NICKEL, PALLADIUM AND PLATINUM, ANNUAL SURVEY COVERING THE YEAR 1980*

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[*] Nickel, Palladium and Platinum; Annual Survey covering the year 1979, see J. Organomet. Chem., 211 (1981) 397-499.

1. INTRODUCTION

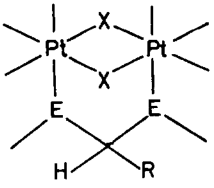
This survey details the accounts of the organometallic chemistry of nickel, palladium and platinum published in 1980. Material from the patent literature has generally been classified according to the year in which it appeared in Chemical Abstracts, and the organisation remains broadly the same as in past surveys. However, it is notable that the number of papers published in this area has increased considerably. Whilst this is true for all sections of the review, the field of the most explosive growth is clearly that of the uses of palladium catalysed and palladium promoted process applied in synthetic organic chemistry [1-4]. To avoid excessive length and uneccesary duplication, certain types of hydride complexes, which have been previously discussed in these surveys, have been omitted, since they are considered in detail in the annual surveys of the coordination chemistry of the metals in Coordination Chemistry Reviews.

A number of rather general reviews have dealt with aspects of the organometallic chemistry of nickel, palladium and platinum [5-10]. Reviews have also focussed on structural studies [11,12], stereochemical effects of bulky phosphine ligands [13], isomerisation mechanisms in square planar complexes [14], dielectric behaviour and molecular structure [15] and the rôle of electron and charge transfer processes [16]. Several reviews have dealt specifically with nickel complexes; monovalent, divalent and trivalent nickel [17], syntheses using electron rich complexes [18], carcinogenic nickel compounds [19,20] and element sensitive detection of volatile organonickel compounds have been discussed [21].

2. METAL CARBON σ-BONDED COMPLEXES

A review detailing metal carbon σ-complexes of the iron, cobalt and nickel triads has been published [22]. Alkyl, alkynyl and carbene complexes of platinum have been reviewed [23].

The reactions of the three isomers of $[Me_2Pt(gly)(H_2O)X]$ (X = Br or OH) with sodium glycinate have been studied. Both water and the oxygen of a glycinate ligand *trans* to a methyl group may be displaced by the nitrogen of glycinate, but groups *cis* to methyl are not displaced at room temperature [24]. Reaction of *fac*-$[(Me_3PtCl)_4]$ with $MeE(CH_2)_nEMe$ (E = S or Se; *n* = 2 or 3) yielded $[Me_3Pt\{MeE(CH_2)_nEMe\}Cl]$ [25]. Variable temperature nmr spectroscopic studies have established the rate of inversion at sulphur or selenium [26]. However, using MeECHREMe (R = H or Me) as the ligand, a bridged system, 1, was formed. In this complex many dynamic processes were identified by nmr spectroscopic studies, including pyramidal inversion at sulphur or selenium, sulphur or selenium switching between platinum atoms, and random cleavage of the halogen bridge bonds, which causes scrambling of the Pt-Me environments [27].



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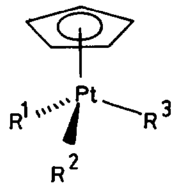

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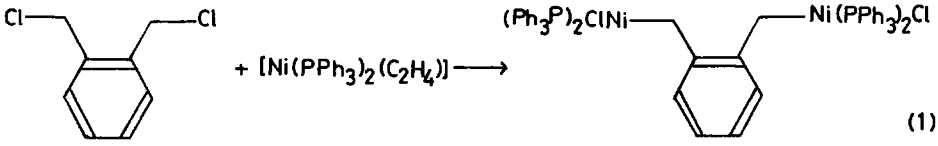
The ^{13}C and ^{1}H nmr spectroscopic parameters for **2** (R^1, R^2, R^3 = Me, Et or $COCH_3$) have been compared with those of known octahedral $\{Me_2Pt(IV)\}$ and $\{Me_3Pt(IV)\}$ complexes. The use of a chiral shift reagent when recording the ^{1}H nmr spectrum of **2** (R^1 = $COCH_3$, R^2 = Me, R^3 = Et) allowed the observation of signals due to the two enantiomers, implying that the complex is stereochemically stable [28]. Mechanical spectroscopy has been used to measure the barrier to ring rotation in **2** (R^1, R^2, R^3 = Me; R^1, R^2 = Me, R^3 = $COCH_3$; R^1 = Me, R^2, R^3 = Et) [29]. Photolysis of **2** (R^1, R^2, R^3 = Me) yielded methane as the major product, together with traces of ethane and ethene. Deuterium labelling studies suggested that the initially formed CH_3 radical abstracted hydrogen from other CH_3 groups, from solvent and, to a minor extent, from the cyclopentadienyl ring [30].

The relative reactivities of MeI and MeOTs with transition metal nucleophiles including $[M(PR_3)_4]$ (M = Ni, Pd or Pt) and $[Me_4Pt]^{2-}$ have been studied. Kinetic data imply an S_N2 mechanism for the process [31]. Benzylic halides undergo facile oxidative addition to metal(0) complexes, for example reactions (1) [32] and (2) [33]. **3** reacted with a range of nucleophiles to give mononuclear species. Treatment of $[Et_2Ni(bipy)]$ with $ArCH_2Cl$ yielded $[ArCH_2Ni(bipy)Cl]$. In this way the derivatives of nitro substituted aryl compounds may be prepared, these having been previously inaccessible by organolithium or Grignard routes [34].



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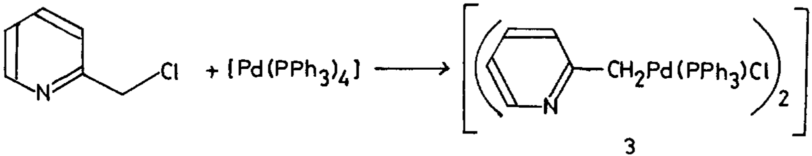

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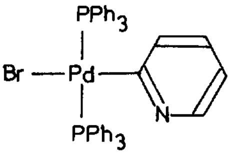
(2)

Palladium atoms reacted with R_fX to give $[R_fPdX]$ where $R_f = C_6F_5$ or CF_3. $[C_6F_5PdBr]$ and $[CF_3PdI]$ were isolated and characterised. Propanone stabilised $[C_6F_5PdBr]$ as a monomer, whilst in ether a trimer was formed. Both complexes reacted with ligands such as PEt_3 to give $[R_fPdL_2X]$, which are not available by classical syntheses [35]. Nickel, however, reacted with C_6F_5I yielding $[Ar_2Ni]$ and NiI_2, formed by disproportionation of [ArNiI]. The latter could be trapped as *trans*-$[ArNi(PR_3)_2Br]$ below -80 °C [36]. $[NiL_2]$, generated electrochemically, reacted readily with aryl halides, ArX, to give $[ArNiL_2X]$. Since this is also electroreducible, ArX could be converted to Ar-Ar by electrochemical reduction in the presence of $[NiL_2X_2]$ [37]. In a similar study nickel(0), generated by electrolysis, reacted with ArX to yield [ArNiX] and nickel(I), their proportions depending on ArX [38]. If the ligand present was dppe, oxidative addition of ArX was inhibited [39]. Kinetic studies have also been reported [40].

Oxidative addition of 2-bromopyridine to $[Pd(PPh_3)_4]$ yielded **4**, the first example of a σ-pyridyl palladium complex. 3- and 4-bromopyridines reacted similarly, and **4** catalysed the coupling of 2-chloropyridine with MeMgBr [41]. By contrast, the reaction of 2-chloropyridine with $[Ni(PPh_3)_4]$ gave the binuclear species **5** (R = 2-pyridyl, X = Cl) [42].



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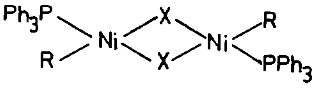

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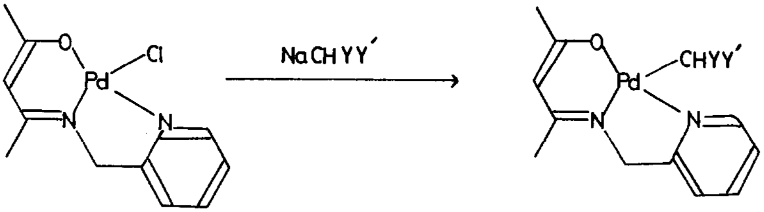
σ-Alkyl metal complexes of nickel, palladium and platinum may be prepared by reaction of alkyl derivatives of more electropositive metals with the appropriate halides. For example, **6** was converted to **7** by stabilised sodium salts (Y = Y' = COOMe, Y = CN, Y' = COOMe, COOEt or CN) [43]. $[R_2ML_2]$ (M = Ni, Pd or Pt; L_2 = bipy, cod, $(PMe_3)_2$, $(PPh_3)_2$ or dppm; R = 1-adamantyl) could be prepared from 1-adamantyl lithium or its Grignard analogue and $[ML_2X_2]$. The proportions of *cis*- and *trans*-isomers depended on the size and nature of L [44]. $[(C_6F_5)_2Pt(diars)]$ was synthesised from C_6F_5Li and $[Pt(diars)Cl_2]$; it reacted with halogens by oxidative addition to yield the platinum(IV) species $[(C_6F_5)_2Pt(diars)X_2]$. Treatment of $[(C_6F_5)_2Pt(tht)_2]$ with $PtCl_2$ gave binuclear *trans*-$[(C_6F_5)_2Pt_2(\mu\text{-}Cl)_2(tht)_2]$ which reacted with diars to yield $[(C_6F_5)Pt(diars)Cl]$. This latter was also oxidised by halogens, but rather slowly [45].



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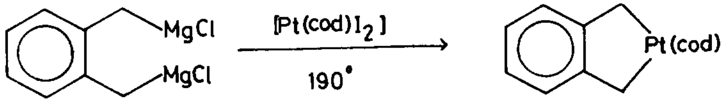
Reaction of the bis Grignard reagent, **8**, with $[Pt(cod)I_2]$ yielded **9**, identified by nmr spectroscopy [46]. An analogous compound was prepared by reaction (3), the conversion of **10** to **11** involving a δ-hydrogen abstraction [47]. Aryl magnesium halides reacted with *cis*-$[Pt(PPh_3)_2Cl_2]$ to give *cis*-$[Ar_2Pt(PPh_3)_2]$. The temperatures necessary for reductive elimination from such species have been determined, and the biaryls formed are linked exclusively at the carbon atoms which were bonded to platinum [48].



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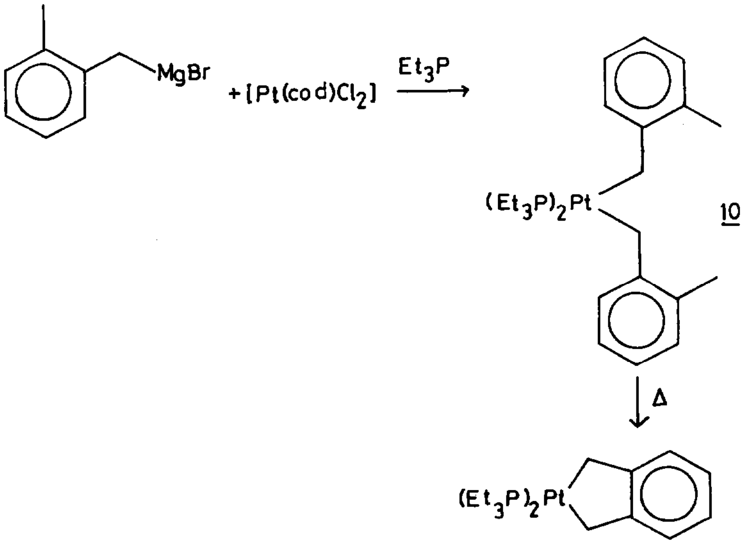

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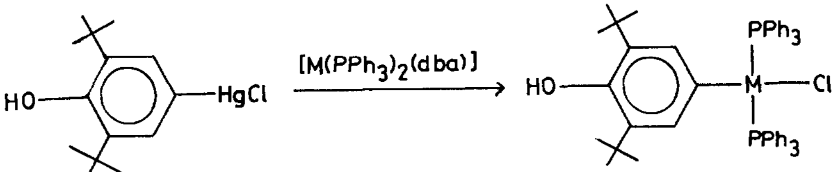
(3)

Two series of alkyl nickel compounds have been synthesised by reactions of Grignards with nickel(II) halides. The first series, formed in reaction (4) (R = CH_3, CH_2Ph or Ph; etp = $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$; Y = BPh_4 or PF_6), inserted SO_2 to yield $[RSO_2Ni(etp)]^+$ salts, one of which was characterised by X-ray crystallography [49].

$$[Ni(etp)X]Y + RMgX \longrightarrow [RNi(etp)]Y \qquad (4)$$

Whilst reaction of dihalides with Grignard reagents generally yields dialkyl complexes, monoalkyl derivatives, *trans*-$[RNiL_2Cl]$ (L = PMe_3 or PMe_2Ph) may be obtained with hindered R groups such as $PhMe_2CCH_2$- or Me_3SiCH_2-. These then reacted with CpTl to yield mixed complexes such as $[PhMe_2CCH_2Ni(Cp)(PMe_3)]$. Alternatively, carbonylation followed by reaction with CpTl yielded $[PhMe_2CCH_2CONi(Cp)(PMe_3)]$ [50].

Organomercury compounds have again proved useful in the synthesis of σ-aryl palladium and platinum complexes. Reactions of **12** with $[M(dba)(PPh_3)_2]$ (M = Pd or Pt) yielded 13. On oxidation of 13 with lead(IV) a rather stable phenoxy radical was formed. Its epr spectrum showed that there is an interaction between the unpaired electron and the metal centre [51]. Treatment of **14** with *trans*-$[Pd(PPh_3)_2Cl_2]$ yielded **15**, which was also formed from $[Pd(PPh_3)_4]$. The *cis*-dichloride was unreactive [52].



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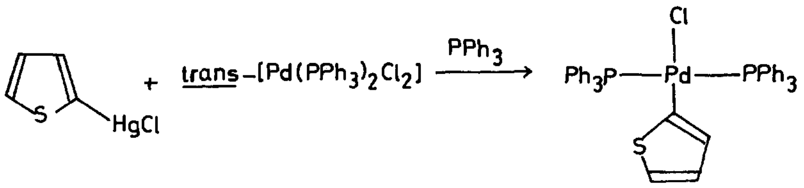

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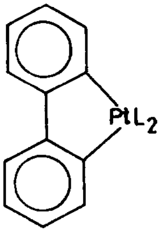
The dibenzostannole compound, $C_{12}H_8SnPr_2$, reacted with $[Pt(cod)Cl_2]$ to give **16** (L_2 = cod). Treatment with PPh_3 or $(CH_3)_3CNC$ yielded **16**, L_2 = $(PPh_3)_2$ and L_2 = $\{(CH_3)_3CNC\}_2$ respectively [53]. The apparent substitution reaction (5) is more strictly an oxidative addition to $[Pt(PPh_3)_2]$, formed by ethene dissociation. **17** decomposed readily to **18**, which was also formed by oxidative addition of Ph_4Pb [54].



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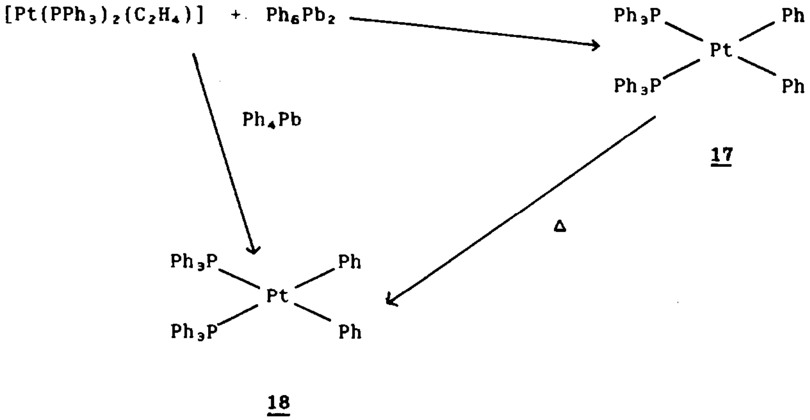


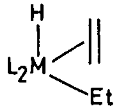
(5)

A wide-ranging paper has summarised the reactions of C_6F_5Li and C_6F_5MgBr with $K_2[MCl_4]$, $[M(tht)_2Cl_2]$ and $[Bu_4N][M_2(\mu\text{-}Br)_2Br_4]$ (M = Pd or Pt) to give anionic complexes such as $[Ar_3M(tht)]^-$, $[Ar_4M]^{2-}$ and $[Ar_4M_2(\mu\text{-}Br)_2]^{2-}$ [55].

Further studies of the uncatalysed *cis* to *trans* isomerisation of $[PhPt(PEt_3)_2X]$ (X = Cl, Br or I) have been reported. The rate does not depend on added halide ion and a suggested mechanism involves a rapid pre-equilibrium with *cis*-$[PhPt(PEt_3)_2(solvent)]$ followed by rate determining isomerisation [56]. Evidence for this pathway included the dependence of the rate of reaction on R in *cis*-$[RPt(PEt_3)_2X]$ [57], and high pressure kinetic data showing $\Delta V^{\ddagger}$ = -12 cm^3 mol^{-1} for the initial step of the process. This is only consistent with a solvolytic associative pathway [58]. Data on the pressure and temperature dependence of the rate of substitution by thiourea in *cis*- and/or *trans*-$[(2,4,6\text{-}Me_3C_6H_2)Pt(PEt_3)_2Br]$ also conformed to the idea of a common associative mechanism [59]. An alternative view was presented by Italian workers for *cis*-$[(3\text{-}MeC_6H_4)Pt(PEt_3)_2Cl]$. They proposed a dissociative pathway for isomerisation, the evidence cited being solvent effects and the fact that solvolysis proceeds considerably more rapidly than isomerisation [60,61]. The isomerisation of $[Pt(CH_2CN)(PPh_3)_2Cl]$ was shown to proceed by an entirely different route [62].

Interest continues in studies of reductive elimination from dialkyl metal complexes. Thermolysis of *cis*-$[Me_2PdL_2]$ L = PPh_3 or PPh_2Me or L_2 = dppe) occurred in the presence of coordinating solvents such as dmso, dmf and thf, yielding ethane. The reaction was intramolecular with no crossover with $[(CD_3)_2PdL_2]$ and $\{PdL_2\}$ could be trapped with Ph-C≡C-Ph. *Trans*-$[Me_2PdL_2]$ (L = PPh_3 or PPh_2Me) isomerised to the *cis*-compound prior to elimination. However, when L_2 was 2,11-bis(diphenylphosphinomethyl)benzo[c]-phenanthrene (TRANSPHOS), isomerisation was impossible and elimination did not occur. Instead, in the presence of CD_3I, CD_3CH_3 was formed *via* a palladium(IV) intermediate [63]. Reaction of $[Me_2NiL_2]$ (L_2 = bipy or $(PEt_3)_2$) with $Ph_2P(CH_2)_nPPh_2$ yielded isolable species $[Me_2Ni(Ph_2P(CH_2)_nPPh_2)]$ for n = 2 or 3. On thermolysis reductive elimination occurred, the reaction being faster for n = 2 than for n = 3. For the biphosphines in which n = 1 or 4 the intermediate was not isolable and the observed products were $[Ni\{Ph_2P(CH_2)_nPPh_2\}_2]$ and ethane [64]. Thermolysis of $[Me_2Ni\{R'N{=}C(R){-}C(R){=}NR'\}]$ yielded alkenes and alkanes together with $[Ni\{R'N{=}C(R){-}C(R){=}NR'\}]$ which disproportionated readily to $[NiL_2]$ and nickel metal [65].

Thermolysis of *trans*-$[R_2Pd(PR'_3)_2]$ yielded alkanes and alkenes in a first order reaction, predominently without dissociation. For R = CH_2CD_3 the major products were $CH_2{=}CD_2$ and CH_2DCD_3, with a kinetic isotope effect k_H/k_D of 1.4 ± 0.1. The reaction kinetics were studied using various R groups and various phosphines. The major pathway involves β-hydride elimination to give **19**, followed by reductive elimination. This may be contrasted with the route followed by the dimethyl compound which loses phosphine prior to simple reductive elimination [66].



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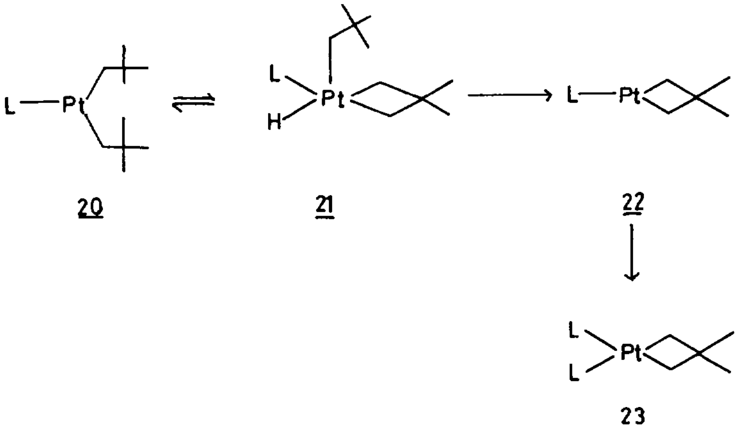
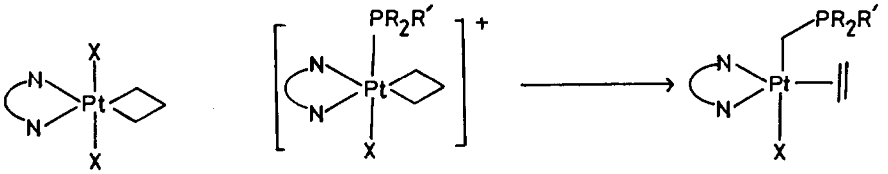
The kinetics of thermal decomposition of $[\{(CH_3)_3CCH_2\}_2Pt(PEt_3)_2]$, in which β-hydride elimination is blocked, have been investigated. The initial step involves loss of phosphine to give **20**, which is in equilibrium with the cyclometallated species, **21**. Reductive elimination from **21** gives $(CH_3)_4C$ and **22**. Transfer of hydrogen from the ligand to the alkyl group has been demonstrated, but occurs at only about 3% of the rate of transfer from the other alkyl group. The driving force for the formation of **23** is thought to be relief of steric strain [67].



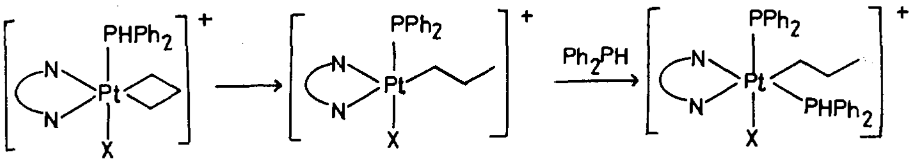
20 21 22 23

Thermal decomposition of *trans*-[ArNiMeL_2] was studied in the presence and absence of Ar'X. Two pathways were discerned. In the absence of additives ArMe was lost in a first order reaction after dissociation of L. The reaction is relatively slow but there is no scrambling of aryl groups. With Ar'X a much faster radical chain process occurred with scrambling of Ar and Ar' moieties. The chain carriers are paramagnetic nickel complexes rather than organic radicals [68].

Platinacyclobutane chemistry has been reviewed [69]. Photolysis of **24** (X = Cl or Br; N N = phen, bipy or Me_4en) in dichloromethane yielded more than 85% propene from direct hydrogen transfer between neighbouring atoms. However, in dmso or CH_3CN, cyclopropane was the major product formed *via* ionisation of X^- and formation of platinum substituted ion radicals [70]. If photolysis or thermolysis was carried out in the presence of PPh_3 or dppm, ethene was the major product. The pathway proposed involoves ionisation of **24** followed by phosphine capture to give 25. 25 yields the ylid, **26**, which readily loses ethene. When the added ligand is $PHPh_2$, **25** gives **27** by hydride transfer. Addition of further $PHPh_2$ gives a compound which may readily eliminate propane, which is the major observed product in this instance [71].

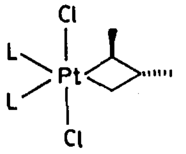


24 25 26



25a 27 28

The reaction of $[Pt_2(C_2H_4)_2(\mu\text{-}Cl)_2Cl_2]$ with *trans*-1,2-dimethylcyclopropane yielded polymeric $[(PtCl_2CHMeCHMeCH_2)_n]$. Treatment of the polymer with L = py or L_2 = phen yielded **29**. With a bulky ligand such as 2-methylpyridine or a weak donor such as MeCN or PhCN, species such as **30** were isolated, formed by ring opening of **29**. *Trans*-1,2-diarylcyclopropanes reacted slowly to give mixtures of **31** and **32**. Three possible mechanisms were considered for isomerisation, involving edge or corner metallated cyclopropane intermediates [72].



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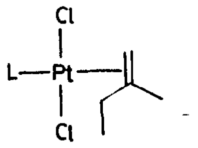

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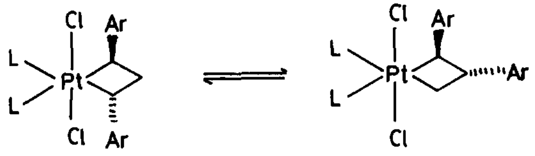
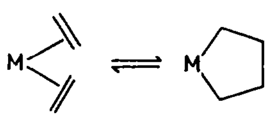
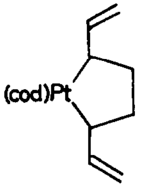


31 32

Theoretical studies of the interconversion of 33 and 34 suggested that if the alkene was unsymmetrically substituted the reaction should be regioselective, placing substituents so that the alkene π^* orbital enters the reaction with the largest lobe β to the metal in the product metallocycle. Heteroatoms more electronegative than carbon, as well as donor groups prefer the α-site, whereas acceptors prefer to be β. The reaction of $[Pt(cod)_2]$ with butadiene yielded **35** in accord with the model, but the model apparently fails with the $[Ni(PR_3)_2(propene)_2]$ system. In this case equilibration was very rapid and the products of protonation of the metallocycle reflected thermodynamic rather than kinetic factors. From an electronic point of view the reaction of methylene cyclopropane with $[Ni(cod)_2]$ should give **36**, but steric factors favour **37**, which yielded on thermolysis **38** and **39** in the ratio 1:3 [73].



33 34



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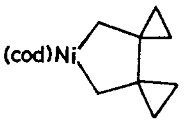

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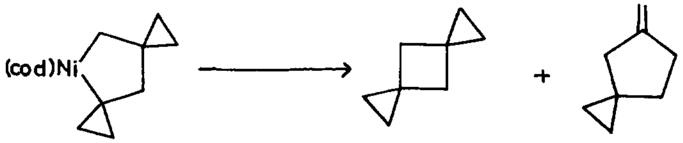
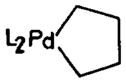


37 38 39

Reaction of $[PdL_2Cl_2]$ (L = Me_4en or dppe) with 1,4-dilithiobutane yielded **40a** (L_2 = Me_4en) and **40b** (L_2 = Me_4en) and **40b** (L_2 = dppe) respectively. **40b** does not carbonylate easily, but compounds with L_2 = Me_4en, bipy, phen or $(PPh_3)_2$ yielded cyclopentanone. Hydride abstraction yielded **41** [74]. Photolysis of **42** (L = PMe_2Ph or PPh_3) resulted in the formation of 1-butene and ethene as the major products. The 1-butene was formed by β-hydride elimination to give **43** (after loss of phosphine) followed by reductive elimination. In the presence of Ph_2PH butane was the major product, formed by a mechanism analogous to that proposed for **25** [75].



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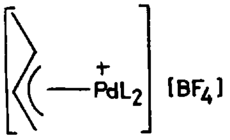

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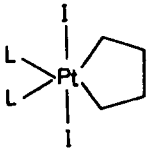

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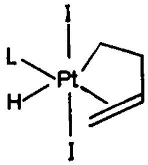

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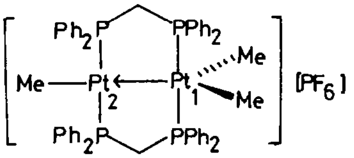
The structure of $[Me_3Pt_2(\mu\text{-dppm})_2][PF_6]$, **44**, has been determined by X-ray crystallography. The Pt-Pt distance of 2.769(1) Å is within bonding range, and it is proposed that the filled d_{z^2} orbital of the Pt(1) atom interacts with a vacant orbital in the square plane of Pt(2) [76]. Both **44** and $[Me_2Pt_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ reacted with $Na[BH_4]$ to give $[Me_2Pt_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$, **45**, the structure of which was determined to be an "A-frame" by X-ray diffraction techniques. Reductive elimination of methane was induced by $PhMe_2P$, but the reaction was slow [77].



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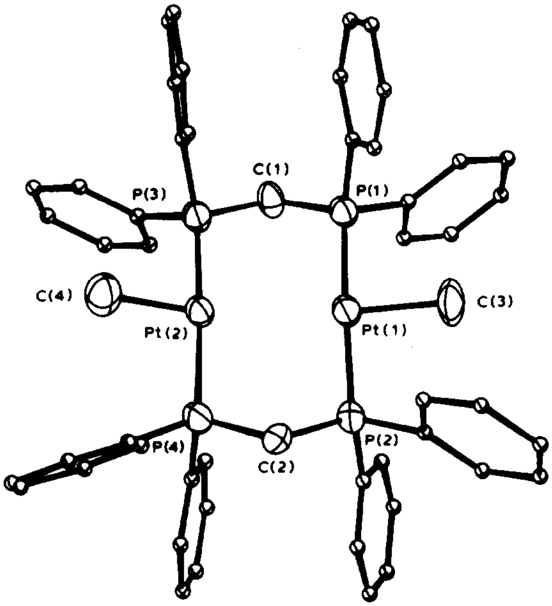


45 (Reproduced with permission from [77])

The reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with alkylcobalamins has been followed by nmr spectroscopy. In the initial adduct, N(3) of the 5,6-dimethylbenzimidazole and N(7) of the 5'-deoxyadenosine are coordinated to platinum(II). Slower demethylation then occurred to yield a {MePt(IV)} species [78].

The ^1H, ^{13}C and ^{195}Pt nmr spectra of $[\{Me_3Pt(\mu_3\text{-}Z)\}_4]$ were reported for Z = Cl, Br, I, OH, N_3, SMe, SPh and SCF_3. The complexes with Z = SPh and SCF_3 were not previously known [79].

Treatment of $[RPt(propanone)L_2]^-$ with KOH yielded *trans*-$[RPt(OH)L_2]$, (R = CH_3, L = $PMe(CMe_3)_2$ or $P(CHMe_2)_3$; R = Ph, L = PCy_3, $PMe(CMe_3)_2$, PMe_2CMe_3, PEt_3, $PMePh_2$ or PMe_2Ph). These hydroxo complexes are strong bases and reacted with CH_3NO_2 and $(CH_3)_2CO$ to give respectively $\{PtCH_2NO_2\}$ and $\{Pt(CH_2COCH_3)\}$ containing species [80]. Reaction of *trans*-$[RPtL_2X]$ (X = Cl, OH or $NHCOCH_3$) with $Na[BH_4]$ or *trans*-$[RPt(CH_3OH)L_2]^+$ with $Na[OCH_3]$ yielded *trans*-$[HPtRL_2]$ (R = Me, L = PPh_3 or $P(CHMe_2)_3$; R = Ph, L = PMe_3, PEt_3, PPh_3, $P(CHMe_2)_3$, $PMe_2(CMe_3)$ or $PMe(CMe_3)_2$) [81].

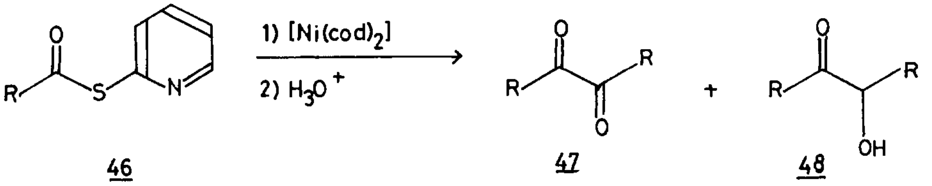
Nmr spectroscopic studies of $[RPt(PPh_3)_3][BF_4]$ (R = Me, Et, CH_2CF_3, CH_2Ph, CH_2CN, CH_2CH_2CN, $(CH_2)_3CN$, CH_2NO_2, CH_2COCH_3 or $CH_2C_6H_4\text{-}2\text{-}CN$) have been reported. An X-ray diffraction study of the complex for which R = CH_2CN revealed the longest Pt-P bond (2.395(5) Å) and the shortest reported sp^3C-Pt bond (2.023(16) Å) [82].

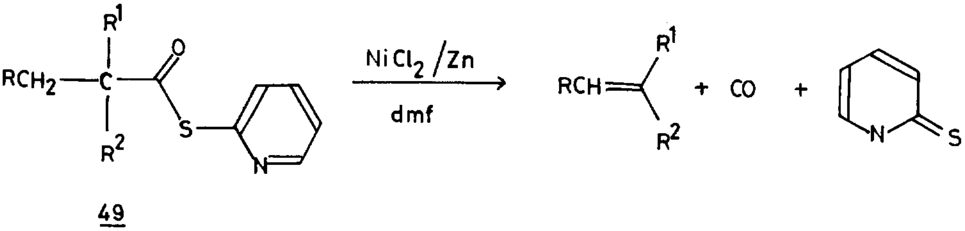
Degradation of $[CpNiR(PPh_3)]$ (R = Me, Et, Ph or $4\text{-}MeC_6H_4$) occurred on photolysis. From the complex with R = Me, CH_4 was the main product; a methyl radical is formed and methane is formed by hydrogen abstraction. For R = Et, β-hydride elimination occurred, followed by reductive elimination yielding ethane and ethene.

The reaction of CH_3I with $[Pt(PPh_3)_3]$ in benzene yielded a 1:1 adduct $[MePt(PPh_3)_2I]$. In thf the only isolable product was $[Pt(PPh_3)_2I_2]$. The reaction proceeds *via* a radical chain mechanism, with the initially formed species from RX being R· and $[Pt(I)L_nX]$. Such platinum(I) intermediates could be trapped by reaction with an appropriate nitroxide [84]. $[Et_2Ni(bipy)]$ also reacted with RNO to yield initially $[Et_2Ni(bipy)(RNO)]$ in which the nitroxide is η^1-bonded to nickel through the nitrogen atom. This unstable paramagnetic species eliminated REtNO [85].

Carbonylation of *trans*-$[PhPt(PR_3)_2X]$ yielded a metastable five coordinate carbonyl complex in non-polar solvents, which, if R_3P was a nucleophilic phosphine, collapsed to the {PhCOPt} species. In more polar solvents the major product was *trans*-$[PhPt(CO)(PR_3)_2]X$ [86]. Carbonylation of $[PhNi(PR_3)_2(CN)]$ (PR_3 = PEt_3, PCy_3 or $\frac{1}{2}(Et_2P(CH_2)_4PEt_2)$) yielded the detectable species $[PhCONi(PR_3)_2(CN)]$. PhCOCN was the major product on decomposition in all cases, together with varying ratios of $[Ni(CO)_2(PR_3)_2]$ and $[Ni(CO)_3(PR_3)]$, according to the pressure of carbon monoxide [87].

A variety of thioesters and esters have been shown to undergo oxidative addition to nickel(0) complexes. For aliphatic species, **46**, the major products were diketones, **47**, and α-hydroxyketones, **48**, suggesting that coupling of the acylnickel complexes was faster than loss of carbon monoxide [88]. When R = aryl, however, the major product was ArCOAr, suggesting that decarbonylation was competitive with coupling [89]. With an alkyl group able to undergo β-hydride elimination as in **49**, alkenes were the major products. Structural factors in these cases may dictate a more rapid loss of CO to give the alkylnickel complex or decarbonylation may be linked to β-hydrogen loss in a concerted process [90]. Phenolic esters may react similarly and the variation of reaction rate with substituents on the phenol suggested that the oxidative addition proceeds *via* a nucleophilic attack of {L_nNi} on the ester [91].





Trans-[PhNi(PPh$_3$)$_2$Br] was cathodically reduced in two steps in acetonitrile solution containing PPh$_3$. Both processes caused activation of the σ-bonded organic group and formation of biphenyl by different pathways (reactions (6) - (9)) [92].

$$[\mathrm{PhNi(PPh_3)_2Br}] + e^- \xrightarrow{\mathrm{PPh_3}} [\mathrm{PhNi(I)(PPh_3)_3}] + \mathrm{Br}^- \qquad (6)$$

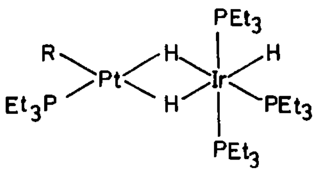
$$[\mathrm{PhNi(I)(PPh_3)_3}] + \mathrm{PPh_3} \xrightarrow{\mathrm{fast}} \tfrac{1}{2}\,\mathrm{Ph\text{-}Ph} + [\mathrm{Ni(PPh_3)_4}] \qquad (7)$$

$$[\mathrm{PhNi(I)(PPh_3)_3}] + e^- \longrightarrow [\mathrm{PhNi(0)(PPh_3)_3}]^- \qquad (8)$$

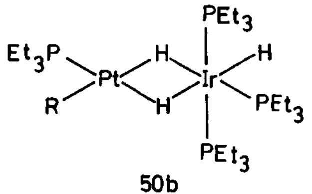
$$[\mathrm{PhNi(0)(PPh_3)_3}]^- + [\mathrm{PhNi(PPh_3)_2Br}] \longrightarrow \mathrm{Ph\text{-}Ph} + [\mathrm{Ni(PPh_3)_4}] \qquad (9)$$

[ArN$_2$][PF$_6$] reacted with [Pd(PPh$_3$)$_4$] to give [(ArN$_2$)Pd(PPh$_3$)$_3$][PF$_6$]. This decomposed at room temperature, in a reaction which could be accelerated photochemically, to [ArPd(PPh$_3$)$_3$] [93].

Trans-$[RPt(CH_3OH)(PEt_3)_2]^-$ reacted with $[H_5Ir(PEt_3)_2]$ to yield mixtures of **50a** and **50b** (R = Ph or H) [94]. Conversion of nitrile complexes, $[RPt(NCR')L_2][BF_4]$ to amide containing species, $[RPt(NHCOR')L_2]$ occurred on treatment with KOH (L = PEt_3, R = Me, R' = Me or $CH{=}CH_2$, L = PEt_3, R = Ph, R' = Me or L = PMe_2Ph, R = Ph, R' = Me or Ph) [95].



50a



50b

Reaction of $H_2[PtCl_6]$ with ArH in the presence of tfaH followed by treatment with SiO_2/NH_3 yielded σ-aryl platinum(IV) complexes, $[NH_4][ArPt(NH_3)Cl_4]$. Mixtures of 3- and 4-substituted isomers were obtained from substituted arenes. Such species are intermediates in chlorination and dimerisation of arenes by $H_2[PtCl_6]$ [96].

The equilibria of reactions (10) and (11) have been investigated; entropy factors appear to be dominant [97].

$$[(2\text{-}MeC_6H_4)Ni(PPh_3)_2Br] + \text{amine} \rightleftharpoons [(2\text{-}MeC_6H_4)Ni(PPh_3)(\text{amine})Br] + PPh_3 \quad (10)$$

$$[(2\text{-}MeC_6H_4)Ni(PPh_3)(\text{amine})Br] + \text{amine} \rightleftharpoons [(2\text{-}MeC_6H_4)Ni(\text{amine})_2Br] + PPh_3 \quad (11)$$

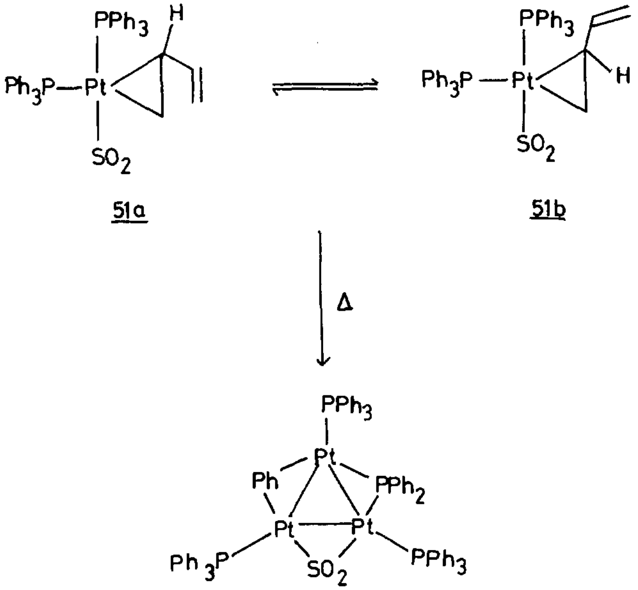
An X-ray diffraction study has established the structure of $[(\pi\text{-}CH_3C_6H_5)Ni(C_6F_5)_2]$. The toluene moiety has a small boat distortion [98]. A similar boat distortion occurs in the $1,3,5\text{-}Me_3C_6H_3$ analogue; calculations suggested that this reflects electronic properties [99].

$[(C_6Cl_5)Pd(PPh_3)_2Cl]$ reacted with $Ag[ClO_4]$ to give the complex $[(C_6Cl_5)Pd(PPh_3)_2(OClO_3)]$. This was readily substituted by $[NO_2]^-$ and $[CH_3COO]^-$ and L (L = py, 2-, 3- or 4-methylpyridine, 2,4- or 3,5-dimethylpyridine or 2,4,6-trimethylpyridine). The palladium-carbon bond in the species produced could not be cleaved by HCl [100].

The preparations of $Q_2[(C_6F_5)_xPd(CN)_{4-x}]$ (Q = R_4N or R_4P; x = 1, 2 (*cis* and *trans*) or 3) have been reported [101]. Reaction of $[(C_6F_5)Pd(PPh_3)_2(CN)]$ with $[R_3Sn(OClO_3)]$ (R = Bu) yielded $[(OClO_3)SnR_3\text{-}N{\equiv}C\text{-}Pd(PPh_3)_2(C_6F_5)]$. With a 2:1 ratio of palladium to tin the perchlorate was displaced giving $[(C_6F_5)Pd(PPh_3)_2\text{-}C{\equiv}N\text{-}SnR_3\text{-}N{\equiv}C\text{-}Pd(PPh_3)_2(C_6F_5)][ClO_4]$ [102]. Perchlorate was also readily displaced from $[RPdL_2(OClO_3)]$ by chelating nitrogen donor ligands, N-N, to yield $[R_2Pd_2(\mu\text{-}N\text{-}N)L_4][ClO_4]_2$ (R = C_6F_5 or C_6Cl_5). Structures were established by IR spectroscopy [103].

In the reaction of $[Pd(acac)_2]$ with L (L = $BuNH_2$, $CyNH_2$, Et_2NH or MeOH) to yield $[Pd(acac)L_2][acac]$. the carbon bonded species [Pd(acac)(acac-*C*-3)L] is not an intermediate, but is in some cases produced subsequently [104].

Reaction of $[Pt(PPh_3)_2(SO_2)]$ with butadiene yielded a mixture of **51a** and **51b**. The interconversion of these species was studied by nmr spectroscopy. Thermolysis of the mixture yielded the cluster **52**, the structure of which was established by X-ray diffraction. This is the first X-ray study of a platinum cluster with a bridging phenyl group [105].

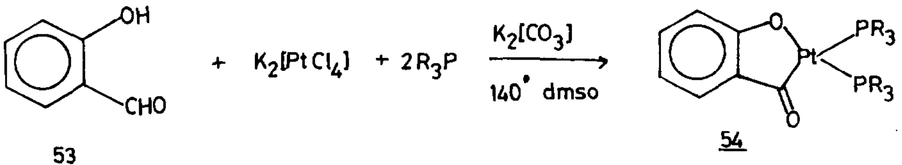


51a

51b

52

Treatment of **53** with $K_2[PtCl_4]$ and R_3P in the presence of base at 140 °C yielded **54** [106]. $[Ni(bipy)(CO)_2]$ reacted with R-C≡C-R to yield species such as **55** which could also be obtained from [Ni(bipy)(R-C≡C-R)] and CO or [Ni(bipy)(cod)], R-C≡C-R and CO. Reactions of **55** were investigated [107].



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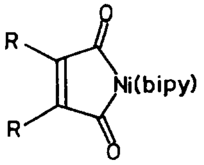
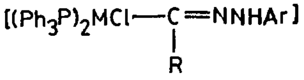


55

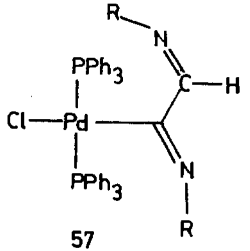
The complexes *trans*-[$RCOPt(PPh_3)_2Cl$] (R = Me, Et or Y-C_6H_4) are relatively difficult to decarbonylate thermally, but in the presence of $SnCl_2$ the reaction is facile. The species produced are *trans*-[$RCOPt(PPh_3)_2(SnCl_3)$] and *trans*-[$RPt(PPh_3)_2(SnCl_3)$], both of which may be isolated. Two factors seem to be important. The $SnCl_3$ ligand stabilises the 5-coordinate intermediate *trans*-[$RPt(PPh_3)_2(CO)(SnCl_3)$], which subsequently loses CO. Also $SnCl_3$ labilises the phosphines and migration of R proceeds faster in the unsaturated species [$RCOPt(PPh_3)(SnCl_3)$] to give [$RPt(CO)(PPh_3)(SnCl_3)$] [108].

Oxidative addition of ArNHN=C(R)Cl to [ML_n] (L = PPh_3) yielded **56** (M = Pd or Pt, Ar = 4-$MeOC_6H_4$, R = $COCH_3$ or COOEt) [109,110]. Treatment of [$Pd(PPh_3)_4$] with RNC/HCl in toluene gave **57** (R = 4-$MeOC_6H_4$) in which the diazadiene may act as a ligand towards other metals [111]. An X-ray diffraction study of the closely related complex, **58**, showed that the coordination about platinum was substantially distorted towards the tetrahedral. The Pd-C distance suggests that there is little π-bonding [112]. The structure of the related copper complex, **59**, has also been determined by X-ray diffraction [113].



$[(Ph_3P)_2MCl—\underset{R}{\underset{|}{C}}=NNHAr]$

56



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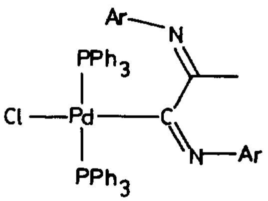

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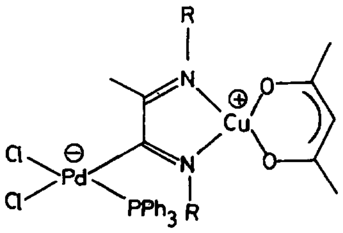
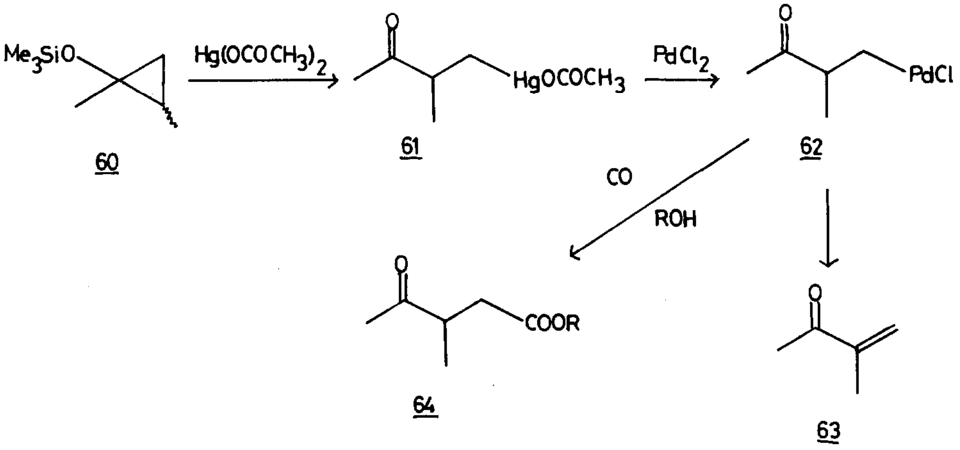


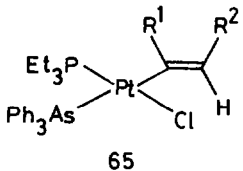
59

Electrophilic opening of the cyclopropene, **60**, by mercury(II) acetate gave **61**. This could be transmetallated by $PdCl_2$ to **62**. **62** β-hydride eliminates to give **63** or may be carboalkoxylated to **64** [114].



3. METAL COMPLEXES FORMED BY INSERTION AND RELATED REACTIONS

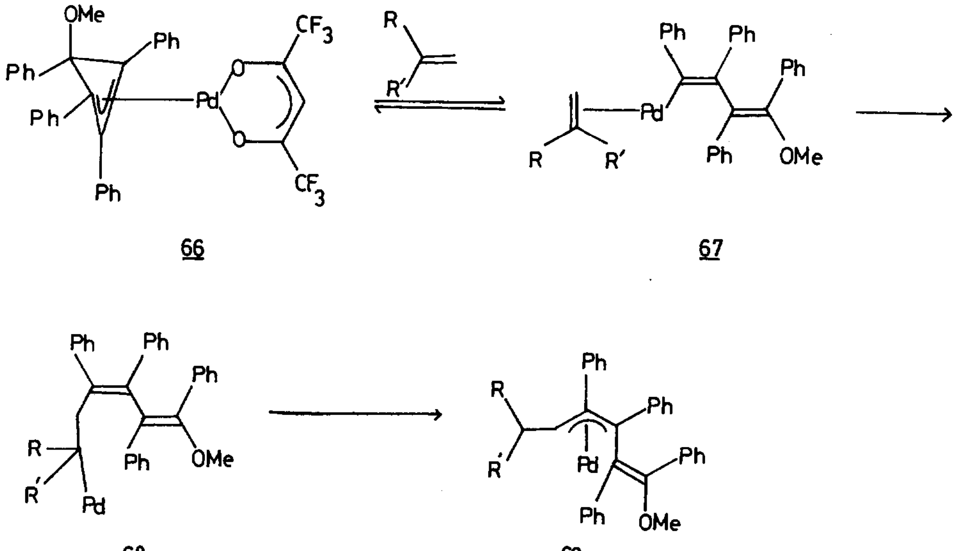
The kinetics of insertion of $MeOOC\text{-}C\equiv C\text{-}COOMe$ into *trans*-$[HPt(PPh_3)_2(MeCN)]$ have been studied by ^{31}P nmr spectroscopy. The rate law followed involves an alkyne dependent and an alkyne independent term [115]. Insertion of $R^1\text{-}C\equiv C\text{-}R^2$ into *cis*-$[HPt(PEt_3)(AsPh_3)Cl]$ gave **65**. The reactions of mono and diethyl analogues were also investigated [116]. **67** is formed on treatment of **66** with $RR'C{=}CH_2$. Insertion yielded **68**, which was converted to **69** *via* a hydride shift. The structure of **69** was determined by X-ray crystallography [117].



65

The insertion of carbon monoxide into transition metal to carbon σ-bonds has been reviewed [118]. The σ-alkyl palladium(II) species, **71** (X = NH, NMe or NCOMe; R = H or Me), an intermediate in heterocyclisation, yielded **72** in the presence of methanol. Insertion of alkenes into **71** is more difficult and is normally restricted to species in which β-hydride elimination is impossible

[119]. Reaction of Ph_2Hg with *cis*-$[Pt(CO)LCl_2]$ yielded $[PhPt(CO)LCl]$ as the initial product. Insertion and dimerisation gave $[(PhCO)_2Pt_2L_2(\mu\text{-}Cl)_2]$ (L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3 or PCy_3) The tendency of the phenyl group to migrate is directly affected by the *trans*-effect of L, unless a critical size of L is exceeded [120].



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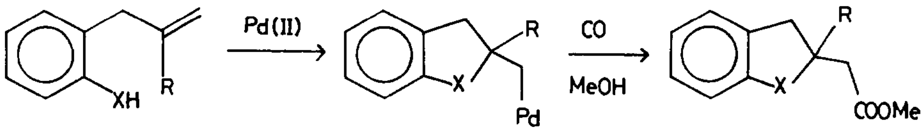

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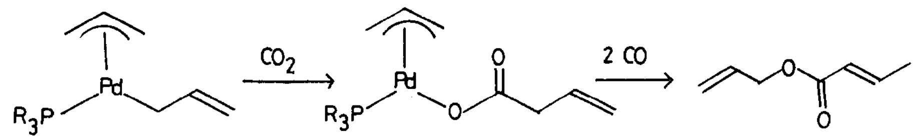
71

72

CO_2 was inserted into the palladium η^1-allyl bond of **73** to give **74**. Reduction of **74** with molecular hydrogen followed by acidification yielded $CH_3CH_2CH_2COOH$ and treatment with CO gave **75**. SO_2 also inserted into **73** [121]. SO_2 inserts preferentially into the Pt-Me bond of *cis*-$[MePhPt(PPh_2Me)_2]$. This contrasts sharply with analogous complexes of main group metals in which insertion occurs prefentially into an aryl metal bond [122]. CS_2 inserted into the Pd-Me bond of **76** yielding **77** [123].



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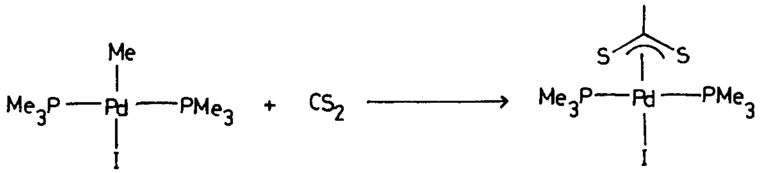
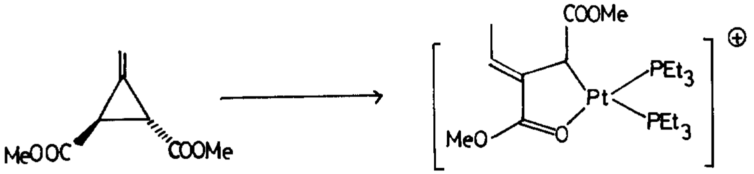


76 77

A range of insertion reactions of metal complexes into strained rings have been reported. Reaction of *trans*-$[HPt(PEt_3)_2(solvent)]^+$ with **78** gave **79**, an η^1-allyl complex. **80**, the first reported metal cyclopropyl complex, could also be obtained under appropriate conditions. X-ray diffraction studies provided structures of **80** and of various salts of **79**. The $[BPh_4]$ salt proved to be an η^1-allyl in the solid state, as shown. However, in the $[PF_6]$ salt the structure was that of an η^3-allyl complex, despite the fact that both salts appear to exist in solution in the η^1-form [124,125].



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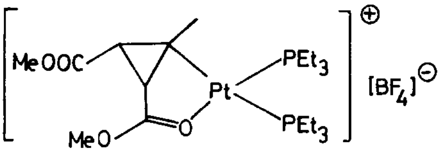
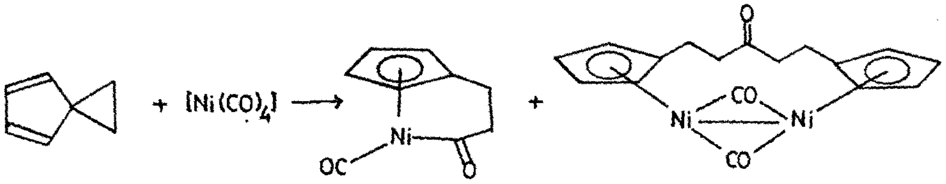


80

Reaction of **81** with $[Ni(CO)_4]$ gave **82** and **83**. The three-membered ring is opened and CO is also inserted [126]. The cyclopropene, **84**, also reacted to give an insertion product, **85**, in eqilibrium with the dimer, **86**. The structures of both **85** and **86** were established by X-ray diffraction [127]. The enthalpy of reaction of $[Pt(PPh_3)_2(E\text{-}PHCH{=}CHPh)]$ with diphenylcyclopropenone to give **87** has been determined to be -94.8 ± 6 kJ mol^{-1}. The reaction with **88** to give **89** is exothermic by only 57.1 kJ mol^{-1}, in keeping with the lower relief of strain in this case [128].



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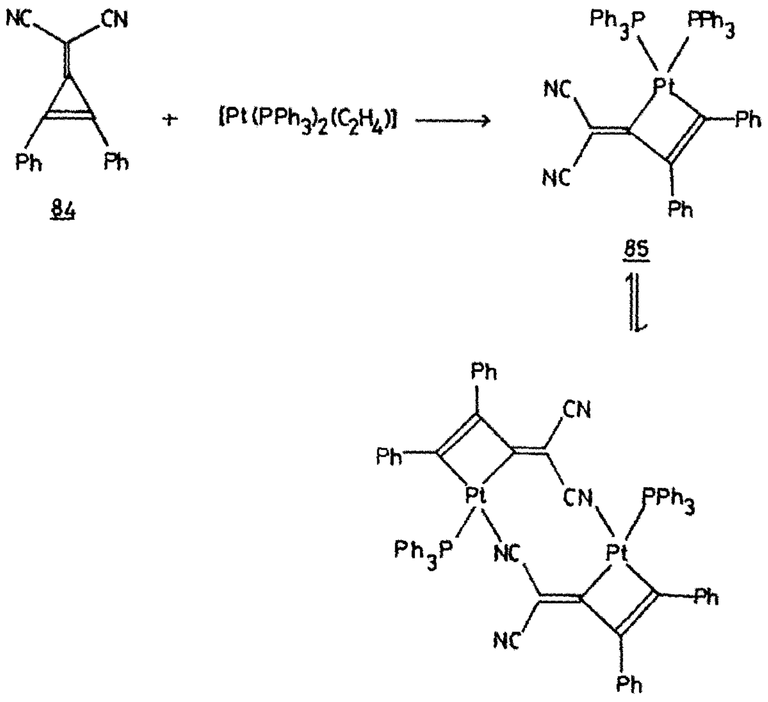

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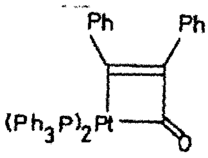
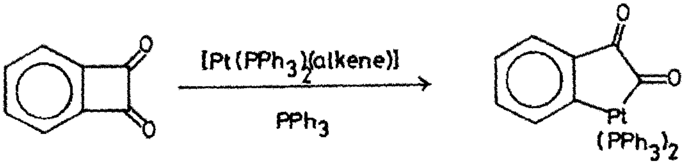
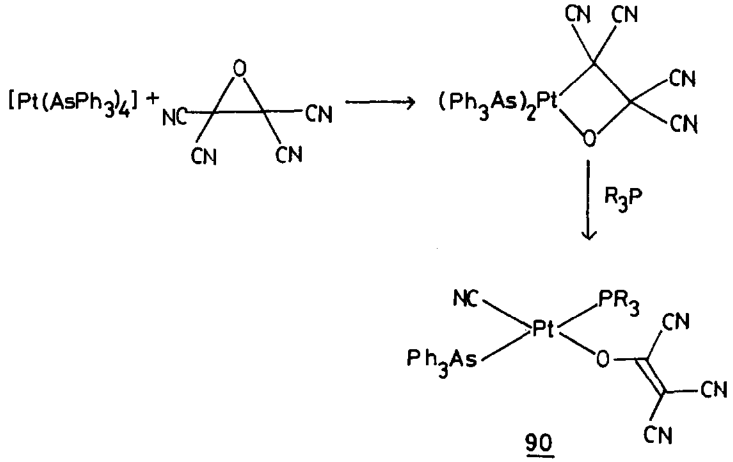




87 88 89

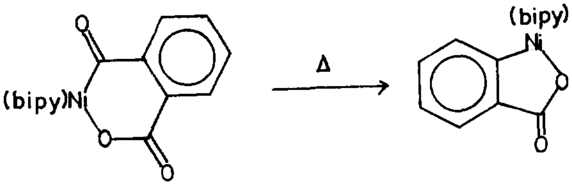
Insertion into epoxides may also occur (reaction (12)). The product reacted with phosphines to give **90** [129].



90

(12)

Whilst [Ni(bipy)(cod)] reacted with maleic anhydride to give complexes bound at C=C and/or C=O, it inserted into phthalic anhydride to yield **91**. Thermolysis resulted in decarbonylation to **92** [130].



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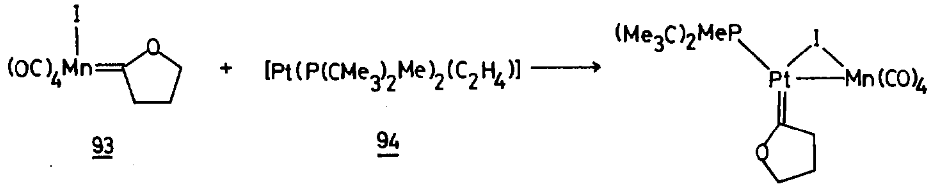
92

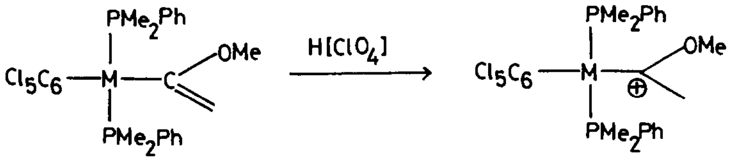
Insertion of [M(0)L$_n$] (M = Pt or Pd, L = PPh$_3$, n = 3 or 4) into a carbon mercury bond in RHgR' may yield either [RHgML$_2$R'] or [RML$_2$HgR']. Both of these species extrude mercury to give *trans*-[RR'ML$_2$]. The intermediate could be isolated for R = R' = Et$_2$NCO [131]. [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] has been shown to insert into the Sn-Me bond of Me$_3$SnCl to give *cis*-[MePt(PPh$_3$)$_2$(SnMe$_2$Cl)] [132]

4. METAL CARBENES, CARBYNES AND YLIDES

Ligand exchange between **93** and **94** yielded **95**, the structure of which was established by X-ray crystallography. However, with PMe$_3$ as the ligand at platinum the main products were [Mn(CO)$_4$(PMe$_3$)I] and the known complex [(OC)$_4$Mn(μ-C$_4$H$_6$O)Pt(PMe$_3$)$_2$] [133]. Reaction of [(C$_6$Cl$_5$)M(PMe$_2$Ph)$_2$Cl] with Li[C(OMe)=CH$_2$] yielded **96** (M = Ni, Pd or Pt). Protonation gave the cationic carbene complex **97**. **97** may also be obtained from the σ-alkynyl species $[(C_6Cl_5)M(PMe_2Ph)_2(C{\equiv}CH)]$ (M = Ni or Pt) by protonation in methanol. The relative ease of protonation of the complexes was in accord with the view that the largest σ-bonding ability is for nickel in **96**, and the largest π-back donor ability for platinum in **97** [134].

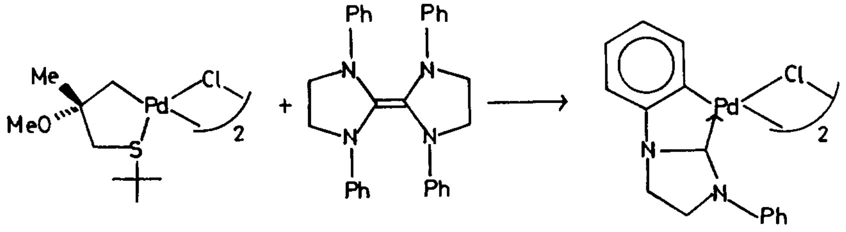


93 94 95



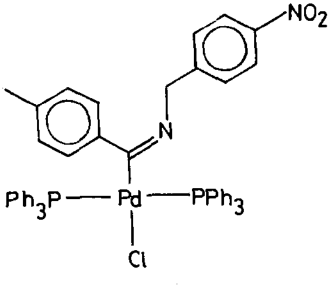
96 97

Reaction of the cyclometallated species, **98**, with **99** yielded the cyclometallated carbene complex, **100**. Bridge splitting occurred with a wide range of ligands including dienes, RCN, $P(OCHMe_2)_3$ and 4-methylpyridine, to give cationic carbene complexes [135,136]. *N*-(4-nitrobenzyl)-4-methylbenzimidoyl chloride reacted with $[Pd(PPh_3)_4]$ giving **101**. Protonation or treatment with $[Et_3O][BF_4]$ has also been shown to yield cationic aminocarbene complexes [137].



98 99 100

Treatment of two equivalents of $[Pd(PPh_3)_2(\eta^2\text{-}CS_2)]$ with one equivalent of $[\{Pd(PPh_3)_2Cl\}_2][BF_4]_2$ gave $[(PPh_3)_2ClPd(\mu\text{-}\eta^1,\eta^3\text{-}CS_2)Pd(PPh_3)_2][BF_4]$. The related species with two platinum centres or one platinum and one palladium centre (such as **102**) were also synthesised. The platinum carbenes were found to be more stable than the palladium analogues [138].



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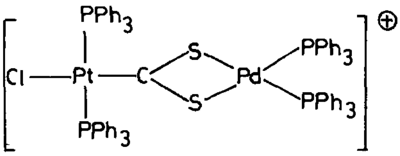
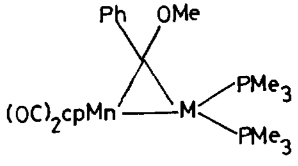


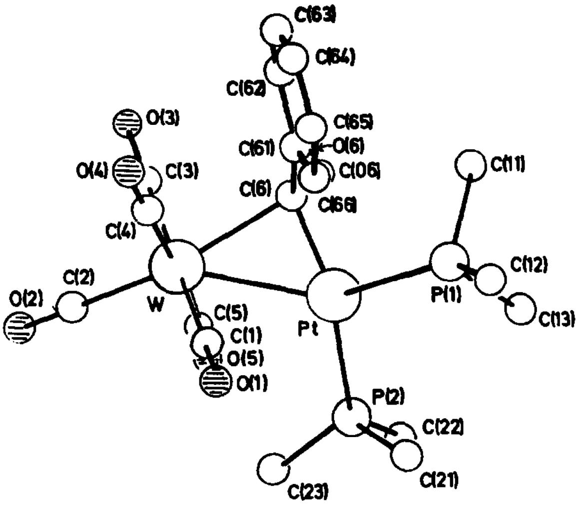
102

More extensive details of the preparations and properties of complexes with Mn-Pt or W-Pt bonds and bridging carbene groups have been published. Reaction of $[Cp(OC)_2Mn{=}C(Ph)OMe]$, **103**, with $[Pt(cod)_2]$ yielded $[Cp(OC)_2Mn\{\mu\text{-}C(Ph)OMe\}Pt(cod)]$. Similarly, $[Pt(C_2H_4)_3]$, $[Pd(dba)_2]$ and $[Ni(cod)_2]$ reacted with **103** in the presence of PMe_3 to yield **104** (M = Ni, Pd or Pt). The PMe_3 ligand *trans* to the carbene is easily replaced be Me_3CNC [139]. Analogous complexes were formed by chromium, molybdenum and tungsten, and the structure of **105** was established by X-ray diffraction [140]. Reaction of $[(OC)_5M{=}C(Ph)OMe]$ (M = Cr or W) with $[Pt(PR_3)(C_2H_4)_2]$ (PR_3 = PCy_3 or $PMe(CMe_3)_2$) which has two readily replaceable ligands, yielded $[MPt_2\{\mu\text{-}C(Ph)OMe\}(CO)_6(PR_3)_2]$. ^{13}C nmr spectroscopy suggests that the carbene bridges the Pt-Pt bond, and this was confirmed by X-ray crystallography. Each platinum atom is coordinated by CO and PR_3 so that the phosphines are on the same side of the Pt-Pt bond and *cis* to the bridging carbene. Two further CO groups are semibridging to platinum [141].

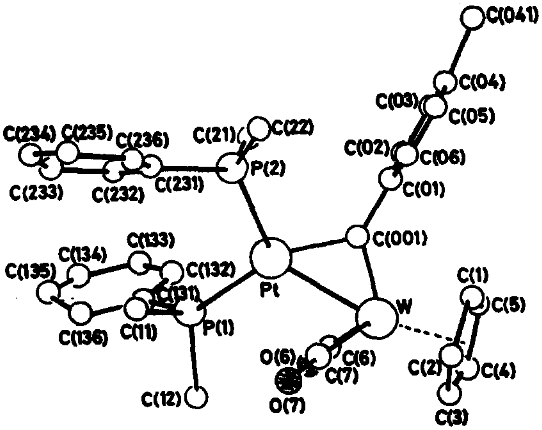


104

Treatment of $[(OC)_2CpW{\equiv}C\text{-}C_6H_4\text{-}4\text{-}Me]$ with $[Pt(PR_3)_2(C_2H_4)]$ (PR_3 = PMe_3 or PMe_2Ph) yielded **106**, the structure of which was established by X-ray diffraction [142]. The sequence of reaction (13) provided a trimetallic cluster, **107**, in which an alkylidene group caps a traingle of transition metal atoms [143].



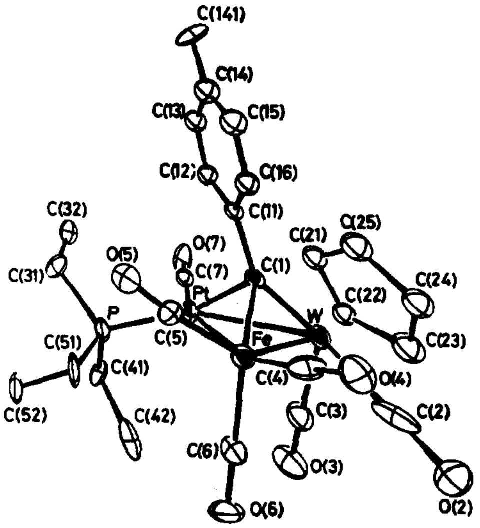
105 (Reproduced with permission from [140])



106 (Reproduced with permission from [142])

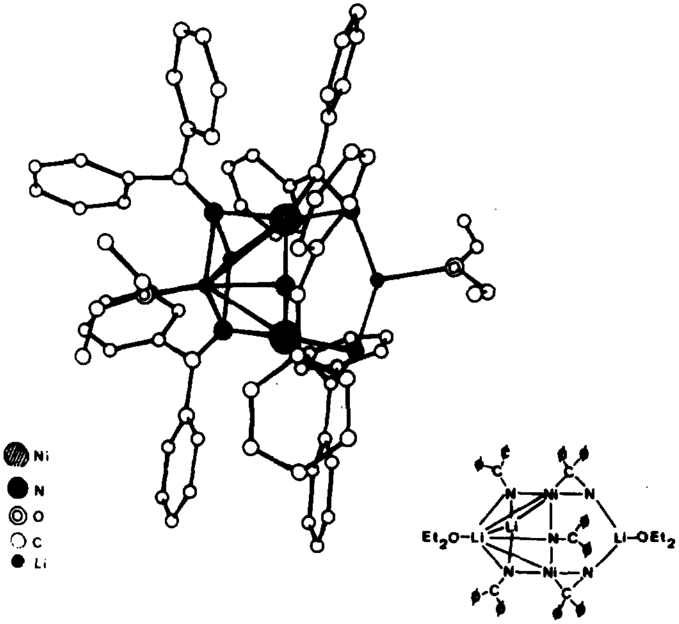
$$[Pt(C_2H_4)_3] + PEt_3 + [Cp(OC)_2W{\equiv}CC_6H_4\text{-}4\text{-}Me] \rightarrow [PtW(\mu_2\text{-}CC_6H_4\text{-}4\text{-}Me)(CO)_2(PEt_3)_2Cp]$$

$$\xrightarrow{[Fe_2(CO)_9]} \underset{\textbf{107}}{[FePtW(\mu_3\text{-}CC_6H_4\text{-}4\text{-}Me)(CO)_4(PEt_3)_2Cp]} \qquad (13)$$



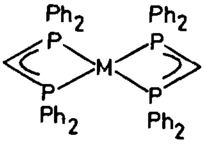
107 (Reproduced with permission from [143])

Reaction of [Ni(cod)$_2$] with two equivalents of [Ph$_2$C=N]Li in the presence of bipy gave **108**, the structure of which was established by X-ray diffraction [144].



108 (Reproduced with permission from [144])

References to ylide complexes have been somewhat sparse this year. Reaction of $[M(PMe_3)_2Cl_2]$ (M = Ni, Pd or Pt) with two equivalents of $Li[CHPPh_2]$ yielded the square-planar bis(phosphino) methanide derivative, **109**. X-ray diffraction revealed a folded ylide ring with the central carbon atom not close to the metal [145].

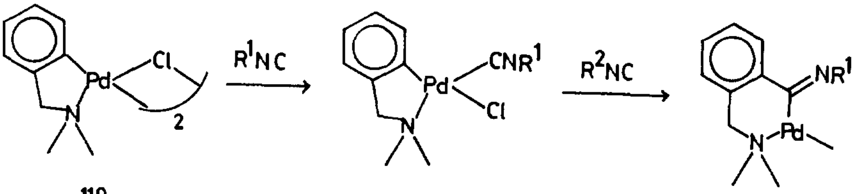


109

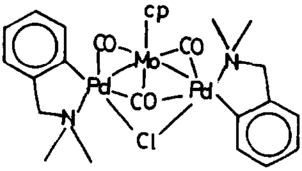
Treatment of $[\{Pt(\eta^3\text{-}CH_2CHCHPh)Cl_2\}_4]$ with 2-methylpyridine, L, gave the ylide complex *trans*-$[Pt(CHLCH_2CH_2Ph)L]$. Deuterium labelling experiments provided strong evidence for carbene and platinacylobutane intermediates [146].

5. INTERNAL METALLATION REACTIONS

A number of transformations of the cylometallated dimer, **110**, have been reported this year. Bridge splitting occurs, using R^1NC, to give **111**. Treatment with a second equivalent, R^2NC, or thermolysis, resulted in intramolecular insertion to **112**. **112** was converted to an α-acyl-*N*,*N*-dimethylbenzylamine on reaction with a Grignard reagent followed by acidic work-up [147]. Reaction of **110** with $Na[Mo(CO)_3(Cp)]$ gave **113**; X-ray diffraction shows that there is no Pd-Pd bond and that two carbonyls bridge Mo-Pd bonds, whilst the third is triply bridging. The carbonyl metallate acts as a three electron donor [148].

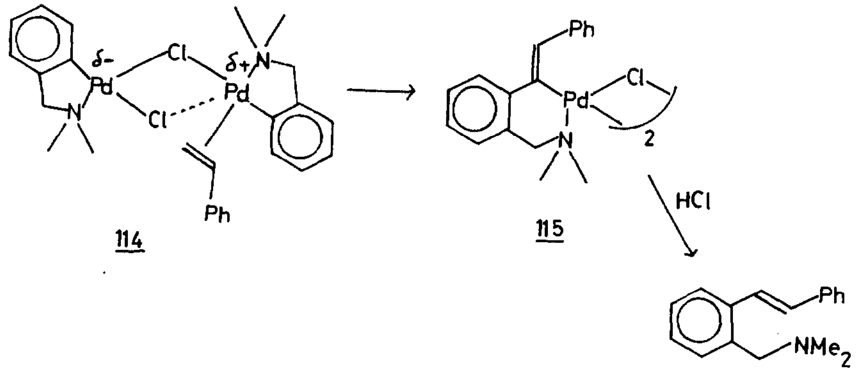


110 111 112



113

110 does not react with styrene in non-polar solvents even in the presence of base, but in an electrolyte such as ethanoic acid, bridge splitting to **124** was accelerated. Insertion gave 115, which could be isolated in good yield, but which was readily converted by acid to **116** and Pd(0) [149]. On reaction with **110**, $[Ph_2PCHCOOEt]^-$ gives products in which it acts either as a chelating or as a bridging ligand. Both **117** and **118** could be isolated using suitable proportions of reactants, their structures being established by X-ray diffraction [150].

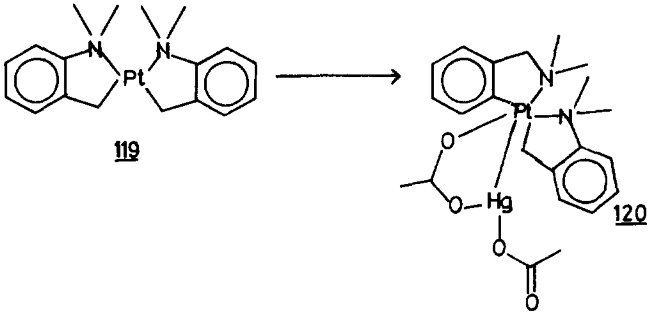


114

115

116

The bis cyclometallated species, **119** reacted with $[Hg(O_2CR)_2]$ (R = Me or $CHMe_2$) to yield the platinum(III) complex, **120**, the structure of which was determined by X-ray crystallography. The stability of such complexes depends on the mutual arrangement of the ligands. The *trans* analogue of 119 gave an unstable species, $[(2\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CMe)_2]$, which decomposed even at -50 °C to mercury metal and $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(IV)(O_2CMe)_2]$ [151]. The absolute configuration of *ortho*-phenylene-bis-α-methylphenylarsine has been determined from the X-ray diffraction data on [{S-dimethyl(α-methylbenzyl)aminato-C^2,N}(S,S-*ortho*-phenylene-bis-α-methylphenylarsine)Pd(II)][PF_6], 121 [152].



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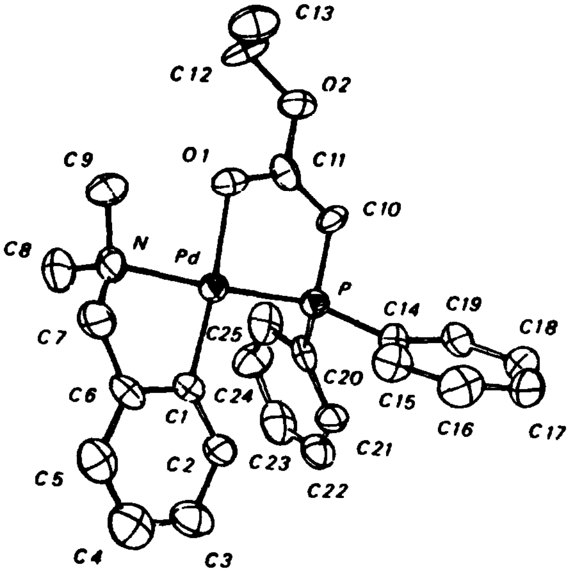
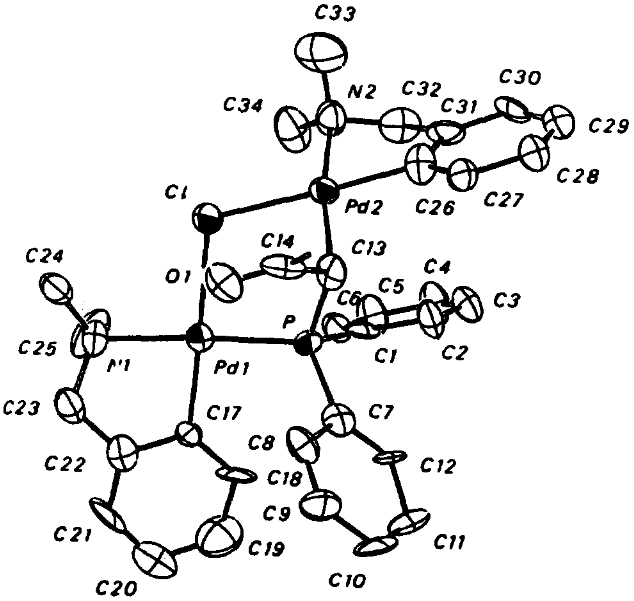


117 (Reproduced with permission from [150])



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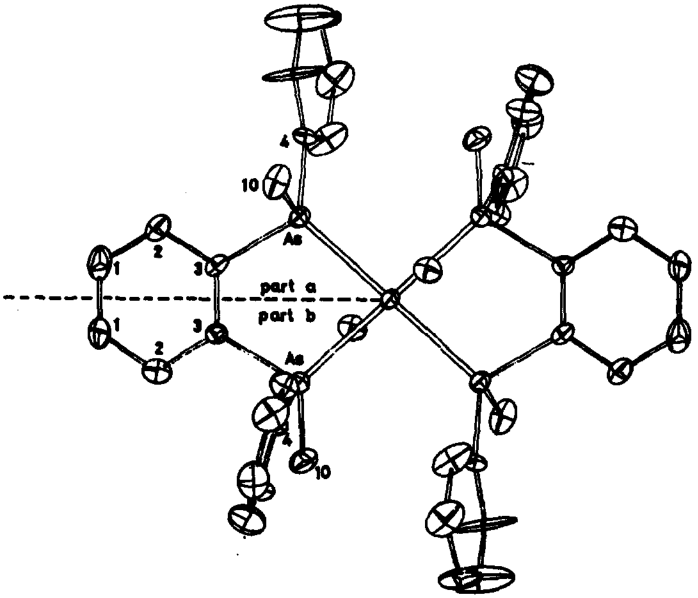
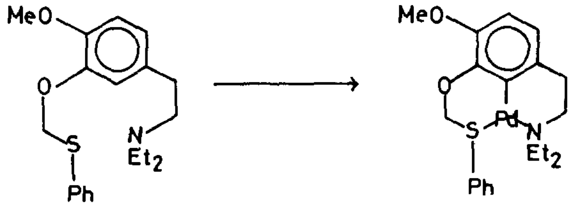


121 (Reproduced with permission from [152])

Treatment of **122** with $Li_2[PdCl_4]$ yielded the cyclopalladated species, **123**. The reaction was less easy in the case of the bis sulphur ligand; **124** was produced initially with metallation of the ring occurring only in the presence of silica [153]. Asymmetric cyclopalladation of dimethylaminomethyl ferrocene was used as the first step in the synthesis of the enantiomers of the useful ligand 1-diphenylphosphino-2-dimethylaminomethyl ferrocene [154].



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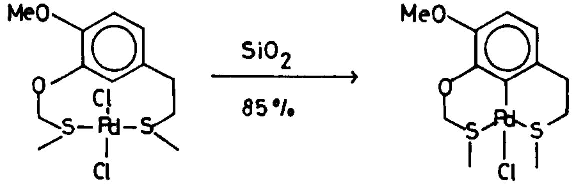
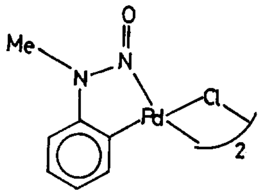


124 **125**

N-nitroso-*N*-methylbenzylamine is not cyclopalladated by $Na_2[PdCl_4]$ but *N*-nitroso-*N*-methylaniline reacted readily to yield **126**. Bridge splitting reactions occurred with acac, dppe, py and PPh_3, the structures of the adducts in the last two cases being determined by X-ray diffraction. The platinum analogues of **126** could not be readily purified but underwent similar bridge splitting reactions [155]. Cyclometallated adducts of the type **127** reacted with bridge splitting with catechol radical anions [156].



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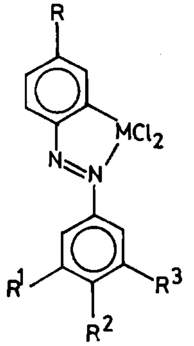
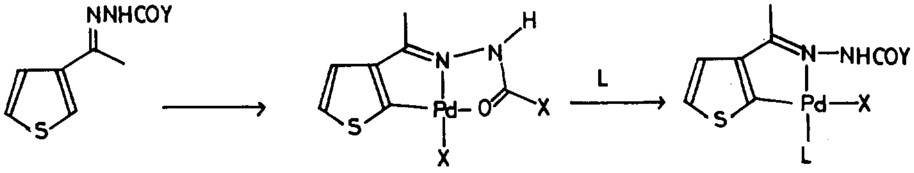
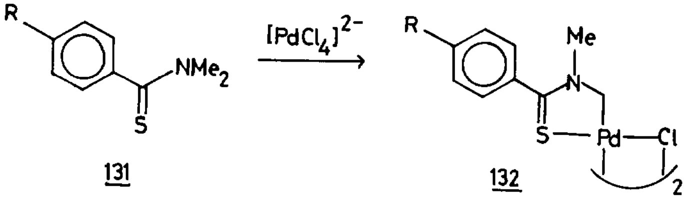


127

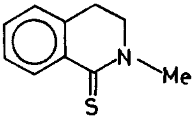
128 (Y = Me or NH_2) reacted with $Li_2[PdCl_4]$ to give **129**. Treatment with ligands such as pyridine or PBu_3 gave **130** by displacement of the carbonyl [157]. The thioamide, **131**, has been shown to metallate at a methyl group in **132**; it is thought that after initial coordination of the metal to sulphur, the aryl ring rotates out of the plane of the thiocarbonyl. In **133**, however, the two potential metallation sites are held at roughly the same distance from the coordinated palladium, which prefers to react at the sp^2 site [158].



128 **129** **130**

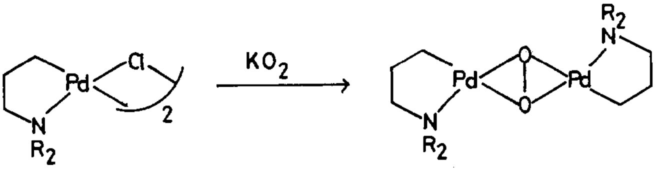


131 132



133

Reaction of **134** with two equivalents of K[O$_2$] yielded **135**; [O$_2$] is coordinated as $[O_2]^{2-}$ and behaves as a strong base [159]. Treatment of **136** with $[Pd(PhCN)_2X_2]$ gave **137**. The reaction of the sulphur analogue suggests that the initial step involves formation of a labile alkene complex, which rearranges in solution [160]. Fluxionality in [{poly(1-pyrazolyl)borato}palladium(II)] cyclometallated complexes has been investigated [161]. Metallation of E-3,3-dimethyl butanone oxime occurred exclusively at the *tert*-butyl group to give an *N*,*C*-bonded 5-membered ring chelate. With the corresponding *N*,*N*-dimethyl hydrazone, palladation occurred at the methyl group, giving **138** [162]. **139** was synthesised from $CH_2{=}C(R^1)CONHR^2$ and $[Ni(cod)_2]$ in the presence of R$_3$P [163].



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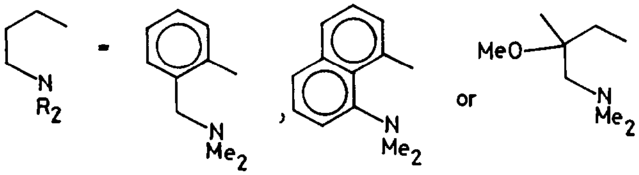

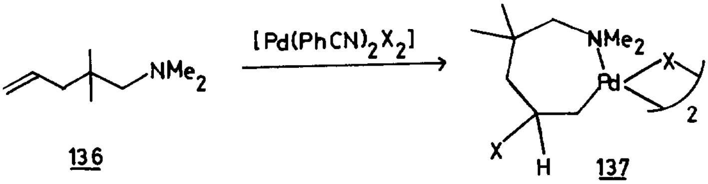

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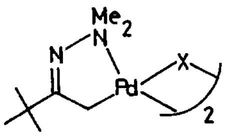

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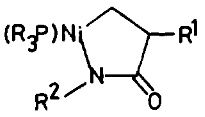
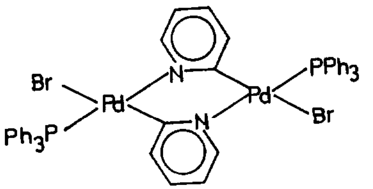


139

Oxidative addition of 2-bromopyridine to [Pd(PPh$_3$)$_4$] yielded the cyclometallated compound, **140**. 3- and 4-bromopyridines gave mononuclear complexes [164]. Cyclometallation of 2-arylpyridines occurred at the *ortho* position of the aryl ring. The reaction was more successful with activated than with deactivated aryl substituents, suggesting that the controlling factor may be electrophilic attack. Steric effects are also important, since it is necessary that the aryl rings be coplanar for metallation to occur [165]. **141** was formed from the free ligand and has the ability to "nick" DNA at rather low concentrations [166]. 2-(4-Methylphenyl)-benzthiazole and benzoxazole gave isomorphous and isostructural cyclometallated adducts such as 142 [176].



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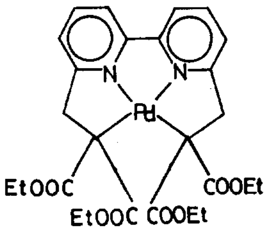

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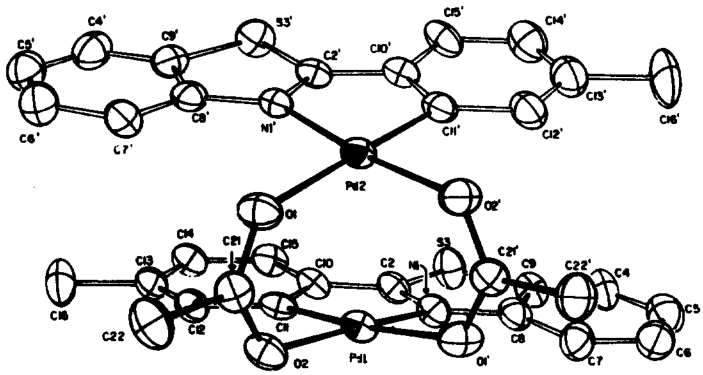
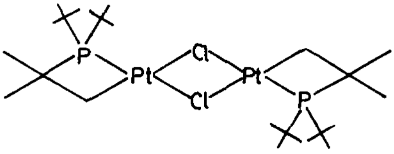


142 (Reproduced with permission from [176])

When *trans*-[Pt(PhCN)$_2$Cl$_2$] was treated with two equivalents of (Me$_3$C)$_3$P the cyclometallated species **143** was formed. Bridge splitting with a wide range of ligands gave mononuclear, *trans*-products [168]. The palladium analogue of **143** has been reacted with methoxide giving the first example of a complex with one methoxy and one chloro bridge [169]. Reaction of [Pd(PhCN)$_2$Cl$_2$] with (Me$_3$C)$_2$PCH$_2$CH$_2$CH(CH$_3$)CH$_2$CH$_2$P(CMe$_3$)$_2$, L, gave [Pd$_2$L$_2$Cl$_2$(μ-Cl)$_2$], whereas with the platinum analogue the metallated species, **144**, was formed in a reaction reminiscent of those of rhodium and iridium complexes with related ligands [170].



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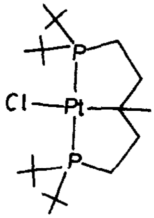
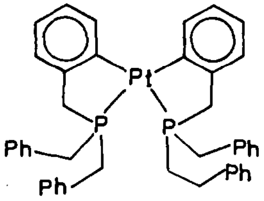


144

The first example of a *cis*-dimetallated platinum phosphine complex, **145**, was synthesised by reaction of [{(η^3-CH$_2$C(CH$_3$)CH$_2$)PtCl}$_2$] with thallium(I) ethanoate and tribenzyl phosphine. In an X-ray diffraction study the 5-membered rings were shown to adopt an envelope conformation [171]. *Cis*-dimetallated species were also formed by reaction of 1-lithio-2-dialkylphosphinomethyl benzene with [Pt(SEt$_2$)$_2$Cl$_2$]. They could be oxidised by Br$_2$ to *trans*-dihaloplatinum(IV) species [172]. Reaction of Pd(OCOCMe)$_2$ with **146** (X = CH=NMe) gave metallation at the 8-position, but no analogous products could be characterised from the substrate with X = *CH$_2$P(CMe$_3$)$_2$ [173]*.



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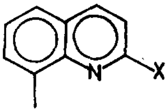
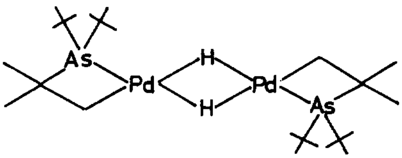


146

Reaction of Na$_2$[PdCl$_4$] with (Me$_3$C)$_3$As gave *trans*-[HPd{As(CMe$_3$)$_2$}$_2$Cl]. This was slowly metallated in benzene solution yielding 147 and its *cis*-isomer. By contrast, the phosphine analogue was rapidly metallated with cleavage of the H-Pd bond [174]. Treatment of 148 with methoxide ion and hfacac yielded the cyclometallated 149; the structures of both complexes were established by X-ray diffraction [175].



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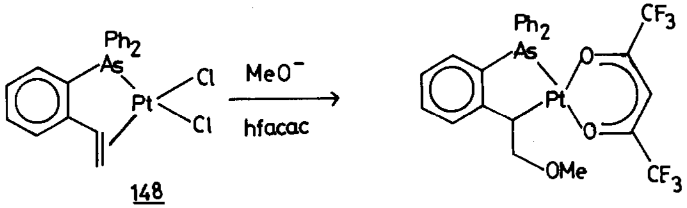
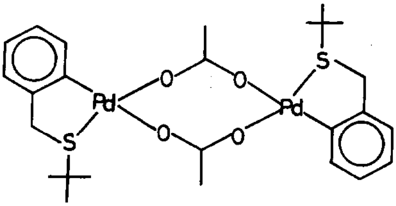


148

149

Reaction of $Pd(OCOMe)_2$ with Me_3CSCH_2Ph gave a sulphur bridged dimer. Thermolysis resulted in metallation of the aryl ring to give **150**. Exchange of ethanoate for chloride bridges was effected by LiCl in thf, and addition of pyridine caused bridge cleavage [176].



150

6. METAL CARBONYLS

The teratogenicity and embryotoxicity of $[Ni(CO)_4]$ in Syrian hamsters has been reviewed [177,178]. Nephrotoxicity of $[Ni(CO)_4]$ in rats [179] and the effect of $[Ni(CO)_4]$ and $NiCl_2$ on kidney DNA have also been investigated. the lung changes which are normally widespread in $[Ni(CO)_4]$ poisoned rats are minimised after treatment with prednisone [181].

The charge exchange mass spectrum of $[Ni(CO)_4]$ has been reported using gasoline exhaust gas as the reactant gas. This method may be used to monitor $[Ni(CO)_4]$ [182]. A sensitive portable detector for $[Ni(CO)_4]$ measures the chemiluminescence produced in the presence of O_3 and CO_2; the method is insensitive to NO [183]. Other methods for detection have also been reported

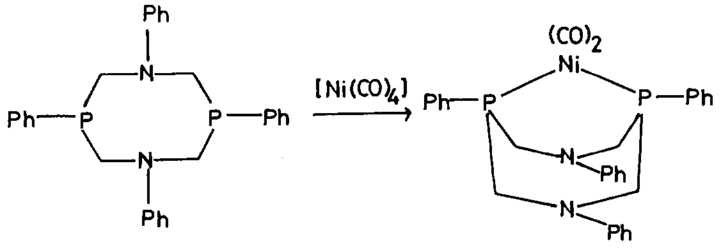
[184]. The lifetime of $[Ni(CO)_4]$ in air has been directly related to the CO concentration and inversely to the oxygen concentration. The first step in decomposition is CO loss, this being followed by rapid reaction of $[Ni(CO)_3]$ with molecular oxygen [185,186].

Semi-empirical quantum mechanical calculations (CNDO and extended Hückel) on $[Ni(CO)_4]$ have led to a resolution of oustanding ambiguities in the signs of the polar tensors [187]. An X_αSW study of the metal to ligand back bonding in $[Ni(CO)_4]$ indicated that the 1.11 electrons back donated from the nickel 3d orbital into the carbonyl π^* were offset by donation into the nickel 4s and 4p levels. The use of the projected, PX_α method allowed avoidance of the ambiguities inherent in the interpretation of the X_αSW distributions [188]. A theoretical study of vibrational interaction coordinates and π-bonding in $[Cr(CO)_6]$ was compared with related work on $[Ni(CO)_4]$ [189]. The force constants, k, for C-O and M-C bonds in $[Ni(CO)_4]$ and other binary carbonyls have been analysed. There is a good correlation between k and the metal carbon bond lengths [190]. Previously unknown transitions of low-lying quintet states of nickel were observed in reactions of $[Ni(CO)_4]$ with metastable argon atoms [191]. The chemiluminescence from collisions of $[Ni(CO)_4]$ with metastable helium, neon and argon atoms has been described. The emission spectra are due to atomic nickel [192].

A model proposed for crystallisation from the gas phase involves three steps. In the first homogeneous reaction of monomer leads to particle formation. This is followed by particle aggregation and heterogeneous reaction on the aggregates. This model has been shown to work well for $[Ni(CO)_4]$ [193]. The thermal decomposition of $[Ni(CO)_4]$ aerosol and formation of nickel aerosol was studied in the temperature range 20-210 °C. This involves dissociation of $[Ni(CO)_4]$ and aggregation of $[Ni(CO)_3]$ [194]. The adsorption binding behaviour and decomposition of $[Ni(CO)_4]$ on zeolites and alumina was studied by ^{13}C nmr spectrsocopy. Highly dispersed metal particles were formed [195]. The properties and catalytic activity in benzene reduction of NaX zeolites modified with $[Ni(CO)_4]$ were studied. Again very dispersed metal particles are produced by decomposition of the nickel carbonyl [196]. Infrared spectroscopy was used to study adsorption of $[Ni(CO)_4]$ on magnesium oxide; small metal carbonyl clusters are formed on the surface [197]. The decomposition of a gaseous mixture of $[Ni(CO)_4]$ and $[Fe(CO)_5]$ streaming between the poles of a permanent magnet yielded a string-like association of metal globules resembling meteoric kamacite [198].

The activation energy for $[Ni(CO)_4]$ formation on sufaces of $Ni_{1-x}Cu_x$ alloys was found to be greater when the metallic substrate is ferromagnetic rather than paramagnetic [199]. The kinetics of formation of $[Ni(CO)_4]$ on nickel surfaces depend strongly on their crystallographic orientation. SEM showed that very sharp (111) facetting of the surface occurred during reaction. A mechanism has been proposed to account both for this and for the available chemisorption data [200]. A theoretical study of the dissolution of $[Ni(CO)_4]$ has been reported [201]. Addition of $[Ni(CO)_4]$ or $[Fe(CO)_5]$ to a butane + recoil-T system resulted in an increased yield of tritiated ethene and light hydrocarbons. The effect was ascribed to an intermediate containing the metal and organic radicals [202].

^{13}C nmr spectroscopic data has been reported for one hundred and sixteen $[NiL(CO)_3]$ complexes. Various trends relating to σ-basicity and π-acidity of L were noted [203]. Monosubstitution of $[Ni(CO)_4]$ with $R_2R^1SnPR^2_2$ yielded $[Ni(CO)_3(R_2R^1SnPR^2_2)]$ [204,205]. Monosubstitution also occurred with the molybenum substituted phosphines $\{Mo(CO)_5PPhH\}_nPPh_{3-n}$ [206]. Bidentate ligands generally give disubstituted products. **151** reacted to give **152** in which the nickel bridges a boat conformation of an eight membered ring [207]. Treatment of $[Ni(CO)_4]$ with $PhHP(CH_2)_3PPhH$ yielded $[Ni(CO)_2(PhPH(CH_2)_3PPhH)]$. An X-ray diffraction study of the *meso* form of the complex showed that the six-membered ring adopts a chair conformation [208]. The complexes **153** (X = O, S or NMe) have been synthesised and characterised by IR spectrsocopy [209]. The potentially bidentate ligands $(Ph_2Sb)_2MMe_2$ (M = C, Ge or Sn) reacted with $[Ni(CO)_4]$ to give $[Ni(CO)_3L]$ as the initial product. These polymerised to materials such as **154** with loss of CO [210].



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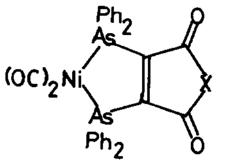

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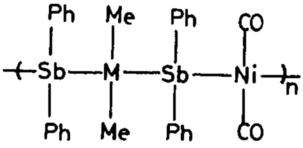


154

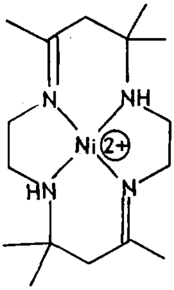
Treatment of $[Ni(PR_3)_2X_2]$ with one atmosphere of CO at room temperature yielded $[Ni(CO)(PR_3)_2X_2]$, which was also obtained from $[Ni(PR_3)_3X_2]$ (R = Me). X-ray diffraction data of the complex for which R = Me, X = I, showed trigonal bipyramidal coordination of nickel with CO and X in the equatorial plane and the phosphine ligands axial [211]. 2,6-Bis(diphenylphosphinomethyl)pyridine (pnp) complexes, [Ni(pnp)XY] (X = Cl or Br, Y = Cl or $[ClO_4]$) reacted with CO in the presence of base to yield $[Ni(pnp)(CO)_2]$ *via* reactions (13) - (16) [212]. Reversible carbonylation of 155 has been noted [213].

$$[Ni(pnp)Cl]^+ \xrightleftharpoons{CO} [Ni(pnp)(CO)Cl]^+ \qquad (13)$$

$$[Ni(pnp)(CO)Cl]^+ + H_2O \longrightarrow [Ni(Hpnp)(COOH)Cl]^+ \qquad (14)$$

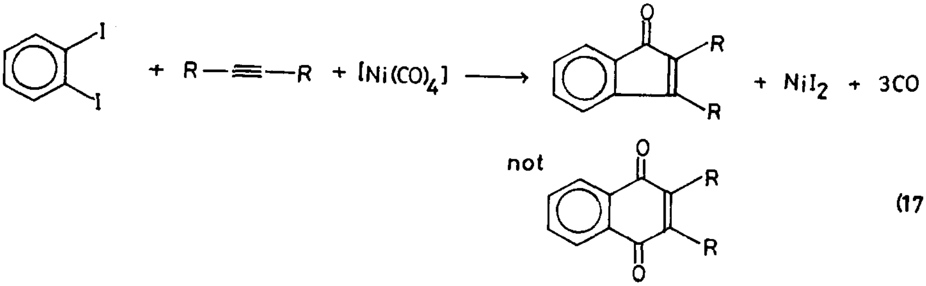
$$[Ni(Hpnp)(COOH)Cl]^+ \xrightarrow{2CO} [Ni(Hpnp)(CO)_2]^+ + CO_2 + HCl \qquad (15)$$

$$[Ni(Hpnp)(CO)_2]^+ \rightleftharpoons [Ni(pnp)(CO)_2] + H^+ \qquad (16)$$



155

The insertion of $[Ni(CO)_4]$ into aryl halides is well known and the acyl nickel complexes produced readily insert alkynes. Using 1,2-diiodobenzene as substrate five rather than the expected six-membered ring products were obtained (reaction (17)) [214]. The nickel carbonyl induced intramolecular coupling of 156 gave only 10 % (*) cubitene, 157. Also conversion was low and there was considerable contamination by dimers [215].



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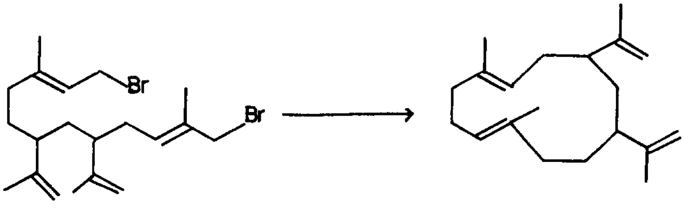


156 157

A preparative scale version of reaction (18) has been described ($[ML_n]$ = $[Ni(CO)(Cp)]$). Reaction of $[Ni(CO)(Cp)]^-$ with acyl halides, RCOCl, yielded $[RCONi(CO)(Cp)]$ with low efficiency, but using Ph_3SnCl, $[Ph_3SnNi(CO)(Cp)]$ was produced in 66 % yield [216]. The reaction between $[R^1CONi(CO)_3]^-$ and the imidoyl chloride, $R^2C(Cl)=NR^3$ yielded diazabutadienes, 1,2-diketones, amides and imidoketones *via* electron transfer processes [217].

$$[ML_n] + NaNp \longrightarrow NpH + Na[ML_n] \qquad (18)$$

A kinetic study of the reduction of copper(II) to copper(I) by carbon monoxide in the presence of $[PdCl_4]^{2-}$ allowed the scheme of reactions (19) to (26) to be proposed [218]. The stoicheiometric reduction of $[PdCl_4]^{2-}$ by CO follows a rather similar route, though some binuclear intermediates with bridging carbonyl groups are also involved. $[Pd(CO)Cl_3]^-$ was isolated as its caesium salt [219].

$$[PdCl_4]^{2-} + CO \rightleftharpoons [Pd(CO)Cl_3]^- + Cl^- \qquad (19)$$

$$[Pd(CO)Cl_3]^- + H_2O \rightleftharpoons [Pd(CO)(H_2O)Cl_2] + Cl^- \qquad (20)$$

$$[Pd(CO)(H_2O)Cl_2] \rightleftharpoons [Pd(CO)(OH)Cl_2]^- + H^+ \qquad (21)$$

$$[Pd(CO)(OH)Cl_2]^- + CO \longrightarrow [Pd(COOH)(CO)Cl_2]^- \qquad (22)$$

$$[Pd(COOH)(CO)Cl_2]^- + [CuCl_4]^{2-} \xrightarrow{\text{fast}} [Pd(CO)Cl] + [CuCl_2]^- + CO_2 + HCl + 2Cl^- \qquad (23)$$

$$[Pd(CO)Cl] + Cu(II) \longrightarrow [Pd(CO)Cl]^+ + Cu(I) \qquad (24)$$

$$[CuCl_2]^- + CO \rightleftharpoons [Cu(CO)Cl] + Cl^- \qquad (25)$$

$$[Cu(CO)Cl] + [PdCl_4]^{2-} \longrightarrow [Pd(CO)Cl_3]^- + CuCl + Cl^- \qquad (26)$$

Mononuclear carbonyl complexes of palladium(0), palladium(I) and palladium(II) have been synthesised. $[Pd(CO)_4]$ is stable over the range 4.2 - 10 K in an argon matrix, whilst $[Pd(CO)_3]$, $[Pd(CO)_2]$ and $[Pd(CO)]$ could be observed by IR spectroscopy between 10 and 20 K. All decomposed above 30 K. Palladium carbonyl phosphine clusters were also discussed [220].

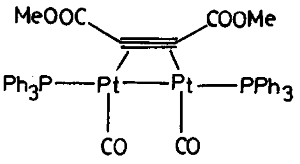
Reaction of the halo-bridged dimers $[(PtLX_2)_2]$ (L = R_3P, R_3As or $PhNH_2$) with CO yielded *trans*-$[Pt(CO)LX_2]$ as the initial product. Isomerisation to the *cis* complex was quite rapid and was catalysed by CO or X^- (*via* a five-coordinate complex), phosphine or UV irradiation. Bound and free CO exchange more rapidly in the *trans* than in the *cis* isomer [221,222]. The signs of $^1J(^{195}Pt-^{13}C)$ and the values of $\delta(^{195}Pt)$ for *cis*- and *trans*-isomers of $[Pt(CO)(PEt_3)Cl_2]$ and $[PhPt(CO)(PEt_3)Cl]$, and all isomers of $[(PhCO)_2Pt_2(PMePh_2)_2(\mu-Cl)_2]$ were determined. $^1J(^{195}Pt-^{13}C)$ was shown to be positive for CO *trans* to phosphine [223]. Calculations to determine the electronic structure of $[Pt(CO)Cl_3]^-$ have been undertaken [224].

Treatment of *trans*-$[HPt(PPh_3)_2(OClO_3)]$ with CO yielded *trans*-$[HPt(PPh_3)_2(CO)][ClO_4]$, since $[OClO_3]^-$ is readily displaced from the metal coordination sphere [225]. *Trans*-$[Pt(CO)(PEt_3)_2Cl]$ was hydrated to yield $[Pt(COOH)(PEt_3)_2Cl]$, which could be characterised and was stable over several hours. It decayed slowly to $[HPt(PEt_3)_2Cl]$ releasing CO_2 [226].

μ_2-Bridging carbonyl systems in transition metal complexes have been reviewed [227]. The structure, as determined by X-ray diffraction, of $[\{Ni(MeCp)(\mu-CO)\}_2]$ has a planar $\{Ni_2(CO)_2\}$ core. However, $[\{Ni(Cp)(\mu-CO)\}_2]$ has two distinct molecules in its crystal, both with a bent $\{Ni_2(CO)_2\}$ core. These were described as individual frames in a motion picture of the dynamic butterfly inversion, with retention of the CO bridges, which occurs in solution [228]. $[\{Ni(\mu-PCy_2)(PCy_2Ph)\}_2]$ retained the PCy_2 bridges on reaction with carbon monoxide to give $[\{Ni(CO)_2(\mu-PCy_2)\}_2]$ [229].

The reaction of $[H_2ML_n]$ with carbon monoxide to yield $[ML_n(CO)]$ and molecular hydrogen is only rarely quantitatively and readily reversible. However, the reaction of the "A-frame" species $[H_2Pt_2(\mu-H)(\mu-dppm)_2][PF_6]$ with CO to yield the new complex $[HPt_2(CO)(\mu-dppm)_2][PF_6]$ was found to fulfill these conditions [230]. The new species $[Pt_2(LL)_2L'(\mu-H)][X]$ (L' = CO or CNR; LL = dppe, dppp, dppb or $Ph_2PCH_2CH_2AsPh_2$) were reported. The structure of $[Pt_2(dppe)_2(CO)(\mu-H)][BF_4]$ was determined by X-ray diffraction [231]. The bridged binuclear platinum(I) complex, **158**, could be obtained either by treatment of $[Pt(CO)_2(PPh_3)_2]$ with the alkyne in an atmosphere of carbon monoxide, or by reaction of carbon monoxide with $[Pt(PPh_3)_2(R_2C_2)]$. The structure of **158** was determined by X-ray diffraction [232].

Treatment of $[Pt\{P(CMe_3)_3\}_2]$, $[H_2Pt\{P(CMe_3)_3\}_2]$ or $[\{HPt(\mu-H)(P\{CMe_3\}_3)\}_2]$ with carbon monoxide yielded the trimer $[Pt_3(\mu-CO)_3\{P(CMe_3)_3\}_3]$. Reaction of this trimer with a limited supply of iodine gave the platinum(I) dimer, **159**, which is stabilised by the steric bulk of the phophines. This is in contrast to earlier studies using an excess of iodine, in which $[Pt(CO)\{P(CMe_3)_3\}I_2]$ was formed and cyclometallated to give $[\overline{Pt(CO)\{P(CMe_3)_2CMe_2C}H_2\}I_2]$ which dimerised with loss of CO [233].



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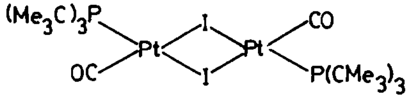
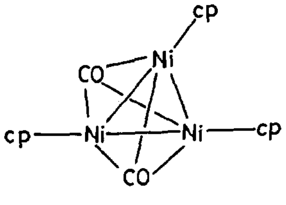


159

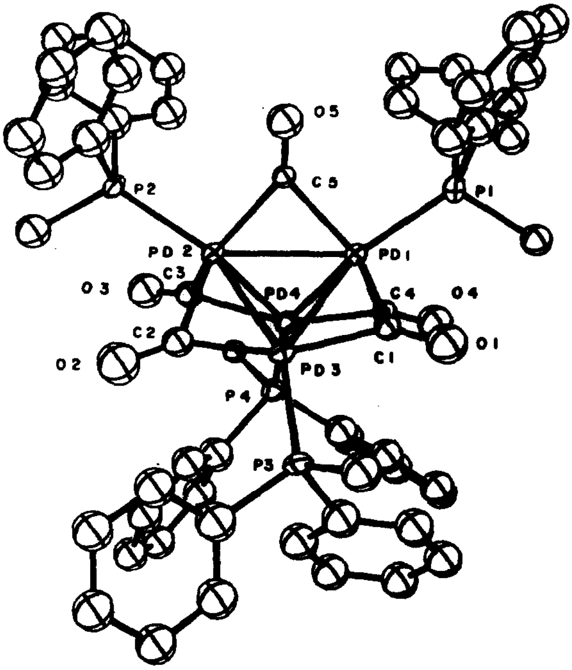
Two reviews have dealt with large metal carbonyl clusters, in particular their catalytic behaviour and their use as models for metal crystallites [234,235]. Extended Hückel molecular orbital calculations have been performed on trinuclear carbonyl complexes of iron, cobalt and nickel. The differences between the structural forms and the rigidity of the complexes containing $[Ni_3(CO)_6]^{2-}$ and $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ were rationalised on the basis of frontier orbital calculations [236]. Detailed consideration has been given to the ^{13}C nmr spectra of $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, $[Ni_9(CO)_{18}]^{2-}$ and $[Ni_{12}(CO)_{21}H_{4-x}]^{x-}$ (x = 2 or 3). At -80 °C the ^{13}C nmr spectra of the $\{Ni_6\}$, $\{Ni_9\}$ and $\{Ni_{12}\}$ complexes were consistent with the reported solid state structures. As the temperature is raised terminal and bridging carbonyls exchange, with the lowest energy process being exchange on the outer triangular faces of the cluster. In $[HNi_{12}(CO)_{21}]^{3-}$ hydrogen migration also occurs. Treatment of $[Ni_6(CO)_{12}]^{2-}$ with $[Ni(CO)_4]$ gave, reversibly, $[Ni_7(CO)_{14}]^{2-}$ which is an intermediate in the formation of $[Ni_9(CO)_{18}]^{2-}$. The structure of this new 102 electron cluster was determined and its fluxional behaviour probed [237].

The cluster $[Ni_3(Cp)_3(CO)_2]$, **160**, was used immobilised on SiO_2/Al_2O_3 to catalyse ethene oligomerisation with high turnover [238]. Reaction with PPh_3 gave $[Ni(PPh_3)_2(CO)_2]$, $[Ni(PPh_3)_3(CO)]$ and $[Ni(Cp)_2]$ as the rather unusual primary products [239]. The tripod ligand, $HC(PPh_2)_3$, has been shown to act as a template for nickel cluster formation; reaction with an excess of $[Ni(CO)_4]$ gave $[Ni_3(tripod)(CO)_6]$, the first reported nickel(0) trimer. The intermediates in the reaction are $[Ni(tripod)(CO)_2]$ and $[Ni_2(tripod)(CO)_5]$. Carbon monoxide is liberated in the formation of these species, and since it inhibits trimer formation it must be removed as it is formed to obtain the product in good yield [240].



160

Reaction of $[PdL_2(NO_2)_2]$ with CO yielded $[Pd_4(CO)_5L_4]$ (L = PPh_3, $PMePh_2$ or $PPhMe_2$). The complex with L = $PMePh_2$, **161**, was characterised by X-ray diffraction; its structure closely resembles that of $[Pt_4(CO)_5(PMe_2Ph)_4]$ [241]. Syntheses of $[Pd_{12}(CO)_{15}(PEt_3)_7]$, $[Pd_{12}(CO)_{15}(PBu_3)_7]$ and $[Pd_{12}(CO)_{17}(PBu_3)_5]$ from $Pd(OCOMe)_2$, CO and PR_3 in varying ratios in tfaH have been described [242].



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The species $[Pt_{19}(CO)_{22}]^{4-}$ and $[Pt_{13}(CO)_{17}]^{4-}$ were obtained by thermal decomposition of $[Pt_3(CO)_6]_n^{2-}$ (n = 2 or 3). In acid these dimerised to yield respectively $[H_4Pt_{38}(CO)_{44}]^{2-}$ and $[H_2Pt_{26}(CO)_{32}]^{2-}$ [243]. The field desorption mass spectra of $[Pt_3(CO)_3(PPh_3)_4]$, $[Pt_4(CO)_5(PPh_3)_4]$ and $[Pt_5(CO)_6(PEt_3)_4]$ all showed M^+ and $\{M-(CO)_n\}^+$ peaks [244].

The syntheses and reactivities of heteronuclear carbonyl clusters have provided many of the most interesting results of this year. Heteronuclear dimetal complexes may be formed by combining 17 electron metal carbonyl units. Among those studied were $\{M(CO)_3(Cp)\}$ (M = Mo, Cr or W), $\{Mn(CO)_5\}$, $\{Co(CO)_4\}$, $\{Fe(CO)_2(Cp)\}$ and $\{Ni(CO)(Cp)\}$. All the possible combinations were synthesised from the homonuclear dimers in benzene. For those containing the $\{Ni(CO)(Cp)\}$ unit the equilibria lie on the side of the mixed complexes [245]. A survey of *n*-vertex metal carbonyl cluster polyhedra for *n* = 12, 13, 14, 15 and 16 included $[Co_4Ni_2(CO)_{14}]^{2-}$, $[Mo_2Ni_3(CO)_{16}]^{2-}$, $[Rh_5Pt(CO)_{15}]^{-}$ and $[W_2Ni_3(CO)_{16}]^{2-}$ [246].

Reactions of either $[Ni(Cp)_2]$ or $[\{Ni(Cp)(CO)\}_2]$ with $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$, or their alkyne derivatives, have yielded many new heteronuclear complexes. The structures of **162** and **163** were established by X-ray diffraction. In **162** one of the CO ligands attached to the basal iron is incipiently semi-bridging [247]. The formation of clusters is not in general very selective, but yields are influenced by relative stabilities [248]. The structure of $[NiFe_2(Cp)(CO)_6(C_2CMe_3)]$, **164**, has also been determined by diffraction methods [249]. The reaction of $[\{Ni(Cp)\}_2(\mu\text{-}C_2Ph_2)]$ with $[Fe_2(CO)_9]$ yielded $[FeNi_2(Cp)_2(CO)_3(C_2Ph_2)]$ and $[Fe_2Ni_2(Cp)_2(CO)_6(C_2Ph_2)]$, providing better syntheses for these known compounds. The tetranuclear species reacted with R_3P to give $[NiFe_2(Cp)(CO)_6(C_2Ph_2)]^-[Ni(Cp)(PR_3)_2]^+$, **165** [250]. New heteronuclear carbide complexes have been synthesised by reactions (27) - (29) [251].

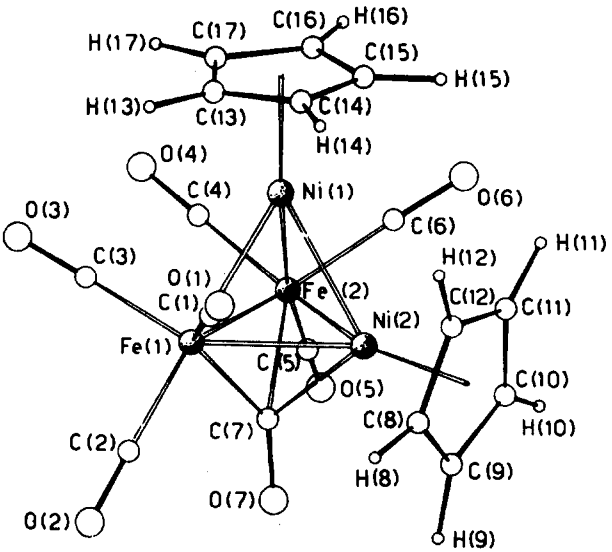
$$[Fe_5C(CO)_{14}]^{2-} + [Ni(cod)_2] \longrightarrow [NiFe_5C(CO)_{13}(cod)]^{2-} \qquad (27)$$

$$[Fe_5C(CO)_{14}]^{2-} + [Ni(cod)_2] + CO \longrightarrow [NiFe_5C(CO)_{15}]^{2-} \qquad (28)$$

$$[Fe_5C(CO)_{14}]^{2-} + [\{(\eta^3\text{-allyl})PdCl\}_2] \longrightarrow [PdFe_5C(CO)_4(\eta^3\text{-allyl})]^{-} \qquad (29)$$

Treatment of $[HRu_3(CO)_9(Me_3CC\equiv CH)]$ with $[\{Ni(Cp)(CO)\}_2]$ gave **166** in which the $\{Ni(Cp)\}$ unit bridges the $\{Ru\text{-}Ru\text{-}C\}$ face of the starting material. One of the carbon atoms of the alkyne ligands interacts with all four metal centres, the other with only one [252]. The allyl ruthenium cluster $[HRu(CO)_9(RCCHCR')]$ yielded a complex of stoicheiometry $[NiRu_3(Cp)(CO)_8(RCCHCR')]$ as the major product. For $R \neq R'$ two isomers could be isolated. X-ray diffraction data showed that the cluster adopts the butterfly structure, **167**, the other isomer having the ethyl and methyl groups transposed [253]. Treatment of $[Ru_3(CO)_{12}]$ with $[Ni(Cp)_2(RC_2R')]$ also yielded mixed clusters, the structure of the chiral species $[NiRu_2(Cp)_2(CO)_3(\mu_3\text{-}CO)(C_2Ph_3)]$ being determined by X-ray diffraction [254]. The structure of $[NiRu_3(Cp)(CO)_9(HC\equiv CCMe_3)]$, **168**, has also been determined [249].

$[Rh_6(CO)_{15}]^{2-}$ reacted with either $[Ni(CO)_4]$ or $[Ni_6(CO)_{12}]^{2-}$ to give



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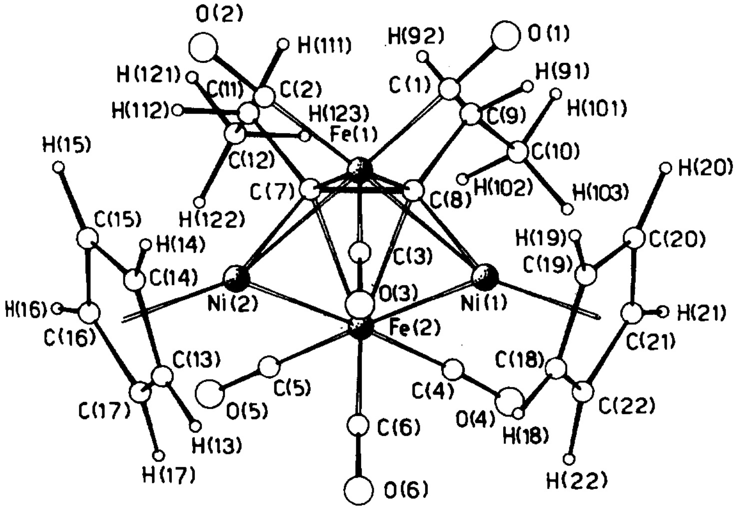

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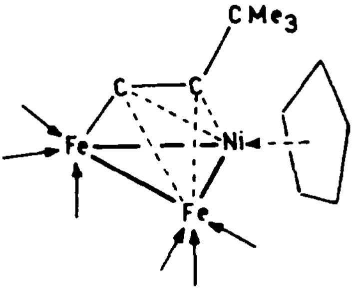

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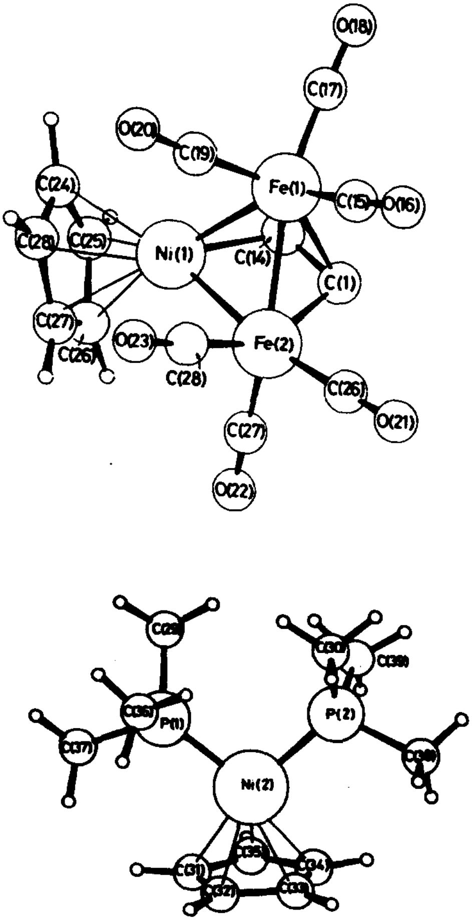

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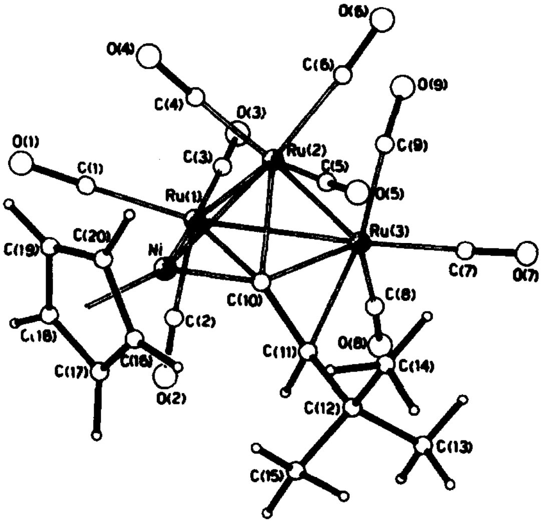

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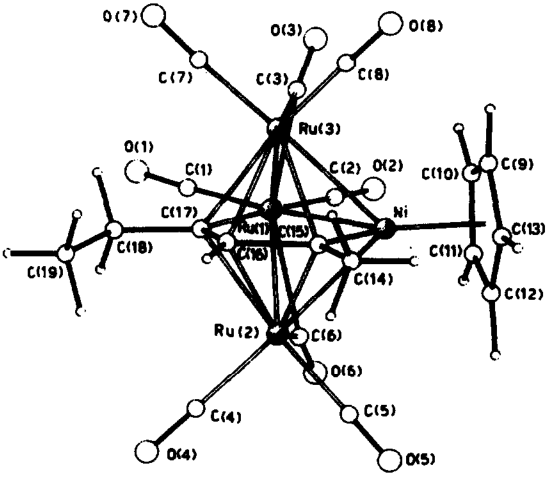

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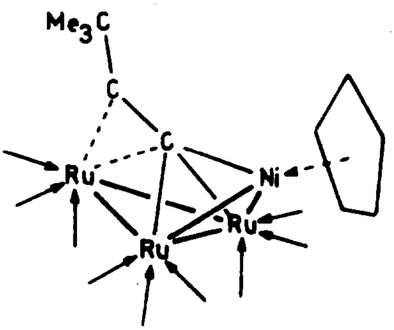

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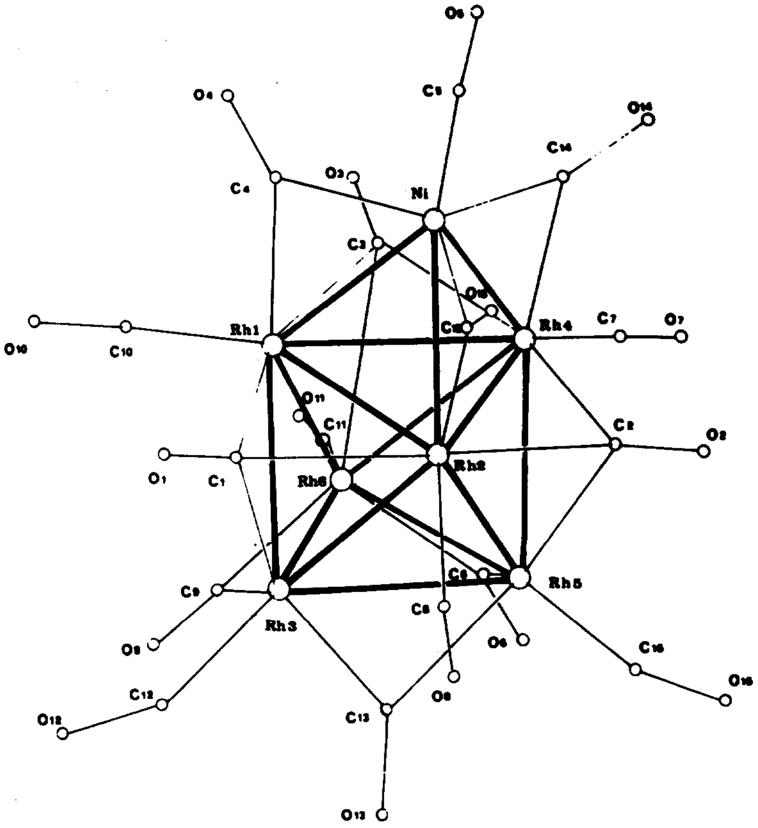


169 (Reproduced with permission from [255])

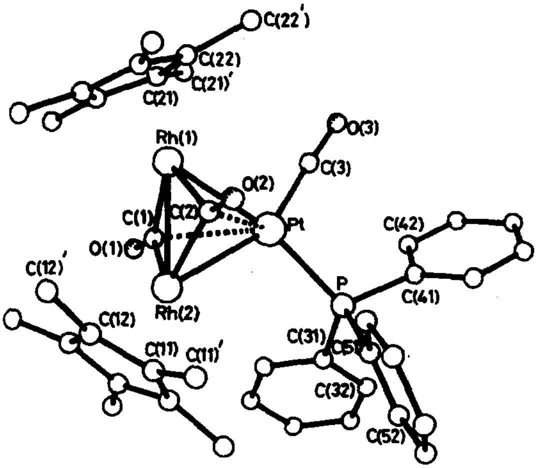
$[NiRh_6(CO)_{16}]^{2-}$, **169**, the structure of which was analysed by diffraction methods. The structure is based on a distorted octahedron of rhodium atoms, capped on one face by nickel. Three carbonyls edge-bridge Ni-Rh bonds, three span bonds of the bottom triangular face, three face bridge three of the six faces of the rhodium antiprism and seven are terminal [255]. $[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ reacted with $[Pt(cod)_2]$ to give $[Rh_2Pt(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2(cod)]$. $[Pt_2(CO)_2(Cp)_2]$ gave $[Rh_2Pt(\mu\text{-}CO)_2(CO)_2(\eta^5\text{-}C_5Me_5)_2]$ (*via* $\{Pt(CO)_2\}$) whilst reaction with $[Pt(PPh_3)_2(C_2H_4)]$ yielded **170** in which two of the carbonyls are semi triply-bridging [256].

Treatment of $[Fe_3(CO)_{11}]^-$ with MCl_2, $K_2[MCl_4]$, $[M(PhCN)_2Cl_2]$ or $[M(Et_2S)_2Cl_2]$ in a 1:0.7 molar ratio gave $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt). Both complexes could be isolated as $[Me_3NCH_2Ph]^+$ salts and their structures were established by X-ray diffraction. In both cases two $\{Fe_2(CO)_8\}$ units are joined to a central palladium or platinum atom, which adopts rectangularly distorted square planar coordination. Each iron bears three terminal CO groups, with a fourth semi-bridging, a somewhat unusual arrangement, at least for palladium. The molar ratio of the reactants is critical. An excess of platinum(II) gave $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_4Pt_6(CO)_{22}]^{2-}$, whilst an excess of palladium(II) resulted in the formation of $[Fe(CO)_5]$ and the precipitation of metallic palladium. A further group of clusters was produced on reaction of $[Fe_4(CO)_{13}]^{2-}$ with $[PdCl_4]^{2-}$. $[Fe_4Pd(CO)_{16}]^{2-}$ was one product but $[Fe_6Pd_6(CO)_{24}]^{4-}$ was also produced in equilibrium with $[HFe_6Pd_6(CO)_{24}]^{3-}$, **171** [257]. $[Fe_4Pt(CO)_{16}]^{2-}$ is an intermediate in the formation of $[Fe_3Pt_3(CO)_{15}]^{2-}$ from platinum(II) and $[Fe_3(CO)_{11}]^{2-}$. When an excess of platinum(II) was used paramagnetic $[Fe_3Pt_3(CO)_{15}]^-$ was formed by oxidation. $[Fe_4Pt_6(CO)_{22}]^{2-}$, formed by loss of $\{Fe(CO)_4\}$ and condensation, could also be isolated. It was suggested that the $[Fe_6M_6(CO)_{24}]^{2-}$ structures are formed from $[Fe_3M_3(CO)_{15}]^{2-}$ by loss of CO and condensation along the C_3 axis in a staggered conformation [258].

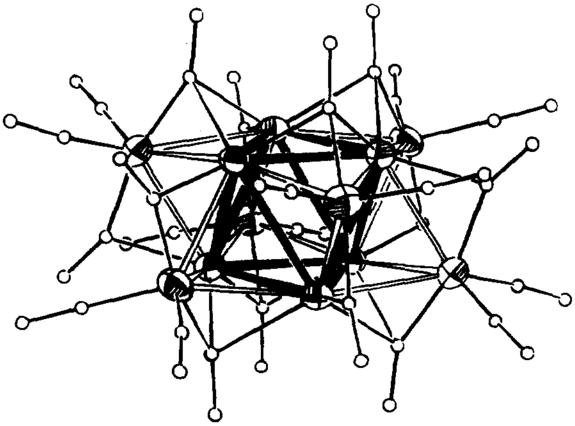
7. METAL ALKENE AND METAL VINYL COMPLEXES

Alkali metal-transition metal π-complexes, including some of nickel, palladium and platinum, have been reviewed [259]. The dissociation energy of the nickel-ethene bond has been calculated using an *ab initio* core potential to account for the chemically inactive core electrons [260].

Calculations on the electronic structure of $[PtLCl_3]^{n-}$ included consideration of the complex for which L = C_2H_4 [224]. The differences between *pseudo* square-planar and *pseudo* tetrahedral coordination for $[PtL(PH_3)_2]$ (L = C_2H_4, C_2H_2 or CS_2) were examined by CNDO. The Pt(dπ) - L(π*) interaction is stronger in the *pseudo* square-planar arrangement, and the Pt-P bond is also



170 (Reproduced with permission from [256])

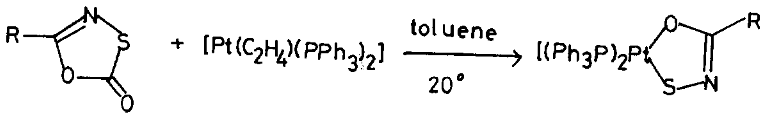


171 (Reproduced with permission from [257])

strengthened [261]. An SCF MO study of $\{Pd(C_2H_4)\}$ suggested that metal ligand bonding was relatively weak [262]. Photolysis of *cis*-$[Pt(C_2H_4)(4\text{-}MeC_5H_4N)Cl_2]$ at the charge transfer $(5d\rightarrow\pi^*(C_2H_4))$ band gave dissociation of ethene with a quantum yield close to unity. Irradiation at longer wavelengths also caused dissociation but less effectively [263].

The ease with which ethene is displaced from $[M(PPh_3)_2(C_2H_4)]$ (M = Pd or Pt) has led to the use of these complexes in the preparation of various coordination compounds [264], as for example in reactions (30) (E = S, Se or Te, M = Pd or Pt) [265] and (31) [266].

$$[Fe_2(\mu_2\text{-}E)_2(CO)_6] + [M(PPh_3)_2(C_2H_4)] \longrightarrow [(CO)_6Fe_2(\mu_3\text{-}E)_2M(PPh_3)_2] \qquad (30)$$



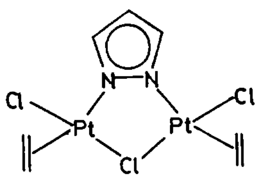
(31)

The kinetics of the reaction of ethene with $[PtCl_n(H_2O)_{4-n}]^{(2-n)+}$ (n = 0, 1, 2, 3 or 4) have been investigated. The results demonstrated that ethene is an inefficient entering ligand. Changes in observed *cis*- and *trans*-effects are consistent with an associative pathway [267]. At -80 °C $[Pt(PPh_3)_3]$ reacted with ethene to yield $[Pt(PPh_3)_2(C_2H_4)]$. Hexene reacted similarly but the reaction of cyclohexene was much slower. At -100 °C the ^{31}P nmr signals of $[Pt(PPh_3)_4]$ and $[Pt(PPh_3)_2(C_2H_4)]$ could be observed. Also at -100 °C butadiene yielded an η^2-complex [268]. Reaction of $[Pt_2(PPr_3)_2Cl_4]$ with a ligand, L, yielded, reversibly, *trans*-$[Pt(PPr_3)LCl_2]$. Carbon monoxide and ethene were the "strongest" ligands used, with the equilibrium being almost entirely in favour of the monomer. In both cases the initially formed *trans*-product was slowly converted to the *cis*-isomer. PhC≡CH was a less effective ligand with only a small amount of the π-bonded form [269].

The structure of *cis*-$[Pt(C_2H_4)(2,6\text{-}Me_2C_5H_3N)Cl_2]$ has been determined by X-ray diffraction. The Pt-Cl distance *trans* to nitrogen is 2.285(6) Å whereas that *trans* to ethene is 2.337(6) Å, demonstrating the *trans* influence of η^2-(C_2H_4) [270]. Treatment of $K[Pt(C_2H_4)Cl_3]$ with pyrazoline yielded **172**. The bridging mode of coordination is certainly unusual, but the complex is not polymeric [271]. In **173** the axial halogens as well as ethene are readily replaced with retention of the trigonal bipyramidal structure. Exchange of alkenes occurred *via* **174** with *cis*-alkenes being more readily coordinated [272].

Reaction of $[Pt(C_2H_4)L_2]$ with CF_3SO_3H yielded ethane (30 - 75 %), $[PtL_2(OSO_2CF_3)_2]$ (78 %) and a little ethene. HCl, by contrast, yielded *trans*-$[HPtL_2Cl]$, indicating that protonation to yield successively

$[HPt(C_2H_4)L_2]^+$, $[EtPtL_2]^+$, $[EtPtL_2X]$ and finally $[PtL_2X_2]$ and C_2H_6 requires a very acidic medium [273].



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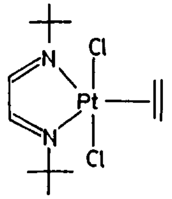

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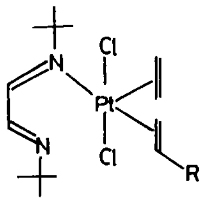
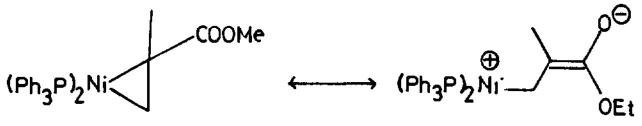


174

The half wave potentials for $[Pt(NH_3)_2LCl]^+$ (L = C_2H_4, C_3H_6, $CH_2{=}CHCH_2OH$ or $PhCH{=}CH_2$) have been determined. The differences between the reduction pathways of the *cis*- and *trans*-forms allows their ready identification [274].

The structure of $[Ni(PPh_3)_2\{CH_2{=}C(Me)COOEt\}]$ has been determined by X-ray diffraction. Only the carbon-carbon double bond of the alkene is coordinated, with the COOEt group directed away from nickel. The nickel carbon distances may be explained by invoking the two resonance forms **175a** and **175b** [275]. $[NiL_3]$ complexes react with alkenes to yield $[Ni(alkene)L_2]$. When L = PCy_3 and the alkene is 1-hexene both this and the species $[Ni(hexene)_2(PCy_3)]$ may be detected. The second species was not detected in platinum or palladium analogues [276].



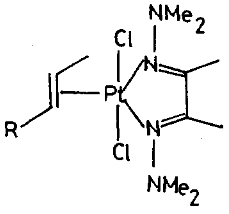
175a

175b

Phenylcyclooctatetraene forms 2:1 and 1:1 complexes with nickel(0). The structures of both were established by X-ray diffraction [277]. $[Ni(cod)_2]$ reduces $[Fe(Cp)(CO)_2Cl]$, $[Mn(CO)_5Cl]$ and $[(\eta^3\text{-}Cp)Fe(CO)_3Cl]$ to yield binuclear products [278].

Reaction of $[Pd(Cp)(PR_3)Br]$ with an alkene and AgX yielded the new class of stable compounds $[Pd(Cp)(PR_3)(alkene)]X$ (R = Ph, Et or Bu; X = $[ClO_4]$ or $[BF_4]$). The ^{13}C nmr spectral data for the complexes in which alkene = $ArCH{=}CH_2$ correlate with σ^+. The alkenes rotate more readily about the Pd-alkene bond than in the platinum analogues, due to less effective π-back-bonding [279]. The thermodynamic parameters for alkene rotation in $[Pt(diamine)(alkene)Cl_2]$ (diamine = R,R or S,S-$(PhCHMeNMeCH_2)_2$) were determined by nmr spectroscopy [280].

η^2-Complexes of alkenes with square-planar platinum(II) have been reviewed, with particular reference to the CD spectra of coordinated alkenes in complexes with chiral amines. When [Pt(C_2H_4)(L-diamine)Cl] reacted with *trans*-2-butene or 2-methyl-2-butene there was considerable asymmetric induction in both the kinetic and the thermodynamic products [281]. Crystallisation of [S-PhCHMeNMe$_3$]$^+$[Pt(alkene)Cl$_3$]$^-$ generally affords a single diastereoisomer through a second order asymmetric transformation. The coordination of *trans*-2-butene was found to be **S,S** [282]. *Trans*-[PtL(**S**-2-methyl-2-butene)Cl$_2$] (X = 4-X-pyridine or 4-X-aniline) may be substituted by a variety of alkenes. A kinetic investigation (by CD) revealed that the σ-character of the platinum nitrogen bond plays an important rôle in the kinetic *trans*-effect [283]. The salt [S-PhCH(Me)NMe$_3$]$^+$[Pt(MeCH=CR$_2$)Cl$_3$]$^-$ reacted with dihydrazones to give **176**, the first five-coordinate platinum(II) complex with an asymmetrically bound prochiral alkene as the only asymmetric ligand [284]. Reaction of a mixture of **177**, **178** and **179** with Na$_2$[PtCl$_4$] yielded only complexes of **177**, which is bonded to platinum through both the sulphur atom and the alkene [285].



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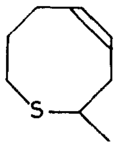

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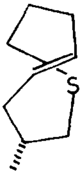

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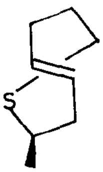
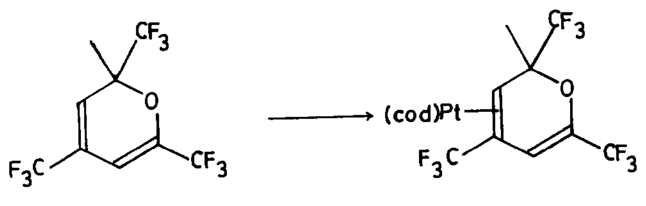


179

Trans-[HPt(PPh$_3$)$_2$(OClO$_3$)] reacted readily with L (L = C_2H_4 or C_3H_6) to give *trans*-[HPtL(PPh$_3$)$_2$][ClO$_4$] [225]. The species [Pt(PR$_3$)QCl$_2$] have been prepared from the reaction of the chloro bridged dimers with Q. X-ray diffraction data are available for the complex in which Q = CH$_2$=CHCH$_2$OH and PR$_3$ = PMe$_2$Ph. The hydroxyl group is bent away from platinum and is hydrogen bonded to chlorine. Nmr spectroscopic data imply that only one conformation is significantly populated at room temperature, and that there is no fast exchange with the free alcohol. At low temperatures the initial bridge-splitting reaction yielded *trans*-[Pt(PR$_3$)QCl$_2$] in which Q is both *O*- and *C*-bonded. Above 260 K isomerisation to the *cis*-compound occurred [286].

^{195}Pt nmr spectroscopic data for a number of platinum-tin complexes including *trans*-[Pt(PPh$_3$)$_2${(EtOOC)C=CHCOOEt}(SnCl$_3$)] have been reported [287]. [Pt(cod)$_2$] reacted with 180 to give 181, characterised by X-ray diffraction techniques. The cyclooctadiene ligand may be readily replaced by PPh$_3$, Me$_3$CNC or 2,6-Me$_2$C$_6$H$_3$NC [288].



180 181

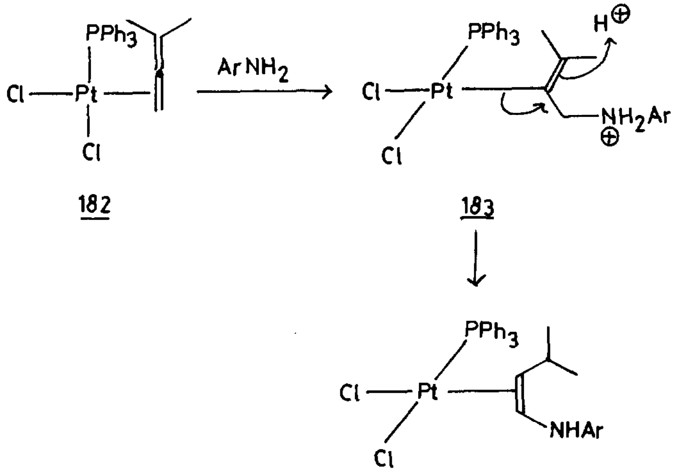
The reaction of $K[Pt(alkene)Cl_3]$ with a diamine was shown to yield $[Pt(diamine)(alkene)Cl_2]$. The diamine used was $\{PhCH(Me)NMe_2CH_2\}_2$ and the alkenes included C_2H_4, C_3H_6, $CH_2{=}CHCHO$, $CH_2{=}CHCN$, *trans*-NCCH=CHCN, maleic anhydride and maleimide. X-ray diffraction data were obtained for the ethene and propene complexes. ^1H nmr spectroscopic data were discussed in terms of alkene rotation. Solid state data as well as the behaviour in solution indicate that asymmetric induction depends on the configuration of the coordinated nitrogen atoms in the complexes. $\Delta G^{\ddagger}$ barriers for alkene rotation in these trigonal bipyramidal complexes are greater than for square planar platinum(II) species [289].

$Na_2[MCl_4]$ (M = Pt or Pd) reacted with L = $Cy_2PC{=}CPCy_2(CF_2)_n$, giving $[PdLCl_2]$ [290]. {Platinum(alkene)(adenine)} complexes have been reported. The π-acidity of the purine causes weakening of the bond to the *trans*-alkene [291].

The reactions of $[M(C_2H_4)L_n]$ with nucleophiles have been the subject of a theoretical study. One of the species investigated was $[Ni(C_2H_4)(PH_3)_2]$, and it was concluded that activation occurred by geometric deformation with slippage of the $\{ML_n\}$ fragment along the alkene [292]. The reaction of the allene complex, **182**, with $ArNH_2$ yielded successively **183** and **184**, the first reported η^2-coordinated enamine. The structure of **184** was determined by X-ray diffraction [293]. When the coordinated allene was $RCH{=}C{=}CMe_2$, **185** was formed, and could be carbonylated to **186** [294].

Further studies reported interactions of amines with coordinated alkenes. **187** reacted with an amine, am, to give the rather unstable **188**. This product could be stabilised by the presence of π-acceptors in the Y and Z positions [295]. Using *cis*-$[Pt(C_2H_4)(amine)Cl_2]^+$, three products, **189**, **190** and **191**, may in principle be obtained by reaction with a further equivalent of amine. **189** was readily identified by nmr spectroscopy, but **190** is a more doubtful intermediate [296].

Treatment of **192** with Me_2NH yielded the cyclic complex, **193**, which was characterised spectroscopically, demonstrating that the formation of such cyclic species is general to platinum(II) chemistry and is not confined to phosphine complexes [297]. Warming of the five-coordinate complex $[Pt(C_2H_4)(Me_4en)Cl_2]$, 194, from -10 °C to 100 °C gave disproportionation to $[Pt_2(C_2H_4)_2(Me_4en)_3Cl_2]^{2+}$ and $[Pt(C_2H_4)Cl_3]^-$. The species of stoicheiometry $[Pt_2(C_2H_4)_2(Me_4en)_3Cl_2]^{2+}$ has the structure $[(Me_4en)ClPtCH_2CH_2NMe_2CH_2CH_2NMe_2CH_2CH_2Pt(Me_4en)Cl]^{2+}$, resulting from the attack of the amine on coordinated ethene [298]. 194, however, dissociates readily to the monochloride, and undergoes substitution reactions [299].



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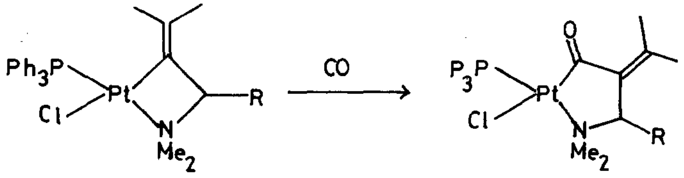

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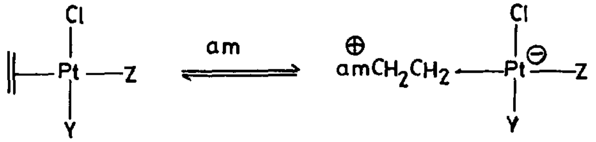

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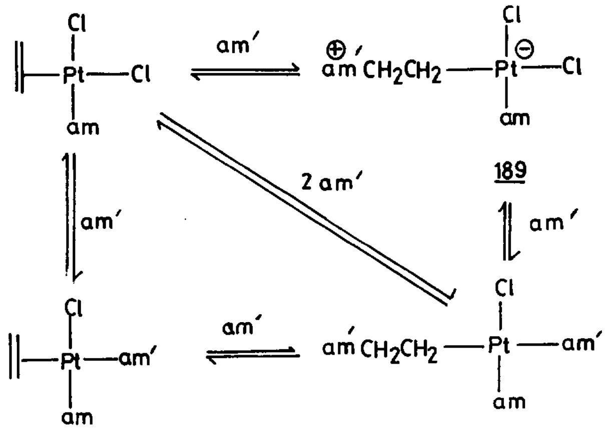

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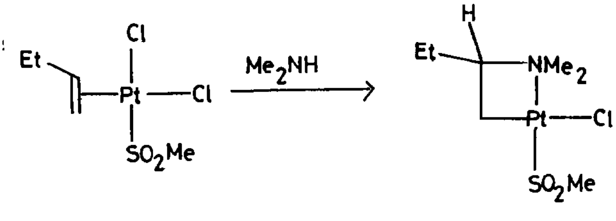
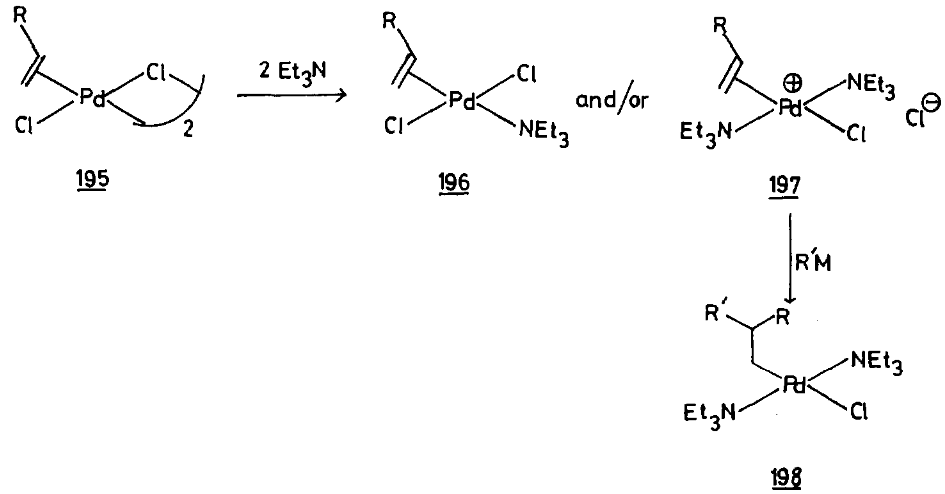
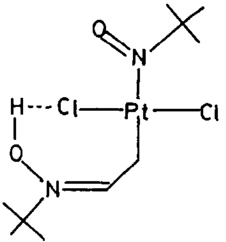


192 193

[Pd(Cp)(C_2H_4)(PR_3)][BF_4] reacted with nucleophiles to yield [$NuCH_2CH_2Pd$(Cp)(PR_3)][BF_4] when Nu = [CH(COOMe)$_2$]$^-$. Amine nucleophiles, by contrast, yielded the products of alkene displacement [279]. More generally [Pd(C_2H_4)LCl_2] reacts with [RR'C(Li)(COOR")] to give [RR'C(COOR")$CH_2CH_2PdL_2Cl$] (L = Et_3N, R" = Me or Et) Decomposition gave RR'C(Et)COOR" and RR'C(CH=CH_2)COOR" in variable ratios [300].

Alkylation of RCH=CH_2 coordinated to palladium requires the presence of two equivalents of Et_3N, proceeding *via* **195**, and **196** or **197**. Attack of R'M is more facile on **196** giving **198** and its regioisomer. Regioselectivity depends on R, R' and the reaction conditions. The intermediate may be reduced by H_2 to RR'CHCH_3 or may β-eliminate to RR'C=CH_2 [301]. Stabilised anions including enolates and malonates have also been used as nucleophiles. Acylation of intermediates such as 198 gave low yields of carboxylate esters [302]. [Pt(C_2H_4)Cl_3]$^-$ reacted with Me_3CNO to give 199 and 200 in the ratio 90:10. The reaction mechanism is unknown, but the product is the first example of this type of nitrosoalkane complex [303].





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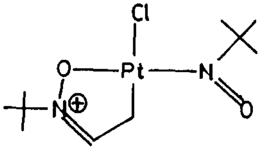

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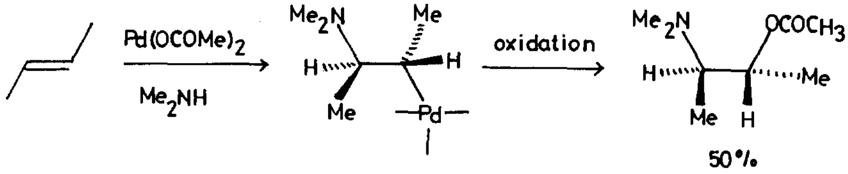
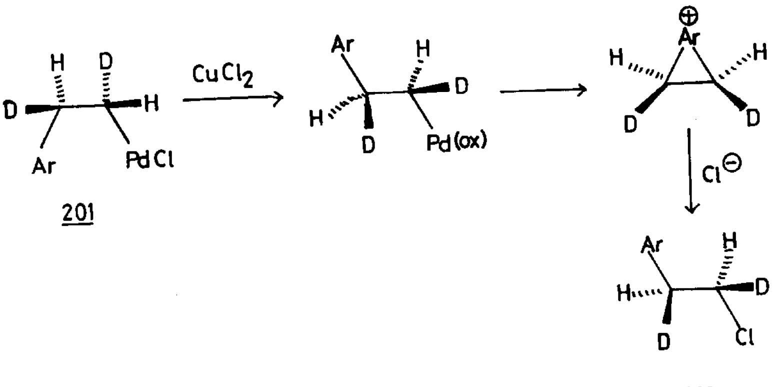
Attack of Me_2NH on a palladium coordinated alkene is responsible for the initial step of Scheme 1. *Trans*-alkenes react faster than their *cis*-analogues in the rate controlling step [304]. *Cis*-addition of ArPdCl to *trans*-CHD=CHD gave **201**. On oxidation, aryl participation results in the formation of **202** with considerable stereoselectivity [305].



Scheme 1 Oxyamination of alkenes



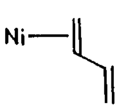
201

202

Two reaction pathways may be discerned for the reaction of [$Pd_2(dba)_3$] with Ph_3Q (Q = P, As or Sb). For the associative pathway, reactivities are in the order Sb > As > P, indicating the importance of π-acceptor ability to the palladium(0) complex. However, with the palladium(II) species, [$Pd(Ph_4C_4)Cl_2$], the rates for the associative pathway are in the order P > As > Sb, showing a dependence on σ-donor ability [306]. ^1H nmr spectroscopic studies of [$M(dba)_3$] (M = Pd or Pt) indicated that the coordinated alkene is fixed in an S-*trans* conformation with the uncoordinated double bond fluxional around an S-*cis* position [307].

Thermolysis of [$Pd(CH_2{=}CHCOOMe)L_2Cl$] or treatment with [$Pd(MeCN)_2Cl_2$] gave dimethyl muconate. $H[BF_4]/CH_2{=}CHCOOMe$ yielded dimethyl 2-hexenedioate. Both routes involve carbene and hydridic intermediates [308].

The reaction between nickel atoms and butadiene under matrix cryogenic conditions has been monitored by optical spectroscopy. A number of species, including 203-206 were identified. Somewhat surprisingly, these seem to be favoured over chelated species [309]. Both 1,4-pentadiene and 2,5-diphenyl-1,5-hexadiene have been shown to react with either $Na_2[PtCl_4]$ or *cis*-[$Pt(PhCN)_2Cl_2$] to give *cis*-[$Pt(diene)Cl_2$] complexes, which could be fully characterised by ir and nmr spectroscopy and X-ray diffraction [310].



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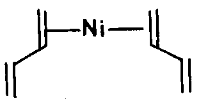

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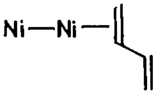

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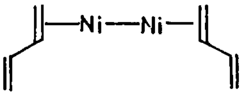

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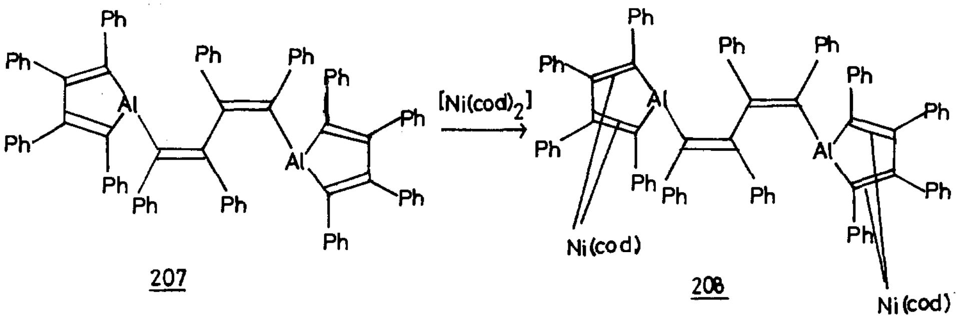
The ir and Raman spectra of the well-known complexes [$M(cod)Cl_2$] (M = Pd or Pt) have been recorded and assigned. Both the total metal ligand interaction and the π-interaction are greater for the platinum complex [311]. An analogous study of [M(norbornadiene)Cl_2] gave broadly similar results [312]. [Ni(cod)$_2$] reacted with **207** in toluene to give **208**. A bis nickel complex was also obtained from **209**. On reaction with $NiBr_2$, however, both **207** and **209** yielded octaphenyl cyclooctatetraene. In both cases the reaction proceeds *via* a nickelacyclopentadiene which collapses to a tetraphenylcyclobutadiene complex prior to dimerisation [313].



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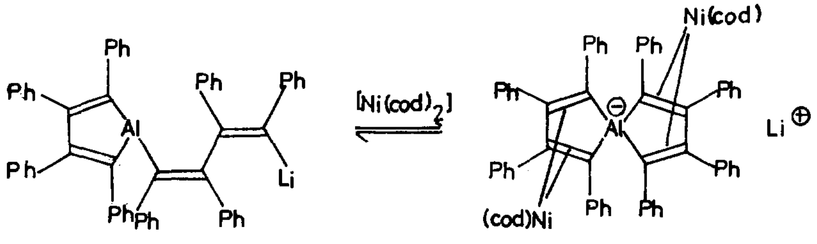

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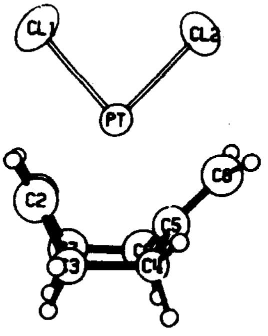
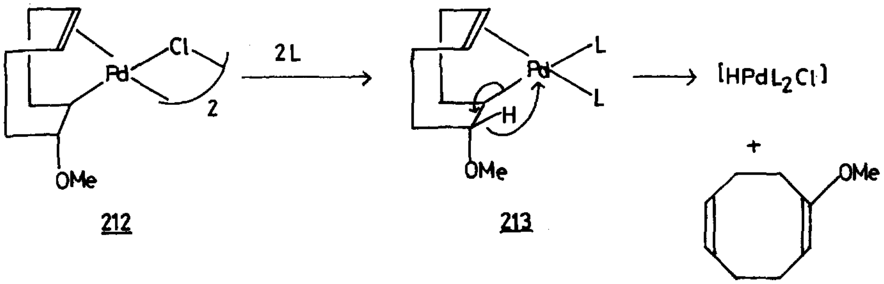
210

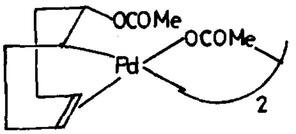
There is considerable interest in preparing complexes, which because of particular geometric constraints, have "in plane" alkene coordination. A new complex of this type is the monomeric species, **211**, which was characterised by X-ray diffraction [314].



211 (Reproduced with permission from [314])

[Pd(cod)Cl$_2$] reacted with sodium hydroxide in methanol to yield [{Pd(C$_8$H$_{12}$OMe)Cl}$_2$], **212**, the product of methoxypalladation. Treatment with hindered phosphine ligands, L (L = PCy$_3$, P(CHMe$_2$)$_3$, PMe(CMe$_3$)$_2$ or PMe(CMe$_3$)$_2$) yielded [HPdL$_2$Cl] *via* **213**, the octadiene being obtained as a mixture of isomers. [HPd{P(CMe$_3$)$_3$}$_2$Cl] reacts further by ligand metallation to give [{Pd({Me$_3$C}$_2$PCMe$_2$CH$_2$)Cl}$_2$] [315]. Some earlier anomalous results reporting the acetoxypalladation of *cis,trans*-1,5-cyclooctadiene have now been fully explained. The diene does react *via* the expected *trans*-acetoxypalladation of the *trans* double bond to give the *cis*-adduct, **214**. The same species was obtained by photoisomerisation of the *trans*-acetoxypalladium complex obtained from *cis,cis*-1,5-cyclooctadiene [316]. Cyclooctadiene reacted with Pd[ClO$_4$] to give **215**. The diene ligand may be readily replaced by phosphines, arsines or chelating diamines [317].





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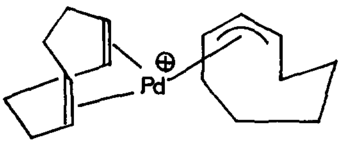
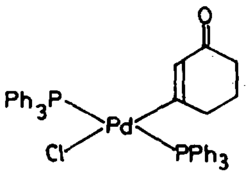


215

The σ-vinyl complex, **216**, prepared by oxidative addition of the β-chloro enone to palladium(0) is, surprisingly, extremely stable. A range of chelating ligands including dppe, Et$_2$NCS$_2$H and phen reacted to yield *cis*-complexes by replacement of PPh$_3$ [318].



216

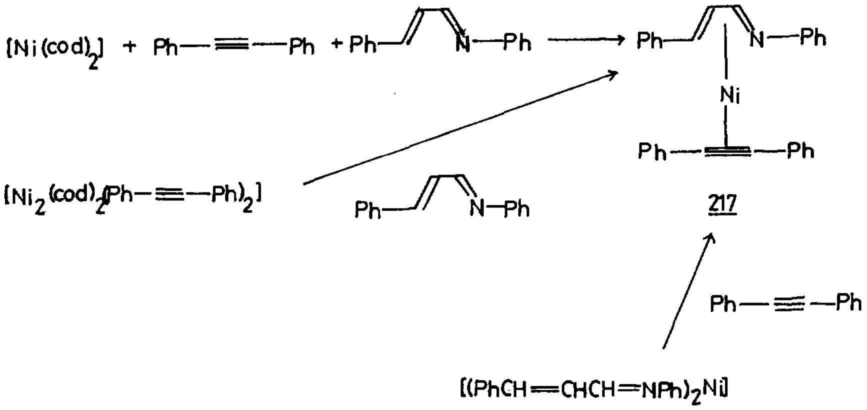
Nickel(0) centres with a high electron density form stable η^2-complexes of ArCHO with a considerable degree of charge transfer (reaction (32)) [319].

$$[Ni(C_2H_4)(PCy_3)_2] + RCHO \longrightarrow [Ni(RCHO)(PCy_3)_2] + C_2H_4 \qquad (32)$$

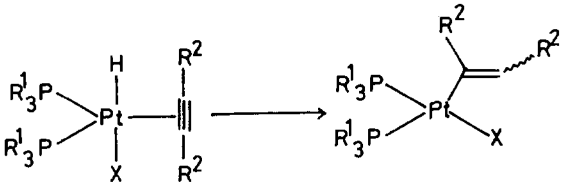
8. METAL ALKYNE AND METAL ALKYNYL COMPLEXES

The important work of Maitlis on palladium complexes of alkynes and cyclobutadienes has been reviewed [320].

The complex 217 has been synthesised by three different routes. $[Ni(Me_4en)(Ph\text{-}C\equiv C\text{-}Ph)]$ was prepared in a similar manner [321]. Treatment of $[\{Ni(Cp)CO)\}_2]$ with $C_6F_5\text{-}C\equiv C\text{-}C_6F_5$ yielded $[Ni(Cp)(\mu\text{-}C_6F_5\text{-}C\equiv C\text{-}C_6F_5)Ni(Cp)]$ which was characterised by X-ray diffraction. The μ-ethyne is bonded to both nickel centres and the carbon-carbon bond length is increased to 1.362 Å from 1.2 Å [322].



Another group have reported the structure of $[Pt(cyclooctyne)(PPh_3)_2]$. Similar results were obtained for cyclohexyne, cycloheptyne and acyclic alkyne complexes [323]. A full paper has given details of the reactions of $[Pt(cod)_2]$ with $R^1\text{-}C\equiv C\text{-}R^2$ to yield $[Pt(R^1\text{-}C\equiv C\text{-}R^2)_2]$. A more facile reaction occurred with $[Pt(C_2H_4)_3]$, enabling the range of complexes synthesised to be considerably extended. When $R^1 = R^2 = Ph$, reaction with $[Pt(cod)_2]$ yielded initially $[Pt(cod)(Ph\text{-}C\equiv C\text{-}Ph)]$, which could be isolated. An excess of the alkyne gave the bis alkyne complex. The coordination of this species was shown by X-ray diffraction to be approximately tetrahedral. Other diaryl alkynes, including those for which $R^1 = R^2 = 4\text{-}MeC_6H_4$, C_6F_5 or $4\text{-}MeOC_6F_4$ gave only [Pt(cod)(alkyne)] complexes. Both these and $[Pt(PhC\equiv CPh)_2]$ reacted with Me_3CNC yielding $[Pt(R^1C\equiv CR^2)(Me_3CNC)_2]$ [324]. Treatment of $[Pt(PR^1_3)_2(R^2C\equiv CR^2)]$ with HX would be expected to give 218 by oxidative addition. Insertion then gives **219** with *cis*-stereochemistry for R^1 = Ph and *trans* with the more sterically demanding R^1 = Cy (R^2 = COOMe). However, no reaction occurred with MeCOOH until PPh_3 was added, at which point **220** was formed by addition of phosphonium ethanoate across the triple bond. This suggests that formation of the metal vinyl complex 219 might in fact occur *via* **221**, the isolation of the analogues of 220 depending on the nature of X [325]. Reaction of $[Pt(PPh_3)_2]$, generated *in situ* from $[Pt(PPh_3)_2Cl_2]$ and hydrazine, with **222** yielded the complex $[Pt(PPh_3)_2(alkyne)]$. Metallation using *n*-BuLi at -90 °C and treatment with dimethyl disulphide led to the substitution of the bromine atoms by thiomethyl groups. Attempts to lithiate the brompyridine directly led to Michael additions. Platinum could be readily removed at the end of the reaction sequence by treatment with $HgCl_2$ [326].



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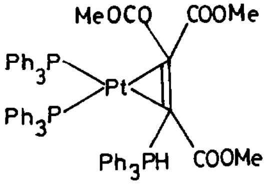

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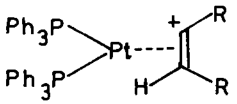

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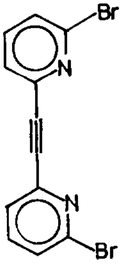
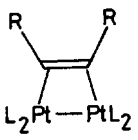


222

Several routes to the binuclear species $[(CO)_3Co\text{-}Ni(Cp)(\mu\text{-}Ph\text{-}C{\equiv}C\text{-}Ph)]$ have been described. These included the reactions of $[Co_2(CO)_8]$ with $[Ni_2(Cp)_2(\mu\text{-}Ph\text{-}C{\equiv}C\text{-}Ph)]$, $[Ni(Cp)_2]$ with $[Co_2(CO)_6(\mu\text{-}Ph\text{-}C{\equiv}C\text{-}Ph)]$ and Ph-C≡C-Ph with $[NiCo_3(Cp)(CO)_9]$. $[(CO)_3Co\text{-}Ni(Cp)(\mu\text{-}Ph\text{-}C{\equiv}C\text{-}Me)]$ was similarly prepared. X-ray diffraction data gave a nickel cobalt bond length of 2.3656(8) Å with the alkyne deviating from linearity by 40.1° [327].

From a mixture of $[Pt(cod)_2]$ and $[Pt(\eta^2\text{-}CF_3C{\equiv}CCF_3)(cod)]$ the bridged complex, **223**, (R = CF_3, L_2 = cod) was isolated together with **224**. The nmr spectrum of **223** showed fluxional behaviour at room temperature with rotation about the metal-alkyne bond and intramolecular exchange of CF_3 groups. However, no dynamic behaviour was observed for 223 (L = Me_3CNC). Protonation of 223 with

$H[BF_4]$ gave initially **225** which could be observed for R = 4-$MeOC_6F_4$, L_2 = cod, but not for R = CF_3. In this latter case insertion rapidly yielded **226** [328].



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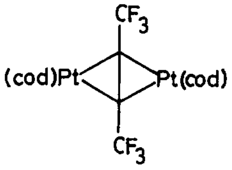

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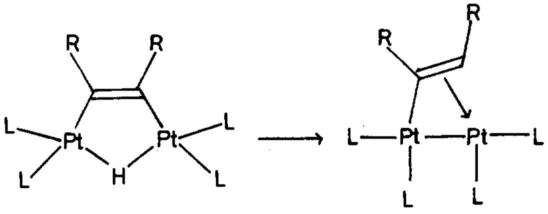
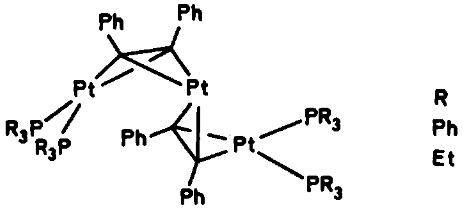


225 226

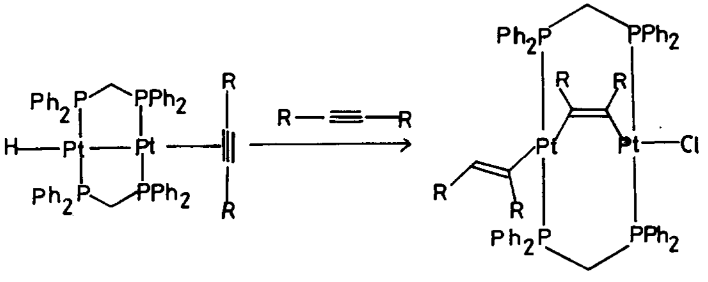
A full paper has now reported the results of the reaction between $[Pt(PhC\equiv CPh)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt_2(PEt_3)_4(\mu\text{-cod})]$ to give $[Pt_2(PhC\equiv CPh)(PR_3)_2(\mu\text{-}PhC\equiv CPh)]$ (R = Ph or Et). Addition of further $[Pt(PR_3)_2(C_2H_4)]$ gave the trimer $[Pt_3(PR_3)_3(\mu\text{-}PhC\equiv CPh)_2]$. X-ray diffraction data showed this to have an open V-shape, **227**. Several analogous species were characterised spectroscopically [329].



227 (Reproduced with permission from [329])

Both $[H_2Pt_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ and $[HPt_2(CO)(\mu\text{-dppm})_2]^+$ reacted with $RC\equiv CR$ to give 228 (R = CF_3 or COOMe; the reaction was unsuccessful with R = H or Ph). Treatment with an excess of $RC\equiv CR$ gave **229** by insertion into the Pt-H bond, the mechanism of the reaction being unknown [330].

With the aim of clarifying the rôle of various intermediates in the cyclisation of alkynes in the presence of $[NiL_2X_2]$, $RC\equiv CH$ was allowed to react with $[Ni(PPh_3)_2(NCS)_2]$ in the presence of Et_2NH to yield *trans*-$[RC\equiv C\text{-}Ni(PPh_3)_2(NCS)]$ (R = Me_2COH, MeCHOH, Et, Ph or CH_2OH) Only bis alkyne species could be isolated from the corresponding chlorides [331]. the related complex, *trans*-$[Ni(PBu_3)_2(C\equiv CH)_2]$, has been prepared by reaction of $[Ni(PBu_3)_2Br_2]$ with $HC\equiv CMgBr$. Coupling with butadiyne in the presence of CuI/Et_2NH gave *trans*-$[Ni(PBu_3)_2(\text{-}C\equiv C\text{-}C\equiv CH)_2]$, but on treatment with $HC\equiv C\text{-}Y\text{-}C\equiv CH$ (Y = C_6H_4 or *trans*-$\{M(PBu_3)_2\}$, M = Ni or Pt) gave high molecular weight polymers [332].



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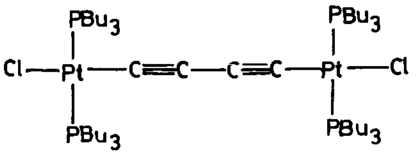
229

The complexes *trans*-$[Pd(C\equiv CR)_2(PEt_3)_2]$ (R = $2\text{-}HC\equiv C\text{-}C_6H_4$ or $4\text{-}HC\equiv C\text{-}C_6H_4$) have been prepared from $[Pd(PEt_3)_2Cl_2]$, alkyne and base, and were characterised by ir and nmr spectroscopy [333]. The preparation and properties of *trans*-$[1,4\text{-}C_6H_4\{C\equiv C\text{-}PdX(PEt_3)_2\}_2]$ (X = Cl, Br, I or NCS) and *trans*-$[1,4\text{-}C_6H_4\text{-}\{C\equiv C\text{-}Pd(PEt_3)_2Y\}_2][ClO_4]_2$ (Y = PEt_3 or py) have been investigated [334].

Treatment of $[HPt(PPh_3)_2Cl]$ with $HC\equiv CCMe_2OH$ gave no insertion into the platinum-hydrogen bond, but in the prsence of a primary alcohol, ROH, $[Pt(PPh_3)_2(C\equiv CCMe_2OR)Cl]$ was formed *via* a tertiary carbocation. Secondary and tertiary alcohols promoted dehydration, giving alkenyl alkyne complexes, also *via* tertiary carbocations [335].

On reaction with butadiyne, $[Pt(PBu_3)_2Cl_2]$ yielded 230, which could be reacted with 1,4-diethynyl benzene in the presence of Et_2NH/CuI to give a copolymer soluble in benzene and dichloromethane, but not methanol [336]. An analogous palladium containing species has been prepared, but proved less stable [337].



230

9. METAL ALLYL COMPLEXES

Reviews this year have dealt with the carbon-carbon bond forming reactions of allyl complexes of nickel, palladium and iron [338] and the stereo and regiochemistry of nucleophilic organometallic displacement reactions of allylic compounds [339]. In a wide-ranging survey ^{13}C and ^{1}H nmr and Raman spectroscopic parameters for $[(\eta^3\text{-allyl})_2M]$ (M = Ni, Pd or Pt) complexes were related to structures determined by X-ray diffraction [340].

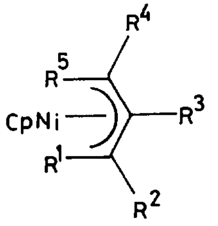
The vertical ionisation potential for $[(\eta^3\text{-allyl})_2Ni]$ has been calculated using a Green's function approximation. The value was in good agreement with experiment and led to a complete assignment of the photoelectron spectrum [341]. X-ray diffraction data for $[\{(\eta^3\text{-allyl})Ni(Cp)\}_2]$ have been compared with those for cobalt analogues [342].

A spectroscopic study compared the formation of $[\{(\eta^3\text{-allyl})NiX\}_2]$ on different supports [343]. ^{1}H nmr spectra of substituted $\{(\eta^3\text{-allyl})Ni(Cp)\}$ complexes have been recorded. δ values for the allylic hydrogens were found to be related by additive increments, and J(vicinal) for *syn*- and *anti*-protons approach as the degree of substitution increases [344]. The η^3-allyl ligand in $[\{(\eta^3\text{-}C_3H_5)Ni(OCOCF_3)\}_2]$ was found to be coordinatively stable on the nmr timescale, but metal to anion bonds were readily broken. The implications of this dynamic process for butadiene polymerisation were explored, but no conclusive arguements for the equibinary distribution obtained could be advanced [345]. The nqr spectra of the halogens in $[\{(\eta^3\text{-}C_3H_5)NiX\}_2]$ (X = Cl, Br or I) implied that the complexes are dimeric but have considerable ionic character [346].

Extended Hückel MO calculations have been undertaken for $[(\eta^3\text{-}C_6H_7)Pt(PH_3)_2]^+$ and $[(\eta^5\text{-}C_6H_7)Pt(PH_3)_2]^+$. These implied that the η^3-compound is only 0.56 eV more stable than the η^5-species, suggesting that such molecules might be fluxional at ambient temperature. The stereochemistry of the observed fluxional behaviour could be rationalised [347]. The He(I) PES of $[(\eta^3\text{-}C_3H_5)_2Pd]$, $[(\eta^3\text{-2-MeC}_3H_4)_2Pd]$ and $[(\eta^3\text{-}C_3H_5)_2Pt]$ have been recorded, and were compared with their nickel analogues. The first seven or eight transitions could be assigned with confidence, and on the basis of these data the first band in the PES of $[(\eta^3\text{-}C_3H_5)_2Ni]$ was reassigned to the ejection of an electron from a $7a_u$ orbital, which is a pure ligand orbital, in accord with theoretical predictions [348]. The structure of $[(\eta^3\text{-}C_3H_5)Pd(MeCN)_2]_2[B_{10}Br_{10}].C_6H_6$ has been determined by X-ray diffraction [349]. $[(\eta^3\text{-allyl})_2M]$ (M = Ni, Pd or Pt) complexes reacted with phosphine ligands to give $[(\eta^3\text{-allyl})_2ML]$, eighteen electron species, which were in equilibrium with sixteen electron complexes, $[(\eta^1\text{-allyl})(\eta^3\text{-allyl})ML]$, as evidenced both by X-ray diffraction and solution spectroscopic data [350].

Two new syntheses of π-allyl nickel complexes have been reported. $[Ni(Cp)_2]$ was reacted with $XMgC(R^4)R^5C(R^3)=CR^1R^2$ to yield $[(Cp)NiC(R^4)(R^5)C(R^3)=CR^1R^2]$, an η^1-allyl species, which was rapidly converted to the η^3-allyl complex, **231**. *Syn-anti* equilibration was shown to occur at 90 °C, whilst allylic equilibration required 120 °C [351]. In an excellent new route to cationic π-allyl complexes, $[allylS-C(NMe_2)_2]^+$ salts acted as precursors (reaction (33)) [352].

$$[CH_2=CHCH_2SC(NMe_2)_2][PF_6] + [Ni(CO)_4] \xrightarrow[Et_2O]{tmtu/MeCN} [(\eta^3-C_3H_5)Ni(tmtu)_2][PF_6] \quad (33)$$



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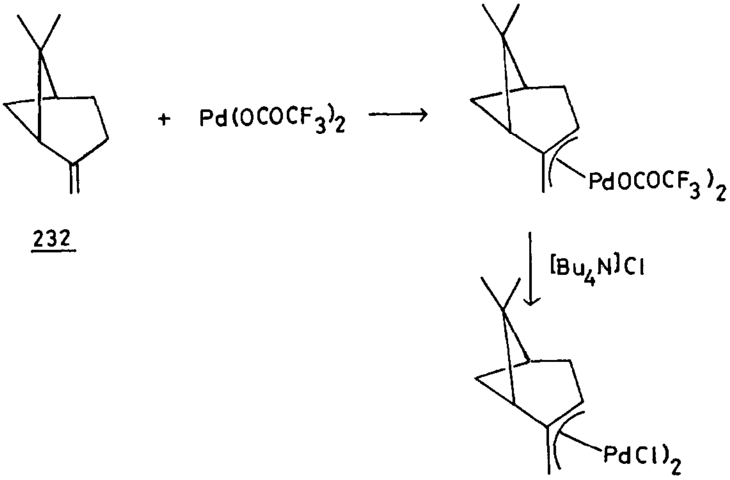
A laboratory experiment, suitable for undergraduate courses, detailed the preparation of $[\{(\eta^3-C_3H_5)PdCl\}_2]$, and described a study of its fluxional behaviour [353].

A new general synthesis of allyl complexes has been reported, involving the reaction of $[Pd_2(dba)_3]$ with $CH_2=CHCH_2X$ ($X = OP(NMe_2)_3$) to yield $[(\eta^3-C_3H_5)Pd(hmpa)_n]^+$. $CH_2=C(R)CH_2SC(NMe_2)_2$ reacted similarly [354]. In another new and fairly general reaction 232 yielded **233**. The process was compatible with both ketones and esters and invariably gave *syn*-allyl complexes. Since the $[CF_3COO]^-$ anion is non-nucleophilic, little competitive oxidation occurred and allyl complexes could be successfully synthesised from 1-alkenes [355].

[6-β-D] and [6-α-D]-cholest-4-ene-3-one were shown to react with $PdCl_2$ in dry thf to give the α-(4-6η)PdCl compound with highly stereoselective loss of the 6-β deuterium or hydrogen (reaction (34)). The α-stereochemistry of the product was established by a full X-ray diffraction analysis of the {α-(4-6η)Pd(acac)} derivative of progesterone. This selectivity could be associated either with an inherently greater reactivity of the *pseudo*-axial 6β-hydrogen or a more general requirement for hydrogen loss from the face *trans* to the incoming metal atom [356]. The study of variously deuterium labelled species such as **234** eliminated the latter possibility and the data were compatible with a mechanism involving metal assisted enolisation of the enone [357]. This is in agreement with the observation that unconjugated steroidal alkenes lose hydrogen *syn* to the incoming metal atom [358].



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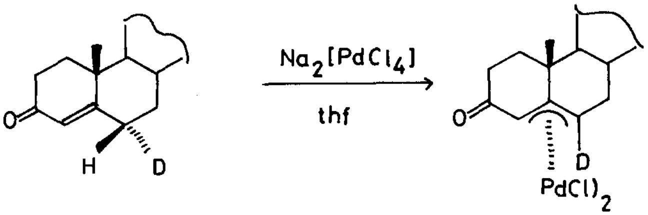

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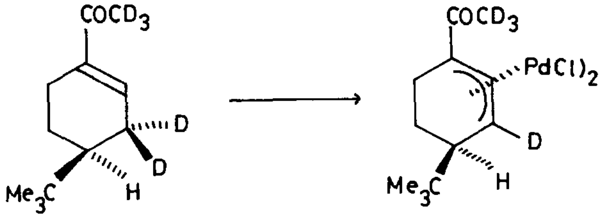

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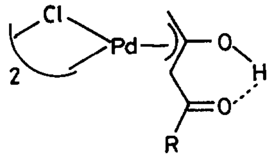
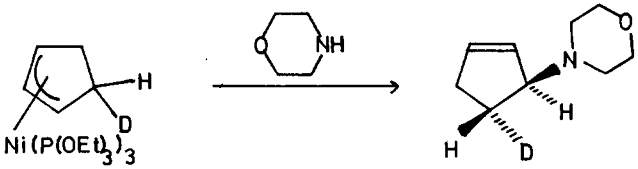
235

Reaction of $[Pt(cod)_2]$ with $CH_2=CHCH_2X$ yielded initially $[(\eta^1\text{-allyl})Pt(cod)X]$, which, on treatment with $Ag[BF_4]$, gave $[(\eta^3\text{-allyl})Pt(cod)][BF_4]$. Variable temperature nmr spectroscopic data on this species were compatible with the reversible coordination of a solvent molecule [359]. When $[Pd(PhCN)_2Cl_2]$ was treated with an equimolar mixture of acac and bipy the product was [Pd(bipy)(acac-C^1)Cl]. However, if the bipy was omitted from the mixture, **236** was formed with η^3-coordination of the 1,3-dione. A series of analogues was also prepared [360].



236

Reaction of the nickel allyl complex, 237, with morpholine gave 238 stereospecifically, by amine attack from the face of the allyl remote from the metal [361]. Treatment of the allyl bromide **239** with [Ni(cod)$_2$] gave **240**. This was coupled with a primary bromide to give a precursor to the pine sawfly pheromone [362].



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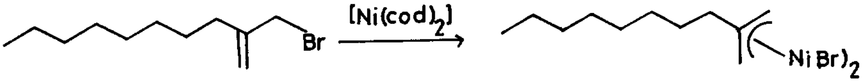

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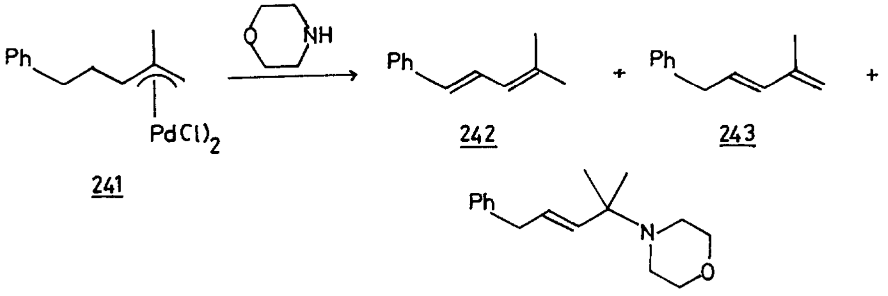
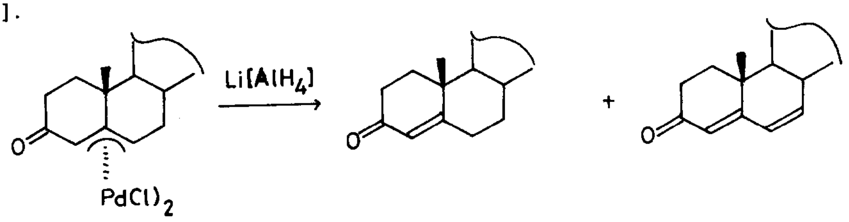
A CNDO MO study of the reaction of hydroxyl ion with allyl palladium complexes has been undertaken. The process was found to be more favourable with complexes of neutral π-acceptor ligands [363]. Various π-allyl palladium chloride dimers have been prepared and their reactions with secondary amines studied. The influence of amine structure and added ligands was compared with the analogous catalytic reactions. For example, treatment of **241** with morpholine gave **242**, **243** and **244** in 40, 6 and 45 % yields respectively. Very similar proportions of products were obtained from 3-methyl-1,3-pentadiene, bromobenzene and morpholine in the presence of Pd(OCOMe)$_2$/P(4-MeC$_6$H$_4$)$_3$. Both amines and dienes could be obtained from the same π-allyl complexes, and it was suggested that elimination of Pd-H occurs from a σ-allyl palladium complex [364].



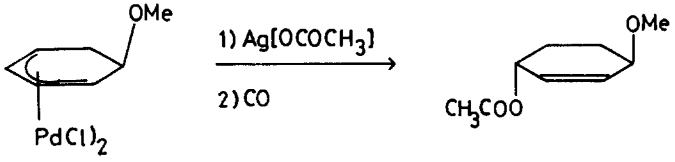
241 242 243 244

Steroidal π-allyl palladium complexes, **245**, reacted with Li[AlH$_4$] giving up to 81 % 246 together with 19 % 247. The more hindered hydride, Li[AlH(OCMe$_3$)$_3$], yielded 75 % **247** [365]. The π-allyl complexes synthesised from RR'C=CHCH$_2$OCOMe reacted with either Na[BH$_4$] or Na[BH$_3$CN] to give mixtures of RR'C=CHCH$_3$ and RR'CHCH=CH$_2$, regioselectivity depending on both steric and electronic factors [366].



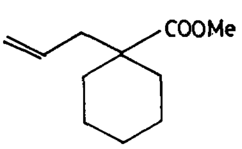
245 246 247

Attack of [MeCOO]$^-$ on **248** gave **249** stereospecifically, indicating that ethanoate attacks *via* palladium [367].



248 249

Reaction of [{(η^3-C$_3$H$_5$)PdCl}$_2$] with the anion of methyl cyclohexylcarboxylate gave a low yield of **250** in the presence of PPh$_3$ using thf as the solvent. However, without phosphine and with an hmpa/thf/Et$_3$N solvent, 251 was formed quite efficiently. Deuterium labelling indicated that attack occurred at the central carbon of the allyl. This may be accounted for by invoking the intermediates **252** and **253**. Branched ester enolates were the only nucleophiles found to be useful and the reaction was limited to relatively unsubstituted allyl complexes [368]. The regiochemistry of reaction of vinylzirconium compounds with **254** was altered by added ligands [369].



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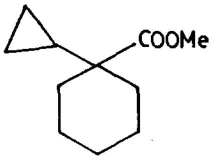

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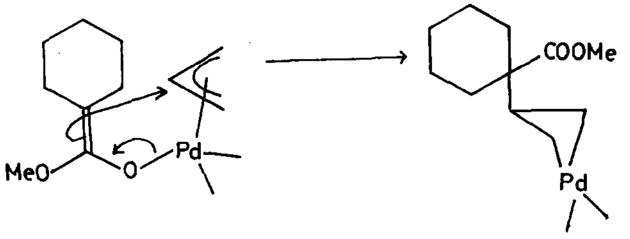

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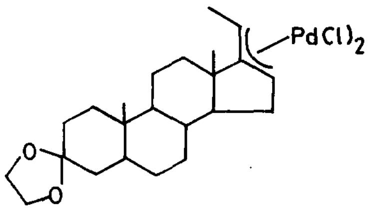
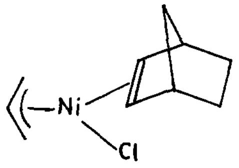


254

Reaction of **255** with CO/H_2O gave **256** by insertion and carbonylation of the resultant alkyl nickel compound. Treatment with molecular oxygen also resulted in double bond insertions followed by oxidation to alcohols or ketones. A radical mechanism was proposed for the oxidation [370]. Carboxylation of $[(\eta^3\text{-}C_3H_5)_2Ni]$ gave butyrolactone in 4 % yield [371].

Isoprene reacted with **257** to give **258**. At -78 °C **258** inserted alkynes, X-C≡C-X, yielding **259**. Sulphur gave the ring closed product, **260**, in only 30 % yield, but in excellent purity. However, CO at -78 °C gave rise to several rearrangements [372].



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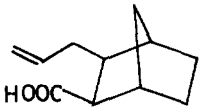

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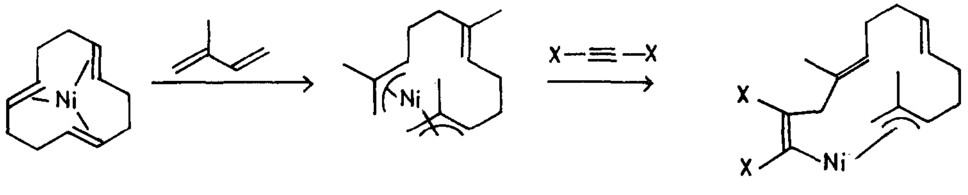

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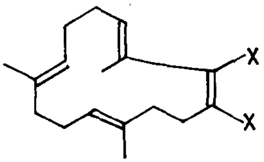
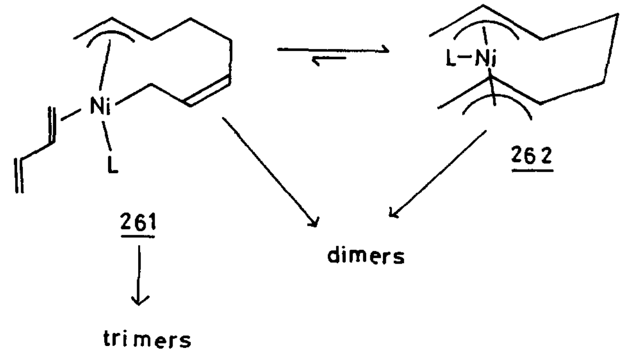
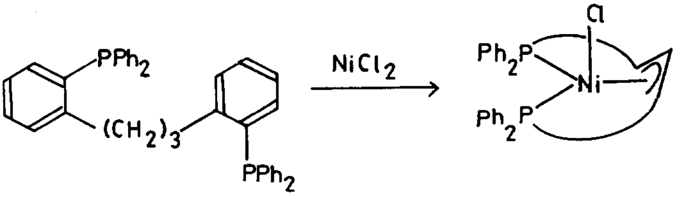


260

The control of the isomer distribution in cyclooligomerisation of butadiene on Ni-L catalysts may be attributed to several mutually independent ligand association processes. The electronic effect of the ligands is postulated to determine the σ-π ⇌ π-π equilibrium of the precursor complexes **261** and **262** [373].



An attempt to form a chelating complex of the phosphine **263** gave instead **264**, which has approximately square pyramidal coordination of nickel [374]. Three stereoisomers of $[(\eta^3\text{-}2\text{-}RC_3H_4)_2Ni_2(\mu\text{-}SH)_2]$ were formed from the bis allyl nickel complex and H_2S. These were stable only at low temperatures, decomposing to NiS and $RC(Me){=}CH_2$ at 20 °C [375]. The interactions of $[\{(\eta^3\text{-}RCHCHCH_2)NiCl\}_2]$ with $[Ni(OCOCCl_3)_2]$ have been studied in the presence of butadienes, with the aim of understanding the factors determining the regioselectivity of butadiene polymerisation [376].



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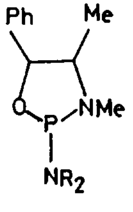
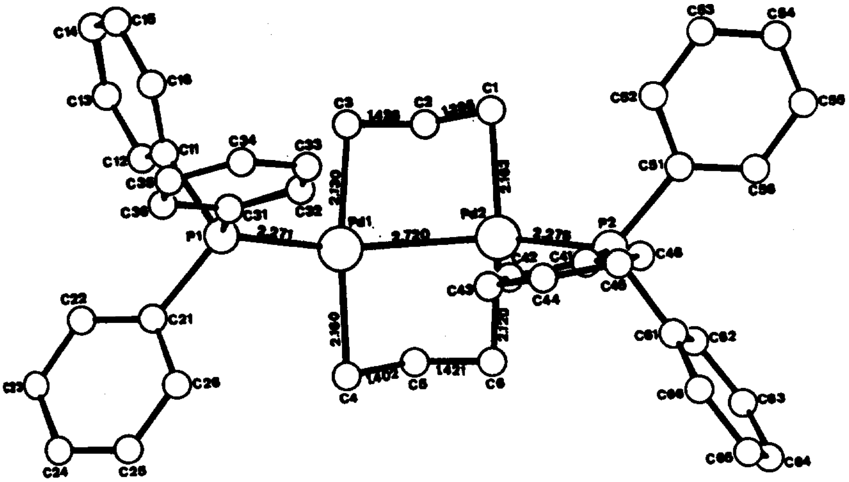
264

$[(2\text{-}MeC_3H_4)_2Pd]$ reacted with Cy_3P to give a monophosphine adduct which showed fluxionality between η^1- and η^3-allyl species at room temperature. The analogue prepared from $P(CHMe_2)_3$ was not fluxional in solution and had one η^1-and one η^3-allyl ligand [377]. $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$, by contrast, reacted with bridge splitting to yield $[(\eta^3\text{-}C_3H_5)PdL_2]Cl$. The complex with L = **265** has now been reported and its conformation determined by CD. These complexes are inefficient catalysts for enantioselective reductions [378]. The reaction of $[M(Cp)(\eta^3\text{-}2\text{-}R'C_3H_4)]$ with R_3P gave a monophosphine adduct. For M = Pd and R' = Me_3C and M = Pt and R' = Me, the coordinated cyclopentadienyl ligand is monohapto and the allyl is η^3-coordinated in solution between -60 °C and +60 °C. X-ray diffraction data showed the same results for the palladium complex in the solid state. However, for M = Pd and R' = Me, two isomers, η^5-Cp, η^1-allyl and η^1-Cp, η^3-allyl, were found to be in equilibrium [379].

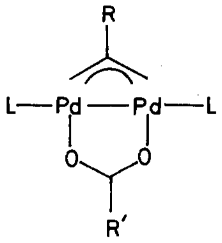


265

The initial adduct formed between $[(\eta^3\text{-allyl})_2Pd]$ and PPh_3 (probably $[(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)Pd(PPh_3)]$) was converted at 0 °C to **266** which was characterised by X-ray diffraction. The phosphines occupy *pseudo cis*-sites, and the allyls are *cis* with the *meso* carbons directed away from the phosphines [380]. An analogous species, 267, was formed from $P(CHMe_2)_3$, L, and $[\{(\eta^3\text{-}2\text{-}RC_3H_4)Pd(OCOR')\}_2]$ [381].



266 (Reproduced with permission from [380])



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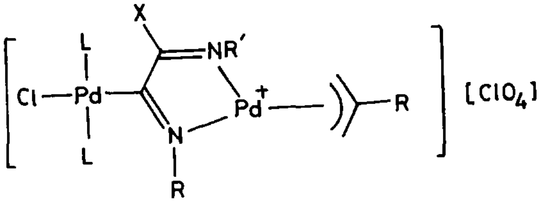
Diazobutadiene palladium(II) complexes also reacted with $[\{(\eta^3\text{-}2\text{-}RC_3H_4)PdCl\}_2]$ in the presence of $Na[ClO_4]$ to give **268**. Without $Na[ClO_4]$, **269** was obtained [382]. A kinetic study suggested that two pathways were involved in the reaction [383]. The other ligands and the polarity of the solvent determine the relative importance of associative and unimolecular pathways [384].

The phenol bearing allyl palladium complexes, 270, could be substituted by $[acac]^-$, PPh_3 and $[Cp]^-$ in predictable reactions. Oxidation of all of these species by PbO_2 gave radicals. The epr spectra of these radicals have been determined and dynamic processes were also discussed [385]. Photolysis of **271** gave **272** in excellent yield. Analogously $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ gave 1,5-dienes [386].



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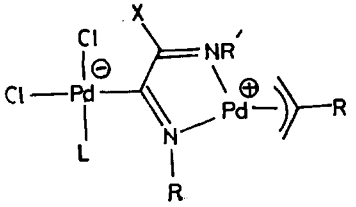

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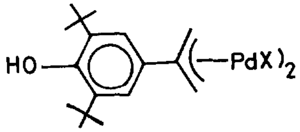

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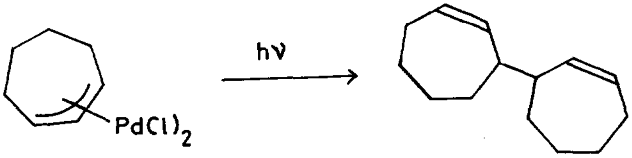

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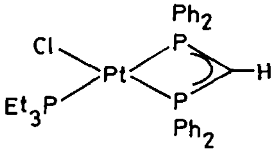
272

Carboxylation of $[(\eta^3\text{-}CH_3CHCHCH_2)_2Pd]$ yielded 2-methyl-3-butenoic acid, by insertion of CO_2 into the γ-position of the allyl, *via* a cyclic transition state. The data suggested that palladium catalysed carboxylation of butadiene also occurred *via* a cyclic transition state, rather than by direct insertion as previously suggested [387].

Palladium allyl complexes may be reacted with base to yield dienes. With complexes derived from steroids dbn has proved a useful base, but yields are still relatively modest [388]. Remote oxidations of secondary alcohols to ketone groups in palladium allyl steroid complexes have been achieved [389].

Platinum σ-allyl complexes such as $[(\eta^1\text{-}C_3H_5)Pt(cod)X]$ (X = Cl or Br) reacted with pyridine yielding the species $[(\eta^3\text{-}C_3H_5)Pt(py)X]$, which dimerised readily in solution. A similar process occurred with PCy_3 as ligand. Cationic complexes reacted similarly and the nmr spectroscopic parameters of a wide range of such species have been reported [390]. [(η^1-allyl)Pt(cod)Cl] reacted with Tl[Cp] yielding [(η^3-allyl)Pt(Cp)]. [Pt(σ-CH_2-CH=CHPh)(cod)(η^1-Cp)] was isolated as an intermediate in the production of the η^3-allyl. Reaction of the η^3-allyl complex with Me_3CNC gave *trans*-[Pt($CNCMe_3$)$_2$(σ-allyl)(Cp)], which was in equilibrium with the more favourable *cis*-isomer. A number of rather complex rearrangements were discussed in detail [391].

Treatment of [Pt(PEt_3)(dppm)Cl] with NaH gave **273**, which was characterised by X-ray diffraction. The central carbon atom was shown to be relatively distant from platinum [392].



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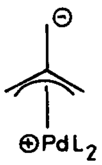
An electronic explanation has been offered for the reason that d^{10} and d^8 [(trimethylenemethane)ML_2] complexes should be η^3- rather than η^4-coordinated [393]. Palladium trimethylenemethane complexes, unlike those of nickel, behave as though the resonance form **274** was the only significant one. Data have come from the reactions of **275**. With **276** complete deuterium scrambling occurs in the formation of **277**. However, the more reactive nucleophile, [$PhSO_2CHCOOMe$]$^-$ yielded only **278** with no deuterium scrambling [394]. Reaction of [Pd($PhCN$)$_2Cl_2$] with **279** gave a 1:1 mixture of **280** and **281**. **280** and **281** were found to be in rather slow equilibrium. Again a non-symmetric trimethylenemethane complex was proposed as an intermediate, for consistency with the deuterium labelling studies [395].

Analogues of the η^5-pentadienyl system, *viz.* [M{X(CH=CH)$_2$BPh}$_2$] have been prepared (X = Me_2C, Me_2Si or CH_2CH_2). X-ray diffraction data were reported for [Ni{Me_2Si(CH=CH)$_2$BPh}$_2$]. This together with ^1H and ^{11}B nmr spectroscopic data imply η^5-coordination and C_2-symmetry [396].



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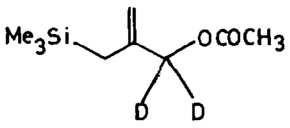

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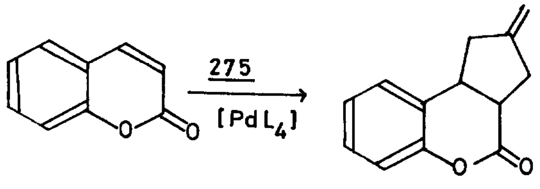

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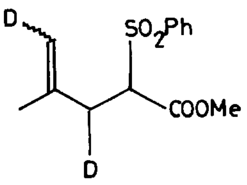

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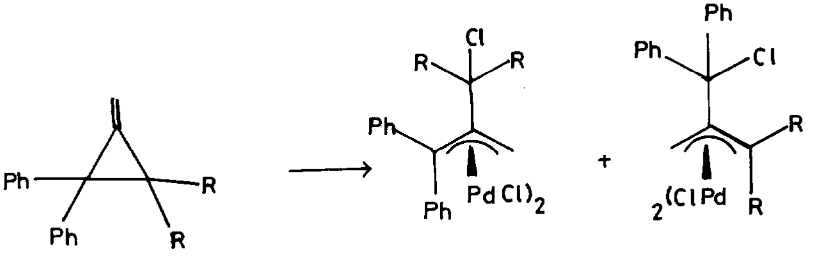
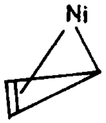


279 280 281

10. COMPLEXES OF DELOCALISED CARBOCYCLIC SYSTEMS AND BORANES

The X-ray diffraction study of $[(Ph_3C_3)Ni(PPh_3)_2][PF_6]$ showed that the three membered ring is coordinated to nickel in an unprecedented unsymmetrical fashion, 282. This is in contrast to its platinum analogue in which the bond lengths in the carbocycle are approximately equal [397]. A theoretical study has investigated the opening of the cyclopropenyl cation in the presence of transition metal complexes [398].



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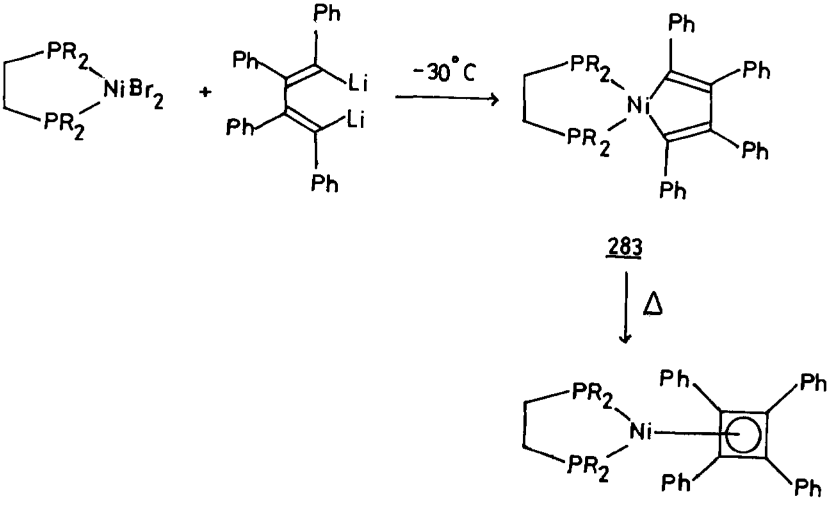
Two papers have reported the synthesis and reactions of new nickel complexes of tetraphenylcyclobutadiene. $[(Ph_4C_4)NiBr_2]$ was reduced by sodium in the presence of cod or cot to give respectively [(Ph_4C_4)Ni(cod)] and [(Ph_4C_4)Ni(cot)]. These diamagnetic complexes were found to be stable up to > 200 °C. Both reacted with bromine to regenerate the starting nickel(II) complex, and with carbon monoxide yielded octaphenylcyclooctatetraene and [$Ni(CO)_4$]. ^{13}C nmr spectroscopic data indicated that cod is more strongly bound than cot [399]. Reduction in the presence of $R_2PCH_2CH_2PR_2$ gave **284**, also obtained by reaction (35). The kinetics of the rearrangement of the nickelacyclopentadiene were studied. Both **283** and **284** gave arenes on reaction with alkynes, **283** being much the more reactive, and both were protonated to yield 1,2,3,4-tetraphenylcyclobutadiene. Carbonylation of 283 at -78 °C gave tetraphenylcyclopentadienone. By contrast, **284** reacted with carbon monoxide only at +60 °C, then yielding [$Ni(CO)_4$] and octaphenylcyclooctatetraene [400].



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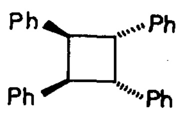
284

(35)

In an analogous manner [$(Ph_4C_4)PdCl_2$] was reduced by sodium or reacted with dilithio tetraphenylcyclobutadiene to yield [$(Ph_4C_4)_2Pd$], the structure of which was established by X-ray diffraction. This was reduced by molecular hydrogen to **285** with good stereospecificity, whilst nitric acid oxidation gave **286** [401]. Cyclobutadiene complexes could also be synthesised by alkyne dimerisation (reaction (36)). The structure of **287** was established by nmr spectroscopy. **287** reacted with HCl in propanone to give [$Pt_2(R_4C_4)_2Cl_4$] with two bridging and two terminal chlorine atoms. The preparations of [Pt{$C_2(CMe_3)_2$}(NCMe)($SnCl_3$)Cl] and *trans*-[Pt_2{$C_2(CMe_3)_2$}$_2$($SnCl_3$)$_2$(μ-Cl)$_2$] were also described. The dimerisations described in this paper were contrasted with the palladium catalysed oligomerisation of alkynes [402].



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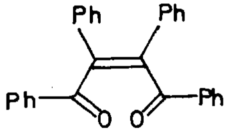

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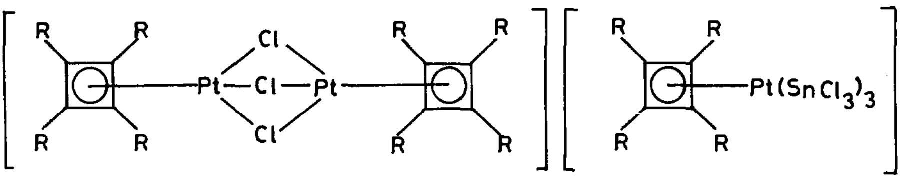
$$[Pt(MeCN)_2Cl_2] + RC\equiv CR + SnCl_2 \longrightarrow [Pt_2(R_4C_4)_2Cl_3][Pt(R_4C_4)(SnCl_3)_3] \quad (36)$$

287



287

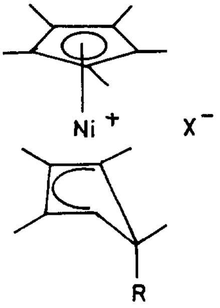
Nickelocene has been used in a new method for the testing and calibration of wire chambers [403]. Addition of nickelocene before vulcanisation was shown to reduce aging in rubbers [404]. Its decomposition in the presence of hydrogen gave thin films of nickel. Cyclopentadiene, cyclopentene and cyclopentane were found among the volatile products. As the decomposition temperature was increased so was the proportion of cyclopentadiene produced [405]. In this way nickel coatings on copper, ceramics and glass have been produced by decomposition of $[Cp_2Ni]$ or $[(propylCp)_2Ni]$ at 150 - 400 °C [406]. The decomposition rate was also found to be a function of the surface on which it takes place, and the catalytic effects of such pyrolytic coatings are determined by the specific nature of the solid phase, rather than solely by surface area [407].

MO calculations, using the all electron SCF multiple scattering X_α method, have been performed for nickelocene and its cation. Calculated spin densities on the metal are in good agreement with epr measurements, and calculated ionisation and electronic excitation energies agree with data from PE and optical absorption spectra [408]. The He(II) PES of $[Cp_2Ni]$ and the He(I) and He(II) spectra of $[(C_5Me_5)_2Ni]$ have been measured. Intensity changes between the He(I) and He(II) spectra gave a reliable guide to band assignment [409]. Bond orders of the carbon-carbon bonds in metallocenes reflect the extent of π-bonding, which determines the strength of the metal-ligand bond. These have been correlated with dissociation energies and used to estimate HOMO levels

[410].

Excitation of [Cp_2Ni] in the range 3750-5200 Å has been shown to lead to collision free multiphoton dissociation. Bare metal atoms were detected by three photon ionisation [411]. An infra-red spectroscopic and mass spectrometric study of [Cp_2Ni] and D_{10}-[Cp_2Ni] has been reported [412]. Infra-red measurements on the [Cp_2Ni][HCl] complex in liquid xenon implied that the π-electrons participate in complex formation. The enthalpy of complexation was determined to be 2.4 kcal mol^{-1} [413]

The oxidation of various metallocenes has been studied and nickelocene was found to be more stable in this respect than vanadium, chromium or cobalt complexes. Some cyclopentadiene was released, possibly *via* an oxygen complex [414]. A comparison of [Cp_2Ni] and [$(C_5Me_5)_2Ni$] suggested that their redox potentials reflect a greater ligand contribution to the e_{1g} orbital in the permethylated compound. Thus, this is the first neutral twenty electron complex to which electrophiles, RX, may be added, yielding **288** [415].

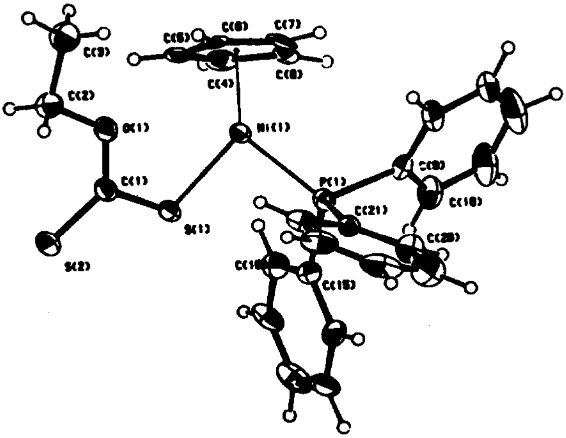


288

At room temperature nickelocene adopts a monoclinic crystal structure, isostructural with ferrocene. However, unlike ferrocene there is found to be no phase change to a triclinic structure on cooling. At 110 K thermal motion is lowered, but the structure is otherwise the same as at room temperature [416].

^{13}C nmr spectra have been successfully measured for the first time on a range of substituted nickelocenes. The linewidths are in excess of 5600 Hz and the δ range greater than 2200 ppm. The long sought for evidence for a strong temperature dependence of δ and $w_{½}$ was presented. In [$(RC_5H_4)_2Ni$] the C_1 carbon is the most shifted. The data allowed the conclusion that both unpaired electrons are in e_{1g} orbitals. There was an 8 ppm shift in the ^{13}C resonance between C_5H_5 and C_5D_5 complexes, the record to date for an isotope shift [417].

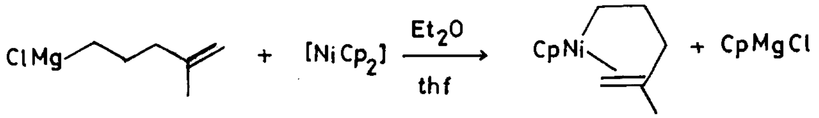
New nickel "sandwich" compounds, including bimetallic sanwiches and triple decker sandwiches, have been reviewed [418]. The relationship between bond length and bond strength of iron, cobalt and nickel hydrides has been explored. Among the complexes discussed were [HNiCp(PCy$_3$)] and [HNiMe(PCy$_3$)$_2$] [419]. The polarographic reduction of π-cyclopentadienyl o-phenylazophenyl nickel in dmf has been reported [420]. An X-ray diffraction study of **289** has shown η^5-binding of the cyclopentadienyl ligand and a monodentate xanthate. Variable temperature ^{1}H nmr spectroscopic measurements indicate equilibration of two inequivalent xanthate conformations. At higher temperatures phosphine dissociation is also important [421].



289 (Reproduced with permission from [421])

[(Me$_5$C$_5$)$_2$Ni] has been prepared from NiBr$_2$ and Li[Me$_5$C$_5$]. Treatment with Ph$_3$P/CCl$_4$ yielded [(Me$_5$C$_5$)Ni(PPh$_3$)Cl]. Then reaction with Tl[Cp] gave the mixed species [CpNi(Me$_5$C$_5$)]. This was protonated by H[BF$_4$] preferentially on the permethylated ring [422]. The reaction of [Cp$_2$Ni] with ω-alkenyl Grignard reagents gave cyclic species such as **290** (reaction (37)). Analogous species, **291**, were obtained from Me$_2$CHMgBr and 1,4-pentadienes (reaction (38)) [423]. Treatment of [Cp$_2$Ni] with 4-methylphenylazide gave **292**, a paramagnetic nickel(I) complex, in 10 % yield, as well as the expected [Ni(N$_4$Ar$_2$)$_2$]. **292** is a nineteen electron complex, and cyclopentadiene is readily displaced by ligands such as Me$_3$CNC [424].

The reaction of nickelocene with [(Ph$_3$Ge)$_2$Cd] (reactions (39) and (40)) has been studied in some detail [425]. The structure of **293** was determined by X-ray diffraction [426] and this area and other advances in the chemistry of polynuclear organometallic compounds with σ-bonded metals was comprehensively reviewed [427].



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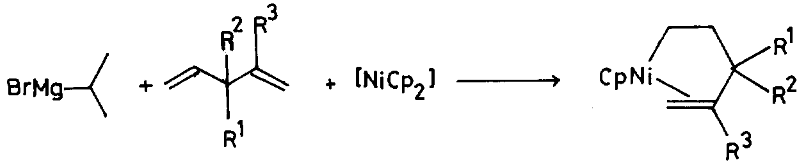

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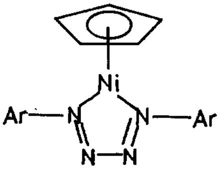
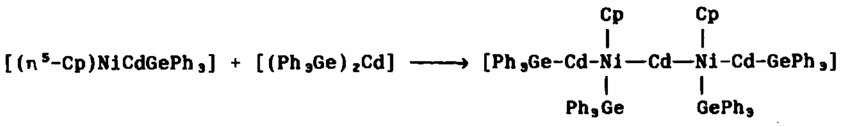


292

$$[Cp_2Ni] + [(Ph_3Ge)_2Cd] \longrightarrow [(\eta^5\text{-}Cp)(\eta^1\text{-}Cp)Ni(CdGePh_3)(GePh_3)]$$

$$\downarrow$$

$$[(\eta^5\text{-}Cp)NiCdGePh_3] + Ph_3GeH + CpH \qquad (39)$$

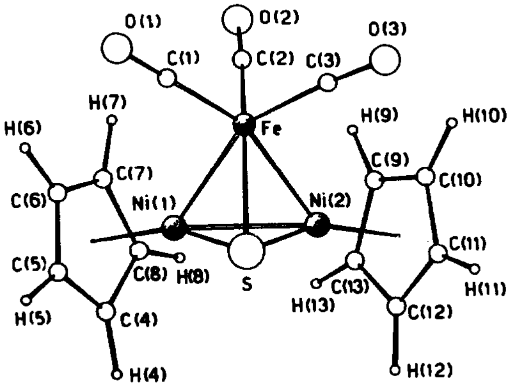


$$[(\eta^5\text{-}Cp)NiCdGePh_3] + [(Ph_3Ge)_2Cd] \longrightarrow [Ph_3Ge\text{-}Cd\text{-}\underset{\displaystyle Ph_3Ge}{\overset{\displaystyle Cp}{Ni}}\text{—}Cd\text{—}\underset{\displaystyle GePh_3}{\overset{\displaystyle Cp}{Ni}}\text{-}Cd\text{-}GePh_3] \qquad (40)$$

293

A correlation has been established between force constants and metal hydrogen bond lengths in both ground and excited states for complexes of iron, cobalt and nickel. Among the compounds considered was $[H_3Ni_4Cp_4]$ [428]. The thermochemistry of binuclear cyclopentadienyl nickel carbonyl complexes has been investigated [429].

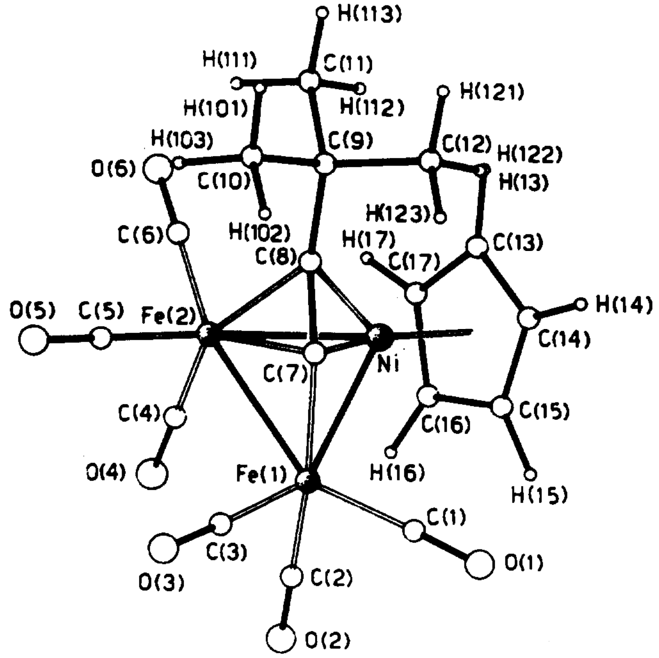
A quantitative procedure for the indirect location of hydrogen atoms bound to transition metal clusters has been described. This was used for $[H_3Ni_4Cp_4]$ and the data thus obtained compared with those from neutron diffraction [430]. $[\{CpNi(CO)\}_2]$ reacted with $[Fe_2(CO)_6S_2]$ to give a 15 % yield of **294**, identified by X-ray diffraction [431]. When $[Cp_2Ni_2(H\text{-}C{\equiv}C\text{-}CMe_3)]$ reacted with $[Fe_3(CO)_{12}]$ in a hydrocarbon solvent the mixed cluster $[CpNiFe_2(CO)_6(C_2CMe_3)]$, **295**, was obtained. X-ray diffraction implied that the deprotonated alkyne interacts with all three metal atoms and acts as a five-electron donor to the cluster. It is σ-bonded to one iron atom and π-bonded to the other iron and to nickel [432]. Reduction of $[Cp_2Ni]$ with sodium naphthalide gave $[Cp_6Ni_6]$, **296** and $[Cp_6Ni_6]^+$, **297**. Chemical oxidation converts **296** to **297**. Both structures were established by X-ray diffraction. **296** is a ninety electron cluster, not conforming with the more usual eighty-six electron count. According to the Wade bonding scheme this should adopt a trigonal prismatic rather than the observed octahedral $\{Ni_6\}$ core. It is presumed that the discrepancy arises from steric interactions of the encapsulating cyclopentadienyl ligands. In **297** the nickel-nickel distance is shorter than that in cubic close packed nickel metal [433].



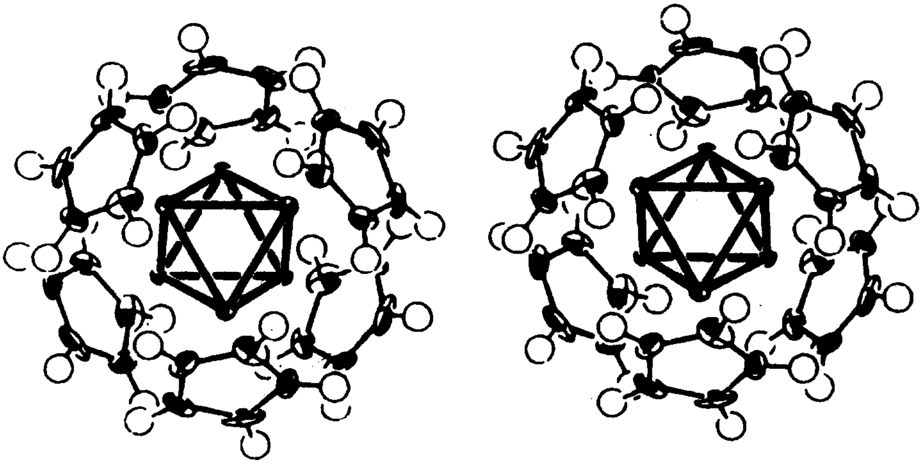
294 (Reproduced with permission from [431])

$[H_3Ni_4Cp_4]$ has been shown to act as a catalyst for the homogeneous hydrogenation of sterically unhindered terminal alkenes, but the cluster μ-hydrides are not involved in the catalysis [434].

Treatment of $[Pd_2Cl_4\{P(OPh)_3\}_2]$ with NaCp gave **298**, a new member of the growing family of palladium dimers bridged by π-bonding ligands. The structure of **298** was established by nmr spectroscopy, but the exact mode of binding is still unclear [435].

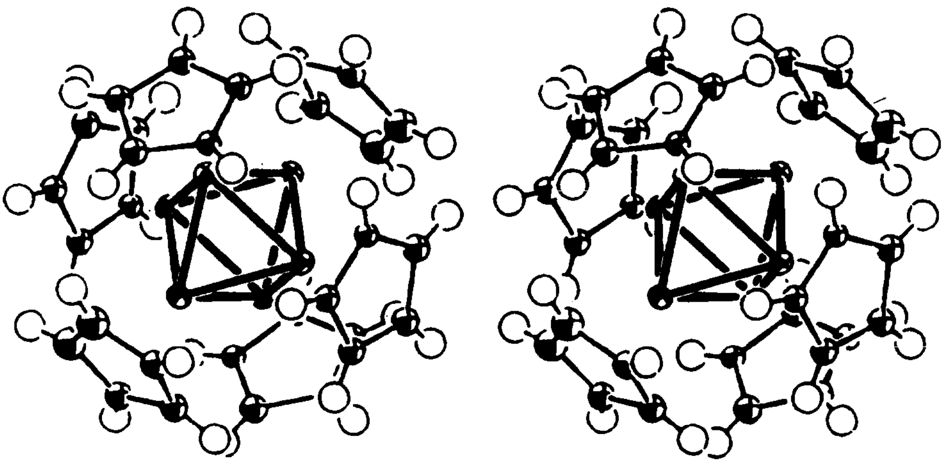


295 (Reproduced with permission from [432])



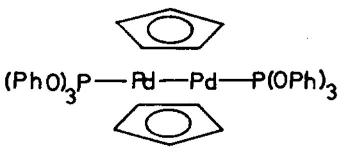
$[Ni_6(h^5\text{-}C_5H_5)_6]^+$

296 (Reproduced with permission from [433])



$Ni_6(h^5\text{-}C_5H_5)_6$

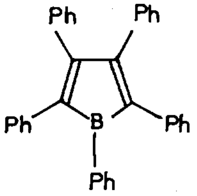
297 (Reproduced with permission from [433])



$(PhO)_3P-Pd-Pd-P(OPh)_3$

298

Treatment of **299** with potassium metal gave the dipotassium salt, $K_2[PPB]$. Reaction of **299** with $[Pt(cod)_2]$ or $K_2[PPB]$ with $[Pt(cod)Cl_2]$ yielded **300**, the analogue of a cyclopentadienyl complex [436].



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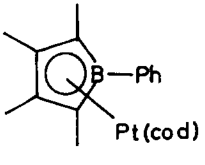
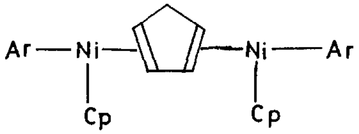


300

Reaction of nickel atoms with C_6F_5Br in the presence of arenes gave $[(C_6F_5)_2Ni(\pi\text{-arene})]$. The arene was particularly easily displaced by ligands including cod, PEt_3 and thf. The π-toluene complex acted as a catalyst for norbornadiene polymerisation, and as a rather short-lived hydrogenation catalyst. Treatment with carbon monoxide yielded C_6F_5-C_6F_5 and $[Ni(CO)_4]$. A rather unusual reaction occurred with cyclopentadiene giving C_6F_5H and $[(C_6F_5)_2Cp_2Ni_2(C_5H_6)]$, 301, in which cyclopentadiene acts as an η^2-ligand to two nickel centres [437]. Reaction of **302** with $Na_2[PdCl_4]$ gave the η^3-phenalenyl complex, **303**. Treatment with PPh_3 gave a rather unstable η^1-species [438].



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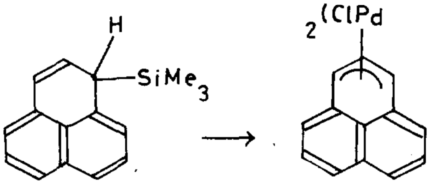
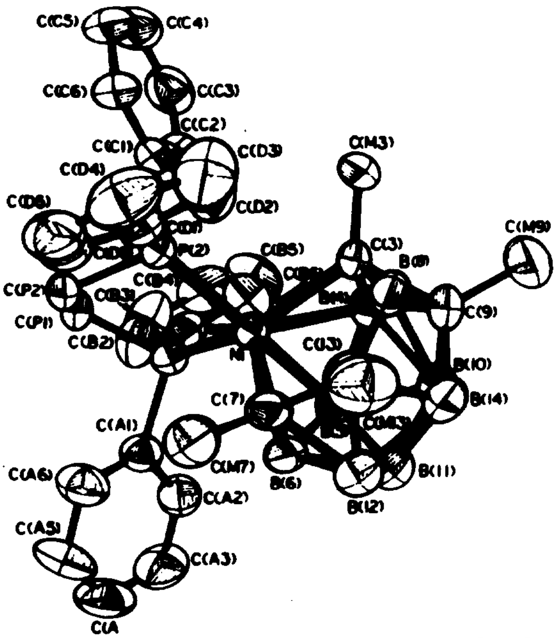


302 303

The dynamic nmr spectrum of [6,7,8,9-η^4-*nido*-decaborato(2-)]$[Pt(PPhMe_2)_2]$ showed a novel type of non-dissociative borane ligand fluxionality [439]. *Nido*-decaboranyl oxide, 6,6'-$(B_{10}H_{13})_2O$, reacted with $[Pt(PMe_2Ph)_2Cl_2]$ to give a mixture of several components including $[Pt_2(\eta^3\text{-}B_6H_9)_2(PMe_2Ph)_2]$. This unprecedented structure was characterised by X-ray diffraction and shown to be a binuclear Pt-Pt bonded compound with two bidentate bridging 2,3,4-η^3-*nido*-hexaboronate ligands [440].

Extended Hückel MO calculations have been performed for the trigonal prismatic platinaboranes and carboranes $[B_8\{Pt(PH_3)_2\}H_8]^{2-}$ and $[B_6C_2[Pt(PH_3)_2\}H_8]$. The observed conformation was accounted for in terms of the nodal characteristics of the frontier orbitals of the $\{Pt(PH_3)_2\}$ and carborane fragments. A description of the bonding in the less symmetric isomer of $[B_6C_2\{Pt(PH_3)_2\}H_8]$ was similarly derived from an analysis of transforming *nido*-$[B_8H_8]^{2-}$ into *arachno*-$[B_8H_8]^{2-}$ [441].

Reaction of $[(MeC)_4B_8H_4]^{2-}$ and $[Ni(dppe)Cl_2]$ gave two isomers of $[Ni(dppe)(CMe)_4B_7H_7]$ and three isomers of $[Ni(dppe)(CMe)_4B_8H_8]$, the structure of one of which, 304, was determined by X-ray diffraction. The thirteen vertex $\{$*nido*-$NiC_4B_8\}$ framework resembles a fourteen vertex *closo* polyhedron from which one vertex has been removed [442].



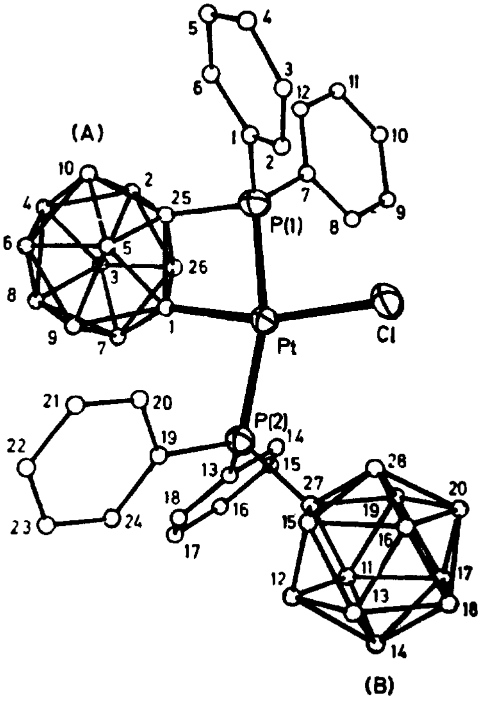
304 (Reproduced with permission from [442])

Reaction of the compounds 4-XB_8H_{12} X = CH, NH or S) with [$Pt(PPh_3)_4$] gave [9,9-$(PPh_3)_2$-6,9-$XPtB_8H_{10}$], isoelectronic with *nido*-[6-CB_9H_{13}]. The structures were characterised by X-ray diffraction [443]. Pyrolysis of the compound for which X = CH gave [9,9-$(Ph_2P)_2(C_6H_4)_2$-6,9-$CPtB_8H_{10}$]. Two intramolecular reactions have occurred giving insertion into a CH bond of the phosphine [444].

The structure **305**, another product formed by insertion, [$PtCl(Ph_2PC_2B_{10}H_{10})(Ph_2PC_2B_{10}H_{11})$], was determined by X-ray diffraction, and the existence of a Pt-P-C-B metallocycle demonstrated [445].

Treatment of *nido*-[4,5-$C_2B_7H_{11}$] with [$Pt(PPh_3)_4$] gave an 80 % yield of *arachno*-[9,9-$(Ph_3P)_2$-5,6,9-$C_2PtB_7H_{11}$], the structure of which was deduced from ^1H and ^{11}B nmr spectroscopic data [446].

Reaction of [$Pt_2(\mu$-cod$)(PEt_3)_4$] with *nido*-[5,6-$C_2B_8H_{12}$] gave **306**, [9H-9,9-$(Et_3P)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$] in 70 % yield. On thermolysis in toluene this was converted to **307**, [9H-9,10-$(Et_3P)_2$-7,8,9-$C_2PtB_8H_9$]. Both polyhedra contain CCPtBB faces and are therefore *nido*, with a single terminal metal hydride. The insertion of the {PtP_2} fragment into the nidocarborane involves incorporation of the metal into an expanded polyhedral framework, and may be contrasted with the reaction with *nido*-[2,3-$C_2B_4H_4R_2$], when the metal inserts into the μ-{B-H-B} function. Conversion of **306** to **307** involves the loss of molecular hydrogen and migration of PEt_3 from Pt(9) to B(10) [447]. A full paper has now reported the thermolysis of *nido*-[$\mu_{4,5}$-{*trans*-HPt(PEt$_3$)$_2$}-$\mu_{5,6}$-H-2,3-Me$_2$-2,3-C$_2$B$_4$H$_4$] with loss of hydrogen to give *closo*-[1,1-(Et$_3$P)$_2$-2,3-Me$_2$-1,2,3-PtC$_2$B$_4$H$_4$], characterised by X-ray diffraction. By contrast, in the non-alkylated analogue, *nido*-[$\mu_{4,5}$-{*trans*-HPt(PEt$_3$)$_2$}-$\mu_{5,6}$-H-2,3-C$_2$B$_4$H$_6$], thermolysis occurred with loss of hydrogen and separation of the cage carbon atoms to give *closo*-[1,1-(Et$_3$P)$_2$-1,2,4-PtC$_2$B$_4$H$_6$], again characterised by X-ray diffraction. Nmr spectroscopic studies showed a lower barrier to rotation of the metal fragment about the axis linking it to the cage than in twelve vertex carbaplatinaboranes [448].

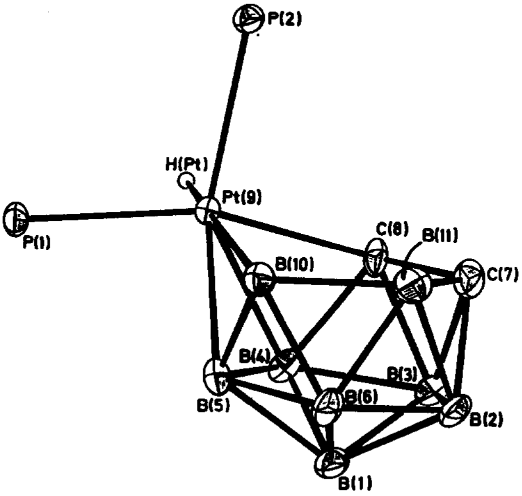


305 (Reproduced with permission from [445])

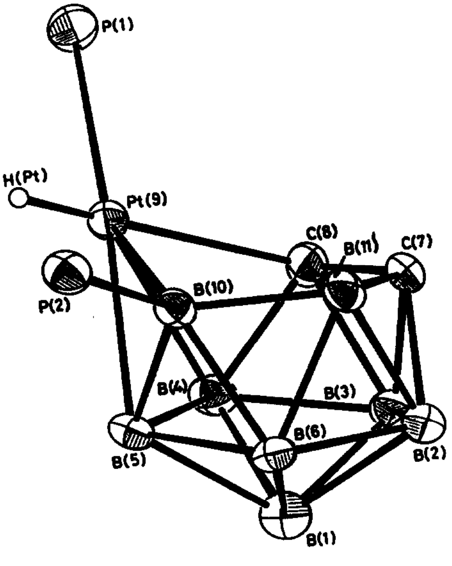
11. METAL ISOCYANIDES

Zerovalent transition metal complexes (including those of nickel, palladium and platinum) of organic isocyanides have been reviewed [449]. The diazo complexes [Ni(N$_2$R)(CNCMe$_3$)$_2$] (R = C$_5$Cl$_4$ or C$_5$Br$_4$) have been prepared from [Ni(CNCMe$_3$)$_2$]. The diazo group is η^2-bonded [450].

The species C≡NNH$_2$ is unstable but may be stabilised by coordination.



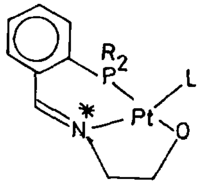
306 (Reproduced with permission from [447])



307 (Reproduced with permission from [447])

However, $C\equiv N\text{-}NPPh_3$ is rather stable and reacted with PdI_2 to yield $[Pd(CCNPPh_3)_2I_2]$. $[Pt(PPh_3)_2Cl]^+$ reacted analogously to give $[Pt(CNNPPh_3)(PPh_3)_2Cl]^+$. The best bonding description which could be proposed was $\{L_nM^-\leftarrow C\equiv N^+\text{-}N^-\text{-}P^+Ph_3\}$ [451]. The preparation of the proposed fulminate complex, *trans*-$[Pt(PPh_3)_2(C\equiv N\rightarrow O)_2]$ has been described. In ethanoic acid this was isomerised to the bis(isocyanate), *cis*-$[Pt(PPh_3)_2(NCO)_2]$ [452].

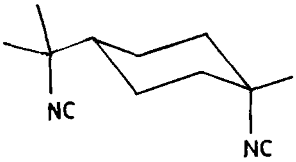
The complexes **308**, in which N^* is ^{15}N were characterised spectroscopically, including that for which L = CyNC [453]. Infra-red and Raman spectra of $[PtL_4][PF_6]_2$, $[Pt_2L_6][PF_6]_2$ and $[PdPtL_6][PF_6]_2$ (L = MeNC) were recorded both in the solid state and in solution, and most of the vibrational modes were assigned. Fluxional behaviour in solution was discussed [454].



308

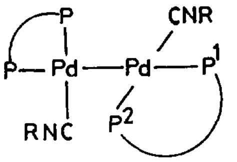
The electroreduction of $[Pt(CNR)_2X_2]$ (R = Cy or Me_3C; X = Cl, Br or I) has been investigated. The first one electron reduction step is irreversible with a half wave potential critically dependent on the nature of X. The product is a paramagnetic platinum(I) compound, and X^- is liberated. The second one electron reduction led to decomposition to platinum metal on the electrode [455]. A platinum(I) species was also formed from the first one-electron reduction of *trans*-$[PtL_2(CNAr)X]^+$ (X = Cl or Br; Ar = 4-NO_2, 4-MeO, 4-Cl or 4-MeC_6H_4; L = PEt_3 or PMe_2Ph). The product was shown to dissociate L giving [Pt(I)L(CNAr)X], which dimerised to $[Pt_2L_2(CNAr)_2X_2]$. A further one-electron reduction gave platinum(0) species. Oxidation occurred irreversibly by a two-electron process to give platinum(III) [456]. The related *cis*-complexes, *cis*-$[M(CNAr)(PPh_3)Cl_2]$ (M = Pd or Pt; Ar = 4-Cl or 4-$MeOC_6H_4$) were also studied. The platinum(II) species were reduced to platinum(0) complexes. Palladium(II) was reduced to palladium(0) at 25 °C but palladium(I) could be detected at 0 °C [457].

Reaction of $NiCl_2$ with **309**, DMB, gave $[Ni_2(DMB)_4Cl][PF_6]$ in which the chloride bridges the two nickel atoms [458]. $[Ni_4(CNR)_6]$, $[Ni_4(CNR)_6L]$, $[Ni_4(CNR)_6(R'C\equiv CR')]$, $[Ni_4(CNR)_7]$ and $[Ni_4(CNR)_4(R'C\equiv CR')_3]$ were all found to be precursors of catalysts for hydrogenation of alkynes, and also some nitriles and isonitriles. Syntheses and solution dynamic behaviour were described for all the clusters. The mechanism of hydrogenation was not defined and either $[Ni_4(CNR)_6]$ or $\{Ni(CNR)_2\}$ may be the active species [459].



309

$[Pd_2(CNMe)_6][PF_6]$ reacted with chelating biphosphines, P-P, to give $[Pd_2(P\text{-}P)_2(CNMe)_2][PF_6]_2$, **310**, (P-P = dppe, dppp, dppb or *cis*-$Ph_2PCH{=}CHPPh_2$). The complexes showed no tendency to insert RCN or CO, but were fluxional on the nmr spectroscopic timescale, with exchange of P^1 and P^2. With $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, all the RNC groups were replaced to give **311** [460]. The electronic, Raman and infra-red spectra of $[Pd_3(CNMe)_8][PF_6]_2$ and $[Pd_3(CNMe)_6(PPh_3)_2][PF_6]_2$ have been measured and assigned. 312 is formally a mixed valence compound with two palladium(I) and one palladium(0) centre [461].



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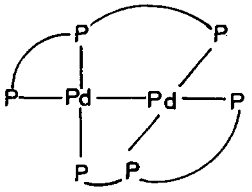

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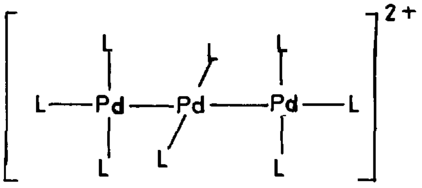


312

The reaction of $[Pt(cod)_2]$ with RNC gave the triangular cluster $[Pt_3(CNR)_3(\mu\text{-}CNR)_3]$ [462]. The species {M-Pt(II)L_2-M} (M = {$Cr(CO)_3Cp$}, {$Mo(CO)_3Cp$}, {$W(CO)_3Cp$}, {$Mn(CO)_5$}, {$Fe(CO)_3(NO)$} or {$Co(CO)_4$}; L = Me_3NC or CyNC) were reduced on platinum or gold electrodes in non-aqueous solvents. All underwent irreversible one-electron reductions to give $\{M\}^-$ and $\{ML_2Pt(I)\}^{\cdot}$, which had low stability but was identified as a platinum(I) species by epr spectroscopy [463].

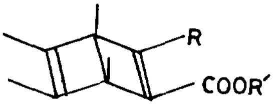
12. CATALYSIS BY METAL COMPLEXES

A number of general reviews have dealt with various aspects of the uses of complexes of nickel, palladium and platinum in catalysis of organic reactions [464-471]. Polymer supported complexes have also received considerable attention [472,473]. Particularly reported have been the synthesis, stability and action of complexes of palladium and platinum on modified silica [474-476]. Preparation of supported metal particles by decomposition of surface organometallic complexes has been discussed [477] as has the effect of substrate complexation on the formation of supported palladium catalysts [478]. The nature of the metal to support bond in nickel complex catalysts has been detailed [479] and there has also been an account of the catalytic properties of complexes of platinum group metals on supports in carbonylation and hydrogenation [480].

12.1 Hydrogenation and Hydrogenolysis

Homogeneous catalytic hydrogenation has been reviewed. Although most of the work discussed dealt with rhodium complexes, some palladium and platinum containing species were also considered [481]. The catalytic properties of palladium complexes fixed on nitrogen and sulphur containing silicas have been discussed [482].

A kinetic study has been performed on the hydrogenation of cyclohexene in the presence of [Ni(acac)$_2$] at 373 K. The mechanism proposed involved the formation of a ternary {Ni(alkene)H$_2$} species which was then slowly converted to products [483]. The new complex [Pd(dppe)(OCOMe)$_2$][ClO$_4$]$_2$ has been shown to have unusually high activity for reduction of styrene at 30 °C and 1 atm H$_2$ [484]. Treatment of ethene with CO/H$_2$O in the presence of K$_2$[PtCl$_4$]/SnCl$_4$ gave ethane by the water gas shift followed by reduction. The reaction was slow but no hydroformylation occurred. The mechanism of Scheme 2 was suggested [485]. The complexes [PtLL'Cl$_2$] (L = PPh$_3$, L' = sulphide or amide) in the presence of SnCl$_2$ were more effective catalysts for styrene reduction than either [PtL$_2$Cl$_2$] or [PtL$'_2$Cl$_2$]. The effect on reactivity of L and L' showed different dependences on *para*-substituents, suggesting that they function differently in the catalytic cycle. It was suggested that the high *trans*-effect of [SnCl$_3$]$^-$ labilises the L' group which then acts as a leaving group [486]. The {Pt/Sn} catalysed hydrogenation of **313** has been investigated [487].



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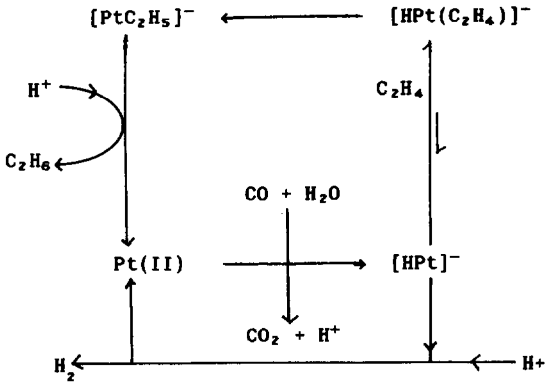
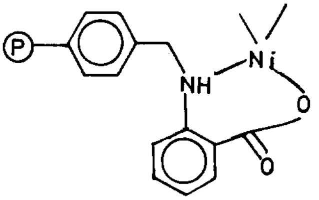


Scheme 2 Mechanism of ethene reduction by H_2/CO in the presence of $[PtCl_4]^{2-}$

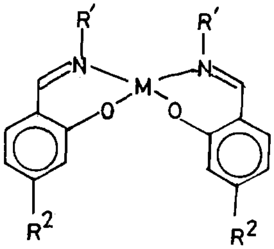
The hydrogenation of ethene over heterogenised complexes of palladium has been investigated [488]. Complexes of poly(vinylpyridine) with $PdCl_2$ have been shown to catalyse hydrogenation of alkenes. Activity depended on the nitrogen:palladium ratio, resin particle size, swelling and solvent coordination ability [489]. The species derived by reduction of $[PdL_2Cl_2]$ with $Na[BH_4]$ could be stabilised by poly(vinylpyrrolidone), and then catalysed reduction or isomerisation of allyl benzene, 1,3-pentadiene, cyclopentadiene, styrene and phenylethyne [490]. $[(\eta^3\text{-}C_3H_5)PdCp]$ on silica or alumina was dried and reduced with molecular hydrogen to give a catalyst for ethene reduction [491]. The kinetics of styrene reduction in the presence of $[PdCl_4]^{2-}$/anion exchange resin have been reported [492]. Reduction of **314** with $Na[BH_4]$ gave a catalyst for hydrogenation of alkenes, but isomerisation and oligomerisation competed [493].



314

The rate of reduction of alkynes in the presence of $[Ni(OCOC_{17}H_{35})_2]/Et_3Al$ was found to be a function of steric hindrance. Up to 85 % of the alkene was obtained in the most favourable cases [494].

The reduction of 1,5,9-cyclododecatriene to cyclododecene was catalysed by **315** (M = Ni or Co) and related species. Activity was increased in polar solvents or with electron donors on the aryl rings [495]. The catalyst formed from $[Ni(acac)_2]/Et_3Al_2Cl_3/PPh_3$ catalysed reduction of isoprene in 1 atm H_2 to give 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene in the ratio 2:1. The monoenes began to isomerise just before completion of hydrogenation. The mechanism was postulated to involve formation of a π-allyl nickel complex which then reacted with hydrogen in the rate-controlling step [496]. The species derived from $[Ni(acac)_2]/Et_3Al$ or $[Ni(acac)_2]/Et_3Al/Na[AlH_2(CH_2CH_2OMe)_2]$ were effective for the hydrogenation of di- and trisubstituted esters from soybean oil, at room temperature and low pressure. However, mixtures of products were still obtained [497]. $PdCl_2$/dmf catalysed the selective reduction of dienes and alkynes to alkenes. Butadiene was reduced to 98.7 % butenes and cyclohexadiene to 95.6 % cyclohexene [498].



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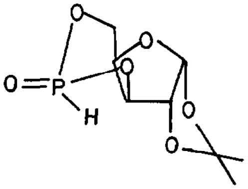
Reduction of soybean oil at 80-140 °C and 1 atm. H_2 was effected in the presence of Ⓟ-PPh_2 and $[Pd(py)_2Cl_2]$. It was suggested that a palladium(0) species, possibly a palladium phosphine cluster, was formed during the observed induction period [499]. Palladium or nickel chloride, immobilised on anthranilic acid derivatised chloromethylated polystyrene, could be reduced by $Na[BH_4]$ to give a catalyst for the reduction of methyl sorbate by 1,2-addition of hydrogen to yield methyl 3-hexenoate [500].

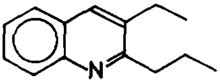
Asymmetric reduction of itaconic acid occurred in the presence of **316**/$[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ in up to 27 % enantiomeric excess [501].



316

Nitroarenes could be reduced to anilines in the presence of $[Pd(PhCN)_2Cl_2]$.

The kinetics of the reaction were studied and a mechanism involving nitrene formation proposed [502]. At 1 atm H_2, the major products were anilines, but at higher pressures only 45 % aniline was isolated, together with 20 % of PhN=N(O)Ph [503]. Nitrobenzene reacted with butanal in the presence of $PdCl_2/CO/H_2O$ to yield **317**, the first step in the reaction presumably being aniline formation [504].



317

The species $[Pd_5(PPh)_2]$ was shown to catalyse reduction of salicylaldehyde at 20 °C and 1 atm. H_2 [505].

$PdCl_2$ supported on functionalised silica catalysed hydrogenolysis of chlorobenzene to benzene at 20 °C and 1 atm. H_2. The reaction was thought to involve oxidative addition of PhCl to $[PdL_n]$ to yield $[PhPdL_mCl]$, which was then reduced [506].

Hydrogenolysis of the alcohols $RR'C{=}CHCH_2OH$ and $RR'CH(OH)CH{=}CH_2$ to give $RR'C{=}CHMe$ and $RR'CHCH{=}CH_2$ was achieved in the presence of $[Pd(acac)_2]/PPh_3/dmf$ using HCOOH as a proton donor [507]. $[Pt(PPh_3)_2Cl_2]$ reacted with hydrogen donors (such as Me_2CHOH or piperidine) to give partial cleavage of the P-C bonds yielding benzene [508].

Estradiol-2-^3H has been synthesised from 2-iodoestradiol by reduction with $Na[B^3H_4]/PdCl_2$ [509]. Acyl halides could be reduced by R_3SnH in the presence of $[Pd(PPh_3)_4]$ to give aldehydes, R'CHO in 75-95 % yield, together with traces of $R'CH_2OCOR'$ [510]. Treatment of allyl ethanoates with $Na[BH_4]$ in the presence of $[Pd(PPh_3)_4]$ resulted in hydrogenolysis *via* a palladium π-allyl complex. Regioselectivity of hydride approach depended on both steric and electronic factors [511].

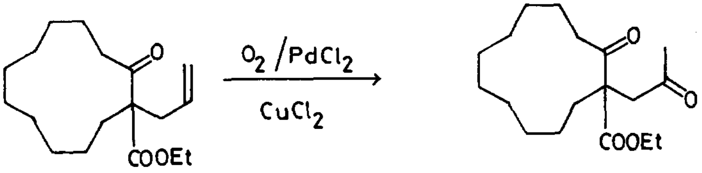
12.2 Oxidation

A new book in the series entitled Catalysis by Metal Complexes has detailed palladium catalysed oxidation of hydrocarbons [512]. New homogeneous catalysts based on heteropolyacids have been reviewed; these have frequently been used as relays for palladium(0) reoxidation [513]. There have also appeared general accounts of the rôle of peroxymetallation in selective oxidation processes [514] and of the oxidation of saturated hydrocarbons by $H_2[SO_4]/Pd[SO_4]/[NO_2]^+$ in 80-100 % $H_2[SO_4]$ [515].

The Wacker reaction continues to attract considerable attention. The addition of 15-30 % by weight ethanoic acid was reported to improve efficiency

[516], and very pure ethanal could be obtained by extractive distillation from the head zone [517]. The mechanism for the reaction proposed by Bäckvall has been disputed by Japanese workers. The pathway of external attack of water on $[Pd(C_2H_4)(OH_2)Cl_2]$ followed by rate-determining loss of Cl^- from $[HOCH_2CH_2Pd(OH_2)Cl_2]$ was said to be incompatible with the measured isotope effects [518]. $Pd(OCOMe)_2$ attached to silica had similar activity for ethene oxidation to the homogeneous system [519]. Reaction of ethene with ethanoic acid in the presence of $[PdX_4]^{2-}$ afforded $HOCH_2CH_2OCOMe$ as the primary product. The mechanism has now been proposed to involve a binuclear π-alkene complex which then isomerises with O_2 or $[ONO]^-$ as nucleophile, to give a σ-organometallic, which is cleaved to the product [520].

Numerous analogues of the Wacker reaction with higher alkenes have been reported. $PdCl_2$ supported on activated charcoal was a catalyst for the vapour phase oxidation of propene to propanone [521]. Patents have reported the conversion of 1-hexene to 2-hexanone using as the catalyst system $PdCl_2/CuCl_2/LiCl/H_3PO_3/[C_{16}H_{33}NMe_3]Br$ [522], 1-octene to 2-octanone with $PdCl_2/CuCl_2/MeO(CH_2CH_2O)_{13}Me$ [523] and styrene to acetophenone with $Pd(OCOMe)_2$ [524]. A number of applications in total synthesis have been noted. **319** was used in the synthesis of muscone [525] and **321** in the preparation of (+)-nookatone [526].



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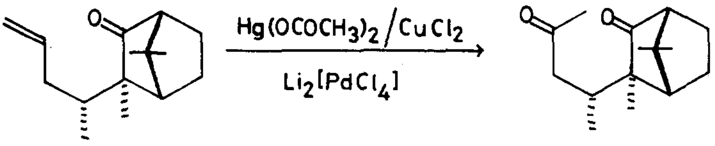
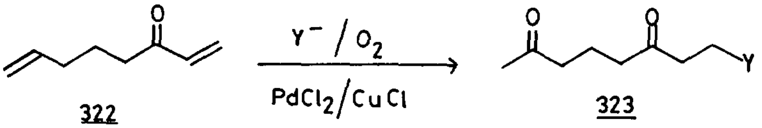
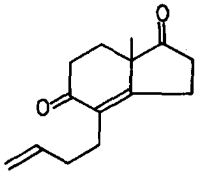


320 321

323, derived from the oxidation of 322, has found uses in the steroid field, and both **324** and **325**, when oxidised to the corresponding methyl ketones, are substrates for aldol reactions to construct steroid A and B rings

[527,528].





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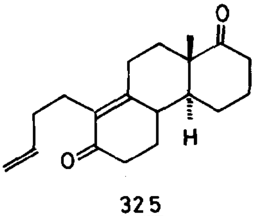

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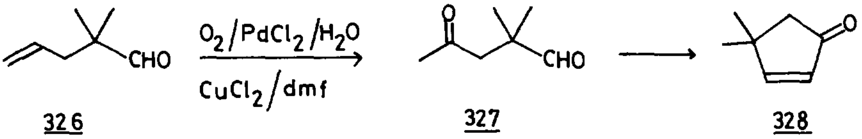
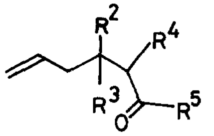
When the oxidation of styrene was carried out in the presence of MeOH/thf instead of the more usual dmf solvent, $PhCH_2CH(OMe)_2$ was obtained in 72 % yield. Not only was the carbonyl product converted *in situ* to the acetal but the usual regiochemistry was also changed, giving a derivative of phenylethanal [529]. The product of oxidation of **326** underwent a facile aldol reaction, providing a convenient synthesis of **328** [530]. A similar reaction of **329** gave, after base catalysed cyclisation, cyclohexenones [531].





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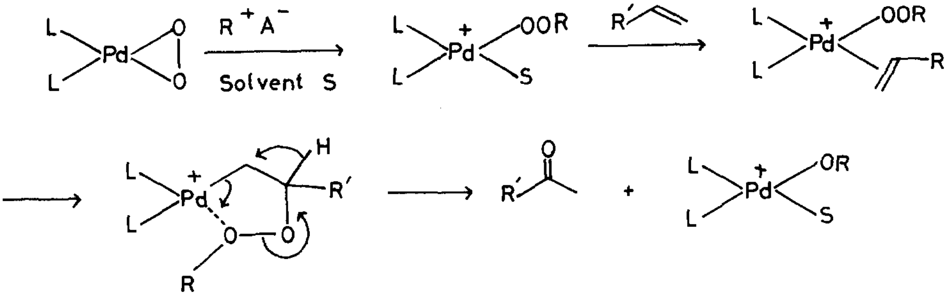
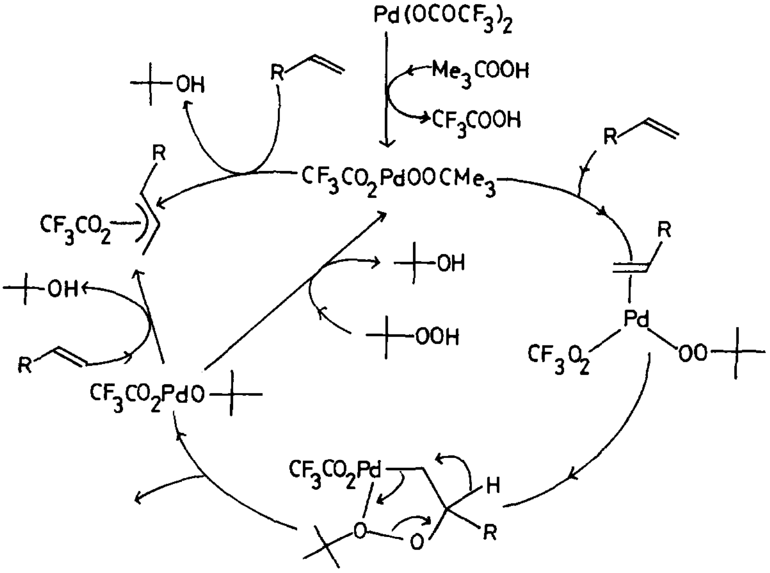
The nucleophilic character of O_2 in $[Pt(PPh_3)_2(O_2)]$ has been established by exchange with *n*-BuLi. The reaction of this complex with ketones was considered as a model for the reaction with alkenes [532]. Reaction of $[Pd(PPh_3)_2(O_2)]$ with 1-octene in the presence of $MeSO_3H$ gave Ph_3PO (36 %) and 2-octanone (50 %). The platinum analogue gave only unreactive dimers. The mechanism proposed is shown in Scheme 3 [533]. An analogous process was proposed for the catalytic oxidation in the presence of Me$_3$COOH (Scheme 4) [534]. A satisfactory catalytic reaction was also obtained using the much less expensive H$_2$O$_2$ [535].



Scheme 3 Mechanism of oxidation of alkenes by [PdL$_2$(O$_2$)]



Scheme 4 Mechanism of catalytic oxidation of alkenes by Me$_3$COOH in the presence of Pd(OCOCF$_3$)$_2$

In the presence of both [{Pd(C$_2$H$_4$)Cl$_2$}$_2$] and [Co(py)(saloph)(NO$_2$)], ethene was oxidised to ethanal. The reaction depends on the oxidation of {Co(NO)} to {Co(NO$_2$)}, and these cobalt species play a similar rôle to copper(II) in the classical Wacker reaction [536]. The precise mechanism of Me$_3$COOH oxidation of αβ-unsaturated esters to β-keto esters in the presence of Na$_2$[PdCl$_4$] has not been established, but it seems more likely that reoxidation of palladium(0) rather than formation of epoxides occurs [537].

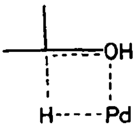
Epoxidation of 2,3-dimethyl-2-butene was achieved using $PhCOC(Ph){=}N_2/O_2/Pd(OCOMe)_2$. The reaction mechanism is not known with certainty, but from a consideration of substituent effects it was concluded that the active species was mildly electrophilic. Epoxidation of *trans*-alkenes gave *trans*-epoxides stereospecifically, but *cis*-alkenes yielded mixtures of *cis*- and *trans*-products [538].

The kinetics of the oxidation of 2-propanol to propanone in the presence of $PdCl_2$ have been investigated. $k(H_2O)/k(D_2O)$ was determined as 1.3 ± 0.1 and k_H/k_D as 1.8 ± 0.1. The mechanism involves a four-centre transition state, 330 [539]. In the presence of HPA-2 ($H_5PMo_{10}V_2O_{40}$) the oxidation involved the reactions (41) - (43) [540].

$$Me_2CHOH + Pd(II) \longrightarrow Me_2C{=}O + Pd(0) + 2H^+ \tag{41}$$

$$Pd(0) + HPA\text{-}2 + 2H^+ \longrightarrow Pd(II) + H_2HPA\text{-}2 \tag{42}$$

$$H_2HPA\text{-}2 + \tfrac{1}{2}O_2 \longrightarrow HPA\text{-}2 + H_2O \tag{43}$$



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[ArHgOCOMe] was shown to react with Pd(II) to give the unstable species [ArPdOCOMe]. Powerful anodic oxidation of this complex suppressed coupling to biaryls, giving instead the oxidised product ArOCOMe [541].

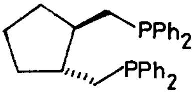
There has been a study of the active species in the catalysis of oxidation of toluene to benzyl ethanoate in the presence of MeCOOH/"Pd". The reactions of $[\{Pd(CO)(OCOMe)\}_4]$ with phen seem to have been well understood but it remains unclear which complex is responsible for catalysis [542]. γ-Benzyl-L-glutamate reacted with sodium hydroxide in the presence of $Na_2[PdCl_4]$ to give palladium(0) and benzaldehyde. A small amount of glutamic acid was also produced, but the main product was pyroglutamate. The reaction mechanism is unknown [543].

12.3 Reactions of Carbon Monoxide and Carbon Dioxide

Hydroformylation of alkenes catalysed by palladium and platinum complexes has been reviewed [544]. $[Pt(CO)(PBu_3)_2Cl][ClO_4]$ together with $SnCl_2$, $ZnCl_2$ or $GeCl_2$ has been used to catalyse hydroformylation of *trans*-2-hexene to give 47 % linear aldehydes. Both isomerisation and H_2/CO addition were promoted [545]. A number of platinum complexes including $[HPt(PPh_3)_2(SnCl_3)]$,

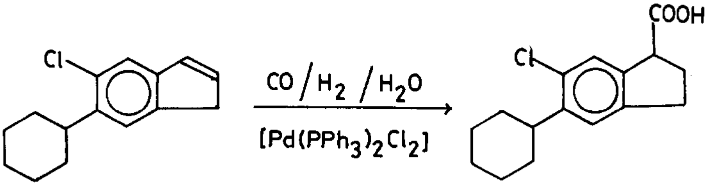
$[Pt(PBu_3)_2Cl_2]/SnCl_2$ and $[Pt(CO)(PPh_3)_2Cl][ClO_4]/SnCl_2$, immobilised on ion exchange resins have been used for hydroformylation of 1-hexene. 97 % aldehydes, of which 97 % were linear, were formed, and metal leaching was low [546]. A binuclear palladium cobalt complex, fixed on phosphinated silica, has been used for hydroformylation of propene [547].

The catalyst formed from $[Pt(PhCN)_2Cl_2]/SnCl_2$ and dppb or **331** gave very high selectivity for the formation of linear aldehydes from 1-alkenes [548]. With $[Pt(DIOP)Cl_2]/SnCl_2$ conditions were found for the conversion of 2-phenylpropene into (+)-3-phenylbutanal in 98 % chemical selectivity but rather modest enantiomer excess [549].



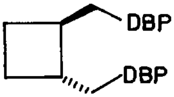
331

A kinetic study of the hydrocarboxylation of 1-nonene in the presence of $[Pd(PPh_3)_2Cl_2]$ has been undertaken [550]. When a mixture of 1-heptene and 2-octene was subjected to hydrocarboxylation conditions in the presence of $[Pt(AsPh_3)_2Cl_2]/SnCl_2$ the 1-alkene reacted selectively, giving a product 89 % selective for the linear ester [551]. **332** was converted to **333** in good yield and regioselectivity using $H_2/CO/H_2O/[Pd(PPh_3)_2Cl_2]$ [552].



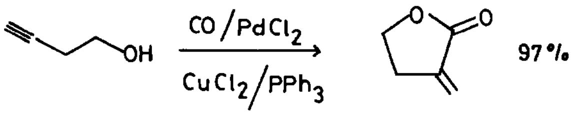
332 333

Asymmetric hydrocarboxylation has generally given rather better optical yields than analogous hydroformylations, since the products are less easily racemised by enolisation under the reaction conditions. Thus $[Pd(PhCN)_2Cl_2]$ with 334 catalysed the reaction of 2-phenylpropene with CO/Me_2CHOH to give the 2-propyl ester of 3-phenylbutanoic acid in 40.3 % enantiomer excess [553].



334

In molecules such as **335**, bearing a suitably positioned hydroxyl group, the reaction may be intramolecular, giving in this case the useful α-methylene lactone, **336** [554]. The unusual oxidative hydrocarboxylation of **337** to **338** occurred in the presence of $PdCl_2/CuCl_2$, but heterogeneous Pd/C gave a better yield [555].



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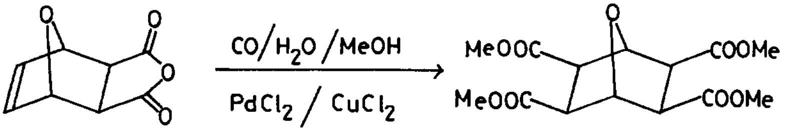


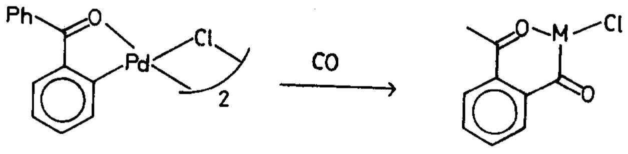
337 338

Two reactions of butadiene with carbon monoxide and alcohols were reported to give somewhat different products. With Me_2CHOH and a catalyst formed from $Pd(OCOMe)_2$/dppe the 3-pentenoate was formed in 26 % yield and the 3,8-nonadienoate in 13.5 % yield. These species are useful as lubricant additives [556]. However, in a phosphine-free system, $PdCl_2/CuCl_2/PrCOONa/HC(OMe)_3$, benzyl alcohol and carbon monoxide with butadiene gave dibenzyl hex-3-ene dioate. Though not explicitly stated it is clear that an oxidation is involved [557] since other patents have reported the isolation of analogous products from substituted dienes using $PdCl_2/CuCl_2$ as catalysts in a CO/O_2 atmosphere [558]. The same product could also be obtained using a CO_2/O_2 atmosphere [559] but conditions were also found for pentadienoate production with up to 80 % selectivity [560].

The carbonylation (1 atmosphere CO) of 1-alkynes in the presence of an alcohol, using $PdCl_2/CuCl_2$ as catalyst, gave $RC\equiv CCOOR'$ in 60-70 % yield. Copper(II) was acting as a reoxidant for palladium(0) [561]. A higher pressure of CO (40 atm.) and a temperature of 180-190 °C was required for carbonylation of benzene to benzophenone, by a pathway thought to involve benzyl chloride. Further reaction gave anthraquinone; the proposed mechanism in this case involved *ortho*-metallation of PhCOPh to give **339**, which is then carbonylated to **340** [562].

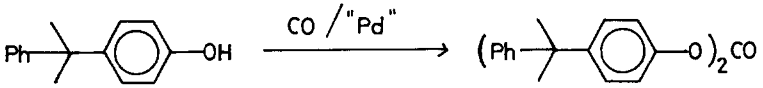
There has been a report of the reactions of carbon monoxide with cyclopropanes. In the presence of $PdCl_2$ in a benzene solvent, cyclopropane gave 73 % chlorobutanoates and 27 % propyl benzene, the proportion of the latter increasing with the ratio of substrate to palladium. Both propyl and

2-methylethyl benzene were obtained using $PtCl_2$. The reaction mechanism is thus far obscure [563].



339 340

Carbonylation of phenols such as 341 gave 342 using a variety of catalyst systems which have been reported in the patent literature. These included $[Pd(PhCN)_2Cl_2]/CuBr/(Me_2CH)_2NEt$ with [564] and without [565] oxygen and molecular sieves, $PdBr_2/[Mn(ON{=}CPhCPhOH)_2]$/1,2,2,6,6-pentamethylpiperidine [566] or $PdBr_2/[Mn(acac)_2]/NaOH/[Bu_4N]Br$ [567,568]. If another alcohol, such as ethanol, was present, mixed carbonates were also obtained [569]. Dihydroxybenzenes gave polycarbonate polymers.



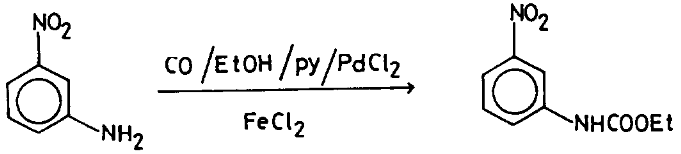
341 342

Carbonylation of allyl alcohol has been shown to occur in the presence of $PdCl_2$, $[Pd(PhCN)_2Cl_2]$ or $[Pd(PPh_3)_2Cl_2]$ to give 3-butenoic acid in up to 82 % yield [570]. A slightly different report described the use of $[Pd(PPh_3)_2Cl_2]/SnCl_2$ to give 2-propenyl-3-butenoate. This complex was also used in carbonylations of benzyl and allyl halides, and reaction mechanisms were proposed [571].

The unusual complexes $[Pd(COOMe)(PPh_3)_2(OCOMe)]$ and $[Pd(COOMe)_2(PPh_3)_2]$ were isolated as intermediates in the catalytic synthesis of dimethyl oxalate from methanol and carbon monoxide in the presence of $[Pd(PPh_3)_2(OCOMe)_2]$ [572].

There has continued to be considerable interest in improving the conditions for conversion, in the presence of palladium complexes, of anilines or nitroarenes to aryl isocyanates [573-576]. An extremely selective reaction of nitrobenzene to give PhNHCOOEt has been reported to occur using $PdCl_2/FeOCl/py/EtOH$ at 180-190 °C and 190 bar CO [577]. Dinitro compounds have been converted both to bis(isocyanates) [578,579] or bis(urethanes) [580]. With 343 the amino group was carbonylated preferentially to 344 [581].

Although the carbonylation of aliphatic amines is a less usual process **345** has been converted to the corresponding isocyanate in the presence of $CO/PdCl_2$. The intermediates proposed include $[Pd(RNH_2)_2Cl_2]$ and $[\{Pd(CO)Cl\}_2]$, and there was some infra-red spectroscopic evidence for these species [582].



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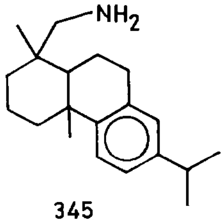
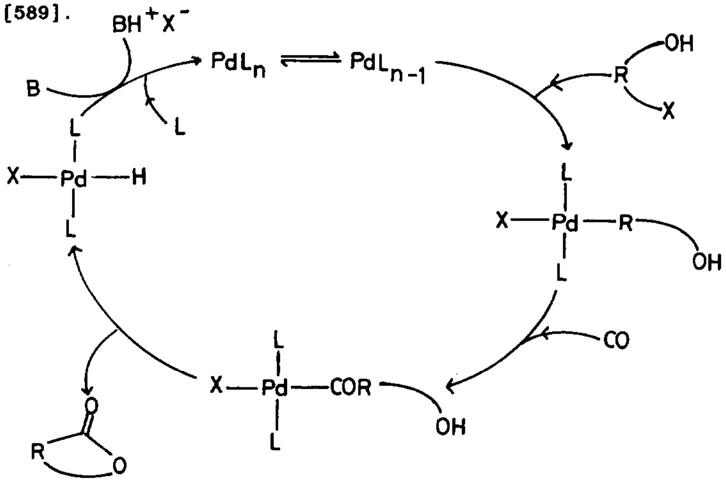


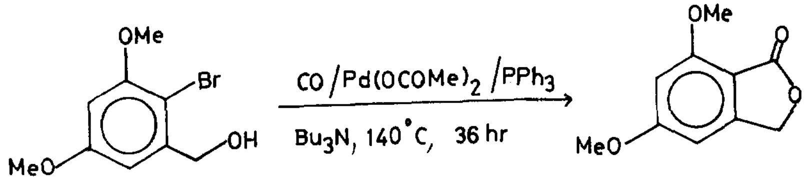
345

Two papers have reported the carbonylation of aryl diazonium salts. These had previously been known to add to palladium(0) to give {ArPdX}. Using CO/[RCOO]Na/Pd(OCOMe)$_2$ in acetonitrile ArCOOCOR was obtained in good yield [583]. Hydrolysis or alcoholysis gave acids or esters, and an overall mechanism was proposed [584].

The carbonylation of aryl, vinyl and benzyl halides in molecules containing an appropriately positioned hydroxyl group proceeds *via* the pathway of Scheme 5. Allyl halides react by an alternative route involving π-allyl complexes [585]. 347 was synthesised in low yield by this route [586] and other syntheses of γ-butyrolactone have been reviewed [587]. The conversion of 348 to 349 was used in the synthesis of zearalenone [588] and 350 to 351 in the preparation of curvalarin [589].



Scheme 5 Palladium catalysed intramolecular hydrocarboxylation of halides



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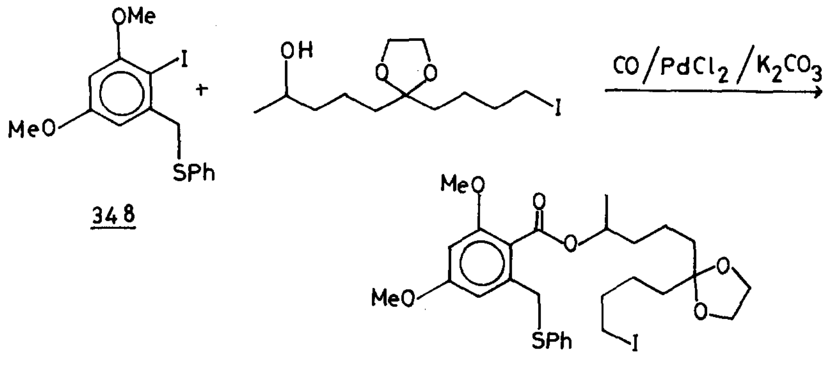

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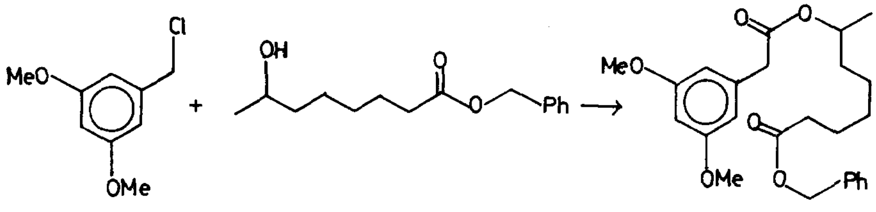
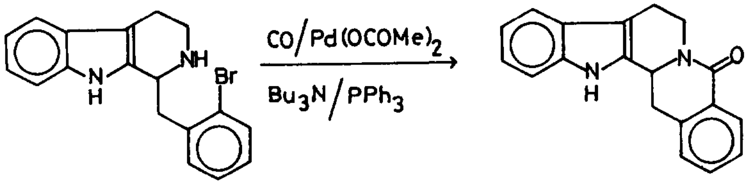


350

351

Amino nitrogen groups may also react with acyl palladium complexes to give amides. 352 yielded 353, 21-oxoyohimbane [590], and the analogous reaction of **354** led to a precursor of sendaverine [591]. The same process occurred with vinyl halides such as **355**, the product being used in a synthesis of (±)-3-aminonocardicinic acid [592].

Catalysed reactions of carbon dioxide are relatively uncommon. Reaction of ethene with CO_2 in the presence of $[Pd(PPh_3)_2Cl_2]$ gave propanoic acid, but with relatively low selectivity [593]. The optimum temperature for reaction of CO_2 with 1,2-propadiene in the presence of $[(\eta^3\text{-}C_3H_5)_2Pd]/Cy_2PCH_2CH_2PCy_2$ was found to be 110 °C. The products were **357**, **358** and **359**. At lower temperatures conversion was lower, and higher temperatures promoted polymer formation. 1,2-Propadiene oligomers were also formed [594]. Carboxylation of 360 in the presence of [Ni(PR$_3$)$_2$] gave a mixture of *cis* and *trans* cyclic carbonates, *via* a radical mechanism [595].



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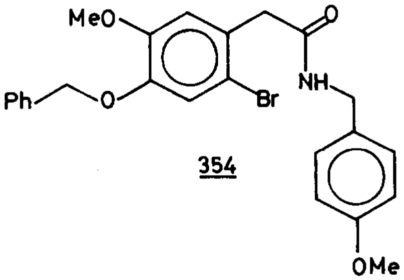

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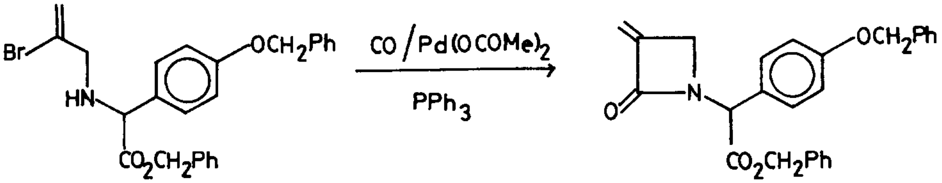

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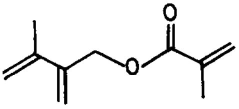

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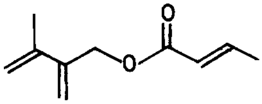

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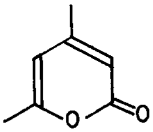

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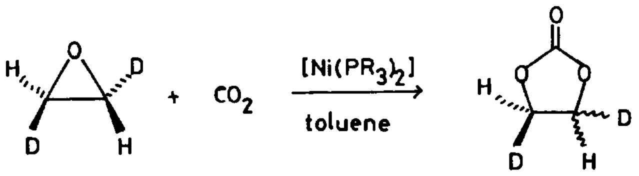

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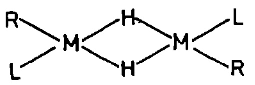
12.4 Hydrosilylation and related reactions

It had previously been reported that $[\{CpNi(CO)\}_2]$, $[Cp_2Ni]$ and $[Ni(cod)(bipy)]^{2+}$ had rather low activity for the hydrosilylation of 1-alkenes. However, η^3-allyl complexes of nickel, activated by PPh_3, are good catalysts. It was suggested that the η^3-allyl nickel intermediates formed were unstable in the absence of phosphine. Regioselectivity was also changed. Phosphine-free $[\{(\eta^3\text{-}C_3H_5)NiCl\}_2]$ gave 100 % α-adducts, but with a phosphine:nickel ratio of 5:1 the β-adduct was the sole product [596]. Acrylonitrile reacted with $MeSiHCl_2$ in the presence of $[Ni(acac)_2]$ to give 80 % $MeCH(SiMeCl_2)CN$ [597].

The Speier catalyst, $H_2[PtCl_6]$, has been proposed to contain $H[Pt(MeCH{=}CH_2)Cl_3]$ as the active species in 2-propanol solution. Aged catalyst contains $[Pt_2(MeCH{=}CH_2)_2Cl_2(\mu\text{-}Cl)_2]$ but the formation of this species could be reversed [598]. The problems of steric effects have been considered for a wide range of substrates, silanes and catalysts. $H_2[PtCl_6]$ was the most regioselective catalyst for addition of Et_2MeSiH to styrene, giving 94.2 % β-adduct [599]. Hydrosilylation of ethene by $C_8H_{17}SiHCl_2$ occurred in 90 % yield in the presence of $H_2[PtCl_6]/Me_2CHOH$ [600]. There was no reaction between dihydrofurans and R_3SiH or R_3GeH in the presence of pure $H_2[PtCl_6]$. Curiously, however, the adducts $R_3MH.H_2[PtCl_6]$ were catalysts, but not for hydrosilylation; 2,3-dihydrofuran gave a polymer and the 2,5-dihydro isomer was isomerised to the 2,3-dihydrofuran [601].

A number of papers have reported the use of $H_2[PtCl_6]$ fixed on ion exchange resins for alkene hydrosilylations. Substrates have included 1-alkenes [602] and allyl alcohols [603]. Activities were improved by pretreatment of the catalyst with silanes [604]. Kinetic and stereochemical studies showed that the reaction was broadly similar to that with the homogeneous analogues [605].

A patent has recorded the use of complexes such as **362** (M = Pd or Pt; R = H, SiR_3 or GeR_3; L = π-acceptor ligand) for alkene hydrosilylation [606]. Enantioselective addition of $HSiCl_3$ to norbornene occurred in the presence of $[(R,S\text{-}PPFA)PdCl_2]$, 363. The *exo*-isomer, 364 was obtained with approximately 50 % enantiomer excess and a similar optical activity was observed in the reaction with styrene [607]. Intramolecular reaction of **365** (M = Si or Ge) was catalysed by $H_2[PtCl_6]$ to give 366 [608].



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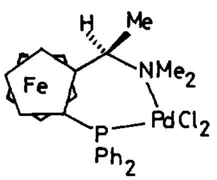

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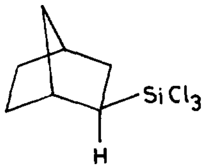

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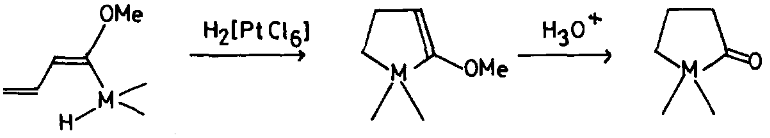
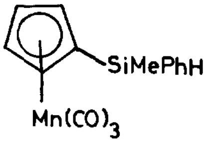


365 366 367

The importance of vinyl silanes in synthetic strategy has made them a significant target to be obtained from alkyne hydrosilylation. The reaction of ethyne with a wide range of silanes using most of the known catalysts has been investigated. Both $[Pt(PPh_3)_2Cl_2]$ and $[Pt(PPh_3)_4]$ proved to be excellent catalysts for vinyl silane production [609]. Further studies reported the use of 362 ($R = R_3Si$, $L = PCy_3$) for alkyne hydrosilylation. Addition of the silane was stereospecifically *cis*, and for 1-alkynes regioselectivity was fair for the anti-Markovnikov product. For internal alkynes, $R\text{-}C{\equiv}C\text{-}R'$, regioselectivity increased as the groups R and R' became more dissimilar [610]. The relative reactivities of different alkynes have been investigated by competition experiments. Terminal alkynes are more reactive than internal ones and rates generally increase with the increasing π-acceptor character of the alkyne [611].

Addition of $Et_nSiCl_{3-n}H$ to $RSi(Cl)(Me)C{\equiv}CH$, in the presence of $H_2[PtCl_6]$, unusually gave $RClMeSiCH{=}CHSiEt_nCl_{3-n}$ (n = 1, 2 or 3) with good regioselectivity but low stereoselection [612]. Analogous hydrosilylation of 1-alkynes using silanes such as 368 and 369 gave mainly linear adducts, 370 [613]. However, with $RCH(OH)C{\equiv}CH$ and **369** the α-adduct was the major product obtained in 36-56 % yield [614].



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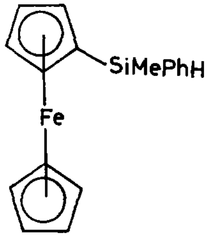

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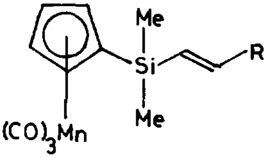

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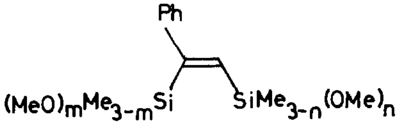
This year has seen an increasing use of disilanes as reagents for silylation. Phenylethyne was thus disilylated to 371 using $(MeO)_mMe_{3-m}SiSi(OMe)_nMe_{3-n}$ in the presence of $[Pd(PPh_3)_4]$. Yields ranged from 34-80 % and addition was essentially *cis* with some *trans*-products formed by *in* *situ* isomerisation. The first step involves splitting the silicon-silicon bond to give **372**, and the regioselectivity observed could be accounted for by considering a four centre transition state, **373** [615]. An analogous reaction occurred using ethyne and $Me_nSi_2Cl_{6-n}$ (n = 2, 3, 4 or 5) [616]. This was also added to dienes to give 1,4-disilylated **Z**-2-butenes stereospecifically [617].



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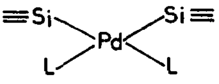

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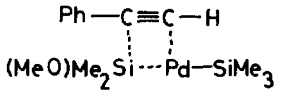

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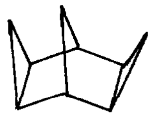
The complexes **362** have also been used to catalyse the 1,4-addition of hydrosilanes to α,β-unsaturated carbonyl compounds. Silyl enol ethers were obtained in good yield as approximately equimolar mixtures of **E**- and **Z**-isomers [618]. Two patents reported the cross-linking of silicone polymers in the presence of $[Pd(2\text{-methylpy})_2Cl_2]$ [619] or $[Pt(\text{dicyclopentadiene})Cl_2]$ [620].

Disproportionation of disilanes was catalysed by $[Ni(PPh_3)_2Cl_2]$ (reaction (44)) [621]. In the presence of $[Cp_2Ni]$/hmpa, allyl halides could be converted by an industrial mixture of $Cl_2MeSiSiMeCl_2$ and $Cl_2MeSiSiMe_2Cl/SiCl_4$ to allyl silanes in good yield [622]. Acyl halides were transformed to $RCOSiMe_3$ by $Me_3SiSiMe_3$ using $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]/P(OEt)_3$ as catalyst. In neither case was there much evidence for the mechanism of the process [623].

$$\mathrm{MeCl_2SiSiCl_2Me} \xrightarrow[58\ \%]{[\mathrm{Ni(PPh_3)_2Cl_2}]} \mathrm{MeSiCl_3} \qquad (44)$$

12.5 Other Additions to Carbon-Carbon Multiple Bonds

Norbornadiene was converted to its bis *exo*-cyclopropane, **374**, by diazomethane in the presence of $Pd(OCOMe)_2$ [624]. Norbornene also gave an *exo*-cyclopropane with Ph_2CN_2, but the yield was low [625]. The reaction of **375**, an aldehyde masked as the ephedrine oxazoline, under the same conditions, was very diastereoselective, giving a cyclopropane of **R**,**R**-configuration [626]. The addition of ethyl diazoethanoate to styrene using $Pd(OCOMe)_2$ as catalyst proceded in 98 % yield to give *trans*- and *cis*-cyclopropanes in a 2:1 ratio. More substituted alkenes were poor substrates, unless strained. Competition experiments demonstrated that the process is very sensitive to steric effects and it was concluded that both alkene and carbene must be simultaneously bonded to palladium [627]. Cyclopropanation of cyclohexene by the α,β-epoxy diazomethyl ketone, **376**, gave a complex mixture of diastereoisomers [628].



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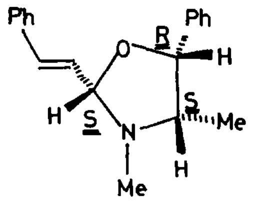

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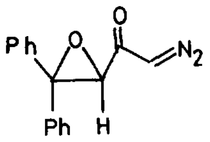

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Hydrocyanation of cyclopentadiene in the presence of $[Ni\{(4\text{-}MeC_6H_4O)_3P\}_4]$ resulted in the addition of one mole of HCN. The mixture of 1-, 2- and 3-cyanocyclopentenes reacted with a further equivalent of HCN using $[NiL_4]/ZnCl_2$ as catalyst to give 1,3-dicyanocyclopentane as the major product [629,630]. Enantioselective hydrocyanation of norbornene to give the *exo*-nitrile was reported to occur with 30 % selectivity in the presence of a complex described as [Pd{(+)-DIOP}]. This stoicheiometry was subsequently shown to be incorrect; the complex was in fact $[Pd\{(+)\text{-DIOP}\}_2]$ [631].

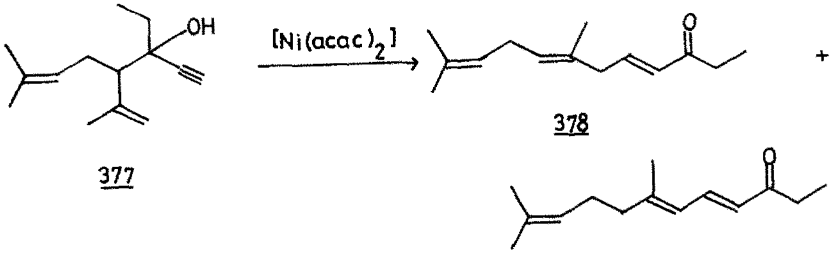
Alkenes were converted to chlorohydrocarbons by HCl addition in the presence of $PdCl_2/CuCl_2/PPh_3$ [632].

12.6 Isomerisation

1-Alkenes have been prepared by isomerisation of internal alkenes in the presence of $[Ni(acac)_2]/Et_3Al/H_2$ [633]. However, 1-alkenes were isomerised selectively to *cis*-2-alkenes in the presence of $[Ni(PPh_3)_3X]$. The reacting species was a nickel hydride, and an addition elimination mechanism was proved by deuterium labelling. Addition of $SnCl_2$ increased both catalyst activity and the *cis:trans* ratio in the product, for reasons which were not well explained [634]. The kinetics of isomerisation of 1-heptene in the presence of $PdCl_2$ have been investigated [635]. Allyl benzene was isomerised using $[Pt(SnX_3)_5X]^{4-}$; the complex for which X = Br was more reactive than that for which X = Cl [636]. 1,5-Cyclooctadiene was converted to 1,4- and 1,3-cyclooctadiene in the presence of *trans*-$[Pt(PPh_3)_2(SnPh_3)Cl]$. The active species is $[HPt(PPh_3)(SnPh_3)]$ and the reaction mechanism involves a series of addition and elimination steps [637].

In the presence of $[Ni(acac)_2]$, **377** could be isomerised to a 2:1 mixture of **378** and **379** [638].

The reversible formation of palladium allyl complexes is responsible for a range of isomerisations. **380** was converted, with good chirality transfer, to **381** in exactly this manner [639]. Allyl alcohols have been similarly interconverted [640]. The oxygen of an epoxide may also act as a leaving group in the formation of an allyl complex. **382** was opened to **383**. The ketone, **384**, was probably formed by a hydride shift and loss of palladium [641]. The mechanism of conversion of α,β-epoxy ketones to diketones was postulated to be somewhat different (Scheme 6) [642].



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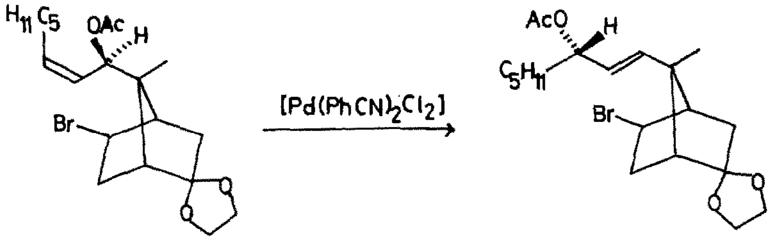

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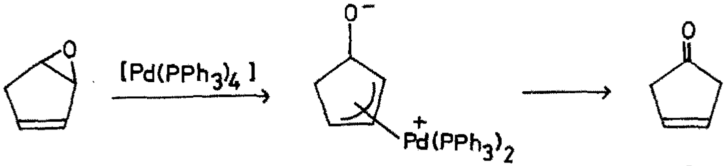

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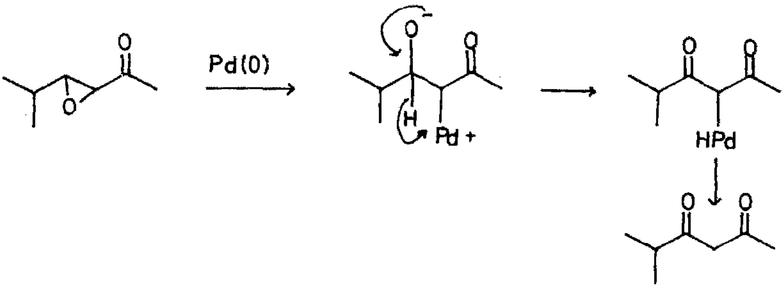
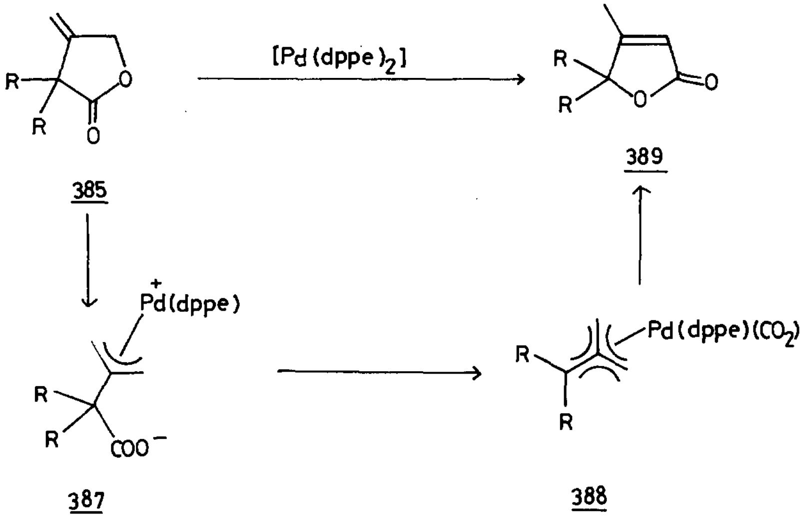
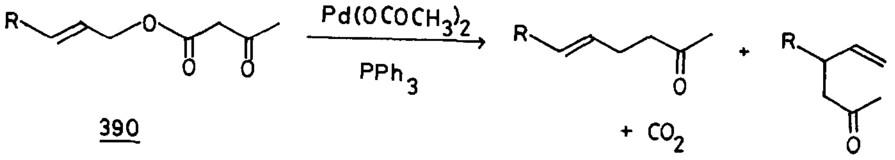


Scheme 6 Palladium catalysed isomerisation of α,β-epoxy ketones to diketones

Opening of five membered rings is similarly facile. 385 was isomerised to 386. The proposed intermediates are 387 and 388 [643]. In this case the mechanism required the reinsertion of CO_2 into the palladium trimethylenemethane complex. In the linear case, 390, however, loss of CO_2 occurred before the enolate anion attacked the palladium allyl complex [644].

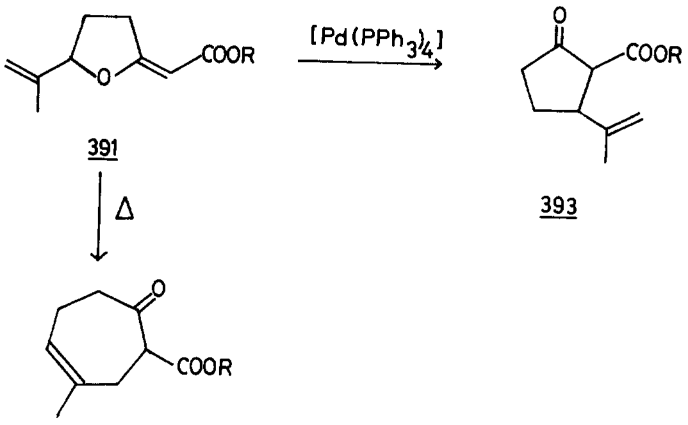




Thermolysis of **391** yielded the seven-membered ring compound, 392, but in the presence of $[Pd(PPh_3)_4]$ a 1,3-shift without allyl inversion yielded 393. The intermediate proposed was **394**, formed by oxidative addition of the allyl ether to palladium(0), The reclosure of **394** occurred preferentially to give a five-membered ring [645]. An analogous process was observed for the prostaglandin precursor, 395 [646].

The Claisen rearrangement of *S*-allyl thioimidates, **396**, was catalysed by palladium(II). Thermolysis, by contrast, gave **398**. Palladium(0) was not a useful catalyst and the mechanism proposed involves a σ-alkyl palladium intermediate, **399**, rather than an allyl complex [647]. An analogous intermediate, **401** was proposed for the palladium catalysed Cope rearrangement of 1,5-dienes, **400**, at room temperature [648]. Similar palladated cyclohexyl cations were thought to be involved in the extremely intricate rearrangement of

403 to **404** in the presence of $PdCl_2$ [649].



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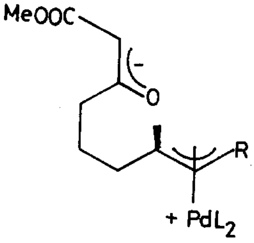

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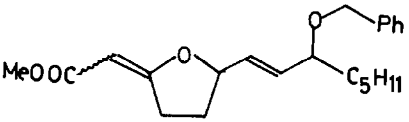

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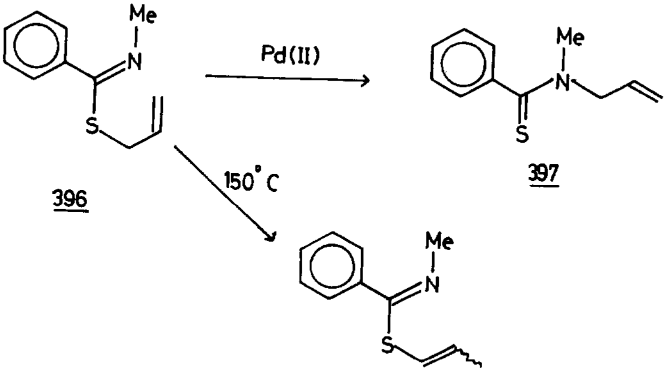

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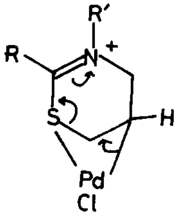

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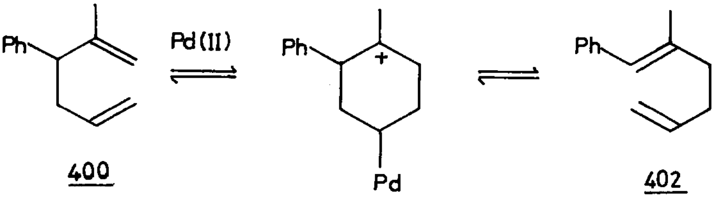

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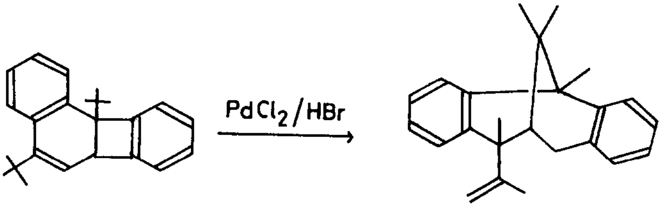

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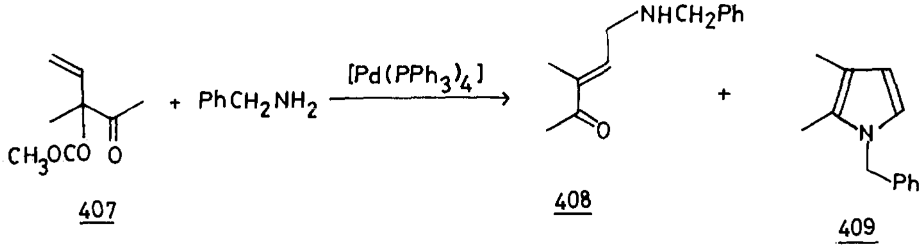
12.7 Substitution of Allyl Derivatives

Rules for selectivity in allylic alkylations catalysed by palladium have been reviewed [650].

Aminations of allyl ethanoates such as **405**, catalysed by [Pd(PPh$_3$)$_4$], gave amino sugars. The reaction was only satisfactory with primary amines; hindered secondary amines promoted elimination to dienes [651]. Reaction of **407** with benzylamine gave a mixture of the expected product **408** and the pyrrole, **409** [652].

An excellent paper by Trost has summarised many of the reactions of allyl ethanoates with carbanions derived from MeOOCCH$_2$X where X is an electron-withdrawing group. The mechanism of the reaction was discussed in great detail and rational explanations for the retention of stereochemistry and the effects on double bond stereochemistry presented [653]. A further paper in this series dealt with intramolecular reactions and the unusual selectivity for the formation of medium and large rings which was shown. Factors affecting intra- and intermolecular reactions were considered, and the syntheses of several naturally occurring macrolides described [654]. Cyclisations of **410** (R = H or Me) have been studied by Tsuji's group. With $P(OPh)_3$ and R = H, 100 % of **413** was formed, whilst with dppe or PBu_3, **411** was the major product. PPh_3 gave up to 51 % of **412**. An analogue of **411** was used in a synthesis of dihydrojasmonate [655] and applications in steroid synthesis were discussed [656]. Conversion of **414** to **415** was the first step reported in a new cyclopentenone annelation to **416** [657].



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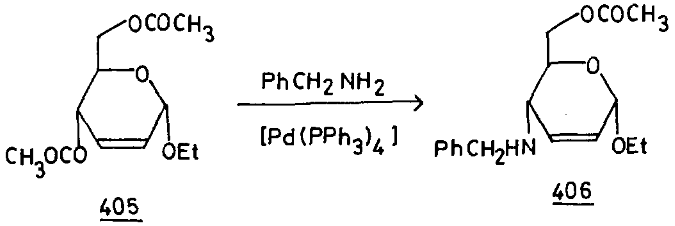

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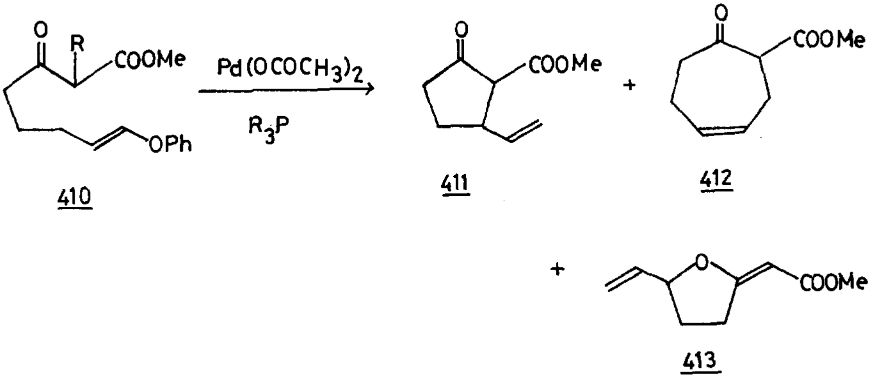

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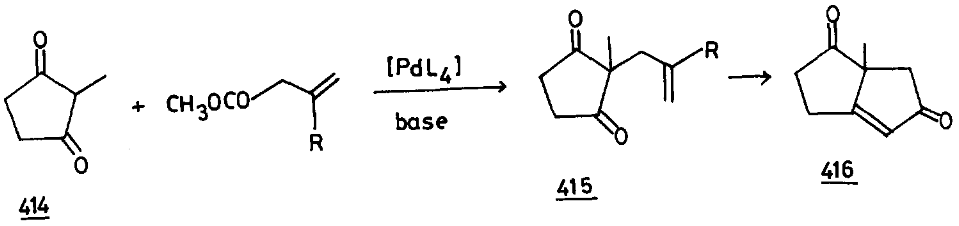
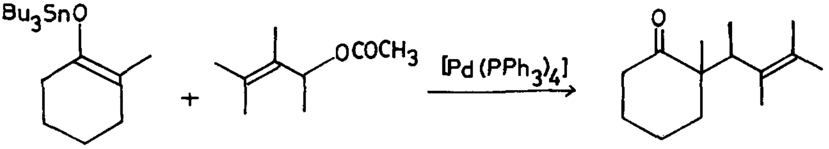


414 415 416

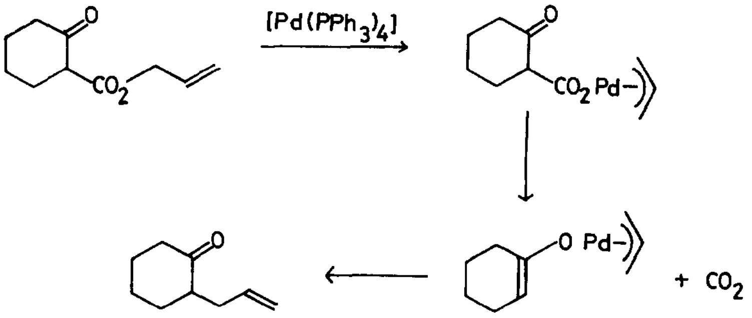
Milder conditions have been found for reactions involving $[(MeOOC)_2CH]^-$ and Cp^- [658]. The anion of $PhSO_2CH_2NO_2$ reacted, as expected, at the less substituted terminus of an intermediate π-allyl palladium complex [659].

Allyl stannanes could be coupled with allyl ethanoates in the presence of $[Pd(PPh_3)_4]$ or $[PhCH_2Pd(PPh_3)_2Cl]$. Only allyl and not alkyl groups could be transferred from tin and some allylic transposition occurred in the stannane fragment [660,661]. Monoallylation of ketones could be achieved using enol stannanes as nucleophiles (reaction (45)). There was good regioselectivity with respect to the allyl ethanoate, with reaction occurring at the less substituted terminus of the allyl. Enolate regioselectivity was more variable, however; with hindered allyl ethanoates, which react slowly, enolate equilibration may occur before alkylation [662].



(45)

Regioselective allylation of ketones could be achieved in good yields by palladium catalysed decomposition of an appropriate allyl ester (Scheme 7). The same products were obtained from the sodium salt of the ester and $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$, although simple ketone enolates do not react readily with palladium allyl complexes [663].



Scheme 7 Preparation of α-allyl ketones

Allyl ethanoates reacted with indole in the presence of $[Pd(acac)_2]/PPh_3$ (1:1) to give mixtures of *N*- and *C*-allylated products, the latter predominating. With a higher P:Pd ratio the *N*-allylated compound was the major product, being converted slowly to the *C*-allyl compound [664].

An allyl sulphone may be regarded as a synthon for a 1,3-dipole. Substitution by $NaCH(COOMe)_2$ occurred in the presence of $[PdL_4]$ (L_4 = $(PPh_3)_4$ or $(dppe)_2$) with retention of stereochemistry at the less substituted site. The process was used in a short synthesis of the sex pheromone of the Monarch butterfly [665].

Allyl alcohols could be substituted by Grignard reagents in low yields in the presence of nickel phosphine complexes. With $[Ni(PHEPHOS)Cl_2]$ as catalyst enantiomer excesses were low but detectable [666]. The use of $[Pd(dppf)Cl_2]$ gave somewhat better yields [667]. A mixture of Me_3SiCl, $CH_2{=}CH{-}CH(CH_2Cl){=}CH_2$ and magnesium metal in the presence of $[Ni(dppp)Cl_2]$ gave as the product $CH_2{=}CH{-}CH(CH_2SiMe_3){=}CH_2$, though the precise sequence of events is not clear [668].

12.8 Coupling of Organometallics with Halides and Related Reactions

Nickel and palladium catalysed cross-coupling reactions of organometallic reagents with organic halides have been reviewed [669] and the applications of such techniques in the formation of aryl-aryl bonds have been included in a review on biaryl synthesis [670].

The heterocoupling reaction of ArMgX with Ar'Br in the presence of $[Ni(acac)_2]$ has been used in the synthesis of several octiphenyls [671]. Selectivities for cross-coupling were reported to be excellent using both this and a range of related nickel complexes as catalysts [672]. Homocoupling of aryl halides was achieved in the presence of Ni(0)/Zn/KI according to reactions (46)-(50) [673].

$$NiX_2 + Zn \longrightarrow Ni(0) + ZnX_2 \tag{46}$$

$$Ni(0) + ArBr \rightleftharpoons ArNiBr \overset{KI}{\rightleftharpoons} ArNiI + KBr \tag{47}$$

$$ArNiI \rightleftharpoons ArI + Ni(0) \tag{48}$$

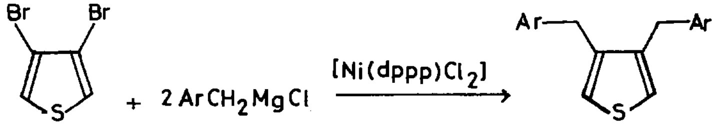
$$2ArNiI \rightleftharpoons Ar_2Ni + NiI_2 \tag{49}$$

$$Ar_2Ni \longrightarrow Ar{-}Ar + Ni(0) \tag{50}$$

Dihaloarenes could be monosubstituted by RMgX or RZnX in the presence of $[Pd(PPh_3)_4]$ or $[Pd(dppb)Cl_2]$. For example, 1,2-dibromobenzene yielded 76 % of 1-bromo-2-butyl benzene with BuMgBr/$[Pd(dppb)Cl_2]$. Only 5 % of the dibutyl compound was formed [674].

Three reactions mechanistically related to these involve phosphorus nucleophiles. $NiCl_2$ reacted with $P(OEt)_3$ to give $[Ni\{P(OEt)_3\}_4]$. Oxidative addition of an aryl iodide was rapid yielding $[ArNi\{P(OEt)_3\}_2I]$ and this was followed by slow reductive elimination of $[ArP(OEt)_3]I$, which collapsed by an Arbusov reaction to $ArP(=O)(OEt)_2$ [675]. Arylation of Ph_2PH with $ArBr/NiBr_2$ gave Ph_2PAr and $[Ph_2PAr_2]X$ [676], and reaction of Ph_2PNR_2 under the same conditions yielded $[Ph_3PNR_2]Br$ [677], but in neither case was the reaction mechanism elucidated. Aryl iodides reacted with $[RS]^-$ in the presence of $[Pd(PPh_3)_4]$ to give aryl thioethers in very good yield [678].

Reactions of heterocyclic halides have been similarly successful and treatment of 417 with $ArCH_2MgCl$ led to 418, which was used as a precursor in a lignan synthesis [679]. Haloisoquinolines have also been successfully reacted with Grignard reagents using $[Ni(dppp)Cl_2]$ as catalyst [680].



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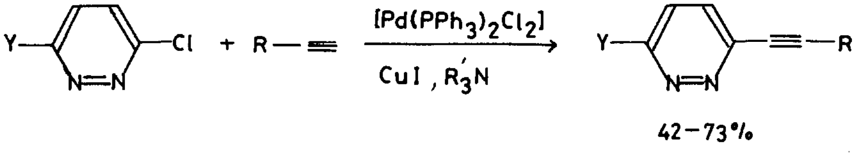
The coupling of 1-alkynes with a variety of halides in the presence of $[Pd(PPh_3)_2Cl_2]/CuI/Et_2NH$ is assumed to involve the transient formation of alkynyl copper compounds. Heterocyclic halides have proved useful substrates (reactions (51) [681] and (52) [682]). Coupling of the alkyne and the halide was thought to be the first step in a one-pot synthesis of 3-dialkylamino indolizines (Scheme 8) [683].



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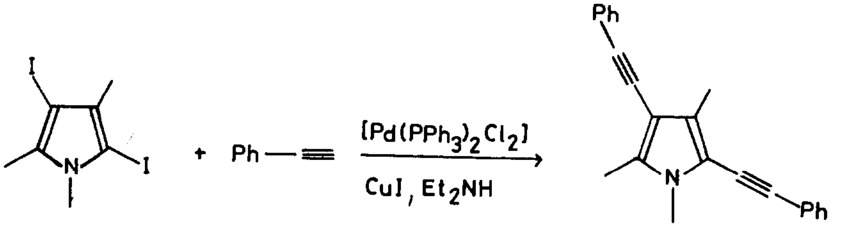

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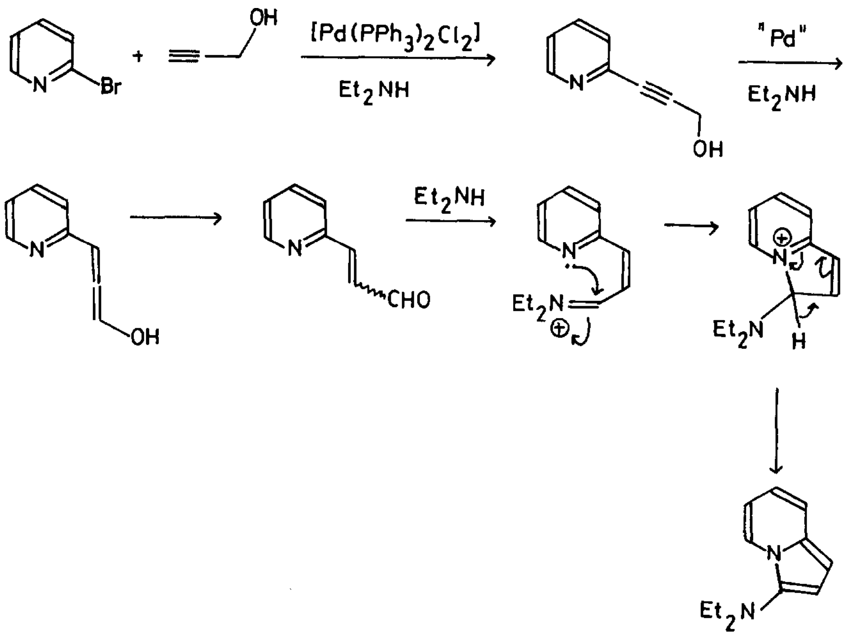
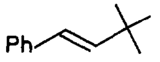


Scheme 8 Synthesis of 3-dialkylamino indolizines

Substitution of vinyl derivatives has continued to be an active area of research, with attention this year focussing on the transformations which can be achieved using leaving groups other than halide. The reaction of Me_3CMgCl with β-bromostyrene in the presence of $[ML_2X_2]$ (L_2 = dppe, dppp, dppb or dppf; M = Ni or Pd) may give **419**, **420** or styrene. The complex with M = Ni and L_2 = dppf gave only 419 in up to 67 % yield. The best selectivity (49 %) for 420 was obtained using $[Pd(dppb)Cl_2]$ [684]. Both the allenyl halide, 421, and the propargyl halide, **422**, reacted with RMgX in the presence of a palladium(0) catalyst formed *in situ* from $PdCl_2/PPh_3/i\text{-}Bu_2AlH$. The predominant product was the allene, 423 [685].



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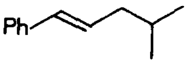

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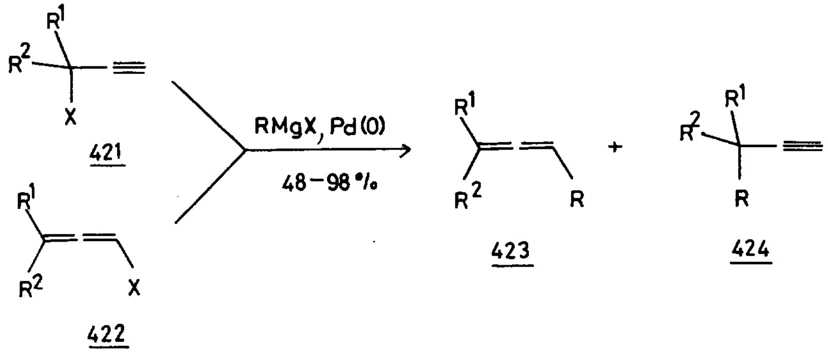
425 has been used as a ligand at nickel for the enantioselective coupling of PhCH(Me)MgCl with vinyl bromide. Despite a slightly dubious method of correction for the optical purity of the ligand, optical yields were impressive (up to 94 % for R = CMe_3) [686]. A polymer bound analogue of **425** gave slower reactions but a similar degree of stereocontrol, and could be reused several times without loss of rate or chiral efficiency [687].



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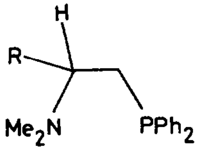
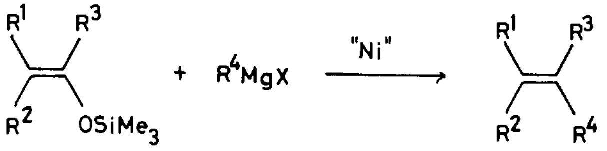


425

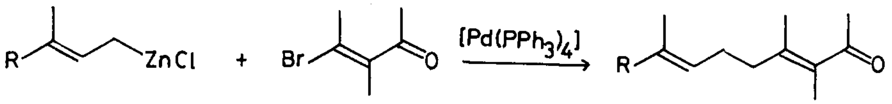
Silyl enol ethers have proved suitable substrates for substitution reactions such as (53). [Ni(acac)$_2$] was the most reactive catalyst, but this was at the expense of the regio and stereochemical purity of the product. [Ni(PPh$_3$)$_2$Cl$_2$] gave slower reactions but higher purity products [688].



(53)

[Ni(dppp)Cl$_2$] has proved a good catalyst for stereospecific substitution of vinyl sulphides [689] and selenides. Aryl and allyl selenides were also substituted, but some Ar-Ar was also obtained. Curiously, PhSeMe >> PhCl > PhSMe in reactivity, a difference which should be of great interest in the preparation of specifically substituted aryl rings [690].

There have been further developments of the nickel and palladium catalysed cross-coupling reactions of organozinc compounds with halides. Reaction (54) was > 95 % stereospecific and the product was used in the synthesis of mokupalide and dendrolasin [691]. Both organozinc and organomercury compounds of this type reacted with R^{2}Cl=CR^{3}R^4 [692]. The intermediate in all such reactions was thought to be **426** which may give **427** by reductive elimination or **428** and **429** by β-hydride elimination. Steric factors seem to be important in determining the path chosen, since Me$_3$C-metal derivatives reacted *via* β-hydride elimination, but *n*-Bu and *sec*-Bu zinc derivatives gave cross-coupling. Homoallyl and homopropargyl zinc halides also work well, despite the existence of a β-hydride elimination pathway which would give a conjugated species [693].



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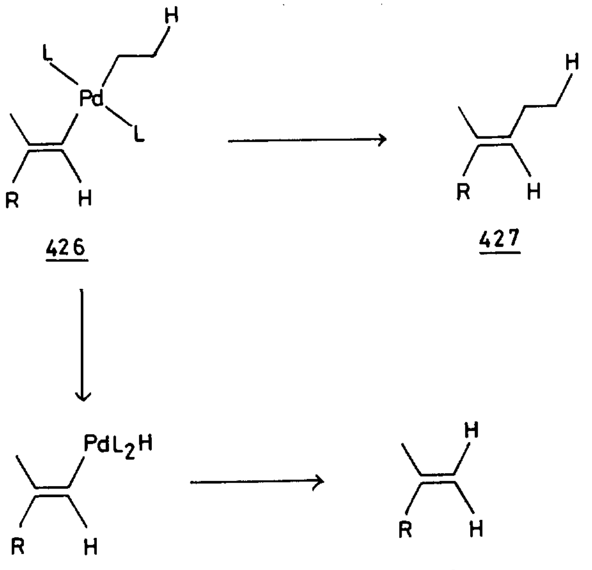


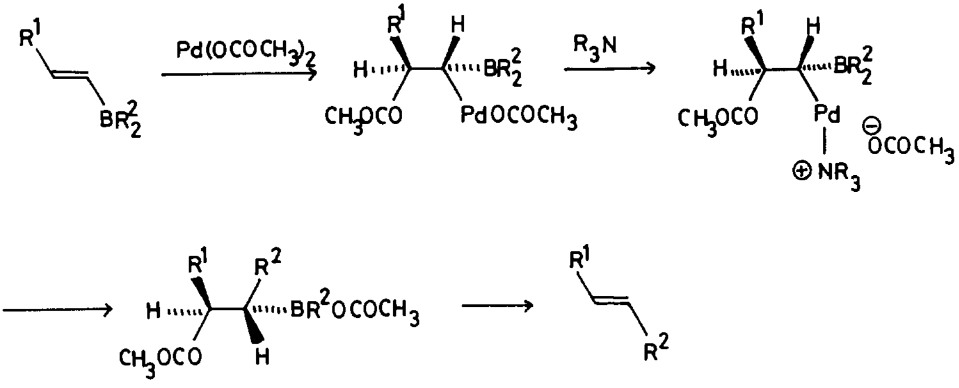
426 427 428 429

Hydroboration of 1-alkynes with HB(Sia)$_2$ gave *trans*-RCH=CHB(Sia)$_2$. These vinyl boranes were coupled with allyl and benzyl halides in moderate to excellent yields in the presence of [Pd(PPh$_3$)$_4$]/base. The presence of a base was essential in forming the "ate" complex; the initial borane is insufficiently nucleophilic to attack palladium [694]. A related reaction, using Pd(OCOMe)$_2$ as catalyst follows a somewhat different pathway (Scheme 9; R^1 = Ph, R^2 = Sia or Bu) [695].

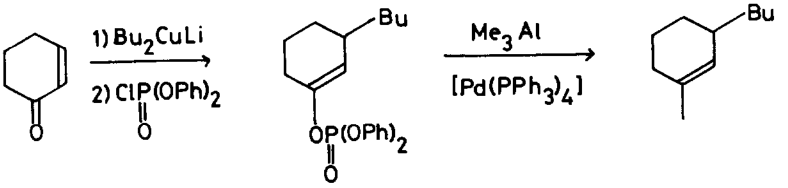
Enol phosphates reacted with Et$_3$Al in the presence of [Pd(PPh$_3$)$_4$] to give vinyl species (reaction (55)) [696]. Vinyl phosphonates, which cannot readily be synthesised by the Arbusov reaction, were made according to reaction (56). The precise mechanism was not known, but it is likely that it involves a vinyl palladium intermediate [697].

Both aryl and vinyl bromides could be substituted by Cl$^-$ in the presence of [(2-MeC$_6$H$_4$)Ni(PPh$_3$)$_2$Br]. The active species involved are probably Ni(I) and

Ni(III) complexes [698].



Scheme 9 Palladium catalysed reactions of vinyl boranes



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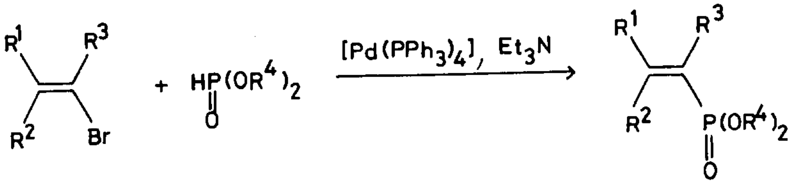

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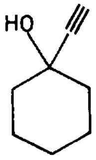
12.9 Oligomerisation, Polymerisation and Telomerisation

The kinetics of ethene dimerisation in the presence of $PdCl_2$ [699] and heterogenised π-allyl nickel complexes [700] have been studied. Other catalyst systems used for ethene or propene dimerisation have included $[\{(\eta^3\text{-}C_3H_5)NiX\}_2]/AlCl_3/ArX$ [701] and $[\{(\eta^3\text{-}C_3H_5)NiBr\}_2]$ with $TiCl_3$, $AlBr_3$, Ph_3P or $(Me_2CH)_3P$. In the last case epr data implied the presence of nickel(I), and a mechanism involving σ- and π-allyl nickel species was proposed [702]. Propene dimerisation in the presence of $[Ni(PCy_3)_2Cl_2]/i\text{-}Bu_2AlCl$ gave, after isomerisation, 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene. The rate of isomerisation depended on the solvent, and bromoarenes are supposed to participate in catalyst regeneration [703]. On a solid supported catalyst nickel is generally fixed as nickel(II). On reaction with $RAlCl_2$ and alkene nickel(0) was formed. In solution this was rapidly deactivated but on the polymer aggregation was retarded and the catalyst had a longer lifetime [704,705].

Oxidative dimerisation of styrene gave 1,4-diphenyl-1,3-butadiene in the presence of palladium(II) fixed on a cation exchange resin. Kinetic studies of this process suggested that the active species may be polynuclear [706]. The analogous process using $Pd(OCOMe)_2$ in solution and 2-phenylpropene as the substrate gave mainly diphenyl hexadienes with some $PhC(=CH_2)CH_2OCOMe$. Increased temperature favoured the allylic oxidation product, but in no cases were the yields really adequate for practical applications. There was evidence for two reaction pathways, one involving $[(\eta^3\text{-}CH_2CHPhCH_2)Pd(OCOMe)]$ which gave the allyl ethanoate, and the other which gave oxidative dimers and some minor products including enol ethanoates. This study gave very different results from most others in this field and, if correct, calls into question many previous data [707].

The complexes $[NiL_2(NCS)_2]$ (L = PBu_3 or PPh_3) were found to be catalysts for the cyclotrimerisation of phenyl ethyne, $HC\equiv C\text{-}CMe_2OH$ and **430**. The monoalkynyl species, *trans*-$[RC\equiv C\text{-}NiL_2(NCS)]$ were intermediates, and if used as catalysts, gave lower induction periods. The ligands, L, influenced both rate and regiochemistry, though **430** gave exclusively the 1,3,5-trisubstituted arene, for steric reasons [708,709]. Cyclotetramerisation of alkynes to cyclooctatetraenes in the presence of nickel complexes has been reviewed [710]. Reaction of 3-hexyne with CO_2 in the presence of $[Ni(cod)_2]$/dppb gave **431** as the major product in up to 57 % yield. The other products were arenes and **432-434**. With $[HNi(dppe)_2]$ as catalyst only **432-434** were obtained [711]. Ethyne and allyl chloride could be codimerised in the presence of $PdCl_2/LiCl$ or $Pd(OCOMe)_2$. During the early stages of the reaction 1-chloro-1,4-pentadiene and 1-chloro-1,3,6-heptatriene were the major products [712].

Polymerisation of 1,2-propadiene using $[Ni(acac)_2]/R_nAlCl_{3-n}$ has been studied. Addition of Lewis acids increased the rate, whilst Lewis bases gave lower rates and changed the selectivity from 1212 to 1221 [713]. Polymerisation of R-2,3-pentadiene in the presence of $[(\eta^3\text{-}C_3H_5)_2Ni]$ gave a largely stereoregular polymer. Both stereoregularity and enantioselectivity were higher at low conversion [714].



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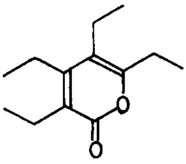

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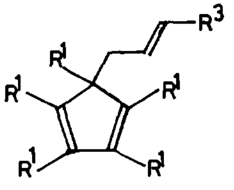

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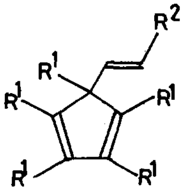

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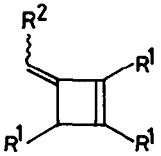


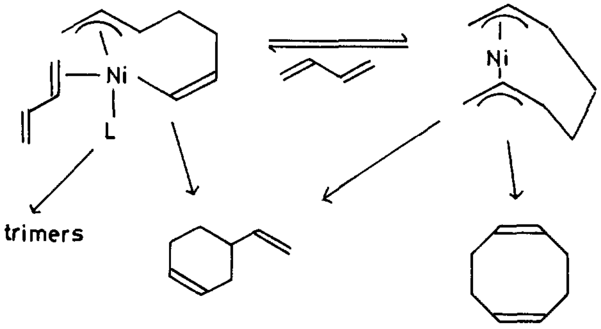
434

The stereoregular and sequence regular polymerisation of butadiene by nickel catalysts has been reviewed [715]. The effect of solvent on the reaction kinetics in the presence of $[\{(\eta^3\text{-}C_3H_5)Ni(OCOCF_3)\}_2]$ has been investigated; polar solvents gave lower rates [716]. Spectroscopic studies of the structure and dynamic behaviour of the catalyst in various solvents threw some light on the problem, which was interpreted in terms of a random solvation sphere from dipolar interactions between the complex and solvent molecules [717]. $[(\eta^3\text{-}C_3H_5)_2Ni]$ fixed on silica and/or alumina gave a catalyst for butadiene polymerisation. An increase in silica content gave an increase in activity and in 1,4-*cis*-segments, but either support alone gave 97 % *trans*-polymer [718]. Two patents have reported the use of $Ni(naphthenate)_2/MeOBF_2/i\text{-}Bu_3Al$ as a catalyst for the production of 97 % *cis*-1,4-polybutadiene [719,720]. 2-Alkyl-1,3-butadienes gave homopolymers and copolymers with a high *trans*-1,4-content using $[\{(\eta^3\text{-}C_3H_5)NiX\}_2]/RCOOH$ as the catalyst system [721]. A system based on nickel(0)/butadiene/Et_2AlCl/PPh_3 had greater ethene oligomerisation activity than the nickel(II) analogue [722].

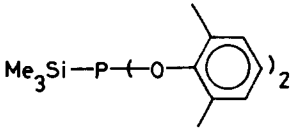
Reductive dimerisation of butadiene gives 1,7-octadiene, and five further patents have reported the use of $[Pd(acac)_2]/HCOOH/P(CHMe_2)_3$, $[Pd(NO_3)_2(OH)_2]/[HCOO]Na/P(CHMe_2)_3$ and $Pd(OCOMe)_2/HCOOH/P(CHMe_2)_3/Et_3N/py$ as catalyst systems with selectivities varying between 87 and 97 % [723-727].

General aspects of the use of metal complexes for cyclooligomerisation of butadiene have been reviewed [728,729]. The changes in distribution of cyclooligomers with conditions [730] and more particularly with added ligand, cannot be explained solely on the basis of the frontier orbital controlled equilibrium of Scheme 10; some kinetic selection must also occur [731].

There have been three reports of very good selectivity for 1,5-cod formation using as catalyst systems $[Ni(acac)_2]/Et_3Al/$**435** [732], $[Ni(acac)_2]/Et_3Al/(PhO)_2PO(CHMeCH_2O)_2PO(OPh)_2$ [733] or $[Ni(acac)_2]/i\text{-}Bu_3Al/PPh_3/$**436** [734,735]. Good selectivity for 4-vinylcyclohexene in the reactions catalysed by $[Ni(acac)_2]/Et_3Al/R_2NH/L$ (L = **437** or **438**) was attributed to blocking of further oligomerisation by the bulk of the phosphine [736]. Similar selectivity was obtained using $[\{Fe(NO)_2Cl\}_2]/[Ni(cod)_2]$ as catalyst, but it seems likely that in this case only an iron species is actively involved [737]. However, as has been previously noted, rather small changes in catalyst give rise to very substantial changes in product ratios. Thus [Ni(acac)$_2$]/(EtO)AlEt$_2$/(RO)$_3$P gave mainly cyclododecatrienes [738].



Scheme 10 Selectivity in cyclooligomerisation of butadiene in the presence of nickel complexes.



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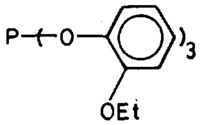

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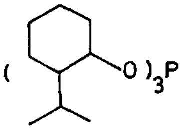

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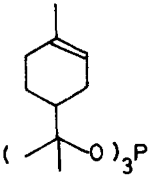

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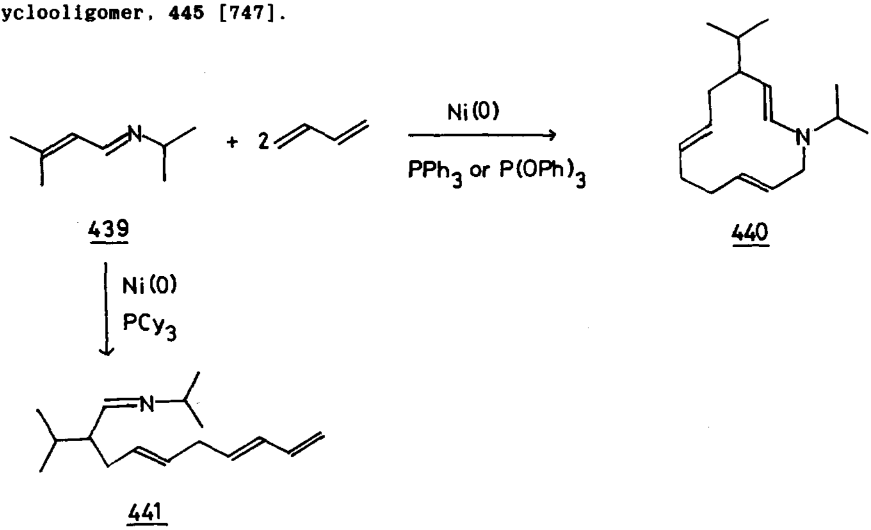
Linear dimers of isoprene were obtained using palladium complexes as catalysts. With [Pd(acac)$_2$/PPh$_3$/[PhO]K, 2,7-dimethyl-1,3,7-octatriene was the major product [739]. Both [{Fe(NO)$_2$Cl}$_2$]/[Ni(cod)$_2$] [740] and [HNi(PCy$_3$)$_2$Cl] [741] gave a variety of cyclodimers and their isomerisation products.

Reaction of butadiene with 1,3-hexatriene gave a copolymer in the presence of [Ni(cod)$_2$]/TiCl$_4$ [742]. Cyclohexadiene and ethene, however, were codimerised by [Ni(cod)$_2$]/Et$_2$AlCl/L (L is a chiral aminophosphine such as MePhCHNMePPh$_2$) to give 3-vinylcyclohexene in up to 87 % chemical and 73.5 % optical yield [743]. Ethene was codimerised with a mixture of octatriene isomers in the presence of $[Ni\{P(OEt)_3\}_4]/H^+$ to give C_{10} trienes with 60-88 % selectivity. A mechanism for the reaction was suggested [744] and propene reacted similarly [745].

Reductive codimerisation of butadiene with 1-butene-3-yne in the presence of $[Pd(NO_3)_2(OH)_2]/P(CHMe_2)_3/Et_3N/HCOOH$ yielded 1-octene-7-yne [746]. Butadiene reacted with the heterodiene **439** to give **440** using $P(OPh)_3$ or PPh_3 as the ligand at nickel(0) and 441 using PCy_3. This is the first example of a change from linear to cyclooligomerisation by changing the ligand in a nickel phosphine complex. The products also changed with the nature of the substituents; for example **442** gave **443** in 90 % yield, but **444** gave the cyclooligomer, 445 [747].



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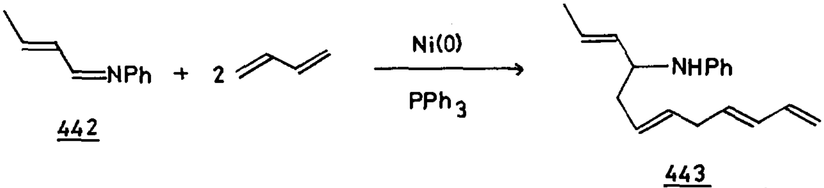

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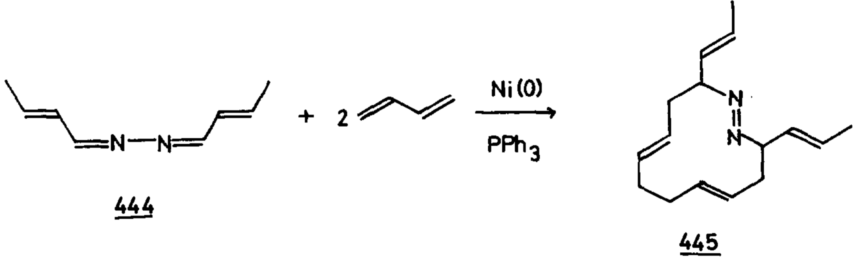
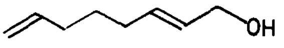


444

445

Telomerisation of butadiene with water in the presence of [Pd(acac)$_2$]/PPh$_3$ with CO$_2$/H$_2$O/dmf or [Ti(acac)$_2$]/Me$_3$COH, gave the linear octadienol, **446**, together with a small amount of the branched compound, **447** [748,749]. Using a catalyst derived from PdCl$_2$/Na[O$_2$SCMe$_3$]/MeOH also gave predominantly a linear telomer [750]. The selectivity of reaction of diols to give mono and dioctadienyl ethers has been examined [751].



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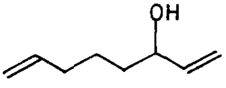
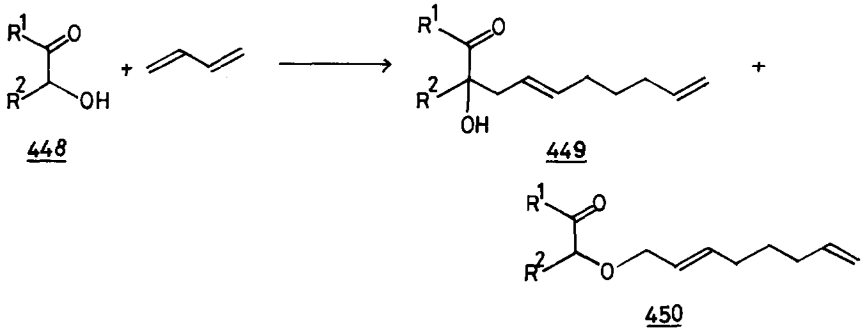
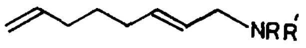


447

The linear telomer of ethanoic acid and butadiene, formed in the presence of Pd(OCOMe)$_2$/PPh$_3$, has been used in a synthesis of curvularin [589]. This linear ethanoate could be equilibrated with the branched isomer, which has been employed in a steroid synthesis [527]. In the presence of CO$_2$ and using palladium bound to silica as catalyst, the usual telomers were not obtained, the major products being diacetoxybutenes [752]. α-Hydroxy ketones such as **448** were telomerised at either carbon or oxygen to give **449** and **450**. The main product was **449** with PdCl$_2$/Na[O$_3$SC$_6$H$_4$-4-Me] but [Pd(PPh$_3$)$_4$] gave mainly 450. The reason for the change is not clear, but it may be related to the difficulty of forming an enol or enolate of 448 in the absence of strong base [753].



Further telomerisations of butadiene with secondary amines in the presence of [Pd(acac)$_2$]/PPh$_3$ or P(OR)$_3$ have been reported to give **451**. Primary amines gave mixtures of mono and dioctadienyl amines [754]. The analogous reaction of isoprene gave mixtures of the telomers, **452-454**, **454** being a previously unobserved type of adduct. Under a nitrogen atmosphere the proportions of **452:453:454** were 20:44:28, changing to 40:32:13 under CO$_2$. Increasing the temperature at which the reaction was conducted favoured 453 and **454** [755].



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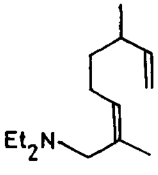

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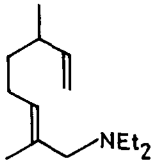

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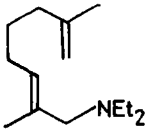

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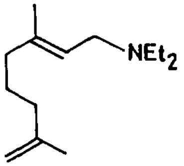
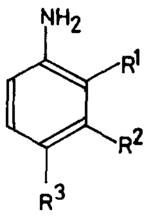


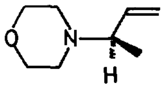
454

Anilines, **455**, could react with butadiene to give mono and dioctadienyl amines. The overall yield of the reaction decreased as the basicity of the aniline decreased. *m*-Substituents promoted bis(octadienyl) amine formation, but *p*-substituted anilines gave mainly 1:1 adducts. Addition of tfaH gave bis products in most cases [756].



455

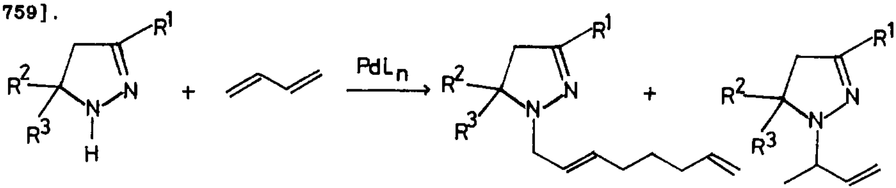
Both piperidine and morpholine have proved useful substrates for telomerisations catalysed by $[Ni(acac)_2]/R_3Al/P(O\text{-}menthyl)_3$. Chemoselectivity was poor compared with palladium catalysts, but impressive enantioselectivitie were noted in some of the products (for example, **456**; a linear isomer of this species and octadienyl amines were also produced) [757].



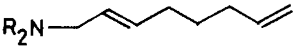
456

The heterocycle, **457**, reacted with butadiene and other dienes to give **458** as the major product, together with a small amount of **459** [758].

Amino alcohols, R_2NCH_2OH, have been shown to give very little of the conventional telomerisation products, either through nitrogen or oxygen. The formation of **460**, **461** and **462** as the major products in the presence of palladium(0) suggests that R_2NCH_2OH gave $(R_2N)_2CH_2$ under the reaction conditions, and that this subsequently decomposed to R_2NH and formaldehyde [759].



457 458 459



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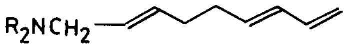
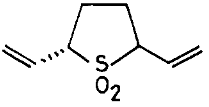


461

462

Sulpholenes and **463** were formed from the reaction of SO_2 and butadiene in the presence of $[Pd(acac)_2]/Et_3Al/PPh_3$. The key intermediate was **464** [760]. The same intermediate is probably crucial in reaction (57) [761].



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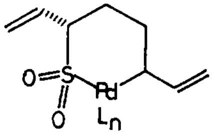

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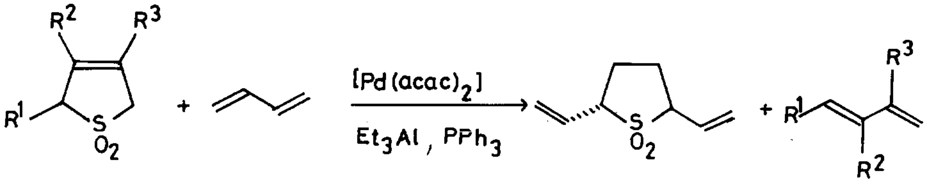
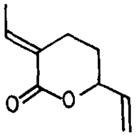


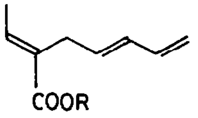
(57)

Telomerisation of CO_2 with butadiene in the presence of palladium(0) gave **465**, **466** and **467** at 80-100 atm. and 70 °C. Hindered phosphines such as PCy_3 and $P(CHMe_2)_3$ gave the best yields of **465** [762].

Telomerisation of butadiene with carbon nucleophiles such as the anion of diethyl malonate was used as an early step in the synthesis of the pine sawfly pheromone [362]. α-Keto amides also reacted exclusively as carbon nucleophiles (reaction (58)), the products being used in amino acid syntheses [763].



465



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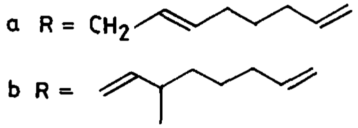

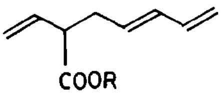

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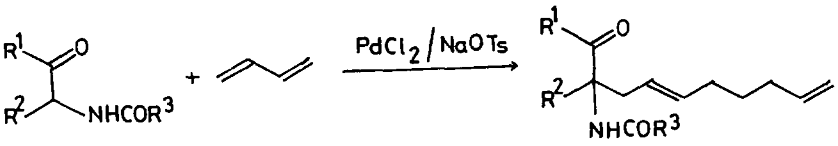
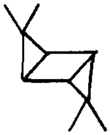


(58)

3,3-Dimethylcyclopropene, gave mainly the dimer, **468**, together with small amounts of trimers and tetramers, in the presence of $[PdL_2]$ (L = cod or dba) or $[Pd(acac)_2]/(EtO)AlEt_2$. However, in the presence of P(*sec*-alkyl)$_3$ the trimer, **469**, was formed in > 90 % yield. Other phosphines gave dimers, trimers, tetramers and higher oligomers in ratios which depended on the phosphine and the P:Pd ratio. A convincing mechanism was proposed [764]. Some further reactions of methylene cyclopropane have been reported. In the presence of $[Pd(PPh_3)_4]$ dimerisation gave **470** *via* a trimethylenemethane palladium complex. Ethene and strained alkenes added to the intermediate to give methylene cyclopentenes such as **472** [765]. 1,2-Propadiene also reacted with **471** to give **473**, **474** and **475** , the exact proportions depending on the palladium complex used as catalyst [766].



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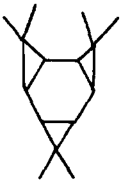
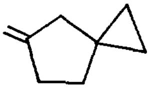


469



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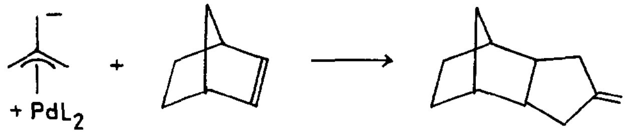
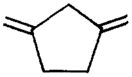


471

472



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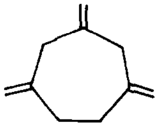

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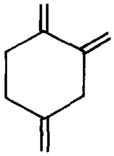
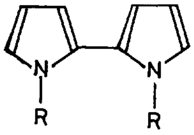


475

Oxidative dimerisation of 1-substituted pyrroles in the presence of $Pd(OCOMe)_2$ gave **476** [767]. Poly-2,5-thienylene was obtained on treatment of 2,5-dibromothiophene with magnesium followed by $[Ni(acac)_2]$ [768].



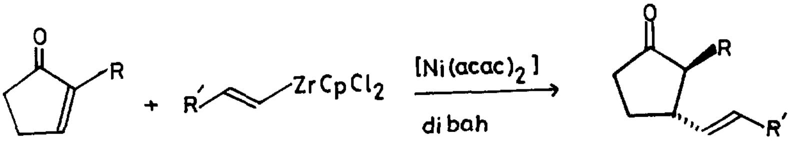
476

12.10 Miscellaneous Coupling Reactions

trans-$[RCH{=}CHZrCpCl_2]$, formed by alkyne hydrozirconation, has been used for conjugate addition to enones in the presence of $[Ni(acac)_2]$ as catalyst. There was no 1,2-addition and in reaction (59) only the *trans*-product was formed [769]. Alkynyl aluminium compounds reacted similarly, with only the alkynyl group being transferred in a synthesis of a prostaglandin precursor (reaction (60)) [770]. Electrochemical studies have elucidated the reaction mechanism (Scheme 11). The precise nature of the complexes is not known and it may be that there are several species with different degrees of aggregation [771]. It seems unlikely, however, that this mechanism operates in the related reaction (61) [772].

The reaction of the cyclopropyl ketone, **477**, with organozirconium compounds also proceeds *via* a one electron transfer from nickel to give a ketyl radical. The ketyl may then couple to give 1,2-addition as previously noted, or may first rearrange to ring-opened products. The ratio of 1,2-addition to rearrangement was shown to depend on the concentration of nickel complexes in a manner implying that two nickel(I) species were involved in the rearrangement

[773].



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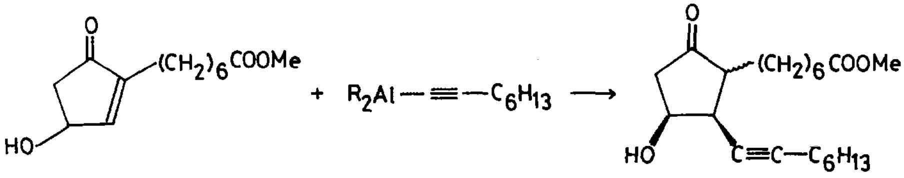

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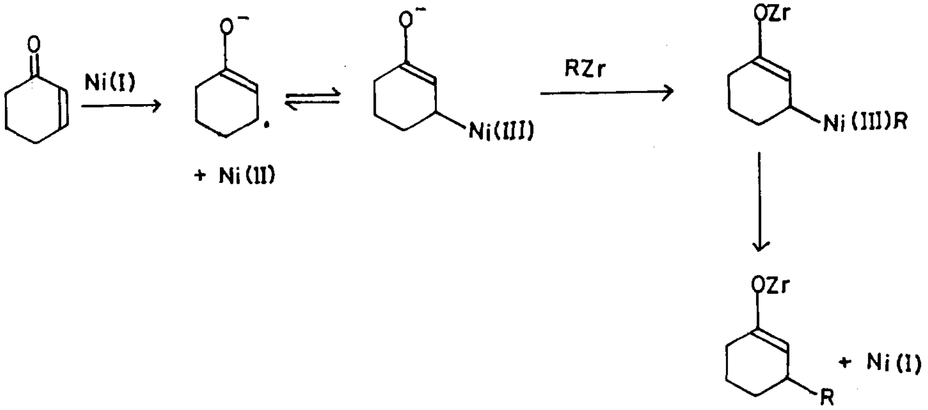
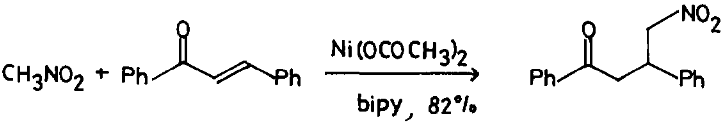
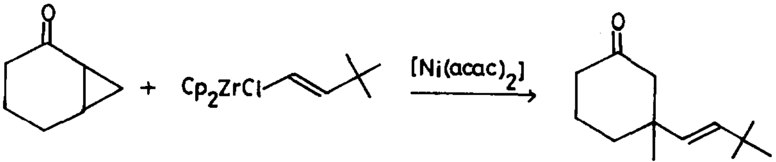


Scheme 11 Mechanism of nickel catalysed conjugate addition to enones



(61)



477

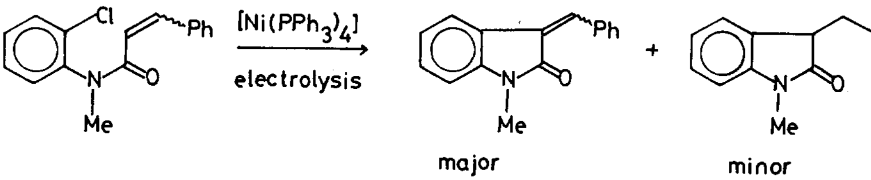
In non-coordinating solvents Na[AlEt$_4$] and Li[AlBu$_4$] acted as alkylating agents towards epoxides, the reaction being greatly accelerated and yields being improved by the presence of nickel halides. Alkylation occurred at the less substituted carbon atom with inversion of configuration [774].

Aryl halides could be coupled readily in the presence of nickel(0) to give biaryls and nickel(II). Electrochemical regeneration of nickel(0) allowed the reaction to be performed catalytically (reactions (62)-(64)) [775]. The nickel(0) complex could be generated electrochemically *in situ* to avoid the need for storage of this sensitive material. The process has been extended to include couplings of the type of reaction (65) [776].

$$[ArNiXL_2] + 2e^- + 2L \longrightarrow Ar^- + X^- + [NiL_4] \tag{62}$$

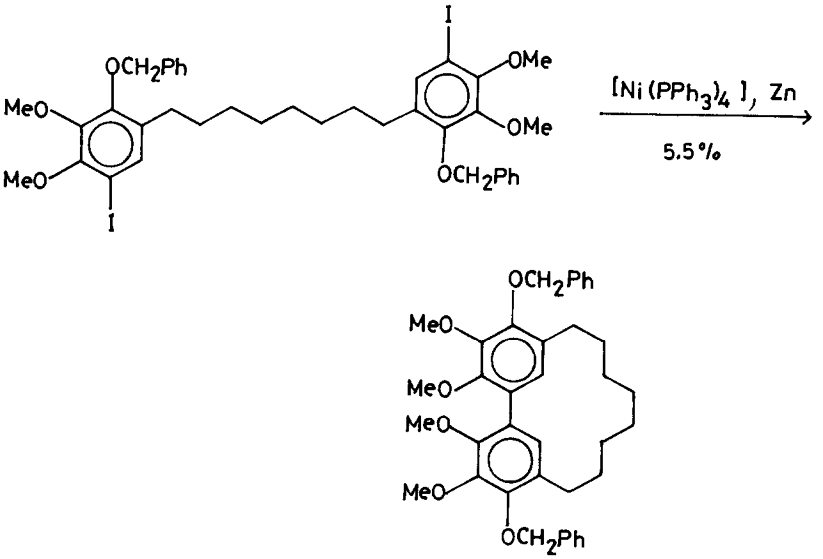
$$[ArNiXL_2] + Ar^- + 2L \longrightarrow ArAr + X^- + [NiL_4] \tag{63}$$

$$[NiL_4] + ArX \longrightarrow [ArNiXL_2] + 2L \tag{64}$$



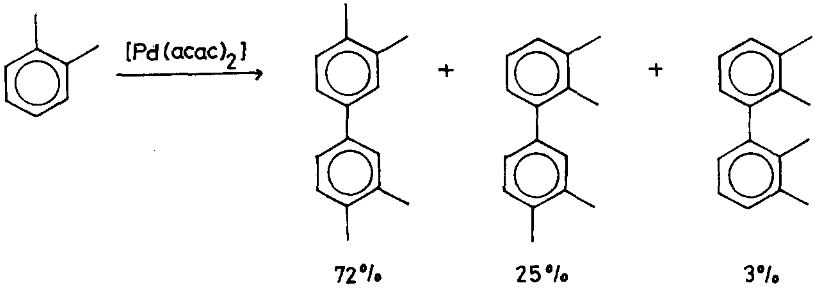
(65)

The alternative reductant commonly used for this reaction is metallic zinc, and further inter and intramolecular reactions have been used in synthesis, for example, reaction (66) [777].



(66)

Oxidative aryl coupling is known to occur in the presence of palladium(II) and further examples have been reported this year (reactions (67) [778] and (68) [779]). Oxidative coupling of ethene and benzene to give styrene occurred in the presence of supported $PdCl_2$ or $Pd(OCOMe)_2$ with $CuCl_2$, $FeCl_3$ or $CrCl_2$ [780].



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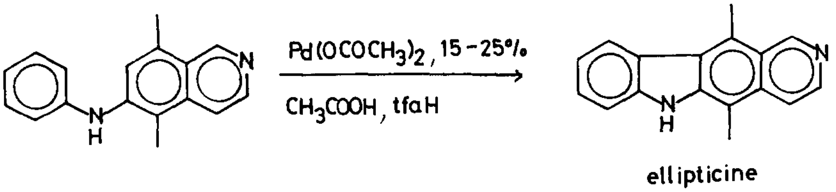
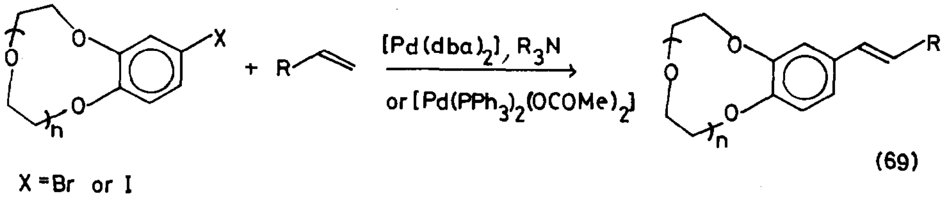


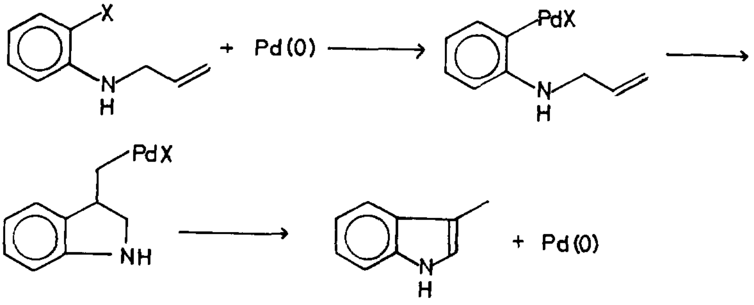
(68)

The couplings between alkenes and aryl halides proceed in most cases *via* initial oxidative addition of the aryl halide to palladium. Substituted crown ethers have been synthesised by reaction (69) (R = Ph, COOH or COOEt; *n* = 3 or 4), the precise catalyst and conditions needed depending on X [781]. Similar reactions of pyrimidines with both alkenes and alkynes have been used in the synthesis of substituted compounds with good regioselectivity [782]. Two intramolecular versions of the reaction have provided indole syntheses (reactions (70) [783] and (71) [784]).



(69)

Treatment of vinylmercury halides with $Hg(OCOMe)_2/Pd(OCOMe)_2$ or vinylmercury ethanoates with $Pd(OCOMe)_2$ resulted in the formation of vinyl ethanoates with good retention of stereochemistry. This has led to the development of a one-pot procedure for difunctionalisation of alkynes (reaction (72)). The process is catalytic in palladium since palladium (0) is reoxidised by mercury(II) [785]. Mercury derivatives of uracil nucleosides and nucleotides were coupled with styrene in the presence of $Li_2[PdCl_4]$ (reaction (73)), the process being tolerant of a wide range of functional groups [786].



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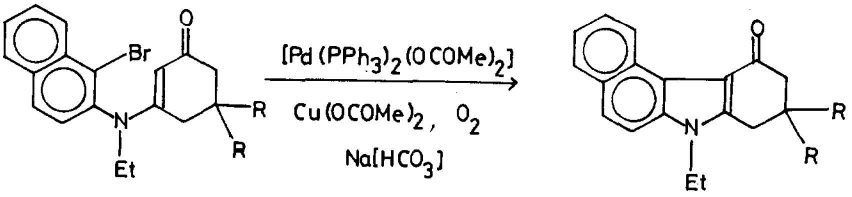

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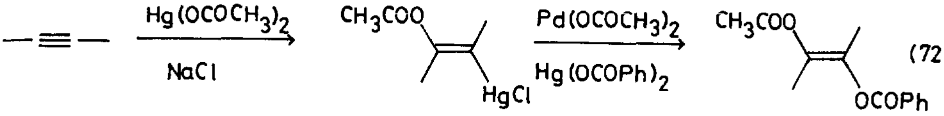

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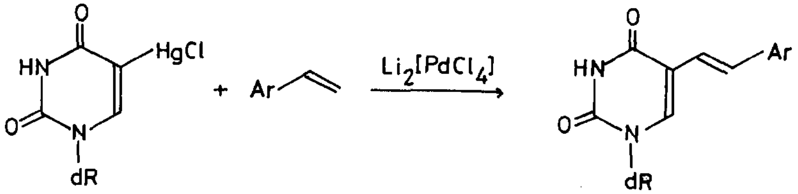
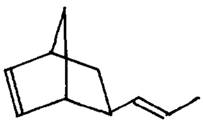


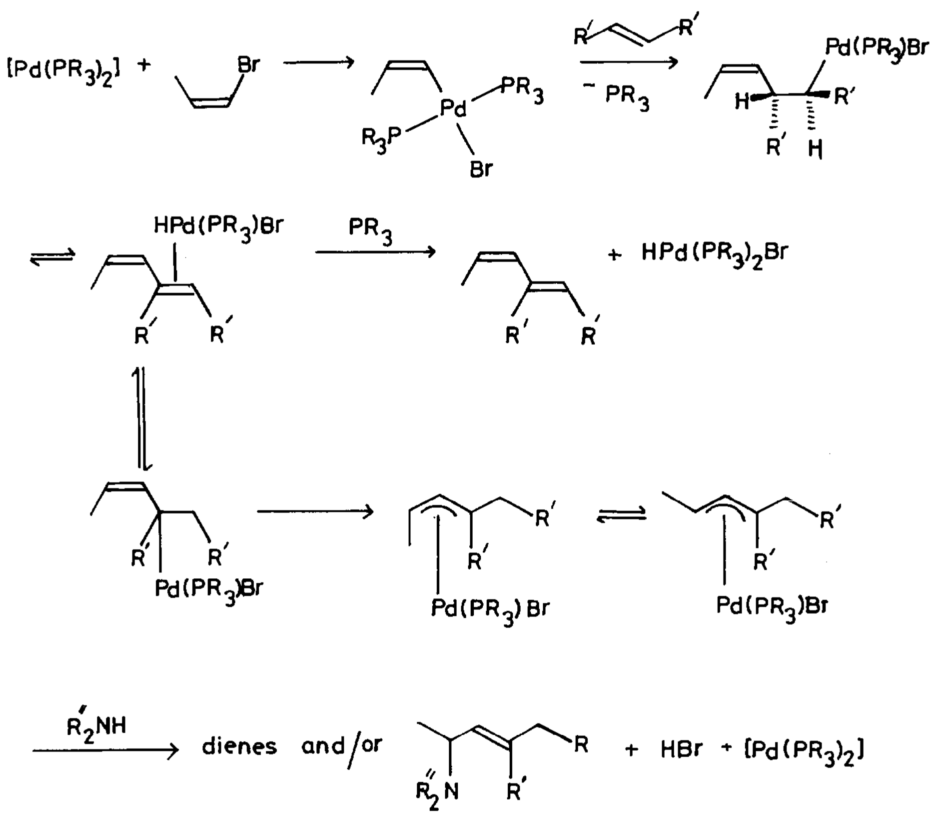
(73)

Oxidative coupling of 1,3-pentadiene with cyclopentadiene (generated *in situ* from its dimer) using $[Pt(PPh_3)_n]$ or $[Ni(PPh_3)_4]$ as the catalyst and hydroquinones as the oxidant gave 478 [787].



478

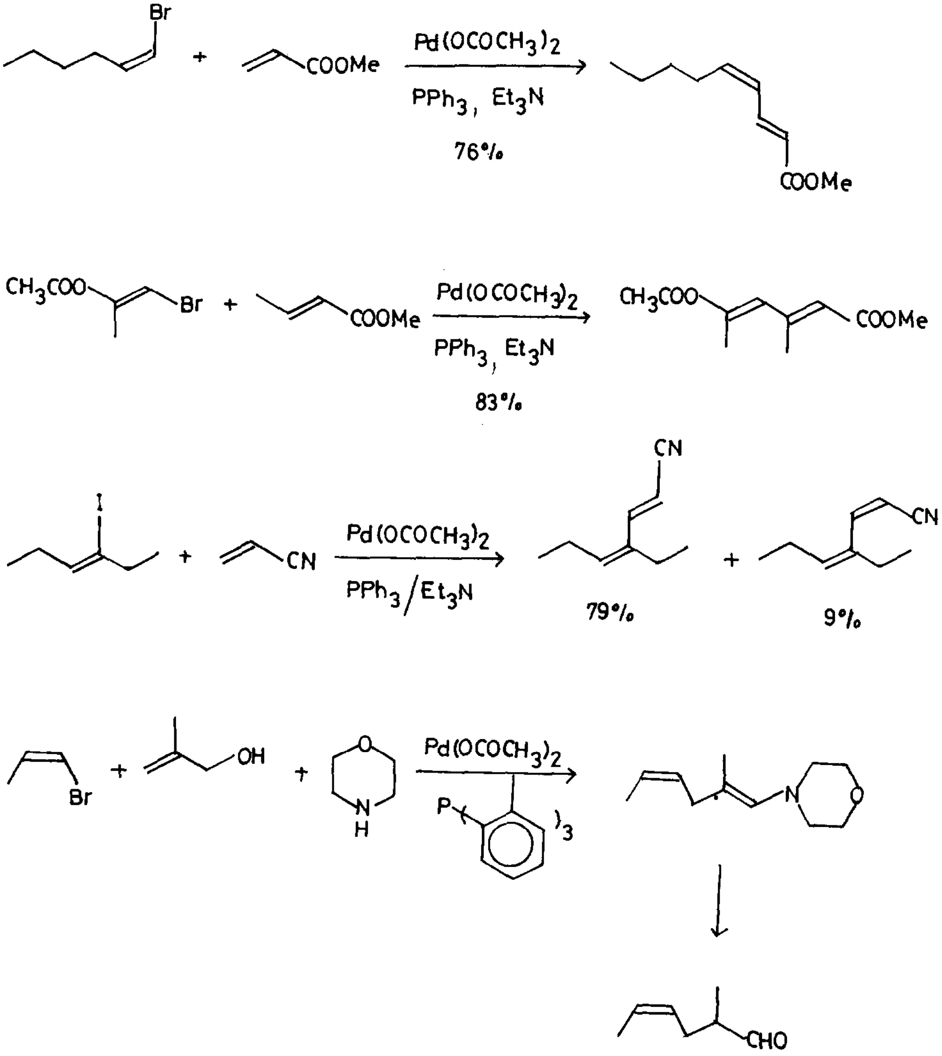
In a wide-ranging review of the Heck reaction the general mechanism was delineated very clearly (Scheme 12) and many examples given (Scheme 13) [788]. A patent has also described one such process using morpholine, 1-hexene and vinyl bromide as the reactants [789].



Scheme 12 Mechanism of the Heck reaction

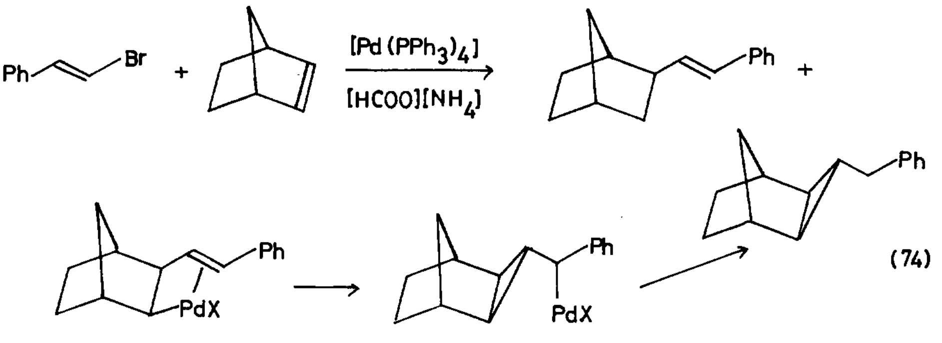
Reductive coupling of β-bromostyrene with norbornene in the presence of $[Pd(PPh_3)_4]$ yielded the coupled product together with a cyclopropane (reaction (74)). The driving force for cyclopropane formation is probably a lack of a facile β-hydride elimination pathway in the intermediate 479 [790].

Treatment of a mixture of benzoyl chloride and methyl acrylate with a nickel(0) complex gave $PhCOCH_2CH_2COOMe$ in 33 % yield. Addition of PPh_3 increased the yield and allowed the isolation of *trans*-$[PhCONi(PPh_3)_2Cl]$ as the first reaction intermediate. In this case the unsaturated ester PhCOCH=CHCOOMe was also formed and a mechanism for the reaction proposed. **480** was isolated and its structure determined by X-ray diffraction. Coordination at nickel was roughly trigonal and the N-C distances were difficult to reconcile with electronic effects, suggesting that steric factors are also important [791].



Scheme 13 Examples of the Heck reaction

A related process occurred when ArOH, RCH=CH$_2$ and {Pd(CO)Cl} reacted in the presence of a base. Some ArOCOCH=CHR was formed together with a compound which appears interestingly as ArOCOCH(OAr)CH$_2$R in one equation and as ArOCOCHRCH$_2$OH in a table of products [792].



(74)

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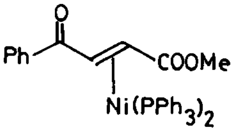
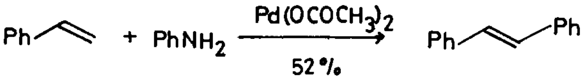


480

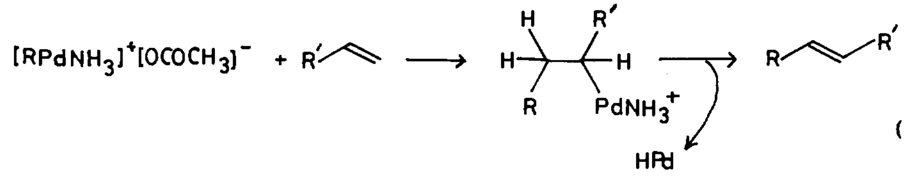
Two new and slightly unusual reagents gave arylation of alkenes. Aryl amines reacted in the presence of $Pd(OCOMe)_2$ (reaction (75)), the mechanism being shown in reactions (76)-(78) [793]. Ph_2TeCl_2 also arylated alkenes in the presence of PdX_2. The crucial step was formation of PhPdX, which may either add to the alkene (which is followed by HPdX elimination) or disproportionate to yield biaryls [794].



(75)

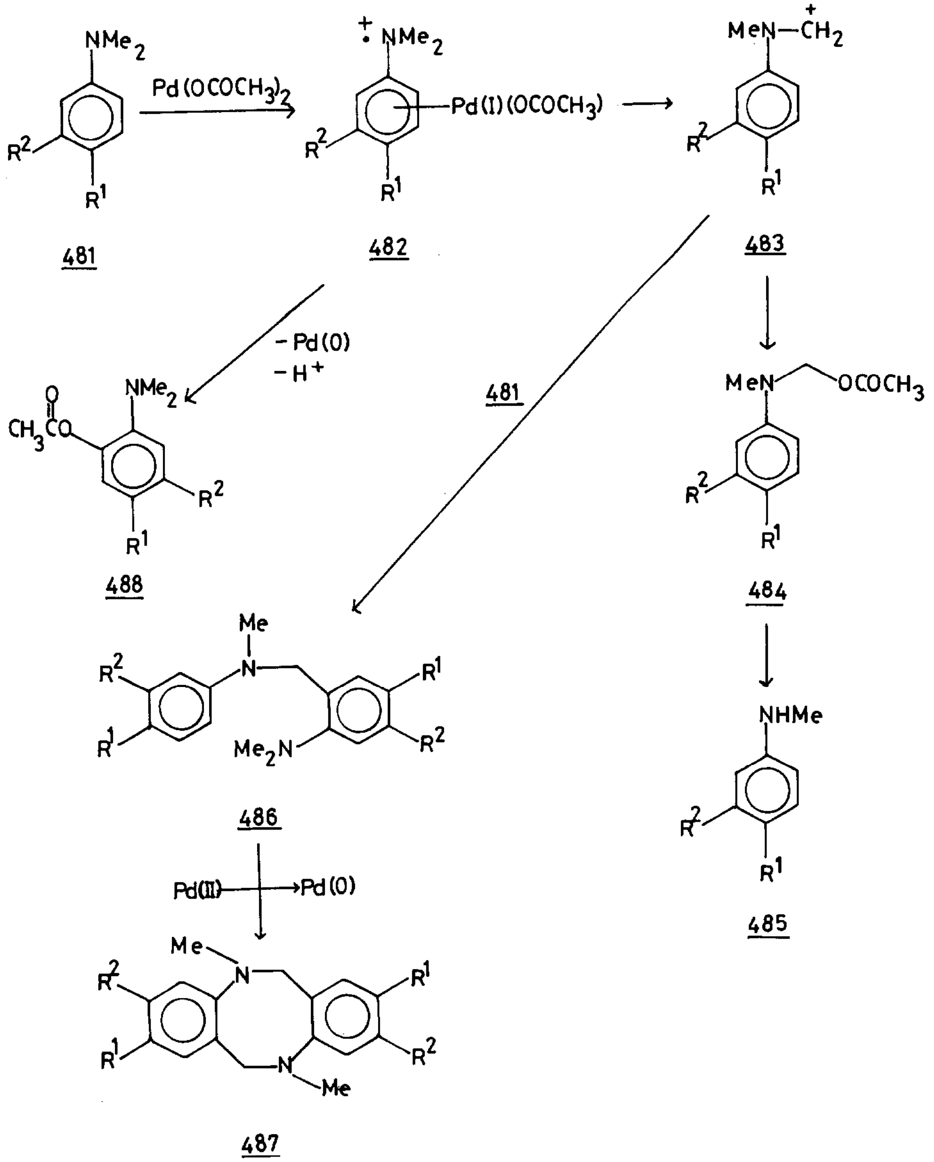
$$RNH_2 + MeCOOH \rightleftharpoons [RNH_3]^+[MeCOO]^- \quad (76)$$

$$[RNH_3]^+[MeCOO]^- + \text{"Pd"} \rightleftharpoons [RPdNH_3]^+[MeCOO]^- \quad (77)$$

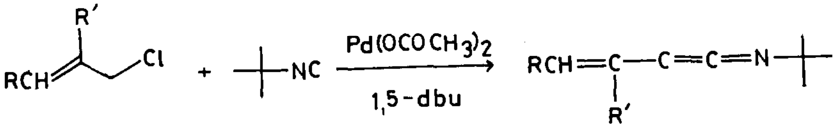


(78)

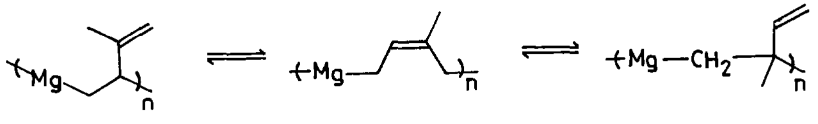
The substituted aniline, **481**, in which R' is an electron donor, reacted with $Pd(OCOMe)_2$ by electron transfer to give a radical cation, **482**. Loss of ethanoic acid and palladium(0) gave the cation, **483**. This was largely captured by another molecule of **481**, but some reacted with ethanoate to give **484** which is reported to be converted to **485**. **486** reacted with further Pd(OCOMe)$_2$ to give 487, whilst reductive elimination from 482 gave 488 and its regioisomer [795].



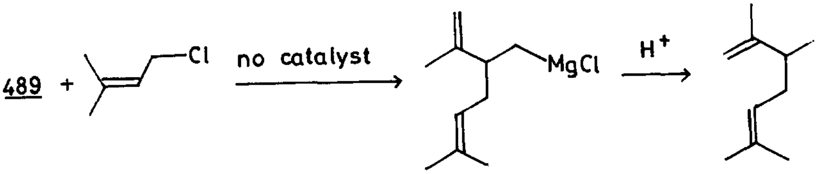
A new synthesis of *N*-CMe$_3$ vinyl ketenimines involved the reaction of an allyl halide with Me$_3$CNC in the presence of Pd(OCOMe)$_2$ and dbu (reaction (79)). The mechanism involves oxidative addition of the halide to palladium, insertion of Me_3CNC into what the authors describe as an alkyl palladium bond, then β-hydride elimination assisted by dbu [796]. The Grignard reagent **489a** is in rapid equilibrium with the isomers **489b** and **489c**. In the absence of a catalyst coupling occurred with an allyl halide, mainly involving **489a** (reaction (80)). However, in the presence of nickel(II) or palladium (II), selective 4,4-coupling of isoprene units occurred (reaction (81) from **489b**) [797].



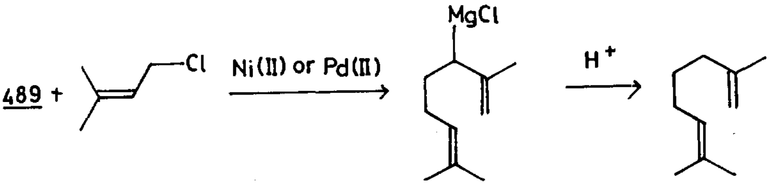
(79)



489a 489b 489c

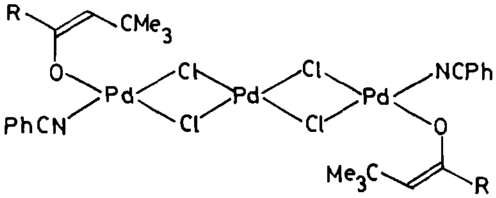


(80)

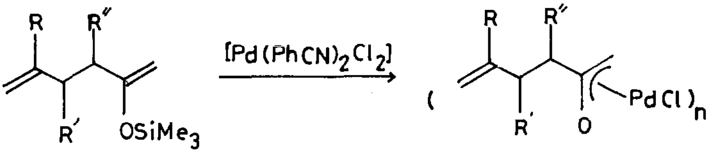


(81)

Treatment of $[Pd(PhCN)_2Cl_2]$ with $RCOCH_2CMe_3$ (R = Ph or CMe_3) in the presence of $Me_3SiOCH=CH_2$ gave **490**; **490** reacted with CO/EtOH to give $RCOCH(CMe_3)COOEt$, and with ethene, by successive insertion and β-hydride elimination, to give $RCOCH(CMe_3)CH=CH_2$. A π-allyl palladium complex is supposed to be the intermediate [798]. Reaction of $[Pd(PhCN)_2Cl_2]$ with **491** gave the oxallyl, **492**. This collapsed *via* a σ-allyl-π-alkenyl species, **493**, to complexes of the type **494**, which were readily isolated and their reactions studied [799].



490



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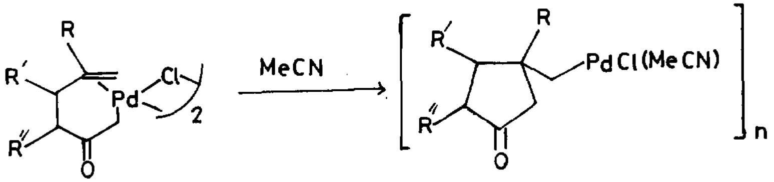

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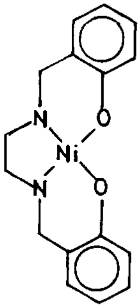
494

12.11 Other Catalytic Reactions

Cyclohexene was dehydrogenated to benzene using molecular oxygen in the presence of $[Pd_5(PPh)_2]$. A kinetic study suggested that cyclohexene was reversibly complexed to the cluster and a C-H bond ruptured in the rate-controlling step [800]. Cyclohexane was catalytically dehydrogenated over nickel phthalocyanines on zeolites [801]. $K[Pd(dmso)Cl_3]$ on a natural mineral support gave a catalyst with enhanced activity for dehydrogenation of isopentenes to isoprene [802].

The complexes $[Pt(H_2O)_{4-n}Cl_n]^q$ (n = 0, 1, 2, 3 or 4) catalysed H-D exchange in cyclohexane. The reaction kinetics were unusual in that the rate is a function of n. This was explained by a theoretical consideration of the effect of the ligand field symmetry on the LUMO structure [803]. **495** catalysed the electrochemical reduction of alkyl bromides. A cyclic voltammetric study showed the steps of reactions (82)-(86) for butyl bromide reduction. With $BrCH_2CH_2OCOMe$ as substrate the reaction pathway involved substitution of the bromide by $[NiL]^-$ followed be elimination to give ethene [804].



495

$$BuBr + e^- \xrightarrow{[NiL]} Bu^\bullet + Br^- \qquad (82)$$

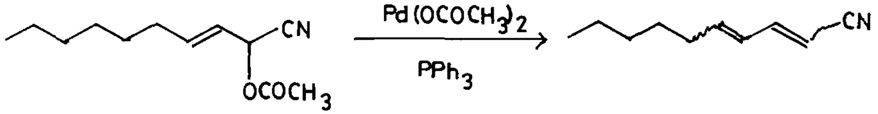
$$2Bu^\bullet \longrightarrow BuBu \qquad (83)$$

$$2Bu^\bullet \longrightarrow BuH + CH_3CH_2CH{=}CH_2 \qquad (84)$$

$$Bu^\bullet + CH_2{=}CHX \longrightarrow BuCH_2\dot{C}HX \longrightarrow BuCH_2CH_2X \qquad (85)$$

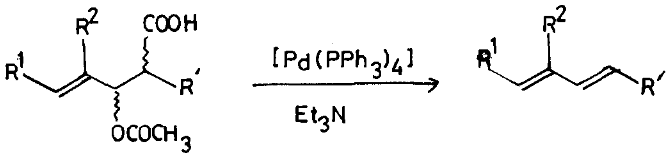
$$BuCH_2\dot{C}HX + CH_2{=}CHX \longrightarrow BuCH_2CHXCH_2\dot{C}HX \longrightarrow \text{polymer} \qquad (86)$$

A number of elimination reactions with rather different mechanisms have been reported this year. 3,4-Dichloro-1-butene was dehydrohalogenated over [Pd(py)$_2$Cl$_2$] on γ-alumina to give 1-butene-3-yne, the yield increasing with increasing temperature. Using [Pd(bipy)Cl$_2$] as the catalyst gave mainly 2-chlorobutadiene [805]. Elimination of ethanoic acid from the allyl ethanoate, **496**, was shown to proceed *via* a π-allyl complex; the product was used in a synthesis of pellitorine [806]. A careful stereochemical study of both diastereoisomers of **497** showed that the **E,E**-alkene, **498**, was the major product under conditions of kinetic control from both. The crucial intermediates were allyl palladium complexes from which loss of CO$_2$ to form a diene was faster than loss of H$^+$ to give a diene carboxylic acid. The stereoselectivity depended both on the steric interactions in the allyls and the relative rates of CO$_2$ loss [807].



496

Addition of water to acrylonitrile to give acrylamide was catalysed by [Pd(bipy)(H$_2$O)(OH)$_2$]. Selectivity was excellent but turnover and yields were low [808]. α-Monosulphonation of anthraquinone was achieved with greater than 99 % selectivity using SO$_3$/SO$_{2(l)}$ in the presence of a range of palladium complexes; the most active was $Pd(OCOMe)_2$ [809].

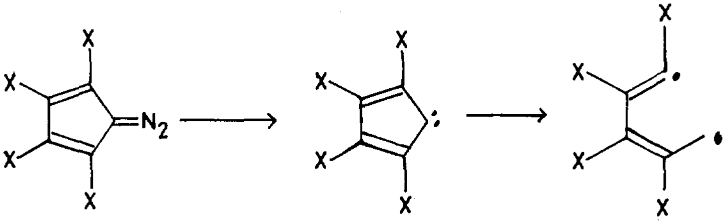


497

498

Nucleophilic substitution at silicon in $CH_2{=}CHSiCl_3$ by the enolate anion of acetone occurred in the presence of $NiCl_2$ to give $CH_2{=}CHSi(OCMe{=}CH_2)_3$ [810]. An oxime may attack CH_2Cl_2 using $[\{(\eta^3CH_2CHMeCH_2)PdCl\}_2]/K[O_2]$ as catalyst to give $(R^1R^2C{=}NO)_2CH_2$ [811]. Vinyl ethanoate reacted with alcohols in the presence of $PdCl_2$ and $Na[WO_4]$ to give $CH_2{=}CHOR$ in excellent yield [812]. For none of these reactions was any convincing mechanistic study carried out.

In the absence of a catalyst **499** (X = Cl or Br) decomposed to the carbene, **500** which was opened to the diradical, **501**, and this then dimerised to give a naphthalene. However, using $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ as catalyst and forming a palladium carbene complex as intermediate, the dimers, **502** could be prepared [813]. The methylation of hydroxyl groups on the gibbane skeleton is catalysed, though somewhat unselectively, by $Pd(OCOMe)_2$ [814].



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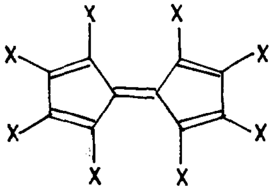
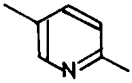


502

The reaction of ethene and ammonia to give **503** (R = H or Et) in the presence of palladium(II) and copper(II) has been investigated [815]. Arylation of alkenes by $ArNH_2$ in the presence of Me_3CONO was catalysed by $[Pd(dba)_2]$ in good yield; the reaction presumably involves a diazonium salt intermediate

[816].



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ABBREVIATIONS

acacH	pentane-2,4-dione
Ar	aryl
atm	atmosphere
bipy	2,2'-bipyridyl
Bu	$-CH_2CH_2CH_2CH_3$
CD	circular dichroism
cod	1,5-cyclooctadiene
cot	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl
Cy	cyclohexyl
dba	*E*,*E*-1,5-diphenylpenta-1,4-diene-3-one
dbn	1,5-diazabicyclo[3.4.0]non-5-ene
DBP	dibenzophosphole
dbu	1,5-diazabicyclo[5.4.0]undec-5-ene
diars	1,2-bis(diphenylarsino)ethane
dibah	di*iso*butylaluminium hydride
DIOP	2,3-O-di*iso*propylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dmf	*N*,*N*-dimethylmethanamide
dmso	dimethylsulphoxide
DNA	deoxyribonucleic acid
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	1,2-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
en	1,2-diaminoethane
epr	electron paramagnetic resonance
Et	$-CH_2CH_3$
eV	electron volt
glyH	H_2NCH_2COOH
hfacacH	1,1,5,5,5-hexafluoropentane-2,4-dione
hmpa	hexamethyl phosphoramide
ir	infra-red

kJ	kilojoule
L	2 electron donor ligand
Me	$-CH_3$
Mecp	methylcyclopentadienyl
nmr	nuclear magnetic resonance
np	naphthalide
nqr	nuclear quadrupole resonance
-OTs	$-OSO_2C_6H_4-4-CH_3$
Ⓟ-	polymer support
Ph	$-C_6H_5$
phen	1,10-phenanthroline
PHEPHOS	R-1,2-bis(diphenylphosphino)-2-phenylpropane
ppm	parts per million
Pr	$-CH_2CH_2CH_3$
py	pyridine
$salophH_2$	*ortho*-phenylenediamine bis(salicylidene imine)
SEM	scanning electron microscopy
tfaH	CF_3COOH
thf	tetrahydrofuran
tht	tetrahydrothiophene
tmen	*N,N,N'N'*-tetramethyl-1,2-diaminoethane
tmtu	*N,N,N',N'*-tetramethylthiourea
UV	ultra-violet
$w_{1/2}$	width at half height
δ	chemical shift