NICKEL, PALLADIUM AND PLATINUM, ANNUAL SURVEY COVERING THE YEAR 1981*

Penny A. Chaloner
School of Chemistry and Molecular Sciences
University of Sussex
Falmer, Brighton, UK

---

* Nickel, Palladium and Platinum, Annual Survey covering the year 1980, see J. Organomet. Chem., 324 (1987) 283-446.

1 INTRODUCTION

This survey details the accounts of the organometallic chemistry of nickel, palladium and platinum published in 1981. Material from the patent literature which was reported in Chemical Abstracts in 1981 is also included, and the organisation remains broadly the same as in past surveys. The number of papers published in this area has increased, the area of greatest growth being the use of palladium complexes to catalyse transformations in synthetic organic chemistry [1-3].

A number of reviews of general interest have appeared. Nickel compounds and their chemical uses have been described [4,5] and annual surveys of the coordination chemistry of nickel [6], palladium and platinum [7] for 1979 have been published. Complexes of the platinum metals containing weak donor ligands have been discussed [8] as has the applied chemistry of these groups [9]. So called "ligand-free" platinum complexes were considered by Stone [10], and the ^{195}Pt nmr spectroscopy of a wide range of complexes reviewed [11]. General discussions of organic reactions of π-complexes [12], carboranes in organic synthesis [13], physical organic studies of organometallic reactions [14] and nitrogen nmr spectroscopy in organometallic and bioinorganic chemistry [15] have all included references to complexes of the nickel triad. ^{31}P nmr spectroscopy of transition metal complexes has also been considered from several viewpoints [16,17].

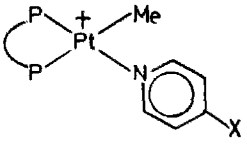
2 METAL CARBON σ-BONDED COMPLEXES

Nickel crystallites formed by clustering of metal atoms in alkane matrices at low temperatures have been studied. Nickel alkyls were formed during decomposition [18].

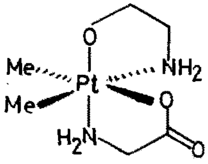
X-ray diffraction data for both *trans*-$[MePt(PEt_3)_2Cl]$ [19] and *trans*-$[MePt(PPh_3)_2Cl]$ [20] have been presented. The platinum-carbon bonds were found in both cases to be similar to those in analogues, and a long platinum-chlorine bond attested to the *trans*-influence of the methyl group. Reaction of $[MePt(\overset{\frown}{P\ P})Cl]$ ($\overset{\frown}{P\ P}$ is a chiral chelating phosphine) with 4-substituted pyridines gave the cationic complexes 1. ^{31}P nmr spectroscopic data for these species could be correlated with ρ_{para} [21].

Further evidence for the *trans*-effect of the methyl group was obtained from the X-ray diffraction data for **2** and **3**. In **2** the Pt-N and Pt-O bonds *trans* to the methyl group were determined to be respectively 2.18 Å and 2.14 Å long, with the Pt-N and Pt-O bonds *cis* to a methyl group measuring

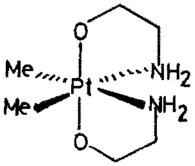
2.07 Å and 2.01 Å [22]. Similar data were established for **3** [23]. The structure of $[MeNi(PMe_3)_4][BPh_4]$ was shown to involve a slightly distorted trigonal bipyramid with the methyl group axial. The distortion involves a shift of the nickel atom towards the axial phosphine on the geometrical reaction path corresponding to homolysis of the nickel methyl bond [24]. Protonation of **4** by $H[BF_4]$ gave **5**, the structures of both complexes being established by diffraction studies. The distance between the two palladium atoms in 5 was shown to be intermediate between that expected for bonded and non-bonded interactions [25].



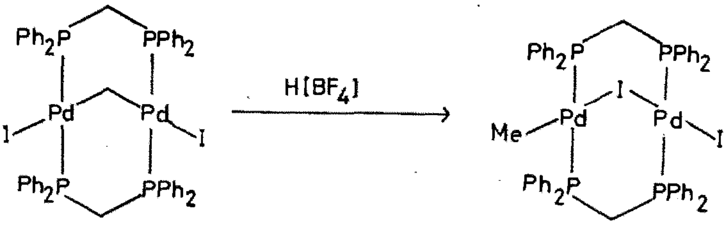
1



2



3

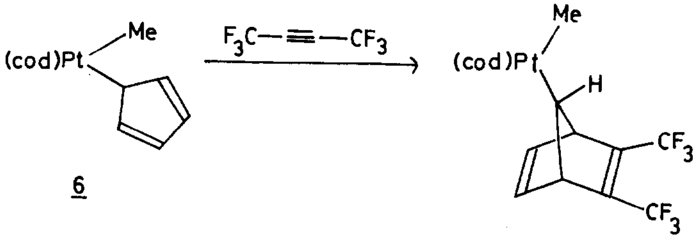


4

5

In **6** it was shown that the palladium alkene bond *trans* to η^1-Cp was shorter than that *trans* to the methyl group [26]. A Diels Alder reaction with CF_3-C≡C-CF_3 gave **7** in which the Pt-alkene bonds are of comparable length, suggesting similar *trans*-effects for the two σ-alkyl groups. Alkyne approach was from the opposite side of the diene to platinum, indicating that the reaction is sterically controlled and that the metal did not participate [27].

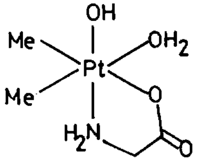
An X-ray diffraction study of *cis*-$[EtPt(PEt_3)_2Cl]$ indicated a Pt-P bond length of 2.21 Å for the phosphine *trans* to chlorine and 2.35 Å for the phosphine *trans* to carbon, once again due to the high *trans*-influence of an alkyl group [28]. The structure of *trans*-$[CF_3Pt(PPh_3)_2Cl]$ was also determined [29].



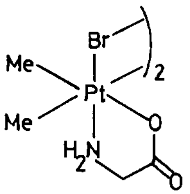
6

7

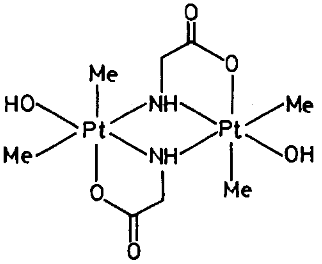
It was hoped that an improved preparation of **8** would result from treatment of 9 with hydroxyl ion. However, **10** was formed instead, and was proved to be the first stable platinum(IV) complex with an amido bridge [30]. The cationic complex, 11, was synthesised by reaction of $[MePt(cod)(acetone)][PF_6]$ with the tridentate ligand. Addition of further ligands, L, including CO, alkenes and alkynes, gave trigonal bipyramidal, five-coordinate species with L equatorial and Me axial, the dynamic behaviour of which was investigated by nmr spectroscopy [31]. Both chloride and phosphine could be displaced by $[CN]^-$ from *trans*-$[MePt(PEt_3)_2Cl]$ in the presence of 18-crown-6, yielding $[MePt(CN)_3]^{2-}$ [32].



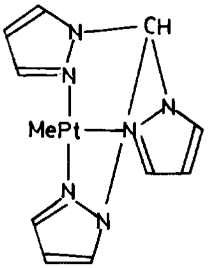
8



9



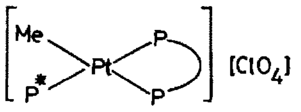
10



11

The variable temperature nmr spectroscopic studies of DL-[$(Me_3PtX)_2(MeSCH_2SeMe)$] established accurate energy barriers for three dynamic processes, *viz.* ligand ring reversal, pyramidal inversion of sulphur and selenium, and ligand commutation between platinum atom pairs with scrambling of the platinum-methyl environments [33]. The new complex [$(Me_3PtCl)_2(SCH_2SCH_2SCH_2)$] was synthesised and was also found to be fluxional on the nmr spectroscopic timescale. X-ray diffraction studies indicated that the trithian adopts a boat conformation. Two dynamic processes were distinguished. The lower energy process involved a series of 60° pivots of the cyclic ligand about individual S-Pt bonds, which averaged the ligand methylene and equatorial platinum-methyl environments. At higher temperatures dissociation and recombination resulted in scrambling of the platinum methyl groups [34-36].

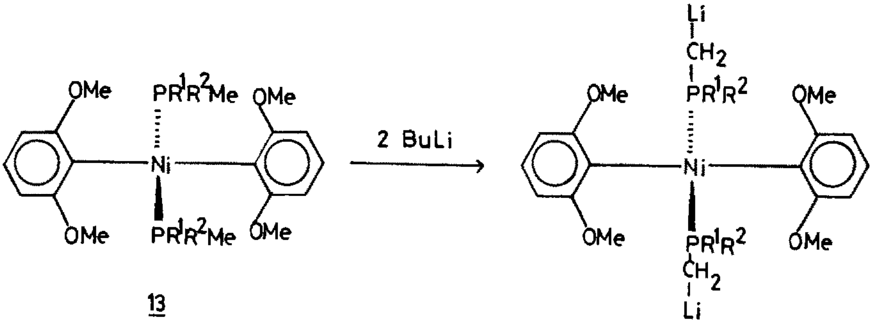
Molecular orbital studies of $^1J(^{195}Pt-^{31}P)$ and $^1J(^{195}Pt-^{195}Pt)$ in platinum phosphine complexes included consideration of $[MePt(PR_3)_3]^+$ [37]. In 12, in which $\widehat{P\,P}$ is a chiral bidentate phosphine and P* is a chiral but racemic phosphine, diastereoisomers could be distinguished and a partial resolution effected. The configuration of the preferentially bound enantiomer ($\widehat{P\,P}$ = CHIRAPHOS, P* = $PhPMe(CH_2Ph)$) was determined by X-ray diffraction and ORD studies [38]. MCD and solution electronic absorption data were recorded at 298 K for *cis*-[$MePt(PEt_3)_2X$], *cis*-[$R_2Pt(PEt_3)_2$] and *trans*-[$RPt(PEt_3)_2X$] (R = Me or Et; X = Cl or Br). Electronic absorption spectra were obtained at 77 K in glassy solution for *cis*-[$Me_2Pt(PEt_3)_2$], *cis*-[$MePt(PEt_3)_2Cl$] and *trans*-[$RPt(PEt_3)_2Cl$]. All the spectra showed intense absorptions assigned to MLCT from a platinum 5d orbital to the empty phosphorus 3d orbitals of the PEt_3 ligands [39]. XPES of platinum complexes including [$Me_2Pt(PEt_3)_2$], [$Me_2Pt(dppm)$], [$Me_2Pt_2(\mu-H)(\mu-dppm)_2$] and [$Me_3Pt_2(\mu-dppm)_2$][$SbF_6$] were reported [40].



12

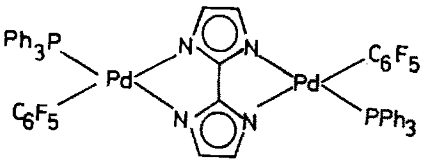
Twenty-one new nickel(II) complexes, *trans*-[$RR'Ni(PR''_3)_2$], and *trans*-[$RNi(PR''_3)_2L$][ClO_4] (R = C_6Cl_5, 2,4,6-$Me_3C_6H_2$, or $Cl_2C{=}C(Cl)-$; L = 3-substituted pyridine; PR''_3 = PMe_2Ph, PMe_3 or $PMePh_2$) have been synthesised [41]. Treatment of [$(C_6Cl_5)Ni(PR_3)_2Cl$] with Na[ClO_4] in the presence of L (pyridine or substituted pyridine) gave $[(C_6Cl_5)Ni(PR_3)_2L]$, $[(C_6Cl_5)NiL_2(PR_3)]$ or $[(C_6Cl_5)Ni(PR_3)_3][ClO_4]$, the product obtained depending principally on solubility in the medium used [42]. Lithiation of **13** to give 14 was readily accomplished using *n*-butyl lithium. It seems likely that the OMe groups enhance reactivity or stabilise the lithiated complex by chelation [43].

Treatment of $[Bu_4N]_2[(C_6F_5)_4Pd_2(\mu\text{-}Cl)_2]$ with L (L = PR_3, $P(OR)_3$ or $PhCH_2NH_2$) gave *cis*-$[Bu_4N][(C_6F_5)_2PdLCl]$. An excess of L yielded *cis*-$[(C_6F_5)_2PdL_2]$ [44]. $[Bu_4N][(C_6F_5)_2Pd(acac)]$ could be prepared in an analogous reaction using Tl[acac], and reacted with $H_2(N\text{-}N)_2$ ($H_2(N\text{-}N)_2$ = H_2BiIm or $H_2BiBzIm$)) to give $[Bu_4N]_2[(C_6F_5)_4Pd_2\{\mu\text{-}(N\text{-}N)\}_2]$. A similar process occurred with $[(C_6X_5)Pd(acac)(PPh_3)]$ giving products such as 15, the related *trans*-structure being ruled out by nmr spectroscopic data [45].$[BiBzIm]^{2-}$ has also been used to bridge different metal centres as in **16** [46].



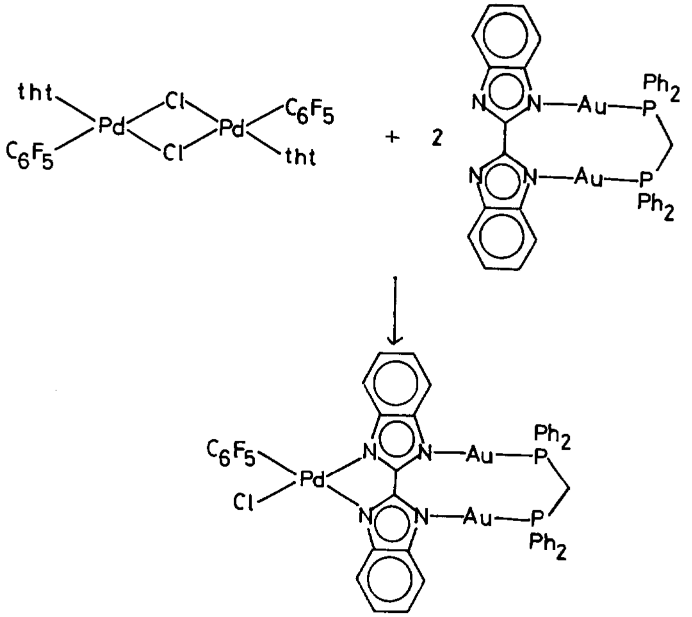
13

14



15

Reaction of $[(C_6Cl_5)Au(PPh_3)]$ with $[Pt(PPh_3)_3]$ resulted in the transfer of the haloaryl group to platinum to give $[(C_6Cl_5)Pt(PPh_3)_2\text{-}Au(PPh_3)]$, and the reaction could best be described as an insertion into the carbon-gold bond [47].

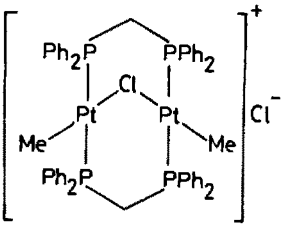


16

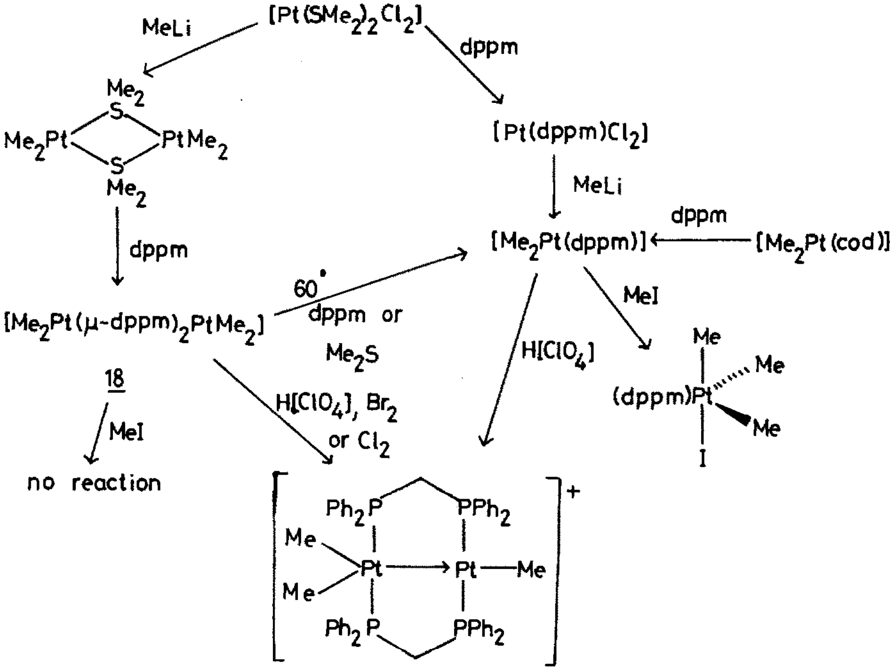
The displacement of halides or other appropriate leaving groups from complexes of the nickel triad by alkyls of electropositive metals is a long-established route for synthesis of alkyl derivatives, and a number of new examples have been reported this year. *Trans*-[$HM(PR_3)_2Cl$] (M = Pd or Pt; R = Cy, Et or *i*-Pr) reacted with MeMgBr to give [$HM(Me)(PR_3)_2$]. The rate of reductive elimination of methane depended on the nature of R [48]. Treatment of [$Pt(dppm)Cl_2$] with MeLi gave [$Me_2Pt(dppm)$], which reacted with HCl to give [HPt(dppm)Cl] and **17**, now isolated in a pure state for the first time. This was characterised spectroscopically, and had earlier been thought to be a non-ionic trimer [49]. Further syntheses of [$Me_2Pt(dppm)$] and some of its reactions were investigated (Scheme 1). An X-ray diffraction study of **18** revealed a Pt-Pt distance of 4.36 Å, and the eight-membered ring adopts a twist-saddle conformation [50]. The monosubstituted complex [$CF_3Ni(PEt_3)_2Br$] could be isolated on treatment of [$Ni(PEt_3)_2Br_2$] with [$(CF_3)_2Cd$], and palladium and platinum analogues were similarly prepared. A second substitution occurred more slowly [51].

Reaction of [$Ni(py)_2Cl_2$] with Me_3SiCH_2MgCl gave the rather unstable species [$(Me_3SiCH_2)_2Ni(py)_2$] which was shown to have *cis*-stereochemistry by an X-ray diffraction study. The pyridine ligands could be readily replaced by monodentate phosphines or by chelating amines or phosphines.

In solution the PMe_3 and PMe_2Ph complexes exist as a mixture of *cis*- and *trans*-isomers, but in the solid state an X-ray diffraction study revealed *trans*-stereochemistry for $[(Me_3SiCH_2)_2Ni(PMe_3)_2]$ [52]. $[Ni(dppe)Cl_2]$ was converted to $[(Me_3SiCH_2)_2Ni(dppe)]$ using Me_3SiCH_2Li, and the product thermolysed to yield $Me_3SiCH_2CH_2SiMe_3$ [53].



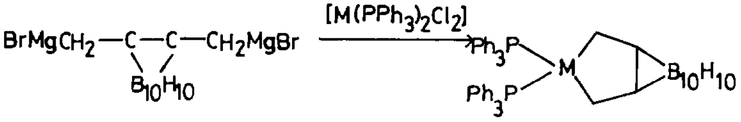
17



Scheme 1 Preparation and reactions of $[Me_2Pt(dppm)]$ [50]

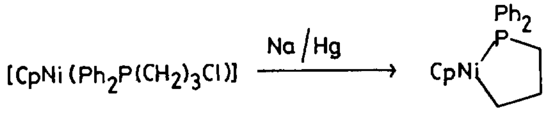
Reactions of two borane substituted Grignard reagents have been reported by Soviet workers. What is described as o-m-$RCB_{10}H_{10}CCH_2MgX$ reacted with

$[CpNi(PPh_3)Cl]$ to give $[\sigma\text{-}(o\text{-},m\text{-}RCB_{10}H_{10}CCH_2)Ni(Cp)(PPh_3)]$ [54]. **19** reacted with $[M(PPh_3)_2Cl_2]$ to give **20** [55]. In neither case do the authors adopt conventional nomenclature for their boranes, nor do they provide structural diagrams through which the interested reader might discern the structure of the ligands for himself.



19 20

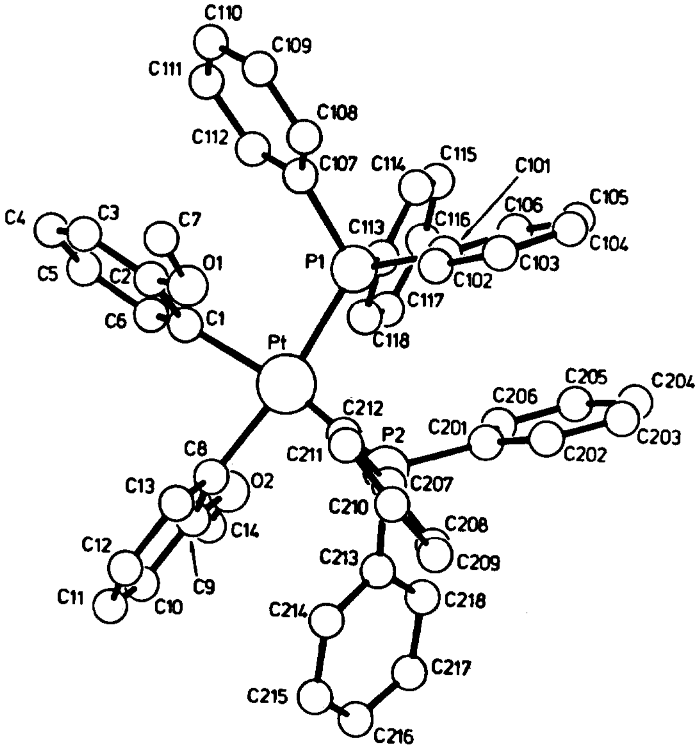
In an intramolecular reaction of this type, **21** reacted with sodium amalgam to give **22** [56].



21 22

σ-Aryl complexes may be synthesised by similar routes, and **23**, characterised by X-ray diffraction, was prepared from *cis*-$[Pt(PPh_3)_2Cl_2]$ and $[2\text{-}MeO\text{-}C_6H_4]Li$ [57]. On treatment with R_2Hg in the melt, the species *trans*-$[RPt(PPh_3)_2Cl]$ were formed in good to excellent yields ($R = 2,5\text{-}Cl_2C_6H_3$, 2,3,4- or $2,4,6\text{-}Cl_3C_6H_2$, 2,3,4,5-, 2,3,4,6- or $2,3,5,6\text{-}Cl_4C_6H$ or C_6Cl_5) [58]. Reaction of $[Ni(cod)_2]$ with $[(2,4,6\text{-}Me_3C_6H_2)_3V]$ was reported to give a species of stoicheiometry $[NiV_2(2,4,6\text{-}Me_3C_6H_2)_6]$ [59]. $K_2[PtCl_4]$ reacted with C_6F_5MgBr to give the unstable intermediate, $[(C_6F_5)_2Pt]$, which was trapped by a range of ligands L as $[(C_6F_5)_2PtL_2]$ (L = NH_3, PPh_3, $AsPh_3$, $SbPh_3$ Ph_3PO or Ph_3AsO) [60]. Similar reactions were noted for the palladium analogue, with the intermediate isolable as $[(C_6F_5)_2Pd(dioxan)_n]$ (n = 1, 2 or 3) [61].

Oxidative addition of organic halides, usually to metal(0) complexes, has again been a popular route for the synthesis of σ-bonded species. The reactions of $[Ni(PCy_3)_2]$ with RX (R = Me, Et, Pr or Ph; X = halide or CN) all involved fission of the RX bond. With R = Et the major product isolated was ethene, together with some butane, whilst longer chain alkyl groups gave mainly alkenes Two processes appear to occur simultaneously. The initial product is $[RNi(PCy_3)_2X]$, which may β-hydride eliminate to give alkenes and $[HNi(PCy_3)_2X]$ or may follow the path or reactions (1) - (5) [62]. When the complex used was $[Ni(bipy)(PPh_3)_2]$ the major nickel containing species isolated was $[Ni(I)(bipy)(PPh_3)X]$. Reactions (6) - (10) were implicated by the electrochemical data [63].



23 (Reproduced with permission from [57])

$$[\mathrm{Ni(PCy_3)_2}] + \mathrm{RX} \longrightarrow [\mathrm{RNi(PCy_3)_2X}] \tag{1}$$

$$[\mathrm{RNi(PCy_3)_2X}] \longrightarrow [\mathrm{Ni(I)(PCy_3)_2X}] + \mathrm{R}\cdot \tag{2}$$

$$[\mathrm{HNi(PCy_3)_2X}] + \mathrm{R}\cdot \longrightarrow [\mathrm{Ni(I)(PCy_3)_2X}] + \mathrm{RH} \tag{3}$$

$$[\mathrm{HNi(PCy_3)_2X}] + [\mathrm{RNi(PCy_3)_2X}] \longrightarrow 2[\mathrm{Ni(PCy_3)_2X}] + \mathrm{RH} \tag{4}$$

$$[\mathrm{RNi(PCy_3)_2X}] \longrightarrow [\mathrm{HNi(PCy_3)_2X}] + \text{alkene} \tag{5}$$

$$[\mathrm{Ni(bipy)(PPh_3)_2}] \rightleftharpoons [\mathrm{Ni(bipy)(PPh_3)}] + \mathrm{PPh_3} \tag{6}$$

$$[\mathrm{Ni(bipy)(PPh_3)}] + \mathrm{RX} \longrightarrow [\mathrm{Ni(I)(bipy)(PPh_3)}]^+[\mathrm{RX}]^- \tag{7}$$

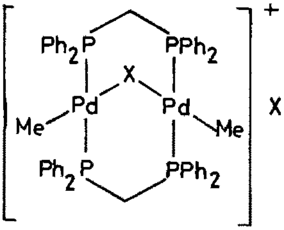
$$[\mathrm{Ni(I)(bipy)(PPh_3)}]^+[\mathrm{RX}]^- \longrightarrow [\mathrm{RNi(I)(bipy)(PPh_3)X}] + \mathrm{R}\cdot \tag{8}$$

$$\begin{aligned}[\mathrm{Ni(I)(bipy)(PPh_3)}]^+[\mathrm{RX}]^- + [\mathrm{Ni(bipy)(PPh_3)}] \longrightarrow {} & [\mathrm{RNi(I)(bipy)(PPh_3)}] + \\ & [\mathrm{Ni(I)(bipy)(PPh_3)X}]\end{aligned} \tag{9}$$

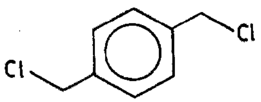
$$2[\mathrm{RNi(I)(bipy)(PPh_3)}] \longrightarrow [\mathrm{Ni(bipy)(PPh_3)_2}] + [\mathrm{R_2Ni(bipy)}] \tag{10}$$

Oxidative addition of iodomethane to aged solutions of [Pt(PR$_3$)$_2$] and [Pt(PR$_3$)$_3$] was followed spectrophotometrically. [Pt(PR$_3$)$_2$] reacted more rapidly, and trialkyl phosphine complexes were more reactive than those of triaryl phosphines [64]. [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] reacted with a range of compounds RCHXY by oxidative addition to give mixtures of *cis*- and *trans*-[(RCHX)Pt(PPh$_3$)$_2$Y] (X, Y = halogen; R = H or Br). The *cis*-complexes were converted entirely to the *trans*-species on heating. Some scrambling indicated the involvement of radicals [65], which were also implicated in the photoinduced oxidative addition of CH$_2$Cl$_2$, yielding *cis*- and *trans*-[(ClCH$_2$)Pt(PPh$_3$)$_2$Cl] and *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] [66]. Addition of RCHX$_2$ to [Pd$_2$(μ-dppm)$_3$] gave [Pd$_2$(μ-dppm)$_2$(μ-CHR)X$_2$] (R = H or Me; X = Cl, Br or I). The halides could be replaced by ligands such as py or MeNC but the palladium-carbon bond resisted the insertion of CO or isocyanides. Halomethanes, however, gave **24**, and the dynamic behaviour of this and the other complexes was investigated by nmr spectroscopy [67].

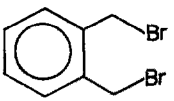
Benzylic halides including **25a** and **25b** reacted with [Ni(C$_2$H$_4$)(PPh$_3$)$_2$] and [Ni(cod)(PCy$_3$)] to give the products of simple oxidative addition [68]. 2-Chloromethylfuran reacted similarly with [Pd(PPh$_3$)$_4$] to give **26**, which was converted to **27**, **28** and **29**. η^3-Complexes of the type **27** were only stable in the presence of σ-donor/π-acceptor ligands such as phosphines [69].



24

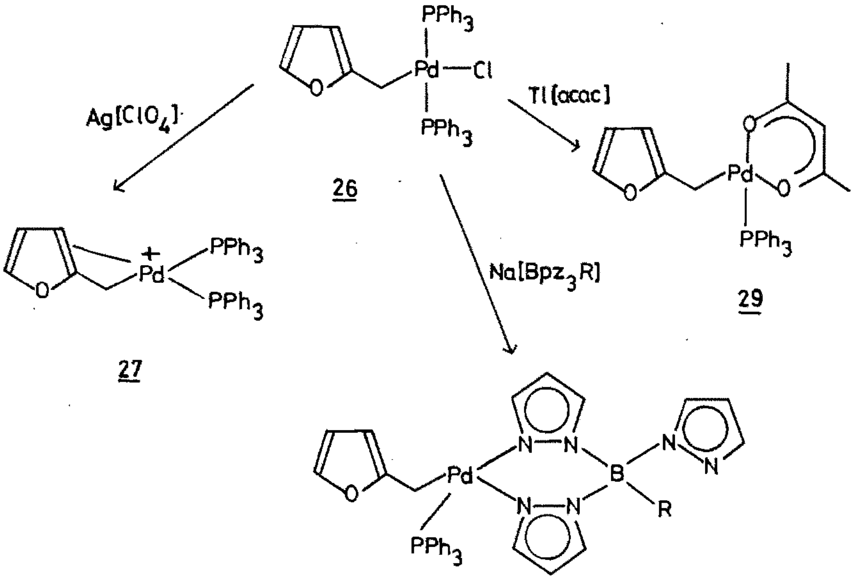


25a



25b

The kinetics of oxidative addition of aryl iodides to palladium(0) in thf in the presence of PPh$_3$ was studied electrochemically. The reaction rate correlated with σ, with a ρ value of +2.0, implying that the reactions are nucleophilic aromatic substitutions with some assistance from an I-Pd interaction [70]. Addition of 2-halopyridines and 2-halopyrazines to [Pd(PPh$_3$)$_4$] proceeded in good yield at 90 °C, yielding binuclear species such as **30**, identified by X-ray diffraction. 3- and 4-halopyridines gave *trans*, mononuclear species, which were relatively stable, unlike their nickel analogues. The product of addition of 2-chloromethylpyridine was less stable, but again binuclear (**31**, identified by X-ray diffraction). Carbonylation of all these species proceeded easily to give palladium acyls such as 32 [71]. 2,6-Dichloropyridine was also reactive, yielding **33** which was converted to $[Pd\{C_5H_3(6\text{-}Cl)N\text{-}C^2\}(PPh_3)_2(ClO_4)]$ on addition of $Ag[ClO_4]$. Bridge splitting occurred with K[acac] yielding 34. In the presence of base *cis*⟶*trans* isomerisation of **34** occurred *via* five-coordinate intermediate [72].

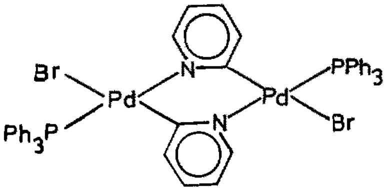


26

27

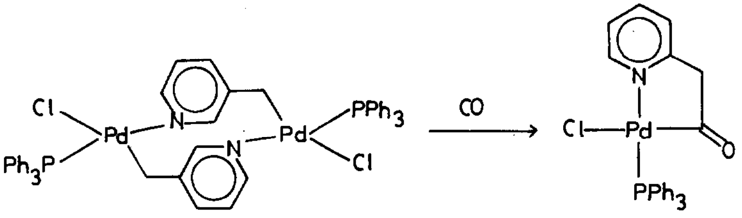
29

28



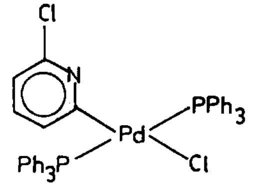
30

The reaction of β-diketonate anions with **35** yielded **36** and related complexes [73], and the analogous reaction (11) (R = $CHNO_2$, CHCN, CHCOMe or CHCOPh), performed *in situ*, was also useful in the synthesis of σ-alkyl derivatives of acidic methylene groups [74].

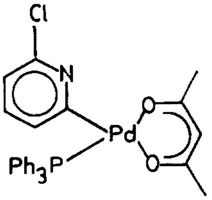


31

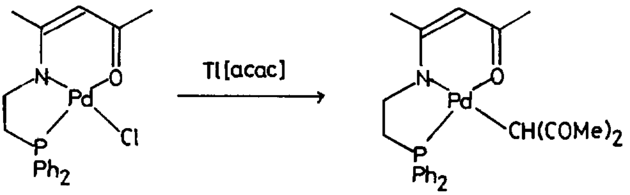
32



33



34

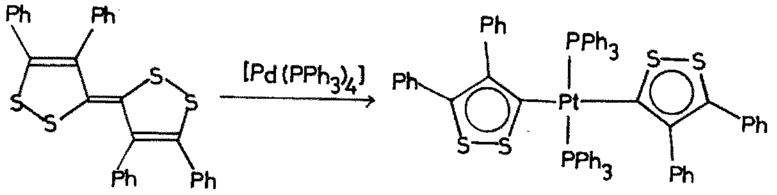


35

36

$$[PtL_2Cl_2] + RH + KOH \xrightarrow{18\text{-crown-6}} [RPtL_2Cl] \qquad (11)$$

$[Pt(PPh_3)_4]$ reacted with **37** to give **38**, the mechanism of the reaction being open to speculation [75]. Palladium or nickel atoms may be condensed at -196 °C with CF_3 radicals to give $[M(CF_3)_2]$. The dialkylpalladium compound has a finite lifetime at room temperature, but $[(CF_3)_2Ni]$ was appreciably less stable. Both could be trapped with PMe_3 at -78 °C [76].



37

38

Several preparative routes to $[Me_3Pt_2(\mu\text{-dppm})_2]^+$ have now been described in detail (reactions (12) - (15)). The complex was isolated and its structure, **39**, determined by X-ray diffraction. The molecule exhibits an unusual class of heteropolar metal-metal bonding involving donation from the filled d_{z^2} orbital of the more substituted platinum into a vacant acceptor orbital of the $\{PtP_2Me\}^+$ unit [77].

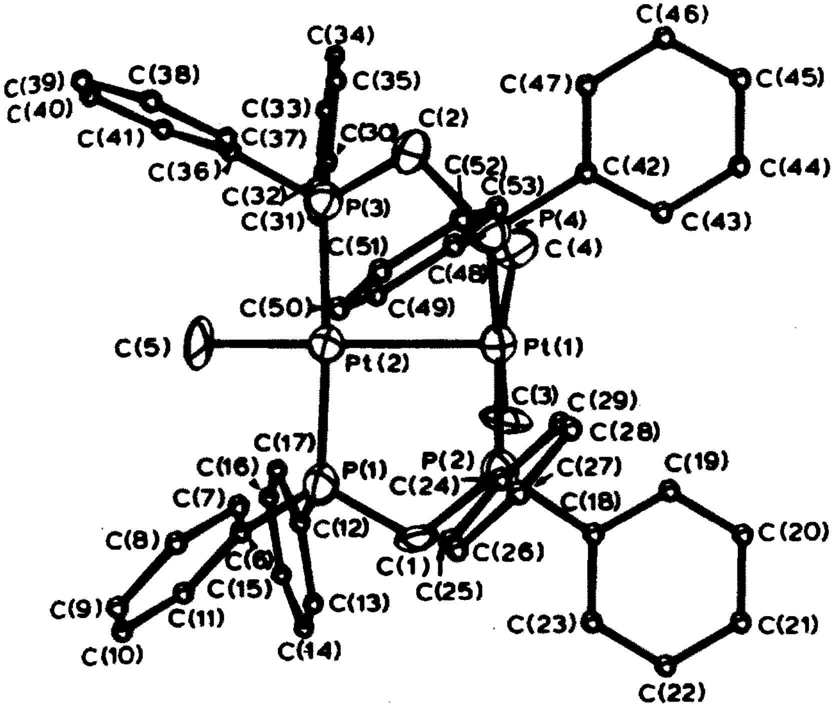
$$[Me_2Pt(dppm)] + [Pt(dppm)Cl_2] \longrightarrow 2[MePt(dppm)Cl] \tag{12}$$

$$[Me_2Pt(dppm)] + [MePt(dppm)Cl] \longrightarrow [Me_3Pt_2(\mu\text{-dppm})_2]^+Cl^- \tag{13}$$

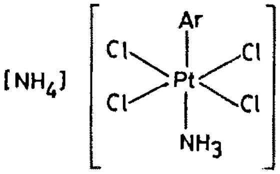
$$[Me_2Pt(dppm)] + H^+ + \text{solvent} \longrightarrow [MePt(dppm)(\text{solvent})]^+ + CH_4 \tag{14}$$

$$[MePt(dppm)(\text{solvent})] + [Me_2Pt(dppm)] \longrightarrow [Me_3Pt_2(\mu\text{-dppm})_2]^+ \tag{15}$$

Reaction of arenes with $H_2[PtCl_6]$ gave anionic σ-aryl platinum(IV) species which could be isolated as **40**, after treatment with SiO_2/NH_3. Monosubstituted arenes including $PhNO_2$, $PhCOCH_3$ and PhCOOH gave mixtures of *m*- and *p*-isomers, the reaction at the *o*-position presumably being prevented by steric hindrance. Electron withdrawing groups were shown to lower the reaction rate [78]. The reaction products from PhF, 1-chloro-2-fluorobenzene and 1-chloro-3-fluorobenzene were studied by ^{19}F nmr spectroscopy, indicating the $\{Pt(NH_3)Cl_4\}^-$ is an electron donor in both the inductive and the resonance sense [79]. The structures of the complexes formed from naphthalene (B-isomer) and 2-nitrotoluene, **41**, were determined by X-ray diffraction [80]. A considerable number of kinetic data have been accumulated, indicating that complex formation has the characteristics of an electrophilic substitution [81,82]. The *meta* and *para*-isomers of the σ-aryl platinum(IV) complex have been shown to isomerise, and multiple H/D exchange in these systems may thus be explained [83].

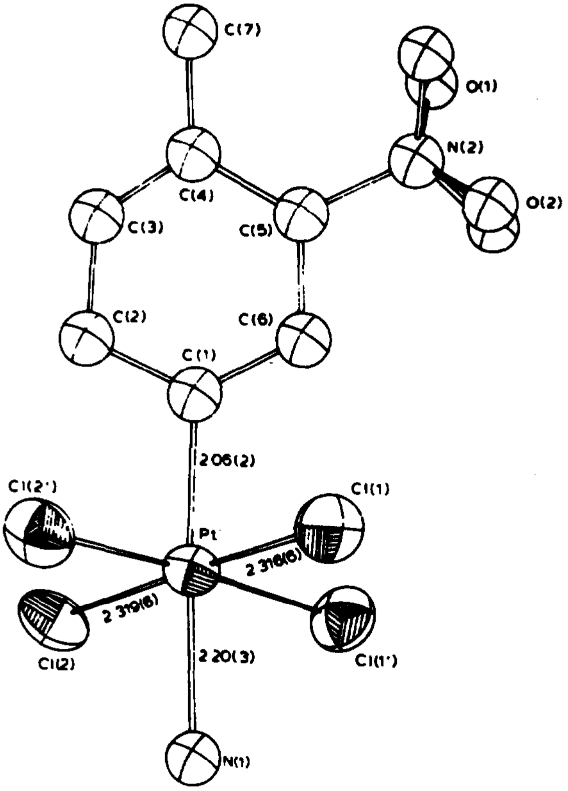


39 (Reproduced with permission from [77])

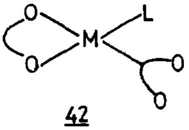


40

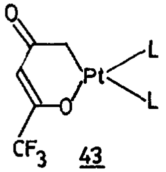
The reactions of $[M(acac)_2]$ with various ligands have been extensively studied over a number of years. One of the products which may be obtained is 42, and this type of species seems to be more favourable for palladium(II) than platinum(II), though the nature of L, particularly if it is a bulky phosphine, is also important. Species such as 42 have been characterised for the systems $[Pd(acac)_2]/PEt_3$ [84], $[Pd(acac)_2]/Me_2NH$, $PrNH_2$ or piperidine and $[Pd(tfacac)_2]$/piperidine [85]. The complex formed from $[Pd(hfacac)_2]$ and Me_2NH was characterised by X-ray diffraction; the Pd-O bond length *trans* to nitrogen was 2.002 Å long whilst that *trans* to carbon measured 2.059 Å [86]. Reaction of **42** (L = PPh_3;$\widehat{O\;O}$ = acac) with hydrogen resulted first in cleavage of the C-Pd bond, followed by O-Pd cleavage [87]. *Cis* or *trans*-[Pt(tfacac)$_2$] reacted with triaryl phosphines, L, to give initially [Pt(tfacac)L_2][tfacac] which was rapidly converted to the γ-acac complex, **43**. This was well characterised, but evidence for [Pt(acac)(γ-acac)L] and [Pt(γ-acac)$_2L_2$] was somewhat more equivocal [89].



41 (Reproduced with permission from [80])



42

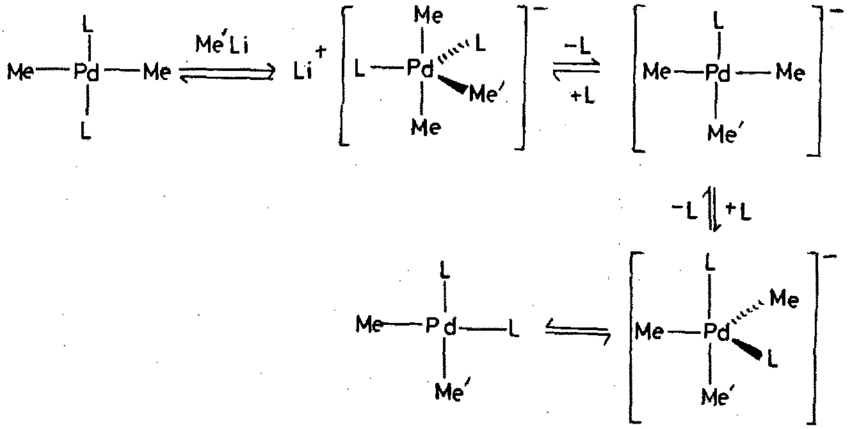


43

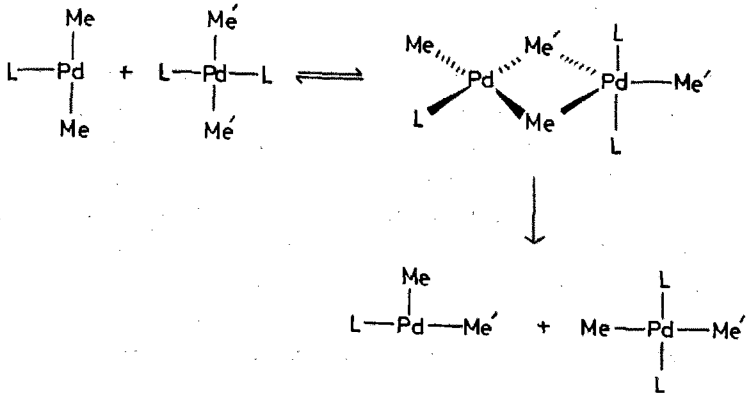
The mechanism of thermal decomposition of dialkyl bis(triethylphosphine) platinum(II) complexes has been reviewed [90]. Three theoretical studies of this process have been published. SCF X_α scattered wave calculations on $[H_2PtL_2]$, $[HPtMeL_2]$, $[Me_2PtL_2]$, $[Me_2NiL_2]$ and $[Me_2PdL_2]$ ($L = PH_3$) indicated that those species which eliminated XY readily had an occupied molecular orbital with pronounced M-X(Y) antibonding character [91]. Consideration of $[R_2M(PR'_3)_2]$ indicated that elimination was favoured by the σ-donor capacity of the leaving group, but that a strong donor *trans* to the leaving group increased the barrier to such a reaction. The barrier is also influenced by the energy of an antisymmetric b_2 orbital which in turn depends on the metal, being lower for nickel than for palladium or platinum. The T-shaped species *trans*-$[R_2PdL]$ was shown to encounter a substantial barrier in rearranging to the *cis*-isomer, which has an open channel for R-R elimination [92]. A theoretical study of the elimination of 1-butene, cyclobutane or ethene from $[L_n\overline{NiCH_2CH_2CH_2C}H_2]$ (n = 1,2 or 3) was also undertaken. In general cyclobutane formation was allowed for square planar geometry and ethene formation in the tetrahedral series, these pathways being mutually exclusive [93].

A kinetic study of the thermolysis of *cis* and *trans*-$[Me_2PdL_2]$ implied that reductive elimination occurred from T-shaped *cis*-$[Me_2PdL\}$ with the rate increasing with the σ-donor capability of the leaving group and the weakness of the donor *trans* to it. In the presence of methyl iodide elimination occurred *via* a six-coordinate platinum(IV) species, evidence for this intermediate coming from the formation of CD_3-CH_3 and CH_3-CH_3 in the presence of CD_3I [94]. Both thermolysis and isomerisation of *cis*- and *trans*-$[R_2PdL_2]$ were studied by Japanese workers. Addition of RLi gave the *cis*-compound selectively *via* the mechanism of reaction (16), which was confirmed using $LiCD_3$. Again reductive elimination of R-R was thought to occur *via* a T-shaped intermediate. The *trans*-isomer must be isomerised to the *cis*-complex before elimination, the data being accounted for by the mechanism of reaction (17) [95].

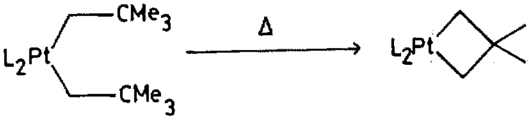
Whitesides' group have been responsible for a large range of kinetic studies on $[Et_2Pt(PEt_3)_2]$. The rate-controlling step is again loss of PEt_3 to give $[Et_2PtL\}$. The interconversion of the isomers of the T-shaped intermediates was in this case faster than reductive elimination. The principal pathway was β-hydride elimination to yield $[HPt(Et)L(C_2H_4)]$ which lost ethane and reacted with L yielding $[Pt(C_2H_4)L_2]$, thus providing a rather convenient and high yielding synthesis of this complex [96]. A detailed investigation of the dependence of the rate on the concentration of PEt_3, L, revealed that for added [L] = 0 the rate determining step was loss of ligand from $[Et_2PtL_2]$, whilst at added [L] = 0.3 M it was ethane elimination from $[HPt(Et)(C_2H_4)L]$. At still higher concentration of added ligand (~1.6 M) the rate determining step was found to be elimination of ethane from $[HPt(Et)(C_2H_4)L_2]$ [97]. The final product, $[Pt(C_2H_4)(PEt_3)_2]$ is a useful synthetic precursor, giving *trans*-$[MePt(PEt_3)_2I]$ cleanly with CH_3I [98]. When the alkyl groups attached to platinum were cyclobutyl or cyclopentyl the path followed was essentially analogous, but σ-cyclopropyl ligands gave anomalous, complex and poorly understood results [99]. Thermolysis of **44** (L = PEt_3) gave **45** with k_H/k_D = 3.0 for deuteration of the C-methyl groups. Metallation of an ethyl or propyl group to give a metallocyclopentane was more favourable (as in the reactions of **46** and **49**) and the rate controlling step was alkane loss from a complex already containing the metallocycle. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ implied that the ring strain in a platinacyclobutane is considerably lower than in cyclobutane itself [100].



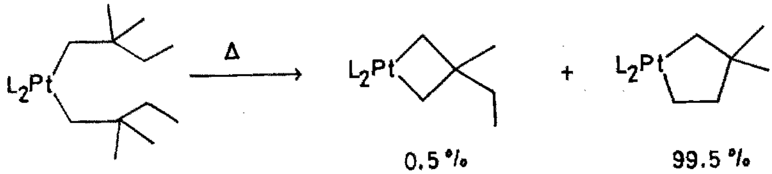
(16)



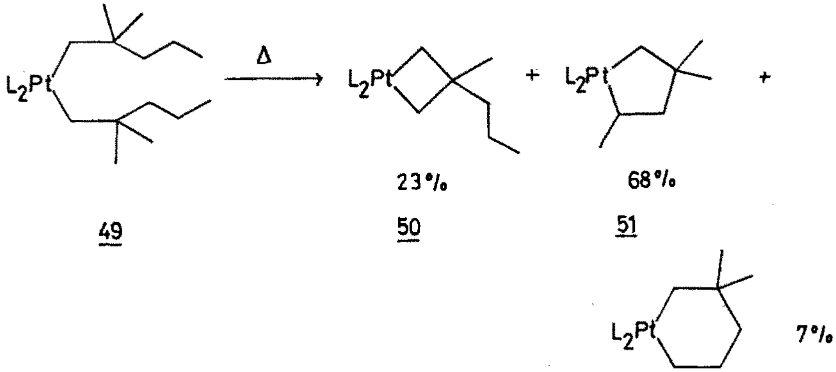
(17)



44 45



46 47 48



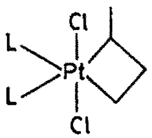
49 50 51

52

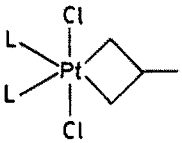
Complexes of the type [RNiL$_n$Y] were prepared by treatment of [R$_2$NiL$_2$] with HY (R = Me or Et; Y = OAr, OCOEt, OCOPh, acac, Cl or oximato; L = PEt$_3$ or bipy). The species [EtNi(bipy)Cl] disproportionated readily to give [Et$_2$Ni(bipy)] and [Ni(bipy)Cl$_2$] [101].

Interest in platinacyclobutane complexes has continued. Reaction of methylcyclopropane with [{Pt(C$_2$H$_4$)Cl$_2$}$_2$] gave [{Pt(C$_3$H$_5$Me)Cl$_2$}$_n$] which reacted with L$_2$ to give a mixture of **53** and **54**. **54** was the major isomer, though the two were readily interconverted. Thermolysis or photolysis of **53** gave the ylide **55**, formed by transfer of hydride from C_3 to C_1, followed by attack of the ligand at C_3. The rate of formation of **55** depended on L, with

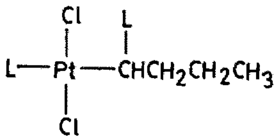
53 and **54** not isolable using the bulky ligand 2-methylpyridine. When L = CD_3CN, however, the products were alkene complexes produced either by α- or β-elimination as shown in Scheme 2 [102].



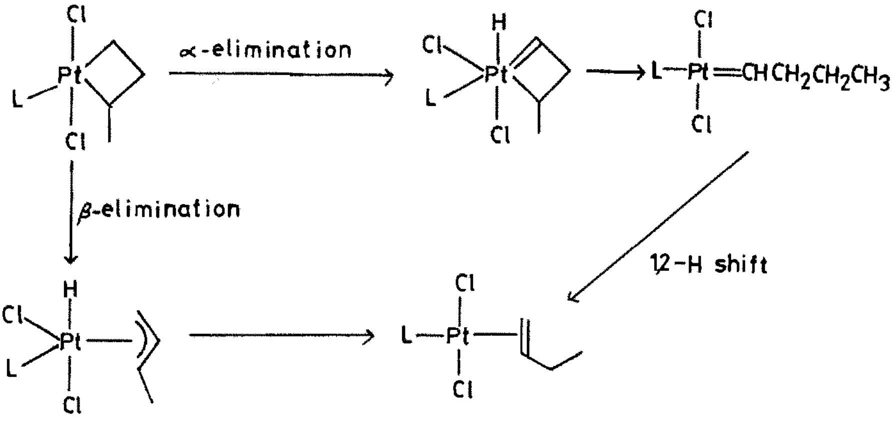
53



54

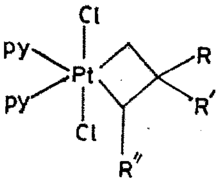


55

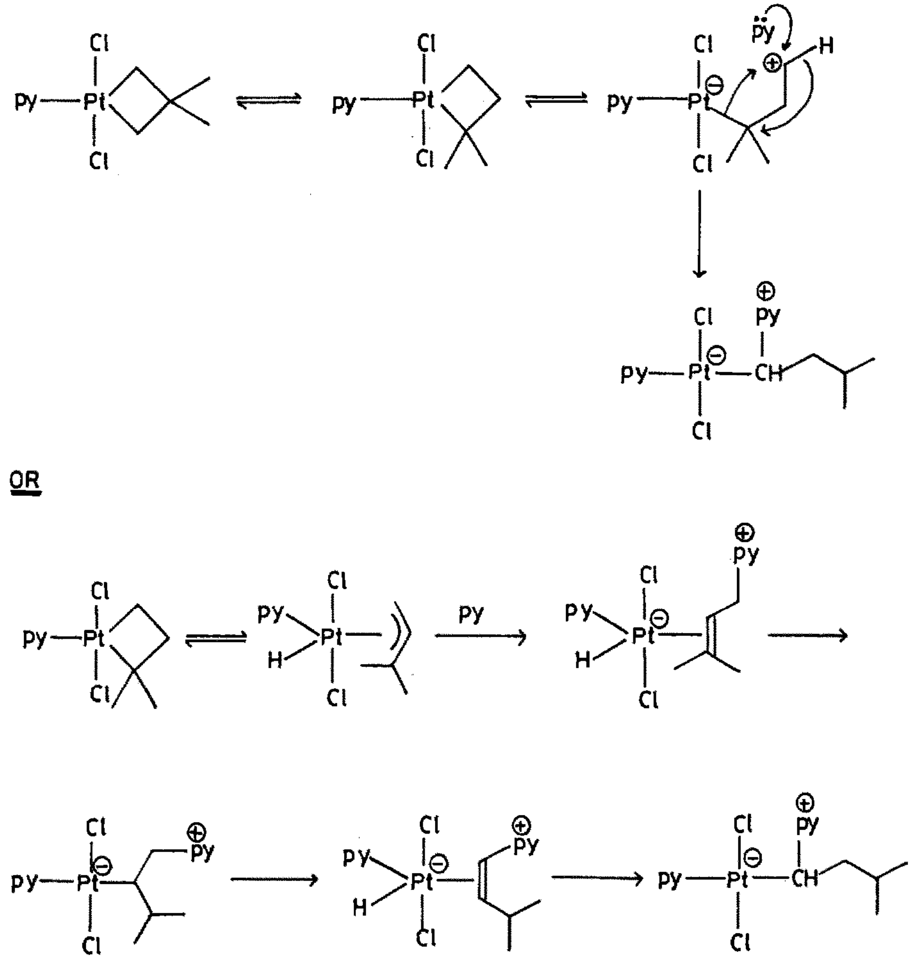


Scheme 2 Mechanisms of formation of alkene complexes from platinacyclobutanes [102].

1,1,2-Trisubstituted cyclopropanes have also been converted, by a similar path, into platinacyclobutanes such as **56**. When R = R' = R" = Me these were thermolysed to alkenes as in Scheme 2, but other complexes (for example R = Me, R' = R" = H and R = R' = Me, R" = H *etc.*) gave ylides. Several pathways were proposed including the hydride transfer scheme (favoured in [102]) and a route *via* an allyl complex (Scheme 3) [103].

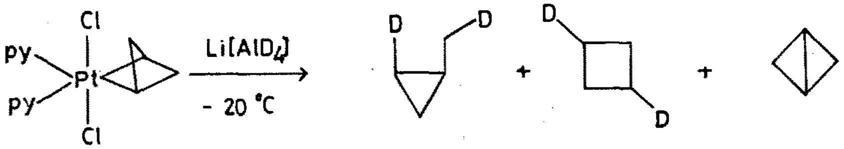


56



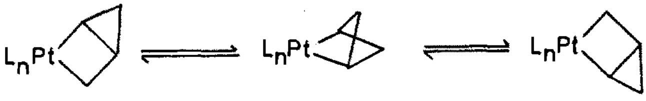
Scheme 3 Mechanisms of formation of ylide complexes from platinacyclobutanes [103]

Treatment of bicyclobutane with [{Pt(C$_2$H$_4$)Cl$_2$}$_2$] gave [{Pt(C$_4$H$_6$)Cl$_2$}$_n$] which could be depolymerised using pyridine to yield **57**, which was stable as a solid at room temperature, but decomposed in solution above -25 °C. Thermolysis of **57** gave mixtures of bicyclobutane, cyclobutene, butadiene, methylcyclopropene and methylene cyclopropane. Reaction with Li[AlD$_4$] at -20 °C gave mixtures of **58**, **59** and bicyclobutane, suggesting that **57** might be in equilibrium with **57a** and **57b** [104].



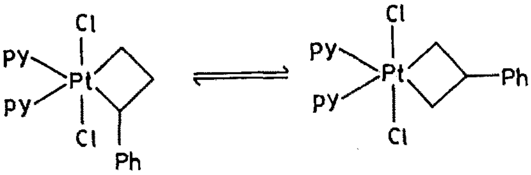
57 58 59

30 % 11 % 53 %



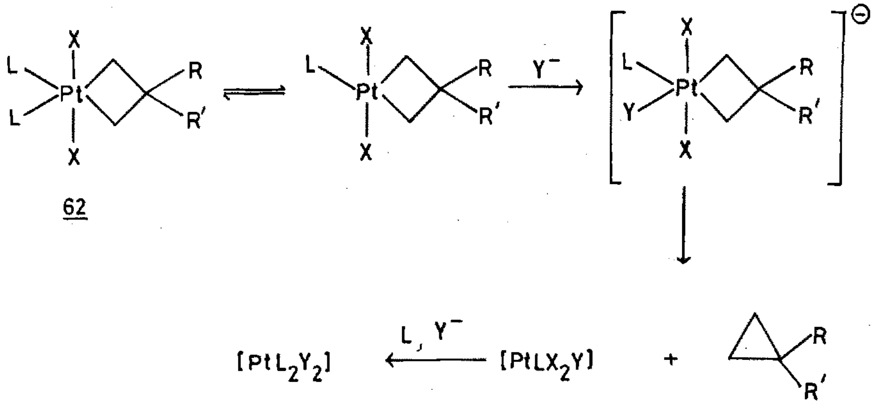
57a 57 57b

60 could be partly resolved using an optically active polymer bearing DIOP units. On thermolysis it was racemised *via* **61**, which is present at equilibrium to the extent of about 50 % of the total material [105]. Treatment of **62** with anions such as I^- or $[SCN]^-$ gave cyclopropanes. A careful study of the kinetics and the effect of additives allowed the mechanism of Scheme 4 to be proposed [106].

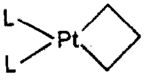


60 61

The electrochemistry of $[Pt(C_3H_6)(bipy)Cl_2]$ has been investigated. A two-electron electrochemical reduction gave $[Pt(II)(C_3H_6)(bipy)]$ which could be converted to **63** (L = R_3P, CO or RNC), in which X-ray diffraction data showed the ring to be almost completely planar. A further one-electron reduction of the bipy complex gave the deep red paramagnetic species $[Pt(I)(C_3H_6)(bipy)]^-$ [107].



Scheme 4 Mechanism of cyclopropane formation from platinacyclobutanes [106].



63

Alkyl tin compounds underwent oxidative addition to platinum(0) complexes to give alkyl derivatives (reaction (18)). Rather complex redistribution reactions proceed *via* platinum(IV) intermediates (reactions (19) - (23)). Additions of alkyl tin halides proceeded in an analogous manner, but in no case was the platinum(IV) intermediate detected [108,109]. Treatment of $[Me_2Pt(bipy)]$ with R_3SnH gave $[HPt(Me)(SnR_3)(bipy)]$ and methane [110]. $K_2[PtCl_4]$ reacted with $RSnMe_3$ (R = Me or Ar) in dmso at 70 - 90 ° to give *cis*-$[R_2Pt(dmso)_2]$ and *cis*-$[RPt(dmso)_2Cl]$, the dmso ligands being sulphur bonded in both cases [111].

$$[Pt(C_2H_4)(PPh_3)_2] + Me_{4-n}SnR_n \longrightarrow \textit{cis}\text{-}[RPt(SnMe_{4-n}R_{n-1})(PPh_3)_2] \tag{18}$$

$$[Pt(C_2H_4)(PPh_3)_2] + Me_3RSn \longrightarrow \textit{cis}\text{-}[RPt(SnMe_3)(PPh_3)_2] \tag{19}$$

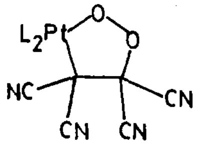
$$\textit{cis}\text{-}[RPt(SnMe_3)(PPh_3)_2] + Me_3RSn \longrightarrow [RPt(Me)(SnMe_3)(SnMe_2R)(PPh_3)_2] \tag{20}$$

$$[RPt(Me)(SnMe_3)(SnMe_2R)(PPh_3)_2] \rightleftharpoons \textit{cis}\text{-}[RPt(SnMe_2R)(PPh_3)_2] + Me_4Sn \tag{21}$$

$$\textit{cis}\text{-}[RPt(SnMe_2R)(PPh_3)_2] + Me_3RSn \longrightarrow [R_2Pt(SnMe_2R)(SnMe_3)(PPh_3)_2] \tag{22}$$

$$[R_2Pt(SnMe_2R)(SnMe_3)(PPh_3)_2] \rightleftharpoons [RPt(SnMe_3)(PPh_3)_2] + R_2Me_2Sn \tag{23}$$

The species $[PhPt(OPPh_2)(RCN)(PPh_3)]$ was formed by reaction of $[Pt(PPh_3)_2L]$ ($L = C_2H_4$ or PPh_3) with two molar equivalents of RNCO, where R is a hindered aryl group. The mechanism of the reaction was not delineated precisely, but it is clear that one of the phenyl groups of the triphenylphosphine ligand has migrated to platinum [112]. The reaction of $[PtL_2(O_2)]$ with electrophiles has been studied ($L = PPh_3$ or PCy_3); tcne was unique in yielding the dioxametallocycle, **64** [113]. Reaction of **65** (= pyrHgOCOMe) with **66** in the presence of $Li_2[Pd(OCOMe)_2Cl_2]$ and PPh_3 gave the isolable alkyl **67**, the reactions of which were investigated [114].

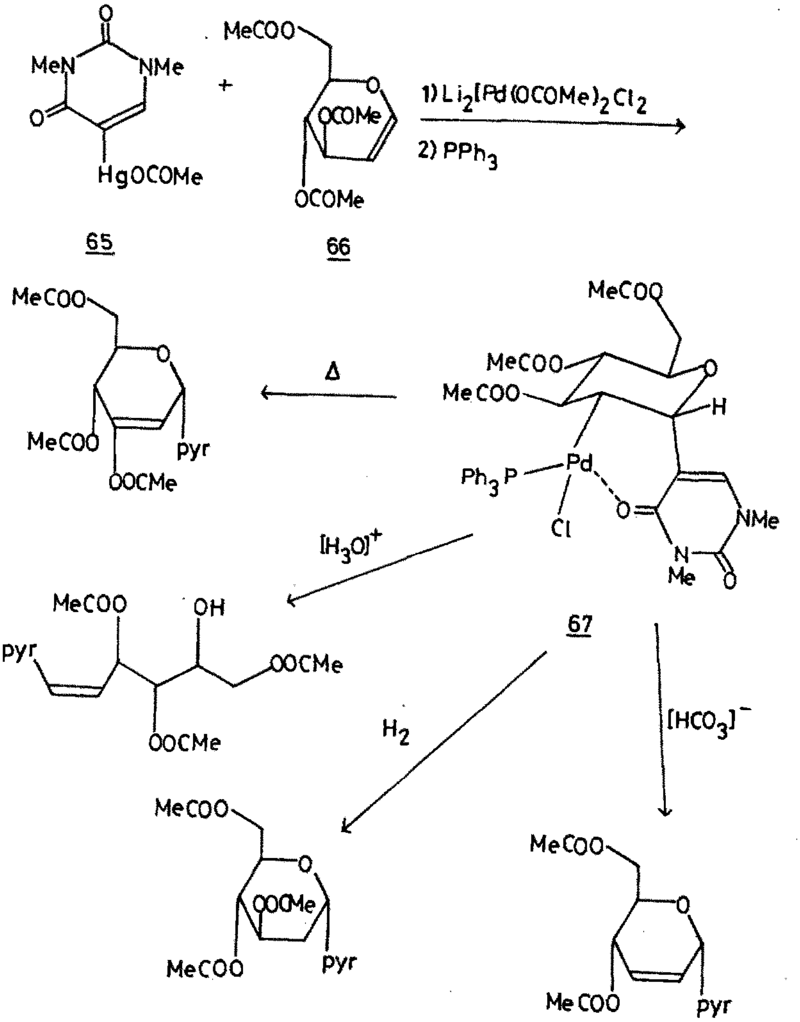


64

Epr investigations of the reactions of $[Et_2Ni(bipy)]$ and $[(PhCH_2)_2Ni(bipy)]$ with nitrosodurene showed considerable differences between them. With the ethyl compound a paramagnetic, unstable, RNO complex was initially observed. This decomposed at -80 °C according to reaction (24). The analogous benzyl complex was not observed for steric reasons [115]. The reactions of similar complexes with R^1R^2NH, in which R^1 and R^2 were electron withdrawing groups able to render the NH function acidic, led to formation of **68** (R = Me or Et; R^1, R^2 = COR; L_2 = bipy, dppe or $(PEt_3)_2$). With imidazole, polymers such as **69** were produced [116]. Activation volumes for the reactions of transition metal compounds in solution have been reviewed, the processes discussed including the isomerisation and substitution of *cis*$[RPt(PEt_3)_2Br]$ [117].

The complex **70** was prepared by oxidative addition of 2,6-dichloropyridine to $[Pd(PPh_3)_4]$ followed by exchange with acac. The methyl groups of the acac ligand were equivalenced by an isomerisation, catalysed by the phosphine liberated, or self-catalysed by the pyridine nitrogen atom [118]. Treatment of **71** with HCl resulted in cleavage of the Pt-Ar bond [119].

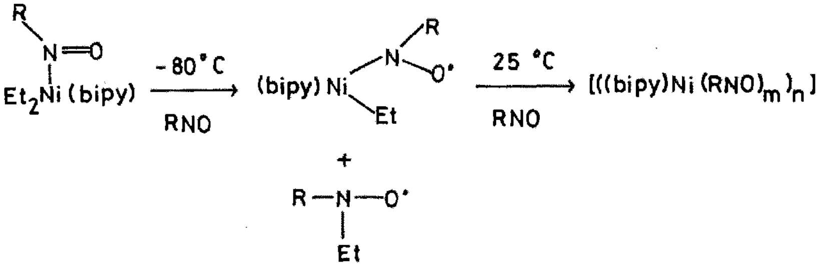
The equilibrium constant for reaction (25) was measured voltammetrically (Y = H, 2-, 3- or 4-CN). K was determined as 6×10^{-3} for Y = H but was lower for the cyano derivatives [120]. Reaction of [PhPt(cod)Cl] with PCy_3 gave initially the dimer **72**, which was converted to **73** by an excess of phosphine. $(2\text{-}MeC_6H_4)_3P$ gave a similar reaction, but $PMePh_2$ gave only mononuclear products, suggesting that the observed process is sterically controlled. The less sterically demanding chelating biphosphines also gave monomeric products [121].



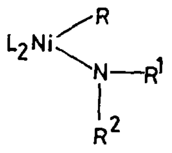
65

66

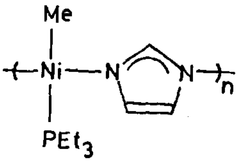
67



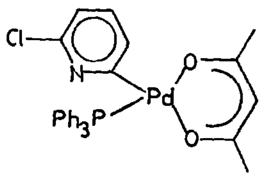
(24)



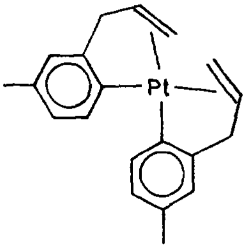
68



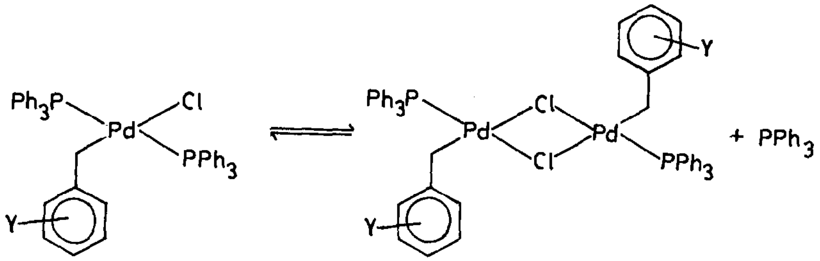
69



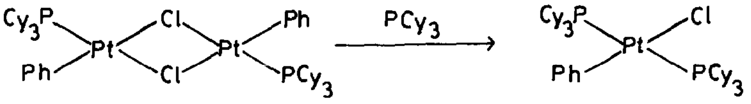
70



71



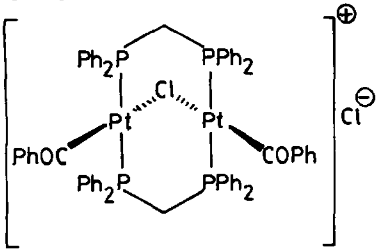
(25)



72

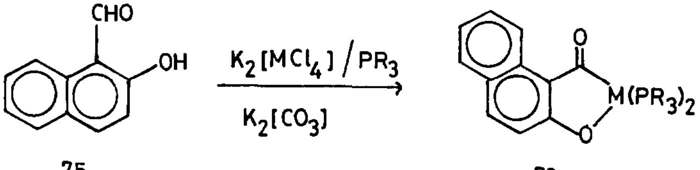
73

Reaction of $H_2[PtCl_6]$ with propene and carbon monoxide in the presence of PPh_3 gave *trans*-[(PrCO)Pt(PPh_3)$_2$Cl], a useful model for intermediates in hydroformylation [122]. [(PhCO)Pt(cod)Cl] reacted with dppm to give the "A-frame" complex, 74, whilst the phenyl complex gave a mixture of [PhPt(dppm)Cl] and the "A-frame". This observation does not substantiate previous work on the methyl platinum complex which had been thought to give trimeric products [123].



74

Reaction of **75** with $K_2[MCl_4]$ in the presence of potassium carbonate and R_3P gave **76**. 2-Hydroxybenzaldehyde gave a similar species, which was protonated by HCl on oxygen to yield *trans*-$[Pt(COC_6H_4\text{-}2\text{-}OH)(PR_3)_2Cl]$. An X-ray diffraction study of **77** revealed a rather long platinum-oxygen bond, in keeping with the fact that this is the site of protonation [124]. Treatment of $[Ni(bipy)(CO)_2]$ with $R^1\text{-}C{\equiv}C\text{-}R^2$ gave **78** (R^1, R^2, R^3 = alkyl or aryl; X = Br or I) the reactions of which were investigated [125].

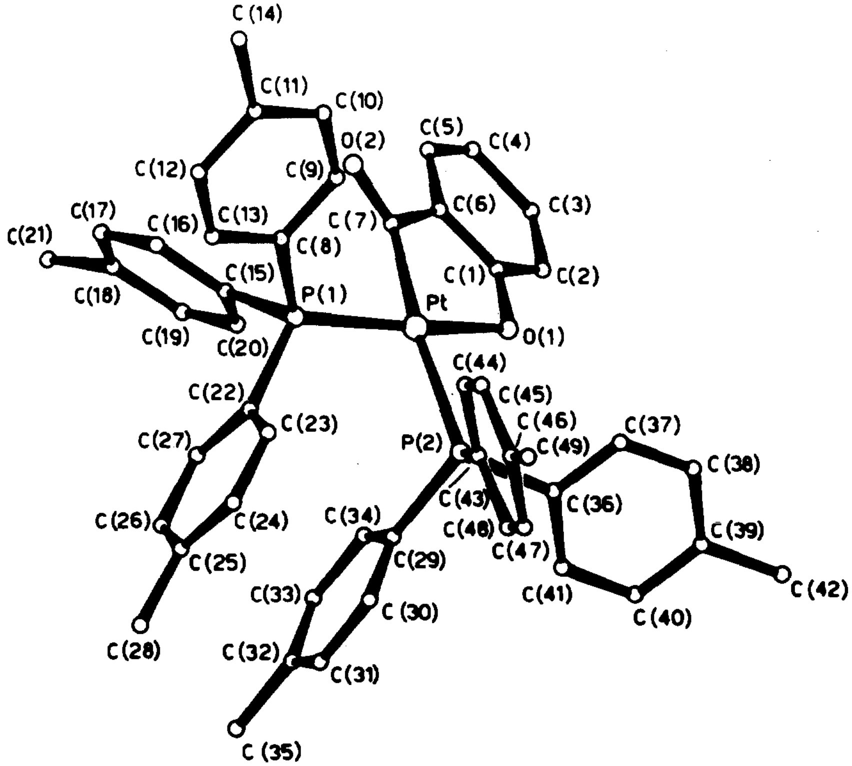


75 76

Oxidative coupling of RCHO and CO_2 on {Ni(0)(bipy)} gave **79**. **80** was proposed as an intermediate [126]. An analogous process occurred with the imine RCH=NR' to give **81**, the reaction regiochemistry being justified on molecular orbital grounds [127].

3 METAL COMPLEXES FORMED BY INSERTION AND RELATED REACTIONS

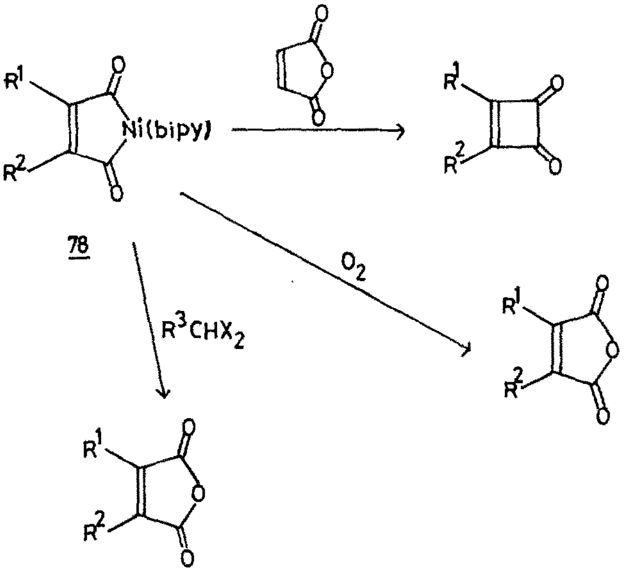
Insertion of carbon monoxide into metal-carbon bonds remains an important route to metal acyl complexes, and has also continued to be popular in model catalytic reactions. It is known that insertion into $[RNi(phenoxide)L_2]$ gives $[(RCO)Ni(phenoxide)L_2]$. Whilst this species is isolable at -78 °C rapid reductive elimination occurs at room temperature to give ArCOOR. More generally, both carbonylation of $[RM(OCOR')L_2]$ (M = Pd or Pt) or oxidative addition of RCOOCOR' to $[Ni(cod)_2]$ in the presence of L gave $[(RCO)M(OCOR')L_2]$. Reductive elimination of RCOOCOR' occurred at room temperature in the presence of CO [128]. Treatment of [RNiL$_2$Y] (R = Me or Et; Y = Cl, succinimide, phthalimide or O-C$_6$H$_4$-2-CN; L = PEt$_3$ or L$_2$ = bipy) gave [RCONiL$_2$Y]; these complexes could be characterised and their reactions were studied [129].



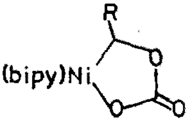
<u>**77**</u> (Reproduced with permission from [124])

Reaction of the allyl complex, 82, with CO gave dienes, alkenes and 83. The selectivity of the reaction depended on the ligand and the ligand to nickel ratio. An increase in donor capacity of L favoured CO insertion, whilst steric hindrance diminished it. The highest yield of **83** was obtained for L:Ni = 1 [130]. Treatment of 84 with [Ni(CO)$_4$] gave 85 in up to 97 % yield, the reaction proceeding non-catalytically *via* **86** and **87** [131]. [ArNiL$_2$X] could be formed by electrochemical reduction of [NiL$_2$X$_2$] in the presence of ArX and L. Further electrolysis in the presence of CO$_2$ gave

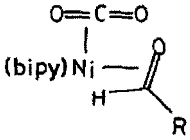
ArCOOH and nickel(0) [132].



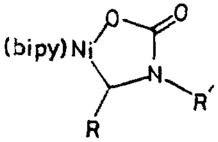
78



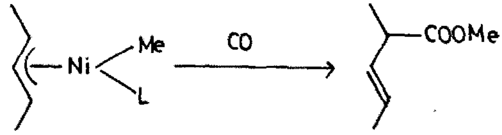
79



80



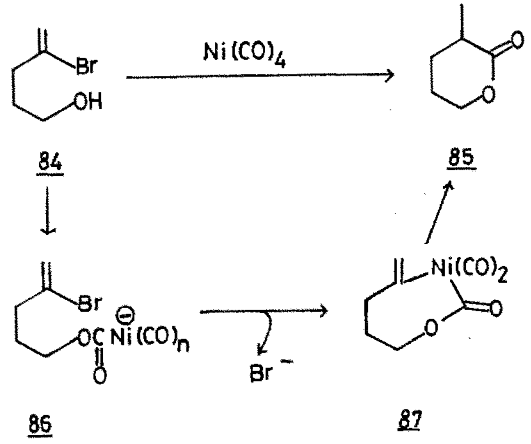
81

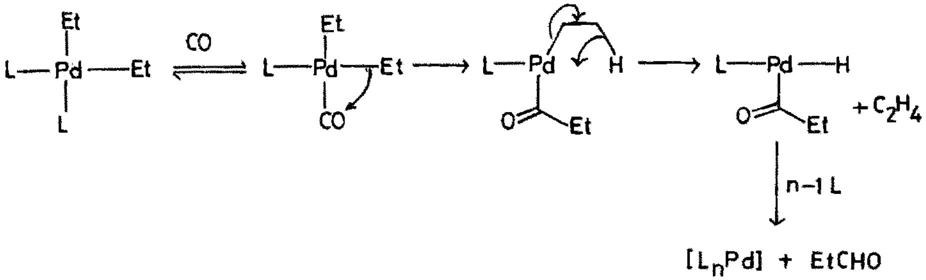


82

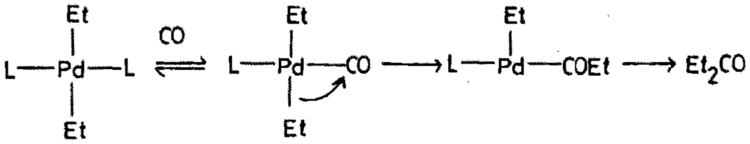
83

The reactions of *cis* and *trans*-[Et_2PdL_2] (L = R_3P) with CO have been studied. The *trans*-isomer gave mainly 3-pentanone whilst the major products from the *cis*-complex were ethene and ethanal. The mechanisms proposed are shown in reactions (26) and (27), the difference between them depending on the configurational stability of the T-shaped intermediates [133].





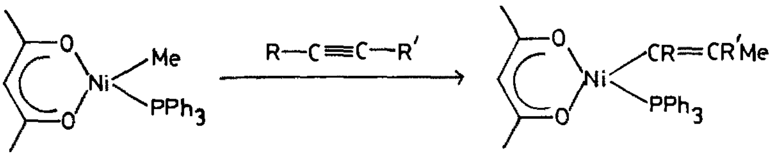
(26)



(27)

When [MePt(PPh$_3$)$_2$I] was treated with CO in KOH/MeOH, *trans*-[MePt(PPh$_3$)$_2$(COOMe)] was formed. The carbonyl stretching frequency was observed at 1655 cm^{-1} [134]. The reaction of [Pt(cod)Cl$_2$] with CO and L (= R$_3$P) to give *cis*-[Pt(CO)LCl$_2$] was studied by infra-red measurements and ^{13}C and ^{31}P nmr spectroscopy. With [R$_2$Pt(cod)] and CO the product was [R$_2$Pt(CO)$_2$], alkene elimination being accelerated by the high *trans*-effect of the alkyl groups. Subsequent addition of PR$_3$ gave [R$_2$Pt(PR$_3$)$_2$] rather than insertion. However, treatment of [RPt(cod)Cl] with CO gave [(RCO)Pt(cod)Cl] [135]. The equilibria between the isomers of [ArPt(CO)(PMePh$_2$)Cl], which undergo insertion, and halide bridged insertion products [(ArCO)$_2$Pt$_2$(μ-Cl)$_2$(PMePh$_2$)$_2$], has been investigated. It was found that electronic effects were critical, with electron donors in the 3- or 4-positions of Ar promoting insertion, and electron withdrawing groups inhibiting the process. Substituents in the 2-position prevented insertion for steric reasons [136].

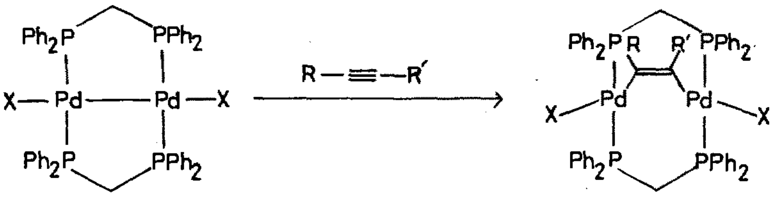
Insertion of alkynes, RC≡CR', into the nickel methyl bond of **88** proceeded with unusual regioselectivity, such that the larger substituent was α to the nickel in the product. Insertion gave the *trans*-product under conditions of kinetic control, *via cis*-addition, but the thermodynamic *cis*-products could also be isolated under some conditions. The reactions of the vinyl nickel compounds to give organic products were studied [137]. X-ray diffraction data are available for 89 (R = R' = Ph) [138].



88

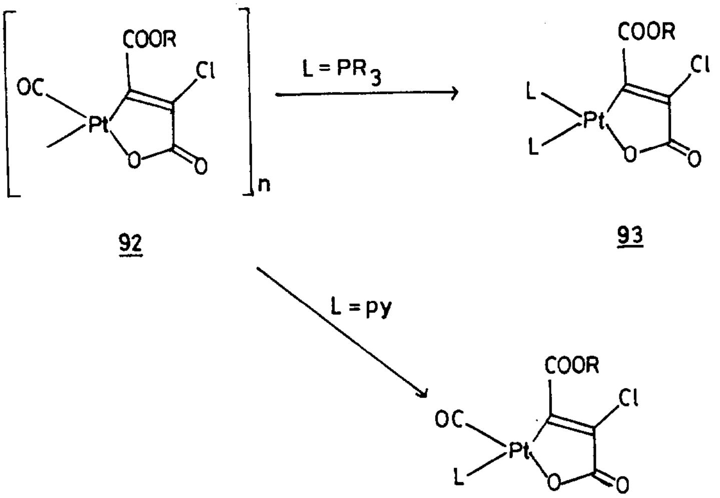
89

The palladium(I) complexes, **90**, insert alkynes bearing electron withdrawing groups to give species such as 91. MeO$_2$CC≡CCO$_2$Me was shown to be able to displace a bridging isocyanide and was trimerised catalytically at 125 °C [139]. Treatment of [Pt(CO)$_2$Cl$_2$] with RO$_2$CC≡CCO$_2$R gave an insoluble polymer assigned the structure **92** (in which the other bond to platinum was not well-defined) which was split by phosphine ligands to give 93. When the added ligand was pyridine or a methylpyridine the mixed complex, **94**, was obtained [140].



90

91



92

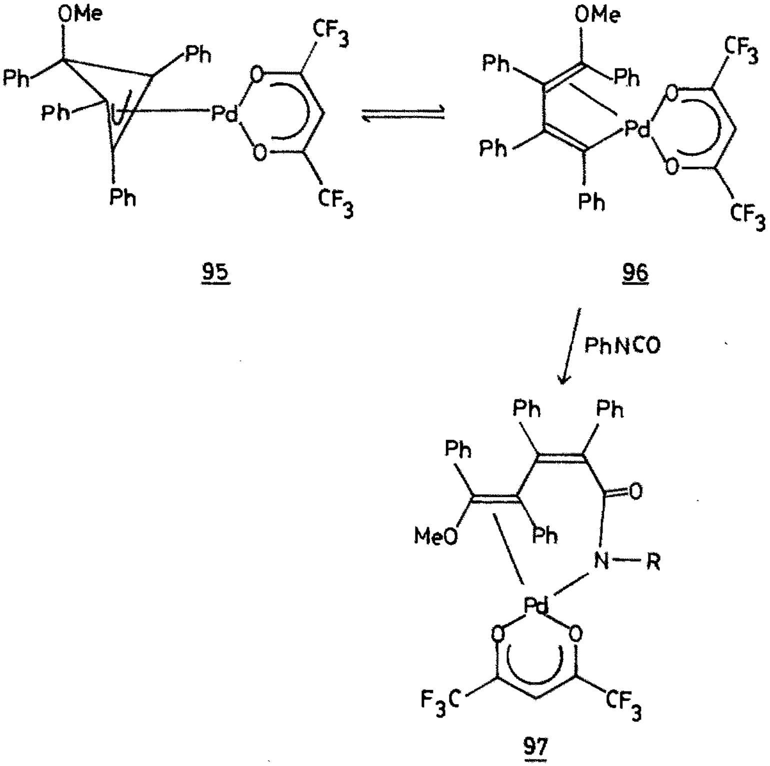
93

94

The cyclobutenyl palladium complex, 95, is thought to be in equilibrium with the open species 96. In this open form RNCO could be inserted to give **97** with kinetics which were shown to be first order in both components. The value of ρ = +1.13 for correlation with σ_p for ArNCO was in accord with the proposed transition state **98** [141]. Alkenes could also be inserted to give initially **99**, which underwent a hydride shift to give the extremely unsymmetrical allyl complex, **100**, characterised by X-ray diffraction [142].

Treatment of **101** with **102** (X = O or S) proceeded *via* insertion of the cyclopentadienyl ligand into a phosphorus-carbon bond of the phosphine to give 103, which was identified by X-ray diffraction techniques. The high yield of the reaction implies that it takes place within the palladium coordination sphere [143].

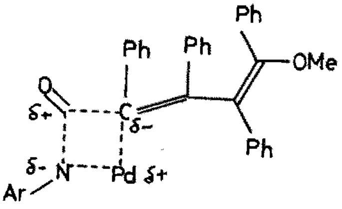
Insertion of nickel into anhydrides such as **104** gave the cyclic species 105, which was readily decarbonylated to **106**. With an acyclic anhydride $(RCO)_2O$, $[(RCO)Ni(bipy)(OCOR)]$ was initially obtained and decomposed on thermolysis to $[Ni(bipy)(OCOR)_2]$, $[Ni(bipy)(CO)_2]$ and R-R (R = Ph), the intermediate probably being 107 [144]. Insertion of $[Ni(PPh_3)_n]$ into the phosphorus-carbon bond of $Ph_3P{=}CHCOPh$ gave 108, which reacted with ethene readily to give successively **109** and 110. The nickel hydride complex **110**, is a catalyst for ethene oligomerisation, yielding mainly linear products [145].



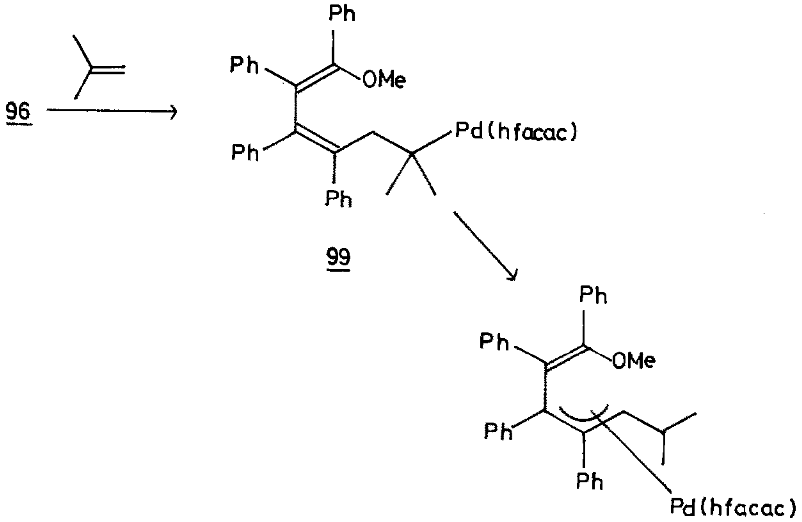
95

96

97



98



96

99

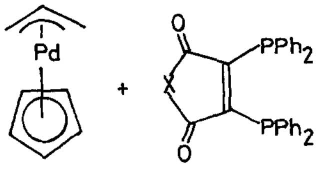
100

4 METAL CARBENE, CARBYNE AND YLIDE COMPLEXES

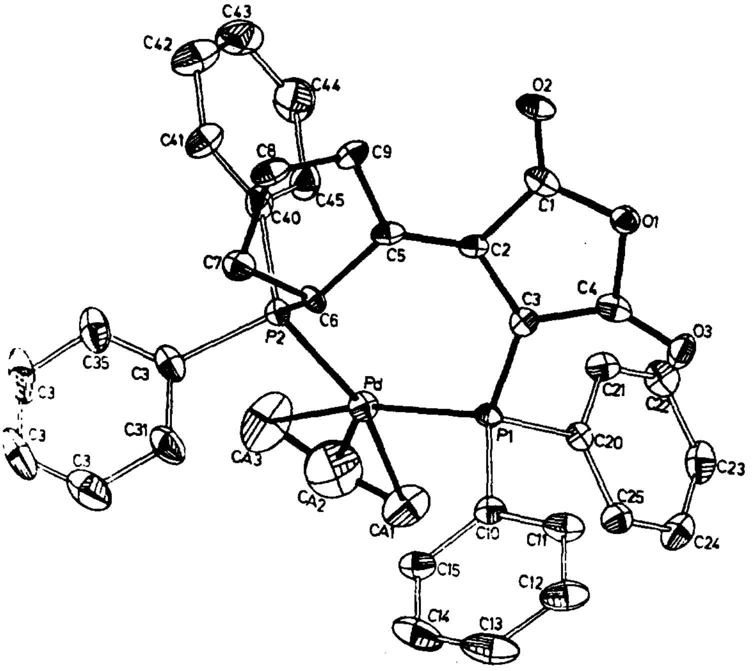
The first application of a non-empirical molecular electronic structure theory to a realistic transition metal carbene complex has been reported for $[(CO)_3Ni{=}CH_2]$. The barrier to rotation about the $Ni{=}CH_2$ bond was calculated to be very low [146]. The nickelacyclopropane, **111**, was postulated to be in equilibrium with the carbene complex, **112**, a fact which was used to account for the products of its thermolysis [147]. Thermolysis of $[Ni(PhN{=}C{=}NPh)(PPh_3)_2]$ in toluene at 60 °C gave irreversibly the corresponding monophosphine species. Reaction of $[Ni(cod)_2]$ with $PhN{=}C{=}NPh$ in thf gave $[Ni(PhN{=}C{=}NPh)_3(thf)]$, the structure, **113**, of which was established by X-ray diffraction. This contains a [3.3.0] nickelabicyclic group in which the carbodiimides are linked to form a 2,5,8-η^3-carbene ligand [148].

Reaction of **114** with the vinyl lithium species **115** gave **116**, which was protonated to **117**. The relative Brønsted acidities of the complexes **117** were in the order $M = Ni < Pd < Pt$ and $\{M{-}^{+}CCH_2CH_2CH_2O\} < \{M{-}^{+}C(OMe)_2\} < \{M{-}^{+}C(CH_2)_4{-}O\}$ [149].

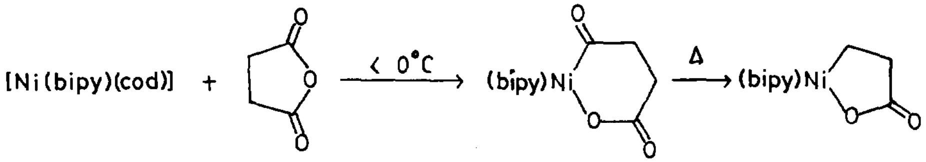
Reaction (28) of an isonitrile complex with a nitrilimine gave a rather stable cyclic carbene complex. An analogous process occurred with a nitrylide [150]. Oxidative addition of an α-ketoimidoyl chloride to $[Pd(PPh_3)_4]$ gave *trans*-$[Pd\{C({=}NR)COMe\}(PPh_3)_2Cl]$, whereas $[Pt(PPh_3)_4]$ or $[Pt(PPh_3)_2(C_2H_4)]$gave



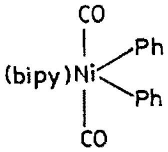
101 102



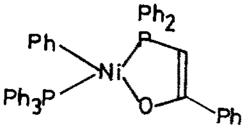
<u>103</u> (Reproduced with permission from [143])



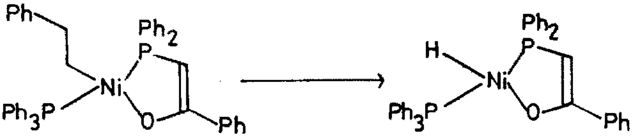
104 105 106



107



108

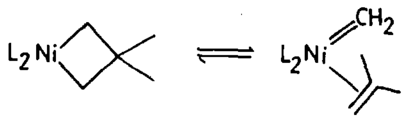


109 110

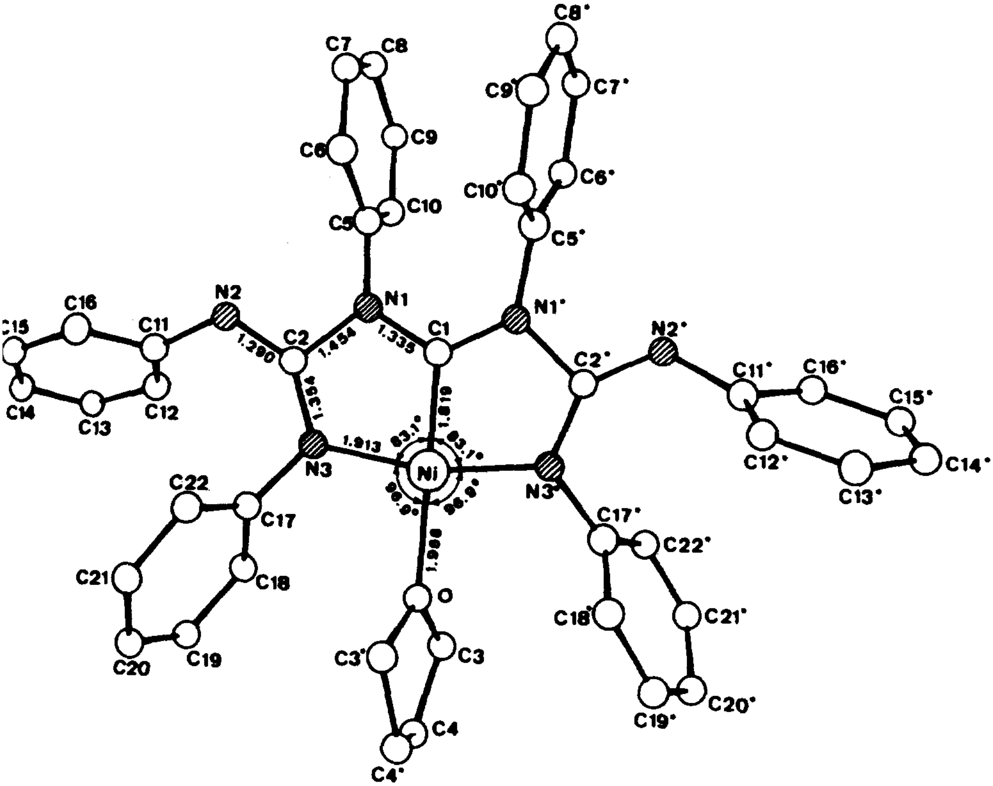
cis-products. Rotation about the metal-carbon bond was shown to be relatively free [151].

Treatment of [$\{Me_3PtI\}_4$] with the electron rich alkene **118** gave the cyclometallated carbene complex, **119**, the reactions of which have been described in a full paper [152]. The carbene complex [$Pt(C(OEt)NHPh)(PEt_3)Cl_2$] reacted with phosgene to give [$Pt(CO)(PEt_3)Cl_2$], and with $AlCl_3/Et_3N$ to yield the isonitrile complex [$Pt(CNPh)(PEt_3)Cl_2$] *via* 120 [153].

Bridging carbene and carbyne complexes of platinum have been reviewed [154]. Addition of a $\{PtL_2\}$ fragment to Fischer carbene complexes such as [$M\{C(OMe)(C_6H_4\text{-}4\text{-}R)\}(CO)_5$] (M = Cr or W; R = Me or CF_3) has been achieved by their admixture with [$Pt(cod)_2$], ethene and a ligand such as R_3P. The properties of these complexes have now been described in detail, and X-ray diffraction studies showed that the carbene bridge in [$PtW\{\mu\text{-}C(OMe)(C_6H_4\text{-}4\text{-}Me)\}(CO)_4(PMe_3)$] was considerably asymmetric with bond lengths C-W = 2.37(1) Å and C-Pt = 2.03(1) Å [155]. Treatment of such bridging methoxycarbene complexes with [Me_3O][BF_4] yielded a carbyne complex such as [$CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3$][$BF_4$] or [$MnPt\{\mu\text{-}C(C_6H_4\text{-}4\text{-}Me)\}(CO)_2(PR_3)_2Cp$]. In the latter case X-ray diffraction

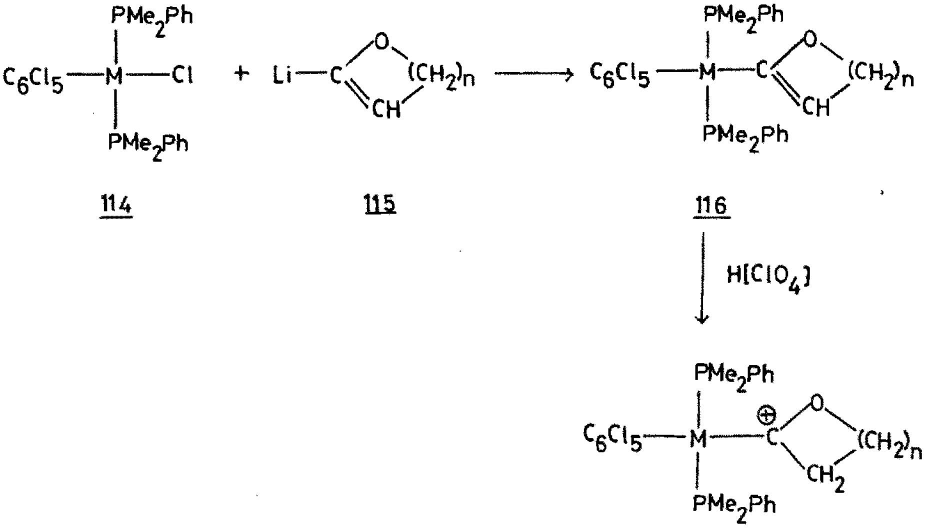


111 112

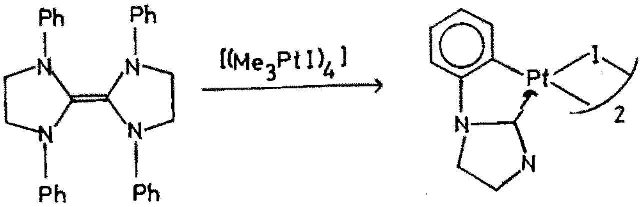


113 (Reproduced with permission from [148])

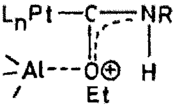
studies revealed that the carbyne was doubly bonded to manganese (C-Mn = 1.829 Å) and singly to platinum (C-Pt = 1.968 Å). The reactions of these carbyne complexes have now been extensively investigated. Addition of ArLi or Na[OEt] to [MPt(μ-CPh)(CO)$_5$(PMe$_3$)$_2$][BF$_4$] gave respectively [MPt(μ-CPhAr)(CO)$_5$(PMe$_3$)$_2$] and [MPt{μ-CPh(OEt)}(CO)$_5$(PMe$_3$)$_2$]. However, if the triphosphine complex [MPt(μ-CPh)(CO)$_4$(PMe$_3$)$_3$][BF$_4$] was treated with Na[OMe], the product was [MPt{μ-C(COOMe)Ph}(CO)$_4$(PMe$_3$)$_3$], 121, characterised by X-ray diffraction [156]. Reaction of the carbyne complex [MPt{μ-C(C$_6$H$_4$-4-Me)}(CO)$_2$(PR$_3$)$_2$(Cp)][BF$_4$] (M = Mn or Re; PR$_3$ = PMe$_3$ or PMe$_2$Ph) with R$_3$P gave 122. When the nucleophile was [Ar'S]$^-$ and M was rhenium the expected {μ-C(SAr')Ar} species was obtained, but with the manganese complex [(OC)(Cp)Mn{μ-C(PR$_3$)Ar}(μ-CO)Pt(SAr')(PR$_3$)] was obtained by migration



114 115 116 117

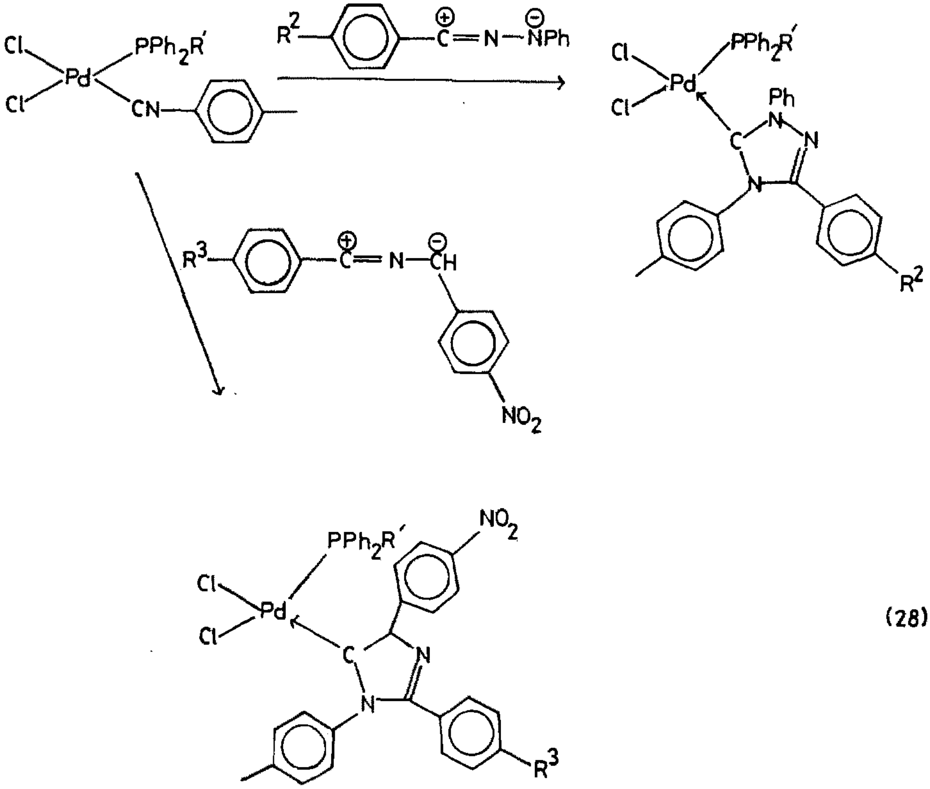


118 119



120

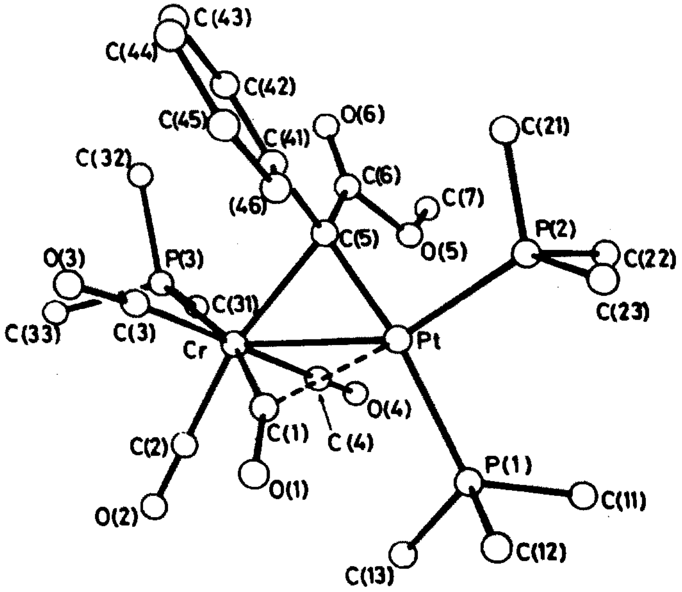
of PR_3 from platinum to carbon [157]. Protonation of **123** by $H[BF_4]$ gave **124**, the structure of which was established by X-ray diffraction. This is the first reported example of the conversion of a μ-carbyne complex to a cationic μ-carbyne. In **124** the aryl ring interacts with tungsten, and one carbonyl is semi-bridging. The coordination needs of tungsten may be satisfied by an additional ligand such as CO or PMe_3. Treatment of 124 with $K[BH(CHMeEt)_3]$



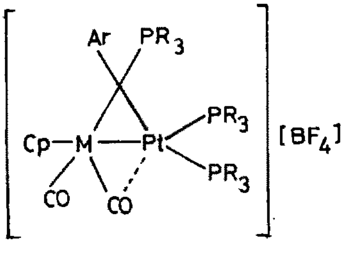
(28)

gave **125**, in contrast to the analogous cobalt complex, which is deprotonated under these conditions [158].

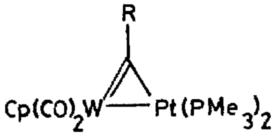
An alternative route to μ-carbyne complexes involved the reaction of $[(Cp)(OC)_2W{\equiv}C-(C_6H_4-4-Me)]$ with complexes of labile ligands such as $[Pt(C_2H_4)_3]$, $[Pd(norbornene)_3]$ or $[Ni(cod)_2]$. The complexes produced all have the formula $[MW_2\{\mu-C(C_6H_4-4-Me)\}_2(CO)_4(Cp)_2]$ but X-ray diffraction studies of the platinum and nickel species revealed slight differences in structure. In the platinum complex, **126**, the terminal carbonyls are arranged such that one is *trans* and one *cis* to the μ-carbyne. The W-Ni-W angle is 175°, whereas the corresponding angle at platinum is 165°. In both cases the bond between the tungsten and the carbyne carbon is short, indicative of its double bond character, and one carbonyl is semi-bridging [159].



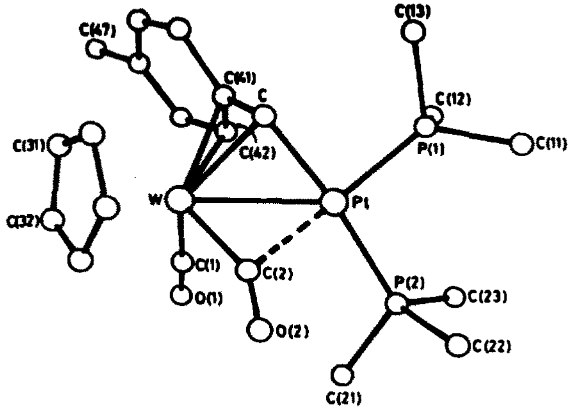
121 (Reproduced with permission from [126])



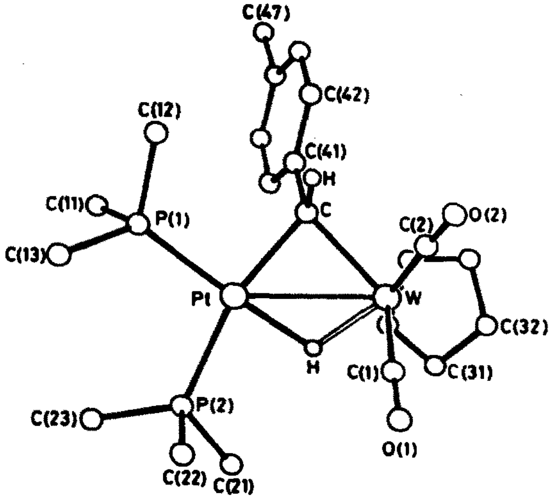
122



123

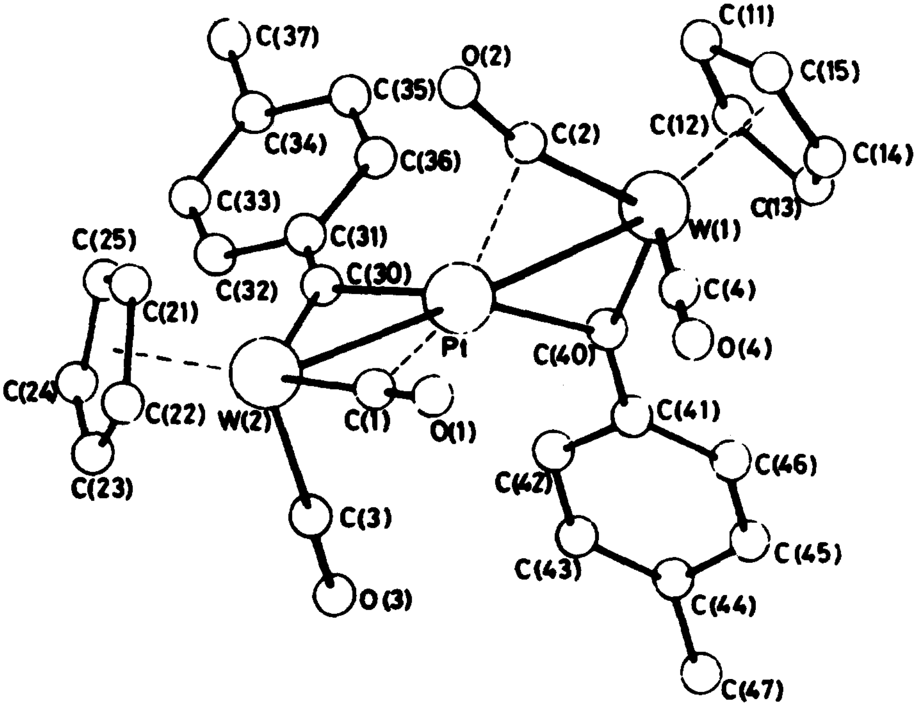


124 (Reproduced with permission from [158])



125 (Reproduced with permission from [158])

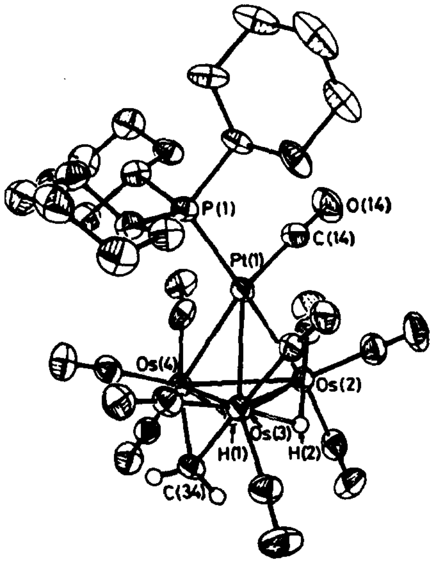
Treatment of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)]$ with diazomethane under conditions of kinetic control gave two isomers of $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}(PCy_3)]$, **127** and **128**, the structures of which were determined by X-ray diffraction. The formation of **127** involves the addition of $:CH_2$ to the short $\{Os\text{-}(\mu\text{-}H)\text{-}Os\}$ bond with hydrogen migration, and the conversion of **127** to the more thermodynamically stable 128 involves rotation of the $\{Pt(CO)(PCy_3)\}$ moiety



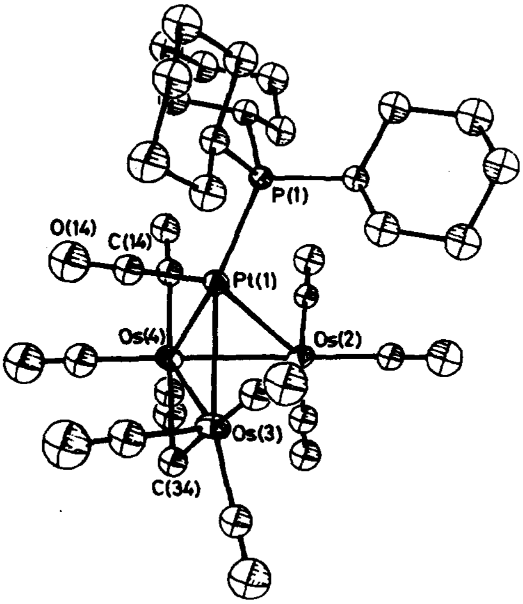
<u>**128**</u> (Reproduced with permission from [159])

about an axis perpendicular to the Os_3 plane, with hydrogen transfer [160]. A theoretical discussion of metalloporphyrins with unusual geometries involved consideration of the carbene complex **129** in which the carbene has been inserted into a metal-nitrogen bond [161].

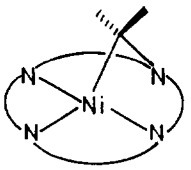
Discussions of ylid complexes seem to be back in vogue this year; the studies of the ylids formed during decomposition of platinacyclobutanes were discussed in Section 2. Reaction of $[CpNi(PPh_3)Br]$ with a range of ylids at room temperature gave species such as $[CpNi(Ph_3PCHR)(PPh_3)]Br$ and analogues derived from $[Ph_3AsCH_2]$, $[Me_2SCH_2]$ and $[Me_2S(=O)CH_2]$. Under more forcing conditions the stabilised ylid $[Ph_3PCHCOPh]$ gave $[CpNi(Ph_3PCHCOPh)_2]Br$ [162]. Using $[Cp_2Ni]$ or $[CpNi(PPh_3)Br]$ and the bis(ylid), $[Ph_3PCH(CH_2)_nCHPPh_3]$ (n = 1 - 3), **130** was formed. Such species were not stable when the ring was larger than six-membered. $[Cp_2Ni]$ and $[Ph_3PCHMe]$ gave, as reported above, $[CpNi(PPh_3CHMe)_2]X$, but using **131**, the ylid derived from cyclopentadiene, resulted in the loss of the original η^5-Cp ligand and the formation of the new ylid metallocene, **132** [163].



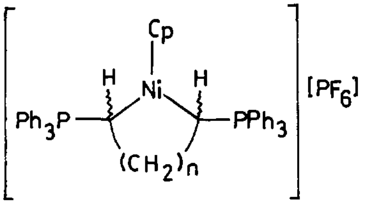
127 (Reproduced with permission from [160])



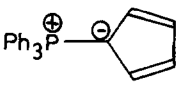
128 (Reproduced with permission from [160])



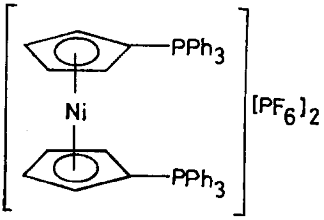
129



130



131

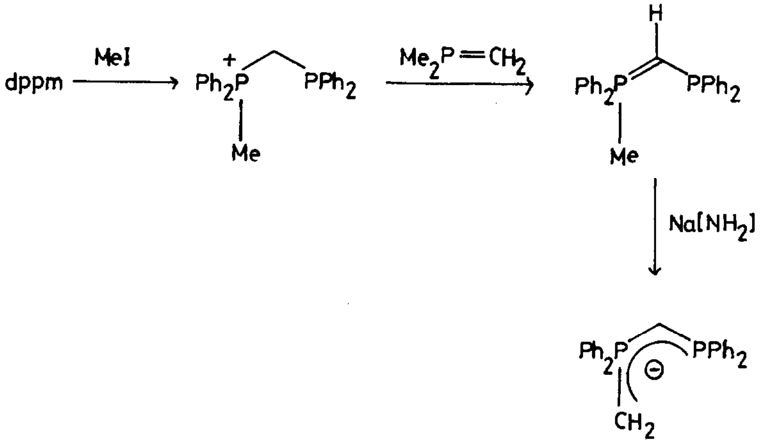


132

The ylid anion, **133**, was prepared according to reaction (29) and could be converted to the two ylid complexes **134** and **135** by reaction with [Ni(PMe_3)$_2$$Cl_2$] in the appropriate molar ratios. An X-ray diffraction study of **135** indicated substantial delocalisation [164]. A similar type of reaction was achieved using **136**; **137** was shown by X-ray diffraction to have a centrosymmetric structure with approximately square planar coordination of nickel [165].

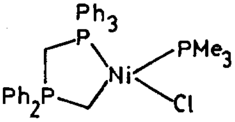
The new nickel ylid complex, **138**, was synthesised according to reaction (30) [166], and numerous analogues were also prepared. All acted as catalysts for the oligomerisation of ethene, and [NH_4][OH] was used to remove nickel ylide residues at the end of the reaction [167,168].

Treatment of *cis*- or *trans*-[$ClCH_2Pt(PPh_3)_2Cl$] with PPh_3 gave the ylid complex *cis*-[$Pt(CH_2PPh_3)(PPh_3)_2Cl$]Cl which yielded *cis*-[$Pt(CH_2PPh_3)(PPh_3)Cl_2$] on thermolysis. Further ylid complexes could be prepared from the latter material on displacement of chloride with Ph_3As, $P(NMe_2)_3$ or dppe [169]. Reaction of the nitrogen ylid, **139**, with [$Pt(SMe_2)_2Cl_2$] resulted in the displacement of the labile sulphides to give **140**. Infra-red, ^1H and ^{13}C spectroscopic data confirmed the structure of **140** in which platinum is coordinated to the ylid carbon and the pyridine nitrogen atoms [170].

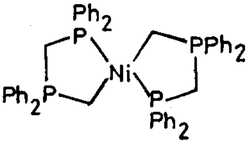


133

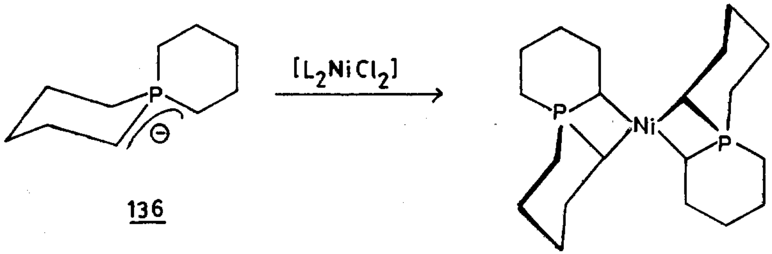
(29)



134

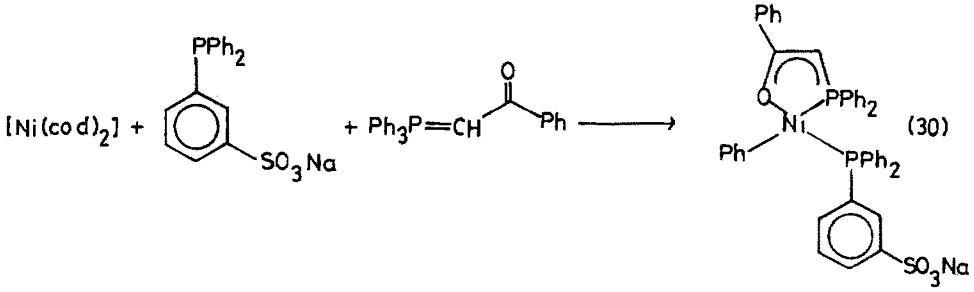


135



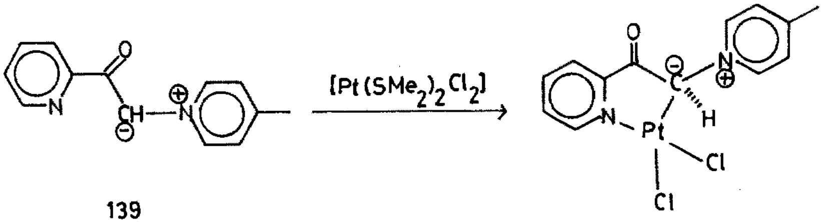
136

137



(30)

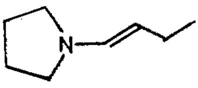
138



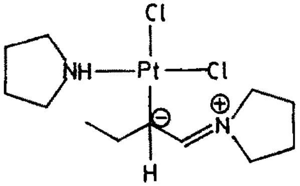
139

140

Treatment of $[\{Pt(C_2H_4)Cl_2\}_2]$ with **141** in ether gave butanal and ethene together with **142**, in which the ylid form of the enamine is coordinated to platinum through a formally anionic carbon atom [171].



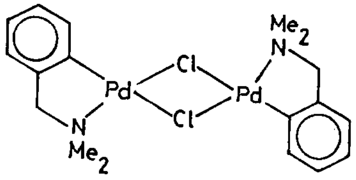
141



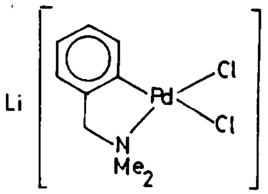
142

5 METAL COMPLEXES FORMED BY INTERNAL METALLATION AND RELATED REACTIONS

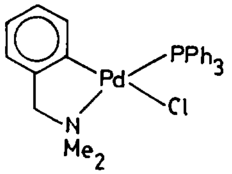
Treatment of the chloro bridged dimer, **143**, with an excess of lithium chloride in ethanoic acid gave the novel anionic species **144**. An analogous anionic complex was also obtained from **145** [172]. Styrene could be inserted into the metal-carbon bond of **143** to give mixtures of **146** and **147**'; the transition state **148** was proposed [173]. Analogous insertions were achieved using **149** [174]. Diazabutadienes, RN=CHCH=NR, gave **150** and **151**, shown to be in exchange by nmr spectroscopy [175].



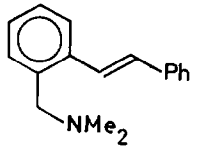
143



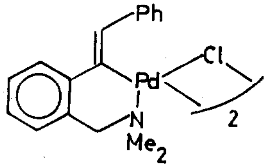
144



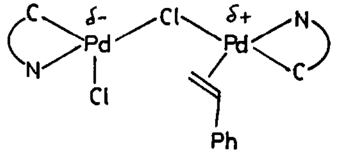
145



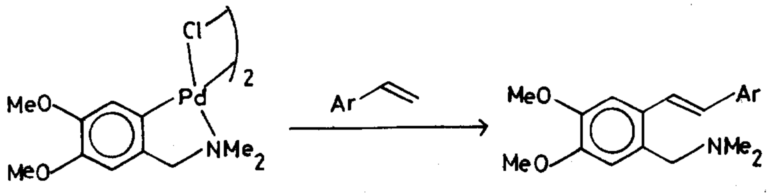
146



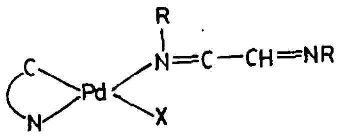
147



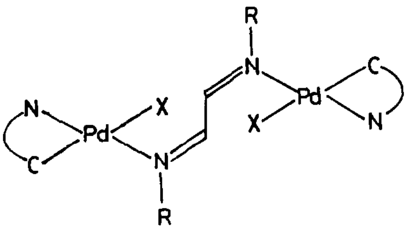
148



149

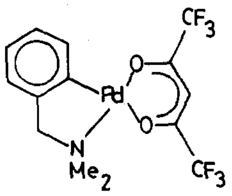


150

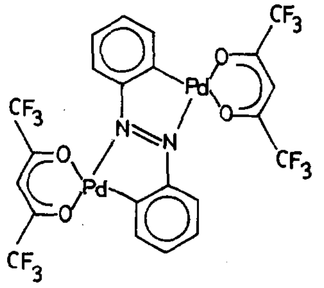


151

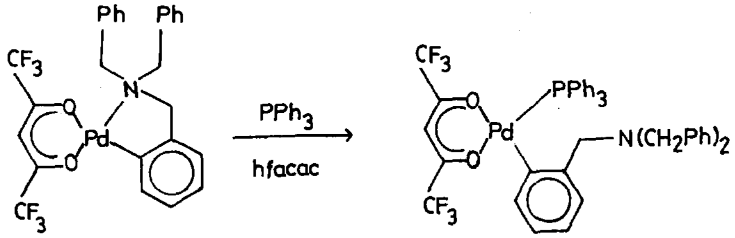
Treatment of [Pd(hfacac)$_2$] with dimethylbenzylamine at -78 °C gave the monodentate species [Pd(hfacac-O,O')(hfacac-O)(Me$_2$NCH$_2$Ph)] which at room temperature was converted to **152**. An analogous sequence was observed with 2-phenylpyridine, PhCH$_2$SMe and (4-MeOC$_6$H$_4$)$_2$C=S, but with azobenzene the intermediate could not be detected and the unusual doubly metallated species, **153**, was also produced [176]. Tribenzylamine yielded **154**, from which the nitrogen could be displaced by PPh$_3$ [85].



152



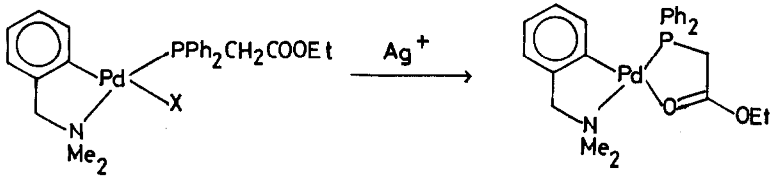
153



154

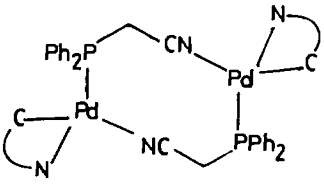
Treatment of **155** with Ag$^+$ resulted in cyclisation to **156**, and both Cp and other *N*-*C*-ligands behaved similarly. With the Ph$_2$PCH$_2$CN derivative, however, **157** was the major product. When dimers such as **143** were reacted with

$[Ph_2PCHY]^-$ (Y = CN or COOEt) the bridged species, **158**, were formed, characterised by X-ray diffraction for $\overset{\frown}{C\ N}$ = dimethylbenzylamine and Y = COOEt [177]. The reaction of **159** with CH_3COCl was retarded by electron-withdrawing groups, indicating that 160 might be the intermediate [178].

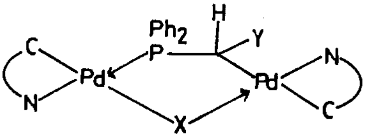


155

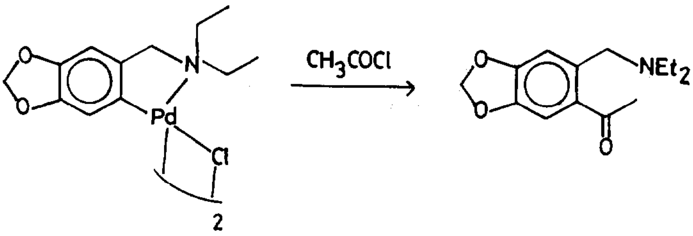
156



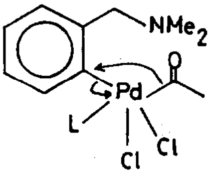
157



158

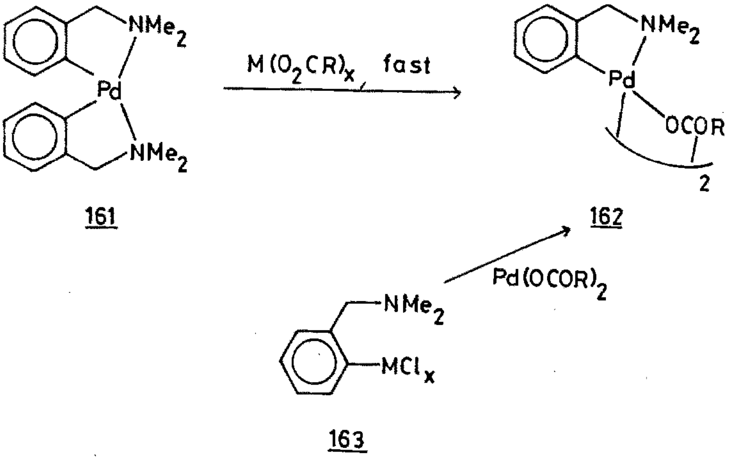


159



160

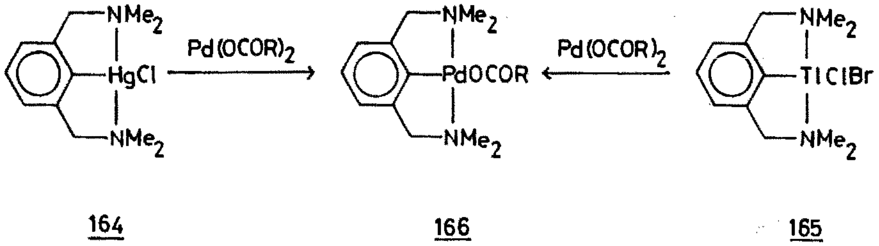
Reaction of the bis(cyclometallated) species, **161**, with $M(O_2CR)_x$ (M = Hg, x = 2 or M = Tl, x = 3) gave **162**, also obtained by treatment of **163** with the palladium alkanoate. **164** or **165** yielded **166** by transmetallation. The ease of transmetallation depended on the stabilisation of the metal-carbon bond by a chelate effect, the strength of the metal-nitrogen bond, and the electronic properties of the metal centres [179].



161

162

163



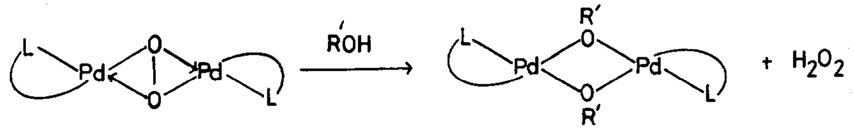
164

166

165

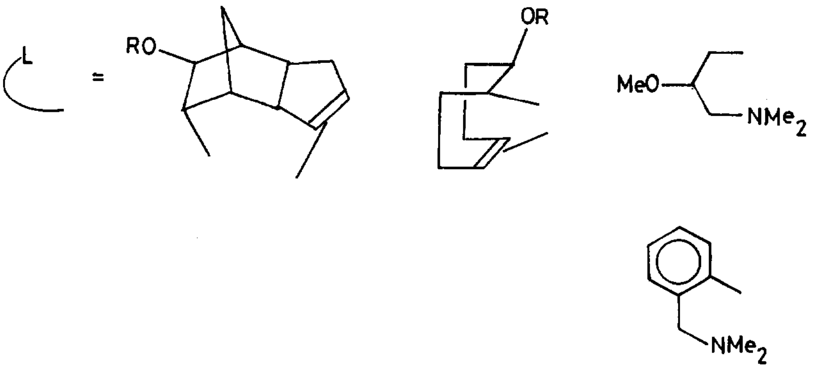
Treatment of **167** with R'OH gave the unstable bridged species, **168**, and hydrogen peroxide (R' = Me or Et) [180].

A number of novel derivatives of metallocenes bearing CH_2NMe_2 groups have been reported this year. $[Co(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_4CH_2NMe_2)]$ reacted with $Li_2[PdCl_4]$/Na[OCOMe] to give **169** which underwent all the expected insertion and bridge splitting reactions (Scheme 5) [181]. Cyclopalladated dimethylaminoferrocene has been resolved *via* its proline derivatives [182].

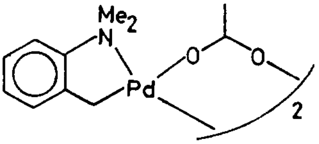


167

168

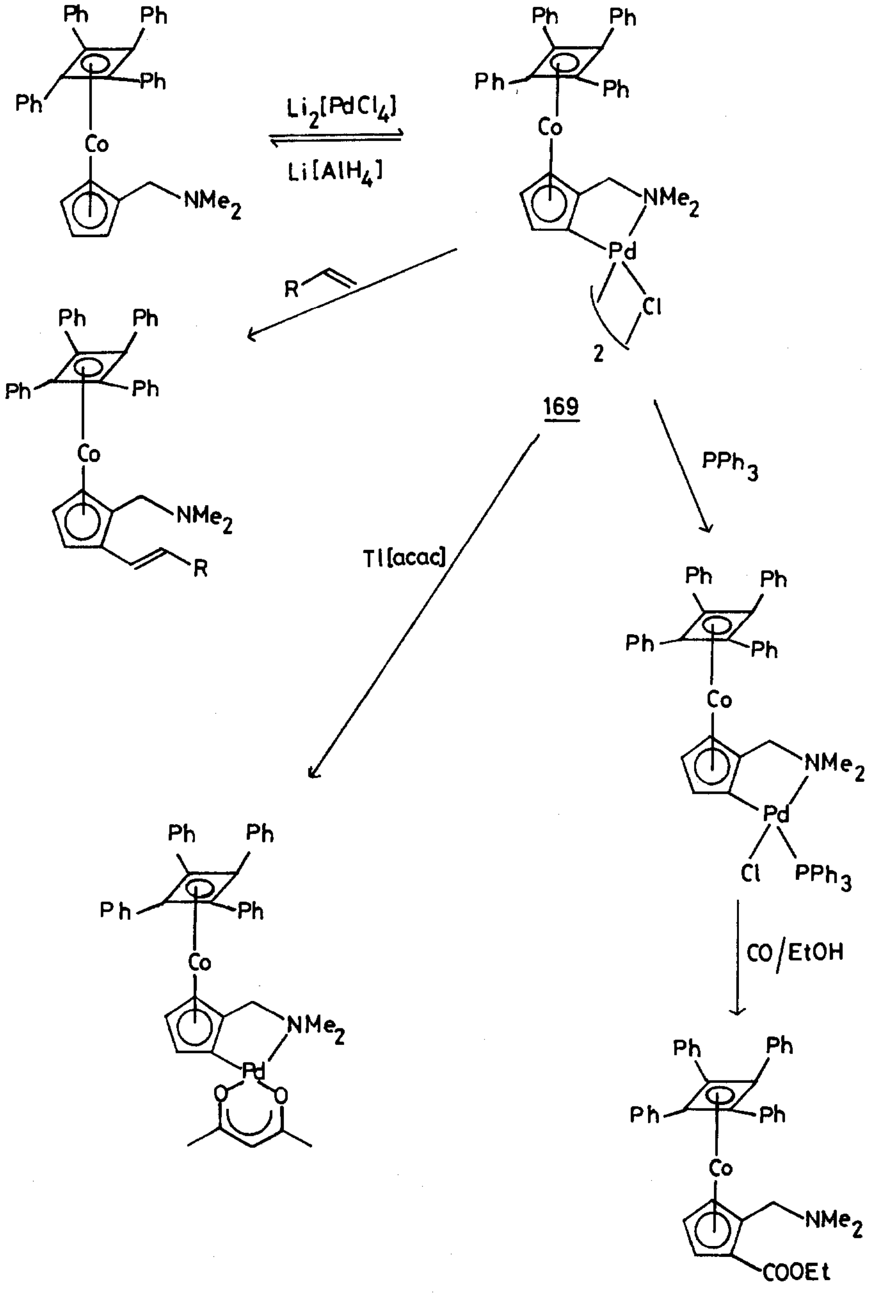


Reaction of 1-alkyl-2-amino benzenes with $Pd(OCOMe)_2$ gave the ethanoate bridged species $[\{Pd(OCOMe)_2L\}_2]$ which yielded $[Pd(OCOMe)_2LL']$ on treatment with L'. These complexes provided a model for intermediates in cyclometallation; the derivative of 2-dimethylaminotoluene gave 170 on warming [183]. Analogous results were reported for other 2-dialkylaminotoluene derivatives [184].

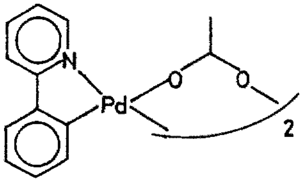


170

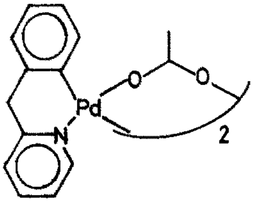
The palladium complexes of 2-arylpyridines were shown to be readily cyclometallated to give species such as **171** [185]. 2-Benzylpyridine reacted similarly and the products, **172**, underwent all the expected bridge splitting and insertion reactions [186]. The synthesis of **173** from the substituted pyridine, $K_2[PdCl_4]$ and pyridine has been described; its structure was determined by X-ray diffraction [187].



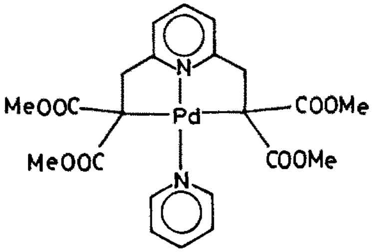
Scheme 5 Reactions of the cyclopalladated complex **169** [181]



171

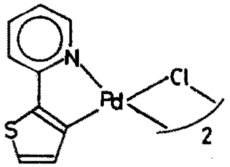


172

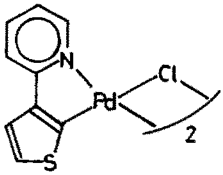


173

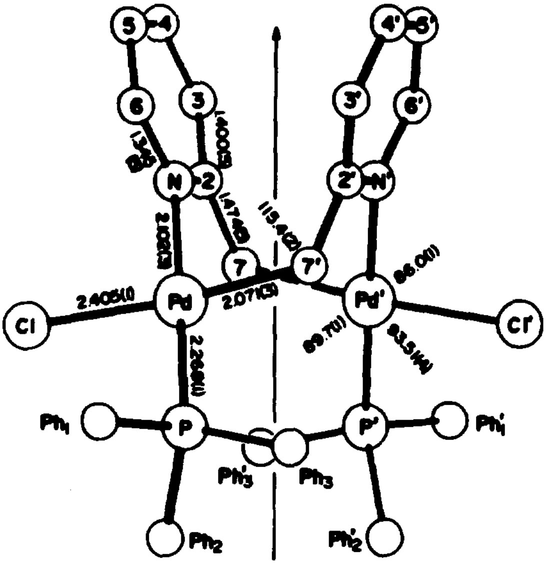
An X-ray diffraction study has established the structure of *trans*-[{(*P*,*N*)-PdCl(μ-C_5H_4N-2-CH_2)(PPh_3)}$_2$], **174**, to contain a boat-like eight-membered ring and no metal-metal bond [188]. Cyclometallated structures, **175** and **176**, were postulated for the products of the reaction of $Li_2[PdCl_4]$ with 2- and 3-thienylpyridine [189]. When **177** was reacted with sodium metallates such as Na[CpMo(CO)$_3$] or Na[Co(CO)$_4$], the rather ionic species, **178**, were produced. With ligands such as CO, py or 4-methylpyridine replacing the phosphine, somewhat less ionic species were obtained [190].



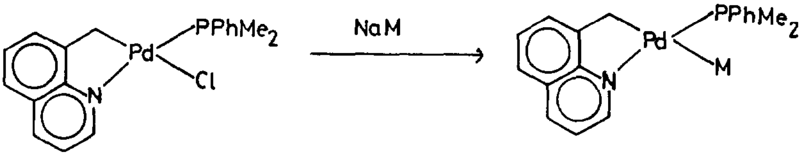
175



176



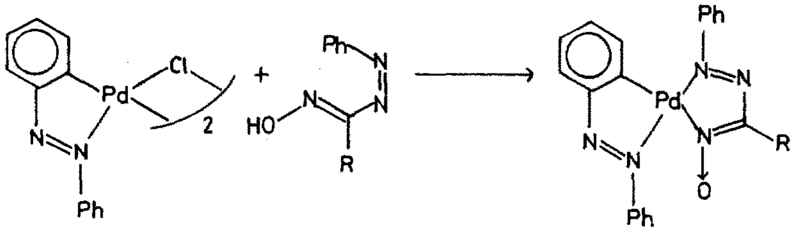
174 (Reproduced with permission from [188])



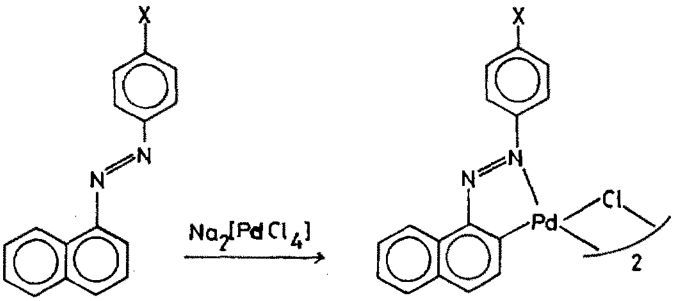
177

178

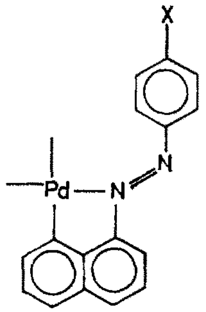
The cyclometallated azobenzene derivative, **179**, reacted with **180** to give 181, the electrochemistry of which was investigated [191]. Treatment of **182** with Na$_2$[PdCl$_4$] gave 183 rather than 184 or 185. It was deduced that the first step in the reaction involved coordination of the less hindered nitrogen atom, and that this was followed by palladation of the more electron rich ring. However, the origin of the selectivity observed in the second step may be steric, since even the ligand for which X = OMe palladated in the same position [192].



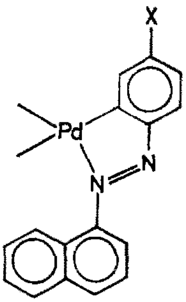
179 180 181



182 183



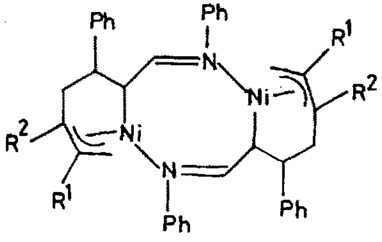
184



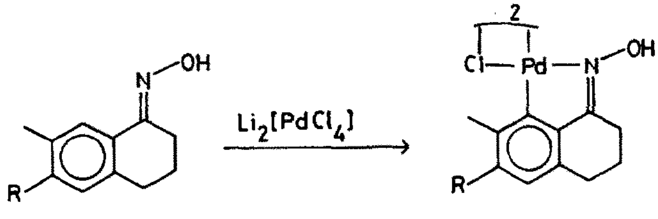
185

2-Phenylthiazole reacted with $Pd(OCOMe)_2$ to give a cyclometallated bridged dimer which underwent the conventional insertion and bridge splitting reactions. $Li_2[PdCl_4]$, however, yielded a simple *trans*-$[PdL_2Cl_2]$ coordination complex [193]. 2-Aryloxazoles showed analogous behaviour [194].

Reaction of a mixture of PhCH=CH-CH=NR and CH_2=CR'-CR"=CH_2 with $[Ni(cod)_2]$ gave **186**, the structure of which was deduced from nmr spectroscopic data [195]. The oxime, **187**, could also be cyclopalladated to give **188** [196].



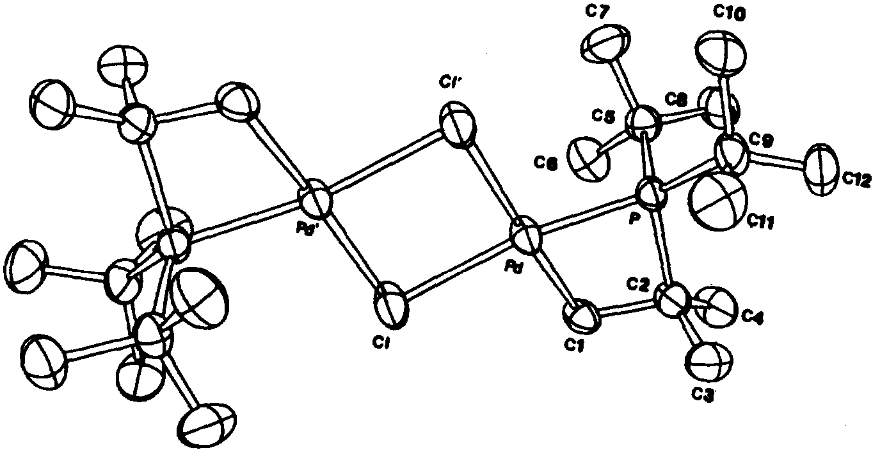
186



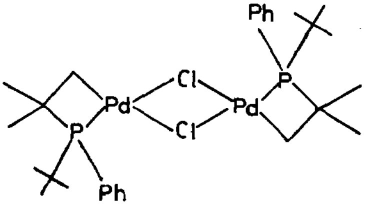
187

188

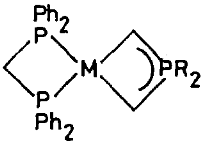
Further data on the cyclometallated species derived from $P(CMe_3)_3$ have been published. The structures of $[\overline{M\{(Me_3C)_2PCMe_2CH_2}\}_2]$ have been established by X-ray diffraction. The platinum complex, **189**, was shown to be isomorphous with its palladium analogue [197]. **189** reacted with a range of ligands to give *trans*-[Pt(*P-C*)LCl], of which the ^{31}P nmr spectra are reported [198]. Reaction of $[Pt\{P(CMe_3)_3\}_2]$ with chloroform gave *trans*-$[HPt(CCl_3)\{P(CMe_3)_3\}_2]$ which decomposed to dichlorocarbene and *trans*-$[HPt\{P(CMe_3)_3\}_2Cl]$. The latter cyclised readily to **189**. Analogous processes, albeit at different rates, were observed using CH_3I, CH_2Cl_2 or I_2 as oxidant [199]. Treatment of $[\{Pd(P\{CMe_3\}_2Ph)Cl_2\}_2]$ with Ag[OCOMe] also resulted in cyclometallation to **190** as a mixture of *syn*- and *anti*-isomers [200]. Lithiated phosphines, $[Ph_2PCH]Li$, reacted with $[M(PMe_3)_2Cl_2]$ (M = Ni, Pd or Pt) to give $[M\{CH_2(PPh_2)_2\}_2]$ which reacted with an ylid, $R_2P(Me)$=CH_2 to give **191** [201].



189 (Reproduced with permission from [198])

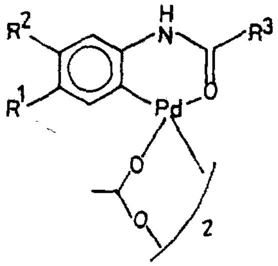


190

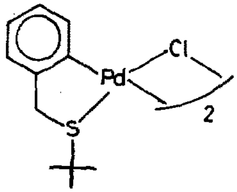


191

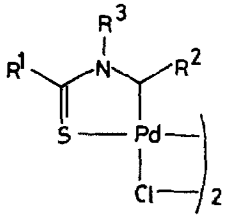
Whilst *C-O*-coordinated ligands are relatively rare in cyclometallated species, 192 has been synthesised by the reaction of the arylamide with Pd(OCOMe)$_2$. Again the expected reactions are duly reported [202]. *S-C*-coordinated ligands have been somewhat more popular; in 193 and its customary derivatives the ^{1}H nmr spectrum showed dynamic behaviour characteristic of the inversion of the Me$_3$C group at sulphur [203]. Similar species were formed from (PhCH$_2$)$_2$S and (PhCH$_2$)$_2$SO [204]. Treatment of R'C(=S)NR^{3}CH$_2$R^2 with PdCl$_2$ gave 194. With 195 the product was 196 in MeOH and 197 in hmpa, for reasons which are not entirely clear [205]. The X-ray diffraction structural determination of 198 indicated that both resonance forms, 198a and 198b contribute significantly to the structure [206].



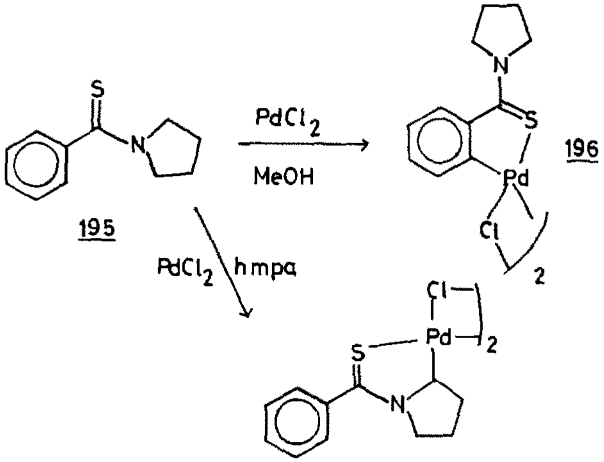
192



193



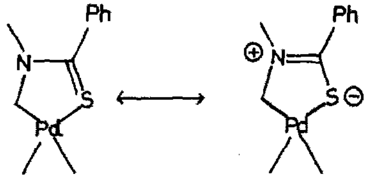
194



195

196

197



198a

198b

6 METAL CARBONYL AND THIOCARBONYL COMPLEXES

Energy optimised Slater orbitals were found for the *nickel* 4s and 4p levels by performing *ab initio* molecular orbital calculations on [Ni(CO)$_4$]

[207]. The frequency and intensity of the C-O stretching modes of [Ni(CO)$_4$] could be explained without recourse to the usual σ-donor/π-back-bond model [208]. Other workers have analysed the infra-red spectrum of [Ni(CO)$_4$] from the point of view of an equilibrium charge-charge flux model of dipolar derivatives [209].

The inner valence shell region of the photoionisation spectrum of [Ni(CO)$_4$] was studied by means of a two-particle-hole Tamm-Dancoff approximation [210]. The dissociation of the molecule has been investigated by the method of laser induced dielectric breakdown [211]. Proton affinities for transition metal complexes including [Ni(CO)$_4$], [Cp$_2$Ni] and [CpNi(NO)] were determined. In [Ni(CO)$_4$] protonation was thought to occur at the metal, but in the other two complexes it is more likely that the Cp ligand is protonated [212].

The concentration of [Ni(CO)$_4$] in air has been determined by glc [213]. Methods for the preparation of steam and gas mixtures with the desired concentrations of [Ni(CO)$_4$] and of detecting low [Ni(CO)$_4$] concentrations were devised [214]. Nickel has been recovered and reactivated by exposure to molecular hydrogen at 600-900 °C, followed by CO at 100 °C, to give [Ni(CO)$_4$] [215]. With ultra-high vacuum techniques and a flow system, the rate of formation of [Ni(CO)$_4$] on Ni(100) was continuously monitored in a field of up to 1000 G, without the detection of any magnetic field effect [216]. Crystals of nickel metal were formed from decomposition of [Ni(CO)$_4$] under specified conditions [217].

The interaction of [Ni(CO)$_4$] with evaporated PdFe surfaces was monitored by XPES [218]. Temperature programmed decomposition of [Ni(CO)$_4$] on γ-alumina gave a substantial amount of methane during catalyst activation. Decomposition occurred at temperatures much lower than those required for methanation [219]. The loss of methanation activity of Ni/Al$_2$O$_3$ was thought to be due to a growth in nickel particle size. The mechanism proposed involves formation of [Ni(CO)$_4$] followed by diffusion and decomposition [220]. Adsorption of [Ni(CO)$_4$] on a zeolite, (MNaX), was studied; adsorption capacity was shown to decrease with the atomic number of the metal in the zeolite [221]. The first stage of decomposition of the adsorbed complex at 70-100 °C involved loss of three moles of carbon monoxide followed by formation of the cyclic species [Ni$_3$(CO)$_3$] [222].

The mechanism of carbon monoxide replacement in [M(CO)$_n$] complexes has been reviewed; for [Ni(CO)$_4$] this follows a dissociative route [223]. When [Ni(CO)$_4$] was subjected to direct or sensitised photolysis using 11.6 or 11.8 eV photons all the ligands were removed in a single step. Excess energy was removed by the metal as electronic excitation [224]. Thermalised tritium atoms reacted with $[Ni(CO)_4]$ to give XT·, which underwent quantitative tritium exchange with Si-H bonds. C-C bonds in hydrocarbons were also reactive, but C-Si and Si-Si moieties were unaffected [225]. $[Ni(CO)_3]^-$ has been prepared in an inert gas matrix at 10 K by vacuum UV irradiation, electron bombardment or cocondensation with alkali metal atoms followed by photolysis. A study of the ^{13}CO labelled species led to the conclusion that $[Ni(CO)_3]^-$ adopted a trigonal planar D_{3h} structure, and that irradiation (visible or UV light) gave photoionisation rather than CO loss [226].

The synthesis of $[Ni(CO)_2\{PhHP(CH_2)_3PHPh\}]$ has been described [227]. Other processes involving displacement of carbon monoxide from $[Ni(CO)_4]$ by various ligands are shown in reactions (31) - (34) [228-231]. $[Ni(CO)_3(MeAsH_2)]$ was found to be too unstable to be isolated, decomposing to CO, H_2 and an insoluble oligomer [232]. Nickel carbonyl complexes of functionalised ferrocenes and cyclometallated palladium complexes of ferrocenyl amines have been reviewed [233].

$$[Ni(CO)_4] + 2\ \underset{HL}{MeC(=NOH)NO} \longrightarrow \textit{cis}\text{-}[NiL(H_2L)] + 4CO \qquad (31)$$

$$[Ni(CO)_4] + Me_2SbSbMe_2 \longrightarrow [(OC)_3Ni(\mu\text{-}Me_2SbSbMe_2)Ni(CO)_3] \qquad (32)$$

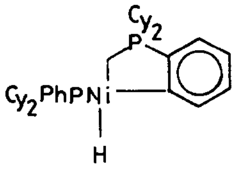
$$[Ni(CO)_4] + [(OC)_5Cr(Me_2PPMe_2)] \longrightarrow [(OC)_3Ni(\mu\text{-}Me_2PPMe_2)Cr(CO)_5] \qquad (33)$$

$$[(OC)_3Ni(\mu\text{-}Me_2PPMe_2)Cr(CO)_5] + [(OC)_5Cr(Me_2PPMe_2)] \longrightarrow [(OC)_2Ni\{(\mu\text{-}Me_2PPMe_2)Cr(CO)_5\}_2] \qquad (34)$$

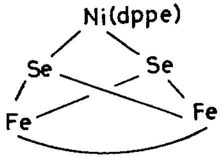
An X-ray crystal structural determination has been reported for $[(OC)_4Cr(\mu\text{-}Me_2PPMe_2)_2Ni(CO)_2]$ [234]. The structure of $[Ni(CO)_2(PCy_3)_2].0.5\ Et_2O$, a catalyst for alkene oligomerisation and hydrocyanation, was shown to involve distorted tetrahedral coordination of nickel [235].

Electrochemical syntheses of nickel carbonyl complexes from $[Ni(acac)_2]$ have been discussed, with particular reference to solvent effects and the problems of cluster formation [236]. Electrochemical syntheses of $[Ni(acac)_2]$, $[Ni(CO)_3(PPh_3)]$ and $[Ni(CO)_2(PPh_3)_2]$ were also described [237]. Treatment of $[Ni(PCy_2Ph)_2Cl_2]$ with sodium metal in the presence of carbon monoxide gave $[Ni(CO)_2(PCy_2Ph)_2]$. However, dissociation of this species gave $[Ni(PCy_2Ph)_2]$, which was cyclometallated to **199** in a reaction sequence leading ultimately to biphenyl [238]. Carbonylation of $[HNi(PPh_3)_3Br]$ in the presence of $H[BF_4]$ gave $[Ni(CO)_2(PPh_3)_2]$ *via* $[HNi(CO)(PPh_3)_3]^+X^-$ [239]. Displacement of carbon monoxide from $[Ni(CO)_4]$ was used to synthesise

$[Ni(DAD)_2]$ (DAD = $R^3N{=}C(R^1){-}C(R^2){=}NR^4$) [240], and from $[Ni(CO)_2(dppe)]$ to give 200 [241]. Nmr spectroscopic parameters were determined for $[Ni(CO)_3\{P(CMe_3)_{3-n}(SnMe_3)_n\}]$ [242].



199



200

The reduction of $FeCl_3$ to $FeCl_2$ by carbon monoxide in the presence of $PdCl_2$ was proposed to occur *via* the steps of reactions (35)-(42) [243].

$$\{Pd(II)\} + CO \rightleftharpoons \{Pd(II)(CO)\} \tag{35}$$

$$\{Pd(II)(CO)\} + CO \rightleftharpoons \{Pd(II)(CO)_2\} \tag{36}$$

$$\{Pd(II)(CO)_2\} + H_2O \longrightarrow \{Pd(0)(CO)\} + CO_2 + 2H^+ \tag{37}$$

$$\{Pd(0)(CO)\} + H_2O \longrightarrow \{Pd(0)(CO)(H_2O)\} \tag{38}$$

$$\{Pd(0)(CO)(H_2O)\} + \text{oxidant} \longrightarrow \{Pd(0)\} + CO_2 + \text{reduced species} + 2H^+ \tag{39}$$

$$\{Pd(0)\} + CO \longrightarrow \{Pd(0)(CO)\} \tag{40}$$

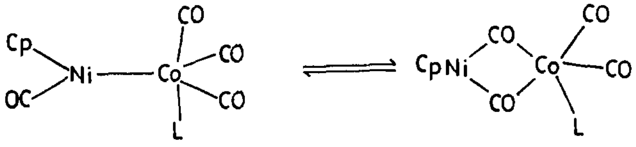
$$\{Pd(0)(CO)\} \longrightarrow \{Pd_2(CO)_2\} \tag{41}$$

$$\{Pd_2(CO)_2\} + \text{oxidant} + 2H_2O \longrightarrow 2CO_2 + 4H^+ + \text{reduced species} + 2Pd(II) \tag{42}$$

Carbonylation of *trans*-$[M_2\{As(CMe_3)_3\}_2(\mu\text{-}Cl)_2Cl_2]$ (M = Pd or Pt) or *trans*-$[Pt\{As(CMe_3)_3\}_2Cl_2]$ gave $[M(CO)\{As(CMe_3)_3\}Cl_2]$. For the palladium bridged dimer the reaction was reversible and yielded a *trans*-complex, but for the platinum species the processes were essentially irreversible giving *cis* products [244]. Treatment of $[Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2]$ with L (L = Me_2SO or Et_2SO) gave *cis*-$[Pt(CO)LCl_2]$. Thermolysis of the product (L = Me_2SO) occurred without isomerisation to give CH_3Cl and CO_2 [245].

Transition metal carbonyl clusters have been reviewed with emphasis on their electronic structures [246], fluxional behaviour [247] and their relationship to supported metal catalysts [248]. Molecular orbital calculations both in bare clusters and metal cluster carbonyls have been discussed in relation to the structural systematics of clusters [249]. A general method of assignment of energies to the M-M bonds of metal carbonyl clusters using the relationship $E = Ad^{-(4-6)}$ (d = metal-metal distance; A = constant which varies between 0.73 and 1.93) gave lower enthalpies than those previously estimated, and implied that metal ligand bonding increased with cluster nuclearity [250].

Reaction of $[Ni_5(CO)_{12}]^{2-}$ with $[Ni(CO)_4]$ gave $[Ni_6(CO)_{12}]^{2-}$ reversibly. The $\{Ni_3(CO)_3(\mu\text{-}CO)_3\}$ unit is common to many clusters including heteronuclear ones such as $[MNi_6(CO)_{17}]^{2-}$ (M = Cr, Mo or W) [251]. Treatment of [CpNiLBr] with $Na[Co(CO)_4]$ gave $[CpNiCo(CO)_4L]$ in which the ligand has migrated from nickel to cobalt. These species exist as mixtures of **201a** and **201b** with the position of the equilibrium affected be temperature and ligands [252]. An analogue of the $[Cp_3Ni_3(\mu_3\text{-}CO)_2]$ system, *viz.* $[Cp_3Ni_2Co(\mu_3\text{-}CO)_2]$, was obtained by reaction of $[Cp_2Ni_2(\mu_2\text{-}CO)_2]$ with $[CpCo(CO)_2]$. Direct evidence was obtained that the unpaired electron occupied an antibonding orbital of the trimetal system [253].



201a

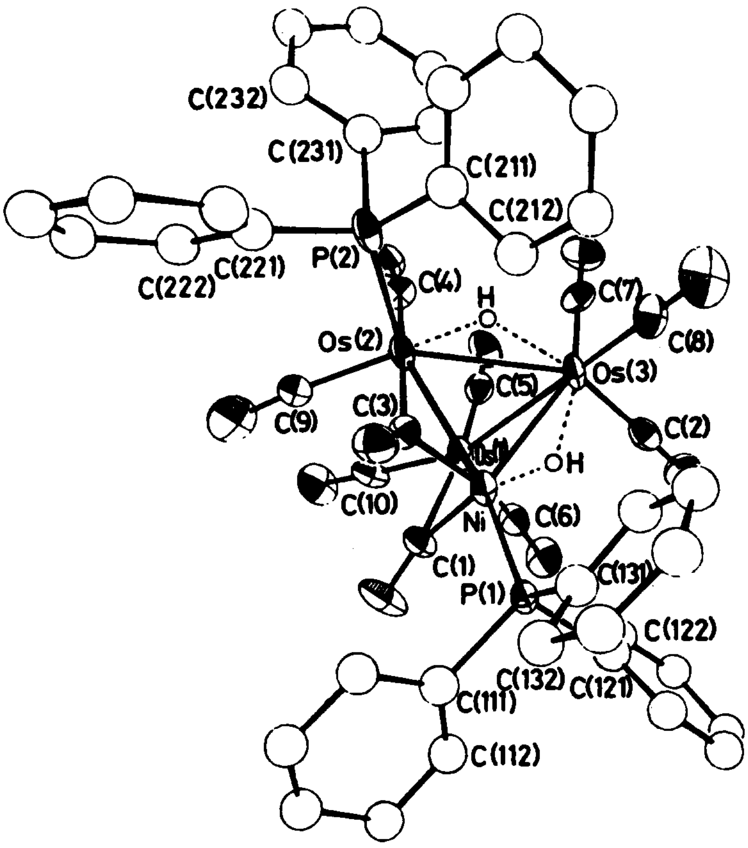
201b

In an attempt to synthesise an $\{NiOs_3\}$ species, $[Cp_3Ni_3Os_3(CO)_9]$ was obtained by reaction of $[Os_3(CO)_{12}]$ with two molar equivalents of $[Cp_2Ni_2(CO)_2]$. The structure of the product, determined by X-ray diffraction, involved a trigonal bipyramidal skeleton with osmium atoms equatorial, two nickel atoms apical and one capping a face of the bipyramid [254]. The sixty-electron complex, $[NiOs_3(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$, **202**, was prepared by reaction of $[Ni(C_2H_4)(PPh_3)_2]$ with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. X-ray diffraction data indicated a distorted tetrahedral structure with two Ni-Os edges bridged by CO and one Ni-Os and one Os-Os bridged by hydride [255]. A further report of mixed Ni-Ru clusters has been published. $[Cp_2Ni_2(C_2Ph_2)]$ reacted with $[Ru_3(CO)_{12}]$ to give $[Cp_2Ru_2Ni(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)]$, **203**. The alkyne is σ-bonded to one ruthenium and one nickel atom and π-bonded to the other ruthenium [256]. Other mixed clusters were synthesised, generally in low yield according to reactions (43) and (44). New materials characterised by X-ray diffraction included $[Cp_2Ni_2Fe(CO)_3(C_2Ph_2)]$ and $[Cp_2Ni_2Ru(CO)_3(C_2Ph_2)]$. These were isostructural, but their reactivities were somewhat different [257]. Strategies for the synthesis of metal carbide clusters have been discussed, and specific syntheses for $[NiFe_5C(CO)_{16}]$, $[PdFe_5C(CO)_{16}]$, $[NiFe_5C(CO)_{15}]^{2-}$, $[NiFe_4(cod)C(CO)_{12}]^{2-}$ and $[Ni_2Fe_4C(CO)_{14}]^{2-}$ described

[258].

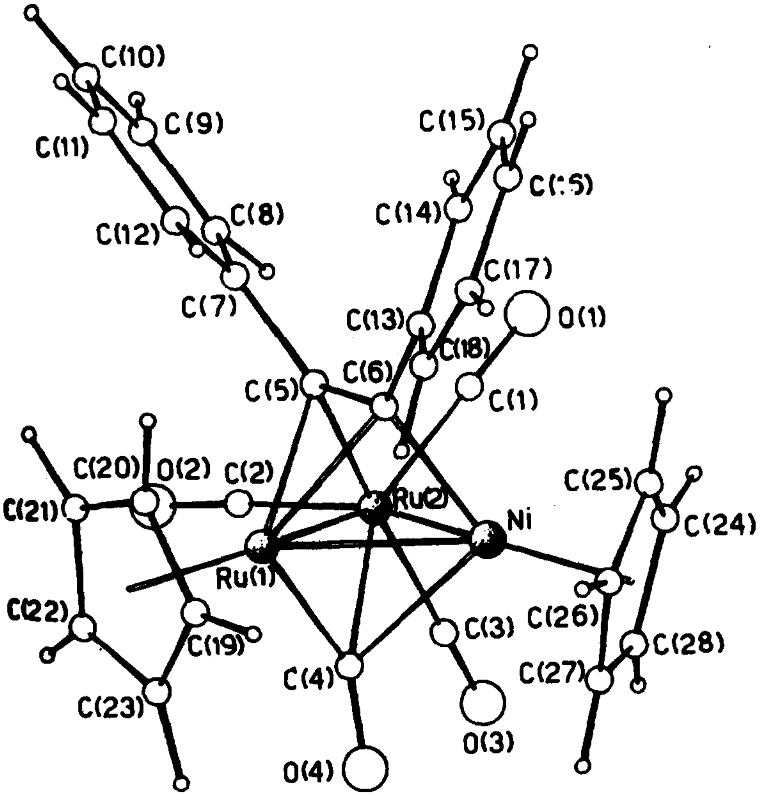
$$[\{CpNi(CO)\}_2] + [Ru_3(CO)_{12}] \longrightarrow [Ni(CO)_4] + [CpNiRu_3(CO)_9] \tag{43}$$

$$[\{CpNi(CO)\}_2] + [Ru_4(CO)_{12}(C_2Ph_2)] \longrightarrow [Ni(CO)_4] + [CpNiRu_3(CO)_9(C_2Ph_2)] + [Cp_2Ni_2Ru(CO)_3(C_2Ph_2)] \tag{44}$$

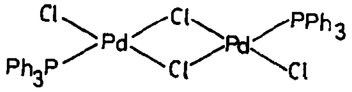


202 (Reproduced with permission from [255])

Treatment of $PdCl_2$ with carbon monoxide at fifty atmospheres pressure gave $[Pd_2(CO)_2Cl_4]$ in 60 % yield. Substitution of PPh_3 to give **204** was found to be faster than bridge splitting, in contrast to the platinum analogue, a fact which has implications for the catalytic function of palladium complexes in carbonylation reactions [259]. $[Pd_2(CO)_2Cl_4]$ was used as a catalyst for the copolymerisation of styrene with 4-vinyl pyridine [260]. The dimeric d^9 Pd(I) dianion $[Pd_2(CO)_2Cl_4]^{2-}$ was shown to have bridging carbonyl groups by both X-ray diffraction and solution IR spectroscopy [261].



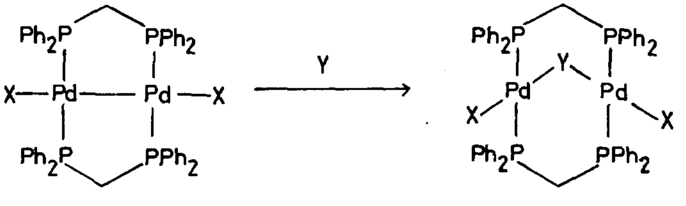
203 (Reproduced with permission from [256])



204

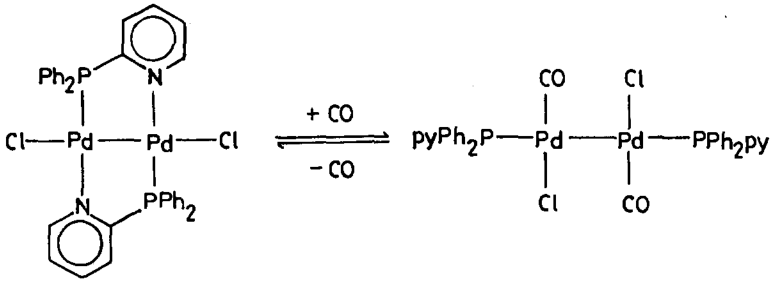
The disproportionation kinetics of $[\{Pd(PR_3)Cl\}_2CO]$ were followed by cyclic voltammetry, and the slow step was shown to be replacement of the bridging carbonyl by solvent molecule(s) *via* an associative mechanism. This was followed by rapid dissociation of the Pd-Pd bond [262]. Ligand substitution by PR_3 in $H_2[Pd_2(CO)_2X_4]$ gave *cis*-$[\{Pd(PR_3)X\}_2CO]$. This initial unstable product was converted to the *trans*-isomer at 60-80 °C [263]. Reaction of $[Pd_4(CO)_4(OCOMe)_2].2MeCOOH$ with 1,10-phen, L, gave $[Pd_2(CO)L_2(OCOMe)_2]$, also obtainable from treatment of $Pd(OCOMe)_2$/phen with carbon monoxide at 50 °C [264].

Insertion of groups Y into **205** gave **206** (Y = CO, CNR or alkynes), these adducts being resistant to exchange and protonation [139]. The electronic structure of such "A-frame" complexes has been discussed [265]. reaction of $[Pd(dppm)Cl_2]$ with carbon monoxide in the presence of $Na[BH_4]$ gave $[Pd(dppm)_2(CO)]$, when conducted in an ethanol solvent. Using $EtOH/Me_2CO$ as solvent $[\{Pd(dppm)Cl\}_2CO]$ was obtained [266]. Carbonylation of **207** was shown to be reversible [267].



205

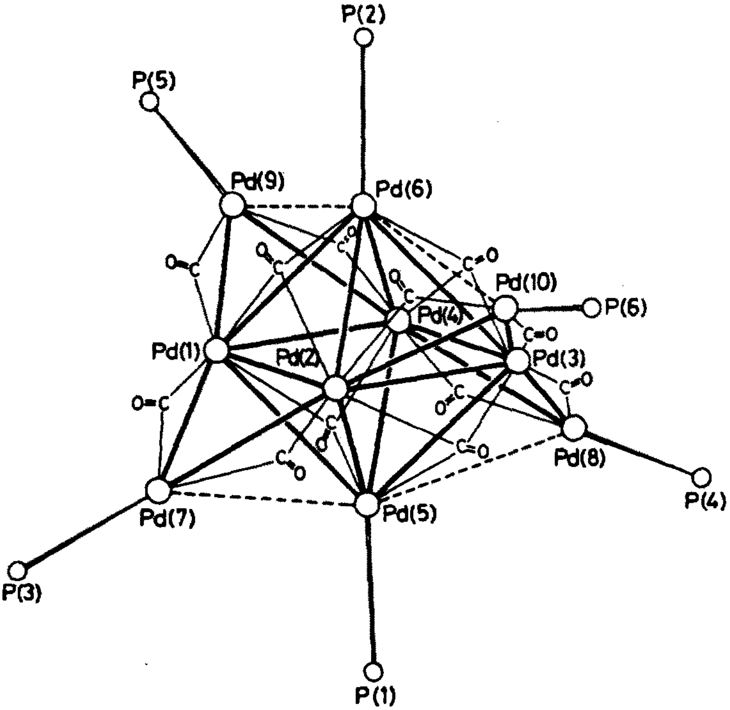
206



207

Reaction of $[M(NO)L_2X]$ (M = Pd or Pt) with carbon monoxide gave initially $[M(CO)_2L_2]$, which was oligomerised to high nuclearity clusters [268]. Treatment of $Pd(OCOMe)_2$ with a phosphine and carbon monoxide in varying proportions, gave rise to a range of species including $[Pd_{10}(CO)_{12}(PR_3)_6]$, $[Pd_{12}(CO)_{15}(PR_3)_7]$, $[Pd_{12}(CO)_{17}(PR_3)_5]$, $[Pd_{13}(CO)_{18}(PR_3)_5]$ and

$[Pd_{15}(CO)_{19}(PR_3)_9$ [269]. The structure of $[Pd_{10}(CO)_{12}(PBu_3)_6]$, **208**, was determined by X-ray diffraction to be a tetracapped octahedron of metal atoms, resembling a distorted fragment of close packed palladium [270]. If the reaction was conducted in the presence of ethanoic acid the major product was found to be the known butterfly cluster, $[Pd_4(CO)_5(PR_3)_4]$ [271]. The presence of tfaH favoured formation of $[Pd_{12}(CO)_{15}(PR_3)_7]$ and $[Pd_{12}(CO)_{17}(PR_3)_5]$ at Pd:P ratios of 1:1.5 - 1:15. At higher Pd:P ratios $[Pd_{13}(CO)_{19}(PR_3)_5]$ and $[Pd_{15}(CO)_{19}(PR_3)_9]$ were formed [272].



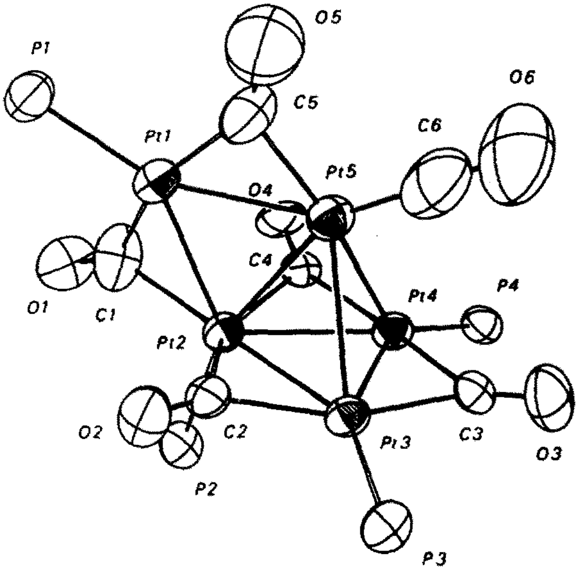
208 (Reproduced with permission from [270])

The ^{31}P nmr spectra of $[Pt_2(CO)(\mu\text{-}S)(PPh_3)_3]$ and a range of derivatives have been analysed in detail [273]. Molecular orbital studies of $J(^{195}Pt,^{31}P)$ and $J(^{195}Pt,^{195}Pt)$ in $[Pt_2(CO)_2(PPh_3)_2(MeOOCC{\equiv}CCOOMe)]$ were discussed [37].

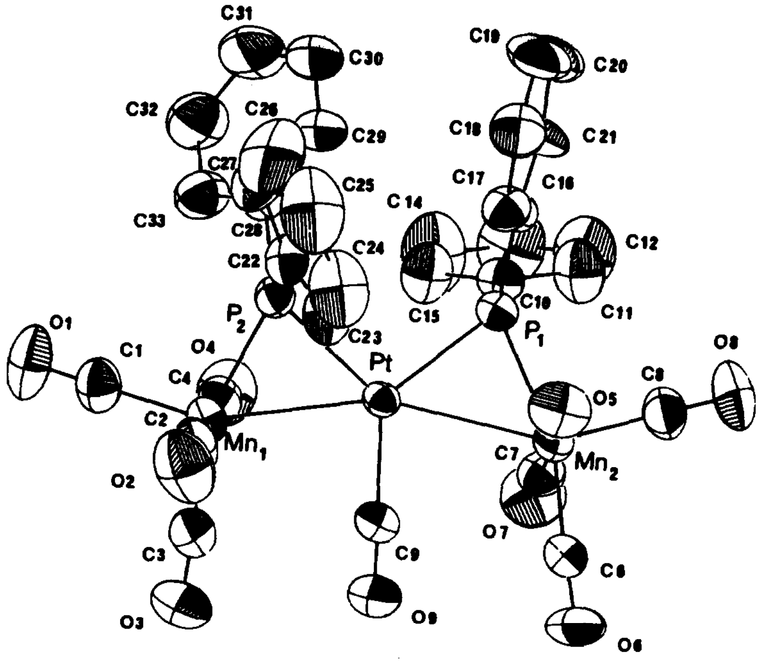
The nuclearity of $[Pt_3(\mu_2\text{-}CO)_3(PR_3)_3]$ was readily determined from ^{31}P and ^{195}Pt nmr spectra [274]. Silica supported platinum was prepared from the metal cluster $[Et_4N]_2[Pt_3(CO)_6]_3$. The increased catalytic activity observed for the hydrogenolysis of hydrocarbons was associated with the small metal crystallite size available from carbonyl cluster precursors [275]. $[Pt_3(\mu_2\text{-}CO)_3(PEt_3)_4]$ on alumina has been used as a hydrocracking catalyst

[276]. $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 5 or 6) was deposited from solution onto alumina. Exposure to air resulted in decarbonylation [277].

Reaction of *cis*- or *trans*-$[PtL_2Cl_2]$ with $K[Fe(CO)_3(NO)]$ gave only $[Pt_5(CO)_6L_4]$ with no mixed cluster formation. The structure of the complex for which L = PPh_3, **209**, was determined by X-ray diffraction. However, $[Pt(PPh_3)_2Cl_2]$ reacted with $[\{CpMo(CO)_3\}_2]$ to give $[Cp_2Pt_2Mo_2(CO)_2(PPh_3)_2]$, albeit in rather low yield [278]. Treatment of $[Pt(PPh_2Cl)Cl_2]$ with $Na[Mn(CO)_5]$ gave a complex mixture of *trans*-$[Pt\{Mn(CO)_5\}_2(CO)_2]$, **210**, **211** and **212**, the structures of the latter complexes being established by X-ray diffraction [279].

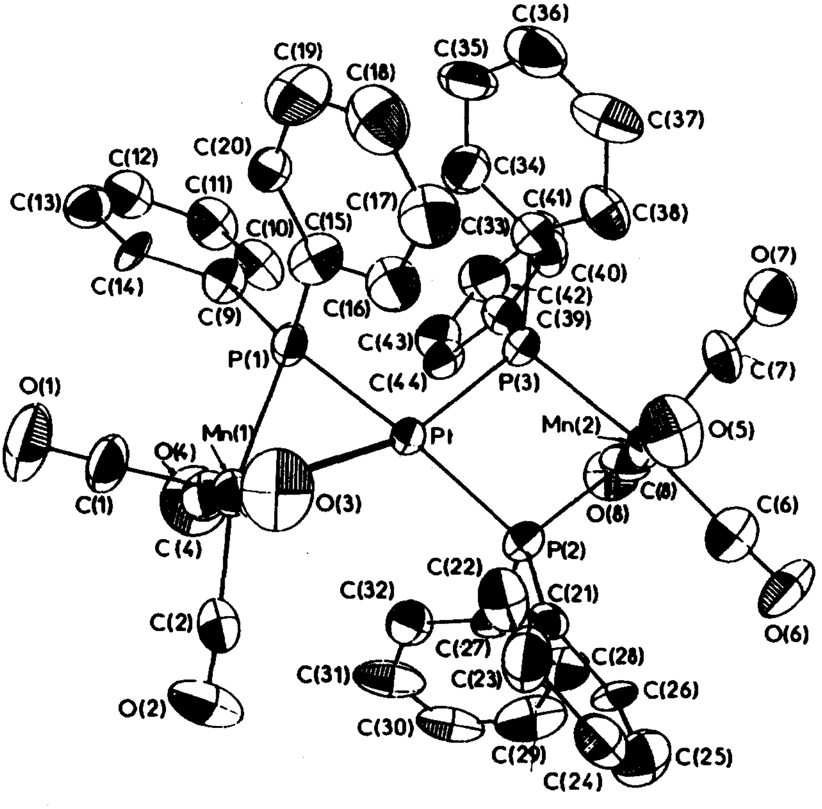


209 (Reproduced with permission from [278])



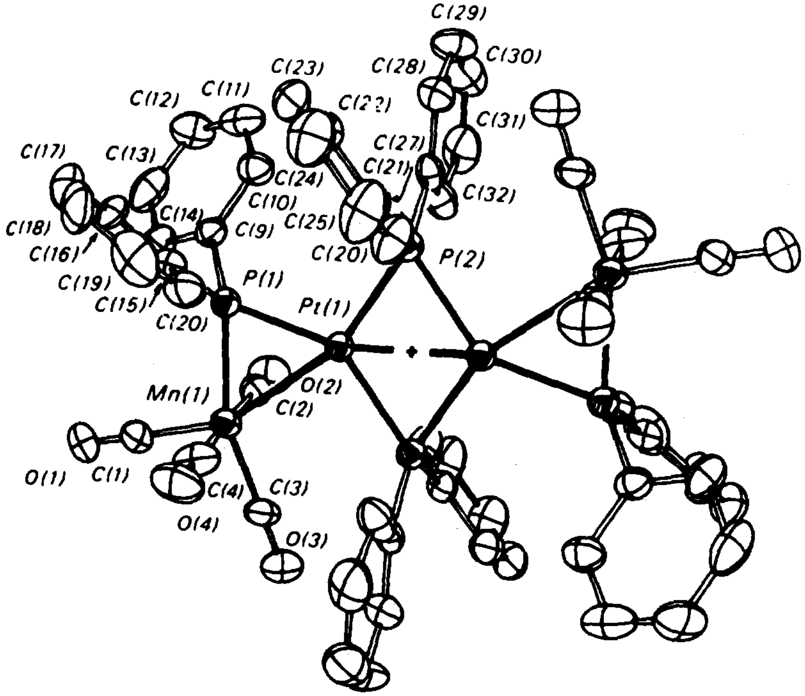
210 (Reproduced with permission from [279])

Mixed cobalt platinum clusters have also been prepared. $[Pt(PPh_3)_2Cl_2]$ reacted with $[Co_2(CO)_8]$ to give $[Pt_2Co_2(CO)_8(PPh_3)_2]$ and $[PtCo_2(CO)_8(PPh_3)]$, 213, the structure of the latter species being determined by X-ray diffraction [278]. The redox behaviour of $[(dppe)PtCo_2(CO)_7]$ and $[(Ph_3P)PtCo_2(CO)_8]$ has been investigated electrochemically. The reductions occurred *via* a one-electron irreversible step which resulted in the release of one $[Co(CO)_4]^-$ anion per mole of cluster. From $[(Ph_3P)PtCo_2(CO)_8]$, $[Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ could be isolated. Both of the $\{PtCo_2\}$ species undergo two one-electron oxidation steps, the first being reversible and the second leading to electrode passivation [280]. The species $[(\text{Ⓟ-}PPh_2)_2Pt_2Co_2(CO)_8]$, which has an open butterfly framework, was a catalyst for ethene hydrogenation at 1 atm H_2 and temperatures below 100 °C. However, closed tetrahedral complexes such as $[H_2PtOs_3(\text{Ⓟ-}PPh_2)_2(CO)_{10}]$ were inactive [281]. Treatment of $[Pt(C_2H_4)_3]$ with the doubly metal-metal bonded species $[Cp^*_2Rh_2(\mu\text{-}CO)_2]$ gave $[Cp^*_4Rh_4Pt(\mu\text{-}CO)_4]$, 214. Protonation of $[Cp^*_2Rh_2Pt(\mu\text{-}CO)_2(CO)(PPh_3)]$ with $H[BF_4]$ gave $[Cp^*_2Rh_2Pt(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)][BF_4]$, 215, the structure of which was established by X-ray diffraction. The complex showed dynamic behaviour on the nmr spectroscopic timescale at room temperature with the {PtLL'} moiety rotating around the axis of the Pt-(Rh=Rh) bond [282].



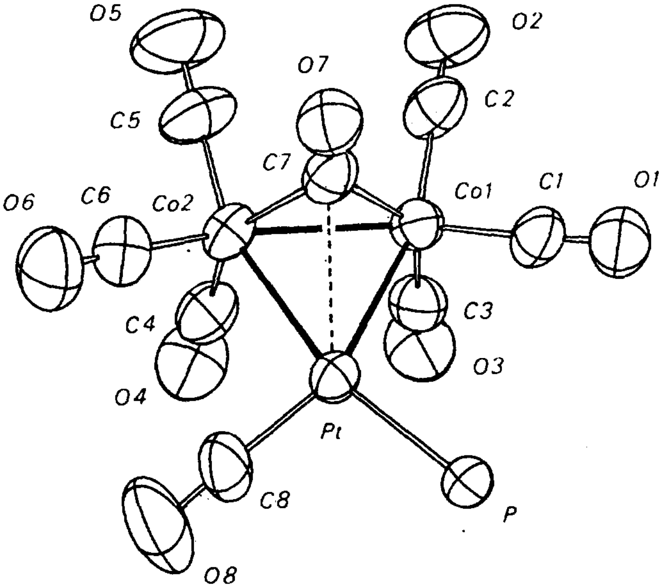
<u>211</u> (Reproduced with permission from [279])

Reaction of $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]^-$ with $[Pt(C_2H_4)(PPh_3)_2]$ gave $[Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, 216, by the displacement of the labile ethene ligand. X-ray diffraction was used for structural characterisation of the species. Protonation gave $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, 217, also characterised by X-ray diffraction. The hydrides bridge the longer Fe-Pt edges. Treatment of $[Pt(cod)(1\text{-}\sigma\text{-}4\text{-}5\text{-}\eta\text{-}C_8H_{13})][BF_4]$ with $[Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ gave **218** [283]. The epr spectrum of $[F_3Pt_3(CO)_{15}]^-$, of which the preparation was reported last year, has been recorded both in solution and in the solid state. The data imply that the unpaired electron is located in a non-degenerate orbital of the triplatinum system, which under idealised D_{3h} symmetry may primarily be the $a_2^{\prime *}$ combination of three d_{xz} platinum orbitals. The stability of the paramagnetic cluster probably derives from the unpaired electron being located on platinum, and from the steric properties of the {μ-Fe(CO)$_4$} group which hinder spin-pairing by dimerisation [284].

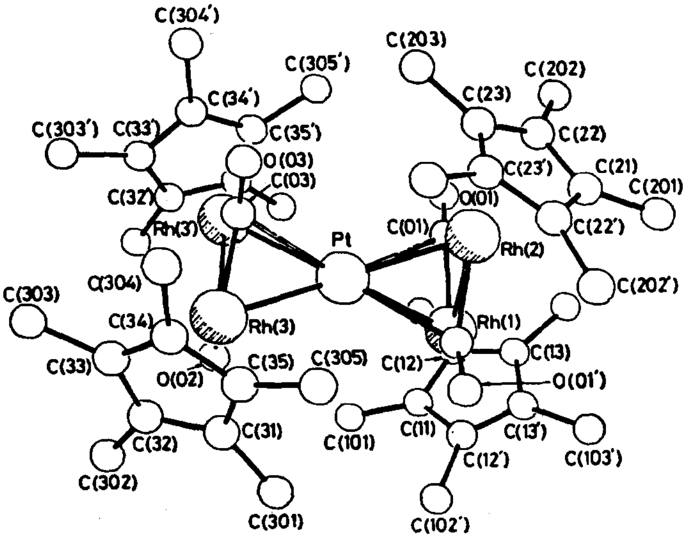


212 (Reproduced with permission from [279])

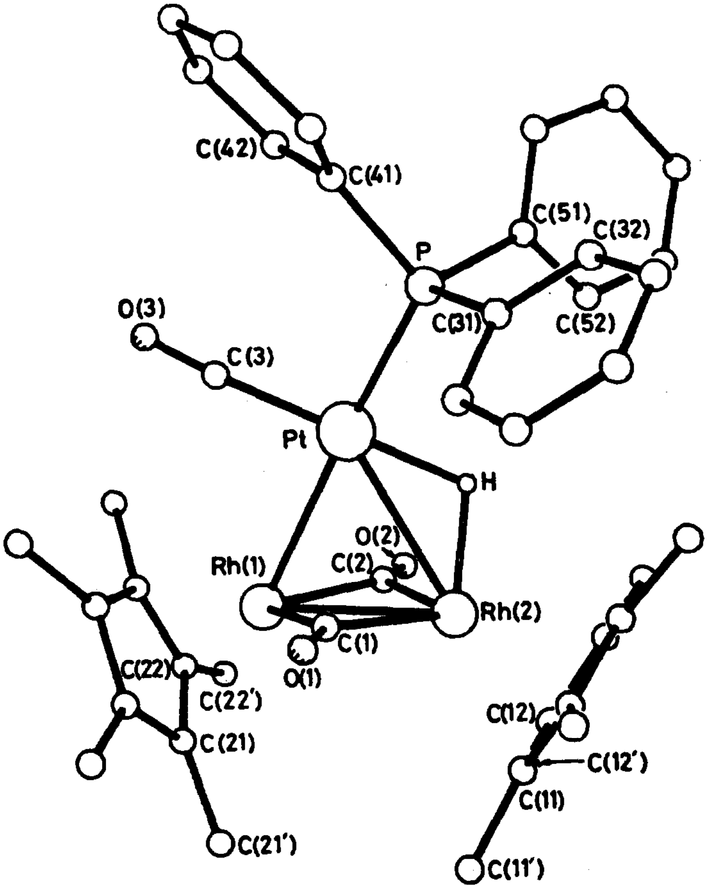
Reaction of [Pt(C_2H_4)$_2$(PR_3)] with [H_2Os(CO)$_4$] in a hydrocarbon solvent at room temperature yielded [Os_2Pt_2(μ-H)$_2$(CO)$_8$(PR_3)$_2$]. The structure of the PPh$_3$ derivative, **219**, was established by X-ray diffraction to be of the butterfly type with osmium atoms on the hinge and platinum atoms at the wingtips [285]. With the same platinum complex, [Os_3(μ-H)$_2$(CO)$_{10}$] gave the fifty-eight electron cluster, [Os_3Pt(μ-H)$_2$(CO)$_{10}$(PR_3)]. The structural determination on the PCy$_3$ complex, **220**, showed that the platinum atom was bound to one carbon monoxide and one phosphine ligand, and that the hydrides bridged the longer of the Os-Os and Os-Pt bonds [286]. Reaction of the product with a further equivalent of ligand, L, (L = CO, PPh$_3$ or AsPh$_3$) gave [Os_3Pt(μ-H)$_2$(CO)$_{10}$(PR_3)L]. In the complex with L = PR_3 = PPh$_3$, **221**, the metal atoms were shown to adopt a butterfly arrangement, in contrast to the tetrahedral structure of the precursor. One phosphine is platinum bound and the other ligated to osmium. On addition of 2-butyne five clusters could be isolated, none of them {Os_3Pt} species. [$OsPt_2(CO)_5(PPh_3)_2\{\mu_3-(CH_3-C\equiv C-CH_3)\}$], 222, was characterised by X-ray diffraction [287].



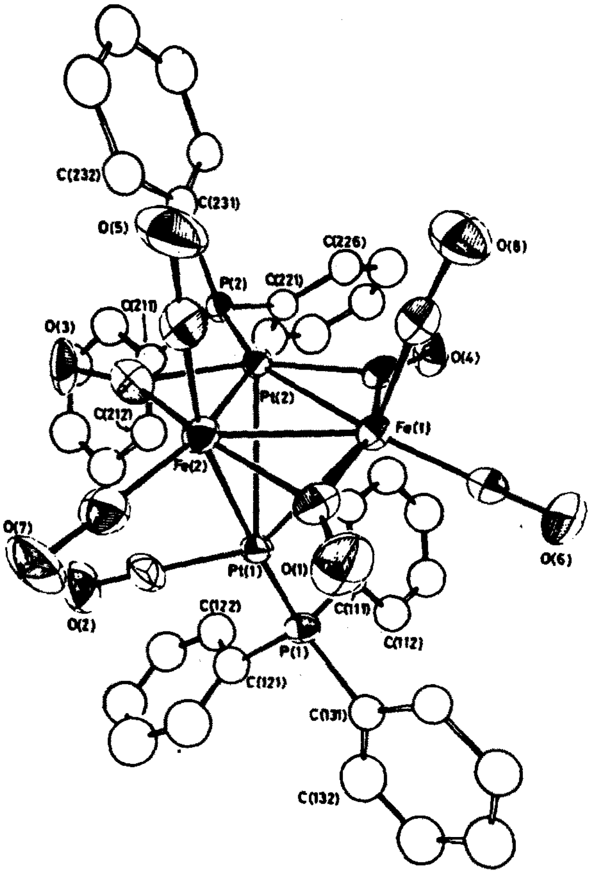
213 (Reproduced with permission from [278])



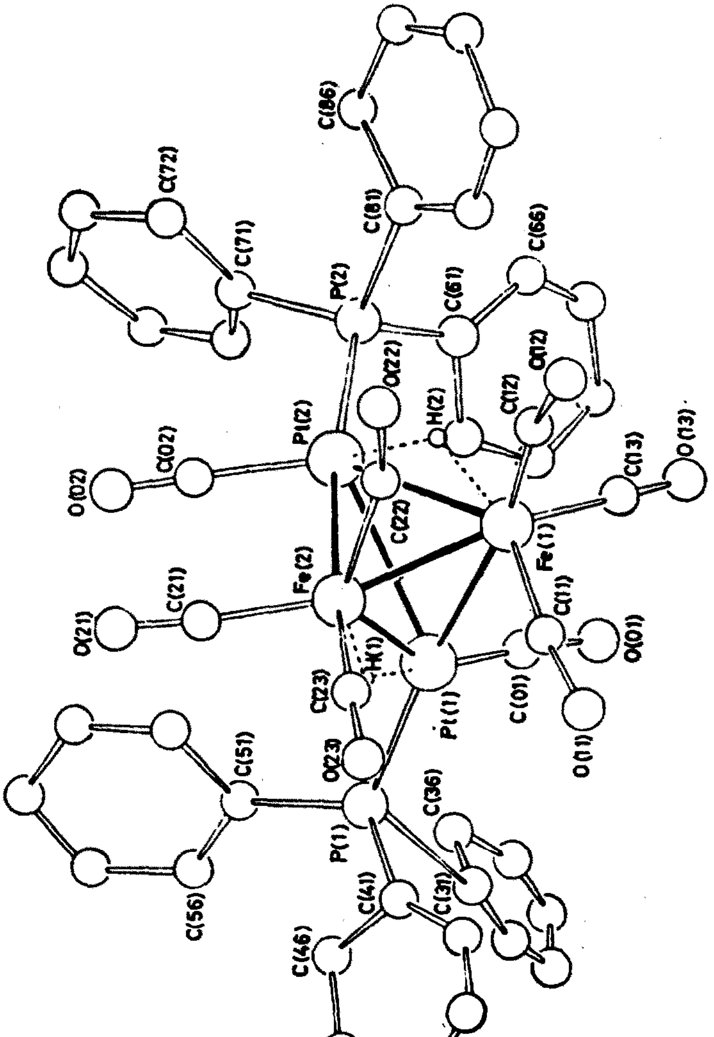
214 (Reproduced with permission from [282])



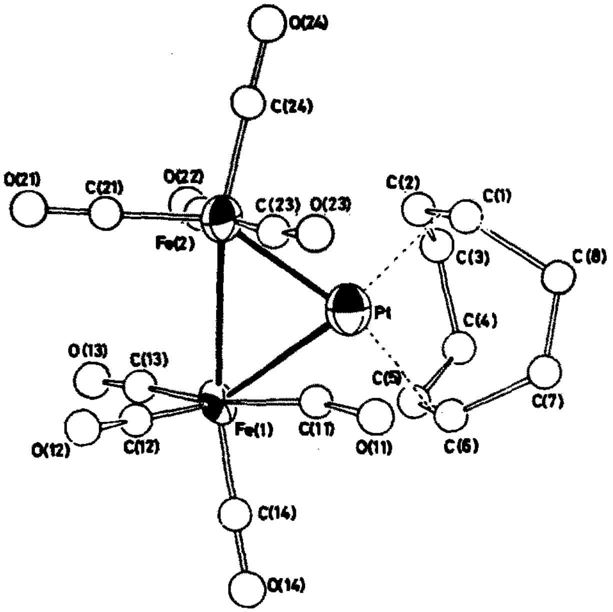
215 (Reproduced with permission from [282])



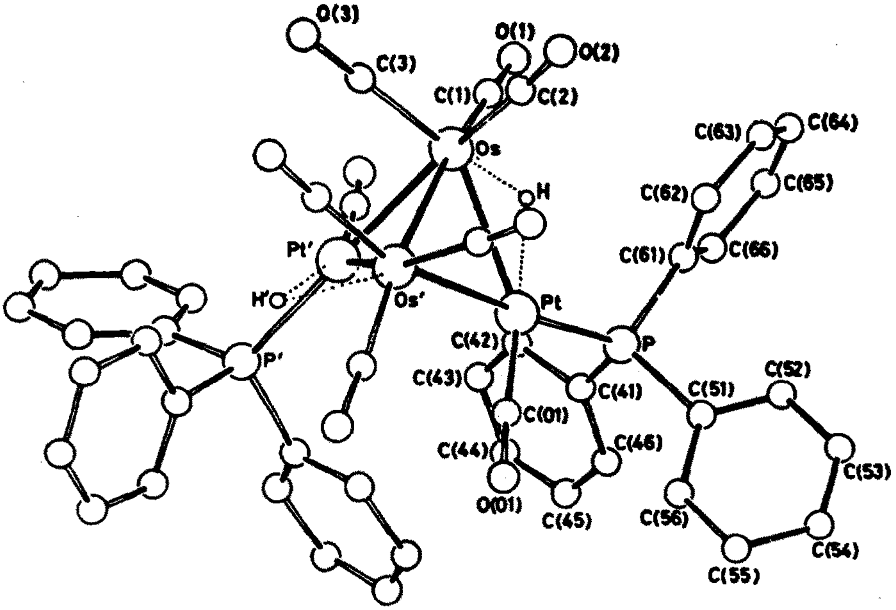
216 (Reproduced with permission from [283])



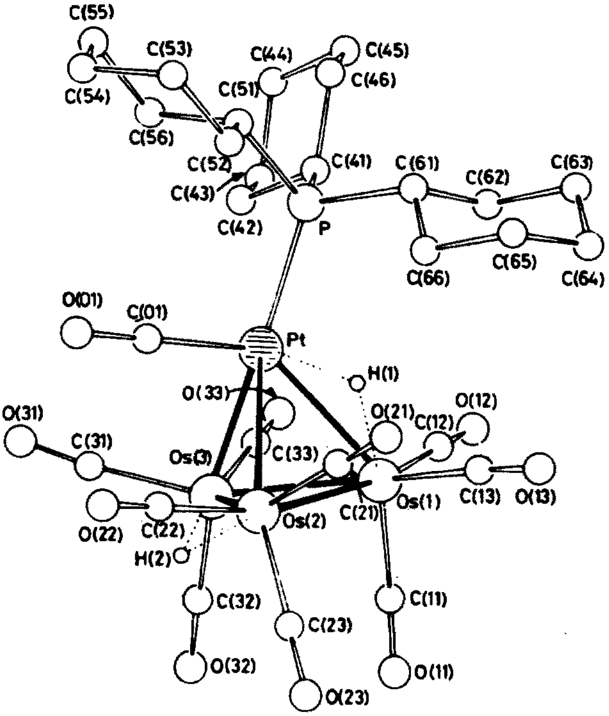
217 (Reproduced with permission from [283])



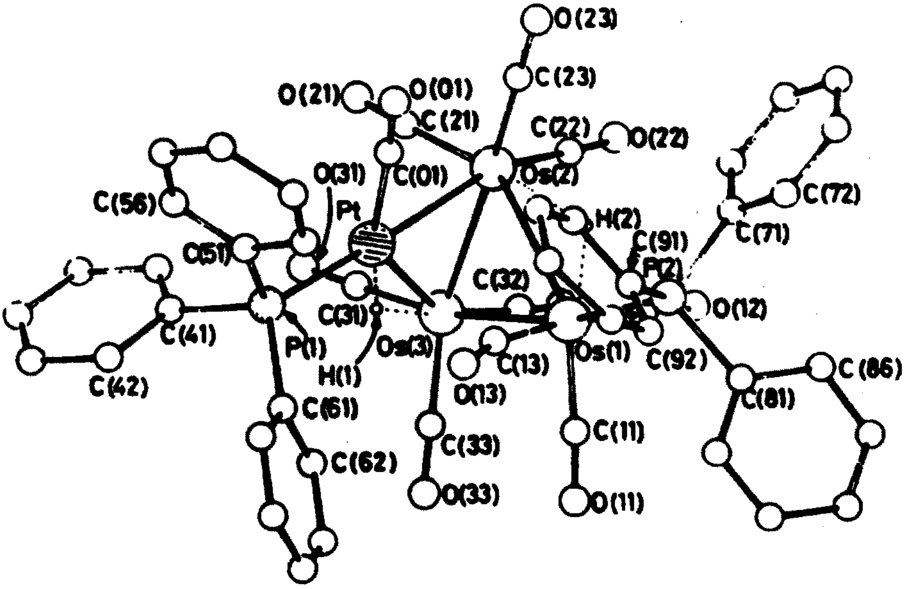
218 (Reproduced with permission from [283])



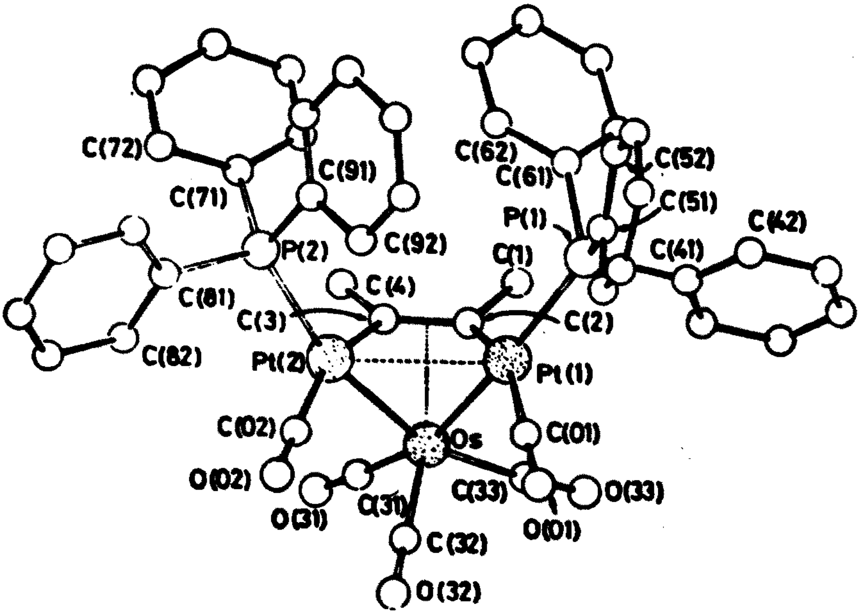
219 (Reproduced with permission from [285])



220 (Reproduced with permission from [286])

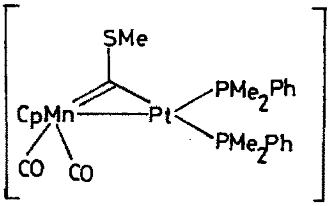


221 (Reproduced with permission from [287])

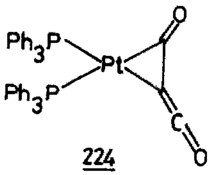


222 (Reproduced with permission from [287])

The thiocarbonyl species [CpM(CO)$_2$(μ-CS)Pt(PR$_3$)$_2$] was synthesised from [Pt(C$_2$H$_4$)(PR$_3$)$_2$] and [CpM(CO)$_2$(CS)] (M = Mn or Re). Both CO and CS undergo bridge/terminal site exchange on the nmr spectroscopic timescale at room temperature. At -60 °C the thiocarbonyl appears static and a value of $\Delta G^{\ddagger}$ = 50±5 kJ mol^{-1} was determined for exchange. The carbon monoxide ligand is still fluxional at this temperature; in the solid state for M = Mn and PR$_3$ = PMePh$_2$ it appeared to be semi-bridging. Reaction with [Me$_3$O][BF$_4$] gave the bridging carbyne, **223** [288].

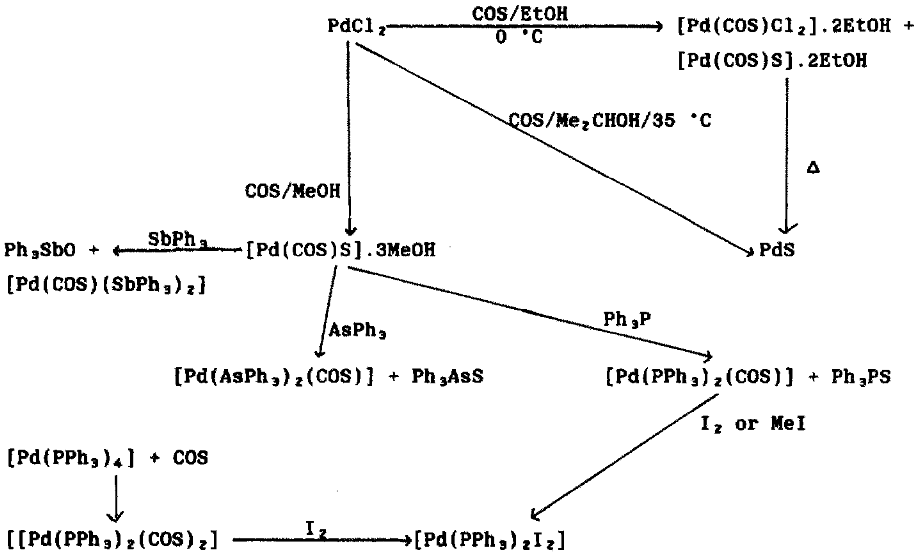


223



224

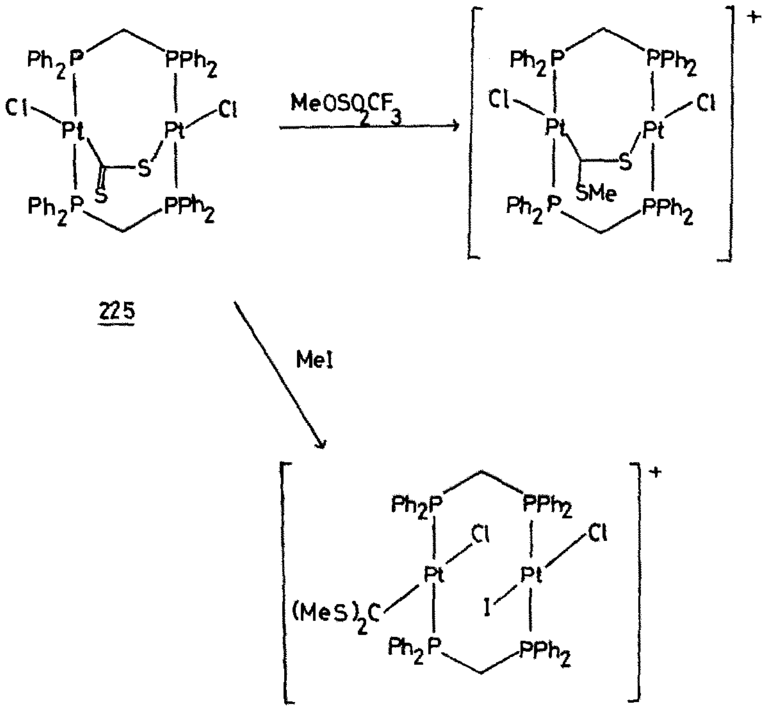
Complexes of carbon dioxide have been reviewed [289]. Carbon suboxide, C$_3$O$_2$, reacted with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] to give **224**, which underwent irreversible two-electron reduction at -1.8 V [290]. Both thermal and photochemical reactions of carbonyl sulphide with $PdCl_2$ in the presence of L (L = PPh_3 or $AsPh_3$) gave $[Pd(COS)L_2]$ [291]. Some further reactions of $PdCl_2$ with COS are shown in Scheme 6. Among the products both η^1- and η^2-COS complexes could be identified [292].

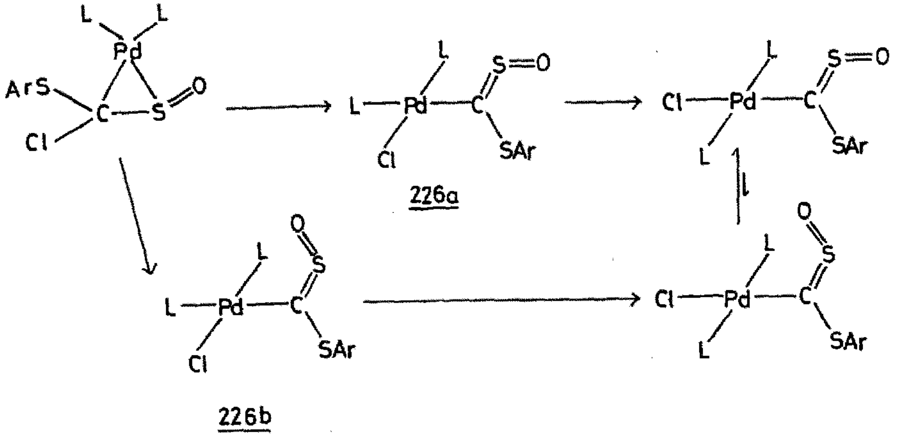


Scheme 6 Reactions of palladium chloride with carbonyl sulphide [292]

In $[Pd(CS_2)L_2]$ (L = PPh_3, $PEtPh_2$ or PCy_3; L_2 = dppe, dppb, bipy or phen) prepared from $[Pd_2(dba)_3]$, L and carbon disuphide, the CS_2 ligand was shown to be π-bonded by infra-red spectroscopy [293]. CS_2 was found to insert into $[Pt_2(\mu\text{-dppm})_2Cl_2]$ to give the A-frame complex $[Pt_2(\mu\text{-}CS_2)(\mu\text{-dppm})_2Cl_2]$, **225**, characterised by X-ray diffraction. Despite the unusual bonding mode, the reactivity of the complex was typical of such species [294].

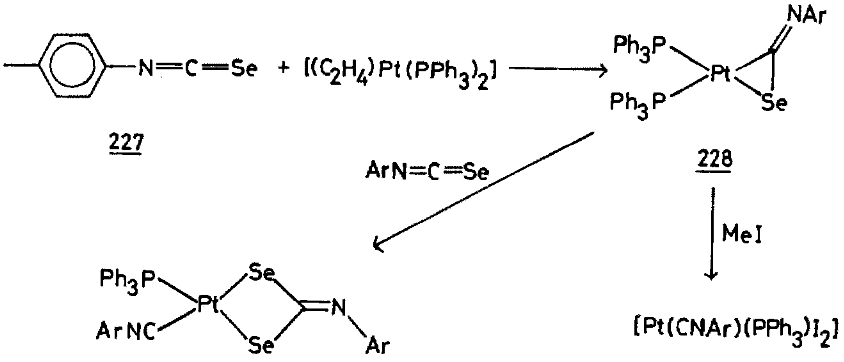
Sulphines, XYC=S=O, have been previously established to coordinate in an η^2-(*C-S*) manner to platinum(0). A further species of this type, $[Pd(PPh_3)_2\{(4\text{-}MeC_6H_4)_2C{=}S{=}O\}]$, prepared by addition of the sulphine to $[Pd(PPh_3)_4]$, has now been reported. It decomposed slowly in solution but did not undergo C-S oxidative addition to palladium, unlike its platinum analogue. If the sulphine used bears a chlorine atom, however, oxidative addition was facile, yielding initially species such a **226** (Scheme 7) [295].





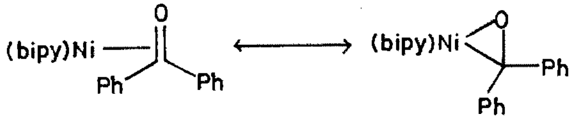
Scheme 7 Reactions of palladium sulphine complexes [295]

In the platinum series replacement of PPh_3 by the bulkier PCy_3 retarded oxidative addition [296]. A full paper has now reported the intramolecular oxidative addition of $[Pt(PPh_3)_2\{(RS)_2C{=}S{=}O\}]$ to give *cis*-E- and *cis*-Z-$[(RS)Pt(PPh_3)_2(RSCSO)]$. The mechanism of the oxidative addition was supposed to be a glide of the $\{Pt(PPh_3)_2\}$ fragment along the S-C=S frame *via* an $\{\eta^3$-SCS$\}$ intermediate [297]. The structure of $[Pt(PPh_3)_2(C_{12}H_8CSO)].0.5\ C_6H_6$, where $C_{12}H_8CSO$ is 9-sulphinyl fluorene, has been determined by X-ray diffraction [298]. $[Pt(C_2H_4)(PPh_3)_2]$ reacted with the related species **227** to give **228**, the first example of an η^2-bonded complex of this type [299]. Treatment of [Ni(bipy)(cod)] with benzophenone gave **229** [300].



227

228



229a

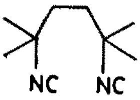
229b

7 METAL ISOCYANIDE COMPLEXES

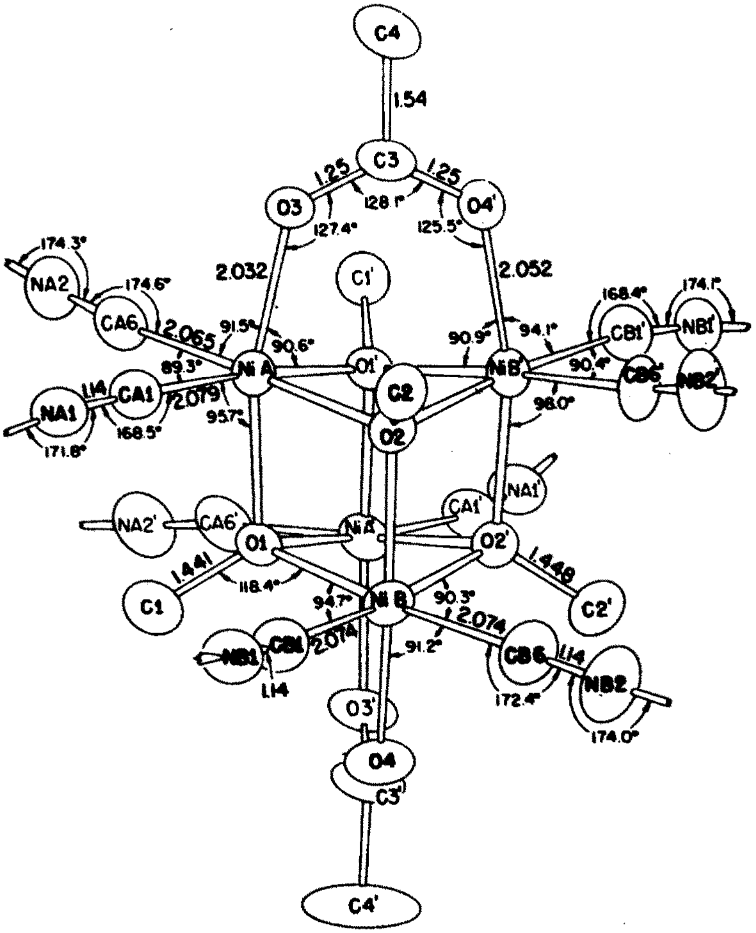
The structure of *cis*-$[(CyNC)_2PdCl_2]$ has been determined by X-ray diffraction techniques. One isocyanide group occupies an axial and the other an equatorial position on the cyclohexane ring [301,302]. Reaction of $[Pt_2(PR_2R^1)_2Cl_4]$ with R^2NC gave *trans*-$[(R^2NC)Pt(PR_2R^1)Cl_2]$. However, with $[Pt_2\{P(CMe_3)_2Pr\}_2I_4]$ and $4\text{-}MeC_6H_4NC$ at -78 °C, the initial product was *cis*-$[Pt\{P(CMe_3)_2Pr\}(CNAr)_2I]I$ [303].

Reaction of $[Ni(Ar_2N_4)_2]$ and $[Ni(cod)_2]$ gave an unidentified brown intermediate, which on treatment with Me_3CNC yielded $[Ni(CNCMe_3)_2(Ar_2N_4)]$

with 80 % effective ligand transfer [304]. Treatment of Ni(OCOMe)$_2$ with 230 followed by Na[BPh$_4$] gave [Ni$_4$(OCOMe)$_2$(OMe)$_4$(230)$_4$][BPh$_4$]$_2$, 231, characterised by X-ray diffraction. The nickel atoms and OMe groups occupy the corners of a cube, with ethanoates bridging metal atoms on opposite faces of the cube [305].

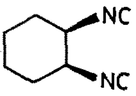


230

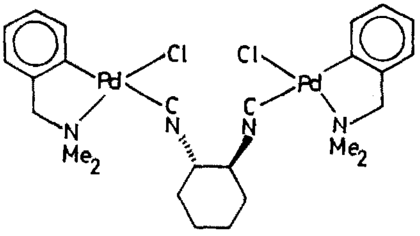


231 (Reproduced with permission from [305])

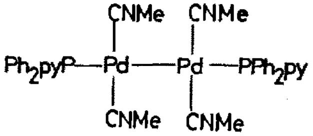
[Pd(cod)Cl_2] reacted with **232**, L, to give [$Pd_2L_2Cl_4$]. **233** was prepared from the appropriate halo bridged dimer [306]. Bridge splitting also occurred with *trans*-$[Ar_4Pd_2(\mu\text{-}X)_2]^{2-}$ to give *trans*-[$Ar_2Pd(CNR)_2$] (Ar = C_6Cl_5 or C_6F_5; X = Cl or F; R = CMe_3, Cy or 4-MeC_6H_4). The related *cis*-isomers could be obtained from tetrahydrothiophene complexes [307]. Reaction of **207** with MeNC or [$Pd_2(CNMe)_6$] with Ph_2(py)P gave 234 [266].



232



233



$$\begin{array}{ccccc} & \text{CNMe} & & \text{CNMe} & \\ & | & & | & \\ \text{Ph}_2\text{pyP}- & \text{Pd} & - & \text{Pd} & -\text{PPh}_2\text{py} \\ & | & & | & \\ & \text{CNMe} & & \text{CNMe} & \end{array}$$

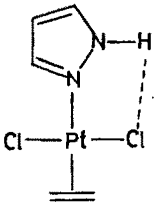
234

8 METAL ALKENE AND METAL ALKENYL COMPLEXES

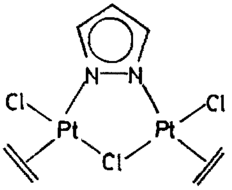
Ab initio molecular orbital calculations have been performed for [$Ni(C_2H_4)(PH_3)_2$] and [$Ni(C_2H_2)(PH_3)_2$]. The bond to the alkyne was thus shown to be stronger than that to the alkene. The relative importance of σ-donation and π-back donation was revealed through analysis of binding energy and electron distribution [308]. The X-ray diffraction data for [$Ni(C_2H_4)(PPh_3)_2$] have been improved; the complex is close to rigorously planar [309]. Infra-red spectroscopic data for various nickel(0) alkene complexes have been reported [310].

The structure and bonding in $[M(C_2H_4)Cl_3]^-$ (M = Pd or Pt) have been investigated by *ab initio* calculations in an extended basis. The calculated geometries agreed with a recent neutron diffraction study and the barrier determined for alkene rotation in Zeise's salt (62 kJ mol^{-1}) was in good accord with the experimental values observed in platinum alkene complexes

[311]. *cis*-$[Pt(C_2H_4)(NH_3)Cl_2]$ has been tested for growth inhibitory effects on corn roots [312]. The structures of two pyrazole platinum ethene complexes, **235** [313] and **236** [314], have been determined by X-ray diffraction techniques.



235



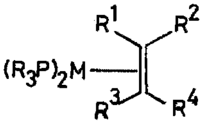
236

Alkene complexes have been used as precursors to coordination compounds in cases in which the alkene is readily displaced (reactions (45) and (46)) [315, 316].

$$[Pt(C_2H_4)_2\{P(CMe_3)_2Ph\}] \xrightarrow{H_2} [H_8Pt_5\{P(CMe_3)_2Ph\}_5] \quad (45)$$

$$[Pd_2(dba)_3] + [(OC)_4Co\text{-}Hg\text{-}Co(CO)_4] + P\text{-}P \longrightarrow [(P\text{-}P)Pd\{Co(CO)_4\}\{HgCo(CO)_4\}] \quad (46)$$

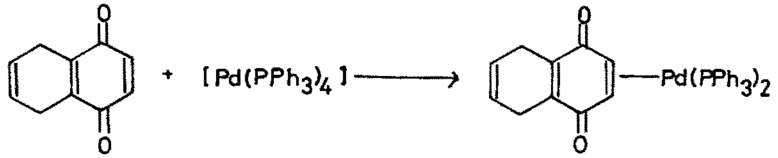
Proton nmr spectroscopic data for a wide range of complexes, *trans*-$[Pt(\eta^2\text{-alkene})(NHMe_2)Cl_2]$, have been reported [317]. A variety of species, **237**, have been synthesised by reaction of $[Pd(PPh_3)_4]$ or $[Pt(C_2H_4)(PPh_3)_2]$ with "push-pull" alkenes (for example, $R^1 = R^2 = OMe$, $R^3 = R^4 = CN$. The cyano group makes the alkene a better acceptor and alkoxy groups have the opposite effect). The data may be interpreted in terms of a "sliding" of the coordinated alkene, resulting in unusually low values for $^2J(Pt,H)$ [318].



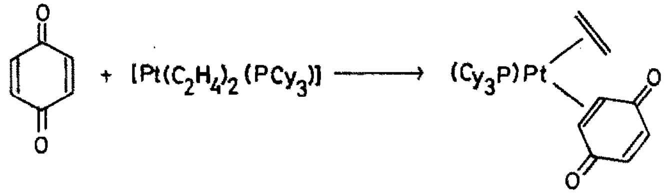
237

A range of quinone complexes have been prepared by reactions such as (47) - (49). In most cases the quinones were η^2-bonded as determined by X-ray diffraction and ^{13}C nmr spectroscopy [319-321]. Exceptions were provided by the platinum complex of tetramethyl quinone (which is η^4-coordinated) and the dinuclear species **238**.

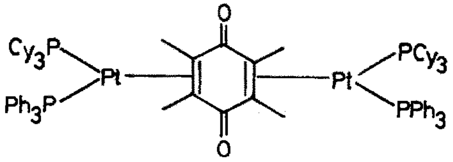
(47)



(48)

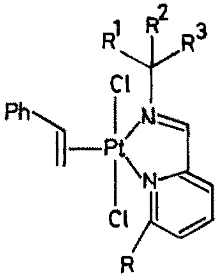


(49)

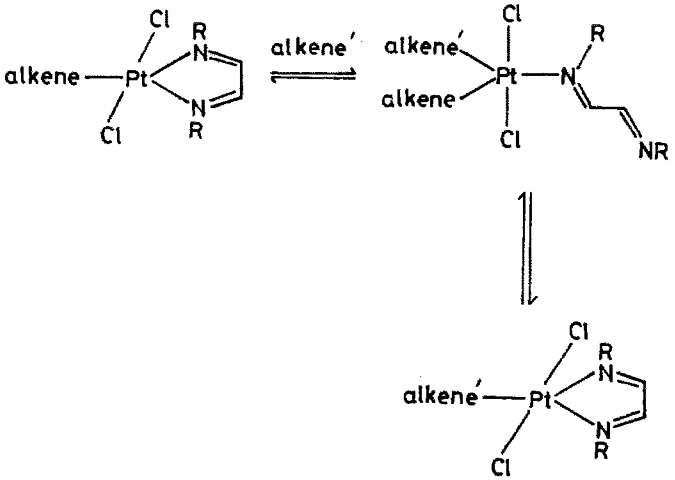


238

It has been suggested that the trigonal bipyramidal platinum(II) complexes such as [Pt(alkene)(N-N)Cl$_2$] (N-N = bridging dinitrogen ligand) should be classified with platinum(0) species such as [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] as Class T, rather than as Class S with [Pt(C$_2$H$_4$)Cl$_3$]$^-$. The underlying reasons were steric rather than electronic [322]. In such species the nitrogen ligands and the alkene occupy the equatorial, and the halides the axial positions. Synthesis generally involves reaction of the ligand with [Pt(η^2-alkene)Cl$_3$]$^-$. The structure of [Pt(η^2-PhCH=CH$_2$)(Me$_3$CN=CH-CH=NCMe$_3$)Cl$_2$] was determined by X-ray diffraction techniques, and solution spectroscopic data indicated little change on dissolution. However, in solution the alkene rotated, without dissociation, about the platinum-alkene bond, $\Delta G^{\neq}$ being determined as 56.2 kJ mol^{-1} for the styrene complex and 66.8 kJ mol^{-1} for the methacrylate containing species [323,324]. The barriers to rotation both here and in **239** were thought to be determined by steric factors [325]. Both the axial halogens and the equatorial substituents could be replaced with retention of the trigonal bipyramidal structure (reaction (50)) [326]. Analogous palladium complexes were prepared from [Pd$_2$(dba)$_3$], a diazabutadiene and an appropriate activated alkene such as tcne or maleic anhydride [327].



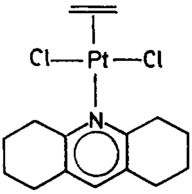
239



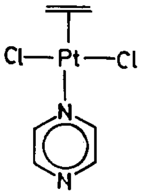
(50)

Reaction of [Pd(DIOP)$_2$] with activated alkenes gave derivatives of dimethyl maleate and maleic anhydride, [Pd(alkene)(DIOP)]. With *trans*-alkenes diastereoisomers were obtained, with modest selectivities, but the binding constant of the alkene decreased rapidly with the degree of substitution [328].

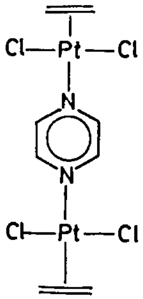
Treatment of $K[Pt(C_2H_4)Cl_3]$ with nitrogen heterocycles gave initial adducts such as **240** and **241**. With an excess of the platinum complex, **241** was converted to **242**. With a ligand such as **243** the chelating complex **244** was formed [329]. Similar complexes were formed from vinyl anilines such as **245** [330]. The stabilities of the complexes **246** were related to Y with a Hammett ρ value of -1.32. ^{13}C nmr spectroscopic data could also be correlated with σ-values [331].



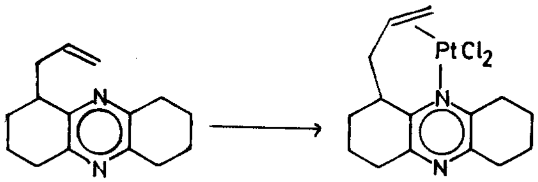
240



241

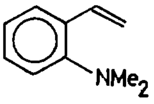


242

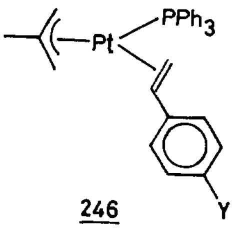


243

244



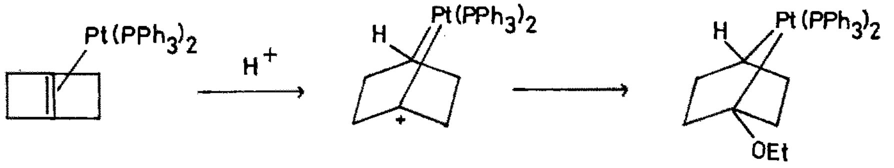
245



246

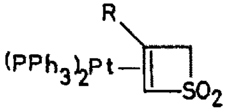
The spectroscopy and photophysics of the species [Pt(alkene)L_2] (alkene = C_2H_4, tcne or fumaronitrile; L = PPh_3 or $AsPh_3$) have been investigated. The luminescence observed was ligand centred but had a lifetime strongly dependent on the heavy atom [332]. Photoassisted isomerisation of carbon-carbon double bonds in the presence of *trans*-[Pt(C_2H_4)(2,4,6-trimethylpyridine)Cl_2] has been studied [333].

Protonation of **247** occurred by a rather unusual route yielding ultimately **248**, identified by X-ray diffraction [334]. Two other cyclobutene complexes, **249** [335] and **250** [336], were synthesised by displacement of other alkenes.

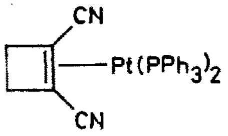


247

248



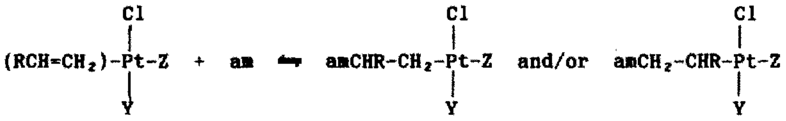
249



250

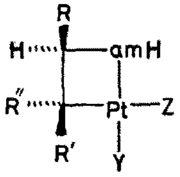
The kinetics of reaction of *trans*-[Pt(S-2-methyl-2-butene)(4-X-Py)Cl_2] with a non prochiral alkene such as 2,3-dimethyl-2-butene or Z-1,2-dichloroethene, leading to alkene displacement, were studied. The basicity of the substituted pyridine had the dominating influence on its *trans*-effect [337]. [Pt(S-2-methyl-2-butene)(1,2-diaminobenzene)Cl][BPh_4] has been obtained as an air-stable crystalline solid. Comparison of its CD spectrum with that of related complexes showed that the coordinating atoms *cis* to the alkene had a dominant effect on the CD pattern in the region 20,000-35,000 cm^{-1} [338].

Theoretical considerations of the mechanism of nucleophilic attack on metal alkene complexes have suggested the proposition that the alkene is activated by "slippage" towards η^1-coordination. The specific cases of $\{PtL_2\}$ and $\{Ni(PR_3)_2\}$ derivatives were considered [339]. Further studies of nucleophilic attack on **251** have been published. The direction of attack was determined by electronic rather than steric factors unless the latter were very large. The reactions were generally incomplete, with equilibrium constants reduced by steric hindrance. Cyclisation to species such as **252**, however, was enhanced by increased steric demand, a phenomenon which may be considered to be an example of a Thorpe Ingold effect [340]. An intramolecular version of the reaction is shown in Scheme 8 [341].



$$(RCH{=}CH_2)\text{-}\overset{Cl}{\underset{Y}{Pt}}\text{-}Z \;+\; am \;\rightleftharpoons\; amCHR\text{-}CH_2\text{-}\overset{Cl}{\underset{Y}{Pt}}\text{-}Z \;\text{ and/or }\; amCH_2\text{-}CHR\text{-}\overset{Cl}{\underset{Y}{Pt}}\text{-}Z$$

251



252

Attack of methoxide ion on 253 gave the unstable species 254 which underwent β-hydride elimination to 255; this complex lost methanol to give 256 and dimerised to 257. 257 was hydrolysed by $[HO]^-/H_2O$ to the vinyl alcohol complex, 258, which has now been isolated for the first time. This was also obtained from 259 by treatment with HCl [342,343].

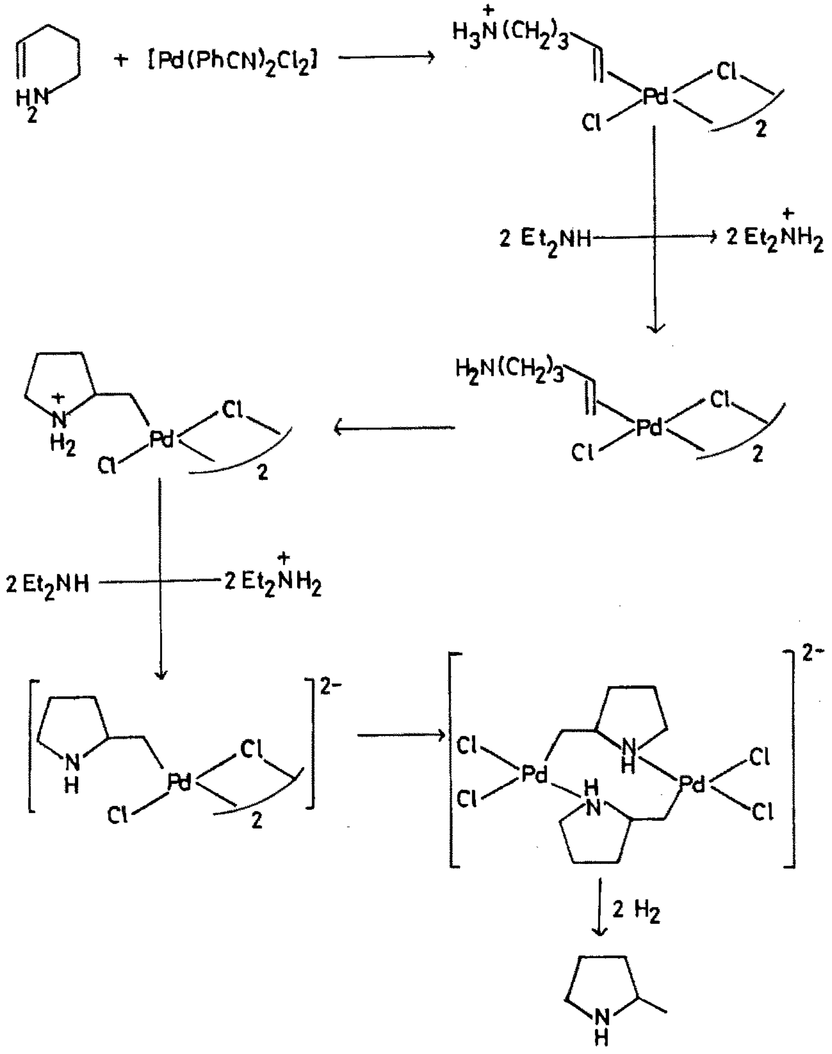
The relative probabilities of intramolecular or intermolecular nucleophilic attack at either of the two carbonyl groups of 260 was examined. The best case corresponded to the formation of a thirteen membered ring, the structure, 261, of which was determined by X-ray diffraction [344].

Treatment of $[Cp_2Ni]$ with $ClMg(CH_2)_3C(CH_3){=}CH_2$ gave 262. The analogous species, 263, was obtained indirectly by reaction (52). 262 and 263 were shown to be rather stable to β-elimination. A full paper now describes an extensive range of substitution patterns in such complexes [345].

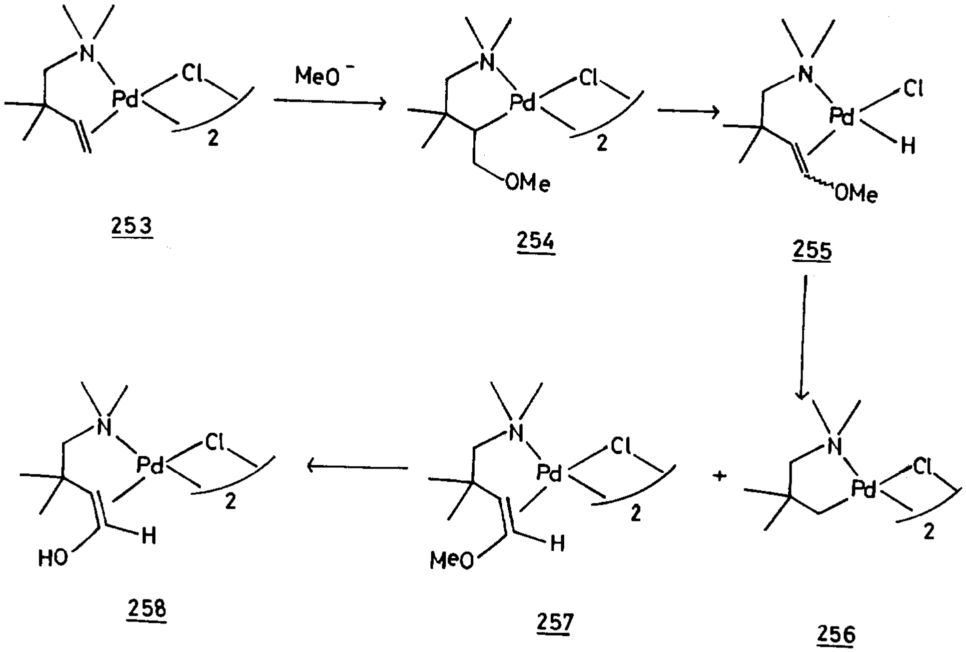
The ease of oxidation of $[Ni(CH_2{=}CHCHO)_2L_2]$ to ethyne, carbon monoxide and nickel(II) was shown to increase in the order L_2 = bipy < $(PPh_3)_2$ < en [346].

$[Pt_2(PMe_2Ph)_2Cl_4]$ reacted reversibly with 1,2-propadiene at 213 K to give *trans*-$[Pt(C_3H_4)(PMe_2Ph)Cl_2]$. At room temperature, however, the *cis*-isomer, 264, was obtained, and η^2-coordination of the allene confirmed by X-ray diffraction. 264 reacted with further $[Pt_2(PR_3)_2Cl_4]$ to give the very insoluble dimer $[(PhMe_2P)Cl_2Pt(\mu\text{-}C_3H_4)Pt(PMe_2Ph)Cl_2]$. An anionic dimer was also synthesised according to reaction (53) (X = Cl, Br or I) [347]. 264 reacted with R_3N to give 265 and with Me_3CNH_2 to give 266 which cyclised to

267 in the presence of an excess of the base. An excess of either $MeNH_2$ or $PhCH_2NH_2$ gave the eight-membered ring complex, **268**; **267** and **268** were characterised by X-ray diffraction. The contrast between the reactions of Me_3CNH_2 (and Me_2NH, which reacted similarly) and the sterically less demanding amines $MeNH_2$ and $PhCH_2NH_2$ may be considered to be another example of the Thorpe-Ingold effect [348].



Scheme 8 Intramolecular amination of a palladium coordinated alkene [341].



253

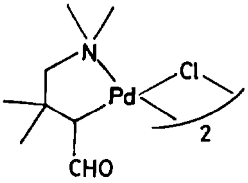
254

255

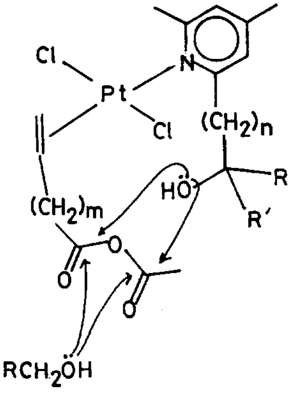
256

257

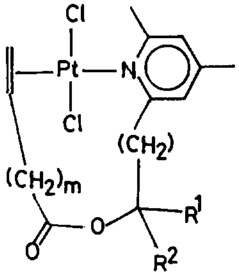
258



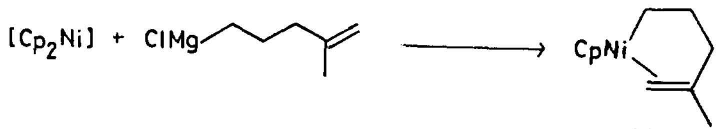
259



260

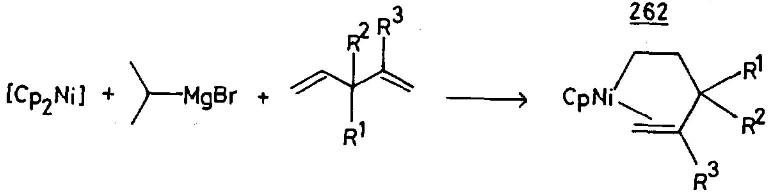


261



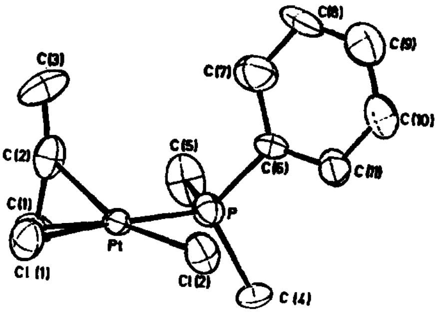
(51)

262



(52)

263

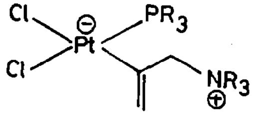


264 (Reproduced with permission from [348])

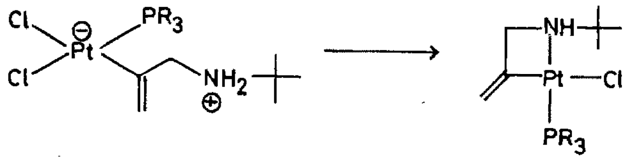
$$[Bu_4N]_2[Pt_2X_6] + C_3H_4 \longrightarrow [Bu_4N][Pt(C_3H_4)X_3]$$

$$\Big\downarrow\ [Bu_4N]_2[Pt_2X_6]$$

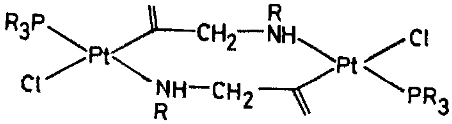
$$[Bu_4N]_2[X_3Pt(\mu\text{-}C_3H_4)PtX_3] \qquad (53)$$



265



266 267



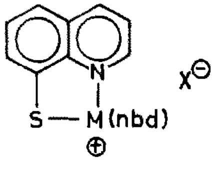
268

The ionisation potentials of the core electrons in [Ni(cod)$_2$] and related species were measured by XPES and could be correlated with the metal oxidation state [349]. Nickelation of PVC could be achieved by treating the polymer with [Ni(cod)$_2$] or [Et$_2$Ni(bipy)]. The IR and visible spectra of the nickelated PVC were reported [350].

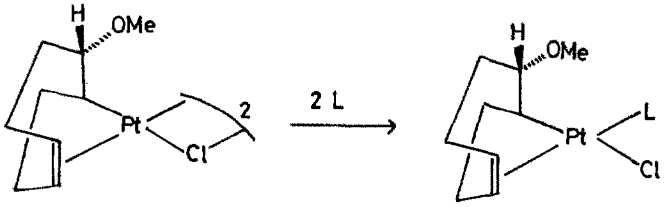
X-ray diffraction data for the complexes [Pd(1,5-cod)Cl$_2$], [Pd(1,4-cod)Cl$_2$] and [Pd(1,5-cyclononadiene)Cl$_2$] have been reported, and [Pd(1,4-cycloheptadiene)Cl$_2$] was characterised spectroscopically. The coordinated diene conformations were compared with minimum energy conformations calculated for the free ligands by molecular mechanics. 1,5-Cyclooctadiene and 1,4-cycloheptadiene were shown to change geometry little on coordination, but for 1,4-cyclooctadiene and 1,5-cyclononadiene, excited state conformations were coordinated [351]. Cyclooctadiene has been readily displaced from [M(cod)Cl$_2$] (M = Pd or Pt), or [Pt(cod)$_2$] by R$_3$P, to give the related phosphine complexes, the R moieties being long chain alkyl groups [352]. Mnt was transferred from [Me$_2$Sn(mnt)] to platinum or palladium in reaction (54) (M = Pd or Pt; X = Cl or Br) [353]. Derivatives of quinoline-8-thiol reacted with [M(nbd)X$_2$] (M = Pd or Pt; X = Cl or Br) to give species such as 269 [354].

$$[\mathrm{Me_2Sn(mnt)}] + [\mathrm{M(cod)Cl_2}] \longrightarrow [\mathrm{M(cod)(mnt)}] + \mathrm{Me_2SnCl_2} \qquad (54)$$

Reaction of [Pt(cod)Cl$_2$] with [MeO]$^-$ is known to yield 270. Reaction of two moles of the ligand L gave the bridge opened species, 271. However, with four molar equivalents of a hindered phosphine the hydride, $[HPt(PR_3)_2Cl]$, ($R = Me_3C$) and methoxycyclooctadiene were formed *via* **272**, providing a synthesis of hydride complexes bearing bulky phosphines, which are otherwise difficult to prepare [355]. Reaction of $[Pt(cod)Cl_2]$ with Ag^+ in methanol gave $[Pt(cod)(MeOH)_x]^{2+}$, which yielded the methoxy bridged analogue of **270** on treatment with $Na_2[CO_3]$. This was identified by X-ray diffraction and is the first methoxy bridged organoplatinum compound to be so characterised [356]. Its reactions with ligands are similar to those of **270**, but it gave $[H_2Pt(PR_3)_2]$, methoxycyclooctadiene and methanal with four moles of R_3P [357].

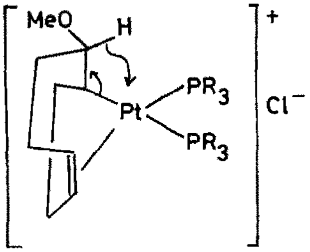


269



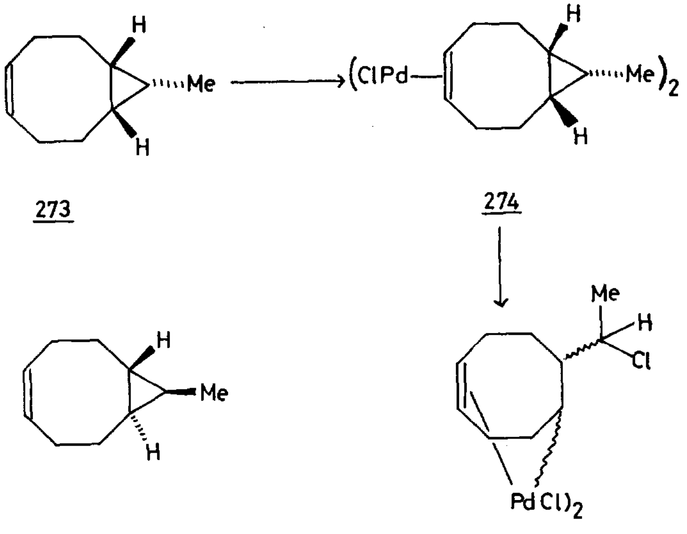
270

271



272

Reaction of **273** with $[Pd(PhCN)_2Cl_2]$ at 0 °C gave **274**, which on standing was converted to **275**. Treatment with cyanide ion led to **276**. That the reaction was stereospecific was proven by the use of the isomer of **273**, although the stereochemistry of **275** was not established in either case. **276** was obtained from both isomers of **275**, derived from either *exo* or *endo*-**273**. The mechanism suggested involves corner palladation of the cyclopropane with attack of Cl$^-$ at the active carbon. The analogous cyclobutane was at least 10^3 times less reactive [358].



273

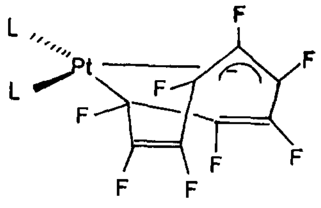
274

276

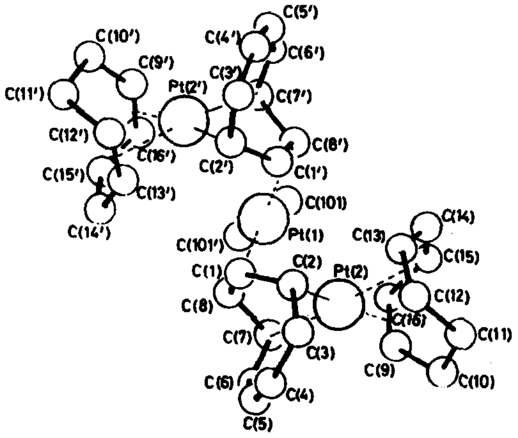
275

Treatment of $[Pt(C_2H_4)L_2]$ (L = PPh_3, $PMePh_2$ or PMe_2Ph) with octafluorocyclooctatetraene (ofcot) gave $[Pt(\eta^2\text{-ofcot})L_2]$. Oxidative addition yielded 1,2,3,6-η^4-complexes, **277** [359]. A mixture of $[Pt(cod)_2]$, ethene and cot yielded $[Pt_3(C_2H_4)(cot)_2(cod)_2]$, characterised by X-ray diffraction. The structure, **278**, indicated that the cod molecules, in a tub conformation, were coordinated η^4 to platinum atoms (2) and (2'). Platinum(1) bears the ethene and the two cot ligands, with the bonds Pt(1)-Pt(2) and Pt(1)-(2') bridged by cot. Platinum(1) is formally platinum(0), whereas platinums(2) and (2') are platinum(II). The dynamic nature of the nmr spectra was described, but was too complex for ready explanation [360].

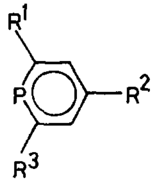
Reaction of $[Ni(cod)_2]$ with **279**, L, gave $[Ni(cod)L_2]$, and several related species including $[Ni(cdt)L]$, $[Ni(C_2H_4)(PCy_3)L]$ and $[Ni(PPh_3)_2L]$ were also prepared. Thermolysis of $[Ni(C_2H_4)(PCy_3)L]$ gave **280** in which L acts both as a η^6-arene and a σ-donor [361].



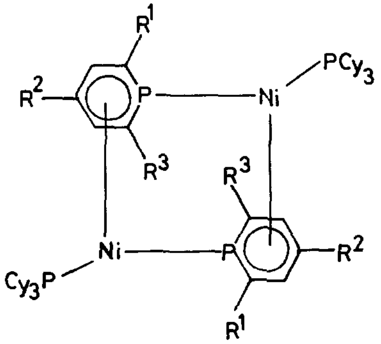
277



278 (Reproduced with permission from [360])

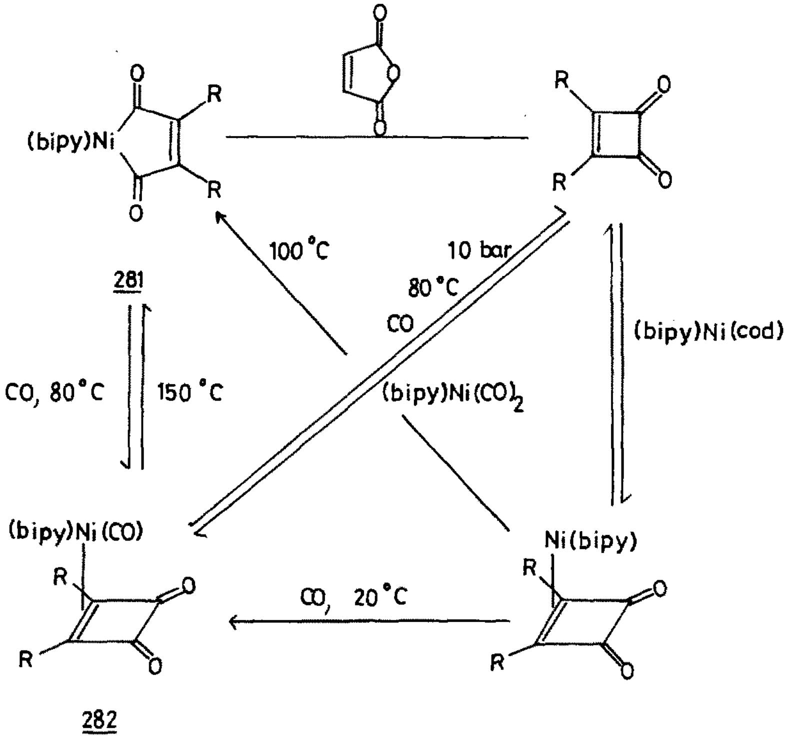


279



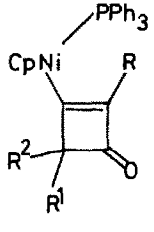
280

Treatment of [Ni(bipy)(CO)$_2$] with RC≡CR gave initially **281**, some reactions of which are shown in Scheme 9. **282** was characterised by X-ray diffraction [362].



Scheme 9 Reactions of the nickelacycle, 281 [362].

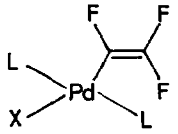
Reaction of a ketene, $R^1R^2C=C=O$, with $[CpNi(PPh_3)(C\equiv CR)]$ gave the 2+2 cycloaddition product, 283. Addition occurred at the triple bond even for R = vinyl. The ketene may be prepared *in situ*, for example from RCH_2COCl/Et_3N, with similar results [363].



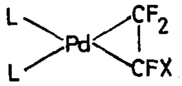
283

$[PdL_4]$ reacted with C_2F_3X to give **284** (L = Ph_2MeP, $PhMe_2P$ or Et_3P; X = Cl or Br). There was no evidence for formation of a three-membered ring with

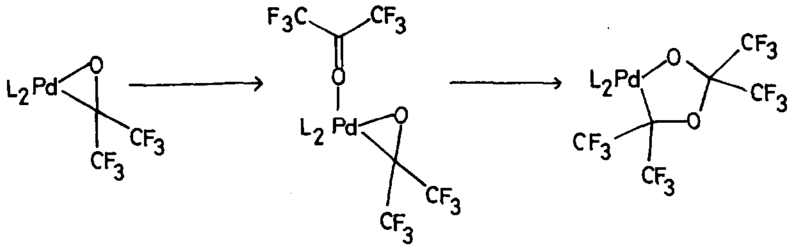
L = Et_3P, but with L = Me_2PhP, the product was **285**. With $(CF_3)_2CO$ and $[Pd(PEt_3)_4]$ both **286** and **288** (formed *via* **287**) were isolated, but with the PPh_3 complex only **286** was formed [364].



284

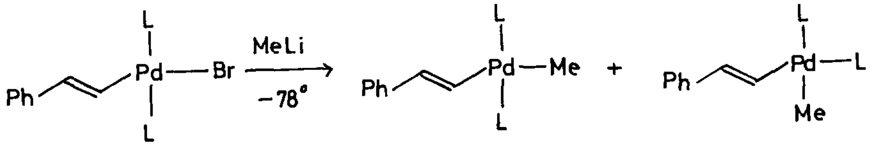


285



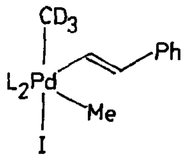
286 287 288

Reaction of the σ-vinyl complex, **289**, with methyl lithium gave E-1-phenyl-1-propene. At -78 °C both **290** and **291** could be observed, presumably being formed *via* a [(PhCH=CH)Pd(solvent)LBr] intermediate. With CD_3I the palladium(IV) complex, **292**, was formed, giving both E-$PhCH=CHCH_3$ and E-$PhCH=CHCD_3$ on reductive elimination [365].

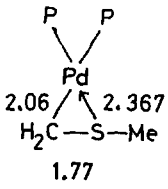


289 290 291

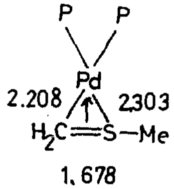
In the complexes $[Pd(CH_2SMe)(PR_3)_2][PF_6]$, **293**, and $[Pd(CH_2SMe)(PR_3)_2][ClO_4]$, **294**, characterised by X-ray diffraction at -160 °C, quite different coordination modes prevail, **293** behaving as a stronger ion pair [366].



292

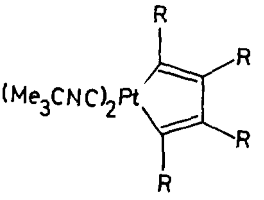


293

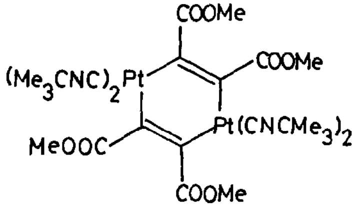


294

Treatment of $[Pt_3(CNCMe_3)_6]$ with RC≡CR (R = Ar) gave the metallocyclopentadiene, **295**, but with $MeO_2CC≡CCO_2Me$ the dimetallocyclohexadiene, **296**, was formed. The interrelationship and interconversions of these and related species were discussed in detail [367].



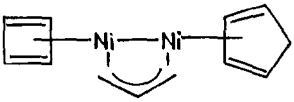
295



296

9 METAL ALLYL AND RELATED COMPLEXES

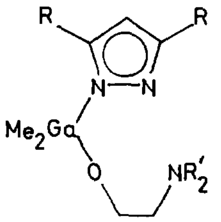
Syntheses of macrocycles *via* π-allyl complexes of nickel have been reviewed [368]. The semi-empirical INDO calculation for **297** showed that the Hartree Fock solution is unstable with respect to singlet, non-singlet and complex variations [369].



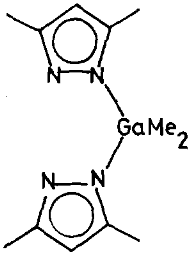
297

Two independent analyses of the X-ray diffraction data for $[\{(\eta^3\text{-}CH_2CHMeCH_2)PdCl\}_2]$ have provided more accurate geometries for the complex [370]. X-ray diffraction data have also been reported for $[\{(\eta^3\text{-}CH_2CH\{CH_2CMe_3\}CH_2)PdCl\}_2]$, synthesised from $H_2[PdCl_4]$ and $Me_3CCH_2C(Me){=}CH_2$ in a hexane/H_2O/Me_2CHOH detergentless microemulsion [371], and other cationic and anionic π-allyl palladium complexes [372].

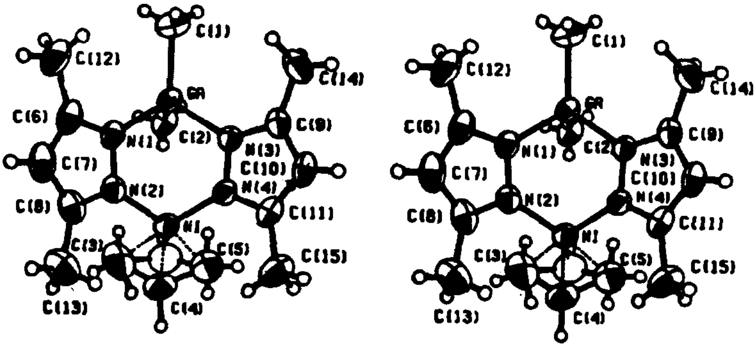
Cocondensation of nickel atoms with $CH_2{=}CHCH_2X$ gave $[\{(\eta^3\text{-}C_3H_5)NiX\}_2]$ [373]. Treatment of $[\{(\eta^3\text{-}C_3H_5)NiBr\}_2]$ with NaL (L = **298**) gave a product not containing nickel allyl groups, but **299** gave both $[(\eta^3\text{-}C_3H_5)NiL]$ and $[(\eta^3\text{-}C_3H_5)PdL]$ derivatives. The structure of 300 was determined by X-ray diffraction, and the dynamic processes discerned by nmr spectroscopy were studied [374].



298

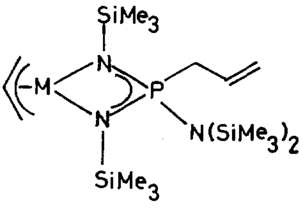


299



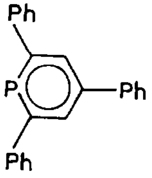
300 (Reproduced with permission from [374])

$[Ni(cod)_2]$ reacted with $CH_2{=}CHCH_2OCOMe$ to give $[\{(\eta^3\text{-}C_3H_5)Ni(OCOMe)\}_n]$ which disproportionated to yield $[(\eta^3\text{-}C_3H_5)_2Ni]$ and $Ni(OCOMe)_2$. In the presence of phosphine, however, $[(\eta^3\text{-}C_3H_5)Ni(OCOMe)(PR_3)]$ was formed, and its reactions with nucleophiles were investigated [375]. $[(\eta^3\text{-}C_3H_5)_2M]$ (M = Ni or Pd) reacted with $(Me_3SiN{=})_2PN(SiMe_3)_2$ to give the fifteen electron species 301, characterised by X-ray diffraction. The complex for which M = Ni catalysed ethene polymerisation, but the palladium analogue was inactive [376].



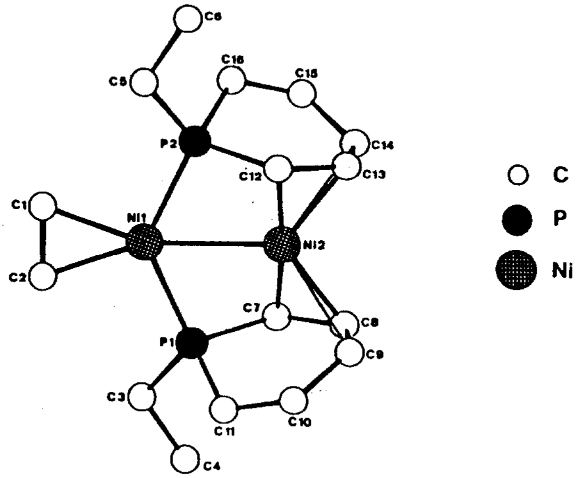
301

New syntheses of $[(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)Ni(cod)][X]$ (X = $AlBr_4$, BF_4 or PF_6) have been described. These complexes were shown to be excellent catalysts for oligomerisation of alkenes and dienes, with butadiene yielding predominently *cis*-1,4-polybutadiene. In one case $[\{\eta^3\text{-}CH_3CHC(CH_3)CHCH_3\}Ni(cod)][PF_6]$ was isolated from the catalytic reaction, implying that cod is still present in the catalytically active species [377]. Reaction of $[Ni(acac)_2]$ and Et_2AlOEt with 302 gave the bis(allyl), **303**, as the initial product. Ethene was readily displaced by other alkenes, alkynes and phosphines. Nmr spectroscopic data indicated that these systems were all fluxional with migration of the allyl function around the six-membered ring [374].



302

The cation $[(\eta^3\text{-}C_3H_5)Pd(RCN)_2]^+$, formed in reaction (55), was stabilised by the $[B_{10}Br_{10}]^{2-}$ and its reactions have been investigated [375]. Bridge splitting of the halide dimer $[\{(\eta^3\text{-}2\text{-}Y\text{-}C_3H_4)PdCl\}_2]$ or the oligomer, $[\{(\eta^3\text{-}C_3H_5)PtCl\}_4]$, also occurred using diazobutadienes (DAB) in the presence of $Na[ClO_4]$ to give $[(\eta^3\text{-}2\text{-}Y\text{-}C_3H_4)M(DAB)][ClO_4]$. Rapid *syn-syn* and *anti-anti* exchange of the allyl hydrogens of complexes containing a non-symmetric DAB was indicated by the room temperature proton nmr spectra, suggesting that DAB may dissociate to give a monodentate DAB complex rather readily [380].

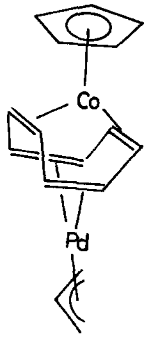


303 (Reproduced with permission from [374])

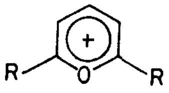
$$[\{(\eta^3\text{-}C_3H_5)PdCl\}_2] + Ag_2[B_{10}Br_{10}] \xrightarrow{RCN} [(\eta^3\text{-}C_3H_5)Pd(RCN)_2][B_{10}Br_{10}] \qquad (55)$$

Halide abstraction from the relevant halo bridged dimers gave $[(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)Pd][BF_4]$, which on reaction with the electron rich complex [CpCo(cot)] yielded the pseudo triple-decker species **304**, identified by ^{13}C nmr spectroscopy [381]. Treatment of $Pd(OCOMe)_2$ with **305** gave the trinuclear species, **306**, characterised by X-ray diffraction. The Pd-Pd distance was shown to be 2.864 Å, indicating some bonding interaction between the metal centres. With the cyclopentadienyl anion the ethanoate bridges were split to yield **307** [382].

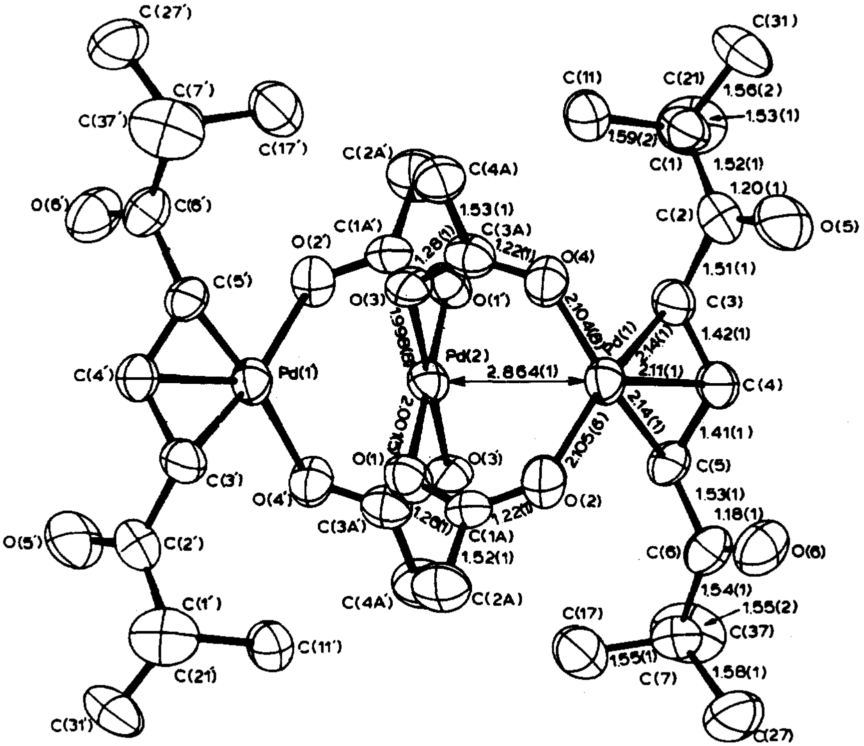
Dynamic nmr spectroscopic studies have been reported for several complexes. In **308** the major fluxional process was rotation about the Pd-P bond [383]. The diastereoisomers of $\{(\eta^3\text{-allyl})Pd\}$ complexes with chiral *cis*- and *trans*-2,3-diphenyl-1,3-oxaphosphorian, **309**, were interconverted *via* formation of σ-allyls and rotation about the C-Pd axis [384]. Reaction of [Pd(β-diketonate(2)C^1-C^3)(bipy)] with a chelating biphosphine gave **310**, and further *in situ* treatment with [Pd(P-P)][ClO_4] yielded **311**. On warming the oxygen atom sites were exchanged, a process which could be monitored by ^{31}P nmr spectroscopy [385].



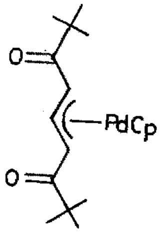
304



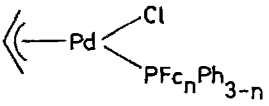
305



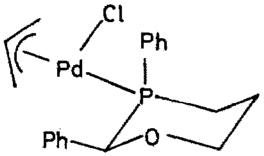
306 (Reproduced with permission from [382])



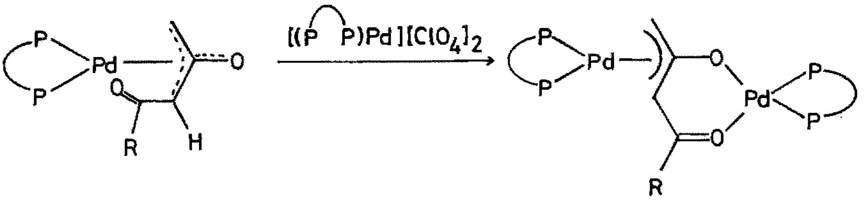
307



308



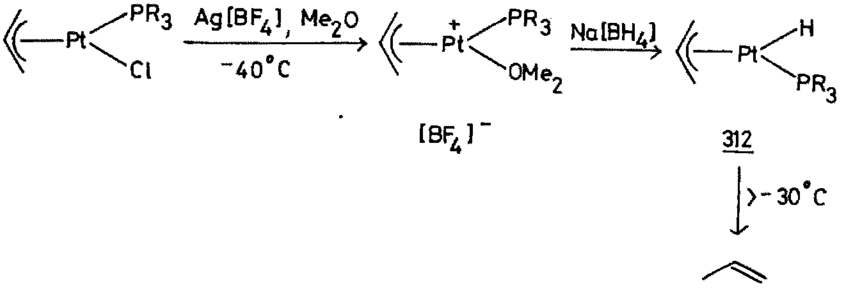
309



310

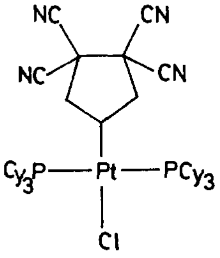
311

As always, reports detailing platinum allyl complexes have been relatively sparse. The allyl hydride, **312**, may be prepared by reaction (56). It decomposed above -30 °C, even in the solid state, but showed dynamic nmr spectra, unusual for a platinum complex [386]. Reaction of the tetramer, $[\{(C_3H_5)PtCl\}_4]$, with PCy_3 gave the new species $[(\eta^1-C_3H_5)Pt(PCy_3)_2Cl]$, which reacted with tcne to give **313**, identified by X-ray diffraction. The reaction formally involves a [3+2] cycloaddition with a 1,2-platinum migration [387].



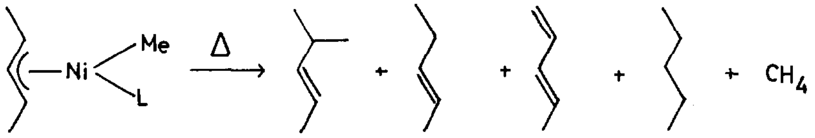
312

(56)

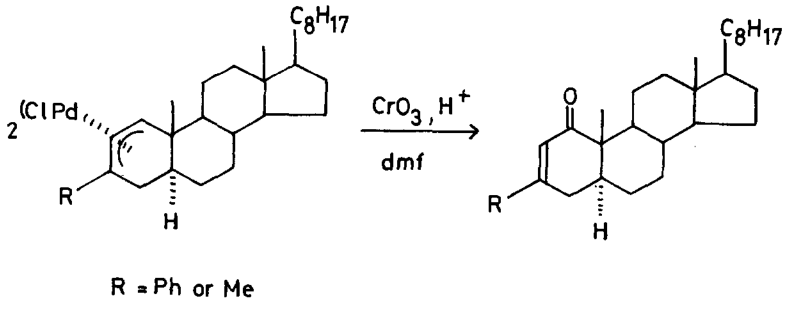


313

Thermolysis of species such as **314** has been investigated thoroughly, and a method for separating the effect of the nature of the ligand from the effect of its concentration devised. The effect of L was about 75 % electronic and 25 % steric in origin when considered in terms of control of the temperature of decomposition, but the effects were more evenly balanced when considering selectivity [388,389]. Photolysis of π-allyl palladium chloride dimers in the presence of oxygen gave enones, in contrast to the dimeric products obtained under an argon atmosphere [390]. Enones were also obtained from CrO_3 oxidation of steroidal π-allyl palladium complexes (reaction (57)) [391].

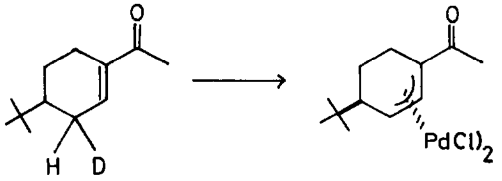


314

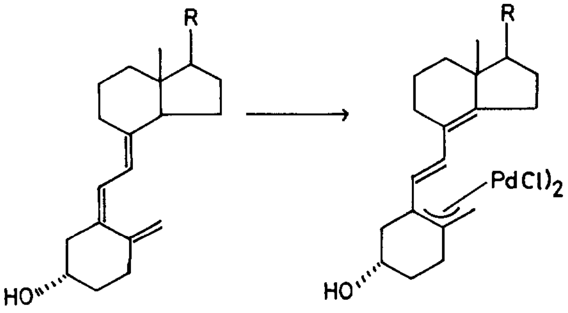


(57)

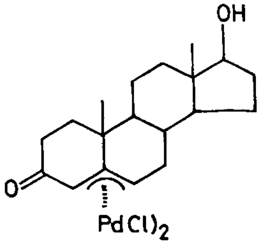
Formation of **316** from **315** occurred with non-stereoselective hydrogen or deuterium loss, in agreement with a mechanism involving palladium assisted enolisation [392]. Formation of **318** gave a mixture of stereoisomers which could not readily be separated, but ergosterol gave only an α-palladium allyl complex [393]. Testosterone also gave a single stereoisomer of the allyl complex, 319, the stereochemistry of which was assigned after an X-ray structure determination on the product of its reaction with PhSO$_2$CH(Na)COOMe, a reaction known to proceed, under specified conditions, with inversion of stereochemistry [394].



315 316

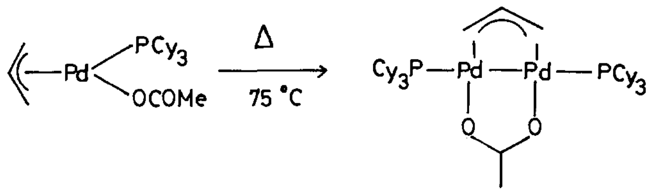


317 318

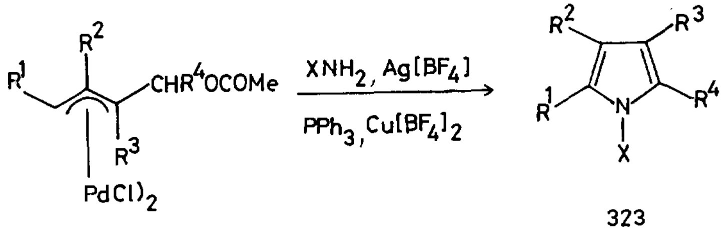


319

Reaction of $[Pd(PCy_3)_2]$ with $CH_2{=}CHCH_2OCOMe$ gave **320** and $[Cy_3P\text{-}CH{=}CHCH_3]^+[OCOMe]^-$. **320** reacted with further PCy_3 to give **321**, which was also obtained by thermolysis [395]. Treatment of a diene, $R^1CH{=}CR^2\text{-}CR^3{=}CHR^4$, with $PdCl_2$ in the presence of CH_3COOH and $CuCl_2$ gave **322** in good yield. For R^1-R^4 = H this reacted with $Ag[BF_4]$ and a nucleophile such as Me_2NH, in the usual way to give $Me_2NCH_2C{=}CHCH_2OCOMe$. However, if an oxidant such as $Cu[BF_4]_2$ was added, the product was the pyrrole, **323** [396]. An analogous process occurred using $Na[SO_2CH_2CMe_3]$, giving only one regioisomeric product in most cases (reaction (58)). Since the palladium is readily removed using dmg in methanol the process is equivalent to regioselective anti-Markovnikov hydrosulphonation [397].

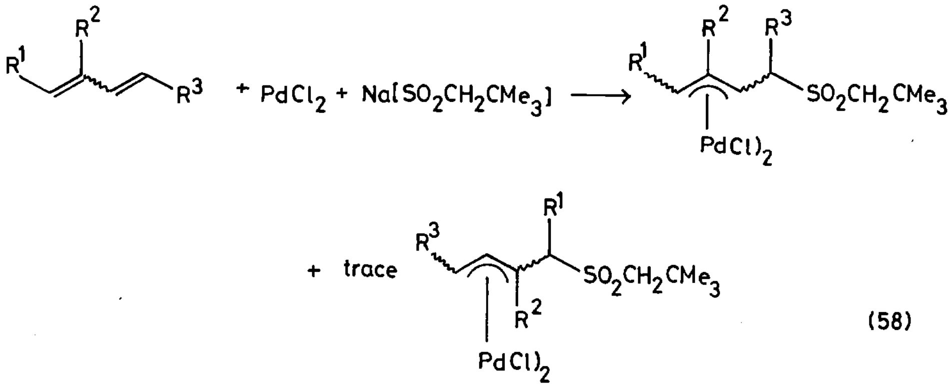


320 321

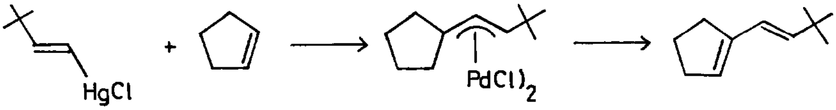


322 323

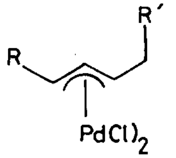
The formation of **324** from *trans*-$[RCH{=}CHHgCl]$, $R^1\text{-}CH{=}CH_2$ and $Li_2[PdCl_4]$ has been presumed to involve the formation of *trans*-$[RCH{=}CHPdL_n]$, *cis*-addition to the alkene, followed by loss of palladium and an allylic hydrogen atom to give a π-complex, and subsequent collapse successively to a σ-allyl and a π-allyl. This story must now be regarded as incomplete since cyclic alkenes also react well (reaction (59)). The new mechanism proposed involves addition of the organopalladium derivative to the alkene followed by successive loss and addition of H[PdCl$_3$] [398]. The stereochemical results of ring opening of **325** with [Pd(PhCN)$_2$Cl$_2$] and its *trans*-isomer were consistent with *cis*-chloropalladation and stereospecific disrotatory ring opening [399].



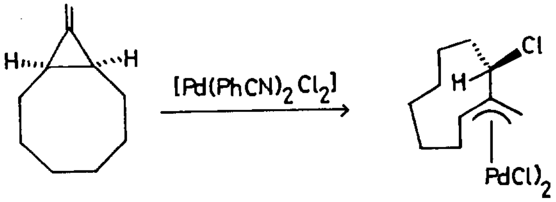
(58)



(59)



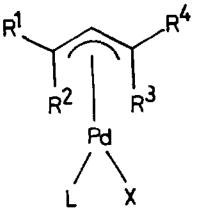
324



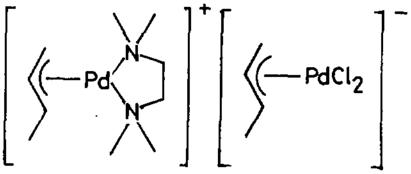
325

326

There continue to be numerous studies of the attack of nucleophiles on palladium allyl complexes. For example, **327** has been reacted with amines, and the structures of the products compared with those obtained by catalytic amination of dienes in the presence of palladium complexes [400]. However, evidence has now been presented that the reaction of tertiary amines or phosphines with π-allyl palladium chloride dimers does not yield cationic π-allyls as had previously been assumed, but rather dynamic σ-allyl palladium complexes. True cations such as 328 were obtained with TMEDA and were characterised by nmr spectroscopy and X-ray diffraction. σ-Allyl complexes such a 329, formed *in situ*, reacted by an S_N2' mechanism to give more substituted products, whereas the π-allyl cations , **330**, were attacked at the less substituted site [401]. Reactions with carbon nucleophiles were also reported [402]. This view of substitution at palladium allyls was supported by comparison of the enantioselectivity of reaction of $Na[CH(COOEt)_2]$ on isolated 331 with the $[Pd(DIOP)_2]$ catalysed substitution of cyclohexenyl ethanoate. The stoicheiometric reaction yielded a product of lower optical purity than that obtained in the catalytic process, indicating a difference in mechanism [403].



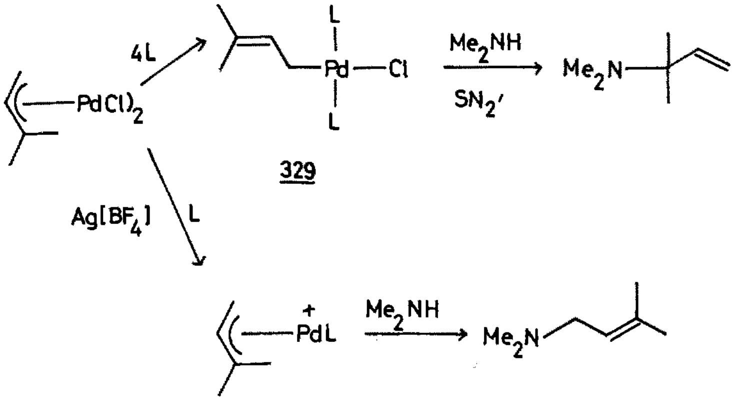
327



328

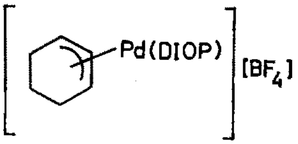
Conditions have been developed for the addition of ketone enolates to palladium allyl complexes. The stereochemistry of the reaction was characterised by the usual *trans*-attack, but yields were modest except for cyclic compounds [404]. Alkenyl zirconium complexes were also useful nucleophiles, giving 1,4-dienes in good yield (reaction (60)). Alkylation at palladium is thought to precede carbon-carbon bond formation [405]. Reactions with alkoxides have also been noted [406].

If allyl suphones could be converted to allyl complexes such as **332**, nucleophilic attack would result in reversal of the usual reactivity of such species. Formation of **332** (in contrast to the previously noted loss of SO_2Ar) has now been achieved under oxidative conditions, and reaction with ethanoate yielded **333** with good regioselectivity [407].

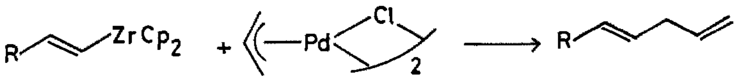


329

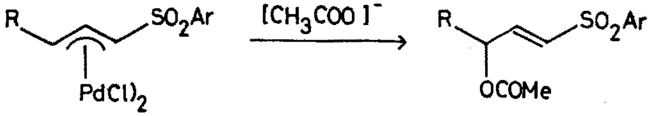
330



331



(60)

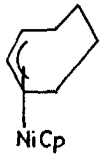


332

333

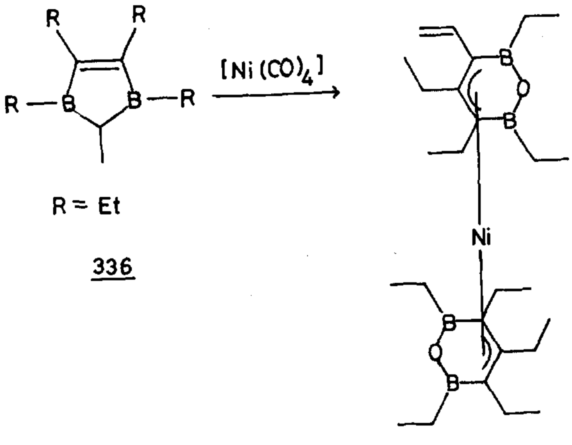
400 and 500 MHz ^{1}H nmr spectra of (η^3-cycloalkenyl)nickel complexes have been studied. When the ring size was 6-8 carbon atoms the uninvolved carbon bridge was shown to be bent away from the nickel atom as in **334** and **335**

[408]. Treatment of 2-methyl-1,3,4,5-tetraethyl-1,3-diborolene (**336**, R = Et) with $[Ni(CO)_4]$ gave 337, characterised by X-ray diffraction [409].



334

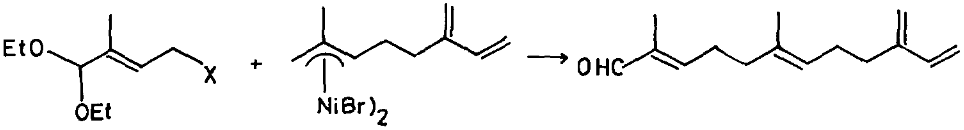
335



336

337

Treatment of **338** with **339**, followed by hydrolysis, yielded the coupled product β-sinesal, **340**, in 50 % yield and with 93 % of the desired *trans*-stereochemistry [410]. Allyl nickel complexes were also used in a synthesis of dihydrocoenzyme Q derivatives [411].

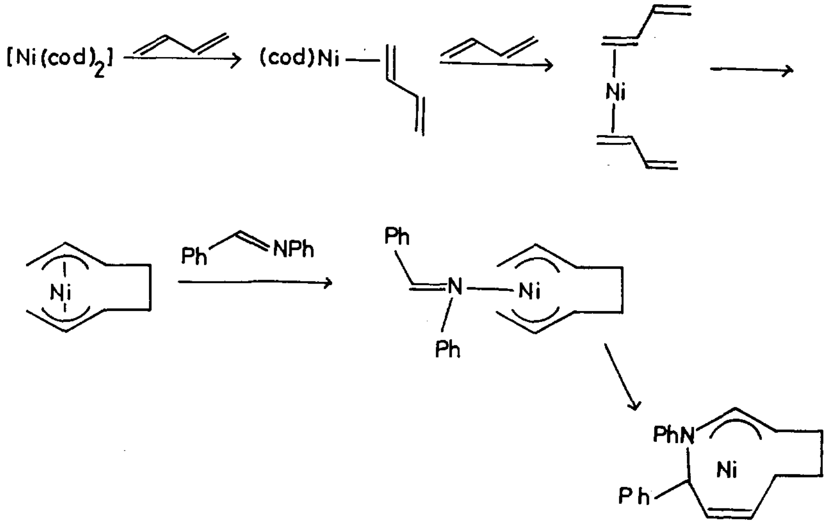


338

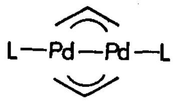
339

340

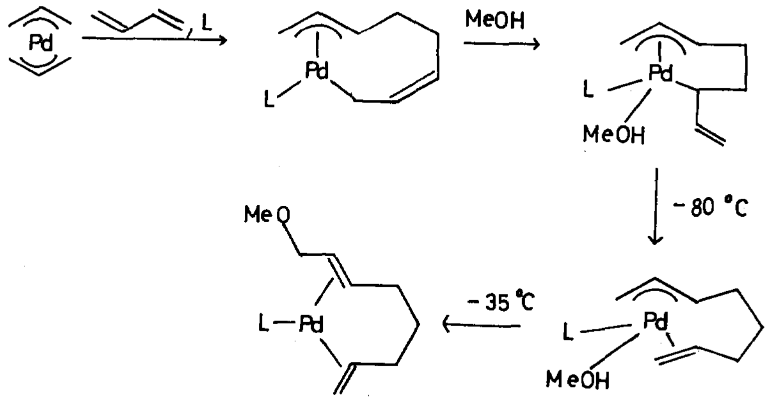
The reaction of $[Ni(cod)_2]$ with 1,3-dienes and azomethines led to oxidative coupling according to Scheme 10 [412]. $[(\eta^3\text{-}C_3H_5)_2Pd]$ reacted with butadiene and two molar equivalents of a ligand, L, to give **341**. With a four molar excess of butadiene over the palladium complex, and methanol as the solvent, the sequence of Scheme 11 was followed [413].



Scheme 10 Reaction of nickel(0) complexes with dienes and imines [412].

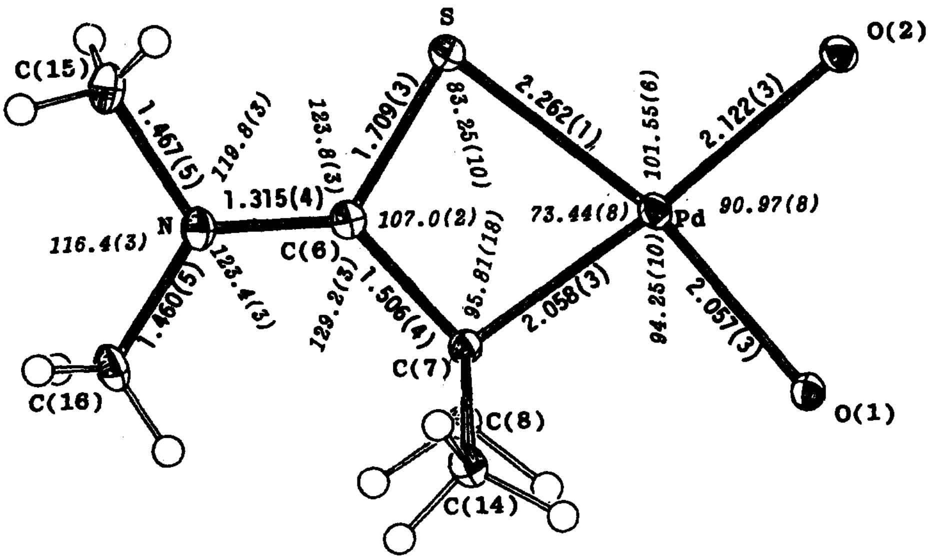


341



Scheme 11 Reaction of palladium(0) complexes with dienes [413].

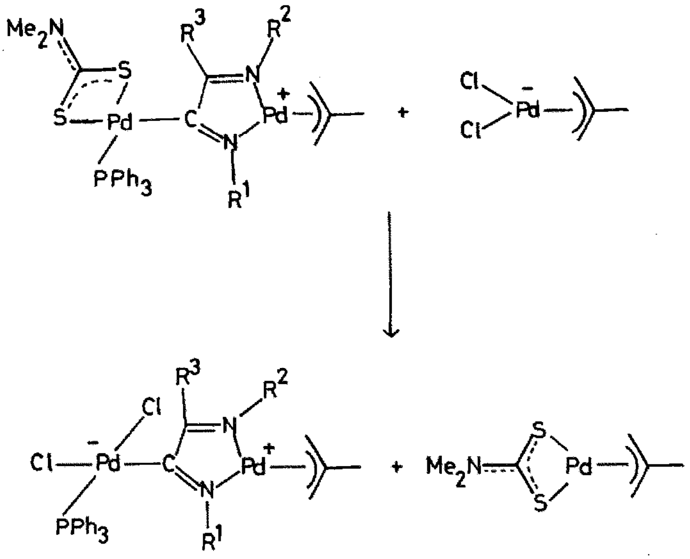
342 was synthesised by reaction of Na[CH(COOMe)$_2$] with [Pd(acac)$_2$] and CH$_2$=C(CH$_3$)-C(=S)NMe$_2$. Its structure was analysed by X-ray diffraction at -160 °C and at +20 °C, with the aim of ascertaining whether the thiallyl was σ- or π-coordianted. The data implied the presence of a carbon-palladium σ-bond together with donation of the sulphur lone pair to the metal [414].



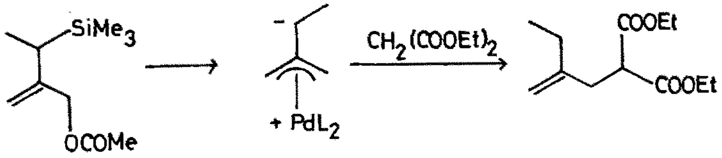
342 (Reproduced with permission from [414])

The mechanism of reaction (61) was investigated. It was proposed that the first step involved fast, reversible formation of an adduct *via* bridging halides [415]. Deallylation of ArOCH$_2$-CH=CH$_2$ required a stoicheiometric amount of [Pd(PhCN)$_2$Cl$_2$], and presumably proceded *via* formation of an allyl complex [416].

Theoretical studies of the bonding in trimethylenemethane palladium biphosphine complexes, slightly surprisingly, indicated that the greatest stability is attained when alkyl groups are bonded to the electron-rich carbon atom, remote from palladium [417,418]. Reaction (62) suggested that protonation of trimethylenemethane complexes occurred more rapidly than their equlibration. Cycloadditions were also studied [419].



(61)



(62)

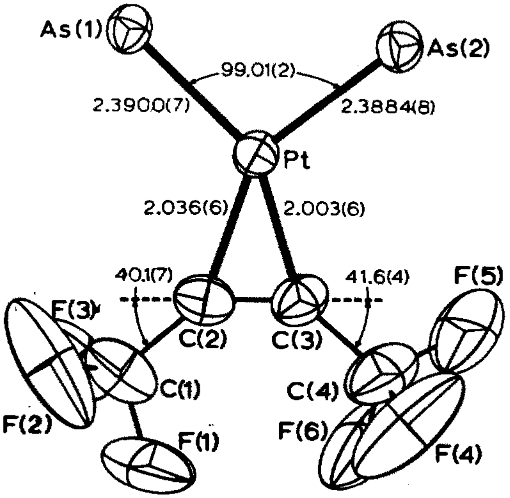
10 METAL ALKYNE AND ALKYNYL COMPLEXES

Molecular orbital studies of complexes such as $[Pt_2(C_2H_4)(PR_3)_4]$ and $[Pt_2(CO)_2(MeO_2CC{\equiv}CCO_2Me)(PPh_3)_2]$ have allowed the prediction of $J(^{195}Pt-^{31}P)$ and $J(^{195}Pt-^{195}Pt)$ in their nmr spectra [37]. The bonding of ethyne in $[Ni(C_2H_2)(CO)_2]$, $[Ni(C_2H_2)(CNH)_2]$ and $[\{Ni(CNH)_2\}_2(\mu-C_2H_2)]$ has been investigated by the non-empirical self-consistent Hartree Fock Slater LCAO method [420].

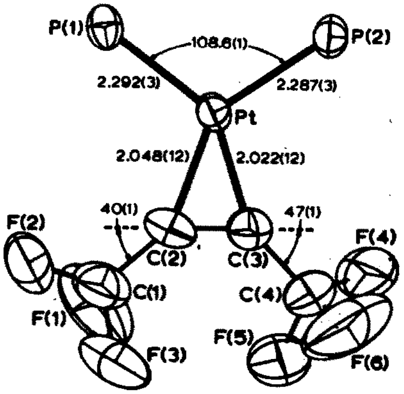
The reaction of nickel vapour with ethyne with and without an inert carrier gas, yielded $[Ni(C_2H_2)_n]$ (n = 1 or 2). Vibrational spectroscopic data favoured simple π-bonding and the complexes decomposed at around 150 K [421].

X-ray diffraction data have been reported for $[Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2]$, 343, $[Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2]$ [422], and $[Pt(CF_3C{\equiv}CCF_3)L_2]$ (L = $PCyPh_2$ or

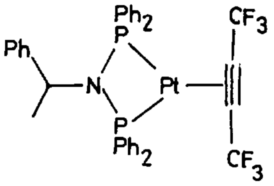
PCy_2Ph, **344**) [423]. The deviation from linearity of the alkynes could be directly related to the steric bulk of the phosphine. **345** was also prepared and its structure determined by X-ray diffraction. The deviation from linearity in this case was greated than would have been expected on purely steric grounds, and it was postulated that electronic effects were also important [424].



343 (Reproduced with permission from [422])

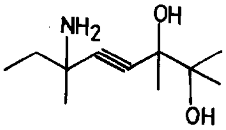


344 (Reproduced with permission from [423])



345

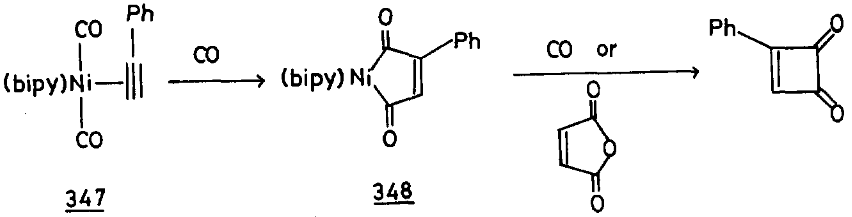
Dehydrochlorination of $[HPt(PPh_3)_2Cl]$ with dbu in the presence of $PhC\equiv CPh$ provided a new synthesis of $[Pt(PhC\equiv CPh)(PPh_3)_2]$ [425]. $[Ni(C_2H_4)(PPh_3)_2]$, $[Ni(PPh_3)_4]$ and $[Ni(cod)_2]/PPh_3$ reacted with $R^1C\equiv CR^2$ to give $[Ni(R^1C\equiv CR^2)(PPh_3)_2]$ (R^1, R^2 = COOH, COOR, CH_2OH or CH_2OR) [426]. Treatment of $K[Pt(Et_2SO)Cl_3]$ with L = **346** was claimed to give two *cis*-complexes of stoicheiometry $[Pt(Et_2SO)LCl_2]$, the difference between them not being made at all clear. IR spectroscopic data did, however, indicate alkyne coordination in both cases [427].



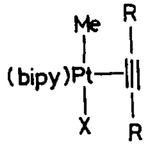
346

^{31}P and ^1H nmr spectra have been recorded for a range of complexes $[Pt(R^1C\equiv CR^2)(PPh_3)_2]$. The ^{31}P resonances were assigned on the basis that $^1J(P\text{-}Pt)$ depends on the $\{\equiv CR\}$ fragment *trans* to it [428]. $\delta(^{195}Pt)$ was found to be dominated by the electronic excitation energy, which was in turn related to the π^* level of the alkyne [429]. In $[Pt(P\equiv CCMe_3)(PPh_3)_2]$ X-ray diffraction showed that the phosphaalkyne was side coordinated, with no interaction between the metal and the phosphorus lone pair. The value of $^1J(Pt\text{-}P)$ = 62 Hz was unusually low [430].

$[Cp_2Ni_2(PhC\equiv CPh)]$ did not add hydrogen at temperatures below 120 °C, at which point gross decomposition occurred. The alkyne exchanged at a measureable rate with other $ArC\equiv CAr$ ligands, probably *via* mononuclear intermediates [431]. $[Ni(CO)_2(bipy)]$ reacted with $Ph\text{-}C\equiv CH$ to give a stable trigonal bipyramidal complex, **347**. Carbonylation gave **348**, from which a cyclobutene dione could be eliminated [432]. Related trigonal bipyramidal species, **349**, were obtained from $[MePt(bipy)Cl]$ and $R\text{-}C\equiv C\text{-}R$, where R was an electron-withdrawing group. The kinetics and mechanism of the thermal dissociation of the alkyne could be related to the ease of halide insertion [433].

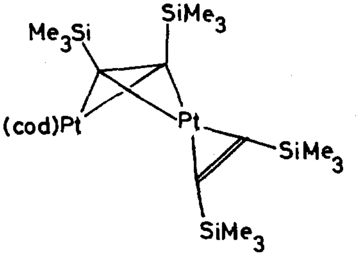


347 348

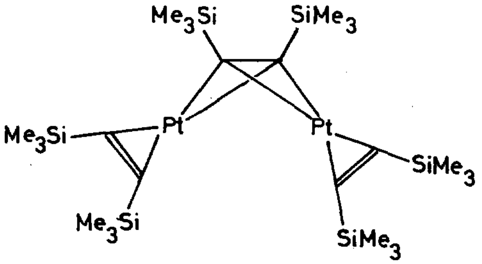


349

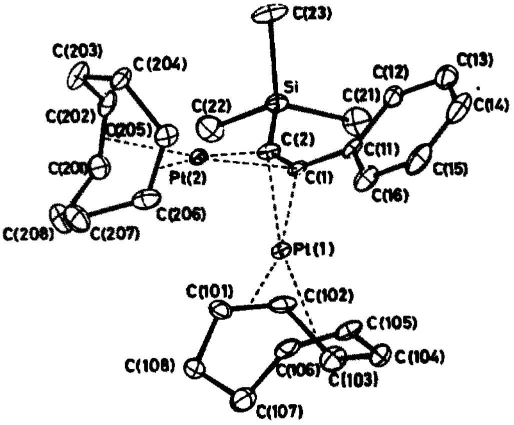
Reaction of $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ with $[Pt(cod)_2]$ gave 350, but with a more easily replaced ligand, $[Pt(C_2H_4)_3]$ yielded 351. With non-symmetrical ligands such as $R\text{-}C{\equiv}C\text{-}SiMe_3$, $[Pt(cod)_2]$ (using a 1:2 alkyne:Pt ratio) gave $[Pt_2(\mu\text{-}R\text{-}C{\equiv}C\text{-}SiMe_3)(cod)_2]$, and nickel analogues were also prepared. These complexes were fluxional in solution as determined by variable temperature nmr spectroscopy, but although several suggestions were made for the origins of the dynamic behaviour, this remained incompletely characterised. The structure of 352 was determined by X-ray diffraction. When the alkyne and $[Pt(cod)_2]$ were mixed in a 1:1 molar ratio $[Pt_3(\mu\text{-}PhC{\equiv}CSiMe_3)_2(cod)_2]$, 353, was formed. Nmr spectroscopic data suggested that there was no direct metal-metal bonding [434].



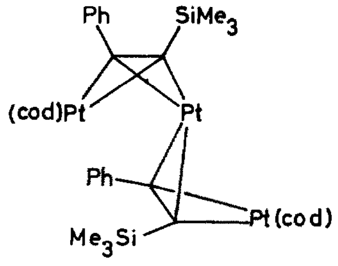
350



351



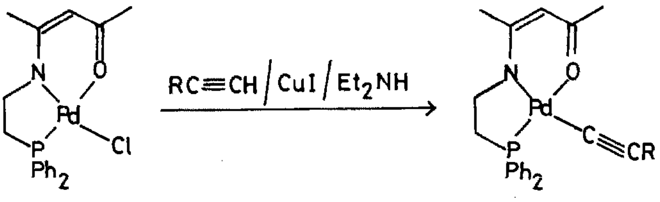
352 (Reproduced with permission from [434])



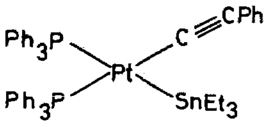
353

The preparation and properties of *trans*-[$(R^1C\equiv C)_2Ni(PR_3)_2$] have been described. X-ray diffraction studies revealed nickel-carbon bond lengths which suggested some double bond character [435]. Reaction of **354** with $R-C\equiv CH/CuI/Et_2NH$ (R = Ph or COOMe) gave a σ-alkynyl species, **355** [73]. Alkynes such as $PhC\equiv CSnR_3$ and related species underwent oxidative addition to [$Pt(C_2H_4)(PPh_3)_2$] to yield complexes, **356**. Intermediate π-alkyne complexes were detectable in some cases [428].

Reactions of $H-C\equiv C-Y-C\equiv C-H$ with [ML_2X_2] (M = Ni, Pd or Pt; L = PBu_3; Y = 1,4-phenylene or 1,1'-biphenylene) in the presence of copper halides gave the oligomer [$X(M-C\equiv C-Y-C\equiv C)_nMX$] (*n* = 5 or 6). Terminal groups could also be introduced [436]. Such species formed lyotropic liquid crystals in C_2Cl_3H or thf [437].



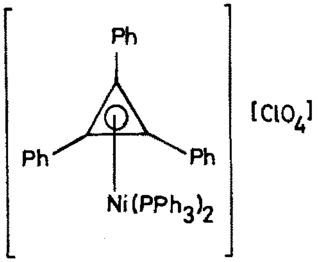
354 355



356

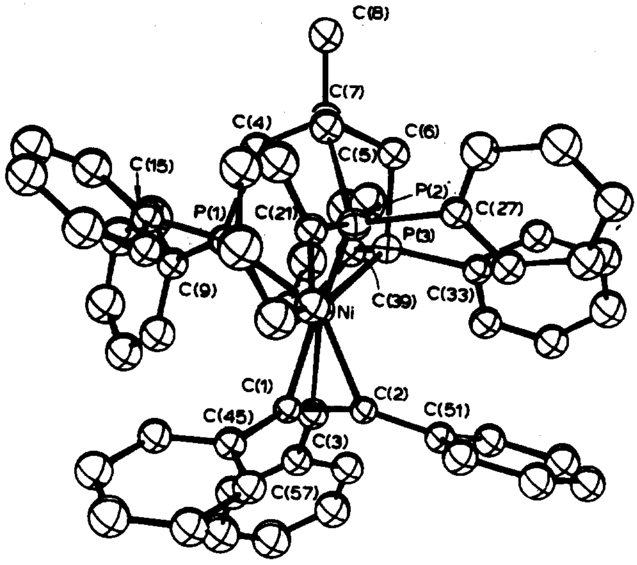
11 COMPLEXES OF DELOCALISED CARBOCYCLIC SYSTEMS

Treatment of 357 with a tridentate ligand L gave [Ni(C_3Ph_3)L]Y. In 358, the structure of which was determined by X-ray diffraction, the {Ph_3C_3} ligand was coordinated in a symmetric η^3-manner [438].



357

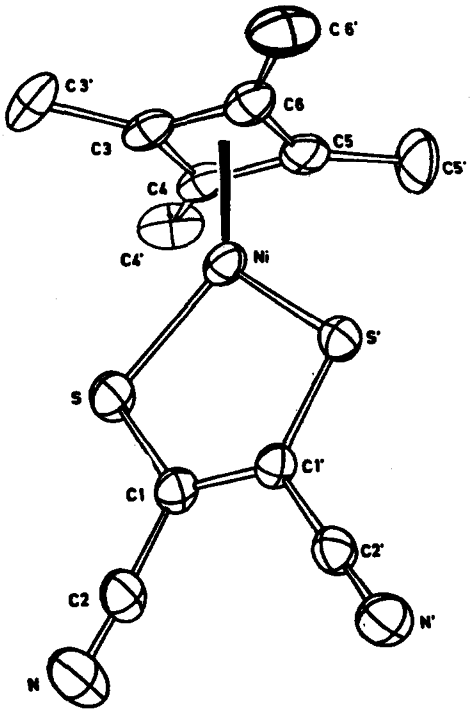
Non-empirical molecular electronic structure theory has been used to study [Ni(C_4H_4)$_2$] as a model for [Ni(Ph_4C_4)$_2$]. It was concluded that eclipsed geometry would be more stable than a staggered structure, and ionisation potentials were predicted [439]. The structure of 359 was determined by X-ray diffraction; the cyclobutadiene ligand was approximately square, with the methyl groups bent away from the nickel atom [440]



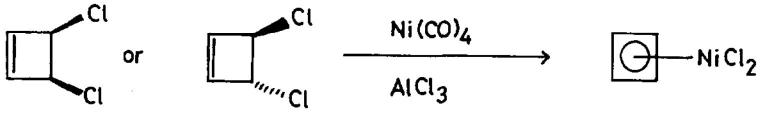
358 (Reproduced with permission from [438])

Treatment of **360** and/or **361** with $[Ni(CO)_4]/AlCl_3$ gave **362**. With the corresponding bromides or iodides the reaction occurred without $AlCl_3$ [441]. Reaction of $[Ni(Ph_4C_4)Br_2]$ with sodium metal in the presence of PPh_3 gave the new nickel(I) complex **363**. The iodo analogue was obtained by oxidation of $[Ni(Ph_4C_4)(cot)]$ using molecular iodine in the presence of PPh_3. Reactions of **363** were studied [442]. Reactions of $[Ni(R_4C_4)X_2]$ (R = Cy or Me_2CH) with two molar equivalents of sodium in the presence of diazabutadienes gave complexes such as **364** [443]. Treatment of $[(Ph_4C_4)Ni(cot)]$ with lithium metal, $[CpCo(C_2H_4)_2]$ or PhCN gave $[(Ph_4C_4)Ni(\mu_2\text{-}\eta^4\text{-cot})Ni(C_4Ph_4)]$ in respectively 47 %, 84 % and 87 % yields [444].

The use of η^5-Cp and η^6-arenes as protecting ligands towards platinum metal complexes has been reviewed [445]. Hartree Fock instabilities in a series of bimetallocenes and bimetallocenylenes of nickel have been investigated by means of a semi-empirical INDO Hamiltonian [446]. Thouless instability conditions in $[CpNi(C_4H_4)]^+$ were examined in the same way. A complete breakdown of the variations of Hartree Fock picture was encountered as singlet, non-singlet and non-real variations of Hartree Fock orbitals were predicted [447]. A quantitative prediction of gas phase enthalpies for the interaction of Lewis acids and Lewis bases has been compared with experimental data. $[CpNi]^+$ was among the Lewis acids considered [448].

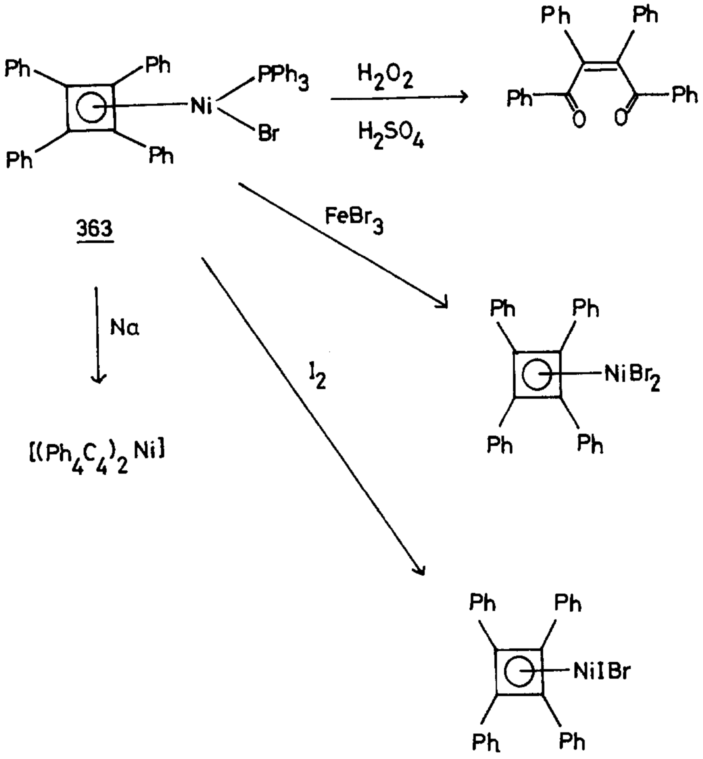


359 (Reproduced with permission from [440])

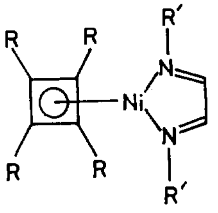


360 361 362

The results of an experimental study of multiphoton ionisation and dissociation of $[Cp_2Ni]$ in effusive and supersonic molecular beams have been reported. Mass spectrometric detection revealed the generation of bare metal ions both by resonant and non-resonant mechanisms [449.450].



363



364

A single crystal X-ray diffraction study of the disordered phase of $[Cp_2Ni]$ at 295 K has been reported. The molecular packing of the metastable ordered phase at 5 K was determined by minimisation of lattice energy [451]. Transition metal complexes have low lying excited electronic states and their electronic properties are therefore rather sensitive to external perturbations. The d^7 complex, $[Cp_2Ni]^+$ is a paramagnetic sandwich with Jahn-Teller degeneracy. The epr spectrum was found to depend on the properties of the host lattice in accord with the prediction of a continuum of energetically equivalent conformations along a circular Jahn-Teller valley [452]. In intercalates of $[Cp_2Ni]$ in FeOCl, solvent and steric effects are more important than ionisation potential effects of the guest molecules [453].

The infra-red and Raman spectra of $[Cp_2Ni]$ and its perdeuterated analogue have been recorded over the temperature range 30-300 K. New assignments for some internal modes were proposed [454]. Calculations of the frequencies and normal modes of vibration in nickelocene and other metallocenes were reported [455,456]. Incoherent quasi-elastic scattering has been used to study the reorientational motions of the cyclopentadienyl ring in $[Cp_2Ni]$ [457]. Fragmentation of $[(\eta^5\text{-}RC_5H_4)_2Ni]$ under electron impact conditions in a mass spectrometer gave fairly distinctive patterns. If the R group bore a hydrogen on the carbon atom α to the ring, fragmentation occurred with hydrogen migration from one ligand to the other, and cleavage of the bond between the metal and the ligand accepting the hydrogen [458].

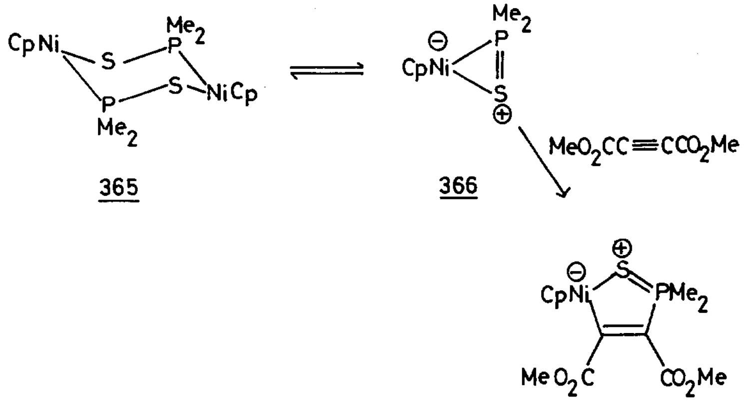
A new and rather efficient synthesis of $[Cp_2Ni]$ from $[Cp_2Mg]$ and $NiCl_2$ has been described [459]. Electrochemical synthesis of $[Cp_2Ni]$, however, was reported to give rather modest yields [460]. Substituted complexes, $[(RC_5H_4)_2Ni]$, could be prepared by reaction (63); yields were good even for cyclopentadienes bearing bulky substituents [461].

$$Ni + Cl_2 \xrightarrow{\text{thf}} [Ni(thf)_xCl_2] \xrightarrow{[RC_5H_4]^-} [(RC_5H_4)_2Ni] \qquad (63)$$

The synthesis of $[(\eta^5\text{-}Me_5C_5)_2Ni]$ was described, and the conversion to mono and dications investigated electrochemically. The decamethyl derivatives were substantially easier to oxidise than the parent nickelocenes [462].

The effect of $[Cp_2Ni]$ on the thermal decomposition of a composite solid propellant has been studied [463].

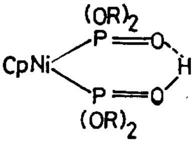
Displacement of a cyclopentadienyl ligand from $[Cp_2Ni]$ was achieved using $Me_2HP{=}S$ to give **365**, characterised by X-ray diffraction. 365 was shown to be in equilibrium with the reactive species, 366, which could be trapped with $MeO_2CC{\equiv}CCO_2Me$ to give 367 [464]. Reaction with $HP({=}O)(OR)_2$ gave **368**, in which the hydrogen bond was thought to be symmetrical [465]. Both this complex and its palladium analogue reacted with $[M'(acac)_n]$ to give $[\{CpM\{(MeO)_2PO\}_2\}_nM']$, where M' = Co(II), Cu(II), Zn(II), Ni(II), Al(III), Cr(III) or Fe(III) [466]. [CpNi{$Ph_2P(CH_2)_nPPh_2$}]X was prepared from [Cp_2Ni], the biphosphine and CX_4 [467]. The structure and stabilities of species such as **369** (M = Cd or Hg) has been investigated [468]. [Cp_2Ni] has been used as a reducing agent in the synthesis of new λ^3-7-phosphanonorbornanes, **370** [469].



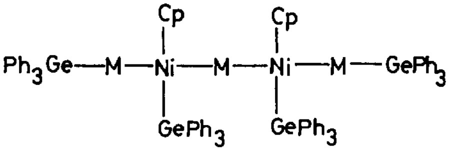
365

366

367



368



369

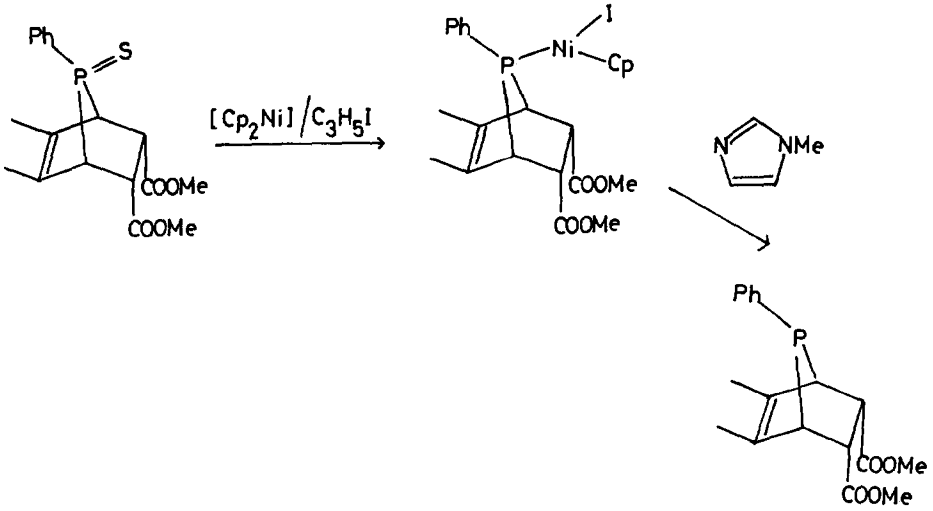
Numerous syntheses of the air-sensitive, paramagnetic nineteen electron nickel(I) complexes, [$CpNiL_2$] (L = R_3P or $(RO)_3P$; L_2 = dppe, arphos, bipy, or phen) have been described (reactions (64)-(67)). Epr spectra were recorded and the structure of the bipy complex established by X-ray diffraction [470]. **372**, synthesised from 371 and [Cp_2Ni] was stable towards β-hydride elimination because the nickel and hydrogen were fixed in *trans*-positions on a rigid ring [471].

$$[Ni(PPh_3)_3Cl] + NaCp \longrightarrow [CpNi(PPh_3)_2] + PPh_3 + NaCl \qquad (64)$$

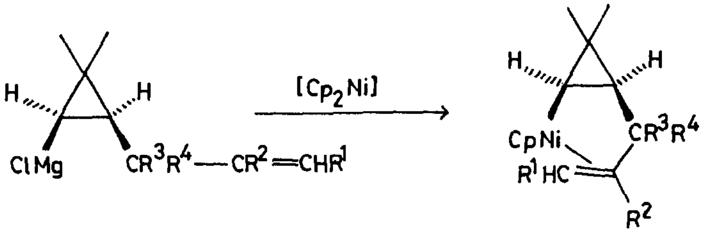
$$[Cp_2Ni] + [NiL_4] \longrightarrow 2[CpNiL_2] \qquad (65)$$

$$[CpNi(NO)] + 2L \longrightarrow [CpNiL_2] + NO \qquad (66)$$

$$[NiL_2X_2] + NaCp \longrightarrow [CpNiL_2] + NaX + X^- \qquad (67)$$



370

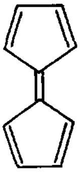


371

372

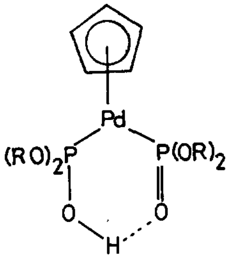
The redox potentials for one-electron reduction of $[CpNiL_2]^+$ (L = PR_3 or $P(OR)_3$ or L_2 = cod, nbd or dppe) have been determined by cyclic voltammetry [472]. In neutral 1:1 molar ratio mixtures of $AlCl_3$ and [1-Bupy]Cl at 40 °C, $[Cp_2Ni]$ underwent a reversible one electron charge transfer reaction with $E_{1/2}$ = −0.165 V. The evidence indicated that $[Cp_2Ni]$ and $[Cp_2Ni]^+$ were unstable in chloride rich melts. Spontaneous oxidation of $[Cp_2Ni]$ to $[Cp_2Ni]^+$ occurred in acidic melts, and a stable dication was formed reversibly at $E_{1/2}$ = +0.912 V. The electronic spectra of the +2, +3 and +4 oxidation levels were recorded [473]. $[CpNi(C_2B_2Et_4CMe)NiCp]$ is a paramagnetic triple decker sandwich. ^1H, ^{11}B and ^{13}C nmr spectra were shown to cover respectively ranges of 60, 1900 and 1000 ppm. Potassium metal reduction gave $[CpNi(C_2B_2Et_4CMe)NiCp]^-$. On the nmr spectroscopic timescale the odd electron was found to be distributed between the metals [474]. The redox properties of trinuclear clusters with two triply bridging ligands, such as $[(CpNi)_3S_2]$ and $[(CpNi)_3(CO)_2]$, were determined electrochemically. The possibility and reversibility of the redox steps depended on the number and type of the ligands [475].

The structure of the diamagnetic complex $[Ni_2L_2]$ (L = **373**) was determined by X-ray diffraction; it was isomorphous with the iron analogue [476].

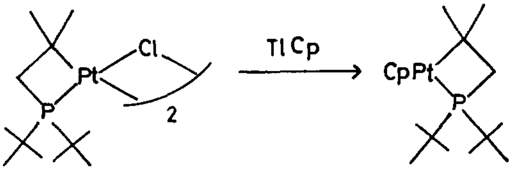


373

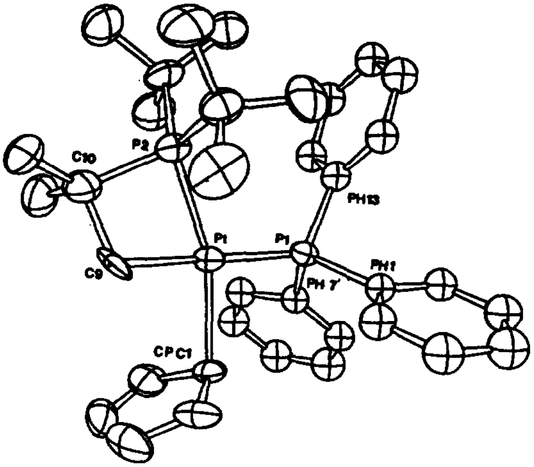
374 was synthesised by reaction of $[(\eta^5\text{-Cp})(\eta^3\text{-CH}_2\text{CHMeCH}_2)\text{Pd}]$ with two molar equivalents of $HP(=O)(OR)_2$, or by treatment of $[\{Pd(\{P(=O)(OR)_2\}_2H)Cl\}_2]$ with TlCp. As with its nickel analogue mentioned previously, IR spectroscopy showed the hydrogen bond to be symmetric [477]. TlCp reacted with the cyclometallated species, **375**, to give **376**. Reaction of 376 with a phosphine or phosphite ligand, L, gave η^1-Cp complexes such as **377**, characterised by X-ray diffraction [478].



374

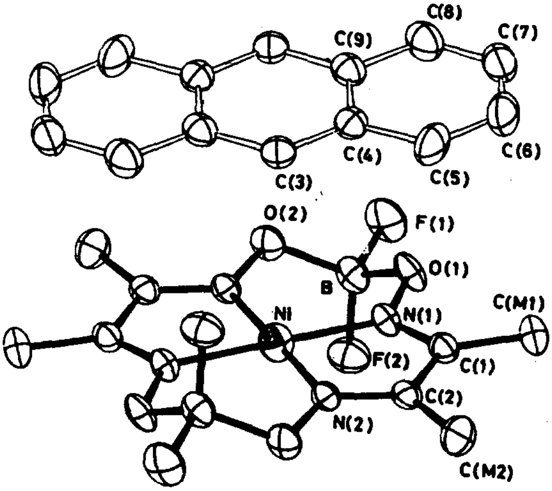


375 376



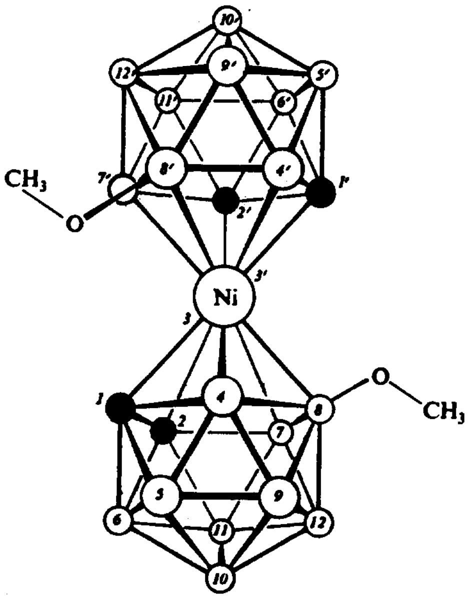
377 (Reproduced with permission from [478])

The structure of the 1:1 adduct of anthracene with bis{difluoroboron(dmg)}Ni(II), 378, was determined by X-ray diffraction. The anthracene and the macrocycle were shown to be almost parallel, implying a high degree of π-π interaction [479].

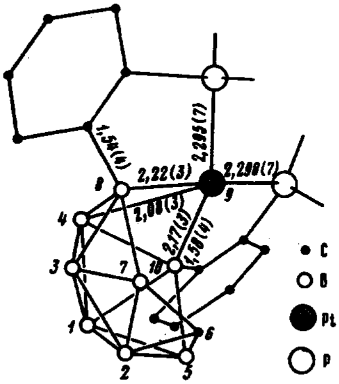


378 (Reproduced with permission from [479])

The structure of [(8-MeO-1,2-$C_2B_9H_{10}$)$_2$Ni(IV)], **379**, has been determined by X-ray diffraction [480]. *Arachno*-[4-CB_8H_{14}] reacted with [Pt(PPh_3)$_4$] to yield *nido*-[9,6-{Pt(PPh_3)$_2$}CB_8H_{12}] in which the heteroborane acted as an η^3-ligand towards platinum. Thermolysis yielded [{CB_8H_{10}($C_6H_4PPh_2$)$_2$}Pt], **380**, in which platinum is coordinated by two phosphorus atoms and one boron atom [481].



379 (Reproduced with permission from [480])



380 (Reproduced with permission from [481])

In extended MO calculations on $[B_4H_4(NiCp)_4]$, the polyhedral skeletal electron pair theory broke down. This and its cobalt analogue were shown to adopt alternative D_{2d} structures based on the dodecahedron; the differences between them were rationalised on the basis of stabilisation of a flattened metal tetrahedron in the cobalt complex and an elongated metal tetrahedron in the nickel based cluster [482].

An improved synthesis of $[(PMe_2Ph)_2PtB_{10}H_{12}]$ from $B_{10}H_{14}$ was reported. This strategy was also applied to 2,2'-, 2,6'- and 1,5'-isomers of $[(B_{10}H_{13})_2]$, to prepare various isomers of $[(R_3P)_2PtB_{10}H_{11}-B_{10}H_{13}]$ differing in the *conjuncto*-linkages or the site of the platinum atom. Detailed nmr spectroscopic studies of fluxional processes in these complexes were undertaken [483]. Treatment of *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ with an excess of $[B_9H_{14}]^-$ gave *arachno*-$[4,4-(PhMe_2P)_2-4-PtB_8H_{12}]$, identified by X-ray diffraction. Treatment with KH and further *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ gave the very stable complex *arachno*-$[6,6,9,9-(PhMe_2P)_4-6,9-Pt_2B_8H_{10}]$, which was topologically similar to *arachno*-$[B_{10}H_{14}]^{2-}$ [484].

13 CATALYSIS BY METAL COMPLEXES

A number of reviews have detailed aspects of metal catalysed reactions. These have included accounts of organic syntheses using palladium complexes [485-487], immobilised transition metal carbonyls [488], and diazabutadiene complexes as catalysts [489]. The mechanisms by which transition metal complexes decompose has been discussed [490], as have σ-π rearrangements [491]. The uses of polynuclear complexes of palladium on phosphine modified silica have been reviewed [492,493].

13.1 Hydrogenation and Hydrogenolysis

Homogeneous asymmetric hydrogenation has been reviewed; various nickel and palladium complexes were described [494]. H/D exchange in biologically active compounds catalysed by transition metal salts, including those of platinum has been reviewed [495], as have mechanistic features of selective hydrogenation in the presence of nickel complexes [496].

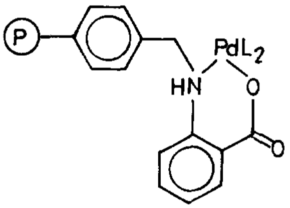
The semiempirical CNDO method has been used to study the interaction of H_2 with $[Pd_2L_2]$, $[PdL_n]$ and $[PtL_2]$. The formation of $\{\mu-H_2\}$ containing species was less favourable for palladium than for platinum. It was suggested that the observed absorption of hydrogen by $\{Pd(PPh_3)_2\}$ resulted in the formation of $[H_2Pd_2(PPh_3)_2]$ [497]. Using the SCF MO LCAO method in the CNDO valence approximation, the electronic structures for the products of the reaction of $[PdL_n]$ with molecular hydrogen were calculated. These calculations indicated that the energy of the $L_nPd—H_2$ interaction decreased as *n* increased [498].

Palladium complexes of amidophosphites of sugars have been tested as hydrogenation catalysts for 1-heptene and nitrobenzene [499]. A kinetic study of the hydrogenation of cyclopentene in the presence of $[Pd_5(PPh)_2]$ has been undertaken. The data were interpreted in terms of the reversible complexation of palladium with the substrate, followed by reaction with molecular hydrogen [500]. A 1:14 mixture of $[Ni(PBu_3)_2Cl_2]:Li[BH_4]$ was effective as a catalyst for 1-hexene reduction [501]. The nickel(II) chloride complex of *N,N*-diethylnicotinamide, when treated with $Na[BH_4]$ gave a catalyst for reduction of alkenes and dienes; using isoprene as the substrate alkenes could be obtained with modest selectivity [502]. Cationic palladium complexes such as $[Pd(dppe)(Me_2CO)_2][ClO_4]_2$ were catalysts for alkene reduction and silane alcoholysis [503,504]. $[Pd_n(P\text{-}P)X]$ $(P\text{-}P = \textcircled{\text{Si}}\!-\!(CH_2CH_2PPh_2)\{(CH_2)_4PPh_2\})$ complexes were used to catalyse cyclohexene disproportionation and alkene reduction. The activity of the complexes depended on *n*, with the species $\{Pd_3(P\text{-}P)\}$ seeming to be the most important [505]. The complexes $[\{Pd_5(phen)_2(OCOMe)\}_n]$ and $[(H_2O)(HO)Pd(\mu\text{-}PPhAr)_2Pd(OH)(OH_2)]$ catalysed the reduction of allyl alcohol [506,507], and $NiCl_2/NaCN/RNH_2$ yielded a catalyst for hydrogenation of cyclopentadiene [508].

Palladium complexes of glycamidophosphites have been used in asymmetric hydrogenation of itaconic acid derivatives with low enantiomer excess [509]. α-Acetamidocinnamate esters have been reduced in the presence of $PdCl_2$/S-α-phenylethylamine. Z-substrates gave S-products and E-substrates yielded R-products, both with rather low optical efficiency [510]. Asymmetric hydrometallation of $R^1R^2C{=}CH_2$ by $L^*/Al(i\text{-}Bu)_3$ (L^* = DIOP, *N,N*-dimethylmenthylamine or *N,N*-dimethylbornylamine) occurred in the presence of $[Ni(mesal)_2]$ to give $[L^*(R^1R^2CHCH_2)_3Al]$, which was protonated to $R^1R^2CHCH_3$, thus achieving enantioselective reduction, albeit with low optical efficiency [511].

Again this year polymer supported complexes have been prominent as catalysts. A silica supported acrylonitrile palladium complex was an active and selective catalyst for reduction of alkenes and nitroarenes, the activity being a function of the N:Pd ratio [512]. Silica supported polyvinylpyrrolidone palladium(II) species have also proved useful, though in this case the activity varied little with the N:Pd ratio [513]. $PdCl_2$, anchored to phosphinated crosslinked polystyrene, has been used for reduction of alkenes [514], polyenes [515], alkynes and carbonyl groups [516]. Polystyrene functionalised with bipy groups was also studied [517], and polyethyleneimine/$PdCl_2$/$Na[BH_4]$ was used for reduction of alkynes to alkenes and dienes to monoenes [518]. Phosphinated silica/$H_2[PtCl_6]$ proved to be an extremely active catalyst for alkenes reduction at 25 °C/1 atm H_2 [519].

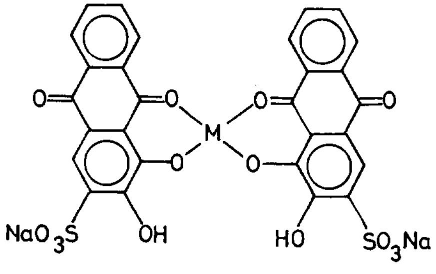
The selective reduction of alkynes to *cis*-alkenes continues to be a desirable goal. For $PhC{\equiv}CPh$, $[Pt(SnCl_3)_2Cl_2]^{2-}$ proved an extremely successful catalyst with 99 % chemoselectivity and 95 % stereoselectivity [520]. $PdCl_2$/amines provided a slightly less selective catalyst system [521]. The system produced *in situ* from $PdCl_2$/py/*i*-Bu_2AlH was also used for reduction of conjugated dienes to alkenes in a reaction promoted by oxygen and water [522]. 381 is a polymer supported analogue of these catalysts; it was less selective than the homogeneous species or than the Lindlaar catalyst, but was air stable and could be stored satisfactorily [523].



381

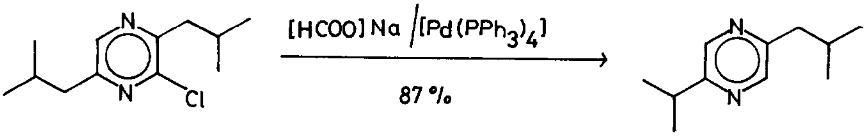
$[\{(\eta^3\text{-}C_3H_5)MSM'(\eta^3\text{-}C_3H_5)\}_x]$ (M = M' = Ni; x = 3) was inactive for reduction of 3-hexyne but the $\{Pd_2\}$ or $\{PdPt\}$ complexes could be used to produce the *cis*-alkene with good selectivity. The $\{Pt_2\}$ species, however, catalysed reduction of the alkene at a significant rate, suggesting that the bimetallic complex must survive intact during catalysis [524].

Nitrobenzene was reduced to aniline in the presence of $PdCl_2$ or $PdX_2/\gamma\text{-}Al_2O_3$ [525]. $[Pd_2(PPh_3)_2Cl_4]$ could also be used as a catalyst in basic ethanol, and the intermediate $[Pd(PhNO_2)(PPh_3)Cl_2]$ was characterised. At 1 atm pressure of hydrogen, $PhNH_2$, PhN=NPh and PhN=N(O)Ph were produced in the ratio 75:5:15, but at elevated pressures only aniline was formed [526]. $[Pd(acac)_2]$ acted as a catalyst for the transfer of hydrogen from 4-vinylcyclohexene to RNO_2, yielding ethylbenzene and RNH_2 [527]. The system $[Pt(dmso)_2Cl_2]/Na[BH_4]$/dmso/quinone catalysed the selective reduction of $PhNO_2$ to PhNHOH, *via* electron transfer and protonation steps [528]. Reductive amination of aldehydes, RCHO, using $PhNO_2$, occurred in the presence of H_2/**382** (M = Pd, Pt or Rh); PhNHOH, $PhNH_2$ and PhNH=CHR were the postulated intermediates [529].

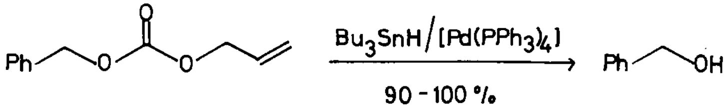


382

Rather few hydrogenolyses have been studied this year and they are a somewhat diverse group. Transfer hydrogenolysis of **383** gave **384** with sodium methanoate as the hydrogen source. The *N*-oxide reacted similarly, without *N-O* bond cleavage [530]. $[Pd(PPh_3)_4]$ could also be useful as a catalyst for the hydrogenolysis of acid chlorides by Bu_3SnH. The process was very selective and even worked well for α,β-unsaturated aldehydes [531]. Bu_3SnH was also used for deprotection of **385**. The reaction was thought to proceed *via* formation of a palladium allyl and $ROCOOSnBu_3$, which readily lost CO_2 [532]. Hydrogenolysis of the alkenyl sulphide, **386**, employed $Me_2CHMgBr$ as the hydrogen source and $[Ni(PPh_3)_2Cl_2]$ as the catalyst. The reaction was stereospecific and no over-reduction occurred, the product being a key intermediate in the synthesis of the Douglas fir tussock moth [533].

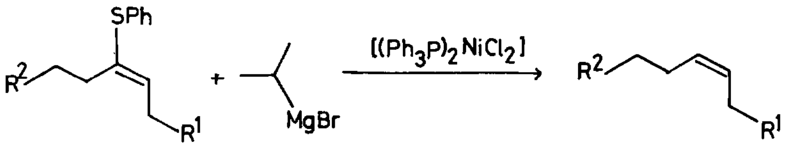


383 **384**



385

There have been further studies of H/D exchange in the presence of Pt(IV)/Pt(II). An intermediate of the type Pt(II)-CH_2- appears to be favoured by the high affinity of platinum for carbon and the low energy of hydration of platinum(II) [534].



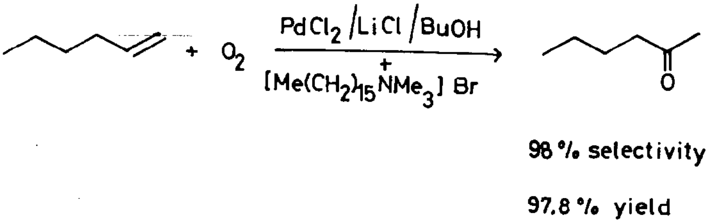
386

13.2 Oxidation

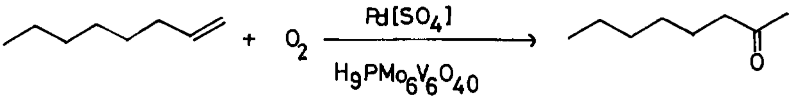
Catalysts for epoxidation of alkenes by ROOH, including nickel phthalocyanine, have been reviewed [535]. The activation of molecular oxygen and the selective oxidation of alkenes in the presence of Group VIII transition metal complexes has also been discussed [536].

Many papers continue to report studies of the Wacker and related reactions. Production of ethanal occurred efficiently in the presence of $Na_2[PdCl_4]/Cu(NO_3)_2/O_2$ [537] or $PdCl_2/FeCl_3/O_2/A^-$ (A = $[H_2PO_4]^-$, $[NO_3]^-$, $[B_4O_7]^{2-}$, $[PO_4]^{3-}$ or $[NO_2]^-$) [538]. 1,2-Dihydroxyethane diethanoate was formed using $PdCl_2/CuCl_2/Cu(OCOMe)_2/LiCl/MeCOOH/O_2$ [539], and a mixture of chlorinated products resulted with $Na_2[PdCl_4]/Cu(NO_3)_2/HCl/O_2$ [537]. The mechanism of formation of the diethanoate and of CH_2=CHOCOMe has been discussed in detail. The arguments for two pathways are somewhat involved [540,541]. Other authors suggested that the species responsible for formation of CH_2=CHOCOMe was a palladium(0) cluster [542]. In the presence of $Pd[SO_4]/K[BrO_3]$ a 2:1 mixture of ethanal and $HOCH_2CH_2Br$ was formed. A kinetic study was undertaken and a mechanism proposed [543]. PdCuNaY zeolites have also been used as catalysts, and the reaction kinetics were compared with homogeneous analogues [544,545].

The oxidation of 1-alkenes continues to be widely used in synthetic sequences. Reactions (68)-(71) [546-549] show some improved protocols for linear alkenes. In (69) the use of $PdCl_2$ as a catalyst gave all three isomeric octanones.

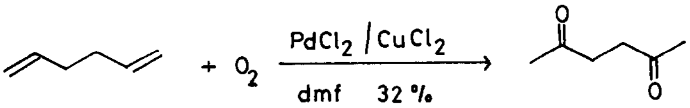


(68)

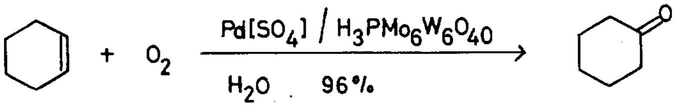


(69)

95 % selectivity

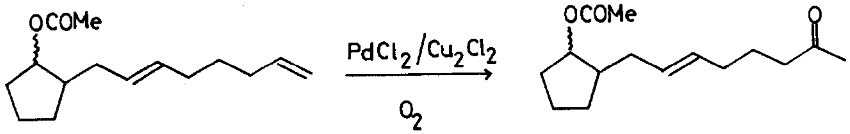


(70)

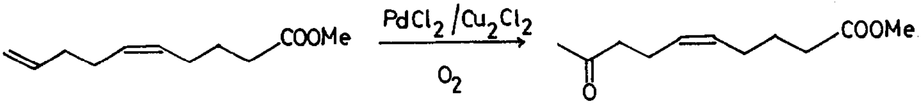


(71)

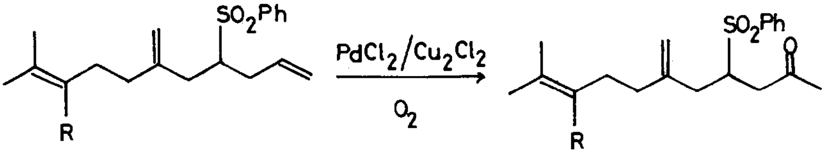
The selectivity for terminal alkenes was high; reactions (72) [550] and (73) [551] gave prostaglandin precursors, whilst the product of reaction (74) was used in ionone and irone syntheses [552]. **387** was readily oxidised to 388, which could be cyclised to the cyclopentenone derivative, **389** [553]. In one case oxidation of a non-terminal alkene in **390** was reported; this was relatively regioselective giving 77 % **391** together with 7 % of the regioisomer [554].



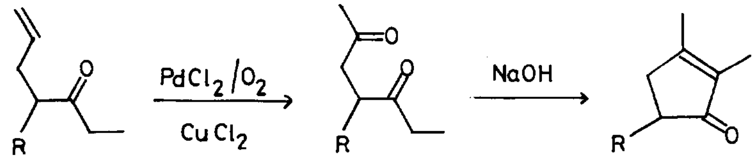
(72)



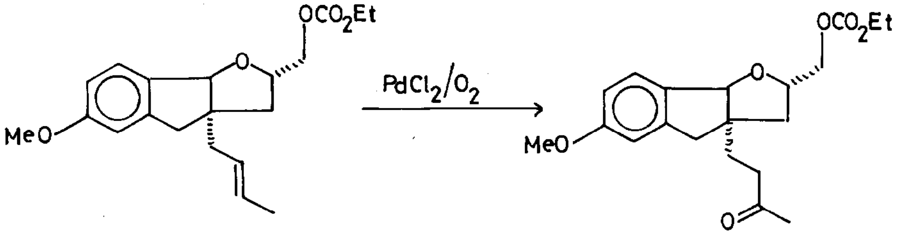
(73)



(74)



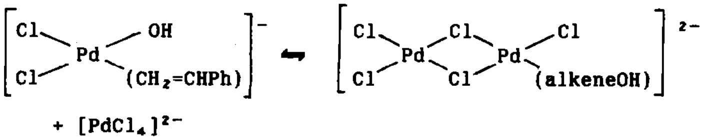
387 388 389



390 391

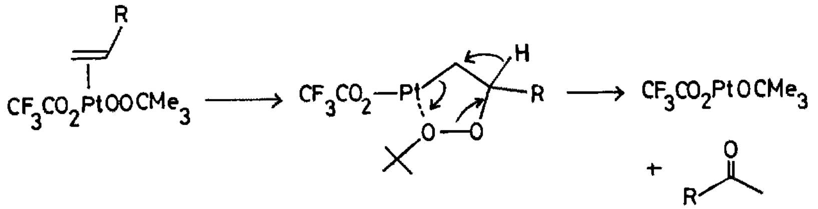
A kinetic investigation of the oxidation of styrene in the presence of [PdCl$_2$]$^{2-}$ revealed the rate equation (75). Various pathways were proposed and it was concluded that the equilibrium (76) was critical [555]. Propene was found to be oxidised by Pd(II)/quinone more rapidly than was ethene, possibly because of the lower stability of the [Pd(0)(propene)$_2$] species [556].

$$\text{Rate} = \frac{k_1[\text{styrene}][\text{PdCl}_4]^{2-}}{[\text{H}_3\text{O}^+][\text{Cl}^-]^2} \qquad (75)$$

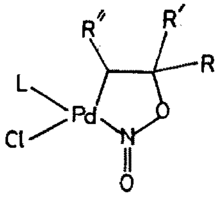


$$\left[\mathrm{Cl_2Pd(OH)(CH_2{=}CHPh)}\right]^- + [\mathrm{PdCl_4}]^{2-} \rightleftharpoons \left[\mathrm{Cl_2Pd(\mu\text{-}Cl)_2Pd(Cl)(alkeneOH)}\right]^{2-} + \mathrm{Cl}^- \qquad (76)$$

Two somewhat different oxidising systems have also been investigated in detail. [Pt(nbd)(O$_2$CCF$_3$)$_2$] reacted with Me$_3$COOH to give [Pt(OOCMe$_3$)(Me$_3$COOH)(O$_2$CCF$_3$)$_2$], which selectively oxidised 1-alkenes to methyl ketones. The mechanism was supposed to be that of reaction (77) [557]. Reaction of [Pd(MeCN)$_2$(NO$_2$)Cl] with RCH=CH$_2$ gave RCOCH$_3$ and [Pd(NO)$_n$Cl], the latter being reoxidised, albeit slowly, by molecular oxygen. ^{18}O labelling implied that the oxygen was transferred from the NO$_2$ group to the alkene, suggesting an intermediate such as 392 [558].

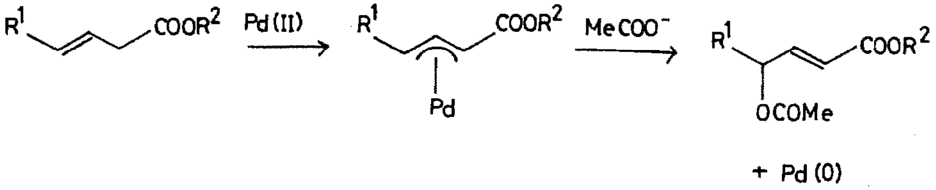


(77)



392

There have been a number of reports of protocols for the allylic oxidation of propene to allyl ethanoate. Catalysts have included Pd(OCOCF$_3$)$_2$ [559], PdCl$_2$/Al$_2$O$_3$/K[OCOMe] [560] and Pd/Na zeolites [561]. XPES was used to study the PdCl$_2$/Al$_2$O$_3$ catalyst, and it was concluded that the active species contained units of the type MeCOO-Pd-Pd-OOCMe [562]. Allylic oxidation of β,γ-unsaturated esters occurred in modest yields *via* the mechanism of Scheme 12 [563].



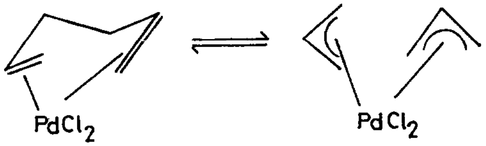
Scheme 12 Palladium catalysed oxidation of β,γ-unsaturated esters [563].

Several papers have reported kinetic studies of the oxidative dimerisation of styrene to *trans,trans*-1,4-diphenylbutadiene in the presence of Pd(OCOMe)$_2$. The reaction was slightly catalytic with respect to palladium even at 1 atm of molecular oxygen. The first steps in the process were suggested to be reactions (78) and (79) [564-566].

$$[Pd_3(OCOMe)_6] + PhCH{=}CH_2 \longrightarrow [\{Pd_3(OCOMe)_6\}^{\ominus}\!\!-\!CH_2\overset{\oplus}{C}HPh] \qquad (78)$$

$$[\{Pd_3(OCOMe)_6\}^{\ominus}\!\!-\!CH_2\overset{\oplus}{C}HPh] \longrightarrow [Pd_3(OCOMe)_5\text{-}CH{=}CHPh] + MeCOOH \qquad (79)$$

In the presence of $[Pd(PhCN)_2Cl_2]$, Cu_2Cl_2 and $CuCl_2$, 1,5-hexadiene was oxidised by molecular oxygen to propanone. The mechanism suggested involved the formation of **393** and **394**, followed by the conversion of the allyl ligands to propanone [567].



393 394

Oxidation of butadiene to furan in moderate yields has been reported in three patents. The catalytic systems investigated and the conditions used were $PdCl_2/[H_9PMo_6V_6O_{40}]/CCl_2F_2/O_2/65\text{-}120$ °C [568], $PdCl_2/TeO_2/Al_2O_3/[NH_4][NO_3]/O_2/H_2O$ [569], and finally the range of catalysts $PdCl_2/[H_{3+n}PMo_{12-n}V_nO_{40}].xH_2O$ (n = 1-10; $0 < x < 32$)/O_2/65-120 °C/pH = 0-2.5 [570]. Oxidation to $CH_2{=}CH\text{-}CH{=}CHOCOMe$ was achieved with 88 % selectivity using $PdCl_2/MgCl_2/Al_2O_3/O_2/MeCOOH$ [571,572], whilst conversion to $MeCOOCH_2CH{=}CHCH_2OCOMe$ was 92 % selective in the presence of $PdCl_2/SnCl_2/TeO_2/MeCOOH$ [573].

The oxidation of arenes has been reviewed. Oxidative coupling and ring acetoxylation in the presence of palladium complexes was particularly considered [574]. It has been postulated that palladium(I) clusters or palladium(0) complexes participate in arene oxidation in the presence of $Pd[SO_4]$ [575]. However, other workers considered that palladium(II) and palladium(IV) species were involved (reactions (80)-(83)) [576].

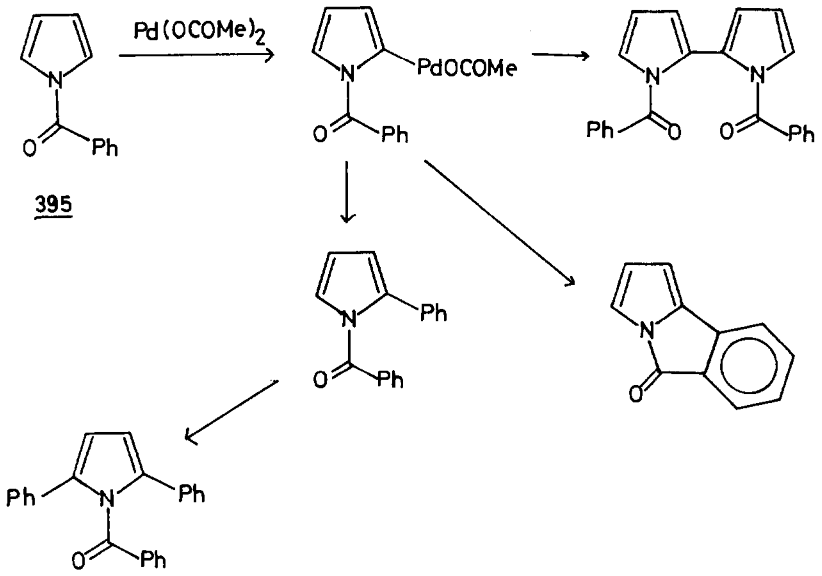
$$ArH + \{Pd(I)(OCOMe)\} \longrightarrow \{ArPd(II)(OCOMe)\} + H^+ \qquad (80)$$

$$\{ArPd(II)(OCOMe)\} + ArH \longrightarrow \{Ar_2Pd(II)\} + MeCOOH \qquad (81)$$

$$\{ArPd(II)(OCOMe)\} \xrightarrow{\text{oxidise}} \{ArPd(IV)(OCOMe)_3\} \qquad (82)$$

$$\{ArPd(IV)(OCOMe)_3\} \longrightarrow ArOCOMe + Pd(OCOMe)_2 \qquad (83)$$

Oxidative coupling of ArR in the presence of $Tl(OCOCF_3)_3/Pd(OCOMe)_2$ gave the *para*-coupled product in good yield and with high regioselectivity [577]. Both intra and intermolecular couplings of **395** could be achieved (Scheme 13) but in all cases the yields were relatively low [578]. Cross coupling of 396 with methyl acrylate gave 397 in low yield, which reacted further to give 398 and 399 [579].

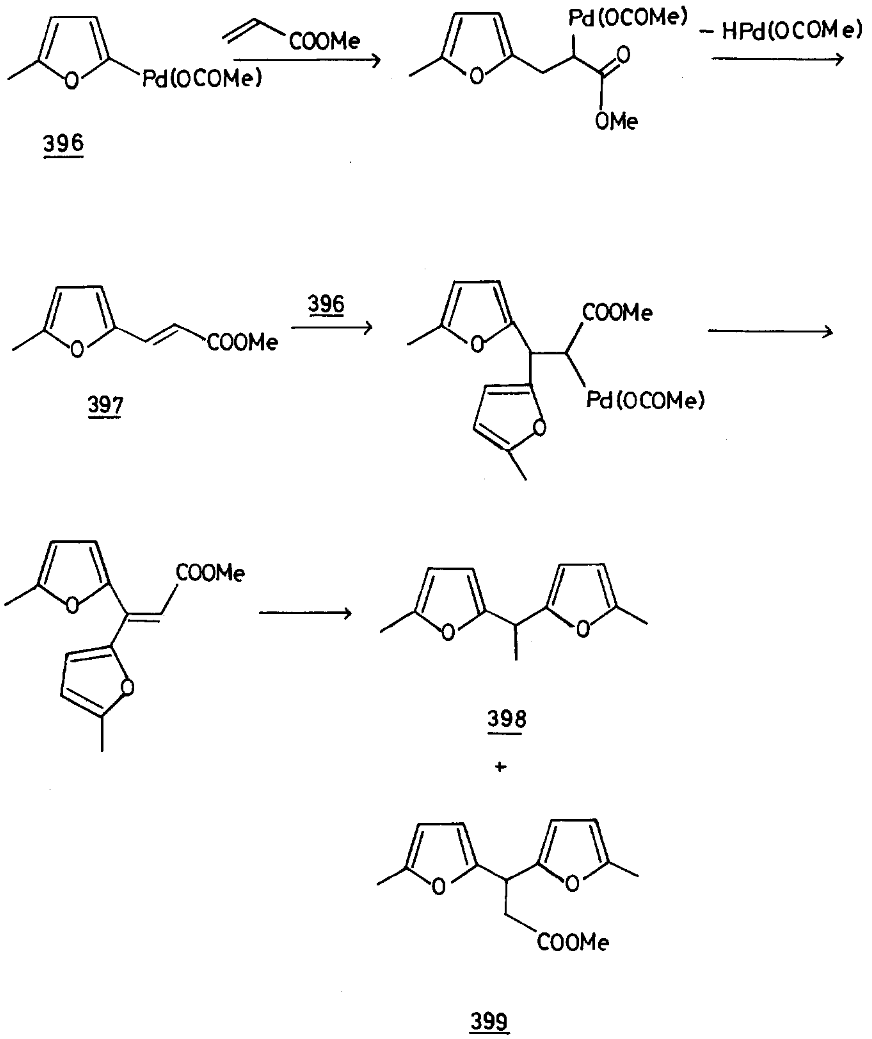


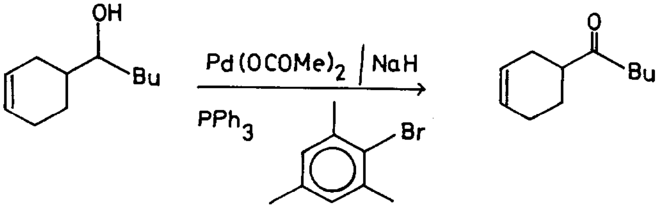
395

Scheme 13 Palladium catalysed intra and intermolecular couplings of pyrrole derivatives [578].

[$Pd_4(CO)_4(OCOMe)_4$], with or without added phen, has proved a good catalyst for oxidation of toluene to benzyl ethanoate. Kinetic schemes were evaluated and it seems likely that the cluster structure is at least partly maintained during catalysis [580,581].

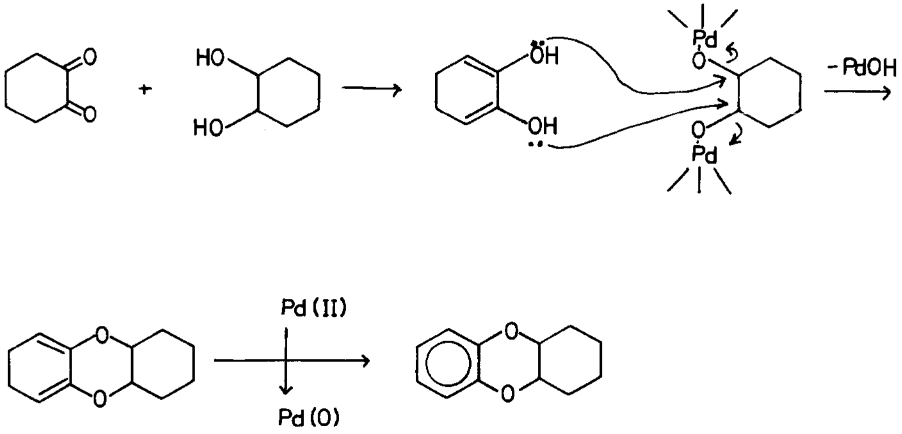
Palladium complexes are not usually thought of as catalysts for alcohol oxidation, but a few examples of this reaction have been reported this year. The system $Pd(OCOMe)_2/PPh_3/NaH$/1-bromo-2,4,6-trimethylbenzene was especially valuable for oxidation of unsaturated alcohols (reaction (84)) [582], and $Pd(OCOMe)_2/Cl^-/K^+$/18C6 was useful for cyclohexanol oxidation [583]. $Pd(OCOMe)_2$ or $PdCl_2$ catalysed the oxidation of secondary alcohols to ketones by tetrachloromethane in basic solution. Primary alcohols were poor substrates [584].


Pd(OCOMe)
COOMe
Pd(OCOMe)
O
OMe
− HPd(OCOMe)
396
COOMe
397
396
COOMe
Pd(OCOMe)
COOMe
398
+
COOMe
399

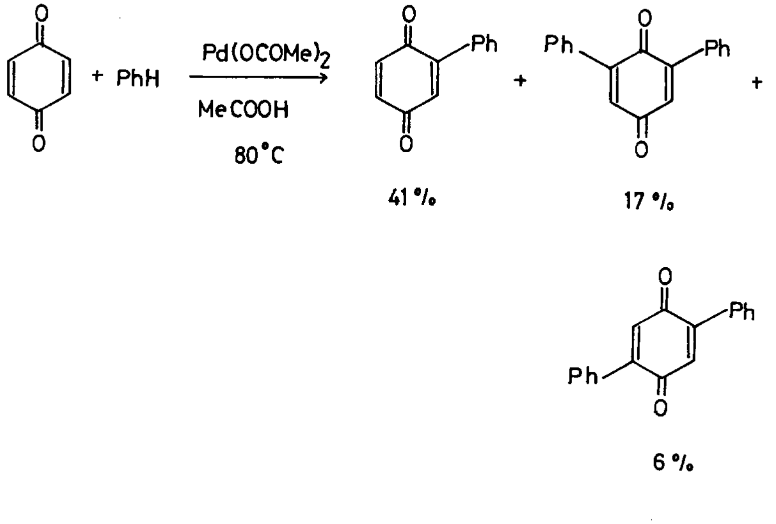

OH
Bu
Pd(OCOMe)₂ / NaH
PPh₃
Br
O
Bu

(84)

Reaction of cyclohexane-1,2-dione with 1,2-diols (Scheme 14) gave phenol derivatives [585]. Oxidative coupling of quinones and arenes (reaction (85)) occurred in the presence of $Pd(OCOMe)_2/MeCOOH$, but the reaction was not strictly catalytic in palladium [586].



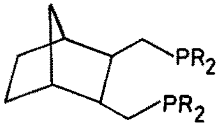
Scheme 14 Palladium catalysed oxidative coupling of diones and diols [585]



(85)

12.3 Reactions of carbon monoxide and carbon dioxide

Hydroformylation of 1-alkenes in the presence of $PtCl_2/SnCl_2$/chelating biphosphine has been investigated. Very high selectivity for linear aldehydes was observed using dppb as the ligand [587]. Using $[Pt(ER_3)(CO)Cl_2]$ (E = P or As) as the catalyst system, the yield of linear aldehyde was maximised by systematic parameter variation. 1-Alkenes reacted with good yield and selectivity, although there was some competitive reduction. Internal and cyclic alkenes, and conjugated double bonds, reacted less rapidly, but there was little competitive addition of hydrogen [588]. Hydroformylation of 1-pentene in the presence of $[Pt(PhCN)_2Cl_2]$/DIOP/SnO gave 75.8 % aldehydes with an *n:iso* ratio of 95:5 [589]. With **400** as the ligand 73.9 % hexanal was obtained together with 13.4 % 2-pentene and 8.4 % pentane [590].

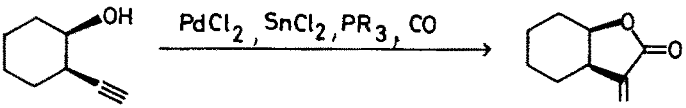


400

In hydrocarboxylation reactions the theme this year has once again been the achievement of selectivity. **Z**-1,4-hexadiene reacted to give Z-methyl-5-heptenoate, but selectivity was poor [591]. Hydrocarboxylation of 1-hexene using $[Pd(PPh_3)_2Cl_2]/SnCl_2$ was reported to give 86 % of the linear product [592] and a polymer bound analogue gave still better selectivity [593]. However, careful adjustment of conditions may lead to a preponderance of the branched ester derived from propene. If the reaction was conducted in an alcohol diluted with an inert solvent in the presence of LiCl and a high pressure of CO, esters of 2-methylpropanoic acid were the major products [594]. The use of $[Pd(AsPh_3)_2Cl_2]$/HCl in *p*-xylene as catalyst has been reported to give similar results [595].

A careful study of the addition of D_2/CO/MeOH to **Z**- and **E**-2-butene in the presence of $[Pt(DIOP)(SnCl_3)Cl]$ demonstrated that the addition of hydrogen and carbon monoxide was predominently *cis*, with any lack of stereoselection almost certainly arising from isomerisation of the starting material [596].

An improved catalyst has been found for the intramolecular hydrocarboxylation of alkynes (reaction (86)) [597].

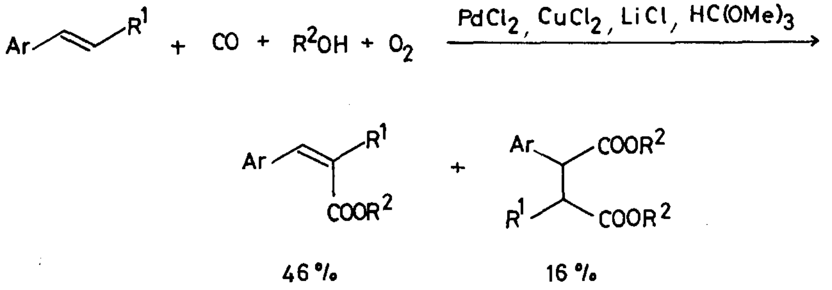


(86)

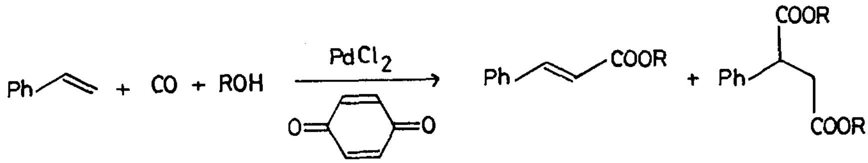
A number of oxidative carbonylations have been reported this year, particularly in the patent literature, and are exemplified by reactions (87) [598] and (88) [599]. Analogous reactions for alkenes have also used as catalysts $PdCl_2/CuCl_2/Et_3N$ [600,601]. Branched alkenes were also suitable substrates, but double carbonylation was a significant competing process (reaction (89)) [602], as it was when benzoquinone was used as an oxidant (reaction (90)) [603]. A double carbonylation of butadiene was achieved using $PdCl_2/CuCl_2$ (reaction (91)) [604]. Carbonylation and polymerisation of ethyne in the presence of $PdBr_2/P(OPh)_3/HBr/ROH$ has also been studied [605].

$$PhCH{=}CH_2 + O_2 + CO + ROH \xrightarrow[\text{75.8 \% conversion}]{PdCl_2/CuCl_2/K[OCOMe]} \underset{\text{82.4 \% selection}}{\textit{trans}\text{-}PhCH{=}CHCOOR} \qquad (87)$$

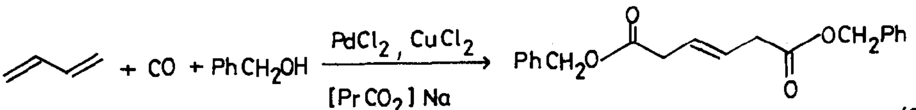
$$CH_2{=}CH{-}CH{=}CH_2 + CO + MeOH \xrightarrow[\text{83 \%}]{PdI_2/CuI/LiI} \textit{trans}\text{-}CH_2{=}CH{-}CH{=}CHCOOMe \qquad (88)$$



(89)



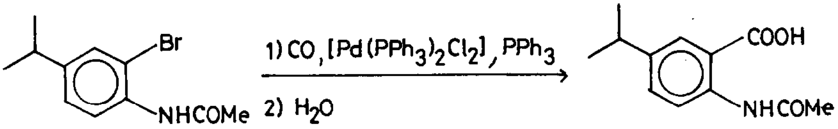
(90)



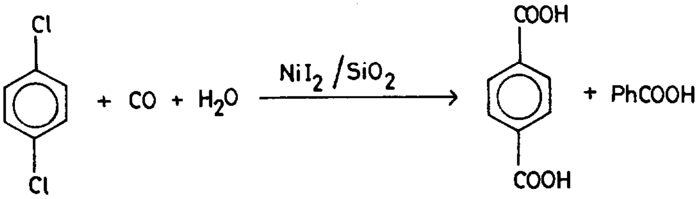
(91)

There continue to be numerous reports of carbonylation reactions of aryl, vinyl and allyl halides. In all cases the initial steps involve oxidative

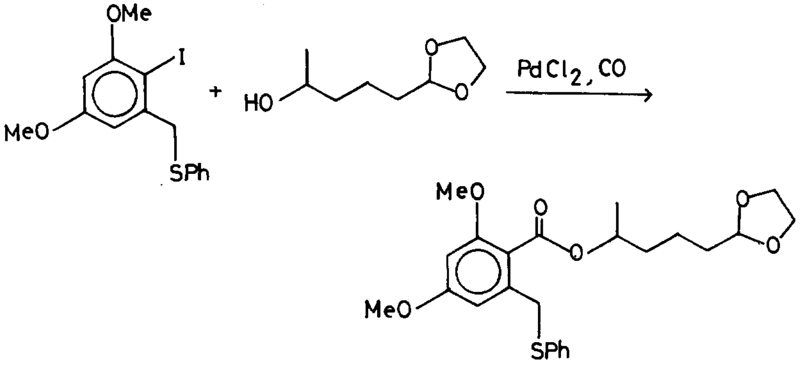
addition of the halide to palladium, to give for example {ArPd(II)X}, and then carbonylation to {ArCOPdX}. The fate of the acyl palladium species then depends on the presence of an appropriate nucleophile, and it is in this area than the most notable developments have come this year. With water as the nucleophile, carboxylic acids could be synthesised (reactions (92) [606] and (93) [607]). Alcohols were also useful nucleophiles, the product of reaction (94) being used in a synthesis of zearalenone [608].



(92)

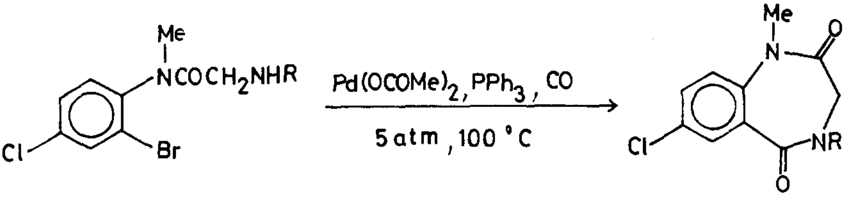


(93)



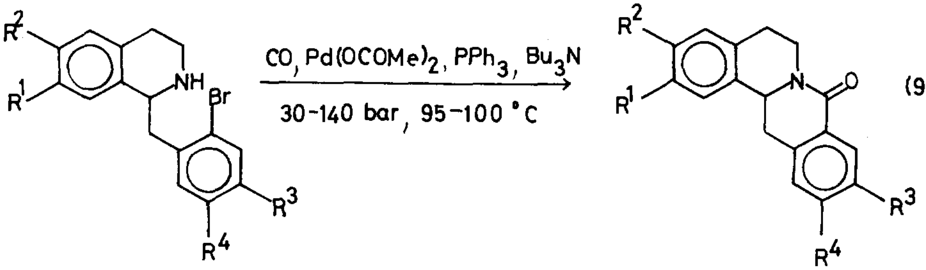
(94)

Amines may also react as the nucleophiles and intramolecular versions of this process are shown in reactions (95) which yielded a diazepam precursor [609], and (96), which gave a product which could be transformed into a berbine alkaloid [610].



(95)

R = COMe or CH$_2$Ph

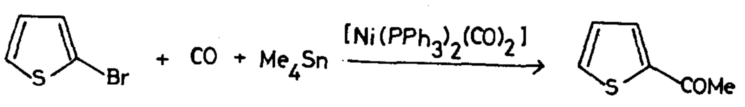


(96)

Less conventionally, but having considerable synthetic scope, several carbon nucleophiles have been used to attack the intermediate acyl palladium complexes. Using [PhPd(PPh$_3$)$_2$I] as catalyst, ArI was converted by CO/[CN]$^-$ to ArCOCN in good yield, this being the first reported example of cyanocarbonylation [611]. Aryl, heteroaryl and vinyl halides, RX, have been converted to RCOC≡CR' by carbonylation in the presence of [Pd(dppf)Cl$_2$]/R$_3$N/R'C≡CH, the nucleophile being the alkynyl anion, generated *in situ* [612].

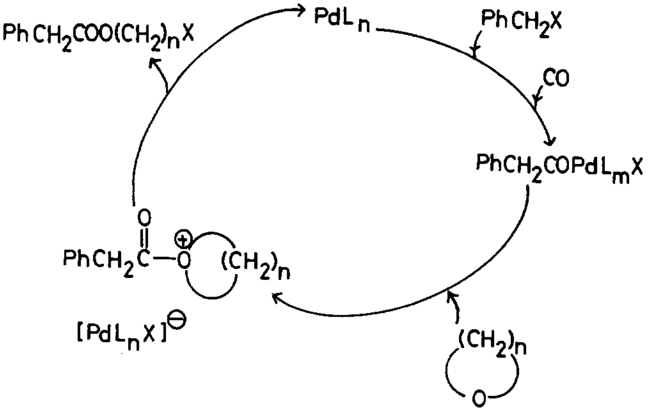
Alkyl tin compounds have also been very popular nucleophiles, examples being given in reactions (97) [613] and (98) [614]. Using ArSnMe$_3$ as the nucleophile only the aryl group was transferred [615]. The first successful carbonylation of halides such as PhCHBrCH$_3$, CH$_3$CHBrCOOEt and PhCHBrCH$_2$CH$_3$ which have β-hydrogen atoms, to give methyl ketones, with CO/Me$_4$Sn/[Pd(AsPh$_3$)$_2$Cl$_2$] has been described. Some competing elimination did occur, but yields were fair although the reaction is rather slow [616].

$$\mathrm{PhI} + \mathrm{Bu_4Sn} \xrightarrow{[\mathrm{PhPd(PPh_3)_2I}]/(\mathrm{Me_2N})_3\mathrm{PO}} \mathrm{PhCOBu} \qquad (97)$$



(98)

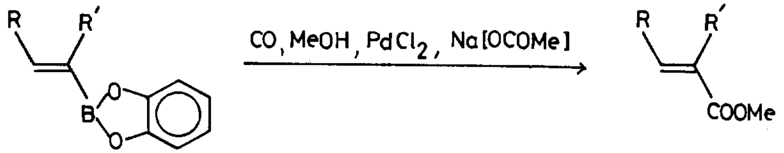
Reaction of benzyl halides, $PhCH_2X$, with cyclic ethers, $[(CH_2)_nO]$, in the presence of $[PhPd(PPh_3)_2I]$ and CO gave $RCOO(CH_2)_nX$. The mechanism proposed is shown in Scheme 15 [617].



Scheme 15 Mechanism of palladium catalysed carbonylation of benzyl halides in the presence of cyclic ethers [617].

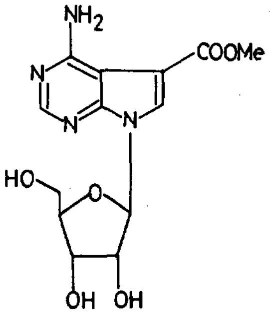
The carbonylation of aryl diazonium salts proceded by a related mechanism, and in the presence of [RCOO]Na, the mixed anhydride ArCOOCOR was produced from $[ArN_2][BF_4]$ [618].

Direct carbonylation of organometallics has been reported for vinyl boranes in reaction (99), which occurred in excellent yield with good stereochemical control [619]. A polymeric heteroaryl mercury compound was carbonylated in the presence of $Li_2[PdCl_4]$ to give the C-5 substituted tubercidin derivative, 401 [620].

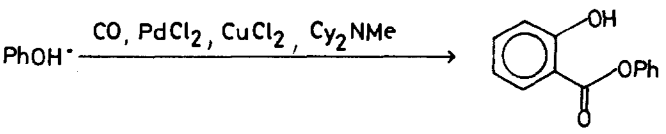


(99)

Various patents have reported the homologation of methanol to ethanoic acid, the catalyst systems used including $[Ni(CO)_4]/Cr(OCOMe)_3/MeI$ [621], $Ni(OCOMe)_2/[VO(acac)_2]/MeI$ [622], $Ni(OCOMe)_2/La(OCOMe)_3/MeCOOH/MeI$ [623] and $[Ni(CO)_4]/KI/MeI/$*N*-methylpyrrolidone [624]. Oxidative carbonylation of phenol to diphenyl carbonate was reported to occur in the presence of $PdBr_2/[R_4N]Br/Na[OH]/[Mn(acac)_2]$/molecular sieves [625]. Trialkylamines could also be used as the bases, and salts of copper, vanadium or cobalt could replace those of manganese as cocatalysts [626]. However, in the absence of oxygen, phenol was converted to **402**, presumably *via* an initial electrophilic attack of palladium on the aryl ring [627].



401

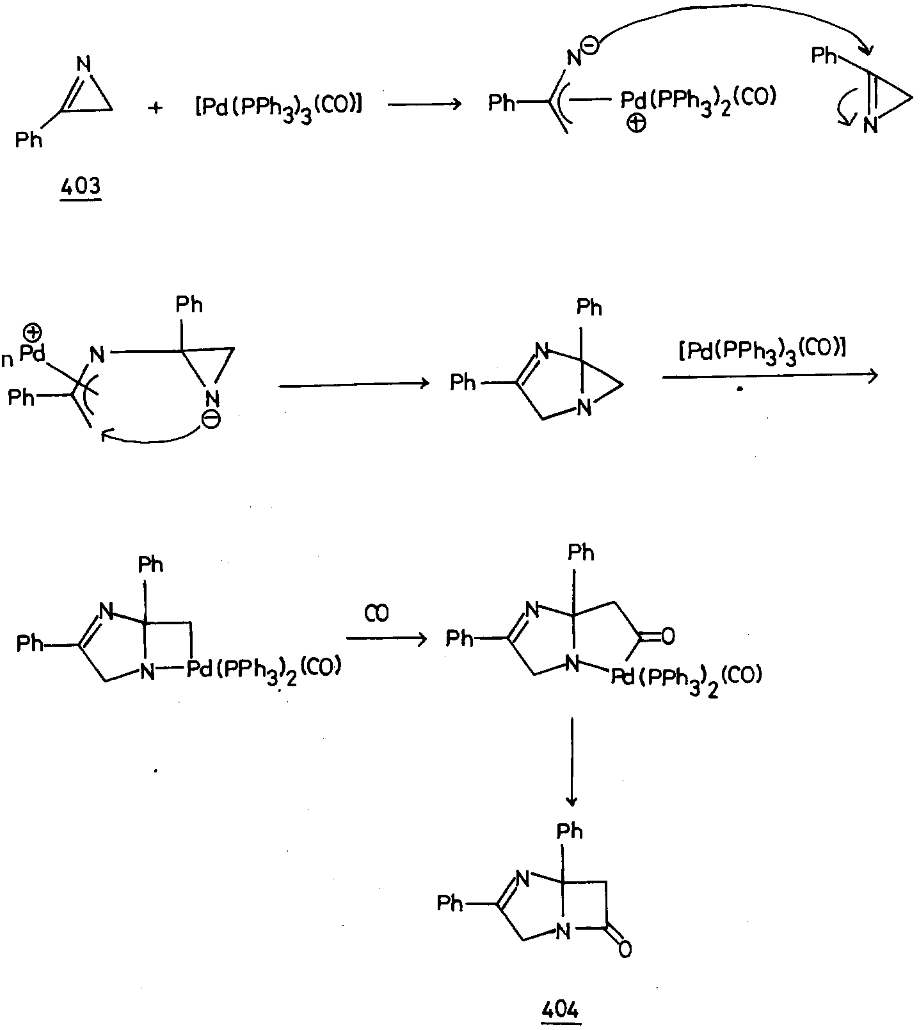


402

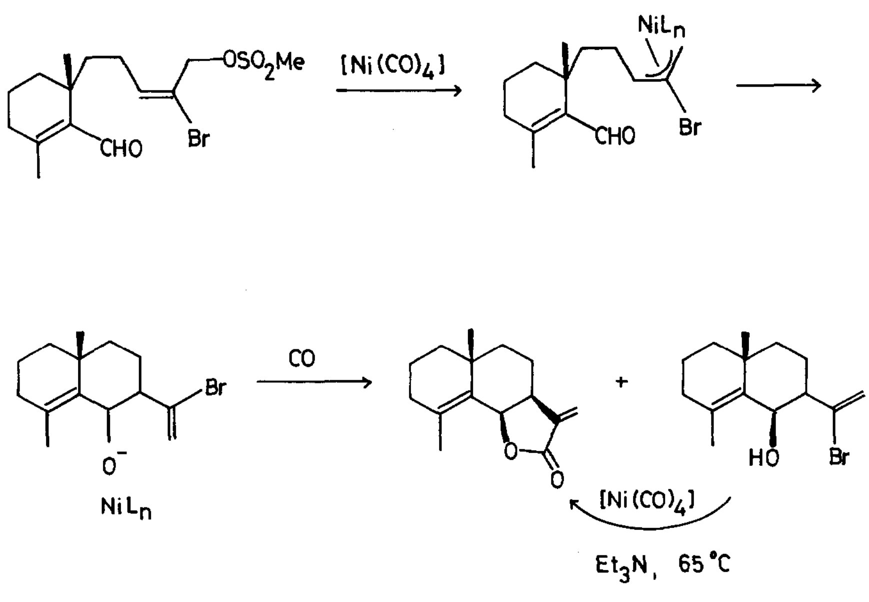
There continues to be considerable interest in improving the conditions for the conversion of nitroarenes to aryl isocyanates [628-635]. Using 2,4-dinitrotoluene as the substrate and [Pd(py)$_2$Cl$_2$] as the catalyst, in the presence or absence of molybdic acid, allowed some control over the selectivity to mono and bis isocyanates [636]. Mechanistic studies led to the conclusion that the reaction proceeds *via* carbonylation of an intermediate nitrene [637,638]. If the reaction was performed in the presence of a suitable alcohol, ROH, the urethane, ArNHCOOR, could be obtained in excellent yield [639-641]. Arylamines could also be carboxylated to urethanes in the presence of PdCl$_2$/FeOCl/CO/O$_2$ [642]. Reaction of nitrobenzene with PhCONHPh and CO in ethanol in the presence of PdCl$_2$ and FeOCl gave PhNHCOOEt with 96 % selectivity [643]. Carbonylation of aliphatic amines, RNH$_2$, in the presence of [Ni(CO)$_4$] gave mainly methanamides, RNHCHO, by an unknown reaction mechanism [644].

The mechanism of the catalytic hydrogenation of carbon monoxide, the Fischer Tropsch process, has been reviewed [645]. When [Et$_2$Ni(bipy)] was used as the catalyst, 3-pentanone was a significant product [646]. Homologation of propanone using methanol in the presence of NiI$_2$/H$_2$/CO at 200 °C gave 2-pentanone as the major product with 67 % selectivity [647]

Carbonylation of the azine, 403, in the presence of [Pd(PPh$_3$)$_4$] under mild conditions (40 °C, 1 atm CO) gave the β-lactam, **404**. The mechanism proposed is shown in Scheme 16 [648]. Scheme 17 shows a carbonylation/cyclisation process in which the intermediate allyl complex cyclises by attack on the adjacent carbonyl group [649].



Scheme 16 Mechanism of azirine carbonylation in the presence of [Pd(PPh$_3$)$_4$] [648]



Scheme 17 Nickel promoted cyclisation/carbonylation in the preparation of α-methylene γ-lactones [649].

13.4 Hydrosilylation and related reactions

Although nickel complexes are not the most popular catalysts for this process, a number of alkene hydrosilylations in their presence have been reported this year. 1-Alkenes, RCH=CH$_2$, reacted with MeSiHCl$_2$ to give RCH$_2$CH$_2$SiMeCl$_2$ and RCH$_2$CH$_2$SiMeHCl in the presence of [Ni(PBu$_3$)$_2$X$_2$] or [Ni{(octyl)$_3$PO}$_2$Cl$_2$] [650]. When magnetic susceptibilities were measured during the reaction the species formed were found to be diamagnetic for the phosphine complexes and paramagnetic for the phosphine oxide containing systems. These measurements, however, shed little light on the reaction mechanism [651]. For 1-hexene the reaction was found to be more successful using the phosphine oxide derivatives [652]. Complexes, [NiL$_2$X$_2$], formed from L = Ph$_2$P(=O)CH=C=CH$_2$, Me$_2$P(=O)C≡CH and related cyclic compounds were paramagnetic, with spectroscopic and magnetic measurements indicating some coordination of the multiple bonds. They were catalysts for the hydrosilylation of 1-alkenes by MeSiHCl$_2$, but yields and selectivities were low [653]. Hydrosilylation of diallyl sulphide, **405**, with HSiCl$_3$ in the presence of [Ni(acac)$_2$]/R^{1}R$^2_2$P gave mixtures of **406**, **407** and **408**. The best yield which could be obtained for **406** was 40 %. The reaction using the nickel complex as catalyst was faster and occurred at lower temperatures than analogous processes in the presence of rhodium and platinum complexes [654]. α-Methylacrylonitrile reacted with trichlorosilane in the presence of $[Ni(PPhMe_2)_2Cl_2]$ to give $Me_2C(SiCl_3)CN$ in 70 % yield [655].

$$\underset{\underline{405}}{CH_2{=}CH{-}CH_2SCH_2{-}CH{=}CH_2} + HSiCl_3 \xrightarrow{[Ni(acac)_2]/R^1R^2_2P} \underset{\underline{406}}{Cl_3Si(CH_2)_3SCH_2CH{=}CH_2} +$$

$$\underset{\underline{407}}{Cl_3Si(CH_2)_3SCH_2CH_2CH_3} + \underset{\underline{408}}{Cl_3Si(CH_2)_3S(CH_2)_3SiCl_3}$$

Palladium complexes are rather rarely used as catalysts for simple alkene hydrosilylation and there are only two reports in this field this year. $RS(CH_2)_nCH{=}CH_2$ was not hydrosilylated by R'_3SiH in the presence of $[Pd(PhCN)_2Cl_2]/PPh_3$, instead yielding $RSSiR'_3$ and $R'_3SiSSiR'_3$ [656]. $[Pd(MDPP)_2Cl_2]$ and $[Pd(NMDPP)_2Cl_2]$ acted as catalysts for the asymmetric hydrosilylation of styrene and cyclopentadiene. Both the regioselectivity and the enantioselectivity observed were accounted for in terms of palladium π-benzyl or π-allyl intermediates [657].

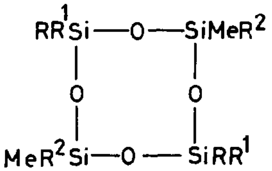
A number of patents reported the hydrosilylation of simple alkenes in the presence of platinum complexes. Examples are shown in reactions (100) and (101) [658-660]. 1-Vinylpyrroles reacted with Et_3SiH, in the presence of $H_2[PtCl_6]$, to give linear silanes with good regioselectivity, the yield being dependent on the substituents on the pyrrole ring [661].

$$ClCH_2CH{=}CH_2 + HSiCl_3 \xrightarrow[82\ \%]{[Pt(PPh_3)_3],\ 100\ ^\circ C} Cl(CH_2)_3SiCl_3 \qquad (100)$$

$$Br(CH_2)_3CH{=}CH_2 + HSiMeCl_2 \xrightarrow{H_2[PtCl_6]} Br(CH_2)_5SiMeCl_2 \qquad (101)$$

Other aryl alkenes were included in a more general study using $HSiMeR_2$, the yield of the linear silane increasing with the degree of conjugation. Competitive isomerisation of aliphatic alkenes increased with increasing catalyst concentration and increasing temperature [662]. Somewhat surprisingly, competitive isomerisation was not reported to be a problem in the conversion of $ArCH_2CH{=}CH_2$ to 3-arylpropyltrichlorosilanes, used as monomers for copolymerisation with ethyl orthosilicate [663]. A systematic study of the hydrosilylation of vinylsilanes in the presence of $H_2[PtCl_6]$ revealed that the proportion of the α-isomer formed increased with the number of electronegative groups on silicon in the vinylsilane, and with the number of methyl groups in the hydrosilylating agent, R_3SiH [664]. Hydrosilylation of divinyl sulphide with $H_2SiEt_2/H_2[PtCl_6]$ resulted in hydrogenation and cyclisation of the mono adducts, yields depending on catalyst concentration. Diallyl sulphide gave mixtures of β- and γ-adducts, with little cyclisation. This is in contrast to the rhodium catalysed reaction, in which the mono adducts reacted readily to give four, five and eight membered rings containing sulphur and silicon [665].

Platinum complexes remain important reagents for the preparation and modification of polysiloxanes by hydrosilylation. A polymer was prepared by reaction of **409** ($R = R^1 = Me$, $R^2 = H$) with **409** ($R = R^1 = Me$, $R^2 =$ vinyl) [666]. Octamethylcyclotetrasiloxane/2,4,6,8-tetramethylsiloxane copolymers were modified by treatment with acrylonitrile or α-chloro acrylonitrile in the presence of $H_2[PtCl_6]$. Some cross-linking occurred at the same time [667]. Polyorganosiloxanes were also hydrosilylated in the presence of $[Pt(PRR^1R^2)_4]/SnX_2$ [668]. A colourless liquid platinum complex was reported to be formed from $[Pt(cod)_2]$ and divinyl-1,1,3,3-tetramethyldisiloxane, and was used to catalyse the hydrosilylation of vinylsiloxanes or SiOH groups in the preparation of silicone resins and rubbers [669].

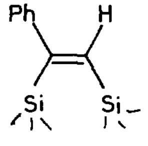


409

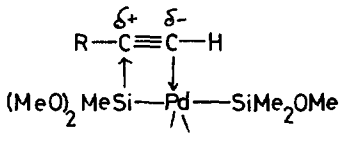
Both aminated silica and anion exchange resins have been used as supports for $H_2[PtCl_6]$ in alkene hydrosilylation. With $SiO_2-(CH_2)_3NH_2/H_2[PtCl_6]$ as catalyst for 1-hexene hydrosilylation by $HSi(OEt)_3$, the linear isomer of the product was produced in quantitative yield [670]. For allyl halides the selectivity was a little lower than in the homogeneous case [671]. A thorough study of the reaction of styrene with $HSiMeCl_2$ in the presence of various catalysts revealed that yields increased in the order $\{-Si-O-Si-(CH_2)_3NMe_3\}_2[PtCl_4]$ < $\{-Si-PPh_2PtCl_n\}$ < $[C_{16}H_{33}NMe_3]_2[PtCl_4]$ < $\{AV-17-8\}[PtCl_4]$ < $H_2[PtCl_6]$. Selectivities for the linear isomer essentially gave a reversal of this order, indicating the importance of steric effects [672]. Rates and selectivities could be correlated with steric, and to a lesser extent, electronic parameters in the substrate, in the reaction of $HSiR^1R^2X$ with 1-hexene in the presence of the anion exchanger $\{AV\text{-}17\text{-}8\}[PtCl_6]^{2-}$ [673].

Addition of Et_3SiH to $HC\equiv CCH_2NR_2$ in the presence of $H_2[PtCl_6]$ gave the expected products, $Et_3SiC(=CH_2)CH_2NR_2$ and *cis*-$Et_3SiCH=CHCH_2NR_2$, but also the unexpected species $Et_3SiCH_2CH=CHNR_2$. Data indicated that this was formed by isomerisation of $Et_3SiCH=CHCH_2NR_2$, probably *via* an allyl complex [674].

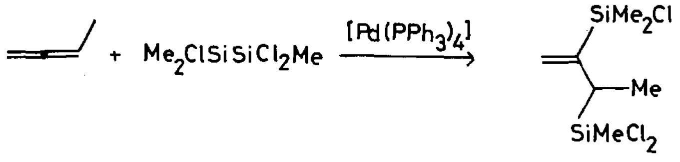
Disilanes have again proved popular reagents for silylation. Reaction of $(MeO)_nMe_{3-n}SiSiMe_{3-m}(OMe)_m$ (m,n = 1 or 2) with phenylethyne in the presence of $[Pd(PPh_3)_4]$ gave **410** with good Z-stereoselectivity and good regioselection. The regioselectivity was readily explained in terms of the electronic demands of a transition state such as **411** [675]. Disilanes reacted with allenes to give substituted 1-alkenes, **412**, with complete regiospecificity, though the origins of this specificity are somewhat obscure [676]. 1,4-Addition to substituted dienes was also noted (reaction (102)) [677].



410



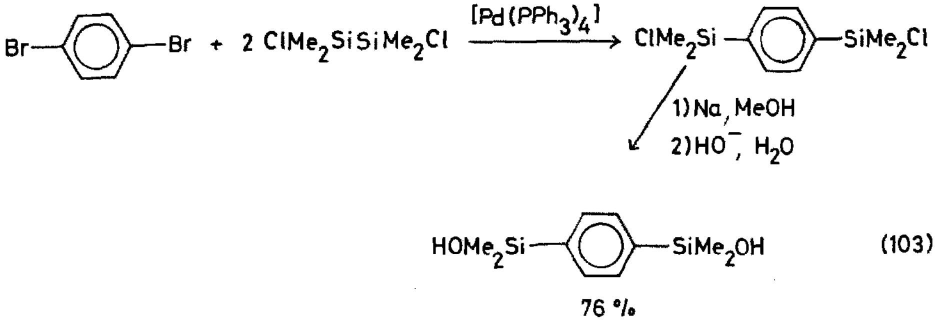
411



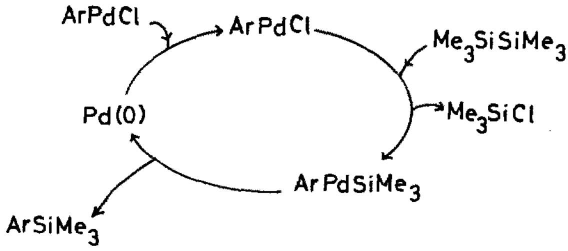
412

$$Cl_{3-n}Me_nSiSiMe_nCl_{3-n} + CH_2=CR\text{-}CR'=CH_2 \xrightarrow{[Pd(PPh_3)_4]} trans\text{-}Cl_{3-n}Me_nSiCH_2CR=CR'CH_2SiMe_nCl_{3-n} \qquad (102)$$

Disilanes have also been used as sources of silicon nucleophiles for substitution of aryl halides (reaction (103)) [678]. The postulated mechanism is shown in Scheme 18 [679].

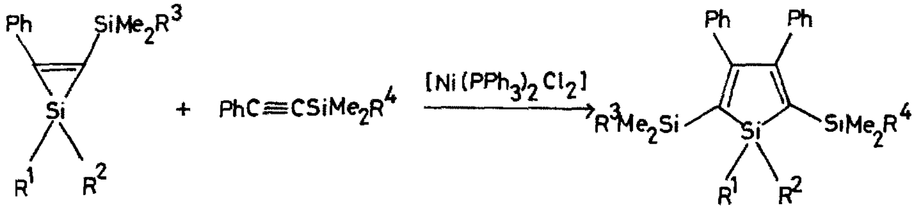


(103)

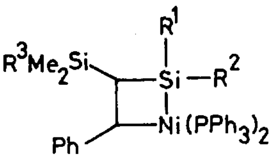


Scheme 18 Mechanism of palladium catalysed conversion of aryl halides to aryl silanes [679]

The mechanism of reaction (104) is not known, but it was postulated that the insertion of nickel into the silacyclopropene gave **413**, which then further inserted alkene [680]. Silanes, R_3SiH, reacted with R'_2BOH in the presence of $H_2[PtCl_6]$ to give $R_3SiOBR'_2$ (R = Et or Ph; R' = Bu or Ph) with elimination of molecular hydrogen [681].



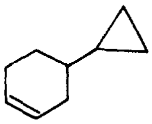
(104)



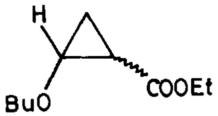
413

13.5 Other additions to carbon-carbon multiple bonds

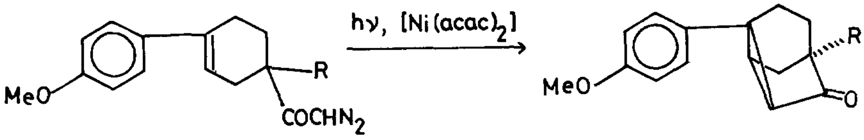
Terminal alkenes may be selectively cyclopropanated by diazomethane in the presence of Pd(OCOMe)$_2$. Thus 4-vinylcyclohexene was converted to 414 [682]. Addition of ethyl diazoethanoate to butyl vinyl ether in the presence of a variety of metal complexes, including [Pd(PPh$_3$)$_4$] and [Pd(PhCN)$_2$Cl$_2$], yielded 415. Catalytic efficiency was correlated with the ease of generation of an ylide intermediate [683]. The intramolecular reaction, (105), occurred on photolysis in the presence of [Ni(acac)$_2$] [684].



414

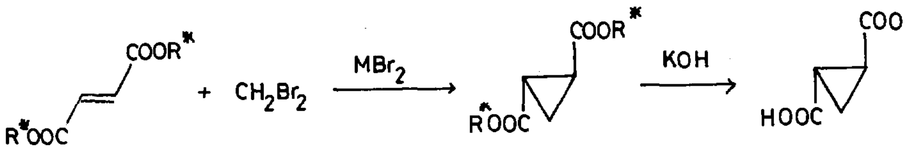


415



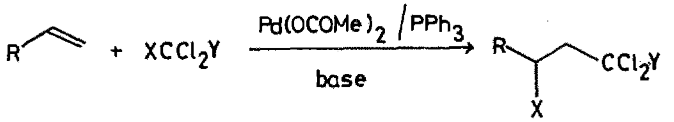
(105)

Enantioselective cyclopropanation of chiral fumarates by CH$_2$Br$_2$ (reaction (106); R* = menthyl or bornyl) gave up to 70 % enantiomer excess with M = Co but only 27 % with nickel bromide [685].

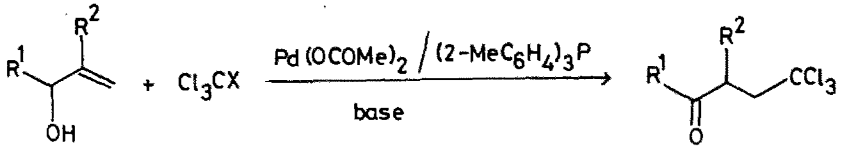


(106)

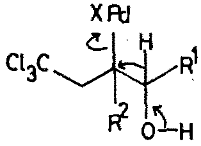
Carbohalogenation of 1-alkenes (reaction (107)) could be achieved in up to 90 % yield in the presence of $Pd(OCOMe)_2/PPh_3$/base (X = Cl or Br; Y = Cl or COOMe) [686]. If the substrate was an allyl alcohol such as **416**, the major product was 417, presumably formed by a hydride shift in the intermediate, 418 [687].



(107)



416 417

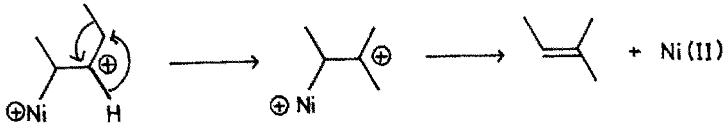


418

A study of the addition of DCN to E-1-deutero-3,3-dimethyl-1-butene in the presence of $[Ni\{P(OPh)_3\}_4]/P(OPh)_3$ and $ZnCl_2$ revealed that addition was >90 % *cis*-stereoselective, giving the *erythro* product [688]. Hydrochlorination of ethyne occurred in the presence of Pd(II)/Hg(II), though oxidation products were also formed [689].

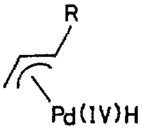
13.6 Isomerisation

Skeletal isomerisation of 1-pentene and 2-methyl-2-butene occurred over nickel sulphate on silica at 200 °C. The yields of the various isomers corresponded to their relative stabilities. A study of the reaction mechanism using ^{14}C labelled 1-pentene indicated that cations such as 419 were formed, and rearranged by known carbocation routes [690]. Isomerisation of racemic 1-alkenes in the presence of $[Ni(mesal)_2]/i\text{-}Bu_3Al$/chiral amine has been studied. The rate of reaction depended both on the alkene and on the amine, and the main products were E-2-alkenes. The reaction was thought to proceed *via* an {H-Ni} addition elimination mechanism [691].



419

The kinetics of isomerisation of 1-butene and Z-2-butene over $PdCl_2$ have been studied [692]. In the presence of $PdCl_2$ 1-heptene was converted to 2- and 3-heptenes, with E-2-heptene as the major product. The consequence of this was that in the palladium(II) catalysed oxidation of 1-heptene, 3-heptanone and 4-heptanone were produced as well as the expected 2-heptanone [693]. The scheme usually proposed for this reaction involved π-allyl palladium(IV) complexes such as **420**. Quite apart from the unfavourability of this oxidation state it was found that the reaction occurred faster in the presence of the more electrophilic complex $[Pd(MeCN)_4]^{2+}$ than with $[Pd(PhCN)_2Cl_2]$. Mechanisms such as those shown in Scheme 19 were proposed, and were supported by deuterium labelling studies [694].

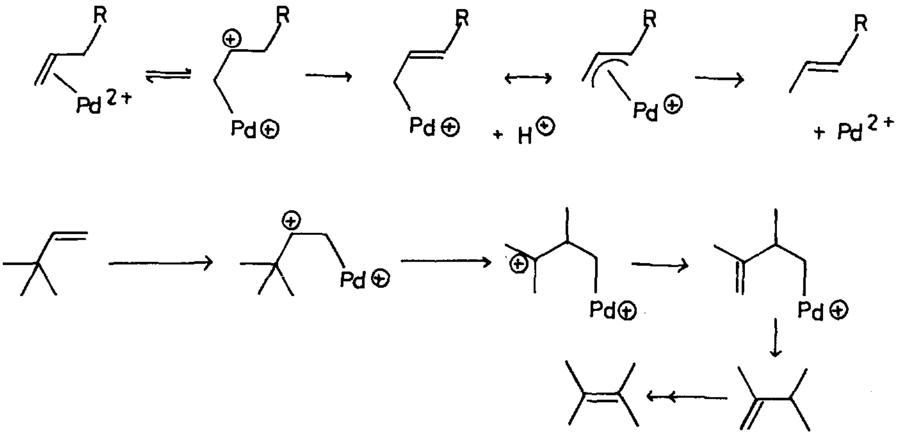


420

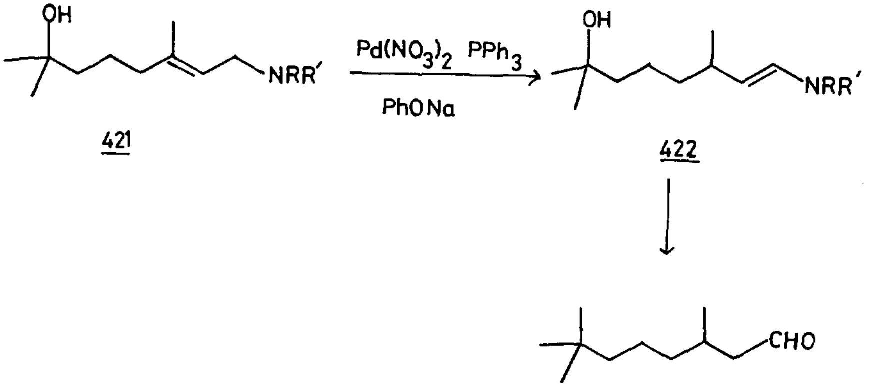
Migration of the double bond of the allylamine, **421**, yielded the enamine, 422, which was hydrolysed to hydroxy citronellal [695].

The isomerisation of 423 to 424 occurred in the presence of palladium(II) during oxidation to acrolein. The most plausible mechanism involves reversible hydroxypalladation (reaction (108)). The rate expression for isomerisation was different from that for oxidation, implying that the intermediate, 425, was not involved in the latter process [696].

The reversible formation of palladium allyl complexes is responsible for a range of isomerisations. A full paper has now described the reaction of **426**, noted last year [697]. 428, formed by isomerisation of **427**, was converted to an isoproterol derivative [698]. In the interconversion of **429** and **430** the position of the equilibrium depended critically on the nature of the substituent. For $R^3 = C_6H_{13}$, $R^1 = R^2 = R^3 = H$, the equilibrium was almost evenly balanced, but 431 was converted to 432 in quantitative yield [699].

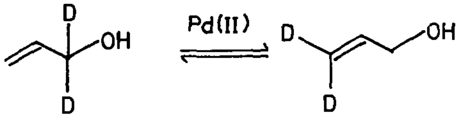


Scheme 19 Mechanism of palladium catalysed alkene isomerisation [694]



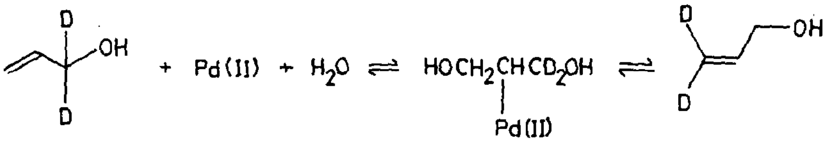
421

422



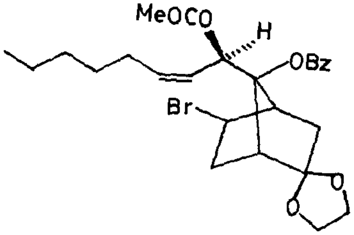
423

424

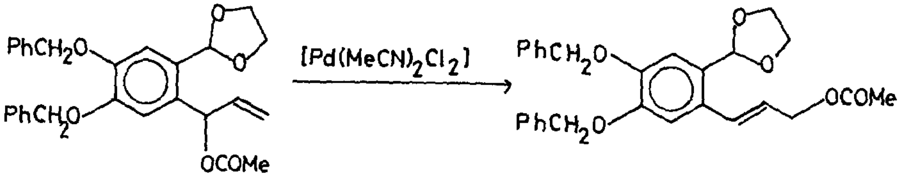


(108)

425

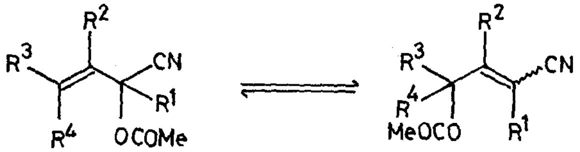


426



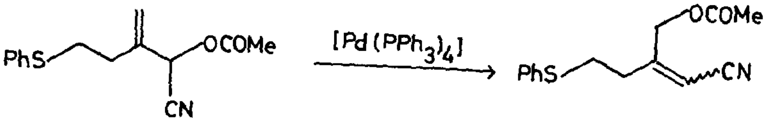
427

428



429

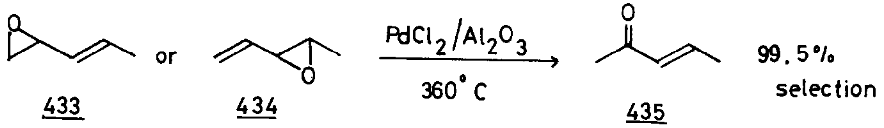
430



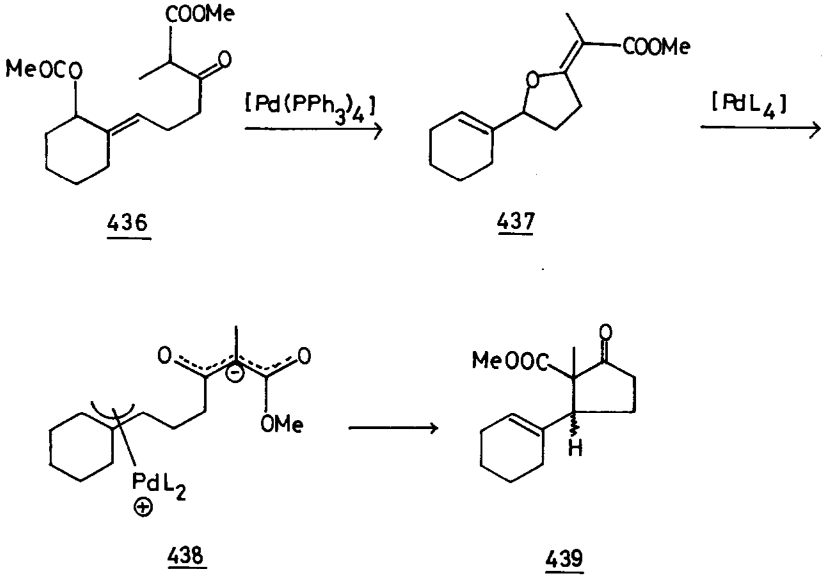
431

432

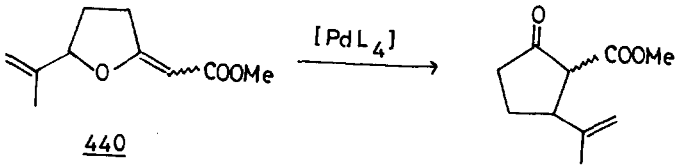
The oxygen atom of an epoxide is also known to be able to act as a leaving group in such processes, and both **433** and **434** were converted to **435** with high selectivity in the presence of $PdCl_2/Al_2O_3$, though the reaction mechanism was not studied [700]. $[Pd(PPh_3)_4]$/dppe has also ben used as a catalyst [701].



The opening of five-membered rings is similarly facile and **437**, formed by the stereoelectronically favoured closure of **436**, was reopened to **438**. **438** closed to the thermodynamic product, **439** [702]. In the conversion of **440** to **441**, the intermediate *syn*-allyl, **442a**, may be interconverted with the *anti*-isomer, **442b**, the degree to which this competes with cyclisation depending on steric hindrance [703]. In some cases cyclisation of the *anti*-allyl to give a cycloheptenone derivative occurred to a small extent. Appropriately substituted cyclopentanones produced by this method have been used in the synthesis of steroids, prostaglandins and carbohydrates [704].

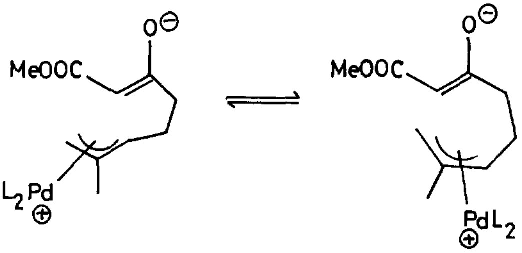


A patent has reported the *O,S*-migration of reaction (109); this probably occurred *via* an allyl derivative but the mechanism was not discussed [705]. Deprotection of allyl esters by palladium catalysed isomerisation and hydrolysis of the resulting enol ester has been further discussed [706].



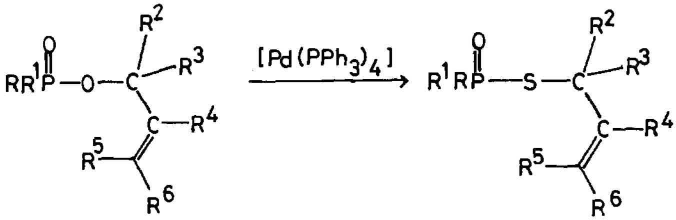
440

441



442a

442b

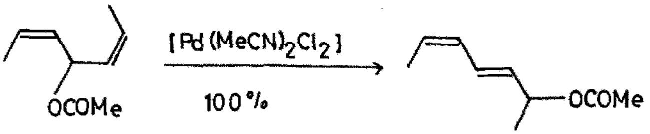


(109)

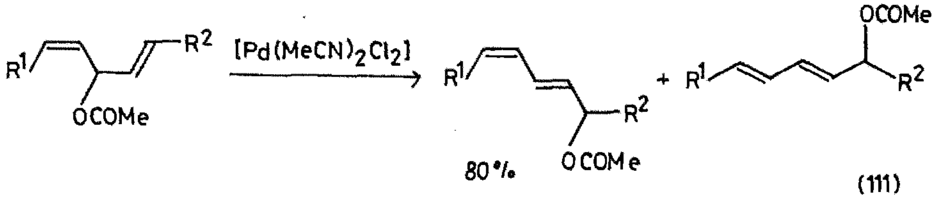
Rearrangements of allyl derivatives in the presence of palladium(II) do not in general proceed *via* η^3-allyl intermediates. For example, reactions (110) and (111) probably proceed *via* an acetoxonium ion, and their stereochemical course was found to be quite different from that reported for palladium(0). Reaction occurred preferentially at **E**-double bonds and had good selectivity for E-products [707]. Palladium(II) was also a useful catalyst for the 1,3-alkyl migration of 1-alkenyl ethyl acetals, **443**, but little or no reaction occurred in the presence of palladium(0) [708].

S-Allylthioimidates underwent *S*-*C* allyl migration on thermolysis, but *S*-*N* migration occurred in the presence of palladium(II) (reaction (112)).

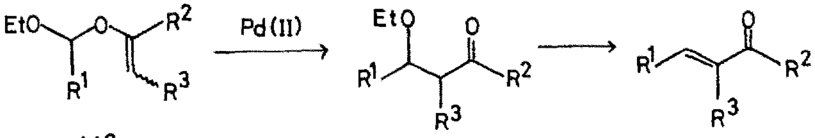
Although the mechanism was not specifically discussed in this case, it may be assumed, as previously suggested, to involve a six-membered ring cationic intermediate rather than a π-allyl complex [709].



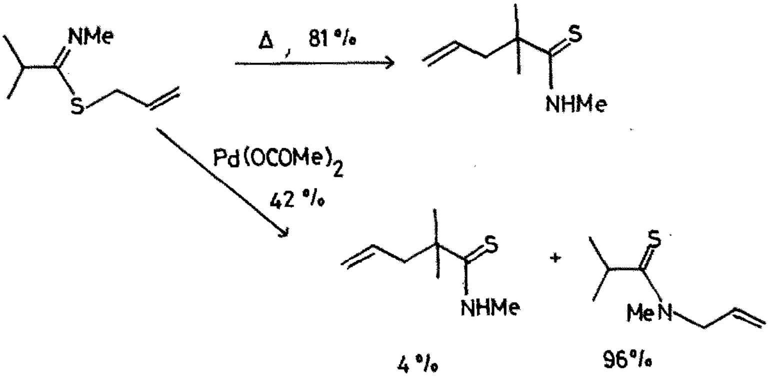
(110)



(111)



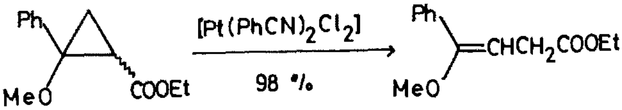
443



(112)

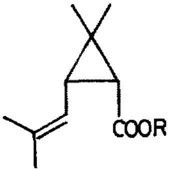
Two phase catalysis using $[MX_n]^{m-}/[R_4N]^+$ has been used for the isomerisation of allyl benzene and allyl alcohols which are insoluble in water. The use of $PdCl_2/HCl$ gave a slow reaction, but $K_2[PtCl_4]$ and $K_2[PtCl_6]$ were inactive [710].

The ring opening of cyclopropanes and epoxides by organometallics has been reviewed [711]. **444** was opened to **445** in the presence of [Pt(PhCN)$_2$Cl$_2$]. The ring substituents were necessary for activation [712]. **446** was converted to its *trans*-isomer at room temperature in the presence of [Pd(RCN)$_2$Cl$_2$], by an unspecified mechanism [713].



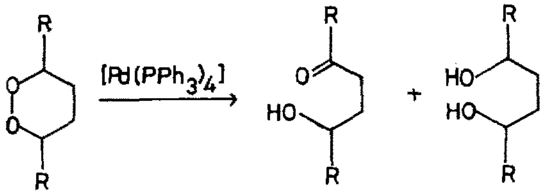
444

445



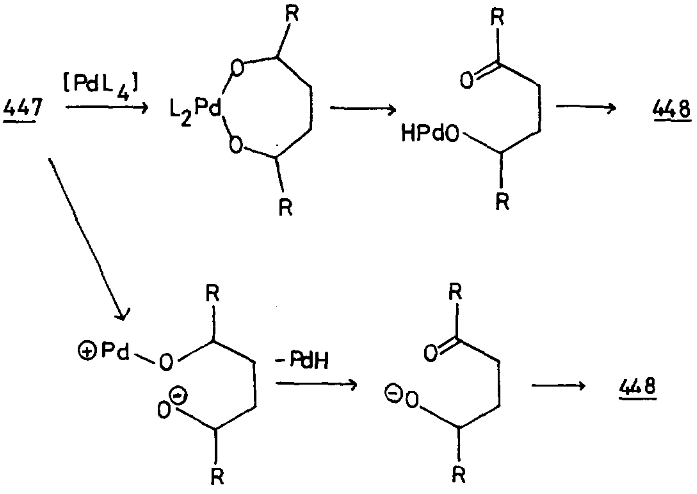
446

Three papers have reported palladium catalysed isomerisation of cyclic peroxides. For example, **447** was converted to **448** and **449** in the presence of [Pd(PPh$_3$)$_4$]. Two mechanisms were proposed for the process (Scheme 20) [714]. A similar mechanism was proposed for the formation of **451**. **449**, **452** and **453** were thought to be formed by the mechanism of Scheme 21, involving palladium(0) and palladium(I) [715].

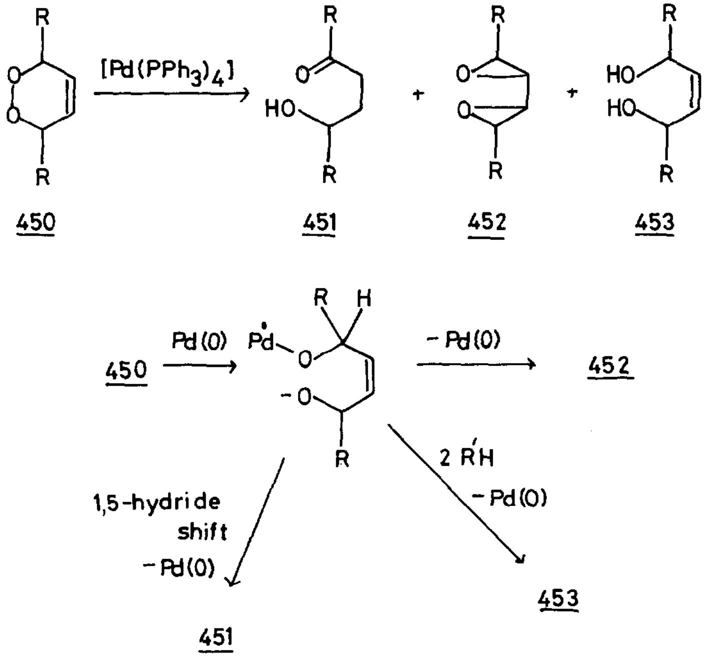


447 448 449

The rearrangement of Ph$_2$PN(Et)(Ph) to [Ph$_3$P-C$_6$H$_4$-NHEt]Br occurred in the presence of NiBr$_2$/PhBr at 200 °C over 24 hours [716].



Scheme 20 Mechanism of palladium catalysed isomerisation of cyclic peroxides [714]

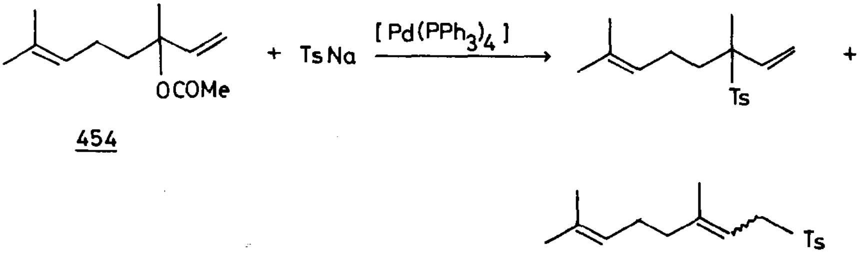


Scheme 21 Mechanism of palladium catalysed isomerisation of cyclic peroxides *via* one-electron processes [715]

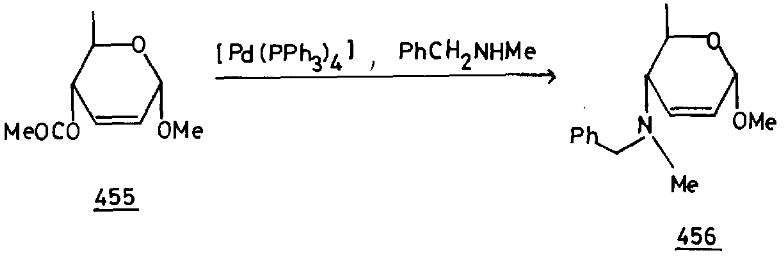
13.7 Substitution of allyl derivatives

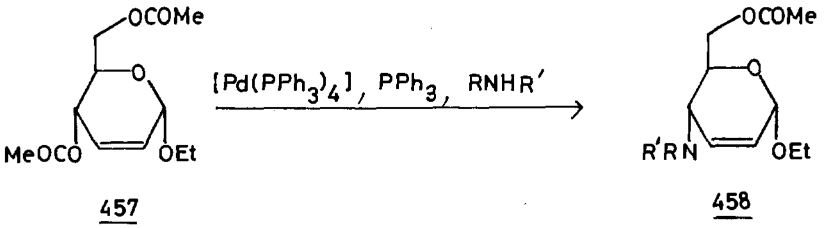
The types of selectivity which may be achieved in palladium catalysed allylic alkylation have been reviewed [717]. Reactions of organotin complexes, including those catalysed by palladium complexes, have also been discussed [718].

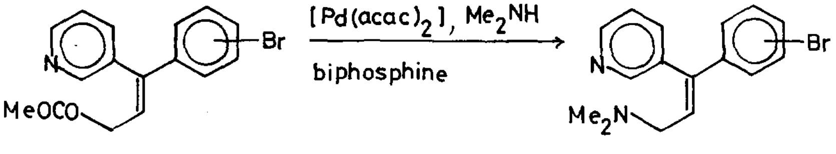
Tosylation of allyl ethanoates was achieved using TsNa and [Pd(PPh$_3$)$_4$] as the catalyst. From **454** the branched tosylate was the kinetic product and the linear species the thermodynamic product (**E**:**Z** $\sim$ 85:15) [719].



Two papers report the amination of allyl ethanoates such as **455** to give amino sugars. **456** was used in the synthesis of methyl α-D-forosaminide [720]. With **457** and R$_2$NH single isomers of the product were generally obtained (70-87 %), but primary amines gave less good results with some *O*-deacylation [721]. Substitution of doubly benzylic allyl ethanoates such as **459** was, as expected, rather facile; **460** was used in the synthesis of the anti-depressant zimelidine [722].

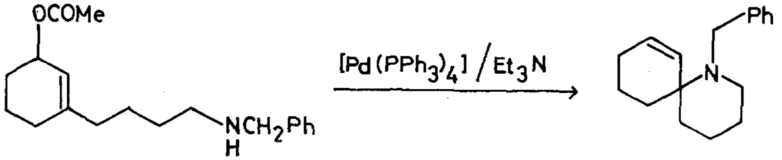






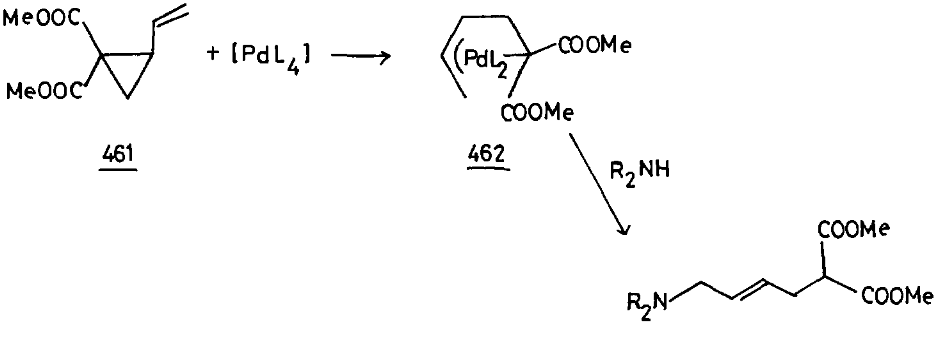
459 460

Intramolecular amination of allyl ethanoates to give spiro compounds has been reported to proceed in excellent yields (reaction (113)) [723].



(113)

Opening of **461** in the presence of [Pd(PPh$_3$)$_4$] gave **462**, and this reacted with R$_2$NH to give 463 in good yield [724].

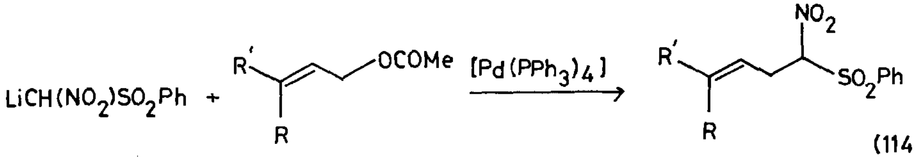


461 462 463

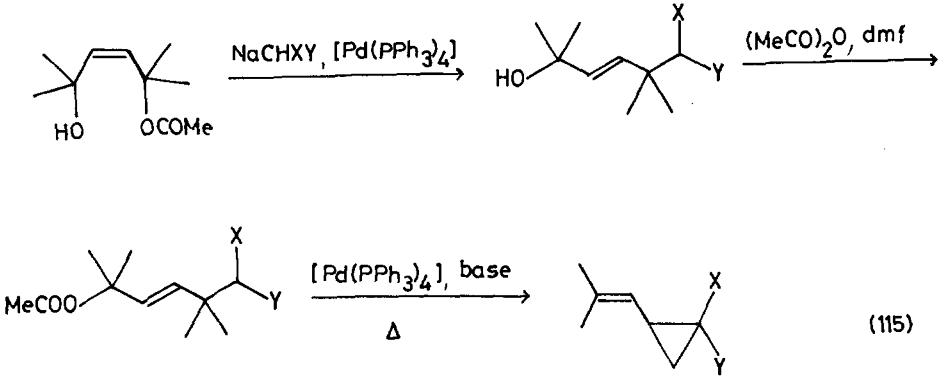
Reactions of stabilised carbanions with allyl ethanoates in the presence of palladium(0) have again been reported (reaction (114)) [725]. That ethanoate is a better leaving group than hydroxyl was demonstrated by reaction (115) (X, Y = electron withdrawing groups); in subsequent steps the hydroxyl group was acetylated and a second allylic substitution gave a cyclopropane [726]. Hydroxyl has, however, been used successfully as a leaving group; allyl alcohols reacted with the anions of β-diketonates [727] and imino esters [728], although yields in both cases were modest. In reaction (116) the nucleophile was an ylid, **464** [729].

Other leaving groups have included the oxygen atoms in lactones (reaction

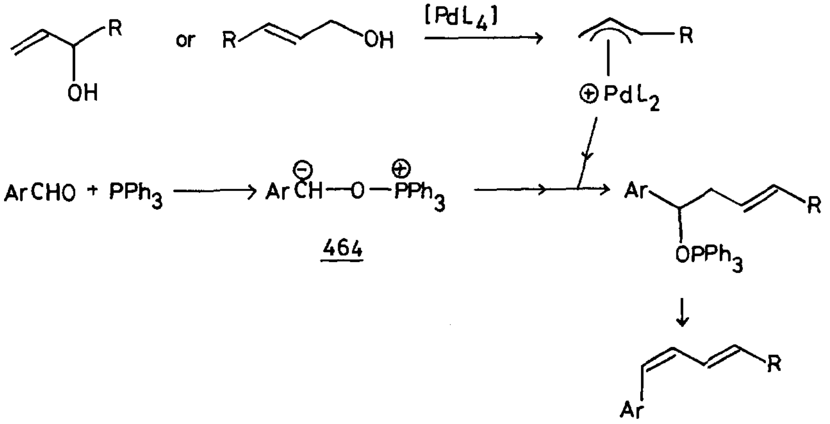
(117)) [730] and ONMe$_2$ (reaction (118)) [731]. If **465** was optically active a racemic product was obtained suggesting a symmetric π-allyl intermediate. Reactions of other nucleophiles, all proceeding an analogous manner, have involved Grignard reagents [732], RSnMe$_3$ [733] and lithium enolates [734].



(114)

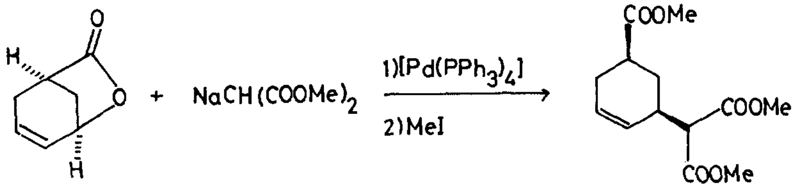


(115)



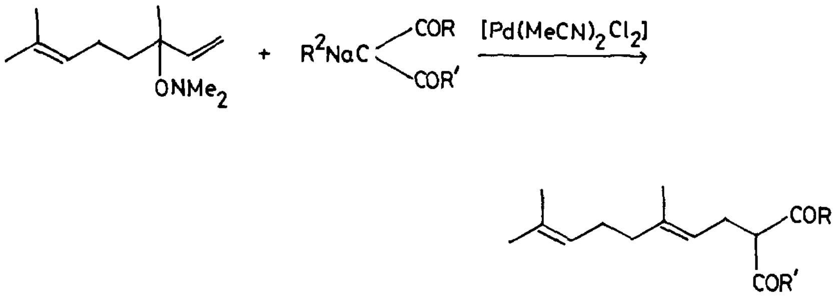
(116)

Functionalised allyl ethanoates have also proved useful substrates. The substitution of **466** by nucleophiles gave regioisomerically pure **467** as an E/Z-mixture [735]. From both **468** and **469** a range of nucleophiles gave vinyl silanes, 470, again as an E/Z-mixture [736].

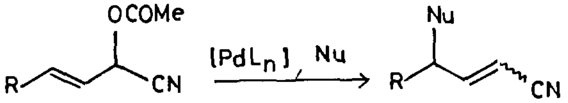


465

(117)

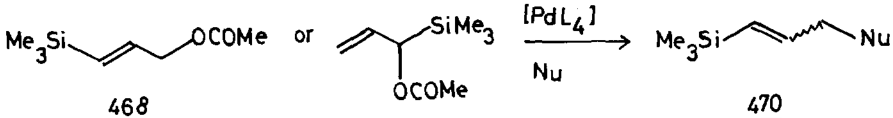


(118)



466

467

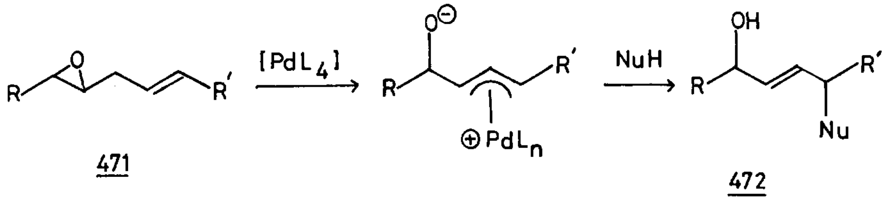


468

469

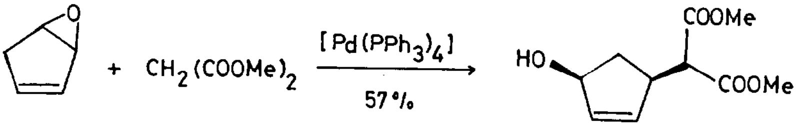
470

Allylic epoxides have also proved suitable substrates for palladium catalysed nucleophilic allylic substitution. Reaction of **471** with $[Nu]^-/[Pd(PPh_3)_4]$ generally gave only **472** ($[Nu]^- = [CH(COOEt)_2]^-$, $[CH_3COCHCOOEt]^-$ or pyrrolidine), without the need for added base [737]. Addition of the nucleophile was stereospecifically *cis*, in accord with a double inversion mechanism (reaction (119)) [738]. Lactones also acted as substrates (reaction (120)). Chirality was transferred with good efficiency in this case [739]. The intramolecular reaction (121) was used in an approach to sarkomycin [740].

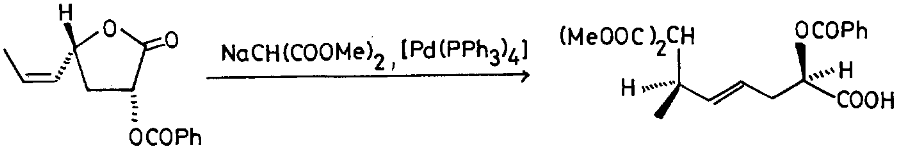


471

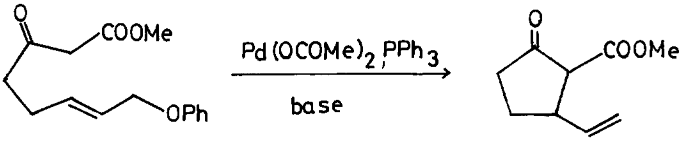
472



(119)

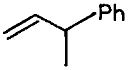


(120)

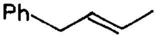


(121)

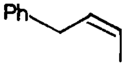
A number of harder organometallic nucleophiles have also been used with success. The reaction of PhMgBr with (+)-**S**-CH_2=CH-CH(CH_3)OH in the presence of [Ni(PPh_3)$_2$$Cl_2$], gave a mixture of the compounds **473**-**476**. **473** was formed mainly with inversion of configuration and a mechanism involving inversion of configuration in nickel allyl formation and retention in the coupling step was proposed [741]. A similar pathway was demonstrated for the reaction of 477 with MeMgI [742]. In reaction (122) it would be expected that **478** would yield initially a *syn*-nickel allyl complex, with **479** giving the *anti*-complex. The optical yield obtained in **481** was 1.2 % **S** from **478** and 14.9 % **R** from **479**, implying that *syn* ⇌ *anti* interconversion was slower than coupling [743].



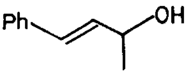
473



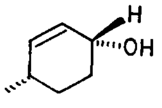
474



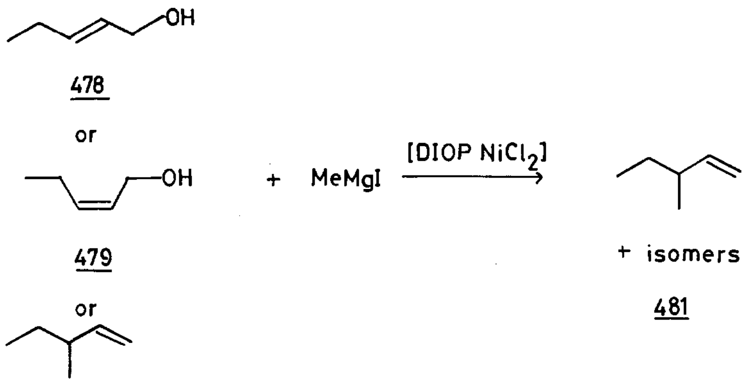
475



476



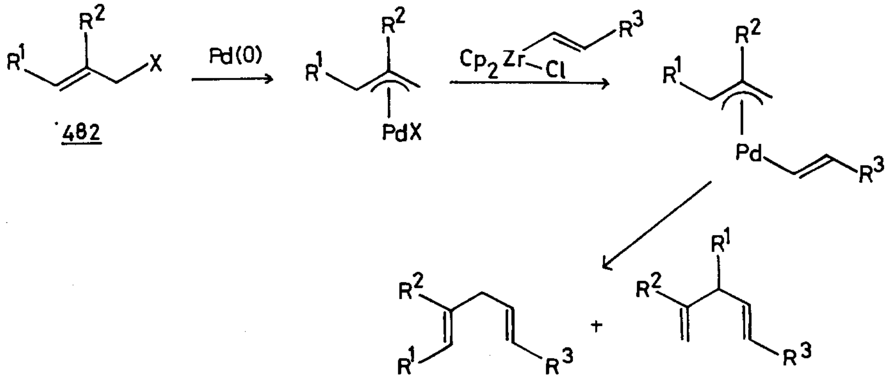
477



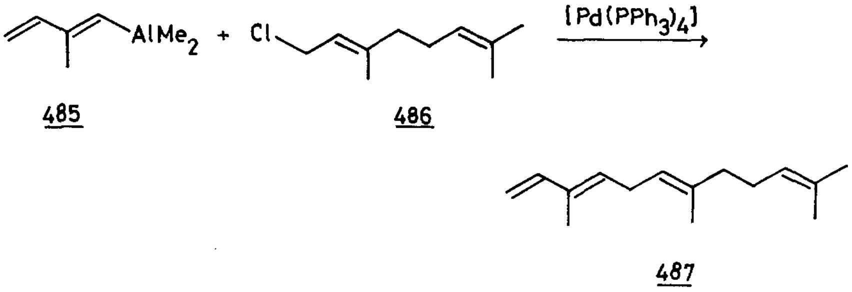
478 479 480 481

(122)

Organozirconium compounds reacted with **482** (X = Br > Cl > OCOMe) in the presence of palladium(0) to give **483** and **484**. If the ligands at palladium were phosphines attack at the more hindered terminus of the allyl was promoted, but maleic anhydride complexes gave the less hindered adduct [744]. **485**, synthesised by zirconium catalysed hydroalumination of buteneyne, reacted with the allyl halide, **486**, to give α-farnesene, **487**, in 86 % yield [745].



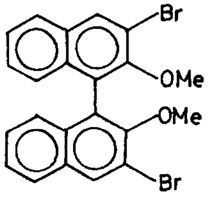
482 483 484



13.8 Coupling of organometallics with halides and related reactions

The use of bimetallic catalyst systems containing titanium or zirconium with nickel or palladium for selected organic syntheses has been reviewed [746].

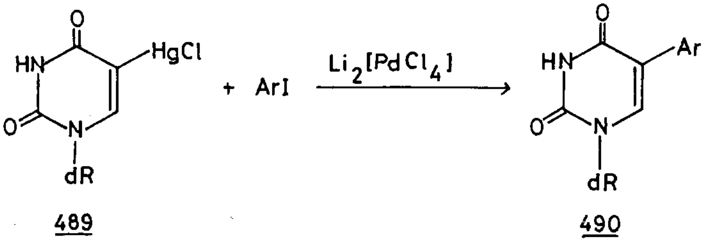
The coupling of ArMgX with aryl iodides in the presence of $[Ni(acac)_2]$ has been used for the preparation of terphenyls [747] and octiphenyls [748] for spectroscopic studies. $[Ni(PPh_3)_2Cl_2]$ was the catalyst of choice for the reaction of **488** with PhMgBr in an approach to chiral binaphthyl crown ether syntheses [749]. Homocoupling of aryl halides has again been achieved in the presence of a variety of nickel catalyst systems including $NiCl_2/Zn/PPh_3$/bipy [750] and $NiCl_2/Zn/PPh_3/NaI$/dimethylethanamide [751]. Aryl polyhalides were similarly converted to polymers [752]. Nickel(0) may be generated and regenerated electrochemically rather than with the use of zinc as a chemical reductant [753]. The mechanism of these reactions was discussed in detail by Semmelhack. His view was that the mechanism involves biarylnickel formation followed by simple reductive elimination, rather than the electron transfer path involving nickel(I) and nickel(III) favoured by Kochi's group. Many examples of the use of the reaction in synthesis were also discussed [754].

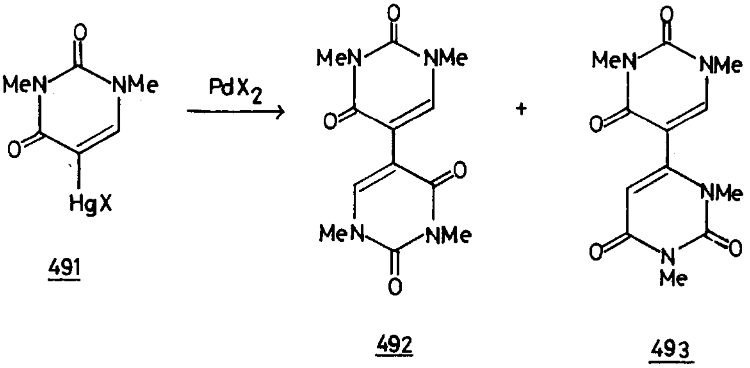


488

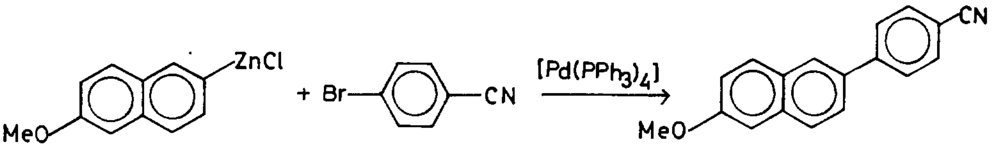
Homocoupling of aryl iodides occurred in the presence of $PdCl_2/N_2H_4/HgCl_2$ in a methanol solvent. Under these conditions the reaction was stoicheiometric and the palladium was recovered as palladium amalgam. An arylpalladium intermediate was thought to be involved [755]. Oxidative coupling of arenes occurred in the presence of $Pd(OCOMe)_2/MeCOOH/H[ClO_4]$. Kinetic studies and consideration of substituent and isotope effects suggested that formation of an arylpalladium(II) complex was the rate controlling step [756].

Diarylmercury compounds, Ar_2Hg, reacted with R'X in the presence of $[PhPd(PPh_3)_2I]/(Me_2N)_3PO/[Bu_4N]I$ to give ArR' in excellent yield. Arylmercury halides reacted more slowly and gave more homocoupled products [757]. **489** could be arylated to **490** but the reaction was not strictly catalytic [758]. **481** also reacted with alkenes in the presence of $Li_2[PdCl_4]$ to give alkenyl derivatives [759,760]. **491** underwent oxidative dimerisation using PdX_2 to give **492** and **493**, with X = Cl favouring **492** and X = OCOMe favouring **493** [761].



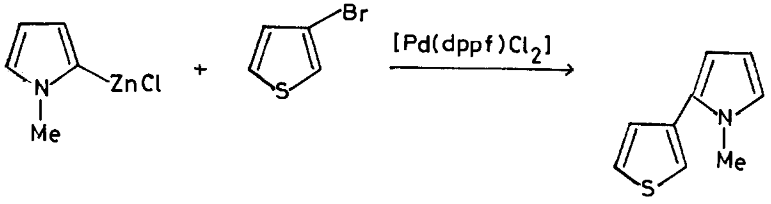


Both aryl and heteroaryl zinc halides were readily coupled with aryl halides (reactions (123) [762] and (124) [763]). **494** was used in a synthesis of liquid crystal compounds.



494

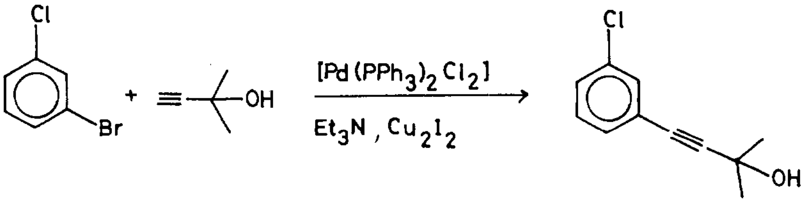
(123)



(124)

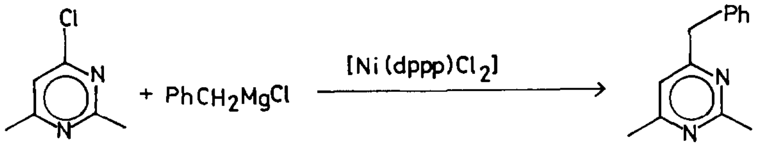
$RSnMe_3$ (R = Ph, 3-Me-C_6H_4 or Ph-C≡C-) reacted with halonitroarenes to give RAr in the presence of $[ArPd(PPh_3)_2I]$. R_2 was in all cases obtained as a by-product and for R = indenyl or fluorenyl as the sole product [764]. Bu_6Sn_2 and Me_6Sn_2 reacted with palladium halides to give $\{PdSnR_3\}$ species which coupled readily with aryl halides bearing additional electron withdrawing groups [765,766]. Benzylic halides also reacted and the aryl or benzyl tin compounds produced are valuable synthetic intermediates for cases in which Grignard or organolithium reagents are unsuitable [767].

Further couplings of 1-alkynes with aryl and heteroaryl halides in the presence of $[Pd(PPh_3)_2Cl_2]$/CuI/base have been reported [768-771]. The reaction was compatible with a free hydroxyl group and $HC{\equiv}CCMe_2OH$ has been a popular substrate [772]. Treatment of the products, $ArC{\equiv}CCMe_2OH$, with sodium hydroxide gave the unsubstituted alkyne [773]. This could also be synthesised by desilylation of $ArC{\equiv}CSiMe_3$ formed by coupling of trimethylsilylethyne [774]. That bromides were substituted more rapidly than chlorides was demonstrated by reaction (125) [775] and monosubstitution of a dibromide could also be achieved [776]. This method was also used for the synthesis of 5-alkyn-1-yl uracil [777].

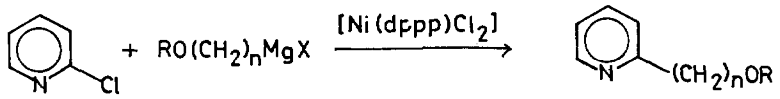


(125)

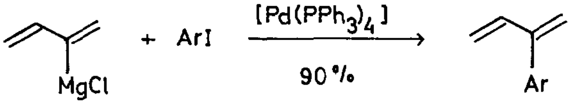
Examples of the coupling of Grignard reagents with aryl halides reported this year have included reactions (126) [778], (127) [779] and (128) [780]. Heteroaryl thioethers were also displaced (reaction (129)) [781].



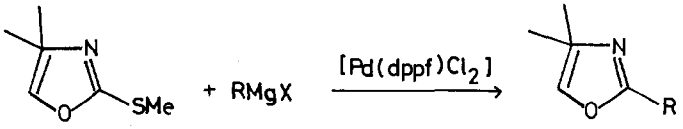
(126)



(127)

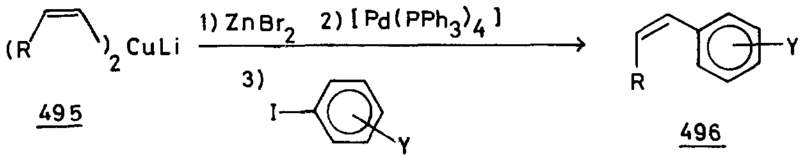


(128)



(129)

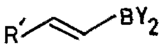
Preformed alkynyl copper compounds were coupled with ArX in the presence of [PhPd(PPh$_3$)$_2$I/hmpt/[Bu$_4$N]I to give Ph-C$\equiv$C-Ar. Without the tetraalkylammonium salt the homocoupled product, Ph-C$\equiv$C-C$\equiv$C-Ph was formed exclusively [782]. Vinyl copper compounds, **495**, reacted with aryl or heteroaryl iodides to give products such as **496** with good stereochemical purity [783].



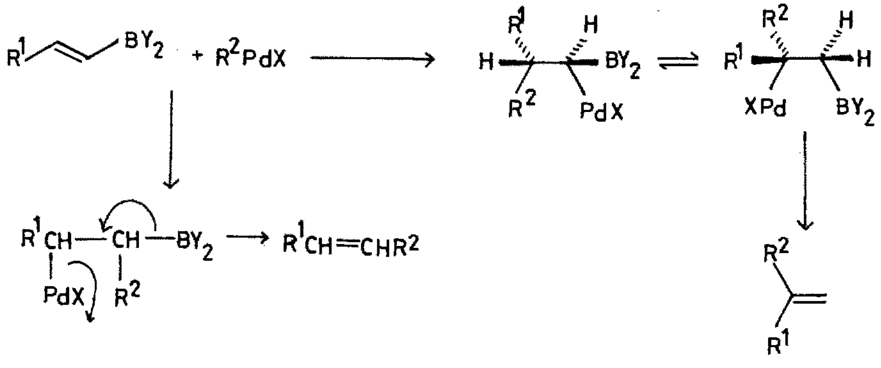
495

496

That vinyl boranes such as **497** coupled readily with ArI in the presence of [Pd(PPh$_3$)$_4$]/base has been known for some time. However, **498** could be made the major product of the reaction (R^2 = Ph or 1-alkenyl; Y_2 = benzodioxacarbonyl) when the palladium catalyst used was palladium black from Pd(OCOMe)$_2$ or [Pd(PPh$_3$)$_4$], and the base used was Et$_3$N. The proposed mechanism (Scheme 22) was in accord with the results of deuterium labelling experiments [784]. Aryl halides could also be coupled with PhB(OH)$_2$to give PhAr in modest to good yields if Na$_2$[CO$_3$] was used as the base [785].



497



498

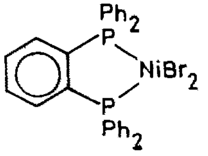
Scheme 22 Mechanism of palladium catalysed coupling of vinyl boranes with organic halides [784].

Substitution of heteroaryl halides by cyanide ion in the presence of [Pd(PPh$_4$)$_4$] has been noted [786]. Aryl halides also reacted in the presence of PdCl$_2$/PPh$_3$/18-crown-6 [787]. Me$_3$SnCN could also be used as the source of cyanide, but the yield of the catalytic reaction was low [788].

Aryl phosphonates were synthesised according to reaction (130), which is closely related to that reported last year for the vinyl derivatives. The synthesis is complementary to the Michaelis Arbusov process for the alkyl substituted case [789].

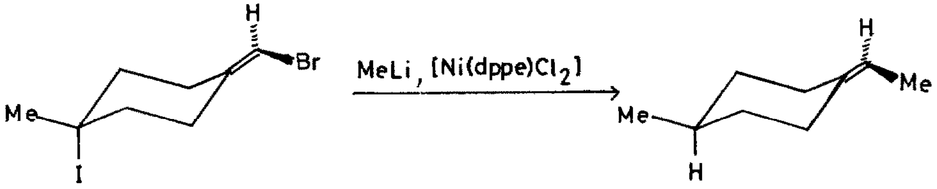
$$\mathrm{ArX} \;+\; \mathrm{H{-}P({=}O)(OR)_2} \xrightarrow[90\ \%]{[\mathrm{Pd(PPh_3)_4}]/\mathrm{Et_3N}} \mathrm{Ar{-}P({=}O)(OR)_2} \qquad (130)$$

Aryl thioethers could be prepared from ArX and $[RS]^-$ in the presence of $[ArM(PPh_3)_2X']$/onium salts/M'OH (M = Ni or Pd; X = Br or I; X' = Cl or Br; M' = Na or K). Haloalkenes were also reactive [790] and **499** could also be used as a catalyst [791]. Aryl ethanoates were prepared from $ArTl(OCOCF_3)_2$] and ethanoic acid in the presence of $PdCl_2$ [792].



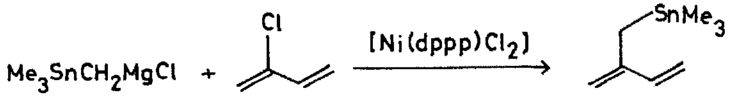
499

Substitution reactions of vinyl halides, catalysed by nickel or palladium complexes, have continued to be applied widely in synthesis. The substitution of 500 by methyl lithium with at least 95 % retention of stereochemistry is readily accommodated by the usual oxidative addition reductive elimination mechanism [793].

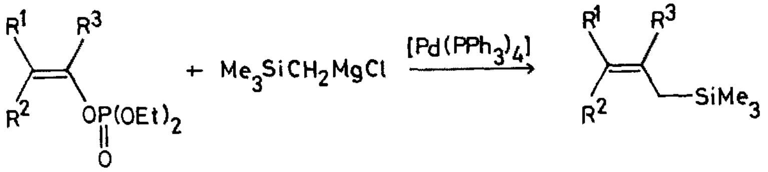


500

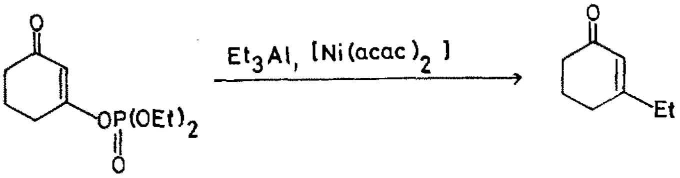
A number of reactions of Grignard reagents have been reported both with vinyl halides (reaction (131) [794]) and other vinyl derivatives (reactions (132) [795], (133) [796] and (134) [797]). $ArOPO(OEt)_2$ could be substituted by RMgX, Et_3Al or $BuCH{=}CHAl\textit{i}\text{-}Bu_2$ in the presence of $[Ni(acac)_2]$ or $[Ni(dppp)Cl_2]$ [798]. In reaction (135) the alkynyl Grignard was formed *in situ* and the product used in a synthesis of the pheromone of the red bollworm moth [799]. The chemospecificity and stereospecificity of reaction (136) was used in the synthesis of the sex pheromone of ***Lobesia botrana*** [800].



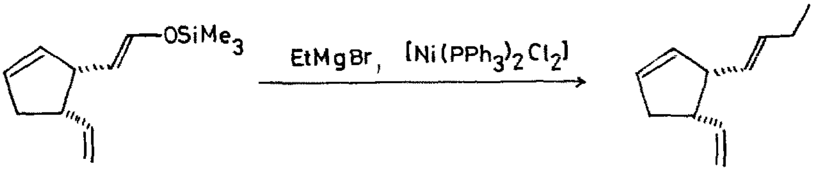
(131)



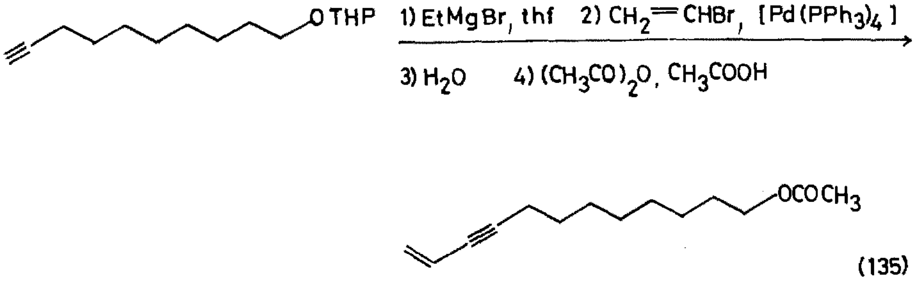
(132)



(133)



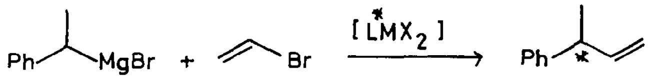
(134)



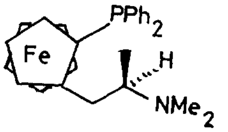
(135)

(136)

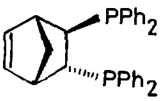
Enantioselective coupling of Grignard reagents in the presence of aminoferrocenyl phosphine nickel complexes has been reviewed [801]. The "classic" reaction of asymmetric Grignard coupling, (137), has been achieved in 88 % optical yield in the presence of **R,R-501**/$NiCl_2$ [802] and 67 % in the presence of **502**/$NiCl_2$ [803]. Using (*)-**503** as the Grignard reagent and **504**/$NiCl_2$ as the catalyst system, kinetic resolutions were modest [804].



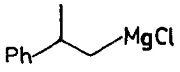
(137)



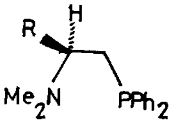
501



502

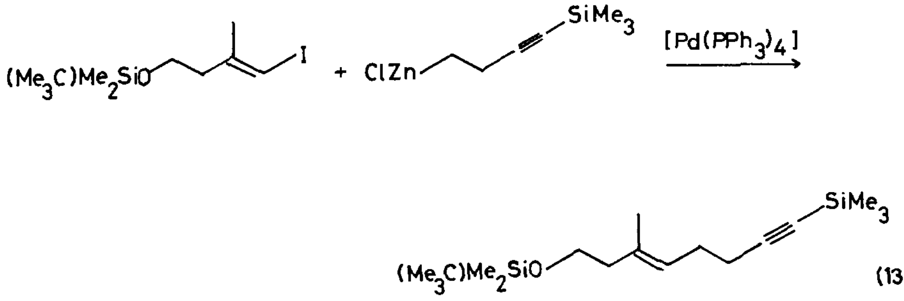


503



504

Organozinc compounds have again been useful reagents for coupling with vinyl halides in the presence of palladium(0) or nickel(0) catalysts (reactions (138) [805], (139) [806] and (140) [807]).

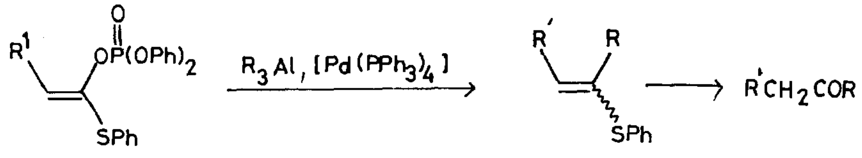


(138)

$$RCH{=}CHBr \ + \ BrZnCH_2COOEt \xrightarrow{[ML_4]} RCH{=}CHCH_2COOEt \qquad (139)$$

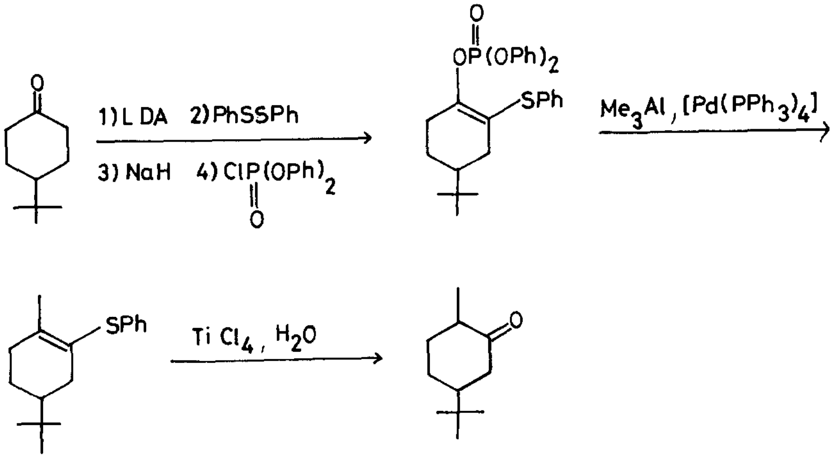
$$RR'C{=}C{=}CHX \text{ or } RR'C(X){-}C{\equiv}CH \ + \ R''ZnCl \xrightarrow[80\text{-}95\ \%]{[Pd(PPh_3)_4]} RR'C{=}C{=}CHR'' \qquad (140)$$

The reaction of organoaluminium compounds with **505** allowed the preparation of **506**, since the phosphate was preferentially displaced. **506** could be converted to R'CH_2COR. Thus the 1,2-carbonyl transposition, with methyl addition, of Scheme 23 was achieved [808].



505

506



Scheme 23 Alkylation and carbonyl transposition of ketones [808]

Organocopper compounds, formed *in situ* from 1-alkynes, were also coupled with vinyl halides, with good stereospecificity, one of the products being used in a synthesis of the sex pheromone of the Egyptian cotton leafworm [809].

Vinyl boranes were coupled with both alkenyl and alkynyl halides in the presence of [Pd(PPh$_3$)$_4$], the products again having been useful in pheromone synthesis [810,811].

Allyl derivatives, CH_2=$CHCH_2X$, have been substituted by E-BuC(Me)=CHAlMe$_2$ in the presence of palladium(0) with rates which depended on X (X = Cl > OCOMe > OAlMe$_2$ > OPO(OEt)$_2$ > OSiMe$_3$ > OSiMe$_2$(CMe$_3$)) [812]. Allyl halides have also been substituted by **489**, but the reaction mechanism seems to involve addition/elimination rather than a π-allyl intermediate [813]. The substitution of allyl alcohols was catalysed by $NiCl_2/Ph_2PCHRCHR'PPh_2$ [814]. Benzyl halides were similarly reactive with organometallic derivatives of zinc, magnesium and aluminium [815].

The haloborane, $[HCB_{10}H_9\text{-}(9\text{-}I)CH]$, (*sic*, unfortunately poorly described in terms of systematic nomenclature) was coupled with $RC\equiv CMgBr$ in the presence of $[Pd(PPh_3)_2Cl_2]$ to give $[HCB_{10}H_9(9\text{-}C\equiv CR)CH]$ in excellent yield [816].

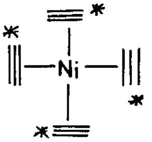
13.9 Oligomerisation, Polymerisation and Telomerisation

The rate of ethene dimerisation in the presence of $[(C_6F_5)Ni(PPh_3)_2Br]$ and $Ag[ClO_4]$ was maximised for Ag:Ni = 2, and the activity varied with the concentration of $[(C_6F_5)Ni(PPh_3)][ClO_4]$, which, it was concluded, was the active species [817]. The catalyst system $[Ni(acac)_2]/Et_2AlCl/PPh_3$ was investigated by epr and conductivity measurements and by UV spectroscopy [818]. It was noted that when this system was supported on Al_2O_3 or Al_2O_3/SiO_2, activity for ethene dimerisation was increased [819]. $[\{(\eta^3\text{-}C_3H_5)NiX\}_2]/Et_3Al_2Cl_3/Al_2O_3$ catalysed the conversion of ethene with good selectivity to a mixture of 1- and 2-butenes. 1-Butene was the primary product and isomerisation occurred *in situ* [820]. Both ethene and higher alkenes were oligomerised in the presence of $[Cp_3Ni_3(CO)_2]/SiO_2/Al_2O_3$ [821-824]. When $[Ni(CO)_4]$ and $CH_2{=}CHCH_2Cl$ were coadsorbed on Al_2O_3, a catalyst, presumed to be a nickel allyl complex, for ethene oligomerisation was obtained [825].

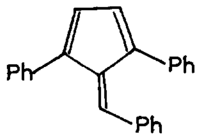
Dimerisation of a mixture of butene isomers was accomplished in the presence of $NiCl_2/EtAlCl_2$ [826]. Both dimers and higher oligomers were obtained using $BuCH(Et)COOH/CF_3COOH/Na_2[CO_3]/NiCl_2$ as the catalyst system [827]. Conversion of a mixture of ethene and propene to pentenes with 46 % selectivity was achieved using gel immobilised $[Ni(acac)_2]/i\text{-}Bu_2AlCl$ [828]. Styrene reacted with propene in the presence of $[Ni(acac)_2]/Et_2AlCl/L$ to give a mixture of $CH_2{=}CHCH_2CH(Ph)CH_3$, $CH_3CH{=}CHCH(Ph)CH_3$ and $CH_3CH(Ph)C(CH_3){=}CH_2$. Both coordination and cationic mechanisms could be proposed [829]. Polymerisation of styrene was catalysed by $[Pd(MeCN)_4]^{2+}$. Ethene was oligomerised under these conditions. That an essentially cationic mechanism operated was demonstrated by the observation that rearrangements typical of carbocations occurred under appropriate conditions [830]. The kinetics of graft polymerisation of methyl methacrylate onto chlorinated natural rubber in the presence of $[Ni\{P(OPh)_3\}_4]$ have been studied [831].

The conversions of carbazole derivatives into polymers and copolymers for photoconductors have exploited many polymerisation techniques. 3-Halocarbazole derivatives with *N*-alkenyl substituents were polymerised using $Pd(OCOMe)_2/PAr_3/R_3N$ [832,833]. *N*-Alkyl-3,6-dihalocarbazoles were copolymerised with divinylbenzene under the same conditions [834]. Treatment of dihalocarbazoles with magnesium followed by polymerisation with $[Ni(PPh_3)_2Br_2]$ gave a polymer of average molecular weight 1000 and polydispersivity 2.0 [835].

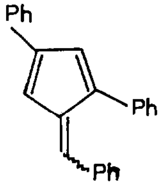
The mechanism of cyclotetramerisation of ethyne to cyclooctatetraene was investigated using ^{13}C-labelled ethyne. The best mechanism which could be proposed involved 507 and a zipper stepwise process [836]. Oligomerisation of phenylethyne in the presence of $[Pd(Al_3Cl_7)_2].2C_6H_6$ gave 508-510, the structures of which were confirmed by independent synthesis. Ethyne gave fulvene polymers [837].



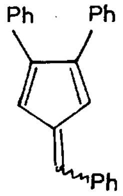
507



508

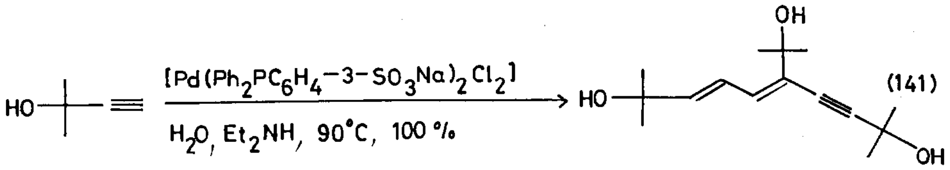


509

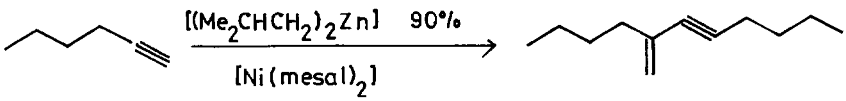


510

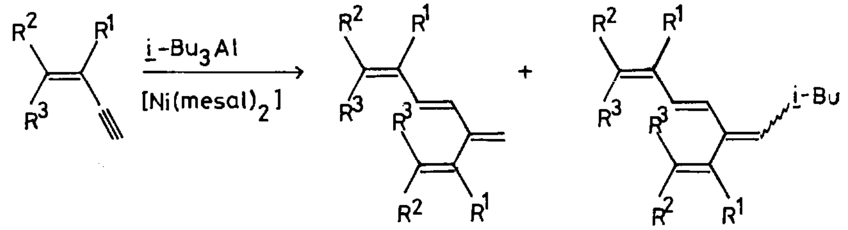
Several other oligomerisations of 1-alkynes (reactions (141)-(143)) have been noted, but their mechanisms remain a matter of speculation [838-840].



(141)



(142)



(143)

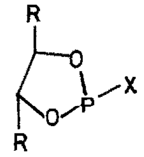
Poly(methylpropynoate) of improved homogeneity was obtained by polymerisation of methyl propynoate in the presence of $[Pd(PPh_3)_2Cl_2]$ [841]. 1,3- and 1,4-diethynylbenzene were polymerised in the presence of $[Ni(acac)_2]/PPh_3$ [842]. Copolymers of $HC\equiv C-Z^1-C\equiv CH$ and $HC\equiv C-Z^2-C\equiv CH$ (Z^1 = 1,4-phenylene, 4,4'-biphenylene and 1,4-naphthylene; Z^2 = $\{M(PBu_3)_2\}$, M = Ni, Pd or Pt) were prepared in the presence of $Cu_2Cl_2/Et_2NH/[Pt(PR_3)_2Cl_2]$ [843].

The system $[Ni(acac)_2]/C_3H_4/i\text{-}Bu_3Al$ was a catalyst for allene polymerisation. ^1H nmr and epr spectroscopic studies at low temperature allowed the identification of two types of nickel(I) complexes, which differed by the coordination of an additional allene ligand [844].

The control of nickel catalysed butadiene oligomerisation has been reviewed [845]. A number of patents have reported butadiene oligomerisation in the presence of nickel complexes. The system $[Ni(acac)_2]/(2\text{-}EtOC_6H_4O)_3P$, together with what is described as $Me_2CHN{:}AlH$, gave mainly cyclooctadiene [846], whilst $[Ni(acac)_2]/PPh_3/i\text{-}Bu_3Al$ gave a 61:39 mixture of cod and 4-vinylcyclohexene [847]. Using $[Ni(acac)_2]/Me_3SiOPh/Et_3Al$, the selectivity for *trans,trans,trans*-1,5,9-cyclododecatriene was 91 % [848]. Using $[Ni(cod)_2]/PPh_3$, a complex mixture of dimers was obtained [849]. Asymmetric dimerisation to 4-vinylcyclohexene occurred in the presence of $[Ni(cod)_2]/511$. This proved a better ligand than related phosphines, giving a higher yield of the desired dimer [850].

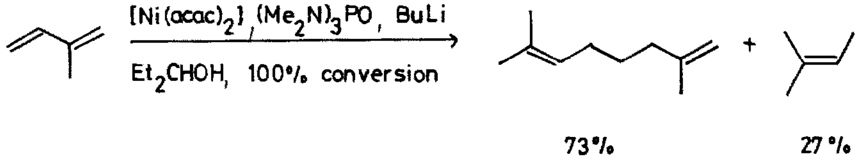
Polymerisation of butadiene occurred in the presence of $NiCl_2$ on $\gamma\text{-}Al_2O_3.MgO.MgCl_2$ [851]. $NiCl_2$ on SiO_2 with Et_2AlCl had a high activity for *cis*-polymerisation [852].

Reductive dimerisation of butadiene to give 1,7-octadiene in the presence of $[Pd(NO_3)_2(OH)_2]/\{P(CHMe_2)_3$ or $P(CMe_3)(OCHMe_2)_2\}/py/HCOOH/Et_3N$ occurred in excellent yield and selectivity [853,854].

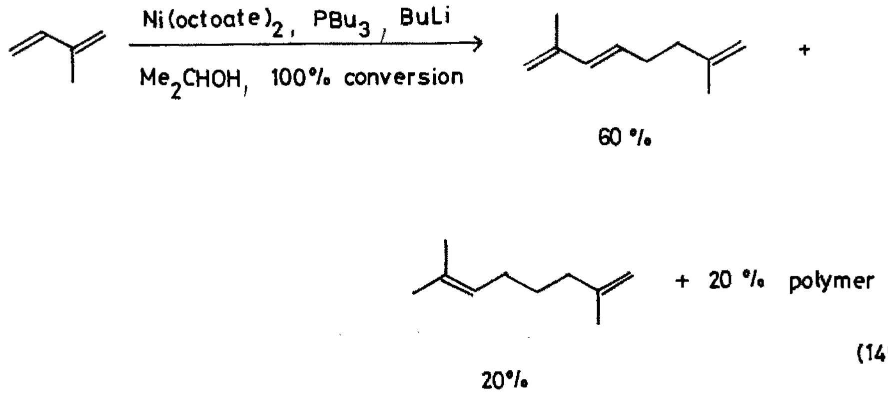


511

Linear dimers of isoprene were obtained in the presence of $[Ni(acac)_2]/BuLi/(Me_2N)_3PO/Et_2CHOH$ (reaction (144)) [855] or $Ni(octoate)_2/Bu_3P/BuLi/Me_2CHOH$ (reaction (145)) [856]. Reductive dimerisation to methylated 1,7-octadienes occurred with modest selectivities in the presence of $[Pd(acac)_2]/P(CHMe_2)_3/\{[HCOO]Na$ or $[HCOO]K\}/dmso$ [857,858].

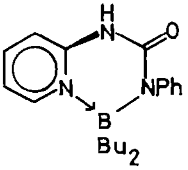


(144)



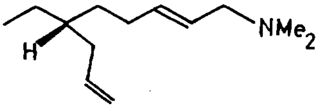
(145)

Using nickel(0) generated *in situ* from $[Ni(acac)_2]/Et_3Al$ or $[Ni(cod)_2]$ together with an appropriate phosphine, for isoprene oligomerisation gave 98 % cyclodimers. Selectivity between the various cyclodimers could be predicted by considering both the cone angle and the x value of the phosphine [859]. Good selectivity for *trans,trans,trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene was obtained in the presence of [Ni(acac)$_2$]/Et$_3$Al/**512** [860].

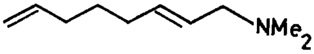


512

Codimerisation of ethene and butadiene in the presence of [Pd(PBu$_3$)$_2$Cl$_2$]/AlCl$_3$/PhNO$_2$ gave 1,5-hexadiene with good selectivity [861]. Reaction of butadiene and CH$_2$=CHCH$_2$NMe$_2$ gave **513** as the major product, together with small amounts of **514** in the presence of [Pd(PPh$_3$)$_2$Cl$_2$]/Et$_3$Al [862]. Enantioselective codimerisation of ethene and cyclohexadiene to give 4-vinylcyclohexene was achieved using [Ni(cod)$_2$]/R-Ph$_2$PNMeCH(Me)Ph [863].

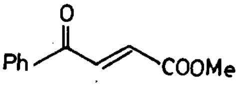


513



514

The reaction of uncomplexed **515** with butadiene was the expected Diels Alder process. However, with **516**, **517** was obtained by the mechanism of Scheme 24 [864].



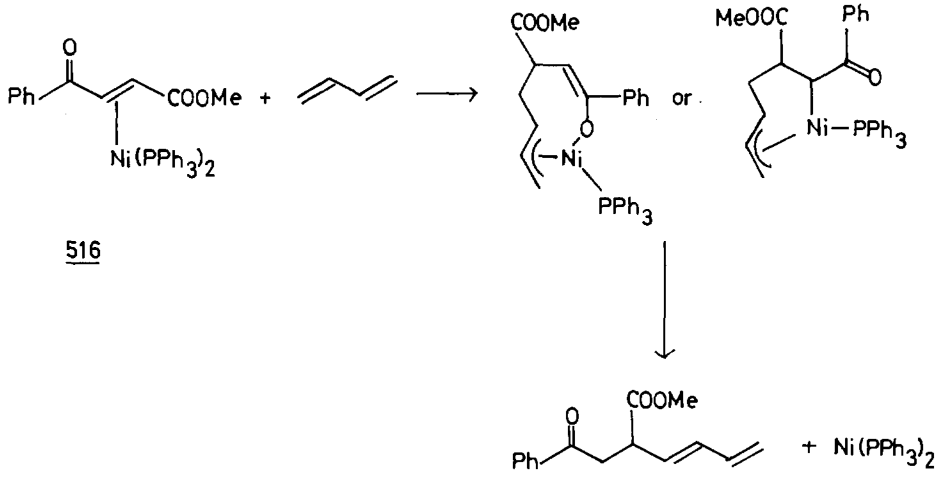
515

Cooligomerisation of butadiene and trimethylvinylsilane in the presence of NiCl$_2$/R$_3$Al/PPh$_3$ gave **518** (n = 1-5) [865]. Cyclododecatriene derivatives were produced from butadiene and styrene using [Ni(acac)$_2$]/Et$_3$Al/PPh$_3$ as the catalyst system. A conventional mechanism was proposed [866].

$CH_3(CH{=}CHCH_2)_n{-}C({=}CH_2)SiMe_3$

518

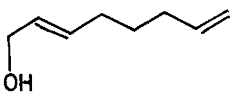
Telomerisation of butadiene with water in the presence of [Pd(acac)$_2$]/PR$_3$/R^{1}NR$^2_2$ gave mixtures of **519** and **520**. Selectivity for **519** was optimised in the presence of Et_3P, whereas PPh_3 gave the maximum yield of **520** [867]. $Pd(OCOMe)_2/H_3BO_3$ gave higher oligomers [868]. If a mixture of butadiene and isoprene was used as the substrate, nonadienols (39 %), octadienols and terpene alcohols (61 %) were obtained. All the products could be separated by gas liquid chromatography, and it was found that isoprene reacted only at its unsubstituted end [869].



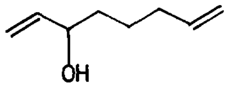
516

517

Scheme 24 Mechanism of reaction of butadiene with an enone nickel complex [864]



519



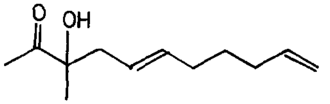
520

Telomerisation of butadiene with methanol in the presence of $[Pd_2(dba)_3]/[CH_2{=}C(CH_3)CH_2OP(NMe_2)_3][PF_6]$ gave mainly linear products, but these comprised a mixture of methoxyoctadienes, dodecatrienes and hexadecatetraenes [870]. Cyclic 1,2-diols yielded octadienyl ethers using butadiene/$[Pd(acac)_2]/PPh_3$ [871].

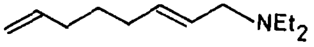
The known linear telomerisation of butadiene with ethanoic acid was used as an early step in the synthesis of dehydroxy-*trans*-resorcylide [872]. Mixtures of telomers and addition products were obtained on reaction of RSO_3H

with butadiene in the presence of $Pd(OCOMe)_2/R^1_3P/R^2_2AlCl$. The product distribution depended on the nature of R^1 and R^2 [873].

The telomerisation of butadiene with α-hydroxyketones in the presence of $PdCl_2/4\text{-}Me\text{-}C_6H_4SO_3Na$ to give products such as **521** (with up to 85 % selectivity), reported last year has been patented [874].

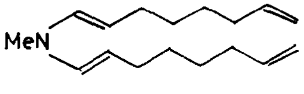


521

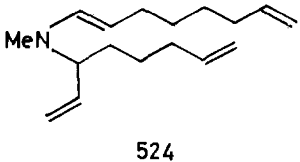


522

Further telomerisations of butadiene with secondary amines have been noted. A palladium(0) complex supported on phosphinated polystyrene gave 2:1 adducts as the major products and could be easily separated and reused with some loss of activity [875]. Complete selectivity for **522** from butadiene/Et_2NH was achieved using $[Pt(PPh_3)_2Cl_2]$/tfaH, which should be compared with 67 % using $[Pd(PPh_3)_4]$ as catalyst [876]. Reactions of primary amines have generally been less selective and this continues to be the case. The catalyst system $[Ni(cod)_2]/PBu_3/BF_3.Et_2O$ gave a mixture of **523** and **524** from $MeNH_2$/butadiene, together with monosubstituted amines [877]. The rather messy reaction of ammonia with isoprene using $[Pd(acac)_2]/P(OR)_3$ as catalyst has been analysed in detail. The product distribution was controlled by the added ligand, and tail to tail coupling of isoprene predominated [878].

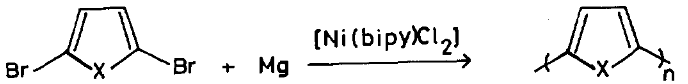


523

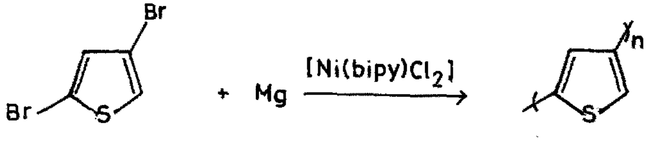


524

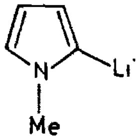
Numerous couplings of heterocycles have been reported for the first time this year. The products are of considerable importance as conducting polymers. Examples include reactions (146) (X = S [879], NPh [880] or Se [881]) and (147) [882]. **525** was oligomerised using $NiCl_2$, by a mechanism which remains undefined [883].



(146)



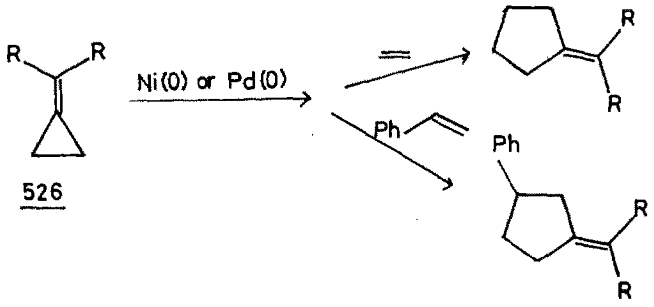
(147)



525

Oxidative coupling of dimethyl phthalate gave 3,4,3',4'- and 2,3,3',3'-substituted biphenyls in the ratio 10:1 in the presence of $Pd(OCOMe)_2$/phen [884].

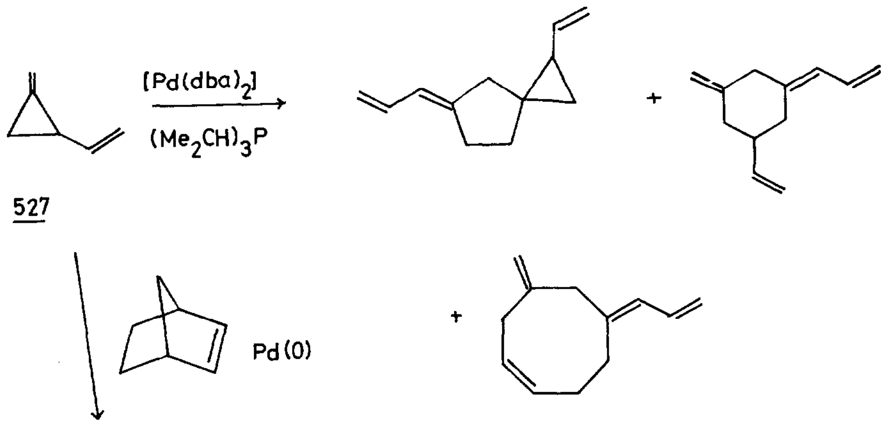
There has been continued work in the study of the catalysed reactions of very strained alkenes such as methylene cyclopropenes. Codimerisation of **526** occurred in the presence of nickel(0) (40-60 °C) or palladium(0) (80-100 °C) [885]. **527** reacted with strained alkenes such as norbornene using palladium(0) as catalyst to give both annelated products and dimers [886]. Cyclodimerisation and oligomerisation of 528 has also been noted [887].

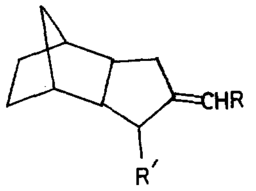


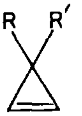
526

13.10 *Miscellaneous coupling reactions*

The coupling reaction (148) was in fact a palladium catalysed substitution of an acyl halide, involving $ArCH_2ZnBr$ and {RCOPdCl} as intermediates [888]. The hydroxypyridine group in **529** was also an excellent leaving group (reaction (149)) [889]. Alkynyl copper compounds were supposed to be formed *in situ* in reaction (150) [890].





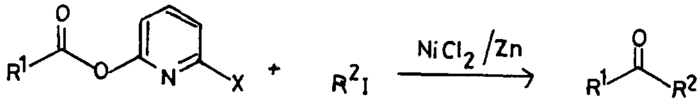


528

R = H R' = vinyl and/or

R = vinyl R' = H

$$PhCH_2Br + RCOCl \xrightarrow[83\ \%]{Zn/[Pd(PPh_3)_2Cl_2]} PhCH_2COR \qquad (148)$$

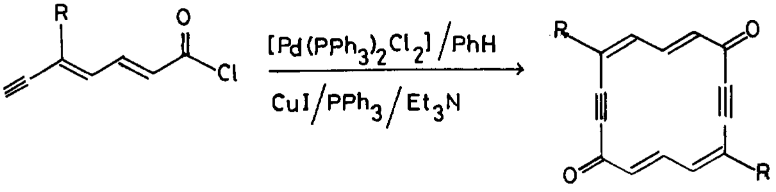


(149)

529

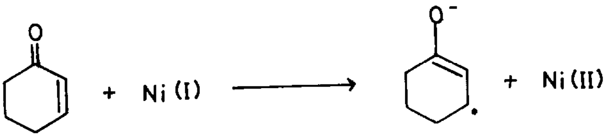
The reactions of ArHgX with enones were catalysed by palladium(II) *via* arylpalladium intermediates. The only unsuitable aryl groups were found to be those bearing strongly electron withdrawing functionalities [891].

The reaction of $R_2CHSZr(Cl)Cp_2$ with methyl vinyl ketone in the presence of [Ni(acac)$_2$] yielded $R_2CHSCH_2CH_2COCH_3$ [892]. Alkynyl alanes behaved as nucleophiles towards cyclopentenones using the [Ni(acac)$_2$]/dibaH catalyst system in a synthesis of 11-deoxyprostaglandin [893]. A study of the reaction mechanism indicated that the steps of reactions (151)-(155) were important [894].



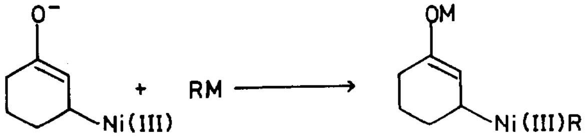
(150)

$$[Ni(acac)_2] \xrightarrow{\text{dibaH}} \{Ni(I)(acac)\} \qquad (151)$$



(152)

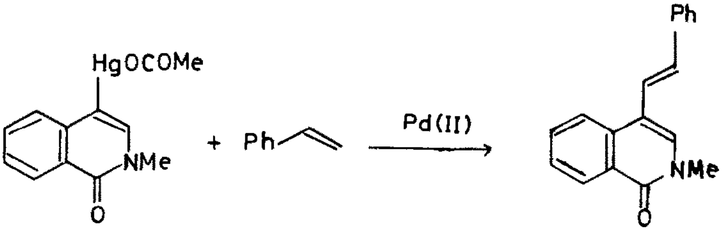
(153)



(154)

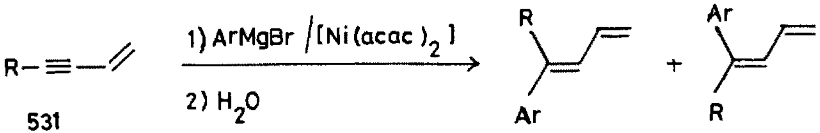
(155)

Coupling reactions forming new bonds between arenes and alkenes have again been numerous and varied. The reaction of $PhHgOCOCF_3$ or Ph_4Sn or Ph_4Sb with acrylic acid in the presence of $H_2[PtCl_6]$ yielded 3-phenylpropenoic acid in respectively 15, 86 an 30 % yield. The intermediate involved was thought to be $[ArPtCl_4]^-$ [895]. An analogous reaction was achieved using **530** [896]. Carbon nitrogen double bonds were also reactive (reaction (156)), but this process was barely catalytic in palladium [897]. With the enyne, **531**, as substrate, reaction with Grignards using $[Ni(acac)_2]$ occurred preferentially at the alkyne to give mixtures of 532 and 533 as well as biaryls [898].



530

$$PhHgCl + CH_2{=}NOH \xrightarrow{Li[PdCl_3]} PhCH{=}NOH \qquad (156)$$



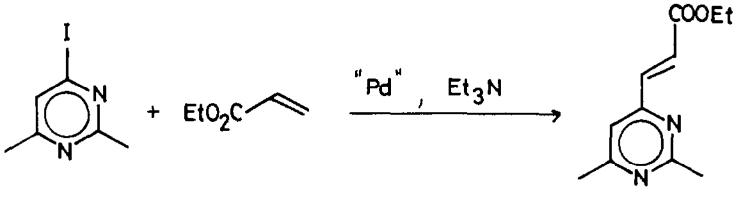
531

532

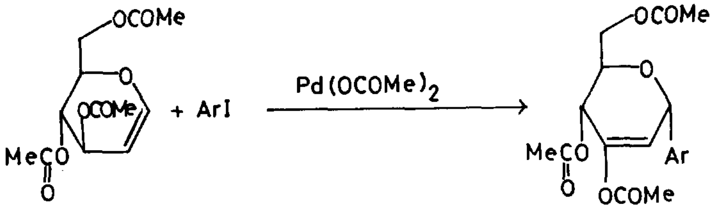
533

The couplings between alkenes and aryl halides proceeded in most cases *via* initial oxidative addition of the aryl halide to a palladium complex. The heteroaryl halide, **534**, was readily coupled with ethyl acrylate, although the yield was best (77 %) using palladium black rather than a defined complex as the catalyst [899].

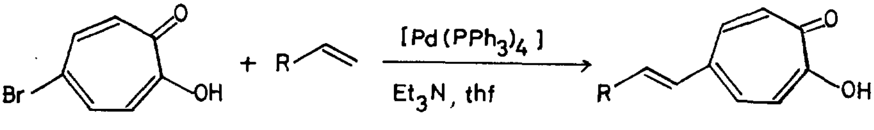
Arylation of fluorinated alkenes, $CF_3CH{=}CH_2$ or $C_6F_5CH{=}CH_2$, by $ArX/PdCl_2$ or $Pd(OCOMe)_2/PPh_3$ was achieved in good yield [900]. The analogous reaction of **535** gave access to 2'-deoxy-*C*-nucleoside precursors [901]. The arenes used have included the tropolone derivative, **536**, [902] and the substituted alkenes have included **537** [903] and $CH_2{=}CHOMe$ (reaction (157) [904]).



534



535

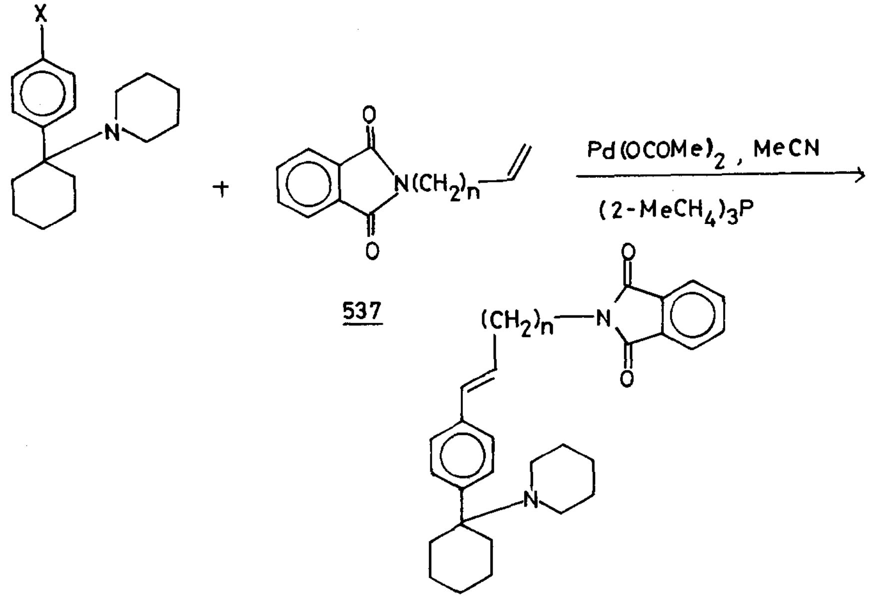


536

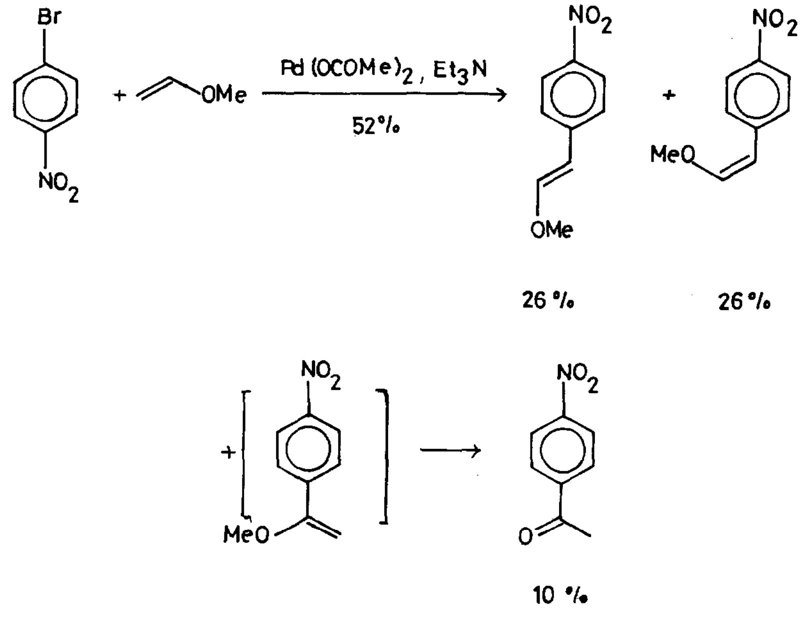
The reactions of allyl alcohols, such as (158), generally gave ketones, since isomerisation occurred after coupling [905]. A modest transfer of chirality was observed in reaction (159); the catalyst interacted preferentially with the *si*-face of the alkene in **538** and the phenyl group was transferred with retention [906]. Allyl silyl ethers also gave ketones in coupling with acyl halides; the proposed mechanism is shown in Scheme 25 [907].

Aryl diazonium salts were readily coupled with alkenes (for example, reactions (160) [908] and (161) [909]) by closely related mechanisms.

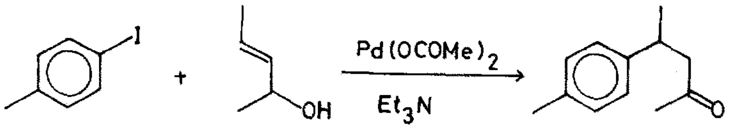
Coupling of benzene with propene in the presence of [$Cp_3Ni_3(CO)_2$]/SiO_2/Al_2O_3 gave mono (26.5 %) and bis(1-methylethyl)benzenes (37 %), by an undefined mechanism [910]. Reaction of 1-alkenes with heterocycles in the presence of Pd(OCOMe)$_2$/air gave species such as **539** and **540** *via* an arylpalladium species and an arylpalladation followed by a dehydropalladation [911]. That indoles react similarly was best exemplified by the intramolecular reaction of **541** to give (±)-epi-ibogamine, albeit in very modest yield [912,913]. The reactions of the metallated heterocycle, 542, were closely related [914].



537

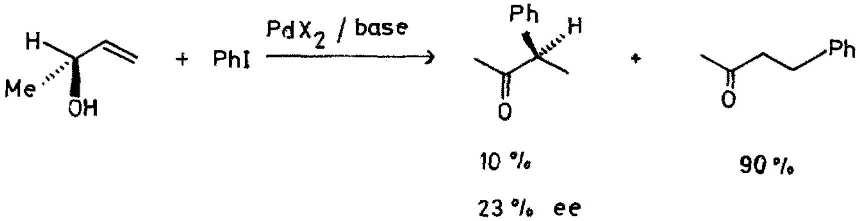


(157)

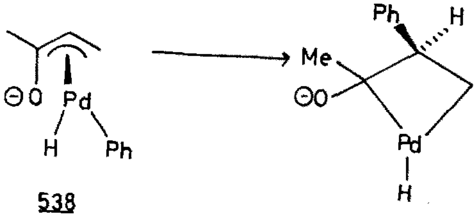


curcumone

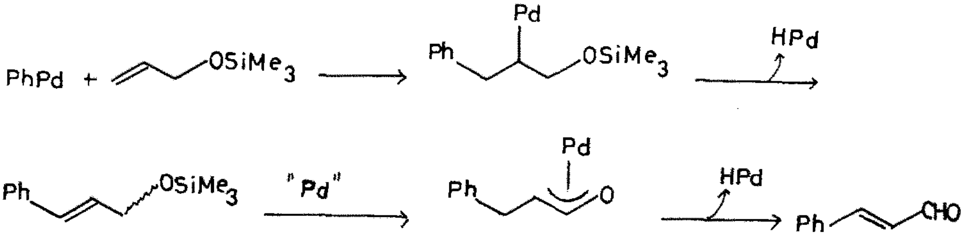
(158)



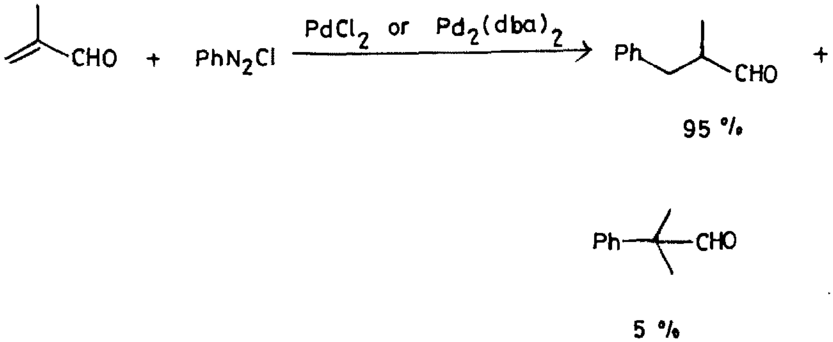
(159)



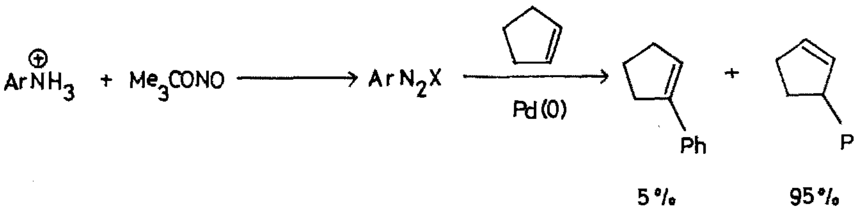
538



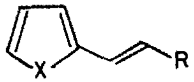
Scheme 25 Mechanism of coupling of arylpalladium complexes with allyl silyl ethers [907]



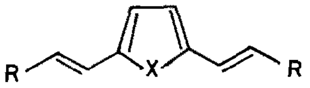
(160)



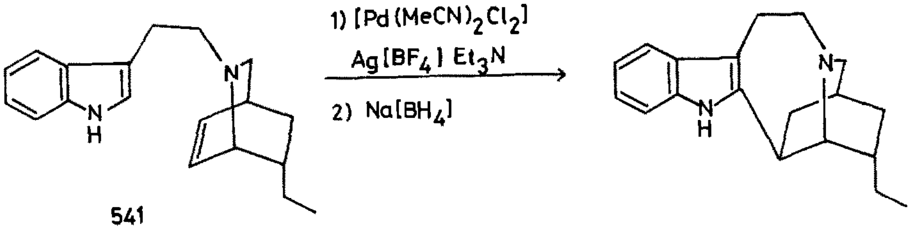
(161)



539

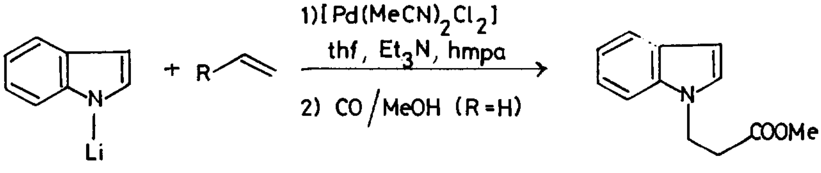


540

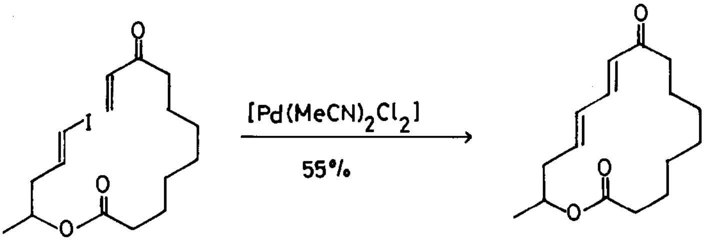


541

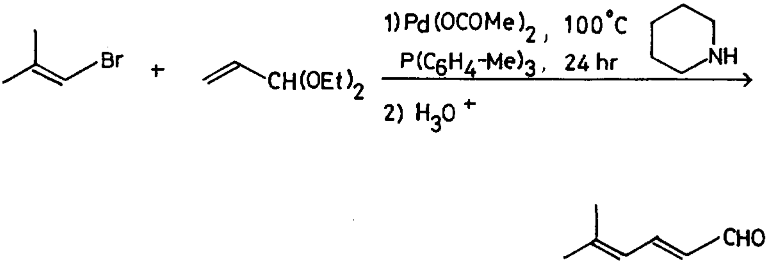
The synthesis of conjugated polyenes *via* the palladium catalysed Heck reaction has been reviewed [915]. Vinyl iodides reacted with methyl vinyl ketone in the presence of $[Pd(MeCN)_2Cl_2]$ to give dienones in good yield and fair stereoselectivity. The process was used in an intramolecular manner for the synthesis of a model of carbonolide B, **543** [916]. Further reactions of unsaturated esters, acids, amides and nitriles have been described in detail [917]. Coupling of vinyl halides with acetals followed by $[H_3O]^+$ work-up also gave dienones, reaction (162) giving an excellent three carbon homologation reaction [918].



542



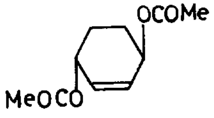
543



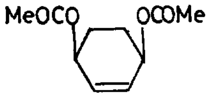
(162)

The reaction of nucleophiles with metal coordinated alkenes has again been important in many syntheses. Treatment of butadiene with BuSH in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$/thf gave $BuSCH_2CH{=}CHCH_3$ and $BuSCH(CH_3)CH{=}CH_2$ in a 7:3 ratio, but in aromatic solvents only the linear product was formed [919]. The reaction between cyclohexadiene and ethanoate in the presence of $Pd(OCOMe)_2$ has been further studied, in some detail. The *trans*-diethanoate, **544**, was obtained using

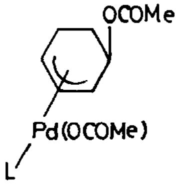
$Pd(OCOMe)_2/Li[OCOMe]/MeCOOH$/benzoquinone, whereas $Li_2[PdCl_4]/Li[OCOMe]/LiCl$ gave **545**. The *trans*-isomer was obtained by *trans*-acetoxypalladation to give **546**, followed by intramolecular transfer of ethanoate. In the presence of an excess of halide the ethanoate at palladium in **546** is replaced by halide, and free ethanoate attacks from the face of the allyl remote from palladium [920].



544

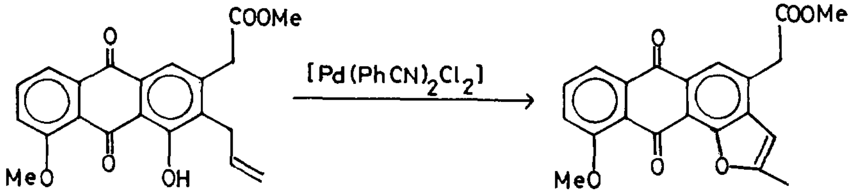


545



546

The intramolecular attack of a hydroxyl group on a palladium coordinated alkene was demonstrated by reaction (163), used in a synthesis of aklavinone [921]. In the presence of the chiral complex, **547**, **548** was produced with an unspecified but significant optical yield. The reaction mechanism proposed was complex, involving **549** as the catalytically active species [922]. The oxygen atom of an ester appears to act as the nucleophile in reaction (164), an efficient synthesis of isocoumarins [923].

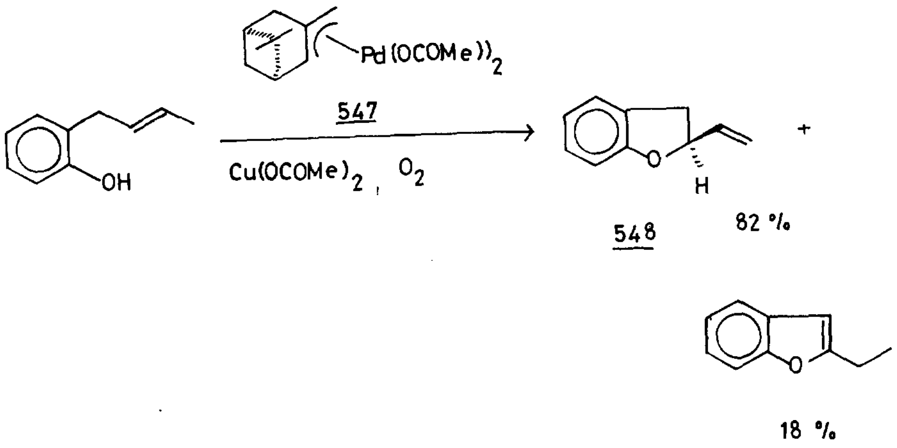


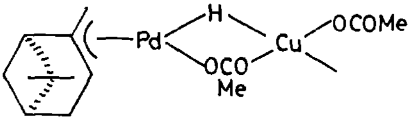
(163)

Nitrogen nucleophiles have been similarly popular, though most of the reported reactions were intramolecular (for example, (165) [924] and (166) [925]). **550** reacted to give 551 and 552 by the mechanism of Scheme 26 [926]. A similar process was used as the first step in an acridine synthesis [927]

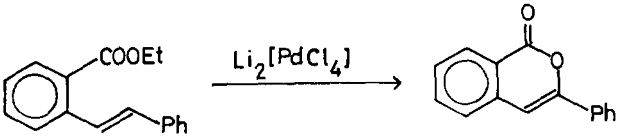
Palladium coordinated alkynes reacted similarly to give pyrroles in 80-100 % yield (Scheme 27 [928]).

Reaction of C_2N_2 with CH_3COCH_2COR in the presence of $[Ni(acac)_2]$ and other acac complexes gave the functionalised pyrimidine, 553, in excellent yield [929]. $[Pd(acac)_2]$, by contrast, gave no reaction [930].

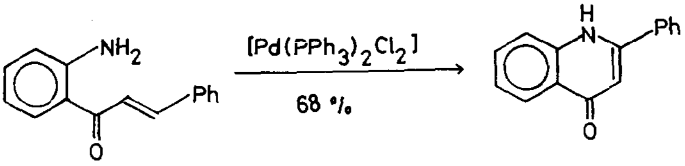




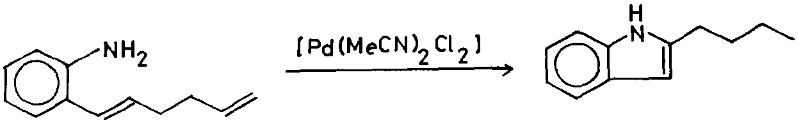
549



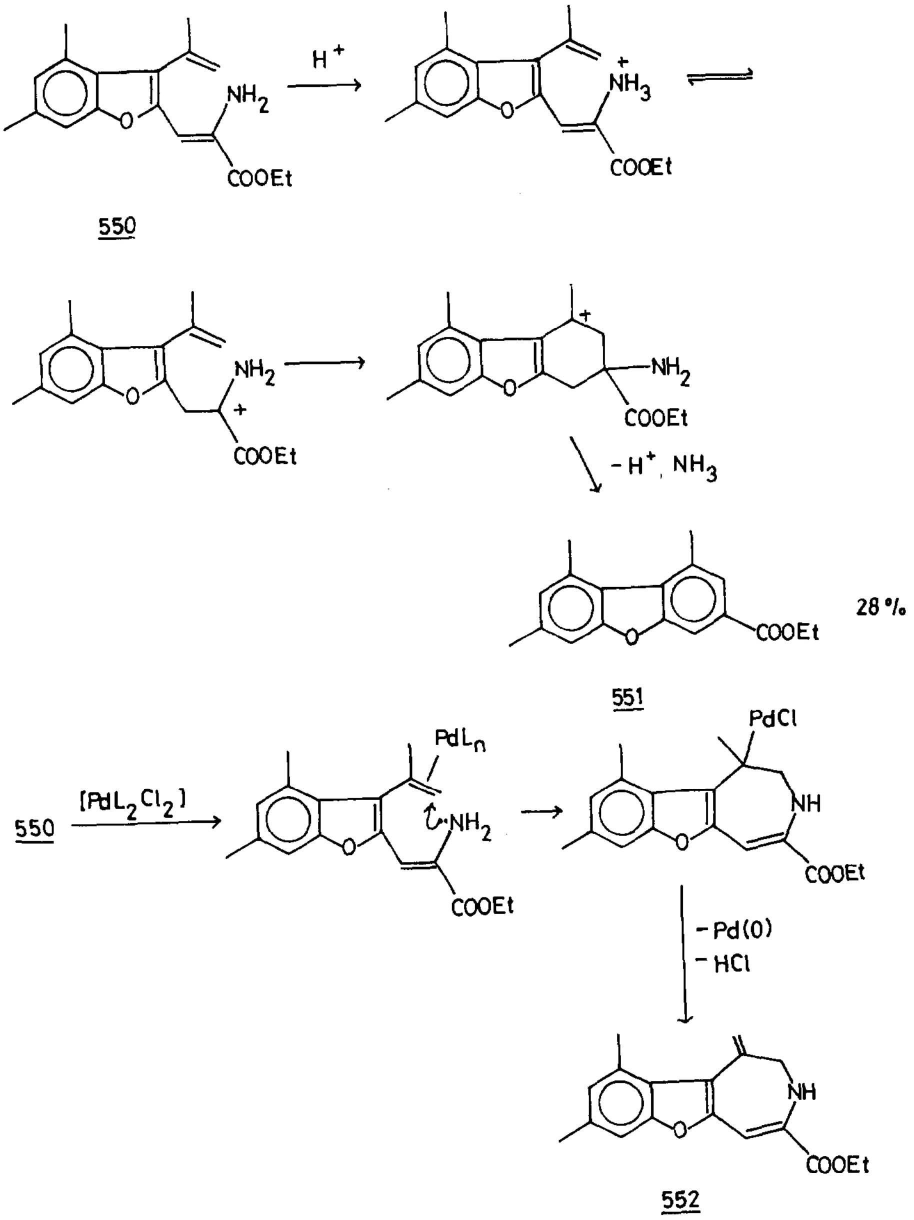
(164)



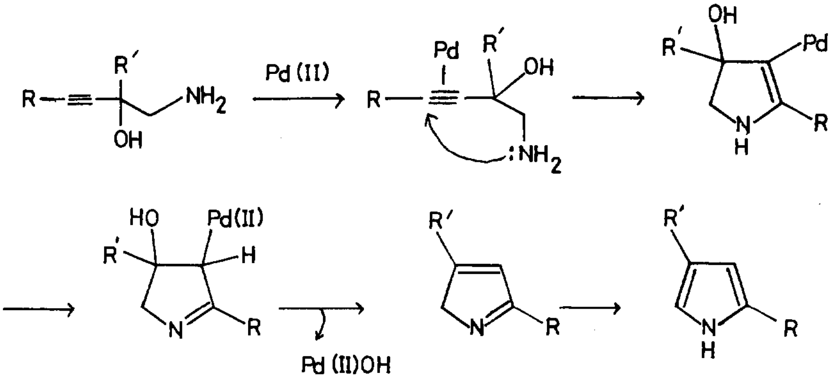
(165)



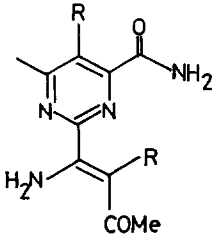
(166)



Scheme 26 Mechanism of palladium catalysed amine/alkene coupling [926]

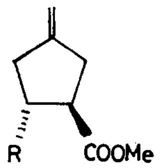


Scheme 27 Mechanism of palladium catalysed amine alkyne coupling in pyrrole synthesis [928]

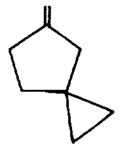


553

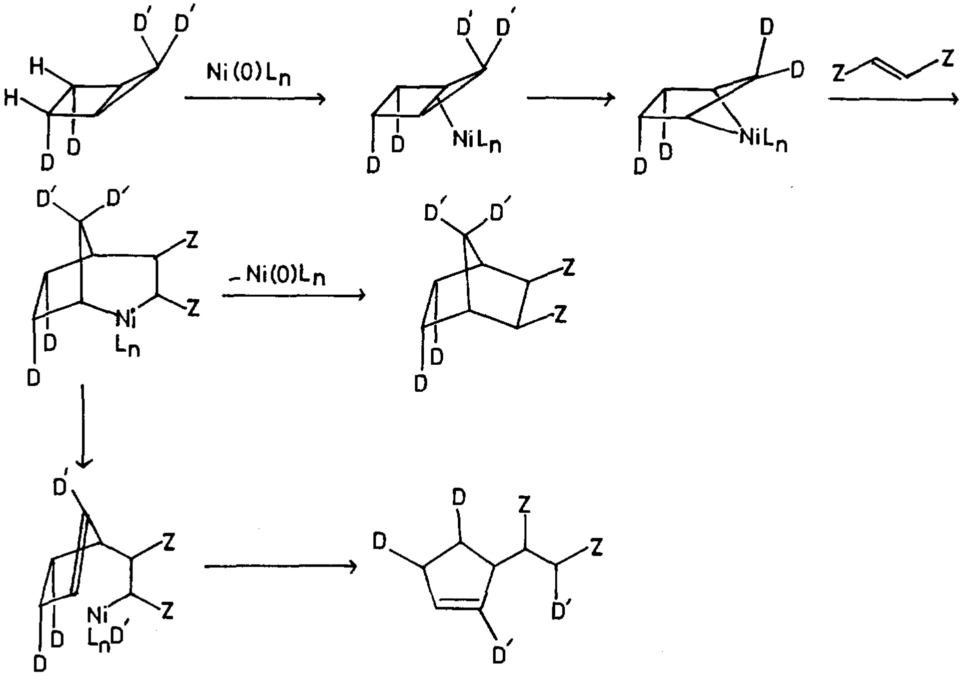
The reaction of methylenecyclopropane with *trans*-RCH=CHCOOMe in the presence of $[Pd(dba)_2]/P(CHMe_2)_3$ gave **554** and **555** *via* a palladium trimethylenemethane complex. The reaction mechanism has now been delineated in detail [931]. Alkenes bearing electron-withdrawing groups reacted with bicyclopentane *via* the mechanism of Scheme 28, deduced from deuterium labelling studies [932]. Bicyclobutane was also reactive, but in this case a metal carbene seemed the likely intermediate (Scheme 29 [933]). The reaction of $RCH_2CH=CH_2$ with MeOOCC≡CCOOMe gave **556** and **557**; the proposed mechanism was very complex [934].



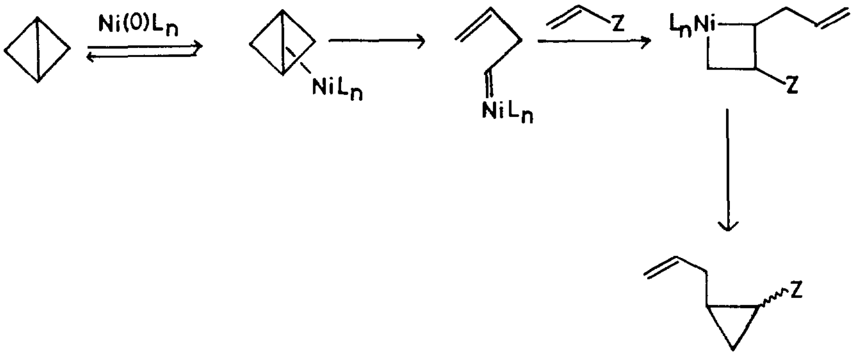
554



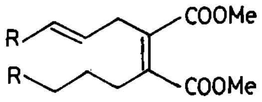
555



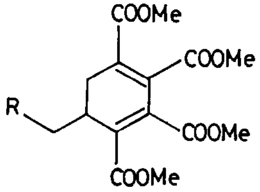
Scheme 28 Mechanism of nickel catalysed coupling of bicyclopentane [932]



Scheme 29 Nickel catalysed coupling of bicyclobutanes [933]



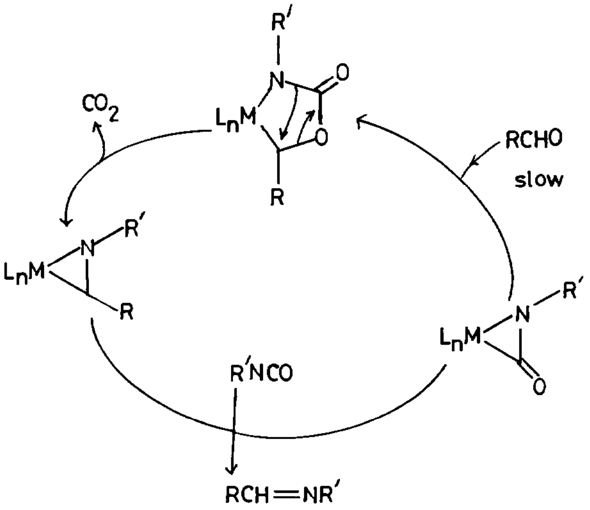
556



557

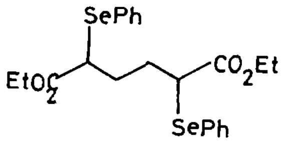
Coupling of RI to give RR was achieved using palladium(0). The PdI_2 produced was reduced back to palladium(0) by hydrazines, substituted reagents giving much better yields than hydrazine itself [935]. Cross-coupling of PhBr with alkyl iodides was carried out in the presence of $[Ni(PPh_3)_4]$, which was generated and continuously recycled electrochemically. A conventional reaction mechanism was proposed [936].

Methyl chloroethanoate and ethanoyl bromide reacted together to give CH_3Br, CH_3COCl and CO_2 in the presence of $[Pd(PPh_3)_4]$. The reaction mechanism was investigated using CD_3COBr [937]. Amination of 3-phenylpropenal was effected by PhNCO with $[Ni(CO)_2(PPh_3)_2]$ as catalyst. The mechanism proposed is shown in Scheme 30 [938]. The coupling of $BrCH_2C(=CH_2)CH=CH_2$ with geranyl bromide using $[Ni(CO)_4]$ gave *trans*-β-farnesene in 66 % yield [939].

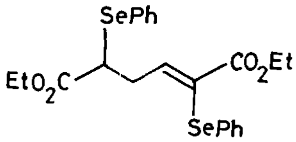


Scheme 30 Mechanism of nickel catalysed coupling of PhNCO and 3-phenylpropenal [938]

Reaction of ethyl acrylate with PhSeBr in the presence of PdCl$_2$/PPh$_3$/Na[OCOMe] gave **558** and **559**. The mechanism proposed involved initial oxidative addition of PhSeBr to palladium(0) followed by a double insertion and reductive elimination steps [940]. Anilines were oxidatively coupled to alkenes bearing electron withdrawing functionalities using [Pd(MeCN)$_2$Cl$_2$]/LiCl/benzoquinone [941]. Coupling of PhNO to give PhN=N(→O)Ph occurred in the presence of a range of catalysts including [Pd$_3$(CO)$_3$(PPh$_3$)$_4$] and [PdL$_2$Cl$_2$] (L = PhNO, ArNH$_2$ or PPh$_3$) [942].



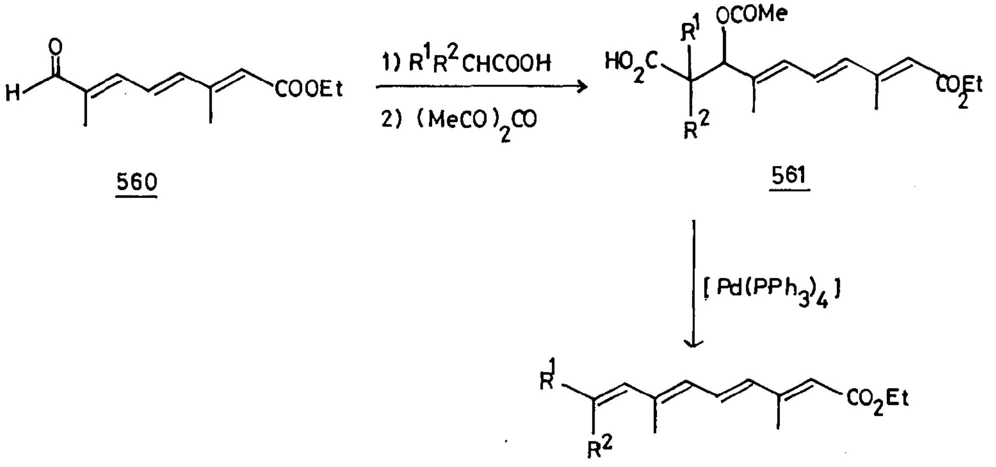
558

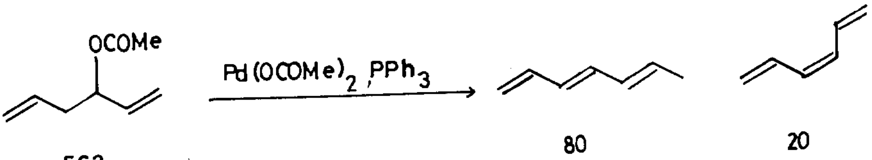


559

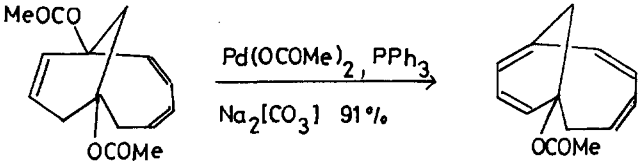
13.11 Other catalytic reactions

Palladium(0) has been used to catalyse a range of elimination reactions. For example, **561**, from R^{1}R^{2}CHCOOH and **560**, lost ethanoic acid readily [943]. The preponderance of the E-isomer in the related reaction of **562** was thought to reflect the preference for the *syn*-isomer of the intermediate π-allyl complex [944]. Ethanoate elimination from **563** gave an intermediate used in the synthesis of 1,5-methano-10-annulene [945]. Methanol was eliminated from **564** to give a precursor of rose oxide [946].

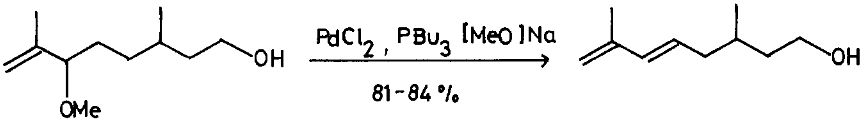




562

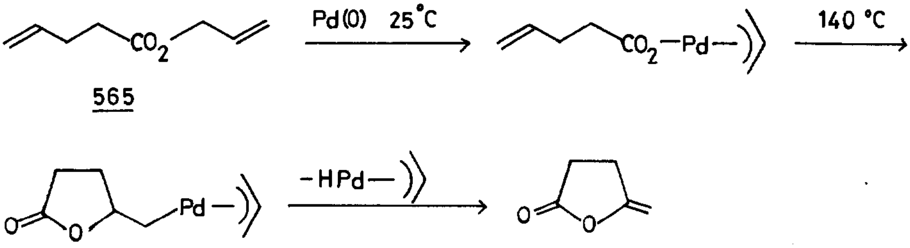


563



564

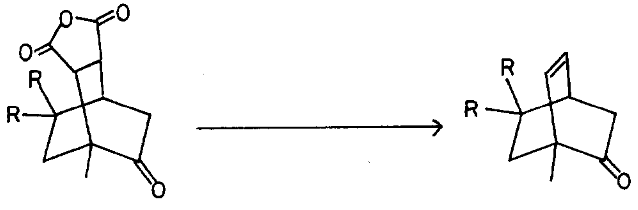
Reaction of the allyl ester, **565**, with [Pd(PPh$_3$)$_4$] provided a useful synthesis of an α-methylene lactone *via* the mechanism of Scheme 31 [947].



Scheme 31 Palladium catalysed synthesis of lactones [947]

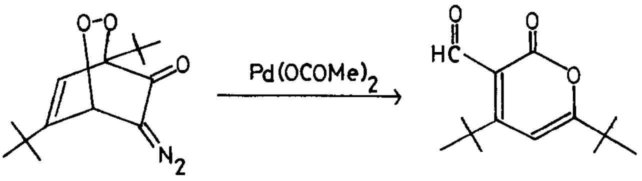
Selective hydration of acetonitrile to CH_3CONH_2 occurred in the presence of [Pd(bipy)(OH)Cl].H_2O. The mechanism involved intramolecular attack of hydroxyl ion on the coordinated nitrile [948].

In the presence of [Ni(CO)$_2$(PPh$_3$)$_2$], **566** underwent quantitative conversion to **567**, presumably *via* successive insertion, decarbonylation and decarboxylation [949].



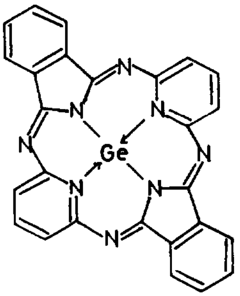
566 567

The conversion of **568** to **569**, using $Pd(OCOMe)_2$ as catalyst, was well established by an X-ray diffraction study of the product, but the reaction mechanism was not defined [950].



568 569

$HpGeCl_2$ reacted with alkynyl Grignard reagents in the presence of $[Ni(PPh_3)_2Cl_2]$ to give **570** [951].



570

$H_4[Pt_3Sn_8Cl_{20}]$ and $[Et_4N]_3[Pt(SnCl_3)_5]$ fixed on alumina catalysed the dehydrogenation of hexane to cyclohexane and methyl cyclopentane [952].

14 REFERENCES

1 L.S. Hegedus, J. Organomet. Chem., 207 (1981) 185.
2 S. Murahashi, Gendai Kagaku, 122 (1981) 26; Chem. Abs., 95 (1981) 60714g.
3 K.M. Halweg and J.A. Gladysz, Strem Chem., 9 (1981) 7.
4 D.H. Antonsen, Kirk-Othmer Encycl. Chem. Technol., 3rd Ed., 15 (1981) 801; Chem. Abstr., 95 (1981) 143228c.
5 E.R. Braithwaite, Spec. Publ. R. Soc. Chem., 40 (Spec. Inorg. Chem.) (1981) 375.
6 A.A.G. Tomlinson, Coord. Chem. Rev., 37 (1981) 221.
7 F.R. Hartley, Coord. Chem. Rev., 35 (1981) 143.
8 J.A. Davies and F.R. Hartley, Chem. Rev., 81 (1981) 79.
9 J. Mink, Termeszet Vilaga, 112 (1981) 202; Chem. Abstr., 95 (1981) 150721m.
10 F.G.A. Stone, Acc. Chem. Res., 14 (1981) 318.
11 P.S. Pregosin, Chimia, 35 (1981) 43.
12 G. Marr and B.W. Rockett, J. Organomet. Chem., 207 (1981) 343.
13 D.S. Matteson, J. Organomet. Chem., 207 (1981) 13.
14 R.G. Bergman, Pure Appl. Chem., 53 (1981) 161.
15 J. Mason, Chem. Rev., 81 (1981) 205.
16 P.E. Garrou, Chem. Rev., 81 (1981) 229.
17 D.W. Meek and T.J. Mazanec, Acc. Chem. Res., 14 (1981) 266.
18 S.C. Davis, S.J. Severson and K.J. Klabunde, J. Am. Chem. Soc., 103 (1981) 3024.
19 R. Bardi, A.M. Piazzesi and G. Bruno, Cryst. Struct. Commun., 10 (1981) 807.
20 R. Bardi and A.M. Piazzesi, Inorg. Chim. Acta, 47 (1981) 249.
21 N.C. Payne and D.W. Stephan, J. Organomet. Chem., 221 (1981) 203.
22 C.H.L. Kennard, J.R. Hall, R.G. Eggins, T.G. Appleton, N.H. Agnew and G. Smith, Cryst Struct. Commun., 10 (1981) 1517.
23 C.H.L. Kennard, J.R. Hall, N.H. Agnew, T.G. Appleton and G. Smith, Cryst Struct. Commun., 10 (1981) 1513.
24 A. Gleizes, A. Kerkeni, M. Dartiguenave, Y. Dartiguenave and H.F. Klein, Inorg. Chem., 20 (1981) 2372.
25 M.M. Olmstead, J.P. Farr and A.L. Balch, Inorg. Chim. Acta, 52 (1981) 47.
26 C.S. Day, V.W. Day, A. Shaver and H.C. Clark, Inorg. Chem., 20 (1981) 2188.
27 D.G. Ibbott, N.C. Payne and A. Shaver, Inorg. Chem., 20 (1981) 2193.
28 R. Bardi, A. Del Pra, A.M. Piazzesi, D. Minniti and R. Romeo, Cryst. Struct. Commun., 10 (1981) 333.
29 R. Bardi, A.M. Piazzesi, R. Ros and P. Cavoli, Cryst. Struct. Commun., 10 (1981) 855.
30 N.H. Agnew, T.G. Appleton and J.R. Hall, Inorg. Chim. Acta, 50 (1981) 137.
31 H.C. Clark and M.A. Mesubi, J. Organomet. Chem., 215 (1981) 131.
32 J.F. Almeida and A. Pidcock, J. Organomet. Chem., 208 (1981) 273.
33 E.W. Abel, K. Kite, K.G. Orrell, V. Šik and B.L. Williams, J. Chem. Soc., Dalton Trans., (1981) 2439.
34 E.W. Abel, M. Booth, K.G. Orrell, G.M. Pring and T.S. Cameron, J. Chem. Soc., Chem. Commun., (1981) 29.
35 E.W. Abel, M. Booth, G. King, K.G. Orrell, G.M. Pring and V. Šik, J. Chem. Soc., Dalton Trans., (1981) 1846.
36 E.W. Abel, Chimia, 35 (1981) 100.
37 Y. Koie, S. Shinoda and Y. Saito, Inorg. Chem., 20 (1981) 4408.
38 N.C. Payne and D.W. Stephan, J. Organomet. Chem., 221 (1981) 223.
39 D.A. Roberts, W.R. Mason and G.L. Geoffroy, Inorg. Chem., 20 (1981) 789.
40 G.M. Bancroft, T. Chan, R.J. Puddephatt and M.P. Brown, Inorg. Chim. Acta, 53 (1981) L119.

41 M. Wada and K. Sameshima, J. Chem. Soc., Dalton Trans., (1981) 240.
42 J.M. Coronas, C. Polo and J. Sales, Inorg. Chim. Acta, 48 (1981) 87.
43 M. Wada, J. Chem. Soc., Chem. Commun., (1981) 680.
44 R Usón, J. Forniés, P. Espinet, F. Martínez and M. Tomás, J. Chem. Soc., Dalton Trans., (1981) 463.
45 R. Usón, J. Gimeno, J. Forniés and F. Martínez, Inorg. Chim. Acta, 50 (1981) 173.
46 R. Usón, J. Gimeno, J. Forniés, F. Martínez and C. Fernandez, Inorg. Chim. Acta, 54 (1981) L95.
47 O. Rossell and J. Sales, Inorg. Chim. Acta, 53 (1981) L1.
48 L. Abis, R. Santi and J. Halpern, J. Organomet. Chem., 215 (1981) 263.
49 S.J. Cooper, M.P. Brown and R.J. Puddephatt, Inorg. Chem., 20 (1981) 1374.
50 R.J. Puddephatt, M.A. Thomson, L. Manojlović-Muir, K.W. Muir, A.A. Frew and M.P. Brown, J. Chem. Soc., Chem. Commun., (1981) 805.
51 L.J. Krause and J.A. Morrison, J. Chem. Soc., Chem. Commun., (1981) 1282.
52 E. Carmona, F. González, M.L. Poveda, J.L. Atwood and R.D. Rogers, J. Chem. Soc., Dalton Trans., (1981) 777.
53 C.S. Chin and M.D. Curtis, Taehan Hwahakhoe Chi, 25 (1981) 311; Chem. Abstr., 96 (1982) 85739c.
54 A.I. Kovredov, M.G. Meiramov, A.V. Kazantsev and L.I. Zakharkin, J. Gen. Chem. USSR, 51 (1981) 708 (Zh. Obshch. Khim., 51 (1981) 854).
55 L.I. Zakharkin and N.F. Shemyakin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1525 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1856).
56 E. Lindner, G. Funk and F. Bouachir, Chem. Ber., 114 (1981) 2653.
57 T. Debaerdemaeker, H-P. Klein, M. Wiege and H.A. Brune, Z. Naturforsch., B, Anorg. Chem., Org. Chem., 36B (1981) 958.
58 O. Rossell, J. Sales and M. Seco, J. Organomet. Chem., 205 (1981) 133.
59 G. Kreisel and D. Walther, Ger. (East) DD 147,628 (1981); Chem. Abstr., 96 (1982) 149889m.
60 I.M. Saez, G. Lopez and G. Garcia, An. Univ. Murcia, Cienc., 1976-1977 (Pub. 1981), 35, 157; Chem. Abstr., 96 (1982) 85723t.
61 G. García and G. López, Inorg. Chim. Acta, 52 (1981) 87.
62 A. Morvillo and A. Turco, J. Organomet. Chem., 208 (1981) 103.
63 E. Uhlig and W. Poppitz, Z. Anorg. Allg. Chem., 477 (1981) 167.
64 S. Franks and F.R. Hartley, Inorg. Chim. Acta, 49 (1981) 227.
65 N.J. Kermode, M.F. Lappert, B.W. Skelton, A.H. White and J. Holton, J. Chem. Soc., Chem. Commun., (1981) 698.
66 O.J. Scherer and H. Jungmann, J. Organomet. Chem., 208 (1981) 153.
67 A.L. Balch, C.T. Hunt, C-L. Lee, M.M. Olmstead and J.P. Farr, J. Am. Chem. Soc., 103 (1981) 3764.
68 B. Hipler, E. Uhlig and J. Vogel, J. Organomet. Chem., 218 (1981) C1.
69 M. Onishi, T. Ito and K. Hiraki, J. Organomet. Chem., 209 (1981) 123.
70 J-F. Fauvarque, F. Pflüger and M. Troupel, J. Organomet. Chem., 208 (1981) 419.
71 K. Isobe and S. Kawaguchi, Heterocycles, 16 (1981) 1603.
72 H. Tanaka, K. Isobe and S. Kawaguchi, Inorg. Chim. Acta, 54 (1981) L201.
73 K. Hiraki, T. Masumoto, Y. Fuchita and Y. Zegi, Bull. Chem. Soc. Jpn., 54 (1981) 1044.
74 J.F. Almeida and A. Pidcock, J. Organomet. Chem., 209 (1981) 415.
75 H. Behringer and E. Meinetsberger, Liebigs Ann. Chem., (1981) 1928.
76 D.W. Firsich and R.J. Lagow, J. Chem. Soc., Chem. Commun., (1981) 1283.
77 M.P. Brown, S.J. Cooper, A.A. Frew, L. Manojlović-Muir, K.W. Muir, R.J. Puddephatt, K.R. Seddon and M.A. Thomson, Inorg. Chem., 20 (1981) 1500.
78 G.B. Shul'pin, J. Organomet. Chem., 212 (1981) 267.
79 G.B. Shul'pin and A.N. Kitaigorodskii, J. Organomet. Chem., 212 (1981) 275.

80 R.B. Shibaeva, L.P. Rozenberg, R.M. Lobkovskaya, A.E. Shilov and G.B. Shul'pin, J. Organomet. Chem., 220 (1981) 271.

81 G.B. Shul'pin, J. Gen. Chem. USSR, 51 (1981) 1808 (Zh. Obshch. Khim., 51 (1981) 2100).

82 G.B. Shul'pin, Kinet. Catal., 22 (1981) 397 (Kinet. Katal., 22 (1981) 520).

83 G.B. Shul'pin and A.T. Nikitaev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1138 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1416).

84 S. Okeya, Y. Nakamura and S. Kawaguchi, Bull. Chem. Soc. Jpn., 54 (1981) 3396.

85 S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B.K. Mohapatra and S. Kawaguchi, Bull. Chem. Soc. Jpn., 54 (1981) 1978.

86 A.R. Seidle and L.H. Pignolet, Inorg. Chem., 20 (1981) 1849.

87 T.I. Bakunina, L.V. Mironova, V.A. Khutoryanskii, Yu.S. Levkovskii, V.L. Beloborodov and F.K. Shmidt, React. Kinet. Catal. Lett., 16 (1981) 281.

88 S. Okeya, Y. Nakamura, S. Kawaguchi and T. Hinomoto, Inorg. Chem., 20 (1981) 1576.

89 B.K. Sahu and B.K. Mohapatra, J. Indian Chem. Soc., 58 (1981) 731.

90 G.M. Whitesides, Pure Appl. Chem., 53 (1981) 287.

91 A.C. Balazs, K.H. Johnson and G.M. Whitesides, Gov. Rep. Announce. Index (U.S), 81 (1981) 2791; Chem. Abstr., 95 (1981) 149694y.

92 K. Tatsumi, R. Hoffmann, A. Yamamoto and J.K. Stille, Bull. Chem. Soc. Jpn., 54 (1981) 1857.

93 R.J. McKinney, D.L. Thorn, R. Hoffmann and A. Stockis, J. Am. Chem. Soc., 103 (1981) 2595.

94 A. Moravskiy and J.K. Stille, J. Am. Chem. Soc., 103 (1981) 4182.

95 F. Ozawa, T. Ito, Y. Nakamura and A. Yamamoto, Bull. Chem. Soc. Jpn., 54 (1981) 1868.

96 T.J. McCarthy, R.G. Nuzzo and G.M. Whiteseides, J. Am. Chem. Soc., 103 (1981) 1676.

97 T.J. McCarthy, R.G. Nuzzo and G.M. Whitesides, J. Am. Chem. Soc., 103 (1981) 3396.

98 R.G. Nuzzo, T.J. McCarthy and G.M. Whitesides, Inorg. Chem., 20 (1981) 1312.

99 R.G. Nuzzo, T.J. McCarthy and G.M. Whitesides, J. Am. Chem. Soc., 103 (1981) 3404.

100 S.S. Moore, R. DiCosimo, A.F. Sowinski and G.M. Whitesides, J. Am. Chem. Soc., 103 (1981) 948.

101 T. Yamamoto, T. Kohara and A. Yamamoto, Bull. Chem. Soc. Jpn., 54 (1981) 2010.

102 R.J. Al-Essa, R.J. Puddephatt, D.C.L. Perkins, M.C. Rendle and C.F.H. Tipper, J. Chem. Soc., Dalton Trans., (1981) 1738.

103 B.M. Cushman and D.B. Brown, Inorg. Chem., 20 (1981) 2490.

104 A. Miyashita, M. Takahashi and H. Takaya, J. Am. Chem. Soc., 103 (1981) 6257.

105 T.H. Johnson, Inorg. Chim. Acta, 53 (1981) L95.

106 G.E. Riley, C.F.H. Tipper and R.J. Puddephatt, J. Organomet. Chem., 208 (1981) 429.

107 R.J. Klingler, J.C. Huffmann and J.K. Kochi, J. Organomet. Chem., 206 (1981) C7.

108 T.A.K. Al-Allaf, C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc., Chem. Commun., (1981) 55.

109 C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc., Dalton Trans., (1981) 1223.

110 J.F. Almeida, H. Azizian, C. Eaborn and A. Pidcock, J. Organomet. Chem., 210 (1981) 121.

111 C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc., Dalton Trans., (1981) 933.

112 W. Beck, M. Keubler, E. Leidl, U. Nagel, M. Schaal, S. Cenini, P. del Buttero, E. Licando, S. Maiorana and A.C. Villa, J. Chem. Soc., Chem. Commun., (1981) 446.

113 Y. Tatsuno and S. Otsuka, J. Am. Chem. Soc., 103 (1981) 5832.

114 I. Arai and G.D. Daves, J. Am. Chem. Soc., 103 (1981) 7683.

115 E. Dinjus, D. Walther, R. Kirmse and J. Stach, Z. Anorg. Allg. Chem., 481 (1981) 71.

116 T. Yamamoto, T. Kohara and A. Yamamoto, Bull. Chem. Soc. Jpn., 54 (1981) 1720.

117 D.A. Palmer and H. Kelm, Coord. Chem. Rev., 36 (1981) 89.

118 H. Tanaka, K. Isobe and S. Kawaguchi, Chem. Lett., (1981) 769.

119 M. Aresta, M. De Fazio, A. Ingrosso and D. Giordano, J. Inorg. Nucl. Chem., 43 (1981) 1415.

120 P. Zanello, R. Seeber, A. Cinquantini and R. Ros, J. Inorg. Nucl. Chem., 43 (1981) 1095.

121 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 3607.

122 G. Cavinato and L. Toniolo, Inorg. Chim. Acta, 52 (1981) 39.

123 G.K. Anderson, H.C. Clark and J.A. Davies, J. Organomet. Chem., 210 (1981) 135.

124 C. Anklin, P.S. Pregosin, F. Bachechi, P. Mura and L. Zambonelli, J. Organomet. Chem., 222 (1981) 175.

125 A. Herrera and H. Hoberg, Synthesis, (1981) 831.

126 E. Dinjus, J. Kaiser, J. Sieler and D. Walther, Z. Anorg. Allg. Chem., 483 (1981) 63.

127 D. Walther and E. Dinjus, Z. Chem., 21 (1981) 415.

128 S. Komiya, A. Yamamoto and T. Yamamoto, Chem. Lett., (1981) 193.

129 T. Yamamoto, T. Kohara and A. Yamamoto, Bull. Chem. Soc. Jpn., 54 (1981) 2161.

130 R. Berger, H. Schenkluhn and B. Weimann, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 272.

131 M.F. Semmelhack and S.J. Brickner, J. Org. Chem., 46 (1981) 1723.

132 M. Troupel, Y. Rollin, J. Perichon and J.F. Fauvarque, Nouv. J. Chim., 5 (1981) 621.

133 F. Ozawa and A. Yamamoto, Chem. Lett., (1981) 289.

134 Y. Djaoued, T.V. Lusyak and I.S. Kolomnikov, Yu.Ya. Kharitonov, Koord. Khim., 7 (1981) 1431.

135 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 1636.

136 R.J. Cross and J. Gemmill, J. Chem. Soc., Dalton Trans., (1981) 2317.

137 J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 3002.

138 J.M. Huggins, Energy Res. Abstr., 6 (1981) Abstr. No. 5132; Chem. Abstr., 95 (1981) 41785q.

139 C. Lee, C.T. Hunt and A.L. Balch, Inorg. Chem., 20 (1981) 2498.

140 F. Canziani, L. Garlaschelli, M.C. Malatesta and A. Albinati, J. Chem. Soc., Dalton Trans., (1981) 2395.

141 C.J. May and J. Powell, J. Organomet. Chem., 209 (1981) 131.

142 W. Wong-Ng and S.C. Nyburg, J. Chem. Soc., Dalton Trans., (1981) 1935.

143 D. Fenske and A. Christidis, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 518.

144 E. Uhlig and B. Nestler, Z. Chem., 21 (1981) 451.

145 W. Keim, Chimia, 35 (1981) 344.

146 D. Spangler, J.J. Wendoloski, M. Dupuis, M.M.L. Chen and H.F. Schaefer, J. Am. Chem. Soc., 103 (1981) 3985.

147 A. Miyashita and R.H. Grubbs, Tetrahedron Lett., 22 (1981) 1255.

148 H. Hoberg, G. Burkhart, C. Krüger and Y.-H. Tsay, J. Organomet. Chem., 222 (1981) 343.

149 M. Wada, Y. Koyama and K. Sameshima, J. Organomet. Chem., 209 (1981) 115.

150 Y. Fuchita, K. Hidaka, S. Morinaga and K. Hiraki, Bull. Chem. Soc. Jpn., 54 (1981) 800.

151 A. Mantovani, G. Facchin, T. Boschi and B. Crociani, J. Organomet. Chem., 206 (1981) C11.

152 K. Hiraki, M. Onishi, K. Ohnuma and K. Sugino, J. Organomet. Chem., 216 (1981) 413.

153 W.P. Fehlhammer, A. Mayr and G. Christian, J. Organomet. Chem., 209 (1981) 57.

154 F.G.A. Stone, Inorg. Chim. Acta, 50 (1981) 33.

155 J.A.K. Howard, K.A. Mead, J.R. Moss, R. Navarro, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 743.

156 J.A.K. Howard, J.C. Jeffery, M. Laguna, R. Navarro and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 751.

157 J.C. Jeffery, R. Navarro, H. Razay and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 2471.

158 J.C. Jeffery, I. Moore, H. Razay and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1981) 1255.

159 T.V. Ashworth, M.J. Chetcuti, J.A.K. Howard, F.G.A. Stone, J.J. Wisbey and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 763.

160 M. Green, D.R. Hankey, M. Murray, A.G. Orpen and F.G.A. Stone, J.Chem. Soc., Chem. Commun., (1981) 689.

161 K. Tatsumi and R. Hoffmann, Inorg. Chem., 20 (1981) 3771.

162 B.L. Booth and K.G. Smith, J. Organomet. Chem., 220 (1981) 219.

163 B.L. Booth and K.G. Smith, J. Organomet. Chem., 220 (1981) 229.

164 H. Schmidbaur, U. Deschler and B. Milewski-Mahrla, Angew. Chem., Int. Ed., Engl., 20 (1981) 586 (Angew. Chem., 93 (1981) 598).

165 H. Schmidbaur, A. Mörtl and B. Zimmer-Gasser, Chem. Ber., 114 (1981) 3161.

166 D.L. Beach and J.L. Harrison, U.S. US 4,293,502 (1981); Chem. Abstr., 96 (1982) 6873r.

167 D.L. Beach and J.J. Harrison, U.S. US 4,293,727 (1981); Chem Abstr., 96 (1982) 85031r.

168 D.L. Beach and J.J. Harrison, U.S. US 4,301,318 (1981); Chem. Abstr., 96 (1982) 68298r.

169 O.J. Scherer and H. Jungmann, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 1663.

170 G. Matsubayashi and Y. Kondo, J. Organomet. Chem., 219 (1981) 269.

171 A.J. Kunin and D.B. Brown, J. Organomet. Chem., 212 (1981) C27.

172 A.D. Ryabov, I.K. Sakodinskaya, V.M. Titov and A.K. Yatsimirsky, Inorg. Chim. Acta, 54 (1981) L195.

173 A.D. Ryabov, A.K. Yatsimirskii and I.V. Berezin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1103 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1378).

174 B.J. Brisdon, P. Nair and S.F. Dyke, Tetrahedron, 37 (1981) 173.

175 H. van der Poel and G. van Koten, J. Organomet. Chem., 217 (1981) 129.

176 A.R. Siedle, J. Organomet. Chem., 208 (1981) 115.

177 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, J. Am. Chem. Soc., 103 (1981) 5115.

178 R.A. Holton and K.J. Natalie, Tetrahedron Lett., 22 (1981) 267.

179 A.F.M.J. van der Ploeg, G. van Koten and K. Vrieze, J. Organomet. Chem., 222 (1981) 155.

180 R. Sugimoto, H. Eikawa, H. Suzuki, Y. Moro-Oka and T. Ikawa, Bull. Chem. Soc. Jpn., 54 (1981) 2849.

181 T. Izumi, M. Maemura, K. Endoh, T. Oikawa, S. Zakozi and A. Kasahara, Bull. Chem. Soc. Jpn., 54 (1981) 836.

182 T. Komatsu, M. Nonoyama and J. Fujita, Bull. Chem. Soc. Jpn., 54 (1981) 186.

183 A.J. Nielson, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 180.

184 J. Dehand, C. Mutet and M. Pfeffer, J. Organomet. Chem., 209 (1981) 255.

185 J. Selbin and M.A. Gutierrez, J. Organomet. Chem., 214 (1981) 253.

186 K. Hiraki, Y. Fuchita and K. Takechi, Inorg. Chem., 20 (1981) 4316.

187 G.R. Newkome, T. Kawato, D.K. Kohli, W.E. Puckett, B.D. Olivier, G. Chiari, F.R. Fronczek and W.A. Deutsch, J. Am. Chem. Soc., 103 (1981) 3423.

188 K. Nakatsu, K. Kafuku Y. Isobe, Y. Nakamura, H. Yamaoka and S. Kawaguchi, Inorg. Chim. Acta, 54 (1981) L69.

189 M. Nonoyama and S. Kajita, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 163.

190 M. Pfeffer, D. Grandjean and G. Le Borgne, Inorg. Chem., 20 (1981) 4426.

191 P. Bandyopadhyay, P.K. Mascharak and A. Chakravorty, J. Chem. Soc., Dalton Trans., (1981) 623.

192 A.J. Klaus and P. Rys, Helv. Chim. Acta, 64 (1981) 1452.

193 K. Hiraki, Y. Fuchita and S. Takakura, J. Organomet. Chem., 210 (1981) 273.

194 T. Izumi, H. Watabe and A. Kasahara, Bull. Chem. Soc. Jpn., 54 (1981) 1711.

195 D. Walther and D. Zeigan, J. Organomet. Chem., 216 (1981) 403.

196 A.J. Nielson, J. Chem. Soc., Dalton Trans., (1981) 205.

197 A.B. Goel, S. Goel and D. Vanderveer, Inorg. Chim. Acta, 54 (1981) L267.

198 A.B. Goel, S. Goel and H.C. Clark, Synth. React. Inorg. Met.-Org. Chem., 11 (1981) 289.

199 R.G. Goel, W.O. Ogini and R.C. Srivastava, J. Organomet. Chem., 214 (1981) 405.

200 H. Werner and H.J. Kraus, J. Organomet. Chem., 204 (1981) 415.

201 H-P. Abicht and K. Issleib, Z. Chem., 21 (1981) 341.

202 H. Horino and N. Inoue, J. Org. Chem., 46 (1981) 4416.

203 Y. Fuchita, K. Hiraki, T. Yamaguchi and T. Maruta, J. Chem. Soc., Dalton Trans., (1981) 2405.

204 R. Rüger, W. Rittner, P.G. Jones, W. Isenberg and G.M. Sheldrick, Angew. Chem., Int. Ed., Engl., 20 (1981) 382 (Angew. Chem., 93 (1981) 389).

205 Y. Tamaru, M. Kagotani and Z. Yoshida, Angew. Chem., Int. Ed., Engl., 20 (1981) 980 (Angew. Chem., 93 (1981) 1031).

206 K. Miki, N. tanaka and N. Kasai, Acta Crystallogr., Sect. B, B37 (1981) 447.

207 L.J. Kirschenbaum, J.M. Howell and A.R. Rossi, J. Phys. Chem., 85 (1981) 17.

208 J.W. Davenport, Chem. Phys. Lett., 77 (1981) 45.

209 A. Garcia-Rodriguez and J.C. Decius, J. Mol. Spectrosc., 87 (1981) 41.

210 D. Saddei, H.J. Freund and G. Hohlneicher, Chem. Phys., 55 (1981) 339.

211 Y. Langsam and A.M. Ronn, Chem. Phys., 54 (1981) 277.

212 A.E. Stevens and J.L. Beauchamp, J. Am. Chem. Soc., 103 (1981) 190.

213 V.A. Luginin, A.E. Samsonov and I.A. Tserkovnitskaya, Probl. Sovrem. Analit. Khimii, (Leningrad) (1981) 104; Chem. Abstr., 96 (1982) 10971p.

214 I.N. Kalitovich, and L.N. Fain, Zavod. Lab., 47 (1981) 12; Chem. Abstr., 95 (1981) 120126d.

215 F. Kacso, E. Campian, L. Szabo and M. Almasi, Rom. 67,180 (1979); Chem. Abstr., 94 (1981) 160470x.

216 G. Greiner and D. Menzel, Surf. Sci., 109 (1981) L510.

217 A.Ya. Kipnis and A.E. Ryumshin, Deposited Doc., (1981) VINITI, 732-81; Chem. Abstr., 96 (1982) 169501g.

218 K. Kishi, Y. Motoyoshi and S. Ikeda, Surf. Sci., 105 (1981) 313.

219 D.A. Hucul and A. Brenner, J. Am. Chem. Soc., 103 (1981) 217.

220 W.M. Shen, J.A. Dumesic and C.G. Hill, J. Catal., 68 (1981) 152.

221 P.N. Galich, Visn. Akad. Nauk Ukr. RSR (1981) 54; Chem. Abstr., 96 (1982) 110848x.

222 A.A. Galinskii, P.N. Galich, G.M. Tel'biz and L.M. Roev, Ukr. Khim. Zh. (Russ. Ed.), 47 (1981) 1040; Chem. Abstr., 95 (1981) 214398w.

223 F. Basolo, Inorg. Chim. Acta, 50 (1981) 65.

224 L. Hellner, J. Masanet and C. Vermeil, Chem. Phys. Lett., 83 (1981) 474.

225 M. Castiglioni and P. Volpe, Gazz. Chim. Ital., 111 (1981) 19.

226 P.A. Breeze, J.K. Burdett and J.J. Turner, Inorg. Chem., 20 (1981) 3369.

227 M. Baacke, Gov. Rep. Announce. Index (U.S.), 81 (1981) 3556; Chem. Abstr., 96 (1982) 20245u.

228 M. Kastner, S. Jonsdottir and G. Klar, Chem.-Ztg., 105 (1981) 232.

229 H.J. Breunig, W. Fichtner and T.P. Knoblock, Z. Anorg. Allg. Chem., 477 (1981) 126.

230 A. Trenkle and H. Vahrenkamp, Chem. Ber., 114 (1981) 1366.

231 A. Trenkle and H. Vahrenkamp, Chem. Ber., 114 (1981) 1343.

232 E. Röttinger and H. Vahrenkamp, J. Organomet. Chem., 213 (1981) 1.

233 W.R. Cullen and J.D. Woollins, Coord. Chem. Rev., 39 (1981) 1.

234 K. Fischer and H. Vahrenkamp, Z. Anorg. Allg. Chem., 475 (1981) 109.

235 A Del Pra, G. Zanotti, L. Pandolfo and P. Segala, Cryst. Struct. Commun., 10 (1981) 7.

236 J. Grobe and B.H. Schneider, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 1.

237 J. Grobe and B.H. Schneider, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 8.

238 C.F. Nobile, G. Vasapollo, P. Giannoccaro and A. Sacco, Inorg. Chim. Acta, 48 (1981) 261.

239 L.S. Isaeva and G.I. Drogunova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1584 (Izv. Akad. Nauk SSSR, Div. Chem. Sci., (1981) 1919).

240 M. Svoboda, H. tom Dieck, C. Krüger and Y-H. Tsay, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 814.

241 D. Seyferth and R.S. Henderson, J. Organomet. Chem., 204 (1981) 333.

242 M. Meissner, H-J. Kroth, K-H. Köhricht and H. Schumann, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 904.

243 V.S. Shestakova, A.F. Kuperman, S.M. Brailovskii and O.N. Temkin, Kinet. Catal., 22 (1981) 279 (Kinet. Katal., 22 (1981) 370).

244 R.G. Goel, W.O. Ogini and R.C. Srivastava, Inorg. Chem., 20 (1981) 3611.

245 I.V. Pakhomova, Yu.N. Kukushkin, Yu.N. Martynov, N.A. Gudova and A.M. Besprozvannyi, J. Gen. Chem. USSR, 51 (1981) 1972 (Zh. Obshch. Khim., 51 (1981) 2292).

246 M.C. Manning and W.C. Trogler, Coord. Chem. Rev., 38 (1981) 89.

247 R.E. Benfield and B.F.G. Johnson, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 131.

248 J. Evans, Chem. Soc. Rev., 10 (1981) 159.

249 R.G. Woolley, Nouv. J. Chim., 5 (1981) 441.

250 C.E. Housecroft, M.E. O'Neill, K. Wade and B.C. Smith, J. Organomet. Chem., 213 (1981) 35.

251 T.L. Hall and J.K. Ruff, Inorg. Chem., 20 (1981) 4444.

252 A.R. Manning, J. Chem. Soc., Dalton Trans., (1981) 1057.

253 L.R. Byers, V.A. Uchtman and L.F. Dahl, J. Am. Chem. Soc., 103 (1981) 1942.

254 E. Sappa, M. Lanfranchi, A. Tiripicchio and M.T. Camellini, J. Chem. Soc., Chem. Commun., (1981) 995.

255 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 171.

256 E. Sappa, A. Tiripicchio and M.T. Camellini, J. Organomet. Chem., 213 (1981) 175.

257 E. Sappa, A.M.M. Lanfredi and A. Tiripicchio, J. Organomet. Chem., 221 (1981) 93.

258 M. Tachikawa, R.L. Geerts and E.L. Muetterties, J. Organomet. Chem., 213 (1981) 11.

259 F. Calderazzo and D.B. Dell'Amico, Inorg. Chem., 20 (1981) 1310.

260 T.W. Smith, US 4,252,677 (1981); Chem. Abstr., 94 (1981) 181533k.

261 P.L. Goggin, R.J. Goodfellow, I.R. Herbert and A. G. Orpen, J. Chem. Soc., Chem. Commun., (1981) 1077.

262 V.K. Polovnyak, V.P. Linev, O.N. Temkin and N.S. Akhmetov, Deposited Doc., (1981) SPSTL 687 Khp-D81; Chem. Abstr., 98 (1983) 167731z.

263 V.P. Linev, O.N. Temkin, V.K. Polovnyak, L.G. Bruk and G.V. Romanov, J. Gen. Chem. USSR, 51 (1981) 2187 (Zh. Obshch. Khim., 51 (1981 2536).

264 M.N. Vargaftik, T.A. Stromnova, T.S. Khodashova, M.A. Porai-Koshits and I.I. Moiseev, Koord. Khim., 7 (1981) 132.

265 D.M. Hoffman and R. Hoffmann, Inorg. Chem., 20 (1981) 3543.

266 B. Denise and R.P.A. Sneeden, J. Organomet. Chem., 221 (1981) 111.

267 A. Maisonnat, J.P. Farr and A.L. Balch, Inorg. Chim. Acta, 53 (1981) L217.

268 S.A. Bhaduri, I. Bratt, B.F.G. Johnson, A. Khair, J.A. Segal and R. Walters, J. Chem. Soc., Dalton Trans., (1981) 234.

269 E.G. Mednikov and N.K. Eremenko, Koord. Khim., 7 (1981) 1399.

270 E.G. Mednikov, N.K. Eremenko, V.A. Mikhailov, S.P. Gubin, Y.L. Slovokhotov and Y.T. Struchkov, J. Chem. Soc., Chem. Commun., (1981) 989.

271 E.G. Mednikov and N.K. Eremenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1980 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2400.

272 E.G. Mednikov and N.K. Eremenko, Koord. Khim., 7 (1981) 1399.

273 C.T. Hunt, G.B. Matson and A.L. Balch, Inorg. Chem., 20 (1981) 2270.

274 A. Moor, P.S. Pregosin and L.M. Venanzi, Inorg. Chim. Acta, 48 (1981) 153.

275 A.F. Simpson and R. Whyman, J. Organomet. Chem., 213 (1981) 157.

276 C. Crouzet, O. Zahraa and F. Gault, Fr. Demande FR 2,462,933 (1981); Chem. Abstr., 96 (1982) 22238t.

277 K.L. Watters, SIA, Surf. Interface Anal., 3 (1981) 55; Chem. Abstr., 94 (1981) 163159p.

278 R. Bender, P. Braunstein, J. Fischer, L. Ricard and A. Mitschler, Nouv. J. Chim., 5 (1981) 81.

279 P. Braunstein, D. Matt, O. Bars, M. Louër, D. Grandjean, J. Fischer and A. Mitschler, J. Organomet. Chem., 213 (1981) 79.

280 P. Lemoine, A. Giraudeau, M. Gross, R. Bender and P. Braunstein, J. Chem. Soc., Dalton Trans., (1981) 2059.

281 R. Pierantozzi, K.J. McQuade and B.C. Gates, Stud. Surf. Sci. Catal., 7 (Pt. B, New Horiz. Catal.) (1981) 941; Chem. Abstr., 95 (1981) 226316f.

282 M. Green, J.A.K. Howard, R.M. Mills, G.N. Pain, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1981) 869.

283 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 1134.

284 G. Longoni and F. Morazzoni, J. Chem. Soc., Dalton Trans., (1981) 1735.

285 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 1274.

286 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 155.

287 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 162.

288 J.C. Jeffery, H. Razay and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1981) 243.

289 A.L. Lapidus and Y.Y. Ping, Russ. Chem. Rev., 50 (1981) 63 (Usp. Khim., 50 (1981) 111).

290 G. Paiaro and L. Pandolfo, Angew. Chem., Int. Ed. Engl., 20 (1981) 288 (Angew. Chem., 93 (1981) 294).

291 S. Datta and U.C. Agarwala, Indian J. Chem., Sect. A, 20A (1981) 1153.

292 S. Datta and U.C. Agarwala, Indian J. Chem., Sect. A, 20A (1981) 1190.

293 R. Uson, J. Fornies and M.A. Uson, Synth. React. Inorg. Met.-Org. Chem., 11 (1981) 517.

294 T.S. Cameron, P.A. Gardner and K.R. Grundy, J. Organomet. Chem., 212 (1981) C19.
295 J.W. Gosselink, G. van Koten and K. Vrieze, J. Organomet. Chem., 222 (1981) 131.
296 J.W. Gosselink, H. Bulthuis and G. van Koten, J. Chem. Soc., Dalton Trans., (1981) 1342.
297 J.W. Gosselink, G. van Koten, A.M.F. Brouwers and O. Overbeek, J. Chem. Soc., Dalton Trans., (1981) 342.
298 J.W. Gosselink, G. van Koten, A.L. Spek and A.J.M. Duisenberg, Inorg. Chem., 20 (1981) 877.
299 P. Haw, A. Walker and M.A. Wiotzik, J. Organomet. Chem., 212 (1981) 419.
300 E. Dinjus and D. Walther, Z. Chem., 21 (1981) 270.
301 Y. Kitano and T. Hori, Acta Crystallogr., Sect. B, B37 (1981) 1919.
302 T. Kajimoto, Y, Kitano, H. Takahashi and J. Tsuji, Bull. Chem. Soc. Jpn., 54 (1981) 2672.
303 J.R. Briggs, C. Crocker and B.L. Shaw, Inorg. Chim. Acta, 51 (1981) 15.
304 P. Overbosch, G. van Koten and K. Vrieze, J. Organomet. Chem., 208 (1981) C21.
305 W.L. Gladfelter, M.W. Lynch, W.P. Schaefer, D.N. Hendrickson and H.B. Gray, Inorg. Chem., 20 (1981) 2390.
306 Y. Ohtani, S. Miya, Y. Yamamoto and H. Yamazaki, Inorg. Chim. Acta, 53 (1981) L53.
307 R. Usón, J. Forniés, P. Espinet and E. Lalinde, J. Organomet. Chem., 220 (1981) 393.
308 K. Kitaura, S. Sakaki and K. Morokuma, Inorg. Chem., 20 (1981) 2292.
309 W. Dreissig and H. Dietrich, Acta Crystallogr., Sect. B, B37 (1981) 931.
310 N.M. Rodionova and O.P. Yablonskii, Ref. Zh., Khim., (1981) Abstr. No. 11B223; Chem. Abstr., 95 (1981) 105599s.
311 P.J. Hay, J. Am. Chem. Soc., 103 (1981) 1390.
312 V.B. Ivanov, P.A. Chel'tsov and R.N. Shchelokov, Izv. Akad. Nauk SSSR, Ser. Biol., (1981) 551; Chem. Abstr., 95 (1981) 181611e.
313 D.A. Johnson, W.C. Deese and A.W. Cordes, Acta Crystallogr., Sect. B, B37 (1981) 2220.
314 W.C. Deese, D.A. Johnson and A.W. Cordes, Inorg. Chem., 20 (1981) 1519.
315 D. Gregson, J.A.K. Howard, M. Murray and J.L. Spencer, J. Chem. Soc., Chem. Commun., (1981) 716.
316 V.V. Sokolov, A.A. Musaev, V.V. Bashilov and O.A. Reutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1988 (Izv. Akad. SSSR, Ser. Khim., (1981) 2409).
317 M. Green and J.K.K. Sarhan, Inorg. Chim. Acta, 54 (1981) L67.
318 M. Lenarda, R. Ganzerla, A. Lisini, M. Graziani and T. Boschi, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 199.
319 M.J. Chetcuti, J.A. Herbert, J.A.K. Howard, M. Pfeffer, J.L. Spencer, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 284.
320 M. Hiramatsu, T. Fujinami and S. Sakai, J. Organomet. Chem., 218 (1981) 409.
321 M.J. Chetcuti, J.A.K. Howard, M. Pfeffer, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 276.
322 F. Hartley, J. Organomet. Chem., 216 (1981) 277.
323 H. van der Poel, G. van Koten, M. Kokkes and C.H. Stam, Inorg. Chem., 20 (1981) 2941.
324 H. Van der Poel, G. van Koten, D.M. Grove, P.S. Pregosin and K.A.O. Starzewski, Helv. Chim. Acta, 64 (1981) 1174.
325 H. van der Poel and G. van Koten, Inorg. Chem., 20 (1981) 2950.
326 H. van der Poel, G. van Koten and G.C. van Stein, J. Chem. Soc., Dalton Trans., (1981) 2164.
327 K.J. Cavell, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 47 (1981) 67.

328 K. Brown and P.A. Chaloner, J. Organomet. Chem., 217 (1981) C25.
329 F. Benayache, J. Jullien and D. Solgadi, J. Chem. Res., S, (1981) 159.
330 M.K. Cooper and D.W. Yaniuk, J. Organomet. Chem., 221 (1981) 231.
331 H. Kurosawa and N. Asada, J. Organomet. Chem., 217 (1981) 259.
332 S. Sostero, M. Lenarda, O. Traverso, W.J. Reed and T.J. Kemp, Inorg. Chim. Acta, 54 (1981) L149.
333 P. Courtot, R. Pichon and J-Y. Salaün, J. Chem. Soc., Chem. Commun., (1981) 542.
334 M.E. Jason and J.A. McGinnety, Inorg. Chem., 20 (1981) 4000.
335 C.R. Hall, E.R. Hamner, R.D.W. Kemmitt and D.J.H. Smith, J. Organomet. Chem., 205 (1981) 417.
336 R.B. Osborne, H.C. Lewis and J.A. Ibers, J. Organomet. Chem., 208 (1981) 125.
337 S. Miya and K. Saito, Inorg. Chem., 20 (1981) 287.
338 S. Miya, K. Kashiwabara and K. Saito, Bull. Chem. Soc. Jpn., 54 (1981) 2309.
339 O. Eisenstein and R. Hoffmann, J. Am. Chem. Soc., 103 (1981) 4308.
340 M. Green, J.K.K. Sarhan and I.M. Al-Najjar, J. Chem. Soc., Dalton Trans., (1981) 1565.
341 B. Pugin and L.M. Venanzi, J. Organomet. Chem., 214 (1981) 125.
342 R. McCrindle, G. Ferguson, M.A. Khan, A.J. McAlees and B.L. Ruhl, J. Chem. Soc., Dalton Trans., (1981) 986.
343 R. McCrindle, G. Perguson, A.J. McAlees and B.L. Ruhl, J. Organomet. Chem., 204 (1981) 273.
344 J.C. Chottard, E. Mulliez, J. Soulié, D. Mansuy and J. Guilhem, Tetrahedron, 37 (Supplement 1) (1981) 31.
345 H. Lehmkuhl, A. Rufińska, R. Benn, G. Schroth and R. Mynott, Liebigs Ann. Chem., (1981) 317.
346 Y. Ohkatsu, E. Sato and T. Osa, Sekiyu Gakkaishi, 24 (1981) 270; Chem. Abstr., 95 (1981) 186400v.
347 J.R. Briggs, C. Crocker, W.S. McDonald and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1981) 121.
348 J.R. Briggs, C. Crocker, W.S. McDonald and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1981) 575.
349 A. Baldy, A. Durocher, H. Rzehak and Y. Limouzin-Marie, Bull. Soc. Chim. Fr., (1981) I-67.
350 T. Yamamoto, Chem. Ind. (London), (1981) 28.
351 M.F. Rettig, R.M. Wing and G.R. Wiger, J. Am. Chem. Soc., 103 (1981) 2980.
352 S. Franks and F.R. Hartley, Inorg. Chim. Acta, 47 (1981) 235.
353 R. Usón, J. Vicente and J. Oro, Inorg. Chim. Acta, 52 (1981) 29.
354 I.A. Zakharova, D.E. Zaruma, M.E. Krasovska, J. Askas and Yu.A. Bankovskii, Russ. J. Inorg. Chem., 26 (1981) 543 (Zh. Neorg. Khim., 26 (1981) 1006).
355 H.C. Clark, A.B. Goel and S. Goel, J. Organomet. Chem., 216 (1981) C25.
356 F. Giordano and A. Vitagliano, Inorg. Chem., 20 (1981) 633.
357 A.B. Goel, S. Goel and D.G. Vanderveer, Inorg. Chim. Acta, 54 (1981) L169.
358 M.F. Rettig, D.E. Wilcox and R.S. Fleischer, J. Organomet. Chem., 214 (1981) 261.
359 A.C. Barefoot, E.W. Corcoran, R.P. Hughes, D.M. Lemal and W.D. Saunders, J. Am. Chem. Soc., 103 (1981) 970.
360 N.M. Boag, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 1051.
361 H. Lehmkuhl, R. Paul and R. Mynott, Liebigs Ann. Chem., (1981) 1139.
362 H. Hoberg and A. Herrera, Angew. Chem., Int. Ed., Engl., 20 (1981) 876 (Angew. Chem., 93 (1981) 924).

363 P. Hong, K. Sonogashira and N. Hagihara, J. Organomet. Chem., 219 (1981) 363.
364 V.A. Mukhedkar and A.J. Mukhedkar, J. Inorg. Nucl. Chem., 43 (1981) 2801.
365 M.K. Loar and J.K. Stille, J. Am. Chem. Soc., 103 (1981) 4174.
366 K. Miki, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jpn., 54 (1981) 3639.
367 N.M. Boag, G.H.M. Dias, M. Green, J.L. Spencer, F.G.A. Stone and J. Vicente, J. Chem. Soc., Dalton Trans., (1981) 1981.
368 K. Sato, O. Miyamoto, S. Inou and S. Uchida, Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai, 39 (1981) 257; Chem. Abstr., 97 (1982) 162791p.
369 M.C. Böhm, Chem. Phys., 60 (1981) 277.
370 G. Bandoli and D.A. Clemente, Acta Crystalogr., Sect. B, B37 (1981) 490.
371 J.B. Murphy, S.L. Holt and E.M. Holt, Inorg. Chim. Acta, 48 (1981) 29.
372 D.J. Olsen, PhD Thesis, Colorado State Univ., (1981), Diss. Abstr. Int. B, 42 (1981) 1022.
373 V.M. Akhmedov and V.G. Mardanov, U.S.S.R., 81,9117 (1981); Chem. Abstr., 95 (1981) 98030u.
374 K.S. Chong, S.J. Rettig, A. Storr and J. Trotter, Can J. Chem., 59 (1981) 996.
375 T. Yamamoto, J. Ishizu and A. Yamamoto, J. Am. Chem. Soc., 103 (1981) 6863.
376 W. Keim, R. Appel, A. Storeck, C. Krüger and R. Goddard, Angew. Chem., Int. Ed., Engl., 20 (1981) 116 (Angew. Chem., 93 (1981) 91).
377 R.B.A. Pardy and I. Tkatchenko, J. Chem. Soc., Chem. Commun., (1981) 49.
378 H. Lehmkuhl, R. Paul, C. Krüger, Y-H.Tsay, R. Benn and R. Mynott, Liebigs Ann. Chem. (1981) 1147.
379 I.A. Zakharova, Yu.L. Gaft, N.T. Kuznetsov, Ya.V. Salyn, L.A. Leites, A.P. Kurbakova and M.M. Kagansky, Inorg. Chim. Acta, 47 (1981) 181.
380 B. Crociani, T. Boschi and P. Uguagliati, Inorg. Chim. Acta, 48 (1981) 9.
381 A. Salzer, T. Egolf and W. von Philipsborn, J. Organomet. Chem., 221 (1981) 351.
382 L.Yu. Ukhin, N.A. Dolgopolova, L.G. Kuz'mina and Yu. T. Struchkov, J. Organomet. Chem., 210 (1981) 263.
383 V.S. Tolkunova, A.Z. Rubezhov, V.I. Bakhmutov and V.D. Vil'chevskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1991) 1826 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2228).
384 A. Zschunke, I. Nehls and H. Meyer, J. Organomet. Chem., 222 (1981) 353.
385 Y. Otani, Y. Nakamura, S. Kawaguchi, S. Okeya and T. Hinomoto, Chem. Lett., (1981) 11.
386 G. Carturan, A. Scrivanti and F. Morandini, Angew. Chem., Int. Ed., Engl., 20 (1981) 112 (Angew. Chem., 93 (1981) 103).
387 M. Calligaris, G. Nardin, G. Carturan and A. Wojcicki, Inorg. Chim. Acta, 54 (1981) L285.
388 H. Schenkluhn, R. Berger, B. Pittel and M. Zähres, Transtion Met. Chem. (Weinheim, Ger.), 6 (1981) 277,
389 H. Schenkluhn, H. Bandmann, R. Berger and E. Hübinger, Transtion Met. Chem. (Weinheim, Ger.), 6 (1981) 287.
390 J. Muzart, P. Pale and J.P. Pete, J. Chem. Soc., Chem. Commun., (1981) 668.
391 J.Y. Satoh and C.A. Horiuchi, Bull. Chem. Soc. Jpn., 54 (1981) 625.
392 B.A.W. Coller, W.R. Jackson, A. Stragalinou and J.U.G. Strauss, Aust. J. Chem., 34 (1981) 171.
393 C. Mahé, H. Patin, M-T. Van Hulle and D.H.R. Barton, J. Chem. Soc., Perkin Trans., I, (1981) 2504.
394 P. Hütter, W. Winter, D. Handschuh and W. Voelter, Liebigs Ann. Chem., (1981) 2045.
395 T. Yamamoto, O. Saito and A. Yamamoto, J. Am. Chem. Soc., 103 (1981) 5600.

396 J-E. Bäckvall and J-E. Nyström, J. Chem. Soc., Chem. Commun., (1981) 59.
397 Y. Tamaru, M. Kagotani, R. Suzuki and Z. Yoshida, J. Org. Chem., 46 (1981) 3374.
398 R.C. Larock, K. Takagi, S.S. Hershberger and M.A. Mitchell, Tetrahedron Lett., 22 (1981) 5231.
399 P.R. Clemens, R.P. Hughes and L.D. Margerum, J. Am. Chem. Soc., 103 (1981) 2428.
400 F.G. Stakem, PhD Theis, Univ. Delaware (1981), Diss. Abstr. Int. B, 42 (1981) 2842.
401 B. Åkermark, G. Åkermark, L.S. Hegedus and K. Zetterberg, J. Am. Chem. Soc., 103 (1981) 3037.
402 B. Åkermark, A. Ljungqvist and M. Panunzio, Tetrahedron Lett., 22 (1981) 1055.
403 J.C. Fiaud and J.L. Malleron, Tetrahedron Lett., 22 (1981) 1399.
404 B. Åkermark and A. Jutand, J. Organomet. Chem., 217 (1981) C41.
405 J.S. Temple, PhD Thesis, Princeton Univ. (1981), Diss. Abstr. Int. B, 42 (1981) 203.
406 A.P. Belov, N.N. Zhdanov and V.V. Lalaev, U.S.S.R., 791,727 (1980); Chem. Abstr., 94 (1981) 191691z.
407 K. Ogura, N. Shibuya and H. Iida, Tetrahedron Lett., 22 (1981) 1519.
408 R. Benn, J. Klein, A. Rufińska and G. Schroth, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 1595.
409 J. Edwin, W. Siebert and C. Krüger, J. Organomet. Chem., 215 (1981) 255.
410 K. Sato, S. Inoue and K. Watanabe, J. Chem. Soc., Perkin Trans., I, (1981) 2411.
411 Eisai Co., Ltd., Jpn. Kokai Tokkyo Koho, 80,124,736 (1980); Chem Abstr., 94 (1981) 192506e.
412 D. Walther, J. Sieler and J. Kaiser, Z. Anorg. Allg. Chem., 472 (1981) 149.
413 A. Döhring, P.W. Jolly, R. Mynott, K-P. Schick and G. Wilke, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 1198.
414 K. Miki, N. Tanaka and N. Kasai, J. Organomet. Chem., 208 (1981) 407.
415 R. Bertani, U. Belluco, P. Uguagliati and B. Crociani, Inorg. Chim. Acta, 54 (1981) L279.
416 J.M. Bruce and Y. Roshan-Ali, J. Chem. Res., S, (1981) 193.
417 D.J. Gordon, PhD Thesis, Univ. Wisconsin, Madison (1981), Diss. Abstr. Int. B, 42 (1981) 2826.
418 D.J. Gordon, R.F. Fenske, T.N. Nanninga and B.M. Trost, J. Am. Chem. Soc., 103 (1981) 5974.
419 B.M. Trost and D.M.T. Chan, J. Am. Chem. Soc., 103 (1981) 5972.
420 P.Guerts, H. Burgers, A. Van der Avoird, Chem. Phys., 54 (1981) 397.
421 G.A. Ozin, D.F. McIntosh, W.J. Power and R.P. Messmer, Inorg. Chem., 20 (1981) 1782.
422 D.H. Farrar and N.C. Payne, J. Organomet. Chem., 220 (1981) 239.
423 D.H. Farrar and N.C. Payne, Inorg. Chem., 20 (1981) 821.
424 D.H. Farrar and N.C. Payne, J. Organomet. Chem., 220 (1981) 251.
425 K.R. Grundy, Inorg. Chim. Acta, 53 (1981) L225.
426 U. Rosenthal, Z. Anorg. Allg. Chem., 482 (1981) 179.
427 I.V. Pakhomova, Yu.N. Kukushkin, E.N. Kalyukova, Sh.S. Samiev, N.V. Vorob'ev-Desyatovskii, J. Gen. Chem. USSR, 51 (1981) 1976 (Zh. Obshch. Khim., 51 (1981) 2295).
428 G. Butler, C. Eaborn and A. Pidcock, J. Organomet. Chem., 210 (1981) 403.
429 Y. Koie, S. Shinoda and Y. Saito, J. Chem. Soc., Dalton Trans., (1981) 1082.
430 J.C.T.R. Burckett-St. Laurent, P.B. Hitchcock, H.W. Kroto and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1981) 1141.
431 S. Slater and E.L. Muetterties, Inorg. Chem., 20 (1981) 1604.
432 A. Herrera, H. Hoberg and R. Mynott, J. Organomet. Chem., 222 (1981) 331.

433 N. Chaudhury and R.J. Puddephatt, Inorg. Chem., 20 (1981) 467.

434 N.M. Boag, M. Green, J.A.K. Howard, F.G.A. Stone and H. Wadepohl, J. Chem. Soc., Dalton Trans., (1981) 862.

435 R. Nast and A. Beyer, J. Organomet. Chem., 204 (1981) 267.

436 Osaka University, Jpn. Kokai Tokkyo Koho JP, 81,118,092 (1981); Chem. Abstr., 96 (1981) 106637k.

437 S. Takahashi, H. Morimoto, Y. Takai, K. Sonogashira and N. Hagihara, Mol. Cryst. Liq. Cryst., 72 (1981) 105.

438 C. Mealli, S. Midollini, S, Moneti and L. Sacconi, J. Organomet. Chem., 205 (1981) 273.

439 R.M. Pitzer, J.D. Goddard and H.F. Schaefer, J. Am. Chem. Soc., 103 (1981) 5681.

440 R. Hemmer, H.A. Brune and U. Thewalt, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 78.

441 C. Fröhlich and H. Hoberg, J. Organomet. Chem., 222 (1981) 337.

442 H. Hoberg, W. Richter and C. Fröhlich, J. Organomet. Chem., 213 (1981) C49.

443 H. Hoberg and C. Fröhlich, J. Organomet. Chem., 209 (1981) C69.

444 C. Fröhlich and H. Hoberg, J. Organomet. Chem., 204 (1981) 131.

445 P.M. Maitlis, Chem. Soc. Rev., 10 (1981) 1.

446 M.C. Boehm, Theor. Chim. Acta, 60 (1981) 233.

447 M.C. Boehm, Chem. Phys. Lett., 83 (1981) 533.

448 M.K. Kroeger and R.S. Drago, J. Am. Chem. Soc., 103 (1981) 3250.

449 S. Leutwyler, U. Even and J. Jortner, Chem. Phys., 58 (1981) 409.

450 S. Leutwyler, U. Even and J. Jortner, J. Phys. Chem., 85 (1981) 3026.

451 G. Clec'h and G. Calvarin, Mol. Cryst. Liq. Cryst., 75 (1981) 345.

452 J.H. Ammeter, L. Zoller, J. Bachmann, P. Baltzer, E. Gamp, R. Bucher and E. Deiss, Helv. Chim. Acta, 64 (1981) 1063.

453 H. Schaefer-Stahl, Synth. Met., 4 (1981) 65; Chem. Abstr., 95 (1981) 114235x.

454 K. Chhor, G. Lucazeau and C. Sourisseau, J. Raman Spectrosc., 11 (1981) 183.

455 V.T. Aleksanyan, T.I. Arsen'eva, N.N. Vyshinskii, I.I. Grinval'd and A.N. Smirnov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 227 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 299).

456 V.T. Aleksanyan, N.N. Vyshinskii, I.I. Grinval'd and T.I. Arsen'eva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 230 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 303).

457 A.B. Gardner, J. Howard, T.C. Waddington, R.M. Richardson and J. Tomkinson, Chem. Phys., 57 (1981) 453.

458 Yu.A. Andrianov, O.N. Druzhkov, A.S. Smirnov and V.A. Dodonov, J. Gen. Chem. USSR, 51 (1981) 2161 (Zh. Obshch. Khim., 51 (1981) 2508).

459 E.G. Perevalova, M.D. Reshetova and D.A. Lemenovskii, Koord. Khim., 7 (1981) 1340.

460 J. Grobe, B.H. Schneider and H. Zimmermann, Z. Anorg. Allg. Chem., 481 (1981) 107.

461 F.H. Köhler, K.H. Doll, E. Fladerer and W.A. Geike, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 126.

462 J.L. Robbins, Energy Res. Abstr., 6 (1981) Abstr. No. 20584; Chem. Abstr., 96 (1982) 6846j.

463 H. Nakamura, H. Goozi, Y. Hara and H. Osada, Kogyo Kayaku, 42 (1981) 345; Chem. Abstr., 97 (1982) 94912b.

464 E. Lindner, F. Bouachir and W. Hiller, J. Organomet. Chem., 210 (1981) C37.

465 H. Werner and T.N. Khac, Z. Anorg. Allg. Chem., 475 (1981) 241.

466 H. Werner, T. Ngo-Khac, C. Friebel, P. Köhler and D. Reinen, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 322.

467 N. Kuhn and M. Winter, Chem.-Ztg., 105 (1981) 376.

468 S.N. Titova, V.T. Bychkov, G.A. Domrachev, G.A. Razuvaev, L.N. Zakharov, G.G. Alexandrov and Yu.T. Struchkov, Inorg. Chim. Acta, 50 (1981) 71.
469 F. Mathey and F. Mercier, Tetrahedron Lett., 22 (1981) 319.
470 E.K. Barefield, D.A. Krost, D.S. Edwards. D.G. VanDerveer, R.L. Trytko, S.P. O'Rear and A.N. Williamson, J. Am. Chem. Soc., 103 (1981) 6219.
471 H. Lehmkuhl, C. Naydowski, R. Benn and A. Rufińska, J. Organomet. Chem., 216 (1981) C41.
472 U. Koelle and H. Werner, J. Organomet. Chem., 221 (1981) 367.
473 R.J. Gale and R. Job, Inorg. Chem., 20 (1981) 40.
474 F.H. Köhler, U. Zenneck, J. Edwin and W. Siebert, J. Organomet. Chem., 208 (1981) 137.
475 T. Madach and H. Vahrenkamp, Chem. Ber., 114 (1981) 505.
476 P.R. Sharp, K.N. Raymond, J.C. Smart and R.J. McKinney, J. Am. Chem. Soc., 103 (1981) 753.
477 H. Werner and T.N. Khac, Z. Anorg. Allg. Chem., 479 (1981) 134.
478 A.B. Goel, S. Goel, D. Van Der Veer and H.C. Clark, Inorg. Chim. Acta, 53 (1981) L117.
479 F.S. Stephens and R.S. Vagg, Inorg. Chim. Acta, 51 (1981) 163.
480 Z. Janoušek, J. Plešek, S. Heřmának, K. Baše, L.J. Todd and W.F. Wright, Coll. Czech. Chem. Commun., 46 (1981) 2818.
481 G.A. Kukina, S.V. Sergienko, M.A. Porai-Koshits, K. Baše and I.A. Zakharova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 2369 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2838).
482 D.N. Cox, D.M.P. Mingos and R. Hoffmann, J. Chem. Soc., Dalton Trans., (1981) 1788.
483 S.K. Boocock, N.N. Greenwood, J.D. Kennedy, W.S. McDonald and J. Staves, J. Chem. Soc., Dalton Trans., (1981) 2573.
484 S.K. Boocock, N.N. Greenwood, M.J. Hails, J.D. Kennedy and W.S. McDonald, J. Chem. Soc., Dalton Trans., (1981) 1415.
485 J. Tsuji, Kagaku, Zokan (Kyoto), (1981) 47; Chem. Abstr., 95 (1981) 96892c.
486 J. Tsuji, Pure Appl. Chem., 53 (1981) 2371.
487 B.M. Trost, Pure Appl. Chem., 53 (1981) 2357.
488 D.C. Bailey and S.H. Langer, Chem. Rev., 81 (1981) 109.
489 G. van Koten and K. Vrieze, Rec., 100 (1981) 129.
490 B.A. Dolgoplosk, Kinet. Catal., 22 (1981) 619 (Kinet. Katal., 22 (1981) 807).
491 K. Tatsumi and M. Tsutsui, J. Mol. Catal., 13 (1981) 117.
492 V.A. Semikolenov, V.A. Likholobov and Yu.I. Ermakov, Kinet. Catal., 22 (1981) 804 (Kinet. Katal., 22 (1981) 1026).
493 V.A. Semikolenov, V.A. Likholobov, P.A. Zhdan, A.I. Nizovskii, A.P. Shepelin, E.M. Moroz, S.V. Bogdanov and Yu.I. Ermakov, Kinet. Catal., 22 (1981) 976 (Kinet. Katal., 22 (1981) 1247).
494 C. Čaplar, G. Comisso and V. Šunjič, Synthesis (1981) 85.
495 L.A. Neiman, Russ. Chem. Rev., 50 (1981) 109 (Usp. Khim., 50 (1981) 196).
496 E.L. Muetteries, Inorg. Chim. Acta, 50 (1981) 1.
497 O.V. Gritsenko, A.A. Bagatur'yants, I.I. Moiseev and I.V. Kalechits, Kinet. Catal., 22 (1981) 1136 (Kinet. Katal., 22 (1981) 1431).
498 O.V. Gritsenko, A.A. Bagatur'yants, I.I. Moiseev, V.B. Kazanskii and I.V. Kalechits, Kinet. Catal., 22 (1981) 266 (Kinet. Katal., 22 (1981) 354).
499 E.E. Nifant'ev, A.T. Teleshev, M.P. Koroteev, S.A. Ermishkina and E.M. Abbasov, Koord. Khim., 7 (1981) 311.
500 A.S. Berenblyum, S.L. Mund, L.G. Danilova and I.I. Moiseev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 686 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 905).
501 V. Kadlec and H. Kadlecova, Czech. CS 190,174 (1981); Chem. Abstr., 96 (1982) 122182p.

502 G.V. Tsintsadze, E.D. Getsadze, E.F. Litvin and L.Kh. Freidlin, Soobshch. Akad. Nauk Gruz. SSR, 104 (1981) 57; Chem. Abstr., 96 (1982) 180693s.

503 F.R. Hartley, J.A. Davies and S.G. Murray, Brit. UK Pat. Appl., 2,058,074 (1981); Chem. Abstr., 95 (1981) 176529e.

504 J.A. Davies, F.R. Hartley, S.G. Murray and G. Marshall, J. Mol. Catal., 10 (1981) 171.

505 V.A. Semikolenov, V.A. Likholobov and Yu.I. Ermakov, Kinet. Catal., 22 (1981) 1174 (Kinet. Katal., 22 (1981) 1475).

506 A.S. Berenblyum, S.L. Mund, T.P. Goranskaya and I.I. Moiseev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 2041 (Izv. Akad. Nauk SSSR, Ser. Chem., (1981) 2472).

507 A.S. Berenblyum, T.V. Turkova and I.I. Moiseev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1918) 361 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 514).

508 L.I. Gvinter, V.Sh. Fel'dblyum, L.N. Suvorova and L.Kh. Freidlin, U.S.S.R., 791,715 (1980); Chem. Abstr., 94 (1981) 191786j.

509 E.E. Nifant'ev, S.A. Rumyantseva, M.P. Koroteev E.M. Abbasov, A.T. Teleshev, V.A. Pavlov and E.I. Klabunovskii, Phosphorus, Sulphur, 12 (1981) 27.

510 L.F. Godunova, E.S. Levitina, E.I. Karpeiskaya and E.I. Klabunovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 595 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 815).

511 G. Giacomelli, L. Bertero and L. Lardicci, Tetrahedron Lett., 22 (1981) 883.

512 Y-J. Li and Y.Y. Jiang, Ts'ui Hua Hsueh Pao, 2 (1981) 42; Chem. Abstr., 95 (1981) 96618t.

513 Y. Li and Y. Jiang, Cuihua Xeubao, 2 (1981) 146; Chem. Abstr., 95 (1981) 203235q.

514 C. Pan, P. Feng and B. Liang, Cuihua Xuebao, 2 (1981) 152; Chem. Abstr., 96 (1981) 6106t.

515 C. Andersson and R. Larsson, JAOCS, J. Am. Oil Chem. Soc., 58 (1981) 675.

516 H. Yukimasa, H. Sawai and T. Takizawa, Makromol. Chem., 182 (1981) 1385.

517 R.S. Drago, E.D. Nyberg and A.G. El A'mma, Inorg. Chem., 20 (1981) 2461.

518 L.P. Shuikina, A.I. Él'natanova, L.S. Kovaleva, O.P. Parenago and V.M. Frolov, Kinet. Katal., 22 (1981) 177.

519 Y. Zhou and J. Yiang, Cuihua Xuebao, 2 (1981) 233; Chem. Abstr., 96 (1982) 41542d.

520 E.F. Litvin, L.Kh. Freidlin, L.F. Krokhmaleva, L.M. Kozlova and N.M. Nazarova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 592 (Izv. Akad. SSSR, Ser. Khim., (1981) 811).

521 V.M. Frolova, O.P. Parenago, G.N. Bondarenko, L.S. Kovaleva, A.I. El'natanova, L.P. Shuikina, G.M. Cherkashin and E.Ya. Mirskaya, Kinet. Catal., 22 (1981) 1072 (Kinet. Katal., 22 (1981) 1356).

522 V.M. Frolov, O.P. Parenago, L.P. Shuikina and G.M. Cherkashin, React. Kinet. Catal. Lett., 16 (1981) 115.

523 N.L. Holy and S.R. Shelton, Tetrahedron, 37 (1981) 25.

524 B. Bogdanović, P. Göttsch and M. Rubach, J. Mol. Catal., 11 (1981) 135.

525 D.V. Sokol'skii, V.F. Pechenkina and B.Zh. Zhanabaev, U.S.S.R., 787,403 (1980); Chem. Abstr., 94 (1981) 174614j.

526 T.K. Banerjee and D. Sen, J. Chem. Technol. Biotechnol., 31 (1981) 676; Chem. Abstr., 96 (1982) 199196d.

527 J.A. Patterson, W.C. Crawford and J.R. Wilson, U.S. 4,233,244 (1980); Chem. Abstr., 94 (1981) 83744k.

528 S.D. Kushch, É.N. Izakovich, M.L. Khidekel' and V.V. Strelets, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1201 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1500).

529 M.V. Klyuev and M.L. Khidekel, J. Org. Chem. USSR, 17 (1981) 2316 (Zh. Org. Khim., 17 (1981) 2595).

530 Y. Akita and A. Ohta, Heterocycles, 16 (1981) 1325.

531 P. Four and F. Guibe, J. Org. Chem., 46 (1981) 4439.

532 F. Guibe and Y. Saint M'Leux, Tetrahedron Lett., 22 (1981) 3591.

533 B.M. Trost and P.L. Ornstein, Tetrahedron Lett., 22 (1981) 3463.

534 E.S. Rudakov, V.P. Tret'yakov, S.A. Mitchenko and A.V. Bogdanov, Dokl. Phys. Chem., 259 (1981) 712 (Dokl. Akad. Nauk SSSR, 259 (1981) 899 [Phys. Chem.]).

535 J. Sobezak and J.J. Ziółkowski, J. Mol. Catal., 13 (1981) 11.

536 H. Mimoun, Pure Appl. Chem., 53 (1981) 2389.

537 R.W. Dale and J.J. Rooney, PCT Int. Appl., 80 02,023 (1980); Chem. Abstr., 94 (1981) 120865y.

538 A.N. Astanina, C.S. Li, A.F. Gamidov and A.P. Rudenko, Azerb. Khim. Zh., (1981) 72; Chem. Abstr., 96 (1982) 180720y.

539 G. Lu, W. Liu, Y. Qi, Y. Zhang, R. Wang and Q. Bai, Huadong Huagong Xueyuan Xuebao, (1981) 13; Chem. Abstr., 97 (1982) 94402k.

540 A.I. Chebaksarov, V.F. Shvets and M.G. Makarov, Deposited Doc., (1981) VINITI, 1512-81; Chem. Abstr., 96 (1982) 217025d.

541 A.V. Devekki, D.V. Mushenko and V.S. Fedorov, J. Org. Chem. USSR, 17 (1981) 2250 (Zh. Org. Khim., 17 (1981) 2519).

542 M.N. Vargaftik, V.P. Zagorodnikov and I.I. Moiseev, Kinet. Catal., 22 (1981) 743 (Kinet. Katal., 22 (1981) 951).

543 N.I. Kuznetsova, V.A. Likholobov and Yu.I. Ermakov, Kinet. Catal., 22 (1981) 133 (Kinet. Katal., 22 (1981) 157).

544 Kh.M. Minachev, N.Ya. Usachev, Ya.I. Isakov, A.P. Rodin and V.P. Kalinin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 199 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 267).

545 Kh.M. Minachev, N.Ya. Usachev, Ya.I. Isakov, A.P. Rodin and V.P. Kalinin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 514 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 724).

546 P.R. Stapp, U.S. 4,237,071 (1980); Chem. Abstr., 94 (1981) 120872y.

547 M. Cihova, M. Hrusovsky, J. Voitko and K.I. Matveev, React. Kinet. Catal. Lett., 16 (1981) 383.

548 Asahi Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho JP 81 99,434 (1981); Chem. Abstr., 96 (1982) 34569q.

549 H. Ogawa, H. Fujinami, K. Taya and S. Teratini, J. Chem. Soc., Chem. Commun., (1981) 1274.

550 G.A. Tolstikov, M.S. Miftakhov and F.A. Valeev, J. Org. Chem. USSR, 17 (1981) 1282 (Zh. Org. Khim., 17 (1981) 1441).

551 G.A. Tolstikov, M.S. Miftakhov and F.A. Valeev, J. Org. Chem. USSR, 17 (1981) 2000 (Zh. Org. Khim., 17 (1981) 2241).

552 T. Mandai, K. Nishikawa, H. Yamaguchi, M. Kawada and J. Otera, Chem. Lett., (1981) 473.

553 M. Ochiai, M. Arimoto and E. Fujita, Tetrahedron Lett., 22 (1981) 1115.

554 S. Takano, C. Kasahara and K. Ogasawara, J. Chem. Soc., Chem. Commun., (1981) 637.

555 J. Vojtko, A. Kaszonyi, M. Čihová and M. Hrušovský, Coll. Czech. Chem. Commun., 46 (1981) 573.

556 E.G. Zhizhina, N.B. Shitova and K.I. Matveev, Kinet. Catal., 22 (1981) 1153 (Kinet. Katal., 22 (1981) 1451).

557 J.M. Bregeault and H. Mimoun, Nouv. J. Chim., 5 (1981) 287.

558 M.A. Andrews and K.P. Kelly, J. Am. Chem. Soc., 103 (1981) 2894.

559 L. Saussine, J.P. Laloz and H. Mimoun, Fr. Demande 2,450,802 (1980); Chem. Abstr., 94 (1981) 208348t.

560 S.F. Politanskii, A.M. Shkitov, V.V. Kharlamov, Kh.M. Minachev, I.I. Moiseev and O.M. Nefedov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1180 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1479).

561 Kh.M. Minachev, O.M. Nefedov, V.V. Kharlamov, S.Yu. Panov and S.F. Politanskii, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1191 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1490).
562 S.F. Politanskii, A.M. Shkitov, E.S. Shpiro, G.V. Antoshin, Kh.M. Minachev, I.I. Moiseev and O.M. Nefedov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1186 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1485).
563 J. Tsuji, K. Sakai, H. Nagashima and I. Shimizu, Tetrahedron Lett., 22 (1981) 131.
564 S.A. Deiko, A.S. Erokhin and A.K. Yatsimirskii, Kinet. Catal., 22 (1981) 459 (Kinet. Katal., 22 (1981) 613).
565 A.K. Yatsimirsky, A.D. Ryabov, V.P. Zagorodnikov, I.K. Sakodinskaya, O.I. Kavetskaya and I.V. Berezin, Inorg. Chim. Acta, 48 (1981) 163.
566 V.P. Zagorodnikov, A.D. Ryabov and A.K. Yatsimirskii, Kinet. Catal., 22 (1981) 113 (Kinet. Katal., 22 (1981) 132).
567 R. Hamilton, T.R.B. Mitchell and J.J. Rooney, J. Chem. Soc., Chem. Commun., (1981) 456.
568 R.V. Lindsey and W.W. Prichard, Eur. Pat. Appl. 31,729 (1981); Chem. Abstr., 95 (1981) 150412m.
569 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 81,123,978 (1981); Chem. Abstr., 96 (1982) 35066k.
570 R.V. Lindsey and W.W. Pritchard, U.S. US 4,298,531 (1981); Chem. Abstr., 96 (1982) 68800y.
571 Japan Synthetic Rubber Co., Ltd., Jpn. Kokai Tokkyo Koho 80 98,138 (1980); Chem. Abstr., 94 (1981) 156333n.
572 Japan Synthetic Rubber Co., Ltd., Jpn. Kokai Tokkyo Koho 80 98,135; Chem. Abstr., 94 (1981) 156334p.
573 N.K.K.K. Toa, Jpn. Kokai Tokkyo Koho 80 69,540 (1980); Chem. Abstr., 94 (1981) 30205d.
574 I.P. Beletskaya and D.I. Makhon'kov, Russ. Chem. Rev., 50 (1981) 534 (Usp. Khim., 50 (1981) 1007).
575 E.S. Rudakov and V.L. Dobachev, Dokl. Chem., 261 (1981) 508 (Dokl. Akad. Nauk SSSR, 261 (1981) 641 [Chem.]).
576 L.M. Stock, K. Tse, J.L. Vorvick and S.A. Walstrum, J. Org. Chem., 46 (1981) 1757.
577 A.D. Ryabov, S.A. Dieko, A.K. Yatsimirsky and I.V. Berezin, Tetrahedron Lett., 22 (1981) 3793.
578 T. Itahara, J. Chem. Soc., Chem. Commun., (1981) 254.
579 O. Maruyama, Y. Fujiwara and H. Taniguchi, Bull. Chem. Soc. Jpn., 54 (1981) 2851.
580 L.A. Katsman, M.N. Vargaftik, M.K. Starchevskii A.A. Grigor'ev and I.I. Moiseev, Kinet. Catal., 22 (1981) 739 (Kinet. Katal., 22 (1981) 947).
581 M.K. Starchevskii, M.N. Vargaftik and I.I. Moiseev, Kinet. Catal., 22 (1981) 467 (Kinet. Katal., 22 (1981) 622).
582 Y. Tamaru, K. Inoue, Y. Yamada and Z. Yoshida, Tetrahedron Lett., 22 (1981) 1801.
583 O.T. Onsager, Stud. Surf. Sci. Catal., 7 (Pt. B, New Horiz. Catal.), (1981) 1510; Chem. Abstr., 95 (1981) 203020r.
584 H. Nagashima and J. Tsuji, Chem. Lett., (1981) 1171.
585 E. Mincione, A. Sirna and D. Covini, J. Org. Chem., 46 (1981) 1010.
586 T. Itahara, J. Chem. Soc., Chem. Commun., (1981) 859.
587 T. Hayashi, Y. Kawabata, T. Isoyama and I. Ogata, Bull. Chem. Soc. Jpn., 54 (1981) 3438.
588 H.C. Clark and J.A. Davies, J. Organomet. Chem., 213 (1981) 503.
589 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho, 80,164,640 (1980); Chem. Abstr., 95 (1981) 97058x.
590 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho, 80,100,331 (1981); Chem. Abstr., 94 (1981) 30191w.

591 J. Kiji, T. Okano, K. Nakajima, K. Odagiri and H. Konishi, Sekiyu Gakkaishi, 24 (1981) 393; Chem. Abstr., 96 (1982) 68280d.
592 J.J. Mrowca, U.S. 4,257,973 (1981); Chem. Abstr., 95 (1981) 97089h.
593 C.U. Pittman and Q.Y. Ng, U.S. 4,258,206 (1981); Chem. Abstr., 94 (1981) 208332h.
594 G. Cavinato and L. Toniolo, J. Mol. Catal., 10 (1981) 161.
595 S.A. Butter, U.S. 4,245,115 (1981); Chem. Abstr., 94 (1981) 156348w.
596 P. Haelg, G. Consiglio and P.Pino, Helv. Chim. Acta, 64 (1981) 1865.
597 T.F. Murray, E.G. Samsel, V. Varma and J.R. Norton, J. Am. Chem. Soc., 103 (1981) 7520.
598 Nippon Synthetic Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho 81 15,242 (1981); Chem. Abstr., 94 (1981) 208566n.
599 H.S. Kesling and L.R. Zehner, US 4,236,023 (1981); Chem. Abstr., 94 (1981) 156342q.
600 Nippon Synthetic Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho 81 22,750 (1981); Chem. Abstr., 94 (1981) 191969w.
601 Nippon Synthetic Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho 81 22,749 (1981); Chem. Abstr., 94 (1981) 191970q.
602 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho, 81 71,039 (1981); Chem. Abstr., 95 (1981) 186892g.
603 M. Katao, K. Kudo and N. Sugita, Bull. Inst. Chem. Res., Kyoto Univ., 59 (1981) 72; Chem. Abstr., 95 (1981) 186300n.
604 J.K. Stille, U.S. 4,259,519 (1981); Chem. Abstr., 95 (1981) 24299s.
605 G.M. Shulyakovskii, L.A. Il'ina and O.N. Temkin, Zh. Prikl. Khim. (Leningrad), 54 (1981) 2739; Chem. Abstr., 96 (1982) 103595j.
606 D. Valentine, J.W. Tilley and R.A. Le Mahieu, J. Org. Chem., 46 (1981) 4614.
607 M. Santra and S.K. Paliit, Indian J. Technol., 19 (1981) 464; Chem. Abstr., 96 (1981) 51926w.
608 T. Takahashi, H. Ikeda and J. Tsuji, Tetrahedron Lett., 22 (1981) 1363.
609 M. Mori, M. Ishikura, T. Ikeda and Y. Ban, Heterocycles, 16 (1981) 1491.
610 G.D. Pandey and K.P. Tiwari, Tetrahedron, 37 (1981) 1213.
611 M. Tanaka, Bull. Chem. Soc. Jpn., 54 (1981) 637.
612 T. Kobayashi and M. Tanaka, J. Chem. Soc., Chem. Commun., (1981) 333.
613 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho 81 02,925 (1981); Chem. Abstr., 95 (1981) 6827h.
614 M. Tanaka, Synthesis, (1981) 47.
615 N.A. Bumagin, I.G. Bumagina, A.N. Kashin and I.P. Beletskaya, Dokl. Chem., 261 (1981) 532 (Dokl. Akad. Nauk SSSR, 261 (1981) 1141 [Chem.]).
616 T. Kobayashi and M. Tanaka, J. Organomet. Chem., 205 (1981) C27.
617 M. Tanaka, M. Koyanagi and T. Kobayashi, Tetrahedron lett., 22 (1981) 3875.
618 K. Kikukawa, K. Kono, K. Nagira, F. Wada and T. Matsuda, J. Org. Chem., 46 (1981) 4413.
619 N. Miyaura and A. Suzuki, Chem. Lett., (1981) 879.
620 D.E. Bergstrom, A.J. Brattesani, M.K. Ogawa and M.J. Schweickert, J. Org. Chem., 46 (1981) 1423.
621 J. Gauthier-Lafaye and R. Perron, Eur. Pat. Appl. EP 37,354 (1981); Chem. Abstr., 96 (1981) 34586t.
622 J. Gauthier-Lafaye and R. Perron, Eur. Pat. Appl. EP 39,652 (1981); Chem. Abstr., 96 (1982) 68351c.
623 J. Gauthier-Lafaye and R. Perron, Eur. Pat. Appl. EP 39,653 (1981); Chem. Abstr., 96 (1982) 85068h.
624 J. Gauthier-Lafaye and R. Perron, Eur. Pat. Appl. EP 18,927 (1980); Chem. Abstr., 94 (1981) 156327p.
625 J.E. Hallgren and G.M. Lucas, J. Organomet. Chem., 212 (1981) 135.
626 J.E. Hallgren, G.M. Lucas and R.O. Matthews, J. Organomet. Chem., 204 (1981) 135.

627 J.E. Hallgren U.S. 4,260,802 (1981); Chem. Abstr., 95 (1981) 61798z.

628 V.I. Manov-Yuvenskii and B.K. Nefedov, Russ. Chem. Rev., 50 (1981) 470 (Usp. Khim., 50 (1981) 889).

629 B.K. Nefedov, V.I. Manov-Yuvenskii, Yu.I. Dergunov, A.I. Rysikhin and A.L. Chimishkyan, Ger. Offen. 2,941,141 (1981); Chem. Abstr., 95 (1981) 61760f.

630 Mitsui Toatsu Chemicals, Inc., Jpn. Kokai Tokkyo Koho JP 81,138,159 (1981); Chem. Abstr., 96 (1982) 52875r.

631 Mitsui Toatsu Chemicals, Inc., Jpn. Kokai Tokkyo Koho 81 68,653 (1981); Chem. Abstr., 95 (1981) 151423c.

632 B.K. Nefedov, V.I. Manov-Yuvenskii, Yu.I. Dergunov, A.I. Rysikhin and A.L. Chimishkayan, U.S. 4,267,070 (1981); Chem. Abstr., 95 (1981) 150162e.

633 K. Schwetlick, K. Unverferth, H. Tietz and M. Pfeifer, Ger. (East), 146,043 (1981); Chem. Abstr., 95 (1981) 115032r.

634 K. Schwetlick, K. Unverferth, H. Tietz and M. Pfeifer, Ger. (East), 145,631 (1980); Chem. Abstr., 95 (1981) 132465b.

635 V.I. Manov-Yuvenskii and B.K. Nefedov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 816 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1055).

636 Mitsui Toatsu Chemicals Inc., Jpn. Kokai Tokkyo Koho JP, 81 61,342 (1981); Chem. Abstr., 96 (1982) 7206n.

637 A.L. Lapidus, V.I. Manov-Yuvenskii and K.B. Petrovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 2282 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2743).

638 A.N. Niyazov, B.K. Nefedov, Kh.O. Khoshdurdyev and V.I. Manov-Yuvenskii, Dokl. Chem., 258 (1981) 267 (Dokl. Akad. Nauk SSSR, 258 (1981) 1120 [Chem.]).

639 R. Becker, J. Grolig and C. Rasp, Ger. Offen. 2,903,950 (1980); Chem. Abstr., 94 (1981) 85125e.

640 A.N. Niyazov, B.K. Nefedov, Kh.O. Khoshdurdyev and V.I. Manov-Yuvenskii, Dokl. Chem., 258 (1981) 242 (Dokl. Akad. Nauk SSSR, 258 (1981) 898).

641 A.L. Lapidus, A.F. Lunin, S.D. Pirozhkov, N.B. Leonchik, P. Neittsel' and K. Shvetlik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1068 (Izv. Akad. Nauk SSSR., Ser. Khim., (1981) 1339).

642 R. Becker, J. Grolig and C. Rasp, Ger. Offen. 2,908,251 (1980); Chem. Abstr., 94 (1981) 65349f.

643 R. Becker, J. Grolig, C. Rasp and G. Stammann, Ger. Offen. 2,908,252 (1980); Chem. Abstr., 94 (1981) 65333w.

644 W.E. Martin and M.F. Farona, J. Organomet. Chem., 206 (1981) 393.

645 C.K. Rofer-De Poorter, Chem. Rev., 81 (1981) 447.

646 W. Keim, M. Berger, A. Eisenbeis, J. Kadelka and J. Schlupp, J. Mol. Catal., 13 (1981) 95.

647 Mitsubishi Gas Chemical Co., Inc., Jpn. Kokai Tokkyo Koho 80,141,426 (1980); Chem. Abstr., 94 (1981) 139228q.

648 H. Alper, C.P. Perera and F.R. Ahmed, J. Am. Chem. Soc., 103 (1981) 1289.

649 M.F. Semmelhack and S.J. Brickner, J. Am. Chem. Soc., 103 (1981) 3945.

650 N.A. Moldavskaya, N.K. Skvortsov, V.O. Reikhsfel'd, V.E. Aleshin, E.D. Ageeva, N.F. Voloshina and Y.N. Kukushkin, U.S.S.R. SU 891,676 (1981); Chem. Abstr., 96 (1982) 199871v.

651 N.A. Moldavskaya, Yu.V. Chebrakov, N.K. Skvortsov, L.V. Krysenko, G.B. Avetikyan, V.O. Reikhsfel'd and Yu.N. Kukushkin, J. Gen. Chem. USSR, 51 (1981) 1959 (Zh. Obshch. Khim., 51 (1981) 2279).

652 N.A. Moldavskaya, N.K. Skvortsov, N.F. Voloshina and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 51 (1981) 1379 (Zh. Obshch. Khim., 51 (1981) 1261).

653 N.A. Moldavskaya, G.G. Peshkova, G.N. Sedova, N.K. Skvortsov and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 51 (1981) 2287 (Zh. Obshch. Khim., 51 (1981) 2654).

654 V.V. Kaverin, I.M. Salimgareeva, I.V. Kovaleva and V.P. Yur'ev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1741 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2119).

655 M. Brenndoerfer, A. Brune and R. Hemmer, Ger. Offen. 3,002,238 (1981); Chem. Abstr., 95 (1981) 187411m.

656 M.G. Voronkov, N.N. Vlasova and S.A. Bol'shakova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 148 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 170).

657 K. Yamamoto, Y. Kiso, R. Ito, K. Tamao and M. Kumada, J. Organomet. Chem., 210 (1981) 9.

658 Chisso Corp., Jpn Kokai Tokkyo Koho 80,145,693 (1980); Chem. Abstr., 94 (1981) 175250z.

659 I. Koga, Y. Terui, M. Oghushi, T. Kitahara and K. Watanabe, U.S. 4,292,433 (1981); Chem. Abstr., 95 (1982) 204149b.

660 I.E. Saratov, I.V. Shpak and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 51 (1981) 322 (Zh. Obshch. Khim., 51 (1981) 396).

661 L.I. Kopylova, S.E. Korotsova, L.N. Sobenina, R.N. Nesterenko, M.V. Sigalov, A.I. Mikhaleva, B.A. Trofimov and M.G. Voronkov, J. Gen. Chem. USSR, 51 (1981) 1522 (Zh. Obshch. Khim., 51 (1981) 1778).

662 A.V. Podol'skii, T.G. Cherezova and V.P. Kachalkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 318 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 404).

663 Y. Chen, J. Liu, Y. Lin, J. Ni, J. You, C. Xiao and Y. Wang, Wuhan Daxue Xuebao, Ziran Kexueban (1981) 61; Chem. Abstr., 97 (1982) 7147q.

664 V.D. Sheludyakov, V.I. Zhun'. S.D. Vlasenko, V.N. Bochkarev, T.F. Slyusarenko, A.V. Kisin, V.N. Nosova, G.N. Turkel'taub and E.A. Chernyshev, J. Gen. Chem. USSR, 51 (1981) 1739 (Zh. Obshch. Khim., 51 (1981) 2022).

665 M.G. Voronkov, S.A. Kirpichenko, V.V. Keiko and E.O. Tseitlina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 152 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 174).

666 A.A. Zhdanov and T.V. Astapova, Vysokomol. Soedin., Ser. A, 23 (1981) 626; Chem. Abstr., 94 (1981) 209261w.

667 E.M. Movsumzade, Azerb. Khim. Zh., (1981) 90; Chem. Abstr., 95 (1981) 220535e.

668 M. Hatakana and S. Nagashima, U.S. 4,256,616 (1981); Chem. Abstr., 95 (1981) 8596f.

669 B.A. Ashby and F.J. Modic, Fr. Demande FR 2,474,890 (1981); Chem. Abstr., 96 (1982) 124298e.

670 L. Wang and Y. Jiang, Cuihua Xuebao, 2 (1981) 236; Chem. Abstr., 96 (1982) 68095x.

671 B. Marciniec, Z.W. Kornetka and W. Urbaniak, J. Mol. Catal., 12 (1981) 221.

672 V.S. Brovko, N.K. Skvortsov and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 51 (1981) 335 (Zh. Obshch. Khim., 51 (1981) 411).

673 T.N. Zaslavskaya, N.A. Filippov and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 51 (1981) 95 (Zh. Obshch. Khim., 51 (1981) 107).

674 L.I. Kopylova, M.V. Sigalov, É.N. Satsuk, M. Čapka, V. Chvalovsky, V.P. Pukhnarevich, É.Ya. Lukevits and M.G. Voronkov, J. Gen. Chem. USSR, 51 (1981) 311 (Zh. Obshch. Khim., 51 (1981) 385).

675 H. Watanabe, M. Kobayashi, M. Saito and Y. Nagai, J. Organomet. Chem., 216 (1981) 149.

676 H. Watanabe, M. Saito, N. Sutou and Y. Nagai, J. Chem. Soc., Chem. Commun., (1981) 617.

677 Toshiba Silicone Co., Ltd., Jpn. Kokai Tokkyo Koho JP 81,122,837 (1981); Chem. Abstr., 96 (1982) 162931p.

678 H. Matsumoto, K. Shono and Y. Nagai, Org. Prep. Proced. Int., 13 (1981) 118.

679 H. Matsumoto, K. Shono and Y. Nagai, J. Organomet. Chem., 208 (1981) 145.

680 M. Ishikawa, H. Sugisawa, O. Harata and M. Kumada, J. Organomet. Chem., 217 (1981) 43.

681 E.V. Chistova, V.N. Alyasov, R.F. Galiullina, V.P. Maslennikov, V.A. Dodonov and Yu.A. Aleksandrov, J. Gen. Chem. USSR, 51 (1981) 899 (Zh. Obshch. Khim., 51 (1981) 1078).

682 M. Suda, Synthesis, (1981) 714.

683 W.H. Tamblyn, S.R. Hoffmann and M.P. Doyle, J. Organomet. Chem., 216 (1981) C64.

684 A.K. Chakraborti, B. Saha and U.R. Ghatak, Indian J. Chem., Sect. B, 20B (1981) 911.

685 H. Matsuda and H. Kanai, Chem. Lett., (1981) 395.

686 J. Tsuji, K. Sato and H. Nagashima, Chem. Lett., (1981) 1169.

687 H. Nagashima, K. Sato and J. Tsuji, Chem. Lett., (1981) 1605.

688 J-E. Bäckvall and O.S. Andell, J. Chem. Soc., Chem. Commun., (1981) 1098.

689 S.M. Brailovskii, O.N. Temkin, V.S. Shestakova and A.F. Kuperman, Kinet. Catal., 22 (1981) 1149 (Kinet. Katal., 22 (1981) 1446).

690 G.V. Isagulyants, K.M. Gitis, L.I. Kovalenko, A.A. Greish, V.N. Kornyshev, M.I. Rozengart and I.N. Nikiforova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 277 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 357).

691 G. Giacomelli, L. Bertero, L. Lardicci and R. Menicagli, J. Org. Chem., 46 (1981) 3707.

692 F. Camacho Rubio, S. Delgado Diaz, R. Arvelo Alvarez, D. Trujillo and J. Del Castillo, Ing. Quim. (Madrid), 13 (1981) 159; Chem. Abstr., 95 (1981) 132022e.

693 M. Cihova, J. Vojtko, M. Hrusovsky and P. Marek, Petrochemia, 21 (1981) 72; Chem. Abstr., 96 (1982) 103574b.

694 A. Sen and T-W. Lai, Inorg. Chem., 20 (1980) 4036.

695 Takasago Perfumery Co., Ltd., Jpn. Kokai Tokkyo Koho 80,162,730 (1980); Chem. Abstr., 95 (1981) 25331h.

696 N. Gragor and P.M. Henry, J. Am. Chem. Soc., 103 (1981) 681.

697 P.A. Grieco, P.A. Tuthill and H.L. Sham, J. Org. Chem., 46 (1981) 5005.

698 A. Reitz, M.A. Avery, M.S. Verlander amd M. Goodman, J. Org. Chem., 46 (1981) 4859.

699 T. Mandai, S. Hashio, J. Goto and M. Kawada, Tetrahedron Lett., 22 (1981) 2187.

700 A.T. Menyailo, M.V. Pospelov, N.N. Kirilash and I.M. Krikun, Neftekhimiya, 21 (1981) 681; Chem. Abstr., 96 (1982) 68268f.

701 Teijin Ltd., Jpn. Kokai Tokkyo Koho 81 15,216 (1981); Chem. Abstr., 95 (1981) 42488g.

702 B.M. Trost and T.A. Runge, J. Am. Chem. Soc., 103 (1981) 7550.

703 B.M. Trost and T.A. Runge, J. Am. Chem. Soc., 103 (1981) 2485.

704 B.M. Trost and T.A. Runge, J. Am. Chem. Soc., 103 (1981) 7559.

705 Sumitomo Chemical Co., Ltd., Jpn. Kokai Tokkyo Koho 81 34,691 (1981); Chem. Abstr., 95 (1981) 169436u.

706 S.W. McCombie, Eur. Pat. Appl. 13,633 (1980); Chem. Abstr., 94 (1981) 103351k .

707 B.T. Golding, C. Pierpoint and R. Aneja, J. Chem. Soc., Chem. Commun., (1981) 1030.

708 M. Takahashi, N. Ishii, H. Suzuki, Y. Moro-Oka and T. Ikawa, Chem. Lett., (1981) 1361.

709 Y. Tamaru, M. Kagotani and Z. Yoshida, Tetrahedron Lett., 22 (1981) 4245.

710 Y. Sasson, A. Zoran and J. Blum, J. Mol. Catal., 11 (1981) 293.

711 H. Alper, Is. J. Chem., 21 (1981) 203.

712 M.P. Doyle and D. Van Leusen, J. Am. Chem. Soc., 103 (1981) 5917.

713 J.L. Williams and M.F. Rettig, Tetrahedron lett., 22 (1981) 385.

714 M. Suzuki, R. Noyori and N. Hamanaka, J. Am. Chem. Soc., 103 (1981) 5606.

715 M. Suzuki, Y. Oda and R. Noyori, Tetrahedron Lett., 22 (1981) 4413.
716 H-J. Cristau, B. Chabaud, A. Chêne and H. Christol, Phosphorus, Sulphur, 11 (1981) 55.
717 B.M. Trost, Stud. Org. Chem. (Amsterdam), 6 (New Synth. Methodol. Biol. Act. Subst.), (1981) 75; Chem. Abstr., 96 (1982) 51457u.
718 M. Pereyre and J-P. Quintard, Pure Appl. Chem., 53 (1981) 2401.
719 K. Inomata, T. Yamamoto and H. Kotake, Chem. Lett., (1981) 1357.
720 H.H. Baer and Z.S. Hanna, Carbohydr. Res., 94 (1981) 43.
721 H.H. Baer and Z.S. Hanna, Can J. Chem., 59 (1981) 889.
722 J.E. Bäckvall, R.E. Nordberg, J-E. Nyström, T. Högberg and B. Ulff, J. Org. Chem. 46 (1981) 3479.
723 S.A. Godleski, J.D. Meinhart, D.J. Miller and S. van Wallendael, Tetrahedron Lett., 22 (1981) 2247.
724 G.P. Chiusoli, M. Costa, L. Pallini and G. Terenghi, Transition Met. Chem. (Weinheim, Ger.), 6 (1981) 317.
725 P.A. Wade, H.R. Hinney, N.V. Amin, P.D. Vail, S.D. Morrow, S.A. Hardinger and M.S. Saft, J. Org. Chem., 46 (1981) 765.
726 J.P. Genet and F. Piau, J. Org. Chem., 46 (1981) 2414.
727 M. Moreno-Mañas and A. Trius, Tetrahedron, 37 (1981) 3009.
728 J.P. Haudegond, D. Commereuc, J. Collin and Y. Chauvin, Fr. Demande FR 2,474,491 (1981); Chem. Abstr., 96 (1982) 85976c.
729 M. Moreno-Mañas and A. Trius, Tetrahedron Lett., 22 (1981) 3109.
730 B.M. Trost and N.R. Schmuff, Tetrahedron Lett., 22 (1981) 2999.
731 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho 80,136,250 (1980); Chem. Abstr., 94 (1981) 209011q.
732 T. Hayashi, M. Konishi, K. Yokota and M. Kumada, J. Chem. Soc., Chem. Commun., (1981) 313.
733 I.P. Beletskaya, A.N. Kasatkin, S.A. Lebedev and N.A. Bumagin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1994 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2414).
734 J-C. Fiaud and J-L. Malleron, J. Chem. Soc., Chem. Commun., (1981) 1159.
735 J. Tsuji, H. Ueno, Y. Kobayashi and H. Okumoto, Tetrahedron Lett., 22 (1981) 2573.
736 T. Hirao, J. Enda, Y. Ohshiro and T. Agawa, Tetrahedron Lett., 22 (1981) 3079.
737 J. Tsuji, H. Kataoka and Y. Kobayashi, Tetrahedron Lett., 22 (1981) 2575.
738 B.M. Trost and G.A. Molander, J. Am. Chem. Soc., 103 (1981) 5969.
739 B.M. Tost and T.P. Klun, J. Am. Chem. Soc., 103 (1981) 1864.
740 Y. Kobayashi and J. Tsuji, Tetrahedron Lett., 22 (1981) 4295.
741 H. Felkin, M. Joly-Goudket and S.G. Davies, Tetrahedron Lett., 22 (1981) 1157.
742 G. Consiglio, F. Morandini and O. Piccolo, J. Am. Chem. Soc., 103 (1981) 1846.
743 M. Chérest, H. Felkin, J.D. Umpelby and S.G. Davies, J. Chem. Soc., Chem. Commun., (1981) 681.
744 Y. Hayasi, M. Riediker, J.S. Temple and J. Schwartz, Tetrahedron Lett., 22 (1981) 2629.
745 H. Matsushita and E. Negishi, J. Am. Chem. Soc., 103 (1981) 2882.
746 E. Negishi, Pure Appl. Chem., 53 (1981) 2333.
747 S. Ozasa, Y. Fujioka, M. Okada, H. Izumi and E. Ibuki, Chem. Pharm. Bull., 29 (1981) 370.
748 S. Ozasa, Y. Fujioka, M. Tsukada and E. Ibuki, Chem. Pharm. Bull., 29 (1981) 344.
749 D.S. Lingenfelter, R.G. Helgeson and D.J. Cram, J. Org. Chem., 46 (1981) 393.
750 I. Colon, L.M. Maresca and G.T. Kwiatkowski, Eur. Pat. Appl., 12,201 (1980); Chem. Abstr., 94 (1981) 65293h.

751 I. Colon, L.M. Maresca and G.T. Kwiatkowski, U.S. 4,263,466 (1981); Chem. Abstr., 95 (1981) 80437x.

752 I. Colon, L.M. Maresca and G.T. Kwiatkowswki, Eur. Pat. Appl. 25,460 (1981); Chem. Abstr., 95 (1981) 62993w.

753 Y. Rollin, M. Troupel, J. Perichon and J.F. Fauvarque, J. Chem. Res., S, (1981) 322.

754 M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L.S. Ryono, J.G. Smith and R.D. Stauffer, J. Am. Chem. Soc., 103 (1981) 6460.

755 R. Nakajima, Y. Shintani and T. Hara, Nippon Kagaku Kaishi, (1981) 249; Chem. Abstr., 95 (1981) 186732e.

756 I.V. Kozhevnikov, React. Kinet. Catal. Lett., 17 (1981) 233.

757 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1993 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2413).

758 C.F. Bigge and M.P. Mertes, J. Org. Chem., 46 (1981) 1994.

759 D.E. Bergstrom and J.L. Ruth, U.S. 4,267,171 (1981); Chem. Abstr., 95 (1981) 62605w.

760 D.E. Bergstrom and J.L. Ruth, U.S. 4,247,544 (1981); Chem. Abstr., 95 (1981) 7706e.

761 I. Arai, R. Hanna and G.D. Daves, J. Am. Chem. Soc., 103 (1981) 7684.

762 U. Lauk, P. Skrabal and H. Zollinger, Helv. Chim. Acta, 64 (1981) 1847.

763 A. Minato, K. Tamao, T. Hayashi, K. Suzuki and M. Kumada, Tetrahedron Lett., 22 (1981) 5319.

764 A.N. Kashin, I.G. Bumagina N.A. Bumagin and I.P. Beletskaya, J. Org. Chem. USSR, 17 (1981) 18 (Zh. Org. Khim., 17 (1981) 21).

765 M. Kosugi, K. Shimizu, A. Ohtani and T. Migita, Chem. Lett., (1981) 829.

766 A.N. Kashin, I.G. Bumagina, N.A. Bumagin, V.N. Bakunin and I.P. Beletskaya, J. Org. Chem. USSR, 17 (1981) 789 (Zh. Org. Khim., 17 (1981) 905).

767 H. Azizian, C. Eaborn and A. Pidcock, J. Organomet. Chem.., 215 (1981) 49.

768 M.S. Shvartsberg, V.P. Mamaev, N.V. Orekhova and I.L. Kotlyarevskii, U.S.S.R. 761,448 (1980); Chem. Abstr., 94 (1981) 102801v.

769 P.M. Hergenrother, Macromolecules, 14 (1981) 898.

770 A.A. Moroz, A.V. Piskunov and M.S. Shvartsberg, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 304 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981)).

771 H. Yamanaka, M. Shiraiwa, E. Yamamoto and T. Sakamoto, Chem. Pharm. Bull., 29 (1981) 3543.

772 E.T. Sabourin and C.M. Selwitz, U.S. 4,204,078 (1980); Chem. Abstr., 94 (1981) 30335w.

773 D.E. Ames, D. Bull and C. Takundwa, Synthesis (1981) 364.

774 W.B. Austin, N. Bilow, W.J. Kelleghan and K.S.Y. Lau, J. Org. Chem., 46 (1981) 2280.

775 E.T. Sabourin and C.M. Selwitz, U.S. 4,210,610 (1980); Chem. Abstr., 94 (1981) 103000v.

776 E.T. Sabourin and C.M. Selwitz, U.S. 4,223,172 (1980); Chem. Abstr., 94 (1981) 103001w.

777 M.J. Robins and P.J. Barr, Tetrahedron Lett., 22 (1981) 421.

778 T. Sakamoto and H. Yamanaka, Heterocycles, 15 (1981) 583.

779 O. Piccolo and A. Martinengo, Synth. Commun., 11 (1981) 497.

780 S. Nunomoto, Y. Kawakami and Y. Yamashita, Bull. Chem. Soc. Jpn., 54 (1981) 2831.

781 L.N. Pridgen and L.B. Killmer, J. Org. Chem., 46 (1981) 5402.

782 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 2366 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2836).

783 N. Jabri, A. Alexakis and J.F. Normant, Tetrahedron Lett., 22 (1981) 3851.

784 N. Miyaura and A. Suzuki, J. Organomet. Chem., 213 (1981) C53.

785 N. Miyaura, T. Yanagi and A. Suzuki, Synth. Commun., 11 (1981) 513.

786 Y. Akita, M. Shimazaki and A. Ohta, Synthesis (1981) 974.

787 B.R. Cotter, U.S. 4,211,721 (1980); Chem. Abstr., 94 (1981) 15412a.

788 M. Kosugi, Y. Kato, K. Kiuchi and T. Migita, Chem. Lett., (1981) 69.

789 T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, Synthesis (1981) 56.

790 M. Foà, R. Santi and F. Garavaglia, J. Organomet. Chem., 206 (1981) C29.

791 H.J. Cristau, B. Chabaud, A. Chêne and H. Christol, Synthesis (1981) 892.

792 U. Knips, Ger. Offen. 2,918,592 (1980); Chem. Abstr., 94 (1981) 174685h.

793 H.M. Walborsky and R.B. Banks, J. Org. Chem., 46 (1981) 5074.

794 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho 80,130,986 (1980); Chem. Abstr., 95 (1981) 7458a.

795 T. Hayashi, T. Fujiwa, Y. Okamoto, Y. Katsuro and M. Kumada, Synthesis (1981) 1001.

796 N. Fukamiya, M. Oki and T. Aratani, Chem. Ind. (London), (1981) 606.

797 G.D. Crouse and L.A. Paquette, J. Org. Chem., 46 (1981) 4272.

798 T. Hayashi, Y. Katsuro, Y. Okamoto and M. Kumada, Tetrahedron Lett., 22 (1981) 4449.

799 R. Rossi, A. Carpita and M.L. Gaudenzi, Synthesis, (1981) 359.

800 V. Ratovelomanana and G. Linstrumelle, Tetrahedron Lett., 22 (1981) 315.

801 M. Kumada, T. Hayashi and K. Tamao, Stud. Org. Chem. (Amsterdam), 6 (New Synth. Methodol. Biol. Act. Subst.) (1981) 55; Chem. Abstr., 96 (1982) 180215n.

802 T. Hayashi, M. Konishi, T. Hioki, M. Kumada, A. Ratajczak and H. Niedbała, Bull. Chem. Soc. Jpn., 54 (1981) 3615.

803 H. Brunner and M. Pröbster, J. Organomet. Chem., 209 (1981) C1.

804 T. Hayashi, K. Kanehira, T. Hioki and M. Kumada, Tetrahedron Lett., 22 (1981) 137.

805 C.L. Rand, D.E. Van Horn, M.W. Moore and E. Negishi, J. Org. Chem., 46 (1981) 4093.

806 J.F. Fauvarque and A. Jutand, J. Organomet. Chem., 209 (1981) 109.

807 K. Ruitenberg, H. Kleijn, C.J. Elsevier, J. Meijer and P. Vermeer, Tetrahedron Lett., 22 (1981) 1451.

808 M. Sato, K. Takai, K. Oshima and H. Nozaki, Tetrahedron Lett., 22 (1981) 1609.

809 V. Ratovelomana and G. Linstrumelle, Synth. Commun., 11 (1981) 917.

810 N. Miyaura, H. Suginome and A. Suzuki, Tetrahedron Lett., 22 (1981) 127.

811 R. Rossi, A. Carpita and M.G. Quirici, Tetrahedron, 37 (1981) 2617.

812 E. Negishi, S. Chatterjee and H. Matsushita, Tetrahedron lett., 22 (1981) 3737.

813 D.E. Bergstrom, J.L. Ruth and P. Warwick, J. Org. Chem., 46 (1981) 1432.

814 G. Consiglio, F. Morandini and O. Piccolo, Congr. Naz. Chim. Inorg., [Atti], 13th, (1980) 349; Chem. Abstr., 95 (1981) 61279f.

815 E. Negishi, H. Matsushita and N. Okukado, Tetrahedron Lett., 22 (1981) 2715.

816 L.I. Zakharkin, A.I. Kovredov and V.A. Ol'shevskaya, J. Gen. Chem. USSR, 51 (1981) 2422 (Zh. Obshch. Khim., 51 (1981) 2807).

817 Y. Ishimura, K. Maruya, Y. Nakamura, T. Mizoroki and A. Ozaki, Chem. Lett., (1981) 657.

818 A. Angelescu and E. Angelescu, Rev. Chim. (Bucharest), 32 (1981) 633; Chem. Abstr., 96 (1982) 6107u.

819 E. Angelescu, A. Angelescu, S. Nenciulescu and I.V. Nicolescu, Rev. Chim. (Bucharest), 32 (1981) 559; Chem. Abstr., 95 (1981) 149504m.

820 D.B. Furman, N.V. Volchkov, L.A. Makhlis, P.E. Matkovskii, F.S. D'yachkovskii, V.É. Vasserberg and O.V. Bragin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1608 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1962).

821 D.L. Beach and T.P. Kobylinskii, U.S. 4,288,648 (1981); Chem. Abstr., 95 (1981) 219764x.

822 D.L. Beach and T.P. Kobylinskii, U.S. 4,272,407 (1981); Chem. Abstr., 95 (1981) 50232j.

823 D.L. Beach and T.P. Kobylinskii, U.S. 4,272,406 (1981); Chem. Abstr., 95 (1981) 50233k.

824 D.L. Beach and T.P. Kobylinskii, U.S. US 4,293,726 (1981); Chem. Abstr., 96 (1982) 34516v.

825 L.A. Makhis, N.V. Volchkov, D.B. Furman, O.V. Bragin and V.E. Vasserberg, Ref. Zh., Khim., (1981) Abstr. No. 2B1469; Chem. Abstr., 95 (1981) 42231t.

826 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho 80,136,236 (1980); Chem. Abstr., 94 (1981) 102802w.

827 D. Le Pennec, D. Commereuc and Y. Chauvin, Eur. Pat. Appl., 24,971 (1981); Chem. Abstr., 95 (1981) 114766w.

828 A.F. Lunin, Z.S. Vaizin, V.M. Ignatov, V.I. Smetanyuk and A.I. Prudnikov, Neftekhimiya, 21 (1981) 199; Chem. Abstr., 95 (1981) 79995w.

829 A.G. Azizov, Kh.Z. Mamedov and S.M. Aliev, Neftekhimiya, 21 (1981) 74; Chem. Abstr., 95 (1981) 42509q.

830 A. Sen and T-W. Lai, J. Am. Chem. Soc., 103 (1981) 4627.

831 P. Nogues, F. Dawans and E. Maréchal, Makromol. Chem., 182 (1981) 3481.

832 Asahi Glass Co., Ltd., Jpn. Kokai Tokkyo Koho 81 86,928 (1981); Chem. Abstr., 95 (1981) 204699f.

833 Asahi Glass Co., Ltd., Jpn. Kokai Tokkyo Koho 81 86,160 (1981); Chem. Abstr., 95 (1981) 204697d.

834 Asahi Glass Co., Ltd., Jpn. Kokai Tokkyo Koho 81 86,159 (1981); Chem. Abstr., 95 (1981) 204698e.

835 Asahi Glass Co., Ltd., Jpn. Kokai Tokkyo Koho 81 88,422 (1981); Chem. Abstr., 95 (1981) 204671r.

836 R.E. Colborn and K.P.C. Vollhardt, J. Am. Chem. Soc., 103 (1981) 6259.

837 G.A. Chukhadzhyan, Zh.I. Abramyan, G.M. Tonyan, L.I. Sagradyan and T.S. Élbakyan, J. Org. Chem. USSR, 17 (1981) 1636 (Zh. Org. Khim., 17 (1981) 1831).

838 G.A. Chukhadzhyan, T.S. Elbakyan and L.I. Sagradyan, Arm. Khim. Zh., 34 (1981) 163; Chem. Abstr., 95 (1981) 80020f.

839 G. Giacomelli, A.M. Caporusso, L. Lardicci and F. Marcacci, Chim. Ind. (Milan), 63 (1981) 482.

840 A,M. Caporusso, G. Giacomelli and L. Lardicci, J. Chem. Soc., Perkin I, (1981) 1900.

841 C. Simionescu, M. Grovu and V. Bulacovschi, Rom. 68,900 (1980); Chem. Abstr., 94 (1981) 157565b.

842 L.M. Levites, T.A. Romanova, L.A. Plyashkevich, L.V. Istomin, Yu.K. Kirilenko and G.I. Kudryavtsvev, Khim. Volokna (1981) 18; Chem. Abstr., 96 (1982) 69716n.

843 Osaka University, Jpn. Kokai Tokkyo Koho JP 81,116,724 (1981); Chem. Abstr., 96 (1982) 35935t.

844 J.G. Van Ommen, J.G.M. Van Rens and P.J. Gellimgs, J. Mol. Catal., 13 (1981) 313.

845 P. Heimbach and H. Schenkluhn, Pure Appl. Chem., 53 (1981) 2419.

846 B. Casensky, J. Hanika, V. Kubanek, V. Ruzicka and K. Sporka, Czech. 184,280 (1980); Chem. Abstr., 95 (1981) 24386t.

847 P. Svoboda, J. Hanika, J. Hetflejs, V. Chvalovsky, V. Ruzicka and K. Sporka, Czech. 183,423 (1980); Chem. Abstr., 95 (1985) 24385s.

848 G.A. Tolstikov, U.M. Dzhemilev, G.I. Rutman, Yu.I. Mitchurov, B.I. Pantuch, S.S. Sasanov, S.R. Rafikov, S.A. Egoriceva, V.P. Yur'ev *et al.*, Ger. Offen. 2,933,852 (1981); Chem. Abstr., 95 (1981) 42489h.

849 J. Thivolle-Cazat, I. Tkatchenko and J.R. Bernard, Fr. Demande 2,437,390 (1980); Chem. Abstr., 94 (1981) 30162n.

850 W.J. Richter, J. Mol. Catal., 13 (1981) 201.

851 K. Soga and K. Yamamoto, Polym. Bull. (Berlin), 4 (1981) 33; Chem. Abstr., 95 (1981) 81593g.

852 K. Soga and K. Yamamoto, Polym. Bull. (Berlin), 6 (1982) 263; Chem. Abstr., 96 (1982) 123405a.

853 K. Nozaki, Eur. Pat. Appl. 12,475 (1980); Chem. Abstr., 94 (1981) 46746s.

854 K. Nozaki, Eur. Pat. Appl. 12,472 (1980); Chem. Abstr., 94 (1981) 46747t.

855 E. Alder, H. Fuellbier and W. Gaube, Ger. (East) DD 152,778 (1981); Chem. Abstr., 97 (1982) 5787z.

856 E. Alder, H. Fuellbier and W. Gaube, Ger. (East) DD 152,779 (1981); Chem. Abstr., 97 (1982) 38482z.

857 K. Nozaki, Eur. Pat. Appl. 19,961 (1980); Chem. Abstr., 95 (1981) 7511n.

858 K. Nozaki, Eur. Pat. Appl. 19,960 (1980); Chem. Abstr., 94 (1981) 192500y.

859 P.W.N.M. van Leeuwen and C.F. Roobeek, Tetrahedron , 37 (1981) 1973.

860 G.A. Tolstikov, B.M. Mikhailov, U.M. Dzhemilev, V.A. Dorokhov and L.Yu. Gubaidullin, U.S.S.R. 791,717 (1980); Chem. Abstr., 95 (1981) 114910p.

861 Agency of Industrial Sciences and Technology Jpn. Tokkyo Koho 80 42,050 (1980); Chem. Abstr., 94 (1981) 156277k.

862 C. Moberg, Tetrahedron Lett., 22 (1981) 4827.

863 G. Buono, C. Triantaphylides, G. Peiffer, A. Mortreux and F. Petit, ACS Symp. Ser., 171 (Phosphorus Chem.), (1981) 499.

864 G.P. Chiusoli, M. Costa, G. Terenghi and I. Vinay, Transition Met. Chem. (Weinheim Ger.), 6 (1981) 125.

865 G.A. Gailunas, G.V. Nurtdinova, F.G. Yusapova, L.M. Khalilov, V.K. Mavrodiev, S.R. Rafikov and V.P. Yuriev, J. Organomet. Chem., 209 (1981) 139.

866 V.M. Akhmedov, A.A. Khanmetov and A.G. Azizov, J. Org. Chem. USSR, 17 (1981) 1479 (Zh. Org. Khim., 17 (1981) 1661).

867 D-L. Deng, K-W. Liu, T-B. Pang, H-F. Zhou, C-Q. Ye and T-L. Wang, Yu Chi Hua Hsueh, 3 (1981) 184; Chem. Abstr., 95 (1981) 149868h.

868 D. Morel, Eur. Pat. Appl. 25,740 (1981); Chem. Abstr., 95 (1981) 114783z.

869 J.P. Bianchini, B. Waegell, E.M. Gaydou, H. Rzehak and W. Keim, J. Mol. Catal., 10 (1981) 247.

870 B. Castro, P. Grenouillet, D. Neibecker, I. Tkatchenko, Fr. Demande 2,459,075 (1981); Chem. Abstr., 95 (1981) 168543q.

871 U.M. Dzhemilev, R.V. Kunakova, N.Z. Baibulatova, G.A. Tolstikov and L.M. Zelenova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 1506 (Izv. Akad. Nauk. SSSR, Ser. Khim., (1981) 1837).

872 T. Takahashi, I. Minami and J. Tsuji, Tetrahedron Lett., 22 (1981) 2651.

873 U.M. Dzhemilev, R.V. Kunakova, R.L. Gaisin, G.A. Tolstikov, R.V. Talipov and S.A. Lomakina, J. Org. Chem. USSR, 17 (1981) 665 (Zh. Org. Khim., 17 (1981) 763).

874 Daicel Chemical Industries, Ltd., Jpn. Kokai Tokkyo Koho 81 45,434 (1981); Chem. Abstr., 95 (1981) 132295w.

875 K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka and S. Teranishi, J. Org. Chem., 46 (1981) 2356.

876 H. Watanabe, A. Nagai, M. Saito, H. Tanaka and Y. Nagai, Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai, 38 (1981) 111; Chem. Abstr., 97 (1982) 181653m.

877 C. Moberg and B. Åkermark, J. Organomet. Chem., 209 (1981) 101.

878 W. Keim and M. Röper, J. Org. Chem., 46 (1981) 3702.

879 Tokyo Institute of Technology, Jpn. Kokai Tokkyo Koho 81 47,421 (1981); Chem. Abstr., 95 (1981) 98612k.

880 I. Khoury, P. Kovacic and H.M. Gilow, J. Polym. Sci., Polym. Lett. Ed., 19 (1981) 395.

881 M.D. Bezoari, P. Kovacic, S. Gronowitz and A-B. Hörnfeldt, J. Polym. Sci., Polym. Lett. Ed., 19 (1981) 347.

882 T. Yamamoto, K. Sanechika and A. Yamamoto, Chem. Lett., (1981) 1079.
883 T. Kauffmann and H. Lexy, Chem. Ber., 114 (1981) 3674.
884 H. Itatani, A. Shiotani and A. Yokota, Eur. Pat. Appl. 19,483 (1980); Chem. Abstr., 94 (1981) 156565q.
885 P. Binger and P. Bentz, J. Organomet. Chem., 221 (1981) C33.
886 P. Binger and A. Germer, Chem. Ber., 114 (1981) 3325.
887 P. Binger and U. Schuchardt, Chem. Ber., 114 (1981) 1649.
888 T. Sato, K. Naruse, M. Enokiya and T. Fujisawa, Chem. Lett., (1981) 1135.
889 M. Onaka, Y. Matsuoka and T. Mukaiyama, Chem. Lett., (1981) 531.
890 Y. Onishi, M. Iyoda and M. Nakagawa, Tetrahedron Lett., 22 (1981) 3641.
891 S. Cacchi, D. Misiti and G. Palmieri, Tetrahedron 37 (1981) 2941.
892 D.E. Laycock and H. Alper, J. Org. Chem., 46 (1981) 289.
893 J. Salaün and J. Ollivier, Nouv. J. Chim., 5 (1981) 587.
894 F.M. Dayrit and J. Schwartz, J. Am. Chem. Soc., 103 (1981) 4466.
895 G.V. Nizova and G.B. Shul'pin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 2211 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2653).
896 S.F. Dyke and M.J. McCartney, Tetrahedron, 37 (1981) 431.
897 P.M. Henry and G.L. Lange, Inorg. Chim. Acta, 53 (1981) L195.
898 L.M. Zubritskii, T.N. Fomina and Kh. V. Bal'yan, J. Org. Chem. USSR, 17 (1981) 63 (Zh. Org. Khim., 17 (1981) 69).
899 T. Sakamoto, H. Arakida, K. Edo and H. Yamanaka, Heterocycles, 16 (1981) 965.
900 T. Fuchikami, M. Yatabe and I. Ojima, Synthesis (1981) 365.
901 S. Czernecki and F. Gruy, Tetrahedron Lett., 22 91981) 437.
902 H. Horino, N. Inoue and T. Asao, Tetrahedron Lett., 22 (1981) 741
903 P.Y. Johnson and J.Q. Wen, J. Org. Chem., 46 (1981) 2767.
904 A. Hallberg, L. Westfelt and B. Holm, J. Org. Chem., 46 (1981) 5414.
905 T.L. Ho, Synth. Commun., 11 (1981) 579.
906 W. Smadja, S. Czernecki, G. Ville and C. Georgoulis, Tetrahedron Lett., 22 (1981) 2479.
907 T. Hirao, J. Enda, Y. Ohshiro and T. Agawa, Chem. Lett., (1981) 403.
908 K. Kikukawa, K. Nagira, F. Wada and T. Matsuda, Tetrahedron, 37 (1981) 31.
909 K. Kikukawa, K. Maemura, Y. Kiseki, F. Wada, T. Matsuda and C.S. Giam, J. Org. Chem., 46 (1981) 4885.
910 D.L. Beach and T.P. Kobylinskii, U.S. 4,293,724 (1981); Chem. Abstr., 95 (1981) 219877m
911 Y. Fujiwara, O. Maruyama, M. Yoshidomi and H. Taniguchi, J. Org. Chem., 46 (1981) 851.
912 H. Tomisawa, H. Hongo, H. Kato, K. Sato and R. Fujita, Heterocycles, 16 (1981) 1947.
913 J.M.D. Fortunak, PhD Thesis, Univ. Wisconsin (1981), Diss. Abstr. Int. B, 42 (1981) 1891.
914 L.S. Hegedus, P.M. Winton and S. Varaprath, J. Org. Chem., 46 (1981) 2215.
915 R.F. Heck, Pure Appl. Chem., 53 (1981) 2323.
916 F.E. Zeigler, U.R. Chakraborty and R.B. Weisenfeld, Tetrahedron, 37 (1981) 4035.
917 J.I. Kim, B.A. Patel and R.F. Heck, J. Org. Chem., 46 (1981) 1067.
918 B.A. Patel, J.I. Kim, D.D. Bender, L-C. Kao and R.F. Heck, J. Org. Chem., 46 (1981) 1061.
919 U.M. Dzhemilev, R.V. Kunakova and R.L. Gaisin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 30 (1981) 2213 (Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2655).
920 J-E. Bäckvall and R.E. Nordberg, J. Am. Chem. Soc., 103 (1981) 4959.
921 B.A. Pearlman, J.M. McNamara, I. Hasan, S. Hatakeyama, H. Sekizaki and Y. Kishi, J. Am. Chem. Soc., 103 (1981) 4248.

922 T. Hosokawa, T. Uno, S. Inui and S. Murahashi, J. Am. Chem. Soc., 103 (1981) 2318.

923 T. Izumi, O. Saito and A. Kasahara, Yamagata Daigaku Kiyo, Kogaku, 16 (1981) 371; Chem. Abstr., 95 (1981) 6979j.

924 A. Kasahara, T. Izumi, H. Watabe and S. Takahashi, Chem. Ind. (London), (1981) 121.

925 S. Varaprath, PhD Thesis, Colorado State Univ., (1981), Diss. Abstr. Int. B, 42 (1982) 4433.

926 S. Hatano, M. Saruwatari, K. Isomura and H. Taniguchi, Heterocycles, 15 (1981) 747.

927 H. Iida, Y. Yuasa and C. Kibayashi, J. Chem. Soc., Chem. Commun., (1981) 114.

928 K. Utimoto, H. Miwa and H. Nozaki, Tetrahedron Lett., 22 (1981) 4277.

929 B. Corain, M. Basato and H-F. Klein, Angew. Chem., Int. Ed., Engl., 20 (1981) 972 (Angew. Chem., 93 (1981) 1034).

930 B. Corain, C. Crotti, A. Del Pra, F. Filira and G. Zanotti, Inorg. Chem., 20 (1981) 2044.

931 P. Binger and U. Schuchardt, Chem. Ber., 114 (1981) 3313.

932 H. Takaya, T. Suzuki, Y. Kumagai, M. Yamakawa and R. Noyori, J. Org. Chem., 46 (1981) 2846.

933 H. Takaya, T. Suzuki, Y. Kumagai, M. Hosoya, H. Kawauchi and R. Noyori, J. Org. Chem., 46 (1981) 2854.

934 K. Itoh, K. Hirai, M. Sasaki, Y. Nakamura and H. Nishiyama, Chem. Lett., (1981) 865.

935 R. Nakajima, K. Morita and T. Hara, Bull. Chem. Soc. Jpn., 54 (1981) 3599.

936 G. Schiavon, G. Bontempelli and B. Corain, J. Chem. Soc., Dalton Trans., (1981) 1074.

937 M. Orisako, Y. Wada, Y. Uchida and M. Hidai, Nippon Kagaku Kaishi, (1981) 1052; Chem. Abstr., 95 (1981) 96669k.

938 J. Drapier, M.T. Hoornaerts, A.J. Hubert and P. Teyssie, J. Mol. Catal., 11 (1981) 53.

939 I. Oprean and H. Ciupe, Rom. RO 70,093 (1981); Chem. Abstr., 97 (1982) 24041t.

940 T-Y. Luh, W.H. So and S.W. Tam, J. Organomet. Chem., 218 (1981) 261.

941 J.J. Bozell and L.S. Hegedus, J. Org. Chem., 46 (1981) 2561.

942 F. Porta, M. Pizzotti and S. Cenini, J. Organomet. Chem., 222 (1981) 279.

943 B.M. Trost and J.M.D. Fortunak, Tetrahedron Lett., 22 (1981) 3459.

944 K. Yamamoto, S. Suzuki and J. Tsuji, Bull. Chem. Soc. Jpn., 54 (1981) 2541.

945 L.T. Scott, W.R. Brunsvold, M.A. Kirms and I. Erden, Angew. Chem., Int. Ed., Engl., 20 (1981) 274 (Angew. Chem., 93 (1981) 282).

946 G. Suzukamo, T. Takano, M. Tamura and K. Ikimi, Eur. Pat. Appl. 21,769 (1981); Chem. Abstr., 95 (1981) 43412q.

947 T. Tsuda, Y. Chujo and T. Saeguso, Synth. Commun., 11 (1981) 775.

948 G. Villain, A. Gaset and P. Kalck, J. Mol. Catal., 12 (1981) 103.

949 P. Yates and G.E. Langford, Can. J. Chem., 59 (1981) 344.

950 H-S. Ryang and C.S. Foote, J. Am. Chem. Soc., 103 (1981) 4951.

951 M. Hanack, K. Mitulla and O. Schneider, Chem. Scripta, 17 (1981) 139.

952 B.N. Kuznetsov, V.K. Duplyakin, V.I. Koval'chuk and Yu.A. Ryndin, Kinet. Catal., 22 (1981) 1183 (Kinet. Katal., 22 (1981) 1484).

15 ABBREVIATIONS

acacH	pentane-2,4-dione
am	amine
Ar	aryl

bipy	2,2'-bipyridyl
Bu	$-CH_2CH_2CH_2CH_3$
i-Bu	$-CH_2CH(CH_3)_2$
Bz	$-CH_2Ph$
CD	circular dichroism
cdt	cyclododecatriene
CHIRAPHOS	S,S-2,3-bis(diphenylphosphino)butane
cod	1,5-cyclooctadiene
cot	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
dba	**E,E**-1,5-diphenylpenta-1,4-diene-3-one
dibah	di*iso*butylaluminium hydride
DIOP	2,3-*O*-di*iso*propylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dmf	*N,N*-dimethylmethanamide
dmg	dimethyglyoxime
dmso	dimethylsulphoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
en	1,2-diminoethane
epr	electron paramagnetic resonance
Et	$-CH_2CH_3$
eV	electron volt
Fc	ferrocenyl
G	Gauss
glc	gas liquid chromatography
$H_2BiBzIm$	2,2'-bibenzimidazole
H_2BiIm	2,2'-biimidazole
hfacacH	1,1,1,5,5,5-hexafluoropentane-2,4-dione
hmpa	hexamethylphosphoramide
H_2Hp	hemiporphrazine
IR	infra-red
kJ	kilojoule
L	2 electron donor ligand
MDPP	Menthyldiphenylphosphine
Me	$-CH_3$
mesal	*N*-methylsalicylaldimine
mnt^{2-}	*cis*-1,2-dicyanoethane-1,2-dithiolate
nbd	bicyclo[2.2.1]heptadiene
NMDPP	(+)-neomenthyldiphenylphosphine
nmr	nuclear magnetic resonance
ofcot	octafluoro-1,3,5,7-cyclooctatetraene
OTs	$OSO_2C_6H_4$-4-Me
Ⓟ-	polymer backbone
Ph	$-C_6H_5$
phen	1,10-phenanthroline
Pr	$-CH_2CH_2CH_3$
i-Pr	$-CH(CH_3)_2$
PVC	polyvinylchloride
py	pyridine
pzH	pyrazole
R	alkyl
SCF	self consistent field

tcne	tetracycanoethene
tfacacH	1,1,1-trifluoropentane-2,4-dione
tfah	CF_3COOH
thf	tetrahydrofuran
THP	tetrahydropyranyl
tht	tetrahydrothiophene
UV	ultra-violet
V	volt
XPES	X-ray photoelectron spectroscopy