NICKEL, PALLADIUM AND PLATINUM. ANNUAL SURVEY COVERING THE YEAR 1982*

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1 INTRODUCTION

This survey details the accounts of the organometallic chemistry of nickel, palladium and platinum published in 1982. Material from the patent literature which was reported in Chemical Abstracts in 1982 is also included, and the organisation remains broadly similar to that in past surveys.

A number of reviews of general interest have appeared, including a wide-ranging one of compounds of the platinum group metals [1]. Oxidative addition in the coordination chemistry of the platinum metals has been discussed [2], as have compounds of palladium(IV) and platinum(IV) [3]. The use of organopalladium intermediates in organic synthesis has again been a growth area [4], and reactions of alkene, allyl and alkylpalladium complexes with nucleophiles have been specifically considered [5]. The relative two-ligand dissociation enthalpies, $\delta D(Ni^{2+}-2L)$ for Ni^{2+} with fifty organic molecules have been determined [6].

2 METAL CARBON σ-BONDED COMPLEXES

SCF X_α SW calculations on $[Me_2ML_2]$ (M = Ni, Pd or Pt), $[H_2PtL_2]$ and $[HPtMeL_2]$ suggested a correlation between molecular orbital character and the rate of reductive elimination. The complexes which eliminated XY readily had occupied molecular orbitals with pronounced M-X(Y) antibonding character, and those which eliminated XY slowly had only vacant M-X(Y) antibonding orbitals [7]. Theoretical analysis of the reductive elimination of methane from $[HPtMe(PX_3)_2]$ showed that elimination should be very facile, in good agreement with experiment [8].

Abel's group have published further studies of the dynamic nmr spectra of methyl platinum complexes. In $[Me_3Pt(X)\{Q(Me)CH_2CH_2Q'(Me)\}]$ (Q = Q' = S or Se or Q = S, Q' = Se), total nmr band-shape fitting methods provided accurate values for the barriers to inversion at sulphur and selenium. The effects of ligand ring size, halide and metal oxidation state were discussed [9]. The complexes $[Me_3Pt(X)(MeSRSeMe)]$ (R = $(CH_2)_2$ or 1,2-C_6H_4) were prepared, and the energy barriers associated with pyramidal inversion of the individual chalcogens determined [10]. Reaction of thiols, RSH, with $[\{Me_3Pt(OH)\}_4]$ gave $[\{Me_3Pt(SR)\}_4]$ [11].

Platinum on alumina catalysts with good reforming activity were prepared from the thermal decomposition of $[\{Me_3PtX\}_4]$ [12]. The reaction of [MePt(cod)Cl] with chelating ligands, LL', gave [MePt(LL')Cl]. Cationic mixed complexes, $[MePt(LL')L''][PF_6]$, could be prepared by further reaction with L" in the presence of $Ag[PF_6]$ [13]. Monosubstitution of only the phosphine ligands in *cis*-[$Me_2Pt(PMe_3)_2$] occurred, to give *cis*-[$Me_2Pt(PMe_3)(CNCMe_3)$] [14].

Oxidation of [$Me_2Pt(NN)$] (NN = bipy or phen) by ROH in the presence of a large counterion, X^-, gave rather stable platinum(IV) complexes, [$Me_2Pt(OR)(NN)]^+X^-$ [15]. *Cis,cis,trans*-[$Me_2Pt(NO_2)_2(PEt_3)_2$] was prepared by reaction of *cis*-[$Me_2Pt(PEt_3)_2$] with nitric oxide; its structure was determined by X-ray diffraction techniques [16]. The structure of $K_4[Pt_2(H_2P_2O_5)_4(Me)I]$ was confirmed by ^1H, ^{13}C, ^{31}P and ^{195}Pt nmr spectroscopy [17].

^{195}Pt chemical shift anisotropy in the solid platinum complexes, [$\{Me_3Pt(acac)\}_2$] and $[Me_3Pt]_2[SO_4]$, was measured. The ^{195}Pt relaxation parameters were found to be strongly field dependent [18].

The rate of oxidative addition of bromomethane to [Me_2PtL_2] to give *fac*-[Me_3PtL_2Br] depended on L. A 2-methoxy group enhanced the reaction rate by electronic interaction with the metal. Oxidative addition of benzyl bromide and α-haloesters was also studied [19]. Reaction of $[PtCl_4]^{2-}$ with iodomethane gave [$MePt(H_2O)Cl_4$]; this reacted with sodium chloride to give chloromethane, and with tin(IV) chloride to give methane [20].

Some reactions of oligomeric methylplatinum complexes have been studied in detail (Scheme 1); the methyl groups generally acted only as spectators [21]. Reaction of [$Me_2Pt(cod)$] with $R_2P(CH_2)_3PHPh$ gave the dimeric species, 1 [22].

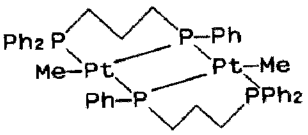
$$[\{Me_2Pt(OH)Br\}_n] \xrightarrow{MeOH} [\{Me_2Pt(MeOH)(\mu\text{-}OH)Br\}_2]$$

K[OH]

$$[\{Me_2Pt(OH)(\mu\text{-}OH)Br\}_2]$$

$$[\{Me_2PtBr_2\}_n] \xrightarrow{MeOH} [Me_2Pt(MeOH)_2Br_2]$$

Scheme 1 Reactions of oligomeric methylplatinum complexes [21]



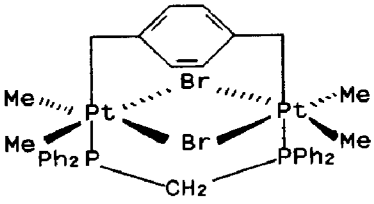
1

Reaction of *cis*-[$Me_2Pt(cod)$] with tris(thiazol-2-yl) phosphine, L, gave *cis*-[Me_2PtL_2]. Many other phosphines substituted with heterocycles gave similarly succesful reactions [23]. The relative proportions of diastereoisomers in [MePt(chelate)L][ClO_4] (chelate = DIOP, CHIRAPHOS or other chiral phosphines; L = R- or S-PhCH(Me)NH_2) were determined by ^{31}P nmr spectroscopy. The structure of [MePt(DIOP)Cl] was determined by X-ray diffraction techniques; the seven-membered chelate ring adopted a twist-chair conformation [24].

Treatment of [$Pt_2(\mu$-dppm$)_3$] with a halomethane gave [$MePt_2(\mu$-dppm$)_2(\eta^1$-dppm)]X. The η^1-dppm ligand could be replaced by PPh_3, PMe_2Ph or pyridine [25]. The "A-frame" complex, [$Me_2Pt_2(\mu$-dppm$)_2(\mu$-H)], could be synthesised by the reaction of [$Me_3Pt_2(\mu$-dppm$)_2$][PF_6] or [$Me_2Pt_2(\mu$-dppm$)_2(\mu$-Cl)][PF_6] with Na[BH_4]. The μ-hydrido species was stable in the solid state and its structure was determined by X-ray diffraction. Some weak metal-metal interaction was detected. On reaction with an excess of PMe_2Ph, methane was evolved, but the reaction was not quantitative and some platinum(0) complexes were also formed [26].

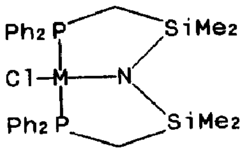
The kinetics of replacement of dmso in *cis*-[$R_2Pt(dmso)_2$] by ligands such as bipy and phen have been studied. The reaction proceeded *via* initial loss of dmso to give an unsaturated three-coordinate complex [27]. The complex *cis*-[$BuPt(PEt_3)_2Cl$] underwent isomerisation to the *trans*-species in 2-propanol. Addition of chloride ion prevented isomerisation and promoted β-elimination, to give mainly 1-butene and Z-2-butene [28].

X-ray diffraction studies of the propanone, ethanonitrile and benzene solvates of [$PdCl(CH_2CN)(PPh_3)_2$] were undertaken. There was little, if any, evidence for the interaction of the nitrogen atom with the metal [29]. The preaparation of 2 was described in detail, and the complex was characterised by X-ray diffraction [30].



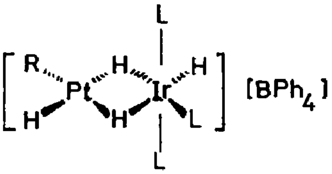
2

Reaction of [Pt(dppm)Cl_2] with RLi gave [$R_2Pt(dppm)$]. Addition of an excess of dppm to this complex gave [$R_2Pt(\eta^1$-dppm$)_2$], which was useful in the synthesis of bimetallic derivatives [31]. The halide in 3 (M = Ni or Pd) was readily replaced by an alkyl group using RMgBr (R = Me, $CH_2CH=CH_2$, Ph or $CH=CH_2$); organolithium reagents gave lower yields [32].



3

The synthesis and properties of $[RCH_2Ni(PMe_3)(S_2CNR'_2)]$ ($R = Me_3Si$ or $Ph_2C(Me)$) were described; the complexes showed dynamic behaviour on the nmr timescale [33]. Reaction of *trans*-$[RPt(MeOH)L_2]^+$ with $[H_5IrL_2]$ gave the binuclear species, 4. *Cis* $\leftrightharpoons$ *trans* isomerisation in 4 occurred *via* the breaking of a Pt-H bond [34].



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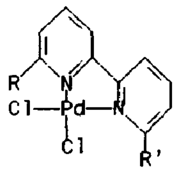
The rate of oxidative addition of RX to $[Ni(PEt_3)_4]$ was found to be ten to twenty fold slower than the related reactions of $[Ni(PEt_3)_3X]$. With halomethanes the main products were methane and ethane, whereas iodoethane gave ethene and ethane [35]. Reaction of $[R_XML_2(OH)]$ with ROOH gave $[R_XML_2(OOR)]$ ($M = Pd$ or Pt, $R = H$ or Me_3C, $R_X = CF_3$ or CH_2CN). The product complexes behaved as oxygen transfer agents towards PPh_3, CO, NO or PhCHO [36].

Numerous papers have described *C*-bonded complexes of *β*-diketonates and related species. Reaction of **5** with the anion of dimethyl propanedioate resulted in substitution of both chlorine ligands [37]. $[Pd(acac)_2]$ reacted with 2-, 3-, or 4-methylpyridines (B) to give complexes of type **6** [38], and a similar reaction occurred when $[Pd(hfacac)_2]$ was treated with a substituted aniline [39,40]. Reactions of the product complexes were studied [41]. Treatment of the terminally bonded acac complex, **7**, with $[M(acac)_n]$ and chelating bis(nitrogen) ligands gave bimetallic species such as **8** [42,43]. Binuclear complexes were also obtained by reaction (1) [44]. Reaction of $[Pd(tfacac)L_2][tfacac]$ ($L = R_3P$) with a base gave initially **9**, which was rapidly isomerised to **10**. $[Pd(tfacac(2-)\text{-}C,O)(PPh_3)(2,6\text{-}Me_2py)].C_6H_6$ was characterised by an X-ray diffraction study, and many spectroscopic data for related complexes were reported [45].



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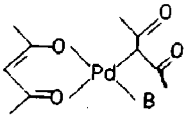

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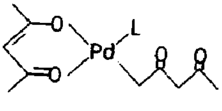

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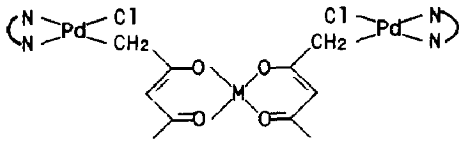

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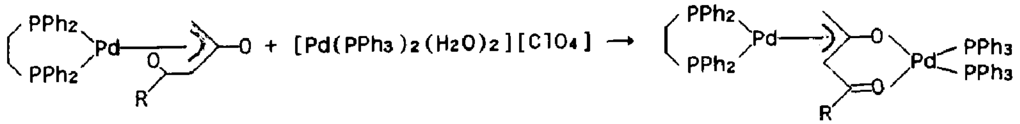
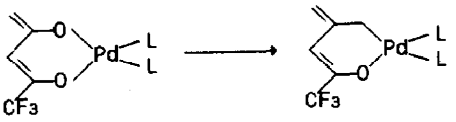


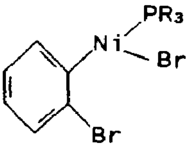
(1)



9 10

Reduction of a species described as [Ph_2Ni] resulted in deposition of nickel metal on ceramics, glass and quartz [46]. Reaction of tris(2,4,6-trimethylphenyl)vanadium with [$Ni(cod)_2$] gave a species of stoicheiometry [NiV_2(2,4,6-trimethylphenyl)$_6$] [47].

The preparations of [$Ni(C_6Cl_5)(PCy_3)_2X$] (X = Cl, I, [NCS], [NCO] or [N_3]) have been described. These complexes were rather reactive due to their steric crowding, and reacted with HCl to give C_6Cl_5H. One of the PCy_3 ligands could be readily replaced by PPh_3 [48]. Reaction of *trans*-[NiL_2Cl_2] with RLi (R = 2,6-dimethoxyphenyl) gave *trans*-[$RNiL_2Cl$] and *trans*-[R_2NiL_2]. Further treatment of *trans*-[R_2NiL_2] with butyl lithium followed by Me_3SiCl (L = PMe_3) resulted in lithiation of the ligand to give *trans*-[$R_2Ni\{PMe_2CH_2SiMe_3\}_2$] [49]. Thallium(III) complexes, [$Tl(C_6F_5)_2Br$], were shown to oxidise nickel(0) species such as [NiL_4] to give [$Ni(C_6F_5)_2L_2$] and thallium(I) salts [50]. Cyclic voltammetry was used to study the reactions of the electrogenerated nickel(0) complex, $[NiL_4]$, with 1,2-dibromobenzene. The initial product was the σ-aryl species, **11**, which could be isolated. This reacted with further nickel(0), and there was some evidence for the production of **12** [51].



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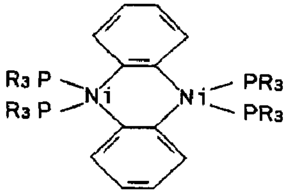
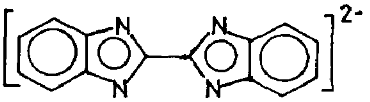


12

A range of complexes of bibenzimidazole, 13, have been prepared, including $[Ar_2Pd(\mu\text{-}BiBzIm)Au_2(dppm)]$ (Ar = C_6F_5 or C_6Cl_5) and $[(C_6F_5)Pd(PPh_3)(\mu\text{-}BiBzIm)Au_2(dppm)]^+$ [52]. Mixed bimetallic complexes such as 14 and 15 (X = [CN] or [SCN]) have been prepared from $[R_4N][(C_6F_5)AuX]$. There was little evidence as to whether the original modes of binding of cyanide or thiocyanate to gold had been preserved in the product complexes [53].



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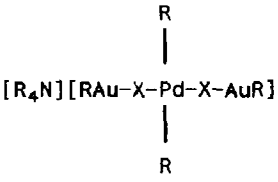
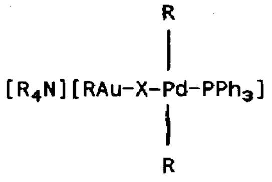


$$[R_4N][RAu\text{-}X\text{-}\underset{R}{\overset{R}{Pd}}\text{-}X\text{-}AuR]$$

14

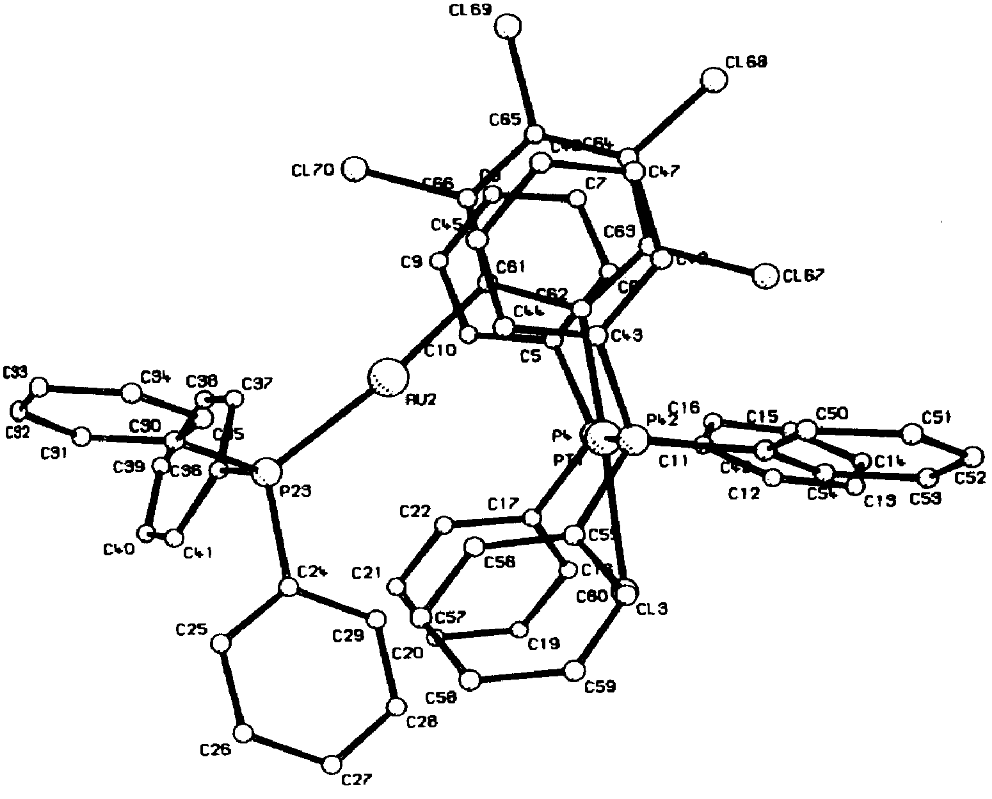


$$[R_4N][RAu\text{-}X\text{-}\underset{R}{\overset{R}{Pd}}\text{-}PPh_3]$$

15

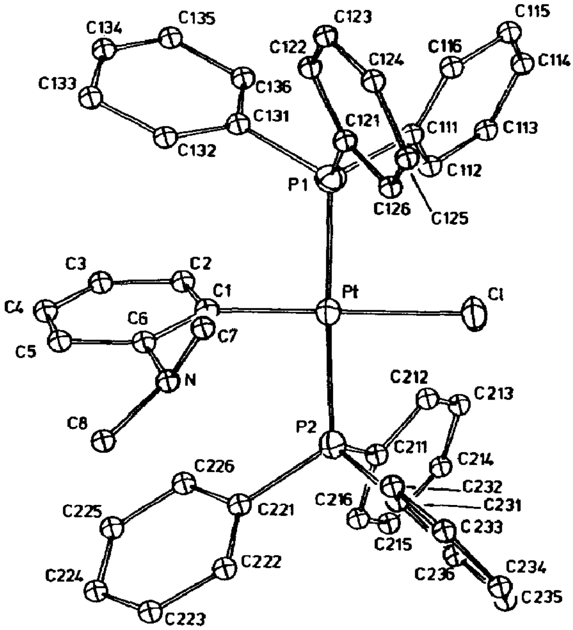
The reaction of $[Pt(PPh_3)_3]$ with $[(C_6Cl_5)Au(PPh_3)]$ gave *trans*-chloro{3,4,5,6-tetrachloro-2-[(triphenylphosphine)auriophenyl] bis(triphenylphosphine) platinum(II), 16, [54]. The structure of this complex has been determined by an X-ray diffraction study. The geometry at gold was distorted linear, whilst that at platinum was approximately square planar. There were no metal-π-interactions. It was considered that the $\{Au(PPh_3)\}$ group activated the adjacent carbon-chlorine bond towards oxidative addition

[55]. The species *cis*-$[(X\text{-}C_6H_4)Pt(PPh_3)_2X']$ (X' = Cl or Br), were synthesised by reaction of the appropriate Grignard reagent with *cis*-$[Pt(PPh_3)_2Cl_2]$ followed by treatment of the product, *cis*-$[Ar_2Pt(PPh_3)_2]$, with hydrogen chloride. The thermal isomerisation in the crystalline phase was studied, and the related *trans*-isomers were characterised [56].



16 (Reproduced with permission from [55])

Reaction of *cis*-$[Pt(PPh_3)_2Cl_2]$ with 2-lithiodimethylaniline in the presence of lithium bromide gave initially the *cis*-monoadduct, *cis*-$[Pt(PPh_3)_2(C_6H_4\text{-}2\text{-}NMe_2)Br]$. This was readily isomerised to the *trans*-compound, 17, which was characterised by X-ray diffraction [57]. Thermolysis of $[(C_6F_5)_2M(dioxan)_n]$ (M = Pd or Pt, n = 2 or 3) gave complexes with only one dioxan ligand. The thermochemistry of the reactions was discussed [58].



17 (Reproduced with permission from [57])

Treatment of the cationic species, $[(M(R_3P)L]^+$ (L = solvent, M = Au or Ag) with *trans*-$[HPt(C_6Cl_5)(PEt_3)_2]$ gave the bridged complexes, $[(R_3P)M(\mu\text{-}H)Pt(PEt_3)_2(C_6Cl_5)]^+$, which were identified by ^1H and ^{31}P nmr spectroscopic techniques [59]. Reaction of $[Pt(PPh_3)_3]$ with R_2Hg resulted initially in oxidative addition to yield $[RPt(PPh_3)_2(HgR)]$. Treatment with tfaH gave $[RPt(PPh_3)_2(OCOCF_3)]$. In the cases in which the R group was a 2-chlorinated aryl the intermediate was unstable and underwent extrusion of mercury to give a diaryl complex [60]. Complexes of the types *cis*-$[RPt(PPh_3)_2(PbR_2R')]$ and *trans*-$[Pt(PBu_3)_2(PbR_3)_2]$ were investigated by ^{31}P, ^{195}Pt and ^{207}Pb nmr spectroscopy [61].

Reaction of *cis*- or *trans*-$[MePt(PMePh_2)_2Cl]$, or $[MePt(cod)Cl]$, with PhLi gave $[Ph_2PtL]$ (L = cod or $(PMePh_2)_2$). However, the preparation of the mixed complexes could be achieved by reactions (2) and (3). The reactions of the mixed complexes were investigated with a view to distinguishing the possible mechanisms of S_E2, and oxidative addition followed by reductive elimination. The S_E2 mechanism seemed to explain both the selectivity and reactivity observed in reaction such as (4) and (5) [62].

$$\textit{cis}\text{-}[Pt(PMe_2Ph)_2(NO_3)_2] + Me_3SnAr \longrightarrow \textit{trans}\text{-}[ArPt(PMe_2Ph)_2(NO_3)] \xrightarrow{MeLi} \textit{cis}\text{-}[MePt(Ar)(PMe_2Ph)_2] \tag{2}$$

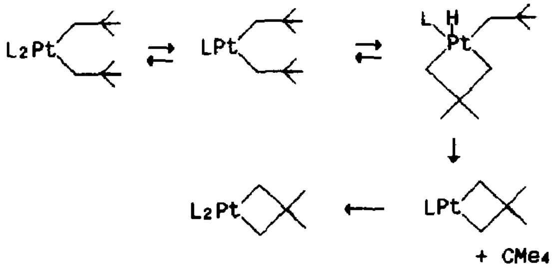
$$[Pt(cod)I_2] + Me_3SnAr \longrightarrow [ArPt(cod)I] \xrightarrow{Ag[NO_3],\ Me_4Sn} [MePt(Ar)(cod)] \tag{3}$$

$$\textit{cis}\text{-}[MePt(Ar)(PR_3)_2] + HCl \longrightarrow CH_4 + \textit{cis}\text{-}[ArPt(PR_3)_2Cl] \tag{4}$$

$$[MePt(Ar)(cod)] + HCl \longrightarrow [MePt(cod)Cl] + ArH \tag{5}$$

The photolysis of $[Et_2PdL_2]$ yielded ethene, ethane and butane in the ratio 2:2:1, irrespective of the stereochemistry of the starting material. Deuterium labelling studies suggested that there was a common intermediate, probably $[Et_2PdL]$, which could adopt a range of geometries [63]. A kinetic study of the thermolysis of $[R^1R^2PtL_2]$ revealed the existence of both dissociative and non-dissociative pathways [64].

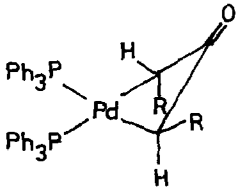
Further work from Whitesides and his coworkers has established the mechanism of reaction for the thermolysis of $[PtL_2(CH_2CMe_3)_2]$ (Scheme 2); the driving force for the reaction would seem to be the release of steric strain [65]. The rate of the decomposition of $[PtL_2(CH_2CMe_2Et)_2]$ was some 10^4 times as rapid, but the same organometallic product was formed. $[PtL_2(CH_2CH_2CMe_3)_2]$ reacted *via* β-hydride elimination [66].



Scheme 2 The mechanism of thermolysis of neopentyl platinum derivatives [65]

The preparations and thermolysis of *cis*-$[Ar_2Pt(PR_3)_2]$ have been described. On thermolysis biphenyl derivatives were produced [67]. *Trans*-$[Ph_2Pt(PPh_3)_2]$ was prepared and its structure was determined by X-ray diffraction. Despite the *trans*-stereochemistry established, thermolysis yielded biphenyl in a clean and high-yielding reaction [68].

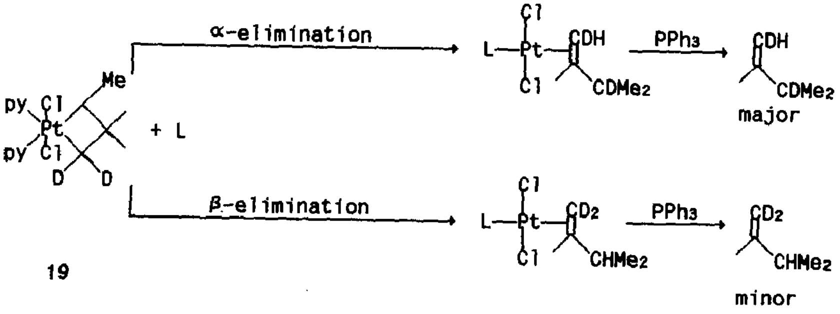
The complex **18** was produced from the reaction of 3-oxoglutarate with $[Pd_2(dba)_3]$ in the presence of PPh_3 and in an oxygen atmosphere. X-ray diffraction studies showed that the ring was appreciably non-planar, implying a strong contribution from structures such as **18a** [69].



18

18a

Thermolysis of $[L_2PtCH_2CMe_2CH_2]$ (L = $P(CHMe_2)_3$ or PCy_3) gave $[PtL_2]$ together with dimethylcyclopropane and a little 2,2-dimethylpropane, by a homogeneous process. The reaction rate decreased with added phosphine indicating that the loss of phosphine was crucial to the process. Two mechanisms were proposed, one involving direct decomposition of the dissociated species, and the other proceeding *via* a reversible cyclometallation of the remaining phosphine [70]. Rearrangement of platinacyclobutanes such as **19** was shown, by a deuterium labelling study, to occur primarily by a 1,3-shift and α-elimination, rather than β-elimination (Scheme 3) [71].

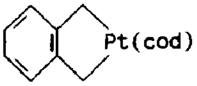


Scheme 3 Mechanism of rearrangement of platinacyclobutane complexes [71]

$[Cl_4Pd(C_3H_6)]^{2-}$ was calculated to be more stable than the related alkene/carbene complex [72].

Reaction of the bis Grignard reagent, C_6H_4-1,2-$(CH_2MgCl)_2$ with $[Pt(cod)I_2]$ gave 20 [73]. When the complex *trans*-$[Pt(O_2CR)_2(py)_2]$ was heated in pyridine, *trans*-$[R_2Pt(py)_2]$ was formed for R = C_6F_5 or 3- or 4-HC_6F_4 [74]. Phenylpalladium intermediates were claimed in the hydrogenation of

[Pd(PPh_3)$_2$$Cl_2$] in the presence of amines [75].



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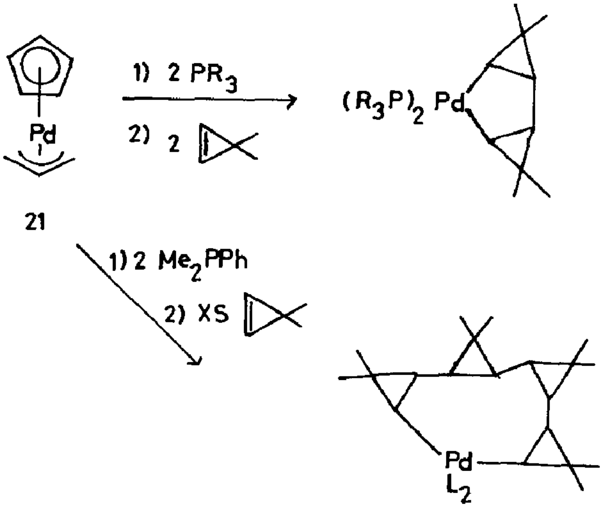
21 rected with two molar equivalents of PMe_3 followed by two moles of 3,3-dimethylcyclopropene to give only **22a**; no further reaction occurred even under forcing conditions. A similar reaction was noted using PMe_2Ph as the ligand. **22b** was also unreactive. However, with PMe_2Ph as the ligand and an excess of dimethylcyclopropene, 23 was the sole product. The thermolyses of 22 and 23 were studied [76].



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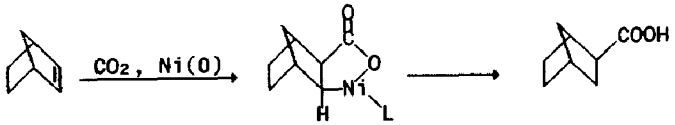
23

22a R = Me
22b R_3P = Me_2PPh

Reaction of norbornene with carbon dioxide in the presence of nickel(0) and a ligand, L, gave **24**; the carboxylic acid was released on hydrolysis [77]. Addition of an organomercurial to norbornene in the presence of palladium(II) chloride yielded **25**, which was used in a synthetic approach to thiophene containing prostaglandins [78].



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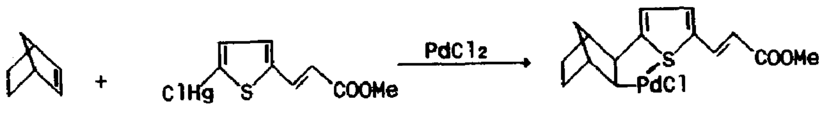
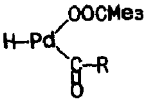


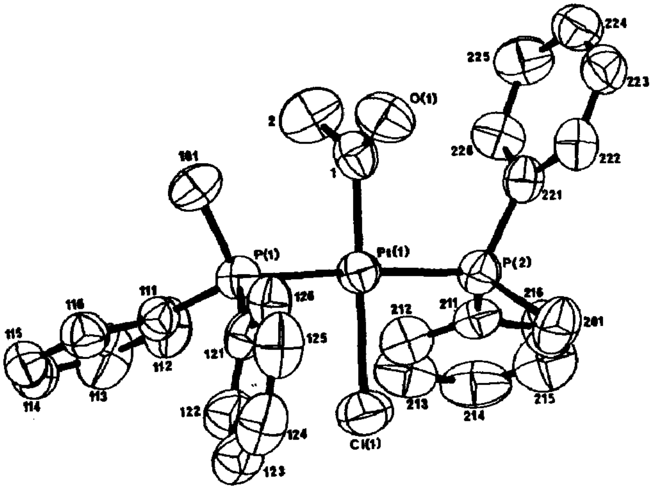
25

Treatment of *trans*-[EtCOPd$(PPh_3)_2$Cl] with Me_3COOH gave [{RCOPd$(PPh_3)_2$}$_2$(μ-Cl)$_2$], which reacted further *via* species such as 26 to give EtC(=O)OOCMe$_3$ [79].

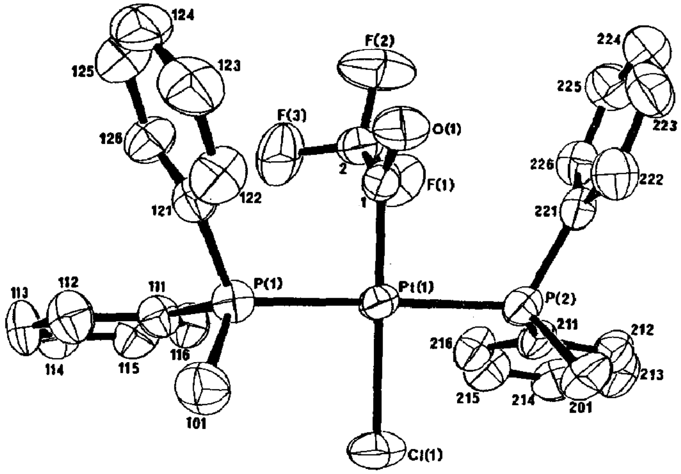


26

Trans-[$(C_6H_{13}COPt(PPh_3)_2Cl$] was isolated from the reaction of hexene and CO with [Pt$(PPh_3)_2Cl_2$]. When $SnCl_2$ was added it proved to be a good catalyst for hydroformylation [80]. The structures of *trans*-[RCOPt$(PMePh_2)_2$Cl (R = CH_3, 27 or R = CF_3, 28) were determined by X-ray diffraction. It was shown that $COCF_3$ formed a shorter and stronger bond to platinum and exerted a larger *cis*- and a smaller *trans*-influence [81].



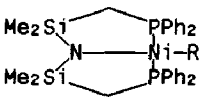
27 (Reproduced with permision from [81])



28 (Reproduced with permisssion from [81])

3 METAL COMPLEXES FORMED BY INSERTION AND RELATED REACTIONS

Insertion of carbon monoxide into metal alkyl bonds is an important route to metal acyl complexes, and the process has been used to prepare models for the intermediates in catalytic cycles. The preparation of $[RCONi(S_2CNR'_2)(PMe_3)]$ both by insertion of carbon monoxide into the metal alkyl and by reaction of $[RCONi(PMe_3)_2]$ with $[R'_2NCS_2]^-$ has been described [82]. Treatment of 29 (R = Me) with carbon monoxide gave 30 as did the complex in which R = π-allyl. The reaction of 29 (R = C_2H_4) was slower and yielded the insertion product, 31, as well as 30. 29 (R = Ph) gave 32, which could be converted to 30 by further carbon monoxide [83].



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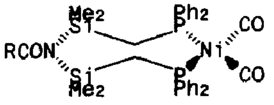
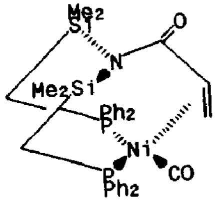


30

Reaction of *trans*-$[PhPtL_2(SnCl_3)]$ (L = PPh_3 or $PMePh_2$) with carbon monoxide was rapid, and gave *trans*-$[PhPt(CO)L_2][SnCl_3]$; insertion to yield *trans*-$[PhCOPtL_2(SnCl_3)]$ was slower. The reaction intermediates were studied by nmr spectroscopy [84]. Treatment of *cis*-$[Pt(PPh_3)_2Cl_2]$ with a mixture of carbon monoxide and propene resulted in the isolation of *trans*-[$PrCOPt(PPh_3)_2Cl$], which was characterised by an X-ray diffraction study. From a hydroformylation reaction in the presence of $SnCl_2$, [$PrCOPt(PPh_3)_2(SnCl_3)$] could be isolated, and was also characterised by X-ray diffraction. It is of note that the tin-free complex did not react with ethanol, unlike its palladium analogue. This is in good accord with the observation that the platinum system catalyses hydroformylation in the presence of $SnCl_2$ and in non-polar solvents, whereas the palladium complex catalyses hydrocarboxylation in the presence or absence of $SnCl_2$ [85].



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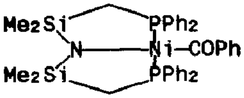
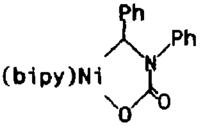


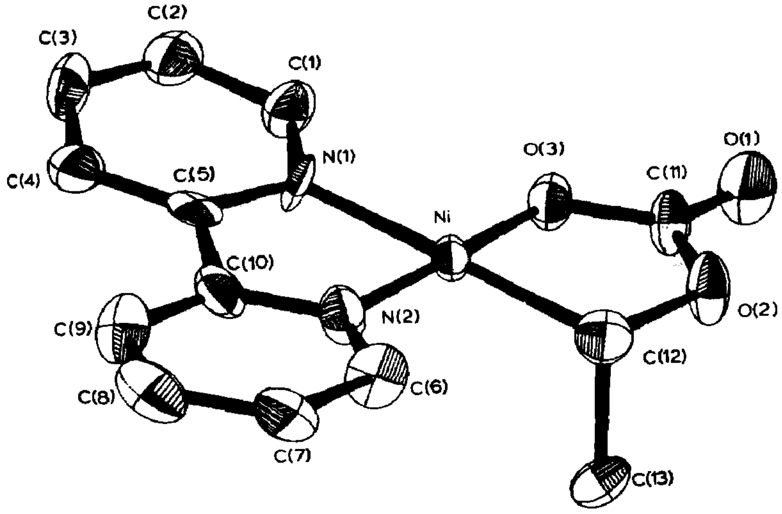
32

PhCH=NPh reacted with [Ni(bipy)(cod)] with the displacement of cod to give [Ni(bipy)(PhCH=NPh)]. This may be considered as an azametallocyclopropane and reversibly and regioselectively inserted carbon dioxide to give 33 [86]. Tmeda complexes reacted analogously [87]. A similar process may be considered for the related reaction with ethanal to give 34, identified by X-ray diffraction, but other mechanisms were also discussed [88]. With 2-butyne, CO_2 and {LNi(0)} 35 was initially obtained, and its reactions were studied [89,90].

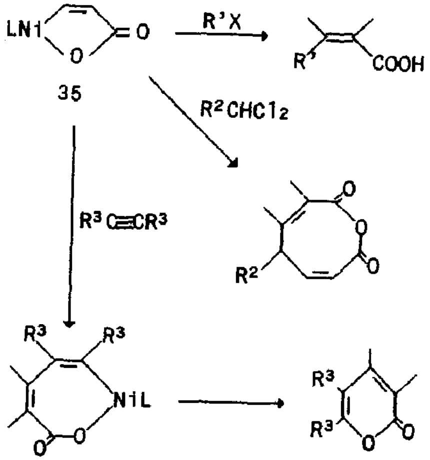


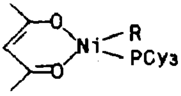
33

The primary process in oligomerisation of ethene has been observed for 36 (R = Me); on exposure to ethene the complexes for which R = Et, Pr and Bu could be observed [91]. Both *trans*- and *cis*-[$HPt(PPh_3)_2(SnX_3)$] inserted ethene at temperatures below -65 °C to give *cis*-[$EtPt(PPh_3)_2(SnX_3)$]. The *trans*-complex reacted rapidly and the *cis*-analogue slowly. Above -60 °C isomerisation to *trans*-[$EtPt(PPh_3)_2(SnCl_3)$] occurred [92]. Insertion of ethene or propene into metal hydride bonds has been observed for {CpNi} complexes (Scheme 4) [93,94].



34 (Reproduced with permission from [88])





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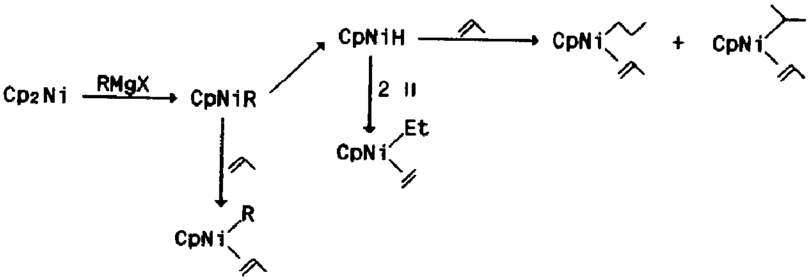
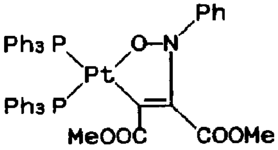


Scheme 4 Insertion of alkenes into nickel hydride bonds [93,94]

Insertion into a pseudometallocycle is responsible for the formation of 37 from $[Pt(PhNO)(PPh_3)_2]$ and $MeO_2C-C\equiv C-CO_2Me$ [95].



37

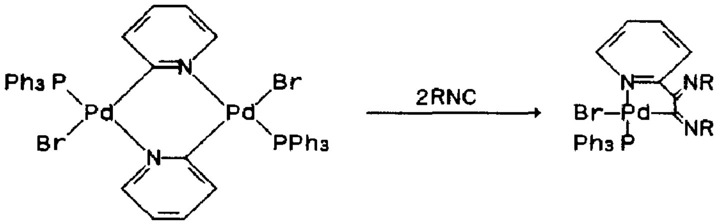
The reaction of Zeise's dimer with 38 followed by treatment with thf/py or dmso gave a poorly defined species, which appeared to be the product of insertion of the platinum into the three-membered ring. Addition of PPh_3 regenerated 38 [96]. Later studies using solid state nmr spectroscopy indicated strongly that the species initially produced was simply related to 39 by the removal of the ligands, L [97].

38

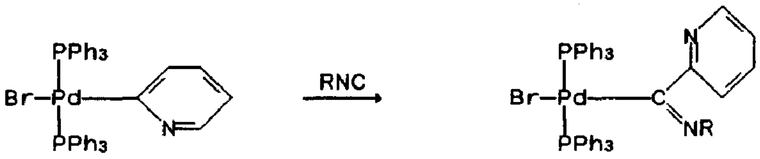
39

Insertion of an isonitrile into the carbon-metal bond of the bridged dimer, 40, gave 41. Insertion also occurred into the σ-aryl species, 42 to give 43 as the final product [98,99].

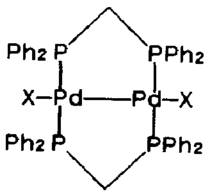
The metal-metal bonded palladium(I) species, 44, are known to insert a variety of small molecules, including CO, RNC, S, SO_2, alkynes and $[PhN_2]^+$. This area has been reviewed and X-ray diffraction studies on the adducts compared. XPES implied that there was little change in oxidation state on insertion. The treatment of [$Pd_2(dppm)_3$] with X_2B (X_2B = $COCl_2$, CH_2I_2 or CH_2Br_2) to give "A-frame" complexes, **45** was described [100]. A detailed description of the reaction of **44** (X = Cl) with CO has been published [101]. Related adducts of the mixed metal complex [PtPd(μ-dppm)$_2$Cl$_2$] have been reported. The carbon monoxide adduct proved to be rather more stable than those of the homometallic species [102]. A {CH_2} group may be inserted into the metal-metal bond of **46** as well as into the metal hydrogen bond. When L = PPh_3 reaction of an excess of diazomethane gave **47**, which on treatment with CH_2Cl_2 yielded **48**, identified by X-ray diffraction [103].



40 **41**



42 **43**



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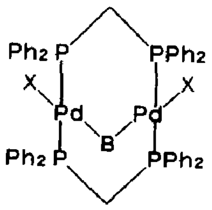

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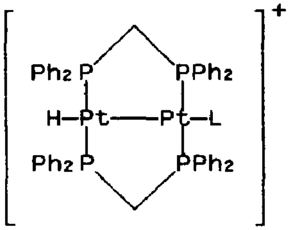

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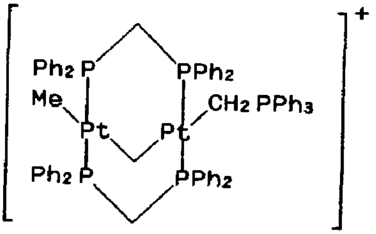

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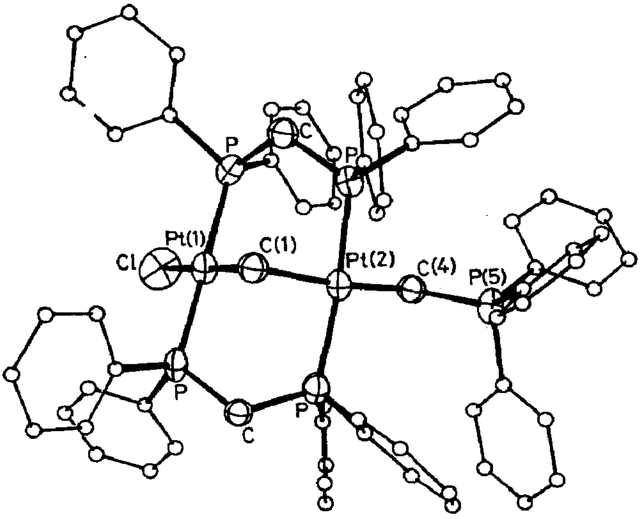
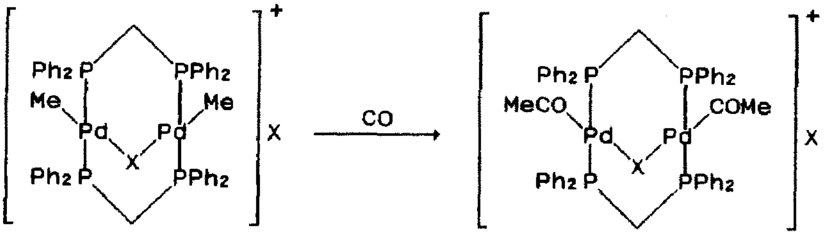


48 (Reproduced with permission from [103])

Selected bond lengths are Pt-P 2.363(6)-2.302(6) and P-C 1.77(3)-1.89(2) Å. The PCP bond angles are equal at 116(1) ° and those involving Pt(1) and Pt(2) atoms deviate from 90 and 180 ° by as much as 9.4 and 12.3 °, respectively.

Carbonylation of 49 (X = I or Br) resulted in insertion of carbon monoxide into both of the palladium-methyl bonds. The related reactions of 50 were also reported; in this case both of the insertion products were shown to have weak metal-metal bonds [104]. Reaction of $[H_2Pt_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ with an alkyne bearing an electron-withdrawing group gave 51 (S = MeCN, PhCN or Me_2CO) as the first identifiable product. Further alkyne in CH_2Cl_2 gave 52 [105]. $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}CH_2)Cl_2]$reacted with $SnCl_2$ by a double insertion process to give $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}CH_2)(SnCl_3)_2]$ [106].



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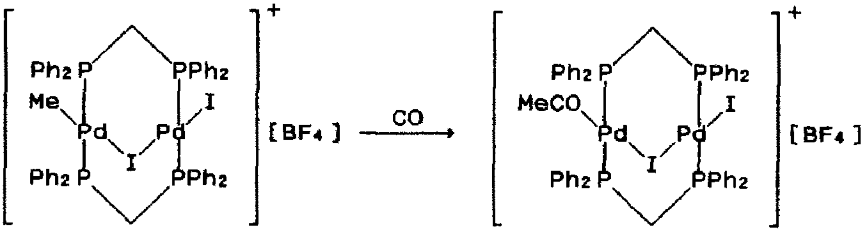
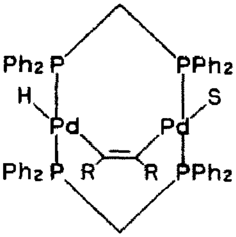
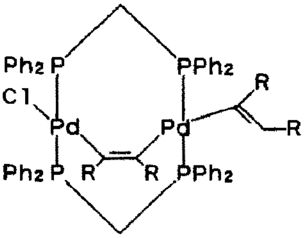


50

$\xrightarrow{\text{MeNCO}}$ $[Pd_2(\mu\text{-dppm})_2(\mu\text{-MeC=NMe})(CNMe)_2]^{3+}$





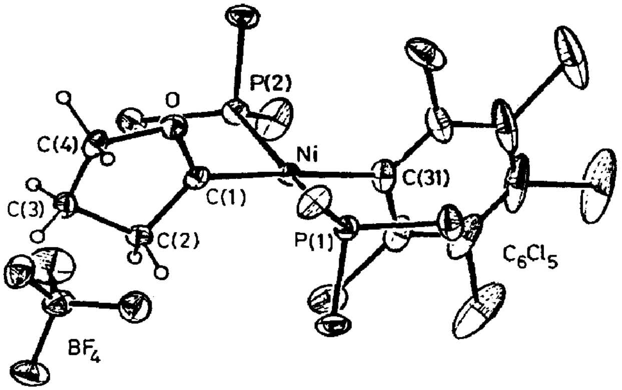
51

52

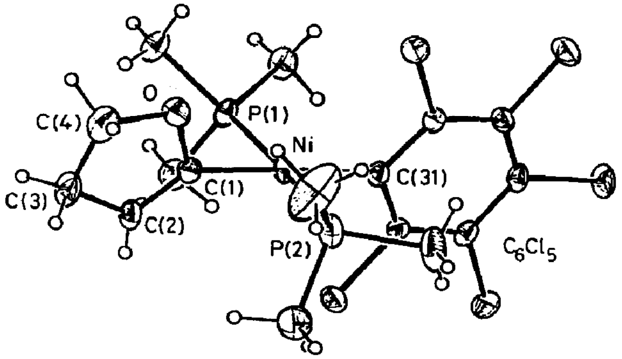
4 METAL CARBENE, CARBYNE AND YLIDE COMPLEXES

The reaction of *trans*-$[Ni(mes)(PMe_3)_2]$ with 1-lithio-3,4-dihydrofuran gave a carbene complex by direct substitution. The related species, 53 and 54 were characterised by X-ray diffraction. The nickel to C(1) bond in 54 was 0.07 Å shorter than a normal Ni-C(vinyl) bond, giving the first clear evidence for π-bonding [107]. Carbene complexes of $\{Ni(C_6H_2\text{-}2,4,6\text{-}Me_3)L_2\}$ have lower

Brønsted acidity than those of $\{Ni(C_6Cl_5)L_2\}$. Barriers to rotation were lower in the mesityl complex, reflecting its stronger *trans*-influence [108].



53 (Reproduced with permission from [107])

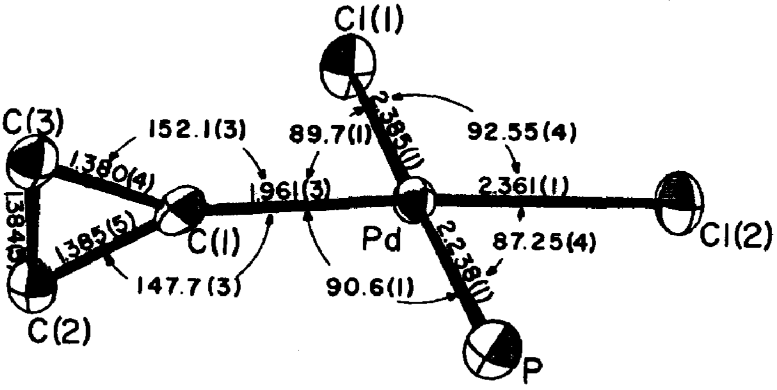


54 (Reproduced with permission from [107])

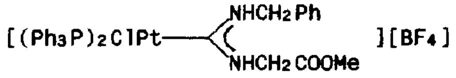
The bonding in complexes of cyclopropenylcarbene complexes has been reviewed. The structure of the palladium derivative, 55 was described [109].

Once again this year aminocarbene complexes have been prepared by reaction of isonitrile derivatives with amines. A simple example was provided by the synthesis of 56 from $[Pt(CNCHPh_2)(PPh_3)Cl_2]$ [110]. In the reaction of Scheme 5 the first step involved the attack of an -SH group on a coordinated isonitrile and was followed by a proton transfer [111}.

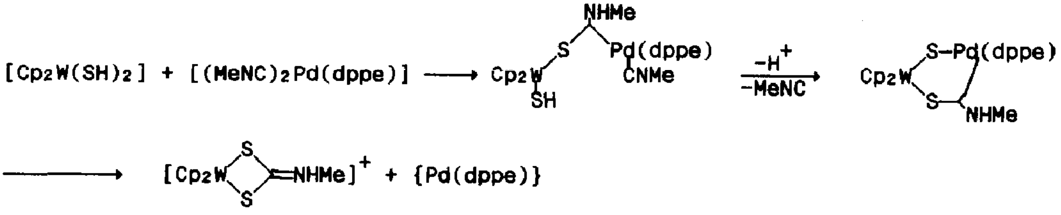
Further work has emerged from Crociani's group on carbene type complexes derived from diazabutadienes. For example, 57 was reacted with $[\{Pd(\eta^3\text{-}2\text{-}R^4C_3H_4)Cl\}_2]$ in the presence of an excess of $Na[ClO_4]$ to give initially 58. 58 could be converted to the binuclear zwitterionic species, 59, on treatment with $[Et_3NCH_2Ph][Pd(\eta^3\text{-}2\text{-}R^4C_3H_4)Cl_2]$, the complex being characterised by an X-ray diffraction study. The kinetics and mechanism of the reaction were investigated in some detail [112,113]. The reactions of 57 with other metal complexes were also reported [114].



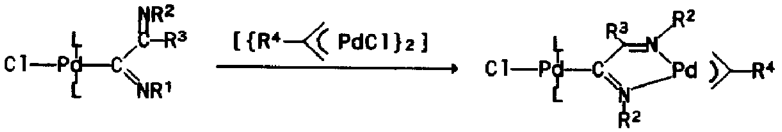
55 (Reproduced with permission from [109])
X-ray structure of the inner coordination sphere of
cis-$[PdCl_2\{C(NCC)_2\}(PBu_3)]$.


$[(Ph_3P)_2ClPt{-}C(NHCH_2Ph)(NHCH_2COOMe)][BF_4]$

56



Scheme 5 Mechanism of reaction of a thiol derivatised tungsten complex with a palladium coordinated isonitrile [111].



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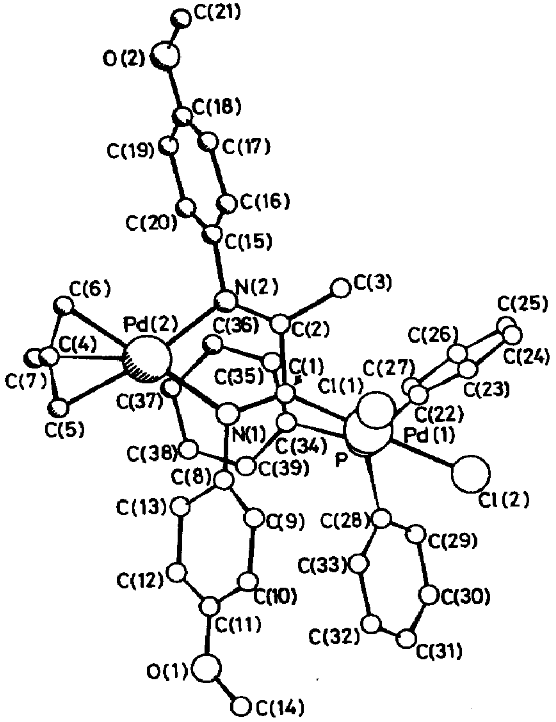
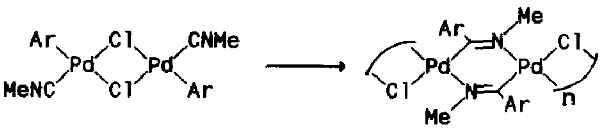
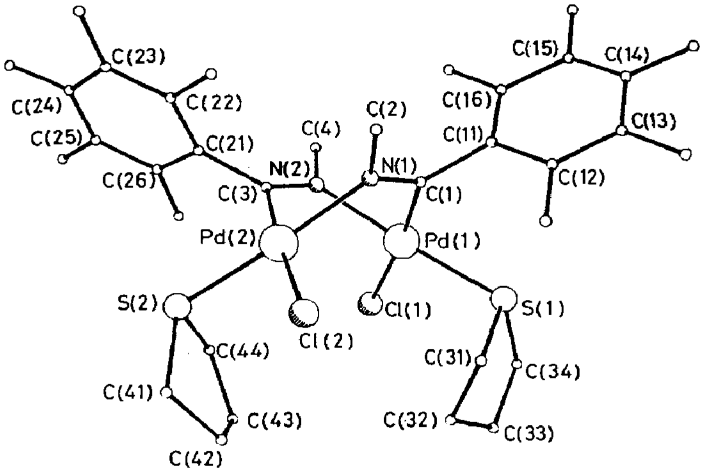


59 (Reproduced with permission from [112])
Projection of the complex viewed along the normal to the five-membered chelate ring including Pd(2)

Thermolysis of the isonitrile complex, 60, gave the bridged species, 61, which was polymeric. However, bridge splitting reactions were relatively easy, with a range of ligands, including [acac]$^-$, isonitriles, pyridines, PPh_3 and tetrahydrothiophene. 62 was characterised by an X-ray diffraction study [115].

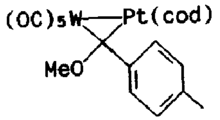


60 **61**



62 (Reproduced with permission from [115])
Atomic radii are arbitrary and hydrogen atoms have been omitted for clarity.
Unmarked atoms are fluorine.

There have been further reports of the chemistry of bridged carbene complexes from Stone's group. Whilst **63** reacted with mono and bidentate phosphines to give the products of cod substitution, with CO or RNC the clusters [$Pt_3\{\mu\text{-}C(OMe)Ar\}_3L_3$] were formed. Two isomers could be detected and, for L = CO, separated. **64** was characterised by an X-ray diffraction study. It was concluded that whilst cod may be replaced by σ-donor ligands, π-acceptors led to fission of the metal-metal bond to give {(OC)Pt=C(OMe)Ar}, which then trimerised [116].



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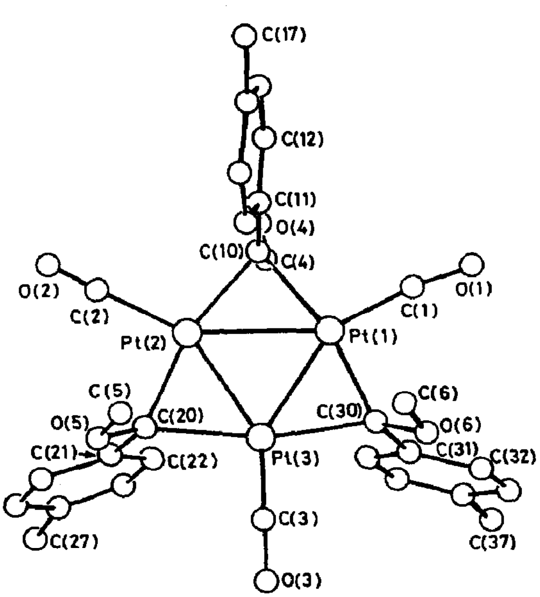
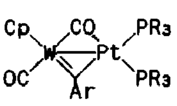


64 (Reproduced with permission from [116])

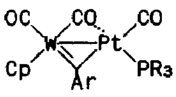
The carbyne complex, **65**, (R_3 = Me_3) reacted with carbon monoxide to give **66** stereospecifically, together with the trimeric species, **67**. The stereospecificity of the reaction reflects the strong *trans*-influence of the bridging carbyne. When the phosphine was PPh_2Me only the trimetallic complex was formed, and **67** (R_3P = Ph_2MeP) was characterised by an X-ray diffraction study. This was a butterfly type cluster related by the isolobal analogy to $[Pt_2L_4(\mu\text{-}RC{\equiv}CR)]$ [117]. The ketenyl complex, **68**, (PR_3 = PMe_3, PMe_2CH_2Ph or PMe_2Ph) reacted with $[Pt(cod)_2]$ to give **69** and analogues, characterised by X-ray diffraction. However, with R_3P = Ph_3P, $[Cp(OC)_2W(\mu\text{-}CAr)Pt(PPh_3)_2]$ was formed [118]. **65** was reacted with $[Fe_2(CO)_9]$ to give $[FePtW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(PR_3)_2Cp]$ when PR_3 = PMe_2Ph, and $[FePtW(\mu_3\text{-}CR)(CO)_6(R_3P)Cp]$ and $[Pt_2W((\mu_3\text{-}CR)(CO)_2(\mu\text{-}CO)_2(PEt_3)_2Cp]$ for R_3P = Et_3P, and $[FePtW(\mu_3\text{-}CAr)(CO)_6(PMePh_2)Cp]$ together with a little $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2Cp]$ for R_3P = Ph_2MeP. X-ray diffraction studies were reported for **70** and **71**; in **70** was found the longest Pt-W bond so far reported [119].

Treatment of $[Cp(OC)_2Mn{=}C{=}CHPh]$ with $[Pt\{P(OEt)_3\}_4]$ was reported to give a mixture of **72** and **73** [120].

Numerous patents have reported the use of ylide complexes such as **74** as catalystss for the oligomerisation of ethene and other alkenes [121-128].



65



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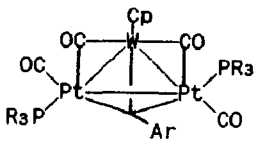

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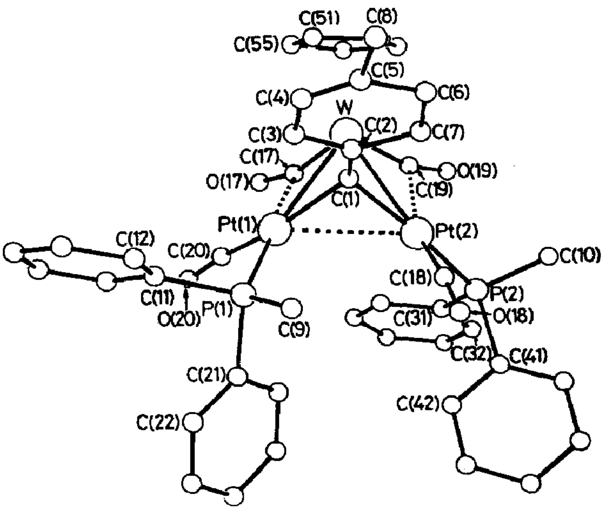
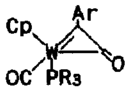


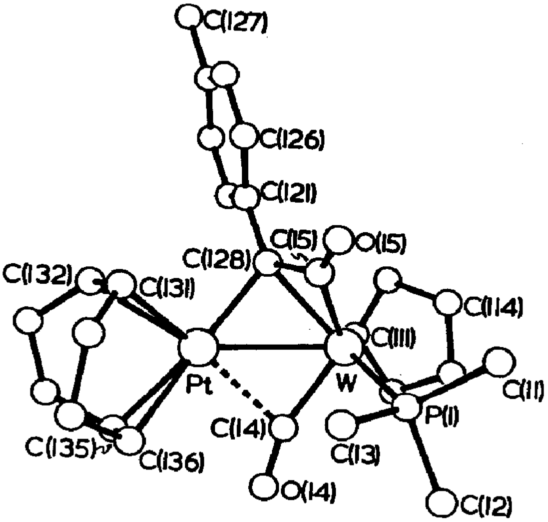
67 (R = $PMePh_2$; Reproduced with permission from [117])



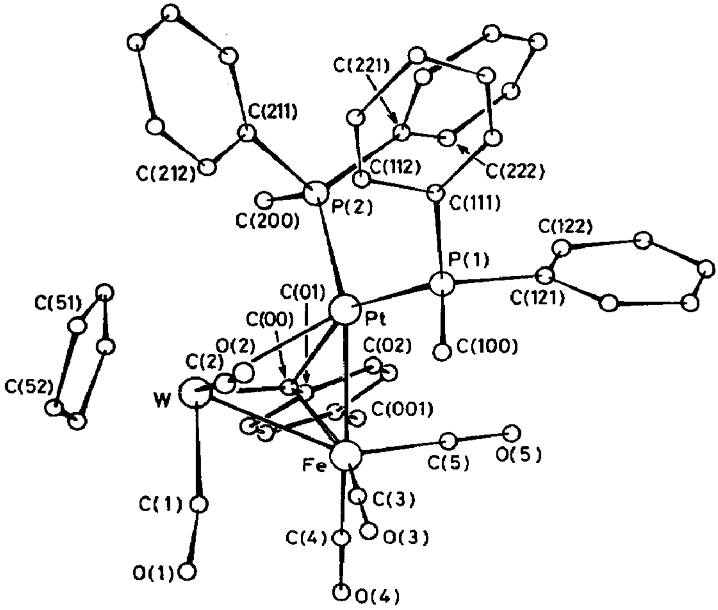
68

Treatment of $[Pt(PEt_3)_3]$ with CH_2I_2 gave the ylide *trans*-$[Pt(CH_2PEt_3)(PEt_3)_2]I$, 75, which was characterised by X-ray diffraction. The intermediate was supposed to be *cis*-$[Pt(CH_2I)(PEt_3)_2I]$, and related complexes were also prepared [129]. In the reaction of *cis*- or *trans*-$[Pt(CH_2Cl)(PPh_3)_2I]$ with PPh_3 a novel migration of chloride from carbon to platinum occurred giving *cis*-$[Pt(CH_2PPh_3)(PPh_3)_2Cl]I$ [130].

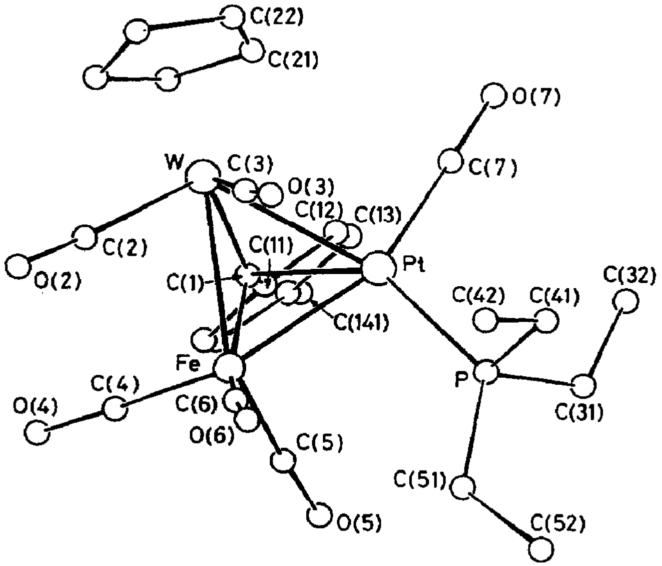
Reaction of the ylide complex, $[Ph_3CH_2Pt(PPh_3)Cl_2]$, with aluminium trichloride resulted in chloride abstraction to give $[Ph_3PCH_2Pt(PPh_3)Cl]^+[AlCl_4]^-$. Additional ligands including Ph_3As and Me_2S were readily coordinated to the cation [131].



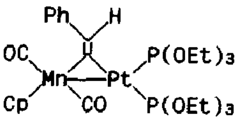
69 (Reproduced with permission from [118])



70 (Reproduced with permission from [119])



71 (Reproduced with permission from [119])



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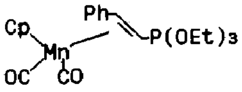

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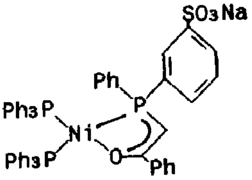
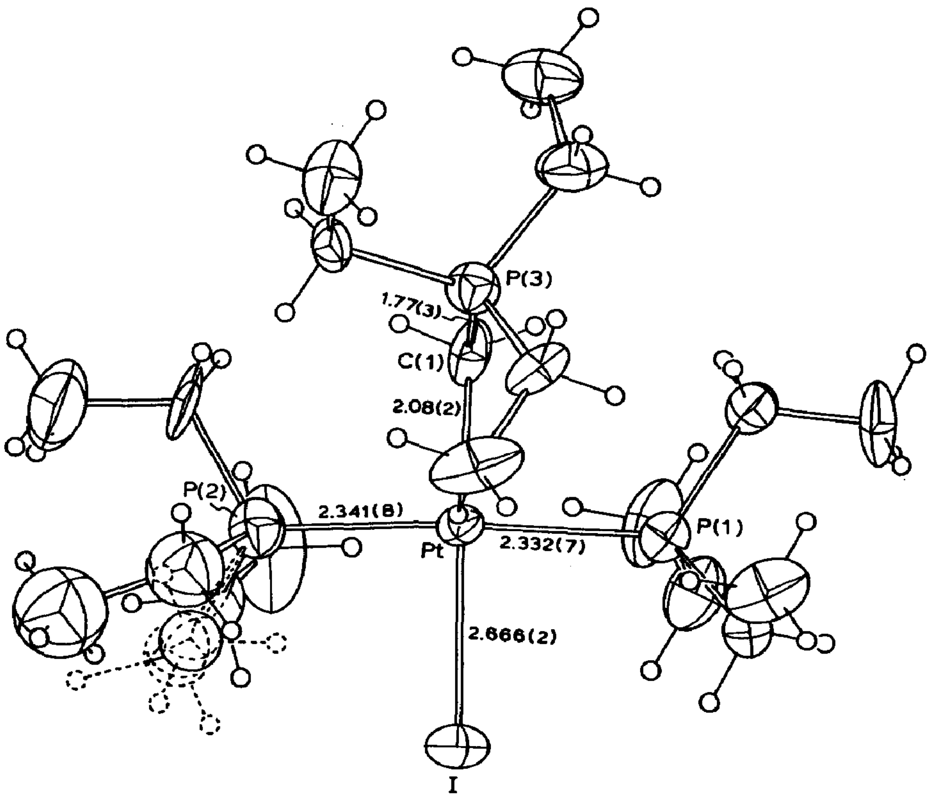
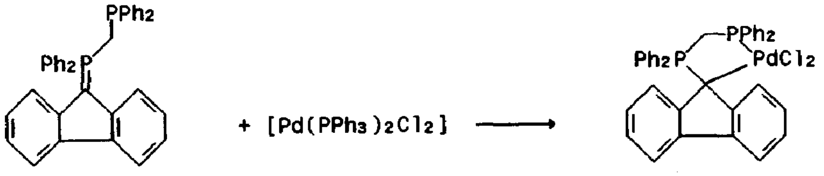


74

Ylide complexes could be prepared by the reactions of the ylides with [CpPd(PPh$_3$)Cl]. The ylides successfully used included [Ph$_3$PCHCOPh], [Ph$_3$PCHCOCH$_3$] and [Me$_2$SCHCOPh] [132]. Ylide complexes were also produced by reaction (6) (M = Pd or Pt). With 76, however, the bis(cyclometallated) species, 77, was obtained [134].

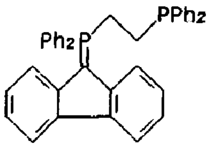


75 (Reproduced with permission from [129])
Projection of the molecular structure of *trans*-[Pt(CH_2PEt_3)(PEt_3)$_2$I]$^+$ normal to the plane of the platinum environment. The ethyl substituents of one of the PEt_3 groups are disordered as shown.



(6)

Carbonylation of the ylide, 78, gave 79, reversibly. Related reactions of ylide complexes derived from decomposition of metallocyclobutanes were also studied [134].



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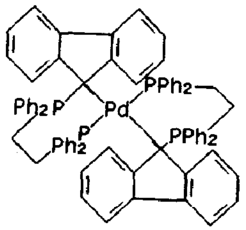

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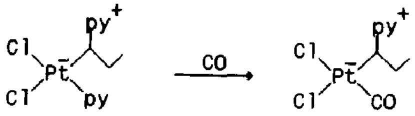
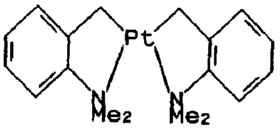


78 79

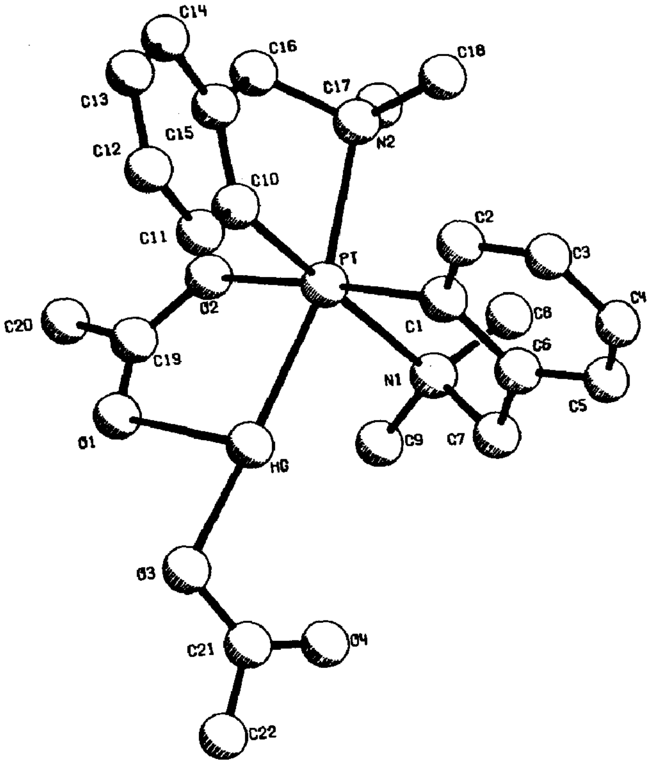
5 METAL COMPLEXES FORMED BY INTERNAL METALLATION AND RELATED REACTIONS

Treatment of $[Pt(SEt_2)_2Cl_2]$ with $2\text{-}Me_2NC_6H_4CH_2Li$.tmeda gave 80. Reaction with $Hg(OCOR)_2$ gave 81, characterised by an X-ray diffraction study. Nmr spectroscopy indicated that the solution structure was fluxional, but essentially similar to that determined in the solid state [135]. Thallium(III) carboxlates were able to oxidise 82 to the platinum(IV) species, $[Pt(N\text{-}C)_2(OCOR)_2]$ as a mixture of two isomers. The major isomer with the carbon ligands *trans* was isomerised in the presence of RCOOH to that in which the nitrogen atoms were *trans* [136].

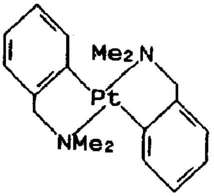


80

The chiral cyclometallated complex, 83, was reacted with chiral chelating biphosphines; ^{31}P and ^{1}H nmr spectrosocopic studies were used to evaluate the diastereomeric mixture of complexes formed. Amounts of the minor diastereoisomer as low as 3 % could be detected [137]. The enantiomer of 83 was used in a similar manner for the resolution of BINAP, separation of the diastereoisomers being effected by fractional crystallisation [138]. The cyclometallated naphthalene complex, 84, reacted with 85 (E = P or As) to give separable diastereomeric complexes. The structure of 86 was established by X-ray diffraction [139].



81 (Reproduced with permission from [135])



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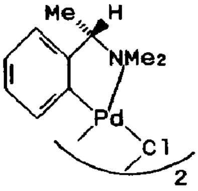

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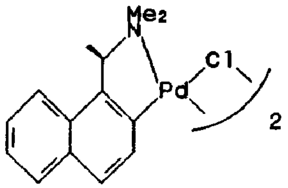

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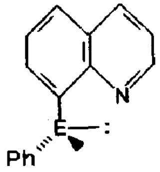

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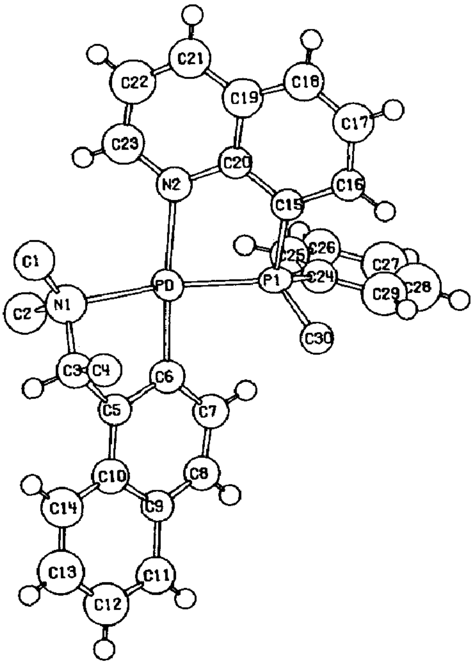
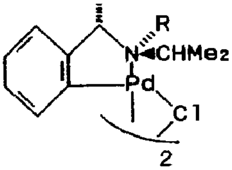


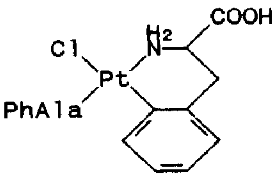
86 (Reproduced with permission from [139]
Molecular geometry and absolute configuration of $(+)_{589}$-R,S-(86)

The stereoselective formation of a second chiral centre at nitrogen in the cyclometallation reaction to form 87 has been studied [140].



87

Whilst methyl phenylglycinate does not cyclometallate on reaction with $Pd(OCOMe)_2$, the ethyl ester reacted surprisingly well [141]. Amongst other products the cyclometalled species, 88, was reported to result from heating *trans*-$Pt[NH_2CH(CH_2Ph)COO\}_2]^{2-}$. This could be induced to react further to give the bis(cyclometallated) complex [142]. Bridge splitting reactions of 89 have been described [143]. The structure of 90 was determined by X-ray diffraction. The geometry at platinum is slightly distorted square planar, and there is some interaction with the CHO group [144].



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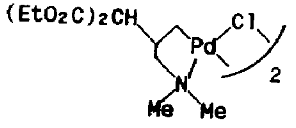

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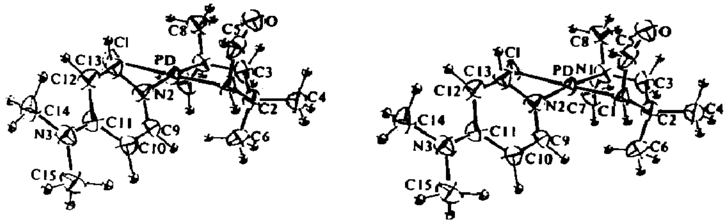
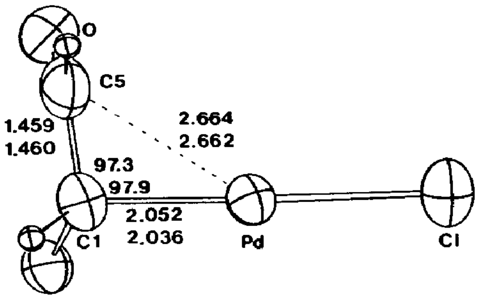
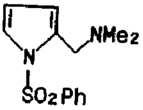


90a Stereoview of a molecule of 90
(Reproduced with permission from [144])



90b Comparison of the dimensions around the methanoyl moiety in 90 (upper) and the related halo bridged dimer (lower) from which 90 was prepared by addition of 4-dimethylaminopyridine
(Reproduced with permission from [144])

Cyclometallation of the pyrrole derivative, 91 took place at the 3-position; 92 was readily carbonylated [145]. In the presence of a chiral acid, cyclometallation of **93** gave **94**, with a new chiral centre; carbonylation followed by reduction yielded **95** [146]. **96** was also resolved using a cyclometallation strategy [147].



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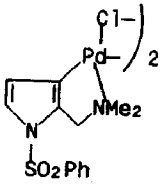

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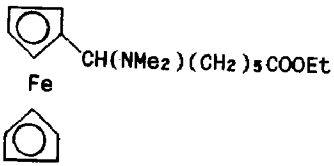

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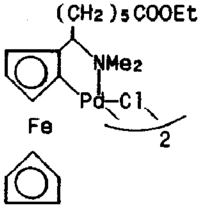

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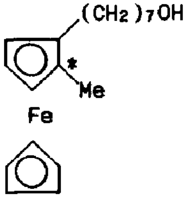

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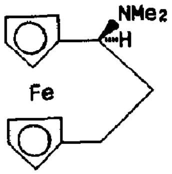
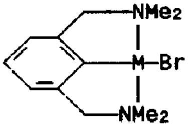


96

A number of papers have reported further reactions of bis(cyclometallated) complexes. **97** was prepared by the reaction of the lithiated arene with either $[Pt(SEt_2)_2Cl_2]/Br^-$ or $[Pd(cod)Br_2]$, and the experimental details of the synthesis have now been published. $Ag[BF_4]$ in water yielded the corresponding aquo complex. The products were air-stable in solution and in the solid state. Methylation with iodomethane occurred at the arene ring to give **98**, which was characterised by X-ray diffraction. The bonding in **98** was discussed in detail [148]. Treatment of **98** with either water or sodium halides resulted in demethylation, but reaction with stronger nucleophiles occurred at the 2- and/or 4-positions of the arene ring. Anions of propane dioate attacked exclusively at the 4-position, whilst reaction with $[Ph-C\equiv C]^-$ occurred only at the 2-position [149].

Reaction of **97** (M = Pt)with Ag[OCOR] gave a monodentate carboxyl complex.

However, the use of Ag[(4-MeC_6H_4)NYNR] (Y = CH or N, R = Me, Et or Pr; Y = CH, R = 4-MeC_6H_4) gave species of the type 99. It was concluded that methanamidino and triazenido ligands had a greater stabilising influence on the Pt-Ag bond than the isoelectronic carboxylates [150]. ^{109}Ag nmr spectroscopy using the INEPT technique provided evidence for a direct platinum to silver bond [151]. Coupling of halo complexes such as 97 with the related aquo derivatives gave bimetallic species such as 100, which was characterised by an X-ray diffraction study [152]. The electrochemistry of 97 and of some of its mercury derivatives was investigated [153].

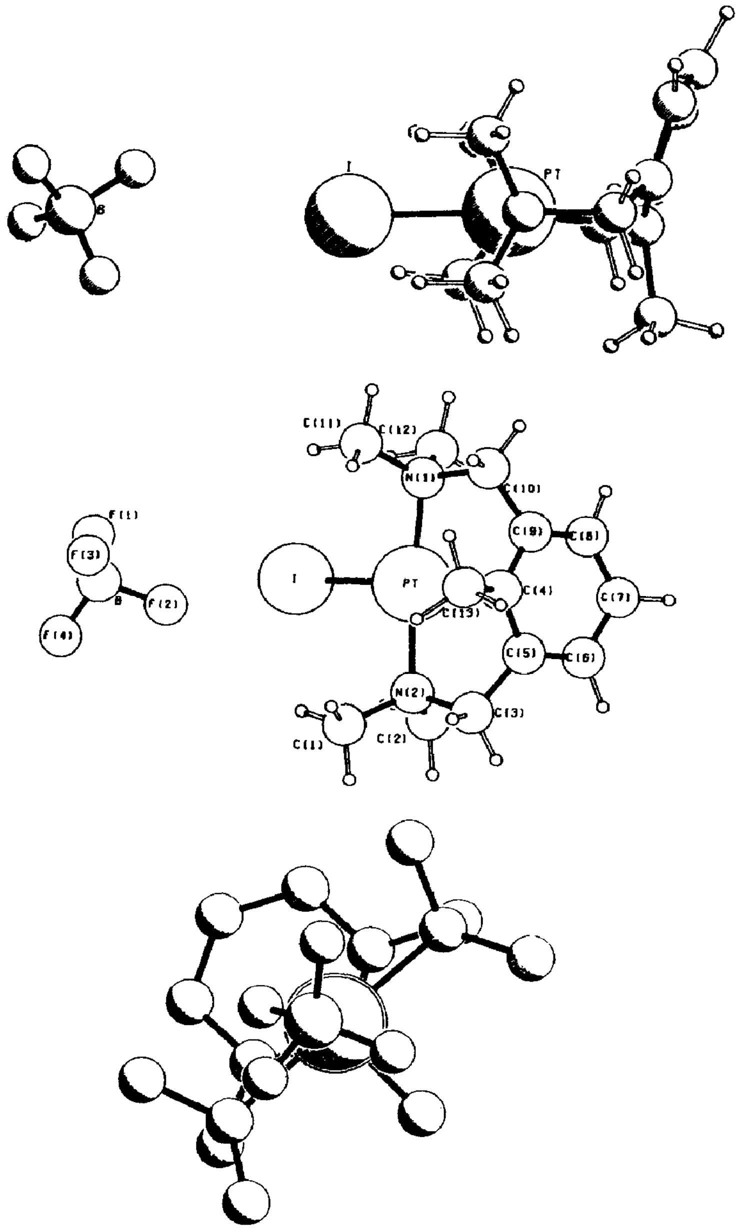


97

The reaction of 97 with Hg{4-MeC_6H_4)NYNR}Cl (Y = CH or N, R = Me, Et or 2-propyl), gave a complex with the structure proposed as 101, involving a platinum to mercury donor bond. Further electron transfer was thought to be inhibited by the tridentate ligand [154]. The structure was formally proven by an X-ray diffraction study of 102. The coordination about platinum was square pyramidal and both metals were formally in the +2 oxidation state [155].

A number of accounts of imine cyclometallation have been published this year. 103 reacted with $Pd(OCOMe)_2$ to give 104 and some unusual regioselectivities were reported with related complexes [156]. Bridge splitting reactions of 105 with ammonia followed the conventional pattern but with an excess of 1,2-diaminoethane 106 was produced, indicating that complexation to the metal had promoted transamination as well as bridge splitting [157]. Cyclometallation of 1,1-dimethylethyl arylaldehyde imines proceeded in good yield, and the products, 107, readily inserted alkenes in a synthetic approach to 3-arylisoquinolines [158,159]. The product of cyclometallation of 108 probably had the structure 109; this yielded the biphenyl, 110, on reaction with a Grignard reagent, followed by imine hydrolysis [160,161].

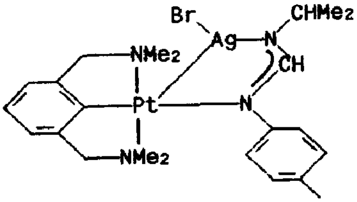
Azobenzenes have long been regarded as excellent substrates for cyclometallation. The regioselectivity of the reaction with 111 was shown to be a function of the relative values of the equilibrium constant for palladium precomplexation at one or other of the nitrogen atoms, the shielding of the azo nitrogens by other substituents, and the blocking of sites by non-coordinating groups. Complexes of the type 112 were formed when the



98 (Reproduced with permission from [148])

PLUTO drawings of the ions as viewed from three approximately perpendicular directions.

substituents on the phenyl ring were either hydrogens or electron donors at the 3- or 4-position. With other substituents complexes of the types 113, 114 and 115 could be detected. The complex or complexes formed depended on the substituents (Table 1), and it was established that the reaction was essentially electrophilic in character [162]. That 111 (R^1 = R^5 = Me, R^3 = OH; R^2, R^4, R^6 and R^7 = H) gave a complex of type 112, and 111 (R^1 = R^5 = R^6 = Me; R^3 = OH; R^2, R^4 and R^7 = H) gave 115 was established by a study of the ^{15}N nmr spectra of labelled species [163].



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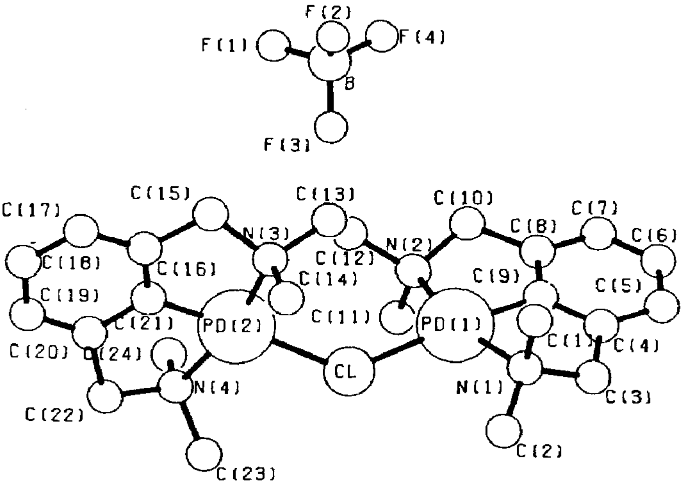

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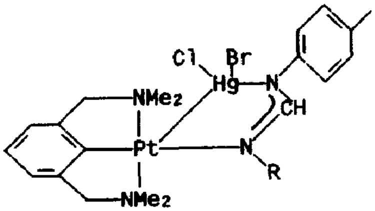

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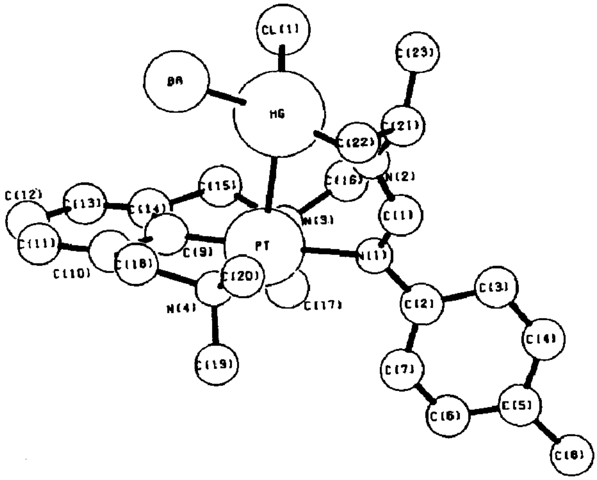

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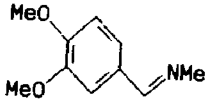

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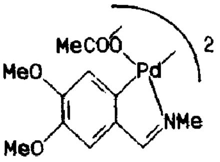

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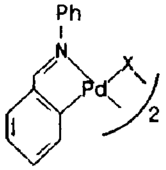

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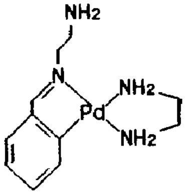

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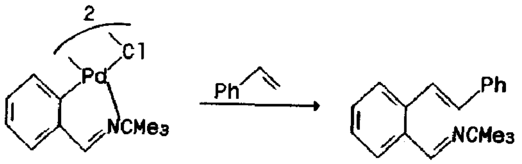

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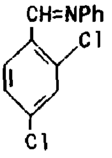

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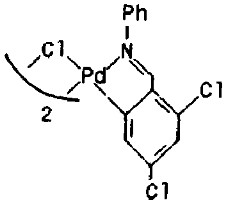

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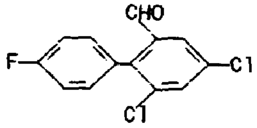

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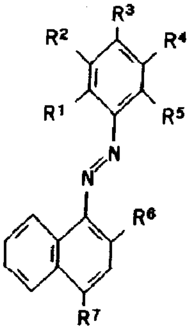

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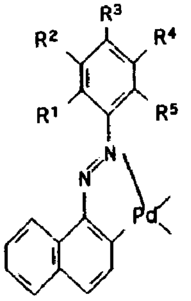

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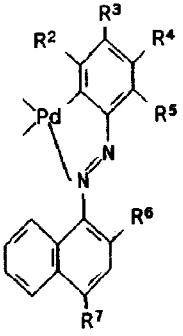
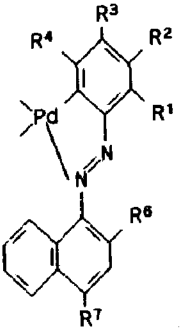
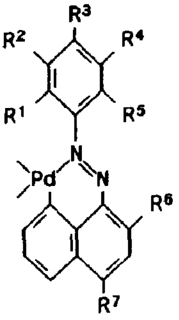


113



114

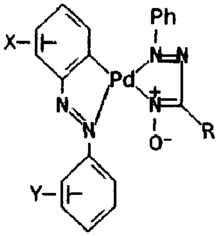


115

About twenty complexes of the type 116 were prepared and characterised. In many cases an inseparable mixture of isomers was obtained; metallation of the more electron rich aryl ring predominated. The electrochemistry of the complexes was investigated, showing that the ligand rather than the metal was readily reduced [164]. Cyclometallated azobenzenes have been shown to give liquid crystals with nematic mesophases [165].

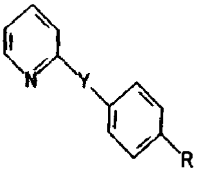
Table 1 Products of cyclometallation of 111 [162]

R^1	R^2	R^3	R^4	R^5	R^6	R^7	Products
H	H	H	H	H	H	H	112
H	H	H	Me	H	H	H	112
H	H	H	OMe	H	H	H	112
H	H	OMe	H	H	H	H	112
H	H	OH	H	H	H	H	112
H	H	H	Me	H	H	NO_2	112 and 113
H	H	OMe	H	H	H	NO_2	112 : 113 = 1:2
H	H	OH	H	H	Ph	H	113, 114 and 115 detected
H	H	OH	Me	H	H	NO_2	112 : 113 = 3:1
H	H	OH	OMe	H	H	NO_2	112 : 113 = 38:62
H	H	OH	H	Me	H	NO_2	113 and 114
Me	H	OH	H	Me	Me	H	115 only



116

Pyridine derivatives have been successfully cyclometallated. For example, 117 (Y = NH; R = H, Me or Cl) gave 118 when reacted with $PdCl_2$ in a 1:1 ratio [166]. The product, 119, derived from the ligand for which Y = CO, reacted readily with styrene [167].



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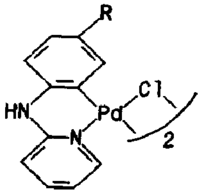

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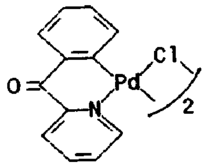
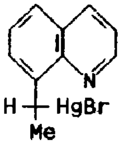
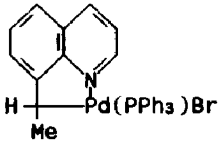


119

A chiral cyclometallated compound, 121, was produced by reaction of the organomercury compound 120 with [Pd(PPh$_3$)$_4$]; the optical purity of the product was not proven [168].

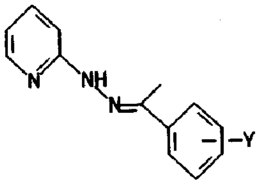


(+)120



(−)121

Treatment of Li$_2$[PdX$_4$] with 122, HL, gave a complex of stoicheiometry [PdLX]. The structure of 123 was established from nmr spectroscopic data [169]. Reaction of 124 with K$_2$[PdCl$_4$] in the presence of a bifunctional but non-chelating ligand, L-L, gave binuclear, bis(cyclometallated) complexes such as 125, characterised by an X-ray diffraction study [170].



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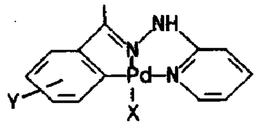

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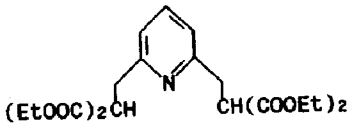

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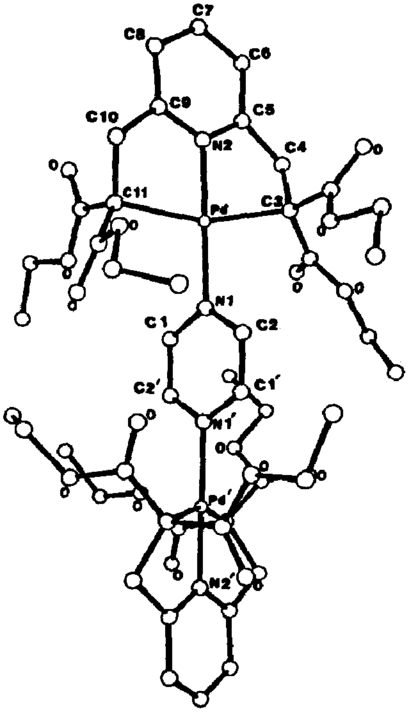
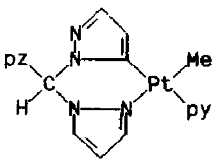


125 (Reproduced with permission from [170])
Perspective drawing of the μ-pyridazine dimer. The atoms designated by primes are related to the unprimed atoms by −x,y,½−z.

Cyclometallation of 5-membered ring heterocycles has also been noted. [$Me_2Pt(cod)$] reacted with $HCpz_3$ to give initially [$Me_2Pt(HCpz_3)$] and cod. Further heating in pyridine, yielded the metallated species, 126. Addition of PPh_3 resulted in the displacement of the nitrogen ligand from the metal and further thermolysis of 127 resulted in metallation of one of the aryl rings of the phosphine [171]. When reacted with $PdCl_2$ in a 1:1 ratio *N*-3-thienylpyrazole yielded a mixture of the cyclometallated species 128 and 129, 128 predominating by a factor of 3:1 [172].



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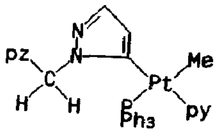

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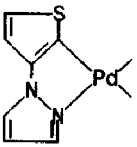

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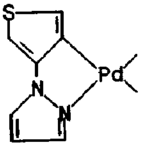
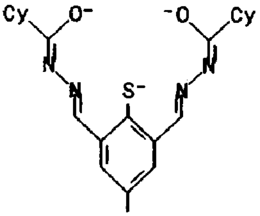


129

When $[LPd_2(OCOMe)]$ (L = 130) reacted with indole, a species of stoicheiometry $[LPd_2(C_8H_6N)]$ was produced. It was shown that the indole had been metallated and was acting as a bridge between the two palladium centres, 131. The related species, 132, and other heterocycle derivatives were also characterised [173].



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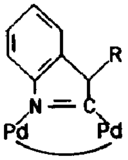

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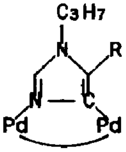
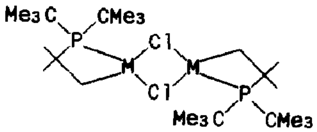


132

Studies of the metallation of tris(1,1-dimethylethyl)phosphine have continued. The phosphine reacted with either $K_2[PdCl_4]$ or $[Pd(PhCN)_2Cl_2]$ to give 133 (M = Pd), characterised by X-ray diffraction. The geometry at palladium was approximately square-planar but the four-membered rings were puckered with a P-Pd-C angle of 70 ° [174]. Reaction of $PtCl_2$ or $K_2[PtCl_4]$ with the phosphine gave initially 134 ($L = P(CMe_3)_3$). Thermolysis resulted in the successive formation of 134 ($L = P(H)(CMe_3)_2$) and *trans*-$[Pt\{P(H)(CMe_3)_2\}_2Cl_2]$ [175]. *Trans*-$[HPt\{P(CMe_3)_3\}_2X]$ cyclometallated slowly at room temperature to give 135. This dimerised with loss of phosphine to give 133 (M = Pt) [176]. Formation of 136 from *trans*-$[Pt\{P(CMe_3)_3\}_2(SnCl_3)Cl]$ was noted [177].



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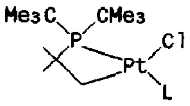

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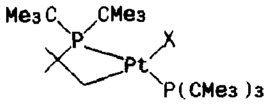

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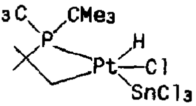


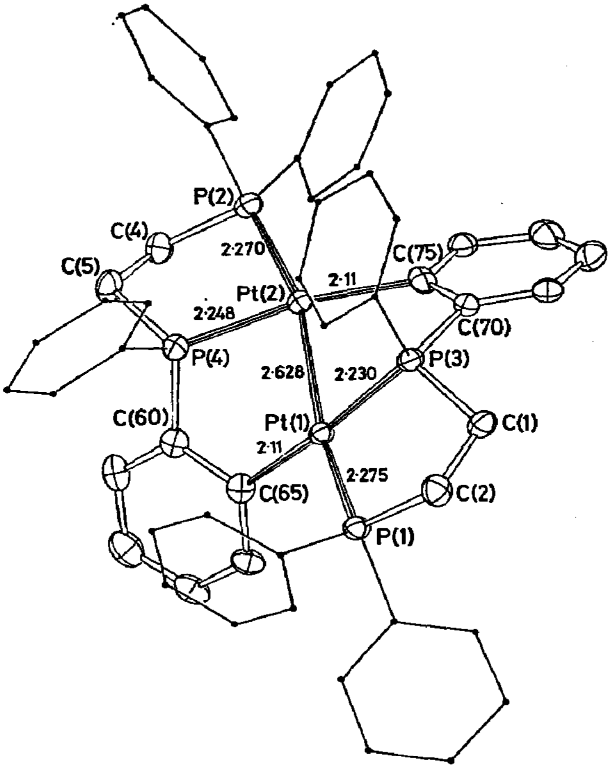
136

Thermolysis of [MePt(OH)(dppe)] yielded [Pt_2(dppe)$_2$], **137**, characterised by an X-ray diffraction study. Only the diastereoisomer with the four phenyl groups on the same side of the average coordination plane was formed [178]. A carbanion displacement route was used in the synthesis of **138**, also characterised by X-ray diffraction [179].

It has long been known that [Pd(cod)Cl_2] reacted with R_3P to give [Pd(PR_3)$_2$$Cl_2$], but with trialkyl phosphines mixtures of *trans*-[Pd_2(PR_3)$_2$(μ-Cl)$_2$$Cl_2$] and species such as **139** were produced [180]. Treatment of [Pt(cod)$_2$] with Cl(CH_2)$_3$$PCy_2$ gave [Pt{Cy_2P(CH_2)$_3$Cl}$_2$], but this species was not isolable and cyclometallated by oxidative addition of a C-Cl bond to platinum(0), to give **140** [181].

The reaction of (Me_3C)$_2$$PCH_2$CH(Me)($CH_2$)$_3$P($CMe_3$)$_2$, L, with [Pd(PhCN)$_2$$Cl_2$] gave **141** in which the methyl group occupied a *pseudo*-equatorial position. In the platinum series, the analogue of **141** could be isolated, but a complex mixture of 16-atom chelates was also formed [182]. When (Me_3C)$_2$P(CH_2)$_5$P(CMe_3)$_2$, L', was reacted with [Pt(Me_3CNC)$_2$$Cl_2$], or [$Pt_2L'_2$$Cl_4$] was treated with CF_3COOH, species such as **142** were isolated, together with an initially unidentified species, which was characterised as **143** by an X-ray diffraction study. In **143** the double bond was disordered [183].

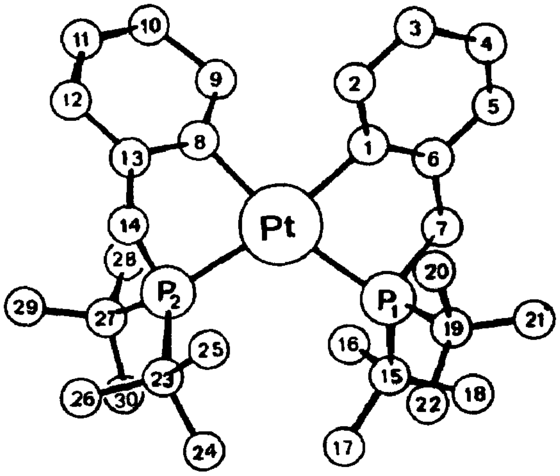
A novel cyclometallated nickel complex, **144**, was prepared from [Ni(PPh_3)$_2$$Cl_2$] and Li[$CH_2$P(=S)$Ph_2$], and was characterised by an X-ray diffraction study. The coordination at nickel was close to square planar [184]. The reactions of [CpNi(CO)I] with a series of halogenated alkyl phosphines, Cl(CH_2)$_n$$PR_2$, has been investigated. The initial product was that of simple CO substitution, and for $n = 1$ cyclometallation yielded **145**, characterised by X-ray diffraction. The six-membered ring adopted a boat conformation. When $n = 3$ or 4 the simple cyclometallated species, **146**, were obtained [185].



137 (Reproduced with permission from [178])

Some reactions of the chelate complex, 147 have been studied; the cyclometallated species, 148, was characterised by an X-ray diffraction study [186].

Treatment of [Ni(cod)$_2$] with 3-butenoic acid in the presence of PCy$_3$ gave the cyclometallated species, 149 (L = PCy$_3$). The PCy$_3$ was easily substituted by dppe. In solution the dppe complex isomerised to 150, presumably *via* β-hydride elimination and readdition [187]. Insertion of alkenes into the carbon-palladium bond of 151 gave 152 [188].



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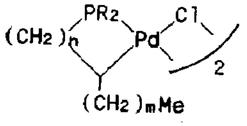

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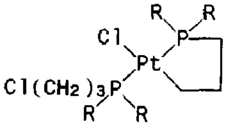

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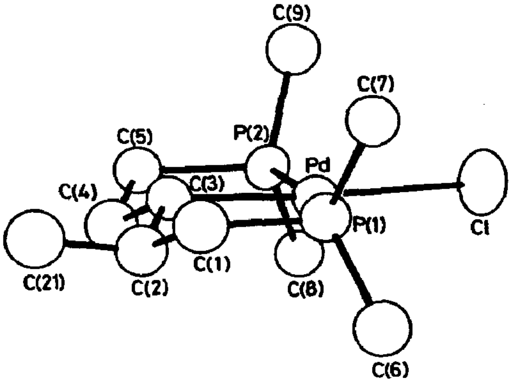
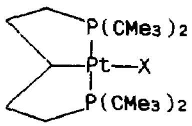


141 (Reproduced with permission from [182])

For clarity the methyl groups of the 1,1-dimethylethyl groups are not shown.



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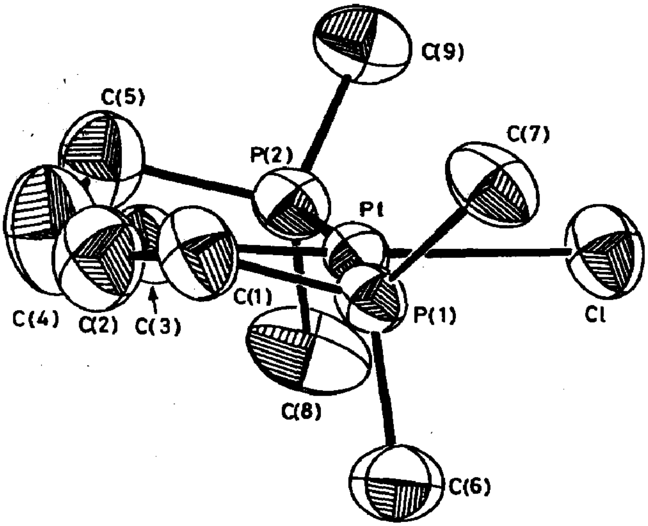
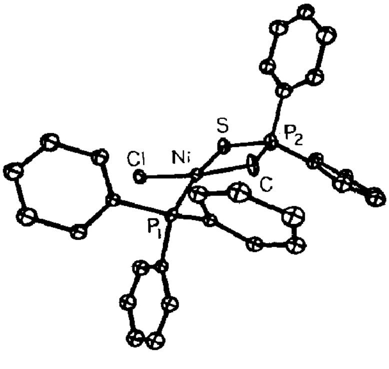
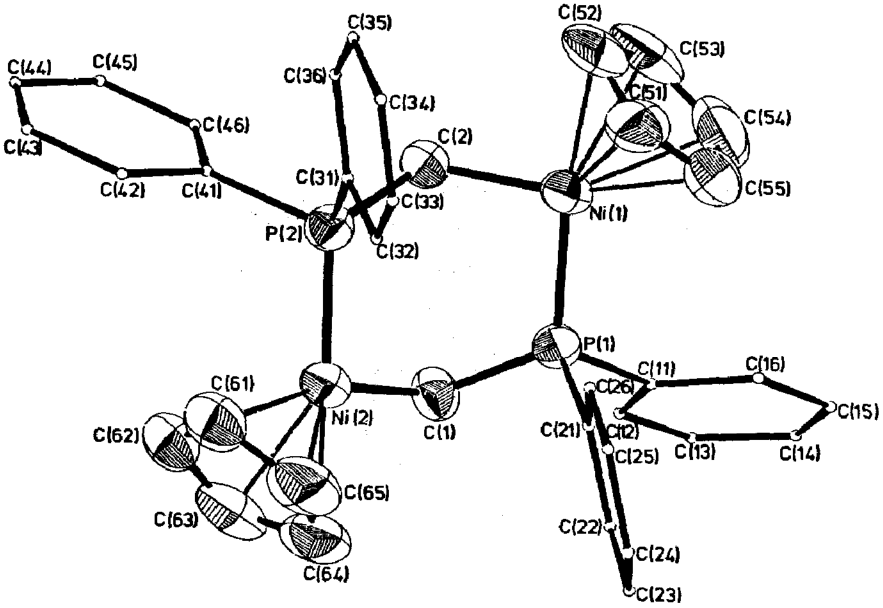


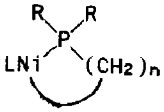
143 (Reproduced with permission from [183])
For clarity the methyl groups have been omitted; 50 % probability thermal ellipsoids are shown. The double bond is disordered between C(2)-C(3) (1.414(23) Å) and C(3)-C(4) (1.430(23) Å)



144 (Reproduced with permission from [184])



145 (Reproduced with permission from [185])



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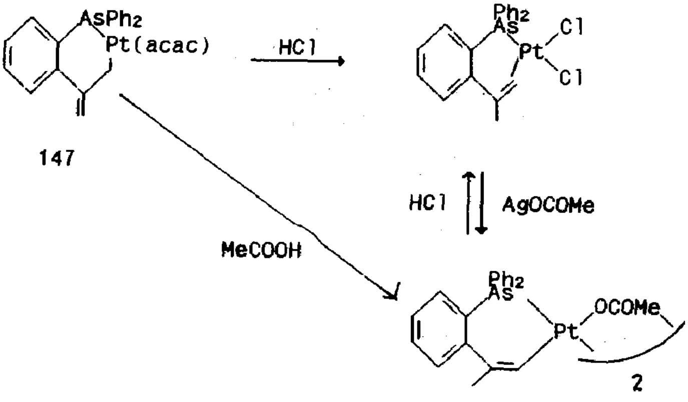

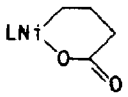

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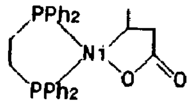

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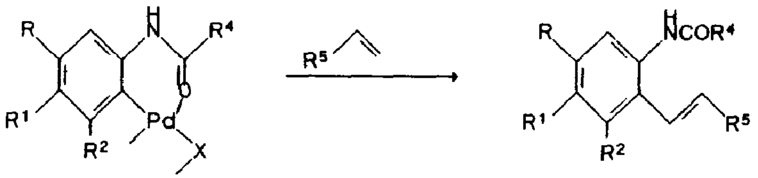

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152

6 METAL CARBONYL AND THIOCARBONYL COMPLEXES

A continuous aerosol ionisation gas analyser has been developed for the monitoring of air pollution, including levels of [Ni(CO)$_4$] [189].

Administration, by inhalation to mice, and intravenously to rats, of [Ni(CO)$_4$] resulted in selective necrosis on non-conciliated bronchiolar epithelial cells, and variable pulmonary parenchymal damage [190].The oral efficacy of the chelating drugs disulfiram, dithiocarb and D-penicillamine was studied in relation to their ability to prevent death due to acute inhalation exposure to [Ni(CO)$_4$] [191]. A series of school experiments in organometallic cehmistry has been described, including the preparations of [Ni(CO)$_4$] and [Ni(CO)$_2$(phen)]; the author clearly has great faith in the skills and safety training of his pupils [192].

Calculations have been performed to determine the electronic configuration and electronic energy levels of [Ni(CO)$_4$]. The photoelectron spectrum of the complex was assigned on the basis of these [193]. MO LCAO calculations of the electronic structure of nickel carbonyl clusters, including [Ni(CO)$_4$] and [Ni$_3$(CO)$_9$], were reported [194]. CI calculations based on an extended CNDO formulation were used to analyse low lying excited states of [Ni(CO)$_4$]. In contrast to the ususal assumptions, atomic d→s and d→p excitations were found to be important in the low energy region. These transitions are responsible for the photochemical reactivity of the carbonyl complex [195].

The ionisation potential of [Ni(CO)$_4$] was calculated using a Green's function perturbation method, based on the INDO approximation. Deviations from Koopman's theorem were analysed [196]. The delta function potential model, based on the variational method and delta-function electronic wave functions, was used to calculate the atomic, bond and molecular polarisabilities of $[Ni(CO)_4]$ [197].

The PES of $[Ni(CO)_n]^-$ (n = 1, 2 or 3) was obtained with a fixed frequency argon-ion laser operating at 488 nm. The spectra allowed the determination of electron affinities for the series of complexes, as well as the symmetric C-O vibration frequencies for the corresponding neutral complexes. Metal to CO bond strengths for the neutral carbonyls $[Ni(CO)_n]$ (n = 1, 2, 3 or 4) were derived from these and other data [198]. The epr spectra of $[Ni(CO)_n]$ (n = 1, 2 or 3) adsorbed on surfaces were discussed [199]. Linear combination of Gaussian type X_α calculations on {Ni(CO)} were described, and their relevance to the mode of CO adsorption on nickel discussed, with the conclusion that it was marginal [200].

The rate of formation of $[Ni(CO)_4]$ by reaction of CO with solid nickel was studied as a function of the composition of the gas used and the initial treatment of the nickel samples. A mechanism was proposed whereby heat treatment activated the surface. In particular a finite number of low coordination nickel sites were activated. These sites were shown to be energetically favoured for $[Ni(CO)_4]$ formation, and were responsible for the transient behaviour observed [201]. Structural aspects of the reaction were studied by field ion microscopy, and several intermediate states were seen. The nickel atoms removed were most commonly taken from <110> atom chains of the {111} planes [202].

The presence of $[Ni(CO)_4]$ in pentane or hexane was shown to reduce the fragmentation of the alkane under γ-irradiation [203]. $[Ni(CO)_4]$ reacted with the ionic species produced on radiolysis, modifying ion-molecule reaction paths. A major effect using butane or pentane as substrate was a tenfold increase in the yield of ethene, and a loss of other light products [204].

Dissociative electron attachment rates were measured for $[Ni(CO)_4]$ as a function of the pressure of carbon dioxide added to relax the epithermal electrons. The thermal rate constant was derived for the formation of $[Ni(CO)_3]^-$ [205].

Ion cyclotron resonance spectroscopy with a pulsed-laser volatilization-ionisation source of atomic metal cations was used to investigate the gas phase chemistry of M^+ with $[Ni(CO)_4]$. The initial product was $[MNi(CO)_n]^+$ (n = 2 or 3, M = Ti, V, Cr, Mn, Fe, Co or Ni), which reacted with further $[Ni(CO)_4]$ to give mixed metal cluster cations [206].

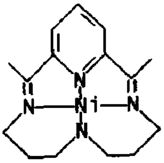
Photolysis of $[Ni(CO)_4]$ in liquid krypton containing nitrogen gave the unstable species $[Ni(CO)_3(N_2)]$, identified by IR spectroscopy [207]. Other substitutions of $[Ni(CO)_4]$ have been of a more conventional type, such as those shown in reactions (7) and (8) (R = styrene/divinylbenzene copolymer). The products were used as catalysts for alkyne oligomerisations [208].

$$\{RR'R''SnPPh_2\}_x + x[Ni(CO)_4] \longrightarrow \{(RR'R''SnPPh_2)Ni(CO)_3\}_x \qquad (7)$$

$$\{RR'R''SnPPh_2\}_x + [Ni(CO)_2(PPh_3)_2] \longrightarrow \{(RR'R''SnPPh_2)Ni(CO)(PPh_3)_2] \qquad (8)$$

Nickel carbonyl complexes have also been prepared by carbonylation; reaction (9) (L = PEt_3, PEt_2Ph or $PEtPh_2$) did not proceed quantitatively in the absence of added ligand or pyridine [209]. Carbonylation of $K[Ni(NPh_2)_3]$ in toluene, ether or thf gave $[Ni(CO)_4]$ and tetraphenylurea. In ether $K[Ni(NPh_2)\}$ was additionally formed, whereas in thf $K_2[Ni_6(CO)_{12}]$ was also produced [210]. Carbonylation of **153** gave a monocarbonyl complex with an axial CO ligand. The electrochemistry of both species was studied [211].

$$[NiL_2Cl_2] + CO \longrightarrow [Ni(CO)_2L_2] + [Ni(CO)_3L] \qquad (9)$$



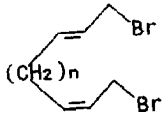
153

Reaction of $[Ni(CO)_4]$ with trifluoroethanoic anhydride gave only $Ni(O_2CCF_3)_2$ [212].

The ^{13}C nmr spectra of the complexes $[Ni(CO)_3(PR_3)]$ have been determined, with a view to studying segmental motion in the phosphine [213]. The structure of the complex $[Cp_2Nb(CO)(\mu\text{-}H)Ni(CO)_3]$, prepared from $[Cp_2Nb(\mu\text{-}H)_2BH_2]$ and $[Ni(CO)_4]$, has been established by an X-ray diffraction study [214].

The cyclocarbonylation of alkynes and alkenes using $[Ni(CO)_4]$ and palladium complexes as carbonylating agents and/or catalysts has been reviewed [215]. The cyclisation of α,ω-bis(allyl bromides) such as **154** by $[Ni(CO)_4]$ has again been noted [216]. A related cross-coupling led to a synthesis of *trans-β*-farnesene [217].

The electronic structures of {PdH}, {PdC} and {Pd(CO)} were investigated by the pseudopotential multireference double excitations configuration interaction method [218]. The relaxation energies, E_R, during ionisation from the valence orbitals of square planar complexes $[PdL_4]$ (L = F, Cl, NH_3, CN or CO) were calculated within the second order perturbation energy. The electronic structures of the ground states were calculated within the INDO method [219]. Calculations on the *trans*-effect in $[PtCl_3X]^-$ (X = CO, among others) purported to show that the nature of the *trans*-influence was related to a d→d transition rather than the nature of X [220]. Calculations on the strengths of metal to ligand bonds in this complex have been undertaken [221].



154

Platinum atoms reacted with oxalyl chloride to give *trans*-$[Pt(CO)_2Cl_2]$ [222]. The complex *cis*-$[Pt(CO)(PPh_3)Cl_2]$ was prepared and studied by ir and nmr spectroscopy and DTA. It was found that structural features of this and related complexes could be related to their catalytic activity in oxidative chlorination of pentane [223]. π-Acceptors such as CO displaced molecular hydrogen from $[H_2Pt(PR_3)_2]$ (R = Me or Et) to give $[Pt(PR_3)_2(CO)_2]$ [224]. Carbonylation of the complex for which R = Cy at low temperature gave $[Pt(PCy_3)_2(CO)_2]$. At ambient temperature this trimerised giving $[Pt_3(PCy_3)_3(CO)_3]$ but at lower temperature the reaction with PBu_3 gave the mixed complex $[Pt(PCy_3)(PBu_3)(CO)_2]$ [225].

The oxidation of $[Pt(CO)Cl_3]^-$ by Cl_2 in $SOCl_2$ to give $[Pt(CO)Cl_5]^-$ was previously reported, but this novel anion has now been isolated as its $[Me_2CHNH_2]^+$ salt. At 2191 cm^{-1}, the carbonyl stretching frequency in the complex is the highest so far recorded [226].

Carbonyl complexes have served as precursors to a number of interesting species. Reaction of $[Pt(CO)_3(SEt_2)(PEt_3)]$ with R_3SnH in methanol gave the hexacoordinate platinum(IV) complex *fac*-$[HPt(PEt_3)(SnR_3)\{R_2Sn(\mu\text{-}OMe)SnR_2(\mu\text{-}OMe)SnR_2\}]$, characterised by an X-ray diffraction study [227]. Treatment of *cis*-$[Pt(PPh_3)(CO)Cl_2]$ with $SnCl_2$ in Me_2CO rather surprisingly gave *cis*-$[Pt(PPh_3)_2Cl_2].Me_2CO$, identified by X-ray diffraction [228]. The carbonyl complex, *trans*-$[Pt(CO)L_2Cl][BPh_4]$ (L = PPh_3 or $AsPh_3$) was converted to the carboxylate type species *trans*-$[PtL_2\{COON(CF_3)_2\}Cl]$ by reaction with $Na[ON(CF_3)_2]$ [229].

A review of the data on the isomerisation of palladium(II) and platinum(II) square planar complexes has been published. It was concluded that the direction of the isomerisation is controlled by the *trans*-effect of the inner sphere ligands [230]. The *cis*$\rightleftharpoons$*trans* isomerisation of $[PtL_2Cl_2]$ (L = PEt_3, PMe_2Ph or $PMePh_2$) was catalysed by carbon monoxide. The intermediate was a five-coordinate carbonyl complex, which underwent ready pseudorotaion. Either chlorine or L could be eliminated from the five-coordinate complex to give species such as $[Pt(CO)L_2Cl][CF_3SO_3]$. The study was extended to isonitrile complexes, which behaved similarly [231].

Carbon monoxide and chlorine react together in $SOCl_2$ in the presence of a suitable catalyst to form phosgene. Catalytic efficiency was in the order $[Au(CO)Cl] > [Pd(CO)Cl_3]^- > [Pt(CO)Cl_3]^-$ [232,233]. Reaction (10) was accelerated by the formation of a bridged complex, $[Cl_3Pd(\mu\text{-}X)(\mu\text{-}CO)CuCl]^{2-}$ [234]. Reaction (11) (M = Pd or Pt, L = PPh_3) was presumed to involve the intermediates $[L_nM(F)CHO]$ and $[HML_n(F)(CO)]$ [235].

$$Pd(II) + CO + H_2O \longrightarrow Pd(0) + CO_2 + 2H^+ \qquad (10)$$

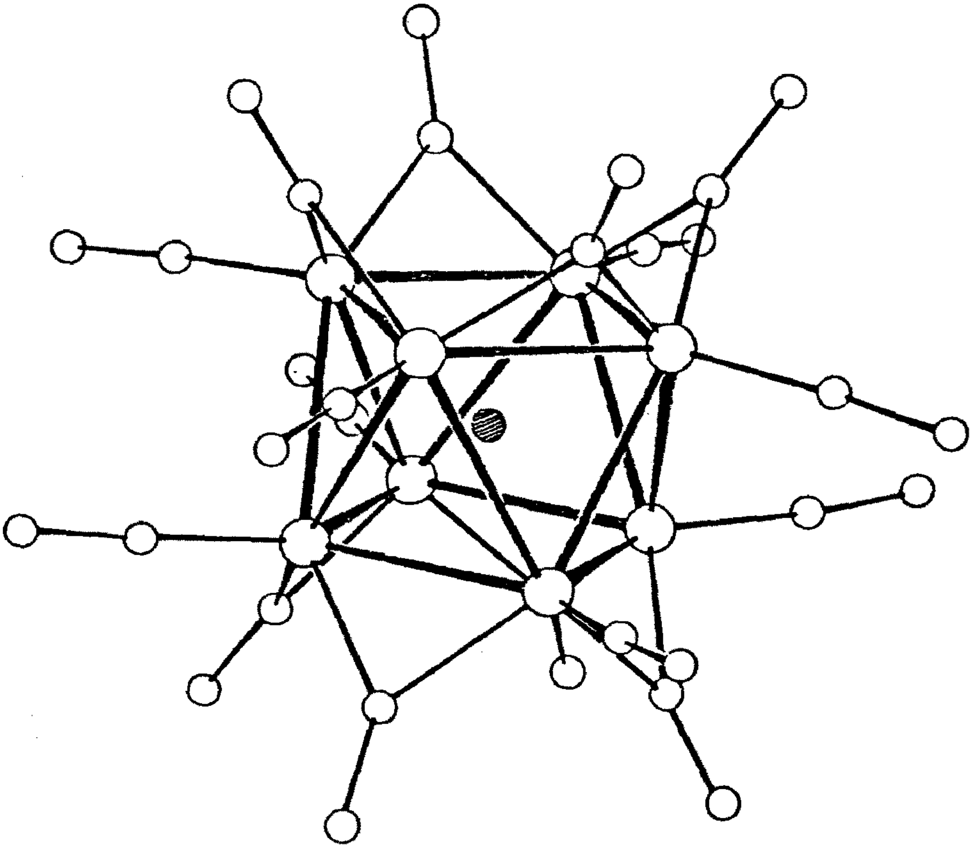
$$[ML_4] + HCOF \longrightarrow [HML_2F] + CO \qquad (11)$$

Successive treatment of $[Ni_6(CO)_{12}]^{2-}$ with $SiCl_4$ and CO/H_2O gave the carbide cluster $[Ni_8C(CO)_{16}]^{2-}$, **155**. $[Ni_9C(CO)_{17}]^{2-}$, **156**, was produced from $[Ni_6(CO)_{12}]^{2-}$, CCl_4 and CO. The structure of this cluster was established by an X-ray diffraction study on its $[Bu_4N]$ salt. It was based on a square antiprism of nickel atoms capped on a square face, with the carbide encapsulated in the nickel cage. The average nickel-nickel bond distance was intermediate between that in nickel metal and that in Ni_3C [236].

^{103}Rh decoupled ^{13}C nmr spectroscopy was used to assign the ^{13}C spectrum of the mixed cluster $[NiRh_6(CO)_{16}]^{2-}$. Variable temperature measurements showed that the fluxional processes observed were different from those in the isostructural complex $[Rh_7(CO)_{16}]$ [237]. Reaction of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CCHMe_2)(PPh_2)]$ with $[\{CpNi(CO)\}_2]$ gave four products. One of these, $[NiRu_4(CO)_9(\mu\text{-}PPh_2)_2(\mu_4\text{-}C{=}CCHMe_2)_2]$, **157**, was characterised by an X-ray diffraction study. The loss of the cyclopentadienyl ligand from nickel is most unusual [238].

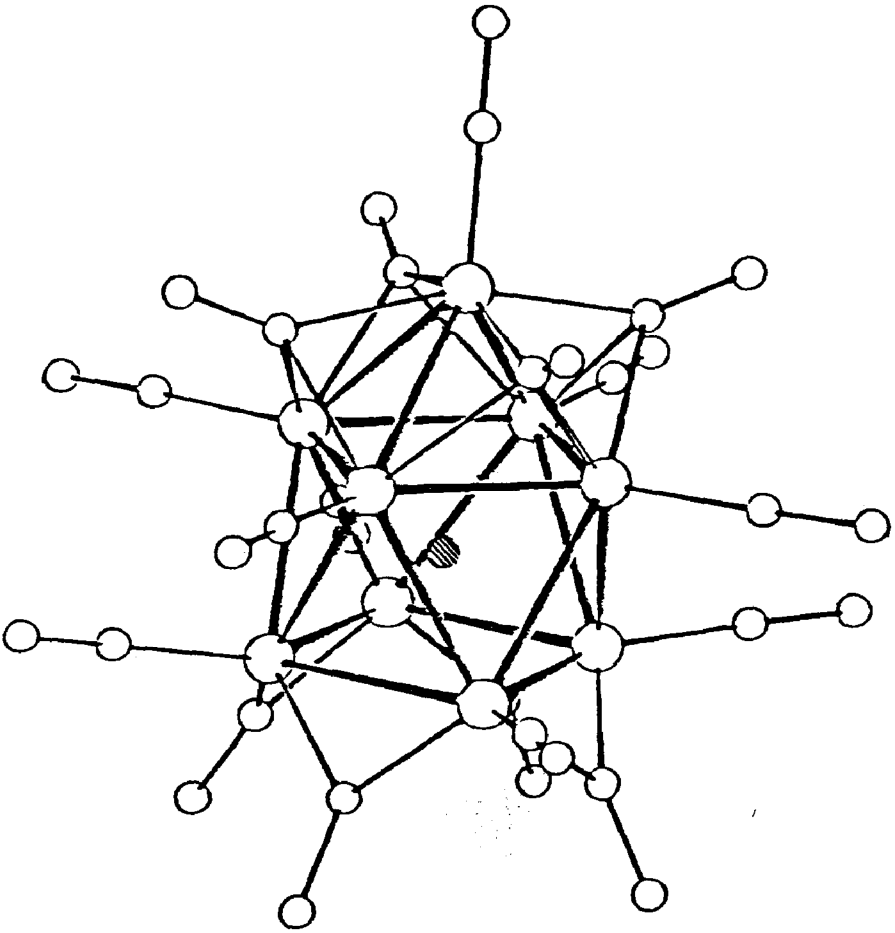
Further studies of palladium carbonyl phosphine clusters have been undertaken. The reaction of $[\{Pd(OCOMe)_2\}_3]$ with carbon monoxide was shown to be first order in $\{Pd(OCOMe)_2\}$ and CO. Numerous intermediates were proposed [239]. In a mixture of dioxan and CF_3COOH, $Pd(OCOMe)_2$ reacted with CO and Bu_3P to give respectively $[Pd_{10}(\mu_3\text{-}CO)_4(\mu_2\text{-}CO)_8(PBu_3)_8]$ and $[Pd_{10}(CO)_{14}(PBu_3)_4]$ at 1:4-1:10 and 1:1.5-1:2.5 molar ratios of palladium to phosphine. If the CF_3COOH was replaced with CH_3COOH the products were $[Pd_4(CO)_5(PBu_3)_4]$ and $[Pd_4(\mu_2\text{-}CO)_6(PBu_3)_4]$. The probable structures of the clusters were discussed [240]. In heptane $[Pd_{10}(CO)_{12}(PBu_3)_6]$ was converted by CO and PBu_3 to $[Pd_4(CO)_5(PBu_3)_4]$ [241]. Carbonylation of $[PdL_2(NO_2)_2]$ gave N_2O, CO_2 and

$[Pd_4(CO)_5L_4]$ (L = $PMePh_2$). Related nickel complexes were also studied [242]. Carbonylation of the allyl complex, $[Pd(\eta^1,\eta^3-C_8H_{12})(PMe_3)]$ in toluene at -30 °C gave $[Pd_7(CO)_7(PMe_3)_7]$, 158, characterised by X-ray diffraction. The structure consisted of a face-capped octahedron of palladium atoms with one phosphine ligand attached to each. Four carbonyl face-bridged the octahedron, whilst the other three bridge the edges to the odd palladium [243].



155 (Reproduced with permission from [236])

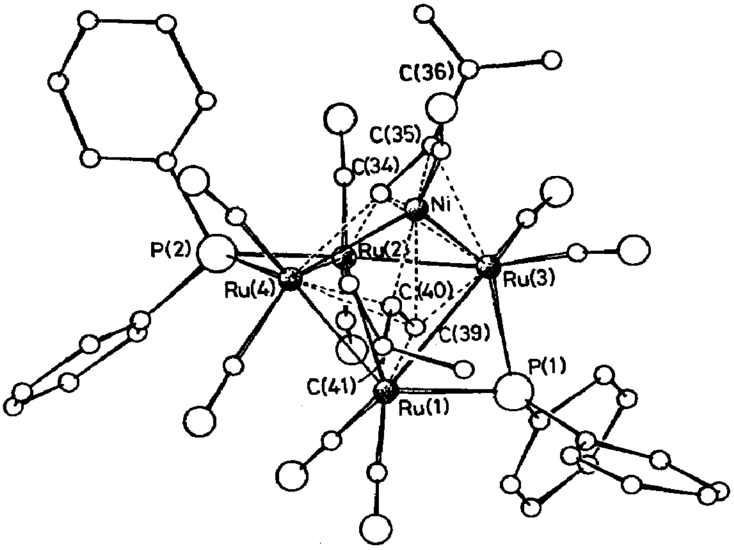
A review of hydride platinum carbonyl clusters has been published [244]. Molecular orbital calculations on phosphine carbonyl clusters of the platinum group metals indicate how they may be encompassed within the framework of the polyhedral skeletal electron pair theory. In particular, $[Pt_4(CO)_5(PR_3)_4]$ was predicted to adopt a butterfly structure, whilst $[Pt_5(CO)_6(PR_3)_4]$ was expected to be an edge-bridged tetrahedron, in accord with the experimental observations [245].



156 (Reproduced with permission from [236])

Selective population transfer techniques were used to identify isotopomers in the ^{31}P nmr spectrum of $[Pt_2(\mu\text{-}S)(CO)(PPh_3)_3]$ [246].

The reaction of $[H_2Pt_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ with carbon monoxide to give $[HPt_2(\mu\text{-}dppm)_2(CO)][PF_6]$ was shown to be reversible. The same product could be produced from $[Pt_2(\mu\text{-}dppm)_2(CO)_2]^{2+}$, 159, on reaction with $[OH]^-$. The trihydride but not the carbonyl hydride acted as a catalyst for the water gas shift. 159 and 160, isolated from a partially oxidised catalytic solution, were characterised by X-ray diffraction studies [247,248]. The chemistry of these and related complexes has been reviewed [249]. Photolysis of $[H_2Pt_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ in the presence of ligands including CO, ArNC, MeCN and pyridine gave $[HPt(\mu\text{-}dppm)_2L]^+$. That the process was intramolecular was shown by deuterium labelling, and quantum yield and sensitisation experiments indicated that reaction probably occurred from the first excited state [250].



157 (Reproduced with permission from [238])

Adsorption of $[Pt_3(\mu\text{-}CO)_3(PEt_3)_4]$ on alumina followed by hydrogenation gave a hydrocracking catalyst [251]. In the triangular complexes $[Pt_3(\mu\text{-}CO)_3L_4]$ (L = PEt_3, PMe_2Ph, $PMePh_2$, PEt_2CMe_3 or $PPh_2(CH_2Ph)$) nmr spectroscopic measurements showed that there were two types of phosphine and two types of platinum atoms with distinctive coupling constants, $^1J_{PtPt}$, in accord with the structure 161 [252]. Carbon monoxide could be substituted by sulphur dioxide in the analogous complex of PPh_3, and reactions (12) and (13) indicated that CO and SO_2 are roughly comparable as bridging ligands. Ir spectroscopy and an X-ray diffraction study of 162 showed that SO_2 bridged two metal atoms *via* the sulphur atom [253].

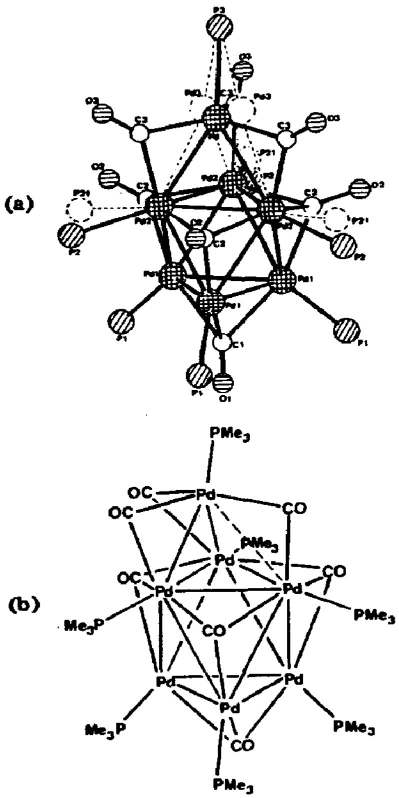
$$[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4] + SO_2 \longrightarrow [Pt_4(\mu\text{-}SO_2)_5(PMe_2Ph)_4] \qquad (12)$$

$$[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4] + SO_2 \longrightarrow [Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)(PPh_3)_4] \qquad (13)$$

162

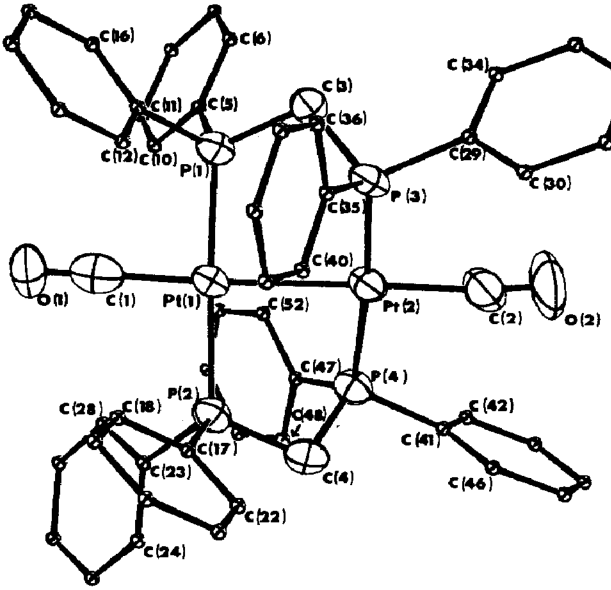
$[Pt_4(CO)_5\{As(CMe_3)_3\}_4]$ was prepared by carbonylation of *trans*-$[H_2Pt\{As(CMe_3)_3\}_2]$ [254]. Some interconversions of large platinum clusters have been studied (reactions (14) and (15)). The structure of

$[Pt_{24}(CO)_{30}]^{2-}$ was shown by an X-ray diffraction study to be a fragment of a cubic close packed structure [255]. A number of large platinum clusters have been used as catalysts for hydrogenation of alkenes, carbonyl groups and nitriles. Ir spectroscopic studies of the catalysis solutions implied the existence of complex equilibria, with the active species containing the unit 163 [256].

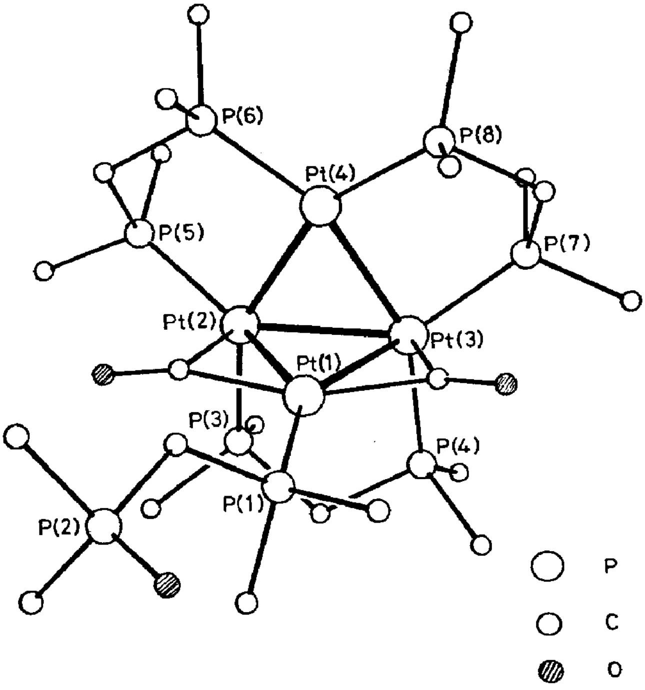


158 (Reproduced with permission from [243])

Structure of $[Pd_7(CO)_7(PMe_3)_7]$ (a) determined in the X-ray experiment. As a result of disorder of the seventh palladium atom on one of the triangular faces of the octahedron the symmetry of individual molecules is reduced to $C_s(m)$. The edge-bridging carbonyl groups, C3-O3, appear disordered in three positions. (b) Idealised structure.

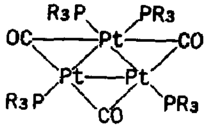


159 (Reproduced with permission from [247])

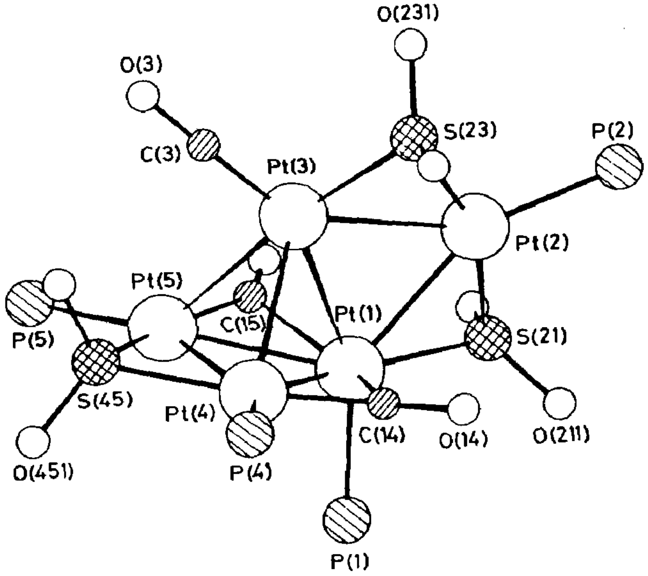


160 (Reproduced with permission from [248])

For clarity hydrogens and five carbons of each phenyl ring are omitted.



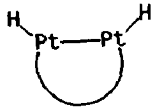
161



162 (Reproduced with permission from [253])
For clarity the phenyl rings have been omitted.

$$[Pt_{15}(CO)_{30}]^{2-} \xrightarrow{\Delta} [Pt_{24}(CO)_{30}]^{2-} \qquad (14)$$

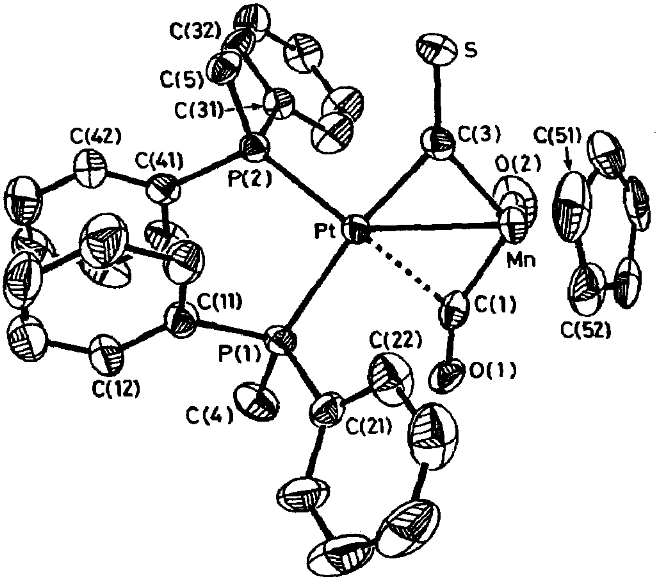
$$[Pt_{24}(CO)_{30}]^{2-} + L \longrightarrow [Pt_{24}(CO)_{29}L]^{2-} \qquad (15)$$



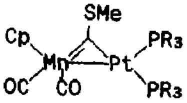
163

Reaction of *cis*-[$Pd(PhCN)_2Cl_2$] with [$(Ph_3P)_2Ir(CO)_2(COOMe)$] gave a species formulated as [$(PPh_3)_2Ir(\mu\text{-}CO)_2PdCl_2$]. The complex was not well characterised [257].

The thiocarbonyl bridged species [$CpM(CO)(\mu\text{-}CS)(\mu\text{-}CO)Pt(PR_3)_2$] (M = Mn, PR_3 = PMe_2Ph or $PMePh_2$; M = Re, PR_3 = PMe_2Ph) were prepared from [$CpM(CO)_2(CS)$] and [$Pt(PR_3)_2(C_2H_4)$]. The the thiocarbonyl was truly bridging and the carbonyl semi-bridging, was clearly demonstrated by an X-ray diffraction study on **164**. Reaction of the bridging thiocarbonyl complex with [Me_3O][BF_4] gave **165**, the first example of a heteronuclear bimetallic complex with a bridging thiocarbyne ligand [258].



164 (Reproduced with permission from [258])



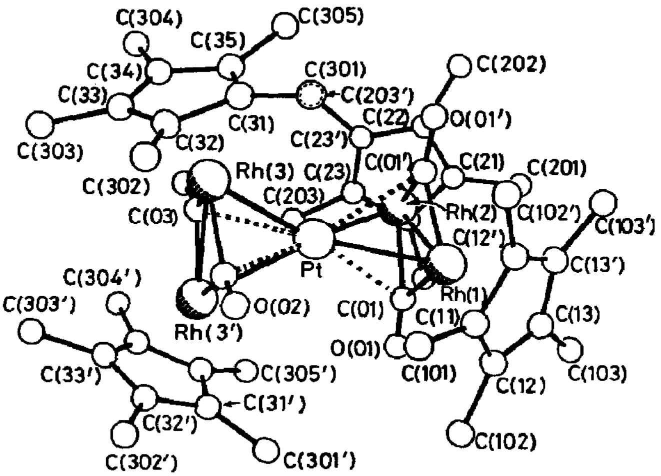
165

The complexes [$Pt_2Co_2(CO)_8(PPh_3)_2$] and [$Pt(CyNC)_2\{CpMo(CO)_3\}_2$] were shown to be poor catalysts for the reduction of alkenes and internal alkynes, but good, though rather unselective, for hydrogenation of terminal alkynes. The {$PtMo_2$} cluster could be recovered essentially unchanged from the reaction, but the {Pt_2Co_2} species was extensively rearranged [259]. Insertion of $SnCl_2$ into the Pt-Pt bond of $[Cl_2(CO)Pt{-}Pt(CO)Cl_2]^{2-}$ gave $[Cl_2(CO)Pt(\mu\text{-}SnCl_2)Pt(CO)Cl_2]^{2-}$, and related platinum halocarbonyl complexes behaved similarly [260].

The reaction of $[Pt_3(\mu_2\text{-}CO)_3L_3]$ (L = $P(CHMe_2)_3$, $PPh(CHMe_2)_2$ or $PEt_2(CMe_3)$) with mercury metal gave the complex $[\{Pt_3(\mu_2\text{-}CO)_3L_3\}_2Hg_2]$ in which the two triangular $\{Pt_3\}$ units were both capped by mercury atoms, the mercury atoms being linked by a weak bond. The bonding arises from a linear combination of an empty σ-type orbital from each of the $\{Pt_3\}$ fragments and the filled 6s orbitals of each mercury atom. This gives rise to one strongly and one weakly bonding molecular orbital to accomodate the four bonding electrons. The weak Hg-Hg interaction arises from the non-bonding character between these two atoms of the HOMO. Reaction of $[Pt_4(\mu_2\text{-}CO)_5(PEt_3)_4]$ with mercury gave $[Hg\{Pt_3(\mu_2\text{-}CO)_3(PEt_3)_3\}_2]$ [261].

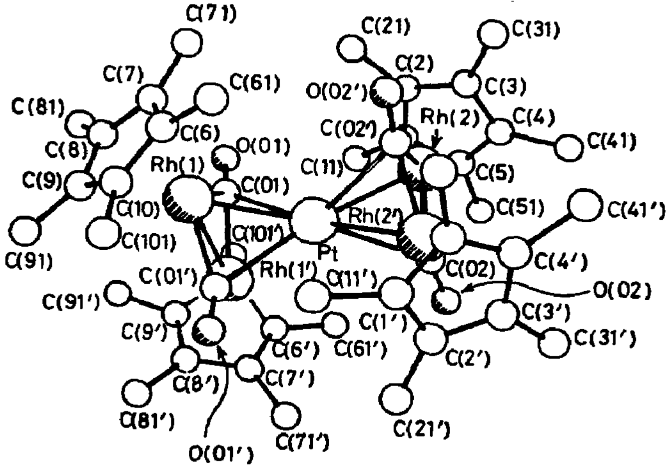
Tris(ethene) platinum is a useful source of mixed clusters since all the ligands are readily displaced. Reaction with $[Cp^*{}_2Rh_2(\mu\text{-}CO)_2]$ gave $[PtRh_4Cp^*{}_4(\mu\text{-}CO)_4]$, **166**, characterised by X-ray diffraction. The rhodium atoms were arranged around the platinum in a pseudotetrahedron and the carbonyls were semi-triply bridging. The cluster possessed D_{2d} symmetry as predicted by degenerate perturbation theory [262]. Cyclooctadiene ligands are a little less easy to displace, and the analogous reaction with $[Pt(cod)_2]$ in a 1:1 molar ratio gave $[PtRh_2(\mu_3\text{-}CO)_2(cod)Cp^*{}_2]$. With two molar equivalents of $[Cp^*{}_2Rh_2(\mu\text{-}CO)_2]$ the major product was $[PtRh_2(\mu\text{-}CO)_2(CO)_2Cp^*{}_2]$. $[Pt(PPh_3)_2(C_2H_4)]$, in which only the ethene is readily displaced, gave a complex mixture of which the major component was **167**; steric crowding led to a lengthening of the Pt-Rh bonds. **167** was also produced in the reaction with $[Pt(PPh_3(C_2H_4)_2]$, along with $[Cp^*{}_2Rh_2Pt(\mu_3\text{-}CO)_2(C_2H_4)(PPh_3)]$ and a little $[Pt_3(\mu\text{-}CO)_3PPh_3)_3]$ [263]. Protonation of a number of these complexes has been studied. Thus treatment of $[Cp^*{}_2Rh_2Pt(\mu\text{-}CO)_2LL']$ (L = L' = CO, L = CO, L' = PPh_3 or LL' = cod) with $H[BF_4]$ gave $[Cp^*{}_2Rh_2Pt(\mu\text{-}H)(\mu\text{-}CO)_2LL']$ in which protonation had occurred on the Pt-Rh edge. All these complexes showed fluxional behaviour on the nmr spectroscopic timescale, apparently involving a shift of the hydride from one Pt-Rh bond to the other. The dynamic process was shown to involve rotation of the $\{Cp^*{}_2Rh_2(CO)_2\}$ fragment about an axis through the platinum atom and the midpoint of the rhodium-rhodium bond. **168** was characterised by X-ray diffraction but the bridging hydride was not directly located [264].

The cluster $[PtRh_{10}N(\mu\text{-}CO)_{10}(CO)_{11}]^{3-}$ was prepared from $[Rh_6N(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^{2-}$, and was characterised by an X-ray diffraction study of its caesium salt, **169**. The cluster has the highest metal to interstitial atom raio known [265].



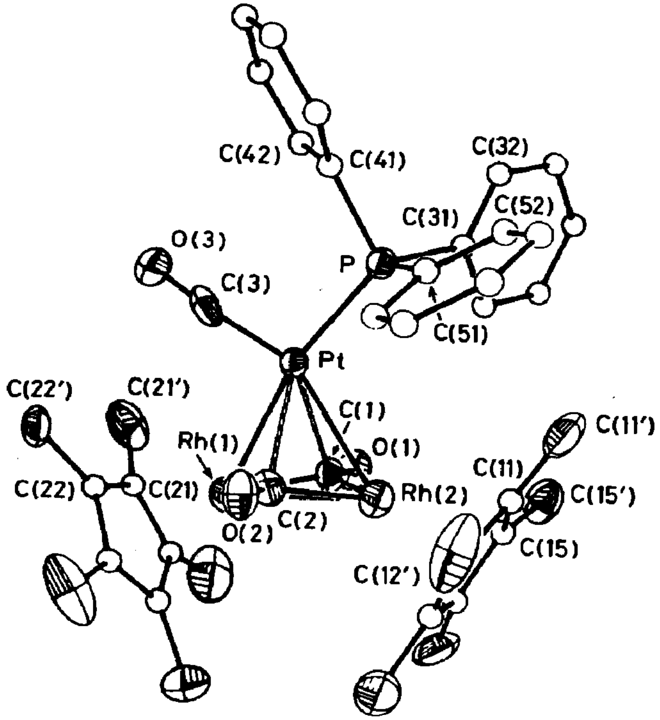
166a Orthorhombic [Cp*$_4$PtRh$_4$(μ-CO)$_4$] The primed and unprimed atoms are related by mirror symmetry

(Reproduced with permission from [262])

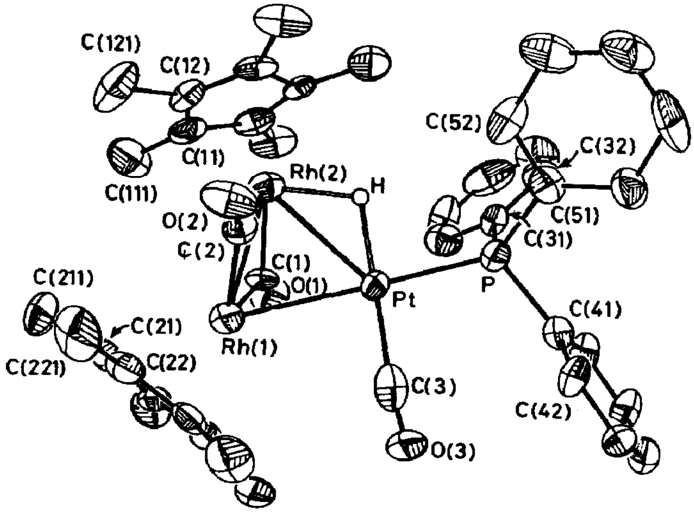


166b Monoclinic [Cp*$_4$PtRh$_4$(μ-CO)$_4$] The primed and unprimed atoms were related by a two-fold rotation axis. Monoclinic crystals were grown at room temperature from light petroleum/CH_2Cl_2. Cooling of the monoclinic crystals to *200 K resulted in a phase change to form a triclinic unit cell*, poorly defined and weakly diffracting. Rewarming to ambient temperature resulted in another irreversible phase change to the orthorhombic structure.

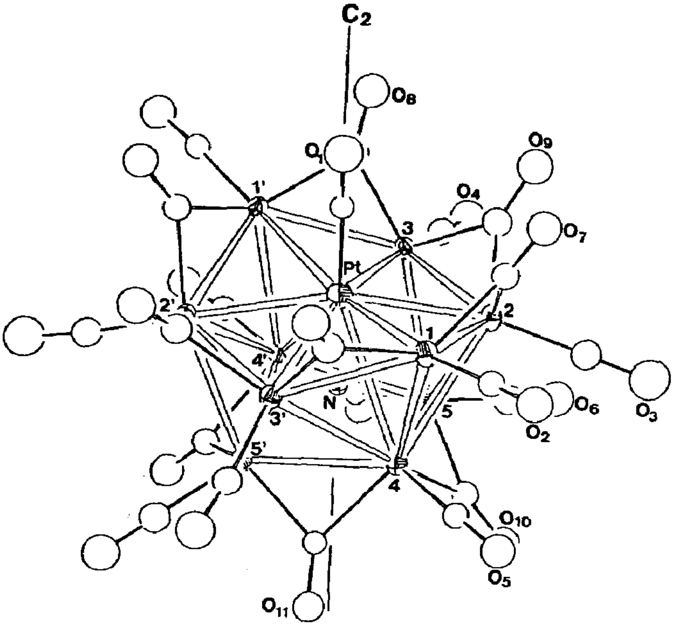
(Reproduced with permission from [262])



167 (Reproduced with permission from [263])

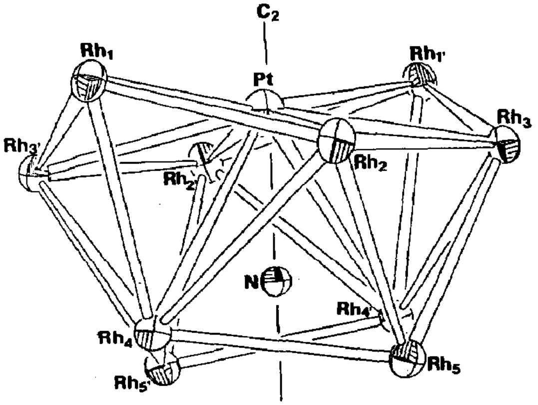


168 (Reproduced with permission from [264])



169a View of the anion [PtRh$_{10}$(μ-CO)$_{10}$(CO)$_{11}$]$^{3-}$. The rhodium atoms are indicated by their sequence numbers and the carbonyl ligands by their oxygen atoms.

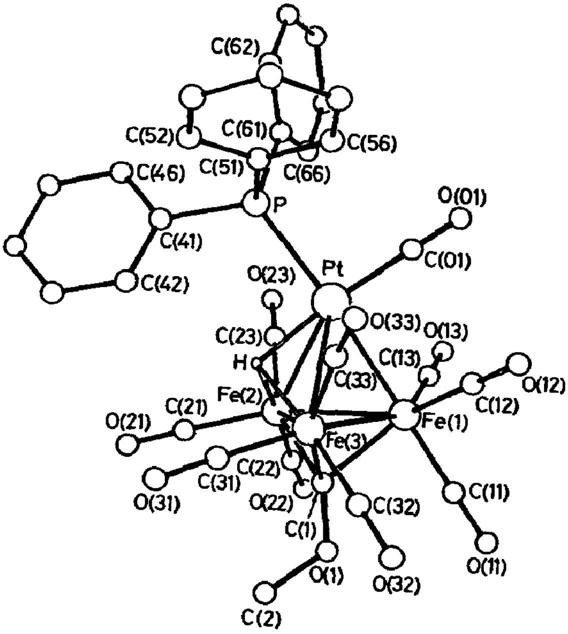
(Reproduced with permission from [265])



169b View of the {PtRh$_{10}$N} moiety

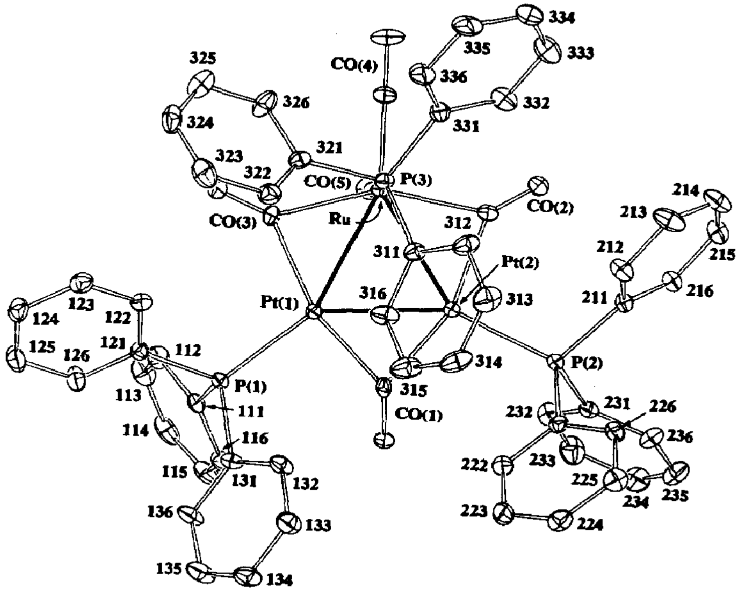
(Reproduced with permission from [265])

Reaction of $[Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ with $[Pt(PPh_3)(C_2H_4)_2]$ gave $[Fe_3Pt(\mu_3\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}(PPh_3)]$, **170**, in which the metal atoms form a distorted tetrahedron, the hydride bridges the $\{Fe_2Pt\}$ face, and the acetyl group bridges the $\{Fe_3\}$ face [266]. The structure of $[Fe_5PtC(CO)_{15}]^{2-}$ was determined and shown to involve an octahedron of metal atoms with the carbidic carbon in the centre. The platinum atom bears one terminal carbonyl group, whilst the iron atoms each bear two. The remaining four carbonyls were bridging [267].



170 (Reproduced with permission from [266])

The reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with $[Ru_3(CO)_{11}(CNCMe_3)]$ was much faster than that with $[Ru_3(CO)_{12}]$, giving, at -30 °C an unstable crimson adduct $[RuPt_2(\mu_2\text{-}CO)_2(CO)_2(PPh_3)_3]$. At room temperature a wide range of products were isolated, including $[Ru_2Pt(CO)_7(PPh_3)_3]$, $[RuPt_2(CO)_5(PPh_3)_3]$, $[RuPt_2(CO)_6(CNCMe_3)(PPh_3)]$ and $[Ru_2Pt_2(CO)_9(CNCMe_3)(PPh_3)]$. Low temperature carbonylation of the crimson intermediate gave $[Pt_2Ru(\mu_2\text{-}CO)_3(CO)_2(PPh_3)_3]$, 171, as the major product. This complex had been prepared before, but has now been definitively characterised by an X-ray diffraction study. Other reactions of the crimson intermediate were also investigated [268]. The structure of $[H_2Os_4Pt(CO)_{12}(dppe)]$, formed from $[H_4Os_4(CO)_{12}]$ and $[R_2Pt(dppe)]$ (R = Ph or Me), was not determined, but was assumed to be closely related to that of the characterised species $[H_2Os_4(CO)_{12}\{Au(PR_3)\}_2]$ [269].



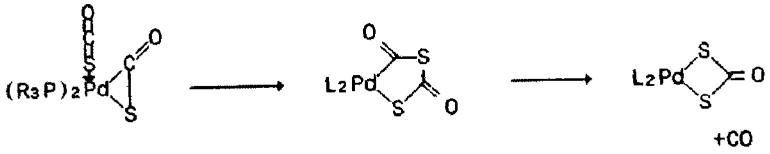
171 (Reproduced with permission from [268])
Molecule of the complex projected normal to the plane of the metal atom triangle.

Ab initio molecular orbital calculations have been performed for the system $\{Ni(PH_3)_2\}/CO_2$. It was concluded that coordination through the central carbon atom was unfavourable, but that η^2-coordination was likely since Ni(0) is able to provide good π-back donation [270]. The reduction of $[Ni(NO_2)_2(PMe_3)_2]$ to $[Ni(NO_2)(NO)(PMe_3)_2]$, by carbon monoxide, was thought to proceed *via* an associative mechanism with transfer of oxygen from nitrogen to carbon in $[Ni(NO_2)_2(CO)(PMe_3)_2]$ [271].

The cod ligand in [Ni(bipy)(cod)] could be substituted by COS, CS_2 or CSSe, but $[Ni(PPh_3)_2(C_2H_4)]$ reacted only with CS_2 and not COS. Reaction with CO_2 occurred only with $[Ni(PCy_3)_3]$ and $[Ni(PEt_3)_4]$. An oligomeric structure was suggested for $[Ni(PPh_3)(CS_2)]$, but was not conclusively proven [272]. Reduction of $[Ni(triphos)(\eta^2-S_2CX)][BPh_4]_n$ (X = SMe, OEt or NEt_2, n = 1; X = PEt_3, n = 2) with $Na[BH_4]$ gave respectively $[Ni(triphos)(\eta^2-CS_2)]$, [Ni(triphos)(CO)], [Ni(triphos)SH] (the structure of this compound was proven by X-ray diffraction) and $[Ni(triphos)(S_2CHPEt_3)]$ [273].

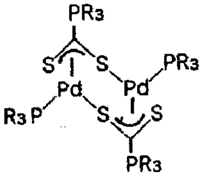
In the complex $[Ni(PCy_3)_2(PhCHO)]$ the aldehyde was shown by an X-ray diffraction study to be η^2-coordinated. The carbon-oxygen bond was lengthened by 0.1 Å due to back donation into the π* orbital [274].

Neither $[Pd(PCy_3)_2]$ nor $[Pt(PCy_3)_2]$ react with liquid CO_2 to give derivatives, but the platinum complex does react with wet CO_2 to give a bicarbonate complex *trans*-$[HPt(PCy_3)_2(O_2COH)]$ [275]. $[PdL_4]$ (L = $PMePh_2$ or PMe_2Ph) and $[PdL'_2]$ (L' = $P(CHMe_2)_3$) all reacted with COS to give complexes of the stoicheiometry $[Pd(R_3P)_2(S_2CO)]$, in which the $\{S_2CO\}$ acted as a chelate through the sulphur atoms. The mechanism of reaction (16) was suggested [276]. By contrast $[Pt(PPh_3)_3]$ reacted with one molar equivalent of COS to give $[Pt(PPh_3)_2(\eta^2\text{-}C,S\text{-}COS)]$, which was stable in solution only below -20 °C. With an excess of COS the dithiocarbonate complex was again formed. The related reaction with $[Pd(PPh_3)_n]$ (n = 3 or 4) was slow and incomplete, giving the unstable complex $[Pd(PPh_3)_2(COS)]$ [277].



(16)

$[Pd\{P(CHMe_2)_3\}_n]$ (n = 2 or 3) and $[Pd(PMePh_2)_4]$ reacted with CS_2 to give complexes with the stoicheiometry $[Pd(PR_3)_2(\eta^2\text{-}CS_2)]$. However, with $[Pd(PMe_3)_4]$ and $[Pd(PPhMe_2)_4]$, $[\{Pd(PR_3)(S_2CPR_3)\}_2]$, with a structure proposed as 172, was produced [278]. Thermolysis of $[Pt(PPh_3)_2(\eta^2\text{-}CS_2)]$ gave a polymer with the proposed structure 173 [279].



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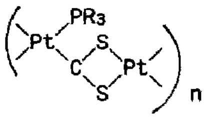
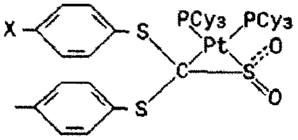


173

A range of palladium(0) phosphine complexes reacted with RNCS to give $[L_2Pd(\eta^2\text{-}C,S\text{-}RNCS)]$ [280]. There have been further investigations of the coordination chemistry of the sulphines, XYC=S=O, with the aim of synthesising unstable sulphines within a metal coordination sphere. The preparation of 174 was achieved by reactions (17) and (18), but the reactions were slow and the process was not competitive with more conventional syntheses [281].

$$[\mathrm{Pt(PCy_3)_2\{\eta^2\text{-}\mathit{C,S}\text{-}E\text{-}(4\text{-}MeC_6H_4S)ClCSO\}}] \xrightarrow{\mathrm{CHCl_3}} \mathit{cis}\text{-}[\mathrm{Pt(PCy_3)_2\{E\text{-}(4\text{-}MeC_6H_4S)CSO\}Cl}] \qquad (17)$$

$$\mathit{cis}\text{-}[\mathrm{Pt(PCy_3)_2\{E\text{-}4\text{-}MeC_6H_4)CSO\}Cl}] \xrightarrow{\mathrm{K[SAr']}} [\mathrm{Pt(PCy_3)_2\{(ArS)_2CSO\}}] \qquad (18)$$



174

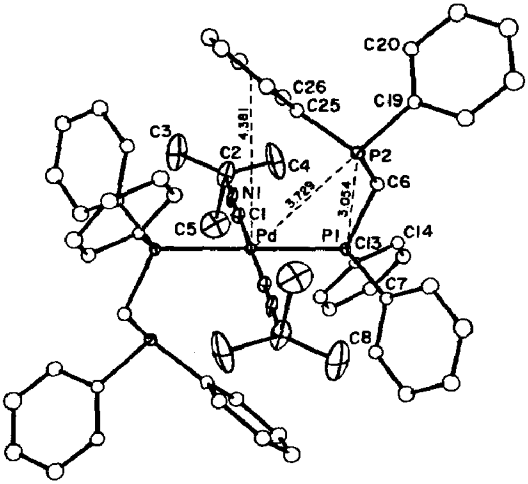
7 METAL ISOCYANIDE COMPLEXES

Substitution of $[\mathrm{Ni(CO)_4}]$ by polymer bound isocyanide groups has been achieved [282]. The complex $[\mathrm{Ni(Ar_2N_4)(CNCMe_3)_2}]$ could be prepared either by reaction of the isocyanide with $[\mathrm{Ni(Ar_2N_4)_2}]$ or from $[\mathrm{Ni(CNCMe_3)_4}]$ and $[\mathrm{Ni(Ar_2N_4)_2}]$ [283]. The paramagnetic complex $[\mathrm{CpNi(Ar_2N_4)}]$ also reacted with $\mathrm{Me_3CNC}$ to give $[\mathrm{Ni(CNCMe_3)_2(Ar_2N_4)}]$ [284].

The structure of 175, prepared by reaction of $[\mathrm{Pd(CNCMe_3)_4}]^{2+}$ with dppm, was determined by an X-ray diffraction study [285]. The reaction of $[\mathrm{Pd(CNCMe_3)_2}]$ with either $[\mathrm{Mo(SCMe_3)_4}]$ or $[\mathrm{Mo(SCMe_3)_2(CNCMe_3)_4}]$ gave the mixed d^4d^{10} bimetallic complex $[\mathrm{(Me_3CNC)_4Mo(\mu\text{-}SCMe_3)_2Pd(CNCMe_3)}]$ [286].

Treatment of $\mathit{cis}\text{-}[\mathrm{Pt\{CNC_6H_3\text{-}2,6\text{-}Me_2)Cl_2\}}$ with the free isonitrile in the presence of sodium amalgam gave $[\mathrm{HgPt_6(CNAr)_{12}}]$ as well as the known species, $[\mathrm{Pt_7(CNAr)_{12}}]$ and $[\mathrm{Pt(CNAr)_5}]$. The structure of this latter compound appeared to be $[\mathrm{(ArNC)_2Pt(2,6\text{-}Me_2C_6H_4imino)_3}]$ but the structure has not yet been determined by X-ray diffraction [287]. $[\mathrm{PtL_3}]$ ($\mathrm{L = Me_3C(SiMe_3)NP{=}NCMe_3}$) reacted with $\mathrm{Me_3CNC}$ to give $[\mathrm{Pt(CNCMe_3)_3(\mu_2\text{-}CNCMe_3)_3}]$ [288].

$[\mathrm{Ni(Ar_2N_4)_2}]$ reacted with $[\mathrm{Pt(cod)_2}]$ in the presence of $\mathrm{Me_3CNC}$ to give $[\mathrm{Ni(Ar_2N_4)Pt(CNCMe_3)_2}]$. A number of related transformations, particularly those giving heterobimetallic complexes, were studied [289].



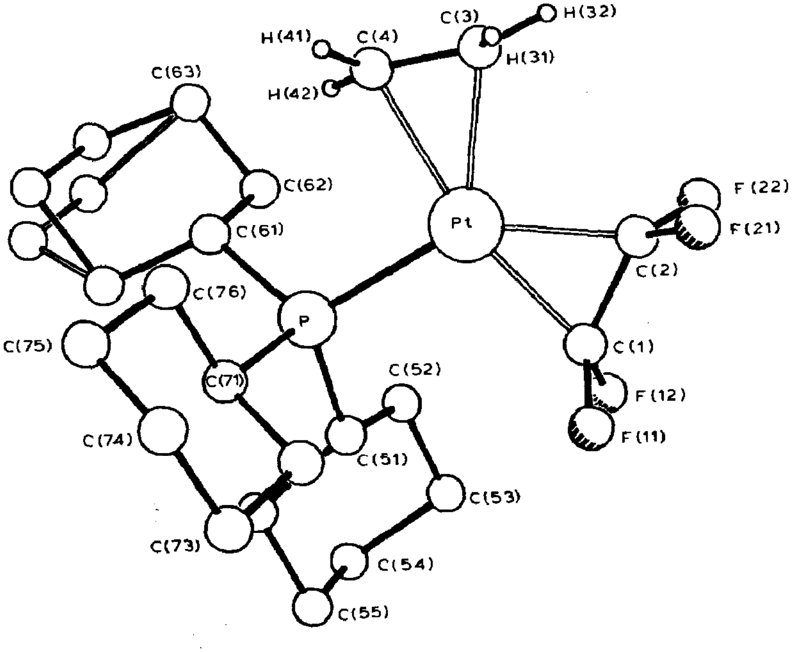
175 (Reproduced with permission from [285]).

8 METAL ALKENE AND METAL ALKENYL COMPLEXES

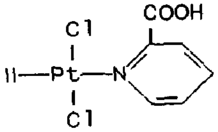
The asymmetric reactions of alkenes with nucleophiles, *via* their metal complexes, has been reviewed. The reactions of palladium alkene complexes were particularly prominent [290]. Calculations on nickel alkene complexes have been undertaken in order to show the rôle of transition metal catalysis in nucleophilic addition to carbon carbon double bonds [291].

The electronic structure of transition metal alkene complexes with lithium containing ligands was investigated by semiempirical MO calculations of the INDO type. Among the models considered was *trans*-$[Ni(C_2H_4)_2\{Li(en)\}_2]$ [292]. Ethene could be displaced from $[Ni(PPh_3)_2(C_2H_4)]$ by $R_3SiCH{=}CH_2$ [293].

The ir and Raman spectra of $[Pt(PPh_3)_2(C_2H_4)]$ have been reported [294]. The low frequency modes of vibration of *trans*-$[Pt(C_2H_4)LCl_2]$ (L = ND_3, CD_3CN, $DCON(CD_3)_2$ or $C_6D_5ND_2$) and *cis*-$[Pt(C_2H_4)\{(CD_3)_2SO\}Cl_2]$ have been studied by inelastic neutron scattering, ir and Raman spectroscopy. In all the complexes the motions of the ethene relative to platinum were assigned, and the barrier to ethene rotation was determined [295]. The structure of 176, $[Pt(PCy_3)(C_2H_4)(C_2F_4)]$, was established by an X-ray diffraction study. The shorter Pt-C(F) and longer C=C(F) bonds reflected the higher $\pi*$ acceptor capacity of C_2F_4 relative to C_2H_4 [296]. The broadening of the ^{195}Pt satellites in the ^1H nmr spectrum of 177 was thought to arise from the ^{195}Pt relaxation *via* a chemical shift anisotropy mechanism [297]. The mass spectrum of *trans*-[$Pt_2(\mu$-$Cl)_2(C_2H_4)_2Cl_2$] has been reported and assigned. Loss of chlorine and ethene were competitive, and fragments containing platinum-platinum bonds were noted [298].



176 (Reproduced with permission from [296])



177

As in the past, platinum ethene complexes have been used as precursors for a wide range of coordination and organometallic complexes, since the ethene ligand may be readily displaced (reactions (19)-(24)) [299-304].

$$[Pt(PPh_3)_2(C_2H_4)] + Ph_2C{=}P(C_6H_2\text{-}2,4,6\text{-}Me_3) \longrightarrow C_2H_4 + [Pt(PPh_3)_2\{Ph_2C{=}P(C_6H_2\text{-}2,4,6\text{-}Me_3\}] \quad (19)$$

$$K[Pt(C_2H_4)Cl_3] + 2L \longrightarrow [PtL_2Cl_2] \quad (20)$$

L = phenothiazine, phenoselenazine or phenoxanthinine

$K[Pt(C_2H_4)Cl_3] + P\text{-}P \longrightarrow trans\text{-}[Pt(P\text{-}P)Cl_2]$ (21)

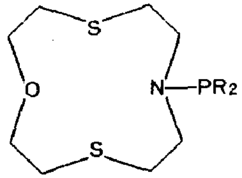
P-P = long chain biphosphine

$[Pt(PPh_3)_2(C_2H_4)] + Sn(acac)_2 \longrightarrow [Pt(PPh_3)_2\{Sn(acac)_2\}_2]$ (22)

$[Pt(PPh_3)_2(C_2H_4)] + [Fe_2(\mu\text{-}S_2)(CO)_6] \longrightarrow [(CO)_6Fe_2(\mu_3\text{-}S)_2Pt(PPh_3)_2]$ (23)

$[\{Pt(C_2H_4)Cl_2\}_2] + L + Ag[BF_4] \longrightarrow [LPtCl_2]$ (24)

L = 178



178

Photolysis of $[Pt(PEt_3)_2(OOCCOO)]$ gave the transient species $\{Pt(PEt_3)_2\}$ which reacted with a range of ligands, L, to give $[Pt(PEt_3)_2L_n]$ including the species in which L = C_2H_4 or C_2F_4 and n = 1 and L_n = $(CO)_2$ [305].

The thermochemistry of oxidative addition reactions has been reviewed, with particular reference to reactions in which Pt(0) is converted into Pt(II). The reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with organic species, AB, generally proceeds with loss of ethene [306]. Transformations of this type were involved in reactions (25) and (26) [307].

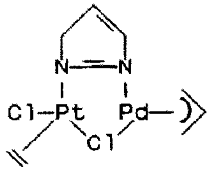
$[Pt(PR_3)_2(C_2H_4)] + HCl \longrightarrow [Pt(PR_3)_2Cl_2] + C_2H_4$ (25)

$[Pt(PR_3)_2(C_2H_4)] + CH_2I_2 \longrightarrow trans\text{-}[Pt(PR_3)_2(CH_2I)I]$ (26)

A reaction of $K[Pt(C_2H_4)Cl_3]$ without loss of ethene has been noted. With diamines, N-N, $[Pt(C_2H_4)(N\text{-}N)Cl_2]$ was prepared [308]. A kinetic study of the reaction of $[Pt(C_2H_4)LCl_2]$ with $[Ru(bipy)_2(CN)_2]$ to give $[Ru(bipy)_2(CN)_2Pt_2(C_2H_4)_2Cl_4]$ has been reported [309].

179 was prepared by treatment of $[Pt(pz)(C_2H_4)Cl_2]^-$ (generated by deprotonation of the adduct of Zeise's salt with pyrazole) with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ [310].

The ethene ligand in $[Pt(C_2H_4)(Me_4en)Cl]^+$ has been shown to be extremely reactive towards nucleophiles. For example, with Et_2NH the bis adduct, **180**, was produced and characterised by an X-ray diffraction study [311,312]. With $[NCO]^-$ as the nucleophile the first product was **181**, which reacted with further $[NCO]^-$ to give **182**, the structure of which was established by X-ray diffraction [301].



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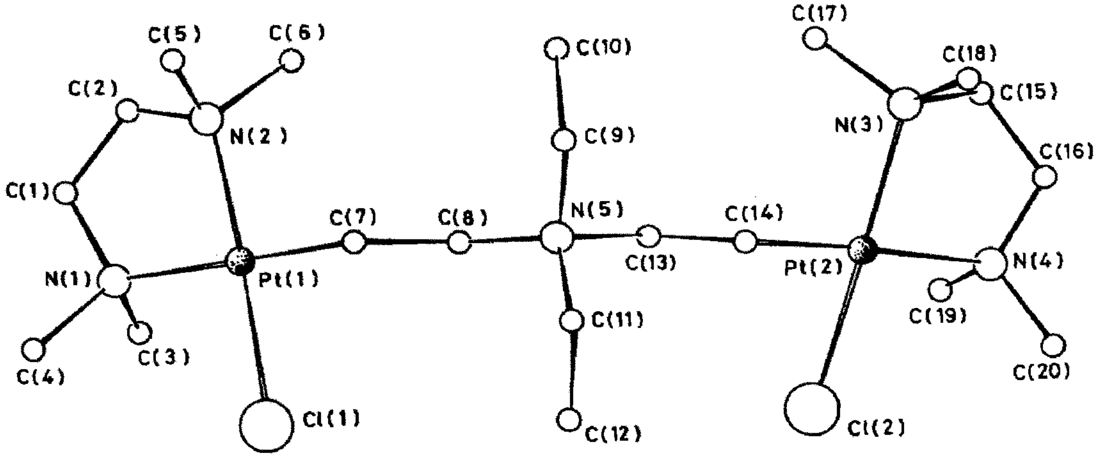
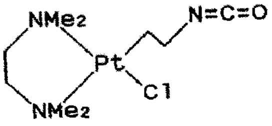


180 (Reproduced with permission from [311])

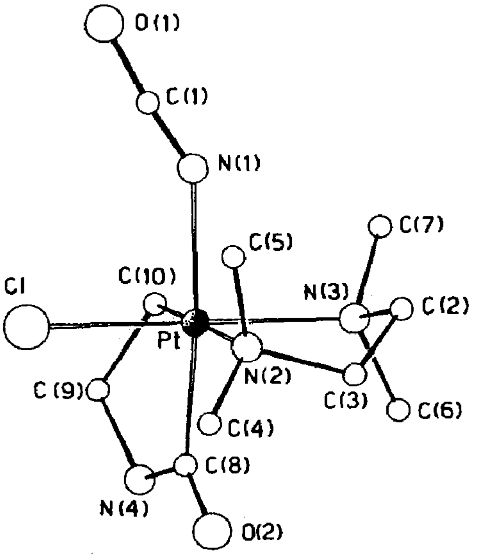


181

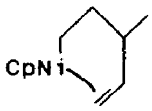
Stabilisation energies have been established for intergroup two ligand transition metal complexes in the gas phase. Complexes studied included $[Ni(CH_2{=}CHMe)]^+$, $[Ni(CH_2{=}CMe_2)(EtCHO)]^+$ and $[Ni(CH_2{=}C{=}CH_2)(MeOH)]^+$ [314].

$^1J_{CC}$ for the alkene moiety in complexes such as **183** was measured. $^1J_{CC}$

values lay between those for alkenes and those for cyclopropanes, giving some insight into the nature of the bonding in **183** [315].

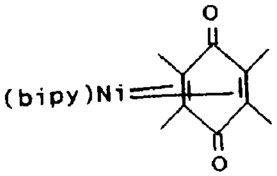


182 (Reproduced with permission from [313])



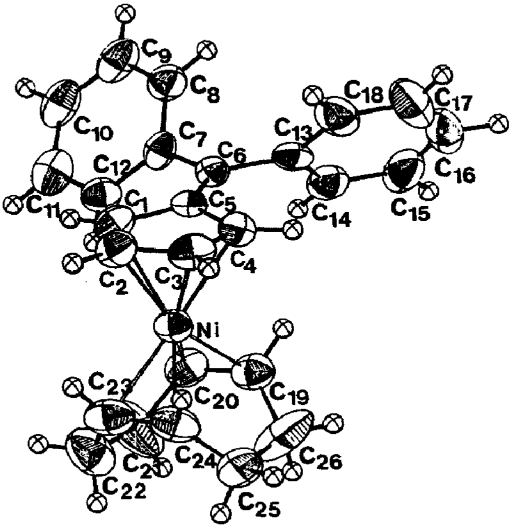
183

The structure of [Ni(bipy)(cod)] has been determined. The cod ligand adopts a twist-boat conformation in the tetrahedrally coordinated complex [316]. On reaction with a range of quinones the cod was displaced giving species such as **184** [317].



184

$[Ni(cod)_2]$ reacted with diphenylfulvene to give **185**, characterised by X-ray diffraction. The remaining cod ligand could be easily substituted by chelating ligands such as bipy [318]. The displacement of cod from $[Ni(cod)_2]$ by phosphines was studied. Reaction of $\{NiL_2\}$ ($L = PPh_3$) with HCOOEt resulted in fragmentation according to the reactions of Scheme 6 [319].



185 (Reproduced with permission from [318])

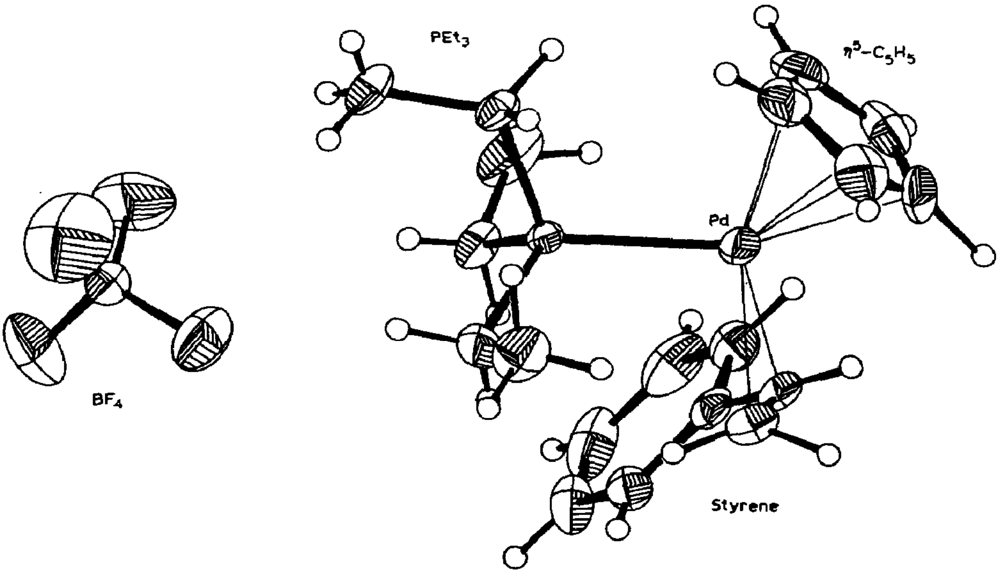
$$\{NiL_2\} + HCOOEt \longrightarrow [HCONi(OEt)L_2] \longrightarrow [HNi(CO)(OEt)L_2]$$

$$\big\downarrow L$$

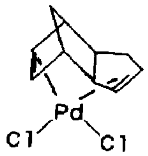
$$[HNi(CO)L_3] + EtOH$$

Scheme 6 Fragmentation of ethyl methanaote in the presence of nickel complexes

The structure of $[CpPd(PhCH{=}CH_2)(PEt_3)][BF_4]$, **186**, was determined by an X-ray diffraction study [320]. The X-ray diffraction study of **187** established that the carbon which is most readily attacked by nucleophiles is the one which is most distant from the metal. In 188 there was substantial slippage of the vinylic carbon-carbon double bond so that the centre of the bond was 0.27 Å out of the coordination plane and C^8 was 0.2 Å closer to platinum than C^7. C^8 was the site of nucleophilic attack. **189** exhibited unusual "in plane" bonding of the exocyclic carbon-carbon double bond, which was also 0.1 Å more distant from platinum than the other. Methoxide ion was shown to attack the "in plane" double bond [321].



186 (Reproduced with permission from [320])
Non hydrogen atoms are represented by thermal ellipsoids at 30 % probability levels, whereas temperature factors of hydrogen atoms are arbitrarily reduced



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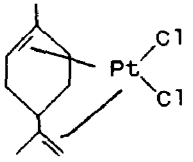

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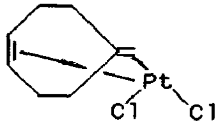
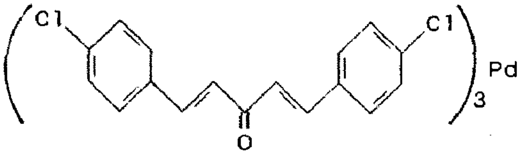


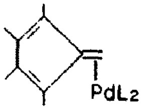
189

There has been a kinetic study of the reaction of $[Pd_2(dba)_3]$ with RPh_2P [322]. **190** was a catalyst for the low-yielding reaction of H_2 and O_2 to give H_2O_2 [323]. A polarimetric and CV study of $[Pd(PR_3)_2(quinone)_n]$ (n = 1 or 2) has been undertaken. The reduction potentials of the quinones were shifted to more negative values on coordination to palladium(0). The extent of the shift was a function of the electron withdrawing ability of the free quinone. On the other hand, the oxidation potentials for palladium(0) in the quinone complexes were at more positive potentials than for [Pd$(PPh_3)_4$] [324].



190

Reaction of [Cp*Pd{η^3-$CH_2C(CMe_3)CH_2$}] with two molar equivalents of PMe_3 or $P(OMe)_3$ gave **191** together with $CH_3C(CMe_3)=CH_2$ [325]. Perfluoronorbornadiene reacted with [M$(PPh_3)_4$] (M = Pd or Pt) to give initially [$(C_7F_8)M(PPh_3)_2$], in which one double bond was coordinated to the metal. For M = Pt the second double bond could be coordinated to a further {Pt$(PPh_3)_2$} moiety [326]. With 192 (R = H or Me_3Sn) coordination occurred only at the fluorinated double bond [327].



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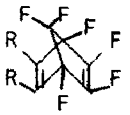


192

A new determination of the structure of [Pt(cod)Cl_2] has been made, with greater accuracy [328]. The structure of [Pt$(cod)_2$] has been determined at 200 K. The four coordinated double bonds occupy approximately tetrahedral sites, but the eight carbon atoms involved are not equidistant from the metal. The small bite angle of the ligand causes strain, which in turn leads to the easy displacement of the diene which is observed [329].

Cyclooctadiene complexes have been used as precursors of a wide range of organometallic and coordination compounds, since the cyclooctadiene is easily displaced (reactions (27)-(31)) [330-334]. [Pt{*cis*-$(RPNCR_3)_2$}$_2$] reacted with alkynes to give species such as [PtL_2(Ph-C≡C-Ph)].

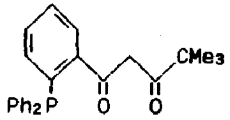
$$[\mathrm{Pt(cod)X_2}] + \mathrm{Ph_2C{=}P(C_6H_2\text{-}2,4,6\text{-}Me_3)} \longrightarrow \mathit{cis}\text{-}[\mathrm{Pt\{\eta^1\text{-}Ph_2C{=}P(C_6H_2\text{-}2,4,6\text{-}Me_3)\}_2X_2}] \qquad (27)$$

$$[\mathrm{Pt(cod)_2}] + \mathit{cis}\text{-}\{\mathrm{RPNCR_3}\}_2 \longrightarrow [\mathrm{Pt}\{\mathit{cis}\text{-}(\mathrm{RPNCR_3})_2\}_2] \qquad (28)$$

$$[\mathrm{Pt(cod)_2}] + \mathrm{Me_3C(Me_3Si)N{-}P{=}NCMe_3} \longrightarrow [\mathrm{Pt\{Me_3C(Me_3Si)N{-}P{=}NCMe_3\}_3}] \tag{29}$$

$$[\mathrm{Pt(cod)Cl_2}] + \mathbf{193} \longrightarrow \textit{cis}\text{-}[\mathrm{Pt}(\mathbf{193}\text{-}P)_2\mathrm{Cl_2}] \tag{30}$$

$$\begin{aligned}[\mathrm{Pd(cod)Cl_2}] + [\mathrm{Ru(Ph_2Ppy)_2(CO)_3}] \longrightarrow [\mathrm{Pd_2(Ph_2Ppy)_2Cl_2}] + [\mathrm{Ru(Ph_2Ppy)(CO)_2Cl_2}]\\ +[\mathrm{Ru(Ph_2Ppy)_2(CO)_2Cl_2}] + [\mathrm{RuPd(Ph_2Ppy)_2(CO)_2Cl_2}]\end{aligned} \tag{31}$$



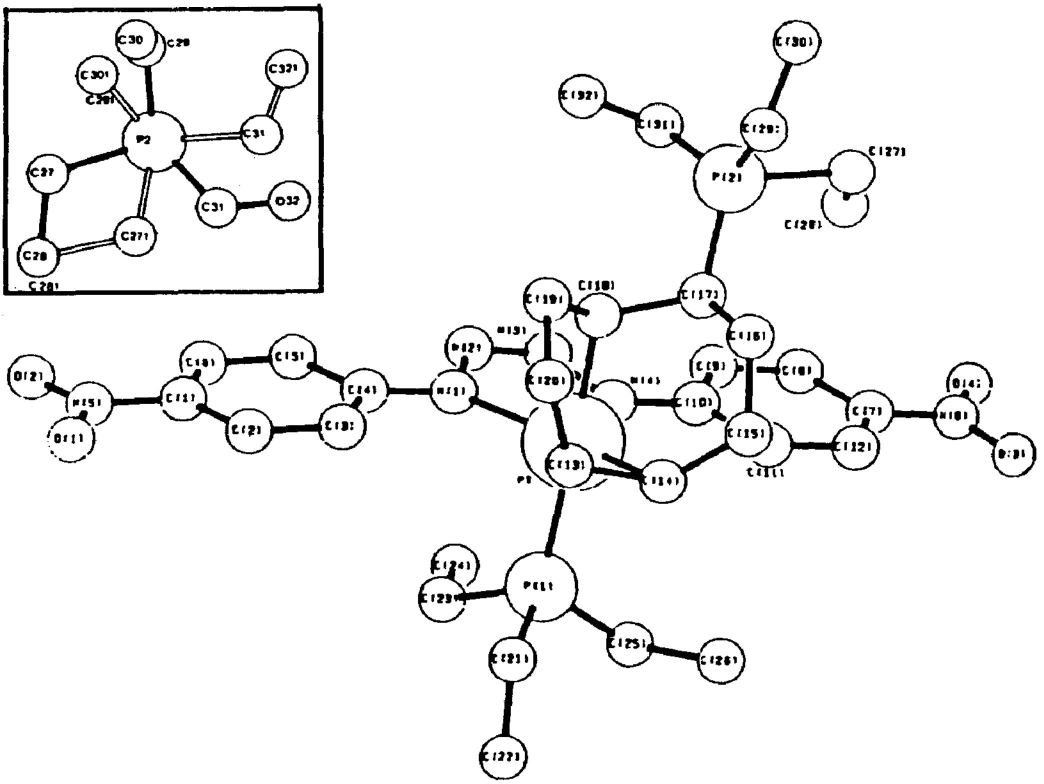
193

The reaction of $[Pt(cod)Cl_2]$ with two molar equivalents of R_3P and an excess of $Na[BH_4]$ was used to synthesise *trans*-$[HPt(PR_3)_2Cl]$ [335].

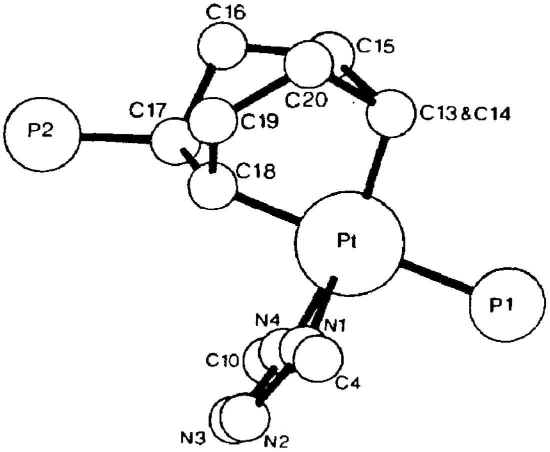
The preparation of complexes of diaryl triazaines, Ar-N=N-NHAr, of the type [PtL(cod)] has been described [336]. Exchange and rearrangement processes of [Pt(RN=N-N=NR)(cod)] have been studied; the cod ligand acts as a spectator [337]. Complexes of the type $[Pt(Ar_2N_4)(cod)$ were prepared from the reaction of an excess of ArN_3 with $[Pt(cod)_2]$. In the species for which Ar = $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$ or $4\text{-}NO_2C_6H_4$ the cod ligand could be substituted by PEt_3 or Me_3CNC. However for Ar = $4\text{-}NO_2C_6H_4$, **194** was also obtained and this bright blue complex was characterised by an X-ray diffraction study [338].

Both *cis*- and *trans*-isomers of the complexes [Pt(amino acid)(alkene)Cl] have been previously reported. Evidence has now been obtained from nmr spectroscopic studies that there is a thermodynamic preference for the isomer with the nitrogen and alkene ligands *cis* [339]. The absolute configuration of (–)-$[Pt(Me_2NN{=}CH{-}CH{=}NNMe_2)LCl_2]$ (L = E-2-butene), prepared by addition of HCl followed by the bidentate nitrogen ligand to *trans*-$[Pt\{S\text{-}(PhCH(Me)NH_2)\}LCl_2]$ has been shown to be S [340]. Resolution of $[Pt(\text{prochiral alkene})Cl_3]^-$ was achieved by crystallisation of its salt with S-$[PhCH(Me)NMe_3]^+$; the optical purities achieved were moderate [341].

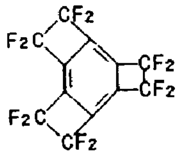
Reaction of **195** with $[Pt(PPh_3)_4]$ gave **196**; X-ray diffraction indicated that this should probably be regarded as a metallocyclopropane [342]. The use of species such as **197** as anti-tumour agents has been discussed; these showed modest cytotoxicity *in vitro*, but none *in vivo* [343].



194a PLUTO drawing of the crystal structure of $[Pt(1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4)\{\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH}_2\}(PEt_3)]$ showing the adopted numbering scheme and the disorder in the PEt_3 moiety.
(Reproduced with permission from [338])



194b View of the central part of the complex as seen along C(13)-C(14)
(Reproduced with permission from [338])



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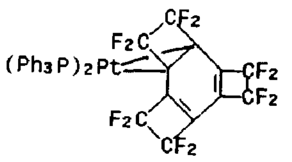

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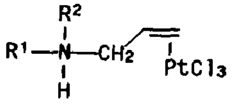
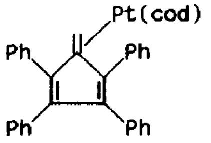


197

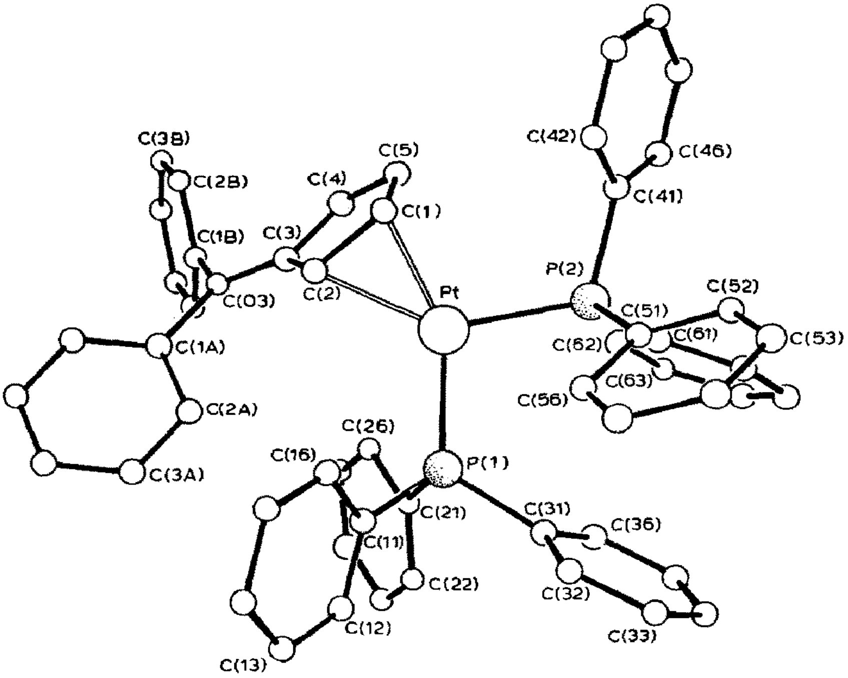
A range of cyano epoxides has been deoxygenated with palladium(0) or platinum(0) complexes. The products were alkene complexes and the structure of $[Pt(PPh_3)_2\{E\text{-}Ph(CN)C{=}CPh(CN)\}]$ was determined by X-ray diffraction techniques [344]. Fulvene complexes of the type **198** were prepared by substitution of $[Pt(cod)_2]$; the remaining cod ligand could be readily displaced by phosphines, arsines or isonitriles. The structure of **199** was determined; the platinum moiety was coordinated to the C^1-C^2 bond in an η^2-manner [345]. Treatment of $[Pt_2(PR_3)_2Cl_4]$ with butadiene gave the species *meso,cis,cis*-$[Pt_2(PR_3)_2(\mu\text{-}C_4H_6)Cl_4]$, **200**. A low temperature nmr spectroscopic study showed an equilibrium with *trans*-$[Pt(PR_3)(C_4H_6)Cl_2]$ (R = Pr). **200** (R = Et) reacted with Me_2NH at -78 °C to give **201**; the *trans*-ring fusion also implied that the **200** was *meso*. At low temperature isoprene reacted reversibly with $[Pt(PMe_2Ph)_2Cl_4]$ to give *trans*-$[Pt(PMe_2Ph)(isoprene)Cl_2]$, which was converted to the *cis*-isomer at room temperature [346].



198

The reaction of [Ni(cdt)] with CO_2 in the presence of Me_4en gave $[Ni(CO)_3(Me_4en)]$ and $[Ni(CO)_4]$. In the presence of 2-butyne, however, **202** was produced. Carbonylation of this complex yielded 2,3-dimethylbutanedioic anhydride, whilst protonation gave E-2-methyl-2-buteneoic acid [347]. Coupling of alkynes, $RC{\equiv}CR$, with isocyanates, $RN{=}C{=}O$, in the presence of nickel(0) and an appropriate ligand gave **203**, the reactions of which were studied [348].

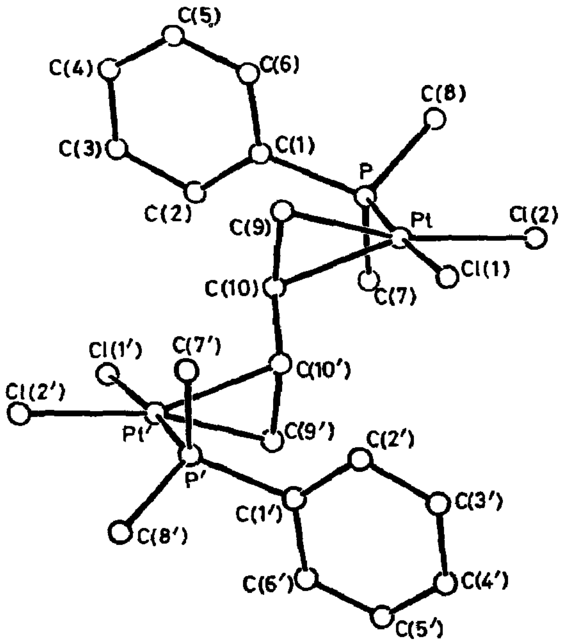
The reactions of palladium alkene complexes with nucleophiles has continued to be a fruitful area for investigation. The reaction of **204** with the chiral organometallics, $PhS(O)CH_2Li$ and $4\text{-}MeC_6H_4S(O)CH(Li)COOCMe_3$ proceeded with up to 40 % asymmetric induction [349]. With *cis*-complexes such as **205**, and using PhCH(Me)NHMe as both ligand and nucleophile, the best enantiomeric excess obtained was 60 % [350]. Aminolysis of the palladium complex of $ArOCH_2CH=CH_2$ to give **206** and **207** proceeded readily, but the reaction was not very practical in a catalytic sense, since the palladium was recovered as $[Pd(R_2NH)_2X_2]$, which was too deactivated to react with further alkene [351].



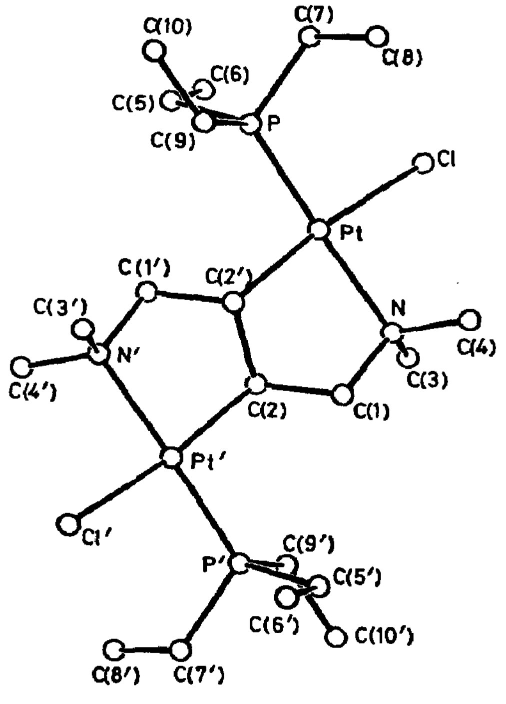
199 (Reproduced with permission from [345])

Alkenes may be oxidised to give ketones using $[Pd(MeCN)_2(NO_2)Cl]$. The intermediates are thought to be **208** and **209**, the first of these being detectable [352].

Reaction of **210** (X = Me, Y = H) with $[Pd(PhCN)_2Cl_2]$ gave bis(μ-chloro)bis{1,4,5-η-8-(α-chloroethyl)cyclooctenyl}dipalladium(II), **211**. The anti orientation of the palladium and the α-chloroethyl groups indicated that electrophilic attack of the palladium at the cyclopropane occurred with inversion of configuration [353]. **212** reacted with aldol, $Me_2C(OH)CH_2COMe$, to give **213** in low yield. A rather complex mechanism was proposed for the reaction [354].



200 (Reproduced with permission from [346])



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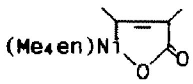

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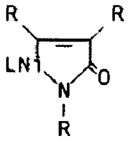

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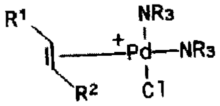

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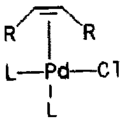

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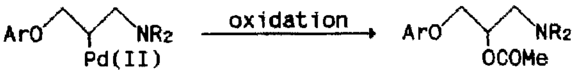

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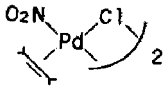

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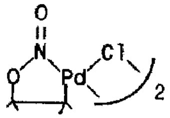

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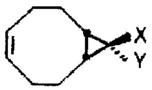
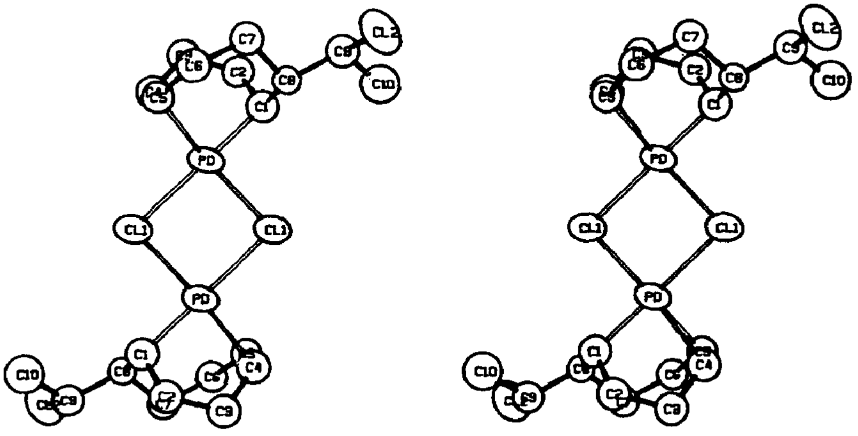
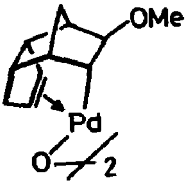


210

Amination of platinum alkene complexes has not yet proved so useful as that of their palladium analogues. However, with *cis*-[Pt(PPh$_3$)(CH$_2$=CHR)Cl$_2$], treatment with R'$_2$NH yielded first **214** and then **215**, which was characterised by an X-ray diffraction study for R = H and R' = Me. The four memberered ring was shown to be markedly non-planar [355]. Imidazole reacted with [Pt(cod)X$_2$] by both displacement of the halide ligands and by attack at the cyclooctadiene ligand. A tetramer, with bridging imidazole ligands, was formed initially and was reacted with ethanoyl chloride and a phosphine ligand to give 216, in which it was demonstrated that the initial attack of imidazole was anti with respect to the metal [356]. Attack of methoxide on a coordinated cyclooctadiene ligand has again been noted, but the evidence given this time for the structures of the products was extremely weak [357].



211 Stereopair drawing. The view is normal to the square plane over the bridge centroid. Hydrogen atoms are omitted for clarity.
(Reproduced with permission from [353])



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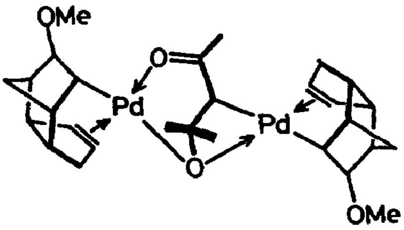
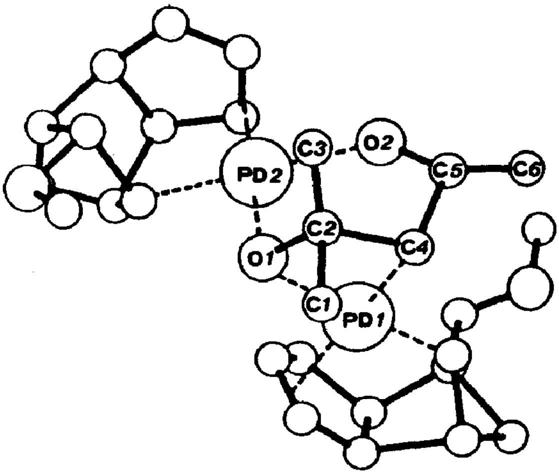
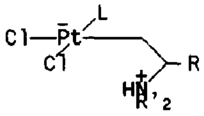


213

The complex [Pt(cyclohexene)(dppe)] reacted with alcohols, ROH, to give the σ-vinyl species, 217; it may be assumed that oxidative addition was followed by insertion [358]. Insertion was also responsible for the transformation of reaction (32) [359].



213 (Reproduced with permission from [354])



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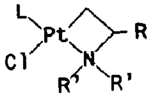

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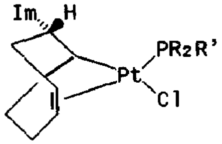

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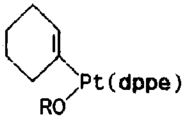

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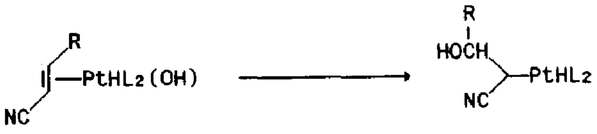


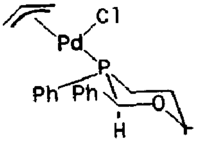
(32)

A variable semiempirical Hamiltonian of the INDO type was used to investigate the magnitude of reorganisation effects (Koopman's defects) in the photoelectron spectrum of 218 [360]. Vertical ionisation potentials were obtained by a Green's function approach and were in good agreement with the experimentally measured values. The nickel 3d ionisation events occurred at lower energies than the lowest ligand band, in contrast to the situation in bis(allyl) nickel. The difference could be traced to less effiecient MLCT in the binuclear complex, leading to a destabilisation of the molecular orbitals with high nickel 3d amplitudes [361].

218

The mechanism of formation of active sites in catalytic systems based on π-allyl complexes of nickel and carbonyl containing acceptors has been studied [362]. ^1H and ^{13}C nmr spectra of η^3-allyl-η^5-cyclopentadienyl nickel complexes have been analysed [363]. The reaction of $[Ni(CO)_4]$ with allyl halides adsorbed on a support has been studied. π-Allyl intermediates were formed, and were calcined to give metallic nickel. On alumina $[\{(\eta^3\text{-}C_3H_5)NiX\}_2]$ was formed, but on MgO metal halides and allenes were produced [364].

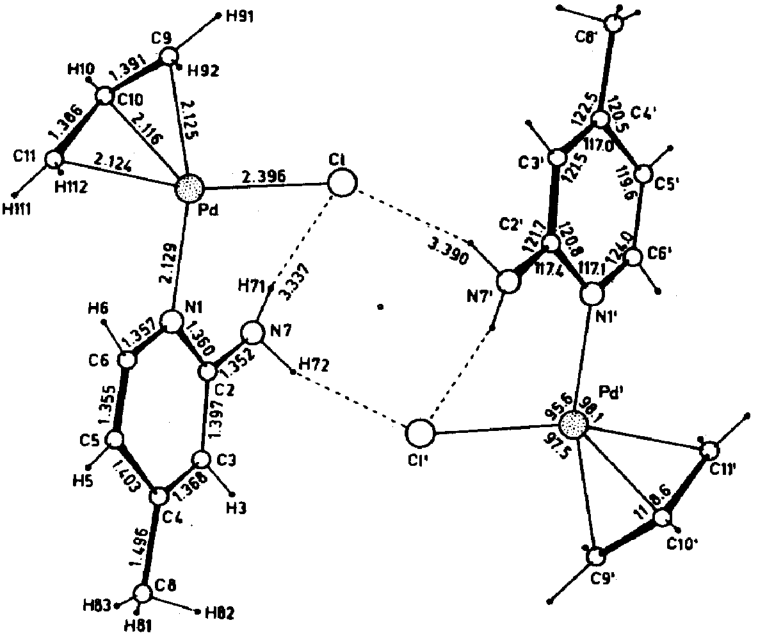
219 has been studied by nmr spectroscopy; the diastereoisomers were shown to interconvert *via* a σ→π transformation with a trigonal bipyramidal array of ligands in the transition state [365].



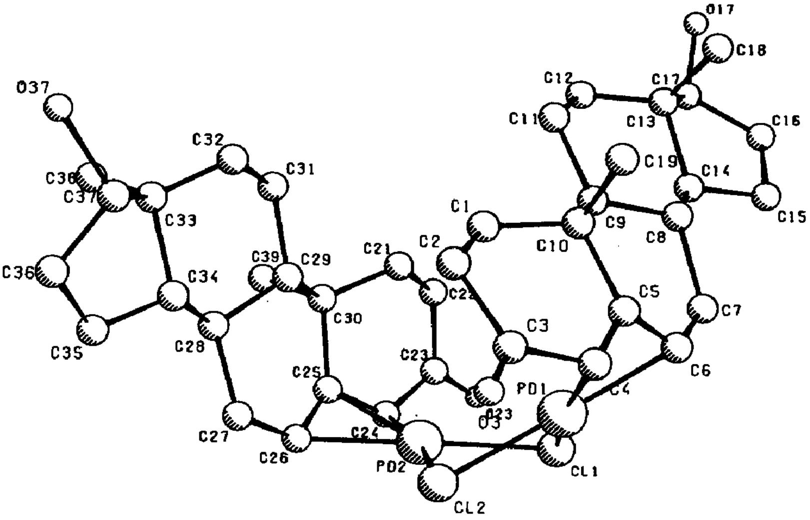
219

The structures of some palladium allyl complexes have been established by X-ray diffraction studies. These have included 220, in which there was strong intermolecular hydrogen bonding [366], and 221, derived from testosterone [367].

The structure of $[(\eta^3\text{-}C_3H_5)Pt(PMe_3)Cl]$ was determined in an X-ray diffraction study [368].

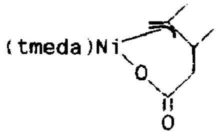


220 (Reproduced with permission from [366])



221 (Reproduced with permission from [367])

Reaction of [Ni(cod)$_2$] with 2,3-dimethylbutadiene, CO$_2$ and tmeda gave 222 [369]. However, with E-3-phenylpropenal anilide the binuclear bis(allyl) species, 223, was formed, and its structure established by an X-ray diffraction study [370]. Allyl nickel complexes such as **224** were prepared from the corresponding allyl bromides with $[Ni(cod)_2]$ or $[Ni(CO)_4]$. **224** was coupled with iodobenzene to give 6-phenyl-1,4-hexadiene in excellent yield [371].



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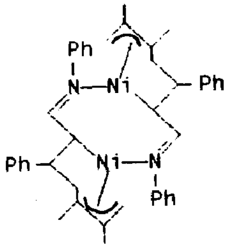
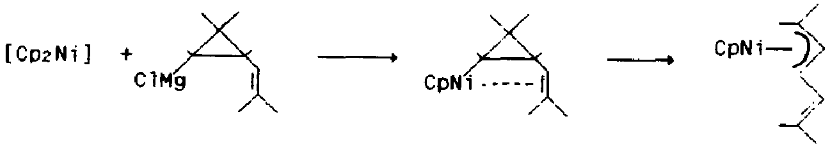


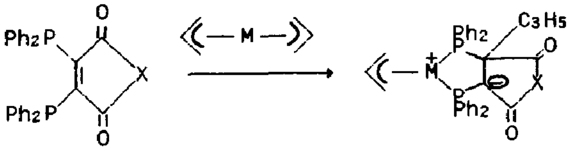
223

224

Reaction of nickel atoms with benzyl bromide or benzyl chloride at −196 K gave a red matrix in which the arene was π-coordinated to nickel. On warming NiX_2 and $PhCH_2CH_2Ph$ were formed. If the cocondensation was carried out on a ceramic surface, warming yielded polybenzyl. It was thought that a π-benzyl intermediate was critical to these processes [372]. Reactions of $[Cp_2Ni]$ with cyclopropyl Grignard reagents led to a synthesis of π-allyl nickel complexes (Scheme 7) [373]. Treatment of bis allyl nickel or palladium with **225** (X = O or NMe) gave the ylide containing species, **226** [374].



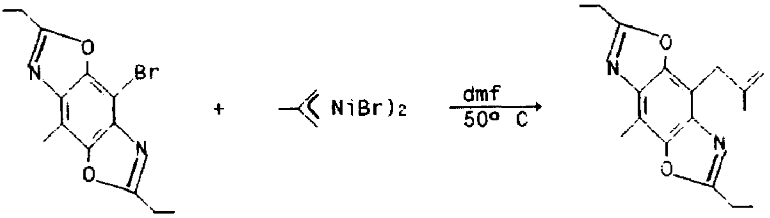
Scheme 7 Reactions of $[Cp_2Ni]$ with cyclopropyl Grignard reagents [373]



225

226

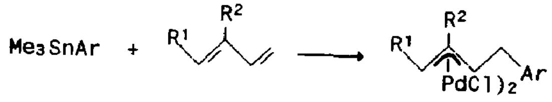
The coupling of aryl halides with nickel allyl complexes (reaction (33)) has been noted [375].



(33)

A number of reactions in which palladium allyl complexes were synthesised have been reported. Treatment of $[\{\eta^3\text{-}C_4H_7)PdCl\}_2]$ with tmeda gave $[Pd(\eta^3\text{-}C_4H_7)(tmeda)][Pd(\eta^3\text{-}C_4H_7)Cl_2]$. This complex showed fluxional behaviour at room temperature in its nmr spectrum, and was characterised by an X-ray diffraction study [376]. The reactions of bis(allyl) complexes with alkyl lithium reagents (RLi) and tmeda were also studied. The major products were $[Li(tmeda)_2][RM(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)]$ (M = Ni, Pd or Pt), and again the molecules were shown to be fluxional on the nmr spectroscopic timescale [377]. *Closo*-borate anions have been used in the stabilisation and isolation of new cationic compounds, including a range of palladium allyl complexes [378].

Palladium allyl complexes have also been synthesised from dienes (reaction (34) provides an example, but the mechanism was not well defined) [379]. Methoxypalladation of dienes was also described (reaction (35)) [380]. 1-Halodienes were reported to react with $[Pd(PPh_3)_4]$ to give the curious species, 227 (*sic*) [381]. Treatment of the bridged complex, 228, with 1,2-propadiene gave 229, characterised by X-ray diffraction. A true insertion of the allene into the Pd-Pd bond has occurred [369].



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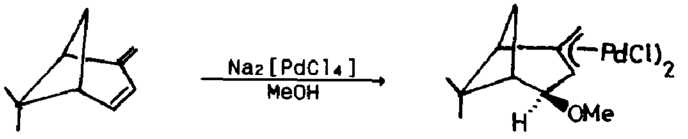

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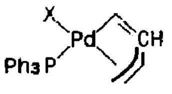

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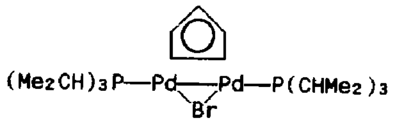

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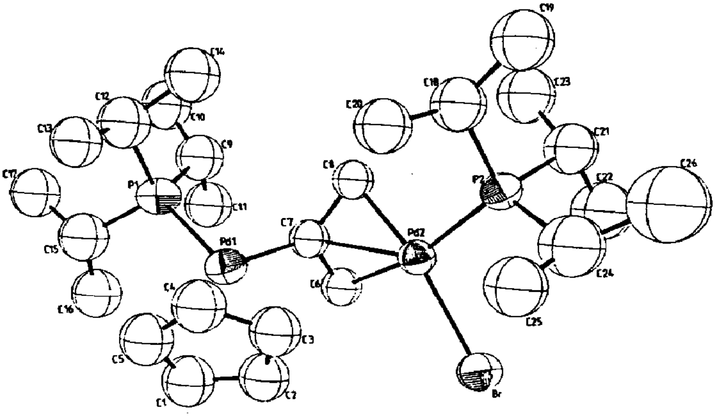
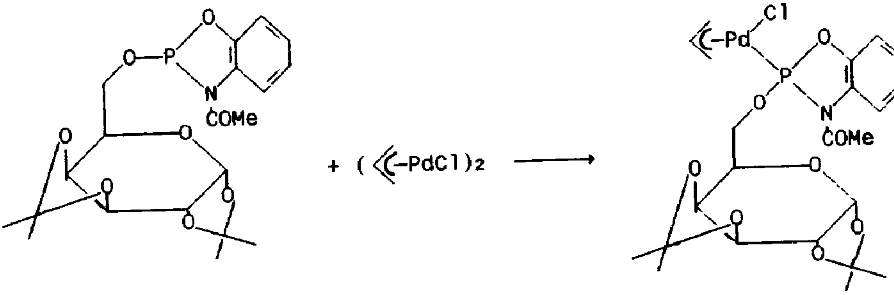


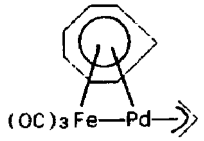
229 (Reproduced with permission from [382])

Bridge splitting reactions of π-allyl palladium halide dimers have again led to the synthesis of new complexes (reaction (36)) [383]. Treatment of $[\{\eta^3\text{-}C_3H_5)PdCl\}_2]$ with $[(C_7H_7)Fe(CO)_3]^-$ gave 230 [384]. Bridge exchange reactions of 231 have been noted [385].



(36)

$[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ was used as a precursor of a bridged coordination complex in reaction (37) [386]. An allyl type complex of pentane-2,4-dione, 232, was prepared by the reaction of $[Pt(acac)_2]$ with $P(4\text{-}Cl\text{-}C_6H_4)_3$ [387]. Reaction of $K_2[PtCl_4]$ with dppm and K[OH] in ethanol gave $[Pt(dppm)_2]$, the first homoleptic complex in which the dppm ligand is chelating [388].



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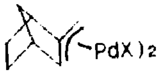

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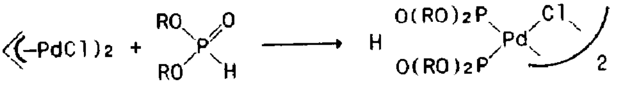

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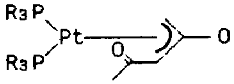
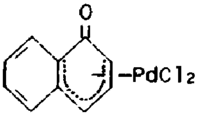


232

The reaction of 1-naphthol with $[Pd(PhCN)_2Cl_2]$ gave 233, but unfortunately only infra-red specroscopy and microanalysis were used in the characterisation of this interesting compound [389]. The ring opening of methylene cylopropanes to give π-allyl complexes has been further studied (reactions (38) and (39)). X-ray diffraction studies inducated that allylic C-C bond distances differred substantially in 234 (X = acac) but not in 235 (X = acac). A rational explanation was provided for the facile $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerisation which resulted in the formation of 235 [390]. Reaction of 236 with $[Pd(PhCN)_2Cl_2]$ gave 237 and 238 in the ratio of 9:1. 239 gave approximately equal amounts of 240 and 241 but 241 was converted to 240 on standing. The related reactions in the cyclohexyl system were reported. A detailed mechanism for chloropalladation was proposed [391-394].



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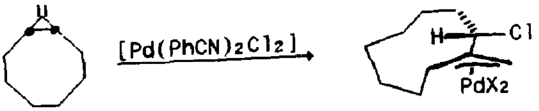

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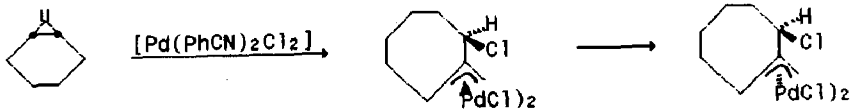

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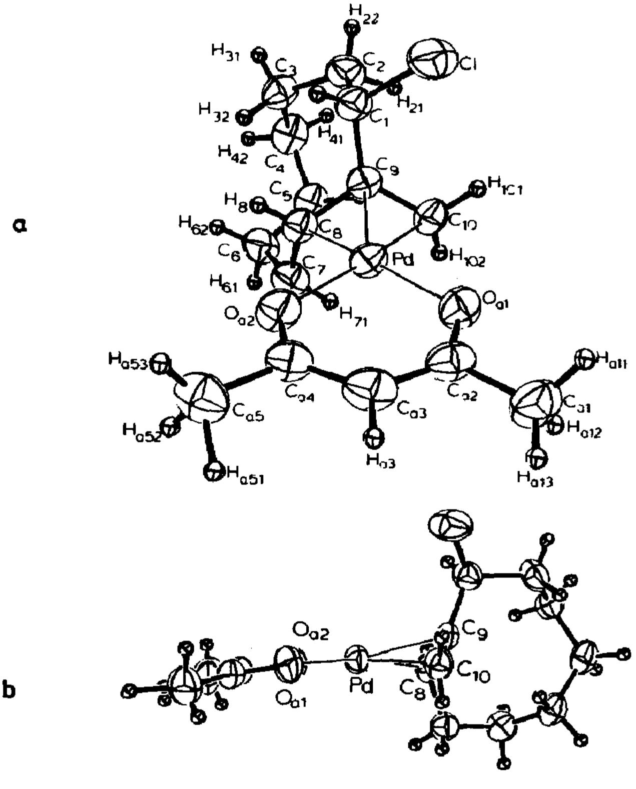
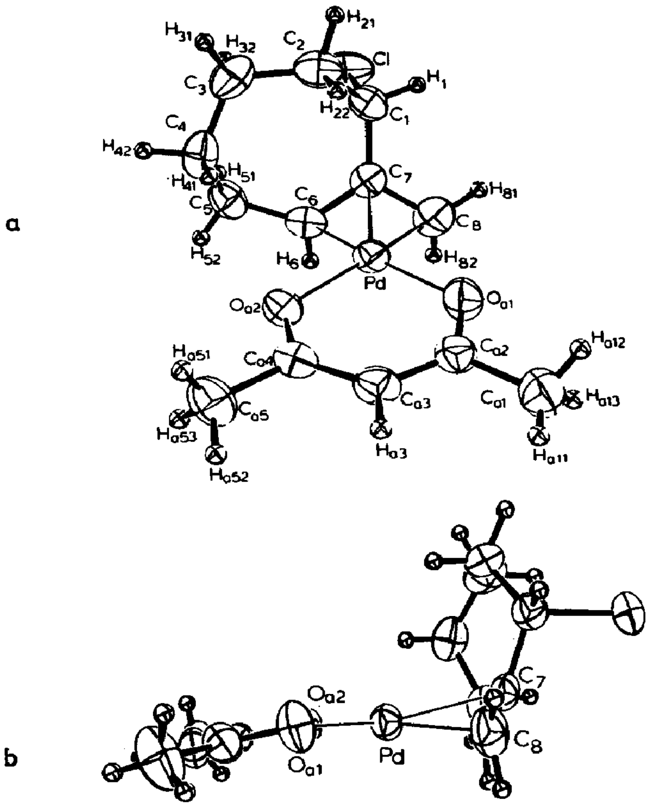
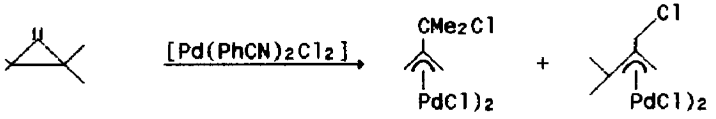


234 (Reproduced with permission from [390]). ORTEP drawing of the solid-state structure of $[Pd\{\eta^3\text{-}CHCl(CH_2)_6\text{-}\mathit{anti}\text{-}CHCCH_2\}(O_2C_5H_7)]$ viewed from (a) the front and (b) the side. Non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50 % of the elctron density. Hydrogen atoms are represented by arbitrarily small spheres which are not representative of their true thermal motion.



235 (Reproduced with permission from [390]). ORTEP drawing of the solid-state structure of $[Pd\{\eta^3\text{-}CHCl(CH_2)_4\text{-}\mathit{syn}\text{-}CHCCH_2\}(O_2C_5H_7)]$ viewed from (a) the front and (b) the side. Atoms are represented as for 234.



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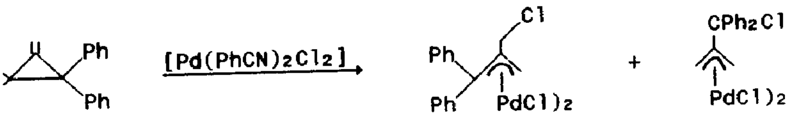
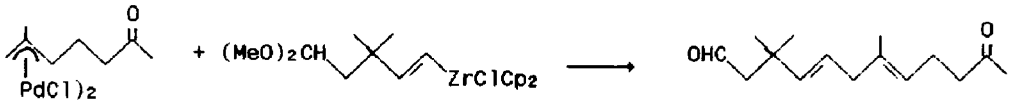


239 240 241

As always, many reactions of palladium allyl complexes with nucleophiles have been studied, and have found significant applications in organic synthesis. Reactions of amines were compared with the palladium catalysed amination reactions of dienes [395]. *Trans*-attack was predominent for the reactions of ethanoate with the palladium allyl complexes of steroids [396]. In a synthesis of humulene, 242 reacted with a vinylzirconium compound to give 243 [397]. A closely related process was used in the synthesis of flexibilene [398].The stereochemistry of such processes was studied for the palladium allyl complex of a steroid [399].



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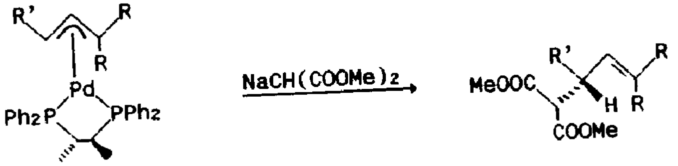
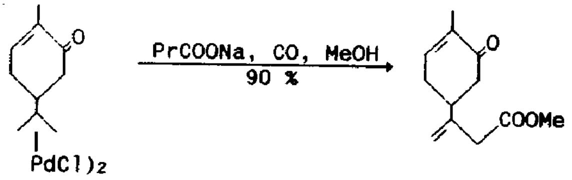
Experiments which allow asymmetric catalytic allylation (for example, reaction (40)) have been reviewed in detail, with particular reference to their mechanism [400].



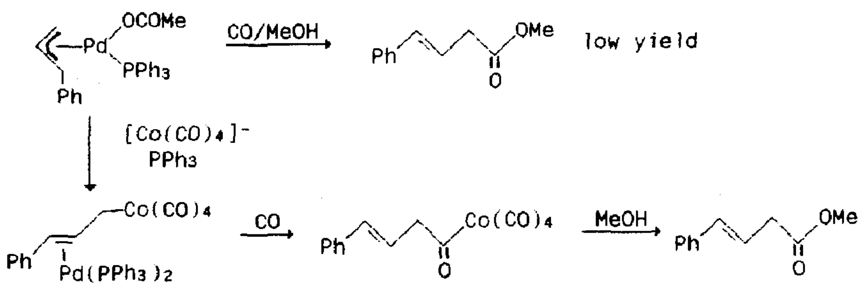
(40)

Carbonylation of palladium allyl complexes has now been achieved under much lower pressures (50 psi) than previously reported (reaction (41)) [401]. The transfer of carbon monoxide from other metal carbonyl and metal acyl species has been investigated; this may provide a usefully catalytic process under mild conditions (Scheme 8) [402].

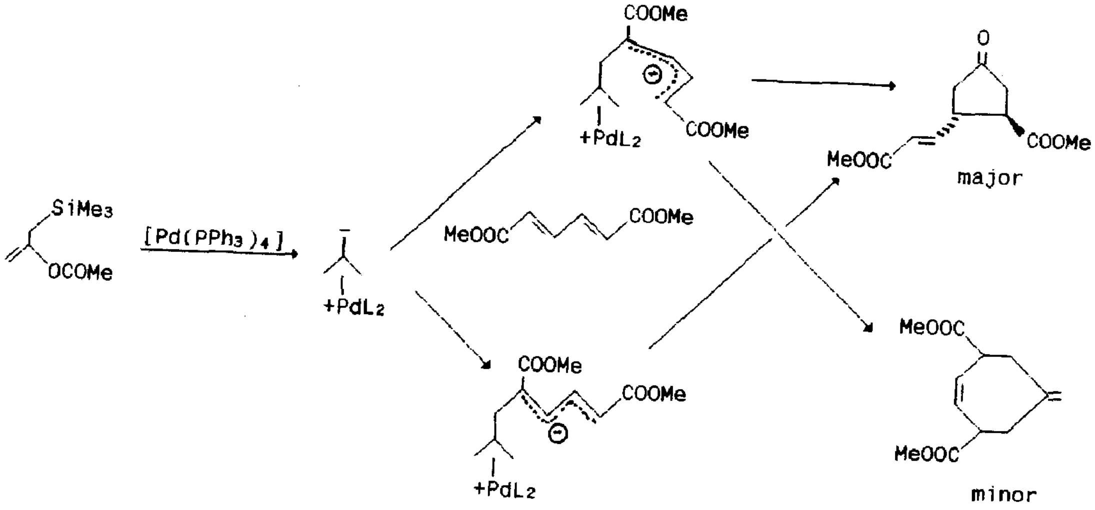


(41)

The uses of palladium trimethylene methane complexes in synthesis have been reviewed with particular reference to the relative rates of protonation and equilibration [403]. The regiochemistry of cycloaddition reactions with dienyl esters has been studied (Scheme 9) [404].

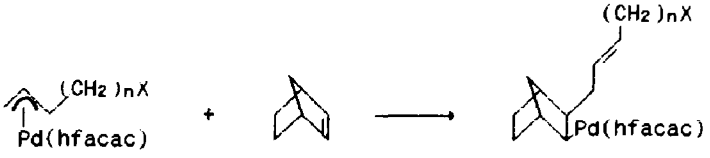


Scheme 8 Carbonylation of palladium allyl complexes [402]



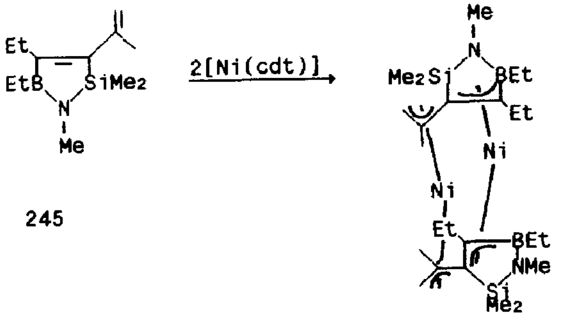
Scheme 9 Regioselectivity in cycloaddition reactions of palladium trimethylene methane complexes [404].

The addition of a palladium allyl complex to norbornene to give **244** was used in a synthesis of prostaglandin endoperoxide analogues [405].



244

Reaction of **245** with [Ni(cdt)] yielded the unusual bis(allyl) bis(borallyl) dinickel complex, **246**, characterised by an X-ray diffraction study [406]. The related bis(borallyl) nickel complex, **247**, was also prepared and characterised [407].



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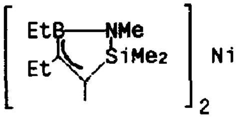
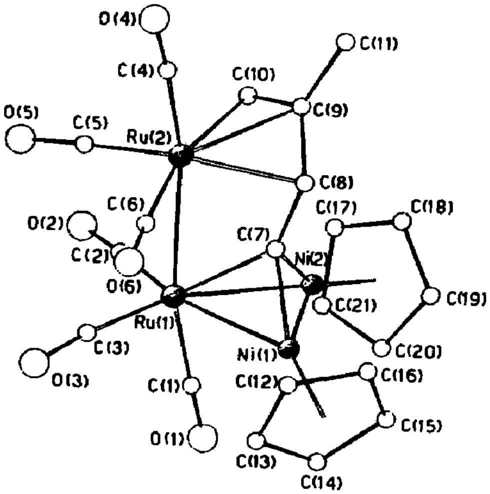


247

10 METAL ALKYNE AND ALKYNYL COMPLEXES

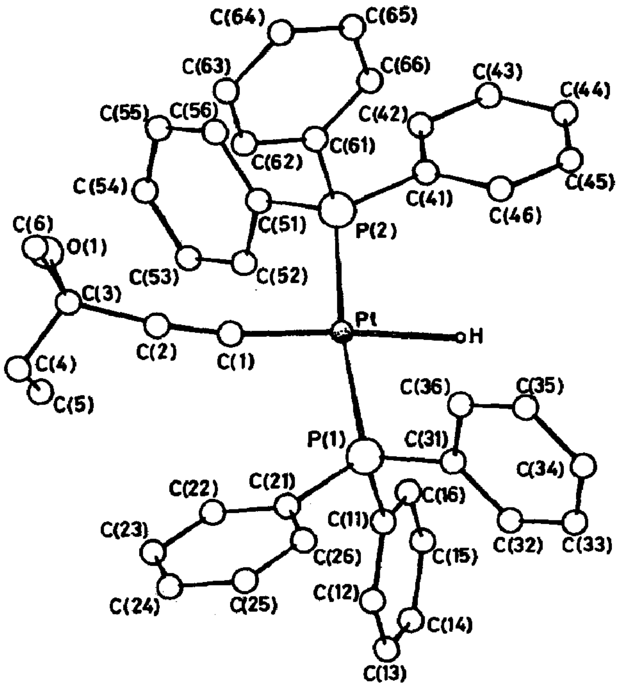
Two types of alkyne complexes may be distinguished by their geometries, *viz.* perpendicular and parallel. Numerous examples of such species have been discussed, in the context of the isolobal analogy [408]. The various interconversions of such species have also been reviewed [409].

Nickel alkyne and nickelacyclopentadiene complexes have been suggested as intermediates in the nickel catalysed cycloligomerisation reactions of alkynes. These may interconvert with nickel cyclobutadiene complexes [410]. Reaction of [$Ni(CO)_4$] with $F_5S-C{\equiv}C-CF_3$ at -196 °C gave a π-complex of the alkyne. At -78 C this could be trapped by triphenylphosphine to give [$Ni(PPh_3)_2(\eta^2-F_5S-C{\equiv}C-CF_3)$], characterised by ^{19}F nmr spectroscopy [411]. A series of complexes of the type [$PdL_2(\eta^2$-substituted alkyne)] have been prepared and characterised [412]. Treatment of [$\{CpNi(CO)\}_2$] with $CH_3C(=CH_2)C{\equiv}CH$ gave a green-brown solution which reacted with [$Ru_3(CO)_{12}$] to give [$Cp_2Ni_2Ru_2(CO)_6\{C_2(H)C(=CH_2)CH_3\}$], **248**, characterised by an X-ray diffraction study. The eneyne is acting as a six-electron donor [413].

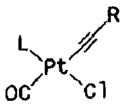


248 (Reproduced with permission from [413])

Bis(alkynyl) metal complexes may be synthesised by the reactions of organolithium compounds or Grignard reagents with appropriate metal halides. [$(HCB_{10}H_{10}CC{\equiv}C)_2Pd(PPh_3)_2$] was prepared in this way [414]. Reaction of *cis*-[$Pt(PPh_3)_2Cl_2$] with *trans*-[$(R-C{\equiv}C)_2Pt(PPh_3)_2$] gave the mono alkynyl complex, *trans*-[$(RC{\equiv}C)Pt(PPh_3)_2Cl$] [415]. A wide range of complexes of the type *trans*-[$HPt(C{\equiv}CR)(PPh_3)_2$] were prepared by reaction of the alkynes with the corresponding halide. **249** was characterised by an X-ray diffraction study [416]. The reaction of *cis*-[$Pt(CO)LCl_2$] with [$Hg(C{\equiv}CR)_2$] to give **250** seemed to proceed conventionally, but a second substitution to give the bis(alkynyl) complex involved an oxidative addition reductive elimination pathway *via* **251**. The reaction mechanism was proved by a ^{13}C labelling study [417].



249 (Reproduced with permission from [416])



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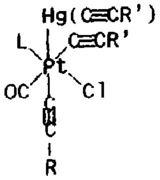
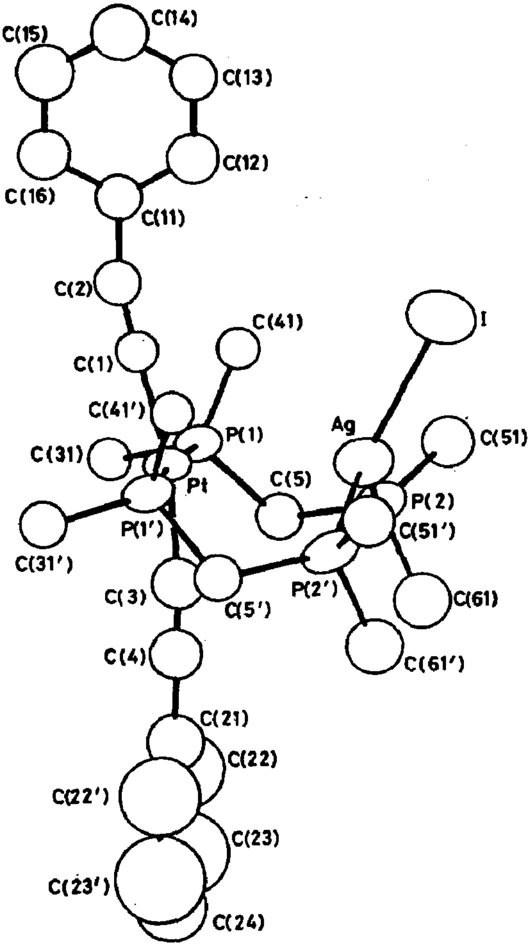
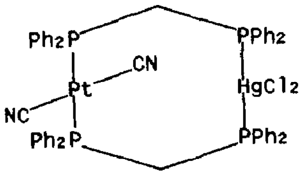


251

The complex [Pt(η^2-dppm)Cl$_2$] reacted with a lithiated alkyne, Li-C≡C-R, to give [Pt$_2$(μ-dppm)$_2$(C≡CR)$_4$], characterised by nmr spectroscopy. The complex *trans*-[Pt(η^1-dppm)$_2$(C≡CR)$_2$] was formed on reaction with an excess of dppm [418]. This proved to be a useful species in the preparation of mixed bimetallic complexes such as [Pt(C≡CR)$_2$(μ-dppm)$_2$Rh(CO)]Cl, in which there is a donor acceptor bond between platinum and rhodium. Related species were prepared by reaction with [Ir$_2$(C$_8$H$_{14}$)$_4$Cl$_2$] and *fac*-[W(CO)$_3$(NCMe)$_3$] [419]. Yet a further paper reported the preparations of gold, silver, mercury and cadmium complexes of analogous structure, 252 being characterised by an X-ray diffraction study [420]. A halogen exchange process was involved in the conversion of *trans*-$[(RC{\equiv}C)_2Pt(\eta^1\text{-dppm})_2]$ to 253 using $Hg(CN)_2$ [421]. Another group reported related reactions using CF_3-C≡C-Li [422].



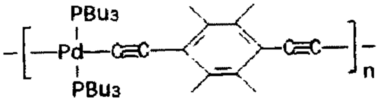
252 (Reproduced with permission from [420])



253

There has been considerable interest in the preparation of metal alkyne containing polymers. For example, 254 was prepared from *trans*-$[Pd(PBu_3)_2Cl_2]$

and the diethynylbenzene in the presence of CuI and a trialkylamine [423]. A related platinum complex has also been synthesised [424], as well as a range of copolymers including 255 [425,426]. Polymers such as 256 (M = Pt, M' = Pd or Ni, or M = Pd, M' = Ni) had lyotropic liquid crystalline phases which could be detected directly using ^{31}P nmr spectrsocopy. The main chain of the polymers aligned itself in a direction perpendicular to the applied field [427].



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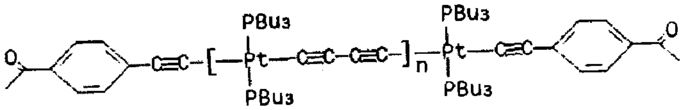

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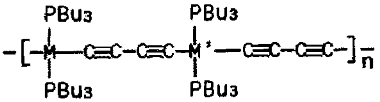


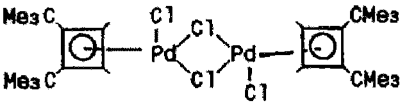
256

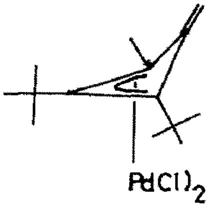
11 COMPLEXES OF DELOCALISED CARBOCYCLIC SYSTEMS

The structures of the complexes $[M(Ph_3C_3)(PPh_3)_2]X$ (M = Ni, X = $[PF_6]$, M = Pd, X = $[ClO_4]$ or $[PF_6]$) have been determined by X-ray diffraction studies. The structures showed a progressive movement of the $\{M(PPh_3)_2\}$ unit over the face of the cation, moving from one η^2-geometry to an equivalent one, accompanied by rotation and other changes. The potential energy surface for the ring whizzing motion was investigated by extended Huckel calculations [428].

The bonding in $[Ni(C_4H_4)_2]$ and $[Ni(C_4H_4)X_2]$ has been studied [429]. Reaction of the σ-complex between $\{Me_4C_4\}$ and $AlCl_3$ with $[Ni(CO)_4]$ gave $[Ni(C_4Me_4)Cl_2]$. However, if 2-butyne, $AlCl_3$ and $[Ni(CO)_4]$ were mixed in CH_2Cl_2 the major product was $[Ni(C_4Me_4)(C_6Me_6)][AlCl_4]_2$. The reaction mechanism was discussed [430].

Treatment of $\{(C_4Me_4)AlCl_3\}$ with $[Pd(PhCN)_2Cl_2]$ gave $[Pd(C_4Me_4)Cl_2]$, the first reported synthesis of a palladium complex of this type [431]. The bridged dimer, 257, underwent bridge splitting reactions with $[R_2NCS_2]^-$ or $L/Ag[BF_4]$ (L = RNH_2, RNC or PPh_3), but with a mild base such as $Na_2[CO_3]$ 258 was formed, and could be converted into 259 by Tl[acac] [432]. The reaction of $4\text{-}MeOC_6H_4C{\equiv}CC_6H_4\text{-}4\text{-}OMe$ with $Na_2[PdCl_4]$ gave initially $[\{(\eta^4\text{-}Ar_4C_4)Pd\}_2Cl_3][Pd_2Cl_6]_{0.5}$. Treatment of this complex with HCl yielded $[\{(Ar_4C_4)Pd\}_2Cl_4]$, 260, which was characterised by X-ray diffraction. The reactions of the complex with nucleophiles were studied in detail [433]. The complex *cis*-$[Pt(CO)_2Cl_2]$ reacted with RC≡CR to give $[Pt_2(C_4R_4)_2Cl_3][Pt(CO)Cl_3]$, 261. A monomeric complex was obtained in this instance on reaction with an excess of chloride ion [434].





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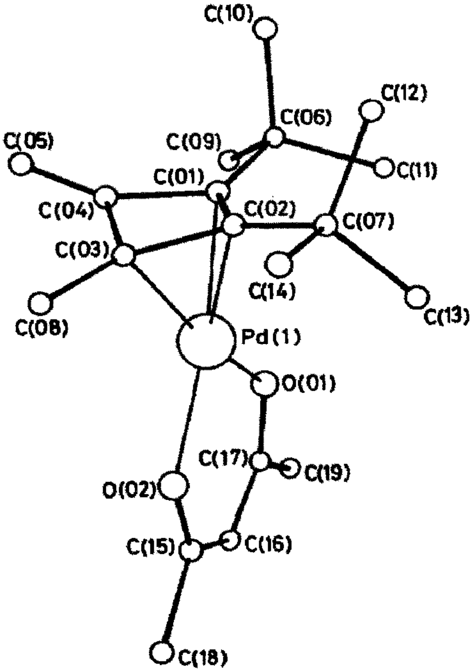
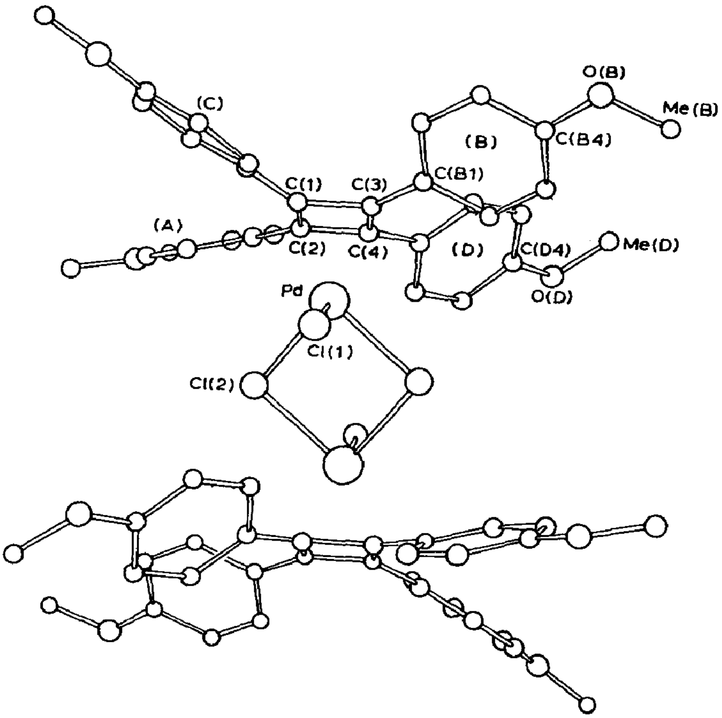
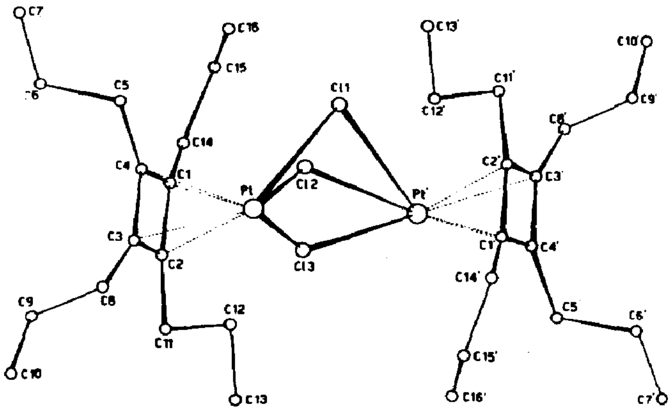


259 (Reproduced with permission from [432])



260 (Reproduced with permission from [433])

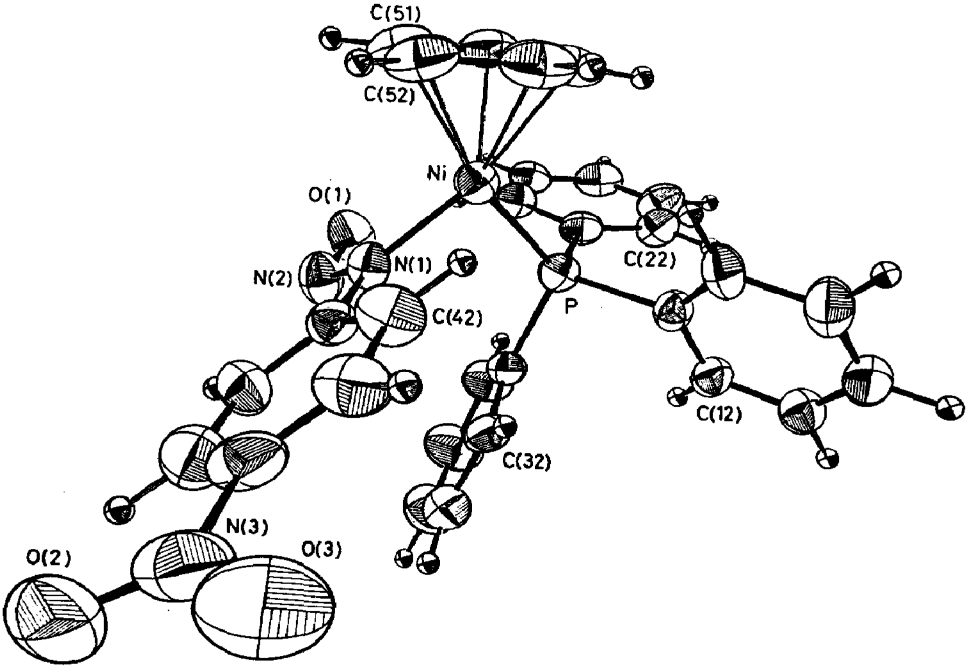


261 (Reproduced with permission from [434])
A perspective view of the cation $[Pt_2(C_4Pr_4)_2Cl_3]^+$

A molecular orbital approach to the determination of MO electronegativities of transition metal fragments included a consideration of

{CpNi} and {(η^3-C_3H_5)Ni} [435]. The electronic configurations of cyclopentadienyl and benzene sandwich complexes of iron, chromium, manganese and nickel have been calculated [436]. The charge separation in [Cp_2M] complexes with different types of bonding has been studied by a theoretical analysis of absolute infra-red spectroscopic intensities, using as a first approximation the effective charge model. Unfortunately, charge separation and bond ionicity were not found to correlate [437]. The magnitudes of reorganisation energies (determined by a Green's function approach with a renormalised approximation for the self energy term) in the PE spectra of transition metal compounds with nickel as a 3d centre were studied by means of a variable INDO Hamiltonian [438].

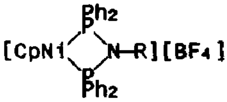
The structures of [CpNi(PPh_3)($MeOCS_2$-*S*)] [439] and [CpNi(PPh_3)(4-NO_2-C_6H_4-N=N-O^-)], 262, have been determined. 262 was prepared by reaction of the diazoate with [CpNi(PPh_3)Cl] and is the first example of a structurally characterised diazoato complex [440].



262 (Reproduced with permission from [440])

The treatment of NaY zeolite with [Cp_2Ni] followed by cation exchange was used to prepare a 3 % nickel catalyst for the hydrodemethylation of toluene [441]. Thermogravimetry, chromatography and smoke generation showed that addition of small amounts of [Cp_2Ni] reduced smoke and HCl generation in the thermal degradation of PVC [442].

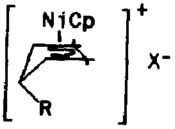
The preparation of [$CpNi(R_2PNR'PR_2)$][BF_4], 263, from [CpNi(nbd)][BF_4] and the ligand has been described. Treatment of 263 with cyanide ion gave [$CpNi(\eta^1-R_2PNR'PR_2)(CN)$] [443]. Substitution of [$CpNi(PPh_3)Cl$] with optically active Me(Ph)(Np)GeLi proceeded with retention of stereochemistry at germanium [444].



263

[$(Me_4HC_5)_2Ni$] was prepared from the corresponding anion and $NiCl_2$. Spectroscopic parameters were reported [445]. [$(EtMe_4C_5)_2Ni$] was similarly synthesised from the thf adduct of $NiCl_2$. Detailed ^1H and ^{13}C nmr spectroscopic studies indicated that there was a change in the redox properties of the complex on peralkylation. The ethyl group underwent hindered rotation with the β-carbon atom turned away from the metal [446]. The generation of titanocene and rhodocene cations from [Cp_2Ni] in the gas phase by a novel metal switching reaction has been reported [447].

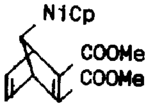
{Cp^*_2Ni} exists in three stable charged forms, *viz.* the neutral 20 electron species, the cationic 19 electron species and the dicationic 18 electron species. The neutral species reacted with electrophiles such as RX to give 264 and had distinctive electrochemical properties [448]. Oxidation of [Cp^*_2Ni] to [Cp^*_2Ni][PF_6] was relatively easy and the cationic species was shown by epr spectroscopy to have a $^2E_{1g}$ ground state. The 18 electron complex [Cp^*_2Ni][PF_6]$_2$ was diamagnetic [449]. Electrochemical reduction of [CpNi(cod)]$^+$ gave the neutral radical [CpNi(cod)], a 19 electron species, stable for 1 hour at -10 °C. It decomposed to [Cp_2Ni] and [$Ni(cod)_2$], but was appreciably more stable than its cobalt analogue [450]. The electrochemical reduction of [$CpNi(PR_3)_2$]$^+$ was studied and found to be appreciably easier than that of [Cp_2Ni] [451].



264

The complex $[CpNi(C_5H_6)][BF_4]$ has proved a useful precursor of mixed complexes, since the $\{C_5H_6\}$ moiety is easily displaced. Among the ligands used were $Ph_2P(=S)(CH_2)_nP(=S)Ph_2$ and $PhS(CH_2)_nSPh$ (n = 1 or 2), which acted as *S,S*-chelates [452,453]. Both $Ph_2As(CH_2)_nAsPh_2$ (n = 1 or 2) and the related phophines reacted similarly, but the arsines were less strongly coordinated and on reaction with lithium iodide gave complexes such as $[CpNi(\eta^1-Ph_2AsCH_2AsPh_2)I]$, under conditions to which their phosphine analogues were inert [454].

Reaction of $[Cp_2Ni]$ with R_2PX/CX_4 gave $[CpNi(R_2PX)X]$ (R = Me_3C, X = Cl or Br). Attack of nucleophiles caused substitution of the halide attached to nickel [455]. The triple decker sandwich, $[Cp_2Ni_2(\mu-Cp)][AlBr_4]$, was synthesised by reaction of $[Cp_2Ni]$ with $AlBr_3$, and was characterised by ir, Raman and nmr spectroscopy. Ligand displacement reactions were also studied [456]. Cleavage of nickel-carbon bonds in **265** occurred with retention of configuration using NBS, or under carbonylation conditions [457].

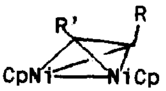


265

The electronic structure of $[\{CpNi(CO)\}_2]$ was investigated by PES, and using Huckel calculations. No net direct nickel-nickel bonding, either σ or π, was found. The source of the stability of the dimer lies in its two in and out of plane back bonding interactions between the d_{xz} and d_{yz} metallic atomic orbitals and the pertinent symmetry combinations of the π^* molecular orbitals of the bridging CO ligands [458]. A study of the vibrational frequencies of μ_2-bridging carbonyl ligands in metal clusters included a consideration of $[\{CpNi(CO)\}_2]$ [459].

The thermal decomposition of $[Cp_3Ni_3(CO)_2]$ has been investigated by ir spectroscopy and thermogravimetric studies. The products included $[Cp_2Ni]$, CO and metallic nickel [460]. $[Cp_3Ni_3(CO)_2]$ on SiO_2/Al_2O_3 has been used as a catalyst for the oligomerisation of propene [461]. Approximate MO calculations have been performed for $[Cp_3Ni_3(\mu_3-S)_2]$ and $[Cp_3Ni_3(\mu_3-CO)_2]$. A novel analysis of the metal-metal bonding indicated that there was no net occupation of orbitals with metal-metal bonding character, but that there were attractive metal-metal interactions. These were dominated by occupation of orbitals on the M_3 triangle which are predominently valence s and p in character. Differences in magnetic and structural characteristics between the two complexes were explained in terms of the different bonding capabilities of CO and sulphur [462].

Photolysis of [{CpNi(CO)}$_2$] in the presence of an alkyne, RC≡CR', gave 266. The bonding in such complexes was discussed and their mass spectra reported [463]. Similar but heterobimetallic clusters of this type, 267 (M = {Co(CO)$_3$}, {Mo(CO)$_4$} or {Mn(CO)$_4$}), have been prepared, and are intrinsically chiral. A new fluxional process was discerned, involving a formal rotation of the M-M and C-C bond vectors. The fluxionality and high reactivity towards added [Fe$_2$(CO)$_9$] were rationalised in terms of Wade's Rules [464]. The reaction with iron complexes gave 268 for M = {Co(CO)$_3$} (a structurally similar complex was produced for M = {CpNi}), R = CO$_2$CHMe$_2$, R' = Ph) and 269 for M = {CpMo(CO)$_2$}. Fluxional process in these complexes were discussed in detail [465]. Substitution of the analogue of 268 for which R = R' = Ph, with PPh$_3$ gave the 48 electron cluster [CpNiCoFe(CO)$_5$(PPh$_3$)(RCCR')], 270 [466].



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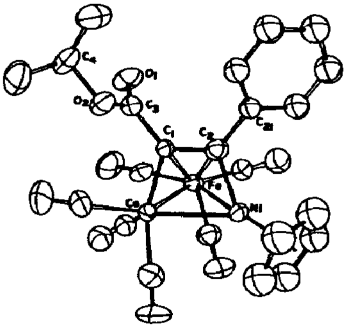
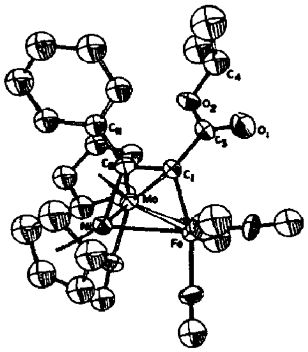
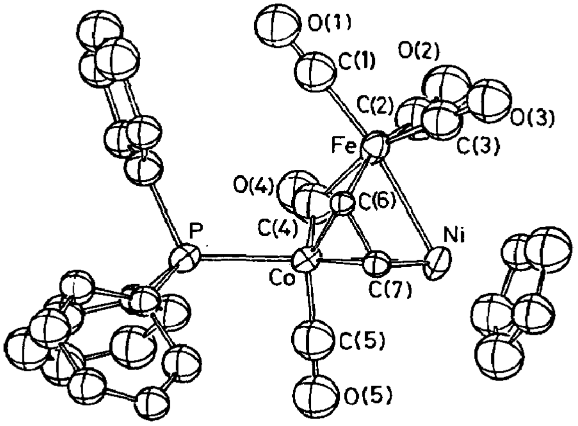


268 (Reproduced with permission from [465])

Reaction of [CpNi]$_2$[Fe$_2$(CO)$_6$(μ_4-C$_2$Ph$_2$)] with PMe$_3$ resulted in a fundamental skeletal rearrangement of the complex to give [CpNi(PMe$_3$)$_2$][CpNiFe$_2$(CO)$_6$(μ_3-C$_2$Ph$_2$)], characterised by X-ray diffraction (271a and 271b show the cation and anion respectively) [467]. Treatment of the alkynyl containing cluster, [HRu$_3$(CO)$_9$(C$_2$R)], with [{CpNi(CO)}$_2$] in the presence of hydrogen gave 272 in better yield than if the reaction was carried out under nitrogen. An X-ray diffraction study shows a butterfly arrangement of the metal atoms with nickel at the wingtips, a σ,π-bonded vinylidene ligand, and a hydride bridging the hinge site [468].



269 (Reproduced with permission from [465])

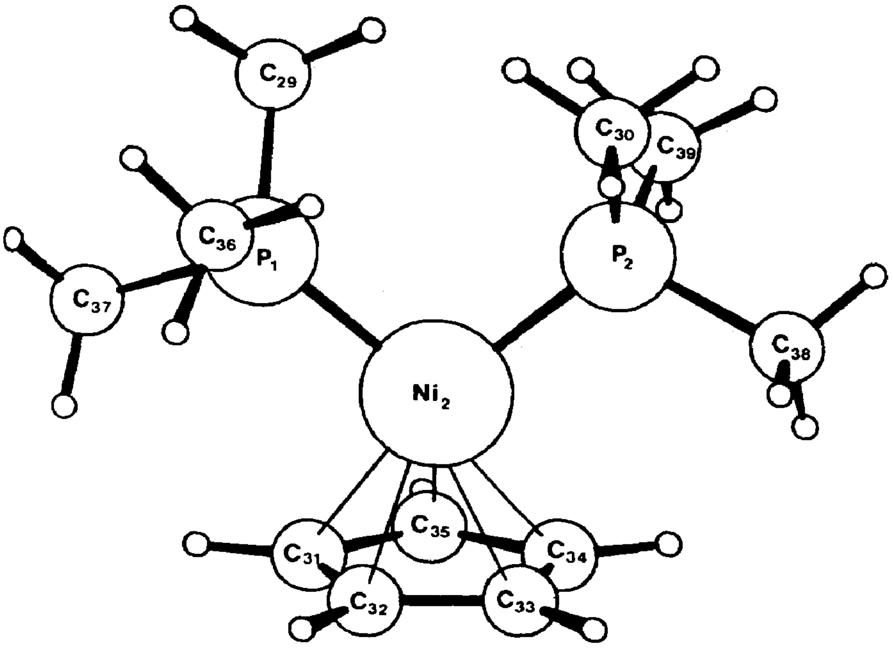


270 (Reproduced with permission from [466])
ORTEP plot (45 % thermal ellipsoids) of [CpNiCoFe$(CO)_5(PPh_3)(C_2Ph_2)$]. The phenyl groups of the alkyne are omitted for clarity.

Reaction of the carbyne complex [CpW($\equiv$CR)$(CO)_2$] with [{CpNi(CO)}$_2$] gave a mixture of [$Cp_3Ni_2W(\mu_3$-CR)$(CO)_2$] and [$Cp_2W_2(\mu$-$RC_2R)(CO)_4$]. A mechanism was proposed for the reaction [469]. The carbide capped complex [$MeCCo_3(CO)_9$] reacted with [{CpNi(CO)}$_2$] to give {Co_2Ni} and {Co_3Ni} containing clusters. Related trimetallic species, including 273 and 274 were also prepared, and were characterised by X-ray diffraction [470].

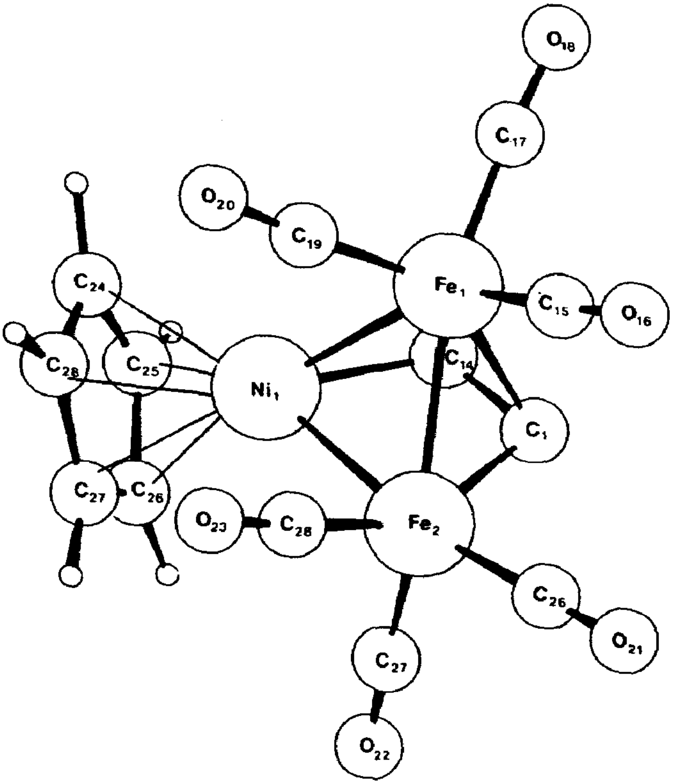
[{CpNi(CO)}$_2$] reacted with CS_2 at 40 °C to give [{$Cp_3Ni_3(\mu_2$-$S)_2$}$_2(C_2S_4)$], 275, in which the [C_2S_4] anion was formed by head-to-head dimerisation of CS_2. However, with the pentamethylcyclopentadienyl analogue, [$Cp*_2Ni_2$][C_2S_4], 276, was produced [471]. Another sulphur bridged cluster was synthesised by the reaction of [{CpCr($SCMe_3$)}$_2$S] with [{CpNi(CO)}$_2$] giving 277,

$[Cp_4Cr_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)]$. The structure deviated from the expected open butterfly with a chromium-chromium bond towards a zig-zag metal chain. The magnetic properties of the cluster were investigated [472].

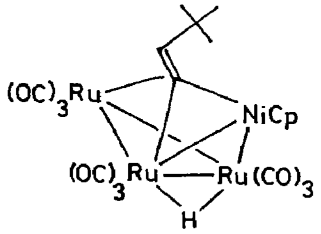


271a (Reproduced with permission from [467])
PLUTO plot of the cation $[CpNi(PMe_3)_2]^+$

A novel one electron reduction of $[Cp_3Ni_3(\mu_3\text{-}CO)_2]$ by potassium naphthalide led to the synthesis and characterisation of $[K(2,2,2\text{-crypt})][Cp_3Ni_3(\mu_3\text{-}CO)_2]$, 278. The related anion, $[Cp^*Cp_2CoNi(\mu_3\text{-}CO)_2]^-$, was similarly prepared. The data provided support for the Strouse-Dahl model in which the HOMO of $[Cp_3Ni_3(\mu_3\text{-}CO)_2]$ is an in plane trimetal antibonding orbital of a nondegenerate a_2' representation under D_{3h} symmetry [473]. $[\{CpNi(CO)\}_2]$ reacted with $[H_2Os_3(CO)_{10}]$ under a hydrogen atmosphere to give $[H_3CpNiOs_3(CO)_9]$, 279, in excellent yield. The yield of 279 was considerably lower when the reaction was carried out under nitrogen [474]. Addition of $[Co_2(CO)_8]$ to $[\{CpFe(CO)_2\}\{CpNi(CO)\}SnCl_2]$ gave 280, $[\{CpFe(CO)_2\}\{CpNi(CO)\}\{Co(CO)_4\}SnCl]$, which adopted an almost perfect tetrahedral geometry at tin. By contrast, reaction of $[\{CpNi(CO)\}_2]$ with $[\{CpFe(CO)_2\}\{Co(CO)_4\}SnCl_2]$ yielded the exchanged product $[\{CpFe(CO)_2\}\{CpNi(CO)\}SnCl_2]$ *via* cleavage of the Sn-Co rather than the Sn-Cl bond [475].



271b (Reproduced with permission from [467])
PLUTO plot of the complex anion [CpNiFe$_2$(CO)(μ_3-C$_2$Ph$_2$)]$^-$



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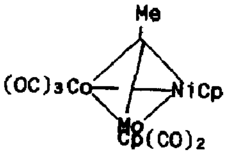

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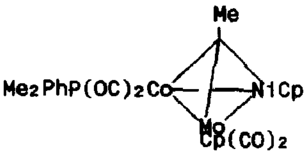

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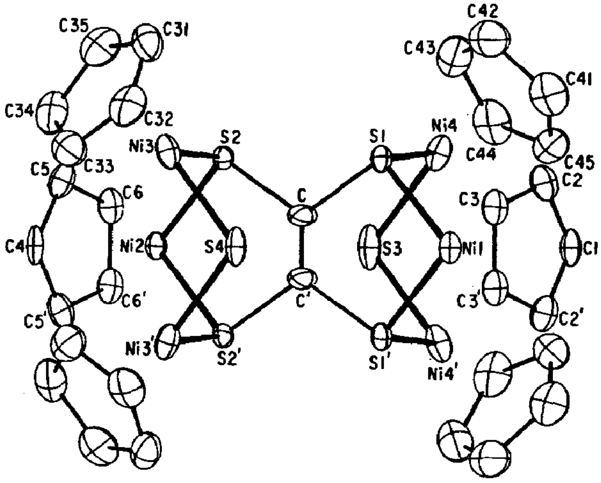
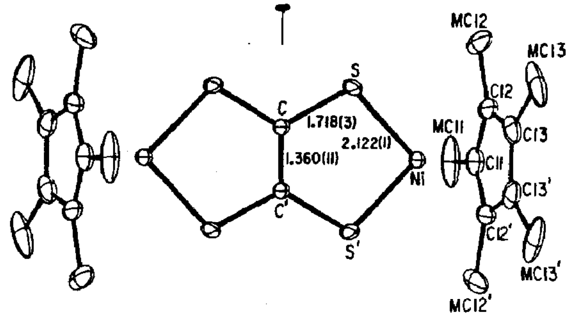


275 (Reproduced with permission from [466])

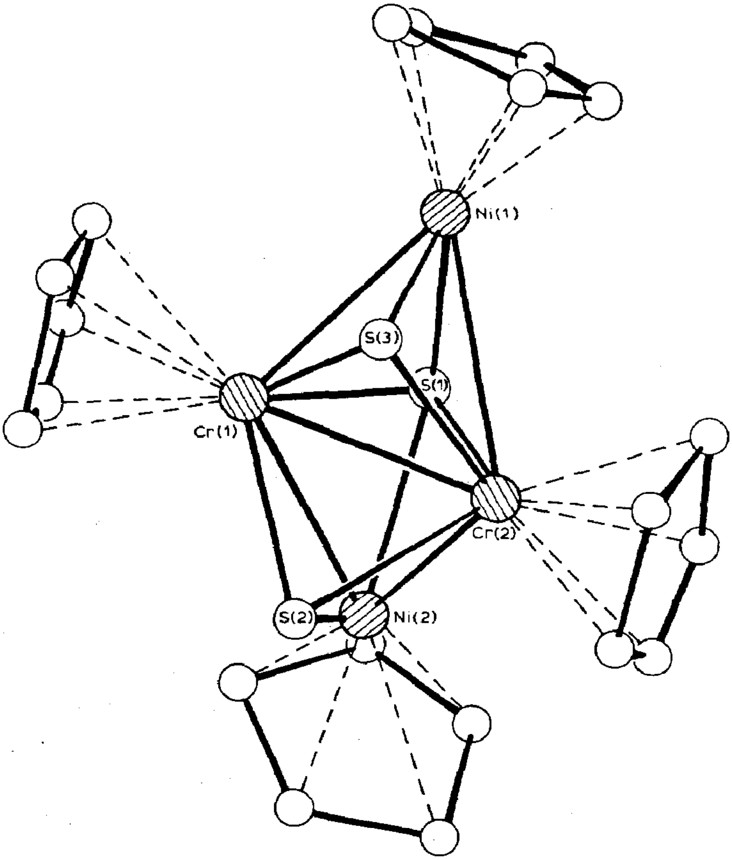
View of the $[\{Cp_3Ni_3(\mu_2\text{-}S)\}_2(C_2S_4)]$ molecule, which possesses crystallographic C_s-*m* site symmetry but closely conforms to a C_{2h}-2/*m* geometry. This hexanickel complex may be viewed as a cycloaddition product of the dinickel molecule (related to 276) formed by the insertion of a CpNi-S-NiCp fragment across each of two *cis*-1,2-dithiolato sulphur atoms to give two-fold related, chair-like six-membered $(NiS)_3$ rings. The fact that the two ethene carbon atoms possess extremely large out-of-plane thermal ellipsoids is indicative of an average structure in which the ethene carbon atoms occupy at least two orientations in the crystalline state. This is also reflected in an artificially short C-C' distance of 1.13 Å, which in turn causes the average C-S distance of 1.84 Å to be abnormally long. This presumed ethene disorder may be attributed to the interaction of the ring sulphur atoms S3 and S4 with C and C', as indicated from the close S3...C and S4...C' distances of 2.27 Å and 2.28 Å respectively.

Reaction of $[NH_4][CpNi\{(MeO)_2P{=}O\}_2]$ with UCl_4 gave $[U\{CpNi(\{MeO\}_2P{=}O)\}_4]$ in which four anionic nickel phosphonate ligands were bonded to uranium through P=O-U interactions [476]. Treatment of 281 with $[Ni(CO)_4]$ resulted in the formation of the four-decker sandwich compound, 282. This reacted with further 1,2,3,4,5-tetraalkyl-1,3-dibora-4-cyclopentene with displacement of the bridging carbonyls to give the penta decker sandwich compound 283 [477].

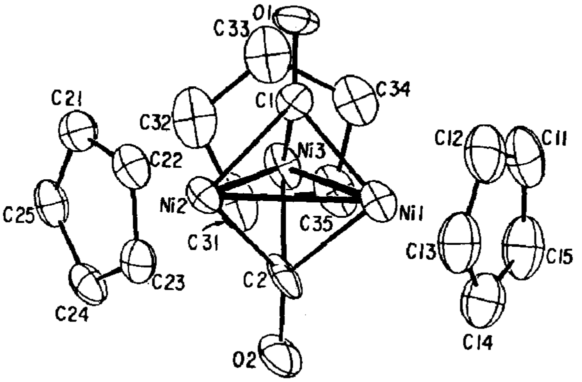


276 (Reproduced with permission from [471])

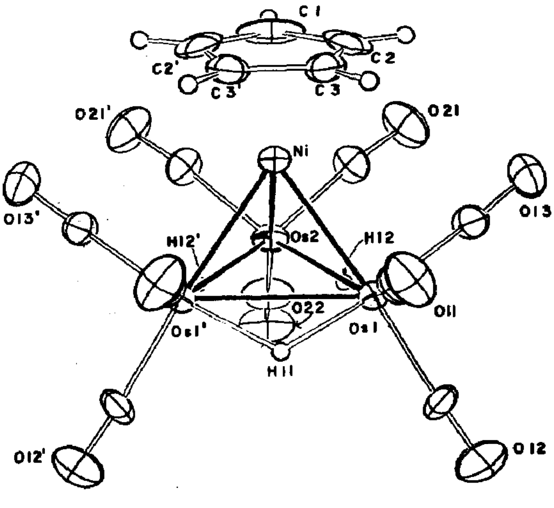
View of the [Cp*$_2$Ni$_2$(C$_2$S$_4$)] molecule which has crystallographic C_{2h}-2/m site symmetry. The NiS$_2$C$_2$S$_2$Ni core of this bimetallic tetrathiolene complex experimentally possesses a planar D_{2h}-mmm gemetry, with extensive π-electron delocalisation indicated from its bond lengths and redox properties.



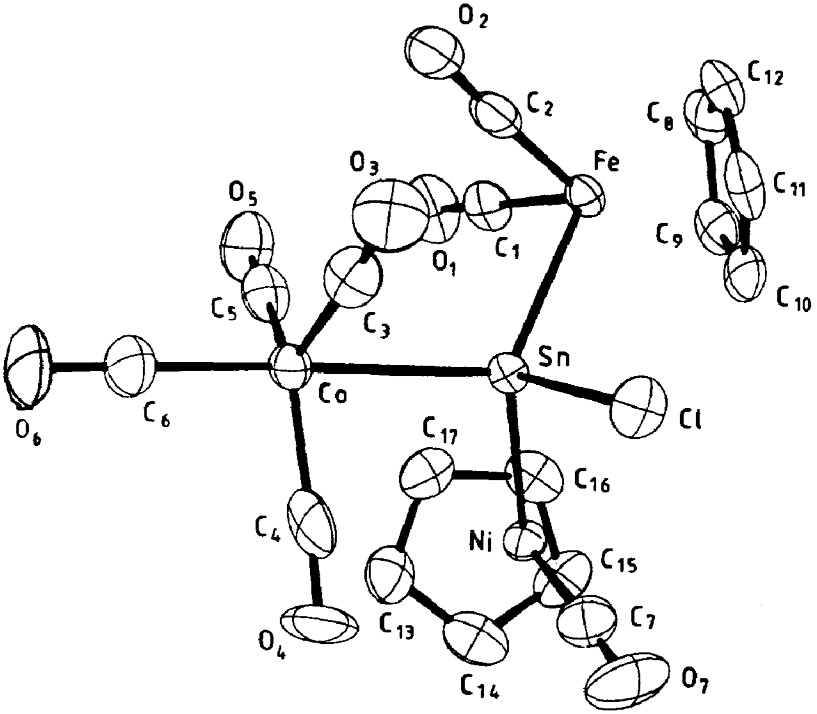
277 (Reproduced with permission from [472])



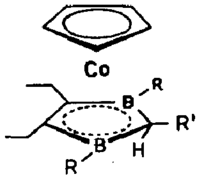
278 (Reproduced with permission from [473])
The diamagnetic monoanion of the neutral paramagnetic Fischer-Palm $[Cp_3Ni_3(\mu_3\text{-}CO)_2]$ parent. The counterion (not shown) was [K(2,2,2-crypt)].



279 (Reproduced with permission from [469])
Geometry of $[H_3CpNiOs_3(CO)_9]$. For each of the crystallographically distinct molecules a crystallographic mirror plane passes through atoms C(1), Ni, Os(2), O(22) and H(11). Note that if we neglect direct osmium-osmium bonds, each osmium atom is in an approximately octahedral coordination environment.



280 (Reproduced with permission from [475])



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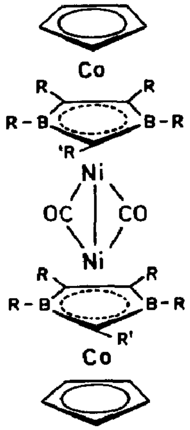

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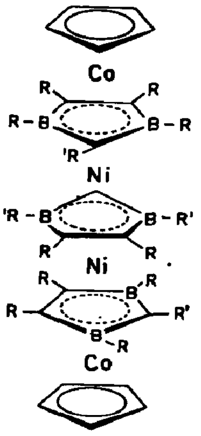
(Reproduced with permission from [477])

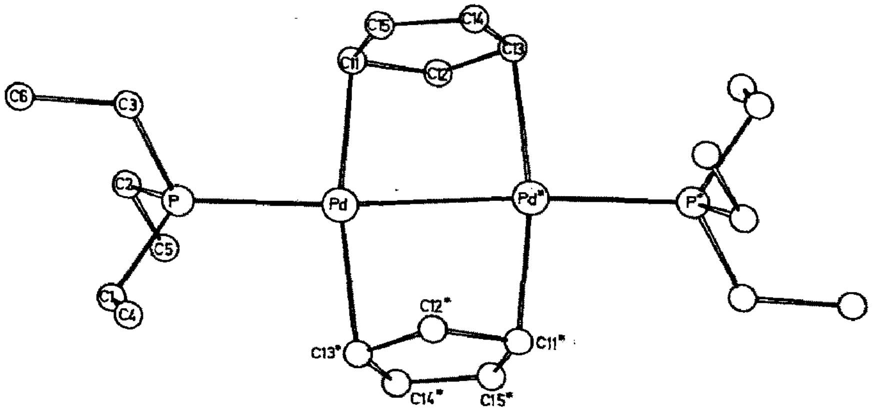


283 (Reproduced with permission from [477])

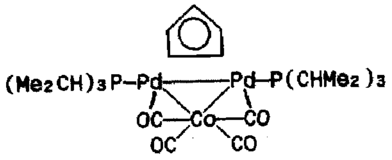
Reports of palladium cyclopentadienyl complexes have, as usual, been more sparse. Reaction of $[CpPd(PR_3)(OCOMe)]$ with sodium potassium alloy yielded $[Pd_2(PR_3)_2(\mu\text{-}Cp)_2]$, which could also be prepared from $[Pd_2(PR_3)_2(\mu\text{-}OCOMe)_2Cl_2]$ and TlCp. 284 was characterised by X-ray diffraction [478]. The compound for which R = $CHMe_2$ underwent oxidation by iodine to give $[CpPd(PR_3)I]$, and oxidative addition with iodomethane to yield $[CpPd(PR_3)I]$ and $[CpPd(PR_3)Me]$. One of the bridges could be readily exchanged for either a bridging carboxylate or a bridging thiolate. Related complexes bridged by allyl ligands were also discussed [479]. $[Pd_2\{P(CHMe_2)_3\}_2(\mu\text{-}Cp)\{\mu\text{-}OC(CMe_3)O\}]$reacted with $Na[Co(CO)_4]$ to give 285 and similar reactions of the allyl bridged species were also reported [480].

A range of complexes $[CpPdL_2][PF_6]$ (L = teriary phosphine, arsine or stibine) were prepared from $[PdL_2Cl_2]$, cyclopentadiene and $Ag[PF_6]$. The bis(triphenylstibine) complex was investigated by X-ray diffraction; the geometry at palladium was found to be approximately trigonal [481]. Treatment of $[M(diene)(Me_2CO)_2][PF_6]_2$ with the ylid 286 yielded $[M(Ph_3PC_5H_4)(diene)][PF_6]_2$ (M = Pd or Pt; diene = cod, nbd or cot) in which the ylid was η^5-bonded to the metal. The complexes were stable as solids, but decomposed in solution [482].

Condensation of nickel vapour with $HSiCl_3$ in the presence of toluene at −196 °C gave a species of stoichiometry $\{HNi(toluene)(SiCl_3)\}$. Warming to room temperature yielded 287 in low yield. 287 could also be prepared from $[Ni(cod)_2]$ and $HSiCl_3$ in toluene, or by condesation of nickel vapour with $Cl_3SiSiCl_3$ and toluene [483]. 288 was prepared from the sodium salt of the ligand and $Ni(CO)_4$]. 289 was obtained by ligand exchange at [$Pt(cod)_2$] [484].



284 (Reproduced with permission from [478])
Hydrogen atoms are omitted for clarity.



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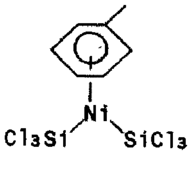

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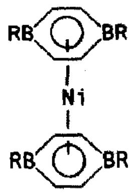

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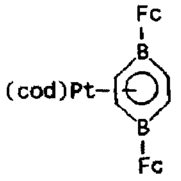

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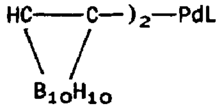
12 METAL CARBORANE AND RELATED COMPLEXES

A simple bonding scheme has been proposed for eight vertex D_{2d} dodecahedral clusters in violation of Wade's rules. The discussion included consideration of $[Cp_4Ni_4B_4H_4]$ [485]. The nature of metal boron bonding in metalloboranes has been explored by extended Huckel calculations. The clusters considered included $[Ni(CO)_2B_3H_7]$ [486]. EHMO claculations on the *closo*-platinacarboranes $[(H_3P)_2PtC_2B_9H_{11}]$ and $[(H_3P)_2PtC_2B_4H_6]$ suggested that the larger slip distortions in the pentagonal bipyramidal derivatives, attributed to metal-ligand interactions, were induced by the different elevation angles of the substituents on the pentagonal faces of the ligands [487].

The reaction of $[Cp_2Ni]$ with $[4\text{-}CB_8H_{13}]Na$ gave initially $[6\text{-}\eta^5\text{-}CpNi\text{-}\eta^5\text{-}1\text{-}CB_8H_9]$, but this cluster could not be isolated in a pure state since it rearranged slowly in solution to give $[10\text{-}\eta^5\text{-}CpNi\text{-}\eta^4\text{-}1\text{-}CB_8H_9]$, characterised by X-ray diffraction [488]. "1-Lithioorthocarborane" reacted with $[PdLCl_2]$ to give a complex with a structure which was rather unhelpfully shown as 290 [489].



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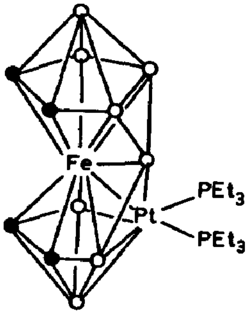
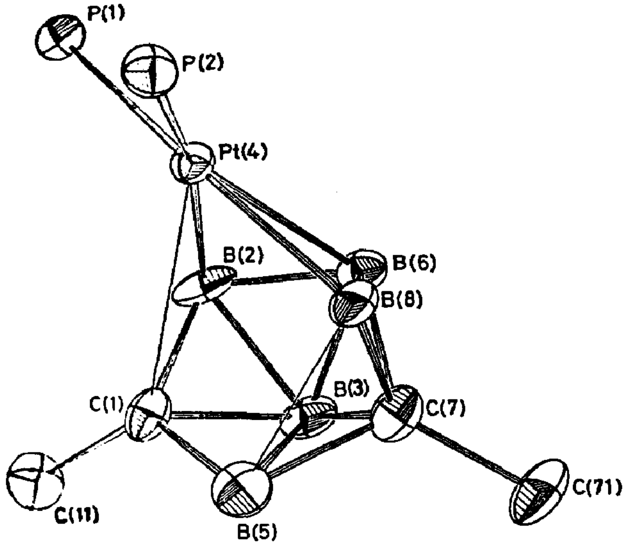
$[Pt_2(\mu\text{-cod})(PEt_3)_4]$ reacted with $[H_2Fe(2,3\text{-}Me_22,3\text{-}C_2B_4H_4)_2]$ to give $[(Et_3P)_2PtFe(Me_4C_4B_8H_8)]$, 291. The cobalt analogue of 291 was characterised by an X-ray diffraction study [490]. The carboranes *closo*-$[2,4\text{-}R_2\text{-}2,4\text{-}C_2B_5H_5]$ (R = H or Me) reacted with $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ to give the carbaplatinaboranes $[4,4\text{-}(Et_3P)_2\text{-}1,7\text{-}R_2\text{-}1,4,7\text{-}CPtCB_5H_5]$ and $[1,1\text{-}(Et_3P)_2\text{-}6,6\text{-}(Et_3P)_2\text{-}4,5\text{-}R_2\text{-}1,4,5,6\text{-}PtC_2PtB_5H_5]$. The structures of the compounds for which R = Me, 292 and 293, were established by X-ray diffraction. The reaction represents an unusual double insertion of a platinum nucleophile into a *closo*-carborane [491].

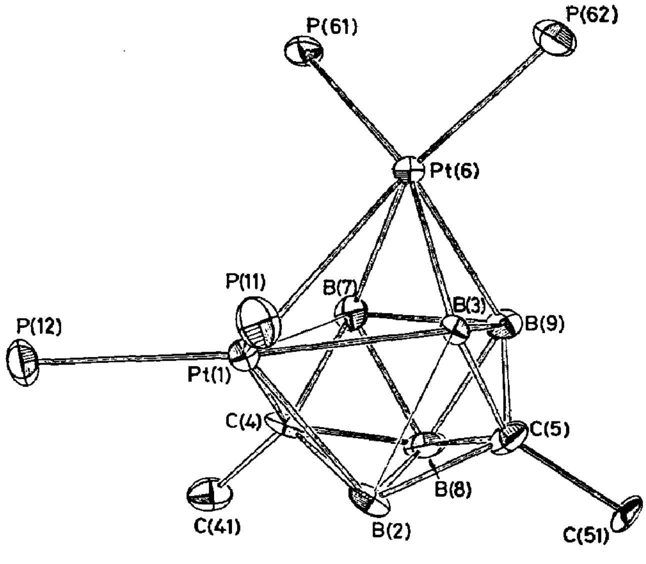


291 (Reproduced with permission from [490])

(•) = CMe; (o) = BH



292 (Reproduced with permission from [491])
The molecular structure of [4,4-$(Et_3P)_2$-1,7-Me_2-1,4,7-$CPtCB_5H_5$] with the ethyl groups omitted for clarity.



293 (Reproduced with permission from [491])
The stereochemistry of [1,1,6,6-$(Et_3P)_4$-1,4,5,6-$PtC_2PtB_5H_5$] with the ethyl functions omitted for clarity.

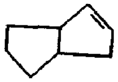
Couplings catalysed by nickel and palladium complexes have been reviewed [492]. A review has also been published of palladium and platinum complexes which are intermediates in organic synthesis [493].

13.1 Hydrogenation and hydrogenolysis

Catalysis by palladium complexes with a palladium-palladium bond has been reviewed. Among the reactions considered were hydrogenation, alkene isomerisation, oligomerisation and carbonylation [494]. Enantioselective hydrogenation in the presence of chiral complexes of rhodium, palladium and cobalt has been discussed [495].

A range of complexes were tested for their efficacy in the interconversion of *ortho* and *para*-hydrogen, a phenomenon known to be diagnostic for the reversible formation of an $\{MH_2\}$ intermediate. $[Pt(PPh_3)_4]$, $[Pt(PPh_3)_2O_2]$ and $[Pt(PBu_3)_2Cl_2]$ were active, but $[Pt(dppe)_2]$ was not, as ligand dissociation is much more difficult [496]. Non-empirical pseudopotential calculations on $[HPd(C_2H_4)Cl_3]^-$ were undertaken, and were related to ethene hydrogenation. A mechanism for collapse to planar $[EtPdCl_3]^-$ was proposed [497].

A 1:14 mixture of $[Ni(PBu_3)_2Cl_2]/Li[BH_4]$ in thf was found to be a very effective catalyst for the reduction of 1-hexene [498]. Several reports of the selective reduction of dienes to alkenes in the presence of nickel complexes have been published. For example, isoprene underwent 1,4-reduction with reasonable selectivity in the presence of $[Ni(acac)_2]/(Me_2N)_3P/[Et_2CHO]Li$ [499], and $[Ni(acac)_2]/Na[HAl(OCH_2CH_2OMe)_2]$ was used as a catalyst for the partial hydrogenation of unsaturated fatty acids [500]. Using $[Ni(acac)_2]/Et_3Al_2Cl_3/PPh_3$, 1,4-cyclohexadiene was reduced to cyclohexene, and 1,3-cyclooctadiene was converted to cyclooctene. However, with 1,5-cyclooctadiene, 294 was formed, rapidly and quantitatively [501].



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The effect of hydrophilic solvents on the reductions of alkenes catalysed by $PdCl_2$ have been investigated. The solvents affect both reaction kinetics and product distributions. The mechanistic implications of the observations for isomerisation and oxidation to carbonyls were discussed [502]. Reduction of acrolein and 295 to the saturated aldehydes was accomplished in the presence of palladium complexes with nitrogen containing ligands [503].

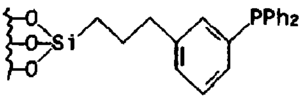
295

^{31}P, ^{119}Sn and ^{195}Pt nmr spectrsocopic studies were used to identify the products of the reaction of $SnCl_2$ with platinum complexes. Species such as $[Pt(SnCl_3)(PR_3)_2L]$ (L = H, alkyl, Cl or $SnCl_3$) were reduction catalysts [504]. Heating $[Pt(PPh_3)_2O_2]$ in hydrogen at 65 °C gave a species described as $\{(Ph_3P)PtO\}$, which was also a catalyst for alkene reduction [505].

$[Pt(PPh_3)_4]$ was used for the preparation of Pt/C and Pt/Al_2O_3 catalysts for hydrogenation, giving superior results to $[Pt(NH_3)_4Cl_2]$ [506]. The kinetics of the hydrogenation of 1-hexene in the presence of aromatic compounds over palladium sulphide have been investigated. The aromatics acted as inhibitors by displacing the adsorbed substrate [507,508].

Again this year polymer supported catalysts have proved to be of great interest. Poly(4-vinylpyridine)/$PdCl_2$ was an effective catalyst for alkene reduction at 30 °C and one atmosphere of hydrogen. The catalyst could be easily removed and reused [509]. Palladium(II) anchored to copolymers of divinylbenzene with either acrylonitrile or *N*-vinylpyrrolidone catalysed alkene reductions at 1 atmosphere pressure of hydrogen and room temperature [510].

Silica has proved a popular support for palladium catalysts [511]. The activities of various palladium complexes on silica for the reduction of sulpholene and thiophene were studied. It was found that there was some increase in activity with the number of palladium atoms in a supported cluster [512]. Attachment of a phosphine bearing side chain to silica was generally accomplished by an exchange reaction with a trialkoxysilane. The product was then reacted with $Na_2[PdCl_4]$ to give the catalyst. Among the ligands prepared in this way, the complexes of which were subsequently used for alkene hydrogenation were 296 [513,514], poly[γ-{4-(diphenylphosphino)phenyl}propyl]siloxane [515], and polo[oxa-7-diphenylphosphino-6-hydroxyheptyl]siloxane [516]. Palladium derivatives of amino functionalised silica have been used as catalysts for the selective reduction of alkynes to alkenes [517]. A palladium polyvinylpyrrolidone complex supported on silica was studied by XPES [519]. A palladium complex of polyphenylquinoxaline supported on silica was an extremely active catalyst for cyclohexene reduction [519].



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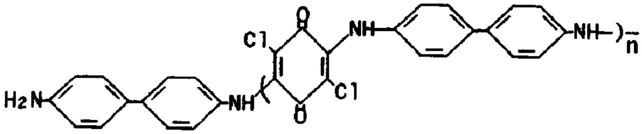
Polyaminochloroquinone, 297, was prepared by interfacial polycondensation of chloranil and benzidine. Its palladium complex was used as a catalyst for the reduction of styrene [520]. Polymeric chelates of palladium with poly(3- or 4-hydroxyphenyl benzoxazoleterephthalimides) as fibres had some activity as catalysts for the reduction of alkenes and dienes [521]. Anthranilic acid, allyl and pyridyl derivatives of layered zirconium phosphate were treated with palladium complexes to give supported species which catalysed the reduction of alkenes, alkynes, nitriles and nitro compounds [522].



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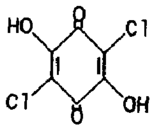
Hydrogenation of alkenes, alkynes, and dienes was accomplished using platinum clusters including $[Pt_2Co_2(CO)_8(PPh_3)_2]$ or $[Pt(CyNC)_2][CpMo(CO)_3]_2$ [523].

Further reductions of nitro groups have been noted. *Trans*-$[Pd(py)_2Cl_2]$ catalysed reduction of nitrobenzene to aniline at room temperature, under 1 atmosphere of hydrogen, in good to excellent selectivity [524]. Reactions of $ArNO_2$ with platinum complexes were studied, and it was concluded that the major products had the nitro group coordinated to palladium *via* an oxygen atom [525]. The activities for nitrobenzene reduction shown by $K_2[PdCl_4]$ and $K_2[PtCl_6]$ on anion exchangers, and $NiCl_2$ and $PdCl_2$ on cation exchangers were determined [526]. Hydrogenation of mixtures of $PhNO_2$ and RCHO in the presence of platinum metals supported on 298 yielded RCH_2NHPh, *via* PhNHOH, $PhNH_2$ and RCH=NPh [527]. In a related process, reaction of $ArNO_2$ with CO/H_2O in the presence of RCH_2CHO and a catalyst yielded mixtures of 299 and 300. 299 was the major product when $[Rh(PPh_3)_3Cl]/PdCl_2$ was used as the catalyst, but up to 45 % 300 was obtained in the presence of $[\{Rh(cod)Cl\}_2]$ [528]. With

1,4-$(NO_2)_2C_6H_4$ or 4-$NH_2C_6H_4NO_2$ as the substrate mixtures of **301**, **302** and **303** were formed [529].



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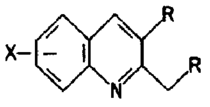

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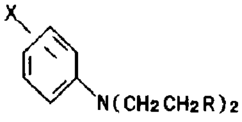

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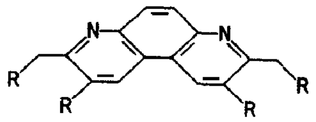

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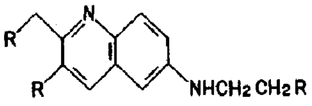

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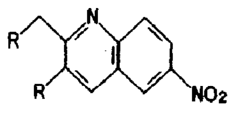

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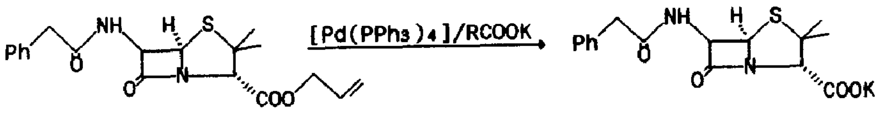
Patents have reported the reduction of MeCOOCOMe to $MeCH(OCOMe)_2$ using either $[Ni(PPh_3)_2(CO)_2]$/MeI/PPh_3/$[Mo(CO)_6]$ or $PdCl_2$ as the catalyst systems [530,531].

Hexane could be dehydrogenated in the presence of platinum polyphthalocyanines. A reaction mechanism was reported [532].

Hydrogenolysis of aryl halides was accomplished using Na[OOCH] as the hydride donor and $[Pd(PPh_3)_2Cl_2]$ as catalyst, together with a phase transfer catalyst [533]. Hydrogenolysis of halothiophenes was accomplished using molecular hydrogen and $PdCl_2$ on modified silica as the catalyst, with CaO or ZnO as the HX acceptor [534,535]. Alkyl halides were reduced to alkanes using Pt(II)/NaI/$H[ClO_4]$ [536,537].

Hydrogenolysis of allyl derivatives in the presence of palladium complexes generally involves hydride reduction of an intermediate π-allyl palladium complex. Thus palladium(0) catalysis has been used to cleave allyl esters, carbonates and carbamates, and thus to unmask acids, alcohols and amines. The reaction is particularly useful in sensitive molecules such as **304** [538]. Allyl ethanoates could be reduced by Bu_3SnH in the presence of $[Pd(PPh_3)_4]$. Certain allylamines also underwent hydrogenolysis [539]. The hydrogenolysis of allyl ethers required the use of a more reactive hydride donor, *viz.* $Li[HBEt_3]$; E-alkenes were generally produced in excellent yield [540].

Bu_3SnH acted as a source of hydride towards α,β-unsaturated aldehydes in the presence of $[Pd(PPh_3)_4]$ to give the saturated compounds. A reaction mechanism was proposed on the basis of deuterium labelling studies [541].



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13.2 Oxidation

Potential applications of the Pd(II)/Pd(IV) redox system in the catalysis of oxidation have been reviewed [542]. Reviews of ethene oxidation with particular reference to catalysis by $Na_2[Pd(NO_2)Cl_3]$ [543] and $Pd(OCOMe)_2/CH_3COOH/Li[NO_3]$ [544] have been published.

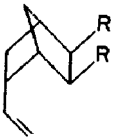
The epoxidation of propene in air was accomplished using $PdCl_2/CuCl_2$ as the catalyst [545].

There have been many further papers reporting reactions related to the Wacker oxidation. Oxidation of ethene to ethanal has been noted in the presence of $[Pd(PhCN)_2Cl_2]/[Co(TPP)(py)(NO_2)]$/diglyme [546], and $PdCl_2/CuCl_2$/NaY zeolite [547]. If the reaction was carried out in the presence of $Pd(OCOMe)_2/Li[NO_3]/CH_3COOH$ it was demonstrated by an ^{17}O nmr spectroscopic study that the oxygen incorporated into ethanal was derived from the $Li[NO_3]$ [548]. $PdCl_2/CuCl_2$ supported on zeolites proved a better catalyst for oxidation of propene than the same species on silica or alumina [549]. A rate study on the oxidation of 1-butene suggested the involvement of a binuclear, $\{Pd_2Cl_4(butene)_2\}$, intermediate [550].

Oxidation of ethenyl benzene using sulpholane as the oxidant and $PdCl_2/CuCl_2/CuCl/H_2O$ as the catalyst system gave 2-phenylethanal with 86 % selectivity, the minor product being 1-phenylethanone (13 %) [551]. Oxidation of styrene was selective for 1-phenylethanone in the presence of $[Pd\{Ph_2P(C_6H_4\text{-}3\text{-}SO_3Na)\}_2Cl_2]$, but conversions were low [552]. Oxidation of alkenes in the presence of $Pd(OCOCF_3)_2/h\nu$ suffered from competition from alkene isomerisation [553].

Oxidation of alkenes and non-conjugated alkadienes by oxygen, achieved in the presence of $[Pd(MeCN)_2(NO_2)Cl]$, generally gave methyl ketones, but epoxides were produced with **305** or **306** as the substrates [554].

1,4-Diketones have been prepared by the regioselective oxidation of β,γ-unsaturated ketones and esters such as **307** [555,556]. Oxidation of unsaturated ethers such as **308** was also quite regioselective [557].



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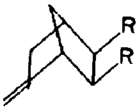

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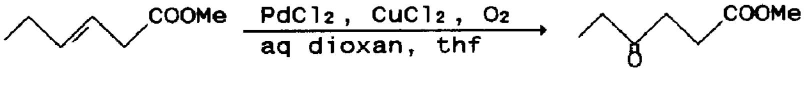

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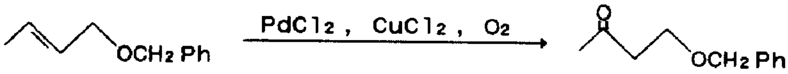


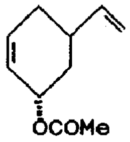
308

Oxidation of ethene to $HOCH_2CH_2OCOMe$ has again been studied. A physicochemical study of the catalytically active solutions in the reaction catalysed by $Pd(II)/CH_3COOH/Fe(NO_3)_3$ indicated that $\{Pd(NO_2)\}$ complexes were formed in the presence, but not the absence, of the substrate [558]. A complex mechanism was postulated, involving inner sphere reaction of ethene with $[NO_2]^-$. The oxygen absorption was associated with oxidation of NO complexes [559]. Just as with the Wacker reaction analogue, the oxygen in $HOCH_2CH_2OCOMe$, formed in the presence of $Pd(OCOMe)_2/Li[NO_3]/CH_3COOH$, was derived from the nitrate group [560]. Deactivation of palladium/nitrate oxidising systems, capable of catalysing formation of diethanoates, was attributed to the formation of insoluble palladium complexes of side products of the catalytic reaction [561]. Oxidation of ethene to ethenyl ethanoate could be achieved in the presence of $[Pd\{PhCON(Ph)O\}_2]/Na[OCOMe]/MeCOOH$ [562].

Oxidation of 1-alkenes to methyl ketones by ROOH in the presence of CO was catalysed by palladium(0) phosphine complexes. Esters and acids were also produced by CO insertion [563].

Allylic oxidation of propene in the presence of MeCOOH was achieved using palladium (0) clusters (formed *in situ* from palladium(II)) as catalysts [564]. Oxidation of cyclopentene using $PdCl_2/TeO_4/Ag[OCOMe]/MeCOOH/Me_3COOH$ gave 3-cyclopentenyl ethanoate as the major product, together with small amounts of cyclopentenone [565]. Allylic oxidation of 4-ethenylcyclohexene gave **309** in

30 % yield, *via* 310-312 [566].



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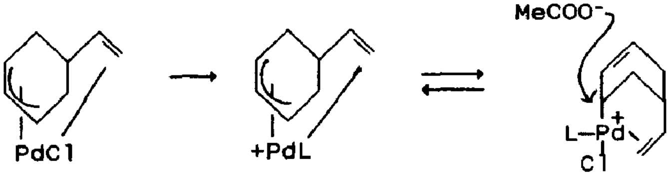
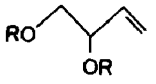


310 **311** **312**

Several patents have reported the oxidation of butadiene to furan. Catalyst systems studied included $PdCl_2/[NH_4][VO_3]/H_2O/Al_2O_3/TeO_2$ [567], $PdCl_2/TeO_2/HCl/H_2O$ [568], and $[H_{3+n}PM_{12-n}V_nO_{40}].xH_2O/PdCl_2/O_2$ (M = W or Mo; n = 1,2,3,4,5,6,7,8,9 or 10; $0<x<32$) [569]. Oxidation in the presence of $PdCl_2/CuCl_2/ROH/O_2$ to give **313** and **314** was noted [570]. Oxidation of ethane-1,2-diol to tetrahydrofuran was accomplished in the presence of $CuCl_2/PdCl_2/O_2$ [571].



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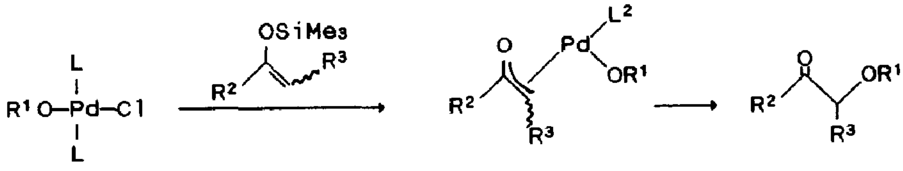
314

$K_2[PtCl_4]$ supported on alumina was an active catalyst for the oxidative chlorination of methane by HCl/O_2 mixtures. Activation of the substrate probably occurred *via* formation of a platinum alkyl complex [572]. Kinetic data for the oxidative carbonylation of methanol in the presence of palladium complexes and benzoquinone was interpreted in terms of palladium(I) and palladium(II) intermediates [573]. Dehydrogenation of cyclohexanone to cyclohexenone occurred in an oxygen atmosphere in the presence of $Pd(OCOCF_3)_2$; the effects of various additives was studied [574].

Oxidation of silyl enol ethers to α-oxygenated ketones was effected by Me_3COCl in the presence of $[Pd(PPh_3)_4]$. **315** and **316** were considered to be the critical intermediates [575]. Oxidative coupling of **317** to give **318** in the presence of palladium ethanoate probably occurred *via* an electron transfer mechanism [576].



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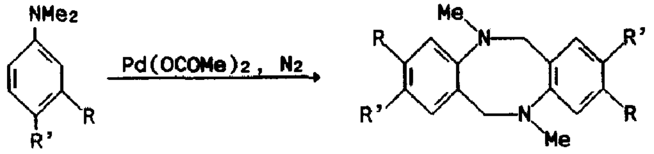


317 318

13.3 Reactions of Carbon Monoxide and Carbon Dioxide

The patent literature has reported several new sets of conditions for the hydroformylation of 1-alkenes to linear aldehydes, with more or less good selectivity, including $[Pt(PhCN)_2Cl_2]/SF_2/$*trans*-1,2-bis(diphenylphosphinomethyl)cycloalkanes [577], and $[Pt(PhCN)_2Cl_2]/Ph_3SnCl/DIOP$ [578]. The reaction using $[Pt(PPh_3)_2Cl_2]/SnCl_2$ has been noted before, and the product aldehyde has now been converted into a linear amine with high selectivity by reductive amination in the presence of a nickel containing catalyst [579].

3,3,3-Trifluoro-1-propene was hydroformylated in the presence of $[Pt(DIOP)Cl_2]$ to give 71 % of the linear aldehyde, although most rhodium and ruthenium complex catalysts gave predominently branched products [580]. Internal alkenes have been hydroformylated in the presence of $[Pt(PR_3)_2(CO)Cl]/SnCl_2$ to give linear aldehydes, but selectivity was low, since three processes, isomerisation, hydroformylation and hydrogenation were in competition. Selectivity could be altered by varying R [581]. Hydroformylation of propene could be accomplished under mild conditions in the presence of a silica supported phospine cobalt complex and $[Pd(PPh_3)_4]$. Selectivity for the linear product was high, and it was suggested that the complexes were acting synergistically [582].

A thorough study has been made of the effect of the addition of chelating biphosphines on the hydroformylation efficiency of the catalyst system $[Pt(PPh_3)_2Cl_2]/SnCl_2$. The rate of the reaction was found to be a function of *n* in $Ph_2P(CH_2)_nPPh_2$ with a maximum for $n = 4$ and a zero rate for $n = 2$. The rate enhancement was accompanied by an increase in selectivity towards the production of aldehydes. It was suggested that whilst the catalyst precursor was a chelating phosphine complex, in the successful catalysts one arm of the phosphine could be readily decoordinated. Kinetic data suggested that the rate controlling step was hydrogenolysis of a metal acyl complex [583].

A rather remarkable asymmetric hydroformylation in the presence of $PtCl_2/SnCl_2$/DBPDIOP was said to result in the formation of $PhCH(CH_3)CHO$ in 94 % optical yield from styrene. More recent work on this system has, however, confirmed that this value for the enantiomeric excess should have been substantially lower [584].

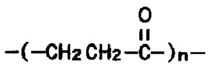
A patent has reported the hydrocarboxylation of propene to methyl 2-methylpropanoate with 81 % selectivity in the presence of $[Pd\{Ph_2P(2\text{-}MeC_6H_4)\}_2Cl_2]/Ph_2P(2\text{-}MeC_6H_4)/MeCOOH/[MeCOO]K/H_2O/MeOH/CO$ [585]. Hydrocarboxylation of propene was accomplished using $[Pd(PPh_3)_4]$ with fluorinated sulphonic acids as the catalyst system [586].

A polymer supported hydrocarboxylation catalyst, in which $[Pd(PhCN)_2Cl_2]$ was reacted with a styrene divinyl benzene copolymer, was found to give linear esters with a higher selectivity, but at a lower rate, than the homogeneous system [587]. $PdCl_2$ supported on chlorinated PVC was said to be an excellent catalyst for conversion of 1-nonene to decanoic acid [588].

The enantioselective hydrocarboxylation of styrene in the presence of a palladium complex, DIOP and CF_3COOH gave PhCH(Me)COOMe in up to 52 % optical yield [589]. Hydrocarboxylation of *N*-ethenyl phthalimide has been studied in detail. The use of $[Pd(DBP)_2Cl_2]$ as the catalyst gave the linear product with very high selectivity, but conversions were low. Complexes of monodentate chiral phosphines gave the branched product with good selectivity, but enantiomeric excesses were negligible [590].

A number of more unusual carbonylation reactions of alkenes have been reported, especially in the patent literature. For example, ethene reacted with CO/MeOH in the presence of $NiI_2/[Mo(CO)_6]/PPh_3/EtI/EtO_2CCH_2CH_3$ to give $EtCO_2Me$, although the source of the components of the product were not made clear [591]. Carbonylation in the presence of $EtCOOH/NiI_2/[Mo(CO)_6]/EtI/PPh_3$ gave the anhydride, EtCOOCOEt, again by an unspecified mechanism [592]. Copolymerisation of ethene and CO to give **319** occurred in the presence of $[Pd(MeCN)_4][BF_4]_2/PPh_3$. The conditions used were mild, and a reaction mechansim was proposed [593].

Several oxidative carbonylations of alkenes have been described. For example, in the presence of MeOH/CO/air and using $PdCl_2/CuCl_2$ as the catalyst system, $PhCH(COOMe)CH_2COOMe$ and *trans*-PhCH=CHCOOMe were produced from ethenyl benzene in the ratio of 1.1:8.4 [594]. Ethene has been reacted with ethanol in the presence of $Pd/C/PdCl_2/HNO_3$ to give $EtOOCCH_2CH_2COOEt$ with 99 % selectivity [595].



$$-(-CH_2CH_2-\overset{O}{\overset{\|}{C}}-)_n-$$

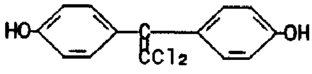
319

A patent has described the carbonylation of butadiene to a mixture of carbonylated and telomerised products [596].

Carbonylation of 1-alkynes to give RC■CCOOMe occurred in the presence of $CO/ROH/PdCl_2/CuCl_2/[MeCOO]Na$ [597]. In a more complex reaction, using $CO/ROH/PdBr_2/PPh_3/HBr$/dmf, both mono and diesters were produced, their ratios depending on the exact conditions employed. In all cases ROCOCH=CHCOOR was a very significant product [598].

Once again this year a number of patents have reported on conditions for the carbonylation of methanol to ethanoic acid. Catalyst systems/conditions have included $[Ni(CO)_4]/MeI/Li[OH]$/180 °C/70 bar [599], $[Ni(CO)_4]/MeI/Cr(OCOMe)_2$ [600], $Ni(OCOMe)_2/VO(acac)_2/MeCOOH/MeI$ [601], $Ni(OCOMe)_2/MeI/MeCOOH/La(OCOMe)_3$ [602] and $[Ni(PPh_3)_2(CO)_2]/[Mo(CO)_6]/PPh_3/MeI$ [603]. Using a catalyst system rather curiously described as $PtCl_4/NaI/dppp/H_2O/CoCO_3$ (*sic*), methanol was converted by CO/H_2 to a mixture of alcohols in which the major component was ethanol [604].

Carbonylation of phenol using $CO/Na[OH]/H_2O$ in the presence of $PdBr_2/[Bu_4N]Br/CH_2Cl_2$/octadecane-2,4,16,18-tetraoato-Mn(II) gave diphenyl carbonate [605]. In an oxidative intramolecular version of the reaction, 320 was converted to 321 [606].



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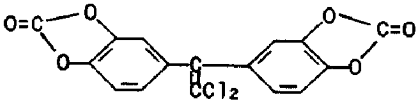

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Methyl ethanoate has again been a popular substrate for carbonylation. Carbonylation to ethanoic anhydride was achieved in the presence of $Ni(OCOMe)_2/MeI/[MePPh_3]I$/tetramethylene sulphone [607], $[Ni(PPh_3)_2CO)_2]/MeI/[Mo(CO)_6]/PPh_3$ at 180 °C and 600 psi carbon monoxide [608], $[Ni(PPh_3)_2(CO)_2]/MeI/[Ph_3PMe]I/Li[OCOMe]$ [609],

$Ni(OCOMe)_2/MeI/NaI/$*N*-methylpyrrolidone at 180 °C and 70 bar carbon monoxide [610], Ni or nickel complexes/2,4-dimethylpyridine/MeI/Li[OCOMe] [611] or $Ni(OCOMe)_2/Mg(OCOMe)_2/MeI/NaI/MeCOOH$ [612]. Methyl ethanoate and/or dimethyl ether reacted with CO/H_2 in the presence of $[Ni(PPh_3)_2(CO)_2]/PPh_3/MeI/[Mo(CO)_6]$ to give $MeCH(OCOMe)_2$ [613]. $Co(OCOMe)_2$ with $[Pd(acac)_2]$, $[Ni(acac)_2]$ or $H_2[PtCl_6]$ were all rather poor catalysts for conversion of methyl ethanoate to ethyl ethanoate using H_2/CO [614].

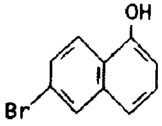
Carbonylation of ethanoic acid in the presence of $Pd(OCOMe)_2/PPh_3/MeI$ gave a mixture of acids including EtCOOH, PrCOOH, BuCOOH and $Me_2CHCOOH$ [615]. Using methyl methanoate as the substrate and $Pd(OCOMe)_2/MeI/PPh_3$ as the catalyst system, ethanoic acid was produced with up to 95 % selectivity [616].

The reaction of carbon monoxide with hydrogen to give alcohols, in particular ethanol, was catalysed by platinum carbonyl clusters [617]. Platinum-ruthenium bimetallic clusters, supported on silica, were prepared *in situ* and were also useful for reaction of CO and H_2, this time to give methane. However, it was found that the platinum-ruthenium dual site was not as successful as a ruthenium-ruthenium site for the catalysis [618]. In the presence of $PdCl_2/H_2O$, $HOCH_2COOH$ and MeCOOH were formed, but the reaction was not efficient [619].

There continue to be many reports of the carbonylation of aryl, allyl and vinyl halides. In all cases these proceed *via* initial oxidative addition of the halide to palladium to give, for example, $[RPdL_2X]$, which is then carbonylated to $[RCOPdL_2X]$. The fate of the palladium acyl then depends on the presence of a nucleophile. When water acts as the nucleophile, acids are formed. Thus, for example, RX was converted to RCOOH using as a catalyst system $[Pd(PhCN)_2Cl_2]/L$ ($L = PR_3$, SbR_3 or R_2S) [620]. Using $ArCH_2X$ as the substrate, the products formed were found to depen on the precise reaction conditions involved. Under phase transfer conditions ($CO/H_2O/CH_2Cl_2/Na[OH]/[Pd(PPh_3)_4]/[(C_6H_{13})_4N][HSO_4]$), $ArCH_2COOH$ was produced, but $[Pd(dba)_2]$ catalysed reduction and coupling of the benzilic halides [621].

Carbonylation of 1-bromo-1-phenylethane gave PhCH(Me)COOMe as the main product using $[(4\text{-}CH_3C_6H_4)Pd(AsPh_3)_2I]$ as the catalyst. However, significant amounts of PhCH(Me)OMe and styrene were also produced [622]. A halonaphthalenene, 322, was successfully thus transformed into the related carbomethoxy compound [623].

An intramolecular version of this reaction (reaction (42)) was used in the synthesis of α-methylene lactones. Cyclisation to give 5-membered rather than 6-membered rings was favoured in molecules, such as 323, in which the option existed [624].



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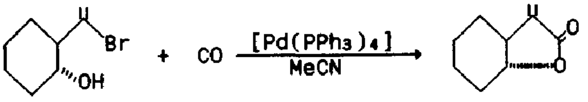

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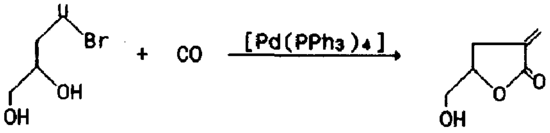

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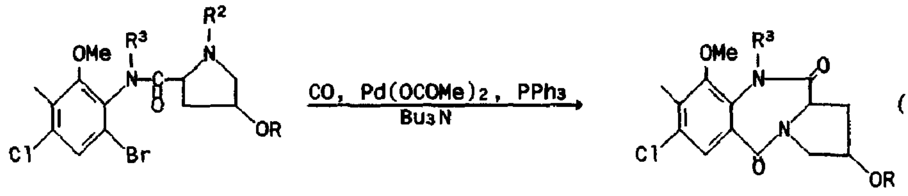
When the added nucleophile is an amine, the product would be expected to be an amide, but it has recently been shown that double carbonylations of halides to give $RCOCONR'_2$ are the main reactions in the presence of $[Pd(dppb)Cl_2]$ [625]. Other workers have reported similar results using $[Pd(PPh_3)_2Br_2]$ or $[Pd(PMePh_2)_2Cl_2]$ as the catalyst [626,627]. The mechanisms proposed have involved either {RCOCOPd} or {$RCOPdCONR'_2$} as the key intermediate [628]. Reaction with trialkylamines proceeded with cleavage of a carbon-nitrogen bond, again giving secondary amides (reaction (43)) [629]. An intramolecular reaction was used in the synthesis of anthramycin (reaction (44)) [630]. When the nucleophile was a urea, RNHCONHR', 324, was converted into a dihydrouracil, 325 [631].

$$PhI + CO + Et_2NPh \xrightarrow{[PhPd(PPh_3)_2I]} PhCONEtPh + EtI \qquad (43)$$

Carbon nucleophiles have also been used in combination with carbonylation reactions. Thus, iodobenzene reacted with phenylethyne in the presence of $CO/Et_3N/[Pd(Ph_3As)_2Cl_2]$ at 120 °C and 20 atm to give $PhCOC\equiv CPh$ in 81 % yield [632]. With Me_4Sn as the nucleophile, phenylethanone was produced in 78 % yield in the presence of $[Ni(PPh_3)_2(CO)_2]/P(NMe_2)_3$ [633].



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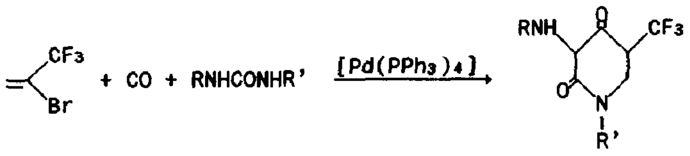


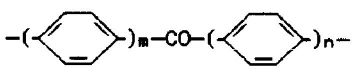
324 325

Carbonylation of aryl nitro compounds to isocyanates has proved a popular field for patents again this year. Catalysts for the conversion of 1,3-dintrobenzene or 2,4-dinitrotoluene have included $[Pd(py)_2Cl_2]$ [634], $[Pd(quinoline)_2Cl_2]/[Cp_2VCl_2]/POCl_3$/quinoline [635], $PdCl_2/py/ThO_2$ [636], $[Pd(quinoline)_2Cl_2]/[V(acac)_3]$/quinoline [637], and $[Pd(py)_2Cl_2]$/1,2-dichorobenzene/molybdic acid [638]. A somewhat different and rather interesting catalyst was the cluster, $[Cp_2Mo_2Pd_2(CO)_6(PPh_3)_2]$, supported on alumina. Both yield and activity were high, and the catalyst was easily recovered [639].

In the presence of alcohols, ROH, nitro compounds are carbonylated to give the esters, ArNHCOOR. Catalysts for the conversion of nitrobenzene to PhNHCOOEt have included $PdCl_2/Fe(OH)(OCOMe)_2/LiCl$ [640], $PdCl_2/FeCl_3$/DBU [641], $[Pt(PPh_3)_2Cl_2]/SnCl_4/Et_3N$ [642], and $PdCl_2/VCl_3$ [643]. Palladium complexes of silica functionalised with sulphur or nitrogen ligands have been used as catalysts for the synthesis both of isocyanates and esters [644].

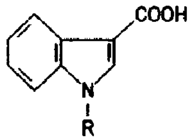
It remains a moot point as to whether arylamines are intermediates in the carbonylation of $ArNO_2$ to ArNHCOOR, but it has been demonstrated that $PhNH_2$ reacted with CO/O_2 in the presence of $Pd(OCOMe)_2/Cu(OCOMe)_2/PhNEt_2$/tetrachlorobenzoquinone to give PhNHCOOEt in 73 % yield [643]. Aryl diazonium salts, ArN_2X, reacted with CO/R_4Sn in the presence of $Pd(OCOMe)_2$ to give ArCOR, thus providing a useful alternative to the Freidel Crafts reaction for deactivated arenes [646].

Some organometallic compounds have been induced to react with carbon monoxide using palladium complexes as catalysts. For example, using RHgCl as substrate and $[PhPd(PPh_3)_2I]/(Me_2N)_3PO/[R_4N]I$ as the catalyst system, R_2CO was obtained in up to 99 % yield [647]. 1,4-Dibromobenzene was converted to its bis(Grignard reagent), and copolymerised with CO to give **326**, using $[\{Ni(dppm)Cl_2\}_2]$ as the catalyst [648].



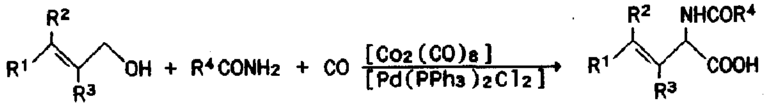
326

Carbonylation of $[Ar_2I]X$ in the presence of an alcohol, ROH, and $PdCl_2$ or $Pd(OCOMe)_2$ as catalyst gave ArCOOR [649]. Oxidative carbonylation of *N*-alkylindoles using $CO/Pd(OCOMe)_2/Na_2[S_2O_8]$ gave 327 [650].



327

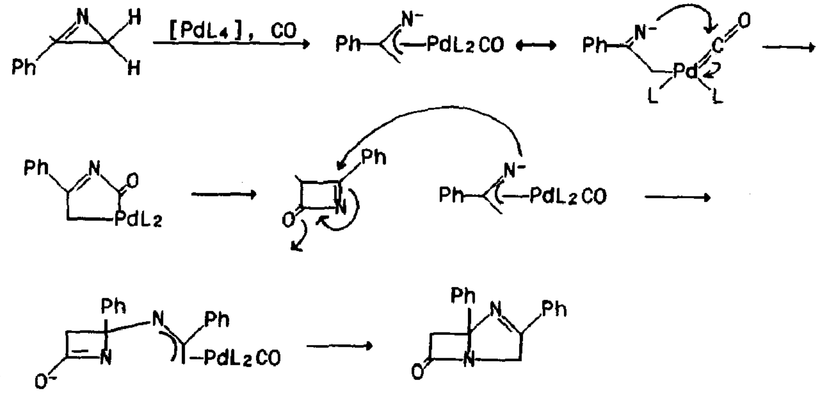
Coupling and amination of CO to give oxamide derivatives such as $Et_2NCOCONEt_2$ was achieved under mild conditions (atmospheric pressure) using $[Ni(Et_2NH)_2Br_2]/Et_2NH$ [651]. The transformation of reaction (45) was achieved in 77 % yield; there was little indication as to the reaction mechanism, or as to the function of the palladium cocatalyst [652].

 (45)

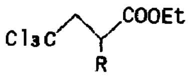
Carbonylation of aziridines led to a very useful *β*-lactam synthesis. Whilst much of the mechanism shown in Scheme 10 is speculative, there are precedents for most of the steps invoked [653].

Carbonylation of 1-alkenes in the presence of CCl_4 and using $Pd(OCOMe)_2$ as the catalyst gave coupled products, **328**, probably *via* a radical mechanism [654].

The reaction of **329** was considered to involve the intermediate $[RCONi(CO)_n]^-Li^+$. **330** was converted through several steps to **331** which underwent an intramolecular carbonylation [655].



Scheme 10 Mechanism of carbonylation of aziridines [653].



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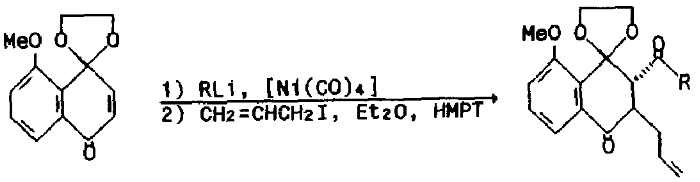

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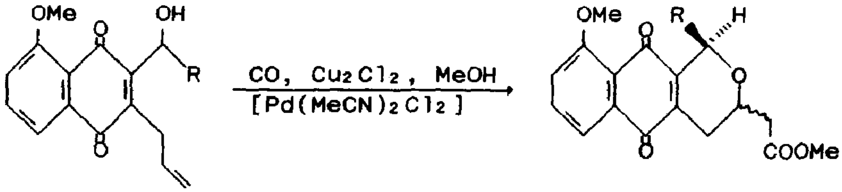

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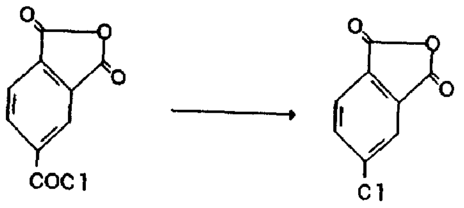
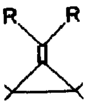
Decarbonylation of 332 was catalysed by $[Pd(PPh_3)_4]$ or $PdCl_2$ in the melt or in the gas phase, in fair to good yields [656].



332

The insertion of CO_2 into methylene cyclopropanes, 333, (R = Me or RR = $(CH_2)_5$) followed a pathway which depended on the nature of the catalyst used. With $[Pd(PPh_3)_4]$ the product was 334, but using $[Pd(dppe)_2]$, 335 was formed. Trimethylenemethane palladium complexes were considered to be likely intermediates [657,658].



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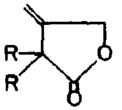

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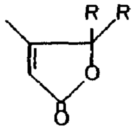


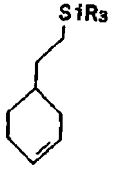
335

13.4 Hydrosilylation and Related Reactions

Hydrosilylation of alkenes was achieved in the presence of $[NiL_2X_2]$ (L = phosphine oxide, X = Cl or Br) [659]. Reaction of 1-alkenes with H_2SiCl_2 in the presence of $[Ni(PPh_3)_2Cl_2]$, $[Pd(PPh_3)_2Cl_2]$ or $[Pd(PPh_3)_4]$ gave $RCH_2CH_2SiHCl_2$, but using $H_2[PtCl_6]$ as the catalyst resulted in the formation of $(RCH_2CH_2)_2SiCl_2$ [660].

The vinyl siloxane, $CH_2{=}CHSi(OR)_3$, reacted with $(R'O)_3SiH$ to give $(R'O)_3SiCH_2CH_2Si(OR)_3$ as the major product, using either $[Ni(acac)_2]$ or $H_2[PtCl_6]$ as the catalyst [661]. In the reaction of $CH_2{=}CHSiCl_3$ with Cl_3SiH the regiochemistry of addition was strongly dependent on the nature of the catalyst used. Using $H_2[PtCl_6]$ the 1,2-disilane was the main product, whilst $[Pd(PPh_3)_4]$ gave mainly the 1,1-isomer. The use of $[Ni(PPh_3)_2Cl_2]$ gave a mixture of the two products [662].

Hydrosilylation of phenylethene by trichlorosilane in the presence of $H_2[PtCl_6]$ has once again been shown to give a mixture of addition products [663]. The reaction of 4-ethenylcyclohexene with trialkylsilanes occurred exclusively at the exocyclic double bond, to give mainly 336. Better yields were obtained if a carboxylic acid was added to the reaction solution [664].



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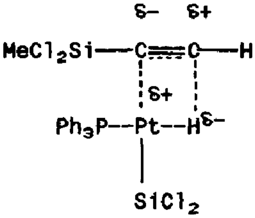
A hydrosilylation catalyst was prepared by addition of $H_2[PtCl_6]$ to silica supported thiols [665]. The kinetic parameters of hydrosilylation in the presence of $H_2[PtCl_6]$ supported on an ion exchange resin were found to be very strongly related to the sorbabilities of the reactants [666].

Hydrosilylations of allyl chloride and allyl amine in the presence of $H_2[PtCl_6]$ have been reported to give mainly linear products [667,668].

Various patents have recorded a range of hydrosilylation reactions of alkynes (reactions (45) and (46)) [669,670]. Most unusually, reaction of $MeCl_2SiC\equiv CH$ with Me_2ClSiH in the presence of $[Pd(PPh_3)_4]$ gave $CH_2{=}C(SiMeCl_2)SiMe_2Cl$ with 96 % regioselectivity. The transition state for the product determining step was proposed to be 337, with the reaction being very sensitive to electronic factors in the alkyne [671]. Hydrosilylation of 338 gave 339, with the yield of the reaction depending on the substituents [672].

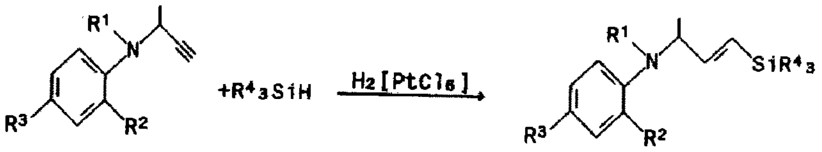
$$HC\equiv CH + HSi(OR)_3 \xrightarrow{[Pt(PPh_3)_4],\ 120\ ^\circ C,\ PhMe,\ 96\ \%} CH_2{=}CHSi(OEt)_3 \qquad (45)$$

$$HC\equiv CH + RSiHCl_2 \xrightarrow{[Pd(PPh_3)_4],\ 78\ \%} RSi(CH{=}CH_2)Cl_2 \qquad (46)$$



337

It was hoped that 340 would prove useful as a chiral catalyst for the enantioselective hydrosilylation of phenylethanone by Ph_2SiH_2, but in practice yields were low and enantioselectivities negligible [673].



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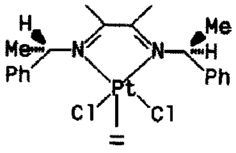


340

Disilylation of dienes has been accomplished using disilanes and a palladium catalyst. Thus, 1,2-propadiene was converted to $CH_2{=}C(SiMe_3)CH(Me)SiMe_2Cl$ by $ClMe_2SiSiMe_3$ in the presence of $[Pd(PPh_3)_4]$ [674], and patents have noted reactions (47) and (48)) [675,676].

$$CH_2{=}CHCH{=}CH_2 + Cl_2MeSiSiMeCl_2 \xrightarrow[82\ \%]{[Pd(PPh_3)_4]} Cl_2MeSiCH_2CH{=}CHCH_2SiMeCl_2 \tag{47}$$

$$CH_2{=}CHCH{=}CH_2 + Me_3SiSiMe_3 \xrightarrow[76\ \%]{[Pd(PPh_3)_4] \text{ or } [Pd(PBu_3)_4]} Me_3Si(CH_2CH{=}CHCH_2)_2SiMe_3 \tag{48}$$

Disilylation of ethyne occurred with good yield and selectivity using $Cl_2MeSiSiMeCl_2$ in the presence of $[Pd(PPh_3)_4]$, to give 96 % $Cl_2MeSiCH{=}CHSiMeCl_2$ with a *cis:trans* ratio of 84:16 [677].

Silylation of haloarenes occurred using disilanes in the presence of $[PdL_2Br_2]$; bromoarenes gave the best results. Bromomethane could similarly be converted into trichloromethylsilane, and acyl halides were transformed to acyl silanes, the latter reaction also being reported in a patent [678,679]. Silylation of benzylic halides has been noted (reaction (49)) [680], but in some cases this has proved quite complex (reactions (50)-(52)) [681].

$$ArCH_2Cl + Cl_2MeSiSiMeCl_2 \xrightarrow{[Pd(PPh_3)_4]} ArCH_2SiMeCl_2 \tag{49}$$

$$ArCHCl_2 + ClMe_2SiSiMe_2Cl \xrightarrow{[Pd(PPh_3)_4]} \tfrac{1}{2}(ArCH{=}CHAr) + 2Me_2SiCl_2 \tag{50}$$

$$ArCHCl_2 + \tfrac{1}{2}(ClMe_2SiSiMe_2Cl) \xrightarrow{[Pd(PPh_3)_4]} \tfrac{1}{2}(ArCHClCHClAr) + Me_2SiCl_2 \qquad (51)$$

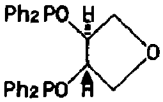
$$PhCHXCHXPh + ClMe_2SiSiMe_2Cl \xrightarrow{[Pd(PPh_3)_4]} PhCH{=}CHPh + 2Me_2SiClX \qquad (52)$$

Silylation of α-halocarbonyl compounds with disilanes gave mixtures of ketones and silyl enol ethers, the reaction being presumed to proceed *via* palladium oxoallyls [682].

13.5 Other Additions to Carbon-Carbon Multiple Bonds

There have been a number of reports this year of hydrocyanation reactions catalysed by platinum group metal complexes. Addition of HCN to 1-alkenes was catalysed by $[Ni\{P(OPh)_3\}_4]/EtAlCl_2$, to give mainly the linear product [683]. Addition to alkynes using $[Ni\{P(OPh)_3\}_4]/P(OPh)_3$ was shown to be stereospecifically *cis* [684].

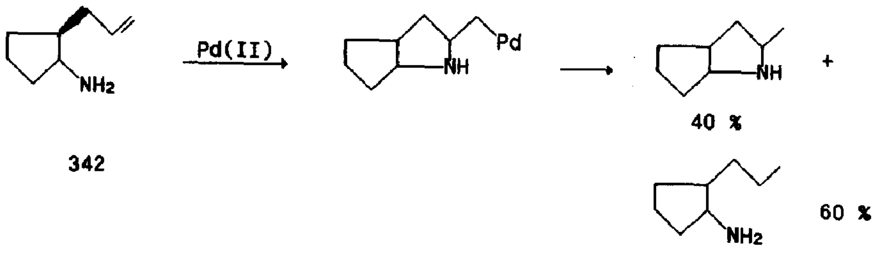
Jackson's group has published several papers on the palladium catalysed addition of HCN to alkenes. It was shown that addition of DCN to both terminal and cyclic alkenes in the presence of $[Pd(DIOP)_2]$ was stereospecifically *cis* [685,686]. This complex was also reported to catalyse chiral hydrocyanation of norbornene in up to 24 % enantiomer excess. Complexes of biphosphines which formed 5-membered chelate rings were inactive, but complexes of **341** proved useful [687,688]. More recent work has cast some doubt on the precision of the enantiomer excesses reported.



341

The hydrocyanation of butadiene in the presence of a nickel(0) phosphite complex has been studied in some detail; allyl intermediates were thought to be involved [689]. A patent has noted conditions for the effective isomerisation/hydrocyanation of a 90:1 mixture of 3-pentene nitrile and 4-pentene nitrile to $NC(CH_2)_4CN$, in 94.4 % yield at 68.9 % conversion [690].

Several patents have reported the addition of alcohols to alkenes, catalysed by palladium complexes. Thus, methanol reacted with 2-methypropene in the presence of $PdCl_2/CuCl_2/LiCl$ to give $MeOCMe_3$ [691], and ethanol with ethenyl ethanoate, using a $PdCl_2$/active carbon catalyst, to give MeCH(OEt)OCOMe, with high selectivity [692]. Oxidation and addition of butanol to CH_2=CHCN in the presence of $PdCl_2$/BuONO gave $(BuO)_2CHCH_2CN$ [693]. In a related reaction the N-H bond of **342** was added across the alkene in the presence of $[Pd(MeCN)_2Cl_2]/LiCl/Na_2[CO_3]$/benzoquinone [694]. Cyclisation of **343** gave **344** [695].



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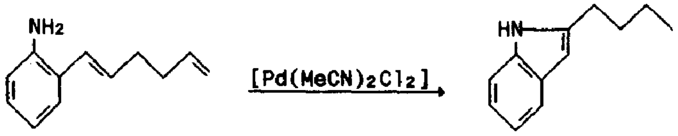

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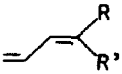
344

Addition of phosphine to CH_2=CHCN in the presence of $H_2[PtCl_6]/P\{CHR(OH)\}_3$ gave $P(CH_2CH_2CN)_3$ [696].

The reactions of Bu_3SnH with various types of carbon-carbon double bonds in the presence of palladium catalysts have been investigated. Whilst enones were reduced to the saturated ketones, α,β-unsaturated nitriles underwent addition (reaction (53)). Aryl allyl ethers were cleaved to give the substituted phenol, propene and Bu_3SnX [697].

$$CH_2{=}CHCN + Bu_3SnH \xrightarrow{[Pd(PPh_3)_4]} MeCH(CN)SnBu_3 \qquad (53)$$

Cyclopropanation of **345** (R = H, R' = Me, Ph, Cl or OMe or R = Me, Ph, Cl or OMe, R' = H) by $N_2CHCOOEt$ in the presence of $[Pd(PhCN)_2Cl_2]$ was found to be quite regioselective [698].

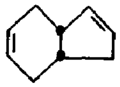


345

Hydrometallation of 1-hexene by MgH_2 or ZnH_2 was catalysed by $NiCl_2/[Cp_2ZrCl_2]$ [699].

13.6 Isomerisation

$[Ni(acac)_2]$ or nickel dioleate/Et_3Al/H_2 provided a catalyst system for the isomerisation of α-alkenes, and for the codimerisation of ethene and isoprene [700]. The non-conjugated diene, **346**, was isomerised in the presence of Pd/C to give only **347** [701].



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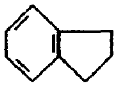
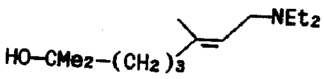


347

The kinetics and mechanism of the isomerisation of 1-nonene in the presence of palladium(II) complexes has been studied [702]. 1-Pentene was isomerised to *cis* and *trans*-2-pentene by $[HPt(PPh_3)_3]X$. The *cis:trans* ratio in the product was greater than 3 only in ether solvents. Lower concentrations of catalyst and/or platinum complex gave higher *cis*-selectivity [703]. Polymers having propenoic acid or 2-propene-1-ol grafted onto them by radical copolymerisation were treated with $PdCl_2$ followed by $Na[BH_4]$/MeOH to give catalysts for the isomerisation of 3-phenyl-1-propene to 1-phenyl-1-propene [704].

The direction of isomerisation of alkenes substituted with polar groups is relatively easy to predict, and most reactions proceed to completion. Thus, in the presence of $Pd[NO_3]_2/PPh_3/Na[OPh]$, **348** was converted to **349**, which could in turn be hydrolysed to 7-hydroxycitronellal [705].



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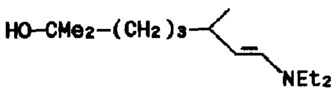
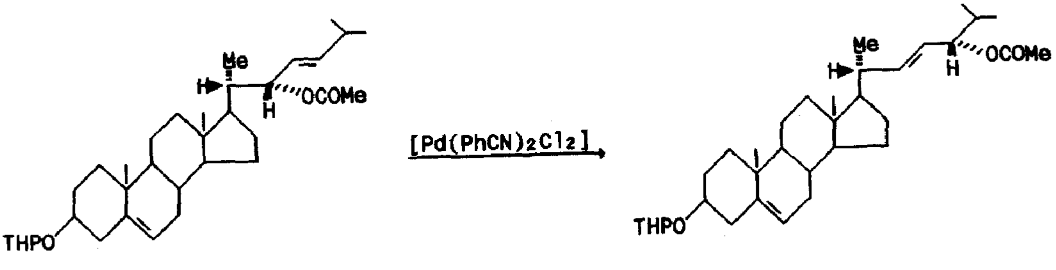


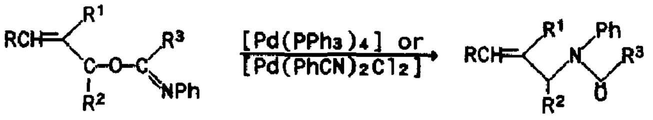
349

The reversible formation of palladium allyl complexes has been responsible for a number of interesting isomerisation reactions. Thus, in the presence of $[Pd(MeCN)_2Cl_2]$ 17-α-ethenyl-17-β-ethanoatoandrost-4-ene-3-one was converted with excellent selectivity to 21-ethanaoatopregna-4,17(20)-dien-3-one [706], and **350** was converted into **351** with 96 % chirality transfer [707].



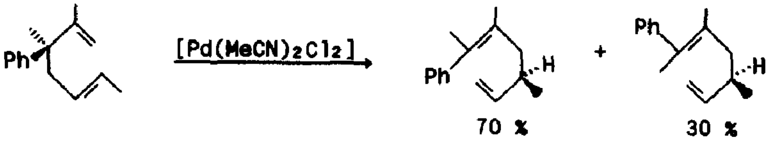
350 351

The conversion of **352** into **353** was catalysed both by palladium(0) and palladium(II) complexes. The reaction in the presence of palladium(II) gave a single isomer of the product, in keeping with a mechanism which involves a σ-bonded palladium intermediate. The reaction in the presence of palladium(0) was assumed to proceed *via* palladium allyl complexes, and as a consequence a mixture of isomeric products was produced [708].



352 353

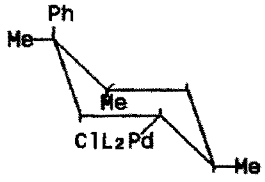
The palladium catalysed Cope rearrangement of **354** proceeded with almost complete chirality transfer. The asymmetric induction was the same as in the thermal Cope rearrangement, suggesting that the catalysed reaction also involved chair topology in the intermediate. An intermediate such as **355** was favoured [709].



354

A wide range of transition metal complexes have been used to catalyse the rearrangement of quadricyclane derivatives to norbornadienes (reaction (54)). When methanol was used as the solvent **356** and **357** were also produced, though in low yield [710]. Oxacyclopropane carboxylate derivatives were isomerised to vinyl ethers in the presence of many transition metal catalysts, including

[M(PhCN)$_2$Cl$_2$] (M = Pd or Pt). The intermediate proposed was 358, and 359 reacted similarly [711].



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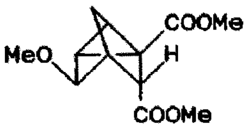

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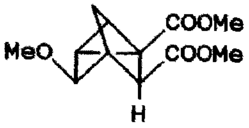

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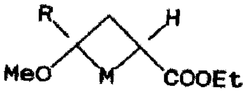

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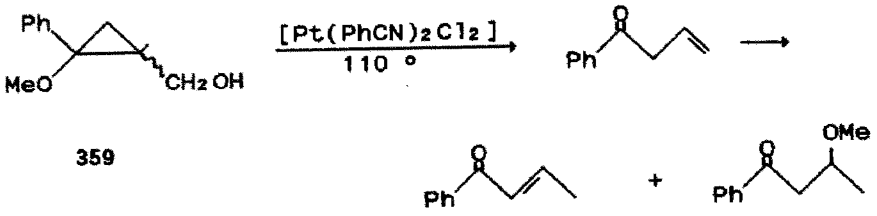
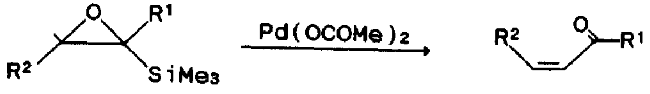


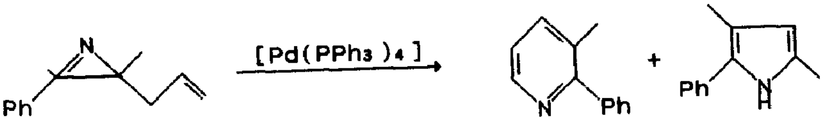
359

The opening of the silylated epoxide, 360, to give the enone 361 was catalysed by Pd(OCOMe)$_2$, [Pd(PhCN)$_2$Cl$_2$] or Pd[NO$_3$]$_2$ [712].



360 361

In the presence of $[Pd(PPh_3)_4]$ 362 was isomerised to 363 (18 %) and 364 (20 %); the reaction was sensitive to the atmosphere in which it was conducted as well as to pressure [713].



362 363 364

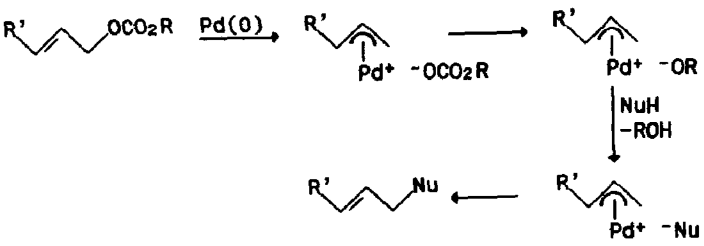
13.7 Substitution of Allyl Derivatives

Catalytic transformations *via* palladium allyl complexes have been reviewed [714], and considerable use has been made of such reactions in organic synthesis.

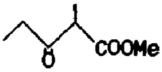
Alkyltrimethyltin compounds, $RSnMe_3$, (R = Ar, allyl or alkenyl) reacted with allyl bromide in the presence of $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$/hmpt, or allyl ethanoate using $[Pd(PPh_3)_4]$ as catalyst, to give in both cases $RCH_2CH{=}CH_2$ [715,716]. Anions α- to nitro groups have also been used successfully as nucleophiles in palladium catalysed reactions of allyl derivatives. In terms of reactivity $CH_2{=}CHCH_2OPh$ > $CH_2{=}CHCH_2OCOMe$ > $CH_2{=}CHCH_2OH$ [717,718].

The use of an allyl carbonate as the substrate for these nucleophilic substitutions has proved to be particularly useful, because of its high reactivity (Scheme 11). Thus 365 reacted with diallyl carbonate in the presence of $[Pd(PPh_3)_4]$ to give 366 in 98 % yield in only 10 minutes [719]. This reaction was also applied to the regiospecific allylation of ketones. Thus 367 reacted with a palladium(0) complex to give the allyl derivative, 368. Decarboxylation gave 369 which could undergo either coupling (L = PPh_3) or elimination (L_2 = dppe, solvent = MeCN) [720].

A number of other leaving groups have also proved useful. Thus 2-propene-1-ol was substituted by the anion of $Ph_2C{=}NCH_2COOEt$ in the presence of $Pd(OCOMe)_2/PPh_3$ to give $Ph_2C{=}NCH(COOEt)CH_2CH{=}CH_2$ in 33 % yield [721]. Nitro compounds were also good substrates, and 370 was converted to 371 with good efficiency and high regioselectivity [722]. The allylic substitution of an allylic nitrile was considered to proceed *via* the mechanism of Scheme 12, but this was not conclusively established [723].



Scheme 11 Mechanism of palladium catalysed substitution of allyl carbonates



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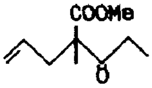

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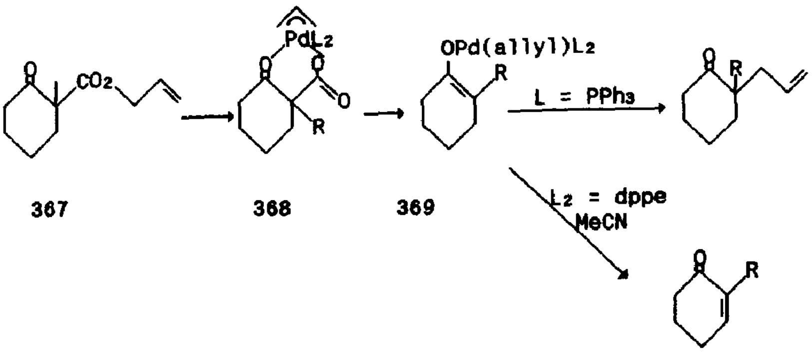
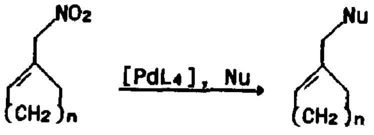
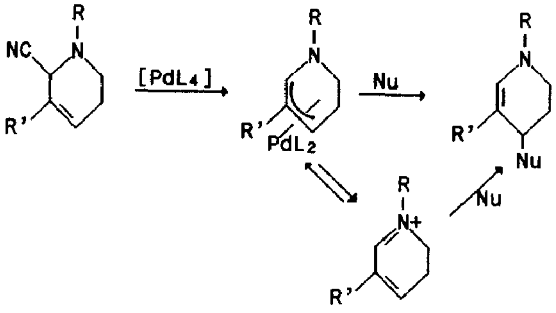


367 368 369

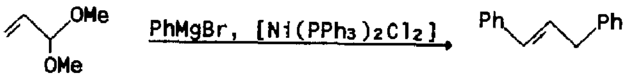


370 371

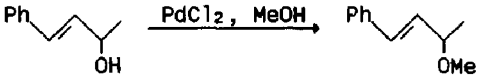


Scheme 12 Mechanism of palladium catalysed substitution of an allylic nitrile

The reaction of enone acetals such as 372 with Grignard reagents was accelerated by $[Ni(PPh_3)_2Cl_2]$, and gave 373 as the sole product. It was suggested that two successive allylic substitutions occurred, the regiochemistry of each depending principally on steric factors [724]. Reaction of 374 with methanol in the presence of $PdCl_2$ gave 375; in practice $RuCl_3$ proved to be a better catalyst [725].



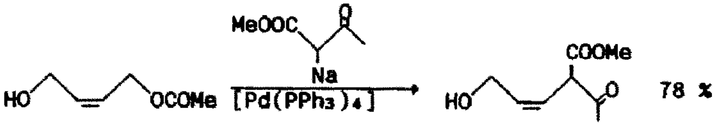
372 373



374 375

Selectivity between leaving groups was observed in the reaction of 376, the ethanoate, predictably, being easier to displace than the OH group.For 376, the Z-isomer gave a 75:25 Z:E mixture of products but the E-isomer reacted stereospecifically [726]. Both 377 and 378 reacted with $NaCH(COOMe)_2$ in the presence of $[Pd(dppe)_2]$ to give 379. If this was then converted to its ethanoate, cyclisation to give cyclopropanes could then be readily accomplished [727].

The regiochemistry of substitution of non-symmetrical allyl derivatives has again been studied. Whilst it is generally accepted that the prevailing regiochemical outcome involved addition of the nucleophile to the less hindered end of the allyl (for example reactions (55) and (56) [728,729]) some unusual reactions have been noted. For example, reaction of sodium 4-methylbenzene sulphonate with **380**, in the presence of $[\{(\eta^3-C_3H_5)PdCl\}_2]$, gave mainly **381** [730]. In reaction (57) the ratio between the amounts of the two products obtained ranged from 1:1 to > 97:3 [731]. The cyclisation of **382** proceeded with high chemo, regio and stereoselectivity [732].



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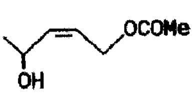

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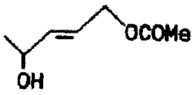

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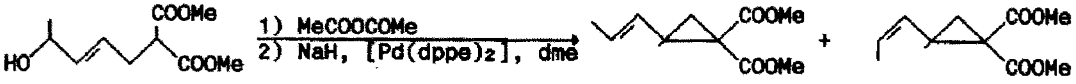

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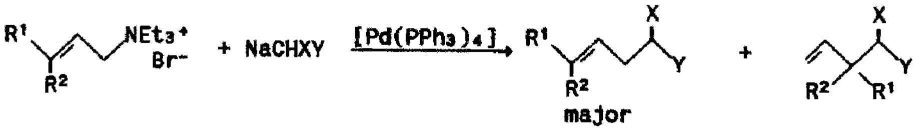

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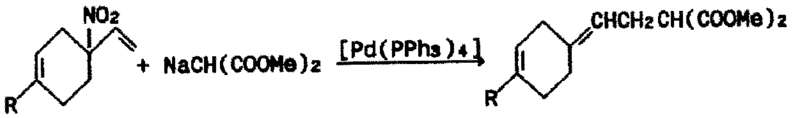

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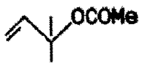

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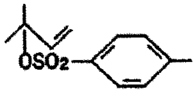

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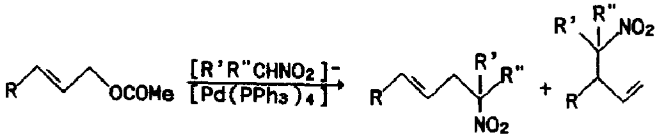

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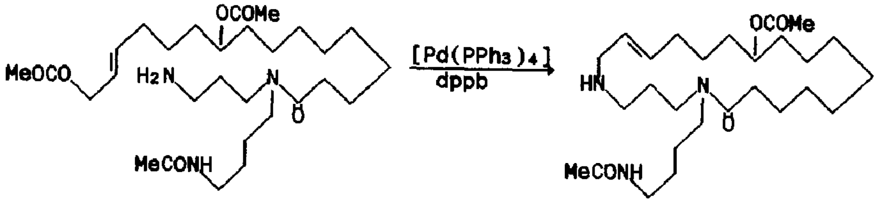
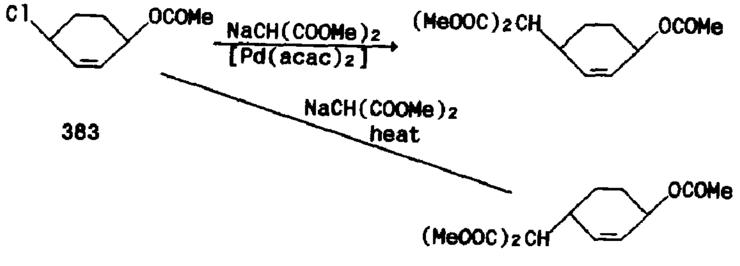


382

The coupling of an alkenylalane with an allylic ester in the presence of [Pd(PPh$_3$)$_4$] has been shown to occur with up to 98 % inversion of configuration at the reaction centre. This was the first demonstration of a reaction in which inversion occurred, since the reactions of stabilised enolates all proceed with retention of configuration [733]. It had been known for some time that addition of two ethanoate groups to cyclic dienes proceeded in the presence of palladium(II) to give 1,4-diethanoates, with a stereochemistry which depended on the relative concentrations of chloride and ethanoate ions in the solution. The reaction was also successful with acyclic dienes. If the concentration of chloride ion in the solution is increased sufficently, the product obtained is predominently that of *cis*-1-halo-4-ethanaoto addition, 383. This compound reacted with the anion of diethyl propanedioate to give the *cis*-product, (*via* double inversion) in the presence of a palladium catalyst, but the *trans*-product (by S_N2 substitution) under normal polar conditions [734]. Substitution of 384 might in principle be expected to give mixtures of 385, 386 and 387, *via* the mechanism of Scheme 13. In practice 385 wass essentially the sole product, the cause of the selectivity not being well-defined [735].

Allylic substitutions in which the palladium allyl complex is formed by opening of a carbocyclic or heterocyclic ring have again attracted some attention this year. For example a vinylborane, 388, reacted with an allylic epoxide to give a mixture of 389 and 390 with both palladium and nickel catalysts [736]. The neutral conditions in which the epoxide reaction is successful (the alkoxide generated by epoxide opening acts to deprotonate the nucleophile) were particularly successful for the cyclisation of 391 in the presence of a polymer supported palladium(0) complex. The sodium salts of related anions did not diffuse successfully into the lipophilic polymer [737].



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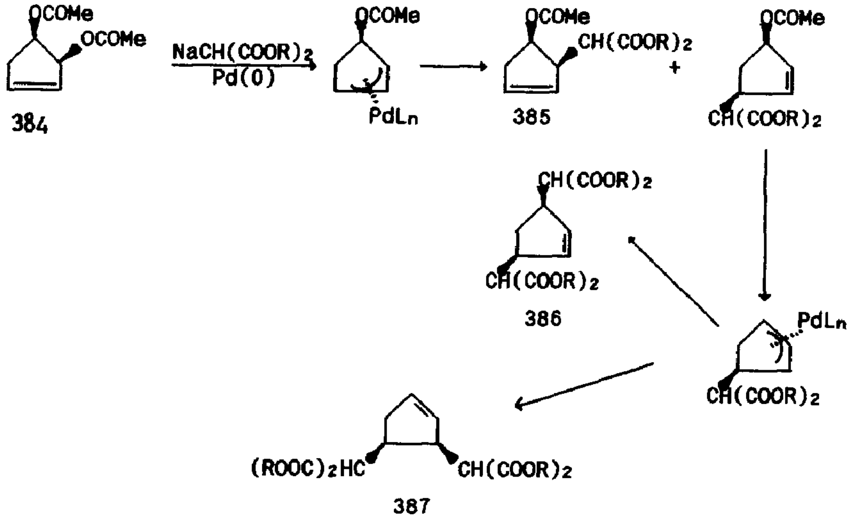
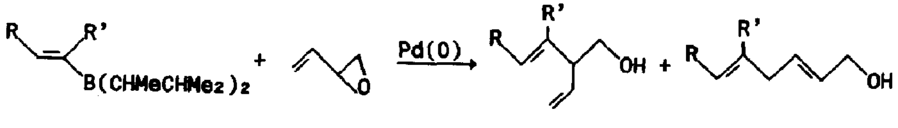


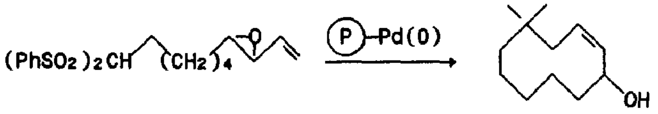
384 385 386 387

Scheme 13 Mechanism of palladium catalysed substitution of 384 [735]



388 389 390

Opening of the cyclopropane ring in 392 gave a palladium dienyl complex and a carbanion. Isomerisation and reclosure yielded 393, which was used in synthetic routes to terpenic cyclopentanoids [738]. The opening and elaboration of allylic lactones has been investigated [739].



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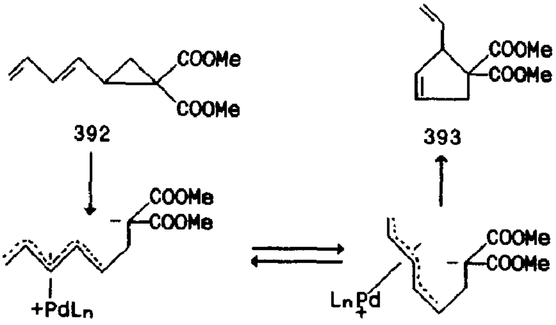
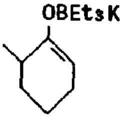


392

393

Potassium enoxyborates (fron potassium enolates and triethylborane) were reacted with allylic halides in the presence of [Pd(PPh$_3$)$_4$] to give α-allylated ketones with retention of enolate regiochemistry and allyl geometry. Thus 394 reacted with neryl ethanoate to give 395 regio and stereospecifically [740]. The palladium trimethylenemethane complex derived from 396 reacted with 397 to give 398 in the presence of [Pd{P(OCHMe$_2$)$_3$}$_4$]. The product was converted into the natural product, albene [741].



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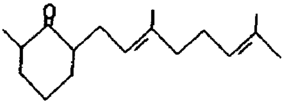
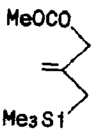


395

There is considerable interest in achieving enantioselective versions of palladium catalysed allylic substitution. The cyclisation reaction, (58), was accomplished in up to 48 % optical yield in the presence of S,R-BPPFA [742]. A novel series of very interesting catalysts, 399, has recently been prepared and used in conjunction with [{(η^3-C$_3$H$_5$)PdCl}$_2$] for the allylation reaction (59). The enantiomer excesses achieved were up to 52 % and it was considered that the remote functionality on the phosphine exerted a guiding effect on the approach of the enolate anion [743].



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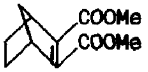

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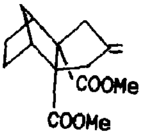

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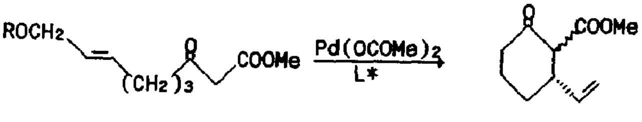

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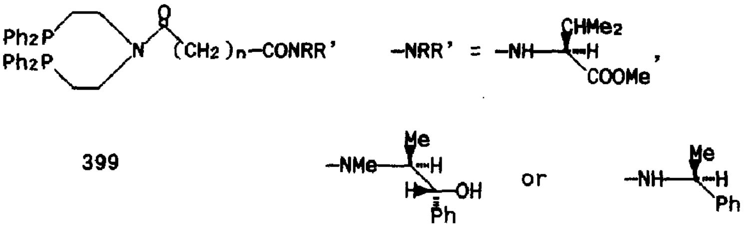

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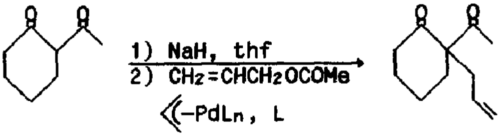

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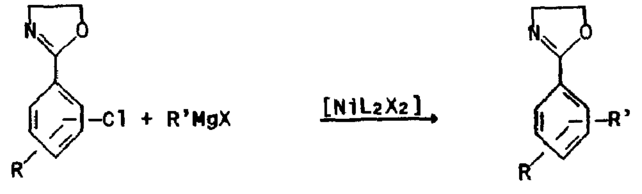
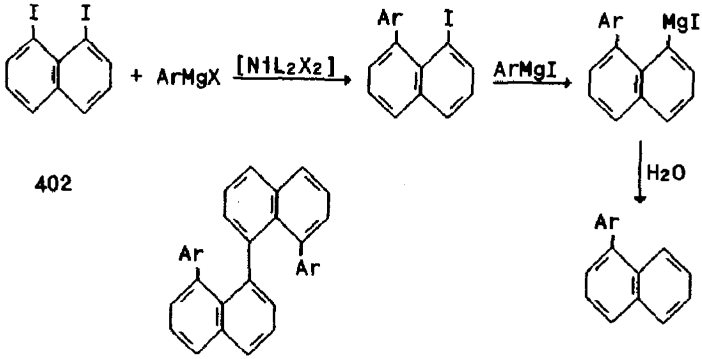
13.8 Coupling of Organometallics with Halides and Related Reactions

Couplings of Grignard reagents with aryl halides have once again been widely reported this year. Thus **400** reacted with RMgX in the presence of $[NiL_2X_2]$ to give **401**. Most yields were excellent, but the reaction with allyl magnesium bromide failed [744]. In the reaction of an aryl Grignard reagent with the diiodonaphthalene, **402**, mixtures of products were obtained, after Grignard exchange [745]. That aryl halides are more readily substituted than aryl thioethers was conclusively demonstrated by the sequence of reaction

(60), in which a selective disubstitution was accomplished [746].



400 401



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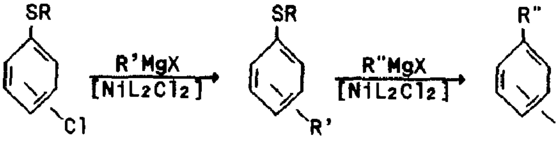

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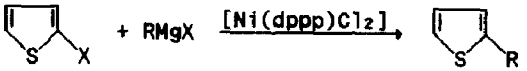
Reactions of heteroaryl halides have also been used in synthesis, as exemplified by reactions (61)-(63) [747-749].



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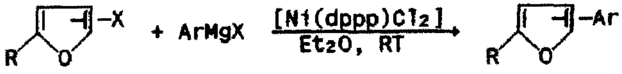
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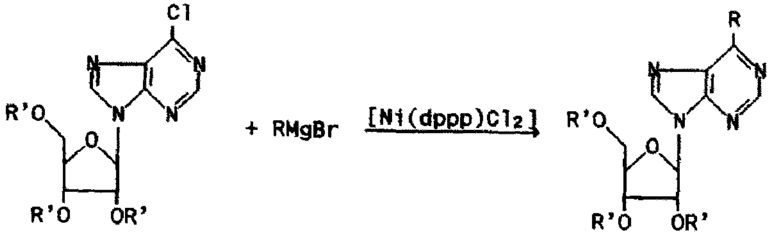
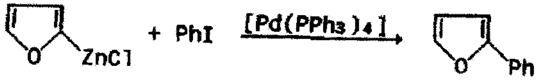
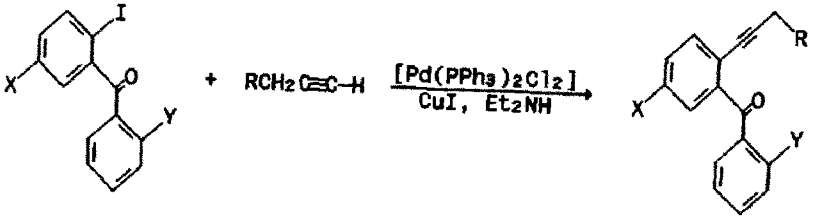

(63)

Derivatives of other metals have also proved very useful, including reactions of vinylzirconium compounds [750], and arylzinc halides (reaction (64)) [751]. Tin enolates were shown to react with aryl bromides in the presence of $[Pd\{P(2\text{-}MeC_6H_4)_3\}_2Cl_2]$ [752], and a tin enolate, formed by exchange from a silyl enol ether, gave a similar result [753]. $CF_2{=}CFSnR_3$ reacted with a range of aryl halides, ArX, to give $CF_2{=}CFAr$ in goood yield and with high selectivity [754].


(64)

The couplings of alkynes and arenes have continued to prove very important. Catalyst systems have included $[Pd(PPh_3)_2Cl_2]/K_2[CO_3]/CuI/dmf$ [755], $[Pd(PPh_3)_2Cl_2]/CuI/Et_3N$ [756], and $[PhPdL_2I]/[Bu_4N]I/hmpt$, which was used together with a preformed alkynyl copper compound [757]. **403** was used in a benzazepine synthesis [758]. Heteroaryl halides have also proved to be useful substrates (reactions (65) and (66)) [759,760].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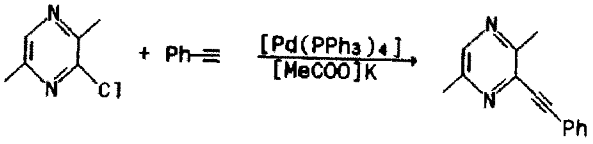

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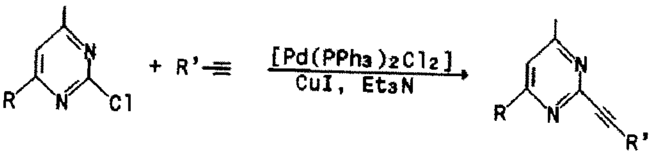
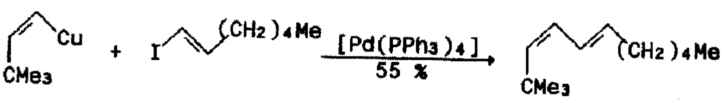


(66)

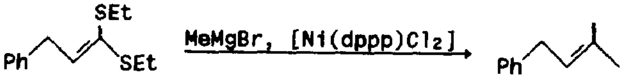
Couplings of organometallics with alkenyl halides follow an essentially analogous course, with examples reported using Grignard reagents [761], alkenyl copper compounds (reaction (67) which proceeded with 98.9 % retention of stereochemistry) [762] and the zinc derivatives of R_fI (R_f = fluoroalkyl) [763]. Alkynylcopper compounds could be prepared *in situ*, and reacted in good yield and stereoselectivity with alkenyl bromides in the presence of $[Pd(PPh_3)_4]/[PhCH_2NEt_3]Cl$ [764]. Alkenyl cyanides were produced by reaction of potassium cyanide with alkenyl halides, using a nickel(0) complex, prepared *in situ* from $[Ni(PPh_3)_2Br_2]/Zn/PPh_3$, as the catalyst [765].



(67)

Other alkenyl derivative have also proved to be useful substrates. BrCH=CHSPh was substituted first at the halide to give RCH=CHSPh using RMgX, with $[Pd(PPh_3)_2Cl_2]$, $[Ni(dppe)Cl_2]$ or $[Ni(dppp)Cl_2]$ as the catalyst. Further substitution of the alkenyl thioether with a second and different Grignard reagent was achieved in the presence of the nickel complexes, with good retention of stereochemistry in both steps [766]. A double substitution of ketene thioacetals such as **404** was achieved [767]. Alkenyltellurium compounds were successfully substituted by Grignard reagents in the presence of $[Ni(PPh_3)_2Cl_2]$, but the retention of stereochemistry was only about 90 % [768]. Alkenyl suphones, **405**, reacted in the presence of $[Ni(acac)_2]$ or $[Fe(acac)_3]$ in 60-80 % yield, with fair stereospecificity [769]. A patent has reported the reaction of **406** with MeMgBr, using $[Ni(acac)_2]$ as the catalyst [770].

A number of relatively unreactive organometallic reagents react poorly with acyl halides in the absence of catalysts. Thus, whilst **407** reacted with RCOCl without a catalyst, the related reactions of **408** and **409** required the presence of $[Pd(PPh_3)_2Cl_2]$ [771,772]. Allyl palladium halide complexes have also been used as catalysts for the process [773]. The reaction of $BrZnCH_2COOEt$ was also catalysed by $[Pd(PPh_3)_4]$, formed *in situ* [774]. Alkynes, $RC\equiv CH$, were coupled with acyl halides in the presence of $[Pd(PPh_3)_2Cl_2]/CuI/Et_3N$, presumably *via* the alkynyl copper compound, formed *in situ* [775]. Diarylmercury compounds reacted with RCOCl using a catalyst system comprising $[PhPd(PPh_3)_2I]/NaI$. Without the added sodium iodide $[Pd(PPh_3)_4]$ was needed as the catalyst, and it was necessary to carry out the reaction under more vigorous conditions [776].



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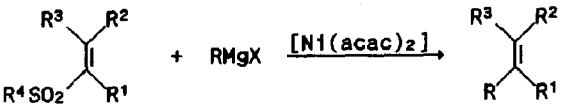

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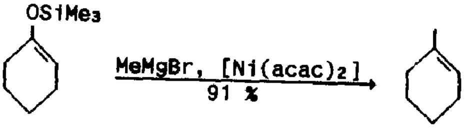

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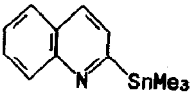

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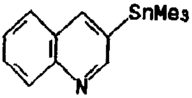

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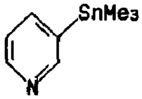

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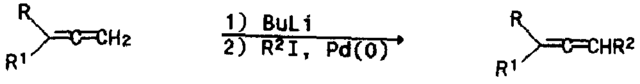
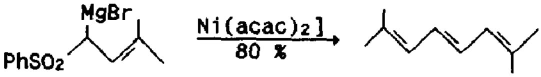
Two coupling reactions of allenyl derivatives have been reported. Thus, RR'C=C=CHM (R = MgCl, Cu, Li, Ag or ZnCl) could be alkylated in the presence of $[Pd(PPh_3)_4]$. The reaction was very regioselective, and no alkynes were formed [777]. An alkenyllithium compound was formed from 410 and was reacted in a one-pot process with iodobenzene or 1-iodo-1-octene, using a palladium(0) catalyst formed *in situ* from $PdCl_2$, PPh_3 and dibaH, to give 411 [778].



410 411

The reaction of phenolate anions, $[ArO]^-$, with tertiary alkyl halides to give species such as $ArOCMe_2R$, was catalysed by $[Ni(acac)_2]$. The reaction failed for strongly electron withdrawing Ar, and conversions were generally moderate, but the products were obtained relatively pure [779]. Couplings of "9-iodo-*o*-$HCB_{10}H_9CH$" with Grignard reagents were reported to be catalysed by $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_2Cl_2]$, but as usual with papers from this Soviet group the details are a little difficult to follow, since they insist on using non-systematic names for the boranes [780].

A number of diverse homo couplings of organometallic complexes have been reported to be catalysed by palladium complexes, and these are included in this section, since this represents an important competitive pathway in cross-coupling processes. Thus ArHgX was converted to ArAr in the presence of $[PhPd(PPh_3)_2I]/I^-$ [781], and $PhB(OH)_2$ yielded PhH and Ph-Ph in the presence of $Pd(OCOMe)_2$. The intermediate in the latter case was assumed to be [PhPd(OCOMe)]. E-PhCH=CHI inhibited both the protonation and the coupling with further $PhB(OH)_2$ of this intermediate, and gave E-PhCH=CHPh in good yield [782]. Homocoupling of 412 was catalysed by $[Ni(acac)_2]$ [783]. The couplings of high-coordinate silicon compounds such as 413 were accomplished in the presence of $PdCl_2$/MeCN. $K_2[PhSiF_5]$ reacted similarly, and 413 underwent cross-coupling with alkenes bearing electron-withdrawing groups. The reaction was thought to proceed *via* oxidative addition of the carbon-silicon bond to palladium to give [PhCH=CHPdX] [784].



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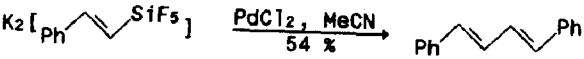

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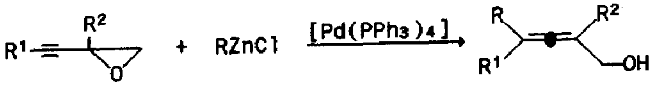
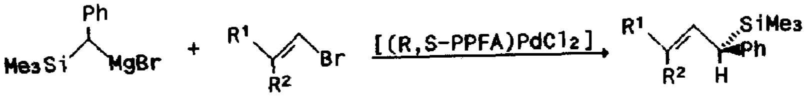
$[(EtOCH=CH)_3B]$ could be converted to the related ate complex in base, and then reacted with aryl or benzyl halides in the presence of [Pd(PPh$_3$)$_4$], [Pd(PPh$_3$)$_2$Cl$_2$] or [Pd(PPh$_3$)$_2$(OCOMe)$_2$] to give RCH=CHOEt, in good yield, and with little formation of biaryl by-products [785]. Alkynyl epoxides, **414**, were opened by RZnCl in the presence of palladium(0) catalysts to give the allenic alcohols, **415**. The process was used in the synthesis of (±)-2,3-octadiene-5,7-diyn-1-ol, a metabolite from the fungus *Cortinellus berkeleyanus* [786].



414 **415**

A number of successful enantioselective couplings of Grignard reagents with alkenyl halides have been noted this year. Using [(S,R-BPPFA)PdCl$_2$] as the catalyst, optical yields up to 46 % were obtained [787]. The use of such ferrocene derived catalysts has been reviewed, and the use of the related reactions of organozinc compounds has proved particularly successful [788]. The couplings of silylated Grignard reagents such as **416** with alkenyl halides was catalysed by [(R,S-PPFA)PdCl$_2$], in up to 95 % optical yield. This represents the first enantioselctive synthesis of chiral silanes in good optical yield [789]. The chiral Grignard reagent, **417**, was coupled with halopyridines in the presence of [Ni(dppe)Cl$_2$], the products being investigated by CD measurements [790].



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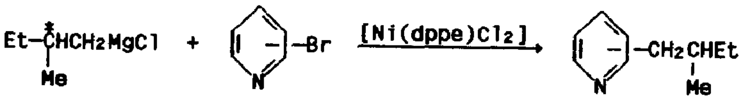

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13.9 Oligomerisation, Polymerisation and Telomerisation

The patent literature has reported the oligomerisation of ethene to 1-alkenes in the presence of $[Ni(cod)_2]/P(CH_2COOH)_3/HOCH_2CH_2OH$ [791], or $[Cp_3Ni_3(CO)_2]$ supported on SiO_2/Al_2O_3 which had been pretreated with K[OCOMe] [792]. Polyethene was produced in the presence of $TiCl_3\{AlCl_3\}_{0.33}(MgCl_2)_6NiCl_2/Et_2AlCl$ [793].

The dimerisation of propene was achieved in the presence of polystyrene functionalised with $-PEt_2$ groups, together with $[(\eta^3-C_4H_7)_2Ni]$ and Et_2AlCl. The selectivity observed was similar to that of the related soluble system. Isomerisation of the initially formed products increased as the temperature was increased [794]. The reaction mechanism has been studied [795]. The main products of dimerisation in the presence of a nickel complex of poly(2-methyl-5-ethenylpyridine), together with $EtAlCl_2$ or $(Me_2CHCH_2)_2AlCl$, were methylpentenes [796]. Oligomerisation of the C_4-alkene fraction was catalysed by Ni(OCOR)(OCOR') [797].

In the presence of $[Ni\{P(OPh)_3\}_4]/CF_3COOH$, styrene was converted to its linear dimer, $PhCH=CHCH(Ph)CH_3$, mainly as the E-isomer. The active catalyst was assumed to be a nickel hydride complex, and a π-benzyl intermediate was proposed [798]. Cationic polymerisation of styrene, 2-phenylpropene, cyclohexadiene and strained alkenes was initiated by $[Pd(MeCN)_4][BF_4]$. This complex also catalysed the polymerisation of ethyne to give a mainly *trans*, highly coloured, high molecular weight polymer [799]. A complex mixture of dimers was obtained by treatment of norbornadiene with $Pt(OCOR)_2$ [800].

The dimerisation of butadiene to 1,3,7-octatriene has been catalysed by $Pd(OCOMe)_2/PPh_3$/sorbitol monopalmitate/H_2O [801] or $PdCl_2/PPh_3$/oleic acid emulsion/Na[OH]/H_2O [802]. The autoxidation products of cod (mainly hydroperoxides and peroxide polymers) have been shown to retard the $[Ni(acac)_2]$ catalysed dimerisation of butadiene to cod. It is thought that the added triphenyl phosphite is oxidised to triphenyl phosphate, which enhances the cyclotrimerisation reaction at the expense of cyclodimerisation [803]. In the presence of $[Ni(acac)_2]/(2-EtOC_6H_4O)_3P/HAl(OCH_2CH_2OMe)_2$, butadiene was converted mainly into cod, together with small amounts of 4-ethenylcyclohexene and cyclododecatriene [804]. In the presence of $HCOOH/Pd(OCOMe)_2/Et_3N/Et_3P$/dmf the major product was 1,7-octadiene, together with the 1,6-isomer [805].

The active species in the polymerisation of butadiene in the presence of $Ni(naphthenate)_2/Et_3Al$ were studied by epr spectroscopy. Both Ni(0) and Ni(I) species were observed [806]. $NiCl_2$ on SiO_2, MgO, Al_2O_3 or $MgCl_2$ was shown to have high activity as a catalyst for the *cis*-polymerisation of butadiene [807]. *Cis*-polybutadiene was also obtained by polymerisation in the presence of a species derived from $[\{(\eta^3\text{-}C_3H_5)NiBr\}_2]$, cod and $Tl[PF_6]$ [808]. The morphology of the polymers obtained in the presence of η^3-allyl nickel halides, together with acceptors such as $TiCl_4$, has been investigated [809].

The dimerisation of isoprene to **418** (60 %) and **419** (20 %) (together with 20 % polymer) was catalysed by nickel octoate/Bu_3P/BuLi/Me_2CHOH [810]. **418** was obtained in 62 % yield from the reaction in the presence of $[Ni(acac)_2]/(Me_2N)_3P/Et_2CHOLi/Et_2CHOH$, together with 8 % **420**, and the isomerisation product, 2-methyl-2-butene [811]. Cyclodimerisation of butadiene occurred in the presence of $[Ni(acac)_2]/Et_3Al/L$ to give a mixture of 1,5-dimethyl-1,5-cyclooctadiene, 1,5,9-cyclododecatriene, **421** and **422**. Phosphites proved to give the most selective catalyst complexes [812].

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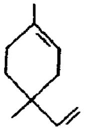

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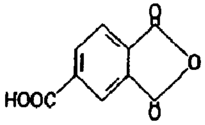
$CF_3-C\equiv C-H$ was polymerised using $PdCl_2$/dmf as the catalyst system, but reaction times were long and yields were low [813]. Using similar conditions $HC\equiv CCOOH$ gave a mixture of a linear polymer and **423**, and $HC\equiv CCOOMe$ reacted similarly [814]. Various isomers of **424** underwent exclusive cyclotrimerisation in the presence of $[Pd(PhCN)_2Cl_2]$ [815]. Chelate complexes of nickel, palladium and copper with *N*-(sulphonyl)salicylaldimines were synthesised, and their activities were determined for the oligomerisation of 3-methyl-1-butyn-3-ol [816]. Reaction (68) was reported to be catalysed by $[Ni(PPh_3)_4]$, but the reaction mechanism was not discussed [817].



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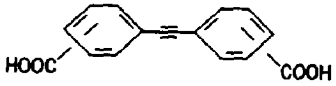

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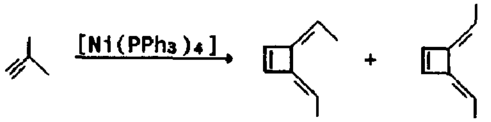
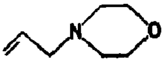


(68)

The copolymerisation of ethyne and butadiene has been reported in several closely related patents; the catalyst was prepared from nickel naphthenate, Et_2AlCl and H_2O [818-821].

The oxidative coupling of arenes by thallium(III) trifluoroethanaote was catalysed by palladium ethanoate. Using PhR (R = Me, Et Cl or OMe) as the substrate, there was high selectivity for coupling at the 4-position. The partial rate factor for coupling at the 4-position was correlated with σ^+, with a ρ value of -6.2, indicating an electrophilic mechanism for substrate activation [822]. Oxidative coupling using $Na_2[S_2O_8]$ in air was also catalysed by palladium ethanoate; in a carbon monoxide atmosphere ArCOOH was formed [823].

The reaction of morpholine with propadiene in the presence of $PdCl_2/PPh_3$ has been studied. The simple addition products, **425**, and **426** and propadiene oligomers were obtained, but the major product was **427**, which could be obtained in up to 95 % yield under optimal conditions [824].



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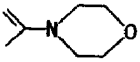

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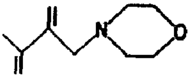

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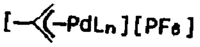
Telomerisation of butadiene with methanol has been reported to occur in the presence of **428**. Variation of the reaction conditions allowed the production of longer chain telomers such as **429** and **430** in substantial yields [825]. The telomerisation of isoprene with phenol in the presence of $[Pd(dba)_2]$ gave phenoxydimethyloctadienes in 45-55 % yield. The products included a head-to-head dimer, which is not normally found in the products of telomerisations with simple alcohols [826].



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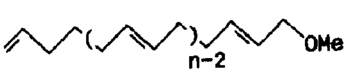
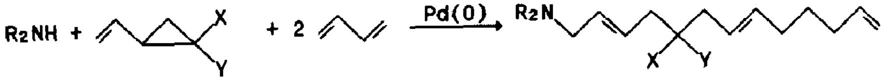


429 *n* = 2 or 4

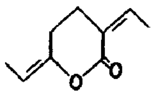
430 *n* = 2,4 or 6

Telomerisation of butadiene with a dialkylamine in the presence of a vinylcyclopropane yielded 431 [827].



431

Reaction of ArMgBr with butadiene in the presence of various nickel complexes yielded $ArCH_2CH{=}CH(CH_2)_3CH{=}CH_2$. Catalyst activities were in the order $[Ni(PPh_3)_2Cl_2]$ > $[Ni(dppe)Cl_2]$ > [Ni(dppe)(acac)] > $[Ni(acac)_2]$ [828]. A patent has described the telomerisation of butadiene and CO_2 (30 bar) in the presence of $[Pd(PPh_3)_2(hydroquinone)]/PPh_3$/hydroquinone/*N*-ethyl piperidine/MeCN to give a mixture of 432, 433 and 434 [829]. Telomerisation with propanone gave mixtures of 435, 436, 437 and 438. The catalyst was formed *in situ* from $Pd(OCOMe)_2$ and R_3P; the best catalysts were derived from trialkylphosphines, although the distribution of products varied widely. The mechanism of formation of 435 and 438 was thought to involve 439 and 440 [830]. The reaction of butadiene with propenoic acid in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$ proved rather complex. The Diels Alder product was partially telomerised with further butadiene to give 441, and the expected linear and branched telomers, 442 and 443, were also obtained [831].



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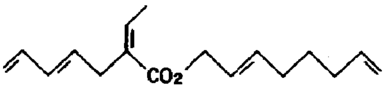

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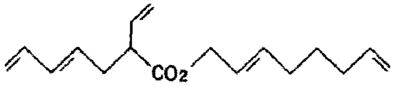

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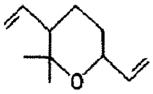

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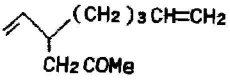

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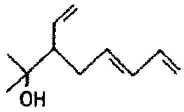

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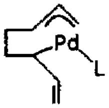

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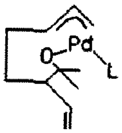

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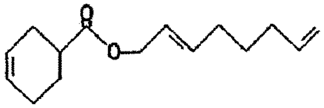

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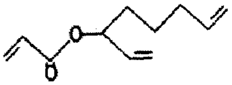
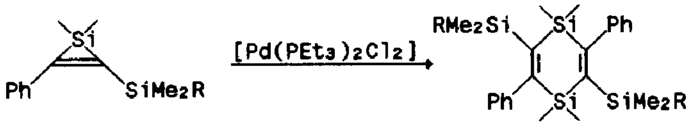


443

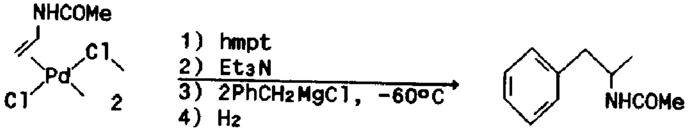
Dimerisation of **444** in the presence of [Pd(PEt$_3$)$_2$Cl$_2$] gave **445** [832]. Polyisobutene reacted with maleic anhydride in the presence of nickel(II) iodide to give polyisobutenesuccinic anhydride [833].



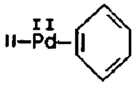
444 **445**

13.10 Miscellaneous Coupling Reactions

The reaction of the palladium alkene complex, **446**, with a Grignard reagent has been used in the synthesis of *N*-ethanoylamphetamine, **447** [834]. Chlorobenzene reacted with ethene in the presence of an excess of zinc metal and $NiCl_2$ as the catalyst to give a mixture of styrene and benzene. The proportion of stryrene increased with temperature, and if a very large excess of zinc was used some biphenyl was also produced [835]. The coupling of ethene and benzene to give Ph_2CHCH_3 was achieved electrochemically in the presence of a nickel complex; it was proposed that a species such as $\{Ni(0)Br\}^-$ was the active species, and that σ-aryl nickel complexes were intermediates [836]. Oxidative coupling of benzene and ethene occurred in the presence of $Pd(OCOMe)_2$, and a kinetic study was undertaken. The rate controlling step involved the conversion of **448** to **449** [837]. Reaction of PhMgBr with $RC{\equiv}C\text{-}CH{=}CH_2$ in the presence of $[Ni(acac)_2]$ gave a mixture of the stereoisomers of $RC(Ph){=}CHCH{=}CH_2$. Epr spectroscopy implied that the reaction followed an electron transfer mechanism [838].



446 **447**



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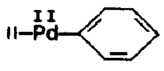
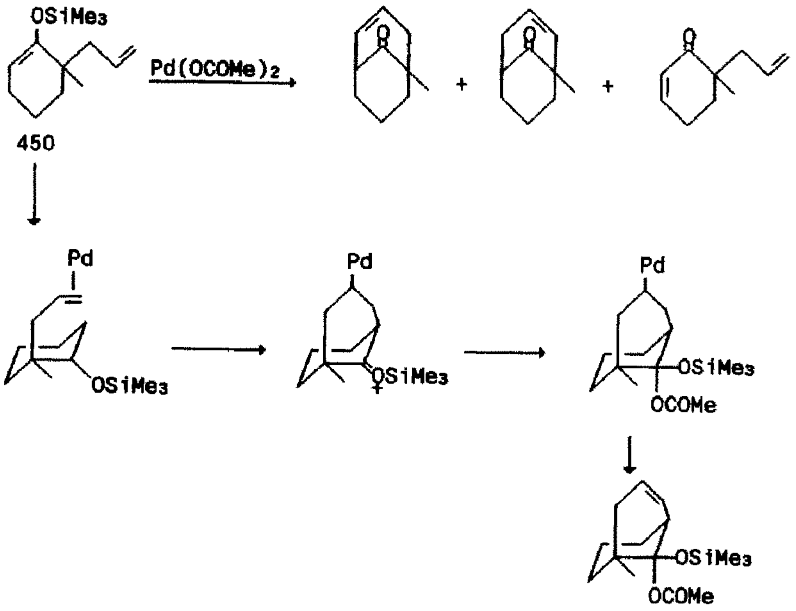


449

It had earlier been proposed that the both the cyclisation and enone forming reactions of **450** involved the intermediacy of a common, desilylated oxo-π-allyl complex. However, it has now been shown that the cylisation proceeds *via* the mechanism of Scheme 14 [839]. The related reaction of **451** has also been noted [848].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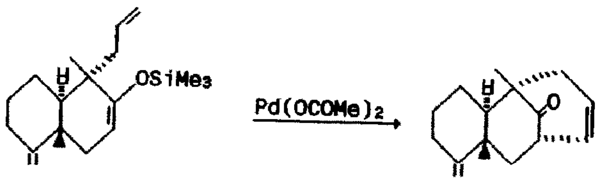
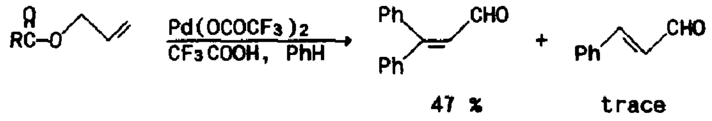
Scheme 14 Mechanism of cyclisation of **450** [839]


451

Acyl-oxygen fission and phenylation of **452** (R = Me or Ph) gave mainly **453**. Addition of sodium ethanoate resulted in an increase in yield, and the reaction was catalytic in palladium in the presence of benzoquinone as a reoxidising agent [841].

The reactions of arylmercury compounds with enones have been shown to be catalysed by $PdCl_2$ under phase transfer conditions. This reaction has now been applied in the synthesis of 2-chromanols and 2-chromenes (Scheme 15) [842]. The $[Ni(acac)_2]$ catalysed reaction of carbanions with levoglucosene gave products suchs as **454** [843].



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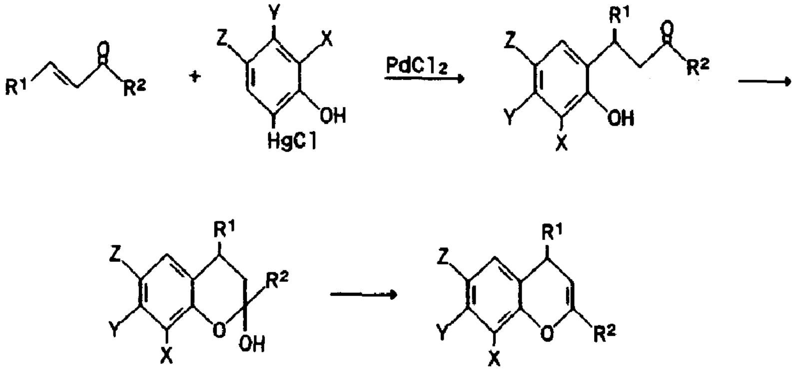
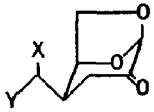


Scheme 15 Palladium catalysed reactions of organomercury compounds



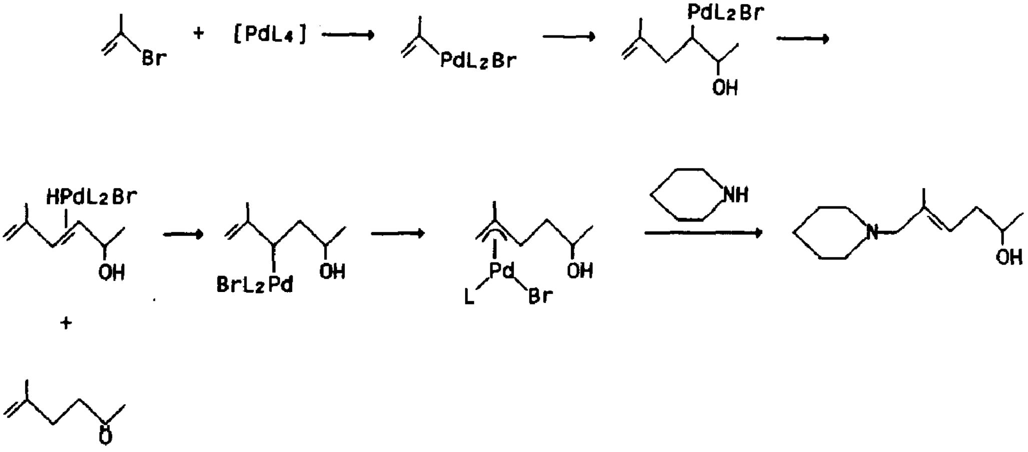
454

There has been a major review of the Heck reaction [844]. The reactions of alkenyl bromides with allyl alcohols and amines has been investigated and the reaction mechanism established (Scheme 16). Many examples (reaction (69)) were given [845]. The arylation and alkenylation of 1,4-dienes has also been studied in detail (Scheme 17, reaction (70)) [846].

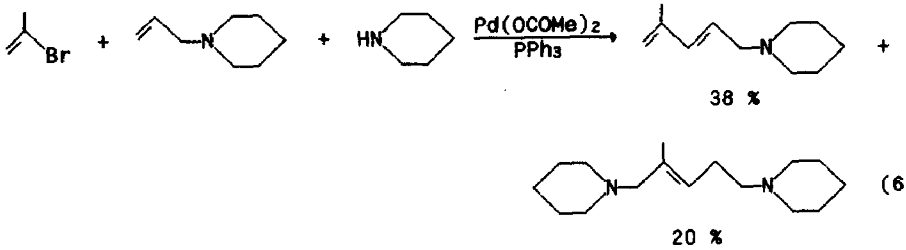
Halogenated enones, such as **455**, have been coupled with alkenes in the presence of $[Pd(PPh_3)_4]$ and/or $[Pd(dba)_2]/Et_3N$ [847].

The reaction of ArCOCl with alkenes, $RCH{=}CH_2$, in the presence of $Pd(OCOMe)_2/Et_3N/Bu_3N$ gave mainly E-ArCH=CHR, *via* the mechanism of Scheme 18. The major competing reaction was that of the addded base with the ArCOCl, and this could be largely avoided by the use of $PhCH_2NMe_2$ [848]. Two patents have also noted this reaction [849,850].

The coupling of an aryl iodide with ethenyltrimethylsilane to give $ArCH{=}CH_2$ occurred in the presence of $Pd(OCOMe)_2/PPh_3$ [851]. 2-Ferrocenylpropenenitriles have been prepared by the palladium catalysed coupling of ferrocenylmercury compounds with propenenitrile [852].



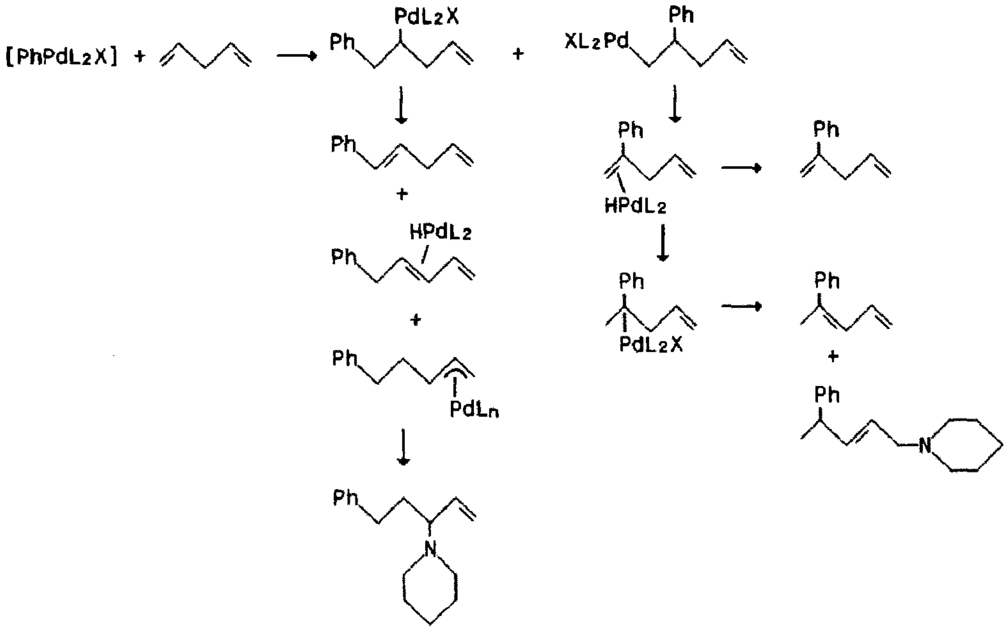
Scheme 16 Mechanism of the palladium catalysed reaction of alkenyl bromides with allyl alcohols and amines.



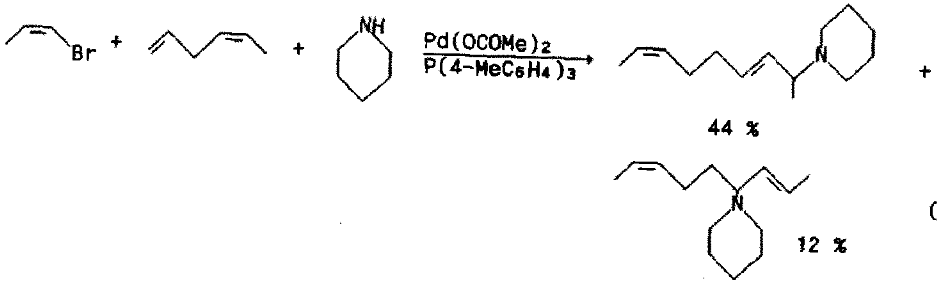
(69)

Several papers have reported the substitution of aryl halides by $HP(=O)(OR)_2$ to give $ArP(=O)(OR)_2$, in the presence of $[Pd(PPh_3)_4]$. The initial step is likely to be oxidative addition of the aryl halide to palladium(0), and alkenyl halides reacted similarly [853-855]. Oxidative addition of the carbon-halogen bond to palladium was also thought to be the initial step in the cyclisation of **456**, although the overall yields of the reaction were low [856]. Initial oxidative addition is also crucial to reactions (71) and (72) [857,858].

Several papers from Chiusoli's group have discussed the addition of alkenylpalladium derivatives to strained alkenes. In reaction (73) the major product was a cyclopropane since there was no facile β-hydride elimination pathway available [859]. If the reaction was undertaken in the presence of an excess of norbornene (Scheme 19) the intermediate ethenylpalladium complex reacted with this to give **457** [860]. In the presence of an alkyne and a base, the intermediate palladium complex was substituted to give the product of *cis*-addition to the norbornene (reaction (74)) [861].



Scheme 17 Mechanism of palladium catalysed arylation of 1,4-dienes



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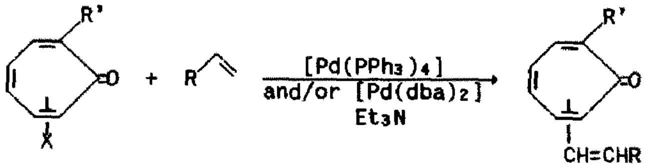
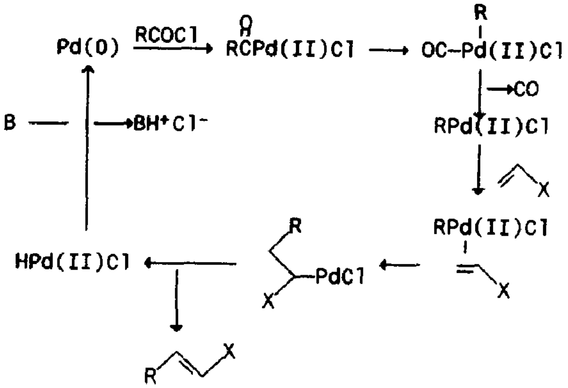
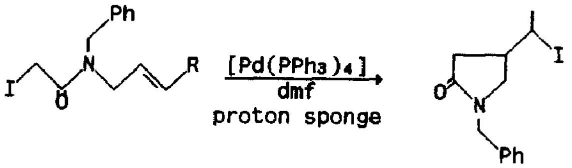


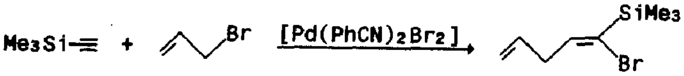
455



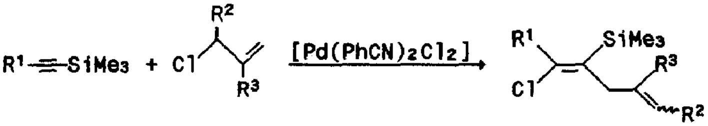
Scheme 18 Mechanism of palladium catalysed couplings of ArCOCl with alkenes [848].



456



(71)



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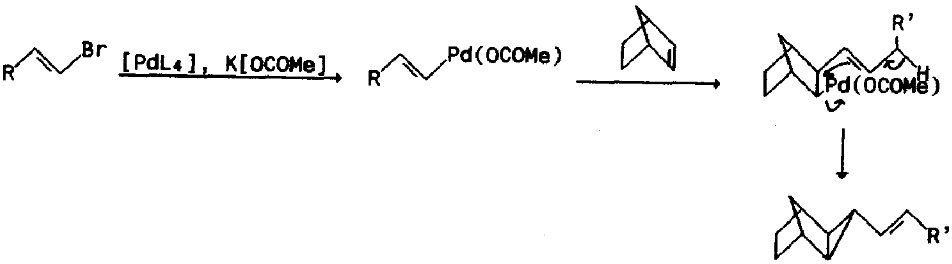

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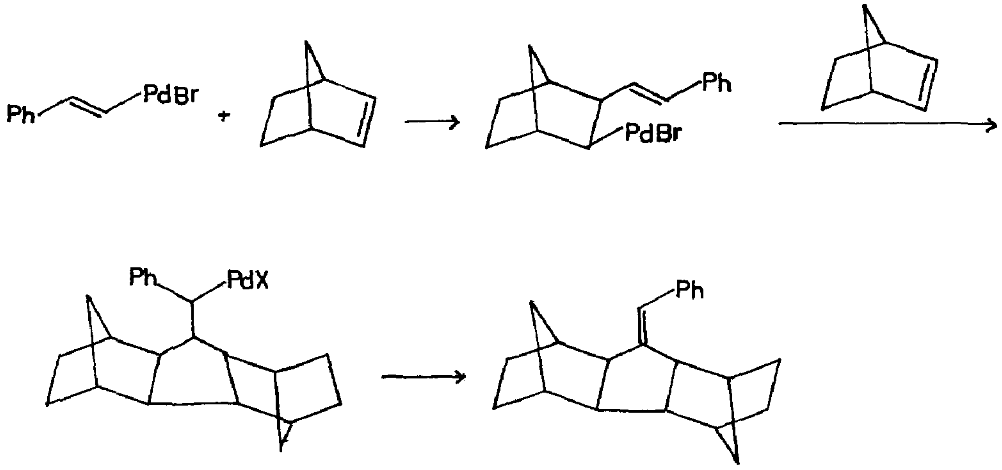
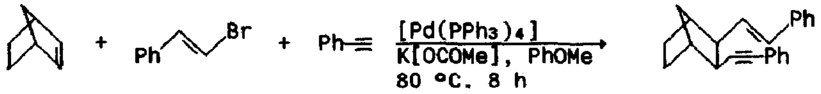


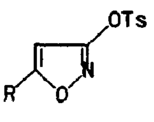
457

Scheme 19 The mechanism of palladium catalysed reaction of alkenyl halides with an excess of norbornene [860].



(74)

The oxidative coupling of **458** with benzene in the presence of $Pd(OCOMe)_2/Cu(OCOMe)_2$/dmso gave **459**, which was used in a synthesis of muscimol [862]. Nickel complexes of polyfluorinated β-diketones, monothio β-diketones and β-aminoenones have been used as catalysts for the nucleophilic substitution of heterocyclic quinones [863]. The cyclisation of **460** was reported in the presence of $PdCl_2/Ag[BF_4]/Et_3N$, but the yields were relatively low and the rôle of the catalyst was not well-defined [864].



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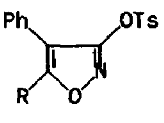
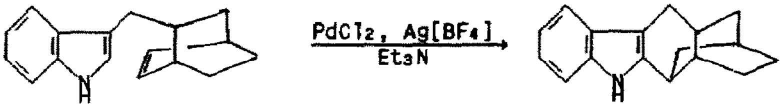


459

Thermolysis of $Me_3COC\equiv COCMe_3$ gave **461**, which was converted to semisquaric acid, **462**. However, in the presence of $[Pd(MeCN)_2Cl_2]$, **463** was produced [865]. [2+2] Cycloaddition of **464** with propenenitrile in the presence of $[Ni(cod)_2]$

or $[Ni(CH_2=CHCN)_2]$ gave **465** and **466**. The reaction was thought to proceed *via* a bis(alkene) nickel complex [866]. The reactions of the vinylcyclopropenes, **467** and **468**, with alkenes in the presence of palladium complexes have been studied. In all cases the two starting materials gave essentially the same products, indicating that the intermediate was a palladium trimethylenemethane complex [867].



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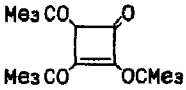

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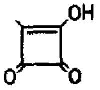

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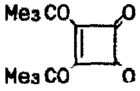


463

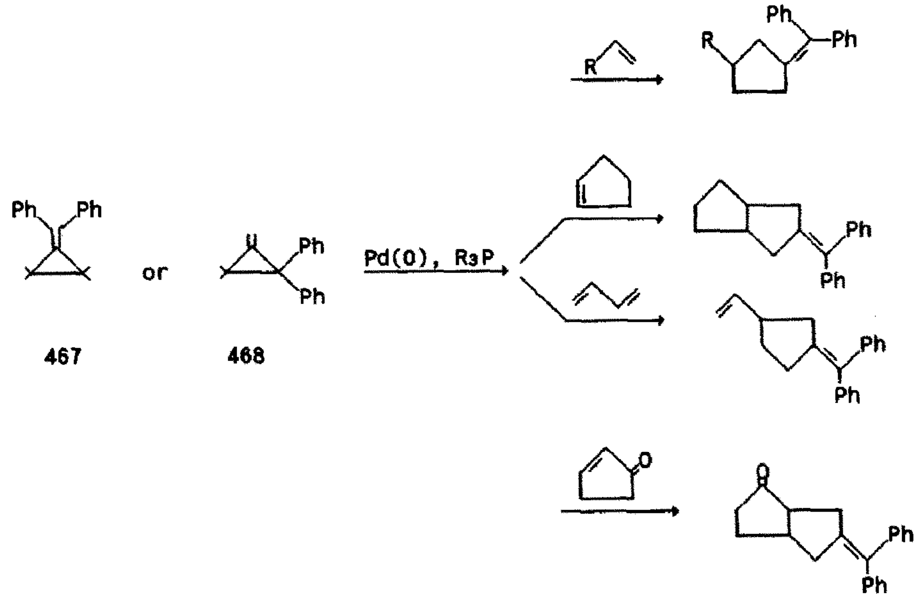
464

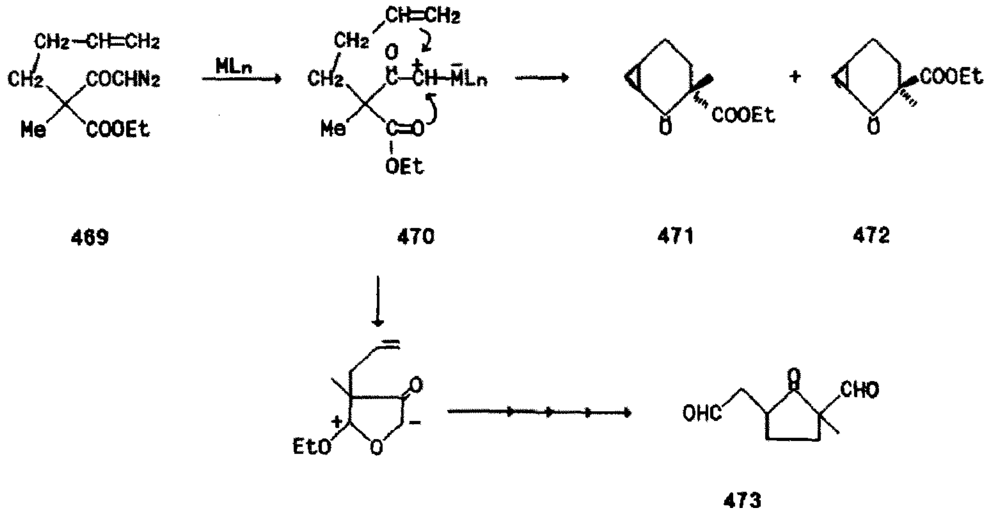
465

466

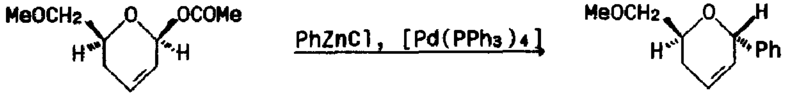
The reaction of the diazo comound, **469**, with metal complexes has been investigated, and the first intermediate proposed was the ylid, **470**. Two pathways were open to this intermediate, giving respectively **471** and **472**, or (*via* a polycylic intermediate) **473**. When the added metal complex was $[\{(\eta^3-C_3H_5)PdCl\}_2]$ the main products were **471** and **472**, with **473** formed in the presence of rhodium complexes [868].

The reaction of nickel metal with aryl halides has led to the production of biaryls. The intermediates were assumed to be "$\{Ar_2Ni\}$" and one of these species could be trapped as $[Ar_2Ni(PEt_3)_2]$ for Ar = C_6F_5 [869]. The reaction of $PdCl_2$ with $PhCH_2MgCl$ resulted in the formation of PhMe (30 %), $PhCH_2CH_2Ph$ (38 %), and a trace of E-PhCH=CHPh. The reaction in the presence of "$PtCl_4$" was similar, but gave less $PhCH_2CH_2Ph$ and more E-PhCH=CHPh [870].

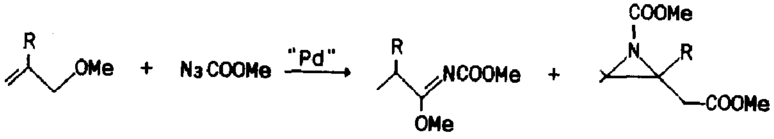




The reaction of 474 with RZnCl in the presence of [Pd(PPh$_3$)$_4$] was reported to give 475, *via* a mechanism involving palladium hydride elimination [871]. Treatment of 476 with N$_3$COOMe in the presence of palladium complexes gave mixtures of **477** and **478**. **477** was obtained in up to 95 % selectivity when $[Pd(PhCN)_2Cl_2]$ was used as the catalyst [872,873]. The mechanism previously proposed for reaction (75) involved the cleavage of a phosphorus-carbon bond by Pd(II). This proposal has now been revised in the light of a study of the reaction kinetics and solvent effects, with a suggestion of a process in which oxidative addition was the key step. Whilst this seems to be in accord with the data, it is extremely complex and it is clear that other, equally likely, schemes could be devised [874].



474 **475**



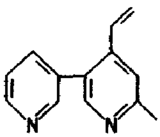
476 **477** **478**

$$PPh_3 + Pd(OCOMe)_2 + PhCH{=}CH_2 \xrightarrow{1)48\ h,\ 25\ ^\circ C;\ 2)[HO]^-;\ 3)H^+} E\text{-}PhCH{=}CHPh +$$

$$E\text{-}PhCH{=}CHOCOMe + Ph_2P({=}O)(OH) + PhP({=}O)(OH)_2 + H_3PO_4 + Ph_3P{=}O \quad (75)$$

13.11 Other Catalytic Reactions

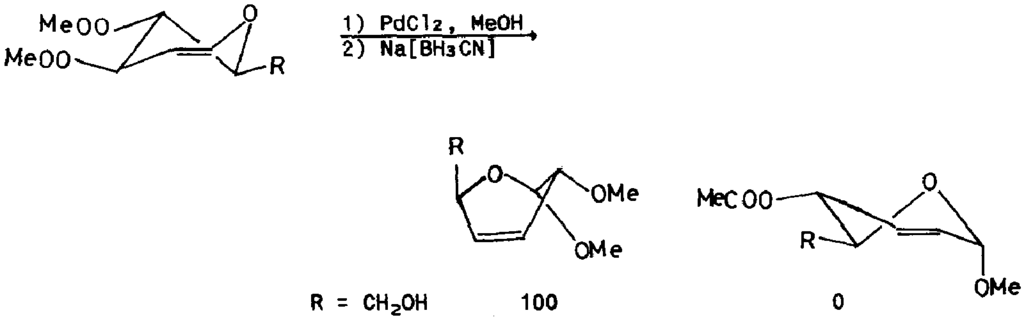
Poly(**479**), when reacted with $Pd(OCOMe)_2$, gave a catalyst for the reaction of PhCOOH with $CH_2{=}CHOCOMe$ to give $PhCOOCH{=}CH_2$ [875]. A similar reaction was reported in the presence of $PdCl_2/K[OCOMe]/CuBr_2$ [876]. Reaction of phenylmethanol with $[Pd(PhCN)_2Cl_2]$ gave $\{PhCH_2OPd\}$, which on treatment with ROH gave an ether. Enols could be similarly converted to enol ethers [877].



479

The chlorination of alkanes, mainly at the 1-position, was reported to be catalysed by a range of platinum(II) complexes [878]. Dehydrochlorination of chloroalkenes occurred in the presence of supported palladium complexes as the catalysts [879]. Dehydrogenation of hexane over metals on active carbon in the presence of $H_2[PtCl_6]$ was selective for hexene [880].

Reaction (76) has been reported to proceed with good chirality transfer, presumably *via* a π-allyl palladium complex. The regioselectivity depended on the nature of the substituent R [881].



R = CH_2OH	100	0
CH_2CN	100	0
CH_2OCOMe	85	15
H	0	100

In the presence of $[PhCH_2Pd(PPh_3)_2Cl]$ and R'_3SnX thf reacted with acyl chlorides to give $RCOO(CH_2)_3CH_2Cl$. Allyl and benzyl ethers were similarly reactive and a mechanism was proposed [882]. Oximes were reported to react with CH_2Cl_2 in the presence of $K[O_2]$ and an allyl palladium halide complex to give $RR'C{=}NOCH_2ON{=}CRR'$ [883].

Catalytic deoxygenation of PhNSO in the presence of [Ni(bipy)(cod)] gave PhN=S=NPh [884]. Reaction of PhCl with $[Ni\{N(CH_2CH_2PPh_2)_3]$ gave $[Ni(I)\{N(CH_2CH_2PPh_2)Cl]$ and a phenyl radical, which underwent a range of hydrogen abstraction, coupling and disproportionation reactions [885].

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15 ABBREVIATIONS

acacH	pentane-2,4-dione
Ar	aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bipy	2,2'-bipyridine
S,R-BPPFA	S-1-[R-1',2-bis(diphenylphosphino)ferrocenyl]ethyl dimethylamine
Bu	butyl
CD	circular dichroism
cdt	cyclododecatriene
CHIRAPHOS	2S,3S-bis(diphenylphosphino)butane
cod	1,5-cyclooctadiene
cot	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
dba	E,E-1,4-diphenyl-1,4-pentadiene-3-one
DBP	dibenzophosphole
DBPDIOP	*trans*-4,5-bis(dibenzophospholomethyl)-2,2-dimethyl-1,3-dioxolan
dibaH	di*iso*butyl aluminium hydride
DIOP	*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan
dmf	*N*,*N*-dimethylmethanamide
dmso	dimethylsuphoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,1-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
DTA	differential thermal analysis
EHMO	extended Huckel molecular orbital
en	1,2-diaminoethane

Et	ethyl
hfacacH	1,1,1,5,5,5-hexafluoropentane-2,4-dione
hmpt	hexamethyl phosphoric triamide
HOMO	highest occupied molecular orbital
ImH	imidazole
INDO	intermediate neglect of differential overlap
ir	infra-red
L	2 electron donor ligand
Me	methyl
mes	2,4,6-trimethylphenyl
MLCT	metal to ligand charge transfer
MO	molecular orbital
nbd	bicyclo[2.2.1]hepta-2,5-diene
NBS	*N*-bromosuccinimide
nm	nanometre
nmr	nuclear magnetic resonance
Np	2-naphthyl
PES	photoelectron spectroscopy
Ph	phenyl
phen	1,10-phenanthroline
PhAlaH	phenyl alanine
S,R-PPFA	S-1-[R-2-diphenylphosphinoferrocenyl]ethyl dimethylamine
Pr	propyl
PVC	polyvinyl chloride
py	pyridine
pzH	pyrazole
R	alkyl
R_f	perfluoroalkyl
tfacac	1,1,1,trifluoropentane-2,4-dione
tfaH	trifluoroethanoic acid
thf	tetrahydrofuran
tht	tetrahydrothiophene
tmeda	*N,N,N',N'*-tetramethyl ethane-1,2-diamine
$TPPH_2$	*meso*-tetraphenylporphyrin
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
X	one electron donor ligand, usually halide
XPES	X-ray photoelectron spectroscopy