation, carbonylation and thermal decomposition of the vinylnickel complexes was also studied. Polystyrene supported nickel catalytic systems containing Ni-C σ-bonds have been prepared and their activity discussed [50,51]. Aromatic substitution of (18a) occurred on chlorination to give (18b) exclusively; heating (18a) in polar solvents gave $[PtCl_3(PEt_3)][PEt_3Ph]$[52].

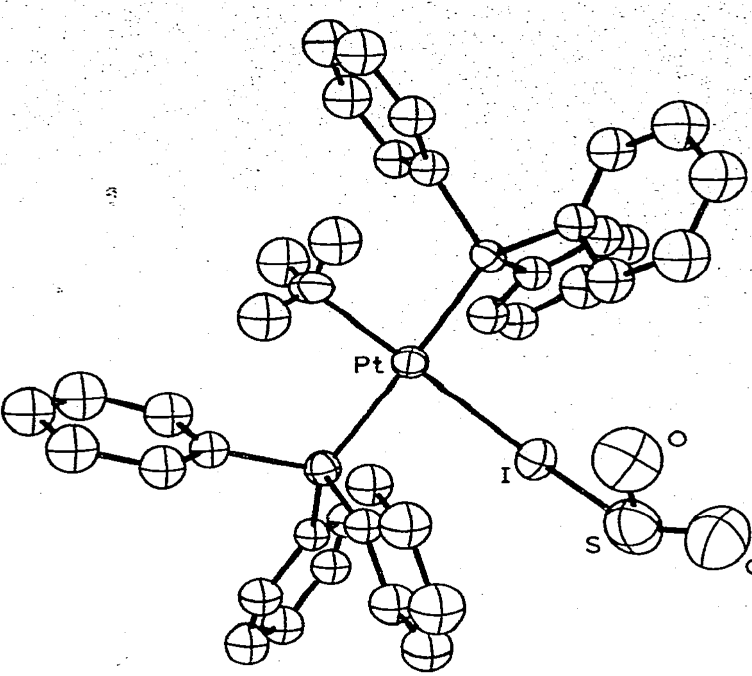


(18a, X = Y = H)
(18b, X = Cl, Y = H)

The reaction of sulphur dioxide with $[PtMe(PPh_3)_2I]$ gave a 1:1 adduct (19) which contained a weak I-S bond (3.391 Å) [53].

From kinetic studies, it was reported that the formation of (20) from $[\overline{PtCH_2CH_2CH_2}(Py)_2Cl_2]$ in benzene occured via a dissociative mechanism [54]. The first alkoxalyl-metal complexes $[MCl(COCO_2R)(PPh_3)_2]$ (M = Pt, or Pd; R = Me or Et) have been prepared by the oxidative addition reaction of $ClCOCO_2R$ to $[M(PPh_3)_4]$; the X-ray structure of the complex where M = Pd and R = Me, has been determined (Pd-C = 1.97 Å) (21) [55].

$[Pt(PPh_3)_2(PbPh_3)_2]$ was found to decompose slowly in dichloromethane to yield <u>cis</u>-$[PtPh(PPh_3)_2(PbPh_3)]$ (22). An X-ray structure of (22) showed a square planar coordination around the platinum atom (Pd-C = 2.055 Å and Pd-Pb = 2.698 Å) [56].



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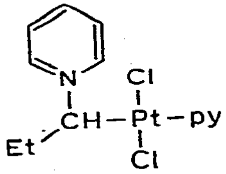

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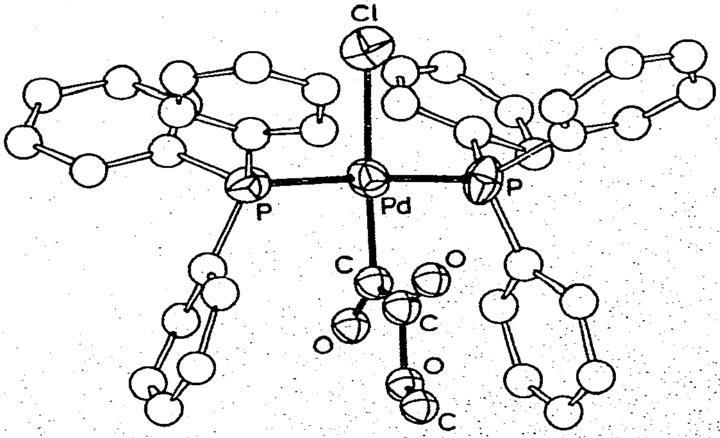

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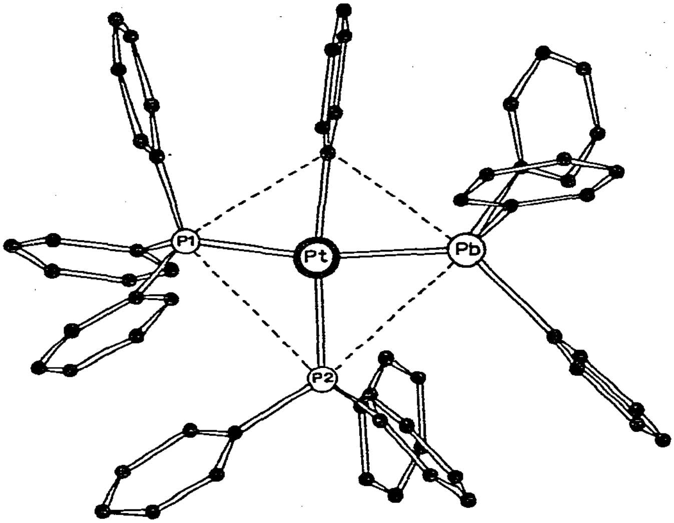
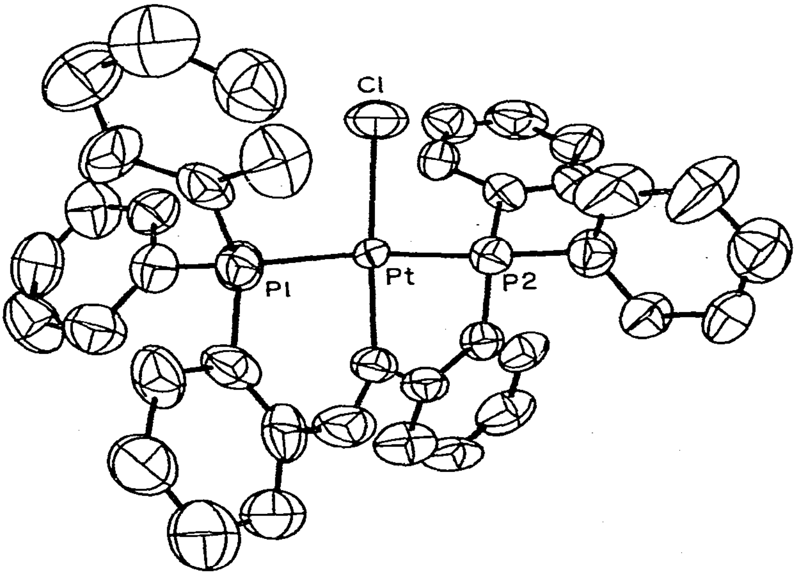


(22)

II Internal Metallation reactions and Metallocycles.

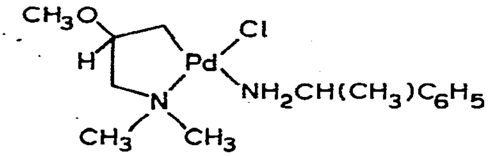
Reaction of the ligands $P(Bu\text{-}t)_2$(*o*-ethylphenyl) or (L=) $P(Bu\text{-}t)_2$(*o*-isopropylphenyl) with $[PtCl_2(PhCN)_2]$ has yielded internally metallated complexes of type $[PtCl_2(P\text{-}C)_2]$ [$P\ \text{-}C = CHMeC_6H_4P(Bu\text{-}t)_2$(P'-C), or $CMe_2C_6H_4P(Bu\text{-}t)_2$]; metallation occured at the α-carbon atom of the ligand. The analogous palladium complex $[PdCl_2(P'\ \text{-}C)_2]$ was prepared but no internally metallated product of palladium could be obtained with L . Bridge-splitting reactions and spectroscopic data for the products were discussed [57]. The first internally metallated complexes containing arsenic donors have been prepared using the ligands As(Bu-t)(*o*-tolyl)$_2$ and As(Bu-t)$_2$(*o*-tolyl). Whereas platinum readily formed internally metallated complexes, analogous palladium complexes could not be prepared [58]. That platinum forms internally metallated complexes more readily than palladium was also demonstrated for a series of triaryl phosphite complexes; thermal elimination of HX from $[MX_2\{P(OAr)_3\}]_2$ (M = Pd or Pt; X = Cl, Br or I; Ar = Ph, *p*-chlorophenyl, *o*-, m- or *p*-tolyl) resulted in *ortho*-metallated products [59]. The action of heat on $[PtMe\{CH_2C_6H_4P(Bu\text{-}t)$(*o*-tolyl)$\}\{P(Bu\text{-}t)$(*o*-tolyl)$_2\}]$ gave three isomeric complexes, including the first example of a dimetallated tridentate ligand. Structures of the three isomers have been determined by X-ray diffraction [60]. It has been suggested that complexes previously formulated as $[Pt(PPh_3)_2]_n$ are the ortho-metallated products $[Pt(PPh_3)(C_6H_4PPh_2)]_n$ (n = 2,3 or 4) [61].

Hydrogen-deuterium exchange occurredin solution for the complexes $[Pt_2Cl_4L_2]$ (L = PPr_3 or PBu_3) specifically at C-3 of the alkyl groups, suggesting the intermediacy of a five-membered internally metallated intermediate [62]. The reactions of (o-vinylphenyl)diphenylphosphine with hydrido-platinum(II) complexes resulted in internally metallated products formed by insertion of olefinic moiety of the phosphine ligand into the Pt-H bond [63]. The complexes $[MCl(o\text{-}Ph_2PC_6H_4C{=}CHC_6H_4PPh_2\text{-}o)]$ (M = Ni, Pd or Pt) have been prepared and an X-ray structure on the platinum complex (23) confirmed that the ligand is tridentate being bonded to the metal via two P atoms and a Pt-C σ-bond (Pt-C = 2.01 Å). The olefinic distance of 1.340 Å is normal for a simple double bond [64]. Internally metallated Pt(IV) complexes have been prepared by the bromination of trans-$[PtBr_2(PEt_3)L]$, where L = 2-(alkenyl)pyridine [65].



(23)

Several reports of internal metallation reactions with N- or S-donor ligands have appeared [66-72]. Complex (24), which contains a metal-carbon σ-bond adjacent to a chiral centre, has been resolved and the absolute configuration of a diastereoisomeric form determined by X-ray crystallography (25) [66]. Bidentate di-N-donor ligands were found to undergo internal metallation reactions with Pt or Pd much less readily than their monodentate analogues. Similar reluctance



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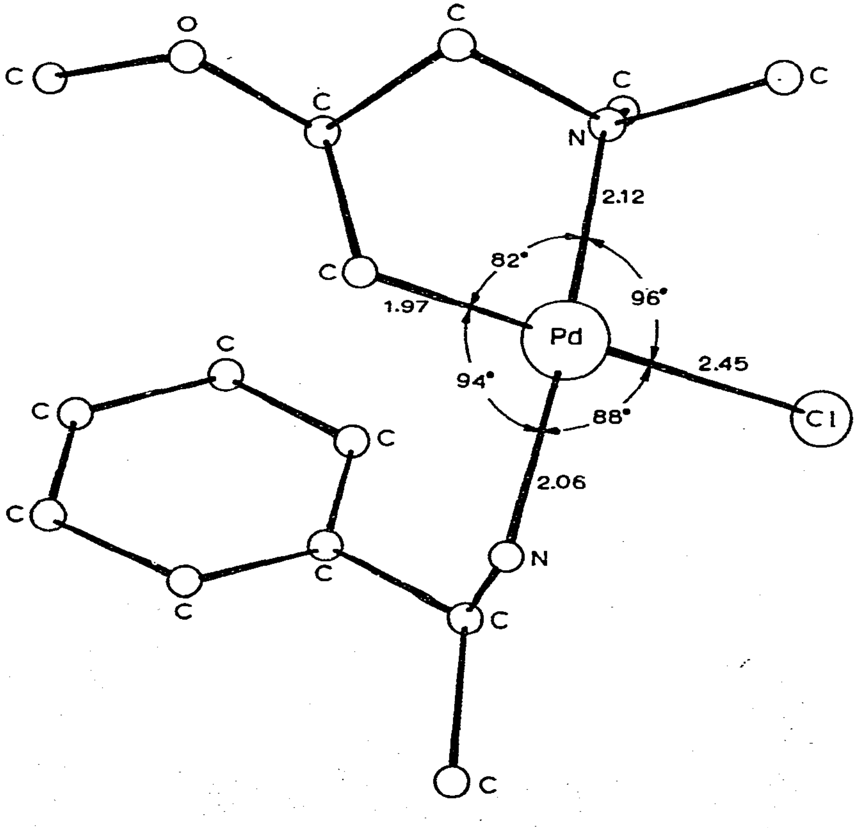
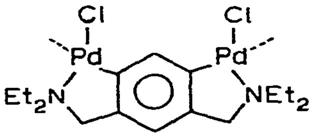


(25)

to undergo metallation was observed for chelating tertiary _o_-tolylphosphines. However, the metallations could be promoted by the presence of acetate ion using a 6-membered chelate ring [67]. From a study on the effect of substituents on the _ortho_-metallation of azobenzenes, it was concluded that palladation occurs via electrophilic substitution of the aryl group [68]. Reactions of N,N-dialkylbenzylamines, N-benzylidine-tert-butylamine or 1-phenylpyrazoles with $[PdCl_4]^{2-}$ gave 5-membered palladiocyclic compounds; N,N,N',N'-tetraalkyl _p_-xylene-α,α'-diamine gave mixtures of 1,2- and 1,4-dipalladiobenzenes whereas N,N,N', N'-tetraethyl-_m_-xylene-α,α'-diamine gave the polymeric 1,3-dipalladiobenzene derivative (26) [69]. Reaction of $[Pd(PhCN)_2Cl_2]$ with biacetyl-bis-(N-methyl,-N-phenyl)-osazone (L) gave $[Pd\ L\ Cl_2]$ which eliminated HCl to give (27); some reactions of these new complexes were discussed [70]. The reactions of the _o_-carbon bonded N,N-dimethylbenzylamine complexes of Pd and Pt $[(Dmba)MCl]_2$ with thallium salts of alkyl or aryl salicylaldimines (Tl Sal=NR) and the quadridentate Schiff base N,N'-ethylenebis (salicylaldimine) (Tl_2salen) gave the compounds [(Dmba)M(sal=N-R)] (28) and $[(Dmba)M]_2$salen [71].

The first _ortho_-metallated complexes containing S-donor ligands with palladium and platinum (29,30) have been synthesized from $[MCl_4]^{2-}$ and thiobenzophenones (M = Pd or Pt; R = Me or OMe) [72].



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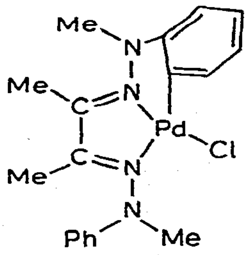

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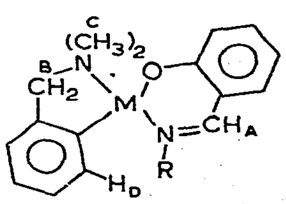

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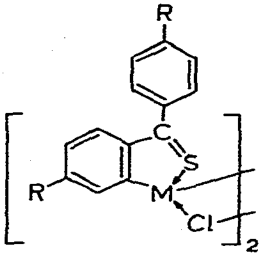

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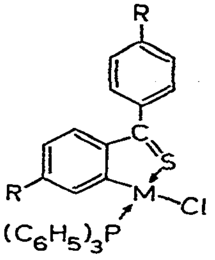
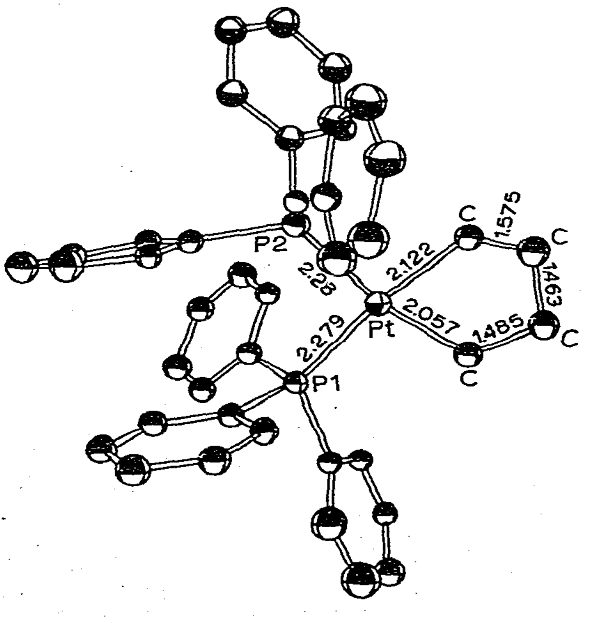


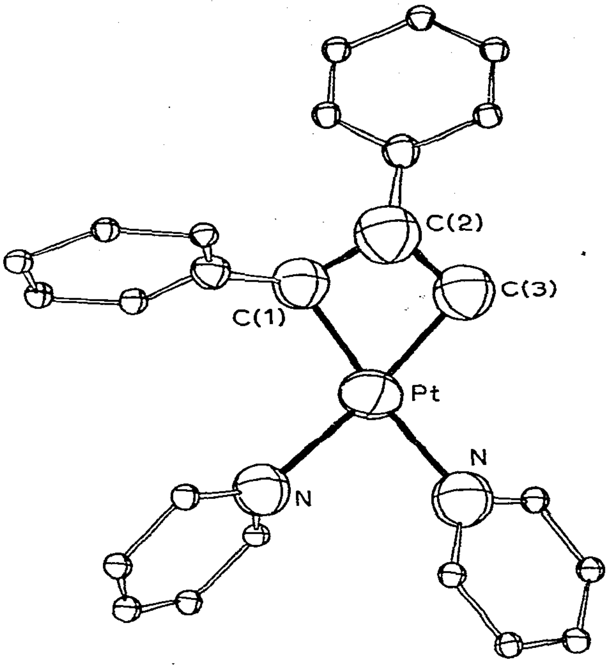
(30)

The importance of metallocyclic intermediates in metal catalyzed reactions e.g. [2 + 2] cycloadditions of olefins and olefin metathesis has been emphasized [73,74]. The X-ray crystal structure of the tetramethylene platinocyclic compound $[Pt(PPh_3)_2(C_4H_8)]$ (31) has been determined [73]. The coordination around Pt was found to be distorted square planar and the metallocyclic ring puckered. The thermal decomposition of several platinocyclic compounds e.g. $[\overline{\mathrm{PtCH_2(CH_2)_nCH_2}}(PPh_3)_2]$ (n = 2,3 or 4) has been studied. The 5- and 6-membered platinocyclic compounds were found to be considerably more thermally stable than their acyclic analogs [74]. The crystal and molecular structure of the



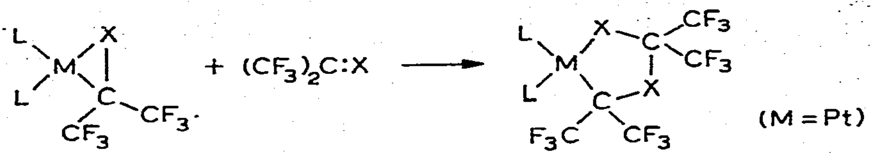
(31)

substituted cyclopropane complex $[PtCl_2(C_3H_4Ph_2)Py_2]$ has been determined by X-ray diffraction [75]. The unit cell was found to contain two non-equivalent complex platinum molecules, although the bonding of the substituted cyclopropane was similar in both. One of these molecules, considering only the coordination around Pt in the equational plane (32), has the following bond parameters: Pt-C(1) = 2.06, Pt-C(2) = 2.60, Pt-C(3) = 2.11, C(1)-C(2) = 1.59, C(2)-C(3) = 1.48 Å.



(32)

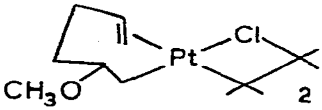
Three papers [76-78], concerning the reactions of low-valent complexes of Ni, Pd or Pt with fluorocarbons have appeared. Reactions of the complexes $[\overline{PtC(CF_3)_2X}L_2]$ (X = O or NH, L = $PMePh_2$ or L_2 = DPE) with $(CF_3)_2CX$ caused ring expansions to occur yielding the 5-membered platinocyclic compounds of type $[\overline{PtC(CF_3)_2X.C(CF_3)_2X}L_2]$ (Scheme 7). The ring expansion reaction can be promoted by use of more basic ligands (L); thus whereas $[Pt\{P(OPh)_3\}_4]$ reacted with hexafluoroacetone to give $[\overline{PtC(CF_3)_2O}\{P(OPh)_3\}_2]$, $[Pt\{P(OMe)_3\}_4]$ gave $[\overline{PtC(CF_3)_2OC(CF_3)_2O}\{P(OMe)_3\}_2]$ [76]. Further information



(scheme 7)

concerning ring expansion reactions has been obtained from a study of reactions of the new complexes [MCF$_2$CFX L] with C_2F_4(M = Ni or Pt; X = F, H or CF_3; L is the potential tridentate ligand MeC(CH_2EPh_2)$_3$ (E = P or As)). The formation of 5-membered metallocyclic complexes was dependent on the ligand L, the coordination number at the metal and the nature of the fluoro-olefin [77]. The crystal structure of the complex [NiCF$_2$CF$_2${MeC(CH$_2$PPh$_2$)$_3$}] has been determined by X-ray diffraction [78]. The fact that the nickel atom is 5-coordinate in this complex is suggested as the reason for its inability to undergo ring expansion with C_2F_4[77,78]. Perfluoroacetone azine complexes of type [MC(CF$_3$)$_2$NN=C(CF$_3$)$_2$L$_2$] (M = Ni, Pd or Pt; L = PPh$_3$, PEt$_3$, PMePh$_2$, Bu-tNC or C$_6$H$_{11}$NC) have been prepared by the reactions of appropriate low-valent metal complexes with bis(trifluoromethyl)diazomethane, (CF$_3$)$_2$CN$_2$. The complexes [M(PhCN)$_2$Cl$_2$] (M = Pd or Pt) reacted with (CF$_3$)$_2$CN$_2$ to yield the insertion products [M(PhCN)$_2${C(CF$_3$)$_2$Cl}$_2$]; possible mechanisms for these reactions were discussed [79].

The reaction of carbon monoxide with dimeric methoxydienylplatinum(II) complexes, e.g. (33) was found to proceed with the formation of monomeric (chloro)carbonyl- or (chloro)methoxycarbonyl-complexes [80]. A ^{1}H and ^{13}C NMR study on (34) and related "enyl" complexes strongly suggested that the norbornenyl ligand is coordinated in a "π-homoallylic" fashion [81].



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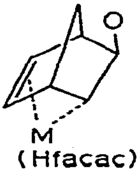
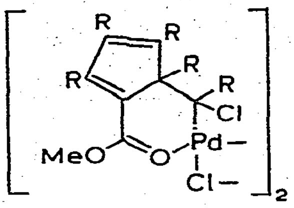


(34)

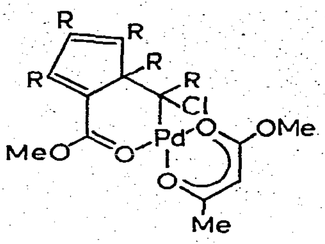
(M = Pd, Pt; R = Me, COMe)

The reaction of [Pd(PhCN)$_2$Cl$_2$] with mad gave the dimer (35) which further reacted with Tl(Acac) to give (36). An X-ray determination has proved the structure of this latter complex (37) (selected bond



(35)

(R = CO_2Me)



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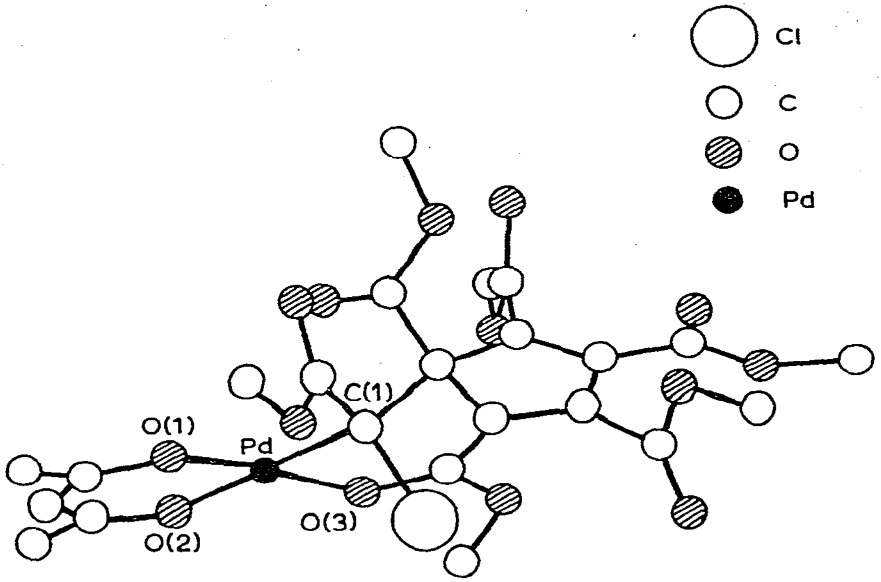
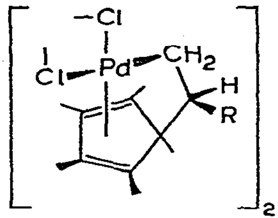


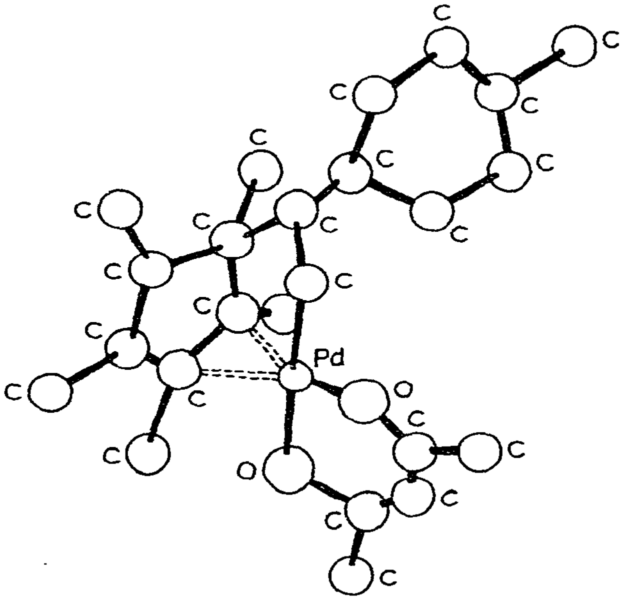
(37)

parameters: Pd—C (1) = 2.04, Pd - O(3) = 2.05, Pd - O(2) = 2.00 and Pd-O(3) = 2.02 Å) [82]. $[Pd(PhCN)_2Cl_2]$ reacted with 2-butyne and diphenylmercury to give (38a). The monomeric species $[\overline{C_5Me_5CHRCH_2Pd}(Acac)]$ were obtained on reaction of (38) with K(Acac); an X-ray structure on the monomer (R = p-tolyl) (39) confirmed the presence of the 5-substituted pentamethylcyclopentadiene ligand in these complexes, which is coordinated to Pd through only one double bond. The fluxional behaviour of complexes (38 and 39) in solution was shown by variable temperature ^1H NMR studies [83] and reactions of this "lightly stabilized" complex with HCl, OMe, H_2, N_2H_4, CO, PPh_3 and Phen have been studied [84]. Although the Pd-C σ-bond in (38a) was not cleaved directly by HCl, it was cleaved



(38)

a = R = phenyl
b = R = p-tolyl

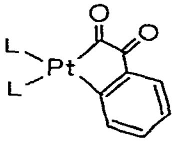


(39)

by methoxide, hydrazine or hydrogen. Carbon monoxide reactions produced several products depending on reaction conditions, but the first step common to these reactions was considered to be carbonyl insertion into the Pd-C σ-bond. Triphenylphosphine gave $C_5Me_5CHPh{=}CH_2$ and $[PdHCl(PPh_3)_2]$ via a β-elimination reaction [84].

The complex $[\overline{PdCH_2COO}(PPh_3)_2]$ reacted with acetylacetone to give $[Pd(CH_2COOH)(PPh_3)(Acac)]$ which contained a C-bonded acetate group; the O-bonded linkage isomer of this latter complex i.e. $[Pd(OCOCH_3)(PPh_3)(Acac)]$, was prepared by another route [85]. Reactions of $[PtL_4]$ ($L = PPh_3$, $PMePh_2$ or $AsPh_3$) with 1,2-benzocyclobutadienequinone gave the unsymmetrical insertion products (37). For L = PPh_3, both red and blue complexes were isolated; these were shown by X-ray crystallography to be conformers of the same species (40). The carboxylate complex (41) was obtained if the reaction of $[Pt(PPh_3)_4]$ with the dione was carried out in the presence of oxygen [86].

Reaction of $[NiCl_2(PMe_3)_2]$ with $Me_3P{=}CH_2$ in THF at 0° gave (42) in which each nickel atom is bonded via four Ni-C σ-bonds [87].



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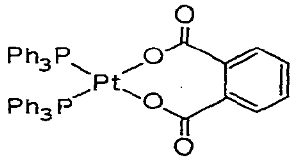

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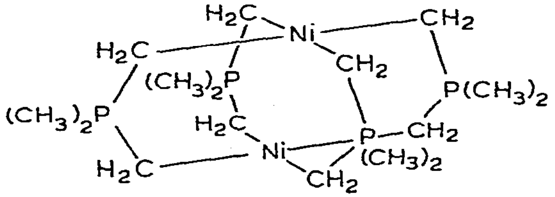
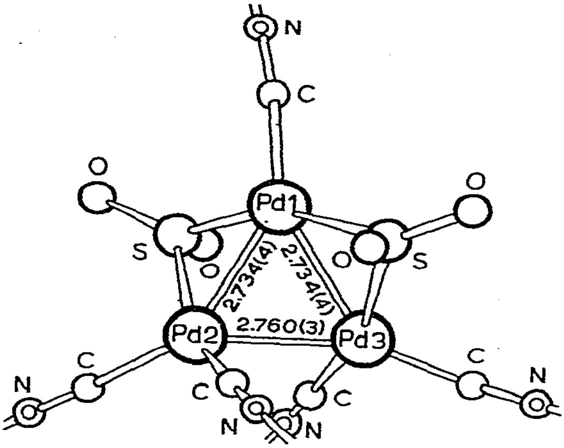


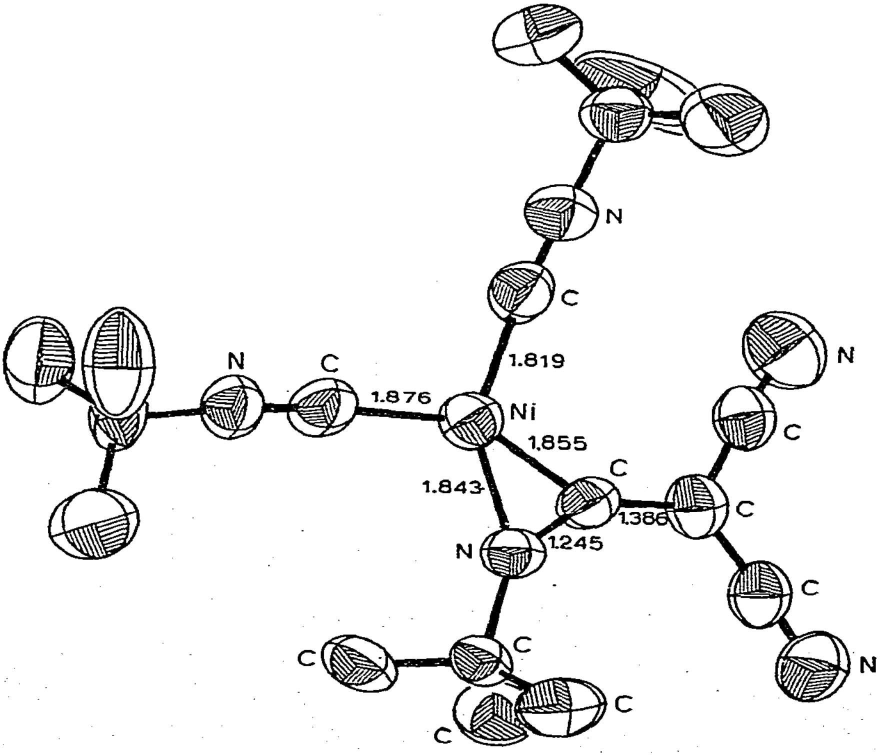
(42)

III Metal isocyanides

The reaction of $[PdCl_2(PhNC)_2]$ with the bidentate ligands en, 2-aminopyridine, *o*-phenylenediamine, ethanoline and allylamine in 1:1 molar ratios have been found to give monocarbene complexes of the type *cis*-$[PdCl_2(PhNC)(carbene)]$. Using a six-fold excess of 2-aminopyridine, the dicarbene derivative $[Pd\{PhNHC(NHC_5H_4N)\}_2Cl_2]$ was obtained [88]. The complex $[Pd(PhNC)_2]$ has been reacted with active mono-olefins and with *p*-quinones to give the 1:1 adducts $[Pd(PhNC)_2L]$ (L = fum, man, *p*-benzoquinone and *p*-napthoquinone). In the case of tetrachloro-*p*-benzoquinone, an adduct was obtained where the Pd:L ratio was 2:1 [89]. The crystal structure [90] of the product of the reaction of $[Pd(Bu^t\ NC)_2]$ with an excess of SO_2 has shown that it is the trinuclear species $[Pd_3(SO_2)_2(Bu^t\ NC)_5].2C_6H_6$


N
C
O
Pd1
O
S
O
O
S
2.734(4)
2.734(4)
Pd2
2.760(3)
Pd3
C
C
N
C
C
N
N
N

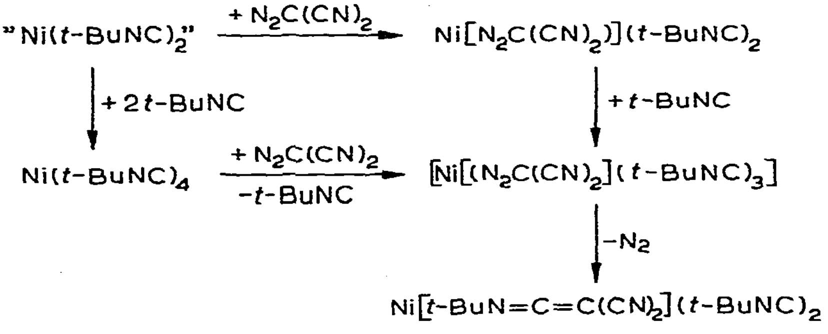
(43)


N
C
N
C
1.819
N
1.876
Ni
N
C
1.855
C
1.843
1.386
C
N
1.245
C
C
N
C
C
C
C

(44)

(43) and not the dimer $[Pd(SO_2)(Bu^t NC)_2]_2$ as originally formulated. The structure shows a triangulo-arrangement of Pd atoms with SO_2 bridges between two of the Pd-Pd bonds. The Pd-Pd bond which has no SO_2 bridge is significantly longer (2.760 Å) than the others (2.734 Å). The thiocyanate isocyanide complexes $[Pd(RNC)_2(SCN)_2]$ (R = Ph, cyclohexyl), $[Pd(RNC)(PPh_3)(SCN)_2]$ (R = Ph, cyclohexyl, p-nitrophenyl) and $[Pd(PhNC)(AsPh_3)(SCN)_2]$ have been prepared by the reaction of the appropriate <u>cis</u>-dichloro- or <u>trans</u>-diodo-derivatives with silver thiocyanate [91]. Whereas the bis-isocyanide complexes contain only S-bonded thiocyanates, the $[Pd(RNC)(PPh_3)(SCN)_2]$ complexes contain partial N-bonded thiocyanates.

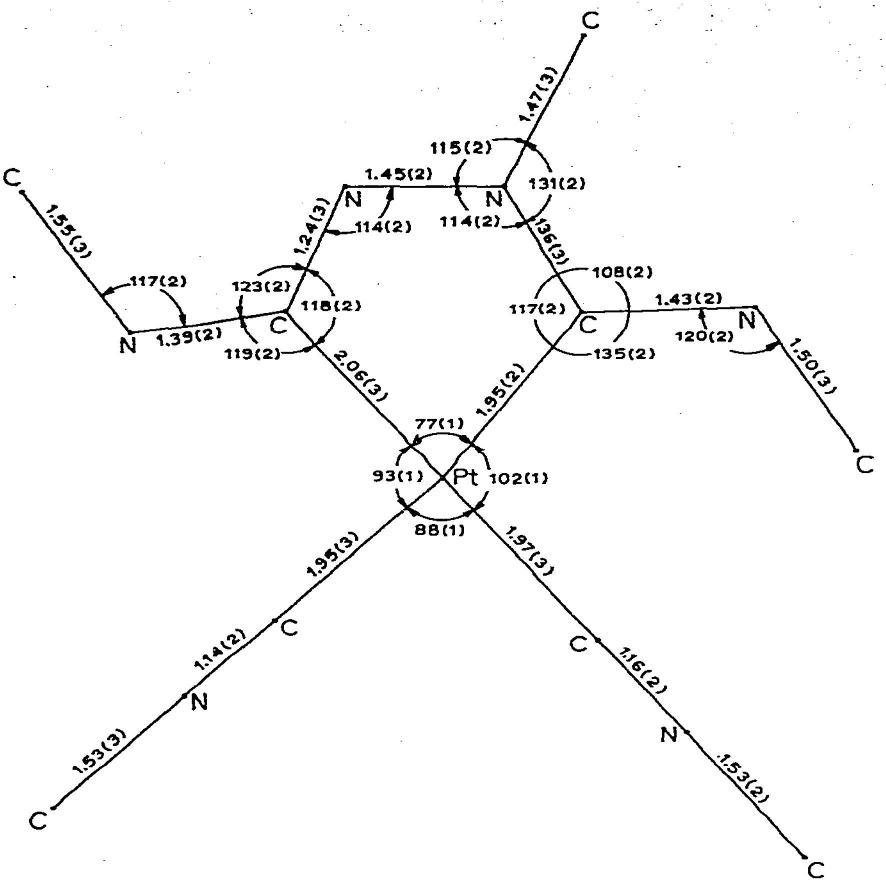
The product of the reaction of $[Ni(Bu^t NC)_4]$ and diazocyanomethane, $N_2C(CN)_2$, has been shown by X-ray crystallography to be the ketenimine complex (44). The mechanism for the formation of (44) is shown in Scheme 8 [92]. The X-ray structure of $[Pt(MeNC)_2(C_4H_8N_4Me)]$ (45) has been reported [93]; this, together with ^1H NMR data, firmly establish that the structure of Chugaev's red cation is (46).



(44)

(scheme 8)

The reactions of methyl and p-chlorophenyl isocyanides (R'NC) with the complexes $[PtXRL_2]$ [94] and $[PtR_2L_2]$ [95] have been studied (X = Br or I; R = Me or Ph; L = tertiary phosphine). The monoalkyl (or -aryl) complexes give initially ionic species $[PtR(R'NC)L_2]X$ which on heating yielded the isocyanide insertion products $[PtX\{C(R)=NR'\}L_2]$. The reactions of the bis-alkyl (or -aryl) complexes with the isocyanides



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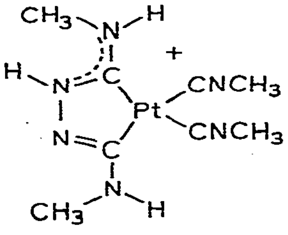
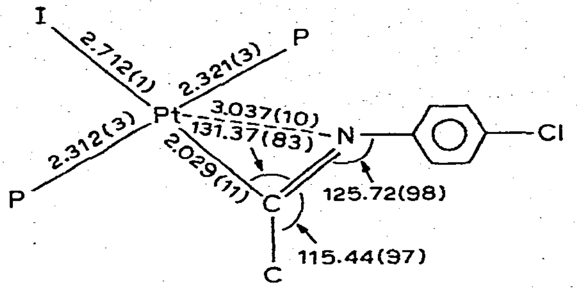


(46)

proceeded with either substitution of a tertiary phosphine ligand to give $[PtR_2(R'NC)L]$ or isocyanide insertion into the carbon-metal bond; the type of reaction occurring being dependent on the nature of the phosphine and isocyanide. The crystal structure of the isocyanide

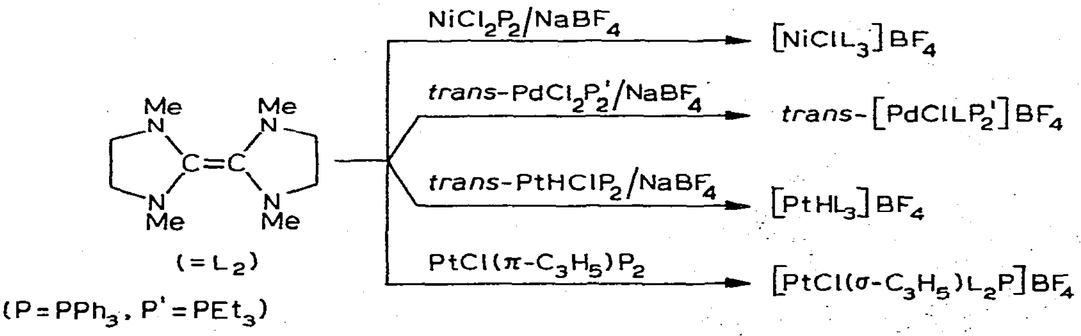


(47)

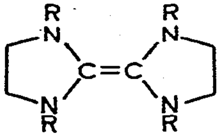
insertion product *trans*-[$PtI\{C(Me)=NC_6H_4Cl\}(PEt_3)_2$] (47) has been determined [96]. The coordination around the platinum is essentially square planar. The non-bonding Pt-N distance of 3.04 Å in (47) is inconsistent with the previously suggested pseudo five-coordinate geometry suggested for this type of complex [96].

IV Metal Carbenes

A series of papers on the synthesis and properties of carbene complexes derived from electron-rich olefins has appeared [97 - 100]. In a preliminary communication, the preparation of a wide range of metal carbene complexes including some of Ni^{II}, Pd^{II} and Pt^{II} has been outlined (Scheme 9) [97]. Reactions of [$M_2X_4L_2$] (M = Pd or Pt; X = Cl or Br; L = tertiary phosphine or tertiary amine) with the electron-rich olefins (48 or 49) gave an extensive series of mononuclear



(scheme 9)



(R = Me, Ph)

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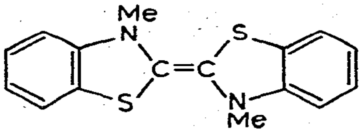
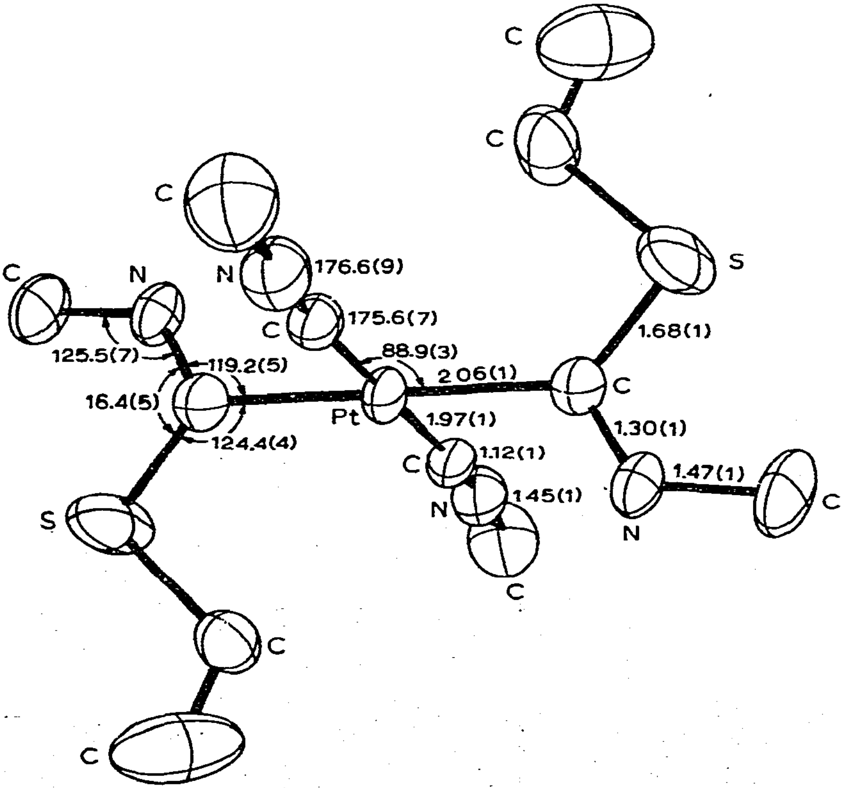


(49)

carbene complexes of type cis- or trans- [MX_2(carbene)L] [98]. Some halide displacement reactions and thermally induced isomerisations of trans-[MX_2(carbene)L] → cis-[MX_2(carbene)L] have been studied [99], and ^{13}C NMR data reported for the new carbene complexes [100]. From this latter study, several trends emerged, a) the ^{13}C chemical shifts occurred at higher fields than in previously reported carbene complexes, b) the chemical shift of the carbene carbon atom was sensitive to the trans-ligand, c) $^3J(^{13}C-^{195}Pt)$ for cis-isomers was ≤ 60 Hz, but ≥ 140 Hz for trans-isomers [100].



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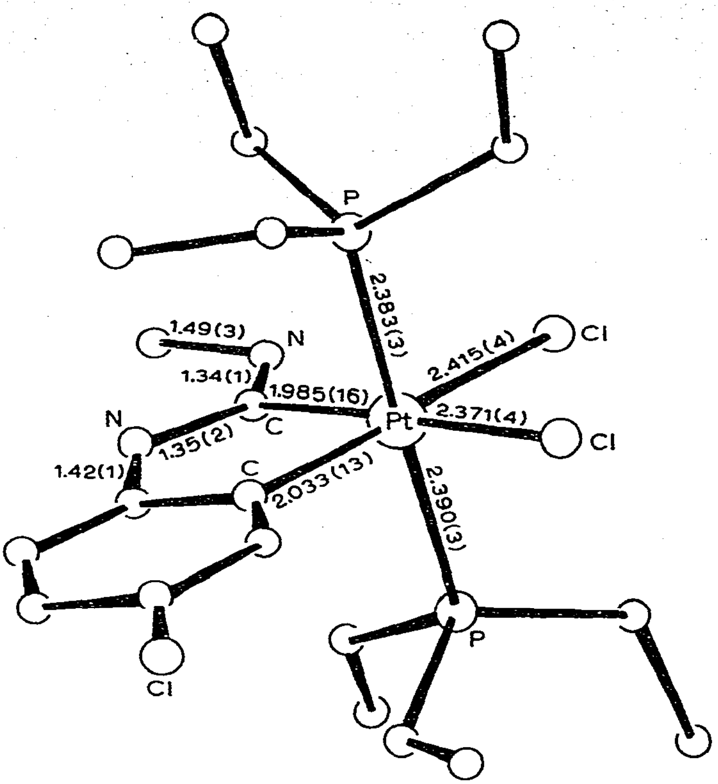


(51)

X-ray crystal structures have been reported for several carbene complexes [101-103]. The structure of *trans*-$[PtMe\{C(OMe)Me\}(PMe_2Ph)_2]^+$ showed essentially square-planar coordination around the platinum and the carbene ligand, which was disordered, adopted the *trans*- configuration, Pt-P = 2.283, Pt-CH_3 = 2.13 and Pt-C (carbene)= 2.13 Å. The unusually long Pt-C (carbene) distance suggests little double-bond character in this bond [101]. The bis-carbene cation *trans*- $[Pt(MeNC)_2\{C(NHMe)(SEt)\}_2]^{2+}$ (50) was found to have square-planar coordination around the metal, and the carbene ligands were shown to exhibit a similar structural *trans* influence to that of tertiary phosphine ligands [102]. The oxidation of *trans*-$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2]ClO_4$ with chlorine gave the Pt^{IV} carbene complex (51) in which one of the aromatic groups of the ligands is metallated [103].

The reaction of nickel tetracarbonyl with $[Al(NMe_2)_3]_2$ gave the polynuclear carbene complex $[(CO)_3Ni\{C(NMe_2)OAl(NMe_2)_2\}]_2$ [104]. The cationic Pt^{II} complex containing a cyclic carbene ligand, $[PtCl\{\overline{CNHCHC(Me)S}\}(PEt_3)_2]^+$, was prepared by the oxidative addition of 2-chloro-4-methylthiazole to $[Pt(PhCH{=}CHPh)(PEt_3)_2]$ followed by protonation at nitrogen [105]. A carbene intermediate has been proposed in the reactions of $[(COD)_2Ni]$ with thionocarbonates of vicinal diols which produced stereospecific alkenes with a high efficiency [106].

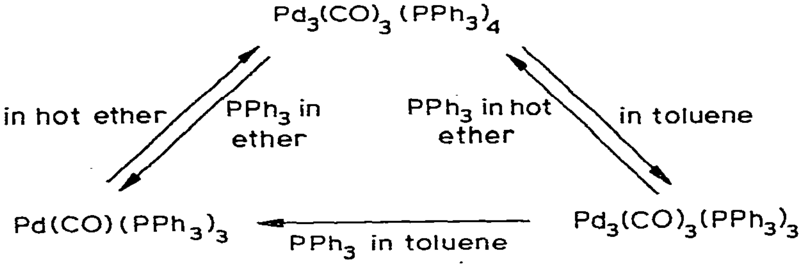
Metal Carbonyls

Four papers [106a, 107-109] have reported matrix IR studies on binary carbonyls of Ni, Pd and Pt. The co-condensation of Ni atoms in various $^{12}C^{16}O/^{14}N_2$, $^{12}C^{16}O/^{14}N_2/Ar$ and $^{12}C^{18}O/^{14}N_2/^{15}N_2/Ar$ mixtures has been studied. The new species $[Ni(N_2)_m(CO)_{4-m}]$ ($m = 1-3$) have been inferred from IR and Raman spectra [107]. The co-condensation of Pd [108] or Pt [109] atoms with carbon monoxide in inert matrices at low temperatures produced the binary carbonyls $[M(CO)_n]$ (M = Pd or Pt; $n = 1-4$); the species were characterized by IR spectroscopy. Both $[Pd(CO)_4]$ and $[Pt(CO)_4]$ were assigned a regular tetrahedral structure on the basis of IR data.

An electrochemical synthesis of metal carbonyls including $[Ni(CO)_4]$ and $[Ni(CO)_2(PPh_3)_2]$ has been reported [110]. $[Ni(CO)_4]$ reacted with tris(trimethylsilylmethyl)phosphine to give only the monosubstituted derivative [111], whereas CF_3PH_2 or $(CF_3)_2PH$ gave both mono- and disubstituted derivatives [112]. ^1H NMR and IR spectra were reported for the new nickel carbonyl complexes. The complex $[Ni(CO)_3(PMe_2Cl)]$, prepared from $[Ni(CO)_4]$ and PMe_2Cl, reacted with $Na[Fe(CO)_2Cp]$ to give the singly bridged product $[(CO)_3Ni(PMe_2)Fe(CO)_2Cp]$ [113]. The complexes $[Ni(CO)_3L]$ were prepared by direct action of $[Ni(CO)_4]$ with the ligands L {L = 2-$(CF_3)_2PB_5H_8$ [114] or 2-chloro-5,5-dimethyl-1,3,2,-dioxaphosphorinane [115]}. Information concerning the nature of M-C and M-P bonds has been obtained by measurements of magnetic molecular rotations in complexes $[M(CO)_n]$ (M = Ni, Fe, Cr or Mo; $n = 4,5$ or 6) and $[M(PF_3)_4]$(M = Ni or Pt) [116].

Reactions of $[Pt_3(CO)_3(PPh_3)_4]$, $[Pt(CO)_2(PPh_3)_2]$ or $[Pd_3(CO)_3(PPh_3)_3]$

with carbon monoxide under pressure in p-xylene solutions have been followed by IR spectroscopy. The spectral changes observed were consistent with the reversible formation of $[M(CO)_3(PPh_3)]$ (M = Pd or Pt) [117]. New syntheses of the complexes $[Pd(CO)(PPh_3)_3]$, $[Pd_3(CO)_3(PPh_3)_3]$ and $[Pd_3(CO)_3(PPh_3)_4]$ have been reported by the reaction of $[PdCl_2(PPh_3)_2]$ with CO in the presence of methanolic solutions of primary or secondary amines; the three complexes were interconvertible (Scheme 10). Use of tertiary amines led to the formation of $[PdCl(COOMe)(PPh_3)_2]$ [118]. Oxidative addition reactions of alkyl halides to $[Pd(CO)(PPh_3)_3]$ under an atmosphere of carbon monoxide yielded the acyl complexes trans-$[PdX(COR)(PPh_3)_2]$ (X = Cl, Br or I; R = $CH{=}CH_2$, $CH_2CH{=}CH_2$, $CH{=}CHMe$, $CH_2CMe{=}CH_2$, CH_2Ph, Me or Ph) [119].



(scheme 10)

The polymeric carbonyl halides $[Pd(CO)X]_n$ (X = Cl or Br) were prepared by the action of carbon monoxide on palladium(II) halides in the presence of HX. It was suggested that compounds previously reported as $[Pd(CO)Cl_2]_2$, $[Pd_2(CO)_2Cl]$, $[PdH(CO)Cl]$ or $[Pd(CO)_2Cl_2]$ were in fact impure samples of the same compound, viz. $[Pd(CO)Cl]_n$. The carbonyl halides $[Pd(CO)X]_n$ reacted with caesium halides to give $[Pd(CO)X_2]_n^-$ and with bis(diphenylarsino)methane(L) to give $[PdLX]_2$ [120]. In a brief communication, the carbonylation of organic substrates, ArX (Ar = Ph or mesityl; X = NO, N = NAr or N_3) by $[Pd(CO)Cl]_n$ has been reported [121].

The unstable thiolate complexes $[CpNi(CO)SR]$ (R = CF_3 or C_6F_5) were identified by IR spectroscopy on irradiating $[CpNi(CO)]_2$ with the appropriate disulphide in a closed system [122]. The oxidative electrochemistry of the thio-bridged complexes $[CpNi(SR)]_2$ (R = alkyl or aryl) has been studied. Both monocationic, $[CpNi(SR)]_2^+$ and dicationic, $[CpNi(SR)]_2^{2+}$ species were detected but could not be isolated. Values of the oxidation potentials for $[CpNi(SR)]_2$ were dependent on the nature of the group R [123]. The effect of pressure on the rates of substitution of metal carbonyls including $[Ni(CO)_4]$, with ligands L in various solvents has been studied [124].

The reactions of $(Me_3Sn)_2X$ (X = O or N) with metal carbonyl species gave complexes containing metal-tin bonds; the complex $[CpNi(CO)SnMe_3]$ was prepared in this way but was too unstable to be fully characterized [125]. Novel heterotrimetallic complexes of type $[CpFe(CO)_2MX_2Ni(CO)Cp]$ (M = Sn or Ge; X = Cl or Br) were prepared by reactions of $[CpFe(CO)_2MX_3]$ with $[CpNi(CO)]_2$, and characterized by IR, ^1H NMR and mass spectroscopy [126]. The ion-cyclotron resonance methods developed to detect the high masses observed due to binuclear metal-organic ions has been described. Ion molecular reactions in the spectra of $[Ni(CO)_4]$ to give $[Ni_2(CO)_6]^-$ have been observed [127]. The fragment patterns obtained from the mass spectral analysis of four dichlorocarbonyl phosphineplatinum(II) complexes are reported [128]. A study of the formation and structure of $[Pt(CO)H_2X_3]^-$ (X = Cl, Br, I) from the reaction $Pt(CO)_2 + 2Fe^{3+} + H_2O + 2X^- \longrightarrow [Pt(CO)H_2X_3]^- + 2Fe^{2+} + CO_2$ has appeared [129].

Several papers [130-132] have reported the use of nickel tetracarbonyl in organic syntheses. The ω-iodoalkynes, $\underline{n}$-$C_4H_9C{\equiv}C(CH_2)_nI$, with $[Ni(CO)_4]/KOBu^t$ yielded the esters $C_4H_9C{\equiv}C(CH_2)_nCO_2Bu^t$ (n = 3 or 5) whereas a mixture of cyclic esters was obtained when n = 4 [130]. Improved yields of γ-lactones were obtained from the reactions of RCOCl (R = Me or Ph) with acetylene and $[Ni(CO)_4]$ in acetone solution. If the reactions were carried out in the presence of tetrabutylammonium halides, the intermediacy of the halotricarbonyl anions, $[Ni(CO)_3X]^-$ (X = Cl,Br,I), was suggested [131]. The reaction of iodobenzene with N-benzylidene-methylamine in the presence of $[Ni(CO)_4]$ was found to be solvent dependent. In DMF, the main product was 1-methyl-2-phenylindolin-3-one, whereas in benzene, coupling of two benzoyl groups to an intervening imine double bond resulted in the formation of N-methyl-N-(α-phenylphenacyl)-benzamide [132].

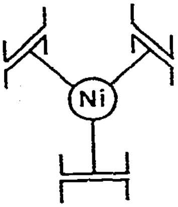
$[PtCl_2(CO)_2]$ reacts with acetylene in MeCN to give $[PtCl(CO)_2(CH{=}CH)_nCH_2CHO]$. In benzene black $[PtCl_2(CO)_2(C_2H_2)_4]$ is obtained which from IR contains a cyclic organic ligand. With PhC≡CH, $[PtCl_2(CO)_2]$

produced $[PtCl_2(CO)_2(PhC{\equiv}CH)_4]$ in MeCN and $[PtCl_2(CO)(PhC{\equiv}CH)_2]$ in benzene. The latter is postulated to contain a cyclic butadiene group with only one Cl ligand bonded to the Pt [133].

VI Olefin complexes

The subject of stereochemical non-rigidity in transition metal π-complexes as investigated by NMR spectroscopy, has been comprehensively reviewed (256 refs.) [134]. A review concerning metal complexes of cyanocarbon and cyanonitrogen ligands, including tetracyanoethylene and dicyanoacetylene, has appeared (96 refs.) [135]. Non-iterative semi-empirical one-electron molecular orbital (NISEMO) calculations have been used to determine the relative energies of zerovalent platinum-olefin and -acetylene complexes. On the basis of these calculations, mechanisms have been proposed for olefin-vinyl rearrangements, HCl addition to π-bonded acetylene- and σ-bonded acetylene-acetylide hydride rearrangement [136].

The synthesis of the first binary metal-ethylene complex, $[Ni(C_2H_4)_3]$, has been reported by the reaction of all-trans-1,5-cyclododecatrienenickel(0) with ethylene at 0°; a trigonal planar structure was suggested for this molecule (52) [137]. With a view to establishing the factors affecting metal-olefin bonding, X-ray crystal structures have been determined for the two complexes $[Ni\{P(o\text{-}MeC_6H_4O)_3\}_2(\text{olefin})]$ (olefin = C_2H_4 or C_2H_3CN) [138]. The coordination around the nickel atoms is trigonal (53,54), with the olefin nearly in the PNiP plane; the olefinic C-C distance is 1.46 Å in both complexes. In the acrylonitrile complex, the olefin is shifted relative to the ethylene complex (53,54) in order to obtain maximum metal-olefin bonding. The structures presented in this study were compared with structures of other metal-olefin complexes.



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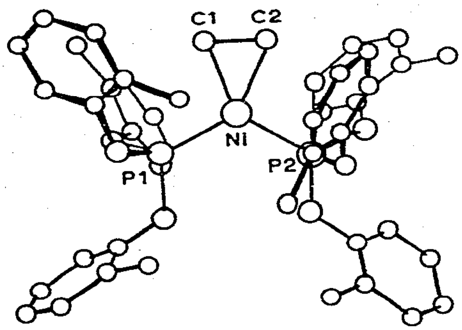

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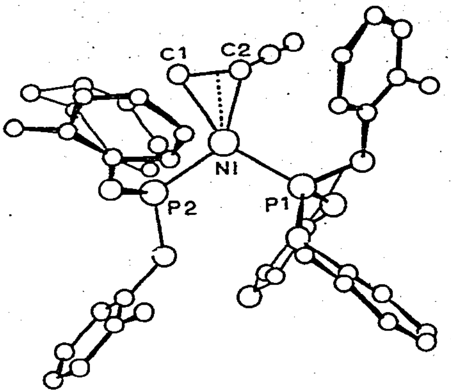


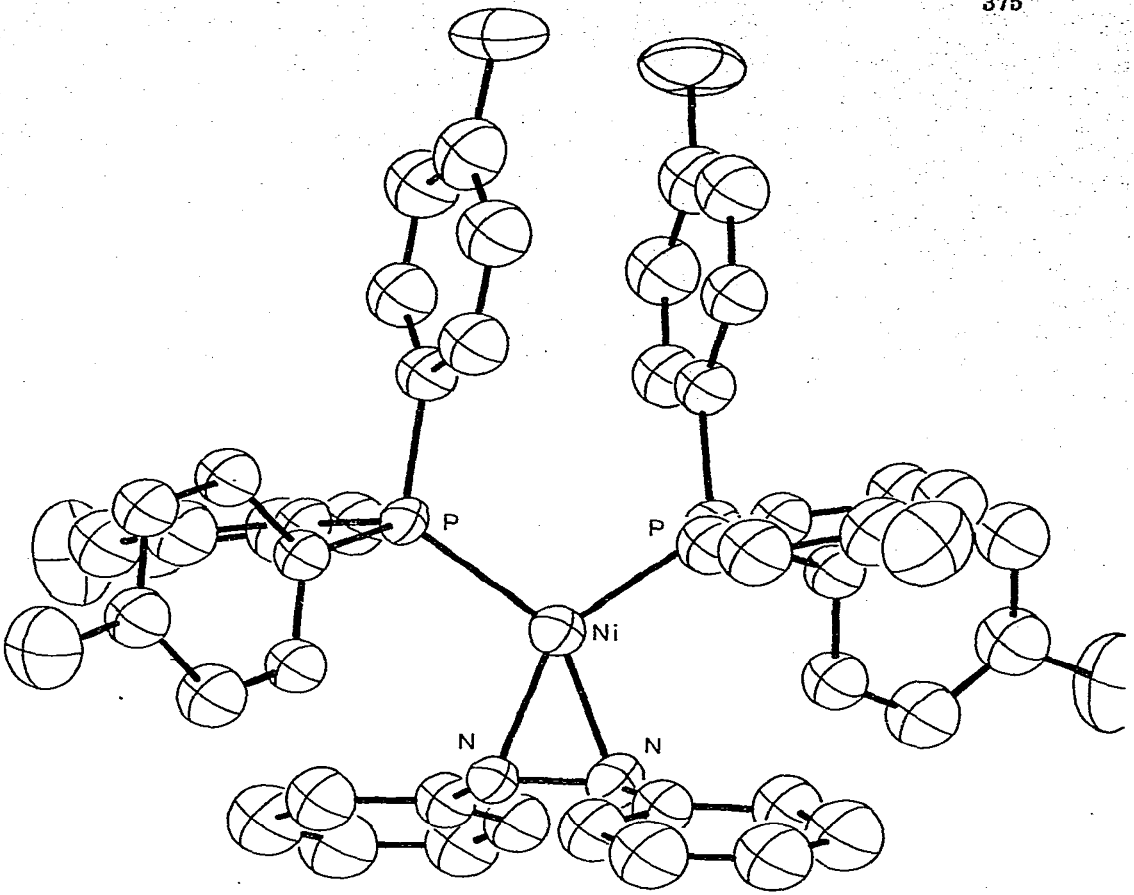
(54)

Electrochemical syntheses of nickel(0) complexes, including [Ni(COT)], [Ni(COT)$_2$], [Ni(COD)$_2$] and cyclododecatrienenickel, have been reported from nickel(II) compounds or nickel metal; mechanisms for these reactions were discussed on the basis of polarographic data [139].

The reaction of [Ni(COD)$_2$] with azobenzene and P(p-MeC$_6$H$_4$)$_3$ gave the diazene complex [Ni{P(p-MeC$_6$H$_4$)$_3$}$_2$(PhN$=\!=$NPh)] (55). An X-ray crystal structure of this complex has been determined and indicates that the π-bonding scheme in metal-olefin complexes may be extended to non-carbon-carbon unsaturated bonds [140]. Reactions of [Ni(COD)$_2$] in the presence of the ligand L , or [Ni(COD)(PPh$_3$)$_2$], with NOCl gave nitrosyl complexes [NiCl(NO)L$_2$] (L = PPh$_3$ or P(OPh)$_3$; L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$, where n = 1,2 or 3) [141].

The dibenzylideneacetone complex [Pd(dba)$_2$] dissociates in solution to give [Pd$_2$(dba)$_3$], and reacts with an excess of dba to give [Pd(dba)$_3$] (Scheme 11) [142,143]. The X-ray crystal structures of (56) and (57) have been determined. The coordination around the palladium atoms in (56) is trigonal with the metal atoms bonding to three olefin groups of bridging dba ligands. The average C=C distance for the six olefin groups is 1.39 Å [142]. In (57) the coordination around the palladium is again trigonal with palladium bonded olefinic C=C distances of 1.39, 1.39 and 1.37 Å [143]. Reaction of [Pt(dba)$_2$] with ligands L gave [Pt(dba)L$_2$] (L = PPh$_3$, PMePh$_2$ or PEt$_3$). These latter complexes reacted with activated olefins, and related molecules, to displace dba giving [PtL'L$_2$] (L' = C$_2$F$_4$, CF$_3$C$_2$CF$_3$, (CF$_3$)$_2$CO or CS$_2$) [144].

Treatment of [PdCl$_2$(PhCN)$_2$] with 4-vinylcyclohexene (=L) gave [PdCl$_2$L$_2$] [145]. The IR and Raman spectra of [MX$_2$(C$_5$H$_8$)]$_2$ (X=Cl, Br; M=Pt, Pd;



(55)

$$[Pd_2(dba)_3] \underset{}{\overset{dba}{\rightleftharpoons}} [Pd(dba)_2] \underset{}{\overset{dba}{\rightleftharpoons}} [Pd(dba)_3]$$

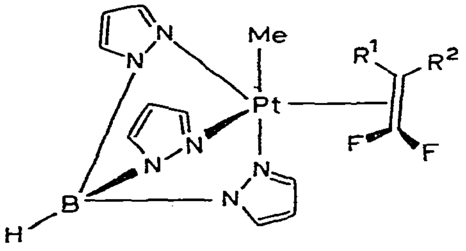
(56) (57)

(scheme 11)

C_5H_8 = cyclopentene) have been recorded and a complete vibrational assignment from 70 to 1 500 cm, completed which required the reassignment of the cyclopentene spectrum [146].

Fumaronitrile complexes $[M(fum)L_2]$ (M = Pd or Pt; L = $AsPh_3$ or PPh_3, L_2 = chelating N, P or As ligands) [147], and maleic anhydride complexes $[Pd(man)L_2]$ (L = P(p-MeC_6H_4)$_3$, $PMePh_2$, P(p-ClC_6H_4)$_3$, $P(OPh)_3$, $P[MeC(CH_2O)]_3$ or PPh_3) [148] have been prepared. ^1H NMR data for all complexes and IR, ν(CO), data for the maleic anhydride complexes were discussed.

Reaction of polymeric [PtMe{HB(pz)$_3$}] with unsaturated organic molecules gave new five-coordinate polypyrazolylborate complexes [PtMe{HB(pz)$_3$}(Un)] (Un = olefin, acetylene or allene) [149]. ^{1}H and ^{19}F NMR studies on the complexes (58) ($R^1 = R^2 = F$, $R^1 = R^2 = H$, $R^1 = H$, $R^2 = F$, $R^1 = F$, $R^2 = H$) suggest that there is through-space H-F coupling between the Pt-Me hydrogens or the 3-H pyrazolyl ring hydrogen and the fluorine nuclei [150]. Reaction of [PtMe(acetone)(PMe$_2$Ph)$_2$]$^+$ with a serie of unsaturated hydrocarbons gave the complexes [PtMe(Un)(PMe$_2$Ph)$_2$]$^+$ (Un = ole diene, allene, vinyl ether, allyl alcohol or allylamine). Vibrational and NMR spectra were reported and used in a discussion on the nature of the metal-olefin bond. The complexes prepared in the present study were compared with the analogous acetylene complexes [PtMe(RC≡CR')(PMe$_2$Ph)$_2$]$^+$ and with [PtH(Un)(PR$_3$)$_2$]$^+$ [151].



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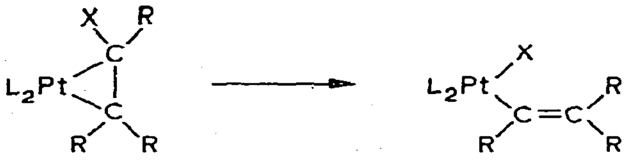
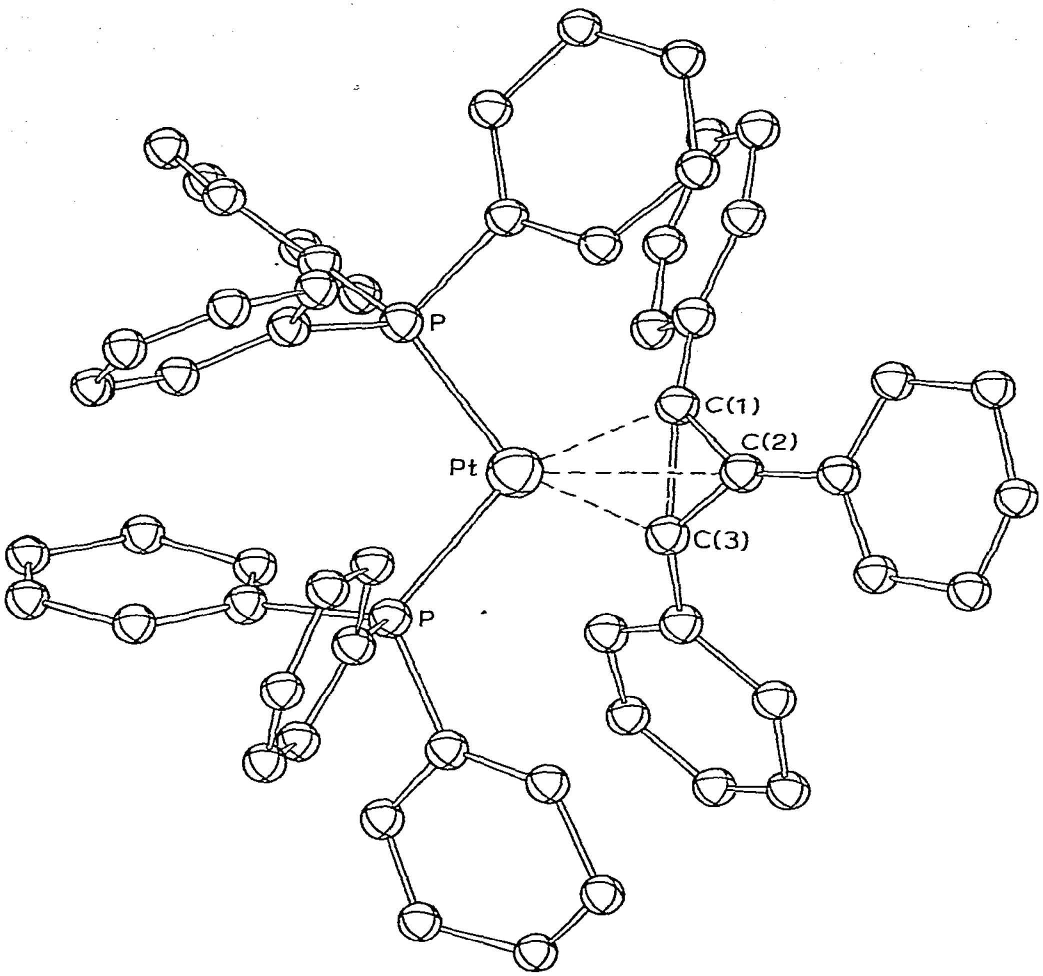
Several papers [152-154] have been concerned with the vinyl rearrangement reaction (Scheme 12). Irradiation of chloroform solutions of [Pt(Tcne)(PPh$_3$)$_2$] at 313 nm produced the percyano-vinyl complex [Pt(PPh$_3$)$_2${C(CN)=C(CN)$_2$}(CN)] [152]. Reactions of [Pt{CF$_2$=CF(CF$_3$)}L$_2$] with SnCl$_4$ gave the vinylplatinum compounds trans-[PtCl{CCl=CF(CF$_3$)}(PPh$_3$)$_2$] or [PtCl{CF=CF(CF$_3$)}DPE]. For the



(scheme12)

complexes where L = $PMePh_2$ or $AsPh_3$ and for $[Pt(C_2F_4)L'_2]$ (L' = PPh_3, $PMePh_2$ or $AsPh_3$), reaction with $SnCl_4$ caused displacement of the fluoro-olefin. Reactions of $[Pt\{\underline{trans}(CF_3)CF{=}CF(CF_3)\}L_2]$ (L = PPh_3 or $PMePh_2$, L_2 = DPE) gave the vinylplatinum complexes $\underline{cis}$-$[PtCl\{\underline{trans}(CF_3)C{=}CF(CF_3)\}L_2]$ [153]. Mechanism for both the photochemical and the Lewis acid-promoted rearrangements were discussed [152,153]. The kinetics of the rearrangement of $[Pt(CF_2{=}CFX)L_2]$ to $[PtX(CF{=}CF_2)L_2]$ (L = PPh_3, X = Cl or Br; L = $PMePh_2$, X = Cl) and the stereochemistry of the rearrangement of $\underline{cis}$- and $\underline{trans}$-$[Pt(CFCl) = CFCl)L_2]$ to $[PtCl(\underline{cis}\text{-}CF{=}CFCl)]$ and $[PtCl(\underline{trans}\text{-}CF{=}CFCl)L_2]$ (L = PPh_3 or $PMePh_2$) have been studied; the data are compatible with a mechanism involving C-Cl bond fission to give an intimate ion-pair [154]. Reactions of $[Pt(CO_3)(AsPh_3)_2]$ with some olefins and acetylenes gave $[Pt(Un)(AsPh_3)_2]$ (Un = C_2F_4, CF_2CFCF_3, C_2F_3H, Tcne or $(CF_3)_2C_2$) whereas vinylplatinum complexes were obtained with the olefins C_2F_3Cl, C_2F_3 Br or C_2Cl_4; the olefin complexes $[Pt(CF_2 = CFX)(AsPh_3)_2]$ rearranged to vinyl complexes in ethanol at 40^o [155].

Cyclopropene and methyl substituted cyclopropenes have been shown to displace ethylene from $[Pt(C_2H_4)(PPh_3)_2]$ to yield $[Pt(\text{cyclopropene})(PPh_3)_2]$. The cyclopropene ligand remains intact on complexation, as shown by X-ray structure determinations on the 3-methylcyclopropene and 1,2-dimethylcyclopropene derivatives, and can be displaced from the complexes by CS_2[156]. The cyclopropenyl complex $[Pt(C_3Ph_3)(PPh_3)_2]^+ PF_6^-$ was prepared by the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $(C_3Ph_3)(PF_6)$ [157]. An X-ray structure of this cation (59) suggested that the platinum is coordinated to a localized double bond in the cyclopropenyl ring. Selected bond parameters for (59) are Pt-C (3) = Pt-C (1) = 2.09, Pt-C (2) = 2.48, C (3)-C (1) = 1.58, C(3)-C(2) = 1.38 and C (2)-C(1) = 1.40 Å [157]. The complexes $[M(C_2H_4)(PPh_3)_2]$ (M = Ni or Pt) have been used in the syntheses of a variety of other complexes [158-163]. Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with diphenylketene or ketene-S,S-acetals caused displacement of ethylene with the formation of 1:1 adducts of $[Pt(PPh_3)_2]$ [158]. $[Ni(C_2H_4)(PPh_3)_2]$ reacted with $LiSnPh_3$ to give $Li_2[Ni(SnPh_3)_2(PPh_3)_2]$ [159] and with quinones to give $[\{Ni(PPh_3)_2\}_2(\text{quinone})]$ [160]. The platinocyclic compound (60) was obtained by the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with hexaphenylcarbodiphosphorane [161]. Reactions of $[Pt(C_2H_4)(PPh_3)_2]$ with $\underline{o}$-$(HMe_2Si)_2C_6H_4$ or $\underline{o}$-$(HMe_2Si)_2C_6H_4CH_2SiMe_2H$ gave complexes containing chelating bis(silyl) ligands; the disiloxane $(HPh_2Si)_2O$ gave a 4-membered cyclic species [162-163].



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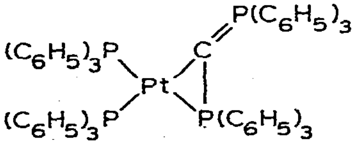
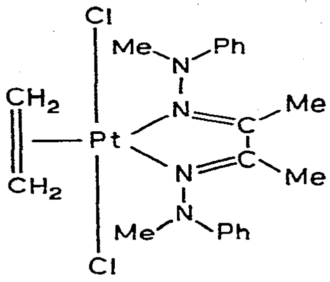


(60)

Thermodynamic parameters obtained from ^{1}H NMR studies of the equilibrium:
(6-acetoxynorbornenyl)Pd(bta) + p-$YC_6H_4CH{=}CH_2 \rightleftharpoons$ (π-p-$YC_6H_4CH{=}CH_2$)-(5-acetoxynortricyclenyl)Pd(bta) (bta = benzoyltrifluoroacetonate; Y = NO_2, F, H, OMe or NMe_2) suggested that the dominant factor affecting the thermodynamic stability of the metal-olefin bond is the olefin-π to metal-d σ- bonding component of the Dewar-Chatt-Duncanson model [164]. Chlorine core binding energies in Zeise's salt and related complexes have been determined and a correlation was found between these energies and ^{35}Cl NQR frequencies; the data is discussed in terms of the electron distribution in the metal-olefin bond [165]. ^{13}C chemical shifts of olefin carbons and ^{195}Pt — ^{13}C coupling constants have been measured for a series of complexes $K[PtCl_3(olefin)]$(olefin = C_2H_4, $MeCH{=}CH_2$, $EtCH{=}CH_2$, trans-$MeCH{=}CHMe$ or cis-$MeCH{=}CHMe$) and this data was compared with ^{13}C NMR parameters for β-methoxyalkylmercuric chlorides. It was concluded that both σ-donation and π-back donation in the Pt-olefin bond were weakened by alkyl substituents on the olefinic carbons, whereas the Hg-C σ-bond was stronger with more alkyl substituents [166]. ^{13}C NMR and IR data have been reported for the platinum complexes trans-[(p-$YC_6H_4CH{=}CH_2)PtCl_2(NC_5H_4Me)$](Y = NMe_2,OEt, Me, H, Cl, COMe or NO_2); the data indicate a significant ionic contribution to the platinum-styrene bond [167]. A reinvestigation of the ^{1}H NMR data for trans-$[PtCl_2(C_2H_4)(isoquinoline)]$ [168] showed that there is not a high-energy barrier to rotation about the Pt-N bond as had been previously suggested.

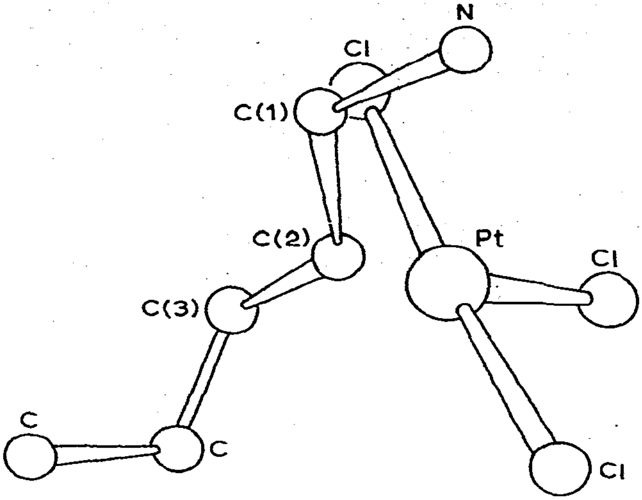
The metathetical replacement of ethylene in Zeise's salt by trimethylvinylsilane gave $K[PtCl_3(Me_3SiCH{=}CH_2)]$ which decomposed in wet acetone-d_6 to give Zeise's salt and hexamethyldisiloxane [169]. The five-coordinate platinum(II) olefin complex (61) was prepared by the reaction of Zeise's salt with biacetyl bismethylphenylhydrazone . (61) slowly decomposes with loss of ethylene in solution or at 100° in the solid state [170]. The reactions of olefins with palladium(II) chloride have been studied [171, 172]. From spectroscopic studies on the equilibria formed between 1-hexene or 1-octene and $Na_2Pd_2Cl_6$ in acetic acid, it was concluded that $Na[Pd_2Cl_5(olefin)]$ was formed at low olefin concentrations whereas $[Pd_2Cl_4(olefin)_2]$ was formed at high olefin concentrations [171]. The geometrical isomerism of complexes $[Pd_2Cl_4(olefin)_2]$ (olefin = C_2H_4, 1-pentene, cis-2, or trans-2-pentene), formed by the reaction of $PdCl_2$ with the olefin, has been studied [172].



(61)

Instability constants for platinum(II) complexes, including *trans*-[$Pt(NH_3)_3(C_2H_4)$][NO_3]$_2$ and [$Pt(NH_3)(C_2H_4)Cl_2$] have been determined by potentiometric titrations with acids in water-acetone solutions [173]. The polarographic reduction of [$Pt(NH_3)_2LCl$]$^+$ (L = C_2H_4, MeCH=CH_2, PhCH=CH_2 or CH_2=CHOH) at a dropping mercury electrode has been studied. The data suggested that the introduction of the π-ligands into the complex increased the ease of reduction of the complexes [174].

An X-ray crystal structure of the zwitterionic complex trichloro-(π-*trans*-pent-2-enylammonium)-platinum(II) (62) has been determined. The coordination around the platinum is square-planar with Pt-C(2) = 2.097, Pt-C(3) = 2.183 and C(2)-C(3) = 1.400 Å [175]. In order to obtain information concerning the bonding of the sulphurdiimine to platinum, the X-ray structure of dichloro(ethylene)di-*t*-butylsulphurdiimineplatinum(II) has been determined (63) [176]. Reaction of [$PtCl_2$(tetramethylallene)]$_2$ with ligands (L) gave the new complexes [$PtLCl_2$(tetramethylallene)] (L = RNH_2, $MeCONH_2$, NH_2CONH_2, CD_3CN, SPh_2 CD_3OD, or *p*-substituted pyridine N-oxides). The fluxional behaviour of the tetramethylallene group in these *trans*-square planar complexes was studied by ^1H NMR spectroscopy [177]. - Nucleophilic addition of amines to coordinated ethylene in complexes e.g. [$Pt(NEt_2H)Cl_2(C_2H_4)$], has yielded products containing a Pt-C σ-bond with the amine coordinated to the β-carbon atom. The reactions were reversible and limited to strongly basic secondary amines [178]. A new method has been reported for the synthesis of the π-vinyl alcohol platinum(II) complexes [Pt(Acac)ClL] (L = π-ethenol or π-propen-2-ol), by the reaction of [$Pt(Acac)Cl(C_2H_4)$] with acetaldehyde or acetone respectively, followed by protonation [179]. The structure of [Pt(Acac)Cl(π-ethenol)] (64) has been



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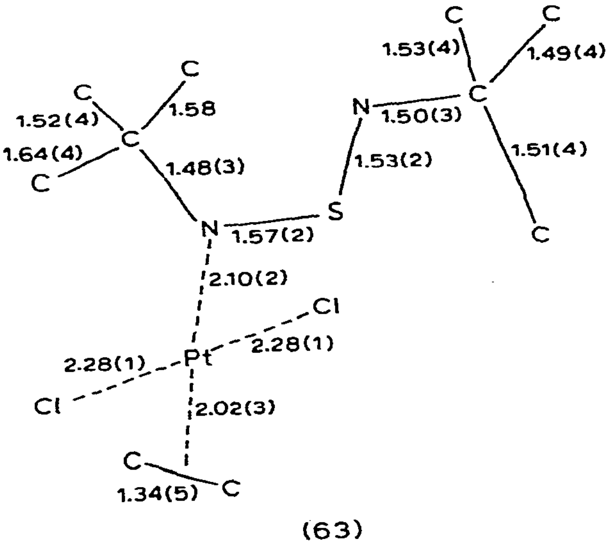
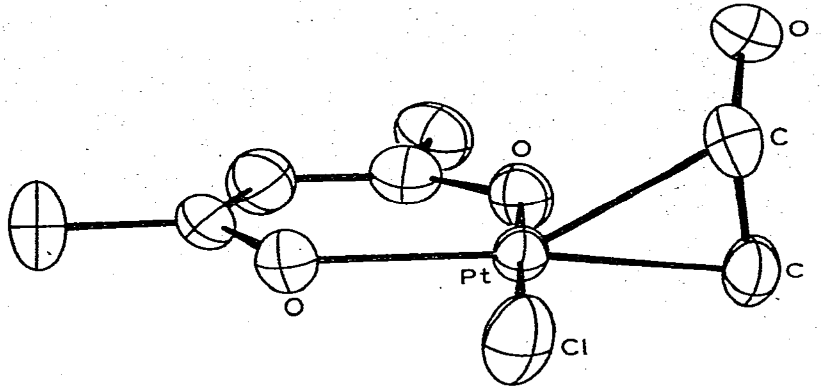


(63)

determined by X-ray crystallography and shows that the principal coordination plane of the molecule does not bisect the olefin bond (65). A bonding model, intermediate between a π-bonded olefin and a σ-bonded aldehyde complex was postulated [180]. Palladium and platinum complexes of o-vinylbenzenethiol, o-allylbenzenethiol or o-allylphenol have been



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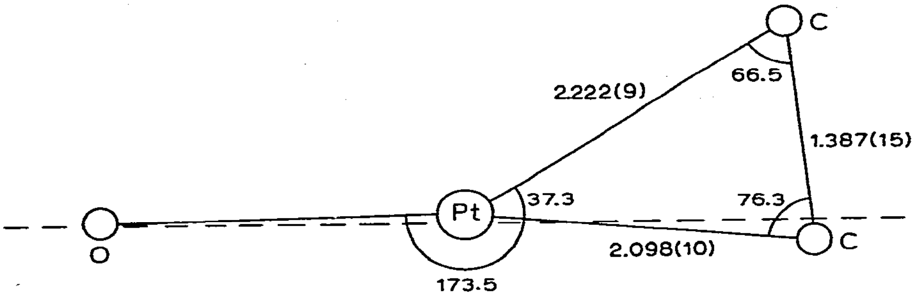
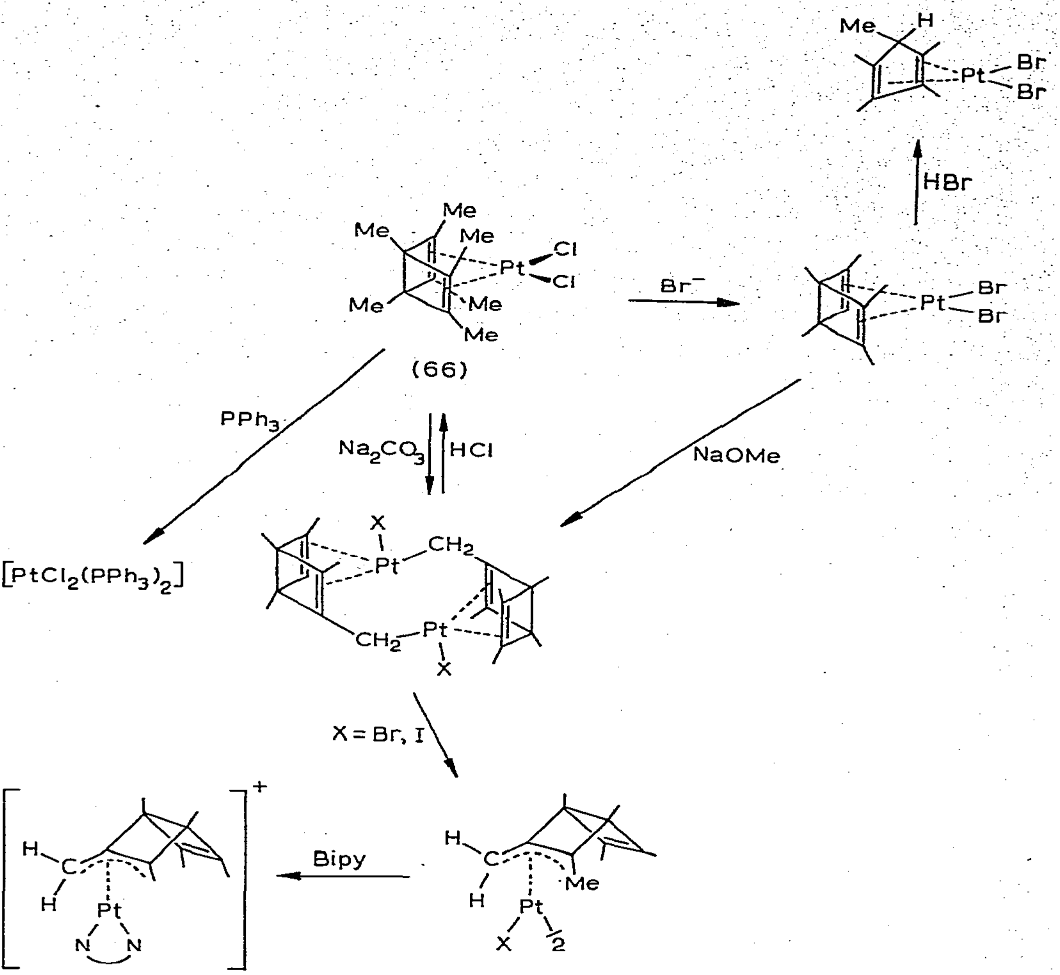


(65)

prepared. The complexes were in most cases monomeric with coordination to platinum through oxygen (or sulphur) and the double bond or solely through oxygen [181].

The synthesis of the complexes $[Pt\{C_6(CF_3)_6\}(PEt_3)_2]$ and $[Ni\{C_2(CF_3)_2\}\{P(OMe)_3\}_2]$ has been reported and their structures determined by X-ray crystallography [182]. In the platinum complex the arene group is bonded in a 1,2-hapto-mode, whereas the nickel is included in a metallocycloheptatriene ring [182]. The reaction of hexamethyl Dewar benzene with either Na_2PtCl_4 or $[Pt_2Cl_4(C_2H_4)_2]$ afforded $[PtCl_2(C_{12}H_{18})]$ (66). Some of the reactions of (66) which have been studied are outlined in Scheme 13. ^1H NMR and IR data were reported and discussed [183]. Vibrational spectra of $[PdX_2(norbornadiene)]$ (X = Cl or Br) have been reported and partial assignments made largely on the basis of Raman

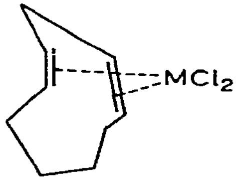


(scheme 13)

polarisation data. Palladium-olefin stretching modes were located at ca. 250 cm^{-1} [184].

The heats of reaction of a number of Rh-and Pd-COD complexes with Py, PPh_3 or $P(OPh)_3$, including the reactions $[PdCl_2(PhCN)_2] + 2B \rightarrow [PdCl_2B_2] + 2PhCN$ (B = Py, PPh_3 or COD) and $[PdCl_2(COD)] + 2P(OPh)_3 \rightarrow [PdCl_2\{P(OPh)_3\}_2]$ + COD, have been measured [185]. The relative replacement energies for the Pd compounds were $PPh_3 > P(OPh)_3 > Py \gg COD$. Several studies on the preparation of palladium-diene complexes from

[$PdCl_2(PhCN)_2$] have been reported [186-189]. Substituted cis,cis-[COD $PdCl_2$] complexes have been prepared from [$PdCl_2(PhCN)_2$] and cis-1,2-divinylcyclobutanes, or the appropriate substituted COD. The configuration of the dienes in the complexes was determined by ^1H NMR spectroscopy [186]. The [$PdCl_2(PhCN)_2$]-induced Cope rearrangement of substituted cis, trans-cyclodeca-1,5-dienes to substituted cis-1,2-divinylcyclohexanes has been studied. Complexes of the type [$PdCl_2L$] (L = substituted cis-1,2-divinylcyclohexane) were isolated [187]. Reaction of [$PdCl_2(PhCN)_2$] with cis, cis-1,4-cyclononadiene gave the complex (67) (M = Pd); no isomerisation of the diene was found to occur on complexation. The analogous Pt^{II} complex was also reported [188]. A series of complexes, [$PdCl_2$(homotropilidene)] (homotropilidene = barbaralone, dihydrobullvalene, bicyclo[5.1.0]octa-2,5-diene, bullvalene or benzobullvalene) have been prepared and characterized by ^1H NMR spectroscopy or sodium borohydride reduction of the palladium-carbon bond. The chemical reactivity and rearrangements of some of the complexes were discussed [189].



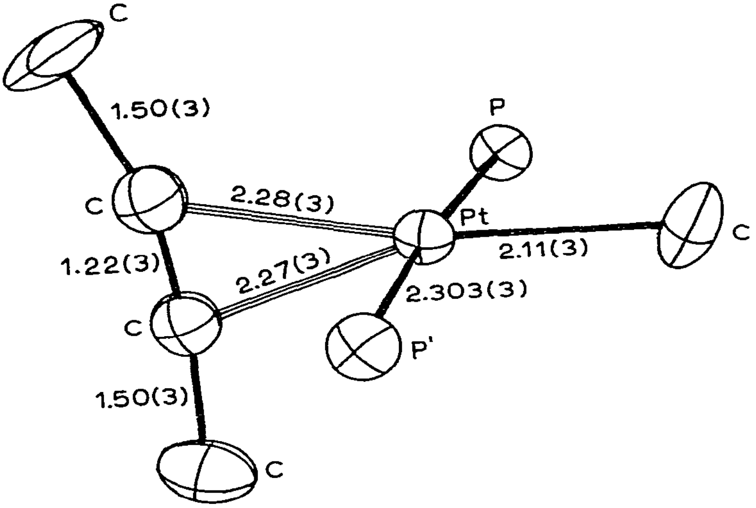
(M = Pd or Pt)

(67)

The reactions of palladium or nickel bis(1,2-ethylenedithiolate) complexes with dienes gave cycloaddition products [190, 191]. That there is no interaction between the double bond of the diene and the metal atom has been shown by X-ray crystallographic determinations on the 1:1 adducts bis(cis-1,2-diphenylethylene-1,2-dithiolato)palladium cyclohexa-1,3-diene [190] and bis(1,2-bis(trifluoromethyl)-1,2- dithiolato) nickel 2,3-dimethylbutadiene [191]. Exchange reactions of a π-vinyl alcohol group in [PtCl(Acac)(vin)] with ^{14}C-labeled CH_3CHO has been observed [192]. The Markovnikov addition of Et_2NH to π-ligands in neutral cis-Pt(II) π-complexes (e.g. [$PtCl_2(C_2H_4)P(OMe)_3$]) is controlled by electronic factors. With bulkier olefin substituents anti-Markovnikov additions were observed [193].

VII Acetylene complexes

The subject of metal-induced carbonium ions, with particular reference to organoplatinum chemistry, has been reviewed. Many of the reactions discussed involve platinum-acetylene complexes [97 refs.] [194]. The crystal structure of $[PtMe(MeC\equiv CMe)(PMe_2Ph)_2]PF_6$ has been determined by X-ray diffraction. The coordination around the platinum is essentially square planar (68) with the acetylene bond approximately perpendicular to this coordination plane [195]. The reactions of $K[Pt(Ac)X_3]$ (Ac = $Me_2C(OH)C\equiv CC(OH)Me_2$; X = Cl or Br) with amines gave as the initial products trans-$[Pt(Ac)(NHR_1R_2)X_2]$ (R_1 = H, R_2 = H, Me, Et, $CHMe_2$ or CMe_3) which then reacted with more amine to give vinyl amine complexes [196]. The structure of $[PtCl_3\{Me_2C(OH)C\equiv CC(OH)Me_2\}]$ BPh_4 , determined by X-ray crystallography, showed square planar coordination of the platinum which was bonded to the acetylene ligand only through the carbon-carbon triple bond [197].

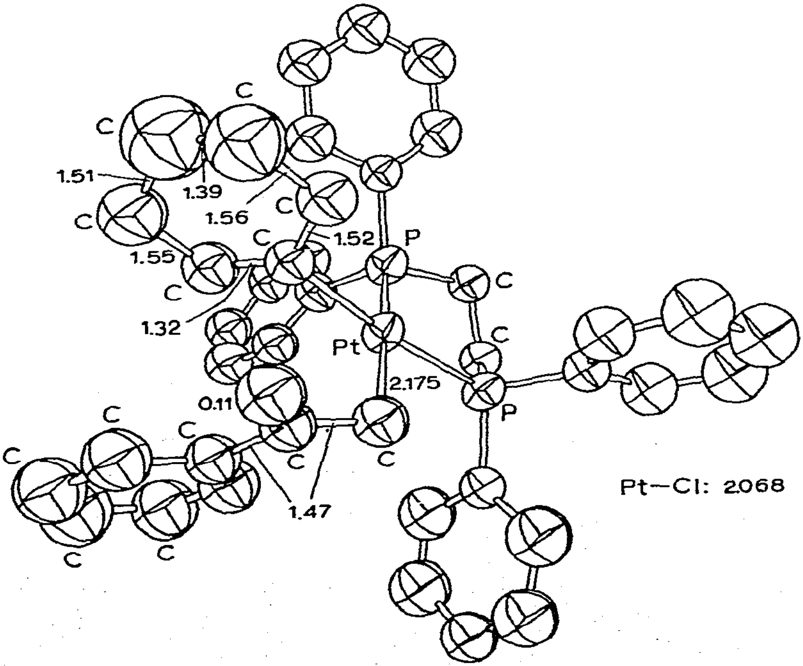


(68)

Kinetic studies on the reaction of $[Pt(PPh_3)_3]$ with $MeC\equiv CPh$ showed that both associative and dissociative pathways are important in the formation of $[Pt(PPh_3)_2(MeC\equiv CPh)]$ [198].

The reaction of palladium acetate with diphenylacetylene in methanol yielded $[Pd_2(\mu\text{-}PhC{\equiv}CPh)(\pi\text{-}C_5Ph_5)_2]$ in 90% yield. The structure of this complex was confirmed by X-ray crystallography and a mechanism for its formation suggested [199].

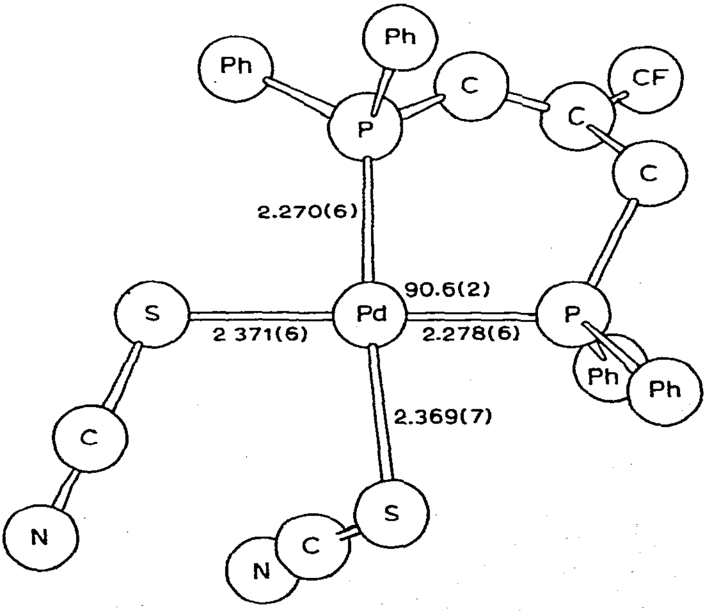
Weak protic acids (HX) readily reacted with the cyclohexyne complex, $[Pt(C_6H_8)DPE]$, yielding the air-stable Pt^{II} complexes $[PtX(C_6H_9)DPE]$ (X = CH_2NO_2, CH_2COMe, CH_2COPh, $CH(CN)Ph$, OH, OMe or *p*-MeC_6H_4O). The new compounds were characterized by IR and ^1H NMR data and also by an X-ray structure determination on $[Pt(CH_2COPh)(C_6H_9)DPE]$ (69). The long Pt-C distance (2.175 Å) of the $PtCH_2COPh$ unit suggested some ionic character in this bond [200]. Reactions of $[M(CF_3C{\equiv}CCF_3)L_2]$ (M = Pd or Pt; L = PPh_3, $PMePh_2$, PMe_2Ph or PEt_2Ph; L_2 = DPE) with CF_3COOH gave the alkenyl complexes $[M(OCOCF_3)(CCF_3{=}CHCF_3)L_2]$ [201,202]. The kinetics of the reactions of $[Pd(CF_3C{\equiv}CCF_3)L_2]$ (L = PPh_3 or DPE) with CF_3COOH, CF_2HCOOH or CCl_3COOH have been investigated and showed that the reactions of the triphenylphosphine complex followed a second order rate law [201]. HgX_2 reacted with $[Pt(CF_3C{\equiv}CCF_3)L_2]$ to give mercurated products of the type $[PtX\{CCF_3{=}C(HgCl)CF_3\}L_2]$ (X = Cl or Br; L = PPh_3 or $PMePh_2$) [202].



(69)

The reactions of Cp-nickel complexes with acetylenes have been investigated [203,204]. Cp_2Ni with $CF_3C{\equiv}CCF_3$ at 85° gave $[CpNi\{C_5H_5(CF_3CCCF_3)_2\}]$ and $[CpNiCF_3CCCF_3]_4$. The latter complex contains four chemically unique nickel atoms and a (π-nickelacyclopentadienyl)-nickel system, as shown by X-ray crystallography. Reaction of $[(CpNi)_2(CF_3CCCF_3)]$ with $CF_3C{\equiv}CCF_3$ at 90° gave the new complex $[Cp_2Ni_3(CF_3CCCF_3)_3]$ [203]. The rates of the reactions of $[CpNi(CO)]_2$ with alkynes, to give $[CpNi_2RC_2R']$ (R = H, R' = Ph or COOMe; R = R' = Et, Ph or COOMe; R = Me, R' = Ph), have been measured and the mechanisms discussed [204].

The reaction of the phosphinoacetylene $Ph_2PC{\equiv}CCF_3$ with $[MX_4]^{2-}$ (M = Pd or Pt; X = Cl or SCN) caused cleavage of the acetylene bond and gave novel complexes of type $[MX_2\{Ph_2PCH_2C(CF_3){=}CHPPh_2\}]$. The crystal structure of the $Pd(SCN)_2$-derivative (70) has been determined by X-ray crystallography [205]. Three isomers of the complex $[Pd(SCN)_2(Ph_2PC{\equiv}CBu^t)_2]$ were prepared; the structure of one of these was determined and showed a) the thiocyanate groups to be S-bonded, b) *trans*-phosphine ligands and c) no interaction between platinum and C≡C [206].



(70)

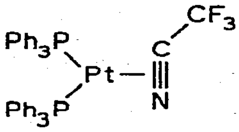
VIII Metal cyanides

IR and Raman spectra have been recorded for the complex anions $[Pt(CN)_5X]^{2-}$ (X = Cl, Br or I) in the regions 2250-2000 and 540-35 cm^{-1} and many of the fundamental frequencies have been assigned. The apical Pt-C and C-N frequencies were shifted to lower energies in the order Cl > Br > I. From IR intensity measurements it was concluded that the metal-C π-back-bonding is considerably less than in metal carbonyls [207]. The polarized single crystal absorption spectrum of $[Ni(CN)_4][N(Bu^n)_4]_2$ has been measured at 5°K and band assignments made [208]. Stopped-flow techniques have been used to study the kinetics of the reaction of CN^- with $[Ni(1,5\text{-diazacyclooctane})_2]^{2+}$. The mechanism for the formation of $[Ni(CN)_4]^{2-}$ via the stable square-planar intermediate $[Ni(1,5\text{-diazacyclooctane})(CN)_2]$ was discussed [209]. An EPR study of the irradiated diamagnetic $[Ni(CN)_4]^{2-}$ in a NaCl lattice identified two paramagnetic species characterised as low-spin d^7 and d^9 complexes and suggested to be $[Ni(CN)_4Cl_2]^{3-}$ and $[Ni(CN)_4Cl_2]^{5-}$ [210].

The reactions of bifunctional phosphonium cations with complex cyanides of Fe, Co and Ni have been studied. For Ni, the products $B^1[Ni(CN)_4].2H_2O$ and $B^2[Ni(CN)_4]$ ($B^1 = [Ph_3P(CH_2)_3PPh_3]^{2+}$, $B^2 = [Ph_3PCH_2C_6H_4\text{-}\underline{p}\text{-}CH_2PPh_3]^{2+}$) were isolated whereas iron and cobalt gave in addition, phosphonium-hydrogen derivatives. IR data were reported and thermal decomposition of some of the complexes was studied [211].

The crystal structure of the dibenzene clathrate complex $[Cu(NH_3)_2Ni(CN)_4\cdot 2C_6H_6]$ has been determined by X-ray crystallography [212]. The copper and nickel ions were linked by cyanide ions to form a polymeric two-dimensional network, the benzene molecules being trapped between the layers of the networks. ESR spectra of the magnetically dilute single crystal of $[(Cd,Cu)(NH_3)_2Ni(CN)_4\cdot 2C_6H_6]$ were recorded and interpreted [212]. The crystal structure, reflectivity spectrum and conductivity anisotropy of $[K_2Pt(CN)_4Br_{0.3}\ 2.3H_2O]$ are reviewed [213].

Reaction of $[Pt(\underline{trans}\text{-stilbene})(PPh_3)_2]$ with CF_3CN yielded the π-bonded trifluoroacetonitrile complex (71). IR spectra showed a drop of 537 cm^{-1} in ν(CN) on coordination of CF_3CN. Some reactions

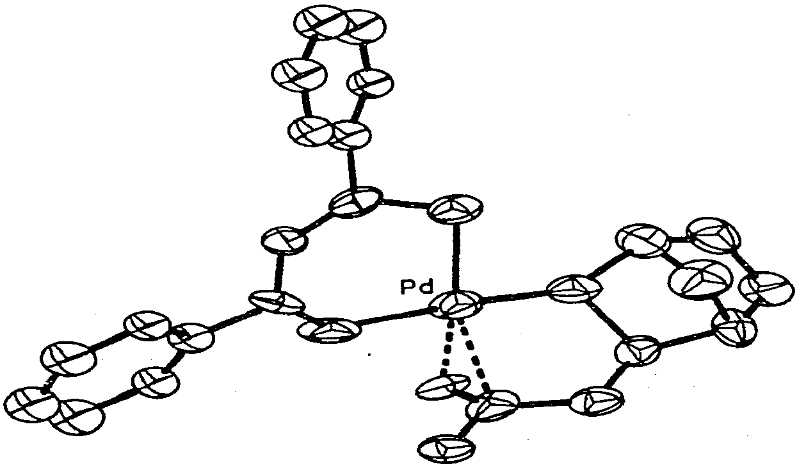


(71)

of (71) including displacement of CF_3CN by $(CF_3)_2CO$ and $PhC\equiv CPh$ were reported [214]. A ^{14}N NMR and spectrophotometric study of the exchange of MeCN on Ni^{II} and Co^{II} complexes of 2,2',2''- triaminotriethylamine and 2,2',2''-tri(N,N-dimethylamino)triethylamine has been made [215]. Reactions of $[Pd(PhCN)_2X_2]$ with carbodi-imides gave complexes $[PdL_2X_2]$ in good yields (X = Cl or Br; L = $MeN{=}C{=}NBu^t$ or $^tBuN{=}C{=}NBu^t$). On the basis of IR data, it was suggested that the carbodi-imide is coordinated through the nitrogen lone pair. The 1,2-addition of methanol to di-o-tolyl-, dicyclohexyl- and methyl-t-butylcarbodi-imides was found to be promoted by Pd^{II} [216].

IX Allyl complexes

The following crystal structures of several π-allyl complexes have been reported; (i) 3-thio-1,3-diphenylprop-2-en-1-one-1-norbornenyl-2-methallylpalladium(II) (72) [217]; (ii) (π-2-methallyl)glycinato)



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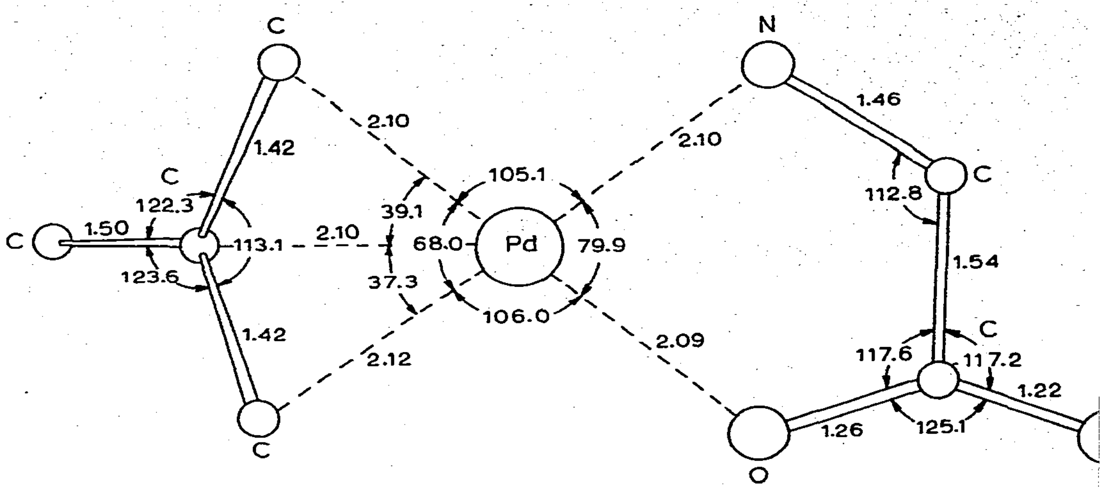
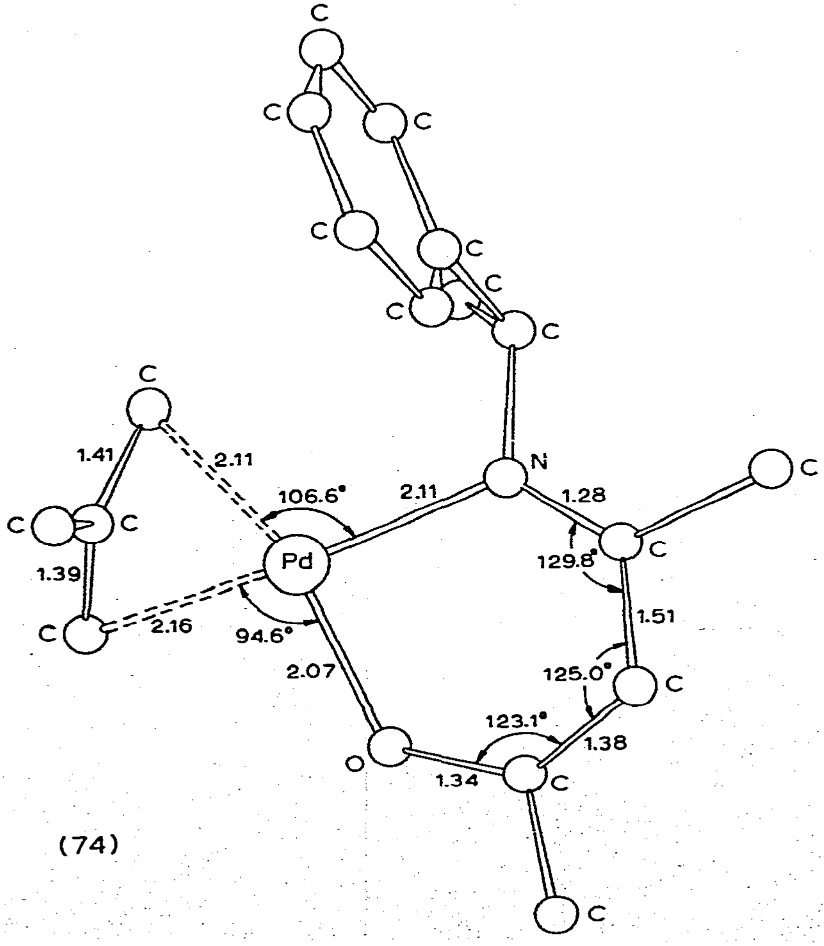

C
N
1.46
2.10
2.10
1.42
C
105.1
C
112.8
122.3
39.1
C
1.50
2.10
68.0
Pd
79.9
C
113.1
1.54
123.6
37.3
106.0
C
1.42
2.09
117.6
117.2
2.12
1.22
125.1
1.26
C
O

(73)


C
C
C
C
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C
C
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C
1.41
2.11
N
C
106.6°
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1.28
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C
Pd
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129.8°
1.39
1.51
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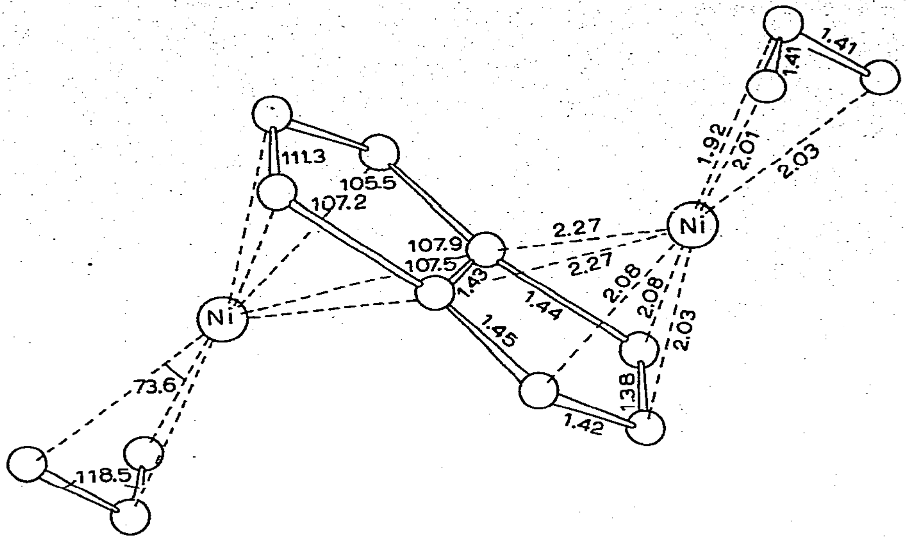
O
1.34
C
C

(74)



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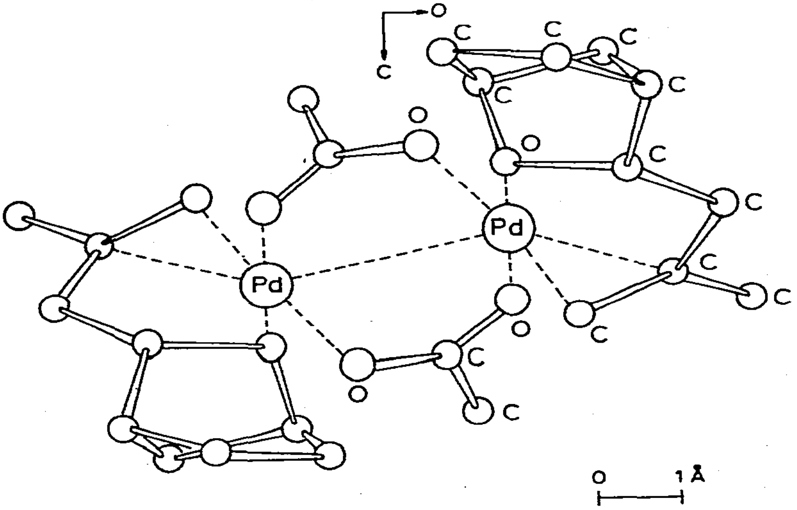
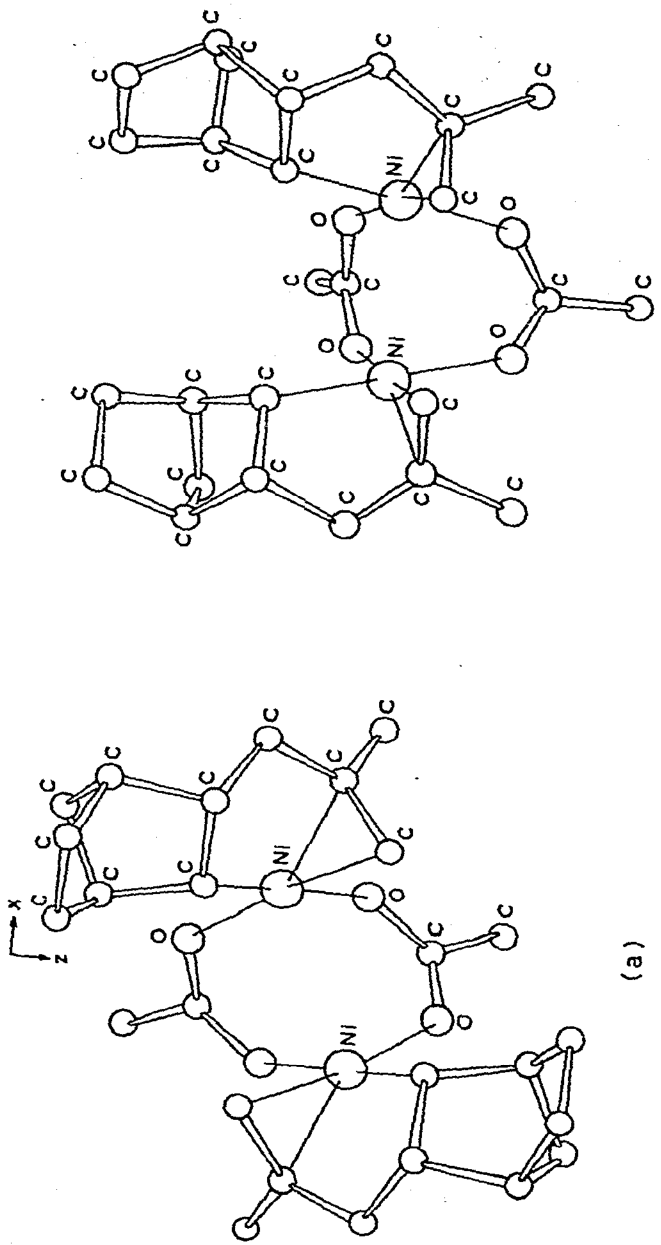


(76)

palladium(II) (73) [218]; (iii) (π-methylallyl)2-(R,S)-α-phenylethylimino-3-penten-4-olato)palladium(II) (74) [219]; (iv) [$C_8H_6Ni_2(C_3H_5)_2$] (75) [220]; (v) di-μ-acetato-bis-[(2-methylallyl-3-norbornyl)palladium(II)](76) [221] which had a distorted square pyramid structure around the Pd with the C=C vinyl bond bent 12.7° away from the normal to the



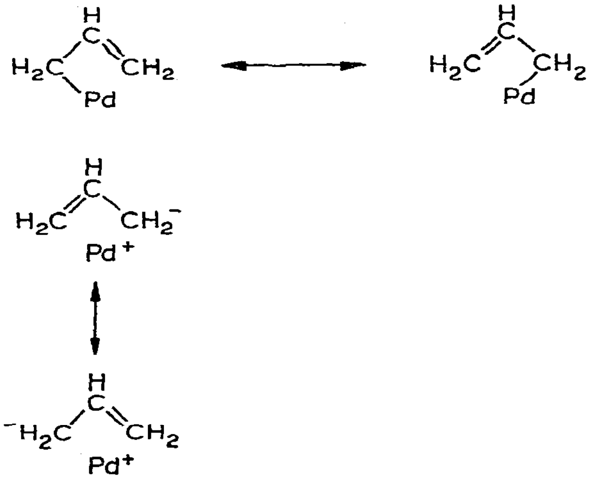
(a)

(b)

(77)

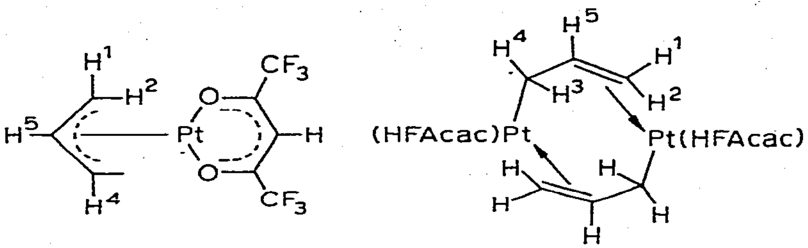
basal plane; (vi) two isomeric forms of the analogous nickel complex (77a and b) [222] in which a strong trans-structural effect was observed for the σ-bonded norbornyl carbon atom.

A detailed examination of the ^1H NMR spectra of the symmetrical allyl Pd complexes, $[PdX_2(C_3H_5)_2]$ (X = Cl or I) and $[PdY(C_3H_5)]$ (Y = Acac, Cp), has shown that the spin system should be described as AA'BB'C. ^{13}C NMR spectral shifts and $J(^{13}C-^1H)$ values were also reported, the former being interpreted in terms of the canonical forms (Scheme 14) [223]. The use of the "simpler" ^{13}C NMR rather than the more complex ^1H NMR spectra for the determination of stereochemistry in bis-phosphine metal complexes has been questioned. The cis phosphine complex $[Pd(2\text{-methallyl})(PEt_2Ph)_2][BF_4]$ exhibited a triplet for the allyl-CH_2 resonance, which, unless analysed for an AAX' system (A = ^{31}P, X = ^{13}C) could be misleading [224].



(scheme 14)

^1H NMR studies have shown that (HFacac)(π-allyl)platinum(II) exists as a monomer/dimer mixture (78) in toluene or chloroform solution. The μ-allyl dimer exhibited temperature dependent tautomerism which did not appear to involve the intermediacy of the monomer [225]. In asymmetric π-allylic β-ketoamine palladium complexes, there is an equilibrium at room temperature between diastereomers, one of the two faces of the allyl group being preferentially bound to the metal atom. Analysis of the ^1H



(78)

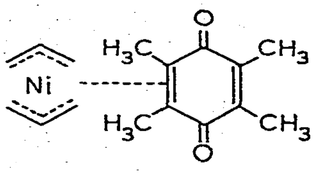
NMR spectra has allowed the assignment of the absolute stereochemistry of the coordinated allylic group provided that the stereochemistry of the chiral ketoamine is known [226].

In the reaction of $[(\pi\text{-}C_4H_7)PdCl]_2$ and Ph_3P, the time-averaged ^{13}C NMR allyl spectra above 40° were interpreted in terms of free and bonded Ph_3P. The kinetics observed from ^{31}P measurements inferred $[(C_4H_7)PdCl\ (PPh_3)_2]$ and $[(C_4H_7)PdCl\ (PPh_3)_3]$ intermediates which decomposed to $[C_4H_7PdClPPh_3]$, $[C_4H_7Pd(PPh_3)_2]^+$ and $[PdCl(PPh_3)_3]^+$ [227]. The downfield shift in the ^{13}C NMR of crotyl or allylpalladium halides in DMSO w.r.t. $CDCl_3$ has been attributed to the formation of $C_4H_7Pd(DMSO)_2^+$ [228].

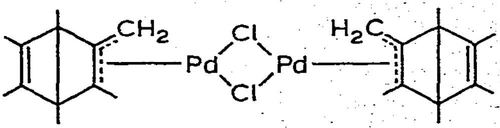
IR and Raman spectra were recorded for $[(\pi\text{-}C_3H_5)_2M]$ (M = Ni, Pd), $[(\pi\text{-methylallyl})_2Ni]$, $[(\pi\text{-}C_3H_5)_3M]$ (M = Rh, Ir) [229], $[(\pi\text{-}C_3H_5)PdX]_2$ (X = Cl, Br) and for X = Cl the perdeuterated analogue [230], and complete vibrational assignments were proposed [229,230].

A disparity between the results of an ab initio computation of the electronic wave function for bis-(π- allyl)-nickel and the photoelectron spectrum of the compound have been rationalised by taking into account the electronic relaxation upon ionization [231].

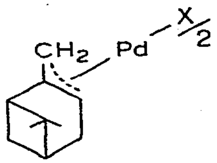
Bis-(π-allyl)nickel reacted with duroquinone (DQ) in ether, at 0° C to give $[(\pi\text{-}C_3H_5)_2NiDQ]$ (79) where only one of the DQ double bonds is coordinated to the nickel and under reflux to give $[(DQ)_2Ni]$ [232]. The improved synthesis of (80) has been achieved under the specific conditions of stirring a solution of hexamethyl bicyclo [2.2.0] hexa-2,5-diene in CH_2Cl_2 together with $[PdCl_2]_n$ at RT for 504 hours [233].



(79)



(80)



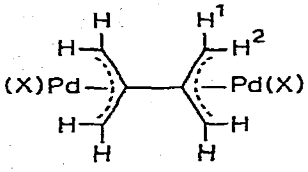
(81)

Treatment of $PdCl_2$ with spiropentane gave $[\pi\text{-}ClCH_2CH_2C(CH_2)_2PdCl]_2$ [234] and (81) was prepared from $[PdCl_2(CN)_2]$ and β-pinene [235].

Using 2,4-hexadiene as a model compound, it has been shown that dienes add stereospecifically to palladium chloride to form (1-chloroalkyl)-π-allylpalladium chloride complexes. The three diene isomers (cis-cis, cis-trans, and trans-trans) formed a pair of epimeric π-allylpalladium diastereomers one of which was formed from both the cis-cis and the trans-trans-isomers, and the other from the cis-trans diene. Excess of a strongly coordinating ligand reversed the reaction. The two diastereomers epimerized when their solutions were warmed to room temperature. This, together with a solvolysis reaction, were studied mechanistically [236].

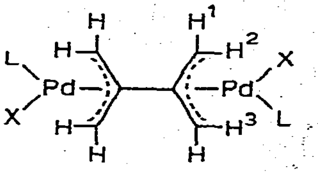
The reaction of methylenecyclobutane with $PdCl_2$ and $[Rh(CO)_2Cl]_2$ has been re-examined and the formation of the π-allylic complexes previously reported must be attributed to some spiropentane impurities. The earlier suggested structures, however, remain uncontradicted [237].

A series of dinuclear palladium(II) complexes containing a bridging 2,2 -bis-π-allyl ligand has been prepared (82a-d). Complex (82a) reacted with basic ligands to yield (83a-c), and with a variety of silver carboxylates to yield (84a-e) in which the two carboxylate ligands bridged the metal atoms. Treatment of (84 a, f, g) with pyridine or triphenylphosphine



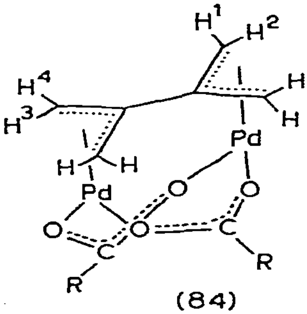
a) : X = Cl
b) : X = Acac
c) : X = Hfacac
d) : X = π-C_5H_5

(82)



a) : X = Cl; L = Py
b) : X = Cl; L = Ph_3
c) : X = Cl; L = $AsPh_3$
d) : X = O_2CCH_3; L = Py
e) : X = O_2CCF_3; L = Py
f) : X = O_2CCCl_3; L = Py
g) : X = O_2CCF_3; L = PPh_3
h) : X = O_2CCCl_3; L = PPh_3

(83)



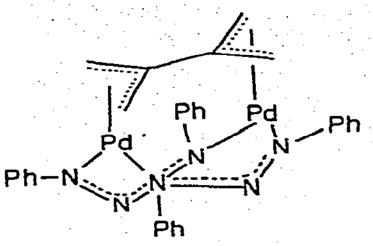
(84)

a): R = CH_3
b): R = C_2H_5
c): R = $(CH_3)_2CH$
d): R = Ph
e): R = $PhCH_2$
f): R = CF_3
g): R = CCl_3

resulted in cleavage of the carboxylate bridge to give (83d-h), while treatment of (84a) with trichloroacetic or trifluoroacetic acid effected carboxylate bridge replacement producing (84f,g). Similarly, reaction of (84a) with 1,3-di-phenyltriazene yielded (85) with the liberation of acetic acid [238].

The reaction of $TiCl_4$ with $[(\pi\text{-}C_3H_5)_2Ni]$ in pentane at -80° produced $[(\pi\text{-}C_3H_5)_2NiTiCl_4]$ and $[(\pi\text{-}C_3H_5)NiCl\ C_3H_5TiCl_3]$ [239].

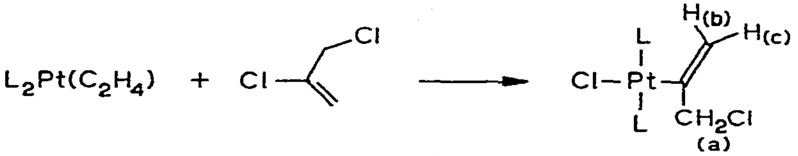
A method for the conversion of conjugated dienes into allenes via allyl Pd and Pt complexes has been reported. Thus, the reaction of choro-



(85)

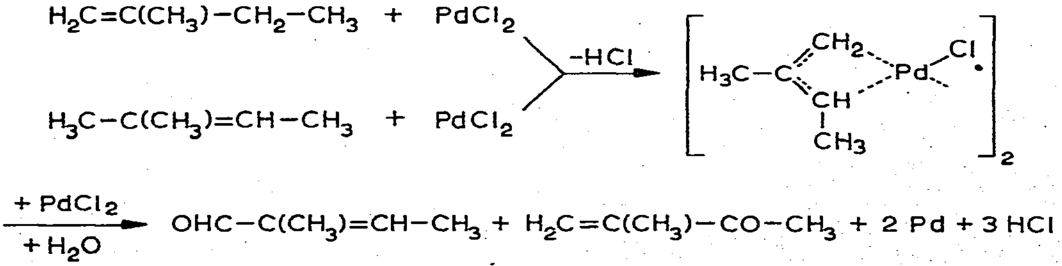
prene, $[Pd(PPh_3)_2Cl_2]$ and methanol produced 1-methoxy-methyl-2-chloro-π-allylpalladium chloride which reacted with an excess of tri-n-butylphosphine to give 4-methoxy-1,2-butadiene. An analogous route via platinum was unsuccessful, leading instead to insertion of the platinum into the vinylic carbon-chlorine bond to give (86) [240].

The reaction of Pd(II) with branched olefins produced a mixture of π-allylic complexes with initial isomerization of the double bond occurring.



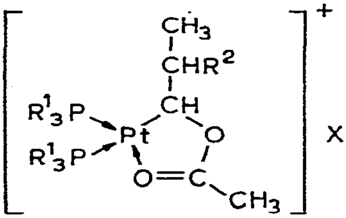
(86)

In branched olefins without substituents at the double bond isomerisations occurred at the thermodynamically most favoured position at the branching point of the olefin which then formed the π-allylic complexes.
Oxidation of these π-allylic complexes produced unsaturated carbonyl compounds in which oxidation occurred at the ends of the allylic system (Scheme 15) [241].



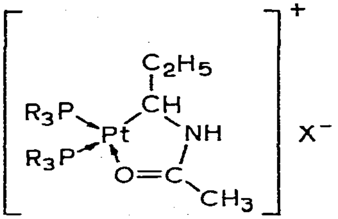
(scheme 15)

Insertion and migration of the C=C bond has been found to occur in the reactions of some allylic acetates and N-allylacetamide with the platinum hydrides trans-$[PtH(PR_3)_2(acetone)]^+$ and trans-$[PtH(PPh_3)_2(ClO_4)]$, to give (87) and (88) [242].



IVa, $PR^1_3 = PPh_2Me, R^2 = H, X = BF_4$
b, $PR^1_3 = PPh_2Me, R^2 = CH_3, X = BF_4$
c $PR^1_3 = PPh_3, R^2 = H, X = ClO_4$

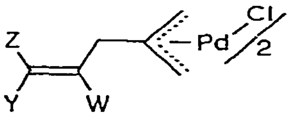
(87)



Va, $PR_3 = PPh_2Me, X = BF_4$
b, $PR_3 = PPh_3, X = ClO_4$

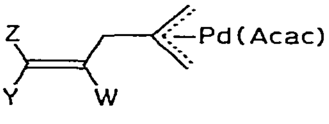
(88)

Insertion of allene, methylallene, 1,1-dimethylallene and 1,3-dimethylallene into the allylic-palladium bonds in the complexes $[(\pi\text{-All})PdX]_n$ (X = Cl, n = 2; X = Acac, HFacac, n = 1) produced the series (89 and 90). A mechanism was proposed in which the 1,2-diene coordinates to palladium via its less substituted olefin function generating a σ-allylic intermediate (Scheme 16) [243]. Addition of the strained olefins norbornene, norbornadiene, benzonorbornadiene, and bicyclo [2.2.2] octene to $[(\pi\text{-All})M(HFacac)]$ (M = Pt, Pd) complexes gave enyl products via a reversible $[(\sigma\text{-allyl})(\pi\text{-olefin})M(HFacac)]$ intermediate. The insertion reaction occurred at the least substituted terminal allylic-metal bond [244].



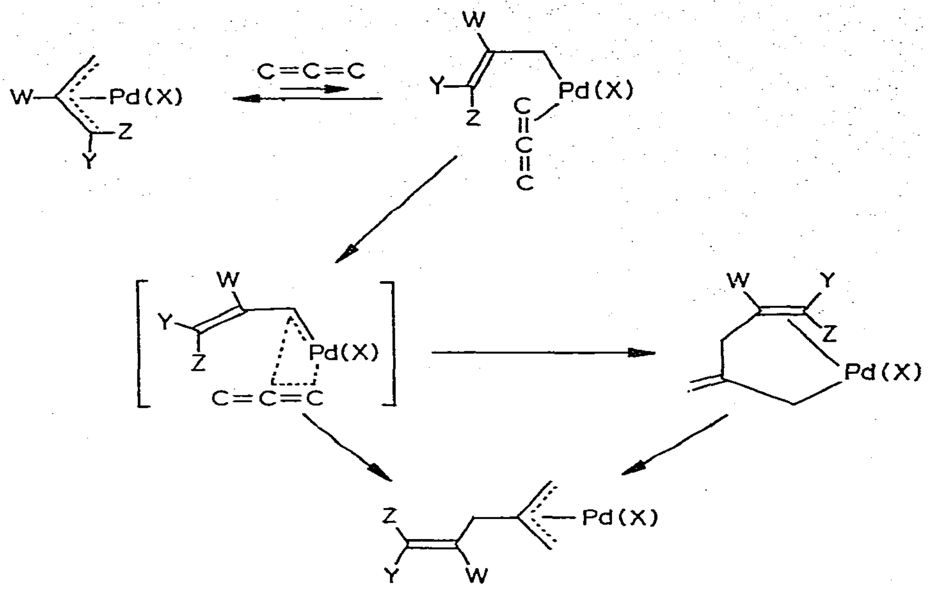
W = Y = Z = H
$W = CH_3; Y = Z = H$
$W = Z = H; Y = CH_3$
$W = H; Y = Z = CH_3$

(89)

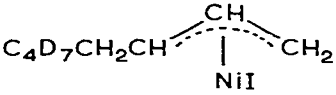


W = Y = Z = H
$W = CH_3; Y = Z = H$
$W = Z = H; Y = CH_3$
$W = H; Y = Z = CH_3$
$W = Z = H; Y = COOCH_3$

(90)



(scheme 16)


$$C_4D_7CH_2CH\cdots\underset{\overset{|}{NiI}}{\overset{CH}{}}\cdots CH_2$$

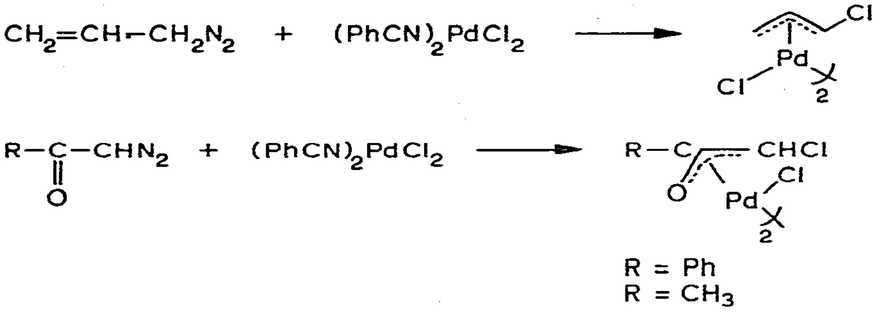
(91)

The reaction of butadiene with [(π-$CD_3CD{=}CDCD_2$)NiI] gave 100% (91). The insertion reaction with other olefins was reported [245].

A kinetic study of the reaction between $PdCl_4^{2-}$ and 1,3-cyclohexadiene in the presence of methanol suggested a mechanism in which a π-1,3-cyclohexadiene intermediate, having only one double bond coordinated to the metal, was formed. Nucleophilic attack from outside the coordination sphere of the metal on the coordinated double bond, was the rate determining step leading to the methoxy-π-allyl product [246].

The kinetics of the oxidation of [(π-C_3H_5)PdCl]$_2$ by p-benzoquinone has been studied as a function of [H^+] and [Cl^-]. Oxidation is first order in π-allyl complex and p-benzoquinone [247]. Pyrolysis of π-crotyl, pentenyl or cyclohexenylnickel chlorides in various solvents has been investigated, and the initial reactions suggested to be cleavage of the Ni-C bond to form radicals [248].

Synthesis of oxo-π-allyl- and π-allyl palladium complexes via diazoketones and vinyldiazomethanes has been reported (Scheme 17) [249].



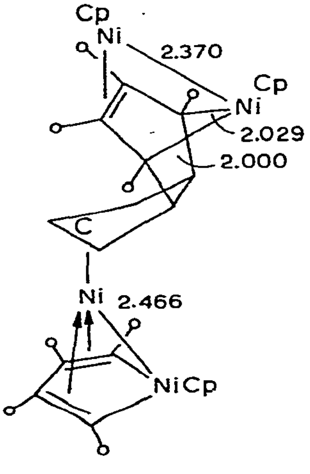
(scheme 17)

^{1}H NMR and ^{13}C NMR spectroscopy and molecular weight studies of a series of hepta-2,6-dienylpalladium(II) carboxylate complexes have shown the existence of an equilibrium between trihapto dimeric complexes with bridging carboxylates and pentahapto monomeric complexes with terminal carboxylate ligands. These systems provide models for the π-allylnickel carboxylate catalysed cis-1,4-polymerization of 1,3-butadiene [250]. The direction of isoprene polymerization has been shown to be a function of the nature of the metal and of the substituents on the allylic ligand. The presence of acidic ligands in the π-allylic complexes of Zr, Cr, Mo, and Co, contributes to 1,4-addition, and for π-allylic nickel complexes, increases the selectivity towards cis-1,4 structure formation [251].

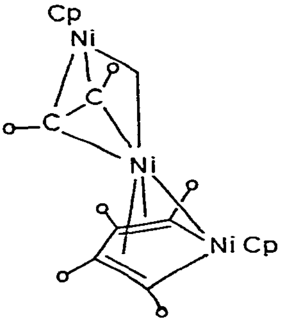
The reaction between $[Ni\{P(OPh)_3\}_4]$, isoprene, and CCl_4 led to the formation of an orange π-allylic Ni(II) derivative without free-radical polymerization of the diene as is the case of the reactions with styrene and methyl methacrylate. A mechanism was proposed, based on kinetic data, involving an initial step of ligand exchange between diene and phosphite followed by a redox reaction with CCl_4 [252].

The comparative chemical characteristics of metallocenes of cobalt and nickel, containing 200 references is reviewed [253].

Complete ligand field perturbation calculations, including spin-orbit coupling, have been carried out for $d^1(d^9)$,$d^2(d^8)$ and $d^3(d^7)$ configurations in axial C^*_α symmetry using the strong field formalism. The application of the results to the interpretation of the d-d electronic spectra of metal sandwich complexes is discussed with particular reference to the vanadium, cobalt and nickel metallocenes [254]. A series of communications reporting the formation reactivity and structural determinations of metallocenes have appeared. $CF_3C \equiv CCF_3$ and [Cp_2Ni] gave the new products $C_6(CF_3)_6$, [$CpNi\{C_5H_5(CF_3CCCF_3)_2\}$][$CpNiCF_3$ $CCCF_3$]$_4$ (92) and [$Cp_2Ni_3(CF_3CCCF_3)_3$] (93). The structure of (92) was verified

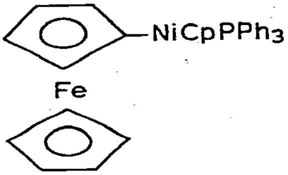


(92)

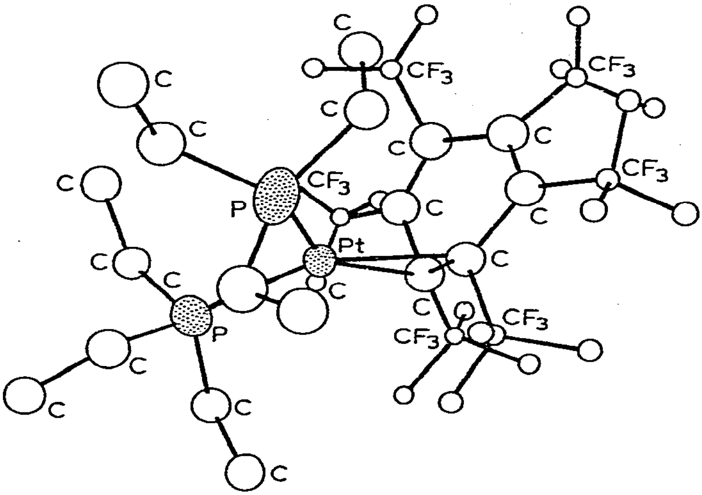


(93)

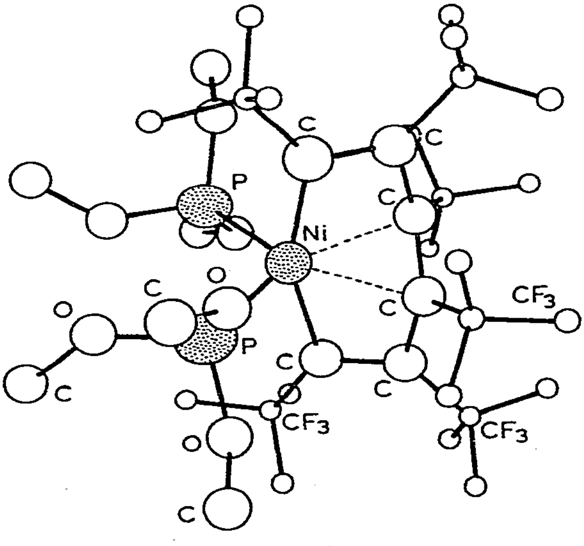
crystallographically [255]. Treatment of [Cp_2Ni] with $P(OR)_3$.(R=Me,Ph) in CCl_4 gave [Cp Ni Cl $P(OR)_3$] [256] whereas [Cp Ni Cl PPh_3] and lithiated chloroferrocene or [$LiC_5H_4Mn(CO)_3$] produced (94) and [$CpNiPPh_3C_6H_4Mn(CO)_3$] respectively [257]. Electronic and ^{31}P NMR spectra of [$CpNiX(PPh_3)$] (X = Cl,Br,I,NCO,NCS, NO_2, CN,$SnCl_3$,$SnPh_3$,$PbPh_3$ alkyl, aryl) have been recorded and a spectrochemical series interpreted [258]. The rate constants for ^2H and ^3H exchanges have been determined for systems of [Cp_2Ni] with Me_3COH-Me_2SO-Me_3COK and $O(CH_2CH_2OH)_2$-Me_3COH-Me_3COK. A


NiCpPPh$_3$
Fe

(94)

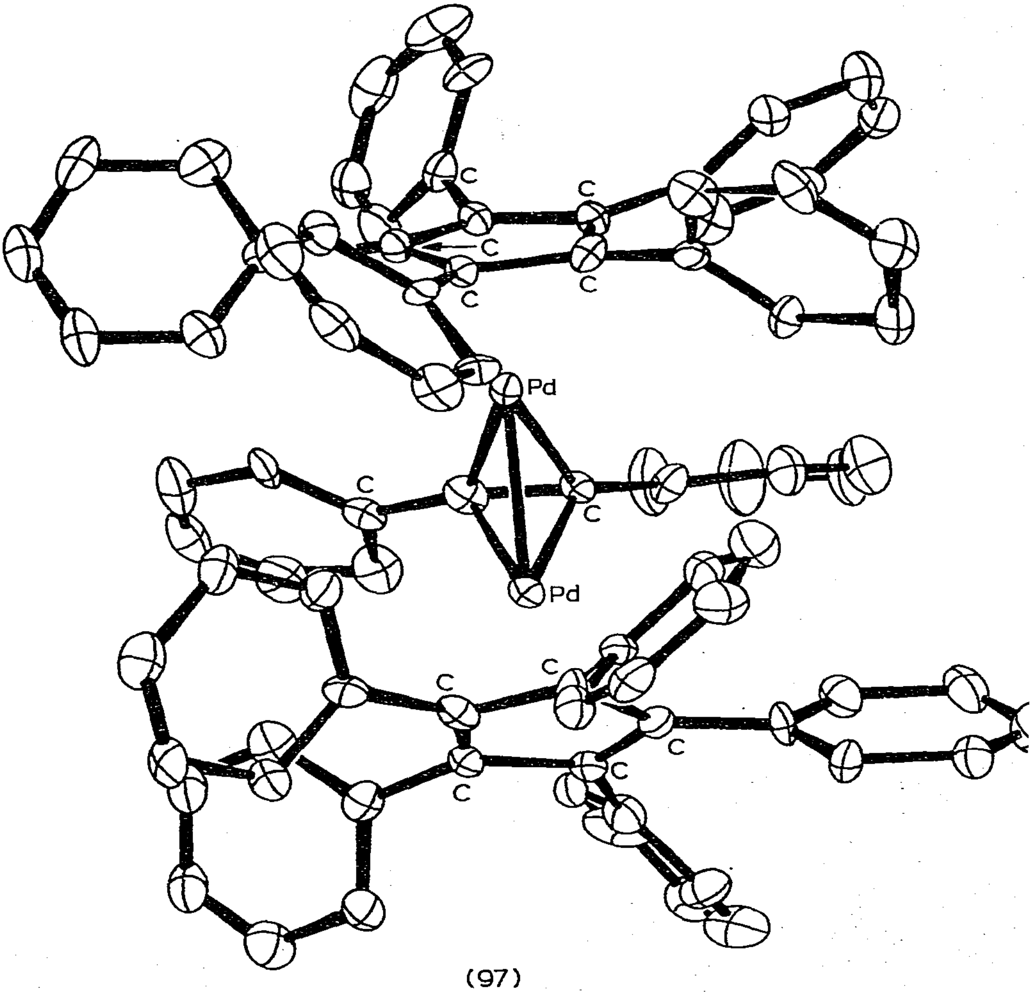

C
CF$_3$
CF$_3$
C
C
C
C
C
C
P
CF$_3$
C
C
CF$_3$
C
Pt
C
C
C
C
C
P
C
CF$_3$
CF$_3$
C
C
C
C

(95)


C
C
P
C
Ni
C
CF$_3$
C
C
P
C
C
C
CF$_3$
CF$_3$
C

(96)

comparison of rates with $[Cp_2Fe]$, Ph_3CH and Ph_2CH_2, found that the kinetic acidity increased in the order $Cp_2Fe < CpMn(CO)_3 < Ph_2CH_2 < Ph_3CH < Cp_2Ni$ [259]. The reaction of $[Pt(PEt_3)_3]$ with $(CF_3)_6C_6$ has afforded $[Pt\{C_6(CF_3)_6\}(PEt_3)_2]$ (95) in which the Pt atom was found crystallographically to be bonded to two adjacent carbon atoms of the non-planar benzene ring [260]. The corresponding nickel analogue and $CF_3C \equiv CCF_3$ gave $[L_2Ni(CF_3CCCF_3)_3]$ ($L = P(OMe)_3$, $AsMe_2Ph$) shown to be (96) ($L = P(OMe)_3$) from initial X-ray data [260]. Additions of tolan and $MeCOOC{\equiv}CCOOMe$(d=dma) to palladium acetate and $[Pd(PhCN)_2Cl_2]$ respectively produced $[(\mu PhC{\equiv}CPh)(\pi\text{-}C_5Ph_5)_2Pd_2]$ (97 [261] and $[Pd\{C_5(CO_2Me)_4(CO_2Me)C(CO_2Me)Cl\}Cl]_2$ [262], the latter of which



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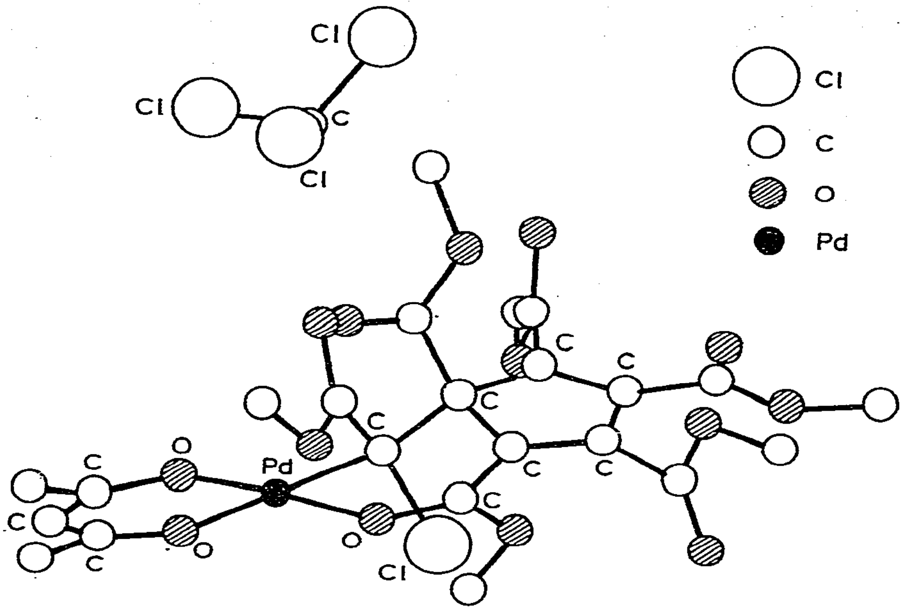
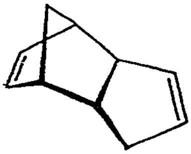
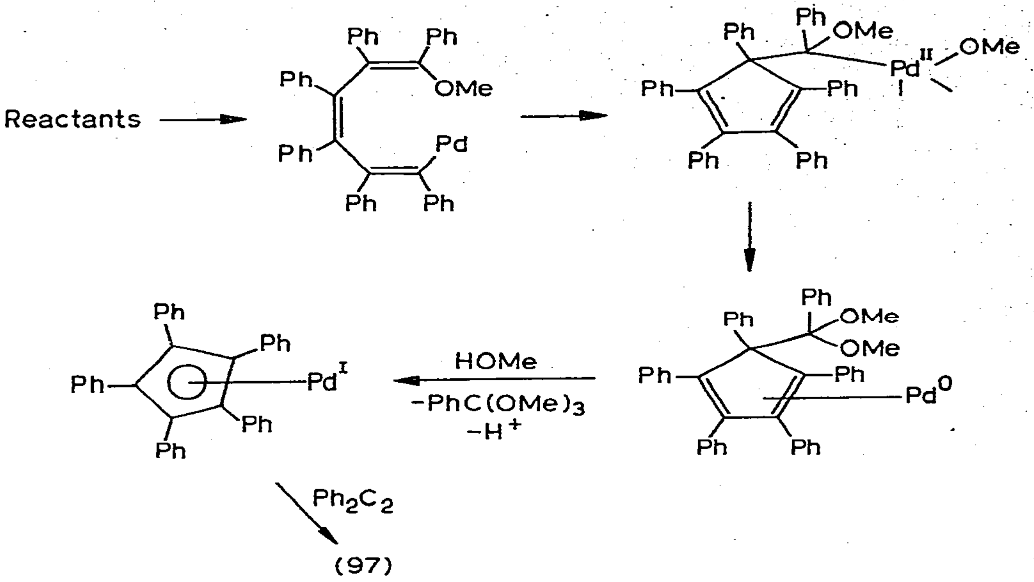


(98)

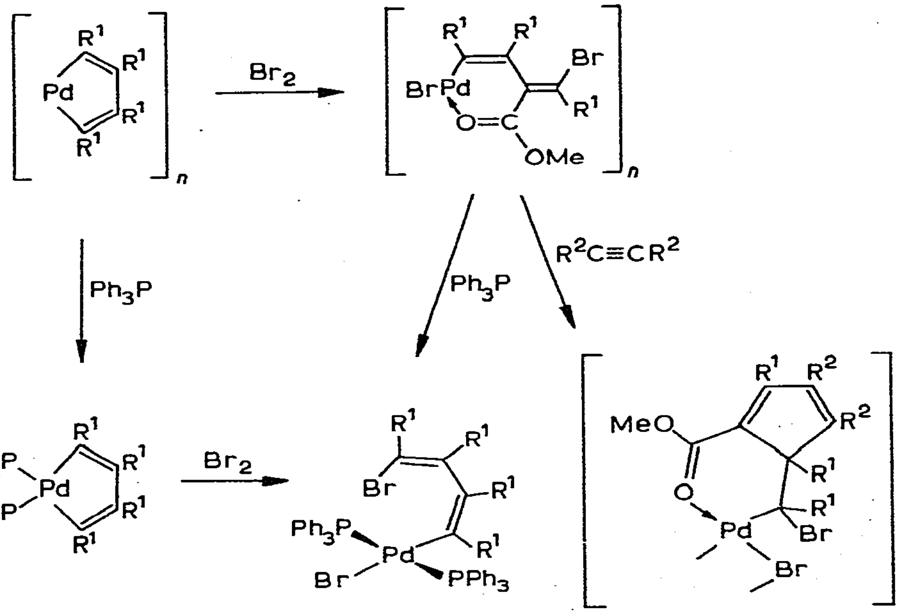


(99)

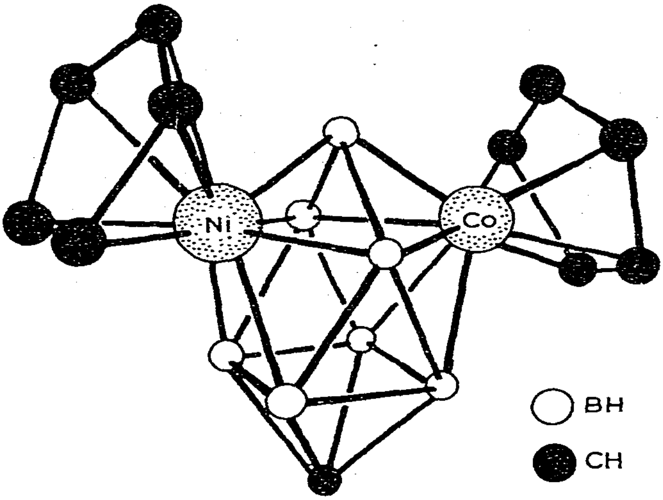
is readily converted to $[Pd\{C_5(CO_2Me)_4(CO_2Me)C(CO_2Me)Cl\}Acac]$ (98) on treatment with TlAcac. Complex (97), which is formally Pd(I) and the first example of an acetylene bridging palladium is structurally analogous to the corresponding nickel product, and to postulated to be formed as in (Scheme 17). Another route to (98) is given in Scheme 18 . The absolute configuration of *endo*-dicyclopentadiene (99) has been determined *via* the crystal structure of $[(+)\text{-}(\text{endo-dicyclopentadiene})PtCl_2]$ (263). Treatment of a sodium naphthalide reduced solution of $[Me_4N][CpCo^{III}(\pi\text{-}CB_7H_8)]$ with NaCp and $[NiBr_2,2C_2H_4(OMe)_2]$ produced $[CpCo^{III}(\pi\text{-}CB_7H_8)Ni^{IV}Cp]$ (100) isolated in at least four isomeric forms [264]. Structural analysis of $[(Me_4C_4)(CF_3)Pt(PMe_2Ph)_2]SbF_6$ (101) indicates a distorted tetrahedral geometry around the Pt atom. Parameters obtained from 2866 observed



(scheme 17)



(scheme 18)



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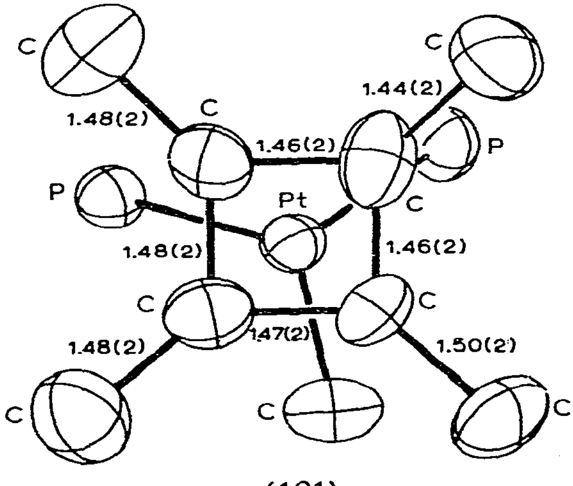
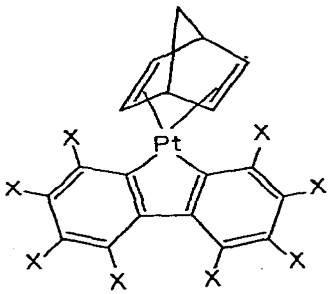
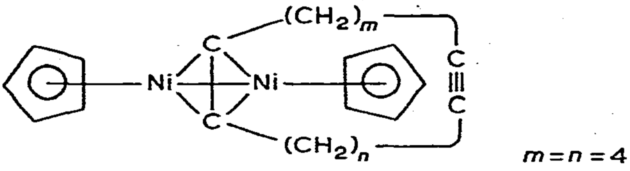


(101)

reflections (R = 0.049) were Pt-P = 2·365(4)Å, Pt-C(CF$_3$) = 2.103(16)Å and C-C(C$_4$Me$_4$) = 1.47(2)Å [265]. Certain alkyl groups in [CpNi(PPh$_3$)R] have been observed to have interesting dynamic NMR properties (Cf. R = CH$_3$, SiMe$_3$,CH$_2$Ph,CH$_2$CH$_2$CH=CH$_2$). To account for the observed low temperature spectra the possibility of diastereotopism from restricted rotation about P-aryl bonds leading to a barrier between enantiomeric conformations which have their origins in H-H repulsions has been initially investigated [266]. Low yields of (102) were obtained from 2,2'-dilithiobiphenyl or 2,2'-dilithiooctafluorobiphenyl and $C_7H_8PtCl_2$[267]. When a propionic anhydride solution of $[Ni_2(C_5H_4R)_3]BF_4$ or $[Ni(C_5H_4R)_2]$ is acidified with HBF_4 in the presence of dienes, the products $[(C_5H_4R)Ni(diene)]$ (R = H, Me, *t*-C_4H_9; diene = norbornadiene, 1,5-COD) result [268]. Bi- and tetrametallic derivatives of macrocyclic alkadiynes of formulae [alkadiyne $(NiCp)_x$](x = 2 (103), 4 (104); alkadiyne = 1,7-cyclododecadiyne) have been characterised. With 1,7-cyclotridecadiyne, 1,7-cyclotetradecadiyne, 1,8-cyclotetradecadiyne and 1,8-cyclopentadecadiyne only (104) is formed [269]. The salt $[CpNi(PBu_3)_2]Cl$ has been utilised as a precursor for the formation of the neutral complexes $[CpNi(PBu_3)L]$ (L = XC_6H_4Y; X = Se,Te, Y = H,*p*-CH_3O, *p*-CH_3, *p*-Cl, *m*-CF_3; X = Se, Y = *m*-Cl, *p*-CH_3CO [270]; L = $SC(S)CH_2C_6H_5$ [271]). Similar compounds prepared were $[CpNi(PPh_3)X]$ (X = $SnMe_3$, $GePh_3$, $SnPh_3$, $PbPh_3$, CN, NCS, NCO, NO_2, CH_2CMe_3) and $[CpNi\{Fe(CO)_2\}PPh_3].C_6H_6$. $[CpNi(PPh_3)SnPh_3)]$ and I_2 gave $[CpNi(PPh_3)I]$ whereas the corresponding germanium and lead analogues gave $[CpNi(PPh_3)Ph]$ [272]. Treatment of $[CpNiPBu_3SC(S)CH_2C_6H_5]$ with HCl gave $[CpNiSC(S)C_6H_5]$ [271]. $[CpNi(Ph_2PCH_2PPh_2)SC_6H_5]$ and $[CpNi(PPh_2CH_2PPh_2)CN]$ can act as bidentate ligands forming $[CpNi\text{-}\mu\text{-}X\text{-}\mu\text{-}(Ph_2PCH_2PPh_2)Mo(CO)_4]$ (X = SPh,CN) with $[C_7H_8Mo(CO)_4]$[273]. A range of complexes of the type $[CpNi(MR_3)L]$ (R = halide, alkyl, aryl; M = Si,Ge,Sn; L = R_3P, R_3As, $C_6H_{11}NC$) are reported [274]. The reactions of Cp_2Ni with thiols RSH gave the derivatives $[CpNiSR]_2$ [275], whereas with $[(DPE)NiX_2]$, $[Cp_2Ni]$ is converted into monomeric or dimeric products depending upon X. For X = Cl, Br the novel ionic salt $[CpNiDPE]_2[NiX_4]$ is obtained, but with X = I, CN,



X = H 10 %
X = F 3.6 %
(102)



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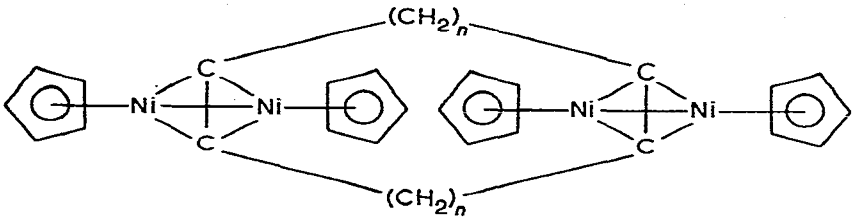

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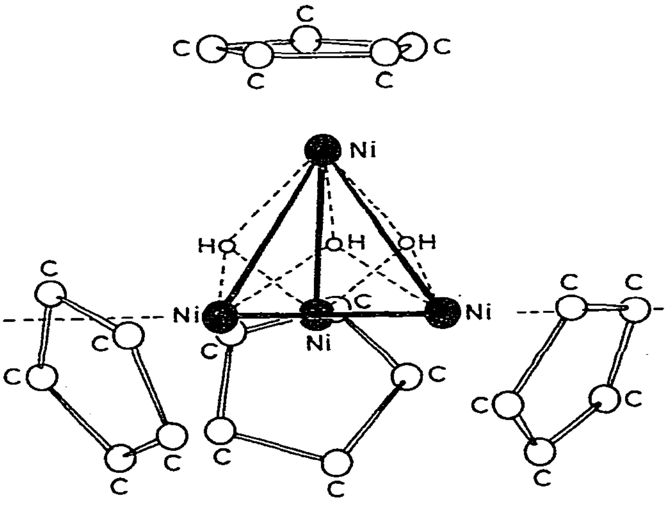
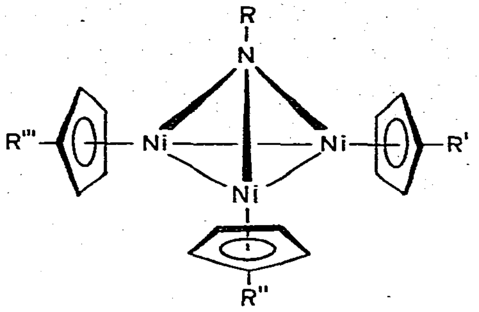


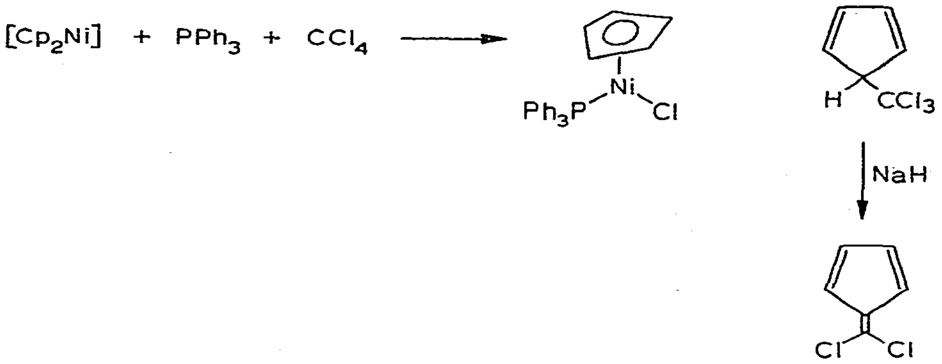
(105)

$[CpNiX]_2$-μ-DPE are the sole isolable products [276]. Evidence has been obtained from IR spectroscopy for the reversible production of the ion pair $CpNi^+NO^-$ by photolysis of [CpNiNO] in an argon matrix at 20K [277]. Binuclear secondary ions have been observed in the mass spectrum of [CpNiNO]. In the presence of donor molecules, L, additional ion molecule reactions occur to form [CpNiL], and even hexane or cyclohexane



R	R'	R''	R'''
C_6H_5	H		
C_6H_5	C_6H_5	H	
C_6H_5	C_6H_5	C_6H_5	H
C_6H_5	C_6H_5	C_6H_5	C_6H_5
t-Bu	H	H	H
t-Bu	*t*-Bu	H	H

(106)



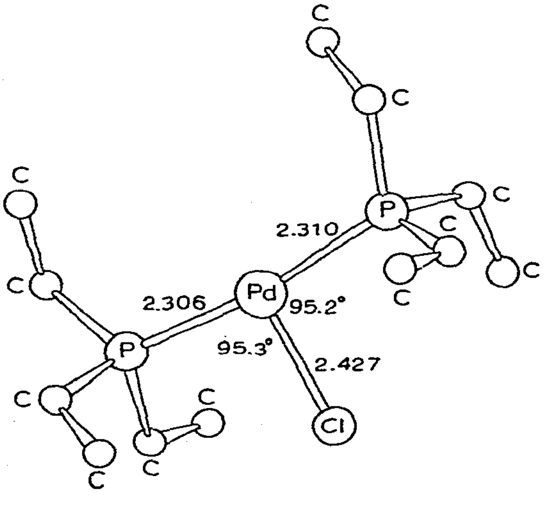
(scheme 19)

produced $[CpNi(ene)]^+$ (ene = hexene, cyclohexene) [278]. Reduction of [CpNiNO] with $LiAlH_4$ + $AlCl_3$ in THF afforded $[Cp_2Ni]$ and a paramagnetic complex assigned as $[CpNi]_4H_3$ (105) from mass spectral, IR and preliminary X-ray data [279]. Bridging organonitrenes of formula$[\{CpNi\}_3\ NR]$(106) are the resultant products obtained from the reactions of LiR(R = Ph, t-Bu) with [CpNiNO] in THF or ether [280]. Addition of PPh_3 to $[Cp_2Ni]$ in the presence of CCl_4 produced (trichloromethyl) cyclopentadiene which was dehalogenated to 6,6-dichlorofulvene (Scheme 19). Analogous reactions with CBr_4 and (trichloromethyl) benzene occured, and 3-bromopropene gave allylcyclopentadiene [281]. The synthesis of a series of platinum metallocycles, together with an examination of their thermal stability is reported. Two features of the data are significant; (i) the platinocycles are much more stable thermally than platinum alkyls and (ii) the products of decomposition suggest that their broad mechanism of formation resembles that established for simple alkyls [282].

XI Metal-Hydrides

A review on transition-metal hydrides containing 287 refs. has appeared [283].

The structure of $[(Et_3P)_2Pd(H)Cl]$ has been resolved crystallographically. The long Pd-Cl bond length (relative to Pd Cl_4^{2-}) is ascribed to the strong trans effect of the hydride ligand (107) [284]. Recent suggestions that the broadening of the hydride resonance in the NMR spectra of trans-$[PtH(NCS)L_2]$ (L = phosphines, Et_3As) is not due to interaction with the ^{14}N nucleus has now been refuted [285]. The first stable dihydride complexes of platinum(II) and palladium II, trans-$[PtH_2L_2]$ (L = PCy_3, PCy_2-i-Pr, PCy_2Et) (Cy = cyclohexyl), and trans-$[PdH_2(PCy_3)_2]$ have been prepared by the reaction of $[M(Acac)_2]$ (M = Pd, Pt) with trialkylaluminium in the presence of bulky tertiary phosphine ligands. A trans-square planar structure was proposed on the basis of IR and ^1H NMR evidence. $[PtH_2(PCy_3)_2]$ reacted with CCl_4 to produce equimolar amounts of the mono-hydride species $[Pt(H)Cl(PCy_3)_2]$ and $CHCl_3$ [286]. $[Pt(PPh_3)_2H(p\text{-}CH_3C_6H_4N\text{-}N{=}N\text{-}C_6H_4\text{-}CH_3\text{-}p)]$ was prepared from cis-$[PtCl_2(PPh_3)_2]$ and p-$CH_3C_6H_4NH\text{-}N{=}N\text{-}C_6H_4CH_3$-p in the presence of $H_2NNH_2H_2O$, and is in dynamic equilibrium at RT probably via a cyclic intermediate [287]. The addition



(107)

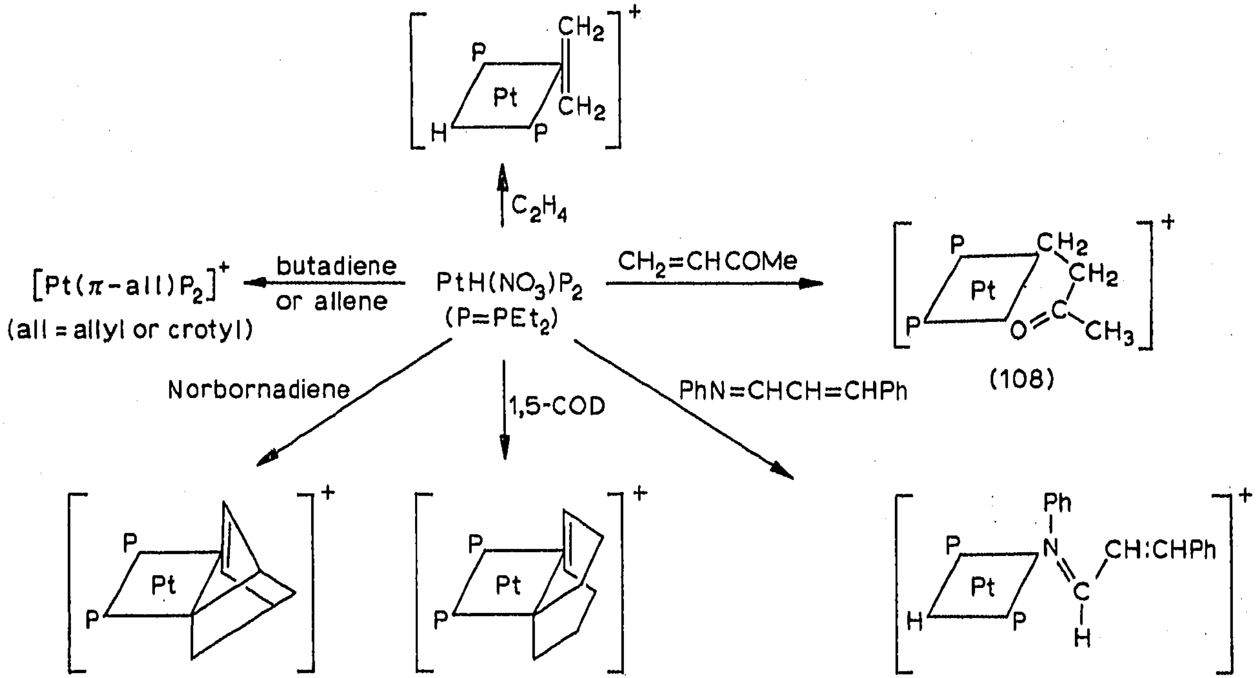
of HX to trans-$[PtHY(PEt_3)_2]$ (X,Y = Cl,Br,I) at 90°, gave cis and trans-$[PtH_2XY(PEt_3)_2]$. Scrambling of the halogens (X≠Y) occurred on allowing the solution to warm to -20° C [288].

Similarly, HX added to trans-$[PtY_2(PEt_3)_2]$ gave $[PtHXY_2(PEt_3)_2]$, with H trans to X. A hydride trans to the lighter halogen was the preferred orientation which was attained by rearrangement if X was heavier than Y. Addition of X_2 to trans-$[PtHX(PEt_3)_2]$ produced a mixture of $[PtH_2X_2(PEt_3)_2]$ and $[PtX_4(PEt_3)_2]$ [288].

The reactionsof trans-$[Pt(PPh_3)_2H(ClO_4)]$ with allyl alcohol, allyl chloride and bromide, in benzene and aqueous acetone have been studied. Allyl alcohol gave the π-allyl complex $[Pt(PPh_3)_2\ (\pi\text{-}C_3H_5)]ClC_4$ in benzene. With C_3H_5X (X = Cl or Br) in benzene, complexes containing a coordinated propene, $[Pt(PPh_3)X(C_3H_6)]ClO_4$ were obtained. In aqueous acetone, the reaction with allyl alcohol gave a mixture of the π-allyl and the propene complexes whereas with allyl halides a mixture of the π-allyl complex and trans-$[Pt(H)X(PPh_3)_2]$ was formed [289].

The insertion of olefins into the Pt-H bonds of trans-$[PtH(NO_3)(PEt_3)_2]$ has been investigated (Scheme 20). The initial step in the insertion was suggested to be the substitution of $NO_3$by the olefin to give a cationic hydrido-olefin intermediate. The Pt-C σ-bond in $[Pt(CH_2CH_2COMe)(PEt_3)_2]BPh_4$ (108) was readily hydrolysed to give $[Pt_2(OH)_2(PEt_3)_4]^{2+}$ and ethyl methyl ketone [290].

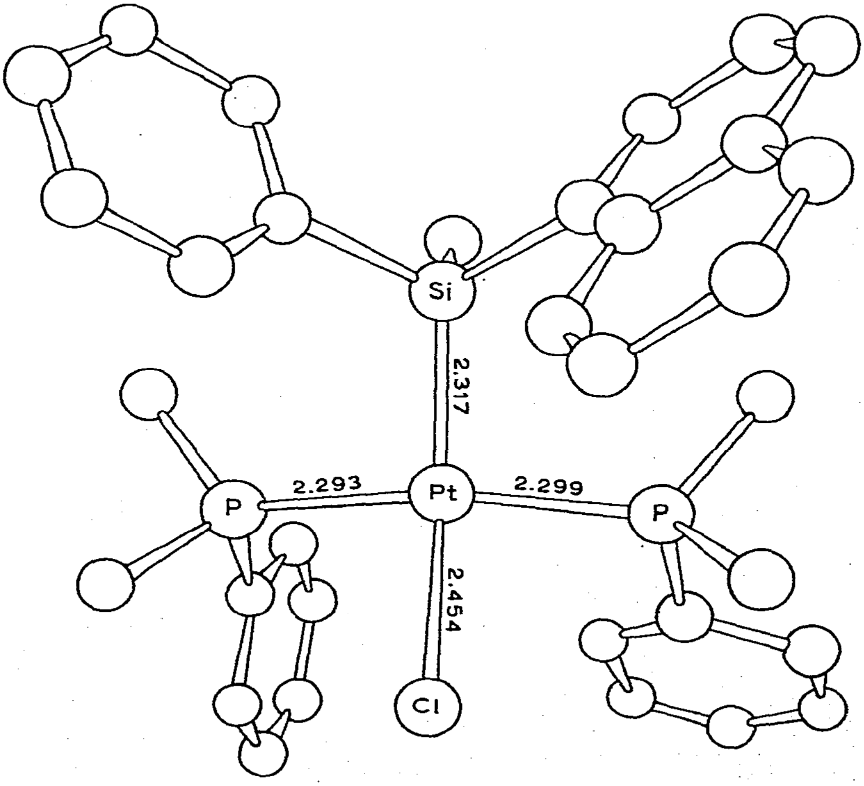
The presumed cationic complex $[PtH(PMe_2Ph)_2]^+\ [SO_3F]^-$, formed from trans-$[Pt(H)Cl(PMe_2Ph)_2]$ and $MeSO_3F$, effectively catalyses the isomerizarion of oct-1-ene, and hex-2-ene [291]. The mechanism of double-bond migration induced by the platinum(II) hydrides, trans-$[PtH(PPh_3)_2(acetone)]^+$, trans-$[PtH(ClO_4)(PPh_3)_2]$, and trans-$[PtH(NO_3)(PPh_2Me)_2]$, has been studied using platinum II-deuterido analogues as well as 2-deuterated allyl methyl ether. Both the stoichiometric reaction of diallyl ether with Pt-H and the catalytic conversion of allyl alkyl ethers to cis-propenyl alkyl ethers were found to involve the initial reversible anti-Markownikov addition of Pt-H across the terminal C = C bond before double bond migration. The isomerization of 1-butene to 2-butene occurred readily at room temperature without stereospecificity [292].


+
P
Pt
H
P
CH_2
CH_2
C_2H_4
$[Pt(\pi\text{-all})P_2]^+$
(all = allyl or crotyl)
butadiene
or allene
$PtH(NO_3)P_2$
$(P{=}PEt_2)$
$CH_2{=}CHCOMe$
(108)
O
C
CH_3
Norbornadiene
1,5-COD
PhN=CHCH=CHPh
Ph
N
C
H
CH:CHPh

(scheme 20)

XII Hydrosilylation/germylation reactions

Structural characterisation of (+)-trans-$[PtCl\{SiMe(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2]$ (109) has revealed an absolute configuration (S) for the molecule [293]. $[Pt(GeCl_3)_5]^{3-}$ has a distorted trigonal bipyramid structure about the Pt; Pt-Ge bond parameters average 2.406(8)Å [294]. A preliminary report on the formation of bissilyl platinum complexes from o-$(HMe_2Si)_2C_6H_4$ and o-$(HMe_2Si)C_6H_4CH_2SiMe_2H$ by reaction with $[Pt(PPh_3)_2C_2H_4]$ or $[Pt(PMe_2Ph)_4]$ has appeared. The products are (110) (n = 0,1). A four membered cyclic species $[Pt(SiR_2OSiR_2)(PPh_3)_2]$ (R = Me,Ph) was also characterised [295]. Silylacetylene and silyl perfluoromethyl acetylene react with trans-$[HPtCl(PEt_3)_2]$ producing trans-$[YC{\equiv}CSiH_2PtCl(PEt_3)_2]$ (Y=H,CF_3). These acetylenes react with $[PtI_2(PEt_3)_2$ to give initially $[HPtI_2(SiH_2CCY)(PEt_3)_2]$ which decomposes to give $[YC{\equiv}CSiHIPtI(PEt_3)_2]$. No evidence for Pt-acetylene interaction was observed [296]. ^{19}F NMR chemical shifts for the complexes trans-$[PtXY(PMe_2Ph)_2]$ (Y = $SiPh_3$,



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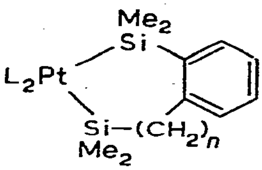


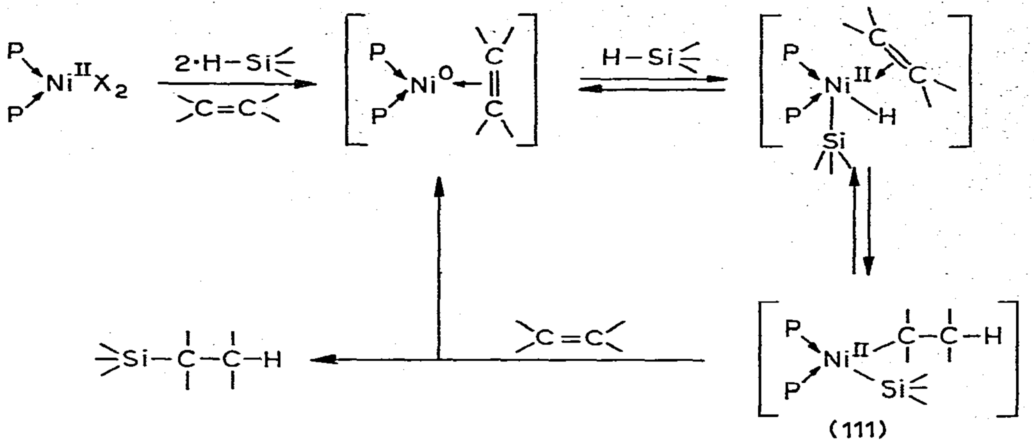
(110)

X = C_6H_4F-*m*, C_6H_4F-*p*; X = C_6H_4F-*m*, Y = Cl) and(*m*- or *p*-$FC_6H_4)_3SiX$ (X=Br,H, Me, Ph, $PtClL_2$-*trans*; L=$AsMe_2Ph$; PMe_2Ph) indicates that the Ph_3Si group acts as a good σ-donor and π-acceptor [297]. A study of the stereochemistry of formation and cleavage of Si-Pt bonds is reported. New complexes identified are (+)-*trans*-$[PtX(SiR_3)L_2]$ (R_3Si = Me($1-C_{10}H_7$)PhSi; X=Cl,Br,I,L=PMe_2Ph; X=H, L=PPh_3). The silicon hydride starting material for these preparations can be regenerated with almost 100% retention of configuration with $LiAlH_4$.

It is suggested that cleavage of Si-Pt occurs via oxidative addition - reductive elimination sequences with almost complete retention of configuration.

Corresponding germanium complexes have been tentatively identified [298].

A highly stereospecific preparative route to $R^1R^2R^3SiH$ involving the reaction between $R^1R^2R^3SiX$(X = OMe,F,Cl) and Grignard reagents possessing β-hydrogens (e.g. Et,Pr^n, Pr^i, Bu^n, Bu^i) activated by $[NiCl_2(PPh_3)_2]$ has been communicated [299]. This reduction was found to take place with retention of configuration at the Si atom for X = MeO or F, and suggested to occur via a Ni-H species formed by β-elimination of the Ni-R intermediate [300]. With non-reductive Grignard reagents and Si-H groups it was found that in the presence of nickel(II) salts Si-C bonds were readily formed [301]. $[CpNiCO]_2$ was found to be a very good catalyst for the addition under mild conditions of $HSiCl_3$ to styrene to form 1-trichloro-silyl-1-phenylethane in high yield [302]. A variety of $[NiX_2L_2]$(L = phosphine) complexes are only effective catalysts for the hydrosilylation of olefins and acetylenes above 90°. Two products were obtained, the ratio of which was found to be dependent upon the donor properties of L [303]. $[Ni(C_2H_4)L_2]$ (L_2 = DPE,DPM) complexes were found to have a lower induction period for hydrosilylation than$[NiX_2L_2]$compounds though the reaction profiles were similar [304]. Above 120° the silylation is accompanied by an interchange of H and Cl on silicon [303]. Isomerisation of the olefin occurred during the reaction, with *cis*-addition taking place preferentially [303] The reactivity of the silcon hydrides decreases in the order $HSiCl_3$>$HSiMeCl_2$> $HSiMe_2Cl$>$HSiMe_3$ [303]. A mechanism for the reaction is proposed [304] (Scheme 21). When the nickel(II) chloride complex with 1,2-bis(dimethylphosphino)-1,2-dicarba-closo-dodecaborane is used as a hydrosilylation catalyst for



(scheme 21)

olefins, internal as well as terminal adducts are formed. The intermediate σ-complex (III in scheme 21) can be regarded as carbanionic in nature and it seems likely that equalisation of stabilities between the primary and secondary carbanions is related to strongly electron accepting carborane ligands [305]. An investigation into the effects by which dinuclear olefin complexes of platinum catalyse hydrosilylation of styrene has shown the retardation effect of donor solvents and ligands [306]. From kinetic investigations the reactions appear to depend upon the halogen-bridge cleavage by the chlorosilanes [307]. The best catalyst for the reactions of Me_3SiOH with butadiene to give 1-trimethylsiloxy-2,7-octadiene was found to be $[PdCl_2(PhCN)_2]$ [308]. Treating H_2PtCl_6 with 3,3-dimethyl-1-butyne in isopropanol gave $H_2[(Me_3CC{\equiv}C)Pt(OCHMe_2)Cl_2]$ whose catalytic activity in the hydrosilylation of butyne and 1-hexyne was studied [309].

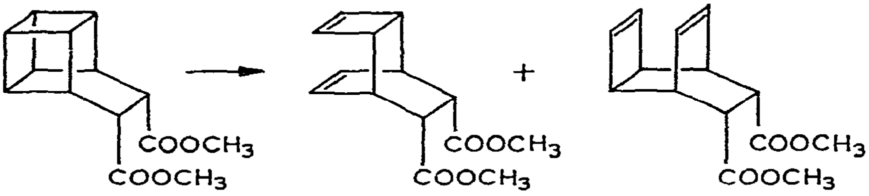
A reinvestigation [310] of the reported reaction of Si_2Cl_6 with $[Pt(PPh_3)_4]$ to form $[Pt(PPh_3)_2(SiCl_3)_2]$ has shown that the product of further reaction of this compound with PPh_3 is not a novel silylene complex but an impure partial hydrolysis product formed from trace ammounts of water. Further reactions of Si_2Cl_6 with transition metal complexes are also reported.

XIII Other Synthetic and Catalytic Reactions Involving Ni,Pd,Pt.

A review containing sections of hydrosilylation and dimerisation of olefins using Ni and Pd catalysts has appeared, [311] and the synthesis of heterocyclic compounds via transition metal intermediates is covered [312]. The multitudinan catalytic reactions stemming from and related to the "Nickel Effect" have been published in memory of Karl Ziegler [313 - 5].

Nickel

A mixture of $LiAlH_4$ and $Ni(Acac)_2$ in THF was found to be a good hydrogenation catalyst for aromatic compounds [316]. The reduction of p-$RC_6H_4NO_2$ (R = Cl,OMe) by $NaBH_4$ with $[NiX_2(PPh_3)_2]$ (X = Cl,Br,I) gave 80-88% of p-$RC_6H_4NH_2$ [317]. The $(COD)_2Ni$ catalysed isomerisation of (112) produced (113) and (114) by an intramolecular [σ2 + σ2]-rearrangement [318]. Methylene cyclopropane is converted quantitatively into (115) by $[NiBr_2(PBu^n_3)_2]$ and Bu^nLi in n-hexane [319]. A study of the catalytic activity of several $[Ni(diphosphine)_2]$/acid systems for the cis-and trans-isomerisations of olefins has found that for 1-pentene the stereoselectivity of the isomerisation is dependent upon the cocatalyst. To explain the different routes for the different catalysts it is suggested that in certain instances a σ-alkyl mechanism is in operation whilst in the other



(112) (113) (114)

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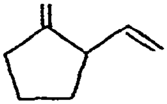
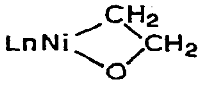


(115)

cases a π-allyl mechanism predominates [320]. The formation of alkylene carbonates from alkylene oxides, CO_2 and nickel(0) catalysts is thought to occur via a repeating sequence of oxidative addition, insertion and reductive elimination steps involving the intermediates (116–118) [321].



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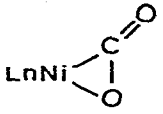

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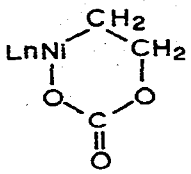
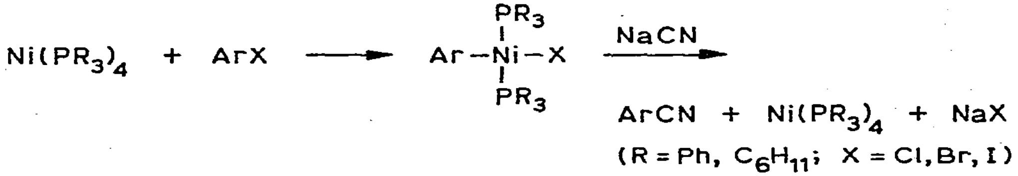
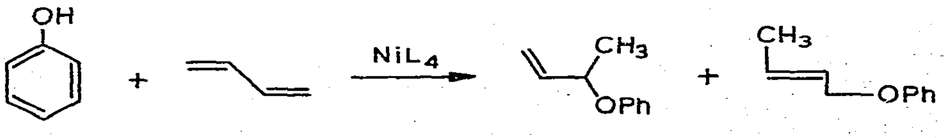


(118)

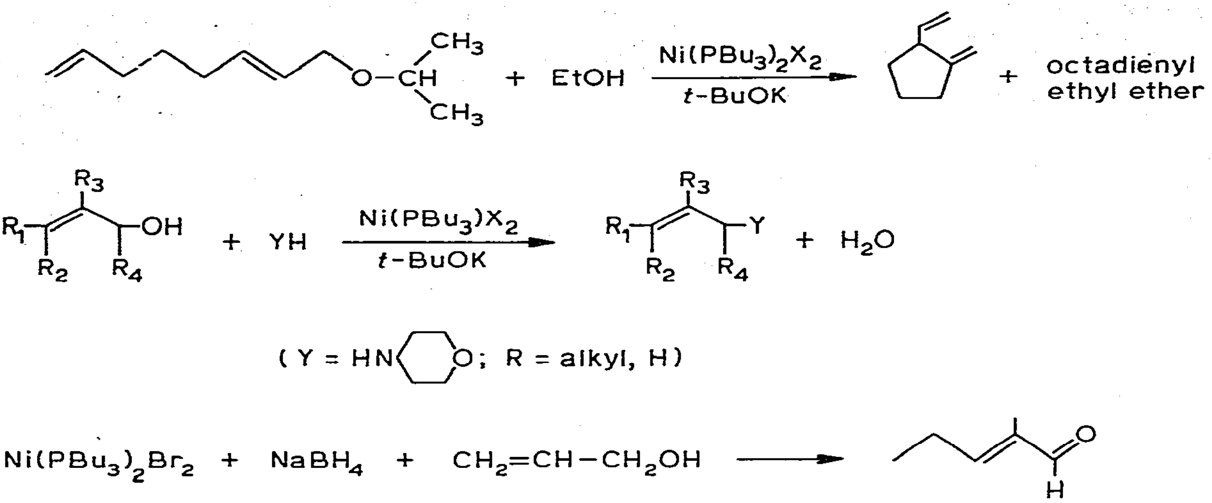
The oxidative addition of aryl halides to nickel(0) complexes and the subsequent reaction of the product with NaCN has been found to be a useful process of converting aryl halides to aryl nitriles (Scheme 22) [322]. Catalytic amounts of certain protic acids (e.g. CF_3CO_2H) to amine, butadiene and $[Ni(COD)_2]$ mixtures enhanced the formation of butenylamine [323]. Phenoxybutenes are the main product of the reaction of phenol, butadiene and nickel(0) complexes when excess phosphorus ligands, good electron donor ligands or a high ratio of phenol to butadiene are used (Scheme 23) [324]. A series of products from allyl transfer reactions in the presence of $[NiX_2(PBu^n_3)_2]$-*t*-BuOK (X = Cl,Br,NO_3) have been obtained (Scheme 24) [325]. The almost total formation of ethane and ethylene from the decomposition of ethyl Grignards by $CoCl_2$ and $NiCl_2$ indicates the absence of radical steps in solution [326]. An improved synthesis of



(scheme 22)

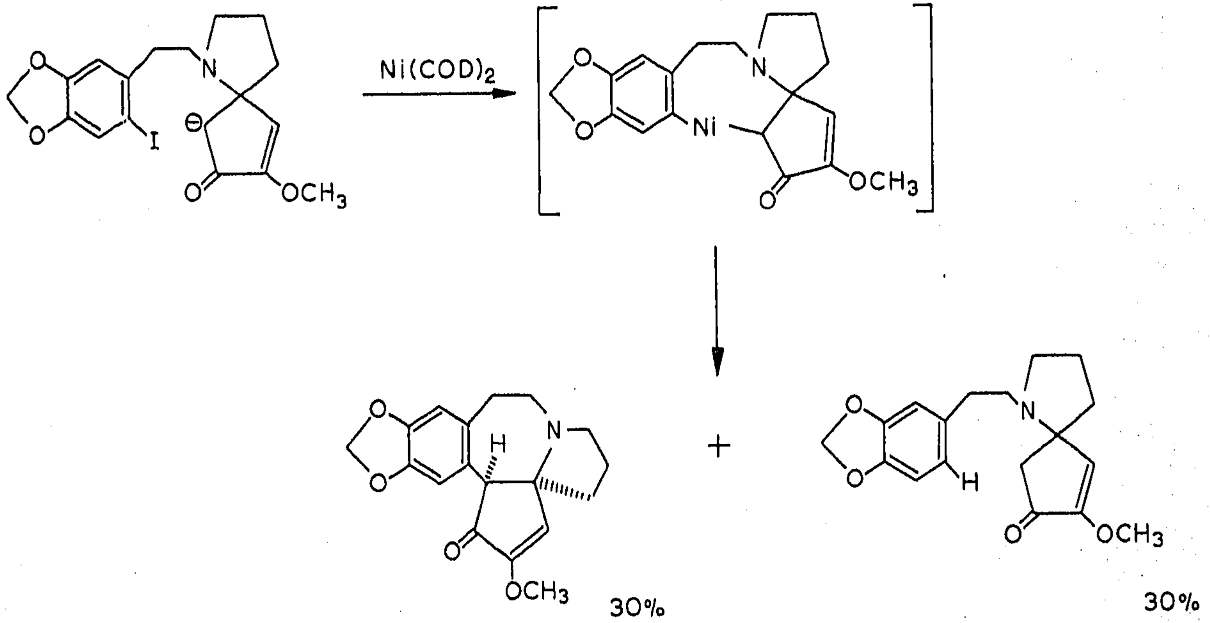


(scheme 23)



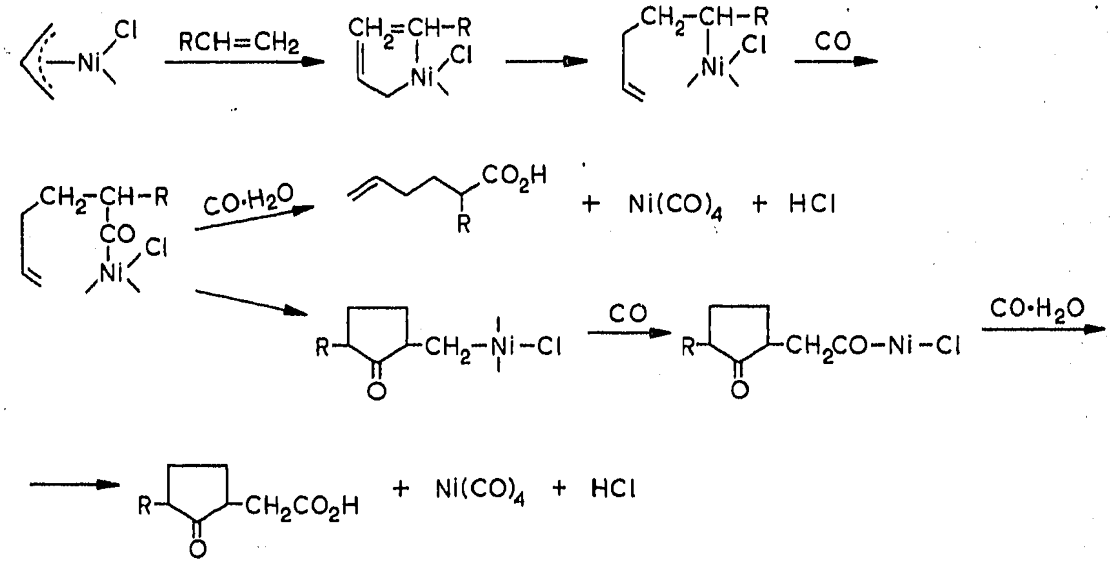
(scheme 24)

cephalotaxinone (119) using $[Ni(COD)_2]$ in one of the steps has been reported (Scheme 25) [327]. A study of the oxidations of benzoylhydrazones of aldehydes, ketones and 1,2-diketones with nickel peroxide has been presented [328]. It has been shown that the alkyl group isomerisation accompanying the nickel-catalysed cross coupling of secondary alkyl Grignards with organic halides depends upon the nature of the halides [329]. The high *cis*-stereoselectivity observed in the alkyl Grignard cross coupling with 1,2-dihaloethylenes catalysed by nickel complexes strongly suggests an elimination-addition mechanism is operative. Under similar conditions with monohaloolefins stereospecific cross-coupled products resulted [330]. High yields of aromatic acids have been obtained from the carbonylation of aromatic halides in dipolar aprotic solvents at atmosheric pressure in the presence of nickel complexes [331]. A mechanism has been suggested to account for the products obtained from the nickel carbonyl induced reactions of olefins and dienes with allyl halides and CO in protic solvent (Scheme 26) [332]. The alkylation of benzaldehyde by allyl chloride using a reduced nickel catalyst occurs in a similar pattern to that of Grignard reagents except that protic solvents can be used [333]. The reaction of norbornadiene and methylenecyclopropane with the aid of phosphine-nickel(0) catalysts gave highly selective [2 + 2] cross-addition (Scheme 27) [334]. A catalyst prepared from $[Ni(COD)_2]$ and various phosphines is an excellent trimerisation catalyst for methylenecyclopropane (Scheme 28) [335].

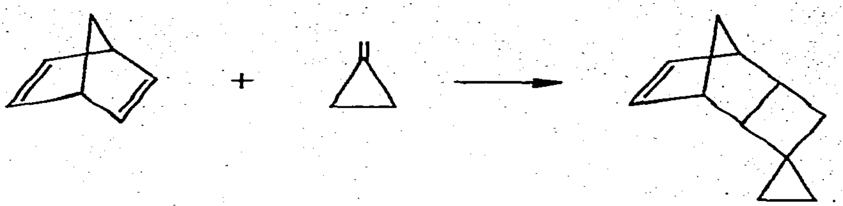


(119)

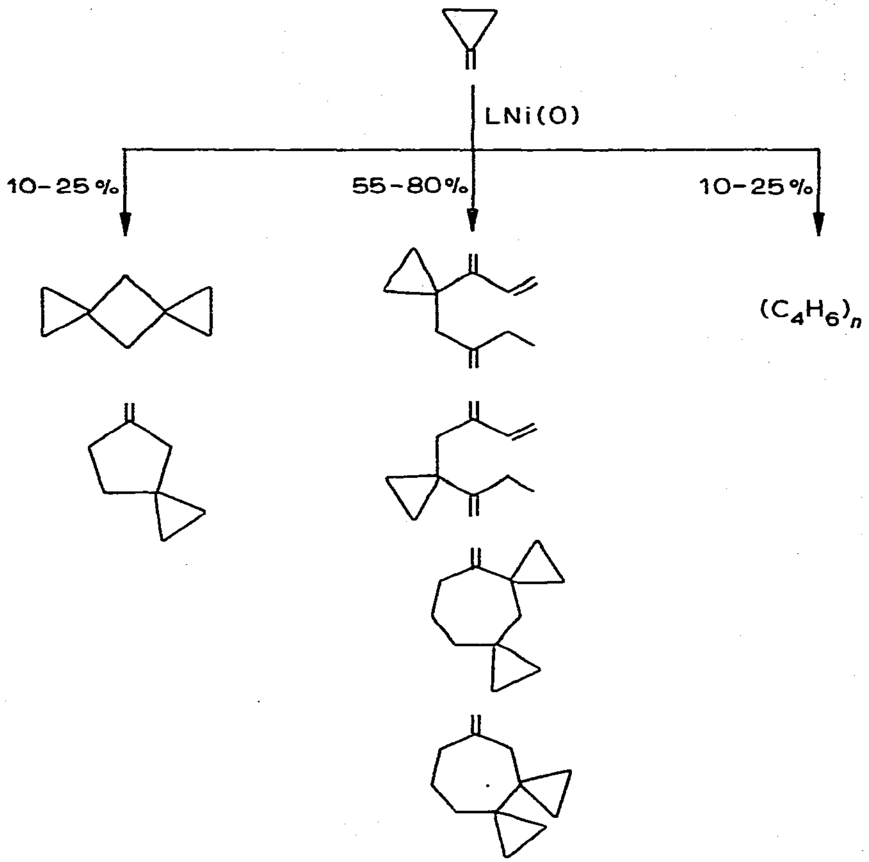
(scheme 25)


Cl
Ni
RCH=CH2
CH2=CH-R
Ni
Cl
CH2-CH-R
Ni
Cl
CO
CH2-CH-R
CO
Ni
Cl
CO·H2O
CO2H
R
+ Ni(CO)4 + HCl
R
CH2-Ni-Cl
O
CO
R
CH2CO-Ni-Cl
O
CO·H2O
R
CH2CO2H
O
+ Ni(CO)4 + HCl

(scheme 26)

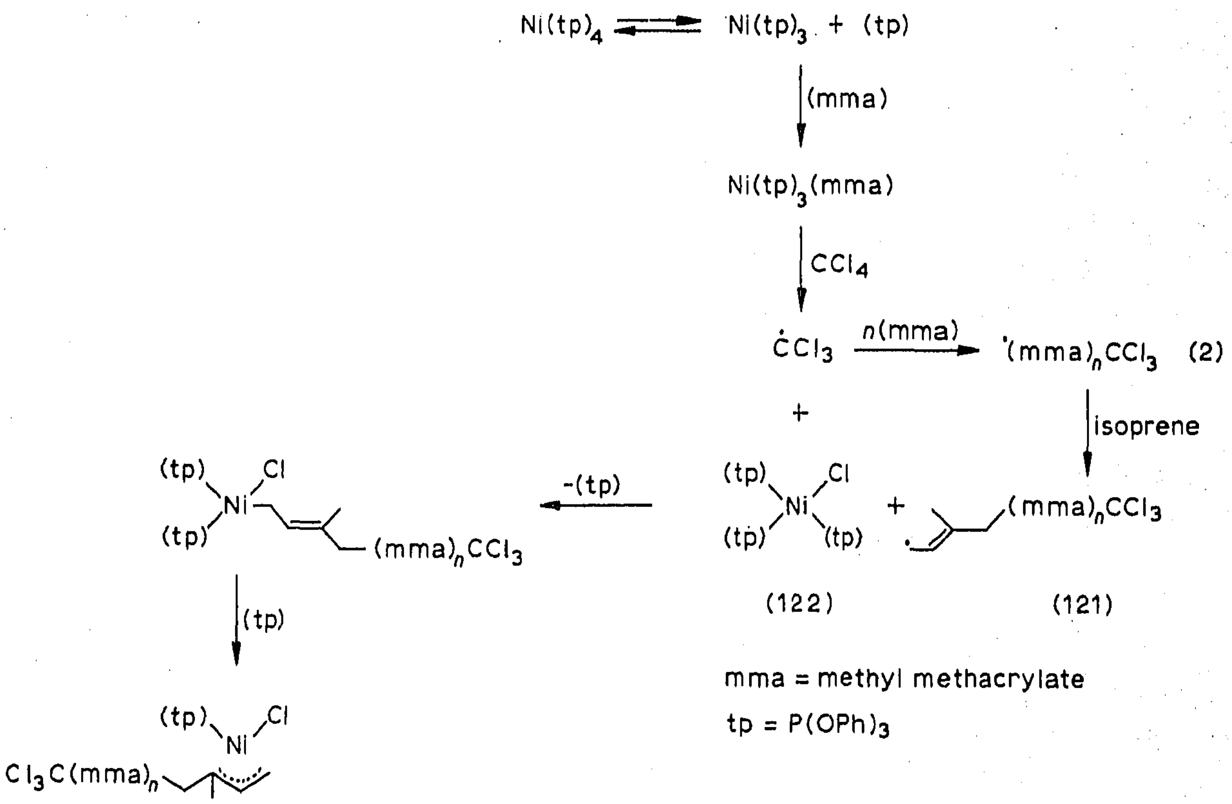


(scheme 27)



(scheme 28)

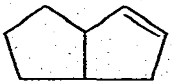
An efficient conversion of COD to (120) using a soluble nickel(II) salt and $EtAlCl_2$ is reported [336]. A series of papers on the oligomerisation of dienes has appeared. The catalyst system $NiX_2(PR_3)_2$+$NaBH_4$ or R^1ONa (X = halogen,R and R^1 = alkyl) produced (115) and n-octatrienes with



mma = methyl methacrylate

tp = $P(OPh)_3$

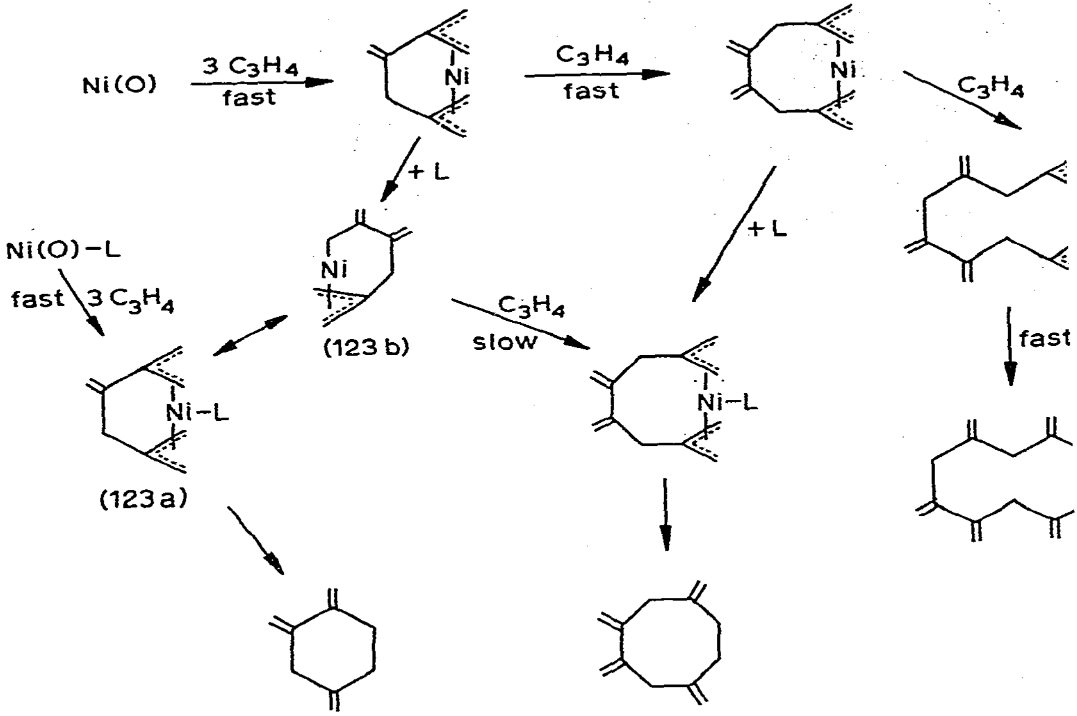
(scheme 29)



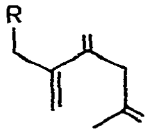
(120)

butadiene [337]. When the system Ni(Acac)$_2$ + PBu$^n_3$ + LiBu^n in methanol is used, the oligomerisation of butadiene produced more isomers than previously reported. Their mechanism of formation was discussed [338]. A survey has appeared on the relative reactivities of a series of dienes in copolymerisation by various catalytic systems of transition metals including nickel [339]. The polymerisation of methyl methacrylate initiated by [Ni{P(OPh)$_3$}$_4$] and CCl$_4$ has been investigated, and a mechanism proposed involving the radical CCl$_3$ as the initiator (Scheme 29). The retardation effect of isoprene on this polymerisation has been explained in terms of an incorporation of isoprene units into the polymer producing (121) which then terminates this polymerisation process by a reaction of (121) with (122) to give a terminal π-allylic unit [340]. The reactions of allenes with nickel(0) catalysts under varying conditions produces a variety of products. Evidence has been presented supporting a multistep reaction path for the metal-assisted cycloadditions. In the nickel-phosphorus ligand systems, the nature of the ligand determines the selective catalytic reaction pathway, by either varying the π-σ- allyl coordination equilibrium (123a-b) or effectively blocking a coordination site (scheme 30) [341]. The major product from the reaction of allene and amine or active methylene compound catalysed by nickel(0) complexes was (124) [342]. [NiBr$_2$(PBu$^n_3$)$_2$] is a regiospecific catalyst for the symmetrical cyclic trimerisation of α-hydroxyacetylenes of formula HC≡C-C(R$_1$)(OH)R$_2$ to give 1,3,5-tris-hydroxyalkylbenzenes in high yields [343].

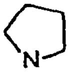
Studies on olefin dimerisation catalysed by [NiBr(1-naphthyl) (PPh$_3$)$_2$] -BF$_3$.Et$_2$O indicated a mechanism involving the steps for e.g. the codimerisation of ethylene 'Ni' + $C_2H_4 \longrightarrow NiH(CH{=}CH_2) \xrightarrow{C_2H_4} Ni(C_2H_5)(CH{=}CH_2) \xrightarrow{C_2H_4} Ni(CH_2CH_2CH_2CH_3)(CH{=}CH_2) \longrightarrow NiH(CH{=}CH_2) + C_4H_8$ [344]. The catalyst activity depended considerably on the solvent used [345]. The products formed from the [Ni(C$_2$H$_4$)$_2$P(CHMe$_2$)$_3$] - BF$_3$.OEt$_2$ oligomerisation of C$_2$H$_4$ were *cis*-2 and *trans*-2-butenes, 3-methyl-1- and 2-pentenes and 1-*trans*-2 and 3-hexene [346]. Butadiene and (125) gave (126) with the catalyst system NaBH$_4$ and [NiBr$_2$(PBu$_3$)$_2$] [347].

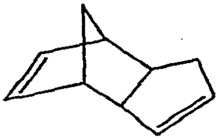


(scheme 30)

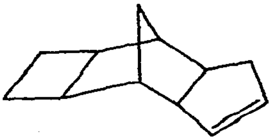


(124)

R = , , PhNH, Ph(COMe)CH, Ph(CN)CH, $(CO_2Et)_2CH$



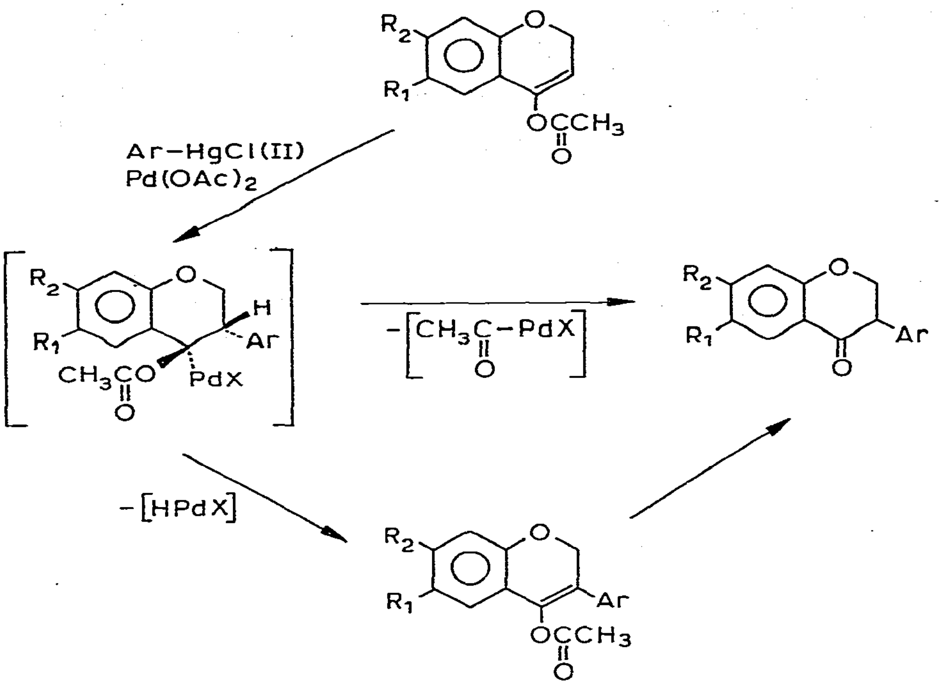
(125)



(126)

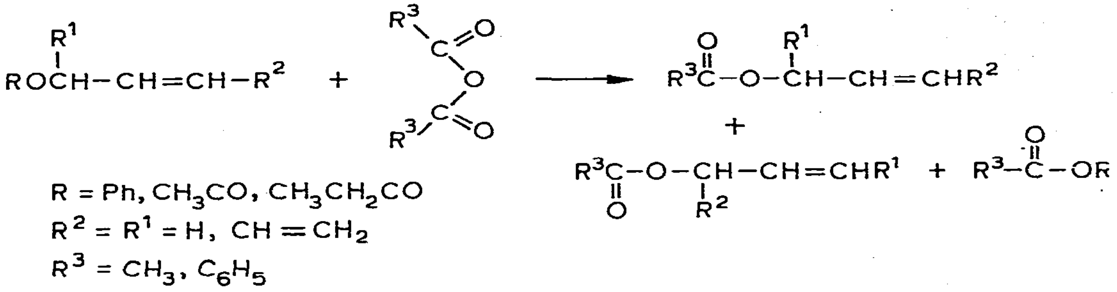
A review of the importance and versatility of the complexes of zerovalent Pd and Pt-phosphine complexes in the field of industrial organic synthesis has appeared (84 refs.) [348].

A reduced solution of $[PdCl_2(PPh_3)_2]$ catalyses the dimerisation and selective hydrogenation of butadiene specifically, in the presence of formic acid. The selectivity of the 1,7-dienes formed was as high as 80% [349]. Catalytic hydrogenation and rearrangement of allyl alcohol and 3-cyclohexenol to propionaldehyde and cyclohexanone has been effected with sulphoxide complexes of Pd [350]. The arylation of a series of olefins with XPh_3 (X = P,As,Sb, Bi) and palladium(II) salts is reported [351-2]. With Ph_3N and styrene only trans-p-diphenylaminostilbene is obtained presumably because of a stronger N-C bond [351]. The mechanism suggested involves initial aryl-palladium formation by cleavage of an X-C bond [351-2]. Aromatic compounds are coupled under oxygen pressure in the presence of palladium salts [353-4]. Addition of Acac or EDTA promoted the yield of coupled products, substituents on the aromatic ring effected yields and isomer distribution, and acids, bases, LiCl and polar solvents inhibited the reaction [354]. A large isotope effect was found for deuterobenzene (k_H/k_D = 2·1 to 2·5) at 150° under oxygen pressure and a two-step hydrogen abstraction mechanism was proposed with oxygen reoxidising reduced palladium(0) species formed during the coupling reaction [355]. Oxidation of C_2D_4 by $PdCl_2$ gave > 95% of CD_3CDO. The kinetic isotope effect $[k(C_2H_4)]/[k(C_2D_4)]$ was 0.8 and the results indicate that hydroxymetallation of ethylene is the rate determining step [356]. Phenylation of nitroolefins are effected strongly by the nitro group and tend to occur on the olefinic carbon atom adjacent to that bearing the nitro group [357]. The metallic palladium catalysed arylation of olefins with iodobenzene has been discussed in terms of an oxidative addition of PhI to a palladium complex of low oxidation state [358]. During the arylation and vinylation reactions of benzo-[b]furan and corresponding deuteroanalogues it was confirmed that no hydride shift occured [359]. Isoflavones have been obtained in high yields by the action of arylpalladium compounds with 4-chromanone enol esters in acetic acid (scheme 31) [360]. In the ^1H-^2H exchange in alkanes in CH_3COOD/D_2O mixtures in the presence of palladium complexes it is suggested that it is more reasonable to regard the ionisation potential correlation for linear hydrocarbons as an index of polarisability of the CH bonds towards electrophilic insertion, which may be a synchronous



(scheme 31)

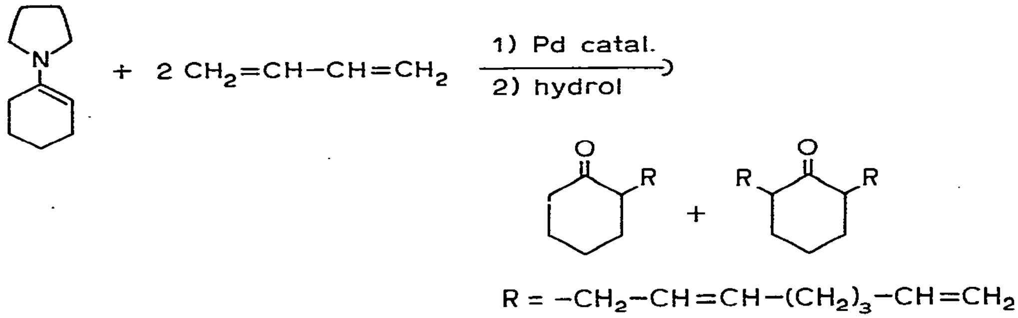
process of ^{2}H insertion and ^{1}H acceptance by a catalyst species such as $[DPtCl_2]^+$ [361]. The near-to-random distribution of deuterium in the palladium(II) catalysed isomerisation of olefins in CH_3COOD and CH_3OD mixtures are consistent with a relatively rapid hydrido-π-olefin mechanism in which the rate determining step in the reaction is the exchange of olefin between catalyst and substrate [362]. Further confirmations for this hydrido-π-olefin isomerisation mechanism have appeared [363-5]. From the microwave analysis of $[^2H_1]$ propenes formed by deuterium exchange of propene with CH_3OD using Pt,Ni and Rh complexes it was inferred that the high deuteration of but-1-ene for platinum was a consequence of preferential anti-Markovnikov Pt-D additions [363]. The isotopic exchange reaction of CH_3OH containing a Pt(II)-Sn(II) chloride mixture, with D_2, is first order in deuterium, and proceeds at a rate which is at a maximum for Sn/Pt ratios of 5.5, indicating that $[Pt(SnCl_3)_5]^{3-}$ is the intermediate [364]. The three-term rate law; rate = $(k_1[Li_2Pd_2Cl_6]/[LiCl] + k_2[Li_2Pd_2Cl_6] + k_3[Li_2Pd_2Cl_6]^{\frac{1}{2}})$[1-chloropropene] has been observed for the palladium(II)-catalysed isomerisation of cis- and trans-1-chloropropene. The k_2 term is explained as resulting from nonstereospecific chloropalladation-dechloropalladation in which the chloride adds to the carbon carrying the methyl and the palladium to the carbon carrying the halide. The k_1 and k_2 terms correspond to formation of monomeric and dimeric π-complexes respectively and the isomerisation is suggested to occur through these π-complexes without π-allyl or Pd-H formations. The mechanism suggested is rearrangement of the π-complex to a Pd(II)-σ-bonded carbonium ion which undergoes rotation before reverting to the π-complex [367]. A mixture of $[PdCl_2(PPh_3)_2]$ and NaOPh is effective for the exchange of ether groups in allyl ethers with carboxylates from acetic anhydrides (Scheme 32) [368]. A series of studies of acetoxylation of olefins are reported [369-72]. A number of oxidants e.g. $K_2Cr_2O_7$, $NaNO_2$, MnO_2, $CuBr_2$, $Pb(OAc)_4$, $Tl(OAc)_3$, $TlCl_3$ and $HAuCl_4$, were found to be effective in increasing the rate at which palladium(II) salts in acetic acid oxidise ethylene to vinyl acetate [369]. The reaction of $PdCl_2$ + NaOAc + CH_3CN



(scheme 32)

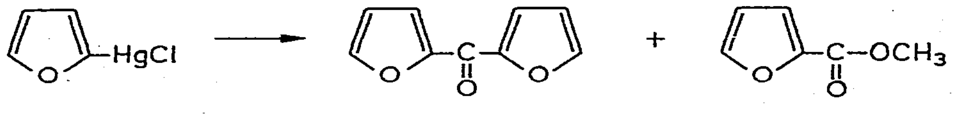
with dihaloethylenes produced trans-diacetoxyethylenes, as well as 1,1-diacetoxyethylene and a small amount of the cis-diacetoxy derivative [370]. The addition of acetic acid to bicyclo [2.2.1]hepta-2,5-diene in the presence of platinum complexes has been shown by the use of CH_3COOD to involve a highly stereoselective skeletal rearrangement of the substrate to produce syn-7-deuterio-exo-5-acetoxybicyclo [2.2.1] hept-2-ene. Possible mechanisms were presented [371]. Quantitative yields of acetoxyoctadienes were obtained and significant degrees of isomer control obtained when o-alkyl or o-aryl substituted triaryl phosphite complexes of palladium were used for the cyclo-oligomerisation of butadiene in acetic acid [372]. Effective removal of allyl groups by formic acid from allyl phenyl ether and allyl carboxylates to give phenol and the corresponding carboxylic acids has been obtained with triphenylphosphine derivatives of palladium [373].

The rate expression for thehydration of vinyl acetate to acetaldehyde is given as; Rate = $k[Li_2Pd_2Cl_6][C_2H_3OAc][H_2O]^n/[LiCl]$ where n is between 1 and 2, and is consistent with attack of non-bonded water on a dimeric palladium(II) vinyl acetate π-complex. The mechanism then postulated is that the enol acetate formed is saponified, and acetaldehyde is released by attack of the acetic acid solvent on a palladium(II) substituted acetaldehyde formed by the saponification process [374]. The oxidative dehydrogenation of 3-hexenedioate to 2,4-hexadienedioate by $PdCl_2$ in acetic acid solution is catalytic in the presence of $CuCl_2$ [375]. The reaction of butadiene with an enamine proceeds via nucleophilic attack of the enamine to give octadienyl products and not cocyclisation compounds when $Pd(Acac)_2$ + PPh_3 are added to the reaction mixture (Scheme 33) [376]. The carbonylation at 100° under CO pressure of a methanol solution of Li_2PdCl_4 and e.g. 2-chloromercurifuran gave (127) and (128) as the major products [377]. The products (130)(131) and (132) were obtained from the dimerisations of (129) (R_1 = CH_3; R_2 = R_3 = H) and (129) (R_1 = H; R_2 = R_3 = CH_3) respectively [378].

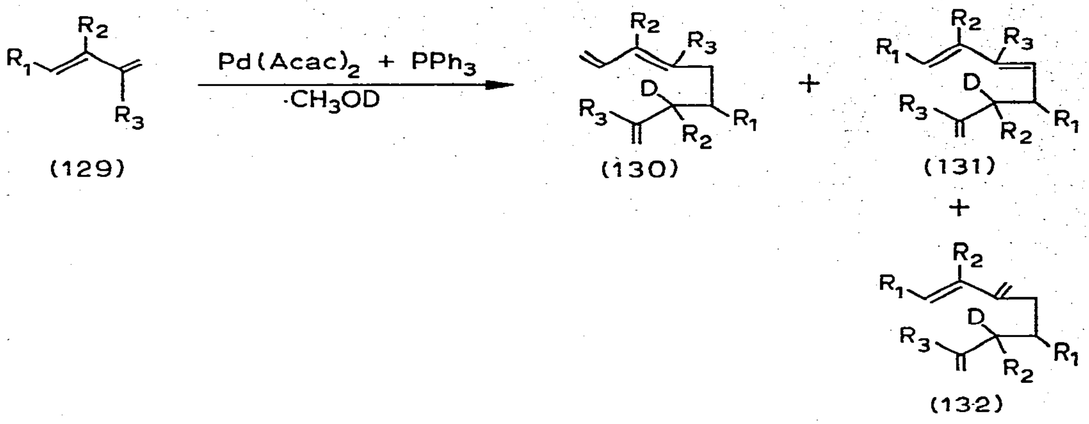


(scheme 33)

Butadiene and methanol gave 1-methoxy-2,7-octadiene with $[PdCl_2(PPh_3)_2]$ and $NaBH_4$ [379]. A mechanism has been proposed for the reaction C_2H_4 + ROH $\longrightarrow CH_2 = CHCO_2R$ catalysed by Pd^{2+} ions [380].

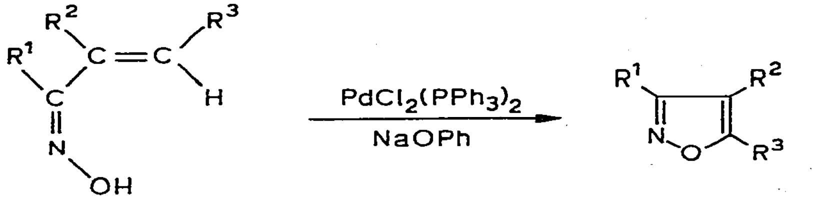


(127) (128)



(129) (130) (131) (132)

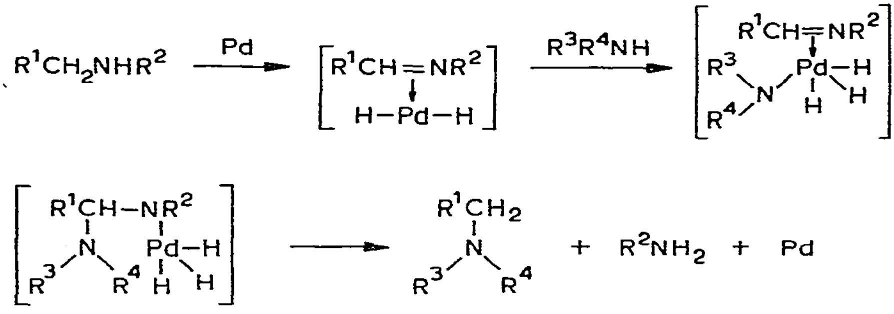
Facile cyclisation of α,β-unsaturated ketoximes with palladium complexes leading to the corresponding isoxazoles has been effected (Scheme 34) [381]. The reactions of p-benzoquinone which is π-bonded to palladium and platinum have been studied. With reagents XY (X = Me, Y = I; Y = Cl, X = CH_3CO, NO, CH_2 = CH - CH) the products $XO-C_6H_4-OX$ were characterised [382], whilst with monoolefins anthraquinone derivatives were formed [383]. The blue complex formed from $[Pd(MeCN)_2(BF_4)_2]$ and tetra-p-anisylethylene in MeCN reacted with 3,5-lutidine to give a phenanthrene derivative. The mechanism of the Pd(II) reaction was suggested as (i) initial formation of a π-complex followed by attack of a nucleophile at a ring position to give an aryl Pd adduct and (ii) attack of a base at an α-hydrogen (if available) to form a benzyl Pd adduct and/or (iii) direct collapse to give a Wheland-type intermediate [384].



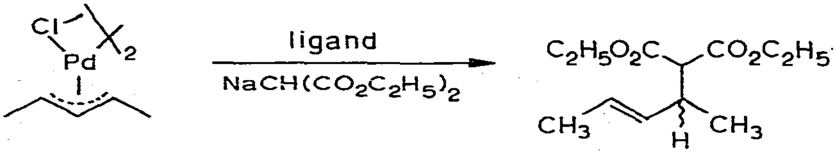
R^1 = Ph, R^2 = H, R^3 = Ph
R^1 = t-C_4H_9, R^2 = H, R^3 = Ph
R^1 = Ph, R^2 = Me, R^3 = i-C_3H_7

(scheme 34)

Aryl cyanides have been synthesised by the substitution reaction of aryl halides with cyanide ions in the presence of palladium(II) salts in DMF [385], whereas with platinum compounds, the hydration of nitriles to carboxamides has been observed [386]. π-Allylpalladium complexes have been found useful for converting various amines to secondary or tertiary amines via a π-complex of Schiff base bearing a Pd-H bond (Scheme 35) [387]. Additions of catalytic amounts of palladium complexes were found to accelerate the dehalogenation of aliphatic and aromatic halogeno derivatives by $NaAlH_2(OC_2H_4OCH_3)_2$ [388]. The alkylation of a π-allylpalladium complex produced a carbon-carbon singlebond with a high optical yield (66–88%) (Scheme 36) [389]. The formation of methyl ethers from the $[PdCl_2(PhCN)_2]$ catalysed rearrangement of (133) has been ascribed to an acid-catalysed ring opening, the acid being formed from the reaction of a π-allylpalladium species with methanol (Scheme 37) [390]. Pd, Pt and Ir(I) complexes catalyse the decomposition of thiirene 1,1-dioxides to SO_2 and the corresponding acetylenes via a thiirene dioxide-metal complex intermediate [391].

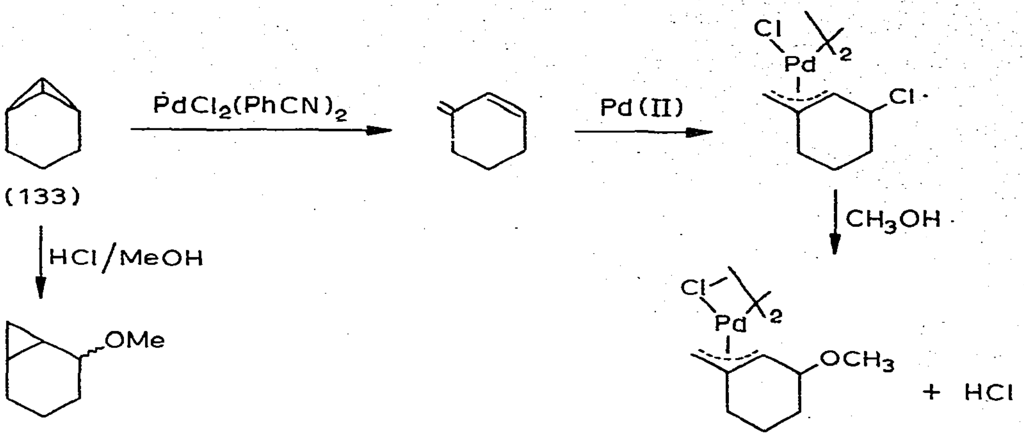


(scheme 35)



(scheme 36)

The β-lactone $CH_2=CH\underline{CHCH_2-\overset{O}{\overset{\|}{C}}-O}$ with Pd^{2+} gave 50–85% of $CH_2=CH-CH=CHCO_2H$ [392].



(133)

(scheme 37)

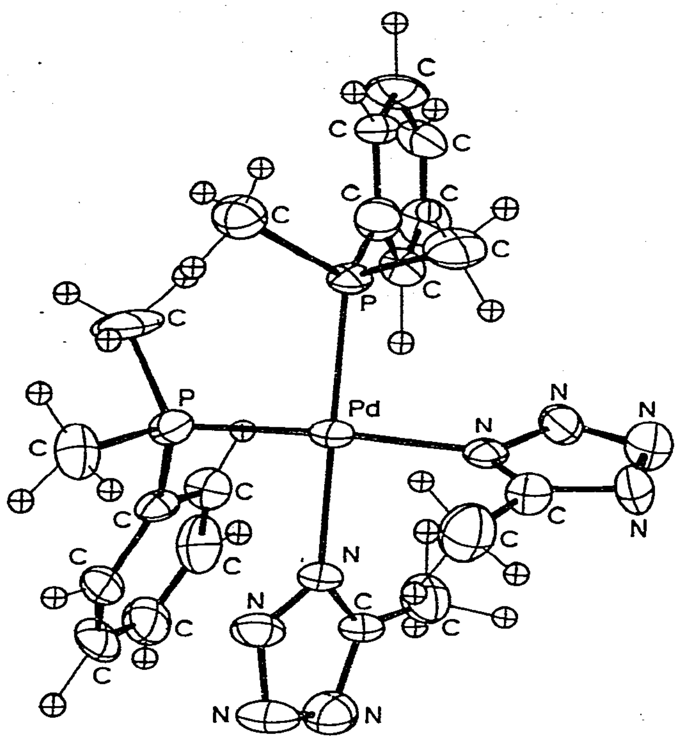
The effect of additions of phenol on the oligomerisation reactions of isoprene catalysed by the [$PdBr_2(DPE)_2$]+PhONa system has been investigated. Five linear dimers were identified from the reaction and the distribution of the isomeric dimers was remarkably effected by the molar ratio of phenol to isoprene [393]. An effective synthesis of 1-phenyl-1,4-hexadiene from the codimerisation of styrene and butadiene in the presence of [(π-C_3H_5)PdCl]$_2$ and $BF_3.PPh_3$ is reported [394]. A catalytic amount of water was found to increase significantly the activity of the [PdCl(aryl)$(PPh_3)_2$]-$BF_3.Et_2O$ system for the formation of 3-phenyl-1-butene from ethylene and styrene [395].

XIV Complexes and Reactions of General Interest

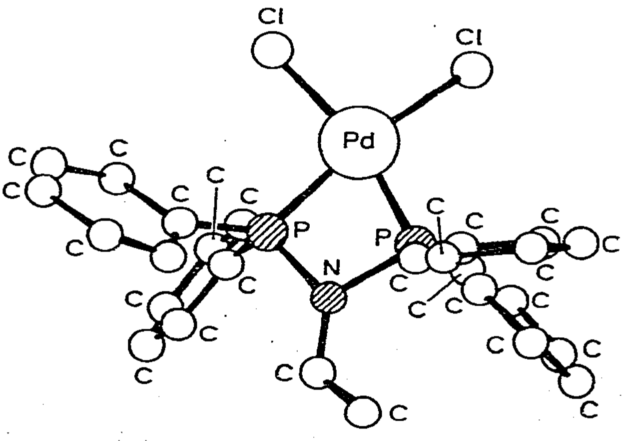
Reviews have appeared on the steric and electronic factors influencing the structure of nickel(II) complexes [396] and on the *trans*-influence, its measurement and significance [397]. A review with 33 refs. on the synthesis of optically active organophosphines and the preparation of the corresponding Ni,Pt and Rh complexes has been published [398].

A general synthesis has been developed for $P(OR)_3$, $P(OR)_2Ph$ and $P(OR)Ph_2$ derivatives of platinum and the coinage metals [399].

X-ray crystal structures of the following compounds have been published; *cis*-bis(dimethylphenylphosphine) bis-(5-methyltetrazolato)palladium(II) (134) [400]; dichloro(bis{diphenylphosphino}ethylamine)palladium(II) (135) [401];


C
C
C
C
C
C
C
C
P
C
P
Pd
N
N
N
C
C
C
N
C
C
C
C
N
N
C
C
C
C
N
N

(134)


Cl
Cl
Pd
C
C
C
C
C
C
C
C
P
P
N
C
C
C
C
C
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C
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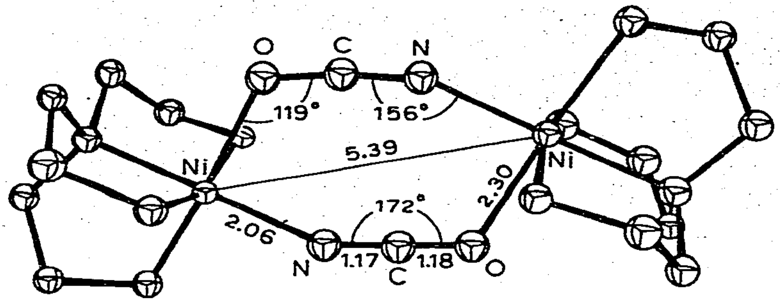
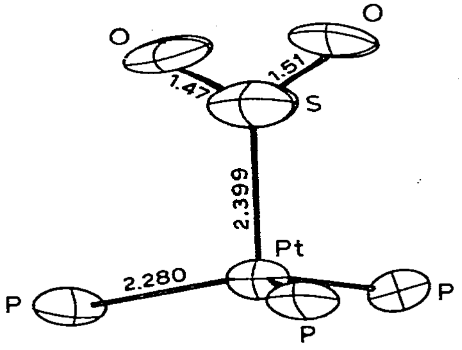
C
C
C
C
C

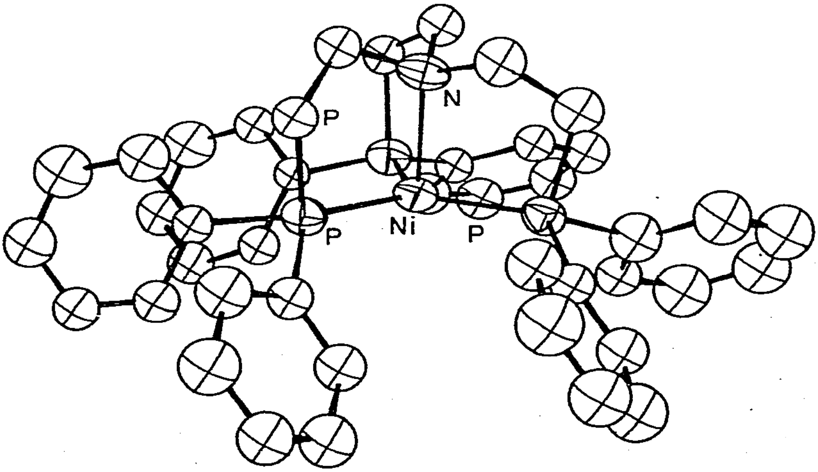
(135)


O
C
N
119°
156°
5.39
Ni
Ni
2.30
172°
2.06
N
1.17
C
1.18
O

(136)


O
O
1.47
1.51
S
2.399
Pt
2.280
P
P
P

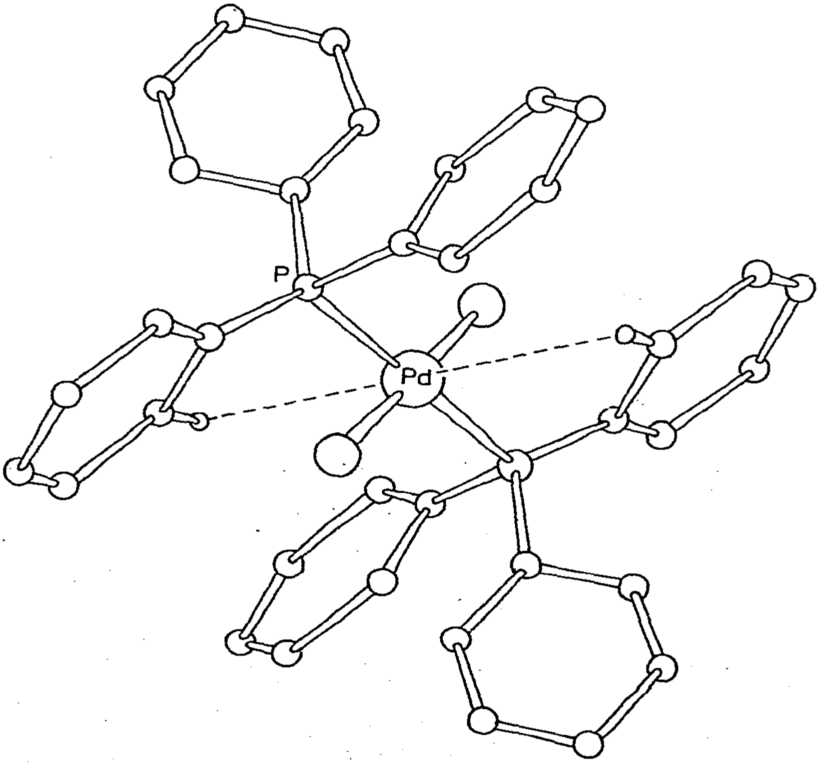
(137)


N
P
P
Ni
P

(138)

[Ni_2(tren)$_2$(NCO)$_2$] BPh_4 [tren = N($CH_2CH_2NH_2$)$_3$] (136) [402], [Pt(SO_2)(PPh_3)$_3$] (137) [403], [NiN(C_2H_4)$_3$] (138) [404], [PdI_2(PPh_3)$_2$] (139) [405], [$NiBr_2$ ($PFBu^t_2$)$_2$] (140) [406], bis(triphenylphosphine)(dibenzoylhydrazido)platinum (141) [407];[(PhLi)$_6Ni_2N_2$(Et_2O)$_2$] (142) [408-9] in which the molecular nitrogen is π-bonded to the transition metal; [$PtCl_2$(B_6H_{10})$_2$] (143) [410]; and *trans*-bis(-1-acetyl-3-*t*-butyl-1,2,L-triazabutadiene)platinum (144) [411].

During attempts to prepare water-soluble complexes of the group(VII) halides for catalytic studies the following complexes were characterised, *cis* or *trans*-[MX_2L_2] [M = Pd or Pt, X = Cl,Br, or I, L = P(CH_2OCOMe)$_3$, PMe (CH_2OCOMe)$_2$, PEt(CH_2OCOMe)$_2$, PMe_2(CH_2OCOMe), PBu^t_2(CH_2OCOMe), PPh_2(CH_2OCOMe), P(CH_2OH)$_3$, PMe(CH_2OH)$_2$, PPh_2(CH_2OH)]. The few water soluble complexes isolat did not show exceptional catalytic behavior [412]. A *cis*-*trans*-equilibrium and the existence of rotamers is proposed to explain the shift differences and temperature dependence of the ^{19}F and ^1H NMR spectra of the new compound



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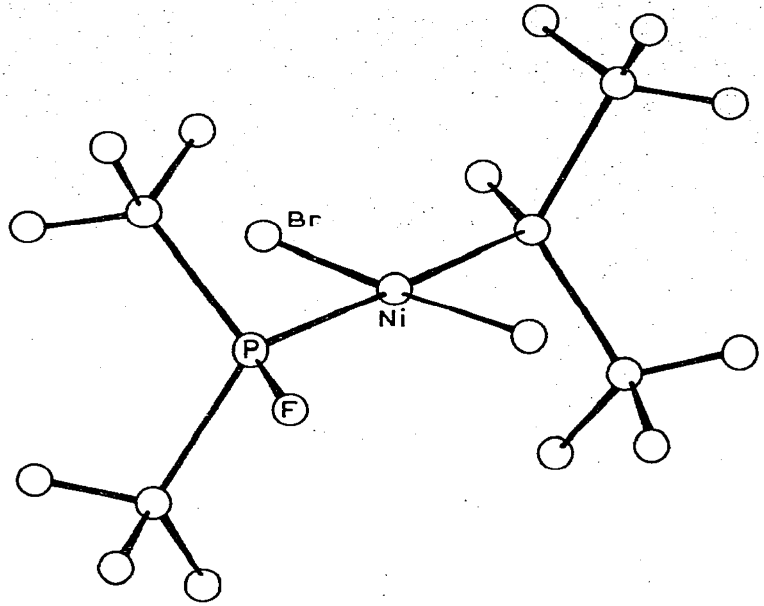
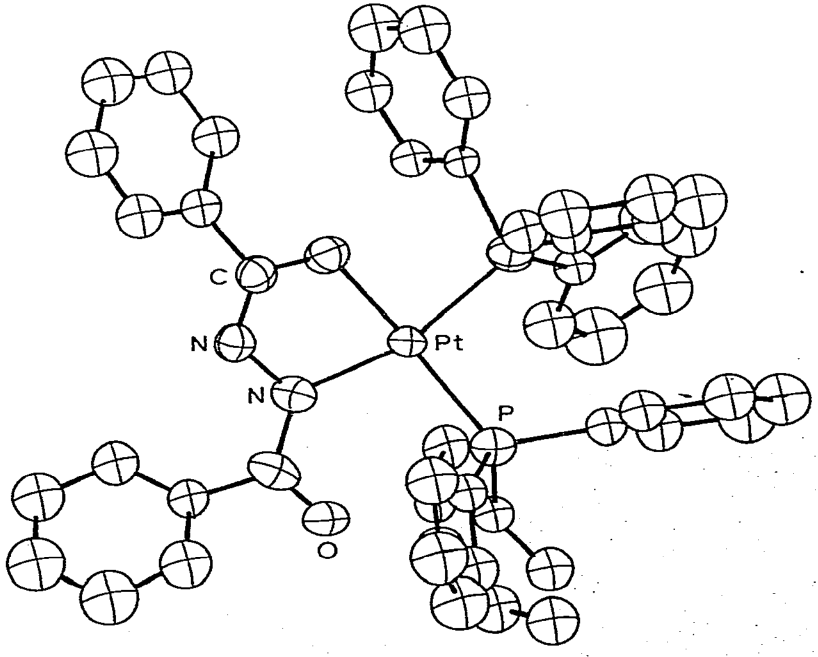
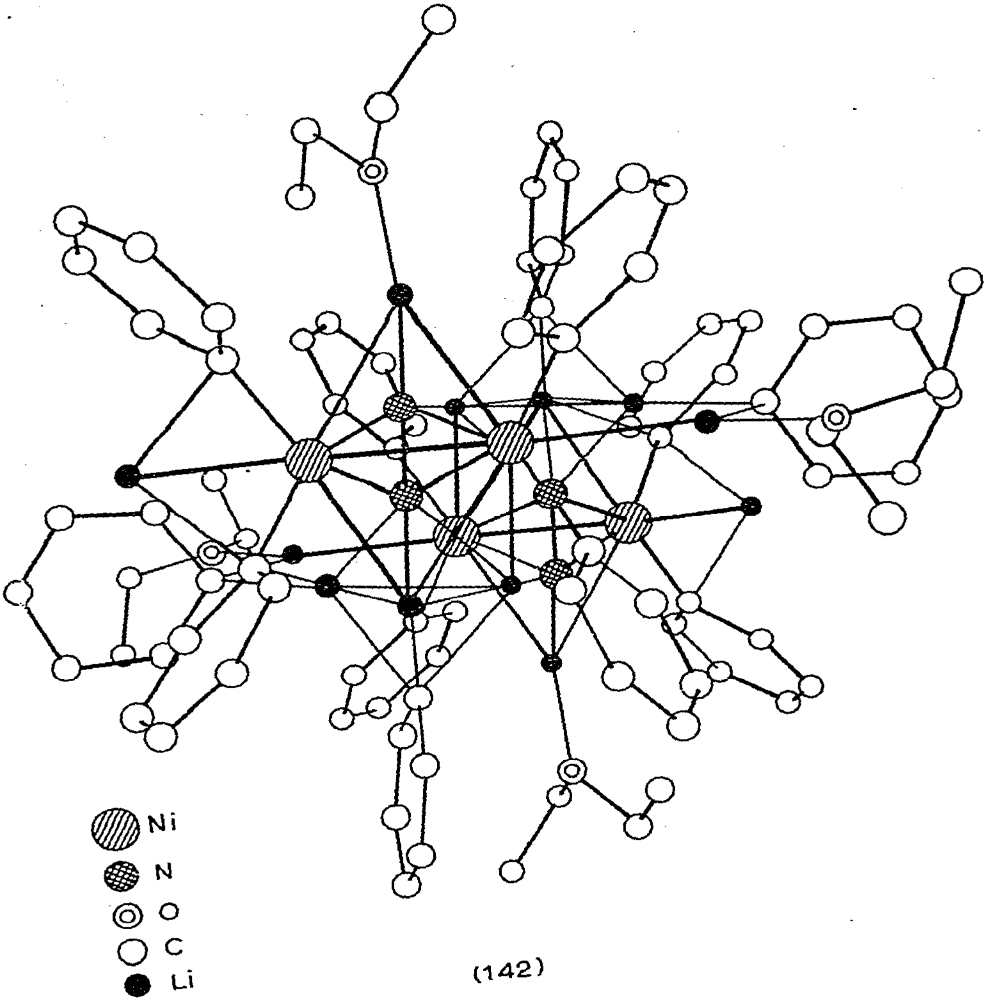


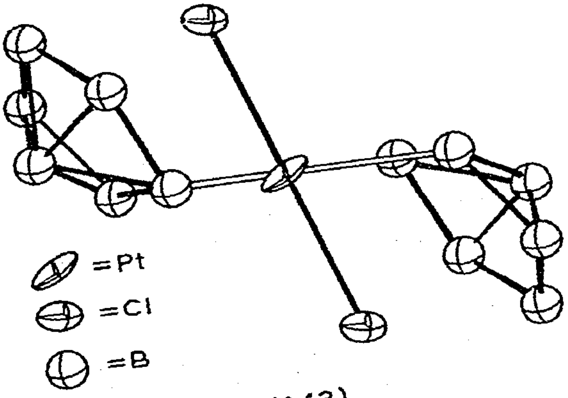
(140)



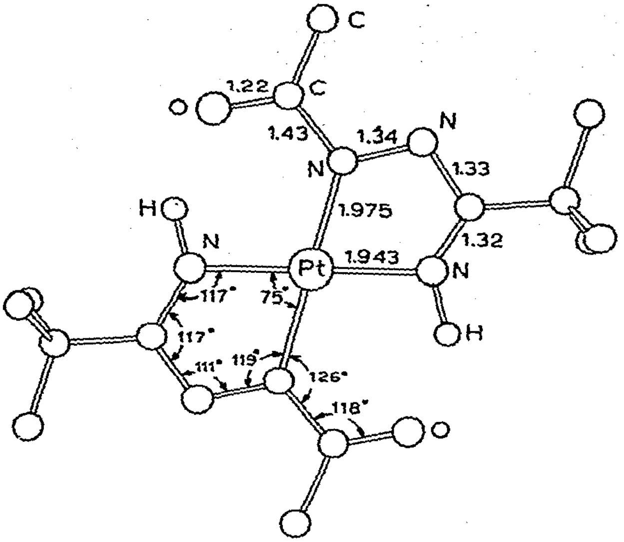
(141)



(142)



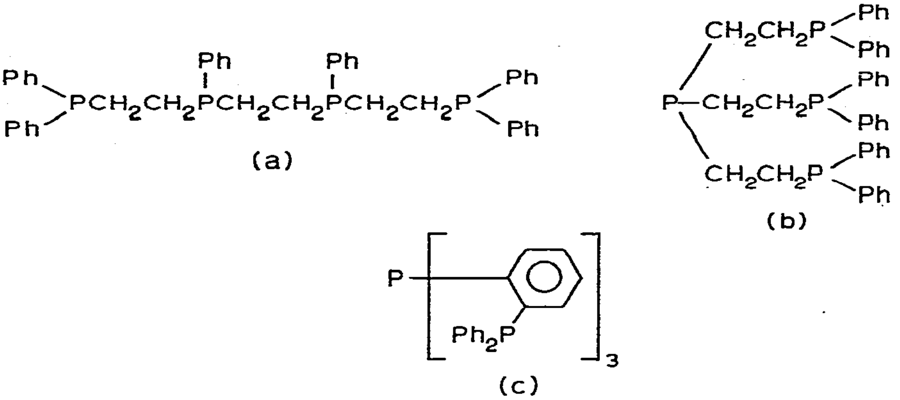
(143)



(144)

$[NiCl_2(PBu^t_2F)_2]$ [413]. The addition of organic acids to $M(PPh_3)_x$ (M = Pd, Pt, X = 3,4) has provided a new route to carboxylate complexes [414].

The following new complexes have been characterised: $[PtX(PPh_2)(PPh_2H)]_2$ (X = Cl,Br,I,NCS) [415]; $[MX_2(tvpp)]$ (M = Ni, X = Cl,Br,I,NCS,CN; M = Co, X = Br,I; M = Pd, X = Cl; tvpp = *trans*-1,2-bisdiphenylphosphinoethylene); $[Pd_2(tvpp)(CNS)_4]$ [416]; $[NiX_2(DPM)]$ (X = Cl,Br,I) where the iodo complex forms a five-coordinate iodo-bridged dimer in CH_2Cl_2 solution [417]; $[NiX_2PhP(CH_2CH_2CH_2PPh_2)_2]$ and $[NiXPhP(CH_2CH_2CH_2PPh_2)_2]PF_6$ (X = Cl,Br) [418]; $[Ni(PH_3)_x\{P(OPh)_3\}_{4-x}]$, (x = 1,2) [419]; *trans*-$[PdX_2L_2]$ (X = Cl,Br,I,NO_2; L = R_2S,Et_2S,Et_2Te,PhRS,PhEtSe) [420]; *cis*- or *trans*-$[M(SCF_3)_2L_2]$ (M = Pt,Pd, Ni; L = PPh_3); *cis*-or *trans*-$[MCl(SCF_3)L_2]$ (M = Pt,Pd; L = PPh_3,PEt_3), *trans*-$[PtH(SCF_3)L_2]$ (L = PPh_3,PEt_3) [421]; $[NiX_2L_2]$ [X = Cl,Br,I,NCS; L_2 = *cis*-(-2-diphenylarsinovinyl)diphenylphosphine(= vasp), 9,10-bis(diphenylphosphino)phenanthrene (=dpph)], $[NiL_2]$ $(ClO_4)_2$, $[Ni(vasp)_2X]Y$ (X=Cl,Br,I,NCS; Y = ClO_4; BPh_4) and $[Ni(dpph)_2NO_3]BPh_4$ [422]; $[NiLX]_n(ClO_4)_n$ (X = Cl, Br, I; L = $Ph_2AsCH_2CH_2N{=}C(CH_3)C(CH_3){=}NCH_2CH_2AsPh_2$) [423]; $[Ni_2L_3(H_2O)](ClO_4)_4$, $[NiLX_2]$ (X = Cl,Br; L = bis(*o*-diphenylarsinophenyl)phenylarsine, bis(*o*-diphenylarsinophenyl), [NiLX]Y (X = Cl,Br,I,NCS,NO_3; Y = Cl,Br,I,CNS,NO_3,BPh_4; L = tris(*o*-dimethylarsinophenyl)stibine) and $[NiL_2]Z$(Z = ClO_4,BPh_4) [424-5]; $[MX_2L_2HgX_2]$ (M = Pd,Pt;X = Cl,Br,I; L = tertiary phosphine or arsine) [426]; and [NiLX] BPh_4 (X = Cl,Br,I; L = (145 a, b or c) [427]).

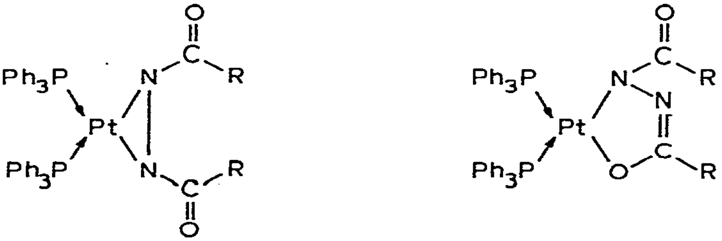

(a)

(b)

(c)

(145)

New preparations of $[Ni(PF_3)_3PH_3]$ [428] and $[Ni\{P(OPh)_3\}_4]$ [429] have been reported. *cis*-Dichlorobis(tertiaryphosphine)platinum(II) reacted in refluxing ethanol with 1,2-dibenzoyl-and 1,2-diacetyl-hydrazines in the presence of sodium bicarbonate to give [1,2-dibenzoyl-and diacetyl-hydrazido] bis(tertiaryphosphine)platinum(II) the structures of which could be (146 a or b) [430]. The complexes $[PtCl_2L_2]$ ($L = M(C_6Cl_5)Ph_2$; $M = P,As$) undergo ligand replacement by more basic phosphines [431]. The *cis*-isomer of $[PtCl_4(PPh_3)_2]$ has been shown to exist [432].


(a)

(b)

(146)

The step-wise complex formation of trialkyl phosphite and nickel(II) thiocyanate has been studied spectro-photometrically [433-4]. U.V. spectroscopy was also used in the study of the step-wise formation of trialkylphosphite complexes of nickel(II) iodide. Instability constants were calculated [435]. Oxidative additions of the organic disulphides RSSR ($R = Ph$, *o*- and *m*-$C_6H_4NO_2$, Bu^t, CN) to $[M(PPh_3)_4]$ ($M = Pd,Pt$) gave the mono and dinuclear compounds $[M(PPh_3)_2L_2]$ [L = SPh, S(*m*-$NO_2C_6H_4$), S(*o*-$NO_2C_6H_4$); M = Pd,Pt] and $[Pt(PPh_3)_2(SPh)_2L]$ (L = $Mo(CO)_4$,$PdCl_2$) which were formed by cleavage of a sulphur-sulphur bond [436].

Stable octahedral, low-spin Ni(III) complexes of the tetradentate ligand 2,3-dimethyl-1,4,8,11-tetraazacyclotetradecane, $[NiLX_2]ClO_4$ (X=Br,Cl,NCO,NO_3, and $\frac{1}{2}$ SO_4) were synthesized by oxidation with $(NH_4)_2S_2O_8$ in aqueous or concentrated HNO_3. Magnetic moment and epr measurements gave unequivocal evidence for the oxidation state of the Ni atom [437].

The new novel nitroso complexes of platinum, *cis*-$[Pt(NO)Cl_3X]$ (X = NH_3, $MeNH_2$, Me_2NH) and $Cs[Pt(NH_3)Cl_4(NO)]$ have been prepared from NO or NO_2 and the *cis*-diamineplatinum(II) complex in HCl [438]. Stability constants for the reversible hydrolysis of a series of acido-tetramine nitrosyl complexes, $[PtA_4(NO)X]^{2+}$ (A = NH_3,CH_3NH_2 or $\frac{1}{2}$ en, X = NO_3^-,HSO_4^-) have been measured [439]. The nature of the ligand *trans* to (NO) was found to be of primary importance in influencing the stability of the complex.

Nickel, palladium and platinum atoms have been inserted into the B_{18} cage in *n*- or *i*-$B_{18}H_{20}{}^{2-}$ by the metathetical reaction of $[MLCl_2]$ (M = Ni,Pd,Pt, L = PPh_3; L_2 = DPE) with *n*- or *i*-$[B_{18}H_{20}]^{2-}$ [440]. The equilibrium between tetrahedral and square planar forms of the complexes $[NiCl_2(PBu^n_3)_2]$ [441] and $[NiX_2L_2]$ (X = halogen; L = PR_3,PR_2Ph,$PRPh_2$, R = cyclopropyl or cyclohexyl) [442] has been studied by NMR. The equilibrium was effected by solvent and ligand electronic effects. A ^{13}C NMR study has shown the major importance of steric effects in dictating the coordination number in some Pd(0) complexes [443]. Extensive NMR data and several NMR studies have been recorded and done on the complexes $[MX_2\{P(OAr)_3\}_2]$ (M = Pd,Pt; X = Cl,Br,I; Ar = Ph,*p*-ClC_6H_4, *o*-,*m*-, or *p*-tolyl) [444]; $[PtCl_{4-n}(R_3P)_n]^{(n-2)+}$ and $[PtCl_{6-n}(R_3P)_n]^{(n-2)+}$ (n = 1-3) [445]; $[MX(PMe_3)_3][NO_3]$ (M = Pd,Pt), *mer*-$[PtX_3(PMe_3)_3][NO_3]$, $[PtI(P\ Me_3)_3][NO_3]$, and $[Pt(PMe_3)_4][BF_4]_2$ [446]; $M[P(OCH_3^-)_3]_5^{2+}$(M = Ni,Pd,Pt) [447]; *cis*-$[PtX_2(PBu_3)_2]$, *trans*-$[PtX_2(PBu_3)_2]$ and $[PtX(PEt_3)_3]$ ClO_4 (X = NO_3,N_3,NCO,NCS,NO_2,CN,halogen) [448].

^{31}P NMR showed that the addition of equimolar amounts of bromine to *trans*-$[PtCl_2(PR_3)L]$ (R = Et, L = Py, 3,5-Me_2Py, 4-Bu^tPy, PEt_3; R = Bu^n, L = Py) or of *trans*-$[PtCl_4(PEt_3)(Py)]$ to *trans*-$[PtBr_4(PEt_3)(Py)]$ resulted in halogen scrambling giving an approximately statistical distribution of *trans*-$[PtBr_xCl_{4-x}(PEt_3)L]$ (x = 0-4) [449].

The ^{1}H NMR spectra of the palladium(II) benzylphosphine complexes $[Ph_{3-n}P(CH_2Ph)_n]_2PdCl_2$ (n = 1,2,3) have been investigated. The complexity of the spectrum for n = 2 was ascribed to hindered rotation around the phosphorus carbon bonds giving rise to a number of rotamers [450].

Kinetic studies on the replacement of tributyl phosphine in the five-coordinate bis(diethyldithiophosphato)nickel(II)(tributyl phosphine) complex with bidentate ligands has shown that the replacement proceeds via a dissociative mechanism [451]. The results of U.V. kinetic studies and variable temperature NMR have supported a consecutive displacement mechanism in the _cis_-_trans_-isomerisation of complexes of the type _cis_-$[PtX_2L_2]$ $\{X = Cl, I,\ L = Me_2PhP,\ (\underline{o}\text{-}MePh)\,Me_2P\}$ and _cis_-and _trans_-$[PdCl_2(Me_2\underline{o}\text{-}tolP)_2]$ catalysed by tertiary phosphine ligands [452-3].

The application of high external pressure produced a solid state structural change between the tetrahedral and square planar forms of $[Ni(Ph_2PCH_2Ph)_2Br_2]$ [454]. Anomalous molecular weights and IR spectra observed for $[(Ph_3P)_2M$(N,N-di-_n_-butylselenocarbamate)] (M = Pd or Pt) in dilute solution suggested the partial dissociation of the Ph_3P ligand as a result of the selenocarbamate ligand acting in a bidentate manner [455]. The relative _trans_-effects of the PPh_3 and $SbPh_3$ ligands in the complexes _trans_-$[Pt(NH_3)_2LCl]^+$ (L = PPh_3, $SbPh_3$) have been determined by measuring the metal-halogen IR stretching frequencies, and in the complexes _trans_-$[Pt(NH_3)_2L\ H_2O]^{2+}$ (L = Ph_3P, Ph_3Sb) by measuring the pka values [456]. The products of the condensation reactions of Ni, Pd and Pt atoms with N_2 at 4.2 - 10°K in Argon, $^{14}N_2$and$^{14}N_2/^{15}N_2$ matrices has been investigated by IR and Raman spectroscopy. The stoichiometries of the products were established as $Ni(N_2)_n$, $Pd(N_2)_m$ (n = 1-4, m = 1-3) [457], $Pt(N_2)_p$ (p = 1-2 [458]; p = 1-3 [459]) and $Pt_x(N_2)_y$ where x or y $\geqslant$ 2 [458]. $Pt(N_2)_2$ was postulated to have "side-on" bonded N_2 ligands [459]. When gaseous oxygen or oxygen argon mixtures were used with Ni, Pd and Pt atoms, the binary transition metal dioxygen complexes MO_2 and $M(O_2)_2$ were formed [460].

Isotopic frequencies and bond intensities were found to be in close agreement with calculations using the Cotton-Kraihanzel approximation which allowed the assignment of structures to the different products [457-59].

The X-ray photoelectron spectra of about 70 compounds of nickel in all its known oxidation states have been measured. The binding energies of the Ni($2p_{3/2}$, $1/2$) levels were correlated with ligand electronegativities, delocalization of charge on the ligands, and stereochemistry. A relationship between paramagnetisms and the shake-up transition was established [461]. Binding energies of the 4F levels have been measured in a series of bis-(triphenylphosphine)platinum(II)pseudohalide complexes by XPS. Although the maximum variation was only 2.8 eV, variations due to the pseudohalogen were observable and were interpreted in terms of current bonding theories [462].

A preliminary account of the reactions of $MeOSO_2F$ and $[Et_3O][BF_4]$ with a variety of organometallic complexes has appeared. Four distinct types of reactions were observed; (i) halogen abstraction occurred in complexes in which the ligands (dienes, Group V ligands) were more strongly bonded than halogen and had no additional electrons, (ii) alkylation of the ligand occurred when the ligand had additional lone pairs available, (iii) oxidative addition occurred in coordinatively unsaturated complexes, (iv) simple oxidation of the metal occurred when the halide was not labile and the other ligands were unreactive [463].

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