NICKEL, PALLADIUM AND PLATINUM. ANNUAL SURVEY COVERING THE YEAR 1983*

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1 INTRODUCTION

This survey details the accounts of the organometallic chemistry of nickel, palladium and platinum published in 1983. Material from the patent literature which was reported in Chemical Abstracts in 1983 is also included, and the organisation remains broadly similar to that in past surveys.

A number of reviews of general interest have appeared, including one of the historical importance of the platinum metals in the development of coordination chemistry [1]. Annual reports on the inorganic chemistry of nickel, iron and cobalt [2], and palladium and platinum [3] have been published. The preparations and uses of nickel, palladium and platinum complexes have been detailed, with particular reference to thermolyses and reactions with carbon monoxide [4]. The preparations of transition metal complexes by reaction of dienes with transition metal salts under Mg/anthracene catalysis has been described in a patent [5], and palladium (I) complexes in coordination chemistry and catalysis have been reviewed [6].

2 METAL CARBON σ-BONDED COMPLEXES

A review has been published of complexes with metal-carbon σ-bonds [7]. The fragmentation of palladium β-diketonato complexes has been shown to involve palladium alkyl intermediates [8].

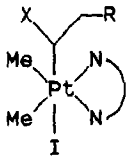
Theoretical models for reductive elimination from transition metal complexes were studied using large scale contracted CI calculations; one of the models was $\{Me_2Ni\}$ [9]. Calculations were also used to study the mechanisms for the concerted elimination and addition reactions of methane and ethane with nickel complexes. The computed barriers for the breaking of a C-H or C-C bond were higher than those for an H-H bond, in agreement with experiment [10]. Reaction of a range of dialkyl nickel complexes with alkyl and acyl halides has been studied, and a range of behaviours observed. With alkyl halides $[Me_2Ni(bipy)]$ and $[Et_2Ni(bipy)]$ gave mainly reductive elimination to ethane and butane respectively, together with oxidative addition of the alkyl halide to yield $[R'NiL_2X]$. *Trans*-$[Me_2Ni(PEt_3)_2]$ reacted with EtBr to give mainly methane, but with bromobenzene to give ethane and $[PhNi(PEt_3)_2Br]$. $[Me_2Ni(dppe)]$ reacted with chlorobenzene to give toluene as the main product [11]. *Cis*-[ArNi(Me)(dmpe)] reacted with added phosphine to give ArMe, by reductive elimination, *via* a 5-coordinate complex. Small added phosphines were most effective in promoting reductive elimination, presumably due to the ease of formation of the 5-coordinate species [12]. The product of partial hydrolysis of Et_3Al reacted with $[Me_2Ni(PPhMe_2)_3]$ to give a complex of stoicheiometry $Et_2AlONiMe.3PhPMe_2$ [13].

The reactions of *cis*- or *trans*-$[R_2PdL_2]$ (R = Me, Et or Ph; L = PR_3) with R'Li (R' = Me or Ph) gave initially $Li[R_2PdR'L]$, with retention of configuration at palladium. The displacement of PEt_3 in $[Ph_2Pd(PEt_3)_2]$ by MeLi was slow and followed a dissociative pathway, whereas the displacement of PEt_2Ph from $Li[Me_3Pd(PEt_2Ph)]$, although also slow, was shown to proceed *via* an associative pathway, involving a 5-coordinate intermediate [14].

The structure of $[\{Me_3PtI\}_4].CCl_4$ was determined by an X-ray diffraction study. The molecule had a pseudocubane structure with platinum and iodine atoms occupying the corners of the cube [15].

Thermolysis of *trans*-$[MePt(PR_3)_2I]$, in which R = CH_3, CD_3, Et, Ph or Cy, gave methane as the main product. Using complexes labelled with deuterium in either the platinum bonded methyl group, or derivatives of $P(CD_3)_3$, two pathways could be distinguished. In the more important one, homolytic fission of the Pt-CH_3 bond occurred to give a methyl radical, which abstracted hydrogen from either the β-alkyl groups or from the solvent. Bimolecular reactions represented a competing, but minor pathway [16]. Thermolysis of $[MePt(PR_3)_2X]$ (X = Cl, Br, I or CN) gave similar results, with the kinetics being determined by the strength of the platinum-carbon bond, in turn determined by the nature of X [17].

The complexes $[Me_2Pt(N\text{-}N)I_2]$ (N-N = bis(1-pyrazolyl)methane, 2,2-bis(1-pyrazolyl)propane or bis(2-pyrazolyl)methane) were prepared from $[Me_2Pt(cod)]$, the chelating dinitrogen ligand, and molecular iodine [18]. A number of papers have reported oxidative addition of alkyl halides to methylplatinum complexes. With $[Me_2Pt(phen)]$ and RX *trans*-addition occurred, but *cis,trans*-$[Me_2Pt(OOCHMe_2)I(phen)]$ was also formed in the reaction with 2-iodopropane, providing evidence for a free radical mechanism for the reaction [19]. In the presence of an electron accepting alkene, CH_2=CHX (X = CN, CHO or COMe), 1 was formed (R = $CHMe_2$ or CMe_3), also by a radical pathway [20]. In the reaction between $[Me_2Pt(phen)]$ and $I(CH_2)_nI$, 2 was the sole product for n = 0,2,3,4 or 5, *via* an S_N2 pathway, but for n = 1 both 2 and 3 were formed. 2 reacted with further $[Me_2Pt(phen)]$ to give the binuclear species, 4 [21].



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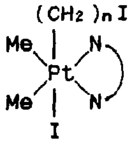

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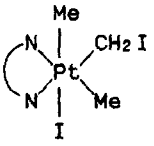

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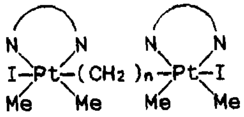

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Methane could be converted to a mixture of methanol and methyl halides in the presence of $[PtCl_4]^{2-}$ as catalyst, and $[PtCl_6]^{2-}$ as oxidant. Intermediate platinum methyl complexes were detected by nmr spectroscopy, and a mechanism for the reaction proposed (reactions (1)-(3)) [22]. Oxidative addition of iodomethane to $[PtCl_4]^{2-}$ gave the platinum(IV) species, $[MePt(H_2O)Cl_4]^-$, but with chloromethane the equilibrium of reaction (4) was set up, and the equilibrium constants determined by ^{195}Pt nmr spectroscopy [23].

$$\mathrm{Pt(II)} + \mathrm{CH_4} \rightleftharpoons \{\mathrm{Pt(II)Me}\} + \mathrm{H^+} \qquad (1)$$

$$\{\mathrm{Pt(II)Me}\} + \mathrm{Pt(IV)} \longrightarrow \{\mathrm{Pt(IV)Me}\} + \mathrm{Pt(II)} \qquad (2)$$

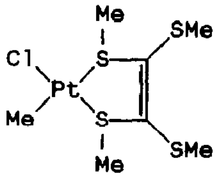
$$\{\mathrm{Pt(IV)Me}\} + \mathrm{Cl^-} + \mathrm{H_2O} \longrightarrow \mathrm{MeOH} + \mathrm{MeCl} + \mathrm{Pt(II)} \qquad (3)$$

$$[\mathrm{PtCl_4}]^{2-} + \mathrm{MeCl} \underset{\mathrm{Cl^-}}{\rightleftharpoons} [\mathrm{MePt(H_2O)Cl_4}]^- \underset{\mathrm{Cl^-}}{\rightleftharpoons} [\mathrm{MePtCl_5}]^{2-} \qquad (4)$$

The demethylation of methylcobalamine by $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$, and related compounds, has been investigated. Platinum in both oxidation states is necessary to the process and methylplatinum(IV) complexes were formed as intermediates [24]. A kinetic study implicated a trinuclear intermediate of the type $\{Me\text{-}B_{12}\cdots Pt(II)\cdots X\cdots Pt(IV)\}$ [25].

The complex $[Me_3Pt(MeSCH_2SCH_2SMe)X]$, in which only the terminal -SMe groups were bound to platinum, was prepared and studied by nmr spectroscopy. The separate energy barriers associated with pyramidal inversion of the sulphur atom, Pt-Me scrambling, and chelate ligand rotation were determined by a complete band shape analysis [26]. In both 5 and 6 inversion at the sulphur atoms was shown to be fast on the nmr spectroscopic timescale at room temperature [27]. $[Me_3Pt\{MeE^1(CH_2)_3E^1Me\}X]$ was reacted with $MeE^2(CH_2)_2E^2Me$ to give $[Me_3Pt\{MeE^2(CH_2)_2E^2Me\}X]$ (E = S or Se), indicating a preference for 5- over 6-membered rings. Selenium containing ligands displaced sulphur containing ones when the ring size was the same. The deductions of the effects of ring size on stability were made using ^{195}Pt, ^{77}Se and ^{13}C nmr spectroscopy

[28].



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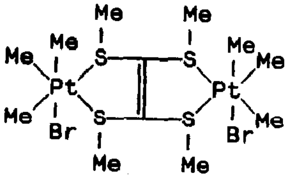

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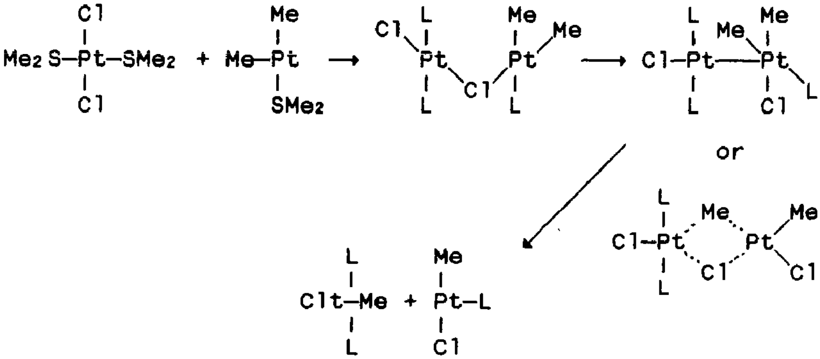
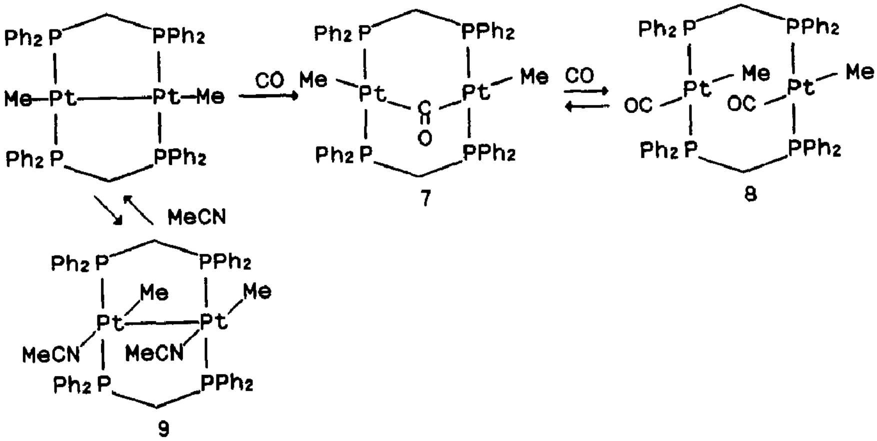
The complex *cis*-$[\mathrm{Me_2Pt(SMe_2)_2}]$ is in equilibrium with $[\mathrm{Me_4Pt_2(\mu\text{-}SMe_2)_2}]$ and $\mathrm{Me_2S}$. Both *cis* and *trans*-$[\mathrm{Pt(SMe_2)_2Cl_2}]$ reacted with *cis*-$[\mathrm{Me_2Pt(SMe_2)_2}]$ to give *trans*-$[\mathrm{MePt(SMe_2)_2Cl}]$. It was clear the dissociation preceded reaction, and the mechanism of Scheme 1 was proposed [29].

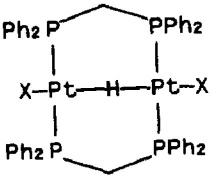


Scheme 1 Mechanism of reaction of *cis*-$[\mathrm{Me_2Pt(SMe_2)_2}]$ with *trans*-$[\mathrm{Pt(SMe_2)_2Cl_2}]$ ($\mathrm{L = SMe_2}$)

Some further reactions of methylated diplatinum complexes have been reported. $[\mathrm{Me_4Pt_2(\mu\text{-}SMe_2)_2}]$ reacted with dmpm to give *cis,cis*-$[\mathrm{Me_2Pt(\mu\text{-}dmpm)_2PtMe_2}]$. Although this was converted to a range of other complexes, details of the reagents used were not given [30]. Fortunately this omission was at least partly remedied in a later paper by the same authors. *cis,cis*-$[\mathrm{Me_2Pt(\mu\text{-}dmpm)_2PtMe_2}]$ reacted with $\mathrm{X_2}$ to give $[\mathrm{Me_3Pt(\mu\text{-}X)(\mu\text{-}dmpm)PtMe}]\mathrm{X}$, and with MeI yielding $[\mathrm{Me_3IPt(\mu\text{-}dmpm)_2PtMe_2}]$. This was the first bridged complex containing platinum(II) and platinum(IV) to be fully characterised [31].

Photolysis of $[\mathrm{Me_3Pt_2(\mu\text{-}dppm)_2}][\mathrm{PF_6}]$ in an appropriate solvent, S, gave $[\mathrm{MePt(\mu\text{-}dppm)_2PtS}]^+$ and ethane, with labelling studies indicating that reductive elimination was at least partially intramolecular. In pyridine $[\mathrm{Me_2Pt(dppm)}]$ and $[\mathrm{MePt(dppm)(py)}]^+$ were obtained, with the dppm acting as a chelating ligand. Quantum yields were high, giving further support to the thesis that these are unimolecular reactions [32]. Reaction of $[Me_3Pt_2(\mu\text{-dppm})_2]^+$ with $[Ph_3C][BF_4]$ gave $[MePt(\mu\text{-dppm})_2PtMe]^{2+}$, which was used in the preparation of the new A-frame complexes, 7, 8 and 9 [33]. A new mechanism has been proposed for the A-frame inversion of $[Pt_2(\mu\text{-dppm})_2(\mu\text{-H})X_2]^{n+}$, involving a linear intermediate 10 [34]. Protonation of $[Pt_2(\mu\text{-dppm})_2(\mu\text{-CH}_2)Cl_2]$ with $H[SbF_6]$ gave $[MePt_2(\mu\text{-dppm})(\mu\text{-Cl})Cl][SbF_6]$, which could be reduced to 11 by $Na[BH_4]$. This A-frame complex also inverted rapidly on the nmr timescale, and the linear transition state was again proposed [35].





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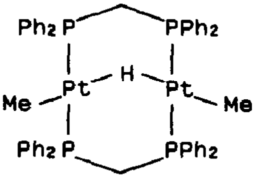

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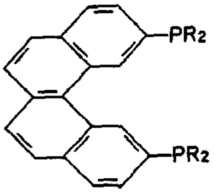
The kinetics of substitution of *trans*-$[MePt(PEt_3)_2Cl]$ by 12, and a number of related reactions, were investigated. The methyl group was found to cause significant steric retardation of the substitution relative to a proton in some cases [36].

The absorption spectra of $[PtL_xL'_{4-x}]$ (L = NH_3, RNH_2, H or alkyl; L' = trialkyl phosphine) have been recorded and assigned [37]. Nitrosodurene reacted with a range of nickel complexes including σ-alkyl, σ-aryl, π- and σ-allyl, and cyclopentadienyl derivatives to give nitrosoduryl radicals which could be detected by epr [38].



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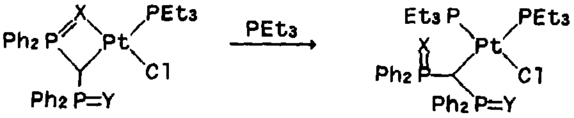
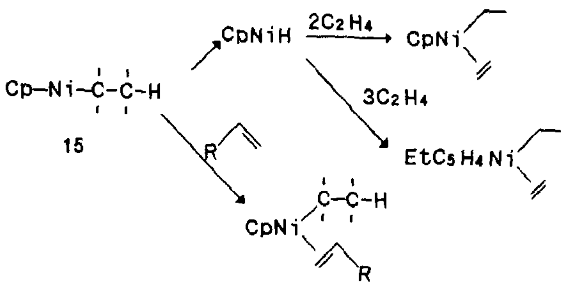
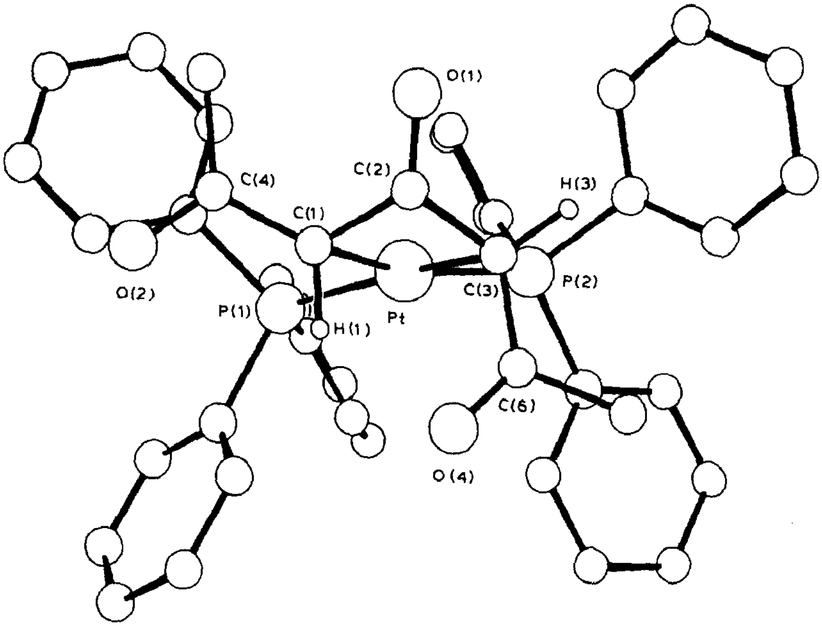
Displacement of ligands by nucleophiles has been used in the synthesis of a few σ-alkyl complexes. For example, $[Ni(acac)_2]$ reacted with $(Me_3SiCH_2)_3Al$ in the presence of bipy to give $[(Me_3SiCH_2)_2Ni(bipy)]$, which could be used as a catalyst for polymerisation and hydrogenation [39]. The reaction of Et_3Al with $[Pd(acac)_2]$ was a complex one, but the initial products are believed to be $Et_2Al(acac)$ and {RPd(acac)}. Subsequent displacement gave $\{R_2Pd\}$, which decomposed readily [40]. Treatment of $[Pt_2(PEt_3)_2Cl_4]$ with $Li[CH(PPh_2X)(PPh_2Y)]$ gave 13 as the initial product, and this could be converted to 14 by addition of triethylphosphine [41]. $[Cp_2Ni]$ reacted with a range of alkyl lithium and Grignard reagents to give initially species such as 15, which could undergo insertion or reductive elimination, followed by further insertion [42]. Reaction of $[ML_2Cl_2]$ (M = Ni or Pd; L_2 = $(PPh_3)_2$ or dppe) with $[NH_4]_2[RSiF_5]$ (R =Me or Ph) gave $[RML_2Cl]$ and/or $[R_2ML_2]$ [43]. The preparation of 16 from $[Pt(CO_3)L_2]$ and RCH_2COCH_2R may be regarded as a double displacement; the product was characterised by nmr spectroscopy and an X-ray diffraction study [44].



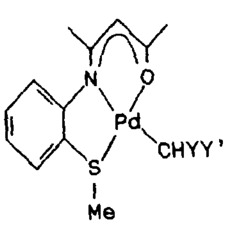
13 14

The complex 17 was prepared by displacement of a halide by $[CHYY']^-$ (Y, Y' = CN, COOMe, *etc.*). The inversion at sulphur was fast on the nmr spectroscopic timescale at temperatures just above ambient [45]. Reaction of $[Pd(tta)_2]$ (ttaH = 18) with bulky bases, including some phosphines, 2-methylpyridine or 2,6-dimethylpyridine, gave a complex assigned the structure 19, although the evidence for this stereochemistry was not very convincing [46]. Reactions of $[Pd(hfacac)_2]$ giving a related product (among others) have been discussed in detail [47].





16 (Reproduced with permission from [44])
H atoms of the phenyl rings and methyl groups have been omitted.



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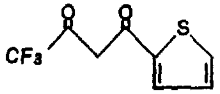

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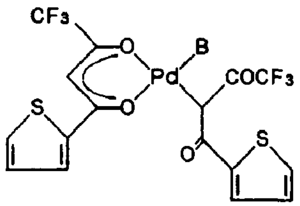
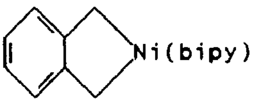


19

Oxidative addition of carbon-halogen bonds has also been a popular method for the preparation of σ-alkyl complexes. Thus, reaction of [PdL_4] (L = PMe_3 or $PMePh_2$) with a three-fold excess of $PhCH_2Br$ gave *trans*-[$PhCH_2PdL_2Br$] [48]. $PhCH_2Br$ reacted similarly with [Ni(bipy)(cod)] to give [$PhCH_2Ni$(bipy)Br], and 20 was prepared *via* a double oxidative addition [49]. Oxidative addition of a benzylic halide to nickel(0) is assumed to be the first step of reaction (5), the nickel(0) being generated *in situ* by lithium metal reduction of NiI_2 [50]. The reactions of platinum(0) and palladium(0) complexes with $ClCH_2SR$ have been investigated. With [$Pd(PPh_3)_4$] the initial product was *trans*-[$MeSCH_2Pd(PPh_3)_2Cl$], which on recrystallisation yielded 21. Phosphine dissociation did not occur to any substantial degree with *trans*-[$PhSCH_2Pd(PPh_3)_2Cl$] or *trans*-[$MeSCH_2Pd(PMePh_2)_2Cl$] [51]. The complex *trans*-[$RSCH_2Pt(PR'_3)_2Cl$ was obtained from [$Pt(PR'_3)_4$] (R = Ph, 4-MeC_6H_4 or Me) and some further reactions were investigated [52].



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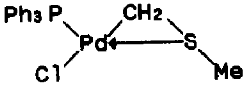

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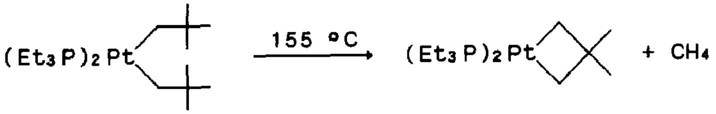
$$ArCH_2X + RCOX' + Ni \xrightarrow{\Delta,\ \text{glyme}} ArCH_2COR + NiXX' \qquad (5)$$

Thienylpalladation of norbornene to give σ-bonded palladium complexes has been used in a synthetic approach to prostaglandin analogues [53]. The complexes *trans*-[$RPt(PR_3)_2(OOCMe_3)$] (R = CH_3, CF_3, Ph, $PhCH_2$ or 2-CNC_6H_4) were prepared by the action of Me_3COOH on the corresponding hydroxo complexes. The complex for which R = Ph was characterised by an X-ray diffraction study [54].

The reductive elimination of 1,1,1-trifluoroethane from the complex *cis*-$[HPt(CH_2CF_3)(PPh_3)_2]$ occurred slowly at temperatures just above ambient, to give a species of stoicheiometry $\{Pt(PPh_3)_2\}$, which was actually an orange-red cluster. This could be used for the preparation of other platinum(0) complexes such as $[Pt(PPh_3)_2(PhC\equiv CPh)]$. The reaction kinetics were in accord with a concerted unimolecular reductive elimination [55]. Photolysis of *trans*-$[HPt(R)(PPh_3)_2]$ ($R = (CH_2)_nCN$, $n = 1$, 2 or 3) gave RH. It was concluded that the *trans*-complexes were isomerised to the *cis*-species prior to reductive elimination, which was intramolecular [56].

Activation of distal C-H bonds in platinum alkyl complexes has been reviewed, with particular reference to reactions such as (6), which could be related to surface chemistry at platinum [57].



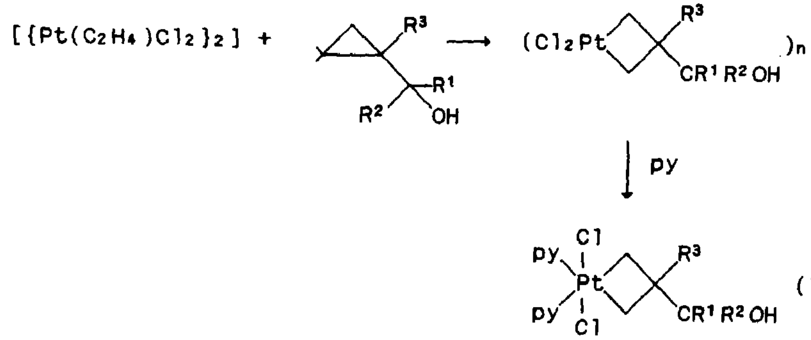
(6)

The preparation of $[(dppe)Pd(CH_2)_4]$ was accomplished by reaction of $[Pd(dppe)Cl_2]$ with 1,4-dilithiobutane. Ligand exchange reactions in the product were studied [58].

Platinacyclobutane chemistry has been reviewed, with particular reference to rearrangement to alkene, ylide and carbene complexes (see also section 4 of this review) [59]. A theoretical study of the rearrangements, using the isolobal analogy, has led to a proposition for a new mechansim for alkene metathesis [60]. New platinocyclobutanes were synthesised *via* reaction (7), the conformation of the four-membered ring in the product being determined by nmr spectroscopy in solution and by an X-ray diffraction study in the solid state (22). The metallocyclobutane was puckered by only 1 ° in the solid state, compared with the 27 ° pucker deduced from solution studies [61]. The sequence of reaction (8) yielded a platinabicyclobutane, 23, which had a rather rigid structure in solution. Reductions with $Li[AlH_4]$ and $Li[AlD_4]$ were studied [62].

The structure of $[HPt(Ph)\{P(CHMe_2)_3\}_2]$ was determined by an X-ray diffraction study [63].

Complexes of the type $[Ar_2M(bipy)]$ (M = Ni or Pt) and $[Ar_2Ni(PR_3)_2]$ ($Ar = C_6F_5$ or $4\text{-}HC_6F_4$) were prepared by the reaction of Ar_2Yb with the appropriate metal halide complexes [64]. Tetraarylmetallates, $[Ar_4M]^{2-}$ (M =Pd or Pt; $Ar = C_6Cl_5$), were prepared from aryl lithium or Grignard reagents, and could be isolated as tetraalkyl ammonium salts. Reaction with HCl gave $[Ar_4M_2(\mu\text{-}Cl)_2]$, and further substitution reactions of these complexes were investigated. These were the first well-characterised anionic palladium or platinum complexes of {C_6Cl_5} [65]. Treatment of $K_2[PtCl_4]$ with two molar equivalents of C_6F_5MgBr in thf/dioxan gave *trans*-$[(C_6F_5)_2Pt(dioxan)_2]$, which has now been isolated, although the yield was lower than for the related palladium complex. The dioxan ligands could be replaced by dmso, dmf, or pyridine-*N*-oxide (*vide infra*) [66].



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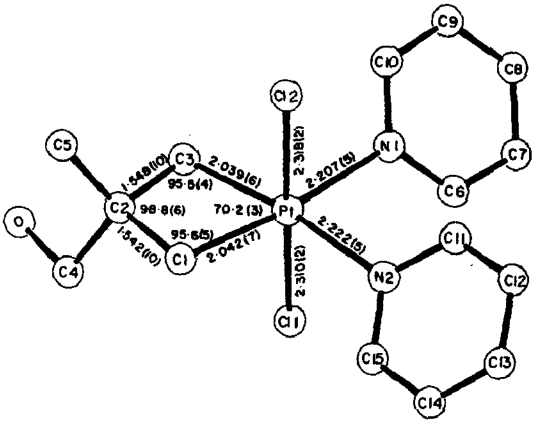
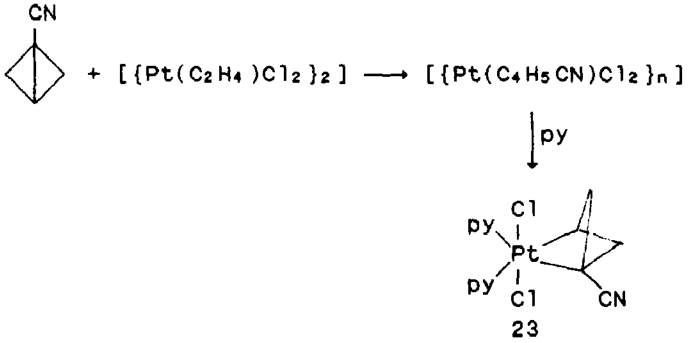


22 (Reproduced with permission from [61])

The hydrogen atoms have been omitted for clarity, and the atoms have been drawn as spheres with arbitrary radii.

Aryl iodides or chlorides in which Ar is C_6Cl_5- or another polychloro derivative, reacted with $[Ni(PPh_3)_4]$ to give $[ArNi(PPh_3)_2X]$. The possibility of nickel(I) intermediates was discussed [67]. Reaction with ArHgX gave the same product, but $(C_6F_5)_2Hg$ yielded $[ArNi(HgAr)(PPh_3)_2]$. The conversion of 24 to the cyclometallated derivative was particularly easy [68]. The complexes

[ML_4] reacted with 2,6-dichloropyridine by oxidative addition to give 25, the temperature needed for the reaction depending on the metal (M = Ni, 20 °C, Pd, 90 °C, Pt, 110 °C). The palladium complex readily inserted carbon monoxide to give a metal acyl complex [69]. Extremely reactive metal powders were obtained by the reduction of anhydrous metal halides by lithium naphthalide. The palladium and platinum powders produced in this way reacted with C_6F_5I to give {ArMI} solvated by ether. With nickel powder, however, the products were {Ar_2Ni} and NiI_2. Reaction of C_6F_5Br with nickel powder gave mainly {ArNiBr} [70].



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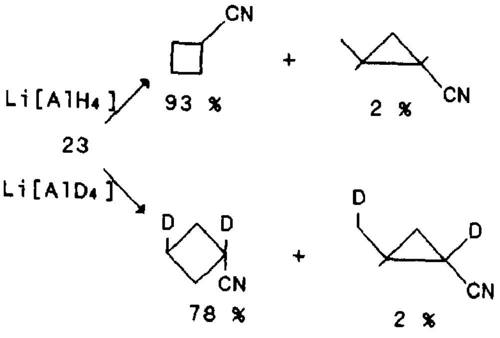

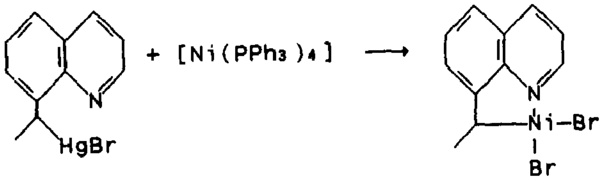

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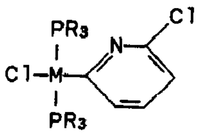

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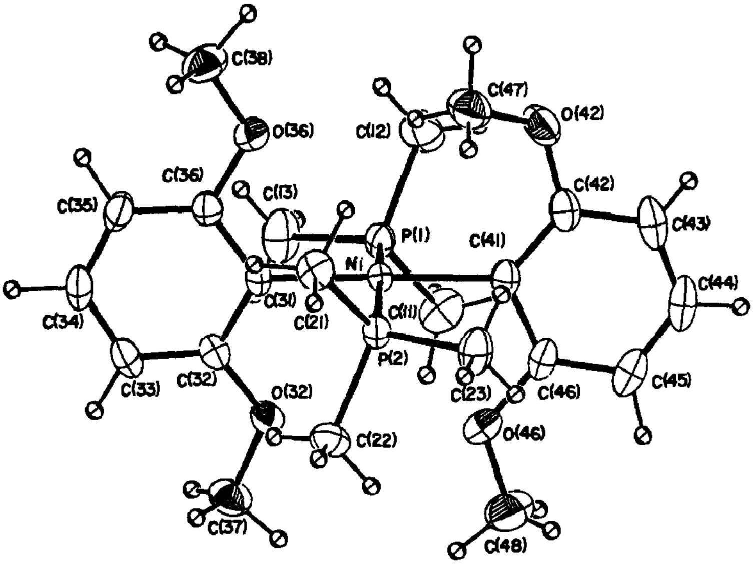
When a mixture of $[PdL_2X_2]$ (L = py or PPh_3 or L_2 = bipy, phen, or dppe) and Tl[OCOAr] (Ar = $C_6F_nH_{5-n}$) was boiled in pyridine, $[Ar_2PdL_2]$ was obtained, generally as a mixture of *cis*- and *trans*-isomers. The reaction was thought to proceed *via* CO_2 elimination from a palladium carboxylate intermediate [71].

A series of papers has described substitution reactions of $\{(C_6F_5)_2M\}$ complexes. In $[(C_6F_5)_2Ni(\eta^6\text{-arene})]$ the arene was readily displaced by a range of ligands including nbd, cod, bipy, thf, tht and py. It was noted that $MeOC_6H_5$ was more easily displaced than toluene [72]. The species *cis*-$[(C_6F_5)_2Pd(dioxan)_2]$ reacted with arylamines to give *cis*-$[(C_6F_5)_2Pd(H_2NAr)_2]$ [73], whilst the *trans*-isomer was substituted with dry thf to give *trans*-$[(C_6F_5)_2Pd(thf)_2]$. If the thf was wet, a butyrolactone derivative was obtained [74]. In the bridged complex *cis*-$[(C_6F_5)_2Pd(\mu\text{-dioxan})_2Pd(C_6F_5)_2]$, the bridging dioxan ligands were substituted by halides from $[RPPh_3]X$ to give a bis phosphonium salt [75]. In a rather confusing paper, *trans*-$[(C_6F_5)_2Pt(dioxan)]$ (*sic*) was said to be substituted by ketones to give species described as *trans*-$[(C_6F_5)_2Pt(ketone)_x]$, with $x = 1$ for propanone, butanone or cyclohexanone, and $x = 1.5$ for 2-hexanone or phenylethanone. The structures of the complexes produced remain far from clear [76].

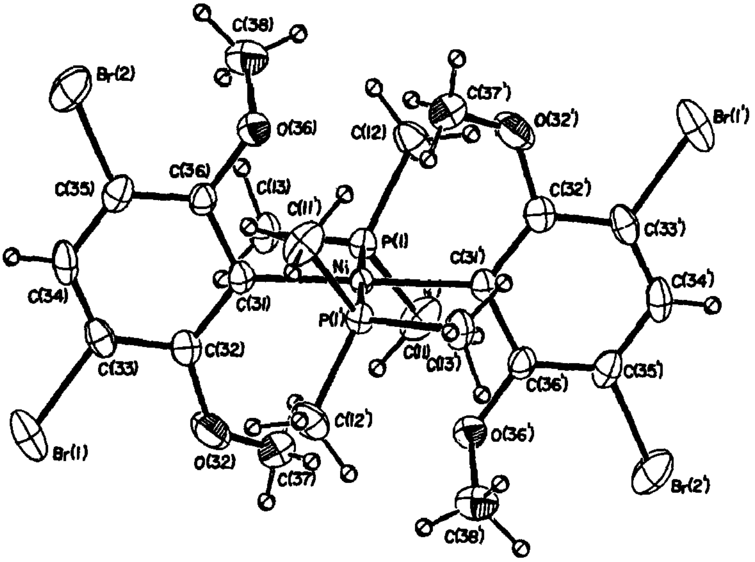
A range of complexes of the types *cis*-$[Ar_2Pt(PPh_3)_2]$ and *cis*-$[ArAr'Pt(PPh_3)_2]$ have been prepared, and their reductive elimination to give biphenyls investigated. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined for the reactions and were related to the pattern of substitution in the aryl rings [77,78].

Two complexes, *trans*-$[R_2NiL_2]$ (L = PMe_3, L = 2,6-$(MeO)_2C_6H_3$ or 2,6-$(MeO)_2$-3,5-Br_2C_6H), were prepared and thier structures established by X-ray diffraction studies (**26** and **27**). Intermolecular exchange of the phosphine ligand was catalysed by CO in **26** but not in **27**. This could be readily explained on the basis that in **26** three of the four methoxyl groups are pointing away from the metal, making CO approach relatively easy. In **27**, by contrast, all the methoxyl groups are directed towards the metal, by the bulk of the bromine atoms, making reaction with CO impossible [79]. Intermolecular halide exchange has been studied in the complexes *trans*-[$(C_6Cl_5)M(PMe_2Ph)_2X$] (M = Ni, Pd or Pt). In a chloride/iodide exchange between nickel and palladium or platinum, nickel chlorides and palladium or platinum iodides were invariably obtained, reflecting differences in the metal-halogen bond energies [80]. The term "coligand isomers" has been proposed to describe the pair of compounds in which one is formed by a reaction of the ligands in the central atom coordination sphere of the other. A few examples were chosen from platinum chemistry [81]. In species such as *trans*-[Ar_2NiL_2] in which Ar = 2-MeC_6H_4 or 2,6-$(MeO)_2$-3-Br-C_6H_2, and L = PMe_2Ph or PMe_3, mixtures of *syn*- and *anti*-isomers with respect to the unsymmetrically substituted ligands could be detected. Some of the isomerisations were catalysed by CO, *via* phosphine/CO exchange. The equilibrium constants were generally close to unity [82].



26 (Reproduced with permission from [79])
Thermal ellipsoids are drawn at the 30 % probability level

The reaction of *trans*-[$ArPt(MeOH)(PEt_3)_2$][BF_4] with Na[OOCH] and Na[BPh_4] gave the cations *trans*-[$ArPt(PEt_3)_2(\mu_2\text{-}H)Pt(PEt_3)_2Ar$], identified by nmr spectroscopic studies. The complex for which Ar = Ph, 28, was isolated and characterised by an X-ray diffraction study [83]. Another hydrido bridged species, 29, was obtained from the reaction of $[Pt(cod)_2]$ with *trans*-$[PhPt(PPh_3)_2(propanone)][BF_4]$ in the presence of molecular hydrogen. It was deduced that the phenyl and PPh_2 ligands were derived from one PPh_3 ligand, rather than from the *Pt*-aryl of the starting material, though the evidence for this could have been stronger [84].

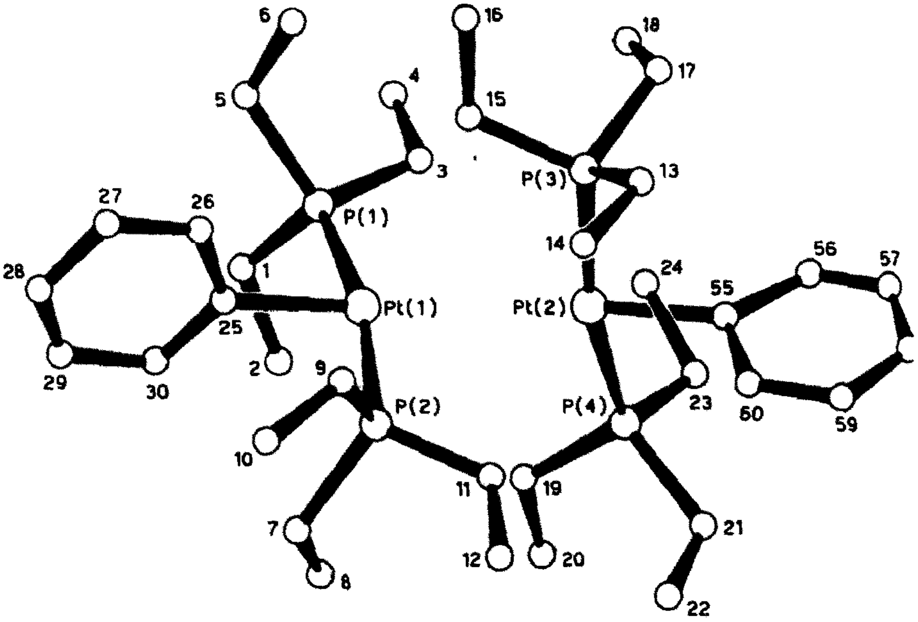


27 (Reproduced with permission from [79])

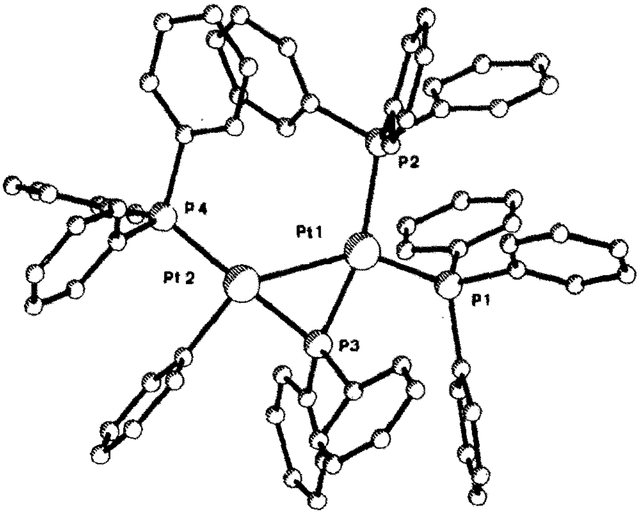
Thermal ellipsoids are drawn at the 30 % probability level.

Treatment of $[Ar_2Pd_2L_2(\mu\text{-}Cl)_2]$ with Ag[CN] gave a species described as $[Ar_4Pd_4L_4(\mu\text{-}CN)_4]$ (L = PEt_3, PPh_3 or $AsPh_3$, Ar = C_6F_5; L = PEt_3, Ar = C_6Cl_5), although the structures were not particularly well-characterised [85]. Reaction of $[ArPd(dppm\text{-}P)_2X]$ (Ar = C_6F_5, X = Cl, Br, I, [NCO] or C_6F_5) reacted with $[Pd_2(dba)_3]$ to give 30, the reactions of which were studied in some detail [86].

Reaction of 31 with ArNHR gave 32. A kinetic study implied that two mechanisms and two distinct transition states were involved [87].

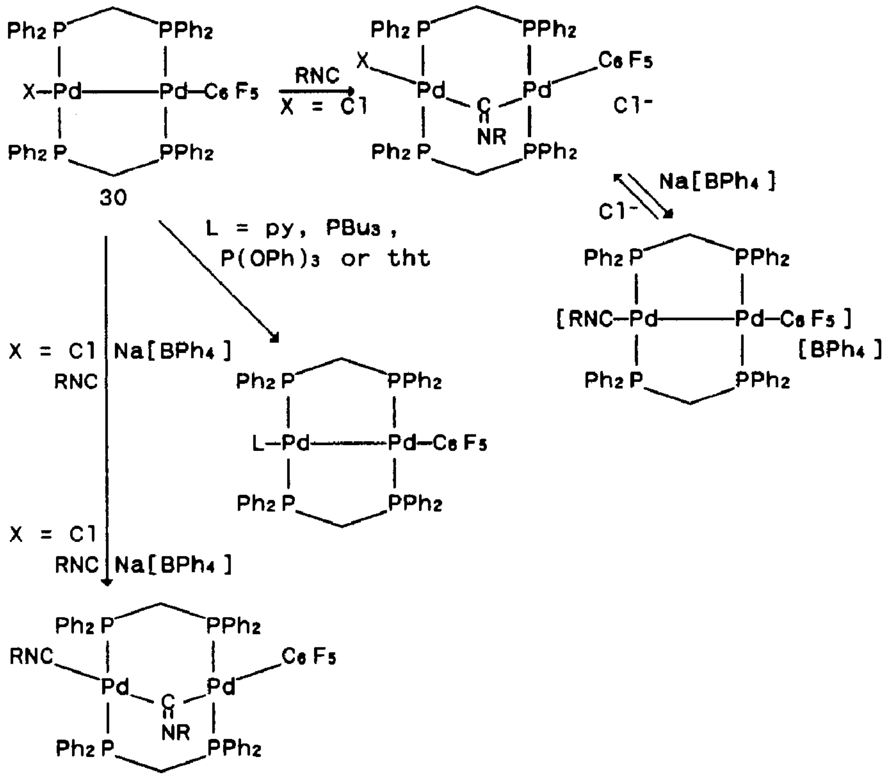


28 (Reproduced with permission from [83])



29 (Reproduced with permission from [84])

A perspective view of the cation $[(Ph_3P)(Ph)Pt(\mu\text{-}H)(\mu\text{-}PPh_2)Pt(PPh_3)_2]^+$. The Pt-Pt bond distances are 2.889(2) and 2.912(2) Å for the two independent molecules in the unit cell.



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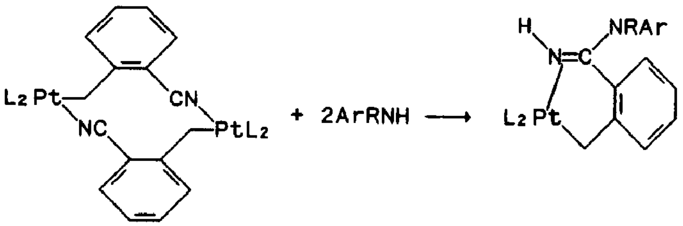

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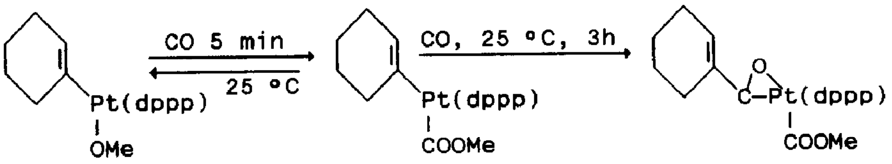
3 METAL CARBON BONDS FORMED BY INSERTION AND RELATED REACTIONS

Calculations have been undertaken on the carbonyl, "bridged" and methanoyl structures of $\{HPd(CO)\}^+$ and $\{HPd(H)(CO)\}$ model complexes using non-empirical SCF MO LCAO methods. It was concluded that an increase in the acceptor power at palladium stabilises the methanoyl structure, and hence favours the catalytic reduction of carbon monoxide by hydrogen at palladium complexes [88]. Calculations have also been used to investigate the reaction path for insertion of CO into a platinum(II)-methyl bond. In [MePt(CO)(PH_3)F] it was concluded that the platinum-methyl bond was stronger when it was *trans* to the PH_3 ligand than when it was *trans* to fluoride. In the insertion product, [MeCOPt(PH_3)F], a T-shaped structure was the most stable. In both *cis*- and *trans*-isomers of the starting material the methyl group migration was feasible, but CO migration was not [89].

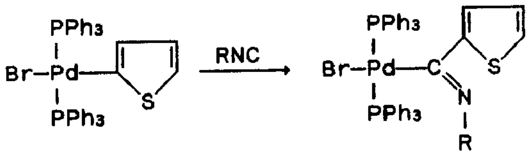
The complex [$R_2Pd_2L_2(\mu\text{-}Cl)_2$] was prepared by the action of R_2Hg on [$Pd_2L_2Cl_2(\mu\text{-}Cl)_2$], and readily inserted CO to give [$(RCO)_2Pd_2(\mu\text{-}Cl)_2L_2$]. The dimeric insertion product reacted with further ligand, L, to give *trans*-[(RCO)PdL_2Cl], which was also obtained by insertion of CO into the metal-alkyl bond of *trans*-[$RPdL_2Cl$]. The possible intermediacy of dimeric complexes in the carbonylation of *trans*-[$RPdL_2Cl$] was discussed [90].

The σ-vinyl complex, **33**, reacted with CO by insertion into the metal-oxygen bond to give **34** in a reversible reaction. The second insertion, which was appreciably slower and irreversible, gave **35**, characterised tentatively by infra-red spectroscopic data [91]. Reaction of Grignard reagents with [$Pd_{10}(CO)_{12}(PBu_3)_6$] gave mononuclear σ-complexes of palladium [92].



33 **34** **35**

The insertion of isonitriles into palladium-aryl bonds has been reported. The initial product was a carbene complex such as **36** [93]. 2-Pyridyl complexes reacted similarly, and ^{31}P nmr spectroscopy suggested an intermediate such as 37 [94]. Insertion of isonitriles in an intramolecular manner occurred in reaction (9) [95].



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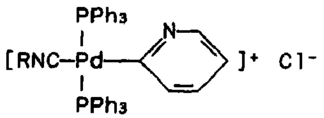

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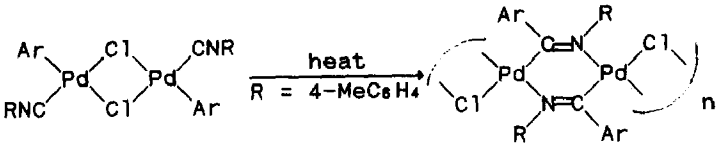
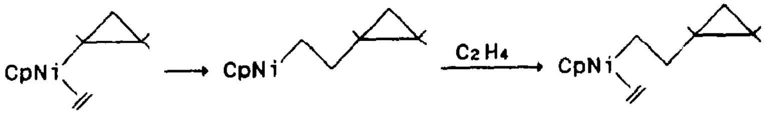


(9)

Insertion of an alkene into a metal-alkyl bond was shown to occur in reaction (10), and 38 reacted to give 39, but this product was rapidly rearranged under the reaction conditions [96]. Insertion of alkenes into metal-OH bonds has been studied from a theoretical point of view [97]. Reaction of $MeOOCC\equiv CCOOMe$ with *trans*-$[PhCH_2Pd(PPh_3)_2Cl]$ gave a σ-vinyl dimeric complex, as a mixture of three stereoisomers. Treatment with Tl[acac] gave 40, and other reactions were also investigated [98].



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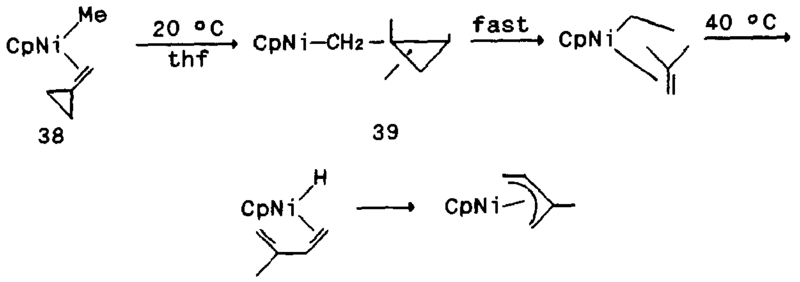

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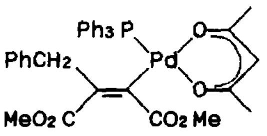

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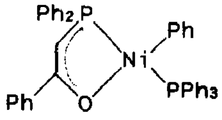
Insertion of CO_2 into the Ni–Ph bond of the ylide complex, **41**, gave [$L_xNiOCOPh$], which reacted with methanol to give PhCOOMe. Insertion of ethene yielded styrene. When coinsertion of ethene and styrene was attempted, some $PhCH_2CH_2COOMe$ was obtained, but yields were low [99]. Reaction of CO_2 and ethene with [Ni(cdt)] in the presnce of a ligand, L, gave **42**. Protonation of **42** yielded EtCOOH, whilst carbonylation gave butane dioate anhydride [100]. Treatement of [Ni(bipy)(cod)] with CO_2 and Cy-N=C=N-Cy gave initially **43**, which on protonation yielded Cy-N=CH-NHCy, CO_2 and $\{Ni(bipy)\}^{2+}$ [101]. In the presence of a substituted butadiene **44** was formed; this could be reacted with RX/HX to give a substituted unsaturated carboxylic acid [102]. A similar synthesis of **45** was described, and the product was shown to be close to planar by an X-ray diffraction study [103].



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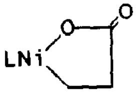

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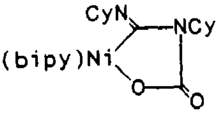

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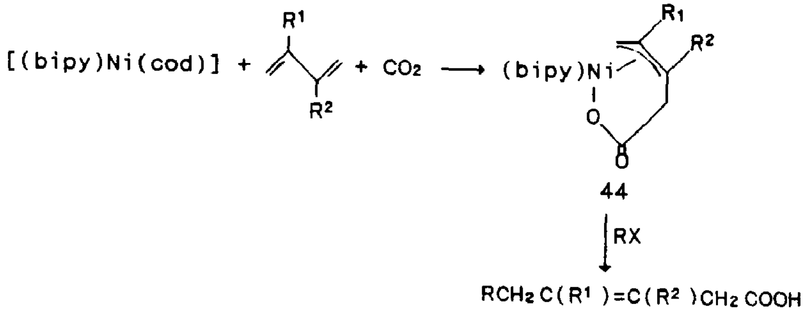
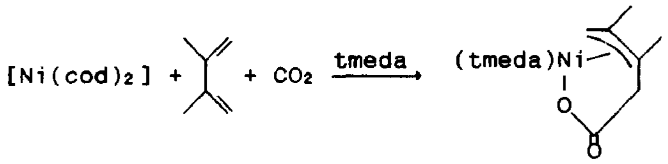


Complexes of the type {LNi(0)} reacted with PhNCO in a manner which depended on L. With L = tmeda head-to-tail linkage occurred to give **46**, which could be hydrolysed and decarbonylated to yield a substituted urea. By contrast, the reaction in the case of L = $\{(Et_3P)_2\}$ gave **47**. The complex was characterised by an X-ray diffraction study, and possible pathways for its formation were discussed [104]. The reaction between {(tmeda)Ni(0)}, PhC≡CPh and PhNCO gave initially 48, which reacted with a second alkyne (R' = COOMe) yielding 49, stable at −20 °C. This could be hydrolysed at low temperature, and decomposed at +20 °C to a pyridone [105].



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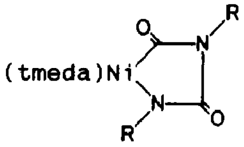

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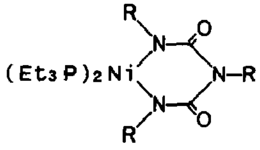

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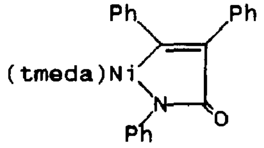

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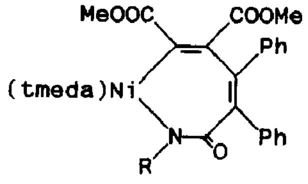

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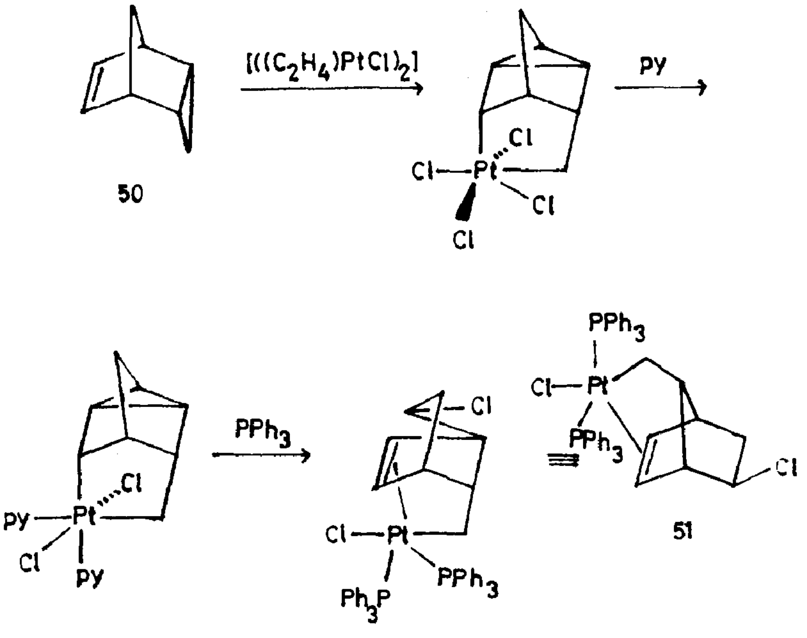
The insertion of a platinum moiety into the strained three membered ring of 50 has been reinvestigated, indicating that earlier work on this reaction was in error. The structure of 51 was determined unequivocally by an X-ray diffraction study, and it was suggested that the initial insertion was followed by a fast sigmatropic shift [106].

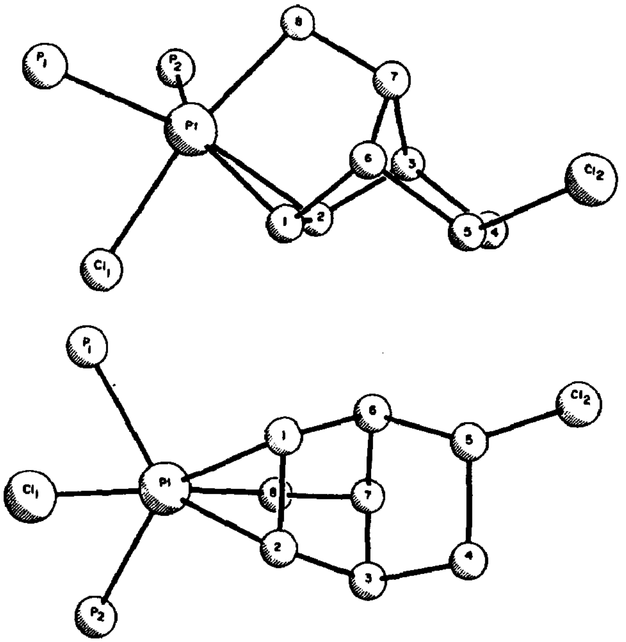
Reaction of $[Pt(PPh_3)_2(PhNO)]$ with $MeO_2CC{\equiv}CCO_2Me$ gave the cyclic insertion product, 52, and a similar reaction was observed for other alkenes and alkynes bearing electron withdrawing groups [107]. In a related process

$[Pt(PPh_3)_2(O_2)]$ reacted with $R_2C{=}C(CN)_2$ (R = CN or Me) to give **53**; an X-ray diffraction study revealed that the platinum adopted distorted square planar geometry, and that the dioxametallocycle adopted a twisted conformation [108]. The oxidation of 1-octene by the $[Pt(PPh_3)_2(O_2)]/CO_2$ adduct, **54**, has been studied (Scheme 2) [109].

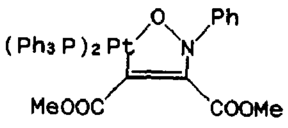


The reaction between $[Pt(cod)_2]$ and butanedioic anhydride in the presence of PCy_3 resulted not only in substitution but also in insertion into a carbon-oxygen bond to give **55**. Treatment of [Ni(bipy)(cod)] with pentane dioic anhydride resulted in insertion and decarbonylation to give **56** [110].

Insertion of platinum(0) into a tin-carbon bond occurred in reaction (11) [111]. Reaction of $[Ni(CO)_4]$ with $[TPP\{C{=}C(4\text{-}ClC_6H_4)_2\}]$ gave $[TPP\{C{=}C(4\text{-}ClC_6H_4)_2Ni\}]$, in which one nickel-nitrogen bond had been broken and one nickel-carbon bond made, relative to a conventional metal porphyrin derivative [112].



51 (Reproduced with permission from [106])
Perspective views of the rearrangement product 51



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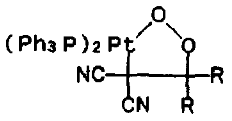

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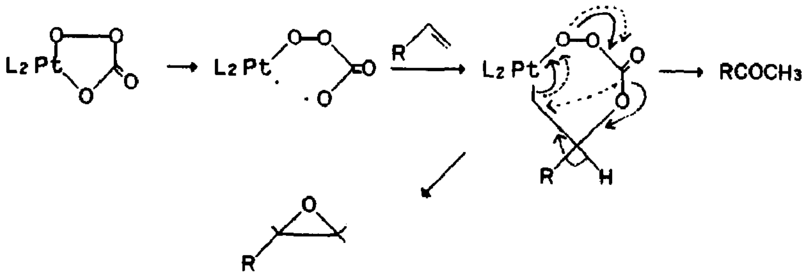
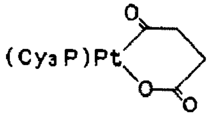


Scheme 2 Mechanism of oxidation of 1-octene by a platinum complex [109]



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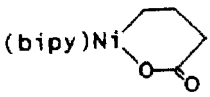

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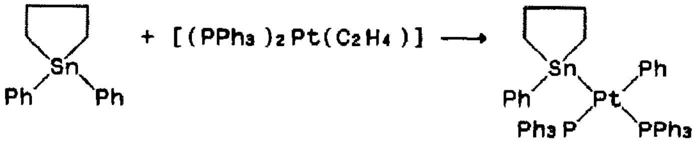


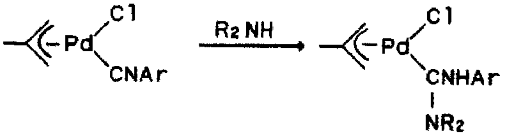
(11)

4 METAL CARBENE, CARBYNE AND YLIDE COMPLEXES

The reactions of Ni^+ with ethene oxide, cyclopropane, ethene or fluorinated hydrocarbons have been examined in an ion beam apparatus. Bond dissociation energies, D^o, for $\{Ni^+-CH_2\}$ and $\{Ni^+-CF_2\}$ were determined respectively as 381±25 kJ mol^{-1} and 198±30 kJ mol^{-1}. However, the difluorocarbene complex had considerable stability; for example reaction (12) was exothermic. The implications for alkene metathesis were discussed [113].

$$\{NiCH_2\}^+ + C_2F_4 \longrightarrow \{NiCF_2\}^+ + CH_2CF_2 \qquad (12)$$

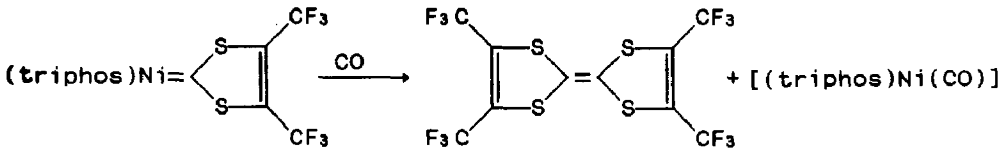
The reactions of amines with isonitrile complexes have again provided a useful route to carbene complexes. In the product of reaction (13) (Ar = 4-Me, 4-MeO or 4-ClC_6H_4, R = Me or Et) the diastereoisomers were interconverted *via* a fairly restricted rotation about the carbene-metal bond [114,115]. Related reactions were also reported [116,117].



(13)

The species $[(triphos)Ni(\eta^2-CS_2)]$ is prepared by reaction of [(triphos)Ni(CO)] with CS_2, and reacted with 1,1,1,4,4,4-hexafluoro-2-butyne to give the carbene complex 57. Carbonylation of 57 gave 58 [118].

The substitution reactions of 59 at the carbonyl carbon atom [119] and 60 at the palladium atom have been studied. The reactions of 61 with MCl_2 (M = Pd or Pt) proceed *via* complex migrations, for which mechanisms were suggested [120]. Reactions of the polymeric species, 62, with monodentate ligands, L, gave initially dimers, and monomers with an excess of L. With chelating ligands such as tmen, however, ylid complexes were produced, and 63 was characterised by an X-ray diffraction study [121].



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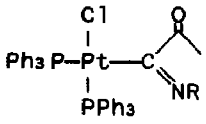

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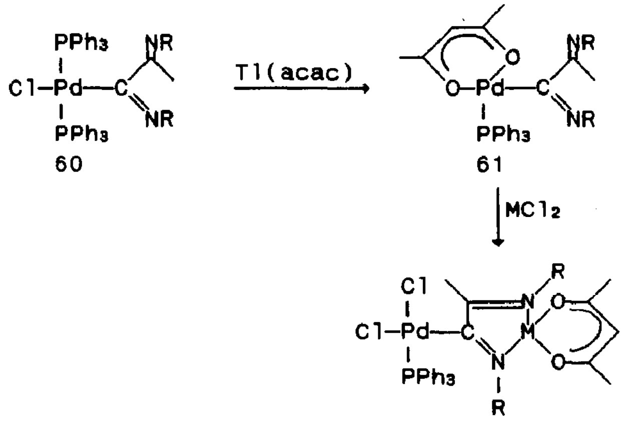

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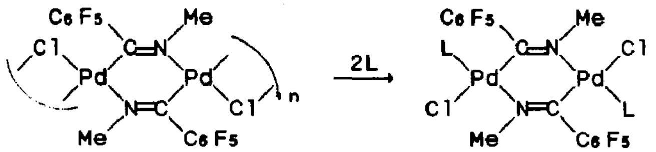

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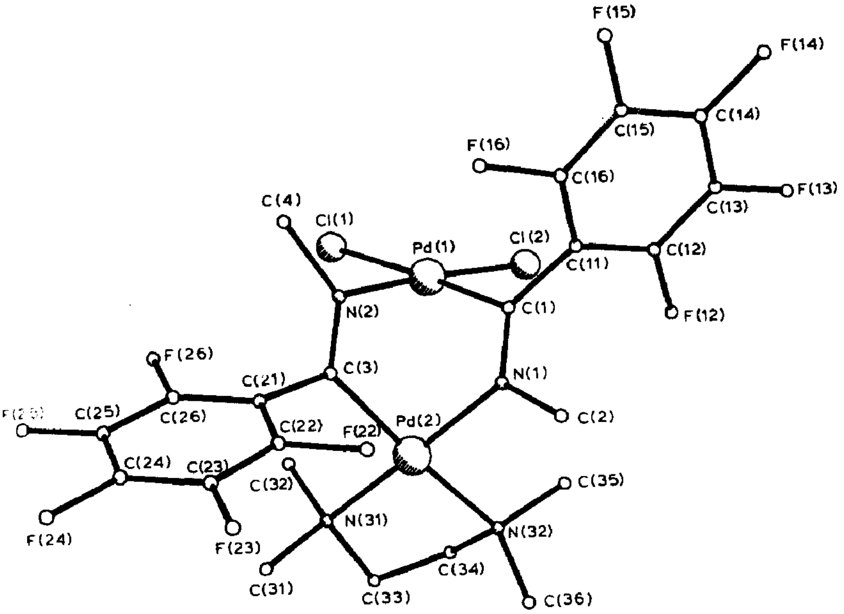


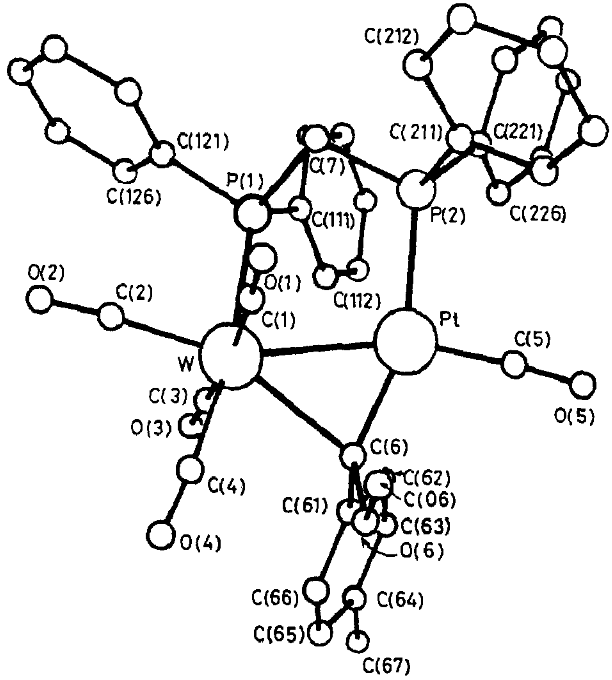
63 (Reproduced with permission from [121])

Reaction of *trans*-$[Pt(PR_3)_2(X)(R'OH)][PF_6]$ (R' = Me or Et) with $Me_3SiC{\equiv}CR^2$ (R^2 = H, Me or $SiMe_3$) gave *trans*-$[Pt(PR_3)_2\{C(OR')CH_2R^2\}][PF_6]$ by a mechanism involving cleavage of the C-Si bond by alcohol attack, and hydride shift in an alkyne complex [122].

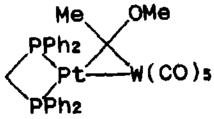
The reaction of diazomethane with $[Pt_2(\mu\text{-dppm})_2X_2]$ gave the A-frame complex $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}CH_2)X_2]$. Kinetic data were obtained for the reaction, suggesting that the rate-controlling step was the transfer of an electron pair from the metal-metal bond of the starting material to the methylene group of diazomethane. The rate of the reaction was considerably reduced when both the halide groups, X, were replaced by a neutral amine or pyridine [123].

Further publications have detailed the work of Stone's group on bridging carbene complexes. Treatment of the carbene complex, $[(cod)Pt\{\mu\text{-}C(OMe)R\}W(CO)_5]$, with dppm gave $[(OC)Pt(\mu\text{-dppm})\{\mu\text{-}C(OMe)R\}W(CO)_4]$ (64, which was characterised by an X-ray diffraction study), $[(\eta^1\text{-dppm})Pt(\mu\text{-dppm})\{\mu\text{-}C(OMe)R\}W(CO)_4]$, and $[Pt_3(CO)_3\{\mu\text{-}C(OMe)R\}_3]$. 64 reacted with $H[BF_4]$ to give the related cationic carbyne complex, and with BBr_3 to give $[BrPt(\mu\text{-}CR)(\mu\text{-dppm})W(CO)_4]$ [124]. For R = Me an initial product, 65, could be isolated. Chromaography of this species on basic alumina gave 66, identified by X-ray diffraction. One of the carbonyl ligands is semibridging to platinum [125]. The Tebbe reagent, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ was able to methylenate the carbon-tungsten double bond of $[(Me_3P)_2Pt(\mu\text{-}CAr)W(CO)_2(\eta^5\text{-}Cp)]$

to give 67. The same species was obtained by an alternative route, *viz.* methylation with $[Me_3O][BF_4]$ to give $[(Me_3P)_2Pt\{\mu\text{-}C(Me)Ar\}W(CO)_2Cp][BF_4]$, followed by deprotonation with sodium hydride [126].

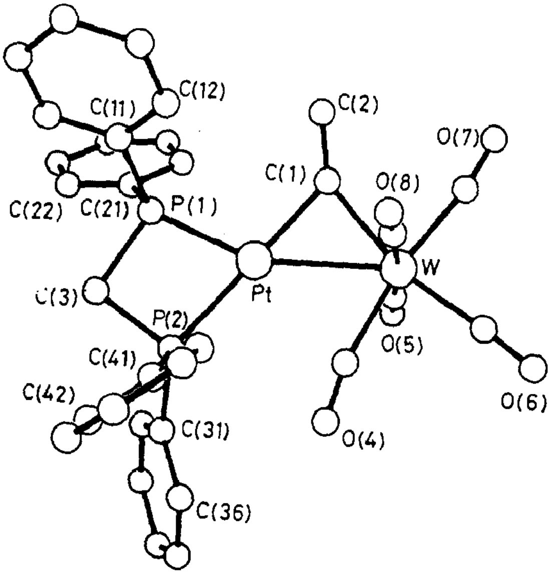


64 (Reproduced with permission from [124])

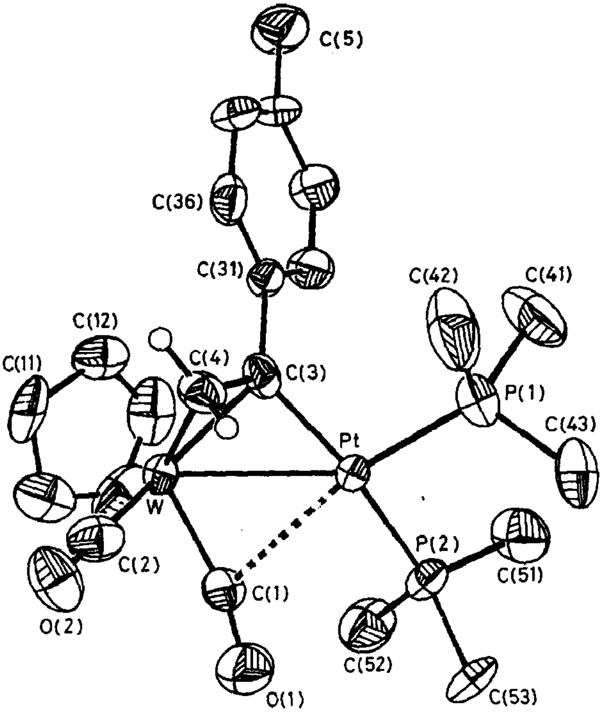


65

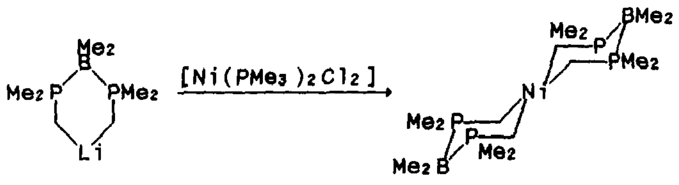
Reports on ylid complexes this year have been extremely diverse. The preparation of 68, was described in detail [127]. A species of the stoichiometry $[Ni(ylid)X_2]$ was obtained by reaction of $CpPPh_3$ with NiX_2; the nature of the bonding was not clear, but a sandwich type structure was favoured by the authors in a very vague paper [128]. Again this year both papers and patents have described the use of ylid complexes such as 69 as catalysts for the oligomerisation of ethene [129-133].



66 (Reproduced with permission from [125])



67 (Reproduced with permission from [126])



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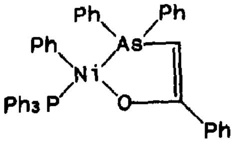
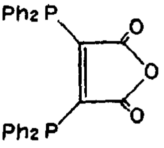


69

Treatment of 70 with [CpPd(η^3-C_3H_5)] gave the ylid complex, 71, which was converted to 72 by oxidation with molecular iodine [134]. The cyclometallated species, 73, reacted with $[Ph_2PCHY]^-$ (Y = CN or COOEt) to give 74. With the neutral ligand 75 was also obtained, and was characterised by an X-ray diffraction study. A mechanism was proposed for the reaction [135]. When $[Pd(PhCN)_2Cl_2]$ reacted with $EtN(CHMe_2)_2$ the product was 76, characterised by X-ray diffraction. Bu_3N and Et_3N reacted similarly. A mechanism involving metallation α to nitrogen, followed by β-hydride elimination and electrophilic attack on the enamine produced was proposed [136].



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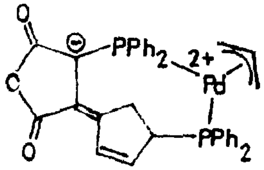

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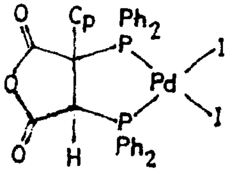

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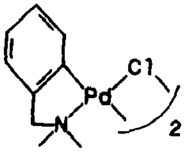

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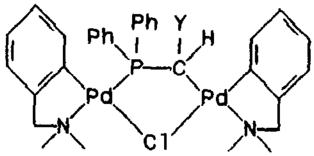

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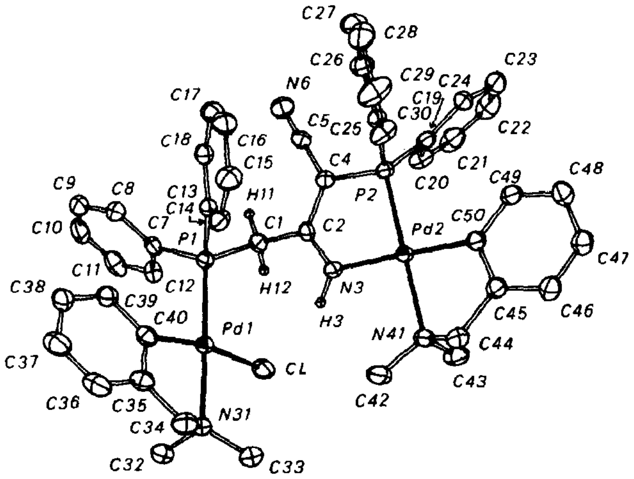
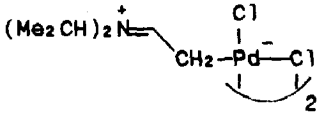


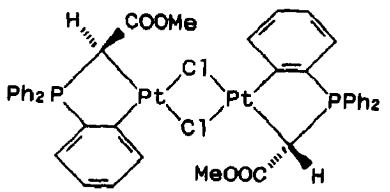
75 (Reproduced with permission from [135])

The two CH_2Cl_2 solvent molecules have been omitted for clarity



76

Reaction of $PtCl_2$ with $Ph_3P{=}CHC({=}O)Me$ in a 1:2 molar ratio yielded 77, characterised by a diffraction study. Spectroscopic data for the complex were discussed [137]. A full paper has now been published concerning the alkylation of 78 (reaction (14)), which proceeds *via* an ylid complex [138].



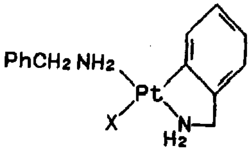
77

$$[Pt(dppm)X_2] \xrightarrow[2)\ RX]{1)\ Li[N(SiMe_3)_2]} [Pt(Ph_2PCHRPPh_2)X_2] \qquad (14)$$

78

5 METAL COMPLEXES FORMED BY INTERNAL METALLATION AND RELATED REACTIONS

There continue to be many reports of the preparations and reactions of cyclometallated complexes of benzylamine derivatives. Reaction of *trans*-$[M(PhCH_2NH_2)_2I_2]$ with two molar equivalents of $Ag[BF_4]$ in propanone followed by treatment with KX gave 79 (X = Cl, I or SCN) for M = Pt. Using the palladium complex as the substrate, however, the starting material was regenerated on addition of KI. 80, prepared by carbonylation of 79 (X = I) in methanol, was characterised by an X-ray diffraction study. It was suggested that the metallation proceeded *via* electrophilic attack of the metal on the aryl ring [139]. Metallation of 81 (x = 2 or 3) occurred only once, giving 82, the mechanism of the reaction being discussed in considerable detail [140].



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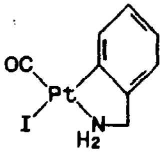
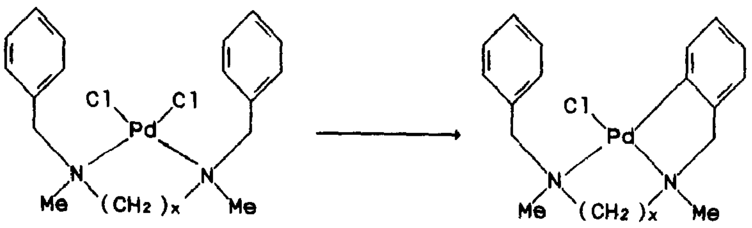


80

Several regioselective metallations have been noted (reactions (15), (16) and (17)). In each case the products were subjected to further interesting transformations [141-143].

83 and its stereoisomers have been prepared and were resolved *via* complexation with 84 [144]. The bridge splitting reactions of 85 with ligands such as 2-phenylethylamine or pyridine could be reversed by treatment with SO_2 in benzene/propanone [145].



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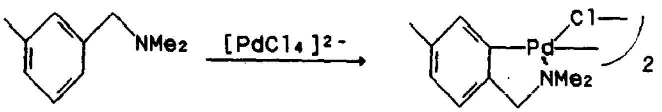
82



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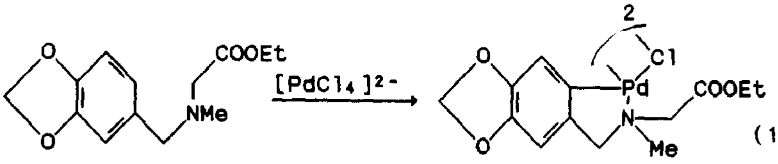

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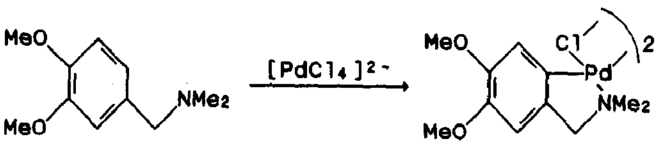

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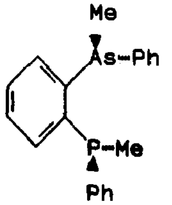

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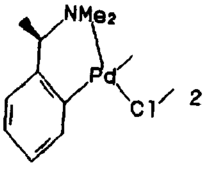
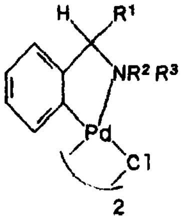


84

The complexes 86 (M = Ni, Pd or Pt) reacted alkynes bearing electron withdrawing groups, such as $CF_3C{\equiv}CCF_3$, by insertion into a palladium-carbon bond to give larger metallocycles [146]. The insertion of an alkene into 87 was subjected to a kinetic investigation, and was found to be complex. The mechanism of Scheme 3 was proposed [147,148].



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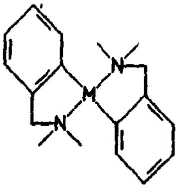

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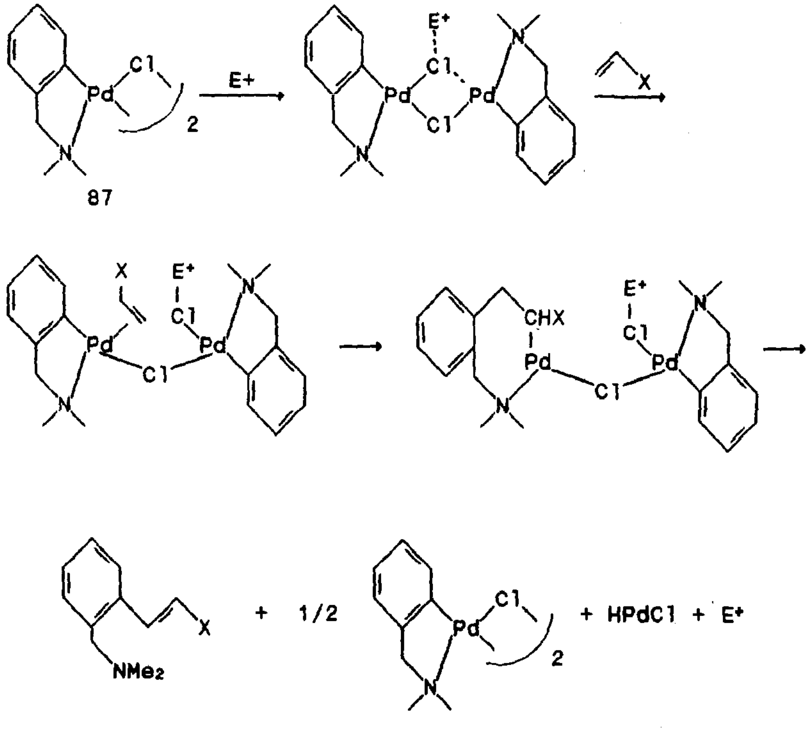
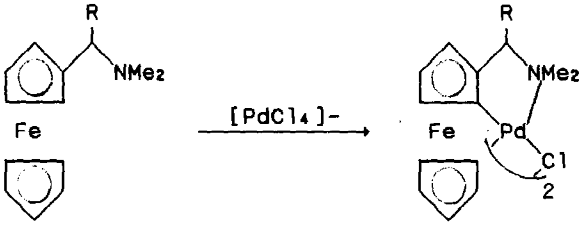


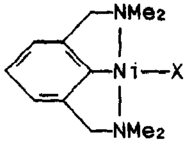
Scheme 3 Mechanism of insertion of alkenes into a cyclometallated palladium complex

A number of related complexes derived from ferrocenes have been studied. Reaction of **88** with $PdCl_2$ gave **89**, with a planar element of chirality. One of these derivatives was used in an enantioselective prostaglandin synthesis [149]. Treatment of **89** with amino acid derivatives to give bridge splitting reactions was investigated [150,151].



88 **89**

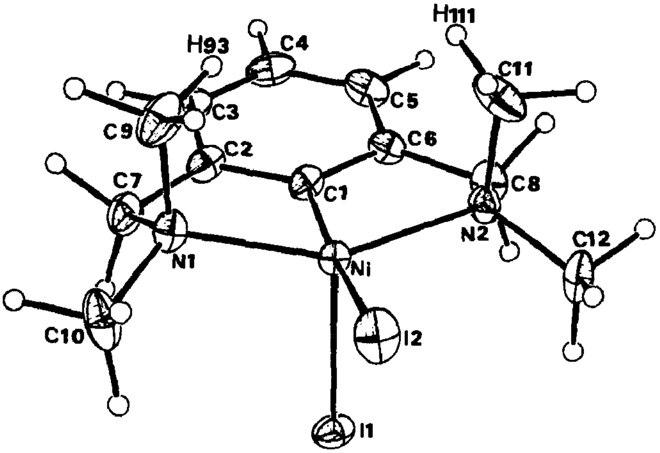
The bis(cyclometallated) species **90** reacted with CuX_2 or half an equivalent of a halogen to give the paramagnetic nickel(III) derivative, **91**. **91** was characterised by an X-ray diffraction study, and its epr spectrum was reported [152]. The related platinum(II) complex was oxidised to the platinum(IV) complex, shown by an X-ray diffraction study to possess octahedral geometry [153]. UVPES date for **90** and the related palladium and platinum derivatives showed strong evidence for π-interaction between the arene ring of the ligand and the metal orbitals [154].



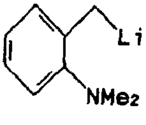
90

The lithium derivative of 2,*N*,*N*-trimethyl aniline, **92**, reacted with $[Ni(PMe_3)_2Cl_2]$ to give **93**. Insertion of $CF_3C{\equiv}CCF_3$ gave **94** which was transformed both in solution and in the solid state to **95**, characterised by an X-ray diffraction study [155].

A few other cyclometallated complexes of simple amines have been reported. Reaction of the mercury compound, **96** with $[Pt(PPh_3)_4]$ gave **97**, the epr spectrum of which was reported [156]. Bridge splitting reactions of **98** were reported [157].



91 (Reproduced with permission from [152])



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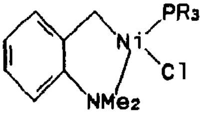

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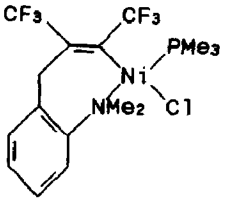
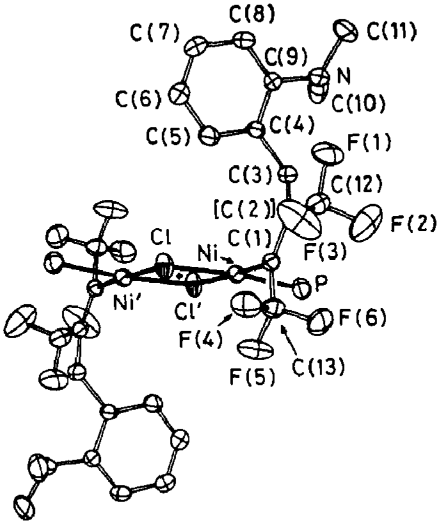
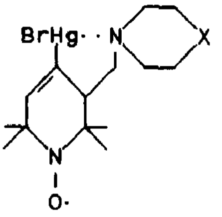


94

Several cyclometallated complexes of imines have been reported. Oxidative addition of the carbon-bromine bond of 99 to $[Pd(dba)_2]$ gave the dimeric species, 100. A number of related examples were also recorded, and bridge splitting reactions were studied [158]. 101 was reported to yield cyclometallated species of stoicheiometry $[\{PdLX\}_2]$ with PdX_2, but the structures of the complexes were not well defined [159]. Some bridge splitting reactions were also investigated [160]. Reaction of 102 with $Pd(OCOMe)_2$ gave 103; some arylation reactions of the product were studied [161].



95 (Reproduced with permission from [155])
Molecular structure of [{Ni(CF$_3$C=C{CF$_3$}CH$_2$C$_6$H$_4$-2-NMe$_2$)(PEt$_3$)(μ-Cl)}$_2$]. The Et groups of the PEt$_3$ are omitted for clarity.



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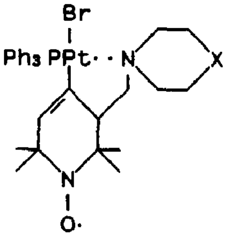

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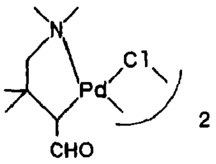

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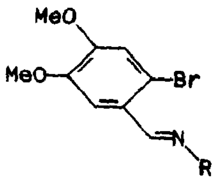

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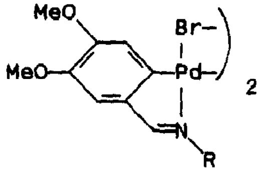

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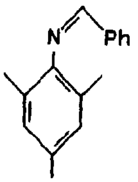

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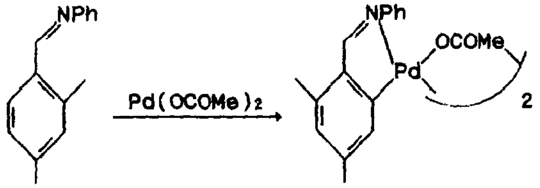
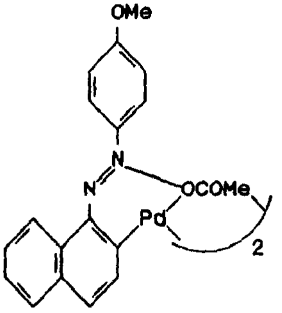


102

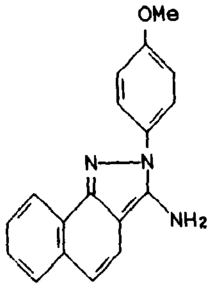
103

Bridge splitting reactions of cyclometallated azoarene complexes such as 104 have been studied. However, in the presence of dppe and [Bu_4N][CN] the 3-amino-benzo[g]indazole, 105, was produced [162].



104

Reaction of 106 with 107 resulted in a condensation reaction [163]. The related palladium complex underwent reversible ring opening in the presence of PBu_3. Deuterium exchange experiments indicated that the process was not simple, with at least two independent reaction pathways involved [164].



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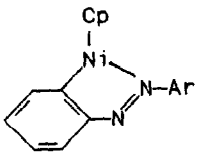

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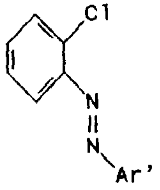
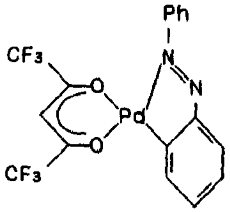


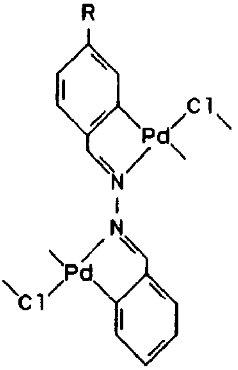
107

The yellow crystalline form of 108 underwent a disordering process on heating and expansion, to give, irreversibly, a red polymorph. The two complexes could, however, be interconverted by recrystallisation. X-ray diffraction studies of the two species revealed very different packing arrangements. Analogous complexes with substituents on the aryl rings do not undergo such changes. It was concluded that the molecular stacks slip on heating by moving [011] in the direction of the long axis of the molecule [165]. The colour change is due to the rotation of the exocyclic phenyl ring into the plane of the phenylazo group [166].



108

Benzalazines, ArCH=N-N=CHAr, reacted with $PdCl_2$ to give the cyclometallated polymer, 109. Bridge splitting reactions were studied [167]. Reaction of the cationic cyclometalled species, 110, with secondary amines, gave 111. Kinetic studies implied that the process occurred *via* direct nucleophilic attack of the amine, followed by hydrogen transfer in a 4-membered transition state [168].



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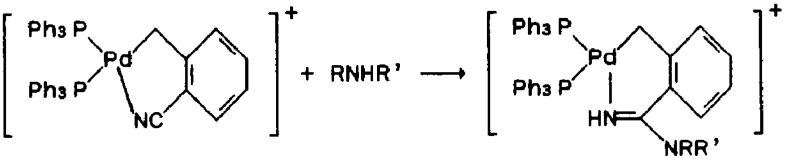
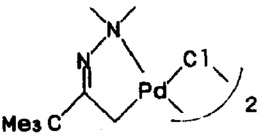


110 111

Reaction of the hydrazone, $Me_3CC(Me)=N-NMe_2$, with $[Pd(RCN)_2Cl_2]$ gave species of stoicheiometry $[PdL_2Cl_2]$ and $[\{PdLClL\}_2]$, Carbopalladation was spontaneous in solution, but was accelerated by the presence of a base giving 112. The mode of hydrazone coordination, and hence the metallation observed, was found to be dependent on both steric and electronic factors [169]. Reaction of 113 with PdX_2 or equivalent gave 114 [170].



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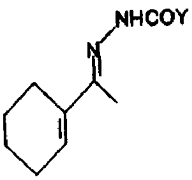

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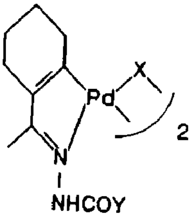
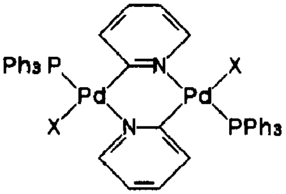


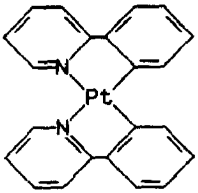
114

There have been further reports of the metallation of pyridine derivatives. The protonation of **115** occurred reversibly at nitrogen to give *cis*-[Pd(2-pyH)(PPh$_3$)X$_2$], this complex being converted to *trans*-[Pd(2-pyH)L$_2$X][ClO$_4$] in the presence of Na[ClO$_4$] and two equivalents of an appropriate ligand. Species of the latter type could also be prepared by protonation of *trans*-[Pt(PPh$_3$)$_2$(2-py)Br] with H[ClO$_4$]. Both the protonation and methylation by dimethyl suphate occurred at nitrogen [171,172].



115

The complex **116** was prepared from the relevant aryl lithium compound and *trans*-[Pt(SEt$_2$)$_2$Cl$_2$]. The red-orange crystals showed very strong emission at room temperature under UV irradiation. Cyclic voltammetry indicated that the complex underwent a reversible reduction at -1.96 V and an irreversible oxidation at +0.46 V. It was concluded that the reduction was ligand centred with the extra electron being accomodated in a π^* orbital. The oxidation on the other hand, was probably metal centred, giving a platinum(III) species, which decomposed rapidly [173]. X-ray diffraction studies of **117** and **118** revealed a boat-like molecular conformation with exact (for **117**) or close (for **118**) two-fold symmetry. The failure of **118** to undergo a second internal metallation was attributed to a shortened palladium-carbon bond in the first formed metallated ring, and the larger constraining angles in the remaining unmetallated ring [174]. Cyclometallation reactions of 2,6-dichloropyridines and related species have been investigated [175].



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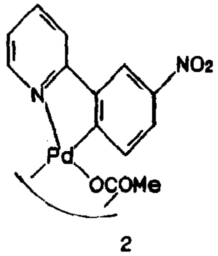

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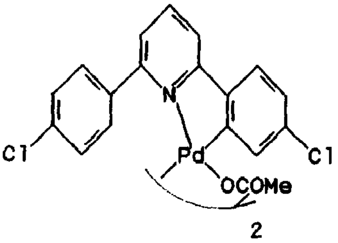
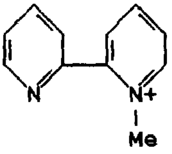


118

Reaction of $K_2[MX_4]$ (M = Pd or Pt, X = Cl or Br) with 119 (bipyMe) resulted in the formation of $[M(bipyMe)X_3]$. The complex for which M = Pt and X = Cl underwent cyclometallation on heating to give 120, or an oligomer [176]. Metallation of 121 occurred on the remote ring to give a *cis*-chelated dimer, 122. Reactions with 123 and 124 resulted in only a single metallation [177]. Metallation of 125 by $Na_2[PdCl_4]$ occurred at the aldehyde group; many spectroscopic data were reported [178].



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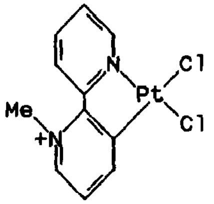
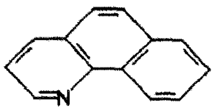


120

Metallation of 2-(CH_2CMe_3)py occurred at one of the methyl groups on treatment with $Pd(OCOMe)_2$. The usual bridge splitting reactions were reported, including the formation of 126 [179]. Reaction of 127 with $PdCl_2$ in the presence of LiCl, MeCN and $K_2[CO_3]$ gave 128. The structure of this species was established by an X-ray diffraction study, and is the first cyclopalladated pyridine complex containing an sp^3 carbon to palladium bond in a six-membereed ring to be so characterised [180]. The reaction of 129 with $Na[HBPz_3]$ resulted in bridge splitting, but with $Na[Bpz_4]$ substitution of the ligand and the halide occurred leaving the bridged dipalladium unit intact [181].



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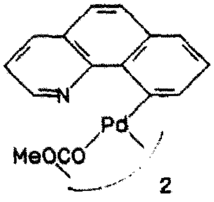

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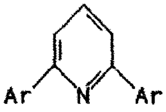

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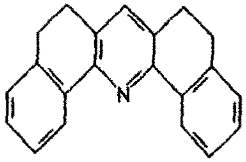

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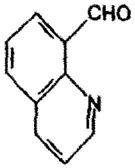

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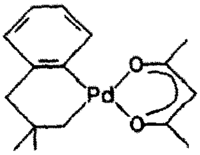

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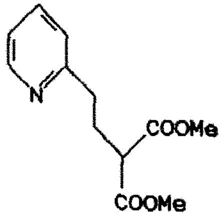
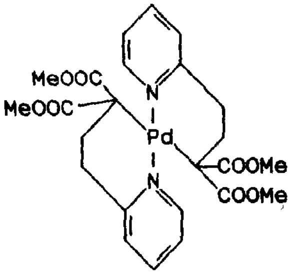


127

Reaction of 130 with $NiBr_2$ gave the cyclometallated species 131, which was also obtained from $[Ni(cod)_2]$ and $Hg(PhPz)_2$ [182]. Tripyrazolylmethane (tpzm) reacted with $[Me_2Pt(cod)]$ to give initially $[Me_2Pt(tpzm)]$. Treatment with hot pyridine yielded 132, characterised by X-ray diffraction, and methane. Both 132 and $[Me_2Pt(tpzm)]$ reacted with PPh_3 in pyridine to give 133, which metallated further on thermolysis to 134 [183]. Bridge splitting reactions of 135 were described [184].



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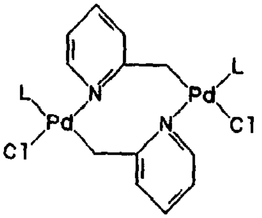

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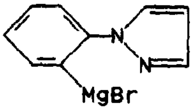

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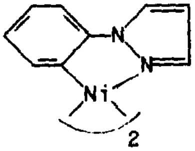

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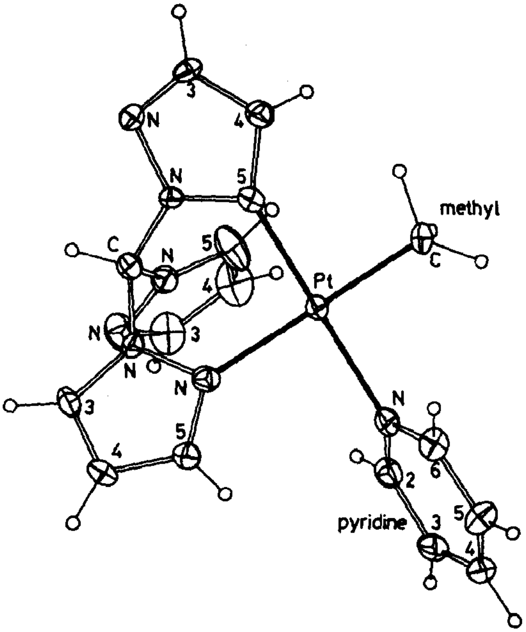
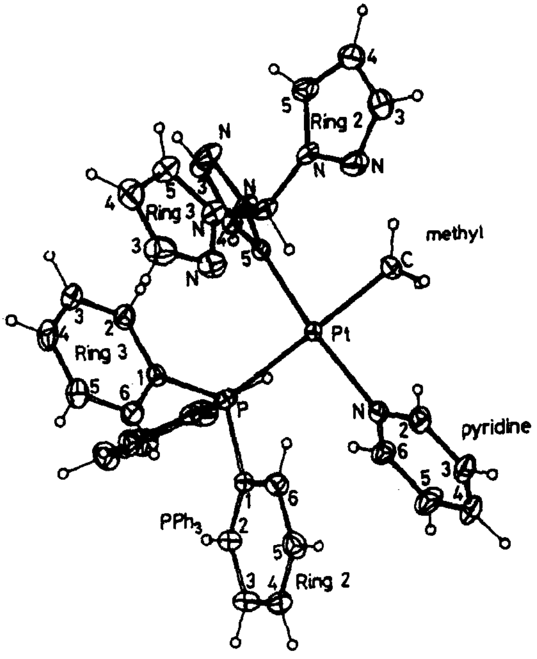
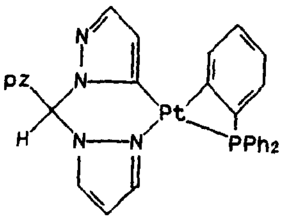


132 (Reproduced with permission from [183])

Molecular projection normal to the platinum coordination plane showing atom labelling. Hydrogen atoms have arbitrary radii of 0.1 Å.



133 (Reproduced with permission from [183])
Molecular projection normal to the platinum coordination plane showing atom labelling. Hydrogen atoms have arbitrary radii of 0.1 Å·



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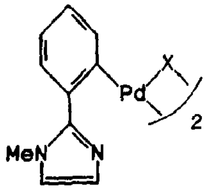
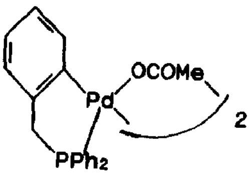


135

This year has seen the publication of rather more papers concerning the internal metallation of phosphine complexes. Reaction of $PhCH_2PPh_2$ with $Pd(OCOMe)_2$ gave 136, which underwent the usual bridge splitting reactions [185]. Internal metallation of 137 occurred at 250 °C. There was some exchange of the hydrogen atoms attached to the 2-position of the $-PPh_2$ groups, implying that some temporary metallation had also taken place at these sites [186].



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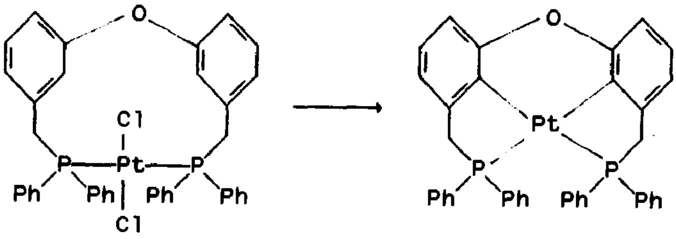
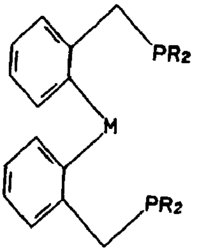


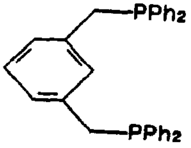
137

When 138 was reacted with butyllithium dimetallation occurred at the benzylic positions, and alkylation was readily achieved [187]. The reactions of the *trans*-isomer, with electrophiles, including bromine and $HgBr_2$, were also studied [188].



138

Treatment of 139 with palladium(II) or platinum(II) halo complexes gave rise to 140 (X = halogen). 140 (X = H, M = Pt) could be produced by reaction of the platinum complex with $Na[BH_4]$, but the related palladium complex decomposed under these conditions [189].



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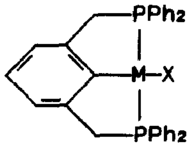
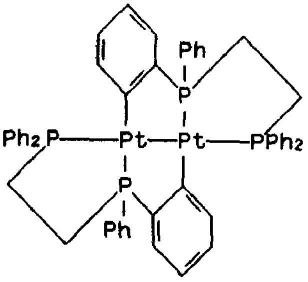


140

The reaction of 141 with iodomethane was investigated, the initial product being postulated as 142. This intermediate reacted with various nucleophiles, and the product of reaction with methyl lithium, 143, was characterised by an X-ray diffraction study [190]. The initial adduct reacted reversibly with sodium methoxide to give 144 [191]. The bridged cationic complex, [Pt$_2$(PPh$_3$)$_2$(μ-dppm)$_2$][PF$_6$]$_2$, could be deprotonated by methoxide ion to give 145. This could be described as a diplatinum(I) species (Pt-Pt = 2.659(2) Å), but might be better considered as having a Pt(0)→Pt(II) bond, which would explain the distortions observed at Pt(1) in the crystal structure [192].



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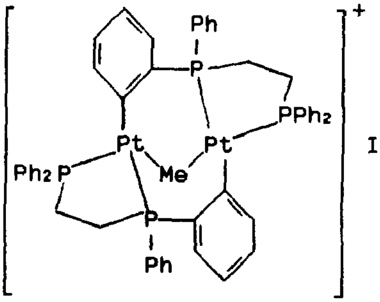

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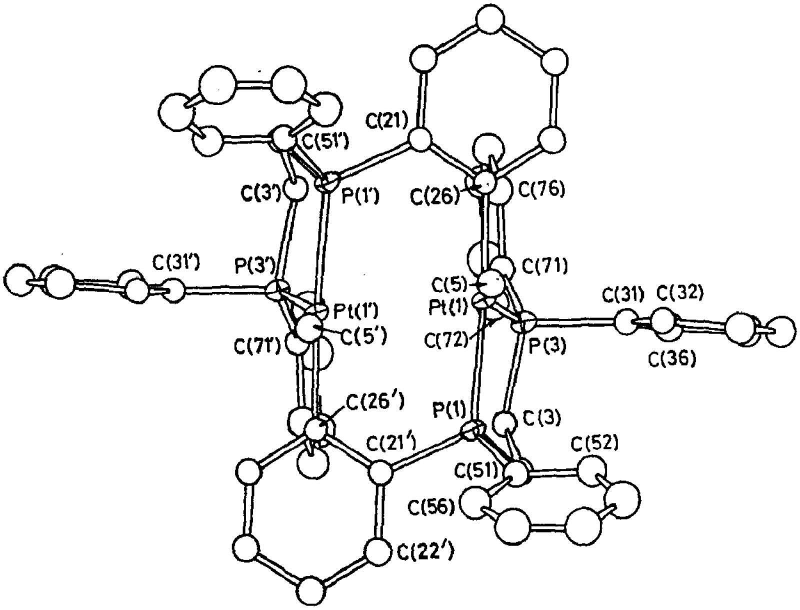
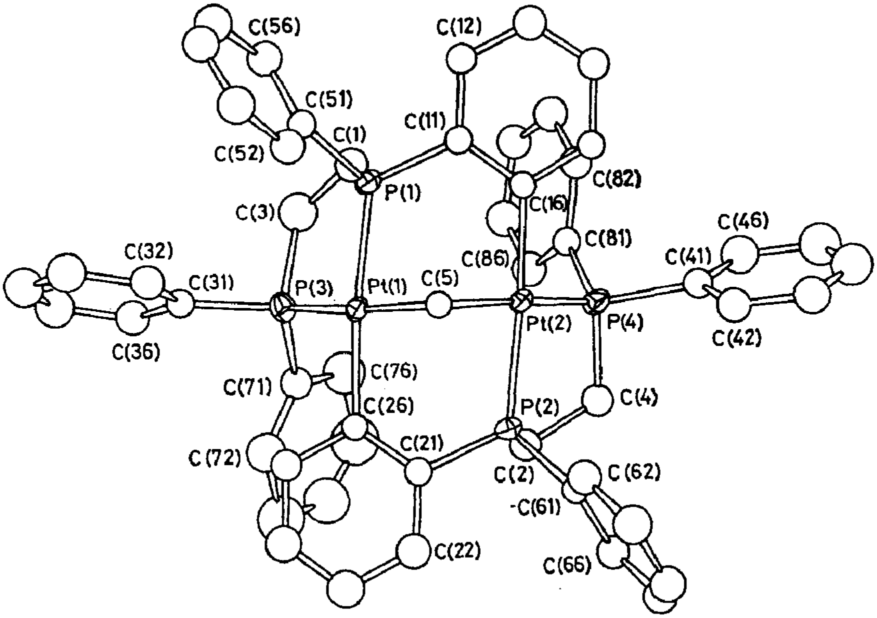


143 (Reproduced with permission from [190])

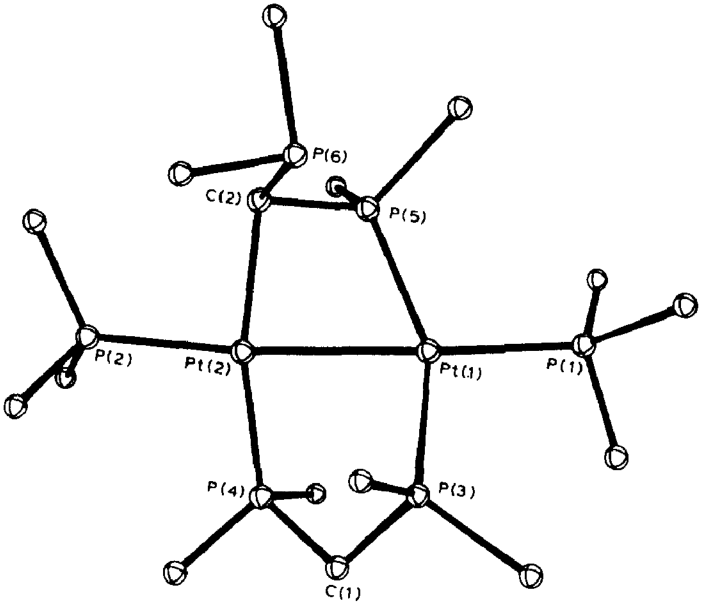
View of the molecule [Me$_2$Pt$_2$(μ-2-C$_6$H$_4$P(Ph)CH$_2$CH$_2$PPh$_2$)$_2$] down the two-fold axis.



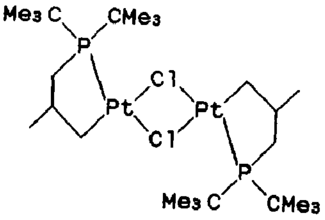
144 (Reproduced with permission from [191])
View of the molecule $[Pt_2(\mu\text{-}2\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2)_2(\mu\text{-}CH_2)]$ down the approximate two-fold axis.

The preparations of $[HPt(P\text{-}C)(PR_3)]$ ($(P\text{-}C) = \text{-}P(CMe_3)_2CMe_2CH_2\text{-}$) from $[Pt(P\text{-}C)Cl(PR_3)]$ and $Na[BH_4]$ have been described [193]. The preparation of $[Pt(P\text{-}C)(SnCl_3)L]$ ($L = PR_3$, $AsPh_3$ or CO)) has also been noted [194]. Reaction of $[Pt(NCCMe_3)_2Cl_2]$ with $Ph_2PCH_2CHMe_2$ resulted in simple substitution, with no cyclometallation, even after prolonged heating. However, with $Me_3CP(CH_2CHMe_2)_2$, both **146** and its *cis*-isomer were formed. Bridge splitting reactions were studied [195].

Ibers' group has published three papers concerning the metallation, with ring opening, of cyclopropyl substituted phosphines. With **147** and $PdCl_2$, *trans*-$[PdL_2Cl_2]$ was initially formed, and was metallated to **148**, by heating in $MeOCH_2CH_2OH$ or CH_3COOH. A chelating π-allyl complex was proposed as the intermediate [196]. Thermolysis of **149** in $MeOCH_2CH_2OH$ gave **150**, this being the first example of the isolation of a σ-allyl complex prepared by the activation of a cyclopropane by a transition metal complex [197]. The structure of the complex was detirmined by an X-ray diffraction study [198].



145 (Reproduced with permission from [192])
A perspective view of the metal coordination polyhedron in the $[Pt_2(PPh_3)_2(Ph_2PCH_2PPh_2)(Ph_2PCHPPh_2)]^+$ cation. For clarity each of the fourteen phenyl rings is represented by its *ipso*-carbon atom only.



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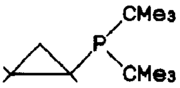

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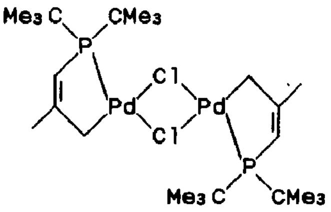

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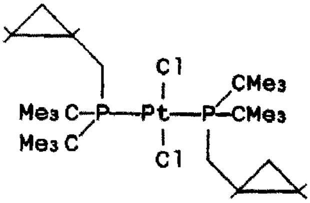
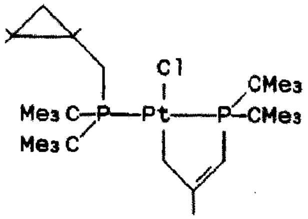


149



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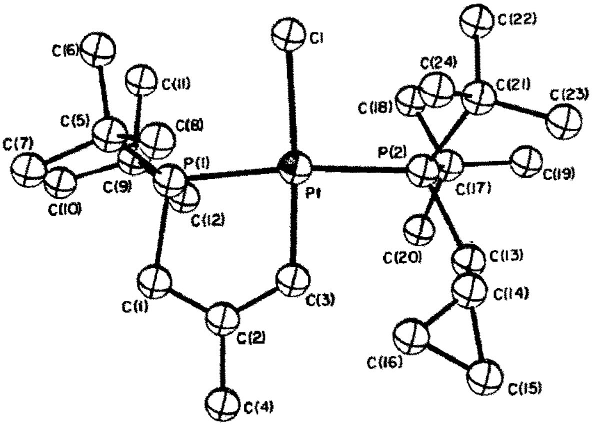
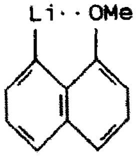
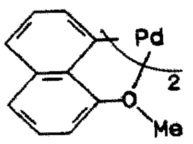


150 (Reproduced with permission from [198])
The atoms have been drawn as spheres with arbitrary radii.

Isolated examples of cyclometallation involving carbon and oxygen coordinated ligands have been reported. Treatment of $[Pd(SEt_2)_2Cl_2]$ with **151** (LiMXN) gave **152**. When reacted with a cyclometallated complex of the type $[\{Pd(C-N)Cl\}_2]$ a bis cyclometallated species was produced. In the case for which (C-N) = 8-methylquinoline, the carbon-palladium bonds were shown to be *cis* by an X-ray diffraction study, but some of the related complexes isomerised readily in solution [199]. The species formed by reaction of $[Pt(dmso)_2Cl_2]$ with nitroarenes were shown to be active catalysts for nitrobenzene hydrogenation. The structure **153** was established [200].



151



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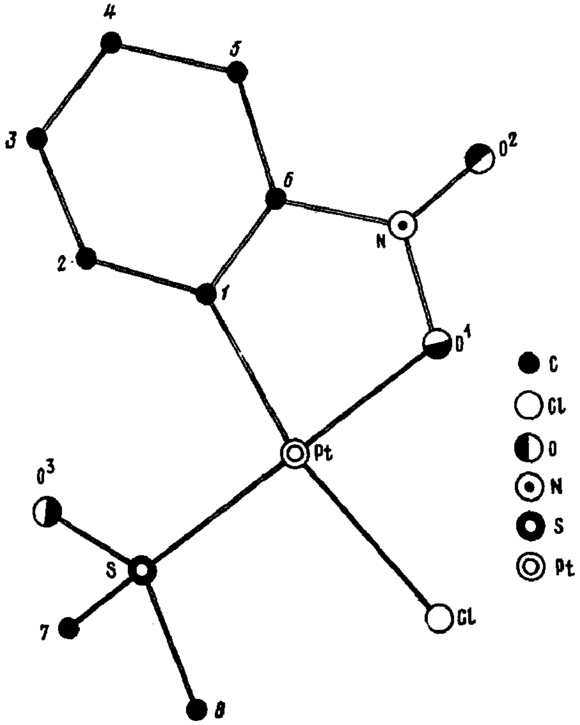
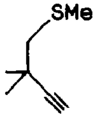


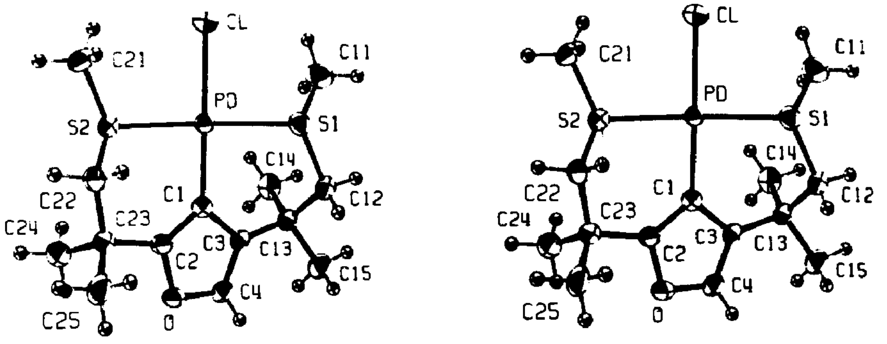
153 (Reproduced with permission from [200])

Reaction of 154 with $[Pd(PhCN)_2Cl_2]$ gave 155, the structure of which was established by an X-ray diffraction study. The two six-membered rings adopted different conformations in the solid state, with one in the twist-boat and one in the twist-chair conformation [201]. A detailed mechanism for the reaction was proposed [202]. The reactions of 156 with base have now been delineated in detail in a full paper [203].

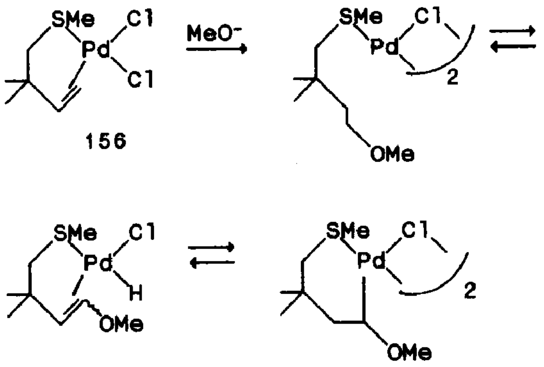


154

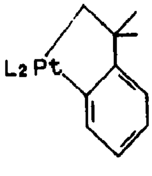
The thermolysis of $[L_2Pt(CH_2CMe_2Ph)_2]$ (L_2 = cod, bipy, bipym or L = PEt_3, PPh_3) to give 157 and $PhCMe_3$ may properly be considered to be a cyclometallation. The rate of the reaction was dependent on L_2, with the fastest rates for PPh_3, and much slower reactions for complexes of chelating ligands [204].



155 (Reproduced with permission from [201])
Stereoview with the crystallographic numbering scheme.



156



157

6 METAL CARBONYL AND THIOCARBONYL COMPLEXES

The electronic energy levels of {Ni(CO)} in different states were calculated by the non-restrictive multiple scattering X_α method. The ground state was found to be $^1\Sigma^+$ rather than $^3\Delta$ as predicted from other methods

[205]. The reaction of carbon monoxide with field emitter surfaces was investigated by pulsed field desorption mass spectrometry at 10^{-6} to 3×10^{-2} Pa and 170-420 K. The species CO^{+}, $\{Ni(CO)\}^{+}$, $\{Ni(CO)_2\}^{+}$ and $\{Ni(CO)_3\}^{+}$ were field desorbed, but $[Ni(CO)_4]^{+}$ was not observed. The rates of formation of the nickel subcarbonyls were deduced [206].

The biological properties of $[Ni(CO)_4]$ have been reviewed [207,208]. FTIR was used to assess the concentration of $[Ni(CO)_4]$ in mainstream tobacco smoke, but none was in fact detected at levels above 0.1 $\mu l\ l^{-1}$ [209]. The use of an aerosol ionisation gas analyser for $[Ni(CO)_4]$ has been described [210]. $[Ni(CO)_4]$ has been determined in argon and nitrogen by gas chromatography with a constant recombination rate detector. Preconcentration was found to be essential for determination in air [211].

The validity of Koopman's theorem in a series of transition metal complexes including $[Ni(CO)_4]$, $[Ni(\eta^3\text{-}C_3H_5)_2]$ and [CpNi(NO)] was discussed [212]. The principal components of the ^{13}C nmr chemical shift tensors of metal carbonyls containing one to six metal atoms (including $[Ni(CO)_4]$) was determined from powder patterns [213].

An improved synthesis of $[Ni(CO)_4]$ has been reported [214].

The overlayers from $[Ni(CO)_4]$ in CO adsorbed onto the Ni <111> surface at 100 K were characterised by high resolution electron energy loss spectroscopy and thermal desorption spectroscopy. Below 135 K molecular $[Ni(CO)_4]$ was adsorbed on a CO saturated Ni <111> surface [215]. The interaction of $[Ni(CO)_4]$ with Cu <111> and <110> single crystal surfaces was studied with ellipsometry, Auger electron spectroscopy, LEED and argon ion depth profiling. At room temperature nickel atoms with some CO ligands remained at the surface, but the amount of nickel deposited was less than one monolayer [216].

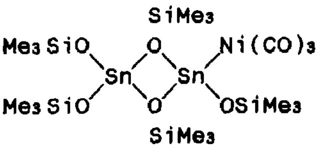
A glass flask was lined with a nickel layer deposited by decomposition of $[Ni(CO)_4]$ vapour at 170-200 °C [217]. Decomposition of $[Ni(CO)_4]$ at 200 °C gave active nickel powder to be used in the synthesis of $[Ni\{P(OR)_3\}_4]$ [218]. Polycrystalline nickel was grown by the decomposition of $[Ni(CO)_4]$ using different wavelengths of visible radiation from a krypton laser [219]. Stable hydrocarbon based nickel ferrofluids were prepared by UV decomposition of $[Ni(CO)_4]$ or reduction of $[Cp_2Ni]$. Transmission electron diffraction showed the particles to be fcc nickel with a lattice parameter a = 3.525 Å. Electron microscopy revealed that the median particle diameters were less than 60 Å and that the size distribution was relatively narrow [220].

Carbon monoxide was extracted from gas mixtures by conversion into $[Ni(CO)_4]$, which was separated, and then decomposed to recover the carbon monoxide [221]. The formation of $[Ni(CO)_4]$ was shown to be important to the transport of nickel from small to large crystallites in Ni/SiO_2 methanation catalysts [222]. Also, the formation of $[Ni(CO)_4]$ and its subsequent deposition on nickel crystals, followed by nickel crystal growth, was shown to be a cause of deactivation of such catalysts [223]. The pressure and the composition of the vapour in the $[Ni(CO)_4]/[Fe(CO)_5]$ sytem has been studied. The thermodynamic characteristics of the overall evaporation process and the dissociation constant of $[NiFe(CO)_9]$ were established [224].

The stereochemistries of the species $[Ni(PH_3)_2(H_2CO)]$ and $[Ni(PH_3)(CO)_2]$ were studied using the *ab initio* MO method. In the case of the methanal complex it was established that the planar side-coordinated geometry was favoured over either the pseudotetrahedral side-on or end-on arrangements, due to stronger back donation. The methanal ligand is greatly distorted, as the distortion relieves the exchange repulsion and enhances back donation [225].

^{13}C nmr spectroscopic parameters have been reported for a range of complexes, $[Ni(CO)_3L]$ ($L = PR_3$, AsR_3, SbR_3 or BiR_3) [226]. In $[Ni(CO)_{4-n}\{P(C{\equiv}CPh)_mPh_{3-m}\}_n]$ (n = 2, 3 or 4; m = 1, 2 or 3), a weak π-acidity for the alkynyl phosphines ($m = 3 > 2 > 1$) could be inferred from the trend in force constants for the stretching of the $C{\equiv}O$ bond [227].

Photolysis of $[Ni(CO)_4]$ in the presence of molecular nitrogen in liquid krypton gave $[Ni(CO)_3(N_2)]$. This decomposed readily, with the reaction giving a two term rate law with both D and I_a components. The $Ni-N_2$ bond energy was estimated to be 42 kJ mol^{-1} [228]. A number of complexes of the type $[Ni(CO)_3L]$ have been prepared by ligand displacement reactions on $[Ni(CO)_4]$, including $[Ni(CO)_3(AsMe_2CH_2CH_2OH)]$ [229], **158** [230,231], **159** [232], and **160**. Further substitution of **160** did not prove possible [233]. Other syntheses of similar complexes have also been noted (reaction (18)) [234].



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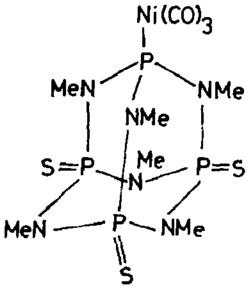
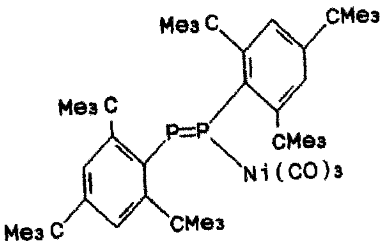


159

Reaction of $[Ni(SiCl_3)_2(\eta^6-PhMe)]$ with CO gave $[Ni(SiCl_3)_2(CO)_3]$, a rare example of a simple carbonyl complex of nickel(II). Infra-red spectroscopy implied that the complex adopted trigonal bipyramidal geometry with the carbonyl ligands occupying axial sites. It could also be prepared from

[Ni(CO)$_4$] and Si$_2$Cl$_6$ in a CO atmosphere at room temperature, and decomposed slowly to give nickel(0) complexes [235].



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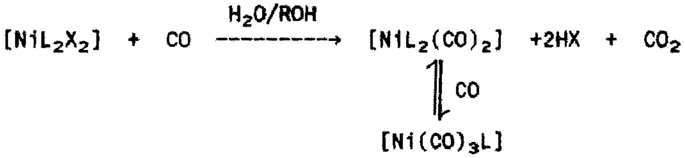
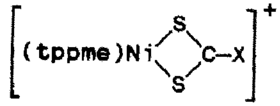


$$[NiL_2X_2] + CO \xrightarrow{H_2O/ROH} [NiL_2(CO)_2] + 2HX + CO_2 \qquad [NiL_2(CO)_2] \underset{}{\overset{CO}{\rightleftharpoons}} [Ni(CO)_3L] \tag{18}$$

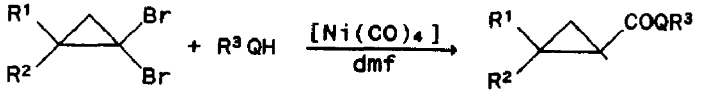
The reaction of Na[Co(CO)$_4$] with [Ni(dppe)X$_2$] in thf or toluene between 30 and 0 °C yielded [Ni(CO)$_2$(dppe)] and [Co$_2$(CO)$_6$(dppe)] [236]. Carbonylation of [Ni(np$_3$)H]$^+$ (np$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$) yielded [Ni(Hnp$_3$)(CO)]$^+$, the tetraphenylborate salt of which was characterised by an X-ray diffraction study. The geometry about nickel was tetrahedral, with three phosphines and CO in the coordination sphere [237]. Reaction of [L$_2$(NO$_2$)Ni-NO$_2$] with CO yielded a simple adduct in a slow and reversible reaction. [L$_2$(NO$_2$)(CO)Ni-NO$_2$] was then rapidly and reversibly converted to [L$_2$(NO)$_2$Ni(CO$_2$)(NO)], which dissociated CO$_2$. There was some spectroscopic evidence for an intermediate such as [L$_2$(NO$_2$)Ni-O-N-O] [238].

When 161 (X = OEt, tppme = MeC(CH$_2$PPh$_2$)$_3$) was treated with [BH$_4$]$^-$, [(tppme)Ni(CO)] was the product. However, with the related species for which X = SMe, [LNi(η^2-CS$_2$)] was formed. [LNi(η^2-*C,S*-COS)] was thought to be the intermediate in the production of the carbonyl complex [239-241].



161

Propene and ethene were codimerised in the presence of $[Ni(CO)_3(PPh_3)]$ supported on alumina. It was established that at least three supported species were present, *viz.*, $[Ni(CO)_2(PPh_3)L]$ ($L = PPh_3$ or Al_2O_3) and $[Ni(CO)_3(PPh_3)]$ [242]. Carbonylation of 162 was effected by $[Ni(CO)_4]$ in the presence of R^3QH (Q = O, NH or NR), and related intramolecular reactions were also noted [243]. Reaction of 163 with $[Ni(CO)_4]$ resulted in the formation of the polymer 164 [244].



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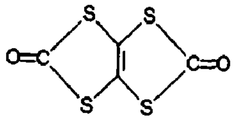

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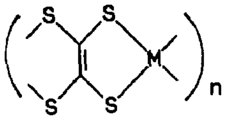


164

Geranyl bromide was coupled with $BrCH_2C(=CH_2)CH=CH_2$ to give *cis*- and *trans*-*β*-farnesene in a 1:1 ratio, by $[Ni(CO)_4]$ [245].

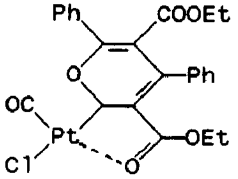
Reports of mononuclear palladium and platinum carbonyl complexes have, as usual, been very much more sparse. A theoretical study of palladium-carbonyl bonding was undertaken using the *ab initio* SCF pseudopotential method with multireference double excitation CI. It was concluded that the Pd_n-CO interaction energy increased with *n* [246]. The introduction of the transition state into the semiconductor method for calculation of ionisation potentials and electronic transition energies of multielectron complex systems, including $[Pd(CO)_4]$, has been studied [247]. Mononuclear palladium carbonyl complexes were proposed as intermediates in the palladium(II) catalysed reduction of iron(III) by carbon monoxide [248].

A semi-empirical method was proposed for the calculation of the electronic structure of complex molecules based on a linear combination of the valence molecular orbitals of fragments; the model was tested on $[Pt(CO)Cl_3]^-$ [249].

Photolysis of $[Pt(PEt_3)_2(\text{oxalate})]$ in the presence of a ligand, L, gave $[Pt(PEt_3)_2L_n]$ (L = CO, *n* = 2 or $L = C_2H_4$, *n* = 1) [250]. Carbonylation of *trans*-$[HPt(NH_3)(PR_3)_2]X$ in propanone gave the cluster $[Pt_3(PR_3)_3(CO)_3]$, *via* $[Pt(PR_3)_2]$, but in CH_2Cl_2 the intermediate *trans*-$[HPt(PR_3)_2(CO)]$ could be isolated [251].

There have been a number of studies on carbonyl complexes related to the intermediates in hydroformylation catalysed by platinum complexes. Reaction of *cis*-$[Pt(PPh_3)(CO)Cl_2]$ with $SnCl_2$ in propanone gave solutions active for alkene hydroformylation. Very complex equilibria, involving insertion of $SnCl_2$ into Pt-Cl bonds, ligand displacement, and rearrangements were studied by nmr spectroscopy [252,253]. Reaction of $[Pt(PR_3)_2Cl_2]$ with CO at one atmosphere pressure in the presence of $[NH_4][PF_6]$ gave *trans*-$[Pt(PR_3)_2(CO)Cl][PF_6]$. This reacted with alcohols to give species such as *trans*-$[Pt(PPh_3)_2(COOR)Cl]$. The alkoxycarbonyl ligand was labile with respect to to photolysis in both solution and the solid state, resulting in dissociation to $[Pt(PPh_3)_2(CO)Cl]^+$ and alkoxide ion [254].

Treatment of $[Pt(CO)_2Cl_2]$ with $PhC\equiv CCOOEt$ gave the complex **165**. Reaction with KCl yielded **166**, which was converted to **167** by PPh_3 [255].



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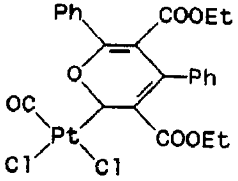

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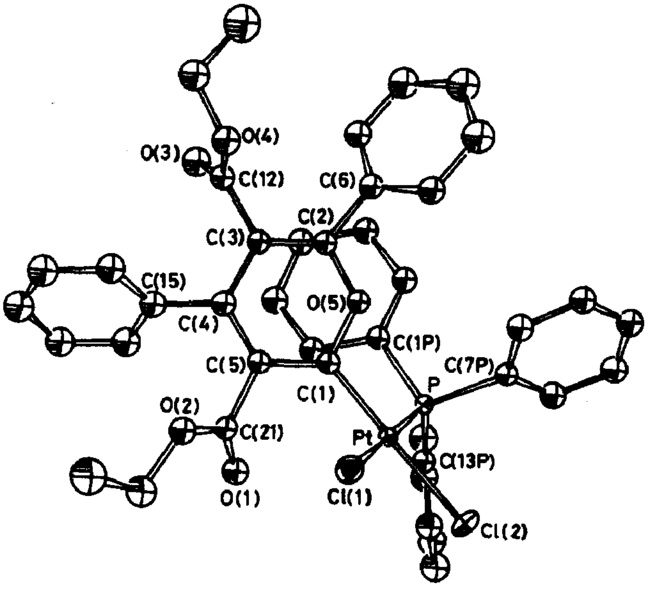
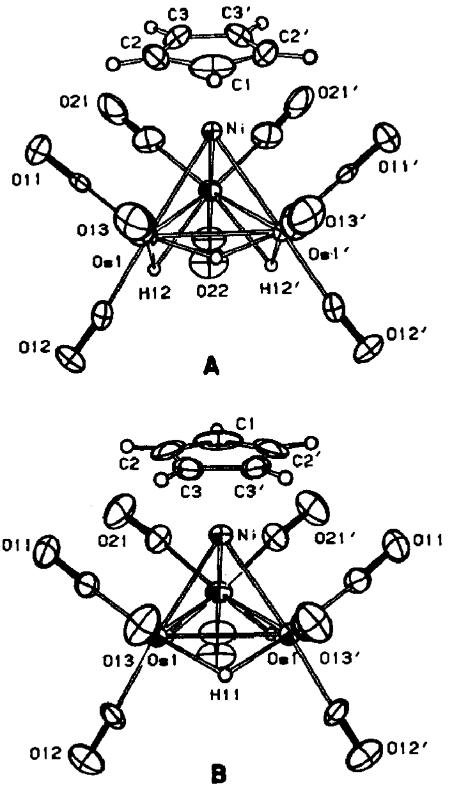


167 (Reproduced with permission from [255])

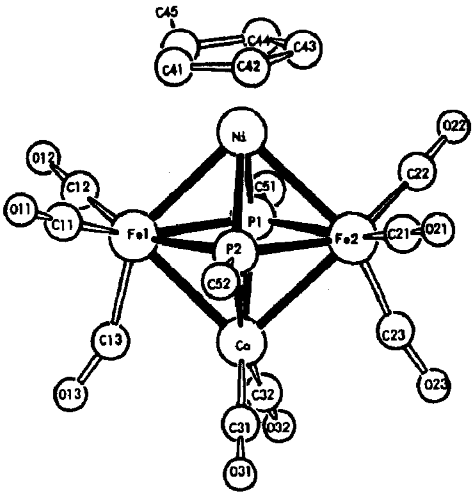
The reaction of polymer bound palladium phosphine complexes with CO has been studied by IR spectroscopy. Both monomeric complexes and dimers with bridging carbonyl groups were identified by IR spectroscopy [256].

The cluster $[H_2Os_3(CO)_{10}]$ has Lewis base character and reacted with $[\{CpNi(CO)\}_2]$ to give a number of new compounds including $[H_3CpNiOs_3(CO)_9]$, 168, [257]. The same product was formed with $[Os_3(CO)_{12}]$ in the presence of hydrogen, and was characterised by an X-ray diffraction study at low temperature [258,259]. Treatment of $[RPFeCo_2(CO)_9]$ with $[\{CpNi(CO)\}_2]$ gave a mixture of products from metal exchange, cluster rearrangement and ligand exchange; 169, $[Fe_2CoNiCp(\mu_4\text{-}MeP)_2(CO)_8]$, and 170, $[FeCoNiCp(\mu_3\text{-}Me_3CP)(CO)_6]$, were characterised by X-ray diffraction studies [260]. The interactions of $[\{CpNi(CO)\}_2]$ and $[Cp_3Ni_3(CO)_2]$ with almost completely dehydroxylated alumina were investigated by IR spectroscopy and gas evolution studies. The trinickel species formed the more stable adducts, mainly by interaction between the carbonyl oxygen and surface aluminium ions [261].



168 (Reproduced with permission from [259])
General views of the two distinct molecules of $[(\mu\text{-}H)_3Os_3Ni(CO)_9(Cp)]$

Carbonylation of either $[\{Ni(\mu\text{-}PCMe_3)(PMe_3)\}_2]$ or $[\{Ni(\mu\text{-}PCMe_3)(PEt_3)\}_2]$ gave $[Ni_2(\mu\text{-}PCMe_3)_2(CO)_2(PR_3)]$, characterised by an X-ray diffraction study [262]. 171 was prepared from $[Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$ and $[Ni(CO)_4]$. The structure may be described as a 62 electron butterfly, with nickel at the wingtips [263].



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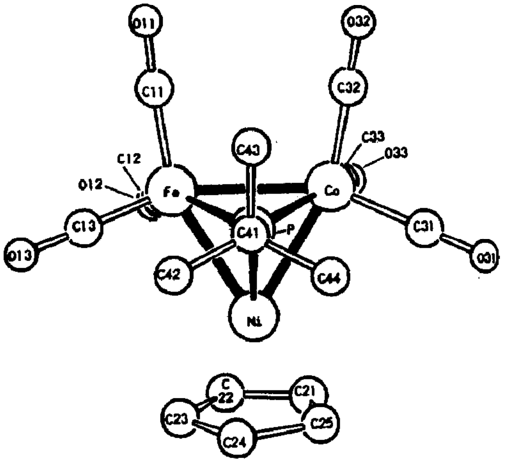
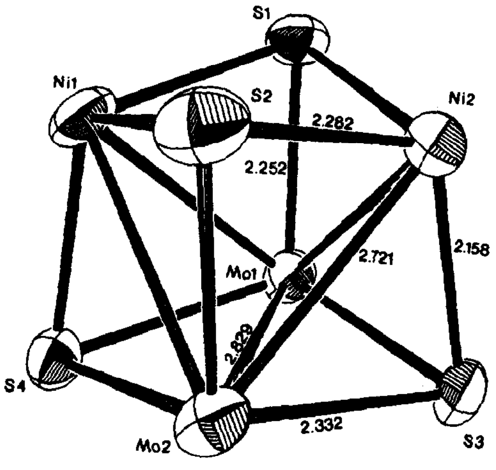


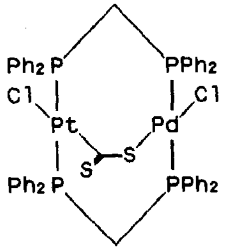
170 (Reproduced with permission from [260])

The bonding in clusters containing bridging carbonyl ligands was analysed using a fragment molecular orbital approach. $[Ni_8(CO)_{12}]^{2-}$ was used to test the model [264]. Treatment of this cluster with buffered water resulted in the formation of $[H_2Ni_{12}(CO)_{21}]^{2-}$ and $[HNi_{12}(CO)_{21}]^{3-}$. Further deprotonation occurred only under severe conditions to give the known species $[Ni_{12}(CO)_{21}]^{4-}$. The clusters could be isolated as ammonium or phosphonium salts, but all were degraded by CO and had limited thermal stability [265]. A wide range of complexes was obtained on reaction of $[Ni_6(CO)_{12}]^{2-}$ with Me_3CPCl_2. They were in general characterised by X-ray diffraction studies, and the ratios in which they were produced depended on the reaction conditions [266]. Reaction of $[Co_3(CO)_9CCl]$ with $[Ni_6(CO)_{12}]^{2-}$ gave the known complex $[Co_3Ni_9(CO)_{20}]^{3-}$ and the new species, $[Co_3Ni_7C_2(CO)_{15}]^{3-}$ and $[Co_6Ni_2C_2(CO)_{16}]^{2-}$, characterised by X-ray diffraction studies. The three-layered metal skeleton of the $\{Co_3Ni_7\}$ species is a distorted bicapped cube derived from either two condensed trigonal prisms, or octahedra sharing a common broken edge. The interstitial carbon atoms were separated by 1.43 Å. The crystals contained two different isomers, differing in the binding mode of one CO ligand. The metal frame of the $\{Co_6Ni_2\}$ species was derived from the condensation of two trigonal prismatic moieties sharing a square face [267].



171 (Rproduced with permission from [263])
Molecular core of the cluster $[Cp_2Mo_2(\mu_3\text{-}S)_4Ni_2(CO)_2]$. Representative distances are noted on the drawings.

Carbonylation of $[PdPt(\mu\text{-dppm})_2Cl_2]$ gave the A-frame species $[PdPt(\mu\text{-dppm})_2(\mu\text{-CO})]$. Alkynes were also inserted, as was CS_2, to give a mixture of 172 and 173 in a reversible reaction [268,269]. The preparation and structural characterisation of $[MnPd(\mu\text{-dppm})_2(CO)_3Br]$, 174, has been described. At least one of the carbonyl ligands appears to be semi-bridging [270]. Reaction of *trans*-$[Rh(Ph_2Ppy)_2(CO)Cl]$ with $[Pd(cod)Cl_2]$ gave the known compound $[RhPd(\mu\text{-}PPh_2py)_2(CO)Cl_3]$. The platinum analogue was obtained on thermolysis of $[Pt(PPh_2py)_2Cl][Rh(CO)_2Cl_2]$ [271].



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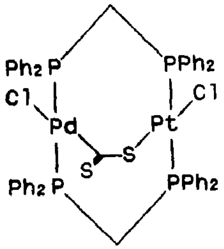

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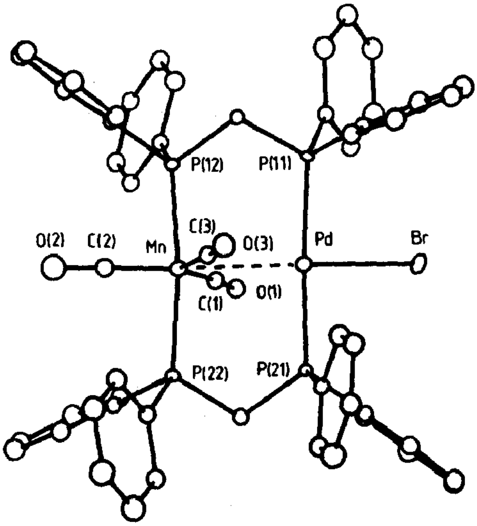


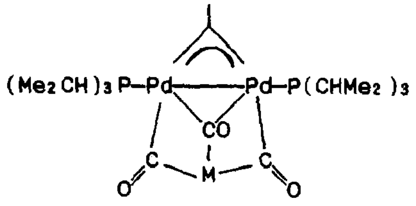
174 (Reproduced with permission from [270])

Molecular orbital calculations have been undertaken on all the isomers of $[Pd_2(CO)_2Cl_4]^{2-}$ and $[Pd_2(CO)_2Cl_4]$. The choice of the bridging ligand (Cl in the palladium(I) species and CO in the palladium(II) complex) was found to depend on the relative energies of the orbitals of the bridging ligands and of the palladium atoms with which they are interacting, *viz.* the HOMO in the palladium(I) compound and the LUMO in the palladium(II) derivative. It was noted that there was no metal-metal bond in the d^9 palladium(I) compound, the short palladium-palladium distance being due to multicentre bonding [272].

The kinetics of the decomposition of $[\{Pd(CO)(OCOMe)\}_4]$ were studied to elucidate the role of the complex as an intermediate in the reduction of palladium ethanoate by carbon monoxide. There was some indication that this was a true intermediate, formed in several steps from the palladium ethanoate trimer [273,274].

Reaction of palladium ethanoate with dppm in the presence of CF_3COOH, and under an atmosphere of carbon monoxide, resulted in the isolation of a 90 % yield of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]$. An X-ray diffraction study revealed that the $\{Pd_3P_6\}$ unit was approximately planar [275]. In the reaction of $[Pd_4(CO)_5(PR_3)_4]$ with metallic mercury the species $[Hg\{Pd_3(CO)_3(PR_3)_3\}_2]$ was formed, in which the mercury atom links the two $\{Pd_3\}$ triangles. The two rings are probably eclipsed, but the nmr spectrum indicated some dynamic behaviour [276].

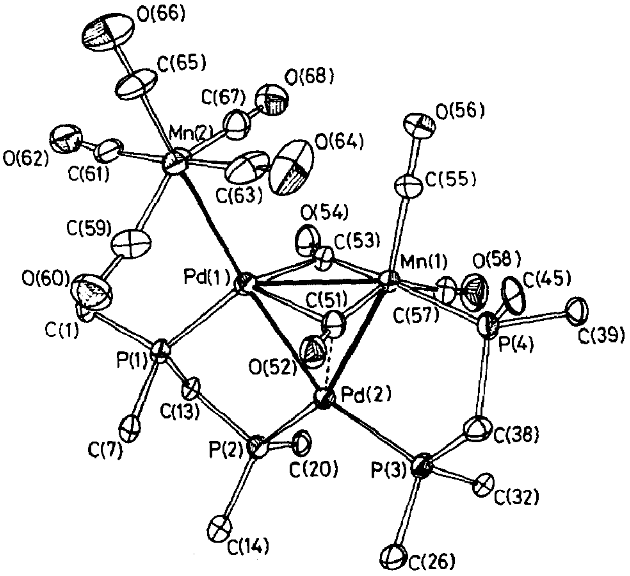
In the presence of MCl_2 (M = Pd or Pt), $[Cp_2Rh_2(\mu\text{-}CO)(CO)_2]$ was converted to $[\{CpRh(\mu\text{-}CO)\}_3]$. $[Cp_2Rh_2(CO)_2(\mu\text{-}MCl_2)]$ was proposed as an intermediate which decomposed to [CpRh(CO)], the latter trimerising rapidly [277]. The bridged dimer $[\{(Me_2CH)_3P\}_2PdPt(\mu\text{-}CH_2CMeCH_2)(\mu\text{-}Br)]$ reacted with $Na[CpM(CO)_3]$ (M = Cr, Mo or W) to give 175, which has an approximately tetrahedral framework [278].



175

Treatment of $[Pd_2(\mu\text{-}dppm)_2Cl_2]$ with $Na[Mn(CO)_5]$ gave $[ClPd(\mu\text{-}dppm)_2Mn(CO)_3]$ and 176, characterised by an X-ray diffraction study [279]. The analogous cobalt compound was also prepared [280].

Another family of heterotetrametallic palladium clusters, $[Pd_2M_2Cp_2(CO)_6(PR_3)_2]$ (M = Cr, Mo or W), has also been prepared and characterised. Two alternative routes for their synthesis were described (reactions (19) and (20)). The structures of the three complexes for which R = Et were determined by X-ray diffraction studies (M = Mo, 177); the four metal atoms were coplanar in a triangulated parallelogram and the 18 electron $[CpM(CO)_3]^-$ fragments acted as four electron donors towards the {L-Pd(I)-Pd(I)-L} unit. The palladium palladium distance, at 2.578 Å, is the shortest ever recorded, being shorter even than that in the bulk metal. The palladium-M distances are also all appreciably shorter than the sums of the covalent radii. The PEt_3 ligand was coordinated to palladium and two of the carbon monoxide ligands were semi-triply bridging on the heterotrimetallic face, with the M-CO bond shorter than the bonds to Pd or Pd' [281]. The complexes exhibited an unexpected irreversible 2e reduction leading to the rupture of the metallic core into identified fragments [282].



176 (Reproduced with permission from [279])

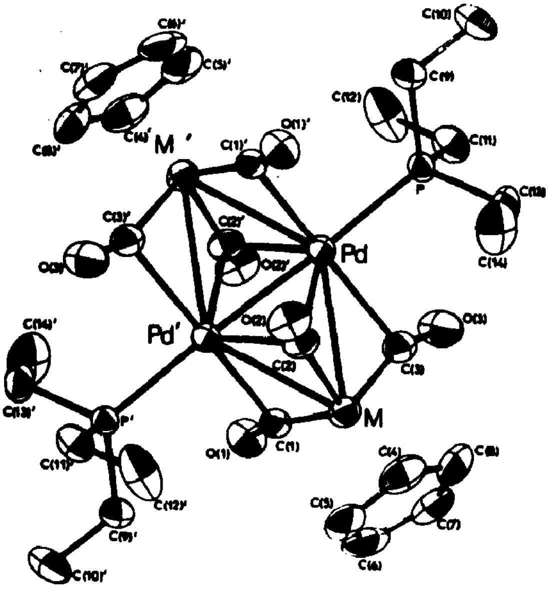
$$[Pd(PR_3)_2Cl_2] + Na[CpM(CO)_3] \rightarrow [Pd_2M_2Cp_2(CO)_6(PR_3)_2] + [Cp_2M_2(CO)_5(PR_3)] \quad (19)$$

$$[Pd(PhCN)_2Cl_2] + Na[CpM(CO)_3] \xrightarrow{\textit{in situ}} [Cp(OC)_3M\text{-}Pd(PhCN)_2\text{-}M(CO)_3Cp] \xrightarrow{R_3P}$$

$$[Pd_2M_2Cp_2(CO)_6(PR_3)_2] \quad (20)$$

Treatment of $[Et_4N][Fe_4MC(CO)_{14}]$ (M = Co or Rh) with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ gave the cluster $[Et_4N][Fe_4MPdC(CO)_{15}]$, a chiral octahedral species [283].

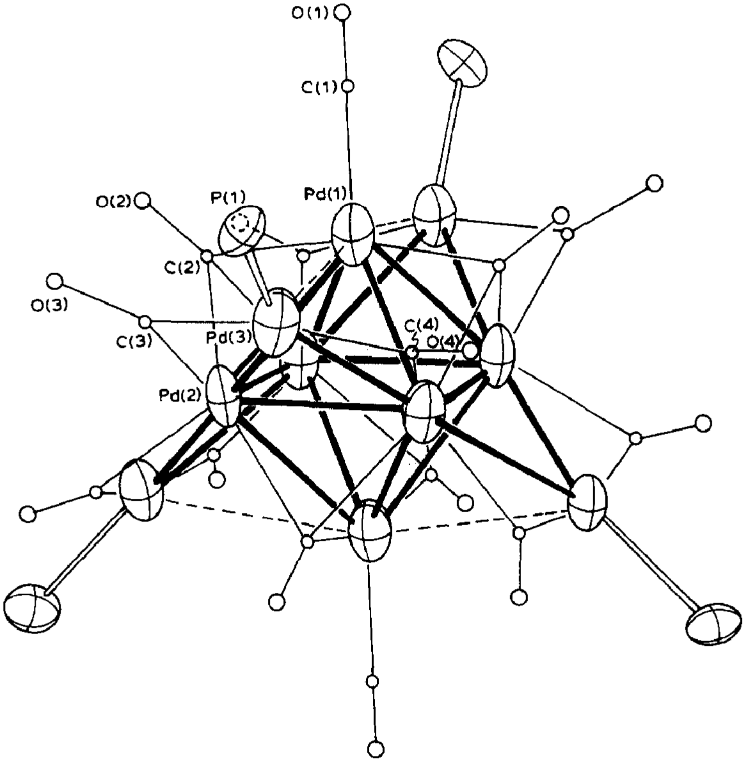
There have been further reports of the synthesis of high nuclearity palladium carbonyl clusters from palladium ethanoate, phosphines and CO in ethanoic acid/propanone [284]. $[Pd_{10}(CO)_{14}(PBu_3)_4]$, 178, was characterised by an X-ray diffraction study. The $\{Pd_{10}\}$ polyhedron is a four-capped octahedron with non-symmetrical caps [285]. Treatment of $[Pd_4(CO)_5(PEt_3)_4]$ with 179 gave $[Pd_4Hg_2(CO)_4(PEt_3)_4Br_2]$, 180, the structure of which was established by an X-ray diffraction study. The structure is a butterfly unit of the four palladium atoms, the wings of which are capped by mercury atoms bonded to bromo ligands [286].



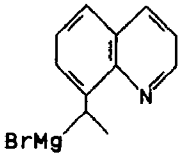
177 (Reproduced with permission from [281])
ORTEP diagram of the molecular structure of the $[Pd_2M_2Cp_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2]$ cluster (M = Mo) illustrating the numebring scheme. Thermal ellipsoids enclose 50 % of the electron density. The ORTEP diagram is identical when M = Cr or M = W.

The orbital interactions in platinum carbonyl clusters have been studied [287]. The structures of condensed platinum cluster compounds were rationalised using the cluster condensation generalisation derived from MO calculations [288].

The mixing of $[Pt(CO)_2Cl_2]$ and $[\{Pt(CO)Cl_2\}_2]$ in the melt had been reported to yield $\{Pt_2(CO)_3Cl_4\}$, but X-ray structural studies revealed that this was a eutectic and not a true compound [289]. A number of binuclear platinum carbonyl complexes have, however, been reported. Reaction of $[Pt(CO)X_3]^-$ (X = Cl, Br or I) with methanoic acid and Pr_3N gave $[Pt_2(CO)_2X_4]^{2-}$. ^{13}C and ^{195}Pt nmr spectroscopic studies were reported, and at 300 K the carbonyls were exchanging between the two platinum atoms. Although all the ligands are terminal in the complexes, bridged intermediates were proposed for the exchange process [290]. The reactions with phosphine ligands were complex (Scheme 4). 181 is a new structural type for a platinum(I) dimer with two approximately planar $\{PtL_3\}$ fragments mutually orthogonal [291].



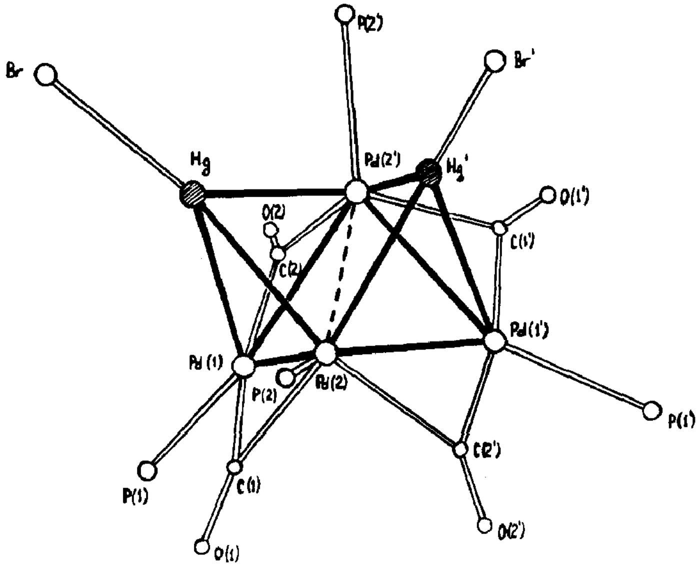
178 (Reproduced with permission from [285].
Butyl substituents have been omitted for clarity



179

Carbonylation of the dimeric species $[Pt_2(\mu\text{-ddpa})_2Cl_4]$ (ddpa = $Ph_2PCH_2NEt_2$)) gave 182 and 183 reversibly. The dimer used seems to be the head to head isomer as shown, but the paper does not give many details on this subject. The related palladium complex was less easy to isolate in a pure form [292]. Treatment of $[H_3Pt_2(L\text{-}L)_2]^+$ (L-L = dppe, dppp or dppb) with CO or RNC (L') gave $[HPtL'(L\text{-}L)_2]$. In most cases IR spectroscopy was consistent with L' being a bridging ligand. Nmr spectroscopy revealed fluxional behaviour. An

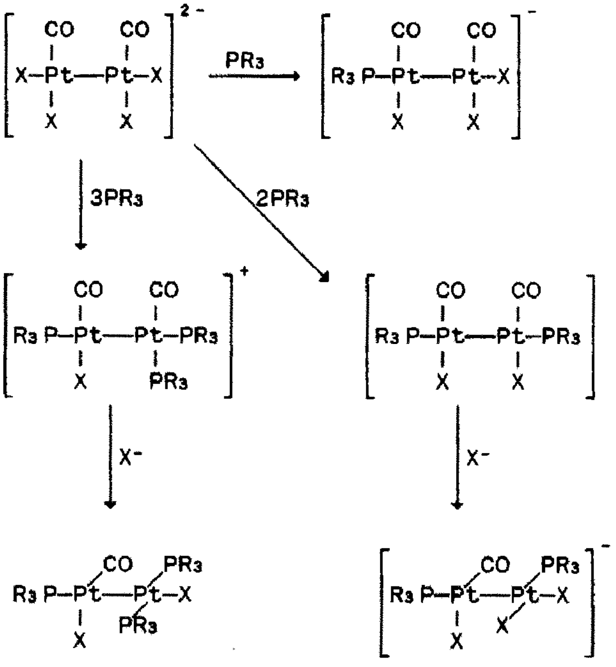
X-ray diffraction study on $[HPt(CO)(dppe)_2]^+$, 184, at 115 K revealed that both the hydride and the CO ligand bridged the platinum atoms, and coordination at each metal was approximately square planar. A mechanism was proposed for the reaction, involving initial rearrangement to a terminal metal dihydride and reductive elimination of molecular hydrogen [293].



180 (Reproduced with permission from [286])
Ethyl substituents have been omitted for clarity

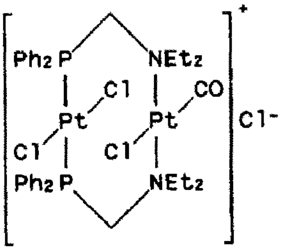
$[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ impregnated onto inorganic supports used for catalysis or chromatography gave $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$, a fact which is important in considering the use of platinum containing clusters in catalysis [294]. Reaction of $[Cp^*Co(\mu\text{-}CO)_2RhCp^*]$ with $[Pt(cod)_2]$ gave 185. $[Cp^*Co(\mu\text{-}CO)(\mu\text{-}CH_2)RhCp^*]$ reacted similarly [295]. $[Fe(CO)_4]^{2-}$ reacted with $[Pt_2(\mu\text{-}dppm)_2Cl_2]$ to give 186, and the related ruthenium and osmium complexes were also prepared. From the mixed complex $[PdPt(\mu\text{-}dppm)_2Cl_2]$ both of the possible isomeric products were isolated [296].

$[\{Pt(CO)_2\}_n]$ reacted with Et_3P in aqueous propanone to give $[Pt_5(CO)_6(PEt_3)_4]$, $[Pt_4(CO)_5(PEt_3)_4]$ and/or $[Pt_3(CO)_3(PEt_3)_4]$, depending on the reaction conditions [297]. The anionic cluster $[Pt_{12}(CO)_{24}]^{2-}$ catalysed the reaction between water and benzoquinone to give hydroquinone and molecular oxygen. Rate constants for the reaction were derived [298].

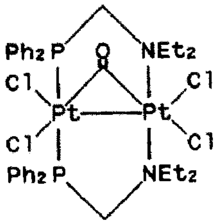


181

Scheme 4 Reactions of $[Pt_2(CO)_2X_4]^{2-}$ with phosphine ligands

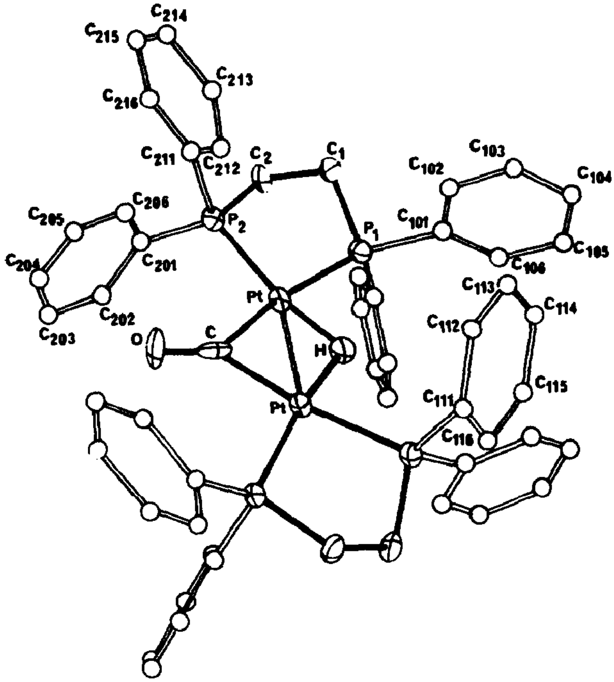


182

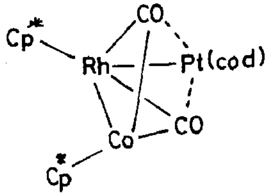


183

The species $[Pt_2Rh_{11}(CO)_{24}]^{3-}$, $[PtRh_{12}(CO)_{24}]^{4-}$, 187, and $[Pt_2Rh_9(CO)_{22}]^{3-}$, 188, were isolated from the controlled pyrolysis of $[PtRh_5(CO)_{15}]^-$. The structures in general resembled those of the isoelectronic homonuclear rhodium species with the platinum atoms in the most highly connected positions. 188 was also obtained from a mixture of $[PtRh_5(CO)_{15}]^-$ and $[PtRh_4(CO)_{12}]^{2-}$. Reaction of $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ with acid caused rearrangement through a multistep process to give $[PtRh_{13}(CO)_{25}]^{3-}$, 189 [299,300].



184 (Reproduced with permission from [293])
ORTEP diagram of the cation. For clarity the carbon atoms of the phenyl groups are depicted as small spheres of arbitrary diameter.



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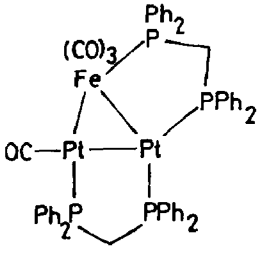
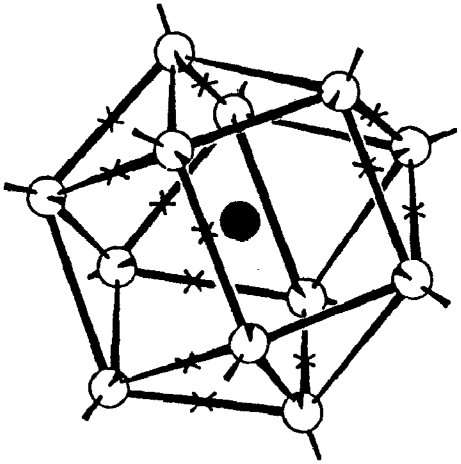
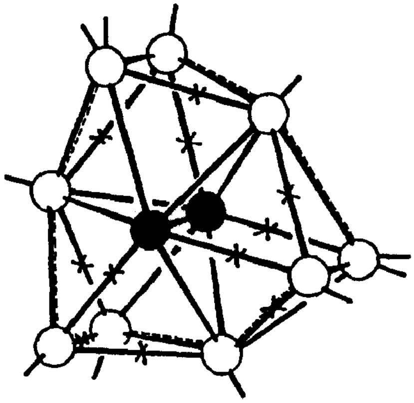


186

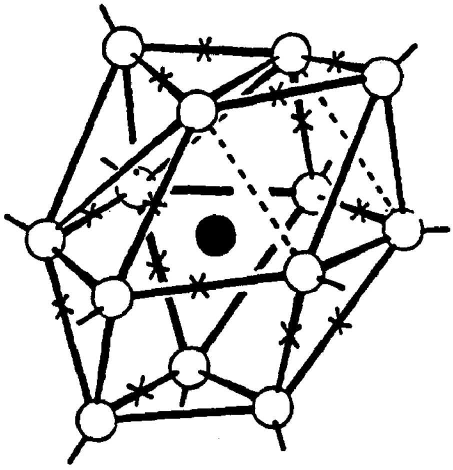
Hydrogenation of the unsaturated cluster [Os$_3$Pt(μ-H)$_2$(CO)$_{10}$(PCy$_3$)] under 200 atm pressure gave 190, characterised by an X-ray diffraction study. The reaction could be reversed by removal of the hydrogen [301]. A new method of preparation of mixed metal clusters using phase transfer catalysis has been noted. The known species [Pt$_2$Co$_2$(μ_2-CO)$_3$(CO)$_5$(PPh$_3$)$_2$] was prepared in this way and had a high catalytic activity for alkene hydroformylation [302]. Like [Fe$_3$Te$_2$(CO)$_9$], [PtFe$_2$Te$_2$(CO)$_6$(PPh$_3$)$_2$] is a 50e cluster. However, a 16e configuration is more favourable for platinum(II), and the $\{Pt(PR_3)_2\}$ is effectively equivalent to $\{Fe(CO)_4\}$, {CpCo(CO)} or {CpRh(CO)}. Thus, although one might expect a *nido* structure on the basis of the electron count, ^{125}Te nmr spectroscopy gave a signal typical of an *arachno* structure [303].



187 (Reproduced with permission from [299])
Each surface metal atom bears one terminal CO ligand and is connected to two bridging carbonyls (X-bridged edges).



188 (Reproduced with permission from [299])
The structure consists of three condensed octahedra with a common edge (Pt-Pt, coincident with the ideal threefold axis). X represents the bridged edges.



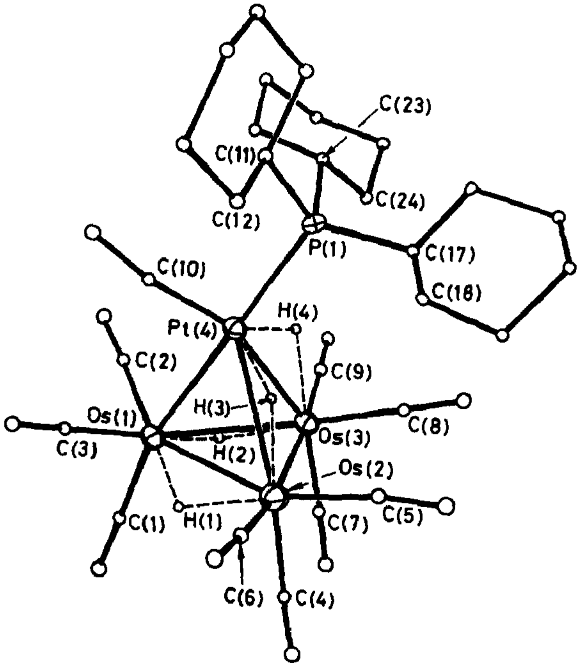
189 (Reproduced with permission from [299])

The metallic skeleton is intermediate between closest packing and bcc. The central platinum atom exhibits nine short metal-metal bonds (2.64-2.73 Å), two longer bonds (mean 2.98 Å) and two very long interactions (3.28 and 3.49 Å). X represents the bridged edges.

Reaction of $[Ni(triphos)(\eta^2-CS_2)]$ with PhNCS gave $[Ni(triphos)(\eta^2-C,S-SCNPh)]$, characterised by an X-ray diffraction study [304]. Treatment of $[Ni(PPh_3)_2(C_3Ph_3)][BPh_4]$ with CS_2 gave $[\{Ni(PPh_3)(\mu-CS_2)\}_2]$, 191 [305]. The same complex was obtained from $[Ni(cod)_2]$, Ar_3P and CS_2. However, with PMe_3 and other basic triaklyl phosphines, 192 was formed. The bonding in these complexes was discussed, and a mechanism was proposed for their formation [306].

Reaction of $[Pd(PPh_3)_4]$ with CSe_2 gave $[Pd(PPh_3)_2(\eta^2-CSe_2)]$. Addition of chelating phosphines resulted in the displacement of PPh_3 [307]. With CSSe a similar reaction occurred, giving a complex bound through carbon and selenium [308]. Oxidation of $[L_2Pd(\eta^2-CS_2)]$ by molecular oxygen gave $[L_2Pd(CS_2O)]$ as a mixture of *S,O*- and *S,S*-isomers [309].

Treatment of $[Pt\{P(CMe_3)_3\}_2]$ with CS_2 gave the trimer $[\{Pt(CS_2)_3(P\{CMe_3\}_3)\}_3]$; this report is claimed as the first synthesis of the species. $[Pt(PCy_3)_2]$ and $[Pt(PCy_3)_2(SO_2)]$, by contrast, gave $[Pt(PCy_3)_2(\eta^2-CS_2)]$ [310]. CS_2 reacted with $[Pt(C_2H_4)_2(PCy_3)]$ to give a species of stoicheiometry $[Pt_3(CS_2)_3(PCy_3)_3]$, of uncertain structure [311]. A thiocarbonyl fragment was transferred from [Pt(dppe)(η^2-CS_2)] to [Pt(PPh_3)$_2$(C_2H_4)] to give 193, which was not isolated, but decomposed to give 194 [312]. The outcome of alkylation reactions of [{Pt(η^2-CS_2)(PPh_3)}$_2$] varied considerably with the hard/soft nature of the alkylating agent [313].

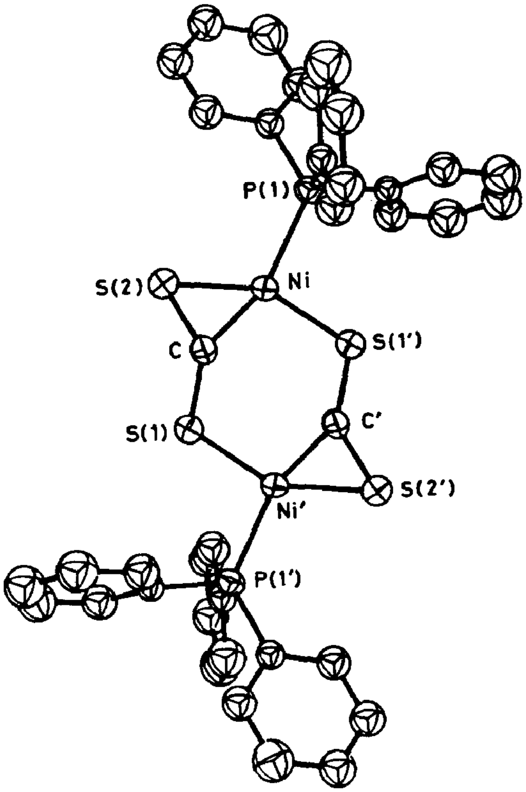


190 (Reproduced with permission from [301])
Molecular geometry of one of the two independent molecules of
[$PtOs_3(CO)_{10}(PCy_3)(\mu$-$H)_4$].

7 METAL ISOCYANIDE COMPLEXES

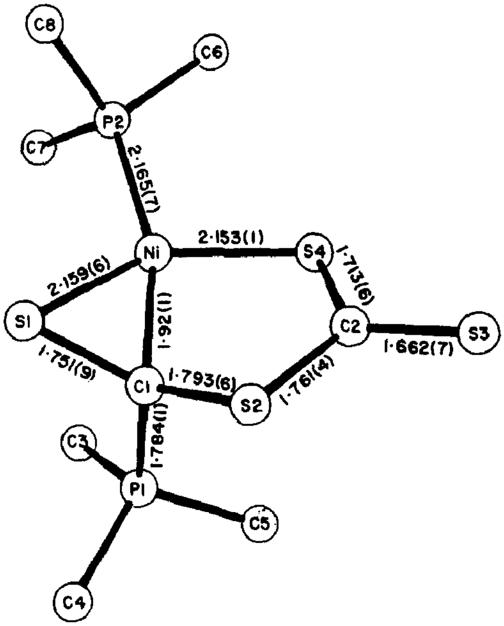
The reaction of the diisonitrile, 195, (R = H or CMe_3) with [Ni(CO)$_4$] gave [Ni(CO)$_2$L] and [NiL$_2$]. These appeared to be mononuclear rather than oligomeric [314]. The ligand for which R = H also reacted with [$PtCl_4$]$^{2-}$ to give [PtL_2][$PtCl_4$], but with 195 (R = CMe_3) the product isolated was *cis*-[$PtLCl_2$] [315].

Treatment of [Pt(cod)Cl_2] with 196 resulted in a simple substitution to give *cis*-[PtL_2Cl_2] [316]. Cleavage of the platinum-platinum bond in [$Pt_2(HPO_4)_4py_2$] was facile in the presence of Me_3CNC, giving [Pt($CNCMe_3$)$_2$(CN)$_2$] as the final product [317].

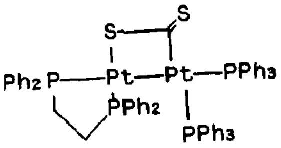


191 (Reproduced with permission from [305])
ORTEP drawing with 50 % probability ellipsoids

Reaction of [Pt(cod)$_2$] with Me$_2$CHNC gave the trimer [Pt$_3$(CNCHMe$_2$)$_6$]. Similar trimers were obtained in the palladium series from [Pd(dba)$_2$]. Treatment of the platinum trimers with electron withdrawing alkenes such as tcne or CF$_2$=CFCl gave [Pt(η^2-alkene)(CNR)$_2$], but in the palladium series oxidative addition occurred to give palladium(II) alkenyl complexes. At room temeprature [Pt$_3$(CNR)$_6$] reacted with HSiMePh$_2$ to give 197 [318]. The reactions of [Pt$_2$(μ-dppm)$_2$X$_2$] with ArNC may give a wide range of products of both insertion (into the metal-metal bond) and halide substitution [319]. Reduction of [Pt(CNC$_6$H$_3$-2,6-Me$_2$)$_2$Cl$_2$] by mercury amalgam gave the cluster [Pt$_7$(CNC$_6$H$_3$-2,6-Me$_2$)$_{12}$], 198. The cluster is derived from a distorted trigonal bipyramidal unit to which two extra platinum atoms have been attached in bridging positions, between one apical and one equatorial platinum atom. One isocyanide is coordinated unusually through the C-N triple bond to three platinum atoms, as a 4e donor, to give a planar cyclic {CNPt$_3$} unit [320].



192 (Reproduced with permission from [306])
The H atoms have been omitted for clarity and the atoms have been drawn as spheres with arbitrary radii. Averaged bond lengths (Å) for the two independent molecules are given.



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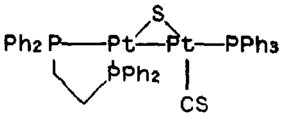

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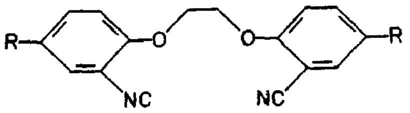

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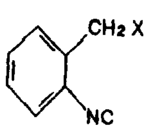

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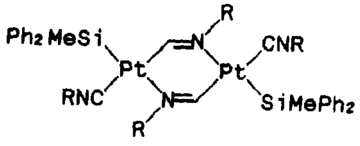

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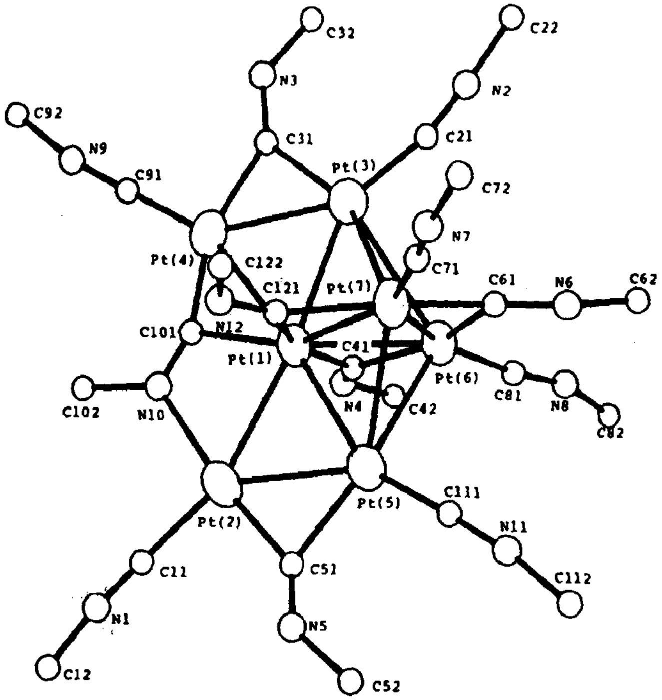
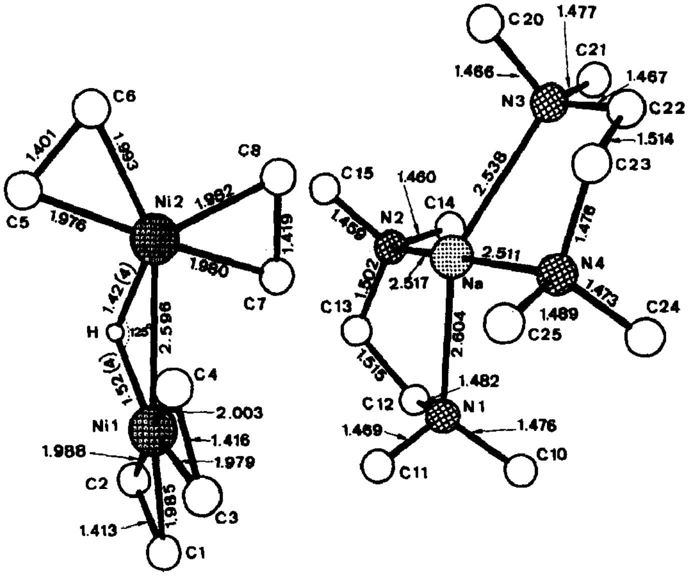


198 (Reproduced with permission from [320])
The central core of [Pt$_6$(2,6-Me$_2$C$_6$H$_3$NC)$_{12}$]. The aromatic groups are omitted for clarity.

Mechanistic studies of the reactions of isocyanide complexes of palladium(II) with ArNH$_2$ have been reviewed [321]. The preparation of the isonitrile complex [ArPdL$_2$(CNR)][ClO$_4$] has been described. Reaction of the species for which L$_2$ = bipy with HY (Y = ArNH, PhNH, Me$_3$CNH, MeO or EtO) resulted in the formation of a carbene complex, [ArPd(bipy){C(NHR)Y}] [322].

The species $[Ni(C_2H_4)_n]$ (n = 1, 2 or 3) could be generated by cryocondensation. The stability of $\{Ni(C_2H_4)\}$ was explained using *ab initio* calculations relating the energy of the complex to various terms of the nickel atom [323]. Reaction of $[Ni(C_2H_4)_3]$ with $M[HAlR_3]$ (M = Li or Na) at temperatures below -70 °C gave $[M(donor)_n]^+[R_3AlHNi(C_2H_4)_2]^-$. In the presence of tmeda and at -40 °C $[M(tmeda)_2][Ni_2(\mu\text{-}H)(C_2H_4)_4]$, 199, was formed, but was stable only below -20 °C. The short metal-metal distance (2.596 Å) suggested that there was significant metal-metal interaction [324]. The ^1H nmr spectra of $[Ni(PMe_3)(C_2H_4)_2]$, $[CpNi(Me)(C_2H_4)]$ and related species have been measured and interpreted [325].



199 (Reproduced with permission from [324])

Crystal structure of the ion pair. The bridging hydride was unambiguously located and its parameters refined.

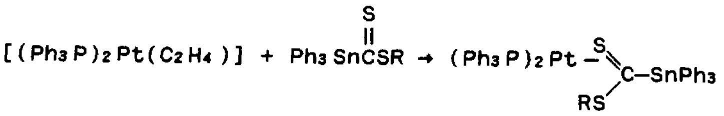
Ethene was oxidised to ethanal in a stoicheiometric reaction by *trans*-$Na[Pd(NO_2)(NH_3)Cl_2]$. In dioxan solution transient ethene complexes were observed, and were invoked as probable intermediates in the reaction [326,327].

$[Pt(PPh_3)_2(C_2H_4)]$ may be prepared by reduction of $[Pt(PPh_3)_2(O_2)]$ by $Na[BH_4]$ in the presence of ethene. Reaction with hexaphenyltrisilane resulted in ethene displacement [328].

IR spectra of the complexes *trans*-[PtL(C_2H_4)X_2] (L = NH_3, py, py-*N*-oxide, $PhNH_2$ or imidazole; X = Cl or Br) were recorded, and were assigned by comparison with deuterated species [329]. IR, UV and ^1H nmr spectra were recorded for *trans*-[Pt(4-$RC_6H_4NH_2$)(C_2H_4)Cl_2]. ν_{Pt-Cl}, ν_{Pt-N} and ν_{C-C} all increased with the electron releasing character of R [330]. ^1H nmr spectrsocopy was used to study ligand exchange processes in *trans*-[PtL(C_2H_4)X_2] (L = pyrazine, imidazole or *N*-methyl imidazole) [331]. The synthesis of the pyrazine complex was described, and the complex was highly fluxional with rapid exchange of the binding site between the two nitrogen atoms, even at very low temperatures [332].

Reaction of K[Pt(C_2H_4)Cl_3] with quinoline-*N*-oxide (L) resulted in the formation of [Pt(C_2H_4)LCl_2] [333]. Both 1:1 and 1:2 adducts were formed with *cis*-[Ru(bipy)$_2$(CN)$_2$], in which the cyanide groups acted as bridges between the two metal centres. In the adducts there were blue shifts in both absorption and emission spectra, enhancement of emission intensity, and an increase in lifetime [334].

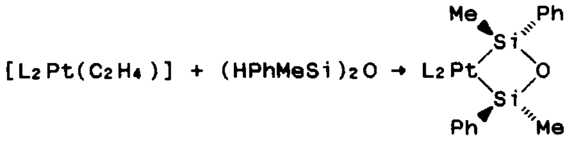
The ethene ligand in [PtL_2(C_2H_4)] is readily displaced and this complex has been used as a precursor to a range of organometallic and coordination compounds (reaction (21)) [335]. In many cases oxidative addition also occurred (reactions (22) (NPht = *N*-phthalimido) [336] and (23) [337]). Examples involving siloxane derivatives have been particularly prominent this year (for example, reaction (24)) [338-340].



(21)

$$[Pt(PR_3)_2(C_2H_4)] \;+\; NphtSSR' \longrightarrow [Pt(PR_3)_2(SSR)(Npht)] \qquad (22)$$

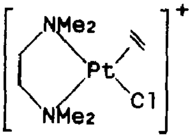
$$[Pt(PR_3)_2(C_2H_4)] \;+\; n\text{-}C_6F_{13}SO_2N_3 \longrightarrow [Pt(PR_3)_2(N_3)_2] \qquad (23)$$



(24)

Photolyis of [PtL_2(C_2H_4)] was assumed to give a transient species {PtL_2}, which reacted with the solvent, CH_2X_2, to give *trans*-[PtL_2(CH_2X)X], *via* a radical process [341]. Ethene could also be readily displaced by Me_2S from the dimeric species [{Pt(C_2H_4)Cl_2}$_2$] [342].

In 200 ethene is strongly activated towards nucleophilic attack, and reactions with a range of nucleophiles have been investigated [343].



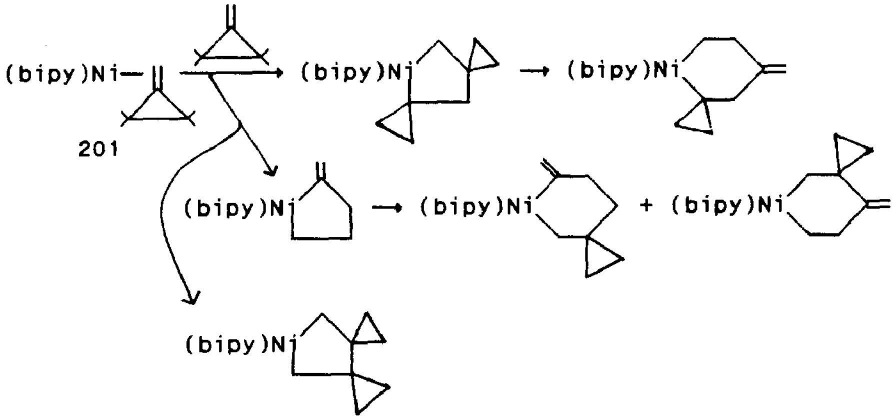
200

When nickel atoms were codeposited with alkenes (alkene = $CHF=CH_2$, $CF_3CH=CH_2$ or $CH_3CH=CH_2$) at -196 °C, thermally unstable complexes of the type $[Ni(alkene)_3]$ were formed, but were not isolated. Reaction with PF_3 gave the species$[Ni(PF_3)_3(alkene)]$, which could be isolated and characterised. At around 0 °C these decomposed to $[Ni(PF_3)_4]$, alkene, and nickel metal [344]. Equilibrium constants for reaction of type (25) were determined spectrophotometrically, and metal-alkene bond strengths measured. K increased considerably for electron withdrawing alkenes, and with bulky ligands at nickel [345]. The substitution of a phosphine ligand by alkenes in $[Ni(PPh_3)_2Cl_2]$ has been investigated [346]. Alkene complexes of nickel(0) could also be prepared by reaction (26); bis(ethenyl)silanes reacted to give chelated complexes [347]. The dinickel derivative of tetraethenylsilane was prepared by substitution of $[Ni(PPh_3)_2(methylenecyclopropane)]$, in turn prepared either by ethene displacement, or from $[Ni(acac)_2]$, Et_2AlOEt, PPh_3 and methylene cyclopropane [348]. Reaction of methylenecyclopropane with [Ni(bipy)(cod)] gave the isolable complex 201, the reactions of which were investigated (Scheme 5) [349].

$$[NiL_4] + alkene \leftrightharpoons [NiL_2(alkene)_2] + 2L \qquad (25)$$

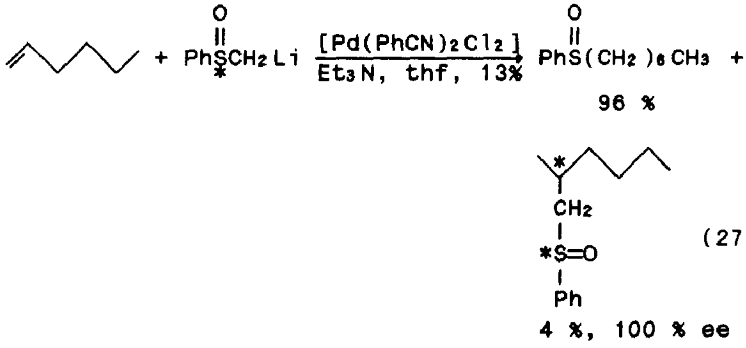
$$[Ni(acac)_2] + PPh_3 + CH_2=CHSiR_3 \xrightarrow{Et_2AlOEt} [Ni(PPh_3)_2(CH_2=CHSiR_3)] \qquad (26)$$

The structures of the complexes $[CpPd(PPh_3)(CH_2=CHAr)][X]$ (Ar = Ph or $4\text{-}MeOC_6H_4$, X = BF_4 or PF_6 or Ar = $4\text{-}ClC_6H_4$, X = BF_4) have been determined in X-ray diffraction studies. The carbon-carbon double bond lies almost perpendicular to the coordination plane, and the bond between the palladium and the aryl substituted alkene carbon atom is shortened with the increasing electron withdrawing nature of Ar [350]. Reaction of $[Pd_2(dba)_3]$ with cod and various quinones led to the synthesis of species [Pd(cod)(quinone)]. The cod ligands were readily substituted by PPh_3, and the electrochemistry of the complexes was investigated [351].



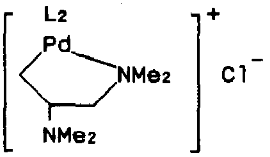
Scheme 5 Reactions of a nickel complex of methylenecyclopropane

The addition of chiral nucleophiles to palladium alkene complexes has been investigated. An alternative strategy involved the addition of achiral nucleophiles in the presence of chiral amines as ligands. The reaction of the anion of a chiral sulphoxide (reaction (27)) gave promising enantioselectivities, but poor chemical yields. Using *N,N*-dimethyl-1-phenylethylamine as the chiral ligand, enantiomer excesses up to 40 % were achieved for the reaction of the anion of diethyl propanedioate with E-1-phenylpropene [352]. Treatment of *N,N*-dimethylallylamine with $Li_2[PdCl_4]$ and dimethylamine gave 202, by attack of the amine on the intermediate palladium alkene complex. Primary amines gave poor results and many side reactions, but potassium phthalimide proved a useful nucleophile [353].

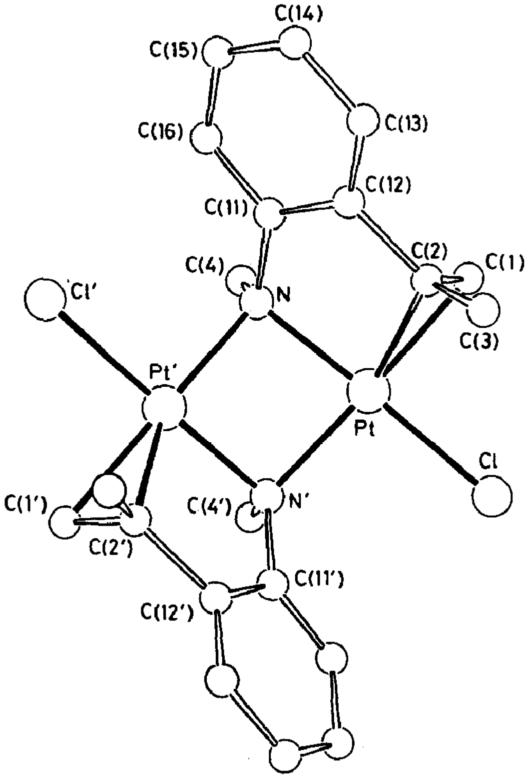


(27)

The preparation of 203, by deprotonation of $[Pt(2\text{-}NHMeC_6H_4CMe{=}CH_2)Cl_2]$ with an anion exchange resin, has been reported, and its structure was established by an X-ray diffraction study [354]. The structure of 204 was also destermined. Remarkably, the carbon-carbon double bond is coordinated in-plane, with the phenyl substituent on the same side of the coordination plane as the methyl group. In the related species, $[CpPd(PPh_3)(PhCH{=}CH_2)]$, the alkene adopted the more normal perperdicular coordination [355].



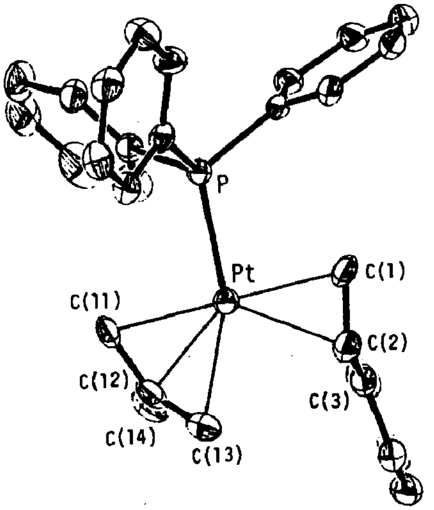
202



203 (Reproduced with permission from [354])

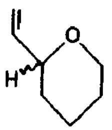
The photolysis of $H_2[PtCl_6]$ in hexane/ethanoic acid gave $[\{(CH_3(CH_2)_3CH{=}CH_2)PtCl_2\}_2]$, *via* a σ-hexyl platinum(IV) complex [356].

The optical purity of trigonal bipyramidal complexes of prochiral alkenes of the type $[Pt(Me_2NN{=}C(Me){-}C(Me){=}NNMe_2)(alkene)Cl_2]$ has been determined using the chiral shift reagent $[Eu(hfc)_3]$ [357]. Complexes of S-3-methyl-1-pentene (SMP) and R,S-3-methyl-1-pentene were studied in solution, and, for SMP, in the solid state [358]. Syntheses of many such hydrazone complexes have been described [359]. The separation of chiral alkenes could be achieved *via* diastereomeric platinum complexes, [Pt(alkene)(OOCCH(Ph)NR^{1}R^2)Cl], using normal or reversed phase liquid chromatography. The influence of alkene structure on complex resolution has been investigated, and several pure enantiomers of alkenes isolated [360]. **205** was resolved *via* a chiral platinum complex with S-PhCH(Me)NH$_2$ [361].



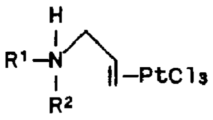
204 (Reproduced with permission from [355])

Atoms are represented by thermal ellipsoids at the 30 % probability level.



205

Complexes of the types **206** and **207** were prepared and examined for their cytotoxic effect. The mechanism of their cytotoxicity is probably different from that of *cis*-platin [362]. The preparation of **208** and its neutral analogues was described. The alkene is more electrophilically activated in the cationic species, and double bond migration occurred *via* a platinum hydride intermediate [363]. The species [PtL$_3$] (L = Me$_3$CN=P-N(CMe$_3$)(SiMe$_3$)) reacted with alkenes bearing electron withdrawing groups to give **209**, which had substantial metallocyclopropane character. Low temperature hydrolysis gave **210**, which was converted at room temperature into the alkenyl derivative **211** [364].



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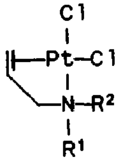

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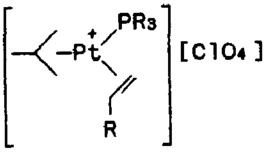

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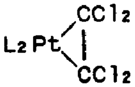

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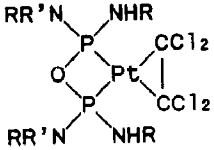

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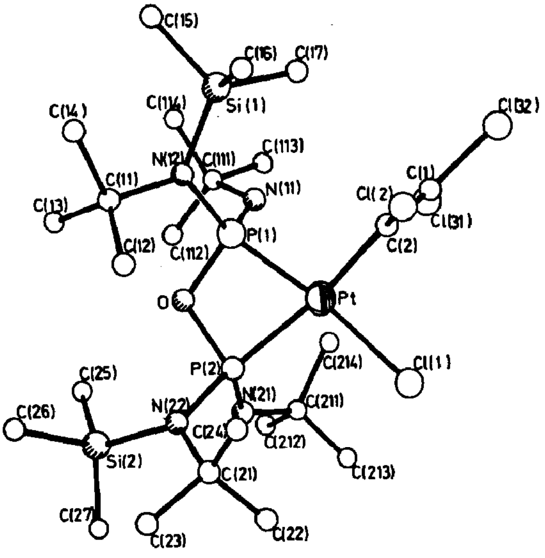
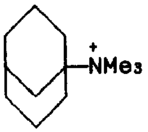


211 (Reproduced with permission from [364])

Hydrolysis of $K[Pt(CH_2=CHCH_2SiMe_3)Cl_3]$ gave the tetrameric species $[\{Pt(MeCH=CH_2)Cl\}_4]$, and $[\{Pt(CH_2=CHCH_2SiMe_3)Cl_2\}_2]$ reacted similarly [365]. Reaction of phenylethene with $H_2[PtCl_6]$ in the presence of $Na[HCO_3]$ and ethanol, was reported to give a platinum alkene complex, which, in 2-propanol, could be used to link ethenyl terminated dimethylpolysiloxane to silica [366].

A range of 1:1, 1:2 and 1:5 (Pt:Sn) complexes were postulated as the products from the reaction of $[\{Pt(MeCH{=}CH_2)Cl_2\}_2]$ with $SnCl_2.2H_2O$. Little evidence was provided for their structures [367]. Photolysis of 1-alkenes in propanone in the presence of $Na_2[PtCl_6]$ gave $[\{Pt(RCH{=}CH_2)Cl_2\}_2]$. The reaction was first order in platinum(IV), and was inhibited by air or water [368]. The homopolymerisation of 2-propene-1-ol in the presence of inorganic salts is generally slow. It has been reported that a hygroscopic, viscous and rather unlikely 1:1 complex is formed with "$PtCl_6$" [369].

Elimination of an amine from 212 gave the anti-Bredt alkene 213, which dimerised rapidly in the absence of other additives. It could, however, be trapped by $[Pt(py)(C_2H_4)Cl_2]$ to give an isolable, stable, complex, 214. In the presence of palladium ethanaote isomerisation occurred *via* an addition elimination mechanism [370].



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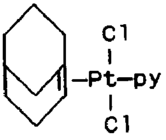
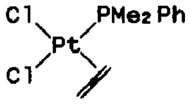


214

The reaction of the allene platinum complex, 215, with the oxime of propanone gave only 216, the structure of which was confirmed by an X-ray diffraction study. Intermediates could be observed by nmr spectroscopy, but could not be isolated [371]. The related complex of 3-methyl-1,2-butadiene reacted with phenol to give $[\{Pt(PPh_3)Cl_2\}_2]$ and 217 [372]. $[Pt(PPh_3)_2(C_2H_4)]$ reacted with butatrienes to give π-complexes by substitution; the regiochemistry of the reactions was investigated for more substituted substrates [373].



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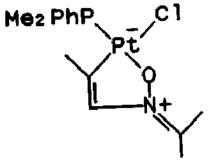

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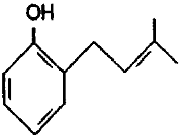
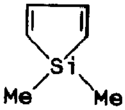


217

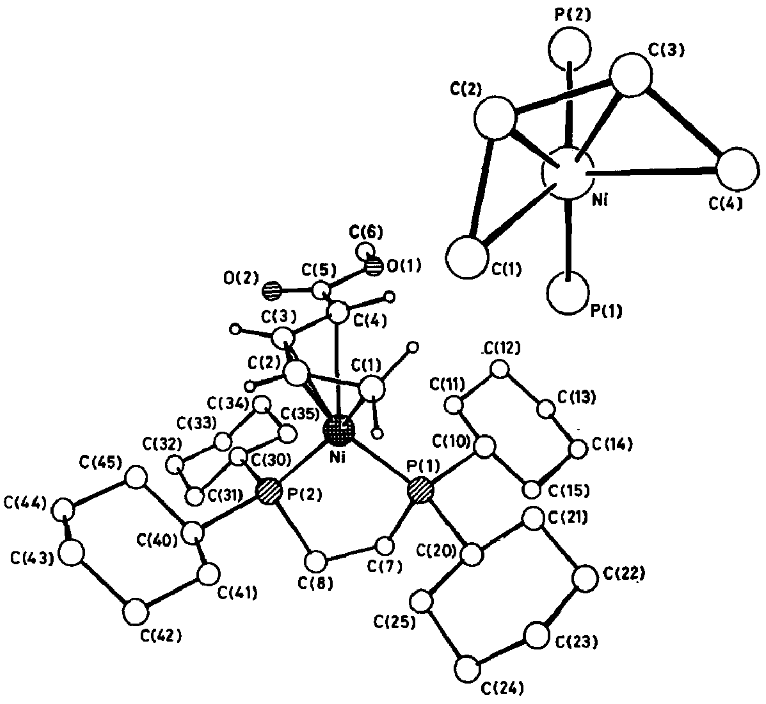
Both [Ni(bipy)(cod)] and $[Ni(cod)_2]$ in the presence of bipy have been used for the desulphurisation of dibenzothiophene to biphenyl. The reaction was proposed to proceed *via* a radical anion [374,375]. $[Ni(cod)_2]$ was substituted by the silacyclopentadiene 218 to give a sandwich type complex [376]. The cod ligand could also be substituted in $[Ni(Cy_2PCH_2CH_2PCy_2)(cod)]$ by methyl 2,4-pentadieneoate to give 219. The nmr spectrum of the complex exhibited fluxional behaviour, suggested dissociation of one of the alkene groups, and there was also a uniquely long nickel-C(4) bond in the solid state [377].



218

The species $[CpNi(Me)(\eta^2\text{-}1,3\text{-diene})]$ was prepared from $[Cp_2Ni]$, the diene, and methyl lithium. With isoprene as the diene, the less hindered double bond was complexed to nickel. The dynamic behaviour of the complexes was studied by nmr spectroscopy [378]. The synthesis and properties of dimeric 1-azadiene ligands such as $PhCH{=}CH{-}CH{=}N(CH_2)_3N{=}CH{-}CH{=}CHPh$, L, were reported. The complex $[\{NiL\}_2]$, 220, was characterised by an X-ray diffraction study. Both metal atoms were three-coordinated [379].

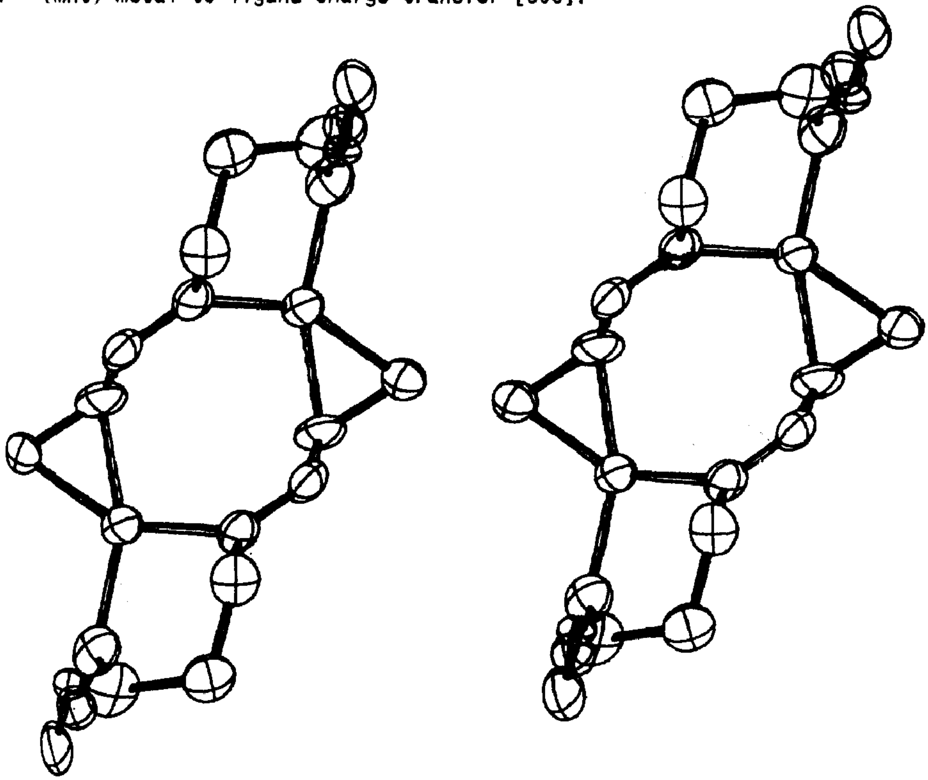
The complex $[Pd_2(dba)_3]$ has been used as a precursor for a range of species, both organometallic and coordination complexes, since the dba ligand is readily displaced. Both diene ligands were displaced by $P(C{\equiv}CPh)_3$ [380], and the rates of reaction with $P(OR)_3$, $P(SR)_3$ or $P(NR_2)_3$ were measured [381]. The displacement of cod from $[Pd(cod)Cl_2]$ by polystyryllithium gave a polystyryl palladium species, which acted as a hydrogenation catalyst [382]. Displacement by Me_2NNS was also noted [383]. The reaction with $[Rh(PPh_2py)_2(CO)Cl]$ gave the head-to-tail isomer of $[Rh(CO)Cl_2(\mu\text{-}PPh_2Py)_2PdCl]$, in which rhodium had sustained the oxidative addition of a Pd-Cl bond [384]. The hydration of $[Pd(nbd)Cl_2]$ in the presence of $Ag[NO_3]$ has been investigated (Scheme 6) [385].



219 (Reproduced with permission from [377])

There have been reports of a number of reactions of [Pt(cod)Cl_2] in which the diene was displaced by other ligands, including dppe [386] and $Ph_2AsCH_2PPh_2$, dapm. In the latter case the first product was *cis*-[Pt(dapm-*P*)$_2Cl_2$], which could be converted to [Pt_2(μ-dapm)$_2Cl_2$] by treatment with [Pt(dba)$_2$] [387]. Reaction with PR_3 under a hydrogen atmosphere gave [$H_2Pt(PR_3)_2$], which was used as a precursor to dihydroplatinum(II) bridged binuclear cations [388]. With the trigonal bipyramidal complex [Ir(NO)L(PPh$_3$)$_2$]$^{2+}$ (L = 3,6-bis(2-pyridyl)pyridazine) and related species, bridged species were formed by replacement of the cod ligand [389,390]. [Pt(cod)Cl_2] reacted with $SnCl_2$ in the presence of [Et_4N]Cl to give [Et_4N][Pt(cod)($SnCl_3$)$_3$], characterised by ^{119}Sn, ^{13}C and ^{195}Pt nmr spectroscopy [391].

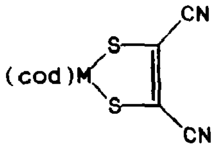
CV studies of [Pt_2(dba)$_3$] and substituted analogues showed that the complexes underwent two reversible one electron reductions and an irreversible oxidation. Substituents on the ligand were shown substantially to affect the LUMO in the complex [392]. The complex 221 showed luminescence in the solid state at room temperature and in frozen glass media. The small Stokes shifts implied that the geometry in the excited state was similar to that in the ground state. The emission-absorption system was assigned to a singlet-triplet d-π^*(mnt) metal to ligand charge transfer [393].



220 (Reproduced with permission from [379])
Stereodrawing of the structure of $[\{Ni(PhCH{=}CH{-}CH{=}N\{CH_2\}_3N{=}CH{-}CH{=}CHPh)\}_2]$. Both central atoms are tricoordinate and there are two modes of azadiene coordination.

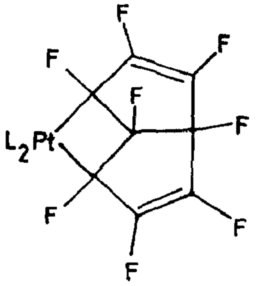
$$\begin{tikzcd}
{[Pd(diene)Cl_2]} \arrow[r, "Ag[NO_3]", "H_2O"'] & {[Pd(diene)(H_2O)_2]^{2+}} \arrow[r, "LL"] \arrow[d, shift left] & {[Pd(diene)LL]^{2+}} \arrow[d, shift left] \\
 & {[Pd(dieneOH)(H_2O)_2]^{+}} \arrow[r, "LL"] \arrow[u, shift left] & {[Pd(dieneOH)LL]^{+}} \arrow[u, shift left] \arrow[d, "{[PF_6]^-}"] \\
 & \text{oxidised products} & {[Pd(dieneOH)LL][PF_6]} \arrow[l]
\end{tikzcd}$$

Scheme 6 Reaction of a palladium complex of a strained diene with water [385].



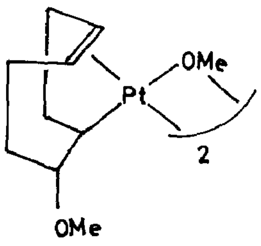
221

In $[Pt\{CH_2{=}C(Ph)CH_2CH_2C(Ph){=}CH_2\}Cl_2]$ the diene could be coordinated in two different conformations. One complex was derived from the *cis*-isomer of $[Pt(PhCN)_2Cl_2]$ and the other from the *trans*-species. The structures of both complexes were established by X-ray diffraction studies [394]. There have been some reassignments of the structures of platinum derivatives of octafluorocyclooctatetraene, such as 222 [395].



222

The complex 223 reacted with PR_3 to give a bridge split derivative, 224. Addition of further phosphine resulted in the displacement of the C=C double bond from the metal, followed by *β*-hydride elimination [396].



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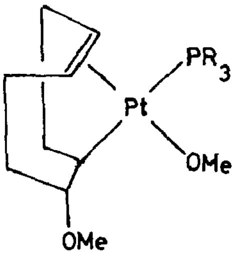
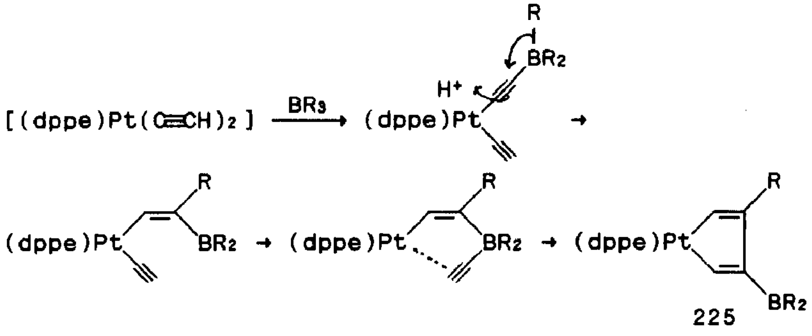
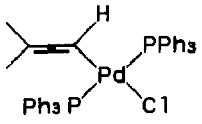


224

Reaction of $[(HC{\equiv}C)_2Pt(dppe)]$ with R_3B yielded the platinacyclopentadiene, 225, *via* the mechanism of Scheme 7 [397]. The related species *trans*-[$(HC\equiv C)_2Pt(PEt_3)_2$] were also hydroborated to give bis-alkenyl derivatives, although in this case cyclisation was impossible [398]. Reaction of the propargyl halide, $Me_2C(X)C\equiv CH$ with [$Pd(PPh_3)_4$] gave the σ-allenyl species 226, which could be readily substituted by organozinc compounds, RZnCl [399].



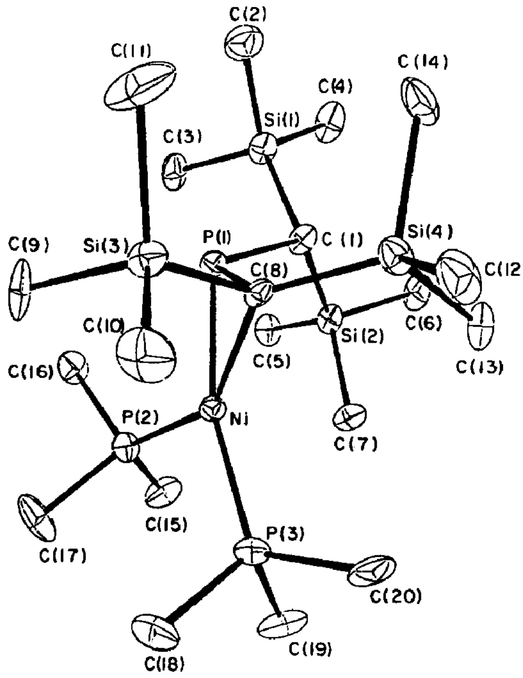
Scheme 7 Mechanism of reaction of [$(HC\equiv C)_2Pt(dppe)$] with boranes.



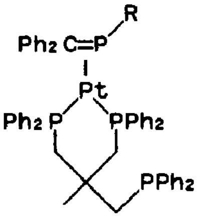
226

A number of papers have reported the preparation of η²-phosphaalkene complexes. An X-ray diffraction study of [$Ni(bipy)(Me_2C_6H_3P=CPh_2)$] indicated η²-coordination of the phosphalkene, but reaction with [$Ni(CO)_4$] gave η¹-complexes, thus demonstrating the influence of the other ligands on the relative importance of σ- and π-bonding [400]. A structural study of 227 also revealed η²-bonding [401].

η²-Coordination was established by spectroscopic techniques for 228, prepared by a simple displacement of PPh_3 from platinum. The phosphaalkyne, $Me_3C\equiv P$, reacted similarly to give an η²-derivative. However, with [$Pt(cod)_2$] and $ArP=CPh_2$ a species of stoicheiometry [PtL_3], in which all the ligands were η¹-*P* coordinated was formed [402,403]. Reaction of 229 (Ar = 2,6-$Me_2C_6H_3$) with [$Pt(PPh_3)_2(C_2H_4)$] gave an η²-derivative, but there was some evidence for an equilibrium with an η¹-complex in solution [404].



227 (Reproduced with permission from [401])
ORTEP view of $[(Me_3P)_2Ni\{(Me_3Si)_2C{=}P\text{-}CH(SiMe_3)_2\}]$



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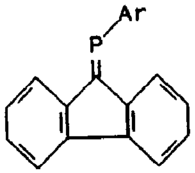
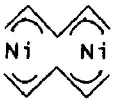


229

9 METAL ALLYL AND RELATED COMPLEXES

There has been a theoretical MO study of $[Ni(\eta^3\text{-}C_3H_5)_2]$ using the X_α SW and Fenske-Hall methods. The HOMO of the complex was shown to be mostly an allyl $a_2(\pi^{NON})$ orbital, and nickel allyl bonding involved both the 4p and 3d functions of nickel. Ionisation potentials were calculated and correlated with the experimental values from XPES [405]. The validity of the Hartree-Fock approximation in 230 and 231 was investigated by means of the Thouless instability conditions in the computational framework of a variable model Hamiltonian [406].



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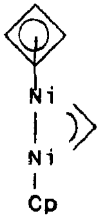
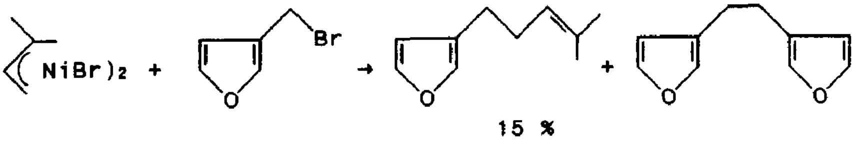


231

[Ni(η^3-C_3H_5)$_2$] reacted with PF_3 by reduction and substitution to yield [Ni(PF_3)$_4$]. Derivatives of PF_2Cl, PCl_3, PF_2NMe_2 and PF_2H were similarly prepared [407]. Treatment of the bridged dimer [Ni_2(η^3-CH_2CRCH_2)$_2$(μ-SH)$_2$] (R = H or Me) with MeLi gave {Ni(η^3-CH_2CRCH_2)SLi(thf)$_x$}, which eliminated lithium sulphide to give a species of stoicheiometry [{Ni(η^3-CH_2CRCH_2)}$_3S_2$Li(thf)$_2$]. One of the thf ligands could be substituted by tmeda to give a complex which was characterised by an X-ray diffraction study; nmr spectroscopic data, however, implied that there were two isomers of the complex present in solution [408].

The nickel allyl complex, 232, prepared from the allyl halide and [Ni(CO)$_4$], reacted with 233 to give some of the substitution product, but the major product was derived from homocoupling of the substrate. A mechanism was proposed which involved the equilibration of allyl complexes [409]. Reaction of pentadiene and CO_2 with {LNi(0)} gave a mixture of the allyl complexes 234 and 235, and the cyclic species, 236. Treatement with butenedioic anhydride yielded 2,4-hexadieneoic acid as a mixture of isomers [410].



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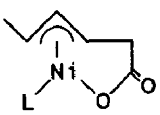

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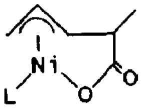

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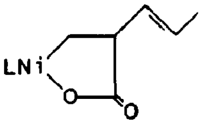
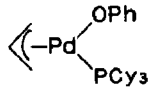


236

There has been an XPES study of π-allyl palladium complexes [411]. The physicochemical properties of "blacks" formed in decomposition of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ and $[CpPd(\eta^3\text{-}C_3H_5)]$ were investigated [412]. The effect of the structure of the precursor allyl complex on the activity of palladium on silica catalysts for the reduction of alkenes and ketones has been studied [413]. $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ underwent reductive decomposition with primary amines in solution. Species such as $[Pd(\eta^3\text{-}C_3H_5)(NH_2R)Cl]$ were supposed to be intermediates [414].

The structures of neutral and cationic complexes with bridging chloride or cyanide groups has been discussed. The bond angles preferred by the bridging ligands may dictate complex nuclearity; in the neutral palladium allyl series the chloro bridged complexes were dimers, whilst the cyano bridged species were tetramers. The cyanide bridges in $[\{Pd(dppe)(CN)\}_3]^{3+}$ were very non-linear; electrostatic repulsion proved to be more important than strain energy in this case [415]. Epr spectra of palladium allyl complexes substituted at the 2-position by a 4-phenoxy radical have been measured, and analysed to probe the interaction of the spin density with palladium [416].

The preparations of a number of palladium allyl complexes have been described. Treatment of phenyl allyl ether with $[Pd(PCy_3)_2]$ gave 237 but with the corresponding thio or selenoethers the dimeric species, 238 (Z = S or Se), were produced [417]. Formation of the allyl derivative from 239 occurred readily, and the product could be substituted by the anion of diethyl propanedioate [418]. Reaction of 240 with $Li_2[PdCl_4]$ gave a halo bridged dimeric allyl complex, which was converted to 241 by Tl[acac]. This is the first η^3-phenalenyl complex to be prepared. It seems to be rigid, and exhibits no dynamic behaviour in its nmr spectrum [419].



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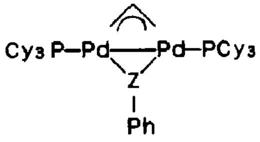
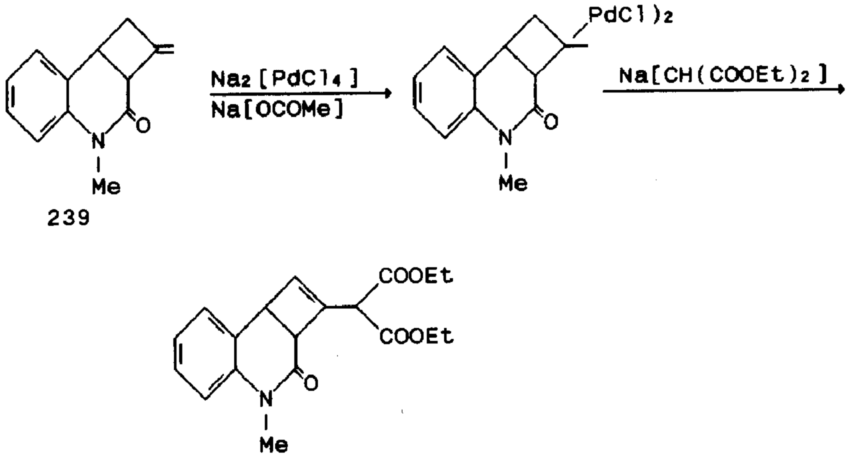


238

The *trans*-strereochemistry of the chloropalladation reaction of 242 was established by an X-ray diffraction study on the product 243 [420]. Conditions for the synthesis of allyl complexes without ring opening for 244 and 245 have been established [421]. The migrations of palladium in 246 have been investigated; the palladium migrates, but remains attached to one face of the molecule [422].



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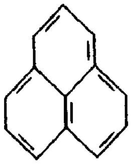

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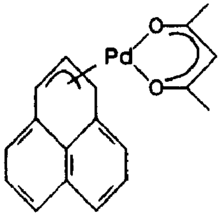

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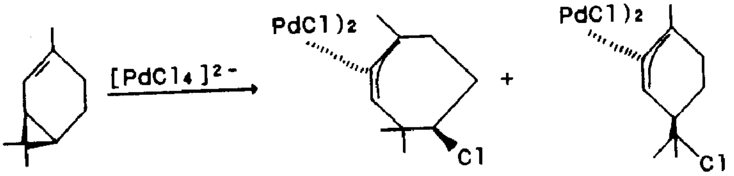

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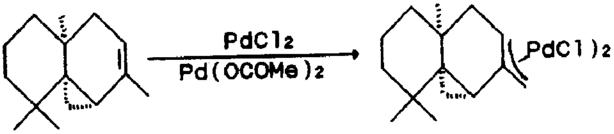

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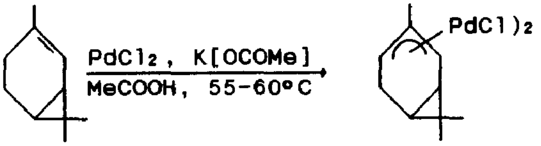

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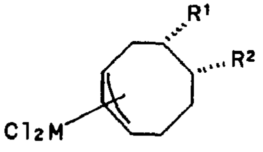
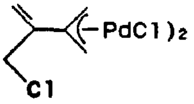


246

The allyl derivative, **247**, was prepared from 1,2-propadiene and $[Pd(PhCN)_2Cl_2]$. Substitution of the allylic halide proved facile, and **248** was cyclised in the presence of a range of nucleophiles [423]. Organomercury halides reacted with 1,4-pentadiene and $Li_2[PdCl_4]$ to give **243** with good regioselectivity for attack at the less substituted double bond. Regiochemical control was also investigated in the cases of more substituted dienes [424]. Reaction of rather substituted dienes with $Na[SO_2R]$ and $PdCl_2$ gave the isomeric allyl derivatives, **250** and **251**. The mechanism and stereochemistry of protiodepalladation was studied in some detail [425].



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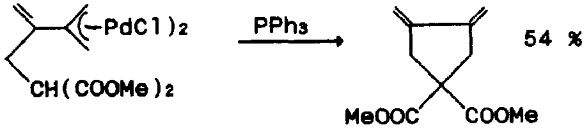

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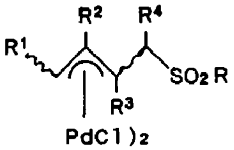

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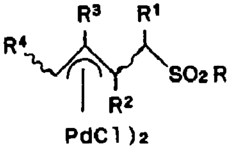
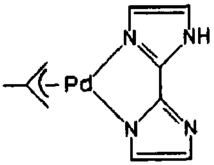


251

Bridge splitting reactions of $[\{Pd(\eta^3-C_3H_5)Cl\}_2]$ have been reported using 2-amino-4-methylpyridine [426], and $P(OEt)_3$ or a chiral, sugar-derived phosphite. In the latter case the products were rather inefficient catalysts for the hydrogenation of 1-decene or 2-methylene-butanedioic acid [427]. $[Pd(\eta^3-C_3H_5)(PPh_3)_2]Cl$, produced by a bridge splitting reaction, was treated with $ArSnMe_3$ to give $ArCH_2CH{=}CH_2$ in low yield in a stoicheiometric process. The related catalytic reaction was somewhat more efficient [428]. When $[\{Pd(\eta^3-CH_2CRCH_2)Cl\}_2]$ was reacted with $Ag[ClO_4]$ followed by H_2L, products such as 252 and 253 were isolated. Alteration of the molar ratio of the reacting species allowed the preparation of 254 [429].



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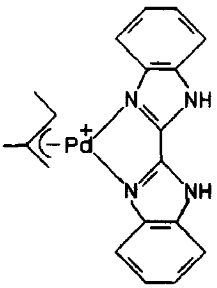

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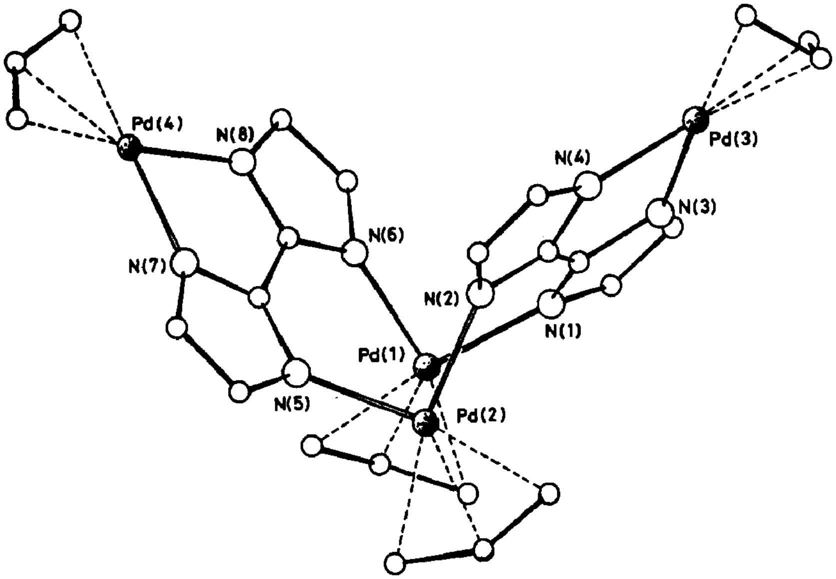
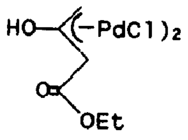


254 (Reproduced with permission from [429])

View of the complex $[Pd_4(\eta^3-C_3H_5)_4(\mu-bim)_2]$ showing its butterfly shape.

Treatment of the oxygen substituted allyl complex 255 with Tl[acac] gave 256. This could be substituted by a range of appropriate ligands, and the dynamic behaviour of the complexes was discussed [430]. Photolysis of 257 in the presence of an alkyl halide, RX, was reported to give the X-bridged analogue. However, in CH_2Cl_2 in the presence of PPh_3, or in dmf, 258 and 259 were formed. An allyl radical or radical complex was postulated as the crucial intermediate [431].



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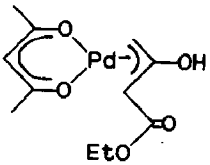

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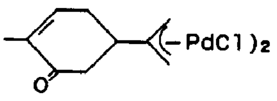

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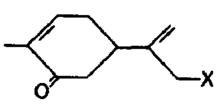

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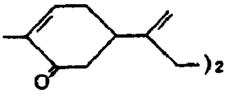
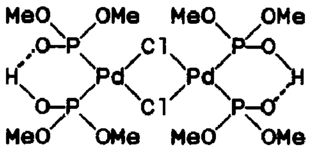


259

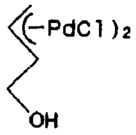
The complex $[CpPd(\eta^3\text{-}CH_2CRCH_2)]$ (R = H or Me) was treated with H_2S at -78 °C to give $[\{Pd(\eta^3\text{-}CH_2CRCH_2)(\mu\text{-}SH)\}_2]$, characterised by IR and nmr spectroscopy. At temperatures above -60 °C decomposition occurred giving PdS and $CH_2{=}CR\text{-}CH_3$. Related platinum complexes were prepared, but they appeared to be oligomeric [432]. Reaction of $[\{Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}SH)\}_2]$ with either bis(allyl)palladium or bis(allyl)platinum gave the mixed complexes $[NiPd(\eta^3\text{-}C_3H_5)_2(\mu\text{-}S)]$ and $[\{NiPt(\eta^3\text{-}C_3H_5)_2(\mu\text{-}S)\}_n]$ [433].

$[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ reacted with $(MeO)_2POH$ to give 260; many related reactions have been noted, and some of the products have been used as catalysts for hydrogenation [434]. $[Pd(\eta^3\text{-}C_3H_5)(MeNO_2)_2][BF_4]$ was a catalyst for the dimerisation and isomerisation of alkenes. The allyl group was retained during the catalytic cycle, and the mechanism proposed was essentially ionic in character [435].



260

The kinetics of the oxidation of 261 by benzoquinone in HCl to give E-$ClCH_2CH{=}CHCH_2OH$ have been investigated [436]. Photooxidation of 262 (R = alkyl, G = electron withdrawing group) gave unsaturated carbonyl compounds [437]. Under an argon atmosphere the main products were allyl dimers, and studies with radical scavengers suggested that both reactions followed a radical path [438]. When a 1-substituted allyl complex was reacted with Me_3COOH in the presence of $[Mo(O_2)(acac)_2]$ the more highly substituted allyl alcohol, such as 263, was obtained [439].



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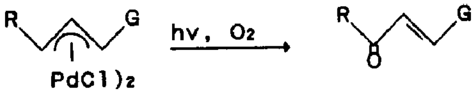

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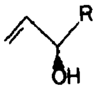
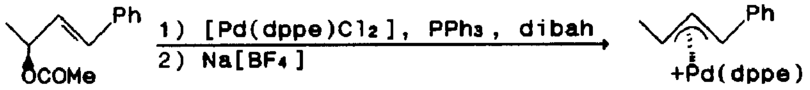


263

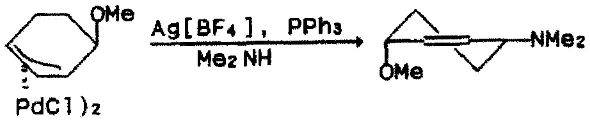
The oxidative addition of the enantiomerically enriched allyl ethanoate, 264, to palladium(0) proceeded with inversion, with 81 % stereoselection. Treatment of 265 with $Na[CH(COOEt)_2]$ resulted in displacement, predominently with a second inversion of stereochemistry. These observations have considerable implications for the stereocontrol observed in allylic substitutions catalysed by palladium complexes [440]. Reaction of 266 with secondary amines in the presence of $Ag[BF_4]/PPh_3$ resulted in external, *trans*-attack, with very high selectivity. Carbonylation in the presence of Et_2NH gave only 267; a σ-allyl was invoked as the critical intermediate [441].



58 % ee

264

265



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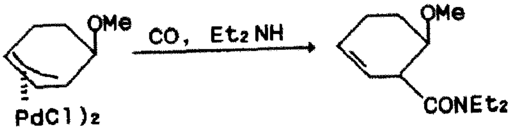
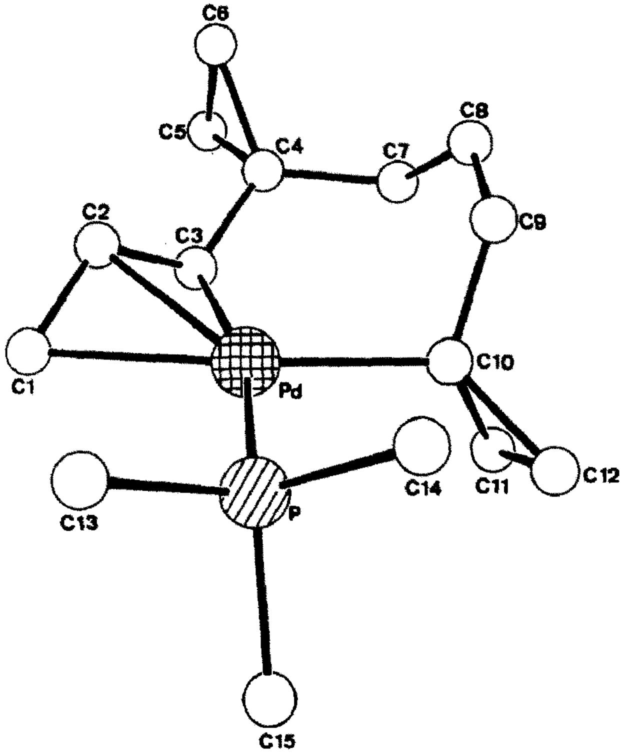


267

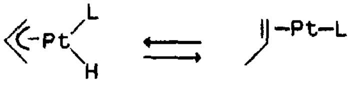
The reaction of [CpPd(η^3-C_3H_5)] with PMe_3 and 268 gave 269, characterised by an X-ray diffraction study [442].

268



269 (Reproduced with permission from [442])

The equilibration between 270 and 271 (L = $P(CMe_3)_3$) was relatively slow, on the nmr timescale, and the complex decomposed above -20 °C to give propene. 270 was a catalyst for the reduction of dienes at low temperature. Kinetic studies implied that hydrogen activation was the rate-controlling step [443]. The reaction of the σ-allyl platinum complex, 272, (L = PPh_3, $PMePh_2$, or PCy_3, *trans*; L_2 = $Ph_2PCH{=}CHPPh_2$, *cis*) with tcne gave 273. Various mechanisms were propsed for the reaction [444].



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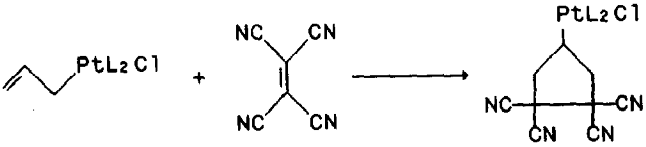


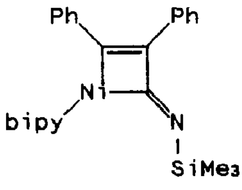
272 273

10 METAL ALKYNE AND ALKYNYL COMPLEXES

Reaction of $[Ni(cod)_2]$ with $PhC{\equiv}CPh$ in the presence of bipy gave $[Ni(PhC{\equiv}CPh)(bipy)]$ in which the η^2-alkyne complex had substantial metallocyclopropene character. Protonation yielded *cis*-1,2-diphenylethene, whilst ring expansion occurred in the presence of Me_3SiNC giving 274, the reactions of which were studied. The metallocyclopropene also inserted other alkynes to give metallocyclopentadienes [445]. When *trans*-$[HPt\{P(CMe_3)_3\}_2]X$ was treated with ethyne an equilibrium was established with *trans*-$[HPt(C_2H_2)\{P(CMe_3)_3\}_2]$, but the alkyne complex could not be isolated [446]. 275 reacted with $K_2[PtX_4]$ to give a species of stoicheiometry $[Pt(275)_2X_2]$, in which it was postulated that the triple bonds were metal coordinated [447].

Alkyne substituted homo and heterometallic clusters of the nickel triad have been reviewed [448]. The UVPES of $[Cp_2Ni_2(\mu\text{-}C_2H_2)]$ and $[Cp_2Ni_2(\mu\text{-}CF_3C{\equiv}CCF_3)]$ have been recorded. For the first time PE spectral features related to ionisation from molecular orbitals involved in metal alkyne back donation have been detected. Analysis of the spectrum of the hexafluorobutyne derivative provided further evidence for the dominant role of the back bonding interaction in the metal alkyne bond

[449]. The dimer $[Cp_2Ni_2(C_2Ph_2)]$ reacted with $[Ru_3(CO)_{12}]$ to give $[Cp_2Ni_2Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}C_2Ph_2)]$. Structural studies revealed a square pyramidal arrangement of the metal atoms with ruthenium at the apex and alternating nickel and ruthenium atoms around the base. The alkyne interacts with the four metal atoms in the basal plane, with a σ-bond to nickel and a π-bond to ruthenium [450]. Reaction of $[Pd_2(\mu\text{-}dppm)_2X_2]$ with alkynes bearing electron withdrawing groups gave $[Pd_2(\mu\text{-}dppm)_2(\mu\text{-}alkyne)X_2]$. The structure of the complex for which the alkyne was $CF_3C\equiv CCF_3$ was established by an X-ray diffraction study [451].



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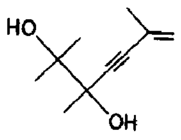
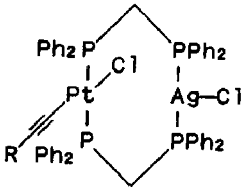


275

The electrochemistry of $[(\eta^5\text{-}Ph_5C_5)_2Pd_2(\mu\text{-}Ph_2C_2)]$ has been studied. Two diffusion controlled, reversible, one electron oxidations were observed, together with a single reversible one electron reduction. The epr spectrum of the moncation was recorded, and this species reacted redily with a range of ligands [452].

^1H, ^{13}C, ^{31}P and ^{195}Pt nmr spectroscopic parameters have been reported for *cis*- and *trans*-$[M(C\equiv CR)_2(PR'_3)_2]$ (M = Ni, Pd or Pt). The data reflected an increase in π-back bonding in the order Pt < Pd < Ni [453]. Alkynes of the type $HC\equiv CCH_2X$ (X = OH, Cl or Br) were polymerised in the presence of $[Ni(PR_3)_2X_2]$ or, more rapidly using $[Ni(C\equiv CCH_2X)(PR_3)_2(NCS)]$ [454].

The complex $[Pd(\eta^2\text{-}dppm)_2]Cl_2$ reacted with $Hg(C\equiv CR)_2$ at -40 °C to give a rather unstable species *trans*-$[(RC\equiv C)_2Pd(\mu\text{-}dppm)_2HgCl_2]$. The mercury could be removed by the action of Na_2S at temperatures below 0 °C to give a fluxional complex *trans*-$[(RC\equiv C)_2Pd(\eta^1\text{-}dppm)_2]$, which reacted with derivatives of other metals to give a range of bimetallic species including [*trans*-$[(RC\equiv C)_2Pd(\mu\text{-}dppm)_2AgX]$ and *trans*-$[(RC\equiv C)_2Pd(\mu\text{-}dppm)_2Rh(CO)]Cl$. In the latter species one of the alkyne ligands was semi-bridging [455]. In the related platinum series the mercury could be displaced directly by rhodium using $[Rh_2(CO)_4Cl_2]$. The bimetallic silver complex, 276, was prepared from $[Pt(\eta^2\text{-}dppm)_2]Cl_2$, AgOCOMe and an alkyne. Silver could also be readily displaced by rhodium [456], or a $\{W(CO)_3\}$ moiety using *fac*-$[W(CO)_3(NCMe)_3]$ [457].



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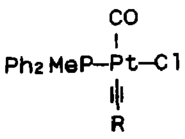
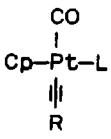
The reaction of 277 with $Hg(C\equiv CR')_2$ in the presence of chloride ion has been reinvestigated. Labelling studies have ruled out an oxidative addition reductive elimination mechanism, and suggest that an S_E2 cyclic process may be operating [458]. Treatment of 277 with CpTl or Cp_2Hg resulted in a simple displacement of the halide. The product, 278, reacted with $HgCl_2$ to give 279 and CpHgCl only. Group transfer between 278 and *cis*-$[PtL(CO)Cl_2]$ involved an S_E2 cyclic mechanism *via* 280 [459].



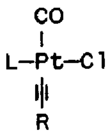
$\mathrm{Ph_2MeP{-}\overset{CO}{\underset{\underset{R}{|||}}{Pt}}{-}Cl}$

277



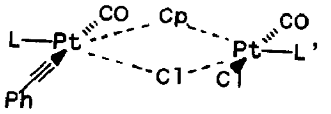
$\mathrm{Cp{-}\overset{CO}{\underset{\underset{R}{|||}}{Pt}}{-}L}$

278



$\mathrm{L{-}\overset{CO}{\underset{\underset{R}{|||}}{Pt}}{-}Cl}$

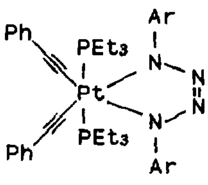
278



280

$[Pt(dppe)Cl_2]$ reacted with either $Me_3SnC\equiv CR$ or $Me_2Sn(C\equiv CR)_2$ to give $[(RC\equiv C)_2Pt(dppe)]$, characterised by nmr spectroscopy [460]. Reaction of the azide, $4\text{-}O_2NC_6H_4N_3$, with *trans*-$[(PhC\equiv C)_2Pt(PEt_3)_2]$ gave 281, characterised by an X-ray diffraction study. On the basis of the bond lengths 281 could be characterised as a platinum(IV) complex of a dianionic ligand [461].

Treatment of $[Pt(\eta^2\text{-dppm})Cl_2]$ with $RC\equiv CLi$ ($R = Ph$, $4\text{-}MeC_6H_4$, $PhCH_2CH_2$ or $C(=CH_2)Me$) gave *trans,trans*-$[(RC\equiv C)_4Pt_2(\mu\text{-dppm})_2]$, which reacted with further dppm to give the mononuclear complex *trans*-$[(RC\equiv C)_2Pt(\eta^1\text{-dppm})_2]$. The latter species was also obtained from $[Pt(\eta^2\text{-dppm})Cl_2]$, $LiC\equiv CR$ and dppm. Mixed metal binuclear complexes could be prepared from the mononuclear derivative, and its oxidation reactions were also investigated [462].



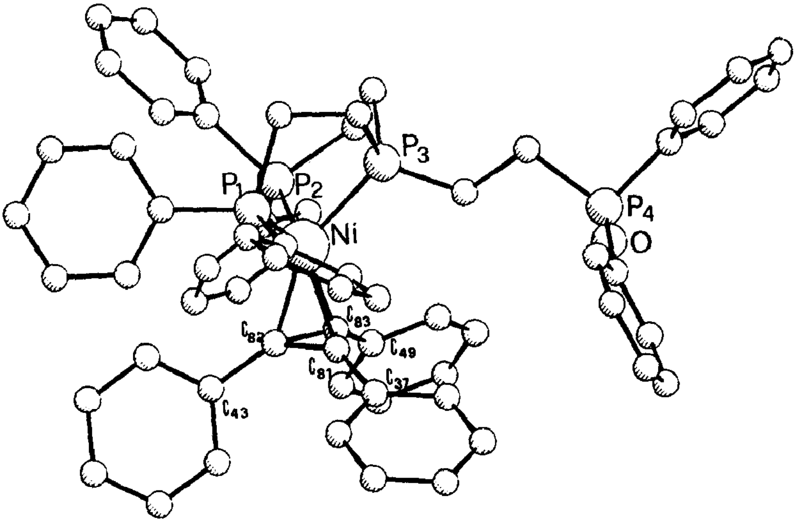
281

Reaction of either [Ni(PCy$_3$)$_2$] or [{Ni(PCy$_3$)$_2$}$_2$N$_2$] with PhCH(R)CN resulted in the formation of an equilibrium mixture of [Ni(PCy$_3$)$_2$(σ-R'CN)] and [Ni(PCy$_3$)(π-R'CN)], the position of the equilibrium depending on the amount of phosphine added. Intramolecular oxidative addition yielded [R'Ni(PCy$_3$)$_n$(CN)] [463]. In the complex [Pt(PPh$_3$)$_2$(η^2-Me$_3$CC$\equiv$P)] there is also a parallel with alkyne chemistry. In no known case is the phosphorus lone pair the sole site of binding, but it may bond to a second metal [464].

11 COMPLEXES OF DELOCALISED CARBOCYCLIC SYSTEMS

A nickel complex of a cyclopropenyl cation could be prepared by the reaction of [Ni(PPh$_3$)$_2$(C$_2$H$_4$)] with [Ph$_3$C$_3$][ClO$_4$] in the presence of P(CH$_2$CH$_2$PPh$_2$)$_3$ or N(CH$_2$CH$_2$AsPh$_2$)$_3$; the mechanism of the reaction was not entirely clear [465]. Reaction of [Ni(Ph$_3$C$_3$)(PPh$_3$)$_2$][ClO$_4$] with P(CH$_2$CH$_2$PPh$_2$)$_3$ (PP$_3$) in the presence of Na[BPh$_4$] gave [Ni(Ph$_3$C$_3$)(PP$_3$)][BPh$_4$]. The PP$_3$ derivative could be selectively oxidised by molecular oxygen in solution to give [Ni(Ph$_3$C$_3$){(Ph$_2$PCH$_2$CH$_2$)$_2$P(CH$_2$CH$_2$POPh$_2$)}][BPh$_4$], 282, characterised by an X-ray diffraction study [466].

A series of metallocenes including [Cp$_2$Ni] was studied by vibrational spectroscopy, quasielastic neutron scattering and calorimetry. Attempts to classify the different order/disorder transitions showed that all three techniques were needed to obtain activation energies and residence times [467]. Incoherent quasi-elastic neutron scattering experiments using different resolutions were carried out on polycrystalline samples of [Cp$_2$Ni], in the temperature range 4-300 K. These showed that a unique 2π/5 reorientational jump process of the cyclopentadienyl rings was taking place below and above the diffuse phase transition at 200 K. A proton correlation time of 4×10^{-12} sec at 300 K, associated with an activation energy of 6.3 kJ mol^{-1}, was in agreement with the literature data. It was concluded that the asymmetry of the double well potential function governing the reorientations of the Cp rings, as deduced from heat capacity and Raman spectroscopy, is too small to be evidenced in neutron scattering experiments [468].



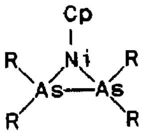
282 (Reproduced with permission from [466])

The cation $[Cp_2Ni]^+$ doped with the magnetic isotope ^{61}Ni has been diluted into several diamagnetic host lattices, and studied by epr at low temperature in polycrystalline samples. From the analysis of the ^{61}Ni hyperfine tensor and EHMO MS X_α calculations, a quantitative comparison of the covalency and the dynamic Jahn-Teller effects with the related d^7 system $[Cp_2Co]$ was possible. Jahn Teller coupling strength was comparable in the two metallocenes [469]. Energies of low-lying negative ion states of the 3d metallocenes, including $[Cp_2Ni]$, were obtained from electron transmission spectroscopy [470].

The complex $[CpNi(PPh_3)Cl]$ supported on silica or alumina was detected by secondary ion mass spectrometry (SIMS). $[Cp_2Ni]$ on silica gave only Ni^+ in the SIMS analysis, which may reflect the presence of oxide supported nickel metal [471]. Silylated and stannylated metallocenes with the central metal being V, Cr, Co or Ni have shown the first paramagnetic shifts in their ^{29}Si and ^{119}Sn nmr spectra. The shifts showed a strong temperature dependence which varied with the electronic structure of the metallocene [472].

Kuhn and Winter have reported the preparation of $[CpNi(\eta^4\text{-}C_5H_6)][BF_4]$ by low temperature protonation of $[Cp_2Ni]$ [473]. The η^4-cyclopentadiene ligand was readily replaced to generate complexes of the type $[CpNiL_2][BF_4]$ ($L = \eta^1\text{-}Ph_2PPPh_2$ [474], $\eta^1\text{-}R_3P{=}Se\text{-}\mathit{Se}$ [475], R_2Se [476], R_2S [477],

η^1-$R_2PCH_2AsR_2$-*P* or η^2-$R_2P(CH_2)_nAsR_2$ (*n* = 1 or 2) [478]) and a large number of very short papers. Treatment with RTeR gave a species of stoicheiometry $[CpNi(R_2Te_2)]$, which may be oligomeric [479]. Reaction with R_3Sb gave $[CpNi(SbR_3)_2][BF_4]$, which was converted to $[CpNi(R_3Sb)I]$ and $[CpNi(Me)(R_3Sb)]$ by LiI and MeLi respectively [480]. Both monomeric, **283**, and dimeric, **284**, structures were proposed for the products of reaction with R_2AsAsR_2 [481]. The mixed complex $[CpNi\{P(NR_2)_3\}Cl]$ was prepared from $[Cp_2Ni]$, $NiCl_2$ and $P(NR_2)_3$ [482]. The reactions of $[Cp_2Ni]$ and $[CpNi(\eta^4$-$C_5H_6)][BF_4]$ with **285** were studied [483].



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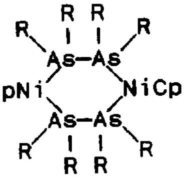

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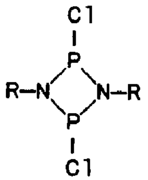
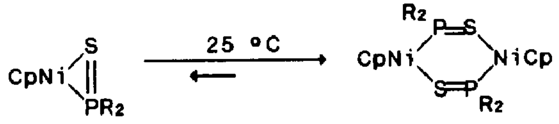
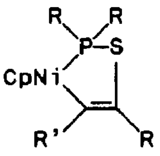


285

$[Cp_2Ni]$ underwent a redox reaction with $\{Cp(OC)_3MoF.BF_3\}$ to give $[\{CpMo(CO)_3\}_2]$ and $[Cp_2Ni]^+$, the latter reacting further to give $[Cp_3Ni_2]^+$ [484]. In solution there was a monomer/dimer equilibrium between **286** and **287**. The monomer inserted alkynes to give a mixture of **288** and its regioisomer **289**, characterised by X-ray diffraction [485].

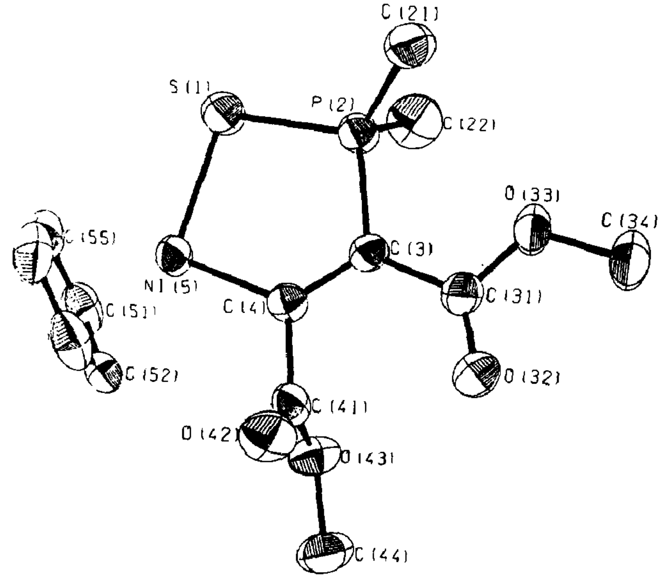


286 **287**

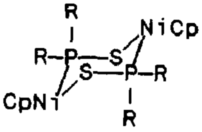


288

$[Cp_2Ni]$ reacted with $HP(O)R_2$ to give $[CpNi\{P(O)R_2\}\{P(OH)R_2\}]$ (R = Me or Et), but with the sulphur analogue, **290** (R = Me, Cy, Ph or OMe) was formed, and its reactions investigated [486]. Desulphurisation of **291** was accomplished reductively using $[Cp_2Ni]$ [487].



289 (Reproduced with permission from [485])



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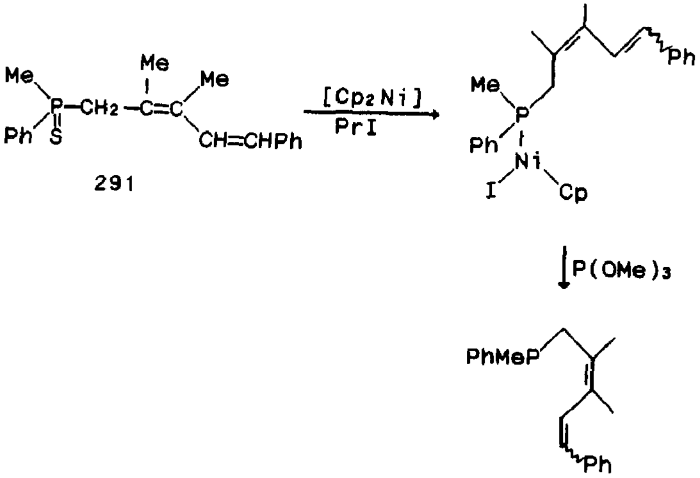
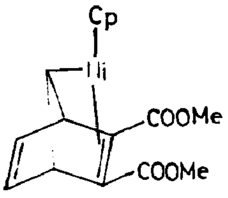


291

Nickel(I) has been shown to act as a catalyst for the equilibration of *syn*- and *anti*-bicycloheptadiene complexes [488]. **292** was oxidised by 3-chloroperbenzoic acid to give **293**, a result which is contrary to previous reports [489]. Some reactions of a cyclopentadienyl nickel alkyl complex are shown in Scheme 8 [490].



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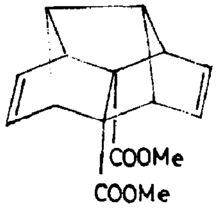

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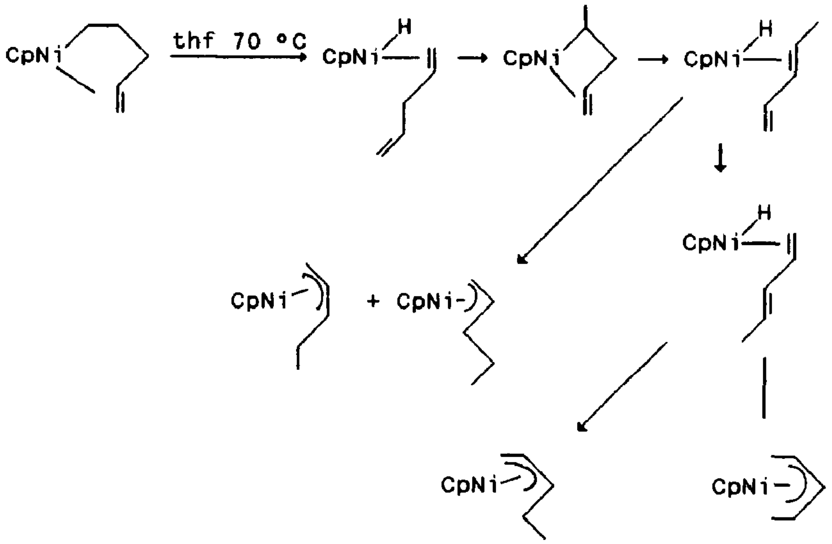
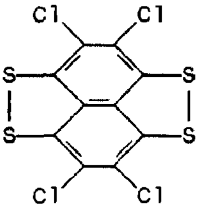


Scheme 8 Interconversion of alkyl, alkenyl and allyl ligands at a nickel centre [490].

The reaction of $[Cp_2Ni]$ and $[Ni(\eta^5\text{-}C_5H_4COOMe)_2]$ with R-PhC≡CCONHCH(Me)Ph gave four products of the $\{Ni_2(alkyne)\}$ type, differing in cluster chirality [491]. In the clusters $[\{CpNiPH_2\}_n]$ (n = 2 or 3), nmr spectroscopy indicated that both phosphorus chemical shifts and ${}^2J_{PP}$ were strongly influenced by ring size [492]. Reaction of $[\{CpNi(CO)\}_2]$ with $C_{10}Cl_4S_4$, **294**, gave **295**, with a butterfly arrangement for the $\{Ni_2S_2\}$ unit. The Ni-Ni distances in the crystallographically distinct molecules, at 2.951(3) and 2.809(3) Å, were very short for non-bonding distances [493].



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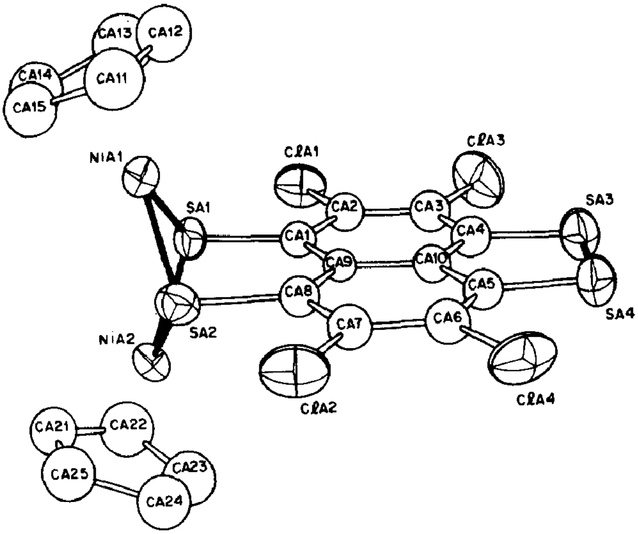
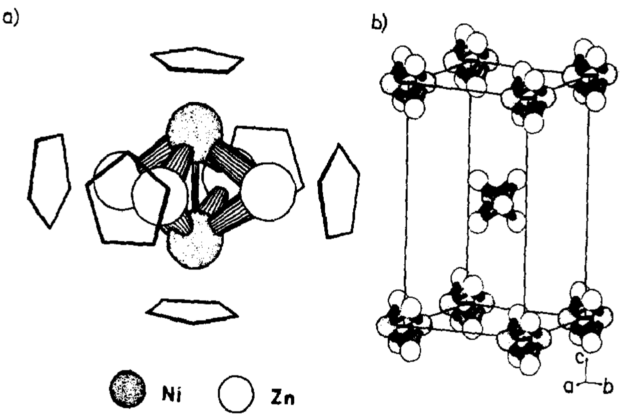


295 (Reproduced with permission from [493])

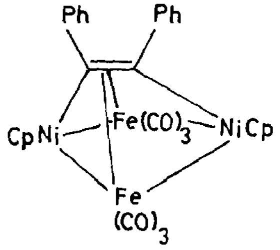
There have been further studies of multi-decker sandwich complexes. The structure of [Cp$_3$Ni$_2$][BF$_4$] has been determined by X-ray diffraction at 190 and 295 K. The structures established were similar, although that at 295 K was more disordered and showed larger thermal motions. DSC revealed a reversible phase transition at 102 K [494]. The structure of [Cp$_2$Ni$_2$(μ_2-C$_5$H$_6$)] has been established by a diffraction study [495]. The species [CpM(μ-C$_3$B$_2$H$_5$)M'Cp] for which M = Ni and M' = Co or Ni were paramagnetic with one unpaired electron. Four-decker sandwiches were also described, and extensive epr and electrochemical studies of these complexes were reported [496].

The reaction of [Cp$_2$Zn] with [Ni(cod)$_2$] gave the mixed cluster [Cp$_6$Zn$_4$Ni$_2$], 296, characterised by an X-ray diffraction study. The cluster consists of an octahedral array of metal atoms with the zinc atoms equatorial and the nickel atoms occupying apical positions. The octahedron is compressed along the Ni-Ni axis [497].



296 (Reproduced with permission from [497])
a) Structure of $[Cp_6Ni_2Zn_4]$. All cyclopentadienyl groups are disordered and only one orientation of each is shown. b) Packing of the $\{Ni_2Zn_4\}$ clusters in the unit cell.

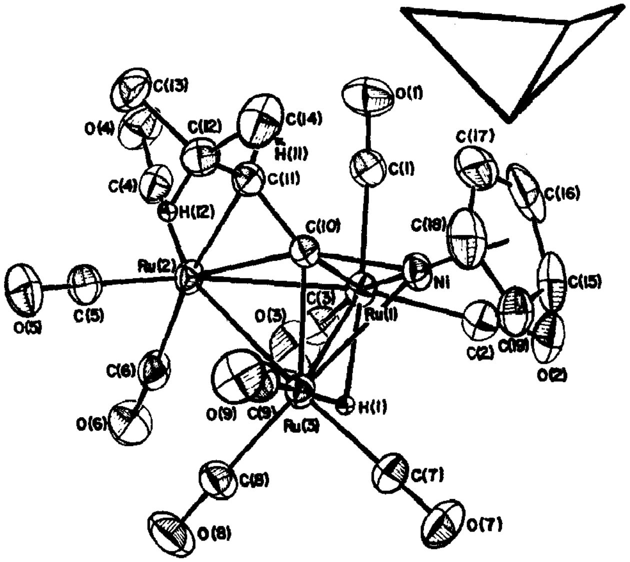
The reaction of $[Cp_2Ni]$ with $[Co_3(CO)_9(CR)]$ ($R = CO_2CHMe_2$) at room temperature yielded $[CpNiCo_2(CO)_6(\mu_3\text{-}CR)]$. If the reaction mixture was heated the products were $[Cp_3Co_3(CO)(CHR)]$ and $[Cp_3Co_2Ni(CO)(CR)]$ [498]. Treatment of 297 with R_3P or alkynes gave low nuclearity products [499].



297

$[\{CpNi(CO)\}_2]$ reacted with $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CCHMe_2)]$ to give $[CpNiRu_3(CO)_9(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{=}CHCHMe_2)]$, 298, which has now been fully characterised by an X-ray diffraction study. The $\{Ru_3Ni\}$ core has a butterfly configuration with the nickel atom at the wingtip site. The vinylidene ligand is σ-bonded to Ru(1), Ru(3) and nickel, and η^2-coordinated to Ru(2). The Ru(1)-Ru(3) edge is bridged by a hydride ligand which was located by the X-ray study. These data suggested that the cluster previously described as $[CpNiRu_3(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CHCMe_3)]$ should be reformulated as a hydride containing species [500]. Both $[Os_3(CO)_{12}]$ and $[H_2Os_3(CO)_{10}]$ reacted with $[\{CpNi(CO)\}_2]$

to give mixtures of [$CpNiOs_3(CO)_9(\mu_2\text{-}H)_3$] and [$Cp_3Ni_3Os_3(CO)_9$]. The tetranuclear cluster was converted to the hexanuclear species either after its use as a catalyst for the hydrogenation of alkynes or, in low yield, by reaction with CO. Complex interelationships of the clusters described were defined experimentally [501]. Reaction of either [$H_2Os_3(CO)_9(C{=}CHCMe_3)$] or [$HOs_3(CO)_{10}(CH{=}CHCMe_3)$] with [$\{CpNi(CO)\}_2$] under an atmosphere of hydrogen gave [$CpNiOs_3(CO)_9(\mu\text{-}H)(C{=}CHCMe_3)$]. The cluster was characterised by an X-ray diffraction study; the metal core consisted of a butterfly arrangement with the nickel atom at a wingtip. The vinylidene ligand was σ-bonded to the nickel and two osmium atoms, and η^2-ccordinated to the third osmium atom [502].



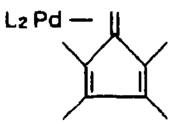
298 (Reproduced with permission from [500])

An ORTEP II perspective view of the molecular structure of [$(\mu\text{-}H)(CpNi)Ru_3(CO)_9(\mu_4,\eta^2\text{-}C{=}CHCHMe_2)$], showing the atomic numbering scheme used. The tetrametal skeleton is shown as an inset.

Reports of palladium and platinum derivatives of cyclopentadienyl ligands have been more sparse. The reaction of $TlCp^*$ with [$\{Pd(PR_3)Cl\}_2(\mu\text{-}OCOMe)_2$] gave [$Cp^*Pd(PR_3)X$]. Initial reports suggested that it was not possible to replace the second halide ligand with either Cp or Cp*. In an X-ray diffraction study of the complex for which R = $CHMe_2$ the five membered ring showed signs of a tendency towards η^1-bonding [503]. However, in a later paper from the same group [$Pd(PR_3)(\eta^5\text{-}Cp)(\eta^1\text{-}Cp)$] was prepared by an analogous reaction. Nmr spectroscopy led to the identification of two dynamic processes. The lower energy of the two was a metallotropic shift. The exchange of η^1- and

η^5-rings was a higher energy process, the rate of which depended on phosphine size [504]. The reaction of Na[C_5Ph_5] with a range of palladium allyl halo bridged dimers has been studied. Reaction of the product species, [(η^5-C_5Ph_5)Pd(η^3-C_3H_5)], with phosphine ligands, gave palladium(0) complexes and coupled organic products [505].

The reaction of [Cp^*Pd(η^3-C_3H_5)] with R_3P gave [Cp^*Pd(η^1-C_3H_5)(PR_3)], and, with an excess of the ligand, 299, characterised for L = PMe_3 by an X-ray diffraction study. A hydrogen atom has been transferred from one of the ring methyl groups to the allyl moiety [506]. A study has attempted to estimate net charge in a number of cyclopentadienyl metal complexes on the basis of ^{19}F nmr spectroscopic studies of derivatives of 300 ($Cp^{\#}$). [$Cp^{\#}$Pd(η^3-C_3H_5)] was among the complexes considered [507].



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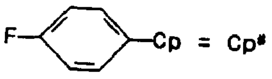
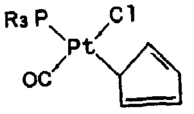


300

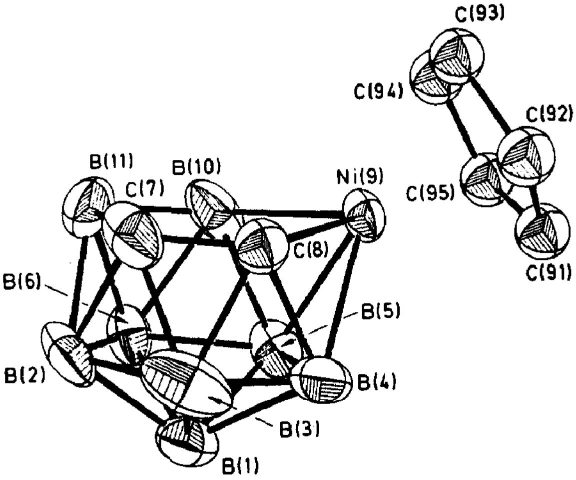
Reaction of *cis*-[Pt(CO)(PR_3)Cl_2] with either CpTl or Cp_2Hg gave only 301. The second chloride could be replaced only with an excess of CpTl to give a bis(η^1-Cp) derivative [508].



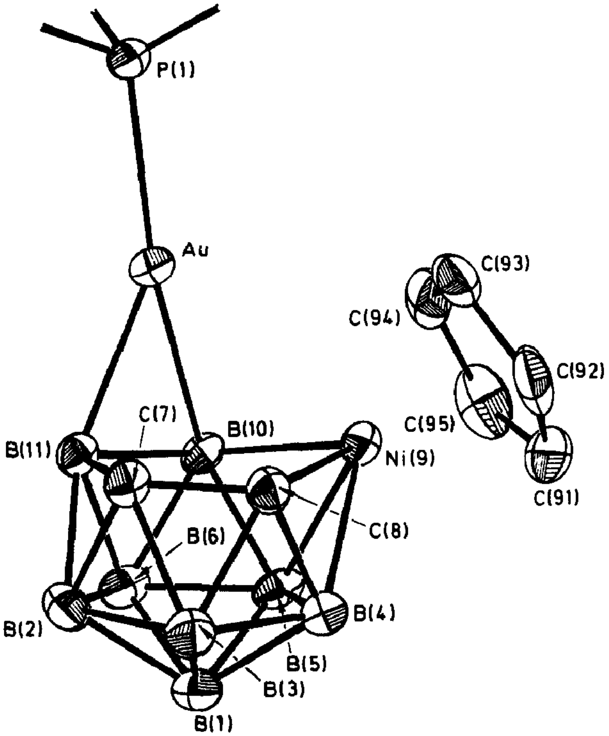
301

12 METAL CARBORANE AND RELATED COMPLEXES

There has been a report of the preparation of complexes of the stoichelometry [σ-($HCB_{10}H_{10}C$)$_2$Ni(bipy)], [CpNi{σ-($CB_{10}H_{10}CH$)}(PPh_3)] and (σ-$HCB_{10}H_{10}CCO_2$)$_2$Ni.$2H_2O$, but few details were given [509]. *nido*-[5,6-$C_2B_8H_{12}$] reacted with [Cp_2Ni] to give *nido*-[9-(Cp)-7,8,9-$C_2NiB_8H_{11}$], 302. The reactivity of the {μ-B-H-B-H} unit was shown by treatment with [MeAu(PPh_3)] yielding *nido*-[9-(Cp)-$\mu_{10,11}$-{Au(PPh_3)}-7,8,9-$C_2NiB_8H_{10}$], 303 [510].

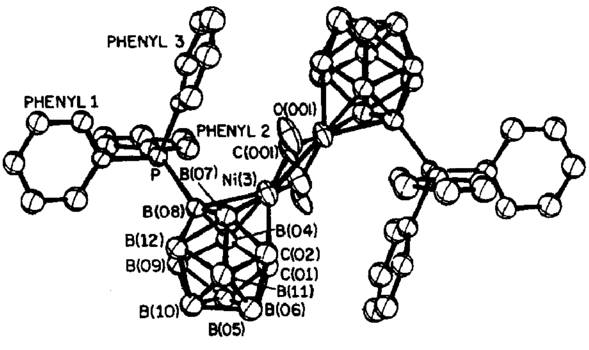


302 (Reproduced with permission from [510])
Molecular structure of *nido*-[9-Cp-7,8,9-$C_2NiB_8H_{11}$], showing only the major components of the disordered structure.



303 (Reproduced with permission from [510])

The reactions of $[NiL_2Cl_2]$ (L = PR_3) with the 7,8-, 7,9- or 2,9-isomers of *nido*-$[C_2B_9H_{11}]$ have been studied and were shown to yield icosohedral bis(phosphine)nickelacarboranes. Thermolysis *at* 80 °C of *closo*-$[3,3\text{-}(Ar_3P)_2\text{-}3,1,2\text{-}NiC_2B_9H_{11}]$ resulted in exchange of the phosphine and hydride ligands, giving *closo*-$[3,8\text{-}(Ar_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}NiC_2B_9H_{11}]$. Ligand substitution reactions of *closo*-$[3,3\text{-}(Ar_3P)_2\text{-}3,1,2\text{-}NiC_2B_9H_{11}]$ were studied, and carbonylation yielded *closo*-$[\{3\text{-}(\mu\text{-}CO)\text{-}8\text{-}(PPh_3)\text{-}3,1,2\text{-}NiC_2B_9H_{11}\}_2]$, 304, characterised by an X-ray diffraction study [511,512].

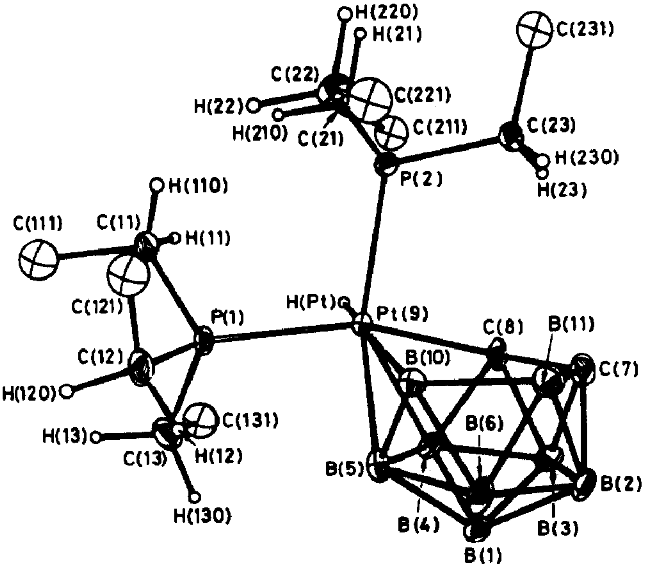


304 (Reproduced with permission from [511])
H atoms have been omitted for clarity.

Treatment of $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ with *nido*-$[5,6\text{-}C_2B_8H_{12}]$ gave $[9\text{-}H\text{-}9,9\text{-}(Et_3P)_2\text{-}\mu_{10,11}\text{-}H\text{-}7,8,9\text{-}C_2PtB_8H_{10}]$, 305, characterised by an X-ray diffraction study. The complex had a structure which approximated to a *nido*-icosohedron with a {CCPtNBB} open face. The reaction was thought to proceed *via* an oxidative insertion of a $\{Pt(PEt_3)_2\}$ unit into a {μ-BHB} function, follwed by interaction of platinum(II) with the boron cage. Thermolysis of 305 at 100 °C in toluene resulted in a the loss of molecular hydrogen and the transfer of a PEt_3 ligand from platinum to boron to give $[9\text{-}H\text{-}9,10\text{-}(Et_3P)_2\text{-}7,8,9\text{-}C_2PtB_8H_9]$. This is formally a derivative of platinum (II), and the structure is distorted towards a closed octadecahedral architecture [513].

13 CATALYSIS BY METAL COMPLEXES

The use of complexes of the platinum metals as catalysts has been reviewed [514]. The uses of palladium catalysts in the synthesis of nitrogen containing heterocycles [515], and applications of $[Pd(PPh_3)_4]$ as a catalyst in pheromone syntheses have been described [516].

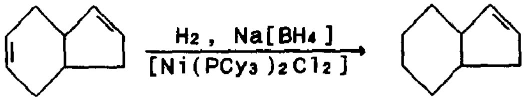


305 (Reproduced with permission from [513])
Thermal ellipsoids are constructed at the 30 % probability level except for H atoms which gave an artificial radius of 0.1 A for clarity.

13.1 Hydrogenation and hydrogenolysis

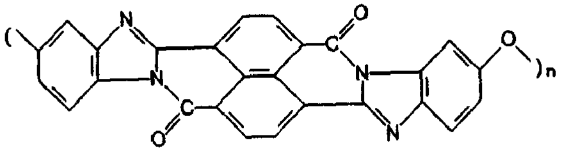
A kinetic and epr study of the catalytic activity of the system $\{2,3,5\text{-}(HO)_3\text{-}(Me_2CH)_2C_6H_2CO_2\}_2Ni/R_3Al$ for hydrogenation of cyclohexene suggested that the active species was a diamagnetic nickel(II) carboxylate salt [517]. The kinetics of the reduction of E-ethyl 3-phenylpropenoate in the presence of $[Ni(acac)_2]$ suggested that the hydrogen became coordinated to the metal prior to interaction with the substrate [518]. The reduction of citral to citronellal in the presence of $NiCl_2/KCN/PrNH_2$ has been reported in a patent [519]. The reduction of 306 could be accomplished with excellent selectivity using either $[Ni(PPh_3)_2Cl_2]/Na[BH_4]/dmf$ or $[Ni(PCy_3)_2Cl_2]/Na[BH_4]$ as the catalyst systems. $H_2[PtCl_6]/SnCl_2/Me_2CHOH$ also gave the product with excellent selectivity, and at a considerable faster rate [520].

The rate of hydrogenation of C_{6-9} alkenes over palladium sulphide was decreased by the presence of either benzene or dimethyl benzenes, which were thought the block the catalytic sites [521]. Palladium sulphide was a useful catalyst for the reduction of benzothiophene to the 2,3-dihydro compound. In order to avoid hydrogenolysis the reaction was not in general run to complete conversion [522].



306

Again this year there have been many reports of the uses of polymer supported palladium catalysts for the reduction of carbon-carbon multiple bonds. Polystyrene functionalised with NMe_2 groups was treated with $PdCl_2$ to give a catalyst for the reduction of alkenes. The rates of reaction decreased with increasing N:Pd ratios, and the catalysts were somewhat sensitive to steric hindrance. They were stable in air and could be reused without loss of activity [523]. $PdCl_2$ supported on silica, alumina, zeolites or aluminosilicate, and treated with Et_3N was a useful catalyst for the selective hydrogenation of alkynes to *cis*-alkenes [524]. Treatment of 307 with $PdCl_2$ gave a catalyst active for the reduction of alkenes and alkynes, for alkene isomerisation, and for disproportionation of 1,3-cyclohexadiene [525]. Palladium complexes of anion exchangers were studied by XPES; palladium complexes of the hydroxy forms of the anion exchangers were found to have the highest activities for hydrogenation [526].

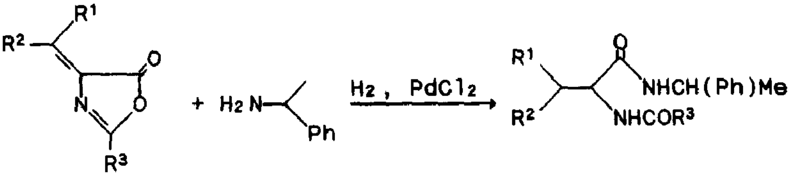


307

Complexes of palladium chloride with acrylamide/acrylic acid or acrylamide/sodium acrylate copolymers were used as catalysts for hydrogenation or reductive alkylation of nitrogen functionalities [527]. The palladium ethanoate complex of 4,4'-diamino-2,2'-bipyridyl was prepared and copolymerised with 2,4-diisocyanatotoluene to give a polyurea. Reduction with $Li[AlH_4]$ gave brown/black material, probably dispersed palladium, which was a good catalyst for alkene reduction [528].

Palladium phthalocyanine proved to be a good catalyst for the reduction of alkenes, carbon-nitrogen double bonds and aryl nitro compounds. Benzyl esters could be cleaved if the pH of the solution was maintained above 11 [529].

$PdCl_2$ may be reacted with primary amines to give a catalyst for the reduction of dienes to monoenes. Some limited evidence has been presented for the intermediacy of halo or hydroxo bridged dimeric species [530]. Reductive aminolysis of 308 in the presence of $PdCl_2$ was thought to involve hydrogenation followed by aminolysis [531]. Further attempts to reduce methyl linoleate and methyl linolenate have been reported using $[M(PR_3)_2Cl_2]/SnCl_2$ (M = Pd or Pt). Since the palladium catalyst functions well in the absence of solvent but the platinum analogue requires methanol for high activity, it was surmised that the rate controlling step may be different for the two catalysts [532,533]. A water soluble catalyst, $[Pd(QS)_2]$ (QS = sulphonated alizarin), has been used for the hydrogenation of fatty acids to cold acclimatise *Anacystis nidulans* [534].



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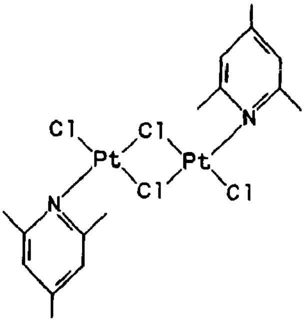
The system $PdCl_2/CH_2Cl_2$/polyethylene glycol is essentially homogeneous and catalyses the reduction of diphenylethyne to Z-1,2-diphenylethene with good selectivity [535]. Prolonged reduction gave 1,2-diphenylethane [536]. Other alkynes also gave good results [537]. Catalysts for the selective reduction of alkynes were reported to have been prepared by the dissolution of $[Pd(dba)_2]$ or a palladium(II) carboxylate in an organic solvent containing either $HC{\equiv}CCH_2OH$ or a compound which was readily hydrogenated [538]. Under an atmosphere of hydrogen, palladium(II) carboxylates reacted with PR_3 to give clusters, $[Pd_5(PPh_2)_2(PPh_3)_2]$, which were useful catalysts for the selective reduction of alkynes to *cis*-alkenes, and also for diene reduction [539]. Reaction of the cluster $[\{(PhP)_2Pd_5\}_n]$ with thioethers, RSR', gave $[(PhP)_2Pd_5(R')(SR)]$, which was hydrogenated to $[(PhP)_2Pd(H)(SR)]$. The active species, $[\{(PhP)_2Pd_5\}_n]$, was regenerated in the presence of a substrate, thus reversing the poisoning [540].

$H_2[PtCl_6]$ was used as a catalyst for the hydrogenation of an acrylamine/sodium acrylate copolymer, in order to remove free monomer [541]. Phosphinated silica was used as a support for $H_2[PtCl_6]$, to be used as a catalyst for the reduction of either benzene or chlorobenzene to cyclohexane. Toluene was reduced initially to methylcyclohexane, and this was then slowly hydrogenolysed to ring opened products. The catalyst was unchanged in air after one year, but there was no real effort made to test for the presence of metal particles [542]. 309 was an extremely active catalyst for the reduction or hydrosilylation of alkenes and enones under mild conditions [543].



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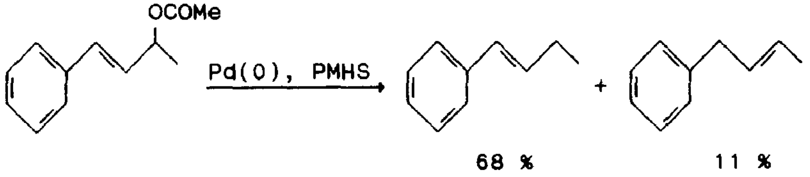
Palladium complexes of silica supported poly-3-cyanopropylsiloxane or poly-3-aminopropylsiloxane catalysed the reduction of aldehydes and ketones at room temperature and 1 atm of hydrogen. The rates of the reactions depended on the temperature and the N:Pd ratio, and the catalysts were stable and reusable. Dialkyl ketones were poor substrates [544,545]. A palladium chloride complex of poly 4-ethenylpyridine gave better rates of reaction for reductive amination of aldehydes with nitrobenzene than did the related solution species [546].

Palladium complexes of silica supported poly(ethenylpyrrolidone) were shown to be catalysts for the reduction of nitrobenzene to aniline, under mild conditions. The catalyst was rather stable and reusable. XPES was used to demonstrate that oxygen and nitrogen were the ligating atoms at palladium [547]. A palladium complex of silica supported 3-(3-$Ph_2PC_6H_4$)propylsiloxane reacted similarly [548].

In the hydrogenolysis of allyl derivatives in the presence of palladium(0) catalysts it has been shown that the site of the double bond in the product may be controlled by the nature of the hydride source. The use of $[NH_4][HCOO]$ resulted in the formation of 1-alkenes, whereas $Li[BEt_3H]$ and $\{(CH_3)_2CHCH_2\}_2AlH$ yielded 2-alkenes, with high maintenance of double bond stereochemistry [549]. Using polymethylhydrosiloxane as the hydride donor resulted in clean hydrogenolysis of 310, mainly with retention of the double bond position. The use of Bu_3SnH led to the formation only of the elimination product, 4-phenyl-1,3-butadiene [550]. Hydrogenolysis of 311 was accomplished using a dihydropyridine as the hydride source, in the presence of

$[Pd(PPh_3)_4]/Li[ClO_4]$. A mixture of alkenes was formed in rather low yields; rhodium complexes were better catalysts [551].



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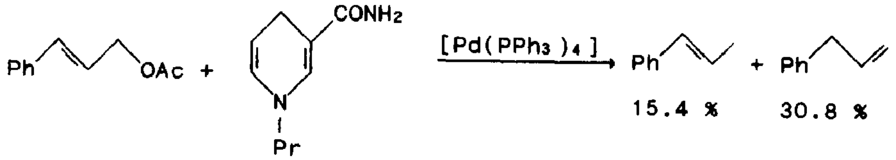


311

Hydrogenolysis of alkenyl sulphones occurred on treatment with BuMgCl in the presence of $NiCl_2/L$, $[Pd(acac)_2]$ or $[Pd(acac)_2]/PBu_3$. Very little coupling was noted [552]. Aryltrimethylsilanes could be protodesilylated in a reaction catalysed by $Li_2[PdCl_4]$ [553].

There has been a quantum chemical study of methane activation by Pt(II) complexes bearing Cl, H_2O or OH ligands, using the CNDO MO method. It was deeduced that the most probably reaction path involves simultaneous coordination of the CH_4 to the platinum centre and the oxygen atom of the ligand [554].

The activity of the species $[Pt(H_2O)_nCl_{4-n}]^{x-}$ (n = 1,2,3 or 4) for H/D exchange in alkanes was directly related to the distortion energy of the complex [555]. For the complexes with n = 0 and 1, the total coordination energy of coordinated alkanes was calculated. It was deduced that the rate controlling step in the reaction was reductive elimination from a binuclear complex [556]. Oxidation of methane by molecular oxygen in the presence of Pt(II), Pt(IV) and HPA-6 was studied. The key step was reaction of CH_4 with platinum(II) to give {MePt} and H^+ [557]. The oxidative dehydrogenation of saturated hydrocarbons using $Pd(II)/H_2[SO_4]$ also involved a C-H cleavage in the rate-determining step, but this time *via* a cyclic transition state [558]. $K_2[PtCl_4]$ was found to be the best catalyst for H/D exchange in most heterocycles [559], but $[Pt(en)_2]Cl_2$ was particularly useful for sulphur containing heterocycles [560].

The uses of palladium complexes as catalysts for selective oxidation has been reviewed, with particular reference to the oxidation of alkenes and dienes [561].

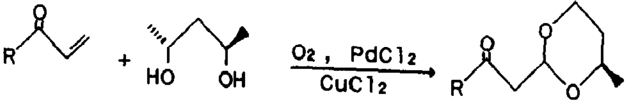
There have been a number of reports detailing palladium catalysed oxidation of ethene. Ethane-1,2-diol monoethanoate was the main product in the presence of $PdCl_2/LiCl/Li[NO_3]/MeCOOH/(MeCO)_2O$ [562]. The reaction in the presence of $PdCl_2/Fe[NO_3]_3/MeCOOH$ gave the same product, and a mathematical model was constructed for the reaction in order to optimise the conditions [563]. With the catalyst system $Pd(II)/HNO_3/MeCOOH$ in dioxan, kinetic data were interpreted in terms of the formation of a $\{Pd(NO_2)\}$ species [564,565]. The reaction of ethene with ethanoic acid in the presence of $Pd(OCOMe)_2$ and $Li[XO_3]$ (X = Cl, Br or I) was first order with respect to palladium and less than first order with respect to $[XO_3]^-$. The data were interpreted in terms of a model in which a palladium alkene complex was initially formed and then interacted with the oxidant [566].

When ethene was oxidised by $MeONO/O_2/NO$ in the presence of $PdCl_2/FeCl_3$ supported on silica, the major product was $MeCH(OMe)_2$ [567]. The clusters $K[Pd_8(phen)(OCOMe)_3Cl_2]$ and $[Pd_8(O_2)_3(phen)(OCOMe)_3]$ were reported to catalyse the oxidation of ethene to ethenyl ethanoate [568].

Branched alkenes have been isolated from mixtures of linear and branched alkenes by the selective oxidation of the linear alkenes in the presence of $PdCl_2/CuCl_2/R_2NH$ [569]. Various 1-alkenes have been oxidised to methyl ketones in the presence of palladium catalysts. Propene was oxidised to propanone using $PdCl_2/CuCl_2/PhMe_2N$ as the catalyst system, with 35 % conversion and 99.4 % selectivity [570]. Palladium cluster complexes were also used as catalysts for oxidation of both propene and toluene [571]. In the presence of $PdCl_2/CuCl_2/PhH/[R_4N]X$ as the catalyst system, 1-alkenes were oxidised to methyl ketones. The course of the reaction depended on the nature of the quaternary ammonium salt, with large lipophilic cations giving the best results, although the reaction was not thought to take place in a micellar environment [572]. The presence of a quaternary ammonium salt also enhanced yields in the oxidation of ω-alkenyl esters such as $CH_2{=}CH(CH_2)_8COOMe$, which gave $CH_3CO(CH_2)_8COOMe$ [573]. The kinetics of 1-butene oxidation were studied; selectivity towards 2-butanone decreased at temperatures above 130 °C [574].

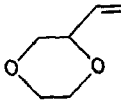
The oxidation of cyclohexene to cyclohexanone was reported to occur with low conversion and selectivity in the presence of $PdCl_2/FeCl_3$ [575,576].

The Wacker oxidation of 2-propenol has been studied in detail; deuterium labelling studies implied that the oxidation followed the same route as for other alkenes [577]. Oxidation of RCOCH=CH$_2$ in the presence of 1,3-diols gave derivatives of aldehydes rather than ketones (for example reaction (28)) [578].



(28)

Mono- and diethanoates were produced by the oxidation of 1-alkenes in the presence of Pd(OCOMe)$_2$/MeCOOH/LiCl/Li[NO$_3$], and rate constants for the reactions were determined [579]. In the presence of ethane-1,2-diol, oxidation of butadiene under Wacker condtitions gave 312 with good selectivity. Various dichlorobutenes were detected in the reaction mixture, and may be intermediates [580].



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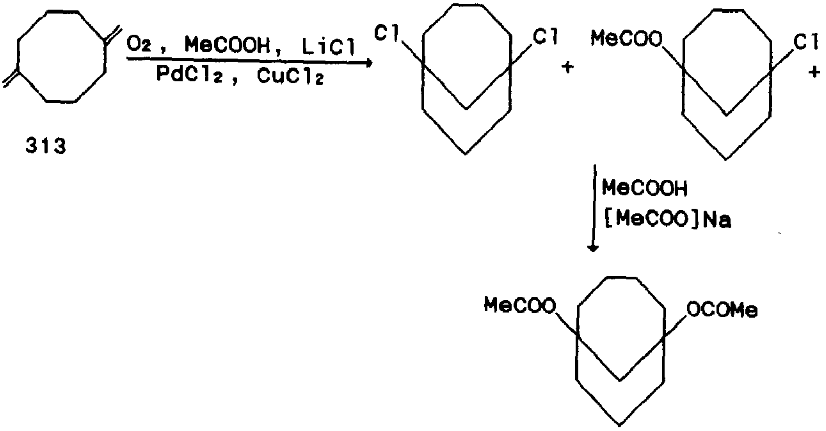
Oxidation of 1,5-dimethylenecyclooctane, 313, in the presence of PdCl$_2$/CuCl$_2$/LiCl/MeCOOH gave a mixture of bicyclic species, with selectivities which varied according to the reaction conditions. The intermediates 314-316 were proposed [581].



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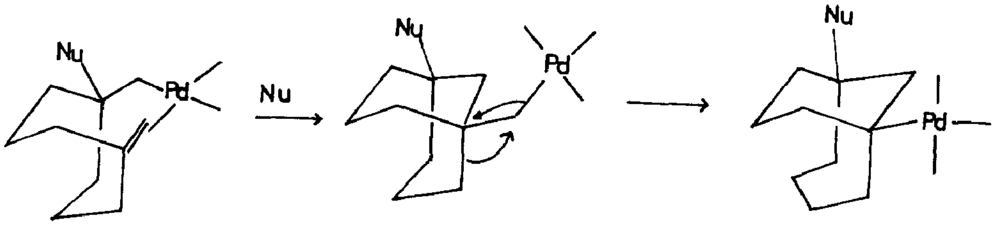
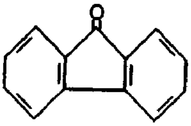


314 315 316

The oxidation of toluene to $PhCH_2OCOMe$ was accomplished in the presence of $Pd(OCOMe)_2/Na[OCOMe]/Cu(OCOMe)_2$/active carbon, and optimum conditions were established for the process [582]. For the reaction using $Pd(OCOMe)_2/Sn(OCOMe)_2/K[OCOMe]$, three kinetic stages could be distinguished. It was suggested that palladium(0) clusters were formed and were the active catalytic species, but little evidence was presented [583]. Fluorene was oxidised to 317 and 318 by molecular oxygen in the presence of nickel or palladium phthalocyanine complexes [584].



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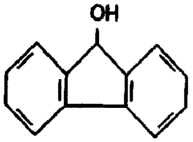


318

The oxidative coupling of hydrocarbons catalysed by palladium(II) has been reviewed [585]. In the oxidative oligomerisation of benzene in solutions containing $PdSO_4$ and H_2SO_4, various terphenyl isomers were formed by a process which involved the formation of a σ-aryl palladium complex as the rate controlling step [586]. Routes involving palladium(I) and palladium(II) could be distinguished in the oxidative dimerisation of toluene under these conditions [587]. When thiophene was reacted in the presence of palladium(II) both hydroxylated and coupled products could be isolated, probably both derived from the same σ-thienyl palladium intermediate [588].

Secondary alcohols could be oxidised to ketones by bromoarenes in the presence of palladium(0) or palladium(II) complexes. The steps proposed are shown in reactions (29)-(32) [589].

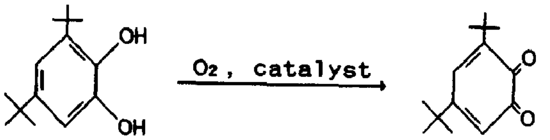
$$[PdL_n] + ArBr \longrightarrow [ArPdL_2Br] \tag{29}$$

$$[ArPdL_2Br] + RR'CHOH \longrightarrow [RR'CHOPd(Ar)L_2] + HBr \tag{30}$$

$$[RR'CHOPd(Ar)L_2] \longrightarrow RR'C{=}O + [HPdArL_2] \tag{31}$$

$$[HPdArL_2] \longrightarrow ArH + [PdL_n] \tag{32}$$

Catalysts for the oxidation of **319** included $[PdL_2Cl_2].H_2O$, $[PdCuL_2Cl_2].H_2O$ and $[PdNiL_2Cl_2].H_2O$ in which L = methionine [590]. When $PdCl_2$ was used as the catalyst for the oxidation of **320**, both conversions and yields were low. Iron and ruthenium salts were more suitable catalysts [591].



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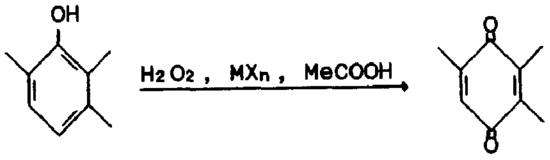
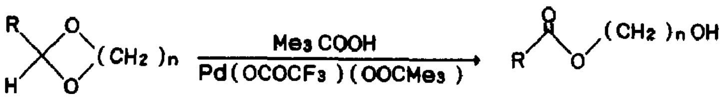


320

There has been a kinetic study of the oxidation of CO to CO_2 catalysed by Pd(II)/Cu(I)/Cu(II). Palladium(I) and palladium(II) carbonyl complexes were proposed as intermediates [592]. Thiocyanates, RNCS, were oxidised to cyanates, RNCO, in dioxan in the presence of $PdCl_2$ [593].

The acetal, **321**, was oxidatively cleaved by Me_3COOH in the presence of $Pd(OCOCF_3)(OOCMe_3)$. $PdCl_2$ and $[Pd(MeCN)_2]$ were also catalysts for the process, but were less effective [594].



313

13.3 Reactions of carbon monoxide and carbon dioxide

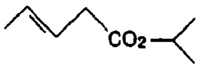
Reduction of carbon monoxide by molecular hydrogen occurred in the presence of $[Bu_4N][Rh_{12}(CO)_{30}]$ and $[Bu_4N][Pt_{12}(CO)_{24}]$ (in the ratio 1:2) in a solution containing *N*-methylpyrrolidine and $(MeOCH_2CH_2OCH_2CH_2)_2O$, to give ethane-1,2-diol, with 75 % selectivity [595]. Among catalysts for the water gas shift reaction were $[PtCl_4]^{2-}/SnCl_4/SnCl_2$, *trans*-$[Pt(SnCl_3)_2Cl_2]^{2-}$, $\{PtCl_2 + 4PbCl_2\}$ and $[Pt(C_2H_4)Cl_3]^-$ [596].

Research into the hydroformylation process continues. Patents have reported the use of $[Pt(PPh_3)_2\{HP(=O)Ph_2\}]$ [597], $[Pt(acac)_2]/SnCl_2/PPh_3$ [598], $[(DIOP)PtCl_2]/Ph_3SnOCOMe$ [599] and $[Pt(PhCN)_2Cl_2]/SnCl_2/dppf$ [600] as suitable catalyst systems, with varying selectivity. The system $[Pt(PPh_3)_2Cl_2]/SnCl_2$ catalysed only hydroformylation even at 100 °C in ethanol with $p(CO) = p(H_2) = 65$ atm. The complex recovered from catalytic solutions was $[HPt(CO)(PPh_3)_2][SnCl_3]$ [601]. The systems *cis*-$[PtL(PR_3)Cl_2]/SnCl_2$ (L = CO, R = alkyl) proved to better catalysts for alkene hydroformylation than *cis*-$[PtL_2Cl_2]$. When L = R_2S or $ArNH_2$, and R = Ar, the species were good catalysts for hydrogenation [602].

$[\{(-)\text{-DBPIOP}\}PtCl_2]$ was last year reported to be a superb catalyst for the asymmetric hydroformylation of ethenyl benzene. This year the spectacular results have had to undergo some modification, with the reported optical yield reduced from 95 % to 73 %. The result remains impressive, when compared to others in this area [603]. A polymer supported version of BPPM has resulted in asymmmetric hydroformylation in up to 70 % optical yield, but regioselectivity was in this case very limited [604].

A number of hydrocarboxylation reactions have been reported. Using a catalyst system consisting of $NiI_2/Mo(CO)_6/PPh_3/EtI$, ethene was converted to EtCOOH [605]. The presence of ethyl propanoate was reported to enhance yields [606]. In the presence of $PdCl_2/FeCl_3/HgCl_2/LiCl/HCl$, ethyne was converted to *E*-ClCH=CHCOOH, *via* chloromercury and chloropalladium intermediates [607]. Branched carboxylic acids were prepared by the reaction of 1-alkenes with CO/H_2O in the presence of $PdCl_2/CuCl_2/O_2/HCl$ [608]. Selectivities were excellent, and substrates included α,ω-dialkenes, and cyclic alkenes [609]. Both *cis*- and *trans*-2-alkenes also gave species of the type RCH(Me)COOMe, and 1-alkynes gave mainly Z-RC(COOR')=CHCOOR' [610]. By contrast, selectivity for linear products was reported to be high in the presence of $[Pd(PPh_3)_2Cl_2]/SnCl_2$ [611]. When ethene was used as the substrate and the catalyst system was $[Pd(acac)_2]/Cu(OCH_2CH_2OMe)Cl$, $MeOCH_2CH_2O_2CCH_2CH_2CO_2CH_2CH_2OMe$ was the major product [612]. Hydrocarboxylations of $R_FCH=CH_2$ (R_F = perfluoroalkyl) were studied in the presence of a range of palladium catalysts; both [Pd(dppb)Cl_2] and [Pd(dppf)Cl_2] gave linear products with better that 99 % selectivity [613].

Hydrocarboxylation of butadiene proceeded with isomerisation to give 322 with 93.2 % selectivity in the presence of $PdCl_2/Me_2CHOH$ [614]. When the catalyst system was [{Pd(η^3-C_3H_5)Cl}$_2$]/[Bu_4P]Cl, and the added alcohol was ethanol, three isomers, 323, 324, and 325 were isolated [615]. Carbonylation of the 1,4-diene, 326, was accomplished in low yield in the presence of [Ni(CO)$_4$] [616]. Hydrocarboxylation of the diyne 327 in the presence of a palladium(II) complex of thiourea gave a mixture of 328 and 329 [617].



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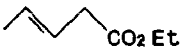

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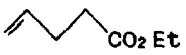

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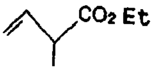

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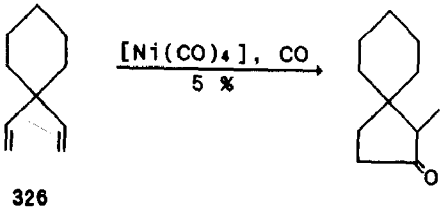

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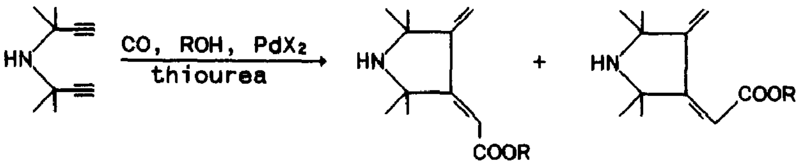


327 328 329

Carbonylation of iodobenzene in the presence of [Pd(PPh_3)$_2$$Cl_2$] in a solvent mixture of py, $(Me_2N)_3PO$ and PhMe gave $PhCONMe_2$ [618]. The kinetics of the reactions of other aryl iodides in methanol to give methyl benzoate derivatives were investigated [619]. When the carbonylation of aryl halides was carried out in the presence of [Pd(PPh_3)$_4$]/Zn/Cu/thf/RX the major product was ArCOR. 2-Substituted aryl halides were poor substrates [620].

Carbonylation of allylic halides in the presence of $[Pd(PPh_3)_4]/Bu_3SnH$ resulted in the formation of the aldehydes in good yield [621]. $RC(Me)=CHCH_2X$ reacted similarly using $CO/H_2/[Pd(PPh_3)_2Br_2]$, but under these conditions allyl bromide was not a suitable substrate and polymerised easily [622].

Carbonylation of methanol in the presence of $PtCl_2/Co(OCOMe)_2/LiI/H_2$ at 195 °C gave ethanal, with modest conversion [623]. Ethanol reacted with $CO/O_2/PdCl_2/CuCl_2/Et_3N/PhNO_2$ to give EtO_2CCO_2Et with 75 % selectivity. In the absence of the nitrobenzene the selectivity was significantly lower [624]. Benzoquinone was also used successfully as an oxidant for this process [625]. Methanol was oxidatively carbonylated to MeOCOOMe by a mixture of CO and air in the presence of a palladium amine complex and 3 Å molecular sieves [626].

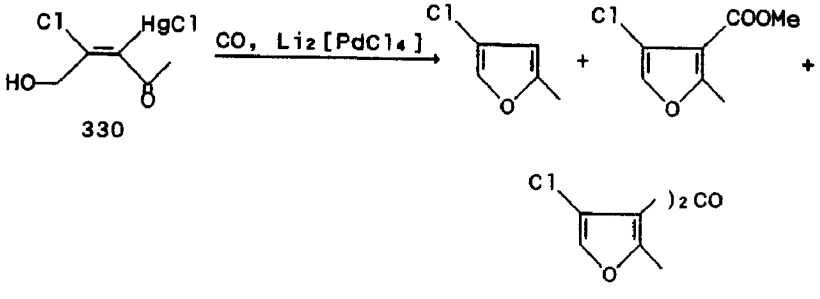
The oxidative carbonylation of ketene in the presence of the catalyst system $[Pd(PPh_3)_2Cl_2]/SnCl_4/Et_3N/Me(CH_2)_4ONO$ gave $CH_2\{CO_2(CH_2)_4Me\}_2$ as the main product [627]. Carbonylation of methyl methanoate to ethanoic acid in excellent selectivity was achieved using $[Ni(PPh_3)_2(CO)_2]/[Mo(CO)_6]/MeI/PPh_3$ as the catalyst system [628]. In the presence of $[Ni(CO)_4]/MeI/NaI/(MeCO)_2O$/15-crown-5, methyl ethanoate was carbonylated to give ethanoic anhydride [629], but when $PdCl_2/RhCl_3/PPh_3/MeI/MeCOOH/H_2$ was used, the sole product was $CH_3CH(OCOMe)_2$ [630]. Oxidative carbonylation of thiophenes to give thiophene-2-carboxylic acids was achieved in the presence of $Pd(OCOMe)_2/Na_2[S_2O_8]$ [631].

Carbonylation of aniline to give PhNHCOOMe was accomplished with good yield and very selectively in the presence of either $CO/O_2/PdCl_2/FeCl_3$/MeOH/magnesium silicate or $CO/O_2/PdCl_2/FeCl_3$/MeOH/molecular sieve [632,633]. Double carbonylation of secondary amines to give $R_2NCOCONR_2$ was reported to occur in the presence of $[NiL_2Br_2]$. Intermediates such as $[L_nNi(CONHR)_2]$ were proposed. Oxalate derivatives could be similarly prepared from alkoxides [634].

Carbonylation of 2,4-dinitrotoluene to give the bis(isocyanate) was reported to be catalysed by $[Pd(quinoline)_2Cl_2]$. Addition of molecular chlorine as a cocatalyst gave increased yields [635]. Modest yields of ArNHCOOR were obtained from $ArNO_2/CO/ROH$ in the presence of $PdCl_2$, deposited on an NaX zeolite, and promoted by $FeCl_3$ and pyridine [636]. Similar products were obtained using $[Pt(PPh_3)_2Cl_2]/SnCl_4$ as the catalyst system. The reaction was proposed to proceed *via* the amine and the isocyanate [637]. In the presence of CO/H_2O and a tertiary amine, $ArNH_2$ was the main product [638]. A mixture of $PhNH_2$ and $PhNO_2$ was carbonylated in the presence of $PdCl_2/FeCl_3/MeOH/H_2$, to give PhNHCOOMe with 94 % selectivity [639].

Carboxylation of benzene was reported to occur using $CO/H_2O/Pd(OCOMe)_2$; yields are thus far rather low, but this reaction holds considerable promise

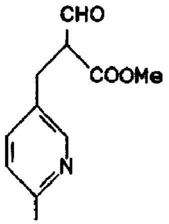
[640]. Reaction of 330 with CO in the presence of $Li_2[PdCl_4]$ gave a mixture of furans. The reaction proceeded *via* transmetallation followed by carbonylation [641].



330

The carbonylation of E-ArCH=CHBr has been studied in detail under a variety of conditions. In a two-phase system ($PhH/NaOH_{aq}$) with a phase transfer catalyst, $[(C_8H_{13})_4N][HSO_4]$, Ar-C≡C-C≡C-Ar was the main product in the presence of $[Pd(dppe)_2]$. $ArCH=CBr_2$ gave the same result, but if the solvent was changed to ROH the diacid $ArCH=C(COOH)_2$ was formed. It seems likely that the reactions involve radical intermediates [642,643].

The reaction of 2-methyl-5-ethenylpyridine with CO and HCOOMe in the presence of $[Pd(dppb)Cl_2]$ was described in a patent to give 331. The mechanism of the reaction has not been delineated [644]. The palladium catalysed carbonylation/alkylation of norbornene has been further studied (reaction (33)) [645].



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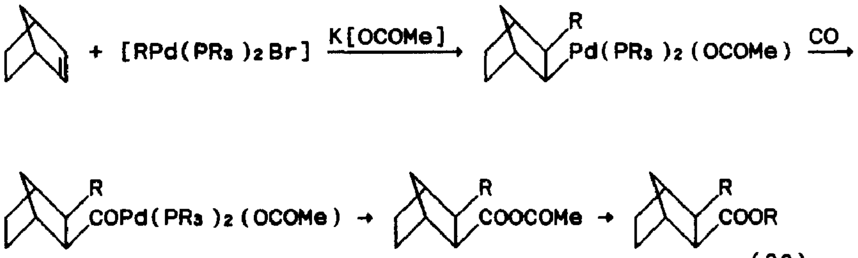
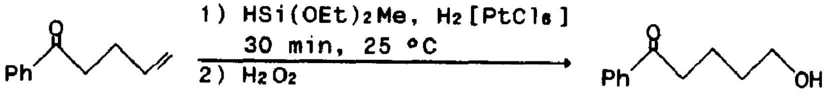


(33)

A silica supported poly(3-mercaptopropylsiloxane) complex of platinum has been reported to be a catalyst for the hydrosilylation of 1-hexene by $(EtO)_3SiH$. It could be reused many times [646]. Good yields of $Ph(CH_2)_3SiR_3$ were obtained from $PhCH_2CH=CH_2$ and R_3SiH ($R_3 = Me_{3-n}Cl_n$, $n = 1$, 2 or 3) in the presence of $H_2[PtCl_6]$ [647]. Hydrosilylation of 332 using $HSi(OEt)_2Me$ and $H_2[PtCl_6]$, followed by treatment with H_2O_2 gave 333 [648].



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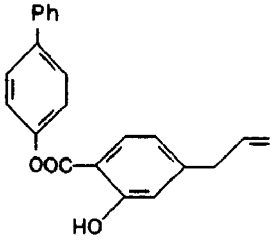
333

Alkenes substituted with polar functional groups have proved popular substrates this year. Ethenyl ethanoate reacted with $HSiCl_3$ in the presence of $H_2[PtCl_6]/CH_2=CHCH_2OH/CH_2=CHCH_2OCH_2CO_2CH_2CH=CH_2$ selectively to give $CH_3COOCH_2CH_2SiCl_3$ in 55 % yield [649]. The ethenyl silane $CH_2=CHSi(OR)_3$ reacted with $HSi(OR')_3$ using either $H_2[PtCl_6]$ or $[Ni(acac)_2]$ as the catalyst to give mainly $CH_3CH\{Si(OR)_3\}_2$; exchange of the alkoxide moieties was faster than hydrosilylation [650].

There have been three reports of catalysts for the hydrosilylation of $CH_2=CHCH_2NH_2$ to $R_3Si(CH_2)_3NH_2$, namely $[\{Pt(4\text{-ethenylcyclohexene})Cl_2\}_2]$ [651], $H_2[PtCl_6]/R_3N$ [652] and $H_2[PtCl_6]/(CH_3)_2CHOH/K[$*nido*-7,8-dicarbaundecaborate]. In this last example some kinetic data were reported [653]. Reaction of $CH_2=CHCH_2OCOMe$ with $HSiCl_3$ in the presence of $H_2[PtCl_6]$ and diethenyltetramethyldisiloxane gave $MeCOO(CH_2)_3SiCl_3$ in 70 % yield [654]. A linear product was also obtained from the reaction of $Me_3SiOCH_2CH=CH_2$ and $HSi(OEt)_3$ in the presence of $H_2[PtCl_6]$ [655]. Modest yields of linear products were obtained under similar conditions for $CH_2=CHCH_2Cl$ and $HSiCl_3$ [656].

Patents have reported the uses of platinum complexes as catalysts in siloxane chemistry. The curing of ethenyl terminated polysiloxanes using $H_2[PtCl_6]$ was noted [657], and ethenyl terminated dimethylsiloxane gums were prepared using a cyclohexene platinum complex as catalyst [658]. From 334, cholesteryl-4-propenyl-2-oxybenzoate and pentamethylcyclopentasiloxane in the presence of dicyclopentadienyl platinum dichloride, German workers were able to synthesise mesogenic cyclosiloxanes for electrooptical display devices [659].



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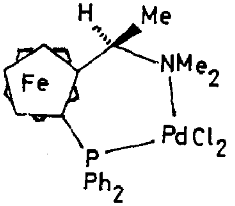
The reaction of cyclopentadiene with $HSiMeCl_2$ in the presence of $[Pd(R,S\text{-}PPFA)Cl_2]$, 335, gave 336 in 22-25 % enantiomeric excess. Less good results were obtained in the reactions of 1,3-cyclohexadiene [660].



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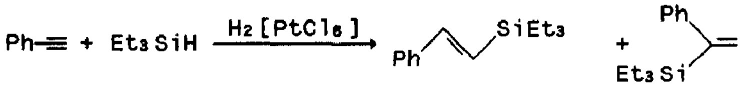
336

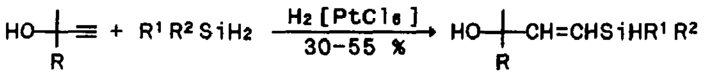
There have been further reports of the hydrosilylation of 1-alkynes in the presence of $H_2[PtCl_6]$ (reactions (34) and (35)) [661,662]. With RC≡CH and $HSiEt_3$, and using $[Pd_2(PPh_3)_4Cl_2][B_{10}Cl_{10}]$ as the catalyst, $RC(SiEt_3)=CH_2$ and $E\text{-}RCH=CHSiEt_3$ were obtained in the ration 78:22 for R = Bu and 44:56 for R = Ph. For R = Bu, and using $[Pt(PPh_3)_3Cl][B_{10}Cl_{10}]$ as the catalyst, only the linear product was obtained, in considerable contrast to the reactions in the presence of $H_2[PtCl_6]$ [663]. Reaction of RC≡CSiMe$_3$ with $HSiCl_3$ in the presence of $H_2[PtCl_6]$ gave exclusively 337, which was used in a synthesis of α-silylketones [664].



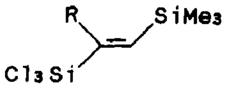
(34)

79 % 21 %

Hydrosilylation of propanone with $HSiMe(OMe)_2$ gave $CH_2=C(Me)OSiMe(OMe)_2$. The catalysts employed included $Ni(SPh)_2$, $Ni(SC_{12}H_{25})_2$ and $NiCl_2/HSiEt_3/PhSH$ [665].



$$HO\text{–}C(R)\text{–}C\equiv CH + R^1R^2SiH_2 \xrightarrow[30-55\ \%]{H_2[PtCl_6]} HO\text{–}C(R)\text{–}CH=CHSiHR^1R^2 \qquad (35)$$



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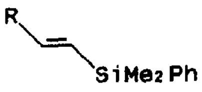
Silylmetallation of $RC\equiv CH$ with $PhMe_2SiLi$ occurred in the presence of a range of platinum and palladium complexes and MX ($MX = MeMgI$, Et_2AlCl or $ZnBr_2$) to give mixtures of 338 and 339. Reasonable selectivity for either product could be achieved. Using *cis*-$[Pt(PBu_3)_2Cl_2]$ as the catalyst and MeMgI as the addend, 338 was favoured by >99:1, but in the presence of $[Pd\{P(2\text{-}MeC_6H_4)_3\}_2Cl_2]$ and with Et_2AlCl as the addend, 339 was favoured by a factor of 85:15 [666].



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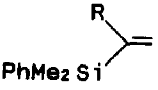

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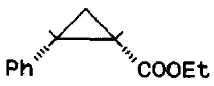
13.5 Other Additions to Carbon-Carbon Multiple Bonds

The addition of HCl to ethyne in the presence of $PdCl_2/FeCl_3$ gave chloroethene, but also yielded 1-chlorobutadiene and a range of products of oxidative oligomerisation. Kinetic data indicated a mechanism involving $ClPd(CH=CH)_nCl$ [667]. When the catalyst system was $PdCl_2/FeCl_3/HgCl_2/LiCl$, the major product was 1-chlorobutadiene. The mechanism proposed involved both chloromercury and chloropalladium alkene derivatives [668].

Hydrocyanation of alkynes has been reported to be stereospecifically *cis* in the presence of $[Ni\{P(OPh)_3\}_4]$. Regioselectivity towards the branched products, $RC(CN)=CH_2$, was about 90 % for 1-alkynes [669]. An equilibrium mixture of 3-pentenenitrile (98 %) and 4-pentenenitile (2 %) was hydrocyanated in the presence of $[Ni\{P(OAr)_3\}_4]/PPh_3$ to give $NC(CH_2)_4CN$ as the major product [670].

Cyclopropanation of ethenylbenzene by $N_2CHCOOEt$ was catalysed by $Pd(OCOMe)_2$, to give 340 and 341 in the ratio of 2:1 [671]. Alkenes bearing electron withdrawing groups (COOMe, CN, COMe or CHO) reacted with CH_2X_2/Zn in the presence of a nickel(0) catalyst and a Lewis acid to give cyclopropanes. The mechanism proposed is shown in Scheme 9 [672]. A similar mechanism was proposed for the cyclopropanation reaction of Z-dimethyl butenedioate in the presence of [Ni(Z-dimethyl butenedioate)$_2$(MeCN)] [673].



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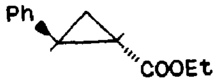

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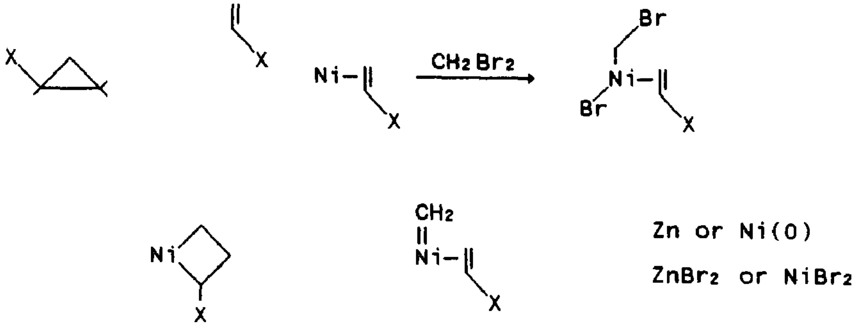
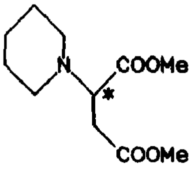


Scheme 9 Mechanism of cyclopropanation of electron poor alkenes in the presence of nickel(0) complexes. The other ligands are omitted for clarity [672].

Addition of an alcohol to 1,5,9-cyclododecatriene under pressure and in the presence of $PdCl_2/CuCl_2$, followed by hydrogenation in the presence of Raney nickel was reported to yield an alkoxycyclododecane [674]. Piperidine was added to dimethyl butenedioates in the presence of [Ni(acac)$_2$]/$PR^1R^2R^3/Et_3Al$ (R^1-R^3 = Ph or menthyl) to give chiral 342 but the optical yields were not stated [675]. Cyclisation of ω-aminoalkenes in the presence of $PdCl_2/CuCl_2$ was used in the synthesis of heterocycles (for example, reaction (36)) [676].



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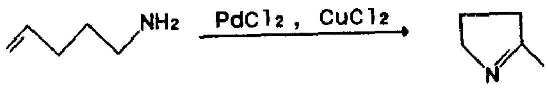
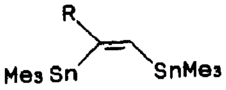


(36)

cis-Addition of Me_6Sn_2 to 1-alkynes, RC≡CH, in the presence of $[Pd(PPh_3)_4]$ gave initially **343**, but this was readily transformed to the E-isomer at 70 °C [677].

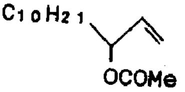


343

13.6 *Isomerisation*

The catalyst system $[Ni(PPh_3)_2(CO)_2]/Et_3Al_2Cl_3/Al_2O_3$ displayed high activity for the isomerisation of 1-alkenes to 2-alkenes over a narrow temperature range [678].

Conversion of **344** to **345** was achieved in the presence of $[Pd(4\text{-}MeC_6H_4SOMe\text{-}S)_2Cl_2]$. Whilst the reaction proceeded well in the presence of complexes of optically active sulphoxides, there was little kinetic resolution. The sulphoxide complexes also catalysed the cyclotrimerisation of diphenylethyne [679]. The allylic transposition of **346** gave a mixture of *cis*- and *trans*-isomers; the products were used in a synthesis of dl-sirenin [680].



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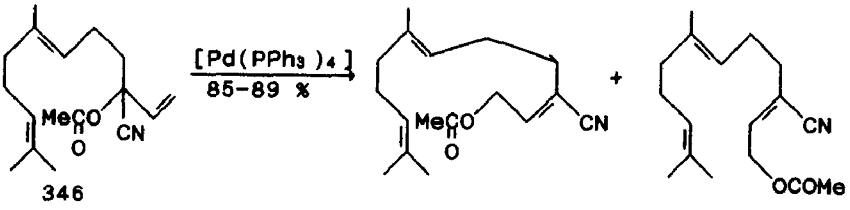

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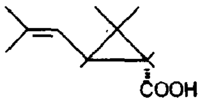
0 °C	7	:	3
30 °C	4	:	6

The *trans*-cyclopropane carboxylic acid, **347**, was prepared by the isomerisation of either the *cis*-isomer or a *cis/trans*-mixture in the presence of [Pd(PhCN)$_2$Cl$_2$] [681]. The carboxylate esters reacted similarly [682].



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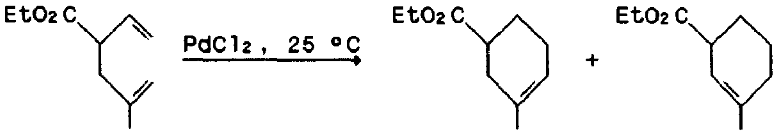
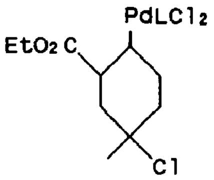
A number of pericyclic rearrangements have been reported to be catalysed by palladium complexes. The cyclisation of **348** gave a mixture of **349** and **350** in the presence of PdCl$_2$. The proposed intermediate was **351**. Without the electron withdrawing group clean Cope rearrangement occurred, but the palladium complex of the Cope product is rather unstable in this case [683]. Substrates bearing additional methyl groups, however, underwent the Cope rearrangement successfully [684].



348 **349** **350**



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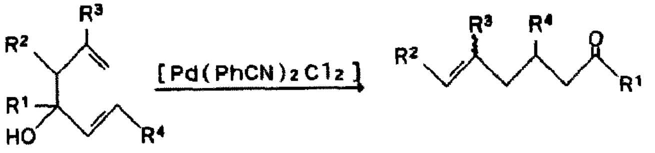
The Cope rearrangement of **352** gave the unsaturated ketone **353** in the presence of [Pd(PhCN)$_2$Cl$_2$]; stereoselection was generally good [685]. Further examples of this process were described in a patent [686]. The hetero Claisen rearrangement of **354** was catalysed by [Pd(PhCN)$_2$Cl$_2$]. The ratio between the products **355** and **356** depended on the substituents (**355**:**356** = 88:12 for R^1 = H or Me and R^2, R^3 = H; **355**:**356** = 30:70 for R^1 = H or Ph, R^2 = Me, R^3 = H) [687].



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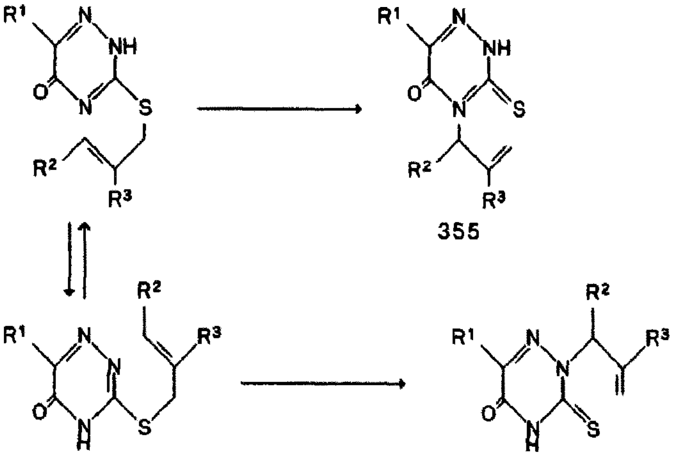
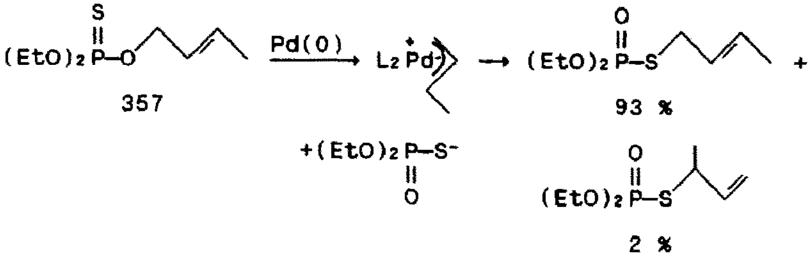


354 355 356

Reaction of 357 with palladium(0) gave a mixture of products, *via* a η^3-butenyl palladium complex [688].



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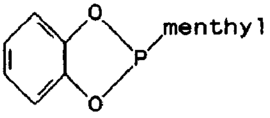
The complexes $[Pd(nbd)Cl_2]$ and $[Pd(PhCN)_2Cl_2]$ were used to catalyse the isomerisation of quadricyclane to norbornadiene. Various mechanisms were considered, and a procees involving radicals was favoured [689]. The conversion of diethenylcyclobutane to 4-ethenylcyclohexene was catalysed by nickel complexes of 358. The asymmetric induction was identical to that observed in butadiene dimerisation, since both reactions proceed *via* 359

[690]. Reaction of 360 with [{Pd(η^3-C_3H_5)Cl}$_2$] gave 361. The reaction mechanism suggested involved oxidative addition to give 362 followed by a 1,3-shift [691].



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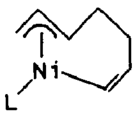

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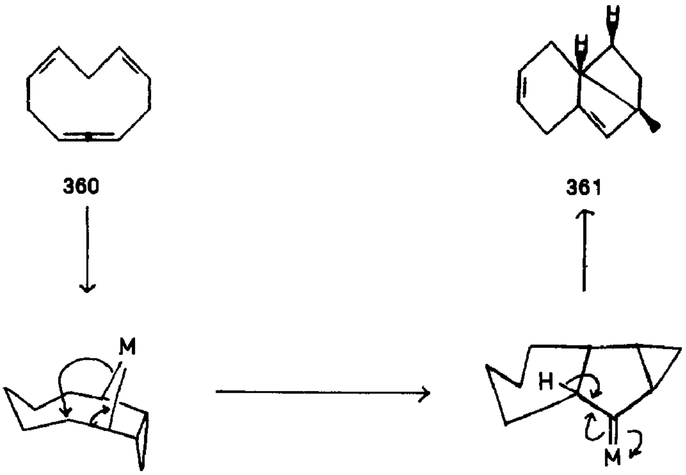

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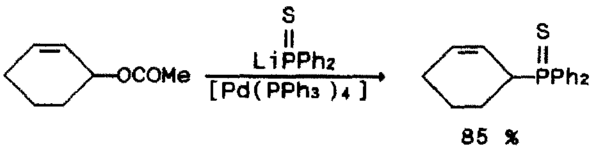
13.7 Substitution of Allyl Derivatives

There have been several reviews of transformations *via* palladium allyl complexes [692-694].

There have been many more examples of allylic substitution of allyl ethanaotes by nucleophiles in the presence of palladium(0) complexes. The cyclohexenyl derivative, 363, was substituted by either Li[PPh_2] or Li[P(=S)Ph_2]. The yields were excellent with the phosphine sulphide, but were poor with Li[PPh_2] [695]. There have been several reports of the reactions of enolates with allylic ethanoates (reactions (37)-(40)) [696-699].

A range of allyl derivatives (X = OH, OMe, OEt, SH, SMe or indole), 364, reacted with Grignard reagents in the presence of [Ni(PPh_3)$_2$$Cl_2$] [700]. In the reaction of zinc metal and CF_3I with $PhCH{=}CHCH_2Br$ in the presence of Pd(OCOMe)$_2$, to give $PhCH(CF_3)CH{=}CH_2$, the likely intermediate is CF_3ZnI [701].

Allyl ethers and allyl ethanoates reacted with $PhSO_2H$ in the presence of $[PdL_n]$, prepared *in situ* from $[Pd(acac)_2]/PPh_3/Et_3Al$ [702]. Grignard reagents, however, successfully displaced $PhSO_2$ groups from $PhSO_2CH_2CH=CH_2$, in the presence of $PdCl_2$ or $[Pd(acac)_2]$, but the reactions were low yielding [703].



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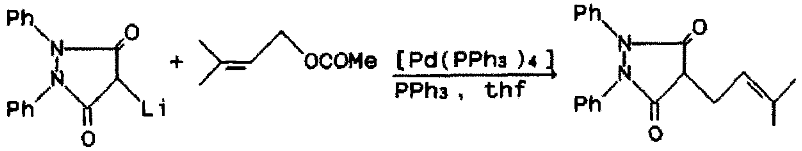

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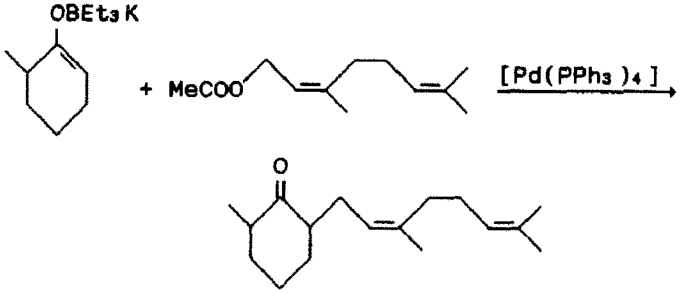

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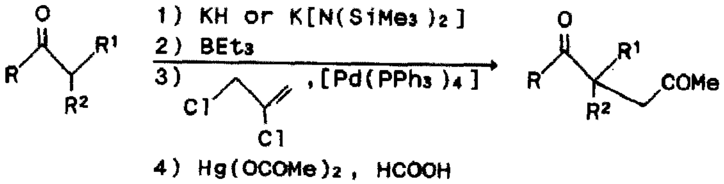

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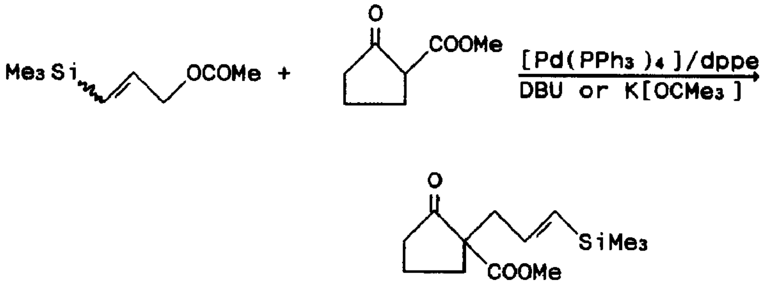

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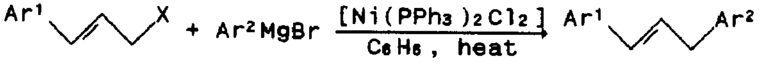
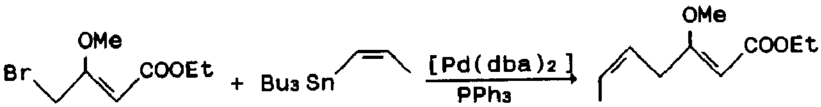


364

Alkenyltin compounds reacted with allylic bromides with good retention of stereochemistry (reaction (41)) [704]. The reaction of allenyltin derivatives with $PhCH{=}CHCH_2OCOMe$ was investigated. Generally both allenyl and alkynyl substituted products such as 365 and 366 were obtained, with the regioselectivity depending on the substitutuents on the allyl group. The mechanism and the side products of the reaction were considered in detail [705].

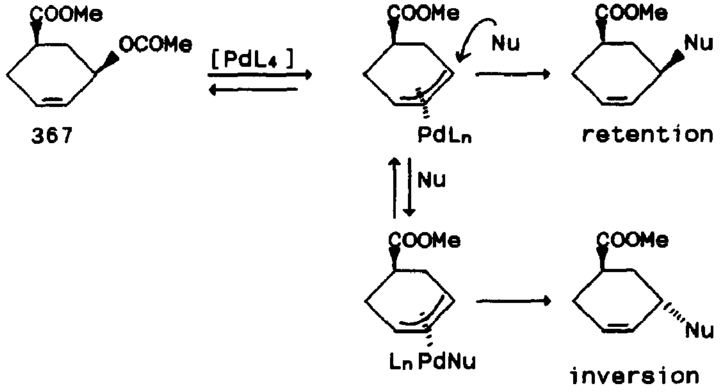


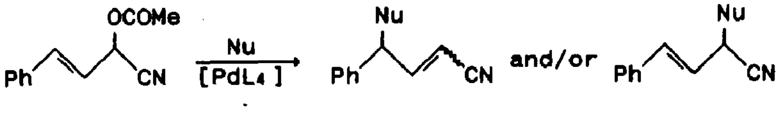
(41)

365

366

The reactions of nucleophiles with 367 have again been studied in detail. Oxidative addition of $[PdL_n]$ invariably proceeds with inversion, with the stereochemistry of attack on the palladium allyl complex being determined by the nature of the nucleophile. $Na[CH(COOMe)_2]$ and related anions, CpNa, and lithium enolates attacked at carbon giving a substituted product with overall retention of configuration. Ethenyl alanes, Grignard and organozinc reagents, and Na[BH_4] attacked initially at palladium with subsequent transfer from the metal to carbon, resulting in substitution with overall inversion. Nucleophiles were also classified in terms of the regioselectivity of their reactions with 368. Group A, soft nucleophiles such as NaCH($COOMe)_2$, Bu_3SnOPh, NaCp and morpholine, attacked at the γ-position, whereas group B, described as intermediate, and including allyl silanes and tin enolates, attacked at the α-position. The hardest nucleophiles, group C, comprising MeLi, PhLi, $PhSnBu_3$, PhZnCl and Na[BH_4] gave rise to reduction [706]. In the related reaction of 369 (X = -OOCOMe or -$OOCCH_2COMe$) the *cis*-product 369 (X = OMe) was the major species formed in the presence of Pd($OCOMe)_2/PPh_3$ [707].





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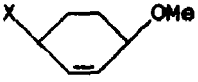
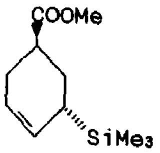


369

Reaction of 367 with $(Me_3Si)_3Al$ in the presence of [Pd($PPh_3)_4$] gave 370 and 371 in the ratio 75:25, but when [Mo($CO)_6$] was used as the catalyst, 371 predominated to the extent of 70:30 [708]. Both **372** and **373** reacted with [acac]$^-$ in the presence of [Pd(PhCN)$_2$Cl$_2$] to give **374** as the major product [709].



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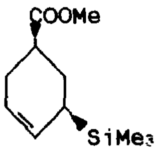

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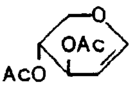

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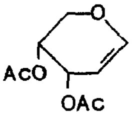

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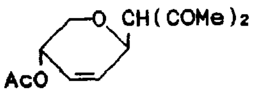
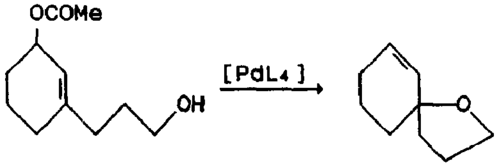


374

A number of papers this year have reported the cyclisation of oxygen and nitrogen nucleophiles onto palladium allyl complexes. With alkoxide nucleophiles both spirocyclic and fused systems were prepared by an appropriate choice of substrate (reactions (42) and (43)) [710]. An allyl benzoate was the substrate in reaction (44), which proceeded with good chirality transfer in the *syn*-sense [711]. Two groups have approached the synthesis of perhydrohistrionicotoxin *via* reaction (45) [712-714].



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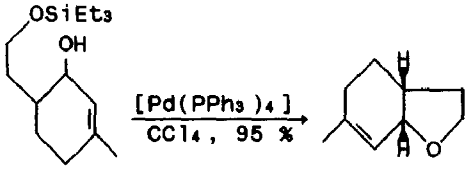

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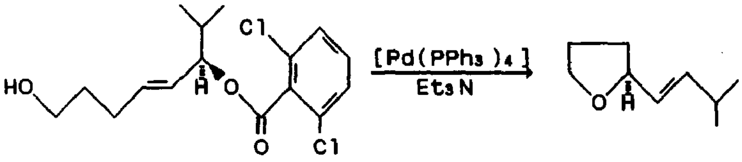

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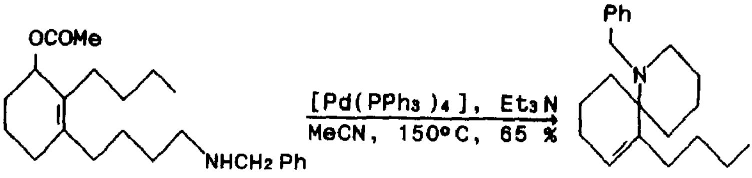
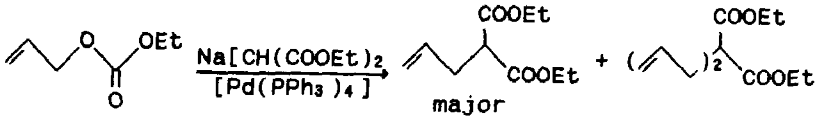


(45)

Allylic carbonates have proved to be popular and successful substrates this year. Reaction of 375 with the anion of diethyl propanedioate gave mainly monoallylated product, together with a little of the bis(allyl) species [715]. Silyl enol ethers were used as nucleophiles towards allyl carbonates in reaction (46); the alkoxide formed in the generation of the palladium allyl derivative removes the silyl group [716]. Enol esters were also suitable substrates if $MeOSnBu_3$ was added to generate the tin enolate (reaction (47)) [717].



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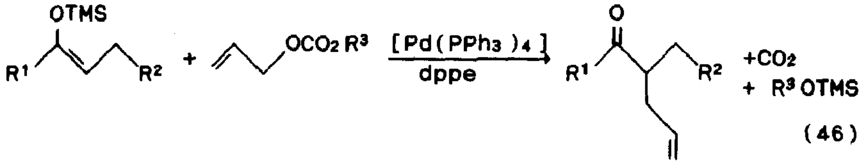

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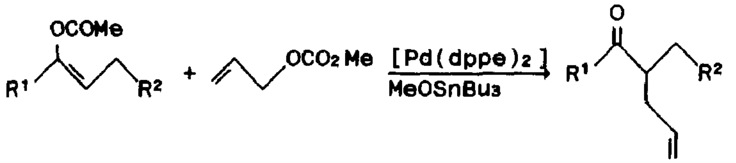
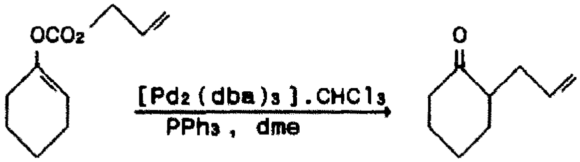


(47)

Reaction of enol allyl carbonates with $[Pd_2(dba)_3]/PPh_3$ resulted in clean and efficent allylation of the enolate. The reaction, (48), involves a palladium allyl complex of the enolate [718]. However, when the palladium containing species was changed to $Pd(OCOMe)_2$/dppe/MeCN, the course of the reaction was altered to give the enone (reactions (49) and (50)). The exact nature of the palladium catalyst is crucial as reaction (51) shows [719].



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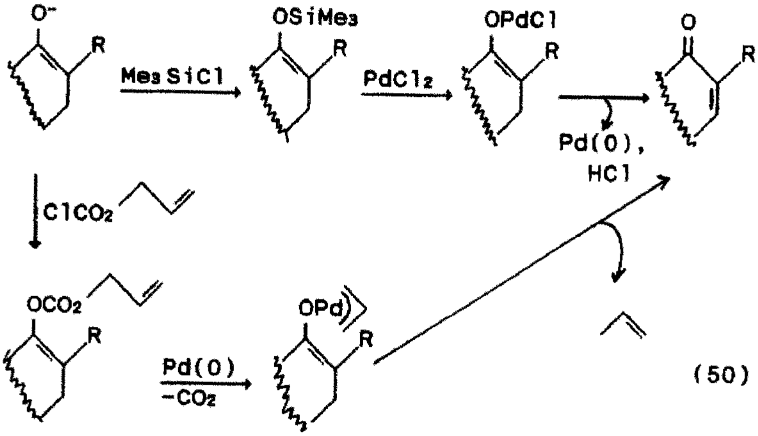
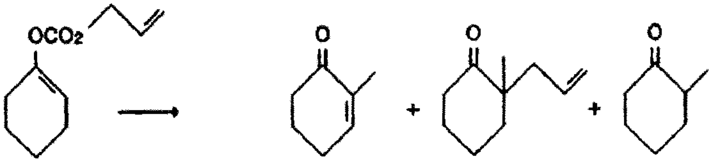


(49)

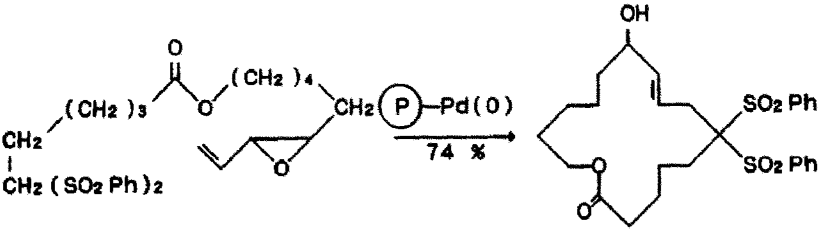
(50)



(51)

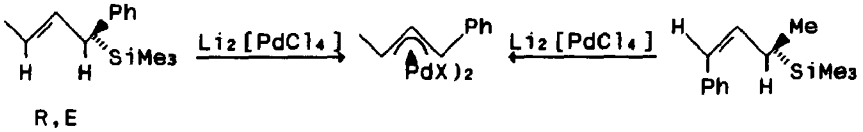
Pd(OCOMe)₂/dppe	98	0	1
Pd(OCOMe)₂ + 2PPh₃	69	18	10
[Pd₂(dba)₃].CHCl₃ + dppe	5	95	0
[Pd(PPh₃)₄]/dppe	5	93	2

The use of alkenyl epoxides as substrates has this year been exemplified by reaction (52); the exact nature of the nucleophile proved to be crucial in this case, and it was suggested that this depended on the ease of its absorption by the polymer [720].



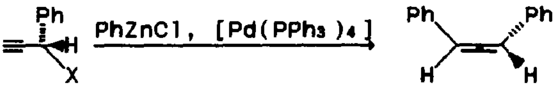
(52)

There is considerable interest in achieving enantioselective allylic substitution in the presence of chiral catalysts. In this context the formation of 376 from either 377 or 378 was investigated. Subsequent complexation with di(+)campholoylmethane revealed that chirality transfer was essentially complete [721].

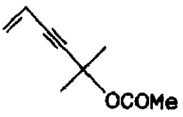


376 377 378

There have been two reports of the use of propargyl derivatives as substrates for palladium catalysed substitution reactions. Treatment of 379 (X = OCOMe, OCOCF$_3$ or OSOMe) with PhZnCl in the presence of [Pd(PPh$_3$)$_4$] gave 380 with good *anti*-stereoselection, although the mechansim bears little relation to those involving allyl derivatives [722]. Reaction of 381 with Et$_3$Al seems to have given 382 in the presence of NiCl$_2$ or [Pd(acac)$_2$], but both were inferior as catalysts to FeCl$_3$ [623]. Reaction (53) appears to be a conventional allyl substitution, but the reaction mechanism was not established [724].



379 380



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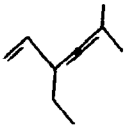

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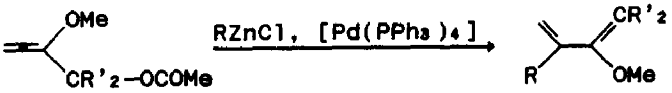
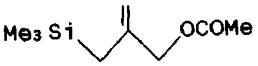


(53)

383 has again been used as an equivalent of trimethylenemethane, and its palladium complex has proved useful in cycloaddition reactions with alkenes

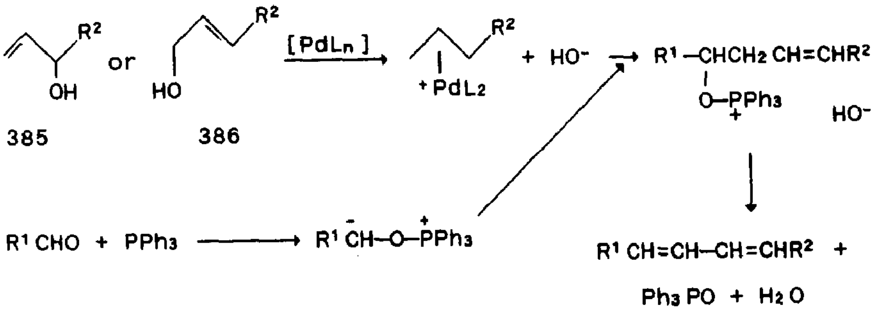
bearing electron-withdrawing groups [725]. The reaction mechanism has been investigated in considerable detail; deuterium labelling studies suggested that 384 was a non-symmetric species which may equilibrate [726].



383

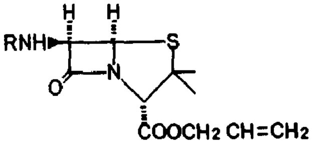
384

Reaction of either 385 or 386 with R^1CHO and PPh_3 in the presence of $[Pd(acac)_2]$ resulted in a substitution; the reaction mechanism is shown in Scheme 10 [727].



Scheme 10 Mechanism of substitution/condensation of 385 with aldehydes [727].

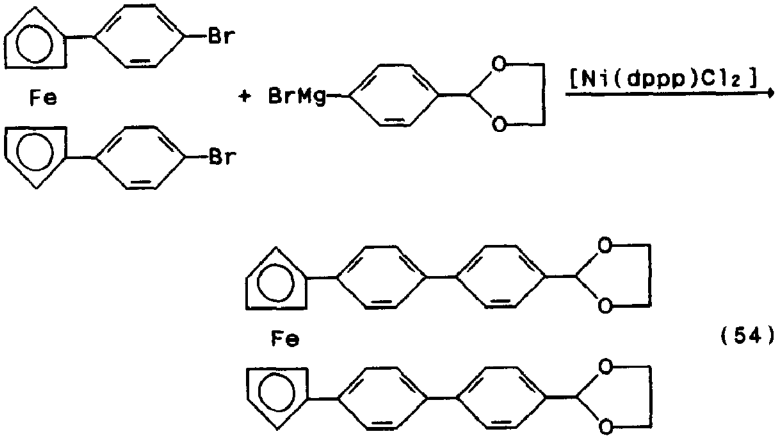
Deallylation of 387 was accomplished using 2-ethylhexanoate in the presence of $[Pd(PPh_3)_4]$ [728].



387

13.8 Coupling of Organometallics with Halides and Related reactions

Couplings of Grignard reagents with aryl halides in the presence of nickel and palladium complexes as catalysts have again been widely reported this year. Reactions (54) [729], (55) [730] and (56) [731] were the simplest examples. In the reaction of 388 it was found to be advantageous to use two molar equivalents of the Grignard reagent; the product was employed in a synthesis of cannabifuran [732]. The best catalyst for reaction (57) was [Ni(H_2O)(2-Cl-benzothiazole)Br_2], and the mechanism suggested was not the usual oxidative addition, but involved 389 [733]. Reaction (58) allowed the preparation of 390, furoventaline, a marine natural product [734]. The substitution of the chloro groups in 391 (X = Cl or F) proceeded selectively and sequentially when R = alkyl [735]. The conversion of the dibromonaphthalene, 392, to the corresponding mono Grignard reagent, followed by treatment with [Ni(acac)$_2$], resulted in the formation of a polymer. Several related polymers were also synthesised [736].



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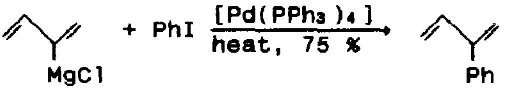

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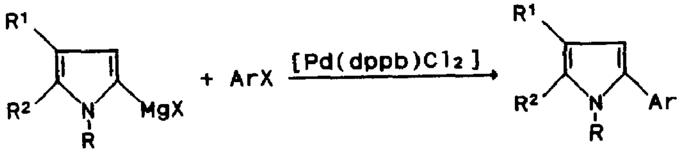

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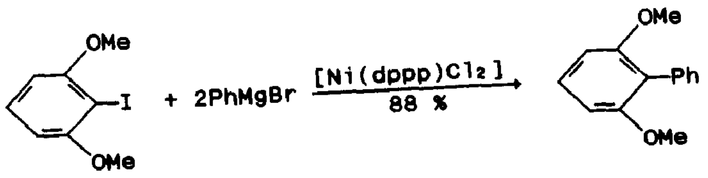

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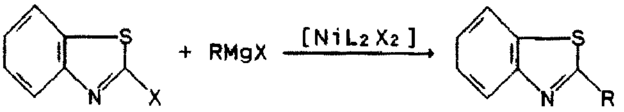

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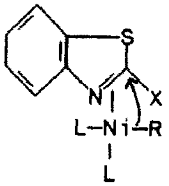

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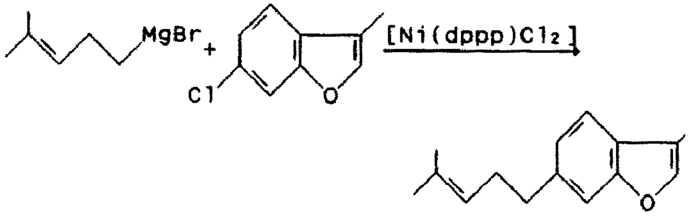

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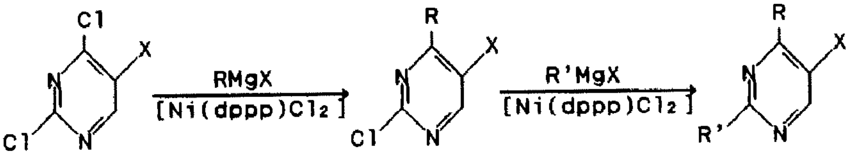

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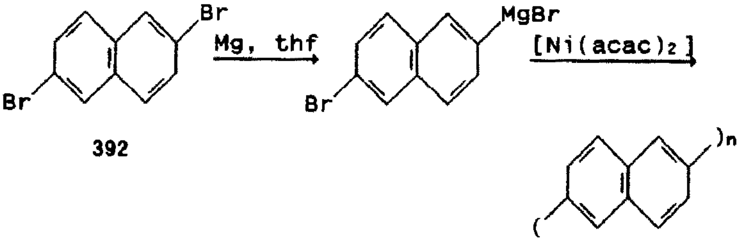
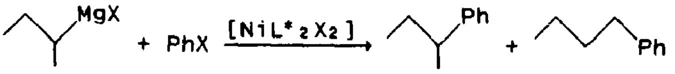


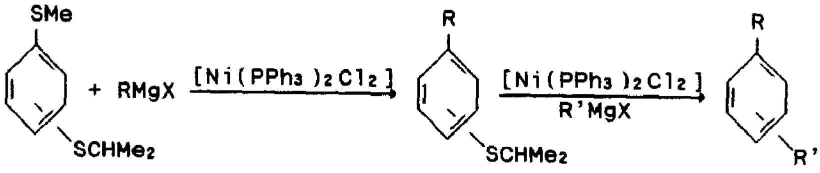
392

Enantioselective coupling of 393 with halobenzenes was accomplished in the presence of $[NiL^*_2X_2]$ (L^*_2 = PROPHOS, CYCPHOS, PHEPHOS or CHIRAPHOS) in up to 50 % enantiomer excess. The reaction appeared to be a complex one with a strong dependence on the nature of the halide and the solvent [737].



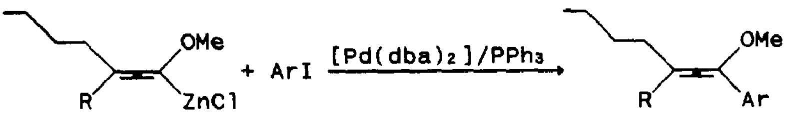
393

Aryl thioethers have also proved to be suitable substrates. In a study of the reactions of 394 the methylthio substituent was the more easily displaced, and good selectivities for the monosubstituted product, or for the products of substitution by two different Grignard reagents, could be obtained [738].



394

Other organometallics have also found wide uses in this coupling reaction. Both aryl and alkenyl halides were readily substituted by organozinc compounds in the presence of $[Pd(PPh_3)_4]$, and $[Ni(PPh_3)_4]$ was a useful catalyst for the aryl halide substrates [739]. Alkoxyallenylzinc halides reacted similarly (reaction (59)) and 395 provided a synthon for the anion of an enone [740].



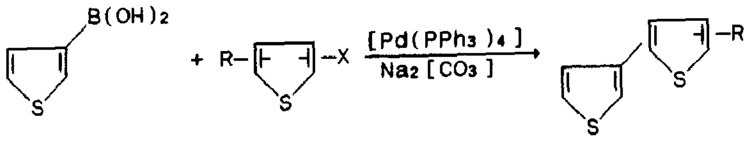
(59)

395

In the presence of iodide anion and $[PhPd(PPh_3)_2I]$, R_2Hg reacted with aryl halides to give mainly RAr, with the formation of the homo coupled products being supressed by the iodide. The reaction proved particularly sensitive to oxygen, since this removed the I^- by oxidation [741]. Thienyl mercury derivatives were coupled with aryl or pyridyl iodides in the presence of $[PhPd(PPh_3)_2I]$, $[Pd(PPh_3)_2Cl_2]$ or $[Pd(MeCN)_2Cl_2]$ [742].

Organotin compounds, $RSnMe_3$ (R = Me, alkenyl, aryl or $PhC{\equiv}C$), coupled with aryl, alkenyl and heteroaryl halides in the presence of $[PhPd(PPh_3)_2I]$, although some homo coupling did also occur [743]. Aryl diazonium compounds reacted similarly [744]. Using Bu_3SnNEt_2 as the attacking nucleophile allowed the direct conversion of aryl halides to anilines, when $[Pd\{P(2\text{-}MeC_6H_4)_3\}_2Cl_2]$

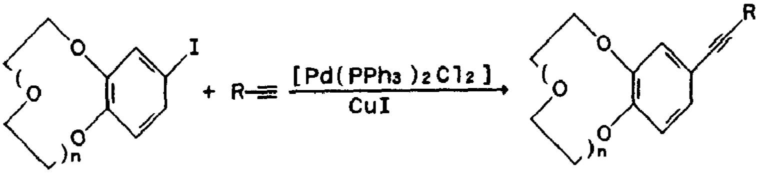
was used as the catalyst [745]. Tin enolates, formed *in situ* from enol ethanoates and Bu_3SnOMe, were coupled with bromobenzene in the presence of $[Pd\{P(2\text{-}MeC_6H_4)_3\}_2Cl_2]$ [746]. It was necessary to convert organoboron derivatives such as **396** to the corresponding ate complexes, before reaction occurred [747].



396

The well-known coupling of 1-alkynes with aryl halides has continued to find wide applications. Reaction (60) gave products which were used as the precursors of bis(ethanoylarylene) carboranes [748], whilst reaction (61) led to the synthesis of an interesting crown ether derivative [749]. Derivatives of nucleic acids such as **397** have been prepared [750,751]. The reactions of $HC\equiv CCMe_2OH$ have been used as an convenient equivalent for the reactions of ethyne itself (for example reaction (62)) [752,753]. Diazonium salts, prepared *in situ*, were suitable substrates (reaction (63)); in this case the product could be desilylated using KOH/MeOH [754]. The coupling of two molar equivalents of phenylethyne with **398** gave **399**; the reaction mechanism is shown in Scheme 11 [755].

$$Ar^1I + HC\equiv CH \xrightarrow[\text{CuI, base}]{[Pd(PPh_3)_2Cl_2]} Ar^1\text{-}C\equiv CH \xrightarrow[\text{CuI, base}]{Ar^2X,\ [Pd(PPh_3)_2Cl_2]} Ar^1C\equiv CAr^2 \qquad (60)$$

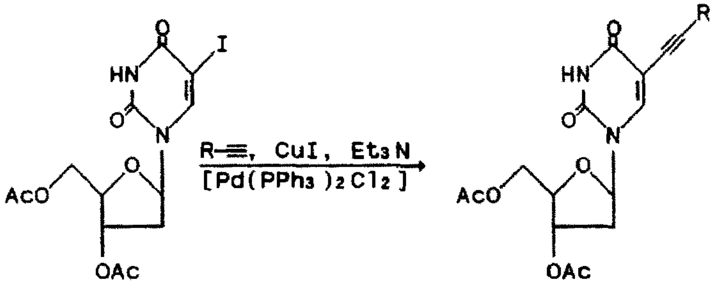


(61)

n = 3,4

Substitution of aryl halides by $[CN]^-$ has been accomplished in the presence of nickel(0) or palladium(0) catalysts. The continued application of a reducing potential was shown to prolong the life of the catalyst, presumably by regenerating an active species from deactivated complexes [756]. The addition of 18-crown-6 also enhanced the reaction of K[CN] in the presence of $[Pd(PPh_3)_4]$, presumably by sequestration of K^+. The reaction was also successful with alkenyl halide substrates, and was in this case stereospecific

[757].



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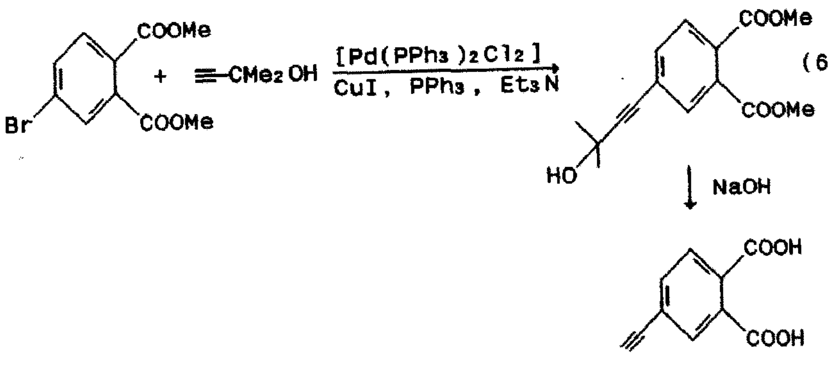

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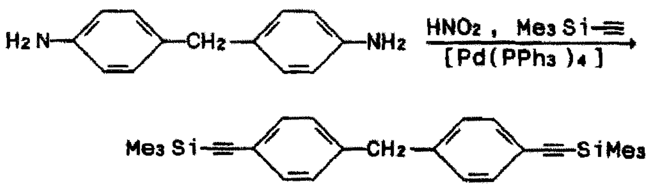


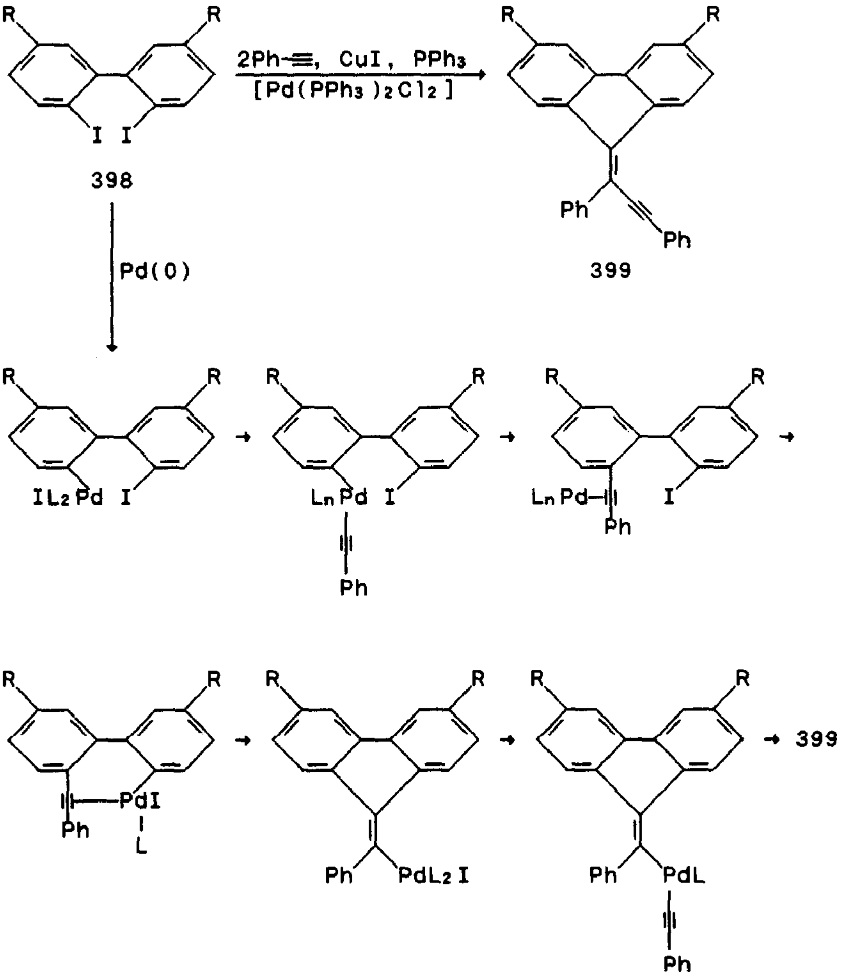
(63)

In the presence of either $[Pd(PPh_3)_4]$ or $Pd(OCOMe)_2$ aryl halides reacted with triarylphosphines to yield quaternary phosphonium salts. Substituents in the 2-position of the aryl halide retarded the reaction [758]. When 400 was reacted with $P(OEt)_3$ in the presence of $PdCl_2$ a modified Arbusov reaction occurred, *via* {ArPdX} [759].

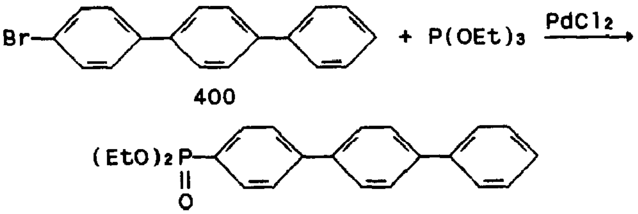
Reduction of NiX_2 with lithium metal gave very reactive nickel powder, which proved useful in catalysing the coupling of aryl halides to biaryls, *via* $[ArNiL_nX]$ [760].

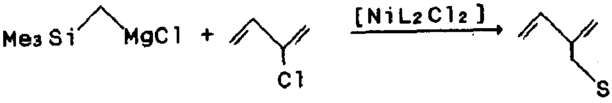
Many of the reactions noted for aryl halides have analogues in the reactions of alkenyl halides. Grignard reagents have been coupled to chloroalkenes in the presence of $[Pd(PPh_3)_4]$ or $[Ni(PPh_3)_4]$ [761], or $[NiL_2Cl_2]$ (L_2 = dppp, dppe or $(PPh_3)_2$, reaction (64)) [762]. $[Ni(dppp)Cl_2]/I_2$

was used as the catalyst for reaction (65) [763]. Both *cis*- and *trans*-alkenyl bromides were reported to react stereospecifically under these conditions [764].



Scheme 11 Mechanism of coupling of phenyl ethyne with a 2,2'bis(iodo)biphenyl in the presence of a palladium complex [755].





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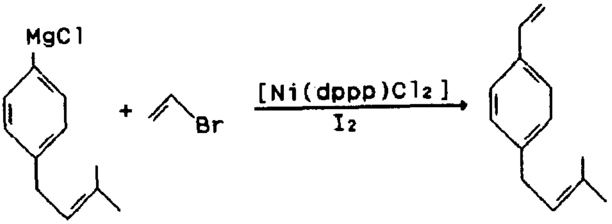
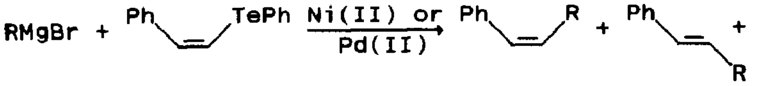
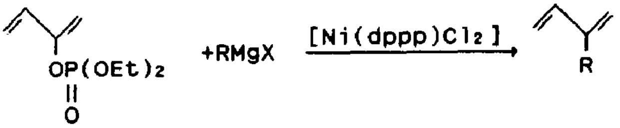


(65)

Some more unusual leaving groups have been investigated, including substrates such as alkenyltelluro ethers (reaction (66)) [765] and mixed alkenyl phosphates (reaction (67)) [766].

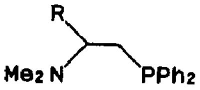


+ PhR (66)



(67)

The enantioselective coupling of branched Grignard reagents with bromoethene has been studied in the presence of complexes of ligands of the type 401, prepared by reduction of amino acids (reaction (68), M = Pd or Ni, L = 401). Enantiomer excesses up to 83 % were obtained [767]. With organozinc compounds and ferrocene derived ligands such as 402 (reaction (69)) optical yields ranged up to 86 %, with excellent chemical yields [768].



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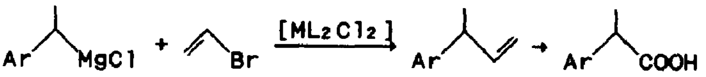
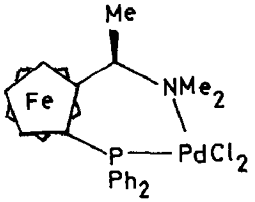


(68)

Reactions using the customary range of other organometallics have been reported, including $(Me_3Si)_3Al$ (reaction (70)) [769], R_4Sn [770], tributyltin enolates [771], and a wide range of alkenyl copper compounds (reaction (71)) [772,773]. Reactions of alkenyl boronates, prepared *in situ*, were generally stereospecific with respect to both components (for example reaction (72)) [774]. The organozinc derivatives of enol ethers such as **403** reacted readily with iodoalkenes in the presence of $[Pd(PPh_3)_4]$; **403** is an acyl anion synthon [775]. Reaction of $HP(O)(OEt)_2$ with alkenyl bomides in the presence of $[Pd(PPh_3)_4]$ and Et_3N gave alkenyl phosphonates with high stereospecificity [776].



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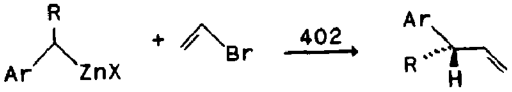

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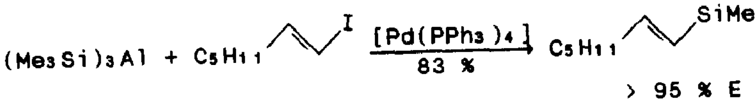

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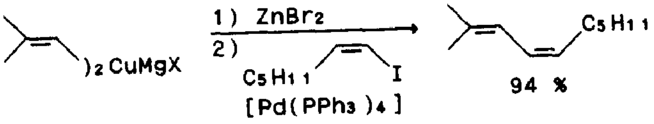

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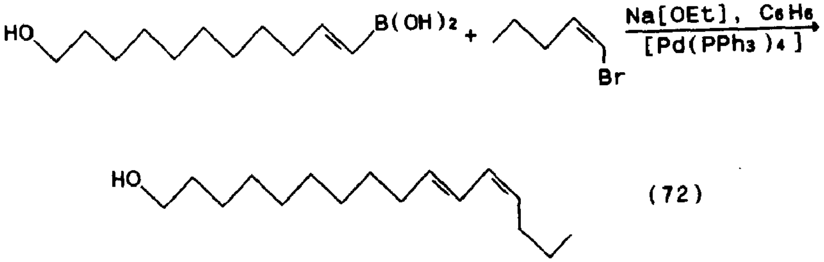

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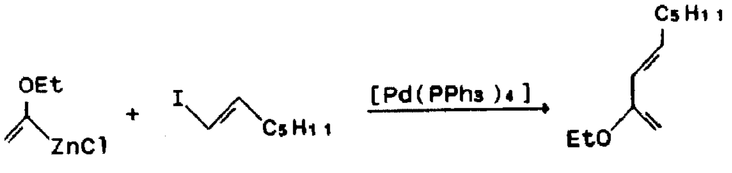
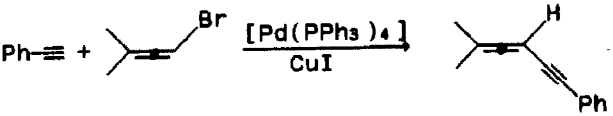


74 %

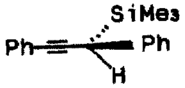
403

Alkynes reacted with allenyl bromides in the presence of [Pd(PPh$_3$)$_4$]/CuI (reaction(73)) [777].



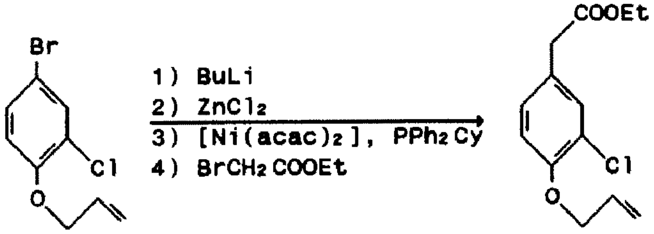
(73)

Treatment of PhC≡CBr with Me$_3$SiCH(Ph)MgBr in the presence of [Pd(R,S-PPFA)Cl$_2$], 402, gave 404 with up to 18 % optical yield [778].



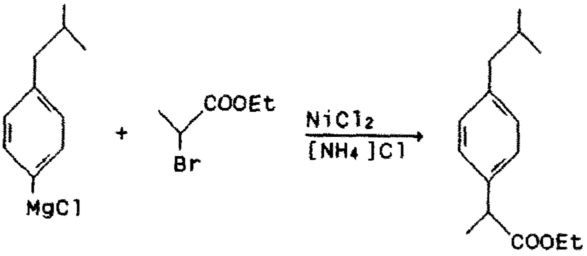
404

Few aliphatic halides undergo sufficiently facile oxidative addition to nickel(0) or palladium(0) complexes to make them good substrates for the catalysed coupling reactions. α-Halo esters are, however, an exception to the rule, and two reactions, (74) and (75), in the presence of nickel complexes, have been noted this year [779,780].



(74)

Whilst the reactions of organometallic reagents with acyl halides might be expected to be generally facile, this is not in practice invariably the case, particularly with the derivatives of poorly electropositive metals. The reactions of organotin compounds have been particularly studied [781]. The reaction of an ttibutylalkenyltin compound, 405, gave a product which was used in a synthesis of pyrenophorin [782]. The allyltin compound, **406**, gave rise to both linear and branched products in proportions which depended on the exact reaction conditions. Only the allyl group was transferred and this is indeed quite generally the case for R_3SnR' in which R = alkyl and R' = alkenyl, alkynyl, aryl, allyl benzyl or CH_2OMe [783]. The related reaction of **407** proceeded in moderate to good yields [784].



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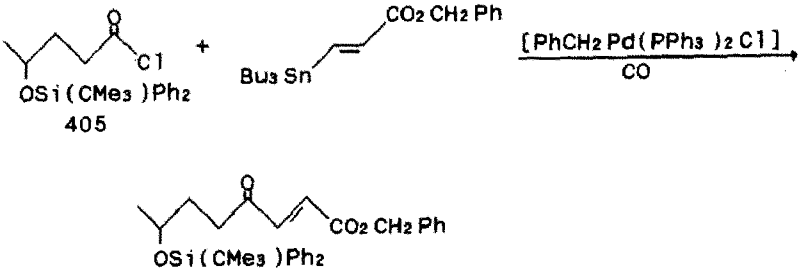

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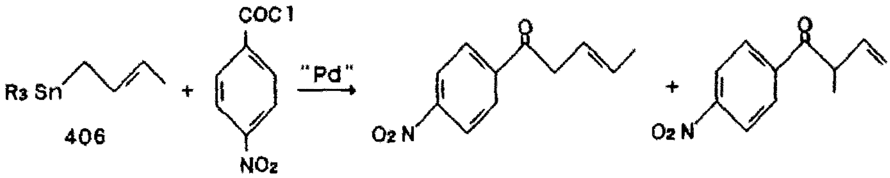
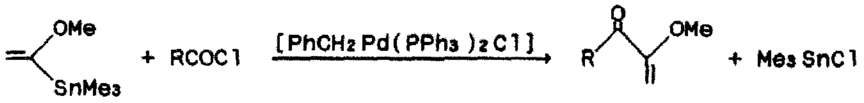


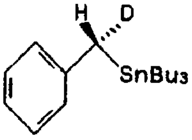
406

[Pd(PPh3)4], R = Me, 65 °C	50	:	50
[PhCH2Pd(PPh3)2], R = Bu, 65 °C	30	:	70
[PhCH2Pd(PPh3)2], R = Bu, 50 °C	17	:	83



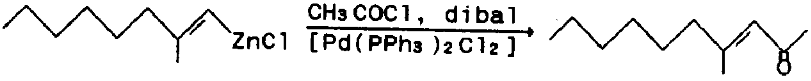
407

The mechanism of the reaction has been investigated. The first intermediate which could be observed by nmr spectroscopy was [$RCOPdL_2Cl$], the product of oxidative addition of the acyl halide to palladium(0). Transmetallation of 408 was about 65 % stereospecific, with inversion of configuration [785]. This process was solvent dependent, and the data were consistent with electrophilic cleavage of the carbon-tin bond with palladium(II) acting as the electrophile [786].



408

The alkenylzinc compound, 409, reacted with ethanoyl chloride in the presence of [$Pd(PPh_3)_2Cl_2$]/dibah to give the enone, 410, in 77 % yield [787]. Alkenylcuprates have also been coupled with acyl halides in the presence of palladium(0) complexes [788].



409 410

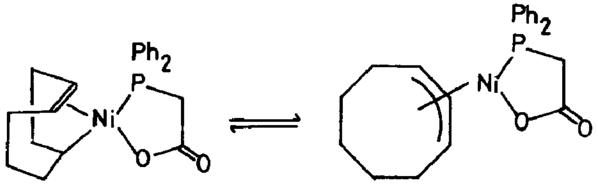
The reaction of aryl halides with $Bu_3SnSnBu_3$ in the presence of [$Pd(PPh_3)_4$] provided a synthesis of $ArSnBu_3$, for aryl groups bearing electron withdrawing functionalities. It was essential to conduct the reaction under mild conditions to avoid coupling of the aryltin compound with unreacted aryl halide [789]. The related reactions of $ArCH_2Cl$ with $ClMe_2SiSiMe_2Cl$ were investigated. The major product was $ArCH_2SiMe_2Cl$ [790]. With $ArCHCl_2$ as the substrate the reaction was greatly more complex, with coupling as well as substitution products being formed, their relative abundances depending on the disilane used [791].

13.9 Oligomerisation, Polymerisation and Telomerisation

The dimerisation of ethene to butenes has been reported to occur in the presence of [$Ni(CO)_2(PPh_3)_2$]/Et_nAlCl_{3-n}/Al_2O_3 (n = 1 or 2) [792,793]. The mechanism proposed involved nickel bis(alkene) complexes and nickel metallocycles [794]. $Ni(NO_3)_2$ supported on silica could be reduced to nickel(I) by molecular hydrogen, and was then used as a catalyst for ethene dimerisation to give 1- and 2-butene in the ratio 1:48 [795]. The complexes $[(C_6F_5)Ni(PPh_3)_2Br]$ and $[(C_6Cl_5)Ni(PPh_3)_2Cl]$ were useful catalysts for the dimerisation of ethene in the presence of $Ag[ClO_4]$. Species such as $\{ArNi(PPh_3)_2(ClO_4)\}$ seemed to be the active intermediates [796].

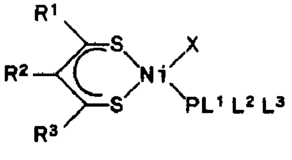
A catalyst system for the dimerisation of propene was prepared from isoprene/$(Et_2Al)_2O$/nickel naphthenate/Cy_3P/2,4,6-trichorophenol [797]. Reaction of butene in the presence of $Ni(OCOCF_3)\{OCOCH(Et)Bu\}/EtAlCl_2$ gave 85 % dimers [798]. Methyl propenoate underwent tail-to-tail dimerisation to give dimethyl 2-hexenedioate in 93 % yield and with 93-96 % selectivity in the presence of $[Pd(MeCN)_4][BF_4]_2/Li[BF_4]$ [799].

Silica supported $[Ni(acac)_2]/\{(CH_3)_2CHCH_2\}_3Al$ was activated by heating to give a catalyst for ethene polymerisation [800]. The complex 411 was a useful model for the oligomerisation of ethene in the SHOP process. In 411 there exists an equilibrating mixture of an allyl complex with an alkyl/η^2-alkene containing species. Oligomerisation of ethene gave more than 95 % selectivity towards linear alkenes. Insertion of ethene into a nickel hydride complex was proposed as the key step in the reaction [801]. A closely related mechanism was proposed for the oligomerisation of 1-butene in the presence of $[Ni(\beta\text{-diketonato})(\eta^3\text{-}C_8H_{13})]$. In this case there was a linear relationship between the acidity of the β-diketone and catalyst activity, and a nickel hydride intermediate could be trapped [802]. Correlations of the inverse volcano type between XPES data and catalytic activity were made [803].



411

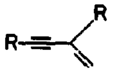
When activated with a cocatalyst such as R_nAlCl_{3-n}, 412 was a very active catalyst for alkene oligomerisation under mild conditions. It was also an excellent isomerisation catalyst [804].



412

The preparation of $[Pd(MeCN)_4][BF_4]_2$ was described, and the complex was used to catalyse the polymerisation of ethenyl benzene. 1,3-Cyclohexadiene and norbornene were also converted to high molecular weight polymers. A number of other reactions including alkylation of arenes, cleavage of strained carbon-carbon bonds, and rearrangement of 3,3-dimethyl-1-butene were also catalysed. In all cases the reactions were assumed to proceed *via* mechanisms involving carbocations [805]. In a very poor paper the effect of platinum(IV) salts on the copolymerisation of ethenylbenzene and 2-propene-1-ol was examined. Unfortunately the authors appear to have some problem in distinguishing between $PtCl_6$ and $H_2[PtCl_6]$ [806].

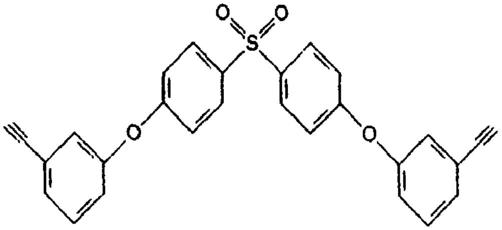
The dimerisation of 1-alkynes to give 413 together with some higher oligomers was catalysed by $[Pd(acac)_2]/L/Et_3N$. The relative abundances of the various products depended on the nature of L; the use of PPh_3 gave substantial amounts of higher oligomers [807]. Two papers have reported cyclotrimerisations of alkynes to give benzene derivatives. With phenylethyne as the substrate and $[Ni(CO)_{4-n}\{P(OCHMe_2)_3\}_n]$ (n = 0,1,2 or 3) as the catalyst 1,2,4-triphenylbenzene was the main product, formed with more than 95 % selectivity [808]. The oligomerisation of $HC{\equiv}CCMe_2OH$ in the presence of $[Ni(cod)_2]$ and a phosphine gave mixtures of arenes, together with linear dimers, trimers and tetramers [809].



413

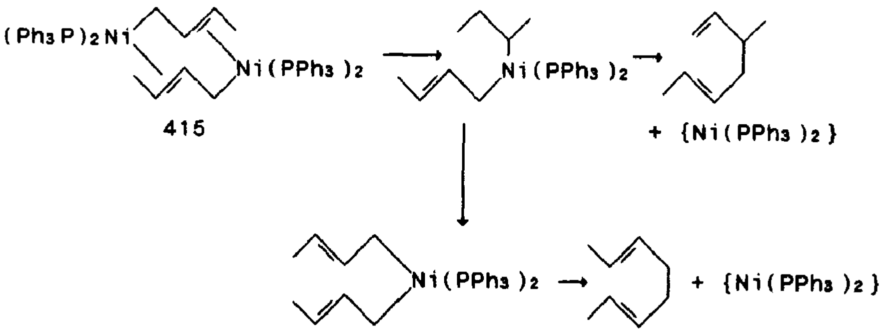
The polymerisation of phenylethyne in the presence of $[Ni(acac)_2]/PPh_3$ was reported to give water and methanol soluble polymer fractions. As the phosphine concentration was increased both the reaction rate and the proportion of the water soluble fraction were increased [810]. Phenylethyne and 1,4-diethynylbenzene were copolymerised using this catalyst [811], whilst $HC{\equiv}CCH_2OH$ and $PhN(CH_2C{\equiv}CH)_2$ reacted in the presence of $PdCl_2$ [812]. The complex $[Ni(PPh_3)_2Cl_2]$ was used to initiate the thermal polymerisation of ATS, 414 [813].

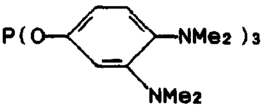
3-Methyl-1,2-butadiene was polymerised in the presence of $[\{Ni(\eta^3\text{-}C_3H_5)Br\}_2]$, *via* a living chain mechanism. The initial reaction is the formation of a 1:1 complex in which the allene has been inserted into the nickel-carbon bond [814].



414

Cyclooctadiene was the principal product of the reaction of butadiene with $[Ni(acac)_2]/H_3Al_2(OCH_2CH_2OMe)_3/P(OR)_3$; the system for which R = 2-ethoxyphenyl gave the most successful results [815]. $[Ni(\eta^3\text{-}MeCHCHCH_2)(PPh_3)_2]^+$ was shown to be a precursor of a catalyst for butadiene oligomerisation. The activation of the catalyst involved the initial formation of **415**, and a $\{Ni(PPh_3)_2\}$ species was the true catalyst [816]. Isoprene was dimerised to 1,5-dimethyl-1,5-cyclooctadiene with good selectivity and conversion in the presence of $[Ni(acac)_2]/Et_3Al/$**416**, this system being considerably superior to nickel naphthenate [817]. The silyl enol ether, **417**, reacted similarly, again with a high degree of regiochemical control [818].





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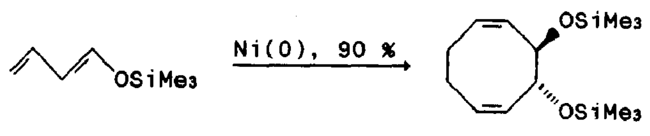
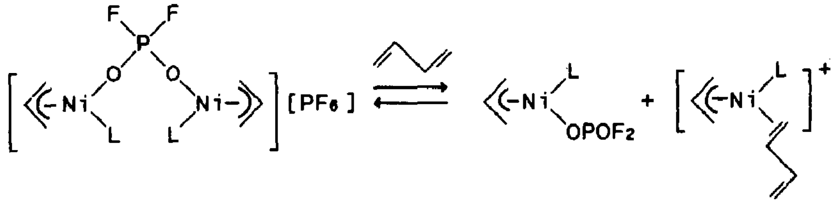


417

Various new catalyst systems have been examined for the polymerisation of butadiene. With $[Ni(acac)_2]/Et_3Al_2Cl_3$ the reaction rate increased with the Al:Ni ratio, but molecular weight was decreased [819]. The molecular weight in the reaction using $Ni(octoate)_2/HF/Bu_2O/(Me_2CHCH_2)_3Al$ could be regulated by the addition of a non-conjugated diene such as 1,4-pentadiene [820]. The strereochemistry of the polymerisation in the presence of a range of nickel complexes was probed by a deuterium labelling study; the rate of allyl isomerisation was critical [821]. Treatment of **418** ($L = P(OAr)_3$) with butadiene gave gave a catalyst which oligomerised butadiene to give mainly a *cis*-product [822].

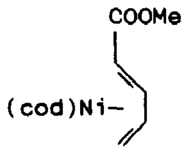


418

Polymerisation of 2-chlorobutadiene in the presence of $[Pd(Ph_2PC_6H_4\text{-}4\text{-}SO_3Na)_2Cl_2]$ gave an excellent yield of a soluble *trans*-1,4-polymer. Long chain aliphatic thiols could be added as chain regulators [823]. Copolymers of butadiene and ethenylbenzene, prepared using a variety of nickel complexes with $Et_3Al_2Cl_3$ as the catalysts, were subjected to an analysis of their microstructures by ^{13}C nmr spectroscopy. The *cis*-content of the polymer decreased as the proportion of ethenylbenzene increased, suggesting a diminution of the *cis*-control normally exerted by the catalyst [824].

Reaction of methyl pentadienoate with $[Ni(cod)_2]$ at 0 °C gave initially **419**, which could be easily converted to **420**. If the pentadienoate, $[Ni(cod)_2]$ and PCy_3 were mixed at 0 °C, however, **421**, the product of tail-to-tail coupling, was isolated as a single isomer. At 80 °C oligomeristaion gave five isomers of cycloooctadiene dimers. Reaction with [Ni(bipy)(cdt)] gave **422** and

423 [825].



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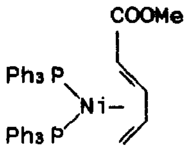

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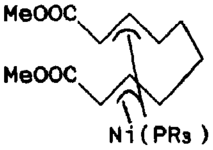

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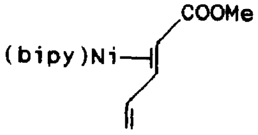

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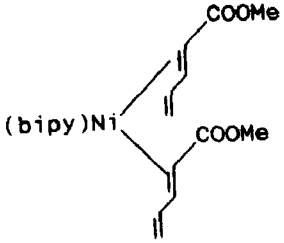
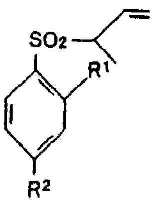


423

Telomerisation of butadiene with water was once again shown to give a mixture of octadienyl alcohols in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$. The reactions of substituted alcohols were also investigated [826]. The telomerisation reactions of isoprene were enhanced by the presence of CO_2, although isoprene dimers were still the major products [827]. Mixtures of the related octadienyl ethers were obtained from alcohols. Palladium complexes of ligands of high basicity and small cone angles were the most active catalysts, and dimeric alkoxy bridged species, which remained intact throughout the catalytic cycle, were involved in the suggested mechanism [828].

Both addition and telomerisation occured in the reactions of arene sulphonic acids with butadiene in the presence of $[PdL_n]$. The proportions of the products, 424, 425 and 426 varied with the precise reaction conditions,and very many data were recorded [829].

When an amino alcohol, $RNHCH_2CH_2OH$, was reacted with butadiene under telomerisation conditions ($[Pd(acac)_2]$ + 2 PPh_3) the major product was the octadienyl amine 427, although some branched amines and octadienyl ethers were also formed [830]. Telomerisation of isoprene with piperidine in the presence of $[Pd(PPh_3)_2Cl_2]$ gave a complex mixture of products with low regioselectivity. However, using $Pd(OCOMe)_2$ + 4 $P(OBu)_3$ as the catalyst system gave mainly **428**, together with a little **429** and **430** [831]. Another group studied related reactions with a range of secondary amines, R_2NH, in the presence of $[Pd\{P(OR)_3\}_n]$. The reactivity of the amines was generally related to their bulk, and the main products were the tail-to-tail telomers such as **431**, together with isoprene dimers [832]. All of the possible telomers and additon products could be obtained from the reaction of Et_2NH with isoprene in the presence of $[Pd(acac)_2]/PR_3$ with and without $BF_3.OEt_2$. Without the Lewis acid the main product was **431** (R = Et), together with a small amount of **432**. However, in the presence of $BF_3.OEt_2$, addition products predominated in the presence of phosphite ligands, but with phosphine additives, **433** and **434** were the main products [833]. An interesting patent has reported the mixed telomerisation of reaction (76), but the mechanism was not investigated [834].



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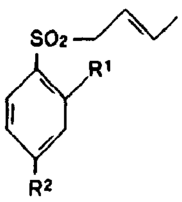

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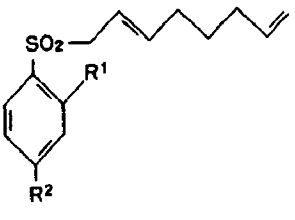

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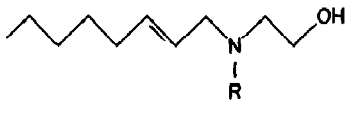

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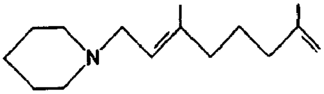
428

Telomerisation of butadiene with an alcohol in the presence of carbon monoxide gave **435**, when $Pd(OCOMe)_2$ + $4R_3P$ was used as the catalyst system [835].



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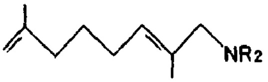

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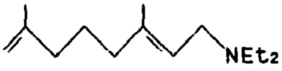

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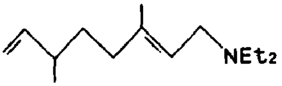

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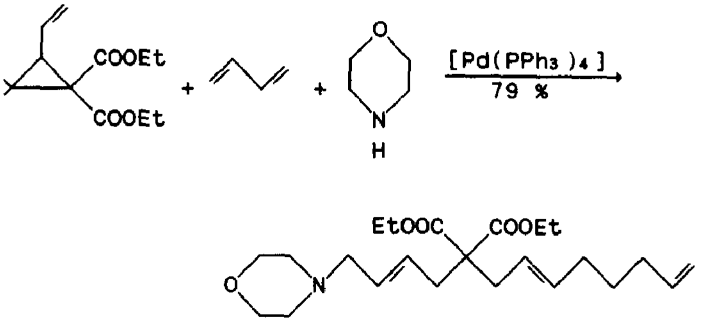

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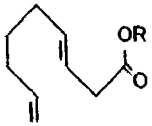
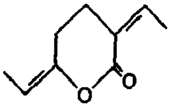


435

As previously reported, the telomerisation of butadiene with CO_2 may lead to a wide variety of products. This year some very selective reactions have been reported. In the presence of a palladium complex of a phosphine with high basicity and high cone angle (such as PCy_3 or $P(CHMe_2)_3$) up to 95 % of 436 was obtained. Using PEt_3 or PBu_3 as the additive, the main products were 437 and 438 [836,837].



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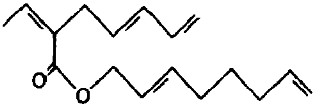

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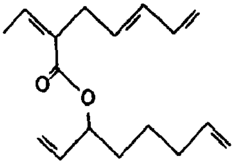
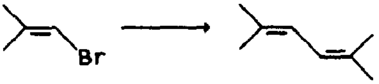


438

Isocyanides have been polymerised to the corresponding poly(iminomethylene) derivatives in the presence of nickel(II). The course of the polymerisation was very strongly influenced by the presence of additional centres in the isocyanides which could interact with the metal [838].

In the presence of a nickel(0) complex 1,4-dibromobenzene was polymerised to polyphenylene. The nickel(0) was generated *in situ* by the electrochemical reduction of $[NiL_2X_2]$ (X = Cl or Br; L = PPh_3 or L_2 = dppe) [839]. Polymerisation of 2,5-dibromo-3-methylthiophene was effected using $[Ni(bipy)Cl_2]$ as the catalyst in the presence of magnesium metal. The reaction presumably proceeded *via* a Grignard coupling process [840].

Dimerisation of alkenyl halides to yield dienes (reaction(77)) occurred in the presence of $NiCl_2$/KI/Zn/KI. The degree of isomerisation in the product was a function of the substituents [841]. Cyclodimerisation of **439** (X = Br or I) gave either four or six-membered ring products in the presence of $[Ni(PPh_3)_4]$. The ratio of the products was strongly dependent on solvent effects [842].



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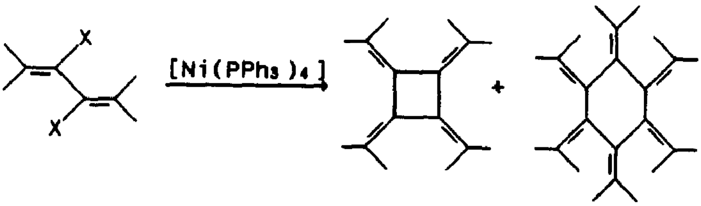
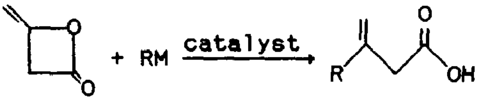


439

13.10 Miscellaneous Coupling Reactions

The enantioselective reaction of Et_2Zn with aldehydes was catalysed by palladium or cobalt somplexes of camphor quinone oximes. Enantioselectivities were in the region of 50 %, but the mechanism of the reaction remains entirely obscure [843]. Silyl enol ethers were converted to tin enolates and reacted with aldehydes in the presence of Bu_3SnF and $[Pd\{P(2\text{-}MeC_6H_4)_3\}_2Cl_2]$. Yields were excellent [844].

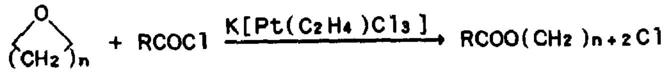
The reactions of a range of organometallics with diketene, **440**, were studied in the presence of nickel or palladium complexes as catalysts. Yields were modest, and the reaction was thought to proceed *via* initial insertion of nickel(0) or palladium(0) into the four membered ring [845]. The best catalyst for the reaction with E-$RCH{=}CHAl(CH_2CHMe_2)_2$ was prepared *in situ* by the reaction of $[Pd(PPh_3)_2Cl_2]$ with dibah. Alkynyl zinc compounds also gave useful reactions, but in this case nickel derived catalysts gave better yields [846].



440

Treatment of benzoic acid with BuMgX in the presence of $[Ni(dppe)Cl_2]$, gave ketones, generally with selectivities in excess of 90 % [847].

Reaction of cyclic ethers with acyl chlorides in the presence of $K[Pt(C_2H_4)Cl_3]$ resulted in ring opening and coupling (reaction (78)). Aliphatic ethers were not suitable substrates, and the mechanism of the reaction was not discussed [848]. Intramolecular coupling of an alkene with a chloromethanoate was accomplished in reaction (79) [849].



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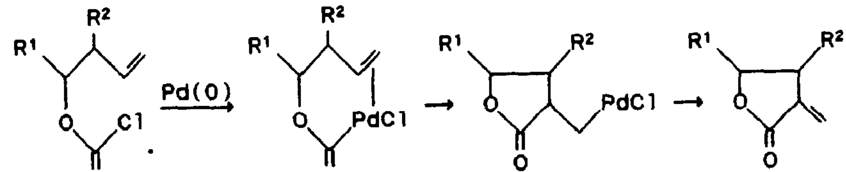
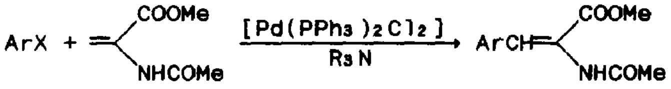


(79)

Many more applications of the Heck reaction and related processes have been reported this year. Aryl iodides underwent conjugate addition to enones using $[Pd(PPh_3)_2(OCOMe)_2]$ as the catalyst. The mechanism involved the formation of ArPdX and addition across the carbon-carbon double bond [850]. Aryl halides were similarly added to dehydramino acids (reaction (80)) [851], and propenenitrile (reaction (81)) [852,853].



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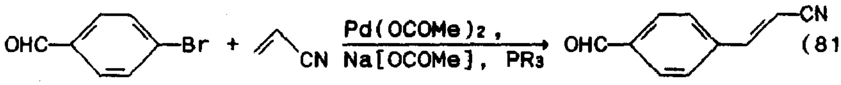
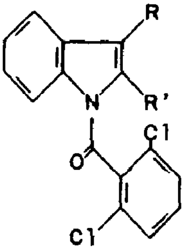


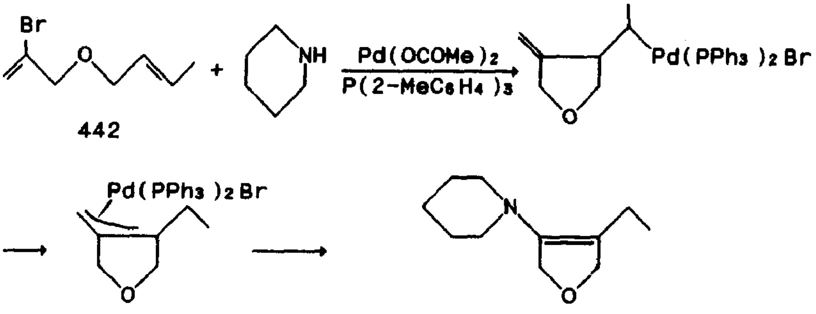
(81)

The reaction of 1-acyl indoles such as **441** with propenoate esters was catalysed by $Pd(OCOMe)_2$. The substrate for which R = H was converted to the 3-alkenyl derivative, but if the 3-position was already substituted (R = Me), alkenylation occurred at the 2-position [854].



441

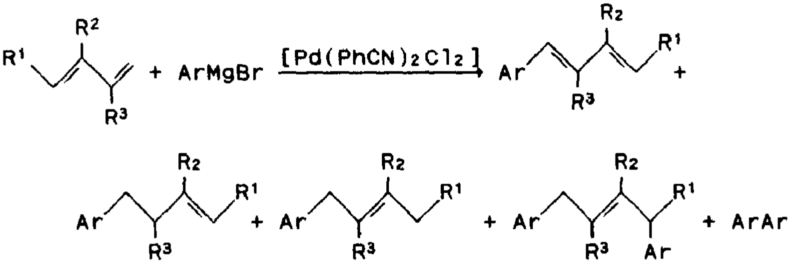
An intramolecular version of the Heck reaction was reported for **442**. It was noted that unsubstituted carbon-carbon double bonds were more reactive than substituted ones, and that the rate of ring formation was in the order 5>6>7 [855].



442

60 %

The reaction of arylmetal compounds with ethenyl benzene to give E-ArCH=CHPh was catalysed by $H_2[PtCl_6]$ in air. The best yields were obtained from Ph_4Sn, but $PhHg(OCOCF_3)$, Ph_2Hg and $Na[Ph_4B]$ were also reactive. A mechanism involving formation of $[ArPtCl_4(H_2O)]$ was proposed [856]. Aryl Grignard reagents underwent both addition and substitution reactions on treatment with substituted butadienes in the presence of $[Pd(MeCN)_2Cl_2]$ (reaction (82)) [857]. Organotin derivatives have been shown to react with ketones in the presence of $[PhCH_2Pd(PPh_3)_2Cl]$. This process has now been effected on halogenated ketones such as **443**; reaction of the alkoxide produced in the first step with the carbon halogen bond led to an efficient synthesis of cyclic ethers [858].



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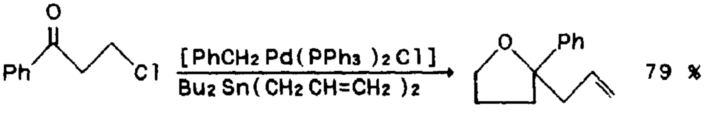


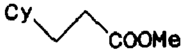
443

The species $ArTl(OCOCF_3)_2$ were efficiently coupled to give biaryls in the presence of $Li_2[PdCl_4]$. No mechanism was defined but the reaction may be assumed to proceed *via* formation of $\{Ar_2Pd\}$, coupling, and reoxidation of the palladium(0) by thallium(III) [859]. Coupling of [PhMg(bipy)Br] to give biphenyl was effected by $[Ni(bipy)X_2]$. The mechanism was complex, involving Ni(I) and Ni(III) derivatives, and $\{(bipy)MgBr\}^{-\cdot}$ radical anions, which were identified from epr data [860]. The treatment of $[Ar_2I]X$ with $[Pd(acac)_2]$ and zinc metal resulted in the formation of the biaryl and aryl halides [861].

Organic halides, in particular aryl halides, have been successfully reductively coupled by N_2H_4 or $ArNHNH_2$ in the presence of $PdCl_2$ or $PdCl_2/HgCl_2$ [862].

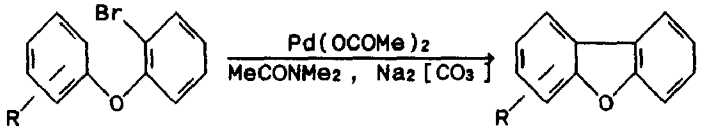
The coupling of bromocyclohexane with ethenyl benzene or methyl propenoate was effected in the presence of $[Ni(PPh_3)_2Cl_2]/Zn$. The two reactions differed in their outcome in that ethenyl benzene yielded the substitution product **444** with better than 90 % selectivity, whereas with methyl propenaoate the additon product **445** was formed, though in lower yield. The reaction mechansim was not discussed [863]. The reaction of aryl halides with alkenes was catalysed by a nickel(0) complex generated and regenerated electrochemically. The most successful and the most closely studied reaction was between iodobenzene and ethene to give ethenyl benzene [864]. A patent reported the reaction of $PhCH_2Cl$ with ethene to give mixtures of ethenyl benzene and E-1,2-diphenylethene in the presence of $Pd(OCOMe)_2/PhCH_2NMe_2$; there is no indication of what would appear to be a most unusual reaction mechanism [865].

444



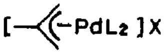
445

An intramolecular arene/aryl halide coupling was used in reaction (83) to prepare a dibenzofuran [866]. Aryl iodides have been reacted with $(Et_3Sn)_2S$ in the presence of $[PhPd(PPh_3)_2I]$ to give symmetric diaryl thioethers. The process was also sucessful when alkenyl bromides were used as the substrates [867]. 1-Alkenes were coupled with pentaborane, B_5H_9, to give 1- and 2-substituted alkenyl pentaboranes, under mild conditions, using $PdBr_2$ as the catalyst [868].



(83)

A range of palladium allyl complexes, **446**, (L_2 = cod, L = hmpt or PBu_3, X = $[BF_4]$ or L = PPh_3 or methyl propenaote, X = $[PF_6]$) have been used to catalyse the Diels Alder reaction between butadiene and methyl propenoate. Conversions were low and considerable amounts of linear dimers were also formed [869]. The cotrimerisation of the diyne **447** and a range of alkynes was catalysed in good yield by nickel(0) phosphite complexes [870].



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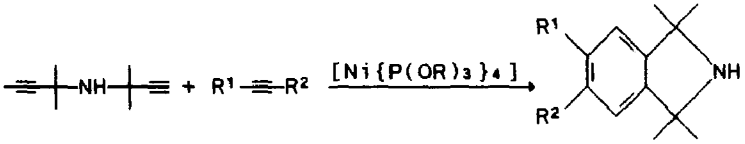
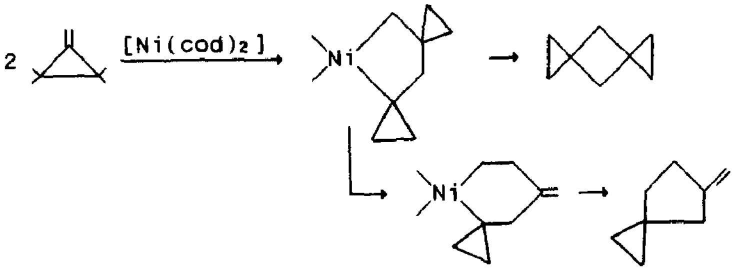


447

There have been further investigations into the reactions of methylene cyclopropane in the presence of Ni(0) complexes. In the absence of other alkenes the products were dimers and trimers (reaction (84)), but cycloaddition occured using methyl propenoate with excellent selectivity (reaction (85)). In the absence of added alkene **448** gave ring opened products, but the cycloaddition reaction was successful, although a mixture of products was obtained. The reactions of **449** were also studied, and the mechanisms of these processes were discussed in detail [871].



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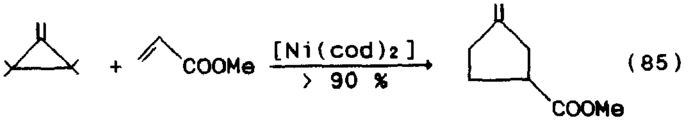

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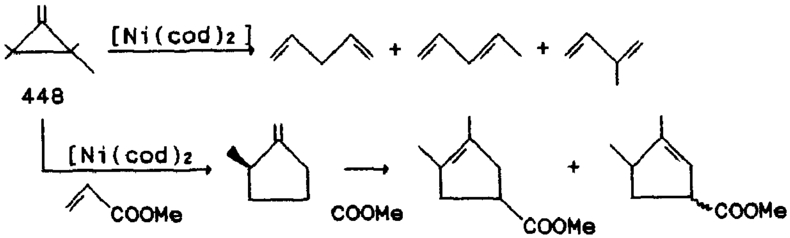
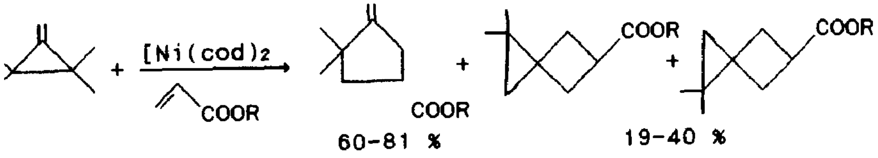
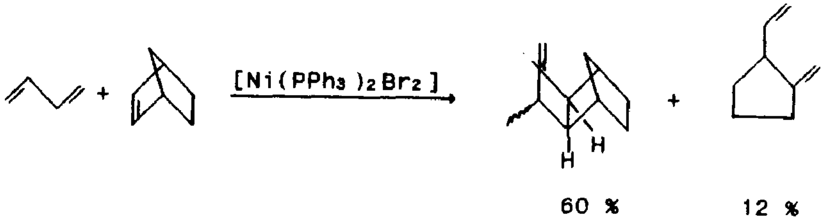


448



449

Couplings to strained alkenes have again been investigated. Norbornene and butadiene underwent 2+2 cycloaddition in the presence of [Ni(PPh$_3$)$_2$Br$_2$] to give 450 as the major product; the *anti*-stereochemistry was carefully assigned [872]. Reaction of aryl bromides with norbornene in the presence of [Pd(PAr$_3$)$_4$] gave mixture of 451 and 452. With (EtO)$_3$CH added as a cocatalyst more 451 was obtained. The reaction was assumed to involve the oxidative addition of the aryl halide to palladium(0) as the initial step [873]. The reaction of norbornene with alkynes in the presence of [Pd(PPh$_3$)$_4$] and ammonium methanoate gave cyclopropanes *via* the mechanism of Scheme 12 [874].



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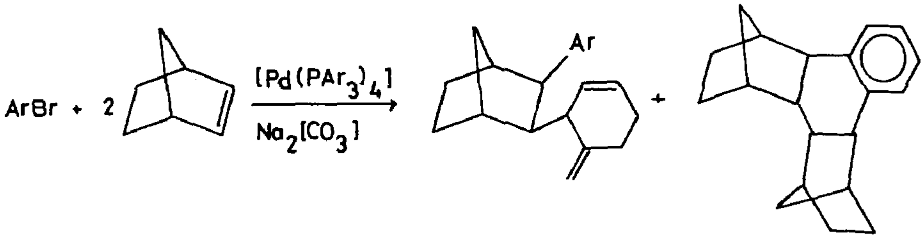
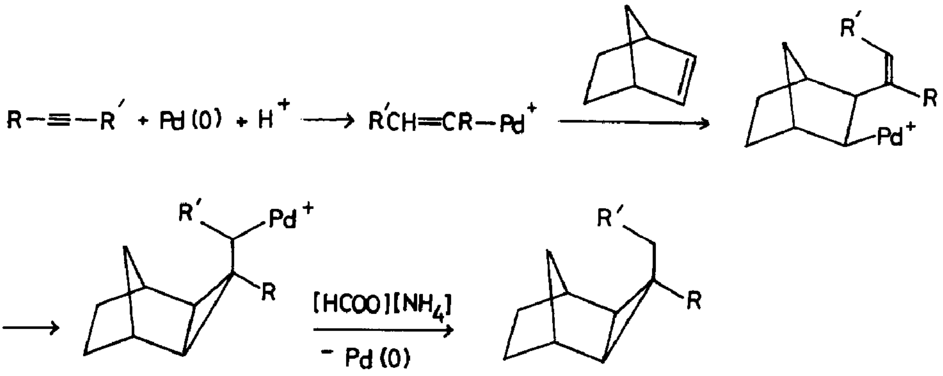
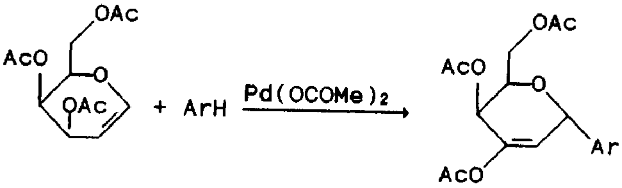


451 452



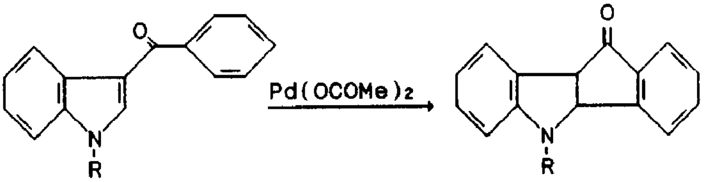
Scheme 12 Mechanism of palladium catalysed reaction of alkynes with norbornene.

Reaction (86) provided a useful synthesis of *C*-aryl glycals. The reaction was thought to proceed *via* addition of {ArPd(OCOMe)} followed by loss of $Pd(OCOMe)_2$ or {HPd(OCOMe)} [875].



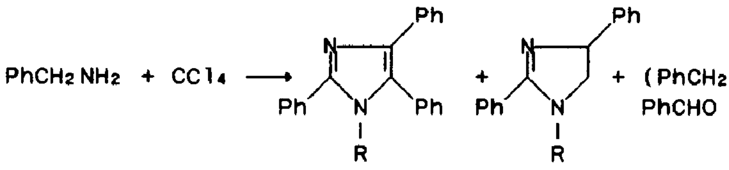
(86)

The intramolecular reaction of **453** in the presence of $Pd(OCOMe)_2$ has been reinvestigated in some detail. The assignment of structure **454** as the product has now been confirmed by an X-ray diffraction study [876].



453 **454**

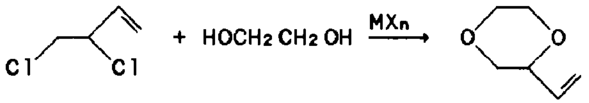
Treatment of ArCOCl with ethene in the presence of $Pd(OCOMe)_2$ gave $ArCH{=}CH_2$ and/or ArCH=CHAr. The yield of the ethenyl arene product increased with an increase in ethene pressure. The reaction presumably involves oxidative addition of the acyl halide to palladium(0) followed by a decarbonylation [877]. A most unusual reaction of $PhCH_2NH_2$ in CCl_4 has been noted (reaction (87), R = H or CH_2Ph). Both $PdCl_2$ and $[Ni(PPh_3)_2Cl_2]$ were catalysts, but in both cases rather inefficient ones [878].



(87)

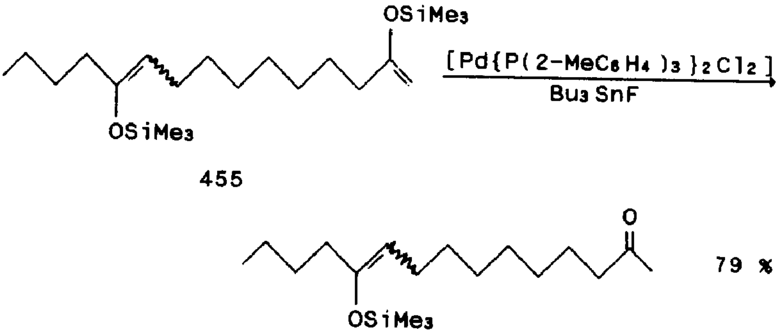
13.11 Other Catalytic Reactions

Reaction of phenols with 2-methyl-2-chloropropane to give the aryl ether was catalysed by [Ni(acac)$_2$] in the presence of Na[HCO$_3$] [879]. PdCl$_2$ catalysed reaction (88), but it was not as successful as CuI [880].



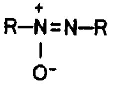
(88)

Hydrolysis of the disilyl enol ether, 455, using Bu$_3$SnF and [Pd{P(2-MeC$_6$H$_4$)$_3$}$_2$Cl$_2$] was extremely selective for the unhindered site. Whilst the reaction will work without a catalyst, it was accelerated dramatically in the presence of the palladium complex [881]. Reaction of α-haloketones with Bu$_3$SnSiMe$_3$ gave a mixture of the ketones and silyl enol ethers in the presence of various palladium catalysts. In the reaction of PhCOCH$_2$Br, the yield of PhCOMe increased with temperature, whilst the best yield of PhC(OSiMe$_3$)=CH$_2$ was obtained at low temperatures and using PdCl$_2$ + 2 P(OMe)$_3$ as the catalyst system [882].



455

The oxidation of RCH$_2$CH$_2$CHO by Ag[OSO$_2$CF$_3$]/[Pd(PhCN)$_2$Cl$_2$]/*N*-Methyl morpholine gave E-RCH=CHCHO [883]. *N*-Hydroxy compounds were oxidised to nitrones in the presence of palladium black. Using PdCl$_2$, Pd(OCOMe)$_2$ or [Pd(MeCN)$_2$Cl$_2$] as the catalyst gave mixtures of nitrones and azoxy compounds, 456 [884].

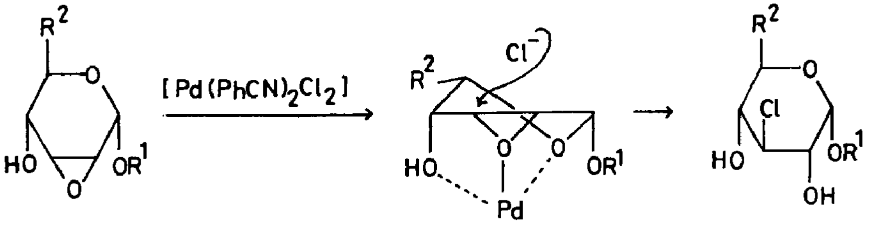


$R-\overset{+}{\underset{O^-}{N}}=N-R$

456

Conversion of *N,N'*-diphenylurea to PhNHCOOEt was accomplished in the presence of $Pd(OCOMe)_2/Cu(OCOMe)_2/CO/EtOH/2,3$-dichloronaphthoquinone/air [885]. In the presence of $NiCl_2$, $PhCH_2NBu_2$ was converted to $MeCONBu_2$ by ethanoic anhydride in excellent selectivity. When $PdCl_2$ was used as the catalyst a mixture of $MeCONBu_2$ (39 %) and $PhCH_2N(Bu)COMe$ (43 %) was produced [886]. Ethanol was converted to ethyl ethanoate in the presence of a range of platinum complexes; $[PtX_6]^{2-}$ gave the fastest rate [887].

The regioselective synthesis of chlorodeoxysugars in the presence of $[Pd(PhCN)_2Cl_2]$ has been described (reaction (89)). The stereochemistry of the product was determined by the most stable conformation of the intermediate. The reaction did not cause epoxide migration and could be used in the presence of acid sensitive functional groups [888,889]. The palladium mediated elimination of ethanoate from **457** has been described; non-allylic oxygen functions were not affected [890].



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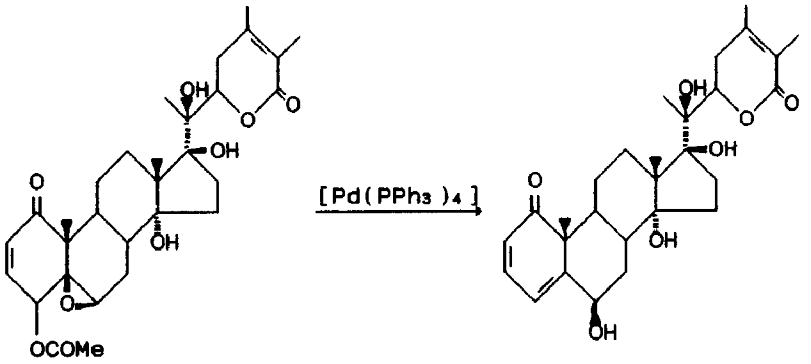
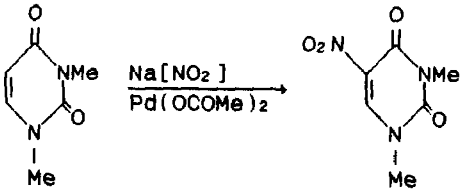


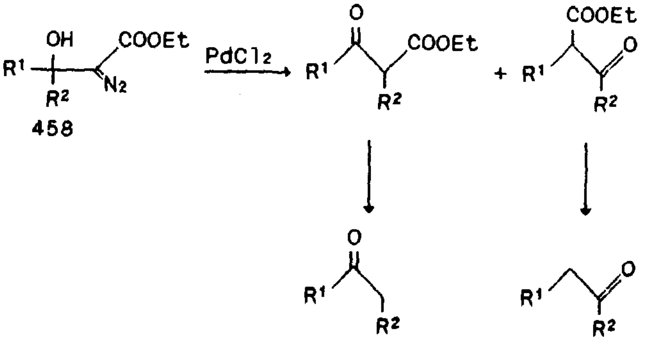
457

Palladium salts supported on Dowex-1, Amberlyst-27, or a polystyrene diethenylbenzene copolymer, catalysed the conversion of cyclohexane hydroperoxide to cyclohexanone and cyclohexanol, together with a small amount of 2-hexenal [891]. Reaction (90) was promoted by $Pd(OCOMe)_2$ [892].



(90)

The diazo compound **458** reacted with migration of one of the R groups in the presence of $PdCl_2$. The less substituted group migrated preferentially, but selectivities were not in general very high [893]. Elimination of R^1X and migration of the aryl group in **459** were catalysed by $PdCl_2$ [894].



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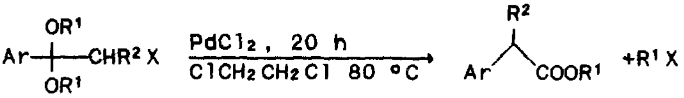

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15 ABBREVIATIONS

A	angstrom
Ac	acetyl
acacH	pentane-2,4-dione
Ar	aryl
bim	2,2'-biimidazole
bipy	2,2'-bipyridine
bipym	2,2'-bipyrimidine
BPPM	2S,4S-*N*-*t*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine
Bu	butyl
cdt	cyclododecatriene
CHIRAPHOS	2S,3S-bis(diphenylphosphino)butane
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
CP*	pentamethylcyclopentadienyl
Cy	cyclohexyl
CYCPHOS	1-cyclohexyl-1,2-bis(diphenylphosphino)ethane
dapm	1-diphenylarsino-1-diphenylphosphinomethane
dba	E,E-1,4-diphenyl-1,4-pentadiene-3-one
DBPDIOP	*trans*-4,5-bis(dibenzophospholomethyl)-2,2-dimethyl-1,3-dioxolan
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dibaH	di*iso*butyl aluminium hydride
dmf	*N*,*N*-dimethylmethanamide
dmpm	bis(bimethylphosphino)methane
dmso	dimethylsuphoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(dipehenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	1,1-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
E	electrophile
EHMO	extended Huckel molecular orbital
en	1,2-diaminoethane
epr	electron paramagnetic resonance
Et	ethyl
FTIR	fourier transform infra-red
hfacacH	1,1,1,5,5,5-hexafluoropentane-2,4-dione
hmpt	hexamethyl phosphoric triamide
HOMO	highest occupied molecular orbital
HPA	heteropolyacid
ir	infra-red
kJ	kilojoule
l	litre
L	2 electron donor ligand
LCAO	linear combination of atomic orbitals
LEED	low energy electron diffraction
LUMO	lowest unoccupied molecular orbital
Me	methyl

mntH$_2$	*cis*-1,2-dicyanoethene-1,2-dithiol
MO	molecular orbital
nbd	bicyclo[2.2.1]hepta-2,5-diene
nmr	nuclear magnetic resonance
Nu	nucleophile
p	pressure
Ⓟ-	polymer backbone
PES	photoelectron spectroscopy
Ph	phenyl
phen	1,10-phenanthroline
PHEPHOS	1-phenyl-1,2-bis(diphenylphosphino)ethane
cis-platin	*cis*-[Pt(NH$_3$)$_2$Cl$_2$]
Pr	propyl
PROPHOS	1,2-bis(diphenylphosphino)propane
py	pyridine
pzH	pyrazole
R	alkyl
SCF	self-consistent field
SIMS	secondary ion mass spectrometry
SW	scattered wave
tcne	tetracyanoethene
tfacac	1,1,1,trifluoropentane-2,4-dione
thf	tetrahydrofuran
tmeda	*N,N,N',N'*-tetramethyl ethane-1,2-diamine
TPPH$_2$	*meso*-tetraphenylporphyrin
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
UV	ultra-violet
UVPES	ultraviolet photoelectron spectroscopy
V	volt
X	one electron donor ligand, usually halide
XPES	X-ray photoelectron spectroscopy
μl	microlitre