Journal of Organometallic Chemistry, 442 (1992) 271–519
Elsevier Sequoia S.A., Lausanne
JOM 22784AS

NICKEL, PALLADIUM AND PLATINUM, ANNUAL SURVEY, 1986*

Penny A. Chaloner

School of Chemistry and Molecular Sciences

University of Sussex

Falmer, Brighton

UK

(Received March 31, 1992)

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*Nickel, Palladium and Platinum, Annual Survey covering the years 1984 and 1985, see J. Organomet. Chem., 432 (1992) 387.
Reprints for this Survey are not available.

1 INTRODUCTION

This survey details the accounts of the organometallic chemistry of nickel, palladium and platinum published in 1986. Material from the patent literature which was reported in Chemical Abstracts in 1986 is also included, and the organisation is broadly similar to that of previous surveys. In view of the time elapsed, there has been much abbreviation of the material, and the author apologises to anyone who feels that their contribution has received less space than it deserves.

A number of reviews of general interest have appeared, including reviews of the coordination chemistry of palladium and platinum in 1982 and 1983 [1,2], and the coordination chemistry of nickel in 1980 and 1981 [3]. The chemistry of iron, cobalt and nickel published in 1985 has been discussed [4] as has the related material for the platinum group metals [5]. Tsuji has published a review of the last 25 years of palladium chemistry [6]. The applications of organonickel complexes in synthesis have been reviewed [7], as have more general applications of transition metals in this field published in 1984 [8]. A wide range of metal complexes were considered in a review of the the reactivity of coordinated ligands [9], and the annual survey of the reactions of selected π-complexes for 1984 was published [10]. Reactions of metal atoms with H_2 and/or methane in inert matrices has been discussed, as have general aspects of C-H activation [11], including reactions of methane with $H_2[PtCl_6]$ [12]. The high resolution nmr spectra of a range of organometallic compounds, incluing many of platinum or nickel have been detailed [13]. Information from molecular spectra and structures of platinum complexes have been considered to derive two empirical "rules" concerning the site of binding of ambidentate ligands [14]. Data concerning ligand substitution reactions of platinum(II) have been considered from the point of view of manifestations of the dependence of the *trans*-effect on the nature of the leaving group [15]. The synthesis and reactions of transition metal complexes with divalent tin and lead as ligands has been reviewed [16].

2 METAL-CARBON σ-BONDED COMPLEXES

Complexes containing only metal-carbon σ-bonds in the iron, cobalt and nickel triads have been reviewed [17], as have transition metal alkyls more generally [18]. In a review of the bonding modes of β-dicarbonyl complexes, many examples are taken from palladium and platinum chemistry [19].

2.1 *Metal Alkyl Complexes*

Reaction of [$NiMe_2(PPh_3)_2$] with Me_3COH gave methane and [$Ni(Me)(OCMe_3)(PPh_3)_2$]. Thermolysis of this complex yielded methane (81 %), ethane (8 %) and 2-methylpropene epoxide (45 %). Deuterium labelling studies indicated that a metallocycle was a likely intermediate. The related palladium complex gave no ethane, more epoxide, and some traces of alkenes [20].

Improved syntheses of [$PtMe_2$(cod)], from various starting materials, have been described [21]. Reaction of [$PtMe_2$(nbd)] with ligands, L, (L = py, NH_3 or dmso or L_2 = bipy, en or tmen) gave *cis*-[$PtMe_2L_2$], the reaction being easier than that of the cod analogue. Attempted reactions with PhCN, MeCN, dmf or water were unsuccessful. Cyanide ion was able to displace either nbd or cod, but there was no reaction with Br^-, Cl^- or $[acac]^-$. Reactions of [$PtMe_2L_2$] with MeI were investigated. For L = nbd, the product was [{$PtMe_3I$}$_4$], whilst for L = py or L_2 = bipy or tmen, [$PtIMe_3L_2$] was produced rapidly at room temperature. Reactions of the en and ammonia derivatives were slow and complex [22]. The preparation of [$PtMe_3$(azol)(L-L) (azol = imidazolate or pyrazolate; L-L = bipy or phen) has been described. Ligand exchange reactions were studied by nmr spectroscopy [23].

Oxidative addition of iodomethane to platinum(II) complexes has been studied. The products from either $K_2[PtCl_4]$ or $K[PtCl_3(C_2H_4)]$ were $K_2[PtCl_5Me]$ and PtI_2, but the alkene complex reacted more slowly because of the lower electron density at platinum [24]. A methylplatinum(IV) complex is also produced from the reaction with $K_2[PtBr_4]$, but this decays, releasing bromide ion [25].

There have been further reports from Abel's group concerning the dynamic behaviour of methylplatinum complexes. The preparation and characterisation of $[PtMe_3\{MeE(CH_2)_nE'(CH_2)_nEMe\}]^+X^-$ has been described [26]. A general method for evaluating rate constants in complex exchange reactions from 2D EXSY (NOESY) nmr spectroscopy has been detailed, and was illustrated by ^{195}Pt two-dimensional nmr spectroscopic studies of the $A \leftrightarrow B \leftrightarrow C$ spin system arising from the inversion of the pyramidal sulphur atom in [$PtMe_3X(MeSCH_2CH_2SMe)$] [27]. The complex [$(PtMe_3X)_2(ECH_2CMe_2CH_2E)$] (E = S or Se), X = Cl, Br or I) is a binuclear structure with a rather strained {Pt_2X_2} ring. Variable temperature nmr spectroscopy identified dynamic processes involving pyramidal inversions of the E atoms and Pt-Me scrambling. $\Delta G^{\neq}$ for pyramidal inversion was 66-75 kJ mol^{-1}, some 20 kJ higher than the usual value for single site inversions, and was clearly associated with the slower synchronous inversions of both E atoms [28]. Reaction of $HC(SMe)_3$ with [{$PtMe_3X$}$_4$] gave [$(PtMe_3X)_2\{HC(SMe)_3\}$] (X = Cl or

Br), and there has been a variable temperature nmr spectroscopic study on the product. Inversion of the pyramidal sulphur atoms was noted as well as a 1,3-metal-pivoting fluxion and scrambling of Pt-Me environments by a {$PtMe_3$} rotation mechanism. The latter two processes are concerted and involve a common transition state [29].

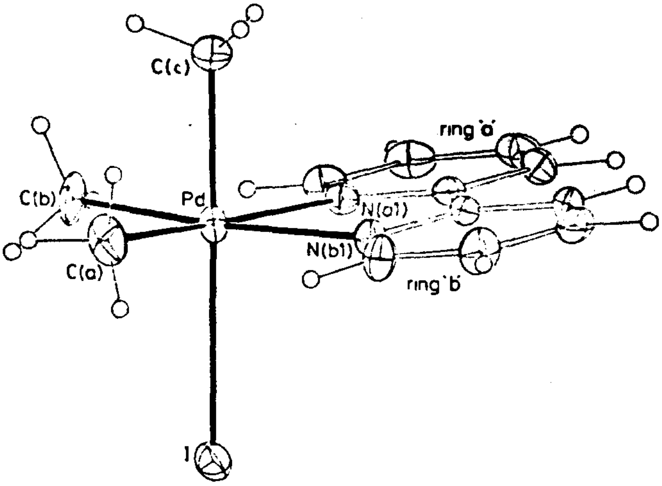
The reactions of CD_3Li with $NiCl_2$, $PdCl_2$ and $PtCl_4$ have been studied. The main products were methane, ethane and ethene, the proportions varying with the metal. The labelling studies suggested that the main mechanism for decomposition of an intermediate methyl derivative was α-elimination to give a carbene intermediate, rather than a radical process [30,31].

Ab initio calculations on {MR_2} have been undertaken to model reductive coupling from [MR_2L_2] ($L = PR_3$). It was concluded that the driving force for reductive elimination from palladium(II) or platinum(II) with the same R approximates to the $s^1d^9 - d^{10}$ splitting, *i.e.* 134 kJ mol^{-1}. Thus the reductive elimination from palladium (prefers d^{10}) is exothermic whilst that from platinum (prefers s^1d^9) is endothermic, when the product complex is d^{10}. The activation barrier for C-C coupling is approximately twice that for C-H coupling, whilst the barrier for elimination of molecular hydrogen was shown to be close to zero. The origin of this trend was shown to be the directionality of the methyl sp^3 orbital which destabilises the transition state for breaking the metal-carbon bond [32]. *Ab initio* calculations have also been undertaken for the systems [$PtMe_2Cl_2(PH_3)_2$] and [$MR^1R^2(PH_3)_2$] (M = Pd or Pt; R^1, R^2 = H or Me). The data explain why C-C elimination is facile for palladium(II), favoured for platinum(IV) and unknown for Pt(II) [33].

The structure of *trans*-[PtMe(MeCOMe)($PPhMe_2)_2$] has been determined in a diffraction study. The platinum adopts slightly distorted square planar geometry, and the propanone ligand has a very weak platinum-oxygen bond and a very small *trans*-influence [34]. The complexes *cis*-[$MMe_2(PR_3)_2$], M = Pd or Pt show very different reactivity, but an X-ray diffraction study showed that they were strictly isostructural. Theoretical studies of the electronic structures of the complexes do not provide an explanation of the fact that the palladium-carbon bond is shorter than the related platinum-carbon bond, and this may be steric in origin [35]. The structures of the complexes of PPh_2Me were detemined at -162 °C. Comparison of the data shows a lengthening of M-C bonds and a shortening of M-P bonds when the metal is changed from palladium to platinum. Other related pairs were compared, and it was concluded that the differences in structure were connected to the ability of the complexes to undergo reductive elimination [36].

Experimental results for high resolution nmr spectroscopy of spin-$\frac{1}{2}$ metals , including ^{195}Pt, in solids have been described. Optimisation of the measurement conditions is discussed, and the complexes considered include *cis*-[$PtCl_4(NH_3)_2$] and *cis*-[$PtMe_2(PR_3)_2$] (R = Ph or Et) [37]. In the latter species it was shown that there are two different platinum-phosphine scalar coupling constants, and an X-ray diffraction study confirms that the phosphine ligands are inequivalent [38].

Oxidative addition of iodomethane to [$PdMe_2$(bipy)] gave *fac*-[$PdIMe_3$(bipy)], 1, the first alkylpalladium(IV) complex to be characterised in an X-ray diffraction study. At 25 °C this decomposes slowly to give ethane and [PdIMe(bipy)], which could also be prepared from *trans*-[{Pd(μ-I)Me(SMe_2)}$_2$] and bipy [39].



1 (Reproduced with permission from [39])

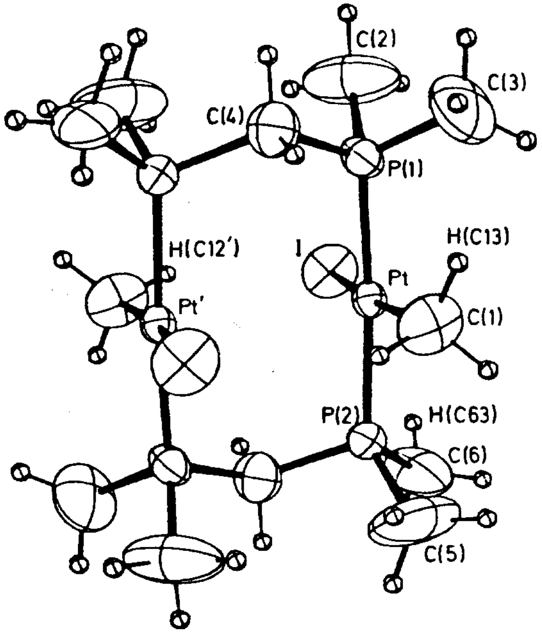
A molecular projection for *fac*[$PdIMe_3$(bipy)], showing selected atomic numbering; 20 % thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms (constrained at estimated idealised positions from difference map locations) have been given an arbitrary radius of 0.1 Å.

The kinetics of the decomposition of [$PtMeCl_5$]$^{2-}$ have been investigated; an S_N2 mechanism with attack of halide at the methyl group explained the observed data [40]. The complex [PtClMe(cod)] did not react with nucleosides, but [PtMe(cod)(MeOH)][NO_3], formed by reaction with Ag[NO_3], reacted with guanosine to give [PtMe(cod)(Guo)][NO_3]. This complex exchanges free and bound guanosine rapidly on the nmr spectroscopic timescale and has substantial *in vitro* cytotoxic activity towards P388 leukemia [41]. Diazomethane reacted with [PtClMe(cod)] to give [Pt(CH_2Cl)Me(cod)], which could also be obtained from methyl lithium and [Pt(CH_2Cl)Cl(cod)]. Reaction of the insertion product with $(CF_3)_2CHOH$ or Ag^+ gave a cationic carbene derivative, [PtMe(=CH_2)(cod)]Cl which rearranged to [PtCl(Et)(cod)]. Further insertions and migrations could be accomplished, providing a model for the polymerisation of diazomethane by transition metal complexes [42].

There have been a number of reports concerning dimeric methylpalladium and methylplatinum complexes. Reaction of [$PdX_2(SMe_2)_2$] (X = Cl, Br or I) with MeI or *trans*-[$PdX_2(SMe_2)_2$] with MeLi/LiI gave [{PdMe(μ-X)(SMe_2)}$_2$]. The stereochemistry of the dimer was shown to be *trans* in an X-ray diffraction study of the chloride [43]. A related phosphine complex, *trans*-[{Pd(μ-Cl)MeL}$_2$] was obtained by reaction of Me_3Al with [{PdCl(μ-Cl)L}$_2$] (L = PEt_3, PBu_3 or PMe_2Ph). Reaction of the dimer with further ligand gave *trans*-[$PdClMeL_2$], whilst carbonylation yielded [{Pd(μ-Cl)L(COMe)}$_2$] [44].

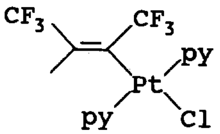
The structure of the complex [$PdCl_2${$Me_2C(pz)_2$}] was established in a diffraction study. There was an agostic interaction between the palladium and the C-Me group [45].

Several reports on related platinum dimers have come from Pudephatt's group. Reaction of *cis,cis*-[Pt_2Me_4(μ-dmpm)$_2$] with two molar equivalents of HCl gave *trans,cis*-[$Pt_2Cl_2Me_2$(μ-dmpm)$_2$]. When dmpm is added to *trans*-[PtIMe(SMe_2)$_2$] the product was *trans,trans*-[$Pt_2I_2Me_2$(μ-dmpm)$_2$], **2**, characterised in a diffraction study. It is thought that steric requirements preclude the formation of the *syn*-isomer in this case. The nmr spectrum of **2** shows fluxionality, and mechanisms for this were discussed [46]. Reaction of [$Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2$] with either [$Pt_2Me_4$($\mu$-$SMe_2$)$_2$] or *cis*-[$PtMe_2(SMe_2)_2$] gave [$Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2$]. Ethene was displaced from the complex by carbon monoxide, disubstituted alkenes or alkynes, and the monomer *trans*-[$PtClMe(C_2H_4)_2$] was formed on treatment with an excess of ethene. Hexafluoro-2-butyne, in the presence of pyridine, gave **3**, by insertion into a platinum-methyl bond [47]. Reaction of [Pt_2Me_4(μ–SMe_2)$_2$] with bipym gave a mixture of [$PtMe_2$(bipym)] and [Pt_2Me_4(μ-bipym)]. Oxidative addition of a range of alkyl halides to these species was investigated [48]. Other studies investigated the related reactions of the ligands, pyen and pypz. Reactivity of both monomeric and dimeric derivatives towards oxidative addition was studied [49]. The oxidative addition reactions of *cis,cis*-[Pt_2Me_4(μ-dmpm)$_2$] with iodomethane have been described [50]. The complexes [$Pt_2X(PPh_3)$(μ–dmpm)$_2$]$^+$ (X = I, Br or Me) have been prepared and characterised. Extensive nmr spectroscopic data were reported [51]. Definitive multinuclear nmr spectroscopic data were reported for [$Pt_2(\mu\text{-}Cl)Me_2$(μ-dppm)$_2$] and [Pt_2Me_3(μ-dppm)$_2$] [52].



2 (Reproduced with permission from [47])

Molecular structure of *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ with vibrational ellipsoids of non-hydrogen atoms displaying 50 % probability. The mid-point of the Pt→Pt' vector coincides with a crystallographically imposed centre of symmetry which related primed with the corresponding unprimed atoms.



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Reaction of $[Pt_2Me_4(\mu\text{-}SEt_2)_2]$ with silver salts of hydroxypyridines, Ag[xhp], in the presence of pyridine, gave $[Pt_2Me_4(\mu\text{-xhp})_2(py)_n]$. A number of the complexes were characterised in diffraction studies, and the geometry of the product complex was dependent on the steric demands of substituents in the xhp ring [53].

The structure of the complex $[Pd\{N(CH_2CH_2PPh_2)_3\}]$ (np_3) has been established in a diffraction study. Only the phosphorus atoms are metal ligated, in a distorted trigonal manner, and there is repulsion between the nitrogen and the palladium. However, reaction with iodomethane or iodoethane gave reasonably stable species, $[PdR(np_3)]I$, in which the metal coordination is trigonal bipyramidal, with the alkyl group *trans* to nitrogen [54].

Gas phase reactivity of first row transition metal complexes with 2-methylpropane has been investigated using a triple quadrupole mass spectrometer. Ni^+ cleaves both C-H and C-C bonds, and there are further reactions of the primary products [55]. Reactions of Pd^+ (as well as Ru^+ and Rh^+) with alkenes in the gas phase have been studied. All of these species dehydrogenate the alkenes by a 1,2-mechanism, in contrast to the 1,4-pathway previously noted for Ni^+. The uniquely high Lewis acidity of Pd^+ results in hydride abstractions as the first step in the mechanism for C-H bond activation, leaving a hydrocarbon-derived species with considerable carbocation character. It was also shown that Pd^+ could insert readily into C-C bonds [56].

The reactions of the macrocyclic complex $[Ni(1R,4R,8S,11S\text{-tmc})]^+$ (tmc = 1,4,8,1-tetramethy-1,4,8,11-tetraazacyclotetradecane) with haloalkenes have been studied. In the presence of base the species $[NiR(tmc)]^+$ was formed, by an electron transfer pathway. The reactions are sensitive to steric constraints [57]. Reaction of $[NiR(tmc)]^+$ with R'X gave various products deriving from combination and disproportionation reactions. The reactivity of R'X increased in the order Me < primary < secondary and Cl < Br < I. An electron transfer process was proposed for the reaction mechanism [58]. The reaction in water with $Br(CH_2)_nCN$ has been specifically investigated [59]. The reaction of the other stereoisomer of the complex, *viz.* $[Ni(R,S,R,S\text{-tmc})]^+$, has been studied kinetically by stopped-flow techniques. The kinetic data indicate that a radical, $R\cdot$, is formed by electron transfer reactions, and this is then captured by a second molecule of $[Ni(tmc)]^+\cdot$ The alkyl product is slowly hydrolysed [60]. The rate was shown to be independent of pH, and to be relatively insensitive to the nature of the iodoalkane [61].

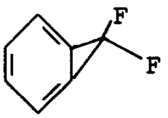
The effect of the nature of the alkyl group in reductive elmination from $[NiMeR(PMe_3)_x]$ ($x = 2$ or 3) has been studied. It was shown that alkyl coupling is intermolecular *via* the formation of a binuclear complex with bridging alkyl groups. Addition of Ni(0) accelarates the reaction by abstracting phosphine ligand [62]. Electrochemical reduction of haloalkenes in the presence of $[Ni(bipy)_2]$ gave RR; dialkylnickel compounds were isolable as intermediates [63].

The thermolysis of $[PdEt_2(bipy)]$ gave ethane and ethene by competitive pathways; ligand dissociation generated the necessary space for β-elimination. However, when methyl propenoate was added to the system to give $[PdEt_2(bipy)(CH_2{=}CHCOOMe)]$, β-elimination was blocked, and reductive coupling gave butane [64]. A similar effect was noted using

E-NCCH=CHCN as the additive. Butane was obtained together with [Pd(bipy)(E-NCCH=CHCN)] [65].

Reaction of $[PtCl_4]^{2-}$ with iodoethane was reversible, giving the unstable species $[PtCl_4R(OH_2)]^-$ and iodide ion. The complex could not be isolated, but was characterised spectroscopically. Reaction with water gave ethanol, and with chloride ion, chloroethane [66]. Under other conditions, with iodoalkanes, the main products were $K_2[PtCl_5R]$, and it was possible to isolate the related caesium salts. Pyrolysis of the complexes for which R = Me or CH_2COMe gave RCl. The reaction rates were different from those observed in solution, and a three-centre transition state was invoked [67].

There has been a review of the synthesis and reactivity of saturated hydrocarbon bridged dinuclear complexes. Among the species discussed were methylene bridged 'A'-frame complexes and $[(cod)Pt(\mu\text{-}C_2F_4)_2Pt(cod)]$ [68]. Reaction of $[Ni(C_2H_4)_3]$ with **4** in the presence of teeda gave **5** identified by nmr spectroscopy [69]. If the reaction was carried out in the presence of a ligand, L, the product was **6**, which could also be prepared from $[NiL_4]$ or $[Ni(cod)L_2]$. The structure of the complex for which L = PEt_3 was established in a diffraction study. The carbon-carbon bond ligated to nickel was 1.514(9) Å long, considerably extended from that expected in an aromatic ring. The complexes are stable at room temperature in the solid state in the absence of oxygen, but revert to starting materials on standing in solution [70].



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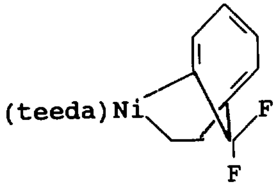

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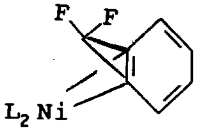

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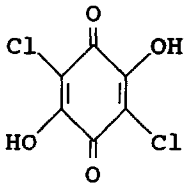
Reaction of $K_2[PtCl_4]$ with **7** gave **8**, identified by comparison with the related palladium complex [71]. The electron impact mass spectra of $[Pt(\eta^1\text{-}C_3H_5)ClL_2]$ ($L = PPh_3$ or L_2 = dppm) and **9** have been discussed in detail [72]. The complex **9** was prepared from an η^1-allyl platinum complex and tcne [73]. Reaction of **10** with *tert*-butyllithium gave the cyclised complex, **11**. The bulk of the base prevents it from abstracting the most acidic hydrogen atom, and it instead deprotonates one of the methyl groups attached to silicon [74]. Oxidative addition of $ICH_2P(=O)(OR)_2$ to $[M(PPh_3)_4]$ (M = Pd or Pt) gave $[M\{CH_2P(=O)(OR)_2\}I(PPh_3)_2]$, both the palladium and platinum complexes being characterised in diffraction studies. The palladium complex decomposed in solution to give $ICH_2P(=O)(OR)_2$ in the presence of air, and mainly $MeP(=O)(OR)_2$ under nitrogen. Reaction of either of the initially formed complexes with $Ag[BF_4]$ gave **12** [75].



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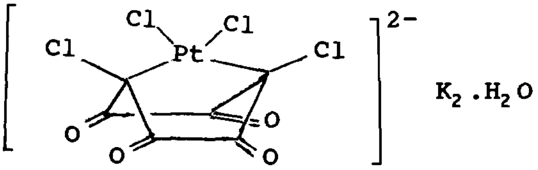

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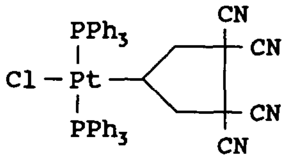

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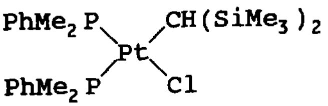

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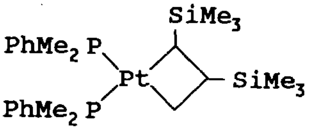

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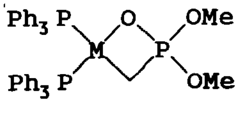

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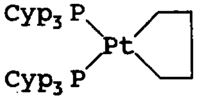
The complex [M(acac-*O,O*)(dppm-*P,P*)][acac] (M = Pd or Pt) has been shown to be in equilibrium with [M(acac-*O,O*)(acac-*C*)(dppm-*P*)] [76].

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $H_2C(SO_2CF_3)_2$ gave *trans*-$[PtH\{CH(SO_2CF_3)_2\}(PPh_3)_2]$, in which there is restricted rotation about the Pt-C bond. Addition of ligands, L, gave *trans*-$[PtHL(PPh_3)_2][CH(SO_2CF_3)_2]$. With weak Lewis bases, however, the product was $[Pt_2(Ph)(PPh_3)_3(\mu\text{-}H)(\mu\text{-}PPh_2)]$ [77].

There have been further reports on reductive elimination from dialkylmetal complexes. Thus **13** (Cyp = cyclopentyl) gave mainly 1-butene and $[Pt(PR_3)_2]$ on thermolysis. The decomposition was slowed both by added phosphine and the products. Deuterium labelling studies indicated that both intra and intermolecular hydrogen transfer were taking place, and cyclometallated intermediates were invoked in the pathways proposed [78]. Reaction (1) was discussed in a review of the activation of C-H bonds [79].



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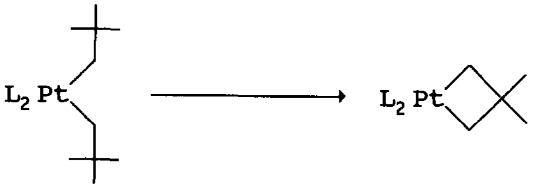
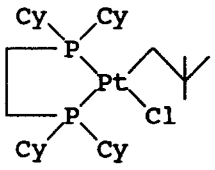


(1)

Reaction of $[PtCl_2(cod)]$ with successively Me_3CCH_2MgCl, concentrated HCl and dcpe gave **14**, which was converted to **15** by $Na[BH(OMe)_3]$. The complex **15** was characterised in an X-ray diffraction study. Thermolysis of **15** resulted in the formation of the transient and highly reactive species [Pt(dcpe)], which may serve as a homogeneous model for an edge atom in a heterogeneous platinum catalyst. Activation and oxidative addition of the C-H bonds of a wide range of compounds was studied, including tetramethylsilane, benzene, cyclopentane, 1,1,2,2,-tetramethylcyclopropane and 1,3,5-trimethylbenzene. Cyclohexane was unreactive [80]. Thermolysis of *trans*-$[Pt(CH_2CMe_3)ClL_2]$ (L = $P(cyp)_3$) gave 1,1-dimethylcyclopropane and *trans*-$[PtHClL_2]$. The reaction mechanism was deduced from kinetic and deuterium labelling studies. The first step is dissociation of L, followed by intramolecular C-H activation to give **16**. Reductive elimination of the cyclopropane is followed by ligand capture. In a related study of **17**, norbornane was reductively eliminated and much of the metal-containing product was a cyclometalled species, though its structure was not definitively established [81]. Protolysis of the analogous complex, *trans*-$[Pt(CH_2CMe_3)Cl(PEt_3)_2]$ has been studied [82]. The complex *cis*-$[Pt(CH_2CMe_2Ph)_2L_2]$ cyclometallates readily to give **18** with ligand loss. This isomerises to **19**, which was characterised in a diffraction study. The distance between the agostic hydrogen atom and the platinum centre was 2.77 Å, and there was a slight tetrahedral distortion of the coordination at the platinum centre [83].



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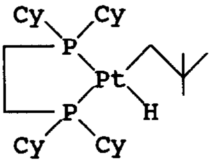

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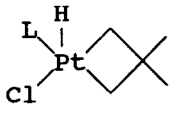

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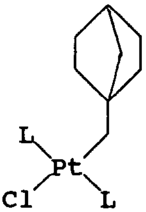

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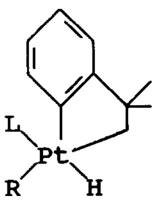

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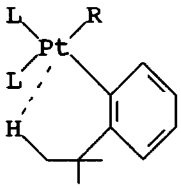


19

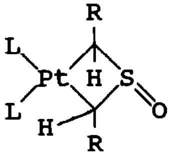
The reductive elimination reactions of monoalkylpalladium complexes which are unable to undergo β-hydride elimination has been investigated. The complex *trans*-[PdCl(CH$_2$Ph)(PPh$_3$)$_2$] was recovered unchanged after heating at reflux for 8 hours in trichloromethane or benzene. However, when [PdCl$_2$(PhCN)$_2$] was added, PhCH$_2$Cl was eliminated, probably *via* a chloro-bridged dimer. When *trans*-[PdCl(CH$_2$Ph)(PPh$_3$)$_2$] was treated with Ag[BF$_4$] in C$_6$D$_6$/CDCl$_3$ the product was C$_6$D$_5$CH$_2$Ph. A radical mechanism for the reaction was ruled out since there was no side chain attack on PhCD$_3$. This represents the first reported example of the electrophilic alkylation of an arene by a transition metal-alkyl compound [84].

The electronic structure of *cis*-[Pt(ascorbate)(NH$_3$)$_2$] has been studied by valence electron SCF calculations. A simpler species, *cis*-[Pt(CH$_2$OH)(OMe)(NH$_3$)$_2$], was used to model the ascorbate complex in a calculation of ligand binding energy. The strength of the platinum-carbon bond was calculated to exceed that of the platinum-oxygen bond by

168 kJ mol^{-1}. The dissociation energies for the NH_3 ligands show the strong effect of the *trans*-influence, with a low dissociation energy for the ammonia ligand *trans* to the platinum-carbon bond [85].

The reaction of $[Ni(CH_2Ph)(PCy_3)X]$ (X = Cl or CN) with oxygen gave benzaldehyde and benzyl alcohol at a rate which depended on X, solvent and temperature. The hydrogen atom needed to form benzyl alcohol is abstracted from the phosphine in a complex of molecular oxygen [86].

Reaction of $PhCOCH_2S(=O)CH_2COPh$ with $[PtCl_2L_2]$ (L = PPh_3) in the presence of Ag_2O gave **20** (R = COPh), the structure of which was determined in a diffraction study. The complex of the related sulphone was also prepared and characterised [87]. Reaction of $[PtMe_2(phen)]$ with RI and CH_2=CHX (X = CN, CHO or COMe) gave the platinum(IV) complex, $[Pt(CHXCH_2R)IMe_2(phen)]$, which was fully characterised. Mechanistic studies indicated that this was produced by a radical chain reaction [88]. Complexes such as **21** have been prepared, and their anti-tumour activity studied [89].



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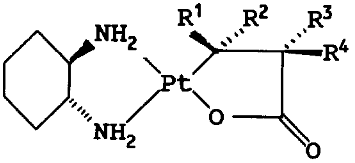


21

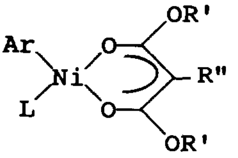
2.2 Metal Aryl Complexes

The reaction of $[Ni(PBu_3)_3]$ with $(4\text{-}MeOC_6H_4)_2S$ gave *trans*-$[Ni(Ar)(SAr)(PBu_3)_2]$, but the complex could not be isolated or purified. The related complex in which Ar = C_6F_5 was more stable, and could be characterised in a diffraction study. This is the first example of the structural characterisation of a complex formed by insertion of nickel into a C-S bond [90]. The reactions of $[NiHBr(PPh_3)_3]$ with various iodoalkenes and iodarenes has been studied. Reaction with iodobenzene gave a rather complex mixture of products, including $[NiI(Ph)(PPh_3)_2]$ [91]. The electrochemistry of $[NiX_2(bipy)]$ and the reactions of Ni(0) with RI depend on the nature of any added ligand. Reactions with bromobenzene have been investigated [92].

^{13}C and ^{1}H nmr spectra of $[M(Ar)X(PEt_3)_2]$ (M = Ni, Pd or Pt) have been reported. Nickel and palladium induce a larger paramagnetic shift at C_{ipso} than does platinum, but there are few differences between the effects of the metals at the other carbon atoms of the aryl ring [93].

Exchange between Ar and Ar' in *trans*-[Ni(Ar)(SAr')$(PEt_3)_2$] and in *cis*-[Ni(Ar)(SAr')(dmpe)] has been shown to involve ArSAr' and {NiL_2} [94]. Reaction of *trans*-[Ni(Ar)(Me)$(PEt_2)_2$] with hydrogen sulphide gave *trans*-[Ni(Ar)(SH)$(PEt_3)_2$] and methane. Thermolysis of the product yielded ArH and $Et_3P{=}S$ as the main products, together with smaller amounts of ArSAr. Reaction of [Pd$(PCy_3)_2$] with ArSH gave [PdH(SAr)$(PCy_3)_2$]. All new compounds were fully characterised [95].

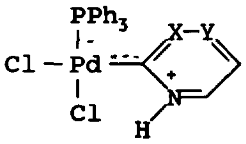
Electrochemical oxidation of [NiRR'L_2], (R, R' = substituted aryl), prepared from R'Li and [NiRXL_2], gave only RR'. The reaction pathway was discussed in detail [96]. Reaction of [Ni(Ar)Cl$(PR_3)_2$] with malonate ion resulted, surprisingly, in the formation of **22**. It was postulated that this is the reason that aryl halides are not readily substituted by malonate under nickel-catalysed conditions. The complex **22** for which Ar = α-Np, L = PPh_3, R' = Et and R" = H was characterised in a diffraction study [97].



22

It has been reported that the reaction of $Pd(OCOMe)_2$ with triphenylphosphine in methanol gave *trans*-[{Pd(Ph)(μ-OCOMe)(PPh_3)}$_2$], characterised in a diffraction study [98]. Treatment of [$PdCl_2(PPh_3)_2$] with RLi gave a species which could not be isolated, but which was relatively stable in solution. Formulations such as {PdLiX$(PPh_3)_2$} or {$PdLi_2X_2(PPh_3)_2$} were proposed for this product. It reacted with iodobenzene to give [PdI(Ph)$(PPh_3)_2$] and with alkenes bearing electron-withdrawing groups to give [Pd(alkene)$(PPh_3)_2$] [99]. There has been a study of the mechanism of oxidation of methylarenes. Both one- and two-electron processes were invoked, and {ArPd(II)} was an important intermediate [100].

Reaction of *trans*-[Pd$(C_6H_4$-4-$CF_3)$I$(PPh_3)_2$] with 2-CH$(OMe)_2C_6H_4$MgBr gave 4-$CF_3C_6H_4C_6H_4$-2-CHO [101]. The complexes [PdCl(Ph)(dppe)] and [Pd$(C_6H_4$-4-$NO_2)$I$(PPh_3)_2$] did not react with NO, but did react with NO_2, to give, respectively, [PdCl(NO_3)(dppe)] and *trans*-[Pd$(NO_3$-*O*$)_2$$(OPPh_3$-*O*$)$$(PPh_3)$], the latter being characterised in an X-ray diffraction study. Reaction mechanisms were suggested [102]. Treatment of **23** with an excess of triphenylphosphine gave **24** which could be deprotonated to **25**. (X = Y = CH, X = CH, Y = N, or X = N, Y = CH). The complexes **25** were in equilibrium with the cyclometallated dimers **26**, the position of the equilibrium being monitored by ^{31}P nmr spectroscopy [103]. Reaction of *trans*-[$PdAr_2L_2$] (L = PEt_2Ph, Ar = C_6H_4-3-Me) with iodomethane gave 1,3-dimethylbenzene with 70 % selectivity, together with some 3,3'-dimethylbiphenyl. Addition of *trans*-[$PdIMeL_2$] resulted in an increase in the reaction rate, and improved selectivity for dimethylbenzene. Kinetic and deuterium labelling studies allowed a mechanism to be proposed; the key intermediate was binuclear with bridging aryl and methyl groups [104].



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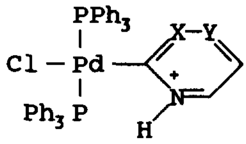

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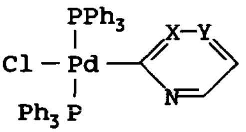

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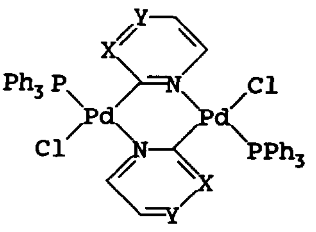

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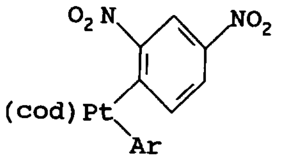
Three papers have reported data concerning the nmr spectra of arylplatinum complexes. ^{13}C and ^{1}H nmr spectroscopic data were correlated with substituent effects in *cis*- and *trans*-[$PtAr_2(PBu_3)_2$] [105]. ^{195}Pt and ^{31}P nmr spectroscopic data were correlated with configuration [106]. IR and ^{1}H nmr spectroscopic criteria for the assignment of stereochemistry have also been discussed [107].

The complexes [PtR_2(cod)] (R = Ph or $PhCH_2$) have been used as fuel additives; they may reduce fuel consumption by up to 3.1 % [108].

Reaction of [$PtCl_6$]$^{2-}$ with ArHgX gave [Pt(Ar)Cl_5]$^{2-}$, but the reaction was unsuccessful with hindered aryl groups. In these cases competing redox reactions were observed [109]. Toluene reacted with [$PtCl_6$]$^{2-}$ at 90 °C, in tfaH, to give [$Pt(C_6H_4$-$CH_3)Cl_5$]$^{2-}$, in which both 3- and 4-isomers were produced. Thermolysis of the product gavce ArAr, with various substitution patterns [110].

The preparations of the complexes **27** and **28** (Ar = 4-XC_6H_4, X = MeO, Me, CF_3 or NO_2, or Ar = C_6H_3-2,4-$(NO_2)_2$) have been discussed. The complexes bearing one electron donating and one electron-withdrawing aryl ring underwent spontaneous reductive elimination of the biaryl. It was suggested that a donor-acceptor interaction was important in the transition state for reductive elimination [111,112]. The synthesis and spectroscopic properties of complexes of the type *cis*-$[Pt(C_6H_4\text{-}4\text{-}X)(Ph)(PPh_3)_2]$ (X = $SiMe_3$, OMe, F, CF_3 or CMe_3) have been described [113]. Reaction of $[PtCl_2(cod)]$ with 1,4-$(SnMe_3)_2C_6H_4$ gave $[Pt_2Cl_2(\mu\text{-}1,4\text{-}C_6H_4)(cod)_2]$, which reacted with 4 molar equivalents of PBu_3 to give *trans,trans*-$[Pt_2Cl_2(\mu\text{-}1,4\text{-}C_6H_4)(PBu_3)_4]$. Reaction of the phosphine complex with phenyllithium yielded *trans,trans*-$[Pt_2Ph_2(\mu\text{-}1,4\text{-}C_6H_4)(PBu_3)_4]$ [114]. Organotin compounds, $XC_6H_4SnMe_3$, were also used to convert $[PtCl_2(cod)]$ to $[PtCl(Ar)(cod)]$. Both these products and $[PtCl_2(cod)]$ reacted with lithiated nitrobenzenes to give $[PtArAr'(cod)]$ [115]. The cyclooctadiene ligand in $[PtAr_2(cod)]$ could be readily replaced by DIOP or related biphosphines. The UV spectra of the complexes were recorded and discussed, as was the wavelength dependence of the photoelimination of ArAr [116]. The complex $[Pt(\alpha\text{-Np-2-OEt})_2(nbd)]$ has been prepared and characterised [117]. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with 1-lithio-2-methylnaphthalene gave *cis*-$[PtAr_2(PPh_3)_2]$ [118].



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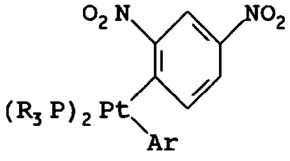


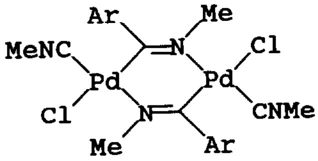
28

Reaction of $[MoI(4\text{-}NHC_6H_4I)\{HB(Me_2pz)_3\}(NO)]$ with either $[Pd(PPh_3)_4]$ or $[Pt(C_2H_4)(PPh_3)_2]$ gave $[MoI\{HB(Me_2pz)_3\}(NO)\{NHC_6H_4M'X(PPh_3)_2\}]$ (M' = Pd or Pt) [119].

Light induced reductive elimination of Ar-Ar from $[PtAr_2(dppe)]$ or $[PtAr_2($*cis*-$Ph_2PCH{=}CHPPh_2)]$ has been studied. The reaction appears to be concerted, and not to involve radical intermediates [120]. Excitation of *cis*-$[Pt(C_6H_4\text{-}4\text{-}X)_2(PBu_3)_2]$ (X = CF_3, Me, OMe or CMe_3) with radiation of wavelengths 287.5 nm or 312 nm gave the 4,4'-substituted biaryl. The complexes were stable to irradiation at 253.5 nm. The elimination reaction is a regiospecific process at platinum, and does not involve radical intermediates [121].

There have been many reports concerning polyhaloaryl complexes. The kinetics of nucleophilic substitution of $[NiBr(C_6Br_5)(PRPh_2)_2]$ by $[SCN]^-$, $[N_3]^-$, $[NO_2]^-$ or I^- have been studied [122]. The reaction mechanism involves competing associative and solvolytic paths [123].

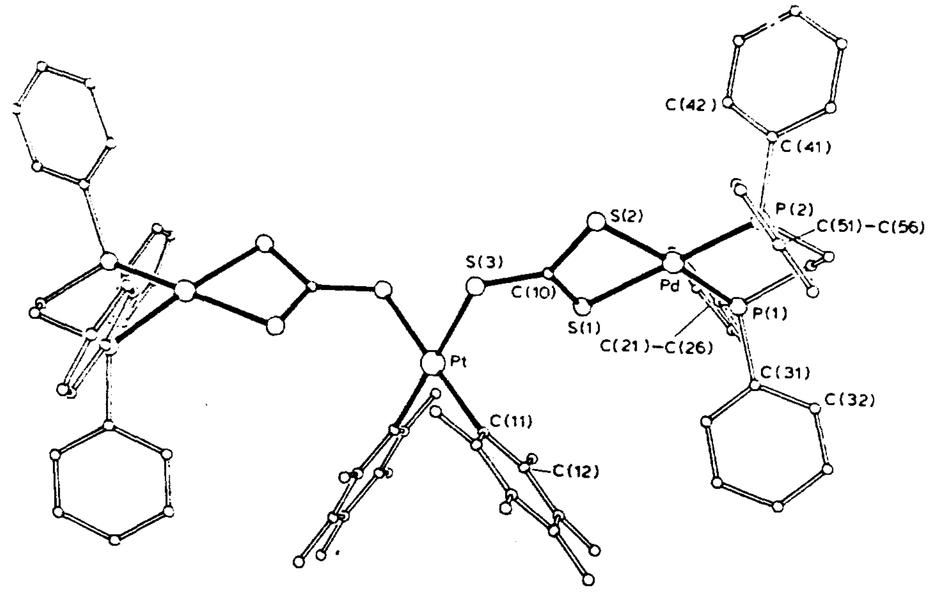
The synthesis of *trans*-$[Pd(C_6Cl_5)X(CNMe)_2]$ (X = Cl, Br I or [SCN]) has been described. Thermolysis resulted in loss of the arene and cyclometallation to **29** [124]. Reaction of $[Pd(C_6F_5)_2(dioxan)]$ with dienes (diene = cod, nbd or dicyclopentadiene) gave $[PdAr_2(diene)]$. These complexes could also be prepared from $[PdAr_2(PhCN)_2]$ and the diene [125]. Treatment of *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ with $[MCl_2L_2]$ (M = Ni or Pd; L_2 = dppe) gave $[PdAr_2(\mu\text{-}Cl)_2L_2]$; spectroscopic date for the products were discussed [126]. Reaction of $[Pd_2(dba)_3]$ with two molar equivalents of $[Pd(Ar)X(\eta^1\text{-}dppm)_2]$ gave $[Pd_2(Ar)X(\mu\text{-}dppm)_2]$ (Ar = X = C_6Cl_5), characterised in a diffraction study. Various insertion and substitution reactions of this type of complex were discussed [127].



29

The use of the complexes $[MAr_2(thf)_2]$ (M = Pd or Pt, Ar = C_6F_5 or C_6Cl_5) as precursors for a range of arylpalladium and arylplatinum comlexes has been reviewed [128]. Reaction of $[MAr_2(thf)_2]$ with $[Cy_3PCS_2]^-$ (M = Pd or Pt); Ar = C_6X_5, X = F or Cl) gave $[MAr_2(S_2CPCy_3)]$ which reacted with a ligand, L (L = PPh_3 or CO) to give $[MAr_2L(\eta^1\text{-}S_2CPCy_3)]$. Both types of complexes were characterised in diffraction studies [129]. When $[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) was reacted with diphenylethyne the product was *cis*-$[M(C_6F_5)_2(PhC{\equiv}CPh)_2]$. Even though there is no significant back-bonding as judged from an X-ray diffraction study, the complexes are stable [130]. When the ligand dppa (dppa = $Ph_2PNHPPh_2$) was added to *trans*-$[Pd(C_6F_5)_2(thf)_2]$ the product was *trans*-$[Pd(C_6F_5)_2(dppa)_2]$. In the platinum series, with *cis/trans*-$[Pt(C_6F_5)_2(thf)_2]$, the products were *cis*- and *trans*-$[Pt(C_6F_5)_2(dppa)_2]$ and $[Pt(C_6F_5)_2(dppa)]$. The complexes *trans*-$[M(C_6F_5)_2(dppa)_2]$ reacted with $Ag[ClO_4]$ to give *trans*-$[M(C_6F_5)_2(\mu\text{-}dppa)_2Ag][ClO_4]$; infra-red spectroscopic studies showed that the NH of the dppa ligand was hydrogen-bonded to the counter-ion. Treatment of $[PdAr(OCLO_3)L_2]$ with dppa gave *trans*-$[Pd(Ar)L_2(\mu\text{-}dppa)Pd(Ar)L_2][ClO_4]_2$ (L = PPh_3, $PMePh_2$ or PEt_3). Reaction of *trans*-$[PdAr_2(dppa)_2]$ with $[Pd_2(dba)_3.CHCl_3]$ gave $[Pd_2(Ar)_2(\mu\text{-}dppa)_2]$, which did not insert CO or SO_2 [131]. Carbonylation of *cis*-$[Pt(C_6X_5)_2(thf)_2]$ (X = F or Cl) gave *cis*-$[PtAr_2(CO)_2]$. The related *trans*-isomer was prepared by carbonylating *trans*-$[Bu_4N][PtCl(C_6F_5)_2(CO)]$ in the presence of Ag[ClO_4]. These complexes reacted with neutral or anionic ligands to give *cis-* or *trans-*[$Pt(C_6X_5)_2(CO)L]^{n-}$ (*n* = 0 or 1) [132].

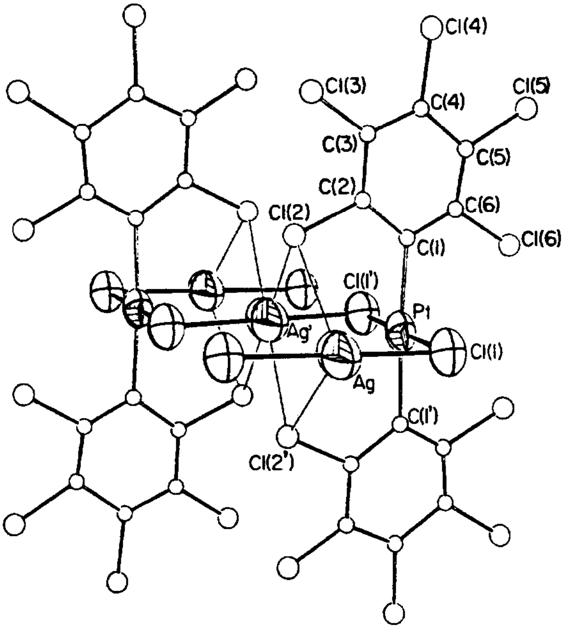
Reaction of [$Pd(C_6F_5)X(\eta^1$-dppm$)_2$] with either [Pt(cod)$_2$] or [$Pt(PPh_3)_4$] gave [PtX(μ-dppm)$_2$Pd(C_6F_5)] (X = Cl, Br or C_6F_5). Chloride could be substituted with [SCN]$^-$, which became *N*-bonded to platinum, and addition of $SnCl_2$ resulted in insertion to give the $SnCl_3$ derivative. A number of insertion products including those with CO, activated alkynes, isocyanides, SO_2, or diazonium cations were prepared [133]. The related bis(platinum) series was also studied [134]. Treatment of [$M(S_2CS)$(L-L)] (M = Pd or Pt; L-L = dppe, dppp or dppb) with [$M'(C_6X_5)_2(thf)_2$] (M' = Pd or Pt, X = F or Cl) gave [{M(μ-S_2CS)(L-L)}$_2$M'($C_6X_5)_2$], the complex **30**, for which M = Pd, M' = Pt, L-L = dppe and X = F being characterised in a diffraction study. Related derivatives of dithiocarbonates were also prepared and characterised [135].



30 (Reproduced with permission from [135])

Structure of [{Pd(μ-S_2CS)(dppe)}$_2$Pt($C_6F_5)_2$] (radii arbitrary, H atoms omitted). The platinum atom lies on a crystallographic two-fold axis at 0,*y*,-1/6.

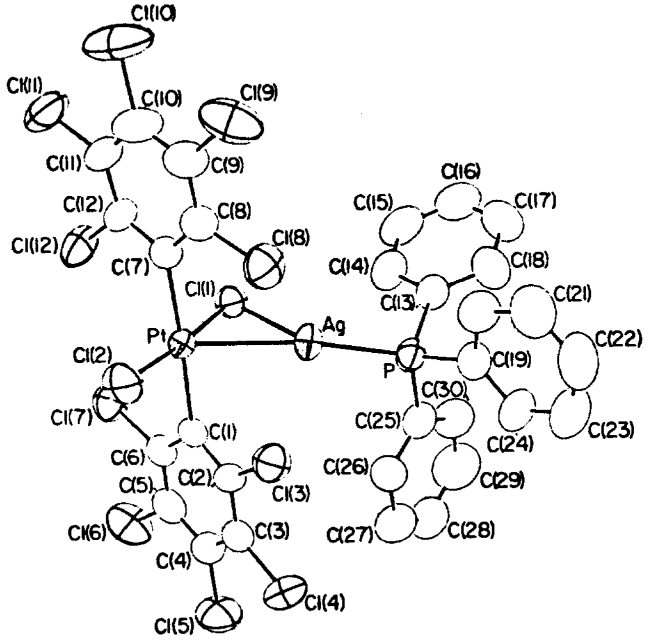
The synthesis and spectroscopic characterisation of [$Bu_4N]_2[Pt(C_6Cl_5)_4$] has been described. Oxidation of this platinum(II) species to the platinum(III) complex, [Bu_4N][$Pt(C_6Cl_5)_4$], could be accomplished using Cl_2, Br_2, I_2 or $TlCl_3$. This was charactersied in a diffraction study, and is the first mononuclear platinum(III) complex to be prepared. It proved to be relatively unreactive, but did react with NO to give [Bu_4N][$Pt(C_6Cl_5)_3(NO)$]. The penatfluorophenyl analogue could not be prepared [136]. Reaction of *trans*-$[Bu_4N]_2[PtAr_2Cl_2]$ (Ar = C_6Cl_5) with $Ag[NO_3]$ or $Ag[ClO_4]$ gave a polymeric species, $[Bu_4N]_x[PtAr_2(\mu\text{-}Cl)_2Ag]_x$, **31**; this reacted with ligands L (L = PPh_3, PEt_3, $AsPh_3$ or $SbPh_3$) to give $[Bu_4N][PtAgAr_2Cl_2L]$, **32**, or $[Bu_4N][PtAgAr_2Cl_2L_2]$ (L = $PMePh_2$, $PEtPh_2$ or PMe_2Ph). These three complexes were characterised in diffraction studies. In **31** the *trans*-$\{PtAr_2Cl_2\}$ units are preserved, and one of the *ortho*-chlorine atoms of the aromatic ring is rather close to the silver atom. In **32** (L = PPh_3) there is a strong, direct platinum-silver bond [137,138].



31 (Reproduced with permission from [137])

ORTEP drawing of one unit of the polymeric anion $[\{Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag\}_x]^{x+}$. Atoms of the C_6Cl_5 ligands are shown as small circles, for clarity. The atoms of the backbone are represented by their 35 % probability ellipsoids.

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $[ArHgPtAr(PPh_3)_2]$ (Ar = tri-, tetra- or pentachlorophenyl) resulted in insertion of the platinum into the arylmercury bond to give $[Hg\{PtAr(PPh_3)_2\}_2]$. Others insertions were also described [139]. When $[Pt(C_2H_4)(PPh_3)_2]$ was reacted with $[Hg(C_6Cl_5)M(Cp)(CO)_3]$ (M = Mo or W), the product was $[Pt(C_6Cl_5)(PPh_3)_2\text{-}Hg\text{-}M(Cp)(CO)_3]$. An X-ray diffraction study established the site of the platinum insertion [140].



32 (Reproduced with permission from [137])

ORTEP drawing of the anion $[PtAgCl_2(C_6Cl_5)_2(PPh_3)]^-$, showing the structure and the atom labelling scheme. All atoms are represented by their 50 % probability ellipsoids.

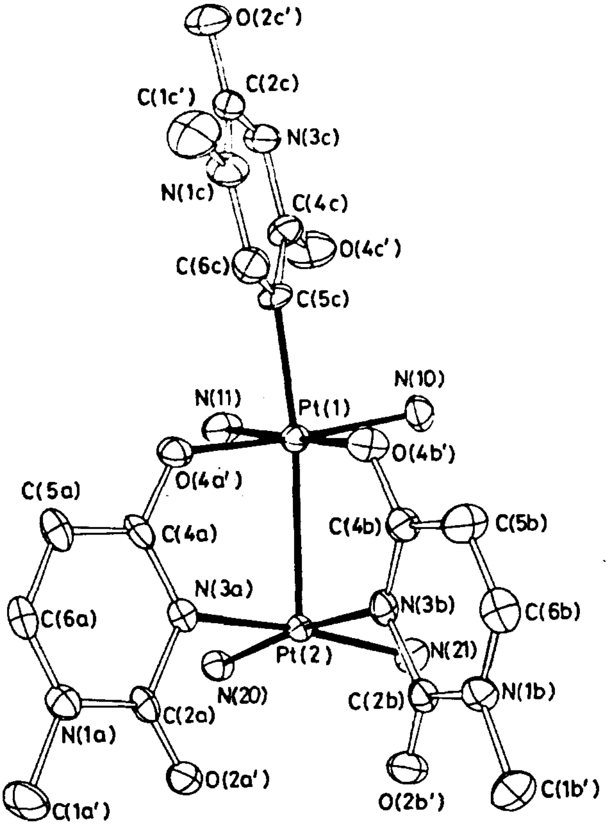
Thermolysis of $[Pt(C_2H_4)(PPh_3)_2]$ gave $[Pt_3(Ph)(\mu\text{-}PPh_2)_3(PPh_3)_2]$; a number of related clusters were described in a review article [141]. The long-lived ($^3A_{2u}$) excited state of the d^8d^8-dimer $[Pt_2(pop)_4]^{4-}$ undergoes reactions with organic substrates, including PhX. The initial product is $[PhPt(pop)_4PtX]^{4-}$, which reacts further to yield biphenyl and $[XPt(pop)_4PtX]^{4-}$ [142].

In studies of platinum complexes for cancer chemotherapy it was found that when $[(NH_3)_2Pt(meu)_2Pt(NH_3)_2(meu)]X_3$ (meu = 1-methyluracil anion) was recrystallised from water and treated with $Na_2[SiF_6]$ the product was $[(NH_3)_2Pt(meu)_2Pt(NH_3)_2(meu)][SiF_6][NO_3]$, **33**, characterised in a diffraction study. This is the first structurally characterised bis{platinum(III)} complex with one five-coordinate and one six-coordinate platinum centre. The bond lengths indicate the high *trans*-influence of the platinum-carbon σ-bond [143].

2.3 Metal acyl complexes

Many metal acyl complexes result from the insertion of carbon monoxide into a metal-carbon bond, and will be considered in the next section. Reaction of $[Ni\{N(CH_2CH_2PPh_2)_3\}]$

([Ni(np$_3$)]) with NCCCOOEt gave [Ni(COOEt)(np$_3$)]$^+$, isolated as the tetraphenylborate salt. With the related nickel triphos complex, the product was [Ni(CN)(COOEt)(triphos)] . Both complexes were characterised in diffraction studies [144].



33 (Reproduced with permission from [143])

Molecular cation $[(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2(C_5H_5N_2O_2)]^{3+}$ with atom numbering.

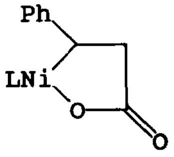
Treatment of FcCOCl with [Pd(PPh$_3$)$_4$] gave *trans*-[PdCl(COFc)(PPh$_3$)$_2$]. This was converted into a range of pyrazolylborane derivatives, the fluxional behaviour of which was studied [145]. Reaction of [PdX$_2$(R$^1{}_3$P)$_2$] with Hg{C(=N$_2$)R}$_2$ gave *trans*-[Pd{C(=N$_2$)R}X(PR$^1{}_3$)$_2$] (R = COOEt or COMe; R^1 = Bu or Ph). With Li[C(=N$_2$)R] as the reagent, the product was *trans*-[Pd{C(=N$_2$)R}$_2$(PR$^1{}_3$)$_2$] (R = COOEt, COMe, Ph, CHMe$_2$, CMe$_3$ or C$_6$H$_4$-4-Me; R^1 = Et, Ph or Bu). Complexes of both types were characterised in diffraction studies. Mass spectrometric fragmentation led to the *in situ* formation of palladium carbene complexes. Their conformations were discussed in detail [146].

Electrochemical reduction of *cis*-[$PtCl_2(PPh_3)_2$] gave a transient 14-electron species, {$Pt(PPh_3)_2$}. This reacted with a wide range of ligands, especially alkynes and underwent oxidative addition of PhCOCl to give *trans*-[$PtCl(COPh)(PPh_3)_2$] [147]. The species derived from the related dppe complex was still more reactive as the 14-electron reduction product is in this case not linear [148].

3 METAL COMPLEXES FORMED BY INSERTION AND RELATED REACTIONS

There have been *ab initio* molecular orbital calculations on the insertion of carbon monoxide into the metal-carbon bond of [$MH(Me)(CO)(PH_3)$] (M = Pd or Pt). It was unequivocally shown that the reaction mechanism involves methyl group migration. The activation energy for the reaction is lower for the palladium complex, and the process is less endothermic, this observation being related to the stronger Pt-CO and Pt-COMe bonds. Substitution of electron-withdrawing groups into the alkyl makes the metal-alkyl bond stronger, and the activation barrier higher [149].

Reaction of phenylethene with CO_2 in the presence of a nickel(0) complex gave **34** and **35**, which reacted with water to yield 3-phenyl- and 2-phenylpropanoic acids respectively. Thermolysis of **34** yielded E-3-phenylpropenoic acid, *via* [LNi(H){OC(=O)CH=CHPh}] [150]. With ethene as the alkene substrate, the product was **36** (L = cod). This reacted with MeOH/HCl to give methyl propanoate, but in the presence of an excess pressure of ethene, **37** was formed. The complex **37** reacted with MeOH/HCl to give methyl pentanoate, or underwent β-hydride elimination to [$LNi(H)\{OC(=O)CH_2CH_2CH=CH_2\}$], which in turn reacted with MeOH/HCl to yield various methyl pentenoates [151].



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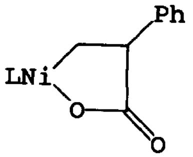

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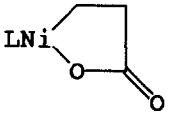

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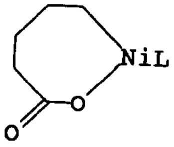
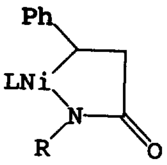


37

The reaction of phenylethene with RNCO in the presence of a nickel(0) complex was regioselective, giving mainly **38** (L = bipy, dcpe, dppe or PCy_3). Hydrolysis of **38** gave $PhCH_2CH_2CONHR$, whilst carbonylation followed by protonation yielded PhCH=CHCONHR [152]. Oxidation of the related complex, **39**, followed by protonation, gave a mixture of RCH=CHCONHPh and $PhNHCOCH_2CH(R)CH(R)CH_2CONHPh$, with the former product predominating in most cases [153]. Spectroscopic characterisation of **38** was reported, and it was shown that phenylethene and PhNCO could be converted catalytically to PhCH=CHCONHPh, if conditions were carefully controlled [154].



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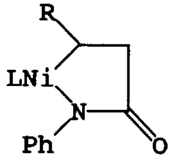
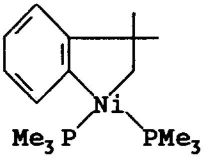


39

Carbonylation of **40** gave **41**, whilst reaction with successively CO_2 and CO gave **42**. With methanal insertion takes place specifically into the alkyl-nickel bond to give **43**, which can be carbonylated to **44** [155].



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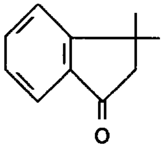

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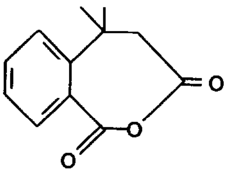

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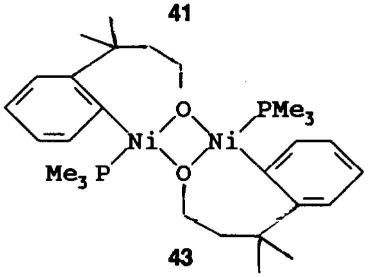

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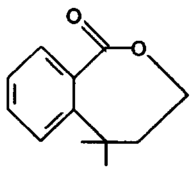
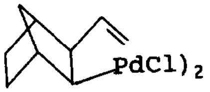


44

Reaction of norbornene with ethenylmercury chloride in the presence of $Li_2[PdCl_4]$ gave **45**. This could be readily carbonylated to give **46** [156]. The related complex **47** was prepared from norbornene and an allylpalladium derivative, and was carbonylated in methanol (R = H) to a mixture of **48** (55 %) and **49** (36 %). The ratio of the products depended on X, and the substituents on the allyl group. Norbornadiene reacted with RCH=CHHgCl and $Li_2[PdCl_4]$ to give **50**. For R = Me, **50** was carbonylated in methanol to give mainly **51** with a trace of **52**, but the outcome depended critically on the reaction conditions and the nature of R [157].



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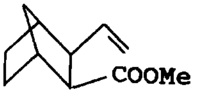

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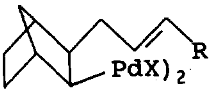

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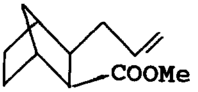

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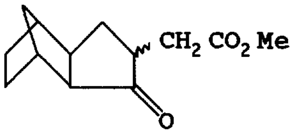

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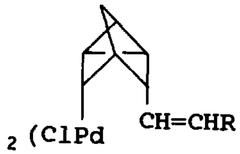

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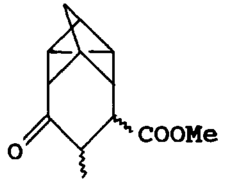

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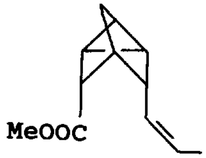
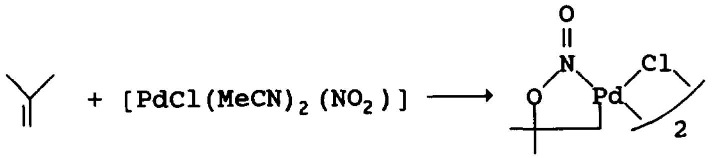


52

The preparations of the complexes, $[Pd_2Cl_2(\mu\text{-dmpm})(\mu\text{-L})]$ (L = CO, MeNC, SO_2 or CS_2), have been described. The complex for which L = CO was characterised in an X-ray diffraction study. CO could be replaced by SO_2, MeNC or CS_2 [158].

Optimised geometries of both the reactants and products have been calculated for the insertion of the alkene into an M-H bond in $[MH_2(CH_2{=}CX_2)(PH_3)]$ (M = Ni, Pd or Pt). Both the activation energy and the nature of the transition state were very dependent on the nature of the metal. A back-donation interaction was responsible for the low activation energy for β-hydride elimination in platinum complexes, by contrast with much higher barriers in the related nickel complexes [159]. Reaction (2) has been reported; carbonylation of the product gave **53** and {PdCl(NO)} [160].



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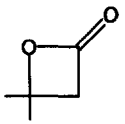


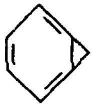
53

Reaction of *trans*-$[PtH_2L_2]$ with RC≡CR resulted in insertion to give the *trans*-product, with both internal and terminal activated alkynes. The structure of *trans*-$[PtH(MeOOCC{=}CHCOOMe)\{P(CMe_3)_2Bu\}_2]$ was established in an X-ray diffraction study. The reaction mechanism was studied in some detail, particularly by epr spectroscopy; radical processes are very significant and steric effects are also important [161]. Insertion of MeOOCC≡CCOOMe into $[Pd_2Cl_2(\mu\text{-}Ph_2Ppy)_2]$ has been noted [162].

The gas-phase chemistry of Ni^+ with alkanes has been investigated. The metal can insert into a range of C-C bonds to give $[RNiR']^+$, but certain types of C-C bonds are strongly favoured [163].

Reaction of **54** with $[Ni(cod)(PMe_3)_2]$ gave **55**, which could be protolysed to **56**, carbonylated to **57** or reacted with H_2O/H_2SO_4 to give **58** [164]. However, with nickel(0) complexes of ligands other than trimethylphosphine the product was more usually **59** (R = Bu, Ph or Et) [165].

Insertion of $[M(C_2H_4)(PR_3)_2]$ (M = Pd or Pt, R = Et or Ph) into **60** gave **61**. The complex **61**, for which M = Pt and R = Et was characterised in a diffraction study [166]. Reaction of **62** with $[PdCl_2(RCN)_2]$ has been studied in detail. Coordination initially involved both the cyclopropane and the double bond, but there was very rapid chloropalladation with cyclopropane ring opening. The initial products of this process were σ,π-chelates, which rearranged to π-allyl complexes [167].



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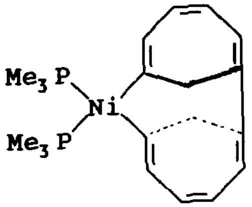

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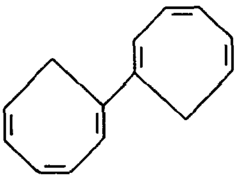

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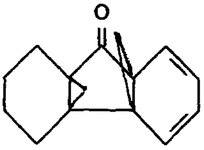

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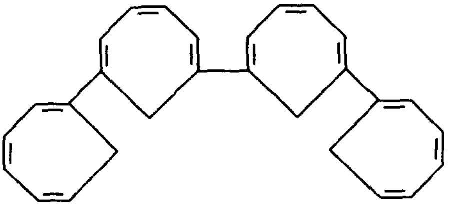

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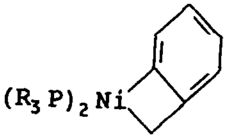

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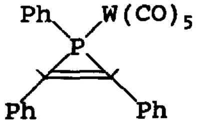

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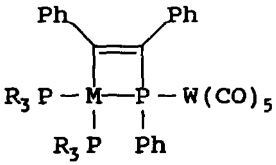
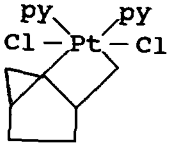


61

62

The insertion of platinum(II) into bicyclopentane had previously been reported. The reaction of **63** with [$\{PtCl_2(C_2H_4)\}_2$] gave **64** and **65**. The product ratio was time dependent, and a detailed reaction mechanism was proposed. The complex **65** could also be prepared from **66** and $[\{PtCl_2(C_2H_4)\}_2]$, and was characterised in an X-ray diffraction study [168]. Reaction of $[\{PtCl_2(C_2H_4)\}_2]$ with **67** gave **68**, which reacted with an appropriate ligand to give **69** as the only isomer detected. Hydrolysis resulted in the formation of **70**. The mechanism of the reaction was discussed in detail [169].

63



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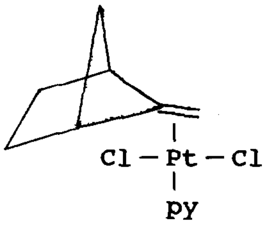

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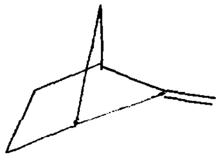

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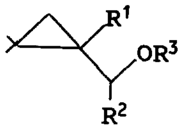

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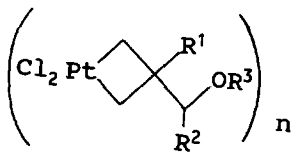

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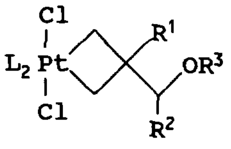

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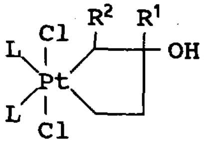
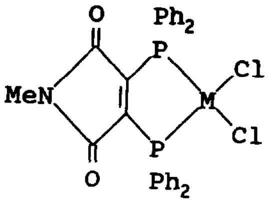


70

The treatment of *trans*-$[PtCl(COR)(PPh_3)_2]$ with $SnCl_2$ gave the related $\{SnCl_3\}$ derivative by insertion, as well as *trans*-$[PtCl\{=C(R)OSnCl_2\}(PPh_3)_2]$ [170]. Reaction of **71** with $[Pt(PPh_3)_4]$ resulted in replacement of the $\{MCl_2\}$ moiety by $\{PtCl(PPh_3)\}$ as well as insertion to give **72**, characterised in a diffraction study [171].



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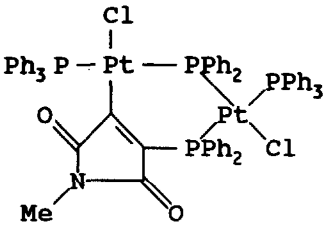
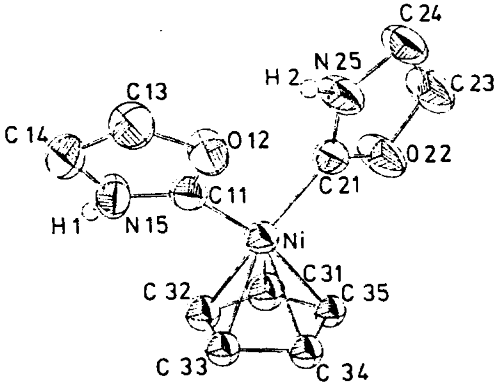


72

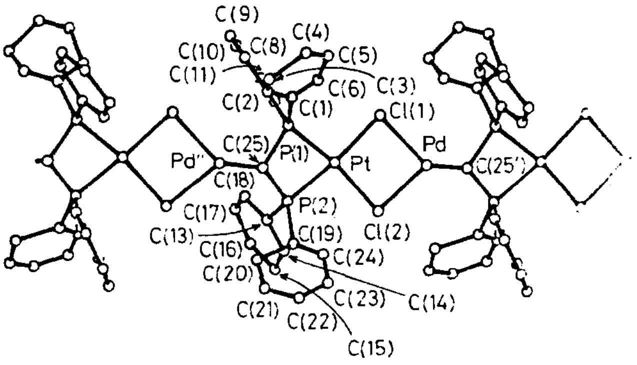
4 METAL CARBENE, CARBYNE AND YLIDE COMPLEXES

The organometallic chemistry of porphyrin complexes, including some carbene derivatives has been reviewed [172]. Metal cluster complexes prepared from [W≡CR(CO)$_2$(Cp)], including many heteropolymetallic carbene and carbyne derivatives of platinum have been reviewed [173]. Reaction of [{Ni(Cp)(CO)$_2$}$_2$] with four molar equivalents of CNCH$_2$CH$_2$OH gave [Ni(Cp)(CNCH$_2$CH$_2$OH)$_2$] which cyclised to **73**, characterised in a diffraction study. Factors influencing the isomerisation were discussed [174].



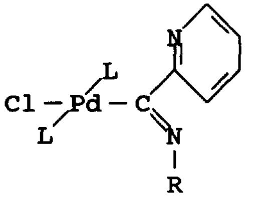
73 (Reproduced with permission from [174])

Calculations have compared the stability of the palladium ethene moiety with a palladium ethylidene complex in [PdCl$_3$(C$_2$H$_4$)]$^-$ [175]. Reaction of [PdCl$_2$(PhCN)$_2$] with [Pt(Ph$_2$PCHPPh$_2$)$_2$] gave an infinite chain mixed metal carbene complex, **74**, characterised in a diffraction study. The same material was obtained, though in lower yield, from [PdPtCl$_2$(μ-dppm)$_2$] and Me$_3$C≡P [176].



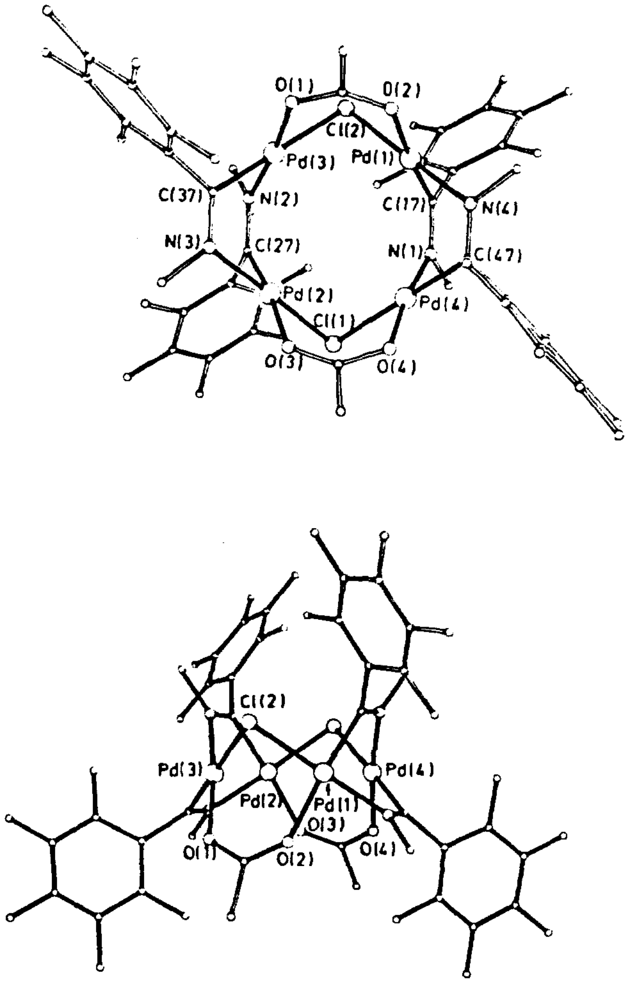
74 (Reproduced with permission from [174])

Treatment of $[PdBr(CH_2COCMe_3)(PPh_3)_2]$ with $[Me_3CO]K$ gave $Ph_3P{=}CHCOMe_3$. The same product was obtained from $Br_2CHCOCMe_3$, $N_2CHCOCMe_3$, $BrCH{=}C(CMe_3)OLi$ or $BrCH{=}C(CMe_3)OSiMe_3$ with $[Pd(PPh_3)_4]$. The intermediate proposed in all the reactions was a palladium alkylidene complex [177]. Reaction of *cis*-$[PdCl_2(PPh_3)_2$(2-pyridylH)] with a ligand, L, gave *trans*-[PdCl(2-pyridylH)L_2]Cl. The chloride ligand could be substitued by RNC, and on treatment with base *trans*-[Pd(2-pyridylH)(CNR)L_2]Cl_2 yielded **75** the conformation of which was studied by nmr spectroscopy. The rate of the migratory insertion reaction was dependent on the nature of the phosphine ligand. The structure of the carbene complex was established in a diffraction study [178]. Reaction of $[\{Pd_2(\mu\text{-}CAr{=}NR')_2(\mu\text{-}Cl)\}]$ with $Ag[OCOR^2]$ gave $[\{(Pd_2\{\mu\text{-}CAr{=}NR'\}_2)(\mu\text{-}Cl)(\mu\text{-}OCOR^2)\}_2]$ (Ar = C_6F_5; R' = Me or C_6H_4-4-Me). The tetrameric nature of the complexes was established as a result of molecular weight determinations, and an X-ray diffraction study on **76** [179].



75

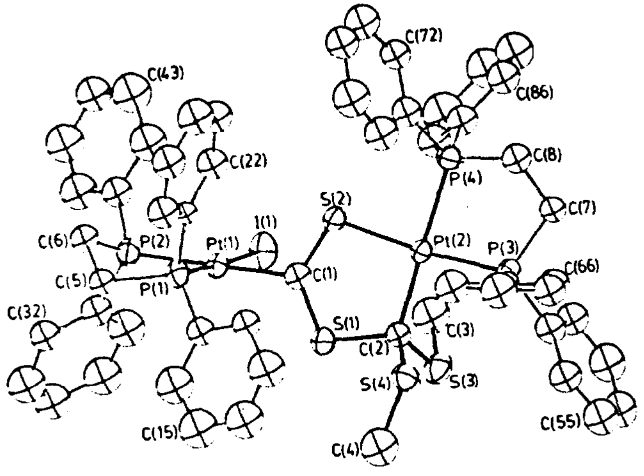
Reaction of $[Pt(dppe)(\eta^2\text{-}CS_2)]$ with iodomethane gave **77**, $[(dppe)IPt\{\mu\text{-}CSSC(SMe)_2\}Pt(dppe)]I$, characterised in a diffraction study. The complex **77** was also obtained from $[Pt(dppe)(\eta^2\text{-}CS_2)]$ and $[PtI(dppe)\{C(SMe)_2\}]I$. This is the first report of the attack of a coordinated CS_2 on a dithiocarbene ligand [180].



76 (Reproduced with permission from [179])
Two approximately perpendicular views of the molecule
$[\{(Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2)(\mu\text{-}Cl)(\mu\text{-}MeCO_2)\}_2]$ showing the atom numbering scheme of the coordination sphere (H-atoms omitted, radii arbitrary).

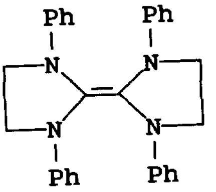
When *trans,trans*-$[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ is treated with **78**, the product is **79** [181]. It has been suggested that the absorption of ethyne on platinum <1.1.1> at low temperature involves μ^3,η^2-binding. A model system has now been studied. Reaction of $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ with ethyne at -80 °C gave **80** which could be observed spectroscopically. On warming this was converted to **81**, which could be isolated [182]. Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with

$[Os_3(CO)_{10}(\mu_2\text{-}CO)(\mu_2\text{-}CH_2)]$ gave $[Os_3Pt(CO)_{11}(\mu_2\text{-}CH_2)(PPh_3)_2]$ in which a diffraction study indicated that the carbene bridges an Os-Pt bond, and the phosphine ligands remain coordinated to platinum [183].



77 (Reproduced with permission from [180])

ORTEP diagram of the cation of $[(dppe)IPt\{\mu\text{-}C(S)C(SMe)_2\}Pt(dppe)]I$ with hydrogen atoms omitted. The thermal ellipsoids are represented by 50 % probability contours.



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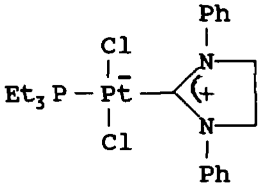

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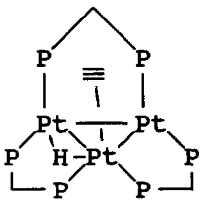

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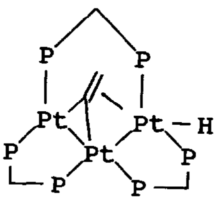
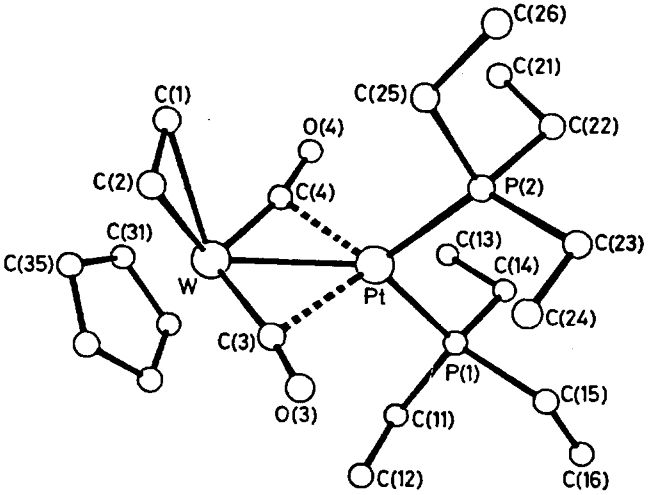


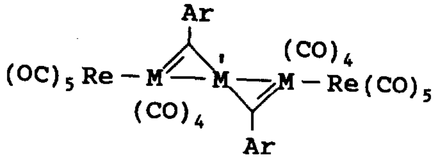
81

There have been further reports from Stone's group concerning carbyne chemistry. Protonation of $[PtW(\mu\text{-}CMe)(CO)_2(PR_3)_2(Cp)]$ (PR_3 = PMe_3, PEt_3, PMe_2Ph or $PMePh_2$) with HBF_4 gave $[PtW(\mu\text{-}CO)_2(PR_3)_2(\eta\text{-}C_2H_4)(Cp)][BF_4]$. The complex **82**, for which R = Et, was characterised in a diffraction study, and was assumed to be formed *via* the methylidene complex. If CF_3COOH was used as the proton source, the product was $[PtW(OOCCF_3)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(Cp)]$. **82** reacted with $Na[BH_4]$ to give $[PtW(\mu\text{-}H)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(Cp)]$ [184]. The preparation of $[PtW(\mu\text{-}CC_6H_4\text{-}4\text{-}Me)(CO)_2(PMe_3)_2\{HB(pz)_3\}]$ from $[RC{\equiv}W(CO)_2\{HB(pz)_3\}]$ and $[Pt(C_2H_4)(PMe_3)_2]$ has been described [185]. Reaction of $[ReM(CC_6H_4\text{-}4\text{-}Me)(CO)_9]$ (M = Cr or W) with either $[Pt(C_2H_4)_3]$ or $[Ni(cod)_2]$ gave $[M_2M'Re_2(\mu\text{-}CAr)_2(CO)_{18}]$, **83** (M' = Pt or Ni). $[ReM(CC_6H_4\text{-}4\text{-}Me)(CO)_9]$ reacted with $[Pt(C_2H_4)_2(PCy_3)]$ to give $[ReMPt(\mu\text{-}CAr)(CO)_{10}(PCy_3)]$. The structure of the related compound, **84**, prepared from $[Pt(C_2H_4)(PMe_3)_2]$, was established in a diffraction study [186]. Treatment of $[Pt(C_2H_4)_3]$ with $[RC{\equiv}W(CO)_2L]$ gave $[PtW_2(\mu\text{-}CR)_2(CO)_4L_2]$. This reacted with one molar equivalent of $[M(cod)_2]$ (M = Pt or Ni) to give $[MPtW_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2]$ and with two molar equivalents of $[Pt(cod)_2]$ to yield $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_2(cod)_2L_2]$. The structure of the complex for which $R = C_6H_4\text{-}4\text{-}Me$ and L = Cp was established in an X-ray diffraction study. The complex consists of two butterfly $\mu_3\text{-}CPt_2W$ fragments sharing a wing-tip platinum vertex. Each terminal platinum bears a cyclooctadiene ligand, and CO semibridges the W-Pt bonds. The complex $[Pt_2W_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2]$ reacted with $[RC{\equiv}W(CO)_2L']$ with displacement of cod to give $[Pt_2W_3(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_6LL'_2]$. In the structure of the complex for which L = L' = Cp there is a planar five-metal atom framework with two edge-bridging and one triply-bridging carbyne. Four of the six carbonyl ligands are semibridging [187]. The structure of $[(\eta^5\text{-}Cp)(CO)_2W\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4\text{-}4\text{-}Me)H\}Pt(PEt_3)_2][BF_4]$, prepared from $[PtH(PEt_3)_2(propanone)][BF_4]$ was determined [188].



82 (Reproduced with permission from [184])

Molecular structure of $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(Cp)][BF_4]$.



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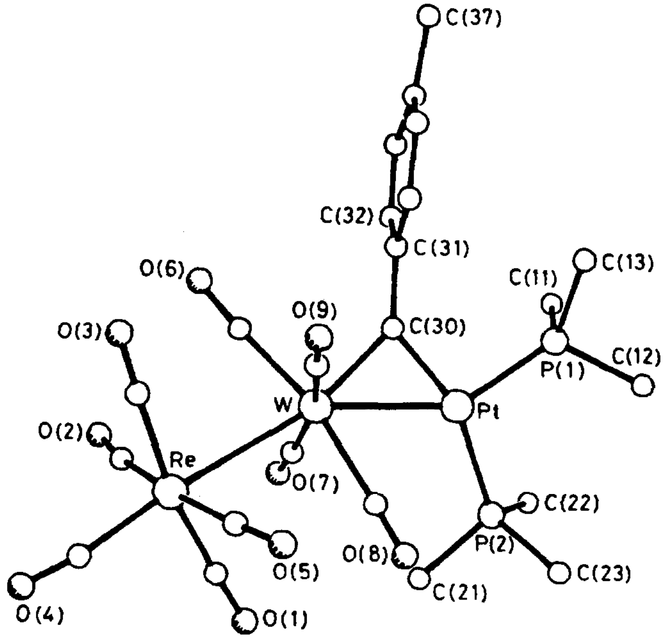
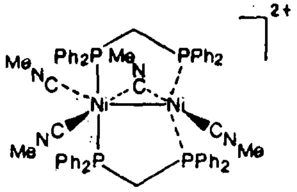


84 (Reproduced with permission from [186])
The molecular structure of [ReWPt(μ-CC_6H_4-Me-4)$(CO)_9(PMe_3)_2$] showing the atom labelling scheme.

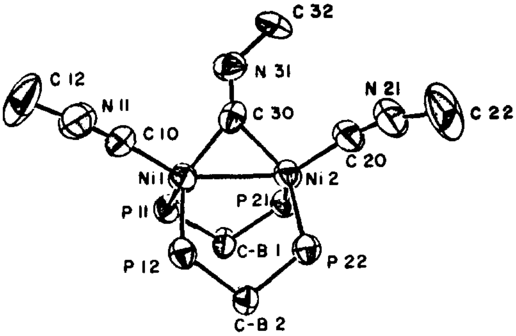
The cluster [$RCCo_3(CO)_9$] reacted with [{Ni(Cp)(CO)}$_2$] to give a mixture of [{NiCp}$_2$Co$(CO)_3$(μ_3-CR)] and [(NiCp){Co$(CO)_3$}$_2$(μ_3-CR)]; several complexes were characterised in diffraction studies [189]. Reduction of **85**, [Ni_2(μ-CNMe)$(CNMe)_3(dppm)_2$][PF_6]$_2$, using sodium amalgam gave the nickel(0) species, **86**, [Ni_2(μ-CNMe)$(CNMe)_2(dppm)_2$]. Protonation of **86** gave **87**, [Ni_2(μ-CNMeH)$(CNMe)_2(dppm)_2$], which seemed to have more aminocarbyne character [190].

Reaction of [Me_3SO]I with [$PdCl_2(PPh_3)_2$] in the presence of Na[OH] and [Bu_4N]I gave a mixture of **88** and **89**, the relative amounts depending on the concentration of Na[OH]. At room temperature **89** was slowly converted to **88**. Reaction of [$PdCl_2(PPh_3)_2$] with the ylid

$Me_2S(=O)CH_2$ gave **88**, **89** and *cis*-$[Pd(CH_2SOMe_2)_2(PPh_3)_2]$ [191]. Reaction of the sulphur ylid with $[PdI_2(PhC{=}CH_2)_2]$ gave a mixture of **90**, **91** and **92**; **92** was characterised in a diffraction study [192].

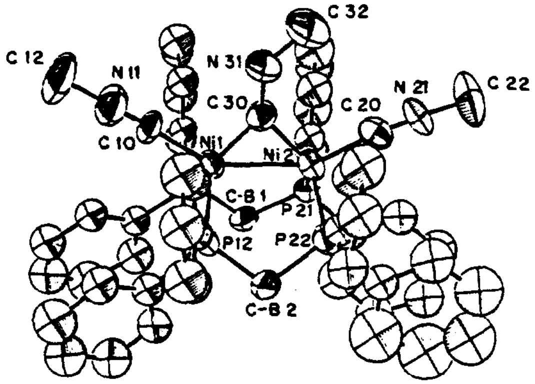


85 (Reproduced with permission from [190])



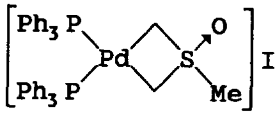
86 (Reproduced with permission from [190])

ORTEP drawing of $[Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2]$ without phenyl rings.



87 (Reproduced with permission from [190])

ORTEP drawing of the $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)_2]^+$ cation, with all non-hydrogen atoms.



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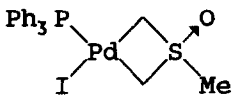

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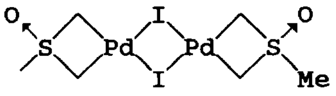

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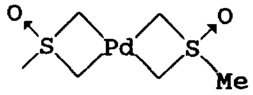

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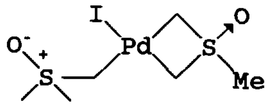
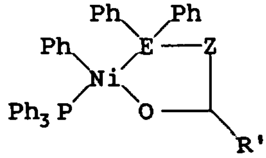


92

The isomerisation of *cis*-$[Pt\{CH_2P(=O)(OMe)_2\}I(PPh_3)_2]$ has been studied by nmr spectroscopy. Interconversion of *cis*- and *trans*-isomers occurred under an atmosphere of CO, but not in the presence of free phosphine. The mechanism proposed involved cyclic ylid complexes [193]. Reaction of $[Pt(PPh_3)_4]$ with CH_2ICl gave $[Pt(CH_2PPh_3)Cl(PPh_3)_3]I$, whilst $[Pt(C_2H_4)(PPh_3)_2]$ yielded $[Pt(CH_2Cl)I(PPh_3)_2]$. Addition of an excess of phosphine to either the *cis*- or the *trans*-isomer of the latter yielded $[Pt(CH_2PPh_3)X(PPh_3)_3]I$, where X = Cl or I, and the chloro complex was characterised in a diffraction study [194].

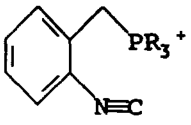
Reaction of $RC(=O)Z=EPh_3$ (E = P or As, Z = CR or N) with $[Ni(cod)_2]$, in the presence of triphenyl phosphine, gave **93**, after transfer of a phenyl ring from E to the metal. The structure of the complex for which E = P and Z = CH was established, and insertion of ethene into the Ni-Ph bond investigated. The resulting $Ni\text{-}CH_2CH_2Ph$ derivative underwent β-hydride elmination to give phenylethene or could be carboxymethylated to yield $PhCH_2CH_2COOMe$. Reactions of phosphorus ylids with other nickel complexes was also discussed [195].



93

Reaction of **94** with various platinum complexes has been studied. With *cis*-$[\{PtCl(PPh_3)_2\}_2][BF_4]_2$, the product was **95**, whilst *trans*-$[PtMe(PR_3)_2(solvent)][BF_4]$

yielded **96**. These and related complexes could be deprotonated with Et_3N to give initially **97**, which isomerised to **98** and **99** [196].



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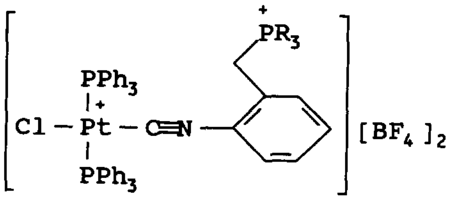

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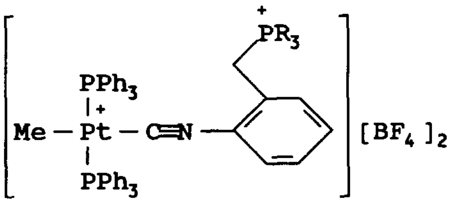

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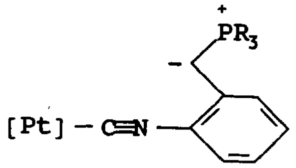

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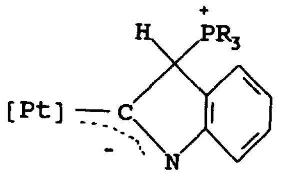

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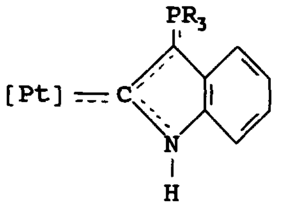


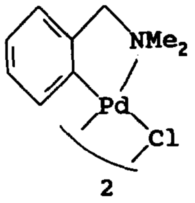
99

5 METAL COMPLEXES FORMED BY INTERNAL METALLATION AND RELATED REACTIONS

The cyclometallation of the platinum metals using nitrogen and alkyl, alkenyl or benzyl carbon donors has been reviewed [197]. In another review of cyclometallation, some alkyne complexes were also discussed [198].

There have been some more reports on cyclometallated derivatives of *N,N*-dimethylbenzylamines. Insertion of an alkyne, RC≡CR, into **100** gave **101** which could lose palladium(0) to give **102**. Alternatively **101** could insert further alkyne to give **103** and **104**. The complex **103** rearranged to **105** and **106**, before losing palladium(0) to give **107** [199]. Insertion of 3,3-dimethylcyclopropene into **100** gave the allyl derivative, **108**,

(R^1, R^2 = H), whereas with 1-carbomethoxy-3,3-dimethylcyclopropene, a mixture of **108** (R^1 = H, R^2 = COOMe) and **109** was obtained [200].



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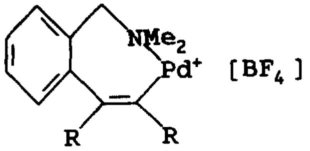

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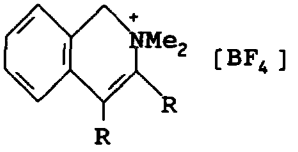

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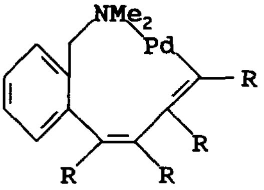

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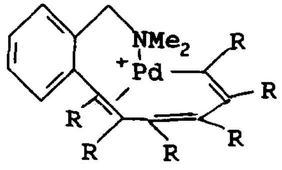

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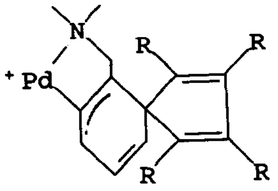

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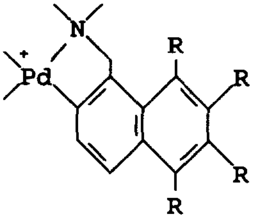

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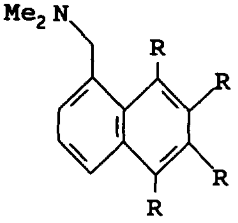

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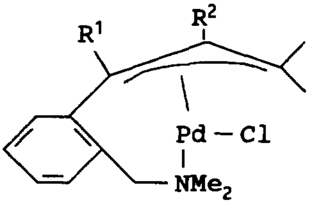

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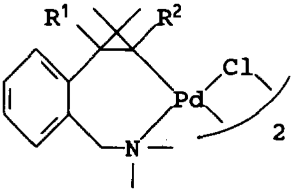
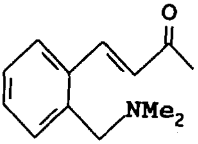


109

It had been previously claimed that reaction of **100** with LiCl gave an anionic species of stoicheiometry $[PdLCl_2]^-$, but this reaction has now been shown to yield $[PhCH_2NHMe_2]_2[PdCl_4]$ [201]. It had also previously been claimed that insertion of 3-butene-2-one into **100** gave **110** in 90 % yield in the presence of triethylamine, but subsequent endeavours gave yields of only 37 % under the conditions which had been described. Better yields were obtained using a mixture of trichloromethane and ethanoic acid as the solvent. If triethylamine was omitted from the reaction only 34 % of **110** was obtained together with 5 % of **111** and 20 % of **112**, this latter being characterised in a diffraction study [202,203]. Reaction of **100** with $PhCH_2PPh_2$ gave a cyclometallated phosphine derivative in low yield, and a similar study was made of carborane substituted phosphines [204]. Exchange of cyclometallated ligand in **100** for another C-N chelate has been investigated [205].



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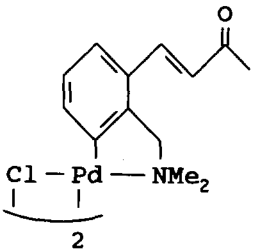
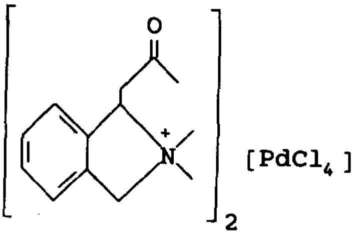


111

Bridge splitting of **100** and related compounds with $[Ph_2PCH_2COO]Na$ has been studied, and one of the products characterised in a diffraction study [206]. Reaction of **113**, a product of insertion into a bis-cyclometallated compound, with PMe_2Ph gave **114** and **115**. Only **114** could be isolated as a pure solid, and its structure was established crystallographically, but **114** and **115** were in equilibrium in solution. The *cis*-isomer of **113** reacted similarly to give a mixture of products [207]. The bis-cyclometallated complex **116** reacted with *trans*-$[PdCl_2(SR_2)_2]$ to give the halo-bridged dimers. The silicon-bearing dimer, **117** reacted with further *trans*-$[PdCl_2(SR_2)_2]$ to give **118**, containing a bridging carbene. Reaction mechanisms were suggested [208].



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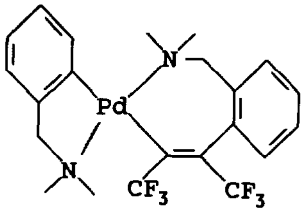

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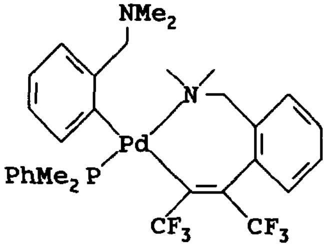

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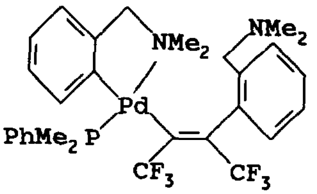

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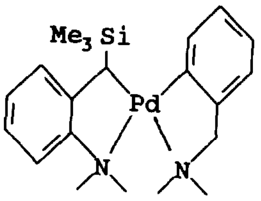

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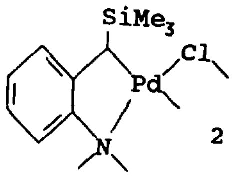

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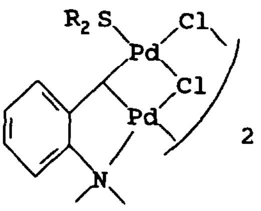
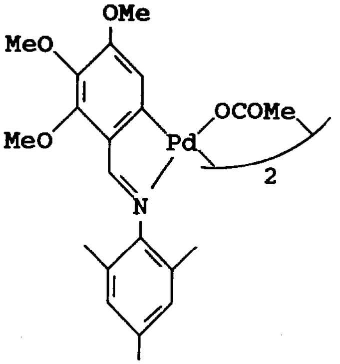


118

The structure of **119** was established in a diffraction study [209]. Reaction of the naphthylamine **120** with $Li_2[PdCl_4]$ gave **121** with good stereoselection at the newly established nitrogen chiral centre [210]. The chirality at nitrogen of one complex was established in a diffraction study after reaction with K[acac] [211]. PhAs(Me)CH_2CH_2SH was resolved by complexation in **122**; the ligand was released after diastereomer separation by treatment with KCN [212].



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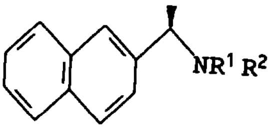

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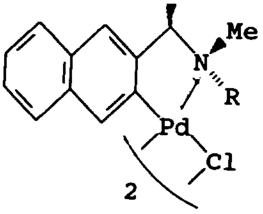

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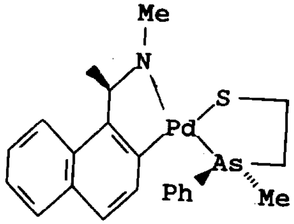
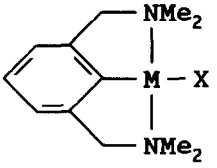


122

There have been several further reports of cyclometallated structures of the type **123**. UVPES data have been reported for the complexes for which M = Ni, Pd or Pt, X = Br and M = Ni or Pt, X = Cl. The experimental data were compared with calculations [213]. Reaction of **123** (M = Pt, X = I) with molecular iodine gave **123** (X = I,I_2) studied by X-ray diffraction. The platinum has a distorted square planar configuration, and the I_2 molecule is η^1-coordinated. Although it might appear that this species would be an intermediate in an oxidative addition, it undergoes no further reaction [214]. Reaction of the cationic version of **123** (M = Pd or Pt, X = OH_2), with the counter-ion as [BF_4] or [CF_3SO_3]) and **124** gave **125** which was the first structurally characterised organometallic complex of a neutral formamidine. Reaction of **125** with Na[OH] resulted in deprotonation to give the neutral species, **126**. In this, at low temperature, nmr spectroscopy indicates that the formamidinate anion is η^1-coordinated, as in the established solid state structure, but at room temperature there is a fluxional process, suggesting that chelate binding may also be important [215].



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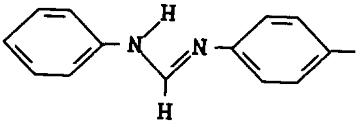

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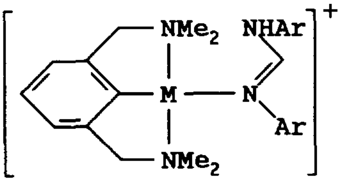

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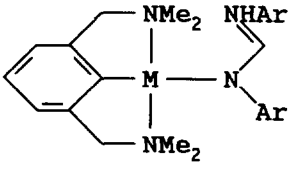
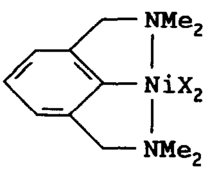


126

There has been a very full report of the reactions of **123** (M = Pd or Pt, X = H_2O) with NaX, and all the complexes have been fully characterised. Reaction of the platinum complex for which X = Br with RLi gave **123** (M = Pt, X = R) [216]. Reaction of **123** with SO_2 at room temperature resulted in the reversible formation of an SO_2 adduct. The structure of the complex for which M = Pt and X = Br was established in a diffraction study; the SO_2 is η^1-ligated, the coordination at platinum is approximately square pyramidal, and the platinum-sulphur distance is quite long. There is no insertion of the SO_2 into the metal-carbon bond, and no formation of sulphate with oxygen [217]. Reaction of **127** with Ag^+ and MX' resulted in halogen exchange for NO_2 or NO_3. With Ag^+ and $[NH_4][NCS]$ the product was **128** (L = H_2O), which reacted with pyridine to give **128** (L = py), characterised in a diffraction study. The epr spectra of **128** (L = H_2O or py) were similar indicating that the Ni(III) had a low-spin d^7-configuration with the unpaired electron associated with nickel [218].



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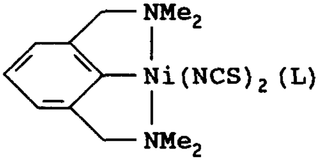
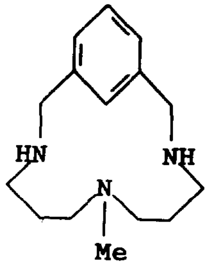


128

Reaction of **129** with palladium ethanoate gave **130**, characterised spectroscopically [219].



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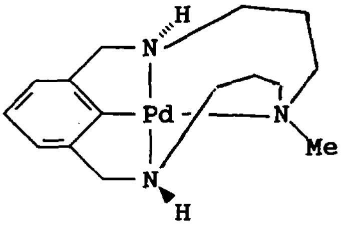
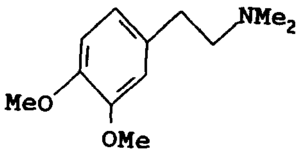


130

A number of other complexes of amines have been reported. Thus **131** reacted with palladium ethanoate to give **132**, which could be carbonylated in the presence of methanol to give an ester, or inserted 3-butene-2-one (after treatment with NaCl to convert **132** to the chloro-bridged analogue) to yield **133** [220]. Mono- and bis-cyclometallation of platinum complexes of phenylalanine has been investigated [221]. Reaction of **134** (M = Pt, X = Y = Cl) with CH_2Cl_2 gave **134** (X = CH_2Cl, Y = Cl) as the sole product, though this does interconvert with the other stereoisomer on warming in $CDCl_3$. It was suggested that the initial product is formed under conditions of kinetic control, by insertion into the Pt-Cl bond with the higher *trans*-influence. Detailed mechanisms were proposed for the reactions [222].



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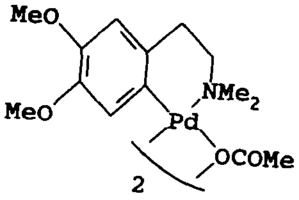

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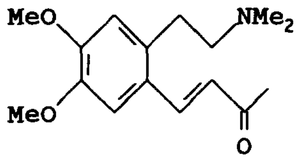

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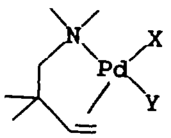
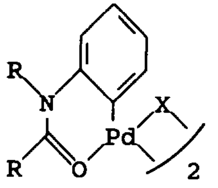


134

There have been a few reports of cyclometallated derivatives of amides. Thus **135** (X = CF_3COO) was prepared from PhNRCOMe and palladium ethanoate in the presence of tfaH [223]. Thermolysis of *trans*-[$PtCl_2$(**136**)$_2$] gave the cyclometallated species **137**, characterised in a diffraction study. The monodentate ligand shows an agostic N-H--Pt interaction, and the agostic hydrogen undergoes relatively easy H/D exchange [224,225].

Reaction of *N,N*-dimethylethanamide with $[PtCl_4]^{2-}$ gave **138**, characterised in a diffraction study. Substantial charge delocalisation was suggested by the observed bond lengths [226].



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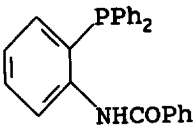

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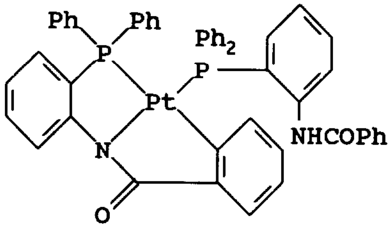

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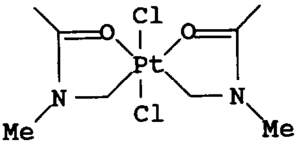
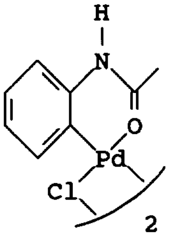


138

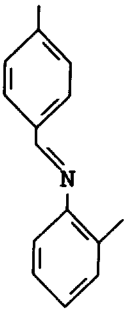
Insertion of phenylethene into the cyclometallated species **139** has been the subject of a kinetic study. It was concluded that the mechanism involved initial coordination of the alkene followed by insertion *via* a weakly polarised transition state [227].



139

Several cyclometallated complexes of imines have been reported. There has been a discussion of the ^{15}N nmr spectra of derivatives of ArCH=NAr'; the dominant factor in determining the value of the ^{15}N chemical shift is the ligand *trans* to nitrogen [228]. The preparation of cyclometallated derivatives of ArCH=NPh with palladium ethanoate has been described; the complexes may be reacted with Ar'MgX , in the presence of a phosphine to give, after hydrolysis, 2-Ar'-ArCHO. Palladium and nickel catalysed coupling reactions are also discussed in this paper [229].

Reaction of **140** with palladium ethanoate gave **141**. Bridge splitting reactions were discussed [230]. The preparation of **142** and its bridge splitting reactions have also been described [231]. Reaction of **143** with palladium ethanoate or lithium chloropalladate gave **144** (X = OCOMe or Cl). Deprotonation of **144** gave the metallo 1,3-dipole **145**, which reacted with **146** to give **147** as a single isomer. Bridge splitting reactions of **144** (X = Cl) were investigated [232].



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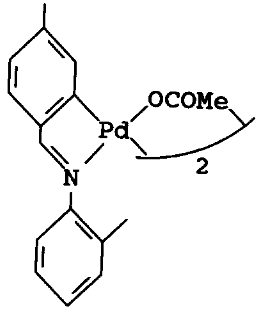

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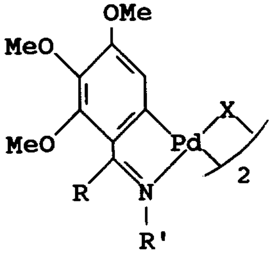

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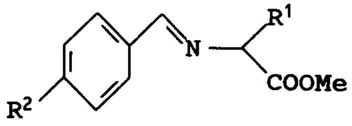

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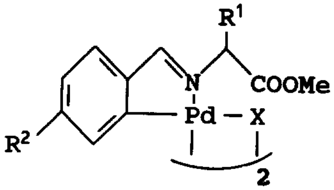

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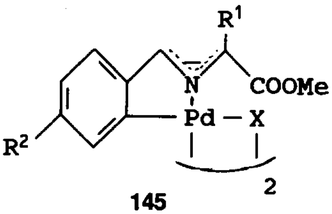
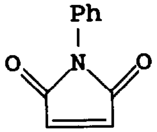


145

Reaction of the imine **148** (*n* = 0, 1 or 2) with palladium ethanoate followed by LiBr gave **149**. This complex is unusual in that cyclometallation reactions usually give five-membered rings; with the imine for which *n* = 1 sp^2-metallation would give a five-membered ring, and metallation of an sp^2-centre is usually favoured over reaction at a saturated site. Bridge splitting reactions were studied, and one of the products was characterised in a diffraction study [233].



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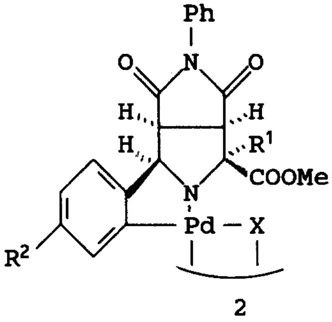

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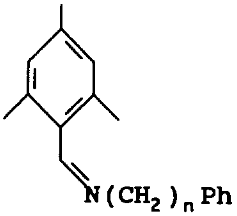

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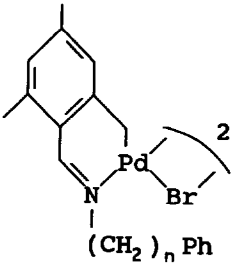
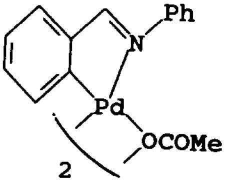


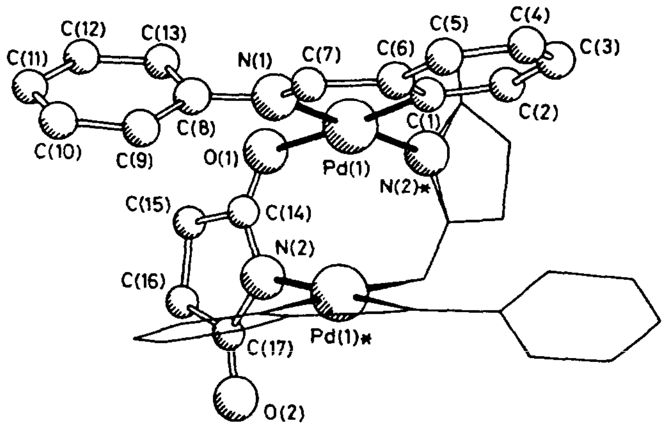
149

Reaction of **150** with the anion of succinimide gave **151**, characterised in a diffraction study [234]. Reactions of **150** with ArCH=NPh resulted in substitution when the incoming ligand bears an electron-withdrawing group. A bis-cyclometallated intermediate was proposed. The usual bridge splitting reactions were also studied for [235]. Coupling of **150** with 2-thienylmagnesium bromide has been reported [236].

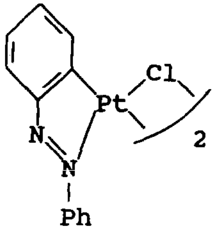


150

Reactions of the cyclometallated azoarene, **152**, have been studied. The bridges were cleaved with carbon monoxide, but the reaction was reversible. Reaction of the monomeric halocarbonyl with TlCp gave **153** [237]. In a further paper from this group the reactions of **154** with phosphines were studied (Scheme 1) [238]. The outcome of the reaction of **155** with $[PdCl_4]^{2-}$ depended on the solvent in which it was undertaken. In ethanol, the product was the cyclometallated derivative **156**, which reacted with water and triphenylphosphine to give **157**. The reaction mechanisms were discussed [239].



151 (Reproduced with permission from [234])



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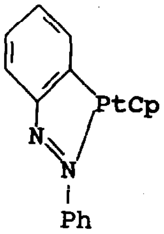
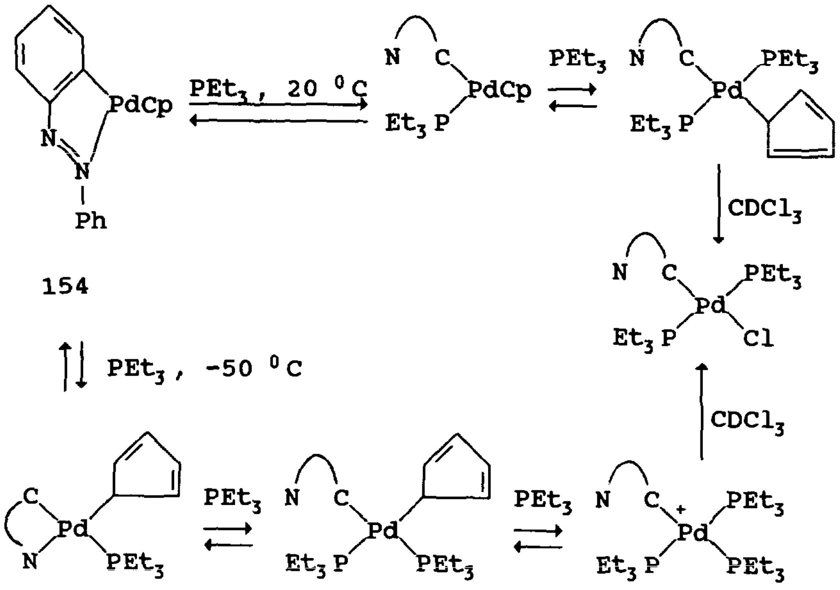


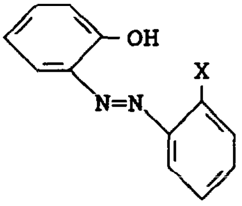
153

The synthesis of the ligand Ph_2PCH_2COPh has been described, and it has been used in bridge splitting reactions with a range of cyclopalladated complexes, including **158** [240]. Metallation of ArCH=N-N=CHAr with palladium ethanoate gave either a monometallated derivative, or the bis-cyclometallated complex, **159**, depending on the reaction stoicheiometry. Species with one ring metallated by palladium and one by platinum were prepared, and bridge-splitting reactions studied [241]. Metallation of **160** resulted in reaction at the methyl group to give **161** [242].

Metallation of pyridine derivatives has again been a popular topic for investigation. Thermolysis of *cis*-$[PtCl_2(py)_2]$ gave a species of stoicheiometry $[PtCl_2(C_5H_4N)_2]$, but the structure was not established definitively. A similar process was reported for the bipy derivative [243]. Reaction of 2-chloropyridine with $[Pd(PPh_3)_4]$ gave **162**, though the reaction needed longer times and higher temperatures than for the related nickel complex. 2-Chloropyrazine reacted similarly, but 2,6-dichloropyridine gave a monomeric complex which was only converted very slowly to a dimer [244].



Scheme 1 Reactions of **154** with phosphines [238]



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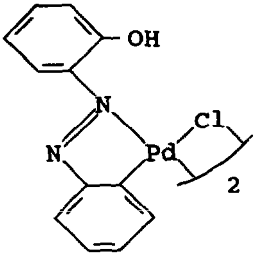
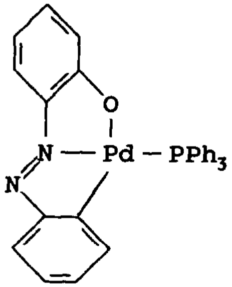


156

Cyclometallation of a quinoline was accomplished by the reaction of **163** with $[PdCl_2(PhCN)_2]$ to give **164** [245].



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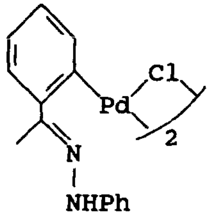

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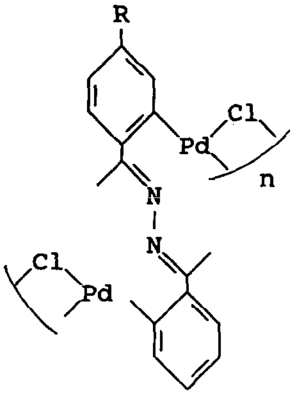

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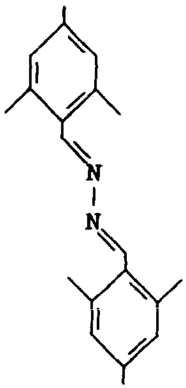

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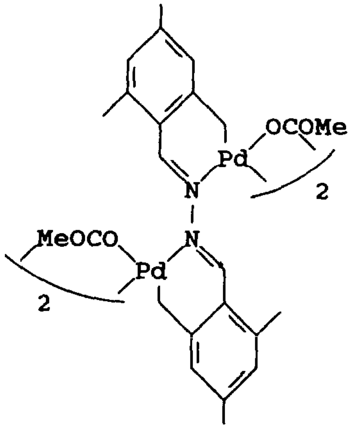

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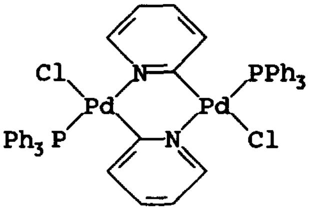

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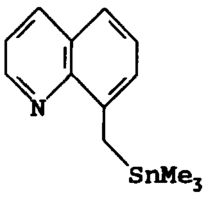

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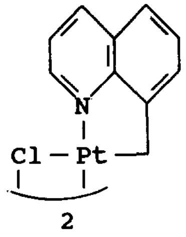
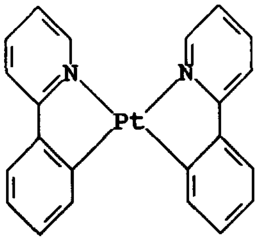


164

The reaction of **165** and **166** with molecular bromine or iodine has been studied, and gave species of stoicheiometry [PtX_2L_2]. Related reactions of other species (*e.g.* MeI, EtI, MeBr or MeCOCl) which could undergo oxidative addition were also studied; initially mixtures of stereoisomeric products were obtained, but on standing, the isomer **167** was the sole product. This could be prepared more rapidly by oxidative addition under photolysis conditions [246]. Photolysis of **165** in CH_2Cl_2 resulted in a simple photooxidation to give [$PtL_2(CH_2Cl)(Cl)$]. The electronic spectrum of **165** was reported; there is a strong and long-lived luminescence with the emitting excited state is the lowest triplet ligand centred excited state, perturbed by metallation [247]. The complex **166** was shown to be photoluminescent in fluid solution at room temperature. In dmf, electrochemical studies showed two one-electron reversible reductions and one irreversible oxidation. In dmf solution electrogenerated chemiluminescence was obtained on pulsing the potential between -1.8 and +0.5 V. The ecl spectrum was identical to the photoluminescence spectrum implying that the chemical reactions which follow the electrochemical processes lead to the same MLCT excited state as is generated by light excitation. Emission was shown to be from the lowest formally triplet MLCT excited state [248]. The dynamics of ring inversion in **168** have been studied spectroscopically, with a range of ligands, L. Inversion rates were insensitive to the electronic nature of L, but were influenced by steric factors. The transition state is planar, but the lowest energy conformation has the six-membered ring in a boat conformation with the aryl rings face-to-face [249].



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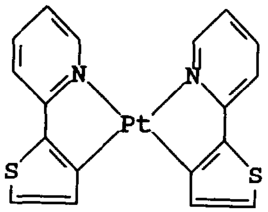

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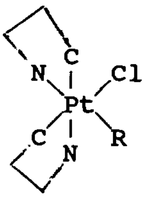

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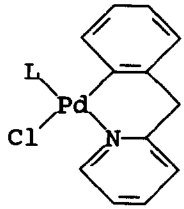
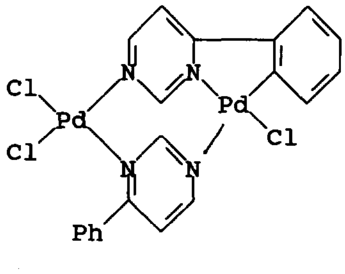


168

Reaction of 4-phenylpyrimidine with palladium chloride in propanone gave the complex *cis*-$[PdCl_2L_2]$, in which N^1 of the pyrimidine is metal coordinated. If the same reaction is carried out in aqueous propanone, the product has the stoicheiometry $[Pd_2Cl_3L(L\text{-}H)]$. Two structures, **169** and **170** were proposed, and some reactions studied [250]. When Ph_2CH-2-py reacted with palladium ethanoate, the product was the cyclometallated species **171** [251].



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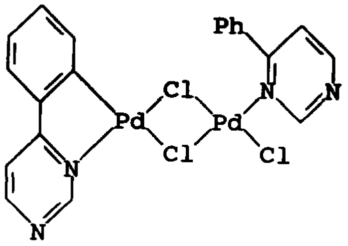
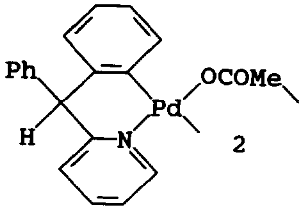


170

The cyclometallation of 6,6'-divinyl-2,2'-bipyridine and related ligands has been studied [252]. The reactions of **172** and **173** with $Na_2[PdCl_4]$ and $K_2[PtCl_4]$ have been studied. The ligand **172** gave conventional bipy derivatives, but **173** gave species of the type **174** with the palladium complex being characterised in a diffraction study [253].



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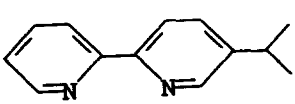

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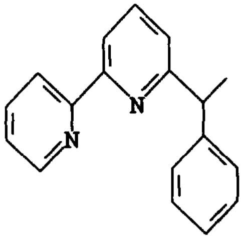

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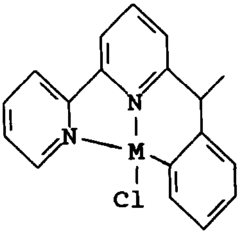
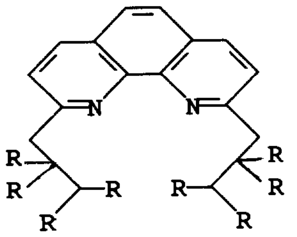


174

Reaction of the bipy derivative, **175** (R = COOEt), with palladium chloride gave **176**, characterised in a diffraction study. With **177**, without the additional ring to augment the ligand "bite", the initial product is a conventional bipy derivative, $[PdCl_2L]$. When this is treated with $K_2[CO_3]$, bis-cyclometallation occurs [254].

There have been a few reported examples of the metallation of 5-membered ring heterocycles. Thus the structure of **178** has been established in a diffraction study [255]. Reaction of **179** with $Li_2[PdCl_4]$ gave *trans*-$[PdCl_2L_2]$, but with further $Li_2[PdCl_4]$ the cyclometallated species **180** was formed, and characterised in a diffraction study. The data obtained show that the Pd-Cl bond *trans* to Pd-C is longer than that *trans* to Pd-N, in accord with the expected *trans*-effect [256].



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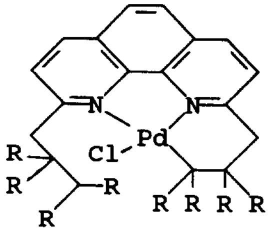

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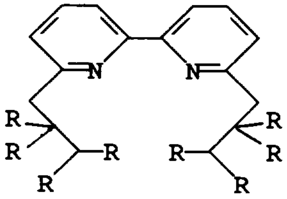

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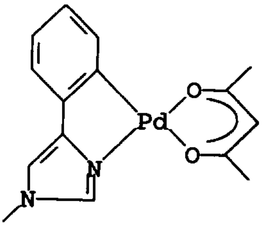

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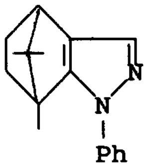

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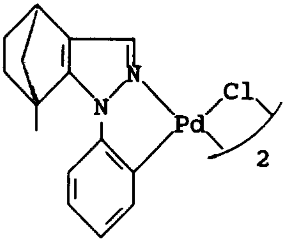
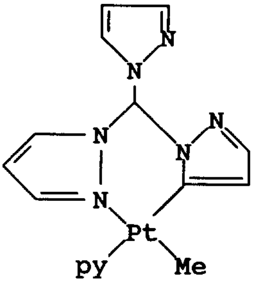


180

On warming the complex of tris(1-pyrazolyl)methane, $CH(pz)_3$, $[Me_2Pt\{CH(pz)_3\}]$, in pyridine, cyclometallation occurred, giving **181** and iodomethane as the initial products. Subsequent oxidative addition yielded the platinum(IV) complex, **182**, characterised in a diffraction study [257]. Reaction of **183** with palladium ethanoate gave **184**. The usual bridge splitting reactions were noted, and carbonylation gave **185** [258].



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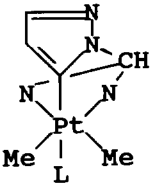

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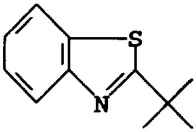

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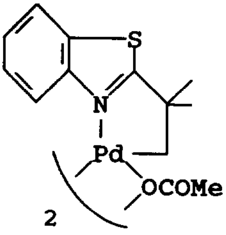

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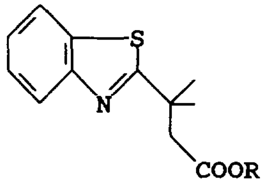
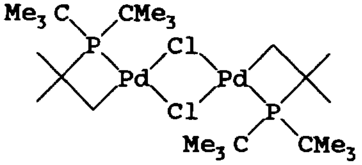


185

There have been rather fewer reports concerning cyclometallated phosphorus ligands this year. Indexed powder data for **186** and **187** have been published, and cell parameters refined [259]. The complex **188** has been shown to be an active catalyst for alkene hydrogenation, although $[PdCl_2\{P(OPh)_3\}_2]$ is inactive [260]. Thermolysis of $[Pt(OMe)_2(dppe)]$ gave methanol, methanal and CO, and **189**. The kinetic data were consistent with an intermediate such as **190**. Various dialkyl and alkoxyalkyl {platinum(dppe)} derivatives were also studied [261].



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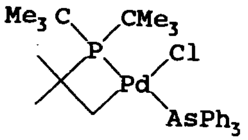

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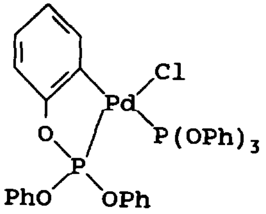

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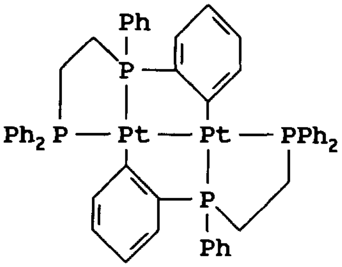

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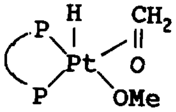
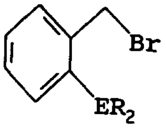


190

Reaction of **191** with [M(dba)$_2$] gave **192** (ER$_2$ = P(CMe$_3$)$_2$ or AsMe$_2$). Bridge splitting reactions were reported, and treatment with 2-LiC$_6$H$_4$CH$_2$PPh$_2$ gave **193** [262]. The ylid APPY, **194**, reacted with platinum chloride to give **195**, and a number of related species were also prepared [263].



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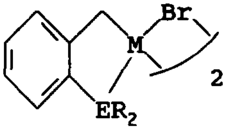

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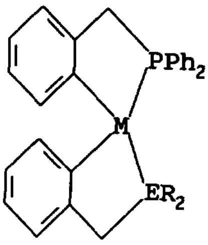

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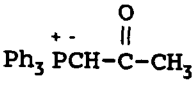
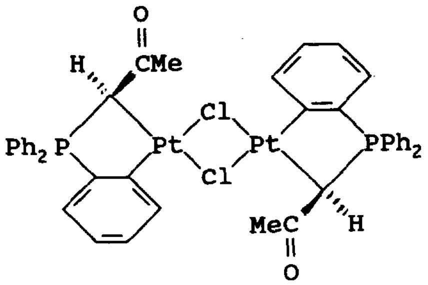


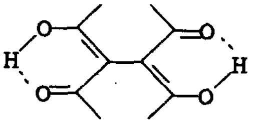
$Ph_3\overset{+}{P}\overset{-}{C}H-\overset{\overset{O}{\|}}{C}-CH_3$

194



195

A range of complexes of **196** have been prepared, in which an $\{ML_2\}$ moiety replaces the hydrogen. In one instance a polymeric species, $[\{Pd(\mathbf{196}\text{-}O,O)(phen)\}_n]$ was obtained, and on attempted dissolution in CH_2Cl_2 this was converted to **197** [264]. Reaction of $Hg(2\text{-}C_6H_4NO_2)_2$ with $PtCl_2$ or $K_2[PtCl_4]$ gave **198**. Reaction with a monodentate ligand such as py, PPh_3 or $AsPh_3$ gave **199** and *cis*-$[PtAr_2L_2]$ in succession [265]. Decomposition of **201** has been studied [266].



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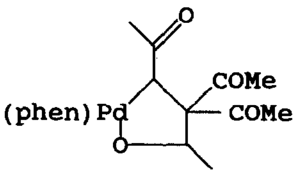

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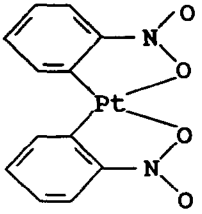

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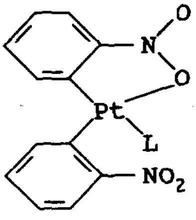

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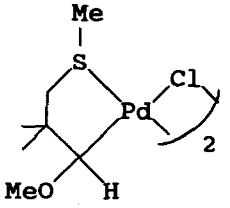

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6 METAL CARBONYL, THIOCARBONYL AND RELATED COMPLEXES

Halocarbonyl complexes of platinum(II) and palladium(II) have been reviewed; nmr and ir spectroscopic data implied that the metal-CO bond has a predominent σ-component [267]. Clusters with opened transition metal polyhedra bearing a wide range of ligands including CO have been detailed [268]. Anionic carbonyl clusters of platinum have been reviewed as homogeneous catalysts for hydrogenation and hydrogen transfer [269]. Heterogenised cluster carbonyls supported on carriers have been discussed [270]. The preparations available for heterometallic carbidocarbonyl clusters have been reviewed, including data on $[Fe_5NiC(CO)_{16}]$ [271]. The infra-red bands from the metal-carbide bonds in such clusters have been discussed [272].

6.1 Mononuclear Carbonyl Complexes

The discrete variation DV-X_α method has been applied to nickel carbonyl and its clusters to investigate core excitation photoemission and inverse photoemission spectroscopy with good results [273]. The nature of CO bonding to transition metal atoms has been analysed using the constrained-space-orbital-variation (CSOV) technique. The cooperative effects for $\{Ni(CO)_2\}$ are different from those for $\{Ni(H_2O)_2\}$, and the bonding in neutral and charged systems is also different. Thus in $\{Ni(CO)\}^+$ there is little π-bonding, but in {Ni(CO)} this is important [274]. Several CSOV analyses were performed for the $^1\Sigma^+$ state of {Ni(CO)}, and it was shown that the importance of the σ-donation from CO, the π-back-donation from Ni and inter-unit polarisations are essentially independent of the order of the CSOV steps, provided that the open-shell 3dσ and 4s nickel orbitals are orthogonalised to the CO. This order of orthogonalisation is consistent with the polarisation of the nickel which is observed in the unconstrained SCF wave function. Comparison of the SCF and CAS descriptions for the $^1\Sigma^+$ state of {Ni(CO)} shows the importance of the s to d promotion and sd hybridisation in reducing the repulsion and increasing the π-bonding [275]. Optimum geometries, vibrational frequencies and IR spectroscopic intensities have been determined by SCF calculations for $\{Ni(CO)_n\}$ (n = 1,2,3 or 4) and some isotopically substituted derivatives. Basis set and correlation effects were examined for {Ni(CO)} to check the reliability of the SCF approach. Detailed comparison with experiment was made [276]. Effective core potentials have been used to study the geometries and binding energies for {M(CO)} and $[M(CO)_4]$ for M = Ni, Pd or Pt). The data obtained correlate reasonably well with experimental data [277]. A procedure for the derivation of an optimised relativistic pseudopotential for platinum has been described, and the results of MO calculations on simple molecules, including {Pt(CO)} given. The bonding was reasonably well described [278].

Exposure of reduced hydrogenase from *chromatium vinosum* to CO resulted in two new epr detectable nickel species, one of which was light sensitive. Illumination of the hydrogen reduced enzyme and the CO treated enzyme gave reversible photodissociation, resulting in the same nickel-containing species. This is in accord with the fact that CO is a competitive inhibitor of the enzyme [279]. The transformation of palladium carbonyl complexes on phosphinated silica in a CO atmosphere has been studied, and the complexes have been used to catalyse hydroformylation reactions [280]. IR emission spectra of CO adsorbed on Pt/alumina have been studied and compared with $[PtCl_3(CO)]^-$ [281].

A preparation of $[Ni(CO)_4]$ from $NiCl_2$, diethylamine and CO in the presence of $[MeOCS_2]K$/MeOH has been reported, but a relatively low yield was obtained, and the reaction mechanism is unknown [282]. Reduction of $[NiCp_2]$ with two molar equivalents of $[V(CO)_6]$ gave $[Ni(CO)_4]$ and $[VCp(CO)_4]$ [283].

Toxicological and environmental properties of $[Ni(CO)_4]$ have again been reported. In a survey of lung function in workers using $[Ni(CO)_4]$ there was found to be little or no change with less than 8 years exposure. However, for males with more than 14 years exposure and females with more than 10 years exposure, there were significant differences from the control group [284]. Toxic effects in workers exposed to 0.007-0.52 mg/m^3 $[Ni(CO)_4]$ over various periods have been studied. EEG profiles were abnormal and MAO levels decreased, implying that $[Ni(CO)_4]$ has neurotoxic effects [285]. Toxic myocarditis, a disorder not previously reported as resulting from exposure to $[Ni(CO)_4]$, was observed in 3 out of a sample of 179 acute $[Ni(CO)_4]$ poisonings in China [286]. Non-occupational exposure to $[Ni(CO)_4]$, mainly from cigarette smoke and automobile fumes, has been studied [287].

Very low concentrations of $[Ni(CO)_4]$ in air have been determined by atomic absorption spectroscopy after preconcentration in a sampling pyrolyzer where $[Ni(CO)_4]$ is decomposed in a graphite crucible [288]. $[Ni(CO)_4]$ at concentrations of 2-50 $\mu g\ m^{-3}$ in air was detected by absorption spectrophotometry following adsorption from 20 L of air by acid washed coconut shell charcoal and desorption with 3 % HNO_3 [289]. A colourimetric method for the determination of $[Ni(CO)_4]$ has also been noted [290].

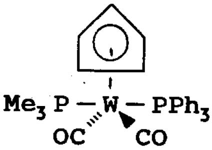
Amorphous alloy coatings were deposited on nickel by decomposition of $[Ni(CO)_4]$; the chemical composition of the coating was investigated using Auger electron spectroscopy [291]. Various experiments have studied the elementary processes involved in laser induced chemical vapour deposition carried out in a pulsed sealed beam of $[Ni(CO)_4]$. These included scattering experiments on real surfaces and deposition experiments under collision free molecular beam experiments [292]. Absorption and thermal decomposition of $[Ni(CO)_4]$ in the cage system of zeolite Y was studied with EXAFS, electron microscopy and IR spectroscopy. $[Ni(CO)_4]$ is absorbed intact in both cation free zeolite Y and NaY. The symmetry changes in NaY were ascribed to the formation of $Na^{+}\cdots OC\text{-}Ni$ bridges. Heating the $[Ni(CO)_4]$/NaY adduct led to the loss of CO, concomitant with the formation of a bimodal nickel phase. Ni-Ni scattering indicated that there was an increase in average particle size with an increase in temperature [293]. Interaction of CO with reduced NiNaY ar NiHY was studied. The samples adsorbed CO onto Ni^{2+} and Ni^{+}, and two forms of adsorbed $[Ni(CO)_4]$ were formed in a slow reversible reaction [294].

A spectroscopic paramatrisation of the CNDO method has been reported for Ni and palladium; $[Ni(CO)_4]$ and $[Pd(CO)_4]$ were used as tests [295]. Recently developed Gaussian basis functions were used in calculations on the ground electronic state of $[Ni(CO)_4]$ [296]. LCGTO-X_{α} calculations on $[Ni(CO)_4]$ gave satisfactory agreement with experimental data for M-C bond lengths and force constants. The deviations were less than in Hartree-Fock calculations [297]. CAD/CAM technology for realtime-simulation of the spectra of molecules, including $[Ni(CO)_4]$, has been described [298].

The HeI (21.2175 eV) PE spectrum of $[Ni(CO)_4]$ has been reinvestigated with improved resolution and molecular beam sampling. The $9T_2$ and 2E PE bands were shown to be intrinsically diffuse, which is attributed to D_{2d} geometries. The ordering of the next seven outer valence electronic states was proposed from a linear least squares fit of the spectrum [299]. The luminescence spectrum resulting from photolysis of $[Ni(CO)_4]$ with an XeCl laser (308 nm) has been described. This was the first observation of an emission from a metal carbonyl compound. Based on LCGTO-X_{α} calculations, a three step mechanism was proposed. Photolysis of $[Ni(CO)_4]$ gave first an excited state, $[Ni(CO)_4]^*$, which then dissociated to the excited state of $[Ni(CO)_3]^*$. This collapsed to the ground state with light emission. The excited states of both $[Ni(CO)_4]$ and $[Ni(CO)_3]$ show pronounced $M\rightarrow CO$ CT character. The luminescence of $[Ni(CO)_3]$ occurs in the visible region of the spectrum since its HOMO-LUMO gap is smaller than for $[Ni(CO)_4]$. This is because there is a lowering of the LUMO energy level as a consequence of the lesser σ-repulsion as well as an increase in the metal 3d levels due to reduced back-donation [300]. A study of the photochemistry of $[Ni(CO)_4]$ led to an appropriate model to account for the prevailing production of nickel atoms at high laser frequencies. Dissociative decay channels into neutral fragments were also considered [301]

Time resolved cluster optical extinction and atomic absorption were used to study the formation of nickel atom clusters from nickel atoms produced by shock wave induced thermal decomposition of [$Ni(CO)_4$] [302,303]. The ion-molecule reaction chemistry of [$Ni(CO)_4$] has been studied; fragments of the type [$Ni(CO)_x$]$^+$ (x = 0,1,2,3 or 4) coalesce to clusters [304].

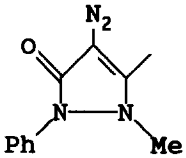
Monosubstitution of [$Ni(CO)_4$] to give [$Ni(CO)_3L$] has been reported using L = **201** [305]. The first complex of this type of a phosphaallene, in which L = η^1-RP=C=CPh_2 has been isolated, and its structure determined in a diffraction study [306]. *Ab initio* MO calculations have been undertaken on the terminal phosphinidine complex [$HPNi(CO)_3$] [307]. Reaction of [$Ni(CO)_4$] with $N_3CF_2CF_2COOMe$ was exothermic, leading to [$Ni(CO)_3(NCF_2CF_2COOMe)$], a nitrene nickel complex. Ellimination of an α-fluoride gave NiF_2 and $NCCF_2COOMe$, whilst carbonylation followed by dissociation yielded $OCNCF_2CF_2COOMe$ [308].



201

The complex [$Cp'_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2$] was mentioned in a review of cyclopentadienyl actinide complexes [309]. MO calculations on the complex indicated a weak donor-acceptor relationship between nickel and thorium, which is made possible by the flexibility of the PPh_2 bridges [310]. Reaction of [$Cp_2Zr(PPh_2)_2$] with [$Ni(CO)_2(PPh_3)_2$] gave [$Cp_2Zr(\mu\text{-}PPh_2)_2Ni(CO)_2$]. With [$Pt(PPh_3)_4$] or [$Pt(CO)_2(PPh_3)_2$] the product was [$Cp_2Zr(\mu\text{-}PPh_2)_2Pt(PPh_3)$] [311].

Reaction of [$Ni(CO)_2(PPh_3)_2$] with **202** resulted in degradation of the nickel complex [312]. Melt processing of capped imide oligomers in the presence or absence of [$Ni(CO)_2(PPh_3)_2$] gave high quality dark films with increased glass transition temperatures [313].



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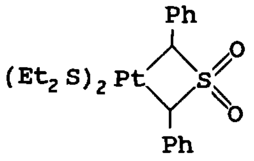
The preparation and ^{31}P nmr spectrum of [$Ni\{P(CH_2CH_2PPh_2)_3\}(CO)$][$BF_4$] has been reported [314]. Carbonylation of [$K18C6]_2[Ni(CN)_2(\eta^2\text{-}PhC{\equiv}CPh)$] gave the isolable species

$[K18C6]_2[Ni(CN)_2(CO)_2]$ and some $[K18C6]_2[Ni(CN)(CO)(\eta^2\text{-PhC}\equiv\text{CPh})]$, but the latter could not be isolated in a pure form [315]. The electrocatalytic properties of $[Ni(cyclam)]^{2+}$ in reduction of CO_2 to CO have been studied (cyclam = 1,4,8,11-tetraazatetradecane). The species $[Ni(cyclam)(CO)]^+$ has been identified by UV spectroscopy and epr spectroscopy. In the initial carboxylation step the N-H protons may favour CO_2 fixation by hydrogen bonding to the incoming ligand [316].

Reaction of $[PtCl_6]^{2-}$ with carbon monoxide in ethanoic acid resulted in reduction to $[PtCl_3(CO)]^-$. Photolysis was shown to increase the reduction rate [317]. The complexes $[PtX_2(CO)_2]$ and $[\{PtX_2(CO)\}_2]$ (X = Cl or Br) have been investigated, and have been shown to have low activity as calatysts for carbonylation of propyne to methyl propenoate [318]. When $[PtCl_3(CO)]^-$ is reacted with tin(II) chloride in dichloromethane, in an atmosphere of CO, salts of *cis*-$[PtCl_2(SnCl_3)(CO)]^-$, *trans*-$[PtCl(SnCl_3)_2(CO)]^-$ and $[Pt(SnCl_3)_4(CO)]^-$ could be isolated. When the solvent was propanone, reduction to the binuclear platinum(I) derivative $[Pt_2(SnCl_3)_4(CO)_2]^{2-}$ was noted, and some clusters were also produced [319]. The reactions of $[PtCl(CO)(PPh_3)_2]^+$ with organosilicon alcohols has been reported [320]. Some reactions of **203** have been studied. Carbonylation gave **204** [321].



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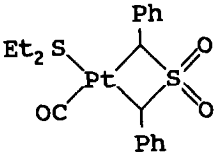
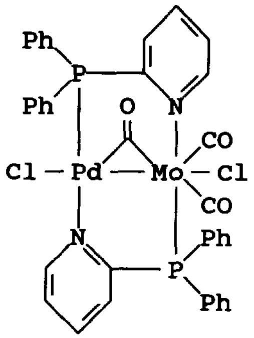


204

6.2 Binuclear Carbonyl Complexes

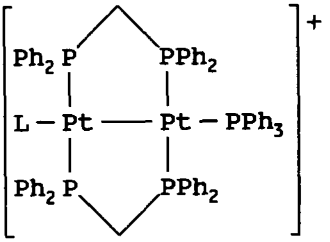
The reaction of $[Ni(CO)_4]$ with dmpm had been previously studied, and the product had been characterised as $[Ni(CO)_2(dmpm)]$. An X-ray diffraction study has now shown that the product is actually $[Ni_2(CO)_4(\mu\text{-dmpm})_2]$, in which the 8-membered ring adopts a boat conformation [322]. MO calculations have been undertaken on $[Ni_2(PMe_3)_2(\mu\text{-CO})(\mu\text{-dmpm})_2]$ [323].

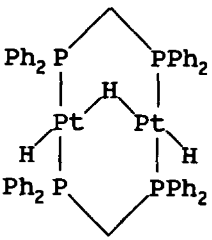
A process for the separation of CO from gas mixtures based on selective reversible CO binding by $[Pd_2(\mu\text{-dppm})_2Br_2]$ has been developed. This allows the separation of CO/N_2 and $CO/H_2/CO_2/CH_4/N_2$ mixtures. In the bound complex the CO is bridging [324]. Some complexes of $Ph_2PCHMePPh_2$ (dppmMe) have been studied; only $[Pd_2Cl_2(\mu\text{-dppmMe})(\mu\text{-dppm})]$ binds CO reversibly to give an A-frame comples [325]. Reaction of $[PdCl_2(cod)]$ with $[Mo(CO)_4(Ph_2Ppy)_2]$ gave **205**, characterised in a diffraction study. The mechanism of the ligand rearrangement which seems to have taken place is not known. The Pd-Mo distance, at 2.817(1) Å, is the shortest thus far determined, and the CO ligand is genuinely bridging, rather than semi-bridging [326].



205

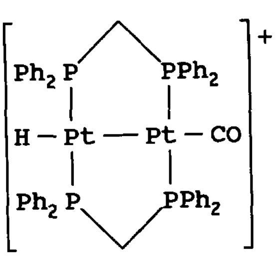
An attempt has been made to correlate the ^{195}Pt-^{31}P coupling constants in **206** with Pt-L and Pt-Pt bond lengths determined crystallographically. It was concluded that the Pt-Pt bond had *trans* and *cis*-influence comparable with that of a hydride. The one-bond coupling, J(Pt-P) is extremely sensitive to the Pt-P bond length, and both $^2J(PPt)_{cis}$ and $^2J(PPt)_{trans}$ were very sensitive to the Pt-Pt bond strength [327]. Carbonylation of **207** to give **208** was shown to be reversible. Reaction of **208** with further CO gave **209** and **210**, which could be observed in solution, but not isolated, these latter being the first reported Pt(0)/Pt(II) complexes [328].





206 **207**

Reaction of $[PtBr_2(cod)]$ with $[Fe(CO)_4(dppm\text{-}P)]$ gave **211**, characterised in a diffraction study. The semibridging interaction of CO with platinum makes a small but significant contribution to the overall bonding. The related palladium complex could be characterised only in solution [329]. When *trans*-$[PtHCl(PR_3)_2]$ was reacted with $Na[M(Cp(CO)_3]$ (M = Mo or W), the product was *cis*-$[PtH\{M(CO)_3(Cp)\}(PPh_3)_2]$. The structure of the molybdenum complex was established in a diffraction study; two of the carbonyl ligands are semibridging, and the square planar environment of the platinum(II) is strongly distorted. In a similar manner *trans*-$[PtHCl(PR_3)_2]$ reacted with $Na[Mn(CO)_5]$ to give **212**; the complex for which R = Et was the subject of a diffraction study. The results of variable temperature nmr spectroscopy on these complexes are presented, and discussed in some detail. In solution all the complexes were slowly transformed to higher nuclearity platinum clusters [330].



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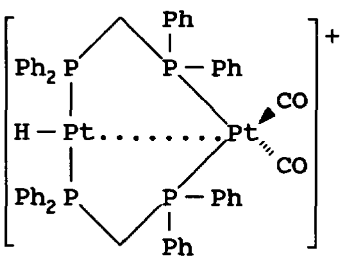

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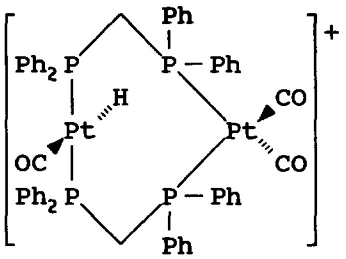

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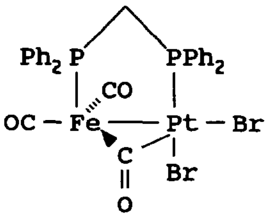

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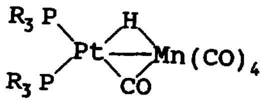
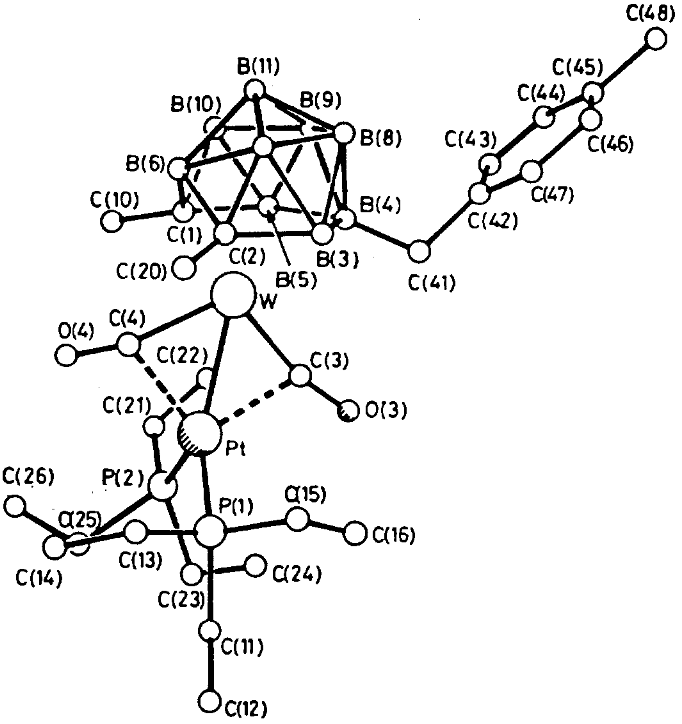


212

Reaction of $[(Ph_3P)_2N][W(CR)(CO)_2(\eta^5\text{-}1,2\text{-}C_2B_9H_8Me_2)]$ with *trans*-$[PtH(PEt_3)_2(\text{propanone})]$ gave $[PtW(CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2R)Me_2\}]$, **213**, in which the carbonyl groups are semi-bridging. Reaction of **213** with PMe_3 or CO gave $[PtW(\mu\text{-}H)\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2R)Me_2\}(CO)_2L(PEt_3)_2]$, in which the carbonyls are not semi-bridging, but the platinum is also coordinated to the carborane [331].



213 (Reproduced with permission from [331])

Molecular structure of $[PtW(CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4\text{-}Me\text{-}4)Me_2\}]$

Reaction of $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ with $LiC{\equiv}CPh$ or phenylethyne/Et_3N gave $[(OC)_2Mn(\mu\text{-}CO)(\mu\text{-dppm})_2Pt(C{\equiv}CPh)]$ in which one carbonyl was weakly semibridging. Protonation yielded $[(OC)_3Mn(\mu\text{-}H)(\mu\text{-dppm})_2Pt(C{\equiv}CPh)][BF_4]$ in a reversible reaction. When $[(OC)_3Mn(\mu\text{-dppm})_2PtBr]$ was reacted with $Na[BH_4]$ or hydrazine, the product was $[(OC)_2Mn(\mu\text{-}CO)(\mu\text{-dppm})_2PtH]$, which could be protonated to yield $[(OC)_2Mn(\mu\text{-dppm})_2Pt(CO)][BF_4]$ or reacted with methoxide to yield $[(OC)_2Mn(\mu\text{-}CO)(\mu\text{-dppm})_2Pt(COOMe)]$. Treatment of $[(OC)_3Mn(\mu\text{-dppm})_2PtBr]$ with Me_3CNC yielded $[(OC)_3Mn(\mu\text{-}CO)(\mu\text{-dppm})_2Pt(CNCMe_3)]$ wich could be protonated reversibly to give $[(OC)_3Mn(\mu\text{-}H)(\mu\text{-dppm})_2Pt(CNCMe_3)][BF_4]$ [332].

6.3 Trinuclear carbonyl complexes

Reaction of $[Co_2M(\mu_3\text{-}CR)(Cp)(CO)_8]$ (M = Mo or W) with $[\{Ni(Cp)(CO)\}_2]$ gave $[CoMNi(\mu_3\text{-}CR)(Cp)_2(CO)_5]$. When R = COOmenthyl the stereoisomers of the complex could be separated by column chromatography, and when R was achiral the enantiomers could be separated on a triethanoylcellulose column [333]. When $[Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ was reacted with $[\{Ni(Cp)(CO)\}_2]$ the major product was $[Fe_2Ni(\mu_3\text{-}COMe)(\mu_3\text{-}CO)(CO)_6(Cp)]$, together with smaller amounts of $[FeNi(\mu\text{-}CO)_2(CO)(Cp)_2]$ and $[Fe_3(\mu_3\text{-}COMe)(\mu\text{-}CO)_2(CO)_6(Cp)]$. An x-ray diffraction study of $[Fe_2Ni(\mu_3\text{-}COMe)(\mu_3\text{-}CO)(CO)_6(Cp)]$ showed that the bridging ethanoyl group almost caps the triangle of metal atoms [334].

When $[Pd_2X_2(CO)L_3]$ ($L = PPh_3$) was reacted with $[PdCl_2(PhCN)_2]$, the product was an oligomeric species $[\{Pd_3X_2(CO)_2L_2\}_n]$. The same species could be generated from $[Pd_4(CO)_5L_4]$ and $[PdCl_2(PhCN)_2]$. The palladium in the complex is in an oxidation state between 0 and 1, and cryoscopy indicated that $n = 1$ or 2 [335]. Some further chemistry of complexes of the type $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (M = Pd or Pt) has been reported [336]. Reaction of $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (M = Pd or Pt) with $[SCN]^-$ gave $[M_3(SCN)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$ in which the thiocycanate caps the face opposite to the CO. When M = Pd this complex loses CO to give $[M_3(\mu_3\text{-}S)(CN)(\mu\text{-}dppm)_3]^{2+}$, characterised in a diffraction study [337].

EHMO calculations of the energies of $[Pt_3(CO)_6]^{2-}$ and $[Pt_{19}(CO)_{22}]^{4-}$ have been undertaken, with a view to using these systems as models for the activation of CO by charged platinum. The calculations indicate that bridging carbonyls are activated more readily than terminal ones [338].

The preparation of $[\{Pt_3(CO)_3(\mu_2\text{-}CO)_3\}_n]^{2-}$ from $[PtCl_6]^{2-}$, CO and Na[OH] has been followed by nmr spectroscopy [339]. The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ has been prepared from $[Pt(OOCCF_3)_2(dppm)]$/CO/MeOH/H_2, and provides a model for CO chemisorbed at a threefold site on a platinum surface [340]. Carbonylation of $[PtCl_2(PPh_3)_2]$ under basic conditions gave mixtures of $[Pt_3(\mu_3\text{-}CO)_3(PPh_3)_4]$ (major product), $[Pt_3(\mu_3\text{-}CO)_3(PPh_3)_3]$, $[PtCl_2PPh_3]$, $[Pt_4(\mu_2\text{-}CO)_5\ [(PPh_3)_4]$ and $[Pt_3(\mu_2\text{-}CO)_5(PPh_3)_4]$ [341]. When ammonia was added to $[\{Pt(CO)_2\}_n]^{2-}$ the nuclearity of the species was altered to give $[\{Pt_3(CO)_6\}_5]^{2-}$. Addition of phosphine gave $[\{Pt_3(CO)_6\}_3]^{2-}$ and $[Pt_3(CO)_3(PPh_3)_4]$ [342].

The decarbonylation of $[Pt_3(CO)_3(PPh_3)_4]$ on alumina or titania *in vacuo* or under an atmosphere of CO has been studied by IR spectroscopy. On alumina, in CO, the products were $[Pt(CO)_2(PPh_3)_x]$ and $[Pt(CO)(PPh_3)_x]$, whilst *in vacuo* CO was lost to give adsorbed platinum phosphine derivatives. The reaction mechanisms were discussed in detail [343].

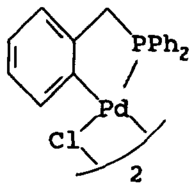
Substitution reactions of $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ by CO or X^- have been facilitiated by the addition of Me_3NO. Thus reaction of $[Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3]$ with CO gave mainly $[Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2(PCy_3)_3]$ together with a small amount of $[Pt_2(\mu\text{-}SO_2)(CO)_2(PCy_3)_2]$. In the presence of Me_3NO, the product was $[Pt_3(CO)_3(PCy_3)_3]$ [344]. $\{Pt_3(\mu_3\text{-}S)\}$ units have been used a a model for the adsorption of H_2S on a platinum <111> surface. Reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ with H_2S gave $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}dppm)_3]^+$ and an analogous process was noted with RSH [345].

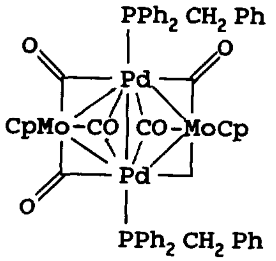
The structure of $[OsPt_2(\mu\text{-}CO)_3(CO)_2(PPh_3)_3]$ has been established. Ecah metal in a triangular array bears one phosphine ligand, and each metal-metal bond is spanned by a bridging CO group. The osmium atom bears two terminal CO ligands. The cluster is isostructural with the ruthenium analogue [346]. Reaction of $[Ir(CO)_2(\eta\text{-}C_9H_7)]$ (η-C_9H_7 = indenyl) with $[Pt(C_2H_4)_2(PCy_3)]$ gave $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ and $[Ir_2Pt(CO)_3(PCy_3)(\eta\text{-}C_9H_7)_2]$. Protonation of the mixed metal clsuter gave $[Ir_2Pt(\mu\text{-}H)(CO)_3(PCy_3)(\eta\text{-}C_9H_7)_2][BF_4]$ in which the hydride bridges an iridium-platinum bond [347].

6.4 Tetranuclear metal carbonyl clusters

Reaction of palladium ethanaote with phen had been previously shown to give $[\{Pd_4H_4(phen)(OCOMe)_2\}_n]$ when Pd:phen = 2:1. The reaction when equimolar amounts of palladium and phen are used has now been studied and shown to give $[Pd_2H(phen)_2(CO)(OCOMe)_2]$ when performed in an atmosphere of CO, and $[Pd_4(CO)_4(phen)_3(OCOMe)_3]$ under H_2/CO. The hydride in the $\{Pd_2\}$ cluster was shown, by labelling studies, to derive from oxidative addition of ethanoic acid to palladium or from orthometallation of a ligand [348].

Reaction of the cyclometallated species, **214**, with $Na[Mo(CO)_3(Cp)]$ in thf gave the tetranuclear cluster $[Pd_2Mo_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(Ph_2PCH_2Ph)_2]$, **215**, characterised in a diffraction study [349]. The preparation of $[Pd_2Fe_2(CO)_5(NO)_2(dppm)_2]$ has been described [350].





214

215

Reaction of $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_2]$ with SO_2 gave $[Pt_3(\mu\text{-}SO_2)_3(PMe_2Ph)_3]$, not the tetranuclear species which had been previously reported. The structure of the mixed CO/SO_2 complex $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4].2CH_2Cl_2.Me_2CHOH$ was also reported in this paper [351].

Bonding in some platinum-gold cluster compounds has been analysed using semiempirical MO calculations. In $[Pt_3Au(\mu\text{-}CO)_3(PR_3)_4]$ the $\{AuPR_3\}$ fragment caps the platinum triangle by using the acceptor orbital of a_1 symmetry localised on gold. The complex $[Pt_2Au_2(PR_3)_4(CNR')_4]^{2+}$ was also discussed in this paper. The Pt-Au bonding involves 3-centre 2-electron bonds between the bonding orbitals of the $\{P_2Au_2\}$ dimer and the frontier orbitals of the T-shaped platinum fragments. The obvious distortions in the molecule could be rationalised [352]. The complex $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ was treated with $[AuCl(PCy_3)]$ to give $[Pt_3Au(\mu\text{-}CO)_3(PCy_3)_4][PF_6]$. This reacted with SO_2 to yield $[Pt_3Au(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PCy_3)_4][PF_6]$, characterised in a diffraction study. Nmr spectroscopic investigations indicated that the solid state structure was maintained in solution [353].

6.5 Higher Nuclearity metal carbonyl clusters

A review of transition metal cluster chemistry, particularly of synthetic routes to large clusters, has included consideration of $[Co_4Ni_2(CO)_{14}]^{2-}$ and $[Pt_{15}(CO)_{27}]^{3-}$ [354]. The relationship of bonding in molecular clusters to that in the bulk metal has been discussed [355]. Magnetic measurements in high nuclearity nickel and platinum clusters have been undertaken. Very unusual low temperature magnetic behaviour was ascribed to quantum-size effects due to the small dimensions of the metal clusters. The experimental data were compared with the results from MO calculations [356].

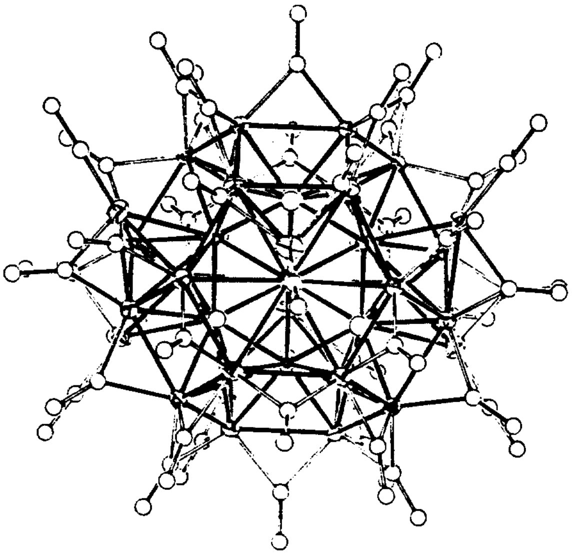
By the use of a modified Föppl notation and replacement methods, the spatial distribution for metal nuclei and ligands of metal clusters can be unequivocally assigned. The discussion included consideration of $[Ni_6(CO)_6]^{2-}$, $[Ni_6(CO)_{12}]$, $[Pt_6(CO)_{12}]$, $[Ni_5(CO)_{12}]^{2-}$ and $[Mo_2Ni_3(CO)_{16}]^{2-}$ [357].

Reaction of $[Me_4N]_2[Ni_6(CO)_{12}]^{2-}$ with $AsPhCl_2$ gave $[Ni_9(AsPh)_3(CO)_{15}]^{2-}$, whereas with $AsMeBr_2$, the product was $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$. Both structures were established in diffraction studies. In the $\{Ni_9As_3\}$ derivative the structure showed a non-centred icosohedral core, corresponding to a *closo*-1,2,12-trisubstituted isomer, unprecedented for a non-boron species. In the $\{Ni_{10}As_2\}$ complex two *trans*-pentagonal nickel faces were capped with arsenic in a 1,12-disubstituted isomer. The bonding in the complexes was discussed [358].

The reactivity of large metal cluster compounds of nickel with cationic group IB and IIB metals has been studied. The structures of $[Me_3NCH_2Ph]_2[Ni_9(CO)_{18}]$ and $[Zn(dmso)_6Ni_{12}H_2(CO)_{21}]$ were established [359]. High yield syntheses of $[Ph_4As]_2[Ni_9(CO)_{18}]$ and $[Me_4N]_3[Ni_{12}(CO)_{21}H]$ have been described, and models for the bonding in the complexes presented. In $[Ni_9(CO)_{18}]^{2-}$ there was a novel triangular metal-stacked core, whilst the positions of the metals in $[Ni_{12}(CO)_{21}H]^{3-}$ were based on an hcp array. Reaction of $[Ni_6(CO)_{12}]^{2-}$ with $[Rh_2Cl_2(CO)_4]$ gave a mixed cluster isolated as $[Ph_3PMe]_3[Ni_6Rh_5H(C)_{21}]^{3-}$. This was fully characterised, including an X-ray structure determination. It is a paramagnetic species of D_{3h} symmetry, which is a geometric isomer of a pentacapped prismatic polyhedron. The rhodium atoms form a trigonal bipyramidal kernel with the nickel atoms on the surface [360].

Reaction of two molar equivalents of $[R_4N]_2[Ni_6(CO)_{12}]$ with hexachloroethane gave a complex mixture of carbide containing clusters including $[Ni_{10}(CO)_{16}C_2]^{2-}$, $[Ni_{16}(CO)_{23}(C_2)_2]^{2}$, $[HNi_{34}(CO)_{38}C_4]^{2-}$ and $[Ni_{34}(CO)_{38}C_4]^{2-}$, the last two of these being interconvertible in an acid/base equilibrium. The structures of $[Me_3NCH_2Ph]_2[HNi_{34}(CO)_{38}C_4]$ and $[Et_4N]_6[Ni_{35}(CO)_{39}C_4]$, which was prepared from $[Et_4N]_2[Ni_6(CO)_{12}]$ and dichloromethane, have been established in diffraction studies. The metal framework consits of a ccp Ni_{20} core, the carbides are bound to square faces, and through condensation of two nickel atoms above each square face they become caged interstitially in four trigonal prismatic cavities to give an $\{Ni_{28}C_4\}$ fragment. Four nickel atoms cap the two pentagonal and two of the four adjacent square faces so that C_i symmetry is maintained. The last two nickel atoms occupy "butterfly" type sites. Ten CO ligands are terminal, 26 doubly bridging and two triply bridging. The $\{Ni_{35}(CO)_{39}\}$ complex has an additional capping $\{Ni(CO)\}$ unit. The data are related to structural changes on carbidization of metal crystallites [361]. Reaction of 1.7 molar equivalents of $[Bu_4N]_2[Ni_6(CO)_{12}]$ with C_3Cl_6 gave the carbide cluster $[HNi_{38}(CO)_{42}C_6]^{5-}$, **216**. The presence of the hydride was deduced only from the observed reversible protonation equilibrium. The structure has an inner core of an empty $\{Ni_8\}$ cube, capped on the six square faces by six carbides [362].

Reaction of $[Ni_6(CO)_{12}]^{2-}$ with $FeCl_3$ gave the Longoni-Chini dianion, $[Ni_9(CO)_{18}]^{2-}$, in quantitative yield. An X-ray structural study showed that this is three stacked $\{Ni_3(CO)_3(\mu\text{-}CO)_3\}$ units oriented so that the $\{Ni_9\}$ core is a previously unknown nine-vertex polyhedron. A qualitative bonding model was presented [363].

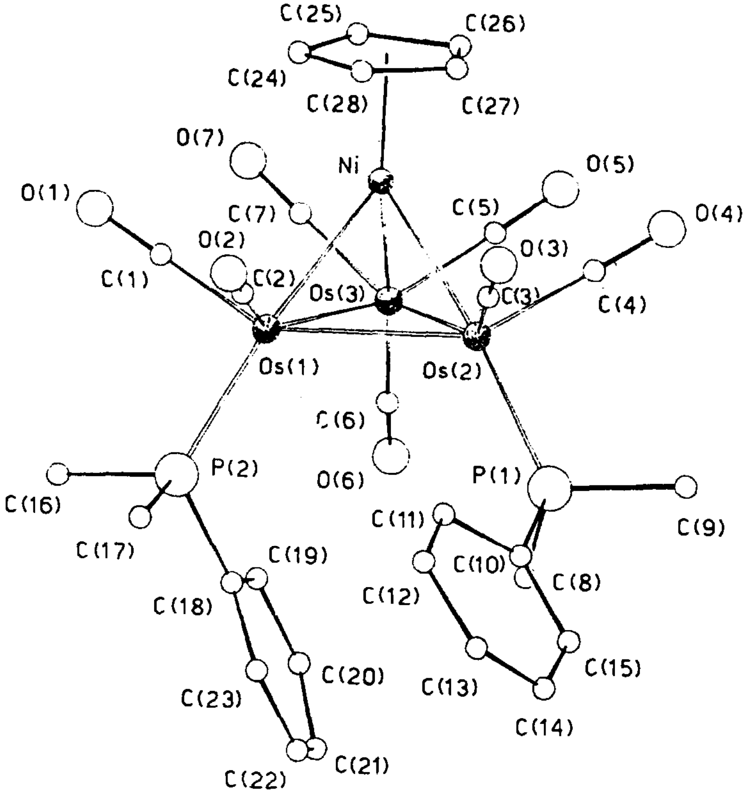


216 (Reproduced with permission from [362])
ORTEP drawing of the $[HNi_{38}(CO)_6(\mu_2\text{-}CO)_{36}C_6]^{5-}$ anion

Reaction of $[NiOs_3(\mu\text{-}H)_3(Cp)(CO)_9]$ with a ligand, L, in the presence of Me_3NO, resulted mainly in monosubstitution, but small amounts of disubstituted products were also obtained. The complex **217**, $[NiOs_3(\mu\text{-}H)_3(Cp)(CO)_7(PMe_2Ph)_2]$ was characterised in a diffraction study; two axial CO ligands have been replaced by phosphines [364].

When $[Ni_6(CO)_{12}]^{2-}$ was reacted with $K_2[PtCl_4]$, $[Ni_9Pt_3H(CO)_{21}]^{3-}$ and a mixture of brown coloured anions was formed. These anions could be carbonylated to give $[Ni_9Pt_3(CO)_{21}]^{4-}$, which, on protonation, yielded $[Ni_9Pt_3H(CO)_{21}]^{3-}$. Further protonation gave $[Ni_9Pt_3H_2(CO)_{21}]^{2}$, this last species decomposing slowly in solution at room temperature. The structure of $[Et_4N]_3[Ni_9Pt_3H(CO)_{21}]^{3-}$, **218** was established in a diffraction study; the structure is related to that of $[Ni_{12}H(CO)_{21}]^{3-}$ with the platinum atoms occupying the inner triangle of the hexametal layer. The unique hydride was not located, but on the basis of ^{195}Pt nmr spectroscopy, probably occupies a trigonal prismatic cavity in the hcp metal fragment [365].

The preparation (from $[Ph_3PMe]_2[Ni_6(CO)_{12}]$ and $[Rh_2Cl_2(CO)_4]$) and characterisation of $[Ni_6Rh_5H_x(CO)_{21}]^{3-}$, **219**, has been described. The metal skeleton adopts a previously unknown D_{3h} close-packed polyhedron with the nickel atoms capping a pentarhodium trigonal bipyramidal core. Epr spectroscopy showed that the complex was paramagnetic with one unpaired electron, implying that *x* is 1 or 3 [366].

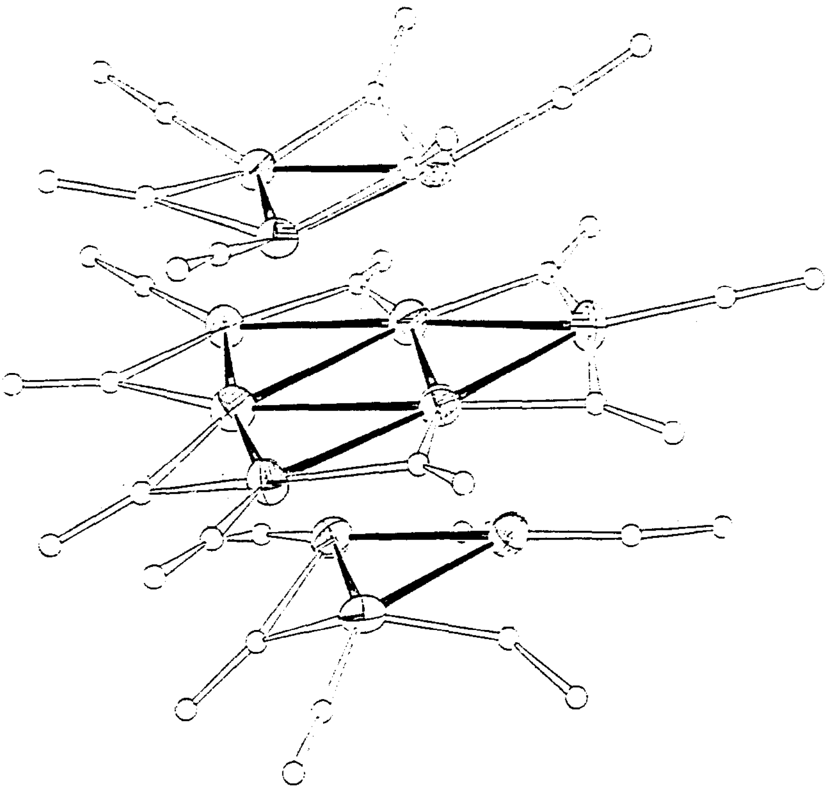


217 (Reproduced with permission from [364])

View of the complex $[NiOs_3(\mu\text{-}H)_3(Cp)(CO)_7(PMe_2Ph)_2]$

The synthesis of $[Fe_5NiC(CO)_{15}]^{2-}$ from nickel(II) chloride and $[Fe_6C(CO)_{16}]^{2-}$ has been described. The metal skeleton is maintained with one iron atom replaced by nickel. Reaction of $[Fe_5NiC(CO)_{15}]^{2-}$ with $[Rh_2Cl_2(CO)_4]$ gave $[Fe_5RhC(CO)_{16}]^{2-}$. $[Fe_5C(CO)_{14}]^{2-}$ reacted with $NiCl_2$ to give $[Fe_5NiC(CO)_{15}]^{2-}$ in low yield [367]. Treatment of $[Et_4N][Fe_4MC(CO)_{14}]$ with $[Ni(cod)_2]$ gave $[Et_4N][Fe_4MNiC(CO)_{15}]$ (M = Rh or Co). With $NiCl_2$, $[Et_4N][Fe_4MC(CO)_{14}]$ yielded $[Et_4N][Fe_3M_3C(CO)_{15}]$ and $[Et_4N][Fe_4MNiC(CO)_{15}]$. The complexes were characterised by nmr and IR spectroscopy [368].

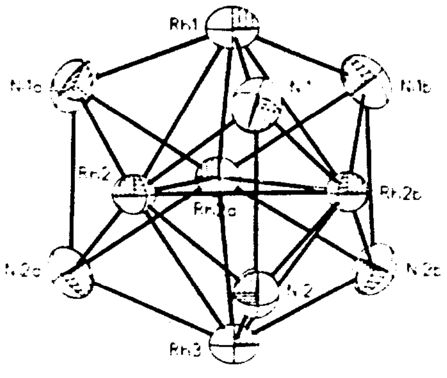
Reaction of palladium ethanoate with $[Pd_{10}(CO)_{12}(PEt_3)_6]$ gave $[Pd_{23}(CO)_{22}(PEt_3)_{10}]$, characterised in a diffraction study. The structure was centrosymmetric with a ccp metal skeleton, though the Pd-Pd distance was somewhat longer than in the bulk metal [369]. Ligand displacement in $[Pd_{10}(CO)_x(PR_3)_y]$ has been investigated [370].



218 (Reproduced with permission from [365])

ORTEP drawing of the $[HNi_9Pt_3(CO)_{21}]^{3-}$ trianion. Interlayer bonds are omitted for clarity.

Previously discussed topological models of metal cluster bonding have now been extended to stacked platinum carbonyl clusters [371]. The magnetic behaviour of large platinum clusters such as $[Bu_4N]_2[Pt_6(CO)_{12}]$, $[Bu_4N]_2[Pt_9(CO)_{18}]$, $[Bu_4N]_3[Pt_{19}(CO)_{22}]$ and $[PPN]_2[Pt_{38}H_x(CO)_{44}]$ has been investigated. The complexes are diamagnetic at room temperature and weakly paramagnetic at low temperature. The observed anomalous paramagnetism was described by the simple Curie law. The Van Vleck temperature independent paramagnetic susceptibility, χ_p, increased with cluster size, which was attributed to the decrease in the energy gap between the occupied and unoccupied states as the size of the cluster is increased. μ_{eff} per atom was 0.1•0.02 μB, close to the value for platinum crystallites of 400 atoms. Thus the clusters are in the quantum size regime, where magnetic properties differ from the bulk, as well as from simple molecules [372]. The structure of $[Pt_5(CO)_6(PPh_3)_4]3C_6H_6$ has been determined, and differs a little from the related toluene solvate [373].

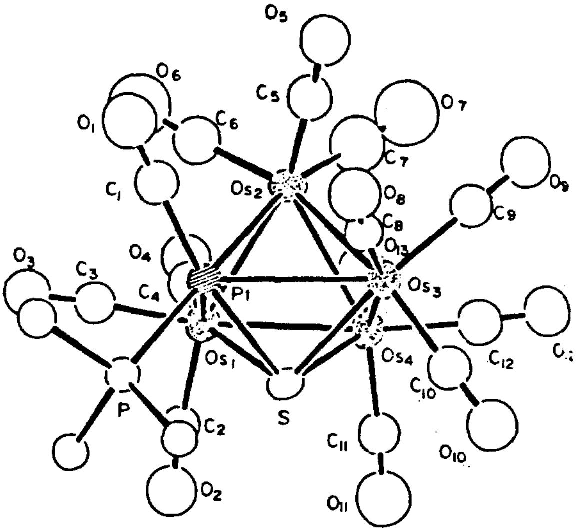


219 (Reproduced with permission from [366])

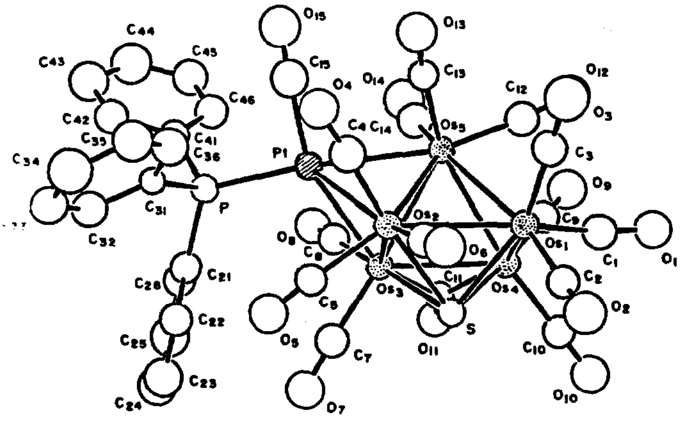
11-Vertex $\{Rh_5Ni_6\}$ core of the paramagnetic $[Rh_5Ni_6(CO)_{21}H_7]^{3-}$ trianion of crystallographic C_3-3 site symmetry. The idealised D_{3h}-62*m* metal architecture suggests that this heterometallic core is formed by nickel capping of a trigonal bipyramidal rhodium kernel.

Reaction of $[Os_5(CO)_{15}(\mu_4\text{-}S)]$ (which has a square pyramidal metal core) with $[Pt(C_2H_4)(PPh_3)_2]$ gave $[Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)]$, **220**, **221** and **222** all of which were characterised in diffraction studies [374]. Treatment of $[Os_4(CO)_{12}(\mu_3\text{-}S)_2]$ with $[Pt(PMe_2Ph)_4]$ gave a mixture of $[PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2]$, **223**, and $[PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2]$, **224**. The pentanuclear complex could be converted to the tetranuclear one by carbonylation. Investigation of **224** by nmr spectroscopy showed that there was rapid rearrangement on the nmr timescale [375]. Treatment of $[Os_6(CO)_{18-n}(NCMe)_n]$ ($n = 1$ or 2) with $[Pt(cod)_2]$ gave $[Os_6Pt_2(CO)_{17}(cod)_2]$ and $[Os_6Pt_2(CO)_{16}(cod)_2]$ respectively. The structure of $[Os_6Pt_2(CO)_{16}(cod)_2]$ was established for the first time; it has an unusual geometry with two edge-fused osmium tetrahedra, one of which is bicapped by platinum. This is a 108e cluster, and is not readily explained by the usual electron counting schemes [376].

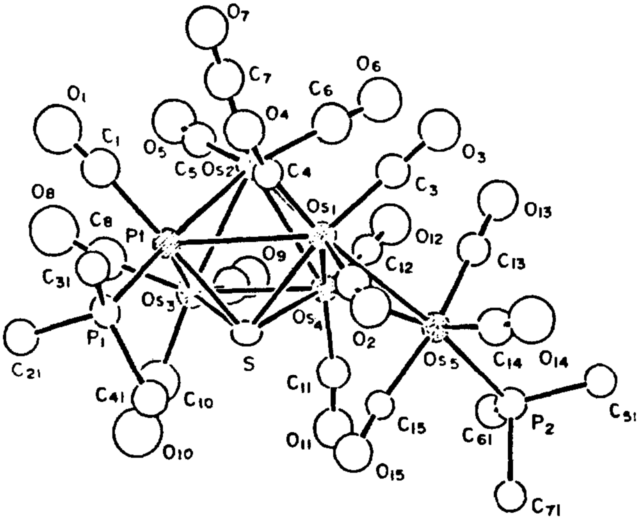
Reaction of $[PtRh_4(CO)_{12}]^{2-}$ with $[Rh_4(CO)_{12}]$ gave $[PtRh_8(CO)_{19}$, **225**, characterised in a diffraction study. The structure is a stack of three triangles generating two face-to-face octahedra. The platinum atom is in the central triangle in one of the positions of highest M-M connectivity. There are 7 terminal CO ligands, 9 edge-bridging and 3 face-bridging. At room temperaure these are completely scrambled on the nmr spectroscopic timescale, and even at -100 °C the structure is still partly dynamic [377].



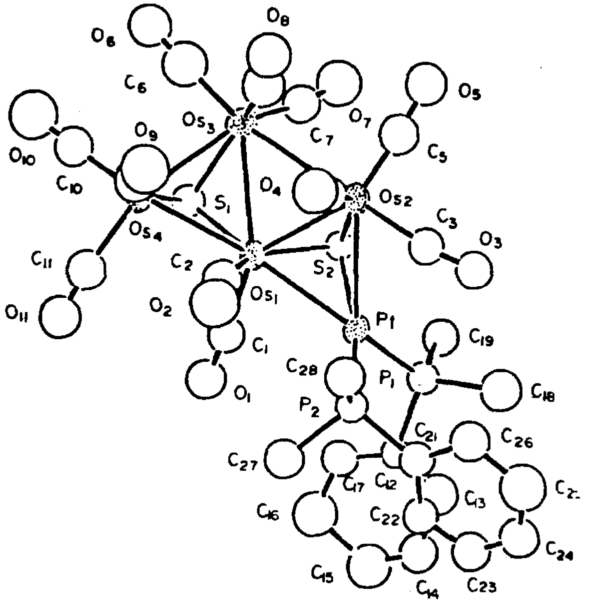
220 (Reproduced with permission from [374])
ORTEP diagram of [$PtOs_4(CO)_{13}(PPh_3(\mu_4-S)$] showing 50 % probability thermal motion ellipsoids. For clarity only the *ipso* carbon atoms of the phenyl rings are shown.



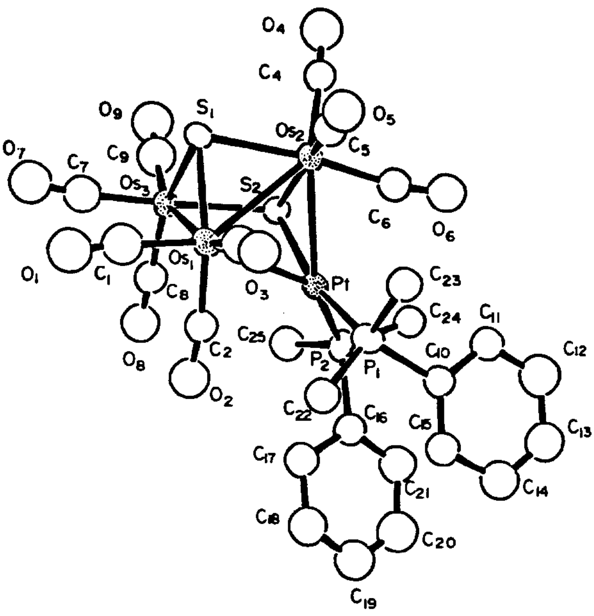
221 (Reproduced with permission from [374])
ORTEP diagram of [$PtOs_5(CO)_{15}(PPh_3)(\mu_4-S)$] showing 50 % probability thermal motion ellipsoids.



222 (Reproduced with permission from [374])
ORTEP diagram of $[PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)]$ showing 50 % probability thermal motion ellipsoids. For clarity only the *ipso* carbon atoms of the phenyl rings are shown.



223 (Reproduced with permission from [375])
ORTEP diagram of $[PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2]$ showing 50 % probability thermal motion ellipsoids.



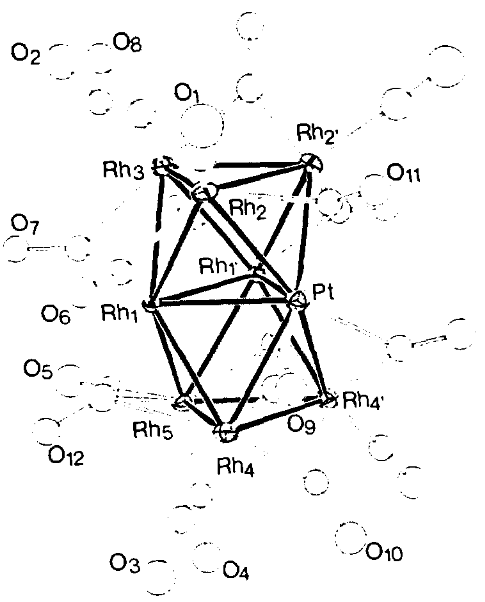
224 (Reproduced with permission from [375])
ORTEP diagram of $[PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2]$ showing 50 % probability thermal motion ellipsoids.

6.6 Complexes of CO_2, and related species

Polymerisation of C_2O_3 has been reported in the presence of a range of platinum complexes [378].

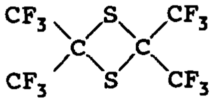
6.7 Thiocarbonyl, carbon disulphide and carbonyl sulphide complexes

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with **226** at low temperature gave **227**, but at 30 °C the product was **228**. **227** could only be converted to **228** at a temperature in excess of 158 °C [379]. Treatment of $[Pt(CS_2)(PPh_3)_2]$ with R_3P gave **229**. When the substrate was $[Pt(CSSe)(PPh_3)_2]$ and the added phosphine PMe_3, the product was **230**. These reactions were compared with that of $[Pt(C_2H_4)(PPh_3)_2]$ with CO_2 to give a carbonate complex [380]. Treatment of $[Pt_3\{2,4,6\text{-}(CMe_3)_3C_6H_2NC\}_6]$ with CS_2 gave $[Pt_2(\mu\text{-}CS_2\text{-}C,S)(ArNC)_4]$ [381]. The syntheses of $[Cp_2Zr(\mu\text{-}PPh_2)_2Pt(\eta^2\text{-}CS_2)]$ and $[Cp_2Zr(\mu\text{-}PPh_2)_2Pt(\eta^2\text{-}PhN{=}C{=}S\text{-}S,C)]$ have been reported [382].



225 (Reproduced with permission from [377])

View of the dianion $[PtRh_8(\mu_3\text{-}CO)_3(\mu\text{-}CO)_9(CO)_7]^{2-}$. Primed atoms are related to unprimed ones by the crystallographic mirror plane passing through Pt, Rh(3) and Rh(5).



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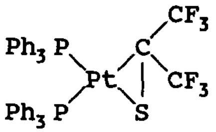

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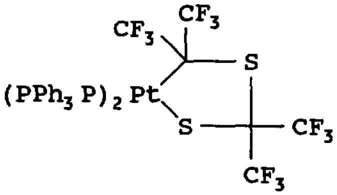

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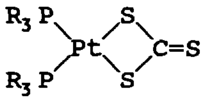

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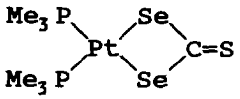
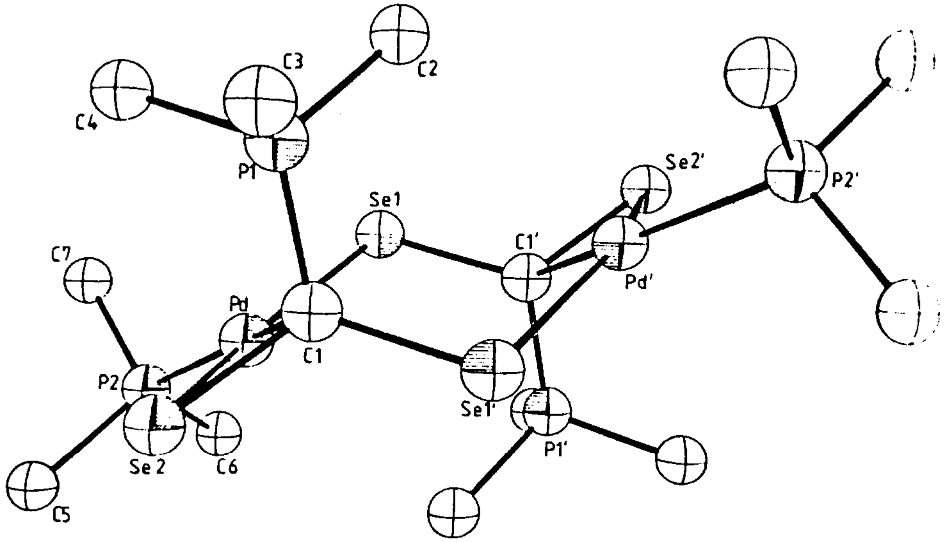


230

MO calculations using effective core potentials have been performed for carbonyl sulphide complexes of palladium and platinum [383].

6.8 Other related complexes

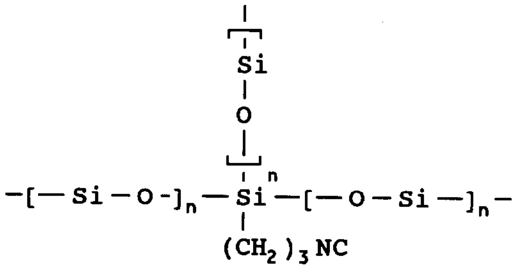
Reaction of [Pt(C_2H_4)(PPh_3)$_2$] with two molar equivalents of $MeNO_2$ gave the fulminate complex *trans*-[Pt(CNO)$_2$(PPh_3)$_2$]. An X-ray diffraction study showed that the CNO groups were linear [384]. Treatment of [Pd(PPh_3)$_4$] with CSe_2 gave **231** characterised in a diffraction study [385].



231 (Reproduced with permission from [385])

7 METAL ISOCYANIDE COMPLEXES

Reaction of [{Ni(μ-{CMe_3}$_2$As)(PMe_3)}$_2$] with 4-MeC_6H_4NC gave [{Ni(μ-{CMe_3}$_2$As)(CNAr)}$_2$] which was characterised in a diffraction study [386]. Treatment of **232** with nickel vapour gave encapsulated nickel isocyanide complexes [387]. The nickel(I) complex [Ni_2(μ–CNMe)(CNMe)$_3$(μ-dppm)$_2$]$^{2+}$ has *cis,trans*-geometry. Reduction with sodium amalgam gave the nickel(0) species, [Ni_2(μ–CNMe)(CNMe)$_2$(μ-dppm)$_2$], which was shown in a diffraction study to have *cis,cis*-diphosphines, and a Ni-Ni distance of 2.572(1) Å. Protonation yielded [Ni_2(μ–CNHMe)(CNMe)$_3$(μ-dppm)$_2$]$^+$ in which the Ni-Ni distance was 2.500(2) Å. The nitrogen of the bridging ligand in [Ni_2(μ–CNMe)(CNMe)$_3$(μ-dppm)$_2$] could also be alkylated by MeI or EtI [388].

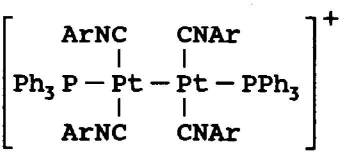


232

Flash photolysis of $[Pd_2(CNMe)_6]^{2+}$ resulted in splitting of the Pd-Pd bond to give the cation radical $[Pd(CNMe)_3]^{\cdot +}$. This could recombine or react with solvent with electron transfer to benzyl viologen to give $[Pd(II)(CNMe)_3(solvent)]^{2+}$. The absorbance of the d^9 intermediate, $[Pd(CNMe)_3]^{\cdot +}$, was more intense and significantly red-shifted compared with the $\sigma \rightarrow \sigma^*$ transition of the starting material or the MLCT band of the d^8 product. The unusually intense transient absorbance was assigned to an allowed d→p electronic transition [389]. Treatment of $[Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_4]$ gave $[Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_2(py)_2]$ which showed substantially lower IR stretching frequencies for the N≡C-bond than those in the starting material. The structure of $[Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_2(py)_2]$ was determined in a diffraction study, showing that the two isocyanides were now bridging. The Pd-Pd distance is longer than in related unbridged complexes. The driving force for bridging was said to be to disperse the increased electron density at the metal centres induced by the electron donating effect of the pyridine ligands [390]. A polymer bearing isocyanide groups produced by dehydration of amides was said to be a good ligand for $PdCl_2$ [391]. There have been other reports of palladium complexes ligated to isonitrile bearing polymers [392].

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ and ArNC ($Ar = 2,6\text{-}Me_2C_6H_4$) gave a mixture of $[Pt_2(PPh_3)_2(CNAr)_4]^{2+}$, **233**, and $[Pt_3(PPh_3)_2(CNAr)_6]^{2+}$, **234** [393]. Potentiostatic electrolysis of $[Pt(CNAr)_4][PF_6]$ yielded $[Pt_2(CNAr)_6][PF_6]_2$ in 14 % yield and $[Pt_3(CNAr)_8][PF_6]_3$ in 45 % yield. Reaction of the trimer with PPh_3 gave **234**, and with dppm, $[Pt_3(\mu\text{-}dppm)_2(CNAr)_4]$, characterised in a diffraction study. This complex has an A-frame structure with a $\{Pt(CNAr)_2\}$ moiety in a bridging position, as an isolobal analogue of CH_2 [394].

Reaction of $[Pt_2Cl_4(PPh_3)_2]$ with **235**, DIBN, gave $[Pt_2Cl_4(PPh_3)_2(DIBN)]$, which was a catalyst for enantioselective hydrosilylation [395].



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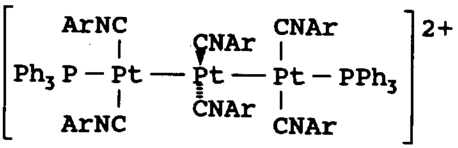

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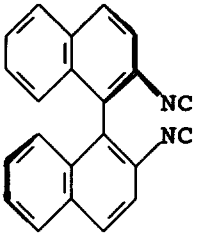

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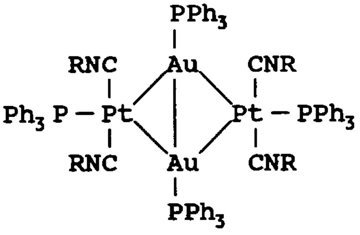
Treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with $[Au(CNAr)]^+$ gave $[Pt_2Au_2(CNAr)_4(PPh_3)_4]^{2+}$, **236**, characterised in a diffraction study. The metal atoms define a distorted flattened butterfly with the gold atoms occupying the higher connectivity sites and forming a short Au-Au bond of 2.593(2) Å. The structure is distorted from D_{2h} to C_{2v} in the solid state, but is probably C_{2v} in solution [396].



241

8 METAL ALKENE AND ALKENYL COMPLEXES

The aminomethylation of alkenes coordinated to, amongst others, the platinum group metals, has been reviewed [397]. Coordination chemistry of α-diimine complexes, including platinum alkene derivatives has been discussed [398]. There has also been a review of the fluxional behaviour of polyene and polyenyl metal complexes which included consideration of some palladium derivatives [399]. Nucleophilic attack on metal alkene and metal arene complexes has been discussed in terms of a new parameter k_{CO}^*, which represents the Cotton-

Kraihanzel CO stretching in the speces in which CO replaces the alkene or arene. Ethene derivatives of nickel palladium and platinum were considered [400].

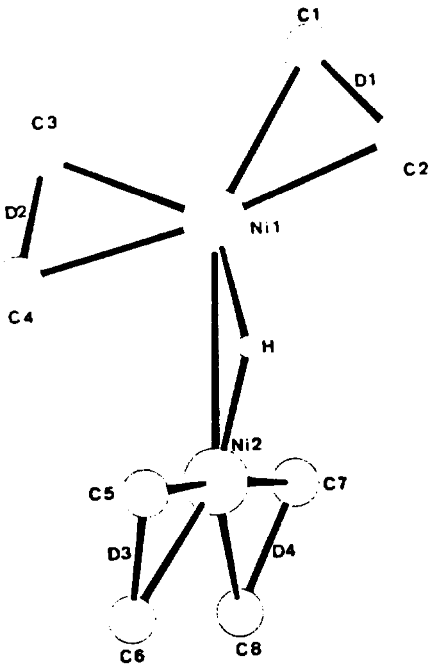
CASSCF CCI calculations have been undertaken in order to understand the bonding in $[Ni(C_2H_4)_2]$. Three different relative orientations of the alkenes were studied. The arrangement with D_{2d} symmetry where the two carbon-carbon double bonds were at right angles had the lowest energy, and it was reasoned that this was a d^8 structure with two simultaneous d_π bonds. The arrangements with D_{2h} and C_{2v} symmetry were shown to be 43 kJ and 134 kJ mol^{-1} higher in energy respectively [401]. The skeletal modes of $[M(C_2H_4)_3]$ (M = Ni or Pt) and $[Bu_4N][PtCl_3(C_2H_4)]$ were measured and assigned. A new model was used for normal coordinate treatment of π-complexes to calculate metal-ligand force constants. It was shown that π-bonding dominates in the metal(0) species, but that σ- and π-bonding are equally important in the platinum(II) derivative [402]. A study of the photodissociation of gas phase organometallic ions by FT mass spectrometry has led to some thermochemical data being obtained. Amongst the complexes studied was $[Ni(C_2H_4)_2]$ [403].

Replacement of ethene in $[Ni(C_2H_4)(PPh_3)_2]$ by PhCH=CHCH=NR (MAD) has been investigated. The initial reaction at -20 °C gave a polymeric derivative, but addition of further PhCH=CHCH=NR yielded a dimer of stoicheiometry $[\{Ni(MAD)(PPh_3)\}_2]$ and a monomer $[Ni(MAD)(PPh_3)_2]$, both of which were characterised in diffraction studies [404,405].

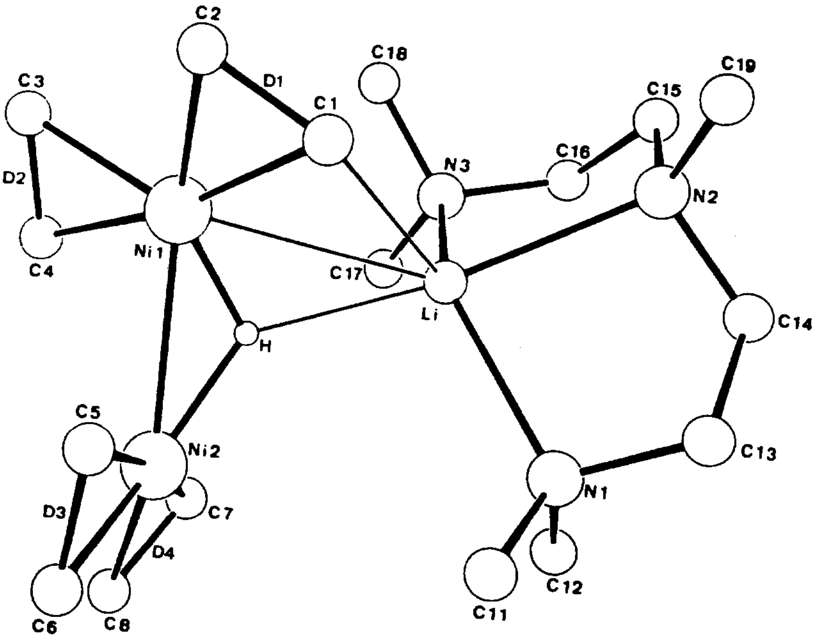
The structures of the complexes $[\{Ni(C_2H_4)_2\}_2H][Na(tmeda)_2]$, **237**, and $[\{Ni(C_2H_4)_2\}_2H][Li(Me_2NCH_2CH_2NMeCH_2CH_2NMe_2)]$, **238**, have been established. In **237** the ions are distinct and well-separated in the unit cell. In **238**, there is ion pair contact between the lithium and one nickel atom. The bonding situation was derived from semi-empirical MO calculations, and was in accord with the electron density distribution [406]. Reaction of 1,2-bis(bromomethyl)benzene with $[Ni(C_2H_4)(PPh_3)_2]$ yielded $[NiBr_2(PPh_3)_2]$ and **239** [407].

Reaction of $[NiCp_2]$ with MeLi and an alkene gave [Ni(Cp)(Me)(alkene)]. The alkenes included ethene, propene, butene, cyclohexene and various dienes [408].

Zeise's salt has been used as a precursor for platinum coordination complexes; the ethene is displaced [409]. Reaction of **240** with Zeise's salt gave **241**. Isomerism and conformation in the complexes was studied by nmr spectroscopy [410]. Simple coordination complexes have also been obtained by displacement of ethene from $[Pt(C_2H_4)(PPh_3)_2]$ [411,412]. Reaction with SO_2 with the palladium analogue gave a mixture of $[Pd(PPh_3)_2(SO_2)]$ and $[Pd(PPh_3)_4]$, formed by disproportionation [413].



237 (Reproduced with permission from [406])



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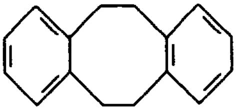

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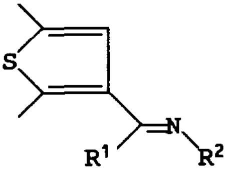
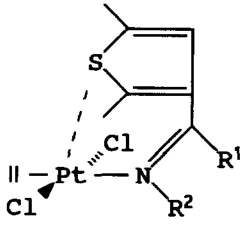


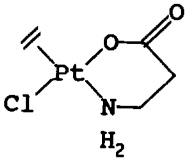


240 **241**

The synthesis of $[Pt(C_2H_4)(PEt_3)_2]$ by reduction of $[PtCl_2(PEt_3)_2]$ with NaCp in an ethene atmosphere, has been described [414]. Another description of a synthesis of the PPh_3 analogue has been given; the reductant in this case was hydrazine [415].

In cases where neutron diffraction data do not provide a clear choice between a centrosymmetric and a non-centrosymmetric space group, it is better to opt for the centrosymmetric one even though disorder may result. The disorder model implies that the crystal is a composite of two or more molecular structures which cannot be distinguished. However, an attempt to refine a single ordered mode in the non-centrosymmetric space group (which should lead to poor convergence) may lead to the erroneous conclusion that a unique structure has been found. An example is provided by $[PtCl_2(C_2H_4)(Me_2N\text{-}N{=}CH\text{-}CH{=}N\text{-}NMe_2)]$. This was described as monoclinic, $P2_1$, and refined. This refinement resulted in a non-symmetric structure with one of the NMe_2 groups planar and the other pyramidal. The structure is better described as $P2_1/m$; the two halves of the hydrazone are now symmetric [416]. The complex $[PtCl(C_2H_4)(Me_4en)][ClO_4]$ is stable, but is very reactive towards nucleophiles. Its structure has been studied by neutron diffraction at 120 K. The complex has square planar geometry at platinum, and, unusually, the ethene is almost perpendicular to the coordination plane. The platinum-carbon bond lengths are slightly longer than in Zeise's salt [417].

The kinetics of the reaction of $[PtCl_3(C_2H_4)]^-$ with 3-aminopropanoic acid anion have been studied. The reaction proceeds by initial displacement of the chloride *trans* to ethene, followed by rapid cyclisation to give **242**, characterised in a diffraction study [418]. Reaction of [$Pt(C_2H_4)(PPh_3)_2$] with **243** gave **244** which underwent ring opening with ethanol to give **245** [419].



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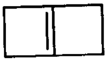

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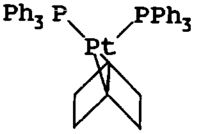

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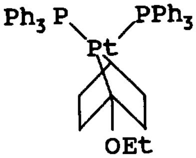

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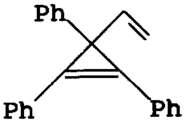
Reaction of **246** with [$Pt(C_2H_4)(PPh_3)_2$] gave the air-stable metallacyclohexa-2,4-diene, **247**, characterised in a diffraction study. The ring is puckered, there is no apparent delocalisation, and no fast ring inversion in solution [420].



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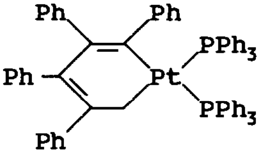

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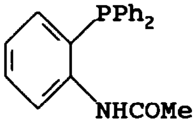
Bonding in the complexes [$Pd\{CH_2{=}C(Me)COOR\}(PMePh_2)_2$] has been studied by ^{13}C and ^{31}P nmr spectroscopy, and various dynamic processes investigated [421]. Reaction of [$Pd_2(dba)_3$] with **248** gave **249**; the possible rotamers in the product were is slow exchange. It was considered of importance to discover why complete substitution of dba did not occur, and it was concluded that the last step in the substitution would need to be associative, and is not possible on a saturated complex [422].

The structure of [$\{PdCl_2L\}_2$] (L = **250**) has been established in a diffraction study. The alkene is palladium bound [423].



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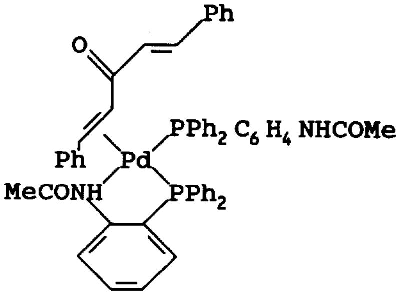

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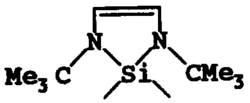


250

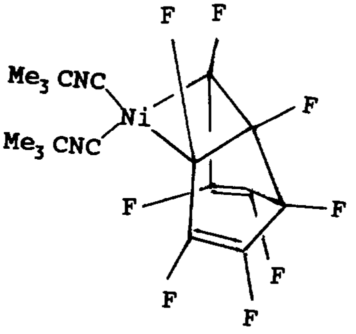
There has been a detailed study of the complexes $[Pt(C_2H_{4-n}CN_n)(PPh_3)_2]$ by IR and Raman spectroscopy. The mode ν(C-C) is relatively insensitive to n, but the changes in ν_{sym} suggest that there is increased rigidity and metallocyclopropane character in the more substituted complexes [424].

Various ^{13}C nmr spectroscopic parameters for complexes of the type $[Pt(alkene)(PPh_3)_2]$ have been reported [425]. The relative stabilities of complexes of the type *trans*-$[PtCl_2L(py)]$ (L = alkene) have been correlated with nmr spectroscopic parameters. They are of higher stability when L is an electron donor. This is consistent with previous results which suggest that alkene to platinum donation is more important than π-back bonding [426].

Reaction of $[Pt(E\text{-}PhCH{=}CHPh)(PPh_3)_2]$ with *trans*-$[Pd\{Ge(CF_3)_3\}\{HgGe(CF_3)_3\}(PPh_3)_2]$ gave *trans,trans*-$[\{(CF_3)_2GePt(PPh_3)_2HgPd(PPh_3)_2\{Ge(CF_3)_2\}]$ [427]. Some diastereomeric platinum complexes of chiral alkenes have been separated by HPLC [428].

Epr spectroscopy has been used to identify the nickel(I) species in solution when $[\{Ni(butadiene)_2\}_n]$ reacts with Et_2AlCl [429]. The reaction of $[M(cod)_2]$ (M = Ni or Pt) with butadiene and a chelating phosphine (PP) have been studied. The initial product was [M(butadiene)(PP)], in which the butadiene acts as a monodentate ligand. The same species could be obtained in the palladium series from allyl palladium derivatives, and the structure of the complex of $(Me_3C)_2PCH_2CH_2P(CMe_3)_2$ was established in a diffraction study. At low temperatures, in the nickel complex, the butadiene acts as a chelating ligand; in general, the mode of ligation is strongly dependent on the nature of the phosphine ligand. Exchange mechanisms and dynamic processes were discussed in detail [430]. Reaction of oligobutadienyl lithium with allyl nickel iodide gave an allyl nickel oligobutadiene derivative [431].

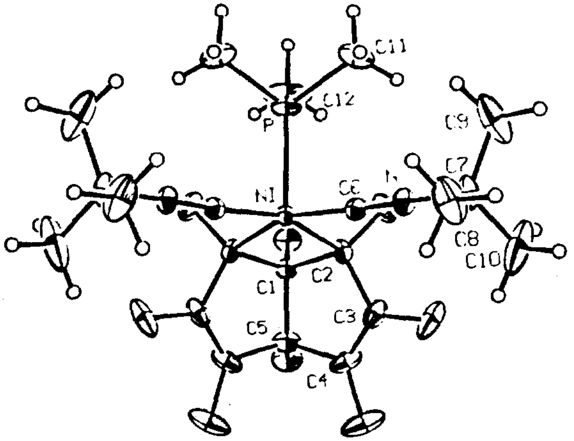
Displacement of cod from [Ni(cod)$_2$] has been used to prepare nickel coordination complexes [432]. It has also been used as a precursor of polymerisation catalysts [433]. [Ni(cod)$_2$] has been used as a hydrogen transfer catalyst in reactions related to coal liquefaction [434]. Reaction of [Ni(cod)$_2$] with L (Me$_3$P or Me$_2$PhP) and C_8F_8 gave [Ni(1,2,5,6-η^4-C_8F_8)L$_2$]. With two moles of Me$_3$NC this was converted to the isonitrile derivative, **251**. This is in contrast to the related reactions in the palladium and platinum series, in which species of the type **251** are the only products formed. **251** reacted with a further mole of ligand to give a 5-coordinate complex such as **252**; this is the first stable 5-coordinate *cis*-dialkylnickel complex to be characterised crystallographically [435].



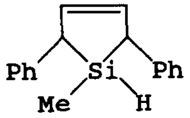
251

Reaction of **253** with [Ni(acac)$_2$] gave [Ni(**253**)$_2$], characterised in a diffraction study. The coordination at nickel is tetrahedral. The complex [Ni(cod)(**253**)] was also prepared [436]. Treatment of [Ni(cod)(bipy)] with Li[AlH$_4$] in thf gave a species of stoicheiometry Li[(bipy)NiAlH$_2$], which was a powerful desulphurising agent [437].

Displacement of cod from [PdCl$_2$(cod)] has been used to prepare various palladium coordination compounds [438]. Palladium diene complexes have been prepared by the addition of the diene to Na[PdCl$_3$(propanone)], giving successively [PdCl$_3$(η^2-diene)] and [PdCl$_2$(η^4-diene)]. The rate of the reaction depended on the diene and reflected the stability of the final product [439]. The structure of 3-(η^2,η^2-1,5-cod)-3-pallada-1,2-dicarba-*closo*-dodecaborane has been established in a diffraction study. The cyclooctadiene has a twist-boat conformation, and metal-diene interactions are smaller than in [$PdCl_2$(cod)]. The significance of the slipping distortion at palladium was discussed [440].



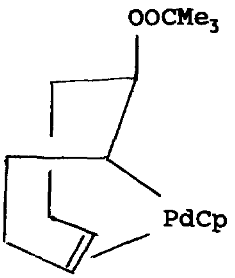
252 (Reproduced with permission from [435])



253

Addition to the cod ligand in palladium cod complexes has again been investigated. Reaction of [Pd(η^3-C_3H_5)(cod)]$^+$ with Me_3COOH at room temperature gave **254**, the reaction being relevant to palladium catalysed oxidations [441]. The complexes **255** are more stable than their methoxy-bridged analogues [442]. Addition of amines to [MCl_2(cod)] (M = Pd or Pt) gave species such as **256** and the product of its deprotonation, **257**. The reaction proceeds more rapidly for the palladium than the platinum complex; palladium(II) is a less effective back-bonder, and nucleophilic attack is facilitated [443].

Displacement of cod from [$PtCl_2$(cod)] [444], [PtI_2(cod)] [445-447] and [Pt$(cod)_2$] [448] has been used in the synthesis of a range of platinum coordination complexes. A 1:1 complex was formed between [PtX_2(cod)] (X = Cl, Br or I) and β-cyclodextrin. γ-Cyclodextrin gave an adduct in good yield from the complex for which X = I, and in low yield from the bromide. The cavity of α-cyclodextrin is too small for these complexes [449].



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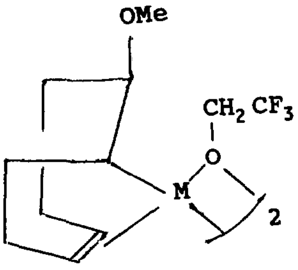

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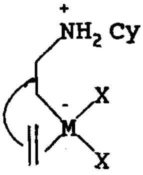

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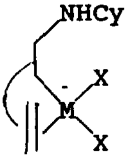
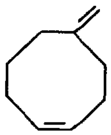


257

The preparation of the complex [Pt(η^2-cycloheptatetraene)(PPh_3)$_2$] has been described, as has that of its benzannelated analogue [450]. There have been structural and mechanistic studies of platinum(II) diene complexes with "crossed" double bonds, such as **258** and **259**. These dienes coordinate to platinum with the endocyclic double bond perpendicular to the coordination planeand the exocyclic bond in the plane. The platinum-carbon bond lengths for the exocyclic alkene are very long [451].



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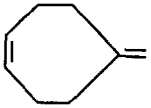
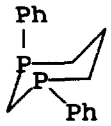


259

The diastereomeric biphosphines, **260** and **261** were separated *via* their platinum complexes [452]. Reaction of [Pt(η^1-Cp)(Ph)(cod)] with PPh_3 gave [Pt(η^1:η^2-C_8H_{12}-C_5H_5)(PPh_3)$_2$] in which the cyclooctadiene and the Cp have become coupled [453].



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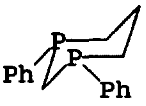
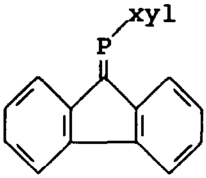


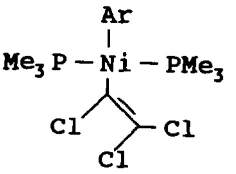
261

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with **262** gave an η^2-coordinated phosphaalkene derivative. The bonding mode was established by comparison of nmr spectroscopic data with those of known complexes. The structure of the complex was established in a diffraction study; the coordination of the phosphaalkene is significantly non-symmetrical [454].



262

Photolysis of **263** gave **264** and **265**; the thermal reaction gave only **264**. The reaction mechanism suggested involved reductive elimination followed by an alternative oxidative addition [455]. Reaction of the dilithiobutadiene, **266**, with $[NiX_2(PR_3)_2]$ gave the nickelole, **267**. This could be protonated to give tetraphenylbutadiene, carbonylated to tetraphenylcyclopentadieneone or reacted with alkynes to give benzene derivatives. A wide range of other reactions were also considered, with particular reference to processes which are important in alkyne trimerisation and tetramerisation [456]. Insertion of $[Ni(PEt_3)_4]$ into **268** gave **269**, which was observed spectroscopically, but could not be isolated. This could be converted into a range of silaheterocycles [457]. Reaction of $[Ni(np_3)]$ with HC≡CCOOEt followed by $Na[BPh_4]$ gave **270** characterised in a diffraction study. The reaction may be interpreted as an oxidative addition [458].



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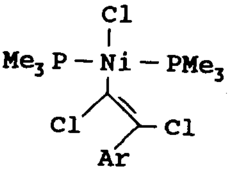

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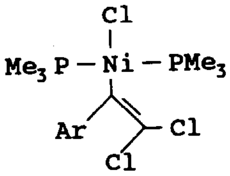

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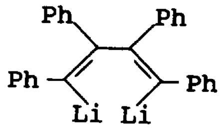

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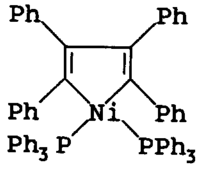

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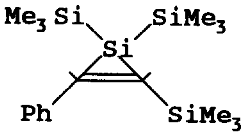

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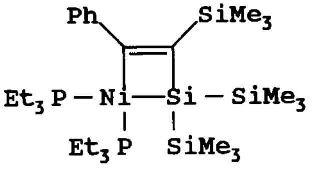

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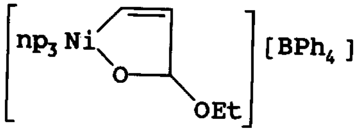
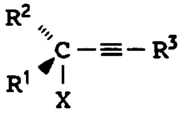


270

Preparation of σ-alkenyl complexes of palladium and platinum of the type *trans*-$[MBr\{C(R)=CR'_2\}(PEt_3)_2]$ using Grignard reagents have been described. Both CO and isonitriles could be inserted into the metal-carbon bonds in suitable examples [459]. Reaction of **271** (X = Cl or OCOMe) with $[Pd(PPh_3)_4]$ gave the σ-allenyl complex **272**, and/or the alkynyl derivative, $R^3C{\equiv}CR^1R^2Pd(PPh_3)_2X$. The reaction was shown to proceed with anti-stereoselectivity, and this type of species is probably an intermediate in the palladium catalysed reactions of organozinc compounds with allene derivatives [460].



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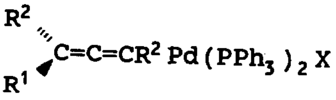
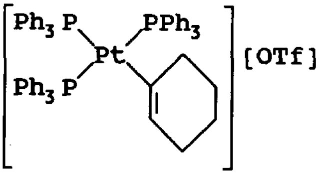


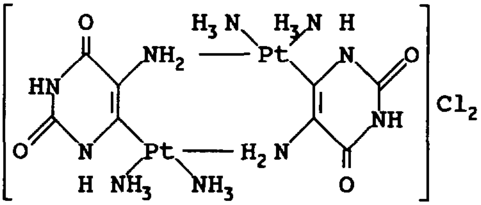
272

Oxidative addition of cyclohexenyl triflate to $[Pt(PPh_3)_4]$ gave **273**. This is a unique structural type, in that the triflate is not metal-coordinated. Reaction of **273** with X^- gave substitution of the phosphine *trans* to the alkenyl ligand, due to its *trans*-effect [461].



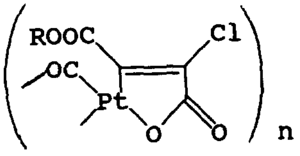
273

The reaction between *cis*-$[PtCl_2(NH_3)_2]$ and 5-aminouracilis is unlike those of other 5-substituted uracils in that it gives the alkenylplatinum complex **274** [462].



274

The complex *cis*-$[PtCl_2(CO)_2]$ reacted with ROOC-C≡C-COOR to give **275** or **276** depending on R. These reacted with L to give **277** or **278**, and all of the complexes could be isolated and characterised [463].



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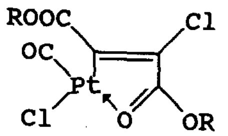

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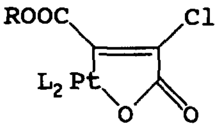

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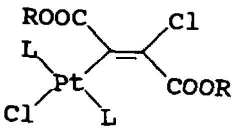
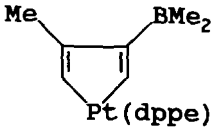


278

Reaction of [Pt(C≡CH)$_2$(dppe)] with Me$_3$B gave **279**, which in CD$_2$Cl$_2$ was converted to **280** [464]. When [Pt(PhC≡CPh)(PPh$_3$)$_2$] was reacted with CH$_2$(SO$_2$CF$_3$)$_2$, the product was **281**, which on recrystallisation from 2-propanol yielded **282**, characterised in a diffraction study [465].



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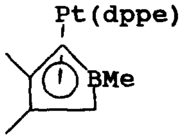

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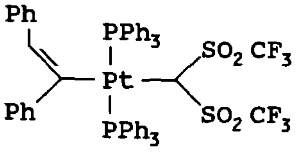

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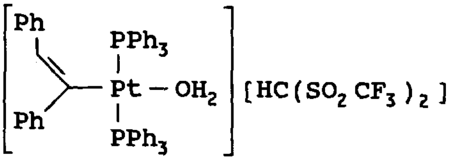


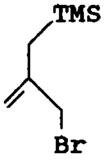
282

Synthetic methods involving π-allyl palladium complexes as intermediates have been reviewed [466], and there has been specific consideration of their uses in the asymmetric synthesis of the side chains of steroids [467]. Uses of oxaallyl complexes in organic syntheses have been described, including numerous palladium derivatives [468].

Correlation effects in the ground state of bis(allyl)nickel have been studied using CI calculations. Redistribution of electron density occurs by increasing the density on the metal compared with that given by an RHF wave function. PES data were compared with ionisation energies calculated using the extended two-particle-hole Tamm-Dancoff method which includes both relaxation and correlation effects. There is good agreement with experimental data,. in contrast to the results with ΔSCF-CI calculations [469]. The predictive capabilities of a simplified semi-empirical Green's function approach and a recent *ab initio* variant for the interpretation of the outer valance ionization energies of bis(allyl)nickel are compared. The *ab initio* version was reported to fail to reproduce the full PE spectrum, and only the older simplified approach was consistent with the experimental data [470]. A reply to this paper compared the Green's function methods in detail. It was claimed that there are some inconsistencies and unexplained facts in the experimental assignments of the PES. It was concluded that both methods have some restrictions [471].

^{13}C and ^{31}P nmr spectroscopic data have been reported for the diastereomeric adducts of $[\{NiBr(\eta^3\text{-}(+)\text{-}1R,5R\text{-pinenyl})\}_2]$ with racemic phosphines. The data allowed the optical purity of the phosphine to be determined [472]. Reaction of **283** with $[Ni(cod)_2]$ gave the allyl derivative, **284**, in 87 % isolated yield. Use of the mesylate, chloride or trifluoroethanaote led to extensive homocoupling, and the palladium analogue desilylated readily to give a trimethylene methane derivative. **284** could be readily coupled with RX to give **285** [473]. Allylation of an aryl bromide by an allyl nickel halide was used in a synthesis of cochliodinol [474]. Oxidation of the π-benzyl complex, $[NiX(CH_2Ph)(PCy_3)]$ (X = Cl or CN) gave benzaldehyde and $PhCH_2OH$, the ratio between the products depending on X, temperature and solvent. Additional hydrogen atoms for alcohol production were derived from the cyclohexyl groups of the ligand [475].

β-Cyclodextrin and γ-cyclodextrin formed 1:1 inclusion complexes with $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$. β-Cyclodextrin also formed a complex with $[\{PdCl(\eta^3\text{-}CH_2CMeCH_2)\}_2]$, but not with $[\{PdCl(\eta^3\text{-}CH_2CHCHMe)\}_2]$. The cavity in α-cyclodextrin was too small for these complexes to be accomodated [476]. The complex $[PdCp(\eta^3\text{-}C_3H_5)]$ was reduced to palladium black by hydrazine [477].



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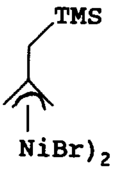

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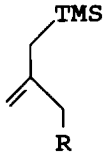
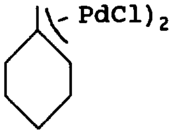


285

Various mechanisms were considered for the conversion of methylene cyclohexane to the palladium allyl complex, **286**. Allylic palladation and isomerisation showed different isotope effects, ruling out rate determining formation of {Pd(allyl)HCl} as a common intermediate. When the solvent is dmf or benzene, abstraction of the allylic hydrogen in **287** probably involves an external base, whereas in ethanoic acid, this hydrogen is lost through elimination of HCl [478]. Reaction of **288** with $Na_2[PdCl_4]$ was reported to give a bridged π-benzyl derivative [479].



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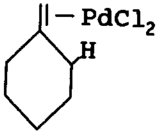

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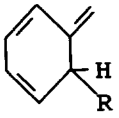
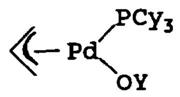


298

The new allyl complexes $[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)(cod)][BF_4]$, $[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)(tmeda)][BF_4]$, $[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)(Cp)]$ and $[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)(tmeda)][BF_4]$ have been synthesised by extensions of standard methods. All were characterised spectroscopically, and two in diffraction studies. In the phenyl substituted complexes the allylic carbon which bears the phenyl group is appreciable further away from the metal than the other one [480]. Complexes of the type $[M_2(\mu\text{-tz})_2(L_2)_2]$ (tz = triazolate, M = Pd, L_2 = allyl) have been prepared and characterised. Coordination of another metal, including a second palladium allyl grouping, at the uncomplexed nitrogen atom of the triazolate was discussed [481].

Reaction of CH_2=$CHCH_2OY$ (Y = COMe or Ar) with $[Pd(PCy_3)_2]$ at room temperature gave **289** and $[Cy_3PCH$=$CHMe][OY]$. Nmr spectroscopy showed that the allyl group in **289** was fluxional, a result which was confirmed by deuterium labelling studies. A wide range of other leaving groups were also discussed [482]. Reactions of allyl thioethers such as CH_3CH=$CHCH_2SPh$ with $[Pd(PCy_3)_2]$ gave bimetallic products such as **290**. The effects of substituents on reactivity were discussed [483].



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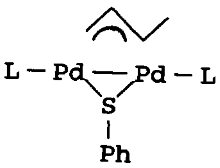

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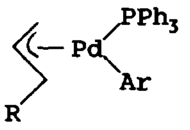
The complexes $[M(\eta^3\text{-allyl})L_2]$ could be reduced by hydride or cathodically to give products which were determined by the nature of L. The reduction potential could be related to the stability of the starting material [484]. The reactivity of palladium allyl complexes with an $[O_2]^{2-}$ bridge has been investigated [485].

Photoreaction of palladium allyl complexes to give 1,5-dienes has been studied by CIDNP. Strong polarisation of the protons of the 1,5-dienes was observed during the reaction. Addition of haloalkanes or PPh_3 resulted in polarisation being observed in the protons of alkylated alkenes. The reaction mechanism was discussed in detail [486]. Reaction of **291** with two molar equivalents of a ligand L gave **292**. **292** (R = H) showed dynamic behaviour with exchange with an undetected η^3-allyl complex, but the complex for which R = Me was not dynamic. Reaction with an electrophile, EX, gave *cis*-$[Pd(Ar)XL_2]$ and CH_2=$CHRE$, with good regioselectivity. By contrast, **291** reacted with EX to yield ArE and **293**. **292** reacted with butenedioate anhydride to give a single stereoisomer of a 1:1 adduct, **294**, characterised in a diffraction study. A mechanism was proposed for the reaction [487].



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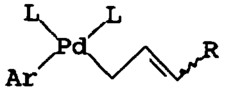

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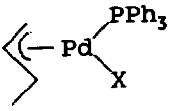

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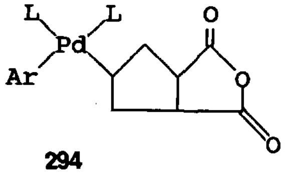
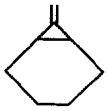


294

Reaction of **295** with [$PdCl_2(MeCN)_2$] gave **296**, the structure of which was assigned spectroscopically. The mechanism of the reaction was thought to involve initial metal coordination to the less hindered face, followed by *cis*-addition of PdCl, and thermal disrotatory ring opening. This initially gives the stereisomer of **296**, but isomerisation to the more stable diastereoisomer appears to be rapid. Several related reactions using substrates with varying substitution were also reported [488]. Substitution of **296** with two molar equivalents of the anion of diethyl propanedioate gave **297** in good yield. With only one molar equivalent of the anion, the product was **298**. The reaction mechanism was discussed [489].



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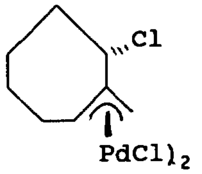

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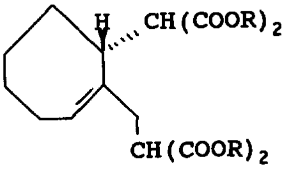

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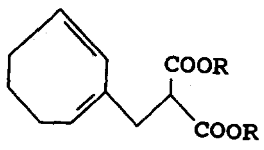
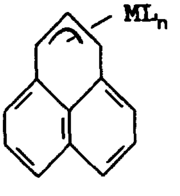


298

In the complex **299** migration of the palladium over all three rings was studied by dynamic nmr spectroscopy on heating [490]. Reaction of **300** (R = Me or OMe) with palladium(0) gives **301**, which may react with a suitable electrophile to yield **302**, which is then deprotonated and cycloadds to an alkene bearing an electron-withdrawing group (ewg) to give **303**. With **300** (R = OMe), this is the main observed pathway. However, **301** may react directly with the acceptor alkene to yield **304**, this being the main product from **300** (R = Me). The reaction mechanism was discussed in detail [491].



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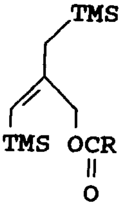

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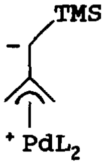

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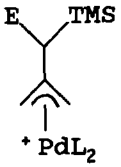

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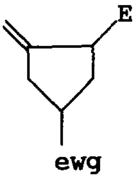

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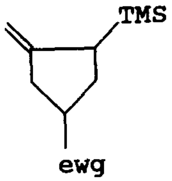
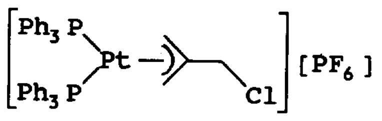


304

In a polar medium, the η^1-platinum complex, $[Pt(CH_2CH{=}CH_2)Cl(Ph_2PCH_2CH_2SR)]$, (R = Me or Ph) was converted to the cationic η^3-derivative $[Pt(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH_2SR)][BF_4]$. Nmr spectroscopic data for the two complexes were compared [492]. The synthesis of $[PtCl(CH_2CH{=}CH_2)L_2]$, and mechanistic studies of its reactions with electrophiles have been described [493]. Reaction of either $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt(PPh_3)_4]$ with $CH_2{=}C(CH_2Cl)CH_2Cl$ in the presence of $K[PF_6]$ gave **305** which reacted with a ligand, L, (L = PPh_3, py or Et_3N) to yield **306**. Treatment of **305** with $[Pt(C_2H_4)(PPh_3)_2]$ resulted in the formation of a trimethylene methane complex, **307** [494]. The structure of **308** has been established in a diffraction study [495].



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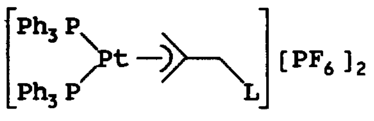

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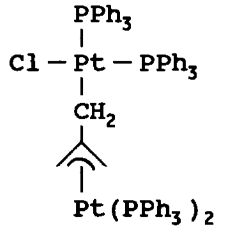

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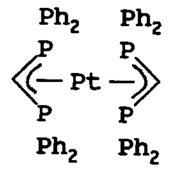

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10 METAL ALKYNE AND ALKYNYL COMPLEXES

There has been a review of new methods for the preparation of heterobimetallic dppm complexes, including alkynyl derivatives [496].

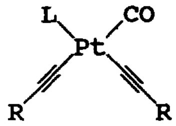
CASSCF and contracted CI calculations have been performed on ethyne complexes of nickel and palladium. The lowest singlet and triplet of the nickel complex, and the lowest singlet of the palladium complex were investigated. Minima were located on both singlet surfaces, and CCI calculations were performed at these geometries. The results were in accord with data for alkynes adsorbed on metal surfaces [497]. Nickel complexes of 1,4,8,11-tetraazaundecane with $[B(C{\equiv}CH)_4]^-$ were studied; at least one alkyne was metal bound [498,499]. The complexes $[CoNiM(RC{\equiv}CR')(CO)_6(Cp)]$ (M = Fe, Ru or Os) have been prepared (from $[CoNi(RC{\equiv}CR')(CO)_6(Cp)]$ and $[Fe_2(CO)_9]$, $[Ru(CO)_5]$ or $[Os(CO)_5]$ respectively). Several structures determined in diffraction studies were discussed in great detail [500].

Simple alkynes such as R-C≡C-H (R = Ph or MeC_6H_4) do not usually react with $[Pd_2Cl_2(\mu\text{-dppm})_2]$, but in the presence of an acid catalyst, the complex $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\eta^2\text{-CH=CR})]$ was formed. Ethyne itself could also be added in this manner, and the known reactions of alkynes bearing electron-withdrawing groups were catalysed. The process could be reversed thermally or photochemically. Reaction of $[Pd(PPh_3)_4]$ with dppm and $CCl_2{=}CH_2$ gave $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-C=CH}_2)]$ in excellent yield. This could be protonated to give $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}\sigma\text{-}\eta^2\text{-CH=CH}_2)][BF_4]$, rather than a bridged carbyne derivative. It was suggested that protonation of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ gave $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-H})]^+$, which reacts more rapidly with alkynes [501].

Phenylethyne has been polymerised by $[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ to give mostly soluble polyphenylethyne [502]. Reaction of $H_2[PtCl_6]$ with $(CH_2{=}CHSiMe_2)_2O$ gave a platinum vinylsiloxane. This was reacted with $PhC{\equiv}CC(Me)(Ph)OH$ to give a platinum alkyne complex which acted as a catalyst for alkene hydrosilylation [503].

Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with $[Ag(C{\equiv}CPh)_2]^-$ gave $[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ and $[AgCl_2]^-$. Similar reactions were noted with the copper alkyne salt [504].

The preparation of **309** and *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$ from *cis*-$[PtCl_2(CO)L]$ and $Hg(C{\equiv}CR)_2$ was previously known. The bis(alkyne) derivative reacted with *cis*-$[PtCl_2(CO)L]$ to give **310**. Now the reaction of *cis*-$[PtCl_2(CO)L]$ with $[Au(C{\equiv}CR)(PPh_3)]$ has been shown not to be stereospecific, and to give both **309** and **310**. Both of these reacted with further gold alkyne to yield *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$. It was also noted that *cis*-$[PtCl_2(CO)L]$ reacted with $[Au(Cp)(PPh_3)]$ to give **311** only [505]. The preparations of *cis*-$[Pt(C{\equiv}CPh)_2L_2]$ either from *cis*-$[Pt(C{\equiv}CPh)_2(cod)]$ and L (L = PPh_3 or $PMePh_2$) or *cis*-$[PtCl_2L_2]$, phenylethyne and Na[OEt], have been described, although the routes were not more generally applicable. Isomerisation to the *trans*-complexes was not successful with nucleophilic catalysts, but was accomplished with $HgCl_2$, HgClPh, CuI or $SnCl_2$. The reaction mechanism was thought to involve alkynyl transfer and isomerisation of a species such as $[PtX(C{\equiv}CPh)L_2]$ [506]. Treatament of *trans*-$[PtCl_2(PEt_3)_2]$ with either $Me_3SnC{\equiv}CR$, or better, $Me_2Sn(C{\equiv}CR)_2$, gave *trans*-$[PtCl(C{\equiv}CR)(PEt_3)_2]$. Addition of further alkynyltin reagent to this gave the bis(alkyne) complex, and addition of $Me_3Sn(C{\equiv}CR')$ gave a complex with two different alkynyl ligands [507].



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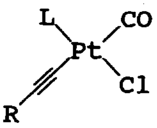

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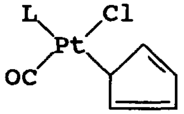

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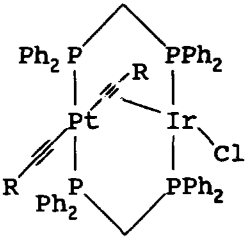
Reaction of *trans*-[Pt(C≡CR)$_2$(η^1-dppm)$_2$] with [Ir$_2$Cl$_2$(cyclooctene)$_4$] gave **312**, which reacted with molecular hydrogen to give **313**. Carbonylation of **313** yielded **314** which could be more readily synthesised from *trans*-[Pt(C≡CR)$_2$(η^1-dppm)$_2$] and *trans*-[IrCl(CO)(PPh$_3$)$_2$]. When **314** was reacted with Na[PF$_6$], the product was [(RC≡C)Pt(μ-dppm)$_2$(μ-C≡CR)Ir(CO)]$^+$ which reacted with molecular hydrogen to give [(RC≡C)Pt(μ-dppm)$_2$(μ-C≡CR)(μ-H)IrH(CO)]$^+$ [508].



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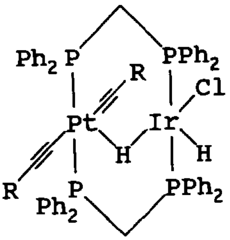

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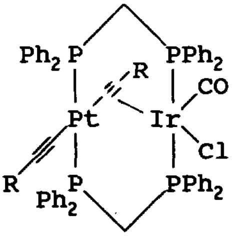
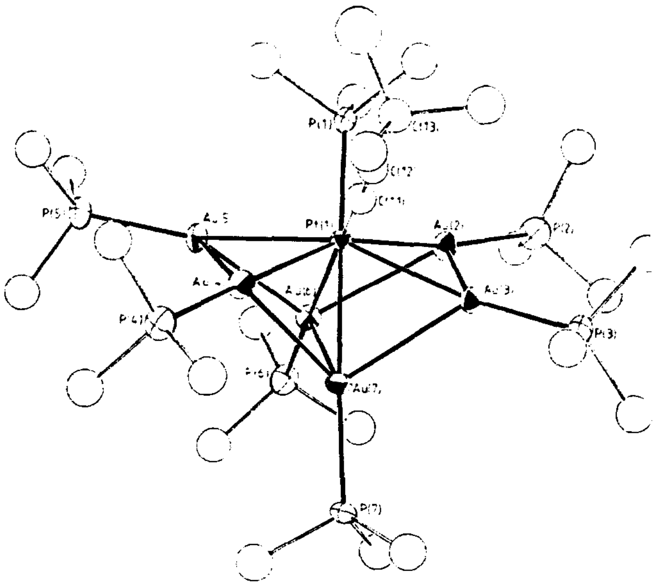


314

Treatment of [Pt(PPh$_3$)$_3$] with [Au(C≡CCMe$_3$)] in toluene gave the cluster complex [Au$_6$Pt(C≡CCMe$_3$)(PPh$_3$)$_7$][Au(C≡CCMe$_3$)$_2$], **315**. This new type of heptametallic cluster consists of two {Au$_4$Pt} square-based pyramids with platinum apical, fused about a common triangular face. The metal core has access to 90 valence electrons and therefore cannot be rationalised by the normal theories of condensed metal polyhedra which require a cluster of this type to have 100 electrons. The cation showed fluxional behaviour on the nmr spectroscopic timescale, with an unprecedental time-averaged structure of a hexagonal pyramid with an {Au$_6$} base and the {Pt(C≡CCMe$_3$)(PPh$_3$} unit rotating [509].

11 COMPLEXES OF DELOCALISED CARBOCYCLIC SYSTEMS

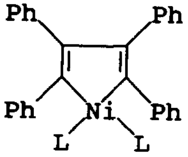
Reaction of [Ni(cod)$_2$] with Ph$_3$C$_3$Br at and Ni:L ratio greater than 0.67 gave [C$_3$Ph$_3$][Ni$_2$(C$_3$Ph$_3$)$_2$(μ-Br)$_3$] characterised in a diffraction study. The six Ni-Br bonds were essentially equivalent. Reaction with [Ni(CO)$_4$] yielded [NiBr(C$_3$Ph$_3$)(CO)$_2$], which lost CO to give [Ni$_2$(C$_3$Ph$_3$)$_2$(μ-Br)$_2$] [510].



315 (Reproduced with permission from [509])

Perspective view (ORTEP, 50 % probability thermal ellipsoids) of the cation $[(Au(PPh_3)_6Pt(PPh_3)(C{\equiv}C\text{-}CMe_3)]^+$ with only the *ipso* carbon atom sof the phenyl rings and no hydrogen atoms shown.

The cyclobutadiene nickel complex, $[NiBr_2(C_4Ph_4)]$ reacted with *tert*-BuLi and L to give the nickelole, **316** [511].



316

Metallocenes in biochemistry, microbiology and medicine have been reviewed, mainly with regard to their use as anti-tumour agents [512]. The complex $[NiCp_2]$ has been used as an example in reviews of the far UV spectra of transition metal complexes [513], doubly charged ion mass spectrometry of metallocenes [514], strengths of metal-ligand bonds in metal arene complexes [515], and electron attachment studies of organometallics [516].

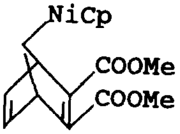
The reaction of $[NiCp_2]$ with CO has been examined by the INDO method. Coordination of CO gives little change in the charge on the metal or in metal-Cp bonding [517]. Organic triplets with energies in the range 0.9-3.2 eV were quenched by [NiCp$_2$] at diffusion controlled rates. This efficient quenching, explainable in terms of a combination of energy and electron transfer, suggests the existence of a low-lying spin-forbidden transition (<0.9 eV) [518]. [NiCp$^*_2$]$^+$ was diluted in various diamagnetic host lattices and studied by epr spectroscopy at low temperature as single crystals and as polycrystalline samples. From analysis of the g-tensor, the Co-hyperfine tensor and EHMO calculations a quantitative comparison of covalency and dynamic Jahn-Teller effects was possible. Covalency and spin distribution were not much affected by methylation. Low temperature epr linewidths in orbitally near-degenerate sandwich compounds were shown to be determined by random strain effects [519]. Large anisotropic g-shifts for [V(C$_6$H$_6$)$_2$] or [V(Cp)(cycloheptatrienyl)] doped into [NiCp$_2$] were observed by X-band epr spectroscopy at 3 K. It was shown by a molecular field analysis that [NiCp$_2$] is a weakly ferromagnetically coupled Van Vleck paramagnet [520].

In one colour experiments, state distributions of nitric oxide photofragments were probed by (2+2) multiphoton ionisation following dissociation of [NiCp(NO)]. The NO (γ = 0-3) is formed in a broad distribution of highly excited rotational states, indicative of dissociation from an excited state having a bent conformation [521]. The electronic structure of [{Ni(CO)(Cp)}$_2$] was examined using the Fenske-Hall MO method. It was possible to correlate the simple valence bond description of the metal-metal bond with the bond order derived from the electronic structure [522].

Nickel dispersed on carbon was prepared by pressure pyrolysis of [NiCp$_2$]/DVB polymer at temperatures <700 °C and 125 mPa. The carbon produced contained uniformly distributed metallic nickel particles <40 nm in size with low crystallinity. [NiCp$_2$]/DVB underwent degradation of the Ni-C bond at low temperature (~280 °C) reflecting the low mean dissociation energy of the metal-carbon bond [523].

The complex [FeCp$_2$]X has been used as a one-electron oxidant for organometallic complexes. Thus [NiCp$_2$] is oxidised to [NiCp$_2$][BF$_4$] in near quantitative yield. The metal-metal bond in [{Ni(CO)Cp}$_2$] is cleaved in the presence of a ligand L (*e.g.* PPh$_3$) to give [NiCpL$_2$][BF$_4$]. Indenyl complexes reacted similarly [524]. [FeCp$_2$][BF$_4$] reacted with [NiCp$_2$][BF$_4$] to give [{FeNiCp$_4$}$_n$][BF$_4$]$_{4n}$, a polymeric material for which a stacked structure was proposed [525].

[NiCp$_2$] reacted with [PH$_4$]I to give successively [Ni(Cp)I(PH$_3$)] and [Ni(Cp)(PH$_3$)$_2$]I. The weak donor properties of the PH$_3$ were illustrated by the reactivity of the compounds and nmr spectroscopic data [526]. Reaction of [NiCp$_2$] with dmad gave **317**, the reactions of which were investigated [527]. Cross linking of the alkyne terminated monomer **318** was accomplished using a range of organometallic complexes, including [$NiCp_2$] [528].



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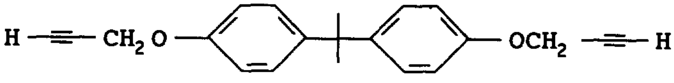


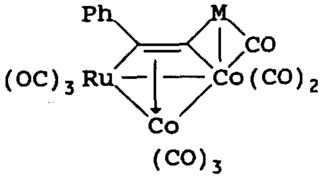
318

The redox behaviour of the 49 electron species [$Ni_3Cp_3(\mu_3\text{-}CO)_2$] has been reexamined. CV studies revealed that both this an its C_5H_4Me analogue undergo reversible one-electron oxidations to 48 electron monocations [529].

A range of iron/nickel cyclopentadienyl cluster complexes have been purified by HPLC [530].

Treatment of [$Ni(CO)_4$] with C_5Ph_5Br gave [$Ni_2(Cp')_2(\mu\text{-}Br)_2$]. The complex was stable to heat, but decomposed in air in solution. The oxidation behaviour of [$NiCp'_2$] was described; the complex was reversibly oxidised at 0.085 V and 0.98 V in dichloromethane to the monocation and dication respectively [531].

Reaction of [{Ni(CO)(Cp)}$_2$] with the 46 electron species [$Ru_3H(CO)_9(\mu\text{-}PPh_2)$] gave [$Ni_2Ru_3(CO)_9(Cp)_2(\mu_5\text{-}PPh)$] with reductive elimination of benzene. The structure of the complex was established; the pentanuclear clusters of metal atoms all interacted with the {PPh} ligand [532]. The preparations of **319**, including the complex for which M = NiCp, have been described [533]. Reaction of [$Ni(CO)(Cp)$]$^-$ with $FpCH_2COCl$ gave [$Cp_2Fe(CO)_2(\mu\text{-}CH_2CO\text{-}C,C)Ni(CO)(Cp)$] [534].



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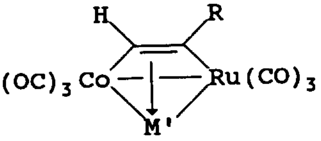
The species {CpNi(P{S}R$_2$)$_2$}$^-$ acts as an *S,S*-chelate ligand with a wide range of divalent metal ions, including Ni^{2+}, Mn^{2+}, Co^{2+} and Fe^{2+} [535]. Reduction of [$Ni_2Cp_2(\mu\text{-}SR)_2$] with Li[$AlH_4$] gave RH (R = Ph, $PhCH_2$, 1-decyl, or 2-Np) [536]. The conversion of [$Mo(Cp)_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$] to [$Mo_2Ni_2(CO)_2(Cp)_2(\mu_3\text{-}S)_4$] and [$Mo_2Ni_2(Cp)_4(S)_4$] has been reported. The complexes were useful catalysts for the hydrogenation of CO [537].

The species [$Cp_4NiB_4H_4$] has been used as an example in a discussion of the structure and bonding in metallboranes [538].

Thermolysis of **320** (M' = NiCp) in hexane at 60 °C, gave **321**, which was also prepared by a metal exchange process [539]. The cluster complex **322** was used as a catalyst for phenylethene hydrogenation [540].



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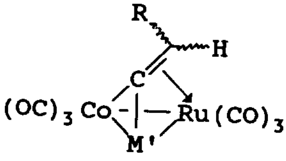

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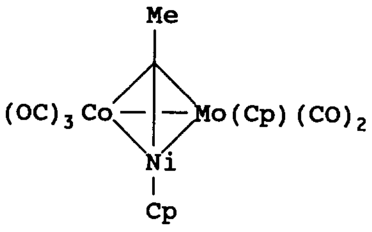

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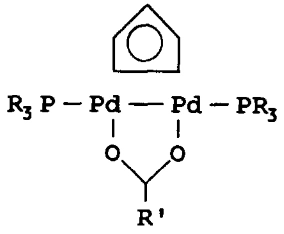
The complexes [$CpNiOs_3(\mu$-$H)_3(CO)_9$] and [$CpNiOs_3(\mu$-$H)_3(CO)_8L$] (L = PPh_2H or $P(C_6H_4$-2-$Me)_3$) have been used as catalysts for diene hydrogenation. There is reasonable selectivity for reduction of the less substituted double bond, and alkynes can be reduced to alkenes. Non-conjugated dienes are isomerised [541]. The complex [$CpNiOs_3(\mu$-$H)_3(CO)_8L$] (L = PPh_2H) was characterised in a diffraction study, and a number of its reactions studied [542].

The reaction of **323** with Na[$CpM(CO)_3$] (M = Cr, Mo or W) gave **324**. The complex for which M = Mo and R = $CHMe_2$ was characterised in a diffraction study; the {$MoPd_2C$} atom skeleton is tetrahedral and the Pd-Mo bond is semibridged by a CO ligand. Reaction of **325** with Me_3SiX gave **326**. Related reactions of an allyl bridged species were also reported [543]. Electrochemical measurements implied that [$Pd_2(\eta^5$-$C_5Ph_5)_2(\mu$-$PhC{\equiv}CPh)$] undergoes two one-electron oxidations and one one-electron reduction at a platinum electrode. Chemical oxidation of [$Pd_2(\eta^5$-$C_5Ph_5)_2(\mu$-$PhC{\equiv}CPh)$] with Ag[PF_6] gave [$Pd_2(\eta^5$-$C_5Ph_5)_2(\mu$-$PhC{\equiv}CPh)$][PF_6] which reacted with ligands, L, to yield [$Pd(\eta^5$-$C_5Ph_5)L_2$][PF_6] [544].



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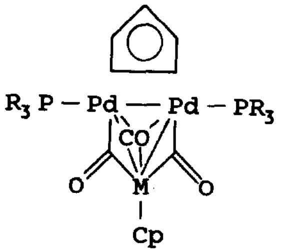

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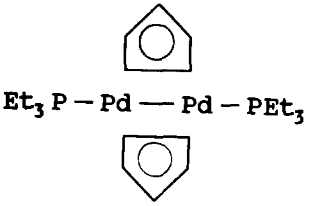

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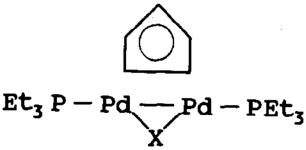


326

The complexes [NiR_2(η^6-arene)] R = $SiCl_3$, SiF_3 or C_6F_5) have displayed high activity as catalysts for alkene isomerisation, especially in bromobenzene solution [545]. The reactions of aromatic guests with [$Ni(NCS)_2(4\text{-}Mepy)_2$] have been further investigated [546].

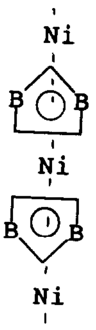
[$Pd(acac)_2$] was reduced by hydrazine in a thf solution of BL6533 to give a palladium(0) dispersion. A similar dispersion was produced on polystyrene, and was analysed by small angle X-ray scattering. The material seems to be isolated palladium atoms, or small clusters stabilised in the polymer by donation from the arene rings [547].

12 METAL CARBORANE AND RELATED COMPLEXES

Polyhedral metallaboranes and metallacarboranes [548] including those containing a {CpFe} unit [549] have been reviewed.

The band structure of the one-dimensional polydecker system, {$Ni(C_3B_2H_5)$} was investigated by means of a semi-empirical crystal orbital formalism based on an improved INDO Hamiltonian. It was concluded that the one-dimensional arrangement was unstable relative towards a unit of two half sandwiches. The band structure properties in the outer valence region were analysed, and the calculated band gap found to be in line with the experimentally observed semiconducting properties of the one-dimensional chain [550]. EHMO calculations have been undertaken to study the electronic structures of multidecker transition metal sandwich complexes including $[CpNi(C_3B_2R_5)CoCp]^+$, $[CpNi(C_3B_2R_5)CoCp]$ and $[CpNi(C_3B_2R_5)NiCp]^x$ (x = +1, 0 or -1) [551].

The synthesis of the 1:1 polymer, **327**, from **328** has been described. **327** is stable to heat, but insoluble in organic solvents, and EXAFS measurements confirmed the polydecker structure [552].



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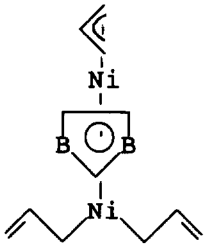

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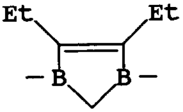
Reaction of $[Ni(C_2H_4)_3]$ with **329** gave **330**, characterised in a diffraction study and an allyl nickel borane. The isolobal analogy of Cp and $[C_3B_3R_5H]^-$ was discussed [553]. The borane *nido*-2,6-$C_2B_7H_{11}$ has recently become available in good yield from a new synthesis. Its reaction with nickel atoms in the presence of 2-butyne has been studied, and yields [5,7,8-Me_3-11,7,8,10-(η^3-C_4Me_4H)$NiC_3B_7H_7$], **331**, characterised in a diffraction study. This is a sandwich complex in which the nickel is bonded to an η^3-cyclobutenyl goup and a C_3-carborane. This complex has a very unusual cage structure, intermediate between *closo*- and *nido*, with the nickel slipped to one side in a *closo*-type structure to form the open face. The structure was compared theoretically with others containing slipped {$Pt(PPh_3)$} groups. The reaction involves extensive rearrangement of the starting material; one of the carbon atoms of the carborane has been reduced and is incorporated in a B-Me group. A plausible but unproven mechanism was proposed [554].



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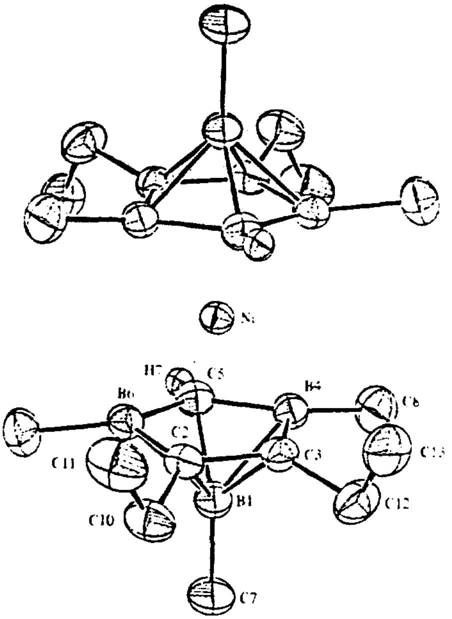


330 (Reproduced with permission from [553])

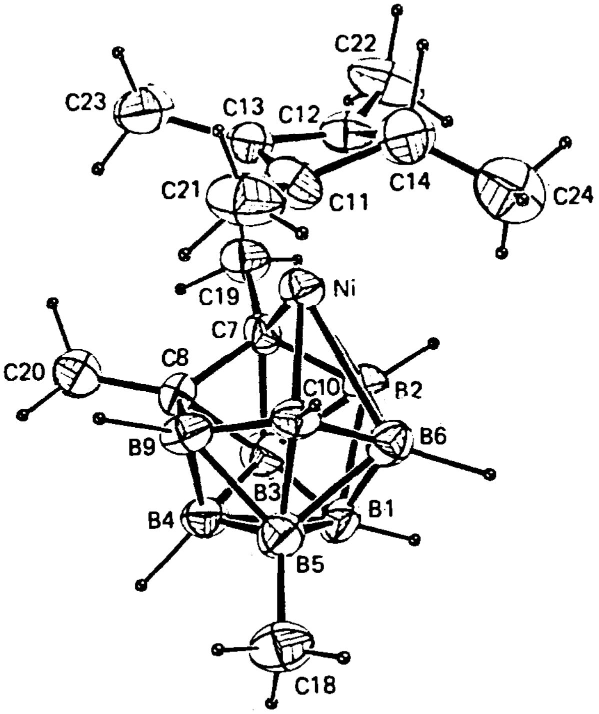
The reaction between [NiX$_2$(dppe)] (X = Cl or Br) and K[C$_2$B$_4$H$_7$] has been studied. For X = Br, the product was 1,1-dppe-2,3-dicarba-1-nickela-*closo*-heptaborane, even at temperatures as low as -80 °C. From the complex for which X = Cl an intermediate 4,5-{μ-Cl(dppe)Ni-2,3-dicarba-*nido*-hexaborane} could be isolated at -80 °C, and this was converted to the heptaborane at room temperature. A plausible mechanism was proposed [555]. Cyclometallated phosphinated carbaboranes have been studied [556].

Reaction of **332**, LH, with [Ni(CO$_4$] gave **333** and an isomer, [Ni(η^6-L)(η^4-LH$_2$)], in which there is a strong nickel-boron interaction. The complex [Ni(η^6-L)(1,4,5-η^3-C$_8$H$_{13}$)] was formed on reaction of **332** with [Ni(cod)$_2$] [557].

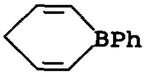
13 CATALYSIS BY METAL COMPLEXES

There have been a number of reviews dealing with the uses of complexes of metal of the nickel triad in organic synthesis [558,559]. These have included discussions of nickel catalysed reactions of zirconium complexes [560], electroorganic syntheses involving nickel complexes [561-563], synthesis of organofluorine compounds using transition metal catalysis [564], and carbon-carbon bond forming reactions catalysed by nickel and palladium complexes [565]. There have been discussions of the uses of palladium complexes in allylation using allyl carbonates and hydrogenolyses [566], reactions of organotin complexes

[567], hydrocyanations and cross-coupling reactions [568], and electrocatalytic reactions [569]. Reaction of $[PdCl_2(PPh_3)_2]$ with two molar equivalents of RLi gave a species of apparent stoicheiometry $\{Pd(PPh_3)_2\}$. This reacted with iodobenzene by oxidative addition, and with added phosphine to give tris and tetrakis phosphine complexes. However, the nature of the halide in the starting material is relevant to the properties of the complex produced. The data were consistent with a formulation as $LiX\{Pd(PPh_3)_2\}$, $Li_2X_2\{Pd(PPh_3)_2\}$ or some aggregate of these. A similar species was produced by reduction with dibal [570].



331 (Reproduced with permission from [554])
ORTEP drawing of $[5,7,8\text{-}(CH_3)_3\text{-}11,7,8,10\text{-}\{\eta^3\text{-}C_4(CH_3)_4H\}NiC_3B_7H_7]$.



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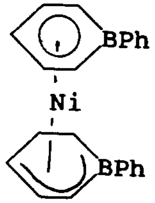
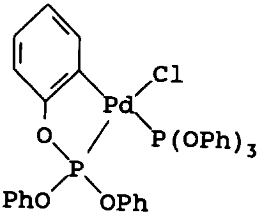


333

There have been reviews of hydrogenations catalysed by palladium and platinum complexes [571]. Anionic carbonyl clusters of platinum have been considered as homogeneous and supported catalysts in hydrogenation and transfer hydrogenation [572], and the hydrogenation of arenes with [Ni(acac)$_2$]/Li[AlH$_4$] has been discussed [573]. The uses of platinum and palladium complexes of organic dyes, which have been immobilised, as catalysts for reduction of dienes, alkynes or nitroarenes has been discussed [574], as have other immobilised palladium and platinum species [575]. Palladium complexes of sulphur ligands are 50-500 times as resistant to thiophene action in hydrogenation reactions than homogeneous or heterogenised species bearing nitrogen ligands [576].

Supported Ziegler catalysts have been used in the reduction of 1-octene [577]. The complex **334** was a catalyst for hydrogenation of simple alkenes, although *cis*-[PdCl$_2${P(OPh)$_3$}$_2$] was inactive [578].



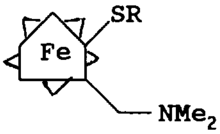
334

Reaction of H$_2$[PtCl$_6$] with an amine, followed by dibal, gave reduced platinum complexes which catalysed reduction of alkenes, dienes and alkynes [579].

The species formed from [NiCp$_2$] and Li[AlH$_4$] catalysed reduction of cyclooctadiene to cyclooctane and E-PhCH=CHCOOMe to PhCH$_2$CH$_2$COOMe [580]. When [Ni(acac)$_2$] was photolysed in the presence of xanthone and hydrogen the products were hydridonickel complexes. These catalysed isomerisation of 1,5-cod successively to 1,4-cod and 1,3-cod, followed by reduction to cyclooctene and cyclooctane. Deuterium labelling studies were used to elucidate the reaction mechanism [581].

The pattern of hydrogenation of the polar lipids of pea chloroplasts incubated in the presence of [Pd(QS)$_2$], a sulphonated alizarin derivative of palladium(II), has been investigated [582]. The carbon-carbon double bonds of the unsaturated fatty acids of the membrane were reduced, but the double bonds of neutral lipids such as chlorophylls, carotenoids, and plastoquinone, were not affected [583].

Reaction of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ with amines gave a catalyst for the selective reduction of dienes or alkynes to alkenes [584]. Ferrocenyl thioether amines such as **335**, complexes with palladium(II) have been used as catalysts for reduction and isomerisation of 1,5-cod and other dienes to monoenes [585].



335

The reduction of $[Pd(\eta^3\text{-}C_3H_5)(Cp)]$ with hydrazine in ethanol gave a palladium black complex which was used as a catalyst for hydrogenation of phenylethyne [586]. Reduction of nitroarenes catalysed by $[\{M(acac)_2\}_n]$ has been discussed; extensive kinetic data were presented [587].

There have been a number of reports of the reactions of polymer supported catalysts. Reduction of 1,4-cyclohexadiene to cyclohexene has been reported to occur in the presence of $[Ni(acac)_2]/Et_3Al_2Cl_3$/phosphinated polystyrene [588]. The cluster complex, $[NiOs_3(\mu\text{-}H)_3(CO)_9(Cp)]$, on γ-alumina, was used as a catalyst for the reduction of alkynes, arenes, CO and CO_2 [589].

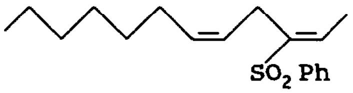
A catalyst derived from a mixture of $[Ni(acac)_2]$/butadiene/phenylethene block copolymer solution/Et_2AlOEt has been used to hydroganate solprene 1205 [590]. Palladium and platinum complexes supported of poly(ethenylpyrrolidone) have been used as catalysts for reduction of alkenes, nitriles, imines and nitro groups. When palladium is supported on polyetheneimine, alkynes may be selectively reduced to *cis*-alkenes [591]. Catalysts preprared from $K_2[PdCl_4]$ and carboxymethycellulose followed by reduction by molecular hydrogen, or by reaction of the polymer with $NiCl_2$ and reduction with $Na[BH_4]$ were used in the hydrogenation of rape seed oil [592].

Montmorillonite was functionalised with phosphines or with pyridine, to form palladium catalysts suitable for reduction of simple alkenes. The catalyst showed low metal leaching

[593]. Long carbon chains bearing phosphinated arenes were grafted on to silica. The material was palladated, and the complexes used as catalysts for alkene hydrogenation [594]. Palladium and platinum complexes supported on silica, alumina or zeolites have been used for reduction of alkenes, dienes and alkynes [595]. With $PdCl_2/(C_9H_{19})_3N$ deposited on a mineral support, it was shown that 5-12 % of the palladium sites were active in reduction of alkenes, dienes and alkynes [596]. A side chain bearing a chelating amine was grafted onto silica or alumina, and then reacted with $PdCl_2$ to give a catalyst for hydrogenation of alkenes and nitro groups [597]. When $PdCl_2$ was reacted with polyetheneimine and then reduced with $Na[BH_4]$, an excellent catalyst for reduction of conjugated dienes was obtained [598]. A palladium complex of an aminated chloromethylated copolymer of phenylethene and bis(ethenyl)benzene was used as a catalyst for reduction of nitroarenes. There was a careful study of the effects of reaction conditions [599]. Silica supported cross-linked poly(2-methylpropenoic acid) palladium and platinum complexes have been prepared and used as catalysts for hydrogenation of alkenes and nitroarenes, under very mild conditions [600].

Hydrogenolysis of aryl halides, ArX, (X = Cl or Br) was accomplished under molecular hydrogen in the presence of $[Pd(PPh_3)_4]$. Aldehyde and nitro groups were not reduced, and the reaction also tolerated free hydroxyl groups, but yields were lower with arenes bearing electron-donating substituents [601]. The same catalyst system was used for chlorinated pyrazine-*N*-oxides; there was no deoxygenation observed [602]. Polymethylhydrosilane has also been used as a source of hydrogen with $[Pd(PPh_3)_4]/(PhCH_2)_3N$ as the catalyst system. With either this or an alternative system based on$[Pd(PPh_3)_4]/[HCOO]Na$, haloarenes, haloalkenes or α-haloketones were hydrogenolysed [603]. Aryl triflates were hydrogenolysed by hydrogen transfer from HCOOH in the presence of $Pd(OCOMe)_2/PPh_3$ or dppf/Et_3N. The reaction is tolerant of a number of functional groups including carbon-carbon double bonds [604]. Similar reaction of $ArOSO_2R_f$ were reported to occur with a catalyst system generated either from $[PdCl_2(PPh_3)_2]$ or $[Pd(PPh_3)_4]$ with $Bu_3N/HCOOH$ [605].

When **336** was reacted with BuMgCl in the presence of $[Pd(acac)_2]/DABCO$ the product was the desulphonated species, **337** [606].



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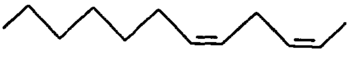
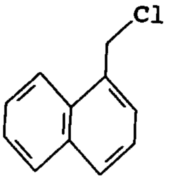


337

Hydrogenolysis of the benzylic halide, **338**, was accomplished by hydrogen transfer from methanoate salts in the presence of palladium complexes of the ligand, **339**. The crown ether moiety of **339** is essential to the success of the reaction, as it acts as a phase transfer catalyst [607].



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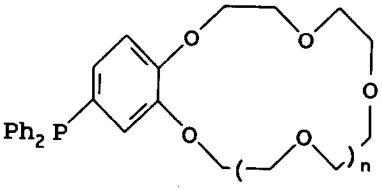
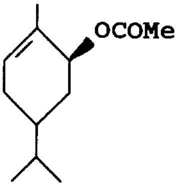


339 (*n* = 1 or 2)

Hydrogenolysis of allyl halides, ethanoates and other derivatives has been described, and usually involves transfer of a nucleophilic hydrogen atom to a π-allyl complex. With Na$[BD_4]$ as the source of "hydride" the reaction of **340** involved predominent inversion of stereochemistry to **341** [608,609]. Reaction of the allylic ethanoate, **342**, with Na$[BH_4]$ or Na$[BH_3CN]$ gave a mixture of **343** and **344** [610]. The allylic tosylates **345** and **346** reacted with Li$[BHEt_3]$ in the presence of $[PdCl_2(dppp)]$ to give **347** and **348** respectively, both with excellent regioselectivity. A related reaction was used in a co-enzyme Q synthesis [611]. A hydrogenolysis of **349** in the presence of Na$[BH_4]$/$[Pd(PPh_3)_4]$/dppe gave **350** and **351** in the ratio of 96:4, in contrast to the reaction which involved hydrogen transfer from $[NH_4][HCOO]$ which yielded the two regioisomeric products **350** and **351** in the ratio 10:90 [612].



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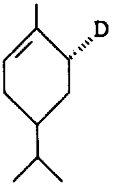

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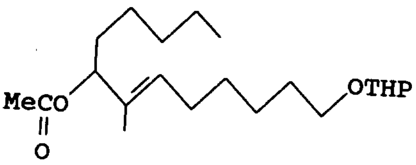

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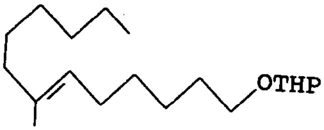

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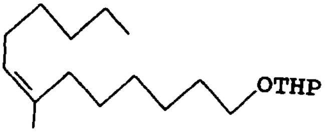

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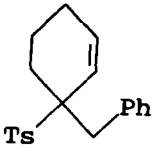

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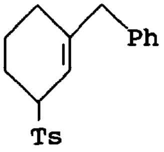

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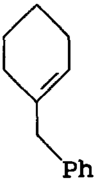

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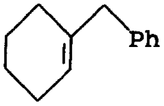

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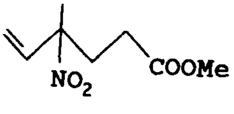

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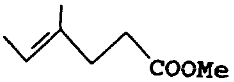

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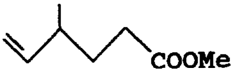
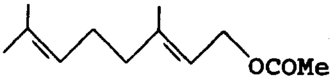


351

The use of Bu_3SnH as a source of hydride has also been described. Reaction with $CH_2=CHCHCl_2$ in the presence of $[Pd(PPh_3)_4]$ gave $CH_3CH=CHCl$ in an E:Z ratio of 62:38. The mechanism was compared with the related radical process, and similar regioselection was noted with $CH_2=CHCH(OCOMe)_2$ [613]. Reduction of $Cl_3CCH=CHCH_2Cl$ with Bu_3SnH/AIBN gave a mixture of $Cl_2HCCH=CHCH_2Cl$ and $Cl_2C=CHCH_2CH_2Cl$. However in the presence of Pd(0) the main product was $Cl_2C=CH\text{-}CH=CH_2$. The reaction mechanism was discussed in detail [614].

Transfer hydrogenolysis of **352** using $[Pd_2(dba)_2].CHCl_3/PBu_3/Et_3N/HCOOH$ gave **353** with good selectivity, at a particularly low ratio of catalyst to substrate [615]. Hydrogenolysis of the epoxide, **354**, was stereospecific to give **355** [616]. Palladium complexes of **356** catalysed transfer hydrogenolysis of $C_6H_{13}CH=CHCH_2Cl$ to give $C_7H_{15}CH=CH_2$ and $C_6H_{13}CH=CHCH_3$ in the ratio 82:17 [617].



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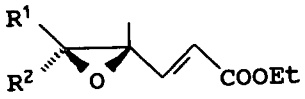

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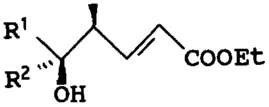

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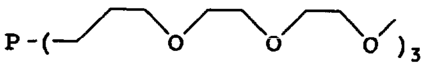

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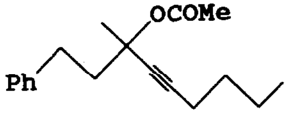
Hydrogenolysis of $PhCH{=}CHCH_2OCOMe$ to give a 20:80 mixture of $PhCH{=}CHMe$ and $PhCH_2CH{=}CH_2$ was accomplished using stoicheiometric SmI_2 and 2-propanol, with a palladium(0) complex as catalyst. The reaction mechanism was thought to involve Sm(II) reduction of a cationic palladium allyl complex to an allyl radical or an allyl anion, which was protonated to yield the observed products [618].

A comparable system was used for hydrogenolysis of **357** to give **358**. In this instance the intermediate proposed was a σ-allenyl palladium complex, which was reduced to an allenyl anion by the samarium(II). The nature of the proton source was shown to be important to selectivity between allenyl and alkyne products [619]. Transfer hydrogenolysis of $RCH(OCO_2Me)C{\equiv}CH$ or $RC{\equiv}CCH_2OCO_2Me$ by $[NH_4][HCOO]/Pd(0)/PBu_3$ gave the allene $RCH{=}C{=}CH_2$ as the initial product, and this could be further reduced by transfer hydrogenation in the same system to $RCH_2CH{=}CH_2$. Again σ-allenyl palladium complexes were invoked as intermediates [620].



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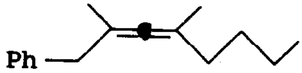

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The hydrogenolysis of RCOCl to give an aldehyde, RCHO, by hydrogen transfer from Bu_2Zn was reported to be catalysed by $[PdCl(CH_2Ph)(PPh_3)_2]$ [621].

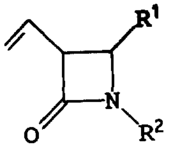
13.2 Oxidation

Oxidation reactions catalysed by palladium complexes have been reviewed [622], as have allyic oxidations of alkenes, inculding some catalysed by palladium derivatives [623].

Oxidation of ethene by molecular oxygen in the presence of $PdCl_2$/CuCl/hmpa at 60 °C/1 atm gave ethanal (67 %) and ethanoic acid (32 %) [624]. Various patents have reported the oxidation of 1-alkenes to methyl ketones, catalytic systems used including $PdCl_2$/CuCl/hmpa/MeCN [625,626], $PdCl_2$/CuCl/hmpa/sulfolane/PhCN/H_2O [627,628], $PdCl_2$/H_3BO_3/phospho-6-molybdo-6-vanadic acid/O_2 (100 psi) [629], $[PdCl(NO_2)(MeCN)_2]$/$CuCl_2$/Me_3COH [630], and $PdCl_2$/$CuCl_2$/HCl/$MeOCH_2CH_2OH$ [631]. The oxidation of phenylethene using $PdCl_2$/$CuCl_2$/H_2O/MeCN/N_2 at 100 °C was unusual, in that the main product was $PHCH_2CHO$, rather than the phenylethanone [632]. The use of the system $PdCl_2$/$CuCl_2$/cyclodextrin/H_2O allowed the oxidation of higher alkenes by molecular oxygen in aqueous solutions, which is not normally possible [633]. A diketone was obtained from $RCOCH_2CH_2CH{=}CH_2$ [634]. MeONO was used as an oxidant in the reaction of $PhOCH_2CH{=}CH_2$ in the presence of $PdCl_2$/H_2O to give $PhOCH_2COMe$ [635]. Oxidation of cyclopentene to cyclopentanone was accomplished in good selectivity and conversion using $PdCl_2$/$CuCl_2$/C/2-propanol [636].

Many synthetic applications have been reported [637]. Thus oxidation of a terminal alkene has been reported as an important step in syntheses of (•)-pentalenene [638], (•)-cephalotaxine [639], the house mouse pheromone [640] and quadrone [641,642]. Oxidation in combination with acetalisation was used in approaches to the host specific substance of the ambrosia beetle [643], and with hemiacetal formation in a synthesis of the eastern half of rosaramicin [644].

Oxidation of **359** by molecular oxygen in the presence of $PdCl_2$/CuCl gave a mixture of **360** and **361** [645]. Oxidation of the disubstituted alkene, **362** gave **363** with good selection, which is quite surprising in view of the fact that PhCH=CHMe is oxidised to a 75:25 mixture of $PhCH_2COMe$ and PhCOEt. The explanation given was that the palladium is coordinated both to the double bond and the adjacent oxygen atom in an intermediate such as **364** [646].



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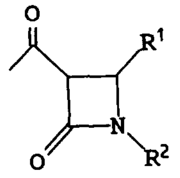

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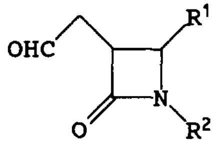

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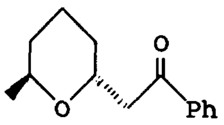

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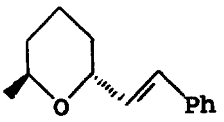

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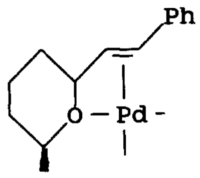

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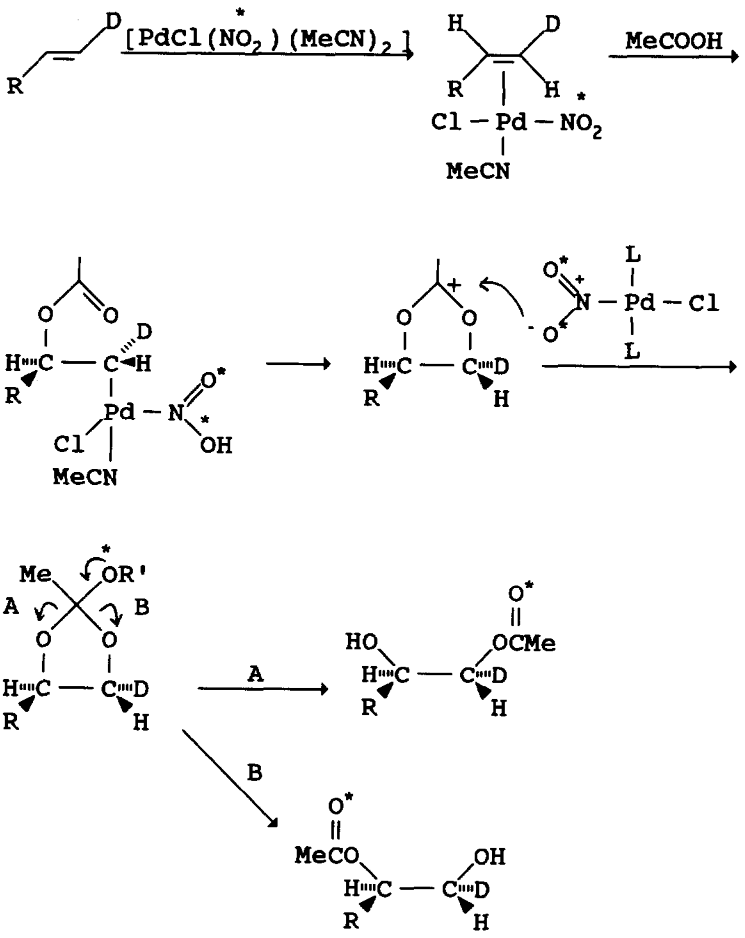
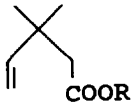
Bäckvall has commented in some detail on Mares' hypothesis for the mechanism of alkene oxidation in the presence of $[PdCl(NO_2)(MeCN)_2]$. An alternative was proposed (Scheme 2), and was justified by a careful study of the reaction stereochemistry and deuterium labelling studies [647]. An oxidation of a 1-alkene, $RCH{=}CH_2$, by molecular oxygen in the presence of $\{Pd(NO_2)L\}/CuCl_2$ has been reported to yield a mixture of RCH_2CHO and RCOMe, whereas only the ketone is obtained in the absence of the copper salt. Phenylethene gave $PHCH_2CH_2CHO$ with 100 % selectivity. A mechanism involving a bimetallic intermediate was proposed [648].

Oxidation of ethene to ethane-1,2-diol mono and diethanoates has been reported in the presence of $PdCl_2/CuCl_2/Cu(OCOMe)_2/MeCOOH$ [649]. Kinetic studies have been undertaken of the reaction of ethene with $PdCl_2/MeCOOH/[MeCOO]Na$/benzoquinone to give ethenyl ethanoate. The kinetics were first order in $PdCl_2$, zero order in benzoquinone and non-linear in ethene and sodium ethanoate [650].There has also been a kinetic study of the liquid phase oxidation of ethene in the presence of giant palladium clusters such as $[Pd_{561}(phen)_{80}][PF_6]_{60}$. It was proposed that the rate controlling step in the reaction was the oxidative addition of a π-coordinated ethene to two palladium atoms on the outside layer of the cluster to give a bis(σ-bonded) complex [651]. There has been an EXAFS study of the palladium cluster [652]. Reaction of **365** with oxygen in the presence of $Pd(OCOMe)_2/Cu(OCOMe)_2/MeCOOH$ gave a mixture of **366**, **367** and **368**. This is in contrast to the reaction in the presence of the chlorides which yields methyl ketones as the main products. Intermediates such as **369** and **370** were proposed [653].



Scheme 2 Mechanism of alkene oxidation catalysed by $[PdCl(NO_2)(MeCN)_2]$ [647].



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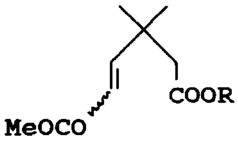

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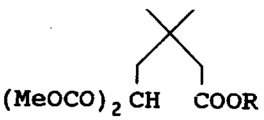

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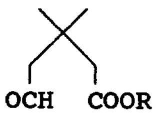

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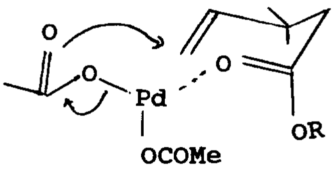

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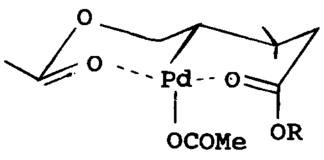

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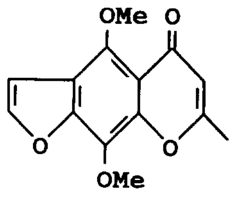
Oxidation of 1,3-pentadiene using $PdCl_2/CuBr_2$ gave 2-methylfuran [654]. Oxidative cleavage of **371** in the presence of $PdCl_2/Cu_2Cl_2$/MeOH gave **372**, *via* a methoxypalladation dehydropalladation sequence [655].



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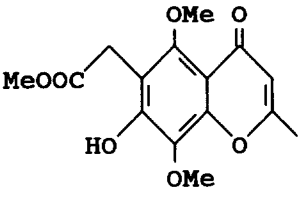
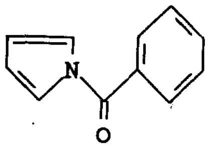


372

Oxidation of disubstituted alkynes in the presence of $Pd(OCOMe)_2/Cu(OCOMe)_2$ gave low yields of ketones and acetals [656].

There has been a report of the oxidation of toluene to $PHCH_2OCOR$ using $O_2/Pd(OCOMe)_2/Pb(OCOMe)_2$/RCOOH. A mixed metal complex, $\{PdPb(OCOMe)_4\}$ was invoked as the true catalyst [657]. A similar reaction was reported with the mixed metal catalyst $\{PdCu(OCOMe)_4\}$ [658]. The mechanisms of oxidation of a range of arenes in the presence of palladium(II) has been discussed. With ArH, the main product is Ar-Ar, formed by reductive elimination from $\{PdAr_2\}$, whilst ArMe is converted by oxidation to $ArCH_2^+$, which may react with nucleophiles or couple with another arene [659]. Coupling of dimethyl benzene-1,2-dicarboxylate in the presence of $Pd(OCOMe)_2/[Cu(acac)_2]$ gave mainly the 1,2,2',3'-substituted biphenyl, whereas good selection for the 2,3,2',3-isomer could be obtained with good selectivity by minor changes in the reaction conditions [660]. It had previously been thought that the intramolecular coupling of **373** in the presence of Pd(II) would give **374**. However, in practice the reaction is much more complex, giving only 28 % of **374**, together with a homocoupling product of **373**, and a substantial amount of benzoic acid [661].



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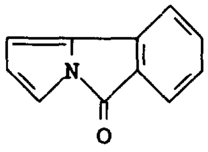

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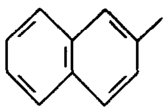
Oxidation of **375** using H_2O_2/MeCOOH/Pd(II)/sulphonated polystyrene resin gave **376**, Vitamin K_3, in 50-60 % yield. The catalyst may be removed by filtration and reused [662]. It was shown that the presence of donating groups at C-2 of the starting material accelerated the reaction, and the mechanism was studied kinetically and theoretically using MINDO/3 [663]. Using the same oxidation system, 2,3-dimethylnapthalene was oxidised to **377** [664].



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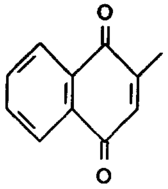

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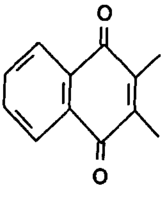


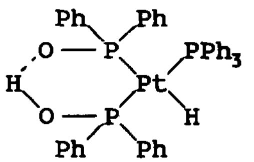
377

There have been a number of synthetic applications for the oxidation of silyl enol ethers to give enones. Thus 1-trimethylsiloxy-3-trimethylsilylmethylcyclohexene was converted to 3-trimethylsilylmethyl-2-cyclohexenone in the presence of palladium ethanoate and diallyl carbonate [665-669].

There has been a review of the synthesis of anti-inflammatory 2-arylpropanoic acids, which includes some discussion of nickel or palladium catalysed carbonylations and carboxylations [670]. Homogeneous and phase transfer catalysed carbonylation reactions have also been reviewed; many palladium complex catalysed reactions were discussed [671].

Reduction of CO with hydrogen has been studied in the presence of $[PPN][PtRh_5(CO)_{15}]$; without additives the product was methanol, but when 2-pyridone was added the major product was ethane-1,2-diol. The exact nature of the catalytic species was not determined, but it seems that it is an intact cluster containing platinum [672].

Reports of hydroformylation catalysts continue to be published. Tris(thienyl)phosphine palladium complexes have been used in reactions of C_3-C_{18} 1-alkenes [673]. The complex **378** was isolated and characterised. This catalyses hydroformylation of 1-alkenes, but also promotes the formation of linear aldehydes from 2-alkenes, since it is able to catalyse isomerisation as well as carbonylation. Reaction of **378** with ethene gave **379** which could be carbonylated to give **380** [674]. Silica bound $\{R_2P(CH_2)_3\}_nSi(OEt)_{4-n}$ ($n = 2$ or 3, R = Cy) was reacted with $[PdCl_2(PhCN)_2]$ to give a catalyst for hydroformylation of propene [675]. There has been a mechanistic study of platinum catalysed hydroformylation. Reaction of *trans*-$[PtHCl(PPh_3)_2]$ with $SnCl_2$ gave *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ and other hydrides. Reaction with ethene at -80 °C gave *cis*-$[PtEt(SnCl_3)(PPh_3)_2]$, which was converted irreversibly at -10 °C to the *trans*-isomer. The presence of CO promotes this isomerisation, even at very low temperature, and the mixture is then slowly converted to *trans*-$[PtEt(CO)L_2]^+[SnCl_3]^-$. At room temperature CO insertion occurs, giving various acyl derivatives, which react with molecular hydrogen to give aldehydes [676].



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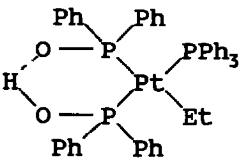

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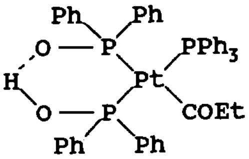
There have also been reports of enantioselective hydroformylations. A catalyst system derived from DIOP, $[Pt(acac)_2]$ and $SnCl_2$ was active for propene hydroformylation, but most of the product was the linear aldehyde [677]. The system $[PtCl(SnCl_3)(DIOP)]$ was used as a catalyst for hydroformylation of $FcCH{=}CH_2$, but much of the product was linear, and the optical yield for the branched isomer was low [678]. Hydroformylation of phenylethene in the presence of a platinum complex of polymer supported DIOP has been reported. Optical yields were a little lower than those obtained with the related soluble system [679].



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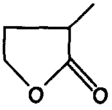
Hydrocarboxylations of alkenes have been widely reported. Ethene reacted with CO and water in the presence of $[PdCl_2(PPh_3)_2]/PPh_3$ to give propanoic acid [680]. Reactions of 1-alkenes using $[PdX_2L_2]$ as catalyst gave a mixture of linear and branched acids. The reaction rate decreased with an increase in phosphine basicity, and an increase in phosphine bulk led to the formation of more of the branched product [681]. Hydrocarboxylation of 1-nonene in the presence of $[PdCl_2(PPh_3)_2]/PPh_3/SnCl_2$ has been studied; more of the linear acid is formed in the presence of the tin(II) salt. $SnCl_2$ retards the carboxylation of cyclohexene [682]. The related reaction of phenylethene in the presence of $[PdCl_2(PPh_3)_2]$ (20 atm pressure CO) gave PhCH(Me)COOH with 93 % selectivity. Addition of $SnCl_2$ or H_2 lowered the selectivity of the reaction, but the yield was still high [683]. Reaction of 3-butene-1-ol with $CO/O_2/PdCl_2/CuCl_2/HCl$ gave **381** [684].



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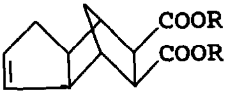
Reaction of ethene with CO in the presence of $Pd(OCOMe)_2/dppp/CF_3COOH/MeOH$ gave a polyketone polymer [685]. With ethene, CO and H_2, and $Pd(OCOMe)_2/CF_3COOH/PPh_3$ as the catalyst system, the product was 3-pentanone [686].

An oxidative carbonylation of ethene to give $MeOOCCH_2CH_2COOMe$ used $CO/Me_3COOCMe_3/PdCl_2/CuCl_2/MeOH$ [687]. Similar reactions have been reported in the patent literature for phenylethene. With $PdCl_2/CuCl_2/Zn(OCOMe)_2$ as the catalyst system, the main product was E-PhCH=CHCOOMe, together with a little $PhCH(COOMe)CH_2COOMe$

[688]. E-PhCH=CHCOOMe was also the main product in the presence of $PdCl_2/CuCl_2/Zn[CO_3]/Zn(OH)_2$ [689] or $Pd(II)/CuCl_2/Ba(OCOMe)_2$ [690].

Further patents from Nissan Chemical Industries have reported the double alkoxycarbonylation of dicyclopentadiene to **382** in the presence of $PdCl_2/CuCl_2$ [691,692].



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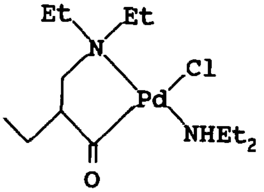
The stoicheiometric reaction of 1-butene with CO, Et_2NH and $[PdCl_2(MeCN)_2]$ gave a mixture of **383** and **384**. Carbonylation of these complexes yielded **385** and **386** [693].



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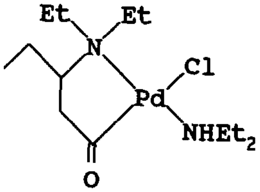

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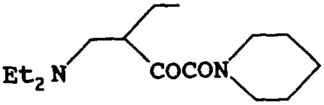

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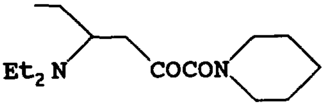

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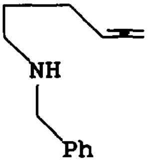
Carbonylation of the allene, **387**, in the presence of CO/Pd(II)/MeOH, resulted in the formation of the cyclised product, **388**, in moderate to good selectivity [694].



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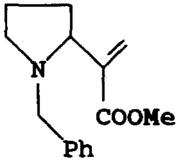
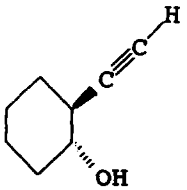


388

Oxidative alkoxycarbonylation of butadiene in the presence of CO/MeOH/$PdCl_2$/H_2SO_4/quinone gave dimethyl 3-hexenedioate [695]. Carboxylation of butadiene by CO_2 in the presence of [Ni(bipy)(cod)] gave an intermediate which could be reacted with bromoethane to yield $PrCH{=}CHCH_2COOH$ [696]. Reaction of $RCH{=}CH\text{-}CH{=}CH_2$ with CO and methanol in the presence of O_2/$PdCl_2$/$CuCl_2$/Aliquat 336 (to prevent polymerisation) gave mainly $RCH(OMe)CH{=}CHCH_2COOMe$ together with some RCH(OMe)CH=CHMe [697].

The synthesis of α-methylene lactones has been reviewed, including intramolecular hydrocarboxylations of alkynes (**389** to **390** in the presence of palladium complexes) and reactions of hydroxylated haloalkenes [698].



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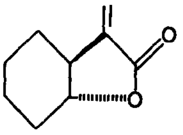


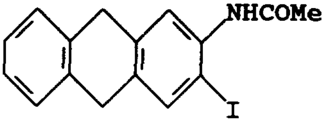
390

Oxidative carbonylation of ethyne in the presence of $PdBr_2$/LiBr/H_2O gave a mixture of Z-butenedioate anhydride and E-butenedioic acid [699]. With CO/BuOH and $[\{PdXL\}_2CO]$ (L = PPh_3 or $AsPh_3$) as catalyst, the major product was BuOOCCH=CHCOOBu [700].

The complexes *cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2(SnCl_3)_2L_2]$ (L = tertiary phosphine or arsine) have been prepared, and their dynamic behaviour investigated by variable temperature nmr spectroscopy. When $SnCl_2$ is added they are catalysts for the conversion of 1-heptyne to $C_5H_{11}CH{=}CHCOOR'$. Yields are moderate, but selectivity is excellent [701]. The conversion of $HOCMe_2C{\equiv}CH$ to $HOCMe_2C{\equiv}CCOOMe$ was accomplished using CO/MeOH in the presence of $PdCl_2$/$CuCl_2$/Na[OCOMe]. The effects of the reaction conditions on the yield were reported [702].

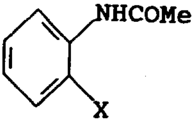
There have been numerous reports of the carbonylation of aryl halides in the presence of a range of additives. In the presence of a hydrogen donor, such as R_3SnH, ArX may be carbonylated to give ArCHO in the presence of $[Pd(PPh_3)_4]$. Many functional groups were tolerated, and a side reaction giving reduction to ArH minimised by slow addition of the R_3SnH. The reaction was readily extended to alkenyl halides (which retained their geometry about the double bond), allylic halides (regioselective for the less hindered site of the allyl) and benzyl and related derivatives. Alkenyl triflates also gave good reactions [703].

Carbonylation in the presence of alcohols generally leads to the formation of carboxylate esters. The reaction has been reported for **391** in the presence of $PdCl_2/Et_3N/MeOH$ [704], and for a range of halides using *trans*-$[PdCl_2L_2]$ (L = 1,2,5-triphenylphosphole) [705]. Aryl triflates were also good substrates and could be converted to esters or amides in the presence of $Pd(OCOMe)_2/Et_3N/PPh_3$ or dppf/dmf/RH (R = OR' or NR'_2) [706]. R_3SnOR may be used as the source of the alkoxy group, and a comparable reaction was noted using R_3SnNR_2 in the presence of $[Pd(Ar)I(PPh_3)_2]$ [707]. The reaction of ArI with CO/wet 2-propanol in the presence of $PdCl_2/PPh_3/K[OCOMe]$ gave benzoic acid and $PhCOCOOCHMe_2$. The optimum yield of the double carbonylation product was obtained with PPh_3:Pd = 2; addition of dppb or $(2\text{-}MeC_6H_4)_3P$ instead of PPh_3 gave less double carbonylation [708]. Electroreductive carboxylation of aryl halides has been reported. The species {ArPdX}, generated on oxidative addition of an aryl halide to palladium(0), was reduced to a radical anion. Further reduction could lead to coupling to give the biaryl, but in the presence of CO_2 the main product was the arene carboxylic acid. Related reactions of alkenyl and allyl derivatives were also discussed in detail [709].



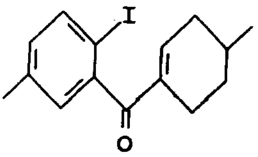
391

In the presence of amines, carbonylation leads to the formation of amides. There has been a review of syntheses of annelated 1,4-benzodiazepines, including a number of palladium catalysed carbonylations of aryl halides with intramolecular attack of amino groups [710]. Examples of this type of reaction have been used in approaches to neothramycin [711] and prothracarcin and tomaymycin [712]. Reaction of **392** (X = Br or I) with CO/Et_2NH in the presence of $[PdCl_2L_2]$ gave a mixture of the mono- and bis-carbonylated products, with product ratios depending on L. Selectivity towards bis carbonylation was enhanced under high pressure of CO, and at lower temperature [713].



394

A few other nucleophiles have proved useful. Thus iodobenzene reacted with $MeCH(COOEt)_2/CO/Et_3N/[PdCl_2(dppf)]$ to give $PhCOCH(COOEt)_2$. Grignard reagents could also be used as nucleophiles, $[PdI(Ph)(PPh_3)_2]$ as catalyst, and alkenyl halides as substrates [714]. When $RAlR'_2$ reacted with R"X under an atmosphere of CO in the presence of $[PdCl_2(MeCN)_2]$, the products were RCOR", RR", R_2CO and RR. The product distribution depended mainly on the nature of the R groups, and selectivities for a wide range of coupling types were checked [715]. Couplings with trialkylboranes were accomplished using $[PdCl_2(PPh_3)_2]/[Zn(acac)_2]$/thf/hmpa [716]. The synthesis of quinones by acylpalladation of iodoaryl alkenyl ketones (for example conversion of **393** to **394**) has been reported [717].



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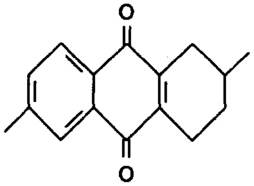
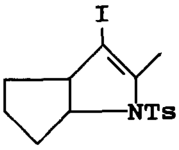


394

There have also been reports of the carbonylation of haloalkenes and related compounds. Conversions of haloalkenes to esters have been used in syntheses of benzazepines [718] and in an intramolecular process to give a lactone in a preparation of cembranoids [719]. Reaction of **395** with CO/MeOH in the presence of $Pd(OCOMe)_2/Bu_3N/P(C_6H_4\text{-}2\text{-}Me)_3$ gave **396** in 61 % yield. Various carbon-carbon coupling reactions with organotin compounds or alkenes bearing electron-withdrawing groups were also discussed [720]. Reaction of chloroethene with CO/NH_3 at 100 °C in the presence of $[Pd(PPh_3)_4]$ gave propenamide [721].



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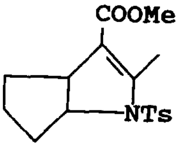

396

A few carbonylations of other types of halides have been reported [722]. Reaction of 2-bromomethylnaphthalene with HCOOR/CO in the presence of Rh(I) gave $ArCH_2COOR$. The process could be applied to aryl and alkyl bromides with a bimetallic Rh(I)/Pd(0) catalyst system [723]. Various mechanisms were considered for the carbonylation of $PhCH_2Cl$ to give $PhCH_2COOMe$ in the presence of $[Pd(PMe_3)_4]$. Since the complex *trans*-$[Pd(CH_2Ph)(COOMe)L_2]$, prepared independently, does not undergo easy reductive elimination under the reaction conditions, it was concluded that the rate-controlling step was methanolysis of an acylpalladium intermediate [724]. Electroreductive carboxylation of ArCH(Me)Cl by CO_2 in the presence of Ni(II) gave ArCH(Me)COOH [725]. A carbon nucleophile was used to attack an acylpalladium intermediate in the reaction of $PhCH_2Cl$ with CO/BuC≡CH in the presence of $[PdCl_2(dppb)]/(Me_2CH)_3N$ to give $PhCH_2COC{\equiv}CBu$ [726].

Reaction of **397** with $RCH{=}CHCH_2X$ and CO in the presence of a palladium complex catalyst gave **398**. Various transformations of the product were discussed [727]. Carbonylation of **399** using $[Pd_2(dba)_3]$ as the catalyst gave **400**, *via* **401** and **402**. The product was readily isomerised to a diene, **403** [728].

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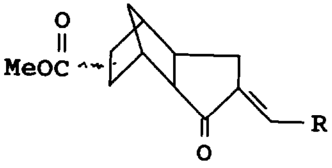

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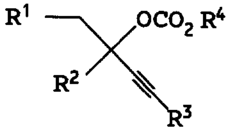

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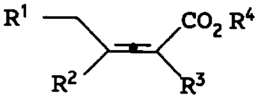

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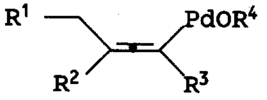

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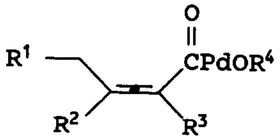

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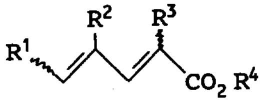
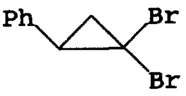


403

Carbonylation of **404** by $[Ni(CO)_4]$ in the presence of $PrNH_2$ gave **405** in a stoicheiometric reaction. The key step in the reaction was a nucleophilic attack of $[RNHC(=O)NiL_m]^-$ on the dibromide [729]. The complexes $[MX_2(PPh_3)_2]$ (M = Ni, Pd or Pt; X = Cl or Br) catalysed reaction of $R^1R^2CBr_2$ with CO and HY in the presence of zinc metal, to give R^1R^2CHCOY and ZnX_2 (R^1, R^2 = H or Me or R^1 = H, R^2 = Me; Y = OMe or NEt_2). The reaction mechanism proposed involved a ketene complex intermediate [730].



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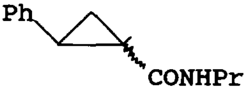
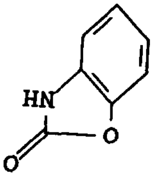


405

Carbonylation of methanol to afford dimethyl carbonate was reported to occur in the presence of $CO/O_2/K_2[Pd(NO_2)_4]/H_5Mo_{10}V_2O_{40}.20H_2O$ [731]. Carbonylation of 2-nitrophenol in the presence of palladium chloride gave **406**, reduction of the nitro group having occurred under the same conditions [732]. The amino alcohol $R'NHCH_2CH(OH)R$ underwent a similar reaction to give **407** with the catalyst system $PdCl_2/CuCl_2/Na[OCOMe]$. The double carbonylation product, **408**, was also obtained, to an extent that depended on the substituents. The diol $HOCH_2CH(OH)Ph$ reacted to give **409** [733].



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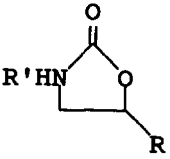

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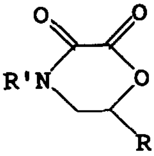

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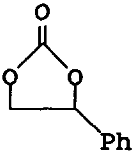


409

Carbonylation of methyl methanoate gave ethanoic acid using CO/H_2 in the presence of $NiCl_2/PdCl_2/KI/Ph_3O$/sulfolane [734]. A silica supported nickel complex has been reported to catalyse carbonylation of methyl ethanoate to ethanoic anhydride, in modest yield, but with excellent selectivity [735].

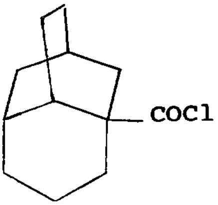
Reaction of diethylamine with carbon dioxide in the presence of $[PdCl_2(MeCN)_2]$ gave $Et_2NC(=O)NEt_2$ and $Et_2NC(=O)H$. When PPh_3 was added the main product was the urea, but in the presence of [HCOO]Na/methylcellosolve the methanamide predominated [736].

Reduction of nitroarenes to aniline derivatives has been accomplished using CO in the presence of $Pd(OCOMe)_2/PR_3$. The hydroxylamine, PhNHOH was shown to be an intermediate, and the cluster $[HPd_2(PPh_3)_4(CO)(HSO_4)]_n$ was isolated from the reaction mixture. A detailed reaction mechanism was proposed [737]. An IR spectroscopic study of the reaction mechanism was reported for the reaction of $ArNO_2$ with CO in the presence of *trans*-$[PdCl_2(py)_2]$ to give ArNCO. Nitrosoarene and nitrene palladium derivatives were invoked as intermediates [738]. Nitrobenzene reacted with CO and aniline in the presence of $[NiX_2L_2]$ to give $(PhNH)_2CO$ and CO_2. Nitrosoarene and nitrene nickel complexes were proposed as intermediates [739].

Thiophene reacted with CO/ROH in the presence of mercury(II) and $PdCl_2$ to give a mixture of thiophene-2-carboxylate ester and bithiophene. The rate of the reaction depended on the nature of the mercury salt, and the first step in the reaction was the formation of the thiophene mercury derivative. This was transmetallated and then the palladium derivative reacted with CO. In the presence of copper(II) the reaction was catalytic in palladium. Similar reactions were noted for furan and pyrrole [740].

Oxidation of CO to CO_2 by a heteropolyacid was catalysed by palladium(II). It has been suggested that the mechanism of the reaction involves palladium(I) CO complexes, including some bimetallic species [741]. A supported version of the catalyst has also been used; the reaction mechanism seems to be similar to that in solution [742].

Decarbonylation of RCOCN to give RCN and CO was accomplished in the presence of $[Pd(PPh_3)_4]$. Esters and ethers survive the reaction. If the substrate bears β-hydrogen atoms, as in RCH_2CH_2COCN, there is β-hydride elimination from the intermediate $\{RCH_2CH_2Pd\}$ to give an alkene [743]. Decarbonylation of the acyl chloride, **410**, using $PdBr_2$ gave **411** as the sole isolated product. The reaction mechanism was discussed in detail [744]. Decarbonylation of methanal was achieved using Ni(0). Both $[Ni(PR_3)_4]$ and $[Ni(C_2H_4)(PR_3)_2]$ reacted with methanal to give $[NiH(CHO)(PR_3)_2]$. Deinsertion yielded $[NiH_2(CO)(PR_3)_2]$ which could lose H_2 and CO to give a catalytic decarbonylation, or react with PR_3 or CO to give respectively $[Ni(CO)(PR_3)_3]$ and $[Ni(CO)_2(PR_3)_2]$ [745].



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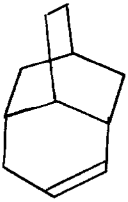
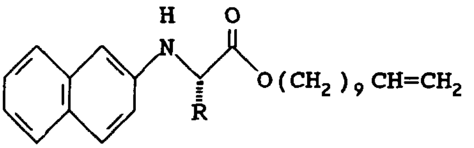


411

There have been a number of reports of the hydrosilylation of 1-alkenes in the presence of $H_2[PtCl_6]$ [746-748], including reactions directed towards the synthesis of polysiloxanes [749-751]. Hydrosilylation of **412** and related reactions were used in preparation of chiral stationary phases for HPLC [752,753]. Reaction of methyl 2-methylpropenoate with $HSiClMe_2$ in the presence of $H_2[PtCl_6]$ gave $ClMe_2SiCMe_2COOMe$ and $ClMe_2SiCH_2CH(Me)COOMe$ in the ratio 2:3, a rather unusual regioselectivity [754]. Hydrosilylation of $(EtO)_3SiCH{=}CH_2$ with $HSi(OEt)_3$ in the presence of $[PtCl_2(Et_2S)_2]$ gave only $(EtO)_3CH_2CH_2Si(OEt)_3$ [755]. A polymer was prepared by hydrosilylation of **413** with $ClHSi(Me)CH_2CH_2CF_3$ [756]. In the absence of solvent both $[Pt(PPh_3)_4]$ and $[Pt(PPh_3)_2(O_2)]$ showed good activity for hydrosilylation of 1-alkenes in the presence of oxygen, but yields were lower under inert atmospheres [757].



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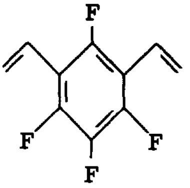


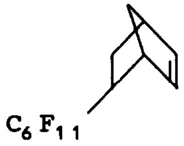
413

Reaction of various platinum complexes which catalyse hydrosilylation with $(EtO)_3SiH$ gave a colloid, and it was concluded that the formation of this colloid is the critical step in hydrosilylation. The material was analysed by TEM, XPES and light scattering experiments. It is believed that a truly homogeneous reaction system is obtained with $[Pd(PPh_3)_4]$ [758].

A range of supported platinum species which catalyse hydroformylation of 1-alkenes has been reported. These included silica attached $[Pt(C_2O_4)L_2]$ [759], Pt(II) and Pt(IV) derivatives of polyamides [760], and aminated or phosphinated polystyrene platinum(II) complexes [761].

The complexes $[Ni(acac)_2L_2]$ ($L = Et_2PhP$, $(PhCH_2)_3P$ or L_2 = dppe) show reasonable catalytic activity for reaction of 1-alkenes with Cl_2MeSiH [762].

Hydrosilylation of **414** by $MeSiHCl_2$ in the presence of $H_2[PtCl_6]$ gave **415**, which was used for surface modification of silica [763]. Two intramolecular hydrosilylation reactions have been noted. The diene **416** reacted with $(HMe_2Si)_2NH$, catalysed by $H_2[PtCl_6]$, to give **417**, which was oxidised by hydrogen peroxide to **418**. Protection, a second intramolecular hydrosilylation, and oxidation yielded **419** with good stereoselection [764]. A related conversion of **420** to **421** and oxidation to **422** was also described [765].



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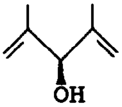

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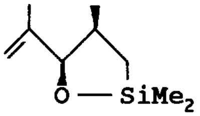

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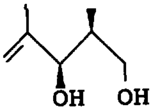

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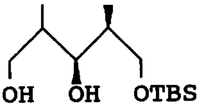

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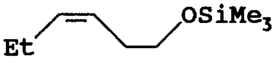

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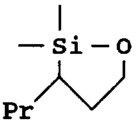

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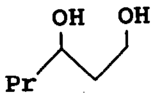
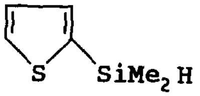


422

Allenes have been shown to inhibit the crosslinking of siloxanes by hydrosilylation, giving increased pot or bath life [766].

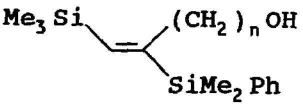
Reaction of ethyne with $HSi(NMe_2)_3$ catalysed by $H_2[PtCl_6]$ gave $CH_2{=}CHSi(NMe_2)_3$ with good selectivity [767]. The effect of additives on the hydrosilylation of ethyne or phenylethyne has been investigated. The halides of Al, Ge, Ce, Nd, Nb or Ta enhance activity and selectivity, but those of Hg, Sn, P, Sb, As, Bi or S inhibit the process [768]. Reaction of **423** with a mixture of 1-alkene and 1-alkyne resulted in reaction only of the alkyne. Regiochemistry varied with substituents [769]. Reaction of $ROOCMe_2C{\equiv}CH$ with Ph_3SiH in the presence of $H_2[PtCl_6]$ gave $ROOCMe_2C(SiPh_3)=CH_2$ with good regioselection [770]. With a catalyst system of $H_2[PtCl_6]$, triethylsilane reacted with $HC\equiv CCH_2Cl$ to give $Et_3SiCH=CHCH_2Cl$. This product reacted with further triethylsilane to give $Et_3SiCH=CHMe$ and Et_3SiCl [771].



423

Hydrosilylation of 5-decyne with $HSiMe(OEt)_2/H_2[PtCl_6]$ resulted in stereospecific *cis*-addition of the silane. Further reactions of the product were discussed [772]. Reaction of $Me_2ClSiC\equiv CSiMe_2Cl$ with $HSiMe_2Cl/H_2[PtCl_6]$ gave $Me_2ClSiCH=C(SiMe_2Cl)_2$ [773].

Reaction of $HSiMeCl_2$ with $PhCH_2CH(Me)C\equiv CSiMe_3$ in the presence of $H_2[PtCl_6]$ was regioselective, and after methylation with MeMgI, the product was E-$PhCH_2CH(Me)C(SiMe_3)=CHSiMe_3$ [774]. Reaction of another silyl alkyne, $Me_3SiC\equiv C(CH_2)_nOH$, was also regioselective, giving, after phenylation with PhMgBr, **424** [775]. Hydrosilylation reactions of **425** occurred at the triple bond only [776].



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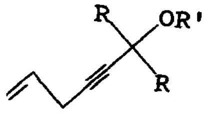


425

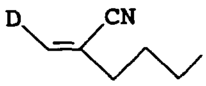
Hydrosilylation of enones to give ketones is best achieved using $Ph_2SiH_2/ZnCl_2/[Pd(PPh_3)_4]$. With a deuterated silane, it was possible to deduce that the deuterium was added to the β-position, from the less hindered face of the molecule [777]. Reaction of RCOX (R = alkyl, X = Cl or Br) with $R^1{}_2R^2SiH$ in the presence of $[Ni(acac)_2]$ gave RCO_2CH_2R and $R^1{}_2R^2SiX$ [778].

Hydrogermylation of $HC\equiv CH(OH)Ph$ with Ph_2GeH_2 in the presence of $H_2[PtCl_6]$ gave $Ph_2Ge\{CH=CHCH(OH)Ph\}_2$ [779].

Alkyl group exchanges between R_4Si and $HSiCl_3$ have been reported to be catalysed by $H_2[PtCl_6]$ [780].

Ligand coupling reactions through hypervalent and valence shell expanded intermediates have been reviewed, including some palladium catalysed addition reactions [781]. There has been a theoretical analysis of palladium catalysed nucleophilic addition reactions to alkenes. The calculations favoured *trans*-addition for water, but *cis*-migration for hydride [782].

Addition of HCN to ethene has been studied, in the presence of $[Ni(C_2H_4)L_2]$ (L = $P(OC_6H_4\text{-}2\text{-}Me)_3$). Intermediates in the catalytic reaction have been detected by nmr spectroscopy, including all 3 stereoisomers of $[Ni(CN)(Et)(C_2H_4)L]$. This is in equilibrium with $[Ni(CN)(Et)(C_2H_4)L_2]$. Kinetic studies allowed a complete catalytic cycle to be proposed [783]. Reaction of 1-hexyne with DCN in the presence of $[Ni\{P(OPh)_3\}_4]$ gave a 6:1 mixture of **426** and **427**. The regioselectivity was discussed in terms of steric and electronic effects. With $Ph_3SiC{\equiv}CCH_2CH_2CH_2CH_3$ the product was **428** [784]. The stereochemistry of the reaction has been studied using **429** which reacted to give *erythro*-**430**. Addition to 1,3-cyclohexadiene gave *cis*-1,2- and *cis*-1,4-addition products. The mechanism proposed was *cis*-addition of {HNi} followed by migration of cyanide [785].



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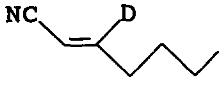

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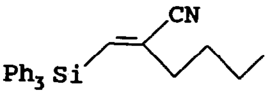

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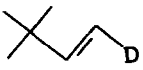

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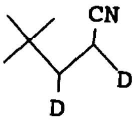

430

Addition of Me_3SiCN to $RCH{=}C{=}CH_2$ was catalysed by $PdCl_2$ or $NiCl_2$ to give an 89:11 E:Z mixture of $RCH{=}C(SiMe_3)CH_2CN$. Various mechanisms were proposed to account for the regiospecificity [786].

Reactions of diazo compounds and alkenes catalysed by palladium complexes formed a part of a review of metal carbene mediated transformations [787]. Cyclopropanation, including palladium catalysed processes has been reviewed [788].

Reaction of **431** with diazomethane in the presence of palladium ethanoate gave **432** [789]. For the related conversion of **433** to **434**, the catalyst was [PdCl$_2$(MeCN)$_2$] [790]. Reactions of chiral esters of E-HOOCCH=CHCOOH with CH$_2$Br$_2$ in the presence of a [Ni(MeOOCCH=CHCOOMe)$_2$(MeCN)] have been investigated; optical yields were modest, and a cobalt complex catalyst gave better results [791].

431

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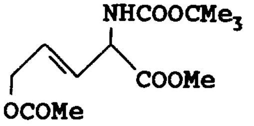

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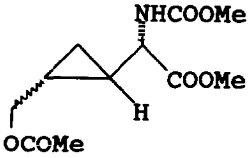
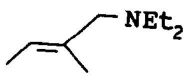


434

Addition of water to 1-hexene was catalysed in the presence of [PtHCl(PMe$_3$)$_2$]/Na[OH]/[PhCH$_2$NEt$_3$]Cl. The reaction mechanism was discussed in detail [792]. A related species also catalysed the hydration of propenenitrile to propenamide [793]. Attack of water on a palladium coordinated ethene molecule has again been considered, in terms of slippage of the metal-alkene bond [794].

Addition of Et$_2$NH to 2-methylbutadiene gave a mixture of **435** and **436**, when palladium ethanoate, triphenylphosphine and the amine hydrochloride are used as the reacting system. An allyl palladium comples was proposed as the reaction intermediate [795]. Indoloquinines have been prepared by palladium(0) catalysed cyclisation of *N*-allyl-2-bromoquinones. Thus **437** was converted to **438**. Reaction of **439** catalysed by palladium(II) gave **440** rather than the indole, though yields were low. However, the palladium(II) catalysed reaction of **441** gave initially **442** which underwent β-elimination to give **443** or insertion to give **444** and **445** [796].



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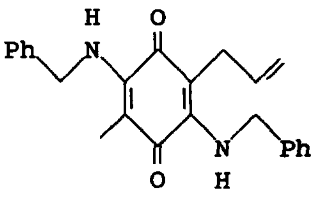

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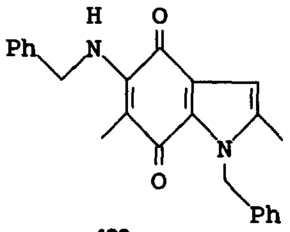

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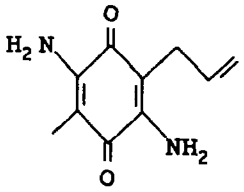

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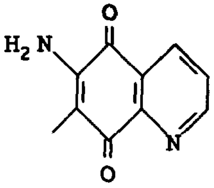

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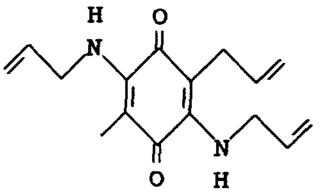

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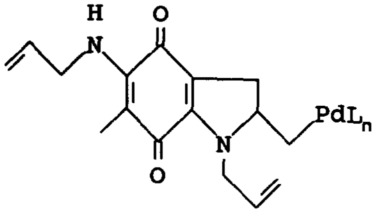

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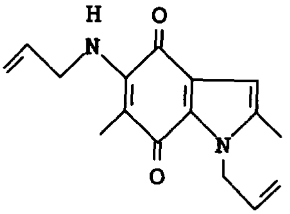

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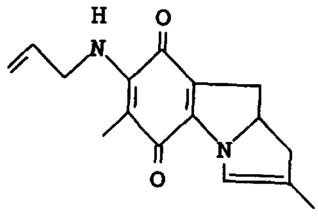
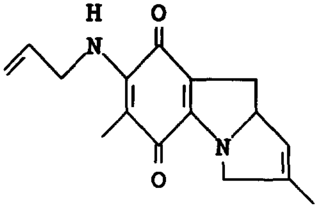


444

Reaction of **446** with chiral PHCH(Me)NH_2 in the presence of $PdCl_2$ under a hydrogen atmosphere gave **447**, which was used in the preparation of chiral amino acids [797]. The reaction mechanism was discussed in detail [798].



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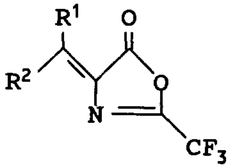

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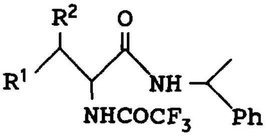
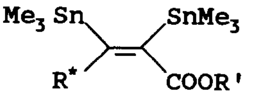


447

cis-Addition of $Me_3SnSnMe_3$ to RC≡CCOOR' was catalysed by $[Pd(PPh_3)_4]$, to give **448**. This underwent *cis/trans*-isomerisation on heating. The rate of isomerisation was faster for the addition product of $RC{\equiv}CCONH_2$ [799]. The initial adducts have also been isomerised photochemically. Addition to propyne gave $Me_3SnCH_2C(SnMe_3){=}CH_2$, though this reaction may involve an allene intermediate [800].

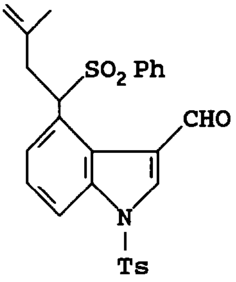


448

The addition of the silastannane, $Me_3SiSnMe_3$ to phenylethyne, catalysed by $[Pd(PPh_3)_4]$, was very regio- and stereoselective, giving only E-$PhC(SnMe_3){=}CHSiMe_3$ [801]. Reaction of $C_{10}H_{21}C{\equiv}CH$ with $PhMe_2SiZnEt_2Li$, in the presence of $[Pd(PPh_3)_4]$, resulted in *cis*-addition to give a 75:25 mixture of $C_{10}H_{21}C{=}CHSiMe_2Ph$ and $C_{10}H_{21}C(SiMe_2Ph){=}CH_2$ [802].

13.6 Isomerisation

Catalytic isomerisation of alkenes using palladium(II) has been studied. Allyl benzene was converted to the conjugated isomer using a palladium complex of γ-aminopropylated silica [803]. Isomerisation of **449** to **450** catalysed by $[PdCl_2(MeCN)_2]$ was used in a synthesis of 6,7-secogroclavine [804].



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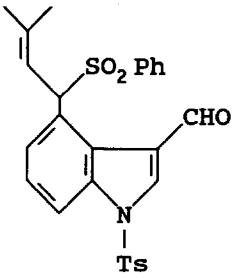
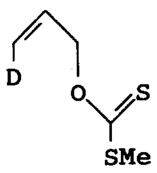


450

The reversible allylic transposition of 1,4-dichloro-2-butene to 3,4-dichloro-1-butene was catalysed by [$NiCl_2(PPh_3)_2$] [805]. Epimerisation of steroidal allylic alcohols was catalysed by [$Pd(PPh_3)_4$]/benzoquinone [806].

There has been an account of the use of palladium(II) or platinum(II) complexes as catalysts for Cope and Claisen rearrangements of *O*-allyl-*S*-methyldithiocarbonates. An example is provided by the conversion of **451** to **452** as the sole product. The 3,3-sigmatropic process occurs cleanly in most cases, *via* a cyclised intermediate, in contrast to the reactions catalysed by rhodium or iridium derivatives [807]. In chiral systems most reactions proceed with prevailing retention of configuration. The reactions catalysed by palladium(0) or platinum(0) derivatives give mixture of the products of 1,3- and 3,3-rearrangements, typical of a process in which the intermediates are π-allyl complexes [808].



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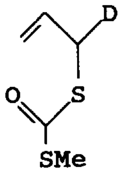
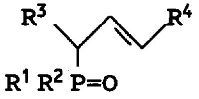


452

Conversion of the allylic phosphite, **453** to allylic phosphonates, **454** and **455**, was catalysed by $NiCl_2$ or [$Ni(cod)_2$]. $R^1R^2P(=O)H$ and dienes were by-products, and the reaction was thought to involve allyl nickel complexes as intermediates [809]. Conversion of **456** to **457** was reported to be catalysed by [$PdCl_2(MeCN)_2$] [810].

Conversion of **458** to **459** was catalysed by [$PdCl_2(RCN)_2$] [811]. In the reaction of **460** to give **461** the yield was strongly dependent on the substituents [812].

453



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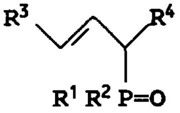

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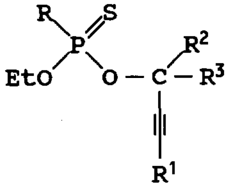

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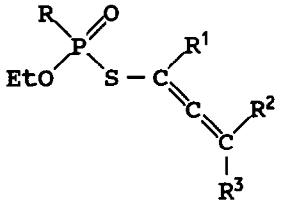

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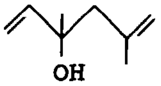

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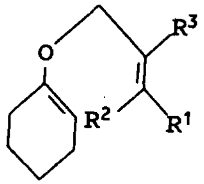

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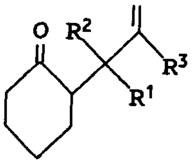
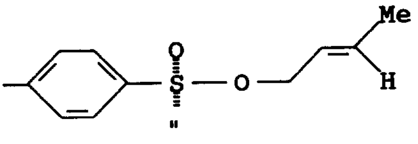


461

Rearrangement of cyclic *S*-allyl thioimidates catalysed by palladium(II) have been studied; only S→N rearrangement occurred [813]. The sulphinate, (•)-**462**, was rearranged in the presence of $[Pd(PPh_3)_4]$/DIOP to give **463** (77 %, enantiomer excess = 87 %) and $ArSO_2CH_2CH{=}CHMe$ (15 %). The reaction mechanism proposed involved $[ArSO_2]^-$ attack on a palladium allyl complex [814].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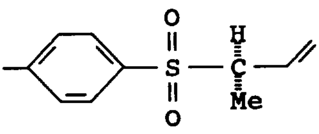
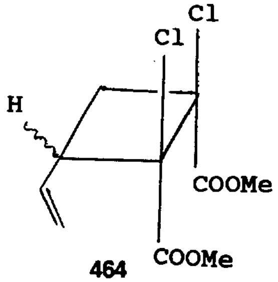

463

Isomerisation of quadricyclane to norbornadiene was catalysed by palladium(II) supported on silica bearing -$(CH_2)_3SH$ side chains. Some activity was lost on recovery and recycling of the catalyst, due to coordination of the product to palladium [815]. A 1,3-sigmatropic shift was involved in reaction of **464** to give **465** promoted by $[Ni(CO)_4]$; the detailed mechanism for the reaction was unknown [816].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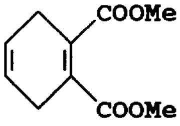
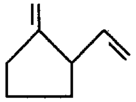

465

Isomerisation of 1,3,7-octatriene in the presence of either $[NiBr_2(PBu_3)_2]$/LiOMe or $[Ni(acac)_2]$/LiOMe gave **466**. The same product could be obtained from butadiene, which is initially oligomerised to the triene [817]. The isomerisation of 1,5-cod with $[Ni(acac)_2]/Et_3Al_2Cl_3/R_3P$ has been investigated. With a PPh_3:Ni ratio in the range 1-3 the main product was **467** with only traces of 1,3-cod and 1,4-cod. With P:Ni in the range 6-10, the reaction is slower, but more of the 1,3- and 1,4-cod isomers are produced. The rate of the reaction increased with a decrease in the electron donor ability of R_3P, and the amounts of the cod isomers increased. Up to 70 % 1,4-cod could be obtained when the additive was a phosphite. A reaction mechanism was proposed [818].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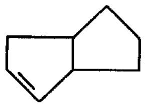
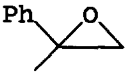

467

Propene epoxide was rearranged in the presence of $[NiBr_2(PR_3)_2]$ to give propanal, and propanone, with propene as a by-product. The product ratios depend on the nature of the phosphine. With **468** as the substrate the reaction in the presence of $[Ni(PPh_3)_4]$ gave

$PhC(Me)=CH_2$ as the main product, but with $[NiBr_2(PPh_3)_2]$ 98 % PhCH(Me)CHO was obtained. A mechanism involving initial insertion of the nickel into the epoxide was proposed [819]. PhCH(Me)CHO was also the main product using $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+$ as the catalyst [820]. Conversion of **469** to $PhCH_2COCH_2OH$ occurred in the presence of $[Pd(PPh_3)_4]$ [821].



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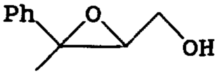


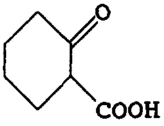
469

Isomerisation of $RCOC{\equiv}CCH_2R'$ using $[Pd(dba)_2]/PPh_3$ gave a 2,5-disubstituted furan [822].

13.7 Substitution of Allyl derivatives and Related Reactions

Palladium catalysed allylic alkylation has been reviewed [823]. Reaction of $PdCl_2$ with 2-propene-1-ol, in an adsorbed layer on the surface of a support such as alumina or MgO, gave a palladium allyl complex anchored to the support. In catalytic and physicochemical properties these catalysts were the same as those obtained from $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ [824]. A range of reactions of 1,3-cyclohexadiene with nucleophiles in the presence of palladium or nickel complexes has been reviewed [825].

Many more examples of substitution reactions of allyl ethanoates have been reported. Allyl ethanoate itself was substituted by $[CHXY]^-$ in the presence of $[Pd(dba)_2]$/dppe/base [826]. With β-ketoacids such as **470**, the product, **471**, has undergone both allylation and decarboxylation [827]. Thiophene-2-magnesium bromide could be allylated with allyl ethanoate, diallyl ether, diallyl sulphide or $CH_2=CHCH_2SO_2Ph$ in the presence of $[Pd(acac)_2]/PPh_3$ [828].



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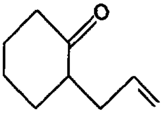
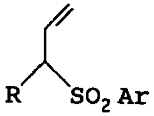


471

Reaction of **472** with $[PhSO_2]Na$ in the presence of $[PdCl_2(MeCN)_2]$ was reported to give mainly **473**, in a reaction which shows regioselection opposite to that normally observed for this type of substitution [829]. **472** reacted with NaN_3 in the presence of $[Pd(PPh_3)_4]$ to give solely $RCH=CHCH_2N_3$, which could be reduced to the amine in good to excellent yields [830]. Substitution of $R'R''C=CHCHR'''OCOMe$ with RM (usually generated electrochemically) gave

R'R"C=CHCHRR'". Variations in both R and M were investigated with regard to changes in regio and stereochemistry of the reaction [831]. Substitution of **474** by Na[CH(SO_2Ph)$_2$] has been investigated [832].

472



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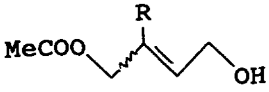
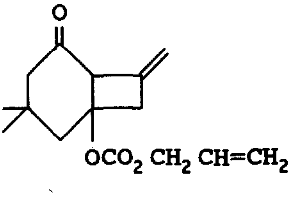


474

There have been several reports of the removal of allyl protecting groups, catalysed by palladium(0) [833]. Cleavage of an allyl ester was important in a total synthesis of mycinolide [834], and in some β-lactam syntheses [835]. $Bu_3SnH/[PdCl_2(PPh_3)_2]$ was used to cleave alloxycarbonyl protected amino acids without racemisation [836]. Similar derivatives of nucleosides were deprotected with $[Pd(PPh_3)_4]$ and $BuNH_2/HCOOH$; TBDMS and DMTr protecting groups were unaffected [837]. Dimethyl propanedioate has also been used as an allyl acceptor in this context [838]. After deprotection using Pd(0), **475**, underwent ring opening to **476** which reacted with the palladium allyl complex generated in the deprotection step to give **477**, used in an approach to the taxane skeleton [839].



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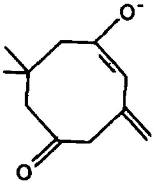
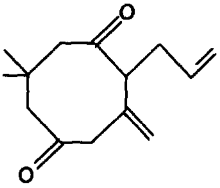


476

Palladium catalysed substitution of allylic ethanoates has been used in a number of cyclisation reactions [840]. Thus **478** was converted to **479**, using NaH/[Pd(dppe)$_2$], the product being used in an approach to the yohimbane skeleton [841]. Cyclisation of **480** gave, after decarboxylation, **481** used in the synthesis of ionophores [842]. Reaction of **482** (R = $OSiMe_2(CMe_3)$) with $Li[Et_3BH]/[Pd(PPh_3)_4]/PPh_3$ gave a mixture of **482** (R = H) and **483** [843]. Cyclisation of **484**, resulted in attack of the nucleophile at the more hindered end of the intermediate allyl complex, to give the six-membered ring product, **485**, rather than the eight membered ring. **485** was used in a synthesis of ergoline [844]. Michael addition of RNH_2 to **486** followed by palladium catalysed cyclisation gave **487**. A similar reaction occurred when the nucleophile was the anion of diethyl propanedioate, but cylohexanone pyrrolidine enamine gave **488** in which there has been no conjugate addition [845].



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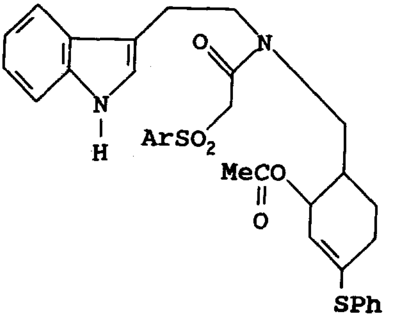

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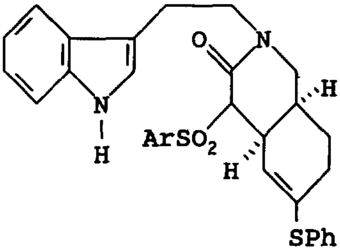

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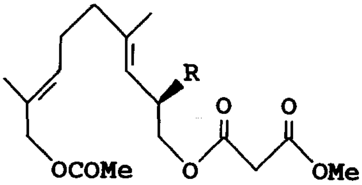

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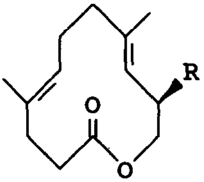

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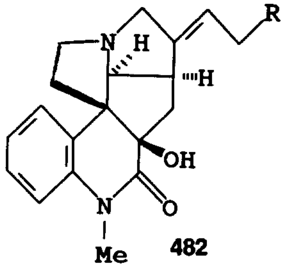

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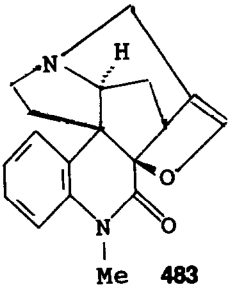

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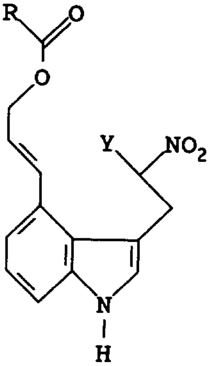

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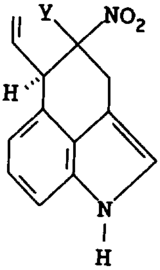

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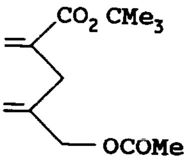

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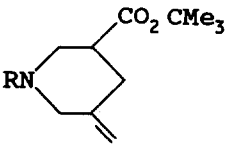

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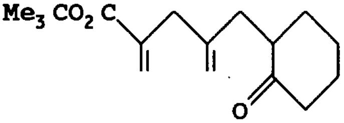
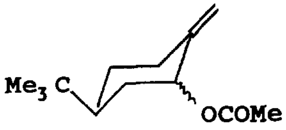


488

Some reactions of allyl ethanoate have been used in synthesis of sugar derivatives and nucleotides [846,847]. The regioselectivity of the reaction of $R^1CH(ZnBr)COOR^2$ with $R^3CH=CHCH(R^4)OCOMe$ has been studied. The organozinc compound always attacks predominantly at the less hindered end of the intermediate palladium allyl complex [848].

Reaction of $R^1CH{=}CHCH_2OCOMe$ with a ketone, R^2COR^3, in the presence of $[Pd(PPh_3)_4]/SmI_2$ gave the homoallyl alcohol $R^1CH{=}CHCH_2C(OH)R^2R^3$. The reaction formally involves samarium iodide induced electrophilic substitution of the palladium allyl complex [849].

There have been a number of reports concerning stereoselective substitution of allyl derivatives [850]. The *cis*-isomer of **489** was recovered in good yield from a *cis/trans*-mixture, when reacted with $[Pd(PPh_3)_4]/[CH(COOEt)_2]^-$. The difference between the isomers was attributed to diastereoselection in forming the intermediate palladium allyl complex [851]. Reaction of the anion of $Ph_2C{=}NCH_2COOMe$ with allyl ethanoate in the presence of $[Pd(dba)_2]$ and a chiral phosphine gave **490** which was hydrolysed to the amino ester. The best optical yield was obtained in the presence of DIOP, up to 57 % at -60 °C [852]. Allylation of $PhSO_2CH_2SO_2Ph$ or dimethyl propanedioate in the presence of a range of chiral phosphines has been studied; optical yields up to 69 % were reported [853].



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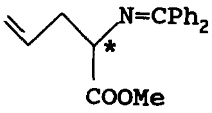
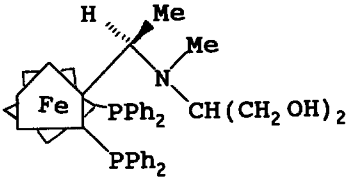


490

Reaction of racemic $RCH(OCOMe)CH{=}CHR$ with a nucleophile in the presence of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$/chiral ligand has been studied. With **491** as the additive, excellent optical yields could be obtained in favourable cases, and it was suggested that the nucleophile was directed by coordination to the remote hydroxyl group of the ligand [854]. Reaction of the non-symmetrical chiral allyl ethanoate, **492**, with the anion of dimethyl propanedioate in the presence of $[Pd(dppe)_2]$ gave mainly **493** with good retention of stereochemistry. However, when the nucleophile was PhZnBr, the reaction proceed with predominant inversion of stereochemistry. In both cases initial oxidative addition of palladium(0) involves inversion. With the propanedioate anion, nucleophilic attack also goes with inversion, but with the organozinc reagent, the nucleophile attacks at palladium and is then transferred to the allyl with retention of stereochemistry [855]. Racemic **494** reacted with the anion of pentane-2,4-dione in the presence of a palladium complex of **491** to give a mixture of the two possible allyl substitution products. The reaction is complicated by the fact that the two enantiomers of the starting material react at different rates, $k_S/k_R = 14$. Thus when 80 % of the starting material has reacted, the remaining **494** could be reisolated in 99 % optical purity.

The product **495** could be obtained in 98 % optical purity after 42 % reaction, but **496** was always formed with much less stereoselection [856].



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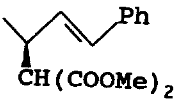

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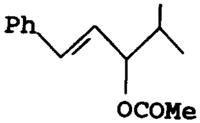

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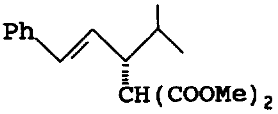

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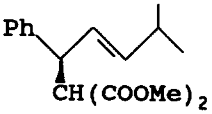
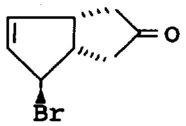


496

There are a few reports of the use of allyl halides as substrates. Reaction of **497** with **498** gave **499**, used in a new route to carbacyclin [857]. Allylation of **500** was achieved using 3-chloro-1-propene in the presence of $Li_2[PdCl_4]$ [858]. Reaction of $PhTiX_3$ with 1-bromo-2-butene in the presence of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ gave 4-phenyl-2-butene, 3-phenyl-1-butene and biphenyl. The selectivity of the reaction depended on the nature of X and on the additives. The best selection for the 2-butene was obtained when hmpa was added, but the yield was low. Addition of phosphine led mainly to the formation of the 1-butene [859].



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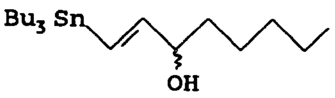

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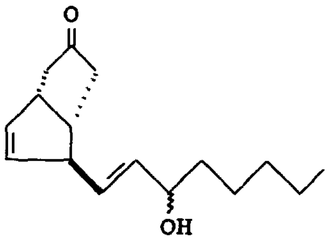

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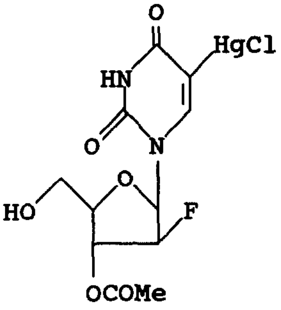
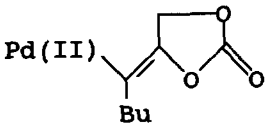


500

Carboxylation of $BuC{\equiv}CCH_2OLi$ gave $BuC{\equiv}CCH_2OCO_2Li$. Cyclisation in the presence of $[PdCl_2(MeCN)_2]$ and reaction of the resultant palladium derivative, **501**, with 3-chloro-1-propene gave **502** which could be hydrolysed to **503** [860]. Reaction of the enolate anion of cyclohexanone with $(EtO)_2P(=O)C(=CH_2)CH_2Cl$ gave **504** which was deprotected and cyclised to **505** in a one pot reaction [861]. Treatment of **506** with the anion of Me_2CHCH_2COOEt in the presence of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ gave a mixture of **507** and **508** [862].



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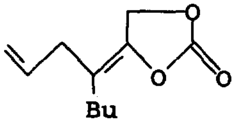

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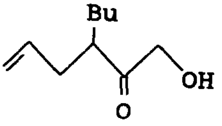

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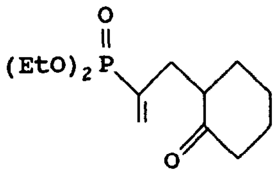

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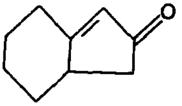

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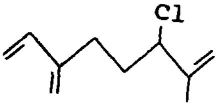

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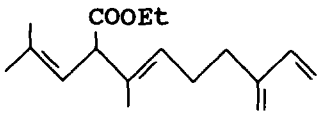

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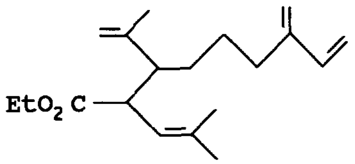
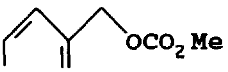


508

Allylic carbonates have been widely used as substrates, and are generally more reactive than the related ethanoates [863]. The main product of the reaction of allyl methyl carbonate with $MeOOCCH_2CN$ in the presence of $[Ni\{P(OEt)_3\}_4]$ was the bis(allylated) species. Reaction of $PhCH_2CN$ gave a mixture of mono and bis(allylated) products [864]. Treatment of **509** with $EtSSiMe_3$ using $[Pd_2(dba)_3]CHCl_3$/dppp as the catalyst system gave **510**, and reactions of vinyl epoxides were also studied [865]. Reaction of $R^1COCH(NO_2)R^2$ with $R^3CH{=}CHCH_2OCO_2Et$ in the presence of $[Pd(PPh_3)_4]$, under neutral conditions at room temperature, gave $R^1COC(NO_2)(R^2)CH_2CH{=}CHR^3$, with good regioselectivity [866]. Neutral conditions were also used for reaction of $ArCH{=}NCH_2COOEt$ with allyl carbonates; a strong base was required with the related ethanoate substrates [867].



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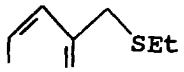
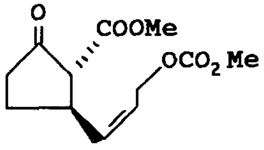


510

Cyclisation of **511** to **512** in the presence of $[Pd(PPh_3)_4]$ gave the product (which was used in the synthesis of cyclopentanoid natural products) in an *exo:endo* ratio of 3:1 [868]. Reaction of **513** with $[PdL_4]$ gave **514** which reacted with the anion of a propanedioate ester to give mainly **515**. A wide range of related reactions and substrates was discussed in detail [869].



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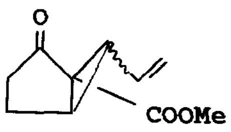

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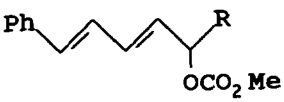

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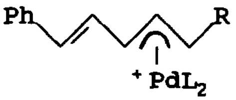

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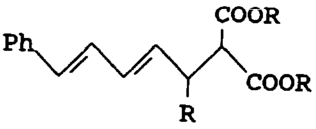
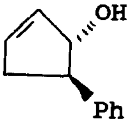


515

Vinyl epoxides have proved to be popular substrates. Thus RHgCl (R = aryl or alkenyl) reacted with butadiene monoepoxide in the presence of lithium chloropalladate to give E-$RCH_2CH=CHCH_2OH$ with good stereoselectivity. However, with **516** a 2:1 mixture of **517** and **518** was obtained [870]. **472** reacted similarly with butadiene monoepoxide to give **519** [871]. A related reaction of 2-nitrocyclohexanone has been noted [872].

516



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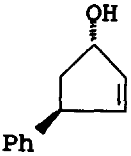

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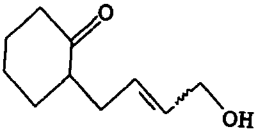
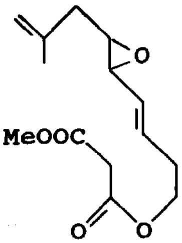


519

The reaction has also been reported in an intramolecular sense, **520** to **521** [873]. Related processes have been used in approaches to the tetrin A skeleton [874] and optically active isoquinuclidines [875].



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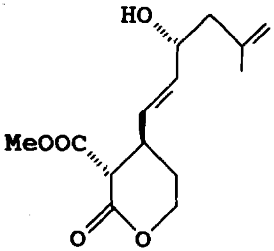
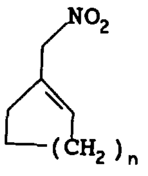


521

Allyl nitro compounds have also been used as substrates. Reaction of **522** with [PhSO$_2$]Na gave mainly **523**, and aliphatic versions of the process were equally regioselective [876]. The regiochemistry of such substitutions seems to be somewhat dependent on the substituents, and particularly on the size of the nucleophile; the larger the nucleophile the more attack at the less hindered terminus of the intermediate allyl complex is favoured [877,878].



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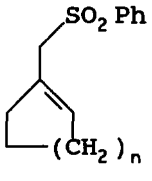
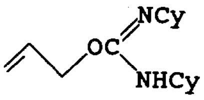


523

Reaction of 1-phenylpropanone with the 2-allylisourea, **524**, gave **525** and **526** in the presence of [Pd(dba)$_2$]/dppe under neutral conditions. Selectivity for monoallylation is fair, and both aldehydes and ketones are good substrates [879]. The intermediate in the reaction is thought to be **527** and this can react with PPh$_3$ to give [CH$_2$=CHCH$_2$PPh$_3$]$^+$ which is deprotonated to give a Wittig reagent [880].



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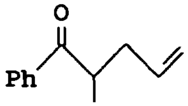

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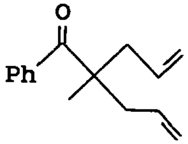

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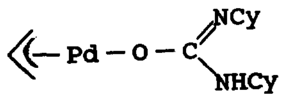
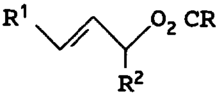


527

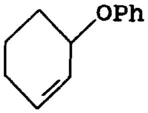
Other leaving groups which have proved useful in one or two instances have included phosphates [881,882], and ethers [883-885].

A few nickel catalysed reactions seem to be closely related. Thus $(C_5H_{11}\text{-}C{\equiv}C)_2Mg$ reacted with allyl sulphides or allyl ethers in the presence of [Ni(acac)$_2$]/PPh$_3$ to give $C_5H_{11}\text{-}C{\equiv}CCH_2CH{=}CH_2$. The best selectivity for this product (99 %) was obtained at low temperature; there was some homocoupling at higher temperatures. Analogous reactions of aryl halides were also noted under the same conditions [886]. Reaction of **528** with (R^{3}O)$_2$P(=O)H in the presence of [Ni(cod)$_2$]/Me$_3$SiCONHSiMe$_3$ gave the allyl phosphonate

[887]. In the reaction of $Me_2C(Z)CH{=}CH_2$ ($Z = SO_2Ph$, $SO_2C_6H_4$-4-Me or OCOMe) with XCH_2Y in the presence of $[NiCl_2L_n]$ (X, Y = electron withdrawing groups) the regioselectivity was shown to be strongly dependent on the nature of L. The stereochemistry of this type of substitution was generally retention, though stereoselection was lower than in related palladium catalysed processes [888]. Substitution of **529** by RMgX in the presence of $[NiCl_2L^*_2]$ (L^* is a chiral phosphine) was accomplished with moderate optical yield [889].

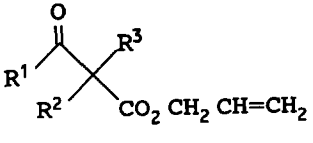


528 (R = Me or OEt)



529

Reaction of **530** with $Bu_3SnH/[PdCl_2(PPh_3)_2]$ followed by NBS gave **531**; the key reaction intermediate was thought to be a tin enolate [890]. An enolate was also formed by decarboxylation in the reaction of **532**; the final step in the reaction was loss of $[Pd(\eta^3\text{-}C_3H_5)(OCOMe)L_n]$ from **533** to give $R^1COC(R^2){=}CH_2$ [891].



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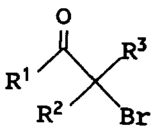

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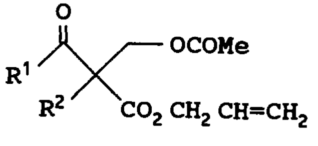

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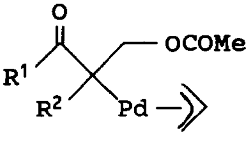
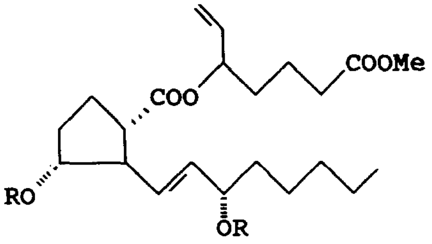


533

Palladium allyl complex formation, decarboxylation, and attack of the enolate produced on the allyl complex were the mechanistic steps involved in conversion of **534** to **535**. The regioselectivity of the reaction was discussed in a number of related cases [892]. The initial steps in the reaction of **536** with palladium(0) were similar. Allyl complex formation followed by decarboxylation gave **537** which either underwent dehydropalladation to give $RCH{=}CHCN$ (Pd:P>1:4) or allyl transfer to give $RCH_2CH(CN)CH_2CH{=}CH_2$ (Pd:P<1:4) [893].



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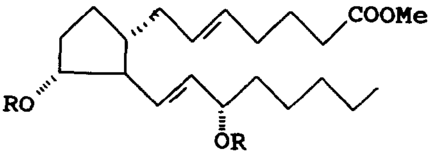

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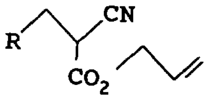

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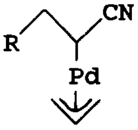
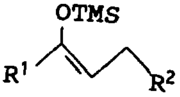


537

Allyl carbonates, CH_2=$CHCH_2OCO_2R$ react with palladium ethanoate and dppe to give $[Pd(\eta^3\text{-}C_3H_5)(dppe)]^+[OR]^-$ This reacts with a silyl enol ether such as **538** to give initially **539**. Dehydropalladation gave the enone [894].



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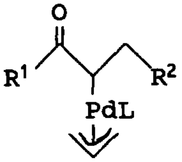
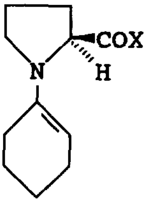


539

Reaction of the chiral enamine, **540** (X = OCH_2CH=CH_2), with $[Pd(PPh_3)_4]$ gave **541** in good optical yield. However, the reaction of **540** (X = OEt) with $PhOCH_2CH$=CH_2 gave **541** in much poorer enantiomer excess [895].



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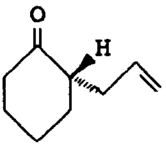
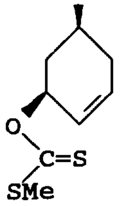


541

Reaction of *O*-allyl-*S*-alkyldithiocarbamates with [Pd(PPh$_3$)$_4$] gave allyl alkyl sulphides with retention of configuration. Palladium catalysed substitution of allyl derivatives by sulphur nucleophiles is often a problem as the sulphur complexes to palladium, precipitating it out of the reaction. In this process the intial step is the formation of [RSCOS]$^-$ and a palladium allyl complex. The anion loses COS to give [RS]$^-$ in the same concentration as the allyl complex. Allylation is substantially faster than any competing Claisen reaction. Thus **542** is converted mainly to **560**; both palladium addition and nucleophilic attack proceed with inversion, giving overall retention of stereochemistry [896].



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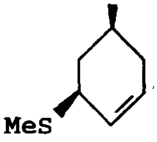
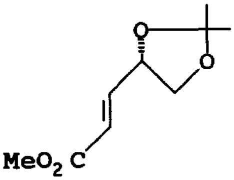


543

There have been more reports of reactions involving palladium trimethylene methane complexes. Thus **544** reacted with **545** in the presence of palladium ethanoate/P(OCHMe$_2$)$_3$ to give **546**, used in an enantiocontrolled synthesis of brefeldin A [897,898]. Reaction of **547** with [PdL$_n$] gave R$_3$MOCOMe and **548** which reacted with R'CHO to yield **549**. Cyclisation gave **550**, but the reaction fails with easily enolised aldehydes [899]. However, **551** (X = OSO$_2$Me, Cl or OCOMe) reacted with [Pd(PPh$_3$)$_4$] or [Pt(PPh$_3$)$_2$(PhCH=CHPh)] to give **552**, rather than a trimethylenemethane derivative. In this series it was found to be advantageous to use nickel complex catalysts to obtain the usual products of cycloaddition of trimethylenemethane intermediates [900].



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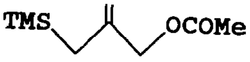

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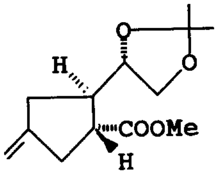

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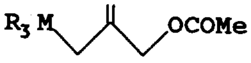

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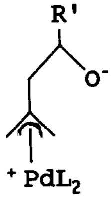

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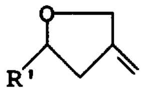

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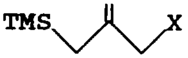

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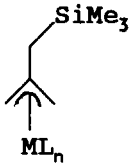
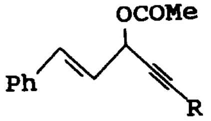


552

Reaction of a propargyl ethanoate, $R^1C\equiv CCR^2R^3OCOMe$, with $PhTi(OCHMe_2)_3$ in the presence of $[Pd(PPh_3)_4]$ gave mainly the allenyl derivative, $R^1C(Ph)=C=CR^2R^3$ [901]. Similarly, $PhCH(OCOMe)C\equiv CMe$ reacted with a vinylzinc compound to give $PhCH=C=C(Me)CH=CH_2$. Reactions of allyl and propargyl systems were compared by a study of **553**. With the anion of dimethyl propanedioate, in the presence of $[Pd(PPh_3)_4]$, the main product was **554**. Reaction with PhZnCl gave **555** indicating that the outcome of the reaction is strongly dependent on the nature of the nucleophile [902].



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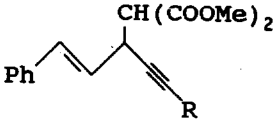

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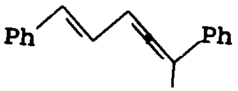
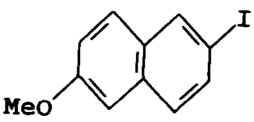


555

Palladium complex catalysis of the coupling reactions of organotin reagents [903] and boranes [904,905] has been reviewed.

Reaction of ethenylmagnesium bromide with **556** in the presence of [Pd(PPh_3)$_4$] gave the alkenylated product which was used in a synthesis of Naproxen [906]. The reaction is relatively general for ArMgX and Ar'MgX with this catalyst, unless there are two *ortho*-substituents [907]. This type of reaction was also catalysed by [$NiCl_2L_2$] (L = R_3P [908] or L_2 = dppe [909,910]). Binaphthyls have also been prepared using this type of catalyst [911]. Reaction of **557** with 4-$MeOC_6H_4MgX$ was achieved in the presence of either [$NiCl_2(PPh_3)_2$] or [Ni(acac)$_2$] to give a coupled product used in the synthesis of 3-aryldopamine analogues [912]. Treatment of 2-bromo-4,6-dimethylbenzonitrile with the Grignard reagent prepared from 2-methyl-4-fluorobromobenzene in the presence of [$NiCl_2(PPh_3)_2$]/dibal gave the coupled biphenyl which was used to prepare antihypercholesterolemic and hypolipemic compounds [913]. [Ni(acac)$_2$] was used as a catalyst for the preparations of poly-*p*-phenylene, poly-2,6-naphthylene, poly-2,7-fluorenylene and poly-2,7-phenanthrylene [914].



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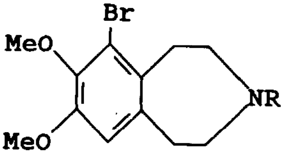


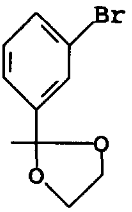
557

Reaction of 1,2-dichlorobenzene with EtMgBr in the presence of [NiCl(dppe)$_2$][PF_6] gave a 4:1 mixture of 2-ethylchlorobenzene and 1,2-diethylbenzene [915]. The coupling of Me_3SiCH_2MgCl with 2-bromo-1,6-methano-[10]-annulene was catalysed by [$NiCl_2(PPh_3)_2$] [916].

There have been some reports of the use of sodium, potassium or lithium salts of stabilised carbanions as nucleophiles towards aryl halides. Thus iodobenzene reacted with K[NCCHCOOEt] [917] or Na[NCCHCN] [918] in the presence of [$PdCl_2(PPh_3)_2$], or Na[NCCHCN] in the presence of [$PdCl_2$(cod)] [919].

There have been several reports of reactions of organozinc compounds. Thus BuZnCl reacted with ArX to give ArBu and ArAr. When the catalyst was [$PdCl_2(PPh_3)_2$], these were formed in the ratio 45:55, but using [$NiCl_2(PPh_3)_2$] the selectivity for ArBu was much better.

Both nickel and palladium complexes gave good selectivity for the catalysed couplings with haloalkenes [920]. Reaction of $EtOOC(CH_2)_nZnI$ ($n = 2$ or 3) with iodoarenes gave good selectivity for $EtOOC(CH_2)_nAr$, when the catalyst used was $[PdCl_2\{P(2\text{-}MeC_6H_4)_3\}_2]$. Nickel or palladium derivatives of PPh_3 gave greater amounts of biaryl. This catalyst also proved to be useful for coupling of the zinc reagent with alkenyl triflates and haloalkenes [921]. Treatment of **558** with successively *tert*-BuLi and $ZnCl_2$ gave an organozinc compound which could be coupled with 1,2-diiodobenzene to give **559** [922]. Reaction of $CH_2{=}CHCH_2CHRCH_2ZnBr$ with iodobenzene, in the presence of $[Pd(PPh_3)_4]$, gave $CH_2{=}CHCH_2CHRCH_2Ph$, and reactions with iodoalkenes, acyl halides and chloromethanoates were also described [923].



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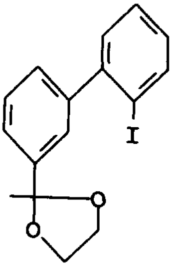
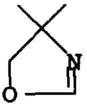


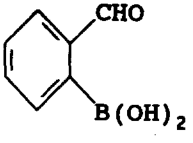
559

Coupling of heteroaryltin derivatives with iodoarenes has been reported to occur in the presence of $[PdCl_2(PPh_3)_2]$ [924]. Reaction of **560** with successively BuLi and Me_3SnCl gave the heteroaryl stannane, which was coupled with ArX in the presence of $[Pd(PPh_3)_4]$ [925].



560

In order for boron derivatives to be coupled to aryl bromides or iodides they must be converted to the more reactive boronates, usually by treatment with base. The complex $[PdCl_2(dppf)]$ has been shown to be a useful catalyst for reaction with aryl halides or with haloalkenes [926]. Aryl boronic acids have been coupled with bromoarenes in the presence of $[Pd(PPh_3)_4]/Na_2[CO_3]$; the reaction of **561** with **562** to give **563** indicates that the process is very tolerant of a wide range of functional groups [927]. Heterocyclic boronic acids have also been studied [928]. Alkenyl boronic acids have been coupled with aryl, alkenyl or allyl halides [929]. An unusual coupling between an aryl boronic acid and an aryl thallium derivative has been noted [930].



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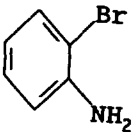

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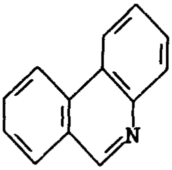
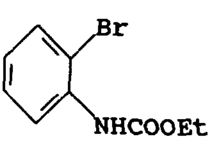


563

Trimethylsilylcyanide reacted with iodoarenes in the presence of $[Pd(PPh_3)_4]/Et_3N$ to give ArCN. Aryl chlorides and bromides were not good substrates, and a conventional reaction mechanism was proposed [931].

Alkynes, in the form of their anions or copper salts, have again been very popular nucleophiles towards aryl halides. Reactions of 1-alkynes with bromoarenes have been reported in the presence of $[PdCl_2(PPh_3)_2]/R_3N/CuI$ [932,933], and related reactions of iodoarenes were also described [934-936]. The coupling of 4-methoxyiodobenzene with 3-butyne-1-ol was used in a synthesis of piperovatine [937]. The reaction is performed under mild conditions, and tolerates aldehydes [938] and nitro groups [939]. A reaction using a polymer supported palladium complex as catalyst has also been reported [940].

Reaction of 2-iodophenol with 1-hexyne in the presence of $[Pd(OCOMe)_2(PPh_3)_2]/CuI$/piperidine/dmf resulted in coupling and cyclisation of the product to give 2-butylbenzofuran [941]. An analogous process was reported with the protected amine, **564**. This was coupled with 1-alkynes in the presence of $[PdCl_2(PPh_3)_2]/Et_3N/CuI$, the protecting group at nitrogen being essential to assure a good yield. Deprotection of the product, **565**, and cyclisation, gave 2-alkylindoles [942]. Related reactions of naphthalene derivatives have also been reported [943]. Cyclisation of the coupling product, **566**, gave the isocoumarin, **567** [944]. Conversion of the coupling product, **568** to its oxime, followed by cyclisation, gave the isoquinoline *N*-oxide, **569** [945].



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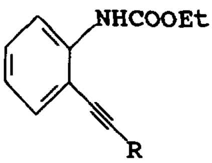

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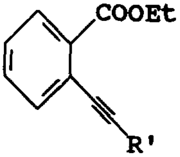

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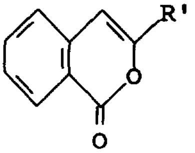

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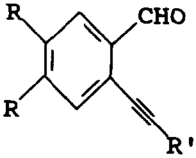

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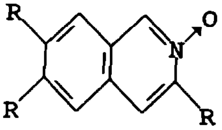

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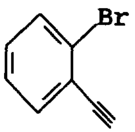
Vollhardt's group have used the coupling of alkynes with haloarenes in their search for ever more complex aromatic structures. Thus coupling of RC≡CH (R = $SiMe_3$ or CMe_2OH) with hexabromobenzene in the presence of $[PdCl_2(PPh_3)_2]/CuI/Et_3N$ gave the hexaalkyne, though yields were modest [946,947]. When the substrate for coupling was 2-iodobromobenzene the iodine could be replaced preferentially. After desilylation, **570** was coupled again with 2-iodobromobenzene to give **571**. Reaction of **571** with $Me_3SiC{\equiv}CH$ gave, after deprotection, **572** used in a synthesis of terphenylene [948]. The tetrabromo compound, **573**, has also been exhaustively coupled with trimethylsilylethyne [949].



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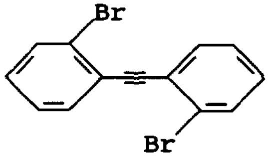

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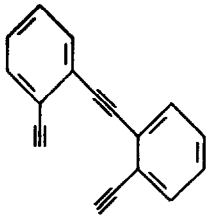

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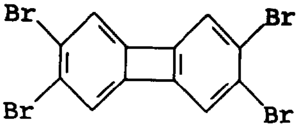

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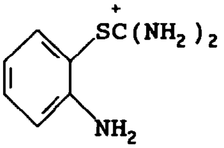
Coupling of $Bu_3SnC{\equiv}CSnBu_3$ with 3-iodoaniline in the presence of $[Pd(PPh_3)_4]$ gave the bis(aryl)ethyne, which was used in the preparation of biphenylene end-capped oligomers [950]. Monocoupling of 1,3-dibromobenzene with $HC{\equiv}CCMe_2OH$ could be achieved in the presence of $[PdCl_2(PPh_3)_2]/CuI/Et_3N$. After reaction with KOH, 1-ethynyl-3-bromobenzene was obtained, and could be polymerised with the same catalyst system. The polymers obtained were of low molecular weight, but had reasonable stability [951]

There have been noted the reactions of a number of phosphorus nucleophiles with aryl halides. Thus 2-bromonaphthalene reacted with PPh_3 in the presence of $NiCl_2$ to give 2-naphthyltriphenylphosphonium bromide [952]. Reaction of ArX with $(RO)_3P$ in the presence of $[Ni\{P(OEt)_3\}_4]$ at 170-200 °C has been reported. The initial steps of the reaction gave an intermediate $[(RO)_3PAr]^+$ which underwent an Arbusov type reaction [953]. An analogous reaction was reported for a bis(bromobenzo)18-crown-6 [954]. The stereochemistry of the reaction of $Me_2CHOP(H)(Me){=}O$ with bromobenzene to give $Me_2CHOP(Me)(Ph){=}O$, catalysed by $[Pd(PPh_3)_4]/Et_3N$ has been studied [955].

The reaction of $ArNH_2$ with Ar'Cl to give ArNHAr' was catalysed by $[PdI(Ph)(PPh_3)_2]$, when both aryl groups bear electron withdrawing groups [956]. Substitution of 2-iodoaniline by thiourea, catalysed by Ni(0) gave initially **574** which cyclised to **575** [957].



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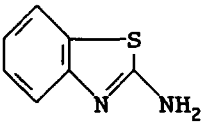

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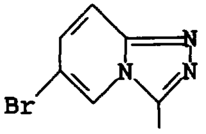
Nickel(0), generated electrochemically, has been used as a catalyst for substitution of bromoarenes by iodide. Bromoalkenes could also be used as substrates [958].

Reactions of heteroarene derivatives generally follow the same pattern, and have also been extensively reported. Reaction of 2-alkoxymethylphenylmagnesium bromide with 4-halopyridines was catalysed by [NiCl$_2$(PPh$_3$)$_2$], and the products used in the preparation of 4-substituted-1-alkylpiperid-3-ones [959]. 2-Alkylthiopyridines were substituted by a range of Grignard reagents in the presence of [NiCl$_2$(dppe)] [960]. Coupling of 3-bromothiophene with alkylmagnesium bromides is readily achieved when catalysed by [NiCl$_2$(dppp)], and the reaction can be performed on a large scale. The products are important in preparation of soluble conducting polymers [961]. Similar coupling could be achieved with 2,3-dibromothiophene as the substrate, and 3-bromomagnesiothiophene as the nucleophile, giving a terthiophene [962]. Various isomers of the oligothiophenes could be produced by suitable choice of substrate and nucleophile [963].

PhZnCl reacted with **576** with [Pd(PPh$_3$)$_4$] as catalyst, to give a relatively low yielding coupling [964]. Reaction of pyridine-3-zinc chloride with **577** in the presence of [Pd(PPh$_3$)$_4$] gave **578** used in a synthesis of cardiotonic agents [965]. Diethylzinc or tetraphenyltin could be coupled with 2-chloropyrazine in the presence of palladium(0) [966]. Reaction of 2,5-dibromothiophene with zinc and [NiCl$_2$(PPh$_3$)$_2$]/PPh$_3$/dmf gave polythiophene [967]. Homocoupling of 2-alkylthiopyridines was reported using Zn/[NiCl$_2$(PPh$_3$)$_2$]/PPh$_3$/dmf. With 2-bromo-6-alkylthiopyridines, coupling occurred at the brominated position [968].



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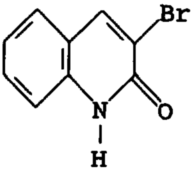

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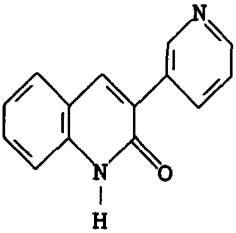

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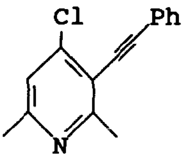
Reaction of stannylated pyridines with bromopyridines in the presence of [Pd(PPh$_3$)$_4$] gave bipyridines [969]. Tetraphenyltin was coupled with chloropyrazines in the presence of [Pd(PPh$_3$)$_4$] [970].

Reaction of thiophene-2-boronic acid with 2,3,5-triiodothiophene in the presence of $[Pd(PPh_3)_4]$ resulted in coupling only at the 2- and 5-positions, to give a UV mediated antibiotic [971]. Boron derivatives of both thiophene and selenophene have been coupled with bromopyrimidines in the presence of either $[Ni(PPh_3)_4]$ or $[Pd(PPh_3)_4]$ [972].

A wide range of coupling reactions with alkynes has been noted. Chloropyrazines were coupled with 1-alkynes using potassium ethanoate and a palladium catalyst. The best catalyst for alkylalkynes was $[Pd(PPh_3)_4]$, but $[PdCl_2(PPh_3)_2]$/CuI gave better results with aryl substituted alkynes [973]. There have been some studies of selectivity in the reaction. Thus 4-chloro-2,6-dimethyl-3-iodopyridine reacted with phenylethyne in the presence of a palladium complex to give substitution only of the iodide. The product, **579**, reacted with Na[SH] to give **580** and several related reactions were described [974]. Similarly, only the iodide was displaced from 2-methylthio-3-iodo-4-chloropyrimidine [975]. Chloride can however, be displaced, as in the conversion of **581** to **582** with RC≡CH in the presence of $[PdCl_2(PPh_3)_2]$/CuI [976].



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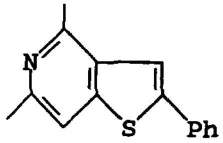

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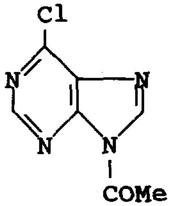

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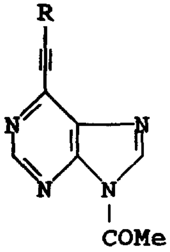

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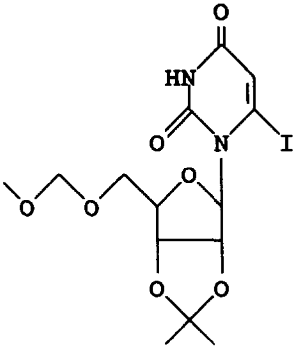
Couplings of **583** [977] and related compounds [978] with 1-alkynes in the presence of $[PdCl_2(PPh_3)_2]$ have been used in the preparation of anti-viral compounds.

Reaction of **584** with propyne in the presence of $[Pd(PPh_3)_4]$/CuI/Na[OH]/TEBAC gave **585**, a compound extracted from tagetes roots [979]. Monocoupling of $HC{\equiv}CCMe_2OH$ with 2,5-dibromothiophene was effected in the presence of $[PdCl_2(PPh_3)_2]/PPh_3/Et_3N$/CuI/py.

After deprotection of the product to give the free alkyne, this was polymerised by the same catalyst system to give. The material produced had a relatively low molecular weight, and lower thermal stability than the phenyl analogue [980].



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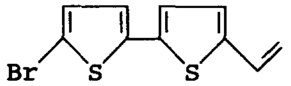

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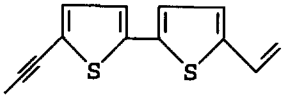
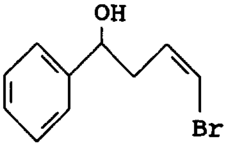


585

Haloalkenes have continued to be popular substrates, and many data have been published. Reaction of chloroethene with simple Grignard reagents in the presence of [Ni(acac)$_2$] resulted in straightforward substitution, but use of $PhCH_2CH_2MgBr$ gave some rearranged products [981]. Chloroethene also reacted with aryl magnesium halides in the presence of [NiCl$_2$(dppp)] [982]. The conditions of the coupling reaction were shown to be compatible with tertiary amines, as in the coupling of $CH_2{=}C(Br)CH_2NMe_2$ with $CH_2{=}C(MgBr)CH_2SiMe_3$ in the presence of [NiCl$_2$(dppp)] [983], and free hydroxyl groups as in the reaction of **586** with EtMgBr with the same catalyst system [984].



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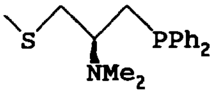
There have been some studies of the selectivity of the reaction. Thus when $PhSCH{=}CHBr$ is reacted with $Me_2CHMgBr$, only the bromine is replaced, and the two main products obtained were $PhSCH=CHCHMe_2$ and $PhSCH=CH(CH_2)_2Me$ [985]. Double substitution of the alkenyl chlorides in $Cl_2C=CH(CH_2)_nCl$ by Grignard reagents was effected in the presence of either $[PdCl_2(PPh_3)_2]$ or $Li_2[CuCl_4]$, the product being used in a pheromone synthesis [986]. Reaction of an E/Z-mixture of $EtCH=CHBr$ with a Grignard reagent in the presence of $[PdCl_2(dppf)]$ resulted in substitution only of the E-isomer; the product was used in a synthesis of isosafrol [987].

There have been further accounts of enantioselective coupling reactions between $PhCH(Me)MgBr$ and bromoethene. Catalysts have included nickel complexes of **587** and **588** [988], and **589** [989]. $[PdCl_2(R,S\text{-}PPFA)]$ was used as a catalyst for coupling of $PhCH(SiMe_3)MgBr$ with bromoethene in 56 % enantiomer excess [990].



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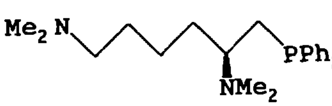

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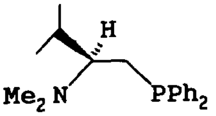


589

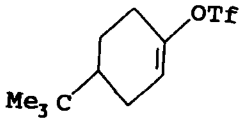
Reaction of $Na[XPh]$ (X = S or Se) with $R^1R^2C=CBr_2$ in the presence of $[NiBr_2(bipy)]$ gave $R^1R^2C=C(XPh)_2$ [991].

Couplings of organozinc compounds with haloalkenes, catalysed by nickel or palladium complexes, have been extensively reported and applied in synthesis [992-995]. Most are stereoselective, retaining the original double bond geometry [996]. When a mixture of E- and Z-$BrCH=CHBr$ was used as substrate, in the presence of $[Pd(PPh_3)_4]$, only the E-isomer was coupled with $RC\equiv CZnCl$, giving E-$RC\equiv C\text{-}CH=CH\text{-}C\equiv CR$ as the sole product, 99.5 % stereoisomerically pure [997]. Similar selectivity was noted with a stereoisomeric mixture of $RCH=CHBr$ [998].

Couplings of organozinc compounds have found applications in the preparation of fluorinated alkenes. Thus fluoroalkenyl iodides were coupled with alkynylzinc compounds in the presence of $[Pd(PPh_3)_4]$ [999]. Alkenylzinc compounds could be coupled with aryl iodides with good stereoselection, and the reaction was not even inhibited by bulky 2-substituents on the aryl ring [1000]. Coupling of $RCF=CFZnCl$ with iodoalkenes, acyl halides or chloromethanoates has been reported in the presence of palladium(0) [1001]. Coupling between E-$CF_3CF{=}CFZnX$ and $CF_2{=}CFI$ in the presence of $[Pd(PPh_3)_4]$ has been reported. The yields were higher with the Z-starting material [1002]. The use of $CF_2{=}CFZnCl$, prepared by lithiation of the chloride and transmetallation, as the nucleophile has been reported [1003].

Reaction of a range of organometallics, including Grignard reagents and organozinc compounds with the chiral allene, $MeC(Et){=}C{=}CHBr$, catalysed either by $[Pd(PPh_3)_4]$ or $[Ni(mesal)_2]$ resulted in substantial racemisation [1004].

The main uses of tin reagents this year have been in coupling reactions with alkenyl triflates [1005]. There has been a careful kinetic study of the reaction of ethenyltributyl tin with **590** in the presence of $[Pd(PPh_3)_4]$/LiCl. Alkenyl, alkyl allyl and alkynyl groups could all be transferred from tin, but benzyltin derivatives gave poor results. The initial step of the reaction was shown to be oxidative addition of the alkenyl triflate to palladium(0) [1006]. Reaction of $Me_3SnSnMe_3$ with 6-methylcyclohexenyl triflate in the presence of $[Pd(PPh_3)_4]$ gave the cyclohexenyl stannane which was used in the preparation of regiochemically pure derivatives of unsymmetrical ketones [1007]. Vinyl stannanes were also obtained by reaction of $(Ph_3Sn)_2Zn(tmeda)$ with alkenyl triflates or iodoalkenes in the presence of $[Pd(PPh_3)_4]$. The stereoselectivity of the process was dependent on the substrate [1008]. Reaction of E-$Me_3SiCH{=}CHSnBu_3$ with Z-$PhCH_2CH(Me)C(Br){=}CHD$ in the presence of $[Pd(PPh_3)_4]$ gave $PhCH_2CH(Me)C({=}CHD)CH{=}CHSiMe_3$, with retention of stereochemistry at both double bonds. The product was used in the synthesis of a substrate for a cobalt catalysed cyclisation reaction [1009]. Alkynylstannanes have also been coupled with alkenyl triflates [1010].



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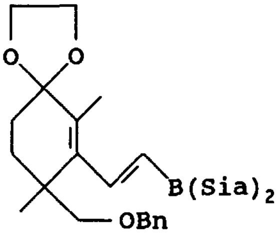
Coupling of Z-$Me_3CCH{=}CHB(OCHMe_2)_3$ with Z-1-bromo-1-octene in the presence of $[Pd(PPh_3)_4]$ gave Z,Z-2,2-dimethyl-3,5-dodecadiene with excellent stereoselectivity, the product being used in a synthesis of bombykol with >98 % isomeric purity [1011]. Reaction of **591** with an iodoalkene in the presence of $[Pd(PPh_3)_4]$/Na[OEt] was used in an approach to (•)-trisporol B [1012].

Coupling of haloalkenes with alkyne anions or their copper derivatives has been reported. Thus, reaction of **592** with $HC{\equiv}C(CH_2)_8COOMe$ in the presence of $[Pd(PPh_3)_4]$/CuI/$PrNH_2$ gave **593**, a new irreversible inhibitor of soybean lipoxygenase [1013]. Related, stereospecific couplings with bromoalkenes have been used in syntheses of Lipoxin A [1014], Lipoxin B [1015], and coriolic acid [1016]. Treatment of **594** with $HC\equiv CCMe_2OH$ was reported in the presence of $[Pd(PPh_3)_4]/CuI/[R_4N]Cl$ [1017]. The reaction of **595** with 1-alkynes in the presence of $[PdCl_2(PPh_3)_2]/CuI/Et_3N$ provides an example of the stereospecific reaction of an iodoalkene. The product was used to study the mechanism of inactivation of serine proteases [1018]. Reactions of chloralkenes are less common, but some have been reported [1019]. A coupling with an alkenyl triflate has been reported ($[Pd(OCOMe)_2(PPh_3)_2]/Bu_3N/Et_2NH/CuI/Na[OCOMe]$), but reaction conditions needed careful control [1020].



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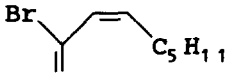

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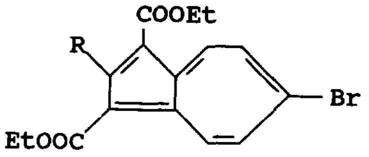

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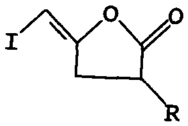
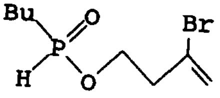


595

A few reactions of phosphorus nucleophiles have been recorded. Thus HP(=O)R(OR') could be coupled with a bromoalkene in the presence of $[PdCl_2(PPh_3)_2]/Et_3N$ with excellent retention of configuration at the double bond. It was assumed that the true catalyst was palladium(0) produced *in situ* [1021]. The reaction also occurred using $[Pd(PPh_3)_4]$ as the catalyst [1022], and intramolecularly, for **596** [1023].

Reaction of benzyl bromide with Me_4Sn was reported in the presence of $[Pd(bipy)(E\text{-}CNCH{=}CHCN)]$/hmpa, to give ethylbenzene. When PhCH(Br)Me was the substrate, a better reaction was obtained using [$PdEt_2$(bipy)] as catalyst. This catalyst system was also used for allyl, alkenyl, aryl and acyl halide coupling reactions [1024].



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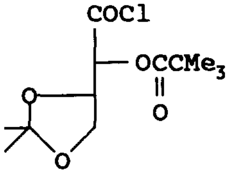
Catalysed coupling reactions of alkyl halides are relatively rare, and most of the substrates used have some special feature, which makes them more susceptible to oxidative addition to a metal. Coupling of Grignard reagents with α-haloesters was catalysed by [$NiCl_2$(dppp)] [1025] or [Ni$(acac)_2$] [1026]. Coupling of ArLi with the homoallyl bromide CH_2=CHC(Me)(OH)CH_2Br, in the presence of [Pd$(PPh_3)_4$], gave CH_2=C(Me)(OH)CH_2Ar in good yield, and without rearrangement [1027]. A catalyst prepared from [Ni$(acac)_2$]/PPh_3 was reported to catalyse coupling of alkynyl magnesium compounds with simple alkyl halides [1028], and reduction of [$PdCl_2$(dppf)] with dibal gave a species able to catalyse coupling between alkyl Grignard reagents and iodoalkanes [1029].

Coupling of acyl halides with complex cuprates, obtained by carbocupration, has been catalysed by [Pd$(PPh_3)_4$], with fairly good retention of double bond geometry in the alkenyl cuprate [1030]. Reaction of 597 with Me_4Sn, catalysed by [PdCl(CH_2Ph)$(PPh_3)_2$] was used in an approach to the hexahydrobenzofuran portion of avermectins and milbemycins [1031]. The alkyne 598 was coupled with PhCOCl in the presence of [$PdCl_2(PPh_3)_2$]/CuI/Et_3N [1032]. Coupling of tin derivatives with RC(Cl)=NR' was catalysed by [$PdCl_2(PPh_3)_2$] [1033].



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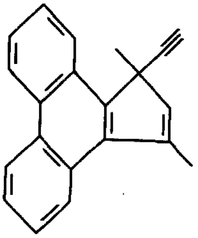

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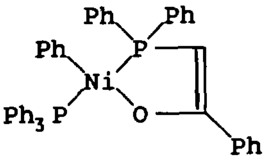
13.9 Oligomerisation, Polymerisation and Telomerisation

Catalytic dimerisation of ethene in the presence of complexes of nickel, palladium or platinum, and of propene with nickel or palladium complexes, has been reviewed [1034].

There has been a review of the use of alkene metal complexes as models for intermediates in ethene oligomerisation [1035].

Complexes of the type $[Ni(\eta^3\text{-}C_3H_5)L_2][PF_6]$ (L = $P(OPh)_3$, $SbPh_3$ or L_2 = cod) were used as catalysts for ethene oligomerisation. The main products were dimers and trimers [1036]. Electrochemical reduction of $[NiX_2L_2]$ gave a catalyst for dimerisation of ethene to 2-butenes with a very high turnover. Propene was dimerised to methypentenes about 100 times more slowly, and the reaction conditions needed to be carefully controlled [1037]. Preconditioning of the reactor for dimerisation of ethene in the presence of $[NiCl_2(PBu_3)_2]/EtAlCl_2$ has been discussed [1038].

The use of **599** as a catalyst for the oligomerisation of ethene and higher alkenes has been discussed. The products produced were highly linear, and supported versions of the catalyst were also described [1039]. Preparation of **600** (Y = CH or N) has been described. This catalyses the oligomerisation of ethene to alkenes which are 85 % linear. 1-Propene, 1-butene and 1-octene were converted to linear dimers with 70-80 % selectivity [1040].



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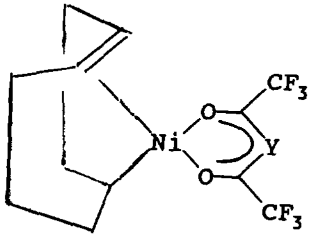

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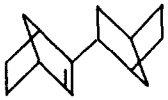
Supported nickel catalysts for dimerisation of ethene and propene have been described [1041]. Ethene dimerisation catalysts have been prepared from Ni(II) on a polymeric support and organoaluminium compounds. These have been subjected to magnetic susceptibility measurements. Nickel clusters (~10 Å) were found, with ferromagnetic exchange. The active centres for catalysis were localised in the boundary of the clusters, and were stabilised by the electronic system of the entire cluster [1042].

EHMO calculations on complexes of ethene and of allenes with $[\{Ni(\eta^3\text{-}C_3H_5)Br\}_2]$ have been performed. The activity of the monomers in oligomerisations was shown to be determined by the elevated charge density of the terminal carbon atom of the allyl ligand *trans* to the halogen. Ethene was less reactive than the allenes [1043].

The effect of the Al:Ni ratio and the reaction temperature on propene oligomerisation has been discussed. With appropriate control, excellent activity, and high selectivity for linear oligomers was achieved [1044]. Dimerisation of propene or 1-butene catalysed by [Ni(hfacac)(η^3-4-cyclooctene-1-yl)] has been noted. The catalyst had good activity and strong selectivity for linear products. A new method of storage, which eliminates deactivation, was described. A reaction mechanism was described in detail; the catalytically active species is a nickel hydride [1045]. The influence of the electronic properties of the β-diketonate ligand on the activity of the catalysts formed with alkylaluminium compounds has been studied. The activity of the system for propene dimerisation increased with a decrease in the electron donating ability of the β-diketonate [1046]. The synthesis of the complex [Ni(sacsac){PR^{1}R^2(CH$_2$)$_n$PR^{3}R^4}]X (n = 1,2,3 or 4) has been described. This is a very good catalyst for oligomerisation and isomerisation of alkenes, with good selection for linear products [1047].

Dimerisation of methyl propenoate to dimethyl 2-hexenedioate catalysed by palladium(II)/Li[BF$_4$] was previously known; the product has now been used in a synthesis of (•)-mitsugashiwalalactone [1048]. Codimerisation of ethene and phenylethene in the presence of [Ni(cod)$_2$]/PPh$_3$/BF$_3$.Et$_2$O gave 3-phenyl-1-butene [1049].

Reaction of norbornene with [NiX$_2$(PR$_3$)$_2$]/Na[BH$_4$] (X = Cl or Br) gave **601**, **602** and **603**. The distribution of products depended on the reaction conditions. With R = Ph and X = Cl, the main products were **601** and **602**, but with R = Bu and X = Br, the reaction gave mainly **603** [1050]. Codimerisation of methyl propenoate and 3,3-dimethylcyclopropene in the presence of Ni(0)/PR$_3$ gave a complex mixture of products, with the composition depending on the nature of the ligand. A similar process was noted for propenenitrile, and the mechanism of the reaction was discussed in detail [1051].



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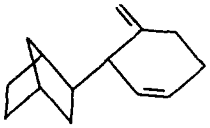
Catalysts for ethene polymerisation discussed during this period have included [NiCl$_2$(2-diphenylphosphinobenzoic acid)]/HO(CH$_2$)$_4$OH/PrOH/K[OH]/Na[BH$_4$] [1052] and [Ni(cod)$_2$]/PPh$_3$/Z-butenedioic acid anhydride [1053]. 1-hexene was polymerised in the presence of [Ni(cod)$_2$]/bis(trimethylsilyl)amino bis(trimethylsilyl)iminophosphorane [1054]. Et_3Al and Et_2Zn acted as chain scission agents and not as chain transfer agents in the polymerisation of phenylethene in the presence of nickel naphthenate/$BF_3.Et_2O/Et_3Al$ [1055].



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PhCH=CHMe was polymerised in the presence of $TiCl_3/Et_2AlCl/NiCl_2$ with some isomerisation to $PhCH_2CH{=}CH_2$, so that both monomer isomers were incorporated into a copolymer. Without the nickel salt, polymerisation still occurs, but there is no isomerisation [1056]. A similar reaction was noted for $PhCH_2CH_2CH{=}CHMe$, though the nickel complex used in this case was [Ni(acac)$_2$] [1057].

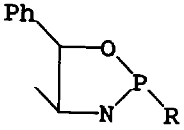
Copolymerisation of ethene and 1-alkenes was reported in the presence of [Ni(cod)$_2$] and the addend of PPh_3 with benzoquinone [1058]. Reaction of ethene and ethyl propenoate in the presence of [Ni(acac)$_2$]/$AlCl_3/Et_3Al/VCl_4$ gave a copolymer with 13-16 % ethyl propenoate content [1059].

Cyclotrimerisation of $RCH_2C{\equiv}CCH_2R'$ (R,R' = OH or OR) in the presence of various nickel(II) complexes gave hexasubstituted benzenes [1060]. The reaction of the dimethoxy compound was specifically discussed. A good turnover was obtained with a catalyst prepared from Ni(II), R_3P and Na[BH$_4$]. A species of stoicheiometry [NiH(BH$_4$)(PCy$_3$)] was said to be isolated [1061]. [Ni(C$_2$H$_4$)(PCy$_3$)$_2$] was also a good catalyst, and some of the hexasubstituted benzenes were employed in podand syntheses [1062].

There has been a full paper describing the mechanism of nickel catalysed cyclotetramerisation of ethyne. The labelling pattern in the cot produced from labelled ethyne was consistent with stepwise coupling, or a zipper mechanism [1063]. Reaction of 1-propyne-3-ol in the presence of [Ni$_2$(PhC≡CPh)$_2$(μ-η^1,η^2-R^{1}N=CH-CH=CHR$_2$)$_2$] gave the 1,3,5,7-tetrasubstituted cot as the main product (70 %) with a smaller amount of the 1,2,4,7-isomer [1064].

Polymerisation of ethyne to *trans*-polyethyne was effected by a species of stoicheiometry $Li_2Ni(OMe)_4$.thf [1065]. Polymerisation of phenyl- or 2-napthylethyne was accomplished in the presence of [M(dmgh)$_2$]/Et$_3$Al (M = Ni or Pd) [1066]. A mechanism has been proposed for the polymerisation of 4-nitrophenylethyne in the presence of PdCl$_2$ [1067].

Dimerisation of butadiene in the presence of [Ni(acac)$_2$]/BuLi/(Me$_2$N)$_3$P/MeOH gave 1,3,6-octatriene and 1,3,7-octatriene, the ratio between the products depending mainly on the concentration of methanol [1068]. 1,3,6-Octatriene was the main product in the presence of [Ni(cod)$_2$]/H$_2$NCH$_2$CH$_2$OPPh$_2$, but some 4-ethenylcyclohexane was also formed [1069]. A range of ligands, **604**, were used as additives to Ni(0) for oligomerisation of butadiene. When R = Ph or Me$_3$C, the main products were cod and bis(ethenyl)cyclobutane, but when R = Me, octatrienes were formed predominantly [1070]. A reductive dimerisation took place in the presence of [Pt(acac)$_2$]/CO$_2$/HCOOH, to give 1,6-octadiene, 1,7-octadiene as well as some 4-ethenylcyclohexene and cyclooctadienyl methanoates [1071].



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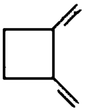
Cyclooligomerisation of butadiene to cdt with 70 % selectivity was achieved in the presence of Ni(0) anchored on linear polethenylpyridine [1072]. Polyethene supported phosphites were good ligand for Ni(0) to act as a catalyst for conversion of butadiene to various cyclooligomers. Similar product selectivities are obtained as with the fully homogeneous systems, and can be manipulated in the same way by changing the L:Ni ratio. At the reaction temperature (100 °C) the solution is homogeneous, but the catalyst is precipitated on cooling,and may be recovered and reused [1073]. Reaction of **605** with [Ni(cod)$_2$]/R$_3$P, gave **606**, **607** and **608** [1074].



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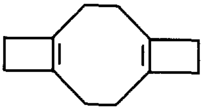

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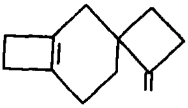

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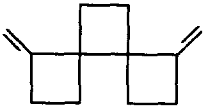
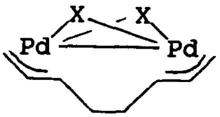


608

The mechanism of stereoregulation in the allyl nickel complex catalysed polymerisation of butadiene has been reviewed [1075].

Telomerisation of butadiene with water under a CO_2 atmosphere in the presence of $[Pd(acac)_2]/PPh_3$/dmf/octadienyl ether gave 78.5 % octadienyl alcohols [1076]. Reaction with methanol using $[Ni(cod)_2]$/dppe as the catalyst system gave initially simple addition products, which were transformed further to hydroxyethers [1077]. Telomerisation of 2-alkylthioethanol in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al/CF_3COOH$ gave octatriene and $RSCH_2CH_2OCH_2CH{=}CH(CH_2)_3CH{=}CH_2$. With $RSCH_2COOH$ as the addend, small amounts of simple addition products as well as telomers were obtained [1078]. The mechanism of reaction of butadiene with ethanoic acid has been investigated. Reaction of palladium ethanoate with butadiene gave **609** (X = OCOMe), isolated from the catalytically active reaction mixture. This reacted with ethanoic acid to give **610**. Reaction of $[Pd(hfacac)_2]$ with butadiene in methanol gave **611**, characterised in a diffraction study. **611** was also a catalyst for the telomerisation of ethanoic acid with butadiene. Thus dimers could be important in the catalytic cycles for this reaction, but the evidence was not conclusive [1079].



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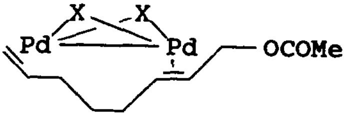

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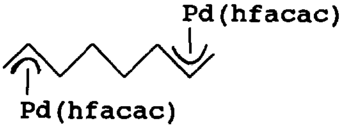
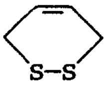


611

Attempted telomerisation of $[PhSO_2]^-$ with butadiene in the presence of $[Pd(PPh_3)_4]/CO_2$ gave a mixture of addition and telomerisation products. With isoprene, the addition product predominated. The reaction is very slow in the absence of CO_2. 1,2-Propadiene reacted to give $PhSO_2CH_2C(=CH_2)C(Me)=CH_2$ [1080].

Reaction of BuSH with butadiene in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$ gave only butenyl sulphides, the products of simple addition. However, with arene thiols, telomers could also be isolated, and the proportions of the products could be adjusted by changes in the added phosphine [1081]. Butadiene reacted with elemental sulphur in the presence of $\{PdL_n\}$ to give **612** and **613** as well as substantial amounts of higher cyclic telomers such as **614**. A reaction mechanism was proposed [1082].



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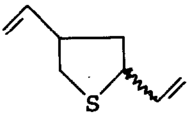

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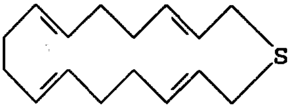
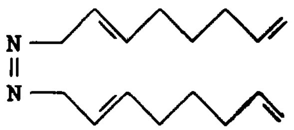


614

Telomerisation of isoprene with PhNHMe has been reported in the presence of various palladium catalysts; the product distribution depends on the additives [1083]. Mono- and bis-octadienylation of amino acids was accomplished in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$. Reaction almost invariably took place at nitrogen, although in a few cases it was shown that octadienyl derivatives of the acid groups were intermediates [1084].

Reaction of hydroxylamine an its *N*-alkyl derivatives also took place mainly at nitrogen but the reaction was not very selective, giving *N,N*-bis(octadienyl)hydroxylamine, tris(octadienyl)amine and octadienol. Reaction of Et_2NOH took place at oxygen [1085]. The reaction of hydrazine with butadiene in the presence of $[Pd(acac)_2]/Et_3Al/CF_3COOH/R_3P$ was, by contrast, quite selective, giving 65 % **615**. When the added phosphine was dppe, up to 31 % **616** was formed [1086].



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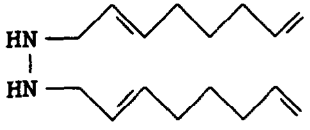
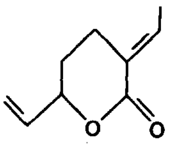


616

Catalytic telomerisation of carbon acids with butadiene was compared with the related stoicheiometric reaction. The mechanism was discussed in considerable detail [1087]. Reaction of $PhSO_2CH_2COOMe$ with 1,3-pentadiene in the presence of $[PdCl_2(PPh_3)_2]/[PhO]Na$ was shown to be reasonably selective [1088].

There have been several reports of telomerisation reactions involving incorporation of CO_2. Reaction in the presence of $[Pd(acac)_2]/HCOOH$/Amberlist A21 gave mostly butadiene oligomers, and some thf, by an unspecified mechanism [1089]. Control of the telomerisation, to give **617**, in the presence of either nickel or palladium complexes as catalysts, has been considered in detail. The structure of *trans*-$[Pd\{OC(=O)C(=CHMe)CH_2CH=CH\text{-}CH=CH_2\}_2\{P(CHMe_2)_3\}_2]$, an intermediate proposed, was established in a diffraction study [1090]. Reaction of 1,3,7-octatriene with CO_2 in the presence of [Ni(bipy)(cod)] resulted in attack only at the diene. The initial product was **618**, which reacted with HCl/MeOH to give methyl 3,8-nonadienoate. Alternatively, further carboxylation gave **619** with reacted with HCl/MeOH to give **620** [1091]. Reaction of butadiene with CO_2 and propene oxide in the presence of $[Pd(acac)_2]/L$ gave **621** and **622** as well as compounds which did not incorporate the oxirane. A reasonable reaction mechanism was proposed [1092].



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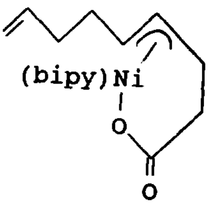

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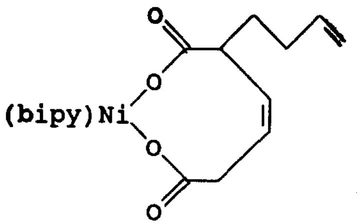

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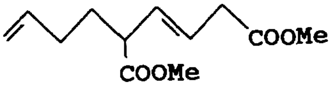

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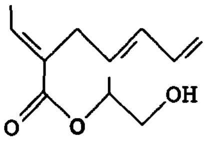

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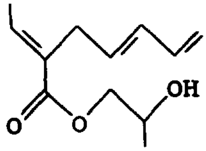

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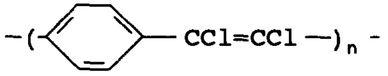
Isonitriles such as Me_3CNC and $MeCH_2CMe_2NC$ were polymerised by Ni(II) in the presence of optically active amines to give helical polymers with enantiomer excesses from 7-61 % [1093]. Reaction of 1,4-bis(trichloromethyl)benzene and $Me_3SiSiMe_3$ in the presence of $[Pd(PPh_3)_4]$ gave the polymer **623** [1094]. Polymerisation of **624** using $NiCl_2$ as the catalyst gave a species which was demethylated by BBr_3 to give a polymer with stacks of donors and acceptors in the side chains [1095].



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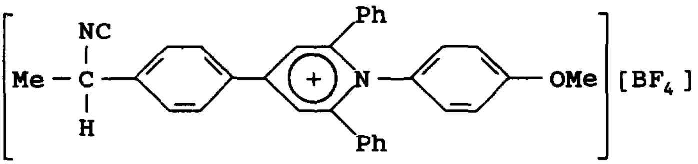
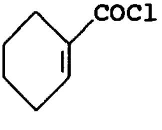


624

Treatment of RCHO (R = alkyl, aryl or thienyl) with CCl_4/Mg in the presence of Ni(0) (generated *in situ* by sodium amalgam reduction of $[NiCl_2(PPh_3)_2]$) and Me_3SiCl gave modest yields of $RCH(OH)CCl_3$ [1096]. Nucleophilic addition of CF_3CX_2ZnX to RCHO was also achieved in the presence of $[NiCl_2(PPh_3)_2]$ or $[PdCl_2(PPh_3)_2]$ [1097]. Reaction of CCl_3CF_3 with Zn/MeCOOCOMe/$[NiCl_2(PPh_3)_2]$ and RCHO gave $RCH{=}CHClCF_3$. The reaction mechanism is not specified, but is presumably related [1098]. Reaction of the alkenyl triflate, $CH_2{=}C(R)OTf$, with R'CHO using $CrCl_2$ and catalytic $NiCl_2$ gave $CH_2{=}C(R)CH(OH)R'$ in good yield. The reaction mechanism involves initial oxidative addition of the triflate to nickel(0), transmetallation to the chromium complex, and addition to the aldehyde [1099]. A related reaction of an iodoalkene has been reported; aldehyde, acetals, silyl and benzyl ethers survived the reaction conditions [1100]

Reaction of Z-$PhC(SnBu_3){=}CHSiEt_3$ with **625** gave **626** in the presence of $[PdCl_2(MeCN)_2]$. Nazarov cyclisations of **626** were studied [1101]. Reaction of **627** with R^3COCl gave **628**, *via* rearrangement of the initial addition product [1102].



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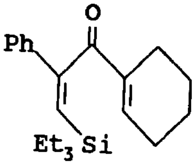

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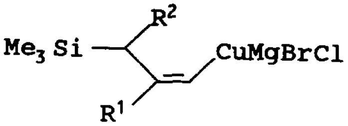

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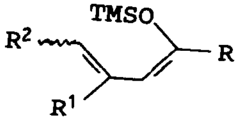

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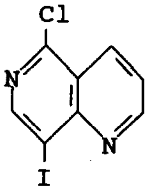
Reaction of Me_3ZnLi with cyclohexenone in the presence of a range of nickel and palladium complexes has been studied. The best conversion to the conjugate addition product was noted in the presence of $[PdCl_2(MeCN)_2]$. Poor results were, however, obtained with very hindered enones [1103]. Conjugate addition of ArBr to methyl propenoate in the presence of Zn/$[NiCl_2(PPh_3)_2]$ may be assumed to involve ar arylzinc compound as the intermediate [1104]. Conjugate addition of an organozirconium compound to an enone in the presence of $[Ni(acac)_2]$ has been used in preparation of a prostaglandin intermediate [1105]. Conjugate addition of β-ketoesters to cyclohexenone in the presence of a Lewis acid such as BF_3 was catalysed by [Ni(acac)$_2$], but the reaction was more successful using a copper based catalytic system [1106].

Reaction of Me_3SiCH_2MgCl with diketene in the presence of nickel(II) gave $Me_3SiCH_2C(=CH_2)CH_2COOH$ [1107]. When ArCOCl was reacted with RR'CHCH(Ph)COCl in the presence of [Pd(PPh$_3$)$_4$]/Et$_3$N, the product was RR'C=C(Ph)COAr. The initial step in the mechanism was the reaction of RR'CHCH(Ph)COCl with the amine to give the ketene, RR'CHC(Ph)=C=O. Oxidative addition of ArCOCl to palladium(0) followed by decarbonylation gave {ClPdAr}, and the ketene was then inserted into the palladium-aryl bond [1108].

Many applications of the Heck reaction continue to be reported. Aryl halides have been added to enones in the presence of [Pd(OCOMe)$_2$(PPh$_3$)$_2$]/Bu$_3$N/HCOOH/dmf [1109]. There have been a number of reactions of methyl propenoate to give ArCH=CHCOOMe, including ones of chloropyrazines in the presence of [Pd(PPh$_3$)$_4$]/dma/K[OCOMe] [1110], halopyrimidines in the presence of Pd(OCOMe)$_2$/PPh$_3$/Et$_3$N [1111] and **629** using palladium ethanoate, the product in this case being used in an approach to the synthesis of matrine and related compounds [1112]. Reaction of ArI with **630** in the presence of [Pd(OCOMe)$_2$(PPh$_3$)$_2$]/Bu$_3$N/HCOOH gave mostly **631** together with some **632**. The starting material, **630**, was prepared by reaction of cyclohexenyl triflate with RCOCH=CH$_2$ catalysed by Pd(OCOMe)$_2$/K$_2$[CO$_3$]/[Bu$_4$N]Cl [1113].



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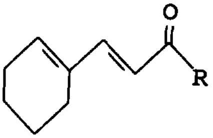

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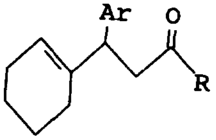

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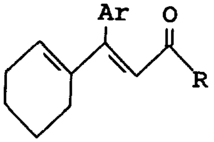

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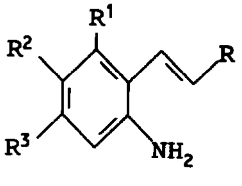
2-Haloanilines were coupled with RCH=CH$_2$ (R = H or Ph) in the presence of Pd(OCOMe)$_2$/Et$_3$N/P(C$_6$H$_4$-2-Me)$_3$ to give, initially, **633**. This was protected as the *N*-tosyl derivative, and cyclised in the presence of Li$_2$[PdCl$_4$] to give, after deprotection, **634** [1114].

In a related process, **635** reacted with a propenoate ester in the presence of $Pd(OCOMe)_2/PPh_3/MeCN$ to give **636** *via* **637** [1115].



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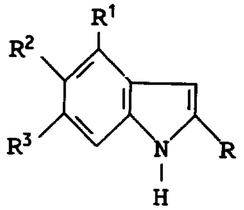

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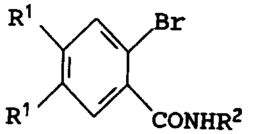

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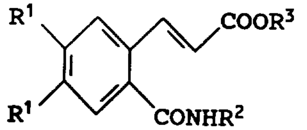

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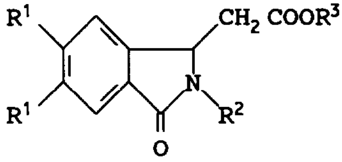
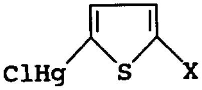


637

Reaction of ArI with $THPOCH_2CH{=}CHCOOMe$ under solid/liquid phase transfer conditions in the presence of $Pd(OCOMe)_2/[Bu_4N]Cl/Na[HCO_3]$/hmpa gave $THPOCH_2C(Ar){=}CHCOOMe$ [1116]. The reaction of RX with $R'CH{=}CH_2$ in the presence of $[Ni(R'CH{=}CH_2)_2(PPh_3)_2]$ gave $RCH{=}CHR'$, RCH_2CH_2R' and RR. The main products were the alkene and the self-coupled product when R' = Ph, bur with R' = COOEt, more of the saturated species was produced [1117].

Reaction of Z-$PhC(OCOMe){=}C(Ph)HgCl$ with ethyl propenoate in the presence of $Li[PdCl_3]/CuCl$ gave Z,Z-$PhC(OCOMe){=}C(Ph){-}CH{=}CH{-}COOEt$ [1118]. A reaction mechanism was suggested, and the effects of the reaction conditions on the amount of by-products from homocoupling reactions investigated [1119]. Addition of MgO allowed the reaction to proceed at room temperature [1120]. In the presence of $Li_2[PdCl_4]$, norbornene reacted with **638** to give, initially, **639**. After treatment with PPh_3, this palladium derivative could be reacted with alkynyllithium compounds, alkenyl tin or alkenyl copper compounds to give compounds which were used in prostaglandin syntheses [1121].



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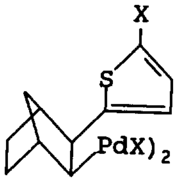
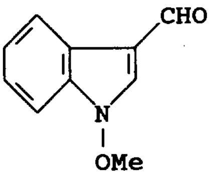


639

Reaction of $PhTl(OCOCF_3)_3$ with phenylethene to give PhCH=CHPh and $PhCH_2CH(OCOCF_3)Ph$, with or without addition of palladium ethanoate has been studied. In ethanoic acid as the solvent, and with added palladium ethanoate, the sole product was PhCH=CHPh. A detailed reaction mechanism was proposed on the basis of kinetic studies [1122]. With $ArTl(OCOCF_3)_3$ and 3-butene-2-one, in the presence of $Li_2[PdCl_4]$, good yields of ArCH=CHCOMe were obtained [1123]. Thallation of **640**, followed by palladium ethanoate catalysed coupling with methyl propenoate, gave **641** as the main product, together with smaller amounts of regioisomers [1124].



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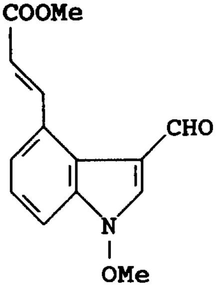
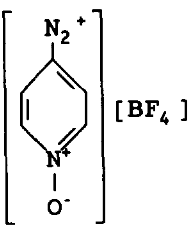


641

Reaction of E- or Z-$RCH=CHSiMe_3$ with $[ArN_2][BF_4]$ in the presence of $[Pd(dba)_2]$ gave a mixture of E-RCH=CHAr and $ArC(R)=CH_2$. The reaction mechanism involves addition of {ArPd} across the double bond of the alkenylsilane, followed by loss of $\{PdSiR_3\}$, and the stereoselection was convincingly explained [1125]. Coupling of an alkenylstannane, $PhC(SnR_3)=CH_2$, with $[ArN_2][BF_4]$, catalysed by $[Pd(dba)_2]$, gave mainly Z-PhCH=CHAr. A similar reaction mechanism was discussed [1126]. The diazonium salt, **642**, reacted with cyclopentene in the presence of $[Pd(dba)_2]$ to give **643**. Although the reaction was successful with cyclohexene and cycloheptene, there was some isomerisation of the position of the double bond in these cases. An addition-elimination mechanism was proposed for the reaction [1127].



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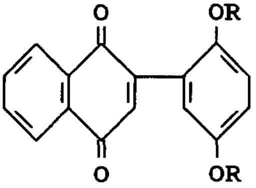
643

Reaction of 4-bromobenzaldehyde with ethene in the presence of $Pd(OCOMe)_2/Bu_3N/P(C_6H_4\text{-}2\text{-}Me)_3$ gave E-1,2-bis(phenyl-4-carbaldehyde)ethene [1128]. The reaction of alkenes with haloarenes in the presence of electrogenerated Ni(0) has been studied. In this case bromobenzene reacted with ethene to give 1,1-diphenylethane, 1,2-diphenylethane and phenylethane [1129]. When iodoarenes were reacted with ethenyltrimethylsilane in the presence of Ag^+ and a palladium catalyst, the product was $ArCH{=}CHSiMe_3$; without the added silver, desilylation occurred giving $ArCH{=}CH_2$. A reaction mechanism was postulated, and the range of functional groups with which the method is compatible explored [1130]. Aryl bromides were reacted with arylethenes in the presence of $[NiCl_2(PPh_3)_2]$ to give ArCH=CHAr' [1131].

Reaction of R_fI (R_f = perfluoroalkyl) with $R'CH{=}CH_2$ in the presence of $[Pd(PPh_3)_4]$ gave R_fCH_2CHIR' in good yield. With R_fI and $RC{\equiv}CH$, the product was $R_fCH{=}CH(I)R$, formed with high regioselectivity. The stereochemistry of the product was mostly E, and the reaction was tolerant of -OH, -COMe and $-SiMe_3$ functional groups [1132]. Compounds such as $ArOSO_2R_f$ reacted with $R'CH{=}CH_2$ to give ArCH=CHR', in the presence of $[PdCl_2(PPh_3)_2]/Et_3N$. Alkynes reacted similarly [1133].

Naphthoquinone reacted with 1,4-dialkoxybenzene in the presence of $Pd(OCOMe)_2$ to give **644** [1134]. Reaction of **645** and **646** in the presence of palladium ethanoate gave **647** in good yield, this product being used in a synthesis of ergot alkaloids [1135]. In a related process **648** reacted with $CH_2{=}CHCH(OH)Me$ to give successively **649**, **650** and **651** [1136].



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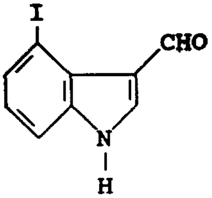

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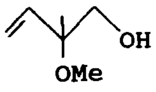

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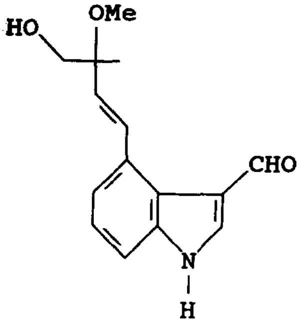

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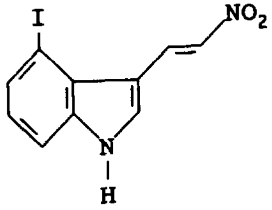

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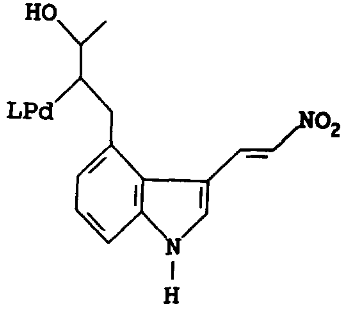

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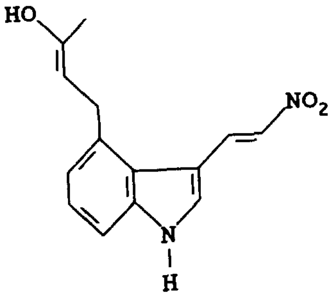

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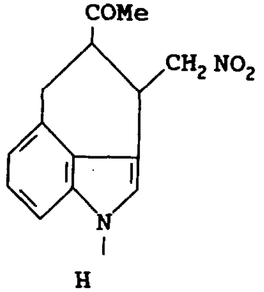
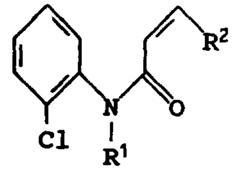


651

Related intramolecular reactions have been reported. Thus **652** reacted under catalysis by $[Ni(acac)_2]/PPh_3/Et_3Al$ to give **653** [1137]. Cyclisation of **654** gave **655**, catalysed by Pd(0) [1138]. Cyclisation of **656** gave **657**, in the presence of $Pd(OCOMe)_2/PPh_3/[Et_4N]Cl/K_2[CO_3]$. This is forced to occur by the 6-*endo-trig* route, since the 5-*endo-trig* route, would give an intermediate lacking a β-hydride for elimination. However, there is a preference, kinetically, for a 5-*exo-trig*, rather than a 6-*endo-trig* reaction, as exemplified by the conversion of **658** to **659** (major) and **660** (minor) [1139].



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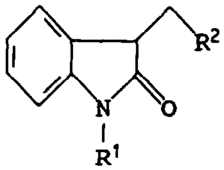

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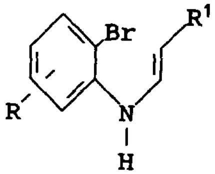

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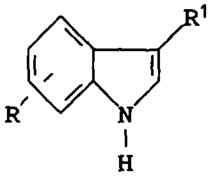

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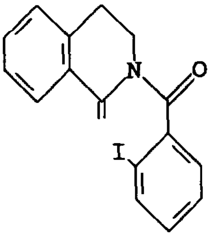

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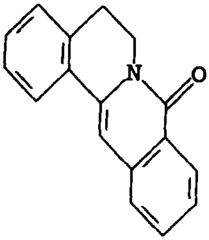

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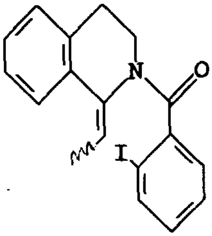

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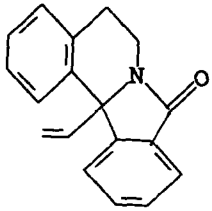

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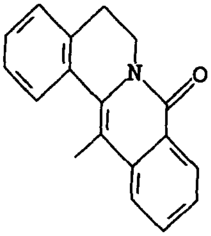
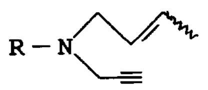


660

Reaction of a disubstituted alkyne, $RC\equiv CR$, with an aryl iodide, catalysed by palladium complexes is known to give $RCH=CR(Ar)$. The reaction has now been applied to $RR'C(OH)C\equiv CAr'$, to give a mixture of $RR'C(OH)CH=CArAr'$ and $RR'C(OH)C(Ar)=CHAr'$ [1140]. Treatment of **661** ($R = CH_2Ph$) with $Pd(OCOMe)_2/PPh_3$ resulted in cyclisation to **662** and **663** in the ration 2:1. The product ratio was dependent on the nature of the added ligand and a reaction mechanism was proposed [1141].



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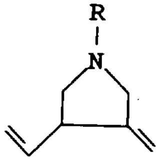

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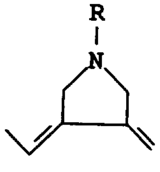
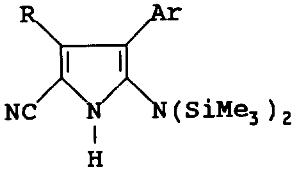


663

Reaction of $RC\equiv CSiMe_3$ with an aryl iodide in the presence of $[Pd(OCOMe)_2(PPh_3)_2]/R_3N/HCOOH/dmf$ gave E-$ArC(R)=CHSiMe_3$ as the main product. This could be readily desilylated to $ArC(R)=CH_2$. A carbopalladation mechanism was proposed, and many functional groups were tolerated [1142]. Treatment of $RC\equiv CAr$ (R = H or aryl) with Me_3SiCN in the presence of $PdCl_2$, $NiCl_2$/dibah or $NiCl_2/Et_3Al$ gave **664** in good yield and with high regioselectivity [1143]. When the substrate was $Me_3Si\text{-}C\equiv C\text{-}C\equiv C\text{-}SiMe_3$, and the catalyst $PdCl_2$, the product was **665**. The mechanism remains unproven, but may involve a palladium cyanide complex or a palladium carbene [1144]. Reactions of $PhC\equiv C\text{-}Si(SiMe_3)_2Mes$ in the presence of $[Ni(PEt_3)_4]$ have been studied. Initial coordination involves rearrangement of one $SiMe_3$ group to give **666**, and subsequent isomerisation to $Me_3SiC\equiv CSi(Ph)(SiMe_3)Mes$. A complex series of reactions of **666** with $PhC\equiv CSiMe_3$ was reported [1145].



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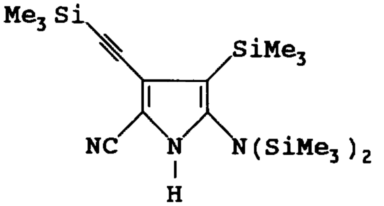

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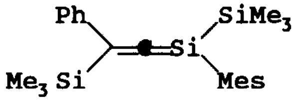


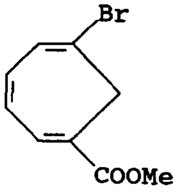
666

A new type of metal-promoted alkyne polyhedral borane insertion reaction has been reported. *nido*-2,3-$Et_2C_2B_4H_6$ reacted with 2-butyne in the presence of NaH and $NiCl_2$ to give *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$. The sodium salt of the starting material and a nickel carborane complex were proposed as intermediates [1146].

Homocoupling reactions are generally regarded as side-reactions to be avoided in desired cross-couplings, but a number have been reported as useful reactions in their own right. Thus aryl triflates were reacted with $NiCl_2$/Zn/PPh_3/NaI/dmf/ultrasound to give 67-95 % biaryl, together with small amounts of reduced ArH. The reaction works well even for hindered substrates with substituents at the 2-position, and naphthyl-1-triflate [1147]. Reactions of aryl chlorides in the presence of $NiCl_2$/M/PPh_3/dmf (M = Zn, Mg or Mn) gave ArAr in up to 98 % yield. Kinetic data supported a complex reaction scheme, with multiple mechanisms, and Ni(0), generated *in situ* is the true catalyst [1148]. Ni(0) for such catalytic reactions has also been generated by electrochemical reduction, and used in coupling of aryl, alkenyl, benzyl, heteroaryl and alkyl halides [1149]. Coupling of 4-$Me_3CC_6H_4X$ to give 98 % biaryl was reported to occur under electrochemical conditions in the presence of $[Pd(PPh_3)_4]$/$[Et_4N][OTs]$/dmf/Ar [1150].

Coupling of $R^1R^2C{=}CHX$ to give $R^1R^2C{=}CH{-}CH{=}CR^1R^2$ was reported to occur in the presence of $Ni(OCOMe)_2$/NaH/$[EtMe_2CO]Na$/bipy/thf or hexane. With the same catalyst system, reaction of $RC(Br){=}CH_2$ gave $RC({=}CH_2){-}C({=}CH_2)R$ when R = alkyl or aryl, and with thf as solvent. When R = alkyl, and the solvent was hexane, the main product was $RC{\equiv}C{-}C({=}CH_2)R$. With R = Ph, in hexane, $Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph$ was formed [1151]. Homocoupling of **667** was accomplished in the presence of $[NiCl_2(PPh_3)_2]$/Zn/$[Et_4N]I$, and the product was used in a synthesis of bis methano-[10]-annulene [1152]. The product of the related coupling of the iodoalkene, **668** was used in a synthesis of a bridged [14]-annulene [1153].

Reaction of 1,2-bis(bromomethyl)benzene with $[Ni(C_2H_4)(PPh_3)_2]$ gave **669**, ethene and $[NiBr_2(PPh_3)_2]$. Intramolecular versions of the reaction were also studied [1154]. Homocoupling of $PhCH{=}CHCH_2Cl$ was catalysed by $PdCl_2$/PPh_3/Bu_3SnCl/$[Et_4N]OTs$/dmf under electroreductive conditions. Alkenyltin compounds were proposed as intermediates [1155].



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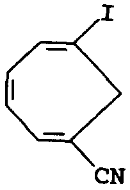

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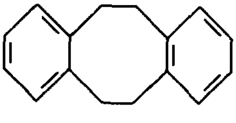
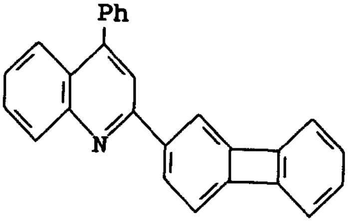


669

Thermolysis of **670** in the presence of [$Ni(CO)_2(PPh_3)_2$] gave **671** in 38 % yield, as well as oligomers. The process may be considered as a model for the curing of polymers such as **762** [1156,1157].



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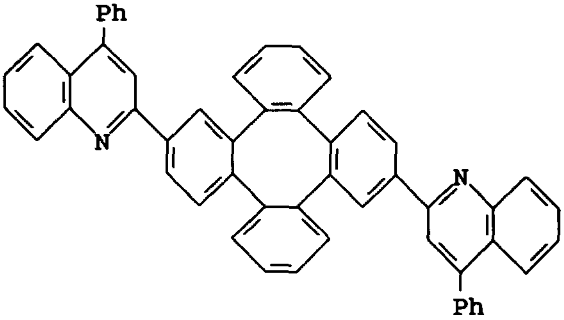

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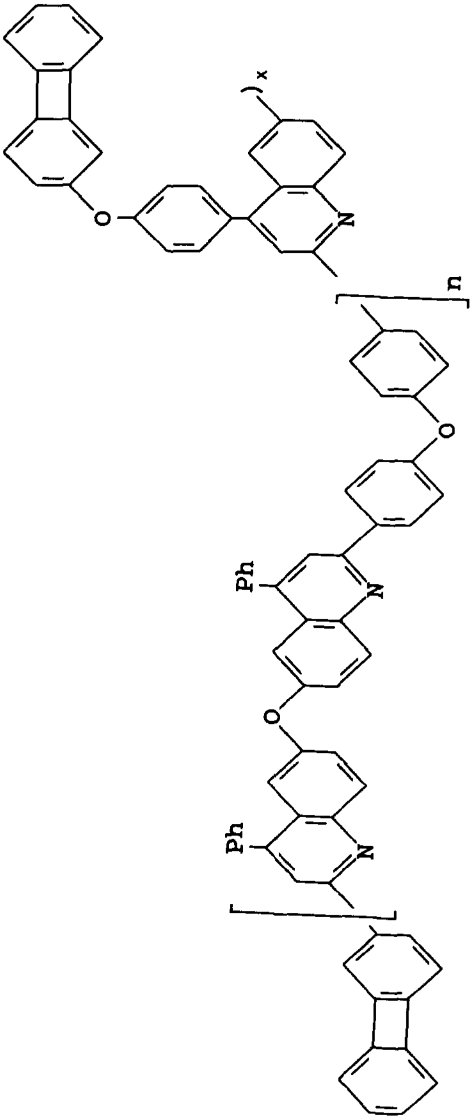
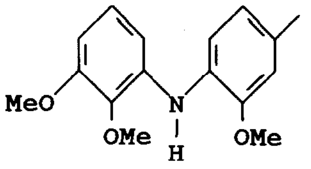


672

Oxidative intramolecular couplings of aryl groups have been reported. Thus **673** is converted to **674**, murrayastine, in the presence of palladium ethanoate [1158]. Homocoupling of **675** in the presence of [$PdCl_2(PPh_3)_2$] gave **676** as a mixture of diastereoisomers. The product was used in a total synthesis of (-)-ancistrocladine [1159].



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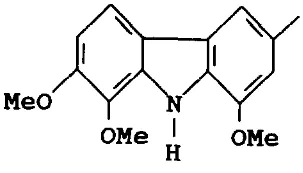

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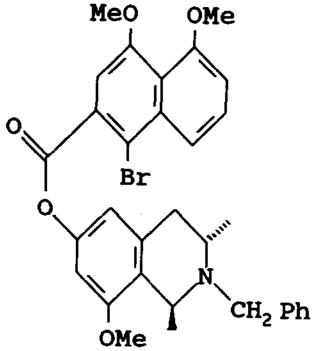

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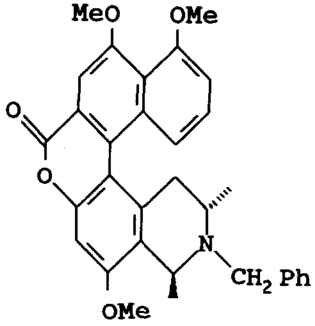
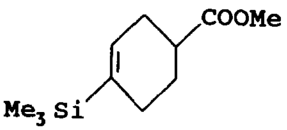


676

Reaction of $CH_2{=}C(SiMe_3)CH(OCOMe)CH_3$ with methyl propenoate in the presence of [$Pd(PPh_3)_4$] gave a mixture of **677** and **678**. The reaction involves 2-trimethylsilylbutadiene as an intermediate, which self condenses, *via* a palladium catalysed mechanism, to 3-trimethylsilyl-1,3,7-octatriene [1160]. Reaction of indole with 2-propene-1-ol in the presence of two molar equivalents of MeMgI and [$NiCl_2(PPh_3)_2$] gave 3-(2-propenyl)indole in 59 % yield. Reaction at nitrogen was not a significant problem [1161]. Palladation of the uracil derivative, **679**, gave **680** which reacted with **681** to give **682**. The reaction could be made catalytic in the presence of a reoxidant such as Ag^+ or copper(II) ethanoate [1162].



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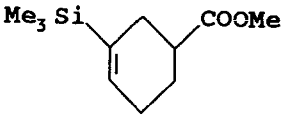

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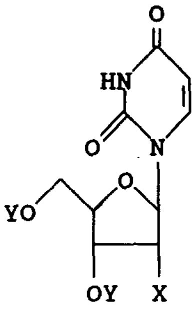

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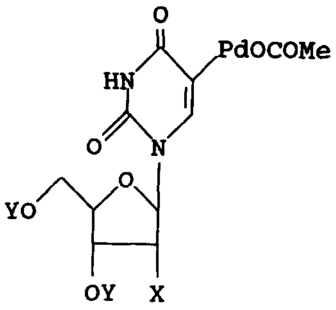

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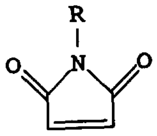

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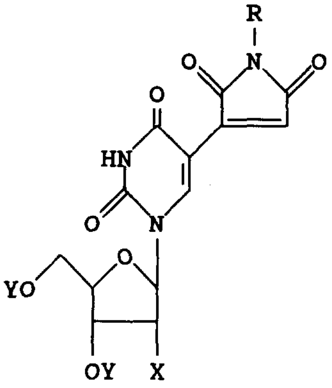
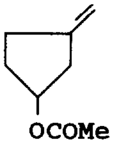


682

Reaction of 1,5-hexadiene with $Pd(OCOMe)_2/MnO_2$/benzoquinone gave a mixture of **683**, **684** and **685**, with **683** predominating. The reactions of substituted hexadienes were also discussed. Conversion of **686** to **687** was accomplished with >95 % selectivity [1163]. Coordination of palladium ethanoate to **688** occurred at the unhindered terminal double bond. The coordinated alkene was then attacked by the silyl enol ether to give **689** in a 6-*endo-trig* process. Dehydropalladation, with or without isomerisation, gave **690** and **691** [1164]. Reaction of **692** with $[Ni(cod)_2]/PPh_3$ gave **693** with good selectivity, though the related reaction to produce a 5/8 fused ring system was more complex [1165].

Reaction of $ArSnBu_3$ with **694** in the presence of $[PdCl_2(PhCN)_2]/CuCl_2$ gave **695** and **696**. In the reaction of **697**, the ratio between the products **698** and **699** depended on the nature of R. The reaction mechanism was discussed [1166]. In the oxygen series, **700** reacted to give **701**, **702** and **703**, with **700** as the main product for Ar = 4-methoxyphenyl. All three products were obtained in comparable amounts when Ar = Ph. The reaction mechanism was described, and syntheses of 5- and 7-membered rings also discussed [1167]. The first steps of the reaction between cyclohexanone pyrrolidine enamine and **704** were those of a conventional allylic substitution to give **705**. The intermediate **705** reacted with ethanoate to give **706** which cyclised to **707** and **708**, 2-ethanoato bicyclo[3.3.1]nonan-9-one derivatives [1168].



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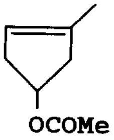

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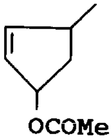

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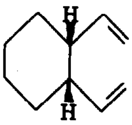

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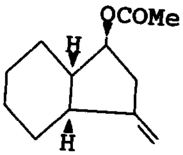

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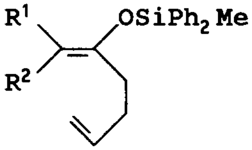

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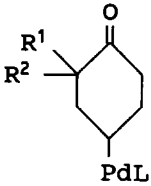

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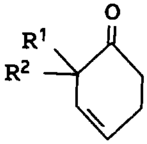

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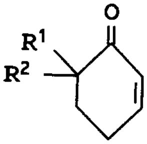

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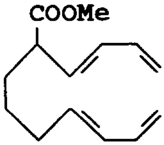

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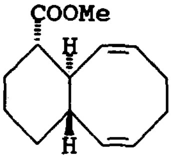

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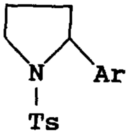

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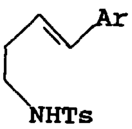

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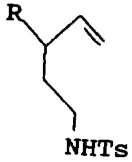

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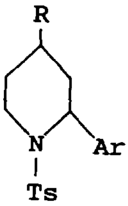

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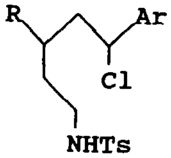

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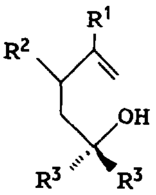

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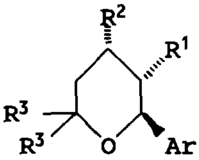
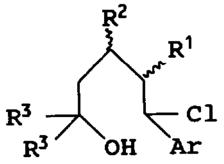


701

Syntheses of α-methylene lactones has been reviewed, including a discussion of palladium catalysed cyclisation of homoallylic carbonochloridates, such as the conversion of **709** to **710** in the presence of palladium(0) [1169]. The related conversion of **711** to **712** and **713** has been studied. The product ratio depended on the catalyst used and the substituents [1170].



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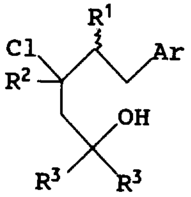

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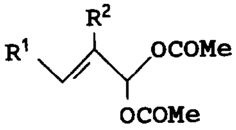

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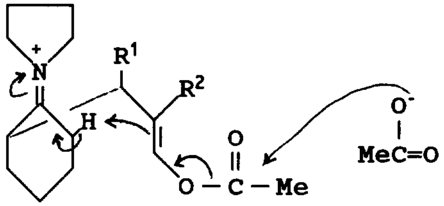

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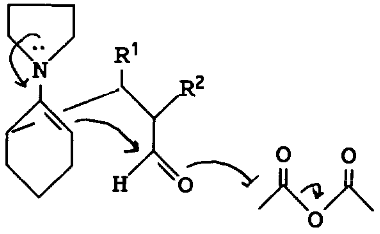

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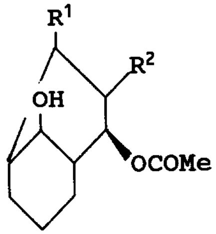

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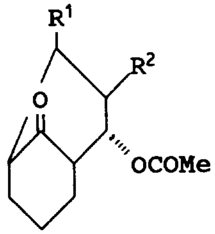

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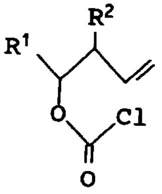

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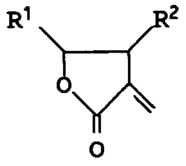

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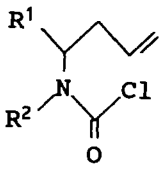

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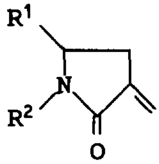

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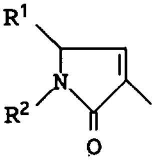
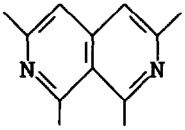


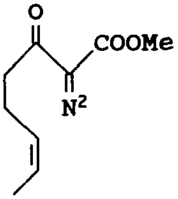
713

Reaction of ethanoyl chloride with ammonia in the presence of $AlCl_3$ gave a mixture of 2,4,6-trimethylpyridine, 2,6-dimethy-4-(CH_2COMe)pyridine and **714**. Various metal halides were investigated as additives; The $AlCl_3$/$PdCl_2$ combination gave the best yield of 2,4,6-trimethylpyridine [1171].



714

Carbene insertion is the key step in the conversion of **715** to **716** mediated by [$PdCl_2(PhCN)_2$] [1172]. The fate of the carbene generated on photolysis of **717** (R = H or OMe; *n* = 1 or 2) in the presence of [$Ni(acac)_2$] depends on *n* and the nature of R [1173].



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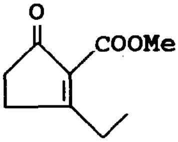

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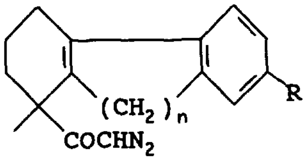
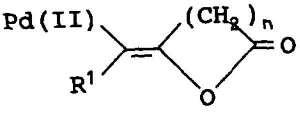


717

Reaction of $R^1C{\equiv}C(CH_2)_nCOOLi$ (R^1 = H or alkyl; n = 2 or 3) with palladium(II) gave **718** stereoselectively. This intermediate reacted regioselectively with γ-attack on $R^2CH{=}CR^3CHR^4Cl$ to give **719** [1174]. Aromatic annelation was accomplished by reaction of 4,*N*-dimethylaniline with dmad in the presence of $Pd(OCOMe)_2$/MeCOOH, yielding **720** and **721** as the major products, together with a small amount of **722**. An electron transfer mechanism was proposed [1175].



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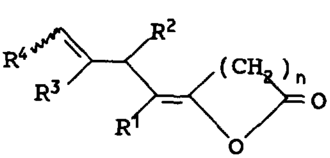

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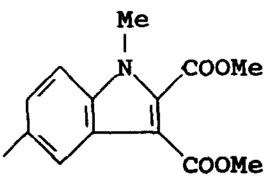

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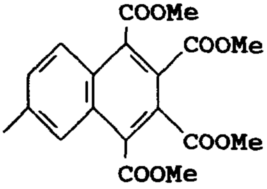

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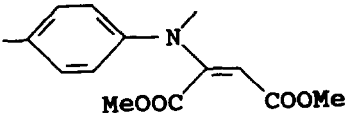
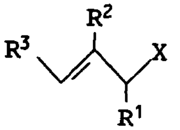


722

Reaction of **723** (X = OCOMe) with diphenylketene in the presence of $[Pd(PPh_3)_4]$ gave **724**. However, with the related carbonate, **723** (X = OCOOMe) and RPhC=C=O, the product was **725**. A complete reaction mechanism was proposed [1176]. When PhN=C=O is reacted with ethene in the presence of $[Ni(cod)_2]/R_3P$, **726** is initially formed. When R = Ph, this β-hydride eliminates to give **727**, which loses Ni(0) to give $CH_2{=}CHCONHPh$ in a reaction which is just barely catalytic. However, when R = Pr and an increased pressure of ethene is applied to **726**, a further insertion to **728** occurs. This then undergoes β-hydride elimination, before or after ring contraction, to give, after Ni(0) loss, a mixture of $CH_2{=}CHCH_2CH_2CONHPh$ and $MeCH{=}CHCH_2CONHPh$ [1177].



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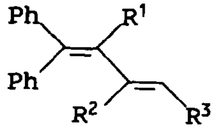

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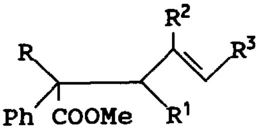

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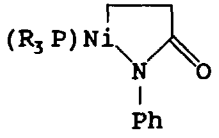

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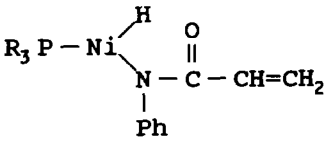

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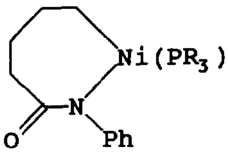
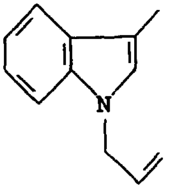


728

Reaction of **729** with $[Pd(MeCN)_4][BF_4]_2$ gave the intermediate **730**. This could be reduced to **731** with $Na[BH_4]$, with hydride attack from the face opposite to palladium, or be carbonylated to **732**. The formation of **730** was said to involve attack of the nitrile on a carbocation generated by palladium(II) addition to the terminal double bond, and the process was compared with the Ritter reaction [1178]. Cyclisation of ω-nitrile aldehydes to pyridines was catalysed by $[NiCl_2(MeCN)_2]$ [1179]. Reaction of $R^1_3SnSiMe_2R^2$ with R^3NC in the presence of $[Pd(PPh_3)_4]$ gave $R^1_3SnC(SiMe_2R^2){=}NR^3$; a reaction mechanism was proposed [1180]. Reaction of bromobenzene with Me_3CNC and $RSnBu_3$ (R = PhS, alkyl, alkoxy or alkylamino) in the presence of $[Pd(PPh_3)_4]$ gave $PhC({=}NCCMe_3)R$, but yields were generally modest [1181].

Carbopalladation of alkylidene cyclopropanes has been exemplified by the conversion of **733** to **734** and **735** with $Na[CH(COOMe)_2]/R'X$ catalysed by Pd(0)/dppe. The intermediates, {R'PdX} and an allyl palladium complex were invoked in the reaction mechanism [1182]. Reaction of **736** with $ZnCl_2$ gives $Zn(CH_2CH_2COOR)_2$, and this could be coupled with ArX in the presence of Pd(0) to yield $ArCH_2CH_2COOR$. Couplings with acyl halides were also studied [1183].



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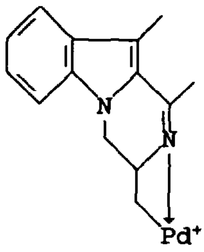

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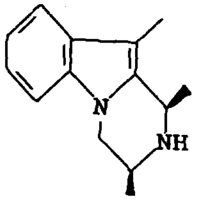

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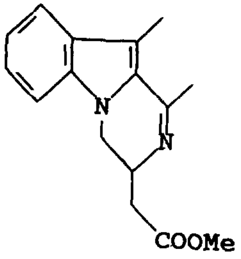

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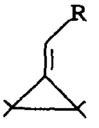

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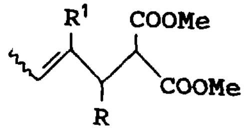

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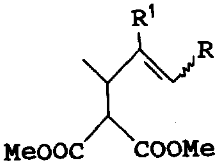

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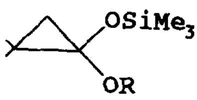
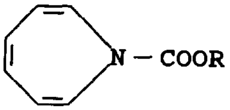


736

Reaction of $(RCH_2CH_2)_3N$ with R_fCF_2I in the presence of $[Pd(PPh_3)_4]$ gave $R_fCF_2C(R){=}CHN(CH_2CH_2R)_2$. A radical process was invoked in the mechanism proposed [1184]. The reaction of $PhCH{=}CHCH_2OH$ with $HC({=}O)(CH{=}CH)_nAr$ in the presence of $[Pd(acac)_2]/PPh_3$ to give $PhCH{=}CH\text{-}CH{=}CH(CH{=}CH)_nAr$ is formally a Wittig process, but probably involves a palladium allyl complex as intermediate [1185].

Reaction of benzene and palladium ethanoate with **737** gave initially **738**. Addition resulted in formation of **739** which lost palladium(0) and ethanoate to give **740**. Attack of water gave **741** in low yield [1186]. Cyclisation of **742** to both diastereoisomers of **743**, catalysed by $[Pd(PPh_3)_4]$, was used in a synthesis of the oxa and carba homocepham skeletons [1187].



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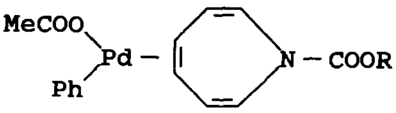

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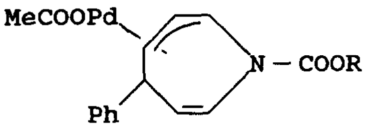

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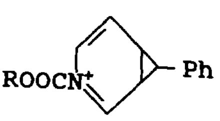

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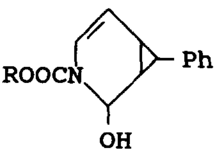

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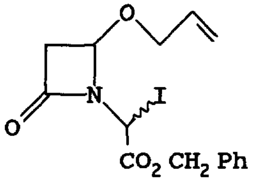

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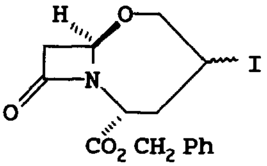
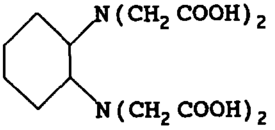


743

13.11 Other catalytic Reactions

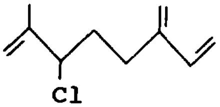
Transesterification of methyl propenoate was catalysed by $[Ni(acac)_2]$/BuLi/L. Depending on the reaction conditions, the products of alcohol addition across the double bond could also be isolated [1188]. Transesterification of RNHCOOR' (R' = CH_2Ph or $CH_2CH{=}CH_2$) with $HSiMe_2(CMe_3)/Pd(OCOMe)_2/Et_3N$ gave $RNHCOOSiMe_2CMe_3$ in excellent yield [1189]. Reaction of $MeOC({=}O)CH_2C({=}CH_2)COOH$ with ethenyl ethanoate in the presence of $Li_2[PdCl_4]$ gave $MeOC({=}O)CH_2C({=}CH_2)COOCH{=}CH_2$ [1190].

Reaction of $[PtHCl(PR_3)_2]$ (R = Me or Et) with $[HO]^-$ in $H_2O/MeCN$ gave a species which catalyses the hydration of propenenitrile to propenamide. The catalyst is very stable, and up to 6000 turnovers were achieved. The species $[PtH(OH_2)(PEt_3)_2]^+$, $[PtH(MeCN))(PEt_3)_2]^+$ and $[PtH(NHCOMe)(PEt_3)_2]$ were characterised spectroscopically [1191]. Reaction of ammonia with propanone and H_2O_2 to give $Me_2C{=}N{-}N{=}CMe_2$, was catalysed by $[Pd(NH_3)_4]Cl_2$ in the presence of **744** [1192].



744

Elimination of HX from RCH_2CH_2X (X = Br or I) by dbu was catalysed by Ni(0); the reaction tolerates ethers, including THP ethers, alcohols, and esters, but acids inhibit the reaction [1193]. Dehydrochlorination of **745** catalysed by $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]/PPh_3/[Bu_4N]Cl$ gave **746**, which has the C_{10} terpene skeleton. There was no isomerisation to give the fully conjugated isomer [1194]. Elimination of diethylamine from **747** to give **748** with up to 93 % selectivity was best catalysed by $[Pd(\eta^3\text{-}C_3H_5)(dppb)]^+$ or $[Pd(\eta^3\text{-}C_3H_5)\{1,5\text{-bis(diphenylphosphino)pentane}\}]^+$. Palladium allyl complexes were proposed as intermediates [1195].



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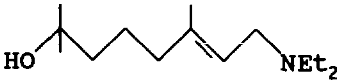

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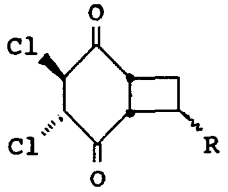
748

Dechlorination of **749** by metallic zinc was catalysed by $[NiBr_2(PPh_3)_2]/[Et_4N]I$ to give **750**. The same catalyst system was also active for hydrogenolysis of aryl halides [1196]. Desulphurisation of phenylethene sulphide using CO in the presence of $[Pd(PPh_3)_4]$ gave a poor yield of phenylethene; $[\{RhCl(CO)_2\}_2]$ was a much better catalyst [1197].



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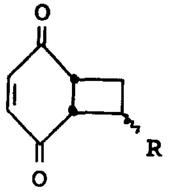
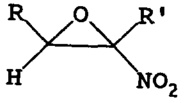


750

Conversion of $RR'C=CBr_2$ to RR'CHCOOH was accomplished using Na[OH] in the presence of $[Pd(dppe)_2]$ under phase transfer conditions. Since the dibromide is prepared from the aldehyde or ketone, RR'CO, this process represents a useful homologation. The reaction mechanism was discussed [1198]. The nitroepoxide, **751** reacted with $Pd(0)/H_2O$ to give RCOCOR' in moderate to good yield [1199].

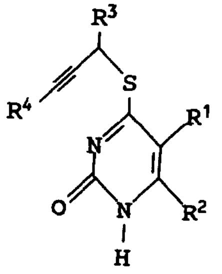


751

Chlorination of toluene, to give mainly side chain reactions by a radical process, was promoted by a range of platinum and palladium complexes [1200].

Reaction of aniline with ethanol to give $PhNEt_2$ was catalysed by $[PtCl_2(PhCN)_2]/SnCl_2$; Without $SnCl_2$, or with added PPh_3, there was low conversion to PhNHEt. The Pt:Sn ratio was critical to good selectivity [1201]. Dehydrocyclisation of 2-ethylaniline over a polymeric platinum phthalocyanine complex gave indole [1202].

Cyclisation of **752** to give **753** was catalysed by palladium(II), and the reaction was accelerated by the presence of methyl groups in the substrate. Several related reactions were also studied [1203].



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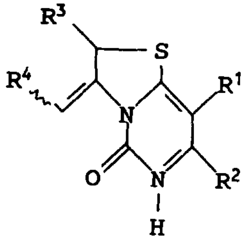
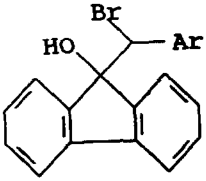


753

Reaction of **754** with $Me_2CHBr/[Ni(acac)_2]$ resulted in ring enlargement to **755** [1204].



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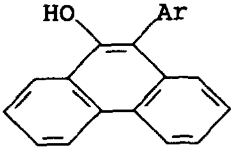

755

ABBREVIATIONS

Å	Ångstrom
acacH	pentane-2,4-dione
AIBN	azoisobutyronitrile ($NCCMe_2N{=}NCMe_2CN$)
Ar	aryl
bipy	2,2'-bipyridine
bipym	2,2'-bipyrimidine
Bu	butyl
CAD/CAM	computer aided design/computer aided machining
CASSCF	complete active space self-consistent field
cdt	cyclododecatriene
CI	chemical ionisation
CIDNP	chemically induced dynamic nuclear polarisation
CNDO	complete neglect of differential overlap
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
CSOV	constrained-space-orbital-variation
CV	cyclic voltammetry
Cy	cyclohexyl
Cyp	cyclopentyl
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	E,E-diphenylpenta-1,4-diene-3-one (dibenzylidene acetone)
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dibalH	diisobutyl aluminium hydride
DIOP	2,3-*O*-diisopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dma	dimethylethanamide
dmad	dimethyl but-2-yne dicarboxylate
dmf	dimethylmethanamide
$dmgH_2$	dimethylglyoxime
dmpm	bis(dimethylphosphino)methane
dmso	dimethylsulphoxide
dppa	$Ph_2PNHPPh_2$
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene

dppm	1,1-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
DVB	1,4-bis(ethenyl)benzene
E	electrophile
EEG	electroencephalogram
EHMO	extended Huckel molecular orbital
en	1,2-diaminoethane
epr	electron paramagnetic resonance
Et	ethyl
eV	electron volt
ewg	electron withdrawing group
EXAFS	extended X-ray absorption fine structure
EXSY	exchange spectroscopy
FAB	fast atom bombardment
Fc	ferrocenyl
Fp	$Fe(CO)_2(Cp)$
FT	Fourier transform
Guo	guanosine
hcp	hexagonal close packed
hfacacH	1,1,1,5,5,5-hexafluoropentane-2,4-dione
hmpa	hexamethylphosphoric triamde
HOMO	highest occupied molecular orbital
HPA	heteropolyacid
HPLC	high pressure liquid chromatography
INDO	intermediate neglect of differential overlap
IR	infra-red
kJ	kilojoule
L	2-electron donor ligand
LCGTO	linear combination of Gaussian type orbitals
LUMO	lowest unoccupied molecular orbital
MAO	monoamine oxidase
Me	methyl
mesal	*N*-methylsalicylaldimine
MINDO	modified intermediate neglect of differential overlap
MLCT	metal to ligand charge transfer
MO	molecular orbital
nbd	[2.2.1]bicyclohepta-2,5-diene
nmr	nuclear magnetic resonance

NOESY	nuclear Overhauser spectroscopy
Np	2-naphthyl
np_3	$N(CH_2CH_2PPh_2)_3$
PES	photoelectron spectroscopy
phen	1,10-phenanthroline
pop	$[P_2O_7]^{2-}$
$[PPN]^+$	$[Ph_3P{=}N{=}PPh_3]^+$
Pr	propyl
py	pyridine
pyen	1,2-bis(2-pyridinealdimino)ethane
pypz	2,3-bis(2-pyridyl)pyrazine
R	alkyl
R_f	perfluoroalkyl
RHF	restricted Hartree Fock
sacsacH	pentane-2,4-dithione
ΔSCF-CI	self consistent field configuration interaction
TBDMS	*tert*-butyldimethylsilyl
tcne	tetracyanoethene
TEBAC	benzyltrimethylammonium chloride
teeda	*N,N,N',N'*-tetramethyl ethane-1,2-diamine
TEM	transmission electron microscopy
tfaH	trifluoroethanoic acid
thf	tetrahydrofuran
THP	tetrahydropyranyl
TMEDA	*N,N,N',N'*-tetramethyl ethane-1,2-diamine
TMS	trimethylsilyl
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
Ts	4-toluene-sulphonyl
UV	ultra-violet
V	volt
X	one electron donor, usually halide
XPES	X-ray photoelectron spectroscopy

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