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NICKEL, PALLADIUM AND PLATINUM, SURVEY COVERING THE YEARS 1984 AND 1985*

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Reprints for this Survey are not available.

1 INTRODUCTION

This survey details the accounts of organometallic chemistry of nickel, palladium and platinum published in 1984 and 1985. Material from the patent literature which was reported in Chemical Abstracts in 1984 and 1985 is also included, and the organisation remains broadly similar to that in past surveys. The author is taking the unusual step of combining the material from two years in an attempt to speed up production, and get the coverage of the survey closer to the present day. In order to keep the length manageable, some abbreviation is essential, and she apologises in advance to any author who feels that their contribution has received less space than it should.

A number of reviews of general interest have appeared, including a discussion of metal-ligand bond energies in organometallic compounds [1], a consideration of the application of the HSAB approach to chemoselectivity in organometallic reactions [2], and an account of the coordination chemistry of secondary phosphorus chalcogenides and their conjugate bases [3]. In reviews specifically of the chemistry of derivatives of the nickel triad, topics covered include the chemistry and spectroscopy of mixed-valence complexes [4], the thermodynamics of oxygen binding in natural and synthetic dioxygen complexes [5], hydroxyoxime complexes [6], the chelate effect in square planar complexes with particular reference to bidentate phosphines and arsines [7], monothio and monoseleno-carbamate complexes [8], and the electrochemistry and redox behaviour of dithiocarbamates [9]. The annual survey of the inorganic chemistry of the platinum group metals has been published [10], as have annual surveys of transition metals in organic synthesis covering hydroformylation, reduction and oxidation [11], and other reactions [12]. Advances in the chemistry of complexes containing heteronuclear metal-metal bonds (other than metal clusters) in 1982-1983 have been detailed [13].

General reviews of nickel chemistry have included discussion of carcinogenicity and mutagenicity of nickel and its complexes [14], complexes of nickel(III) and nickel(IV) [15], and matrix isolation of nickel complexes [16]. The angular overlap model for the description of the paramagnetic properties of transition metal complexes, including nickel, has been reviewed [17], as have crystal field aspects of their vibrational spectra [18], Arbuzov-like dealkylation reactions of nickel phosphite complexes [19], and geometric and electronic factors relating to N_2 activation on nickel complexes [20].

A book has been published concerning the uses of palladium reagents in organic synthesis [21]. The electronic structure and reactivity of palladium complexes, especially those of palladium(II) and palladium(0) has been reviewed [22].

The industrial toxicology of palladium and platinum derivatives has been reviewed [23]. In a discussion of palladium-ligand and platinum-ligand bond energies, both coordination and organometallic complexes were considered [24]. "Odd" oxidation states (I and III) of platinum and palladium have been detailed, with particular reference to bimetallic compounds, carbonyl clusters, A-frames and isocyanide complexes [25]. An annual survey reviews X-ray data on clusters, carbonyl complexes, and complex reactivity [26].

A discussion of the history of organometallic chemistry begins with a consideration of Zeise's salt [27], and the molecular tectonics of platinum clusters have been reviewed [28].

2 METAL CARBON σ-BONDED COMPLEXES

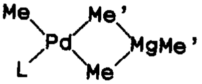
There have been review articles on complexes containing metal-carbon σ-bonds [29], and of μ-(α,ω)alkanediyl derivatives of transition metals [30]. Methylation and dealkylation reactions of platinum(II) and platinum(IV) with alkyl cobalamins have been discussed [31]. In a review of alkoxo complexes of palladium and platinum, a number of derivatives in which there is also a metal alkyl or metal allyl are discussed [32].

2.1 Metal Alkyl Complexes

Thermolytic decomposition of the complexes $[MR_2X_2]$ (M = Ni, Pd or Pt) has been reviewed. Possible 3-, 4- or 5-coordinated intermediates are discussed, as is the relative importance of reductive elimination and β-hydride elimination pathways [33]. The reductive elimination of methane from $[PtH(Me)(PPh_3)_2]$ is easy at -25 ^{o}C, but $[PtMe_2(PPh_3)_2]$ is stable up to 237 ^{o}C. Activation seems to be extremely sensitive to the nature of the bond being formed, and calculations were undertaken which provided an explanation for the trends observed [34]. There has also been a theoretical study of the mechanism of the reaction between molecular hydrogen and $\{Pt(PH_3)_2\}$, and of the decomposition of $[PtH(Me)(PH_3)_2]$. In the oxidative additon of hydrogen, an early transition state is on an approach to a *cis*-product, but phosphine repulsions intervene to ensure formation of the *trans*-derivative. The large deuterium isotope effect found experimentally in the reductive elimination of CH_3D was accounted for by the calculated reaction path [35]. There have also been calculations on the $\{Ni(CH_3)H\}$ system [36].

Addition of a ligand, L', promotes the elimination of ethane from *cis*-$[NiL_2Me_2]$. A molecular orbital analysis of the problem indicated that elimination is easy from a *cis*-dialkyl square pyramidal complex, or from an intermediate with trigonal bipyramidal geometry, but not from other possible intermediates [37]. Reaction of CD_3Li or CD_3MgBr with $NiCl_2$ or $PdCl_2$ has been studied. Metal carbene as well as metal alkyl intermediates were proposed [38]. In the thermolysis of $[Ni(CH_2{=}CHCH_3)(Cp)(R)]$, (R = CH_3 or CD_3), H/D exchange was noted between the complexed propene and the alkyl group, prior to decomposition to methane and ethane. For the complexes in which R = Et or Pr, β-hydride elimination was the major decomposition pathway [39].

Thermolysis of $[Pd(PEt_3)_2(R)X]$ (R = CH_3 or CD_3; X = Br, I or CN) in the temperature range 120-160 °C gave methane, ethane, and ethene in ratios which were a function of temperature. Deuterium labelling studies suggested that the methane was formed through intramolecular hydrogen abstraction from the phosphine ligands, rather than fission of the palladium-carbon σ-bond. At higher temperatures the P-ethyl bonds were also cleaved to give ethene and ethane. The reaction proceeded faster in the presence of molecular oxygen, with a change in mechanism to a radical process [40]. Reaction of *trans*-$[PdMe_2(PEt_2Ph)_2]$ with Me_2Mg or MeMgBr resulted in equilibration with the *cis*-isomer, followed by rapid reductive elimination. 1 was proposed as a likely reaction intermediate, in accord with deuterium labelling studies [41].

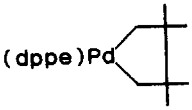


1

The electrochemistry of $[Ni(phen)_3]^{2+}$ has been studied in some detail. If reduction is carried out in the presence of an alkyl bromide, RBr, $[Ni(phen)R_2]$ is formed, and further reduction brings about catalytic reductive coupling of the alkyl bromide in solution [42].

An *ab initio* calculation on the optimum geometry for $[Pd(Et)(H)(PH_3)]$ revealed that the β-hydrogen of the ethyl group has an agostic interaction with the palladium. The path to β-hydride elimination to give *cis*-$[Pd(C_2H_4)H_2(PH_3)]$ is a smooth continuation of the agostic interaction, and has a low activation energy. The transition state is both tight and late. β-Hydride elimination is predicted to be supressed in the related $\{PdCH_2CHF_2\}$ derivative; in this case the β-hydride is insufficiently donating for an agostic interaction [43,44].

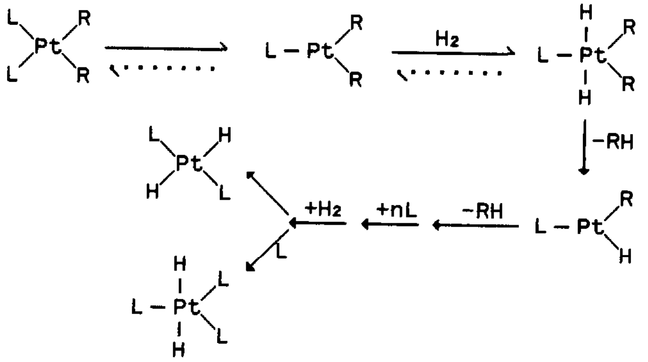
The preparation and thermolysis of $[Pd(bipy)Et_2]$ has been described. The products of thermolysis are almost entirely ethane and ethene, in contrast to the observation on the related nickel complex, which gives 50 % butane. The formation of butane from the palladium complex is achieved in the presence of π-acceptor ligands such as methyl propenoate [45]. By contrast, with *cis*-$[PdEt_2L_2]$ (L = PMe_2Ph, dppe, dppp or dppb), butane is the major product, and ethane and ethene are obtained only on addition of an additional ligand. The mechanism of the reaction in this case was entirely different, as was revealed by a deuterium labelling experiment, and involved orthometallation of the ligand [46]. Reaction of $[PdCl_2L_2]$ with Me_3CCH_2MgBr or Me_3CCH_2Li gave $[Pd(CH_2CMe_3)_2L_2]$, probably with *cis*-geometry. Thermolysis yielded only 2,2,5,5-tetramethylhexane, and no products of disporoprtionation or γ-hydrogen elination, in contrast to the platinum analogues. Carbonylation resulted in the insertion of CO between the two alkyl groups to give the symmetric ketone. When $[PdCl_2(dppe)]$ was reacted with $LiCH_2CMe_2CMe_2CH_2Li$ the isolable metallocyclopentane, 2, was formed. This is the first metallocyclopentane to be isolated in which both of the α-carbon atoms are of the neopentyl type. At temperatures above 200 °C, 1,1,2,2,-tetramethylcyclobutane is formed [47].



2

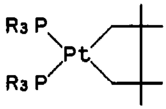
Enthalpies and activation energies for β-hydride elimination from *cis*- and *trans*-$[PtCl(PEt_3)_2R]$ (R = Et, Pr or Bu) were obtained from DSC [48]. The thermolysis reactions of $[Pt(CD_2CH_3)_2(cod)]$ and $[Pt(CD_2CH_3)(cod)X]$ (X = Cl or I) were investigated. The data were fitted to an appropriate kinetic model [49]. The mechanism of decomposition of *trans*-$[PtCl(Et)(PEt_3)_2]$ in cyclohexane at 158 °C was investigated by means of a careful kinetic study [50].

The reaction of Me_3CCH_2MgBr with "$PtCl_4$" has been investigated [51]. Hydrogenation of *cis*-$[Pt(CH_2CMe_3)_2(PEt_3)_2]$ gave Me_4C and *trans*-$[PtH_2(PEt_3)_2]$. The mechanism proposed for the reaction is shown in Scheme 1. If the concentration of added ligand is zero, ligand dissociation is the rate controlling step, and there is no H_2/D_2 isotope effect. When the concentration of added ligand is > 0.1M, phosphine loss is reversible, and either H_2 addition or 2,2-dimethylpropane loss is rate-limiting, with K_H/K_D = 1.9 [52]. Thermolysis of 3 gave 2,2,3,3-tetramethylbutane *via* heterogeneous processes catalysed by platinum metal, and 1-methyl-1-(1,1-dimethylethyl)cyclopropane under strictly homogeneous conditions [53].



L = PEt3 , R = CH2CMe3

Scheme 1 Mechanism of hydrogenation of $[Pt(CH_2CMe_3)_2(PEt_3)_2]$ [52]



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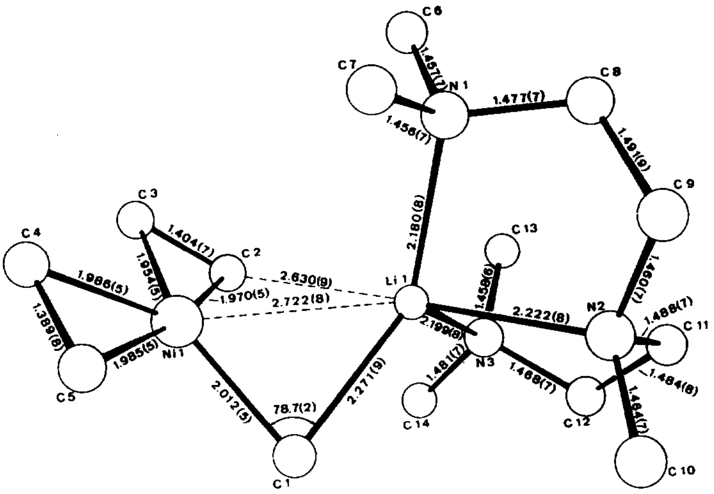
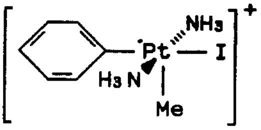
A species described as $\{Me_3NiLi\}$ reacted with cyclohexenone to give 3-methylcyclohexanone in 2 % yield and 1-methyl-2-cyclohexene-1-ol in 14 % yield [54]. The principle of structural correlation was applied to 78 5-coordinate nickel complexes to give a map of the reaction coordinate for association at square planar 4-coordinate nickel centres. $[Ni(Me)(PMe_3)_4]$ was the only organometallic complex considered [55]. Reaction of MeLi with $[Ni(C_2H_4)_3]$ in the presence of pmdta gave 4, characterised by an X-ray diffraction study. Related species were produced from $[Ni(CO)_4]$ and [Ni(cdt)]. Chemical properties and spectroscopic data indicated that the Me-Ni bond was essentially covalent in the carbonyl derivative, but was more polar in character in the cdt and ethene complexes [56]. Treatment of $[MCl_2L_2]$ (M = Ni or Pt; L = PPh_3 or L_2 = dppe) with $[NH_4]_2[RSiF_5]$ (R = Me or Ph] gave a mixture of $[MClL_2R]$ and $[ML_2R_2]$ [57].

The gas phase reaction of Pd^+ with H_2 and C_2H_6 has been studied in an ion beam apparatus as a function of relative kinetic energy. The bond dissociation energy for Pd^+-Me was shown to be 247±21 kJ mol^{-1} and the bond was largely covalent in character [58]. Theoretical calculations have been performed for the migration process shown in reaction (1). These suggested that the starting material was initially deformed at the phosphorus centre. In a comparable process, $[Pt(NH_3)_2(Ph)]^+$ reacted with MeI to give 6, *via* a migration process in the initial oxidative addition product, 5 [59].



4 (Reproduced with permission from [56])

(1)



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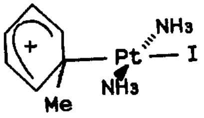


6

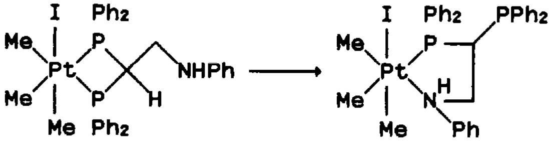
The complexes *cis*- and *trans*-$[Pd(PMe_3)_2R_2]$ and *cis*-$[Pd(dmpe)R_2]$ (R = Me, CH_2Ph, CH_2CMe_2Ph, or CH_2SiMe_3) were prepared from $Pd(OCOMe)_2$, and the relevant Grignard reagent, in the presence of phosphine [60]. Treatment of $[PdCl_2(SMe_2)_2]$ with halide free methyl lithium, in the presence of a ligand, L, gave $[PdLMe_2]$ (L are poly-(pyrazol-1-yl)methane ligand) [61].

Reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with Me_3Al gave $[Pd_2Cl(\mu\text{-dppm})_2Me]$, which could be characterised, but was not very stable. Thermolysis yielded $[Pd_2Cl_2(\mu\text{-dppm})_2Me_2]$, whereas treatment with ethanol gave

$[Pd_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2(H)(Me)]^+$. This complex was in equilibrium with an isomer in which the hydride was bridging and the chloride ligand terminal [62,63].

Reaction of $[Pt(AsPh_3)(Me)_2(PEt_3)]$ with one molar equivalent of HCl gave *trans*-$[Pt(AsPh_3)Cl(Me)(PEt_3)]$, characterised by an X-ray diffraction study [64]. The ligand $Ph_2PCH_2P(Ph)CH_2PPh_2$, dpmp, forms chelate complexes such as $[Pt(dpmp)Me_2]$, in which only the terminal phosphines are metal-coordinated. The "internal" phosphine is thus free for coordination to other metal centres, forming species such as *trans*-$[RhCl(CO)\{(\mu\text{-}dpmp)PtMe_2\}_2]$, and *cis*-$[PtCl_2\{(\mu\text{-}dpmp)PtMe_2\}_2]$ in which the metal centres are remote from each other [65]. The preparations of $[Pt(dppm\text{-}P,P)R_2]$ (R = Me, Et, CH_2Ph, CH_2CMe_3, or Ar) from RMgBr and $[PtCl_2(dppm\text{-}P,P)]$ have been described. Reaction of the chelating complexes with an excess of dppm resulted in an equilibrium with $[Pt(dppm\text{-}P)_2R_2]$. The rate at which the equilibrium was established depended on the steric hindrance provided by the R groups. For hindered R groups selective protolysis was possible with HCl to yield $[PtCl(dppm\text{-}P,P)R]$. Oxidative addition of MeI gave the *trans*-platinum(IV) complex in most cases, but for R = $2\text{-}MeOC_6H_4$ the final product was $[Pt(dppm\text{-}P,P)I(R)]$ [66]. Treatment of $[Pt(cod)Me_2]$ with dpam gave *cis*-$[Pt(\mu\text{-}dpam)_2Me_2]$, since the arsine is a less successful chelate than dppm. Addition of an excess of dpam yielded $[Pt(dpam\text{-}As)_2Me_2]$. *trans*-$[PdCl_2(dpam\text{-}As)_2]$ was also prepared and its reactions with other metals studied [67].

The reactivity of *trans*-$[PtClL_2(R)]$ (R = Me, L = PPh_3, or R = Ph, L = PEt_3) has been studied. Treatment with Na[OMe]/MeOH followed by $Na[BH_4]$/MeOH gave *trans*-$[Pt(H)L_2(R)]$. The same complex was obtained from *trans*-$[PtL_2(R)(solvent)][BF_4]$ or *trans*-$[PtL_2(NHCOCH_3)(R)]$. The intermediate *trans*-$[PtL_2(OMe)(R)]$ was isolated in an impure form and could be characterised spectroscopically. Reductive elimination of RH occurred only at high temperatures. Loss of benzene was facilitated in an atmosphere of CO, which catalyses *cis* $\leftrightharpoons$ *trans*-isomerisation, and inhibited by Et_3P, suggesting that the mechanism requires phosphine dissociation [68]. Reaction of *trans*-$[\{Pt(C_2H_4)(Me)\}(\mu\text{-}Cl)_2\{Pt(C_2H_4)Me\}]$ with the bis *N,N*-dimethylhydrazone of butane-2,3-dione gave a 5-coordinate complex in wich the methyl and chloro ligands occupied the axial positions. The use of a chiral chelating ligand gave two diastereomeric complexes with differing chirality at the platinum centre. Recrystallisation gave a single diastereoisomer, *via* a second order asymmetric transformation [69]. The ligand $(Ph_2P)_2C{=}CH_2$ is very reactive towards Michael additon reactions when it is complexed to platinum. A range of such reactions for $[PtMe_2\{(Ph_2P)_2C{=}CH_2\}]$ with amines and hydrazines have been described. Oxidative additon of MeI to give *fac*-$[PtI(Me)_3\{(Ph_2P)_2C{=}CH_2\}]$ allowed the study of similar reactions in the platinum(IV) series. The products in these cases, such as 7, rearranged to give *P,N*-chelates, which were somewhat less strained [70].



7

Oxidative addition reactions have been studied for a number of $\{PtMe_2\}$ derivatives. Reaction of RX with $[Me_2Pt(LL)]$ (LL = bipy or phen) gave $[Pt(LL)(Me)_2(R)X]$ (R = Me, Et, Pr or Bu) by an S_N2 mechanism. By contrast a radical mechanism was involved in the reaction with CH_2X_2 to give $[Pt(CH_2X)(LL)(Me)_2X]$ [71]. Reactions of α,ω-dihalides were also studied [72]. The complex *cis*-$[PtMe_2(py)_2]$ was extremely reactive towards oxidative addition, reacting rapidly with CF_3I or ROH. By contrast, oxidative addition of CF_3I to *cis*-$[Pt(CF_3)_2(py)_2]$ required more forcing conditions [73]. The photochemically initiated oxidative addition of 2-iodopropane to $[PtMe_2(phen)]$ has been studied. Irradiation of the lowest energy MLCT band of the complex leads to iodine atom abstraction from the substrate. The MLCT excited state of the complex was shown to have triplet character using a triplet sensitiser (Ph_2CO) and a triplet quencher (pyrene). This is followed by free radical addition, with the 2-propyl radicals, these being the chain carriers. Termination occurs by radical attack at the methyl or phen ligands rather than recombination or disproportionation [74]. Further insight into the reaction was obtained when it was carried out in oxygen. In this case one of the products obtained was *cis*-$[Pt(LL)I(Me_2)(OOCHMe_2)]$, formed by reaction of oxygen with the 2-propyl radicals [75]. Treatment of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with bipym gave the mononuclear species $[Pt(bipym)Me_2]$, the oxidative addition reactions of which were studied in some detail. Reaction with alkyl iodides, RI, yielded $[Pt(bipym)I(Me)_2(R)]$, and with $I(CH_2)_nI$ (n = 3, 4 or 5), $[Pt(bipym)\{(CH_2)_nI\}I(Me)_2]$ and $[\{Pt(bipym)I(Me_2)\}\{\mu\text{-}(CH_2)_n\}\{Pt(bipym)I(Me)_2\}]$. Reactions of the mononuclear complexes with further $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give binuclear species such as $[(Pt\{(CH_2)_nI\}I(Me)_2)(\mu\text{-}bipym)\{PtMe_2\}]$ were also investigated [76].

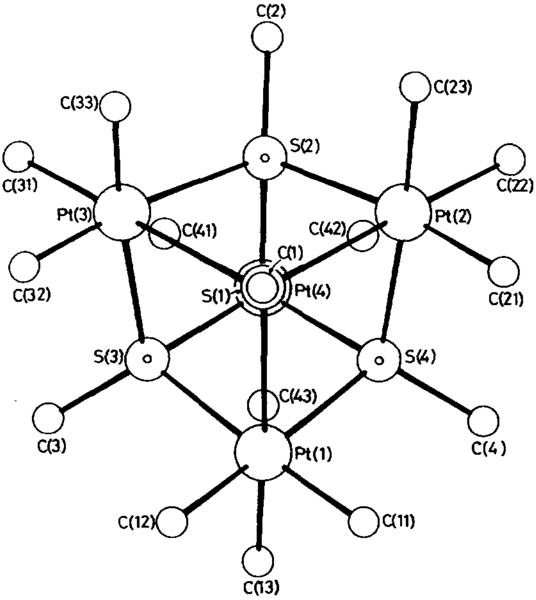
Reaction of iodomethane with $[PtCl_4]^{2-}$ in aqueous solution gave $[PtCl_4(Me)(OH_2)]^-$ and iodide ion as the initial products. This complex was hydrolysed to give methanol, and reacted with halide to give chloromethane, both pathways operating simultaneously in aqueous solution [77]. The species

$[PtCl_5(Me)]^{2-}$ lost chloromethane in an intramolecular elimination, and also reacted with external halide [78]. Photolysis of $[PtCl_6]^{2-}$ with Me_4Sn gave $[PtCl_5(Me)]^{2-}$ which decomposed slowly to chloromethane and $[PtCl_4]^{2-}$. With Me_2Et_2Sn or Me_2Et_2Ge, $[PtCl_5(Me)]^{2-}$ was again formed, but this was accompanied by formation of $[\{Pt(C_2H_4)Cl_2\}_2]$, *via* $[PtCl_5(Et)]^{2-}$. In all cases an electron transfer mechanism was proposed for the reaction [79]. The electrophilic assistance of Hg(II) in the reaction of iodomethane with $[PtCl_4]^{2-}$ was cited as evidence for an S_N2 mechanism in oxidative addition [80]. The facile methyl transfer reaction of methyl aquo(3,5,6-trimethylbenzimidazolyl)cobamide requires the presence of platinum in both platinum(II) and platinum(IV) oxidation states. It is proposed that $[PtCl_4]^{2-}$ complexes to the methyl corrinoid prior to the rate controlling methyl transfer step. The reaction mechanism is discussed in detail [81]. The interactions of methylcobalamin with $[PtCl_4]^{2-}$, $[Pt(CN)_4]^{2-}$ or $[Pt(SCN)_4]^{2-}$ in aqueous solution have been studied. There are at least three platinum binding sites. One site is located on the Co—Me side of the macrocycle, and is involved in methyl transfer in the presence of platinum(IV). For $[Pt(SCN)_4]^{2-}$ an additional site is provided by N(3) of the benzimidazole [82].

The structure of $[\{Me_3Pt(SMe)\}_4]$, **8**, has been determined in an X-ray diffraction study. There are three independent, but essentially isostructural, tetramers in the asymmetric unit. In each tetramer the four metal atoms are linked together by bridging {SMe} groups, with three methyl ligands completing the octahedral coordination [83]. A series of complexes has been prepared of the type $[PtMe_3(NN)X]$ (NN = pz_2CH_2, $(Me_2pz)_2CH_2$ or py_2CH_2), by reaction of the heterocyclic ligand with $[\{PtMe_3X\}_4]$. The structure of **9**, the derivative of $(Me_2pz)_2CH_2$, was determined in an X-ray diffraction study [84].

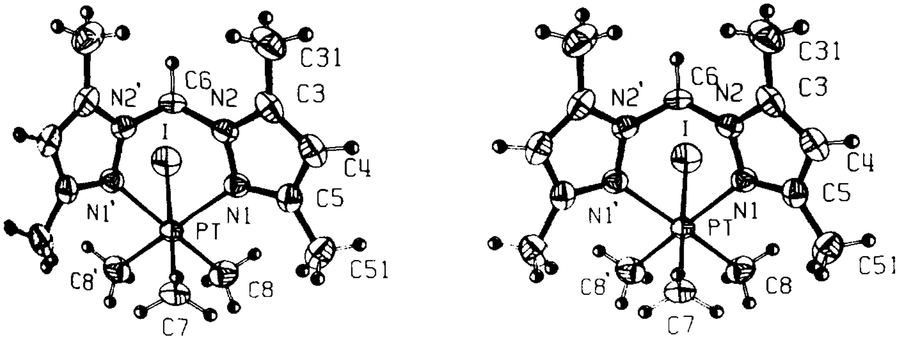
Treatment of $[\{PtIMe_3\}_4]$ with Ag[SeCN] resulted in the formation of $[\{PtMe_3(SeCN)\}_4]$. Pyridine derivatives, including $[PtMe_3(py)_2(SeCN)]$ and $[\{PtMe_3(py)(SeCN)\}_2]$ were also prepared, and structures proposed [85]. Reaction of alcohols, ROH, with $[PtMe_2(NN)]$ (NN = bipy or phen) resulted in oxidative addition to yield $[PtMe_2(NN)(OR)(OH_2)][OH]$. The complexes were fully characterised, and could be converted to $[PF_6]$, $[BF_4]$ or $[ClO_4]$ salts. The platinum(IV)-alkoxide bond was unusually stable towards solvolysis [86]. The complex *cis*-$[PtMe_2(SMe_2)_2]$ reacted with MeI to give *fac*-$[PtIMe_3(SMe_2)_2]$. When the reaction was carried out in CD_3CN the intermediate *fac*-$[Pt(CD_3CN)(Me)_3(SMe_2)_2]I$ was observed. When the bridged complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was used as the substrate, *fac*-$[PtIMe_3(SMe_2)_2]$ and $[\{PtIMe_3\}_4]$ were produced. Both complexes undergo oxidative addition *via* an S_N2 mechanism, but the monomer reacted an order of magnitude more rapidly. Both monomer and dimer also react with bis-1,2-(bromomethyl)benzene to give

10, but in this case it is the dimer which reacts the more rapidly [87]. Reaction of $[PtMe_4(NN)]$ (NN = bipy or phen) with HX yielded *fac*-$[PtMe_3(NN)X]$ (X = Cl, OPh, SPh, OMe, $[CF_3CO_2]$ or $[MeCO_2]$). Reactions of other electrophiles were also studied, and it was concluded that they involved initial electrophilic attack on one of the mutually *trans* methyl-platinum bonds (HX or SO_2) or electron transfer from a platinum-carbon σ-bond to the reagent (C_2F_4 or $C_2(CN)_4$) [88]. Reaction of $[Me_3SiC_5H_4]^-$ with $[\{PtIMe_3\}_4]$ gave $[Pt(\eta^5\text{-}C_5H_4SiMe_3)Me_3]$, which was used as a hydrosilylation catalyst [89].

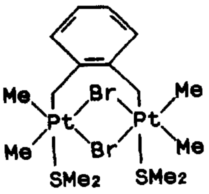


8 Molecular configuration and atom naming scheme for $[\{PtMe_3(SMe)\}_4]$ viewed down the *pseudo*-three fold axis. (Reproduced with permission from [83])

There have been further reports from Abel's group on the dynamic stereochemistry of complexes of the type $[Pt(LL)Me_3X]$. Multinuclear nmr spectroscopy was used to characterise the invertomers in $[PtMe_3(MeECH{=}CHEMe)X]$ (E = S or Se; X = Cl, Br or I). The structure of $[PtCl(Me)_3(MeSeCH{=}CHSeMe)]$ was described as *meso*-1 in type, 11, with the two *Se*-methyl groups on the same side as the chloride ligand. By contrast, the iodo analogue was of the *meso*-2 type, 12, with the two methyls on the opposite side to the iodide. The major invertomers in solution were the same as those found in the solid state. Barriers to inversion were determined [90]. The complex $[\{Me_3PtX\}_2(\text{tetrathia-8-C-4})]$, 13 (X = Cl) was also characterised in a diffraction study. The platinum atoms are each coordinated to two adjacent sulphur centres, and the ligand has a chair conformation. Two fluxional processes observed (pivoting at the metal and Pt-Me intramolecular rearrangements) are considered to be different manifestations of one transition state rather than independent rearrangements [91]. The preparation of $[\{PtMe_3X\}_2(Me_2CCH_2EECH_2)]$ (E = S or Se; X = Cl, Br or I) has been described, and the structure of 14 was determined in a diffraction study. Nmr spectroscopic studies in solution revealed that the two selenium centres invert synchronously, the first authenticated case of this phenomenon [92].



9 A stereoview of the $[PtMe_3\{(Me_2pz)_2CH_2\}]$ complex with the crystallographic numbering scheme. (Reproduced with permission from [84])



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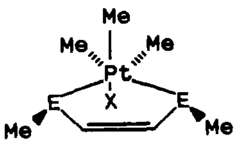

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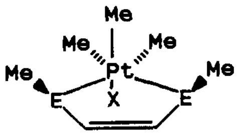

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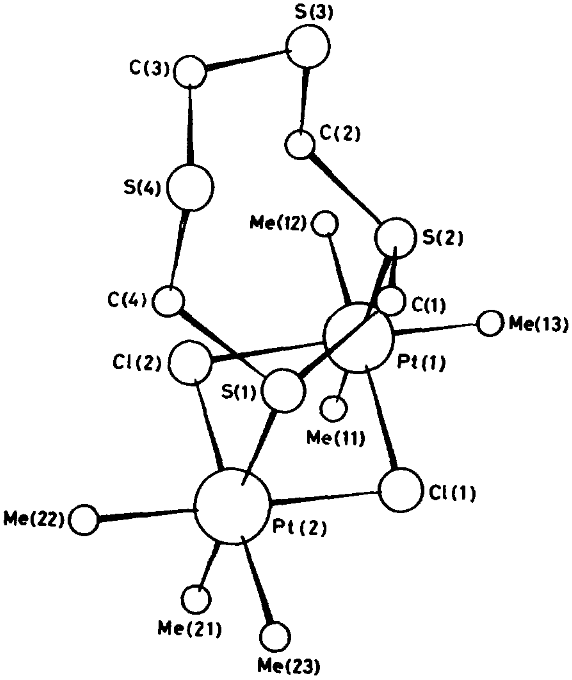
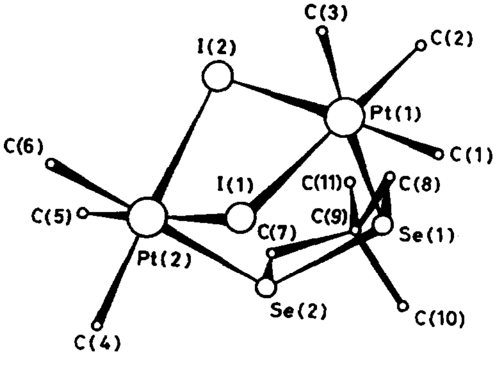


13 A PLUTO perspective drawing of the molecular structure of $[(PtClMe_3)_2(SCH_2SCH_2SCH_2SCH_2)]$ showing the numbering scheme. (Reproduced with permission from [91])



14 (Reproduced with permission from [92])

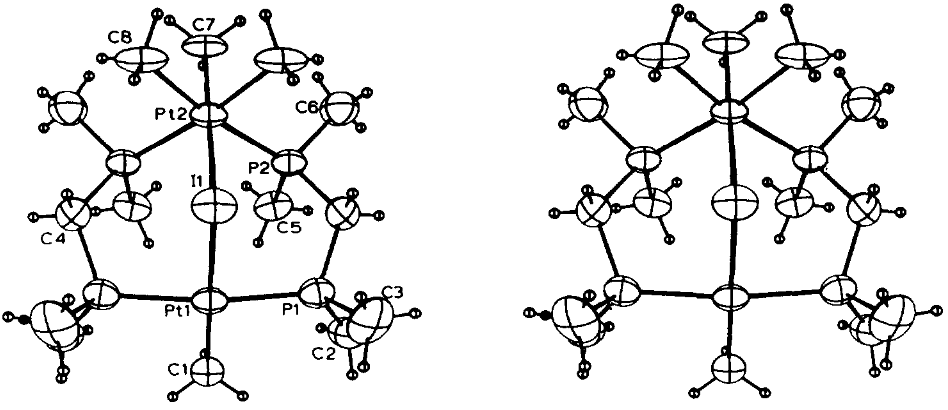
The thermal decomposition of $[\{PtIMe_3\}_4]$ in the presence of an alkene and R_3SiH gave a catalyst for alkene hydrosilylation. Two complexes could be identified in the reaction mixture, $[PtIMe(RCH{=}CH_2)_2]$ and $[PtMe_2(RCH{=}CH_2)_2]$

and both seemed to be effective catalysts [93].

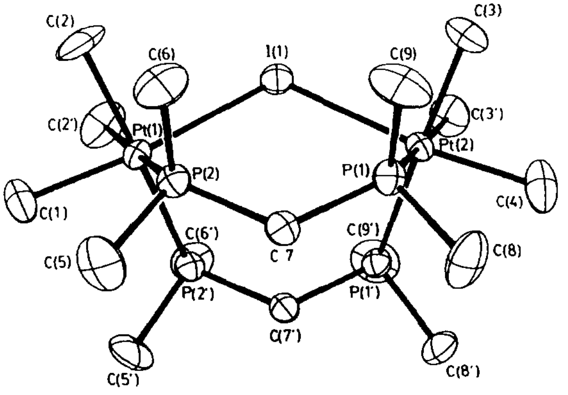
Various binuclear complexes containing palladium-methyl or platinum-methyl units have been studied. The complex $[Pt_2(dppm))_3]$ reacted with iodomethane to yield succesively $[Pt_2(\eta^1\text{-dppm})(\mu\text{-dppm})_2Me][PF_6]$ and $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}I)Me_2][PF_6]$. Treatment of $[Pt_2H(\mu\text{-}H)(\mu\text{-dppm})_2Me][SbF_6]$ with an added phosphine ligand, L, gave $[Pt_2(\mu\text{-dppm})_2(L)Me_2][SbF_6]$. The likely intermediate is $[\{PtH(L)\}(\mu\text{-dppm})_2(\mu\text{-}H)PtMe]$, but the mechanism was not proven unequivocally [94]. Photolysis of $[\{PtMe\}(\mu\text{-}H)(\mu\text{-dppm})_2\{PtH\}]$ in the presence of a solvent, S, (S = py, MeCN or Me_2O) yielded $[\{PtMe\}(\mu\text{-dppm})_2\{PtS\}]^+$ and molecular hydrogen. The same organometallic product, together with methane, was obtained from $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}H)Me_2]^+$. Ethane was eliminated from $[Me_3Pt_2(\mu\text{-dppm})_2]^+$. Both methane and ethane elimination reactions were mostly intramolecular (as established by labelling studies). The rates of the thermal reactions depended strongly on the complex involved, but related photochemical reactions all proceded at approximately the same rate [95].

The reactions of $[Pt(R_2PCH_2PR_2)Cl_2]$ with MeLi were studied. When $R = Me_2CH$, only a mononuclear species, $[PtMe_2(R_2PCH_2PR_2)]$, was isolated. When R = Me or Et, only $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ was formed, but with R = Ph, both mono and dinuclear complexes could be isolated. When $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was reacted with $R_2PCH_2PR_2$ mononuclear species were isolated only when $R = CHMe_2$, with the other phosphines giving binuclear products. Mono and dinuclear species did not interconvert thermally, but in the presence of an added ligand such as Me_2S or dppm, interconversion did occur slowly at 60 °C. The structures of the dimeric complexes were determined for R = Me or Ph; there was no metal-metal bonding. The dimer derived from dmpm reacted readily with I_2 or MeI, in oxidative addition reactions, but the dppm derived analogue was more crowded, and hence reaction with MeI or I_2 resulted in electrophilic cleavage reactions [96]. The structure of $[\{PtL\}(\mu\text{-}I)(\mu\text{-}Me_2PCH_2PMe_2)_2\{PtMe_3\}]I_3$ has been determined in an X-ray diffraction study (L = 0.45 I, 0.55 Me). Iodination of $[Pt_2(\mu\text{-dmpm})_2Me_4]$ involves both oxidative addition and methyl transfer [97].

Oxidative addition and methyl group transfer was studied in more detail for the reactions of $[Pt_2(\mu\text{-dmpm})_2Me_4]$ with X_2, (X = Cl, Br or I) giving $[\{PtMe_3\}(\mu\text{-}X)(\mu\text{-dmpm})_2\{PtMe\}]X$. The species 15 was characterised in an X-ray diffraction study, and a mechanism for the reaction was proposed [98]. The outcome of reactions of $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ with iodomethane depended on the bulk of R. When R = Me, the reaction yielded succesively $[\{Pt(I)Me_3\}(\mu\text{-dmpm})_2\{PtMe_2\}]$ and $[Pt_2(\mu\text{-dmpm})_2(\mu\text{-}I)Me_6]^+$, but when R = Ph, there was no reaction. When R = Et, the reaction was still reversible, but very much slower, and the intermediacy of $[\{PtMe_3\}(\mu\text{-}I)(\mu\text{-depm})_2\{PtMe_3\}]I$, 16, was established. The oxidative addition of CD_3I was shown not to be stereospecific [99].



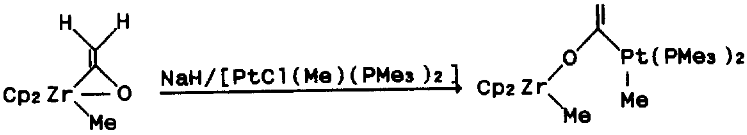
15 Stereoview of the $[\{PtMe_3\}(\mu\text{-dmpm})_2(\mu\text{-I})\{PtMe\}]^+$ cation showing the atom numbering scheme. (Reproduced with permission from [98])



16 A perspective view of the structure of $[\{PtMe_3\}(\mu\text{-dmpm})_2(\mu\text{-I})\{PtMe_3\}]^+$ showing 50 % probability of vibrational ellipsoids. (Reproduced with permission from [99])

Reaction of $[PtCl_2(SMe_2)_2]$ with an excess of MeLi, followed by an excess of MeI yielded $[Pt_2Me_8(\mu\text{-SMe}_2)_2]$, the first binuclear octamethyl complex of this type. Addition of a ligand, L, caused bridge splitting to give *cis*-$[PtL_2Me_4]$. Reaction of the dimer with HX (X = Cl or OH) yielded $[\{PtXMe_3\}_4]$ [100].

Treatment of $[Pt(cod)R_2]$ or $[Pt(dmso)_2R_2]$ with bipym gave mono or binuclear complexes, according to the stoicheiometry of the added ligands [101]. The complexes [Pt(Me)(Me$_2$MPz)L] (L = CO, PPh$_3$, PhC≡CPh; M = B or Ga) were prepared, and their fluxional behaviour on the nmr spectroscopic timescale investigated [102]. Reaction of 17 with a base such as NaH, in the presence of [MClL$_2$X] yieled 18 (Y = Z = Me; M = Pt; L = PMe$_3$) [103]. The preparation of 19 from [PtMe$_4$(SO$_4$)] and the potassium salt of the ligand was reported [104].



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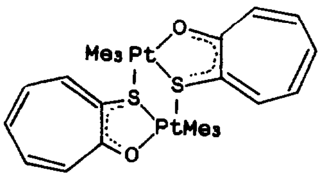


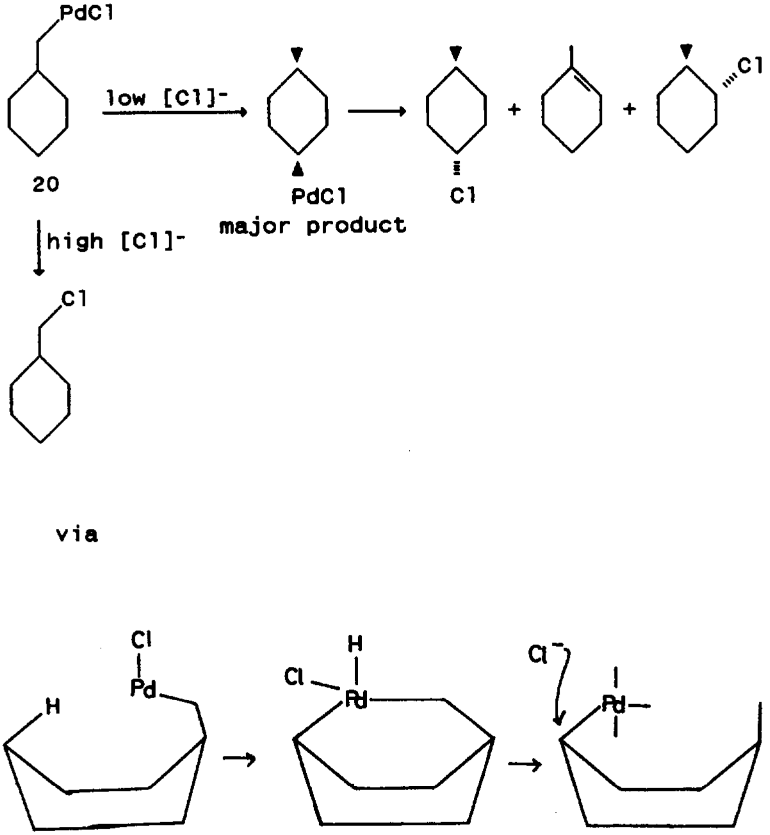
19

An EHMO calculation has assessed the ability of *trans*-[PtH(PPh$_3$)$_2$X] (X = Cl, Br or I) to add oxidatively a C-H bond of pentane. The calculations indicated that the rate of the reaction is related to the difference in energy levels and the overlap integral between the HOMO of the complex, and the LUMO of pentane, as well as the stability of the transition state. The results were consistent with the experimentally determined ease of reaction, $Cl^- > Br^- > I^-$ [105].

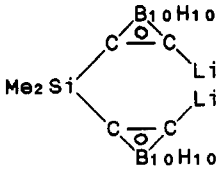
^{195}Pt, ^{119}Sn and ^{31}P nmr spectroscopic experiments have been used in the study of *trans*-[Pt(PEt$_3$)$_2$(R)(SnCl$_3$)] (R = Me, CH$_2$Ph, COPh, C$_6$Cl$_5$ or C$_6$H$_4$Y). Most of the data could be correlated with electronic effects. The structure of the complex for which R = COPh was established in an X-ray diffraction study; the longest Pt-Sn bond observed in complexes of this type (2.634 Å) was related to the strong *trans*-influence of the benzoyl group [106]. An electrochemical study of the reaction between NiX$_2$ (X = Cl or acac), PR$_3$ or P(OR)$_3$ and R'$_3$Al suggested the presence of σ-alkylnickel complexes as intermediates [107]. In a related study, UV spectrsocopy indicated the intermediacy of {RNi(acac)} and {R$_2$Ni}, and suggested that the reactions of the analogous palladium complexes followed a similar course [108].

Reaction of $[\{Pt(Ge\{CF_3\}_3)(PPh_3)_2\}_2Hg]$ with R_2Hg (R = Et, Cl or GeR'_3) gave $[RHgPt(PPh_3)_2R]$, as the initial product [109]. With RHgR' and $[Pt(PPh_3)_3]$ $[Pt(PPh_3)_2(R)HgR']$ was obtained (R = Me or Et, R" = chloroaryl). Demercuration to give $[Pt(PPh_3)_2RR']$ was frequently very rapid [110].

Treatment of $[NiCl_2(PMe_3)_2]$ with Me_3CCH_2MgCl gave *trans*-$[Ni(CH_2CMe_3)Cl(PMe_3)_2]$, which readily inserted carbon monoxide into the nickel-carbon bond. Related species, inculding $[Ni(NCS)(PMe_3)_2R]$ (R = CH_2CMe_3) and [Ni(Cp)(L)(R)] (L = PMe_3 or PPh_3) were also studied, and the structure of *trans*-$[Ni(CH_2CMe_3)_2(PMe_3)_2]$ was established in an X-ray diffraction study [111]. With the mercury compound, Me_3CCH_2HgCl, and palladium(II) in the presence of copper(II), the metal alkyl complexes were unstable, and gave rearrangement products, *via* carbocations. The reactions of 20 were investigated in detail (Scheme 2) [112]. Reaction of 21 (*sic*) with $[M(bipy)Cl_2]$ (M = Ni or Pd) gave the dialkyl complex [113].



Scheme 2 Reactions of cyclohexylmethyl palladium chloride [112]



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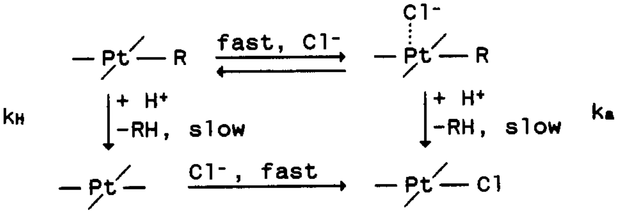
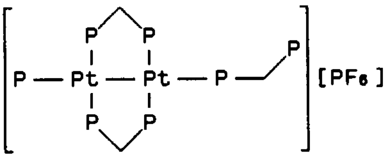
A kinetic analysis was performed on the decomposition reactions of *cis*-[$PtCl(PEt_3)_2(R)$] (R = Pr or Bu). With added lithium chloride the main products are alkenes, formed by β-hydride elimination, but when Et_3P is added isomerisation to the stable *trans*-complex is catalysed, and is much faster than elimination [114]. The mechanism of electrophilic cleavage of the platinum-carbon bond in *trans*-[$Pt(PEt_3)_2(R)X$] (R = Me, Et, Pr, Bu or $PhCH_2$; X = Cl or Br) or *cis*-[$Pt(PEtPh_2)_2Ph_2$] by H^+ in the presence of X^-/MeOH has been studied. The mechanism shown in Scheme 3 was proposed, and explains all the previously observed results [115].



Scheme 3 Mechanism of electrophilic cleavage of platinum-alkyl bond [115].

The complex [$Pt_2(\mu\text{-dppm})_3$] reacted with alkyl iodides, RI, in the presence of $[PF_6]^-$ to give 22 (R = Me, Et, Pr, Bu, H or CH_2CD_3). Thermolysis or photolysis of the ethyl derivative gave ethene and ethane as the main products in the ratio 2:1. The reaction is quite slow, suggesting that the platinum-platinum bond does not activate the alkyl group towards β-elimination. With the deuterated analogue there was no scrambling (implying that the β-elimination reaction is irreversible), and no kinetic isotope effect. Two mechanisms could be proposed for the reaction, one involving initial splitting of the metal-metal bond, and the other dissociation of one of the μ-dppm ligands [116]. Reaction of [PtL_4] with $BrCH_2CH_2OPh$ gave *trans*-[$PtBr(CH_2CH_2OPh)L_2$]. Thermolysis of this complex at 100 °C gave ethene and phenylethenyl ether in the ratio 1:2, consistent with competitive β-elimination of hydride and phenoxyl. The effect of varying the ligand on the outcome was studied. A dissociative mechanism was proposed for β-hydride elimination, and an associative one for phenoxy elimination. In 23, the proposed transition state, the electrophilicity of the platinum centre increases with the π-acceptor character of L' [117].



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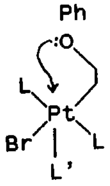


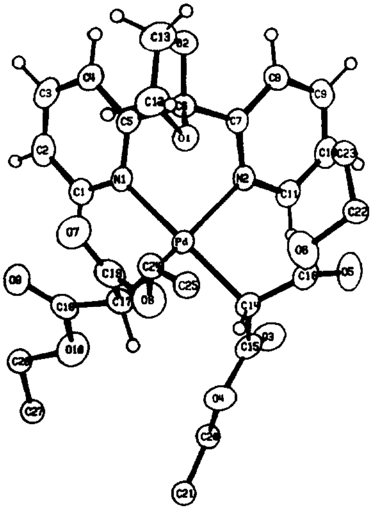
23

There have been a range of reports in which the alkyl ligand is a carbon-bonded β-diketonate or a β-diester. When palladium bis(β-diketonato-*O,O*) complexes, $[PdL_2]$, were treated with pyridine and a trifluoromethyl containing β-diketone, L' (L' = CF_3COCH_2COR, R = CH_3, CF_3, CMe_3 or 2-thienyl), complexes of the type $[PdL(L'\text{-}C^3)py]$ were formed [118]. Similarly tfacacH and hfacacH readily replaced the *O*-bonded acac ligand in [Pt(acac-*O,O*)(acac-*C*)(py)] [119].

Reaction of thallium β-diketonates with *cis*- or *trans*-$[PtCl_2(Et_2S)_2]$ gave products in which the β-diketonate ligand was bonded to the platinum through carbon. With an excess of added β-diketonate, the second halide and one of the sulphide ligands was displaced to give $[Pt(\beta\text{-dik-}C)(\beta\text{-dik-}O,O)(SEt_2)]$ [120]. Halides could also be displaced from $[PdCl_2(NN)]$ (NN = bidentate nitrogen ligand) by $K[CH(COOR)_2]$. That the propanedioates were *C*-bonded was confirmed by spectrsocopic studies, and by an X-ray diffraction study of 24 [121]. Reaction of diethyl propanedioate with $Na_2[PdCl_4]$ in the presence of K[OH] gave $[Pd_2\{CH(COOEt)_2\}_4(\mu\text{-}Cl)_2]^{2-}$ and $[Pd_2\{CH(COOEt)_2\}_4(\mu\text{-}C_2O_4)]^{2-}$. The bridging oxalato ligand is considered to be formed from metal catalysed reactions of diethyl propanedioate [122].

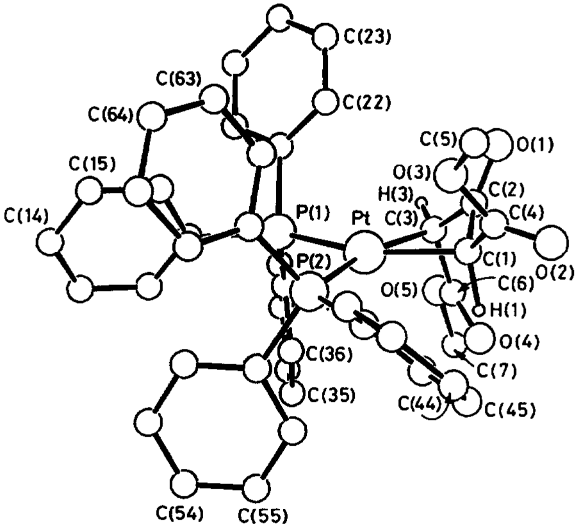
Dimethyl-3-oxo-pentanedioate reacted with $[Pt(PPh_3)_4]$ at room temperature, to give 25. This may be characterised as a highly puckered platinacyclobutan-3-one ring with a weak transannular platinum-carbon bond, or as a slipped η^3-oxodimethylenemethane compound. Nmr spectroscopic data showed that the ring was inverting, *via* a planar transition state [123]. In a related process, heptane-2,4-6-trione reacted with $[Pt(CO_3)L_2]$ to give 26, which had very similar properties [124]. Reaction of $[Pd_2(dba)_3]$ with $RO_2CCH_2COCH_2COOR$ in the presence of a ligand, L, gave 27 (L = PPh_3, $AsPh_3$, bipy, PMe_2Ph, $PMePh_2$

or PEt_3; R = Me, Et or Pr). A diffraction study established the structures of the complexes with R = Me, L = $AsPh_3$ or PPh_3 or L_2 = bipy. They were best formulated as slipped η^3-oxodimethylenemethane derivatives [125].

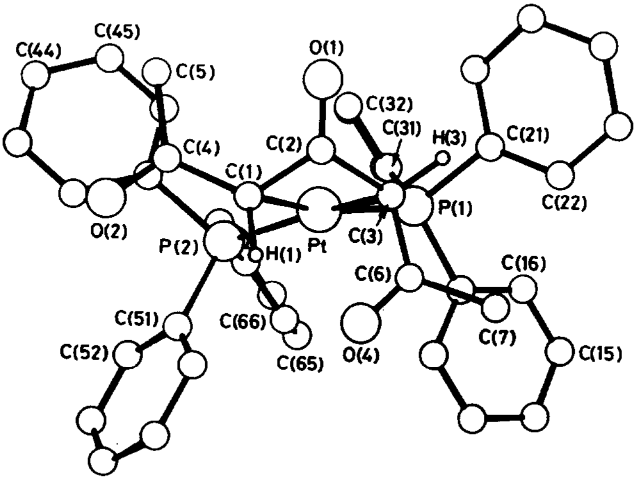


24 ORTEP drawing of bis(diethylpropanedioato-*C*){2,2-bis(2-pyridyl)-1,3-dioxolane} palladium(II). Some of the hydrogen atoms have been omitted for clarity, and the ethyl carbon atoms are represented by circles of arbitrary radius. (Reproduced with permission from [121])

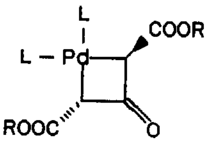
Reaction of $[Ni(C_2H_4)(PPh_3)_2]$ with 1,2-bis(bromomethyl)benzene gave dibenzocyclooctadiene and $[NiBr_2(PPh_3)_2]$, but when the substrate was $[Ni(cod)(PCy_3)]$ the oxidative addition product, 28, was isolated in good yield [126]. When the reaction between $[Ni(C_2H_4)(PPh_3)_2]$ and $4\text{-}RC_6H_4CH_2Cl$ was carried out at -20 °C, the intermediate $[Ni(CH_2Ar)Cl(PPh_3)_2]$ could be observed. Carboxylation using CO_2, followed by an aqueous work-up, gave $ArCH_2COOH$. Treatement of the σ-benzyl derivative with butadiene resulted in insertion to yield an allyl complex [127]. A range of oxidative addition products, including cyclophanes, were reported from the reaction of $[Ni(C_2H_4)(PPh_3)_2]$ with $C_6H_x(CH_2X)_{6-x}$ (x = 0, 1, 2, or 3; X = Cl or Br) [128]. Both σ-benzyl and π-benzyl nickel complexes have also been prepared by a contrasting route, from $[NiCl_2(PMe_3)_2]$ and $2\text{-}MeC_6H_4CH_2MgCl$. The presence of a small amount of adventitious water in the reaction mixture led to the isolation of the cluster 29, characterised in an X-ray diffraction study [129]. Reaction of $ArCH_2X$ with nickel(0) and PhCOX gave $ArCH_2COPh$; a number of similar couplings were also promoted [130].



25 Molecular structure showing the atom numbering scheme. Atoms are drawn as circles with arbitrary radii. Phenyl and methyl hydrogen atoms have been excluded. (Reproduced with permission from [123])



26 Atoms are drawn as circles with arbitrary radii. Phenyl and methyl hydrogen atoms have been excluded. (Reproduced with permission from [124])



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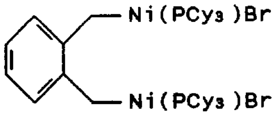

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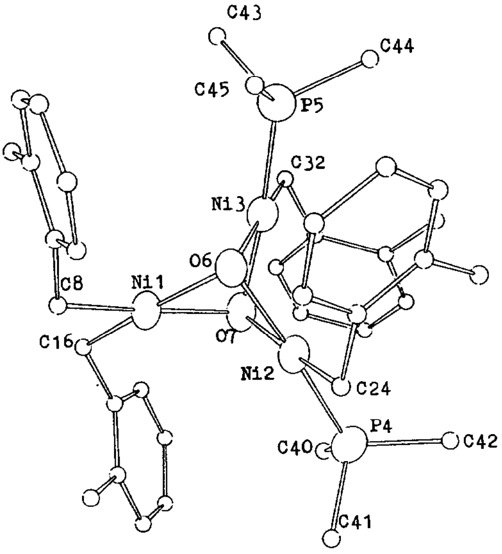
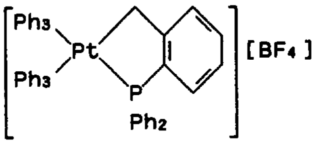


29 The C_6H_4-Me labels have been omitted for clarity. (Reproduced with permission from [129])

Photolysis of propanone in the presence of $[PtCl_6]^{2-}$ resulted in the initial formation of the relatively stable species $[CH_3COCH_2PtCl_5]^{2-}$. More prolonged photolysis gave CH_3COCH_2Cl and $[PtCl_4]^{2-}$, whereas treatment with ammonia and silica yielded $[NH_4][Pt(CH_2COCH_3)Cl_4(NH_3)]$. EPR spectroscopy in a frozen matrix indicated that platinum(II) and $CH_3COCH_2\cdot$ radicals were involved in the photolytic reaction [131]. The same type of product was formed thermally from $K_2[PtCl_4]$ and iodopropanone [132].

Reaction of $[Pt_2L_4(\mu\text{-}S)_2]$ (L = PPh_3) with CH_2I_2 afforded $[Pt(CH_2I)_2I_2L_2]$ in ethanol and $[PtL_2(CH_2I)I]$ in ether solution. Other alkyl halides react at sulphur [133]. Treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with CH_2XX' gave *cis*- and *trans*-$[Pt(CH_2X')(PPh_3)_2X]$ (X = X' = I, X = Br, X" = Cl or X = I, X' = Cl). Treatement with $Ag[BF_4]$ in the presence of an excess of phosphine yielded 30 [134]. Oxidative addition of CH_2XX' to a platinum allyl complex was also studied [135].



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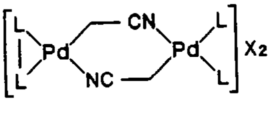
The reactions of *trans*-$[Pd(CH_2CN)Cl(L)_2]$ (L = PPh_3) have been investigated; ligand replacement occurs relatively readily. When the derivative of a chelating ligand, LL, $[Pd(CH_2CN)Cl(LL)]$ was treated with AgX the dimeric species 31 was formed [136]. Treatment of $[NiCl_2L_2]$ with $LiCH_2PMe_2$ gave 32, in which $\{CH_2PMe_2\}$ acts as an η^2-ligand [137]. Nickel(II) bromide reacted with $LiCH_2SPh$ to give a species of stoicheiometry $\{Ni(CH_2SPh)_2\}$ which decomposed to $[Ni(SPh)_2]$, together with ethene and propene [138]. The complex $[Ni(CH_2SMe)(Cp)(PPh_3)]$ has been prepared by several different routes, including oxidative additon of CH_3SCH_2Cl to $[Ni(C_2H_4)(PPh_3)_2]$ and reaction of $[Ni(Cp)(PPh_3)X]$ with $LiCH_2SMe$. In the latter case the ylide $Me_2S^+CH_2^-$ has also been used as the nucleophile, giving 33 and 34, $[Ni_2\{\mu\text{-}CH_2S(Me)CH_2\}(PPh_3)_2]^+$ [139].



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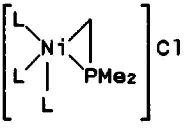

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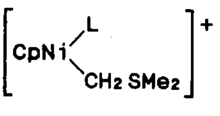
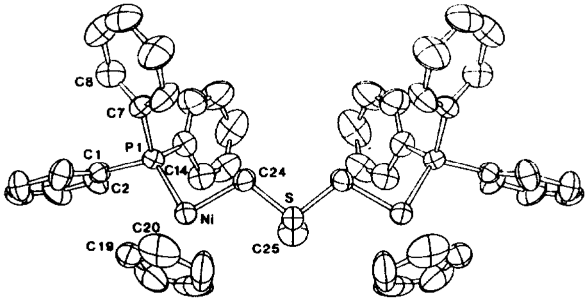


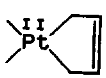
33

The treatment of *trans*-$[Pd(CH_2SR')(PRPh_2)X]$ with an excess of HX' (R = Me or Ph; X = Cl, Br, I or [SCN]; R' = Me or Ph; X' = Cl or $[OCOCF_3]$) gave MeSR' and *trans*-$[Pd(PPh_2R)_2XX']$. With $[Pd(\eta^2\text{-}CH_2SMe)(PPh_3)X]$, HX' reacted more slowly to give *trans*-$[Pd_2(PPh_3)_2X'_2(\mu\text{-}X)_2]$ [140]. Attempted alkylation of *trans*-$[Pd(CH_2SR')(PPh_2R)_2X]$ with R"X' resulted only in halide exchange. With the η^2-{CH_2SMe} derivative, halide exchange also occurred, but was very slow [141].



34 ORTEP drawing of the cation $[Ni_2\{\mu\text{-}CH_2S(Me)CH_2\}(Cp)_2(PPh_3)_2]^+$. Hydrogen atoms are not shown. Probability ellipsoids are at the 50 % level. (Reproduced with permission from [139])

^{195}Pt nmr spectrsocopy has been used to distinguish between platinum(0) and platinum(II) in alkene and diene complexes; 35 and 36 were distinguished in this way [142]. It had previously been reported that metallocyclopentane ions had been synthesised in the gas phase by the decarbonylation of cyclopentanone by Ni^+. A study of the reaction with cyclobutanone now shows that a similar course, leading to a nickelacyclobutane, is followed. However, the product is unstable with respect towards β-hydride transfer, to give propene complexes. The reaction of Ni^+ with cyclopentane and cyclohexane was also studied; carbon-carbon bond cleavage occurred, and alkenes and dienes were the main products [143].



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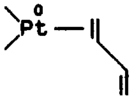
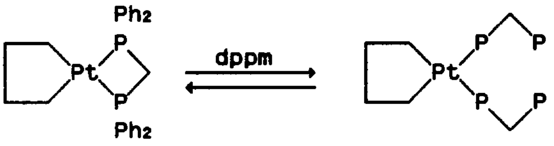
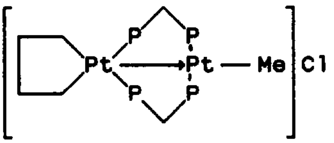


36

Reaction of $[PtCl_2(dppm\text{-}P,P)]$ with 1,4-dilithiobutane gave 37 which reacted with an excess of dppm to give 38, readily isolated as a pure compound. The complex 38 reacted with other metal derivatives, to give a range of binuclear complexes, including 39 [144]. Trityl cation has been widely used as a hydride abstraction agent, and reacts with $[Pd(CH_2)_4L_2]$ to give $[Pd(\eta^3\text{-}CH_2CHCHCH_3)L_2]^+$. That the initial abstraction is of a β-hydride was shown by a deuterium labelling study, and the first intermediate was a σ-3-butenyl complex [145].

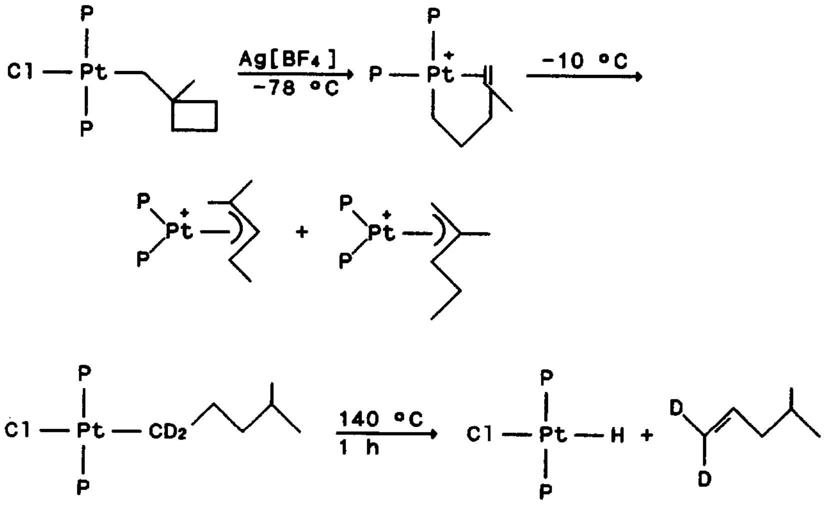


37 **38**



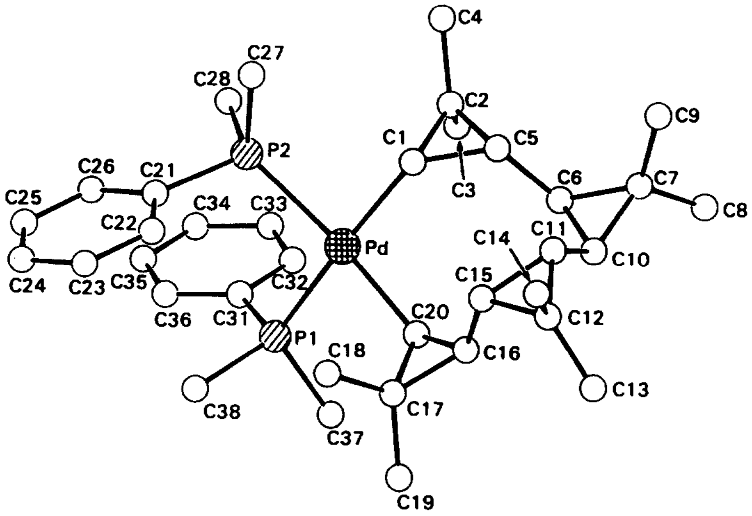
39

A range of complexes *trans*-$[PtCl(PMe_3)_2R]$ have been prepared. Pyrolysis of the complex for which R = $(CH_2\overline{C(Me)CH_2CH_2C}H_2)$ gave *trans*-$[PtClH(PMe_3)_2]$ and 2-methyl-1,4-pentadiene. The thermolysis was inhibited by the presence of free PMe_3, and the related *cis*-complex [PtCl(dmpe)R] also reacted much more slowly. Some further reactions are shown in Scheme 4 [146].

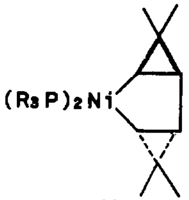


Scheme 4 Reactions of $[PtCl(PMe_3)_2R]$ [146]

The structure of **40** was established in an X-ray diffraction study; the conformation of the ring was best compared with the all *cis* boat conformer of 1,3,5,7-cyclononatetraene, and the cyclopropane rings adopted an *anti,syn,anti,syn*-arrangement [147]. Reaction of 3,3-dimethylcyclopropene with [Ni(PPh$_3$)$_3$] gave 41, which could be oxidised in air to 42 [148].



40 (Reproduced with permission from [147])



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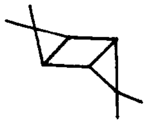
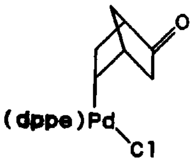


42

The protolysis of 43 has been studied; with DCl, 44 was the sole product, and $K_H/K_D = 4$. This suggests a three-centre transition state and an SE_2 mechanism [149]. Reaction of [Pd(PPh$_3$)$_4$] with 45 (M = Pd or Pt; X = O or NR) in toluene gave 46 [150,151].



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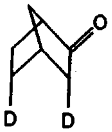

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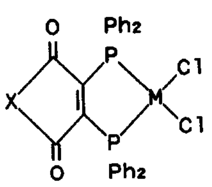

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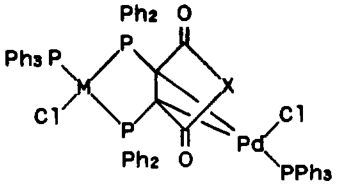
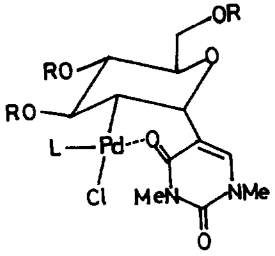


46

The complexes 47 and 48, prepared *via* organomercury compounds, proved to be surprisingly stable towards β-hydride elimination, presumably because there are conformational barriers to the proper alignment of the palladium for elimination [152]. The structure of 49, prepared from sodium ascorbate and *cis*-[Pt(dach)$(H_2O)_2$][NO_3]$_2$, has been established. This is the first example of an ascorbate ligand which is metal bound at C(2) and O(5) [153]. Reaction of 50 with [Pt(C_2H_4)$(PPh_3)_2$] resulted in oxidative addition to yield a *trans* platinum alkyl complex, *via* a radical process [154].



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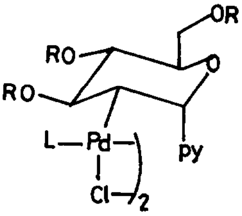

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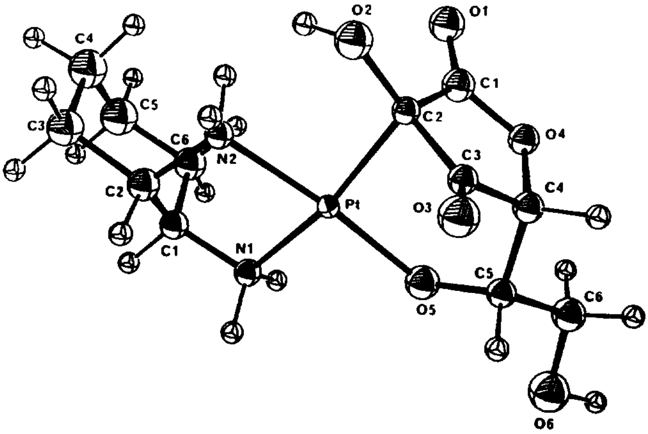
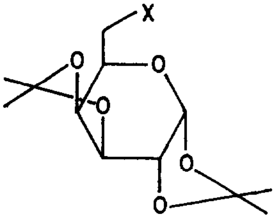


49 ORTEP illustration of the structure of [Pt(*cis*-dach)(ascorbate)] showing the 40 % probability ellipsoids for all non-hydrogen atoms. (Reproduced with permission from [153])



50

2.2 Metal aryl complexes

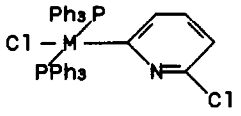
Advances in the synthesis and polymerisation of metal-containing monomers, including *trans*-[M(Ar)Cl(PR$_3$)$_2$] (M = Ni, Pd or Pt) and metal alkynyl derivatives have been reviewed [155].

The complexes [PtAr$_2$(cod)], *cis*- and *trans*-[PtAr$_2$(PBu$_3$)$_2$] have been studied by ^{1}H, ^{13}C and ^{31}P nmr spectroscopy. The coupling constants, ^{1}J(PPt), ^{1}J(PtC), ^{3}J(PtH) and ^{2}J(PC) show a clear correlation with the ligand configuration at platinum, and may be used for configuration determination [156]. Spectroscopic data have also been reported for *trans*-[Pt(C$_6$H$_4$Y)(PEt$_3$)$_2$X] and [Pt(C$_6$H$_4$Y)(PEt$_3$)$_3$][BF$_4$]. Good correlations were obtained between a range of spectroscopic parameters and the electronic and steric parameters for Y [157].

A number of structural studies on σ-aryl complexes have been reported. The complex *trans*-[NiBr(C$_6$Br$_5$)(PMePh$_2$)$_2$] showed slightly distorted square planar coordination [158], and in *trans*-[PtCl(Ph)(PPh$_3$)$_2$] the platinum-carbon bond was shortened in comparison with platinum-alkyl complexes [159]. The structures of [NiAr$_2$(nbd)] and [NiAr$_2$(cod)] (Ar = C$_6$F$_5$) have been established, and the bonding in the complexes was discussed in detail [160]. Reaction of [Bu$_4$N]$_2$[Pt(C$_6$Cl$_5$)$_4$] with either X$_2$ or TlCl$_3$ gave the blue paramagnetic platinum(III) derivative, [Bu$_4$N][Pt(C$_6$Cl$_5$)$_4$], the first fully authenticated monomeric platinum(III) complex to be structurally characterised. Diffraction studies, of both starting materials and products, showed that the structure of the anions was essentially identical [161].

Reaction of platinum atoms with C$_6$F$_5$Br yielded {PtBr(C$_6$F$_5$)}, which disproportionated at room temperature in propanone to give [Pt(C$_6$F$_5$)$_2$(Me$_2$CO)$_2$] and PtBr$_2$. The solvate reacted with ligands such as PEt$_3$ to yield *trans*-[Pt(C$_6$F$_5$)$_2$(PEt$_3$)$_2$]. The comparable reaction with PhBr was less favourable, but PhCH$_2$Cl gave what appeared to be an η^3-benzyl derivative, which reacted readily with phosphite ligands [162].

A number of preparations of σ-aryl derivatives have resulted from oxidative addition reactions. For example, [Pd(PPh$_3$)$_4$] was reacted with 18 haloarenes, RX (R = chloroaryl; X = Cl, Br or I) to give *trans*-[Pd(PPh$_3$)$_2$(R)X]. The products for which X = I reacted with iodine to yield [PdI$_3$(PPh$_3$)$_2$(R)]; the protolysis and decomposition of these complexes was discussed [163]. Reaction of ArX (Ar = dichlorophenyl, X = I) with [NiBr(PPh$_3$)$_3$] yielded [NiAr(PPh$_3$)$_2$X]. Various mechanisms were proposed for the reaction [164]. Oxidative addition to [Pd(PPh$_3$)$_4$] also occurred with 3- or 4-bromopyridines, to give *trans*-[PtBr(het)(PPh$_3$)$_2$], the reactions of which were explored in detail. When the substrate was 2,6-dichloropyridine, a single oxidative addition occurred [165]. Reaction of the product, 51, with Me$_2$SO$_4$ resulted in *N*-methylation; spectroscopic data indicated that there was partial double bond character and restricted rotation about the metal-carbon bond [166]. Photochemically induced oxidative addition of chlorobenzene to [Pd(PPh$_3$)$_4$] gave a low yield of *trans*-[PdCl(Ph)(PPh$_3$)$_2$] [167]. Reaction of [Ni(depb)$_2$] (depb = Et$_2$P(CH$_2$)$_4$PEt$_2$) with PhCN gave an equilibrium mixture of *trans*-[Ni(CN)(depb-*P*)$_2$(Ph)] and *trans*-[Ni$_2$(CN)$_2$(*μ*-depb)$_2$(Ph)$_2$]. Rate and equilibrium constants for all the processes involved were established, and radical processes discounted on the basis of a lack of EPR or CIDNP signals [168].



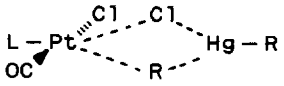
51

Substitution reactions using organolithium and organomagnesium compounds have been well represented in syntheses reported in this period. Reaction of *cis*-[PtCl$_2$(PBu$_3$)$_2$] with LiC$_6$H$_4$X gave *cis*-[PtAr$_2$(PBu$_3$)$_2$]. Protolysis with one molar equivalent of HCl yielded *trans*-[Pt(Ar)Cl(PBu$_3$)$_2$], which could be further substituted by Ar'Li, giving *trans*-[PtArAr'(PBu$_3$)$_2$] [169]. The complex *cis*-[Pt(PBu$_3$)$_2$(Ph)$_2$] could be lithiated at the 4-position of the aryl rings using Me$_3$CLi, and the dilithio derivative reacted readily with a range of electrophiles [170]. Other mixed biaryl complexes have been prepared for study of their thermolysis [171].

Reaction of C$_6$Br$_5$MgBr with [NiCl$_2$(PRPh$_2$)$_2$] gave [NiBr(C$_6$Br$_5$)(PRPh$_2$)$_2$]. The bromide could then be substituted by a range of other anions including [N$_3$]$^-$, Cl$^-$, I$^-$, [NO$_2$]$^-$ or [SCN]$^-$, but the rate of the reaction was slower than for the {C$_6$Cl$_5$} derivative [172]. The species [Ni(C$_6$Cl$_5$)Cl(PRPh$_2$)$_2$] was prepared in the same way; in this case the chloride ligand could also be substituted by a range of aryl and alkynyl nucleophiles [173].

Treatment of *cis*-[$PtCl_2(PPh_3)_2$] with 2-X-C_6H_4Li gave the *cis*-[$PtAr_2(PPh_3)_2$] derivative, for X = CF_3, NMe_2 or MeO, but the reaction failed for X = NO_2, F or Me. However, when the other ligands at platinum were tmeda or cod, the less reactive lithioarenes gave successful reactions [174]. The reaction was more generally tested later, and a wide range of complexes of the types [$Pt(C_6H_4$-2-$X)_2(PPh_3)_2$] and *cis*-[$Pt(C_6H_4$-2-$X)(C_6H_4Y)(PPh_3)_2$] were prepared [175]. When the lithioarene was 2,6-$(MeO)_2C_6H_3Li$, only a monosubstituted product was obtained from [$Pt(PPh_3)_2X_2$], but [$PtAr_2L_2$] was formed from [$PtCl_2$(tmeda)] [176].

Whilst it had been known that reaction of R_2Hg with *cis*-[$PtCl_2(CO)L$] gave a single isomer of [PtCl(CO)(L)(R)] (R and L *trans*), when R is a 2-substituted aryl group, the reaction is very slow, and for R = 2,4,6-$Me_3C_6H_2$, both possible stereoisomers are obtained in approximately equal amounts. The isomer with R and L *trans* was considered to have been produced by an S_{E2} cyclic mechanism *via* 52, with the other isomer formed by a non-cyclic process [177]. Treatment of [$PtCl_2L_2$] (L = py or L_2 = bipy or phen) with $Ba[O_2SR]_2$ (R = C_6F_5 or 4-HC_6F_4) gave [R_2PtL_2], $BaCl_2$ and SO_2. Partial substitution to yield [$Pt(Ar)ClL_2$] was also possible by careful control of the ratio of the reactants. {RSO_2} derivatives were thought to be intermediates in the reaction [178].



52

Various new aryl complexes have been prepared by ligand exchange reactions on existing aryl complexes. Thus [$Ni(C_6Cl_5)\{P(CH_2Ph)_3\}_2X$] (X = Cl, Br, I, [NCS] or [NCO]) were prepared [179]. Nucleophilic substitution of [$Ni(C_6Cl_5)(PPh_2R)_2X$] (R = Me, Et or Pr; X = Cl, Br or I) with methanol, ethanol, Na[NO_2] or K[CNS] has been noted [180]. The kinetics of the substitution reaction of *trans*-[$NiCl(C_6Cl_5)(PPh_2Me)_2$], with substituted pyridines have been investigated. The rate constants were found to be controlled by steric effects rather than amine basicity [181]. Reaction of [$Ni(bipy)Br(C_6H_2$-2,4,6-$Me_3)$] with RLi (R - 2,4,6-$Me_2C_6H_2$ or Me) gave [$Ni(bipy)(C_6H_2$-2,4,6-$Me_3)(R)$]. The latter reacted with iodine to give [$Ni(bipy)I_2$] and RC_6H_2-2,4,6-Me_3 [182].

Ligand exchange reactions of *trans*-[$Pd(C_6F_5)_2(dioxan)_2$] gave *trans*-$[Pd(C_6F_5)_2L_2]$ (L = ketone)] [183]. A larger range of ligands, both mono and bidentate, was used for reaction with *cis*-$[Pd(C_6F_5)_2(dioxan)_2]$ [184]. With *cis*-$[Pd(C_6F_5)_2(thf)_2]$ as the substrate, and CO as the incoming ligand, *cis*-$[Pd(C_6F_5)_2(CO)_2]$ was the product. The stretching frequency, ν_{CO} = 2186 cm^{-1}, indicated that back-bonding to the metal was negligible [185].

The complex $[Bu_4N][M(C_6F_5)_3(CNR)]$ (M = Pd or Pt; R = Me, Cy, Me_3C or 4-MeC_6H_4) was prepared from $[Bu_4N][M(C_6F_5)_3(tht)]$ and RNC. These triaryl complexes were unreactive towards amines, but *trans*-$[Pd(C_6F_5)_2(CNR)_2]$ reacted slowly with $PhCH_2NH_2$ to give the carbene complex *trans*-$[Pd(C_6F_5)_2\{C(NHR)NHCH_2Ph\}_2]$. The bis(aryl)platinum complexes were less reactive [186]. A range of reactions of $[Pd(\beta\text{-dik})(PPh_3)(R)]$ (R = 2-, 3-, or 4-pyridyl) with nucleophiles has been studied, as have the reactions of *trans*-$[RPd(PEt_3)_2X]$ with $Tl[\beta\text{-dik}]$. The nmr spectra and fluxional behaviour in the products were discussed [187].

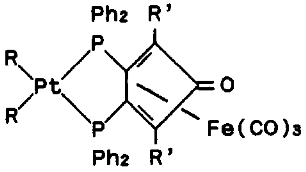
Ligand exchange reactions of *trans*-$[Pt(C_6F_5)_2(dioxan)_2]$, leading to *trans*-$[Pt(C_6F_5)_2L_2]$ (L = Et_2NH, $PhNH_2$ or piperidine) have been studied [188]. Both *cis*- and *trans*-$[Pt(C_6Cl_5)(OCHO)(PEt_3)_2]$ were readily decarboxylated to give the related hydrides. The complex $[Pt(C_6Cl_5)Cl(PEt_3)_2]$ reacted with $Ag[BF_4]$ to give $[Pt(C_6Cl_5)(PEt_3)_2(solvent)][BF_4]$, and further reactions of these and related species were studied [189].

The normal mode of substitution of *cis*-$[Pt(dmso\text{-}S)_2(Ph)_2]$ is associative. However, with chelating ligands, L-L, both dissociative and bimolecular processes were observed. The strong *trans*-influence of the phenyl ligand is necessary to weaken and lengthen the platinum-sulphur bond sufficiently that dissociation to $[Pt(\eta^2\text{-dmso})(Ph)_2]$ occurs [190].

Reaction of $[Pt(dppm\text{-}P)_2(Np)_2]$ with $[Rh_2Cl_2(CO)_4]$ gave $[\{PtNp_2\}(\mu\text{-dppm})_2\{RhCl(CO)\}]$. A number of related complexes were also studied [191]. Treatment of $[Pt(PPh_2C\equiv CR')_2R_2]$ (R = 2-MeC_6H_4, C_6F_5 or CF_3; R' = Ph, Cy or $SiMe_3$) with $[Fe_2(CO)_9]$ gave 53, together with some of the complex which has lost the $\{Fe(CO)_3\}$ unit; the structure of the iron-free complex for which R = C_6F_5, R' = Ph was established in an X-ray diffraction study [192]. Reaction of *trans*-$[Pt(PCH_2Ph)_2(Ph)_2]$ with CO_2 gave *trans*-$[\{Pt(P\{CH_2Ph\}_3)_2(Ph)\}_2(\mu\text{-}CO_3)]$, 54, the structure of which was established in an X-ray diffraction study. The reaction was considered to proceed in a stepwise manner *via* hydrogen carbonate intermediates [193].

Various aryl derivatives of platinum(IV) have been reported. Complexes of the type $[Pt(Ar)Cl_n]^{x-}$ were prepared from ArI and $K_2[PtCl_4]$ in H_2O/tfaH [194]. Arenes reacted with $[PtCl_6]^{2-}$ under irradiation, to give aryl platinum(IV) complexes, which were isolated as the ammonia adducts $[NH_4][Pt(Ar)Cl_4(NH)_3]$

[195]. In a thermal reaction, $H_2[PtCl_6]$ reacted with toluene to give $[Pt(Ar)Cl_5]^{2-}$. The kinetics of complex formation as well as of interconversion of the 3- and 4-substituted isomers were studied. These suggested the formation of Wheland intermediates, which were able to interconvert in solution [196]. More detailed studies suggested that in the thermal reaction the initially formed intermediate was a π-bonded arene complex, but in the photochemical reaction, an electron transfer pathway was dominant [197].



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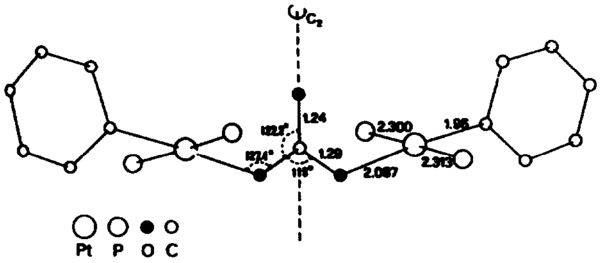
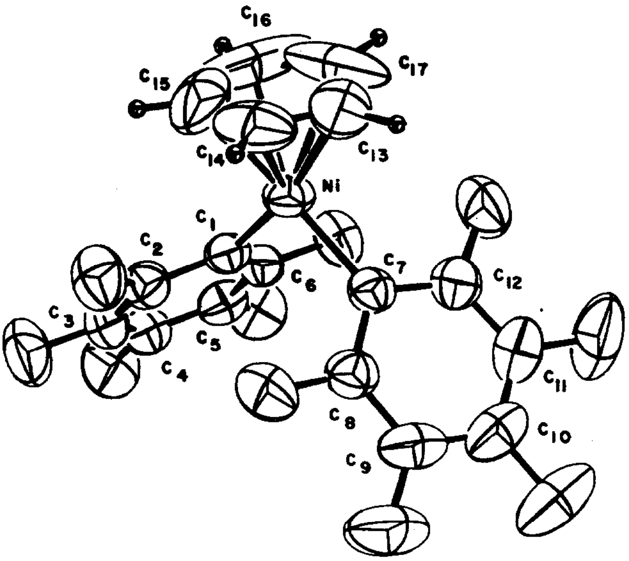


54 A sketch of the dimer with some bond lengths and angles of interest. E.s.d.'s are 0.004 for Pt-P, 0.007 for Pt-O, and 0.01-0.02 for the other bond lengths. Only the donor atoms of the phosphines are shown. (Reproduced with permission from [193])

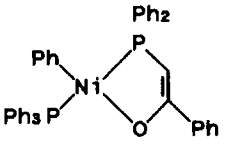
Reaction of $[PtCl_6]^{2-}$ with ethenylbenzene gave a platinum(II) ethenylbenzene complex. Irradiation of $[PtCl_6]^{2-}$ in the presence of hexane yielded a platinum(II) complex of 1-hexene. With PhOMe a 4-platinated aryl complex was the sole isolated product. Again the kinetics of the reaction have been studied in detail, and competition between electron transfer pathways and electrophilic substitution reactions considered [198]. Treatment of $[PtCl_6]^{2-}$ with ArHgX, followed by reaction with NH_3/SiO_2 gave $[Pt(Ar)Cl_4(NH_3)]^-$. This is a convenient reaction for the specific preparation of 3- or 4-substituted species, since mixtures are generally obtained in reactions with arenes. Ph_4Sn and Ph_4Pb give lower yields in this reaction [199].

The ^{195}Pt nmr spectra of $[ArPt(NH_3)Cl_4]^-$ have been reported, and the data correlated with the substituents on the aryl ring [200]. The thermal behaviour of $[Ar]_2[PtCl_6]$ (Ar = *N*-alkyl-py) has been investigated. Initially on heating HCl is lost to give, for example, $[N\text{-Mepy}][PtCl_5(N\text{-Mepy-H})]$, in which one of the heterocyclic rings has been metallated [201].

Kinetic data for oxidative addition reactions of Ni(0) with ArX have been published. The arylnickel complexes produced readily inserted alkenes, to give arylated alkenes and {HNiX} [202]. Reaction of $[Ni(C_6F_5)_2(\eta^6\text{-}C_6H_5Me)]$ with TlCp followed by $[Et_4N]I$ gave the new class of compounds $[Et_4N][Ni(C_6F_5)_2Cp]$. In the structure of 55 there is a non-planar deformation of the Cp ligand, and this is the first example of the direct replacment of an arene ligand by $[Cp]^-$ [203]. Reaction of $[Ni(cod)_2]$ with PPh_3 and $Ph_3PCHCOPh$ gave 56, the structure of which was established in a diffraction study [204].



55 Computer drawing of the $[Ni(C_6F_5)_2(\eta^5\text{-}C_5H_5)]^-$ ion as it exists in crystals of the $[(C_2H_5)_4N]^+$ salt. Anisotropic ellipsoids are represented at 50 % probability and hydrogen atoms have been reduced in size for clarity. (Reproduced with permission from [203])



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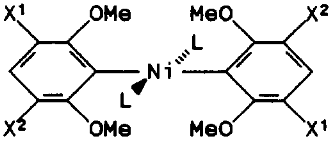
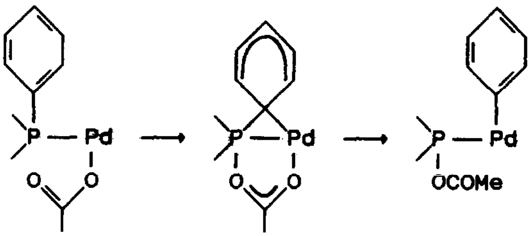
The electrochemical reduction of *cis*[$NiBr(C_6H_4$-4-Br)$Ni(PPh_3)_2$] in MeCN gave a polymer coating of nickel containing poly *para*-phenylene. The coating, which contains nickel-aryl units, undergoes a two-electron reversible reduction, and a one-electron reversible oxidation. There is thus a large potential window in which the polymer is not destroyed [205]. Poly-2,5- and poly-2,6-pyridine coatings were produced on glassy carbon electrodes by the nickel catalysed reduction of dibromopyridines in MeCN. The complexes *trans*-[$NiBr(PPh_3)_2$(2-pyridyl-5-Br)] and *trans*-[$NiBr(PPh_3)_2$(3-pyridyl-6-Br)], formed by the addition of the dibromopyridines to [$Ni(PPh_3)_4$], were used as the starting materials [206]. The photolysis reactions of 57 (L = PMe_3 or PMe_2Ph; X^1 = H or Br, X^2 = H or Br) have been investigated [207]. Reduction of [$Ni(C_6F_5)(PPh_3)_2X$] (X = (C_6F_5) or Br) with [BH_4]$^-$ gave an unstable species [$Ni(Ar)(PPh_3)_3$]$^-$, which was not fully characterised. In the presence of CO, the reaction yielded [$Ni(Ar)(CO)_2(PPh_3)_2$]. Some related alkynyl complexes were also studied [208]. Reaction of $NiCl_2$ with NaH, [RO]Na and bipy in the ratios 4:2:1:2 gave an incompletely characterised nickel(0) complex, which catalysed homocoupling of aryl haides, and haloalkenes [209].



57

Reaction of palladium ethanoate with PPh_3 gives [{$Pd(OCOMe)_2(PPh_3)$}$_2$] or [$Pd(OCOMe)_2(PPh_3)_2$] depending on the reaction stoicheiometry. Thermolysis of the products gave biphenyl and phenyl ethanoate, possibly *via* the initial sequence of reaction (2) [210]. When *trans*-[$Pd(Ar)I(PPh_3)$] is treated with $RSnMe_3$ (R = Ph or 4-MeC_6H_4) cross-coupling to yield RAr occurred. The reaction mechanism was discussed in terms of initial halide substitution followed by isomerisation and reductive elimination [211].

The complex *trans*-[$M(C_6F_5)(OClO_3)(PR_3)_2$] reacted with [$R'_3PCS_2$] to give *trans*-[$M(C_6F_5)(PR_3)_2(R'_3PCS_2)$][$ClO_4$] (M = Pd, R = R' = Et or Bu, R_3 = R'_3 = Et_2Ph, R = Bu, R' = Cy, or R = Ph, R' = Et or Bu; M = Pt, R = R' = Et or Bu). The same type of complex was also obtained by reacting CS_2 with [$Pd(C_6F_5)(PEt_3)_3$][ClO_4]. The structure of 58 was established in an X-ray diffraction study; the {Et_3PCS_2} moiety acts as a unidentate ligand, bound at sulphur [212].



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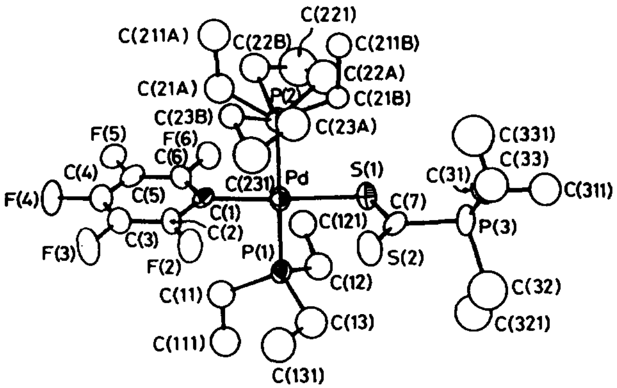


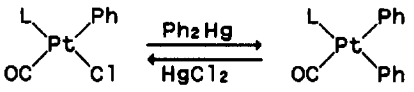
58 Perspective view of the cation *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2CPEt_3)]^+$ with thermal ellipsoids constructed at the 30 % electron probability level. (Reproduced with permission from [212])

The reductive elimination of biaryls from *cis*-$[Pt(Ar)_2(PPh_3)_2]$ has been studied. The influence of the substituents on the aryl ring on the rate of the reaction was considerable, and $\Delta H^{\ddagger}$ was linearly correlated with the substituent constants and with $^1J(PPt)$ [213]. A further range of complexes of the types *cis*-$[Pt(Ar)(C_6H_4\text{-}4\text{-}Me)(PPh_3)_2]$ and *cis*-$[Pt(Ar)(C_6H_4\text{-}4\text{-}OMe)(PPh_3)_2]$ were similarly investigated [214].

The kinetics of dmso exchange in the complex *cis*-$[Pt(dmso)_2(Ph)_2]$ were investigated by stopped-flow techniques. Ligand replacement reactions with bipy, dppe or phen were also studied, and it was concluded that the reaction proceeded by a dissociative mechanism [215]. Isomerisation, solvolysis and thiourea substitution of *cis*-$[Pt(C_6H_4\text{-}4\text{-}F)Cl(PEt_3)_2]$ have been reported. The data were consistent with a dissociative mechanism, and the reactivity tended to be dominated by the solvation of the departing halide [216].

The complex *trans*-[Pt(Ar)(H)L_2] could be prepared by reaction of *trans*-[Pt(Ar)(OH)L_2] with methanol, *trans*-[Pt(Ar)L_2X] (X = Cl or NHCOMe) with $[MeO]^-$/MeOH or Na[BH_4]/MeOH or *trans*-[Pt(Ar)L_2(solvent)][BF_4] with $[MeO]^-$/MeOH or Na[BH_4]/MeOH. Reductive elimination from the products occurred only at high temperatures, and their stability increased with an increase in the bulk of the phosphine ligand, L. Loss of benzene from *trans*-[Pt(H)(PEt_3)$_2$(Ph)] was accelerated by CO, and inhibited by PEt_3 [217]. Protonation of [Bu_4N][Pt(C_6F_5)$_4$] with one molar equivalent of HCl gave [Bu_4N][Pt(C_6F_5)$_3$Cl], whereas with two molar equivalents the product was [Bu_4N]$_2$[Pt_2(C_6F_5)$_4$(μ-Cl)$_2$]. The related salts of [(Ph_3P)$_2$N], PPN, were also studied with particular reference to replacement of the halide ligand by dppm. Mixed metal dimers and trimers were prepared, including [($PtAr_3$)(μ-dppm){Pd(Ar)(PPh_3)$_2$}] and [Bu_4N][Ag{$PtAr_3$(μ-dppm)}$_2$] [218].

A detailed paper has been published regarding the reactions of complexes of the type [PtCl(CO)L(Ph)] with organomercury compounds. For the reaction between Ph_2Hg and 59, the group *trans* to the phosphine is replaced in both forward and reverse reactions, because PR_3 has a stronger *trans*-influence than CO. The mechanism probably involves an SE_2 cyclic pathway, with a transition state 60 [219].



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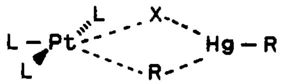
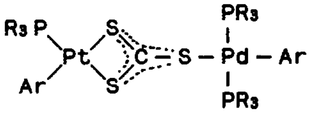


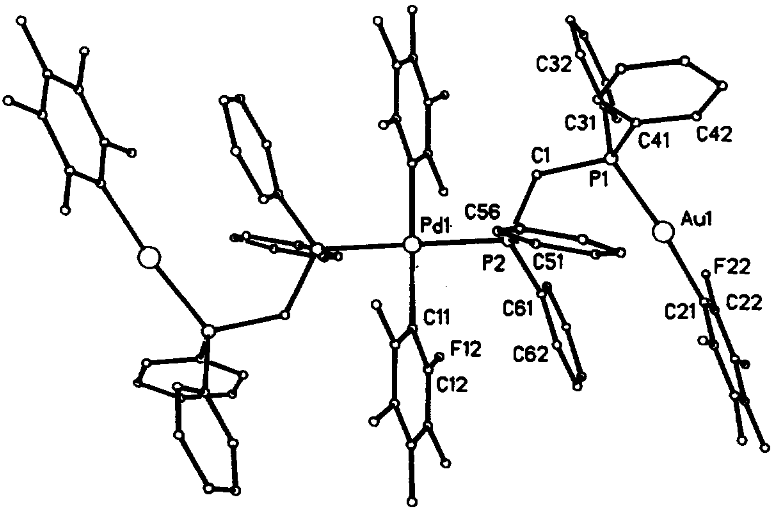
60

Various binuclear σ-aryl complexes have been noted. Reaction of [Pd(C_6F_5)L_2X] with [Pd(C_6F_5)L_2($OClO_3$)] gave the dimer *trans,trans*-[{Pd(Ar)L_2}$_2$(μ-X)][ClO_4] (X = [CN], [SCN] or [N_3], L = PPh_3). However, the scope of reaction of the bipy complexes is greater, and the bridging group may also be chloride or bromide. Some complexes of higher nuclearity were also prepared [220]. When the perchlorate derivative was reacted with Tl_2[CS_3] the product was 61. With [Pd(η^2-CS_3)(PR_3)$_2$], the related species [L_2Pd(μ-S_2CS)Pd(Ar)L_2][ClO_4] was formed [221].



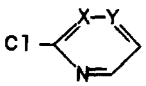
61

A series of binuclear complexes were prepared by the reaction of [Pd(η^1-dppm)$_2$RR'] (R = R' = C_6Cl_5 or C_6F_5 or R = C_6F_5, R' = Cl) with various gold complexes, bearing ligands which could be easily displaced. Examples included [(PdRR')(μ-dppm)$_2$AuCl], [(PdRR')(μ-dppm)$_2${Au(C_6X_5)}] (X = Cl or F) and [RR'Pd{(μ-dppm)AuCl}$_2$] The structure of 62 was established in a diffraction study [222]. Oxidative addition of 63 (X or Y = N) to [Pd(PPh_3)$_4$] gave a mixture of *trans*-[Pd(Ar)Cl(PPh_3)$_2$] and the binuclear complex, 64. The proportion of the binuclear complex could be increased by addition of H_2O_2, which removed free phosphine by oxidation. Nmr spectroscopic data indicated that there was restricted rotation about the C-Pd bond in the mononuclear species, suggesting that $d_{\pi}\rightarrow\pi^*$ back bonding was important [223].



62 (Reproduced with permission from [222])

The complexes [{M(PR_3)}(μ-H){Pt(C_6Cl_5)(PEt_3)$_2$}]$^+$ (M = Ag or Au, R = Et or Ph) were prepared from *trans*-[Pt(C_6Cl_5)(H)(PEt_3)$_2$] and [ML(PR_3)]$^+$ [224]. Reaction of [Bu_4N][Pt(C_6F_5)$_3$(SC_4H_8)] with [Ag($OClO_3$)(PPh_3)] gave [PtAg(C_6F_5)$_3$(PPh_3)(SC_4H_8)] characterised in a diffraction study. At 2.637(1) Å this possesses the shortest known Pt-Ag bond [225].The tetranuclear complex $[Bu_4N]_2[Pt_2Ag_2(C_6F_5)_4Cl_4]$, 65, was formed by treatment of $[Bu_4N]_2[Pt(C_6F_5)_2Cl_2]$ with $Ag[NO_3]$ and was characterised in a diffraction study. The bonds between the two silver atoms and between platinum and silver are quite strong, and there is a weak interaction between the platinum atoms. The 2-fluorine substituents on the aryl rings are quite close to the silver atoms [226]. Addition of PPh_3 allows replacement of a chloride ligand, and splitting to give the dimer $[Bu_4N][PtAg(C_6F_5)_2Cl(\mu\text{-}Cl)(PPh_3)]$, 66. By contrast, reaction with $AsPh_3$ or $SbPh_3$ gave *trans*-$[PtAr_2L_2]$ and *trans*-$[Bu_4N]_2[PtAr_2Cl_2]$ [227].



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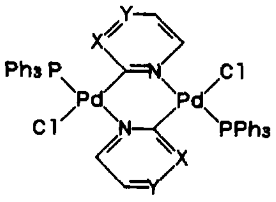

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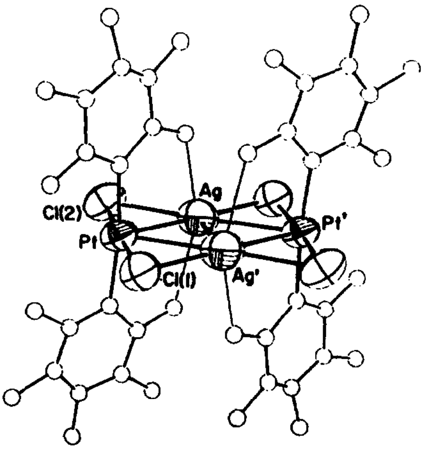
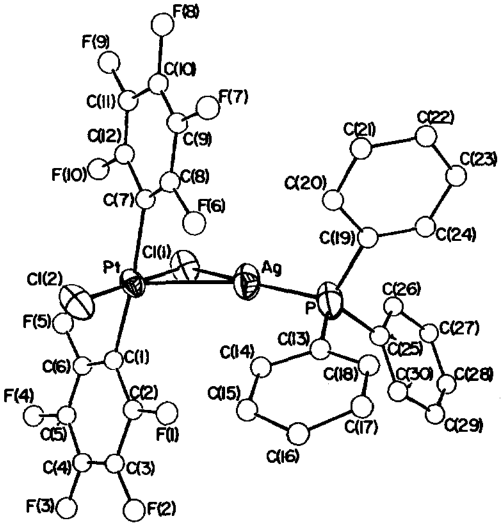


65 ORTEP drawing of the $[Pt_2Ag_2(C_6F_5)_4Cl_4]^{2-}$ ion. (Reproduced with permission from [226])

Photochemically induced oxidative addition of aryl bromides or iodides to $[Pt_2(\mu\text{-}P_2O_5H_2)_4]^{4-}$ gave $[Pt_2(\mu\text{-}P_2O_5H_2)_4ArX]^{4-}$. The chloride could be prepared by halide exchange, though not by direct oxidative addition. The mechanism of the addition involves double activation induced by single electron transfer

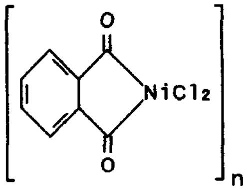
[228].



66 ORTEP drawing of the complex anion $[PtAg(C_6F_5)_2Cl_2(PPh_3)]^-$ showing the atom labelling scheme. Carbon and fluorine atoms are shown as small circles, for clarity. Pt, Ag, C and P atoms are represented by their 40 % probability ellipsoids. (Reproduced with permission from [227])

2.3 *Metal acyl complexes*

Many metal acyl complexes result from insertion of carbon monoxide into a metal-carbon bond, and will be considered in the next section. Treatment of $[Ni(CO)(np_3)][BPh_4]$ ($np_3 = N(CH_2CH_2PPh_2)_3$) with ethoxide ion gave $[Ni(COOEt)(np_3)][BPh_4]$. This reacted with BH_3.thf to give the four-coordinate complex $[Ni(CO)(Hnp_3)][BPh_4]$ and $[NiH(np_3)][BPh_4]$, which is five-coordinate. The intermediate is assumed to be $[Ni(CHO)(np_3)]^+$ or $[Ni(CO)(H)(np_3)]^+$, which may lose CO or H^+ [229]. Reaction of benzene-1,2-dicarboxylic acid dichloride with $[Ni(CO)_4]$ was reported to give 67, but the species was not fully characterised. An analogous species was obtained from 1,2-diiodobenzene, in which the carbonyl units of the metal acyl are assumed to have been derived from the nickel carbonyl. A related reaction is described for $[Pd(PPh_3)_4]$ [230]. The acylnickel complex $[Ni(CO)_n(COR)]^-$ was prepared from RLi and $[Ni(CO)_4]$, and reacted readily with unhindered enones (reaction (3)) [231].



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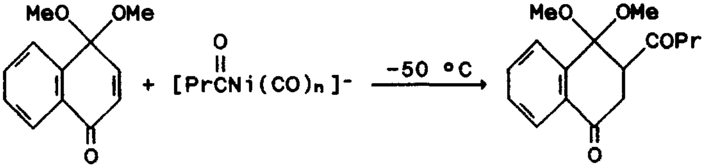
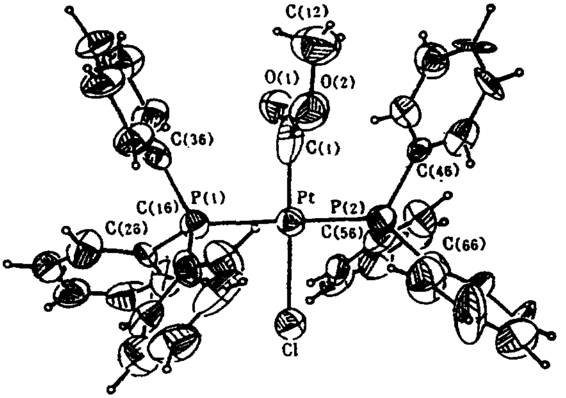


(3)

The structure of *trans*-[PtCl(COOMe)(PPh$_3$)$_2$], 68, has been determined [232]. Reaction of *trans*-[PtCl(COhexyl)(PPh$_3$)$_2$] with SnCl$_2$ has been studied by ^{31}P nmr spectrsocopy. The species *trans*-[Pt(COhexyl)(PPh$_3$)$_2$(SnCl$_3$)] was formed, together with a species which was not fully characterised, but seemed to contain a chloride ligand bridging the platinum and tin centres. The complexes were discussed as models for intermediates in catalytic hydroformylation [233].

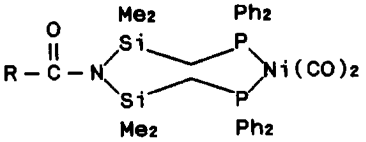


68 (Reproduced with permission from [232])

3 METAL COMPLEXES FORMED BY INSERTION AND RELATED REACTIONS

The carbonyl insertion reactions of square planar complexes have been reviewed; the reactions of platinum and palladium complexes have particular relevance to the mechanisms of carbonylation reactions [234]. Calculations have been performed to optimise the transition state for the insertion reaction of [Pd(CO)(H)Me(PH_3)] to give [Pd(COMe)H(PH_3)]. The reaction takes place by methyl migration with a low activation energy, and provides an model for the carbonylation of *trans*-[$PdMe_2(PR_3)_2$] [235].

Carbonylation of [Ni{N($SiMe_2CH_2PPh_2$)$_2$}R] gave a compound, originally thought to be 69, in a rapid reaction. However, for R = CH=CH_2 small amounts of material characterised as 70 were also formed, and "69" (R = CH=CH_2) lost CO slowly to give this compound. Thus it is clear that the originally formed 69 underwent a novel rearrangement to give 71. All the complexes showed enhanced intramolecular silyl group exchange between oxygen and nitrogen, due to the proximity of the nitrogen lone pair of the {C=NSi} group to the transannular {O-Si} moiety [236]. The complexes [PtCl(Ph)(PY)] (PY = dppp, $Ph_2PCH_2CH_2SMe$ or $Ph_2PCH_2CH_2NMe_2$) underwent CO insertion to give [PtCl(COPh)(PY)], but the derivatives of dppe and $Ph_2PCH_2CH_2AsPh_2$ were unreactive. It was concluded that dissociation of (PY) was essential for coordination of CO prior to insertion [237].



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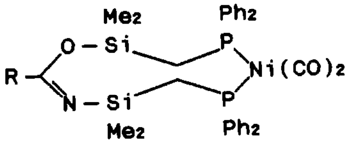

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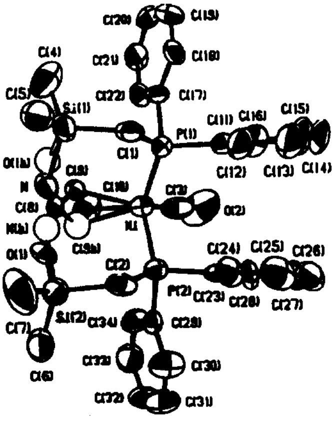
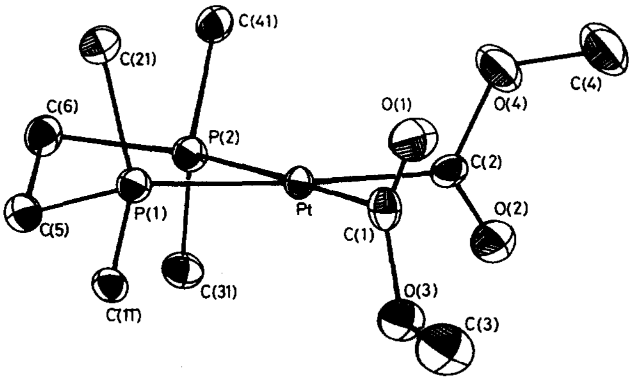


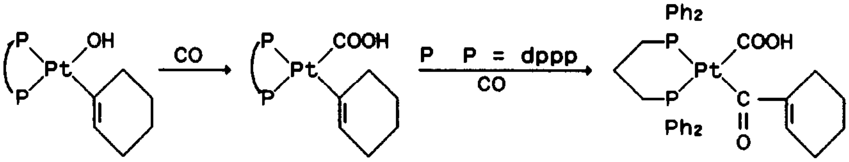
70 ORTEP diagram and numbering scheme for the complex [Ni(CO){(η^2-C_2H_3)C=N($SiMe_2CH_2PPh_2$)O$SiMe_2CH_2PPh_2$}]. The unshaded thermal ellipsoids represent the disorder in the backbone. (Reproduced with permission from [236])

There have been a number of reports of insertion of CO into metal-heteroatom bonds. Reaction of [PtCl(dppe)(Me)] with Na[OMe] resulted in substitution to yield [Pt(dppe)(Me)(OMe)] Carbonylation gave [Pt(COOMe)(dppe)Me], whilst reaction with C_2F_4 yielded [[Pt(CF_2CF_2OMe)(dppe)Me]. In neither case was any insertion into the platinum-carbon bond noted. Labelling studies suggested the intermediacy of a five-coordinate complex. Alkenes bearing electron withdrawing groups, such as CH_2=CHCN or CH_2=CHCOOMe, gave less than 10 % yield of insertion products [238,239]. The thermally unstable species [Pt(dppe)$(OMe)_2$] was prepared similarly, and could be mono and dicarbonylated. The dicarbonylation product, 72, was characterised in an X-ray diffraction study. At 80 °C it decomposed to give a mixture of CO, methanol, methanal and oligomers. Oxidation with a range of oxidising agents gave dimethyl oxalate, dimethyl carbonate, methyl methanoate, CO, CO_2 and methanol [240]. However, reaction of [ML_2Me_2] (M = Pd or Ni, L_2 = bipy or $(PEt_3)_2$) with ArOH gave [ML_2(Me)(OAr)] which was carbonylated to [M(COMe)L_2(OAr)]. Thermolysis of the acyl palladium complex gave MeCOOAr, but heating the nickel complex resulted in deinsertion of CO. The reaction mechansims were discussed [241].



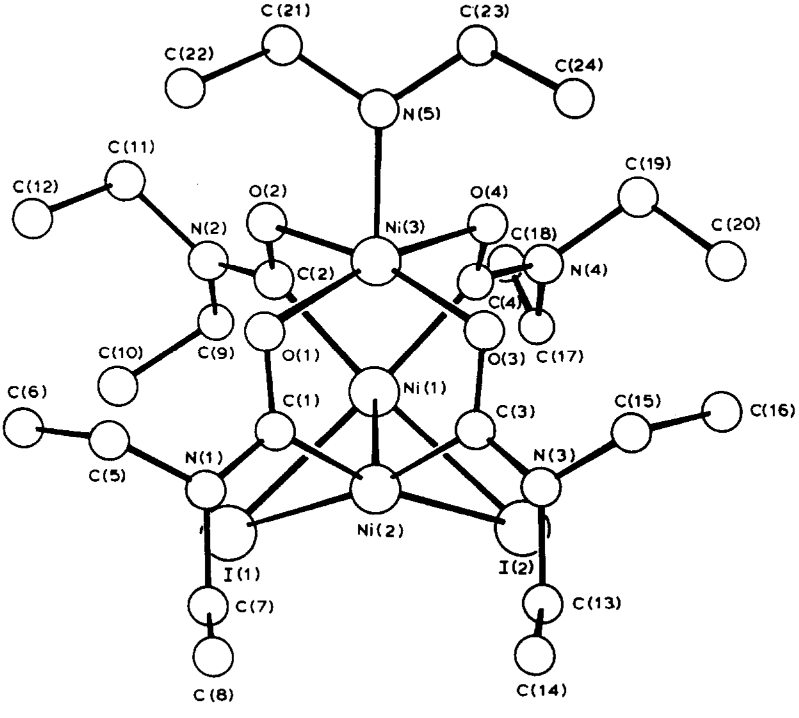
72 Perspective drawing of the coordination sphere in [Pt$(COOMe)_2$(dppe)]. Only the *ipso*-phenyl carbon atoms are indicated and the hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. (Reproduced with permission from [240])

Addition of water to [Pt(cyclohexyne)(PP)] ((PP) = dppe, dppp, dppb or vdpp) gave 73, which inserted CO first into the platinum-oxygen bond. When (PP) was dppp, a second, slower insertion into the platinum alkenyl bond occurred. The platinum carboxylic acids were relatively stable and did not readily decarboxylate. They could be converted to esters and amides. Labelling studies suggested that [Pt(CO)(PP)R][OH] was an intermediate in the carbonylation [242]. Reaction of $[MCl_2(pnp)]$ (M = Pd or Pt; pnp = 2,6-bis(diphenylphosphinomethyl)pyridine) with CO and alkoxide ion gave [M(COOR)(pnp)]Cl, and amides could be prepared similarly [243].

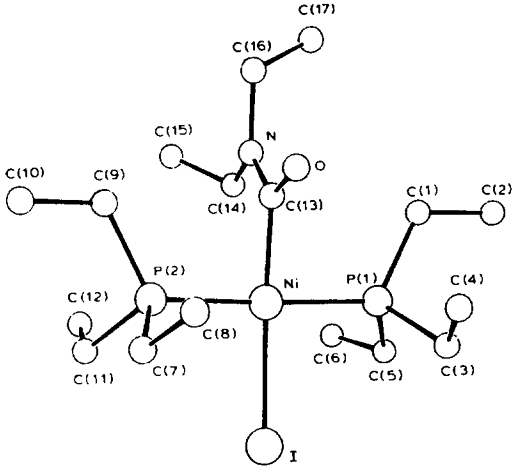


73

Carbonylation of $[NiI_2(NHEt_2)_2]$ in the presence of free Et_2NH gave $[Ni(CONEt_2)I(NHEt_2)_2]$. This underwent substitution of the amine ligands with Et_3P and insertion of $PhC\equiv CPh$ to give $[Ni\{C(Ph)=C(Ph)CONEt_2\}I(NHEt_2)_2]$ [244]. These carbamoyl complexes could also be prepared directly from NiI_2, CO and Et_2NH. When the carbamoyl complex is reacted with $[NiI_2(NHEt_2)_2]$ a trinuclear cluster, 74, is formed, and was characterised in a diffraction study. Addition of PEt_3 gave a mononuclear species, 75 [245].



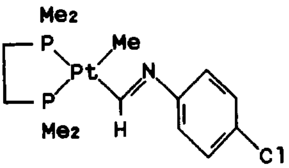
74 (Reproduced with permission from [245])



75 (Reproduced with permission from [245])

Reaction of [$NiCl_2$(pnp)] with CO and RNH_2 gave {NiCl(CONHR)(pnp)]}, the structure of the complex not being described. If the pK_a of the amine is greater than 4.0, no additional base is needed, but for less basic amines, addition of $Na_2[CO_3]$ or Et_3N was necessary. Base treatment of the carbamoyl complex resulted in deprotonation to give an isocyanate derivative, which reacted with an excess of the amine to give a urea [246]. The halide ligand in the complex [$PtClL_2R$] (L_2 = dppe, R = Me, Ph or $PhCH_2$; L_2 = dmpe, R = Me) could be substituted by $LiNHCH_2Ph$ to give a relatively unstable product. Carbonylation then gave the isolable species [$Pt(CONHCH_2Ph)$(dppe)Me], and there was no insertion into the platinum-alkyl bond [247].

Insertion of $4\text{-}ClC_6H_4NC$ into [Pt(dmpe)H(Me)] occurred exclusively at the platinum-hydride bond to give 76 as a single isomer. This implies that hydride migration is stereoelectronically controlled with the new C-H bond *trans* to the developing lone pair on nitrogen. Reaction of the aryl isocyanide with [$Pt(dmpe)Me_2$] in methanol gave 77, again as a single isomer, characterised by a diffraction study. Above -30 °C the Z- and E-isomers equilibrate. The mechanism of the reaction is thought to involve methanol attack on a coordinated isonitrile, followed by protonation at platinum and methane elimination. If the reaction is conducted in toluene, insertion of the isocyanide into the platinum-methyl bond does occur, but the reaction is some 10^8 times slower than that of the methyl hydride complex, and is neither clean nor stereospecific [248].



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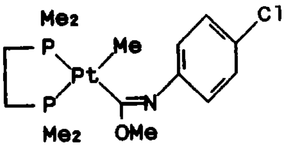
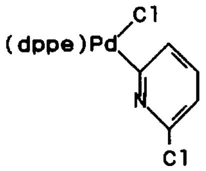


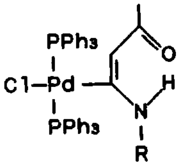
77

There has been a kinetic study of the insertion of isocyanides into the palladium-aryl bond of 78 [249]. The steps proposed for the the reaction of related complexes of non-chelating phosphines were similar and various substitution reactions on the product were described [250].



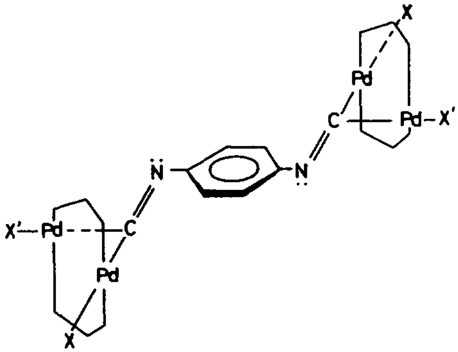
78

Reaction of $[Pd(PPh_3)_4]$ with chloropropanone gave *trans*-$[Pd(CH_2COCH_3)Cl(PPh_3)_2]$, which readily inserted RNC (R = Me or 4-$MeOC_6H_4$) to give 79 [251]. The bis(isocyanide), 1,4-CNC_6H_4NC, reacted with $[Pd_2(\mu\text{-dppm})_2X_2]$ (X = Cl, Br, I, [NCO] or [SCN]) by a double insertion reaction to give the A-frame complex 80 [252].

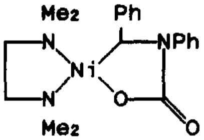


79

There have been a number of reactions reported which may be considered to be insertions of CO_2, though in most cases the mechanisms were not delineated in detail. Thus 81 was prepared from $[Ni(cod)_2]$, $Me_2NCH_2CH_2NMe_2$, PhCH=NPh and CO_2 [253]. A similar process allowed the synthesis of 82 by carboxylation of $[NiL(RC\equiv CR)]$, or from Ni(0), $RC\equiv CR$, L and CO_2. Carbonylation of 82 gave the anhydride, and alkynes could also be inserted into the nickel-carbon bond. A similar process was reported using alkenes, to give 83. In the case in which a non-symmetrical alkene, $RCH=CH_2$, is used as the substrate, two insertion products, **84a** and **84b** were formed, their proportions depending on the temperature at which the reaction was carried out [254]. With allene as the substrate and a basic ligand, L, such as bipy or dcpe, the product was **85**. Reactions with substituted allenes were regioselective (reaction (4)) [255]. With butadiene the three products obtained, **86a**, **86b**, and **86c**, were in equilibrium. Carboxylation of the mixture gave **87** which could be readily opened with methanol [256].



80 (Reproduced with permission from [252])



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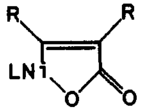

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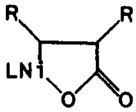

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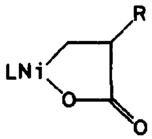
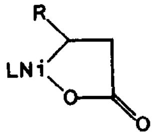
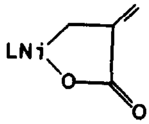


84a



84b



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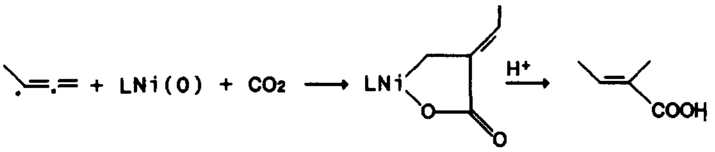
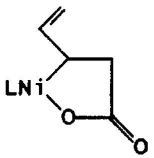
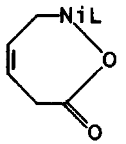


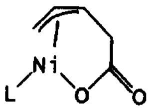
(4)



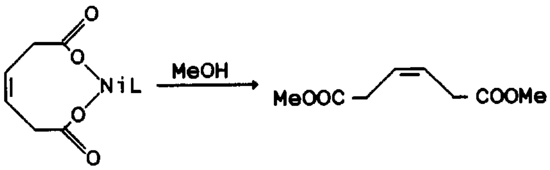
86a



86b

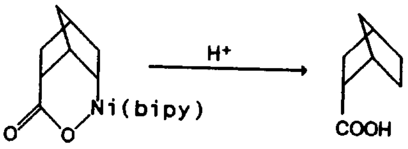


86c



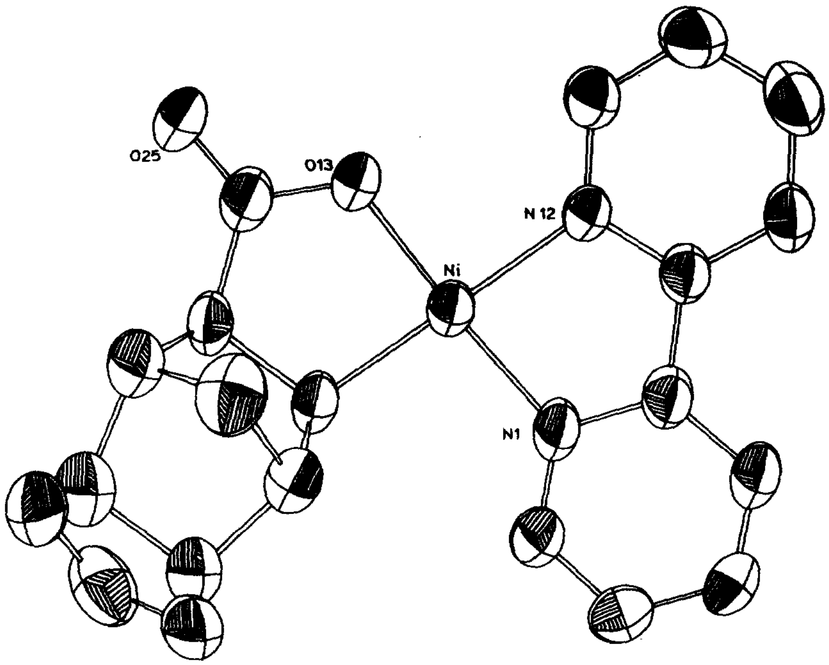
87

Quadricyclane reacted with [Ni(bipy)(cod)] and CO by insertion into one of the strained three membered rings. Carboxylation then gave 88, which could be protonated to 89. A number of related reactions with strained double bonds were also described [257]. Reaction of dicyclopentadiene with {Ni(0)(bipy)} and CO_2 gave 90, in a stereoselective reaction [258]. The insertion product 91 was readily isomerised to 92. Although the diastereomeric excess was initially small, it rose to 54 % S after 10 h at 24 °C [259].

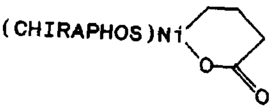


88 **89**

The insertion of isocyanates into nickel complexes is closely related to the insertion of CO_2, and several new reactions have been reported. Reaction between 1,1-dimethylallene, [Ni(cdt)], RCNO and an appropriate ligand, L, gave 93, as the major product. A range of reactions was discussed [260]. Oxidation resulted in bimolecular coupling to give 94 [261]. Under the same conditions RCHO yielded 95 [262]. With ethene, and a reaction at low temperature, 96 was formed; thermolysis yielded CH_2=CHCONHR, rather than a β-lactam [263]. The complex 96 may react with further ethene to give an expanded ring, prior to β-elimination [264]. In the absence of addend, the isocyanates are coupled to give 97 and/or 98, but all the yields were low [265].



90 (Reproduced with permission from [258])



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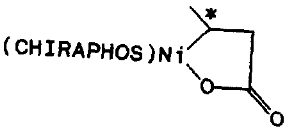

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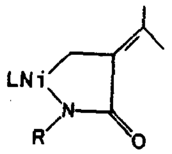

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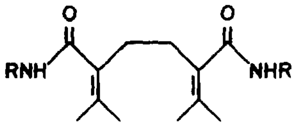

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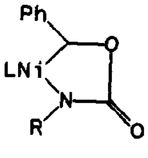

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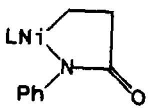

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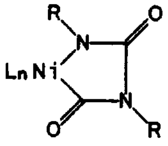

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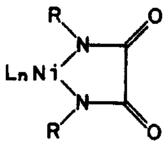


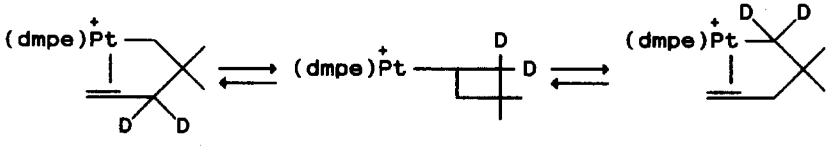
98

The insertion of alkenes into metal hydride bonds is a fundamental step in most hydrogenations catalysed by transition metal complexes. The mechanism of alkene hydrogenation and isomerisation in the presence of platinum complexes has been reviewed. The alkene insertion into the platinum hydride bond in *trans*-$[PtH(PR_3)_2(SnX_3)]$ was followed by multinuclear nmr spectroscopy. Insertion was faster for the *trans* than for the *cis*-complex [266]. The complex $[Pd(OCOCF_3)_2(PPh_3)_2]$, in the presence of tfaH, catalysed isotope exchange between H_2 and H_2O, *via* $[PdH(PPh_3)_3][X]$. Addition of ethene lowered the rate of reaction, and a mixture of CO and ethene inhibited it completely. Under these conditions $[PdH(PPh_3)_3]^+$ reacted with ethene to give $[Pd(Et)(PPh_3)_nX]$, which further inserted CO to yield $[Pd(COEt)(PPh_3)_mX]$. Insertion of more ethene and protolysis gave EtCOEt [267].

The facile insertion of perhaloalkenes has been again demonstrated by the reaction of [Pt(dppe)Me(OMe)] with C_2F_4 to give $[Pt(CF_2CF_2OMe)(dppe)Me]$ [268].

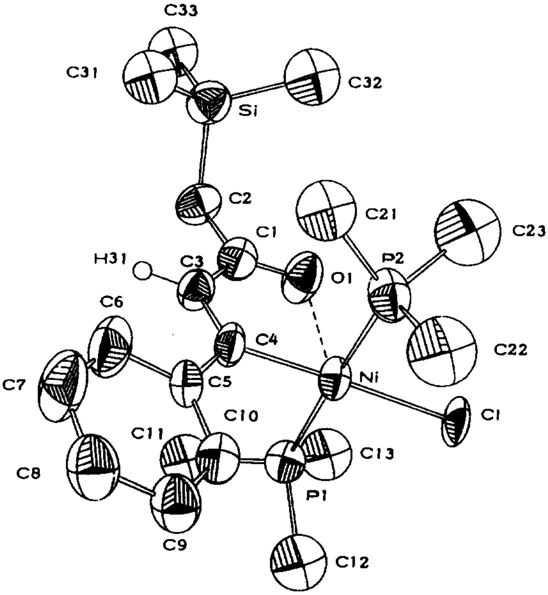
Insertion of $CH_2{=}CHCOOMe$ into the unstable species *trans*-$[PtCl(H)\{P(OMe)_3\}_2]$ gave only *cis*-$[Pt\{CH(Me)COOMe\}Cl\{(P(OMe)_3\}_2]$. The fact that only the branched product is formed is quite distinct from the the reactions of the related PEt_3 derivatives [269]. Reaction of a zinc porphyrin derivative, bearing peripheral organomercury functionality, with $CH_2{=}CHCOOMe$ in the presence of $Li[PdCl_3]$ gave the corresponding porphyrin bearing {CH=CHCOOMe} units, but some complications did occur due to overmercuration [270].

In a heterogeneous reaction, under an ammonia atmosphere, $[Pt(C_2H_4)Cl_2(NH_3)]$ yielded $[Pt(CH_2CH_2NH_2.HCl)(NH_3)_3]Cl$ [271]. The complex 99 was in equilibrium with its isotopomer *via* the insertion product, 100 [272].



99 100

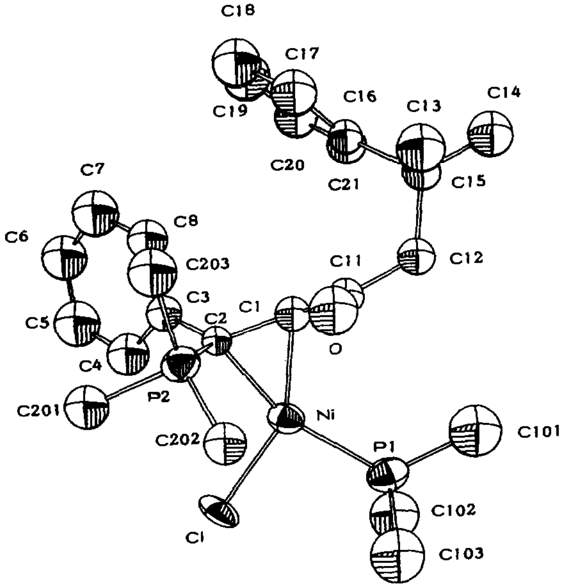
Similarly, insertion of alkynes into metal hydride and metal-carbon bonds are key processes in their hydrogenation and oligomerisation respectively. Reaction of $PhC\equiv CH$ with *trans*-$[NiCl(COR)(PMe_3)_2]$ gave 101, in which the nickel atom is 5-coordinate, and has distorted square pyramidal geometry. For the complex in which R = CH_2CMe_2Ph the square pyramidal species was in equilibrium with the novel ylide complex 102 [273]. Cycloinsertion of 103 and related species was studied. As predicted by the work of Thorn and Hoffman, kinetic studies show that the insertion step involves a 4- rather than a 5-coordinate intermediate [274].



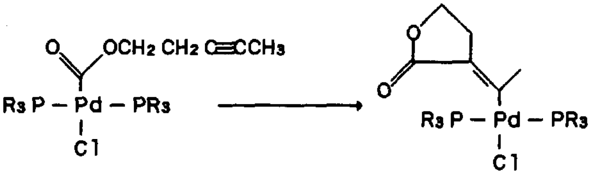
101 (Reproduced with permission from [273])

Insertion of dmad into 104 involved reaction of the platinum-chlorine bond. The reaction did not occur in systems with less bulky phosphine ligands, suggesting that 5-coordinate intermediates were not likely in this case [275].

Reaction of $[Pt(\eta^2\text{-}PhNO)(PPh_3)_2]$ with dmad gave 105, *via* insertion of the alkyne into the Pt-N bond of the η^2-bonded ArNO ligand. Insertion of alkenes bearing electron withdrawing groups was also studied [276]. Reaction of the amino carborane, 106, with $PhC\equiv CPh$, gave 107 [277]. Treatment of *sym,trans*-$[Pt_2(\mu\text{-}Cl)_2(PEt_3)_2(SnCl_3)_2]$ with two molar equivalents of $CF_3C\equiv CCF_3$ resulted in insertion into both the Pt-Sn bonds, to give 108 as the major product, in equilibrium with its *cis*-isomer. One plausible mechanism advanced for the reaction involved formation of cationic platinum alkyne complexes by substitution, followed by attack of $[SnCl_3]^-$ at the alkyne [278].



102 (Reproduced with permission from [273])



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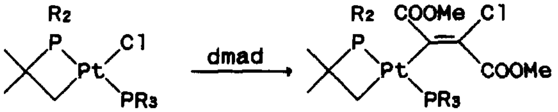
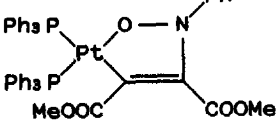


R = CMe3

104



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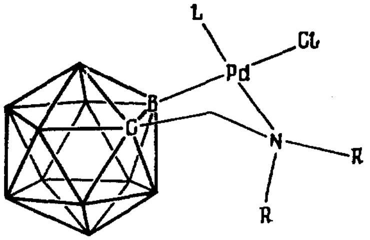
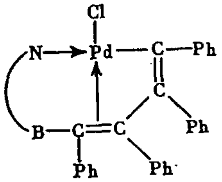
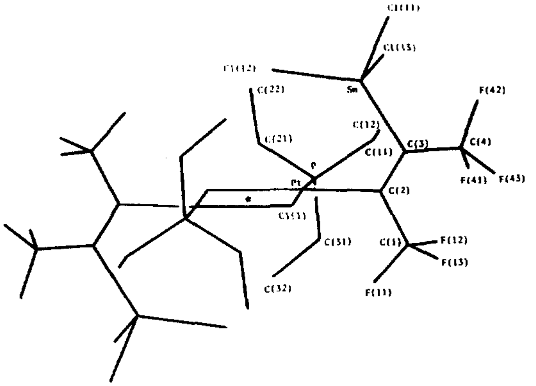


106 (Reproduced with permission from [277])

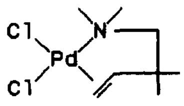


107 (Reproduced with permission from [277])



108 Line drawing of the dimeric double insertion product. (Reproduced with permission from [278])

Reaction of 109 with CH_2N_2 gave 110, by insertion of $\{CH_2\}$ into a metal-chloride bond [279]. Insertion of methylene also occurred with $[Pt(cod)X_2]$ (X = Cl or I) to give the stable complex $[Pt(CH_2X)_2(cod)]$ [280]. Reaction of cyclooctene with PhN_3 in the presence of $PdCl_2$ gave 111, characterised by a diffraction study. By-products included cyclooctanone, phenylimine, and a bis(aziridine) palladium complex. The aziridine complex was formed in larger quantities from $[PdCl_2(coe)_2]$ and phenyl azide. The initial step in both processes is probably insertion of PhN_3 into a metal alkene bond [281].



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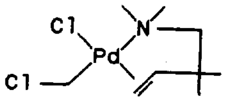

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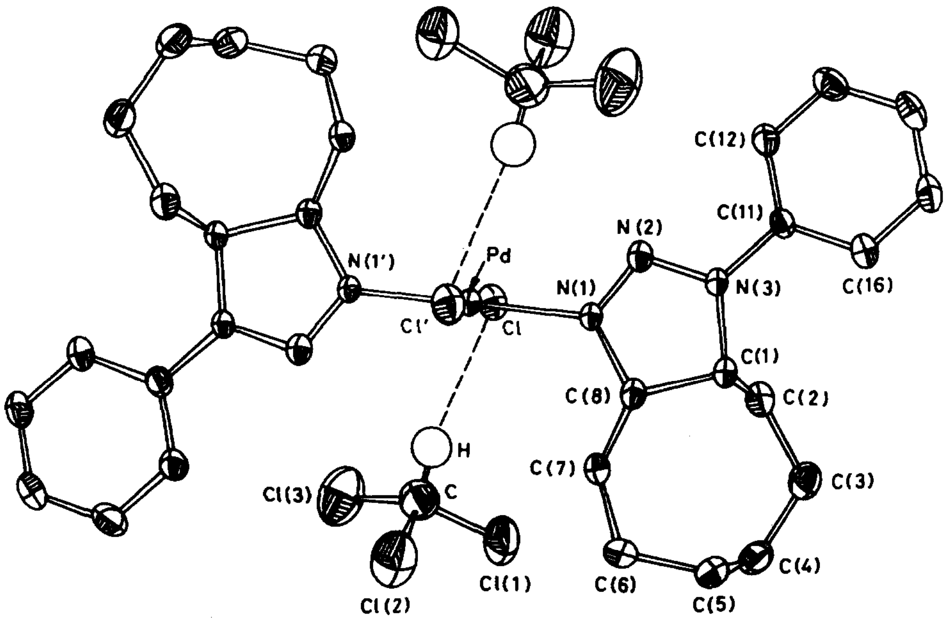
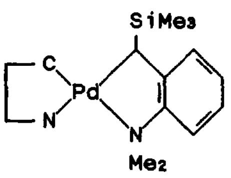


111 ORTEP view of *trans*-dichlorobis(11-phenyl-9,10,11-triazabicyclo[6.3.0]undec-9-ene) palladium(II)-chloroform (1/2). Thermal ellipsoids are drawn at 30 % probability. (Reproduced with permission from [281]).

Insertion of $CF_3C\equiv CCF_3$ into 112 ($\overset{\frown}{C\ N}$ = 2-dimethylaminomethylphenyl) gave a double insertion product, 113. A complex mechanism was proposed [282].



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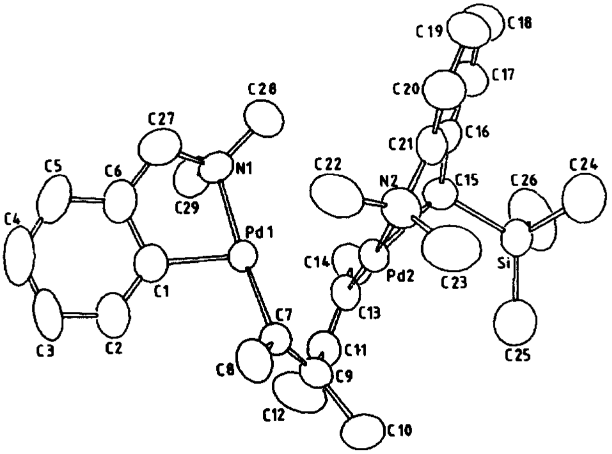
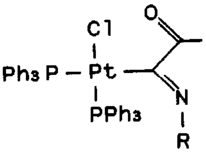
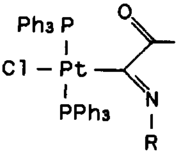


113 Molecular structure of the double insertion product. The fluorine and hydrogen atoms are omitted for clarity. (Reproduced with permission from [282])

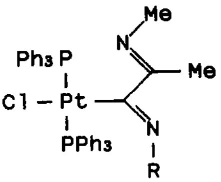
A number of insertion reactions have the opposite sense, that is they are the insertions of metal complexes into organic molecules. Thus in the reaction of [Pt(PPh_3)$_4$] with RN=C(Cl)-C(Me)=O the products are 114a and 114b, in the ratio 9:1. Reaction of the mixture with $MeNH_2$ gave mainly 115. A range of reactions of 115 with other metal complexes was reported [283].



114a

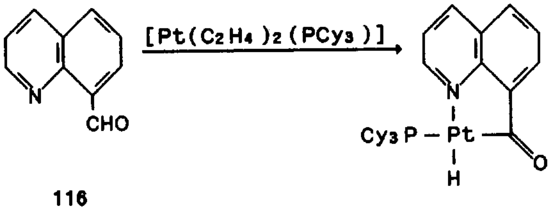


114b



115

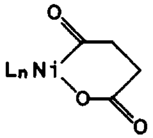
The activation of methane by *trans*-[Pt$(H_2O)_2Cl_2$] has been studied from a theoretical perspective. As the reactants approach, the repulsion energy decreases initially as a result of distortion of the metal complex, but at a later stage as a result of deformation and stretching of the C-H bonds in methane [284]. Reaction of [Pt$(C_2H_4)_2(PCy_3)$] with 116 resulted in insertion of the metal complex into the C-H bond of the aldehyde. Related reactions were also considered [285].



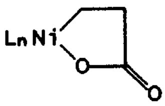
116

Reaction of [Pt$(PPh_3)_3$] with R_2Hg (R = 2,4,6-$Cl_3C_6H_2$ or 2,3,5,6-Cl_4C_6H) gave [Pt(HgR)$(PPh_3)_2$(R)], by insertion of the platinum into the alkyl-mercury bond. Further reaction with [Pt$(C_2H_4)(PPh_3)_2$] gave the trimetallic species [Hg{Pt$(PPh_3)_2$(R)}$_2$], indicating that the second alkyl-mercury bond is not deactivated towards insertion by the reaction of the first [286]. When [Pt$(PPh_3)_4$] reacted with 4-FC_6H_4HgCl, the product was [Pt(C_6H_4-4-F)Cl$(PPh_3)_2$]; insertion had occurred into the Ar-Hg bond, followed by elimination of mercury. With PhHgSC_6H_4-4-F, insertion of platinum into both the Ar-Hg and the S-Hg bonds took place, to yield, after mercury elimination, [Pt(Ph)$(PPh_3)_2$(SAr)] and [Pt(Ar)$(PPh_3)_2$(SPh)] [287].

Insertion of nickel(0) into butane-1,4-dioic acid anhydride gave intitially 117 (L_n = bipy or dppe), which was not isolated, but lost CO in a reversible reaction, to give 118. When the reaction was carried out using a substituted, non-symmetrical, anhydride, regioselectivity was generally low and depended on the ligand [288]. A similar reaction was reported for [Ni$(C_2H_4)(PPh_3)_2$] with benzene-1,2-dicarboxylic acid anhydride [289].

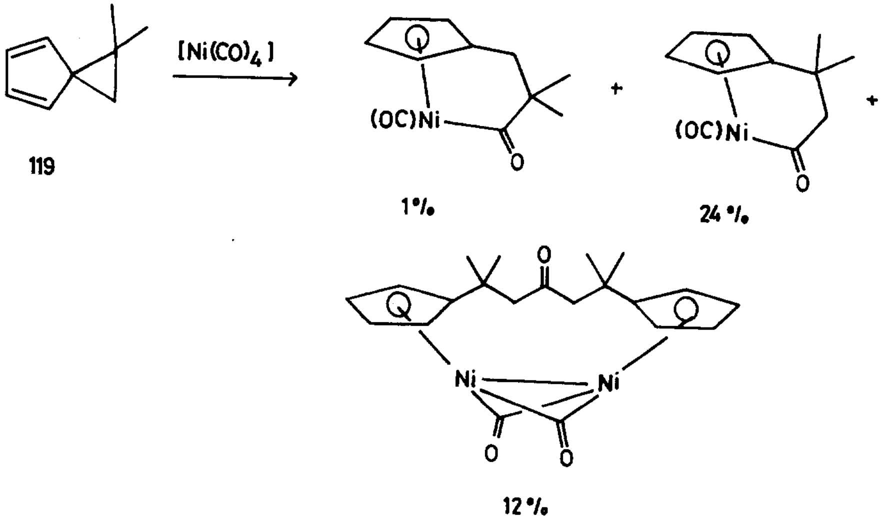


117



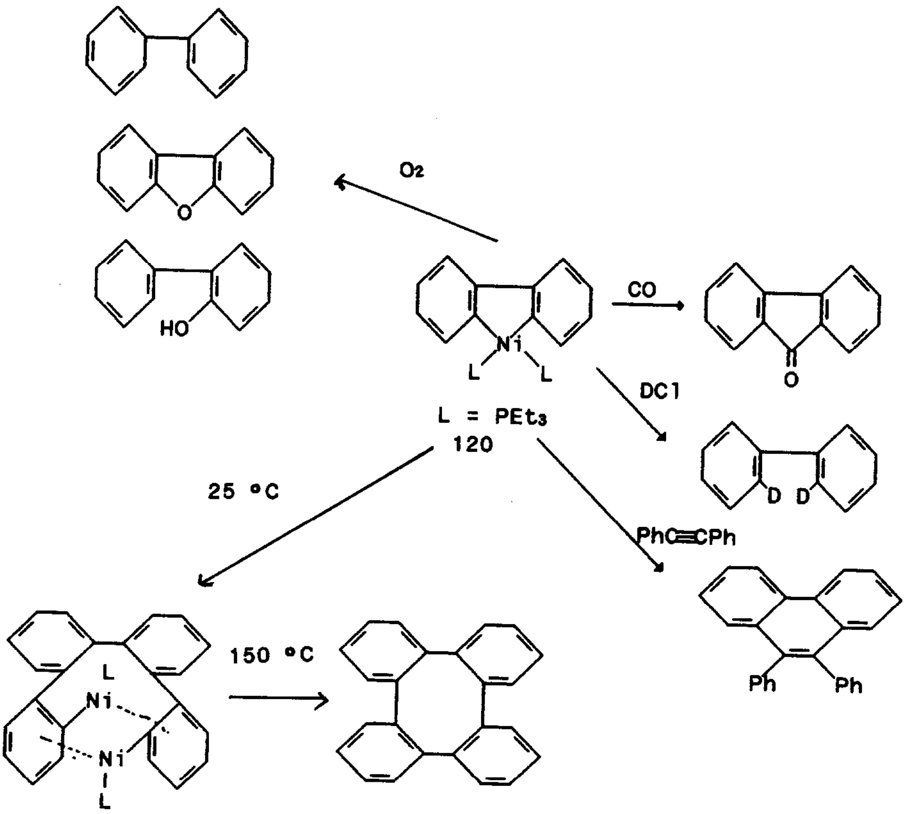
118

Insertion of [Ni$(CO)_4$] into the strained ring of 119 gave three products; their relative proportions indicated that the major opening was of the less hindered bond, with retention of configuration. The related substrate bearing four methyl groups on the cyclopropane ring was unreactive [290]. Insertion of $\{L_nNi\}$ into the strained ring of biphenylene depended on the nature of L, with the reactivity order $[Ni(bipy)(cod)] < [Ni(PPh_3)_4] < [Ni(C_2H_4)(PPh_3)_2] < [Ni(Et_3P)_4)]$ being established. The reactions of 120 were investigated (Scheme 5) [291]. Biphenylene end-capped polyquinoline and polyimide prepolymers were melt processed in the presence of $[Ni(CO)_2(PPh_3)_2]$ at 325-340 °C and 500 psi to give high quality transparent films. The curing involves insertion of Ni(0) into the four-membered ring of the biphenylene, followed by dimerisation [292,293].

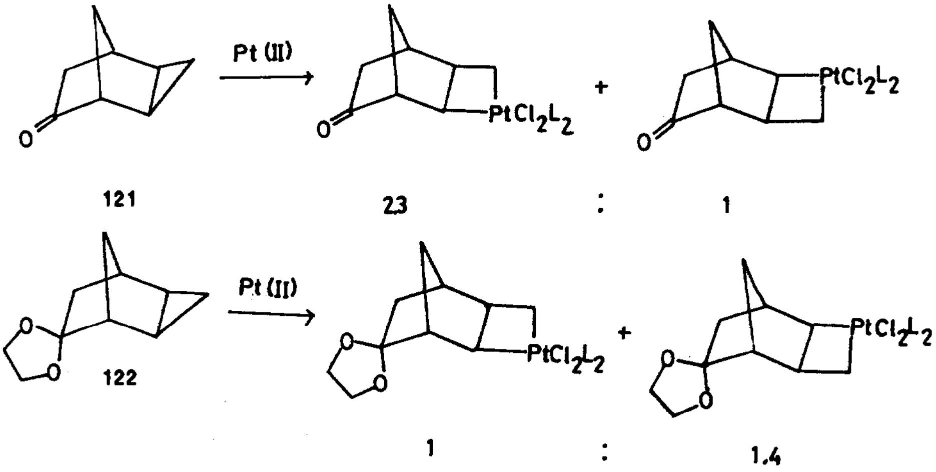


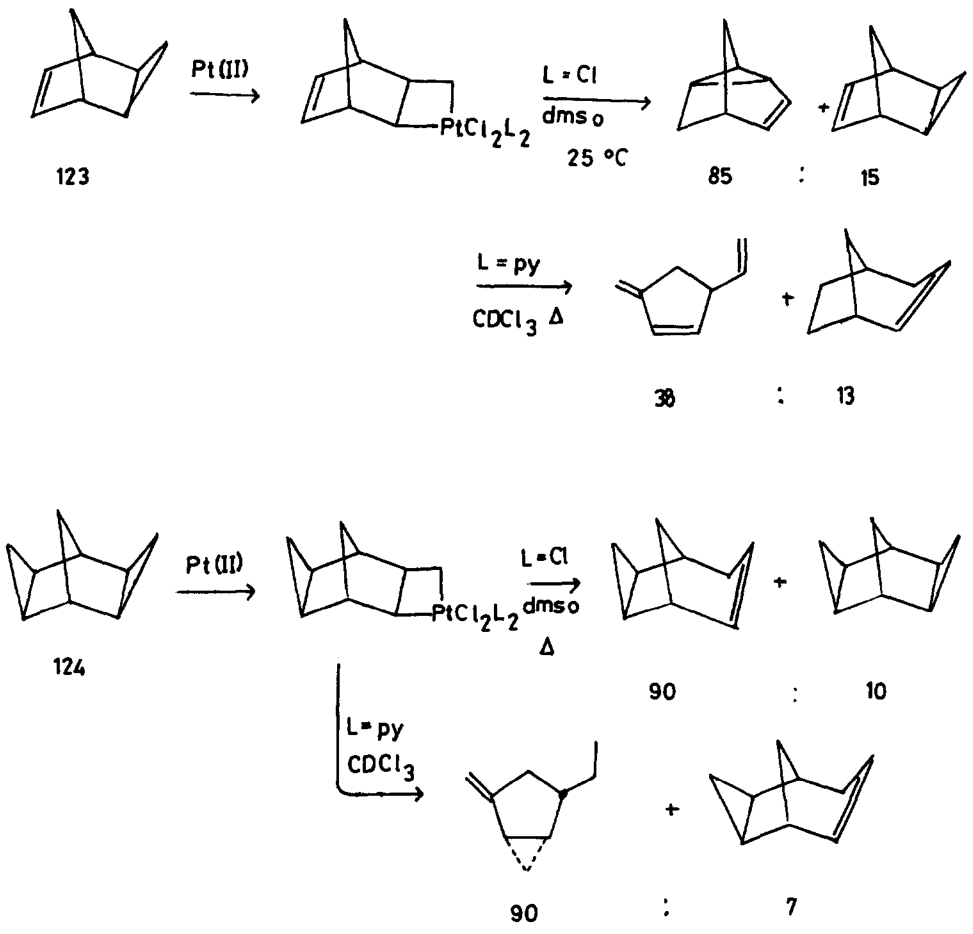
119

Insertion of platinum(II) from Zeise's dimer into 121 gave two platinacyclobutanes in the ratio 2.3:1. Protection of the ketone as an acetal, in 122, resulted in different regioselectivity, and an accelerated reaction [294]. The reactions of 123 and 124 proceeded similarly, but the products of their decomposition depended strongly on the nature of L (Scheme 6) [295].



Scheme 5 Reactions of 120 [291]





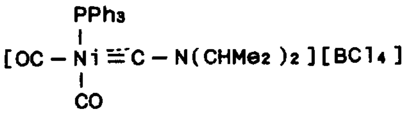
Scheme 6 Formation and decomposition of platinacyclobutanes [295].

4 METAL CARBENE, CARBYNE AND YLIDE COMPLEXES

Reviews have discussed the structural consequences of bonding in transition metal carbene complexes [296], and the reactions of such complexes with unsaturated hydrocarbons [297].

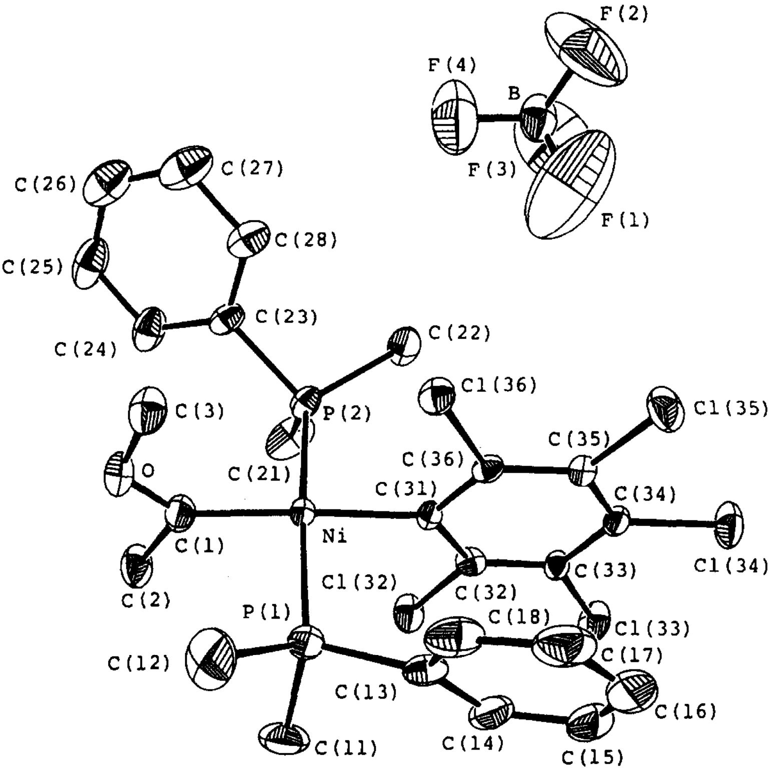
Reaction of $[Ni(CO)_4]$ with $LiN(CHMe_2)_2$ followed by $[Et_3O][BF_4]$ gave the carbene complex $[Ni(CO)_3\{C(OEt)N(CHMe_2)_2\}]$. Replacement of one of the carbonyl ligands by PPh_3 gave a more stable complex, which was reacted with BCl_3 to yield 125 as the final product [298]. When [Ni(cdt)] was treated with $Me_3P{=}CH_2$, $[Ni(cdt)(CH_2PMe_3)]$ was formed. This, and the related species

$[Ni(C_2H_4)_2(CH_2PMe_3)]$, decomposed at room temperature to give, respectively, $[Ni(cdt)(PMe_3)]$ and $[Ni(C_2H_4)_2(PMe_3)]$. In the presence of ethene, cyclopropane was formed, suggesting a strong carbene character for the complexes [299]. The structure of the previously reported complex, 126, has been determined in an X-ray diffraction study. The nickel adopts square planar geometry, and the short nickel-carbon bond length suggests that π-back-bonding is very important [300].



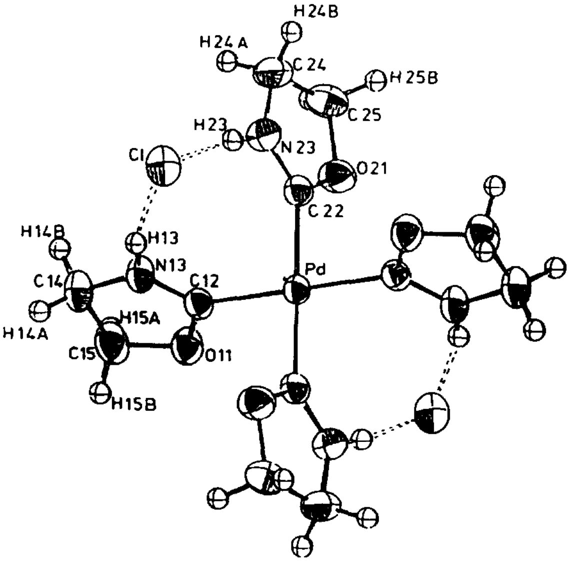
$$[OC-\underset{\displaystyle CO}{\overset{\displaystyle PPh_3}{Ni}}\equiv C-N(CHMe_2)_2][BCl_4]$$

125



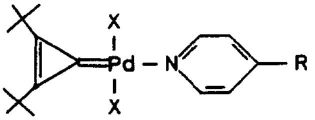
126 Atoms are represented by thermal ellipsoids at 30 % probability levels. Hydrogen atoms are omitted for clarity. (Reproduced with permission from [300])

Reaction of either MX_2 or $[ML_2X_2]$ (M = Ni, Pd or Pt; L = MeCN, PhCN or PPh_3) with HOCH(R)CH(R')NC (R = R' = H, R' = Et, R = H or R' = H, R = Me) gave tetraoxazolinium metal complexes such as 127. The four five-membered rings are approximately perpendicular to the coordination plane, and the structure is stabilised by extensive hydrogen bonding. The related complexes containing six-membered rings could also be synthesised, and in some cases intermediates with some of the ligands cyclised and the others not could be observed [301].



127 (Reproduced with permission from [301])

The conversion of quadricyclane to norbornadiene has been catalysed by 128 (X = halogen, R = H, alkyl or CN) [302]. The reactions of σ-heteroaryl complexes such as 129 (L = PMe_2Ph) have been extended. This complex may be considered to be carbene like in character, and *O*-methylation with Me_2SO_4 was readily accomplished. Reaction with RNC gave 130, but carbon monoxide could not be inserted [303].



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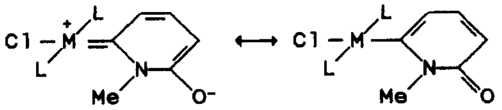
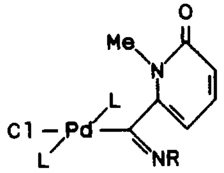


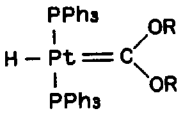
129a

129b



130

The complex *trans*-[Pt(CF_3)(H)(PPh_3)$_2$] reacted with alcohols or thiols in the presence of H[BF_4] to give carbene complexes such as 131. Similar reactions were noted for *trans*-[(CF_3)Pt(PMe_2Ph)$_2$Cl] [304]. Treatment of H_2[Pt(CN)$_4$] with an propene oxide resulted in the formation of 132. The opposite regiochemistry was noted, but not explained, for ethenylbenzene oxide [305]. Reaction of the isocyanide complex, 133, with base gave an ylid which cyclised to the carbene complex 134 (M = *cis*- or *trans*-{PtCl$_2$(PR'$_3$)}) [306].



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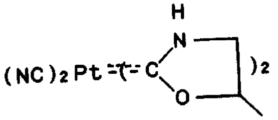

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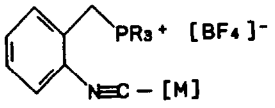

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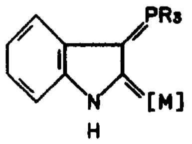
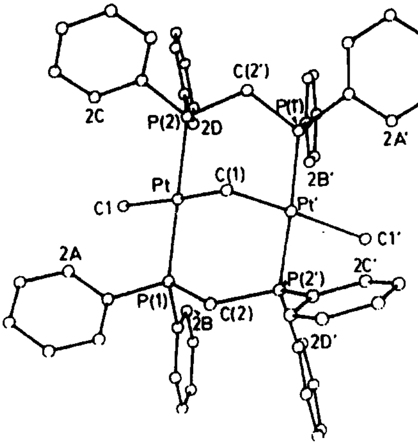


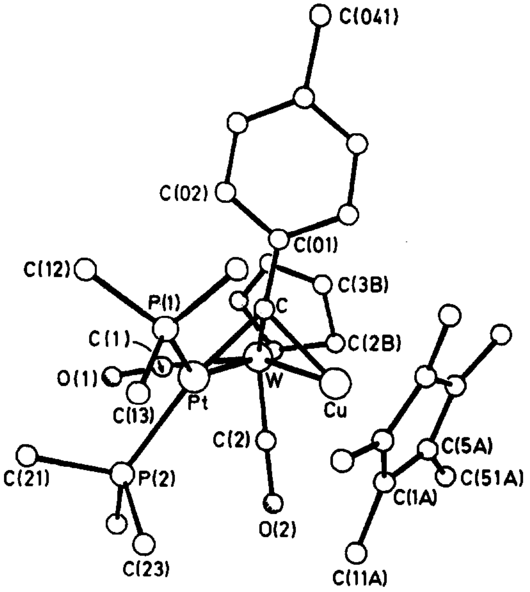
134

There have been a number of reports concerning bridging carbene complexes. Reaction of diazomethane with [Pt_2Cl_2(μ-dppm)$_2$] gave [Pt_2(μ-CH_2)Cl_2(μ-dppm)$_2$] [307]. A similar insertion into the platinum-platinum bond was reported for [Pt_2(μ-dppm)$_2$(H)L] (L = PPh_3), but in this case insertion also occurred into the Pt-L and Pt-H bonds to yield [{Pt(Me)}(μ-CH_2)(μ-dppm)$_2${Pt(CH_2L)}]$^+$. When the ligand, L, was CO or PMe_2Ph, insertion into the M-L bond was suppressed. The structures of [Pt_2(CH_2L)Cl(μ-dppm)$_2$]$^+$ and [Pt_2(μ-CH_2)Cl_2(μ-dppm)$_2$], 135, were established in diffraction studies. When [Pt_2(μ-CH_2)(CO)(μ-dppm)$_2$(Me)] was reacted with Na[BD_4], CH_4 and CO were evolved, and extensive deuteration was noted in the product, [{Pt(CH_2D)}(μ-D)(μ-$Ph_2PCD_2PPh_2$)$_2${Pt(CH_2D)}] [308].

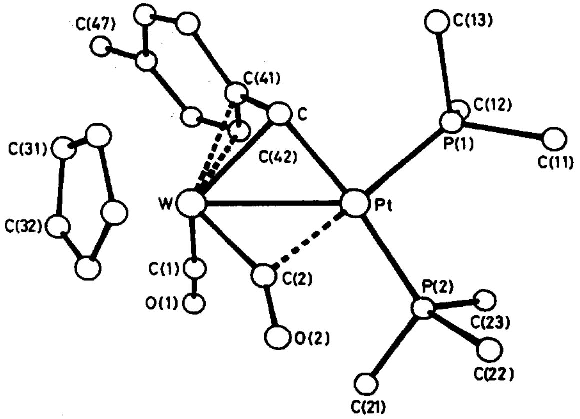


135 Molecular structure of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ viewed approximately along the crystallographic diad axis passing through C(1). Hydrogen atoms are omitted. (Reproduced with permission from [308])

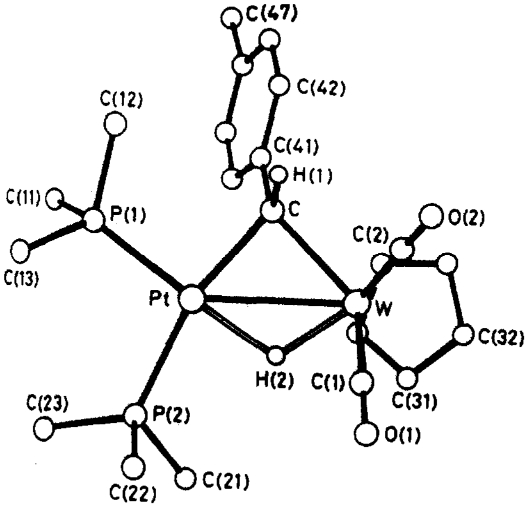
As ever, much new work has emerged from Stone's group, concerning bridging carbene and carbyne complexes. The reaction of $[PtW(CO)_2(Cp)(\mu\text{-}CR)(PMe_3)_2]$ with $[Cu(Cp^*)(thf)]$ gave $[CuPtW(CO)_2(Cp)(Cp^*)(\mu_3\text{-}CR)(PMe_3)_2]$, 136, characterised in a diffraction study. The four atoms, {CCuPtW}, adopt a butterfly configuration with platinum and copper at the wingtips, no Cu-Pt bond, and one of the carbonyls semi-bridging between platinum and tungsten. Complexes with bridging alkynes were also described [309]. Protonation of $[PtW(CO)_2(Cp)(\mu\text{-}CR)(PR'_3)_2]$ (R = MeC_6H_4-4-Me; PR'_3 = PMe_3, PMe_2Ph or $PMePh_2$) gave $[PtW\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4\text{-}4\text{-}Me)\}(CO)_2(Cp)(PR_3)_2][BF_4]$, 137, in which two carbon atoms of the aryl ring have an η^2-attachment to tungsten, and one of the CO ligands is semibridging [310]. 137 reacted with CO to give $[PtW(\mu\text{-}CHR)(CO)_3(Cp)(PR_3)_2][BF_4]$, or R_3P to yield $[PtW(\mu\text{-}CHR)(CO)_2(Cp)(PR_3)_3][BF_4]$. Reduction of 137 using $K[BH(CHMeEt)_3]$ gave $[PtW(CO)_2(Cp)(\mu\text{-}CR)(\mu\text{-}H)(PR_3)_2]$, which existed as a mixture of diastereoisomers in solution. The structure of 138 was established; a single diastereoisomer was isolated in the solid state [311]. 137 reacted slowly with 2-butyne, in contrast to the {CoW} analogue, for which the reaction is much faster. In the product, 139, the carbene forms a symmetric bridge, with the CO ligand semi-bridging [312]. The species $[PtW(CO)_2(Cp)(\mu\text{-}CR)(PMe_3)_2]$ reacted with $[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$ to give 140. The spectroscopic properties of the product were discussed, and mechanisms for the reactions proposed [313].



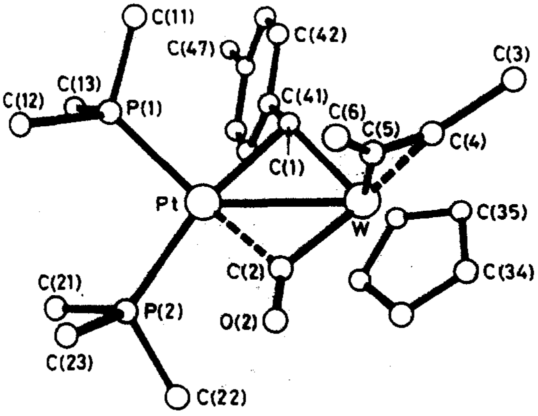
136 (Reproduced with permission from [309])



137 Molecular structure of the cation of $[PtW\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4\text{-}4\text{-}Me)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$. (Reproduced with permission from [310])



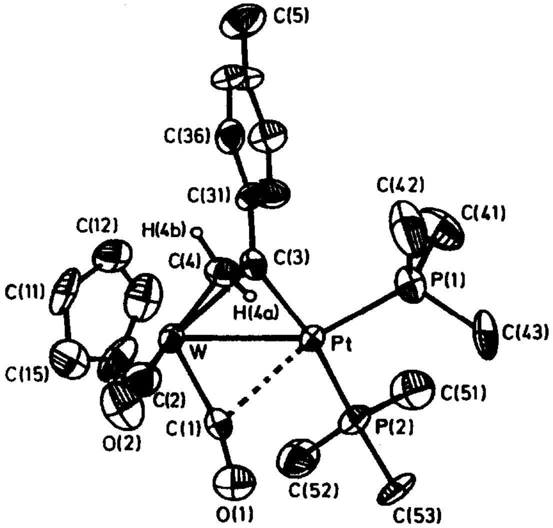
138 (Reproduced with permission from [311])



139 (Reproduced with permission from [312])

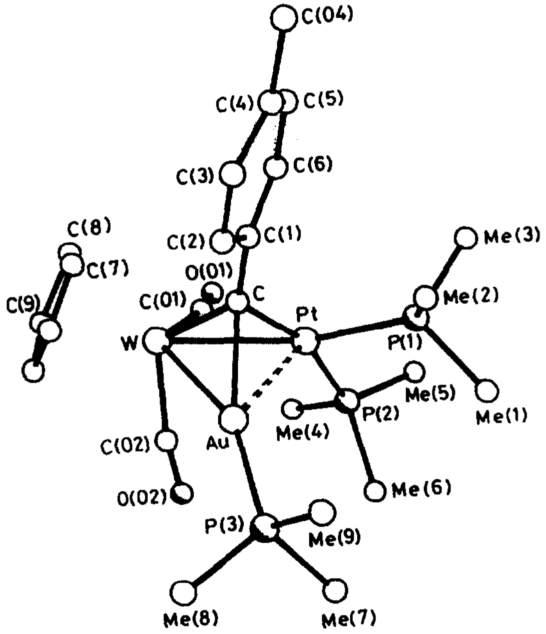
Reaction of $[Au\{W{\equiv}CR(CO)_2(Cp)\}_2][PF_6]$ with $[Pt(C_2H_4)(PMe_3)_2]$ gave 141, which could also be prepared from $[Au(PMe_3)(thf)][PF_6]$ and $[PtW(CO)_2(Cp)(\mu\text{-}CR)(PMe_3)_2]$ [314]. The tetranuclear cluster, $[Os_3Pt(\mu_4\text{-}C)(CO)_{10}(\mu\text{-}H)_2(PCy_3)]$, 142, and the pentanuclear species, $[Os_3Pt_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9(\mu\text{-}H)_2(PCy_3)_2]$, 143, were prepared from $[Os_3(\mu_3\text{-}CH)(CO)_{10}(\mu\text{-}H)]$ and $[Pt(C_2H_4)_2(PCy_3)]$ at 80 °C in toluene. In 142 the carbide is irregularly bonded to all four metal atoms. Each osmium bears three

CO ligands, and platinum is ligated by CO and PCy_3. In 143 four metal atoms, $\{Os_2Pt_2\}$ form an approximate square plane, with Os(3) bridging the Os-Os edge. The carbide is approximately equidistant from all five metal atoms, and the hydride ligands bridge the Os(1)-Os(3) and Os(2)-Os(3) bonds. When $[Pt(C_2H_4)_2(PCy_3)]$ was reacted with $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$, the major product was $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_8(PCy_3)_2]$, 144. Two platinum and two osmium atoms are arranged in a buckled square plane, with Os(3) bonded only to Os(1). All the metal carbide bonds are approximately equal in length, and the hydride bridges the shorter of the two Pt-Os edges. Nmr spectroscopic data were consistent with the solid state structure, but there was some dynamic behaviour. This paper represents a rather uncommon report of the generation of carbide complexes from non-carbide precursors [315].

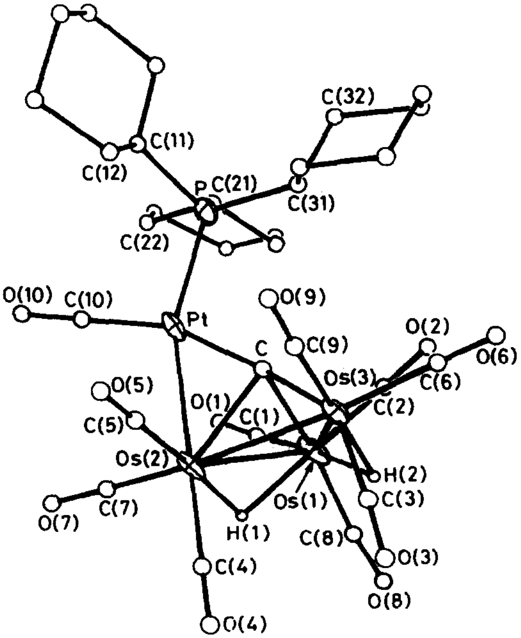


140 The hydrogen atoms on C(4) are shown at calculated positions. (Reproduced with permission from [313])

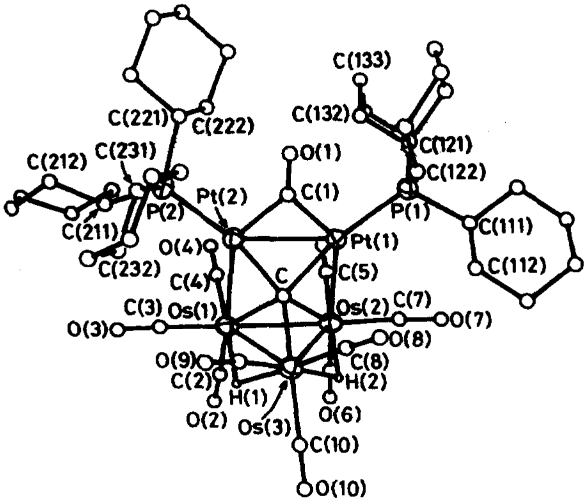
The bridging carbene complex $[PtW(\mu\text{-}CHAr)(\mu\text{-}CO)(CO)(Cp)(PEt_3)_2][BF_4]$ (Ar = $4\text{-}MeC_6H_4$) has been prepared in a single step from $[Pt(H)(PEt_3)_2(propanone)][BF_4]$ and $[W(CAr)(CO)_2(Cp)]$, this preparation being appreciably more convenient than the two-step process previously reported by Stone for the PMe_3 derivative [316]. When $[PtH(PEt_3)_2(propanone)]$ is reacted with *trans*-$[Pt(C\equiv CPh)_2(PEt_3)_2]$, 145 is obtained, by *cis*-addition of the platinum hydride across one of the carbon-carbon triple bonds [317].



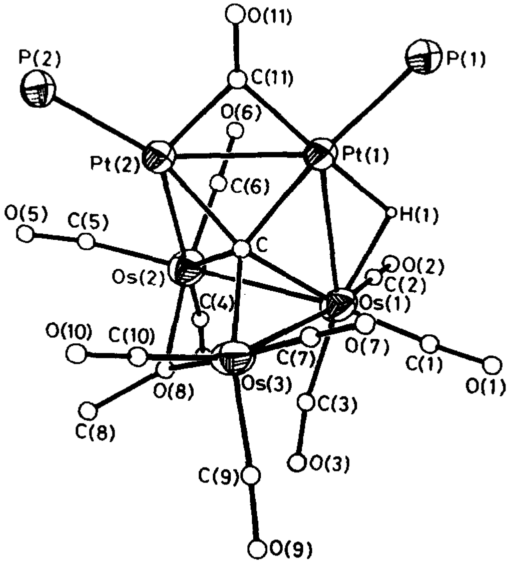
141 (Reproduced with permission from [314])



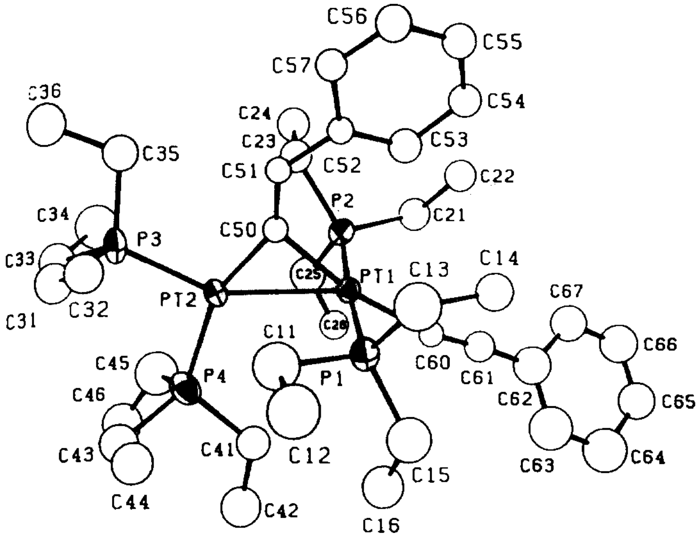
142 (Reproduced with permission from [315])



143 (Reproduced with permission from [315])

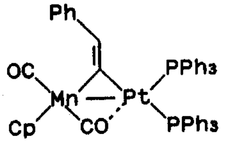


144 Cyclohexyl groups have been omitted for clarity. (Reproduced with permission from [315])



145 ORTEP view (thermal ellipsoids at 15 % probability) of the cation $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4][BF_4]$. (Reproduced with permission from [317])

Reaction of the manganese alkylidene carbene, $[Mn({=}C{=}CHPh)(CO)_2(Cp)]$ with $[PtL_4]$ or $[PtL_2($*trans*-stilbene$)]$ gave **146**, fully characterised spectroscopically [318]. Some reactions of the complex with nucleophiles were studied, and the PPh_3 ligand *trans* to the μ-carbene could be readily replaced by CO [319]. When the complex was reacted with $[Fe_2(CO)_9]$, $\{Fe(CO)_3\}$ adducts were obtained, but the structures were not described in detail [320].

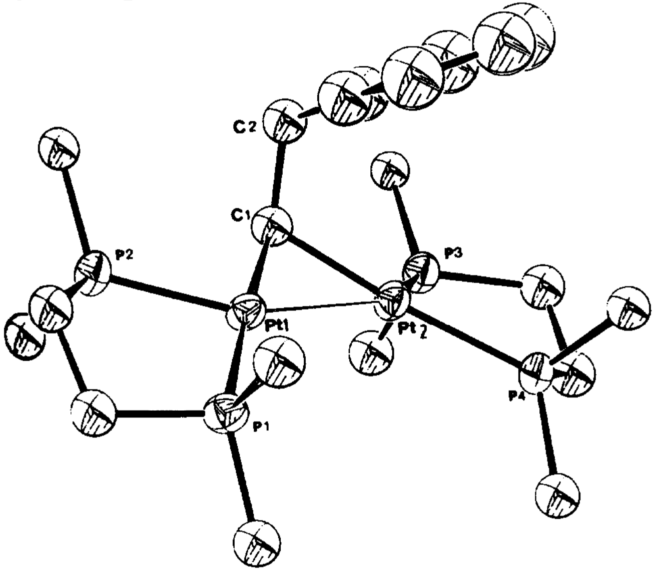


146

When $[\{PtH(PP)\}(\mu\text{-}H)_2\{Pt(PP)\}]$ (PP = dppe) is treated with styrene in the presence of molecular hydrogen, the stable complex $[Pt_2(\mu\text{-}CHCH_2Ph)(\mu\text{-}H)(PP)_2]$, **147**, was obtained, and characterised in a diffraction study. The μ-alkylidene is symmetrically bound, and the hydride, although not located, is probably not symnetrically ligated [321].

A range of metal complexes have been reacted with the metallocyclobutane $[Ti(CH_2CRR'CH_2)(Cp)_2]$ to give $[\{Ti(\mu\text{-}CH_2)(Cp)_2\}(\mu\text{-}X)ML_n]$ and $RR'C{=}CH_2$. Among the complexes studied were $[PtCl(Me)(PMe_3)_n]$ (n = 1 or 2) and

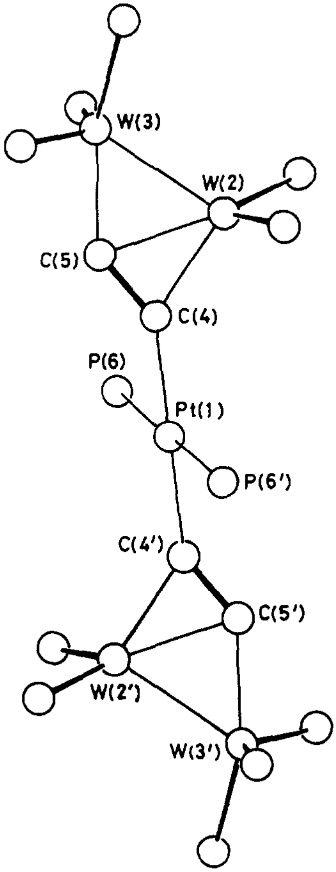
$[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ [322].



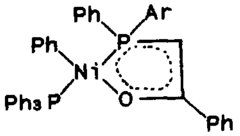
147 ORTEP view of the structure of the cation in the crystal of $[Pt_2(\mu\text{-}CHCH_2Ph)(dppe)_2(\mu\text{-}H)][BF_4]$. The bridging hydride was not located and only one carbon of each *P*-phenyl group is shown. (Reproduced with permission from [321])

Reaction of $[W_2(OCMe_3)_6]$ with *trans*-$[Pt(C\equiv CH)_2(PMe_2Ph)_2]$ gave *trans*-$[Pt(C\equiv CH)\{C_2W_2(OCMe_3)_5\}(PMe_2Ph)_2]$, which, over a period of 4-5 days was converted to *trans*-$[Pt\{C_2W_2(OCMe_3)_5\}_2(PMe_2Ph)_2]$, 148, characterised in a diffraction study. The $\{PtP_2C_2\}$ unit is planar, with the platinum formally in the +2 oxidation state. The $\{C_2\}$ unit is coordinated as $[C_2]^{4-}$, and this is the first complex of this type to be characterised. The bonding resembles that of a μ_2,η^2-alkyne, but the carbon carbon bond is substantially longer [323].

Reports on ylids have, as usual, been very diverse. There have been further reports on complexes of the type 149, used as catalysts for ethene oligomerisation [324]. Reaction of $[Ni(cod)_2]$ with $Ph_3P{=}CHCOPh$ and $Me_3P{=}CH_2$ gave a complex formulated as 150 (*sic*) [325], used for ethene oligomerisation and polymerisation [326], and polymerisation of ethyne to give a predominently *trans*-product [327]. The product of reaction of $[Ni(cod)_2]$ with $Ph_3P{=}CHCOPh$ and $Me_3SiN{=}PPh_3$, also proved to be a useful catalyst for ethene polymerisation [328]. Reaction of $Me_2\overset{+}{S}\overset{-}{C}HCOAr$ with NiX_2 gave $[Ni_2X_4(ylide)_2]$. The structure is probably dimeric with bridging halides [329]. A similar reaction was reported for $PdCl_2$ [330].



148 A ball and stick view of the central *trans*-$\{PtP_2(C_2W_2O_5)_2\}$ moiety of the centrosymmetric *trans*-$[Pt\{C_2W_2(OCMe_3)_5\}_2(PMe_2Ph)_2]$ molecule looking nearly down the PPtP axis, showing the PtC_2W_2 unit. [Reproduced with permission from [323])



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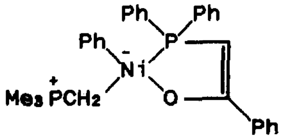
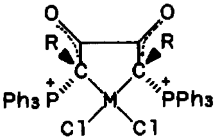


150

Reaction of the bis(ylide), $Ph_3P{=}CRCOCOCR{=}PPh_3$, with $[Pd(PhCN)_2Cl_2$ gave 151, characterised spectroscopically. The halides could be replaced by (en) [331]. Similar complexes were prepared of the monodentate ylid $Ph_3P{=}CHCOOR$.

Solid state IR spectroscopic data implied that the product was *trans*-[$PdCl_2L_2$], but solution data indicated that the *cis*-form is also important. Both *meso* and *dl*-isomers were obtained [332].



151

When $PdCl_2$ was treated with two molar equivalents of $(Me_2N)_3P{=}CH_2$, {PdL_2Cl_2} was obtained. A similar reaction converted PtI_4 to {PtI_4L_4}. The products were unstable in chlorinated solvents at room temperature, and their structures were not conclusively established [333]. [$Pd(PPh_3)_4$] reacted with E-XCH=CHCOOR by oxidative addition to give *trans*-[Pd(CH=CHCOOR)$(PPh_3)_2$X] as the initial product, but this was rapidly converted to 152, characterised in a diffraction study [334].

Treatment of [$Pd(C_6F_5)L_2(OClO_3)$] with Ph_3P-CHCOMe, appy, gave [Pd(appy)(Ar)L_2][ClO_4]. In this complex appy was *O*-coordinated, which was unprecedented for keto stabilised ylid complexes of palladium. In [Pd(appy)(Ar)Cl(tht)], prepared from appy and [$Pd_2Ar_2(\mu\text{-}Cl)_2(tht)_2$], the normal *C*-coordination obtained [335].

The electrochemistry of 153 has been investigated [336]. Studies of the formation and decomposition of a range of platinum ylid complexes have again been reported by Puddephatt's group (Schemes 7 and 8) [337].

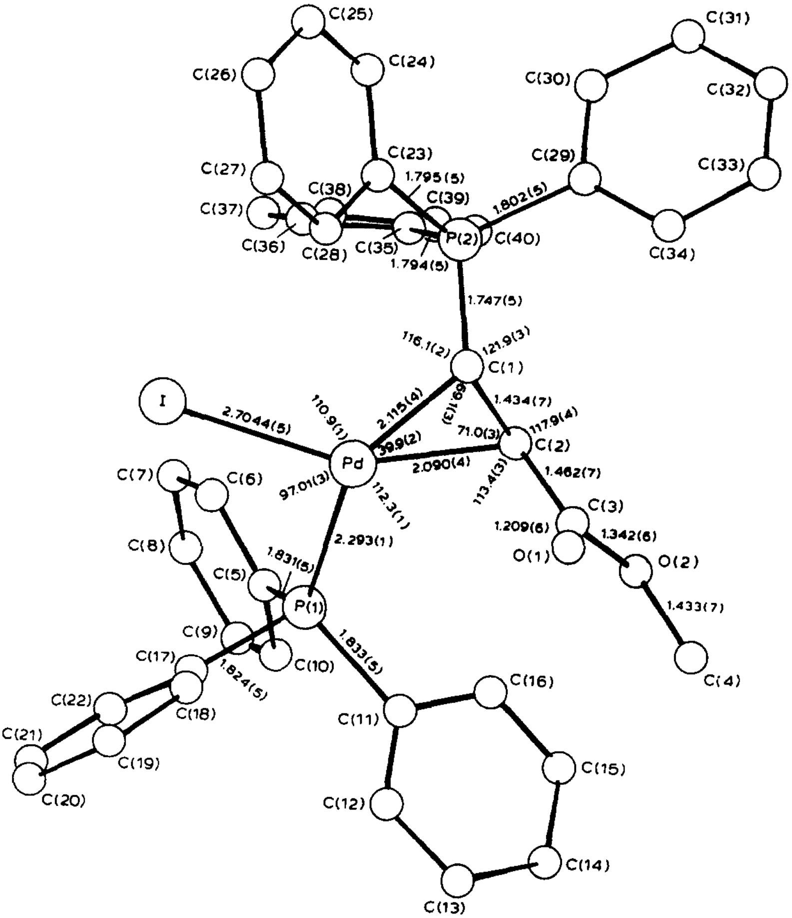
Reaction of [$PdCl_2(MeCN)_2$] with R_3N gave complexes of the type 154, the first characterised enamine palladium complexes. For example, the use of $EtN(CHMe_2)_2$ gave 154a (R^1, R^2 = $CHMe_2$, R^3, R^4 = H) in 17 % yield, and 154b (R^1 = Et, R^2 = $CHMe_2$, R^3 = Me, R^4 = H) in 38 % yield [338].

5 METAL COMPLEXES FORMED BY INTERNAL METALLATION AND RELATED REACTIONS

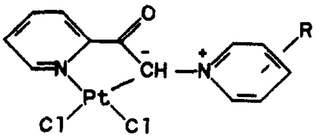
There has been a useful review of the uses of cyclometallated complexes in synthesis [339], and a most comprehensive account of applications involving cyclopalladated species [340]. The *C*-metallation of phosphine complexes has been discussed [341].

There continue to be many reports of the preparations and reactions of cyclometallated complexes of benzylamine derivatives. The reaction of *trans*-[PtI_2L_2] with successively $PhCH_2NH_2$, Ag[BF_4]/propanone and KI, to give 155 has been shown to be strongly solvent dependent [342]. Reaction of

$[PdCl_4]^{2-}$ with $PhCH_2NHR$ (R = H or Me) gave $[PdCl_2L_2]$, but with $PhCH_2NMe_2$, cyclometallation occurred rapidly. Similar reactions were noted for palladium ethanoate. In the reaction of $[\{PdL(OCOMe)(\mu\text{-}OCOMe)\}_2]$ with $PhCH_2NMe_2$ nmr spectroscopic studies were used to show that interaction between the metal and the aryl ring protons preceded cyclometallation [343]. The oxidative addition reaction, (5), allowed a more general synthesis of cyclometallated complexes of primary and secondary benzylamines, and the products of bridge splitting, such as 156 and 157 were characterised fully for the first time [344].



152 (Reproduced with permission from [334])



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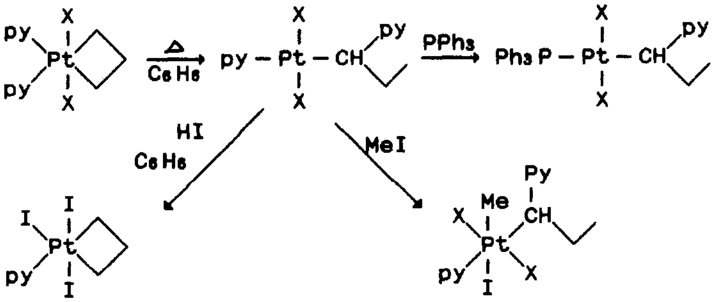
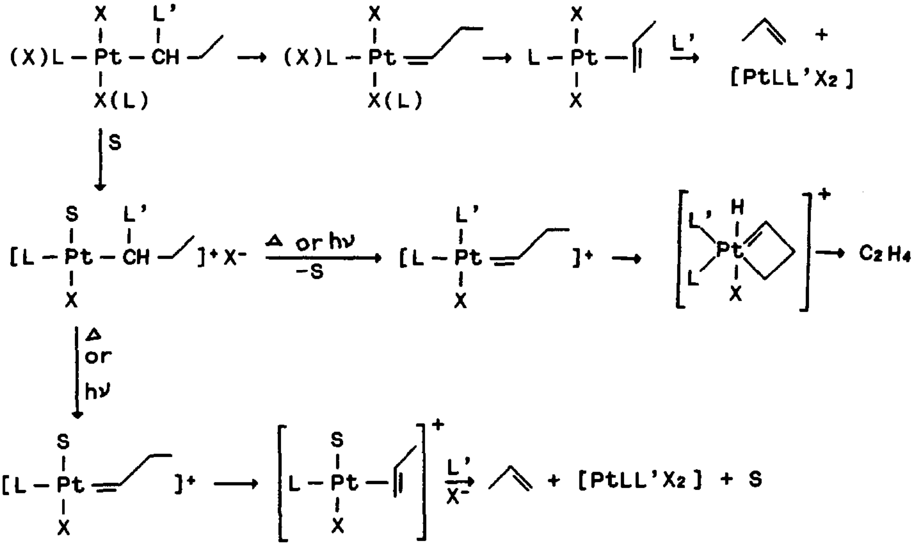
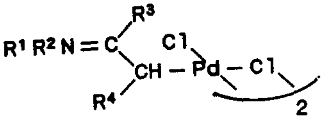


Scheme 7 Formation of ylids from cyclometallated platinum complexes [337]



Scheme 8 Decomposition of platinum ylid complexes (X = Cl, L' = py, L = py or PPh_3, S = dmso) [337]



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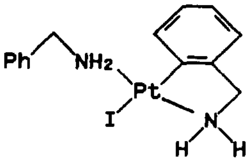

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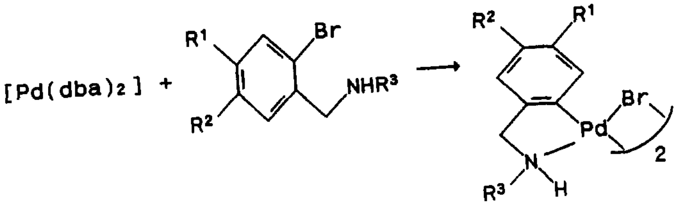

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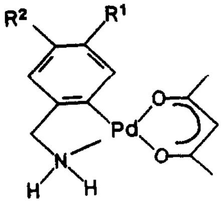

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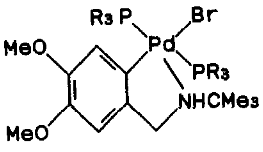
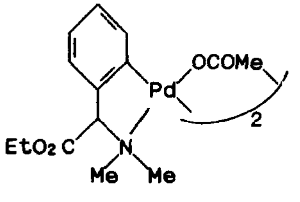


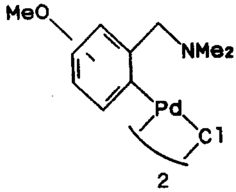
157

There have been more reports of the preparation of cyclometallated derivatives of *N,N*-dimethylbenzylamines. A kinetic study using palladium ethanoate indicated that ligand coordination was rate controlling, and palladation to give the five-membered ring was then rapid. The kinetic isotope effect was negligible, and the reaction rate was not very sensitive to substituents on the aromatic ring [345]. A more detailed full paper considered the reaction in terms of the palladium ethanoate oligomers [346]. Reaction of palladium ethanoate with $PhCH(COOEt)NMe_2$ gave 158, and the usual exchange and bridge splitting reactions were reported [347]. A chloro bridged dimer was obtained with $Li_2[PdCl_4]$. The corresponding acid, $PhCH(COOH)NMe_2$, gave *N,O*-chelate complexes [348].



158

The structures of the three isomers of 159 were established in X-ray diffraction studies; all adopted *trans*-geometry in the solid state [349]. ^{13}C nmr spectroscopic data have been reported for the range of complexes 160 and 161. No quadrupolar broadening due to coupling to ^{105}Pd was noted [350]. The structure of the bis(cyclometallated) complex, 162, was established; the palladium atom adopts slightly distorted square planar geometry, and the bond lengths are in accord with *trans*-effect considerations [351].



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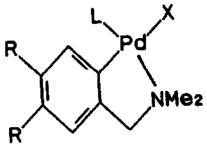

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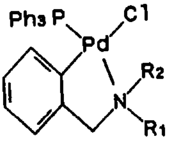

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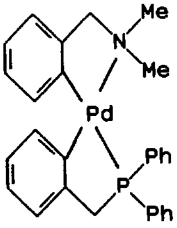
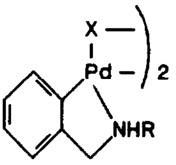


162

Carbonylation of 163 gave the insertion product, 164, whereas R^2NC yielded initially only the bridge split derivative. Insertion occurred on subsequent heating [352]. Reaction of 165 with $LiCl/CH_3COOH$ at room temperature resulted in cleavage of the Pd-N bond. Heating the product, 166, in ethanoic acid at 80 °C yielded $PhCH_2NEt_2$ and $[\{Pd(PPh_3)(\mu\text{-}Cl)Cl\}_2]$ [353]. Reaction of 167 with Na[M] ([M] = $[Co(CO)_4]$, $[Mo(CO)_3(Cp)]$ or $[Fe(CO)_3(NO)]$) gave 168, and related reactions were noted for derivatives of 8-methylquinoline or 2,*N*,*N*-trimethylaniline. One bridging metal could be replaced by another, and the fluxional behaviour of the complexes was probed by nmr spectroscopy [354].



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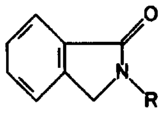
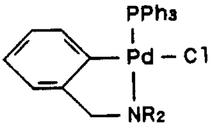


164

An interesting bridge splitiing reaction for 167 with 169 was reported [355].

Soviet workers have reported new syntheses of cyclometallated complexes by exchange of the cyclometallated ligands (reaction (6)). The reaction mechanism was shown to involve bridge splitting followed by protolysis of a palladium-carbon bond, the presence of ethanoic acid as a cosolvent being essential. The final rapid step is palladation of the incoming ligand. The reaction is useful not only as an example of ligand exchange, but also as a method for the palladation of relatively unreactive substrates [356-358].



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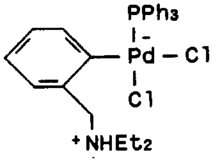

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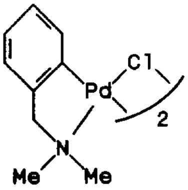

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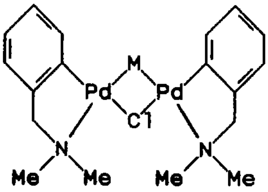

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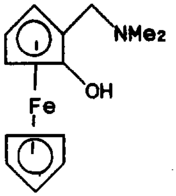

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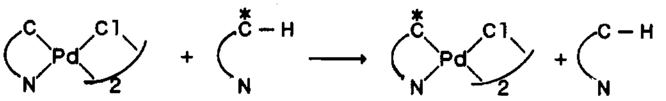
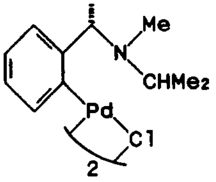


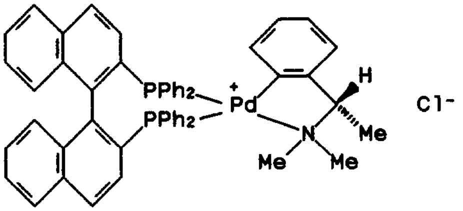
(6)

Cyclometallation reactions of α-substituted, chiral benzylamines have received much attention. The preparation of 170 was reported [359]. With PhCH(R^1)NHR^2 and $Li_2[PdCl_4]$ a mixture of $[PdCl_2L_2]$ and the cyclometallated species was obtained, their relative proportions depending on the substituents. The usual bridge splitting reactions were reported [360]. When $PdCl_2$ was reacted with S-PhCH(Me)NH_2 in the presence of molecular hydrogen, a dark brown solution was obtained. Whilst these complexes were poorly defined, the derivatives of the *N,N*-dimethyl analogue were more easily characterised, and acted as precursors to enantioselective catalysts for the reduction of azlactones. The true catalysts are thought to be oligomeric palladium(0) species [361].



170

When a chiral bidentate phosphine is used to split an optically actice chloro bridged dimer, species such as 171 are obtained, and were used as a check on the optical purity of the phosphine [362]. A similar strategy was used for the resolution of asymmetric bidentate aminophosphines and aminoarsines, 172 (E = P or As), involving fractional crystallisation of 173 [363]. The ligands PhAs(Me)$CH_2CH_2NH_2$ and PhAs(Bu)$CH_2CH_2NH_2$ were resolved similarly [364]. When the nitrogen atom is substituted by two different groups, as in 174, two diastereoisomers are obtained on cyclometallation. One diastereomer generally predominates, to an extent which depends on the size of the substituents at nitrogen. The complex 175, with an S-configuration at carbon and R-stereochemistry at nitrogen, was characterised in a diffraction study [365].



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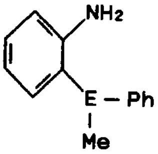

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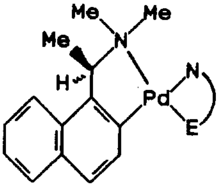

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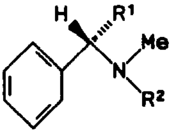

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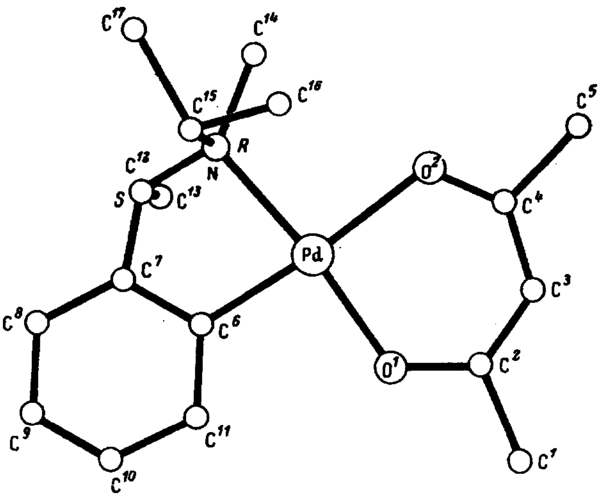
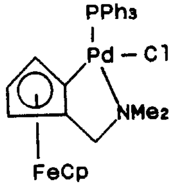


175 (Reproduced with permission from [365])

The cyclometallation of $FcCH_2NMe_2$ with $[PdCl_4]^{2-}$ has been studied, and a range of bridge splitting reactions discussed [366]. Protolysis of 176 gave the amine and *trans*-$[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ [367]. The cyclometallated derivative of the chiral substrate, 177, was used in a prostaglandin synthesis [368].



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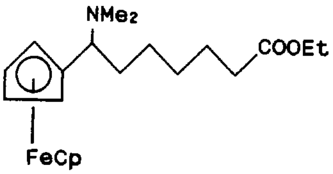
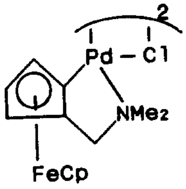


177

Carbonylation of 178 in the presence of the prochiral species $HOCH_2CH(OBn)CCH_2OH$ gave $HOCH_2CH(OBn)CH_2OCOFc$ with 36 % asymmetric induction [369,370].

Oxidative addition of 2,6-bis(dimethylaminomethyl)bromobenzene to $[Ni(cod)_2]$ gave 179 (M = Ni, X = Br). The bromide could be readily substituted by a sequence involving reaction with $Ag[BF_4]$ to give the aquo derivative, followed by substitution by X^- (X^- = Cl^-, Br^-, I^-, $[NO_2]^-$, $[NO_3\text{-}O]^-$, $[HO]^-$, $[O_2CR]^-$ or $[CF_3SO_3]^-$). Somewhat surprisingly, the methanoate salt, 180, was stable at 80 °C in benzene [371]. The platinum complex, 179, (M = Pt, X = OCOH) lost CO_2 readily at 50 °C in benzene [372]. The reaction of this platinum aquo complex with iodomethane had been noted previously, and a full paper has now discussed this reaction in more detail [373].



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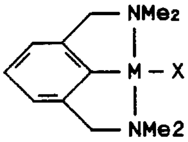

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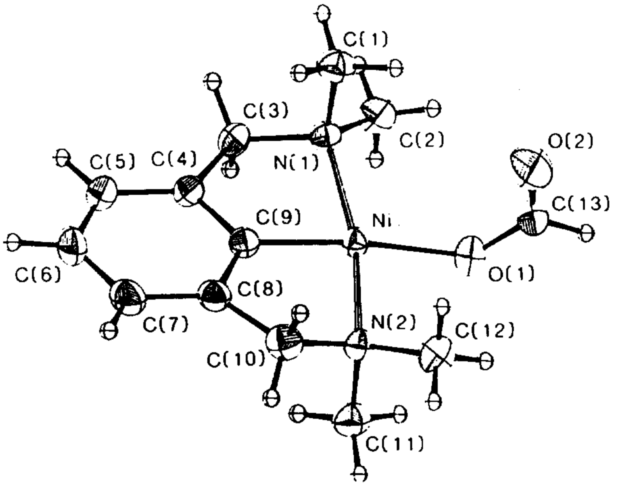
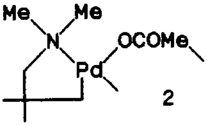


180 (Reproduced with permission from [371])

There have been isolated reports of cyclometallated derivatives of simple amines. One is discussed in a review of organometallic chelates of the π-π and n-π types [374]. When palladium ethanaote reacted with $Me_2NCH_2CMe_3$, the product was 181, which underwent the usual bridge splitting reactions [375]. Reaction of 182 with $[Pd_2(dba)_3]$ gave 183, with retention of configuration at the chiral centre. In the presence of pyridine, the monomer, 184, was formed [376].



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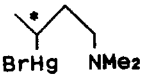

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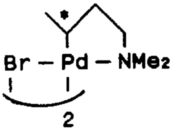

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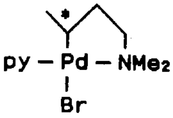
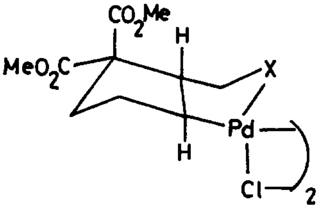


184

The amine $(MeO_2C)_2CHCH_2CH_2CH{=}CHCH_2NMe_2$ reacted with $Li_2[PdCl_4]$ to give 185 (X = NMe_2), which could be reduced with $Na[BH_4]$ to 186. Related reactions of allylthioethers were also reported [377]. The complex 187 (X = Cl) reacted with diazomethane to give palladium(0) and insertion products (187, X = CH_2Cl, CH_3 and/or CH_2OEt depending on the reaction conditions) [378].



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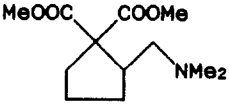

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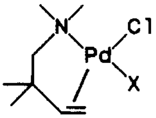
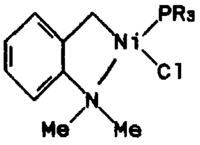


187

Reaction of 2-dimethylamino benzyl lithium with $[NiCl_2(PR_3)_2]$ gave 188. A similar reaction was noted with the α-trimethylsilylated analogue. Insertion of $CF_3C{\equiv}CCF_3$ into the nickel carbon bond occurred cleanly for R = Me, but with the complex of the bulkier PEt_3 ligand, 189 was obtained [379]. When 190 was reacted with Ag[OCOMe], the ethanoate bridged species was obtained, and was shown to be non-rigid in solution. However, when palladium ethanoate was reacted with 2,*N*,*N*-trimethylaniline, a trimer, $[(C\text{-}N)Pd(\mu\text{-}OCOMe)_2Pd(\mu\text{-}OCOMe)_2Pd(C\text{-}N)]$ ((C-N) is the cyclometallated aniline) was formed [380].



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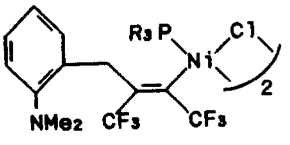

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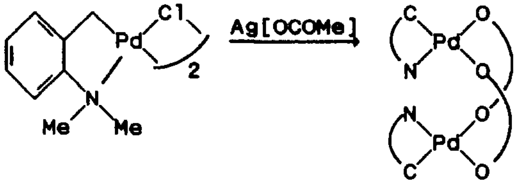
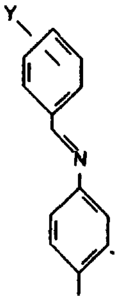


190

Several cyclometallated complexes of imines have been reported. Reaction of 191 with palladium ethanoate gave 192, which could be carbonylated in methanol to 193. The rate of the reaction depended on the nature of Y; electron withdrawing groups retarded the reaction, and rates could be correlated with ^{13}C nmr spectroscopic parameters [381]. The related complex 194 was characterised in an X-ray diffraction study. If the analogue of 194 with halo bridges was subjected to carbonylation conditions the sole product was 195, and 194 reacted with CO in the presence of PPh_3/methanol to give 196. Related reactions of isocyanides were also studied [382].



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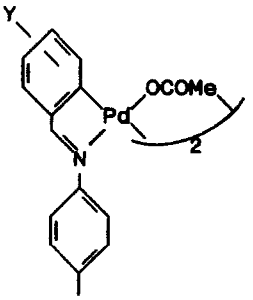

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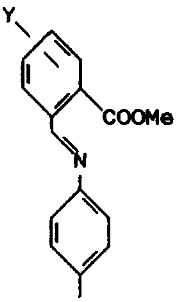
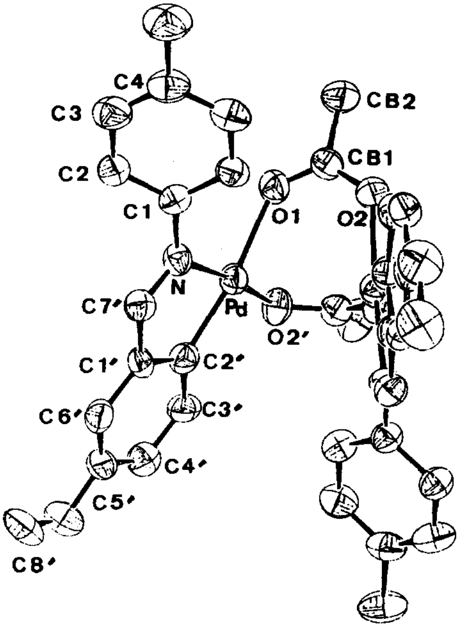


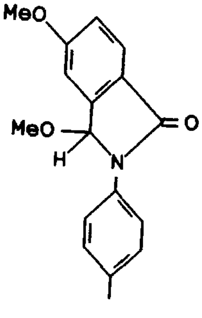
193

Reaction of 197 with $[Pd(dba)_2]$ led to a useful preparation of cyclopalladated benzalimines; the usual bridge splitting reactions on the products were demonstrated [383]. The metallation of $PhCH=N(C_6H_4-2-Me)$ has been noted [384]. Reaction of 198 with PdX_2 (X = Cl or (OCOMe)} gave only 199

[385]. Cyclometallation reactions of 200 have been reported [386].



194 (Reproduced with permission from [382])



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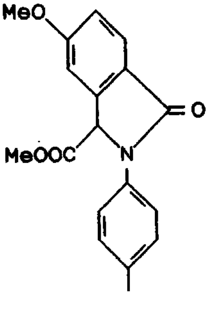

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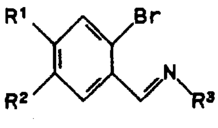

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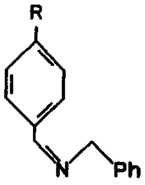

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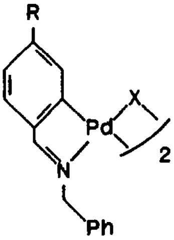

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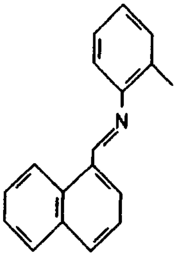
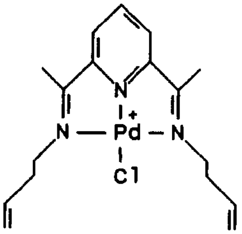


200

In 201, spectroscopic data make it clear that the alkene is not metal coordinated. However, the pendant alkene may be coordinated by palladium by addition of [Pd(MeCN)$_2$Cl$_2$], and the alkene complex reacted with water to give 202. β-Hydride elimination resulted in a coordinated enol, and in the final product, both of the pendant alkenes had been oxidised to methyl ketones [387]. Bridge splitting reactions on the polymeric species, 203 (Ar = C$_6$F$_5$), using Ph$_2$PH, have been investigated. In benzene solution, the dimer, 204, was formed, but in the presence of K[OH], the product was 205, in which a C-P bond has been formed at the expense of a C-F bond [388].



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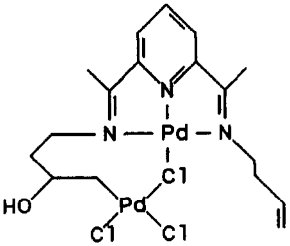

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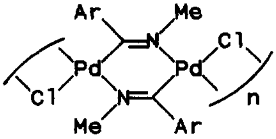

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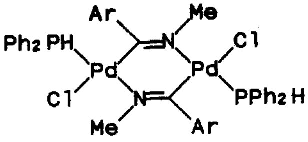

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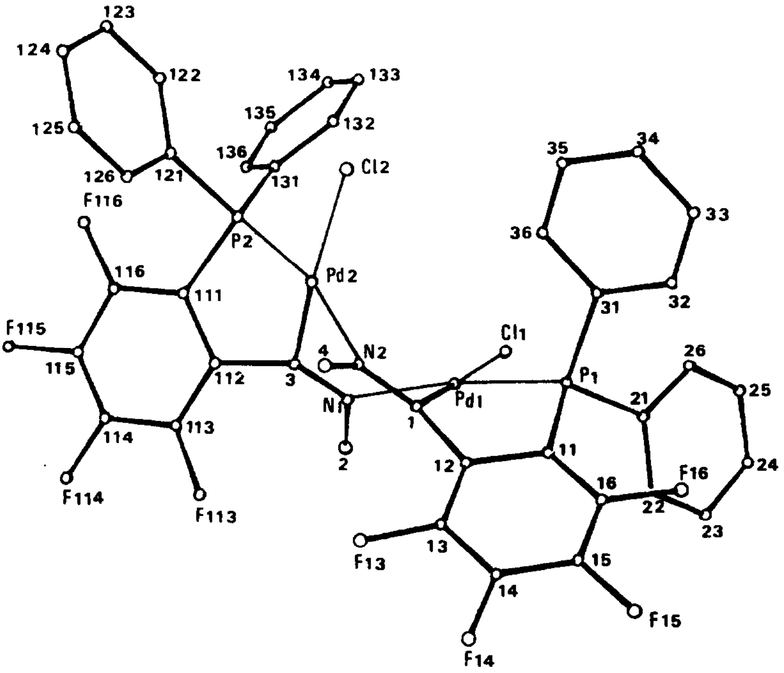
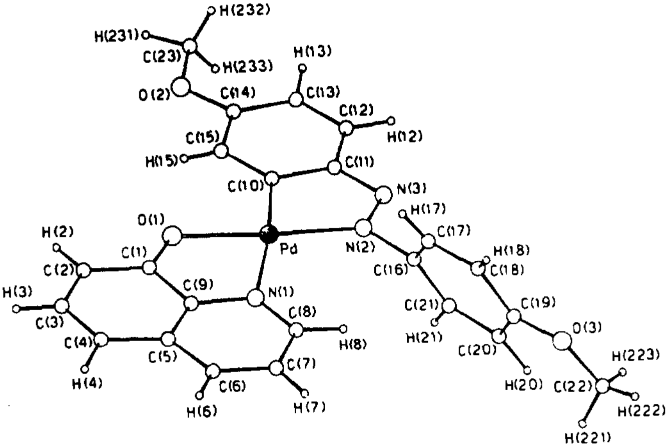


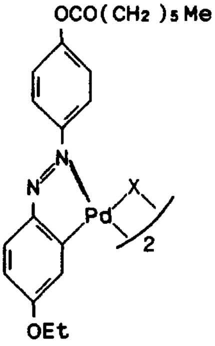
205 (Reproduced with permission from [388])

Further cyclometallated azoarene complexes have been prepared. For example, 4-$MeOC_6H_4$-N=N-C_6H_4-4-OMe reacted with $K_2[PdCl_4]$ to give a metallated halo bridged dimer, which was treated with 8-hydroxyquinoline to yield 206. The metallated complexes, unlike the ligand itself, lacked thermotropic mesophases [389]. The complexes 207 (X = Cl, Br or I) underwent the usual bridge splitting reactions with pyridine, quinoline or $PhNH_2$. When X =Cl, 207 showed a strongly birefringent and fluid nematic mesophase at temperatures between 190 and 205 ^{o}C. The mononuclear derivatives of pyridine and quinoline were also liquid crystalline, and a layered smectic phase was present [390].

Metallation of non-symmetrical azoarenes was shown to be regioselective, when the electronic character of the substituents on the rings was highly dissimilar. Thus 4-$Me_2NC_6H_4$-N=N-C_6H_4-4-NO_2 was metallated only in the electron rich aromatic ring, but both possible products were obtained from 4-$MeOC_6H_4$-N=N-Ph. A range of complexes were prepared, and their electronic spectra described. Whilst the free ligands do not luminesce, intraligand fluorescence was noted for the metallated species [391]. Metallation of 208 with $[PdCl_4]^{2-}$ occurred initially to give 209. However, if the naphthalene *peri*-position was blocked, as in 210, metallation occurred at the exocyclic position, to give 211 as the final product [392].



206 (Reproduced with permission from [389]



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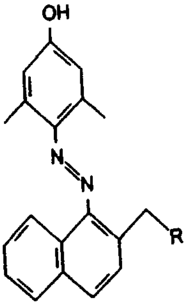

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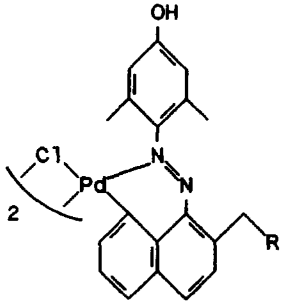

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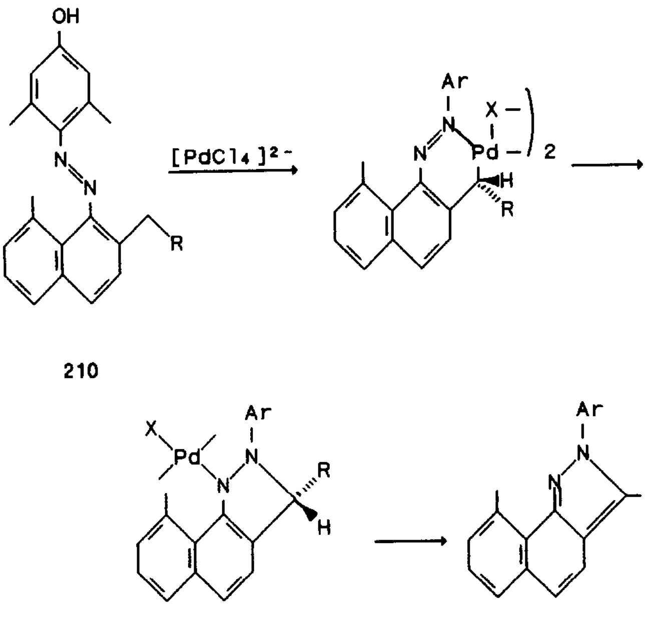

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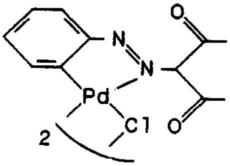
211

The azo compound Ph-N=N-CH(COMe)$_2$ does not react with PdCl$_2$, but with the copper complex, 212 was formed [393]. Bridged palladated complexes of azobenzene have been used as catalysts for the hydrogenation of nitrobenzene or benzaldehyde [394].

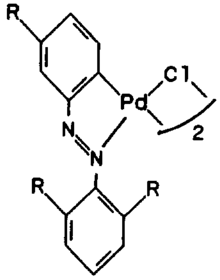


212

Oxidation of 213 with 3-ClC$_6$H$_4$CO$_3$H gave 214 by apparent insertion of oxygen into the metal-carbon bond. Various transformations of the product were discussed [395].

Bridge splitting reactions of the cyclometallated benzalazine polymer, 215, have been studied [396]. The ease of cycloplatination of (4-RC$_6$H$_4$C=N)$_2$ depended on the nature of R; no cyclometallation occurred for R = NO$_2$, H or NMe$_2$, but the reaction was facile for R = Cl [397]. Monocyclopalladation of benzalazines gave the dimer, 216, and this could be further reacted with

$K_2[PtCl_4]$ to give an oligomer. Bridge splitting of the oligomer with PEt_3 gave 217, the first mixed metal complex of this type to be characterised [398].



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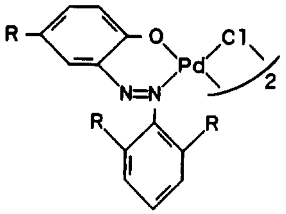

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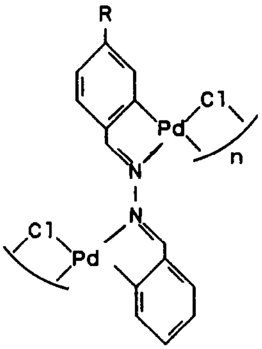

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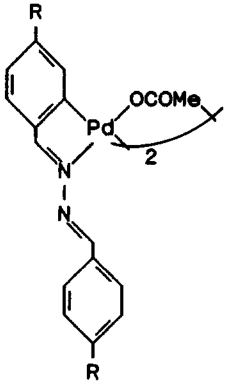

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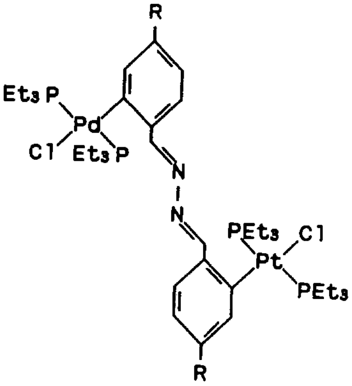
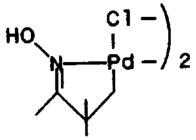


217

Metallation of the oxime of lanost-8-ene-3-one with $Na_2[PdCl_4]$ has been reported. Various reactions of the metallated oxime were reported [399]. It had been previously reported that palladation of $Me_3CC(Me)=NOH$ yielded 218. Reaction of 218 with successively pyridine, $Pb(OCOMe)_4$ and $Na[BH_4]$ gave the functionalised compound $MeC(=NOH)CMe_2CH_2OCOMe$. The latter was also readily metallated to give 219, which was similarly functionalised to $MeC(=NOH)(CH_2OCOMe)_2$ [400]. Other reactions of 218 to give chlorinated and reduced derivatives were also reported [401].

Reaction of $Bu_3SnCH_2CH_2C(Me)C=NOR$ (R = H or OCOMe) with $[PdCl_2(PhCN)_2]$ gave 220. Related reactions leading to complexes containing six-membered rings were also reported [402].



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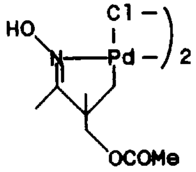

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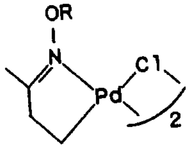
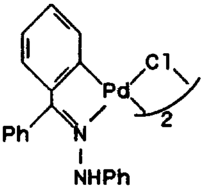


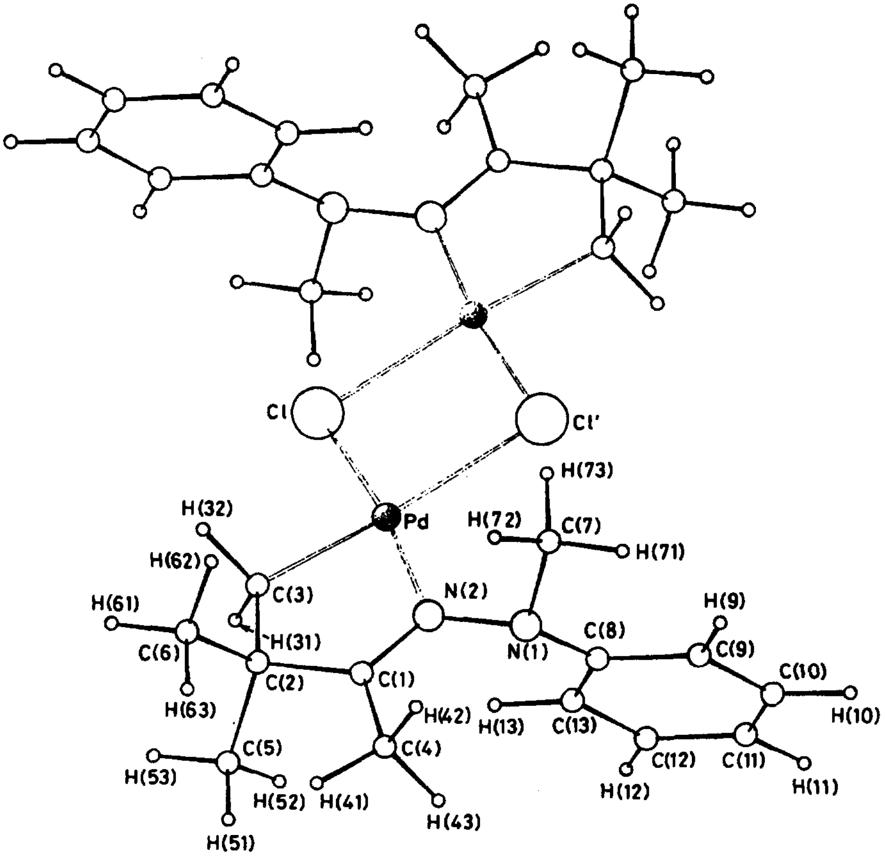
220

Metallation of the hydrazone derivative, $Ph_2C=NNHPh$, with $Li_2[PdCl_4]$ gave 221, characterised in a diffraction study. The dimer adopts *trans*-stereochemistry [403]. Reaction of $Me_3CC(Me)=NNMePh$ with PdX_2 gave 222 and 223. The temperature dependence of the nmr spectrum of 222 was interpreted on the basis of *cis*⇌*trans* isomerism and hindered rotation about the N-N bond [404].



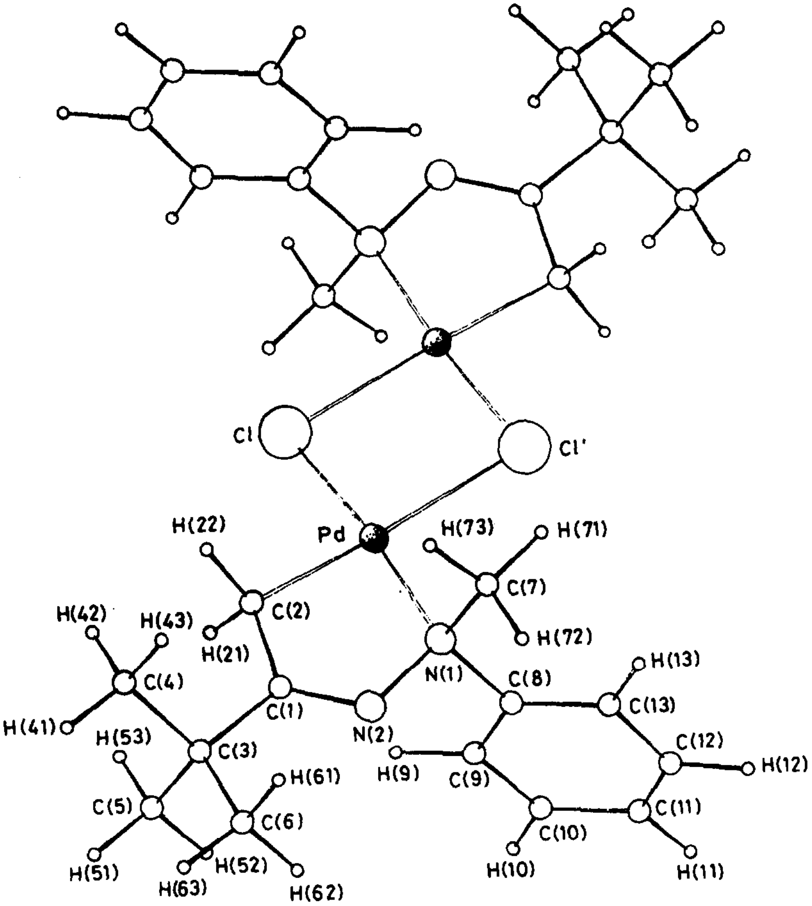
221

The reactions of 224 with HX had been previously described. There has now been a kinetic study of the reaction with aniline, indicating that the first step in the reaction is the displacement of the cyanide ligand by the aniline. In a second step the aniline attacks the nitrile, with assistance from the metal, to give 225 [405]. Both primary and secondary amines follow a similar pathway, unlike the related reactions in the platinum series, and the nucleophilicity of the amine enhances the rate of the second step in the reaction [406]. 224 was among a range of complexes reviewed as catalysts for nitrile hydration [407].



222 (Reproduced with permission from [404])

There have been further reports of the metallation of pyridine derivatives. The structure of 226 was established in a diffraction study; the central six-membered ring adopts a boat conformation, with a Pd-Pd distance of 3.165 Å [408]. Reaction of $[PdCl_2(py\text{-}4\text{-}Me)_2]$ with 227 gave *trans-N,N*-[{PdCl(μ-pyCHPh-*N,C*)(py-4-Me)}$_2$], 228, characterised in a diffraction study [409]. Reaction of polyethene bearing pyridine side-chains with $Na_2[PdCl_4]$ in the presence of 2,6-bis{$CH_2CH(COOMe)_2$}pyridine gave 229. The polymer bound palladium complex showed significant activity in catalysis of hydrogenation of PhCH=CHCOOH [410].



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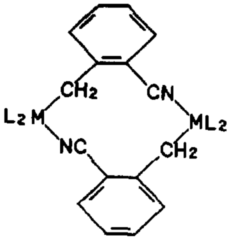

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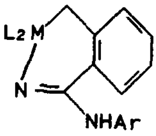

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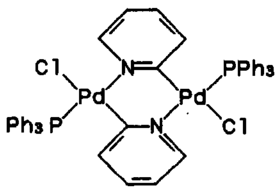

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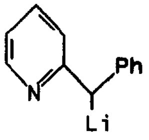

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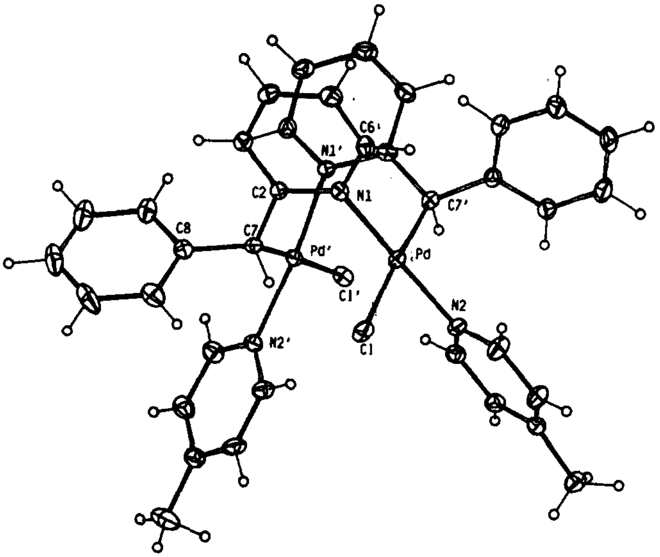
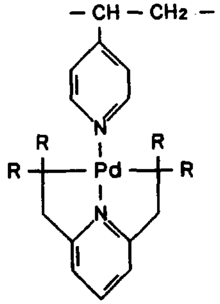
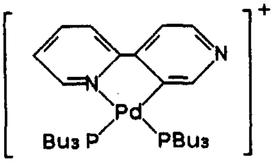


228 ORTEP drawing of *trans-N,N*-[{PdCl(μ-pyCHPh-*N,C*H)(py-4-Me)}$_2$]. (Reproduced with permission from [409])



229 (R = COOMe)

Reaction of 2,4'-bipy with Pd(OCOMe)$_2$ gave [{Pd(C$_{10}$H$_7$N$_2$)(μ-OCOMe)}$_2$] which was converted to the chloro bridged dimer with LiCl. Various bridge split products, including 230, were characterised, and it seems likely that *metallation of bipy is more common than has generally been believed* [411]. Thermolysis of [$PtAr_2$(bipy)] (Ar = C_6H_4-4-X; X = H, CMe_3 or CF_3) resulted in the loss of one mole of the arene, and metallation of bipy to give an unstable species, [$PtAr(C_{10}H_7N_2)$], which was trapped by py-4-CMe_3 to give 231 [412].



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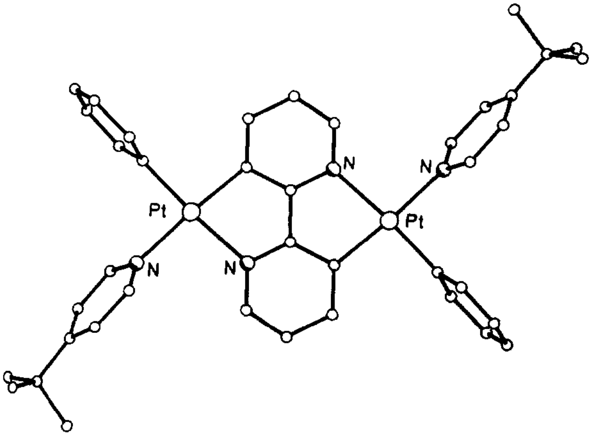
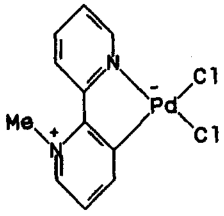


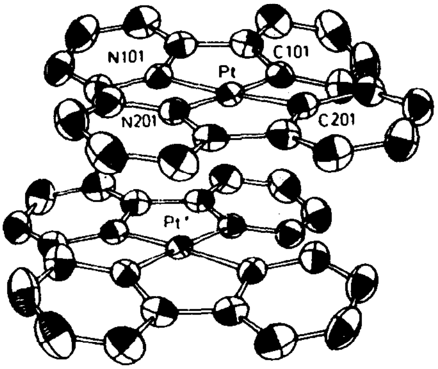
231 Molecular structure of [{Pt(Ph)(py-4-CMe_3)}$_2$(μ-bipy-2H)]. The main distortion in the square planar metal coordination is the N-Pt-C chelate angle of 81.7(4) °. (Reproduced with permission from [412])

When [$PdCl_4$]$^{2-}$ is treated with [*N*-Mebipy]$^+$ the initial product is [Pd(bipy-*N*-Me)Cl_3]. Thermolysis results in ligand metallation to give the unusual monomeric 232; the halides may be substituted with a range of ligands including py or bipy. Related reactions were reported for the platinum analogues [413,414].



232

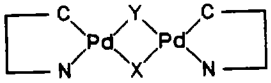
The complex *cis*-[Pt(2-Phpy-H)$_2$], 233, was prepared from *trans*-[PtCl$_2$(SEt$_2$)$_2$] and 2-(2-lithiophenyl)pyridine. An X-ray diffraction study showed bow-like distortions of the ligands. Cyclic voltammetry showed that the complex underwent an irreversible one electron oxidation and an almost reversible one electron reduction. Reaction with bromine gave [PtBr$_2$(2-Phpy)$_2$] [415]. Absorption spectra, emission spectra and emission lifetimes were established for this and several related species. Low energy absorption bands in the near UV and visible regions were assigned to MLCT transitions. Strong and structured luminescence emissions observed in the 500-600 nm region (lifetimes in the microsecond range at 77 K) were assigned to MLCT excited states [416].



233 ORTEP plot of the [Pt(Phpy)$_2$] dimer. (Reproduced with permission from [415])

Derivatives of the type 234 of 8-methylquinoline or *N,N*-dimethylbenzylamine have been prepared and characterised, in which X was a halide and Y = {Ph$_2$PCHCOOEt}, {Ph$_2$PCHCN}, {Mo(CO)$_3$(Cp)}, {Co(CO)$_4$} or {Fe(CO)$_3$(NO)}. Reaction of the complex in which the bridge is {Mo(CO)$_3$} with

$Ag[BF_4]$ gave $[\{Pd(8\text{-mq})\}_3\{\mu_3\text{-}Mo(CO)_3(Cp)\}(\mu_3\text{-}Cl)][BF_4]$, 235. The molybdenum and all three carbonyl groups are metal bonded, an unprecedentated arrangement [417]. Reaction of 236 (R = H or Me) with $[PdL_4]$ gave 237. The authors favoured a radical mechanism for the reaction [418,419]. Chiral 237 (R = Me) was similarly prepared and structurally characterised [420].



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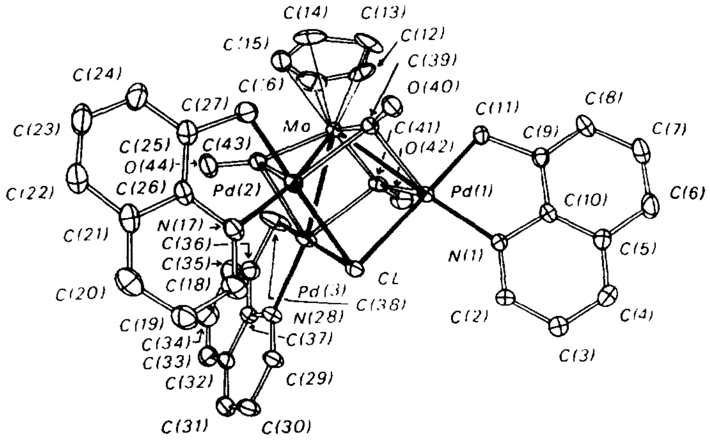
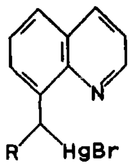


235 (Reproduced with permission from [417])



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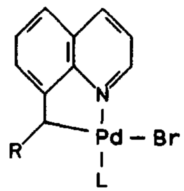
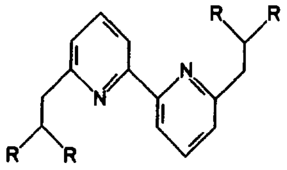


237

Reaction of 238 (R = COOEt) with $Li_2[PdCl_4]$ gave the *N,N*-bipy complex as the initial product. Treatment with $K_2[CO_3]$ or $K_2[CO_3]/Ag[NO_3]$ resulted in successive cyclometallations to yield 239 [421,422]. $[PdCl_4]^{2-}$ reacted with 240 to give 241 [423]. When palladium ethanoate was treated with 1,3-bis(2-pyridyl)propane, metallation occurred at the central carbon atom of the aliphatic chain to give 242; this is the first example of insertion into a

CH_2 group to give a doubly chelated compound [424].



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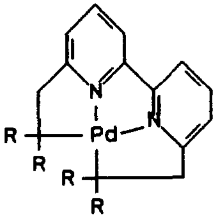

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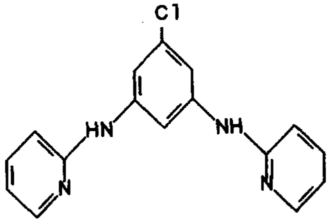

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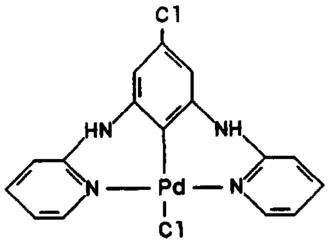

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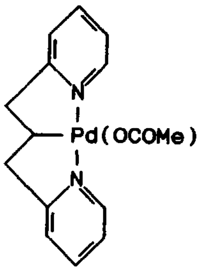


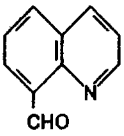
242

The bridge splitting reaction of *trans*-$[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ with 243 gave 244 at room temperature. A diffraction study showed that the non-bonded H...Pt distance was 2.3 Å, suggesting that platinum activated the C-H bond in the conversion, on heating, to 245 [425].

The ligand 2-(1-pyrrolyl)pyridine was metallated in the pyrrole ring on reaction with $Li_2[PdCl_4]$ to give 246 [426].

Two groups gave reported complexes of the type 247 in which the X-Y bridge is a carbon-metallated heterocyclic moiety [427,428].

Various internal metallations of phosphines have been described. Thermolysis of $[PdI_2\{P(C_6H_4\text{-}2\text{-}Me)_3\}_2]$ gave 248, in which the metallation has been facilitated by steric congestion. This metallated complex is formed at early stages in the Heck reaction, is catalytically inactive, and redissolves on heating [429].



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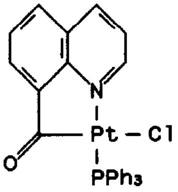

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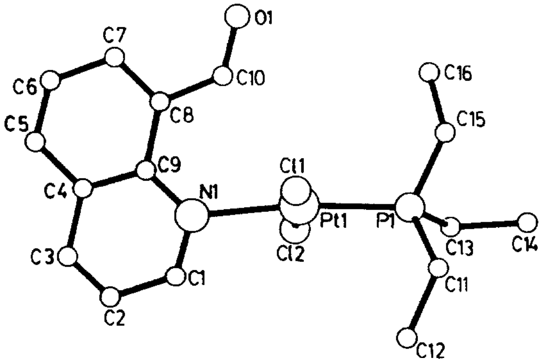
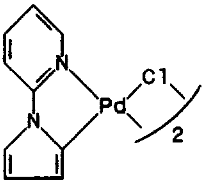


244 (Reproduced with permission from [417])

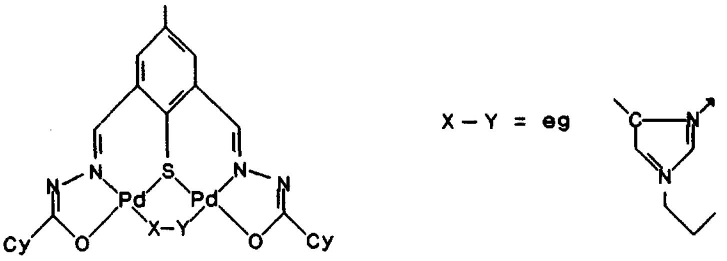


246

The reaction of 249 (X = Cl) with dppm has been investigated. Addition of 2 molar equivalents of dppm gave a {μ-dppm}-complex. Reactions with diarsines, and arsinophosphines were also studied [430]. Bridge replacement was also accomplished from the μ-halo to the μ-SR derivative [431], and with pyrazoles, to give species such as 250 [432].

Reaction of *trans*-[PtCl(L)(P-C)] ((P-C) = $CH_2CMe_2P(CMe_3)_2$); L = Ph_3As, Ph_3Sb, CO, PCy_3 or PPh_2Me) with $SnCl_2$ gave *trans*-[PtL(P-C)($SnCl_3$)]. Many spectroscopic data were reported [433]. The decomposition of [PtH(L)(P-C)]

(L = PPh_3) in solution has been studied [434].



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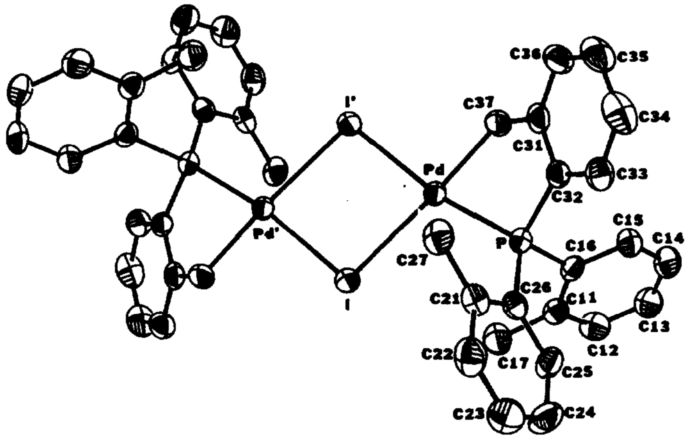
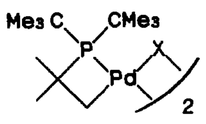
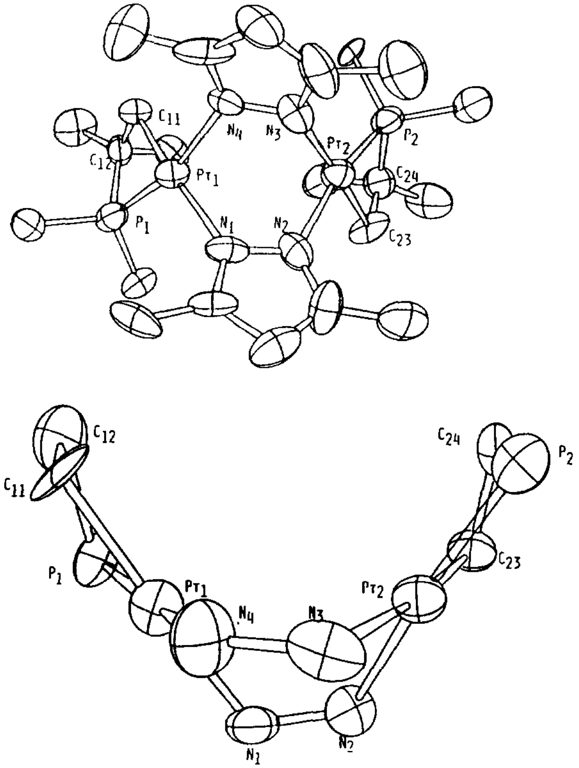


248 Molecular structure and labelling scheme for $[\{(\mu\text{-I})(\overline{PdP\{C_6H_4\text{-}2\text{-}Me\}_2\{C_6H_4\text{-}2\text{-}CH_2}\})\}_2]$. Hydrogen atoms have been deleted to improve clarity. A crystallographic inversion centre is located in the centre of the $\{Pd_2I_2\}$ rhombus. (Reproduced with permission from [429])

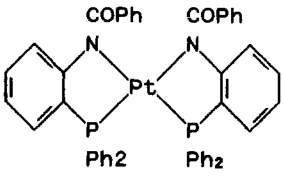


249

Thermolysis of 251 in MeCN, benzene or trichloromethane, gave 252, *via* 253. The complex 253 was formed by C-H metallation, and the final product by N-H reductive elimination [435].



250 ORTEP drawings of the complex $[Pt_2(C_5H_7N_2)_2\{CH_2CMe_2P(CMe_3)_2\}_2]$. The methyl groups of the non-metallated $-CMe_3$ groups are omitted for clarity. (Reproduced with permission from [432])



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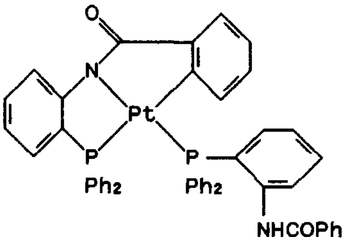
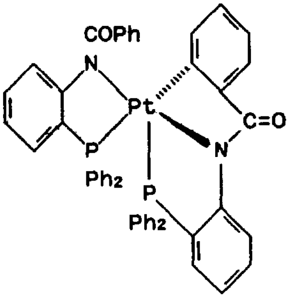


252

The bis(cyclometallated) complex, 254, reacted with $Ag[CF_3SO_3]$/propanone to give the propanone solvate. The solvate could be substituted by Na[HCOO] to give 255 as the final product, this complex being surprisingly stable [436].



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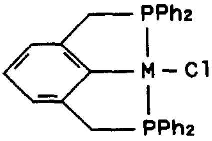

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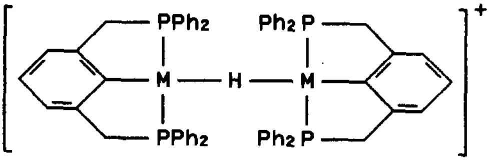
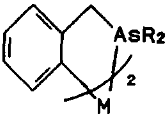


255

Reaction of 2-lithiated dialkylarsinomethylbenzene with $[MCl_2(SEt_2)_2]$ gave 256 (M = Pt, R = Me or M = Pd, R = Ph). Bridge splitting of 257 with the same lithio complex gave mixed bis(metallated) complexes [437,438].



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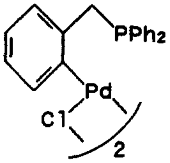
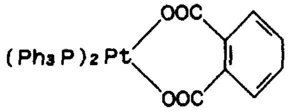


257

Thermolysis or photolysis of 258 gave 259. A number of related species including 260 were also characterised [439]. Metallation of PhNHCOMe with $Pd(OCOMe)_2$ gave the isolable complex 261. This underwent oxidative addition with iodomethane to give $2\text{-}MeC_6H_4NHCOMe$ as the final product. The reaction could be made barely catalytic [440].

Metallation of $4\text{-}MeC_6H_4CH_2SCH_2C_6H_4\text{-}4\text{-}Me$ with palladium ethanoate gave 262, *via* metallation only at the more electron rich 2-position [441]. Reaction of $[\{Pt(tmtu)Br_2\}_2]$ with an excess of tmtu gave 263, with close to perfect octahedral coordination. Nmr spectroscopic data indicated that there was considerable delocalisation of electron density between the nitrogen and sulphur atoms. The reaction is unusual in that the metal is oxidised with the loss of molecular hydrogen [442].



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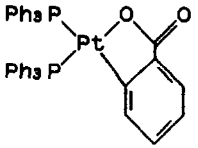

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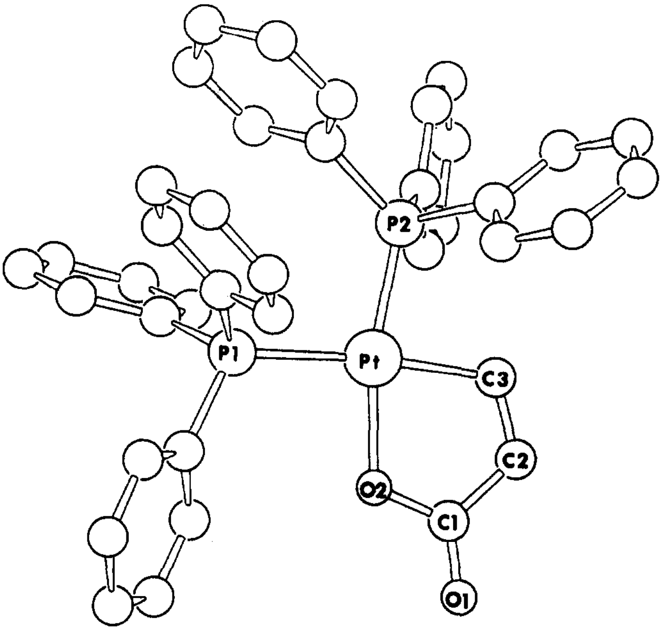
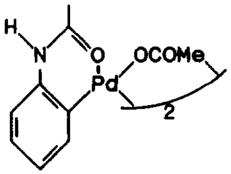
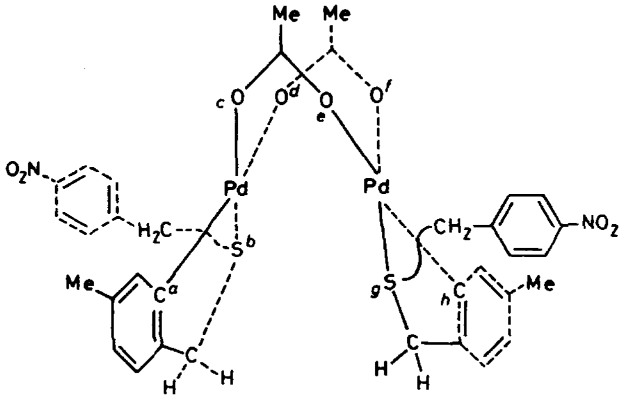


260 (Reproduced with permission from [439])

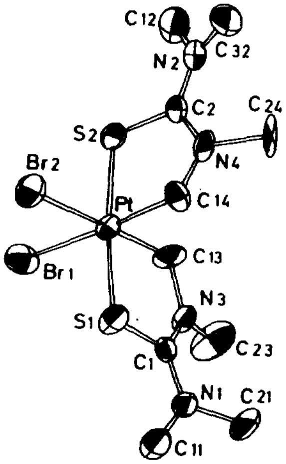


261

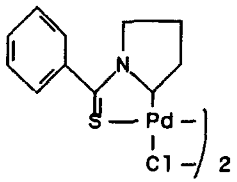
The outcome of the reaction of PhC(=S)N$(CH_2)_4$ with $PdCl_2$ depends on the solvent. In hmpt the *C,S* coordinated complex, 264, was obtained, but in methanol, 265, metallated in the arene ring, was formed [443,444].



262 (Reproduced with permission from [441])



263 ORTEP illustration of the structure of the cyclometallated $[PtBr_2(tmtu^*)_2]$ complex; tmtu* denotes the deprotonated form of tmtu. (Reproduced with permission from [442])



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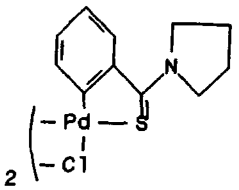


265

Carbonyl phosphine clusters of palladium and platinum have been reviewed [445], as have the uses of platinum carbonyl complexes in homogeneous catalysis [446]. A review of three-membered ring metallocycles included a number of species with {Ni_2Co}, {Ni_2Fe} and {PtWFe} cores [447].

6.1 Mononuclear carbonyl complexes

The mechanism of catalytic methanation of CO_2 over nickel catalysts involves {Ni(CO)} intermediates [448].

Reviews have been published concerning the environmental effects of $[Ni(CO)_4]$ [449], and its safe storage, toxicity and handling [450]. Biological monitoring of nickel complexes in general and $[Ni(CO)_4]$ in particular have also been discussed [451]. In poisoning of rats by $[Ni(CO)_4]$ the antidotal action of tetraethylpentamine was tested. This was as good an antidote as diethyl dithiocarbamate, and the two may act synergistically [452]. Diethyldithiocarbamate has been shown to affect the distribution of ^{63}Ni in mice exposed to $[^{63}Ni(CO)_4]$. ^{63}Ni concentrations in lung tissue were depressed, but there was some increase in the concentrations in brain tissue [453].

Potential energy curves for the $^3\Delta$ and $^1\Sigma^+$ states of {Ni(CO)} have been calculated by an *ab initio* CI method employing a large basis set. It was concluded that the ground state of {Ni(CO)} is $^1\Sigma^+$. Some molecular properties of the two states were computed and compared [454]. The theoretical background of the model potential method was reviewed, with the emphasis on practical aspects of preparation of atomic model potentials. The newly constucted basis sets and model parameters were used in calculations on a number of species, including {Ni(CO)} and $[Ni(CO)_4]$ [455]. The interaction of nickel with CO, H_2O or R_3P was studied at the CASSCF and contracted CI level. The effects of adding one, two or four CO ligands were discussed in detail [456]. Effective core potentials were used to calculate SCF equilibrium geometries and properties of mono and tetracarbonyls of nickel, palladium and platinum [457].

Calculations on the electronic structure of $[Ni(CO)_4]$ by the method of SCF X_α wave scattering have been undertaken. The results of the calculations were compared with experimental data from X-ray emission, X-ray absorption and PES [458]. The geometry of $[Ni(CO)_4]$ was optimised with basis sets of varying size, the larger ones being of near Hartree-Fock quality. The best basis sets give a metal-ligand bond distance 0.097 Å longer than that determined experimentally. Relativistic corrections were obtained at the level of first-order perturbation theory, and yield a nickel-carbon bond contraction of 0.026 Å [459]. Assuming tetrahedral symmetry, an optimisation of the geometry of [Ni(CO)$_4$] was performed using the LCGTO X_α method. The results obtained for the metal-carbon bond length, the dissociation energy and the stretching frequency were compared with experiment; the calculation leads to an overestimate of the metal-carbon bond strength [460].

Calculations of the X-ray absorption spectra and diffuse LEED intensity patterns were used to illustrate the extraction of local structural parameters for atomic and molecular adsorbates on clean surfaces. Among the sytems considered was [Ni(CO)$_4$] on Ni<111> [461]. The results for the first overlapping sphere Z_α-SW chemical shift calculation proved useful in reproducing ^{13}C nmr spectroscopic data for [Ni(CO)$_4$] [462].

The concept of absolute electronegativity was used to show that the transition metal acts as a Lewis base and carbon monoxide as a Lewis acid in the neutral metal carbonyls of nickel, palladium and platinum. π-Bonding is dominant, and estimates of the mean bond strength could be made [463]. Hartree-Fock-Slater calculations were reported on protonation energies for nickel, palladium and platinum tetracarbonyls [464].

There have been a number of reports of the use of [Ni(CO)$_4$] as a precursor of the metal, in the form of films or coatings [465]. One interesting patent abstract described the formation of a nickel coating from [Ni(CO)$_6$]! [466]. Passivation coatings for surfaces of iron recording powders with thicknesses of 2.5-30 Å were prepared by contacting the iron powder with [Ni(CO)$_4$] and decomposing the carbonyl [467,468]. Aluminium powder of 50-100 µm was coated with nickel by dissociation of [Ni(CO)$_4$] vapour, and the procedure was recommended for gas-spray coating of protective layers [469]. Plasma decomposition of [Ni(CO)$_4$]/PH$_3$ in argon or hydrogen as the carrier gas gave black or silver films respectively. The films formed in the hydrogen atmosphere were three times as conductive, but both were phosphorus enriched, and contained chemisorbed carbon monoxide [470].

In the decomposition of [Ni(CO)$_4$] adsorbed on the surface of activated X-ray amorphous lamellar silica, the structure crystallises. When the nickel is then selectively removed from the silica matrix, the skelton of the newly formed structure does not change [471]. Quartx optical fibres were coated with nickel from [Ni(CO)$_4$] to improve tensile strength [472]. Cu/Ni methanation catalysts were prepared by a two step method involving precipitation of copper on silica, followed by deposition of nickel by decomposition of [Ni(CO)$_4$] [473].

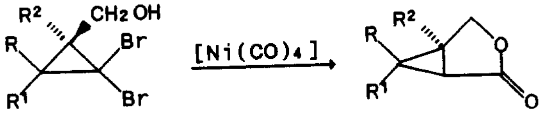
A dispersion of PTFE was added to a mixture of [Ni(CO)$_4$] powder and water, and blended to make a paste, to which ethanol was added to give a gum-like aggregate useful for thin water repellant films for electrodes [474].

A chromatographic method has been used to determine $[Fe(CO)_5]$ and $[Ni(CO)_4]$ in fluid streams, using 10 % squalene on Chromosorb W [475]. Zeolite X shows a high capacity, up to 25 % by weight, for $[Ni(CO)_4]$. Some decoposition occurs at room temperature under nitrogen to give an orange species which is very reactive, and which has spectroscopic properties consistent with the unsaturated $\{Ni(CO)_3\}$. Thermolysis gave black material with an undefined metal phase [476]. The influence of composition and distillate formation rate on the temperature of condensation of a gaseous mixture of $[Ni(CO)_4]$ and $[Fe(CO)_5]$ has been studied experimentally and predicted theoretically [477].

A review of the chemiluminescence of organometallics included discussion of $[Ni(CO)_4]$ [478]. A portable chemiluminescent detector for $[Ni(CO)_4]$ has been improved [479].

Laser induced vibrational energy transfer in $[Fe(CO)_5]$ has been studied. The deactivation of excited species by collision with $[Ni(CO)_4]$ was measured [480]. A frequency doubled CO_2 laser of modest output energy has been used to study, for the first time, the IR multiphoton absorbtion by, and dissociation of $[Ni(CO)_4]$. The multiphoton cross section was measured, and shown to be high (σ approx. 2×10^{-17}). Pressure measurements showed that the final products were Ni and CO, and the extensive decarbonylation along the ground state surface is consistent with recent studies of the photochemistry of the molecules from excited electronic states [481].

A number of coupling reactions requiring stoicheiometric $[Ni(CO)_4]$ have been reported (reactions (7-11)) [482-488].



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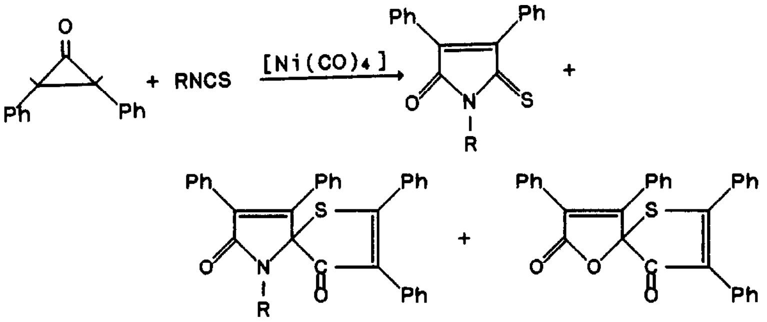

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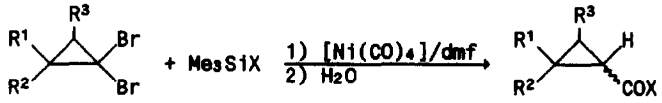

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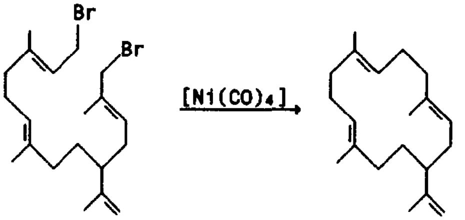

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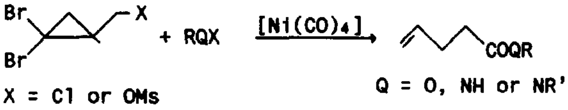

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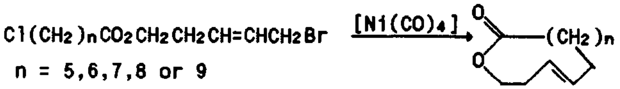

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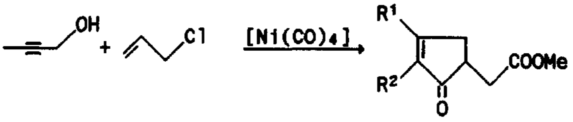
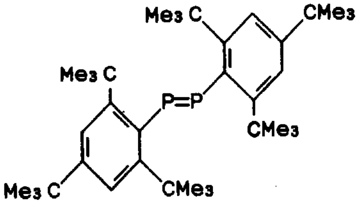


(13)

R^1 = Me, R^2 = CH_2OH 80 %
R^1 = CH_2OH, R^2 = Me 20 %

Monosubstitution of $[Ni(CO)_4]$ to give $[Ni(CO)_3L]$ has been noted using L = Me_2NPF_2 and related compounds [489], 266 [490] 267 [491] 268 [492] or 269 [493]. When $Me_2PCH_2P(Me)CH_2PMe_2$ was used as the ligand, the initial product was $[\{Ni(CO)_3\}_3L]$, but this lost $[Ni(CO)_4]$ to give the chelate 270 [494]



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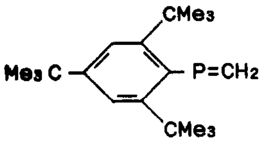

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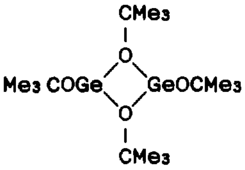

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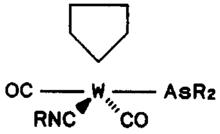

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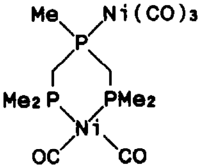
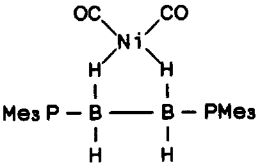


270

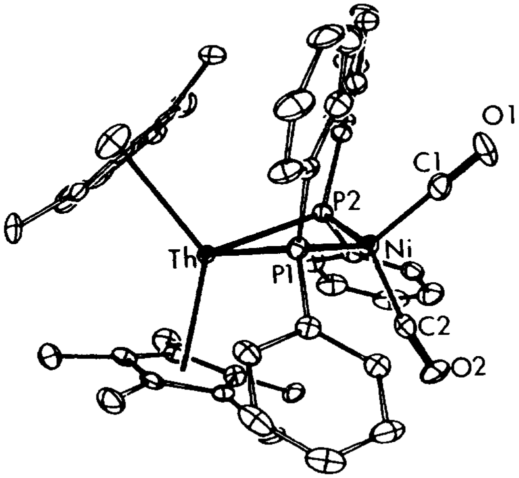
Double substitution of $[Ni(CO)_4]$ with biphosphines [495] or dmpm [496] gave complexes of the type $[Ni(CO)_2(LL)]$. When the added ligand was $P(OCH_2CF_3)_3$, $[Ni(CO)L_3]$ or $[Ni(CO)_2L_2]$ were formed, their proportions depending on the reaction stoicheiometry [497]. With $B_2H_4.2PMe_3$ the species 271 was formed in an equilibrium reaction [498].



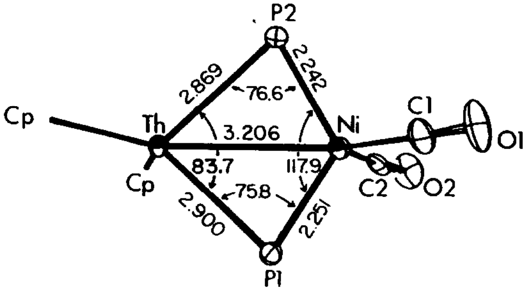
271

The complexes $[HfCp_2(PEt_2)_2]$ and $[ThCp^*_2(PPh_2)_2]$ both reacted with $[Ni(CO)_4]$ to give $[\{MCp_2\}(\mu\text{-}PPh_2)_2\{Ni(CO)_2\}]$. The structure of 272 was established in a diffraction study; the metal-metal distance is rather short

[499,500].

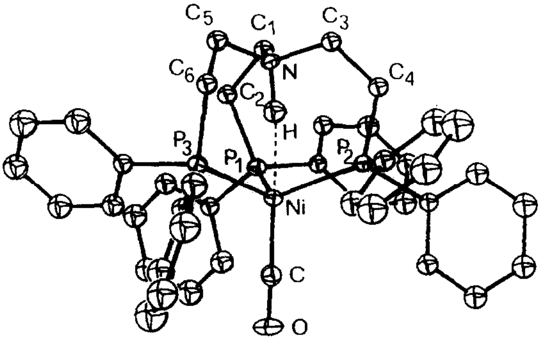


272a Overall geometry of the [$\{ThCp*_2\}(\mu-PPh_2)_2\{Ni(CO)_2\}$] molecule (ORTEP II diagram, 30 % thermal ellipsoids). (Reproduced with permission from [500])



272b Geometry of the $\{Th(\mu-P)_2Ni\}$ core with distances shwon in Ångstroms and angles in degrees. (Reproduced with permission from [500])

A number of syntheses of nickel carbonyl complexes involve carbonylation reactions. For example, reaction of [$Ni(\eta^6-C_6H_6)(SiCl_3)_2$] with carbon monoxide gave [$Ni(CO)_3(SiCl_3)_2$]. The structure of this pentacoordinate complex was established in a diffraction study; the nickel adopts trigonal bipyramidal geometry with the silicon ligands axial [501]. The complex [Ni(cdt)(CO)] could be produced by low temperature carbonylation of either [$Ni(cdt)(PPh_3)$] or [Ni(cdt)]. A range of reactions of the product were studied [502]. Carbonylation of [$NiH(np_3)$][BPh_4] (np_3 = $N(CH_2CH_2PPh_2)_3$) gave [$Ni(CO)(Hnp_3)$][BPh_4], 273. The coodination of nickel was shown to be tetrahedral, but there is a significant interaction between the metal and the proton on the nitrogen atom [503]. Carbonylation of $[(ZrCp^{*})(\mu\text{-}OCH_2PPh_2)_3\{Ni(PPh_2CH_2OH)\}]$ gave $[(ZrCp^{*})(\mu\text{-}OCH_2PPh_2)_3\{Ni(CO)\}]$, characterised in a diffraction study [504].



273 Perspective view of the complex cation $[Ni(CO)(Hnp_3)]^{+}$; ORTEP drawing with 30 % thermal ellipsoids. (Reproduced with permission from [503])

The electrochemical synthesis of $[Ni(PPh_3)_4]$ from $[Ni(acac)_2]$ has been described. If the reaction was carried out under carbonylation conditions a mixture of $[Ni(CO)_3(PPh_3)]$ and $[Ni(CO)_2(PPh_3)_2]$ was obtained; carbonylation occurs after reduction [505]. Carbonylation of a mixture of $[Ni(NHAr)_x(PPh_3)_2]$, $x = 1$ or 2, gave a mixture of $[Ni(CO)_2(PPh_3)_2]$ and *cis*-$[Ni(CO)_2(NHAr)_2]$ [506].

Carbonylation of $Ni(CN)_2$ gave $[Ni(CO)_2(CN)_2]$, which reacted with $[R_4N][OH]$ to yield $[R_4N][Ni\{C(=N)OH\}(CN)(CO)_2]$. Proton transfer and loss of $\{HNCO\}$ yielded $[R_4N][Ni(CN)(CO)_3]$, which was able to undergo oxidative addition of allyl halides, giving $[Ni(\eta^1\text{-}CH_2CH=CH_2)(CN)(CO)_2]$. Overall, catalytic carboxylation of the organic halide was accomplished [507].

Electrochemical reduction of nickel perchlorate in the presence of CO and phosphines gave only nickel(0) carbonyl phosphine complexes, with no evidence for nickel(I) or nickel(II) carbonyl intermediates [508]. Reaction of $[Ni(PCy_3)_2]$ with C_3O_2 gave successively $[Ni(CO)_2(PCy_3)_2]$ and $[Ni(CO)_3(PCy_3)]$. When the reaction was followed by IR spectrsocopy a band at 2080 cm^{-1} appeared rapidly, and decayed gradually. This was atrributed to a ketene type intermediate [509].

The complex $[Ni(np_3)]$ reacted with methanal to give a paramagnetic nickel(I) complex, $[Ni(np_3)(CHO)]$ which was more slowly transformed to $[Ni(CO)(np_3)]$ [510]. Reaction of $MeC(CH_2X)_3$ (X = Br or I) with $[Ni(CO)(Cp)]^{-}$ gave $[\{Ni(CO)(Cp)\}_2]$, $[Ni_3(CO)_2(Cp)_3]$ and $[Ni(C_5H_9)(CO)(Cp)]$, in which $\{C_5H_9\}$

was 1-methylcyclopropylmethyl. A mechanism for the reaction, and for the formation of the small amounts or ring-opened product seen, was proposed [511].

The structure of $[Ni(bipy\text{-}2,4\text{-}Me_2)(CO)_2]$ was established in an X-ray diffraction study; the torsion angle between the rings of the bipy ligand was 4.3 ° [512].

Geometry optimisation within the CNDO version of the MO-LCAO-SCF approach for complexes $[NiL_3X]^q$ (L = Cl or NH_3; X includes CO) has been described [513]. The He(I) and He(II) PES for $[Ni(CO)_2(Me_3CN{=}CH\text{-}CH{=}NCMe_3)]$ have been analysed [514]. EPR spectroscopic data were obtained for $[Ni(CO)_2(PPh_3)_2]$ grafted onto $\gamma\text{-}Al_2O_3$ or SiO_2 and reacted with $EtAlCl_2$; these showed the presence of nickel(I) derivatives [515]. A study of the complexes $[Ni(CO)_3(PR_3)]$ was used to determine the χ values for 157 phosphine ligands. The deviations from Tolman's additivity rule followed a predictable pattern [516].

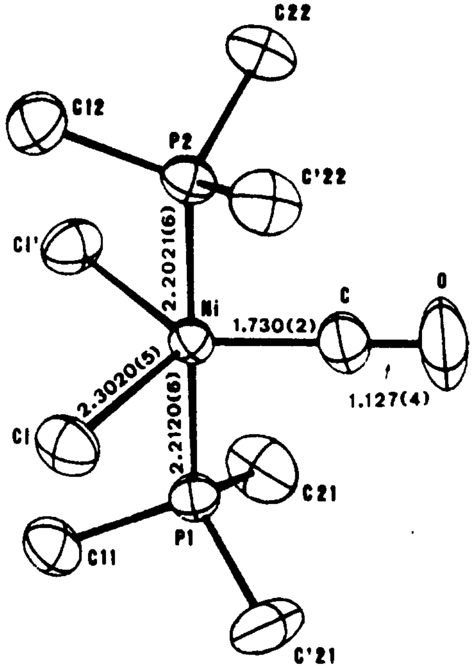
Reaction of $[Ni(CO)_2(PPh_3)_2]$ with cyanogen gave $[Ni(CN)_2(PPh_3)_2].C_2N_2$. A diffraction study showed that the cyanogen was trapped in the solid matrix, but not nickel bonded [517,518].

In the previously described complex $[Ni(CO)I_2(PMe_3)_2]$ the nickel carbon bond was the shortest recorded. The chloride complex, 274, has now been shown to be isomorphous, with a similar nickel-carbon bond length [519].

Reaction of $[Ni(CO)_4]$ with Ph_2PLi gave $Li[(OC)_3Ni(\mu\text{-}PPh_2)Ni(CO)_3]$, which could be converted to the $[Ph_3P\text{-}N{=}PPh_3]^+$ salt. In trichloromethane coupling of the nickel centres occurred, giving $[Ni_2(CO)_4(\mu\text{-}PPh_2)_2]$ with a nickel-nickel bond [520].

The electronic structure of {Pd(CO)} was studied by means of effective core potential calculations, including configuration interaction. A study of the $^3\Sigma^+$ and $^1\Sigma^+$ states showed that the low spin states are bound, and the high spin states repulsive. The bonding energy was estimated as 30.1 kJ mol^{-1} and the equilibrium bond length as 4.03 au [521].

The concept of absolute electronegativity has been used to show that transition metals act as Lewis bases and carbon monoxide as a Lewis acid in neutral metal carbonyls. This implies that π-bonding is dominant, with some σ-bonding being induced. Values of absolute electronegativity and absolute hardness were calculated for the metals in low spin valence states. Thus the instabilities of $[Pd(CO)_4]$ and $[Pt(CO)_4]$ were correctly predicted [522]. Equilibrium geometries and harmonic frequencies of {PtXY} (XY = CO, N_2 $[CN]^-$ or $[NO]^+$) in the $^1\Sigma^+$ states were calculated by the *ab initio* SCF method with gradients using appropriate effective core potentials. The calculated results for {Pt(CO)} and {Pt(N_2)} were compared with IR spectroscopic data for the matrix isolated species [523]. The electronic properties of $[PtLCl_3]^n$ (L = $[CN]^-$, CO, $[NO]^+$ or N_2) were calculated by the linear combination of fragment MOs within the CNDO approximation. The donor properties of the ligands were discussed in terms of MO populations [524].

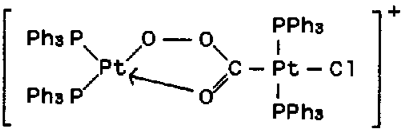


274 ORTEP drawing of $[NiCl_2(CO)(PMe_3)_2]$. (Reproduced with permission from [519])

Cocondensation of platinum atoms with oxalyl chloride gave *cis*-$[PtCl_2(CO)_2]$ as colourless crystals [525]. It has been reported that this complex may exist in tetrahedral or *cis*-planar forms, depending on the aggregate state and the solvent [526,527]. The structures and properties of platinum films obtained from $[Pt(CO)_2Cl_2]$ in MeCN by thermal dissociation on amorphous alumina, single crystal KCl or glass ceramics, have been studied [528].

Reaction of $[PdX_4]^{2-}$ (X = Br, (OCOMe), or X_2 = (SO_4)) with CO gave $[Pd(CO)X_3]^-$ in a reversible reaction. Hydrolysis of the product yielded CO_2 and palladium(0), and the reaction was accelerated in the presence of oxygen. Carbonylation of $[Pt(CH_3CN)Cl(PPh_3)_2]+$ gave $[PtCl(CO)(PPh_3)_2]X$ (X = $[PF_6]^-$, $[ClO_4]^-$ or $[OTs]^-$) [530].

Reaction of $[Pt(PPh_3)_2(O_2)]$ with $[PtCl(CO)(PPh_3)_2]^+$ gave 275, which could be substituted with PPh_3 to yield 276 [531]. When *cis*-$[Pt\{As(CMe_3)_3\}Cl_2(CO)]$ reacted with PR_3, the arsine was the ligand replaced, giving the *cis*-product [532]. Reaction of $[PtCl_2(\mu\text{-}Cl)_2(CO)_2]$ with CO gave *trans*-$[PtCl_2(CO)_2]$ as the kinetic product, which was converted to the *cis*-isomer as the thermodynamic product. The same reaction is not possible in the palladium series, because of the lower Pd-CO bond strength [533].



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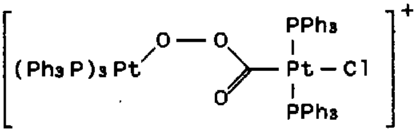

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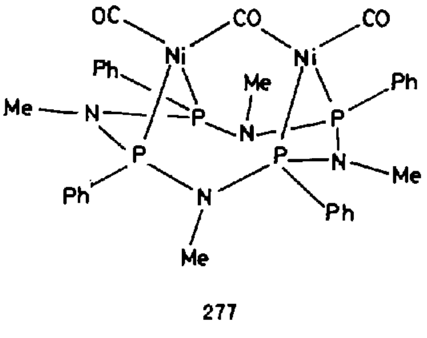
6.2 Binuclear carbonyl complexes

γ-Irradiation of $[Ni(CO)_4]$ in a krypton matrix at 77 K gave three binuclear nickel carbonyl radicals, detected by EPR spectrsocopy. The species $[Ni_2(CO)_8]^+$ and $[Ni_2(CO)_6]^+$ each had two bridging carbonyl ligands, whilst $[Ni_2(CO)_7]^-$ had a single carbonyl bridge [534]. The photochemical disproportionation of metal-metal bonded carbonyl dimers, including $[\{Ni(CO)(Cp\}_2]$ has been reviewed [535].

Reaction of the ligand $(MeNPPh)_4$ with $[Ni(CO)_4]$ gave $[LNi_2(CO)_3]$, 277. This could be oxidised to $\{MeNP(=O)Me\}_4$ [536]. Two isomers of $[Ni_2(CO)_4\{\mu\text{-}P_3(CHMe_2)_3\}_2]$ were formed from the reaction of the ligand with $[Ni(CO)_4]$. They were characterised by nmr spectroscopy [537].



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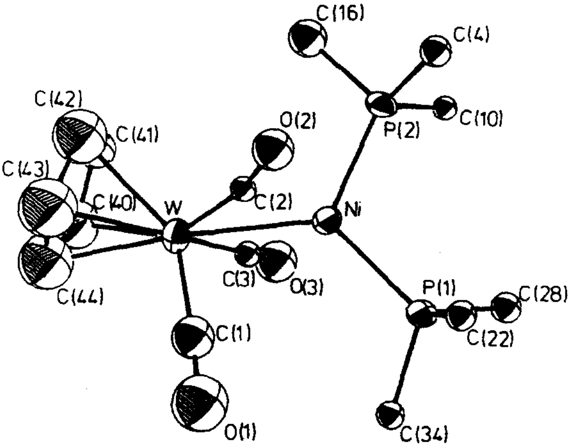
When $[NiCl_2(PPh_3)_2]$ was treated with $Na[M(CO)_3Cp]$ (M = Mo or W), 278, with two semibridging carbonyl groups, was formed. Calculations suggested that the metal-metal interation was not very strong. CV studies indicated a reversible one-electron oxidation to $[NiW(CO)_3(Cp)(PPh_3)_2]^+$ [538].



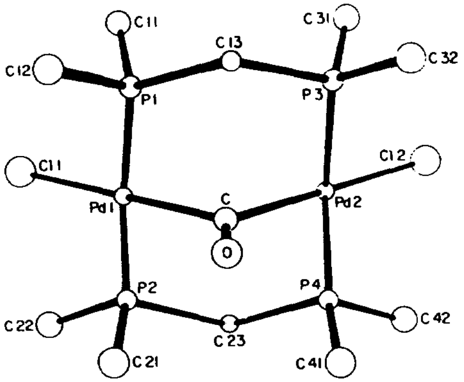
278 X-ray crystal structure of $[NiW(CO)_3(PPh_3)_2(\eta_5\text{-}C_5H_5)]$. Apart from the carbon atoms bonded to phosphorus, the remaining phenyl group carbon atoms have been omitted for clarity. (Reproduced with permission from [538])

The preparation of $[Pd_2Cl_4(CO)_2]$ from $PdCl_2$ and CO in $SOCl_2$ was studied as a function of temperature and CO pressure. The data obtained were used to deduce a value of 100 kJ mol^{-1} for the palladium-carbon bond energy. Reaction of the dimer with CO in ethanoic anhydride gave the polymer $[\{PdCl(CO)\}_n]$ [539]. Carbonylation of $[PdH(PPh_3)_3]^+$ gave $[\{Pd(PPh_3)_2\}(\mu\text{-}CO)(\mu\text{-}H)\{Pd(PPh_3)_2\}]$, *via* reaction of $[PdH(PPh_3)_3]^+$ with $[Pd(CO)(PPh_3)_2]$ [540].

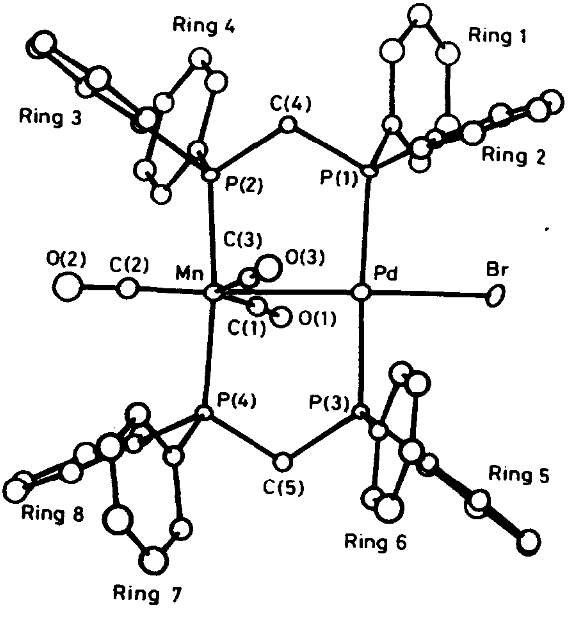
Carbonylation of $[Pd_2Cl_2(\mu\text{-}dmpm)_2]$ gave the A-frame complex, 279, characterised in a diffraction study. The related reaction with $[Pd_2(\mu\text{-}dmpm)_2(OH)_2]$ was reversible, and with the {OPh} derivative, insertion into both the Pd-Pd and the Pd-O bonds occurred [541]. The kinetics of the carbonylation of $[Pd_2(\mu\text{-}dppm)_2X_2]$ to give $[Pd_2(\mu\text{-}CO)(\mu\text{-}dppm)_2X_2]$ (X = Cl, Br or [NCO]) were studied. Insertion of CO is very selective over reaction with O_2, CO_2, H_2, C_2H_4 or C_2H_2 [542].

When $[Pd(dba)_2]$ was treated with $[Mn(CO)_5X]$ in the presence of dppm, the complex $[MnPd(CO)_3(\mu\text{-}dppm)_2X]$ was produced (X = Cl, Br or I). The bromo complex, 280, was structurally characterised, and two of the CO ligands were semi-bridging [543].

Carbonylation of *head-to-tail*-$[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SMe)_2]$ gave $[Pt_2Cl_2(CO)_2(Ph_2PCH_2SMe\text{-}P)_2]$, in which there was an unsupported metal-metal bond [544].



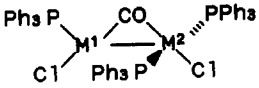
279 Drawing of $[Pd_2Cl_2(\mu\text{-CO})(\mu\text{-dmpm})_2]$ showing all non-hydrogen atoms. (Reproduced with permission from [541])



280 (Reproduced with permission from [543])

Reaction of $Ph_2AsCH_2PPh_2$ (dapm) with $[Pt(cod)X_2]$ gave either $[Pt(dapm)X_2]$ or *cis*-$[Pt(dapm\text{-}P)_2X_2]$, depending on the reaction stoicheiometry. The latter species (X = Cl) reacted with $[Pt(dba)_2]$ to give $[Pt_2Cl_2(\mu\text{-dapm})_2]$, which could be carbonylated to $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dapm})_2]$ as a mixture of *head-to-head* and *head-to-tail* isomers [545]. The complex *cis,mer*-$[MnCl(CO)_2(dppm\text{-}P,P')(dppm\text{-}P)]$ reacted with $[Pt(PPh_3)_4]/CO$ to give $[MnPtCl(CO)_3(\mu\text{-dppm})_2]$, in which two of the carbonyl groups were semi-bridging [546].

Treatment of $[M^1(CO)(PPh_3)_3]$ with $[M^2(PhCN)_2Cl_2]$ (M^1, M^2 = Pd or Pt) gave 281. If the asymmetric carbonyl ligand is formally assigned to M^1, both metals may be considered to be 16e centres [547]. The μ-phosphido metal hydride complex 282 (M = Cr, W or Mo) was formed by oxidative addition of a phosphorus-hydrogen bond to platinum(0). Insertion of cod into the metal hydride yielded 283, and further reactions were studied (Scheme 9) [548]. A similar reaction was noted for $[Re(CO)(Cp)(NO)(PCy_2H)]^+$ and $[Pt(C_2H_4)(PPh_3)_2]$ (Scheme 10) [549], and some further reactions of molybdenum and tungsten complexes were noted (Scheme 11). In this case there were differences between the molybdenum and tungsten series, related to the greater ease of oxidation of tungsten, and the greater bond strengths af third *versus* second row metal hydride bonds [550].



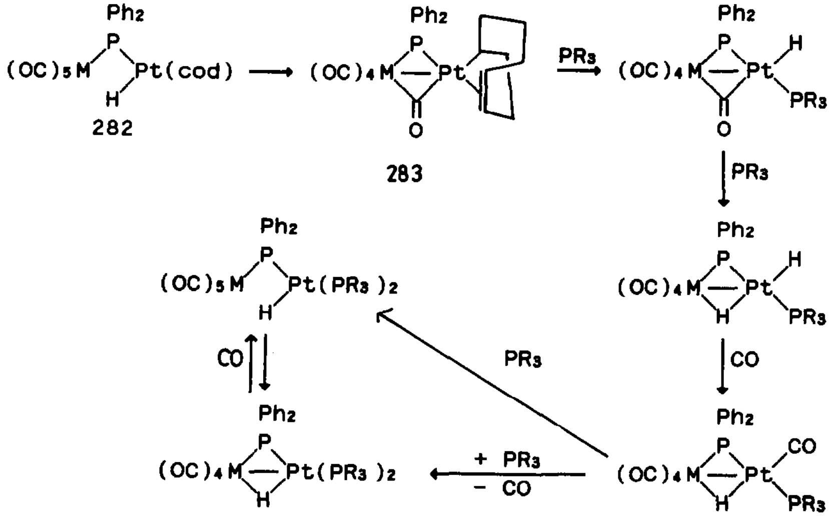
281

The structure of 284 has been established in a diffraction study. Fluxional behaviour was noted in the ^1H nmr spectroscopic timescale, attributed to a unique rotation of the $\{PtL_2\}$ unit about the Mn-H bond [551].

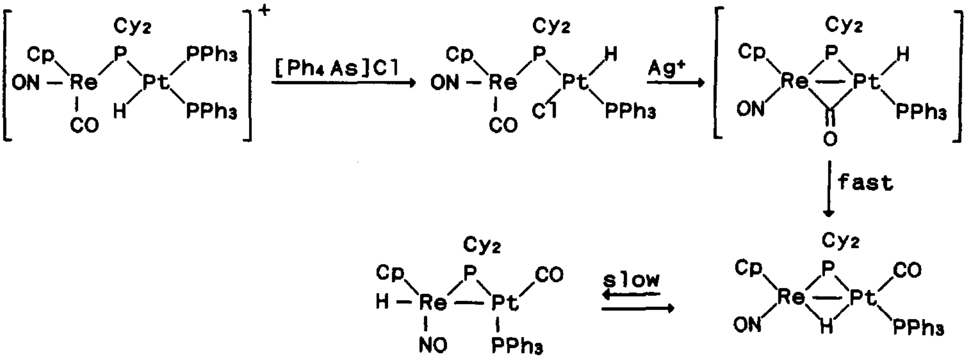
6.3 Trinuclear carbonyl complexes

The cluster $[(\mu_3\text{-}Me_3CP)\{Co(CO)_3\}\{Fe(CO)_3\}\{Ni(CO)_2(Cp)\}]$ has been investigated electrochemically. The radical anion, generated in this way, undergoes fragmentation under all conditions [552].

Carbonylation of $[Pd(dppm)(OCOMe)_2]$ in the presence of an excess of trifluoroethanoic acid gave $[Pd_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, *via* binuclear derivatives. Spectroscopic evidence was presented for some of the intermediates in the reaction [553]. The trimeric complex reacted reversibly with anions, X^-, (X = Cl, Br, I or $[CF_3CO_2]^-$), to give $[Pd_3(\mu_3\text{-CO})(\mu\text{-dppm})_3(\mu_3\text{-X})]^+$. The equilibrium constants were in the order $I^- > Br^- > Cl^- > [CF_3CO_2]^-$, as might have been expected for covalent interaction with the soft palladium centre. The structure of the chloro derivative was established in a diffraction study; the Pd-Cl distances at 2.741-3.161 Å are too long for ordinary covalent bonding [554].

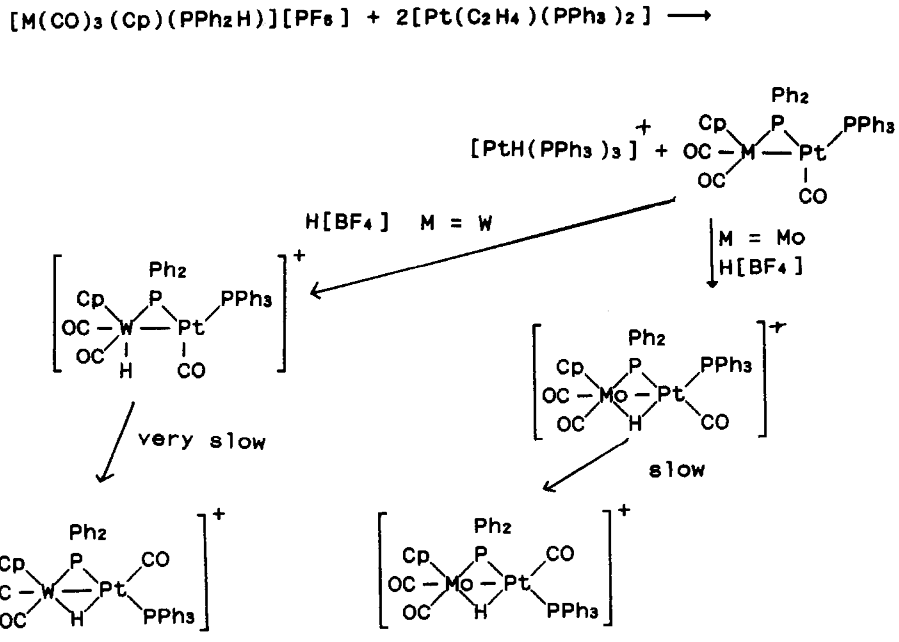


Scheme 9 Reactions of platinum carbonyl μ-phosphido complexes [548]

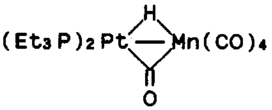


Scheme 10 Reactions of rhenium platinum μ-phosphido complexes [549].

When $[Pd_2Cl_2(\mu\text{-dppm})_2]$ was reacted with $Na_2[Fe(CO)_4]$ the product was $[Pd_2Fe(CO)_4(\mu\text{-dppm})_2]$, 285, which catalysed reaction (14). When the substrate was the mixed palladium platinum dimer both possible product isomers were obtained, and could not be separated [555]. Comparable reactions were noted between $[PdPtCl_2(\mu\text{-dppm})_2]$ and $Na[Co(CO)_4]$ or $Na[Mn(CO)_5]$, except that in these cases the trinuclear core was attached to a further $\{Co(CO)_4\}$ or $\{Mn(CO)_5\}$ unit as in 286. In these cases a palladium-phosphorus bond was opened regioselectively [556].



Scheme 11 Reactions of platinum carbonyl μ-phosphido complexes [550].



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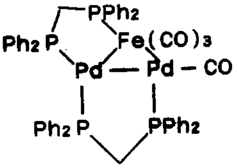

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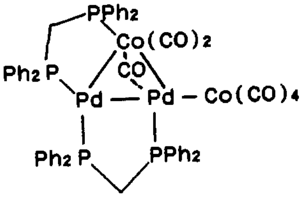

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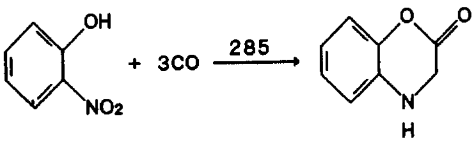


(14)

Metal-metal bonding and antibonding orbitals were considered for triangular complexes of the type $[M_3L_6]$; $[Pt_3(CO)_6]^{2-}$ was taken as a classic example of a 44e unsupported structure with three terminal and three bridging ligands [557].

The structure of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ was established in a diffraction study [558]. Reaction of $[Pt_3(\mu\text{-}X)_3(PCy_3)_3]$ (X = CO or SO_2) with dppp gave $[Pt_3(dppp)(PCy_3)_2(\mu\text{-}X)_3]$. The structure of the SO_2 bridged complex was established in a diffraction study, and that of the CO bridged species was comparable. The chelating biphosphine adopted a low symmetry conformation with respect to the $\{Pt_3\}$ plane, so that the other two phosphine ligands were inequivalent on the nmr spectroscopic timescale at low temperature [559].

Phosphine exchange in the complexes $[Pt_3(\mu\text{-}CO)_3L_3]$ (L = $P(CMe_3)_3$, $P(CMe_3)_2Ph$ or PCy_3) with added phosphine L' (L' = $P(CMe_3)_2Ph$, $P(CMe_3)Ph_2$, PCy_3 or $P(CHMe_2)_3$) has been studied. The process was shown to be an associative one, with the $\{Pt_3\}$ unit remaining intact. ^{13}CO was scrambled between clusters in a much slower reaction. Reactions of the clusters with CS_2 COS or SO_2 to give dimers was discussed [560]. Skeletal rearrangements of methylcyclopentane were reported to be catalysed by $[Pt_3(CO)_3L_4]$ (L = phosphine ligand) on alumina, but it was not clear what was the catalytically active species [561].

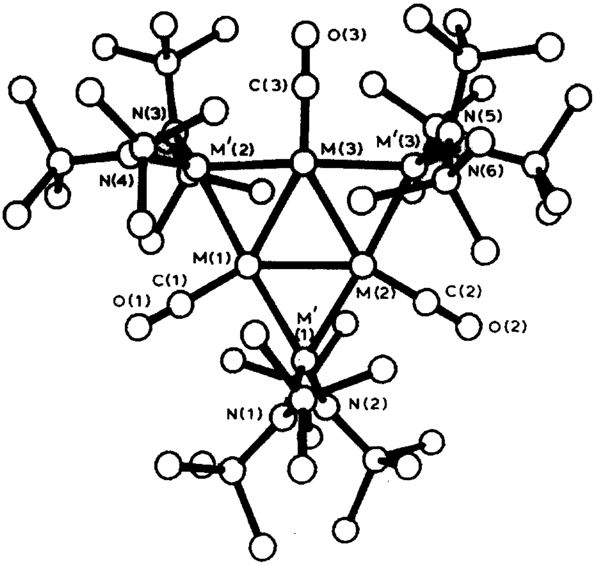
Reduction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ with $Na[BH_4]$ gave $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3(\mu_3\text{-}H)]^+$. This lost CO to give $[Pt_3(\mu\text{-}dppm)_3(\mu_3\text{-}H)]^+$, which was also obtained directly by sodium amalgam treatment of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ [562].

The preparation and characterisation of $[\{M(\mu_2\text{-}M'\{NR_2\}_2)(CO)\}_3]$ (M = Pd or Pt, M' = Ge or Sn, R = $SiMe_3$) has been reported. The complexes undergo reversible one electron reduction in thf at -1.2 V to give radical anions characterised by EPR spectrsocopy. The structure of 287 was established in a diffractions study [563].

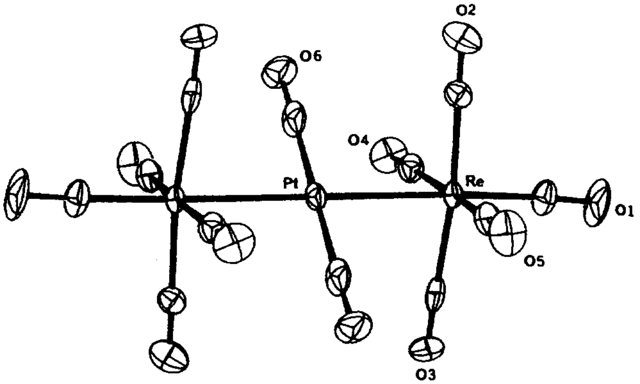
Reaction of $[Pt(cod)Me_2]$ with an excess of $[HM(CO)_5]$, under an atmosphere of CO, gave $[PtM_2(CO)_{12}]$ (M = Re or Mn). the presence of $[M_2(CO)_{10}]$ as a by-product of the reaction suggests that it proceeds through a radical pathway. In 288 the platinum adopts square planar geometry [564,565]. The structure of the manganese derivative has also been established [566].

Reaction of $[MoRh(\mu\text{-}CO)_2(CO)(Cp)(PPh_3)]$ with $[Pt(C_2H_4)(PPh_3)_2]$ gave $[MoPt(CO)_2(Cp)(PPh_3)_2(\mu\text{-}PPh_2)]$ and the trinuclear species, $[MoRhPt(\mu\text{-}1\text{-}\sigma\text{:}1\text{-}2\text{-}\eta\text{-}C_6H_5)(\mu\text{-}CO)_2(Cp)(PPh_3)_2(\mu\text{-}PPh_2)]$, 289, the structure of which was established in a diffraction study. The Mo-Rh bond is bridged by two CO ligands and the Mo-Pt bond by $\{PPh_2\}$. The Rh-Pt bond is bridged by a phenyl group; one carbon atom is σ-bonded to platinum and the adjacent π-bond is η^2-ligated to rhodium [567]. Thermolysis of the known butterfly cluster $[Co_2Pt_2(CO)_8(PPh_3)_2]$ in the solid state gave

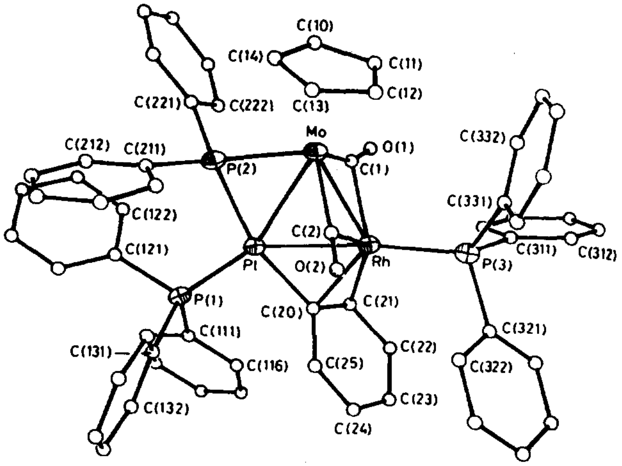
$[CoPt_2(\mu\text{-}CO)_2(CO)(PPh_3)_3(\mu\text{-}PPh_2)]$. The platinum-platinum distance falls in the appropriate range for {Pt(I)-Pt(I)}, and a formal description of the structure would therefore be that it is bridged by $\{\mu\text{-}PPh_2\}^-$ and $\{\mu\text{-}Co(CO)_3(PPh_3)\}^-$, both acting as 4e donors [568].



287 The molecular structure and atom numbering scheme for $[\{M(\mu_2\text{-}Sn\{NR_2\}_2)(CO)\}_3]$, M = Pd or Pt. The $\{M_3Sn_3\}$ units are nearly coplanar. (Reproduced with permission from [563])



288 ORTEP diagram of the molecular structure of $[Re_2Pt(CO)_{12}]$. The platinum-rhenium bond length is 2.8309(5) Å and the carbonyl groups on rhenium are eclipsed. (Reproduced with permission from [564])



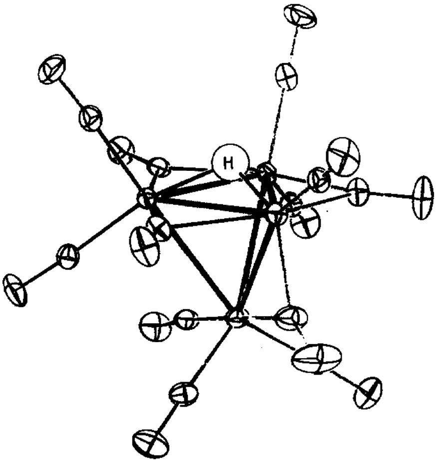
289 The molecular structure of $[MoRhPt(\mu\text{-}C_5H_5)(\mu\text{-}1\text{-}\sigma\text{:}1\text{-}2\text{-}\eta\text{-}C_8H_8)(\mu\text{-}CO)_2(PPh_3)_2(\mu\text{-}PPh_2)]$ showing the crystallographic numbering scheme. (Reproduced with permission from [567])

6.4 Tetranuclear metal carbonyl clusters

MO LCAO INDO theory has been applied to $\{Ni_4\}$ and higher nuclearity nickel clusters. The main contributor to bonding is the nickel-ligand interaction, but there are also significant contributions from metal-metal bonding. Among the species considered were $[Ni_4(CO)_6(\mu_2\text{-}CO)_3]^{2-}$ and $[Ni_4(CO)_6(\mu_2\text{-}CO)_3H]^-$ [569].

When $[Ni(CO)_4]$ is reacted with $[Fe_3(CO)_{11}]^{2-}$, the product is $[Fe_3Ni(CO)_{12}]^{2-}$, which may be protonated to give $[Fe_3Ni(CO)_{12}H]^-$. Salts of both anions could be isolated, and the structure of the benzyltrimethylammonium salt of the hydride, 290, was established in a diffraction study. The metal atoms form a tetrahedron with eight terminal and four edge-bridging carbonyl groups. The hydride is located over the centre of an $\{Fe_2Ni\}$ face at a distance of 0.60(3) Å from the trimetal plane [570].

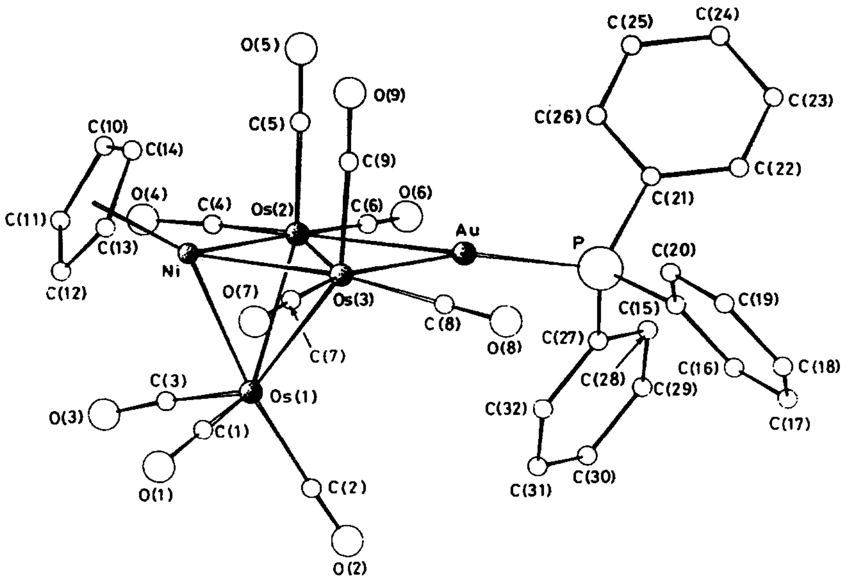
It has been noted that $[Os_3(CO)_{10}H_2]$ reacts with $[\{Ni(CO)(Cp)\}_2]$ under a hydrogen atmosphere to give $[NiOs_3(CO)_9(Cp)H_3]$ [571]. Reaction between $[Os_3(CO)_{10}H_2]$ and $[NiCl(H)(PCy_3)_2]$ gave $[NiOs_3(CO)_{10}(H)_2(PCy_3)]$. The structure of the product was assigned on the basis of spectroscopic data, and comparison with the platinum analogue. The metal atoms form a tetrahedron with each osmium atom ligated by three terminal carbonyl ligands, and the nickel atom by PCy_3. One Os-Os and one Ni-Os bond are bridged by hydride ligands, and one carbonyl ligand bridges an Os-Ni bond [572]. Treatment of $[NiOs_3(CO)_9(Cp)(\mu\text{-}H)_3]$ with NaH resulted in hydride abstraction to yield $[NiOs_3(CO)_9(Cp)(\mu\text{-}H)_2]^-$. This product reacted with $[MCl(PPh_3)]$ (M = Au or Cu) to give $[NiOs_3(CO)_9(Cp)(\mu\text{-}H)_2\{\mu\text{-}M(PPh_3)\}]$; the gold complex, 291, was characterised in a diffraction study. The $\{NiOs_3\}$ unit is a tetrahedron, with an Os-Os bond bridged by a gold atom [573]. The complex $[NiOs_3(CO)_9(Cp)(\mu\text{-}H)_3]$ has been shown to be an active catalyst for the hydrogenation of alkenes, alkynes and dienes [574].



290 Perspective view of the $[Fe_3Ni(CO)_{12}H]^-$ anion with thermal ellipsoids drawn to enclose 20 % probability. (Reproduced with permission from [570])

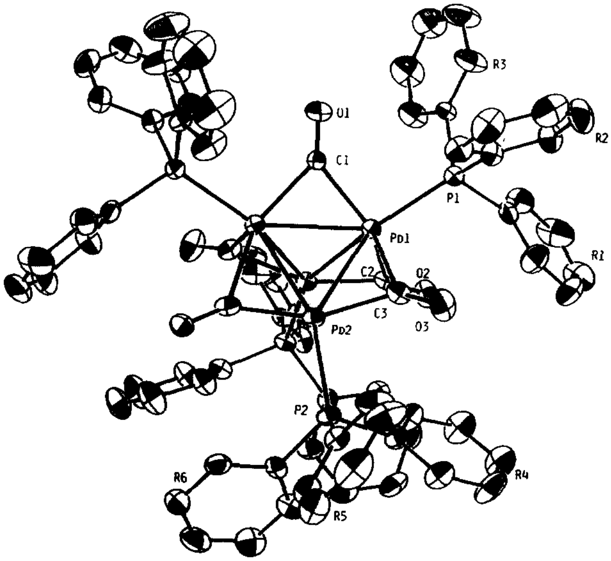
Carbonylation of $[PdL_2(NO_2)_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph or PEt_3) gave $[Pd_4(CO)_5L_4]$. The structure of the complex for which L = PPh_3, 292, was established in a diffraction study; the palladium atoms are at the corners of a distorted tetrahedron in which five of the six edges are bridged by CO. Dimeric products were obtained from PEt_2Ph derivatives [575].

The complexes $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (L = PEt_3, $PEt_2(CMe_3)$ or $PMePh_2$) were prepared from $[Pt(cod)_2]$, L, C_2H_4 and CO. The structure of the purple modification of the PMe_2Ph complex, 293, was determined in a diffraction study. The $\{Pt_4\}$ unit is a distorted edge-opened tetrahedron with five edge-bridging carbonyls and four terminal phosphine ligands [576]. The PEt_3 derivative was also reported to have been prepared from $[Pt(cod)_2]/PEt_3/CO/Me_2CO/NH_3$ [577], and its structure was established [578].

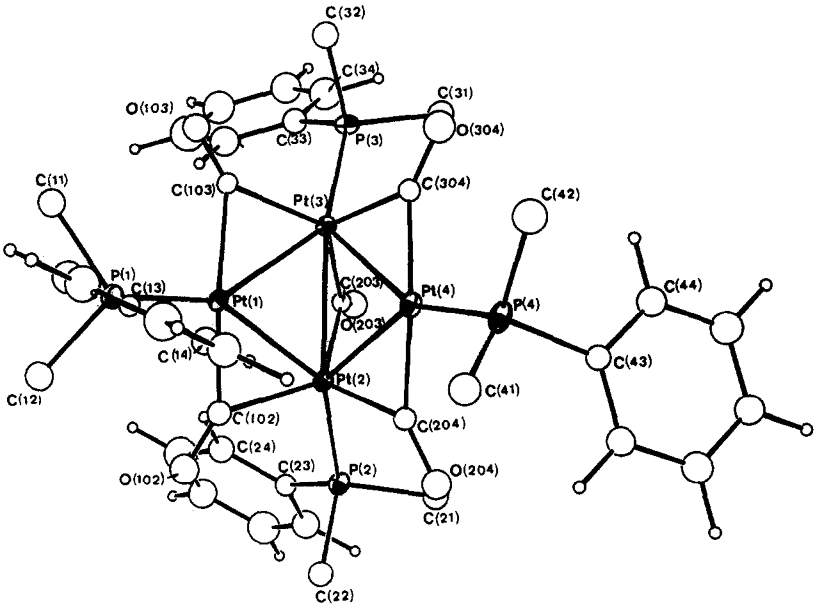


291 View of the molecule [NiOs$_3${μ-Au(PPh$_3$)}(η-C$_5$H$_5$)(CO)$_9$(μ-H)$_2$] showing the atom numbering scheme. The hydride ligands, which bridge the Os(1)-Os(2) and Os(1)-Os(3) bonds, are not represented. (Reproduced with permission from [573])

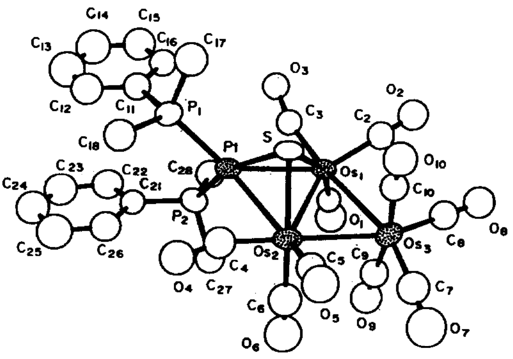
Reports of osmium-platinum clusters have been numerous. A number were discussed in a review of the synthesis, reactivity, structure and bonding of such species [579]. When [Os$_3$(CO)$_{10}$(μ_3-S)] was reacted with [Pt(PMe$_2$Ph)$_4$], the products were [Os$_3$Pt(CO)$_{10}$(PMe$_2$Ph)$_2$(μ_3-S)], 294, [Os$_3$Pt(CO)$_9$(PMe$_2$Ph)$_3$(μ_3-S)], 295, [Os$_3$Pt(CO)$_9$(PMe$_2$Ph)$_2$(μ_3-S)], and [Os$_3$Pt(CO)$_8$(PMe$_2$Ph)$_3$(μ_3-S)], 296. The complexes 294 and 295 both possess approximately planar arrays of one platinum and three osmium atoms, with sulphur bridging a {PtOs$_3$} face. Photolysis of 295 gave 296 and [Os$_3$Pt(CO)$_7$(H)(PMe$_2$Ph)$_2$(PMe$_2$C$_6$H$_4$)(μ_3-S)], 297. This latter has a tetrahedral array of metal atoms with the sulphur bridging the {Os$_3$} face [580-582].



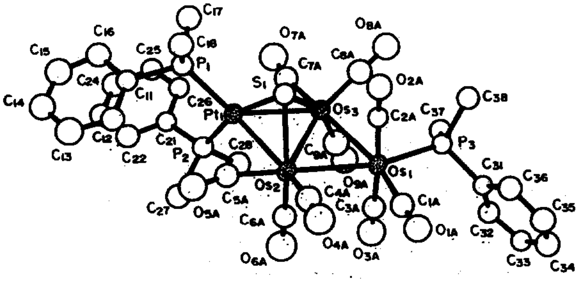
292 Molecular structure and numbering scheme for $[Pd_4(CO)_5(PPh_3)_4]$. The hydrogen atoms are omitted for clarity. (Reproduced with permission from [575])



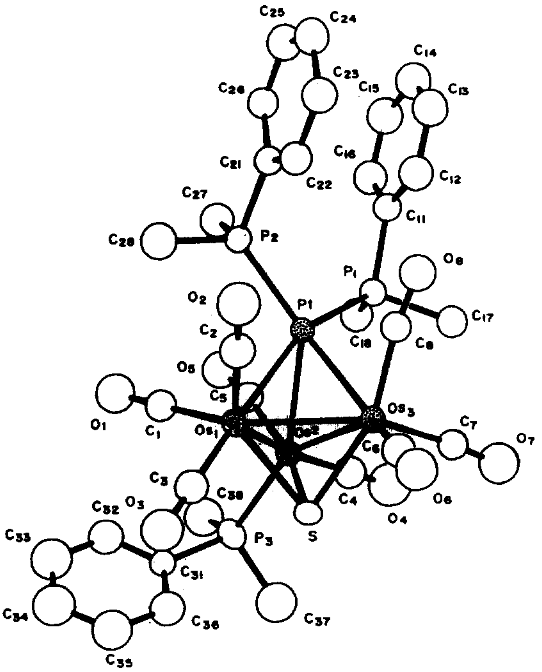
293 Perspective view and atomic numbering scheme for $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$. Thermal ellipsoids are constructed at the 30 % electron probability level except for hydrogen atoms which have an artificial radius of 0.1 Å for clarity. (Reproduced with permssion from [576])



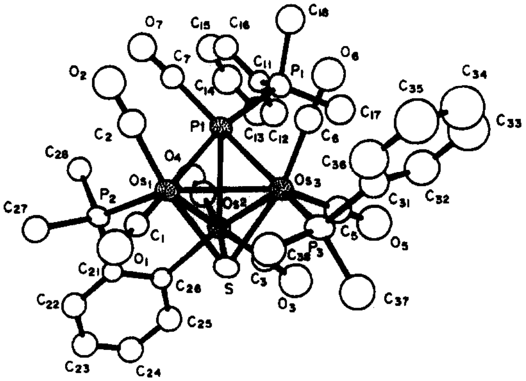
294 ORTEP diagram of $[Os_3Pt(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)]$ showing 50 % probability ellipsoids. (Reproduced with permission from [580])



295 ORTEP diagram of one of the two crystallographically independent molecules of $[Os_3Pt(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)]$ showing 50 % probability ellipsoids. (Reproduced with permission from [580])

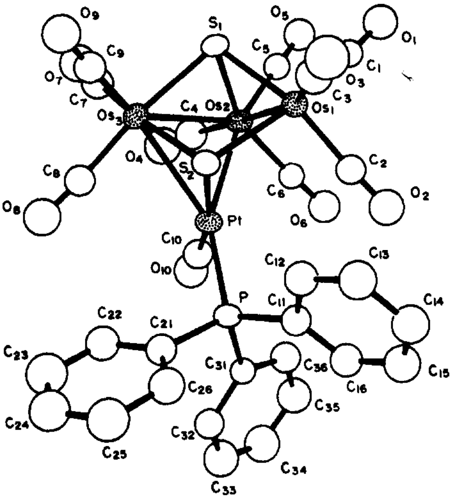


296 ORTEP diagram of [Os$_3$Pt(CO)$_8$(PMe$_2$Ph)$_3$(μ_3-S)] showing 50 % probability ellipsoids. (Reproduced with permission from [580])



297 ORTEP diagram of [Os$_3$Pt(CO)$_7$(H)(PMe$_2$C$_6$H$_4$)(PMe$_2$Ph)$_2$(μ_3-S)] showing 50 % probability ellipsoids. (Reproduced with permission from [580])

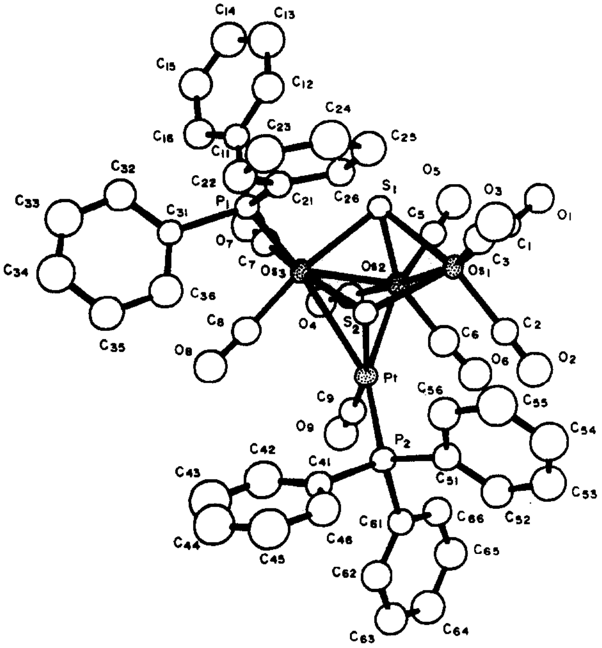
Reaction of [Os$_3$(CO)$_9$(μ_3-S)$_2$] with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] under a nitrogen atmosphere gave 34 % of [PtOs$_3$(CO)$_{10}$(PPh$_3$)(μ_3-S)$_2$], 298, and 24 % of [PtOs$_3$(CO)$_9$(PPh$_3$)$_2$(μ_3-S)$_2$], 299. When the reaction was carried out under an atmosphere of CO, the decacarbonyl was essentially the sole product. Both products were characterised by diffraction studies, and consisted of triangular $\{PtOs_3\}$ clusters with the third osmium atom linked to one of the others *via* a metal-metal bond and a bridging sulphide. The clusters are formed by insertion of $\{PtL_2\}$ into an osmium sulphur bond, followed by rearrangement [583].



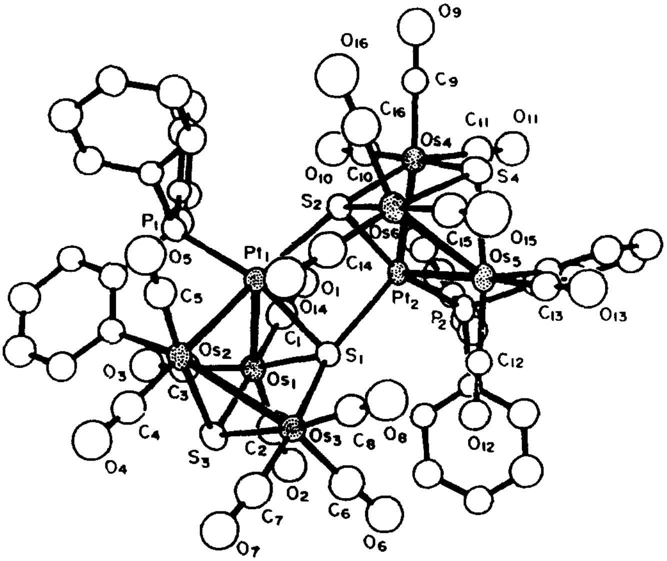
298 ORTEP diagram of $[Os_3Pt(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2]$ showing 50 % probability ellipsoids. (Reproduced with permission from [583])

Oxidation of $[Os_3Pt(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2]$ with Me_3NO resulted in decarbonylation to give a dimer, $[\{Os_3Pt(CO)_8(H)(PPh_2C_6H_4)(\mu_3\text{-}S)(\mu_4\text{-}S)\}_2]$, 300. The hydride lgands are believed to bridge the elongated osmium-osmium bonds [584].

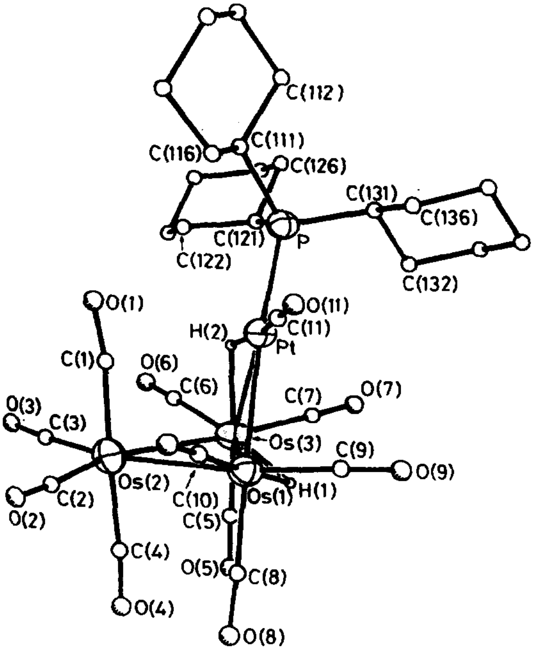
Reactions of the unsaturated cluster $[Os_3Pt(CO)_{10}(\mu\text{-}H)_2(PCy_3)]$ have been studied. Carbonylation gave the known species $[Os_3Pt(CO)_{11}(\mu\text{-}H)_2(PCy_3)]$, 301, now characterised in a diffraction study for the first time. The metal atoms adopt a butterfly arrangement with the platinum at the wingtip. One hydride bridges the Os-Os vector of the "body" and one an Os-Pt bond. The platinum atom is ligated by PCy_3 and one carbonyl, the wingtip osmium bears four carbonyls and the others three each. Hydrogenation of the unsaturated cluster gave $[Os_3Pt(CO)_{10}(\mu\text{-}H)_4(PCy_3)]$, 302, in a reversible reaction. In this case the metal atoms adopt a *closo*-tetrahedral arrangement, and the hydrides occupy edge bridging sites on two Os-Pt and two Os-Os bonds. The $\{M_4\}$ unit has D_{2d} symmetry with two short unbridged edges and four longer bridged ones. Reaction of $[Os_3Pt(CO)_{10}(\mu\text{-}H)_2(PCy_3)]$ with diazomethane gave $[Os_3Pt(\mu\text{-}CH_2)(CO)_{10}(\mu\text{-}H)_2(PCy_3)]$ as an equilibrium mixture of two isomers. In the orange-yellow form, 303, the {CH_2} bridges the Os-Os edge cisoid to the phosphine at platinum, whilst in the red form, 304, it bridges the edge transoid to PCy_3. In the orange form, hydrides bridge the other two Os-Os edges, whereas in the red form they are thought to bridge one Os-Os and one Os-Pt edge. Nmr spectroscopic studies indicated that these structures were maintained in solution and equilibrated only slowly [585].



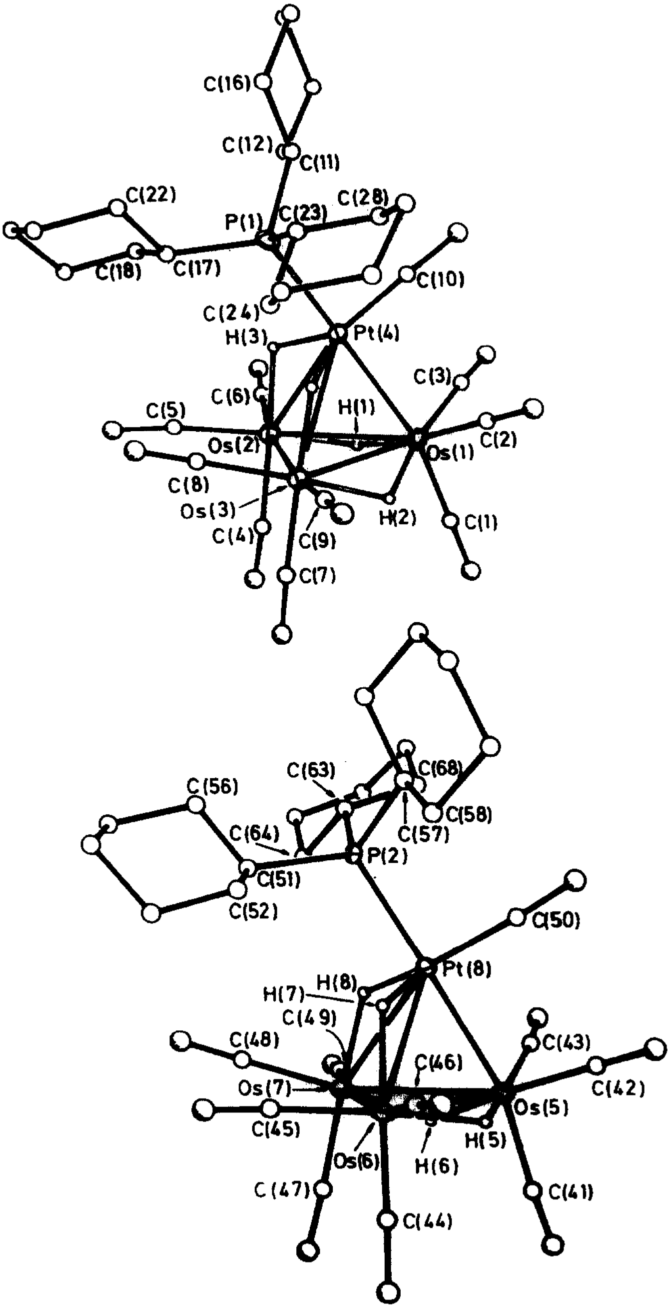
299 ORTEP diagram of $[Os_3Pt(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2]$ showing 50 % probability ellipsoids. (Reproduced with permission from [583])



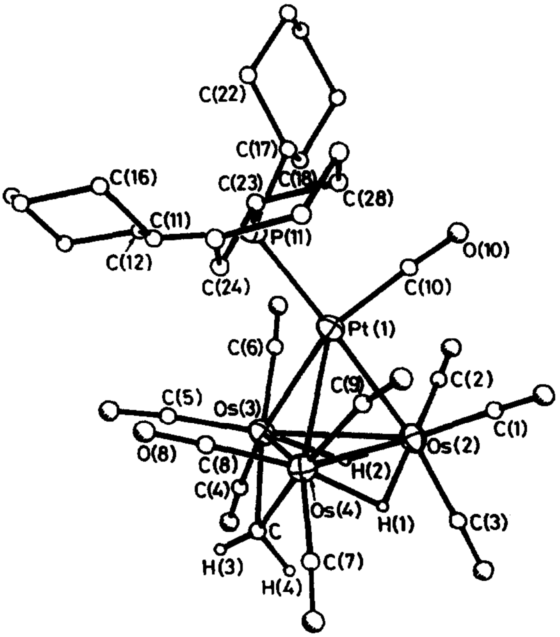
300 ORTEP diagram of [{$Os_3Pt(CO)_8(H)(Ph_2PC_6H_4)(\mu_3$-S)($\mu_4$-S)}$_2$] showing 50 % probability ellipsoids. (Reproduced with permission from [584])



301 (Reproduced with permission from [585])



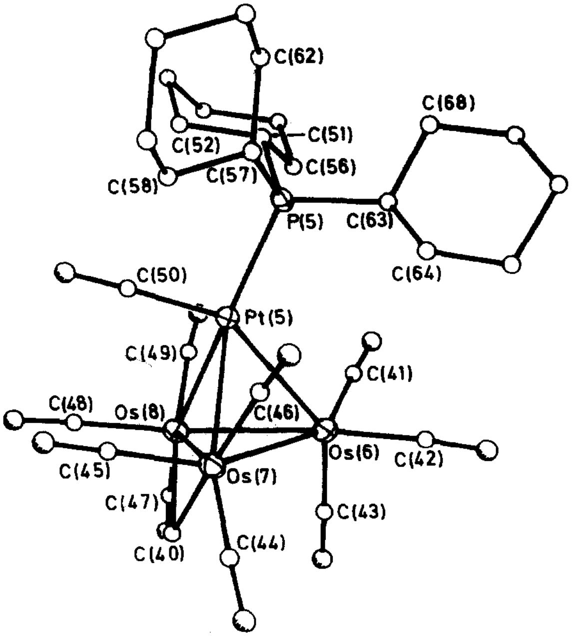
302 Molecular structure of the complex [$Os_3Pt(CO)_{10}(\mu\text{-}H)_4(PCy_3)$] showing the two crystallographically independent molecules and the atom numbering scheme. (Reproduced with permission from [585])



303 Molecular structure of the complex $[Os_3Pt(\mu\text{-}CH_2)(CO)_{10}(\mu\text{-}H)(PCy_3)]$ (yellow-orange isomer) showing the crystallographic numbering scheme. (Reproduced with permission from [585])

When $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ was treated with $[Au(PCy_3)Cl]$, the product was $[Pt_3Au(\mu_2\text{-}CO)_3(PCy_3)]^+$, isolated as the $[PF_6]^-$ salt, 305. The $\{Au(PCy_3)\}$ fragment occupies an apical site above the $\{Pt_3\}$ triangle, and the phosphines bend 17 ° out of plane to minimise steric repulsion and maximise bonding [586]. Breakup of the high nuclearity cluster resulted from the reaction of $[Pt_{12}(CO)_{24}]^{2-}$ with $[IrCl(CO)(PPh_3)_2]$ to give the butterfly cluster $[Ir_2Pt_2(CO)_7(PPh_3)_2]$, 306, which was shown to be a catalyst for alkene hydrogenation [587].

Strategies for the preparation of mixed metal clusters, $\{M_2Pt_2\}$, where M is Cr, Mo or W have been discussed. It was noted that the reaction of $[PtCl_2L_2]$ with Na[M] ($[M]^- = [(Cp)M(CO)_3]^-$ or $[Mn(CO)_5]^-$ and L = RNC or PhCN) gave complexes of the type *trans*-$[PtL_2M_2]$. However, when L = PR_3, the desired species, such as $[M_2Pt_2(CO)_6(Cp)_2(PR_3)_2]$, were formed. The preparation and characterisation of a wide range of new complexes was described. All the structures were based on a planar triangulated parallelogram framework for the metal core, as in 307 [588]. The electrochemistry of the clusters has been studied, and a two-electron reduction and two distinct one-electron oxidations noted. Both reduction and the second oxidation led to decomposition [589].

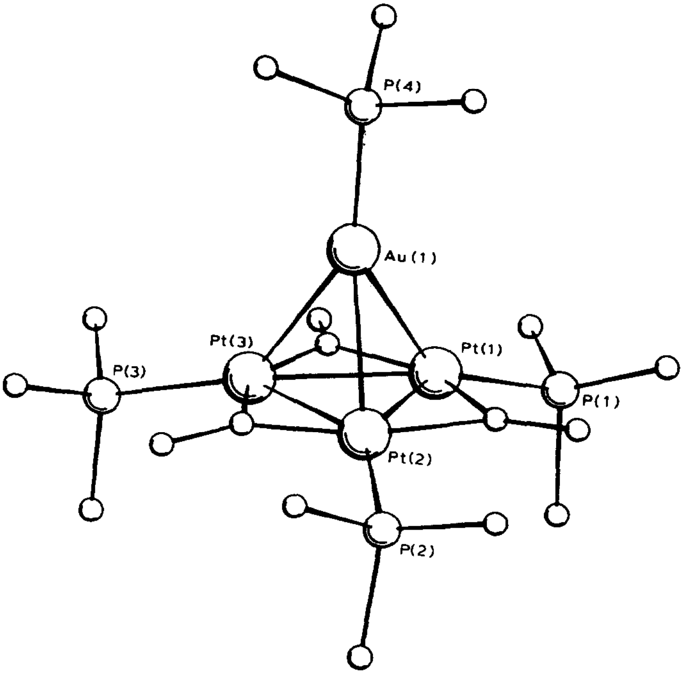


304 Structure of one of the two crystallographically independent molecules in the crystal of $[Os_3Pt(\mu\text{-}CH_2)(CO)_{10}(\mu\text{-}H)(PCy_3)]$ (red isomer). (Reproduced with permission from [585])

6.5 *High nuclearity metal carbonyl clusters*

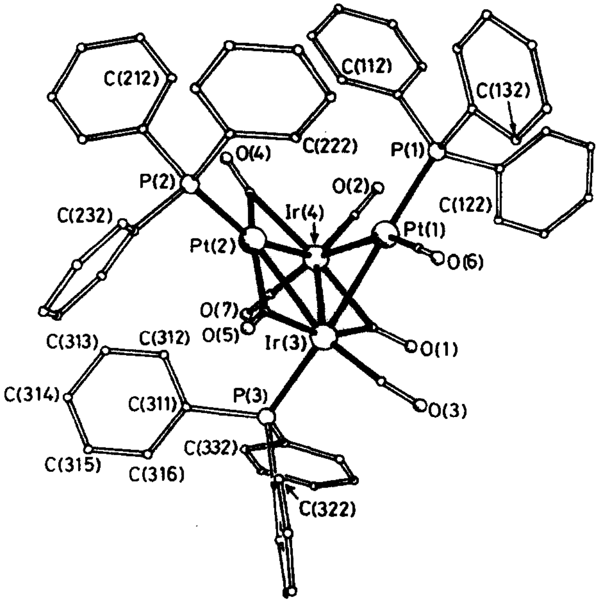
The structures of metal clusters, including those of nickel, palladium and platinum, have been reviewed [590]. A review of the polyhedral skeletal electron pair approach included extensive discussion of carbonyl nickel and platinum clusters [591].

A new topological electron counting theory, based on Euler's theorem and the effective atomic number rule, has been developed to predict the electron counts of a large number of polyhedral metal clusters, including homo and heteronuclear species from the nickel triad [592,593]. Stone's Tensor Surface Harmonic Theory has been successfully applied to three connected polyhedral molecules of main group and transition elements, including $[Ni_8(PPh)_6(CO)_8]$ [594].



305 Structure of the $[AuPt_3(CO)_3(PCy_3)_4]^+$ cation. For reasons of clarity, the cyclohexyl rings have been omitted except for the *ipso*-carbon atoms. (Reproduced with permission from [586])

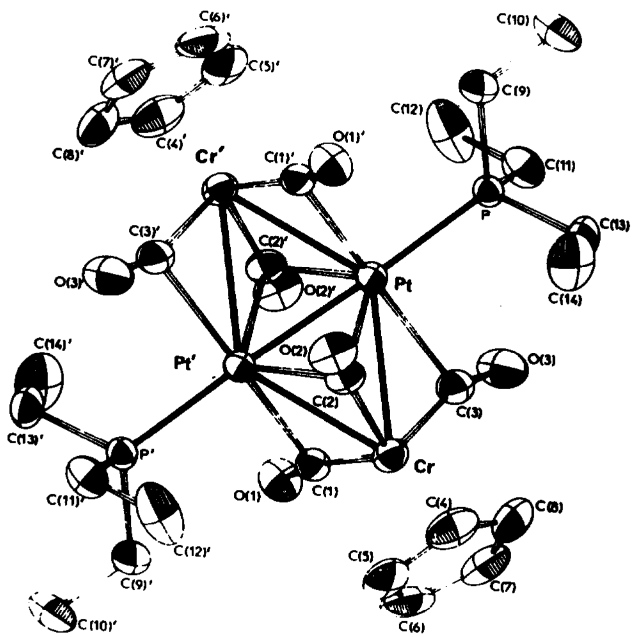
The reaction of $NiCl_2$ with PPh_3 and $(Me_3Si)_2PPh$ did not proceed to completion, but the brown material obtained could be converted by CH_3COCl to a mixture of $[Ni_8Cl_4(\mu_4\text{-}PPh)_6(PPh_3)_4]$ and $[Ni_8(CO)_4(\mu_4\text{-}PPh)_6(PPh_3)_4]$, 308. The structures of both products were determined, and methods for their interconversion described. Both are based on a cubic array of eight nickel atoms with each face coordinated by a $(\mu_4\text{-}PPh)$ ligand [595]. The cluster $[Ni_8Cl_4(\mu_4\text{-}PPh)_6(PPh_3)_4]$ could be reduced with Na/Hg in the presence of CO to give 308, and $[Ni_8(\mu_4\text{-}PPh)_6(PPh_3)_4]$ reacted directly with CO to give the same product. Isocyanide complexes were prepared similarly [596]. In a related reaction $[Ni_8Cl_2(PPh_3)_6S_6]$ was reduced by Na/Hg under a CO atmosphere to give $[Ni_8(CO)_2(PPh_3)_6S_6]$ [597].



306 (Reproduced with permission from [587])

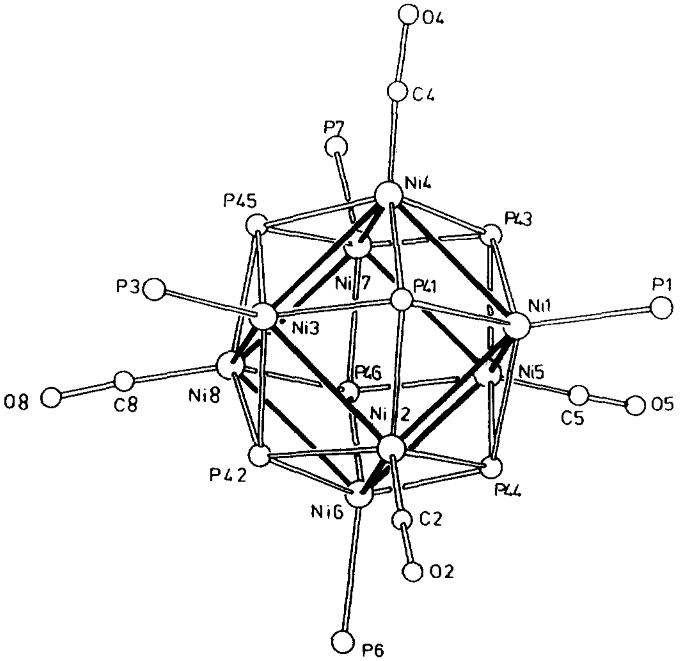
Ultrasound treatment of NiX_2 under an atmosphere of CO gave $[Ni_6(CO)_{12}]^{2-}$, but in low yield [598]. The complex $[Ni_5Cl(CO)_6\{(Me_3Si)_2CHP=PCH(SiMe_3)_2\}_2]$, 309, was prepared by reaction of $(Me_3Si)_2CHPCl_2$ with $Na_2[Ni_6(CO)_{12}]$, and its structure determined. Four of the five nickel atoms adopt a butterfly configuration, and the phosphine acts as a σ-donor to nickel [599].

A number of papers have reported nickel carbonyl carbide clusters. For example, reaction of $[Ni_6(CO)_{12}]^{2-}$ with tetrachloromethane gave $[Ni_{10}C(CO)_{18}]^{2-}$, $[Ni_9C(CO)_{17}]^{2-}$ and $[Ni_8C(CO)_{16}]^{2-}$. The $\{Ni_{10}\}$ species is succesively carbonylated to give the other two clusters, the structures of which were established in diffraction studies [600]. When the chlorocarbon added contained two carbon atoms, as in tetrachloroethene or hexachloroethane, the product was $[Ni_6C_2(CO)_{16}]^{2-}$, which was isolated and characterised as the tetraphenylarsonium salt, 310 [601]. When the related species $[Ni_{10}(CO)_{16}C_2]^{2-}$ was reacted with PPh_3, cluster condensation occurred, giving $[Ni_{16}(CO)_{23}C_4]^{4-}$, 311. This is a unique hexadecanuclear truncated ν_2-octahedron caging two interstitial $\{C_2\}$ moieties with a very short interatomic separation of 1.38 Å. *It was envisaged that the new cluster could be formed by the fusion of two* $\{Ni_{10}\}$ units with the loss of a unique interstitial nickel atom [602].

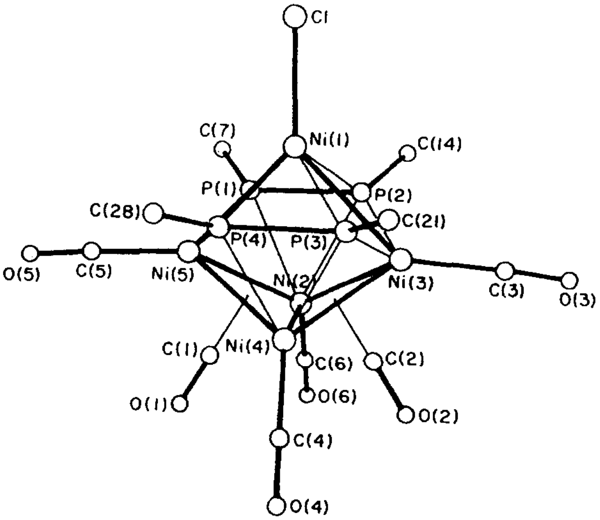


307 ORTEP diagram of the molecular structure of the $[Cr_2Pt_2(\mu\text{-}CO)_4(\mu_3\text{-}CO)_2(Cp)_2(PEt_3)_2]$ cluster. Thermal ellipsoids enclose 50 % of the electron density. (Reproduced with permission from [578])

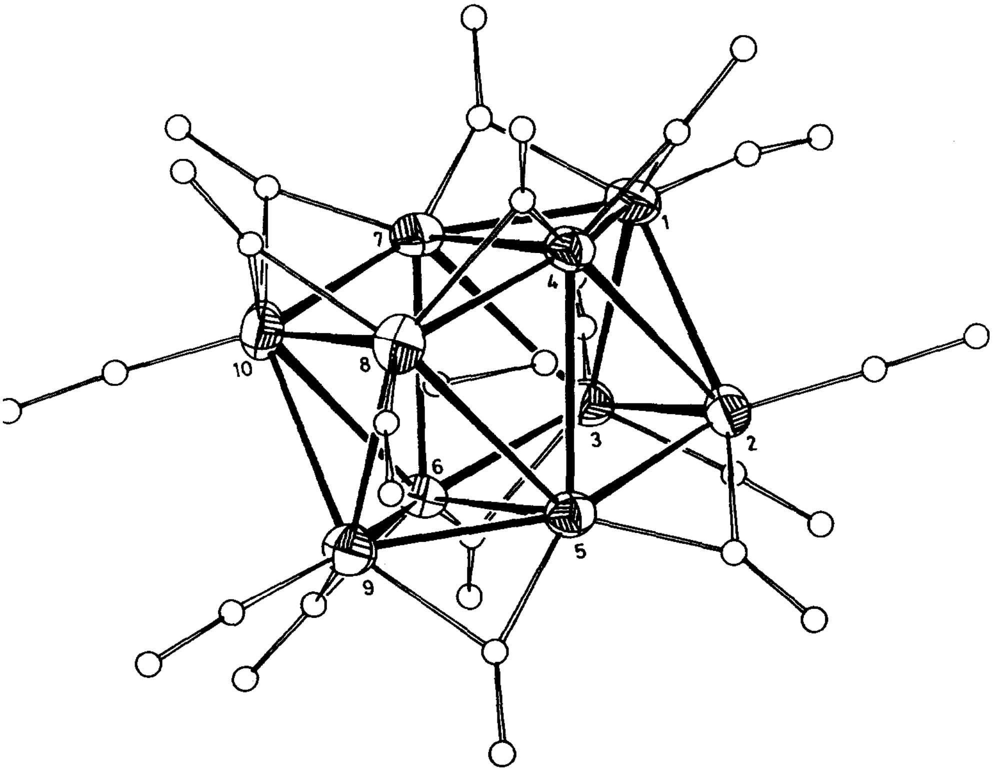
Reaction between $[Ni_6(CO)_{12}]^{2-}$ and $[Co_3CCl(CO)_9]$ gave a complex mixture of clusters from which $[Co_3Ni_9C(CO)_{20}]^{3-}$ could be isolated pure, and its structure determined. It has an unprecedented metal framework with a square antiprism of metal atoms tetracapped on two alternative pairs of triangular faces [603]. When the added nickel complex was $[Ni_9C(CO)_{17}]^{2-}$, $[Co_3Ni_7C_2(CO)_{16}]^{2-}$ was formed, and the structure of its tetraphenylphosphonium salt, 312, determined. The anion has a metal framework based on a 3,4,3-C_{2h} stack, and may be regarded as resulting from the condensation of two octahedra or two trigonal prismatic moieties. Cobalt and nickel sites were not distinguished, and the metals are probably randomly distributed. The $\{C_2\}$ unit inside the cluster has a carbon-carbon bond length of 1.48 Å [604]. The ketenylidene cluster $[Fe_3(CCO)(CO)_9]^{2-}$ reacted with either $[Ni(CO)_4]$ or $[\{Ni(CO)(Cp)\}_2]$ to give $[Fe_3Ni_3C(CO)_{13}]^{2-}$ [605].



308 Molecular structure of $[Ni_8(CO)_4(\mu_4\text{-}PPh)_6(PPh_3)_4]$ (without phenyl groups). P(1), P(3), P(6), P(7) and P(41)-P(46) represent respectively the P-atoms of the PPh_3 and PPh ligands. (Reproduced with permission from [595])

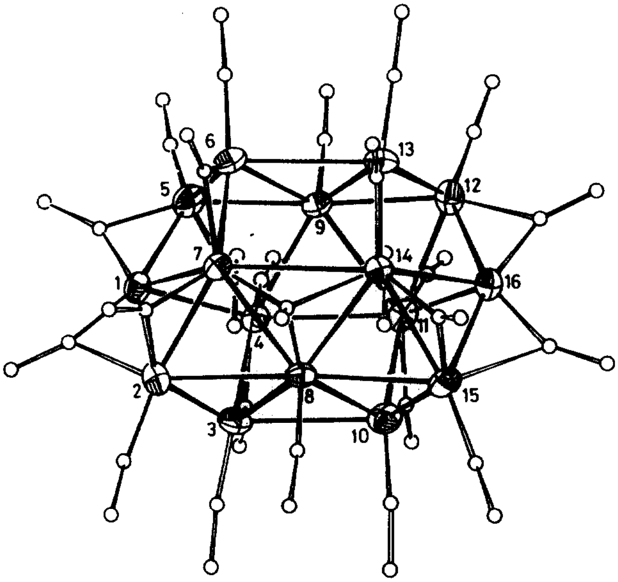


309 The $SiMe_3$ groups are omitted for clarity. (Reproduced with permission from [589])



310 (Reproduced with permission from [601])

The complexes $[Ni_{38}Pt_6(CO)_{48}H_{6-n}]$ (n = 3,4,5 or 6) were prepared from $[Ni_6(CO)_{12}]^{2-}$ and $PtCl_2$ or $K_2[PtCl_4]$ under varying conditions, and could be interconverted by protonation/deprotonation. The structures of $[Ph_4As]_2[Ni_{38}Pt_6(CO)_{48}H_2]$ and $[Ph_4As]_2[Bu_4N]_3[Ni_{38}Pt_6(CO)_{48}H]$ were established in diffraction studies. The metal frameworks consist of an inner octahedron of six platinum atoms fully encapsulated by a ν_3 octahedron of thirty-eight nickel atoms. The metal cluster has the same structure as a fragment of a ccp metal lattice. Preliminary measurements suggested unusual magnetic behaviour [606].

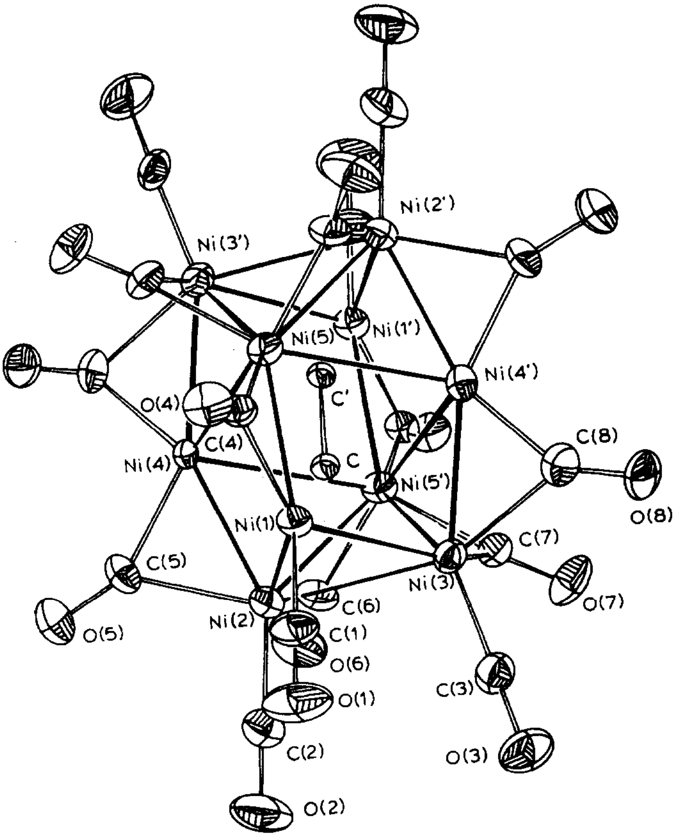


311 ORTEP drawing of the structure of the $[Ni_{16}(C_2)_2(CO)_{12}(\mu\text{-}CO)_{10}(\mu_3\text{-}CO)]^{4-}$ tetraanion. (Reproduced with permission from [602])

Palladium and platinum phosphine carbonyl clusters have been reviewed [607]. In the palladium ethanoate catalysed reduction of $H[ClO_4]$ by CO, the only palladium compound which could be separated from the reaction mixture was the polymer $[\{PdCl(CO)\}_n]$. This does not seem to be the active catalyst, but rather a deactivation product. The tetranuclear species $[Pd_4(CO)_4(OCOMe)_4]$ was isolated from the related reduction of HNO_3, but again this is not the active catalyst [608]. $[\{PdCl(CO)\}_n]$ was used as a source of palladium in the preparation of $[Pd_2Cl_2(\mu\text{-}dmpm)_2]$ [609].

The clusters $[Pd_{10}(CO)_{12}(PR_3)_4]$, $[Pd_3(CO)_3(PR_3)_4]$ and $[Pd_4(CO)_5(PR_3)_4]$ were prepared from palladium ethanoate, CO and PR_3, under a variety of conditions [610]. Oxidative carbonylation of $[Pd_4(CO)_5(PPh_3)_4]$ or $[Pd(PPh_3)_4]$ gave $[Pd_{10}(CO)_{12}(PPh_3)_6]$; the oxidant acts to increase the cluster nuclearity by removing phosphine ligands as phosphine oxide [611].

The mixed carbide cluster $[CoFe_4C(CO)_{14}]^-$ reacted with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ to give $[CoFe_4PdC(CO)_{15}]^-$, which has not yet been fully structurally characterised [612].



312 (Reproduced with permission from [604])

An excellent review has been published on homonuclear platinum clusters [613]. The uses of platinum carbonyl clusters in catalysis has also been reviewed, including both homo and heteronuclear clusters [614]. The new topological electron counting theory based on Euler's theorem and the effective atomic number rule has been used to predict electron counts of a large number of polyhedral electron clusters including $[\{Pt_3(CO)_6\}_n]^{2-}$ [615]. Th theory permits a better understanding of the interrelationships between cluster geometries [616-618].

Electronic structure calculations for $[M_3(CO)_6]_n^{2-}$ (M = Ni or Pt, n = 1,2 or 3) show that the highest occupied state in these diamagnetic dianions is a low lying molecular orbital from the $2\pi_z$ CO system, and that the unoccupied molecular orbitals of $2\pi_z$ origin are at least 0.7 eV higher in energy. The data are used to discuss the different configurations of the nickel and platinum complexes, and the absence of a palladium series [619]. The structures of $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 2,3,4,5,6 or 10) have been considered. For n = 2 there is some departure from ideality, in that there is a lateral slip of one $\{Pt_3\}$ triangle relative to the other. In the trimer there is a helical twist of 13 ° from one unit to the next, and in the pentamer the angular distortion is confined to the middle three $\{Pt_3\}$ units [620].

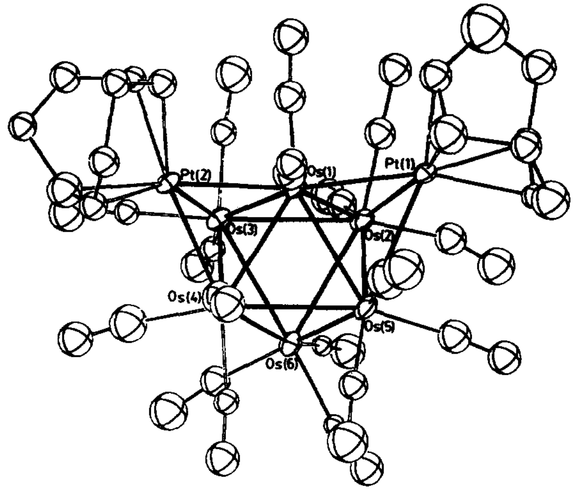
Bonding in high nuclearity clusters with close packed arrangements of metal atoms is dependent primarily on radial interactions between the surface and interstitial atoms. Radial bonding interactions were shown to predominate in $[Pt_{19}(CO)_{22}]^{4-}$ and $[Pt_{26}(CO)_{32}]^{2-}$, but in $[Pt_{24}(CO)_{30}]^{2-}$ tangential bonding interactions also make a partial contribution [621].

There have been several reports of the uses of platinum carbonyl clusters in catalytic reactions. For example, chlorided γ-alumina impregnated with $[Et_4N]_2[Pt_{15}(CO)_{30}]$ and $[Re_2(CO)_{10}]$, followed by reduction and sulphidation, gave a catalyst for reformation of n-heptane [622]. Isocyanates were produced from $ArNO_2/CO$ in the presence of $[Pt_{15}(CO)_{30}]^{2-}$ [623]. Rate parameters were established for generation of oxygen from water by a redox reaction with hydroquinone in the presence of $[Pt_{12}(CO)_{24}]^{2-}$ [624]. Layered compounds with the formula $A_x^{2+}B_y^{3+}(OH)_{2x+3y-nz}D_3^{n-}.tH_2O$ (D is a polyanion including $[Pt_{18}(CO)_{36}]^{2-}$ and $[Ni_3Cr(CO)_{18}]^{2-}$; $x,y,z,t > 0$, $n = 1-10$, $0.5 \leqslant x/y < 10$) are suitable as ion exchangers and exhaust gas and hydrocarbon conversion catalysts [625].

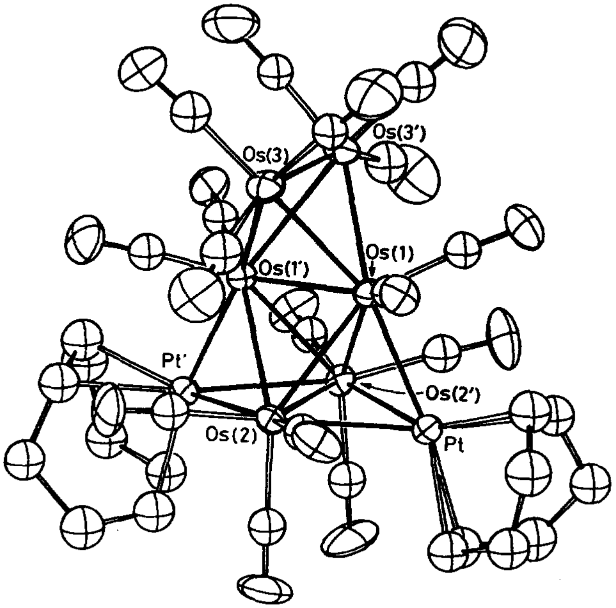
The amberlite anion exchange resin, IRA 401, has been used as a support for $[Pt_{15}(CO)_{30}]^{2-}$ and $[PtRh_5(CO)_{15}]^{-}$. XPES revealed the presence of platinum(IV) impurities. On the surface the homonuclear complex may be decarbonylated, but the reaction is not reversible, and recarbonylation leads to a different complex. Both supported complexes are active catalysts for the hydrogenation of benzaldehyde, and the heteronuclear species also catalyses the reduction of certain arene rings [626].

Thermolysis of $[Pt_{15}(CO)_{30}]^{2-}$ under a nitrogen atmosphere, gave $[Pt_{24}(CO)_{30}]^{2-}$. An X-ray diffraction study revealed that the metal framework resembled a fragment of a cubic close packed structure. Hydrogenation and substitution reactions were studied [627].

Reaction of $[Pt(cod)_2]$ with $[Os_8(CO)_{20}]$ gave the 110 electron cluster $[Os_6Pt_2(CO)_{17}(cod)_2]$, 313, characterised by a diffraction study [628]. Similarly, $[Os_6(CO)_{16}(MeCN)_2]$ gave $[Os_6Pt_2(CO)_{18}(cod)_2]$, 314, in which a regular octahedron of osmium atoms is face-capped by two $\{Pt(cod)\}$ units [629].

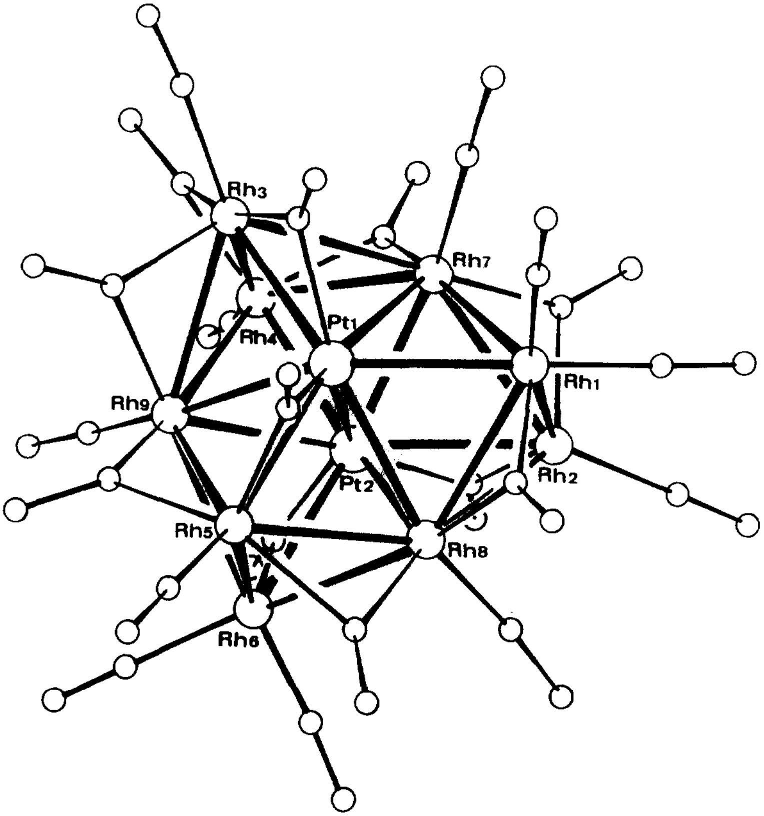


313 (Reproduced with permission from [628])



314 (Reproduced with permission from [629])

Thermolysis of the mixed cluster $[PtRh_5(CO)_{15}]^-$ gave $[Pt_2Rh_9(CO)_{22}]^{3-}$, 315, which was isolated and characterised in an X-ray diffraction study. The metal skeleton has ideal D_{3h} symmetry and is composed of three face-to-face condensed octahedra. The platinum atoms lie on the three fold axis in the positions of maximum connectivity [630]. Reaction of $Na_2[PtCl_6]$ with $RhCl_3.xH_2O$ under an atmosphere of CO gave a mixture of $[PtRh_5(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^-$. The latter species was isolated, and could be converted reversibly to $[PtRh_4(CO)_{12}]^{2-}$, by carbonylation/decarbonylation. This is the first example of a facile interconversion of two trigonal bipyramidal clusters with 76 and 72 CVE's, but it is noteable that the site of the platinum changes in the interconversion, which may be mechanistically complex. A scheme was proposed for the interconversion of the complexes [631].



315 (Reproduced with permission from [630])

Treatment of $[Ir(CO)_2Cp^*]$ with $[Pt(C_2H_4)_3]$ in ether at 0 °C, gave $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(Cp^*)_3]$, 316. The central triangle of platinum atoms has each edge bridged by an $\{Ir(Cp^*)(CO)_2\}$ unit, and the complex undergoes dynamic behaviour on the nmr spectroscopic timescale [632].

$$[\mathrm{PtCl_6}]^{2-} \xrightarrow{[\mathrm{HO}]^-/\mathrm{CO}} [\mathrm{PtCl_3(CO)}]^- \xrightarrow{[\mathrm{HO}]^-/\mathrm{CO}} [\{\mathrm{Pt_3(CO)_6}\}_n]^{2-} \quad n = 4,5 \text{ or } 6$$

$$\mathrm{RhCl_3} \xrightarrow{[\mathrm{HO}]^-/\mathrm{CO}} [\mathrm{RhCl_2(CO)_2}]^-$$

$$[\mathrm{RhCl_2(CO)_2}]^- + [\{\mathrm{Pt_3(CO)_6}\}_m]^{2-} \xrightarrow{[\mathrm{HO}]^-/\mathrm{CO}} [\mathrm{PtRh_5(CO)_{15}}]^- + \mathrm{A} \xrightarrow{[\mathrm{HO}]^-/\mathrm{CO}}$$

$$m = 4 \text{ or } 5 \qquad\qquad [\mathrm{PtRh_4(CO)_{14}}]^{2-} + \mathrm{B}$$

By-products A are $[\mathrm{Rh_{12}(CO)_{30}}]^{2-}$, $[\mathrm{Rh_5(CO)_{15}}]^-$ if Pt:Rh < 1:5

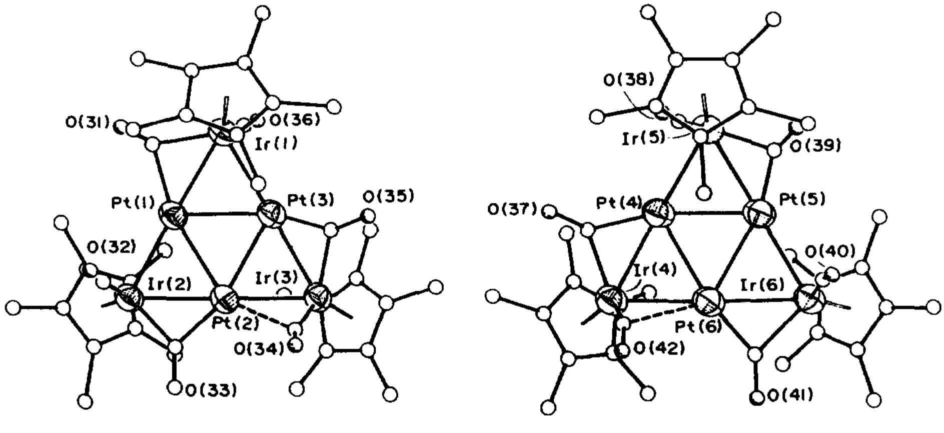
$[\{\mathrm{Pt_3(CO)_6}\}_p]^{2-}$ (p = 3 or 4) if Pt:Rh > 1:5

By-products B are $[\mathrm{Rh_6(CO)_{15}}]^{2-}$ and $[\mathrm{Rh_7(CO)_{16}}]^{3-}$ if Pt:Rh < 1:4

$[\{\mathrm{Pt_3(CO)_6}\}_3]^{2-}$ if Pt:Rh > 1:4

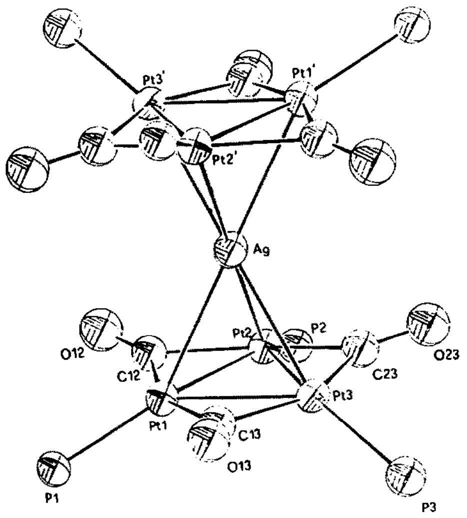
$$\begin{tikzcd}
{[\mathrm{PtRh_4(CO)_{14}}]^{2-}} \arrow[r, shift left, "\mathrm{N_2}\text{ or vacuum}"] \arrow[d, "{[\mathrm{Rh(CO)_2(MeCN)_2}]^+}"] \arrow[rd, "{[\mathrm{Rh_6(CO)_{16}}]}"] & {[\mathrm{PtRh_4(CO)_{12}}]^{2-} + 2\mathrm{CO}} \arrow[l, shift left, "\mathrm{CO}"] \\
{[\mathrm{PtRh_5(CO)_{15}}]^- + \mathrm{CO}} & {[\mathrm{PtRh_5(CO)_{15}}]^- + [\mathrm{Rh_5(CO)_{15}}]^-}
\end{tikzcd}$$

Scheme 12 Interconversions of platinum rhodium carbonyl complexes [631]



316 The molecular structures of the two crystallographically independent molecules of $[\mathrm{Ir_3Pt_3(\eta\text{-}C_5Me_5)_3(CO)_3(\mu\text{-}CO)_3}]$ showing the atom numbering scheme. (Reproduced with permission from [632])

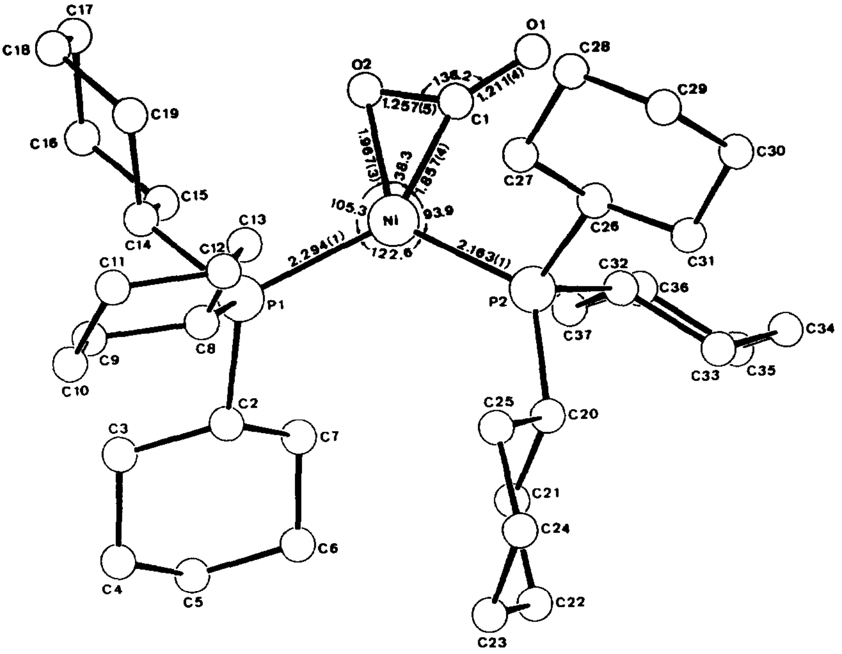
Reaction of $[Fe_5C(CO)_{14}]^{2-}$ with $[Pt(PPh_3)_4]$ gave $[Fe_5PtC(CO)_{14}(PPh_3)]^{2-}$, but the structure of the product was not given [633]. When the trimer $[Pt_3(CO)_3\{P(CHMe_2)_3\}_3]$ reacted with $Ag[CF_3SO_3]$ two $\{Pt_3\}$ units were coupled by silver in $[Ag\{Pt_3(\mu_2\text{-}CO)_3(P\{CHMe_2\}_3)_3\}_2][CF_3SO_3]$, 317. The silver ion links two staggered $\{Pt_3\}$ triangles, which rotate on the nmr spectroscopic timescale [634].



317 ORTEP diagram of the $[Ag\{Pt(\mu_2\text{-}CO)_3(P\{CHMe_2\}_3)_3\}_2]$ cation in the $[Ag\{Pt(\mu_2\text{-}CO)_3(P\{CHMe_2\}_3)_3\}_2][CF_3SO_3]$ crystal. Only the phosphorus atoms of the phosphine ligands are shown. (Reproduced with permission from [634])

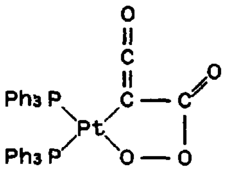
6.6 Complexes of CO_2, and related species

Calculations have been performed on $[Ni(CO_2)(PH_3)_2]$ and $[Ni(CS_2)(PH_3)_2]$, with particular reference to modes of binding and fluxional behaviour [635]. Reaction of [Ni(cdt)] with CO_2 in the presence of a phosphine ligand, L, gave $[Ni(\eta^2\text{-}CO_2)L_2]$. The toluene solvate of the complex with L = PCy_3, 318, was structurally characterised [636]. Reaction of CO_2 with $[Ni(\eta^2\text{-}CS_2)(triphos)]$ gave $[Ni(CO_2)_x(triphos)]$ as the initial product. This could also be obtained by carboxylation of [Ni(CO)(triphos)}. Decomposition of the CO_2 derivative gave [Ni(CO)(triphos)] and [Ni(triphosO)]. Further carboxylation of the phosphine oxide complex yielded $[Ni(CO_3)\{Ph_2P(=O)CH_2C(CH_3)(CH_2PPh_2)_2\}]$ as the final product [637].



318 (Reproduced with permission from [636])

Reaction of [Pt(O_2)(PPh_3)$_2$] with C_3O_2 gave a species of stoicheiometry [Pt(C_3O_4)(PPh_3)$_2$], with the postulated structure 319. Good crystals could not be obtained in this case, but the structure of the benzylamine adduct, 320, was unequivocally established [638]. Reaction of 319 with PPh_3 gave 321; a mechanism was proposed but not proven for this reaction [639]. Reaction of C_3O_2 with [Pt(C_2H_4)(PPh_3)$_2$] at 0 °C under CO_2 gave 322 or 323 depending on the stoicheiometry. Further reactions of the complexes were discussed [640].



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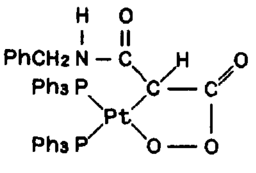

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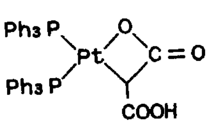

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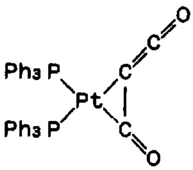

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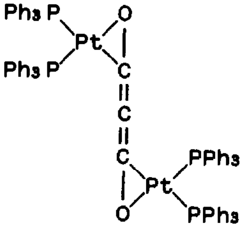

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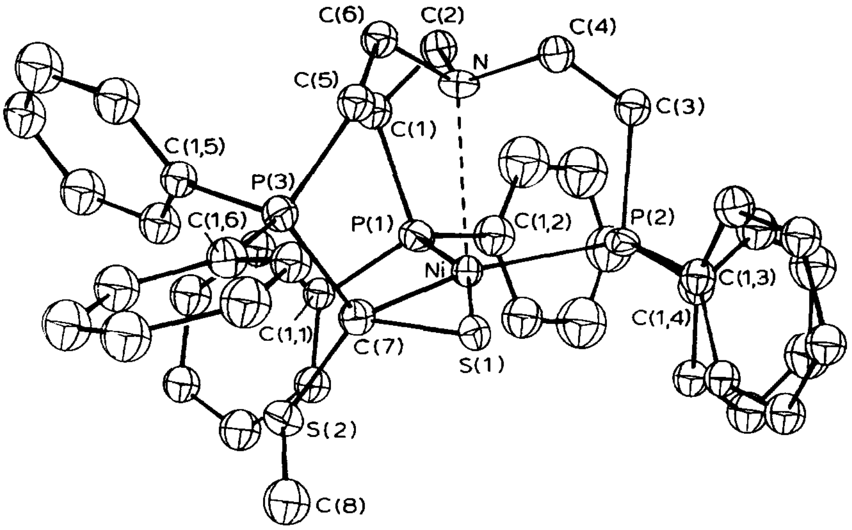
6.7 Thiocarbonyl, carbon disulphide and carbonyl sulphide complexes

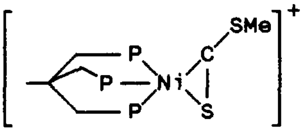
Transition metal thiocarbonyl [641] and carbonyl sulphide [642] complexes have been reviewed.

Reaction of $[Ni(np_3)]$ ($np_3 = N(CH_2CH_2PPh_2)_3$) with CS_2 gave the simple η^2-adduct, $[Ni(CS_2)(np_3)]$. This was treated successively with $MeOSO_2F$ and $Na[BPh_4]$ to give 324, characterised in a diffraction study. This was thought to be formed by phosphine attack on an η^2-dithiomethyl ester formed *in situ*. The reaction of $[Ni(np_3)]$ with PhNCS also gave an η^2-*C,S*-adduct, the structure being assigned on the basis of the comparison of the IR spectroscopic data with the related triphos complex. The reaction with COS gave only $[Ni(CO)(np_3)]$, the η^2-COS adduct being too labile for isolation [643]. The structures of $[Ni(\eta^2\text{-}CS_2)(triphos)]$ and $[Ni(\eta^2\text{-}PhNCS\text{-}S,C)(triphos)]$ have been established in diffraction studies, and the data evaluated in theoretical terms [644]. Protonation of $[Ni(triphos)(CS_2)]$ with $H[BF_4]$ gave $[\{Ni(triphos)\}_2S][BF_4]_2$, whilst methylation with $MeOSO_2F$ yielded 325. Oxidation with molecular oxygen resulted in oxidation of one of the phosphine centres and of the CS_2 ligand to give 326 [645]. Reaction with $CF_3C{\equiv}CCF_3$ gave the carbene complex, 327, the further reactions of which were studied [646].

The reactions of palladium(0) phosphine complexes with CS_2 have been studied; the steric bulk of the phosphine controls the nature of the complex precipitated, either $[Pd(\eta^2\text{-}CS_2)L_2]$ or $[Pd_2(\mu\text{-}CS_2)_2L_2]$. Dimers were also obtained from reactions of $[Pd_3(CO)_3L_3]$ [647]. When $[Pd(\eta^2\text{-}CS_2)(PCy_3)_2]$ was reacted with an excess of CS_2, $[Pd(CS_2)(PCy_3)]$ and $Cy_3P^+CS_2^-$ were obtained. IR spectroscopic data indicated that the complexes formed were probably polymeric [648]. The same polymers were obtained from a reaction between $[Pd(\eta^2\text{-}CS_2)L_2]$ and $[Pd(bipy)(C_6F_5)(OCOMe)]$ [649].



324 ORTEP drawing of the complex cation with 30 % probability ellipsoids. (Reproduced with permission from [643])



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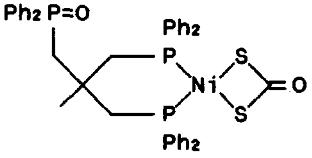

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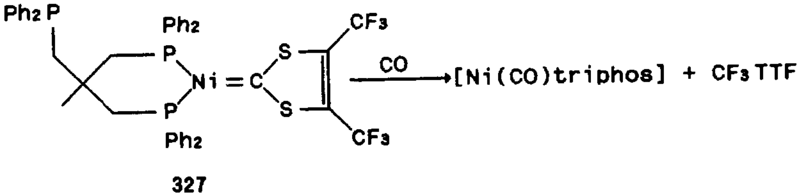

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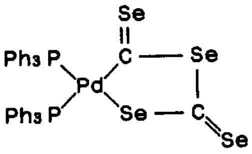
The reactions of $[M_3(CO)_3L_3]$ (M = Pd or Pt) with CS_2 were compared. With bulky ligands such as $P(CMe_3)_2Ph$ or $P(CMe_3)_3$, the dimers $[M_2(\mu\text{-}CS_2)_2L_2]$ were obtained; spectroscopic monitoring of the reaction mixture indicated that the mechanism involves monomeric species [650]. Treatment of $[Pd(PPh_3)_4]$, $[Pt(PPh_3)_4]$ or $[Pt\{P(CHMe_3)_3\}_2]$ with CEE' (E = E' = S or Se, or E = S, E' = Se) gave $[M(\eta^2\text{-}CEE')(PR_3)_2]$. When M = Pd, an excess of CSe_2 yielded 328. Reaction of $[Pd(\eta^2\text{-}CSe_2)(PPh_3)_2]$ with a small phosphine such as PMe_3 or PMe_2Ph gave 329 [651]. When $[M(\eta^2\text{-}CES\text{-}C,E)(PP)]$ ((PP) = dppe or 1,2-bis(diphenylphosphino)benzene; E = S or Se) was treated with

$[Pt(C_2H_4)(PPh_3)_2]$ 330 was obtained; the structure of the complex for which M = Pt and E = Se was established in a diffraction study [652].



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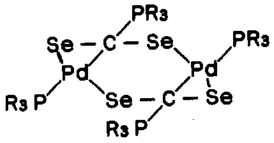

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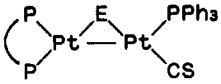

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A full paper has been published detailing an extremely thorough study of the reactions of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ (Scheme 13) [653].

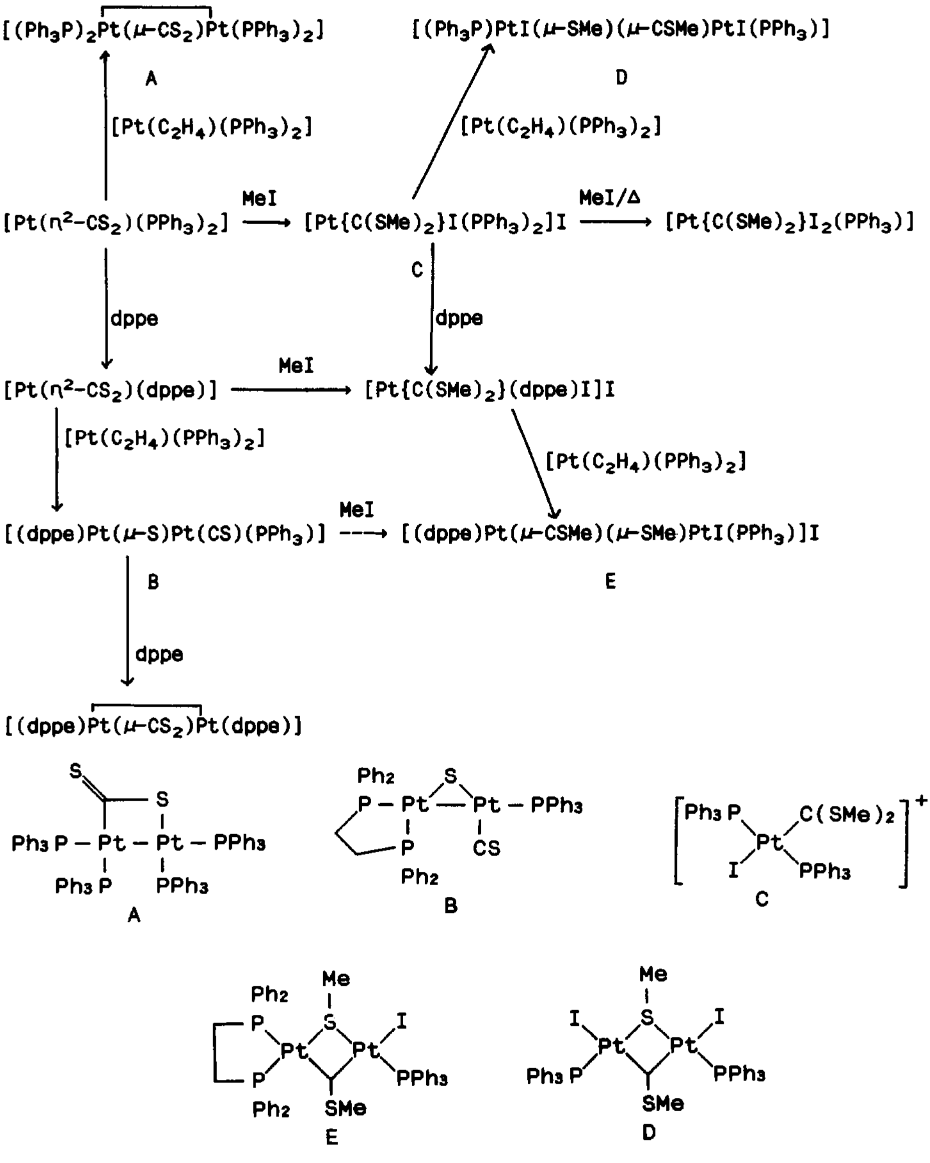
In a review of CS_2 chemistry, the displacement of 1,1,1,4,4,4-hexafluoro-2-butyne, hfb, from $[Pt(hfb)(PPh_3)_2]$ to give $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ was noted [654]. The complex 331 was mentioned in a review of stannanedithiocarboxylate ligands [655].

There have been effective core potential calculations on {Ni(OCS)} and {Pt(OCS)}. With the nickel species bonding may be to carbon or to sulphur, or to both, in the closed shell configuration. All electron calculations using Gaussian 80 indicated approximately η^2-*C,S*-ligation. For the platinum analogue, in the closed shell configuration, there is a preference for bonding to oxygen [656].

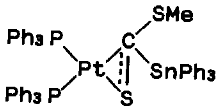
6.8 Other related complexes

The coordination of EtO_2CCOCO_2Et to an $\{M(PCy_3)_2\}$ fragment (M = Pd or Pt) has been described. Oxidation of 332 gave 333 [657]. In a study of the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $R_2P(=S)C(=S)SR'$ the data were consistent with the displacement of ethene and η^2-coordination of the ligand through the carbon-sulphur double bond. $PhNHC(=S)PR_2$ gave a similar adduct initially, and further reactions of these complexes were discussed [658].

Carbonylation of 334, reaction of $[Ni(PPh_3)_4]$ with ketene, or treatment of $[Ni(PPh_3)_4]$ with CH_2Br_2/Zn followed by CO, gave the ketene complex 335. Thermolysis resulted in the loss of ethene, and the formation of the polymeric species $[\{Ni(CO)(PPh_3)\}_n]$ [659]. Reaction of $[Ni(cod)_2]$ with $[R_2N{=}CH_2]X$ (R = Me or $PhCH_2$) in thf gave a red insoluble product, characterised with difficulty as $[R_2N{=}CH_2][Ni(\eta^2\text{-}CH_2{=}NR_2)X_2]$. Thermolysis gave $[Ni(R_2NCH_2CH_2NR_2)X_2]$ [660].



Scheme 13 Reactions of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ [653].



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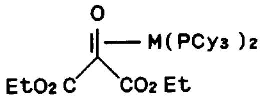

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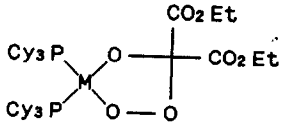

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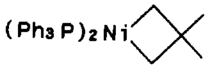

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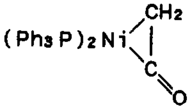
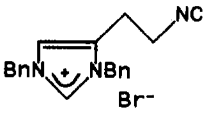


335

7 METAL ISOCYANIDE COMPLEXES

The interaction of nickel atoms with MeNC in an argon matrix gave mononuclear species [Ni(MeNC)$_n$] at low nickel concentrations, and polynuclear species with bridging isocyanides at higher nickel concentrations [661]. The reaction of [Ni(CO)$_4$] with CF$_3$NC gave [Ni(CNCF$_3$)$_4$], which was treated with [NiCp$_2$] to yield [Ni$_2$(μ-CNCF$_3$)$_2$(Cp)$_2$] [662,663]. [NiCp$_2$] reacted directly with isocyanides, RNC, (R = Cy or Me$_3$C) to give [Ni(CNR)$_2$(Cp)]Cl. With [NiCl$_2$(CNR)$_2$] (R = Cy) the product was [NiCl(CNR)(Cp)] [664]. The synthesis of CN(CH$_2$)$_n$OH has been described. The ligand was stabilised in an open-chain form in complexes such as [Ni(CNCH$_2$CH$_2$OH)$_4$(PPh$_3$)$_2$][PF$_6$]$_2$ and [Pd{CN(CH$_2$)$_n$OH}$_2$I$_2$] (n = 3 or 5) [665].

Oxidation of [Ni(CNCMe$_3$)$_4$] gave [Ni(CNCMe$_3$)$_2$(O$_2$)]. In combination with [MoBr$_2$O$_2$(Ph$_3$PO)$_2$], this effected the oxidation of cyclohexene to 1,2-dibromohexane. When the two complexes were mixed at -40 °C a yellow paste and a red solution were obtained. The yellow paste was a molybdenum complex which was poorly characterised, but which appeared to be a peroxide. From the red solution needle-like crystals of *cis,cis,trans*-[NiBr$_2$(CNR)$_2$(Ph$_3$PO)$_2$] were isolated [666,667]. The isonitrile 336 was polymerised in the presence of Ni^{2+}, *via* [Ni(CNR)$_4$]$^{2+}$ [668].



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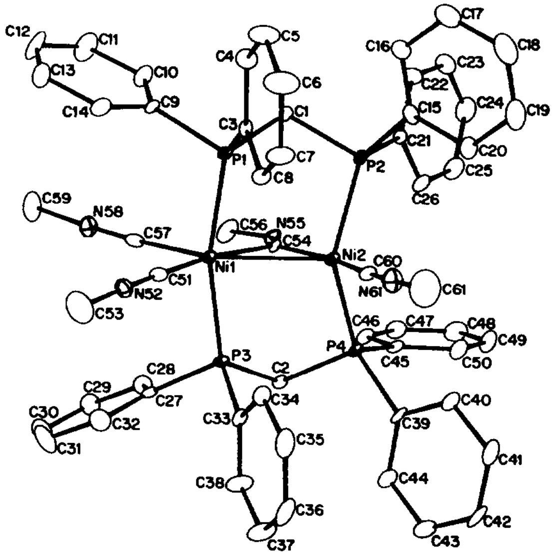
Reaction between the nickel(II) complex, [Ni(CNMe)$_4$][PF$_6$]$_2$, and the nickel(0) species, [Ni(CNMe)$_4$], gave the diamagnetic nickel(I) dimer

$[Ni_2(CNMe)_6]^{2+}$. With the addition of dppm this yielded 337, characterised in a diffraction study. The complex is extremely non-symmetrical, with one nickel atom adopting square pyramidal coordination, and the other being a distorted trigonal bypyramid. The complex showed fluxional behaviour on the nmr spectroscopic timescale [669]. The cluster $[Ni_4(CNCMe_3)_7]$ reacted with $R_2N\text{-}P\text{=}NR$ to give $[Ni_4(CNCMe_3)_4(\mu_3\text{-}\eta^2\text{-}CNCMe_3)(\mu_3\text{-}\eta^2\text{-}R_2NP\text{=}NR)_2]$, 338 [670].

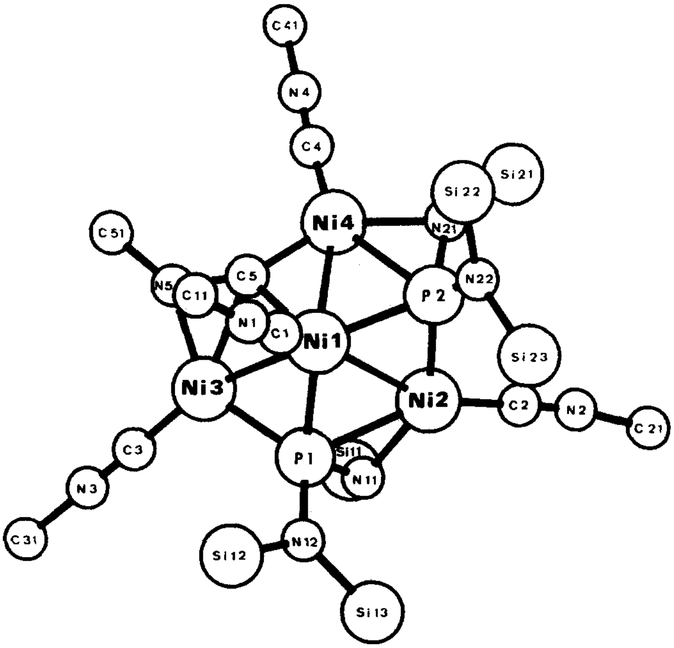


337 ORTEP drawing of the $[Ni_2(CNMe)_3(\mu\text{-}CNMe)(\mu\text{-}dppm)_2]^{2+}$ dication with all the non-hydrogen atoms. (Reproduced with permission from [669])

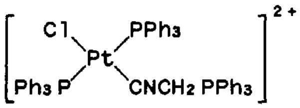
The complex $[PdCl_3(CNCH_2PPh_3)]$ was prepared from $[Ph_3PCH_2NC]X$. The related phosphine complex, 339, reacted with fluorenone to give the Wittig product, 340, (*sic*) [671]. Derivatives of L, 341, $[PdL_2X_2]$ have been noted [672], as have a range of complexes of 342 [673].

Condensation between $[Pt(CNH)_2(PPh_3)_2]^{2+}$ and 4-methyl-3-pentene-2-one gave $[Pt(CNCMe_2CH_2COCH_3)_2(PPh_3)_2]^{2+}$ [674]. Reactions of 2-chloromethylbenzene isocyanide with a range of complexes have been studied (Scheme 14) [675].

Potentiostatic reduction of *cis*-$[PtCl_2(CNR)_2]$ at a mercury pool electrode resulted in one-electron reduction to give $[\{PtCl(CNR)_2\}_2]$, 343, characterised in a diffraction study. Two electron reduction yielded $[Hg\{Pt_3(CNR)_6\}_2]$ for $R = 2,4,6\text{-}(Me_3C)_3C_6H_2$ [676]. The related palladium complex, prepared from $[Pd_2(dba)_3].CHCl_3$ and RNC, was also structurally characterised [677]. The photolysis of the complexes was investigated. Irradiation resulted in the breaking of the metal-metal bond to give the 15e species $[M(CNR)_3]^{\bullet}$. In the presence of CX_4, the sole photoproduct was $[M(CNR)_3X]^+$ [678].



338 Structure of $[Ni_4(CNCMe_3)_4(\mu_3\text{-}\eta^2\text{-}CNCMe_3)(\mu_3\text{-}\eta^2\text{-}R_2N\text{-}P{=}NR)_2]$. methyl groups have been omitted for clarity. (Reproduced with permission from [670])



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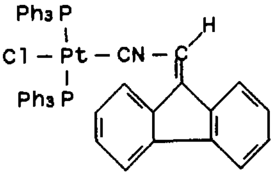

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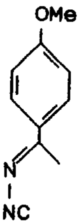

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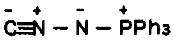
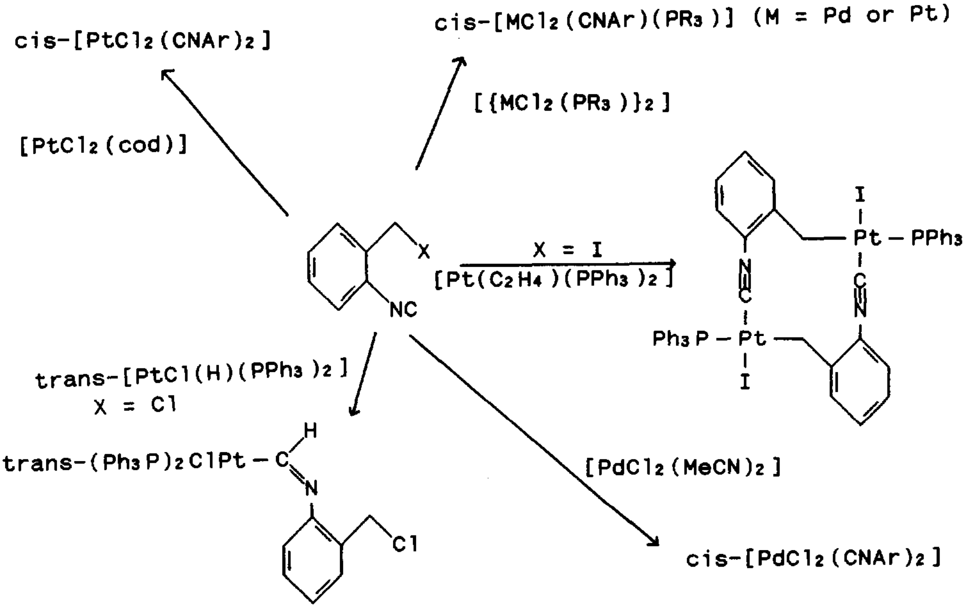
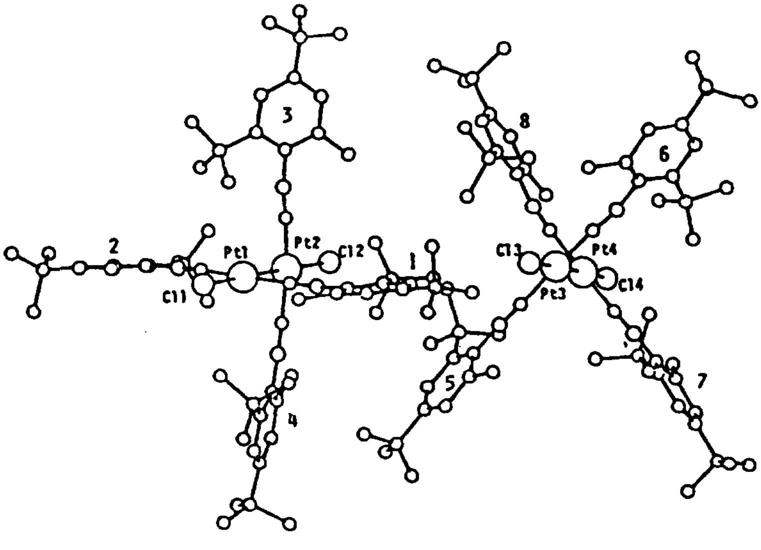


$$\bar{C}{\equiv}\overset{+}{N}-\bar{N}-\overset{+}{P}Ph_3$$

342

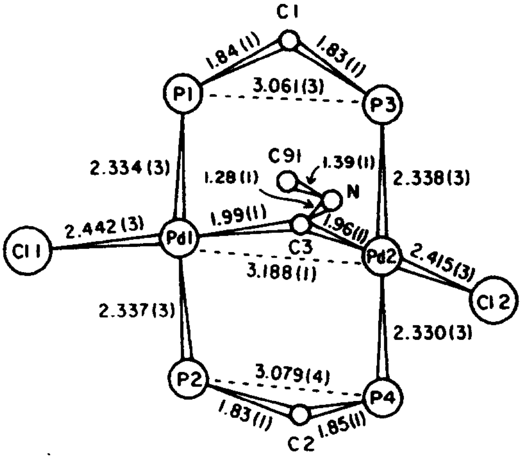


Scheme 14 Reactions of 2-chloromethylbenzene isocyanide with palladium and platinum complexes [675].

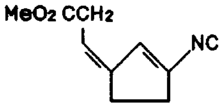


343 (Reproduced with permission from [676])

The structure of $[Pd_2Cl_2(\mu\text{-}CNPh)(\mu\text{-}dppm)_2]$, 344 was established in a diffraction study. The structure consists of discrete molecules packed in a spiral fashion along the 4_1-axis, with an unusually large channel though the structure, almost 10 Å in diameter. The complex was photosensitive, giving, on irradiation, [PdCl$_2$(dppm)] amongst other products [679]. The structure of the related derivative of **345** was also established. However, there were some problems in the structure determination in that the {COOMe} group extends into a channel in the structure, has very high thermal motion, and could not be located [680].



344 Selected bond lengths and atomic numbering scheme for [Pd$_2$Cl$_2$(μ-CNPh)(μ-dppm)$_2$]. (Reproduced with permission from [679])

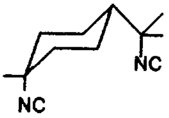


345

Reaction of [PtCl$_2$(dppm)] with Me$_3$CNC gave [Pt$_2$(CNCMe$_3$)$_4$(μ-dppm)$_2$]$^{4+}$, whereas [M(dppm)$_2$]Cl$_2$ yielded [M(CNR)$_2$(dppm-P)$_2$] (M = Pd or Pt). Mixed metal complexes were obtained from the latter by reaction with silver, gold or rhodium complexes; thus [M(dppm)$_2$]Cl$_2$ reacted with [AgCl(CNR)] to give [{AgCl(CNR)}(μ-dppm)$_2${AgCl}]$^+$ [681].

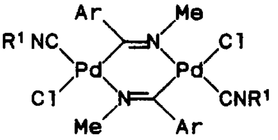
The structure of [Pd$_2$(CNMe)$_4$I$_2$], prepared from [Pd(CNMe)$_4$] and [Pd(CNMe)$_4$]I$_2$, was established in a diffraction study. Although IR spectroscopic date had implied that the iodo ligands were bridging, the solid state structure is an example of a rare unbridged structure, in accord with theoretical expectations. The Pd-Pd distance, at 2.533 Å, is similar to other Pd(I)-Pd(I) bonds, and the Pd-I distances (2.697 and 2.699 Å) are long, reflecting the high *trans*-effect of the metal-metal bond [682]. The structure of $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]$ has been reported [683].

Reaction of the ligand dmb, 346, with Pd^{2+}, in an aprotic medium, gave $[Pd_2(dmb)_4]^{4+}$, which reacted further with X^- to encapsulate the anion between the metal atoms in $[Pd_2(dmb)_4X]^{3+}$ [684].



346

The bridged complex 347 (Ar = C_6F_5) reacted with R^2NC to give 348, characterised for $R^2 = R^1 = Me$ in a diffraction study [685].



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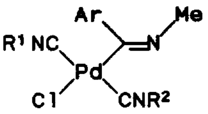
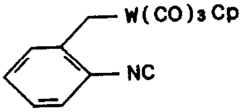


348

Reaction of 349 with *trans*-$[PtCl(H)(PPh_3)_2]$ gave 350. Simple *cis*-diisocyanide derivatives were prepared from $[PtCl_2(cod)]$ or $[PdCl_2(MeCN)_2]$ [686].



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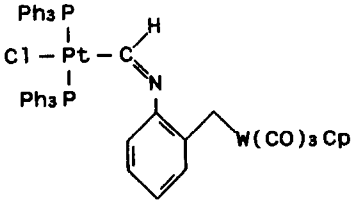
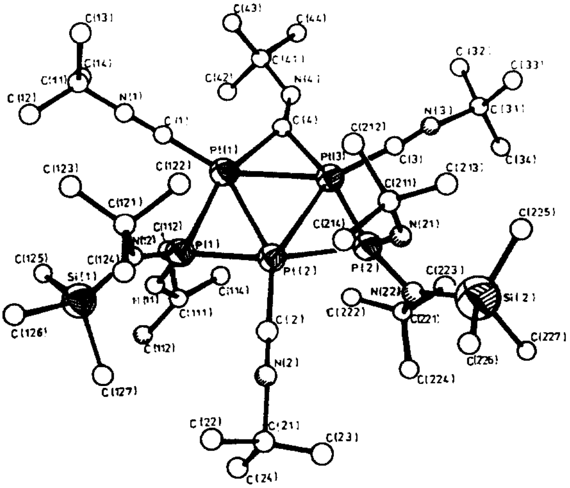


350

Few palladium isonitrile clusters have been defined. When palladium vapour was allowed to react with CyNC, the sole product was $[Pd_3(CNCy)_6]$, the structure of which was very similar to that of $[Pt_3(CNCMe_3)_6]$ [687]. Reaction of $[PtL_3]$ ($L = R^1R^2N\text{-}P{=}NR^3$) with Me_3CNC gave the trimeric complex $[Pt_3(CNMe_3)_3(\mu\text{-}CNCMe_3)(\mu\text{-}L)_2]$, 351, which could also be obtained from the reaction of $[Pt_3(CNCMe_3)_3(\mu\text{-}CNCMe_3)_3]$ with L [688]. When $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ was reacted with three molar equivalents of 2,6-dimethylphenylisocyanide (CNAr), the product was $[Pt_3(CNAr)(\mu\text{-}CNAr)_2(\mu\text{-}CO)(PCy_3)_2]$. When five molar equivalents of the isonitrile were used, $[Pt_3(CNAr)_2(\mu\text{-}CNAr)_2(PCy_3)]$ was the main product. Structural studies showed that the bridging isocyanides were severely bent about nitrogen, and their steric requirements are incompatible with the presence of bulky PCy_3 ligands on both the adjacent metal atoms. Thus replacement of the bridging CO by ArNC labilises the adjacent terminal PCy_3 to substitution [689].

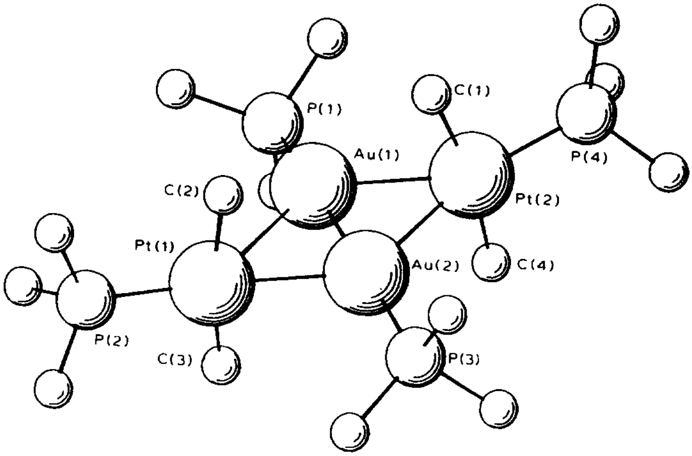


351 (Reproduced with permission from [688])

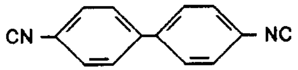
Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $[Au(CNC_6H_3\text{-}2,6\text{-}Me_2)_2]^+$ gave the tetrameric cluster $[Au_2Pt_2(CNAr)_4]^{2+}$, 352, isolated as the $[PF_6]^-$ salt. The metal atoms define a flattened butterfly, with the gold atoms at the higher connectivity sites [690]. Reaction of either $[Pd(\eta^3\text{-}C_3H_5)(Cp)]$ or $[Pt(cod)_2]$ with 353 gave an oligomeric species $[\{M(L)_x\}_n]$, in which $x = 1.82 \pm 0.12$ for M = Pd and $x = 1.25 \pm 0.2$ for M = Pt. The complexes were used as catalysts for the heterogeneous hydrogenation of alkenes or alkynes [691].

8 METAL ALKENE AND ALKENYL COMPLEXES

A number of reviews have been published in this area, including discussions of organic reactions of π-complexes [692], nucleophilic addition to coordinated cyclic π-hydrocarbons [693], the thermodynamics of complexation of unsaturated hydrocarbons with silver, nickel or zinc [694], palladium(II) assisted reactions of alkenes [695] and crystal structural analyses of platinum alkene complexes [696].



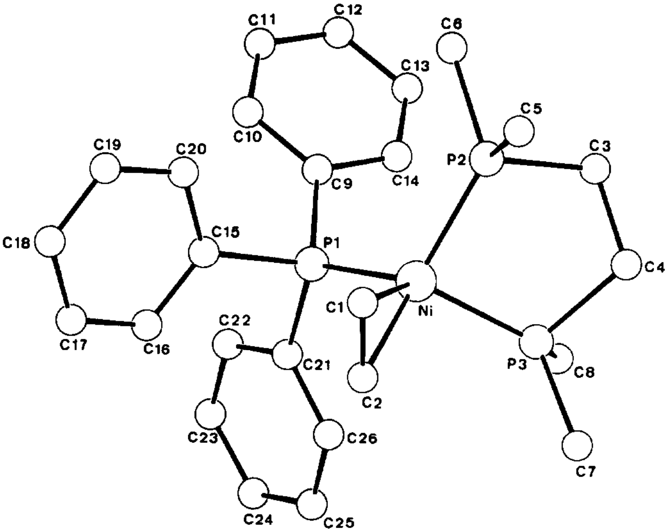
352 Molecular structure of the $[Au_2Pt_2(CNC_6H_3\text{-}2,6\text{-}Me_2)_4(PPh_3)_4]^{2+}$ dication. For reasons of clarity the phenyl groups have been omitted. (Reproduced with permission from [690])



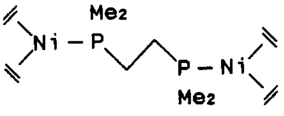
353

Hatree Fock Slater calculations have been undertaken to determine bonding energies in ethene, ethyne and dioxygen complexes of $\{M(PH_3)_2\}$ (M = Ni, Pd or Pt). Back donation of charge from the metal was shown to be more important than donation from ligands to metal, and the bonding energies were in the order Ni > Pt > Pd [697]. Complete active space SCF and contracted CI calculations were performed on the lowest singlet and triplet potential surfaces for $\{Ni(C_2H_4)\}$. The ground state was shown to be $^1A_1$ with an energy minimum corresponding to a distorted ethene moiety with a carbon-carbon bond length of 1.45 Å and the hydrogen atoms tilted 21 ° away from the C-C axis. The triplet $^3A_1$ state is essentially unbound, which is not in agreement with previous calculations [698]. Calculations were used to predict ^{13}C chemical shifts for nickel ethene and ethyne complexes [699].

The reaction between $[Ni(C_2H_4)_3]$, dmpe and R_3P at -20 °C gave $[Ni(C_2H_4)(dmpe)(PR_3)]$, the complex for which R = Ph, 354, being characterised in a diffraction study. Various intermediates were observed [700]. In the absence of added R_3P, $[Ni_2(C_2H_4)_4(dmpe)]$, $[Ni_2(C_2H_4)_3(dmpe)_2]$ and $[Ni_2(C_2H_4)_2(dmpe)_3]$ were formed, their proportions depending on the reaction stoicheiometry. The structures, 355, 356 and 357 were assigned using nmr spectroscopy [701].



354 (Reproduced with permission from [700])



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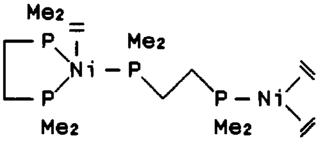

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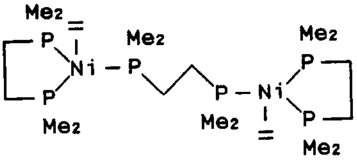
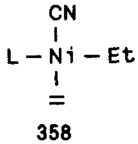


357

The complex $[Ni(C_2H_4)(CH_3)LX]$ (L = PH_3, X = Cl) was considered as a model for a polymerisation catalyst using the Cossée mechansim. From MO symmetry considerations a rearrangement requiring rotation of the alkene around the metal-alkene bond is necessary before reaction occurs. The barrier to rotation is a function of the *trans*-effect of the ligand and the steric interactions [702]. Reaction of $[NiCp_2]$ with RLi or RMgX in the presence of ethene gave $[Ni(C_2H_4)(Cp)R]$, the alkene being necessary to stabilise the metal alkyl

[703].

Reaction of $[Ni(C_2H_4)_3]$ with $M[R_3M'H]$ (M = Li or Na; M' = Al or Ga; R = Me, Et or Me_2CHCH_2) at temperatures below -70 °C in Et_2O or Et_2O/thf, gave $[M(solvent)_n][Ni(C_2H_4)_2(H)(M'R_3)]$. The complex was rather unstable, and was readily converted to carbonyl derivatives [704]. Treatment of $[Ni(C_2H_4)L_2]$ with ethene and HCN gave 358, from which slow reductive elimination in the presence of L gave EtCN. Kinetic data, however, suggest that the processes involved in catalytic hydrocyantion of ethene are more complex [705].



$$L-\overset{\overset{CN}{|}}{\underset{\underset{=}{|}}{Ni}}-Et$$

358

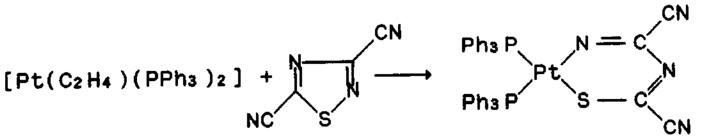
Ab initio calculations on the reactions of $\{Pd(C_2H_4)\}$ with different coordinated nucleophiles (including H^-, Me^-, $[HO]^-$ or F^-) have been undertaken. They show weak $\pi^*\rightarrow d_{yz}$ back donation in all cases. Analysis of the reactivity of the coordinated nucleophiles towards migration to the alkene involved estimating the bond strength and energy of the orbital describing the Pd-Nu bond. It was concluded that frontier orbital controlled *cis*-migration is possible only for H^- and CH_3^-, with F^- and $[HO]^-$ being too unreactive [706,707].

Adsorption of ethene on the <110> surface of palladium at 110 K gave rise to two related but distinguishable electron energy loss spectra corresponding to low and high ethene coverage. Most of the spectroscopic features suggest π-complexation of the ethene, but at very high coverage there are some features which suggest that there are a small number of doubly σ-bonded complexes, involving pairs of palladium atoms [708].

Applications of a closed flow thermostable titration vessel to a study of the reaction of *sym,trans*-$[Pd_2(C_2H_4)_2Cl_2(\mu\text{-}Cl)_2]$ with secondary amines have been discussed [709]. The complexes $[M(C_2H_4)(PPh_3)_2]$ (M = Pd or Pt) reacted with S_4N_4 to give $[M_2(PPh_3)_2(\mu\text{-}S_2N_2)_2]$ [710].

Calculations on the platinum atom with variation of the number of electrons in the $5d_{3/2}$, $5d_{5/2}$ and $6s_{1/2}$ levels indicated that the energy of the $4f_{7/2}$ electrons depends on the ratio between the number of upper d- and s-electrons. On the basis of semi-empirical calculations on the $\{Pt(C_2H_4)\}$ complex, the interaction of the platinum atom with the ligand leads to an increase in the population of the 6s atomic orbital. The bonding of the ethene was discussed [711]. An *ab initio* MO study on $[Pt(C_2H_4)Cl_3]^-$ indicated that both donation and back donation contributed comparably to the stability of the complex [712].

The complex $[Pt(C_2H_4)(PPh_3)_2]$ has again been widely used as a source of the $\{Pt(PPh_3)_2\}$ fragment, since the ethene is readily displaced. Among the added ligands which were used to replace ethene were ArP=C=PAr [713]. In other cases oxidative addition to the $\{Pt(PPh_3)_2\}$ fragment occurred (reactions (15) [714], (16) [715], (17) [716], (18) [717] and (19) [718]. Additionally, $[Pt(C_2H_4)(PPh_3)_2]$ reacted with $[Co(E_2S)(triphos)][BF_4]$ to give $[(triphos)Co(E_2S)Pt(PPh_3)_2][BPh_4]$, (S = P or As) in which platinum may be described as either having bridged, or inserted into the S-E bond of the S_2E ring [719].



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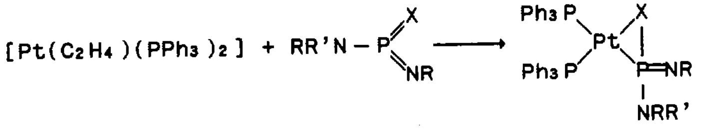


(16)

R = Me₃C, R' = SiMe₃ ; X = S or Se

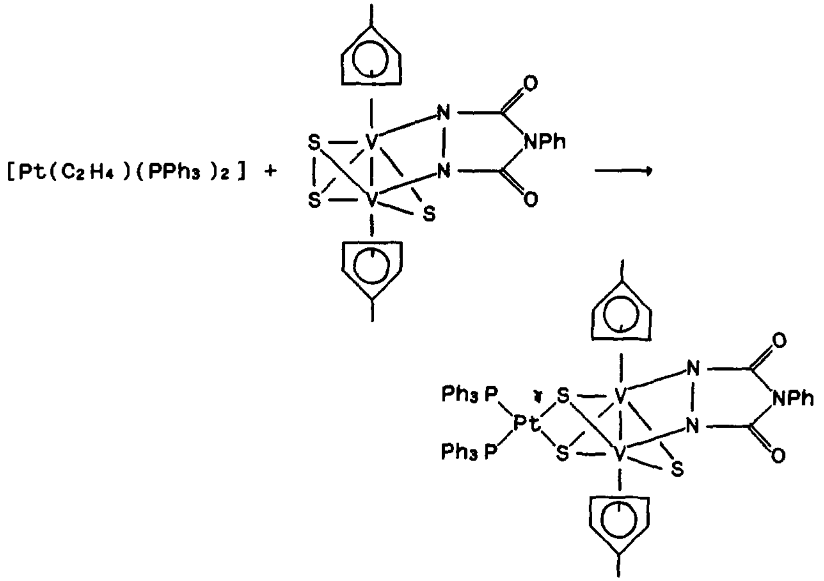
$[Pt(C_2H_4)(PPh_3)_2] + RHgCl \longrightarrow [PtCl(HgR)(PPh_3)_2]$ (17)

R = C_6Cl_5, 1,3,4,6-Cl_4C_6H, 2,3,5,6-Cl_4C_6H or 2,4,6-$Cl_3C_6H_2$

$[Pt(C_2H_4)(PPh_3)_2] + (Me_3SiN)_2S \longrightarrow$ *cis*-$[Pt(NSNSiMe_3)_2(PPh_3)_2]$ (18)

The FAB mass spectra of $[Pt(C_2H_4)(PPh_3)_2]$ and related metal cumulene complexes have been reported. Loss of ethene is the principal fragmentation, but a loss of 14 mass units suggests the formation of a platinum carbene complex [720].

The reaction of $[Pt(C_2H_4)_3]$ with molecular oxygen at -46 °C gave $[Pt(O_2)(PPh_3)_2]$, but the complex decomposes at -20 °C to give ethene and oxygen. In the reaction with the complex in the solid state, some ethene oxide was formed [721]. Reaction of the biphosphine, 359, with $[Pt(C_2H_4)_3]$ gave $[\{Pt(C_2H_4)L\}_n]$ (n = 1 or 2). The ethene could be displaced by other alkenes (such as methyl propenoate), alkynes, CO, or phosphines to give monomeric species [722].



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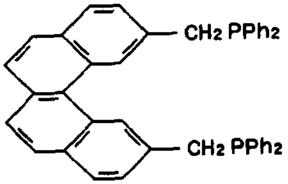
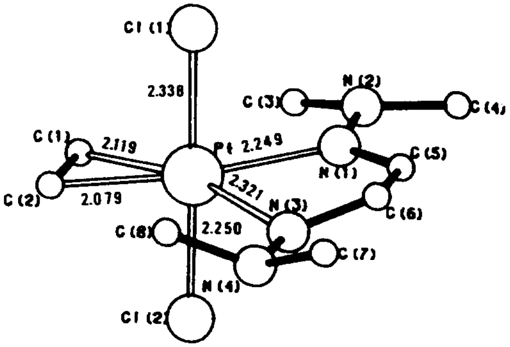


359

The complex $[Pt(C_2H_4)\{PPh(CHMe_2)_2\}_2]$ acted as a catalyst for the reaction of $[H_7Re(PR_3)_2]$ with ethene to give $[Re(C_2H_4)_2H_3(PR_3)_2]$ [723].

Single crystal polarised electronic absorption spectra of $K[Pt(C_2H_4)Cl_3].H_2O$ have been recorded at 10 K. Ligand field and CT transitions were assigned, vibronic structure assigned, and excited state absorptions interpreted. Somewhat surprisingly, the ethene was shown to be an excellent σ-donor (better than ammonia) and a very weak π-acceptor. The relevance of the excited state assignments to the photochemical reactivity of the salt were discussed [724]. The neutron inelastic scattering spectrum of the salt was also recorded in the range 300-1700 cm^{-1}. The vibrational modes of the ethene were assigned [725].

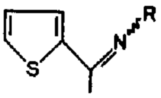
The structure of 360 has been established. The complex is not very symmetric, in accord with ^1H nmr spectroscopic studies which suggest that there is an equilibrium between 4- and 5-coordination in solution [726]. ^1H nmr, ir and electronic spectra have been reported for 16 complexes of the type *trans*-$[Pt(ArNH_2)Br_2(C_2H_4)]$. The chemical shift of the ethene protons was not affected by the electronic character of Ar, but both $\nu(Pt-C_2)$ and $\nu(Pt-N)$ increased with electron releasing aryl groups. The $\pi \rightarrow \pi^*$ transition was also very sensitive to the electronic character of the aryl ring [727]. ^1H and ^{13}C nmr spectroscopic data were reported for complexes *trans*-$[Pt(amine)(C_2H_4)Cl_2]$, in which the amine was a pyrazine, phenazine, quinoxaline or phenazine *N*-oxide. The orientation of the plane of the heterocyclic ligand with respect to the coordination plane was variable, and sensitive to steric effects [728].



360 Perspective view of the molecule down the <121> direction with coordination distances (Å). (Reproduced with permission from [726])

The barrier to alkene rotation in $[Pt(C_2H_4)(\eta^3-CH_2CMeCH_2)(PPh_3)][PF_6]$ was shown to be very low in comparison with those in other platinum(II) ethene complexes, presumably due to a lack of steric hindrance. However, the barrier in $[Pt(C_2H_4)(Cp)(PPh_3)]$ is higher, although it would seem that the steric constraints should be similar. Nmr spectroscopic data suggest that $\{Pt(Cp)(PPh_3)\}$ is a better π-donor to the alkene than is the allyl containing fragement [729].

Reaction of 361 with $K[Pt(C_2H_4)Cl_3]$ gave *trans*-$[Pt(C_2H_4)Cl_2(imine)]$, in which the imine acted as a unidentate *N*-coordinated ligand. The imine complex underwent ready amine/imine exchange [730]. The preparation of 362 has been described [731]. When *sym,trans*-$[Pt_2(C_2H_4)_2Cl_2(\mu-Cl)_2]$ was treated with $[Pt_2Me_4(\mu-SMe_2)_2]$, *sym,trans*-$[Pt_2Cl_2(\mu-Cl)_2Me_2]$ was obtained. The ethene does not rotate or dissociate readily on the nmr spectroscopic timescale. A wide range of further reactions of the complex were discussed [732].



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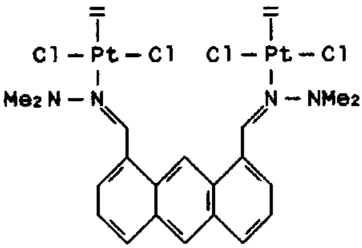


362

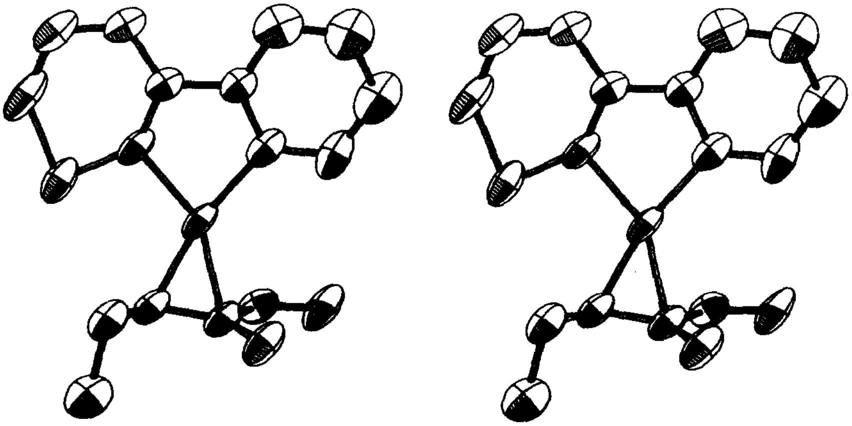
Low temperature photolysis of [Pt(C_2H_4)Cl_2L] (L = substituted pyridine) in a coordinating solvent, S, gave [PtCl_2LS], which was converted to a mixture of *cis*- and *trans*-[PtCl_2L_2] at room temperature [733]. Reaction of the complex with [Ru(bipy)$_2$(CN)$_2$] gave [Ru(bipy)$_2$(μ-CN)$_2${Pt(C_2H_4)Cl_2}$_2$] [734].

In the complexes [Pt(C_2H_4)Cl(diamine)]$^+$ the nature of the amine was shown to be critical in the stabilisation of the complex. In general it was found that 5-membered rings were more stable than six-membered ones, and the Thorpe-Ingold effect was also important [735]. Reaction of *cis*-[Pt(C_2H_4)Cl_2Y] with an excess of amine gave *cis*-[Pt(CH_2CH_2am)Cl_2Y] (Y = dmso or PPh_3). Further reactions replaced one of the chloro ligands by an amine, and for Y = PPh_3, dmso or Me_2NH, cyclic compounds were the eventual products [736]. The kinetics of the reactions for *trans*-[Pt(amine)Cl_2L] (L = C_2H_4, CO or PPh_3) with Cl^- to give [PtCl_3L]$^-$ have been studied. Only in the case of the ethene complex was there a dependance on [Cl^-], and this was reduced when the amine was bulky. The data could be partially explained in terms of the *trans*-effect and the *trans*-influence, but steric effects in the transition state were also very important [737].

Nickel, fluoroethene and PF_3 vapours were cocondensed and reacted at a temperature between -90 °C and -120 °C. The reaction product, presumed to be an alkene complex, was distilled off and condensed on a substrate where it decomposed to a nickel coating, fluoroethene and [Ni(PF_3)$_4$] [738].

Complexes of the type [Ni(alkene)L_2] have been prepared from [Ni(cod)$_2$], alkene and two molar equivalents of L. The relationship between ν(C=C) and the size and electronic character of L was investigated, and a number of reactions of the complexes described [739]. A related reaction with methylene cyclopropane has also been described [740]. [Ni(cod)$_2$] reacted with *trans*-$PhSO_2CH$=CHCOOMe (sma) to give [Ni(cod)(sma)], the second cod ligand not being replaced even in the presence of a large excess of sma. An X-ray structure determination revealed that the the carbon-carbon double bond in sma prefers an in-plane conformation, as predicted by theory. Reaction of [Ni(cdt)] with sma did give small amounts of $[Ni(sma)_2]$. Reactions of [Ni(cod)(sma)] with phosphorus or nitrogen donor ligands resulted in the replacement of cod, whilst maleic anhydride replaced sma [741].

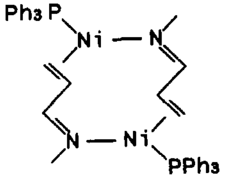
The electrochemistry of the Ni(II) complex $[Ni(NCMe)_6]^{2+}$ has been investigated. Ni(I) species were stabilised by the addition of alkenes bearing electron withdrawing groups, including acrylonitrile, fumaronitrile, and diethylmaleate [742]. The structure of $[Ni(bipy)\{CH_3CH_2CH{=}C(CH_3)CHO\}].H_2O$, 363, was established in a diffraction study. As well as coordination of the carbon-carbon double bond, there is a significant interaction with the neighbouring carbonyl group, so that the structure is intermediate between an alkene and an allyl complex [743].



363 Molecular structure of $[Ni(bipy)\{CH_3CH_2CH{=}C(CH_3)CHO\}]$. (Reproduced with permission from [743])

The role of mono and diazadiene complexes in catalytic reactions has been reviewed. In $[Ni(PhCH{=}CH\text{-}CH{=}NPh)(PPh_3)_2]$ a diffraction study shows that only the carbon-carbon bond is metal coordinated, but in $[Ni_2(CH_2{=}CH\text{-}CH{=}NMe)_2(PPh_3)_2]$, 364, the S-*trans*-ligand interacts at nitrogen with another metal centre [744].

The preparations of the ligands $(CH_2{=}CHCH_2CH_2)_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$ (n = 1, tasol, n = 2 dasdol) have been described. The reaction of tasol with Ni(II) gave $[Ni(tasol)X]^+$ for X = Cl or Br, the complexes having trigonal bipyramidal geometry with the halide axial, and the alkene coordinated in the equatorial plane. However, $[Ni(tasol)I_2]$ adopted square pyramidal geometry, with iodide at the apex and the alkene uncoordinated. Reaction of $[NiCl(tasol)][ClO_4]$ with water resulted in displacement of the alkene from the coordination sphere to give [NiCl(H_2O)(tasol)][ClO_4] in which the cation had a square pyramidal coordination sphere. No dasdol complexes with coordinated alkene were prepared [745]. Reaction of 2-ethenylphenyldiphenylphosphine (SP) with [M(C_2H_4)(PPh_3)$_2$] (M = Ni, Pd or Pt) gave [M(PPh_3)$_2$(SP)]. The complexes all disproportionated in solution. In the solid state the nickel and platinum complexes adopted tetrahedral geometry with SP acting as a bidentate ligand, but the alkenyl group was uncoordinated in the palladium complex. Exchange reactions and dynamic behaviour in the complexes were investigated by nmr spectroscopy [746].



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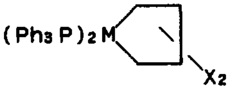
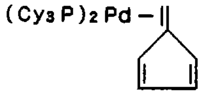
Reaction of either [Ni(C_2H_4)(PPh_3)$_2$] or [Ni{$(CH_2)_4$}(PPh_3)$_2$] with an alkene, XCH=CH_2, gave [Ni(CH_2=CHX)$_2$(PPh_3)$_2$] (X = CN or COOMe), which was in equilibrium with 365. Reductive elimination gave the *trans*-substituted cyclobutane [747].



365

Photolysis of [M(C_2O_4)L_2] (M = Pd or Pt; L = R_3P or Et_2S) gave CO_2 and {ML_2}, the latter reacting readily with L' to give [ML_2L'], with L' = alkene, alkyne or R_3P. Oxidative addition reactions of {NiL_2} with alkyl, aryl and allyl halides were also described [748]. Reaction of [Pd(η^3-C_3H_5)(η^5-MeC_5H_4)] with PCy_3 gave the fulvene complex 366. The metal fulvene bond is strong, and the ligand is not easily liberated [749]. When Pd(OCOMe)$_2$ was treated with a stoicheiometric amount of acrylonitrile the products were $MeCO_2CH$=CHCN and palladium metal, but with an excess of the alkene, a species of composition {Pd(CH_2=CHCN)(OCOMe)$_2$} was isolated and characterised. A diffraction study of 367 showed that the complex has a tetrameric structure, with a cyanoethylethanoate acting as a bridging ligand between two metals of different dimeric units. The palladium atoms of the dimers are joined by double ethanoate bridges arranged around the crystallographic 4_1 axis [750].



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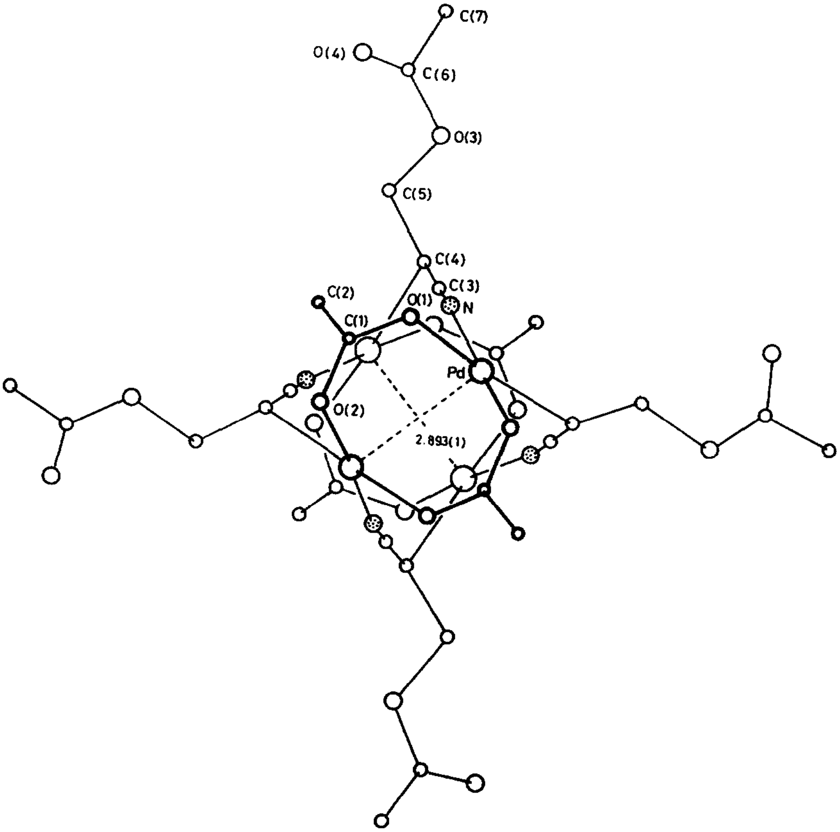
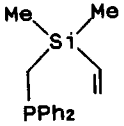


367 A view of two dimeric units of "Pd(CH_2=CHCN)(OCOMe)$_2$" along the crystallographic 4_1 axis with the numbering scheme of the independent atoms shown. Pd-Pd distance in Å. (Reproduced with permission from [750])

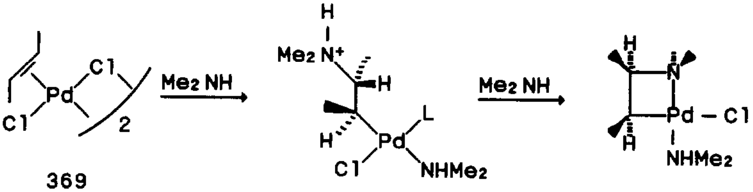
When tasol was reacted with $[PdX_4]^{2-}$ the species {Pd(tasol)X_2} (X = Cl, Br or I) were produced. In solution these were four coordinate species of the type [Pd(tasol)X]X, and the alkene was not metal bound. Similar results were noted for the platinum series. In the solid state both the palladium and the platinum complexes were 5-coordinate, with the palladium series having an $\{As_3X_2\}$ coordination sphere, and the platinum having $\{As_3(alkene)X\}$ ligation [751]. In complexes of 368, such as $[MLCl_2]$, the ligand was bidentate with phosphine and alkene both metal coordinated [752].



368

Some reactions of $[\{Pd(\alpha\text{-pinene})Cl_2\}_2]$ have been reported [753]. Voltammetric studies of palladium and platinum complexes containing diimine and alkene ligands indicated that the LUMO of the complexes was dominated by the diimine π^* orbital [754].

The reactions of palladium coordinated alkenes with amines continue to be investigated. Conversion of 369 to the characterisable product 370 proves that amine addition is stereospecifically *trans* [755]. Addition of diethylamine to $PhOCH_2CH{=}CH_2$ in the presence of palladium ethanoate, followed by oxidation, gave only $PhOCH_2CH(OCOMe)CH_2NEt_2$. However, when the attacking amine was $PhCH(Me)NMe_2$ and the reaction time was short, both regioisomeric products were produced. This suggests that the aminopalladation step is reversible, and that the anti-Markownikoff product may be formed under conditions of kinetic control, possibly for steric reasons [756].



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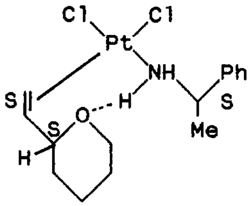
370

The structure of 371 was established in an X-ray diffraction study. The complex was prepared from *cis*-$[Pt(C_2H_4)Cl_2\{S\text{-}PhCH(NH_2)CH_3\}]$ and the racemic alkene, followed by fractional crystallisation of the diastereoisomers. Hydrogen bonding is important in determining the arrangement of the coordinated ligands [757].



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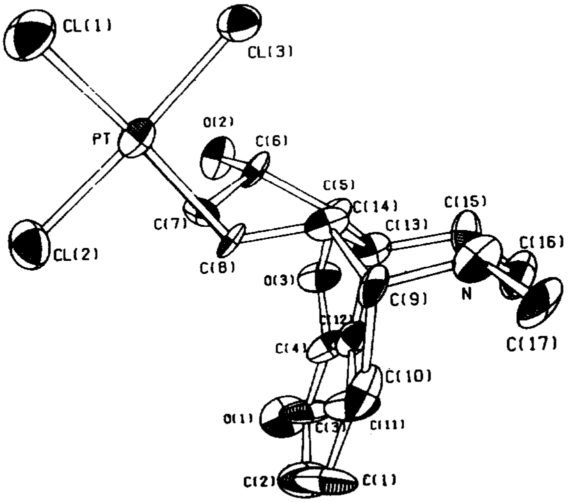
The ir spectrum of K[Pt($CD_3CD=CD_2$)Cl_3] was recorded and assigned [758]. Alkene rotation in *cis*-[PtCl_2(4-Me$C_6H_4NH_2$)(RCH=CH_2)] (R = H or OEt) was studied by ^{1}H nmr spectroscopy. In the ethene complex, both the amine and the alkene rotate fairly freely at temperatures above -25 °C. Howver, in the complex of ethyl vinyl ether, neither the amine nor the alkene rotate; a strong hydrogen bond stabilises one rotamer [759]. XPES of seven five-coordinate complexes of the type [Pt(alkene)Cl_2(NN)] (NN = diimine or diamine chelating ligand) reveal differences from the related four-coordinate platinum(II) derivatives. The platinum 4f and nitrogen 1s signals gave evidence for π-back-donation from platinum both to the alkene and the chelating nitrogen ligands. The π-back donation is more significant, and the platinum atoms more positive, in the five- than in the four-coordinate complexes. These results are in keeping with the decrease in reactivity with nucleophiles for the alkenes in the five-coordinate complexes [760].

A general synthesis of platinum(II) alkene complexes has been reported (reactions (20) and (21); yields were moderate to excellent. The thermal reaction is thought to proceed *via* [PtCl_5]$^-$, to give [RCH^+-CHR'-PtCl_5^-], whereas in the photochemical process, electron transfer gives rise to [RCH=CHR']$^{+\cdot}$ and [Pt(III)Cl_5]$^{2-}$ [761]. A range of complexes *cis*-[Pt($CH_3CH=CH_2$)Cl_2(PR_3)] was prepared by reaction of [Pt(η^3-C_3H_5)Cl(PR_3)] with HCl [762].

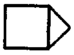
$$\begin{tikzcd}
{[PtCl_6]^{2-} + RCH{=}CHR'} \arrow[r, "\Delta \text{ or } h\nu"] & {[\{PtCl_2(RCH{=}CHR')\}_2]} \arrow[r, "py"] & {[PtCl_2(py)(RCH{=}CHR')]} & (20) \\
{[PtCl_6]^{2-} + RCH_2CHR'OX} \arrow[r, "\Delta"] & {[\{PtCl_2(RCH{=}CHR')\}_2]} \arrow[ur, "py"'] & & (21)
\end{tikzcd}$$

X = H or COMe

Reaction of $K_2[PtCl_4]$ with morphine hydrochloride gave the zwitterion [Pt(morphinium)Cl_3], 372, characterised in a diffraction study. The {$PtCl_3$} unit is π-bonded to the C(7)-C(8) double bond [763]. When 373 was treated with $K[Pt(C_2H_4)Cl_3]$ the products were cyclopentene and [{PtCl(μ-Cl)(cyclopentene)}$_2$]. Related reactions were also discussed [764]. When 374 was generated in the presence of $[Pt(C_2H_4)Cl_2(py)]$, the product was the stable species 375. An anomalously large change in δ on complexation for C^1, as well as enhanced values of $^1J(PtC)$ suggest that this complex has strong metallocyclopropane character. The related reaction in the palladium series was much more complex, resulting in isomerisation of the anti-Bredt alkene [765]. The initial reaction of 376 with platinum(II) gave an alkene π-complex. When this was reacted with [{$Pt(C_2H_4)Cl(\mu$-Cl)}$_2$], the product was the most unusual platinum(IV) alkene complex, 377, characterised in a diffraction study [766].



372 ORTEP drawing of the [(morphinium)$PtCl_3$] zwitterion. The ellipsoids correspond to 50 % probability. (Reproduced with permission from [763])



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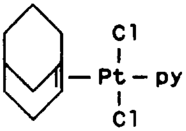

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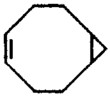

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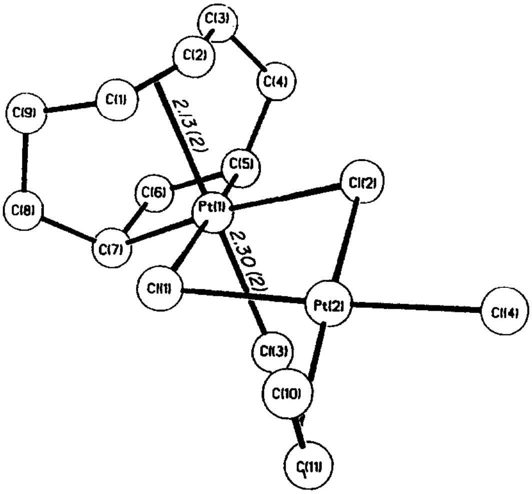
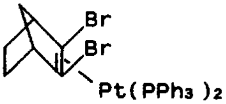


377 (Reproduced with permission from [766])

Complexes of $\{Pt(PPh_3)_2\}$ with cycloalkynes have previously been prepared by sodium amalgam reduction of 1,2-dibromocycloalkenes in the presence of $[Pt(PPh_3)_3]$. However, 378 gave only the alkene complex, whether Na/Hg was added or not. The groups X and Y must be electron withdrawing for the reaction to be successful. Thermolysis of 379 resulted in insertion into the carbon-bromine bond to give 380, characterised in a diffraction study [767].

378



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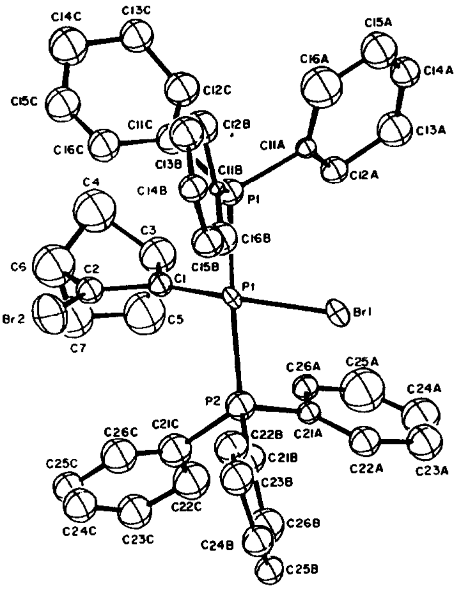
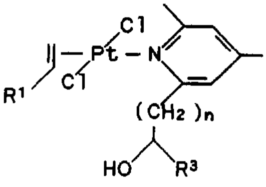


380 (Reproduced with permission from [767])

Transition metals are known to yield more stable complexes of Z- rather than E-alkenes. A study of the complexes $[Pt(\eta^3-CH_2CMeCH_2)L(PPh_3)][PF_6]$, in which L may be a range of alkenes, provides the first contrary example. Complexes of E-MeCH=CHMe, E-MeCH=CHEt or E-MeCH=CHPh were more stable than those of their Z-isomers. Some insight into this was provided by structural sudies on the complexes of Z- and E-MeCH=CHMe. For the complex of the Z-isomer the carbon-carbon bond lay in the coordination plane, whereas in the E-isomer it was at 67.1 ° to the plane [768].

^1H nmr spectroscopy of *cis*-$[Pt(alkene)Cl_2(4-MeC_6H_4NH_2)]$ (alkene = 1-butene, 4,4-dimethyl-1-pentene, Z-CH_3CH=CHOEt, $MeOCH_2CH=CH_2$ or $Me_3COCH=CH_2$) indicated that the coordination of the alkene was stereoselective, with a single isomer in solution [769]. Alkene exchange reactions of 381 have been studied. Exchange was hindered by substituents at the 2- and 6-positions of the pyridine ring, but the -OH group provided an intramolecular catalyst, *via* 382 [760].

The complex (+)-*trans*-$[PtCl_2(E\text{-}MeCH=CHMe)\{MeC(=NNMe_2)C(=NNMe_2)Me\}]$ was prepared from resolved *trans*-$[PtCl_2(E\text{-}MeCH=CHMe)\{S\text{-}PhCH(Me)NH_2\}]$, and the bis(hydrazone). The structure of the product was established in a diffraction study, and it was shown that the absolute configuration of the alkene was unchanged [771]. The reaction of 383 with 1-alkenes gave a mixture of diastereoisomers which could be separated on a preparative scale by liquid chromatography. Addition of a chiral alkene gave four separable diastereoisomers, and 384 was thus resolved [772].



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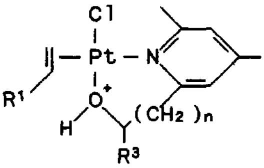

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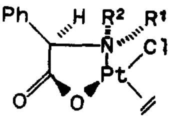

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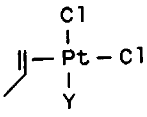
384

The reaction between 385 and $PhCOCH_2CH_2NMe_2$ to give 386, and the subsequent cycloelimination to give 387 were followed by ^{195}Pt and ^{31}P nmr spectroscopy [773]. The partition of 388 between 389 and 390 was investigated. Cyclic products were more likely when the amine is secondary and the alkene is substituted. Complexes of the type 390 were isolated in a number of cases [774].



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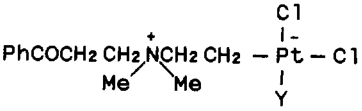

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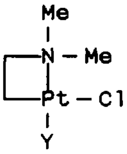
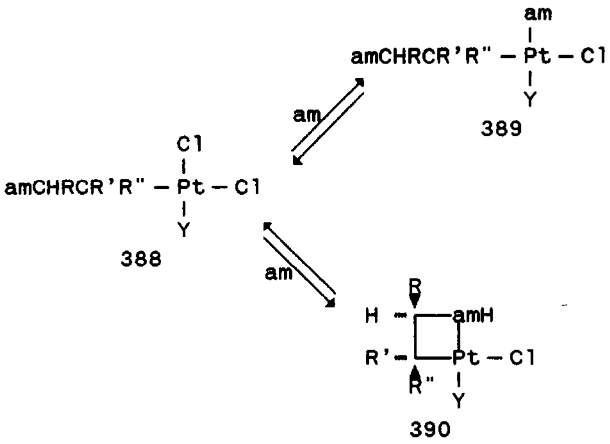
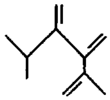


387

When $SnCl_2$ was reacted with $[Pt(alkene)Cl_3]^-$ the initial product was *cis*-$[Pt(alkene)Cl_2(SnCl_3)]^-$. Further addition of $SnCl_2$ resulted in alkene loss for the ethene complex, but when $[PtCl_2(cod)]$ was treated with $SnCl_2$ and $[SnCl_3]^-$, the five-coordinate complex, $[Pt(cod)(SnCl_3)_3]^-$, was the final product [775]. Photolysis of hexane in the presence of $[PtCl_6]^{2-}$ and pyridine gave a low yield of $[PtCl_2(1\text{-hexene})(py)]$. An electron transfer mechanism was proposed for the reaction [776]. Platinum alkene complexes were implicated in the decomposition of 2,2,6,6,-tetramethylcyclohexane carboxylic acid on platinum films [777].



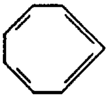
The reactions between $[Ni(PPh_3)_3]$ and allenes have been studied. $MeCH=C=CH_2$, $Me_3CH=C=CH_2$ or $Me_2C=C=CH_2$ reacted reversibly to form mono and bis(allene) complexes at teperatures below -70 °C. In all cases π-complex formation involved the less substituted double bond. $PhCH=C=CH_2$ and $CH_2=C=CHCN$ reacted rapidly and irreversibly at this temperature. The stability of the complexes formed was discussed in terms of both steric and electronic effects, and carbonylation reactions were also described [778]. Oligomerisation of 1,1-dimethyl allene in the presence of $[Ni(PPh_3)_3]$ gave 391 as the major product, together with smaller amounts of other dimers and trimers. The mechanism of the reaction was discussed in considerable detail [779].



391

The ethene ligand in $[Pt(C_2H_4)(DIOP)]$ was readily substituted by allene to give an η^2-complex, or by CO [780]. Base catalysed elimination of HBr from 1-bromo-1,3,5-cycloheptatriene gave the cycloallene 392, which reacted with $[Pt(PPh_3)_3]$ to give successively $[Pt(392)(PPh_3)_2]$ and $[Pt(392)_2(PPh_3)_2]$. The latter underwent ligand dimerisation, in what appeared to be a radical reaction, to yield 393, characterised in a diffraction study [781]. The reaction of the benzannelated complex was similar [782]. Treatment of $[PtL_4]$ with CH_2Br_2, CO and zinc metal gave $[Pt(CH_2=C=O)L_2]$, the same complex being derived from the reaction of $[PtL_4]$ and ketene. Spectroscopic data for the complex were consistent with η^2-coordination of the carbon-carbon double bond.

Deuterium labelling studies of the decomposition of the complex were consistent with a mechanism invoving a carbene complex [783].



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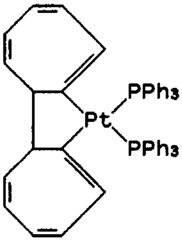


393

Reaction of $[Ni(C_2H_4)_3]$ with butadiene and bipy gave $[Ni(bipy)(\eta^2\text{-}C_4H_6)(\mu\text{-}\eta^4\text{-}C_4H_6)Ni(\eta^2\text{-}C_4H_6)(bipy)]$, 394, characterised in a diffraction study. The relevance of this structure to the catalytic oligomerisation of butadiene has been discussed [784]. Low temperature matrixes of butadiene containing nickel or platinum atoms were prepared by codeposition at -190 °C. With nickel, the charge transfer complex $\{Ni(C_4H_6)\}$ was formed initially, giving yellow $[Ni(C_4H_6)_2]$ on warming to -130 °C. At higher temperatures the red polymer $[\{Ni(C_4H_6)\}_n]$ was formed, but decomposed at temperatures above -80 °C [785].

Various nickel cyclooctadiene complexes have been used as precursors for organometallic or coordination complexes, since cod is relatively easily displaced (reactions (22), n = 2 or 3; m = 1 or 2; L = PPh_3, Cy_2PH or Cy_3P, or L_2 = tmeda, bipy, phen or dppe) [786], (23) [787] and (24) [788]. Oxidative addition with replacement of cod has also been noted (reactions (25) (L = PEt_3 or L_2 = bipy) [789], and (26) [790]).

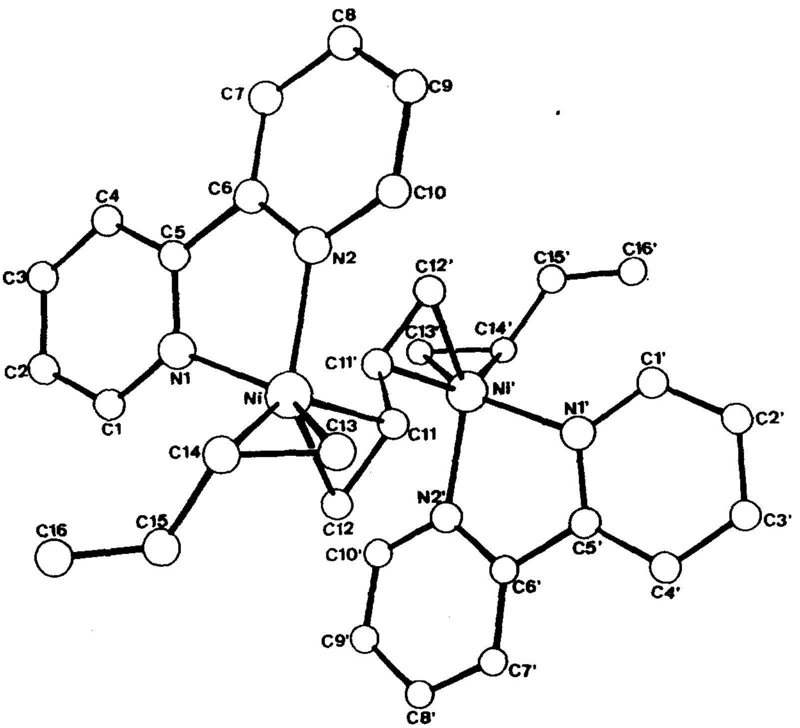
$$[Ni(cod)_2] + nL + mSO_2 \longrightarrow [Ni(SO_2)_mL_n] \qquad (22)$$

$$[Ni(cod)_2] + [Zr(CH_2PMe_2)_2(Cp)_2] \longrightarrow [\{Cp_2Zr(CH_2PMe_2)_2\}_2Ni] \qquad (23)$$

$$[Ni(cod)_2] + Me_3Si\text{-}C{\equiv}C\text{-}SO_2Ph \longrightarrow [Ni(cod)(Me_3Si\text{-}C{\equiv}C\text{-}SO_2Ph)] \qquad (24)$$

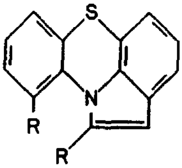
$$[Ni(cod)_2] + ArSSAr + 2L \longrightarrow [Ni(SAr)_2L_2] \qquad (25)$$

$$[Ni(cod)_2] + PPh_3 + I_2 \longrightarrow [Ni(cod)(PPh_3)I] \qquad (26)$$



394 (Reproduced with permission from [784])

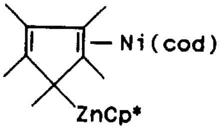
The complex [Ni(cod)$_2$] proved to be the best doping agent for MgH$_2$ or Mg/H$_2$ as a system for hydrogen storage [791]. Desulphurisation of 395 was reported in the presence of [Ni(bipy)(cod)], but the reaction mechanism was not discussed [792].



395

Reaction of [Ni(cdt)] with M[AlR$_3$H] in Et$_2$O or thf at temperatures below -50 °C gave [M(solvent)$_n$]$^+$[R$_3$Al-H...Ni(cdt)]$^-$ (M = Li or Na, R = Me, Et or CH$_2$CHMe$_2$), in which there is a three-centre Al-H-Ni bond [793]. Electron transfer between [Ni(bipy)(cod)] and phthalimide gave a nickel radical cation, and a phthalimide radical anion as the initial products. Further reactions in this system involved partial decarbonylation, and insertion of the metal into the N-H bond [794].

The catalyst derived from $[Ni(cod)_2]$ and bipy ruptures carbon-sulphur bonds in ArSAr at temperatures below 100 °C and in the absence of molecular hydrogen. The desulphurisation is enhanced by the presence of main group hydrides such as $Li[AlH_4]$ [795]. Reaction of $[Ni(cod)_2]$ with $Cp^*{}_2Zn$ gave $[\{Ni(Cp^*)_2\}_2(C_{16}H_{24})]$ *via* **396**, **397** and **398**, followed by radical dimerisation [796]. In the reaction of benzoquinone with $[Ni(C_2H_4)(PCy_3)_2]$ electron transfer gave initially **399**. The reactions of naphthaquinones were also discussed [797].



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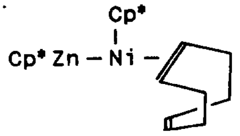
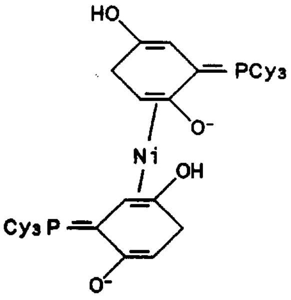


397

$[Ni(\eta^2\text{-}cod)(Cp^*)]^\bullet$

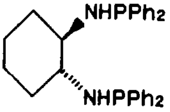
398



399

Reaction of $Na_2[PdCl_4]$ with 1-trimethylsilyl-2,4-pentadiene gave the $[PdCl_2(diene)]$ complex. The preparations of clusters of unknown structure, $[Pd_5(CH_2{=}CH{-}CH{=}CHCH_2X)Cl_9(OMe)]$ (X = SPh, SePh or PPh_2) were also described [798]. The synthesis of $[Pd(cod)L]^{2+}$ (L = **400**) was noted [799]. Two stages were discerned in the reaction of $[PdCl_3(OH_2)]^-$ with dienes. In the first rapid step $[PdCl_3(\eta^2\text{-diene})]^-$ was formed, and this was more slowly converted to $[PdCl_2(\eta^4\text{-diene})]$. As the water content of the reaction solvent was increased, the formation of some colloidal palladium was noted, indicative of hydroxypalladation of the diene. This seems to take place from the η^2- not the η^4-complex [800]. The synthesis of $[PdCl_2(3\text{-methylcycloocta-1,4-diene})]$, **401**, was reported. The methyl group perturbs the conformational energies of the

1,4-diene so that the only conformation observed in the complexed state is the boat-chair. The rearrangement of this complex to [$PdCl_2$(3-Me-1,5-cod)] involved a σ-allyl intermediate. Methoxypalladation of the complexes was discussed [801].



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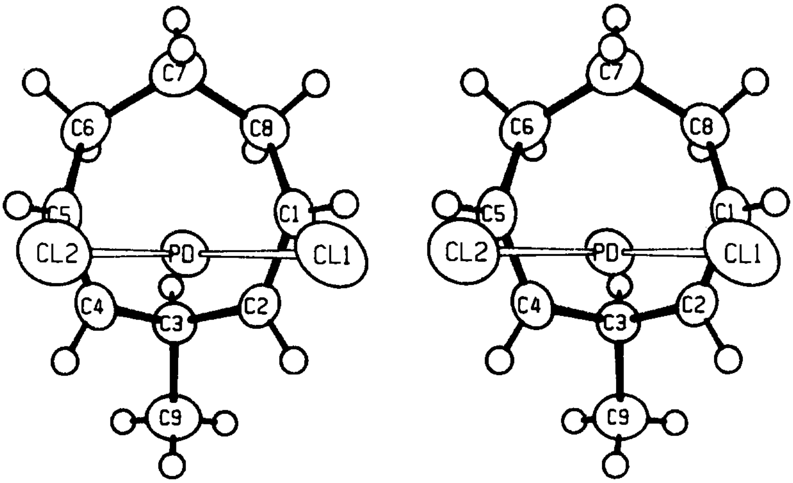
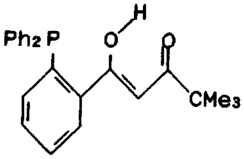


401 Stereopair drawing of the molecular structure of [$PdCl_2$(3-Me-1,4-cycloooctadiene)]. (Reproduced with permission from [801])

Microcalorimetric measurements of enthalpies of thermal decomposition of palladium and platinum complexes have been made. The species discussed included [MCl_2(cod)] [802].

Cyclooctadiene was displaced from [M(cod)Cl_2] (M = Pd or Pt) by HacacP, 402, to give [MCl_2(HacacP-*P*)$_2$] [803]. The homoleptic metal d^{10} complexes [M{M'$(NR_2)_2$}$_3$] (M = Pd or Pt; M' = Sn or Ge; R = $SiMe_3$) were prepared from [Pd(cod)Cl_2] and five molar equivalents of M'$(NR_2)_2$ or [Pt(cod)$_2$] and four equivalents of M'$(NR_2)_2$ [804]. Reaction of [Pt(cod)I_2] with [IrL(NO)$(PPh_3)_2$] (L = 403) gave [IrL(NO)(PPh_3PtI_3)]$^+$ supposed to contain a bridging nitrosyl group. However, with $PtCl_2$(cod)], the product was [$IrCl_2L(PPh_3)_2$]$^+$ [805].



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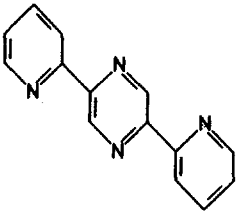
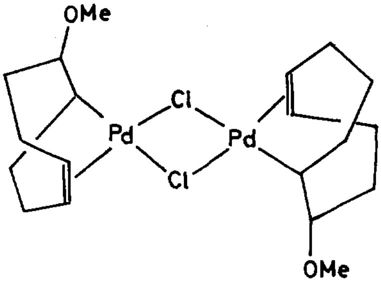


403

The well known reaction of $[Pd(cod)Cl_2]$ with methoxide ion to give 404 has been adapted for use as an undergraduate experiment [806]. The complex 404 reacted with thallium catechol salts to give species such as 405, for which EPR spectroscopic data were reported [807]. Reaction of $[PdCl_2(nbd)]$ with methanol gave 406, and a number of further transformations of this complex were discussed [808]. The mechanism of reaction (27) is not known, but may be assumed to involve a palladium alkene complex [809].



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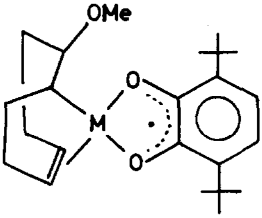
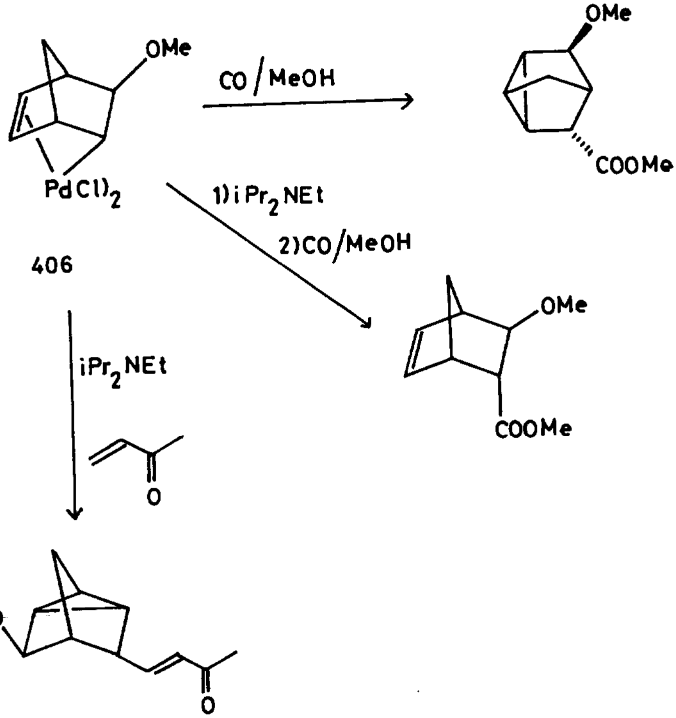


405

A low temperature X-ray study of $[PtCl_2(cod)]$ failed to confirm the earlier reported room temperature study, which suggested non-symmetric metal alkene bonding. This had been thought to be responsible for the activation of the diene towards nucleophilic attack [810]. The structure of $[Pt(acac)(cod)][BF_4]$ has been published twice. The cod ligand adopts a tub conformation [811,812].

Displacement of cod from $[PtCl_2(cod)]$ has been noted using dapm [813] or crown ether analogues [814] as the incoming ligands. $[Pt(cod)_2]$ was used as a precursor for $[PtL_3]$ and/or $[PtL_4]$ ($L = P(OBu)_3$, $AsBu_3$ or $SbBu_3$). In a reaction in which there was insufficient of the added ligand, complexes of the solvent, toluene, were also formed [815]. Reaction of 407 with $[PtCl_2(cod)]$ gave a polymeric yellow solid, which did not contain cod, but the material was too insoluble for the structure to be determined [816].



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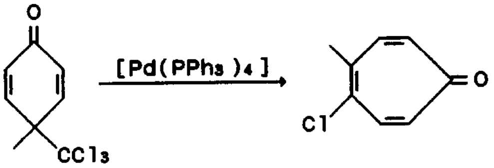

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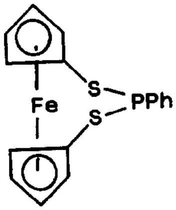
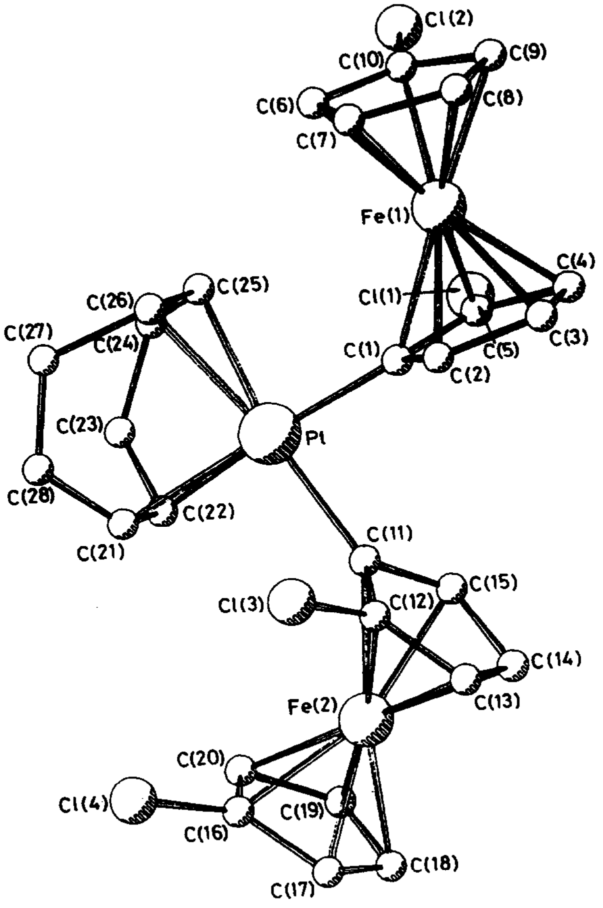


407

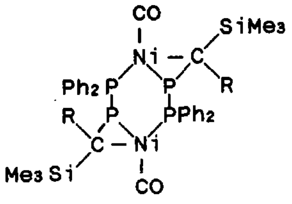
When $[Pt(cod)X_2]$ was reacted with 1-lithio-1'2-dichloroferrocene, the product was 408, characterised in a diffraction study. The ferrocenyl groups adopt a D_h arrangment, with a single crystal consisting of molecules of only one enantiomer [817].



408 A molecule of $[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$ showing the numbering scheme used in the crystallographic results. (Reproduced with permission from [817])

Reaction of $[PtCl_2(cod)]$ with silver ethanoate gave successively $[Pt_2(C_8H_{12}OCOMe)_2Cl_2]$ and $[Pt_2(C_8H_{12}OCOMe)_2(OCOMe)_2]$. The latter species could also be conveniently prepared by treatment of $[Pt_2(C_8H_{12}OMe)_2(OMe)_2]$ with an excess of ethanoic acid [818]. Treatment of $[PtCl_2(cod)]$ with $M'(NR_2)_2$ (M' = Sn or Pb; R = $SiMe_3$) gave *cis*-$[Pt(cod)\{M'Cl(NR_2)_2\}_2]$, which decomposed at temperatures above 0 °C [819].

A number of papers have reported complexes of phosphaalkenes. Reaction of $[Ni(CO)_4]$ with $ClP=C(SiMe_3)_2$ gave $[Ni\{\eta^2\text{-}ClP=C(SiMe_3)_2\}_2(CO)]$. When the added ligand was $Ph_2PP=C(SiMe_3)R$ (R = $SiMe_3$ or Ph), the initial product was an η^1-complex, coordinated to $\{Ni(CO)_3\}$ at the diphenylphosphine group. Thermolysis yielded **409** [820]. The reaction between $[NiCl_2(PMe_3)_2]$ and $[\{(Me_3Si)_2CH\}_2P]Na$ gave $[Ni\{\eta^2\text{-}(Me_3Si)_2C=PCH(SiMe_3)_2\}(PMe_3)_2]$, 410. The mechanism of the reaction was discussed [821].



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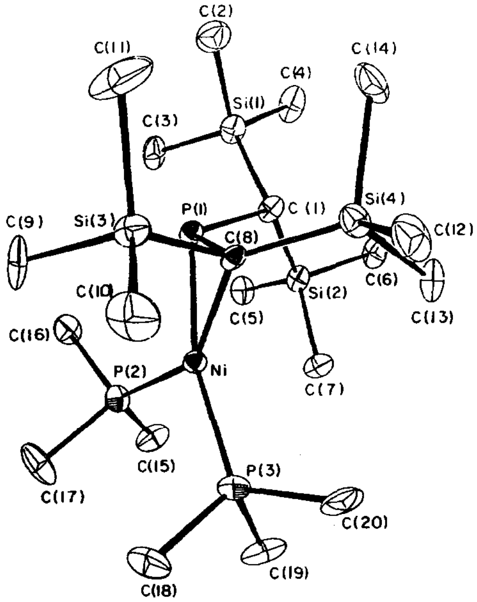
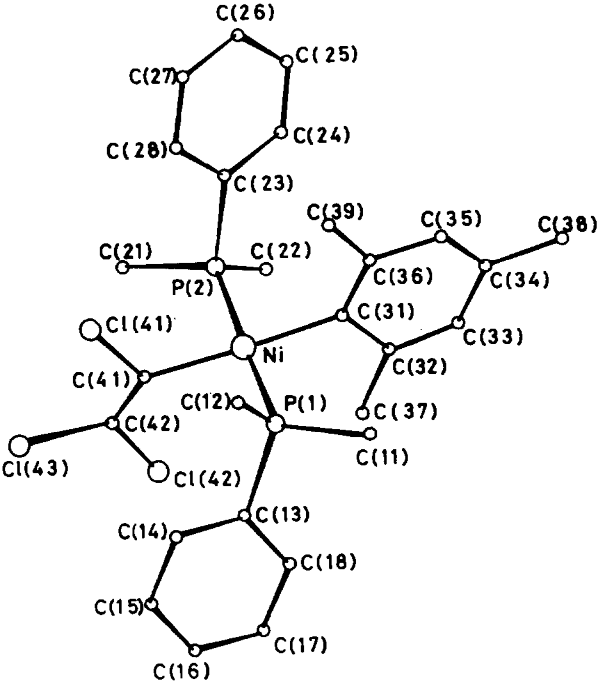


410 ORTEP view of $[Ni\{(Me_3Si)_2C=PC(H)(SiMe_3)_2\}(PMe_3)_2]$. (Reproduced with permission from [821])

The equilibration of η^1- and η^2-$MesP=CPh_2$ in complexation with $\{Pt(PPh_3)_2\}$ has been studied. In the solid state, a diffraction study proved the presence of an η^1-complex, but the theoretically favoured η^2-complex was observed in solution [822]. Solid state ^{31}P nmr spectroscopic data indicate that the coordination is η^1 in the solid, but solution data were quite different, suggesting a predominence of the η^2-form [823].

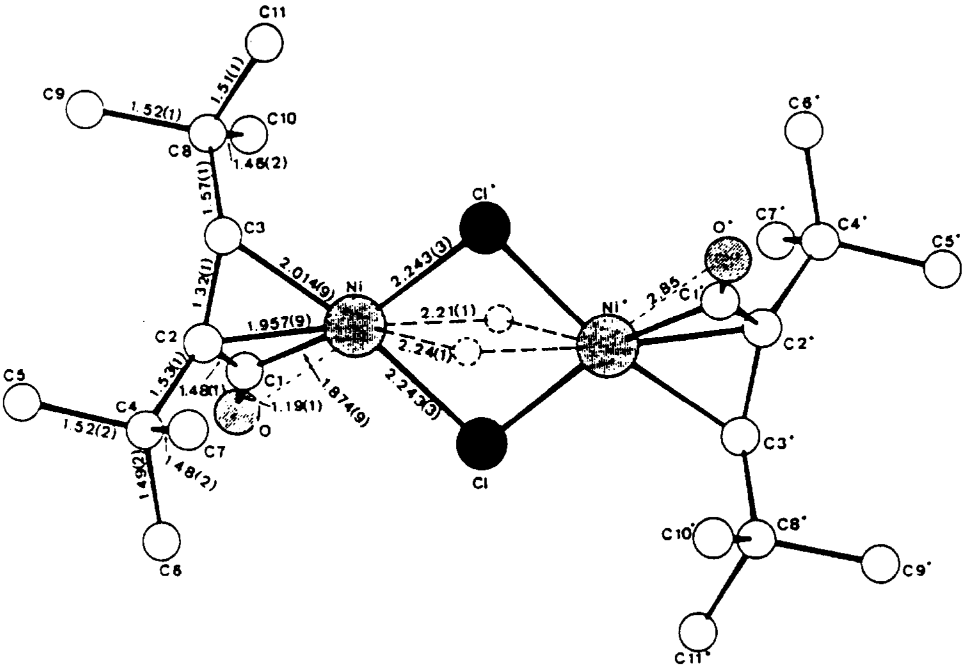
When *trans*-$[Ni(Ar)\{C(Cl)=CCl_2\}(PMe_3)_2]$ was thermolysed, the main product was *trans*-$[Ni\{C(Cl)=C(Cl)Ar\}Cl(PMe_3)_2]$, but the configuration of the double bond was not determined. The stability and reactions of various aryl complexes was discussed [824]. Treatment of $[Ni(PPh_3)_n]$ with RCl (R = $CCl=CCl_2$, $CH=CCl_2$, $C(Cl)=CH_2$ or $CH=CHCl$) gave *trans*-$[NiCl(PPh_3)_2(R)]$. Further reactions of the complexes were studied in detail [825]. The preparation of $[NiL_2RR']$ for which L = PMe_2Ph, R = C_2Cl_3 and R' = Ar was described for a wide range of complexes. The structure of *trans*-$[Pt\{2,4,6\text{-}Me_3C_6H_2C(Cl)=CCl_2\}(PMe_2Ph)_2]$, 411, was established in a diffraction study [826].



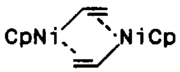
411 (Reproduced with permisssion from [826])

Reaction of $Me_3CC{\equiv}CCMe_3$ with $[Ni(CO)_4]$ and HCl gave a species of stoicheiometry $[Ni_2Cl_2(CO)_2\{C(CMe_3)=CH(CMe_3)\}]$. IR, ^1H and ^{13}C nmr spectroscopy indicated that the halides were bridging, but an X-ray structure determination revealed that the structure was actually 412. Further reactions of the complex were discussed [827]. The treatment of $[NiCp_2]$ with ethenyl lithium gave 413, which was converted to 414. In the presence of ethene,

$[Ni(C_2H_4)(CH{=}CH_2)(Cp)]$ was formed, and underwent a variety of insertion reactions [828].



412 (Reproduced with permission from [827])



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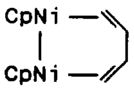


414

9 METAL ALLYL AND RELATED COMPLEXES

Reviews have been published concerning the use of π-allyl nickel halides as selective reagents in organic synthesis [829], and more specifically in carbon-carbon bond forming reactions [830]. A more general review of the chemistry of such complexes has also appeared [831].

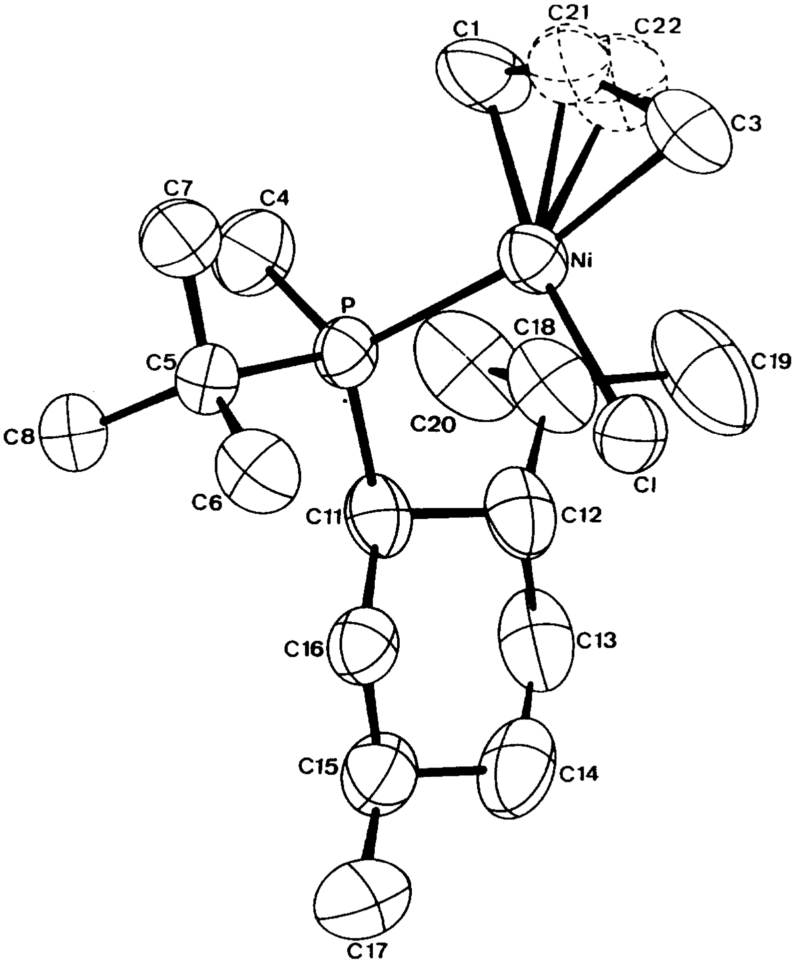
Ab initio SCF calculations at the double ζ-level have shown that the total energy of bis(allyl) nickel is lowered by 187 kJ mol^{-1} when the hydrogen atoms are allowed to move out of the plane. The most stable geometry involves the *syn*- and *meso*-hydrogen atoms being bent by 6.7 ° and 13.4 ° respectively towards the metal, with the *anti*-hydrogen atoms being bent 31.4 ° away. The calculations were confirmed by a neutron diffraction study at 100 K, the experimentally determined angles being 8.9 °, 15.8 ° and 29.4 ° respectively. The change in the total energy is derived from three effects, the reduction in the repulsion between the nickel and the *anti*-hydrogens, destabilisation of the allyl ligands, and enhancement of metal allyl bonding by rehybridisation [832].

Correlation effects in the ground and ionic states of bis(allyl) nickel were investigated by the use of large-scale configuration interaction calculations. In the ^1A_g molecular ground state the dominant correlation involves the b_g metal-ligand bonding electrons, and results in an increase in the metal 3d electron density compared to that found at the RHF level of approximation. Calculations on the ionic states reveal differential electron correlation for the metal and ligand ionised states, which must be considered for an interpretation of the PES of the molecule. Calculation of the ionisation energies of the complex by the *ab initio* Green's function method leads to a satisafactory assignment of the PES, in contrast to the results of SCF calculations [833,834].

Theoretical studies of transition metal π-allyl complexes have been undertaken using a pseudopotential *ab initio* MO method, with particular reference to intermediates in the oxidation of propene to propenal. In the cases in which there is a large charge transfer from the allyl anion bonding orbital to an s metal orbital and/or an important backbonding interaction, the result is complete oxidation (Co(II), Fe((II), Mn(II) or Cr(II)). In other cases, including Ni(II), the reaction is more selective [835].

The EI mass spectra of $[\{Ni(\eta^3-C_3H_5)X\}_2]$ (X = Cl, Br or I) have been recorded. The main fragmentation involves the loss of C_3H_5X, and the dimer was cleaved only for X = I [836]. The spectra of nine complexes of the type $[NiBr(\eta^3-C_3H_5)L]$ were also recorded. The main process noted was the reversal of the reaction by which the complexes were made, leading to L and $[\{NiBr(\eta^3-C_3H_5)\}_2]$. The relative strengths of the nickel-ligand bonds, derived from the mass spectrometric data, were compared with their influence on the selectivity of $[Ni(\eta^3-C_3H_5)L_2][PF_6]$ as a catalyst for the 1,4-polymerisation of butadiene [837].

In $[Ni(\eta^3-C_3H_5)LX]$, where L is a chiral phosphine, there are chiral centres at both phosphorus and carbon, as well as the possibility of several accessible rotamers. The structure of $[Ni(\eta^3-C_3H_5)Cl\{PMe(CMe_3)(menthyl)\}]$, **415**, was established in a diffraction study, and its relevance to the enantioselective codimerisation of alkenes discussed [838].



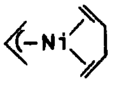
415 The molecular structure of [Ni(η^3-C_3H_5)Cl{Pmenthyl(Me)CMe$_3$}] showing the arbitrary numbering scheme. The *meso*-carbon of the η^3-allyl group is disordered at C21 and C22. (Reproduced with permission from [838])

The preparations and properties of a range of complexes [Ni(η^3-C_3H_5)L_2][PF_6] (L = $P(OR)_3$; R = Et, $CHMe_2$, Ph, 2-MeC_6H_4 or 2-PhC_6H_4) have been described. The electronic and steric effects of the ligands control both activity and selectivity in butadiene polymerisation, although solvent effects are also important [839]. The species [Ni(Cp)H] was generated by the reaction of $Me_2CHMgCl$ with [$NiCp_2$], followed by loss of propene from [Ni($CHMe_2$)Cp]. It reacted with cyclic 1,3-dienes to give allyl complexes such as 416 [840].

416

π-Allyl nickel halide dimers supported on Al_2O_3 and activated by Lewis acids, preferably aluminium halides, are good catalysts for propene dimerisation. Methylpentenes and hexene were obtained in a 3:1 ratio. The supported system was both more active and more stable than the related homogeneous catalyst [841]. Other 1-alkenes could also be dimerised [842]. Electrochemical reductive coupling of allyl derivatives in the presence of $[Ni(PPh_3)_4]$ gave 1,5-hexadiene. A study of the reaction has revealed that the key intermediate is a bis(allyl) nickel(I) complex, which is reduced electrochemically [843].

The complexes $[Ni(\eta^3\text{-}C_3H_5)L_2][PF_6]$ (L = PPh_3, $AsPh_3$, $SbPh_3$, MeCN, Me_3CNC or cod) are catalysts for the stereoselective 1,4-polymerisation of butadiene. As the strength of the metal ligand bond was decreased, both activity and *cis*-selectivity increased, due to a predominence of 417 over 418, the former leading to *cis*- and the latter to *trans*-products [844]. The complex $[\{Ni(\eta^3\text{-}C_3H_5)(OOCCF_3)\}_2]$ has also been used as a living coordination initiator for the polymerisation. The stereoselection could be directed up to 99 % to give either *cis*- or *trans*-product, by choice of additives and conditions [845].



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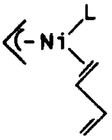

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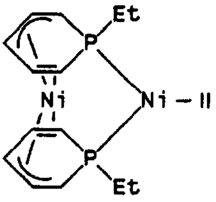
Reaction of $[Ni(\eta^3\text{-}CH_2CMeCH_2)_2]$ with $HSiCl_3$ in toluene gave 2 moles of 2-methylpropene and $[Ni(SiCl_3)_2(\eta^6\text{-}C_6H_5Me)]$, providing an alternative synthesis to the metal atom reactions [846]. When $[Ni(\eta^3\text{-}C_3H_5)(PRR'_2)X]$ was reacted with [Ni(cdt)] and PRR'_2, the product was 419. This could also be obtained, though in lower yield, from reaction with $[Ni(cod)_2]$ or from $[\{Ni(\eta^3\text{-}C_3H_5)X\}_2]$ and $[Ni(C_2H_4)(PRR'_2)_3]$ [847].

The reaction of 420 with 1-alkenes resulted in the displacement of ethene and the formation of the 1-alkene complex. The nmr spectra of the propene and 1-octene complexes were temperature dependent because of the valence isomerisation in the phosphorus ligand, and alkene roation. Other ligands also displaced ethene. Reaction with a diene, $CH_2=C(R)-CH=CH_2$, resulted in insertion into the nickel allyl bond to give 421, characterised in a diffraction study [848].

419



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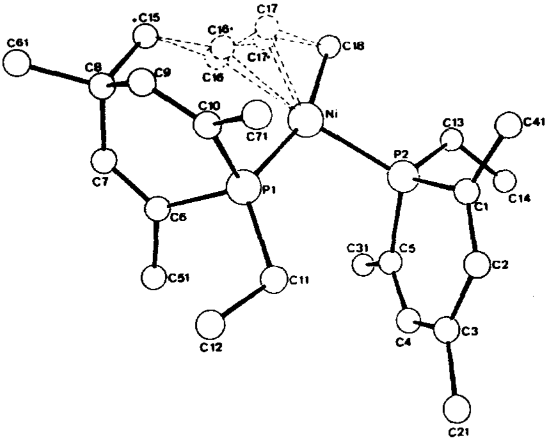
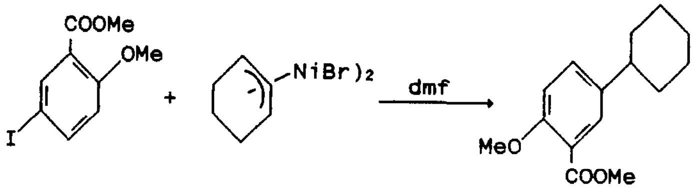


421 (Reproduced with permission from [848])

A number of stoicheiometric reactions of nickel allyl complexes have been used in organic syntheses. The coupling with an aryl iodide (reaction (28)) was used in the synthesis of the antheridium inducing factor of the fern *Anemia phyllitidis* [849], whilst reaction (29) was used in a synthesis of caryopterone [850]. The allyl bromide 422 was converted to 423 by either $[Ni(CO)_4]$ or $[Ni(cod)_2]$, and reacted with 3-bromomethylfuran to give a complex mixture of homo and cross-coupled products used in pheromone synthesis [851].



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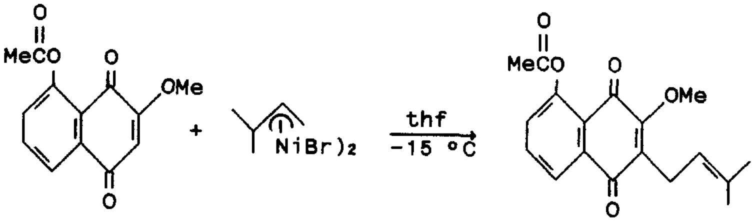

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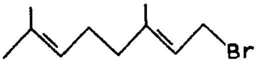

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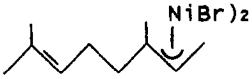

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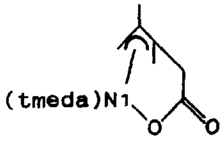
Nickel allyl complexes are intermediates in a wide range of oligomerisations, cooligomerisations and telomerisations, and some of the chemistry associated with these reactions has again been investigated. Reaction of $[NiL_n]$ with butadiene and CO_2 gave nickelacarboxylates, and the influence of the ligands on the regioselectivity was investigated [852]. Reaction of 424 with R_3P resulted in the displacement of the tmeda ligand. Addition of 1,4-diazadienes gave bis(diazadiene) nickel complexes [853]. Reaction of [Ni(bipy)(cod)] with CO_2 and PhN=CH-CH=CHPh gave an equilibrium mixture of 425 and 426 [854]. The complex 427 was prepared by oxidative coupling of 2,3-dimethylbutadiene with CO_2 and $\{L_nNi(0)\}$. The structure of 428 was established in a diffraction study [855].

Reaction of either $[Ni(cdt)(PR_3)]$ or $[Ni(cod)_2]/PR_3$ (R = Cy, $CHMe_2$ or OC_6H_4-2-Ph)) with two molar equivalents of butadiene gave 429, but with R = Ph, the main product was 430 at temperatures above -10 °C. Reaction of 429 (R = Cy) with CO or cod gave 4-ethenylcyclohexene, whereas addition of PPh_3 caused decomposition to butadiene. Insertion reactions of alkynes were discussed [856].



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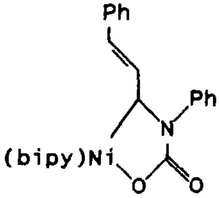

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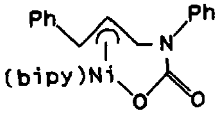

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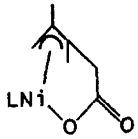

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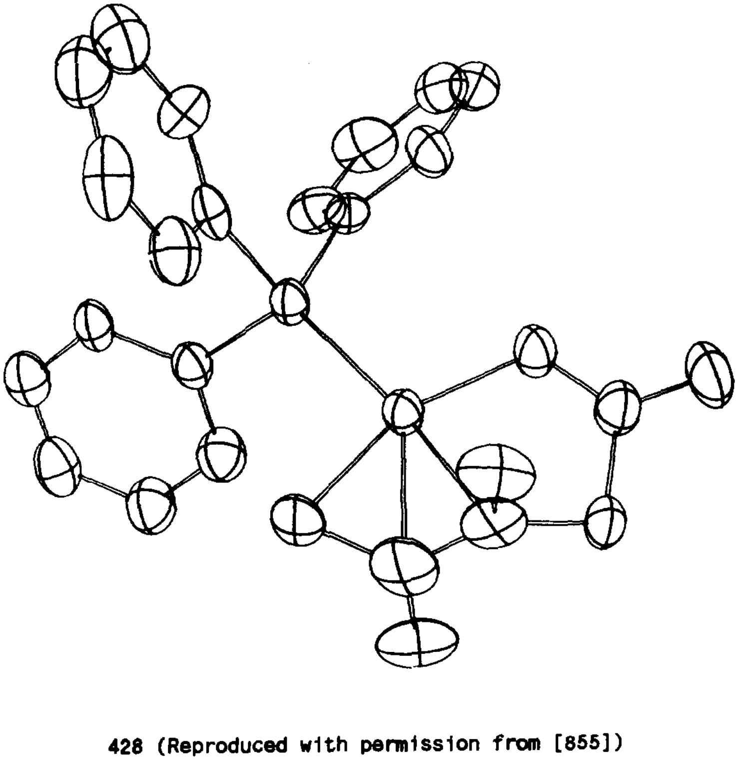
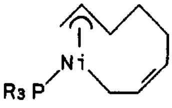


428 (Reproduced with permission from [855])



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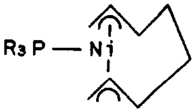
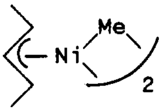


430

The mechanism of the reaction between [{Ni(η^3-C_3H_5)X}$_2$] and RX to give $RCH_2CH=CH_2$ and NiX_2 has been studied. The reaction appears to be very complex with competing pathways, but the first step is clearly an electron transfer reaction to give $[RX]^{-\cdot}$ and [Ni(III)(η^3-C_3H_5)X]$^{+\cdot}$ [857]. Reaction of 431 with R_3P and CO gave 432. If the added phosphine was chiral, then 432 was formed with a fair optical yield. The extent and direction of the optical yield depended on the concentration and nature of the chiral phosphine [858].



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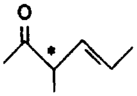
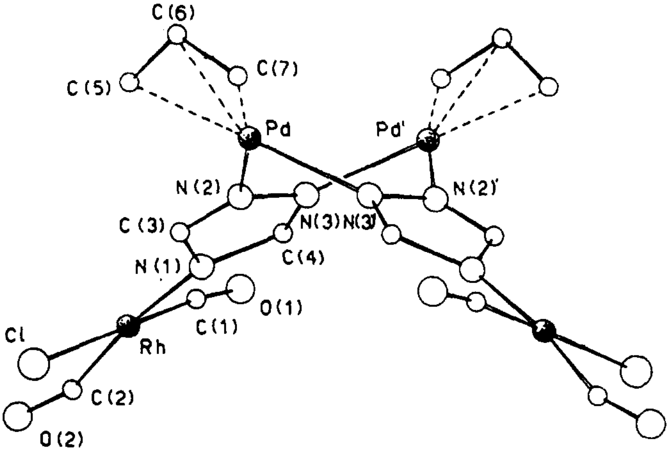


427

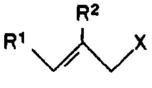
A wide ranging review of palladium allyl complexes, with particular relevance to their rôle in catalytic reactions has been published [859]. The reader is referred also to the section of this review which discusses the substitution of allyl derivatives catalysed by palladium complexes.

The structure of the cluster complex [Pd_2Rh_2(η^3-C_3H_5)$_2Cl_2(CO)_4$(μ_3-tz)], 433, (tz = 1,2,4-triazole), prepared from [Pd_2(η^3-C_3H_5)$_2Cl_2$], Htz and [Rh(acac)$(CO)_2$], was established in a diffraction study [860].

There has been a stereochemical study of the formation of palladium allyl halide complexes from alkenes, using $CH_2=CH-CHDR$. The ratio of deuterium to protium loss was dictated by the kinetic isotope effect, the data being consistent only with a stereospecific process. The hydrogen *syn* to the metal is lost from the alkene, with rate controlling insertion of the palladium into the C-H bond [861]. The effects of the steric bulk of the substituents on the formation of allyl complexes from trisubstituted alkenes has also been examined [862]. The preparation of 435 from 434 (X = I or Br) was accomplished by treatment with palladium black under ultrasonic irradiation [863].



433 (Reproduced with permission from [860])



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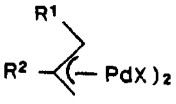
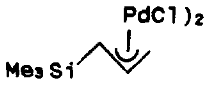


435

Reaction of **436** with $Li_2[PdCl_4]$ gave **437**, which could be reacted with Na[CHXY] (X = Y = COOEt or COMe or X = COOEt, Y = COMe) to give **438** with good regio and stereoselectivity [864]. The reaction of **439** with $PdCl_2$ gave **440** stereospecifically. Thermolysis of **440** gave **441**, and mechanisms for the reactions were proposed. Reactions with nucleophiles and phosphines were also investigated (Scheme 15), and the structure of **442** defined in a diffraction study [865].

436



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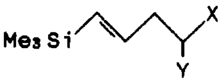
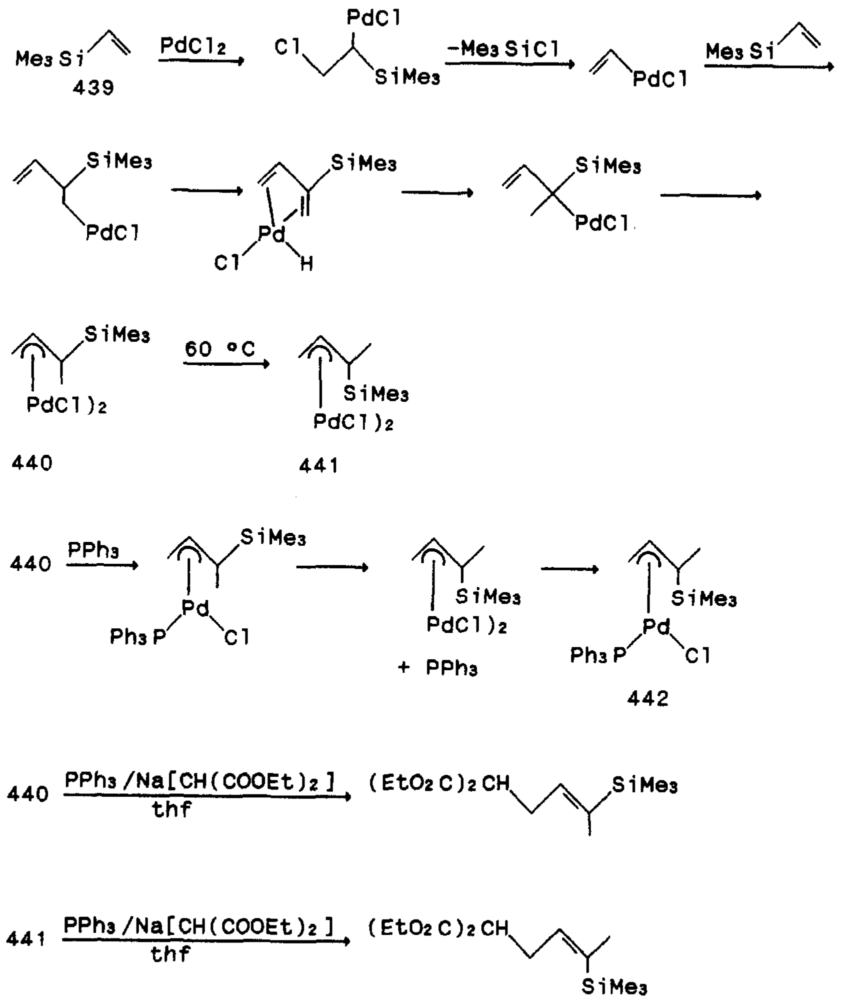


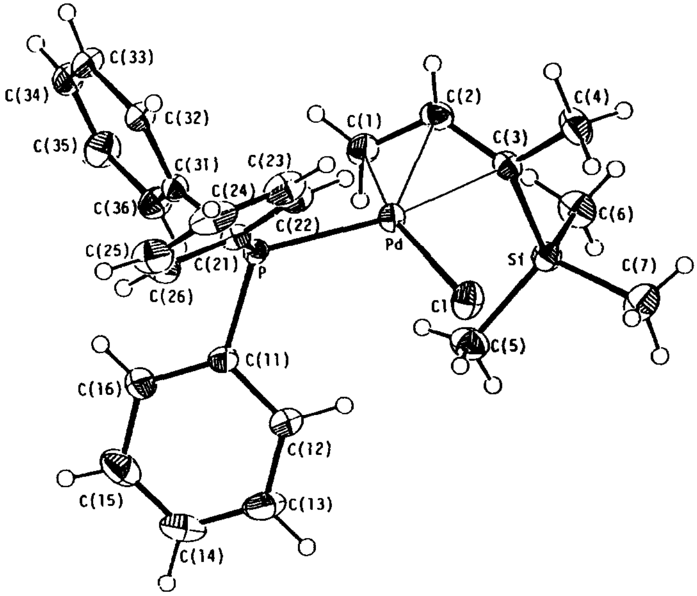
438

The cyclohexenes **443** [866] and **444** [867] were converted to their palladium allyl complexes, and reactions with nucleophiles studied.

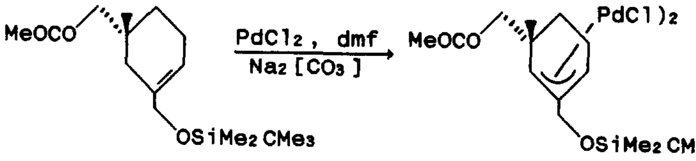


Scheme 15 Mechanism of formation and reactions of some trimethylsilyl substituted palladium allyl complexes [868].

Reaction of 445 with either $PdCl_2$/Na[OCOMe], or better with $Li_2[PdCl_4]$, gave the dimeric palladium phenalenyl complex. This was converted to the monomer 446 using Tl[acac]. This a rare example of a palladium allyl complex of a polycylic aromatic hydrocarbon, and there is no evidence for any dynamic behaviour [868].



442 Non-hydrogen atoms are represented by thermal ellipsoids at 30 % probability, whereas temperature factors of hydrogen atoms are arbitrarily reduced for clarity. (Reproduced with permission from [865])



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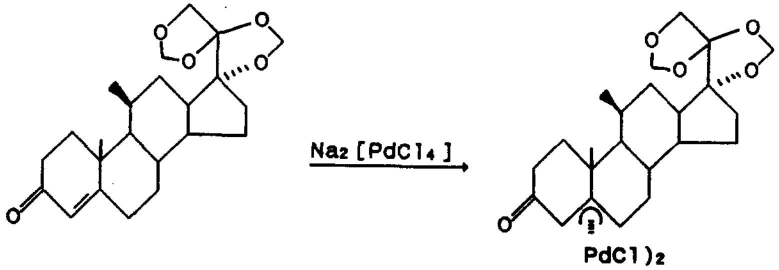

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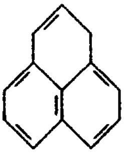

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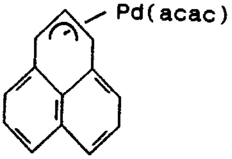
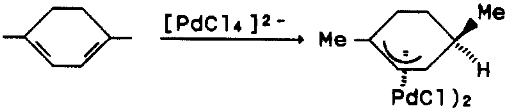


446

There have been a number of reports of the preparation of palladium allyl complexes from dienes. For example, 1,4-disubstituted 1,3-cyclohexadienes such as **447** gave a single isomer of the allyl complex on reaction with $[PdCl_4]^{2-}$. However, other substitution patterns gave mixtures of isomers [869]. 1,2-Dimethyl-1,4-cyclohexadiene reacted with $[Pd(MeCN)_2Cl_2]/MeOH/K[HCO_3]$ to give **448**. Under conditions of kinetic control, in the presence of base and at low temperature, 1,4-dimethyl-1,4-cyclohexadiene gave **449** as the major product, *via* **450**. If the base is omitted, **450** undergoes acid catalysed isomerisation to the less hindered **451**, which gives the thermodynamic product **452**. The authors concluded that the primary process was distal addition of palladium and methanol, followed by palladium migration with retention of stereochemistry [870].



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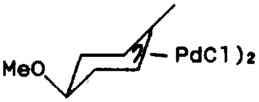

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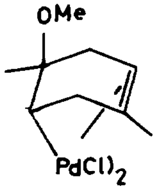
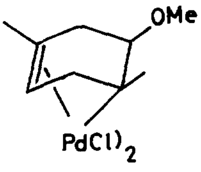


450

Geranyl chloride reacted with palladium(0) to give an equilibrium (1.1:1) mixture of **453** and **454**. When the mixture was treated with $[Ag(MeCN)_4]^+$ an equilibrating mixture of **455**, **456** and **457** was obtained. Addition of ligands such as PPh_3, bipy or tmeda allowed complexes of good isomeric purity to be obtained, and the donor/acceptor properties of the ligands influenced the regiochemistry of a subsequent amination reaction [871].



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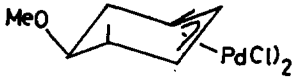

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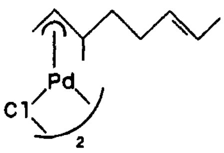

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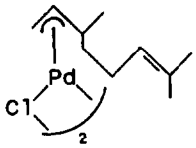

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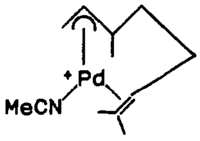

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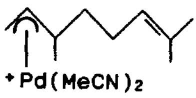

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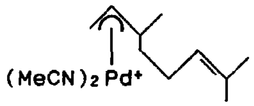
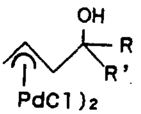


457

Complexes such as 458 were prepared by heating substituted butadienes in water with $Li_2[PdCl_4]$ [872]. In the reaction of β-myrcene, 459, with $[PdCl_2L_2]$ in the presence of an alcohol and other solvent, the chemical and regiochemical outcome of the reaction was determined by the solvent mixture. In H_2O/hmpa, 460 (R = H) was the major product, whilst 461 was favoured by H_2O/propanone. In pure methanol 462 was the main product. The reaction mechanism was discussed in detail [873].



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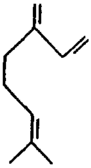

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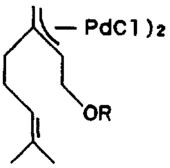

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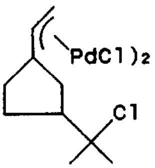

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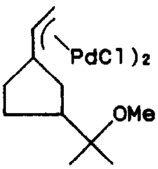
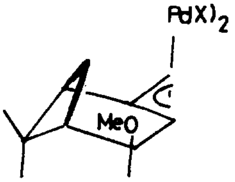


462

Reaction of 463 with $[PdCl_4]^{2-}$ in methanol gave 464 (X = Cl) stereospecifically. The related 464 (X = OCOMe) could be used as a catalyst for the enantioselective cyclisation of 465 [874].

463



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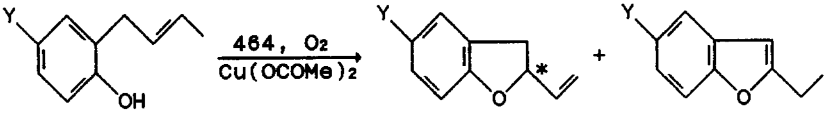
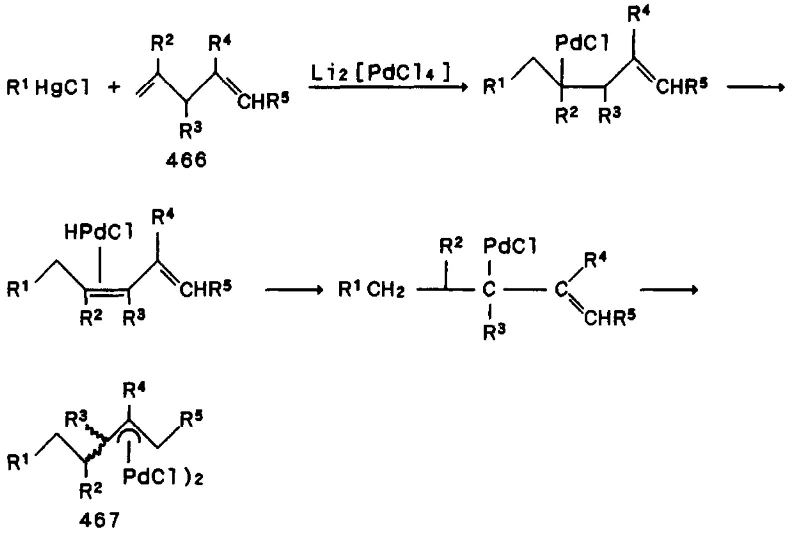


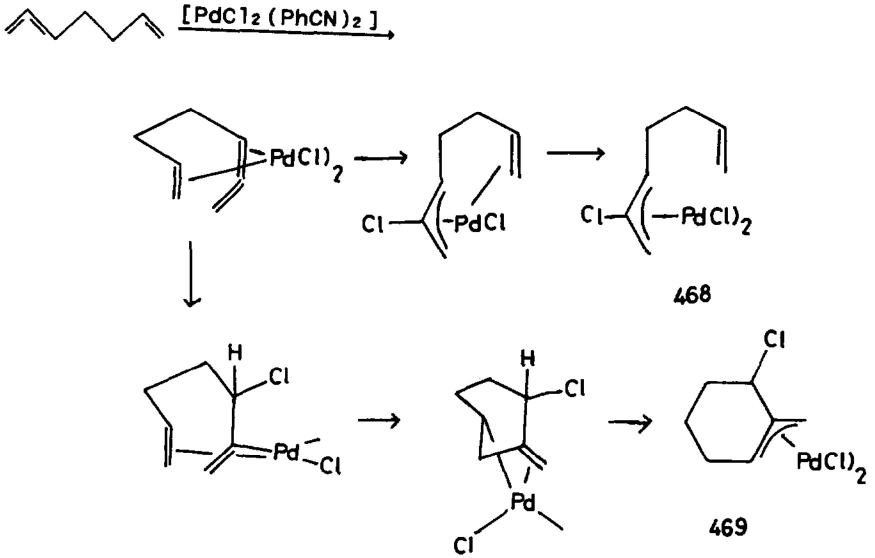
465

The reaction of R^1HgCl with the 1,4-diene 466 in the presence of $Li_2[PdCl_4]$ gave 467 by the mechanism of Scheme 16. A similar reaction was noted for 1,5- and 1,6-dienes, but 1,7-octadiene gave a mixture [875]. 1,2,6-Heptatriene reacted with $[PdCl_2(MeCN)_2]$ to give an inseparable mixture of 468 and 469, the ratio between the complexes depending on the temparature of the reaction. A mechanism for the reaction was proposed (Scheme 17). 1,2,8-Nonatriene gave no cyclised product, since it is unable to act as a chelating ligand [876].

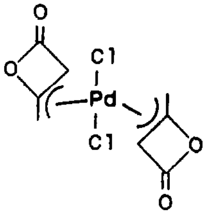
The reaction of diketene with $[PdCl_2(PhCN)_2]$ was reported to yield 470, identified by ir and nmr spectrsocopy [877]. In the presence of water, palladium (II) catalysed diketene hydrolysis, the effecive catalyst being the initially formed 471 [878].



Scheme 16 Formation of palladium allyl complexes from 1,4-dienes [875].



Scheme 17 Mechanism of reaction of palladium(II) with 1,2,6-heptatriene [862].



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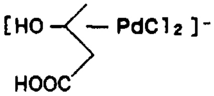
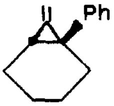


471

The reaction of **472** with [$PdCl_2L_2$] in dichloromethane gave a mixture of **473** and **474**, **474** being the thermodynamic product. The complex **474** does not react with methanol, but if the ring opening is carried out in the presence of methanol, **473**, **474** and **475** are obtained. This suggests that the product of the intital ring opening has carbocation character (perhaps **476**), and may be captured by solvent as well as halide [879]. The stereochemistry of the ring opening of **477** to **478** was studied [880]. In non-nucleophilic solvents **479** reacted with [$PdCl_2(MeCN)_2$] to give **480** and **481**, the ratio between the products depending on the solvent. In alcohols, the products were **480** and **482**. The stereochemistry of the reaction was studied in detail [881].



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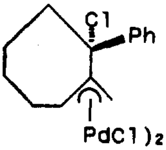

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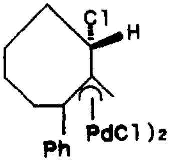

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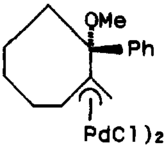

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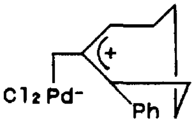

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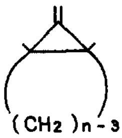

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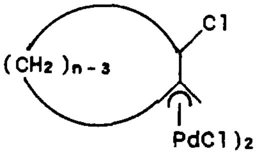

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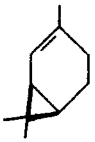

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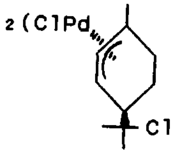

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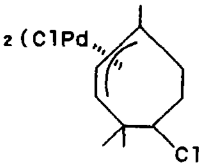

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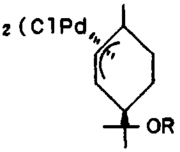
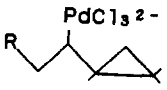


482

Reaction of $[PdCl_3(R)]^{2-}$, prepared *in situ* from RHgCl and $[PdCl_4]^{2-}$, with ethenylcyclopropane resulted in initial addition across the double bond to yield 483. Ring opening of the cyclopropane gave 484, which was isomerised in several steps to 485. Ethenyl and methylene cyclobutanes underwent related reactions [882].



483

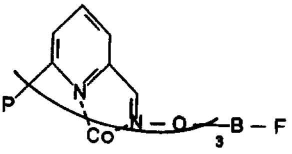
484

485

Ir spectroscopy and XPES were used to study palladium blacks prepared from allyl palladium complexes, $[Pd(\eta^3-C_3H_5)L_2]^n$ (L = Cl, Cp or PPh_3). The palladium oxidation state is close to zero, and the activity of the catalyst for the liquid phase hydrogenation of ethyne depended on the nature of the ligand in the starting complex [883]. The effect of the ligand on particle size was also investigated [884]. The reduction of [Pd(acac)$_2$] gave colloidal palladium particles which could be used as a catalyst for alkyne hydrogenation. It was noted that in anhydrous [Pd(acac)$_2$] there is an interaction between the palladium and C(*3*) of an adjacent molecule [885]. A phosphor bronze sheet was immersed in xylene containing [{Pd(η^3-CH$_2$CMeCH$_2$)Cl}$_2$] at 120 °C to be coated with palladium [886].

The complex [{Pd(η^3-CH$_2$CMeCH$_2$)Cl}$_2$] was mixed with Udel P-1700 and polysulphone polymer 5, and formed into a conducting film [887]. The complex also acted as a phase transfer agent to solubilse KO$_2$ in the reaction which it promotes between oximes R^{1}R^{2}C=NOH and CH$_2$Cl$_2$ to give (R^{1}R^{2}C=NO)$_2$CH$_2$ [888].

The complex **486** was used as a paramagnetic shift reagent analogue of a phosphine ligand to elucidate the structure of palladium allyl complexes. When the exchange reaction with the palladium allyl halide dimer is rapid there are substantial shifts noted for both *syn-* and *anti-* protons [889]. The shift reagent data predicted that the terminal protons in **487** would be twisted out of the allyl plane, a fact later confirmed by an X-ray diffraction study [890].



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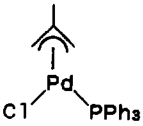
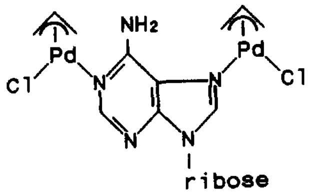


487

The reaction of [{Pd(η^3-C$_3$H$_5$)Cl}$_2$] with a base, L, (L = inosine, adenosine, guanosine or cytosine) gave complexes of stoicheiometry [Pd(η^3-C$_3$H$_5$)ClL]. With adensoine, and an appropriate reaction stoicheiometry, the bridged species **488** could also be obtained [891]. When [Ni$_2$(PNNP)$_2$]$^{2+}$ (PNNPH = **489**) was reacted with [{Pd(η^3-C$_3$H$_5$)Cl}$_2$], **490** was obtined in a metal transfer synthesis [892]. When the potentially *N,P*-bidentate ligand, **491**, was added to [{Pd(η^3-CH$_2$CMeCH$_2$)Cl}$_2$] the first product was the *P*-ligated species **492**, characterised in a diffraction study. The cationic *P,N*-chelate complex was also prepared, and used as a catalyst for the oligomerisation of butadiene [893].

The chloro bridges in a range of palladium allyl chloride dimers were replaced by [O$_2$]$^{2-}$ in reactions with KO$_2$ [894]. Reaction of [{Pd(η^3-C$_3$H$_5$)Cl}$_2$] with less than one molar equivalent of SnCl$_2$ was reported to yield 3-chloro-1-propene and a {Pd$_3$Sn} cluster. With an excess of SnCl$_2$ and [Me$_4$N]Cl the product was reported to be [Me$_4$N][Pd(η^3-C$_3$H$_5$)(SnCl$_2$)(SnCl$_3$)] (*sic*) [895].



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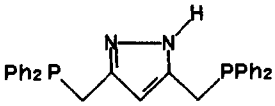

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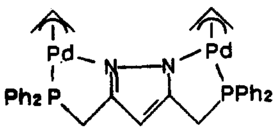

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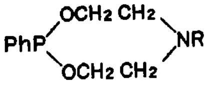

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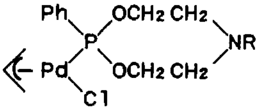
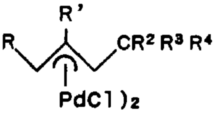


492

Restricted rotation and isomerisation in 493 have been studied by ^{1}H nmr spectroscopy [896]. The rotation of the R group in 494 was shown not to be free, for the side chains $-CH_2Cl$, $-CH_2OH$, $-CH_2OMe$ or $-CH_2CH_3$, but this was not thought to be connected to any direct interaction between the metal and the side chain [897]. ^{1}H nmr spectroscopic and PES data were reported for 495 [898]. The preparation of 496 has been described, and spectroscopic data were reported [899].



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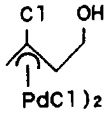

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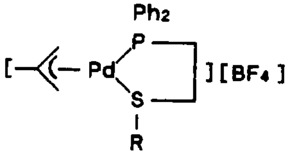
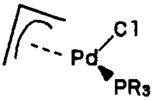


496

${}^1H$ nmr spectroscopy at high pressure was used to study the reversible reaction between $[\{Pd(\eta^3\text{-}CH_2CMeCH_2)Cl\}_2]$ and PPh_3 to give $[Pd(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)]$. It was found that $\Delta V^{\ddagger}$ at room temperature was close to zero, due to the cancelling of opposite volume contributions from partial bond cleavage in the dimer, and association with the monomer. At higher temperatures the activation volume becomes significantly positive and bridge cleavage is thought to be the dominant process under these conditions [900]. The exchange between the diastereoisomers 491 and 492, where PR_3 is a bulky phosphine, has been studied by 2D nmr spectroscopy. Two processes are occuring. The $\eta^3 \leftrightharpoons \eta^1$-conversion may take place with only C-C bond rotation, or with both C-C and C-Pd rotation, both processes being slowed by the presence of a bulky phosphine [901].



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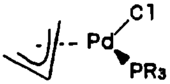
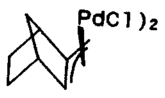


498

Very detailed nmr spectroscopic studies have been undertaken on the reaction of **499**, *prepared from norcamphene, and* PPh_3. *With 0.5 molar* equivalents of PPh_3, some starting material remained, and 500 and 501 were formed in the ratio 1.3:1. With PPh_3:Pd = 1, 500 and 501 were the exclusive products again in the ratio 1.3:1. When between 1 and 2 moles of PPh_3 were added, fluxional nmr spectra were obtained at room temperature. Cooling showed the presence of some 502, which was the exclusive product with a large excess of PPh_3. However, there was also evidence for an equilibrium between 502 and 503, which was strongly temperature dependent. The structure of the $[PF_6]^-$ salt, 504, was established in a diffraction study. The reaction of propanedioateanion proceeded with the same regiochemistry for all the complexes, with attack at the less hindered exocyclic position, but attack of the harder nucleophile, PhLi, proceeded *via* the metal to give both possible regioisomers, in amounts which depended on the exact nature of the complex [902].



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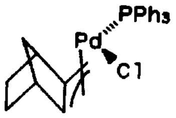

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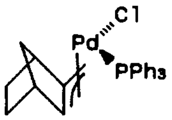

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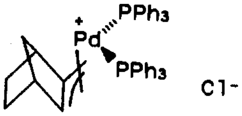

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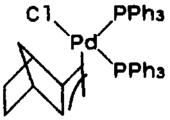

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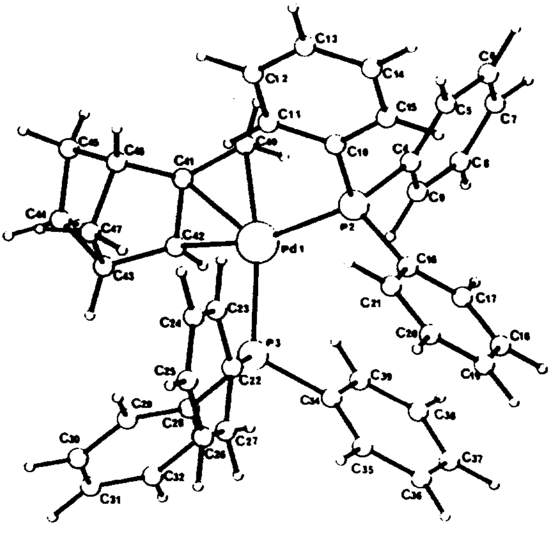
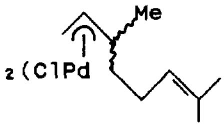


504 (Reproduced with permission from [902])

Treatment of 505 with Ag[BF$_4$] in MeCN gave 506, characterised in a diffraction study. This revealed a remarkable coordination of the alkene, which forms an angle of 26 ° to the coordination plane, and is thus much closer to the "in plane" geometry than the "upright" geometry. The allyl group is tilted, both effects being due to the steric and geometric constraints of chelation. Addition of strongly coordinating ligands displaces the alkene, and the system was considered as a model for butadiene oligomerisation [903].

Reaction of $[\{Pd(\eta^3-C_3H_5)Cl\}_2]$ with R_3MH (R = Cl or Me; M = Si, Ge or Sn) resulted in initial oxidative addition to give **507**. Hydrogen transfer yielded **508**, which decomposed by a radical pathway [904].



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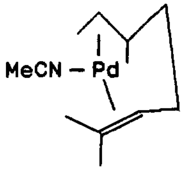

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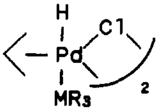

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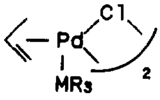
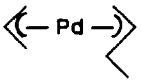


508

Reductive elimination from $[Pd(Ar)(\eta^3-CH_2CRCH_2)L]$ in the presence of an excess of L, gave $CH_2=C(R)CH_2Ar$. A kinetic study showed that the rate of the reaction was independent of [L] up to a concentration of 0.26 M, suggesting that the rate controlling step is not dissociation of L. The electron donor ability of L is important, but insufficient, to explain the kinetic data [905]. The reaction of EX with $[(dppe)Pd(\eta^1-CH_2CH=CHR)Ar]$ gave $CH_2=CH(E)R$ and $[Pd(Ar)(dppe)X]$, whereas the reaction with the η^3-complex, $[Pd(Ar)(\eta^3-CH_2CHCHR)(PPh_3)]$ yielded ArE and $[Pd(\eta^3-CH_2CHCHR)(PPh_3)X]$ (EX = Br_2, NBS, C_6F_5Br, or allyl halides). The mechanisms of these processes were not well understood [906]. Addition of PPh_3 to $[Pd(\eta^3-CH_2CRCH_2)(PPh_3)R']$ (R = H or Me, R' = Ph, R = H or Me, R' = $C_6H_3Cl_2$-2,5) did not result in the formation of a new species, but the *syn* and *anti*-protons exchanged rapidly on the nmr spectroscopic timescale. This suggests that some *cis*-$[Pd\{\eta^1-CH_2C(R)=CH_2\}(PPh_3)_2(R')]$ may be formed, but it is probably not involved in catalysis involving these complexes. However, when $CH_2=C(R'')CH_2X$ is added, $CH_2=C(R)CH_2R'$ is rapidly formed, together with $[Pd(\eta^3-CH_2CR''CH_2)(PPh_3)X]$. The data presented were deemed to be consistent with the involvement of palladium(IV) intermediates in palladium catalysed allylation reactions [907].

Reaction of **509** with maleic anhydride in the presence of butadiene gave 4-ethenyl cyclohexene and 1,3,6,11-dodecatriene. Reductive elimination from a bis(allyl) palladium complex was thought to provide the "naked" palladium species needed for butadiene oligomerisation [908]. When [{Pd(η^3-C_3H_5)Cl}$_2$] was reacted with $R_3SnCH_2CH{=}CH_2$, the product was a bis(allyl) palladium complex. Reductive elimination to yield 1,5-dienes was achieved only in the presence of maleic anhydride. The reaction could also be accomplished catalytically, but most yields were modest [909]. When Grignard reagents were substitututed for allyltin derivatives, yields were much improved, with head-to-head dimers predominating in most reactions of substituted allyls (reaction (30)) [910,911]. A study of the reductive elimination reactions of [Pd(Ar)($AsPh_3$)(η^3-C_3H_5)] in the presence of alkenes, showed that the intermediate in the reaction was [Pd(alkene)(Ar)(η^3-C_3H_5)] resulting from $AsPh_3$ displacement. The best rates were obtained with alkenes bearing electron withdrawing groups [912].



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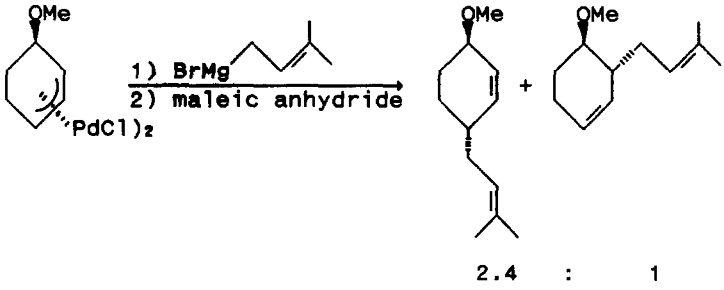
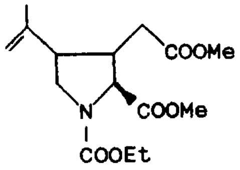


(30)

The factors affecting the regiochemistry of the attack of nucleophiles on palladium allyl complexes have been investigated. The 3-methyl butenyl complex reacts predominently with the anion of dimethyl propanedioate at the more substituted site, but with the anion of diethyl propanedioate at the less substituted position. The distribution of products in the stoicheiometric reaction is similar to that in the related catalytic process. Both neutral and cationic species were considered to be important, but η^1-complexes were not significant [913]. Reaction of 510 with 511 gave 512, as a mixture of stereoisomers [914].

Thermolysis of [Pd(η^3-C_3H_5)(PPh_3)$_2$]$^+$ gave [Pd(Ph)(PPh_3)($PPh_2C_3H_5$)]$^+$ *via* a carbon-phosphorus bond cleavage process [915].



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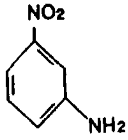

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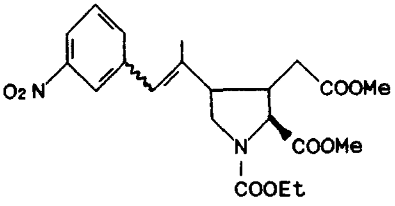
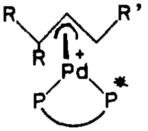


512

The general characteristics of asymmetric allylation using palladium allyl complexes have been investigated. *anti*-Disposed substituents on the inetermediate π-allyl complex were the major source of the discrimination in the reaction [916]. The reactions of chiral complexes were studied in detail. Provided that the complexes 513 and 514 (PP = CHIRAPHOS) were in rapid equilibrium, successful asymmetric allylation could be achieved [903]. Reaction of 515 with Na[CH(COOMe)$_2$] gave 516 with inversion of stereochemistry, and good chirality transfer. The reaction of dimethylamine was similar, but with PhMgBr the reaction proceeded with lower specificity, but mainly retention of the configuration of the allyl complex, this reaction proceeding *via* initial attack of the nucleophile at palladium [918].



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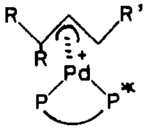

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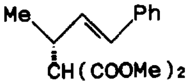
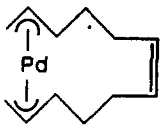
515



516

Reaction of [Pd(dba)$_2$] or [Pd(bipy)(dba)] with butadiene gave 517, which was unstable at temperatures above -20 °C in the absence of butadiene. Addition of dppe gave 518, the largest metallocycle thus far reported. Addition of DCl to 518 gave 519, in contrast to the related nickel complexes, which cyclise readily [919]. The complex $[Pd(\eta^3\text{-}CH_2CMeCH_2)_2]$ reacted with butadiene in the presence of PR_3 to give 520. The reactions of this complex, and their relationship to palladium catalysed oligomerisation reactions of dienes were noted [920]. The insertion reactions of 520 with alkynes were studied [921].



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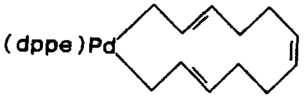

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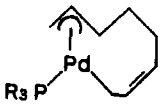
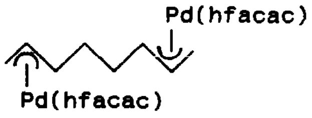


520

Reaction of the bis(allyl) complex, 521, with $(Me_2CH)_3P$ gave 522. The latter reacted with CO_2 by insertion, and addition of HCl gave 523 [922]. Under pressure, 524 reacted with 2-methylpropene to give a mixture of 525 and 526. Other insertion reactions were also discussed [923].



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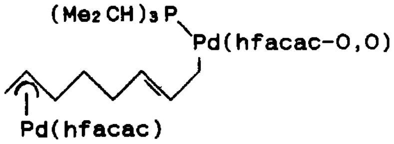

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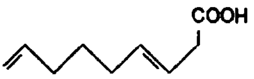

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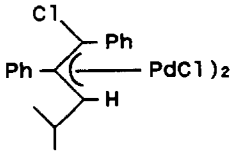
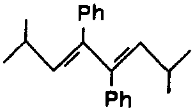


524

Complexes such as 527 could be opened to give palladium allyl complexes, at rates which depended on the nature of the substituents on the azirine ring [924].



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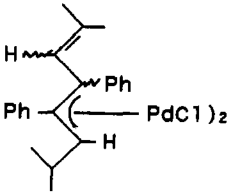

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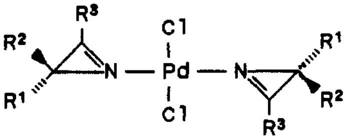
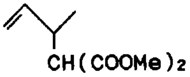


527

There has been continuing work on the reactions of palladium trimethylene methane with alkenes bearing electron withdrawing groups. Direct attack at the allyl complex occurred, in a distal manner [925]. The palladium complexes of trimethylene methane have been compared with those of other metals [926].

Reports on platinum allyl complexes have, as always, been sparse. The ^{1}H nmr spectrum of $[Pt_2(acac)_2(\eta^1,\eta^2-C_3H_5)_2]$ was consistent with the structure established for the complex in the solid state. Data from a magnetisation transfer experiment were consistent with pairwise exchange of allyls ($\Delta G^{\ddagger}$ = 66.1 KJ mol^{-1}), consistent with the platinum atoms reversing their bonding to each allyl group [927]. The complex E-[Pt(butenyl)(DIOP)]$^+$ has been prepared from either $[Pt(\eta^3-CH_2CHCHMe)(PPh_3)_2]^+$ or from $[Pt(cod)_2]$. The complex exists as an equilibrating mixture of diastereoisomers, the equilibria being followed by ^{31}P nmr spectroscopy. Diastereoisomer exchange and E $\rightleftharpoons$ Z isomerisation occurred *via* σ-allyl complexes, and both processes were catalysed by PPh_3. Diastereoisomer interconversion was faster than isomerisation. The complex catalysed the reaction of $E-CH_3CH=CHCH_2OCOMe$ with $Na[CH(COOMe)_2]$ to give a mixture of 528 (ee = 11 %) and 529 in the ratio 4:1. Labelling experiments indicated that the allyl was a true intermediate in the reaction [928].

Reaction of tcne with $[Pt(\eta^3-C_3H_5)_2]$ gave $[Pt(C_3H_5)_2(tcne)]$, characterised by nmr spectroscopy at low temperature. Reactions of the complexes were studied and are shown in Scheme 18 [929]..



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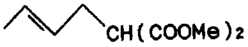

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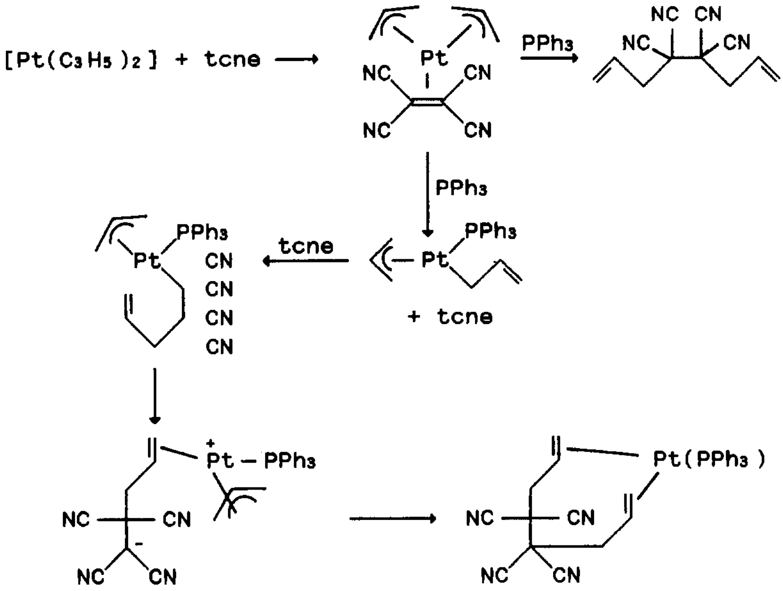
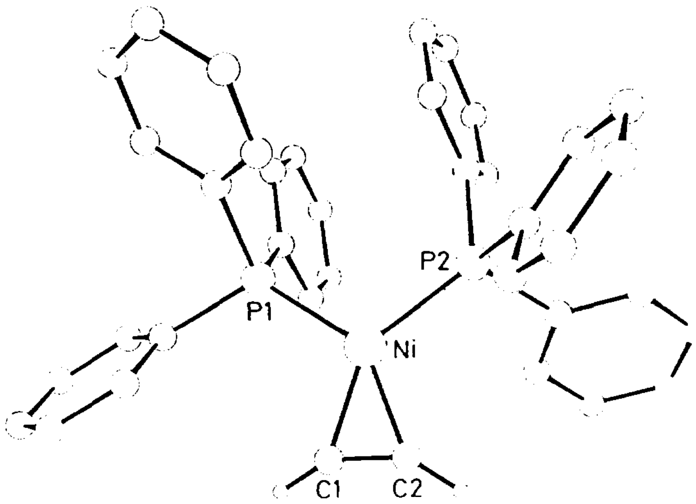


Scheme 19 Reaction of bis allyl platinum with tcne [929]

10 METAL ALKYNE AND ALKYNYL COMPLEXES

The reactions of alkynes with metal atoms including Ni, Pd and Pt, have been reviewed [930]. Catalytic and stoicheiometric reactions of alkynes with nickel(II) or palladium(II) have been described [931].

The reaction of $[Ni(C_2H_4)(PPh_3)]$ with ethyne at temperatures between -78 °C and -60 °C gave $[(C_2H_4)(Ph_3P)Ni(\mu\text{-}C_2H_2)Ni(C_2H_4)(PPh_3)]$. At temperatures above -30 °C this decomposed to give $[Ni(C_2H_2)(PPh_3)_2]$, 523, stable in the solid state [932].



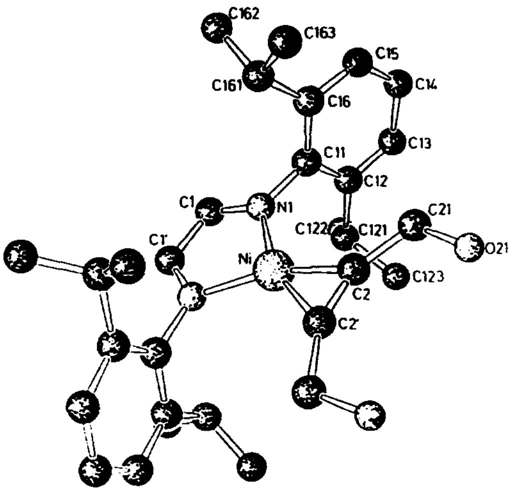
530 (Reproduced with permission from [932])

Displacement of ethene by alkynes from $[Ni(C_2H_4)L_2]$ was readily accomplished with a wide range of alkynes bearing CH_2NR_2 substituents [933]. Reactions of alkynes with $[Ni(C_2H_4)(PMe_3)_2]$ or $[Ni(C_2H_4)(dmpe)]$ were also studied, and $[Ni(C_2Ph_2)(dmpe)]$ was characterised in a diffraction study [934]. The cyclooctadiene ligand in [Ni(cod)(dad)] (dad = diazadiene) could be substituted by alkynes, and 531 was characterised in a diffraction study [935]. With appropriate alkynes diazadienes could be displaced from bis(diazadiene) complexes [936].

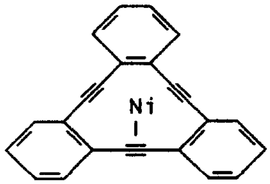
The complex $K_4[Ni(CN)_4]$ is extremely insoluble in solvents with which it does not react, but in the presence of $PhC\equiv CPh$ and 18-crown-6 the species $[K(18C6)]_2[Ni(CN)_2(PhC\equiv CPh)]$ was formed, the first organometallic derivative from $[Ni(CN)_4]^{4-}$ to be isolated. 3-Hexyne gave a similar derivative, but in this case the product was unstable [937].

The dehydroannulene complex, 532, (prepared from $[Ni(cod)_2]$ and the dehydroannulene ligand) was shown in a diffraction study to stack in a manner reminiscent of TTF/TCNQ or undoped nickel phthalocyanine. It was noted that there was a very low distortion from linearity in the alkyne, possibly imposed by the rigid structure [938]. Reaction of 533 with sodium amalgam gave [Ni(benzyne)(dcpe)], 534, characterised in a diffraction study. The "alkyne" carbon-carbon bond is somewhat longer than in alkyne nickel(0) complexes. Reactions of the complex with a range of nucleophiles were discussed [939].

Reaction of $[NiBr(Cp)(PPh_3)]$ with $RC\equiv CR'$ (R = Ph, R' = H or Ph) gave a species of stoicheiometry $\{(NiCp)_2(RC\equiv CR')\}$. The structure of the product was not definitievely established, but it seems likely that the alkyne is bridging the two nickel centres [940].



531 SCHAKAL plot of the molecular structure of $[(Ni(dad)(HOCH_2C\equiv CCH_2OH)]$. (Reproduced with permission from [935])



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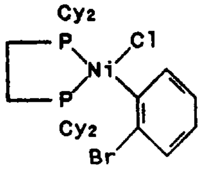
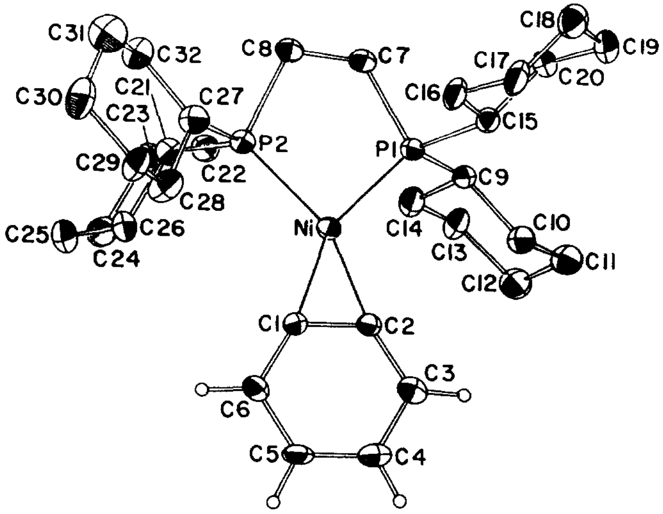


533

There have been several reports of nickel alkyne cluster complexes. When $[NiOs_3(CO)_9(Cp)(\mu\text{-}H)_3]$ reacted with $Ph_2P\text{-}C\equiv C\text{-}CHMe_2$ the product was $[NiOs_3(CO)_8(Cp)(\mu\text{-}H)_3(Ph_2P\text{-}C\equiv C\text{-}CHMe_2)]$, 535, which reacted with $[Co_2(CO)_8]$ to give 536 [941].

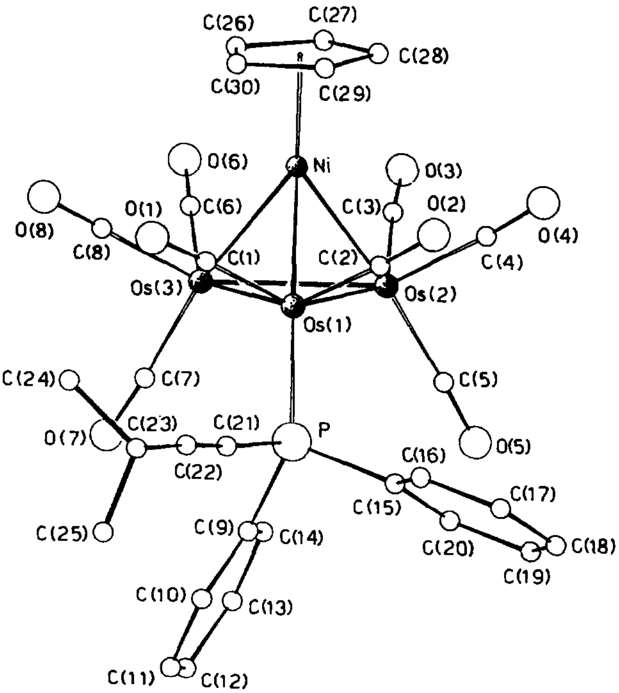
The complex $[Ni_2Cp_2(C_2Ph_2)]$ reacted with $[Ru_3(CO)_{12}]$ under a hydrogen atmosphere to give $[Ni_2Ru_3(CO)_6(\mu\text{-}CO)_2(Cp)_2(\mu_4,\eta^2\text{-}C_2Ph_2)]$, 537, as well as other products. An X-ray diffraction study showed the complex to have a square pyramidal arrangement of the metal atoms, with $Ph\text{-}C\equiv C\text{-}Ph$ coordinated in a σ-manner to a basal plane nickel, and π-bonded to ruthenium [942]. The reaction of $[NiRu_3(\mu_4,\eta^2\text{-}C{=}CNCMe_3)(CO)_9(Cp)(\mu\text{-}H)]$ with alkynes gave complex mixtures of organic products, including oligomers, products of carbon-carbon cleavage and hydrogenolysis, and metathesis products [943].



534 Molecular structure of $[Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)]$. Thermal ellipsoids depict 30 % probability surfaces. Methylene and methine hydrogen atoms of the phosphine ligand have been omitted for clarity. (Reproduced with permission from [939])

The structure of $[Fe_2Ni_2(CO)_6(Cp)_2(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ has been established in a diffraction study. The two iron and two nickel atoms adopt a slightly distorted square planar arrangement with the alkyne interacting with all four metals. Reactivity was discussed; Lewis acidity was associated with the unsaturated nature of the cluster, and cluster expansion was also investigated involving reactions which generated pentametallic complexes *via* completion of the pentagonal bipyramid [944].

Reaction of $Li_2[W(CO)_4(PPh_2)_2]$ with $[M(PPh_3)_2X_2]$ gave $[(CO)_4W(\mu\text{-}PPh_2)_2M(PPh_3)]$ (M = Ni, Pd or Pt). The platinum and palladium complexes (R = H or COOMe) reacted with $RC{\equiv}CCOOMe$ to give $[(OC)_4W(\mu\text{-}PPh)_2)_2M(RC{\equiv}CCOOMe)]$, with 538 characterised in an X-ray diffraction study [945].



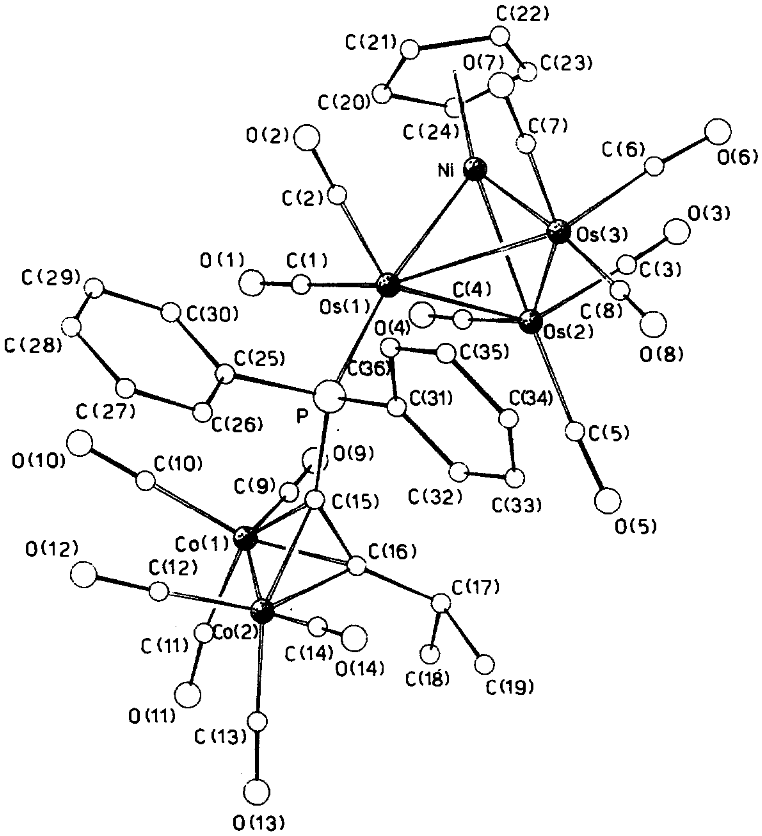
535 (Reproduced with permission from [941])

Reaction of [Pt(cyclohexyne)L_2] with chelating biphosphines (dppe, dppp or dppb) resulted in the displacement of L. When treated with HY, 539 was formed [946]. In the polymer [$\{PtLX_2\}_n$] (L = 540) L was said to be coordinated to platinum at both the alkyne and alkene, but the evidence was weak [947].

The structures of [$PtL_2(RC{\equiv}CR)$], [$Pt_2L_4(\mu\text{-}RC{\equiv}CR)$] and related higher oligomers were investigated theoretically [948].

New routes have been developed for the preparation of σ-alkynyl complexes of nickel. Reaction of [NiCl(Cp)(PPh_3)] with PhC$\equiv$CH in the presence of CuI and Et_3N gave [Ni(C$\equiv$CPh)(Cp)(PPh_3)] in good yield, the procedure being more convenient that that previously reported using a Grignard reagent [949].

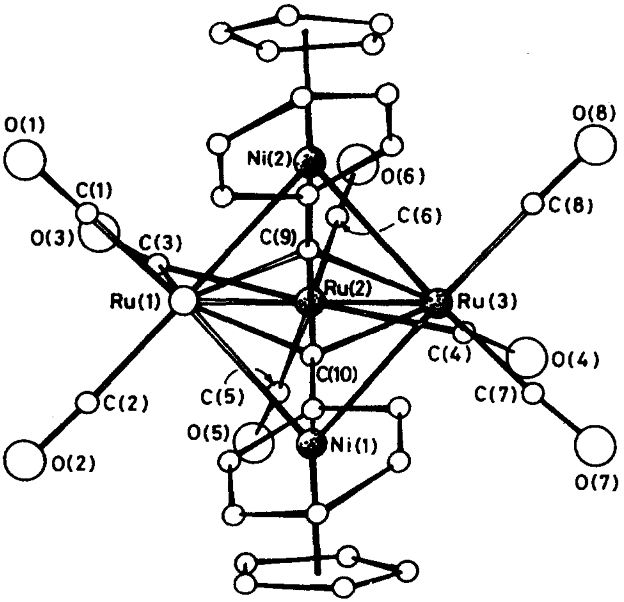
The reaction of [$PdCl_2$(dppe)] with $Me_2Sn(C{\equiv}CR)_2$ gave [PdCl(dppe)($SnMe_2Cl$)] and RC$\equiv$C-C$\equiv$CR. The palladium species could be converted to [Pd(C$\equiv$CR)(dppe)($SnMe_2Cl$)] by a further molar equivalent of the tin reagent. The initial reaction is supposed to proceed *via* oxidative addition of a tin-carbon bond to palladium to give 541, which rearranged to 542, followed by reductive elimination [950].



536 (Reproduced with permission from [941])

UVPES data have been presented for *trans*-$[M(PEt_3)_2X_2]$ (M = Pd or Pt; X = C≡CH or C≡CMe), and compared with Hartree-Fock-Slater MO calculations. The upper valence bands were assigned in good agreement with the calculations. There was a strong π-interaction between the metal and the filled alkynyl orbitals both in and out of the plane, but no significant metal to ligand back bonding [951].

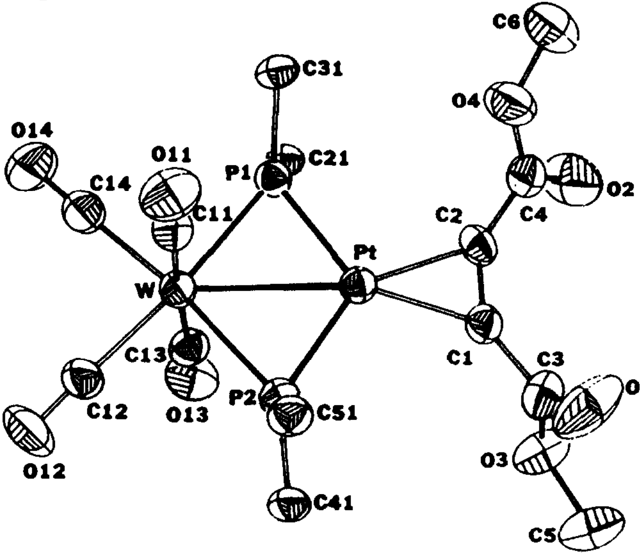
Reaction between $[M(C{\equiv}CH)_2(PR_3)_2]$ and $[MCl_2(PR_3)_2]$ in the presence of CuCl and Et_2NH gave $[M(C{\equiv}CH)Cl(PBu_3)_2]$ for R = Bu, but with R = Me the dimer, **543** was formed, and further reactions invesigated [952]. A new series of liquid crystalline materials containing metal atoms, such as **544** and **545** have been prepared. These form liquid crystals in concentrated trichloroethene solutions, and ^{31}P nmr spectrsocopic data suggested that the polymer molecules respond to the magnetic field, and align perpendicular to the applied field [953]. Optical transitions under high pressure were recorded for **546** (M = Pd or Pt) at room temperature and 77 K. There were three emission bands the highest energy one being due to the excitation of the MLCT in the UV region of the spectrum. This excitation energy could be transferred to the anthracene moiety, which then gave rise to the other two bands [954].



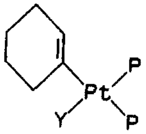
537 Molecular structure of the complex $[Ni_2Ru_3(CO)_8(\mu\text{-}CO)_2(Cp)_2(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ showing approximately C_2 symmetry. (Reproduced with permission from [942])

A range of reactions have been used to prepare $[Pt(C{\equiv}CR)_2L_2]$ from the alkynes. In general these have involved displacement of a halide or other anions by the acetylide anion. Conditions were found in which halides could be displaced by acetylenic alcohols, without dehydration. The structure of 547 was established [955]. The oxalate anion could also be displaced from $[Pt(C_2O_4)(dppe)]$ by the anion of $PhC{\equiv}CH$. In oxalic acid, $[Pt(C{\equiv}CPh)_2(dppm)]$ was rearranged to give *cis,cis*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-}dppm)_2]$ [956].

The complex *cis*-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ could be prepared either from *cis*-$[PtCl_2(PMePh_2)_2]$, and phenylethyne in the presence of NaOEt, or by reaction of *cis*-$[PtCl_2(CO)L]$ with $(PhC{\equiv}C)_2Hg$ to give *cis*-$[Pt(C{\equiv}CPh)_2(CO)L]$, followed by displacement of CO with L. $[Au(C{\equiv}CPh)(PPh_3)]$ was also used as a transfer agent for phenylethyne [957]. It was established that Au(I) > Hg(II) > Pt(II) in transferring alkynyl groups. The stereochemistry of several reactions of this type was studied in detail [958]. A single isomer of the mixed complex $[Pt(C{\equiv}CR)(C{\equiv}CR')(CO)L]$ could be prepared by reaction of 548 with $Hg(C{\equiv}CR')_2$ [959].



538 An ORTEP drawing of $[(CO)_4\overline{W(\mu\text{-}PPh_2)_2Pt}(MeO_2CC{\equiv}CCO_2Me)]$. For clarity only the phenyl carbon atoms attached to phosphorus are shown. (Reproduced with permission from [945])



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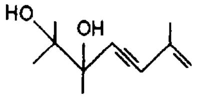

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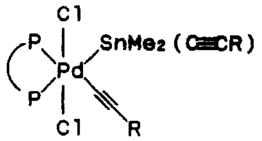

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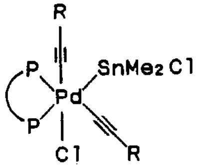

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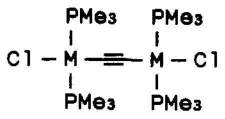
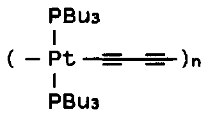


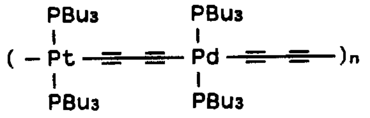
$\mathrm{Cl-\underset{PMe_3}{\overset{PMe_3}{M}}-\!\equiv\!-\underset{PMe_3}{\overset{PMe_3}{M}}-Cl}$

543



$\mathrm{(-\underset{PBu_3}{\overset{PBu_3}{Pt}}-\!\equiv\!-\!\equiv\!-)_n}$

544



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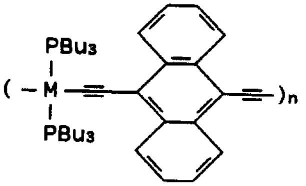

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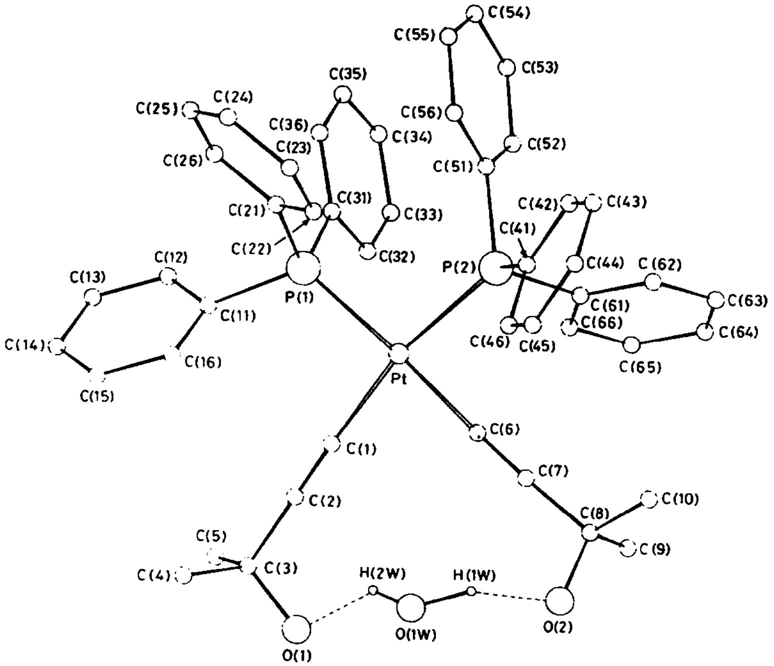
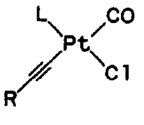


547 (Reproduced with permission from [955])

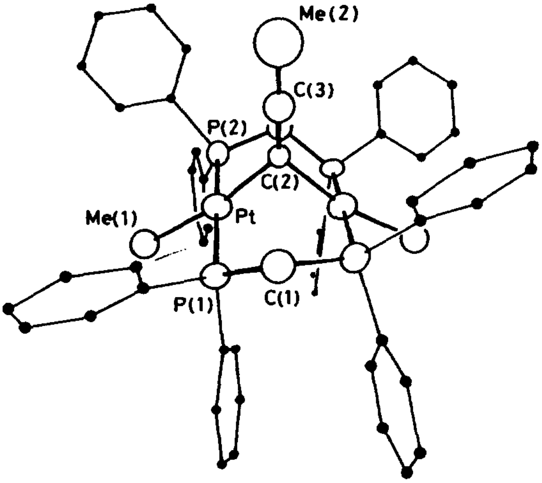


548

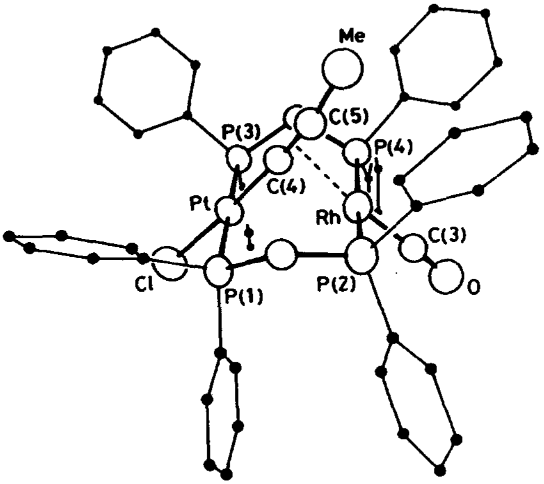
The rearrangement of $[Pt(C{\equiv}CR)_2(dppm)]$, (R = H, Me, Ph or CMe_3) prepared from the chloride and $Me_2Sn(C{\equiv}CR)_2$, to give *trans,trans*-$[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ was catalysed by phosphines [960]. In a more extensive study, Puddephatt showed that the outcome of such reactions was crucially dependent on the substituents on the bridging phosphine. When the alkyne was propyne, the dppm derivative gave only the *trans,trans*-complex, but the dmpm complex gave only the *cis,cis*-isomer. The depm derivative gave a mixture of all the possible isomers [961].

The reaction of *trans*-$[Pt(C\equiv CR)_2(dppm\text{-}P)_2]$ with *trans*-$[PtCl(H)(PPh_3)_2]$ gave $[Pt_2(C\equiv CR)_2(\mu\text{-}dppm)_2(\mu\text{-}H)]Cl$ in good yield. This could be deprotonated with an alkoxide base to give $[Pt_2(C\equiv CR)_2(\mu\text{-}dppm)_2]$, and further reactions of this species with CS_2, SO_2 or $MeO_2CC\equiv CCO_2Me$ to give A-frame complexes were studied [962]. When $[Pt_2(\mu\text{-}dppm)_2Me_2][BF_4]_2$ was reacted with propyne in propanone, the product was **549**, a rare example of a complex in which the alkyne is symmetrically bonded in a μ,η^1-manner. Reaction of $[Pt(dppm\text{-}P,P')_2]Cl_2$ with propyne and silver ethanoate gave $[\{Pt(C\equiv CMe)Cl\}(\mu\text{-}dppm)_2AgCl]$, which reacted with $[Rh_2Cl_2(CO)_4]$ to give $[\{Pt(C\equiv CMe)Cl\}(\mu\text{-}dppm)_2Rh(CO)]^+$, the structure of the $[PF_6]$ salt, **550**, being established in a diffraction study. In this case the alkyne is bonded in a σ-fashion to platinum, and π-bonded to rhodium. The reason for the difference from **549** is thought to be electronic in origin, and the high *trans*-influence of the methyl groups weakens the σ,π-bonding mode of the alkyne [963]. Fluxional behaviour of this and related rhodium carbonyl complexes was investigated. Reaction of $[Pt(C\equiv CR)_2(dppm\text{-}P)_2]$ with $[Rh_2Cl_2(coe)_4]$ gave a complex formulated as $[(RC\equiv C)Pt(\mu\text{-}dppm)_2(\sigma,\eta^2\text{-}C\equiv CR)RhCl]$, but the complex could not be successfully purified. Rhodium also readily replaced silver or mercury from species such as $[(RC\equiv C)_2Pt(\mu\text{-}dppm)_2HgCl_2]$ or $[Cl(RC\equiv C)Pt(\mu\text{-}dppm)_2AgCl]$ [964].

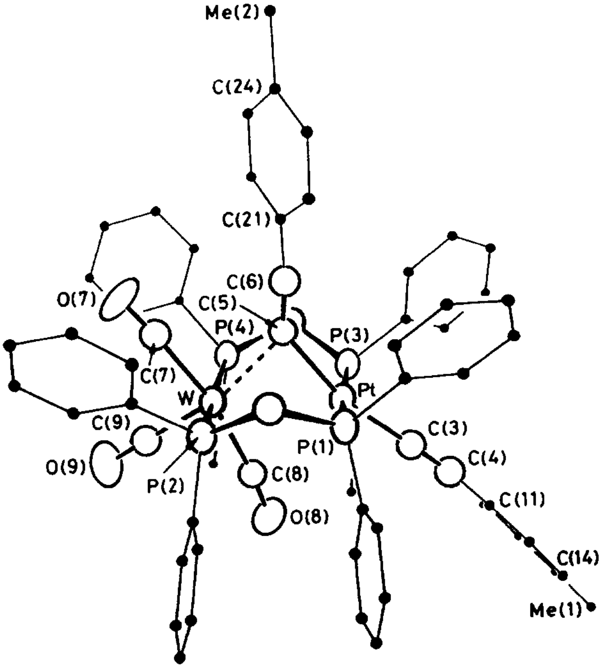
Reaction of the complex *trans*-$[Pt(C\equiv CR)_2(dppm\text{-}P)_2]$ with AgX gave $[(RC\equiv C)_2Pt(\mu\text{-}dppm)_2Ag][X]$ for X = $[NO_3]$ or $[PF_6]$, and $[\{(Ph_3P)AgX\}_4]$ could be used in the same way for X = Cl or I. Related reactions of copper and gold complexes were aslo studied [965]. Reaction with $[W(CO)_3(NCMe)_3]$ gave $[(RC\equiv C)Pt(\mu\text{-}C\equiv CR)(\mu\text{-}dppm)_2W(CO)_3]$, **551**, and $[Pt_2(C\equiv CR)_4(\mu\text{-}dppm)_2]$. The related molybdenum complex could be obtained from $[Mo(CO)_4(cod)]$ or $[Mo(CO)_3(cycloheptatriene)]$, but yields were low. Better yields were obtained by a metal exchange reaction with $[(RC\equiv C)_2Pt(\mu\text{-}dppm)_2AgX]$, and by this route the chromium complex was also succesfully prepared. Protonation with CF_3COOH was reversible, giving $[(RC\equiv C)Pt(\mu\text{-}C{=}CHR)(\mu\text{-}dppm)_2W(CO)_3]^+$. The structure of **551** was established in a diffraction study. The triple bond was shown to be perpendicular to the $\{PtP_4W\}$ plane, with a short Pt-C distance and a longer W-C interaction [966].



549 Molecular structure of the $[Pt_2(\mu\text{-}\eta^1\text{-C}\equiv\text{CMe})(\mu\text{-dppm})_2Me_2]^+$ cation in $[Pt_2(\mu\text{-}\eta^1\text{-C}\equiv\text{CMe})(\mu\text{-dppm})_2Me_2][BF_4]$. (Reproduced with permission from [963])



550 Molecular structure of a $[ClPt(\mu\text{-}\sigma\text{-}\pi\text{-C}\equiv\text{CMe})(\mu\text{-dppm})_2Rh(CO)]^+$ cation in $[ClPt(\mu\text{-}\sigma\text{-}\pi\text{-C}\equiv\text{CMe})(\mu\text{-dppm})_2Rh(CO)][PF_6]$. The asymmetric unit in the crystal structure comprises two vitually identical cations and two $[PF_6]^-$ anions. (Reproduced with permission from [963])

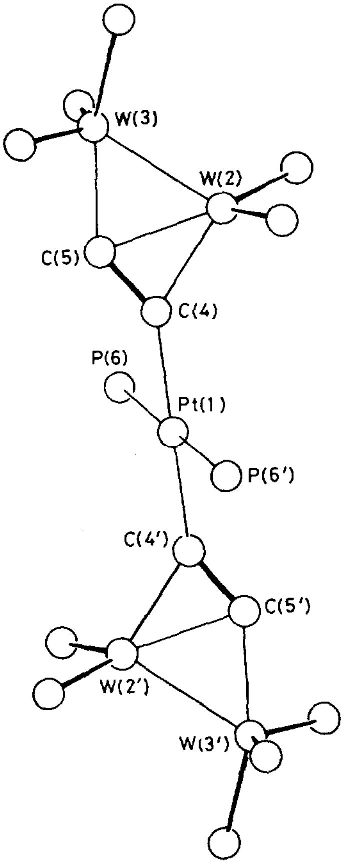


551 (Reproduced with permission from [966])

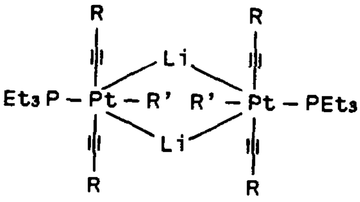
When *trans*-[Pt(C$\equiv$CH)$_2$(PMe$_2$Ph)$_2$] was treated with [W$_2$(OCMe$_3$)$_6$], 2-methyl-2-propanol and *trans*-[Pt(C$\equiv$CH){C$_2$W$_2$(OCMe$_3$)$_5$}(PMe$_2$Ph)$_2$] were obtained. Further addition of [W$_2$(OCMe$_3$)$_6$] gave *trans*-[Pt{C$_2$W$_2$(OCMe$_3$)$_5$}$_2$(PMe$_2$Ph)$_2$], 552, characterised in a diffraction study. The C_2W_2 unit is planar and roughly perpendicular to the PtP_2C_2 plane. The Pt-C distances are consistent with single and the C-C and W-W distances with double bonds [967].

The reaction of *trans*-[Pt(C$\equiv$CR)$_2$(PEt$_3$)$_2$] with R'Li (R = Me, Bu or Ph; R' = Bu, Ph or CMe$_3$) in hydrocarbon solvents, gave [Pt$_2$(C$\equiv$CR)$_4$(PEt$_3$)$_2$(R')$_2$(μ-Li)$_2$], 553. In the presence of better donors such as Et_2O or thf the product was *trans*-[Pt(C$\equiv$CR)$_2$(PEt$_3$)R']$^-$ [968].

Platinum complexes of phosphaalkynes have been reviewed [969]. RC$\equiv$P may act as a 2,4 or 6-electron donor in its complexes with transition metals. The complex [Pt(dppe)(Me$_3$CC$\equiv$P)], in which the phosphalkyne is η^2-bonded, reacted with [Fe$_2$(CO)$_9$] or [Fe$_3$(CO)$_{12}$] to give [PtFe$_2$(dppe)(CO)$_8$(Me$_3$CC$\equiv$P)], 554. In this structure the phosphorus atom of the phosphalkyne is coordinated to all three metals, and the phosphorus-carbon bond length is typical of a doubly bonded species [970]. When [Pt(PPh$_3$)$_2$(Me$_3$CC$\equiv$P)] was reacted with [Pd(PPh$_3$)$_4$] the product was [Pd$_2$Pt$_3$(PPh$_3$)$_5$(Me$_3$CC$\equiv$P)$_3$], 555. The metals are arranged in a trigonal bipyramid with palladium axial and platinum equatorial, each metal bearing one PPh_3 ligand. The phosphaalkynes are bridging, so that the structure has overall C_3 symmetry, in accord with predictions made on the basis of the cluster condensation generalisation [971].



552 A ball and stick view of the central *trans*-{$PtP_2(C_2W_2O_5)_2$} moiety of the centrosymmetric *trans*-[$Pt\{C_2W_2(OCMe_3)_5\}_2(PMe_2Ph)_2$] molecule looking nearly down the P-Pt-P axis showing the planar PtC_2W_2 unit. (Reproduced with permission from [953])



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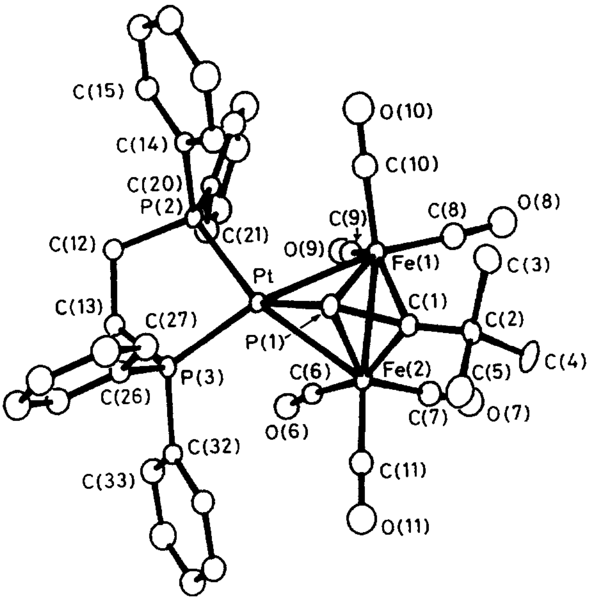
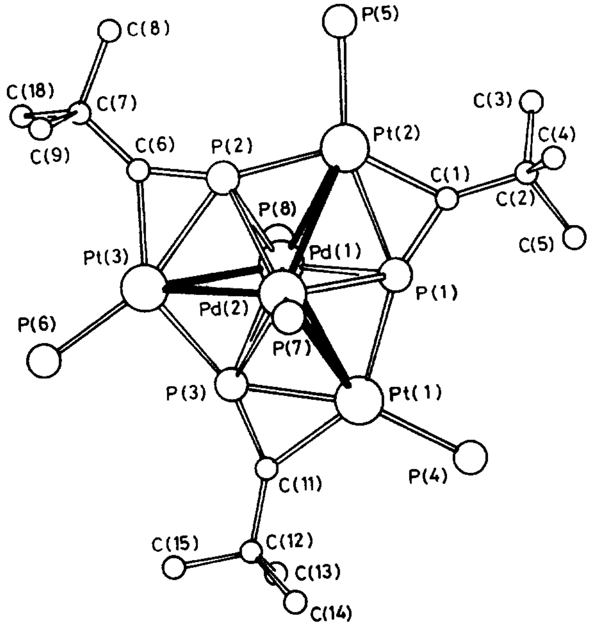
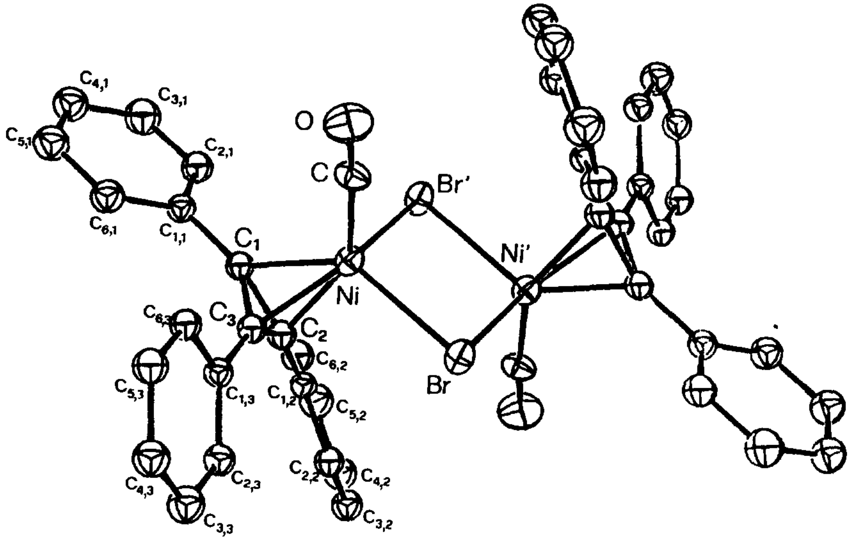


554 Molecular structure of [$Fe_2Pt(CO)_6(dppe)(Me_3CC\equiv P)$]. (Reproduced with permission from [970])



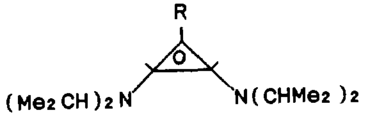
555 (Reproduced with permission from [971])

The complex of stoicheiometry $\{Ni(C_3Ph_3)(CO)Br\}$ was originally formulated as a dimer, and later as a monomer. An X-ray diffraction study has now established its dimeric structure, 556 [972].



556 Perspective view of $[\{NiBr(CO)(C_3Ph_3)\}_2]$; ORTEP drawing with 30 % probability ellipsoids. (Reproduced with permission from [972])

There has been a theoretical study of the stereochemistry and reaction path for ring whizzing in cyclic d^{10} $\{ML_2(polyene)\}$ complexes. Extended Huckel calculations were performed for $[Pt(C_3H_3)(PH_3)_2]^+$, $[Ni(C_4H_4)(PH_3)_2]$, and $[Ni(C_6H_6)(CO)_2]$ [973]. The cation 557 (R = H) was readily lithiated using BuLi, and then reacted with *trans*-$[PtCl_2(PBu_3)_2]$ to give 558 [974].



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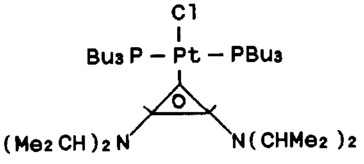
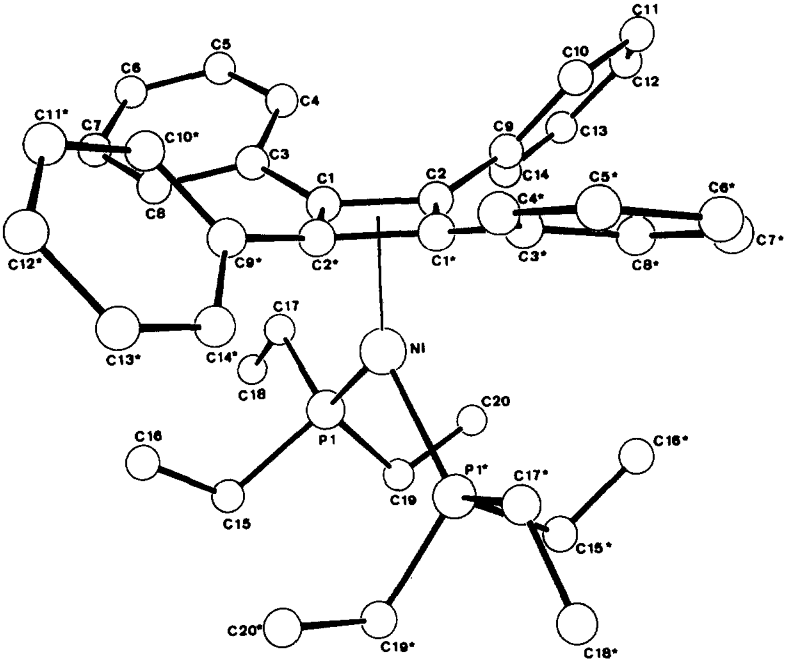


558

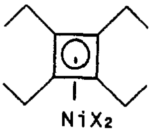
There has been a theoretical study of the rearrangenemt of $\{ML_2\}$ groups from one coordination site to another in $\{ML_2(polyene)\}$ complexes. Among the species considered were $[Ni(C_4H_4)(PH_3)_2]$, $[Ni(C_6H_6)(CO)_2]$ and $[Pt(CO)_2(Cp)]^-$

[975]. The electrochemical reduction of $[Ni(\eta^4-C_4R_4)(\eta^5-C_5R'_5)]^+$ (R = Me or Ph; R' = H or Me) was studied by CV, chronopotentiometry and chronoamperometry. A reversible 1-electron reduction to give a 19-electron species was noted when R = Ph, R' = H or Me, but this was irreversible for R = Me [976].

Reaction of the complex $[NiBr_2(C_4Ph_4)]$ with successively Me_3CLi and Et_3P gave $[Ni(C_4Ph_4)(PEt_3)_2]$, 559. Carbonylation of 559 gave octaphenylcyclooctatetraene, and reaction with alkynes gave arenes. The relationship of these processes to the Reppe reaction was discussed [977]. The complex 560 was isolable in significant amounts from the cyclotrimerisation of 3-hexyne in the presence of NiX_2/Mg/thf [978].



559 (Reproduced with permission from [977])



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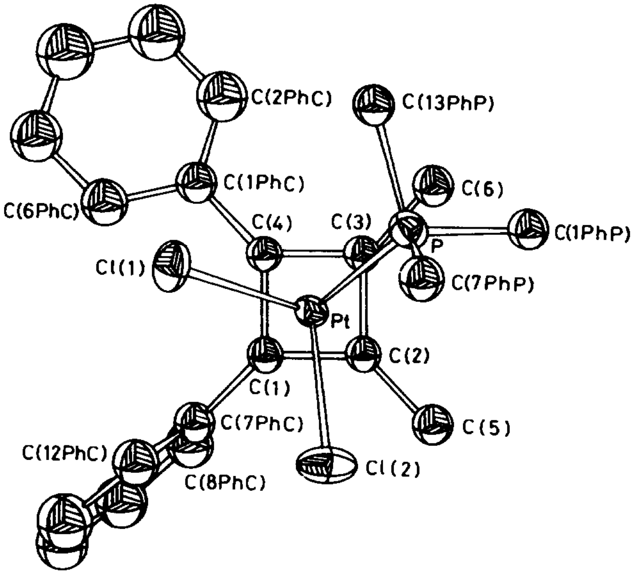
Reaction of *cis*-$[PtCl_2(CO)_2]$ with PhC≡CMe gave

$[Pt_2(\mu\text{-}Cl)_3(C_4Me_2Ph_2)][PtCl_3(CO)]$, characterised spectroscopically. When treated with $[Et_4N]Cl$ in MeCN, $[Pt_2Cl_2(C_4Me_2Ph_2)_2]$ was formed. Monomeric species $[PtCl_2(C_4Ph_2Me_2)L]$ could be obtained on addition of a suitable ligand, and 561 was characterised in a diffraction study. The geometry at platinum was distorted tetrahedral, and the four membered ring was not symmetrically coordinated in the solid state, though the solution structure seems to be more symmetric [979].



561 View of the coordination around the platinum atom projected along a normal to the *cb* plane. The phenyl rings of the phosphine are omitted for clarity. (Reproduced with permission from [979]).

The photochemistry of metallocenes, including $[NiCp_2]$, has been reviewed [980]. Hartree Fock calculations have been undertaken on selected sandwich and half sandwich compounds, including $[NiCp_2]$ and $[Ni(Cp)(NO)]$. The errors in computed metal-ligand distances were compared to determine the type of correlation effects which are important in a discussion of bonding. It was concluded that charge transfer effects were much more important than ring-ring dispersion forces [981]. The far UV spectra of the metallocenes $[MCp_2]$ (M = Ni, Fe or Co) were recorded in the vapour phase. It was suggested that the Rydberg bands originating with the metal 3d and ligand π-orbitals made significant contributions to the spectra [982]. Orbital reorganisation energies in the PE spectra of 15 transition metal complexes, including

[Ni(Cp)(NO)], were determined by means of the Green's function formalism. The results were compared with experimental data [983]. The band structures of 11 one dimensional poly-decker sandwich compounds, including nickel complexes of Cp and/or η^5-B_5H_5 were studied using the semiempirical crystal orbital procedure based on the INDO approach [984].

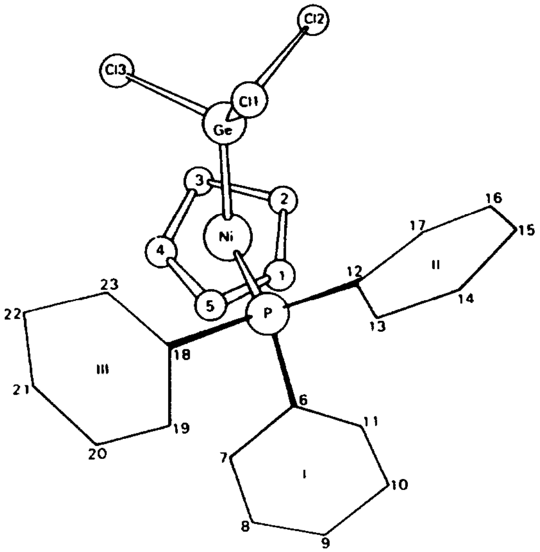
Films of nickel suitable for soldering and <2-3 μ thick were deposited by thermal dissociation of [$NiCp_2$] in a hydrogen containing atmosphere [985]. Joining of homogeneous porous ceramics was accomplished by metalising the surfaces to be joined by pyrolysis of [$Ni(arene)_2$] followed by welding in vacuum [986]. In a thermodynamic study of the thermal decomposition and hydrogenation of metallocenes, nickelocene was shown to be the least resistant to decomposition of the series [987]. There has been a gas chromatographic study of the products of hydrogenation of [$NiCp_2$] during nickel coating of quartz units [988]. Tetrakis(allyl) molybdenum in pentane was abosrbed onto alumina, the pentane removed and the material treated with hdrogen at 600 °C for 16 h. Further treatment with [$NiCp_2$] led to the preparation of a mixed metal catalyst for hydrogenation [989].

The complexes [$NiCp_2$] and [$FeCp_2$] have pseudoisomorphous structures at room temperature, but only ferrocene undergoes a second order phase tranformation on cooling [990]. The structure of $[NiCp(dppp)]_2[B_{12}H_{12}]$ has been established; the six-membered ring adopts a boat conformation [991]. Reaction of [$NiCl(Cp)(PPh_3)$] with Cs[$GeCl_3$] gave [$Ni(Cp)(GeCl_3)(PPh_3)$], 562. There was shown to be some indication of localised bonding in the Cp ligand, which deviates from planarity [992].

The standard heat of sublimation of [$NiCp_2$] was established as 70.2 kJ mol^{-1}, and the entropy of sublimation as 144.4 J mol^{-1} [993]. ^{199}Hg nmr spectroscopic parameters were established for [$Hg\{(\eta^5-Cp)(GePh_3)NiHgGePh_3\}_2$] [994]. Spectroscopic properties of [$Ni(\eta^5-RC_5H_4)_2$] (R = H, Me, Et, Bu or $PhCH_2$) have been reported [995]. Two photon ionisation of saturated vapours of organic compounds including [$NiCp_2$] has been investigated. This technique allows one greatly to decrease the radiation exposure and to obtain laser tracks with practically any distribution of energies [996].

The species [$MgCp_2$] was prepared electrochemically in various aprotic solvents, and used in preparations of [$NiCp_2$] and [NiCp(NO)] [997]. Electrolysis of a cyclopentadiene solution at a nickel anode, followed by treatment with NO gave [Ni(Cp)(NO)] in low yield [998]. Reaction of [$M(acac)_2$] (M = Fe, Co or Ni) with Cp*Li gave [M(acac)Cp*] [999]. In the nickel series, a further reaction with CpNa gave [NiCpCp*], whilst treatment with MeMgI under an atmosphere of CO yielded [Ni(CO)(Cp*)(Me)] as an unstable violet liquid

[1000]. The complex $[Ni(\eta^5-C_5H_4Cl)_2]$ was prepared from $[NiBr_2(dme)]$ and the thallium chlorocyclopentadienide [1001]. With Cp^*Li, at −10 °C, $[Ni(dme)X_2]$ gave $[\{NiCp^*X\}_2]$ which could be further reacted with a range of donor ligands to give species such as $[Ni(Cp^*)(PPh_3)X]$ or $[Ni(cod)(Cp^*)]^+$ [1002]. Treatment of $[Ni(cod)_2]$ with Cp_2Zn in the presence of PPh_3 gave $[(CpZn)_2(\mu\text{-}Cp)\{\mu\text{-}Ni(Cp)(PPh_3)\}]$, 563, in which two {CpZn} units are bridged by the nickel of $\{Ni(Cp)(PPh_3)\}$ and a Cp. The mechanism for the reaction was discussed [1003].

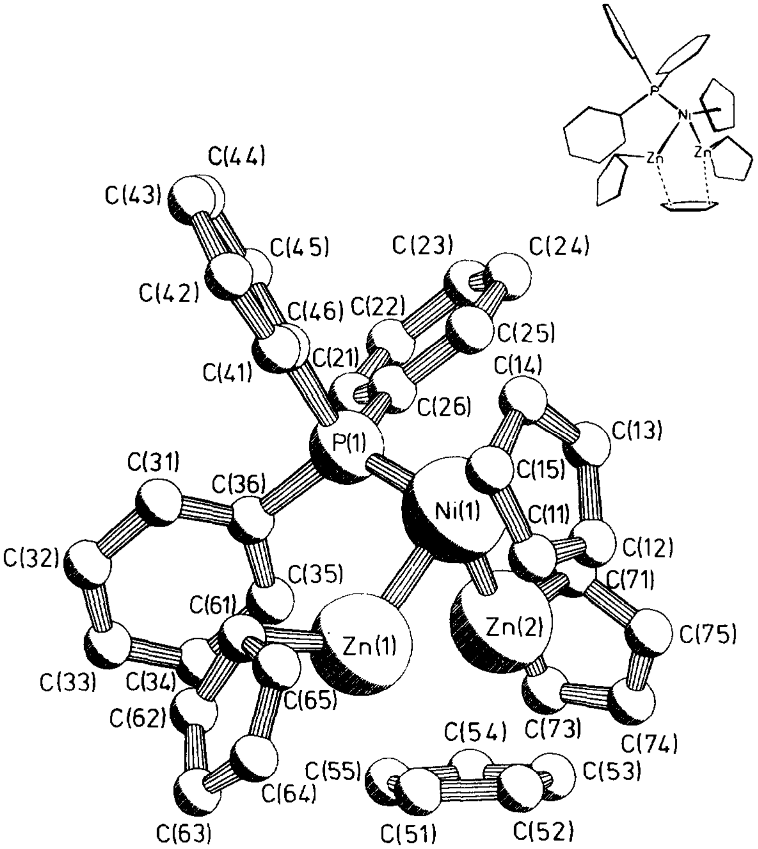


562 Structure of $[Ni(Cp)(GeCl_3)(PPh_3)]$; hydrogen atoms and benzene of crystallisation have been omitted for clarity. (Reproduced with permission from [977])

A series of salts $[NiCp(PPh_3)_2]_2[B_nX_m]$ (X = H or Cl) were prepared by reaction of $[NiCl(Cp)(PPh_3)]$ with $[Et_4N]X$ in the presence of PPh_3 at room temperature [1004]. Related dppe derivatives were also prepared [1005].

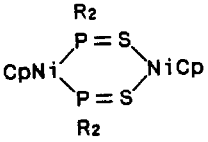
Reaction of $[NiCp(SMe_2)_2][BF_4]$ with $R_2NCH_2CH_2NR_2$ gave the stable species $[CpNi(R_2NCH_2CH_2NR_2)][BF_4]$, the chemical and spectroscopic properties of which were discussed [1006]. The complex $[NiCp(\eta^4\text{-cyclopentadiene})][BF_4]$ reacted with $AsMe_3$ with the displacement of the diene to give $[Ni(AsMe_3)_2(Cp)][BF_4]$, which on treatment with halide, X^-, yielded the neutral species $[Ni(AsMe_3)(Cp)X]$ [1007]. Reaction of $[NiBr(Cp)(PPh_3)]$ with $Tl[BF_4]$ in the presence of PCy_3 yielded $[Ni(Cp)(PCy_3)(PPh_3)][BF_4]$. Sodium amalgam reduction of such complexes gave the unstable $[Ni^I(Cp)L_2]$, whilst carbonylation yielded

[{Ni(CO)(Cp)}$_2$] [1008]. Reaction of [{CpNi(CO)}$_2$] with [Cp$_2$FeX] in the presence of a ligand, L, gave [CpNiL$_2$]X [1009].



563 PLUTO drawing of [Cp$_3$Zn$_2$Ni(Cp)(PPh$_3$)]. (Reproduced with permission from [987])

Halide was displaced from [NiCl(Cp)(PPh$_3$)] by PhSCH$_2$Li to give [Ni(η^1-CH$_2$SPh)(Cp)(PPh$_3$)] as green crystals. Protonation yielded PhSMe. With [NiCp$_2$] and PhSCH$_2$Li in the presence of PPh$_3$, the same complex was obtained, together with small amounts of [NiCp(PPh$_3$)(SPh)] and [{NiCp(SPh)}$_2$], this latter being the major product in the absence of PPh$_3$ [1010]. The synthesis of [NiCp{Me$_2$P(S)P(S)Me$_2$}] and the related anion have been described. Reaction with [Ni$_2$Cp$_3$] gave a weakly paramegnetic species, **564**. A temperature dependent singlet-triplet spin equilibrium was observed, essentially localised on the {NiCpS$_2$} unit [1011].



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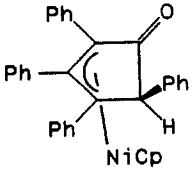
The 17-electron vanadium(0) complex, $[V(CO)_6]$, was oxidised to the 18-electron vanadium(I) species, $[V(CO)_4(Cp)]$, by $[NiCp_2]$, the other product being $[Ni(CO)_4]$ [1012]. The reduction of $[NiCp_2]$ has been studied by CV. One 1-electron irreversible reduction, and one reversible 1-electron oxidation were noted at room temperature. A further 1-electron oxidation was irreversible at room temperature, but reversible at low temperature. In the reduction process the initial product is $[NiCp_2]^-$, which decomposes to give Cp^- and {NiCp}, the latter being stabilised by thf coordination, or further reduced and trapped by CO to give $[Ni(CO)(Cp)]^-$. High pressure of CO resulted in the formation of $[Ni(CO)_4]$ [1013]. A species derived from $[NiCp_2]$ and $Li[AlH_4]$ was used to cleave carbon-sulphur bonds in thiols, sulphides and thioacetals, but the active species was not fully characterised [1014].

The reactions of organometallics with XeF_2 in the presence and the absence of air has been studied. Among the complexes investigated were $[Ni(\eta^5-C_5H_4SiMe_3)_2]$ and $[Ni(CH_2=CHSiMe_3)(PPh_3)_2]$, both of which gave rise to low intensity chemiluminescence [1015].

The complexes $[Ni(Cp)(L)(PR_3)][BF_4]$ (L = SMe_2 or $Me_3P=S$) were stabilised when the phosphine was bulky. A range of substitution reactions was discussed [1016]. There had been previously demonstrated a reversible reaction between $[NiCp_2]$ and an appropriate ligand, L, in the presence of LiI to give $[Ni(\eta^1-Cp)(Cp)L]$, and a number of such species were characterised. Now reactions giving rise directly to $[NiCpI(L)]$ (L = PR_3, AsR_3 or $SbMe_3$), or $[Ni(Cp)(LL)]I$ using a chelating ligand, LL, (LL = $R_2PCH_2CH_2PR_2$) are reported [1017].

Reaction of $[NiCp_2]$ with tetracyclone at 170 °C in the melt gave bis(tetracyclone)nickel together with small amounts of **565** and **566**. It is likely that **565** is an intermediate in the reduction of tetracyclone to **566**, since either its reaction with $[NiCp_2]$ or thermolysis gave mainly **566** [1018]. When $[NiCp(nbd)][BF_4]$ was treated with Me_3P, the product was $[Ni(C_7H_8PMe_3)(Cp)][BF_4]$, **567**. This disproportionated quite readily to give the starting material and $[Ni(Cp)(PMe_3)_2][BF_4]$ [1019].



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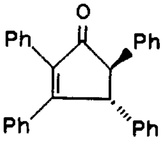

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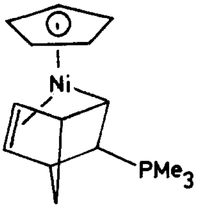

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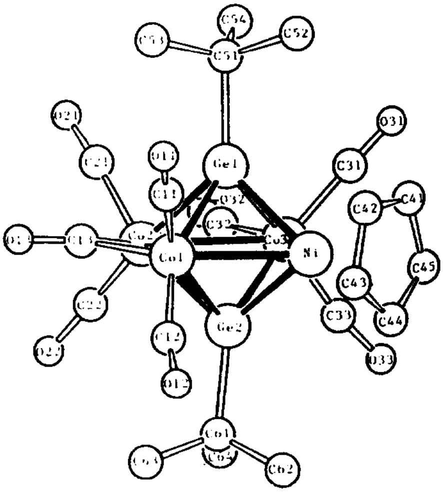
There have been many reports of the involvement of {NiCp} units in cluster complexes. The complex [{Ni(Cp)(PH_2)}$_3$] crystallised in the rhomohedral space group R3. the six-membered {Ni_3P_3} ring adopted a chair conformation and the cyclopentadienyl ligands were disordered [1020]. Reaction of [$NiCp_2$] with either [ReCl(CO)$_5$] or [Mo(CO)$_3$(MeCN)$_3$] resulted in the formation of [Ni_3(CO)$_2$(Cp)$_3$], characterised in a diffraction study. The nickel atoms form an equilateral triangle with C_{3h} symmetry. The intermediate proposed in the rhenium series was [Ni(Cp)(η^1-Cp)(μ-Cl)Re(CO)$_5$] [1021]. When [$NiCp_2$] was treated with [RNO_2H][BF_4] in the presence of acid, the product was the triple-deacker sandwich, [Ni_2Cp_3][BF_4]. A mechanism was proposed for the reaction [1022].

A range of reactions between [MCp_2] and M'L have been studied in the gas phase. With nickelocene the main processes were ligand displacement and metal switching. This allowed the determination of limits for the values of ionisation potentials, ΔH(formation) of complexes, and some bond energies. Secondary reactions were also discussed, including those of {$CoNiCp_2$} and {$FeNiCp_2$} [1023].

The reaction of [Co_3(CO)$_9$CR] with [$NiCp_2$] gave [$NiCo_2$(CO)$_6$(Cp)(μ_3-CR)], which reacted further with [Fe_2(CO)$_9$] to give [Co_2FeNi(Cp)(CO)$_9$CR]. Replacement of both cobalt atoms by nickel was achieved in [Co_2Mo(CO)$_8$(Cp)(μ_3-CR)] using [$NiCp_2$], but with [{Ni(CO)(Cp)}$_2$] only a single replacement was accomplished [1024]. A metal exchange reaction was also reported for one of the cobalt atoms in [Co_4(CO)$_{11}$(GeR)$_2$], to give 568 characterised in a diffraction study [1025]. Reaction of

[$Co_2Mo(CO)_8(Cp)(\mu_3$-GeR)] with [{Ni(CO)(Cp)}$_2$] resulted in the replacement of one of the cobalt atoms of the cluster [1026]. When the phospaalkyne $Me_3CC{\equiv}P$ was reacted with [{Ni(CO)(Cp)}$_2$] the product was the tetrahedral cluster 569. With [$Co_2(CO)_6(Me_3CC{\equiv}P)$] the product was the heteronuclear tetrahedral species 570, which could also be obtained by reaction of [$Co_2(CO)_8$] with [{Ni(CO)(Cp)}$_2$] followed by treatment with the phosphaalkyne. The phospaalkyne could not, however, displace an alkyne from the related alkyne derivative [1027].



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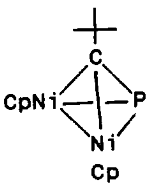

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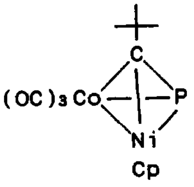

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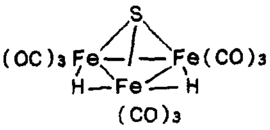
Some similar reactions of [$NiCp_2$] with iron clusters have also been noted. Reaction with 571 gave 572 and 573. The bridging hydride in 572 could be readily replaced by {$Au(PPh_3)$} by reaction with KH followed by [$Au(R_3P)X$] [1028]. The reaction of [$Ni_2Cp_2\{H_2CC(=CH_2)CH_3\}$] with [$M_3(CO)_{12}$] (M = Fe or Ru) under a hydrogen atmosphere gave [$Fe_2Ni_2\{C_2HC(=CH_2)CH_3(CO)_6(Cp)_2\}$], 574, characterised in a diffraction study. In this complex, the alkyne interacts with all the metal centres through either σ- or π-bonds [1029].



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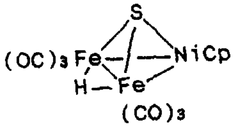

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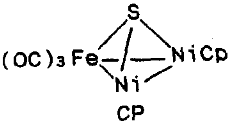

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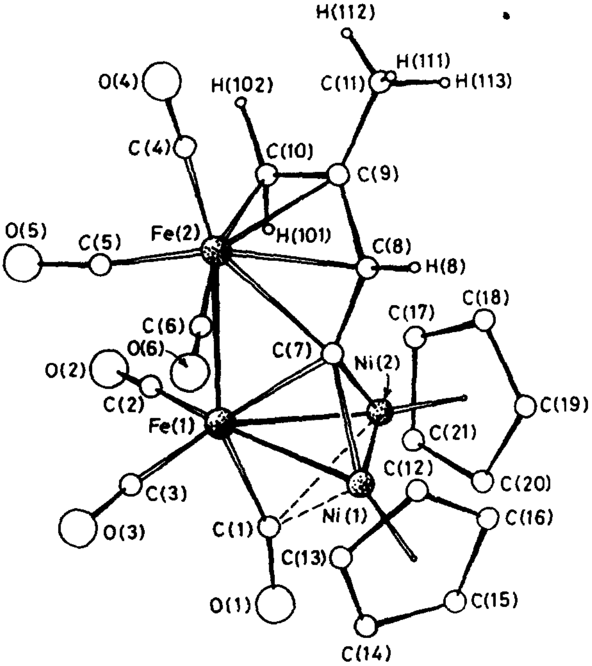
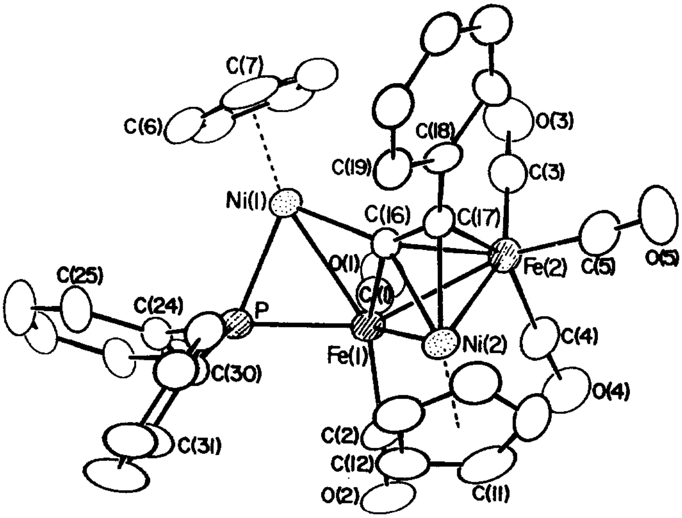


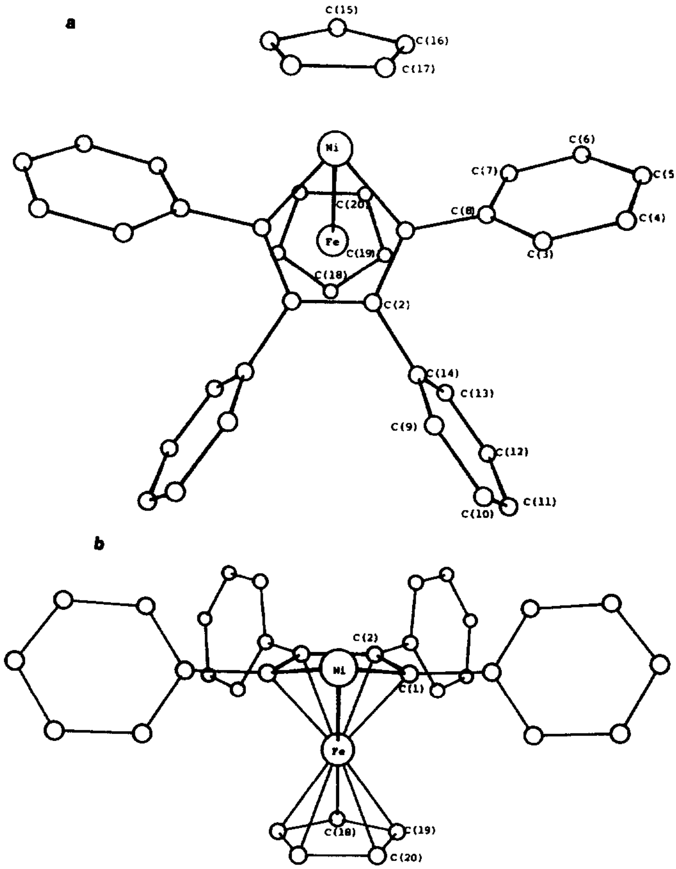
574 *View of the molecular structure of* $[Fe_2Ni_2\{C_2(H)C(=CH_2)CH_3\}(CO)_6(Cp)_2]$ showing the atomic numbering scheme. (Reproduced with permission from [1013])

When $[Fe_2(CO)_9]$ was allowed to react with $[MM'(PhC\equiv COOCHMe_2)]$ the square pyramidal chiral cluster $[FeMM'(CO)_3(PhC\equiv CCOOCHMe_2)]$ was formed ($M = \{NiCp\}$, $M' = \{Mo(CO)_3(Cp)\}$, $\{Co(CO)_3\}$ or $\{NiCp\}$). The derivative for which $M' = \{NiCp\}$ racemises on the nmr spectroscopic timescale, whilst in the other cases the diastereoisomers interconvert. The mechanisms of the rearrangement reactions were discussed in detail, and all the structures were established in *diffraction studies [1030]. The bridged alkyne complex* $[Fe_2(\mu_2\text{-}\eta^2\text{-}C\equiv CPh)(CO)_6(\mu\text{-}PPh_2)]$ reacted with $[\{Ni(CO)(Cp)\}_2]$ to give $[Fe_2Ni_2(\mu_4\text{-}\eta^2\text{-}C\equiv CPh)(CO)_5(Cp)_2]$, 575, in good yield. The μ_4-alkyne is bonded to a spiked triangular metal skeleton with σ-bonds to Fe(1) and Ni(1) in a three centre interaction, and is η^2-bonded to Fe(2) and Ni(2), overall acting as a five electron donor [1031]. The alkyne derivative [$Fe_2(CO)(\mu$-CO){μ-σ;η^3-CO)(Cp)$_2$(RC≡CR')] reacted with nickelocene to give the novel metallocycle analogue of ferrocene, [CpFe{μ-σ:η^4(CpNiC$_4$R$_2$R'$_2$)}], 576. The iron atom is sandwiched between approximately parallel η^5-Cp and σ:η^4-NiC$_4$Ph$_4$ ligands, and is displaced somewhat towards the nickel [1032].



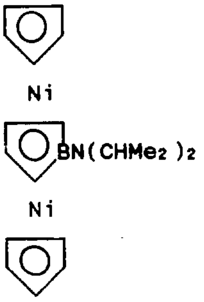
575 (Reproduced with permission from [1031])

Reaction of [Ni(cod)$_2$] with [Cp$_2$Zn] gave the very stable cluster [Ni$_2$Zn$_4$Cp$_6$]. The metal atoms adopt an octahedral arrangement with the nickel atoms apical, and the zincs equatorial, and some compression along the Ni-Ni axis. The bonding in the cluster, and the mechanism of its formation were discussed [1033]. The triple-decker species [Ni$_2$Cp$_3$][BF$_4$] reacted with [TiCp(SR)$_2$] or [MoCp(SR)$_2$] to give [Cp$_2$M(μ-SR)$_2$NiCp][BF$_4$]. The temperature dependence of the ^{1}H nmr spectrum was explained by inversion of the bridging sulphur atoms. However, ^{1}H and ^{13}C nmr parameters for the Cp ring coordinated to nickel in [Cp$_2$Mo(μ-SCMe$_3$)$_2$Ni(C$_5$H$_4$R)]$^+$ were explained in terms of a temperature dependent equilibrium between diamagnetic low spin, and paramagnetic high spin isomers. MO calculations suggested that the spin crossover was a consequence of the flattening at the sulphur atoms caused by the bulky CMe$_3$ substituents. The structure of the complex for which R = H was established in a diffraction study, and the sulphur atoms are indeed less pyramidal than in related structures [1034].



576 a Perspective drawing of [$CpFe\{\mu$-σ-η^4-$(CpNiC_4Ph_4)\}$] showing the atom numbering scheme. b Drawing of [$CpFe\{\mu$-σ-η^4-$(CpNiC_4Ph_4)\}$] showing the sandwich structure. Atoms of the nickel bound cyclopentadienyl ring are omitted for clarity. (Reproduced with permission from [1016])

Boron containing analogues of the cyclopentadienyl ligand have been studied. For example, $Li_2[C_4H_4B$-$N(CHMe_2)_2]$ reacted with $NiCl_2$ to give the metallocene analogue, and with [Ni(cod)(Cp)][BF_4] to give 577, though in low yield [1035]. A paramagnetic mixed metallocene, [Ni(Cp)(578)] was prepared from [{Ni(CO)(Cp)}$_2$] and 578. This disproportionated quite readily, and could not be stacked to give triple decker complexes [1036]. With 579 and [$Ni(\eta^3$-$C_3H_5)_2$], the mixed species, [$Ni(\eta^3$-$C_3H_5)$(579)] was thought to be the initial product, but 580 and some higher oligomers were isolated [1037]. This could be stacked with further units by reaction with [Co(Cp)(579)], to give the first hexadecker complex isolated [1038].



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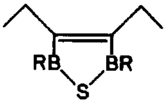

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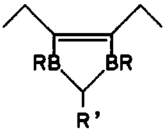

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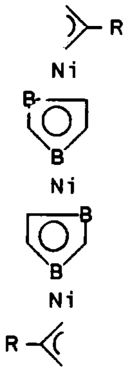

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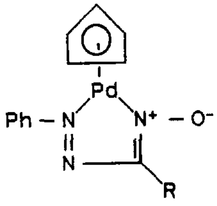
Examples of palladium or platinum metallocenes have, as always, been scattered. A method for estimating the contributions of different factors to ^{13}C nmr chemical shifts of a ligand has been proposed, based on elimination of the charge effect, and a determination of the combined effect of the remaining factors. A relationship was established between ^{13}C nmr spectroscopic data, and chemical properties of a range of cyclopentadienyl metal complexes, including [Pd(η^3-C_3H_5)(Cp)] [1039]. Reaction of CpTl with [Pd_2(arylazooximate)$_2Cl_2$] gave the monomer 581. The starting material could be regenerated with HCl, and the redox properties of the complex were investgated by CV [1040]. The preparation of 582 from [{$PdCl_2(PREt_2)$}$_2$] and the thallium salt of the ligand has been reported [1041].

Some reactions of 583 have been described; 584 was characterised in a diffraction study [1042].



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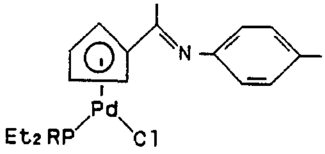

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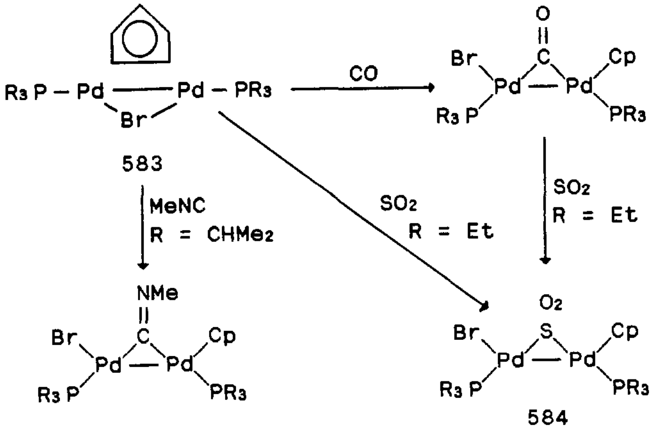
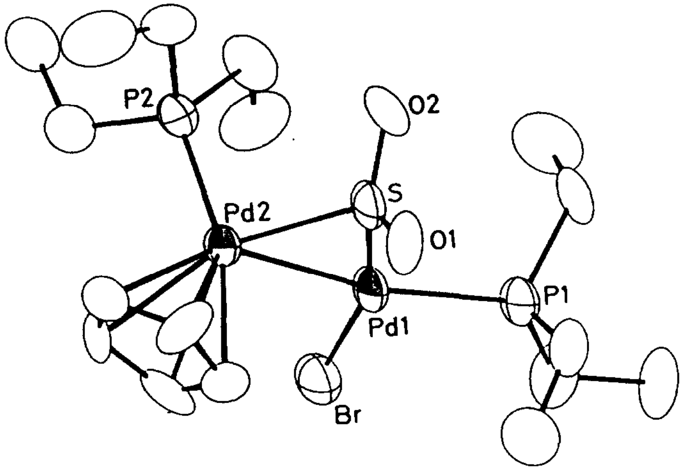
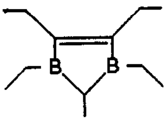




584 Reproduced with permission from [1042])

Reaction of **585** (HL) with MX_2 (M = Pd or Pt) and NaCp gave the mixed metallocene analogue **586**. Low yields of [PtL_2] were also obtained, and this reacted with potassium metal to give mono and dianions [1043]. From this 3- and 4-decker complexes such as **587** could be obtained by reaction with $CpML_n$ [1044].



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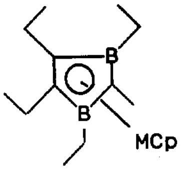

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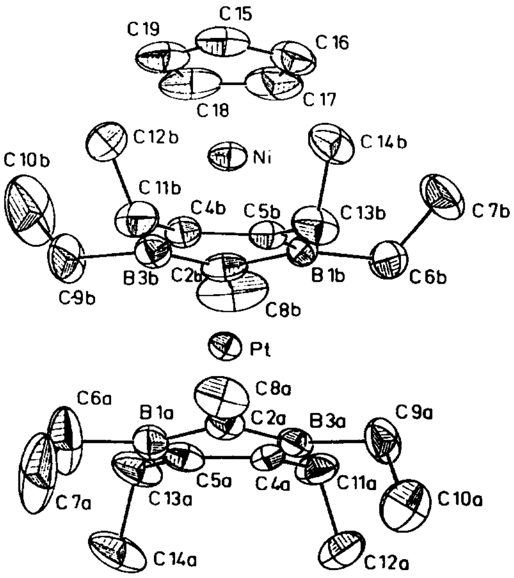


587 (Reproduced with permission from [1044])

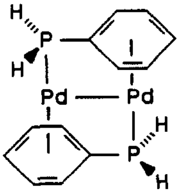
The codeposition of atomic nickel with benzene or toluene at -196 °C has been studied. IR spectroscopic data indicated that unstable bis(π-arene) nickel complexes were formed, from a precursor with 1:1 stoicheiometry [1045]. The reaction of nickel atoms with toluene was also studied by another group, and at -196 °C was thought to lead to the formation of a labile species, {Ni(toluene)}. This reacted readily with bipy to give [$Ni(bipy)_2$] [1046].

Reaction of [$Ni(\eta^3\text{-}CH_2CMeCH_2)_2$] with R_3SiH and toluene gave [Ni(toluene)SiR_3] and 2-methylpropene. Toluene also reacted with [$NiBr(C_6F_5)$]

to give $[Ni(C_6F_5)_2(toluene)]$, which was also obtained from $[Ni(C_6F_5)_2(OEt_2)]$ and toluene in the presence of BF_3 [1047].

The preparation and characterisation of $[Ni(C_5H_5BMe)(\mu\text{-}CO)\}_2]$, a nickel complex of a borabenzene, has been reported [1048].

Proton resonance linewidths and proton spin lattice relaxation parameters have been measured as a function of temperature for crystalline $[(AlCl_3)(\mu\text{-}Cl)Pd(\mu\text{-}C_6H_6)_2Pd(\mu\text{-}Cl)(AlCl_3)]$. The benzene ligand performs a reorientational motion around a 6-fold symmetry axis both at room temperature and at -196 °C, with E_a = 5.9 kJ mol^{-1} [1049]. CNDO calculations have been performed on the electronic structure of models for $[Pd_2(PPh_3)_2]$, for the purpose of studying the role of intramolecular Pd-arene coordination in stabilisation of the complex. It was concluded that the complex was stabilised by a donor-acceptor interaction of the weakly populated 5s and 5p atomic orbitals of the palladium with the filled orbitals of the aryl rings, suggesting a structure such as 588 [1050].



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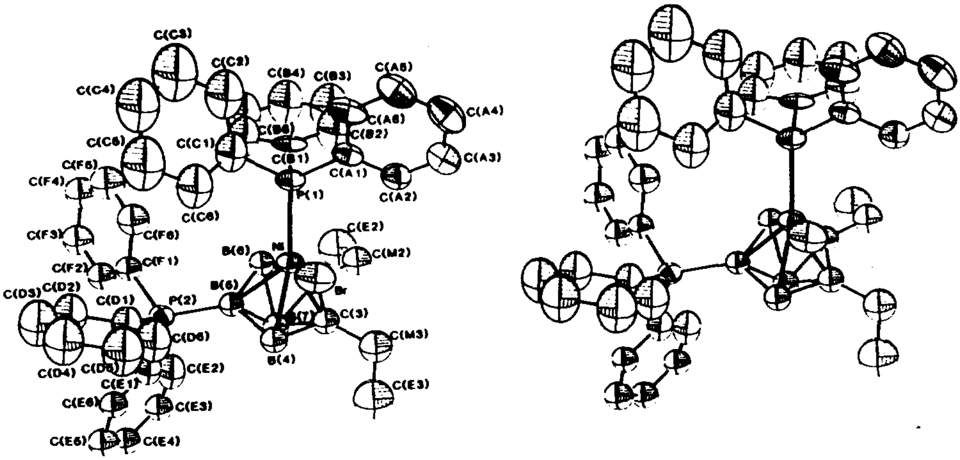
There has been a study of the interaction of 54 aromatic and quinonoid compounds with platinum thin layer electrodes, to establish the surface coordination chemistry of polycrystalline platinum with these compounds in aqueous solution. Both π- (for quinones) and σ-modes (for thiophenols, and heterocyclic amines) of coordination were noted [1051].

12 METAL CARBORANE AND RELATED COMPLEXES

Metallocarboranes, including nickel and platinum complexes, have been reviewed [1052].

The reaction of *nido*-$Na[Et_2C_2B_4H_5]$ with $[NiBr_2(PPh_3)_2]$ in thf at room temperature gave $[1\text{-}Br\text{-}1,5\text{-}(PPh_3)_2\text{-}1,2,3\text{-}NiEt_2C_2B_4H_3]$, 589, characterised in a diffraction study, and by mass spectrometry and high field nmr spectroscopy. The $\{NiC_2B_4\}$ unit has regular *closo*-geometry, as expected for a 7-vertex 16-skeletal electron structure [1053].



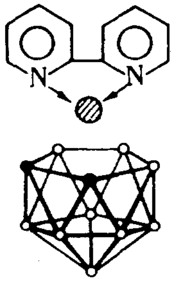
589 Stereoview of the molecular structure of $[1,2,3\text{-}(Ph_3P)(Br)Ni(Et_2C_2B_4H_3\text{-}5\text{-}PPh_3)]$. (Reproduced with permission from [1053])

The structure of *closo*-$[6,7\text{-}(\eta^5\text{-}Cp)_2\text{-}6,7,1\text{-}Ni_2CB_{10}H_8]$ has been established in a diffraction study. The structure involves a distorted bicapped square antiprism, the vertices of which are occupied by 2 nickel, 1 carbon and 7 boron atoms. The nickel atoms are bonded, and are located in a square face of the antiprism, with a boron over the centre. The carbon atom is located over the centre of the opposite face. The core of the complex contains one unpaired electron localised in one of the Ni-Ni antibonding orbitals [1054]. The structure of $[Ni(8\text{-}MeO\text{-}C_2B_9H_{10})_2]$ was established in a diffraction study; the two dicarbollide ligands were coordinated by their π-pentagonal faces to nickel, to form a new staggered conformation, with the cages distorted at 112 ° to each other [1055].

Electrolysis of $K[C_2B_9H_{12}]$ at a nickel anode in dmso gave $[Ni(C_2B_9H_{11})_2]^-$ and $[Ni(C_2B_9H_{11})_2]$ [1056]. Complexes of the stoichelometry $\{Cb_2Ni(III)\}_2\{Ni(II)L_4\}$ (Cb = π-(3)-1,2-$C_2B_9H_{11}$; L_2 = bipy or L = py) have been studied. Thermolysis of the complex with bipy as the ligand gave 3-bipy-3,1,2-nickeladicarbadodecaborane [1057].

Reaction of $[NiCp_2]$ with $[Bu_4N]_2[B_6H_6]$ gave the stable, isolable species $[Bu_4N][CpNiB_6H_6]$, formed in a new example of polyhedron expansion. The product adopts *closo*-geometry in a pentagonal bipyramid with the nickel atoms in the equatorial position [1058]. With $Na[4\text{-}CB_8H_{13}]$ and $[NiCp_2]$ at 130-140 °C the initial product was the unstable $[6\text{-}(\eta^5\text{-}Cp)Ni(\eta^5\text{-}1\text{-}CB_8H_9)]$, which was converted on standing to $[10\text{-}\eta^5\text{-}(Cp)Ni\text{-}\eta^4\text{-}1\text{-}CB_8H_9]$, which adopts a *closo*-geometry [1059].

Thermolysis of $[(\sigma\text{-}HCB_{10}H_{10}CCOO)_2Ni(bipy)]$ gave $[(\sigma\text{-}HCB_{10}H_{10}C)_2Ni(bipy)]$, which had previously been prepared. Further thermolysis gave 590 [1060].



⊘Ni, ●CH, ○ BH

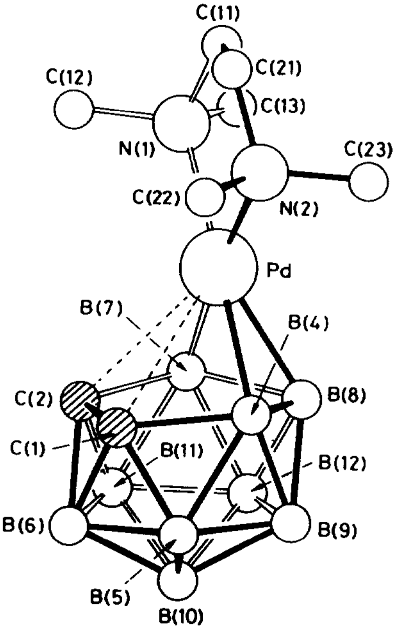
590 (Reproduced with permission from [1060].

Reaction of $[PdCl_2(tmeda)]$ with $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ gave $[3\text{-}tmeda\text{-}3,1,2\text{-}PdC_2B_9H_{11}]$, 591, shown in a diffraction study to have a slipped structure. The tmeda could be displaced by PMe_3 to give 592, which was shown both in a diffraction study and by ^{11}B nmr spectroscopy, to have a more symmetric structure. The distortions were thought to be caused by electronic effects [1061].

The anion $[6,9\text{-}C_2B_8H_{10}]^{2-}$ was allowed to react with each of $[PtCl_2L_2]$ and $[NiCl_2(dach)]$ to give *nido*-$[\mu\text{-}6,9\text{-}ML_2\text{-}6,9\text{-}C_2B_8H_{10}]$, in which the metal bridges the carbon atoms. The data provided on the products were limited [1062]. The structures of $[9\text{-}(Ph_3P)_2Pt\text{-}6\text{-}CB_8H_{12}]$ and $[9\text{-}(PPh_3)_2Pt\text{-}6\text{-}SB_8H_{12}]$ were elucidated [1063]. Thermolysis of $[9\text{-}(Ph_3P)_2Pt\text{-}6\text{-}CB_8H_{12}]$ was also studied, and the products characterised [1064]. The complex $[3,3'\text{-}Pt(1,2\text{-}C_2B_9H_{11})_2]$, was characterised in an X-ray diffraction study, and has been used as a catalyst for alkene hydrosilylation [1065].

13 CATALYSIS BY METAL COMPLEXES

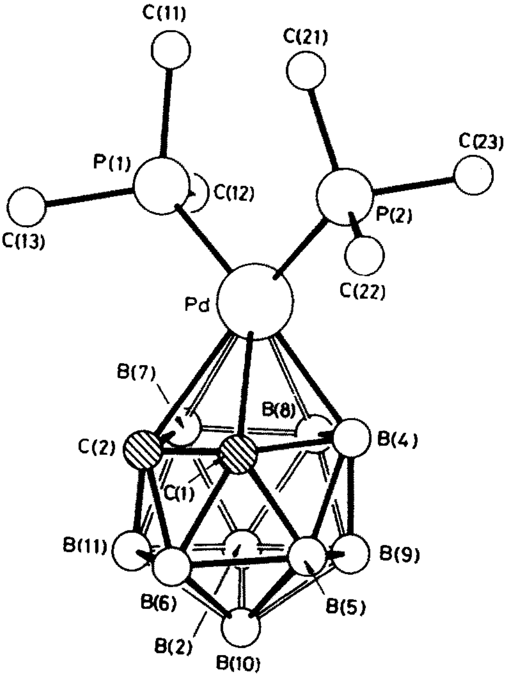
There have been a number of reviews dealing with the uses of complexes of metals of the nickel triad in organic synthesis. These have included an account of carbon-carbon bond forming reactions and functional group preparations [1066], hydroformylation, hydrogenation and oxidation [1067], and applications in the chemical industry [1068]. Catalysis by complexes containing a palladium-palladium bond has been discussed [1069], as have some uses of palladium and platinum complexes of pyridine monocarboxylic acids [1070]. A review of reactions of epoxides has included a discussion of the various ring opening reactions catalysed by palladium complexes [1071], and the preparation of oxygen and nitrogen containing heterocycles *via* palladium catalysed reactions of organomercury compounds has been discussed [1072]. The HSAB theory has been applied to homogeneous catalysis involving nickel, palladium and platinum complexes [1073].



591 Molecular structure of [3-tmeda-3,1,2-$PdC_2B_9H_{11}$], hydrogen atoms being omitted. (Reproduced with permission from [1061])

13.1 Hydrogenation and Hydrogenolysis

Criteria have been developed for distinguishing homogeneous and heterogeneous catalysis based on the observation that whilst monomers are generally reduced by either, polymers are reduced only by homogeneous catalysts. It was established that the catalyst produced from Ni(2-ethylhexanoate)$_n$ and Na[BH_4] definitely contains dispersed metal, and is comparable with supported metal catalysts [1074]. In the catalyst derived from nickel napththenate and Et_3Al the effect of dilution was to increase the rate, probably due to the deaggregation of less active polynuclear complexes [1075].

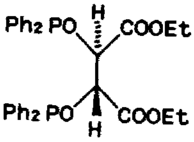


592 Molecular structure of [3-$(PMe_3)_2$-3,1-2-$PdC_2B_9H_{11}$], hydrogen atoms being omitted. (Reproduced with permission from [1061])

The hydrogenation of dicyclopentadiene has been reported in the presence of a catalyst derived from $NiCl_2$ and Na[BH_4] [1076]. $NiCl_2$ was chemically bonded to silica and then converted to NiH_x to give a stable and finely divided catalyst. The catalytic activity for the reduction of linear and cyclic dienes was a maximum when the bound $NiCl_2$ was reduced with two molar equivalents of Li[AlH_4] [1077]. The hydrogenation reactions of phenylethene, 2-phenylpropene and 2-pentene were investigated in the presence of [MeC{$Co(CO)_3$}(NiCp){$MoCp(CO)_2$}], but activity was low [1078].

The enantioselective hydrogenation of E-ethyl 2-methyl-2-butenoate was achieved using the catalyst system [Ni(DIOP)Cl_2]/2Et_3N, but optical yields were low [1079]. A copolymer containing 593 was treated with $NiCl_2$ and used in the asymmetric hydrogenation of acetamidocinnamic acid [1080].

Changes in catalysts derived from nickel stearate during the hydrogenation of vegetable oil have been investigated [1081]. Hydrogenation of a mixture of Z,E,E- and E,E,E-cdt over [$NiI_2(PPh_3)_2$] was more than 95 % selective for the monoene [1082]. Hydrogenation of a block butadiene/styrene rubber was accomplished using [$Ni(acac)_2$] as the catalyst [1083].



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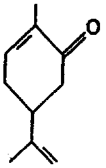
Cyclopentadiene was selectively reduced to cyclopentene in the presence of [Ni(acac)$_2$]/Et$_3$Al/py [1084]. Disproportionation of 1,3-cyclohexadiene in the presence of [Ni(acac)$_2$]/dibalH at 20 °C gave a mixture of cyclohexene and benzene, but at 80 °C gave benzene and cyclohexane [1085].

A supported catalyst derived from NiBr$_2$ on polyethyne was used for the hydrogenation of phenylethyne to phenylethene and ethylbenzene. At low loading, selectivity for phenylethene was reasonable [1086]. The use of a range of nickel complexes as catalysts for the reduction of arenes and heteroarenes has been reviewed [1087].

The use of palladium clusters in the catalysis of hydrogen transfer reactions has been reviewed [1088]. Catalysts for the reduction of 1-hexene, phenylethyne or 1,3-pentadiene included [{(PhP)$_2$Pd$_5$}$_n$]. The effect of sulphur compounds on the reaction rate was studied [1089]. Reduction of the conjugated double bond in 594 was accomplished using Bu$_3$SnH/CF$_3$SO$_3$SnBu$_3$/[PdCl$_2$(PPh$_3$)$_2$]. A radical mechanism was proposed [1090].



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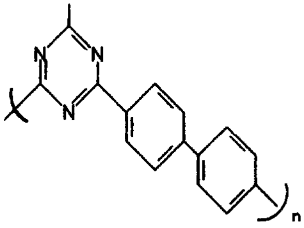
A number of polymer supported palladium complexes have been used as catalysts for alkene reduction. Catalysts were prepared from reaction of PdCl$_2$ with polyvinylpyrrolidone and Et$_3$N [1091] and PdCl$_2$ with 595 [1092], but details of the reactions actually catalysed were limited. Selective alkene hydrogenation was reported with palladium complexes of polymeric bipyridines [1093], and Pd(OCOMe)$_2$, anchored to polystyryl bipyridine, catalysed alkene reduction under 1 atm of hydrogen, with little isomerisation. Treatment with Li[AlH$_4$] gave a catalyst which caused extensive alkene isomerisation [1094]. The grafting of PdCl$_2$ with a tertiary amine onto microporous zeolites, macroporous zeolites and macroporous adsorbants has been studied. Preactivation of the grafted catalysts enhanced the rate of hydrocarbon reduction [1095].



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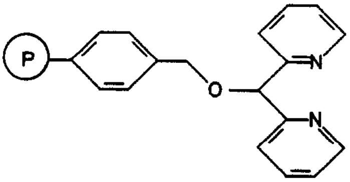
Reaction of [Pd(PPh$_3$)$_4$] with chloromethylated crosslinked polystyrene gave a supported palladium(II) complex, which proved to be an active catalyst for hydrogenation of alkenes and alkynes [1096]. Catalysts of reduced and unreduced palladium chloride with hydrazine hydrate deposited on polyaminochloroquinones or polyaminochlorohydroquinones were prepared and used for reduction of phenylethene to ethyl benzene. IR spectroscopy of the catalyst indicated the presence of Pd-N and Pd-Cl bonds [1097]. The polymer 596 was prepared and reacted with Pd(OCOMe)$_2$ to give a catalyst which was useful for the reduction of alkenes and alkynes. With 1-octene as the substrate there was also some competing alkene isomerisation. The observation that there was an induction period suggested that the palladium(II) underwent reduction to palladium(0) prior to catalysis [1098]. Catalysts prepared from reaction of palladium(II) with poly-4-ethenylpyridine or poly-2-ethenylpyridine could be used in the presence or absence of Na[BH$_4$] for the reduction of 2-propenyl-1-ol [1099,1100].



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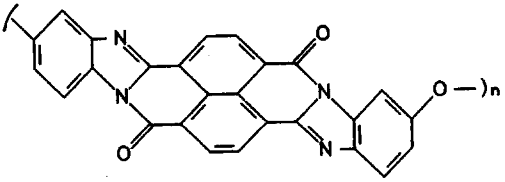
A catalyst system was prepared by impregnating 597 with Na$_2$[PdCl$_4$], and reducing the product, to obtain a material containing palladium clusters about 35±10 Å across. This was useful for reduction and isomerisation of alkenes [1101]. The hydrogenation and isomerisation of 3-phenyl-1-propene was investigated in the presence of a range of palladium complexes of amine modified silicas [1102].



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The catalyst system $PdCl_2/RNH_2/i\text{-}Bu_2AlH$ on a mineral support proved to be useful for the selective reduction of dienes or alkynes to alkenes [1103]. A related homogeneous system was also investigated [1104]. Crosslinked polystyrene functionalised with $[Pd(bipy)Cl_2]$ was used as a catalyst for the selective reduction of 1,5-cyclooctadiene [1105].

The hydrogenation of soybean oil in the presence of $[Pd(acac)_2]$ at 60-170 ^{o}C, and 150 psi of H_2, with 1-60 ppm palladium has been studied. The best selectivity for linolenate was obtained in the temperature range 80-120 ^{o}C. Addition of Et_3Al allowed an increase of the rate at low temperature [1106]. *In situ* modification of lipids in a chloroplast membrane was accomplished using a homogeneous water soluble catalyst, $[Pd(QS)_2]$, in which QS is a sulphonated alizarine incorporated into the thykaloids of isolated chloroplasts. Polyunsaturated acids were reduced more rapidly than the monounsaturated compounds [1107]. Homogeneous and heterogeneous palladium catalysts for the reduction of methyl 2,4-pentadienoate have been compared. $[Pd(acac)_2]$ is a better catalyst than Pd/C, and gives mainly methyl 2-pentenoate [1108].

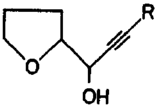
Reduction of 1,4-cyclohexadiene in the presence of polyethyleneimine/$PdCl_2$ gave mainly cyclohexane together with some benzene [1109]. However, 1,3-cyclohexadiene was a better substrate with this system [1110].

Palladium complexes of primary amines were active catalysts for reduction of ethyne to ethene with 98-99 % selectivity. 1-Alkenes were isomerised to internal alkenes, which are not reduced. The nature of the starting palladium salt was not critical, and activity was largely governed by the reducing agent [1111]. Selective reduction of alkynes to *cis*-alkenes was accomplished in the presence of $PdCl_2/Na[BH_4]$/polyethylene glycol/CH_2Cl_2 [1112].

Reaction of $[Pd(dba)_2]$ with phenylethyne gave a complex $[Pd_n(PhC{\equiv}CH)_{n-1}]$ (n = 4 or 5), which catalysed the reduction of phenylethyne to phenylethene. Kinetic studies showed that the rate controlling step was the interaction of molecular hydrogen with the coordinated alkyne [1113]. There has been a kinetic study on the reduction of phenylethyne in the presence of

$[Pd(acac)_2]/PPh_3$, and a reaction mechanism was proposed [1114].

Catalysts prepared by supporting $PdCl_2/R_3N$ on an inorganic oxide have been used as catalysts for the selective reduction of alkynes to *cis*-alkenes [1115]. Substrates discussed in detail have included diaryl alkynes [1116,1117], dialkyl alkynes [1118] and 598 [1119]. Layered zirconium phosphates were derivatised with allyl anthranilic acid and pyridine, and then treated with $K_2[PdCl_4]$ or $[PdCl_2(PhCN)_2]$ to give a catalyst which could be used for the selective reduction of alkynes to *cis*-alkenes, but also for reduction of arenes, alkenes, aryl nitro compounds and aryl nitriles. There is probably some reduction to metallic palladium with this system [1120]. The phosphinated polysaccharide 599 was reacted with $PdCl_2$ to give a catalyst with high activity for reduction of conjugated alkenes and allyl compounds. Phenylethyne was reduced to phenylethene with 95 % selectivity. The catalyst could be recycled twice with only 15 % loss of activity, and was also useful in promoting arene alkene coupling and butadiene telomerisation [1121].



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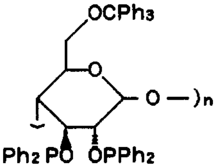

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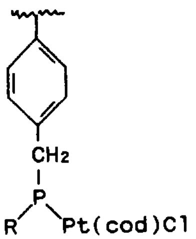
There has been an XPES study of the platinum complex of silica supported poly(γ-diphenylphosphinopropylsiloxane), which is a hydrogenation catalyst. The catalytic properties with repect to arene hydrogenation were affected by the P:Pt ratio and the amount of HCl present [1122]. This complex also catalysed the slow hydrogenolytic ring opening of the product cyclohexanes in some cases [1123]. The phosphinated polystyrene complex 600 was shown to catalyse the hydrogenation of benzene or toluene at 45 ^{o}C and 2 atm H_2. With D_2 the reaction was totally stereospecific, and it was shown that the metal was in the +2 oxidation state both before and after the reduction [1124]. Hydrogenation of linear diene dimers such as 601 and 602 in the presence of $H_2[PtCl_6]/SnCl_2$ gave up to 75 % 4-methylnonadienes [1125]. Several mixed metal complexes containing platinum, such as $[Co_2Pt(CO)_7(dppm)]$ could be used for hydrogenation of dienes and alkynes. They were also reactive in oligomerisation, hydroformylation and isomerisation [1126].



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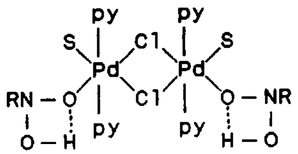
The other main class of compound reduced in the presence of palladium and platinum complxes has been nitroarenes. Complete reduction results in the formation of aniline derivatives, but in some cases the intermediates in the reaction may be readily isolated. Amongst the catalyst systems which are useful for the reduction of nitrobenzene to aniline were polybenzimidazole/Pd(0) (25 °C, 3 atm) [1127,1128], *trans*-$[PdCl_2L_2]$ (L = quinoline or isoquinoline [1129], or 3-aminocoumarin [1130]) or SiO_2 supported polyvinylpyrrolidone palladium complexes [1131]. Palladium(II) on a polyethylene imine composite was also useful in this context, methanoic acid being used as the hydrogen source [1132]. Reduction of 4-chloronitrobenzene proceeded without hydrogenolysis in the presence of a catalyst derived from the $Na[BH_4]$ reduction of palladium complexes of polymers such as polyvinylimidazole, polyvinylamine or polyacrylonitrile. Rates and yields were very much improved by the addition of a mole of anthroquinone per mole of palladium [1133]. The complex $[PdCl_2(PhCN)_2]$ and a supension of polyethylene were grafted onto polyvinylcarbazole, and the product was used as a catalyst for the reduction of 4-chloronitrobenzene [1134]. The complexes *trans*-$[Pd(py)_2X_2]$ (X = Cl, Br or I) have been used for the reduction of nitroarenes to anilines. An intermediate of stoicheiometry $[Pd_2Cl_2(EtOH)_2(PhNO_2H)_2(py)_4]$ was characterised, and the structure 603 proposed [1135]. Silica supported methacrylic acid palladium and platinum complexes were used for reduction of nitroarenes, alkenes, aldehydes and ketones [1136]. The supported complex 604 proved to be a very active catalyst with excellent lifetime and stability [1137]. Reaction of RCHO with $PhNO_2$ in the presence of molecular hydrogen and palladium(II) supported on an anion exchange resin gave $PhNHCH_2R$, *via* reductive amination of the aldehyde by the initially formed aniline [1138].



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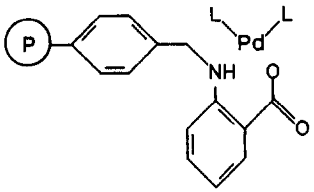
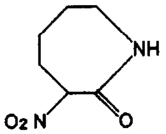


604

Reduction of the nitro group of **605** to the corresponding amine was accomplished with a reported 11 % enantiomer excess in the presence of a palladium complex of S-1-phenylethylamine. Presumably, the proton which is α both to the carbonyl and the nitro group is sufficiently labile that some kinetic resolution occurs [1137]. Hydrogenation of **606** in the presence of $PdCl_2/R_3N$ has been studied [1140].



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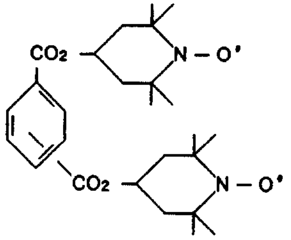
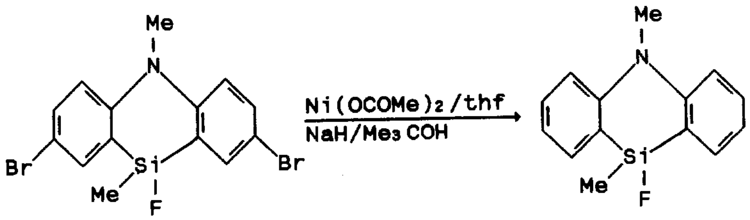


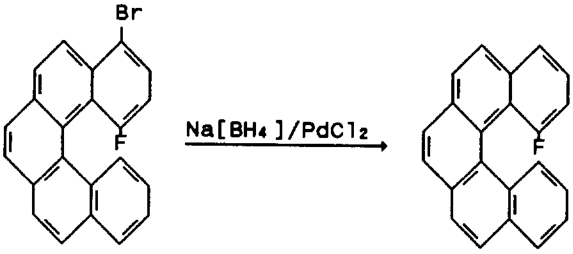
606

Reactions which may formally be classed as hydrogenolyses have been very diverse in their nature and mechanistic type. The cleavage of the C-Br bond in **607** was accomplished using sodium hydride, with $Ni(OCOMe)_2$ as the catalyst [1141].



607

Hydrogenolyses of aryl halides in the presence of palladium complexes have also been reported. In the reaction of **608** the source of hydrogen is the hydride ion, and the product was used in a helicene synthesis [1142]. Hydrogenolysis of 2-halopyridines was accomplished in the presence of $PdCl_2$ immobilised on silica modified by γ-aminopropyl groups. The reactions of the halopyridines were faster than those of related furan and thiophene derivatives [1143]. Formally speaking, hydride is the source of hydrogen in the hydrogenolysis of aryl halides by **609** in the presence of palladium ethanoate; carbonyl, nitro and alkene groups were unaffected [1144]. Transfer hydrogenolysis of aryl halides was accomplished using benzyl alcohol as the hydride source in the presence of $[PdCl_2(PPh_3)_2]$/phase transfer catalyst. The reaction mechansim was discussed in detail [1145]. Hydrogenolysis of $PhCO_2CH_2Ph$ by Et_3SiH in the presence of $PdCl_2/Et_3N$ gave $PhCO_2H$ [1146].



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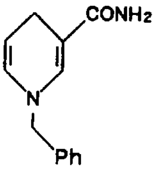
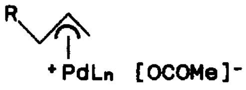


609

Hydrogenolyses of allyl derivatives in the presence of palladium complexes have also been widely reported. An electrolytic reaction involved the initial formation of a cationic allyl complex such as **610**, which was reduced to **611**, and reacted with electrophiles to give $RCH{=}CHCH_2E$ ($E = H^+$ or Me_3SiCl) [1147]. The effect of the leaving group in the allylic position in the reaction with $Pd(0)/Na[BH_4]$ has been discussed; the ethanoate group has many advantages [1148]. $Na[BH_3CN]$ was used as the source of hydride ion in the reaction of **612** [1149].



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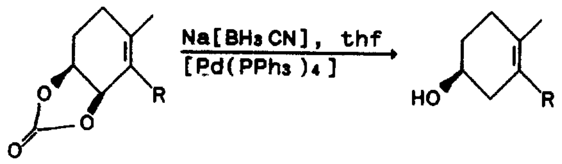
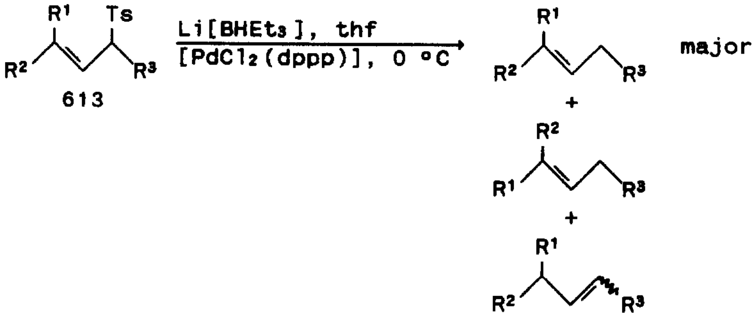
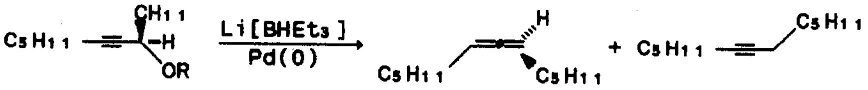


612

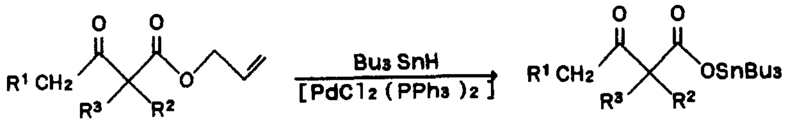
Hydrogenolysis of **613** was accomplished in the presence of $[PdCl_2(dppp)]$ and $Li[HBEt_3]$; the ratio of the products was determined by the substituents in the starting material [1150]. $Li[HBEt_3]$ was also used as the hydride source in the reaction of **614**; stereoselection was good for the mesylate, but poor for the phosphate [1151].





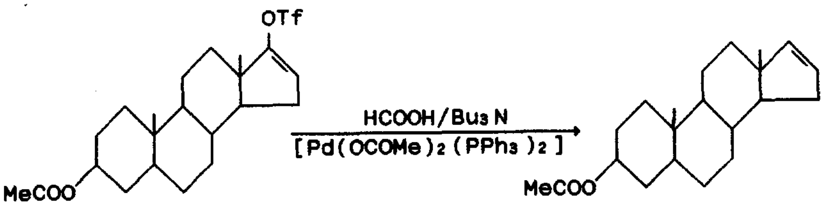
614

Tributyltin hydride acted as the hydride source in the palladium catalysed reaction of **615**. Thermolysis of the product was discussed [1152]. Methanoate anion was used as the source of hydrogen in other hydrogenolyses of allyl derivatives, yields being excellent when $[Pd(PBu_3)_n]$ was used as the catalyst [1153].



615

Hydrogenolysis of the enol triflate, 616, was accomplished using $HCOOH/Bu_3N$ in the presence of $[Pd(OCOMe)_2(PPh_3)_2]$. The enol triflate was prepared from the ketone, and it was noted that ethanoate esters, ketones and tertiary alcohols survived the procedure [1154]. Hydrogenolysis of 617 involved molecular hydrogen in the presence of $[PdCl_2(PPh_3)_2]/Et_3N$; a mechanism for the reaction involving oxidative addition of the carbon-chlorine bond to palladium(0) was proposed [1155]. Reaction of Me_2NCHO with $HSiR_nCl_{3-n}$ (R = Me or Et; n = 1 or 3) in the presence of $[NO]_2[PtCl_6]$ gave Me_3N and $Cl_{3-n}R_nSiOSiR_nCl_{3-n}$ [1156].



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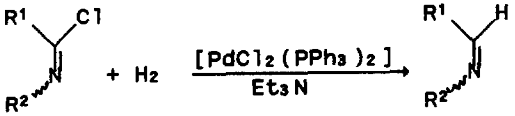


617

The complex $[Pd(PR_3)_n]$ (n = 3 or 4) has been shown to catalyse the H/D exchange between D_2O and organic molecules, at rates which are related, but not simply, to their pKa values. A mechanism was proposed for the reaction [1157].

There has been a kinetic study of H/D exchange and oxidation of alkenes in the presence of platinum complexes [1158]. The effect of halide ion concentration has been studied [1159]. Isotope exchange in $ArCH_2CH(NH_2)COOH$ in the presence of $K_2[PtCl_4]/D_2O$ has been studied, with the main exchange occurring in the aryl ring [1160]. Deuteration of the aryl ring was also noted for $PhCH(NH_2)COOH$ [1161].

13.2 Oxidation

There have been reviews of palladium catalysed oxidation of alkenes to ketones [1162], and of the uses of supported platinum complexes for the dehydrogenation of higher alkanes [1163]. Palladium catalysed reactions were included in a general review of epoxidation methods [1164].

Oxidation of ethene to ethanal has been accomplished using $PdCl_2/CuCl/MeCN/hmpt/O_2$ [1165], and to a mixture of ethane 1,2-diol mono and diethanoates using $PdCl_2/CuCl_2/Cu(OCOMe)_2.MeCOOH/LiCl/O_2$ [1166,1167]. The composition of the copper complexes involved in the catalytic cycle has been studied [1168].

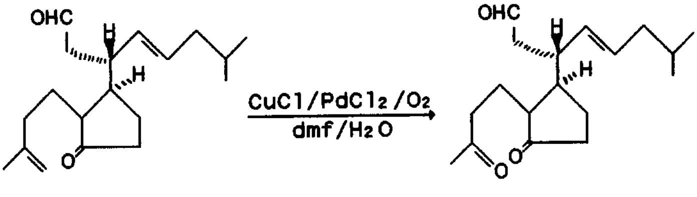
The oxidation of 1-alkenes to methylketones, under a range of conditions, has again found wide use in synthesis. The patent literature has reported oxidation of 1-decene using $O_2/PdCl_2/CuCl_2/H_2O$/sulpholane [1169], or $O_2/PdCl_2/CuCl_2/[RNMe_3]Cl/H_2O/C_6H_6$ [1170], 1-butene with $O_2/PdCl_2/H[PMo_6V_6O_{40}]/[RNMe_3]Br/H_2O$/decane [1171] or with added perfluorodecalin [1172]. A mixture of 1- and 2-butene was oxidised to give 2-butanone as the major product [1173]. Pure E-2-butene yielded 2-butanone in low conversion, but with excellent selectivity in the presence of $O_2/PdCl_2/CuCl_2/H_2O$/*N*-methylpyrrolidone [1174]. Propene or 1-hexene were oxidised using $O_2/PdCl_2/CuCl_2/CuCl/MeCOOH/Zn(OCOMe)_2/H_2O$ [1175]. In one case nitro compounds were used as the oxidant [1176]. A Wacker type catalyst containing palladium, a heteropolyacid and surfactant was recycled by removing the organic phase, and removing water from the aqueous phase until a solid was obtained. Water was added to the solid, and the catalyst solution could then be reused [1177].

A reliable procedure has been described for the oxidation of 1-decene to 2-decanone in the presence of $PdCl_2/CuCl$ [1178]. The presence of an ester group in $CH_2{=}CH(CH_2)_8COOCMe_3$ was tolerated in its oxidation to $CH_3CO(CH_2)_8COOCMe_3$ [1179]. The use of PEG-400 as a phase transfer catalyst in these reactions has been reported; the products were mostly 2-alkanones, but some others resulted from isomerisation of the starting material followed by oxidation [1180]. An electrochemical reaction was reported in the presence of $[PdCl_4]^{2-}$; the reoxidation of the palladium is accomplished electrochemically using the Fe(III)/Fe(II) couple as a transfer agent [1181]. The use of HPA's as oxidants in the Wacker system has been discussed. The system

$Pd[SO_4]/H_3PMo_6W_6O_4$ was found to be the most useful for the oxidation of cycloalkenes, with the yield increasing with the size of the ring [1182]. All the HPA's were effective for the palladium reoxidation, but varied in their ability to be reoxidised by molecular oxygen [1183]. Oxidation of 1-butene to 2-butanone, butane-2,3-dione and ethanal was achieved in the presence of $PdSO_4/VOSO_4/H_2O/C$ [1184]. When $PhOCH_2CH{=}CH_2$ was reacted with $MeOH/PdCl_2/MeONO$, the product was the acetal $PhOCH_2C(OMe)_2CH_3$ [1185].

Three patents have reported the oxidation of cyclopentene to cyclopentanone, the systems used being $O_2/PdCl_2/Me_3COH$ [1186], $O_2/[PdCl_2(MeCONR_2)_2]/ROH/25$ °C [1187] and $O_2/PdCl_2/CuCl_2$ [1188]. Oxidation of 1-undecene-5-one under the usual Wacker conditions gave 2,5-undecanedione, used in a jasmone synthesis [1189]. The regiochemistry of the reaction with internal alkenes has been studied with a wide range of substrates [1190].

Further applications of this reaction in steroid synthesis have been described [1191], including reaction (31) [1192]. Synthetic approaches using this route have been described for 4-oxopentanals and 5-oxohexanals [1193]. Oxidation of **618** was the last step in a synthesis of brevicomin [1194]. The oxidation of **619** was a key step in a recent synthesis of vetispirene [1195]. In the oxidation of **620** ($R = SiMe_2CMe_3$), the oxidant, unusually, was an alkyl hydroperoxide [1196].



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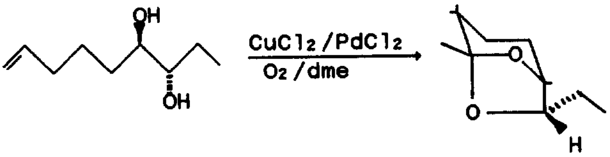
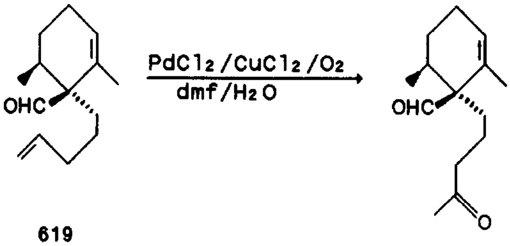


618

Three papers have discussed in detail the palladium catalysed oxidation of 2-propene-1-ol. A kinetic study in the presence of $PdCl_2$ and $Cu(OCOMe)_2$ showed a reaction first order in the alcohol, zero order in copper, and of order −1 in $[Cl^-]$ [1197]. In a study of the reaction of the 2,2-dideutero substituted compound, a new and unexpected mode of hydroxypalladation was reported in solution. The two processes have different rate expressions, and in the new pathway external water attacks the coordinated alkene. The evidence is that this hydroxypalladation, and not the normal reaction, is the one leading to 2-chloroethanol in the oxidation of ethene in the presence of $CuCl_2$ and a high chloride ion concentration [1198]. Detailed product studies were also undertaken, and routes for the formation of all the minor products proposed [1199].



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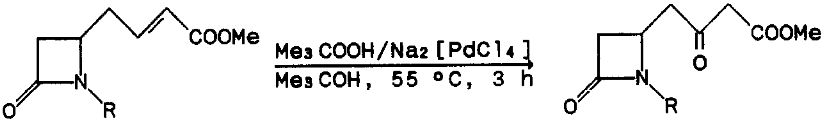
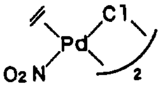


620

There have been a number of studies of oxidations in the presence of palladium nitro complexes. In the presence of $[PdCl(MeCN)_2(NO_2)]$, norbornene was oxidised by molecular oxygen to give the epoxide [1200]. When terminal alkenes were reacted with $[Pd(MeCN)_2(NO_2)_2]$ the major products were 2-nitroalkenes. The reaction is limited to terminal alkenes, with internal alkenes giving ketonic products. Reactions with cyclic and strained alkenes were also studied [1201]. The reaction of ethene with *cis*-$[PdCl(MeCN)_2(NO_2)]$ gave 621 as the initial product. More slowly this was transformed to 622, which decomposed to give oxidised products and $\{(Pd(NO)Cl)_n\}$. The palladium complex is able to oxidise alkenes both stoicheiometrically and catalytically to give mixtures of ketones, epoxides and allylic alcohols. ^{18}O-labelleing studies showed that the oxygen derived from the NO_2 group, and not from added oxygen by Wacker chemistry. The most likely route was considered to be intramolecular attack of the nitro group on the coordinated alkene [1202]. The related complex $[\{PdCl(cyclooctene)(NO_2)\}_2]$ was characterised, and the structure of 623 established in a diffraction study [1203]. The mechanism of oxygen transfer from the nitro group was compared in reactions using palladium complexes alone, and those with a bimetallic cobalt/palladium catalyst system [1204].



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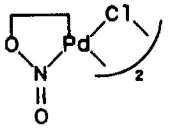

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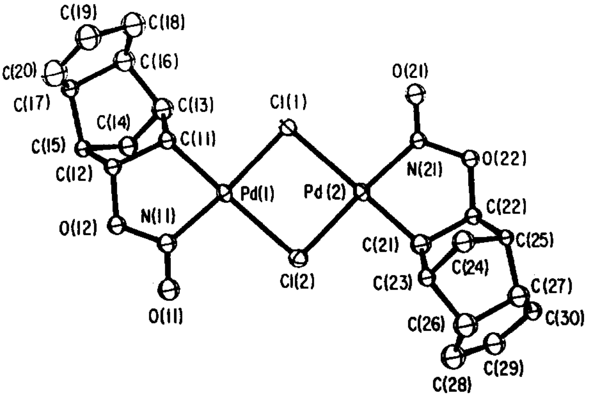
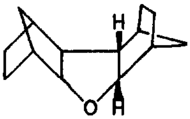


623 (Reproduced with permission from [1203])

It has been shown that strained alkenes are selectively epoxidised by O_2 in the presence of $[PdCl(RCN)_2(NO_2)]$. A mechanism was proposed for the reaction, and side products were accounted for [1205]. The reaction of norbornene was studied in detail. At low norbornene concentration the epoxide was formed with very high selectivity, but at higher substrate concentration the main product was 624. It was concluded that there were two competing catalytic cycles which had the common intermediate 625 [1206]. There has been a study of the oxidation of 1-alkenes to 1,2-diol monoethanoates using $O_2/[PdCl(MeCN)_2(NO_2)]/MeCOOH$. An ^{18}O labelling study showed that there was transfer of oxygen from the NO_2 only into the ethanoate. Mechanisms were proposed for the formation of all the products, and the catalytic system was compared with the bimetallic Pd/Co system [1207].

Epoxidation of alkenes was catalysed by 626 using dilute H_2O_2 as the oxidant. Selectivity was excellent [1208,1209].



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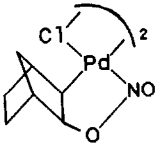

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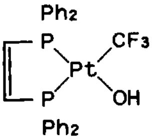
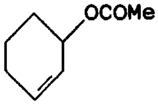


626

Oxidation of cyclohexene in the allylic position, giving **627**, was accomplished in the presence of Pd(OCOMe)$_2$/MnO$_2$/CH$_3$COOH/benzoquinone in excellent selectivity. Other cycloalkenes proved to be less useful substrates, and the reaction mechanism was not definitively established [1210]. Allyic oxidation of geranyl ethanoate, **628**, in the presence of Pd(OCOCF$_3$)$_2$/CH$_3$COOH/MeOC$_6$H$_4$-2-COMe/benzoquinone gave **629** which was used in syntheses of helminthogemacrene and *β*-elemene [1211]. Allylic oxidation of cycloalkenes to cycloalkenols occurred in air in the presence of *cis*-[PdCl(MeCN)$_2$(NO)$_2$]. Other alkenes gave epoxides, ketones or enones, and the selectivity could be rationalised in terms of the ease of *β*-hydride elimination from the intermediates of type **622** [1212]. Allylic oxidation of α-pinene to give verbenone as the major product, together with some verbenol, was catalysed by PdCl$_2$/CuCl$_2$/LiCl/H$^+$ [1213].



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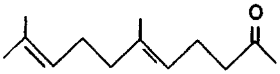

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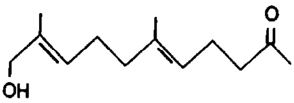
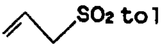


629

A number of other oxidations of alkenes have been reported. Oxidation of decene in the presence of {Pd(PPh$_3$)$_2$} (*sic*), Pd(OCOMe)$_2$ or [Pd(CNS)$_2$(PPh$_3$)$_2$] was reported to yield 1-decene-2-one as the major product, *via* a decene palladium complex [1214]. Treatment of **630** with O$_2$/Pd(OCOCF$_3$)$_2$/Me$_2$CO/hν gave **631** which was also obtained by palladium catalysed isomerisation of the Z-isomer. Reaction of **630** with PdCl$_2$/CuCl$_2$/NaCl/Na[OCOMe] gave **632**. A mechanism involving a hydroperoxide intermediate was proposed [1215].



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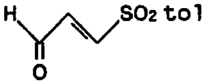

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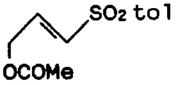
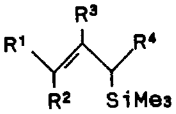


632

Reaction of 633 with oxygen in the presence of palladium(II) under photolytic conditions gave 634. Yields were low when R^1-R^4 = H, but much better when R^4 = OTs [1216]. Reaction of 635 with $[Pd(PPh_3)_4]$/636 gave 637, generally with good regio and stereoselectivity [1217]. Arylalkenes could be oxidised to methyl ketones by 638 in the presence of palladium ethanoate. A hydroperoxide palladium alkene complex was invoked as an intermediate [1218].



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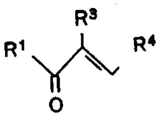

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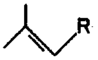

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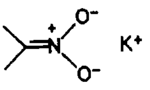

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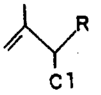

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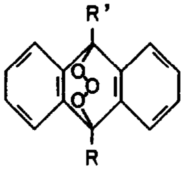
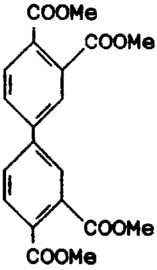


638

In the presence of palladium ethanoate supported on oligo-4-phenyleneterphthalamide, Z-alkenes were converted to alkynes with excellent selectivity, when the reaction solvent was $EtOH/H_2O/H[ClO_4]$, but in dioxan the main products were ketones [1219]. Reaction of 1-alkenes, $RCH{=}CH_2$, with $CO/O_2/HOCH_2CH_2OH$ in the presence of $PdCL_2/CuCl_2/HCl$/25 °C/1 atm gave $RCH(Me)CO_2(CH_2)_nOH$ as the major product, as well as some isomers [1220]. When 1-hexene was treated with the species prepared from $Pd(OCOMe)_2$ and Me_3COOH, the main products were 2-hexanone and 2-ethanoato-1-hexene. The reaction mechanism was assumed to involve insertion of an alkene into {PdOOR} or {PdOCOMe} followed by a β-hydride shift, or β-hydride elimination [1221].

There have been a number of studies of the oxidation of alkylarenes. Using molecular oxygen as the oxidant and $K_2[Pd(OCOMe)_4]$ as the catalyst, toluene was oxidised in RCOOH to $PhCH_2OCOR$ [1222]. The same type of reaction occurred using $Pd(OCOMe)_2/Na[OCOMe]/Cu(OCOMe)_2$/active carbon [1223]. A kinetic study of the reaction in the presence of $Pd(OCOMe)_2/Sn(OCOMe)_2/K[OCOMe]$ showed that there were three distinct kinetic regions, with the deposition of palladium metal at the end of the second phase, with the metal also acting as a catalyst [1224].

The oxidation of toluene to biaryls and diarylmethanes, using palladium(II) in CF_3COOH, has been reinvestigated. There is evidence that the reaction proceeds *via* an SET pathway, rather than the traditionally invoked two-electron route. Radical intermediates were detected by EPR spectroscopy [1225]. In a study of the related reactions of xylenes, it was suggested that whilst the reaction of the 1,2-isomer was essentially an electrophilic substitution, SET and radical intermediates were important for the reactions of 1,4-dimethylbenzene [1226]. Oxidative coupling of PhR (R = H, Me, Et, Cl or OMe) was accomplished using stoicheiometric $Tl(OCOCF_3)_3$, and $Pd(OCOMe)_2$ as the catalyst [1227]. A low yield of **639** was obtained from oxidative coupling of dimethyl benzene 1,2-dicarboxylate using $[Pd(NO_2)_2(phen)]/Cu(OCOMe)_2/H_2O$/air [1228].



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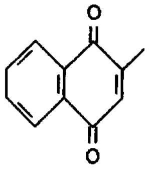
2-Methylnaphthalene was oxidised to **640** by hydrogen peroxide in the presence of palladium(II) supported on a polystyrene sulphonic acid resin. The catalyst could be recovered and reused [1229]. Diphenyl ether was converted to dibenzofuran by molecular oxygen in the presence of $Pd(OCOMe)_2/RCOOH$ [1230].

Catalytic oxidation of methane by molecular oxygen in solutions of platinum salts and heteropolyacids has been reported, but details were lacking [1231]. Nickel(II) was bound to Amberlite 15 by ion exchange, and was used to catalyse oxidation of 1-methylethyl benzene by molecular oxygen, initially to 2-phenyl-2-propanol, which was further converted to phenol and propanone [1232]. Chloroethane was oxidised by molecular oxygen in the presence of $PdCl_2/SiO_2$ to give ethanoic acid, with excellent conversion [1233].



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Oxidation of primary and secondary alcohols has been reported using $PdCl_2/CCl_4/K_2[CO_3]$; the tetrachloromethane acts as the oxidant. Both aldehydes and esters were obtained from primary alcohols. Reactions of allylic alcohols resulted both in oxidation of the alcohol and addition to the double bond. The reaction mechanism was discussed in detail [1234]. Oxidation of secondary alcohols to ketones by molecular oxygen has been reported in the presence of $Pd(OCOMe)_2/Na[HCO_3]/[Bu_4N]Cl/PhI/dmf$ [1235].

The dehydrogenation of methanol to CO and H_2 has been reported to occur in the presence of $H_2[PtCl_6]/CeO_2/Al_2O_3/[NH_4]_2[S_2O_3]$ [1236]. In the presence of $[Pd_2Cl_2(dppm)_2]$ a photochemical reaction gave more mixed products, including CH_2O, $CH_2(OMe)_2$, $HOCH_2CH_2OH$, Me_2CHOH, $Me_2C(OH)CH_2OH$ and $CH_3CH(OH)CH(OH)CH_3$ [1237].

Palladium induced dehydrogenations of cyclopentanones have been used in syntheses of coriolin [1238], hirsutic acid C [1239] and related compounds [1240].

There have been a number of reports of palladium catalysed oxidations of carbon monoxide. In the presence of aquo complexes of palladium(II) and vanadium(V) or iron(III), and heteropolyacids, CO_2 was formed. The reaction kinetics were investigated, and a mechanism proposed [1241-1243]. Supported palladium complexes have also been used as catalysts [1244]. Cerium(IV) and chromium(VI) have also been used as oxidants [1245], as have benzoquinone [1246], and $[S_2O_8]^{2-}$ [1247]. In the reaction in the presence of $Pd(II)/Fe(III)/Na[NO_2]$ together with chloride or bromide, the rate is better with bromide salts [1248].

The oxidation of CO by O_2 over [NiPc] has been studied. A dual site mechanism with a bridging $\{CO_3\}^-$(*sic*) as the intermediate has been proposed [1249]. A catalytic cycle has been proposed for the reaction in the presence of $[NiL_2X_2]$ [1250]. When $PdCl_2/LiCl$/benzoquinone/ROH was used as the catalyst, the product was that of oxidative coupling, ROOCCOOR. The reaction mechanism was discussed, and an alternative pathway discerned in the presence of palladium(I) [1251].

13.3 Reactions of Carbon Monoxide and Carbon Dioxide

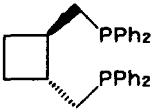
The use of transition metal complexes to catalyse hydrogenation of CO or CO_2 to hydrocarbons has been reviewed [1252].

Several patents have reported catalysts for the hydrogenation of CO with molecular hydrogen to give alcohols. In the presence of $[Ru_3(CO)_{12}]/K_2[PtCl_4]/SnCl_2/[C_7H_{15}PPh_3]Br$ the main product was ethanol, with traces of methanol, propanol, ethanoic acid and ethanaote esters [1253], whilst with a polyethenylpyrrolidone platinum complex together with [Fe(TPP)] and 1,2-dimethylimidazole the main product was methanol, although conversion was low [1254]. Methanol and ethanol were obtained in comparable quantities in the presence of nickel complexes such as $NiCl_2$, $[NiCp_2]$ or $[Ni(acac)_2]$ [1255], but with the system $RhCl_3/NiCl_2/TiCl_4$, ethanol was the main product, with fair selectivity [1256]. Preparation of higher alcohols from CO/H_2 in the presence of silica supported palladium or nickel catalysts has been reviewed [1257].

The uses of the water gas shift reaction in tandem with platinum catalysed hydroformylation reactions have been reviewed [1258]. The complexes $[NiCl_2L_2]$ were shown to catalyse the WGSR at temperatures above 90 °C [1259]. The catalysis of the WGSR by $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ has been studied. The active species is the neutral dihydroxy species $[Pd_2(\mu\text{-dmpm})_2(OH)_2]$; this is carbonylated to a μ-CO derivative, and then CO is inserted into the metal oxygen bonds. Some IR spectrsocopic data for the intermediates were presented [1260].

Reports of hydroformylation catalysts continue to be published. From the patent literature systems reported to be useful for the reaction of propene include $[Pt(PPh_3)_4]/SnCl_4/1,4\text{-}Me_2C_6H_4$ [1261] and $[Pt(acac)_2]/dppf/SnCl_2$ [1262]. Palladium exchanged silica catalysts showed excellent activity for the conversion of ethene to ethanal, at 1 atm pressure and room temperature [1263].

A number of patents have also reported enantioselective hydroformylations in the presence of chiral phosphines. For example, in the presence of $[Pt(641)Cl_2]$ propene was converted predominently to the linear product [1264,1265]. C_4-Aldehydes were also obtained using $[Pt(DIOP)_2]/PhSnCl_3$, again with good selectivity for linear products [1266]. The hydroformylation of a range of alkenes using $[PtCl(DIOP)(SnCl_3)]$ has been reinvestigated. Both isomerisation and hydrogenation were shown to be competing reactions, and optical yield and regioselectivity were a function of conversion. The degree of asymmetric induction was shown to be determined before or during the formation of the metal alkyl intermediates [1267]. Hydroformylation of styrene using $[PtCl_2(DBPDIOP)]$ gave a product with 78 % ee, considerably better than with DIOP [1268]. Polymer supported versions of DIOP [1269] or BPPM [1270] were used with results similar to their homogeneous analogues. With $[Pt(CHIRAPHOS)Cl(SnCl_3)]$ as catalyst, and 1-butene as substrate, the best optical yield obtained was 40 %S, and most of the product was linear [1271].



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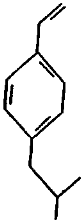
Hydrocarboxylations of alkenes have been widely reported. Reaction of ethene with $H_2/CO/H_2O$ in the presence of $NiI_2/[Mo(CO)_6]/LiI/EtI$ gave propanoic acid in good yield [1272]. Production of octanoic acid with 85 % selectivity from 1-heptene was accomplished in the presence of $[PdCl_2(PPh_3)_2]/SnCl_2$/dioxan/$H_2O/H_2/CO$ [1273]; the influence of solvent and added alkene has been investigated [1274]. High selectivity for the linear product was observed using a similar system and 1-nonene, especially in the presence of a small excess of PPh_3 [1275,1276]. Reaction of 642 in the presence of $[PdCl_2(PPh_3)_2]/3\text{-}ClC_6H_4CO_3H/CO/H_2/HCl$ gave 643 in enhanced yield and selectivity, relative to the reaction in the absence of the peracid [1277]. Palladium salts supported on anion exchange resins have been used as catalysts for conversion of 1-hexene to carboxylic acids [1278].



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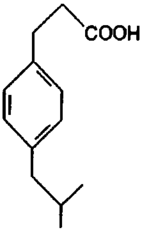

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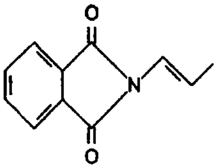
Reaction of ethene with CO and 1-butanol in the presence of $[PdCl_2(PPh_3)_2]/HSnCl_3$ gave butyl propanoate. A reaction mechanism and kinetic scheme were proposed [1279]. The rates of palladium catalysed carboxymethylation of ethene and higher alkenes increased when homogeneous or heterogeneous perfluoroalkene sulphonic acids were used as cocatalysts [1280]. Various patents have reported hydrocarboxylation reactions of 1-alkenes, with catalyst systems including $PdCl_2/CuCl_2/HCl$ [1281], $[Pd(PPh_3)_4]/PPh_3/CF_3SO_3H$ [1282] or $[PdCl_2(PPh_3)_2]/HCl$ [1283]. The reaction of 1-nonene in the presence of $[PdCl_2(PPh_3)_2]/ROH$ gave a mixture of linear and branched esters; the reaction yield increased with the size of R, but selectivities were unchanged. Some increase in selectivity could be obtained by the addition of propanone [1284]. Selectivity could also be increased by the addition of PPh_3 [1285]. When the added alcohol was a diol, $HO(CH_2)_nOH$, selective monoesterification and carbonylation of $RCH{=}CH_2$ gave $RCH(Me)(CH_2)_nOH$ as the predominent regioisomer [1286].

The reaction mechanism was probed by the preparation of *trans*-$[PtCl(COC_8H_{13})(PPh_3)_2]$, characterised in a diffraction study. The palladium-chlorine bond is long, due to the *trans*-effect of the acyl ligand [1287].

The hydrocarboxylation of an E/Z mixture of $MeSCH_2CH{=}CHOCOMe$ in the presence of $[PdCl_2(PPh_3)_2]$ gave a mixture of $MeSCH_2CH_2CH(OCOMe)COOMe$ (29 %) and $MeSCH_2CH_2CH(OCOMe)C({=}S)OMe$ [1288]. The hydrocarboxylation of $CH_2{=}CHCH_2COOEt$ using CO/EtOH in the presence of $[PdCl_2(PPh_3)_2]/PPh_3$ involves the ethanol acting as a hydrogen donor. More of the linear product was obtained in polar solvents or with extra PPh_3. The effects of conditions and additives on yield and selectivity was thoroughly investigated [1289].

The enantioselective hydrocarboxylation of ethenylbenzene and 2-phenylpropene has been studied in the presence of $[PdCl_2(PhCN)_2]$ and an added chiral ligand; dibenzophosphole derivatives generally gave the best enantiomer excesses, and addition of LiCl dramatically increased conversion without loss of enantioselectivity [1290]. Hydrocarboxylation reactions of **644** were also studied. Whilst regioselectivity was generally fair, enantioselectivities in the presence of DIOP and related chiral phosphines were low [1291].



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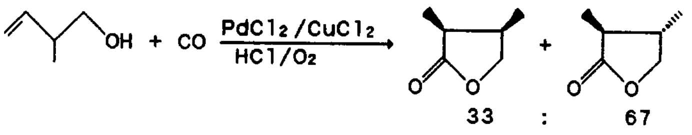
Related intramolecular hydrocarboxylation reactions have also been noted. The formation of six-membered rings was favoured over that of seven-membered ones, and the accessibility of five-membered rings was shown to depend on alkene geometry [1292]. Lactones were formed in reactions (32) and (33) under very mild conditions [1293,1294].



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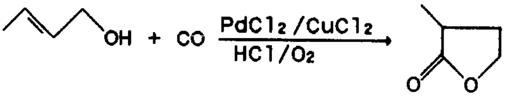
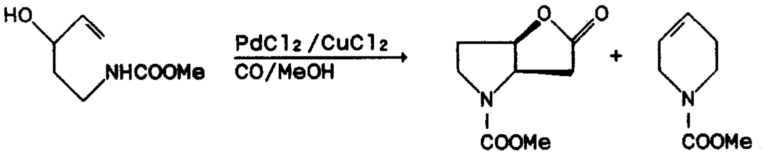


(33)

Reaction of **645** resulted in a double cyclisation to give **646** and **647** *via* an allyl palladium complex intermediate [1295]. With **648** (X = H) a double cyclisation gave **650** *via* **649** in the presence of $PdCl_2/CH_3COOH/Na[OCOCH_3]$, but for X = OCOMe, using $[Pd(PPh_3)_4]/Et_3N/thf$, palladium allyl chemistry dominated, resulting in elimination to **652** *via* **651** [1296].



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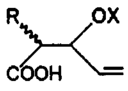

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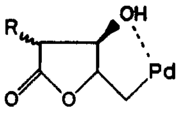

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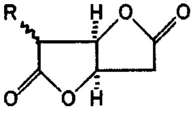

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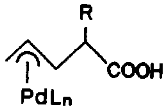

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652

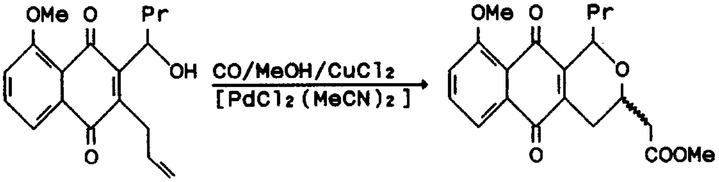
Hydrocarboxylation of phenyl ethyne in the presence of $PdCl_2$/thiourea gave a mixture of mono and dicarboxylated products, with Z-PhC(COOMe)=CHCOOMe as the major one. The best selectivity was accomplished using $PdCl_2/4tu/12dba$ [1297]. Ethyne was converted to E-BuOOCCH=CHCOOBu in the presence of $PdCl_2/FeCl_3/H_2SO_4/BuOH$; the reaction was though to involve an unstable palladium cluster [1298]. Reactions of 1-alkynes gave mixtures of E- and Z-RC(COOR')=CHCOOR', with the Z-isomer as the major product. Yields were generally good [1299].

Reaction of allene with CO/MeOH in the presence of $PdCl_2/CuCl_2/HCl/O_2$ gave $MeOCH_2C(=CH_2)COOMe$. Reactions of 1,1-disubstituted allenes, $R_2C=C=CH_2$ gave $R_2C(OMe)C(=CH_2)COOMe$, with good regioselection, but in poor yield [1300]. Butadiene, reacted with CO/H_2O in the presence of $PdCl_2/[Bu_4N]Cl/HCl$, gave mainly $E-CH_3CH=CHCH_2COOH$, together with small amounts of other addition products [1301].

A number of patents, mostly from Nissan Chemical industries, report the double alkoxycarbonylation of dicyclopentadiene to give 653 in the presence of $PdCl_2/CuCl_2/MeOH$ [1302-1306].

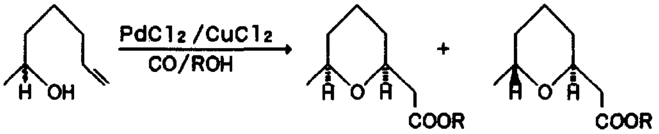
653

A hydrocarboxylation reaction was combined with an intramolecular nucleophilic attack in the conversion of 654 to 655 using CO/MeOH in the presence of $CuCl_2/[PdCl_2(MeCN)_2]$. The product was used in an approach to naphthaquinone antibiotics [1307]. A mixture of diastereoisomers was obtained on cyclisation of 656, but in both this and related cases one was generally strongly favoured [1308]. In the reaction of 657 the hydrocarboxylation is also an intramolcular reaction [1309].



654 655

Alkoxycarbonylation of bicyclo-[2.2.1]-heptadiene under oxidative conditions $(CO/MeOH/Na[OCOMe]/Pd(OCOMe)_2/CuCl_2)$ has been studied, and shown to be a complex reaction. Mixtures of 658, 659, 660 and 661 were obtained, their proportions depending on the exact reaction conditions. The major product was generally 658, but 659 was obtained in the absence of Na[OCOMe] [1310].



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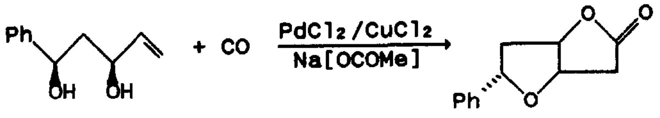

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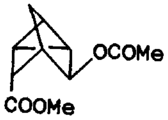

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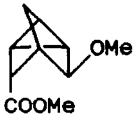

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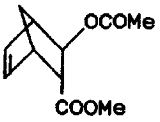

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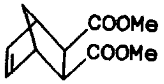
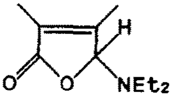


661

A radical reaction pathway was proposed for the reaction of 1-alkenes, $RCH{=}CH_2$, with CO and CCl_4 in the presence of $Pd(OCOMe)_2/PPh_3$, to give a mixture of $RCH(COOR)CH_2CCl_3$ and $RCHClCH_2CCl_3$. The proportion of the carboxylated product increased with the pressure of CO [1311].

The reaction of 2-butyne with CO/Et_2NH in the presence of $[NiBr_2(Et_2NH)_2]$ at 70 °C and 15 atm CO gave $CH_3C(CONEt_2){=}C(CONEt_2)CH_3$, but at higher temperature and lower CO pressure the main product was 662 [1312]. When 1-alkynes were used as the substrates the products included $RC{\equiv}CCONEt_2$, $RC(CONEt_2){=}CHCONEt_2$ and $Et_2NCOCONEt_2$, with the product selectivity being a function of temperature and the halide ion in the nickel catalyst. A mechanism was proposed for the reactions [1313].



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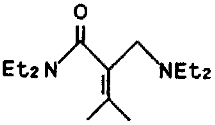
When 1,1-dimethylallene was reacted with CO/Et_2NH in the presence of [$Ni(Et_2NH)_2I_2$] the main products were 663 and 664; the mechanism proposed was complex [1314].



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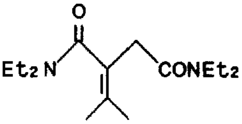


664

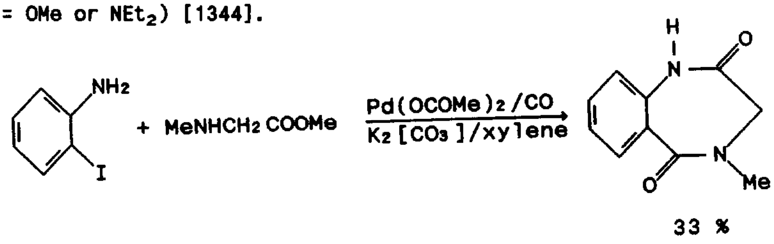
There have been numerous reports of the carbonylation of aryl halides in the presence of a range of additives. In the presence of a hydrogen donor, ArX may be carbonylated to ArCHO using [$Pd(PPh_3)_4$]/$(PhCH_2)_3N$, with the reactivity in the order X = I > Br > Cl [1315]. Poly(methylhydrosiloxane) has been used as the hydrogen donor [1316]. Using molecular hydrogen as the hydrogen source required the use of [$PdCl_2(PPh_3)_2$]/R_3N as the catalyst system [1317,1318].

Carbonylation in the presence of alcohols generally leads to the formation of carboxylate esters. The reaction has been reported for bromobenzene and phenol in the presence of [$PdBr_2(PPh_3)_2$]/PPh_3/Bu_3N [1319], and various heterocyclic halides in the presence of [$PdCl_2(PPh_3)_2$]/R_3N [1320-1322]. In a two-phase system, bromobenzene was converted to [PhCOO]Na with excellent selectivity [1323]. Reaction of iodobenzene with $CH_3CH_2CH(CH_3)CH_2OH$ in the presence of [$PdCl_2(PPh_3)_2$]/Et_3N/CO gave $CH_3CH_2CH(CH_3)CH_2OCOPh$ with 77 % selectivity [1324]. However, in some cases the outcome of the reaction has been shown to be strongly solvent dependent, giving rise to both mono and doubly carbonylated products, ArCOOR and ArCOCOOR [1325]. Using [$PdCl_2(PCy_3)_2$] as the catalyst system, and iodobenzene as the substrate, monocarbonylation was favoured in CH_2Cl_2/DBU, and dicarbonylation in C_6H_6/Et_3N [1326]. Careful mechanistic studies suggest that the intermediates involved are [$M(CO)(COR)L_n$] and [$M(CONu)(COR)L_n$], rather than [$M(COCOR)L_n$], since this latter spontaneously loses carbon monoxide at room temperature [1327-1329]. $B(OR')_3$ was used as an alkoxy group source in alkoxycarbonylation of both activated and unactivated halides in the presence of [$Pd(PPh_3)_4$]/[{$RhCl(nbd)$}$_2$] [1330].

In the presence of amines, carbonylation of halides leads to the synthesis of amides. In this area also studies of double carbonylation reactions have been widely reported [1331,1332]. In the patent literature it has been noted that iodobenzene reacts with CO/Et_2NH in the presence of $PdCl_2$ to give mainly $PhCOCONEt_2$; using $[PdI(Ph)(PPh_3)_2]$ as the catalyst gave both mono and dicarbonylated products [1333]. Good selectivities towards dicarbonylated products were also reported for reactions involving $Me_3CNH_2/PdCl_2/CO$ [1334] and $Et_2NH/PdCl_2/CO/Cy_2P(CH_2)_4PCy_2$ [1335]. Aryl and alkenyl bromides and iodides have been reported to react similarly [1336]. Using $PhI/CyNH_2/CO$ in the presence of $PdCl_2$, the main product was PhC(=NCy)CONHCy, a condensation product of the initially formed dicarbonyl derivative [1337].

There have been a number of mechanistic studies of the reaction. As with the related ester formation, the exact nature of the catalyst and solvent are crucially important to selectivity. The catalytic cycles for mono and dicarbonylation are quite distinct, and the key intermediate is $[Pd(COAr)(CONR'_2)L_2]$ rather than $[Pd(COCOAr)L_n]$ [1338-1340].

A number of other amidation reactions have been used in total syntheses. In reaction (34) an α-halo aniline is carbonylated to give a mixture of 7- and 5-membered ring products, in an approach to benzodiazepine syntheses [1341]. A related process (reaction (35)) gave an intermediate for synthesis of quinazoline derivatives [1342]. Carbonylation of **665** in the presence of **666** and $[PdCl_2(PPh_3)_2]$ gave the related amide [1343]. In some instances the nucleophile may be introduced by reaction with a tin derivative, R_3SnNu (Nu = OMe or NEt_2) [1344].



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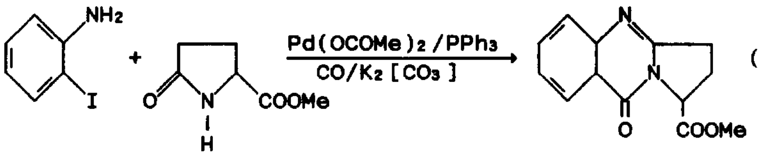

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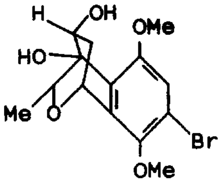

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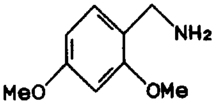

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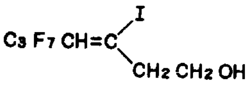
A few other nucleophiles have proved useful. Reaction of ArI with $PhC{\equiv}CH/CO$ in the presence of $[PdCl_2(PPh_3)_2]/Zn/Cu/[Cp_2TiCl_2]$ gave ArCOCH=CHPh as the major product in most cases. Traces of alkynyl ketones were formed [1345]. Using $(Me_2CHCH_2)_3Al$ as the nucleophile in the presence of $[PdCl_2(PPh_3)_2]/PPh_3$/dme yielded $ArCH(OH)CH_2CHMe_2$, in some cases in excellent yields. Aryl bromides were not good substrates [1346]. Ketones, ArCOR, were also the major products from ArX/RX/CO/(1 atm)/$[Pd(PPh_3)_4]$/Zn/Cu/thf [1347]. Reaction of $[Ar_2I]X$ (X = Cl, Br, I or $[BF_4]$) with CO in the presence of palladium(II) gave Ar_2CO and ArCOCOAr. An increased CO pressure resulted in higher proportions of ArCOCOAr [1348].

There have also been many reports of the carbonylation of vinyl halides and related compounds. Carboxylic acids were produced by carbonylation of $CH_2{=}C(CF_3)X$ (X = Cl or Br) using CO/H_2O in the presence of $[PdCl_2(PPh_3)_2]/KI/Et_3N$ [1349,1350]. E-PhCH=CHBr was converted to E-PhCH=CHCOOBu in the presence of $CO/[Ti(OBu)_4]/[Pd(PPh_3)_4]$ [1351], and $(MeO)_2CO$ was used as the source of alkoxide in a reaction of 2-bromopropene in the presence of $[PdCl_2(PPh_3)_2]$, to give methyl 2-methylpropenoate [1352]. $[Al(OR)_3]$ has also been used as an alkoxide source [1353]. The treatment of **667** with CO in the presence of $[PdCl_2(PPh_3)_2]/K_2[CO_3]$ resulted in an intramolecular reaction to give the lactone **668** [1354]. The reaction of Z-PhCH=CHTePh with $CO/PdCl_2/LiCl$ was studied in detail. At high pressures of CO, the Z-product was the major one, but E-PhCH=CHCOOMe was formed exclusively in reactions from which the LiCl was omitted [1355]. Reaction of steroidal enol triflates with CO/MeOH in the presence of $Pd(OCOMe)_2/PPh_3/Et_3N$ gave the corresponding unsaturated esters [1356].



$C_3F_7CH{=}C(I)CH_2CH_2OH$

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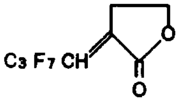

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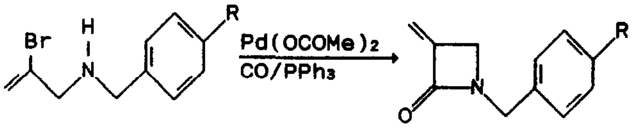
β-Lactams have been formed in intramolecular amidocarbonylations of alkenyl halides such as reaction (36) (R = COOMe, Me or OMe) [1357-1360].



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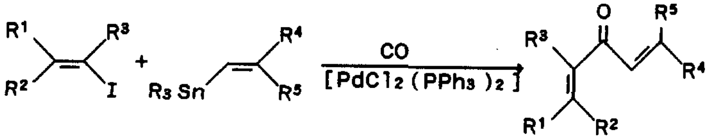
Tin nucleophiles have also been used in conjunction with alkenyl halide carbonylation, to give dienones (reactions (37) and (38)) [1361,1362]. Ureidocarbonylation of $CH_2{=}C(CF_3)Br$ by $R^1NHCONHR^2$ gave 669 in the presence of $[PdCl_2(PPh_3)_2]$ [1363]. When there is an appropriately positioned double bond, as in 670, carbonylation may be followed by insertion, giving, ultimately, a γ-ketoester (reaction (39)) [1364].



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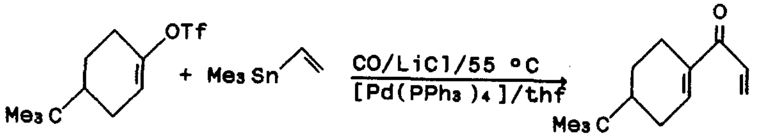

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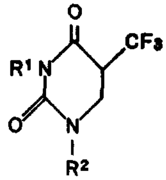

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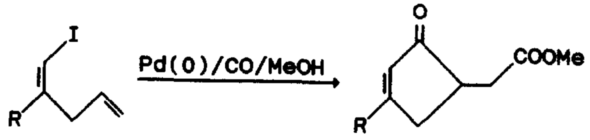

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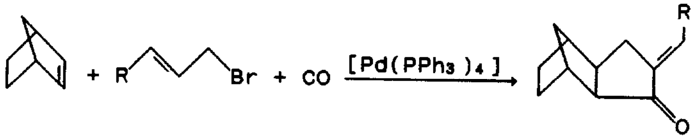
A few carbonylations of other types of halides have been reported. Allyl halides have been converted to the corresponding acids in the presence of $CO/[Ni(CO)_4]/NaOH/H_2O/C_6H_6/[R_4N]X$ [1365], and allyl phosphonates such as $CH_3CH_2CH_2CH{=}CHCH_2OP({=}O)(OEt)_2$ reacted with $CO/Et_2NH/[Pd(PPh_3)_4]/[Bu_4N]Cl$ to give a mixture of $CH_3CH_2CH_2CH{=}CHCH_2CONEt_2$ and $CH_3CH_2CH_2CH{=}CHCH_2NEt_2$ [1366]. Benzylic halides reacted using $[M(LL)X_2]$ (M = Ni or Pd, LL = $R_2P(CH_2)_xPR_2$, $x \leqslant 3$) as the catalyst [1367]. Reactions of allyl halides with organotin compounds in the presence of CO and a palladium complex gave mixtures of products derived from simple coupling, and coupling with carbonyl insertion [1368,1369]. Carbonylation was also combined with coupling in reaction (40) [1370].



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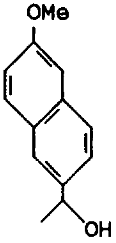
The patent literature again affords many examples of catalytic systems for methanol carbonylation. Methyl ethanoate was the product in the presence of $PtCl_2/Co(OCOMe)_2/LiI$ [1371], whilst a mixture of methyl ethanoate and ethanoic acid was obtained using $[Ni(CO)_2(PPh_3)_2]/[Mo(CO)_4(PPh_3)_2]$ [1372]. Catalyst systems yielding ethanoic acid as the main product included $NiI_2/[M(CO)_6]/MeI/LiI$ (M = Cr, Mo or W) [1373] and $Pd(OCOMe)_2/NiCl_2/MeI/LiI/$*N*-methylpyrrolidone [1374]. Ethanol was obtained using $NiCl_2/[Co_2(CO)_8]/Bu_3P$ with [1375] or without Ph_3N [1376], or $PdCl_2/[Co_2(CO)_8]/Bu_3P$ [1377]. There has been a thorough investigation of the reaction in the presence of *cis*-$[Pt(CO)_2(PEt_3)_2]$, which gives methyl methanoate and dimethyl oxalate [1378]. Under oxidative conditions methanol is carbonylated to give mixtures of dimethyl carbonate and dimethyl oxalate; catalysts have included $PdI_2/Cu(OCOMe)_2$ [1379], $[\{PdCl(CO)\}_n]/LiCl$/benzoquinone [1380] or $PdX_2/CuCl_2/Na_5H_2Mo_8V_4O_{40}$ [1381]. Oxalate syntheses in the presence of palladium(0) complexes have been reviewed [1382].

An interesting carbonylation of ROH (R = alkyl, cycloalkyl or arylalkyl) to give ROCOOR has been reported to occur in the presence of $K_2[PdCl_4]/CuBr/K[OCOMe]$ [1383]. Dibutyl carbonate was obtained with excellent selectivity from BuONO and BuOH when treated with CO/O_2 in the presence of $PdCl_2$ [1384]. Reaction of 671 with CO, HCl and 2-propanol in the presence of $[PdCl_2(PPh_3)_2]$ gave 672 [1385]. Reaction of allylic carbonates with CO in the presence of $Pd(OCOMe)_2/PPh_3$ gave β,γ-unsaturated esters, in an effective carbonylation of allylic alcohols. The reaction mechanism involves a palladium allyl complex, and allylic transposition was important in many cases

[1386,1387].



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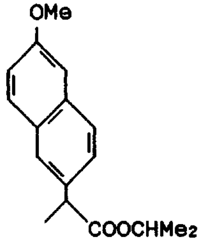

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The patent literature also funishes a number of examples of the catalysed carbonylation of methyl ethanoate. Ethanal was the product of the reaction with CO/H_2 in the presence of $PdCl_2/RhCl_3/K[OCOMe]/MeI$/active C [1388], and a mixture of ethanal and ethanoic acid when the active carbon was omitted [1389]. The commonest product was ethanoic anhydride, formed in the presence of $[Ni(acac)_2]$/butyrolactone/*N*-methylimidazolium iodide [1390], $[Ni(acac)_2]/MeI$/butyrolactone/Ph_2PNEt_2 [1391], $NiCl_2/MeI/Ph_3PO/[Bu_4N]I$ [1392], $NiI_2/[M(CO)_6]/LiI/MeI/CH_3COOH$ (M = Cr, W or Mo) [1393,1394], $[Ni(acac)_2]/[VO(OCHMe_2)_3]/MeI/[Bu_3MeP]I$ [1395] or $PdCl_2$ [1396]. Either methyl ethanoate or dimethyl ether were converted to ethanoic anhydride in the presence of $[Ni(acac)_2]/MeI/PPh_3/\gamma$-valerolactone [1397], $[Ni(CO)_4]/MeI/CH_3COOH$/butyrolactone [1398], $[Ni(CO)_4]/[Ti(OBu_4)]/[Bu_3MeP]I/MeI$ [1399] or $[Ni(acac)_2]/MeI$/butyrolactone/$[R_4N]X$ [1400]. Using $[Ni(acac)_2]/MeI/Et_3N$/butyrolatone as the catalyst system, one patent reports that both ethanoic anhydride and ethanoic acid were obtained [1401], and with $PdCl_2/VCl_3/MeI/[Bu_3MeP]Cl$, traces of $CH_3CH(OCOMe)_2$ were also formed [1402]. The acetal type product could be made the major one in the presence of $Pd(OCOMe)_2/RhCl_3/Bu_3P/MeI$ [1403]. A rather curious patent reports the conversion of $Me_3COOCMe_3$ to $Me_3COOCCOOCMe_3$ in the presence of $[Pd(acac)_2]/CuCl/py/Me_2CO$ [1404].

Carbonylation of $ArNH_2$ under oxidative conditions and in the presence of an alcohol, ROH, gave ArNHCOOR when $PdCl_2/CuCl_2$ was used as catalyst. The reaction could be carried out under unusually mild conditions, at room temperature and atmospheric pressure [1405]. Palladium black could also be used as a catalyst for this reaction, with {RNHCOPd} invoked as a surface bound intermediate [1406].

Carbonylation of aromatic nitro compounds to yield isocyanates has again been widely reported. Catalyst systems have included $[Bu_4N][PdCl_3(CO)]/VCl_3$

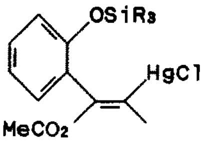
[1407] and $[Bu_4N]_2[Pd_2Cl_4(CO)_2]/VOCl_2$ [1408], with the reaction rate increasing for nitroarenes bearing electron donating groups in the 4-position [1409]. Other catalysts giving mainly isocyanates were $PdCl_2/Fe(III)/py$ [1410], $[Bu_4N]_2[Pd_2Cl_6]$ [1411], $[PdCl_2(py)_2]$ [1412] and $[PdCl_2(isoquinoline)_2]$ [1413]. Using $[Pt_{15}(CO)_{30}]^{2-}$ as the catalyst gave a mixture of ArNCO, $ArNH_2$ and $(ArNH)_2CO$ [1414], whereas mainly amines were obtained in the presence of $[PtCl_2L_2]$ (L = PhCN or PPh_3) [1415]. Urethanes were the main product using $PdCl_2/py/V_2O_5/EtOH$ [1416] or Pd/C, and in the latter case both selectivity and conversion were greatly improved by addition of 2,4,6-trimethyl benzoic acid [1417]. Reaction of 2,4-dinitrotoluene with CO/EtOH in the presence of $[PtCl_2(PPh_3)_2]/FeCl_3/Et_3N$ gave the bis(NHCOOEt) derivative [1418]. Carbonylation of $PhNO_2$ in the presence of $[PtCl_2(PPh_3)_2]/SnCl_4/R'COOH$ gave mainly PhNHCOR'. Possible mechanisms were proposed which involved either the arylamine or any aryl isocyanate reaction with the carboxylic acid [1419].

The reaction of nitroarenes and anilines with CO in the presence of $[PtCl_2(PPh_3)_2]/SnCl_4/Et_3N$ yielded ArNHCONHAr, but attempts to make mixed urea derivatives by this method were not very successful, leading to a complex mixture of products [1420]. Carbonylation of $ArNO_2$ in the presence of $PdCl_2/NaX/FeX_3/MeOH$ gave ArNHCOOMe as the final product. The intermediacy of ArN(O)=NAr and ArN=NAr was said to be established on the basis that the same final product was obtained from azobenzene and azoxybenzene [1421]. However, other workers considered that azobenzene is not an intermediate, preferring a mechanism involving metal nitrene complexes [1422]. Azo- and azoxy benzene were among the products formed from carbonylation of PhNO [1423]. Some evidence for palladium(I) intermediates in the reaction was obtained from PES measurements [1424].

There have been a few reports of the carbonylation of organomercury compounds. Reaction of RHgX with CO and R'OH gave RCOOR' in the presence of $[PdCl_2L_2]$ (R = Ar, R'OH = H_2O) or $[PdL_4]$ (R, R' = alkyl) [1425]. Similarly, **673** was converted to **674** using CO/MeOH in the presence of $Li_2[PdCl_4]$ [1426]. Under oxidative conditions, in the presence of a $Pd(OCOMe)_2/Hg(OCOMe)_2/Na[OCOMe]$, PhHgOCOMe was converted to a mixture of PhCOOCOPh and PhCOOR. Yields were excellent and conditions mild [1427]. An attempt was made to achieve a cross-coupling of Ph_2Hg and ArI in the presence of $[PdI(Ph)(PPh_3)_2]/I^-$, but the main product was Ph_2CO. Substantial amounts of PhAr and PhPh were also obtained, and the yield of PhCOAr was low [1428].

Various other carbonylation reactions have been noted. Reaction of methanal with CO and $CH_3(CH_2)_4ONO$ in the presence of $[PdBr_2(PPh_3)_2]/SnCl_2/[Bu_4N]Cl$ gave mainly $CH_2\{COO(CH_2)_4\}_2$ [1429]. When 4-hydroxybenzaldehyde was treated with CO/HCl/EtOH in the presence of

$[PdCl_2(PPh_3)_2]$ the main product was reported to be ethyl 4-hydroxybenzoate, but there was no indication of the course of the reaction [1430]. Patents reported the reaction of diketene with CO and MeONO in the presence of $PdCl_2/CuCl_2$ to give $MeO_2CCH_2COCH_2COOMe$ [1431,1432].



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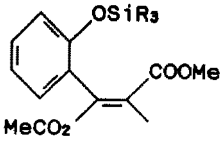

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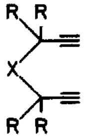
The substituted alkyne $R^1R^2C(OH)C{\equiv}CH$ reacted with $CO/MeOH/PdCl_2/CuCl_2$ to give $R^1R^2C(OH)C{\equiv}CCOOMe$ [1433]. Reaction of 1-alkynes with CO (20 atm), and organic halides, RX, in the presence of $[PdCl_2(PP)]$ (PP = phosphine ligand(s)) gave ketones $RCOC{\equiv}CR'$. Yields varied widely with the nature of PP, and were best using the dppf complex [1434]. The α,ω-diyne, 675 (X = NH, R = Me, or X = CH_2, R = H) reacted with CO in the presence of palladium(0) to give the dienone, 676, which was not isolated, but could be characterised as its Diels Alder dimerisation product [1435]. In the presence of $[NiBr_2(Et_2NH)_2]$ butadiene reacted with CO/Et_2NH to give $CH_2{=}CH{-}CH{=}CH{-}CONEt_2$in modest yields. A mechanism involving a π-allyl nickel complex was proposed [1436]. Reductive carbonylation of $[ArN_2][BF_4]$ with CO/Et_3SiH in the presence of $Pd(OCOMe)_2$ gave ArCHO together with a small amount of ArH. The reaction mechanism proposed is related to that for the carbonylation of aryl halides to aldehydes, but the reaction conditions needed are much milder [1437].



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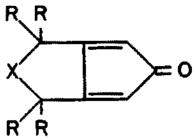

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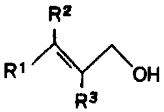
Copolymerisation of ethene and CO was accomplished in the presence of $Pd(OCOMe)_2/dppp/TsOH/MeOH$ [1438]. Dialkyl ketones have been prepared from 1-alkenes, CO and H_2, with excellent selectivity under mild conditions, using $[PdL_2X_2]/CF_3COOH$ as the catalyst. A detailed reaction mechanism was proposed [1439]. Cleavage of a phosphorus-carbon bond in PPh_3 to give PhCOOH occurred using CO/NO in the presence of $PdCl_2$. Some PhCOPh and anthroquinone were also obtained [1440]. Reaction of 667 with CO, H_2 and $[Co_2(CO)_8]/[PdCl_2(PPh_3)_2]$ gave 678 (R, R^1 = Me, R^2, R^3 = H) with good yield [1441].



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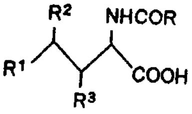

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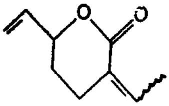
The catalytic fixation of CO_2 by metal complexes has been reviewed [1442]. In the presence of $Pd(OCOMe)_2$, ArH was carboxylated to ArCOOH in low yield, and with modest regioselectivity. Addition of Me_3COOH increased the yield, and substituent effects indicated that the reaction had the character of an electrophilic substitution [1443]. The reaction has also been reported to occur in the presence of $Pd(NO_3)_2/CCl_4$ [1444], and the yield may be increased by the addition of $Fe(NO_3)_3$ [1445].

Carboxylation of aryl halides, bearing either electron acceptors or moderate electron donors, has been accomplished in an electrochemical reaction in the presence of $[NiBr_2L_2]$, but conversions were low [1446]. Reaction of 2-bromopropene with CO_2/MeOH in the presence of $[PdCl_2(PPh_3)_2]/Bu_3N$ yielded methyl 2-methylpropenoate [1447].

Carboxylation of butadiene in the presence of $[Pd(acac)_2]/P(CHMe_2)_3$ gave mainly 679, which was isomerised thermally in the presence of the palladium catalyst to 680 [1448]. Reactions of other dienes were also investigated [1449]. Using [Ni(bipy)(cod)] as the catalyst, and oxidative conditions, 681 was converted to 682 [1450].



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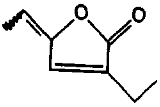

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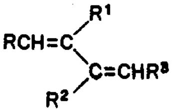

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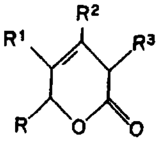

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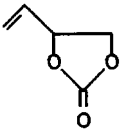
The reactions of CO_2 with alkynes in the presence of nickel catalysts have been reviewed [1451]. The apparent insertion of CO_2 into the epoxide **683** to give **684**, catalysed by $[Pd(PPh_3)_4]/PPh_3$, involved the intermediacy of the allyl derivatives **685** and **686** [1452]. Methylenecyclopropane was carboxylated to **687** in the presence of $[Pd(\eta^3\text{-}C_3H_5)(Cp)]/PPh_3$ [1453].

683



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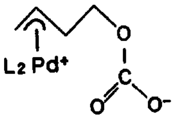

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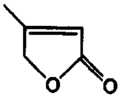

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13.4 Hydrosilylation and Related Reactions

Organochlorosilane chemistry, including hydrosilylation, has been reviewed [1454]. Heterogenised platinum catalysts for hydrosilylation have been discussed [1455], as has the use of other platinum or rhodium complexes as catalysts [1456]. A report refers to hydrosilylation with homogeneous and heterogeneous silicon ion *(sic)* complexes of platinum [1457].

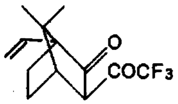
There have been a number of reports of the hydrosilylation of 1-alkenes in the presence of $H_2[PtCl_6]$ [1458-1460], including a kinetic study [1461]. There have been several reports of such hydrosilylations of γ-alkenyl amines and amides leading to the preparation of chiral stationary phases for hplc [1462-1465]. Monomers to be used in the preparations of polysiloxanes have also been synthesised [1466]. There have been two reports of the hydrosilylation of the strained double bond of a bicycloheptene derivative, using $H_2[PtCl_6]$ as catalyst [1467,1468].

A mechanism has been proposed for the hydrosilylation of 1-octene by $MeSiHCl_2$ in the presence of $[NiCl_2(PBu_3)_2]$ [1469]. A kinetic study of the reaction revealed that the reaction rate depended on both the steric and the electronic character of the phosphine ligand [1470]. $NiCl_2$ on silica supported γ-methyldiethyoxysilyl propyl dibutylphosphine oxide has been used as a hydrosilylation catalyst [1471].

There has been a range of reports of catalysts for the hydrosilylation of phenylethene and its derivatives, including platinum salts on silica [1472] or an anion exchange resin [1473,1474] for reaction with $MeSiHCl_2$. In a patent abstract it was stated that reaction of $4\text{-}Me_3C_6H_4CH{=}CH_2$ with Me_2SiCl_2 in the presence of $[PtCl_2(PhCN)_2]$ gave $4\text{-}Me_3CC_6H_4CH_2CH_2SiClMe_2$, but it seems likely that the reagent was $HSiMe_2Cl$ [1475]. Dihydrofuranyl substituted silanes reacted with phenylethene in the presence of $H_2[PtCl_6]$ [1476].

The hydrosilylation of alkenyl silanes with $HSiR_3$ in the presence of $H_2[PtCl_6]$ has been studied; variation of either the catalyst or the solvent may alter the α/β ratio. An alkenyl silane platinum complex was propsed as an intermediate [1477]. With $R_3SiCH{=}CH_2$ and R'_3SiH there was also some exchange between the R and R' groups [1478]. Reactions in the presence of a range of palladium(II) or palladium(0) complexes gave mainly $R_3SiCH_2CH_2SiR'_3$, except when both R and R' = Cl [1479].

Reaction of $CF_3CH{=}CH_2$ with $MeSiHCl_2$ in the presence of $[PdCl_2(PhCN)_2]/PPh_3$ gave $CF_3CH(CH_3)SiMeCl_2$ as the sole product, this being a potent new monomer for production of fluorosilicones. Reaction under photolytic conditions or in the presnce of $H_2[PtF_6]$ gave exclusively the β-product. Treatment with trichlorosilane gave the β-product under all conditions [1480]. Hydrosilylation of 688 with $HSiCl_3$ in the presence of $H_2[PtCl_6]$ gave only 689 [1481].



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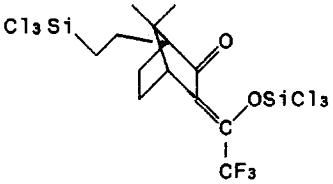

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Hydrosilylation of 3-amino-1-propene by $(EtO)_3SiH$ in the presence of $H_2[PtCl_6]$ gave $(EtO)_3Si(CH_2)_3NH_2$ [1482]. With $RR'NCH_2CH{=}CH_2$ and $HSiX_2Y$, however, regiochemistry was strongly dependent on the nature of the substituents [1483]. A linear product was formed from $Me_3SiNHCH_2CH{=}CH_2$ and $HMeSi(OSiMe_3)_2$ [1484]. Hydrosilylation of the allyl ether, $PhOCH_2CH{=}CH_2$, with $HSiCl_3$ in the presence of $H_2[PtCl_6]$ gave exclusively $PhO(CH_2)_3SiCl_3$ [1485]. Linear products were also obtained from $Me_3SiOCH_2CH{=}CH_2$ and $HSiMe_2Ph$ using $H_2[PtCl_6]$ on ion exchange resin [1486], and $CH_2{=}CHCH_2OCOC(CH_3){=}CH_2$ and $HSiMe_2Cl$ in the presence of $[PtCl_2(Et_2S)_2]$ [1487].

The reaction of 3-chloro-1-propene with 2-dichlorohydrosilylthiophene in the presence of $H_2[PtCl_6]$ gave propene and 2-trichlorosilylthiophene as well as the normal hydrosilylation products [1488]. Reaction of 3-chloro-1-propene with trichlorosilane in the presence of a polysiloxane supported platinum catalyst gave $Cl(CH_2)_3SiCl_3$ with 77 % selectivity [1489].

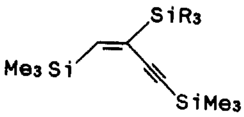
There have been further studies of the regiochemistry of 1-alkyne hydrosilylation in the presence of platinum or palladium complexes [1490]. Using $H_2[PtCl_6]$ as the catalyst, 1-octyne reacted with R_3SiH to give $E\text{-}R_3SiCH{=}CHC_6H_{13}$ as the major product, together with a small amount of the Z-isomer, and α-addition product [1491]. Using $H_2[PtCl_6]/I_2$ as the catalyst system, however, the major product was $RC{\equiv}CSiR'_3$, with little competing hydrosilylation [1492]. Mixtures of substitution and addition products were obtained with $H_2[PtCl_6]/LiI$ [1493]. Addition of either Et_3SiH or $EtSiCl_2H$ to 1-alkynes, $RC{\equiv}CH$, in the presence of platinum(II) salts gave E-addition products stereospecifically, with the regiochemistry of the reaction dependent on R [1494]. Additions to $AdC{\equiv}CH$ (Ad = adamantyl), using $H_2[PtCl_6]$ as catalyst, gave only E-β-products [1495].

Hydrosilylation of phenylethyne may give mixtures of both possible regioisomeric products. It was shown that $[PtCl_2(1,2,4\text{-triazole})_2]$ had very high catalytic activity for the reaction, but the the regiochemistry of the reaction was dependent primarily on the nature of the added silane [1496]. The regiochemistries of the reactions of a wide range of 1-alkyne substrates were tested [1497].

Hydrosilylation of $HC{\equiv}CCMe_2OH$ with $PhMeSiH_2$ in the presence of $H_2[PtCl_6]$ gave a mixture of $PhMeHSiOCMe_2C{\equiv}CH$, $PhMeSi(CH{=}CHCMe_2OH)_2$ and $PhMeHSiCH{=}CHCMe_2OH$, the last product predominating [1498,1499]. With $HC{\equiv}CCMe(Bu)OH$ and $PhMeSiH_2$, the major product was similarly $PhMeHSiCH{=}CHCMe(Bu)OH$. In neither case was the product stereochemistry specified, but it may be assumed that E-products predominate [1500].

Hydrosilylation of $Me_2OCCH_2CH_2OCH_2C{\equiv}CH$ occurred with $RR'SiH_2$ in the presence of $H_2[PtCl_6]$, giving $(MeO_2CCH_2CH_2OCH_2CH{=}CH)_2SiRR'$ [1501,1502]. Both double and single hydrosilylation were reported for the related reaction of $HC{\equiv}CCH_2OCOMe$ [1503]. The products of both α- and β-addition were observed for the reaction of $HC{\equiv}CCH_2Cl$ with R_3SiH [1504].

Reaction of $Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3$ with R_3SiH in the presence of a platinum complex gave a mixture of **690** and **691**, with **690** being slowly converted to **691** under the reaction conditions. Using $[Pt(PPh_3)_4]$ or $H_2[PtCl_6]$ as the catalyst, the main product was **690**, but the outcome of the reaction was also dependant on the nature of the phosphine [1505]. The enyne, **692** (R = COOMe), reacted with $BuMeSiH_2$ in the presence of $H_2[PtCl_6]$ to give mainly **693**, though no stereochemistry was specified [1506,1507].



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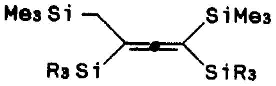

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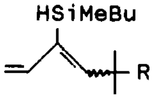

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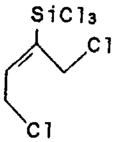
There has been a kinetic study of the platinum catalysed hydrosilylation of $PhC\equiv CCRR'OH$ with Pr_3SiH [1508]. Addition of hydrosilanes or hydrogermanes to $Me_3SiOCH_2C\equiv CCH_2OSiMe_3$ was also noted [1509]. Reaction of $ClCH_2C\equiv CCH_2Cl$ with $HSiCl_3$ in the presence of $H_2[PtCl_6]$ gave **694** in near quantitative yield [1510]. Reaction of Et_3SiH with $Me_3SiC\equiv CCOR$ gave a 5:1 mixture of **695** and **696** [1511].



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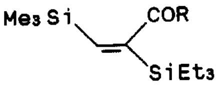

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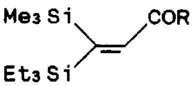

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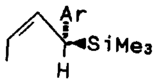
Enantioselective hydrosilylation of $ArCH=CH-CH=CH_2$ with $HSiCl_3$ in the presence of $[PdCl_2\{(R)-(S)-PPFA)]$ gave, after work-up and reaction with MeLi, a mixture of 1,4- and 1,2-addition products, **697** and **698** with respectively 29 % and 55 % enantiomer excess. A mechanism invoving a π-allyl intermediate was proposed [1512].



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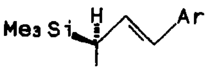

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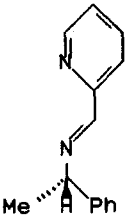
There have been many reports of the use of hydrosilylation and related reactions in polymer preparation and curing. Polysiloxane graft copolymers have been prepared by reaction of polysiloxanes with allyl derivatives in the presence of $H_2[PtCl_6]$ [1513-1515]. Reactions between vinyl terminated siloxanes and Si-H terminated siloxanes have been noted [1516-1519], and the kinetics of the hydrosilylation of oligomeric butadiene rubber have been investigated [1520]. Various other processes have been more or less clearly reported in the patent literature [1521-1530].

Enantioselective hydrosilylation of ketones has been studied in the presence of $K[Pt(C_2H_4)Cl_3]$ with an added ligand such as 699; most of the reported enantiomer excesses were modest [1531]. Hydrosilylation of the oxime, 700, gave a mixture of 701, 702 and 703, with 703 as the major product, though overall yields were low [1532]. Hydrosilylation of enones by Ph_2SiH_2 in the presence of $[Pd(PPh_3)_4]$ required the addition of $ZnCl_2$ for success, giving the saturated carbonyl compound in good yield. With Ph_2SiD_2 deuterium labelling was exclusively β to the carbonyl, whilst the use of D_2O in the work-up resulted in α-labelling [1533].



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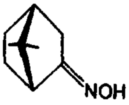

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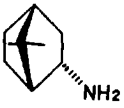

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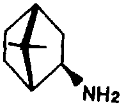

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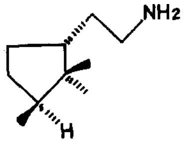

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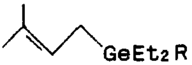
Addition of R_3GeH to 1-alkynes has been accomplished in the presence of $H_2[PtCl_6]$, the major product being E-$RCH{=}CHGeR_3$, but the outcome being somewhat dependent on the nature of R. When $[PtCl_2(PPh_3)_2]$ was used as the catalyst considerable, and unexplained, isomerisation to the Z-addition product was noted [1534]. Hydrogermylation of isoprene with $HGeEt_2Br$ has been studied in the presence of $[Ni(acac)_2]/PPh_3$. 1,4-Addition gave 704 as the main product [1535]. With butadiene and Et_2GeH_2 the main products were Z-$CH_3CH{=}CHCH_2GeHEt_2$ and 705, from 1,4-*cis*-addition [1536]. Hydrogermylation of methyl propenoate by $AdGeMe_2H$ in the presence of $H_2[PtCl_6]$ gave exclusively $AdGeMe_2CH_2CH_2COOMe$ [1537].



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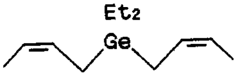
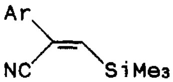


705

Silylcyanation of ArC≡CH with Me_3SiCN in the presence of $PdCl_2$/py gave 706 with high regio and stereoselectivity. The reaction was compatible with acetals, ethers, chlorides and fluorides, but aryl bromides were substituted by cyanide under the reaction conditions [1538]. Reaction of Me_3SiCN with 707 in the presence of $Pd(OCOMe)_2$ gave a mixture of 708 and 709, the ratio depending on the nature of R_f and R [1539].



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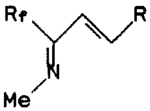

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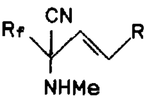

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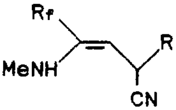
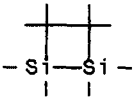


709

Reaction of the disilane, 710, with RC≡CH in the presence of $[PdCl_2(PPh_3)_2]$ gave 711. With butadiene the products were disilacyclooligomers, and with propadiene, 712 was formed [1540]. The palladium catalysed reaction of disilanes $Me_{3-n}X_nSiSiX_nMe_{3-n}$ with dienes CH_2=CH-C(R)=CH_2 (R = H or Me) has been studied, and shown to give 713 as the main product. The product for which *n* = 0 and R = H was converted to muscone in a short synthesis [1541].



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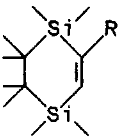

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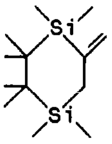

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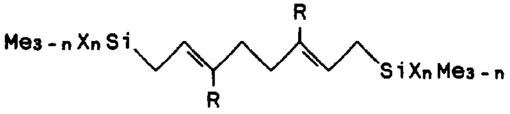

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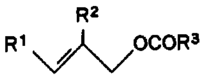
Reaction of an allyl ethanoate, 714, with $Me_3SiSiMe_3$ in the presence of a palladium(0) complex gave a mixture of 715 and 716, the product ratios depending on the exact nature of the catalyst and the substituents [1542]. Substitution of 717 to give an acyl silane was accomplished using $Me_3SiSiMe_3$ in the presence of $[\{Pd(\eta^3\text{-}C_3H_5)Cl_2]/P(OEt)_3$. By products included R_2CO and RCOCOR [1543].



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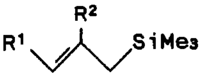

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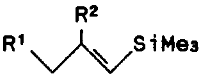

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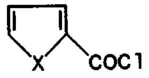

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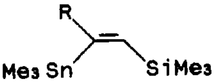
Silylstannation of $RC\equiv CH$ with $Me_3SiSnMe_3$ was stereospecific and generally regiospecific in the presence of $[Pd(PPh_3)_4]$, giving 718. However, for the substrate with R = COOMe, equal amounts of the regioisomers 718 and 719 were obtained. Reaction with 3-methyl-1,2-butadiene gave a 1:1 mixture of 720 and 721 [1544]. The reaction of $Me_3SnSiMe_2CMe_3$ with $RC\equiv CH$ in the presence of $[Pd(PPh_3)_4]$ gave only 722 [1545]. The distannation of 1-alkynes has been known for some time to give Z-1,2-distannaalkenes. However, when propyne reacted with Me_6Sn_2, the major product was 723, thought to be formed *via* an allene. The reactions of allenes were studied in some detail; both kinetic and thermodynamic products could be obtained under appropriate conditions, and the intermediacy of a palladium allyl complex was proposed [1546]. Reaction of Me_6Sn_2 with ArCOCl resulted mainly in the formation of Ar_2CO, when the catalyst was $[PdI(Ph)(PPh_3)_2]$, but gave more of ArCOCOAr with $[PdI(Ph)\{P(OEt)_3\}_2]$. A mechanism was proposed for the reaction [1547]



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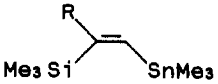

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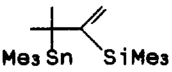

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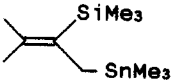

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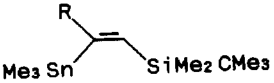

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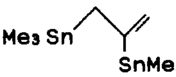

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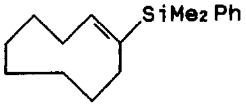
Reaction of $RC\equiv CH$ with $PhMe_2SiZnR'_2Li$ in the presence of $[Pd(PPh_3)_4]$ gave a mixture of E-$RCH=CHSiMe_2Ph$ and $RC(SiMe_2Ph)=CH_2$. The regioselectivity was inferior to that in the reaction catalysed by CuCN [1548]. Reaction of $RC\equiv CH$ with $(Bu_3Sn)_2Zn$ gave a mixture of E-$RCH=CHSnBu_3$ and $RC(SnBu_3)=CH_2$. For R = Ph, and using $[PdCl_2(PPh_3)_2]$ as catalyst, E-$RCH=CHSnBu_3$ was the main product, but for $R = C_{10}H_{21}$ using $[Pd(PPh_3)_4]$, $RC(SnBu_3)=CH_2$ was formed with >95 % selectivity [1549,1550]. Cyclonona-1,2-diene reacted with $(PhMe_2Si)_2M$ (M = Zn or $AlEt_2$) in the presence of $[PdCl_2(PR_3)_2]$ (R = Bu or 2-MeC_6H_4) to give a mixture of **724** and **725**, the ratio between the products depending on R and M [1551].



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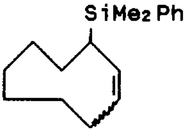

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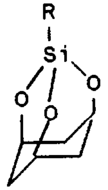
Trichlorosilane reacted with $R_2SiR'_2$ in the presence of $H_2[PtCl_6]$ to give $RSiHCl_2$ and RR'_2SiCl. Methyl groups migrated most easily, and selectivity was generally good [1552]. Reaction of $RSiH_3$ with *cis*-cyclohexane-1,3,5-triol in the presence of either $[PtCl_2(PPh_3)_2]$ or $H_2[PtCl_6]$ gave **726**. However, $[RhCl(PPh_3)_3]$ was a more useful catalyst [1553]. When Et_3SiH was reacted with $H_2NC(=S)NHR$ in the presence of $H_2[PtCl_6]$, the product was $Et_3SiNHC(=S)NHR$, which decomposed to give Et_3SiNCS and RNH_2 [1554]. The allylic Grignard reagent, 727, reacted with R_3SiH using $[NiCl_2(dppf)]$ as the catalyst to give 728 as the main product. Minor products were the Z-isomer and $CH_2{=}CHCH(Me)SiR_3$ [1555].



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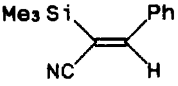
13.5 Other Additions to Carbon-Carbon Multiple Bonds

The mechanism of hydrocyanation of alkenes in the presence of nickel complexes as catalysts has been investigated in detail. There are two catalytic loops, one involving the addition of HCN to $[Ni(C_2H_4)L_2]$, and the other ethene addition to $[Ni(CN)(H)L_2]$. Steric crowding leads to a preponderance of linear products, but 91 % branched products were obtained from phenylethene, due to the intermediacy of a π-benzyl nickel complex. Addition of Lewis acids accelerates carbon-carbon bond formation, destabilises branched alkyl intermediates relative to linear ones, and increases catalyst lifetime [1556]. Hydrocyanation of $PhC{\equiv}CSiMe_3$ in the presence of $[Ni\{P(OPh)_3\}_4]$ gave mainly 729, but more of the other regioisomer was obtained when the substituents at silicon were larger [1557].



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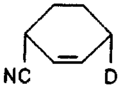
Addition of DCN to cyclohexa-1,3-diene in the presence of $[Ni\{(P(OPh)_3\}_4]$ gave both 730 and 731, in comparable amounts, thus establishing the intermediacy of a π-allyl intermediate in the reaction pathway. It was proposed that *cis*-addition of $[Ni(CN)(D)L_3]$ gave 732, with cyanide then being transferred from the metal to either end of the allyl unit [1558]. Addition of DCN and $H^{13}CN$ to pentenenitiles in the presence of $[Ni\{P(OC_6H_4\text{-}4\text{-}X)_3\}_4]$/Lewis acid has been studied. H/D exchange occurred *via* orthometallation when X = MeO, but not when X = Me. It was shown that $CH_3CH(CN)CH_2CH_2CN$ was derived mainly from 4-pentene nitrile and $CH_3CH_2CH(CN)CH_2CN$ from 3-pentene nitrile

[1559]. Hydrocyanation of $RCH=C=CH_2$ using $[Ni\{P(OPh)_3\}_4]$ as catalyst gave a mixture of products depending on R and the reaction conditions. Competing oligomerisation and polymerisation lowered the yields [1560].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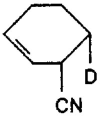
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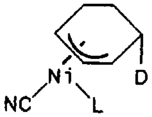
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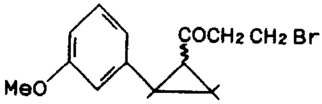
Cyclopropanation of 3-methoxyphenylethene by $N_2CHCOCH_2CH_2Br$ in the presence of a palladium salt gave 733 with a *trans:cis* ratio of 7:1. The product was used in a steroid synthesis [1561]. With phenylethene and $N_2CHCOOEt$ in the presence of [NiPc] the *trans:cis* ratio was 2.2:1, and the yield 97 % [1562]. Reaction of norbornene with diazomethane in the presence of a range of palladium salts led to efficient cyclopropanation; it was considered that the active species was metallic palladium formed *in situ.* Selectivity was for the least hindered double bond; thus 4-ethenyl cyclohexene was converted mainly to 734 [1563]. In the presence of $[PdCl_2(PhCN)_2]$, 735 reacted with Ph_2CN_2 to give 736. Using $Rh_2(OCOMe)_4$, which does not coordinate alkenes readily, the main product was 737 [1564]. A range of catalysts was compared for the reaction of ethyl diazoethanoate with substituted alkenes. The *trans:cis* ratio was generally lower for $[PdCl_2(PhCN)_2]$ or $Pd(OCOMe)_2$ catalysed reactions than when rhodium or copper complexes were used [1565]. Reaction of norbornene with E-1-bromo-2-phenylethene and R_2NH in the presence of $[Pd(PPh_3)_4]$ gave 738. The reaction mechanism involves oxidative addition of the haloalkene to palladium(0) followed by norbornene insertion and cyclisation [1566]. In an analogue of a Simmons Smith reaction, E-dialkyl butene-1,4-dioates were cyclopropanated by CH_2Br_2 in the presence of nickel(II) and zinc metal. An enantiomer excess of up to 65 % was obtained using the menthyl esters [1567].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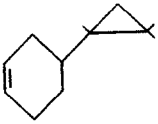
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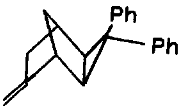

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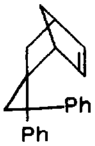

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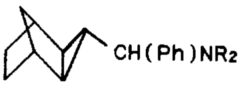

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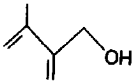
Addition of water to propadiene in the presence of $[Pd(dba)_2]/PPh_3/CO_2$ gave 739 selectively. The reaction with methanol or ethanol proceeded in the absence of CO_2 [1568]. Reaction of butadiene with ROH in the presence of $PdCl_2/CuCl_2$ gave 740 and 741 [1569].



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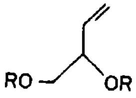

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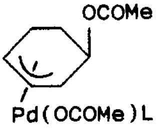
Isoprene was reported to react with Na[OMe]/MeOH in the presence of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]/PBu_3$ to give 46 % methoxyalkenes, but details were sparse [1570]. Reaction of alcohols with $BnOC(=CH_2)CH_2F$ using $[PdCl_2(cod)]$ as a catalyst gave $BnOC(OR)(CH_3)CH_2F$. This acetal was rather resistant to hydrolysis because of the electron withdrawing fluorine, but could be hydrogenolised to regenerate ROH [1571].

Reaction of butadiene with $Pd(OCOMe)_2/MeCOOH/MnO_2$/benzoquinone gave 742, *via* a palladium allyl complex. The reaction stereochemistry could be controlled by the conditions. Transfer of ethanoate from palladium in 743 gave 744. This transfer could be blocked by addition of halide to give 745; then external attack of ethanoate gave 746. The process was used to prepare a key intermediate for a synthesis of shikimic acid [1572]. The reaction also works readily for acyclic substrates, and 747 was prepared with good selectivity [1573].

742



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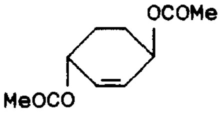

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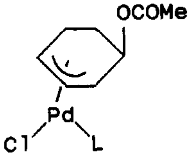

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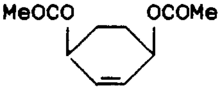
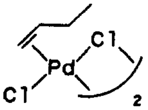


746

747

There has been a careful study by nmr spectrsocopy, of the palladium promoted addition of amines to alkenes. The intermediates 748-752 were invoked; 752 could be isolated at low temperature and was converted to the addition product by hydrogenation or reaction with hydride [1574].



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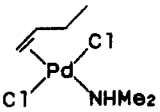

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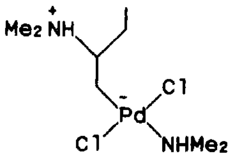

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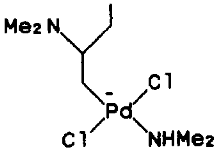

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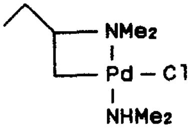
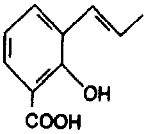


752

Cyclisation of 753 to give the benzofuran was accomplished under an oxidising atmosphere in the presence of $PdCl_2$/CuCl [1575]. Using the chiral palladium complex 754 as catalyst, the major product of cyclisation of 755 was the ethenyl furan 756, but optical yields were generally low [1576]. A mechanism was proposed for the palladium(II) catalysed cyclisation of 757 to 758 [1577]. The regiochemistry of cyclisation of substrates such as 759 and

760 was analysed in terms of Baldwin's rules [1578].



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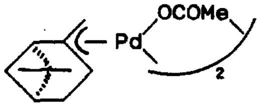

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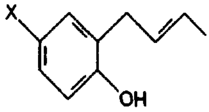

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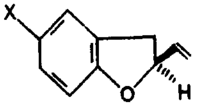

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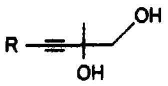

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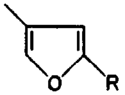

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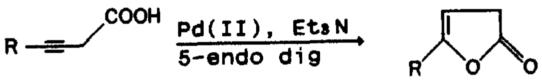

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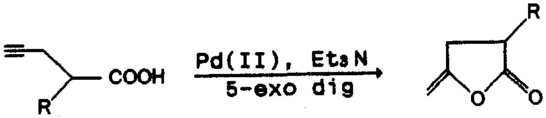

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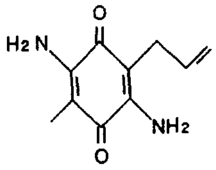
The presence of a palladium(II) catalyst facilitates the cyclisation of 761 to 762, but is not essential. 763, however, gave 764 and 765 *via* palladium catalysed alkene amination [1579]. The cyclisation of 766 to 767 has been described in detail [1580]. A five-membered ring was also formed in the cyclisation of 768 [1581]. Reaction of 769 with [$PdCl_2(PhCN)_2$] involves *cis*-addition to give 770, which may be carbonylated to 771 or undergo elimination to 772. The chloropalladium intermediate 773 is isolable in the *trans*-series, since there is no facile *cis*-elimination pathway, and may undergo carbonylation or hydrogenolysis [1582]. In the reaction of 774, each of the adjacent nitrogen atoms may be involved in attack on the palladium coordinated alkyne [1583].



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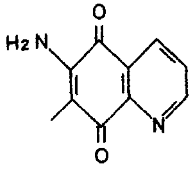

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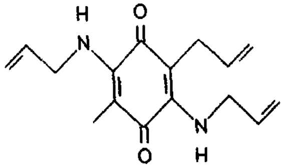

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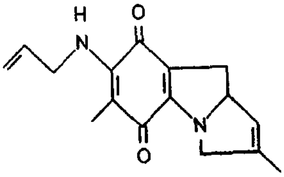

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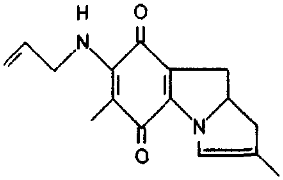

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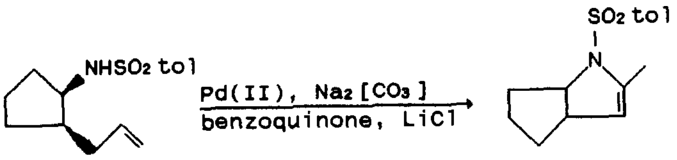
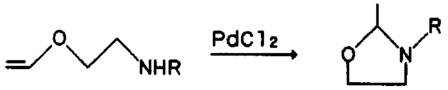


766 **767**



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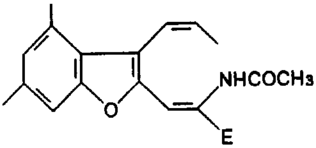

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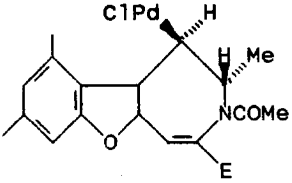

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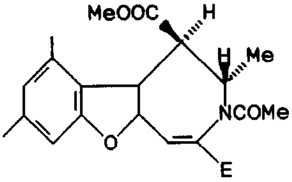

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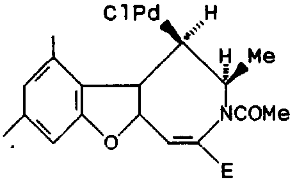

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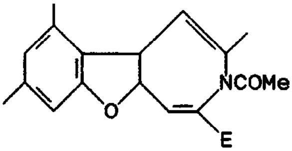

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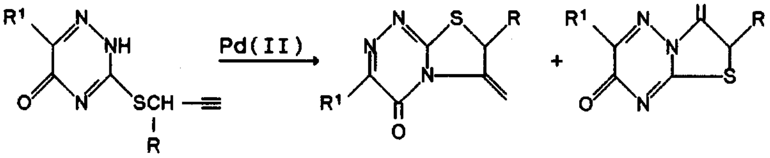

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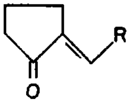
13.6 Isomerisation

The catalytic isomerisation of alkenes by palladium(II) has been studied. It was concluded that the reaction does not involve oxidative addition or a Pd(IV) intermediate; basic phosphines attenuate activity, which is the opposite effect from the one expected for a mechanism involving Pd(IV). Alkenyl, σ-alkyl and π-allyl complexes were invoked as intermediates [1584]. Isomerisation of **775** in the presence of $[PdCl_2(PhCN)_2]$ gave the conjugated product [1585], and reaction of **776** gave the endocyclic enone [1586]. The isomerisation of 3-pentene nitrile by $[Ni\{P(OR)_3\}_4]/CF_3SO_3H$ was studied. There is a kinetic preference for the formation of 4-pentene nitrile, which is formed and hydrocyanated before any significant amount of the conjugated isomer is produced (see also section *13.5*) [1587]. In the presence of $PdCl_2/CuCl$, *cis,trans*-1,5-cyclododecadiene was converted to *cis,cis*-1,6-cyclododecadiene [1588]. $[Pd(SnCl_3)_4]^{2-}$ fixed on AV-17-8 anion exchange resin has been shown to catalyse double bond migration in hexene [1589].

775



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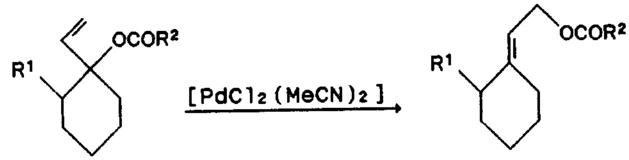
There continue to be examples of the removal of allyl protecting groups by isomerisation and hydrolysis (see also section *13.7*). Allyl ethers of carbohydrates have been isomerised and cleaved in the presence of *trans*-$[PdCl_2(NH_3)_2]$ in excellent yield [1590], and alloxycarbonyl derivatives of sugars were deprotected in the presence of both allyl ethers and prop-2-enylidene acetals using $[Pd(PPh_3)_4]$ as the catalyst [1591]. Allyl esters were used as protecting groups in the synthesis of aspartyl peptides, and could be removed using $[Pd(PPh_3)_4]$ and dimedone or morpholine [1592]. Deallylation of an ester using $[Pd(PPh_3)_4]/PPh_3/[RCOO]Na$ was used in a synthesis of penem derivatives [1593], and a related process in an approach to the amaryllidacae alkaloids [1594]. Allyl groups have been removed in the presence of trityl and silyly groups [1595]. Deallylation of allyl phosphonate esters has been noted in the presence of $[Pd(PPh_3)_4]$ [1596].

Various transpositons of allyl esters have been noted (reaction

(41)) [1597], and reaction (42) was used in a synthesis of (±)-α-(methylenecyclopropyl)glycine [1598]. Reaction of 777 with catalytic [Pd(PPh$_3$)$_4$] gave 778 in good yield. With substrates of the type 779, the major product, 780 was formed by elimination from a π-allyl palladium complex [1599]. In the conversion of reaction (43), product formation is supposed to be driven by the formation of an *S,O*-chelated nickel complex, but the reaction mechanism was not proven in detail [1600].



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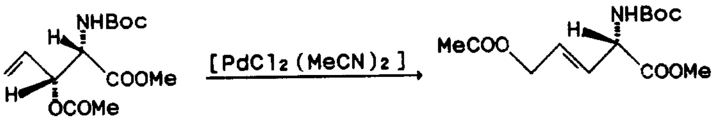

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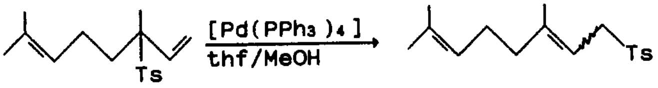

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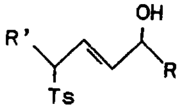

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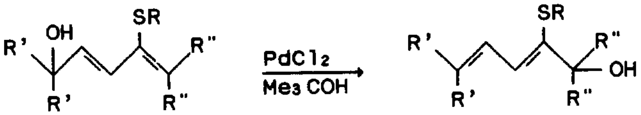
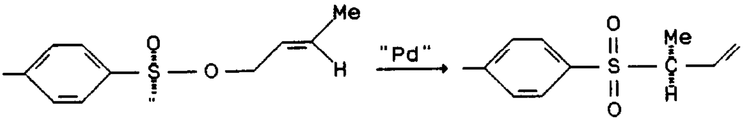


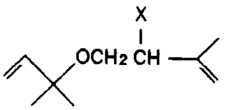
(43)

The sulphinate/sulphone rearranegment of reaction (44) proceeds with good retention of stereochemistry in the presence of either [$Pd(PPh_3)_4$] or [$Pd(dppe)_2$]; the reaction mechanism proposed involves a π-allyl intermediate [1601]. The regiochemical outcome of the reaction was studied with a range of substrates [1602].



(44)

Conversion of 781 to 782 in the presence of $Pd(OCOMe)_2/PPh_3$ was thought to involve a palladium allyl intermediate [1603].



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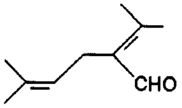
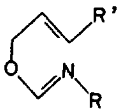


782

There has been a review of palladium catalysed Cope and Claisen rearrangements, and more generally, of 3,3-sigmatropic reactions [1604,1605]. Rearrangements of 783 have been carefully studied. In the presence of palladium(II), 784, the product of a 3,3-sigmatropic reaction is the exclusive outcome. When the catalyst is palladium(0), a mixture of 784 and 785 is formed. The palladium(II) catalysed reaction involves an intermediate such as 786, and the observed stereoselection depends on the chair topolgy of the six-membered ring intermediates. The palladium(0) reaction is not generally either regio or stereospecific. Deuterium labelling studies indicate a π-allyl palladium intermediate, which may be attacked at either end by $[O{=}CH{-}NPh]^-$ [1606]. Related reactions include (45) [1607], (46) [1608] and (47) [1609]. Chirality transfer is generally good [1610].



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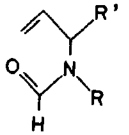

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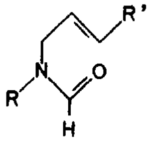

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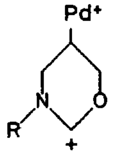

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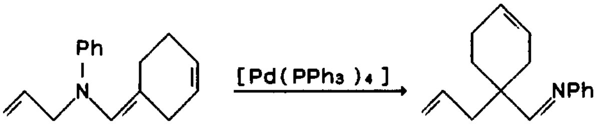
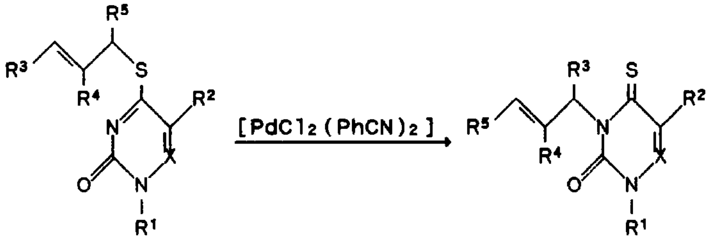
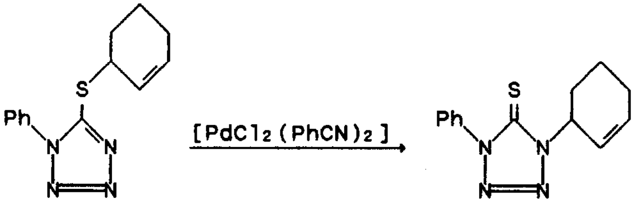


(45)



(46)

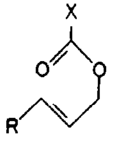
X = N or CR



(47)

In the palladium(II) catalysed reaction of 787, comparable amounts of the E- and Z-isomers of 788 were formed [1611]. For 789 (X = Me or NMe_2) 790 is the main product, but some of the Z-isomer of the starting material was also noted. This latter reacts very slowly [1612]. In the rearrangement of 791 to 792 and 793, the N(1) alkylated product, 792, generally predominates, but substitution at the 6-position ($R^2 \neq H$) reverses this trend [1613]. 794 was isomerised to 795 in the presence of $[PdCl_2(MeCN)_2]$ [1614].

787 788



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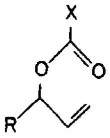

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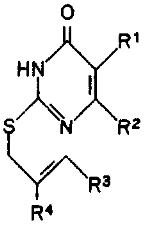

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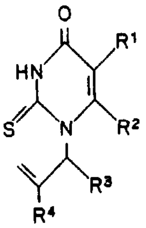

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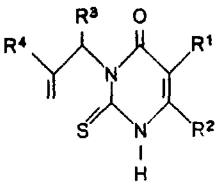

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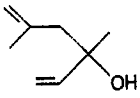

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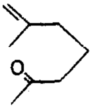
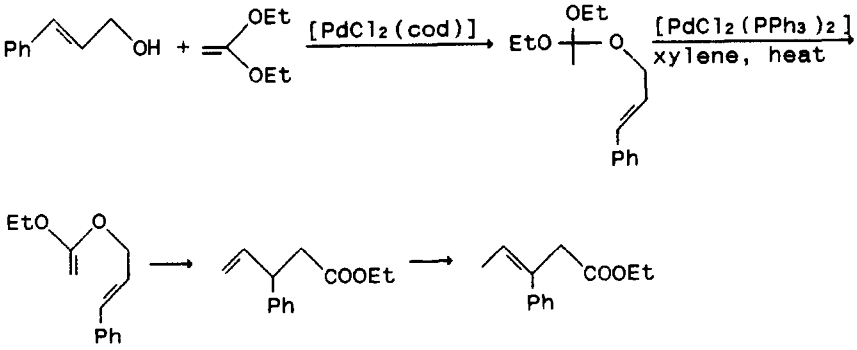


795

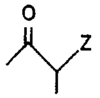
A facile synthesis of γ,δ-unsaturated esters (Scheme 19) involves a palladium catalysed rearrangement in the key step [1615]. The alkoxyallylation of 796 (Z = electron withdrawing group) was accomplished using the rearrangement of 797 at 200 °C in the presence of [Ni(acac)$_2$] [1616].

Conversion of 798 to 799 in the presence of Ni(0) involves a sigmatropic shift, and gives an epimer of the compound produced in the thermal reaction [1617].

There has been reported the first example of a 3,3-sigmatropic shift of a 1,5-enyne in organophosphorus chemistry (reaction (48)) [1618,1619].



Scheme 19 Palladium catalysed synthesis of unsaturated esters [1615].



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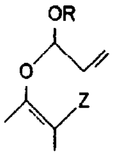

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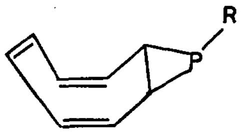

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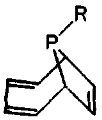

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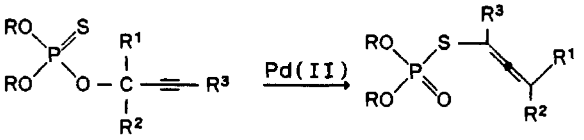
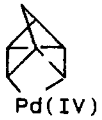


(48)

The rearrangement of quadricyclane to norbornadiene continues to be investigated. Photolysis in the presence of [$PdCl_2$(nbd)] proceeds with a quantum yield greater than 10^2 [1620]. Related reactions were also reported for substituted quadricyclanes [1621]. A kinetic study of the reaction in the presence of $PdCl_2$ suggested a palladium(IV) intermediate such as 800, formed reversibly [1622]. When [$Pd(acac)_2$]/Et_3Al/PR_3 was used as the catalyst system a complex range of norbornadiene oligomers was also obtained by reaction of the first formed product [1623]. The substituted quadricyclane, **801**, was isomerised to the related norbornadiene in the presence of $[PdI_2(Ph_3Sb)_2]$, without damage to the allene unit [1624].

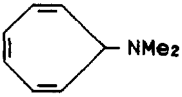


800

801

In the presence of $[Ni(CO)_2(PPh_3)_2]$, **802** was converted successively to **803** and **804**, the reaction proceeding *via* the norbornadiene [1625]. The opening of three-membered rings in tri- and tetracyclic species in the presence of palladium complexes has also been noted [1626,1627].

802



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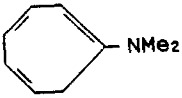
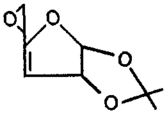


804

The rearrangement of the vinyl epoxide **805** gave **806**, which was used to prepare a synthon for pentenomycin [1628]. The ring opening of **807**, catalysed by $[Pd(dba)_2]$, gave **808**, used as an intermediate in the synthesis of canthaxanthin [1629]. Ring expansion of the aziridine **809** probably proceeds *via* a palladium allyl complex; six-membered rings were similarly obtained from azetidines [1630].



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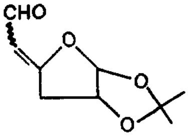

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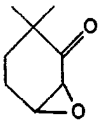

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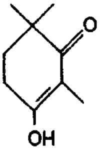

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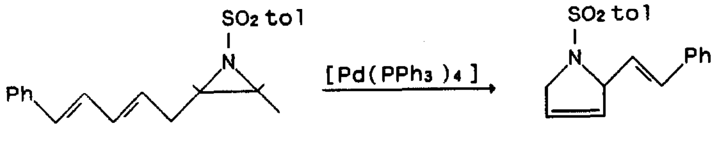
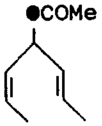


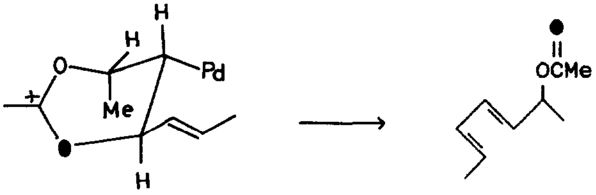
809

Isomerisation of methyl methanoate to ethanoic acid in the presence of CO/MeI was catalysed by a range of complexes, including [Pd(acac)$_2$] [1631]. Conversion of ethanal to ethyl ethanoate was catalysed by a giant cluster formulated as $\{Pd_{561}(phen)_{60}\}\{OCOMe\}_{180}$ [1632].

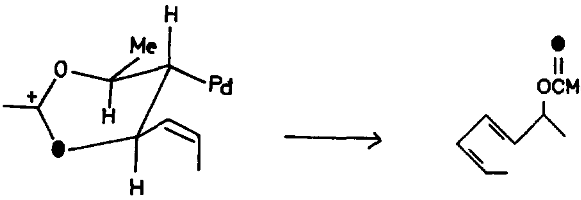
The isomerisation of 810, labelled with ^{17}O, has been studied in some detail. Reaction with palladium(II) gave either 811 or 812. The thermodynamic product, 813, is the minor one, presumably because of the unfavourable steric interactions in 811 [1633].



810 ● = ^{17}O

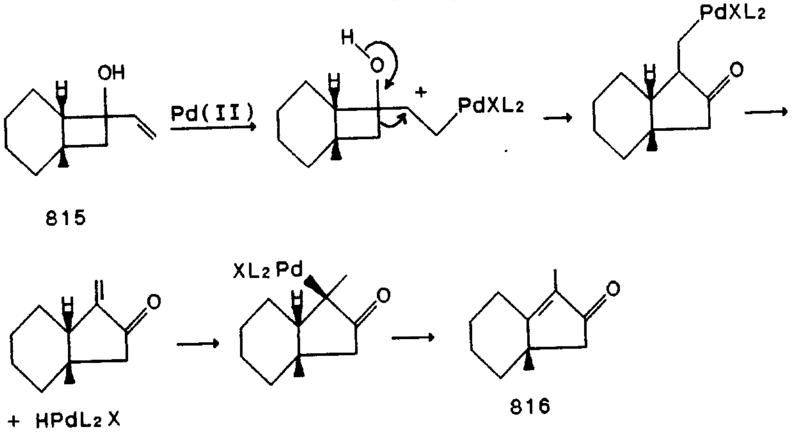


811 813

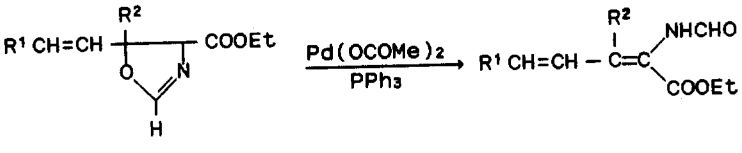


812 814

Ring enlargement of **815** to **816** was proposed to involve the mechanism of Scheme 20 [1634]. Isomerisation of **817** to **818** probably involves a π-allyl intermediate, and β-elimination of PdH [1635].



Scheme 20 Palladium catalysed ring expansion [1634].



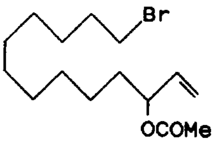
817 **818**

13.7 Substitution of Allyl Derivatives and Related Reactions

There have been two reviews of syntheses involving palladium allyl complexes [1636,1637].

Many more examples of substitution reactions of allylic ethanoates have been reported. Allyl ethanoate itself has been substituted by [Cp]Na in the presence of $[Pd(dba)_2]$/dppe [1638], [TsNH]Na in the presence of $[Pd(PPh_3)_4]$ [1639], PhZnBr using $[Pd(acac)_2]/PPh_3$ [1640] and Me_6Sn_2 using $[Pd(PPh_3)_4]$ as the catalyst [1641]. In a new type of coupling allyl ethanoate reacted with ArBr and Bu_6Sn_2 in the presence of $[PdCl_2(dppf)]$ to give $ArCH_2CH{=}CH_2$. The mechanism proposed involved two rôles for the palladium complex. The initially formed π-allyl complex reacted with Bu_6Sn_2 followed by {ArPdBr} to give $\{Pd(\eta^3\text{-}C_3H_5)(Ar)\}$. This could also be obtained from $ArSnBu_3$ and the allyl complex. Coupling then released the product [1642]. Palladium complexes on alumina catalysed the reaction of allyl ethanoate with species with pKa's between 5 and 13, without the necessity to preform the carbanions [1643]. The enolate of 2-methyl cyclopentane-1,3-dione was also a suitable nucleophile [1644].

Treatment of 819 with Bu_3SnOPh in the presence of $[Pd(PPh_3)_4]$ gave a mixture of 820 and 821. On thermolysis in the presence of palladium(0), elimination yielded 822. Synthetic applications of this reaction in carbohydrate chemistry were discussed [1645]. Substitution of 823 by $[ArSO_2]Na$ in the presence of $[Pd(PPh_3)_4]$ gave only 824 [1646]. Palladium metal dispersed on graphite or alumina, with PPh_3 added, was used as a catalyst for the substitution of allyl ethanoates, phosphates or cabonates by $[PhSO_2]Na$. Without the added phosphine there was considerable formation of the conjugated isomers of the type $CH_3CH{=}CHSO_2Ph$. The use of palladium on graphite was compared with $[Pd(PPh_3)_4]$; using the heterogeneous catalyst resulted in the formation of more branched products [1647]. New methodology for the use of alkoxide nucleophiles has been described [1648].



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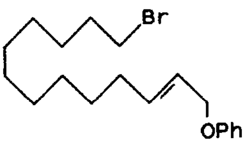

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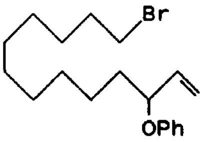

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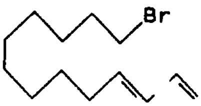

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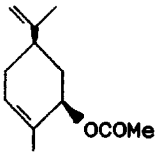

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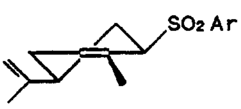
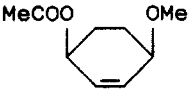


824

Reaction of 825 with 5 molar equivalents of Et_2NH in the presence of $[Pd(PPh_3)_4]$ gave the *cis*-product, 826, with more than 95 % stereospecificity. However, with the *trans*-isomer of the starting material, the stereochemical results depended strongly on the exact reaction conditions; the isomerisation of the starting material competes with the substitution reaction [1649]. Phthalimide reacted with allyl ethanoate, but the conditions needed were realtively harsh, and yields were low. The best leaving group proved to be an isourea [1650].



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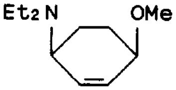
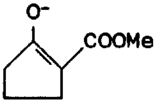


826

Diethyl propanedioate reacted with CH_2=$CHCMe_2OCOMe$ in the presence of $[Pd(PPh_3)_4]/PPh_3$ to give a mixture of the two possible regioisomers, in unspecified proportions [1651]. Similarly, $Na[ROOCCHNO_2]$ reacted smoothly with CH_2=$CMeCH_2OCOMe$, or the related carbonate or phenyl ether [1652]. The 2-carbomethoxy cyclopentanone enolate, **827**, reacted with **828** to give the less hindered of the two possible regioisomers, which was used in a steroid synthesis [1653]. Reactions of the stabilised anion formed from **829** also gave the less hindered regioisomer [1654]. The cyclopentanone enolate, **830**, reacted with a range of allyl ethanoates to give products such as **831**, which was formed with good stereoselection, and was used in a prostaglandin synthesis [1655,1656]. The use of CH_2=$CClCH_2OCOMe$ as substrate gave a side chain which could be readily hydrolysed to $-CH_2COCH_3$ [1657]. The tin enolate of 4-*tert*-butylcyclohexanone reacted successfully with Me_3SiCH=$CHCH_2OCOMe$ to give both diastereoisomers of **832** [1658].



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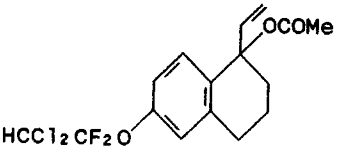

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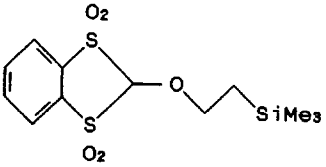

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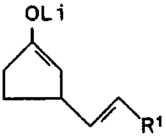

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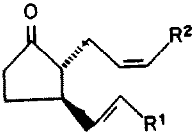

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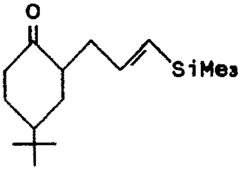
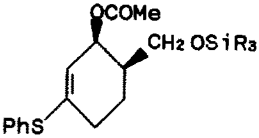
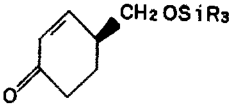


832

In an aim to establish a stereospecific Michael equivalent, 833 was reacted with a propanedioate ester in the presence of [Pd(dppe)$_2$]. The reaction was stereospecific, with retention of configuration, in contrast with the *trans*-stereochemistry obtained in the Michael reaction of 834 [1659].

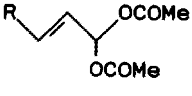


833



834

There have been two reports of the use of allylic acetals such as 835 as substrates. With propanedioate nucleophiles, two products were formed, 836 and 837. The intermediate 838 reacted with the stabilised anion at the acetyl group, to give RCH=CHCHO and $CH_3COCH(COOR)_2$. The anion formed from the latter then reacted with the allyl palladium complex in the more usual way to give the observed products [1660]. Trost's group, however, obtained somewhat different results. The expected substitution product, 841, was initially obtained from 839 and 840, but its fate depended on the nature of R. When R = H, elimination yielded 842, but for R = $CH(COOMe_2)$ cyclisation occurred giving 843 [1661].



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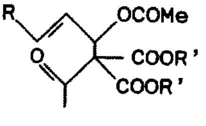

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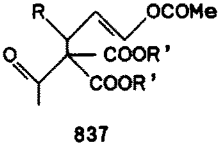
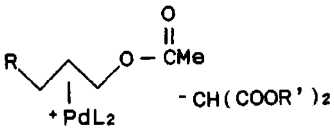


837

The reaction of $Et_2AlSnBu_3$ with $RCH{=}CHCH_2OCOMe$ in the presence of Pd(0) gave $RCH{=}CHCH_2SnBu_3$, which is a very soft source of the allyl anion, and proved useful for reaction with allyl and aryl palladium(II) complexes. It was shown that substitution occurred with inversion of stereochemistry; the tin attacks first at palladium and is then transferred to the allyl unit [1662]. Reaction of **844** with Me_6Sn_2 in the presence of $Pd(OCOMe)_2/PPh_3$ gave **845** *via* **846** and **847** [1663].



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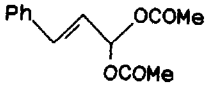

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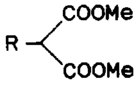

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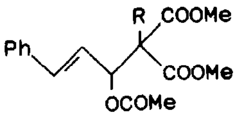

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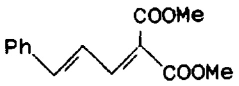

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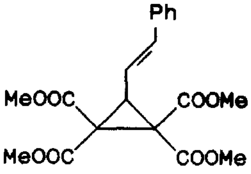

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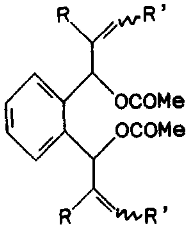

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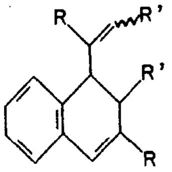

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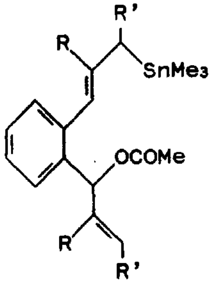

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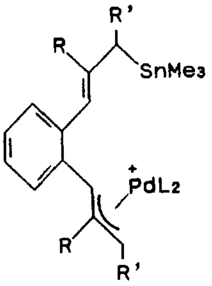
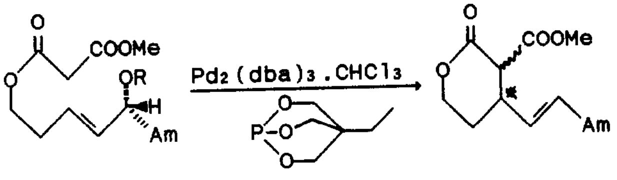


847

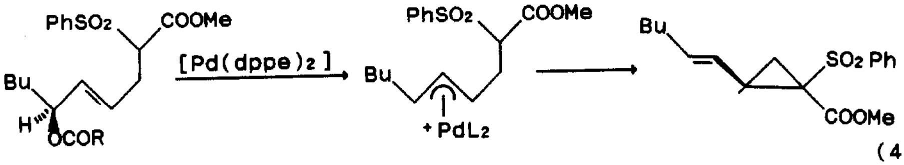
Substitution of a range of allyl derivatives by Grignard reagents has been noted in the presence of $[MCl_2L_2]$ (M = Ni or Pd, L_2 = dppe, dppf or dppf). The branched product, $ArCH(Me)CH{=}CH_2$, was the major regioisomer obtained from

ArMgBr and either $CH_3CH{=}CHCH_2X$ or $CH_2{=}CHCH(CH_3)X$ (X = $OSiR_3$, OPh, Cl, OTHP or OH) [1664]. An enantioselective version of the reaction was reported in the presence of [Ni(CHIRAPHOS)Cl_2] [1665].

Intramolecular reactions may lead to cyclic products. In the reaction of 848 transfer of chirality was 75 % efficient for R = COMe, but 100 % effiecient for R = COOMe [1666]. Complete chirality transfer was also achieved in reaction (49), which was used in the first enantioselective synthesis of dictyopterene A [1667].

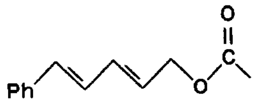


848



(49)

There have been several studies of the regiochemistry of the reaction. In general catalysis by palladium(0) complexes leads to the formation of the less hindered product, in contrast to tungsten catalysed reactions, for which regiochemistry is dominated by electronic factors. Thus 849 reacts with Na[CH$(COOMe)_2$] to give mainly 850, and 851 gives mainly 852 [1668]. Both 853 and 854 react with [Pd$(PPh_3)_4$] to give 855, with substitution occurring at the terminal position. There is apparently no significant migration of the palladium along the chain [1669]. In a more general study, it was shown that amines, enolates and alkoxides react at the less hindered terminus of an allyl, but reaction with PhZnCl is selective for the more hindered site, even when the difference between the two sites is small [1670].



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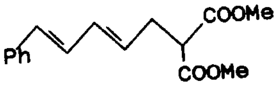

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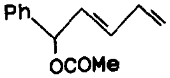

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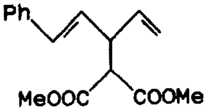

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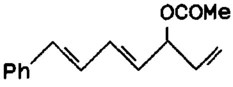
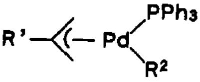


854

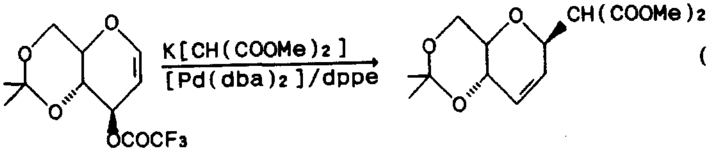
855

One mechanistic study has suggested that the Pd(II)/Pd(IV) rather than the Pd(0)/Pd(II) couple is the important one in catalytic allylation. Addition of PPh_3 to **856** resulted in no significant change in the rate of reductive elimination, implying that there is little of any η^1-allyl palladium(II) intermediate. However, addition of CH_2=$CHCH_2X$ resulted in a substantial rate increase, and the added allylic substrate is incorporated into the products. This observation is consistent with the intermediacy of a palladium(IV) complex, formed by oxidative addition of the allylic substrate [1671]. The mechanism of the coupling of PhZnCl with allyl ethanoate has been studied in the presence of palladium(0) and chiral phosphines. A π-allyl intermediate was proposed, and enantiomer excesses were low [1672].



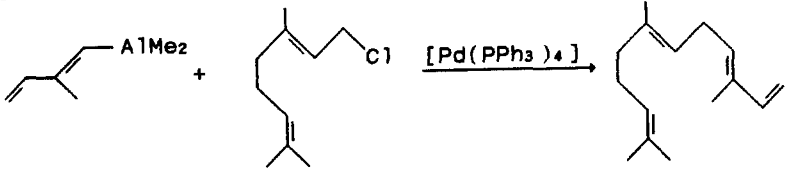
856

Trifluoroethanoate was used as the leaving group in reaction (50); neither ethanoate nor phosphate derivatives gave useful results [1673].



(50)

Halides have also been used as leaving groups; reaction (51) shows the synthesis of α-farnesene [1674] and reaction (52) the preparation of humulene [1675]. There has been a report of the reaction of $[PhTi(OEt)_3]$ with $RCH=CHCH_2X$ (X = Cl or Br) to give $RCH=CHCH_2Ph$ as the major product, together with a smaller amount of $CH_2=CHCHRPh$. Biphenyl was a substantial by-product [1676].



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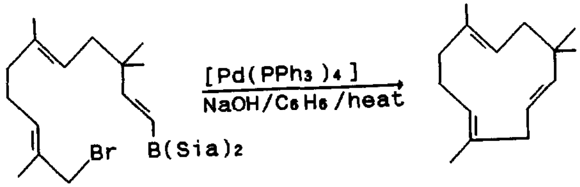
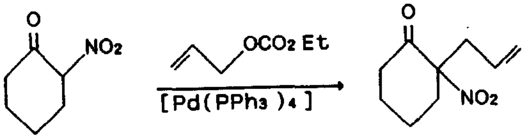


(52)

Allyl carbonates have also been popular substrates, and a number of simple substitutions have been reported (reactions (53) [1677] and (54) [1678]). Tsuji's group have noted reactions with a very wide range of nucleophiles [1679], including trimethylsilyl ketene acetals (reaction (55)) [1680]. Intramolecular reactions have also been successful. 857 reacted with good chirality retention in the presence of NaH, since cyclisation was faster than allyl racemisation, but without added base a racemic product was obtained [1681].



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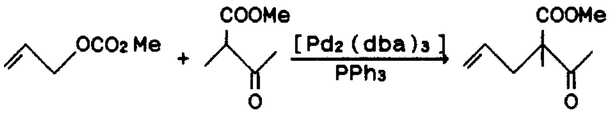

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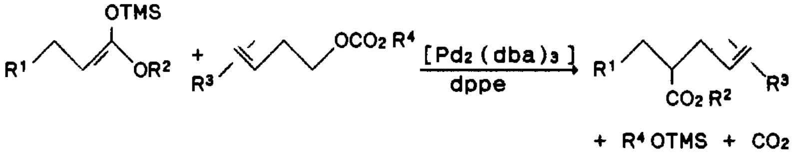

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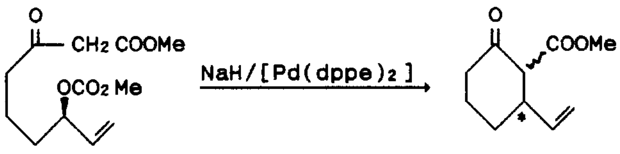
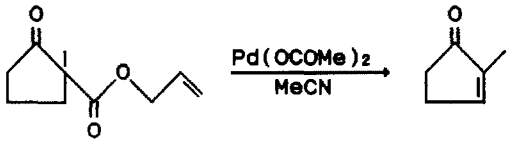


857

There have been a number of reports of reactions such as (56) [1682]. The reaction mechanism involves the initial formation of an intermediate such as 858, which is readily decarboxylated to an enolate equivalent [1683]. The enolate may then be protonated [1684-1687], or may react with the palladium allyl complex to give an α-allylated ketone [1688,1689]. The precise outcome of the reaction depends on the exact nature of the substrate and the reaction conditions. Reaction of either 859 or 860 with $[PdL_n]$, or $RC(OSiMe_3)=CHCH_2R'$, $CH_2=CHCH_2OCO_2R^3$ and $[PdL_n]$, gave an equilibrating mixture of 861 and 862. Three possible fates were noted for this mixture. β-Elimination gives 863, protonation 864, and allylation 865. Addition of mono or bidentate phosphines promoted allylation, and a "ligand free" environment (MeCN solvent) gave mainly elimination [1690]. The Carroll rearrangement of alkenyl allyl carbonates proceeds thermally at 170-200 °C. However, the conversion of 866 or 867 to 868 occurs under very mild conditions in the presence of transition metal complex catalysts. $[Ni\{P(OEt)_3\}_4]$ was active in thf at reflux temperature; the mechanism is probably analogous to that previously reported for palladium complexes, but was not investigated in detail [1691].



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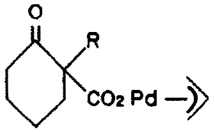

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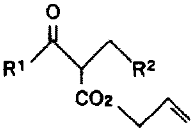

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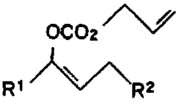

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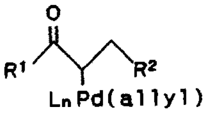

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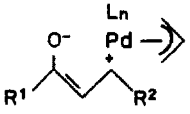

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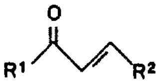

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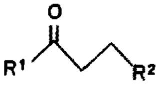

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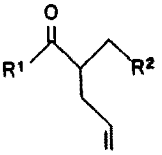

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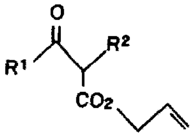

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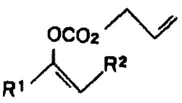

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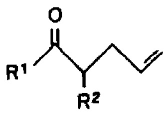
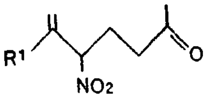


868

A number of papers have reported the use of allyl nitro compounds as substrates. For example, 869 reacted with Na[CH(COOMe)$_2$] in the presence of

$[Pd(PPh_3)_4]$ to give **870** (E:Z = 89:11), the product being used in terpene synthesis [1692]. Substitution of **871** by $Na[SO_2Ph]$ gave a mixture of regiosiomers, with **872** predominent [1693]. Nitroalkenes may be isomerised to allyl nitro compounds in the presence of base, and then substituted by $Na[SO_2Ph]$ in the presence of $[Pd(dppe)_2]$ [1694]. Amine nucleophiles also gave successful results [1695].



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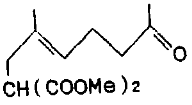

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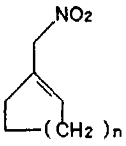

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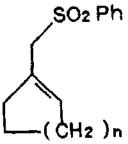
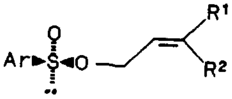


872

Reaction of R_3Al with $PhSO_2CH_2CH{=}CH_2$ in the presence of a catalyst gave $RCH_2CH{=}CH_2$. Low yields were obtained with either $[Ni(acac)_2]$ or $[Pd(acac)_2]$, copper salts being much better catalysts [1696]. Reaction of **873** with $Na[CH(COOMe)_2]$ gave **874**, with 83 % stereospecificity, together with **875** [1697].



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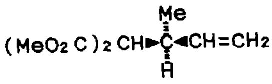


$(MeO_2C)_2CH\overset{Me}{\underset{H}{C}}CH{=}CH_2$

874

$MeCH{=}CHCH_2CH(COOMe)_2$

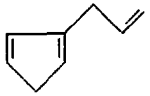
875

The influence of leaving group on substitution regiochemistry has been studied for **876** and **877** (Z = OCOMe or $SO_2C_6H_4$-4-Me). By judicious choice of catalyst and leaving group almost complete regioselection, for either product, was accomplished [1698].

876

877

Coupling of CpMgBr with diallyl ether gave a mixture of **878** and **879**, in the presence of $[Pd(acac)_2]/PPh_3$. Other leaving groups were equally effective [1699]. With $PhSCH{=}CHCH_2OMe$ and RMgX in the presence of $[Ni(dppe)Cl_2]$ the product was $PhSCH{=}CHCH_2R$, formed with good regioselectivity. Elaboration of the product was discussed [1700]. Reaction of the enolate of $R^1COCH_2R^2$ with *N,N'*-dicyclohexyl-*O*-allyl isourea using $[Pd(dba)_2]$/chelating phosphine as the catalyst system, gave a mixture of mono and diallylated products [1701]. The use of $R^1R^2NCO_2CH_2CH{=}CH_2$ as a reagent for allylation has also been considered [1702]. In reaction (57) the leaving group is an aluminium alkoxide [1703]. Attack on $CH_2{=}CHCH(OMe)_2$ by alkenyl alanes or organozinc halides in the presence of $[Pd(PPh_3)_4]$ was exclusively at the γ-position (for example, reaction (58)). Orthoesters were also useful substrates [1704].



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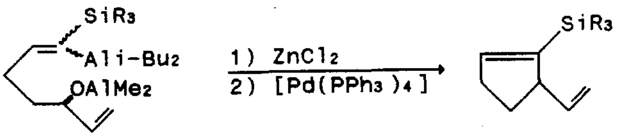

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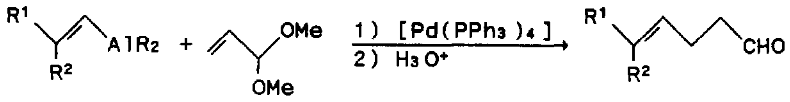
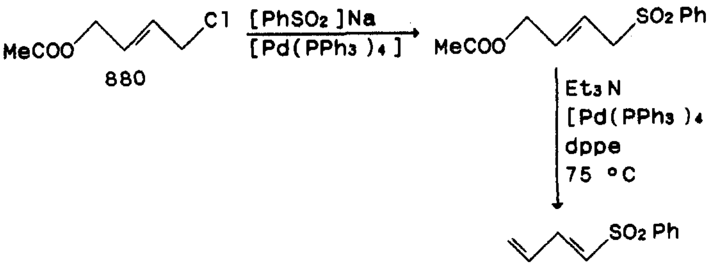
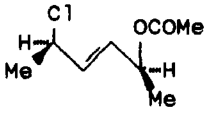


(58)

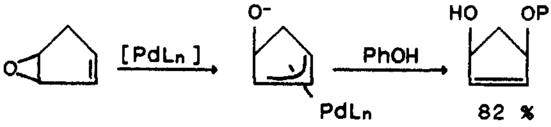
The relative reactivities of organometallics and leaving groups were studied in the series $CH_2{=}CHCH_2X$ (X = Br, OCOMe, OPh and NEt_3) [1705]. Bäckvall's group has studied the reactions of compunds such as **880** prepared by palladium catalysed oxidation of dienes. The halide is preferentially substituted in a palladium catalysed reaction, and the ethanoate may then be eliminated in a further palladium catalysed process to yield a substituted diene [1706]. Alternatively the ethanoate may be substituted by a second, different nucleophile [1707]. The diene oxidation may be controlled to give a diasteromerically pure product such as 881, which may then be substituted in a stereocontrolled manner. This process has been exploited in a synthesis of the pheromone of the carpenter bee [1708].





881

There have been reported several examples of the use of allylic epoxides as substrates for substitution. The initial oxidative addition of palladium(0) generates an alkoxide, which may be used to deprotonated an appropriate incoming nucleophile (reaction (59)) [1709]. This has been exploited in the regio and stereoselective introduction of the 15β-hydroxy group and various side chains to steroid nuclei [1710], and a synthesis of digitoxigenin [1711]. Reaction with CO_2 has been studied (reaction (60)); in this case it is necessary to use a phosphine other than PPh_3, since the latter is displaced from palladium by CO_2 [1712].



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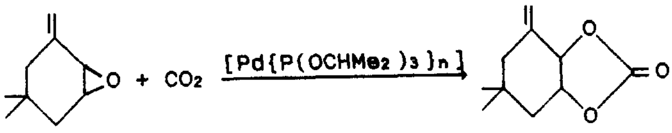
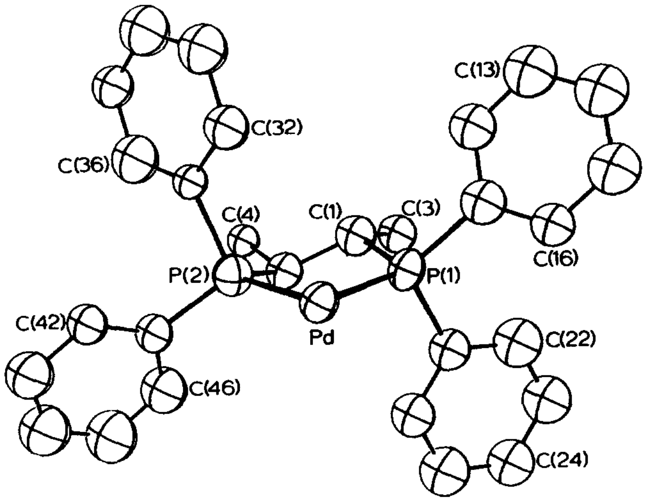


(60)

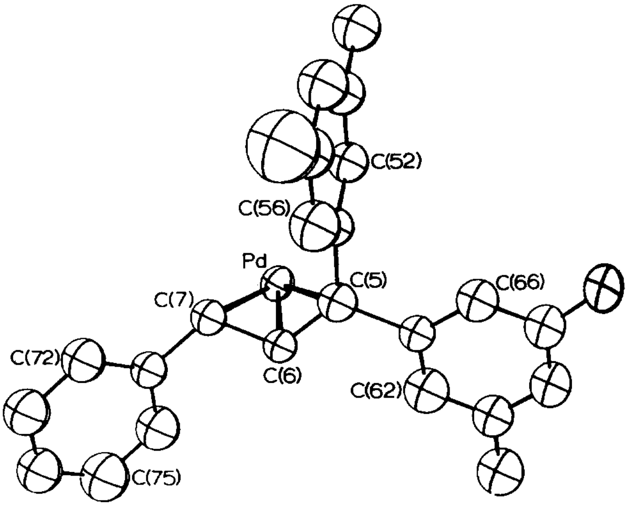
There has been continued work on the mechanism of palladium catalysed enantioselective catalytic allylation. It was shown that π-allyl intermediates epimerise 10-100 times faster than they are attacked by nucleophiles, so that nucleophilic attack is both turnover limiting and the step which determines enantioselection [1713]. The crystal structure and absolute configuration of the major diastereoisomer of a CHIRAPHOS complex has been established in an X-ray diffraction study. In 882 the chelating biphosphine adopts a gauche conformation with a S-configuration, and the phenyl-bearing terminus of the allyl is forced to adopt the R-configuration [1714].



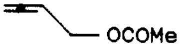
882a Structure of [Pd{η^3-C(C_6H_3-3,5-Me_2)$_2$CHCHPh}(S,S-CHIRAPHOS)][BF_4] showing the CHIRAPHOS ligand bonded to palladium. (Reproduced with permission from [1714])

The reactions of allenyl ethanoates and related compounds with nucleophiles in the presence of palladium complexes may appear to be similar to those of allyl substrates. Thus 883 is converted to 884, which may be cyclised and alkylated in a further palladium catalysed process to give a mixture of 885 and 886, the regioselectivity being controlled by the nature of

R [1715]. However, it is not clear that the reaction mechanism is entirely analogous to that with allyl substrates; in the substitution reaction of **887**, the intermediates **888**, **889** and **890** were all considered [1716]. Similar intermediates were proposed in related reactions where the leaving group was OR, OCOR or OSO_2R [1717]. Reaction of **891** with an aryl halide in the presence of palladium(0) yielded an enone, *via* initial addition of RPdX to the allene [1718]. Addition of R^2PdX to $R^1CH{=}C{=}CH_2$ proceeed similarly *via* addition at C(2) of the allene. The allyl **892** was reacted with R_2NH to give **893**, generally in good yield [1719]. Substitution of the propargyl halide **894** gave the allene **895**, though probably not *via* a palladium π-allyl intermediate [1720,1721]. Reaction of $HC{\equiv}CCH_2OCOOMe$ with a range of nucleophiles in the presence of $[Pd_2(dba)_3]$/dppe gave species of the type **896**. Thus with dimethyl propanedioate a mixture of **897** and **898** was obtained, with **897** being isomerised to **898** on heating. A complete reaction mechanism was proposed, invoking both σ- and π-bonded palladium intermediates [1722].



882b Structure of $[Pd\{\eta^3\text{-}C(C_6H_3\text{-}3,5\text{-}Me_2)_2CHCHPh\}(S,S\text{-}CHIRAPHOS)][BF_4]$ showing the η^3-allyl ligand bonded to palladium. (Reproduced with permission from [1714])



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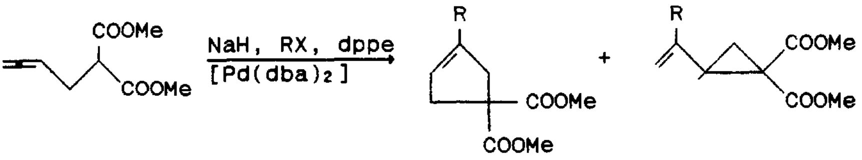
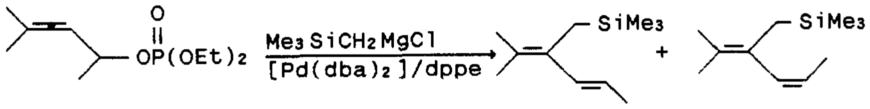
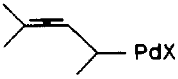


884 **885** **886**



887



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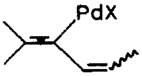

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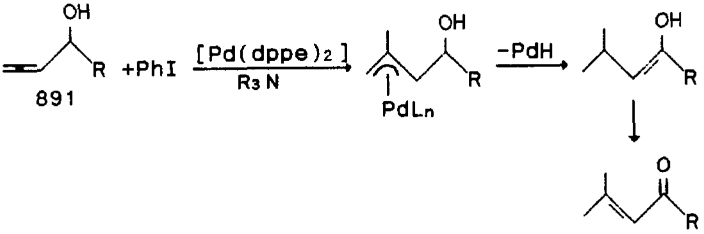
890



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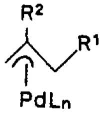

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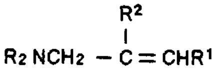
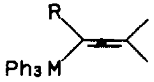


$$R_2NCH_2-\overset{\overset{\displaystyle R^2}{|}}{C}=CHR^1$$

893

Ph$_3$M – C≡C–C(CH$_3$)$_2$–Cl

894



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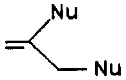

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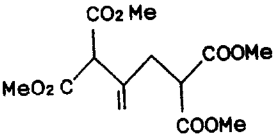

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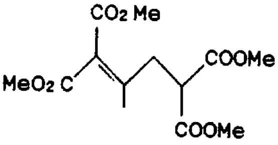
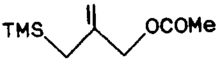


898

Cyclopentannulation reactions in organic synthesis have been reviewed, with particular reference to the use of trimethylene methane (TMM) palladium complexes [1723]. The reaction of the TMM precursor, **899**, with **900** in the presence of $Pd(OCOMe)_2/P(OCHMe_2)_3$ gave **901**, a potential precursor of pentalene [1724]. The stereoselectivity of the reaction of **899** with **902** was shown to be strongly solvent dependent [1725]. In the cyclopentannulation of cyclopentenone with **903**, better yields were obtained when the palladium(0) catalyst was generated *in situ*. The main by-products arose from isomerisation and protodesilylation, and the product, **904**, was used in a synthesis of loganin aglucon [1726].



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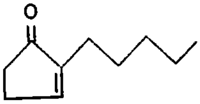

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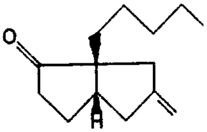

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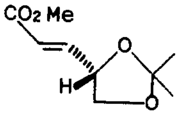

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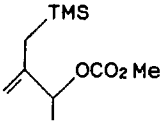

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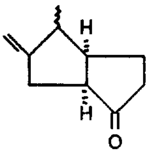
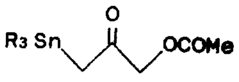
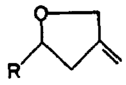


904

Trost's group have reported the synthesis of a range of TMM complex precursors, and a wide-ranging study of their reactions [1727]. It has been shown that tin compounds such as **905** are also useful precursors of palladium TMM complexes; the reaction with aldehydes, RCHO, gave **906** [1728].

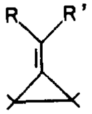


905



906

TMM complexes are also derived from the reactions of palladium(0) or nickel(0) with methylene cyclopropane complexes. Thus the reaction of **907** with **908** in the presence of $[Ni(cod)_2]/P(OC_6H_4\text{-}2\text{-}Ph)_3$ gave a mixture of **909**, **910** and **911**, the amounts of the regioisomers depending on the substituents, although the reaction mechanism was not proven [1729]. Both TMM complexes and nickelacycle intermediates were invoked to explain reaction (61) [1730].



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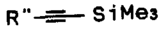

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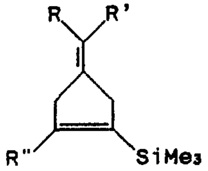

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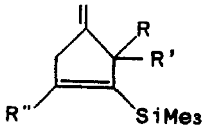

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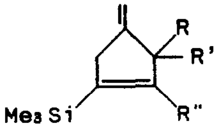

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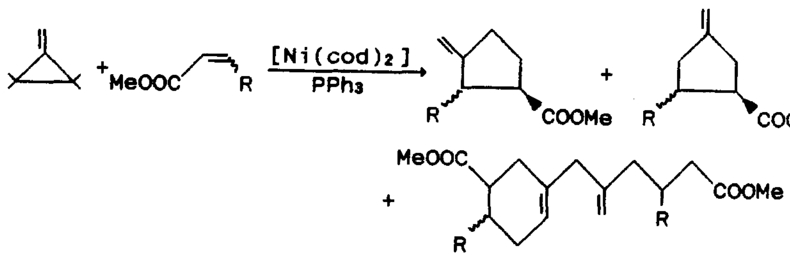
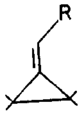
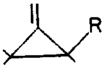


(61)

Reaction of either **912** or **913** with $Ph_2C{=}C{=}NPh$ in the presence of palladium(0) gave a mixture of **914** and **915**, which were readily isomerised to the related pyrroles [1731]. Carboxylation of methylenecyclopropane in the presence of Pd(0) gave a very wide range of oligomeric products, but **916** could be obtained in up to 80 % yield by careful control of the reaction conditions [1732]. The more substituted carboxylation product **917**, obtained similarly, could also be used as a convenient precursor of the palladium TMM complex (reaction (62)) [1733].



912



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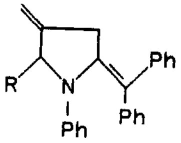
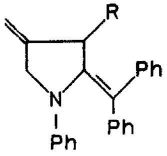


914



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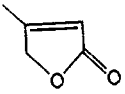

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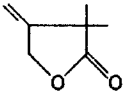
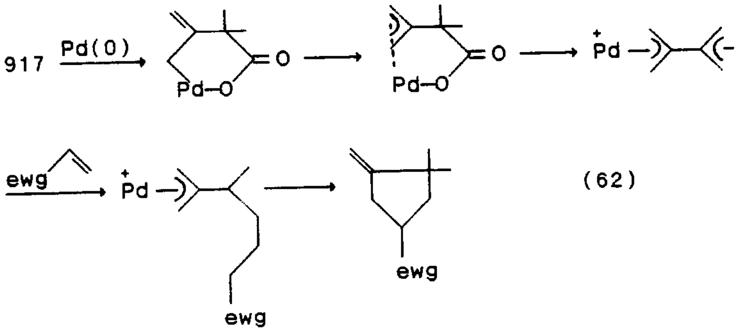
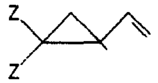


917

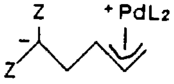


(62)

Some reactions of alkenyl cyclopropanes have been studied. Thus **918** (Z = electron withdrawing group) reacts with [Pd(PPh$_3$)$_4$] to give the anion **919**. This may deprotonate a potential nucleophile, CH$_2$ZZ', which then substitutes the allyl complex to give **920**. Yields depend on the ease of proton transfer [1734]. Intermediates such as **919** also react with CH$_2$=CHZ' to give, after cyclisation, 921 [1735].



918



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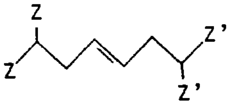

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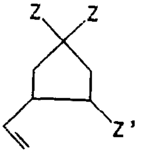
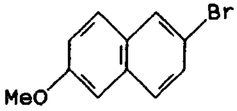


921

13.8 Coupling of Organometallics with Halides and Related Reactions

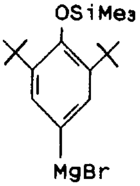
The couplings of a wide range of nucleophiles with aryl, heteroaryl, vinyl, benzyl and other halides have continued to prove popular in synthesis, and a number of reviews have been published [1736-1739].

The coupling of Grignard reagents with aryl chlorides in the presence of [NiCl$_2$(dppe)] allowed the synthesis of 1,3,5-trialkylbenzenes in good yields, with litle contamination by mono and dialkylated species. Under the same conditions 1,2,3-trichloroarenes yielded dialkylated products [1740]. The reactions of a number of dichloroarenes with Grignards in the presence of [NiCl(triphos)][PF$_6$] has been studied. The major product was the monoalkylated species, and the regiochemistry in more substituted dihaloarenes depended on the nature of the Grignard reagent [1741]. The reaction of ethenylmagnesium bromide with 922 in the presence of [NiCl$_2$(dmpe)] gave the alkenylated product, which was hydrocyanated using [Ni{P(OC$_6$H$_4$-4-Me)$_3$}$_4$] as the catalyst, to give a naproxen precursor. Ibuprofen was synthesised similarly [1742].



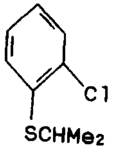
922

The coupling of the 923 with 9-bromoanthracene has been reported to be catalysed by [Ni(acac)$_2$] [1743], whilst the best catalyst for the reaction of ArMgBr with 4-Br-2,2-paracyclophane was [NiCl$_2$(PPh$_3$)$_2$] [1744]. In the coupling of *sec*-BuMgBr with bromobenzene, catalysts of the type [Pd(chelating biphosphine)Cl_2] were surveyed. The succes of [$PdCl_2$(dppf)] was ascribed to the large $P\hat{Pd}P$ and the small $Cl\hat{Pd}Cl$ angle, established in an X-ray diffraction study [1745].



923

Reaction of 2-MeC_6H_4MgBr with **924** in the presence of [$NiCl_2(PPh_3)_2$] gave **925** by the preferential displacement of the halide. However, with **926** as the substrate, the sulphur containing ring was readily opened, yielding **927**. A range of reactions with benzothiophene as the substrate was also reported [1746]. The methylthio group was displaced from **928** by MeMgBr in the presence of [$NiCl_2$(dppe)] [1747], and reactions of a range of aryl, heteroaryl and alkenyl thioethers in the presence of [$NiCl_2(PPh_3)_2$] have also been noted [1748]. Reaction (63) proceeds in the absence of a catalyst, but the yields are increased in the presence of [$NiCl_2(PPh_3)_2$]. When the methyl group is replaced with a chiral moiety, chiral biaryls are obtained from the uncatalysed, but not the catalysed coupling reaction, indicating that these proceed by different mechanisms [1749].



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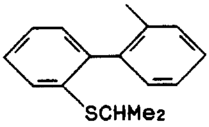

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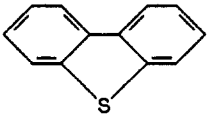

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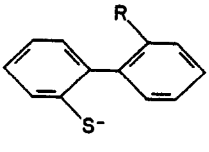

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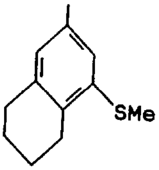

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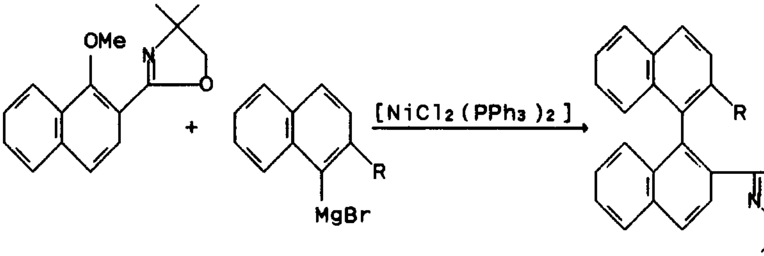
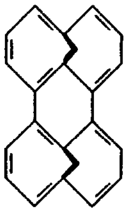


(63)

There have been a number of reports of the use of sodium or potassium salts of stabilised carbanions as nucleophiles towards aryl halides. $[Pd(PPh_3)_4]$ was used as the catalyst in the reaction of sodio ethylcyanoethanoate with aryl bromides or iodides [1750], and the potassium derivative has been reported to react in the presence of $[PdCl_2(PPh_3)_2]$, giving ArCH(CN)COOR in moderate to excellent yields [1751]. $Na[CH(CN)_2]$ reacted with ArX in the presence of $[Pd(PPh_3)_4]$ or $[PdCl_2(PPh_3)_2]$ [1752]. With 1,4-diiodobenzene double substitution occurred, but with 1,4-dibromobenzene, the initially formed $4\text{-}Br\text{-}C_6H_4CH(CN)_2$ was inert to further reaction [1753].

1,1'-Dilithioferrocene reacted with 1-iodonaphthalene in the presence of $[Pd(PPh_3)_4]$ to give a reasonable amount of a mono coupled product. Using $[PdCl_2(dppf)]$ as the catalyst, and 1,8-diiodonaphthalene as the substrate, bis alkylation predominated [1754]. The homocoupling of 2,10-dibromo-1,6-methano-[10]annulene in the presence of $Zn/[NiCl_2(PPh_3)_2]/[Et_4N]I$ has been studied; both the *syn*-product, **929**, and its *anti*-isomer were formed in the ratio 4:3 [1755]. A patent has reported the enantioselective coupling reaction of the lithium enolate of $EtCO_2CMe_3$ with 930 in the presence of $[NiCl_2\{Ph_2PCH(Ph)CH_2PPh_2\}]$, in the synthesis of naproxen [1756].



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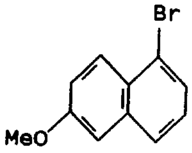


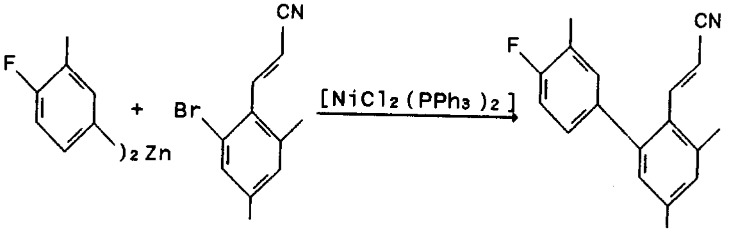
930

The use of organotin nucleophiles continues to prove popular, most particularly because of their tolerance of a wide range of functional groups. The field has been reviewed, with the inclusion of a wide range of halide types as substrates, as well as consideration of similar reactions in the presence of CO to give ketones [1757]. Tin nucleophiles used have included $RSnMe_3$, where R = alkenyl, aryl or alkynyl [1758], and $ArSnBu_3$ [1759]. In both cases a wide range of aryl substrates, bearing either electron donors or electron withdrawers have been used. With Bu_3SnCH_2CN, aryl groups bearing strong electron withdrawers in the 4-position proved to be unsatisfactory substrates [1760].

There have been reports of the reactions of Bu_3SnCH_2OR (R = H or Me) with aryl halides, in the presence of $[PdCl_2(PPh_3)_2]$. Aryl halides bearing either electron-withdrawing or electron-donating groups in the 4-position proved to be satisfactory substrates when R = Me [1761], but with R = H poor results were obtained with substrates bearing strongly electron-withdrawing groups [1762]. The use of Bu_3SnNEt_2 or Bu_3SnSPh as nucleophiles has also been reported [1763,1764].

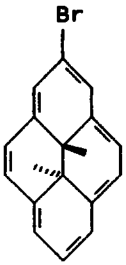
Tin enolates have also been used as nucleophiles, in the presence of a range of palladium derived catalysts; yields were moderate to good [1765-1767]. Soviet workers have employed R_6Sn_2 as nucleophile, in the presence of allyl palladium halide derived catalysts; good yields were obtained only with halides bearing strongly electron withdrawing groups [1768-1770].

Reaction of $CF_2=CFZnCl$ with aryl iodides occurred in the presence of either $[PdL_4]$ or $[PdClL_2Ph]$ to give $CF_2=CFAr$, though the reaction fails with some aryl groups which are substituted with strong electron acceptors [1771]. Diarylzinc compounds reacted with aryl halides in the presence of $[NiCl_2(PPh_3)_2]$ as, for example in reaction (64), which was used in a novel synthesis of β-hydroxy-δ-lactone HMGCoA reductase inhibitor [1772].



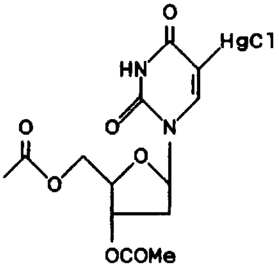
(64)

The catalyst $[Ni(PR_3)_2]$, generated *in situ* from $[NiCl_2L_2]$, was used for the homocoupling of aryl, alkenyl or heteroaryl haildes in the presence of zinc metal [1773]. Homocoupling of methano-[10]-annulene halides was similarly accomplished [1774]. In the attempted homocoupling of 931 in the presence of $[NiCl_2(PPh_3)_2]/Zn$, 41 % of the homocoupled product was obtained. A significant by-product was PhAr, derived from aryl transfer from PPh_3 [1775].



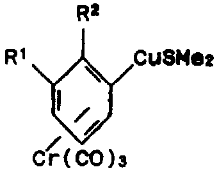
931

The organomercury compound, **932**, reacted with a range of aryl iodides in the presence of [Pd(PPh$_3$)$_4$] to give 5-aryl substituted 2'-deoxyuridines [1776]. A competition experiment has been undertaken in the reaction of (4-MeC$_6$H$_4$)$_3$Al with a mixture of PhCOCl and 4-MeOC$_6$H$_4$I in the presence of [PdCl$_2$(MeCN)$_2$]. The acyl halide proved to be the more reactive substrate, and related carbonylation/coupling reactions were also undertaken [1777]. A series of experiments were undertaken to ascertain the relative reactivities of a range of metal complexes, including derivatives of zinc, cadmium, lithium, magnesium, copper, boron, aluminium, tin and titanium [1778].



932

The preparation of (R^{1}R^{2}NCO)$_2$CuLi and its reaction with iodobenzene in the presence of [PdCl$_2$(PPh$_3$)$_2$]/PPh$_3$/dibal has been shown to yield R^{1}R^{2}NCOPh in moderate to good yield [1779]. Reaction of **933** with R^{3}X (R^3 = vinyl, phenyl or 2-pyridyl) in the presence of [Pd(PPh$_3$)$_4$] gave **934**. The reaction yields were better in cases in which one equivalent of [Pd(PPh$_3$)$_4$] was used to preform ArPdX [1780]. Reaction of **935** with ArI using [PdI(Ph)(PPh$_3$)$_2$] as catalyst could be accomplished using aryl halides bearing either electron donors or electron-withdrawing groups, but the reaction rate was much slower with substrates bearing donor groups [1781].



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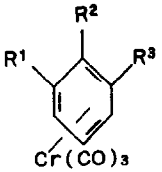

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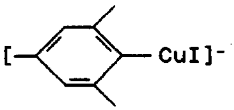
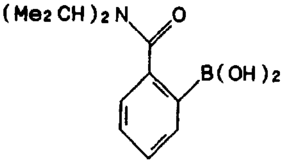


935

Whilst organoboranes are insufficiently nucleophilic to participate directly in substitution reactions of this type, they may be coverted by base to the more nucleophilic boronates. Thus 936 reacted with aryl bromides in the presence of $Na_2[CO_3]/[Pd(PPh_3)_4]/H_2O/PhMe$. Benzylic halides were also good substrates, but alkenyl or allyl halides were unsuitable [1782]. The reaction was also successful with 2,6-disubstituted aryl bromides [1783]. Similar reactions of 937 with aryl halides have been described [1784,1785].



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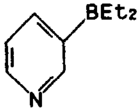
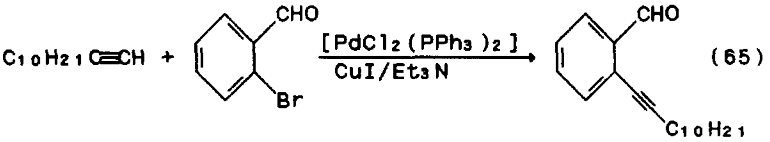
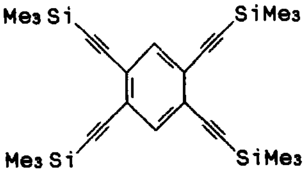


937

Alkynyl metal derivatives needed for coupling to aryl halides are usually generated *in situ* from the alkyne, using CuI/R_3N. A wide range of such reactions have again been described in this period. Coupling of phenyl ethyne with 1,4-dihaloarenes was used as a model for polymer synthesis [1786], and reaction (65), used in the synthesis of a novel class of leucotriene antagonists, demonstrates that the process is compatible with the presence of an unprotected aldehyde group [1787]. The reactions of $HC{\equiv}CCH_2OH$ with aryl and alkenyl halides in the presence of $[PdCl_2(PPh_3)_2]/CuI/Et_3N$, have been studied; the products, $ArC{\equiv}CCH_2OH$ could be converted to $ArC{\equiv}CH$ by reaction with MnO_2/KOH [1788-1790]. The complex $[PdI(Ph)(PPh_3)_2]$ could also be used as a catalyst in this reaction, and for aryl and alkyl substitued alkynes [1791]. A similar process used $HC{\equiv}CCMe_2OH$ as the substrate. After deprotection of the initial product, a second alkyne was coupled to give diaryl alkynes [1792]. Vollhardt's group has made use of the reaction in the coupling of 1,2,4,5-tetraiodobenzene with $Me_3C{\equiv}CH$ to give 938 [1793,1794]. The substitution of the chromium chlorobenzene complex, 939, was achieved in the presence of $[PdCl_2L_2]$ or $[PdL_4]$ [1795].





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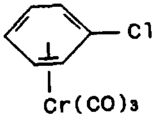
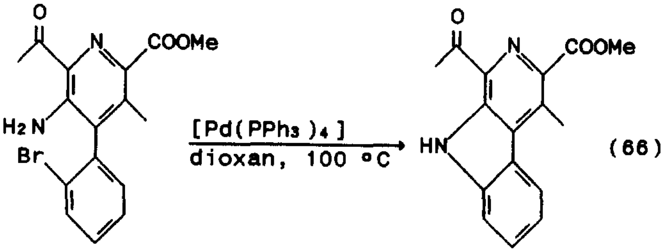
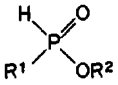


939

Reaction of a nitrogen nucleophile with an aryl halide may be catalysed by $[Pd(PPh_3)_4]$; reaction (66) was used in the synthesis of lavendamycin methyl ester [1796,1797].



Carbon-phosphorus bond formation appears to follow a similar course, but the mechanism has not been studied in detail. Thus reactions of **940** [1798] and **941** [1799] have been reported by Chinese workers. An intramolecular version of the reaction has also been noted [1800]. Reaction of **942** with $HP(=O)(OEt)_2$ in the presence of $[Pd(PPh_3)_4]$ gave **943** in good yield, but pyridines were less satisfactory substrates [1801]. Substitution of **944** by R_3P was catalysed by $NiBr_2$ to give **945**, and a mechanism was proposed for the reaction [1802]. Reactions (67) [1803] and (68) [1804] were reported in the patent literature.



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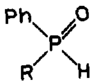

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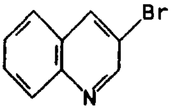

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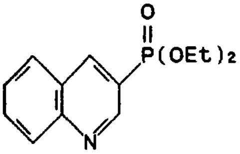

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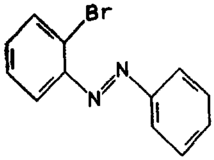

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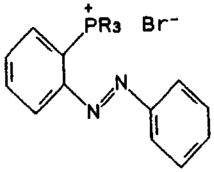

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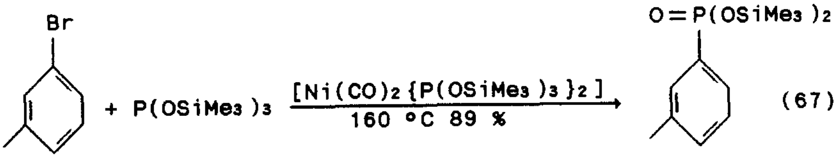

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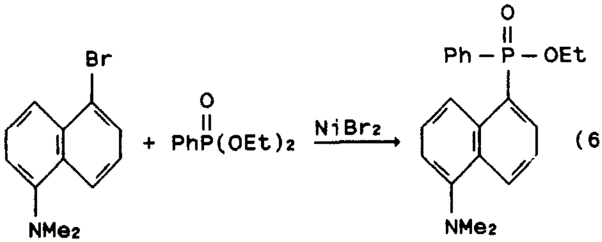
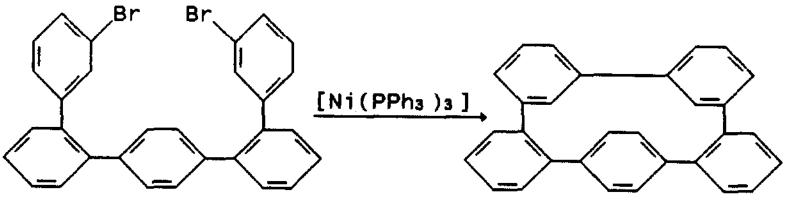


(68)

The homocoupling of halobenzenes or halopyridines has been reported to occur electrochemically in the presence of Pd(0) and/or Pd(II); excellent yields of biaryls were obtained except for 2-methoxy and 2-dimethylethyl substituted compounds. In the latter cases the reduced arene was the main product [1805]. The well-known coupling of aryl halides by nickel complexes was used in reaction (69); yields were low, and Mg/$CuCl_2$ was a superior reagent for this purpose [1806]. In the reaction of 746 with 747 in the presence of [Ni(cod)$_2$], the two component have comparable reactivities, and a complex mixture of homo and hetero coupled products was obtained [1807].



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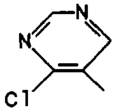

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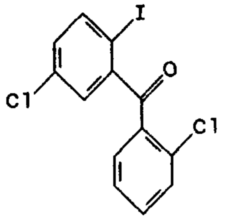
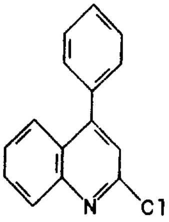


947

The reaction of $Me_3SiCH{=}CH_2$ with iodoarenes to give ethenyl arenes bears a superficial resemblance to the other reactions in this section, but is probably mechanistically distinct. It is catalysed by a range of Pd(0) and Pd(II) complexes [1808].

A similar range of reactions has been described for heteroaryl halides. Thus **948** was substituted by MeMgBr [1809], and **949** by various RMgBr [1810] in the presence of [$NiCl_2L_2$]. The reaction of 3-$MeOC_6H_4MgBr$ with 3-bromopyridine in the presence of [$NiCl_2(PPh_3)_2$] was used in a synthesis of (−)-3-(3-hydroxyphenyl)-*N*-propylpiperidine [1811], whilst its reaction with **950** was used in a synthesis of a dopamine receptor agonist [1812]. A double coupling of 4-$MeOCH_2C_6H_4MgBr$ with **951** in the presence of [$NiCl_2(PPh_3)_2$] has been reported [1813]. A variety of Grignard reagents has also been coupled with **952** in the presence of [$NiCl_2$(dppp)] [1814].



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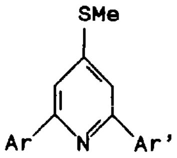

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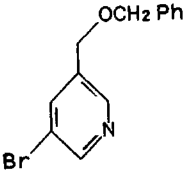

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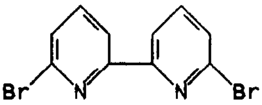

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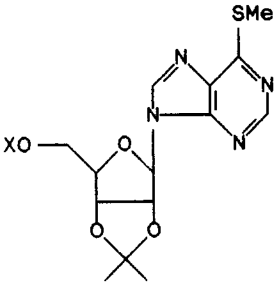
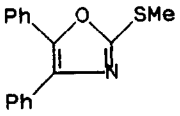


952

The coupling of furan thioethers with Grignard reagents has been reported to occur in the presence of [$NiCl_2$(dppp)] [1815]. 3-Bromothiophene and 3,4-dibromothiophene were coupled with various Grignard reagents in the presence of [$NiCl_2$(dppp)], to give monomers for the preparation of soluble conducting polythiophenes [1816]. Reactions of 2-halothiophenes have been directed towards the same ends [1817]. The heterocyclic thioether **953** could be coupled with RMgX in the presence of either [$NiCl_2$(dppe)] or [$PdCl_2$(dppf)], to give the 2-substituted oxazole [1818].

Reaction of **954** with Reformatskii reagents was acomplished using either [$Pd(PPh_3)_4$] or [$PdCl_2(PPh_3)_2$] as the catalyst. Only iodides gave good yields, and the reaction seems to work well only when the halide is at an activated position of the pyrimidine. When the halide is β- to nitrogen, some homocoupled products, or unreacted starting material are obtained [1819]. Nucleosides substituted at C-5 by a carbocycle or heterocycle were obtained in low yields by coupling of RZnCl with **955** [1820]. Bipyridines were obtained from 2-halopyridines and $Zn/NiCl_2/PPh_3$/dmf, and all the bipyrimidine isomers could be similarly prepared [1821].



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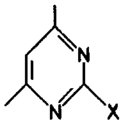

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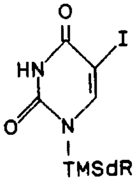
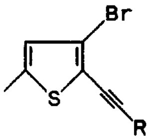


955

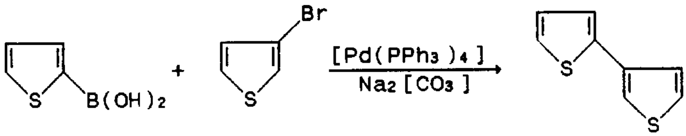
Organozinc compounds were coupled with 3-bromothiophene in the presence of $[PdCl_2(PPh_3)_2]$, but yields were generally lower than those with the related Grignard reagents [1822]. 3-Bromo-2-iodo-5-methylthiophene reacted selectively with $RC{\equiv}CZnCl$ using $Pd(OCOMe)_2/PPh_3$ as the catalyst system to give **956** [1823].



956

Various bithiophene isomers have been synthesised by reactions such as (70) [1824], and thiophene/pyridine coupling was accomplished in analogous reactions [1825]. Whilst **957** and **958** could be coupled using copper metal, and a $[PdL_n]$ catalyst, a better yield was obtained from **958** and $3\text{-}O_2NC_6H_4B(OH)_2$ in the presence of $[PdL_n]$/base [1826].

Trimethylaluminium has been reacted with **959** in the presence of $[Pd(PPh_3)_4]$ to give the methyl substituted compound, and selective monosubstitution of dichloro derivatives has also been accomplished [1827]. Chloro substituted pyrazine *N*-oxides may also be successfully substituted, without reduction of the *N*-oxide functionality [1828,1829].



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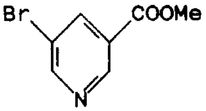

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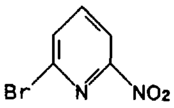

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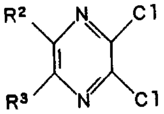
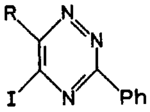


959

The coupling of alkynes with halogenated heterocyles has been widely reported again, with substrates including **960** [1830], **961** [1831] and **962** [1832]. In the reaction of **963** with $HC\equiv CCMe_2OH$, both mono and bis-substitution products were obtained [1833]. The product of the reaction of **964** (X = I or Br) with $HC\equiv CSiMe_3$ was used in a synthesis of azabiphenylene [1834].



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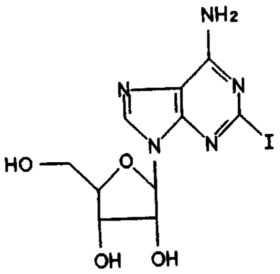

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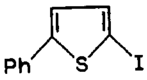

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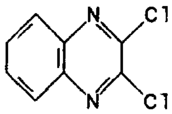

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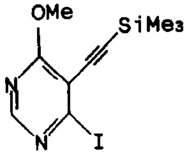
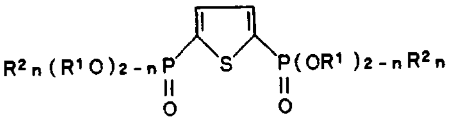


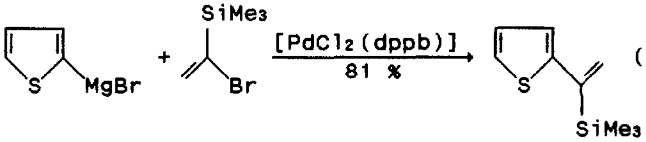
964

The reaction of 2,5-dibromothiophene with $R^2{}_nP(OR^1)_{3-n}$ in the presence of $NiCl_2$ gave **965**. A reasonable mechanism was suggested, but it was not extensively tested [1835].



965

Most of the reactions of alkenyl halides and other alkenyl derivatives are closely related mechanistically to those of the aryl and heteroaryl compounds; the same range of organometallics and catalysts may generally be used. Some examples of simple couplings of Grignard reagents with vinyl halides are shown in reactions (71) to (73) [1836-1838]. The product of reaction (74) was used in a study of regiospecific cycloadditions [1839], that of reaction (75) in a pheromone synthesis [1840] and that of reaction (76) in an approach to the hydrophenanthrene nucleus [1841].



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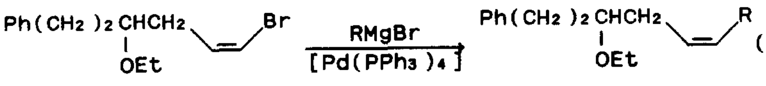

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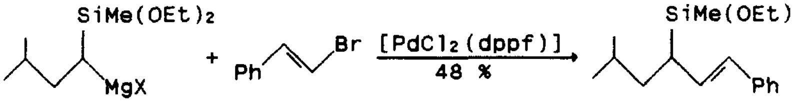

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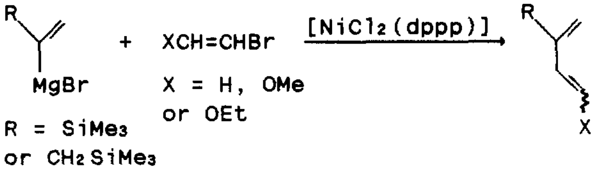

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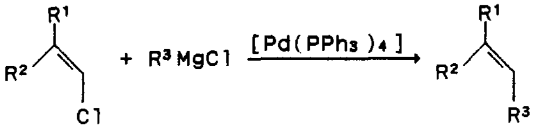

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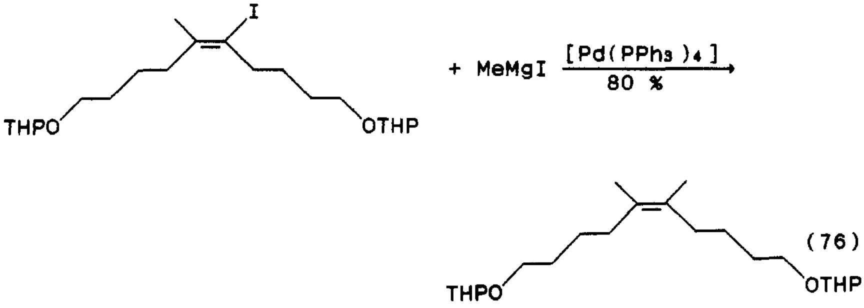
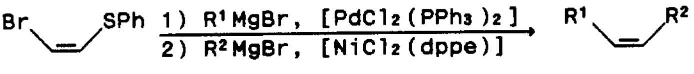
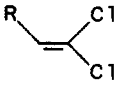


(76)

There have ben a number of studies of the selective reactions of polyfunctionalised alkenes. For example, in 966 the initial substitution reaction is of the halide, but the thioether may also be displaced in a subsequent reaction. Both steps are sterospecific, and the products were used in pheromone syntheses [1842]. E-1,2-Dichloroethene reacts twice with most Grignards [1843,1844], but trichloroethene gave only 967 R = hexyl, octyl, Cy or dimethylcyclohexyl) with 98 % purity [1845]. Reaction of 1,6-diiodocyclohepta-1,3,5-triene with RMgX in the presence of $[Pd(PPh_3)_4]$ or $[NiCl_2(dppp)]$ gave a mixture of mono and bis-substituted products, their ratio depending on R and the the nature of the catalyst. $Li_2[CuCl_4]$ proved to be a more suitable catalyst [1846].

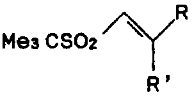


966



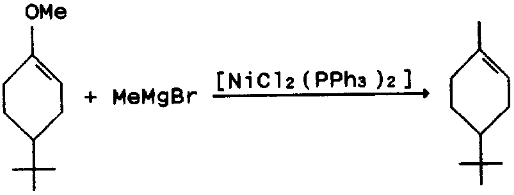
967

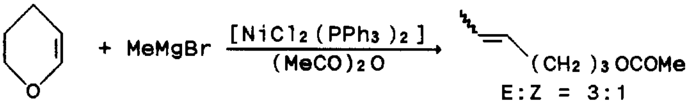
Reaction of **968** with Grignard reagents in the presence of $[Ni(acac)_2]$ gave coupling with retention of stereochemistry, under carefully controlled conditions [1847].



968

It has been shown that alkenyl ethers may be substituted by Grignard reagents in the presence of $[NiCl_2(PPh_3)_2]$ (reaction (77)). This has now been applied to cyclic substrates such as **969**; retention of sterochemistry predominates. Benzofurans such as **970** may also be opened, again with retention of stereochemistry. The process has been used in the synthesis of the termite trail pheromone and the Douglas fir beetle aggregation pheromone [1848,1849]. Reaction of furans under these conditions leads to a double substitution, since the alkenyl ether initially produced reacts a second time with the Grignard reagent. The Z,Z-product generally predominates (reaction (78)) [1850].

 (77)



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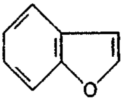

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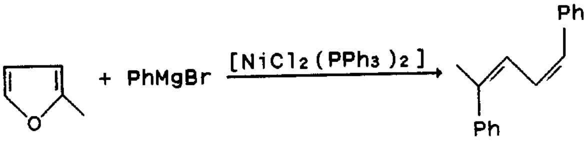
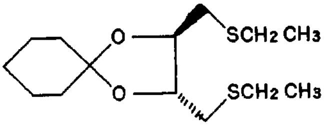


(78)

There have been further reports of enantioselective coupling of PhCH(Me)MgX with bromoethene in the presence of nickel(II) complexes of chiral ligands such as 971 [1851] and 972 [1852], but in neither case were good optical yields achieved. A wide range of chiral diamines, biphosphines and aminophosphines were studied by Brunner's group. The use of the diamines resulted in poor optical yields, whilst with 973 32 % ee was obtained [1853]. Aminophosphine ligands which also contain a thioether functionality have also been investigated; the ee was up to 65 % S using 974 [1854].



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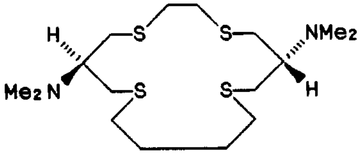

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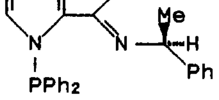

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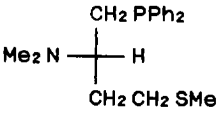
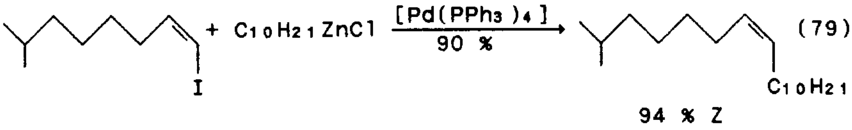


974

Reactions of organozinc compounds with alkenyl halides have also been noted. The coupling of reaction (79) was used in a pheromone synthesis [1788], whilst that shown in reaction (80) led to a short synthesis of Tamoxifen [1856]. Excellent isomeric purity was obtained in reaction (81) [1857]. Alkynyl zinc compounds have also successfully been used as reagents [1858]. The preparation of R_fZnX from R_fX and zinc metal was accelerated by ultrasound, and the organometallic could then be coupled with alkenyl or allylic halides in the presence of palladium complexes [1859]. Homocoupling of 2-bromotropone was achieved in good yield using $Zn/[NiBr_2(PPh_3)_2]/[Et_4N]I$ [1860].



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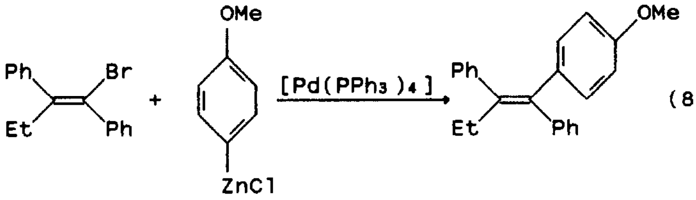

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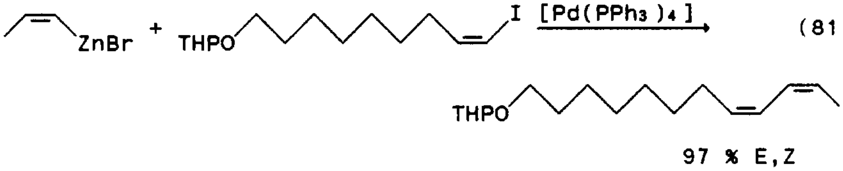
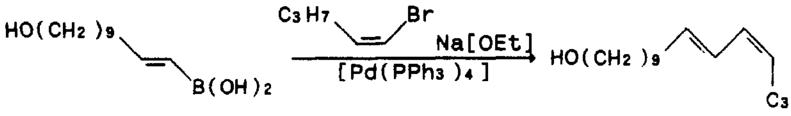


(81)

Organoboron derivatives react readily with alkenyl derivatives in the presence of a base able to convert them to their ate complexes, as previously noted for aryl halides. Reaction (82) is a synthesis of bombykol [1861] and other regio and stereospecific reactions have been reported and reviewed [1862,1863]. Heteroaryl substituted boranes have also proved to be useful reagents [1864,1865].

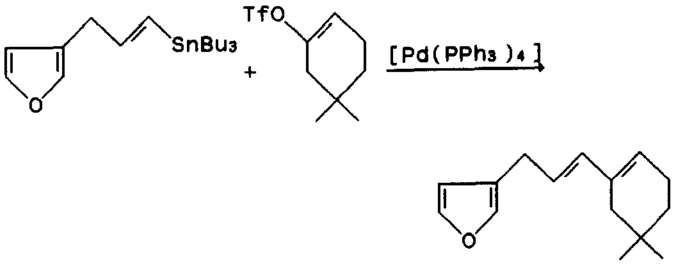


(82)

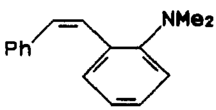
The coupling of E-RCH=CHAli-Bu$_2$ with E-1,2-dichloroethene gave **975** with > 99 % isomeric purity in the presence of either [Ni(PPh$_3$)$_4$] or Pd(OCOMe)$_2$/PPh$_3$. The product was further coupled with an alkyne under the influence of [Pd(PPh$_3$)$_4$]/CuI/Bu$_3$N [1866]. Enol phosphates were substituted by a range of organoaluminium compounds, using [Pd(PPh$_3$)$_4$] as the catalyst [1867].

975

The coupling of alkenyltin compounds with alkenyl triflates has been catalysed by [Pd(PPh$_3$)$_4$]/LiCl. The lithium chloride serves to covert the initially formed alkenylpalladium triflate to the more easily substituted chloride. Reaction (83) was used in a short synthesis of Pleraplysillin-1 [1868]. *N*,*N*-Dimethylaniline is readily lithiated in the 2-position, and then reacts with Z-PhCH=CHBr in the presence of PdCl$_2$/PPh$_3$ to give **976** [1869].

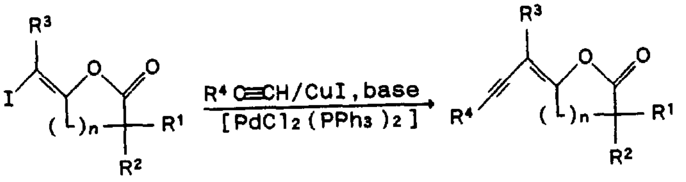


(83)

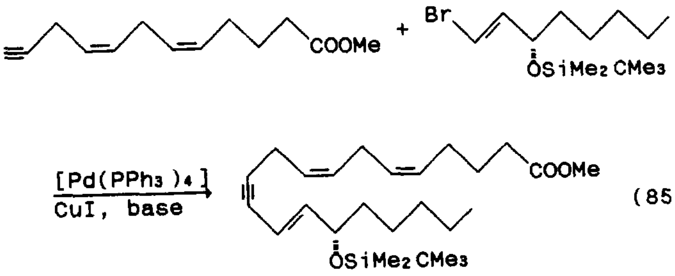


976

Synthetic applications of the coupling of alkynes with alkenyl derivatives continue to be reported. Reaction (84) was used in a synthesis of a suicide inhibitor of serine protease [1870], and reactions (85) and (86) in the preparation of products of the enzymatic oxidation of arachidonic acid [1871-1873]. Reaction of $HC{\equiv}CCH_2CH_2CO_2Et$ with Z-1,2-dichloroethene in the presence of $[Pd(PPh_3)_4]/CuI/BuNH_2$ gave selectively a mono-coupling product, which was used in the synthesis of large ring lactone [1874]. A more extensive study from Vollhardt's group showed that bis-coupling could also be achieved using this catalyst system, the major by-product in their reactions being alkyne dimers and trimers [1875].



(84)



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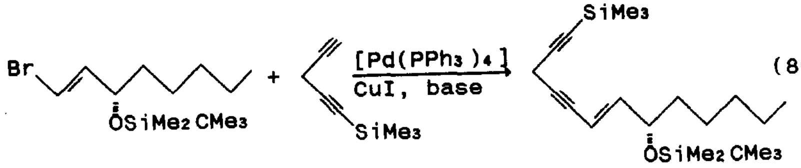
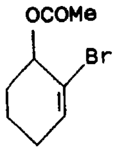


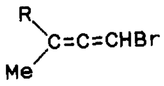
(86)

Two possible substitutions could be envisaged for the substrate 977, since it might behave either as an alkenyl bromide or as an allyl ethanoate. Using either palladium(0) or palladium(II) as the catalyst, and an alkyne as the nucleophile, only the bromide was substituted, though yields were low. When carbonate replaced the ethanoate as the leaving group, the main product was that of elimination [1876,1877].

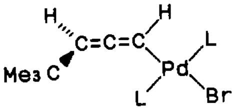


977

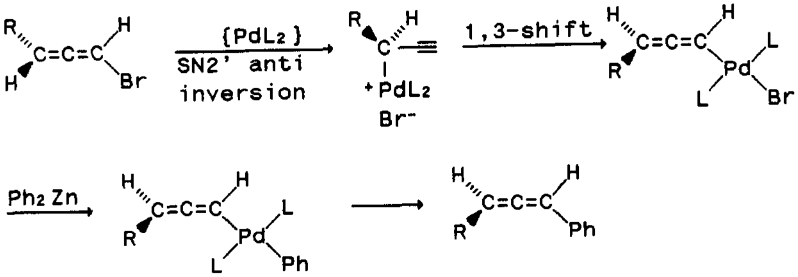
A number of reactions of allenyl halides have been reported. Reaction of 978 with either Grignard reagents or organoaluminium compounds was catalysed by [Ni(mesal)$_2$], [NiCl$_2$(dppe)] or [NiCl$_2$(dppp)]. With chiral substrates the reaction proceded with inversion, the degree of stereoselection depending on the organometallic reagent [1878]. Using Ph$_2$Zn in the presence of [Pd(PPh$_3$)$_4$] the reaction went with inversion for bromides and chlorides, but with retention for allenyl iodides. The mechanism for the reaction with chlorides and bromides is shown in Scheme 21; the intermediate 979 was isolated. With the iodides it was proposed that the reaction involved atom transfer, with the radical, [Pd^{I}IL$_2$] as an intermediate [1879,1880].



978

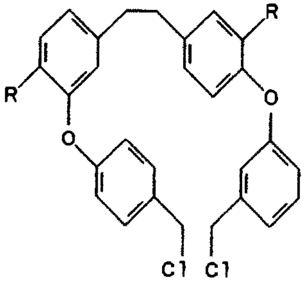


979



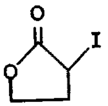
Scheme 21 Mechamism of substitution of allenyl halides by organozinc compounds in the presence of palladium(0).

Two papers have reported the homocoupling of benzylic halides in the presence of nickel complexes and zinc metal. $ArCH_2X$, in the presence of $Zn/[NiBr_2(PPh_3)_2]/[Et_4N]I$, gave $ArCH_2CH_2Ar$ in good to excellent yields, with ArMe as the by-product [1881]. The intramolecular coupling of **980**, using $Zn/[Ni(PPh_3)_n]/[Et_4N]I$ led to a synthesis of Riccardin B [1882].



980

Simple alkyl halides are not generally good susbtrates for the coupling reaction, as the do not undergo rapid oxidative addition to Pd(0) or Ni(0). It has been reported that $[Pd(PPh_3)_4]$ catalyses the coupling of PhYbI with iodobutane, but yields are poor and a large amount of biphenyl is formed. Copper complexes were more suitable catalysts for the cross-coupling reaction [1883]. An exception to the general rule is found for α-halocarbonyl compounds. Thus the α-iodolactone **981** reacted readily with $RSnR'_3$ in the presence of $[PdCl_2(PPh_3)_2]$ [1884] Reactions with α-haloketones were found to be sensitive to steric hindrance [1885]. Homocoupling of $ArCOCH_2Cl$ gave $ArCOCH_2CH_2COAr$ in moderate to good yields in the presence of $Zn/[NiCl_2(PPh_3)_2]/[Et_4N]I$ [1886].



981

There have been two reports of the use of $[PdCl_2(PPh_3)_2]$ as a catalyst for the coupling of Grignard reagents with iodocarboranes [1887,1888].

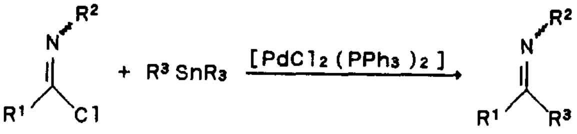
In general acyl halides react readily with organometallics without the need for catalysis. However, there are exceptions, and a number of catalysed reactions have been reported. Grignard reagents reacted with PhSCOCl in the presence of $[NiCl_2(dppe)]$ to give RCOSPh, which was coupled with R'MgX in the presence of Fe(III), thus effecting an overall synthesis of non-symmetric ketones in excellent yield [1889].

The reaction of R_2Zn with R'COCl was catalysed by either $[PdCl_2(dppf)]$ or $[Pd(CH_2Ph)Cl(PPh_3)_2]$ to give ketones in > 90 % yield [1890]. With RZnI as the nucleophile, $[Pd(PPh_3)_4]$ was found to be a good catalyst [1891]. Perfluoroalkenylzinc reagents were coupled with acyl, alkenyl or aryl halides in the presence of $[Pd(PPh_3)_4]$ [1892].

When Et_6Sn_2 was reacted with RCOCl in the presence of various palladium complexes, mixtures of products were obtained, including RCOCOR, R_2CO and RR, but not the unsymmetrical ketone [1893]. Non-symmetrical α-diketones could be obtained by the reaction of $R^1COSnBu_3$ with R^2COCl in the presence of $[PdCl_2(PPh_3)_2]$ [1894].

Non-symmetrical ketones have been prepared in good yields from R_3Al and R'COCl in the presence of $[Pd(PPh_3)_4]$ [1895]. Reaction of Ph_2Hg with PhCOCl using $[PdI(Ph)(PPh_3)_2]/[Bu_4N]I$ as the catalyst system gave mainly Ph_2CO with some biphenyl. Non-symmetrical ketones, including some derived from alkynylmercury compounds, were also prepared [1896].

The reaction of 982 is assumed to proceed by a similar mechanism [1897].



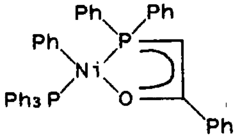
982

13.9 Oligomerisation, Polymerisation and Telomerisation

The dimerisation of ethene has been reported to occur in the presence of heterogeneous $PdCl_2$ based catalysts [1898]. Using $[Ni(cod)_2]/Cy_2PH/TsOH$ as the catalyst system, the products contained 97.5 % butenes, with 98.7 % selectivity for 1-butene [1899]. Both 1- and 2-butenes were obtained using nickel naphthenate/Et_2AlCl or nickel complexed to a polymeric carrier [1900]. Electroreduction of Ni(II) in the presence of PPh_3 and ethene, in propylene carbonate, gave a nickel(I) complex able to catalyse dimerisation of ethene to give mainly E-2-butene, although more 1-butene was observed in the early stages of the reaction [1901].

Cationic allyl nickel complexes catalyse the oligomerisation of ethene, giving mainly linear trimers [1902]. In the presence of $NiCl_2/MeCONMe_2$/2-diphenylphosphinophenol/$Na[BH_4]$, ethene was converted to 39 %

C_4-C_{24} alkenes [1903]. Addition of the 2-diphenylphosphinophenol ligand to either allyl or alkene complexes of nickel also gave catalysts for conversion of ethene to very linear alkene mixtures [1904]. The industrial production and use of α-alkenes prepared using catalysts such as **983** has been reviewed [1905]. Impregnation of **983** on silica or alumina gave good catalysts, but there was some enhancement of double bond migration [1906].



983

The dimerisation and oligomerisation of propene in the presence of $[Ni(hfacac)_2]/i\text{-}Bu_3Al$ or $[Ni(cod)_2]$/hfacac has been studied, and a reaction mechanism proposed [1907]. Other catalysts for this reaction include $[Pd(acac)_2]/R_3P/BF_3.Et_2O$ [1908], and $Pd(CN)_2$ [1909]. In the presence of $[NiCl(PPh_3)(sacsac)]/Et_2AlCl$, the propene dimerisation products dimethylbutene, methylpentene and hexene were formed in the ratio 10:74:16 [1910]. When $[Ni(acac)_2]$ was loaded onto a cross-linked ethene/propene/dicyclopentadiene synthetic rubber functionalised with $-P(=O)(OR)_2$ groups, and treated with $EtAlCl_2$, a catalyst for propene dimerisation was obtained. As the reaction temperature was increased the yields of linear hexenes and 2-methyl-1-pentene increased, whilst that of 4-methyl-1-pentene fell [1911].

Gel-immobilised $NiL_2.nH_2O$, activated by water loss, and treated with R_nAlX_{3-n}, was used as a catalyst for alkene dimerisation. The nature of the active site was discussed [1912]. Butenes have been dimerised over nickel octanoate/$EtAlCl_2$ activated with H_2 to give *n*-octenes and branched species [1913].

Propene oligomerisation has been shown to occur in the presence of $[Ni(hfacac)_2]/i\text{-}Bu_2AlH$, with the activity of the catalyst increasing with increasing temperature [1914]. In a study of $[Ni(hfacac)_2]$ with a range of additives, catalytic activity was shown to increase with the Lewis acidity of the added aluminium compound [1915]. NiO prepared by dehydration of nickel oxide and basic nickel carbonate, supported on a range of surfaces, was compared with $[Ni(Cp)_2]/SiO_2$ or homogeneous $[Ni(acac)_2]$ [1916]. Nickel(II) immobilised on polyvinylpyridine grafted ethene-ethylidenenorbornene-propene rubber was used for dimerisation and polymerisation of a range of alkenes [1917]. Oligomerisation of 1-hexene using nickel methanoate/Et_3Al gave vinylene dimers and trimers [1918].

Oligomerisation and cooligomerisation reactions of ethenyl monomers containing functional groups have been reviewed [1919]. The reactions of propenoate esters have again been prominent in this area. The dimerisation of methyl propenoate to give a 7:1 mixture of **984** and **985** was catalysed by $[Pd(RCN)_4][BF_4]_2$ [1920]. The rate of reaction in the presence of $[PdCl_2(PhCN)_2]$ was enhanced by the addition of Lewis acids, and a palladium hydride complex was invoked as an intermediate [1921]. When the catalyst was $[Pd\{\eta^3\text{-}CH_2C(Me)CH_2\}(cod)][PF_6]/Bu_3P$, **984** was the main product [1922], but lower selectivities were obtained when the added phosphine was less basic [1923]. Linear diesters were the main products of the reaction in the presence of $[Ni(\eta^3\text{-}C_3H_5)_2]/Me_3P/H[BF_4]$ [1924], but with $[Ni(acac)_2]/P(NEt_2)_3/BuLi$ as the catalyst system, **986** was formed exclusively [1925]. Dimerisation of methyl 2-methylpropenoate in the presence of $[PdCl_2(RCN)_2]/Ag[BF_4]$ gave mainly **987**. Codimerisation experiments with methyl propenoate indicated that the latter was the more reactive [1926].

984

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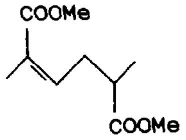
986

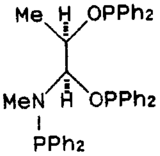


987

Catalysts for ethene polymerisation discussed during this period have included $[Ni(cod)_2]/C_3F_7COOH/Cy_2PH$ [1927], $[Ni(cod)_2]/PPh_3/Ph_3PO$/benzoquinone [1928,1929] and $[Ni(acac)_2]/Bu_2Mg/Et_3Al_2Cl_3/[Ti(OBu)_4]$ [1930]. Active sites in Ziegler Natta catalysts have been studied, including some based on $NiCl_2$ [1931].

$H_2[PtCl_6]$ has been used as a catalyst for the polymerisation of methyl propenoate and methyl 2-methyl propenoate [1932]. The cationic species $[Pd(MeCN)_4][BF_4]_2$ has been shown to catalyse the polymerisation of phenylethene, norbornene or 1,3-cyclohexadiene [1933].

Codimerisation of ethene with phenylethene in the presence of $[Ni(N,N\text{-diethyldithiocarbamate})_2]/EtAlCl_2$ gave mainly 4-phenyl-1-butene. A kinetic study indicated that the addition of phosphine ligands lowered the activation energy for alkene insertion, but increased the activation barrier to alkene coordination [1934]. Using $NiX_2/P(OPh)_3/Et_3Al/BF_3.Et_2O$ as the catalyst system, the main product was 3-phenyl-1-butene, together with a little 2-phenyl-2-butene. Nickel hydride complexes were invoked as the intermediates in this case [1935]. Codimerisation of phenylethene with propene in the presence of $[Ni(acac)_2]/R_3P/Et_2AlCl$ gave a mixture of 4-phenyl-2-pentene, 4-phenyl-1-pentene and 2-methyl-3-phenyl-1-butene [1936]. Enantioselective codimerisation of ethene with 1,3-cyclohexadiene in the presence of $[Ni(cod)_2]/Et_2AlCl/$**988** gave **989** in up to 93 % optical yield [1937].



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989

The copolymerisation of phenylethene and methyl propenoate has been reported to occur in the presence of $H_2[PtCl_6]$, which acts as a chain transfer agent [1938]. A similar function for the platinum salt was proposed in the copolymerisation of propene nitrile and 2-propene-1-ol [1939].

Anionic polymerisation of phenylethene was initiated by BuLi in cyclohexane, and then the reaction mixture was added to 1,3-butadiene/nickel naphthenate/$BF_3.Et_2O$ to give a transparent copolymer with 90 % 1,4-*cis*-stereochemistry in the polybutadiene block [1940].

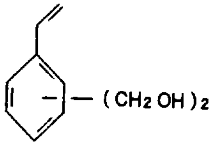
Copolymerisation of ethene and carbon monoxide to give a high melting point solid was achieved in the presence of $[Pd(PPh_3)_n(MeCN)_{4-n}][BF_4]_2$ (n = 1, 2 or 3). The mechanism proposed involved a single mode of chain growth with alternate insertions of CO and C_2H_4 into a palladium alkyl bond [1941,1942]. An alternate copolymer of butadiene monoepoxide and CO_2 was obtained on reaction with $[Pt(C_2H_4)Cl_2(py)]$ [1943].

An important paper has been published concerning the mechanism of the cyclotetramerisation of ethyne to cot in the presence of nickel complex catalysts. Using ^{13}C-labelled ethyne it was shown that the only reasonable mechanisms were either a stepwise or a concerted zipper type mechansim. Cyclobutadiene and benzenoid intermediates were ruled out, and there was no break up of individual ethyne units [1944].

The electrochemical synthesis of $[Ni(CO)_2(PPh_3)_2]$ has been described, and it was used in a one-pot trimerisation of ethyne to benzene [1945].

Cyclooligomerisation of phenylethyne in the presence of $[Ni(CO)_3\{P(OCHMe_2)_3\}]$ gave 1,2,4-triphenylbenzene with > 95 % selectivity [1946]. Cyclotrimerisation of $HOCH_2C{\equiv}CCH_2OH$ using $[Ni(cod)(PR_3)_2]$ gave $C_6(CH_2OH)_6$ [1947].

Dimerisation of buteneyne to give ethenylbenezene occurs thermally, but the reaction yield is increased in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$ [1948]. Buteneyne also reacted with propynyl alcohol in the presence of $[Ni(CO)_2(PPh_3)_2]$ to give a mixture of **990** and the alcohol cyclotrimer. Various other cotrimers were similarly prepared [1949]. In the presence of diazabutadiene nickel complexes, $RC{\equiv}CCOOR'$ was cyclotrimerised to give mainly 1,2,4-substituted benzenes [1950]. Reaction of **991** with $RC{\equiv}CR'$ in the presence of $[Ni\{PPh(OCHMe_2)_2\}_4]$ gave 2,3-isoindolines, **992** [1951]. Using $[Ni(cod)_2]$ as the catalyst, **993** gave diyne oligomers; in the presence of RNCO no pyridones were formed, in contrast with the cobalt catalysed reaction. However, 1-phenyl-1-butyne reacted with $PhCH_2CH_2NCO$ to give **994** as the sole product [1952]. Cooligomerisation of ethyne and nitriles was reported to occur in the presence of $[Ni\{P(OC_6H_4\text{-}2\text{-}Me)_3\}_4]$ [1953]. Reaction of 1-alkynes with **995** in the presence of $[PdCl_2(PPh_3)_2]$ gave **996** in good yield. Related cyclocooligomerisation of allenes and butadienes were also noted [1954].



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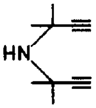

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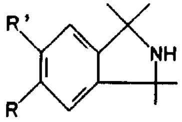

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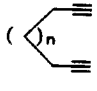

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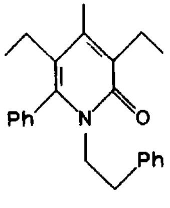
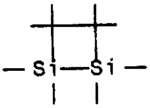


994

The first cyclotetramerisation of a propynyl ether has been described. Thus **997** reacted in the presence of **998** to give the highly symmetric 1,4,5,8-tetrasubstituted cyclooctatetraene, a hitherto unknown pattern [1955]. With related catalysts, $HC{\equiv}CCOOR$ gave mainly 1,3,6,8-substituted cyclooctatetraenes, together with some cyclotrimer [1956]. The diyne, **999**, reacted in the presence of $[Ni\{PPh(OCHMe_2)_2\}_4]$ or $[Ni(cod)_2]/R_3P$ to give 1000 and some 1001 [1957].



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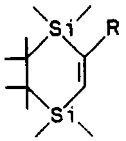

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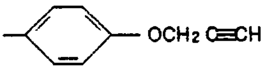

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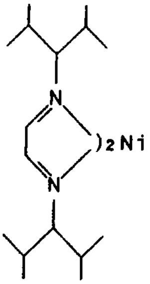

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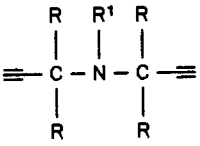

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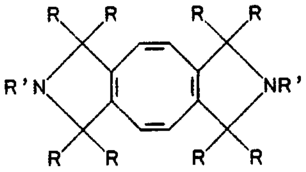

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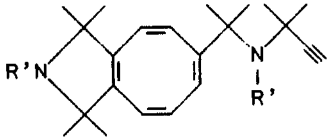
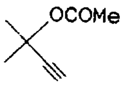


1001

Head-to-head coupling of $RC{\equiv}CH$ to give $RC{\equiv}CC{\equiv}CR$ (and for R = alkyl also some $RC{\equiv}C\text{-}C(=CHR)(C{\equiv}CR)_2$) was achieved in the presence of $[Pd(PPh_3)_4]/CuI/Et_3N$, the process proving to be a useful alternative to the Glaser reaction [1958]. Reaction of 1002 in the presence of $[PdCl_2(MeCN)_2]$ gave 1003 as the main product, but numerous isomerised and hydrolysed products were also obtained [1959]. The related alcohol, 1004, gave mainly dimers in the presence of $Pd(OCOMe)_2/CuI/Et_3N/L$, but the products contained more trimers when the CuI was omitted from the mixtures. For L = $PPh(OCHMe_2)_2$ conversion was 62 %, and selectivity towards the dimer 90 %. In this case a single dimer, 1005, was obtained. Various cross-dimerisations were also discussed [1960].



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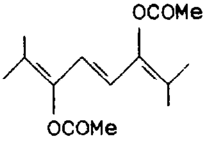

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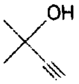

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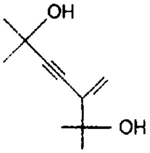


1005

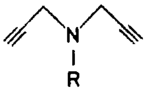
The polymerisation of alkynes has been reviewed, with particular reference to the use of the catalyst system $[NiCl_2(PR_3)_2]/Na[BH_4]$ [1961]. Related systems detailed in patents included $NiCl_2$/white phosphorus/H_2O [1962], $NiCl_2/H_3PO_2/H_2O$ [1963], and $NiCl_2/Na[BH_4]$ [1964]. Polyacetylene was deposited on a platinum surface by electrochemical polymerisation of ethyne in a cell with a platinum strip as cathode, a nickel strip as anode, and $NiBr_2$ in MeCN as electrolyte. A mechanism for the reaction was proposed [1965].

Polyphenylethyne was obtained using $[PdCl_2(PPh_3)_2]/PPh_3/CuI/Et_3N/PhMe$ as the catalyst system [1966]. The polymerisation of **1006** to give a fibre forming polymer was catalysed by $[Ni(acac)_2]/PPh_3$; the effect of changes in the reaction conditions was studied [1967,1968]. The same system was used to prepare polymers and copolymers of carborane substituted phenylethyne [1969].

1006

Buteneyne was polymerised under the influence of $PdCl_2$ or $[Pd(acac)_2]$ selectively at the alkyne to give a *trans*-polyene, but the chain lengths were fairly short [1970,1971]. In the presence of $[Ni(PR_3)_2X_2]$ MeSC≡CSMe was converted to a polymer useful for the preparation of conducting materials [1972].

Polymerisation of **1007** in the presence of $PdCl_2$ at 150-185 °C gave a soluble material, **1008**, which became conducting on doping with I_2 or TCNQ [1973,1974].



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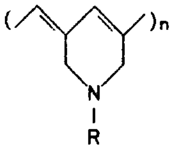
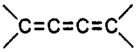


1008

Reaction of the cumulene **1009** with [Ni(bipy)(cod)] gave **1010**, believed to be an intermediate in catalytic oligomerisation. Reactions of **1010** were studied [1975]. Oligomerisation of **1011** in the presence of $[Ni(PPh_3)_3]$ gave mainly **1012**. Using $[Ni(cod)_2]$ a mixture of **1013** and **1014** was obtained, whilst $[Ni(cod)(PPh_3)]$ gave **1012** and **1013**. The reaction mechanism was discussed in detail [1976]. The cumulene **1009** was prepared by dehalogenation of $Me_2C{=}C(X)C(X){=}CMe_2$ (X = Br or I) using Ni(0). The nickel(0) then catalysed cyclooligomerisation to **1015** and/or **1016** [1977].



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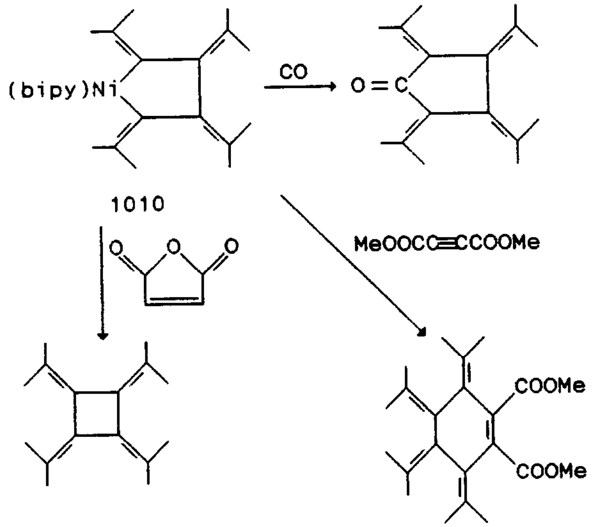

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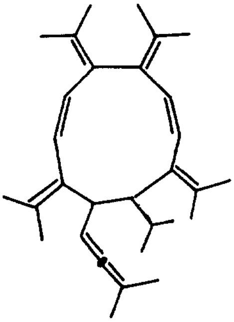

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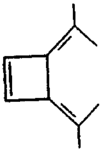

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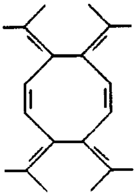

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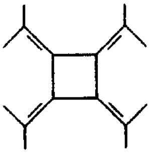

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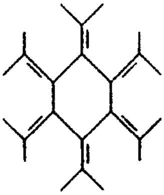
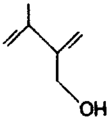


1016

Telomerisation of propadiene with water in the presence of [Pd(acac)$_2$]/PPh$_3$/CO$_2$ gave 1017 and 1018 [1978]. Reaction with PdCl$_2$ gave initially 1019 which reacted with CuCl$_2$ to give the chlorinated dimer 1020 in a catalytic reaction. Polyhalogenated dimers and trimers were prepared from more substituted allenes [1979].



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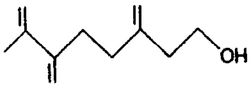

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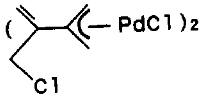

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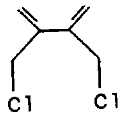
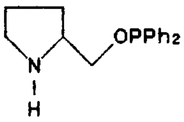


1020

Rather clean linear dimerisation of butadiene to 1,3,6-octatriene was shown to have occurred in the presence of [Ni(cod)$_2$]/1021. After a longer time, the main product was 2,4,6-octatriene [1980]. Linear dimerisation of isoprene gave 1022 and 1023 in the presence of [Pd(η^3-CH$_2$CMeCH$_2$)(cod)][PF$_6$]/R$_3$P. The ratio of the products was dependent on the solvent and the phosphine, with up to 90 % selectivity for 1022 under appropriate conditions. The ratio of P:Pd at 1:1 is critical, since the 2:1 complex is inactive [1981].



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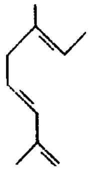
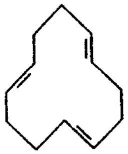


1022

1023

A nickel catalyst anchored on polyethenylpyridine was used to cyclooligomerise butadiene to give cyclododecatrienes, mainly 1024 [1982]. A varient on an earlier reported procedure for the dimerisation to give 1025, involving [NiCl$_2$(PEt$_3$)$_2$]/BuLi, has been described [1983].



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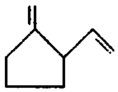
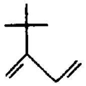


1025

Dimerisation of isoprene in the presence of [Ni(acac)$_2$]/Et$_3$Al/R$_2$NH was said to give 1026 [1984]. With 1027 as the substrate and [Ni(cod)$_2$] in toluene as the catalyst, two dimers, 1028 and 1029, were obtained in a 9:1 ratio. 1031 was the main dimer from 1030, but the reaction was less selective. In contrast to the reaction of butadiene, addition of PR$_3$ had an inhibitory effect [1985].

1026



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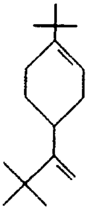

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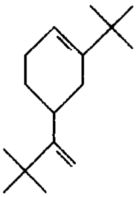

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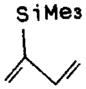

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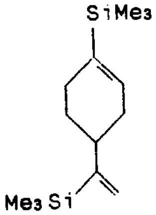
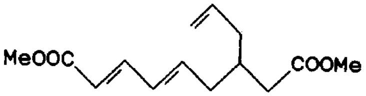


1031

The nickel catalysed oligomerisation of functionalised dienes including 1032 has been studied, with particular reference to the effect of substituents on selectivity [1986]. There has been an extensive study of the reactions of 1033. With $[Ni(acac)_2]/PPh_3/Et_2AlOEt$ a mixture of cyclic diesters was obtained, whilst using $Pd(OCOMe)_2/L$, the main product was **1034**. Nickel catalysed dimerisation of 1035 gave 1036 and 1037, with the product ratio depending on the exact nature of the catalyst, whilst the use of $Pd(OCOMe)_2/L$ again gave linear dimers. Codimerisation reactions of both these ester substrates were also reported [1987,1988]

1032

1033



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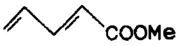

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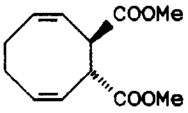

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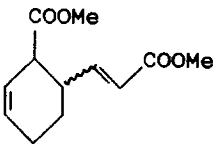
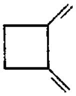


1037

Dimerisation of **1038**, using $[Ni(acac)_2]/P(OAr)_3/Et_3Al$ in an aromatic solvent as the catalyst system, gave up to 90 % of **1039**. Codimers were also studied [1989]. Oligomerisation of cyclopentadiene in the presence of $[Pd(acac)_2]/PR_3$ gave **1040** and **1041** [1990].



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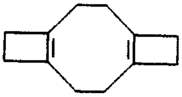

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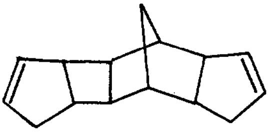

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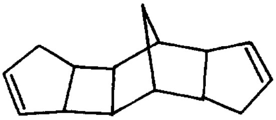
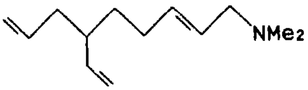


1041

Cooligomerisation of butadiene and ethene gave E,Z-cyclodeca-1,5-diene using $NiCl_2/Et_3N/Et_3Al$ as the catalyst system [1991]. Reaction of butadiene with $CH_2{=}CHCH_2NMe_2$ in the presence of $Pd(II)/PPh_3/Et_3Al$ gave mixtures of **1042**, **1043** and **1044**, the product ratios depending on the exact reaction conditions. **1042** is formed by *C-N*-cleavage followed by regioselective addition of the amine function to the 1- and 6-positions of a butadiene dimer. The reaction resembles telomerisations of dienes with other nucleophiles, except that the allyl group replaces a proton [1992]. Reaction of butadiene with tetraethenylsilane in the presence of $Ni(0)/PPh_3$ gave a mixture of **1045** and **1046** [1993]. Reaction of butadiene with diazabutadienes in the presence of Ni(0)/L gave **1047** in yields up to 96 %, as well as butadiene oligomers. Reactions of hydrazones and imines have also been detailed [1994,1995]. Cooligomerisation of a range of ethenyl derivatives $CH_2{=}CHX$ ($X = OR$, SPh, CMe_3 or $SiMe_3$) with butadiene in the presence of Ni(0) catalysts has been studied. Only $CH_2{=}CHSiR_3$ reacted by cooligomerisation, giving both linear and cyclic products in ratios which depended on both steric and electronic parameters of added phosphine ligands [1996].



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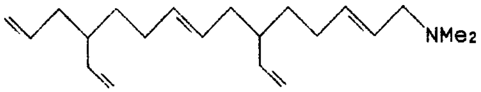

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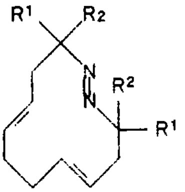


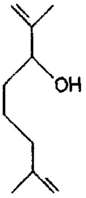
1047

Organometallic catalysis of diene and cycloalkene polymerisation has been reviewed, with specific reference to the mechanism of stereoregulation of butadiene polymerisation in the presence of nickel allyl complexes [1997]. Two patents have reported catalyst systems for the production of predominently *cis*-polybutadiene, *viz.* aged nickel naphthenate/$BF_3.Et_2O/AlEt_3$ [1998], and $[Ni(C_2H_4)(PPh_3)_2]/PhCH_2Cl/AlBr_3$ [1999]. A 1:1 mixture of *cis*-1,4- and 1,2-poybutadiene was reported to have been obtained using nickel naphthenate/phen/*i*-Bu_3Al, although the system was less active than those using other metal naphthenates [2000]. Conditions for obtaining *cis*-, *trans*- or mixed *cis/trans*-polybutadiene in the presence of various nickel allyl complexes have been carefully established [2001]. A ^{31}P nmr spectroscopic study of the reaction of $[Ni(\eta^3-C_3H_5)\{P(OAr)_3\}_2]^+$ with butadiene has been used to propose an origin for the stereoselectivities observed in polymerisation [2002].

Reaction of a 10:1 ratio of butadiene and ethene in the presence of nickel naphthenate/Et_2AlCl/H_2O gave a useful copolymer [2003].

Telomerisation of isoprene with water in the presence of $[Pd(acac)_2]/PPh_3/CO_2$ gave dimethyloctadieneols, as well as isoprene dimers [2004]. Using a polymer supported palladium catalyst gave **1048** as the main product, and the results were compared with the related homogeneous system

[2005].

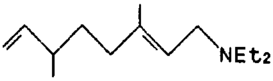


1048

Reaction of isoprene with methanol in the presence of $[\{PdCl(\eta^3-C_3H_5)\}_2]$ gave dimethyloctadienol methylethers, as well as oligomers [2006]. In a reaction using $[Pd(acac)_2]/PPh_3$ as the catalyst system, the ratio of products was strongly dependent on the nature of the reacting alcohol [2007]. A patent has reported telomerisation of butadiene with 1,4-butane diol, to give products useful in the synthesis of surfactants [2008].

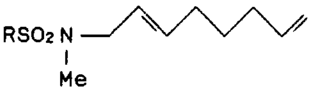
Both addition and telomerisation reactions occurred when Et_2NH was reacted with isoprene in the presence of $[Pd(dppe)(py)_2][BF_4]_2$. The tail-to-head and head-to-head telomers, 1049 and 1050, were the favoured products, and a palladium hydride complex was proposed as the active intermediate [2009]. Telomerisation of butadiene with substituted 2-aminopyridines gave both secondary and tertiary amines, in ratios which could be controlled by altering the butadiene concentration [2010].

1049



1050

A mixture of linear and branched telomers was obtained from phthalimide and butadiene in the presence of $[Pd(acac)_2]/PR_3/Zn$, the reaction providing an alternative to the Gabriel synthesis [2011]. Reaction of butadiene with RSO_2NHMe gave a mixture of 1051 and 1052, in good yields in most cases [2012]. Both mono- and bis-octadienylated sulphonamides could be obtained from $ArSO_2NH_2$ in the presence of $\{PdL_n\}$; the ratio of products depended on L and the reaction solvent. Isoprene and 1,3-pentadiene gave both addition and telomerisation products [2103].



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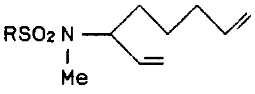
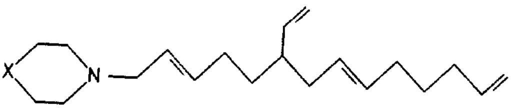


1052

The octadienylamine 1053 reacted with butadiene in the presence of $\{PdL_n\}$ to give 1054, with 1055 being obtained when CF_3COOH was added. It was assumed that the original allylamines was cleaved under the reaction conditions, and this view was supported by deuterium labelling studies [2014]. Reaction of methanamide with butadiene using $[Pd(acac)_2]/PPh_3/Et_3Al$ in CF_3COOH gave both linear and branched *N*-octadienyl amides. However, in dmso, the starting material was cleaved to give ammonia, which reacted to give mainly trioctadienyl amine [2015].

1053



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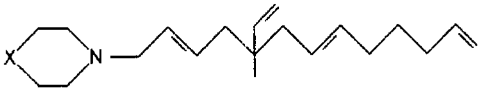
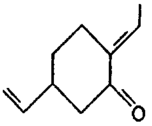


1055

Reaction of butadiene with ethanol under CO pressure in the presence of $Pd(OCOMe)_2/PPh_3$ gave 1056, used in a pheromone synthesis [2016]. There have been further reports of the reactions of CO_2 with butadiene in the presence of palladium catalysts. The formation of 1057 was favoured by the use of PCy_3 as the added ligand [2017], and conditions have been found which favour C_9-acids [2018]. With the catalyst system $[Pd(dba)_2]/PPh_3/Na[OCOMe]/DCC$, the main product was the *N*-acyl urea of 1058 [2019]. Reaction of butadiene with ethene carbonate in the presence of $[Ni(cod)_2]/Et_3P$ gave 1059, which underwent radical polymerisation to give a translucent homopolymer [2020].

1056



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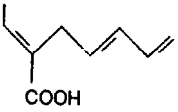

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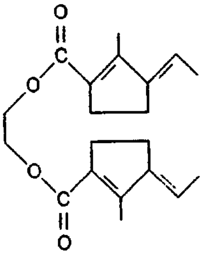
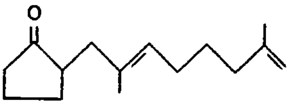


1059

Telomerisation of butadiene with carbon acids, including cycloalkanones, has been reported to occur using $[\{Pd(OCOMe)(\eta^3\text{-}CH_2CMeCH_2)\}_2]/PPh_3$ as the catalyst. The reaction mechanism was discussed in detail; the key species was $[HPdL_3][OH]$ which enolised the ketone for subsequent nucleophilic attack on the palladium allyl complex [2021]. The reaction between isoprene and cyclopentanone under these conditions gave mainly the tail-to-tail coupled product 1060 [2022]. With cyclohexenone the product was 1061 formed by conjugation of the original telomer [2023].



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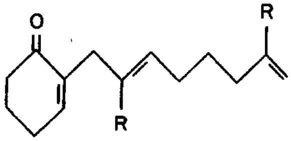
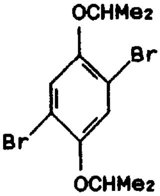


1061

Polymerisation of a chiral isocyanide, RNC, using a nickel(II) catalyst gave atropoisomeric polymers with a rigid helical structure [2024]. Isocyanide terminated tripeptides have been converted to chiral polymers with $NiCl_2$ [2025,2026]. The isocyanide group of RR'C=CHNC is readily polymerised by $[Ni(acac)_2]$ to give polyvinyliminomethylenes, the pendant vinyl groups being identified by nmr spectroscopy [2027,2028].

Polymerisation of 4-bromothiophenol by nucleophilic susbtitution was catalysed by $[Pd(PPh_3)_4]$ [2029] or $[NiBr_2(PPh_3)_2]$ [2030].

Polyphenyl was obtained by electrochemical reductive polymerisation of 1,4-dibromobenzene in the presence of Ni(0), though the chain lengths obtained were relatively short [2031]. Conversion of 1062 to its magnesium derivative was followed by coupling catalysed by $[Ni(bipy)Cl_2]$ to give a polymer with an average molecular weight of 3700 [2032]. Crystalline polythiophene was similarly prepared from 2,5-dibromothiophene [2033], and the related zinc derivative was coupled using $[NiCl_2(dppe)]$ [2034]. Magnesium derivatives were used for the prepararation of polymers from 2,5-dibromo-3-methylthiophene [2035] and other 3-alkyl-2,5-dibromothiophenes [2036]. The monomer prepared from 4-chlorophenol and bis(4-chlorophenyl)sulphone was polymerised using $Zn/NiCl_2/PPh_3$/bipy/dma to give a thermoplastic with reduced viscosity [2037].



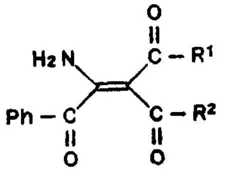
1062

13.10 *Miscellaneous Coupling Reactions*

Reaction of Bu_3SnCH_2CN with ArCHO was catalysed by $[PdCl_2L_2]$, to give $ArCH(OH)CH_2CN$. The reaction was restricted to aryl aldehydes bearing electron withdrawing groups. When L was a chiral phosphine, chiral alcohols were obtained in low optical yields [2038]. α-Haloesters reacted with aryl aldehydes and ketones in the presence of $SnCl_2/Et_2AlCl/[Pd(PPh_3)_4]$ to give Reformatsky products, the process presumably involving the *in situ* formation of an organotin intermediate [2039]. An organozinc intermediate was invoked in a complex mechanism for the reaction of R_fI, Zn and RCHO to give $R_fCH(OH)R$ in the presence of $[MCl_2(PPh_3)_2]$ (M = Pd or Ni) [2040].

There have been several reports of the conjugate addition of dialkyl or diarylzinc compounds to enals or enones in the presence of $[Ni(acac)_2]$ [2041]. The reaction of $Zn(C_6H_4\text{-}4\text{-}Me)_2$ with 3,4,4-trimethylcyclopent-2-ene-1-one gave β-cuparenone, with essentially no competing 1,2-addition [2042]. The enolate produced in the initial addition reaction may be captured by an appropriate electrophile [2043]. The reaction was also extended to RZnBr [2044].

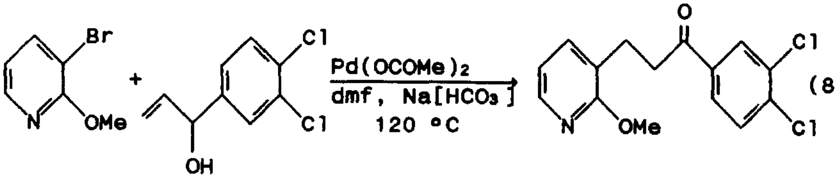
Reaction of 1-alkynes with diphenylketene in the presence of $[Pd(PPh_3)_4]$ resulted in decarbonylation and coupling to give $Ph_2CHC\equiv CR$ [2045]. PhCOCN reacted with β-diketones in the presence of [Ni(acac)$_2$] to give 1063. The key stage in the reaction involved coordination of the cyanide to nickel, favouring attack at that carbon atom [2046]. Ring opening of cyclohexene epoxide by ethenylmagnesium bromide was catalysed by [PdCl$_2$(MeCN)$_2$] [2047].



1063

Applications of the Heck reaction in synthesis continue to be reported. Aryl halides have been added to enones in the presence of [Pd(OCOMe)$_2$(PPh$_3$)$_2$]/HCOOH/Bu$_3$N [2048], enals [2049], unsaturated amides [2050] or unsaturated esters using Pd(OCOMe)$_2$/P(C$_6$H$_4$-2-Me)$_3$/Et$_3$N [2051]. A highly efficient phosphinated polymer supported palladium catalyst was shown to involve metallic palladium [2052]. The reaction of aryl iodides with CH$_2$=CHCOR in the presence of [Pd(OCOMe)$_2$(PPh$_3$)$_2$] gave initially ArCH=CHCOR, but this reacted further, by a second catalysed conjugate addition, to yield Ar$_2$CHCH$_2$COR, isolable in 50-70 % yield [2053]. The reaction of iodobenzene with methylpropenoate has been conducted under exceptionally mild conditions (at or near room temperature) using as the catalytic system Pd(OCOMe)$_2$/Na[HCO$_3$]/[Bu$_4$N]Cl under solid liquid phase transfer conditions [2054].

The reaction of aryl chlorides with propenenitrile was catalysed by Pd(OCOMe)$_2$/PR$_3$/Na[OCOMe], but yields and stereoselectivities were low [2055,2056]. Reaction (87) shows an application involving an allylic alcohol [2057].



(87)

Dialkenylated benzenes have been prepared by the sequence shown in Figure 22. X and Y are electron-withdrawing groups, and the overall yields for the three step reaction are 30-50 %. 2-, 3- and 4-bromobenzoic acids all proved to be suitable substrates [2058]. Heck reactions such as (88) were used in an approach to the ergot alkaloids [2059].

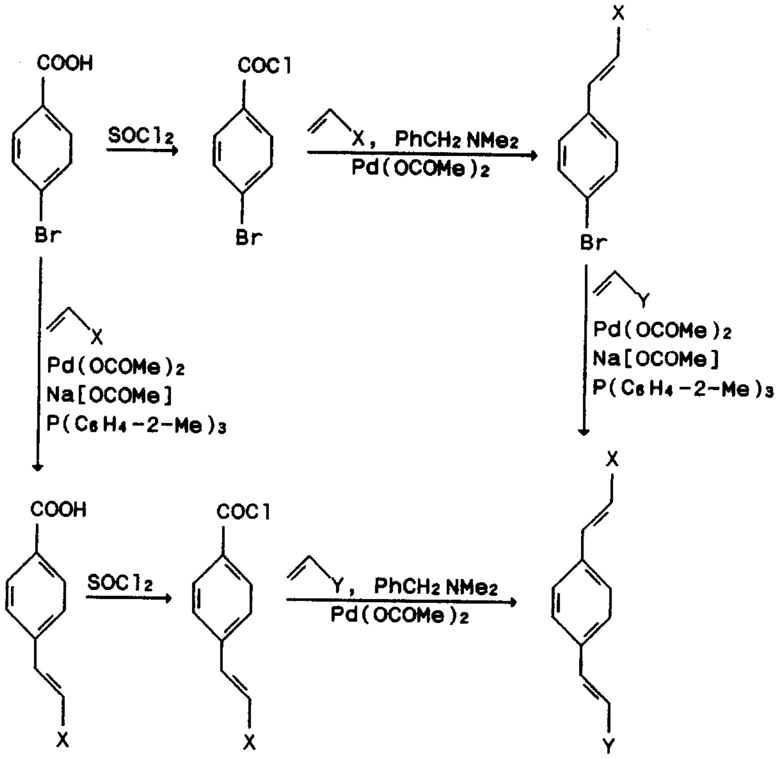
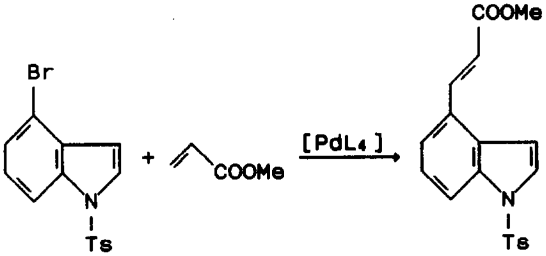


Figure 22 Synthesis of dialkenylated arenes [2058]

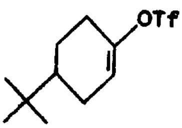


(88)

There has been a detailed study of the reaction of bromobenzene with isoprene catalysed by $Pd(OCOMe)_2/P(C_6H_4\text{-}2\text{-}Me)_3/Et_3N$, which gave PhCH=CH-C(Me)=CHPh in low yield. Better yields were obtained with arenes bearing electron withdrawing substituents [2060].

The Heck reaction of E-BuCH=CHI with methyl propenoate catalysed by

$Pd(OCOMe)_2/Na[HCO_3]$ under phase transfer conditions, gave E,E-BuCH=CHCH=CHCOOMe in 94 % yield. Stereoselectivity was poorer with the Z-substrate, but could be improved by the use of $K_2[CO_3]$ as the base [2061]. The reaction of 1064 with methyl propenoate gave 1065 in the presence of $[PdCl_2(PPh_3)_2]/Et_3N$, in a reaction which was relatively insensitive to air [2062].



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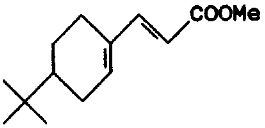


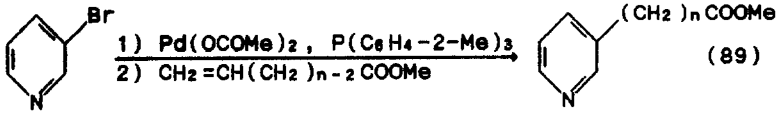
1065

There have been a number of reports of the reactions of aryl halides with alkenes which do not bear electron withdrawing groups. The reaction of aryl iodides with ethenyltrimethyl silane in the presence of $Pd(OCOMe)_2/PPh_3/Et_3N$ was known to give ethenyl arenes. When $Ag[NO_3]$ was added to the reaction mixture the product was E-ArCH=CHSiMe_3 [2063]. When $[ArN_2][BF_4]$ was used as substrate and palladium(0) as the catalyst, the main product was the ethenylarene at a 1:1 ratio of reactants, and ArCH=CHSiMe_3 with an excess of the ethenylsilane. A convincing reaction mechanism was proposed [2064].

There have been two reports of alkene arylation using, for the first time, unactivated aryl chlorides. Thus chlorobenzene reacted with phenylethene in the presence of $Pd(OCOMe)_2$/dppe/Na[OCOMe] to give PhCH=CHPh with an E:Z ratio of 4:1. The nature of the base used proved to be very important, and the turnover was low, with quite rapid deactivation of the catalyst [2065]. In another report, ethene reacted with chlorobenzene using $Pd(OCOMe)_2/Cu(OCOMe)_2/MeCOOH$ as the catalyst system under oxidising conditions to give a chlorinated ethenylbenzene [2066].

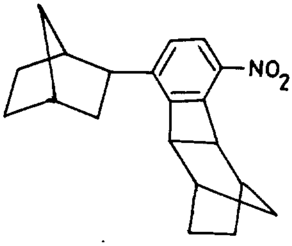
There has been a report of electroreductive coupling of aryl halides with alkenes or alkynes in the presence of Pd(0) to give $ArCH_2CH_2R$ or ArCH=CHR. Yields were generally excellent [2067].

Reaction of $RCH(OH)(CH_2)_nCH=CH_2$ (n = 1, 2 or 3) with aryl halides in the presence of a palladium catalyst gave $RCO(CH_2)_{n+1}CH_2Ar$ as the major product. A deuterium labelling study suggested that a key step was a regioselective 1,2-hydride shift in a Wacker type intermediate [2068]. Coupling of ethenylbenzene with a range of aryl halides has been reported to occur in the presence of $Na_2[PdCl_4]$/proton sponge/dmf; iodides were better substrates than bromides [2069]. Reaction (89) was used in the synthesis of a new class of thromboxane A_2 synthetase inhibitors [2070].

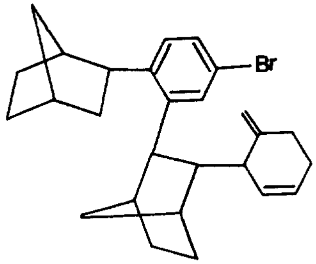


(89)

Chiusoli's group continues to pursue the study of addition of aryl halides to norbornene. Reaction with 4-nitrobromobenzene in the presence of $[Pd(PPh_3)_4]$ gave 1066, characterised in an X-ray diffraction study. The possibility of an aryne intermediate was discussed [2071]. With 1,4-dibromobenzene as the substrate, 1067 was formed, as well as 1068 and the analogue of 1066. It is clear that C-H activation in this system is subject to very subtle influences [2072]. The reaction mechanism has been discussed in detail, both in this case [2073], and for aryl halides with other substitution patterns [2074]. The influence of the nature of the base used has also been studied [2075]. A full paper has now reported the details of reaction (90) (R = alkenyl), and the reaction mechanism was discussed [2076]. The related reactions of norbornene and norbornadiene with S-1-octyne-3-ol and $3\text{-ClCH}_2C_6H_4OCH_2CO_2Me$ have also been studied [2077]. Three types of product could be formed in reaction (91), the proportions of which depended to some extent on the nature of the added amine [2078].

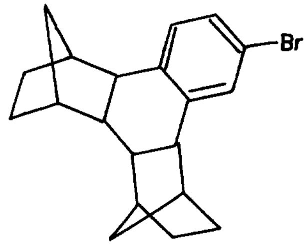


1066



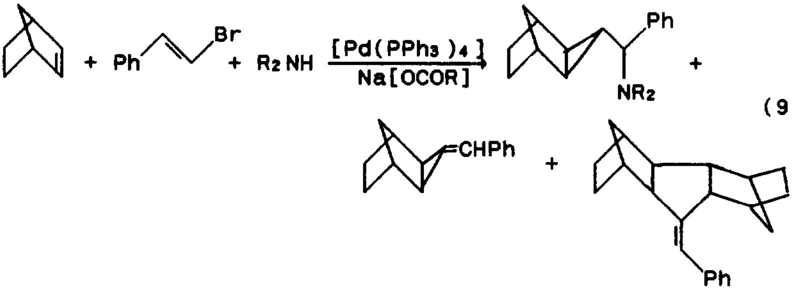
1067

Coupling of arenes with RCH=CHY, where Y is an electron-withdrawing group, catalysed by a palladium complex, gave ArRC=CHY [2079]. Indoles such as 1069 reacted with propenoate esters at the 3-position to give 1070, catalysed by $PdCl_2/Cu(OCOMe)_2$ [2080]. The *N*-substituted pyrrole, 1071, reacted at the 2- and 5-positions using $Pd(OCOMe)_2$ as the catalyst [2081]. *N*-Methyl-2-pyridone was substituted at the 5-position, as was furfural [2082].



1068

(90)



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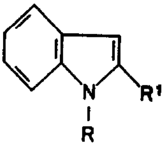

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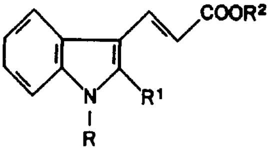

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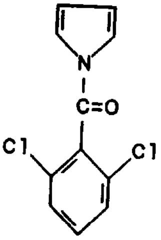
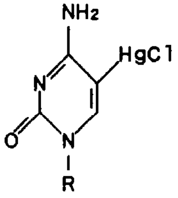


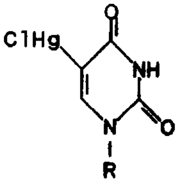
1071

There has been a careful study of the conditions for the coupling of Ph_2Hg

in the presence of $[PdI(Ph)(PPh_3)_2]$ to give biphenyl. Coupling of PhHgCl was also possible, but yields were low, and rhodium complexes proved to be better catalysts [2083]. The organomercury compound 1072 could be coupled with ethene or methyl propenoate in the presence of $Li_2[PdCl_4]$. Other palladium mediated routes to the same products were also tested [2084]. The coupling of 1073 with 1,1,1-trifluoropropene was effected in the presence of $Li_2[PdCl_4]$; the reaction mechanism was explored in some detail [2085]. The palladium mediated coupling of an aryl or heteroaryl mercury compound with a cyclic enol ether has been investigated, with the intermediates in the reaction being analysed by FAB mass spectrometry [2086].

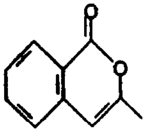


1072

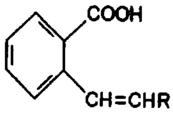


1073

Thallation of benzoic acid with $Tl(OCOCF_3)_3$ gives a 2-substituted product, which could be reacted with 3,3-dimethyl-1-butene in the presence of $PdCl_2/LiCl$ to give the isocoumarin 1074. With propene or phenylethene as the substrate the amounts of isocoumarin obtained were smaller, and substantial amounts of 1075 were also formed [2087]. Reaction of 1076 with PhMgBr gave 1077 as the main product in the presence of $PdCl_2$, $[Pd(PPh_3)_4]$ or $[NiCl_2(PPh_3)_2]$. The reaction mechanism is clearly complex, and may involve the equilibration of intermediate allyl Grignard reagents [2088].



1074



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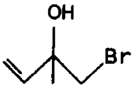

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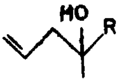
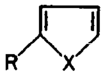


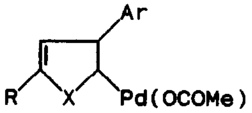
1077

Diaryliodonium salts, $[Ar_2I]Cl$, may be coupled in the presence of zinc metal and palladium ethanoate to give biaryls [2089]. With mixed salts, [PhArI]X, homo and heterocoupled products were obtained [2090]. The salts could be coupled to phenylethene to give 1,2-diphenylethene in the presence of either Pd(0) or Pd(II) and a base [2091]. Coupling with $CH_2=C(Me)CH_2OH$ gave $ArCH_2CH(Me)CHO$, although Pd/C was an even better catalyst in this instance [2092].

Reaction of arenes with palladium ethanoate gives {ArPd(OCOMe)}, which may be added across a double bond of a furan or thiophene derivative, 1078 (X = O, R = CHO or X = S, R = CHO or COMe), to give 1079. β-Hydride elimination gave the substituted heterocycle, 1080. The use of unsubstituted substrates resulted in homocoupling [2093]. The process is also useful for 2,3-disubstituted furans or thiophenes [2094]. Similarly reaction of {ArPd(OCOMe)} with the benzoquinone, 1081, gave 1082, which lost {HPd(OCOMe)} to give 1083 [2095]. {PhPd(OCOMe)} may also be readily generated from $[PhN_2][OCOMe]$ and $[Pd(dba)_2]$, and was then reacted with Z-RCH=$CHSiMe_3$ to give 1084 stereospecifically, by *syn*-addition followed by *syn*-elimination [2096].



1078



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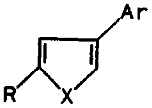
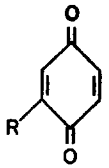
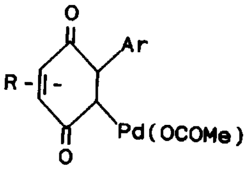


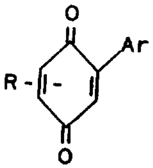
1080



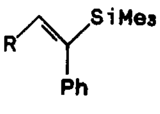
1081



1082

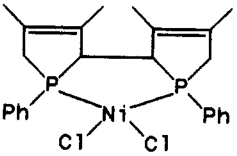


1083

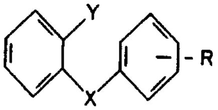


1084

Reaction of 3,4-dimethyl-1-phenylphosphole with $NiCl_2$ gave R,R and S,S-1085, with no *meso*-dimer [2097]. Coupling of diaryl ethers to give dibenzofurans had previously been shown to occur in the presence of stoicheiometric palladium(II). Using 1086 as the substrate (Y = I or Br), the reaction could be made catalytic [2098].



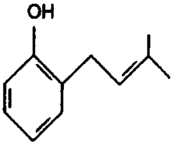
1085



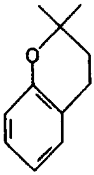
1086

Iodobenzene reacted with diphenylethyne in the presence of $[Pd(OCOMe)_2(PPh_3)_2]/HCOOH/Et_3CN/MeCN$ to give triphenylethene. The key step in the reaction was addition of $[PdI(Ph)(PPh_3)_2]$ across the triple bond [2099]. With a non-symmetrical alkyne the reaction may be made regioselective if one end is substituted by a bulky group such as $-CR^1R^2OH$ [2100].

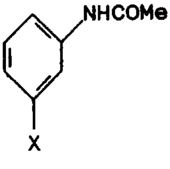
Reaction of phenol with isoprene to give 1087 and 1088 was catalysed by $[Pr_4N][PtCl_3(C_2H_4)]$; a mechanism for the reaction was proposed [2101]. The reaction between 1089 and $[PtCl_2(3,3\text{-dimethylpropa-1,2-diene})(PPh_3)]$ gave 1090 [2102].



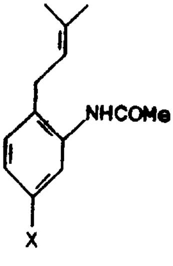
1087



1088

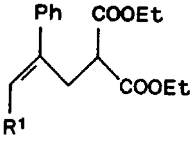


1089

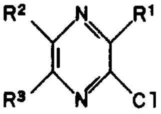


1090

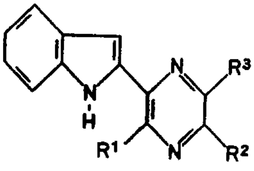
Coupling of a monosubstituted allene with iodobenzene and diethyl propanedioate, catalysed by $[Pd(PPh_3)_4]$, gave 1091. Haloalkenes were also satisfactory substrates, and a palladium allyl complex was invoked as an intermediate [2103]. Ethenylbenzene was coupled with the aryl group of ArN(NO)COMe in the presence of $[Pd(dba)_2]$ to give mainly E-ArCH=CHPh. When $[PhN_2][BF_4]$ had been used as the source of the arylpalladium intermediate, mixtures of products were obtained with either 1-octene or cycloheptene. With ArN(NO)COMe cycloheptene was converted exclusively to 3-phenyl-1-cycloheptene. The reaction mechanism was not fully elucidated [2104]. Coupling of 1092 with indole using $[Pd(PPh_3)_4]/K[OCOMe]$ or $[PdCl_2(PPh_3)_2]/CuI/K_2[CO_3]$ as the catalyst system gave the unusual 2-coupled product, 1093 [2105].



1091

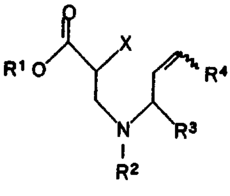


1092

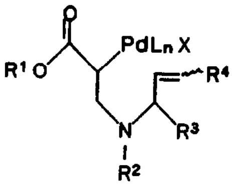


1093

There have been a number of reports of coupling reactions between alkenes and organic halides. Thus treatment of 1094 with palladium(0) gave 1095 which was then added across the nearby double bond. The reaction was completed either by reductive elimination to give 1096 or dehydropalladation to give 1097. Six-membered rings could also be prepared in this way (reaction (92)) [2106]. Reactions such as (93) of α-haloamides were also reported [2107,2108]. A related reaction of aryl halides in the presence of nickel complexes has been studied; in this instance the competing reactions were hydrogenolysis and reduction (reaction (94)) [2109,2110]. A similar process led to a useful indole synthesis (reaction (95)) [2111].

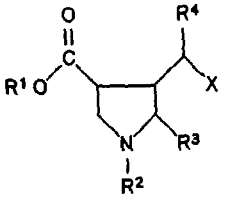


1094

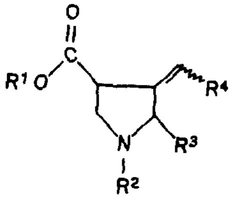


1095

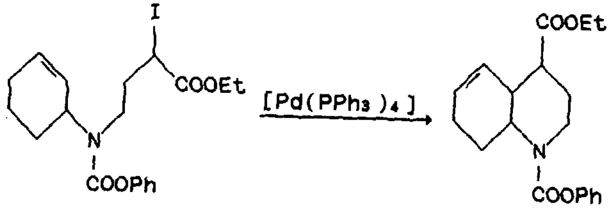
In the reaction of 1098 with a palladium catalyst two possible routes to cyclisation could be envisaged, *viz.* 5-*exo-trig* to give 1099 and 6-*endo-trig* to give 1100. The use of $[Pd(PPh_3)_4]$ resulted in the formation of mainly the six-membered ring product, whereas the use of $[RhCl(PPh_3)_3]$ gave mostly 1099. It was proposed that the five-membered ring was the kinetic and the six-membered ring the thermodynamic product [2112].



1096



1097



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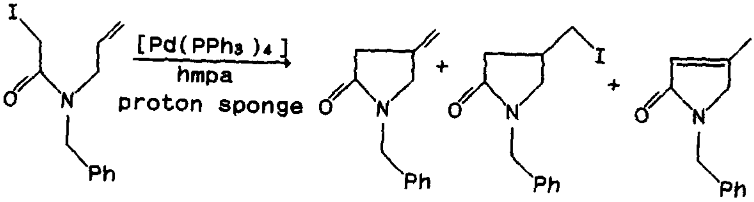

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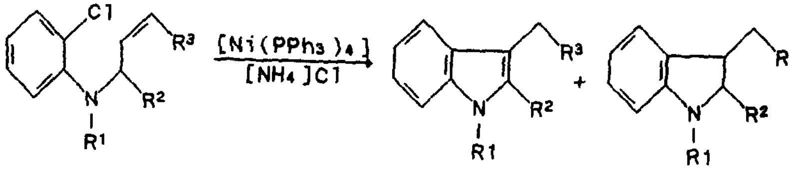
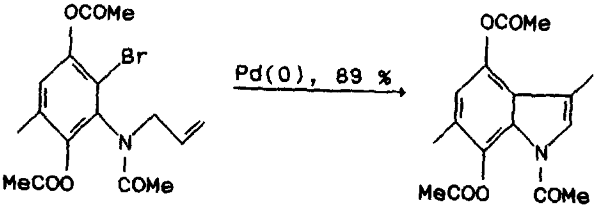


(94)



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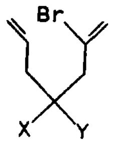
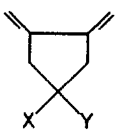
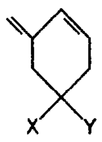


1098

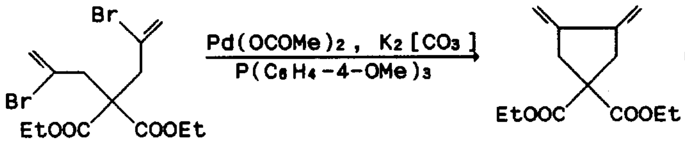


1099



1100

Intra and intermolecular couplings of haloalkenes have been used to prepare 1,3-dienes for use as Diels Alder substrates (reactions (96) and (97)) [2113].



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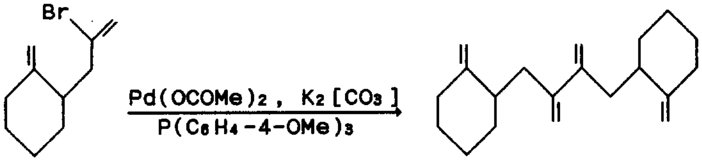
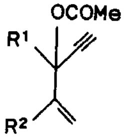


(97)

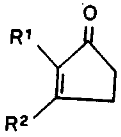
Reaction of alkyl halides, RBr, with phenylethene occurred in the presence of $Zn/py/[NiCl_2(PPh_3)_2]$, giving E-RCH=CHPh. The best substrates were those where R was secondary [2114]. Addition of R_fI to alkenes has been catalysed by $[Ni(CO)_2(PPh_3)_2]$; the reaction also succeeds with alkynes, and probably involves a radical chain process [2115]. Reaction of $I(CF_2)_6I$ with ethene using this catalyst gave $I(CH_2)_2(CF_2)_6(CH_2)_2I$ [2116], and $[Pd(PPh_3)_4]$ has also been used as a catalyst [2117].

The cyclisation of 1101 in the presence of $[PdCl_2(MeCN)_2]$ gave 1102 in moderate to excellent yield. The intermediate was suggested to be 1103, and a mechanism involving Pd(II) and Pd(IV) suggested [2118,2119]. When the silylated alkyne 1104 was used as the substrate, the products were 1105 and 1106 in the ratio 1.2:1. These were readily hydrolysed, and/or rearranged *via* hydride shifts, but could be trapped as Diels Alder adducts of *N*-phenylmaleimide [2120]. The alkene unit of the eneyne substrates could be replaced by a cyclopropane, as in 1107. The initial product was 1108, which could be trapped as a Diels Alder adduct, or hydrolysed to 1109 and 1110

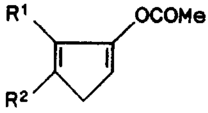
[2121].



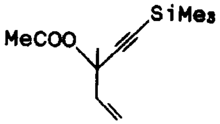
1101



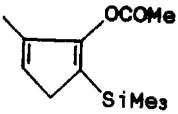
1102



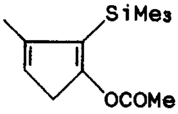
1103



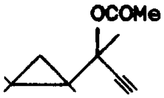
1104



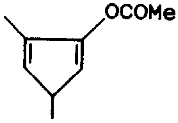
1105



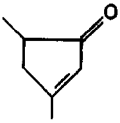
1106



1107



1108



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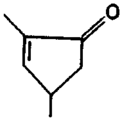
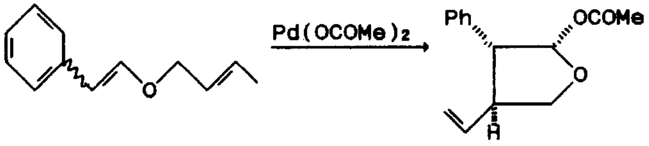
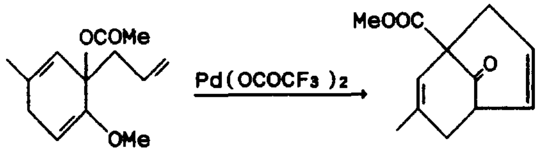


1110

Reaction (98) may be viewed as a nucleophilic attack of the enol ether on the palladium complexed alkene [2122]. In the related reaction of 1111 cyclisation predominates over Claisen rearrangement [2123]. The effect of additives on reaction (94) was studied; the yields were low under most conditions [2124].



1111



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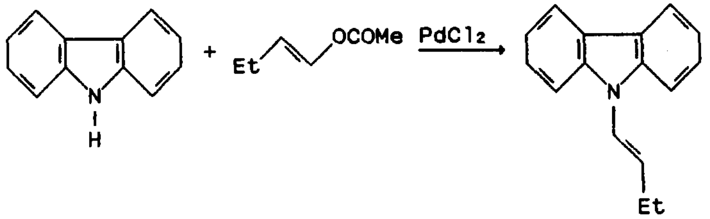
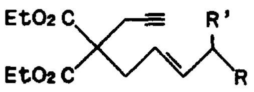
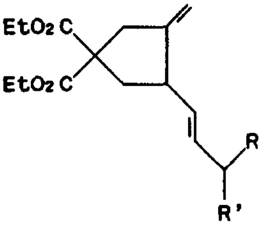


(99)

The enyne 1112 was prepared by palladium catalysed allylation of a stabilised carbanion. On reaction with palladium(II) it was cyclised to give 1113 (R, R' ≠ H) in good yield, *via* a carbometallation/cyclisation process involving 1114 as the key intermediate [2125,2126]. The same product isomer was obtained in both reactions (100) and (101) [2127]. A similar process may be initiated by reaction of PhHgCl/CuCl$_2$/PdCl$_2$, when PhPdX adds across the triple bond of 1115 to give 1116, which subsequently cyclises [2128].



1112



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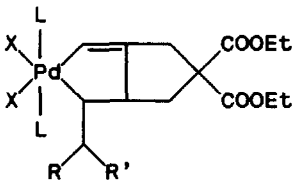

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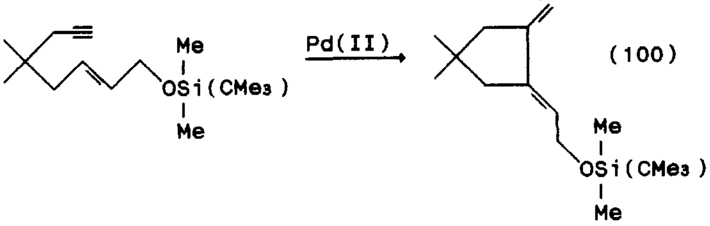

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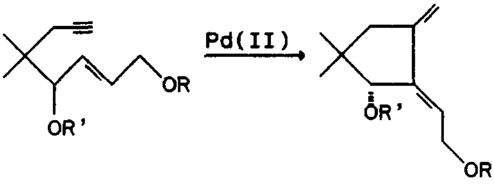

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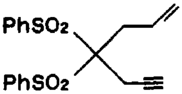

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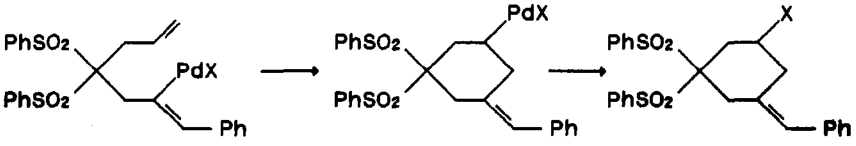
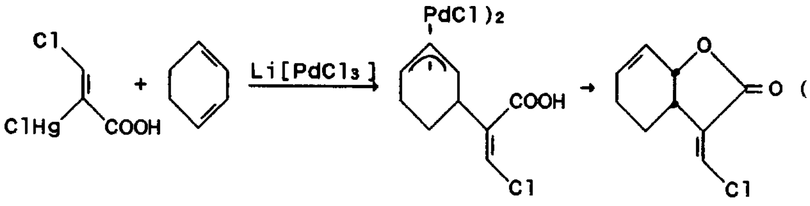


1116

Reaction of 1,1,-dibromo-2,2-diphenylethene with $[Ni(PPh_3)_3]$ in thf gave a complex mixture of products including 1,2-diphenylethene, diphenylethyne, triphenylethene and 1,1,4,4-tetraphenyl-1,3-butadiene. However, the reaction in benzene yielded 1,1,4,4-tetraphenylbutatriene in 60 % yield. A number of related reactions were noted, and possible reaction mechanisms proposed [2129].

When 1,3-cyclohexadiene was reacted with organomercury compounds containing a protic functional group, in the presence of $Li[PdCl_3]$, annulation resulted from addition followed by cyclisation onto an intermediate palladium allyl complex (reaction (102)). Internal nucleophiles which gave successful results included -COOH, -OH, NHCOMe and NH_2 [2130]. Reaction of 1,3-pentadiene with PhN=C=O in the presence of Ni(0) gave initially the equilibrating mixture 1117a and 1117b Protonation yielded 1118 and 1119, whilst low temperature extrusion of nickel yielded 1120 [2131].



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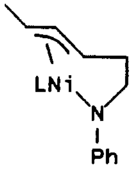
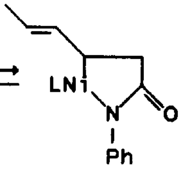


1117a



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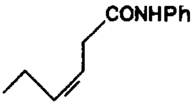

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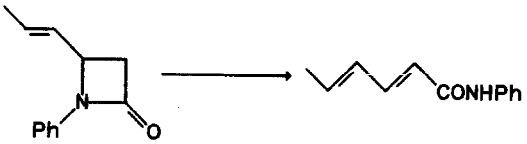
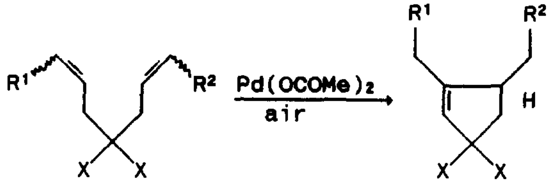


1120

Intramolecular oxidative coupling of alkenes occurred in air, catalysed by $PdCl_2$ or $Pd(OCOMe)_2$ (reaction (103); X = COMe). The presence of the carbonyl substituents is crucial to the success of the reaction. It may be assumed that the initial step in the reaction is coordination to the metal, and the related complex 1121 has been characterised in a diffraction study. The 1,6-diene is complexed in a chair conformation. A complete mechanism was proposed for the reaction [2132].



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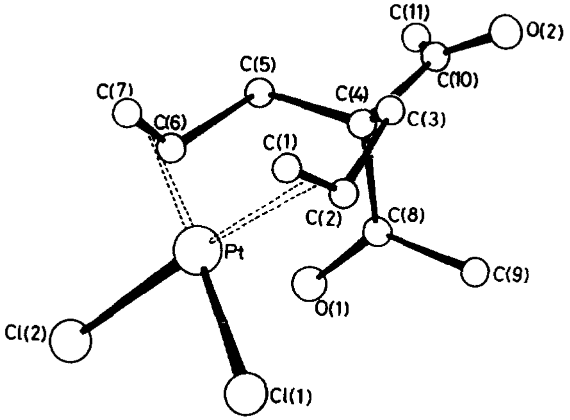
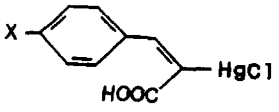
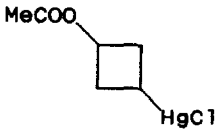


1121 (Reproduced with permission from [2132])

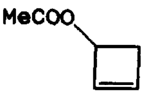
Oxidative dimerisation of 1122 was catalysed by $Li_2[PdCl_4]$, to give a mixture of E,Z and Z,Z-products [2133]. Reaction of 1123 with stoicheiometric $Li_2[PdCl_4]$ gave a mixture of homocoupled product (60 %) and 1124 (40 %) [2134, 2135]. Cyclopropylmercury chloride reacted with methyl propenoate in the presence of $Li[PdCl_3(MeCN)]$ to give methyl hexa-2,4-dienoate. The reaction mechanism proposed involved transmetallation, followed by addition and ring opening. The mechanism was supported by deuterium labelling studies, and reactions with other alkenes were also described [2136].



1122

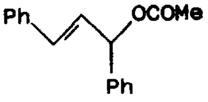


1123

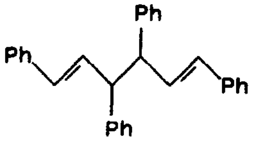


1124

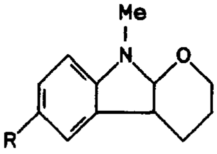
Reaction of 1125 with zinc metal in the presence of $[Pd(PPh_3)_4]$ gave the homocoupled product 1126 in excellent yield. A radical mechanism was assumed for the process, but it was not studied in great detail [2137]. A radical process also seems to be the most likely for the reaction of RCF_2I with Et_3N to give $RCF_2CH{=}CHNEt_2$ in the presence of $[Pd(PPh_3)_4]$ [2138]. The reaction of *N,N*-dimethyl arylamaines with thf to give 1127 as the main product involves initial single electron transfer yielding 1128 [2139].



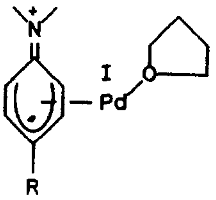
1125



1126

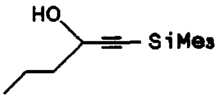


1127

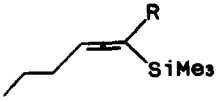


1128

Reaction of RMgX with 1129 to give 1130 in the presence of nickel(0) was thought to involve initial addition of $\{RNiL_n\}$ across the triple bond [2140].

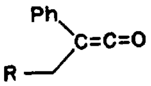


1129



1130

Photolysis of methanal in water gives rise to HCOCOH; $PdCl_2$ accelerated the reaction and increased the yield [2141]. Coupling of ketenes such as 1131 with ArCOCl to give 1132 was catalysed by $[Pd(PPh_3)_4]$; a palladium carbene complex was proposed as an intermediate [2142].



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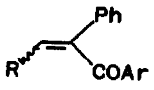
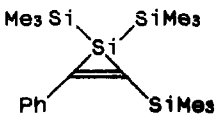


1132

Reaction of 1133 with $PhC{\equiv}CSiMe_3$ in the presence of $[NiCl_2(PEt_3)_2]$ gave a mixture of 1134 and 1135. The initial step in the mechanism proposed was insertion of nickel into the three-membered ring, and this was followed either by ring opening to give a species such as 1136 or ring expansion to 1137 [2143].



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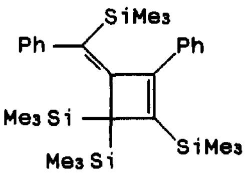

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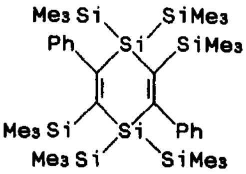

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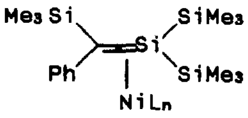

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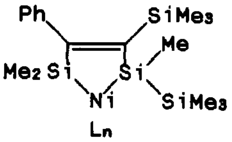
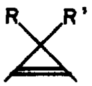


1137

Reaction of $RCH{=}CH_2$ with CXY_3 (X,Y = halogen) in the presence of $[Pd(PPh_3)_4]/Me_3Al$ gave $RCHYCH_2CX_3$. The reaction does occur without the catalyst, but yields are low [2144].

Reaction of 1138 with methyl propenoate in the presence of $[Ni(cod)_2]$ gave 1139, its *cis*-isomer and the dimer, 1140 [2145].



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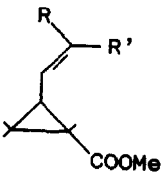

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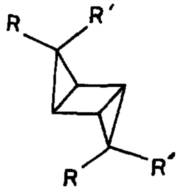
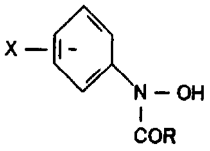


1140

13.11 Other Catalytic Reactions

Transesterification of methyl propenoate by ROH was catalysed by $[Ni(acac)_2]/BuLi$. Propenoate dimers were a by-product [2146]. Selectivity for transesterification with 2-propanol was 72 % using $[Ni(acac)_2]/BuLi/P(OPh)_3$ [2147]. Preparation of alkenyl esters of carboxylic acids was accomplished by their reaction with $CH_2{=}CHOCOMe$ in the presence of

$Pd(OCOMe)_2/K[OCOMe]/Cu(OCOMe)_2/KBr$ [2148]. *N*-Hydroxy compounds such as 1141 also reacted with $CH_2{=}CHOCOMe$ in the presence of $Li_2[PdCl_4]$ to give initially 1142, which underwent a 3,3-sigmatropic rearrangement to 1143, which then cyclised to the indole derivative 1144 [2149,2150]. Reaction of an alcohol, ROH, with $CH_2{=}C(OBn)CH_3$ in the presence of $[PdCl_2(cod)]$ gave the protected alcohol, $Me_2C(OBn)OR$. Deprotection was accomplished by hydrogenolysis [2151]. Hydrolysis of acetals has been reported to be catalysed by $[PdCl_2(MeCN)_2]$; MEM ethers and $Ph_2(Me_3C)SiO{-}R$ groups were inert, but $Me_2(Me_3C)SiO{-}R$ was cleaved under the reaction conditions [2152].



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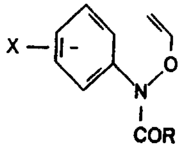

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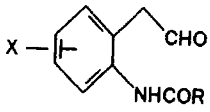

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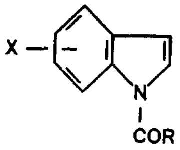
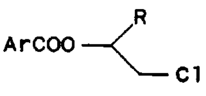


1144

Reaction of aroyl chlorides, ArCOCl, with monosubstituted epoxides in the presence of a range of transition metal complexes, gave a mixture of 1145 and 1146, 1145 being the main product using $[Pd(PPh_3)_4]$. 1146 was the main product using ruthenium complexes as catalysts, and was produced in greater yield when the aryl group was electron donating [2153]. Amberlite supported $PdCl_2$ catalysed the reaction of 2,6-$(Me_3C)_2C_6H_3OH$ with methanal and hydrogen to give 1147 with 93 % selectivity and 97.5 % conversion [2154]. Reaction of phosphine with methanal in the presenece of $NiCl_2$ gave $P(CH_2OH)_3$; a mathematical model was proposed to establish the best reaction conditions [2155]. The aldol condensation of propanal was catalysed by $[Ni(bipy)Et_2]$ [2156].

A range of elimination reactions have been reported to be catalysed by palladium complexes. Thus 1148 was heated in the presence of $[Pd(PPh_3)_4]$ to give 1149 in good isomeric purity [2157], and $RCO_2CH_2CH_2C(Me){=}CHCH_2X$ (X = Cl, Br or OCOR) gave $RCO_2CH_2CH_2C({=}CH_2)CH{=}CH_2$ using $Pd(OCOMe)_2/PPh_3$, $[Pd(PPh_3)_4]$ or $[Ni(CO)_2(PPh_3)_2]$ as the catalyst [2158]. Dehydrohalogenation of

$ClCH_2CHClCH=CH_2$ to 2-chlorobutadiene was shown to be best catalysed by $K[PdCl_3(dmso)]$ [2159]. Dehydrochlorination of 1150, in the presence of [PdL$_n$] was thought to involve a palladium allyl complex as intermediate [2160].



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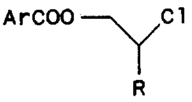

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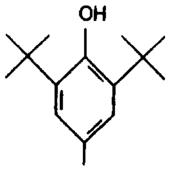

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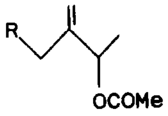

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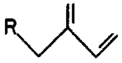

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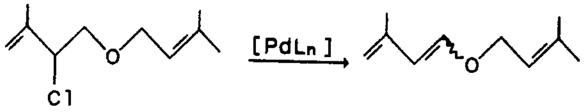
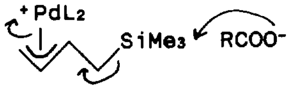


1150

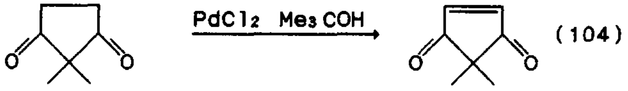
Acyl halides could be converted to stable acyl esters, $RCOOCH_2CH=CHCH_2SiMe_3$, on reaction with $HOCH_2CH=CHCH_2SiMe_3$. On reaction with $[PdL_4]$ the allyl complex 1151 was formed, and was attacked by the liberated $[RCOO]^-$ to give butadiene and $RCOOSiMe_3$, which was readily hydrolysed under very mild conditions. The overall yield for the deprotection step was 80-98 % [2161].



1151

Thermolysis of 2-hydroxypropanoic acid in the presence of $[PtH(PEt_3)_3]^+$ gave a complex mixture of products, including those of double bond hydrogenation, alcohol dehydration, transfer hydrogenation, decarbonylation and the water gas shift [2162].

The dehydrogenation of ketones in the presence of palladium chloride is not strictly a catalytic reaction, but is most conveniently considered here. It has been used in a synthetic approach to dodecahedrane [2163], and for reaction (104) [2164]. When β-amino ketones were used as the substrates, the reaction was extremely regioselective, to give enamines (reaction (105)) [2165]. In a related process, silyl enol ethers are converted to enones using $Pd(OCOMe)_2$ under oxidising conditions [2166-2168].



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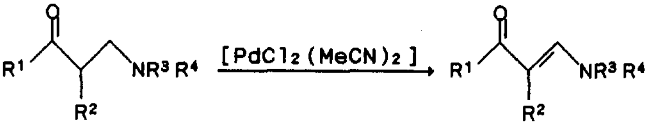
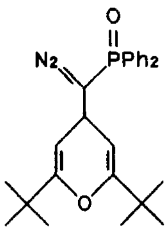


(105)

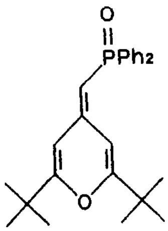
Primary amines, RNH_2, were converted to R_2NH on thermolysis in the presence of $[PtCl_2(PPh_3)_2]/SnCl_2$, generally in good yield. The reaction was supposed to involve formation of the imine followed by attack of RNH_2 and elimination of ammonia [2169]. Aryl exchange occurred on reaction of $Ar^1{}_3P$ with $Ar^2{}_3P$ in the presence of a range of transition metal complexes. $[Pd(PPh_3)_4]$ and $[Ni(CO)_2(PPh_3)_2]$ were relatively poor catalysts, with rhodium complexes being much more successful [2170]. Both PPh_3 and $SbPh_3$ underwent P-C bond cleavage in the presence of palladium ethanoate, giving biphenyl as the main isolated product [2171].

The diazo compound 1152 was cleanly converted to 1153 in the presence of $[\{Pd(\eta^3-C_3H_5)Cl\}_2]$ [2172]. A similar reaction was noted for the related sulphur containing heterocycle. The process involves a 1,2-hydride shift, and there was no competing carbon shift [2173]. However, with 1154, no hydride shift is possible, and ring expansion allows the synthesis of 1155 [2174]. A similar rearrangement must be invoked in reaction (106) [2175].

A range of nickel(0) complexes have been shown to catalyse the transalkylation of R_3Al with $R'CH{=}CH_2$; the mechanism involves σ-alkyl and π-alkene complexes [2176].



1151



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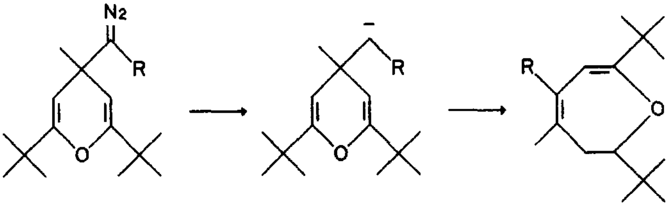

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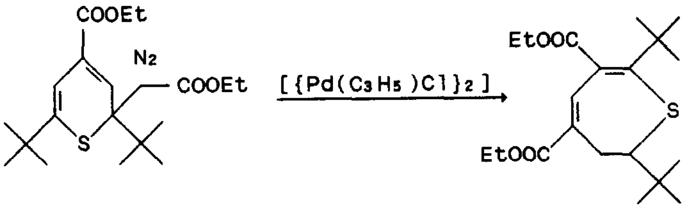
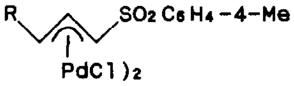


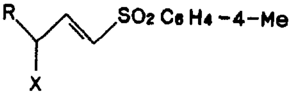
(106)

Reaction of 1156 with $PdCl_2$ gave the allyl complex 1157 which reacted with either ethanoate or halide in the presence of an excess of Cu(II) to give 1158 (X = OCOMe or Cl). The reaction intermediates need not be isolated [2177].

1156



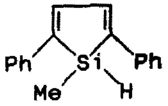
1157



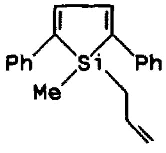
1158

Reaction of allylmagnesium bromide with 1159 in the presence of

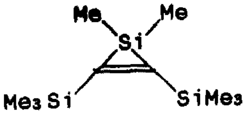
$[NiCl_2(PPh_3)_2]$ resulted in formation of 1160 [2178]. When 1161 was treated with phenylethene in the presence of $[PdCl_2(PPh_3)_2]$, 1162 was formed in an exothermic reaction. The mechanism of the reaction is complex, and is described in detail, with the first step being palladium insertion into the three membered ring [2179]. Metallosilylcyclobutanes were also key intermediates in reaction (107) [2180].



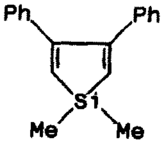
1159



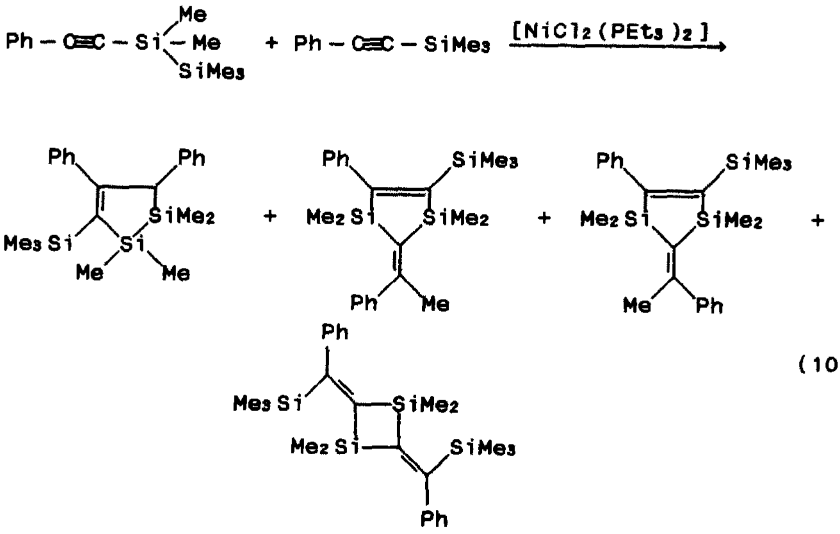
1160



1161

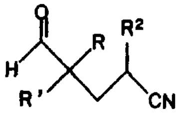


1162

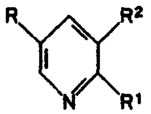


(107)

A patent has described the reaction of 1163 with $Me_2CHNH_2/[NiCl_2(PPh_3)_2]$ to give the pyridine derivative 1164 [2181]. The intended coupling of 1165 with a propargyl alcohol in the presence of $Pd(II)/Cu(II)/Et_3N$ resulted in cyclisation to 1166. The other oxime stereoisomer underwent hydrogenolysis; presumably the propargyl alcohol acted as the reductant [2182]. Two papers have described the reaction of 1167 with $Zn/NiCl_2/KI$ to give a mixture of 1168 and 1169. The key step appears to be the selective demethylation, but the reaction mechanism was not elucidated [2183,2184].



1163



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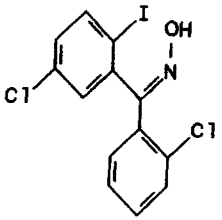
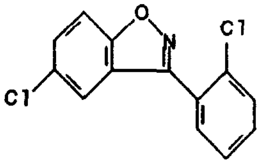
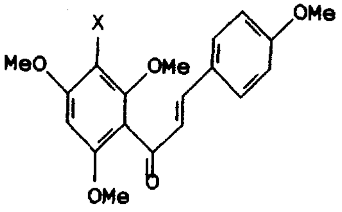


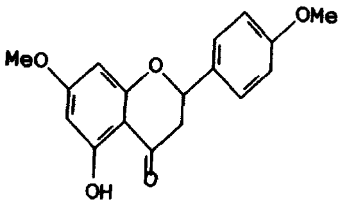
1165



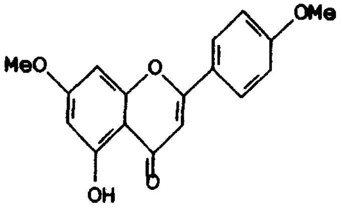
1166



1167



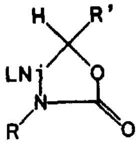
1168



1169

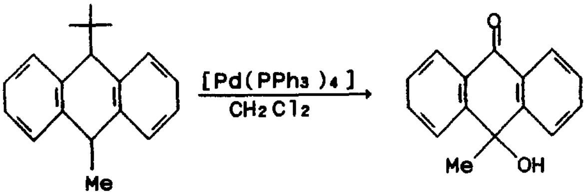
Dimerisation of $1,5-C_2B_3H_5$ was effected by $PtBr_2$ to give $2:2'[1,5-C_2B_3H_4]_2$, the reaction mechansim being related to that for palladium promoted arene dimerisation [2185].

Reaction of RNCO with R'CHO and $[Ni(0)L_n]$ gave the 1170 isolable at low temperature. On heating $[NiL_n]$ was regenerated, and CO_2 evolved to yield R'CH=NR. The complex reaction mechanism was discussed in detail [2186].



1170

Reaction (108) proceeded slowly, but with excellent conversion. Its mechanism is not known [2187].



(108)

ABBREVIATIONS

A	Angstrom
acacH	pentane-2,4-dione
Ad	adamantyl
Ar	aryl
bipy	2,2'-bipyridine
bipym	2,2'-bipyrimidine
Bn	benzyl
BPPM	2S,4S-*N-tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine
i-Bu	*iso*-butyl
Bu	butyl
CASSCF	complete active space self consistent field
ccp	cubic close-packed
cdt	cyclododecatriene
CI	chemical ionisation
CIDNIP	chemically induced dynamic nuclear polarisation
CHIRAPHOS	2S,3S-bis(diphenylphosphino)butane
CNDO	complete neglect of differential overlap
cod	1,5-cyclooctadiene
coe	cyclooctene
cot	cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
CV	cyclic voltammetry
CVE	cluster valence electron
Cy	cyclohexyl
dach	1,2-diaminocyclohexane
dad	diazadiene
dapm	1-diphenylarsino-1-diphenylphosphinomethane
dba	E,E-1,4-diphenyl-1,4-pentadiene-3-one
DBPDIOP	*trans*-4,5-bis(dibenzophospholomethyl)-2,2-dimethyl-1,3-dioxolan
DCC	*N,N'*-dicyclohexylcarbodiimide
dcpe	1,2-bis(dicyclohexylphosphino)ethane
depb	1,4-bis(diethylphosphino)butane
depm	1,1-bis(diethylphosphino)methane
dibalH	diisobutyl aluminium hydride
DIOP	*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan
dma	*N,N*-dimethylethanamide
dmad	dimethyl but-2-yne dioate
dmf	*N,N*-dimethylmethanamide
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
dmso	dimethyl sulphoxide
dpmp	$Ph_2PCH_2P(Ph)CH_2PPh$
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
DSC	differential scanning calorimetry
EHMO	extended Huckel molecular orbital
EI	electron impact
EPR	electron paramagnetic resonance
Et	ethyl
ewg	electron withdrawing group
Fc	ferrocenyl

hfacaacH	1,1,1,5,5,5-hexafluoropentane-2,4-dione
hmpt	hexamethylphsophoric triamide
HOMO	highest occupied molecular orbital
HPA	heteropolyacid, $H_{3+n}PMo_{12-n}V_nO_{40}$, n = 2-8
hplc	high pressure liquid chromatography
HSAB	hard and soft acid and base
INDO	intermediate neglect of differential overlap
IR	infra-red
kJ	kilojoule
L	2 electron donor ligand
LCAO	linear combination of atomic orbitals
LCGTO	linear combination of Gaussian type orbitals
LEED	low energy electron diffraction
LUMO	lowest unoccupied molecular orbital
Me	methyl
MEM	2-methoxyethoxymethyl
Mes	methane sulphonate
MLCT	metal to ligand charge transfer
MO	molecular orbital
8-mqH_2	8-methylquinoline
nbd	bicyclo[2.2.1]heptadiene
NBS	*N*-bromosuccinimide
nmr	nuclear magnetic resonance
Np	naphthyl
np_3	$N(CH_2CH_2PPh_2)_3$
Nu	nucleophile
Pc	phthalocyanine
PES	photoelectron spectroscopy
Ph	phenyl
phen	1,10-phenanthroline
pmdta	*N,N,N',N",N"*-pentamethyldiethylene triamine
pnp	2,6-bis(diphenylphosphino)pyridine
R,S-PPFA	(R)-*N,N*-dimethyl-1-{(S)-2-diphenylphosphinoferrocenyl)ethylamine
Pr	propyl
PTFE	polytetrafluoroethene
py	pyridine
pzH	pyrazole
R	alkyl
R_f	perfluoroalkyl
RHF	restricted Hartree Fock
sacsacH	pentane-2,4-dithione
SCF	self-consistent field
SET	single electron transfer
tcne	tetracyanoethene
TCNQ	7,7,8,8-tetracyanoquinodimethane
THP	tetrahydropyranyl
TfOH	trifluoromethane sulphonic acid
tfacacH	1,1,1-trifluoropentane-2,4-dione
tfaH	trifluoroethanoic acid
thf	tetrahydrofuran
tmeda	*N,N,N',N'*-tetramethylethane-1,2-diamine
TMM	trimethylene methane
tmtu	*N,N,N'N'*-tetramethylthiourea
tol	4-methylphenyl
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
TsOH	4-toluene sulphonic acid
TTF	tetrathiofulvalene
tu	thiourea
UV	ultra-violet
UVPES	ultraviolet photoelectron spectroscopy

vdpp	ethenyldiphenylphosphine
WGSR	water gas shift reaction
X	one electron donor ligand, usually halide
XPES	X-ray photoelectron spectroscopy
β-dik	β-diketonato

REFERENCES

1 H.A. Skinner and J.A. Connor, Pure Appl. Chem., 57 (1985) 79.
2 T.-L. Ho, Tetrahedron, 41 (1985) 1.
3 B. Walther, Coord. Chem. Rev., 60 (1984) 67.
4 R.J.H. Clark, Chem. Soc. Rev., 13 (1984) 219.
5 E.C. Niederhoffer, J.H. Timmons and A.E. Martell, Chem. Rev., 84 (1984) 137.
6 M.E. Keeney, K. Osseo-Asare and K.A. Woode, Coord. Chem. Rev., 59 (1984) 141.
7 D.M.A. Minahan, W.E. Hill and C.A. McAuliffe, Coord. Chem. Rev., 55 (1984) 31.
8 B.J. McCormick, R. Bereman and D. Baird, Coord. Chem. Rev., 54 (1984) 99.
9 A.M. Bond and R.L. Martin, Coord. Chem. Rev., 54 (1984) 23.
10 W. Levason, Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., 81(A) (1985) 269.
11 L. Markó, J. Organomet. Chem., 283 (1985) 221.
12 L.S. Hegedus, J. Organomet. Chem., 283 (1985) 1.
13 M.I. Bruce, J. Organomet. Chem., 283 (1985) 339.
14 A. Reith and A. Broegger, IARC Sci. Publ., 53 (Nickel Hum. Environ.) (1984) 175; Chem. Abstr., 103 (1985) 66090f.
15 F. Brezina, Acta Univ. Palacki Olumuc., Fac. Rerum Nat., 82 (Chem.-24) (1985) 5; Chem. Abstr., 104 (1986) 44902r.
16 R.B. Hitam, K.A. Mahmoud and A.J. Rest, Coord. Chem. Rev., 55 (1984) 1.
17 A. Bencini, C. Benelli and D. Gatteschi, Coord. Chem. Rev., 60 (1984) 131.
18 D.A. Thornton, Coord. Chem. Rev., 55 (1984) 113.
19 T.B. Brill and S.J. Landon, Chem. Rev., 84 (1984) 577.
20 P. Pelikán and R. Boča, Coord. Chem. Rev., 55 (1984) 55.
21 R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, 1985; Chem. Abstr., 104 (1984) 87788a.
22 O.V. Gritsenko, A.A. Bagatur'yants, I.I. Moiseev and V.B. Kazanskii, Russ. Chem. Rev., 54 (1985) 1151; Usp. Khim., 54 (1985) 1945.
23 A.V. Roschin, V.G. Veselov and A.I. Panova, J. Hyg., Epidemiol., Microbiol., Immunol., 28 (1984) 17; Chem. Abstr., 100 (1984) 214724w.
24 C.T. Mortimer, Rev. Inorg. Chem., 6 (1984) 233.
25 A.L. Balch, Comments Inorg. Chem., 3 (1984) 51.
26 W. Levason, Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., 80 (1984) 245.
27 L.B. Hunt, Platinum Met. Rev., 28 (1984) 76; Chem. Abstr., 101 (1984) 71753n.
28 N.N. Greenwood, Chem. Soc. Rev., 13 (1984) 353.
29 A.K. Smith, Organomet. Chem., 12 (1984) 225.
30 J.R. Moss and L.G. Scott, Coord. Chem. Rev., 60 (1984) 171.
31 Y.-T. Fanchiang, Coord. Chem. Rev., 68 (1985) 131.
32 R.C. Mehrotra, S.K. Agarwal and Y.P. Singh, Coord. Chem. Rev., 68 (1985) 101.
33 A. Yamamoto, T. Yamamoto, S. Komiya and F. Ozawa, Pure Appl. Chem., 56 (1984) 1621.
34 J.J. Low and W.A. Goddard, J. Am. Chem. Soc., 106 (1984) 8321.
35 S. Obara, K. Kitaura and K. Morokuma, J. Am. Chem. Soc., 106 (1984) 7482.
36 E. Bauwe and G. Rasch, Z. Chem., 24 (1984) 304.
37 K. Tatsumi, A. Nakamura, S. Komiya, A. Yamamoto and T. Yamamoto, J. Am. Chem. Soc., 106 (1984) 8181.
38 N.N. Kostitsyna, I.A. Oreshkin, B.A. Dolgoplosk, E. Tinyakova and A.I. Mikaya, Dokl. Chem., 277 (1984) 268; Dokl. Akad. Nauk SSSR, 277 (1984) 1405 [Chem.].
39 S. Pasynkiewicz and H. Lehmkuhl, J. Organomet. Chem., 289 (1985) 189.
40 A. Morvillo and A. Turco, J. Organomet. Chem., 276 (1984) 431.
41 F. Ozawa, K. Kurihara, T. Yamamoto and A. Yamamoto, J. Organomet. Chem., 279 (1985) 233.

42 W.H. Smith and Y.-M. Kuo, J. Electroanal. Chem., Interfacial Electrochem., 188 (1985) 189.

43 K. Morokuma, K. Ohta, N. Koga, S. Obara and E.R. Davidson, Faraday Symp. Chem. Soc., 19 (1984) 49.

44 N. Koga, S. Obara, K. Kitaura and K. Morokuma, J. Am. Chem. Soc., 107 (1985) 7109.

45 J. Lau and R. Sustmann, Tetrahedron Lett., 26 (1985) 4907.

46 F. Ozawa, K. Kurihara, T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Jpn., 58 (1985) 399.

47 P. Diversi, D. Fasce and R. Santini, J. Organomet. Chem., 269 (1984) 285.

48 G. Alibrandi, D. Minniti, R. Romeo, G. Cum and R. Gallo, J. Organomet. Chem., 291 (1985) 133.

49 H.E. Bryndza, J. Chem. Soc., Chem. Commun., (1985) 1696.

50 R.L. Brainard and G.M. Whitesides, Organometallics, 4 (1985) 1550.

51 I.A. Kop'eva, I.A. Oreshkin and B.A. Dolgoplosk, Dokl. P. Chem., 284 (1985) 882; Dokl. Akad. Nauk SSSR, 284 (1985) 162 [Phys. Chem.].

52 R.H. Reamey and G.M. Whitesides, J. Am. Chem. Soc., 106 (1984) 81.

53 G.M. Whitesides, M. Hackett, R.L. Brainard, J.-P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown and E.M. Staudt, Organometallics, 4 (1985) 1819.

54 T. Kauffmann and M. Bisling, Tetrahedron Lett., 25 (1984) 293.

55 T.P.E. Auf der Heyde and L.R. Nassimbeni, Inorg. Chem., 23 (1984) 4525.

56 K.-R. Pörschke, K. Jonas, G. Wilke, R. Benn, R. Mynott, R. Goddard and C. Krüger, Chem. Ber., 118 (1985) 275.

57 V.O. Efe and B.N. Ghose, Rev. Port. Quim., 25 (1983) 151; Chem. Abstr., 101 (1984) 130854w.

58 M.L. Mandich, L.F. Halle and J.L. Beauchamp, J. Am. Chem. Soc., 106 (1984) 4403.

59 J.V. Ortiz, Z. Havlas and R. Hoffmann, Helv. Chim. Acta, 67 (1984) 1.

60 R. Tooze, K.W. Chiu and G. Wilkinson, Polyhedron, 3 (1984) 1025.

61 P.K. Byers and A.J. Canty, Inorg. Chim. Acta, 104 (1985) L13.

62 B. Kellenberger, S.J. Young and J.K. Stille, J. Am. Chem. Soc., 107 (1985) 6105.

63 J.K. Stille, Energy Res. Abstr., 10 (1985) Abstr. No. 51954; Chem. Abstr., 106 (1987) 176635g.

64 A.B. Goel, S. Goel and D. Vanderveer, Polyhedron, 3 (1984) 373.

65 A.L. Balch, R.R. Guimerans and J. Linehan, Inorg. Chem., 24 (1985) 290.

66 F.S.M. Hassan, D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1501.

67 G.B. Jacobsen and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1985) 692.

68 D.P. Arnold and M.A. Bennett, Inorg. Chem., 23 (1984) 2110.

69 A. De Renzi, G. Morelli, A. Panunzi and A. Vitagliano, Gazz. Chim. Ital., 115 (1985) 247.

70 X.L.R. Fontaine, F.S.M. Hassan, S.J. Higgins, G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985) 1635.

71 P.K. Monaghan, PhD Thesis, Univ. Western Ontario; Diss. Abstr. Int. B, 45B (1985) 3814.

72 P.K. Monaghan and R.J. Puddephatt, Organometallics, 4 (1985) 1406.

73 T.G. Appleton, J.R. Hall, D.W. Neale and M.A. Williams, J. Organomet. Chem., 276 (1984) C73.

74 R.H. Hill and R.J. Puddephatt, J. Am. Chem. Soc., 107 (1985) 1218.

75 G. Ferguson, P.K. Monaghan, M. Parvez and R.J. Puddephatt, Organometallics, 4 (1985) 1669.

76 J.D. Scott and R.J. Puddephatt, Inorg. Chim. Acta, 89 (1984) L27.

77 V.V. Zamashchikov, A.N. Kitaigorodskii, S.L. Litvinenko, E.S. Rudakov, O.N. Uzhik and A.E. Shilov, Bull. Acad. Sci USSR., Div. Chem. Sci., 34 (1985) 1582; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 1730.

78 V.V. Zamashchikov, E.S. Rudakov, S.A. Mitchenko and T.M. Pekhtereva, Koord. Khim., 11 (1985) 69; Chem. Abstr., 102 (1985) 85082a.

79 G.B. Shul'pin, G.V. Nizova, A.N. Kitaigorodskii and M.V. Serdobov, J. Organomet. Chem., 275 (1984) 273.

80 V.V. Zamashchikov, S.L. Litvinenko and O.N. Uzhik, Kinet. Catal., 25 (1984) 653; Kinet. Katal., 25 (1984) 765.

81 Y.-T. Fanchiang, Inorg. Chim. Acta, 105 (1985) 209.

82 Y.-T. Fanchiang and J.J. Pignatello, Inorg. Chim. Acta, 91 (1984) 147.

83 G. Smith, C.H.L. Kennard and T.C.W. Mak, J. Organomet. Chem., 290 (1985) C7.

84 H.C. Clark, G. Ferguson, V.K. Jain and M. Parvez, J. Organomet. Chem., 270 (1984) 365.

85 S. Aros M. and A. Nettle Z., Afinidad, 42 (1985) 158.

86 P.K. Monaghan and R.J. Puddephatt, Organometallics, 3 (1984) 444.

87 R.J. Puddephatt and J.D. Scott, Organometallics, 4 (1985) 1221.

88 J.E. Hux and R.J. Puddephatt, Inorg. Chim. Acta, 100 (1985) 1.

89 T.J. Drahnak, U.S. US 4,510,094 (1985); Chem. Abstr., 103 (1985) 38798z.

90 E.W. Abel, S.K. Bhargava, K.G. Orrell, A.W.G. Platt, V. Šik and T.S. Cameron, J. Chem. Soc., Dalton Trans., (1985) 345.

91 E.W. Abel, G.D. King, K.G. Orrell, V. Šik, T.S. Cameron and K. Jochem, J. Chem. Soc., Dalton Trans., (1984) 2047.

92 E.W. Abel, P.K. Mittal, K.G. Orrell, V. Šik and T.S. Cameron, J. Chem. Soc., Chem. Commun., (1984) 1312.

93 S.L. Pratt and R.A. Faltynek, J. Mol. Catal., 24 (1984) 47.

94 K.A. Azam, M.P. Brown, R.H. Hill, R.J. Puddephatt and A. Yavari, Organometallics, 3 (1984) 697.

95 K.A. Azam, R.H. Hill and R.J. Puddephatt, Can. J. Chem., 62 (1984) 2029.

96 L. Manojlović-Muir, K.W. Muir, A.A. Frew, S.S.M. Ling, M.A. Thomson and R.J. Puddephatt, Organometallics, 3 (1984) 1637.

97 L. Manojlović-Muir and K.W. Muir, Croat. Chem. Acta, 57 (1984) 587.

98 S.S.M. Ling, N.C. Payne and R.J. Puddephatt, Organometallics, 4 (1985) 1546.

99 S.S.M. Ling, I.R. Jobe, L. Manojlović-Muir, K.W. Muir and R.J. Puddephatt, Organometallics, 4 (1985) 1198.

100 M. Lashanizadehgan, M. Rashidi, J.E. Hux, R.J. Puddephatt and S.S.M. Ling, J. Organomet. Chem., 269 (1984) 317.

101 V.V. Sutcliffe and G.B. Young, Polyhedron, 3 (1984) 87.

102 S. Nussbaum and A. Storr, Can. J. Chem., 63 (1985) 2550.

103 S.C.H. Ho, D.A. Straus, J. Armantrout, W.P. Schaefer and R.H. Grubbs, J. Am. Chem. Soc., 106 (1984) 2210.

104 R. Contreras and Y.A. Nettle Z., Bol. Soc. Chil. Quim., 30 (1985) 21; Chem. Abstr., 104 (1985) 6003r.

105 G. Li, F. Ding, F. Dai and L. Zhang, Huaxue Xuebao, 43 (1985) 878; Chem. Abstr., 105 (1986) 5911u.

106 A. Albinati, U. von Gunten, P.S. Pregosin and H.J. Ruegg, J. Organomet. Chem., 295 (1985) 239.

107 G.A. Tolstikov, N.R. Popod'ko, A.A. Pozdeeva, R.I. Khusnutdinov, S.I. Zhdanov, D.K. Galeev and U.M. Dzhemilev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1186; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 1293.

108 T.V. Dmitrieva, G.V. Ratovskii and F.K. Shmidt, Sov. J. Coord. Chem., 10 (1984) 113; Koord. Khim., 10 (1984) 213.

109 M.N. Bochkarev, N.L. Ermolaev, L.N. Zakharov, Yu.N. Saf'yanov, G.A. Razuvaev and Yu.T. Struchkov, J. Organomet. Chem., 270 (1984) 289.

110 M. Crespo, O. Rossell, J. Sales and M. Seco, J. Organomet. Chem., 273 (1984) 415.

111 E. Carmona, M. Paneque, M.L. Poveda, R.D. Rogers and J.L. Atwood, Polyhedron, 3 (1984) 317.

112 A. Heumann and J.-E. Bäckvall, Angew. Chem., Int. Ed. Engl., 24 (1985) 207; Angew. Chem., 97 (1985) 228.

113 L.I. Zakharkin and N.F. Shemyakin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1985) 2572; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1985) 2807.

114 G. Alibrandi, D. Minniti, R. Romeo and P. Vitarelli, Inorg. Chim. Acta, 81 (1984) L23.
115 G. Alibrandi, D. Minniti, R. Romeo, P. Uguagliati, L. Calligaro, U. Belluco and B. Crociani, Inorg. Chim. Acta, 100 (1985) 107.
116 M.P. Brown, A. Yavari, R.H. Hill and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1985) 2421.
117 S. Komiya and T. Shindo, J. Chem. Soc., Chem. Commun., (1984) 1672.
118 G.C. Dash, R.C. Mishra, D. Panda and B.K. Mohapatra, Polyhedron, 4 (1985) 1297.
119 G.C. Dash and B.K. Mohapatra, J. Indian Chem. Soc., 62 (1985) 14.
120 F. Sasakura, K. Isobe and S. Kawaguchi, Bull. Chem. Soc. Jpn., 58 (1985) 657.
121 G.R. Newkome, V.K. Gupta, H.C.R. Taylor and F.R. Fronczek, Organometallics, 3 (1984) 1549.
122 T. Kawato, T. Uechi, H. Koyama, H. Kanatomi and Y. Kawanami, Inorg. Chem., 23 (1984) 764.
123 D.A. Clarke, R.D.W. Kemmitt, M.A. Mazid, P. McKenna, D.R. Russell, M.D. Schilling and L.J.S. Sherry, J. Chem. Soc., Dalton Trans., (1984) 1993.
124 A. Imran, R.D.W. Kemmitt, A.J.W. Markwick, P. McKenna, D.R. Russell and L.J.S. Sherry, J. Chem. Soc., Dalton Trans., (1985) 549.
125 R.D.W. Kemmitt, P. McKenna, D.R. Russell and L.J.S. Sherry, J. Chem. Soc., Dalton Trans., (1985) 259.
126 E. Uhlig and B. Hipler, Tetrahedron Lett., 25 (1984) 5871.
127 B. Hipler and E. Uhlig, Z. Anorg. Allg. Chem., 510 (1984) 11.
128 B. Hipler and E. Uhlig, Proc. Conf. Coord. Chem., 10th (1985) 153; Chem. Abstr., 106 (1987) 5201h.
129 E. Carmona, J.M. Marín, P. Palma, M. Paneque and M.I. Poveda, Organometallics, 4 (1985) 2053.
130 S. Inaba and R.D. Rieke, J. Org. Chem., 50 (1985) 1373.
131 G.V. Nizova, M.V. Serdobov, A.T. Nikitaev and G.B. Shul'pin, J. Organomet. Chem., 275 (1984) 139.
132 V.V. Zamashchikov, E.S. Rudakov, S.A. Mitchenko, G.V. Nizova, A.N. Kitaigorodskii and G.B. Shul'pin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1520; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 1657.
133 C.E. Briant, C.J. Gardner, T.S.A. Hor, N.D. Howells and D.M.P. Mingos, J. Chem. Soc. Dalton Trans., (1984) 2645.
134 Z.-Y. Yang and G.B. Young, J. Chem. Soc., Dalton Trans., (1984) 2019.
135 Z. Yang, X. Han and T. Ji, Huaxue Xuebao, 43 (1985) 476; Chem. Abstr., 104 (1985) 18660r.
136 N. Ishio, Y. Nakamura and S. Okeya, Bull. Chem. Soc. Jpn., 57 (1984) 1012.
137 H.H. Karsch, Chem. Ber., 117 (1984) 783.
138 D. Steinborn and R. Taube, Z. Anorg. Allg. Chem., 521 (1985) 183.
139 J.G. Davidson, E.K. Barefield and D.G. Van Derveer, Organometallics, 4 (1985) 1178.
140 H.D. McPherson and J.L. Wardell, Inorg. Chim. Acta, 81 (1984) 33.
141 H.J. McPherson and J.L. Wardell, Inorg. Chim. Acta, 81 (1984) 39.
142 R. Benn, R.-D. Reinhardt and A. Rufińska, J. Organomet. Chem., 282 (1985) 291.
143 D.B. Jacobson and B.S. Freiser, Organometallics, 3 (1984) 513.
144 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 849.
145 P. Barabotti, P. Diversi, G. Ingresso, A. Lucherini and F. Nuti, J. Chem. Soc., Dalton Trans., (1984) 2517.
146 T.C. Flood and J.A. Statler, Organometallics, 3 (1984) 1795.
147 H.M. Büch and C. Krüger, Acta Crystallogr., Sect. C, C40 (1984) 28.
148 T.A. Peganova, P.V. Petrovskii, L.S. Isaeva, D.N. Kravtsov, D.B. Furman, A.V. Kudryashev, A.O. Ivanov, S.V. Zotova and O.V. Bragin, J. Organomet. Chem., 282 (1985) 283.
149 E. Rotondo, F.P. Cusmano, G. Neri, A. Donato and R. Pietropaolo, J. Organomet. Chem., 292 (1985) 429.

150 D. Fenske and W. Bensmann, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1819.
151 D. Fenske and W. Bensmann, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 1093.
152 U. Hacksell, H.T. Kalinkoski, D.F. Barofsky and G.D. Daves, Acta Chem. Scand., B39 (1985) 469.
153 L.S. Hollis, A.R. Amundsen and E.W. Stern, J. Am. Chem. Soc., 107 (1985) 274.
154 Y. Nagel and W. Beck, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 1181.
155 A.D. Pomogailo and V.S. Savostyanov, J. Macromol. Sci., Rev. Macromol. Chem. Phys., C25 (1985) 375.
156 H.A. Brune, J. Unsin, H.G. Alt, G. Schmidtberg and K.-H Spohn, Chem. Ber., 117 (1984) 1606.
157 D.P. Arnold and M.A. Bennett, Inorg. Chem., 23 (1984) 2117.
158 Z. Zhang, S. Wang, G. Yang, C. Shen and Y. Fang, Jiegou Huaxue, 3 (1984) 119; Chem. Abstr., 103 (1985) 62902z.
159 W. Conzelmann, J.D. Koola, U. Kunze and J. Strähle, Inorg. Chim. Acta, 89 (1984) 147.
160 M.W. Eyring and L.J. Radonovich, Organometallics, 4 (1985) 1841.
161 R. Usón, J. Forniés, M. Tomás, B. Menjón, K. Sünkel and R. Bau, J. Chem. Soc., Chem. Commun., (1984) 751.
162 S.T. Lin and K.J. Klabunde, Inorg. Chem., 24 (1985) 1961.
163 J. Doménech and J. Sales, An. Quim., Ser. B, 80 (1984) 182; Chem. Abstr., 102 (1985) 132226n.
164 M. Anton, N. Clos and G. Muller, J. Organomet. Chem., 267 (1984) 213.
165 H. Tanaka, K. Isobe, S. Kawaguchi and S. Okeya, Bull. Chem. Soc. Jpn., 57 (1984) 456.
166 B. Crociani, F. Di Bianca, A. Giovenco and A. Scrivanti, J. Organomet. Chem., 269 (1984) 295.
167 J.V. Caspar, J. Am. Chem. Soc., 107 (1985) 6718.
168 G. Favero and A. Morvillo, J. Organomet. Chem., 260 (1984) 363.
169 W.-D. Müller, G. Schmidtberg and H.-A. Brune, Chem. Ber., 118 (1985) 4653.
170 W.-D. Müller and H.A. Brune, Chem. Ber., 118 (1985) 4347.
171 H.A. Brune, R. Hess and G. Schmidtberg, Chem. Ber., 118 (1985) 2011.
172 Z. Zhang and H. Wang, Gaodeng Xuexiao Huaxue Xuebao, 6 (1985) 910; Chem. Abstr., 105 (1986) 226941f.
173 X. Wang, Z. Zhang and D. Wei, Goadeng Xuexiao Huaxue Xuebao, 6 (1985) 49; Chem. Abstr., 104 (1986) 208418d.
174 H.-A. Brune, M. Wiege and T. Debaerdemaeker, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 359.
175 H.A. Brune, G. Schmidtberg and M. Wiege, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 517.
176 H.A. Brune, M. Wiege and T. Debaerdemaeker, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 907.
177 R.J. Cross and J. Gemmill, J. Chem. Res., S, (1984) 30.
178 G.B. Deacon and I.L. Grayson, J. Organomet. Chem., 292 (1985) 1.
179 J.M. Lopez and B.N. Spevak, Rev. Cienc. Quim., 16 (1985) 161; Chem. Abstr., 108 (1988) 186954r.
180 R. Chen, Q. Zhang, X. Wang, X. Wang and Z. Zhang, Gaodeng Xuexiao Huaxue Xuebao, 5 (1984) 869; Chem. Abstr., 102 (1985) 95812c.
181 Q. Zhang, Y. Li, J. Chen, R. Chen, Z. Zhang and X. Wang, Wuli Huaxue Xuebao, 1 (1985) 460; Chem. Abstr., 104 (1986) 40565k.
182 H.-P. Abicht, H. Schmidt and K. Issleib, Z. Chem., 25 (1985) 410.
183 G. Garcia, G. Lopez, J. Ruiz and G. Sanchez, An. Univ. Murcia, Cienc., 43 (1984-1985, pub 1984) 21; Chem. Abstr., 103 (1985) 123678e.
184 G. Lopez, G. Garcia, C. De Haro, G. Sanchez and M.C. Vallejo, J. Organomet. Chem., 263 (1984) 247.

185 R. Usón, J. Forniés, M. Tomás and B. Menjón, Organometallics, 4 (1985) 1912.

186 R. Usón, J. Forniés, P. Espinet, R. Navarro and E. Lalinde, Transition Met. Chem., 9 (1984) 277.

187 H. Tanaka, K. Isobe, S. Kawaguchi and S. Okeya, Bull. Chem. Soc. Jpn., 57 (1984) 1850.

188 N. Cutillas Aullo, G. Garcia Sanchez and G. Lopez Lopez, An. Univ. Murcia, Cienc., 43 (1984-1985, pub. 1984) 13; Chem. Abstr., 103 (1985) 71479u.

189 D. Carmona, S. Chaloupka, J. Jans, R. Thouvenot and L.M. Venanzi, J. Organomet. Chem., 275 (1984) 303.

190 S. Lanza, D. Minniti, R. Romeo, P. Moore, J. Sachinidis and M.L. Tobe, J. Chem. Soc., Chem. Commun., (1984) 542.

191 A.T. Hutton, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1677.

192 T. Rukachaisirikul, S. Arabi, F. Hartstock, N.J. Taylor and A.J. Carty, Organometallics, 3 (1984) 1587.

193 R.A. Michelin, G. Strukul, N. Bresciani-Pahor, E. Zangrando and L. Randaccio, Inorg. Chim. Acta., 84 (1984) 229.

194 S.L. Litvinenko, V.V. Zamashchikov, E.S. Rudakov, M.P. Goncharenko and V.F. Galat, Koord. Khim., 11 (1985) 356; Chem. Abstr., 102 (1985) 173378g.

195 G.B. Shul'pin, G.V. Nizova, A.E. Shilov, A.T. Nikitaev and M.V. Serdobov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2454; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 2681.

196 A.T. Nikitaev, V.V. Lontsov, G.V. Nizova and G.B. Shul'pin, J. Org. Chem. USSR, 20 (1984) 2339; Zh. Org. Khim., 20 (1984) 2570.

197 G.B. Shul'pin, G.V. Nizova and A.T. Nikitaev, J. Organomet. Chem., 276 (1984) 115.

198 M.V. Serdobov, G.V. Nizova and G.P. Shul'pin, J. Organomet. Chem., 265 (1984) C12.

199 G.B. Shul'pin and G.V. Nizova, J. Organomet. Chem., 276 (1984) 109.

200 A.N. Kitaigorodskii, V.M. Nekipelov, A.T. Nikitaev and G.B. Shulpin, J. Organomet. Chem., 275 (1984) 295.

201 Yu.N. Kukushkin, A.N. Belyaev, V.N. Demidov and E.A. Bychkov, Russ. J. Inorg. Chem., 30 (1985) 389; Zh. Neorg. Khim., 30 (1985) 689.

202 M. Troupel, Y. Rollin, G. Meyer and J. Perichon, Nouv. J. Chim., 9 (1985) 487.

203 M.M. Brezinski, K.J. Kalbunde, S.K. Janikowski and L.J. Radonovich, Inorg. Chem., 24 (1985) 3305.

204 H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meicheng and T. Youqi, J. Organomet. Chem., 287 (1985) 419.

205 G. Schiavon, G. Zotti and G. Bontempelli, J. Electroanal. Chem. Interfacial Electrochem., 161 (1984) 323.

206 G. Schiavon, G. Zotti and G. Bontempelli, J. Electroanal. Chem. Interfacial Electrochem., 194 (1985) 327.

207 M. Wada and M. Kumazoe, J. Chem. Soc., Chem. Commun., (1985) 1204.

208 E. Hernandez, I. Saez and P. Royo, J. Organomet. Chem., 293 (1985) 249.

209 R. Vanderesse, J.-J. Brunet and P. Caubere, J. Organomet. Chem., 264 (1984) 263.

210 A.B. Goel, Inorg. Chim. Acta, 85 (1984) L25.

211 N.A. Bumagin, I.G. Bumagina and I.P. Beletskaya, J. Org. Chem. USSR, 20 (1984) 411; Zh. Org. Khim., 20 (1984) 457.

212 R. Usón, J. Forniés, R. Navarro, M.A. Usón, M.P. Garcia and A.J. Welch, J. Chem. Soc., Dalton Trans., (1984) 345.

213 H.A. Brune, M. Falck, R. Hemmer and H.G. Alt, Chem. Ber., 117 (1984) 2803.

214 H.-A. Brune, R. Hess and G. Schmidtberg, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1772.

215 S. Lanza, D. Minniti, P. Moore, J. Sachinidis, R. Romeo and M.L. Tobe, Inorg. Chem., 23 (1984) 4428.
216 M.J. Blandamer, J. Burgess, D. Minniti and R. Romeo, Inorg. Chim. Acta., 96 (1985) 129.
217 D.P. Arnold and M.A. Bennett, Inorg. Chem., 23 (1984) 2110.
218 R.Usón, J. Forniés, M. Tomás and R. Fandos, J. Organomet. Chem., 263 (1984) 253.
219 R.J. Cross and J. Gemmill, J. Chem. Soc., Dalton Trans., (1984) 205.
220 R. Usón, J. Forniés, P. Espinet and R. Navarro, Inorg. Chim. Acta, 82 (1984) 215.
221 R. Uson, J. Fornies, M.A. Uson and M.A. Orta, Inorg. Chim. Acta, 89 (1984) 175.
222 R. Usón, A. Laguna, J. Forniés, I. Valenzuela, P.G. Jones and G.M. Sheldrick, J. Organomet. Chem., 273 (1984) 129.
223 B. Crociani, F. Dibianca, A. Giovenco and A Scrivanti, J. Organomet. Chem., 291 (1985) 259.
224 A Albinati, M. Lehner, P.S. Pregosin and L.M. Venanzi, Congr. Naz. Chim. Inorg., [Atti], 15th, 1982, 53; Chem. Abstr., 100 (1984) 202359t.
225 R Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton and L.R. Falvello, J. Am. Chem. Soc., 107 (1985) 2556.
226 R. Uson, J. Forniés, M. Tomas, F.A. Cotton and L.R. Falvello, J. Am. Chem. Soc., 106 (1984) 2482.
227 R. Usón, J. Forniés, B. Menjón, F.A. Cotton, L.R. Falvello and M. Tomás, Inorg. Chem., 24 (1985) 4651.
228 D.M. Roundhill, J. Am. Chem. Soc., 107 (1985) 4354.
229 C. Bianchini and A. Meli, J. Organomet. Chem., 276 (1984) 413.
230 L.S. Liebeskind, S.L. Baysdon, M.S. South, S. Iyer and J.P Leeds, Tetrahedron, 41 (1985) 5839.
231 M.F. Semmelhack, L. Keller, T. Sato, E.J. Spiess and W. Wulff, J. Org. Chem., 50 (1985) 5566.
232 F. Wang, Y. Fan and Q. Cong, Gaodeng Xuexiao Huaxue Xuebao, 5 (1984) 699; Chem. Abstr., 101 (1984) 201996g.
233 A. Scrivanti, G. Cavinato, L. Toniolo and C. Botteghi, J. Organomet. Chem., 286 (1985) 115.
234 G.K. Anderson and R.J. Cross, Acc. Chem. Res., 17 (1984) 67.
235 N. Koga and K. Morokuma, J. Am. Chem. Soc., 107 (1985) 7230.
236 M.D. Fryzuk and P.A. MacNeil, J. Am. Chem. Soc., 106 (1984) 6993.
237 G.K. Anderson and G.L. Lumetta, Organometallics, 4 (1985) 1542.
238 H.E. Bryndza, J.C. Calabrese and S.S. Wreford, Organometallics, 3 (1984) 1603.
239 H.E. Bryndza, Organometallics, 4 (1985) 1686.
240 H.E. Bryndza, S.A. Kretchmar and T.H. Tulip, J. Chem. Soc., Chem. Commun., (1985) 977.
241 S. Komiya, Y. Akai, K. Tanaka, T. Yamamoto and A. Yamamoto, Organometallics, 4 (1985) 1130.
242 M.A. Bennett and A. Rokicki, Organometallics, 4 (1985) 180.
243 G. Vasapollo, C.F. Nobile and A. Sacco, J. Organomet. Chem., 296 (1985) 435.
244 H. Hoberg and F.J. Fañanás, Angew. Chem., Int. Ed. Engl., 24 (1985) 325; Angew. Chem., 97 (1985) 320.
245 H. Hoberg, F.J. Fañanás, K. Angermund, C. Krüger and M.J. Romão, J. Organomet. Chem., 281 (1985) 379.
246 A. Sacco, P. Giannoccaro and G. Vasapollo, Inorg. Chim. Acta, 83 (1984) 125.
247 H.E. Bryndza, W.C. Fultz and W. Tam, Organometallics, 4 (1985) 939.
248 N.W. Alcock, J.M. Brown and T.D. MacLean, J. Chem. Soc., Chem. Commun., (1984) 1689.
249 A. Campagnaro, A. Mantovani and P. Uguagliati, Inorg. Chim. Acta., 99 (1985) L15.

250 B. Crociani, F. Dibianca, R. Bertani and C.B. Castellani, Inorg. Chim. Acta, 101 (1985) 161.

251 R. Bertani, C.B. Castellani and B. Crociani, J. Organomet. Chem., 269 (1984) C15.

252 R. Usón, J. Forniés, P. Espinet and C. Fontuño, Inorg. Chim. Acta, 87 (1984) 207.

253 D. Walther and E. Dinjus, Ger. (East) DD 205,908 (1984); Chem. Abstr., 101 (1984) 55347c.

254 H. Hoberg, D. Schaefer, G. Burkhart, C. Krüger and M.J. Romão, J. Organomet. Chem., 266 (1984) 203.

255 H. Hoberg and B.W. Oster, J. Organomet. Chem., 266 (1984) 321.

256 H. Hoberg and B. Apotecher, J. Organomet. Chem., 270 (1984) C15.

257 A. Behr and G. Thelen, C_1 Mol. Chem., 1 (1984) 137.

258 D. Walther, E. Dinjus, J. Sieler, L. Anderson and O. Lindqvist, J. Organomet. Chem., 276 (1984) 99.

259 K. Sano, T. Yamamoto and A. Yamamoto, Chem. Lett., (1984) 941.

260 H. Hoberg and K. Sümmermann, J. Organomet. Chem., 275 (1984) 239.

261 H. Hoberg, E. Hernandez and K. Sümmermann, J. Organomet. Chem., 295 (1985) C21.

262 H. Hoberg and K. Sümmermann, J. Organomet. Chem., 264 (1984) 379.

263 H. Hoberg, K. Sümmermann and A. Milchereit, Angew. Chem., Int. Ed. Engl., 24 (1985) 325; Angew. Chem., 97 (1985) 321.

264 H. Hoberg, K. Sümmermann and A. Milchereit, J. Organomet. Chem., 288 (1985) 237.

265 H. Hoberg, K. Radine and A. Milchereit, J. Organomet. Chem., 280 (1985) C60.

266 V.S. Petrosyan, A.B. Permin, V.I. Bogdashkina and D.P. Krut'ko, J. Organomet. Chem., 292 (1985) 303.

267 V.N. Zudin, V.A. Rogov, V.A. Likholobov, V.A. Shmachkov, L.A. Sazonov and Yu.I. Ermakov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1577; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 1726.

268 H.E. Bryndza, Organometallics, 4 (1985) 406.

269 W.R. Meyer and L.M. Venanzi, Angew. Chem., Int. Ed. Engl., 23 (1984) 529; Angew. Chem., 96 (1984) 505.

270 K.M. Smith, K.C. Langry and O.M. Minnetian, J. Org. Chem., 49 (1984) 4602.

271 Yu.N. Kukushkin, N.V. Vorob'ev-Desyatovskii and K.M. Patrabansh, J. Gen. Chem. USSR, 55 (1985) 410; Zh. Obshch. Khim., 55 (1985) 464.

272 T.C. Flood and S.P. Bitler, J. Am. Chem. Soc., 106 (1984) 6076.

273 E. Carmona, E. Gutiérrez-Puebla, A. Monge, J.M. Marín, M. Paneque and M.L. Poveda, Organometallics, 3 (1984) 1438.

274 E.G. Samsel and J.R. Norton, J. Am. Chem. Soc., 106 (1984) 5505.

275 A.B. Goel, Indian J. Chem., Sect. A, 24A, (1985) 311.

276 S. Cenini, F. Porta, M. Pizzotti and G. La Monica, J. Chem. Soc., Dalton Trans., (1984) 355.

277 V.N. Kalinin, A.V. Usatov and L.I. Zakharkin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1510; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 1646.

278 H.C. Clark, G. Ferguson, A.B. Goel and B.L. Ruhl, Organometallics, 3 (1984) 15.

279 G. Ferguson and B.L. Ruhl, Acta Crystallogr., Sect C, C40 (1984) 2020.

280 R. McCrindle, G.J. Arsenault and R. Farwaha, J. Organomet. Chem., 296 (1985) C51.

281 F. Porta, M. Pizzotti, G. La Monica, L.A. Finessi, S. Cenini, P.L. Bellon and F. Demartin, J. Chem. Soc., Dalton Trans., (1984) 2409.

282 F. Maassarani, M. Pfeffer, G. Le Borgne, E. Wehman and G. Van Koten, J. Am. Chem. Soc., 106 (1984) 8002.

283 A. Mantovani, M. Pelloso, G. Bandoli and B. Crociani, J. Chem. Soc. Dalton Trans., (1984) 2223.

284 S.M. Vinogradova and A.F. Shestakov, Khim. Fiz., 3 (1984) 371; Chem. Abstr., 100 (1984) 208901k.

285 J.J. Koh, W.-H. Lee, P.G. Williard and W.M. Risen, J. Organomet. Chem., 284 (1985) 409.

286 O. Rossell, M. Seco, I. Torra, X. Solans and M. Font-Altaba, J. Organomet. Chem., 270 (1984) C63.

287 S.I. Pombrik, A.A. Bezrukova, L.S. Golovchenko, A.S. Peregudov, A.Z. Rubezhov and D.N. Kravtsov, J. Organomet. Chem., 293 (1985) C1.

288 K. Sano, T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Jpn., 57 (1984) 2741.

289 E. Uhlig and O. Reitman, Z. Chem., 24 (1984) 103.

290 P. Eilbracht, W. Fassmann and W. Diehl, Chem. Ber., 118 (1985) 2314.

291 J.J. Eisch, A.M. Piotryowski, K.I. Han, C. Krüger and Y.H. Tsay, Organometallics, 4 (1985) 224.

292 J.P. Droske and J.K. Stille, Macromolecules, 17 (1984) 1.

293 J.P. Droske, U.M. Gaik and J.K. Stille, Macromolecules, 17 (1984) 10.

294 R.A. Ekeland and P.W. Jennings, J. Organomet. Chem., 281 (1985) 397.

295 P.W. Jennings, R.E. Ekeland and M.D. Waddington, J. Organomet. Chem., 285 (1985) 429.

296 U. Schubert, Coord. Chem. Rev., 55 (1984) 261.

297 A.I. Syatkovskii and B.D. Babitskii, Russ. Chem. Rev., 53 (1984) 672; Usp. Khim., 53 (1984).

298 E.O. Fischer and J.R. Schneider, J. Organomet. Chem., 295 (1985) C29.

299 K.-R. Pörschke, G. Wilke and R. Mynott, Chem. Ber., 118 (1985) 298.

300 D. Xu, K. Miki, Y. Kai, N. Kasai and M. Wada, J. Organomet. Chem., 287 (1985) 265.

301 W.P. Fehlhammer, K. Bartel, U. Plaia, A. Völkl and A.T. Liu, Chem. Ber., 118 (1985) 2235.

302 Z. Yoshida and S. Miki, Eur. Pat. Appl. EP 118,801 (1984); Chem. Abstr., 102 (1985) 78439u.

303 B. Crociani, F. Di Bianca, A. Giovenco and A Scrivanti, J. Organomet. Chem., 269 (1984) 295.

304 R.A. Michelin, G. Facchin and R. Ros, J. Organomet. Chem., 279 (1985) C25.

305 W. Beck, W. Weigand, U. Nagel and M. Schaal, Angew. Chem., Int. Ed. Engl., 23 (1984) 377; Angew. Chem., 96 (1984) 377.

306 G. Facchin, R. Campostrini and R.A. Michelin, J. Organomet. Chem., 294 (1985) C21.

307 S. Muralidharan and J.H. Espenson, J. Am. Chem. Soc., 106 (1984) 8104.

308 K.A. Azam, A.A. Frew, B.R. Lloyd, L. Manojlovic-Muir, K.W. Muir and P.J. Puddephatt, Organometallics, 4 (1985) 1400.

309 G.A. Carriedo, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1555.

310 J.C. Jeffery, J.C.V. Laurie, I. Moore, H. Razay and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1563.

311 J.C. Jeffery, I. Moore and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1571.

312 J.C. Jeffery, I. Moore, H. Razay and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1581.

313 M.R. Awang, R.D. Barr, M. Green, J.A.K. Howard, T.B. Marder and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985) 2009.

314 G.A. Carriedo, J.A.K. Howard, F.G.A. Stone and M.J. Went, J. Chem. Soc., Dalton Trans., (1984) 2545.

315 L.J. Farrugia, A.D. Miles and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985) 2437.

316 J.H. Davis and C.M. Lukehart, Organometallics, 3 (1984) 1763.

317 D. Afzal, P.G. Lenhert and C.M. Lukehart, J. Am. Chem. Soc., 106 (1984) 3050.

318 A.B. Antonova, S.V. Kovalenko, E.D. Korniyets, P.V. Petrovsky, G.R. Gulbis and A.A. Johansson, Inorg. Chim. Acta, 96 (1985) 1.

319 A.B. Antonova, S.V. Kovalenko, E.D. Korniyets, P.V. Petrovsky, A.A. Johansson and N.A. Deykhina, Inorg. Chim. Acta, 105 (1985) 153.

320 A.B. Antonova, S.V. Kovalenko, N.A. Deikhina, E.D. Korniets, P.V. Petrovskii and A.A. Ioganson, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2624; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 2827.

321 G. Minghetti, A. Albinati, A.L. Bandini and G. Banditelli, Angew. Chem., Int. Ed. Engl., 24 (1985) 120; Angew. Chem., 97 (1985) 119.

322 P.B. Mackenzie, K.C. Ott and R.H. Grubbs, Pure Appl. Chem., 56 (1984) 59.

323 R.J. Blau, M.H. Chisholm, K. Folting and R.J. Wang, J. Chem. Soc., Chem. Commun., (1985) 1582.

324 D.L. Beach and J.J. Harrison, U.S. US 4,529,554 (1985); Chem. Abstr., 103 (1985) 178461j.

325 K.A. Ostoja-Starzewski and J. Witte, Angew. Chem., Int. Ed. Engl., 24 (1985) 599; Angew. Chem., 97 (1985) 610.

326 K.A. Ostoja-Starzewski and J. Witte, Ger. Offen. DE 3,228,865 (1984); Chem. Abstr., 100 (1984) 175519m.

327 K.H.A. Ostoja-Starzewski and J. Witte, Ger. Offen. DE 3,403,493 (1985); Chem. Abstr., 103 (1985) 215958z.

328 K.H.A. Ostoja Starzewski, J. Witte and H. Bartl, Eur. Pat. Appl. EP 101,927 (1984); Chem. Abstr., 101 (1984) 7797c.

329 R.S. Tewari and A.K. Awasthi, J. Organomet. Chem., 271 (1984) 403.

330 R.K. Singhal, A.K. Awasthi and N.K. Mishra, Indian J. Chem., Sect. A, 23A (1984) 1046.

331 R. Sanehi, R.K. Bansal and R.C. Mehrotra, Indian J. Chem., Sect. A, 24A (1985) 398.

332 R. Sanehi, R.K. Bansal and R.C. Mehrotra, Indian J. Chem., Sect. A, 24A (1985) 1031.

333 Y. Yamamoto, Bull. Chem. Soc. Jpn., 57 (1984) 43.

334 L.V. Rybin, E.A. Petrovskaya, M.I. Rubinskaya, L.G. Kuz'mina, Yu.T. Struchkov, V.V. Kaverin and N.Yu. Koneva, J. Organomet. Chem., 288 (1985) 119.

335 R. Usón, J. Forniés, R. Navarro, P. Espinet and C. Mendívil, J. Organomet. Chem., 290 (1985) 125.

336 G. Matsubayashi and K. Ueyama, Polyhedron, 4 (1985) 173.

337 R.J. Puddephatt, M.C. Rendle and C.F.H. Tipper, J. Organomet. Chem., 269 (1984) 305.

338 R. McCrindle, G. Ferguson, G.J. Arsenault, A.J. McAlees and D.K. Stephenson, J. Chem. Res., S, (1984) 360.

339 A.D. Ryabov, Synthesis (1985) 233.

340 A.D. Ryabov, Russ. Chem. Rev., 54 (1985) 153; Usp. Khim., 54 (1985) 253.

341 H.-P. Abicht, Z. Chem., 25 (1985) 318.

342 A. Avshu and A.W. Parkins, J. Chem. Res., S, (1984) 245.

343 T.C. Jones, A.J. Nielson and C.E. Rickard, Aust. J. Chem., 37 (1984) 2179.

344 P.W. Clark and S.F. Dyke, J. Organomet. Chem., 281 (1985) 389.

345 I.K. Sakodynskaya, A.D. Ryabov, A.K. Yatsimirski and I.B. Berezin, Dokl. Chem., 284 (1985) 295; Dokl. Akad. Nauk SSSR, 284 (1985) 634 [Chem.].

346 A.D. Ryabov, I.K. Sakodinskaya and A.K. Yatsimirsky, J. Chem. Soc., Dalton Trans., (1985) 2629.

347 A.D. Ryabov, V.A. Polyakov and A.K. Yatsimirsky, Inorg. Chim. Acta, 91 (1984) 59.

348 V.M. Titov and A.D. Ryabov, Russ. J. Inorg. Chem., 30 (1985) 1072; Zh. Neorg. Khim., 30 (1985)

349 N. Barr, S.F. Dyke, G. Smith, C.H.L. Kennard and V. McKee, J. Organomet. Chem., 288 (1985) 109.

350 N. Barr, S.F. Dyke and R.L.W. Frost, Org. Magn. Reson., 22 (1984) 277.

351 K. Peters, E.M. Peters, H.G. von Schnering and H.-P. Abicht, Z. Kristallogr., 171 (1985) 313.

352 R.D. O'Sullivan and A.W. Parkins, J. Chem. Soc., Chem. Commun., (1984) 1165.

353 A.D. Ryabov, J. Organomet. Chem., 268 (1984) 91.
354 M. Pfeffer, J. Fischer and A. Mitschler, Organometallics, 3 (1984) 1531.
355 M. Onishi, K. Hiraki and A. Iwamoto, J. Organomet. Chem., 262 (1984) C11.
356 A.D. Ryabov and G.M. Kazankov, J. Organomet. Chem., 268 (1984) 85.
357 A.D. Ryabov, Sov. J. Coord. Chem., 11 (1985) 875; Koord. Khim., 11 (1985) 1532.
358 A.D. Ryabov and A.K. Yatsimirsky, Inorg. Chem., 23 (1984) 789.
359 V.V. Dunina, O.A. Zalevskaya and V.M. Potapov, J. Gen. Chem. USSR, 54 (1984) 406; Zh. Obshch. Khim., 54 (1984) 455.
360 V.V. Dunina, O.A. Zalevskaya and V.M. Potapov, J. Gen. Chem. USSR, 54 (1984) 347; Zh. Obshch. Khim., 54 (1984) 389.
361 E.I. Karpeiskaya, L.F. Godunova, E.S. Levitina, M.R. Lyubeznova, E.I. Klabunovskii, E.D. Lubuzh and A.I. Lutsenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 73; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 85.
362 K.J. Brown, M.S. Berry, K.C. Waterman, D. Lingenfelter and J.R. Murdoch, J. Am. Chem. Soc., 106 (1984) 4717.
363 J.W.L. Martin, J.A.L. Palmer and S.B. Wild, Inorg. Chem., 23 (1984) 2664.
364 Y. Shigetomi, M. Kojima and J. Fujita, Bull. Chem. Soc. Jpn., 58 (1985) 258.
365 O.A. Zalevskaya, V.V. Dunina, V.M. Potapov, L.G. Kuzmina and Yu.T. Struchkov, J. Gen. Chem. USSR, 55 (1985) 1191; Zh. Obshch. Khim., 55 (1985) 1332.
366 J.C. Kotz, E.E. Getty and L. Lin, Organometallics, 4 (1985) 610.
367 A.D. Ryabov, V.M. Titov, G.M. Kazankov and A.B. Belova, Koord. Khim., 11 (1985) 805; Chem. Abstr., 104 (1986) 109904q.
368 V.I. Sokolov, N.S. Khrushcheva, L.L. Troitskaya and O.A. Reutov, Dokl. Chem., 274 (1984) 15; Dokl. Akad. Nauk SSSR, 274 (1984) 342 [Chem.].
369 L.L. Troitskaya and V.I. Sokolov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1548; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 1689.
370 L.L. Troitskaya and V.I. Sokolov, J. Organomet. Chem., 285 (1985) 389.
371 D.M. Grove, G. van Koten, H.J.C. Ubbels, R. Zoet and A.L. Spek, Organometallics, 3 (1984) 1003.
372 D.M. Grove, G. van Koten, H.J.C. Ubbels, R. Zoet and A.L. Spek, J. Organomet. Chem., 263 (1984) C10.
373 J. Terheijden G. van Koten, I.C. Vinke and A.J. Spek, J. Am. Chem. Soc., 107 (1985) 2891.
374 N.I. Rybinskaya and V.V. Krivykh, Russ. Chem. Rev., 53 (1984) 476; Usp. Khim., 53 (1984) 825.
375 Y. Fuchita, K. Hiraki and Y. Matsumoto, J. Organomet. Chem., 280 (1985) C51.
376 V.V. Bashilov, E.V. Maskaeva, P.V. Petrovskii and V.I. Sokolov, J. Organomet. Chem., 292 (1985) 89.
377 R.A. Holton and J.R. Zoeller, J. Am. Chem. Soc., 107 (1985) 2124.
378 R. McCrindle and D.W. Sneddon, J. Organomet. Chem., 282 (1985) 413.
379 C. Arlen, F, Maassarani, M. Pfeffer and J. Fischer, Nouv. J. Chim., 9 (1985) 249.
380 M. Pfeffer, E. Wehman and G. van Koten, J. Organomet. Chem., 282 (1985) 127.
381 P.S. Pregosin and R. Rüedi, J. Organomet. Chem., 273 (1984) 401.
382 A. Albinati, P.S. Pregosin and R. Rüedi, Helv. Chim. Acta, 68 (1985) 2046.
383 P.W. Clark and S.F. Dyke, J. Organomet. Chem., 276 (1984) 421.
384 A. Suarez, J.M. Vila, E. Gayoso and M. Gayoso, An. Quim., Ser. B, 81 (1985) 251.
385 J. Albert, J. Granell and J. Sales, J. Organomet. Chem., 273 (1984) 393.
386 A. Suarez, J.M. Vila, E. Gayoso and M. Gayoso, Rev. Port. Quim., 26 (1984) 21; Chem. Abstr., 101 (1984) 72931f.
387 A Lavery and S.M. Nelson, J. Chem. Soc., Dalton Trans., (1984) 615.
388 R. Usón, J. Fornies, P. Espinet, A. Garcia, M. Tomas, C. Foces-Foces and F.H. Cano, J. Organomet. Chem., 282 (1985) C35.

389 A.M.M. Lanfredi, F. Ugozzoli, M. Ghedini and S. Licoccia, Inorg. Chim. Acta, 86 (1984) 165.

390 M. Ghedini, S. Licoccia, S. Armentano and R. Bartolino, Mol. Cryst. Liq. Cryst., 108 (1984) 269.

391 Y. Wakatsuki, H. Yamazaki, P.A. Grutsch, M. Santhanam and C. Kutal, J. Am. Chem. Soc., 107 (1985) 8153.

392 M. Hugentobler, A.J. Klaus, P. Ruppen and P. Rys, Helv. Chim. Acta, 67 (1984) 113.

393 E.A. El-Sawi and S.M. Shendy, Bull. Soc. Chim. Belg., 94 (1985) 171.

394 P.K. Santra and C.R. Saha, Chem. Ind. (London), (1984) 713.

395 A.K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay and A. Chakravorty, J. Chem. Soc., Chem. Commun., (1984) 999.

396 J. Granell, J. Sales and J. Vilarrasa, Transition Met. Chem., 9 (1984) 203.

397 R.M. Ceder and J. Sales, J. Organomet. Chem., 294 (1985) 389.

398 R.M. Ceder and J. Sales, J. Organomet. Chem., 276 (1984) C31.

399 K. Carr and J.K. Sutherland, J. Chem. Soc., Chem. Commun., (1984) 1227.

400 J.E. Baldwin, C. Nájera and M. Yus, J. Chem. Soc., Chem. Commun., (1985) 126.

401 J.E. Baldwin, R.H. Jones, C. Najera and M. Yus, Tetrahedron, 41 (1985) 699.

402 H. Nishiyama, M. Matsumoto, T. Matsukura, R. Miura and K. Itoh, Organometallics, 4 (1985) 1911.

403 P.W. Clark, S.F. Dyke, G. Smith, C.H.L. Kennard and A.H. White, Acta Crystallogr., Sect. C, C41 (1985) 1742.

404 B. Galli, F. Gasparrini, B.E. Mann, L. Maresca, G. Natile, A.M. Manotti-Lanfredi and A. Tiripicchio, J. Chem. Soc., Dalton Trans., (1985) 1155.

405 P. Uguagliati, U. Belluco, R.A. Michelin and P. Guerriero, Inorg. Chim. Acta, 81 (1984) 61.

406 L. Calligaro, Polyhedron, 3 (1984) 117.

407 E.N. Zil'berman, Russ. Chem. Rev., 53 (1984) 900; Usp. Khim., 53 (1984) 1548.

408 T.A. Anderson, R.J. Barton, B.E. Robertson and K. Venkatasubramanian, Acta Crystallogr., Sect. C, C41 (1985) 1171.

409 A.J. Canty, N.J. Minchin, L.M. Engelhardt and A.H. White, Inorg. Chim. Acta, 102 (1985) L29.

410 G.R. Newkome and A Yoneda, Makromol. Chem., Rapid Commun., 6 (1985) 77.

411 E.C. Constable, J. Chem. Soc., Dalton Trans., (1985) 1719.

412 A.C. Skapski, V.F. Sutcliffe and G.B. Young, J. Chem. Soc., Chem. Commun., (1985) 609.

413 F.L. Wimmer and S. Wimmer, Transition Met. Chem., 10 (1985) 238.

414 F.L. Wimmer and S. Wimmer, Polyhedron, 4 (1985) 1665.

415 L. Chassot, E. Müller and A. von Zelewsky, Inorg. Chem., 23 (1984) 4249.

416 M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet and A. von Zelewsky, Chem. Phys. Lett., 122 (1985) 375.

417 P. Braunstein, J. Fischer, D. Matt and M. Pfeffer, J. Am. Chem. Soc., 106 (1984) 410.

418 V.V. Bashilov, É.V. Maskaeva, A.A. Musaev, V.I. Sokolov and O.A. Reutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1466; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 1597.

419 A.A. Musaev, B.T. Usubaliev, A.A. Guliev, V.V. Bashilov and V.I. Sokolov, J. Struct. Chem. USSR, 26 (1985) 643; Zh. Strukt. Khim., 26 (1985) 166.

420 L.G. Kuz'mina, Yu.T. Struchkov, V.V. Bashilov, A.A. Musaev and V.I. Sokolov, Sov. J. Coord. Chem., 11 (1985) 881; Koord. Khim., 11 (1985) 1543.

421 G.R. Newkome, W.E. Puckett, G.E. Kiefer, V.K. Gupta, F.R. Fronczek, D.C. Pantaleo, G.L. McClure, J.B. Simpson and W.A. Deutsch, Inorg. Chem., 24 (1985) 811.

422 W.E. Puckett, PhD Thesis, Louisiana, State Univ., 1983; Diss. Abstr. Int. B, 44 (1984) 2757.

423 M. Nonoyama, Polyhedron, 4 (1985) 765.

424 K. Hiraki, Y. Fuchita and Y. Matsumoto, Chem. Lett., (1984) 1947.

425 A. Albinati, C.G. Anklin and P.S. Pregosin, Inorg. Chim. Acta, 90 (1984) L37.

426 M. Nonoyama, J. Organomet. Chem., 262 (1984) 407.

427 B.F. Hoskins and I.A.S. McDonald, Aust. J. Chem., 37 (1984) 1395.

428 T.E. Crossley, P. Davies, M. Louey, R. Robson and T.N. Huckerby, Inorg. Chim. Acta, 85 (1984) 199.

429 A.L. Rheingold and W.C. Fultz, Organometallics, 3 (1984) 1414.

430 A.B. Goel and S. Goel, Inorg. Chim. Acta, 98 (1985) 67.

431 H.C. Clark, V.K. Jain and G.S. Rao, J. Organomet. Chem., 279 (1985) 181.

432 A.B. Goel, S. Goel and D. Vanderveer, Inorg. Chim. Acta, 82 (1984) L9.

433 A.B. Goel and S. Goel, Inorg. Chim. Acta, 82 (1984) 41.

434 A.B. Goel and S. Goel, Inorg. Chim. Acta, 90 (1984) L33.

435 D. Hedden, D.M. Roundhill, W.C. Fultz and A.L. Rheingold, J. Am. Chem. Soc., 106 (1984) 5014.

436 H. Rimml and L.M. Venanzi, J. Organomet. Chem., 260 (1984) C52.

437 H.-P. Abicht, Z. Chem., 24 (1984) 387.

438 H.-P. Abicht and K. Issleib, J. Organomet. Chem., 289 (1985) 201.

439 O.J. Scherer, K. Hussong and G. Wolmershäuser, J. Organomet. Chem., 289 (1985) 215.

440 S.J. Tremont and H. Ur Rahman, J. Am. Chem. Soc., 106 (1984) 5759.

441 K. Hiraki, Y. Fuchita and Y. Kage, J. Chem. Soc., Dalton Trans., (1984) 99.

442 P. Castan, J. Jaud, N.P. Johnson and R. Soules, J. Am. Chem. Soc., 107 (1985) 5011.

443 V.V. Dunina. O.A. Zalevskaya, I.P. Smolyakova and V.M. Potapov, Dokl. Chem., 278 (1984) 323; Dokl. Akad. Nauk SSSR, 278 (1984) 628 [Chem.].

444 V.V. Dunina, O.A. Zalevskaya, I.P. Smolyakova and V.M. Potapov, J. Gen. Chem. USSR, 54 (1984) 2049; Zh. Obshch. Khim., 54 (1984) 2290.

445 N.K. Eremenko, E.G. Mednikov and S.P. Gubin, Koord. Khim., 10 (1984) 617; Chem. Abstr., 101 (1984) 32227z.

446 H.C. Clark and V.K. Jain, Coord. Chem. Rev., 55 (1984) 151.

447 S.P. Gubin, Russ. Chem. Rev., 54 (1985) 305; Usp. Khim., 54 (1985) 529.

448 D.J. Darensbourg, C.G. Bauch and C. Ovalles, Rev. Inorg. Chem., 7 (1985) 315.

449 L. Filkova, Cesk. Hyg., 30 (1985) 243; Chem. Abstr., 103 (1985) 26401b.

450 Anon., Dangerous Prop. Ind. Mater. Rep., 5 (1985) 76; Chem. Abstr., 103 (1985) 200143f.

451 A. Aitio, IARC Sci. Publ., 53 (Nickel Hum. Environ.) (1984) 497; Chem. Abstr., 103 (1985) 75471h.

452 D.C. Jones, P.M. May, D.R. Williams, M.C. Reid and F.W. Sunderman, Inorg. Chim. Acta, 91 (1984) L51.

453 H. Tjalve, S. Jasim and A. Oskarsson, IARC Sci. Publ., 53 (Nickel Hum. Environ.) (1984) 311; Chem. Abstr., 103 (1985) 66255p.

454 T.K. Ha and M.T. Nguyen, J. Mol. Struct. (Theochem) 109 (1984) 331.

455 S. Huzinaga, M. Klobukowski and Y. Sakai, J. Phys. Chem., 88 (1984) 4480.

456 M.R.A. Blomberg, U.B. Brandemark, P.E.M. Siegbahn, K.B. Mathisen and G. Karlström, J. Phys. Chem., 89 (1985) 2171.

457 C.M. Rohlfing and P.J. Hay, J. Chem. Phys., 83 (1985) 4641.

458 K.M. Neiman, A.V. Kondratenko, L.N. Mazalov, V.A. Nasluzov and P.V. Avramov. Zh. Strukt. Khim., 26 (1985) 22; Chem. Abstr., 104 (1986) 215659y.

459 K. Fægri and J. Almlöf, Chem. Phys. Lett., 107 (1984) 121.

460 H. Jörg and N. Rösch, Chem. Phys. Lett., 120 (1985) 359.

461 D.D. Vvedensky, D.K. Saldin and J.B. Pendry, Surf. Sci., 156 (1985) 845.

462 X. You, R.F. Fenske and D.G. Freier, Gaodeng Xuexiao Huaxue Xuebao, 6 (1985) 146; Chem. Abstr., 103 (9185) 114827a.

463 R.G. Pearson, Inorg. Chem., 23 (1984) 4675.
464 T. Ziegler, Organometallics, 4 (1985) 675.
465 T.R. Jarvis, J. Appl. Phys., 58 (1985) 1400.
466 M.P. Neary and T.A. Wilson, Fr. Demande FR 2,526,333 (1983); Chem. Abstr., 100 (1984) 105834m
467 Hitachi Maxell, Ltd., Jpn. Kokai Tokkyo Koho JP 59 27,505 [84 27,505] (1984); Chem. Abstr., 101 (1984) 32215u.
468 Semiconductor Energy Research Institute Co., Ltd., Jpn Kokai Tokkyo Koho JP 59 98,504 [84 98,504] (1984); Chem. Abstr., 101 (1984) 203093j.
469 L.V. Biketova, A.T. Belyaevskii, A.S. Mnukhin and A.N. Shteinberg, Tsvetn. Met. (Moscow), (1984) 79; Chem. Abstr., 101 (1984) 175784q.
470 A.K. Hays, Mater. Res. Soc., Symp. Proc., 38 (Plasma Synth. Etching Electron. Mater.) (1985) 337; Chem. Abstr., 103 (1985) 79707n.
471 M.V. Tsodikov, Ya. R. Katsobashvili, O.V. Bukhtenko, G.A. Korneeva and S.M. Loktev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 663; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 727.
472 Fujikura Cable Works, Ltd., Jpn. Kokai Tokkyo Koho JP 59,102,843 [84,102,843] (1984); Chem. Abstr., 101 (1984) 156369s.
473 C.M.A.M. Mesters, J.W. Geus, E.G.M. Kuijpers and O.L.J. Gijzeman, Ger. Offen. DE 3,347,677 (1985); Chem. Abstr., 103 (1985) 90185m.
474 Toyo Soda Mfg. Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,164,621 [83,164,621] (1983); Chem. Abstr., 100 (1984) 175893d.
475 B.A. Lasoski, U.S. US 4.426,452 (1984); Chem. Abstr., 100 (1984) 95780z.
476 N. Herron, G.D. Stucky and C.A. Tolman, Inorg. Chim. Acta, 100 (1985) 135.
477 A.A. Ginzburg and A.M. Verblovskii, J. Appl. Chem. USSR, 57 (1984) 2230; Zh. Prikl. Khim. (Leningrad), 57 (1984) 2423.
478 G.A. Tolstikov. R.G. Bulgakov and V.P. Kazakov, Russ. Chem. Rev., 54 (1985) 1058; Usp. Khim., 54 (1985) 1789.
479 D.A. Hikade, D.H. Stedman and J.G. Walega, Anal. Chem., 56 (1984) 1629.
480 Y. Langsam and A.M. Ronn, J. Chem. Phys., 80 (1984) 749.
481 M.-K Au, P.A. Hackett, M. Humphries and P. John, Appl. Phys. B, B33 (1984) 43.
482 K. Kabushiki, S. Ueno and K. Oyo, Jpn. Kokai Tokkyo Koho JP 58,167,581 [83,167,581] (1983); Chem. Abstr., 100 (1984) 103162s.
483 Y. Ohshiro, H. Nanimoto, H. Tanaka, M. Komatsu, T. Agawa, N. Yasuoka, Y. Kai and N. Kasai, Tetrahedron Lett., 26 (1985) 3015.
484 T. Hirao, S. Nagata, Y. Yamana and T. Agawa, Tetrahedron Lett., 26 (1985) 5061.
485 O.P. Vig, R. Nanda, R. Gauba and S.K. Puri, Indian J. Chem., Sect. B, 24B (1985) 918.
486 T. Hirao, S. Nagata and T. Agawa, Tetrahedron Lett., 26 (1985) 5795.
487 S. Inoue, S. Uchida, M. Kobayashi, S. Sato, O. Miyamoto and K. Sato, Nippon Kakagu Kaishi (1985) 425; Chem. Abstr., 103 (1985) 215039a.
488 F. Camps, J. Coll. J.M. Moretó and J. Torras, Tetrahedron Lett., 26 (1985) 6397.
489 S.S. Snow, D. Jiang and R.W. Parry, Inorg. Chem., 24 (1985) 1460.
490 A.H. Cowley, J.E. Kilduff, J.G. Lasch, N.C. Norman, M. Pakulski, F. Ando and T.C. Wright, Organometallics, 3 (1984) 1044.
491 R. Appel, C. Casser and F. Knoch, J. Organomet. Chem., 293 (185) 213.
492 M. Grenz, E. Hahn, W.-W du Mont and J. Pickardt, Angew. Chem., Int. Ed. Engl., 23 (1984) 61; Angew. Chem., 96 (1984) 69.
493 M. Luksza, U. Wanka and W. Malisch, J. Organomet. Chem., 266 (1984) 237.
494 D.J. Brauer, S. Hietkamp, H. Sommer, O. Stelzer, G. Müller, M.J. Romão and C. Krüger, J. Organomet. Chem., 296 (1985) 411.
495 L.I. Zakharkin, A.V. Kazantsev and M.G. Meiramov, J. Gen. Chem. USSR, 54 (1984) 1368; Zh. Obshch. Khim., 54 (1984) 1536.
496 R.B. King and K.S.R. Veer, Inorg. Chem., 23 (1984) 2482.
497 J.M. Shreeve and S.M. Williamson, Organometallics, 3 (1984) 1104.
498 S.A. Snow and G. Kodama, Inorg. Chem., 24 (1985) 795.

499 R.T. Baker, T.H Tulip and S.S. Wreford, Inorg. Chem., 24 (1985) 1379.

500 J.M. Ritchey, A.J. Zozulin, D.A. Wrobleski, R.R. Ryan, H.J. Wasserman, D.C. Moody and R.T. Paine, J. Am. Chem. Soc., 107 (1985) 501.

501 S.K. Janikowski, L.J. Radonovich, T.L. Groshens and K.J. Klabunde, Organometallics, 4 (1985) 396.

502 K.R. Pörschke and G. Wilke, Chem. Ber., 117 (1984) 56.

503 F. Cecconi, C.A. Ghilardi, P. Innocenti, C. Mealli, S. Midollini and A. Orlandini, Inorg. Chem., 23 (1984) 922.

504 G.S. Ferguson and P.T. Wolczanki, Organometallics, 4 (1985) 1601.

505 J. Grobe and H. Zimmerman, Z. Naturforsch., B; Anorg. Chem., Org. Chem., 39B (1984) 808.

506 B. Cetinkaya, P.B. Hitchcock, M.F. Lappert, M.C. Misra and A.J. Thorne, J. Chem. Soc., Chem. Commun., (1984) 148.

507 F. Joó and H. Alper, Organometallics, 4 (1985) 1775.

508 G. Bontempelli, F. Magno, B. Corain and G. Schiavon, Transition Met. Chem., 10 (1985) 8.

509 L. Pandolfo and G. Paiaro, Gazz. Chim. Ital., 115 (1985) 561.

510 C. Bianchini and A. Meli, Organometallics, 4 (1985) 1537.

511 R. Poli, G. Wilkinson, M. Motevalli and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985) 931.

512 J. Sieler, N.-N. Thon, R. Benedix, E. Dinjus and D. Walther, Z. Anorg. Allg. Chem., 522 (1985) 131.

513 P. Pelikan, R. Boca, M. Breza, M.M. Gofman and V.I. Nefedov, Proc. Conf. Coord. Chem., 10th (1985) 317; Chem. Abstr., 105 (1986) 12491k.

514 R.R. Andréa, L.N. Louwen, M.W. Kokkes, D.J. Stufkens and A. Oskam, J. Organomet. Chem., 281 (1985) 273.

515 V.A. Shvets, L.A. Makhlis, V.É. Vasserberg and V.B. Kazanskii, Kinet. Catal., 25 (1984) 1287; Kinet. Katal., 25 (1984) 1496.

516 T. Bartik, T. Himmler, H.-G. Schulte and K. Seevogel, J. Organomet. Chem., 272 (1984) 29.

517 B. Corain, M. Basato, G. Favero, P. Rosano and G. Valle, Inorg. Chim. Acta, 85 (1984) L27.

518 M. Basato, B. Corain, G. Favero and P. Rosano, J. Chem. Soc., Dalton Trans., (1984) 2513.

519 G. Elbaze, F. Dahan, M. Dartiguenave and Y. Dartiguenave, Inorg. Chim. Acta, 85 (1984) L3.

520 D.J. Brauer, G. Hasselkuss, S. Morton, S. Hietkamp, H. Sommer, O. Stelzer and W.S. Sheldrick, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 1161.

521 J. Koutecký, G. Pacchioni and P. Fantucci, Chem. Phys., 99 (1985) 87.

522 R.G. Pearson, Inorg. Chem., 23 (1984) 4675.

523 H. Basch, Chem. Phys. Lett., 116 (1985) 58.

524 O.V. Sizova, G.B. Perminova, N.V. Ivanova, V.I. Baranovskii and A.B. Nikol'skii, Vestn. Leningr. Univ., Fiz., Khim., (1985) 102; Chem. Abstr., 103 (1985) 42835b.

525 P.R. Brown, F.G.N. Cloke and M.L.H. Green, Polyhedron, 4 (1985) 869.

526 S.M. Kim, V.Zh. Ushanov and O.V. Agashkin, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., (1985) 26; Chem. Abstr., 102 (1985) 194233w.

527 S.M. Kim and O.V. Agashkin, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., (1984) 51; Chem. Abstr., 102 (1985) 102632z.

528 N.O. Ivanova, A.V. Yarovchuk, G.N. Kravchenko and S.P. Pak, Izv. Vyssh. Uchebn. Zaved., Fiz., 28 (1985) 105; Chem. Abstr., 102 (1985) 153257p.

529 V.A. Golodov and E.L. Kuksenko, C_1 Mol. Chem., 1 (1984) 109.

530 M. Kubota and F.S. Rosenberg, Synth. React. Inorg. Met.-Org. Chem., 15 (1985) 1037.

531 M. Kubota, F.S. Rosenberg and M.J. Sailor, J. Am. Chem. Soc., 107 (1985) 4558.

532 R.C. Srivastava, J. Chem. Res., S, (1985) 330.

533 D.B. Dell'Amico, F. Calderazzo, C.A. Veracini and N. Zandonà, Inorg. Chem., 23 (1984) 3030, 4781.

534 J.R. Morton and K.F. Preston, Inorg. Chem., 24 (1985) 3317.
535 A.E. Stiegman and D.R. Tyler, Coord. Chem. Rev., 63 (1985) 217.
536 K.D. Gallicano and N.L. Paddock, Can. J. Chem., 63 (1985) 314.
537 M. Baudler, F. Salzer, J. Hahn and E. Därr, Angew. Chem., Int. Ed. Engl., 24 (1985) 415; Angew. Chem., 97 (1985) 410.
538 L. Carlton, W.E. Lindsell, K.J. McCullough and P.N. Preston, Organometallics, 4 (1985) 1138.
539 D.B. Dell'Amico, F. Calderazzo and N. Zandona, Inorg. Chem., 23 (1984) 137.
540 V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Likholobov and Yu.I. Yermakov, J. Organomet. Chem., 289 (1985) 425.
541 M.L. Kullberg and C.P. Kubiak, Organometallics, 3 (1984) 632.
542 C.-L. Lee, B.R. James, D.A. Nelson and R.T. Hallen, Organometallics, 3 (1984) 1360.
543 B.F. Hoskins, R.J. Steen and T.W. Turney, J. Chem. Soc., Dalton Trans. (1984) 1831.
544 G.K. Anderson and R. Kumar, Inorg. Chim. Acta, 97 (1985) L21.
545 A.L. Balch, R.R. Guimerans, J. Linehan and F.E. Wood, Inorg. Chem., 24 (1985) 2021.
546 S.W. Carr, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1985) 2131.
547 R. Bender, P. Braunstein, A. Tiripicchio, and M. Tiripicchio-Camellini, J. Chem. Soc., Chem. Commun., (1984) 42.
548 J. Powell, M.R. Gregg and J.F. Sawyer, J. Chem. Soc., Chem. Commun., (1984) 1149.
549 J. Powell, J.F. Sawyer and M.V.R. Stainer, J. Chem. Soc., Chem. Commun., (1985) 1314.
550 J. Powell, J.F. Sawyer and S.J. Smith, J. Chem. Soc., Chem. Commun., (1985) 1312.
551 P. Braunstein, G.L. Geoffroy and B. Metz, Nouv. J. Chim., 9 (1985) 221
552 P.N. Lindsay, B.M. Peake, B.H. Robinson, J. Simpson, U. Honrath, H. Vahrenkamp and A.M. Bond, Organometallics, 3 (1984) 413.
553 B.R. LLoyd and R.J. Puddephatt, Inorg. Chim. Acta, 90 (1984) L77.
554 L. Manojlović-Muir, K.W. Muir, B.R. Lloyd and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1985) 536.
555 P. Braunstein, J. Kervennal and J.-L. Richert, Angew. Chem., Int. Ed., Engl., 24 (1985) 768; Angew. Chem., 97 (1985) 762.
556 P. Braunstein, C. De M. De Bellefon and M. Ries, J. Organomet. Chem., 262 (1984) C14.
557 C. Mealli, J. Am. Chem. Soc., 107 (1985) 2245.
558 A. Jiang and Q. Cong, Jiegou Huaxue, 4 (1985) 96; Chem. Abstr., 105 (1986) 124739d.
559 M.F. Hallam, N.D. Howells, D.M.P. Mingos and R.W.M. Wardle, J. Chem. Soc., Dalton Trans., (1985) 845.
560 C.S. Browning, D.H. Farrar, R.R. Gukathasan and S.A. Morris, Organometallics, 4 (1985) 1750.
561 O. Zahraa, Int. Congr. Catal., [Proc.] 8th, 5 (1984) V87; Chem. Abstr., 105 (1986) 103354j.
562 B.R. Lloyd and R.J. Puddephatt, J. Am. Chem. Soc., 107 (1985) 7785.
563 G.K. Campbell, P.B. Hitchcock, M.F. Lappert and M.C. Misra, J. Organomet. Chem., 289 (1985) C1.
564 M.A. Urbancic, S.R. Wilson and J.R. Shapley, Inorg. Chem., 23 (1984) 2954.
565 M.A. Urnbanic, PhD Thesis, Univ. Illinois, Urbana, Diss. Abstr., Int. B, 45 (1984) 182; Chem. Abstr., 101 (1984) 142819b.
566 O. Bars, P. Braunstein and J.M. Jud, Nouv. J. Chim., 8 (1984) 771.
567 L.J. Farrugia, A.D. Miles and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 2415.
568 R. Bender, P. Braunstein, B. Metz and P. Lemoinè, Organometallics, 3 (1984) 381.

569 P. Fantucci, G. Pacchioni and V. Valenti, Inorg. Chem., 23 (1984) 247.
570 A. Ceriotti, P. Chini, A. Fumagalli, T.F. Koetzle, G. Longoni and F. Takusagawa, Inorg. Chem., 23 (1984) 1363.
571 S.G. Shore and W.L. Hsu, U.S. US 4,515,278 (1985); Chem. Abstr., 103 (1985) 178460h.
572 B.F.G. Johnson, J. Lewis, P.R. Raithby, S.N. Azman, B. Syed-Mustaffa, M.J. Taylor, K.H. Whitmire and M. Clegg, J. Chem. Soc., Dalton Trans., (1984) 2111.
573 P. Braunstein, J. Rosé, A.M. Manotti-Lanfredi, A. Tirippicchio and E. Sappa, J. Chem. Soc., Dalton Trans., (1984) 1843.
574 M. Castiglioni, R. Giordano, E. Sappa, G. Predieri and A. Tiripicchio, J. Organomet. Chem., 270 (1984) C7
575 R.D. Feltham, G. Elbaze, R. Ortega, C. Eck and J. Dubrawski, Inorg. Chem., 24 (1985) 1503.
576 A. Moor, P.S. Pregosin, L.M. Venanzi and A.J. Welch, Inorg. Chim. Acta, 85 (1984) 103.
577 V.F. Yudanov, N.K. Eremenko, E.G. Mednikov and S.P. Gubin, J. Struct. Chem. USSR, 25 (1984) 41; Zh. Strukt. Khim., 25 (1984) 49.
578 R.F. Klevtsova, E.N. Yurchenko, L.A. Glinskaya, E.B. Burgina, N.K. Ermenko and V.V. Bakakin, Zh. Struct. Khim., 26 (1985) 84; Chem. Abstr., 103 (1985) 14872t.
579 R.D. Adams, Polyhedron, 4 (1985) 2003.
580 R.D. Adams and T.S.A. Hor, Inorg. Chem., 23 (1984) 4723.
581 R.D. Adams, T.S.A. Hor and P. Mathur, Organometallics, 3 (1984) 634.
582 R.D. Adams and S. Wang, Inorg. Chem., 24 (1985) 4447.
583 R.D. Adams, T.S.A. Hor and I.T. Horváth, Inorg. Chem., 23 (1984) 4733.
584 R.D. Adams and T.S.A. Hor, Organometallics, 3 (1984) 1915.
585 L.J. Farrugia, M. Green, D.R. Hankey, M. Murray, A.G. Orpen and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985) 177.
586 C.E. Briant, R.W.M. Wardle and D.M.P. Mingos, J. Organomet. Chem., 267 (1984) C49.
587 S. Bhadhuri, K.R. Sharma, W. Clegg, G.M. Sheldrick and D. Stalke, J. Chem. Soc., Dalton Trans., (1984) 2851.
588 R. Bender, P. Braunstein, J.-M. Jud and Y. Dusausoy, Inorg. Chem., 23 (1984) 4489.
589 R. Jund, P. Lemoine, M. Gross, R. Bender and P. Braunstein, J. Chem. Soc., Dalton Trans., (1985) 711.
590 Yu.L. Slovokhotov and Yu.T. Struchkov. Russ. Chem. Rev., 54 (1985) 323; Usp. Khim., 54 (1985) 556.
591 D.M.P. Mingos, Acc. Chem. Res., 17 (1984) 311.
592 B.K. Teo, Inorg. Chem., 23 (1984) 1251.
593 B.K. Teo, G. Longoni and F.R.K. Chung, Inorg. Chem., 23 (1984) 1257.
594 R.J. Johnston and D.M.P. Mingos, J. Organomet. Chem., 280 (1985) 407.
595 D. Fenske, R. Basoglu, J. Hachgenei and F. Rogel, Angew. Chem., Int. Ed. Engl., 23 (1984) 160; Angew. Chem., 96 (1984) 160.
596 D. Fenske, J. Hachgenei and F. Rogel, Angew. Chem., Int. Ed. Engl., 23 (1984) 982; Angew. Chem., 96 (1984) 959.
597 D. Fenske, J. Hachgenei and J. Ohmer, Angew. Chem., Int. Ed. Engl., 24 (1985) 706; Angew. Chem., 97 (1985) 684.
598 K.S. Suslick and R.E. Johnson, J. Am. Chem. Soc., 106 (184) 6856.
599 M.M. Olmstead and P.P. Power, J. Am. Chem. Soc., 106 (1984) 1495.
600 A. Ceriotti, G. Longoni, M. Manassero, M. Perego and M. Sansoni, Inorg. Chem., 24 (1985) 117.
601 A Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, L. Resconi and M. Sansoni, J. Chem. Soc., Chem. Commun., (1985) 181.
602 A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, G. Piro, L. Resconi and M. Sansoni, J. Chem. Soc., Chem. Commun., (1985) 1402.
603 A. Ceriotti, R. Della Pergola, G. Longoni, M. Manassero and M. Sansoni, J. Chem. Soc., Dalton Trans., (1984) 1181.

604 A. Arrigoni, A. Ceriotti, R. della Pergola, G. Longoni, M. Manassero and M. Sansoni, J. Organomet. Chem., 296 (1985) 243.
605 J. A. Hriljac, P.N. Swepston and D.F. Shriver, Organometallics, 4 (1985) 158.
606 A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva and M. Sansoni, Angew. Chem., Int. Ed. Engl., 24 (1985) 697; Angew. Chem., 97 (1985) 708.
607 N.K. Eremenko, E.G. Mednikov and S.S. Kurasov, Russ. Chem. Rev., 54 (1985) 394; Usp. Khim., 54 (1985) 671.
608 R. Ugo, A. Chiesa and A. Yatsimirski, J. Chem. Soc., Dalton Trans., (1985) 1971.
609 M.L. Kullberg, F.R. Lemke, D.R. Powell and C.P. Kubaik, Inorg. Chem., 24 (1985) 3589.
610 E.G. Mednikov, N.K. Eremenko and S. P. Gubin, Koord. Khim., 10 (1984) 711; Chem. Abstr., 102 (1985) 142160a.
611 E.G. Mednikov and N.K. Eremenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2547; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2781.
612 V.E. Lopatin, S.P. Gubin, N.M. Mikova, M. Ts. Tsybenov, Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organomet. Chem., 292 (1985) 275.
613 D.M.P. Mingos and R.W.M. Wardle, Transition Met. Chem., 10 (1985) 441.
614 H.C. Clark and V.K. Jain, Coord. Chem. Rev., 55 (1984) 151.
615 B.K. Teo, Inorg. Chem., 23 (1984) 1251.
616 B.K. Teo, G. Longoni and F.R.K. Chung, Inorg. Chem., 23 (1984) 1257.
617 B.K. Teo, Inorg. Chem., 24 (1985) 4209.
618 B.K. Teo and N.J.A. Sloan, Inorg. Chem., 24 (1985) 4545.
619 D.W. Bullett, Chem. Phys. Lett., 115 (1985) 450.
620 D.J. Underwood, R. Hoffmann, K. Tatsumi, A. Nakamura and Y. Yamamoto, J. Am. Chem. Soc., 107 (1985) 5968.
621 D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1985) 1352.
622 T. Ohmori, T. Fujiso, E. Yasui, S. Nomura and Y. Aizawa, Fr. Demande FR 2,545,095 (1984); Chem. Abstr., 102 (1985) 187845u.
623 S. Bhadhuri, K.R. Sharma and G.S. Kalpathi U.S. US 4,491,670 (1985); Chem. Abstr., 102 (1985) 166489r.
624 A. Basu, S. Bhadhuri and K.R. Sharma, J. Chem. Soc., Dalton Trans., (1984) 2315.
625 G.M. Woltermann, U.S. US 4,454,244 (1984); Chem. Abstr., 101 (1984) 60992p.
626 S. Bhadhuri and K.R. Sharma, J. Chem. Soc., Dalton Trans., (1984) 2309.
627 A. Ceriotti, P. Chini, G. Longoni, M. Marchionna, L.F. Dahl, R. Montag and D.M. Washecheck, Cong. Naz. Chim. Inorg., [Atti], 15th (1982) 93; Chem. Abstr., 100 (1984) 166992h.
628 C. Couture, D.H. Farrar and R.J. Goudsmit, Inorg. Chim. Acta, 89 (1984) L29.
629 C. Couture and D.H. Farrar, J. Chem. Soc., Chem. Commun., (1985) 197.
630 A. Fumagalli, S. Martinengo and G. Ciani, J. Organomet. Chem., 273 (1984) C46.
631 A. Fumagalli, S. Martinengo, P. Chini, D. Galli, B.T. Heaton and R. Della Pergola, Inorg. Chem., 23 (1984) 2947.
632 M.J. Freeman, A.D. Miles, M. Murray, A.G. Orpen and F.G.A. Stone, Polyhedron, 3 (1984) 1093.
633 V.E. Lopatin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2623; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2827.
634 A Albinati, K.-H. Dahmen, A. Togni and L. M. Venanzi, Angew. Chem., Int. Ed. Engl., 24 (1985) 766; Angew. Chem., 97 (1985) 760.
635 C. Mealli, R. Hoffmann and A. Stockis, Inorg. Chem., 23 (1984) 56.
636 A. Döhring, P.W. Jolly, C. Krüger and M.J. Romão, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 484.
637 C. Bianchini, C. Mealli, A. Meli and M. Sabat, Inorg. Chem., 23 (1984) 2731.

638 L. Pandolfo, G. Paiaro, G. Valle and P. Ganis, Gazz. Chim. Ital., 115 (1985) 59.
639 L. Pandolfo, G. Paiaro, G. Valle and P. Ganis, Gazz. Chim. Ital., 115 (1985) 65.
640 L. Pandolfo, F. Morandini and G. Paiaro, Gazz. Chim. Ital., 115 (1985) 711.
641 P.V. Broadhurst, Polyhedron, 4 (1985) 1801.
642 K.K. Pandey and H.L. Nigam, Rev. Inorg. Chem., 6 (1984) 69.
643 C. Bianchini, C.A. Ghilardi, A. Meli and A. Orlandini, J. Organomet. Chem., 270 (1984) 251.
644 C. Bianchini, D. Masi, C. Mealli and A. Meli, Inorg. Chem., 23 (1984) 2838.
645 C. Bianchini, C.A. Ghilardi, A. Meli and A. Orlandini, J. Organomet. Chem., 286 (1985) 259.
646 C. Bianchini, A. Meli and G. Scapacci, Organometallics, 4 (1985) 264.
647 D.H. Farrar, R.R. Gukathasan and K. Won, J. Organomet. Chem., 275 (1984) 263.
648 R. Usón, J. Forniés and M.A. Usón, Synth. React. Inorg. Met.-Org. Chem., 14 (1984) 355.
649 R. Usón, J. Forniés and M.A. Usón, Inorg. Chim. Acta, 81 (1984) L27.
650 D.H. Farrar, R.R. Gukathasan and S.A. Morris, Inorg. Chem., 23 (1984) 3258.
651 H. Werner, M. Ebner and W. Bertleff, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 1351.
652 M. Ebner, H. Otto and H. Werner, Angew. Chem., Int. Ed. Engl., 24 (1985) 518; Angew. Chem., 97 (1985) 522.
653 E. Ma, G. Semelhago, A. Walker, D.H. Farrar and R.R. Gukathasan, J. Chem. Soc., Dalton Trans., (1985) 2595.
654 M. Yokoyama and T. Imamoto, Synthesis (1984) 797.
655 U.R. Kunze, J. Organomet. Chem., 281 (1985) 79.
656 C.C. Hinckley, L.V. Dunkerton and J. Tyrell, Energy Res. Abstr., 10 (1985) Abstr. No. 49238; Chem. Abstr., 106 (1987) 167787f.
657 A. Grassi, P. Longo, A. Musco, W. Porzio and A. Scrivanti, J. Organomet. Chem., 289 (1985) 439.
658 S.W. Carr, R. Colton and D. Dakternieks, Inorg. Chem., 23 (1984) 720.
659 A. Miyashita, H. Shitara and H. Nohira, J. Chem. Soc., Chem. Commun., (1985) 850.
660 E.K. Barefield, A.M. Carrier, D.J. Sepelak and D.G. Van Derveer, Organometallics, 4 (1985) 1395.
661 M Seidel and H. Hobert, Wiss. Z.-Friedrich-Schiller-Univ. Jena: Naturwiss. Reihe, 34 (1985) 701; Chem. Abstr., 104 (1986) 218095x.
662 D. Lentz, Chem. Ber., 118 (1985) 560.
663 D. Lentz, Ann. Chim. (Paris), 9 (1984) 665; Chem. Abstr., 103 (1985) 142128s.
664 N. Kuhn and M. Winter, Chem.-Ztg., 109 (1985) 12.
665 W.P. Fehlhammer, K. Bartel, B. Weinberger and U. Plaia, Chem. Ber., 118 (1985) 2220.
666 H. Arzoumanian, R. Lai, J. Metzger and J.-F. Petrignani, J. Organomet. Chem., 267 (1984) 207.
667 H. Arzoumanian, A. Baldy, M. Pierrot and J.F. Petrignani, J. Organomet. Chem., 294 (1985) 327.
668 J.M. van der Eijk, V.E.M. Richters, R.J.M. Nolte and W. Drenth, Rec. Trav. Chim. Pays.-Bas, 103 (1984) 46.
669 D.L. Delaet, D.R. Powell and C.P. Kubiak, Organometallics, 4 (1985) 954.
670 O.J. Scherer, R. Walter and W.S. Sheldrick, Angew. Chem., Int. Ed. Engl., 24 (1985) 115; Angew. Chem., 97 (1985) 132.
671 G. Zinner and W.P. Fehlhammer, Angew. Chem., Int. Ed. Engl., 24 (1985) 979; Angew. Chem., 97 (1985) 990.
672 B. Weinberger, F. Degel and W.P. Fehlhammer, Chem. Ber., 118 (1985) 51.
673 B. Weinberger and W.P. Fehlhammer, Chem. Ber., 118 (1985) 42.

674 M. Schaal, W. Weigand, U. Nagel and W. Beck, Chem. Ber., 118 (1985) 2186.

675 R.A. Michelin, G. Facchin and P. Uguagliati, Inorg. Chem., 23 (1984) 961.

676 Y. Yamamoto, K. Takahashi and H. Yamazaki, Chem. Lett., (1985) 201.

677 Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Jpn., 58 (1985) 1843.

678 M.K. Reinking, M.L. Kullberg, A.R. Cutler and C.P. Kubiak, J. Am. Chem. Soc., 107 (1985) 3517.

679 M.A. Khan and A.J. McAlees, Inorg. Chim. Acta, 104 (1985) 109.

680 A.W. Hanson, A.J. McAlees and A. Taylor, J. Chem. Soc., Perkin Trans I, (1985) 441.

681 C.R. Langrick, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 1233.

682 N.M. Rutherford, M.M. Olmstead and A.L. Balch, Inorg. Chem., 23 (1984) 2833.

683 A.F.M.M. Rahman, PhD Thesis, Wayne State University, (1984); Diss. Abstr., Int. B, 45 (1985) 3815.

684 C.-M. Che, F.H. Herbstein, W.P. Schaefer, R.E. Marsh and H.B. Gray, Inorg. Chem., 23 (1984) 2572.

685 R. Usón, J. Forniés, P. Espinet, E. Lalinde, P.G. Jones and G.M. Sheldrick, J. Organomet. Chem., 288 (1985) 249.

686 G. Facchin, P. Uguagliati and R.A. Michelin, Organometallics, 3 (1984) 1818.

687 C.G. Francis, S.I. Khan and P.R. Morton, Inorg. Chem., 23 (1984) 3680.

688 O.J. Scherer, R. Konrad, E. Guggolz and M.L. Ziegler, Chem. Ber., 118 (1985) 1.

689 C.E. Briant, D.I. Gilmour, D.M.P. Mingos and R.W.M. Wardle, J. Chem. Soc., Dalton Trans., (1985) 1693.

690 C.E. Briant, D.I. Gilmour and D.M.P. Mingos, J. Organomet. Chem., 267 (1984) C52.

691 I. Jaffee, M. Segal and A. Efraty, J. Organomet. Chem., 294 (1985) C17.

692 G. Marr and B.W. Rockett, J. Organomet. Chem., 278 (1984) 331.

693 L.A.P. Kane-Maguire, E.D. Honig and D.A. Sweigart, Chem. Rev., 84 (1984) 525.

694 G. Deng, L. Wang and Y.T. Chen, Gaodeng Xuexiao Huaxue Xuebao, 5 (1984) 532; Chem. Abstr., 101 (1984) 138251t.

695 L.S. Hegedus, Tetrahedron, 40 (1984) 2415.

696 K. Miki, K. Masaki and K. Yamatodani, Kessho Kaiseki Kenkyu Senta Dayori, 6 (1985) 31; Chem. Abstr., 103 (1985) 45932s.

697 T. Ziegler, Inorg. Chem., 24 (1985) 1547.

698 P.-O Widmark, B.O. Roos and P.E.M. Siegbahn, J. Phys. Chem., 89 (1985) 2180.

699 E. Bauwe and G. Rasch, Z. Chem., 24 (1985) 26.

700 K.R. Pörschke, R. Mynott, C. Krüger and M.J. Romão, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1076.

701 K.R. Pörschke and R. Mynott, Z. Naturforsch., B; Anorg. Chem., Org. Chem., 39B (1984) 1565.

702 B.M. Trzcinska, J.P. Fackler and A.B. Anderson, Organometallics, 3 (1984) 319.

703 H. Lehmkuhl, C. Naydowski, F. Danowski, M. Bellenbaum, R. Benn, A. Rufińska, G. Schroth, R. Mynott and S. Pasynkiewicz, Chem. Ber., 117 (1984) 3231.

704 W. Kleimann, K.-R. Pörschke and G. Wilke, Chem. Ber., 118 (1985) 323.

705 R.J. McKinney and D.C. Roe, J. Am. Chem. Soc., 107 (1985) 261.

706 J.E. Bäckvall, E.E. Björkman, L. Pettersson and P. Siegbahn, J. Am. Chem. Soc., 106 (1984) 4369.

707 J.E. Bäckvall, E.A. Björkman, L. Pettersson and P. Siegbahn, J. Am. Chem. Soc., 107 (1985) 7265.

708 M.A. Chesters, G.S. McDougall, M.E. Pemble and N. Sheppard, Appl. Surf. Sci., 22-23 (1985) 369.

709 L.-F. Olsson, Chem. Script., 25 (1985) 194.

710 C.A. Ghilardi, S. Midollini, S. Moneti and O. Orlandini, J. Organomet. Chem., 286 (1985) 419.

711 S.G. Gagarin, Yu.A. Teterin and I.G. Fal'kov, Koord. Khim., 10 (1984) 1243; Chem. Abstr., 102 (1985) 35909e.

712 S. Sakaki, K. Maruta and K. Ohkubo, Nippon Kagaku Kaishi (1985) 598.

713 C.A. Akpan, M.F. Meidine, J.F. Nixon, M. Yoshifuji, K. Toyota and N. Inamoto, J. Chem. Soc., Chem. Commun., (1985) 946.

714 H.W. Roesky, H. Hofmann, P.G. Jones and G.M. Sheldrick, Angew. Chem., Int. Ed. Engl., 23 (1984) 971; Angew. Chem., 96 (1984) 971.

715 O.J. Scherer, H. Jungmann, C. Krüger and G. Wolmershäuser, Chem. Ber., 117 (1984) 2382.

716 J. Calvet, O. Rossell and M. Seco, Transition Met. Chem., 9 (1984) 208.

717 N.P.C. Walker, M.B. Hursthouse, C.P. Warrens and J.D. Woollins, J. Chem. Soc., Chem. Commun., (1985) 227.

718 C.M. Bolinger, T.B. Rauchfuss and S.R. Wilson, J. Am. Chem. Soc., 106 (1984) 7800.

719 M. Di Vaira, S. Moneti, M. Peruzzini and P. Stoppioni, J. Organomet. Chem., 266 (1984) C8.

720 T.R. Sharp, M.R. White, J.F. Davis and P.J. Stang, Org. Mass Spectrom., 19 (1984) 107.

721 W.-S. Hwang, Polyhedron, 3 (1984) 513.

722 P. Boron-Rettore, D.M. Grove and L.M. Venanzi, Helv. Chim. Acta, 67 (1984) 65.

723 N.J. Hazel, J.A.K. Howard and J.L. Spencer, J. Chem. Soc., Chem. Commun., (1984) 1663.

724 T.-H. Chang and J.I. Zink, J. Am. Chem. Soc., 106 (1984) 287.

725 H. Jobic, J. Mol. Struct., 131 (1985) 167.

726 A. Bavoso, M. Funicello, G. Morelli and V. Pavone, Acta Crystallogr., Sect. C, C40 (1984) 2035.

727 G.A. Foulds, P.S. Hall and D.A. Thornton, J. Mol. Struct., 117 (1984) 95.

728 R.A. Newmark and A.R. Siedle, Magn. Reson. Chem., 23 (1985) 67.

729 H. Kurosawa, N. Asada, A. Urabe and M. Emoto, J. Organomet. Chem., 272 (1984) 321,

730 I.M. Al-Najjar, S.S. Al-Showiman and H.M. Al-Hazimi, Inorg. Chim. Acta, 89 (1984) 57.

731 V. De Felice, A. De Renzi, G. Morelli and A. Panunzi, Inorg. Chim. Acta, 90 (1984) L35.

732 J.D. Scott and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1984) 193.

733 J. Auffret, P. Courtot, R. Pichon, R. Rumin and J.Y. Salaun, J. Organomet. Chem., 262 (1984) C19.

734 C.A. Bignozzi, F. Scandola, C. Bartocci and V. Carassiti, Congr. Naz. Chim. Inorg. [Atti], 15th (1982) 214; Chem. Abstr., 100 (1984) 184718c.

735 C. Bisi-Castellani, L. Maresca and G. Natile, Inorg. Chim. Acta, 89 (1984) 157.

736 J.K.K. Sarhan, M. Green and I.M. Al-Najjar, J. Chem. Soc., Dalton Trans., (1984) 771.

737 L. Canovese, M.L. Tobe and L. Cattalini, J. Chem. Soc., Dalton Trans., (1985) 27.

738 A.D. Berry, U.S. Pat. Appl. US 531,387 (1984); Chem. Abstr., 100 (1984) 107905j.

739 U. Rosenthal and W. Schulz, Z. Chem., 25 (1985) 227.

740 P. Binger, T.R. Martin, R. Benn, A. Rufińska and G. Schroth, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 990.

741 H.M. Büch, P. Binger and C. Krüger, Organometallics, 3 (1984) 1504.

742 G. Bontempelli, F. Magno, B. Corain and G. Schiavon, Inorg. Chim. Acta, 99 (1985) 19.

743 E. Dinjus, H. Görls, E. Uhlig, D. Walther, J. Sieler, O. Lindqvist and L. Andersen, J. Organomet. Chem., 276 (1984) 257.

744 H. Tom Dieck, L. Stamp, R. Diercks and C. Müller, Nouv. J. Chim., 9 (1985) 290.

745 F.M. Ashmawy, F.R. Benn, C.A.McAuliffe and D.G. Watson, J. Organomet. Chem., 287 (1985) 65.

746 M.A. Bennett, C. Chiraratvatana, J. Organomet. Chem., 296 (1985) 255.

747 A. Miyashita, S. Ikezu and H. Nohira, Chem. Lett., (1985) 1235.

748 R.S. Paonessa, A.L. Prignan and W.C. Trogler, Organometallics, 4 (1985) 647.

749 G.T. Crisp, S. Holle, P.W. Jolly, R. Mynott and H. Werner, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 990.

750 M. Lenarda, G. Nardin, G. Pellizer, E. Brayé and M. Graziani, J. Chem. Soc., Chem. Commun., (1985) 1536.

751 F.M. Ashmawy, F.R. Benn, C.A. McAuliffe, D.G. Watson, W.E. Hill and W.D. Perry, Inorg. Chim. Acta, 97 (1985) 25.

752 E.C. Alyea, R.P. Shakya and A.E. Vougioukas, Transition Met. Chem., 10 (1985) 435.

753 V. Sirakova, D. Dimitrov and R. Stefanova, Dokl. Bolg. Akad. Nauk, 37 (1984) 1343; Chem. Abstr., 103 (1985) 6481z.

754 N. Ito, T. Saji and S. Aoyagui, Bull. Chem. Soc. Jpn., 58 (1985) 2323.

755 B. Åkermark and K. Zetterberg, J. Am. Chem. Soc., 106 (1984) 5560.

756 J.-E. Bäckvall and E.E. Björkman, Acta Chem. Scand., B38 (1984) 91.

757 R. Lazzaroni, G. Uccello-Barretta, S. Bertozzi, C. Bertucci and F. Marchetti, J. Chem. Res., S, (1984) 286.

758 R. Řeřicha and M. Zdražil, Coll. Czech. Chem. Commun., 50 (1985) 2647.

759 R. Lazzaroni, G. Uccello-Barretta, S. Bertozzi and P. Salvadori, J. Organomet. Chem., 275 (1984) 145.

760 G. Morelli, G. Polzonetti and V. Sessa, Polyhedron, 4 (1985) 1185.

761 G.B. Shul'pin, G.V. Nizova and P. Lederer, J. Organomet. Chem., 275 (1984) 283.

762 J.W. Fitch and F.C. Willims, Inorg. Chim. Acta, 97 (1985) 9.

763 J.-P. Macquet and A.L. Beauchamp, Inorg. Chim. Acta, 91 (1984) L25.

764 J.T. Burton Ph.D. Thesis, Univ. West. Ontario, Diss. Abstr. Int. B, 45 (1984) 1463.

765 S.A. Godleski, K.B. Gundlach and R.S. Valpey, Organometallics, 4 (1985) 296.

766 E.J. Parsons, R.D. Larsen and P.W. Jennings, J. Am. Chem. Soc., 107 (1985) 1793.

767 P.G. Gassman and I.G. Cesa, Organometallics, 3 (1984) 119.

768 K. Miki, K. Yamatoya, N. Kasai, H. Kurosawa, M. Emoto and A. Urabe, J. Chem. Soc., Chem. Commun., (1984) 1520.

769 R. Lazzaroni, G. Uccello-Barretta, S. Bertozzi and P. Salvadori, J. Organomet. Chem., 297 (1985) 117.

770 G. Guillot-Edelheit and J.-C. Chottard, J. Chem. Soc., Dalton Trans., (1984) 169.

771 V.G. Albano, F. Demartin, B. Di Blasio, G. Morelli and A. Panunzi, Gazz. Chim. Ital., 115 (1985) 361.

772 J. Köhler, A. Deege and G. Schomburg, Chromatographia, 18 (1984) 119.

773 I.M. Al-Najjar, Inorg. Chim. Acta, 83 (1984) L53.

774 M. Green, J.K.K. Sarhan and I.M. Al-Najjar, Organometallics, 3 (1984) 520.

775 A. Albinati, P.S. Pregosin and H. Rüegger, Angew. Chem., Int. Ed. Engl., 23 (1984) 78; Angew. Chem., 96 (1984) 63.

776 G.B. Shul'pin, G.V. Nizova and A.T. Nikitaev, J. Gen. Chem. USSR, 55 (1985) 1251; Zh. Obshch. Khim., 55 (1985) 1403.

777 V. Amir-Ebrahimii, J. Grimshaw, E.A. McIlgorm, T.R.B. Mitchell and J.J. Rooney, J. Mol. Catal., 27 (1984) 337.

778 D.J. Pasto, N.-Z. Huang and C.W. Eigenbrot, J. Am. Chem. Soc., 107 (1985) 3160.

779 D.J. Pasto and N.-Z. Huang, Organometallics, 4 (1985) 1386.

780 J.M. Brown, S.J. Cook and S.J. Kimber, J. Organomet. Chem., 269 (1984) C58.

781 W.R. Winchester, M. Gawron, G.J. Palenik and W.M. Jones, Organometallics, 4 (1985) 1894.

782 W.R. Winchester and W.M. Jones, Organometallics, 4 (1985) 2228.

783 A. Miyashita, H. Shitara and H. Nohira, Organometallics, 4 (1985) 1463.

784 W. Mayer, G. Wilke, R. Benn, R. Goddard and C. Krüger, Monatsh. Chem., 116 (1985) 879.

785 I.C. Hisatsune, Spectrochim. Acta, Part A, 40A, (1984) 391.

786 E. Wenschuh, T. Hoffmann and D. Walther, Z. Chem., 24 (1984) 385.

787 H.H. Karsch, G. Müller and C. Krüger, J. Organomet. Chem., 273 (1984) 195.

788 J.J. Eisch, M. Behrooz and S.K. Dua, J. Organomet. Chem., 285 (1985) 121.

789 T. Yamamoto and Y. Sekine, Inorg. Chim. Acta, 83 (1984) 47.

790 H. Hoberg, K. Radine, C. Krüger and M.J. Romão, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 607.

791 B. Bogdanovic, Ger. Offen. DE 3,247,360 (1984); Chem. Abstr., 101 (1984) 133325k.

792 T. Klingstedt, A. Hallberg, P. Dunbar and A. Martin, J. Het. Chem., 22 (1985) 1547.

793 K.-R. Pörschke and G. Wilke, Chem. Ber., 118 (1985) 313.

794 B. Nestler and E. Uhlig, Z. Anorg. Allg. Chem., 530 (1985) 196.

795 J.J. Eisch, L.E. Hallenbeck and M.A. Lucarelli, Fuel, 64 (1985) 440.

796 B. Fischer, J. Boersma, B. Kojić-Prodić and A.L. Spek, J. Chem. Soc., Chem. Commun., (1985) 1237.

797 R. Fischer, M. Rudolph and E. Uhlig, Z. Anorg. Allg. Chem., 520 (1985) 93.

798 T. Kauffman and K.-R. Gaydoul, Tetrahedron Lett., 26 (1985) 4071.

799 M.K. Doh, C.L. An and B.G. Kim, Kich'o Kwahak, Yongu (Yuengnam Taehakkyo), 5 (1985) 145; Chem. Abstr., 107 (1987) 198620w.

800 H.M. Asfour and M. Green, J. Organomet. Chem., 292 (1985) C25.

801 G.R. Wiger, S.S. Tomita, M.F. Rettig and R.M. Wing, Organometallics, 4 (1985) 1157.

802 G. Al Takhin, H.A. Skinner and A.A. Zaki, J. Chem. Soc., Dalton Trans., (1984) 371.

803 D.A. Wrobleski, C.S. Day, B.A. Goodman and T.B. Rauchfuss, J. Am. Chem. Soc., 106 (1984) 5464.

804 P.B. Hitchcock, M.F. Lappert and M.C. Misra, J. Chem. Soc., Chem. Commun., (1985) 863.

805 F. Neve and M. Ghedini, Congr. Naz. Chim. Inorg., [Atti], 16th (1983) 136; Chem. Abstr., 100 (1984) 78833b.

806 C.T. Bailey and G.C. Lisensky, J. Chem. Ed., 62 (1985) 896.

807 G.A. Abakumov, I.A. Teplova, V.K. Cherkasov, K.G. Shal'nova and G.A. Razuvaev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1291; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1402.

808 R.C. Larock and D.R. Leach, J. Org. Chem., 49 (1984) 2144.

809 V.A. Nikanorov, G.V. Gavrilova, V.I. Rozenberg and O.A. Reutov, Bull. Acad. Sci. USSR, 33 (1984) 2428; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2647.

810 A. Syed, E.D. Stevens and S.G. Cruz, Inorg. Chem., 23 (1984) 3673.

811 K. Venkatasubramanian, Proc.-Indian Acad. Sci., Chem. Sci., 93 (1984) 1237; Chem. Abstr., 102 (1985) 103969b.

812 K. Venkatsubramanian, Indian J. Phys., Part A, 56A (1982) 201.

813 R.R. Guimerans, F.E. Wood and A.L. Balch, Inorg. Chem., 23 (1984) 1307.

814 E.P. Kyba, C.N. Clubb, S.B. Larson, V.J. Schueler and R.E. Davis, J. Am. Chem. Soc., 107 (1985) 2141.

815 D.H. Goldsworthy, F.R. Hartley, G.L. Marshall and S.G. Murray, Inorg. Chem., 24 (1985) 2849.

816 A.G. Osborne, R.E. Hollands, R.F. Bryan and S. Lockhart, J. Organomet. Chem., 288 (1985) 207.

817 R.E. Hollands, A.G. Osborne, R.H. Whiteley and C.J. Cardin, J. Chem. Soc., Dalton Trans., (1985) 1527.

818 A.B. Goel and D. Vanderveer, Inorg. Chim. Acta, 87 (1984) L19.
819 M. F. Lappert and P.P. Power, J. Chem. Soc., Dalton Trans., (1985) 51.
820 R. Appel, C. Casser and F. Knoch, J. Organomet. Chem., 297 (1985) 21.
821 A.H. Cowley, R.A. Jones, J.G. Lasch, N.C. Norman, C.A. Stewart, A.L. Stuart, J.L. Atwood, W.E. Hunter and H.-M. Zhang, J. Am. Chem. Soc., 106 (1984) 7015.
822 T.A. van der Knaap, F. Bickelhaupt, J.-G. Kraaykamp, G. van Koten, J.P.C. Bernards, H.T. Edzes, W.S. Veeman, E. de Boer and E.J. Baerends, Organometallics, 3 (1984) 1804.
823 H.W. Kroto, S.I. Klein, M.F. Meidine, J.F. Nixon, R.K. Harris, K.J. Packer and P. Reams, J. Organomet. Chem., 280 (1985) 281.
824 M. Wada, K. Nishiwaki and M. Kumazoe, J. Chem. Soc., Chem. Commun., (1984) 981.
825 J. Carvajal, G. Muller, J. Sales, X. Solans and C. Miravitlles, Organometallics, 3 (1984) 996.
826 J.M. Coronas, G. Muller, M. Rocamora, C. Miravitlles and X. Solans, J. Chem. Soc., Dalton Trans., (1985) 2333.
827 B. Fell, H.-U. Hög and C. Krüger, J. Mol. Catal., 30 (1985) 57.
828 H. Lehmkuhl and C. Naydowski, J. Organomet. Chem., 277 (1984) C18.
829 D.C. Billington, Chem. Soc. Rev., 14 (1985) 93.
830 G.P. Chiusoli and G. Salerno, Chem. Met.-Carbon Bond, 3 (1985) 143; Chem. Abstr., 103 (1985) 215350v.
831 I. Omae, Coord. Chem. Rev., 53 (1984) 261.
832 R. Goddard, C. Krüger, F. Mark, R. Stansfield and X. Zhang, Organometallics, 4 (1985) 285.
833 D. Moncrieff, I.H. Hillier, V.R. Saunders and W. von Niessen, Inorg. Chem., 24 (1985) 4247.
834 D. Moncrieff, I.H. Hillier, V.R. Saunders and W. von Niessen, J. Chem. Soc., Chem. Commun., (1985) 779.
835 M. Merchan, I. Nebot-Gil, R. Gonzalez-Luque and F. Tomas, J. Mol. Struct., 120 (1985) 479 (THEOCHEM, 21 (1985) 479).
836 N. Stransky, R. Herzschuh, J.-P. Gehrke and R. Taube, J. Organomet. Chem., 270 (1984) 353.
837 N. Stransky, R. Herzschuh, J.-P. Gehrke and R. Taube, J. Organomet. Chem., 270 (1984) 357.
838 H. Brandes, R. Goddard, P.W. Jolly, C. Krüger, R. Mynott and G. Wilke, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1139.
839 R. Taube, U. Schmidt, J.-P. Gehrke and U. Anacker, J. Prakt. Chem., 326 (1984) 1.
840 H. Lehmkuhl, A. Rufińska, C. Naydowski and R. Mynott, Chem. Ber., 117 (1984) 376.
841 S.Ş. Zhukovskii, B.M. Fedorov, A.M. Taber, I.V. Kalechits and V.É. Vasserberg, Kinet. Catal., 25 (1984) 50; Kinet. Katal., 25 (1984) 62.
842 B.M. Fedorov, S.S. Zhukovskii, Deposited Doc., (1984) VINITI 3201-84, 23; Chem. Abstr., 103 (1985) 104486z.
843 G. Bontempelli, S. Daniele and M. Fiorani, J. Electroanal. Chem. Interfacial Electrochem., 160 (1984) 249.
844 R. Taube, J.-P. Gehrke and U. Schmidt, J. Organomet. Chem., 292 (1985) 287.
845 P. Hadjiandreou, M. Julémont and P. Teyssié, Macromolecules, 17 (1984) 2455.
846 S.T. Lin, T.J. Groshens and K.J. Klabunde, Inorg. Chem., 23 (1984) 1.
847 R. Hanko, Angew. Chem., Int. Ed., Engl., 24 (1985) 704; Angew. Chem., 97 (1985) 707.
848 H. Lehmkuhl, J. Elsässer, R. Benn, B. Gabor, A. Rufińska, R. Goddard and C. Krüger, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 171.
849 E.J. Corey and A.G. Myers, J. Am. Chem. Soc., 107 (1985) 5574.
850 T. Matsumoto, A. Ichihara, M. Yanagiya, T. Yuzawa, A. Sannai, H. Oikawa, S. Sakamura and C.H. Eugster, Helv. Chim. Acta, 68 (1985) 2324.

851 A. Carpita, F. Bonaccorsi and R. Rossi, Gazz. Chim. Ital., 114 (1984) 443.

852 H. Hoberg, D. Schaefer and B.W. Oster, J. Organomet. Chem., 266 (1984) 313.

853 D. Walther and E. Dinjus, Z. Chem., 24 (1984) 63.

854 D. Walther and E. Dinjus, Z. Chem., 24 (1984) 298.

855 D. Walther, E. Dinjus, H. Görls, J. Sieler, O. Lindqvist and L. Andersen, J. Organomet. Chem., 286 (1985) 103.

856 R. Benn, B. Büssemeier, S. Holle, P.W. Jolly, R. Mynott, I. Tkatchenko and G. Wilke, J. Organomet. Chem., 279 (1985) 63.

857 L.S. Hegedus and D.H.P. Thompson, J. Am. Chem. Soc., 107 (1985) 5663.

858 T. Bartik and I. Gerdes, J. Organomet. Chem., 291 (1985) 253.

859 P.W. Jolly, Angew. Chem., Int. Ed. Engl., 24 (1985) 283; Angew. Chem., 97 (1985) 279.

860 A. Tiripicchio, F.J. Lahoz, L.A. Oro, M.T. Pinillos and C. Tejel, Inorg. Chim. Acta, 100 (1985) L5.

861 D.E. Smith, Ph.D. Thesis, USC, 1983; Diss. Abstr. Int. B, 44 (1984) 3411.

862 N.J. Trivedi, Ph.D. Thesis USC, 1983; Diss. Abstr. Int. B, 44 (1984) 3411.

863 Y. Inoue, J. Yamashita and H. Hashimoto, Synthesis (1984) 244.

864 R.J.P. Corriu, N. Escudié and C. Guerin, J. Organomet. Chem., 271 (1984) C7.

865 T. Ohta, T. Hosokawa, S. Murahashi, K. Miki and N. Kasai, Organometallics, 4 (1985) 2080.

866 H. Shibuya, S. Tsuji, Y. Yamamoto, H. Miura and I. Kitagawa, Chem. Pharm. Bull., 32 (1984) 3417.

867 D.A. Hunt, J.M. Quante, R.L Tyson and L.W. Dasher, J. Org. Chem., 49 (1984) 5262.

868 K. Nakasuji, M. Yamaguchi, I. Murata, K. Tatsumi and A. Nakamura, Organometallics, 3 (1984) 1257.

869 S. Imaizumi, T. Matsuhisa and Y. Senda, J. Organomet. Chem., 280 (1985) 441.

870 S.S. Hall and B. Åkermark, Organometallics, 3 (1984) 1745.

871 B. Åkermark and A. Vitagliano, Organometallics, 4 (1985) 1275.

872 M.K. Andari, A.V. Krylov and A.P. Belov, Zh. Strukt. Khim., 25 (1984) 167.

873 M. Takahashi, H. Urata, H. Suzuki, Y. Moro-Oka and T. Ikawa, J. Organomet. Chem., 266 (1984) 327.

874 T. Hosokawa, Y. Imada and S. Murahashi, Bull. Chem. Soc. Jpn., 58 (1985) 3282.

875 R.C. Larock and K. Takagi, J. Org. Chem., 49 (1984) 2701.

876 J. Powell and N.I. Dowling, J. Organomet. Chem., 264 (1984) 387.

877 A.V. Devekki and Yu.I. Malov, Russ. J. Inorg. Chem., 30 (1985) 1378; Zh. Neorg. Khim., 30 (1985) 2418.

878 S. Okeya and S. Kawaguchi, Bull. Chem. Soc. Jpn., 57 (1984) 1217.

879 W.A. Donaldson, J. Organomet. Chem., 269 (1984) C25.

880 W.A. Donaldson and B.S. Taylor, Tetrahedron Lett., 26 (1985) 4163.

881 D. Wilhelm, J.-E. Bäckvall, R.E. Nordberg and T. Norin, Organometallics, 4 (1985) 1296.

882 R.C. Larock and S. Varaprath, J. Org. Chem., 49 (1984) 3432.

883 A.B. Fasman, N.V. Perkas and V.F. Vozdvizhenskii, Kinet. Catal., 26 (1985) 592; Kinet. Katal., 26 (1985) 680.

884 N.V. Perkas, A.B. Fasman and V.N. Ermolaev, Vestn. Akad. Nauk Kaz. SSR, (1984) (11) 36; Chem. Abstr., 102 (1985) 51528k.

885 L.V. Mironova, Yu.S. Levkovskii, L.B. Belykh, G.V. Lobza, N.A. Ivanova, G.V. Ratovskii, E.I. Dubinskaya and F.K. Shmidt, Koord. Khim., 11 (1985) 1689; Chem. Abstr., 104 (1986) 40520s.

886 Nissan Chemical Industries, Ltd., Jpn. Kokai Tokkyo Koho JP 60 96,764 [85 96,764] (1985); Chem. Abstr., 103 (1985) 146043h.

887 M. Takakura, S. Kondo and T. Nogami, Eur. Pat. Appl. EP 125,617 (1984); Chem. Abstr., 102 (1985) 83111k.
888 T. Hosokawa, T. Ohta, Y. Okamoto and S. Murahashi, Bull. Chem. Soc. Jpn., 58 (1985) 194.
889 J.W. Faller, C. Blankenship and S. Sena, J. Am. Chem. Soc., 106 (1984) 793.
890 J.W. Faller, C. Blankenship, B. Whitmore and S. Sena, Inorg. Chem., 24 (1985) 4483.
891 Y. Rosopulos, U. Nagel and W. Beck, Chem. Ber., 118 (1985) 931.
892 T.G. Schenck, J.M. Downes, C.R.C. Milne, P.B. Mackenzie, H. Boucher, J. Whelan and B. Bosnich, Inorg. Chem., 24 (1985) 2334.
893 S. Agbossou, M.C. Bonnet and I. Tkatchenko, Nouv. J. Chim., 9 (1985) 311.
894 P.J. Chung, Taehan Hwahakhoe Chi, 28 (1984) 135; Chem. Abstr., 101 (1984) 91174c.
895 H. Stegemann, P.G. Antonov, W. Gaube and Yu.N. Kukushkin, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 28(9) (1985) 14; Chem. Abstr., 105 (1986) 43054z.
896 M.K. Andari, A.V. Krylov and A.P. Belov, Khim. Svyaz Str. Mol. (1984) 208; Chem. Abstr., 104 (1986) 149111k.
897 A.P. Belov and M.K. Andari, Dokl. Chem., 275 (1984) 107; Dokl. Akad. Nauk SSSR, 275 (1984) 629 [Chem.].
898 T.N. Petukhova, M.K. Andari, A.V. Ryabtsev, A.P. Belov and G.A. Grigor'ev, Koord. Khim., 10 (1984) 999; Chem. Abstr., 101 (1984) 152051j.
899 M. Bressan, L. Dal Mas, F. Morandini and B. Prozzo, J. Organomet. Chem., 287 (1985) 275.
900 R.L. Batstone-Cunningham, H.W. Dodgen, J.P. Hunt and D.M. Roundhill, J. Organomet. Chem., 289 (1985) 431.
901 H. Meyer and A. Zschunke, J. Organomet. Chem., 269 (1984) 209.
902 S.A. Godleski, K.B. Gundlach, H.Y. Ho, E. Keinan and F. Frolow, Organometallics, 3 (1984) 21.
903 R. Ciajolo, M.A. Jama, A. Tuzi and A. Vitagliano, J. Organomet. Chem., 295 (1985) 233.
904 P.J. Ssebuwufu, F. Glockling and P. Harriott, Inorg. Chim. Acta, 98 (1985) L35.
905 H. Kurosawa and M. Emoto, Chem. Lett., (1985) 1161.
906 H. Kurosawa and A. Urabe, Chem. Lett., (1985) 1839.
907 H. Kurosawa, M. Emoto and A. Urabe, J. Chem. Soc., Chem. Commun., (1984) 968.
908 A. Goliaszewski and J. Schwartz, Organometallics, 4 (1985) 415.
909 A. Goliaszewski and J. Schwartz, Organometallics, 4 (1985) 417.
910 A. Goliaszewski and J. Schwartz, J. Am. Chem. Soc., 106 (1984) 5028.
911 A. Goliaszewski and J. Schwartz, Tetrahedron, 41 (1985) 5779.
912 H. Kurosawa, M. Emoto, A. Urabe, K. Miki and N. Kasai, J. Am. Chem. Soc., 107 (1985) 8253.
913 B. Åkermark, S. Hansson, B. Krakenberger, A. Vitagliano and K. Zetterberg, Organometallics, 3 (1984) 679.
914 G.A. Conway, J.S. Park, L. Maggiora, M.P. Mertes, N. Galton and E.K. Michaelis, J. Med. Chem., 27 (1984) 52.
915 A.B. Goel, Tetrahedron Lett., 25 (1984) 4599.
916 P.R. Auburn, P.B. Mackenzie and B. Bosnich, J. Am. Chem. Soc., 107 (1985) 2033.
917 P.B. Mackenzie, Ph. D. Thesis, Univ Toronto, 1983; Diss. Abstr. Int. B, 44 (1984) 3075.
918 T. Hayashi, M. Konishi and M. Kumada, J. Chem. Soc., Chem. Commun., (1984) 107.
919 R. Benn, P.W. Jolly, R. Mynott and G. Schenker, Organometallics, 4 (1985) 1136.
920 R. Benn, P.W. Jolly, R. Mynott, B. Raspel, G. Schenker, K.-P. Schick and G. Schroth, Organometallics, 4 (1985) 1945.

921 R. Benn, G. Gabor, P.W. Jolly, R. Mynott and B. Raspel, J. Organomet. Chem., 296 (1985) 443.
922 A. Behr and G. Von Ilsemann, J. Organomet. Chem., 276 (1984) C77.
923 I.G. Dinulescu, S. Staicu, A. Dumitru, A. Ghenciulescu, F. Chiraleu and M. Avram, Rev. Roum. Chim., 30 (1985) 585.
924 P.F. Dos Santos Filho and U. Schuchardt, J. Organomet. Chem., 263 (1984) 385.
925 B.M. Trost and T.N. Nanninga, J. Am. Chem. Soc., 107 (1985) 1075.
926 M.D. Jones and R.D.W. Kemmitt, J. Chem. Soc., Chem. Commun., (1985) 811.
927 B.P. Gracey, B.E. Mann and C.M. Spencer, J. Organomet. Chem., 297 (1985) 375.
928 J.M. Brown and J.E. MacIntyre, J. Chem. Soc., Perkin Trans. II, (1985) 961.
929 R. Bertani, G. Carturan, A. Scrivanti and A. Wojcicki, Organometallics, 4 (1985) 2139.
930 R.W. Zoellner and K.J. Kalbunde, Chem. Rev., 84 (1984) 545.
931 G. Sartori, A. Furlani, M.V. Russo, P. Carusi, S. Licoccia and L. Suber, Kem. Kozl., 61 (1984) 1; Chem. Abstr., 103 (1985) 53360u.
932 K.R. Pörschke, Y.-H. Tsay and C. Krüger, Angew. Chem., Int. Ed. Engl., 24 (1985) 323; Angew. Chem., 97 (1985) 334.
933 U. Rosenthal, Z. Anorg. Allg. Chem., 513 (1984) 151.
934 K.R. Pörschke, R. Mynott, K. Angermund and C. Krüger, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 199.
935 R. Diercks, J. Kopf and H. tom Dieck, Acta Crystallogr., Sect. C, C40 (1984) 363.
936 R. Diercks, L. Stamp, J. Kopf and H. tom Dieck, Angew. Chem., Int. Ed. Engl., 23 (1984) 893; Angew. Chem., 96 (1984) 891.
937 R. del Rosario and L.S. Stuhl, J. Am. Chem. Soc., 106 (1984) 1160.
938 J.D. Ferrara, C. Tessier-Youngs and W.J. Youngs, J. Am. Chem. Soc., 107 (1985) 6719.
939 M.A. Bennett, T.W. Hambley, N.K. Roberts and G.B. Robertson, Organometallics, 4 (1985) 1992.
940 P. Royo, T. Cuenca, E. Hernandez and R. Serrano, Rev. R. Acad. Cienc. Exactas, Fis. Nat. Madrid, 78 (1984) 391; Chem. Abstr., 105 (1986) 115156j.
941 E. Sappa, G. Predieri, A. Tiripicchio and M. Tiripicchio-Camellini, J. Organomet. Chem., 297 (1985) 103.
942 A. Tiripicchio, M. Tiripicchio-Camellini and E. Sappa, J. Chem. Soc., Dalton Trans., (1984) 627.
943 M. Castiglioni, R. Giordano and E. Sappa, J. Organomet. Chem., 275 (1984) 119.
944 E. Sappa, A.M.M. Lanfredi, G. Predieri, A. Tiripicchio and A.J. Carty, J. Organomet. Chem., 288 (1985) 365.
945 E.D. Morrison, A.D. Harley, M.A. Marcelli, G.L. Geoffroy, A.L. Rheingold and W.C. Fultz, Organometallics, 3 (1984) 1407.
946 M.A. Bennett and A. Rokicki, Aust. J. Chem., 38 (1985) 1307.
947 Yu.N. Kukushkin, I.V. Pakhomova and A.N. Arbatov, J. Gen. Chem. USSR, 54 (1984) 1420; Zh. Obshch. Khim., 54 (1984) 1595.
948 D.J. Underwood, M. Nowak and R. Hoffmann, J. Am. Chem. Soc., 106 (1984) 2837.
949 M.I. Bruce, M.G. Humphrey, J.G. Matisons, S.K. Roy and A.G. Swincer, Aust. J. Chem., 37 (1984) 1955.
950 C. Stader and B. Wrackmeyer, J. Organomet. Chem., 295 (1985) C11.
951 J.N. Louwen, R. Hengelmolen, D.M. Grove, A. Oskam and R.L. DeKock, Organometallics, 3 (1984) 908.
952 H. Ogawa, T. Joh, S. Takahashi and K. Sonogashira, J. Chem. Soc., Chem. Commun., (1985) 1220.
953 S. Takahashi, Mem. Inst. Sci. Ind. Res., Osaka Univ., 42 (1985) 1; Chem. Abstr., 103 (1985) 46329n.

954 K. Sonogashira, K. Asami and N. Takeuchi, J. Mat. Sci. Lett., 4 (1985) 737.

955 A. Furlani, S. Licoccia, M.V. Russo, A.C. Villa and C. Guastini, J. Chem. Soc., Dalton Trans., (1984) 2197.

956 G.K. Anderson and G.J. Lumetta, J. Organomet. Chem., 295 (1985) 257.

957 R.J. Cross and M.F. Davidson, Inorg. Chim. Acta, 97 (1985) L35.

958 R.J. Cross, M.F. Davidson and A.J. McLennan, J. Organomet. Chem., 265 (1984) C37.

959 R.J. Cross and J. Gemmill, J. Chem. Soc., Dalton Trans., (1984) 199.

960 A. Sebald and B. Wrackmeyer, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 1481.

961 A.J. McLennan and R.J. Puddephatt, Organometallics, 4 (1985) 485.

962 C.R. Langrick, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 1015.

963 A.T. Hutton, B. Shebanzadeh and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1984) 549.

964 A.T. Hutton, C.R. Langrick, D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 2121.

965 G.R. Cooper, A.T. Hutton, C.R. Langrick, D.M. McEwan, P.R. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 855.

966 A. Blagg, A.T. Hutton, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1984) 1815.

967 R.J. Blau, M.H. Chisholm, K. Folting and R.J. Wang, J. Chem. Soc., Chem. Commun., (1985) 1582.

968 A. Sebald, B. Wrackmeyer, C.R. Theocharis and W. Jones, J. Chem. Soc., Dalton Trans., (1984) 747.

969 E.A. Ishmaeva and I.I. Patsanovskii, Russ. Chem. Rev., 54 (1985) 243; Usp. Khim., 54 (1985) 418.

970 S.I. Al-Resayes, P.B. Hitchcock, M.F. Meidine and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1984) 1080.

971 S.I. Al-Resayes, P.B. Hitchcock, J.F. Nixon and D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1985) 365.

972 C.A. Ghilardi, S. Midollini and A. Orlandini, J. Organomet. Chem., 295 (1985) 377.

973 J. Silvestre and T.A. Albright, Nouv. J. Chim., 9 (1985) 659.

974 Z. Yoshida, Jpn. Kokai Tokkyo Koho JP 58,154,594 [83,154,594] (1983); Chem. Abstr., 100 (1984) 121362m.

975 J. Silvestre and T.A. Albright, J. Am. Chem. Soc., 107 (1985) 6829.

976 T. Ding and U. Koelle, Wuli Huaxue Xuebao, 1 (1985) 232; Chem. Abstr., 103 (1985) 78194f.

977 J.J. Eisch, A.M. Piotrowski, A.A. Aradi, C. Krüger and M.J. Romão, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 624.

978 P. Mauret and P. Alphonse, J. Organomet. Chem., 276 (1984) 249.

979 F. Canziani, C. Allevi, L. Garlaschelli, M.C. Malatesta, A. Albinati and F. Ganazzoli, J. Chem. Soc., Dalton Trans., (1984) 2637.

980 N.S. Kochetkova, M.-G.A. Shvekhgeimer and L.V. Balabanova, Russ. Chem. Rev., 53 (1984) 1168; Usp. Khim., 53 (1984) 2009.

981 J. Almlöf, K. Fægri, B.E.R. Schilling and H.P. Lüthi, Chem. Phys. Lett., 106 (1984) 266.

982 G. Richer and C. Sandorfy, J. Mol. Struct. (THEOCHEM), 123 (1985) 317.

983 M.C. Böhm, J. Phys. B: 17 (1984) 3103.

984 M.C. Böhm, Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys., 39A (1984) 223.

985 Yu.A. Kaplin, L.S. Chernysheva, M.M. Chesnokova and M.M. Protasova, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 27 (1984) 943; Chem. Abstr., 101 (1984) 214993d.

986 V.F. Korzo, O.P. Gludkin, D.N. Gogiya, Z.I. Mgebrishvili and V.N. Korotkov, U.S.S.R. SU 1,071,610 (1984); Chem. Abstr., 101 (1984) 11471j.

987 V.I. Tel'noi and I.B. Rabinovich, J. Appl. Chem. USSR, 38 (1985) 124; Zh. Prikl. Khim. (Leningrad), 58 (1985) 134.

988 G.N. Bortnikov, Yu.A. Kaplin, L.S. Chernysheva, M.M. Chesnokovo and T.V. Tal'nikova, Ref. Zh., Khim., (1985); Abstr. No. 19G242; Chem. Abstr., 104 (1986) 81331z.

989 Y.Y.P. Tsao, U.S. US 4,513,098 (1985); Chem. Abstr., 103 (1985) 8826q.

990 D.C. Levendis and J.C.A. Boeyens, J. Crystallogr. Spectrosc. Res., 15 (1985) 1.

991 L. Chen, K. Pan, X. Chen and L. Zhang, Jiegou Huaxue, 3 (1984) 125; Chem. Abstr., 103 (1984) 62903a.

992 N.A. Bell, F. Glockling, A. McGregor, M.L. Schneider and H.M.M. Shearer, Acta Crystallogr., Sect. C, C40 (1984) 623.

993 A.K. Baev, A.A. Barkatin and L.M. Dyagileva, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, (5) (1984) 60; Chem. Abstr., 102 (1985) 132199f.

994 Yu.K. Grishin, V.A. Roznyatovskii, Yu.A. Ustynyuk, S.N. Titova, G.A. Domrachev and G.A. Razuvaev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1780; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 1928.

995 Z. Zhang, D. Wei, Y. Chen and X. Wang, Kexue Tongbao (Foreign Lang. Ed.) 29 (1984) 281; Chem. Abstr., 101 (1984) 91184f.

996 E.M. Gushchin, A.N. Lebedev and S.V. Somov, Zh. Tekh. Fiz., 54 (1984) 1366; Chem. Abstr., 101 (1984) 199839n.

997 A.B. Sutormin, V.L. Shirokii, N.A. Maier and Yu.A. Ol'dekop, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk (2) (1985) 74; Chem. Abstr., 103 (1985) 142152v.

998 V.L. Shirokii, A.B. Sutormin, N.A. Maier and Yu.A. Ol'dekop, J. Gen. Chem., USSR, 54 (1984) 1280; Zh. Obshch. Khim., 54 (1984) 1436.

999 J.M. Manriquez, Simp. Quim. Inorg. "Met. Transicion", 1st (1985) 101; Chem. Abstr., 105 (1986) 172675b.

1000 E.E. Bunel, L. Valle and J.M. Manriquez, Organometallics, 4 (1985) 1680.

1001 B.G. Conway and M.D. Rausch, Organometallics, 4 (1985) 688.

1002 U. Kölle, B. Fuss, F. Khouzami and J. Gersdorf, J. Organomet. Chem., 290 (1985) 77.

1003 P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk, A.L. Spek and A.J.M. Duisenberg, J. Organomet. Chem., 287 (1985) C13.

1004 L. Zhang, Y. Huang, X. Chen and J. He, Gaodeng Xuexiao Huaxue Xuebao, 6 (1985) 872; Chem. Abstr., 105 (1986) 191365s.

1005 L. Zhang, X. Chen, E. Li and J. He, Youji Huaxue (1984) 446; Chem. Abstr.,102 (1985) 132108a.

1006 N. Kuhn and M. Winter, J. Organomet. Chem., 276 (1984) C16.

1007 V.M. de Bellis, N. Kuhn and M. Winter, Inorg. Chim. Acta, 104 (1985) L11.

1008 E. Hernandez and P. Royo, J. Organomet. Chem., 291 (1985) 387.

1009 H. Schumann, J. Organomet. Chem., 290 (1985) C34.

1010 R. Taube, D. Steinborn and W. Höbold, J. Organomet. Chem., 284 (1985) 385.

1011 W. Kläui, K. Schmidt, A. Bockmann, P. Hoffmann, H.R. Schmidt and P. Stauffert, J. Organomet. Chem., 286 (1985) 407.

1012 F. Calderazzo and G. Pampaloni, J. Chem. Soc., Chem. Commun., (1984) 1249.

1013 J.D. Payne and N. El Murr, J. Chem,. Soc., Chem. Commun., (1984) 1137.

1014 M.-C. Chan, K.-M. Cheng, M.K. Li and T.-Y. Luh, J. Chem. Soc., Chem. Commun., (1985) 1610.

1015 R.G. Bulgakov, G.Ya. Maistrenko, V.N. Yakovlev, S.P. Kuleshov, G.A. Tolstikov and V.P. Kazakov, Dokl. Chem., 282 (1985) 173; Dokl. Akad. Nauk SSSR, 282 (1985) 1385 [Chem.].

1016 N. Kuhn, N. Heuser and M. Winter, J. Organomet. Chem., 267 (1984) 221.

1017 N. Kuhn and M. Winter, J. Organomet. Chem., 269 (1984) C47.

1018 D.W. Slocum, M. Moronski, R. Gooding and S. Duraj, J. Organomet. Chem., 260 (1984) C26.

1019 N. Kuhn, U. Schwenk, M. Winter and R. Mynott, J. Organomet. Chem., 260 (1984) C43.

1020 B. Deppisch, H. Schäfer, D. Binder and W. Leske, Z. Anorg. Allg. Chem., 519 (1984) 53.

1021 A.A. Pasynskii, A.D. Shaposhnikova, Yu.V. Skripkin V.R. Zalmanovich, I.L. Eremenko, A.S. Antsyshkina and V.K. Bel'skii, Sov. J. Coord. Chem., 11 (1985) 563; Koord. Khim., 11 (1985) 988.

1022 H. Schumann, Chem.-Ztg., 108 (1984) 289.

1023 D.B. Jacobson and B.S. Freiser, Organometallics, 4 (1985) 1048.

1024 M. Mlekuz, P. Bougeard, B.G. Sayer, R. Faggiani, C.J.L. Lock, M.J. McGlinchey and G. Jaouen, Organometallics, 4 (1985) 2046.

1025 P. Gusbeth and H. Vahrenkamp, Chem. Ber., 118 (1985) 1746.

1026 P. Gusbeth and H. Vahrenkamp, Chem. Ber., 118 (1985) 1770.

1027 R. Bartsch, J.F. Nixon and N. Sarjudeen, J. Organomet. Chem., 294 (1985) 267.

1028 K. Fischer, W. Deck, M. Schwarz and H. Vahrenkamp, Chem. Ber., 118 (1985) 4946.

1029 M.L.N. Marchino, E. Sappa, A.M.M. Lanfredi and A. Tiripicchio, J. Chem. Soc., Dalton Trans., (1984) 1541.

1030 M. Mlekuz, P. Bougeard, B.G. Sayer, S. Peng, M.J. McGlinchey, A. Marinetti, J.-Y. Saillard, J.Ben Naceur, B. Mentzen and G. Jaouen, Organometallics, 4 (1985) 1123.

1031 C. Weatherell, N.J. Taylor, A.J. Carty, E. Sappa and A. Tiripicchio, J. Organomet. Chem., 291 (1985) C9.

1032 S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 4 (1985) 1594.

1033 P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk, A.L. Spek and A.J.M. Duisenberg, Organometallics, 4 (1985) 680.

1034 H. Werner, B. Ulrich, U. Schubert, P. Hofmann and B. Zimmer-Gasser, J. Organomet. Chem., 297 (1985) 27.

1035 G.E. Herberich and H. Ohst, Chem. Ber., 118 (1988) 4303.

1036 W. Siebert, M. El-Din, M. El-Essawi, R. Full and J. Heck, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 458.

1037 T. Kuhlmann and W. Siebert, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1032.

1038 T. Kuhlmann and W. Siebert, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 167.

1039 N.A. Ogorodnikova and D.N. Kravtsov, Polyhedron, 4 (1985) 311.

1040 P. Bandyopadhyay and A. Chakravorty, Indian J. Chem., Sect. A, 24A (1985) 638.

1041 M. Onishi, K. Hiraki, Y. Ohama and A. Kurosaki, J. Organomet. Chem., 284 (1985) 403.

1042 P. Thometzek, K. Zenkert and H. Werner, Angew. Chem., Int. Ed. Engl., 24 (1985) 516; Angew. Chem., 97 (1985) 520.

1043 H. Wadepohl and W. Siebert, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 50.

1044 H. Wadepohl, H. Pritzkow and W. Siebert, Chem. Ber., 118 (1985) 729.

1045 A.L. Shobert, I.C. Hisatsune and P.S. Skell, Spectrochim. Acta, Part A, 40A (1984) 609.

1046 B.J. Henne and D.E. Bartak, Inorg. Chem., 23 (1984) 369.

1047 S.-T. Lin, R.N. Narske and K.J. Klabunde, Organometallics, 4 (1985) 571.

1048 G.E. Herberich, H.J. Becker, B. Hessner and L. Zelenka, J. Organomet. Chem., 280 (1985) 147.

1049 E.R. Mognaschi and A. Chierico, J. Phys. C, 18 (1985) 3815.

1050 O.V. Gritsenko, R.V. Vysotskaya, A.A. Bagatur'yants and V.B. Kazanskii, Sov. J. Coord. Chem., 10 (1984) 771; Koord. Khim., 10 (1984) 1397.

1051 M.P. Soriaga, E. Binamira-Soriaga, A.T.Hubbard, J.B.Benziger, and K.-W.P. Pang, Inorg. Chem., 24 (1985) 65.

1052 A.I. Yanovskii, Russ. Chem. Rev., 54 (1985) 515; Usp. Khim., 54 (1985) 881.

1053 H.A. Boyter, R.G. Swisher, E. Sinn and R.N. Grimes, Inorg. Chem., 24 (1985) 3810.

1054 K.A. Solntsev, L.A. Butman, I.Yu. Kuznetsov, N.T. Kuznetsov, B. Štibr, Z. Janoušek and K. Baše, Sov. J. Coord. Chem., 10 (1984) 627; Koord. Khim., 10 (1984) 1132.

1055 V. Petříček, K. Malý, A. Petřina, K. Baše and A. Línek, Z. Kristallogr., 166 (1984) 1; Chem. Abstr., 101 (1984) 31453h.

1056 A.A. Erdman, Z.P. Zubreichuk, V.L. Shirokii, N.A. Maier and Yu.A. Ol'dekop, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, (4) (1984) 86; Chem. Abstr., 101 (1984) 192180g.

1057 N.A. Maier, A.A. Erdman, Z.P. Zubreichuk, V.P. Prokopovich and Yu.A. Ol'dekop, J. Organomet. Chem., 292 (1985) 297.

1058 D.M. Vinitskii, V.L. Lagun, K.A. Solntsev, N.T. Kuznetsov, K.N. Marushkin, J. Janoušek, K. Base and B. Stibr, Russ. J. Inorg. Chem., 29 (1984) 984; Zh. Neorg. Khim., 29 (1984) 1714.

1059 B. Štíbr, Z. Janoušek, K. Baše, J. Plešek, K.A. Solntsev, L.A. Butman, I.I. Kuznetsov and N.T. Kuznetsov, Coll. Czech. Chem. Commun., 49 (1984) 1660.

1060 V.P. Prokopovich, A.A. Érdman, N.A. Maier and Yu.A. Ol'dekop, Dolk. Chem., 278 (1984) 360; Dokl. Akad. Nauk SSSR, 278 (1984) 1141 [Chem.].

1061 H.M. Colquhoun, T.J. Greenhough and M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans., (1985) 761.

1062 B. Štíbr, Z. Janoušek, K. Baše, S. Heřmánek, J. Plešek and I.A. Zakharova, Coll. Czech. Chem. Commun., 49 (1984) 1891.

1063 G.A. Kukina, M.A. Porai-Koshits, V.S. Sergienko, Yu.V. Zefirov and G.G. Sadikov, Sov. J. Coord. Chem., 11 (1985) 220; Koord. Khim., 11 (1985) 385.

1064 G.A. Kukina, V.S. Sergienko and M.A. Porai-Koshiots, Sov. J. Coord. Chem., 11 (1985) 234; Koord. Khim., 11 (1985) 400.

1065 N.I. Kirillova, A.I. Gusev, N.V. Alekseev, L.K. Knyazeva, Z.V. Belyakova, V.V. Strelets and S.V. Kukharenko, Dokl. Chem., 280 (1985) 56; Dokl. Akad. Nauk SSSR, 280 (1985) 1148 [Chem.].

1066 L.S. Hegedus, J. Organomet. Chem., 261 (1984) 283.

1067 L. Markó, J. Organomet. Chem., 261 (1984) 485.

1068 G.W. Parshall, W.A. Nugent, D.M.T. Chan and W. Tam, Pure Appl. Chem., 57 (1985) 1809.

1069 I.I. Moiseev, Ref. Zh., Khim., (1984) Abstr. No. 16B4121; Chem. Abstr., 101 (1984) 190616e.

1070 G.K. Kornienko, Ref. Zh., Khim., (1984) Abstr. No. 4B4078; Chem. Abstr., 101 (1984) 190642k.

1071 J.G. Smith, Synthesis, (1984) 629.

1072 C.-L. Liu, PhD Thesis, Iowa State University, 1983; Diss. Abstr. Int. B, 44 (1984) 3788.

1073 J. Hagen, Chem.-Ztg., 109 (1985) 63, 203.

1074 J.P. Collman, K.M. Kosydar, M. Bressan, W. Lamanna and T. Garrett, J. Am. Chem. Soc., 106 (1984) 2569.

1075 N.F. Noskova, G.Kh. Azerbaeva, A.R. Brodskii, N.I. Margulis, S.R. Savel'ev and G.N. Sharifkanova, Russ. J. Phys. Chem., 58 (1984) 1408; Zh. Fiz. Khim., 58 (1984) 2319.

1076 L.I. Gvinter, V.M. Ignatov, G.D. Kharach and L.Kh. Freidlin, U.S.S.R. SU 1,066,976 (1984); Chem. Abstr., 101 (1984) 6695f.

1077 A.Ya. Yuffa, N.N. Lebedeva and G.V. Lisichkin, Neftekhimiya, 25 (1985) 183; Chem Abstr., 103 (1985) 122934y.

1078 D. Mani and H. Vahrenkamp, J. Mol. Catal., 29 (1985) 305.

1079 K. Yoshinaga, T. Kito, H. Oka, S. Sakaki and K. Ohkubo, J. Catal., 87 (1984) 517.

1080 W. Guo, Y. Chen and Y. Ma, Huaxue Tongbao, (9) (1985) 16; Chem. Abstr., 104 (1986) 207811b.

1081 J. Zajic and V. Filip, Fette, Seifen, Anstrichm., 86 (1984) 313; Chem. Abstr., 101 (1984) 194106m.

1082 B. He, J. Sun, H. Li and Y. Wang, Huaxue Shiji, 6 (1984) 257; Chem. Abstr., 102 (1985) 131567n.

1083 J. Molova, P. Svoboda, J. Hetflejs and M. Sufcak, Czech. CS 227,105 (1985); Chem. Abstr., 103 (1985) 72445s.

1084 Y. Chen, X. Zhu and S. Yu, Huaxue Shiji, 7 (1985) 106; Chem. Abstr., 103 (1985) 12029z.

1085 J.L. Costa, A.F. Noels, A.J. Hubert and Ph. Teyssie, Tetrahedron Lett., 25 (1984) 649.

1086 D.H. Whitney and G.E. Wnek, Polym. Mater. Sci. Eng., 53 (1985) 659.

1087 E.A. Karakhanov, A.G. Dedov and A.S. Loktev, Russ. Chem. Rev., 54 (1985) 171; Usp. Khim., 54 (1985) 289.

1088 A.S. Berenblyum, Ref. Zh., Khim., (1984) Abstr. No. 7B4077; Chem. Abstr., 101 (1984) 54306b.

1089 A.S. Berenblyum, S.L. Mund and V.V. Karellskii, Kinet. Catal., 26 (1985) 545; Kinet. Katal., 26 (1985) 626.

1090 Y.T. Xian, P. Four, F. Guibé and G. Balavoine, Nouv. J. Chim., 8 (1984) 611.

1091 H.J. Schmidt, Ger. Offen. DE 3,226,865 (1984); Chem. Abstr., 100 (1984) 74767k.

1092 Y. Wang and F. Lu, Gaofenzi Tongxun, (1984) 181; Chem. Abstr., 102, (1985) 46359b.

1093 D.C. Neckars, Met.-Containing Polym. Syst., (1985) 385; Chem. Abstr., 103 (1985) 166794g.

1094 A. Modelli, F. Scagnolari, G. Innorta, A. Foffani and S. Torrini, J. Mol. Catal., 24 (1984) 361.

1095 E.Ya. Mirskaya, A.I. Él'natanova, L.S. Kovaleva, O.P. Parenago and V.M. Frolov, Dokl. Chem., 276 (1984) 224; Dokl. Akad. Nauk SSSR, 276 (1984) 1407 [Chem.].

1096 S.D. Nayak, V. Mahadevan and M. Srinivasan, J. Catal., 92 (1985) 327.

1097 O. Butufei, M. Mazare, I. Deaconescu, G. Rolea, C. Pascu and I.V. Nicolescu, J. Macromol. Sci., Chem., A22 (1985) 889.

1098 B. Elman and C. Moberg, J. Organomet. Chem., 294 (1985) 117.

1099 D.V. Sokol'skii, A.K. Zharmagambetova, S.G. Mukhamedzhanova, E.A. Bekturov, S.E. Kudaibergenov and S.S. Saltybaeva, Dokl. Phys. Chem., 283 (1985) 728; Dokl. Akad. Nauk SSSR, 283 (1985) 678 [Phys. Chem.].

1100 E.A. Bekturov, S.E. Kudaibergenov, S.S. Saltybaeva, D.V. Sokolskii, A.K. Zharmagambetova and N.V. Anisimova, React. Polym., Ion Exch., Sorbents, 4 (1985) 49; Chem Abstr., 104 (1986) 110900s.

1101 A.A. Belyi, L.G. Chigladze, A.L. Rusanov, G.T. Gurgenidze and M.E. Vol'pin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 32 (1983) 2400; Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 2678.

1102 V.Z. Sharf, M.A. Nesterov, L.P. Finn and I.B. Slinyakova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2178; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2384.

1103 G.M. Cherkashin, L.P. Shuikina, O.P. Parenago and V.M. Frolov, Kinet. Catal., 26 (1985) 958; Kinet. Katal., 26 (1985) 1110.

1104 O.P. Parenago, G.M. Cherkashin and L.P. Shuikina, Neftekhimiya, 25 (1985) 589; Chem. Abstr., 105 (1986) 133300f.

1105 N.A. Maly, Eur Pat. Appl., EP 109,915 (1984); Chem. Abstr., 101 (1984) 111604y.

1106 S. Koritala, JAOCS, J. Am. Oil. Chem. Soc., 62 (1985) 517.

1107 L. Vigh, F. Joó, M. Droppa, L.I. Horváth and G. Horváth, Eur. J. Biochem., 147 (1985) 477.

1108 J.A. Heldal and E.A. Frankel, JAOCS, J. Am. Oil Chem. Soc., 61 (1984) 756.

1109 R.Sh. Abubakirov, G.A. Sytov, V.N. Perchenko, T.O. Omaraliev and N.S. Nametkin, Dokl. Chem., 272 (1983) 279; Dokl. Akad. Nauk SSSR, 272 (1983) 113 [Chem.].

1110 V.N. Perchenko, G.A. Sitov, R.Sh. Abubakirov, T.O. Omaraliev and N.S. Nametkin, Dokl. Chem., 282 (1985) 141; Dokl. Akad. Nauk SSSR, 282 (1985) 109 [Chem.]

1111 G.M. Cherkashin, L.P. Shuikina, L.S. Kovaleva, O.P. Parenago and V.M. Frolov, Neftekhimiya, 24 (1984) 188; Chem. Abstr., 101 (1984) 72336r.

1112 N. Suzuki, Y. Kaneko, T. Tsukanaka, T. Nomoto, Y. Ayaguchi and Y. Izawa, Tetrahedron, 41 (1985) 2387.

1113 A.I. Min'kov, O.A. Efimov, O.V. Kapshutar and N.K. Eremenko, Kinet. Catal., 25 (1984) 926; Kinet. Katal., 25 (1984) 1090.

1114 L.V. Mironova, L.B. Belykh, I.V. Usova and F.K. Schmidt, Kinet. Catal., 26 (1985) 413; Kinet. Katal., 26 (1985) 469.

1115 V.M. Frolov, O.P. Parenago, L.S. Kovaleva, A.V. Novikova, A.I. El'natanova, E.Ya. Mirskaya and E.G. Kliger, U.S.S.R. SU 1,066,975 (1984); Chem. Abstr., 100 (1984) 191349m.

1116 V.M. Frolov, O.P. Parenago, L.S. Kovaleva, E.Ya. Mirskaya, A.I. El'natanova, Neftekhimaya, 24 (1984) 783; Chem. Abstr., 102 (1984) 166283u.

1117 E.Ya. Mirskaya, A.I. El'Natanova, L.S. Kovaleva, O.P. Parenago and V.M. Frolov, Deposited Doc., (1983) VINITI 5349-83; Chem. Abstr., 102 (1985) 112651u

1118 E.Ya. Mirskaya, Deposited Doc., (1984) VINITI 3201-84, 3; Chem. Abstr., 103 (1985) 141221e.

1119 V.M. Frolov, R.A. Karakhanov, O.P. Parenago, M.M. Vartanyan, E.Ya. Mirskaya, T.Yu. Solov'eva, A.I. Elnatanova and L.S. Kovaleva, React. Kinet. Catal. Lett., 27 (1985) 375.

1120 R.H. Lane, K.P. Callahan, R. Cooksey, P.M. DiGiacomo, M.B. Dines and P.C. Griffith, Prepr. - Am. Chem. Soc., Div. Pet. Chem., 27 (1984) 624; Chem. Abstr., 101 (1984) 130760n.

1121 K. Kaneda, H. Yamamoto, T. Imanaka and S. Teranishi, J. Mol. Catal., 29 (1985) 99.

1122 D. Wang, Y. Zhou and Y. Jiang, Gaofenzi Tongxun (1984) 89; Chem. Abstr., 101 (1984) 111629k.

1123 Y. Zhou, L. Zhao and J. Jiang, Huaxue Shiji, 7 (1985) 187; Chem. Abstr., 105 (1986) 5965r.

1124 R.A. Jones and M.H. Seeberger, J. Chem. Soc., Chem. Commun., (1985) 373.

1125 L.I. Gvinter, V.M. Ignatov, V.Yu. Egorova, V.K. Krylov, P.S. Belov and L.Kh. Freidlin, Neftekhimiya, 24 (1984) 790; Chem. Abstr., 102 (1985) 166284v.

1126 C.U. Pittman, W. Honnick, M. Absi-Halabi, M.G. Richmond, R. Bender and P. Braunstein, J. Mol. Catal., 32 (1985) 177.

1127 J.M.J. Fréchet and N.H. Li, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 26(2) (1985) 251; Chem. Abstr., 104 (1986) 185622m

1128 N.-H. Li and J.M.J. Fréchet, J. Chem. Soc., Chem. Commun., (1985) 1100.

1129 P. Khandual, P.K. Santra and C.R. Saha, Proc. Indian Natl. Sci. Acad., Part A, 51 (1985) 538; Chem. Abstr., 104 (1986) 224414s.

1130 L.M. Ryzhenko and A.D. Shebaldova, Khim. Tekhnol Elementoorg. Soedin. Polim., (1984) 14; Chem. Abstr., 102 (1985) 77977f.

1131 Y. Li and Y. Jiang, Gaofenzi Tongxun (1984) 53; Chem. Abstr., 100 (1984) 191469a.

1132 G.P. Roger, W.S. Chow and K.S. Hatton, J. Mol. Catal., 31 (1985) 1.

1133 M.V. Klyuev, T.B. Pogodina and Yu.G. Erykalov, Russ. J. Phys. Chem., 59 (1985) 1223; Zh. Fiz. Khim., 59 (1985) 2063.

1134 A.D. Pomogailo and M.V. Klyuev, Deposited Doc., (1984) VINITI 414-84; Chem. Abstr., 102 (1985) 84983h.

1135 S. Bhattacharya, P.K. Santra and C.R. Saha, Indian J. Chem., Sect. A, 23A (1984) 724.

1136 X-Y. Guo, H.-J. Zong, Y.-J. Li and Y.-Y. Jiang, Makromol. Chem., Rapid Commun., 5 (1984) 507.

1137 E. Baralt and N. Holy, J. Org. Chem., 49 (1984) 2626.

1138 M.V. Klyuev, J. Org. Chem. USSR, 20 (1984) 1741; Zh. Org. Khim., 20 (1984) 1908.

1139 E.I. Klabunovskii, E.I. Karpeiskaya, L.S. Levitina, L.F. Godunova and L.N. Kaigorodova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1996; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2157.

1140 K.A. Saptova, G.M. Cherkashin, L.P. Shuikina, O.P. Parenago, Sh.S. Sarymsakov, E.G. Rozantsev and V.M. Frolov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1064; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1159.

1141 J.Y. Corey, E.R. Corey, V.H.T. Chang, M.A. Hauser, M.A. Leiber, T.E. Reinsel and M.E. Riva, Organometallics, 3 (1984) 1051.

1142 M. Gorsane and R.H. Martin, Bull. Soc. Chim. Belg., 94 (1985) 205.

1143 A.S. Gurovets, V.Z. Shaff and L.I. Belen'kii, Khim. Geterotsikl. Soedin., (1985) 1229; Chem. Abstr., 105 (1987) 24156t.

1144 S. Yasui, K. Nakamura, N. Fujii and A. Ohno, J. Org. Chem., 50 (1985) 3283.

1145 A. Zoran, Y. Sasson and J. Blum, J. Mol. Catal., 27 (1984) 349.

1146 Y. Watanabe, Y. Maki, K. Kikuchi and H. Sugiyama, Chem. Ind. (London) (1984) 272.

1147 S. Torii, H. Tanaka, T. Katoh and K. Morisaki, Tetrahedron Lett., 25 (1984) 3207.

1148 J. Huang, B. Li and X. Lu, Kexue Tongbao (Foreign Lang. Ed.) 29 (1984) 1038; Chem. Abstr., 102 (1985) 112790p.

1149 J.K. Sutherland and G.B. Tometzki, Tetrahedron Lett., 25 (1984) 881.

1150 M. Mohri, H. Kinoshita, K. Inomata and H. Kotake, Chem. Lett., (1985) 451.

1151 Y. Colas, B. Cazes and J. Gore, Tetrahedron Lett., 25 (1984) 845.

1152 F. Guibé, Y.T. Xian, A.M. Zigna and G. Balavoine, Tetrahedron Lett., 26 (1985) 3559.

1153 J. Tsuji, I. Shimizu and I. Minami, Chem. Lett., (1984) 1017.

1154 S. Cacchi, E. Morera and G. Ortar, Tetrahedron Lett., 25 (1984) 4821.

1155 M. Tanaka and T. Kobayashi, Synthesis (1985) 967.

1156 L.I. Kopylova, N.D. Ivanova and M.G. Voronkov, J. Gen. Chem. USSR, 55 (1985) 1467; Zh. Obshch. Khim., 55 (1985) 1649.

1157 G.K. Anderson and A.K. Phipps, J. Organomet. Chem., 266 (1984) C15.

1158 V.P. Tret'yakov and E.S. Rudakov, Ref. Zh., Khim., (1984) Abstr. No. 7B4454; Chem. Abstr., 101 (1984) 54305a.

1159 A.I. Mustafin, Ref. Zh., Khim., (1984) Abstr. No. 5V125; Chem. Abstr., 101 (1984) 61062x.

1160 M. Kanska, J. Radioanal. Nucl. Chem., 87 (1984) 95; Chem. Abstr., 101 (1984) 230976f.

1161 M. Kańska, J. Radioanal. Nucl. Chem., 85 (1984) 233.

1162 J. Tsuji, Synthesis (1984) 369.

1163 A.N. Startsev, V.R. Gurevich, L.B. Abdullaeva and Z.A. Sadykhova, Ref. Zh., Khim., (1984) Abstr. No. 22B4169; Chem. Abstr., 102 (1985) 78162y.

1164 V.G. Dryuk, Russ. Chem. Rev., 54 (1985) 986; Usp. Khim., 54 (1985) 1674.

1165 Y. Nishimura, M. Yamada, Y. Arikawa, T. Kamiguchi, T. Kuwahara and H. Tanimoto, Eur. Pat. Appl., EP 128,745 (1984); Chem. Abstr., 102 (1985) 95250t.

1166 G. Lu, G. Huang, Y. Guo, R. Wang, Q. Bai, C. Li and H. Qi, Shiyou Huagong, 14 (1985) 262; Chem. Abstr., 104 (1986) 170513c.

1167 G. Lu, T. Guo, R. Wang, G. Huang, R. Zhu, Q. Bai and H. Qi, Huadong Huagong Xueyuan Xuebao, 11 (1985) 261; Chem. Abstr., 103 (1985) 197657u.

1168 S.A. Lange, Kh.E. Khcheyan and R.V. Saifetdinova, Ref. Zh., Khim., (1985) Abstr. No. 10B4171; Chem. Abstr., 103 (1985) 110616h.

1169 T.K. Shioyama, U.S. US 4,507,506 (1985); Chem. Abstr., 102 (1985) 203610w.

1170 H. Alper, K.R. Januszkiewicz and D.J.H. Smith, Eur. Pat. Appl. EP 106,590 (1984); Chem. Abstr., 101 (1984) 38136r.

1171 T.P. Murtha, T.K. Shioyama, U.S. US 4,434,082 (1984); Chem. Abstr., 100 (1984) 174277u.

1172 S.G. Kukes and T.K. Shioyama, U.S. US 4,448,892 (1984); Chem. Abstr., 101 (1984) 38137s.

1173 Showa Denko K.K., Showa Acetyl Chemical Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60 81,138 [85 81,138] (1985); Chem. Abstr., 103 (1985) 123002e.

1174 Toa Nenryo Kogyo K.K., Jpn. Kokai Tokkyo Koho JP 59 93,023 [84 93,023] (1984); Chem. Abstr., 101 (1984) 191146p.

1175 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,128,345 [84,128,345] (1984); Chem. Abstr., 101 (1984) 191145n.

1176 M. Nakai and T. Enomiya, Eur. Pat. Appl., EP 101,223 (1984); Chem. Abstr., 101 (1984) 54715j.

1177 T.K. Shioyama and J.J. Straw, U.S. US 4,419,525 (1983); Chem. Abstr., 100 (1984) 138600k.

1178 J. Tsuji, H. Nagashima and H. Nemoto, Org. Synth., 62 (1984) 9.

1179 T. Hirao, K. Hayashi, Y. Fujihara, Y. Ohshiro and T. Agawa, J. Org. Chem., 50 (1985) 279.

1180 H. Alper, K. Januszkiewicz and D.J.H. Smith, Tetrahedron Lett., 26 (1985) 2263.

1181 H.H. Horowitz, J. Appl. Electrochem., 14 (1984) 779.

1182 H. Ogawa, H. Fujinami, K. Taya and S. Teratani, Bull. Chem. Soc. Jpn., 57 (1984) 1908.

1183 S.F. Davison, B.E. Mann and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1984) 1223.

1184 Y. Izumi, Y. Fujii and K. Urabe, J. Catal., 85 (1984) 284.

1185 Ube Industries Ltd., Jpn. Kokai Tokkyo Koho JP 60 64,941 [85 64,941] (1985); Chem. Abstr., 103 (1985) 104710t.

1186 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 60 81,139 [85 81,139]; Chem. Abstr., 103 (1985) 87547a.

1187 K. Takehira, T. Hayakawa and H. Orita, Chem. Lett., (1985) 1835.

1188 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,144,345 [83,144,345] (1983); Chem. Abstr., 100 (1984) 67892u.

1189 M. Yamashita, K. Matsumiya, M. Tanabe and R. Suemitsu, Bull. Chem. Soc. Jpn., 58 (1985) 407.

1190 H. Alper, K. Januszkiewicz and D.J.H. Smith, Tetrahedron Lett., 26 (1985) 2263.

1191 A.J. Pearson and T. Ray, Tetrahedron Lett., 26 (1985) 2981.

1192 T. Takahashi, H. Ueno, M. Miyazawa and J. Tsuji, Tetrahedron Lett., 26 (1985) 4463.

1193 J. Tsuji, I. Shimizu and Y. Kobayashi, Isr. J. Chem., 24 (1984) 153.

1194 K. Mori and Y.-B. Seu, Tetrahedron, 41 (1985) 3429.

1195 G. Balme, Tetrahedron Lett., 26 (1985) 2309.

1196 Nippon Kayaku Co. Ltd., Jpn. Kokai Tokkyo Koho JP 58,167,564 [83,167,564] (1983); Chem. Abstr., 100 (1984) 85507b.

1197 I. Ahmad and C.M. Asraf, Arab Gulf J. Sci Res., 2 (1984) 417; Chem. Abstr., 102 (1985) 184557r.

1198 N. Gregor, K. Zaw and P.M. Henry, Organometallics, 3 (1984) 1251.

1199 K. Zaw, M. Lautens and P.M. Henry, Organometallics, 4 (1985) 1286.

1200 M.A. Andrews, C.W. Chen and K.P. Kelly, U.S. Pat. Appl., US 398,508 (1983); Chem. Abstr., 101 (1984) 7771q.

1201 M.A. Andrews, T.C.-T. Chang, C.-W.F. Cheng, L.V. Kapustay, K.P. Kelly and M.J. Zweifel, Organometallics, 3 (1984) 1479.

1202 M.A.Andrews T.C.-T. Chang, C.-W.F. Cheng and K.P. Kelly, Organometallics, 3 (1984) 1777.

1203 M.A. Andrews, T.C.-T. Chang, C.-W.F. Chang, T.J. Emge, K.P. Kelly and T.F. Koetzle, J. Am. Chem. Soc., 106 (1984) 5913.

1204 M.A. Andrews, T.C.-T. Chang and C.-W.F. Cheng, Organometallics, 4 (1985) 268.

1205 F. Chauvet, A. Heumann and B. Waegell, Tetrahedron Lett., 25 (1984) 4393.

1206 P.K. Wong, M.K. Dickson and L.L. Sterna, J. Chem. Soc., Chem. Commun., (1985) 1565.

1207 F. Mares, S.E. Diamond, F.J. Regina and J.P. Solar, J. Am. Chem. Soc., 107 (1985) 3545.
1208 G. Strukul and R.A. Michelin, J. Chem. Soc., Chem. Commun., (1984) 1538.
1209 G. Strukul and R.A. Michelin, J. Am. Chem. Soc., 107 (1985) 7563.
1210 A. Heumann and B. Akermark, Angew. Chem., Int. Ed. Engl., 23 (1984) 453; Angew. Chem., 96 (1984) 443.
1211 J.E. McMurry and P. Kočovský, Tetrahedron Lett., 26 (1985) 2171.
1212 M.A. Andrews, T.C.-T. Chang and C.-W.F. Cheng, Organometallics, 3 (1984) 1777.
1213 D. Dimitrov, V. Sirakova and R. Stefanova, Oxid. Commun., 7 (1984) 399; Chem. Abstr., 104 (1986) 88854f.
1214 E.A. Efanova and D.N. Gazizova, Khim. Tekhnol. Pererab Nefti Gaza, (1985) 7; Chem. Abstr., 108 (1988) 36976k.
1215 J. Muzart, A. Riahi and J.P. Pete, J. Organomet. Chem., 280 (1985) 269.
1216 A. Riahi, J. Cossy, J. Muzart and J.P. Pete, Tetrahedron Lett., 26 (1985) 839.
1217 S. Suzuki, T. Onishi, Y. Fujita and J. Otera, Synth. Commun., 15 (1985) 1123.
1218 A. Matsuura, Y. Ito and T. Matsuura, J. Org. Chem., 50 (1985) 5002.
1219 G. Cum, R. Gallo, S. Ipsale and A. Spadaro, J. Chem. Soc., Chem. Commun., (1985) 1571.
1220 S.B. Fergusson and H. Alper, J. Chem. Soc., Chem. Commun., (1984) 1349.
1221 E.P. Talsi, V.P. Babenko, V.A. Likholobov, V.M. Nekipelov and V.D. Chinakov, J. Chem. Soc., Chem. Commun., (1985) 1768.
1222 A.B. Goel, Inorg. Chim. Acta, 90 (1984) L15.
1223 T.N. Shakhtakhtinskii, A.M. Aliev, N.V. Bairamov, R.Yu. Agaeva and R.M. Babaev, Azerb. Khim. Zh., (6) (1983) 25; Chem. Abstr., 102 (1985) 61891n.
1224 S. Ivanov and S. Tanielyan, Oxid. Commun., 7 (1984) 69; Chem. Abstr., 103 (1985) 70754t.
1225 I.V. Kozhevnikov, V.I. Kim, E.P. Talzi and V.N. Sidelnikov, J. Chem. Soc., Chem. Commun., (1985) 1392.
1226 I.V. Kozhevnikov, V.I. Kim and E.P. Talzi, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2001; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2167.
1227 S.A. Deiko, A.D. Ryabov and A.K. Yatsimirskii, Kinet. Katal., 25 (1984) 335.
1228 Ube Industries Ltd., Jpn. Kokai Tokkyo Koho JP 60 51,151 [85 51,151] (1985); Chem. Abstr., 103 (1985) 71063d.
1229 S. Yamaguchi, M. Inoue and S. Enomoto, Chem. Lett., (1985) 827.
1230 A.B.Goel, U.S. US 4,490,550 (1984); Chem. Abstr., 102 (1985) 95529r.
1231 Yu.V. Geletii and A.E. Shilov, Ref. Zh., Khim., (1984) Abstr. No. 11B4210; Chem. Abstr., 101 (1984) 210255s.
1232 C. Iditoiu, M. Bura and C. Alexandrescu, Rev. Chim., (Bucharest); 35 (1984) 109; Chem. Abstr., 101 (1984) 56826.
1233 H. Inoue, Jpn. Kokai Tokkyo Koho JP 59,163,339 [84,163,339]; Chem. Abstr., 102 (1985) 95260w.
1234 H. Nagashima, K. Sato and J. Tsuji, Tetrahedron, 41 (1985) 5645.
1235 B.M. Choudary, N.P. Reddy, M.L. Kantam and Z. Jamil, Tetrahedron Lett., 26 (1985) 6257.
1236 Nissan Motor Co., Ltd., Jpn Kokai Tokkyo Koho JP 58,177,153 [83,177,153] (1983); Chem. Abstr., 100 (1984) 26534k.
1237 H. Yamamoto, S. Shinoda and Y. Saito, J. Mol. Catal., 30 (1985) 259.
1238 L. Van Hijfte and R.D. Little, J. Org. Chem., 50 (1985) 3940.
1239 A.E. Greene, M.-J. Luche and A.A. Serra, J. Org. Chem., 50 (1985) 3957.
1240 R.L. Funk, G.L. Bolton, J.U. Daggett, M.M. Hansen and L.H.M. Horcher, Tetrahedron, 41 (1985) 3479.
1241 E.G. Zhizhina, K.I. Matveev and L.I. Kuznetsova, Kinet. Catal., 26 (1985) 404.

1242 E.G. Zhizhina, K.I. Matveev and L.I. Kuznetsova, Kinet. Katal., 26 (1985) 461.
1243 L.I. Kuznetsova and K.I. Matveev, Kinet. Katal., 25 (1984) 1274.
1244 L.I. Kuznetsova, K.I. Matveev and E.G. Zhizhina, Kinet. Catal., 26 (1985) 887; Kinet. Katal., 26 (1985) 1029.
1245 E.G. Zhizhina, L.I. Kuznetsova and K.I. Matveev, Kinet. Catal., 25 (1984) 930; Kinet. Katal., 25 (1984) 1095.
1246 E.G. Zhizhina, L.I. Kuznetsova and K.I. Matveev, Kinet. Catal., 26 (1985) 1161; Kinet. Katal., 26 (1985) 1349.
1247 M.T. Abilov and V.A. Golodov, Kinet. Catal., 26 (1985) 1276; Kinet. Katal., 26 (1985) 1481.
1248 V.M. Belousov and T.A. Pal'chevskaya, Ukr. Khim. Zh. (Russ. Ed.), 51 (1985) 712; Chem. Abstr., 103 (1985) 166856d.
1249 B.V. Romanovskii and T.G. Borisova, Oxid. Commun., 6 (1984) 157.
1250 P. Giannoccaro, E. Pannacciulli and G. Vasapollo, Inorg. Chim. Acta, 83 (1984) 99.
1251 L.N. Zhir-Lebed' and O.N. Temkin, Kinet. Catal., 25 (1984) 255,263; Kinet. Katal., 25 (1984) 316,325.
1252 A.L. Lapidus and N.M. Savel'ev, Russ. Chem. Rev., 53 (1984) 535; Usp. Khim., 53 (1984) 925.
1253 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,172,33 [83,172,333] (1983); Chem. Abstr., 100 (1984) 23759b.
1254 Nippon Mining Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 88,436 [84 88,436] (1984); Chem. Abstr., 101 (1984) 229986c.
1255 J.J. Lin, U.S. US 4,434,248 (1984); Chem. Abstr., 100 (1984) 194008k.
1256 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58 62,123 [83 62,123] (1983); Chem. Abstr., 100 (1984) 36132s.
1257 J.G. Goodwin, S.C. Chuang, Energy Res. Abstr., 11 (1986) Abstr. No. 260. Chem. Abstr., 107 (1988) 6728p.
1258 P. Escaffre, A. Thorez and P. Kalck, J. Mol. Catal., 33 (1985) 87.
1259 P. Giannoccaro, E. Pannacciulli and G. Vasapollo, Inorg. Chim. Acta, 96 (1985) 179.
1260 M.L. Kullberg and C.P. Kubiak, C_1 Mol. Chem., 1 (1984) 109.
1261 C.Y. Hsu and P.E. Ellis, Eur. Pat. Appl. EP 125,055 (1984); Chem. Abstr., 102 (1985) 78367u.
1262 C.Y. Hsu, U.S. US 4,528,278 (1985); Chem. Abstr., 103 (1985) 106619u.
1263 M. Kobayashi, Chem. Lett., (1984) 1215.
1264 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,185,534 [83,185,534] (1983); Chem. Abstr., 100 (1984) 102758d.
1265 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,203,640 [84,203,640] (1984); Chem. Abstr., 102 (1985) 101283z.
1266 C.Y. Hsu, J.E. Lyon and P.E. Ellis, U.S. US 4,524,142 (1985); Chem. Abstr., 103 (1985) 195821u.
1267 P. Haelg, G. Consiglio and P. Pino, J. Organomet. Chem., 296 (1985) 281.
1268 L.I. Flowers, PhD Thesis, Univ. Alabama (1983), Diss. Abstr. Int. B, 44 (1984) 2426.
1269 J.K. Stille, Chem. Ind. (Dekker), 22 (1985) 23; Chem. Abstr., 104 (1986) 129560c.
1270 J.K. Stille, J. Macromol. Sci., Chem., A21 (1984) 1689.
1271 G. Consiglio, F. Morandini, M. Scalone and P. Pino, J. Organomet. Chem., 279 (1985) 193.
1272 N. Rizkalla, Ger. Offen. DE 3,335,639 (1984); Chem. Abstr., 101 (1984) 25380r.
1273 A.D. Karpyuk, A.V. Protchenko, É.S. Petrov and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1971; Izv. Akad. Nauk SSSR, Ser. Khim., 33 (1984) 2155.
1274 A.D. Karpyuk, É.S. Petrov and I.P. Beletskaya, Dokl. Phys. Chem., 285 (1985) 1119; Dokl. Akad. Nauk SSSR, 285 (1985) 389 [Phys. Chem.].

1275 A.D. Karpyuk, N.D. Kolosova, M.I. Terekhova, É.S. Petrov and I.P. Beletskaya, Dokl. Chem., 277 (1984) 266; Dokl. Akad. Nauk SSSR, 277 (1984) 1402 [Chem.].

1276 M.I. Terekhova, A.B. Sigalov, N.E. Petrova and É.S. Petrov, J. Gen. Chem. USSR, 55 (1985) 842; Zh. Obshch. Khim., 55 (1985) 944.

1277 Mitsubishi Petrochemical Company., Ltd., Jpn. Kokai Tokkyo Koho JP 59 10,545 [84 10,545] (1984); Chem. Abstr., 100 (1984) 209176q.

1278 A.L. Lapidus, S.D. Pirozhkov, M.A. Buiya, A.F. Lunin, L.P. Karapetyan and K.M. Saldadze, Bull. Acad. Sci. USSR, 34 (1985) 2612; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2816.

1279 S. Xu, Z. Nie, X. Deng, Z. Li, B. Xue, J. Ling, D. Guo, J. Zhou and Z. Kong, Cuihua Xuebao, 6 (1985) 252; Chem. Abstr., 105 (1986) 5910t.

1280 F.J. Waller, Catal. Convers. Synth. Gas Alcohols Chem., [Proc. Symp.] 1983 (Pub. 1984) 193; Chem. Abstr., 101 (1984) 40197e.

1281 H. Alper, B. Despeyroux, D.J.H. Smith and J.B. Woell, PCT Int. Appl. WO 84 01,376 (1984); Chem. Abstr., 101 (1984) 110369p.

1282 F.J. Waller, U.S. US 4,414,409 (1983); Chem. Abstr., 100 (1984) 34125t.

1283 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 59,216,849 [84,216,849] (1984); Chem. Abstr., 102 (1985) 184840c.

1284 A.D. Karpyuk, M.I. Terekhova, N.D. Kolosova, É.S. Petrov and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 221; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 233.

1285 A.D. Karpyuk, M.I. Terekhova, N.D. Kolosova, É.S. Petrov, V.A. Chernoplekova and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 583; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 639.

1286 S.B. Fergusson and H. Alper, J. Chem. Soc., Chem. Commun., (1984) 1349.

1287 R. Bardi, A.M. Piazzesi, A. del Pra, G. Cavinato and L. Toniolo, Inorg. Chim. Acta, 102 (1985) 99.

1288 J.D. Burrington and M.C. Cesa, Eur. Pat. Appl. EP (1985) 133,796; Chem. Abstr., 103 (1985) 105316f.

1289 G. Cavinato, L. Toniolo and C. Botteghi, J. Mol. Catal., 32 (1985) 211.

1290 T. Hayashi, M. Tanaka and I. Ogata, J. Mol. Catal., 26 (1984) 17.

1291 G. Delogu, G. Faedda and S. Gladiali, J. Organomet. Chem., 268 (1984) 167.

1292 C.C. Bodurow, PhD Thesis, Princeton Univ., 1984; Diss. Abstr. Int. B, 45 (1984) 1468.

1293 H. Alper and D. Leonard, J. Chem. Soc., Chem. Commun., (1985) 511.

1294 H. Alper and D. Leonard, Tetrahedron Lett., 26 (1985) 5639.

1295 Y. Tamaru, T. Kobayashi, S. Kawamura, H. Ochiai and Z. Yoshida, Tetrahedron Lett., 26 (1985) 4479.

1296 Y. Tamaru, H. Higashimura, K. Naka, M. Hojo and Z. Yoshida, Angew. Chem., Int. Ed. Engl., 24 (1985) 1045; Angew. Chem., 97 (1985) 1070.

1297 G.P. Chiusoli, M. Costa, P. Pergreffi, S. Reverberi and G. Salerno, Gazz. Chim. Ital., 115 (1985) 691.

1298 Z. Nie, S. Xu, Y. Chen and J. Ma, Cuihua Xuebao, 6 (1985) 149; Chem. Abstr., 103 (1985) 195779m.

1299 H. Alper, B. Despeyroux and J.B. Woell, Tetrahedron Lett., 24 (1983) 5691.

1300 H. Alper, F.W. Hartstock and B. Despeyroux, J. Chem. Soc., Chem. Commun., (1984) 905.

1301 J. Jenck, Fr. Demande FR 2,529,885 (1984); Chem. Abstr., 100 (1984) 209175p.

1302 C.B. Anderson and R. Markovic, Glas. Hem. Drus. Beograd, 49 (1984) 445; Chem. Abstr., 103 (1985) 87537x.

1303 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 59,139,343 [84,139,343] (1984); Chem. Abstr., 102 (1985) 5776s.

1304 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 60 64,946 [85 64,946] (1985); Chem. Abstr., 103 (1985) 104615r.

1305 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 60,104,036 [85,104,036] (1985); Chem. Abstr., 103 (1985) 141524f.

1306 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 60,104,039 [85,104,039] (1985); Chem. Abstr., 103 (1985) 160147b.

1307 M.F. Semmelhack, J.J. Bozell, L. Keller, T. Sato, E.J. Spiess, W. Wulff and A. Zask, Tetrahedron, 41 (1985) 5803.

1308 M.F. Semmelhack and C. Bodurow, J. Am. Chem. Soc., 106 (1984) 1496.

1309 Y. Tamaru, T. Kobayashi, S. Kawamura, H. Ochiai, M. Hojo and Z. Yoshida, Tetrahedron Lett., 26 (1985) 3207.

1310 C.B. Anderson and R. Marković, J. Serb. Chem. Soc., 50 (1985) 125; Chem. Abstr., 105 (1985) 152574q.

1311 J. Tsuji, K. Sato and H. Nagashima, Tetrahedron, 41 (1985) 5003.

1312 H. Hoberg and F.J. Fañanás, J. Organomet. Chem., 262 (1984) C24.

1313 F.J. Fañanás and H. Hoberg, J. Organomet. Chem., 277 (1984) 135.

1314 F.J. Fañanás and H. Hoberg, J. Organomet. Chem., 275 (1984) 249.

1315 I. Pri-Bar and O. Buchman, J. Org. Chem., 49 (1984) 4009.

1316 I. Pri-bar and O. Buchman, J. Org. Chem., 49 (1984) 4009.

1317 P.C. Fiedler and R. Braden, Ger. Offen. DE 3,242,582 (1984); Chem. Abstr., 101 (1984) 191338c.

1318 Nissan Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 59,29,664 [84 29,664] (1984); Chem. Abstr., 101 (1984) 110739j.

1319 Ube Industries, Ltd., Jpn. Kokai Tokkyo Koho JP 59 29,641 [84 29,641] (1984); Chem. Abstr., 101 (1984) 130409e.

1320 R.A. Head, Tetrahedron Lett., 25 (1984) 5939.

1321 R.A. Head and A. Ibbotson, Eur. Pat. Appl. EP 127,276 (1984); Chem. Abstr., 102 (1985) 113312w.

1322 A. Carpita and R. Rossi, Gazz. Chim. Ital., 115 (1985) 575.

1323 M.K. Alekseev, E.G. Freidlin, V.M. Zarytovskii, V.V. Kaverin and V.P. Yur'ev, J. Appl. Chem. USSR, 58 (1985) 281; Zh. Prikl. Khim. (Leningrad), 58 (1985) 325.

1324 Ube Industries Ltd., Jpn. Kokai Tokkyo Koho JP 60 19,750 [85 19,750] (1985); Chem. Abstr., 103 (1985) 5904c.

1325 M. Tanaka, T. Kobayashi, T. Sakakura, H. Itatani, S. Danno and K. Zushi, J. Mol. Catal., 32 (1985) 115.

1326 F. Ozawa, N. Kawasaki, T. Yamamoto and A. Yamamoto, Chem. Lett., (1985) 567.

1327 J.-T. Chen and A. Sen, J. Am. Chem. Soc., 106 (1984) 1506.

1328 A. Yamamoto, T. Yamamoto and F. Ozawa, Pure Appl. Chem., 57 (1985) 1799.

1329 M. Tanaka, T. Kobayashi and T. Sakakura, J. Chem. Soc., Chem. Commun., (1985) 837.

1330 K.E. Hashem, J.B. Woell and H. Alper, Tetrahedron Lett., 25 (1984) 4879.

1331 A. Yamamoto, F. Ozawa, H. Nakazawa and T. Yamamoto, New. Front. Organomet. Inorg. Chem., Proc. China-Jpn-U.S.A. Trilateral Semin., 2nd, 1982 (Pub. 1984) 217; Chem. Abstr., 102 (1984) 148331d.

1332 A. Yamamoto, T. Yamamoto and F. Ozawa, Pure Appl. Chem., 57 (1985) 1799.

1333 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,213,742 [83,213,742] (1983); Chem. Abstr., 100 (1984) 209417u.

1334 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,213,724 [83,213,724] (1983); Chem. Abstr., 100 (1984) 209418v.

1335 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,213,745 [83,213,745] (1983); Chem. Abstr., 100 (1984) 209188v.

1336 A. Yamamoto, Jpn. Kokai Tokkyo Koho JP 58,152,846 [83,152,846] (1983); Chem. Abstr., 100 (1984) 51461s.

1337 T. Kobayashi and M. Tanaka, Ger. Offen. DE 3,311,026 (1983); Chem. Abstr., 100 (1984) 68020v.

1338 F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto and A. Yamamoto, J. Am. Chem. Soc., 107 (1985) 3235.

1339 F. Ozawa, T. Sugimoto, Y. Yuasa, M. Santra, T. Yamamoto and A. Yamamoto, Organometallics, 3 (1984) 683.

1340 F. Ozawa, T. Sugimoto, T. Yamamoto and A. Yamamoto, Organometallics, 3 (1984) 692.
1341 M. Mori, M. Kimura, Y. Uozumi and Y. Ban, Tetrahedron Lett., 26 (1985) 5947.
1342 M. Mori, H. Kobayashi, M. Kimura and Y. Ban, Heterocycles, 23 (1985) 2803.
1343 M.F. Semmelhack, Y. Appapillai and T. Sato, J. Am. Chem. Soc., 107 (1985) 4577.
1344 N.A. Bumagin, Yu.V. Gulevich and I.P. Beletskaya, J. Organomet. Chem., 285 (1985) 415.
1345 Y. Tamaru, H. Ochiai and Z. Yoshida, Tetrahedron Lett., 25 (1984) 3861.
1346 Y. Wakita, T. Yasunaga and M. Kojima, J. Organomet. Chem., 288 (1985) 261.
1347 Y. Tamaru, H. Ochiai, Y. Yamada and Z. Yoshida, Tetrahedron Lett., 24 (1983) 3869.
1348 M. Uchiyama, T. Suzuki and Y.Yamazaki, Nippon Kagaku Kaishi (1984) 585; Chem. Abstr., 101 (1984) 72378f.
1349 Sagami Chemical Research Center, Jpn. Kokai Tokkyo Koho JP 60 94,933 [85 94,933] (1985); Chem. Abstr., 103 (1985) 141461h.
1350 Sagami Chemical Research Center, Jpn. Kokai Tokkyo Koho JP 58,154,529 [83,154,529] (1983); Chem. Abstr., 100 (1984) 85276a.
1351 J.B. Woell, S.B. Fergusson and H. Alper, J. Org. Chem., 50 (1985) 2134.
1352 R.T. Klun and T.W. Regulski, U.S. US 4,451,667 (1984); Chem. Abstr., 101 (1984) 91627c.
1353 H. Alper, S. Antebi and J.B. Woell, Angew. Chem., Int. Ed. Engl., 23 (1984) 732; Angew. Chem., 96 (1984) 710.
1354 T. Fuchikami and I. Ojima. Tetrahedron Lett., 25 (1984) 303.
1355 S. Uemura, K. Ohe, J.-R. Kim, K. Kudo and N. Sugita, J. Chem. Soc., Chem. Commun., (1985) 271.
1356 S. Cacchi, E. Morera and G. Ortar, Tetrahedron Lett., 26 (1985) 1109.
1357 M. Mori and Y. Ban, Heterocycles, 23 (1985) 317.
1358 M. Okita, M. Mori, T. Wakamatsu and Y. Ban, Heterocycles, 23 (1985) 247.
1359 M. Mori, K. Chiba, M. Okita, I. Kayo and Y. Ban, Tetrahedron, 41 (1985) 375.
1360 K. Chiba, M. Mori and Y. Ban, Tetrahedron, 41 (1985) 387.
1361 W.F. Goure, M.E. Wright, P.D. Davis, S.S. Labadie and J.K. Stille, J. Am. Chem. Soc., 106 (1984) 6417.
1362 G.T. Crisp, W.J. Scott and J.K. Stille, J. Am. Chem. Soc., 106 (1984) 7500.
1363 I. Ojima, T. Fuchikami and K. Hirai, New. Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd, 1982, Pub. 1984, 169; Chem. Abstr., 102 (1985) 203330e.
1364 J.M. Tour and E. Negishi, J. Am. Chem. Soc., 107 (1985) 8289.
1365 H. Des Abbayes, Is. J. Chem., 26 (1985) 249.
1366 S. Murahashi and Y. Imada, Chem. Lett., (1985) 1477.
1367 J.F. Fauvarque, A. Jutand, C. Chevrot, F. Pfluger and M. Troupel, Fr. Demande FR 2,530,266 (1984); Chem. Abstr., 101 (1984) 14051h.
1368 J.H. Merrifield, J.P. Godschalx and J.K. Stille, Organometallics, 3 (1984) 1108.
1369 F.K. Sheffy, J.P. Godschalx and J.K. Stille, J. Am. Chem. Soc., 106 (1984) 4833.
1370 E. Amari. M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 285 (1985) 383.
1371 G.R. Steinmetz, J. Mol. Catal., 26 (1984) 145.
1372 Z. Zhang, X. Wang, D. Wei, W. Zhao, S. Zhang and Y. Fang, Huaxue Xuebao, 43 (1985) 650; Chem. Abstr., 103 (1985) 170967h.
1373 N. Rizkalla, Ger. Offen. DE 3,335,595 (1984); Chem. Abstr., 100 (1984) 212088t.
1374 E. Drent, Eur. Pat. Appl. EP 124,160 (1984); Chem. Abstr., 102 (1985) 78376w.

1375 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 59,110,637 [84,110,637] (1984); Chem. Abstr., 101 (1984) 151406s.

1376 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,135,830 [83,135,830] (1983); Chem. Abstr., 100 (1984) 5840s.

1377 Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 58,135,828 [83,135,828] (1983); Chem. Abstr., 100 (1984) 5842u.

1378 R.A. Head and M.I. Tabb, J. Mol. Catal., 26 (1984) 149.

1379 G. Schroeder and E. Baumgartner, Ger. Offen. DE 3,342,291 (1985); Chem. Abstr., 103 (1985) 214874g.

1380 L.N. Zhir-Lebed and O.N. Temkin, Kinet. Katal., 25 (1984) 325.

1381 L.I. Kuznetsova and K.I. Matveev, Kinet. Catal., 25 (1984) 1089; Kinet. Katal., 25 (1984) 1274.

1382 F.J. Waller, J. Mol. Catal., 31 (1985) 123.

1383 E. Baumgartner, G. Schroeder and S. Besecke, Ger. Offen. DE 3,212,535 (1983); Chem. Abstr., 100 (1984) 51081t.

1384 Toa Nenryo Kogyo K.K., Jpn. Kokai Tokkyo Koho JP 60 94,943 [85 94,943] (1985); Chem. Abstr., 103 (1985) 160110j.

1385 Mitsubishi Petrochemical Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 98,037 [84 98,037] (1984); Chem. Abstr., 101 (1984) 151606g.

1386 J. Tsuji, K. Sato and H. Okumoto, J. Org. Chem., 49 (1984) 1341.

1387 E.P. Woo and D.J. Murray, U.S. US 4,450,285 (1984); Chem. Abstr., 101 (1984) 72292y.

1388 Kuraray Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 13,745 [84 13,745] (1984); Chem. Abstr., 100 (1984) 191378v.

1389 Kuraray Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,144,340 [83,144,340] (1983); Chem. Abstr., 100 (1984) 5856b.

1390 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 93,026 [84 93,026] (1984); Chem. Abstr., 103 (1985) 37099k.

1391 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,144,730 [84,144,730] (1984); Chem. Abstr., 102 (1985) 78383w.

1392 E. Drent, Eur. Pat. Appl. EP 111,949 (1984); Chem. Abstr., 101 (1984) 130248b.

1393 N. Rizkalla, Ger. Offen. DE 3,335,594 (1984); Chem. Abstr., 100 (1984) 194023m.

1394 N. Rizkalla, Ger. Offen. DE 3,335,694 (1984); Chem. Abstr., 100 (1984) 194024n.

1395 W. Vogt, E. Jaegers and H. Glaser, Ger. Offen. DE 3,232,066 (1984); Chem. Abstr., 101 (1984) 22992f.

1396 V.A. Mamyan, S.D. Sominskii, S.D. Pirozhkov, V.L. Barsegyan, V.D. Vardanyan and A.L. Lapidis, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2095; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2265.

1397 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 39,848 [84 39,848] (1984); Chem. Abstr., 101 (1984) 54580m.

1398 W. Vogt, H. Glaser and E. Jaegers, Ger. Offen. DE 3,300,256 (1984); Chem. Abstr., 101 (1984) 191161q.

1399 W. Vogt, H. Glaser and E. Jaegers, Ger. Offen. DE 3,231,154 (1984); Chem. Abstr., 100 (1984) 209185s.

1400 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 93,026 [84 93,026] (1984); Chem. Abstr., 101 (1984) 191164t.

1401 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,161,327 [84,161,327] (1984); Chem. Abstr., 102 (1985) 95264a.

1402 W. Vogt and E. Jaegers, Ger. Offen. DE 3,230,307 (1984); Chem. Abstr., 101 (1984) 6634k.

1403 K. Kudo, S. Mori and N. Sugita, Chem. Lett., (1985) 265.

1404 G.E. Morris, PCT Int. Appl. WO 84 02,340 (1984); Chem. Abstr., 101 (1984) 170719m.

1405 H. Alper and F.W. Hartstock, J. Chem. Soc., Chem. Commun., (1985) 1141.

1406 S. Fukuoka, M. Chono and M. Kohno, J. Chem. Soc., Chem. Commun., (1984) 399.

1407 H. Tietz and K. Schwetlick, Z. Chem., 25 (1985) 147.

1408 H. Tietz, K. Schwetlick and G. Kreisel, Z. Chem., 25 (1985) 290.

1409 H. Tietz and K. Schwetlick, Z. Chem., 25 (1985) 149.

1410 V.I. Manov-Yuvenskii, A.L. Lapidus and K.B. Petrovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1561; Izv. Akad. Nauk SSSR, Ser. Khim., 34 (1985) 1709.

1411 G.A. Abakumov, I.L. Knyazeva, N.N. Vavilina, L.V. Gorbunova and S.V. Zhivtsova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1242; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1352.

1412 S.P. Gupte and R.V. Chaudhari, J. Mol. Catal., 24 (1984) 197.

1413 S.B. Halligudi, R.V. Chaudhari and L.K. Doraiswamy, Ind. Eng. Chem. Process Des. Dev., 23 (1984) 794; Chem. Abstr., 101 (1984) 129913h.

1414 Indian Explosives Ltd., Chemicals and Fibres of India Ltd., Jpn. Kokai Tokkyo Koho JP 59,148,750 [84,148,750] (1984); Chem. Abstr., 102 (1985) 24305d.

1415 Y. Watanabe, Y. Tsuji, T. Ohsumi and R. Takeuchi, Bull. Chem. Soc. Jpn., 57 (1984) 2867.

1416 W.R. Pretzer and R.B. Pannell, U.S. US 4,411,820 (1983); Chem. Abstr., 100 (1984) 51282j.

1417 E. Alessio and G. Mestroni, J. Mol. Catal., 26 (1984) 337.

1418 Y. Watanabe, Y. Tsuji and R. Takeuchi, Bull. Chem. Soc. Jpn., 57 (1984) 3011.

1419 Y. Watanabe, Y. Tsuji, T. Kondo and R. Takeuchi, J. Org. Chem., 49 (1984) 4451.

1420 Y. Tsuji, R. Takeuchi and Y. Watanabe, J. Organomet. Chem., 290 (1985) 249.

1421 V.I. Manov-Yuvenskii, K.B. Petrovskii and A.L. Lapidus, Bull. Acad. Sci USSR, Div. Chem. Sci., 33 (1984) 543; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 593.

1422 V.I. Manov-Yuvenskii, K.B. Petrovskii and A.L. Lapidus, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2486; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2717.

1423 G. Vasapollo, C.F. Nobile, P. Giannoccaro and F. Allegretta, J. Organomet. Chem., 277 (1984) 417.

1424 H. Tietz, P. Neitzel, K. Schwetlick and R. Szargan, Z. Chem., 24 (1984) 186.

1425 W.C. Baird, R.L. Hartgerink and J.H. Surridge, J. Org. Chem., 50 (1985) 4601.

1426 R.C. Larock and L.W. Harrison, J. Am. Chem. Soc., 106 (1984) 4218.

1427 A. Chiesa and R. Ugo, J. Organomet. Chem., 279 (1985) 215.

1428 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2368; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2586.

1429 Ube Industries Ltd., Jpn. Kokai Tokkyo Koho JP 59 67,243 [84 67,243] (1984); Chem. Abstr., 101 (1984) 110373k.

1430 Mitsubishi Petrochemical Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60 38,343 [85 38,343] (1985); Chem. Abstr., 103 (1985) 53812t.

1431 S. Uchiumi and K. Ataka, Eur. Pat. Appl. EP 108,332 (1984); Chem. Abstr., 101 (1984) 90431x.

1432 Ube Industries Ltd., Jpn Kokai Tokkyo Koho JP 60,120,838 [85,120,838] (1985); Chem. Abstr., 103 (1985) 195833z.

1433 B.A. Trofimov, Yu.M. Skvortsov, A.G. Mal'kina and A.I. Gritsa, J. Org. Chem. USSR, 21 (1985) 1850; Zh. Org. Khim., 21 (1985) 2020.

1434 M. Tanaka, T. Kobayashi and T. Sakakura, Nippon Kagaku Kaishi, (1985) 537; Chem. Abstr., 104 (1986) 129561d.

1435 G.P. Chiusoli, M. Costa, M. Gerbello and G. Salerno, Gazz. Chim. Ital., 115 (1985) 697.

1436 H.J. Riegel and H. Hoberg, J. Organomet. Chem., 260 (1984) 121.

1437 K. Kikukawa, T. Totoki, F. Wada and T. Matsuda, J. Organomet. Chem., 270 (1984) 283.

1438 E. Drent, Eur. Pat. Appl. EP 121,965 (1984); Chem. Abstr., 102 (1984) 46423t.

1439 V.N. Zudin, G.N. Il'inich, V.A. Likholobov and Y.I. Yermakov, J. Chem. Soc., Chem. Commun., (1984) 545.

1440 A.B. Goel, H.J. Richards and J.H. Kyung, Tetrahedron Lett., 25 (1984) 391.

1441 I. Ojima, K. Hirai, M. Fujita and T. Fuchikami, J. Organomet. Chem., 279 (1985) 203.

1442 S. Inoue and H. Koinuma, Rev. Inorg. Chem., 6 (1984) 291.

1443 H. Sugimoto, I. Kawata, H. Tanmiguchi and Y. Fujiwara, J. Organomet. Chem., 266 (1984) C44.

1444 Teijin Ltd., Jpn. Kokai Tokkyo Koho JP 59,163,338 [84,163,338] (1984); Chem. Abstr., 102 (1985) 78572g.

1445 H. Sugimoto, I. Kawata, H. Taniguchi and Y. Fujiwara, J. Organomet. Chem., 266 (1984) C44.

1446 J.F. Fauvarque, C. Chevrot, A. Jutand, M. François and J. Perichon, J. Organomet. Chem., 264 (1984) 273.

1447 R.T. Klun, C.B. Murchison and D.A. Hucul, U.S. US 4,480,121 (1984); Chem. Abstr., 102 (1985) 46415s.

1448 W. Keim, A. Behr and K.D. Juszak, Ger. Offen. DE 3,317,013 (1984); Chem. Abstr., 102 (1985) 78723g.

1449 A. Behr, K.D. Juszak and R. He, Int. Congr. Catal., [Proc.], 8th, (1984) 5, V565-V572; Chem. Abstr., 106 (1987) 101530k.

1450 E. Dinjus and D. Walther, Ger. (East) DD 222,023 (1985); Chem. Abstr., 103 (1985) 195995d.

1451 A. Behr, Bull. Soc. Chim. Belg., 94 (1985) 671.

1452 T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa and S. Sakai, Chem. Lett., (1985) 199.

1453 P. Binger and H.J. Weintz, Ger. Offen. DE 3,403,793 (1985); Chem. Abstr., 103 (1985) 215149m.

1454 R. Müller, Z. Chem., 25 (1985) 309.

1455 V.O. Reikhsfel'd, N.K. Skvortsov and V.S. Brovko, Ref. Zh., Khim., (1984) Abstr. No. 22B4193; Chem. Abstr., 102 (1985) 132126e.

1456 M.G. Voronkov and V.B. Pukhnarevich, Ref. Zh., Khim., (1984) Abstr. No. 7B4114; Chem. Abstr., 101 (1984) 171324s.

1457 V.S. Brovko, N.K. Skvortsov, L.A. Payanen and V.O. Reikhsfel'd, Kremniiorg. Soedin. Mater. Ikh. Osn., Tr. Soveshch Khim. Prakt. Primen. Kremniiorg Soedin., 5th, 1981 (Pub 1984) 43; Chem. Abstr., 101 (1984) 230594e.

1458 M. Capka and J. Hetflejs, Czech. CS 206,394 (1983); Chem. Abstr., 101 (1984) 23711a.

1459 M. Capka, M. Rmoutil, I. Rosenberg and A. Holy, Czech CS 215,473 (1984); Chem. Abstr., 103 (1985) 71492t.

1460 G.V. Motsarev, V.R. Rozenberg, V.T. Inshakova, A.D. Raskina and A.A. Ushakov, Zh. Vses. Khim. O-va. im D.I. Mendeleeva, 30 (1985) 233; Chem. Abstr., 103 (1985) 178316r.

1461 X. Yi, Q. Xu, X. Zhang and C. Wang, Wuhan Daxue Xuebao, Ziran Kexueban (4) (1985) 108; Chem. Abstr., 105 (1986) 191209u.

1462 W.H. Pirkle and M.H. Hyun, J. Chromatogr., 322 (1985) 295.

1463 H. Shih-Hsien, S.D. Fazio, S.A. Tomellini, J.B. Crowther and R.A. Hartwick, Chromatographia, 20 (1985) 161.

1464 W.H. Pirkle, M.H. Hyun and B. Bank, J. Chromatogr., 316 (1984) 585.

1465 W.H. Pirkle, M.H. Hyun and B. Bank, J. Chromatogr., 316 (1984) 585.

1466 Y. Kawakami and Y. Yamashita, ACS Symp. Ser., 286 (1984) 245.

1467 V.J. Eddy and J.E. Hallgren, U.S. US 4,542,226 (1985); Chem. Abstr., 103 (1985) 196235t.

1468 R.A. Sultanov, G.A. Saryev, T.Sh. Gazarov and G.K. Bairamov, Dokl. Akad. Nauk Az. SSR, 41(8) (1985) 48; Chem. Abstr., 106 (1986) 102366y.

1469 V.O. Reikhsfel'd, Kremniiorg. Soedin. Mater. Ikh. Osn., Tr. Soveshch. Khim. Prakt. Primen. Kremniiorg. Soedin., 5th, 1981 (pub. 1984) 5 ; Chem. Abstr., 102 (1985) 46274v.
1470 N.K. Skvortsov, N.F. Voloshina, N.A. Moldavskaya and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 55 (1985); Zh. Obshch. Khim., 55 (1985) 2323.
1471 L.V. Krysenko, V.S. Brovko, N.K. Skvortsov, V.G. Shiballo and V.O. Reikhsfel'd, U.S.S.R. SU 1,128,978 (1984); Chem. Abstr., 102 (1985) 138490r.
1472 V.O. Reikhsfel'd, Kremniiorg. Soedin. Mater. Ikh. Osn., Tr. Soveshch. Khim. Prakt. Primen. Kremniiorg. Soedin., 5th, 1981 (pub. 1984) 5; Chem. Abstr., 102 (1985) 46274v.
1473 A.V. Nikitin and V.O. Reikhsfel'd, J. Gen. Chem. USSR, 55 (1985) 1846; Zh. Obshch. Khim., 55 (1985) 2079.
1474 V.O. Reikhefel'd and A.V. Nikitin, Deposited Doc. (1984) VINITI 4717-84; Chem. Abstr., 103 (1985) 59965s.
1475 B.C. Arkles, U.S. US 4,469,881 (1984); Chem. Abstr., 102 (1985) 6797m.
1476 E. Lukevics, V. Gevorgyan, Y. Goldberg, J. Popelis, M. Gavars, A. Gaukhman and M. Shimanska, Heterocycles, 22 (1984) 987.
1477 V.D. Sheludyakov, V.I. Zhun', S.D. Vlasenko, V.N. Bochkarev, T.F. Slyusarenko, G.N. Turkel'taub, A.V. Kisin and V.M. Nosova, J. Gen. Chem. USSR, 55 (1985) 1372; Zh. Obshch. Khim., 55 (1985) 1544.
1478 V.D. Sheludyakov, V.I. Zhun' and S.D. Vlasenko, J. Gen. Chem. USSR, 55 (1985) 1594; Zh. Obshch. Khim., 55 (1985) 1795.
1479 B. Mariniec, W. Maćkowska, J. Guliński and W. Urbaniak, Z. Anorg. Allg. Chem., 529 (1985) 222.
1480 I. Ojima, T. Fuchikami and M. Yatabe, J. Organomet. Chem., 260 (1984) 335.
1481 S.A. Matlin, W.J. Lough, L. Chan, D.M.H. Abram and Z. Zhou, J. Chem. Soc., Chem. Commun., (1984) 1038.
1482 N.S. Chu, B. Kanner and C.L. Schilling, U.S. US 4,481,364 (1984); Chem. Abstr., 102 (1985) 95816g.
1483 E.A. Chernyshev, Z.V. Belyakova, V.M. Shevchenko, L.A. Yagodina, A.V. Kisin, A.A. Bernadskii, V.D. Sheludyakov and V.N. Bochkarev, J. Gen. Chem. USSR, 54 (1984) 1812; Zh. Obshch. Khim., 54 (1984) 2031.
1484 V.V. Kireev. V.A. Kovyazin, V.M. Kopylov, M.G. Zaitseva and I.M. Kostylev, J. Gen. Chem. USSR, 54 (1984) 327; Zh. Obshch. Khim., 54 (1984) 367.
1485 M. Capka, I. Rosenberg, A. Holy and J. Hetflejs, Czech. CS 224,790 (1984); Chem. Abstr., 103 (1985) 196230n.
1486 L.N. Burova, N.N. Krylova, T.E. Buyakova, N.K. Skvortsov, N.S. Fedotov and V.O. Reikhsfel'd, Kremniiorg. Soedin Mater. Ikh Osn., Tr. Soveshch. Khim. Prakt. Primen. Kremniiorg. Soedin., 5th, 1981 (pub 1984) 55; Chem. Abstr., 102 (1985) 78946g.
1487 G.G. Cameron and M.S. Chisholm, Polymer, 26 (1985) 437.
1488 Z.V. Belyakova, A.A. Dmitriev, V.I. Savushkina, V.N. Bochkarev and E.A. Chernyshev, J. Gen. Chem. USSR, 55 (1985) 555; Zh. Obshch. Khim., 55 (1985) 627.
1489 P. Panster, R. Michel, W. Buder and P. Kleinschmidt, Ger. Offen. DE 3,404,703 (1985); Chem. Abstr., 103 (1985) 196232q.
1490 M.G. Voronkov. N.I. Ushakova, V.B. Pukhnarevich and M.I. Tsykhanskaya, Ref. Zh., Khim., (1984) Abstr. No. 1B4139; Chem. Abstr., 101 (1984) 23573q.
1491 A. Onopchenko, E.T. Sabourin and D.L. Beach, J. Org. Chem., 49 (1984) 3389.
1492 M.G. Voronkov, V.B. Pukhnarevich, N.I. Ushakova, I.I. Tsykhanskaya, A.I. Albanov and V.Yu. Vitkovskii, J. Gen. Chem. USSR, 55 (1985) 80; Zh. Obshch. Khim., 55 (1985) 94.
1493 M.G. Voronkov, N.I. Ushakova, I.I. Tsykanskaya and V.B. Pukhnarevich, J. Organomet. Chem., 264 (1984) 39.

1494 V.B. Pukharevich, I.I. Tsykhanskaya, N.I. Ushakova, M.I. Gel'fman and M.G. Voronkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2540; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2774.

1495 E. Lukevits, R.Ya. Sturkovich, O.A. Pudova, Ya.Yu. Polis and A.P. Gaukhman, J. Gen. Chem. USSR, 55 (1985) 553; Zh. Obshch. Khim., 55 (1985) 624.

1496 L.I. Kopyleva, N.D. Ivanova, V.N. Voropaev, E.S. Domnina, G.G. Skvortsova and M.G. Voronkov, J. Gen. Chem. USSR, 55 (1985) 923; Zh. Obshch. Khim., 55 (1985) 1036.

1497 E. Lukevics, R.Ya. Sturkovich and O.A. Pudova, J. Organomet. Chem., 292 (1985) 151.

1498 L.G. Kulieva, R.M. Mustafaev and S.I. Sadykh-Zade, Zh. Vses. Khim. O-va., 29 (1984) 231; Chem. Abstr., 101 (1984) 38531r.

1499 S.I. Sadykh-Zade, L.G. Kulieva, R.M. Mustafaev and S.M. Mamedov, Dokl. Akad. Nauk Az. SSR, 40 (1984) 41: Chem. Abstr., 102 (1985) 78956k.

1500 R.M. Mustafaev, L.G. Kulieva and S.I. Sadykh-Zade, Zh. Vses. Khim. O-va. im. D.I. Mendeleeva, 29 (1984) 456; Chem. Abstr., 102 (1984) 6624c.

1501 R.A. Sultanov, G.A. Sayev and M.Sh. Sultanova, Dokl. Akad. Nauk Az. SSR, 41 (6) (1985) 29; Chem. Abstr., 104 (1986) 129971n.

1502 R.A. Sultanov, T.Sh. Gazarov and Sh.A. Tarverdiev, Dokl. Akad. Nauk Az. SSR, 41 (7) (1985) 34; Chem. Abstr., 105 (1986) 191182e.

1503 R.M. Mustafaev, L.G. Kulieva and S.I. Sadykhzade, Azerb. Khim. Zh., (2) (1983) 58; Chem. Abstr., 101 (1984) 23570d.

1504 E. Lukevits, O.A. Pudova, R.Ya. Sturkovich and A.P. Gaukhman, J. Gen. Chem. USSR, 55 (1985) 1352; Zh. Obshch. Khim., 55 (1985) 1520.

1505 T. Kusumoto and T. Hiyama, Chem. Lett., (1985) 1405.

1506 T.Sh. Gazarov, G.A. Saryev, R.A. Sultanov and Sh.A. Tarverdiev, Zh. Vses. Khim. O-va., 29 (1984) 232; Chem. Abstr., 101 (1984) 38532s.

1507 G.A. Saryev, T.Sh. Gazarov, R.A. Sultanov and Z.M. Pashaev, Azerb. Khim. Zh., (5) (1985) 80; Chem. Abstr., 106 (1987) 102369b.

1508 D.N. Machavariani and L.M. Sepiashvili, Soobshch. Akad. Nauk Gruz. SSR, 117 (1985) 61; Chem. Abstr., 103 (1985) 142068x.

1509 E. Lukevics, V.N. Gevorgyan, Y.S. Goldberg and M.V. Shymanska, J. Organomet. Chem., 263 (1984) 283.

1510 F. Sato, H. Uchiyama and A.K. Samaddar, Chem. Ind. (London), (1984) 743.

1511 V.B. Pukhnarevich, I.I. Tsykhanskaya and M.G. Voronkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 390; Izv. Akad Nauk SSSR, Ser. Khim., (1984) 427.

1512 T. Hayashi and K. Kabeta, Tetrahedron Lett., 26 (1985) 3023.

1513 R. Zentel, J. Wu and H.-J. Cantow, Makromol. Chem., 186 (1985) 1763.

1514 Y. Chujo, K. Murai, Y. Yamashita and Y. Okumura, Makromol. Chem., 186 (1985) 1203.

1515 C. Aquilera and L. Bernal, Polym. Bull. (Berlin), 12 (1984) 383; Chem. Abstr., 102 (1985) 54271g..

1516 F.J. Modic, Ger. Offen. DE 3,423,742 (1985); Chem. Abstr., 102 (1985) 133722h.

1517 A.A. Zhdanov, V.M. Kotov, B.D. Lavrukhin and T.A. Pryakhina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1691; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1851.

1518 T. Matsushita and K. Shimizu, Eur. Pat. Appl. EP 98,985 (1984); Chem. Abstr., 100 (1984) 122940k.

1519 T.J. Drahnak, Eur. Pat. Appl. EP 122,008 (1984); Chem. Abstr., 102 (1985) 47489f.

1520 L.M. Khananashvili, V.M. Kopylov, M.I. Shkol'nik, K.M. Gogoberishvili, R.Sh. Tkeshelashvili and N.A. Konovalenko, Vysokomol. Soedin., Ser. B, 27 (1985) 752; Chem. Abstr., 104 (1986) 150506z.

1521 Shin-Etsu Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,143,844 [83,143,844] (1983); Chem. Abstr., 100 (1984) 57416c.

1522 T. Matsushita, Eur. Pat. Appl. EP 96,888 (1983); Chem. Abstr., 100 (1984) 69682z.

1523 Toray Silicone Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,226,036 [84,226,036] (1984); Chem. Abstr., 102 (1985) 151062x.
1524 R.P. Sweet, Eur. Pat. Appl. EP 91,737 (1983); Chem. Abstr., 100 (1984) 8210x.
1525 Toshiba Silicone Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,174,482 [83,174,482] (1983); Chem. Abstr., 100 (1984) 122896a.
1526 Toshiba Silicone Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,174,481 [83,174,481] (1983); Chem. Abstr., 100 (1984) 122897b.
1527 Toray Silicone Co., Ltd., Jpn Kokai Tokkyo Koho JP 58,194,762 [83,194,762] (1983); Chem. Abstr., 100 (1984) 125758t.
1528 Shin-Etsu Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 12,760 [84 12,760] (1984); Chem. Abstr., 101 (1984) 24479t.
1529 R.A. Faltynek, U.S. US 4,529,553 (1985); Chem. Abstr., 103 (1985) 161668j.
1530 J.A. Brossas and G. Friedmann, Ger. Offen. DE 3,342,766 (1984); Chem. Abstr., 101 (1984) 111978y.
1531 H. Brunner, B. Reiter and G. Riepl, Chem. Ber., 117 (1984) 1330.
1532 H. Brunner and R. Becker, Angew. Chem., Int. Ed. Engl., 24 (1983) 703; Angew. Chem., 97 (1985) 713.
1533 E. Keinan and N. Greenspoon, Tetrahedron Lett., 26 (1985) 1353.
1534 H. Oda, Y. Morizawa, K. Oshima and H. Nozaki, Tetrahedron Lett., 25 (1984) 3221.
1535 N.G. Bogatova, I.M. Salimgareeva and V.P. Yur'ev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1983) 856; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 930.
1536 I.M. Salimgareeva, N.G. Bogatova, A.A. Panasenko, Yu.B. Monakov and V.P. Yur'ev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1272; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 1391.
1537 T.K. Gar, O.N. Chernysheva, A.V. Kisin and V.F. Mironov, J. Gen. Chem. USSR, 55 (1985) 942; Zh. Obshch. Khim., 55 (1985) 1057.
1538 N. Chatani and T. Hanafusa, J. Chem. Soc., Chem. Commun., (1985) 838.
1539 Y. Yamasaki, T. Maekawa, T. Ishihara and T. Ando, Chem. Lett., (1985) 1387.
1540 D. Seyferth, E.W. Goldman and J. Escudié, J. Organomet. Chem., 271 (1984) 337.
1541 H. Sakurai, Y. Eriyama, Y. Kamiyama and Y. Nakadaira, J. Organomet. Chem., 264 (1984) 229.
1542 H. Urata, H. Suzuki, Y. Moro-oka and T. Ikawa, Bull. Chem. Soc. Jpn., 57 (1984) 607.
1543 A. Ricci, A. Degl'Innocenti, S. Chimichi, M. Fiorenza, G. Rossini and H.J. Bestman, J. Org. Chem., 50 (1985) 130.
1544 T.N. Mitchell, H. Killing, R. Dicke and R. Wickenkamp, J. Chem. Soc., Chem. Commun., (1985) 354.
1545 B.L. Chenard, E.D. Laganis, F. Davidson and T.V. RajanBabu, J. Org. Chem., 50 (1985) 3666.
1546 H. Killing and T.N. Mitchell, Organometallics, 3 (1984) 1318.
1547 N.A. Bumagin, Yu.V. Gulevich and I.P. Beletskaya, J. Organomet. Chem., 282 (1985) 421.
1548 Y. Okuda, K. Wakamatsu, W. Tückmantel, K. Oshima and H. Nozaki, Tetrahedron Lett., 26 (1985) 4629.
1549 S. Matsubara, J. Hibino, Y. Morizawa, K. Oshima and H. Nozaki, J. Organomet. Chem., 285 (1985) 163.
1550 J. Hibino, S. Matsubara, Y. Morizawa, K. Oshima and H. Nozaki, Tetrahedron Lett., 25 (1984) 2151.
1551 Y. Morizawa, H. Oda, K. Oshima and H. Nozaki, Tetrahedron Lett., 25 (1984) 1163.
1552 R.A. Benkeser and M.-H. Yeh, J. Organomet. Chem., 264 (1984) 239.
1553 H. Sakurai, M. Shoji, M. Yajima and A. Hosomi, Synthesis (1984) 598.
1554 N.N. Vlasova, A.E. Pestunovich and M.G. Voronkov, J. Gen. Chem. USSR, 55 (1985) 550; Zh. Obshch. Khim., 55 (9185) 621.

1555 T. Hayashi, K. Kabeta and M. Kumada, Tetrahedron Lett., 25 (1984) 1499.
1556 C.A. Tolman, W.C. Seidel, J.D. Druliner and P.J. Domaille, Organometallics, 3 (1984) 33.
1557 N.J. Fitzmaurice, W.R. Jackson and P. Perlmutter, J. Organomet. Chem., 285 (1985) 375.
1558 J.-E Bäckvall and O.S. Andell, J. Chem. Soc., Chem. Commun., (1984) 260.
1559 J.D. Druliner, Organometallics, 3 (1984) 205.
1560 Y. Sakakibara, S. Matsuzaka, S. Nagamine, M. Sakai and N. Uchino, Nippon Kagaku Kaishi (1985) 409; Chem. Abstr., 104 (1986) 108998m.
1561 A.R. Daniewski and T. Kowalczyk-Przewłoka, J. Org. Chem., 50 (1985) 2976.
1562 G.V. Pazynina, E.A. Luk'yanets and I.G. Bolesov, J. Org. Chem. USSR, 20 (1984) 730; Zh. Org. Khim., 20 (1984) 802.
1563 Yu.V. Tomilov, V.G. Bordakov, I.E. Dolgii and O.M. Nefedov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 533; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 582.
1564 M.P. Doyle, L.C. Wang and K.-L. Loh, Tetrahedron Lett., 25 (1984) 4087.
1565 M.P. Doyle, R.L. Dorow, W.E. Buhro, J.H. Griffin, W.H. Tamblyn and M.L. Trudell, Organometallics, 3 (1984) 44.
1566 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 275 (1984) 257.
1567 H. Kanai and H. Matsuda, J. Mol. Catal., 29 (1985) 157.
1568 Y. Inoue, Y. Ohtsuka and H. Hashimoto, Bull. Chem. Soc. Jpn., 57 (1984) 3345.
1569 L.Yu. Gubaidullin, E.I. Logunov, L.M. L'vovich and V.P. Yur'ev, J. Gen. Chem. USSR, 55 (1985) 1382; Zh. Obshch. Khim., 55 (1985) 1554.
1570 H. Stegemann, H. Fuellbier, W. Gaube and E. Alder, Ger. (East) DD 206,989 (1984); Chem. Abstr., 101 (1984) 170703c.
1571 T. Mukaiyama, M. Ohshima, H. Nagoaka and M. Murakami, Chem. Lett., (1984) 615.
1572 J.-E. Bäckvall, S.E. Byström and R.E. Nordberg, J. Org. Chem., 49 (1984) 4619.
1573 J.E. Bäckvall, J.-E. Nyström and R.E. Nordberg, J. Am. Chem. Soc., 107 (1985) 3676.
1574 L.S. Hegedus, B. Akermark, K. Zetterberg and L.F. Olsson, J. Am. Chem. Soc., 106 (1984) 7122.
1575 Mitsui Petrochemical Industries Ltd., Jpn. Kokai Tokkyo Koho JP 59,104,374 [84,104,374] (1984); Chem. Abstr., 101 (1984) 191676m.
1576 T. Hosokawa, C. Okuda and S. Murahashi, J. Org. Chem., 50 (1985) 1282.
1577 Y. Wakabayashi, Y. Fukuda, H. Shiragami, K. Utimoto and H. Nozaki, Tetrahedron, 41 (1985) 3655.
1578 C. Lambert, K. Utimoto and H. Nozaki, Tetrahedron Lett., 25 (1984) 5323.
1579 P.R. Weider, L.S. Hegedus, H. Asada and S.V. D'Andreq, J. Org. Chem., 50 (1985) 4276.
1580 L.S. Hegedus, M.S. Holden and J.M. McKearin, Org. Synth., 62 (1984) 48.
1581 B.F. Kukharev, V.K. Stankevich, V.P. Terent'eva and V.A. Kukhareva, J. Org. Chem. USSR, 20 (1984) 1222; Zh. Org. Khim., 20 (1984) 1344.
1582 K. Isomura, N. Okada, M. Saruwatari, H. Yamasaki and H. Taniguchi, Chem. Lett., (1985) 385.
1583 M. Mizutani, Y. Sanemitsu, Y. Tamaru and Z. Yoshida, Tetrahedron Lett., 26 (1985) 1237.
1584 A. Sen and T.-W. Lai, Inorg. Chem., 23 (1984) 3257.
1585 S.H. Dai, C.Y. Lin, D.V. Rao, F.A. Stuber, P.S. Carleton and H. Ulrich, J. Org. Chem., 50 (1985) 1722.
1586 Toray Industries Inc., Jpn. Kokai Tokkyo Koho JP 59 29,051 [84 29,051] (1984); Chem. Abstr., 102 (1985) 45526s.
1587 R.J. McKinney, Organometallics, 4 (1985) 1142.
1588 G.A. Dzhemileva, V.N. Odinokov and U.M. Dzhemilev, U.S.S.R. SU 1,097,586 (1984); Chem. Abstr., 101 (1984) 191211f.
1589 N.V. Borunova, P.G. Antonov, K.V. Kotegov, R.Kh. Karymova and L.Kh. Freidlin, J. Gen. Chem. USSR, 54 (1984) 1167; Zh. Obshch. Khim., 54 (1984) 1304.

1590 T. Bieg and W. Szeja, J. Carbohydr. Chem., 4 (1985) 441.
1591 M. Kloosterman, J.H. van Boom, P. Chatelard, P. Boullanger and G. Descotes, Tetrahedron Lett., 26 (1985) 5045.
1592 H. Kunz, H. Waldmann and C. Unverzagt, Int. J. Pept. Protein Res., 26 (1985) 493.
1593 C. Battistini, S. Vioglio, C. Scarafile and G. Franceschi, Heterocycles, 23 (1985) 1929.
1594 S.F. Martin and S.K. Davidsen, J. Am. Chem. Soc., 106 (1984) 6431.
1595 Y. Hayakawa, M. Uchiyama, H. Kato and R. Noyori, Tetrahedron Lett., 26 (1985) 6505.
1596 M. Kamber and G. Just, Can J. Chem., 63 (1985) 823.
1597 Y. Tamaru, Y. Yamada, H. Ochiai, E. Nakajo and Z. Yoshida, Tetrahedron, 40 (1984) 1791.
1598 N. Kurokawa and Y. Ohfune, Tetrahedron Lett., 26 (1985) 83.
1599 K. Inomata, Y. Murata, H. Kato, Y. Tsukahara, H. Kinoshita and H. Kotake, Chem. Lett., (1985) 931.
1600 K.S. Kyler, A. Bashir-Hashemi and D.S. Watt, J. Org. Chem., 49 (1984) 1084.
1601 K. Hiroi, R. Kitayama and S. Sato, J. Chem. Soc., Chem. Commun., (1984) 303.
1602 X. Lu and Y. Huang, Huaxue Xuebao, 42 (1984) 835; Chem. Abstr., 101 (1984) 191243t.
1603 Kuraray Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,106,434 [84,106,434] (1984) ; Chem. Abstr., 101 (1984) 171559x.
1604 R.P. Lutz, Chem. Rev., 84 (1984) 205.
1605 L.E. Overman, Angew. Chem., Int. Ed. Engl., 23 (1984) 579; Angew. Chem., 96 (1984) 565.
1606 T.G. Schenck and B. Bosnich, J. Am. Chem. Soc., 107 (1985) 2058.
1607 S. Murahashi and Y. Makabe, Tetrahedron Lett., 26 (1985) 5563.
1608 M. Mizutani, Y. Sanemitsu, Y. Tamaru and Z. Yoshida, Tetrahedron, 41 (1985) 5289.
1609 H. Quast and U. Nahr, Chem. Ber., 118 (1985) 526.
1610 E.J. Jacobsen, PhD Thesis, UC, Irvine, 1983, Diss. Abstr. Int. B, 45 (1984) 190.
1611 L.E. Overman and A.F. Renaldo, Tetrahedron Lett., 24 (1983) 3757.
1612 A.C. Oehlschlager, P. Mishra and S. Dhami, Can. J. Chem., 62 (1984) 791.
1613 M. Mizutani, Y. Sanemitsu, Y. Tamaru and Z. Yoshida, J. Org. Chem., 50 (1985) 764.
1614 E.P. Serebryakov and G.D. Gamalevich, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1740; Izv. AKad. Nauk SSSR, Ser. Khim., (1985) 1890.
1615 M. Ohshima, M. Murakami and T. Mukaiyama, Chem. Lett., (1984) 1535.
1616 R.M. Coates and S.J. Hobbs, J. Org. Chem., 49 (1984) 140.
1617 W.J. Richter, Chem. Ber., 118 (1985) 97.
1618 Y. Yamada, G. Suzukamo, H. Yoshioka, Y. Tamaru and Z. Yoshida, Tetrahedron Lett., 25 (1984) 3599.
1619 Sumitomo Chemical Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60,115,594 [85,115,594] (1985); Chem. Abstr., 103 (1985) 215553p.
1620 N. Borsub and C. Kutal, J. Am. Chem. Soc., 106 (1984) 4826.
1621 C.K. Kelley and C. Kutal, Organometallics, 4 (1985) 1351.
1622 T.B. Patrick and D.S. Bechtold, J. Org. Chem., 49 (1984) 1935.
1623 R.I. Khusnutdinov, V.A. Dokichev, I.O. Popova, O.M. Nefedov, G.A. Tolstikov and U.M. Dzhemilev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 433; Izv. AKad. Nauk SSSR, Ser. Khim., (1985) 475.
1624 R.W. Hoffmann, A. Riemann and B. Mayer, Chem. Ber., 118 (1985) 2493.
1625 R.W. Hoffmann and W. Barth, Chem. Ber., 118 (1985) 634.
1626 K.-D. Baumgart, H. Harnisch, U. Szeimies-Seebach and G. Szeimes, Chem. Ber., 118 (1985) 2883.
1627 R.B. Taylor, PhD Thesis, Montana State Univ., Diss. Abstr. Int. B, 45 (1984) 566.

1628 S. Achab, J.-P. Cosson and B.C. Das, J. Chem. Soc., Chem. Commun., (1984) 1040.

1629 T. Lukac, M. Soukup and E. Widmer, Eur. Pat. Appl. EP 133,711 (1985); Chem. Abstr., 103 (1985) 104604m.

1630 K. Fugami, Y. Morizawa, K. Oshima and H. Nozaki, Tetrahedron Lett., 26 (1985) 857.

1631 M. Roeper, E.O. Elvevoll and M. Luetgendorf, Erdoel Kohle, Erdgas, Petrochem., 38 (1985) 38; Chem. Abstr., 102 (1985) 133950.

1632 V.P. Zagorodnikov and M.N. Vargaftik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2457; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2652.

1633 E. Curzon, B.T. Golding, C. Pierpoint and B.W. Waters, J. Organomet. Chem., 262 (1984) 263.

1634 G.R. Clark and S. Thiensathit, Tetrahedron Lett., 26 (1985) 2503.

1635 Y. Ito, T. Matsuura and T. Saegusa, Tetrahedron Lett., 26 (1985) 5781.

1636 B.M. Trost, Fundam. Res. Homogeneous Catal., 4 (1984) 117; Chem. Abstr., 100 (1984) 209446c.

1637 J. Tsuji. Sel., Goal Synth. Effic., Proc. Workshop Conf. Hoechst, 14th 1983, Pub. 1984; Chem. Abstr., 101 (1984) 210041u.

1638 J.-C. Fiaud, B. Denner and J.-L. Malleron, J. Organomet. Chem., 291 (1985) 393.

1639 S.E. Byström, R. Aslanian and J.-E. Bäckvall, Tetrahedron Lett., 26 (1985) 1749.

1640 D.L. Minsker, A.G. Ibragimov and U.M. Dzhemilev, J. Org. Chem. USSR, 20 (1984) 873, Zh. Org. Khim., 20 (1984) 959.

1641 N.A. Bumagin, A.N. Kasatkin and I.P. Beletskaya, Bull. Acad. Sci USSR, Div. Chem. Sci., 33 (1984) 588; Izv. Akad. Nauk SSSR. Ser. Khim., (1984) 636.

1642 Y. Yokoyama, S. Ito, Y. Takahashi and Y. Murakami, Tetrahedron Lett., 26 (1985) 6457.

1643 D. Ferroud, J.P. Genet and J. Muzart, Tetrahedron Lett., 25 (1984) 4379.

1644 H.J. Bestmann, G. Schade, H. Lütke and T. Mönius, Chem. Ber., 118 (1985) 2640.

1645 E. Keinan, M. Sahai, Z. Roth, A. Nudelman and J. Herzig, J. Org. Chem. 50 (1985) 3558.

1646 B.M. Trost and N.R. Schmuff, J. Am. Chem. Soc., 107 (1985) 396.

1647 G.P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Organomet. Chem., 268 (1984) 97.

1648 S.A. Stanton, PhD Thesis, Univ. Rochester, 1984, Diss. Abstr. Int. B, 45 (1984) 199.

1649 R.E. Nordberg and J.-E. Bäckvall, J. Organomet. Chem., 285 (1985) C24.

1650 Y. Inoue, M. Taguchi, M. Toyofuku and H. Hashimoto, Bull. Chem. Soc. Jpn., 57 (1984) 3021.

1651 M. Julia and T. Cuvigny, Fr. Demande FR 2,541,997 (1984); Chem. Abstr., 102 (1985) 131548g.

1652 J.P. Genet and D. Ferroud, Tetrahedron Lett., 25 (1984) 3579.

1653 S.G. Will, P. Magriotis, E.R. Marinelli, J. Dolan and F. Johnson, J. Org. Chem., 50 (1985) 5432.

1654 B.M. Trost and P. Quayle, J. Am. Chem. Soc., 106 (1984) 2469.

1655 F.-T. Luo and E. Negishi, Tetrahedron Lett., 26 (1985) 2177.

1656 F.-T. Luo and E. Negishi, J. Org. Chem., 50 (1985) 4762.

1657 P.F. Schuda and B. Bernstein, Synth. Commun., 14 (1984) 293.

1658 B.M. Trost and C.R. Self, J. Org. Chem., 49 (1984) 468.

1659 S.A. Godleski and E.B. Villhauer, J. Org. Chem., 49 (1984) 2246.

1660 X. Lu and Y. Huang, J. Organomet. Chem., 268 (1984) 185.

1661 B.M. Trost and J. Vercauteren, Tetrahedron Lett., 26 (1985) 131.

1662 B.M. Trost and J.W. Herndon, J. Am. Chem. Soc., 106 (1984) 6835.

1663 B.M. Trost and K.M. Pietrusiewicz, Tetrahedron Lett., 26 (1985) 4039.

1664 T. Hayashi, M. Konishi, K. Yokota and M. Kumada, J. Organomet. Chem., 285 (1985) 359.

1665 T. Hiyama and N. Wasaka, Tetrahedron Lett., 26 (1985) 3259.

1666 T. Takahashi, Y. Jinbo, K. Kitamura and J. Tsuji, Tetrahedron Lett., 25 (1984) 5921.

1667 F. Colobert and J.-P. Genet, Tetrahedron Lett., 26 (1985) 2779.

1668 B.M. Trost and M.-H. Hung, J. Am. Chem. Soc., 106 (1984) 6837.

1669 B.M. Trost, M. Lautens, M.-H. Hung and C.S. Carmichael, J. Am. Chem. Soc., 106 (1984) 7641.

1670 E. Keinan and M. Sahai, J. Chem. Soc., Chem. Commun., (1984) 648.

1671 H. Kurosawa, M. Emoto and A. Urabe, J. Chem. Soc., Chem. Commun., (1984) 968.

1672 J.-C. Fiaud and L. Aribi-Zouioueche, J. Organomet. Chem., 295 (1985) 383.

1673 T.V. RajanBabu, J. Org. Chem., 50 (1985) 3642.

1674 E. Negishi and H. Matsushita, Org. Synth., 62 (1984) 31.

1675 N. Miyaura, H. Suginome and A. Suzuki, Tetrahedron Lett., 25 (1984) 761.

1676 G.A. Tolstikov and A.N. Kasatin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2599; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2835.

1677 V.I. Ognyanov and M. Hesse, Synthesis (1985) 645.

1678 I. Minami, I. Shimizu and J. Tsuji, J. Organomet. Chem., 296 (1985) 269.

1679 J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura and K. Takahashi, J. Org. Chem., 50 (1985) 1523.

1680 J. Tsuji, K. Takahashi, I. Minami and I. Shimizu, Tetrahedron Lett., 25 (1984) 4783.

1681 K. Yamamoto, R. Deguchi, Y. Ogimura and J. Tsuji, Chem. Lett., (1984) 1657.

1682 J. Tsuji, M. Nisar, I. Shimizu and I. Minami, Synthesis (1984) 1009.

1683 J. Tsuji, M. Nisar and I. Shimizu, J. Org. Chem., 50 (1985) 3416.

1684 J. Tsuji, I. Shimizu, H. Kataoka, Y, Mitsuda and K. Goto, Ger. Offen. DE 3,316,306 (1983); Chem. Abstr., 100 (1984) 67888x.

1685 H. Kataoka, T. Yamada, K. Goto and J. Tsuji, Eur. Pat. Appl. EP 133,548 (1985); Chem. Abstr., 103 (1985) 37129v.

1686 Nippon Zeon Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,186,939 [84,186,939] (1984); Chem. Abstr., 102 (1985) 184763e.

1687 Nippon Zeon Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60 32,745 [85 32,745]; Chem. Abstr., 103 (1985) 104605n.

1688 T. Tanaka, N. Okamura, K. Bannai, A. Hazato, S. Sugiura, K. Manabe and S. Kurozumi, Tetrahedron Lett., 26 (1985) 5575.

1689 A. Hazato, T. Tanaka, K. Watanabe, K. Bannai, T. Toru, N. Okamura, K. Manabe, A. Ohtsu, F. Kamamoto and S. Kurozumi, Chem. Pharm. Bull., 33 (1985) 1815.

1690 J. Tsuji, I. Minami, I. Shimizu and H. Kataoka, Chem. Lett., (1984) 1133.

1691 J. Tsuji, I. Minami and I. Shimizu, Chem. Lett., (1984) 1721.

1692 N. Ono, I. Hamamoto and A. Kaji, Synthesis (1985) 950.

1693 R. Tamura, K. Hayashi, M. Kakihana, M. Tsuji and D. Oda, Tetrahedron Lett., 26 (1985) 851.

1694 R. Tamura, K. Hayashi, M. Kakihana, M. Tsuji and D. Oda, Chem. Lett., (1985) 229.

1695 R. Tamura, K. Hayashi, Y. Kai and D. Oda, Tetrahedron Lett., 25 (1984) 4437.

1696 U.M. Dzhemilev, A.G. Ibragimov and D.L. Minsker, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 625; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 675.

1697 K. Hiroi, R. Kitayama and S. Sato, Chem. Lett., (1984) 929.

1698 T. Cuvigny, M. Julia and C. Rolando, J. Organomet. Chem., 285 (1985) 395.

1699 U.M. Dzhemilev, A.G. Ibragimov, E.V. Gribanova and L.M. Khalilov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2374; Izv. Akad. Nauk SSSRO, Ser. Khim., (1985) 2562.

1700 H. Sugimura and H. Takai, Chem. Lett., (1984) 1505.

1701 Y. Inoue, M. Toyofuku and H. Hashimoto, Chem. Lett., (1984) 1227.

1702 I. Minami, Y. Ohashi, I. Shimizu and J. Tsuji, Tetrahedron Lett., 26 (1985) 2449.

1703 S. Chatterjee and E. Negishi, J. Organomet. Chem., 285 (1985) C1

1704 S. Chatterjee and E. Negishi, J. Org. Chem., 50 (1985) 3406.
1705 N.A. Bumagin, A.N. Kasatkin and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1696; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1858.
1706 B. Åkermark, J.-E. Nyström, T. Rein, J.-E. Bäckvall, P. Helquist and R. Aslanian, Tetrahedron Lett., 25 (1984) 5719.
1707 M. Nikaido, R. Aslanian, F. Scavo, P. Helquist, B. Åkermark and J.-E. Bäckvall, J. Org. Chem., 49 (1984) 4738.
1708 J.-E. Bäckvall, S.E. Byström and J.E. Nyström, Tetrahedron, 41 (1985) 5761.
1709 D.R. Deardorff, D.C. Myles and K.D. MacFerrin, Tetrahedron Lett., 26 (1985) 5615.
1710 T. Takahashi, A. Ootake, J. Tsuji and K. Tachibana, Tetrahedron, 41 (1985) 5747.
1711 J. Wicha and M.M. Kabat, J. Chem. Soc., Perkin Trans., 1, (1985) 1601.
1712 B.M. Trost and S.R. Angle, J. Am. Chem. Soc., 107 (1985) 6123.
1713 P.B. Mackenzie, J. Whelan and B. Bosnich, J. Am. Chem. Soc., 107 (1985) 2046.
1714 D.H. Farrar and N.C. Payne, J. Am. Chem. Soc., 107 (1985) 2054.
1715 M. Ahmar, B. Cazes and J. Gore, Tetrahedron Lett., 26 (1985) 3795.
1716 D. Djahanbini, B. Cazes, J. Gore and F. Gorbet, Tetrahedron, 41 (1985) 867.
1717 D.Djahanbini, B. Cazes and J. Gore, Tetrahedron Lett., 25 (1984) 203.
1718 I. Shimizu, T. Sugiura and J. Tsuji, J. Org. Chem., 50 (1985) 537.
1719 I. Shimizu and J. Tsuji, Chem. Lett., (1984) 233.
1720 K. Ruitenberg, H. Westmijze, H. Kleijn and P. Vermeer, J. Organomet. Chem., 277 (1984) 227.
1721 K. Ruitenberg and P. Vermeer, Tetrahedron Lett., 25 (1984) 3019.
1722 J. Tsuji, H. Watanabe, I. Minami and I. Shimizu, J. Am. Chem. Soc., 107 (1985) 2196.
1723 M. Ramaiah, Synthesis (1984) 529.
1724 R. Baker and R.B. Keen, J. Organomet. Chem., 285 (1985) 419.
1725 B.M. Trost, J. Lynch and P. Renaut, Tetrahedron Lett., 26 (1985) 6313.
1726 B.M. Trost and T.N. Nanninga, J. Am. Chem. Soc., 107 (1985) 1293.
1727 B.M. Trost, T.N. Nanninga and T. Satoh, J. Am. Chem. Soc., 107 (1985) 721.
1728 B.M. Trost and P.J. Bonk, J. Am. Chem. Soc., 107 (1985) 8277.
1729 P. Binger, Q.-H. Lü and P. Wedemann, Angew. Chem., Int. Ed. Engl., 24 (1985) 316; Angew. Chem., 97 (1985) 333.
1730 P. Binger and P. Wedemann, Tetrahedron Lett., 26 (1985) 1045.
1731 H.-J. Weintz and P. Binger, Tetrahedron Lett., 26 (1985) 4075.
1732 P. Binger and H.-J. Weintz, Chem. Ber., 117 (1984) 654.
1733 Y. Inoue, S. Ajioka, M. Toyofuku, A. Mori, T. Fukui, Y. Kawashima, S. Miyano and H. Hashimoto, J. Mol. Catal., 32 (1985) 91.
1734 K. Burgess, Tetrahedron Lett., 26 (1985) 3049.
1735 I. Shimizu, Y. Ohashi and J. Tsuji, Tetrahedron Lett., 26 (1985) 3825.
1736 J.K. Stille, Pure Appl. Chem., 57 (1985) 1771.
1737 A. Suzuki, Pure Appl. Chem., 57 (1985) 1749.
1738 Z. Rappoport, Recl. Trav. Chim. Pays-Bas, 104 (1985) 309.
1739 A.K. Yatsimirskii, A.D. Ryabov and I.V. Berezin, Ref. Zh., Khim., (1984) Abstr. No. 9B4138; Chem. Abstr., 101 (1984) 44034x.
1740 K.C. Eapen, S.S. Dua and C. Tamborski, J. Org. Chem., 49 (1984) 478.
1741 G.S. Reddy and W. Tam, Organometallics, 3 (1984) 630.
1742 W.A. Nugent and R.J. McKinney, J. Org. Chem., 50 (1985) 5370.
1743 D.E. Wellman, K.R. Lassila and R. West, J. Org. Chem., 49 (1984) 965.
1744 P. Kuś and A. Zemanek, Pol. J. Chem., 59 (1985) 281.
1745 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, J. Am. Chem. Soc., 106 (1984) 158.
1746 M. Tiecco, M. Tingoli and E. Wenkert, J. Org. Chem., 50 (1985) 3828.
1747 R.K. Dieter and Y.J. Lin, Tetrahedron Lett., 26 (1985) 39.

1748 H. Sugimura, H. Okamura, M. Miura, M. Yoshida and H. Takei, Nippon Kagaku Kaishi, (1985) 416; Chem. Abstr., 104 (1986) 108625n.

1749 J.M. Wilson and D.J. Cram, J. Org. Chem., 49 (1984) 4930.

1750 K. Seto, S. Takahashi and T. Tahara, J. Chem. Soc., Chem. Commun., (1985) 122.

1751 M. Uno, K. Seto, W. Ueda, M. Masuda and S. Takahashi, Synthesis (1985) 506.

1752 M. Uno, K. Seto and S. Takahashi, J. Chem. Soc., Chem. Commun., (1984) 932.

1753 M. Uno, K. Seto, M. Masuda, W. Ueda and S. Takahashi, Tetrahedron Lett., 26 (1985) 1553.

1754 M.-T. Lee, B.M. Foxman and M. Rosenblum, Organometallics, 4 (1985) 539.

1755 E. Vogel, K.-D. Sturm, A. de F. Dias, J. Lex, H. Schmickler and F. Wudl, Angew. Chem., Int. Ed. Engl., 24 (1985) 590; Angew. Chem., 97 (1985) 590.

1756 G.W. Erickson, Eur. Pat. Appl. EP 110,671 (1984); Chem. Abstr., 101 (1984) 170907x.

1757 J.K. Stille, Pure Appl. Chem., 57 (1985) 1771.

1758 N.A. Bumagin, I.G. Bumagina and I.P. Beletskaya, Dokl. Chem., 274 (1984) 39; Dokl. Akad. Nauk SSSR, 274 (1984) 818 [Chem.].

1759 M. Kosugi, T. Ishikawa, T. Nogami and T. Migita, Nippon Kagaku Kaishi, (1985) 520; Chem. Abstr., 104 (9186) 68496n.

1760 M. Kosugi, M. Ishiguro, Y. Negishi, H. Sano and T. Migita, Chem. Lett., (1984) 1511.

1761 M. Kosugi, T. Sumiya, T. Ogata, H. Sano and T. Migita, Chem. Lett., (1984) 1225.

1762 M. Kosugi, T. Sumiya, K. Onhashi, H. Sano and T. Migita, Chem. Lett., (1985) 997.

1763 M. Kosugi, M. Kameyama, H. Sano and T. Migita, Nippon Kagaku Kaishi, (1985) 547; Chem. Abstr., 104 (1986) 129990t.

1764 N.A. Bumagin, Yu.V. Gulevich and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 879; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 953.

1765 M. Kosugi, I. Hagiwara, T. Sumiya and T. Migita, Bull. Chem. Soc. Jpn., 57 (1984) 242.

1766 A. Duchêne and J.-P. Quintard, Synth. Commun., 15 (1985) 873.

1767 M. Kosugi, Y. Negishi, M. Kameyama and T. Migita, Bull. Chem. Soc. Jpn., 58 (1985) 3383.

1768 N.A. Bumagin, I.G. Bumagina and I.P. Beletskaya, Dokl. Chem., 274 (1984) 53; Dokl. Akad. Nauk SSSR, 274 (1984) 1103 [Chem.].

1769 N.A. Bumagin, Yu.V. Gulevich, G.A. Artamkina and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1098; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1195.

1770 N.A. Bumagin, Yu.V. Gulevich and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 1044; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1137.

1771 R.S. Sorokina, L.F. Rybakova, I.O. Kalinovskii and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1506; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 1647.

1772 M. Sletzinger, T.R. Verhoeven, R.P. Volante, J.M. McNamara, E.G. Corley and T.M.H. Liu, Tetrahedron Lett., 26 (1985) 2951.

1773 K. Takagi, N. Hayama and K. Sasaki, Bull. Chem. Soc. Jpn., 57 (1984) 1887.

1774 M. Iyoda, K. Sato and M. Uda, Tetrahedron Lett., 26 (1985) 3829.

1775 R.H. Mitchell, M. Chaudhary, T.W. Dingle and R.V. Williams, J. Am. Chem. Soc., 106 (1984) 7776.

1776 G. Chang and M.P. Mertes, Tetrahedron Lett., 25 (1984) 2431.

1777 N.A. Bumagin, A.B. Ponomaryov and I.P. Beletskaya, Tetrahedron Lett., 26 (1985) 4819.

1778 N.A. Bumagin, A.B. Ponomaryov and I.P. Beletskaya, J. Organomet. Chem., 291 (1985) 129.

1779 Y. Wakita, S. Noma, M. Maeda and M. Kojima, J. Organomet. Chem., 297 (1985) 379.
1780 P.J. Beswick, S.J. Leach, N.F. Masters and D.A. Widdowson, J. Chem. Soc., Chem. Commun., (1984) 46.
1781 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, J. Organomet. Chem., 267 (1984) C1.
1782 M.J. Sharp and V. Snieckus, Tetrahedron Lett., 26 (1985) 5997.
1783 R.B. Miller and S. Dugar, Organometallics, 3 (1984) 1261.
1784 M. Ishikura, M. Kamada and M. Terashima, Heterocycles, 22 (1984) 265.
1785 M. Ishikura, M. Kamada and M. Terashima, Synthesis, (1984) 936.
1786 K. Sanechika, T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Jpn., 57 (1984) 752.
1787 C. Perchonock, M.E. McCarthy, K.F. Erhard, J.G. Gleason, M.A. Wasserman, R.M. Muccitelli, J.F. DeVan, S.S. Tucker, L.M. Vickery, T. Kirchner, B.M. Weichman, S. Mong, S.T. Crooke and J.F. Newton, J. Med. Chem., 28 (1985) 1145.
1788 N.A. Bumagin, A.B. Ponomarev and I.P. Beletskaya, Dokl. Chem., 283 (1985) 212; Dokl. Akad. Nauk SSSR, 283 (1985) 630 [Chem.].
1789 A.I. Kovredov, Zh.S. Shaugumbekova, A.V. Kazantsev and L.I. Zakharkin, J. Gen. Chem. USSR, 54 (1984) 509; Zh. Obshch. Khim., 54 (1984) 577.
1790 N.A. Bumagin, A.B. Ponomaryov and I.P. Beletskaya, Synthesis (1984) 728.
1791 N.A. Bumagin, A.B. Ponomaryov and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 1561.
1792 A. Carpita, A. Lessi and R. Rossi, Synthesis (1984) 571.
1793 B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdagh and K.P.C. Vollhardt, J. Am. Chem. Soc., 107 (1985) 5670.
1794 H.E. Helson, K.P.C. Vollhardt and Z.-Y. Yang, Angew. Chem., Int. Ed. Engl., 24 (1985) 114; Angew. Chem., 97 (1985) 120.
1795 D. Villemin and E. Schigeko, J. Organomet. Chem., 293 (1985) C10.
1796 D.L. Boger, S.R. Duff, J.S. Panek and M. Yasuda, J. Org. Chem., 50 (1985) 5790.
1797 D.L. Boger and J.S. Panek, Tetrahedron Lett., 25 (1984) 3175.
1798 X.Xu and J. Zhang, Synthesis (1984) 778.
1799 Y. Xu, Z. Li, J. Xia, H. Guo and Y. Huang, Synthesis (1984) 781.
1800 Y. Xu and J. Zhang, Tetrahedron Lett., 26 (1985) 4771.
1801 J.J. Bulot, E.E. Aboujaoude, N. Collignon and P. Savignac, Phosphorus Sulfur, 21 (1984) 197.
1802 D.W. Allen, I.W. Nowell, L.A. March and B.F. Taylor, J. Chem. Soc., Perkin Trans. 1, (1984) 2523.
1803 K. Issleib, K. Balszuweit, S. Richter and J. Koetz, Ger. (East) DD 219,776 (1985); Chem. Abstr., 103 (1985) 215558u.
1804 L. Horner and H.W. Fleming, Ger. Offen. DE 3,400,509 (1985); Chem. Abstr., 103 (1985) 196254y.
1805 S. Torii, H. Tanaka and K. Morisaki, Tetrahedron Lett., 26 (1985) 1655.
1806 Y. Fujioka, Bull. Chem. Soc. Jpn., 57 (1984) 3494.
1807 D.L. Coffen, B. Schaer, F.T. Bizzarro and J.B. Cheung, J. Org. Chem., 49 (1984) 296.
1808 N.M. Chistovalova, I.S. Akhrem, E.V. Reshetova and M.E. Vol'pin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2139; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2342.
1809 A.A. Alhaider, M.A. Abdelkader and E.J. Lien, J. Med. Chem., 28 (1985) 1394.
1810 E. Wenkert, J.M. Hanna, M.H. Leftin, E.L. Michelotti, K.T. Potts and D. Usifer, J. Org. Chem., 50 (1985) 1125.
1811 S.-O. Thorberg, L. Gawell, I. Csöregh and J.L.G. Nilsson, Tetrahedron, 41 (1985) 129.
1812 T.R. Kelly, H.R. Howard, B.K. Koe and R. Sarges, J. Med. Chem., 28 (1985) 1368.
1813 H.E. Katz, J. Org. Chem., 50 (1985) 2086.
1814 H. Sugimura and H. Takei, Bull. Chem. Soc. Jpn., 58 (1985) 664.

1815 R. Okazaki, Y. Negishi and N. Inamoto, J. Org. Chem., 49 (1984) 3819.
1816 J.-P. Monthéard, J.-F. Delzant and M. Gazard, Synth. Commun., 14 (1984) 289.
1817 A. Carpita, R. Rossi and C.A. Veracini, Tetrahedron, 41 (1985) 1919.
1818 L.N. Pridgen, Synthesis (1984) 1047.
1819 H. Yamanaka, M. An-naka, Y. Kondo and T. Sakamoto, Chem. Pharm. Bull., 33 (1985) 4309.
1820 P. Vincent, J.P. Beaucourt and L. Pichat, Tetrahedron Lett., 25 (1984) 201.
1821 M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, Synthesis (1984) 736.
1822 P. Vincent, J.P. Beaucourt and L. Pichat, Tetrahedron Lett., 25 (1984) 201.
1823 J.O. Karlsson, A. Svensson and S. Gronowitz, J. Org. Chem., 49 (1984) 2018.
1824 S. Gronowitz, V. Bobosik and K. Lawitz, Chem. Scr., 23 (1984) 120.
1825 S. Gronowitz and K. Lawitz, Chem. Scr., 24 (1984) 5.
1826 W.J. Thompson and J. Gaudino, J. Org. Chem., 49 (1984) 5237.
1827 A. Ohta, A. Inoue and T. Watanabe, Heterocycles, 22 (1984) 2317.
1828 A. Ohta, A. Inoue, K. Ohtsuka and T. Watanabe, Heterocycles, 23 (1985) 133.
1829 A. Ohta, A. Inoue, K. Ohtsuka, T. Watanabe and Y. Akita, Heterocycles, 23 (1985) 187.
1830 S. Konno, S. Fujimura and H. Yamanaka, Heterocycles, 22 (1984) 2245.
1831 A. Matsuda, M. Shinozaki, T. Miyasaka, H. Machida and T. Abiru, Chem. Pharm. Bull., 33 (1985) 1766.
1832 A. Carpita, A. Lezzi, R. Rossi, F. Marchetti and S. Merlino, Tetrahedron, 41 (1985) 621.
1833 D.E. Ames, J.C. Mitchell and C.C. Takundwa, J. Chem. Res., S, (1985) 144.
1834 V. Bakthavachalam, M. d'Alarcao and N.J. Leonard. J. Org. Chem., 49 (1984) 289.
1835 E.A. Krasil'nikova, O.L. Nevzorova and V.V. Sentemov, J. Gen. Chem. USSR, 55 (1985) 1145; Zh. Obshch. Khim., 55 (1985) 1283.
1836 A. Minato, K. Suzuki, K. Tamao and M. Kumada, Tetrahedron Lett., 25 (1984) 83.
1837 A. Hosomi, M. Ando and H. Sakurai, Chem. Lett., (1984) 1385.
1838 K. Tamao, T. Iwahara, R. Kanatani and M. Kumada, Tetrahedron Lett., 25 (1984) 1909.
1839 A. Hosomi, Y. Sakata and H. Sakurai, Tetrahedron Lett., 26 (1985) 5175.
1840 V. Ra tovelomanana and G. Linstrumelle, Synth. Commun., 14 (1984) 179.
1841 M. Malacria and K.P.C. Vollhardt, J. Org. Chem., 49 (1984) 5010.
1842 V. Fiandanese, G. Marchese, F. Naso and L. Ronzini, J. Chem. Soc., Perkin Trans., 1, (1985) 1115.
1843 J.A. Walker, S.P. Bitler and F. Wudl, J. Org. Chem., 49 (1984) 4733.
1844 J.-P. Monthéard and J.-C. Dubois, J. Het. Chem., 22 (1985) 719.
1845 V. Ratovelomanana, G. Linstrumelle and J.F. Normant, Tetrahedron Lett., 26 (1985) 2575.
1846 R. Okazaki, M. O-oka, N. Tokitoh and N. Inamoto, J. Org. Chem., 50 (1985) 180.
1847 J.-L. Fabre, M. Julia and J-N. Verpeaux, Bull. Chem. Soc. Fr., (1985) 762.
1848 E. Wenkert, E.L. Michelotti, C.S. Swindell and M. Tingoli, J. Org. Chem., 49 (1984) 4894.
1849 E. Wenkert, V.F. Ferreira, E.L. Michelotti and M. Tingoli, J. Org. Chem., 50 (1985) 719.
1850 E. Wenkert, M.H. Leftin and E.L. Michelotti, J. Chem. Soc., Chem. Commun., (1984) 617.
1851 M. Lemaire, J. Buter, B.K. Vriesema and R.M. Kellog, J. Chem. Soc., Chem. Commun., (1984) 309.

1852 M. Lemaire, B.K. Vriesema and R.M. Kellog, Tetrahedron Lett., 26 (1985) 3499.
1853 H. Brunner, W. Li and H. Weber, J. Organomet. Chem., 288 (1985) 359.
1854 J.H. Griffin and R.M. Kellog, J. Org. Chem., 50 (1985) 3261.
1855 K. Koumaglo and T.H. Chan, Tetrahedron Lett., 25 (1984) 717.
1856 R.B. Miller and M.I. Al-Hassan, J. Org. Chem., 50 (1985) 2121.
1857 F. Björkling, T. Norin and R. Unelius, Synth. Commun., 15 (1985) 463.
1858 E. Negishi, N. Okukado, S.F. Lovich and F.-T. Luo, J. Org. Chem., 49 (1984) 2629.
1859 T. Kitazume and N. Ishikawa, J. Am. Chem. Soc., 107 (1985) 5186.
1860 M. Iyoda, K. Sato and M. Oda, J. Chem. Soc., Chem. Commun., (1985) 1547.
1861 H.C. Brown and V. Somayaji, Synthesis (1984) 919.
1862 N. Miyaura, K. Yamada, H. Suginome and A. Suzuki, J. Am. Chem. Soc., 107 (1985) 972.
1863 A. Suzuki, Pure Appl. Chem., 57 (1985) 1749.
1864 M. Ishikura, M. Kamada, T. Ohta and M. Terashima, Heterocycles, 22 (1984) 2475.
1865 M. Ishikura, I. Oda and M. Terashima, Heterocycles, 23 (1985) 2375.
1866 V. Ratovelonanana and G. Linstrumelle, Tetrahedron Lett., 25 (1984) 6001.
1867 K. Takai, M. Sato, S. Oshima and H. Nozaki, Bull. Chem. Soc. Jpn., 57 (1984) 108.
1868 W.J. Scott, G.T. Crisp and J.K. Stille, J. Am. Chem. Soc., 106 (1984) 4630.
1869 S. Murahashi, T. Naota and Y. Tanigawa, Org. Synth., 62 (1984) 39.
1870 T.F. Tam, R.W. Spencer, E.M. Thomas, L.J. Copp and A. Krantz, J. Am. Chem. Soc., 106 (1984) 6849.
1871 K.C. Nicolaou, T. Ladduwahetty and E.M. Elisseou, J. Chem. Soc., Chem. Commun., (1985) 1580.
1872 K.C. Nicolaou and S.E. Webber, J. Am. Chem. Soc., 106 (1984) 5734.
1873 K.C. Nicolaou, C.A. Veale, S.E. Webber and H. Katerinopoulos, J. Am. Chem. Soc., 107 (1985) 7515.
1874 D. Guillerm and G. Linstrumelle, Tetrahedron Lett., 26 (1985) 3811.
1875 K.P.C. Vollhardt and L.S. Winn, Tetrahedron Lett., 26 (1985) 709.
1876 G.C. Nwokogu, Tetrahedron Lett., 25 (1984) 3263.
1877 G.C. Nwokogu, J. Org. Chem., 50 (1985) 3900.
1878 A.M. Caporusso, F. Da Settimo and L. Lardicci, Tetrahedron Lett., 26 (1985) 5101.
1879 C.J. Elsevier and P. Vermeer, J. Org. Chem., 50 (1985) 3042.
1880 C.J. Elsevier, H.H. Mooiweer, H. Kleijn and P. Vermeer, Tetrahedron Lett., 25 (1984) 5571.
1881 M. Iyoda, M. Sakaitani, H. Otsuka and M. Oda, Chem. Lett., (1985) 127.
1882 M. Iyoda, M. Sakaitani, H. Otsuka and M. Oda, Tetrahedron Lett., 26 (1985) 4777.
1883 K. Yokoo, T. Fukagawa, Y. Yamanaka, H. Taniguchi and Y. Fujiwara, J. Org. Chem., 49 (1984) 3237.
1884 J.H. Simpson and J.K. Stille, J. Org. Chem., 50 (1985) 1759.
1885 M. Kosugi, I. Takano, M. Sakurai, H. Sano and T. Migita, Chem. Lett., (1984) 1221.
1886 M. Iyoda, M. Sakaitani, A. Kojima and M. Oda, Tetrahedron Lett., 26 (1985) 3719.
1887 L.I. Zakharkin, A.I. Kovredov and V.A. Ol'shevskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 809; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 888.
1888 L.I. Zakharkin, A.I. Kovredov, V.A. Olshevskaya and V.A. Antonovich, J. Organomet. Chem., 267 (1984) 81.
1889 C. Cardellicchio, V. Fiandanese, G. Marchese and L. Ronzini, Tetrahedron Lett., 26 (1985) 3595.
1890 R.A. Grey, J. Org. Chem., 49 (9184) 2288.
1891 Y. Tamaru, H. Ochiai, F. Sanda and Z. Yoshida, Tetrahedron Lett., 26 (1985) 5529.

1892 J.-P. Gillet, R. Sauvetre and J.-F. Normant, Tetrahedron Lett., 26 (1985) 3999.

1893 N.A. Bumagin, Yu.V. Gulevich and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2600; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2835.

1894 J.-B. Verlhac, E. Chanson, B. Jousseaume and J.-P. Quintard, Tetrahedron Lett., 26 (1985) 6075.

1895 K. Wakamatsu, Y. Okuda, K. Oshima and H. Nozaki, Bull. Chem. Soc. Jpn., 58 (1985) 2425.

1896 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2144; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2347.

1897 T. Kobayashi, T. Sakakura and M. Tanaka, Tetrahedron Lett., 26 (1985) 3463.

1898 E.D. Chekurovskaya, N.I. Kuvshinova, Ref. Zh., Khim., (1984) Abstr. No. 4Zh106; Chem. Abstr., 101 (1984) 131176p.

1899 R.D. Knudsen, U.S. US 4,487,847 (1984); Chem. Abstr., 102 (1985) 112866t.

1900 A.D. Pomogailo, F.A. Khrisostomov and F.S. D'yachkovskii, Kinet. Catal., 26 (1985) 953; Kinet. Katal., 26 (1985) 1104.

1901 S. Sibille, J. Coulombeix, J. Perichon, J.-M. Fuchs, A. Mortreux and F. Petit, J. Mol. Catal., 32 (1985) 239.

1902 D. Neibecker, R.F. De Souza and I. Tkatchenko, Actas Simp. Iberoam. Catal., 9th, 2 (1984) 1501; Chem. Abstr., 102 (1985) 79357c.

1903 D.M. Singleton, U.S. US 4,472,522 (1984); Chem. Abstr., 102 (1985) 46405p.

1904 D.M. Singleton, U.S. US 4,472,525 (1984); Chem. Abstr., 102 (1985) 85118s.

1905 A. Behr and W. Keim, Arabian J. Sci. Eng., 10 (1985) 377; Chem. Abstr., 104 (1986) 186862b.

1906 M. Peuckert and W. Keim, J. Mol. Catal., 22 (1984) 289.

1907 K. Zhou, Z. Gao and W. Keim, Int. Cong. Catal., [Proc.], 8th, 5 (1984) V429-V439; Chem. Abstr., 106 (1987) 137726t.

1908 M.L. Chernyshev, Mater. Vses. Nauchn. Stud. Konf. "Stud. Nauchno-Tekh. Prog.": Khim., 22nd (1984) 3; Chem. Abstr., 107 (1987) 236005j.

1909 E.J. Smutny, U.S. US 4,436,946 (1984); Chem. Abstr., 100 (1984) 191351f.

1910 A.F. Masters and K.J. Cavell, PCT Int. Appl. WO 83 02,907 (1983); Chem. Abstr., 100 (1984) 7392w.

1911 G.P. Potapov and V.A. Shepelin, React. Kinet. Catal. Lett., 28 (1985) 287.

1912 V.A. Kabanov, G.A. Grishin, M.A. Martynova, A.I. Prudnikov, L.M. Rozenberg, V.I. Smetanyuk and R.V. Chediya, Kinet. Catal., 26 (1985) 1230; Kinet. Katal., 26 (1985) 1427.

1913 G.M.K. Mathys, Eur. Pat. Appl. EP 91,232 (1983); Chem. Abstr., 100 (1984) 120495v.

1914 Z. Gao, Z. Liu, H. Wang and K. Zhou, Gaodeng Xuexiao Huaxue Xuebao, 6 (1985) 1127; Chem. Abstr., 104 (1986) 207783u.

1915 K. Zhou, Z. Gao, J. Jiang, G. Wang and W. Keim, Dalian Gongxueyuan Xuebao, 24 (1985) 1; Chem. Abstr., 103 (1985) 196446n.

1916 S. Kvisle, U. Blindheim and O.H. Ellestad, J. Mol. Catal., 26 (1984) 341.

1917 T.V. Budantseva, I.A. Litvinov, V.I. Smetanyuk and V.A. Kabanov, Vysokomol. Soedin., Ser. A, 26 (1984) 588; Chem. Abstr., 101 (1984) 7684p.

1918 O.A. Sycheva, V.N. Mel'nikov and L.I. Vladimirova, Neftepererab. Neftekhim. (9) (Moscow), (1984) 20; Chem. Abstr., 102 (1985) 78282n.

1919 V.P. Yur'ev, G.A. Gailyunas and O.T. Kofanova, Russ. Chem. Rev., 53 (1984) 783; Usp. Khim., 53 (1984) 1352.

1920 W.A. Nugent, U.S. US 4,451,665 (1984); Chem. Abstr., 101 (1984) 151436b.

1921 W.A. Nugent and R.J. McKinney, J. Mol. Catal., 29 (1985) 65.

1922 I.B.M. Tkatchenko, D. Neibecker and P. Grenouillet, Fr. Demande FR 2,524,341 (1983); Chem. Abstr., 100 (1984) 67850d.

1923 P. Grenouillet, D. Neibecker and I. Tkatchenko, Organometallics, 3 (1984) 1130.

1924 G. Wilke, K. Sperling and L. Stehling, Ger. Offen. DE 3,336,691 (1985); Chem. Abstr., 103 (1985) 54563z.

1925 H. Fuellbier and M. Helms, Ger. (East) DD 212,507 (1984); Chem. Abstr., 102 (1985) 96214w.

1926 G. Oehme, J. Prakt. Chem., 326 (1984) 779.

1927 R.D. Knudsen and S.E. Reiter, U.S. US 4,482,640 (1984); Chem. Abstr., 102 (1985) 79447g.

1928 K.H.A. Ostoja-Starzewski, J. Witte and H. Bartle, Ger. Offen DE 3,336,500 (1985); Chem. Abstr., 103 (1985) 142517t.

1929 K.H.A. Ostoja-Starzewski, J. Witte and H. Bartl, Ger. Offen. DE 3,345,785 (1985); Chem. Abstr., 103 (1985) 178787v.

1930 Stamicarbon B.V., Neth. Appl. NL 82 04,876 (1984); Chem. Abstr., 101 (1984) 171945v.

1931 K.S. Minsker and M.M. Karpasas, Dokl. Chem., 283 (1985) 253; Dokl. Akad. Nauk SSSR, 283 (1985) 1201 [Chem.].

1932 A.R. Khan and S.A.K. Lodhi, Pak. J. Sci. Ind. Res., 28(1) (1985) 18; Chem. Abstr., 103 (1985) 124035e.

1933 T.-W. Lai, PhD Thesis, Penn. State Univ., 1983; Diss. Abstr. Int. B, 44 (1984) 2429.

1934 A.G. Azizov, D.B. Akhmedov and S.M. Aliev, Neftekhimiya, 24 (1984) 353; Chem. Abstr., 101 (1984) 110309u.

1935 G.A. Mamedaliev and A.G. Azizov, Polym. J. (Tokyo), 17 (1985) 1075; Chem. Abstr., 104 (1986) 34390.

1936 A.G. Azizov, Kh.Z. Mamedov and S.M. Aliev, Neftekhimiya, 25 (1985) 780; Chem. Abstr., 105 (1986) 42220p.

1937 G. Buono, C. Siv, G. Peiffer, C. Triantaphylides, P. Denis, A. Mortreux and F. Petit, J. Org. Chem., 50 (1985) 1781.

1938 A.R. Khan and S.A.K. Jodhi, Pak. J. Sci. Ind. Res., 28 (1985) 81; Chem. Abstr., 103 (1985) 178689q.

1939 S.A.K. Lodhi and A.R. Khan, Pak. J. Sci. Ind. Res., 26 (1983) 162; Chem. Abstr., 100 (1984) 86164z.

1940 Japan Synthetic Rubber Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60 26,016 [85 26,016] (1985); Chem. Abstr., 103 (1985) 23636x.

1941 T.-W. Lai and A. Sen, Organometallics, 3 (1984) 866.

1942 A. Sen, Energy Res. Abstr., 9 (1984) Abstr. No. 16985; Chem. Abstr., 101 (1984) 111462a.

1943 C.E. Carraher, T.A. Manek, D.J. Giron, M.L. Trombley, K.M. Casberg and W.J. Scott, Polym. Sci. Technol. (Plenum) 25 (New Monomers Polym.) (1984) 133; Chem. Abstr., 101 (1984) 16903m.

1944 R.E. Colborn and K.P.C. Vollhardt, J. Am. Chem. Soc., 108 (1986) 5470.

1945 J. Grobe, B.H. Schneider and H. Zimmerman, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 957.

1946 A. Mantovani, A. Marcomini and U. Belluco, J. Mol. Catal., 30 (1985) 73.

1947 U. Rosenthal, Ger. (East) DD 207,704 (1984); Chem. Abstr., 101 (1984) 170872g.

1948 U.M. Dzhemilev and F.A. Selimov, U.S.S.R. SU 1,097,588 (1984); Chem. Abstr., 101 (1984) 111557k.

1949 G.D. Jones and H.E. Doorenbos, J. Macromol. Sci., Chem., A22 (1985) 161.

1950 R. Diercks and H. tom Dieck, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 180.

1951 G.P. Chiusoli, L. Pallini and G. Terenghi, Eur. Pat. Appl. EP 93,467; Chem. Abstr., 100 (1984) 103173w.

1952 R.A. Earl and K.P.C. Vollhardt, J. Org. Chem., 49 (1984) 4786.

1953 H. Boennemann and B. Bogdanovic, Ger. Offen. DE 3,205,550 (1983); Chem. Abstr., 100 (1984) 22805b.

1954 D. Seyferth, E.W. Goldman and J. Escudié, J. Organomet. Chem., 271 (1984) 337.

1955 R. Diercks, L. Stamp and H. tom Dieck, Chem. Ber., 117 (1984) 1913.

1956 R. Diercks and H. tom Dieck, Chem. Ber., 118 (1985) 428.
1957 G.P. Chiusoli, L. Pallini and M.G. Terenghi, Transition Met. Chem., 10 (1985) 350.
1958 R. Rossi, A. Carpita and C. Bigelli, Tetrahedron Lett., 26 (1985) 523.
1959 V. Rautenstrauch, Tetrahedron Lett., 25 (1984) 3845.
1960 E.T. Sabourin, J. Mol. Catal., 26 (1984) 363.
1961 A.M. Saxman, R. Liepins and M. Aldissi, Prog. Polym. Sci., 11 (1985) 57.
1962 H. Naarmann, V. Muench and K. Penzien, Ger. Offen. DE 3,237,735 (1984); Chem. Abstr., 101 (1984) 91644f.
1963 H. Naarmann, V. Muench and K. Penzien, Ger. Offen. DE 3,237,736 (1984); Chem. Abstr., 101 (1984) 91645g.
1964 H. Naarmann and G. Koehler, Ger. Offen. DE 3,315,854 (1984); Chem. Abstr., 102 (1985) 62680e.
1965 S.-A. Chen and H.-J. Shy, J. Polym. Sci., Polym. Chem. Ed., 23 (1985) 2441.
1966 Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59 89,310 [84 89,310] (1984); Chem. Abstr., 101 (1984) 152511j.
1967 M.I. Cherkashin, M.G. Chauser, K.M. Dyumaev, Yu.K. Kirilenko, T.Ya. Vlasenko, L.A. Plyashkevich, G.I. Kudryavtsev and M.N. Belitsin, Vysokomol. Soedin., Ser. B, 27 (1985) 9; Chem. Abstr., 102 (1985) 114052y.
1968 Yu.K. Kirilenko, L.A. Plyashkevich, E.P. Perepechkina, B.A Batik'yan, G.I. Kudryavtsev and M.I. Cherkashin, Vysokomol. Soedin., Ser. B, 26 (1984) 368; Chem. Abstr., 101 (1984) 55600e.
1969 Yu.K. Kirilenko, L.A. Plyashkevich, V.K. Shitikov, V.N. Kalinin, G.I. Kudryavtsev, V.A. Sergeev, L.I. Zakharkin and B.P. Parfenov, Vysokomol. Soedin., Ser. A, 26 (1984) 1898; Chem. Abstr., 101 (1984) 231078b.
1970 S.G. Grigoryan, A.M. Arzumanyan, A.M. Gromov, G.V. Matirosyan and A.A. Matnishyan, Polym. Sci. USSR, 27 (1985) 1886; Vysokomol. Soedin., Ser. A, 27 (1985) 1681; Chem. Abstr., 104 (1985) 19856w.
1971 S.G. Grigoryan, M.M. Davtyan and A.A. Matnishyan, Elektron. Org. Mater., (1985) 87; Chem. Abstr., 107 (1987) 40378.
1972 E. Fanghaenel, A.M. Richter and J.M. Richter, Ger. (East) DD 211,118 (1984); Chem. Abstr., 102 (1985) 25247y.
1973 G.V. Ambartsumyan, S.B. Gevorkyan, V.G. Kharatyan, V.B. Gavalyan, A.A. Saakyan, S.G. Grigoryan and L.A. Akopyan, Arm. Khim. Zh., 37 (1984) 188; Chem. Abstr., 101 (1984) 73144p.
1974 Y. Okamoto and E.F. Hwang, U.S. US 4,497,727 (1985); Chem. Abstr., 102 (1985) 141864w.
1975 L. Stehling and G. Wilke, Angew. Chem., Int. Ed. Engl., 24 (1985) 496; Angew. Chem., 97 (1985) 505.
1976 D.J. Pasto and N.-Z. Huang, J. Org. Chem., 50 (1985) 4465.
1977 M. Iyoda, K. Nishioka, M. Nose, S. Tanaka and M. Oda, Chem. Lett., (1984) 131.
1978 R.V. Kunakova, V.V. Sidorova and U.M. Dzhemilev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2431; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2624.
1979 L.S. Hegedus, N. Kambe, Y. Ishii and A. Mori, J. Org. Chem., 50 (1985) 2240.
1980 P. Denis, A. Mortreux, F. Petit, G. Buono and G. Peiffer, J. Org. Chem., 49 (1984) 5274.
1981 D. Neibecker, M. Touma and I. Tkatchenko, Synthesis (1984) 1023.
1982 U. Schuchardt and F. Santos Dias, J. Mol. Catal., 29 (1985) 145.
1983 G.S. Groenewold and M.L. Gross, J. Am. Chem. Soc., 106 (1984) 6569.
1984 U.M. Dzhemilev, R.N. Fakhretdinov and A.G. Telin, U.S.S.R. SU 1,085,967 (1984); Chem. Abstr., 101 (1984) 91286r.
1985 T. Bartik, P. Heimbach, T. Himmler and R. Mynott, Angew. Chem., Int. Ed. Engl., 24 (1985) 313; Angew. Chem., 97 (1985) 345.
1986 A. Tenaglia, P. Brun and B. Waegell, J. Organomet. Chem., 285 (1985) 343.

1987 A. Tenaglia, P. Brun and B. Waegell, Tetrahedron Lett., 26 (1985) 3571.

1988 P. Brun, A. Tenaglia and B. Waegell, Tetrahedron Lett., 26 (1985) 5685.

1989 U.M. Dzhemilev, R.I. Khusnutdinov, N.A. Shchadneva, L.M. Khalilov, G.A. Tolstikov and O.M. Nefedov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2094; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2294.

1990 A. Behr and W. Keim, Angew. Chem., Int. Ed. Engl., 24 (1985) 314; Angew. Chem., 97 (1985) 326.

1991 R.N. Fakhretdinov, U.M. Dzhemilev, G.N. Koshel, A.G. Telin, R.M. Marvanov and T.N. Antonova, U.S.S.R. SU 1,129,196 (1984); Chem. Abstr., 103 (1985) 5936q.

1992 T. Antonsson and C. Moberg, Organometallics, 4 (1985) 1083.

1993 G.A. Gailyunas, F.G. Yusupova, L.S. Isaeva, T.A. Peganova, F.F. Kayumov and V.P. Yur'ev, J. Gen. Chem. USSR, 54 (1984) 2029; Zh. Obshch. Khim., 54 (1984) 2269.

1994 P. Brun, A. Tenaglia and B. Waegell, Tetrahedron, 41 (1985) 5019.

1995 T. Bartik, A. Behler, P. Heimbach, P. Ndalut, J. Sebastian and H. Sturm, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1529.

1996 T. Bartik, P. Heimbach and T. Himmler, J. Organomet. Chem., 276 (1984) 399.

1997 B.A. Dolgoplosk and E.I. Tinyakova, Russ. Chem. Rev., 53 (1984) 22; Usp. Khim., 53 (1984) 40.

1998 J. Dunkel, K. Dreschler, H.D. Lehmann, W. Schulz and U. Taeglich, Ger. (East) DD 213,934 (1984); Chem. Abstr., 102 (1985) 96773c.

1999 E. Uhlig and B. Hipler, Ger. (East) DD 208,981 (1984); Chem. Abstr., 101 (1984) 111576r.

2000 Z. Zhang and H. Zhang, Fenzi Kexue Yu Huaxue Yanjiu, 4 (1984) 279; Chem. Abstr., 101 (1984) 131150a.

2001 F. Dawans and J.P. Durand, Macromol. Synth., 9 (1985) 18; Chem. Abstr., 103 (1985) 71773k.

2002 R. Taube, J.-P. Gehrke and R. Radeglia, J. Organomet. Chem., 291 (1985) 101.

2003 Nippon Paint Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,142,929 [83,142,929] (1983); Chem. Abstr., 100 (1984) 53309x.

2004 R. Berger, L. Klimke, P. Schröder and W. Gaube, Z. Chem., 25 (1985) 226.

2005 J.-P. Bianchini, E.M. Gaydou, B. Waegell, A. Eisenbeis and W. Keim, J. Mol. Catal., 30 (1985) 197.

2006 W. Gaube and H. Stegemann, J. Prakt. Chem., 326 (1984) 729.

2007 R. Berger and W. Gaube, J. Prakt. Chem., 327 (1985) 643.

2008 P. Hayden and D. Wright, Brit. UK Pat. Appl. GB 2,114,974 (1983); Chem. Abstr., 100 (1984) 53561y.

2009 M. Röper, R. He and M. Schieren, J. Mol. Catal., 31 (1985) 335.

2010 R.N. Fakhretdinov, R.N. Khusnitdinov, I.B. Abdrakhmanov and U.M. Dzhemilev, J. Org. Chem. USSR, 20 (1984) 1002; Zh. Org. Khim., 20 (1984) 1101.

2011 U.M. Dzhemilev, R.N. Fakhretdinov and R.M. Safuanova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 1937; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2098.

2012 U.M. Dzhemilev, M.M. Sirazova, R.V. Kurakova, A.A. Panasenko and L.M. Khalilov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 339; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 372.

2013 U.M. Dzhemilev, R.V. Kunakova and M.M. Sirazova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2563; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2766.

2014 R.N. Fakhretdinov, A.G. Telin and U.M. Dzhemilev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2560; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2763.

2015 R.M. Safunova, R.N. Fakhretdinov and U.M. Dzhemilev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 653; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 703.

2016 N.T. Byrom, R. Grigg, B. Kongkathip, G. Reimer and A.R. Wade, J. Chem. Soc., Perkin Trans. 1 (1984) 1643.
2017 A. Behr, K.-D. Juszak and R. He, Int. Congr. Catal., [Proc.], 8th, (1984) 5, V565-V572; Chem. Abstr., 106 (1987) 101530k.
2018 U.M. Dzhemilev, R.V. Kunakova and V.V. Sidorova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 34 (1985) 2102; Izv. Akad. Nauk SSSR, Ser. Khim., (1985) 2273.
2019 Y. Inoue, R. Ohashi, M. Toyofuku and H. Hashimoto, Nippon Kagaku Kaishi, (1985) 533.
2020 M.J. Mullins U.S. US 4,431,592 (1984); Chem. Abstr., 100 (1984) 210620m.
2021 R. Bortolin and A. Musco, J. Mol. Catal., 22 (1984) 319.
2022 A. Citterio, E. Comunale and A. Musco, J. Chem. Res., S, (1984) 77.
2023 A. Citterio, P. De Angelis, P. Longo and A. Musco, J. Chem. Res., S, (1985) 316.
2024 T. Harada, M.C. Cleij, R.J.M. Nolte, A.M.F. Hezemans and W. Drenth, J. Chem. Soc., Chem. Commun., (1984) 726.
2025 H.G.J. Visser, R.J.M. Nolte, J.W. Zwikker and W. Drenth, J. Org. Chem., 50 (1985) 3133.
2026 H.G.J. Visser, R.J.M. Nolte, J.W. Zwikker and W. Drenth, J. Org. Chem., 50 (1985) 3138.
2027 R.B. King and L. Borodinsky, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 26(1) (1985) 266.
2028 R.B. King and L. Borodinsky, Macromolecules, 18 (1985) 2117.
2029 Asahi Glass Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,185,625 [83,185,625] (1983); Chem. Abstr., 100 (1984) 192567t.
2030 Asahi Glass Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,185,626 [83,185,626] (1983); Chem. Abstr., 100 (1984) 192566s.
2031 J.-F. Fauvarque, A. Digua, M.-A. Petit and J. Savard, Makromol. Chem., 186 (1985) 2415.
2032 Dainippon Ink and Chemicals, Inc., Jpn. Kokai Tokkyo Koho JP 59,176,317 [84,176,317] (1984); Chem. Abstr., 102 (1985) 62696q.
2033 Showa Denko K.K., Jpn. Kokai Tokkyo Koho JP 59,221,330 [84,221,330] (1984); Chem. Abstr., 102 (1985) 149973b.
2034 T. Yamamoto, K. Osakada, T. Wakabayashi and A. Yamamoto, Makromol. Chem., Rapid Commun., 6 (1985) 671.
2035 Tokyo Industrial University, Jpn. Kokai Tokkyo Koho JP 58,147,426 [83,147,426] (1983); Chem. Abstr., 100 (1984) 86315z.
2036 C. van Pham, R.S. Macomber, H.B. Mark and H. Zimmer, J. Org. Chem., 49 (1984) 5250.
2037 Union Carbide Corp., Jpn. Kokai Tokkyo Koho JP 58,118,826 [83,118,826] (1983); Chem. Abstr., 100 (1984) 35026y.
2038 S.S. Labadie and J.K. Stille, Tetrahedron, 40 (1984) 2329.
2039 S. Matsubara, N. Tsuboniwa, Y. Morizawa, K. Oshima and H. Nozaki, Bull. Chem. Soc. Jpn., 57 (1984) 3242.
2040 N.J. O'Reilly, M. Maruta and N. Ishikawa, Chem. Lett., (1984) 517.
2041 C. Petrier, J.-L. Luche and C. Dupuy, Tetrahedron Lett., 25 (1984) 3463.
2042 A.E. Greene, J.-P. Lansard, J.-L. Luche and C. Petrier, J. Org. Chem., 49 (1984) 931.
2043 C. Petrier, J.C. de Souza Barbosa, C. Dupuy and J.-L. Luche, J. Org. Chem., 50 (1985) 5761.
2044 J.C. de Souza Barboza, C. Pétrier and L.-L. Luche, Tetrahedron Lett., 26 (1985) 829.
2045 T. Mitsudo, M. Kadokura and Y. Watanabe, Tetrahedron Lett., 26 (1985) 3697.
2046 M. Basato, B. Corain, M. Cofler, A.C. Veronese and G. Zanotti, J. Chem. Soc., Chem. Commun., (1984) 1593.
2047 F. Henin and J. Muzart, Synth. Commun., 14 (1984) 1355.
2048 S. Cacchi and G. Palmieri, J. Organomet. Chem., 282 (1985) C3.
2049 S. Cacchi, F. La Torre and G. Palmieri, J. Organomet. Chem., 268 (1984) C48.

2050 Y.T. Hong, J.T. Lee, C.M. Ryu and J.I. Kim, Taehan Hwahakhoe Chi, 29 (1985) 287; Chem. Abstr., 104 (1986) 19393t.

2051 G.R. Newkome and A. Yoneda, Makromol. Chem., Rapid Commun., 6 (1985) 451.

2052 C.M. Andersson, K. Karabelas, A. Hallberg and C. Andersson, J. Org. Chem., 50 (1985) 3891.

2053 S. Cacchi and G. Palmieri, Synthesis (1984) 575.

2054 T. Jeffery, J. Chem. Soc., Chem. Commun., (1984) 1287.

2055 A. Spencer, J. Organomet. Chem., 270 (1984) 115.

2056 A. Spencer, Eur. Pat. Appl. EP 103,544 (1984); Chem. Abstr., 101 (1984) 72454c.

2057 T.M. Bargar, T. Wilson and J.K. Daniel, J. Het. Chem., 22 (1985) 1583.

2058 A. Spencer, J. Organomet. Chem., 265 (1984) 323.

2059 P.J. Harrington and L.S. Hegedus, J. Org. Chem., 49 (1984) 2657.

2060 T. Mitsudo, W. Fischetti and R.F. Heck, J. Org. Chem., 49 (1984) 1640.

2061 T. Jeffery, Tetrahedron Lett., 26 (1985) 2667.

2062 W.J. Scott, M.R. Peña, K. Swärd, S.J. Stoessel and J.K. Stille, J. Org. Chem., 50 (1985) 2302.

2063 K. Karabelas and A. Hallberg, Tetrahedron Lett., 26 (1985) 3131.

2064 K. Kikukawa, K. Ikenaga, K. Kono, K. Toritani, F. Wada and T. Matsuda, J. Organomet. Chem., 270 (1984) 277.

2065 J.B. Davison, N.M. Simon and S.A. Sojka, J. Mol. Catal., 22 (1984) 349.

2066 A.G. Kurbanov, A.M. Aliev, A.R. Babaeva and L.E. Ternorutskii, Azerb. Khim. Zh., (2) (1985) 9; Chem. Abstr., 104 (1986) 206790g.

2067 S. Torii, H. Tanaka and K. Morisaki, Chem. Lett., (1985) 1353.

2068 W. Smadja, G. Ville and G. Cahiez, Tetrahedron Lett., 25 (1984) 1793.

2069 W.H. Daly and C.H. Sun, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 26(1) (1985) 90; Chem. Abstr., 103 (1985) 104620p.

2070 N.F. Ford, L.J. Browne, T. Campbell, C. Gemenden, R. Goldstein, C. Gude and J.W.F. Wasley, J. Med. Chem., 28 (1985) 164.

2071 G. Bocelli, M. Catellani, G.P. Chiusoli and S. Larocca, J. Organomet. Chem., 265 (1984) C9.

2072 G. Bocelli, M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 279 (1984) 225.

2073 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 286 (1985) C13.

2074 M. Catellani, G.P. Chiusoli and S. Ricotti, J. Organomet. Chem., 296 (1985) C11.

2075 M. Catellani, G.P. Chiusoli, S. Ricotti and F. Sabini, Gazz. Chim. Ital., 115 (1985) 685.

2076 M. Catellani, G.P. Chiusoli and A. Mari, J. Organomet. Chem., 275 (1984) 129.

2077 R.C. Larock and S. Babu, Tetrahedron Lett., 26 (1985) 2763.

2078 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 275 (1984) 257.

2079 J. Tsuji and H. Nagashima, Tetrahedron, 40 (1984) 2699.

2080 Y. Murakami, Y. Yokoyama and T. Aokai, Heterocycles, 22 (1984) 1493.

2081 T. Itahara, K. Kawasaki and F. Ouseto, Bull. Chem. Soc. Jpn., 57 (1984) 3488.

2082 T. Itahara and F. Ouseto, Synthesis (1984) 488.

2083 N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2364; Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2580.

2084 M.E. Perlman, K.A. Watanabe, R.F. Schinazi and J.J. Fox, J. Med. Chem., 28 (1985) 741.

2085 D.E. Bergstrom, J.L. Ruth, P.A. Reddy and E. De Clercq, J. Med. Chem., 27 (1984) 279.

2086 H.T. Kalinoski, U. Hacksell, D.F. Barofsky, E. Barofsky and G.D. Daves, J. Am. Chem. Soc., 107 (1985) 6476.

2087 R.C. Larock, S. Varaprath, H.H. Lau and C.A. Fellows, J. Am. Chem. Soc., 106 (1984) 5274.

2088 S. Araki, M. Ohmura and Y. Butsugan, Bull. Chem. Soc. Jpn., 58 (1985) 1607.

2089 Y. Yamazaki, T. Suzuki and M. Uchiyama, Eur. Pat. Appl. EP 119,065 (1984); Chem. Abstr., 102 (1985) 61912v.
2090 M. Uchiyama, T. Suzuki and Y. Yamazaki, Nippon Kagaku Kaishi, (1984) 580; Chem. Abstr., 101 (1984) 90474p.
2091 K. Sugioka, M. Uchiyama, T. Suzuki and Y. Yamazaki, Nippon Kagaku Kaishi, (1985) 527.
2092 A. Nishimura, M. Uchiyama, T. Suzuki and Y. Yamazaki, Nippon Kagaku Kaishi, (1985) 558.
2093 T. Itahara, J. Org. Chem., 50 (1985) 5272.
2094 T. Itahara, M. Hashimoto and H. Yumisashi, Synthesis (1984) 255.
2095 T. Itahara, J. Org. Chem., 50 (1985) 5546.
2096 K. Kikukawa, K. Ikenaga, F. Wada and T. Matsuda, Tetrahedron Lett., 25 (1984) 5789.
2097 F. Mercier, F. Mathey, J. Fischer and J.H. Nelson, J. Am. Chem. Soc., 106 (1984) 425.
2098 D.E. Ames and A. Opalko, Tetrahedron, 40 (1984) 1919.
2099 S. Cacchi, M. Felici and B. Pietroni, Tetrahedron Lett., 25 (1984) 3137.
2100 A. Arcadi, S. Cacchi and F. Marinelli, Tetrahedron, 41 (1985) 5121.
2101 V. de Felice, A. de Renzi, M. Funicello, A. Panunzi and A. Saporito, Gazz. Chim. Ital., 115 (1985) 13.
2102 A. de Renzi, A. Panunzi, A. Saporito and A. Vitagliano, J. Chem. Soc., Perkin Trans., 1, (1985) 1095.
2103 M. Ahmar, B. Cazes and J. Gore, Tetrahedron Lett., 25 (1984) 4505.
2104 K. Kikukawa, M. Naritomi, G.-X. He, F. Wada and T. Matsuda, J. Org. Chem., 50 (1985) 299.
2105 Y. Akita, A. Inoue, K. Yamamoto, A. Ohta, T. Kurihara and M. Shimizu, Heterocycles, 23 (1985) 2327.
2106 M. Mori, Y. Kubo and Y. Ban, Tetrahedron Lett., 26 (1985) 1519.
2107 M. Mori, N. Kanda, I. Oda and Y. Ban, Tetrahedron, 41 (1985) 5465.
2108 M. Mori, Y. Kubo, N. Kanda, I. Oda and Y. Ban, Heterocycles, 23 (1985) 220.
2109 J.G. Rodriguez and L. Canoira, J. Het. Chem., 22 (1985) 883.
2110 L. Canoira and J.G. Rodriguez, J. Het. Chem., 22 (1985) 1511.
2111 L.S. Hegedus, T.A. Mulhern and A. Mori, J. Org. Chem., 50 (1985) 4282.
2112 R. Grigg, P. Stevenson and T. Worakun, J. Chem. Soc., Chem. Commun., (1984) 1073.
2113 R. Grigg, P. Stevenson and T. Worakun, J. Chem. Soc., Chem. Commun., (1985) 971.
2114 S.A. Lebedev, V.S. Lopatina, T.V. Luk'yanova, S.S. Berestova, R.R. Shifrina, N.N. Shapet'ko, É.S. Petrov and I.P. Beletskaya, J. Org. Chem. USSR, 21 (1985) 652; Zh. Org. Khim., 21 (1985) 721.
2115 K. von Werner, J. Fluorine. Chem., 28 (1985) 229.
2116 K. von Werner, Ger. Offen. DE 3,338,299 (1985); Chem. Abstr., 103 (9185) 214858e.
2117 Q. Chen and Z. Yang, Huaxue Xuebao, 43 (1985) 1118; Chem. Abstr., 105 (1986) 152495q.
2118 V. Rautenstrauch, J. Org. Chem., 49 (1984) 950.
2119 V. Rautenstrauch, Eur. Pat. Appl. EP 110,142 (1984); Chem. Abstr., 101 (1984) 170776d.
2120 V. Rautenstrauch, U. Burger and P. Wirthner, Chimia, 39 (1985) 225.
2121 V. Rautenstrauch, Chimia, 39 (1985) 227.
2122 A.S. Kende, R.A. Battista and S.B. Sandoval, Tetrahedron Lett., 25 (1984) 1341.
2123 A.S. Kende and D.J. Wustrow, Tetrahedron Lett., 26 (1985) 5411.
2124 V.P. Lopatinskii, S.A. Tuzovskaya and V.M. Sutyagin, J. Org. Chem. USSR, 20 (1984) 2020; Zh. Org. Khim., 20 (1984) 2217.
2125 B.M. Trost and M. Lautens, J. Am. Chem. Soc., 107 (1985) 1781.
2126 B.M. Trost and M. Lautens, Tetrahedron Lett., 26 (1985) 4887.
2127 B.M. Trost and J.Y.L. Chung, J. Am. Chem. Soc., 107 (1985) 4586.
2128 B.M. Trost and K. Burgess, J. Chem. Soc., Chem. Commun., (1985) 1084.

2129 M. Iyaoda, M. Sakaitani, T. Miyazaki and M. Oda, Chem. Lett., (1984) 2005.
2130 R.C. Larock, L.W. Harrison and M.H. Hsu, J. Org. Chem., 49 (1984) 3662.
2131 H. Hoberg and E. Hernandez, Angew. Chem., Int. Ed. Engl., 24 (1985) 961; Angew. Chem., 97 (1985) 987.
2132 R. Grigg, J.F. Malone, T.R.B. Mitchell, A. Ramasubbu and R.M. Scott, J. Chem. Soc., Perkin Trans., 1, (1984) 1745.
2133 D.C. Gautam and R.A. Misra, Synth. React. Inorg. Met.-Org. Chem., 14 (1984) 293.
2134 N.M. Abramova, S.V. Zotova and O.A. Nesmeyanova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 33 (1984) 2578.
2135 N.M. Abramova, S.V. Zotova and O.A. Nesmeyanova, Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 2813.
2136 W. Fischetti and R.F. Heck, J. Organomet. Chem., 293 (1985) 391.
2137 S. Sasaoka, T. Yamamoto, H. Kinoshita, K. Inomata and H. Kotake, Chem. Lett., (1985) 315.
2138 Y. Huang, Q. Zho and J. Li, Youji Huaxue, (1985) 332; Chem. Abstr., 103 (1985) 177933c.
2139 T. Sakakibara, S. Karasumaru and I. Kawano, J. Am. Chem. Soc., 107 (1985) 6417.
2140 E. Wenkert, M.H. Leftin and E.L. Michelotti, J. Org. Chem., 50 (1985) 1122.
2141 Q. Fang, G. Xi, Z. Zhang and R. Wang, Huaxue Xuebao, 43 (1985) 92; Chem. Abstr., 102 (1985) 203406j.
2142 T. Mitsudo, M. Kadokura and Y. Watanabe, Tetrahedron Lett., 26 (1985) 5143.
2143 M. Ishikawa, S. Matsuzawa, T. Higuchi, S. Kamitori and K. Hirotsu, Organometallics, 4 (1985) 2040.
2144 K. Maruoka, H. Sano, Y. Fukutani and H. Yamamoto, Chem. Lett., (1985) 1689.
2145 P. Binger, J. McMeeking and H. Schäfer, Chem. Ber., 117 (1984) 1551.
2146 M. Helms and H. Fuellbier, Wiss. Z. Ernst-Moritz-Arndt-Univ. Greifsw. Math.-Naturwiss. Reihe, 34 (1985) 34; Chem. Abstr., 104 (1986) 206431r.
2147 H. Fuellbier and M. Helms, Ger. (East) DD 215,306 (1984); Chem. Abstr., 103 (1985) 54570z.
2148 F. Kawamoto, S. Tanaka and Y. Honma, U.S. US 4,425,277 (1984); Chem. Abstr., 100 (1984) 120533f.
2149 P. Martin, Helv. Chim. Acta, 67 (1984) 1647.
2150 P. Martin, Brit. UK Pat. Appl. GB 2,114,568 (1983); Chem. Abstr., 100 (1984) 6338w.
2151 T. Mukaiyama, M. Ohshima and M. Murakami, Chem. Lett., (1984) 265.
2152 B.H. Lipshutz, D. Pollart, J. Monforte and H. Kotsuki, Tetrahedron Lett., 26 (1985) 705.
2153 A. Roloff, Chimia, 39 (1985) 392.
2154 Mitsubishi Petrochemical Co., Ltd., Jpn. Kokai Tokkyo Koho JP 58,162,542 [83,162,542] (1983); Chem. Abstr., 100 (1984) 51249d.
2155 R.K. Valetdinov, A.Ya. Dorfman, A.A. Kutuev and I.T. Shaikhutdinova, Khim. Tekhnol. Elementoorg. Soedin. Polim., (1984) 22.
2156 E. Dinjus and D. Walther, Ger. (East) DD 208,607 (1984); Chem. Abstr., 101 (1984) 151422u.
2157 A. Carpita, F. Bonaccorsi and R. Rossi, Tetrahedron Lett., 25 (1984) 5193.
2158 Kuraray Co., Ltd., Jpn. Kokai Tokkyo Koho JP 59,175,451 [84,175,451] (1984); Chem. Abstr., 102 (1985) 78384x.
2159 Yu.N. Usov, E.D. Chekurovskaya, T.G. Vaistub, A.N. Akimov, O.A. Bozhenova, V.I. Bystrenina and N.N. Sorokin, Khim. Tekhnol. Elementoorg. Soedin. Polim., (1984) 3; Chem. Abstr., 102 (1985) 95195d.
2160 S. Suzuki, K. Kanehira, Y. Fujita and J. Otera, Nippon Kagaku Kaishi, (1985) 552; Chem. Abstr., 104 (1986) 109962g.
2161 H. Mastalerz, J. Org. Chem., 49 (1984) 4092.

2162 B. Odell, G. Earlam and D.J. Cole-Hamilton, J. Organomet. Chem., 290 (1985) 241.
2163 G. Mehta and M.S. Nair, J. Am. Chem. Soc., 107 (1985) 7519.
2164 K.A. Parker, K.A. Koziski and G. Breault, Tetrahedron Lett., 26 (1985) 2181.
2165 S. Murahashi, T. Tsumiyama and Y. Mitsue, Chem. Lett., (1984) 1419.
2166 S. Danishefsky, D.F. Harvey, G. Quallich and B.J. Vang, J. Org. Chem., 49 (1984) 392.
2167 Nippon Zeon Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60 45,544 [85 45,544] (1985); Chem. Abstr., 103 (1985) 123001d.
2168 M. Ihara, M. Toyota, K. Fukumoto and T. Kametami, Tetrahedron Lett., 26 (1985) 1537.
2169 Y. Tsuji, J. Shida, R. Takeuchi and Y. Watanabe, Chem. Lett., (1984) 889.
2170 A.J. Abatjoglu and D.R. Bryant, Organometallics, 3 (1984) 932.
2171 A.B. Goel, H.J. Richards and J.H. Kyung, Tetrahedron Lett., 25 (1984) 391.
2172 M. Regitz and S.G. Khbeis, Chem. Ber., 117 (1984) 2233.
2173 S.G. Khbeis, G. Maas and M. Regitz, Tetrahedron, 41 (1985) 811.
2174 K.-L. Hoffmann, G. Maas and M. Regitz, Chem. Ber., 118 (1985) 3700.
2175 K. Yamamoto, A. Matsukawa and I. Murata, Chem. Lett., (1985) 1119.
2176 K. Fischer, K. Jonas, A. Mollbach and G. Wilke, Z. Naturforsch., B, Anorg. Chem., Org. Chem., 39B (1984) 1011.
2177 K. Ogura, N. Shibuya, K. Takahashi and H. Iida, Bull. Chem. Soc. Jpn., 57 (1984) 1092.
2178 J. Corey, C. Guérin, B. Henner, B. Kolani, W.W. Choy, W.C. Man and R. Corriu, C.R. Acad. Sci. Paris, 300 (1985) 331.
2179 D. Seyferth, M.L. Shannon, S.C. Vick and T.F.O. Lim, Organometallics, 4 (1985) 57.
2180 M. Ishikawa, S. Matsuzawa, K. Hirotsu, S. Kamitori and T. Higuchi, Organometallics, 3 (1984) 1930.
2181 Z. Lysenko and R.G. Pews, U.S. US 4,435,573 (1984); Chem. Abstr., 100 (1984) 191748r.
2182 D.L. Coffen, B. Schaer, F.T. Bizzarro and J.B. Cheung, J. Org. Chem., 49 (1984) 296.
2183 S.M. Ali, J. Iqbal and M. Ilyas, J. Chem. Res., S, (1984) 236.
2184 S.M. Ali, J. Iqbal and M. Ilyas, Chem. Ind. (London), (1985) 276.
2185 E.W. Corcoran and L.G. Sneddon, J. Am. Chem. Soc., 106 (9184) 7793.
2186 H. Hoberg and K. Sümmermann, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 1032.
2187 A. Matsuura, A. Nishinaga, Y. Ito and T. Matsuura, Chem. Lett., (1985) 993.