Coordination Chemistry Reviews, 72 (1986) 1—195
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

1. PALLADIUM AND PLATINUM

P.A. CHALONER

CONTENTS

0010-8545/86/$68.25

INTRODUCTION

This review covers mainly the papers recorded in Chemical Abstracts between Volume 97, issue 21 and Volume 99, issue 24, as well as the 1983 issues of the major English language inorganic chemistry journals. Thus, although most of the papers covered were published in 1983, many from 1982 are also included, together with earlier work slow to reach Chemical Abstracts.

As always, the number of references has increased overall, but some general trends may also be noted. More papers are reported in the sections dealing with lower oxidation states and in particular with chemistry related to catalytic reactions. In this context many data concerning tin complexes of platinum are considered, since this is an important catalytic system for a range of transformations. The importance of the complexes of biomolecules continues to be noted by many groups and a newly fashionable area seems to be that of porphyrin complexes and their analogues.

A number of reviews have been published. The historical importance of the platinum metals in the development of chemistry, particularly coordination chemistry, is considered by Soviet workers [1]. The whole of the platinum group and the chemistry of their complexes is included in the account of Wallbridge [2], whilst Bailar reviews only coordination compounds of platinum(II) and platinum(IV) [3]. "Classic" and "modern" aspects of palladium and platinum coordination compounds are discussed by Beck [4].

1.1 PALLADIUM (VI) AND PLATINUM(VI)

$[PdF_6]$ was synthesised by reaction of palladium powder with fluorine atoms. This dark red material is thermally unstable and decomposes at a significant rate even at 273 K to yield $[PdF_4]$ and molecular fluorine [5]. Both $[PdF_6]$ and $[PtF_6]$ have body-centred cubic structures at room temperature with an orthorhombic form at higher temperature. The stabilities and

structures of the platinum metal fluorides are also reviewed [6]. The general chemistry of palladium and platinum in higher oxidation states (Pt(VI), Pt(IV) and Pd(IV)) has been reviewed [7].

Palladium(V) complexes are said to be formed on oxidation of metal fluorides by $[PdF_6]$ [5] but no other papers dealing with palladium (V) or platinum(V) have been published in the last year.

1.2 PALLADIUM(IV) AND PLATINUM(IV)

The thermodynamics of the formation of outer sphere complexes of coordination compounds of platinum(IV) and other platinum group metals have been reviewed [8]. The best separation of platinum(IV) from rhodium(III) is reported to be achieved using ascorbic acid as a reducing agent under carefully controlled conditions [9].

1.2.1 Complexes with Group VII donor ligands

The structure of $[BrF_2]_2[PtF_6].(BrF_2)_2$, formed on reaction of $[PtF_4]$ with $[BrF_3]$, was determined by X-ray diffraction and ^{19}F NMR spectroscopy [10]. A general valence force field has been applied to hexahalide anions of Pt(IV) ($[PtF_6]^{2-}$, $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$) using the molecular kinetics constants method to determine the charactertistic molecular constants [11]. Analysis of the biexponential luminescence decay curves for $K_2[PtX_6]$ (X = F, Cl or Br) gave two time constants. The contribution of the faster relaxation component increases on transition from $[PtF_6]^{2-}$ to $[PtBr_6]^{2-}$, as well as on increasing the temperature from 77 K to 300 K [12]. The bimolecular rate constants for luminescence quenching of $[Cr(bipy)_3]^{3+}$, $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ by $[PtX_6]^{2-}$ (X = F, Cl, Br or SCN) have been determined [13].

The chlorine K X-ray absorption spectra of $K_2[PdCl_6]$, $K_2[PtCl_6]$, $K_2[PdCl_4]$ and $K_2[PtCl_4]$ have been obtained. An intense white line at the

absorption threshold with a chemical shift related to the ionisation potentials of palladium and platinum corresponds to the transition from the Cl 1s level to the lowest unoccupied antibonding orbital originating from the Pd 4d, Pt 5d or Cl 3p orbitals [14]. Relativistic multiple scattering X_α calculations on $[PtCl_6]^{2-}$ in octahedral symmetry have been undertaken. The theoretical predictions concerning photoionisation and optical spectra are in good agreement with experimental data [15].

By applying a rigid sphere model, using the assumption of free cation motion within a spherical cavity consisting of twelve halogen atoms, the stability condition for $K_2[PtCl_6]$ has been determined. The temperature at which cubic $K_2[PtCl_6]$ should undergo distortion was calculated and conforms to the experimental observation [16]. The low temperature tunnel splittings of reorienting $[NH_4]^+$ in a tetrahedral surround were determined for $[NH_4]_2[MCl_6]$ (M = Pt, Re or Te), and found to depend exponentially on lattice dimensions [17].

Theoretical calculations were used to assist in assigning experimental spectra of $L_2[MCl_6]$, L = $[(C_8H_{17})_3NH]^+$ and M = Os, Re, Ir or Pt. The N-H stretching frequency is substantially affected by the nature of the metal [18].

The reduction of $H_2[PtCl_6]$ by iron(II) sulphate in aqueous H_2SO_4 in the presence of an alumina catalyst was shown to be first order in Pt(IV), 0.56 in Fe(II) and -0.21 in Cl^-. The initial product is $Fe[PtCl_6]$ which is adsorbed on the alumina and reduced by Fe(II) to give, ultimately, a thin platinum metal film [19]. $[PtCl_6]^{2-}$ is also very rapidly reduced by ferrocene, the products at room temperature being $[PtCl_4]^{2-}$ and ferrocinium cation. At higher temperatures more extensive reduction gives platinum metal [20]. The adsorption of $H_2[PtCl_6]$ on alumina to give reforming catalysts has been studied [21].

Solid state thermolysis of $[(py)_2I]_2[PtX_6]$ (X = Cl or Br) yields *cis*-$[Pt(py)_2X_4]$, whilst $[(py)_2Br]_2[PtCl_6]$ gives $[Pt(py)_2Cl_4]$ and $[pyH]_2[PtCl_6]$

[22]. Disproportionation constants for Pt(IV) and Pt(II) halides and the equilibrium constant for reaction (1) (X = Cl or Br) have been determined [23]. The effect of HCl concentration on extraction distribution coefficients, when chloro complex acids of Pd(IV) and Pt(IV) are extracted by tributyl phosphate was examined [24].

$$[PtX_6]^{2-} + H_2O \rightleftharpoons [PtX_5(OH_2)]^- + X^- \qquad (1)$$

Oxidation of $[PtCl_4]^{2-}$ by molecular bromine in HBr solution yielded *trans*-$[PtCl_4Br_2]^{2-}$, whereas in HCl, $[PtCl_5Br]^{2-}$ is obtained. A sample of *trans*-$[PtCl_4Br_2]^{2-}$ was obtained in very high purity when CH_2Cl_2 is used as solvent. The literature concerning *trans*-$[PtCl_4Br_2]^{2-}$ has been critically discussed [25]. The ^{195}Pt NMR spectra of $[PtCl_nBr_{6-n}]^{2-}$ (n = 1 - 5) have been measured. The *cis-trans* isomerisations of $[PtCl_nBr_{6-n}]^{2-}$ (n = 2 or 4) and the *fac-mer* isomerisation of $[PtCl_3Br_3]^{2-}$ are sufficiently slow on the NMR timescale to allow the unambiguous assignments of the ^{195}Pt signals. *cis*- and *fac*-isomers give rise to signals at 12 - 15 ppm lower field than the *trans*- and *mer*-compunds [26].

The structures of the *cis, cis, trans*-, *trans, trans, trans*- and *cis, trans, cis*-isomers of $[PtCl_2(NH_3)_2(OH)_2]$ have been studied by ^{15}N and ^{195}Pt NMR spectroscopy and by X-ray diffraction. All are octahedral with normal bond lengths and an extensive network of hydrogen bonds. A facile isomerisation of the *trans, trans, trans*- to the *cis, trans, cis*-isomer on recrystallisation from water is thought to involve dissociation of $[HO]^-$ or H_2O_2 since it is suppressed by the presence of H_2O_2 [27].

The phases of the complex $[Me_4N]_2[PtBr_6]$ have been studied by NMR spectroscopic techniques, X-ray powder diffraction and DTA. At room temperature an E_{d3c} cubic structure is adopted, with an F_{m3m} cubic phase at higher temperatures [28]. Crystals of M_2PtI_6 (M = K, Rb, Cs, NH_4 or Tl) were obtained by heating $[PtI_4]$ or $H_2[PtCl_6]$ in highly concentrated solutions of MI

containing HI and I_2. The complexes for M = Rb, Cs or NH_4 adopt the cubic $K_2[PtCl_6]$ structure and are poorly soluble in water. For M = K or Tl, a tetragonally distorted structure is determined from single crystal data, and the complexes are more soluble [29]. $[N_2H_5]_2[PtI_6]$ and $[N_2H_5]_2[PtI_5(H_2O)]$ were obtained from $H_2[PtCl_6]$, HI and hydrazine hydrochloride in aqueous solution. $[N_2H_5]_2[PtI_6]$ was shown by X-ray diffraction to have a structure similar to that of $K_2[PtCl_6]$ whereas $[N_2H_5]_2[PtI_5(H_2O)]$ resembles the linear chain mixed valence compounds (*vide infra*) and has anisotropic properties [30].

x.2.2 Complexes with Group VI donor ligands

The first X-ray structural study of a heteropolytungstate containing platinum(IV), $Na_5[H_3PtW_6O_{24}].20\ H_2O$ is reported. The polyanion, synthesised from $Na_2[Pt(OH)_6]$ and $Na_2[WO_4]$, has approximately D_{3d} symmetry analogous to the Anderson type heteropolytungstate anion in $[MnW_6O_{24}]^{8-}$ [31]. An X-ray powder study of $Ca[Pd(OH)_6]$ is reported [32].

Treatment of $[Pt(NH_3)_5Cl]Cl_3$ with CF_3SO_3H, followed by ether at 5 °C yields $[Pt(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_3$. Triflate acts as a monodentate *o*-donor weak field ligand and is an excellent leaving group, allowing the facile synthesis of a wide range of complexes of the type $[Pt(NH_3)_5L][CF_3SO_3]_4$ [33]. In $[Pt\{(H_2N)_2CO\}Cl_4]$, prepared from urea and $H_2[PtCl_6]$, the Pt(IV) is octahedral and the urea is coordinated through oxygen [34].

Oxidation of $[Pt(C_2O_4)_2]^{2-}$ by X_2 (X = Cl, Br, I or OH) yields the platinum(IV) complexes *trans*-$[Pt(C_2O_4)_2X_2]^{2-}$, which were isolated as the $[Bu_4N]^+$ salts. The complexes were characterised by IR, Raman and electronic spectroscopy and show intense ligand to metal charge transfer bands in the UV/visible region [35]. β-Diketonate complexes of octahedral platinum(IV) were shown to be generally more volatile than those of square planar platinum(II) [36].

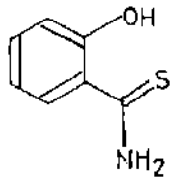
Rate data for reaction (2) are consistent with a mechanism involving

direct addition of S(IV) to the Pt-OH moiety without Pt-O cleavage. (1) is the first example of a stable, isolable, *o*-bonded sulphito complex. In the

$$[Pt(NH_3)_5(OH_2)]^{4+} \xrightarrow{[HSO_3]^-,\ SO_2,\ H_2O} [Pt(NH_3)_5(OSO_2)]^{2+}.SO_3.2H_2O \quad (2)$$

(1)

presence of an excess of sulphite, (1) is slowly converted to *cis*-$[Pt(NH_3)_4(SO_3)_2].2H_2O$ [37]. Platinum(IV) complexes of (2), (LH), of composition $[PtL_2(LH)_2]Cl_2$, contain two ligands which act as *o,s*-chelates and two which are bonded only through sulphur [38].



(2)

The lowest excited ligand field state has been shown to be responsible for the photochemical reactions of $[Pt(SCN)_6]^{2-}$ to yield platinum(II). The quantum yield may be determined by monitoring $[SCN]^-$ produced on photolysis [39]. Precipitation of the platinum group metals (including Pt(IV) and Pd(II)) in the presence of $(PhS)_3P$ occurs *via* reactions such as (3) and (4) [40].

$$(PhS)_3P + H_2O \longrightarrow PhSH + (PhS)_2POH \quad (3)$$

$$[PdCl_4]^{2-} + 2PhSH \longrightarrow [(PhS)_2Pd] + 2H^+ + 4Cl^- \quad (4)$$

Definitive syntheses for $[NH_4]_2[Pt(S_5)_3]$ and $[Pr_4N]_2[Pt(S_5)_3]$ have been published. Platinum(IV) is coordinated in a pseudooctahedral manner to three pentasulphide ligands [41]. New preparative methods are reported for $[PtMe_3(MeE(CH_2)_nE'Me)]$ (X = Cl, Br or I; n = 2 or 3; E, E' = S or Se) and

the variation of stability with ring size assessed ^{195}Pt, ^{77}Se and ^{13}C NMR spectroscopic parameters were correlated with structures [42]. The new complex $[Pt(MeSCH_2CH_2SMe)_2][ClO_4]_2$ has been compared with known analogues. It was concluded that the rate of inversion at the coordinated sulphur atom depends strongly on the nature of the metal ion, but much less on the ligand *trans* to sulphur [43].

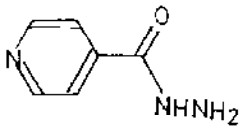
$[Pt(pmdtc)_2(pip)_2]Cl_2$ (Hpmdtc = pentamethylene dithiocarbamic acid) has been shown to be a 6-coordinate octahedral complex with each carbamic acid acting as an *S,S*-chelating agent [44].

1.2.3 Complexes with bidentate Group VI/Group V donor ligands

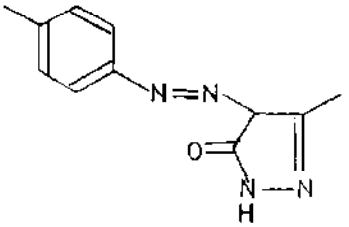
There have been further reports of platinum(IV) complexes of iminodiacetic acid (H_2L). Reaction of H_2L with $K_2[PtBr_6]$ in a 1:1 ratio gives $K_2[Pt(HL)Br_5]$, in which the ligand is *N*-bonded and one of the carboxyl groups is deprotonated. With a 2:1 ratio of H_2L to $K_2[PtBr_6]$ the major product is $K[Pt(HL)(H_2L)Br_4]$. Under analogous conditions $K_2[PtBr_4(OH)_2]$ gives $K[PtLBr_3]$ and $[Pt(HL)_2Br_2]$ respectively. These data are curiously at variance with those noted last year for the chloro analogues [45]. The thermal decomposition of $K[PtLCl_3]$, $K_2[Pt(HL)Br_5]$, $K_2[Pt(HL)Cl_2(OH)_2]$ and $[Pt(HL)_2(NH_3)_2Cl_2]$ has been investigated by DTA. The initial process in all cases is decarboxylation [46].

Isonicotinic acid hydrazide (**(3)**, L) coordinates to platinum(IV) through the nitrogen atom of the NH_2 group and the carbonyl oxygen in $[PtL_2Cl_2]Cl_2$ [47]. 3-Methyl-4-(4-methylphenylazo)pyrazol-5-one, **(4)**, HL', forms octahedral complexes of stoicheiometry $[Pt(HL')Cl_4]$. Despite some slightly dubious statements to the contrary, the data presented do not allow a clear distinction of the binding site(s) involved [48].

Trans-$[PtLX_2(AA)]$ and *trans*-$[PtLL'_2X_2]$ have been prepared by oxidative addition of halogens to $[PtL(AA)]$ and $[PtLL'_2]$ (H_2AA =



(3)



(4)

HOOC-COOH, $HOOCCH_2COOH$ or $HOOCCH(C_2H_5)COOH$; L = $H_2NCH_2CH_2OH$ or $H_2NCH_2CH_2SH$; H_2L' = HCOOH, CH_3COOH, H_2NCH_2COOH or $CH_3CH{=}CHCOOH$). In all cases L acts as a chelating bidentate ligand [49]. The structure of *cis-N,N'-trans-O,O'*-bis(2-aminoethanolato)*cis*-dichloro platinum(IV) has been determined by X-ray diffraction. This complex has unusually low anti-tumour activity [50].

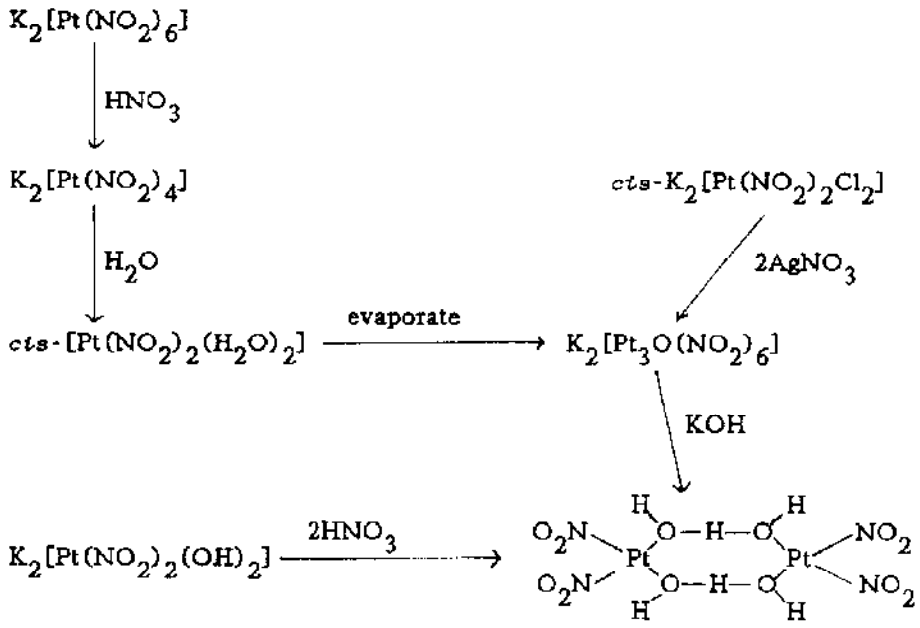
1.2.4 Complexes with Group V donor ligands

The two photon, four electron redox reaction of $[Pt(N_3)_6]^{2-}$ to platinum(II) and finally colloidal platinum metal has been shown to proceed initially *via* reaction (5), with oxidative cleavage of the ligands [51].

$$[Pt(N_3)_6]^{2-} \xrightarrow{h\nu,\ CH_2Cl_2} [Pt(N_3)_4]^{2-} + 3N_2 \qquad (5)$$

Reaction of $[NH_4]_2[PtX_6]$ (X = Cl, Br or I) with liquid ammonia at -40 °C gives mixtures of $[Pt(NH_3)_{6-n}X_n]X_{4-n}$, where n = 0, 1, 2 or 3. After several weeks $[Pt(NH_3)_6]X_4$ is isolated as the major product. At room temperature (X = Cl or Br) the bridged dimer $[\{Pt(NH_3)_4\}_2(\mu\text{-}NH_2)_2]X_6$ is obtained. Treatment of $[NH_4]_2[PtX_6]$ with gaseous or liquid ammonia followed by an excess of KNH_2 yields $K_2[Pt(NH_2)_6$ [52]. The heat capacity of *trans*-$[Pt(NH_3)_4Br_2]Br_2$ was determined in the temperature range 55-310 K; γ-type anomalies correspond to phase transitions [53].

The interrelationships of platinum(IV) and platinum(II) nitro complexes have been further investigated (Scheme 1) [54].

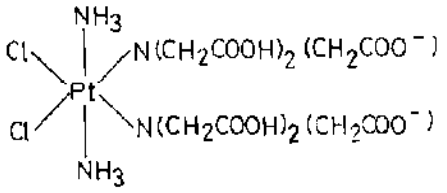


Scheme 1 Interconversion of platinum(II) and platinum(IV) nitro complexes [54]

The preparations of *cis*-$[PtL_2X_2].nH_2O$ and *trans*-$[PtL_2X_2(OH)_2]$ (L = Me_2CHNH_2; X_2 = Cl_2, Br_2, C_2O_4 or $CH_2(COO)_2$) have been described. *trans*-$[PtL_2(C_2O_4)(OH)_2]$ is the most useful for supression of L 1210 leukaemia in rats [55]. Treatment of *cis,cis,trans*-$[Pt(NH_3)_2Cl_2(NO_3)_2]$ with a range of amines, L, yields *cis,cis,trans*-$[Pt(NH_3)_2L_2Cl_2][NO_3]_2$ [56]. The dissociation constants for $[PtA_2X_2(H_2O)_2]^{2+}$ and $[PtA_2X_2(H_2O)(OH)]^{+}$ (A = NH_3, $MeNH_2$, Me_2NH or $EtNH_2$; X = Cl, CN or NO_2) have been determined [57].

A range of complexes of nitrilotriacetic acid, H_3L, have been prepared from *trans*-$[Pt(NH_3)_2Cl_4]$. Using a 1:1 molar ratio the complex *trans*-$[Pt(NH_3)_2(H_2L)Cl_3]$ is formed, whereas with two moles of H_3L the product is **(5)**. *Trans,cis,cis*-$[Pt(NH_3)_2Cl_2(NO_3)_2]$ yields **(5)** together with the mixed

species, $[Pt(NH_3)_2(H_2L)Cl_2(NO_3)]$ [58].

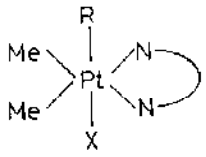


(5)

The preparation and characterisation of platinum(IV) complexes of 1-vinyl imidazole, 1-vinyl benztriazole, 1-vinylbenzimidazole and 1-vinylpyrazole has been reported. In all cases coordination occurs through the sp^2 nitrogen of the heterocycle and the vinyl group is uncoordinated [59,60].

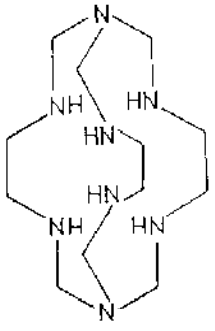
$H_2[PtX_6]$ (X = Cl or Br) reacts with thioproline, LH, to give $[HL]_2[PtX_6]$; whilst this shows some cytostatic activity *in vitro* it is not useful *in vivo* [61].

The formation of the outer sphere complexes $[Pt(en)_3(SO_4)_n]^{4-2n}$ and $[Pt(en)(phen)_2(SO_4)_n]^{4-2n}$ (n = 1 or 2) was established by solubility studies. The most stable outer sphere complexes are formed by $[Pt(en)_3]^{4+}$ [62]. Outer sphere association constants were also determined for $[Pt(phen)_2(en)L_n]^{4-n}$, the trend in stability being L = $HCOO^-$ < CH_3COO^- < $C_2H_5COO^-$ < $C_3H_7COO^-$ [63]. A number of octahedral palladium(IV) complexes, $[Pd(L\text{-}L)Cl_4]$ (L-L = bipy, phen, dppe, $Me_2ECH_2CH_2EMe_2$, {E = N or P}, $Ph_2AsCH_2CH_2AsPh_2$ or $Me_2As(CH_2)_3AsMe_2$) were prepared by chlorination of $[Pd(L\text{-}L)Cl_2]$. Analogous bromination and the reactions of $[Pd(L\text{-}L)_2]Cl_2$ were also investigated [64]. $[Me_2Pt(phen)]$ hase been demonstrated to undergo stereospecifically *trans* oxidative addition of alkyl halides to yield (6) by a radical pathway [65].



(6)

Platinum(IV) complexes of (7) have been synthesised from $[Pt(en)_3]^{4+}$ by treatment with methanal and ammonia, and characterised by X-ray diffraction. Addition of one electron, either electrolytically or radiolytically, gives transient monomeric platinum(III) ions with a lifetime in the millisecond range [66]. [Pd(*meso*-tetrakis{*N*-methyl-4-pyridyl}porphine)]$^{4+}$ has been shown to be an efficient photoreductant for Fe(III), and hence a promising material for solar energy conversion [67].



(7)

The centrifugal distortion constants of $[PtL_2X_4]$ (X = Cl or Br; L = PMe_3, $AsMe_3$ or SMe_2) have been obtained using Cyvin's modified theory, and the previously reported force constants and structural parameters [68].

1.2.5 Complexes with Group IV donor ligands

The kinetics of reduction of $K_2[Pt(CN)_5I]$ by $[BH_4]^-$ have been

investigated spectrophotometrically. Two pathways were established, as shown in reactions (6) - (10) [69].

$$[Pt(CN)_5I]^{2-} + [BH_4]^- \longrightarrow [Pt(CN)_5]^{3-} + I^- + H^+ + BH_3 \quad (6)$$

$$[Pt(CN)_5]^{3-} \longrightarrow [Pt(CN)_4]^{2-} + CN^- \quad (7)$$

$$[Pt(CN)_5I]^{2-} + CN^- \longrightarrow [Pt(CN)_5(ICN)]^{3-} \quad (8)$$

$$[Pt(CN)_5(ICN)]^{3-} \longrightarrow [Pt(CN)_4]^{2-} + CN^- + ICN \quad (9)$$

$$ICN + [BH_4]^- \longrightarrow I^- + CN^- + H^+ + BH_3 \quad (10)$$

The kinetics and mechanism of the reduction of $[Pt(CN)_4(OH)Br]^{2-}$ by inorganic ions has been reviewed [70], whilst another account deals specifically with the extremely complex reaction with $[S_2O_3]^{2-}$ [71].

1.3 PALLADIUM AND PLATINUM COMPLEXES WITH MIXED IV/II OXIDATION STATES

The chemistry of one dimensionally ordered mixed valence compounds has continued to be an active area of investigation. The structure of $[Pt(NH_3)_4][Pt(NH_3)_4Br_2][HSO_4]_4$ has been determined by X-ray diffraction. It contains linear chains comprising alternately arranged octahedral $[Pt(NH_3)_4Br_2]^{2+}$ and square planar $[Pt(NH_3)_4]^{2+}$ cations in the direction of the c-axis [72]. $[PtL_2][PtL_2Cl_2][BF_4]_4$ {L = $H_2N(CH_2)_3NH_2$} and its bromo analogue also form 1-dimensionally ordered structures in which no distinction was made between the platinum oxidation states [73]. The electronic, IR and resonance Raman spectra of the species $[Pt(1,2\text{-pn})_2][Pt(1,2\text{-pn})_2X_2]Y_4$ (1,2-pn = 1,2-diaminopropane; X = Cl, Br or I; Y = ClO_4 or BF_4) have been reported [74]. $[Pt(dien)I][Pt(dien)I_3]I_2$ has been prepared by oxidation of $[Pt(dien)Cl]Cl$ with dilute HI. Although the electronic and resonance Raman spectra are typical of a linearly ordered compound, the X-ray structure determination shows that there is significant bending (21 °) about the

bridging iodine. This is the first mixed valence chain to be prepared with a single positive charge or a tridentate ligand [75]. Two routes (reactions (11) and (12)) have been developed for the synthesis of an analogous mixed

$$[LPd]^{2+} + [LPdCl_2]^{2+} \xrightarrow{HClO_4/H_2O} [LPd][LPdCl_2][ClO_4]_4 \quad (11)$$

$$[LPd]^{2+} + Cl_2 \xrightarrow{HClO_4/H_2O} [LPd][LPdCl_2][ClO_4]_4 \quad (12)$$

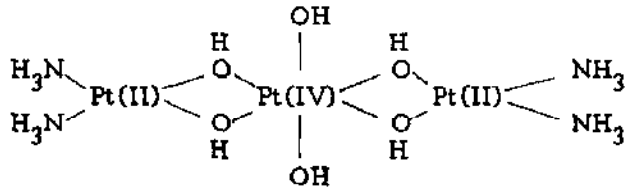
valence compound of 1,4,8,11-tetraazacyclotetradecane, L. X-ray diffraction studies show that the macrocycles adopt the most stable conformation, and the Pd(II) and Pd(IV) units are linked by N-H---O---H-N hydrogen bonds. The electronic interaction between Pd(II) and Pd(IV) in this complex is weaker than that in $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$ as judged by the Pd-X distances and electronic spectroscopic data [76]. The Ni(II)---X---Pt(IV) chain in $[Ni(en)][Pt(en)_2X_2][ClO_4]_4$ (X = Cl or Br) is more conducting than the comparable Pt(II)---X---Pt(IV) chain [77].

Reaction of $K_4[Pt_2(pop)_4]$ with X_2 ($H_2pop = (HO)_2POP(OH)_2$; X = Cl, Br or I) has been shown to yield $K_4[Pt_2(pop)_4X]$, the X-ray structural determination of which shows linear chains of -Pt-Pt-X-Pt-Pt-X- atoms. The bridging halides provide a continuous path for electrical conduction [78].

Simple preparations of one dimensional tetracyanoplatinate complexes containing platinum atom chains have been described. The species synthesised include $Cs_2[Pt(CN)_4]Cl_{0.3}$, $K_2[Pt(CN)_4][HF_2]_{0.3}.3H_2O$, $Cs_2[Pt(CN)_4][N_3]_{0.25}.xH_2O$ and $Cs_3[Pt(CN)_4][O_3SOHOSO_3]_{0.46}$ [79]. Application of high pressures to $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ and $Rb_2[Pt(CN)_4][HF_2]_{0.4}$ induces phase transitions observable in X-ray diffraction studies [80]. The preparation and properties of a new type of partially oxidised salt exemplified by $Pb_{0.77}K_{0.23}[Pt(CN)_4].1.5H_2O$ are reported. The partial oxidation in this case arises only from the presence of a non-stoicheiometric proportion of univalent and bivalent cations [81]. A

somewhat different stoicheiometry, $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}$, is obtained on electrolysis of $K_2[Pt(CN)_4]$ in the presence of $Pb[NO_3]$. The divalent cations are said to stiffen the lattice, reduce λ, the electron phonon coupling constant, and increase conductivity [82].

Photolysis of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ at 251 nm yields a blue mixed valence compound in which the ratio of Pt(II) to Pt(IV) is two. The blue compound has the structure **(8)**, and it is suggested that a dimeric or trimeric platinum(II) compound is the photoactive species [83].



(8)

A number of papers report mixed valence compunds of thiourea (tu) and analogues. $K_2[PtCl_6]$ reacts with tu to yield $[Pt(tu)_4][PtCl_6]$ [84], but more generally complexes of stoicheiometry $Pt_2L_4Cl_6$ may be $[Pt(II)L_4][Pt(IV)Cl_6]$ or $[Pt(IV)L_2Cl_2][Pt(II)L_2Cl_4]$. ^{13}C NMR spectroscopy confirms that sulphur is the coordinating atom in all cases. ^{195}Pt NMR spectroscopy is used to distinguish the other species, and the type of complex formed depends both on the method of preparation and the nature of the ligand [85-87].

1.4 PALLADIUM(III) AND PLATINUM(III)

$Na[PdF_4]$ may be prepared from the solid state reaction of 2 moles of NaF with $[Pd_2F_5]$ at 600 °C/70 kbar. The EPR spectrum at 8 K indicates the presence of Pd^{3+} with the unpaired electron in the d_z2 orbital. The complex is low spin $t_{2g}^{6}\ e_g^{1}$ with a significant Jahn-Teller effect [88]. $LaPd_xAl_{1-x}O_3$ solid solutions ($0.004 < x < 0.09$) in which Pd(III) is stabilised have been prepared by the ceramic method using a $Pd/La_2O_3/\gamma\text{-}Al_2O_3$ mixture [89].

The lifetimes of electronically excited states of $[M(bipy)_3]^{3+}$ (M = Cr, Os or Ru) have been obtained from luminescence spectra as functions of the concentration of the platinum(II) quenchers. Energy transfer is the dominant mechanism of the luminescence quenching using $K_2[PtBr_4]$ and $K_2[PtCl_4]$ or the osmium or ruthenium complexes, but with $[Cr(bipy)_3]^{3+}$ and $[Pt(SCN)_4]^{2-}$ or $[Pt(C_2O_4)_2]^{2-}$ electron transfer to yield platinum(III) is involved [90].

The range of $\{Pt_2\}^{6+}$ units fully characterised by X-ray crystallography has been further extended during the last year and the results are summarised below [91, 92].

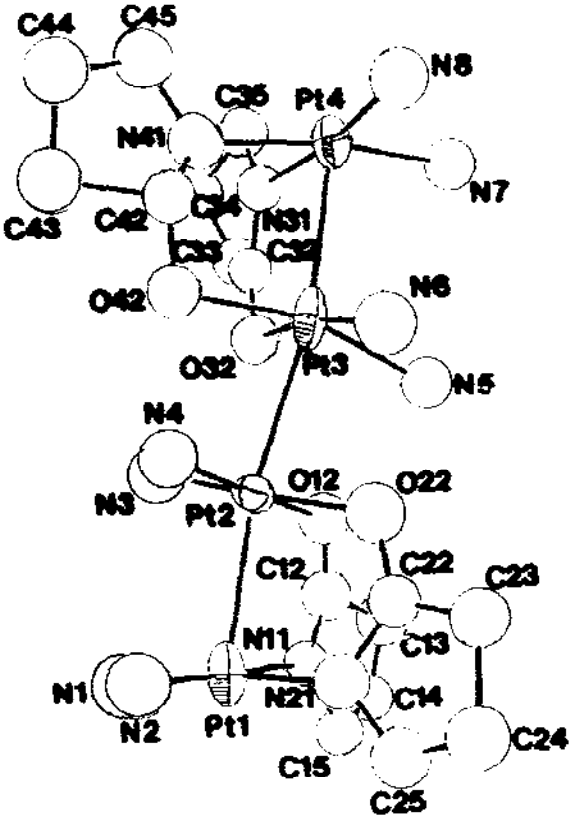
Complex	r(Pt-Pt)/(Å)
$[pyH]_2[Pt_2(H_2PO_4)(HPO_4)_3(py)_2].H_2O$	2.494
$[X(NH_3)_2Pt(pyridonate)_2Pt(NH_3)_2X][NO_3]_2$	2.582 (X = Br)
	2.576 (X = NO_2)
	2.584 (X = Cl)
$[(NO_3)(NH_3)_2Pt(pyridonate)_2Pt(NH_3)_2(H_2O)][NO_3]_3$	2.540

The complexes $[Pt_2(CH_3CS_2)_4X_2]$ (X = Cl, Br or I) have been synthesised by oxidative addition of X_2 to the Pt(II) dimer, and the oxidation states confirmed by XPES. If only one half of the stoicheiometric amount of iodine is employed $[Pt_2(CH_3CS_2)_4I]$ is formed, in which the average oxidation state of platinum is 2.5. The Pt-Pt bond (2.677 Å) lies between values typical of $\{Pt(II)_2\}$ and $\{Pt(III)_2\}$, and iodine bridges the $\{Pt_2\}$ units in Pt-Pt···I···Pt-Pt [94]. When $[Pt_2(HPO_4)_4]^{2-}$ is treated with a base, L (L = py, 4-methylpyridine or 3,4-dimethylpyridine), the major product is $[LH]_2[Pt_2(HPO_4)_4L_2]$, (9), contaminated with small amounts of the mixed salt $[LH][Pt_2(H_2PO_4)(HPO_4)_3L_2].H_2O$, (10). During attempts to grow crystals

of **(9)** (L = py), **(10)** was isolated and its structure determined by X-ray diffraction [91]. The ^{195}Pt NMR spectra of $[Pt_2(SO_4)_4X_2]^{n-}$ and $[Pt_2(HPO_4)_4X_2]^{n-}$ (X = H_2O, Cl or Br; n = 2 or 4) were measured. It was found that $^1J_{Pt\text{-}Pt}$ is very sensitive to small variations in electronic structure which have little effect on molecular structure [95]. The IR and Raman spectra of $[Pt_2(pop)_4X_2]^{2-}$ (X = Cl, Br or I) were compared with those of the Pt(II) analogue, $[Pt_2(pop)_4]^{4-}$. It was concluded that Pt(III)-Pt(III) is a much stronger bond than Pt(II)-Pt(II) [96].

Treatment of the head-to-tail platinum(II) α-pyridonate dimer *cis*-$[\{Pt(NH_3)_2(C_5H_4NO)\}_2]^{2+}$ with nitric acid in the presence of X^- (X = NO_2, Cl or Br) results in oxidative addition and metal-metal bond formation to give the Pt(III) dimer. The Pt-Pt bond lengths in the complexes parallel the *trans*-influence of the axial ligand, X, whilst elongation of the Pt-X bond reveals that the Pt-Pt bond has a very strong *trans*-influence [93]. Treatment of *cis*-diammine platinum α-pyridone blue with nitric acid results in the loss of three electrons from the four Pt(2.25) centres and cleavage of the tetranuclear unit to a Pt(III) dimer. In this case a dimer with a head-to-head arrangement of the α-pyridones is obtained, but the head-to-tail isomer $[(O_2N)(NH_3)_2Pt(pyridonate)_2Pt(NH_3)_2(NO_2)][NO_2]_2.2H_2O$ is obtained from nitric acid oxidation of $[(NH_3)_2Pt(pyridonate)_2Pt(NH_3)_2][NO_2].2H_2O$. The electrochemistry of these complexes has been studied [94].

cis-Diammine α-pyrrolidone tan was obtained unexpectedly during a synthesis of platinum blues. Its structure has now been determined by X-ray diffraction to be bis[bis{μ-α-pyrrolidinato(1-)-N^1,O^2}bis{*cis*-diammine platinum(II,III)}] hexanitrate dihydrate **(11)**. The cation has a tetranuclear chain structure similar to *cis*-diammine-α-pyrrolidone blue except that the average oxidation state is 2.5 rather than 2.25. This may thus be considered as possessing two Pt(II) and two Pt(III) centres, but since the complex is diamagnetic, the two unpaired electrons must be strongly coupled and delocalised over all four atoms [97].



(11)

Reaction of $K_2[PtCl_4]$ with a very large excess of acetamide gives a polymeric compound $\{Pt(C_2H_4NO)_2Cl\}_n$. However, using $K_2[PdCl_4]$ as the substrate, $[Pd_4(C_2H_4NO)_7(OH)_2]$ is obtained. Analytical and spectroscopic data imply that this has a polynuclear structure with bridging ligands and partially oxidised metal centres. This is the first isolated palladium analogue of the platinum blues [98].

A variety of platinum complexes of the ethanoate ligand are reported by Soviet workers. Among these are $[\{Pt(OOCMe)(OH)_2(H_2O)\}_4]$ and $[\{Pt(OOCMe)_3\}_4]$ [99].

1.5 PALLADIUM(II) AND PLATINUM(II)

1.5.1 Complexes with Group VII donor ligands

The absorption spectra of palladium(II) in melts of LiCl, NaCl, KCl and CsCl at a chromophore concentration of 0.01 mol % and a temperature of 1087 K have been examined [100]. Reaction of $PdCl_2$ and KCl yields $K_2[PdCl_4]$ which melts congruently at 534 °C. The $K_2[PdCl_4]/Na_2[PdCl_4]$ systems have been shown to be stable sections of the $KCl/NaCl/PdCl_2$ system [101].

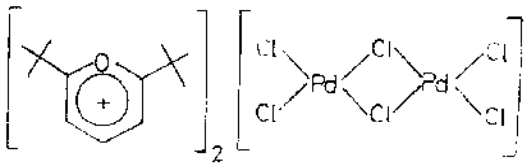
A potentiometric study using an iodide selective electrode has established a value of 3.73×10^{-16} for the solubility product of PdI_2. Radiometric data give a value of 2.55×10^{-16} [102]. The stability constants fo chloro complexes of platinum(II) in aqueous solution at 60 °C have been determined spectrophotometrically [103].

The electronic structure of $K_2[MCl_4]$ (M = Pd or Pt) has been investigated by the Xα SCF method and by X-ray spectroscopy [104]. X-ray diffraction studies allow the detection of charge distribution in crystals of $K_2[PtCl_4]$. The 5d electrons have an aspherical distribution in a square planar ligand field [105].

The complexes $[(py)_2I]_2[PtX_4]$ (X = Cl or Br) have been prepared by reaction of $[(py)_2I][NO_3]$ with $K_2[PtX_4]$ in DMF. $[(\gamma\text{-picoline})_2I]_2[PtCl_4]$ and $[(py)_2Br]_2[PtCl_4]$ are similar. The thermal behaviour of the complexes was studied by thermogravimetry, IR spectroscopy, conductivity measurements and X-ray diffraction [106]. $[C_2H_5NH_3]_2[PdCl_4]$ has not been characterised crystallographically but near IR and IR transmission spectra and unpolarised Raman spectra allow the authors to conclude that it closely resembles members of the series $[C_2H_5NH_3]_2[MCl_4]$ (M = Mn, Cu or Cd) [107].

X-ray crystallographic studies have been performed on $CsPd_2F_5$, $CsMPdF_5$ (M = Mg, Zn or Ni), Rb_3PdF_5, Cs_3PdF_5 and Rb_2CsPdF_5. Half of the Pd^{2+} ions are surrounded octahedrally by fluoride, whilst the others are in a square

planar environment [108]. In 2,6-di-*tert*-butylpyrilium hexachlorodipalladate(II), (12), each palladium has approximately square planar coordination, but the four membered $\{Pd_2Cl_2\}$ ring is not planar [109].



(12)

The rules governing the variation of M-L bond lengths on transition of complexes to excited states of the d-d type have been reviewed, with especial reference to $[PtCl_3L]^n$ (L = NO, CO, CN, Cl, NH_3 or H_2O) [110]. Vibrational and laser Raman spectra of the mononuclear square planar coordination compounds, $[MX_4]^{2-}$ and $[MX_3L]^{n-}$ (M = Pd or Pt; X = halogen) have been reviewed [111].

Extraction of $[PdCl_4]^{2-}$ by $[R_3NH]Cl$ (R = octyl) gives both $[R_3NH]_2[PdCl_4]$ and $[R_3NH]_2[Pd_2Cl_6]$ as detectable species in the organic phase [112]. The kinetics of the interactions of $K_2[PtX_4]$ (X = Cl, Br, CNS, NO_2 or CN) complexes with the surfaces of $Ln_2O_3.nH_2O$ between 40 and 80 °C have been investigated [113].

The oxidation of molecular hydrogen under conditions in which platinum metal is not formed has been studied. The species $[Pt(II)Cl_n(H_2O)_{4-n}]$ (n = 1, 2 or 3) are active, but $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ do not react with H_2 [114].

The mass spectrum of $[(C_2H_4)_2Pt_2(\mu\text{-}Cl)_2Cl_2]$ has been reported and assigned. Fragmentation results in competitive loss of chlorine and ethene with the formation of species containing a Pt-Pt bond [115].

Conditions for determination of platinum by spectrophotometry have been studied, and it was shown that the colour reaction is always preceded by reduction to platinum(II) [116].

1.5.2 Complexes with Group VI donor ligands

1.5.2.1 Unidentate oxygen donor ligands

The emission spectrum of PtO has been studied betwee 3800 and 8900 Å and several new transitions analysed [117]. The thermogravimetric properties of PdO from 800 - 1040 K have been investigated [118].

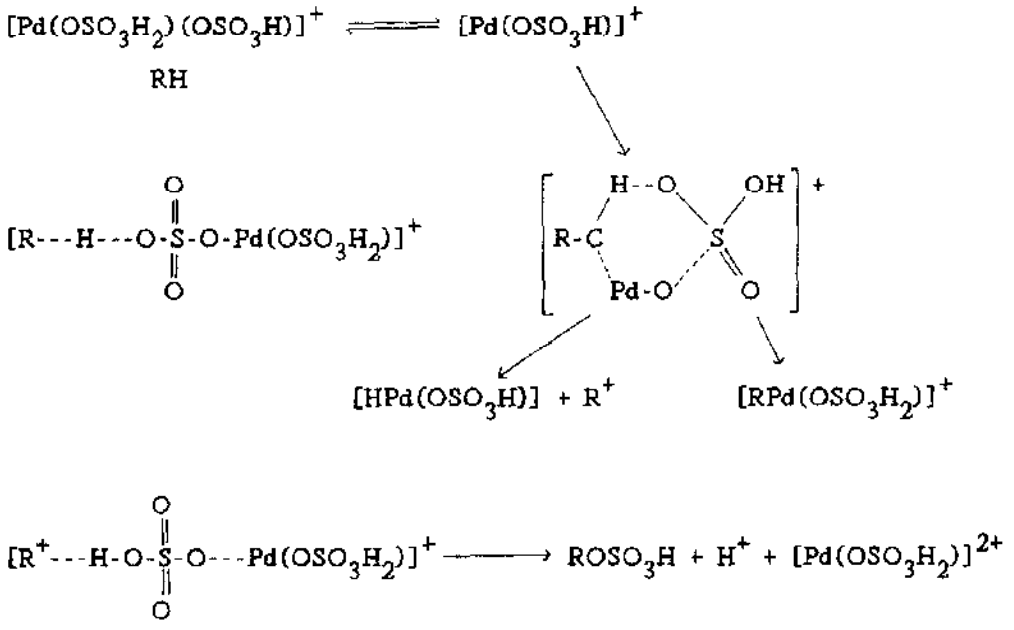
Thermolysis of $[Pd(NO_3)_2].2H_2O$ occurs in three stages yielding colloidal platinum *via* $[Pd(NO_3)(OH)(H_2O)]$ and $[Pd(OH)_2]$ [119].

Stable monomeric *trans*-$[(R_3P)_2Pt(R_x)(OO\text{-}CMe_3)]$ complexes (R_x = CF_3, 2-CNC_6H_4 or Ph) have been prepared from $[(R_3P)_2Pt(R_x)(OH)]$ and Me_3COOH. ^1H, ^{19}F and ^{31}P NMR spectroscopic studies and X-ray diffraction confirm that the peroxide is end-bonded, and suggest considerable covalent character for the Pt-O bond. All the complexes, except those of $(PhCH_2)_3P$, are effective in oxygenation of 1-octene to 2-octanone [120].

Oxidative dehydrogenation of saturated hydrocarbons occurs in the presence of Pd(II) in H_2SO_4 by a mechanism which involves C-H cleavage in the rate determining step. A possible mechanism is shown in Scheme 2 [121]. A quantum chemical study of CH_4 activation by platinum(II) complexes with Cl, H_2O or OH ligands has been carried out by the CNDO MO method. The most probable path involves simultaneous coordination of CH_4 to platinum and the oxygen atom of the ligand [122].

1.5.2.2 Bidentate and multidentate oxygen donor ligands.

There continue to be numerous studies of the chemistry of bis(β-diketonato) complexes. $[Pd(R^1COCHCOR^2)_2]$ (R^1 = CH_3, Ph or 2-thienyl, R^2 = CF_3; R^1 = Ph or 2-thienyl, R^2 = C_2F_5 or C_3F_7; R^1 = 2-thienyl, R^2 = CHF_2) areprepared from $K_2[PdCl_4]$ and the diketone. In solution they are square planar and exist as a mixture of *cis* and *trans* isomers, which were separated by HPLC for R^1 = CH_3, R^2 = CF_3 [123]. A mixture of the *cis* and *trans*



Scheme 2 Pathways in alkane dehydrogenation in the presence of palladium(II) [121].

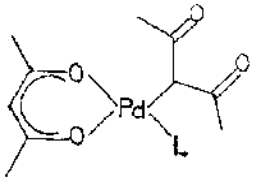
isomers of $[Pd(PhCOCHCOCH_2CH_2CH_3)_2]$ was formed serendipitously when (13) was reacted with $PdCl_2$ with the intention of synthesising the allyl complex. The additional oxygen atom was derived from Na_2CO_3, which had been added to prevent polymerisation of the enone [124].

(13)

The preparation of $[Pd(HCOCHCHO)_2]$ was described; relatively few metals form characterisable complexes with this ligand. Its sublimation behaviour was compared with other analogous palladium chelates. It is the most volatile of the series, but also the least stable, and on volatilisation 50-65% of the metal is deposited as a palladium mirror [125]. Mass spectrometric studies of

bis(β-diketonato)palladium complexes all show the ions $[L_2Pd]^{2+}$ and $[L_2Pd\text{-}R]^{2+}$, where R is one of the substituents [126].

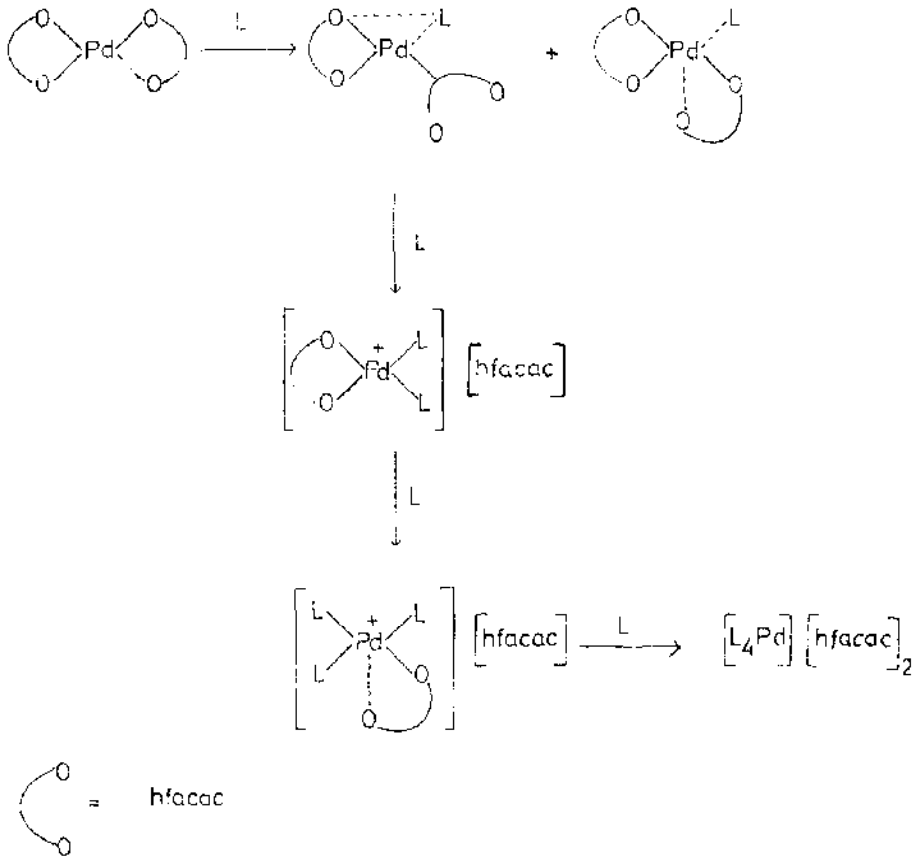
Studies of the reactions of bis(β-diketonato) complexes with nucleophiles have mainly involven nitrogen and phosphorus donors this year, and further insight into the complex series of pathways possible has been obtained. $[Pd(acac)_2]$ reacts with 2-, 3-, or 4-methylpicoline, L, to yield stable complexes of structure (14) [127]. Similar reactions are observed with complexes of hfacac and tfacac [128]. Platinum bis(β-diketonato), (β-dik), complexes react with ligands, L, to give $[Pt(\beta\text{-dik})L_2][\beta\text{-dik}]$, $[Pt(\beta\text{-dik-}o)_2L_2]$, $[Pt(\beta\text{-dik})(\beta\text{-dik-}c)L]$ or $[PtL_4][\beta\text{-dik}]_2$, depending on β-dik and L (β-dik-*o* and β-dik-*c* act as unidentate ligands bonding through *o* and *c* respectively). All the products are stable and, unlike their palladium analogues, do not readily isomerise. Generally reactions with primary amines are said to yield $[PtL_4][\beta\text{-dik}]_2$, whilst secondary amines give $[Pt(\beta\text{-dik})L_2][\beta\text{-dik}]$ and/or $[Pt(\beta\text{-dik-}o)L_2]$. However, reaction of 2-methyl aniline with $[Pt(hfacac)_2]$ gives $[Pt(hfacac)(hfacac\text{-}C^3)L]$ as the major product [129].



(14)

$[Pd(hfacac)_2]$ crystallises from the vapour phase as a molecular crystal with no strong metal metal interactions. X-ray diffraction confirms its planar structure. The reactions of the complex with pyridines have been systematically studied and are shown in Scheme 3. An exemplary member of each class of complexes has been characterised by NMR spectroscopy and X-ray diffraction. The point at which the sequence stops is primarily determined by

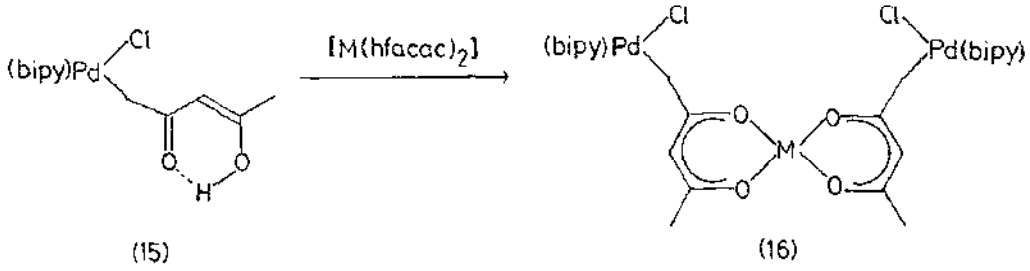
steric effects, and the scope of the process derives from the strong acceptor character of the metal centre and the relative weakness of the metal oxygen bonds [130].



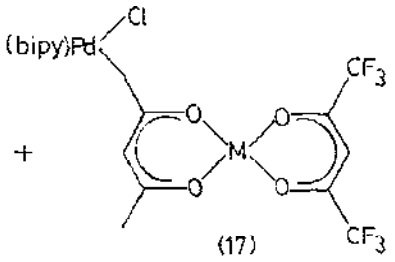
Scheme 3 Reactions of $[Pd(hfacac)_2]$ with pyridines, L [130].

A rather curious report details the conversion of **(15)** to **(16)** or **(17)** on treatment with varying proportions of $[M(hfacac)_2]$ (M = Cu or Pd) [131]. By contrast, **(18)** does not react rapidly with $[M(acac)_n]$ [132].

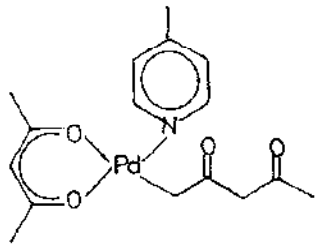
The X-ray crystallographic structure of **(19)**, formed by reaction of $(2\text{-methylphenyl})_3P$ with $[Pd(hfacac)_2]$ has been determined. The Pd-O bond *trans* to phosphorus is 0.03 Å longer than the other, and the unidentate hfacac ligand has a *trans*-planar structure [133].

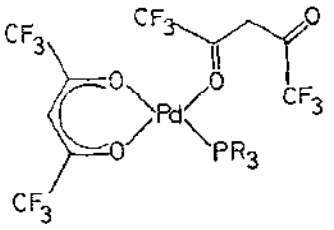


(15) (16)



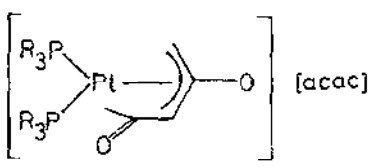
(17)

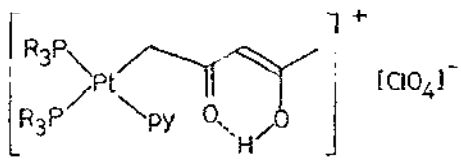




(18) **(19)**

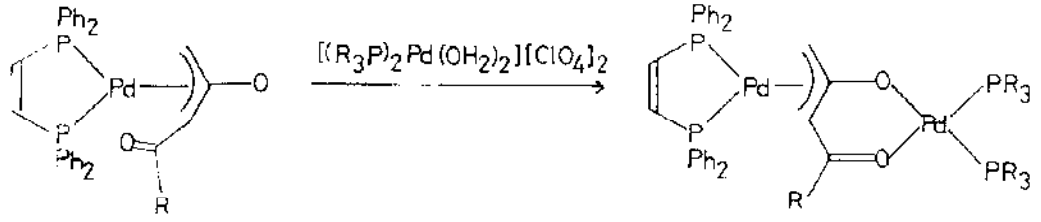
Pentane-2,4-dione may act, under appropriate circumstances, as a trihapto ligand. Reaction of $[Pt(acac)_2]$ with $(4\text{-chlorophenyl})_3P$ yields (20), the first example of a platinum complex of this type. Treatment with $[pyH][ClO_4]$ gives (21) [134].





(20) **(21)**

Reaction of an analogue of **(20)**, **(22)**, with $[(R_3P)_2Pd(H_2O)_2][ClO_4]_2$ yields **(23)** and mixed metal complexes are obtained on reaction with $[(Ph_3P)_2Pt(H_2O)_2]^{2+}$ and $[Ni(acac)_2]$ [135].



(22) **(23)**

Treatment of $[Pd(tfacac)_2]$ with R_3P followed by pyridine yields $[Pd(tfacac(2-)\text{-}C,\text{-}O)(PR_3)(py)]^+$, the structure of which was determined in solution by spectroscopic means. X-ray diffraction studies were performed on the complex with PPh_3 and 2,6-dimethylpyridine, demonstrating that the nitrogen atom is *trans* to carbon and the phosphorus atom *trans* to oxygen in a square planar species [136].

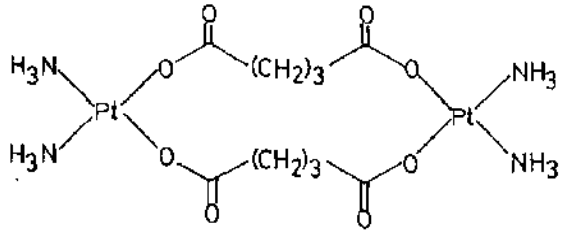
The IR and Raman spectra of $[Pd(acac)_2]$ and its 3-bromo derivatives reflect the changes in electron distribution on bromination [137].

Photolysis of palladium(II) oxalate in a water matrix at 77 K led to reduction of the central atom [138]. Photolysis of $K_2[Pd(C_2O_4)_2].4H_2O$ crystals also gives reduction, this time to palladium metal with the other products being $K_2[C_2O_4]$ and CO_2. Palladium particles are formed preferentially on structural defects [139].

Determination of the standard enthalpy of formation of solid complexes of the type [(diamine)Pt(dicarboxylic acid dianion)] has led to estimates of the mean bond dissociation enthalpies for Pt-N and Pt-O in these species. For diamine dicarboxylates, the mean dissociation enthalpy for the Pt-O bond is considerably greater than in Pt(II) β-diketonato complexes [140].

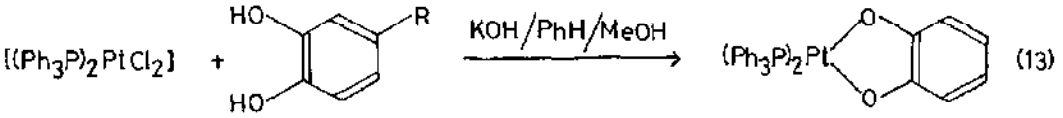
Treatment of *cis*-$[Pt(NH_3)_2(OH_2)_2][SO_4]$ with glutaric (H_2L) or

succinic acid (H_2Q) in the presence of $Ba(OH)_2$ leads to the formation of $[\{Pt(NH_3)_2L\}_2].H_2O$ and $[\{Pt(NH_3)_2Q\}_2].H_2O$ respectively. $[\{Pt(NH_3)_2L\}_2]$ is a centrosymmetric dimer, (24) in which the *cis* square planar arrays about platinum are bridged by L to give a 16-membered ring [141]. Tartaric and malic acids act as *cis*-chelating ligands in the complexes $[Pt(NH_3)_2L]$ prepared from *cis*-$[Pt(NH_3)_2Cl_2]$ and Ag_2L [142].



(24)

A wide range of catechol complexes **(25)** has been synthesised according to equation (13). These were tested for their anti-tumour activity and the best results obtained when R = CH_2COOH or $CH(OH)CH_2NHCH(CH_3)_2$ [143].



(13)

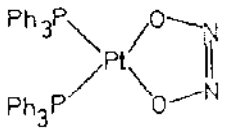
(25)

$[Pd\{(\{CH_3\}_2CHO)_2P(O)CH_2CONEt_2\}(NO_3)_2]$ was prepared by the reaction of $Pd(NO_3)_2$ with the phosphonate in acid solution. X-ray diffraction demonstrates that $[NO_3]^-$ acts as a monodentate ligand, whilst the phosphonate binds through the carbonyl oxygen and the phosphoryl group [144].

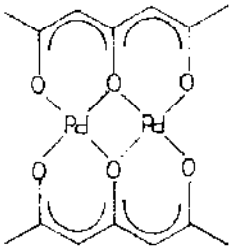
The ionic radius for Pd^{2+} was calculated to be 0.721 Å from the absorption maximum of its "salicylfluoronone" complex, the structure of which is somewhat imprecisely described [145].

Amongst a range of other complexes of the platinum metals the ^{15}N NMR

spectrum of (26) has been determined [146].

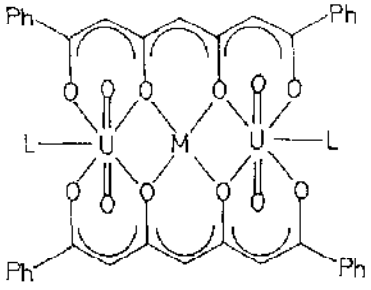


(26)



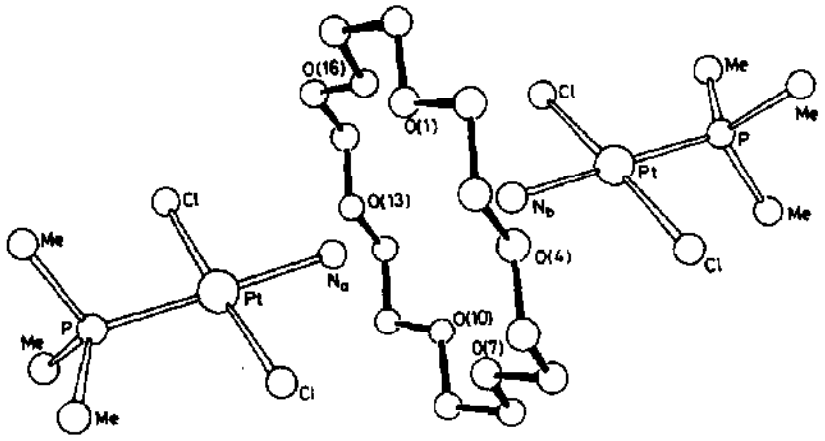
(27)

The complexes $[Pd(HL)_2].nH_2O$ where H_2L is a β,ε-triketone or a β-ketophenol are reported. The nature of the complex formed depends both on the temperature and on the L:Pd ratio. Binuclear complexes of the type **(27)** are formed under appropriate conditions [147]. Mixed metal complexes such as **(28)** (M = Pd(II) amongst others) have been prepared. They are strongly coloured and two almost reversible one electron transfers are associated with the redox properties of $\{UO_2\}^{2+}$ [148].



(28)

Crown ethers form isolable adducts wth *trans*-$[Pt(NH_3)(PMe_3)Cl_2]$, *trans*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(en)_2][PF_6]_2$. An X-ray diffraction study of the adduct between dibenzo-18-crown-6 and *trans*-$[Pt(NH_3)(PMe_3)Cl_2]$ shows that the crown ether is bound to two moles of the complex with association to the ammine in **(29)**. The other two complexes both give polymeric species with alternating crown ether and platinum complex constituents [149].



(29)

1.5.2.3 Ambidentate oxygen sulphur donor ligands

An X-ray diffraction study of $[(en)Pt(dmso)_2][PF_6]_2.dmso.H_2O$ revealed approximately square planar coordination with *cis*-*S*-bonded sulphoxides and a gauche conformation for en [150].

Thermolysis of $[(CH_3)_3SO]_2[Pt_2I_6]$ in air or helium yields $[Pt_2(dmso)_2I_4]$, (30) and two moles of iodomethane. (30) was identified by IR spectroscopy and contains *trans*-*S*-bonded sulphoxides. This represents the first example of the transfer of an alkyl cation in thermolysis of an onium complex of platinum and is related to the Anderson rearrangement [151].

Several studies report the kinetics of reaction of platinum complexes with sulphoxides. Reaction (14) has been studied with a wide variety of sulphoxides. It was noted that the second order rate constants decreased with

$$[PtCl_4]^{2-} + R^1R^2SO \longrightarrow [Pt(R^1R^2SO)Cl_3]^- + Cl^- \qquad (14)$$

increasing bulk of the sulphoxide, but electronic effects were small. There is some evidence that an *O*-bonded sulphoxide complex is formed initially with subsequent rapid conversion to the more usual *S*-bonded species

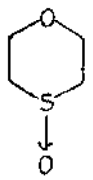
[152]. Palladium analogues were also studied and it was found that the second displacement to yield *trans*-$[Pd(dmso)_2Cl_2]$ was very much less favourable, presumably due to the strong *trans*-effect of dmso [153].

In the reactions of *trans*-$[Pt(py)_2Cl_2]$ with methyl aryl sulphides and sulphoxides to yield $[Pt(py)_2L_2]^{2+}$, sulphoxides are about twenty-five times less reactive than sulphides. Kinetic studies revealed that $k_{obs} = (k_1 + k_2[L])$ [complex]; the first displacement of chloride is rate controlling [154].

The kinetics of reaction (15) (L = dmso or H_2O) were studied with a range of nucleophiles, Y. A simple second-order rate law is observed. The substrate in which L = dmso is more reactive than the aqua complex, and additionally shows a significantly greater ability to distinguish between nucleophiles. The mutual labilising effect of the sulphoxides is due, at least in part, to the ability of this ligand to stabilise the five-coordinate intermediate by acting as a π-acceptor [155].

$$[Pt(en)(dmso)L]^{2+} + Y^{n-} \longrightarrow [Pt(en)(dmso)Y]^{(2-n)+} + L \qquad (15)$$

Thioxane *S*-oxide, **(31)** reacts with $K_2[PtCl_4]$ to give the monosubstitution product $K[PtLCl_3]$, or if added in excess, *cis*-$[PtL_2Cl_2]$. Further interconversions were investigated (reactions (16) - (18) [156].



(31)

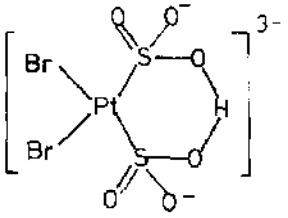
$$K[PtLCl_3] + [Pt(NH_3)_4]Cl_2 \longrightarrow [Pt(NH_3)_4][PtLCl_3]_2 \qquad (16)$$

$$K[PtLCl_3] + py \longrightarrow trans\text{-}[Pt(py)LCl_2] \qquad (17)$$

$$K[Pt(py)Cl_3] + L \longrightarrow cis\text{-}[Pt(py)LCl_2] \qquad (18)$$

X-ray diffraction studies of K_3[*cis*-dibromo(hydrogenbissulphito)

platinum(II)] monohydrate, (32) reveals a distorted square planar structure. Short Pt-S bonds and long Pt-Br bonds confirm the strong *trans*-influence of sulphite. A very short asymmetric hydrogen bond links the sulphite ligands to form a six membered ring [157]. The out-of-plane modes of the hydrogen bond in the chloro analogue of (32) were assigned from the inelastic neutron scattering spectra [158].



(32)

1.5.2.4 Bidentate oxygen sulphur donor ligands

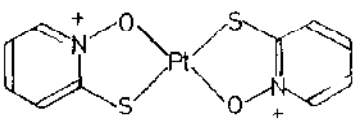
The preparation of $[Pt(RCSCH_2COCF_3)_2]$ (R = CH_2CMe_2) has been described and its spectroscopic parameters determined [159]. *Trans*-$[Pt(NH_3)_2Cl_2]$ reacts with $HSCH_2COOH$ (H_2L), with or without HCl, to give *trans*-$[Pt(NH_3)_2Cl(HL)]$ or $[Pt(NH_3)_2L]$. Further transformations are detailed in reactions (19) and (20) [160].

$$[Pt(NH_3)_2L] + HCl \xrightarrow{50 - 60\ ^\circ C} cis\text{-}[Pt(NH_3)_2(HL)Cl] \qquad (19)$$

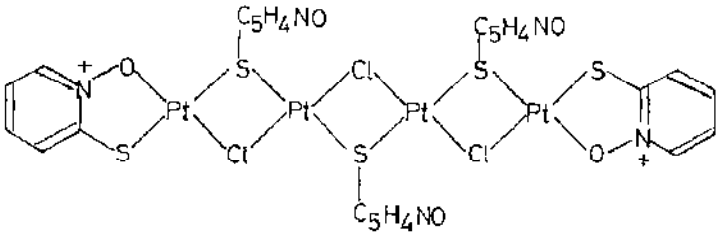
$$trans\text{-}[Pt(NH_3)_2Cl_2] + 2H_2L \xrightarrow{H_2SO_4} [Pt_2(NH_3)_4(HL)_2][SO_4] \qquad (20)$$

$K[Pt(C_2H_4)Cl_3]$ reacts with quinoline *N*-oxide to give a complex of stoicheiometry $[Pt(C_2H_4)LCl_2]$ but a similar reaction with pyridine-2-thione *N*-oxide yields (33) and (34). $K_2[PtCl_4]$ gives only (34). (34) reacts with phosphines to give monomeric species by displacement of oxygen. Their dynamic behaviour has been studied by NMR spectroscopy [161].

The extraction kinetics of Pd^{2+} from HNO_3 solutions by sulphides have been determined. The ligands used included both simple sulphides and 10-hexyl-7,13-dithia-10-azanonadecanol, 10,10-dioxa-7,16-dithiadocosane and 10,13,16-trioxa-7,19-dithiapentacosane [162].

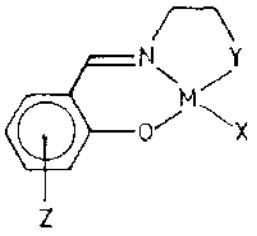


(33)



(34)

The kinetics of substitution of [LMX], (35) by Y^- was studied by normal and stopped flow spectrophotometry [163].



M = Pd or Pt

Y = NEt_2, SEt or S^-

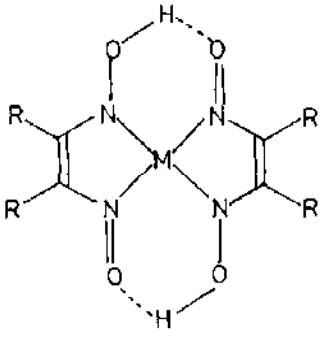
(35)

1.5.2.5 Ambidentate oxygen nitrogen donor ligands

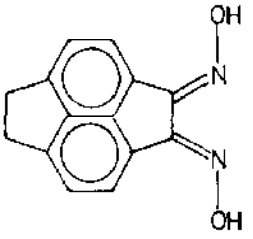
The metal substitution of $[ML_2]$ (HL = dimethylgyloxime, M = Ni, Cu or Pd) was studied by electron impact mass spectrometry. The ease of reaction (21) depends primarily on the counter ion (M' = Ni, Cu or Pd; X = Cl, $[NO_3]$, $[OCOCH_3]$, or 1/2 $[SO_4]$) with Pd(II) rather easily replaced by Ni(II) [164].

$$ML_2 + M'X_2 \longrightarrow M'L_2 + M^{2+} + 2X^- \qquad (21)$$

The mass spectra of the complexes (36) (M = Pd, Pt or Ni; R = Me or 2-furanyl) differ significantly. The stability is in the order Pt > Ni > Pd, as expected, and the abundance of fragments with M-C σ-bonds increases in the order M = Ni < Pd < Pt [165].



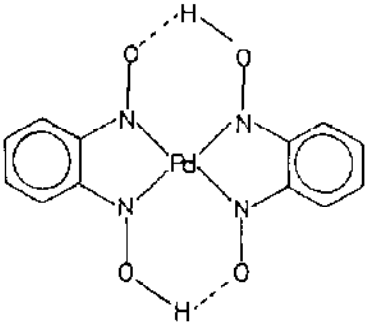
(36)



(37)

A bis(oxime) complex, all *N*-bonded, is formed by the ligand (37) with both palladium(II) and platinum(II) [166].

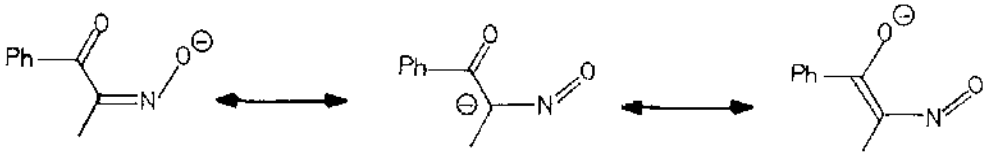
Bis(1,2-benzoqinone)dioximato palladium(II), (38), crystallises in two forms at room temperature. In the α-form the planar coordination complexes are stacked with their molecular planes rigorously perpendicular to the stack, whereas in the β-form the planes are angled at 25° to the stack. The crystal structure of the α-form varies as a function of temperature with a second order phase transition at 110 K, to give a supercell below this temperature [167].



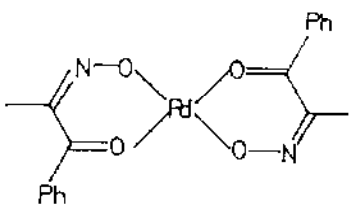
(38)

trans-Bis(D-camphoroxime)$PdCl_2$ has been prepared from $Na_2[PdCl_4]$ and D-camphor oxime. An X-ray diffraction study showed that the oxime is *N*-bonded and that steric factors are unhelpful to cyclometallation, which does not occur, even under forcing conditions [168].

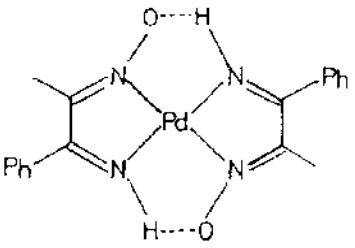
Both *O,O*- and *N,O*-chelation are theoretically possible in complexes of isonitrosopropriophenone, **(39)**. IR data for the palladium(II) complex imply a *trans*, symmetric square planar structure, **(40)**, with *O,O*-chelation in contrast to the nickel(II) analogue, which is *N,O*-chelated. The isonitroso iminato complex, **(41)**, is *N,N*-chelated [169].



(39a) **(39b)** **(39c)**



(40)

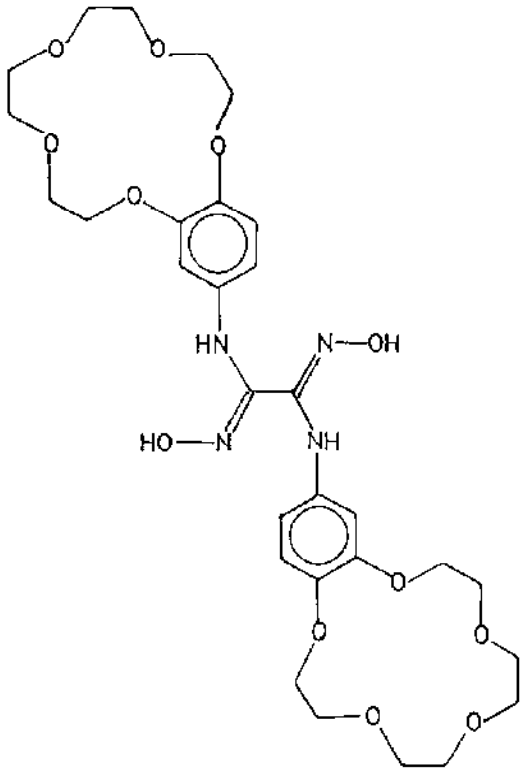


(41)

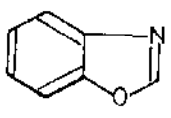
The ligand, **(42)**, which has a crown ether portion to complex sodium as well as a potentially chelating amino oxime moiety, forms six-membered ring chelates bonding through nitrogen and oxygen to palladium or platinum in $M(HL)_2.4Na[ClO_4]$ [170].

Benzoxazole, **(43)** and 2-methylbenzoxazole, **(44)** might also act as *N*- or *O*-donors. Their complexes $[ML_2X_2]$ (M = Pd or Pt; X = Cl, Br, I, NO_3, or SCN) were characterised by IR and electronic spectroscopy and conductivity measurements. These data demonstrated that most of the complexes adopted

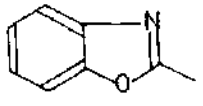
trans, square-planar geometry with **(43)** bonded through *N* and **(44)** bonded through *o* [171].



(42)

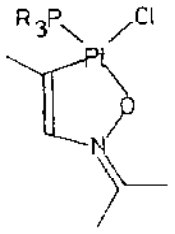


(43)

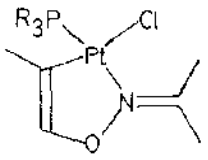


(44)

Reaction of the allene complex, *cis*-$[Pt(PMe_2Ph)(C_3H_4)Cl_2]$ with propanone oxime gave a product for which two structures, **(45a)** and **(45b)** could initially be proposed. Both X-ray diffraction and NMR spectroscopic data indicated that the material produced was in fact **(45a)** [172].



(45a)



(45b)

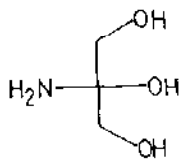
1.5.2.6 Bidentate and multidentate oxygen nitrogen donor ligands

The preparation of the species $[PtL^1L^2]$ (L^1 = $H_2NCH_2CH_2OH$ or $H_2NCH_2CH_2SH$; H_2L^2 = HOOCCOOH or $HOOCCH_2COOH$) has been described. Oxidative addition of halogens yields the corresponding *trans* platinum(IV) complexes [173]. Reactions of Pd(II) with mono-, di- and triethanolamine (eoa, deoa and teoa) were investigated spectrophotometrically. $[Pd(eoa)Cl_2]$, $[Pd(deoa)Cl_2]$ and $[Pd(teoa)Cl_2]$ were all isolated and analysed, and numerous other structures including $[Pd(eoa)]^+$, $[Pd(deoa)_3]$, $[Pd(eoa)_2Cl_4]$ and $[Pd_2(eoa)Cl_3$ were proposed to exist in solution. In all cases the ethanolamine is thought to act as an *N,O*-chelate [174].

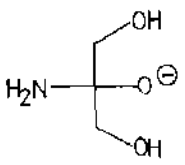
The kinetics for ring closure for *trans*-$[PtL_2Cl_2]$ (L = (46)) in the presence of $[HO]^-$ (reactions (22) and (23); L-H = (47)) have been investigated. The exact pathway followed depends on pH, and the species $[Pt(L\text{-}H)_2]$ has the structure (48) [175].

$$[PtL_2Cl_2] + HO^- \xrightarrow{\text{fast}} [PtL(L\text{-}H)Cl] + Cl^- + H_2O \qquad (22)$$

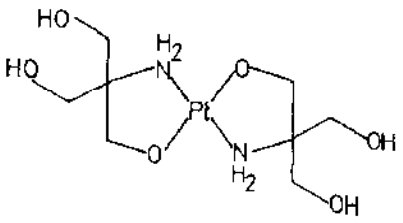
$$[PtL(L\text{-}H)Cl] + HO^- \xrightarrow{\text{slow}} [Pt(L\text{-}H)_2] + Cl^- + H_2O \qquad (23)$$



(46)



(47)



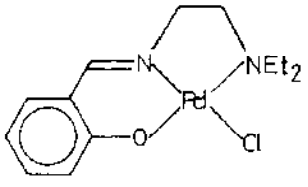
(48)

Reaction of Th^{4+} with $[PdL]^{2-}$ (H_4L = H_4edta) results in an equilibrium with [ThL] and Pd^{2+}. Measurement of the equilibrium constant gives the stabilty constant of $[PdL]^{2-}$ relative to [ThL] [176]. The reactions of $[(HOOCCH_2)_2N(CH_2)_6N(CH_2COOH)_2]$ with Pd(II) have been investigated. 1:1 and 2:1 complexes are reported and both carboxylate and nitrogen may be bound under appropriate conditions, but the precise structures involved are not defined [177]. Thermal decomposition of complexes of the substituted H_4edta, $[(HOOCCH_2)_2NCH(CH_3)CH_2N(CH_2COOH)_2]$, ($H_4L$) such as $[Pd(H_3L)X].2H_2O$ and $[Pd_2(H_2L)(NCS)_2].2H_2O$, have been studied by DTA. Decarboxylation occurs in two stages, with free COOH groups lost first [178]. The thermal properties of $Na_3[PdLCl_3].2H_2O$ (HL = iminodiacetic acid) were also investigated [179].

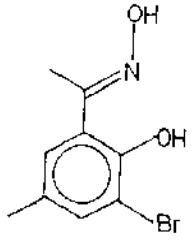
Reaction of α-pyridone with $[Pt(en)(H_2O)_2][NO_3]_2$ yields the head-to-tail isomer of $[Pt_2(en)_2(C_5H_4NO)_2][NO_3]_2$. X-ray diffraction in the solid state shows that this is a dimer of dimers with r(Pt-Pt) = 2.992 Å for the binuclear unit and 3.236 Å for the interdimer distance. Both of these values are slightly greater than is observed in the *cis*-diammine complex, which is attributed to a greater repulsion between adjacent in-plane ligands. This argument is also used to account for the fact that isomerisation is easier, but oxidation to Pt(III) more difficult [180]. The reversible intramolecular head/head to head/tail isomerisation was studied by ^{195}Pt NMR

spectroscopy, and it was concluded that the reaction occurred dissociatively *via* initial cleavage of the Pt-N bond [181]. The reaction of α-pyridone with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ gives both the head-to-head and the head-to-tail bridged dimers, $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$. X-ray diffraction studies are compared with those of the analogous platinum pyridone blue [182]. Both 5-chloro and 5-methyl α-pyridonates form bridged binuclear complexes of the type $[M_2L_4]$; across the transition series X-ray diffraction studies show a progression to longer M-M and shorter M-O and M-N bonds [183].

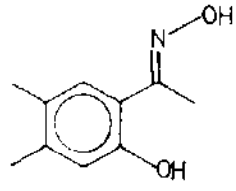
A range of *O,N*-chelating ligands where the oxygen donor atom is a phenol have been studied. **(49)** is formed from the tridentate ligand, *N*-(2-diethylaminoethyl)salicylaldimine and has been studied by X-ray diffraction. The complex is close to planar, though the copper analogue shows somewhat greater distortion [184].



(49)

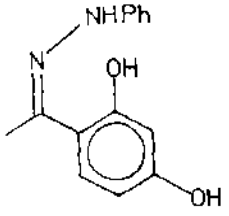


(50)

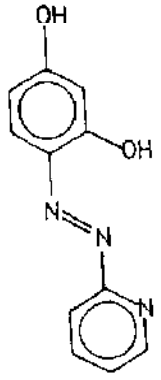


(51)

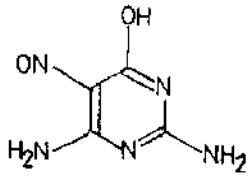
The two oximes, (50) and (51) form complexes of stoicheiometry $[PdL_2]$. These have been studied by IR, electronic and Mossbauer spectroscopy [185] and thermogravimetric techniques [186], all of which support the assumption of an *O,N*-chelated structure. The complexes $[M(HL)_2].2H_2O$ of resacetophenone phenyl hydrazone (H_2L, (52)) have been prepared and characterised. Coordination occurs through the azomethine nitrogen and the adjacent phenolic oxygen, in a square-planar, but polymeric complex [187].



(52)



(53)



(54)

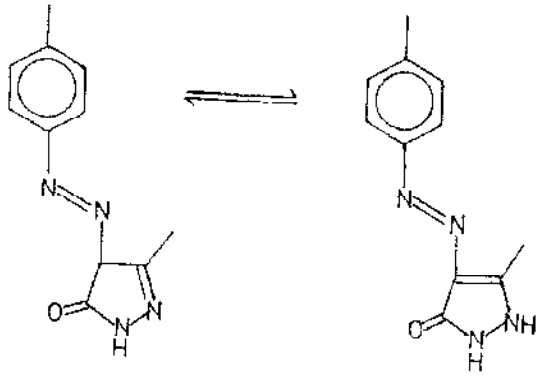
The kinetics of complexation of platinum(II) with 4-(2-pyridylazo)resorcinol, (53), and analogues have been investigated in various solvents [188].

2,6-Diamino-4-hydroxy-5-nitrosopyrimidine, (54), forms a tridentate palladium(II) complex, $[PdLCl].2H_2O$, which was characterised by IR spectroscopy and DTA. Coordination is said to occur through OH, NH_2 and the ring *N*-3 [189].

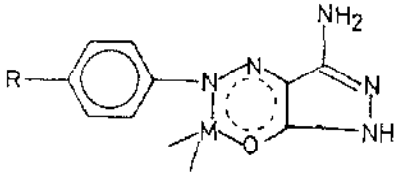
The complexes, $[PdL_2]$, of 3-methyl-4-(4-methylphenylazo)pyrazol-5-one, (55), and analogues are reported to be square-planar. Neither the mode of ligand binding nor the stereochemistry of the complexes are specified [48]. Somewhat better data were provided for complexes of 3-amino-4-arylazopyrazolones. Again it is the anion which is metal bound with the structure (56) proposed for the $[L_2Pd]$ complex. The structure of $[PdL_4(H_2O)_2]$ is less clear [190].

Many hydrazides, including malonodihydrazide and ethanoyl hydrazide, form metal complexes as unidentate nitogen donor ligands. However, $HCONHNH_2$ acts as an *O,N*-bidentate ligand in $[LPdCl_2]$ with binding from the carbonyl oxygen and the terminal NH_2 group [191]. 3-Phenylhydrazono-5-methyl tetronic acid, (57), LH, and 3,4-di(phenylphydrazono)-5-methyl tetronic acid, (58), HQ,

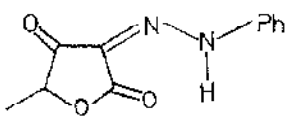
exist as a mixture of several tautomers. Reactions with *trans*-$[Pd(NH_3)_2(NO_3)_2]$ give respectively $[PdL_2]$ and $[PdQ_2(NH_3)_2]$, the structure (59) being proposed for $[PdL_2]$ [192].



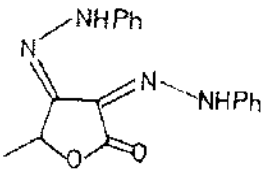
(55a) (55b)



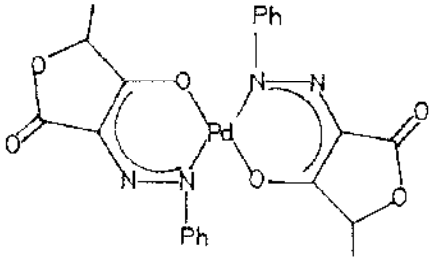
(56)



(57)

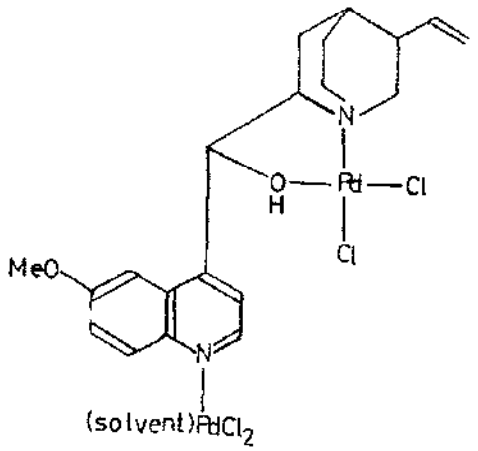


(58)

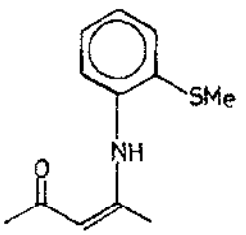


(59)

The CD spectra of $[(quinine)PdCl_2].2H_2O$ and $[(quinine)(PdCl)_2].5H_2O$ have been determined in dmf and dmso. There are strong Cotton effects in the d-d range. Quinine is thought to act as an *O,N*-chelate in **(60)** [193].



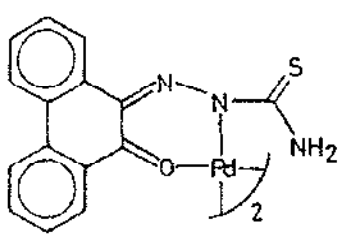
(60)



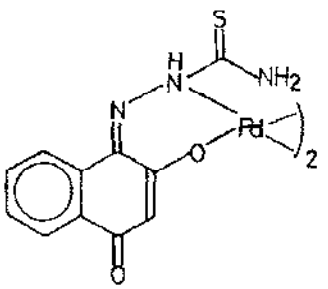
(61)

Ligands capable of multidentate coordination continue to be developed. 4-[2-(Methylthio)anilino]-3-pentene-2-one, **(61)** was prepared by condensation of pentane-2,4-dione with 2-methylthioaniline. Reaction with $Na_2[PdCl_4]$ gives [Pd{**(61)**}Cl] in which L is *O,S,N*-coordinated. Transformations of this complex are shown in Scheme 4 [194].

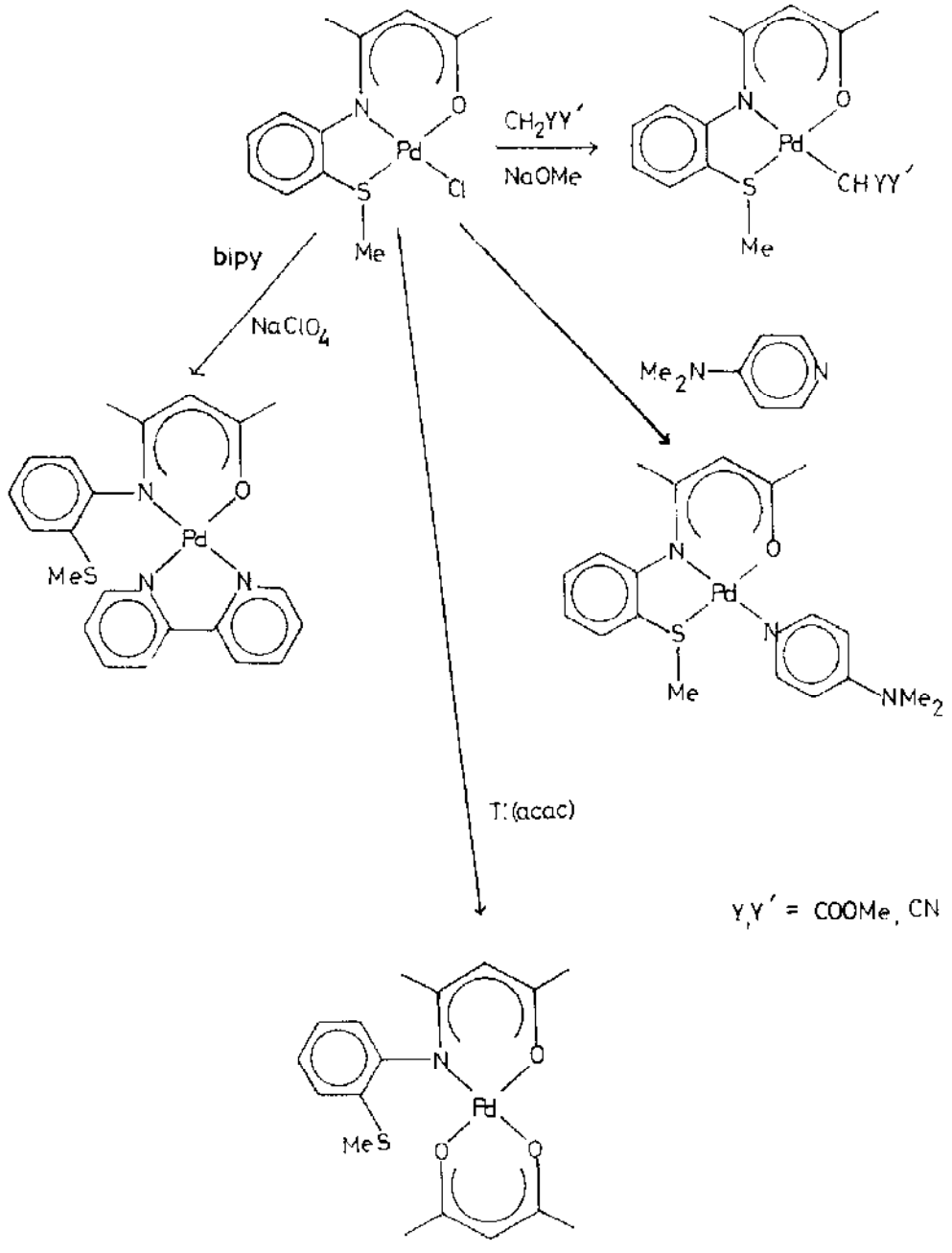
The complexes, $[PdL_2]$, of phenanthroquinone monothiosemicarbazone, **(62)** and 2-hydroxy-1,4-naphthoquinone thiosemicarbazone, **(63)**, were prepared and characterised; their stereochemistry is not known [195].



(62)



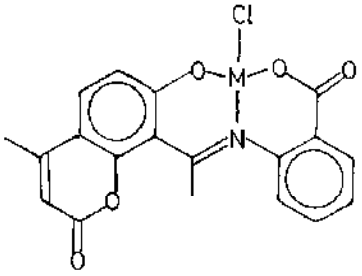
(63)



Scheme 4 Transformations of [Pd(61)L] [194].

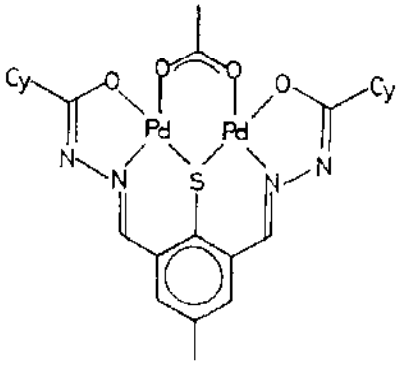
(64) (M = Cu, Pd or Pt) is prepared by heating under reflux a mixture of MCl_2 with the ligand in ethanol. The ligand is prepared from anthranilic acid

and 4-methyl-7-hydroxy-8-acetylcoumarin [196].

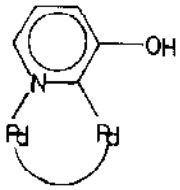


(64)

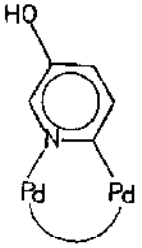
Reaction of the binuclear complex, (65), with indole causes replacement of the acetate bridge with an indole bridge. Using 3-hydroxypyridine, two isomers, both *N,C*-bridged, are formed, (66) and (67); in (67) the OH function is linked to another molecule [197]. Binuclear complexes of structure (68), are formed from 2-(α-pyridonimino)propanoic acid (X = CH_2CH_2) and 2-(α-pyridonimino)benzoic acid, have been prepared and characterised [198].



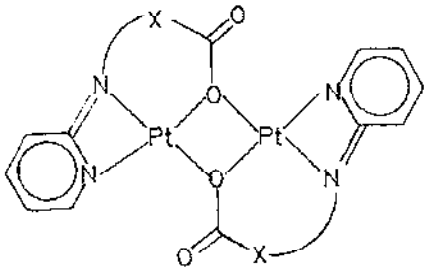
(65)



(66)



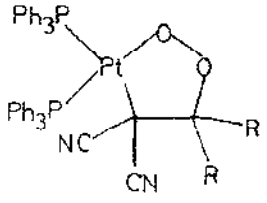
(67)



(68)

1.5.2.7 Bidentate oxygen carbon donor ligands

Reaction of $[Pt(PPh_3)_2(O_2)]$ with an alkene $R_2C{=}C(CN)_2$ (R = CN or Me) gives a cyclic species **(69)**. An X-ray diffraction study of the complex with R = Me reveals distorted square planar coordination about platinum with a twisted five-membered ring [199].



(69)

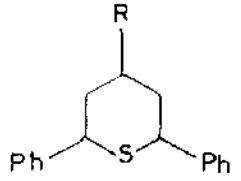
1.5.2.8 Unidentate sulphur donor ligands

The rate law and temperature dependence of ligand exchange of dimethyl sulphide in $[(Me_2S)_2PdCl_2]$ was studied by ^1H NMR spectroscopy in various solvents. ΔV^* is correlated with the solvent electrorestriction parameter, implying a highly symmetrical associative ligand exchange pathway with a trigonal bipyramidal transition state or intermediate [200].

The rate of reaction of R_2S with $[(dien)PtBr]^+$ was studied in 95% methanol; the second-order rate constant is relatively insensitive to the electronic effect of R, but is reduced for bulky R groups [201]. The *cis*-effect of the ligands L = R_2S or R_2SO on substitution reactions of $[(en)PtLX]^+$ by halide was studied potentiometrically. An associative mechanism

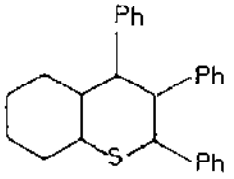
is proposed with the *cis*-influence decreasing in the order Me_2SO > Me_2S > Et_2SO > Et_2S > Pr_2SO > Pr_2S [202].

Trans-$[ML_2Cl_2]$ (M = Pd or Pt; L = (70), (71) or (72)) may be prepared by reaction of $K_2[MCl_4]$ with L. The complexes were characterised by IR spectroscopy and DTA and their antibacterial activity studied [203]. Dynamic NMR spectroscopic studies of analogous complexes of thiacyclohexane, thiacyclobutane and 1-thia-3-methylcyclobutane have been carried out. The variation of the rate of inversion at the pyramidal sulphur atoms with pressure was determined; $\Delta V^{\ddagger}$ is very small, implying that there is little or no participation from solvent in the process [204].

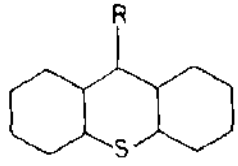


R = H, CH_3 or Ph

(70)



(71)



R = CH_3 or Ph

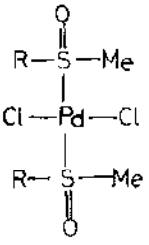
(72)

Fusion *in vacuo* of $[PtL_2(SR)_2]$ (L = PPh_3 or PMe_2Ph; R = CH_2Ph or 4-methyl-C_6H_4) yields the dimer $[\{LPt(SR)(\mu\text{-}SR)\}_2]$ from both *cis*- and *trans*-isomers. An X-ray diffraction study of $[\{Pt(PMePh_2)(SCH_2Ph)(\mu\text{-}SCH_2Ph)\}_2]$ shows that it has *cis*-geometry, with the benzyl groups of the bridging thiolato ligands *anti* to each other [205].

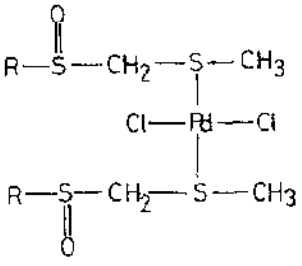
That sulphides coordinate to palladium more strongly than the corresponding sulphoxides received an interesting confirmation in a study of the complexes (73)-(75) (R = 4-methyl-C_6H_4). (73) is the best catalyst both for cyclotrimerisation of diphenylethyne and isomerisation of allyl ethanoates. In both processes a vacant metal coordination site is essential and the sulphide sulphur is too strongly bound for facile dissociation [206].

The thermochemical aspects of the conversion of the Magnus salt

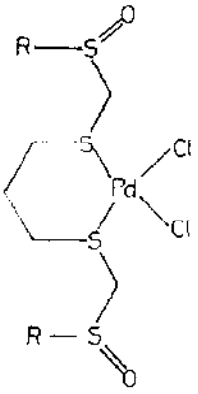
compounds $[PtL_4][PtCl_4]$ (L = R_2S, R_3N or R_3P) to $[PtL_2Cl_2]$ have been investigated [207].



(73)



(74)



(75)

The complexes $[PtL_4]X_2$ (where L is a thiourea and X = Cl, I, $[BF_4]$, $[BPh_4]$, $1/2[SO_4]$, $1/2[C_2O_4]$ or $1/2[SiF_3]$) have been investigated. They are comparatively weak electrolytes since the NH_2 of the thiourea forms hydrogen bonds to X, the strength of which increases with decreasing size and increasing charge on X^- [208]. The mechanism of reaction (24) has been investigated [209].

$$trans\text{-}[Pt(NH_3)_2Cl_2] + tu \xrightarrow{Na[ClO_4]} trans\text{-}[Pt(NH_3)_2(tu)Cl]Cl \qquad (24)$$

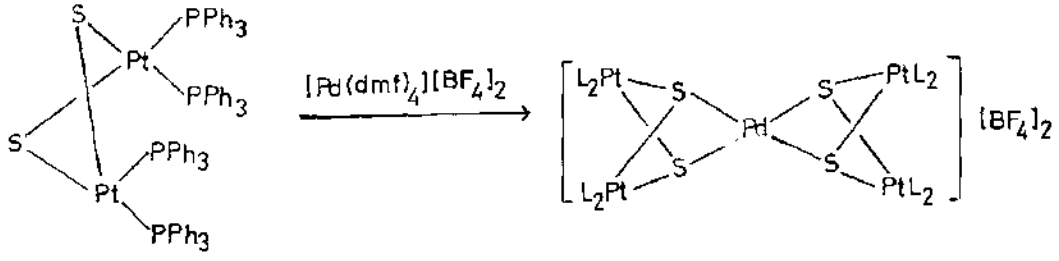
The nephrotoxicity shown by *cis*-$[Pt(NH_3)_2Cl_2]$ in cancer treatment is alleviated by coadministration of sodium diethyldithiocarbamate, so the reactions of thiocarbamates with platinum complexes is of some interest. The preparation of *trans*-$[ML_2X_2]$, M = Pd or Pt, L = *N,N*-dimethyl-*O*-ethylthiocarbamate, **(76)**, and *N*-methyl-*O*-ethylthiocarbamate, **(77)**, by a new method, has been described. The complexes were themselves tested for cytostatic activity; derivatives of **(76)** gave poor results, whereas moderate activity was detected in the platinum complexes of **(77)** [210]. 1:2, 1:3 and 1:4 derivatives, $[ML_2X_2]$, $[ML_3X]X$ and $[ML_4]X_2$ (M = Pd or Pt; X = Cl, Br or I) of *O*-ethylthiocarbamate have also been synthesised. IR

spectroscopy does not allow unambiguous structural assignment and L is partly dissociated [211].

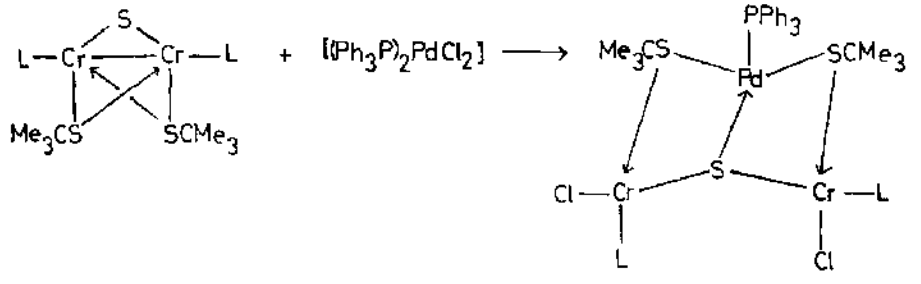
Reaction of $[PdX_2]$ (X = Cl or Br) with Ph_3PS or Ph_3PSe gives complexes of stoicheiometry $[PdLX_2]$ or $[Pd_2L_3Br_4]$ [212].

1.5.2.9 Bidentate and multidentate sulphur donor ligands

The bridged bimetallic species **(78)** functions as a bidentate ligand towards other metal ions including Ni(II), Pd(II), Hg(II) and Au(I) to give heterobimetallic species such as **(79)** [213]. Tridentate and bidentate bridging sulphur atoms are also found in **(81)** which is formed by the reaction of **(80)** (L = cp) with $[Pd(PPh_3)_2Cl_2]$ [214].

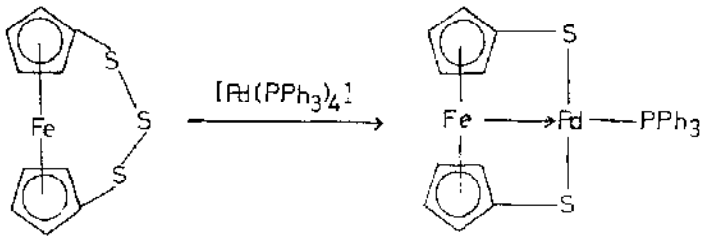


(78) **(79)**



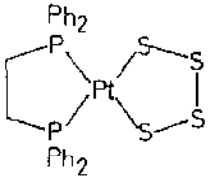
(80) **(81)**

Oxidative addition of **(82)** to $[Pd(PPh_3)_4]$ yields **(83)**, which was fully characterised by X-ray diffraction [215].



(82) **(83)**

The structure of $[(dppe)PtS_4]$ has been established by X-ray diffraction to be **(84)**; the central S-S bond is shorter than the others [216].

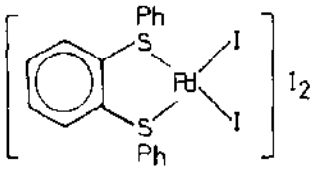


(84)

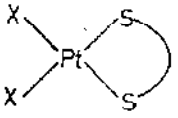
Diallyl sulphide, L, reacts with $K_2[PtCl_4]$ to give 1:1 and 1:2 complexes $[Pt_2(\mu\text{-}L)_2Cl_4]$ and $[Pt_2(\mu\text{-}L)Cl_6]^{2-}$ in which L is bidentate and bridges through the sulphur atom [217].

Stereochemical aspects of the complexes of bidentate thioethers have been investigated. The ^{195}Pt NMR chemical shift in $[\{R^1SCH(R^2)CH_2SR^1\}PtCl_2]$ depends both on ligand basicity and molecular conformation. The δ-λ transition is relatively easy in the five-membered ring [218]. X-ray diffraction studies of **(85)** show that in the solid state the palladium has square planar coordination with the phenyl groups *anti*. Adjacent molecules are linked by I--I-I--I bridges giving an essentially linear I_4 arrangement [219, 220]. Palladium(II) is extracted from $[PdCl_4]^{2-}$ solutions by $C_8H_{17}SCH_2CH_2SC_8H_{17}$, L, as a five-membered neutral chelate [221]. Total band shape fitting methods in the NMR spectra of **(86)** and **(87)** where the chelating ligands include $MeSCH_2CH_2SMe$, $MeSeCH_2CH_2SeMe$, $MeS(CH_2)_3SMe$, *cis*-MeSCH=CHSMe or **(88)** and X = Cl, Br or I, provide accurate inversion barriers at sulphur

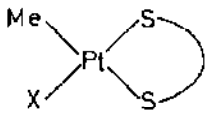
and selenium. 3p-2p π-conjugation between sulphur and the conjugated backbones causes a lowering of the barrier by 10-12 kJ mol^{-1} [222]. In both **(89)** and **(90)** sulphur inversion was found to be fast at room temperature. If bromine is replaced by chlorine in **(90)** the barrier is lowered by about 20 kJ mol^{-1} [223].



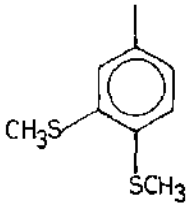
(85)



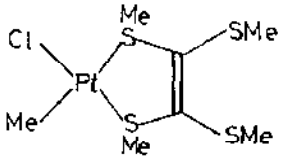
(86)



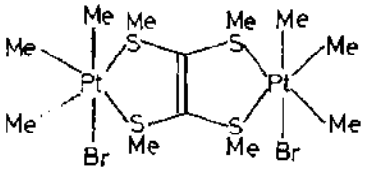
(87)



(88)



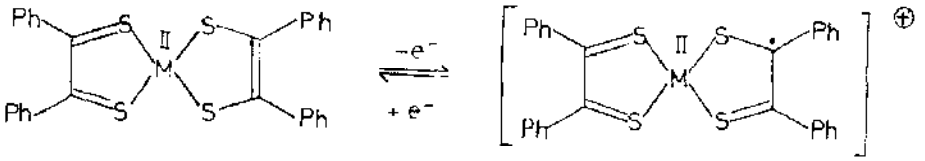
(89)



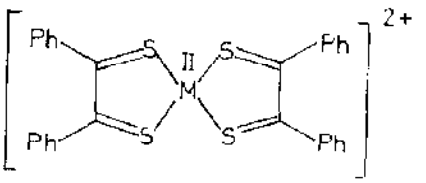
(90)

More detailed studies of dithiolates have been published. The structure of $[Pt(S_2C_2Ph_2)_2]$ is described [224]. EPR spectra of the one-electron reduction products of this and its palladium analogue confirm that the reductions are ligand based. Cyclic voltammetric studies show a *quasi* reversible redox process (reaction (25)); in **(91)** the unpaired electron is delocalised over both metals and to some extent the central metal atom [225]. Two reversible reductions were also noted for **(92)** (M = Ni, Pd or Pt;

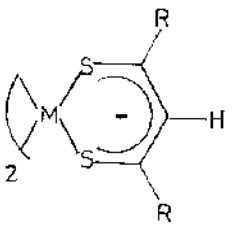
R, R' = CMe_3, CF_3, Me or Ph); again the electron transfers are ligand centred [226]. The electrical conductivities of $[Et_4N][Pt(S_2C_2Ph_2)_2]$ and $[Et_4N][Pt(S_2C_2Me_2)_2]$ have been measured. The monoanions bearing a phenyl substituent are more conducting by a factor of 10^3 than the cyano analogues, possibly due to increases mobility of the charge carriers [227].



(91)



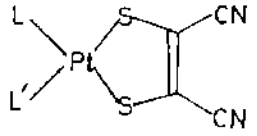
(25)



(92)

The new complexes **(93)** have been prepared; they luminesce in the solid state at room temperature and in frozen glass media. The small Stokes shifts imply that the excited and ground state geometries are similar and the emission absorption system is assigned to a singlet triplet d–π^*(mnt) metal to ligand charge transfer [228].

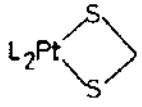
Simple dithiolates of the type $[L_2Pt(SR)_2]$ (L = PPh_3, PMe_2Ph or PPh_2Me) are prepared by treating the corresponding chlorides with RSH/Et_3N. The



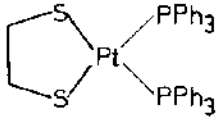
L,L' = cod, $P(OEt)_3$, $P(OPh)_3$ or dppm

(93)

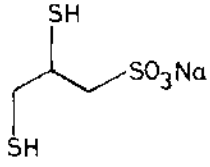
cis-complex is isolated for R = $CH_3CH_2CH_2$, $(CH_3)_2CH$ or $PhCH_2$, whilst the *trans* species is obtained with R = 4-methylphenyl. The cyclic compound, **(94)** is obtained from *cis*-$[PtL_2Cl_2]$ with $H_2S/K_2CO_3/CH_2Cl_2$ [229]. The structure of **(95)** has been determined by diffraction methods [230]. In the palladium(II)/unithiol, **(96)**, system, intermediates with palladium:L ratios 1:2, 1:1 and 2:1 were detected by electronic spectroscopy [231].



(94)

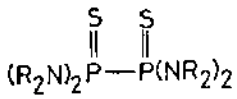


(95)

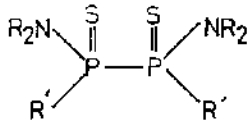


(96)

Complexes of bidentate phosphine sulphides are somewhat more stable than those of monodentate analogues. $Me_2P(S)P(S)Me_2$ forms a five-membered chelate complex whilst $Ph_2P(X)CH_2P(X)Ph_2$ (X = S or Se) form six-membered chelates $[LPdX'_2]$ [212]. $R^1R^2P(S)P(S)R^1R^2$ also forms five-membered chelate complexes with palladium(II) and platinum(II) [232]. Complexes, $[LPdCl_2]$ of (97) and **(98)** have been studied by diffraction methods; the ligand adopts the gauche conformation [233].



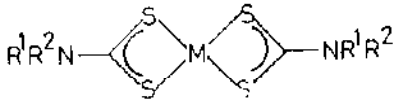
(97)



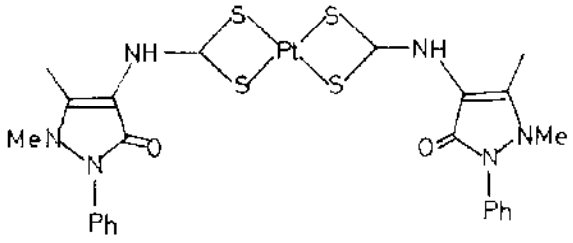
R = Et, R' = Cy

(98)

Interest in dithiocarboxamide complexes has continued. The bis(dithiocarbamate), **(99)**, is prepared from $Na[S_2CNR^1R^2]$ and $PdCl_2$ or $K_2[PtCl_4]$. Infrared spectroscopy confirms the bidentate structure [234]. Thermolysis of **(99)** (R^1 = R^2 = 4-ethoxyphenyl) yields palladium sulphide [235]. Restricted rotation about the C-N bonds in **(99)** (R^1 = H, R^2 = CH_2CH_2Ph) has been studied by high performance liquid chromatography. $\Delta H^{\ddagger}$ for the rotation was determined to be 83 ± 5 kJ mol^{-1} [236]. By contrast, **(100)**, on thermolysis, yields initially $Pt[SO_4]$ and finally PtO [237].

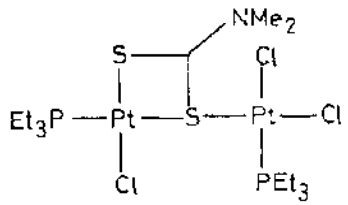


(99)

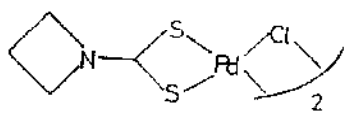


(100)

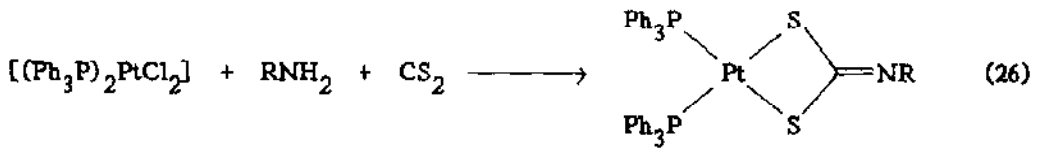
Reaction of $Na[S_2CNMe_2]$ with $[Pt_2(PEt_3)_2Cl_4]$ gives the curious binuclear complex **(101)**. IR spectroscopy shows that the C-N linkage has considerable double bond character [238]. **(102)** was prepared in 40-65% yield *via* reaction (26) [239]. A monodentate dithiocarbamate is reported to be present in the complex $[PdL_2(pip)_2].2H_2O$ (L = pentamethylenedithiocarbamic acid) [44]. **(103)** is one of the complexes which, when anchored to silica gel, is a catalyst for carbonylation of $ArNO_2$ to ArNHCHO and ArNHCOOH [240].



(101)



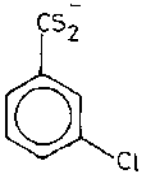
(103)



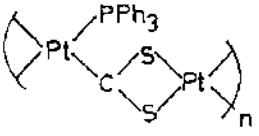
(102)

R = CH_2COOEt, CH_2COOH, CH_2Ph or $C(CH_3)_3$

The metal atomic charges in nickel, palladium and platinum chelate complexes of dithiocarboxylates were calculated from atomic polarizability determinations and by the generalised Born-Haber cycle [241]. Reactions of **(104)** with $H_2[PdCl_4]$ and $K_2[PtCl_4]$ were reported to give respectively $[PdL_2]$ and $[PtL_4]$. Curiously, however, the authors describe both as complexes of the metals in the +2 oxidation state [242].

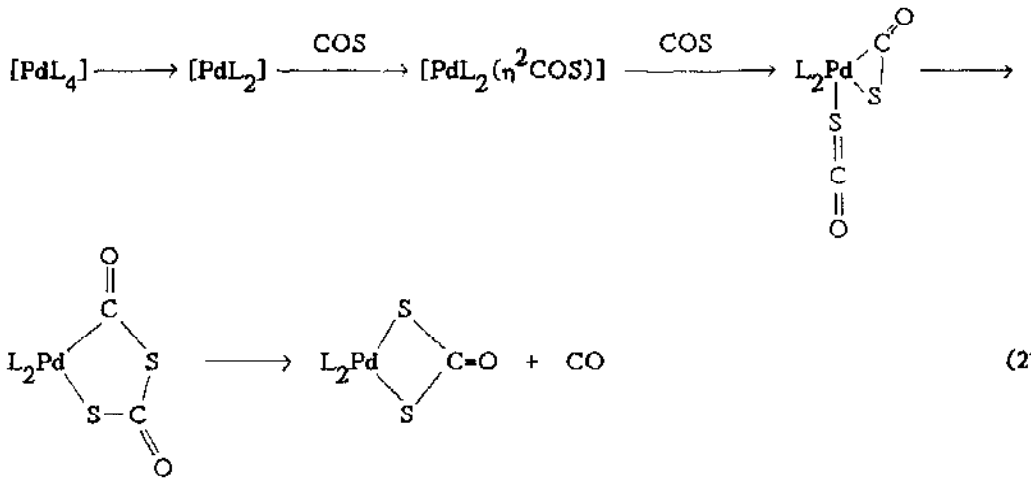


(104)



(105)

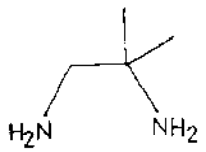
Thermolysis of the formally Pt(0) complex $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ yields PPh_3 and a polymer of structure (105) [243]. Oxidative addition of COS to $[Pd(PR_3)_4]$ gives $[Pd(PR_3)_2(S_2CO)]$ in which the S_2CO moiety is coordinated through both sulphur atoms. The structure of the complex for which R_3P = Me_2PhP was determined by diffraction methods. A possible mechanism for the process is shown in reaction (27) [244].



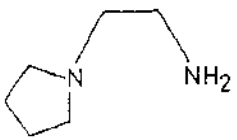
(27)

1.5.2.10 Ambidentate sulphur-nitrogen donor ligands

Studies of linkage isomerism in thiocyanate complexes continue. A systematic study of [(diamine)Pd(SCN)$_2$] species is reported, including diffraction studies of complexes of **(106)** and **(107)**. It was concluded that an increase in steric hindrance in the amine promotes *N*-bonding on the part of the thiocyanate, but the bonding mode is also influenced by the physical state of the complex, kinetic factors and the solvent in which the complex is prepared or crystallised [245]. IR spectral data were used to establish the mode of SCN coordination in eight palladium(II) thiocyanate complexes with phosphorus donor ligands [246].



(106)



(107)

The linkage isomerism of [Pd(Et$_4$dien)(SCN)]$^+$ was studied as a function of temperature and thiocyanate concentration in water and dmf. Conventional wisdom suggests that *S*-coordinated SCN adopts a bent conformation and hence is

more sterically demanding than the linear *N*-coordinated isomer. The steric effect of the ethyl groups in this case makes the *N*-bonded isomer more stable by about 9 kJ mol^{-1}. The mechanism of interconversion of the two isomers involves both direct $[SCN]^-$ attack and a solvent modified pathway, both I_a [247].

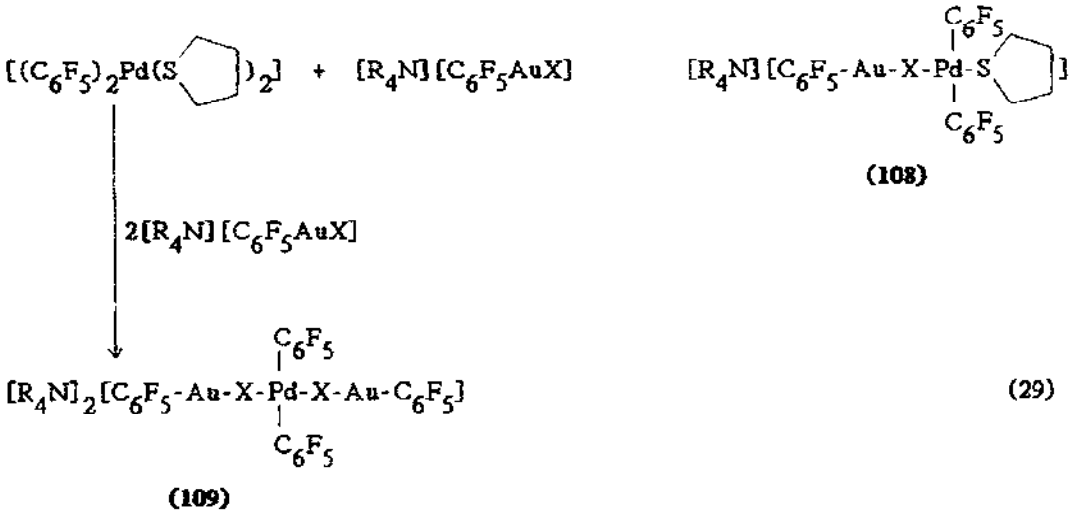
The kinetics of ligand replacement in reaction (28) (L = sulphides, selenides or sulphoxides) were studied in 0.1 M $Na[ClO_4]$ solutions. The *cis*-effect of the ligands decreased in the order $Me_2SO > Me_2S > Me_2Se > Et_2Se > Pr_2SO > Pr_2S > Et_2SO > Et_2S$ [248].

$$[Pt(en)LCl]^+ + [SCN]^- \longrightarrow [Pt(en)L(SCN)]^+ + Cl^- \qquad (28)$$

The mechanism of sorption of a Pd(II) thiocyanate complex by a polyether type of polyurethane foam has been investigated. At low thiocyanate concentration palladium is extracted as $Pd(SCN)_2$. At high thiocyanate concentration the reaction is more complex; $[Pd(SCN)_4]^{2-}$ is the major species involved, but the detailed process depends on the complexation of the cation by the foam [249].

A bridging mode of coordination is proposed in (108) and (109), prepared in reaction (29) (X = CN or SCN). There is no evidence as to whether the original Au-SCN or Au-CN linkage is retained or whether isomerisation occurs [250].

The ligands $Me_2Si(NCS)_2$ and $MeSi(NCS)_3$ complex to $PdCl_2$ through sulphur in $[LPdCl_2]$, though with harder acids *N*-coordination predominates [251].



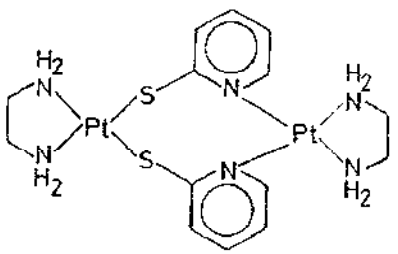
(108)

(109)

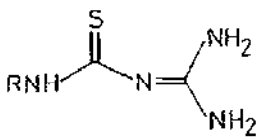
(29)

1.5.2.11 Bidentate and multidentate sulphur nitrogen donor ligands

The complexes [PtLL'] (L = $HSCH_2CH_2NH_2$ or 2-aminothiophenol; H_2L' = $H_2C_2O_4$ or $RCH(COOCH_3)COOH$) have been prepared and characterised; L acts as an *N,S*-chelate [252]. (110) is synthesised from $[Pt(en)Cl_2]$ and 2-thiopyridine; in the solid state it closely resembles the head-to-tail isomer of the corresponding α-pyridonate complex [253].



(110)

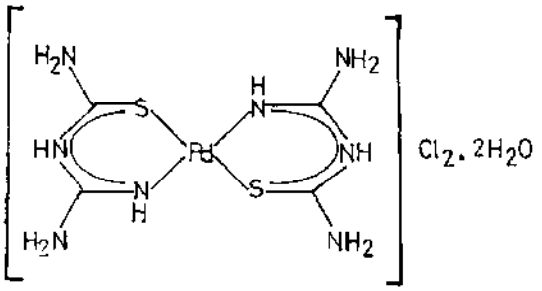


R = H, Me or Et

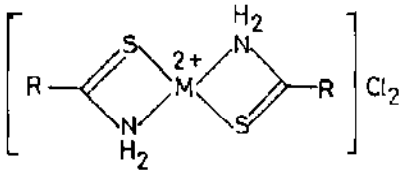
(111)

A range of complexes of 2-amidino-2-thioureas, **(111)**, of the type $[ML_2X_2]$ (M = Pd; X = Cl or Br) have been prepared; all are *S,N*-bonded [254]. Preliminary diffraction data on bis(1-amidino-2-thiourea) palladium, (112), have been reported [255].

Complexes $[ML_2]Cl_2$ (M = Pt, Pd or Hg; L = a thioamide) have the

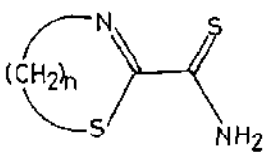


(112)



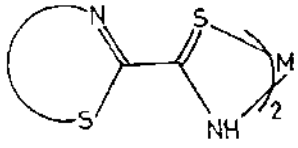
(113)

structure (113). $[MLCl_2]$ species have also been isolated [256]. Thioamides such as (114) form related complexes (115) but species with the alternative ligation (116) were also characterised [257].

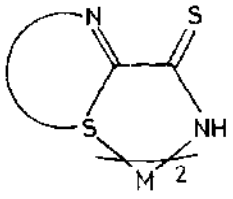


(114a) n = 2

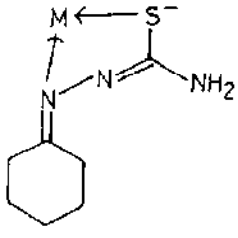
(114b) n = 3



(115)



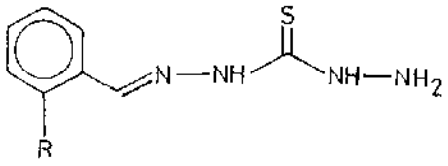
(116)



(117)

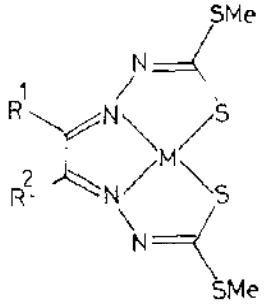
Cyclohexanone thiosemicarbazone (HL), acts as an *S,N*-bidentate ligand in $[M(HL)_2]X_2$ (M = Pd or Pt; X = Cl, Br or I). Under alkaline conditions the main species isolated is $[ML_2]$; the ligand is still *S,N*-coordinated, this time through the enol form, (117) [258]. An *S,N*-chelated complex $[PdL_2]Cl_2.nH_2O$ is also formed from **(118)**, coordination occuring through sulphur and the NH_2 group [259]. α-Diketone and α-ketoaldehyde bishydrazones derived from

hydrazine-*s*-methylcarbodithioate are proposed to give complexes such as **(119)** [260].



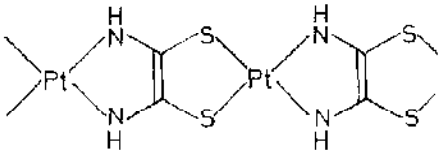
(118)

R = H or OH



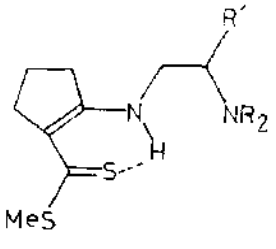
(119)

The infrared spectrum of the polymeric species $[Pt(HNSCCSNH)]_n$ has been analysed indicating, albeit rather vaguely, a square-planar structure with a *cis*-configuration **(120)** [261].

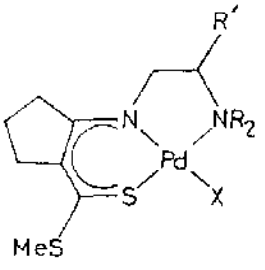


(120)

The ligand **(121)** (HL) forms tridentate complexes **(122)** with palladium(II). Treatment with $Ag[ClO_4]$ in the presence of a coordinating solvent, S, yields $[PdLS][ClO_4]$ and the solvent may be replaced from this species by a variety of Lewis bases [262].

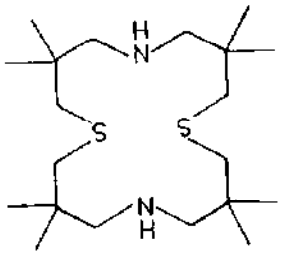


(121)



(122)

1:1 complexes between (123) and $PdCl_2$ and $Pd[PF_6]_2$ have been prepared. In the chloride, palladium is five-coordinate with a trigonal bipyramidal structure and two isomers, the *cis,cis,cis* and the *cis,cis,trans*, have been crystallised [263].

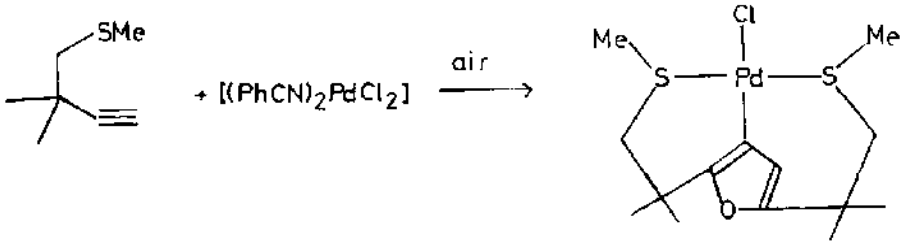


(123)

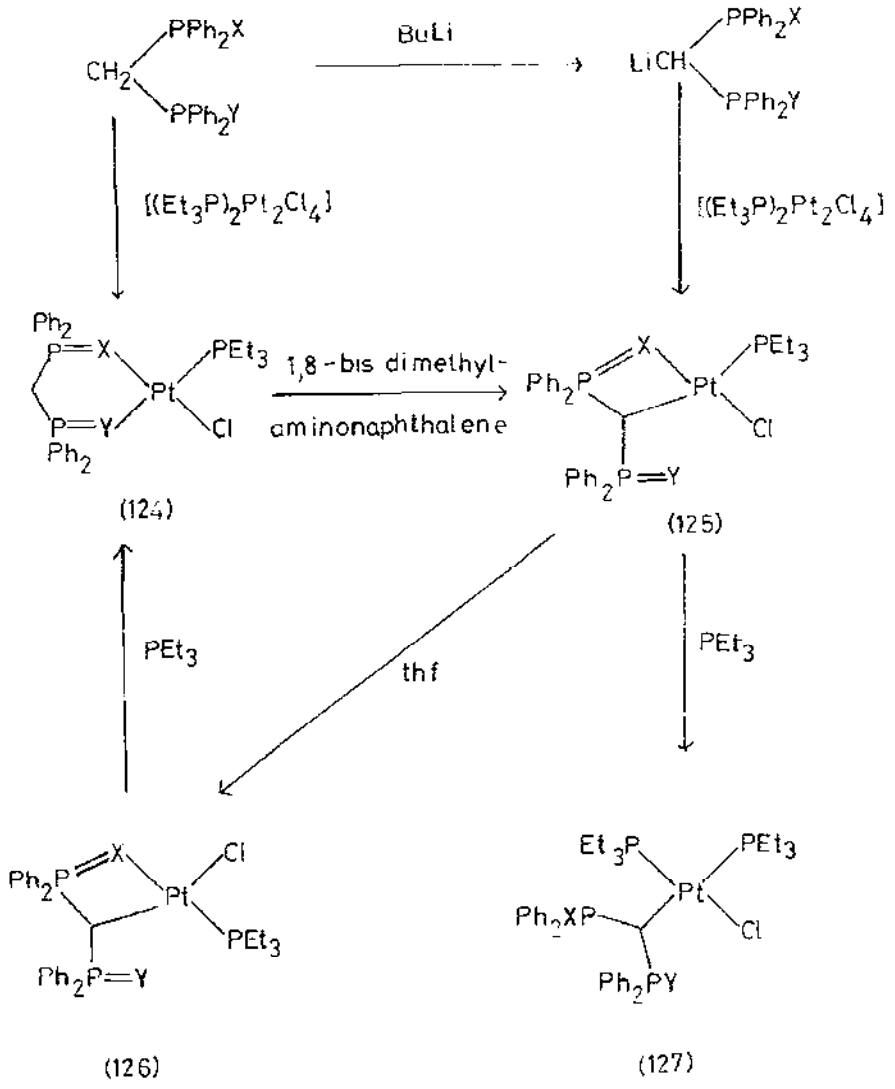
1.5.2.12 Bidentate sulphur carbon donor ligands

A complex series of transformations (Scheme 5) has been established for complexes of the ligands $XPh_2PCH_2PPh_2Y$ where X and Y are oxygen, sulphur or selenium. All the complexes **(124)-(127)** have been characterised for X = Y = S, including a diffraction study of **(126)** which shows the four membered ring to be essentially planar. **(124)** and **(125)** were characterised for X = S, Y = O, but the complexes in which X = Y = Se were less stable [264].

Reaction of **(128)** with $[Pd(PhCN)_2Cl_2]$ yields (129), the structure of which was established by X-ray diffraction. The two six-membered rings adopt different conformations, one being a twist-boat and the other a twist-chair [265].



(128) (129)



Scheme 5 Transformations of complexes of bidentate sulphur carbon donor ligands [264]

Further coordination chemistry of sulphines, XYC=S=O, has been investigated with the aim of synthesising unstable sulphines in a metal coordination sphere. Reaction of *cis*-Z-[$(Ph_3P)_2$Pt(II)(4-methyl-C_6H_4-S-C=S=O)Cl] with K[4-X-C_6H_4S] gives *cis*-E- and *cis*-Z-[$(Ph_3P)_2$Pt(II)(4-X-C_6H_4S)(4-methyl-C_6H_4-S=C=O)] [266].

1.5.2.13 Selenium donor ligands

A detailed preparation of mixed ligand diselenocarbamates by reactions (30) and (31) has been published; the diselenocarbamates are synthesised from CSe_2 and amines [267].

$$[Pd(Se_2CNEt_2)_2] + [Pd(PPh_3)_2Cl_2] \longrightarrow 2[Pd(PPh_3)(Se_2CNEt_2)Cl] \quad (30)$$

$$[Pt(Se_2CNEt_2)_2] + [Me_2Pt(PPh_3)_2] \longrightarrow 2[Pt(PPh_3)(Me)(Se_2CNEt_2)] \quad (31)$$

1.5.3 Complexes with amino acids, peptides and nucleic acids

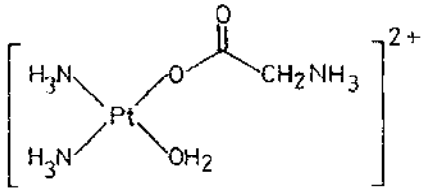
Since most biologically important molecules bind to palladium and platinum through Group VI and Group V donor atoms, the practice of considering them between ligands belonging to these two groups is continued. The interactions of palladium(II) and platinum(II) with proteins and nucleic acids have been reviewed [268].

1.5.3.1 Amino acids

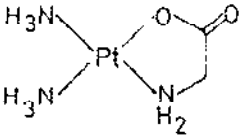
The reaction of *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ with glycine has been studied in some detail. The initial reaction gives the *O*-bonded complex **(130)**, which is in equilibrium with **(131)**. Slow irreversible loss of H_3O^+ from (130) gives the *O,N*-chelate **(132)** in a self-inhibiting process. As the reaction proceeds the pH falls from 4.5 to 1.5 and the process is substantially accelerated by addition of base. Other amino acids undergo an analogous process [269]. The system $PdCl_2$/glycine/H_2O has been studied by potentiometric titration to determine the stability constants of 1:1 and 2:1 complexes [270].

A careful and detailed study of the IR spectral parameters of the *cis*- and *trans*-isomers of the complexes $[Pt(NX_2CH_2COO)_2]$, $[Pt(NX_2CH_2COOH)_2Cl_2]$ and $[Pt(NX_2CH_2CONXCH_2COOEt)_2Cl_2]$ (X = H

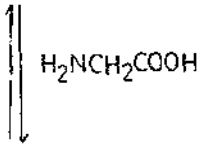
or D) failed to reveal any changes which could be attributed to different *trans*-effects in *cis*- and *trans*-isomers [271]. Glycine complexes of palladium(II) and platinum(II) react with amide acetals to yield *o,o*-chelated species (reaction (32)). The structure of (133) was established by X-ray diffraction [272].

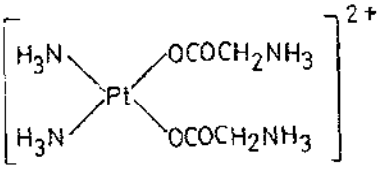


(130)

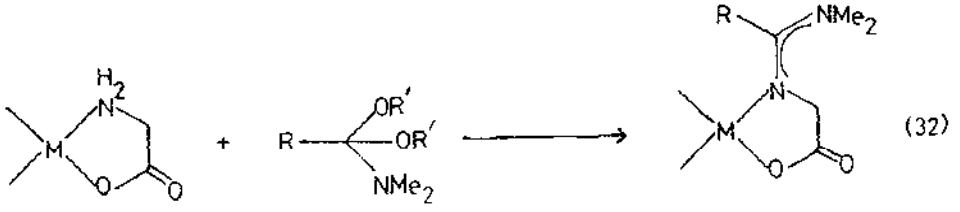


(132)



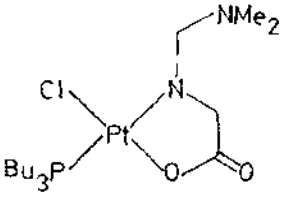


(131)



(32)

M = Pd, Pt or Cu **R = H or Ph; R'= Me or Et**



(133)

The kinetics of the reaction between $[Pd(en)(OH_2)_2]^{2+}$ and glycine ethyl ester have been studied [273].

The syntheses of sixteen new neutral complexes of the types $[PtA_2I_2]$ (A = DL-alaOEt, L-alaOEt, DL-pheOEt, L-pheOEt, DL-aspOEt, L-aspOEt, DL-serOEt or L-lysOEt) and $[PtA'_2Cl_2]$ (A' = DL-alaOEt, L-alaOEt, DL-serOEt, DL-pheOEt, DL-aspOEt or L-aspOEt) from $K_2[PtX_4]$ and the relevant ester in water have been reported. Dipole moment data suggest that all the iodides have *cis*-stereochemistry. The chloro complexes of DL-alaOEt, D-alaOEt and DL-serOEt are also *cis*, but other chlorides are *trans* [274]. The structures of *trans*-dichlorobis(L-ethylphenylalanate)Pt(II) [275] and *cis*-dichlorobis(diethylaspartate)Pt(II) [276] were established by X-ray diffraction. Both are square planar.

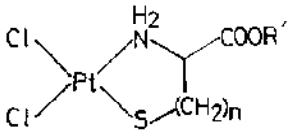
Substantial differences in the optical activity of the *cis*-bis chelates, $[PtL_2]$ (L = ala, ile, D-leu, pro or norvaline) and *cis*-[Pt(pro)L'] (L' = ala, ser, val or sarcosine) between aqueous solutions and a KBr dispersion have been noted. The differnces are less pronounced for the *trans*-isomers. Analysis of electronic absorption and CD spectra of the solids and the solutions implies that there are strong intermolecular interactions in solid samples of *cis*-$[Pt(val)_2]$, *cis*-$[Pt(norvaline)_2]$ and *trans*-[Pt(pro)(ser)], possibly attributable to hydrogen bonding [277]. Unidentate amino acid Pt(II) complexes of the type $[Pt(LH)_2(thio)_2]Cl_2$ (thio = thiocarbamide; LH = L-alaH, L-valH, L-tyrH or L-hydroxyproline) have been prepared and their electronic and CD spectra studied in aqueous and dmf solutions [278].

L-histidine complexes have been studied by potentiometric titration. $[Pd(hisH)_2]Cl_2$, $[Pd(hisH)Br_2]$ and $[Pd(hisH)Cl_2]$ all have the amino acid coordinated through the amino group and the nitrogen of the imidazole ring [279].

Reaction of amino acids with $[Pt(bipy)Cl_2]$ yields [Pt(bipy)L]Cl (L = gly, ala, leu, ser, cys or met). Conductivity measurements show that these are 1:1 electrolytes and ^1H nmr spectroscopy demonstrates that gly, ala, leu and

ser bond through oxygen and nitrogen, whilst cys and met are *N,S*-coordinated. All except the leucine complex show antiviral activity against tobacco mosaic virus [280]. Kinetic data have been obtained for *cis-trans* isomerisation of [Pt(amino acid)(dmso)Cl] by Cl^- or dmso (amino acid = gly, *N,N*-Me_2gly, pro or sarcosine). The *cis-N,S*-isomer is favoured for amino acids unsubstituted at nitrogen. Rate data (from NMR spectroscopic and radioisotope techniques) imply, unusually, that ismoerisation *via* pseudorotation of [Pt(amino acid)(dmso)Cl_2]$^-$ predominates by a factor of 4-20 over consecutive displacements for the Cl^- catalysed reaction. The dmso catalysed isomerisation proceeds *via* consecutive displacements [281].

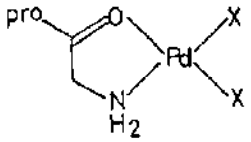
Amino acids containing sulphur have more modes of metal coordination available to them, and complexes employing these alternatives are well known. The vibration frequencies and forms of vibrations for the $\{MO_2S_2\}$ fragments of *cis-* and *trans*-$[ML_2]$ (M = Pd or Pt; LH = cysteine) have been calculated and compared with experimental IR spectra [282, 283]. Reaction of $K_2[PtCl_4]$ with D or L forms of cysteine, methionine or methyl methionate hydrochloride gives *cis*-$[PtLCl_2]$, which are the first reported well-characterised enantiomerically pure neutral complexes of this type. Sulphur and nitrogen are the preferred ligating atoms in (134) and stereochemical inversion at sulphur is slow on the nmr spectroscopic timescale [284]. S and N are also the preferred ligating atoms in complexes of *S*-benzyl cysteine, whilst gly-*S*-benzylcysteine is an *S,N,N*-donor [285]. In reactions of *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ with cysteine, methionine and glutathione, the initial product has the amino acid ligated to platinum *via* sulphur. On treatment with base the *S,N*-chelate is formed from the methionine complex and the *S,O*-chelate with cysteine [286]. A CD study on coordination of methionine and methionine containing peptides to palladium(II) shows that the amino acid is normally *N,S*-coordinated, whilst gly-met is an *N,N,S*-donor [287].



(134) R,R' = H or Me; x = 1 or 2

1.5.3.2 Peptides

$[PdCl_4]^{2-}$ reacts with the dipeptide gly-pro to give the 1:1 complex **(135)** and $[proCOCH_2NH_2)_2PdCl_2]$. Gly-gly-pro coordinates in a similar manner. Coordination of cytidine to these palladium(II) dipeptide complexes is *via* N(3); a monocytidine complex is formed where the peptide is gly-pro, but the gly-gly-pro species gives a bis(cytidine) derivative [288]. Cysteine containing peptide complexes of palladium(II) have been synthesised and studied by ^1H and ^{13}C NMR spectroscopy. Only the thiolato group is coordinated in *trans*-$[Pd(peptide)_2Cl_2]^{2-}$ [289]. Binding of $K_2[Pt(CN)_4]$ to bovine liver rhodanese has been studied by diffraction methods; binding occurs at one site at the entrance of the active site pocket with interactions with arginine-186 and lysine-240 [290].

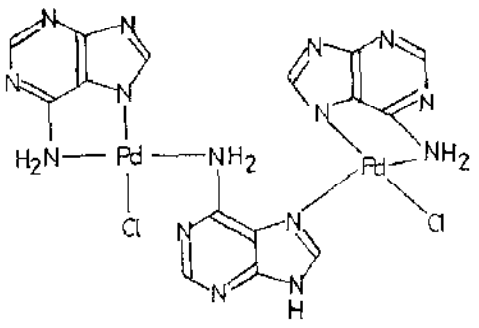


(135)

1.5.3.3 Nucleic acids and nucleosides

The complex $[Pd_2Cl_2Ad_2(AdH)].2H_2O$ (AdH = adenine) has been isolated and characterised. The most probable structure is **(136)** [291].

The reaction of $[Pd(en)(OH_2)_2]^{2+}$ with purine nucleosides and nucleotides was studied by NMR spectroscopy. For inosine, guanosine, adenosine, 5'-IMP,



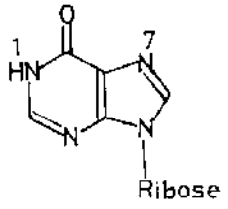
(136)

5'-GMP, 5'-AMP, 5'-ATP and 2'3'-AMP reaction occurs at N(7) in acid solution and N(1) in base. Near neutral pH polymers and mixtures were formed. Earlier work suggesting that N(7)-O(6) chelation might be important was largely discredited [292]. The complex $[Pd(en)(AMP)]^{2+}$ enhances the stacking of AMP to a greater extent than the analogue, $[Pd(dien)(AMP)]^{2+}$. It is thought that AMP may bridge {Pd(en)} units by coordination through both N(1) and N(7) [293]. This series of complexes closely resemble those reported last year with the *cis*-$[Pt(NH_3)_2]$ unit.

Treatment of $[Pd_2(\mu\text{-}Cl)_2Q_2]$ (HQ = methylcysteinate) with nucleosides, HL, yields [PdQ(HL)Cl] in dmso solution. N(7) of the nucleoside is bound *trans* to the sulphur of methyl cysteinate. In water guanosine and inosine are said to bind through O(6) as well as N(7), but chelating and dimeric structures were not distinguished [294]. *cis*-$[PtLL'Cl_2].nH_2O$ (L = gly or ala; L' = adenosine, guanosine, inosine, cytidine or uridine) have been prepared. The amino acids bind as monodentate ligands through the amino nitrogen, adenosine and guanosine coordinate at N(7), inosine at N(1) and cytidine and uridine at N(3) [295].

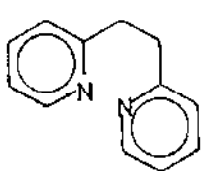
Reaction of inosine, (137), with $[Pd(en)Cl_2]$ has been monitored by stopped flow techniques. At pH < 5 initial coordination is to N(7) and the reaction mechanism involves a substantial contribution from a solvent mediated

pathway [296].

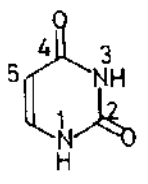


(137)

A range of complexes of inosine, guanosine and xanthosine and their derivatives has been prepared, including *cis*-$[PdL_2]$, *cis*-$[Pd(HL)_2Cl_2]$ and $[ML^1L^2Cl]$ (M = Pd or Pt; HL = triacetylinosine, triacetylguanosine or triacetylxanthosine; L^1 = py; HL^2 = inosine, guanosine or xanthosine). The authors concluded that N(7)-O(6) binding occurs from IR spectroscopic evidence, but some of their assignments lack rigour [297]. $[Pt(bipy)(nucleoside)_2]Cl_2$ complexes of guanosine and inosine and their analogues using bipy, *o*-phenylene diamine and 4,5-dimethyl *o*-phenylene diamine (LL) are prepared by treating $[Pt(LL)Cl_2]$ with an excess of nucleoside. Spectroscopic data indicate the customary N(7) binding [298]. Similar complexes, *cis*-$[PtL^1{}_2L^2{}_2]^{2+}$, (L = guanosine or 9-methylhypoxanthine; L^2 = $H_2N(CH_2)_3NH_2$, bipy or (138)) were prepared by Dutch workers and studied by NMR spectroscopy. Rotation of L^1 about the Pt-N(7) bond is fast on the NMR timescale for $H_2N(CH_2)_3NH_2$ complexes but slower for those of $Me_2N(CH_2)_3NH_2$. In the complexes with **(138)**, rotation is fast at room temperature but may be slowed by cooling [299].



(138)



(139)

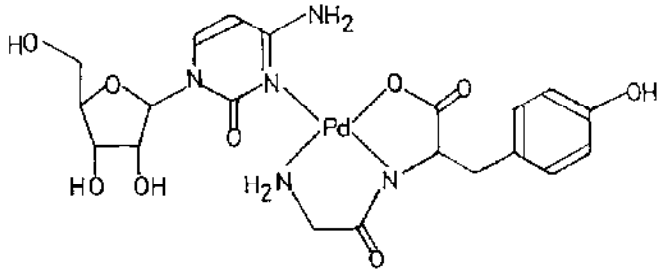
X-ray diffraction studies generally give the only definitive verdict as to the involvement of O(6) interactions in metal coordination of the purine necleotides. In [Pt(9-methylguanineH)Cl_3].H_2O diffraction methods show that platinum is bound only at N(7) with no interaction with O(6). The structure of [9-methylguanineH]$_2$[$PtCl_6$].H_2O was also determined; this is a true salt with guanine protonated at N(7) [300].

Reaction of *cis*-[$Pt(NH_3)_2Cl_2$] with uracil, HL, (139) yields *cis*-[$Pt(NH_3)_2LCl$]. However, when the 5-position is substituted with F or Cl, *cis*-[$Pt(NH_3)_2L_2$] is the main product. The 5-bromo and 5-nitro compounds give mixtures. 5-Nitrouracil coordinates through N(1), as does uracil in *cis*-[$Pt(NH_3)_2LCl$], but all the other complexes are N(3) bound [301]. An analogous complex, *cis*-[$Pt(NH_3)_2LCl$] (L = 1-methyluracil, N(3) bound) is also reported. Treatment with Ag^+ may yield *cis*-[$(NH_3)_2LPt(\mu\text{-}OH)PtL(NH_3)_2$]. The head-to-head dimer, **(140)** may be obtained by reaction (33). In **(140)** diffraction studies show that N(3) and O(4) are metal bound [302]. Reactions of *cis*-[$Pt(NH_3)_2(OH_2)_2$]$^{2+}$ with uracil, thymine or cytosine in the presence of air generate a new series of platinum blues. Their structures are not yet well defined but the complexes inhibit two mitochondrial enzymes and DNA synthesis in *E. coli* [303]

$$cis\text{-}[Pt(NH_3)_2(H_2O)_2]^{2+} + cis\text{-}[Pt(NH_3)_2L_2] \longrightarrow \underset{\textbf{(140)}}{cis\text{-head-to-head-}[\{Pt(NH_3)_2L\}_2]^{2+}} \qquad (33)$$

The reactions of {(en)Pd(II)} with uridine, cytidine and their 5'-monophosphates have been used as a model for the analogous interactions of the *cis*{-$(NH_3)_2Pt$} moiety. The process is extremely complex with five different complexes identified using uridine and seven with cytidine. Stability constants indicate that Pt(II) binds nucleobases about thirty times more strongly than Pd(II) [304].

Two papers report the binding of cytidine to palladium(II) peptide complexes. NMR spectroscopic studies of the species formed from (gly-gly-OEt)Pd(II), (gly-tyr)Pd(II) or (asp)Pd(II) indicate that two types of complex are formed in which the donor atom of the nucleoside is N(3) of the pyrimidine ring. The complexes differ only in their conforamation about the Pd-N(3) bond [305]. An X-ray diffraction study of [(gly-tyr)Pd(cytidine)].$6H_2O$ gives somewhat more definitive information. In **(141)** there is a hydrogen bond from the tyrosine OH to the glycine carbonyl in the next molecule [306].

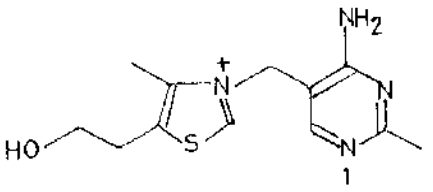


(141)

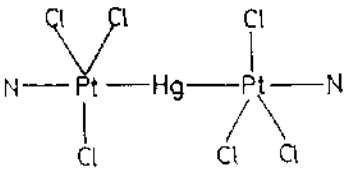
An X-ray diffraction study of a second modification of the head-to-tail dimer, bis(*μ*-1-methylthyminato-*N(3),O(4)*) bis{*cis*-diammine platinum(II)} dinitrate 4.5 hydrate, is reported. Differentiation of the head-to-head and head-to-tail dimers is not easy by IR or NMR spectroscopy. However addition of Cl^- cleaves Pt-O but not Pt-N bonds yielding *cis*-[Pt$(NH_3)_2$(1-MeT)$_2$] (1-MeT = 1-methylythyminato) and *cis*-[Pt$(NH_3)_2Cl_2$] from the head-to-head isomer and *cis*-[Pt$(NH_3)_2$(1-MeT)Cl] from the head-to-tail compound [307].

Reaction of $K_2[PtCl_4]$ with [Hg(HTh)Cl_4].H_2O (HTh = thiamine, **(142)**) yields [$HgPt_2Th_2Cl_6$]. Two possible structures, (143) and (144), where N is N(1) of the thiamine may be proposed. Related complexes [$CdPtThCl_3$] and [$ZnPtThCl_3$] were also synthesised [308]. Oxythiamine, in which the NH_2 group of **(142)** is replaced by OH, is less basic than thiamine and hence coordinates

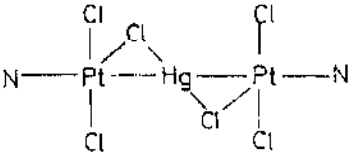
less strongly to both Pd(II) and Pt(II). The 1:1 complex formed with $[PtCl_4]^{2-}$ is easily isolable but that from $[PdCl_4]^{2-}$ is not so tractable [309].



(142)



(143)



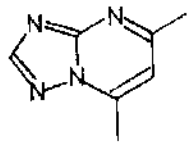
(144)

Interactions of *cis*-$[Pt(NH_3)_2Cl_2]$ with small oligonucleotides have been studied as models for the binding of this chemotherapeutic agent to DNA. Reaction of the dinucleotide guanylyl(3'-5')adenosine (GpA) with *cis*-platin gives two 1:1 products in which $\{Pt(NH_3)_2\}^{2+}$ binds to the N(7) sites of guanine and adenine. With $[Pt(NH_3)_3Cl]Cl$ four products may be isolated; the main component is a 1:1 species in which $[Pt(NH_3)_2]^{2+}$ binds to N(7) of guanine [310].

Conformational analysis of d(GpCpG) and *cis*-$[(NH_3)_2Pt\{d(GpCpG)\}]$ has been performed by NMR spectrosopy at 500 MHz. Platination affects the sugar conformational equilibrium to favour the *N*-conformation, with an increase of anomeric effect. In the platinated complex the cytosine turns away, giving a bulge [311]. The products from the reactions of *cis*-$[Pt(NH_3)_2Cl_2]$ with d(CpCpGpG), d(GpCpG), d(CpGpCpG), d(GpCpGpC) and d(CpGpCpG) were characterised spectroscopically. Platinum always binds at N(7) of guanine, where possible to two guanines. No

interstrand complexes were formed, despite the self-complimentary nature of the oligonucleotides [312].

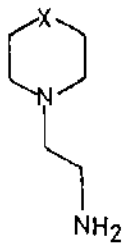
The preparation of $[Pt(dmtp)_4][Pt(SCN)_6]$ (dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine, **(145)**) has been described. The complex was characterised by X-ray diffraction; dmpt acts as a monodentate ligand through N(3) of the triazole with no participation from the pyrimidine N(4). This is the first example of an X-ray determination of the structure of the *S*-bonded $[Pt(SCN)_6]^{2-}$ anion [313].



(145)

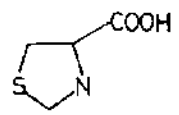
1.5.3.4 Cancer chemotherapy

The complexes *cis*-$[Pt(Me_2CHNH_2)_2X_2].nH_2O$ (X = Cl, Br, $1/2[C_2O_4]^{2-}$ or $1/2[OOCCH_2COO]^{2-}$) were prepared by reduction of $K_2[PtCl_6]$ by N_2H_4 followed by reaction with the appropriate anion. Oxidation with H_2O_2 yields *trans*-$[Pt(Me_2CHNH_2)_2X_2(OH)_2]$; the complex with X_2 = oxalate was the most effective in suppression of L-1210 leukaemia in mice [314]. Diamine complexes, $[PtLX_2]$ (X = Cl, Br or I) of **(146)** and **(147)** were prepared and characterised. Their anti-tumour activity and toxicity are lower than that of *cis*-$[Pt(NH_3)_2Cl_2]$ [315]. Analogous palladium and platinum complexes of thioproline, **(148)** also show some cytostatic activity [61].



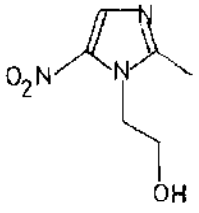
X = CH_2 **(146)**

X = O **(147)**

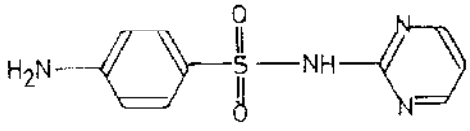


(148)

cis-[Pt(metronidazole)$_2$Cl$_2$] is prepared from K$_2$[PtCl$_4$] and the ligand **(149)**. On melting, the *trans*-isomer is formed and both were characterised by X-ray diffraction as being coordinated through the sp^2 nitrogen atom. The *cis*-compound has been used as a radiosensitiser of hypoxic tumour cells towards X-irradiation [316]. In *cis*-[Pt(HL)$_2$Cl$_2$] (HL = sulphadiazine, (150)) platinum is, as usual, coordinated to the softer basic atom, the nitrogen of the pyrimidine ring. In *cis*-K[PtLCl$_2$] additional coordination is thought to occur through oxygen. Both compounds are cytotoxic *in vitro* to HeLa cells and *cis*-K[PtLCl$_2$] showed anti-tumour activity against P388 leukaemia. These first reported platinum sulphadiazine complexes are less potent than *cis*-platin, but also less toxic [317].



(149)



(150)

The reaction of [Pt(dien)Cl]Cl with salmon sperm DNA has been investigated. Binding at N(7) of guanine occurs at levels of fixation of < 0.1 Pt/DNA. Above this level coordination to N(7) of adenine is also important [318].

1.5.4 Complexes with Group V donor ligands

1.5.4.1 Unidentate amine donor ligands

The electronic structures of *cis*- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] have been studied by the CNDO/2 method [319] and their IR and Raman spectra were used to clarify structrural features [320]. The *cis*-isomers of [Pt(NH$_3$)$_2$X$_2$] (X = Cl, Br, I or SCN) had lower stability towards γ-irradiation than the *trans*-analogues, in accord with data previously reported for [Pt(NH$_3$)$_2$XY].

cis-$[Pt(NH_3)_2Y_2]$ {Y_2 = oxalate or $(NO_2)_2$} have anomalously high stability [321].

Further studies of the oligomerisation reactions of *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ between pH 4 and 5 have been published. The bis μ-hydroxo dimer is the only detectable product under these conditions [322]. The reaction of this species with adenosyl cobalamin and alkyl cobalamins has been studied. An adduct involving the "base-off" form of the organocobalamin is formed rapidly and reversibly, followed by rate determining ligand exchange between N(3) of a 5,6-dimethylbenzimidazole ligand and H_2O at platinum [323].

The reactions between *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ and $H_2NCH_2SO_3H$ (HL) have been studied in some detail {reactions (34) and (35)}. However, on reaction with *cis*- and *trans*-$[Pt(NH_3)_2(NO_2)_2]$ either ammonia or NO_2 is preferentially displaced, according to stereochemistry, in reactions (36) and (37). In all cases the ligand is bonded through nitrogen [324, 325].

$$cis\text{-}[Pt(NH_3)_2Cl_2] + 2HL \longrightarrow cis\text{-}[Pt(NH_3)_2L_2] + [Pt(NH_3)L_2(HL)]$$

$$cis\text{-}[Pt(NH_3)_2L_2] \xrightarrow{H_2O_2} [Pt(NH_3)_2(OH)_2L_2] \qquad (34)$$

$$trans\text{-}[Pt(NH_3)_2Cl_2] + 2HL \longrightarrow trans\text{-}[Pt(NH_3)_2L_2] \qquad (35)$$

$$cis\text{-}[Pt(NH_3)_2(NO_2)_2] + 2HL \longrightarrow cis\text{-}[Pt(HL)_2(NO_2)_2] \qquad (36)$$

$$trans\text{-}[Pt(NH_3)_2(NO_2)_2] + 2HL \longrightarrow trans\text{-}[Pt(NH_3)_2(NO_2)L] + trans\text{-}[Pt(NH_3)_2L_2] \qquad (37)$$

Microcalorimetric measurements of enthalpies of thermal decomposition of *cis*-$[PtL_2X_2]$ (L = NH_3, amine or pyridine; X = Cl, Br or I) have allowed the determination of the standard enthalpies of formation of these complexes. Bond dissociation eneergies are slightly less for pyridine complexes than for those of ammonia [326].

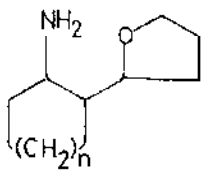
The kinetics of substitution by $[CN]^-$ of $[Pt(NH_3)_4]^{2+}$, $[Pt(py)_4]^{2+}$ and

$[Pt(en)_2]^{2+}$ have been studied spectrophotometrically. the kinetic trend is similar to that for the kinetic *trans*-effect [327]. The interaction of $[Pt(NH_3)_4]^{2+}$ and $Fe(NO_3)_3$ on a silica gel surface during bimetallic catalyst preparation has been investigated [328]. Reactions of *trans*-$[Pt(NH_3)_2(ROH)Cl][ClO_4]$ with azobenzene and aminoazobenzene have been studied [329].

The reaction of $[PtLCl_3]^-$ (L = PMe_3, PEt_3, PBu_3, PPh_3, $P(OMe)_3$ or $AsEt_3$) with a range of amines (am) to yield *trans*-$[Pt(am)LCl_2]$ has been investigated from a kinetic standpoint. The lability of chloride is strongly dependent on the nature of the donor atom in L. The equilibrium constant for the reaction also depends on L, but the variation, which represents a *trans*-influence, is less than the *trans*-effect and does not follow the same sequence [330].

Oxidation of *cis*- or *trans*-$[Pt(RNH_2)_2Cl_2]$ by $[AuCl_4]^-$ in the presence of $[Et_4N]Cl$ has been investigated kinetically and reaction mechanisms proposed [331].

Trans-complexes $[ML_2Cl_2]$ (M = Pd or Pt; L = (151a) or (151b)) have been prepared and characterised by IR spectroscopy, conductivity measurements and DTA. Both ligands act as monodentate *N*-donors and the platinum complex is more stable than the palladium analogue [332]. Further 1:1 and 1:2 complexes of palladium with iminodiacetic acid are reported [333].



(151a) n = 2

(151b) n = 3

The preparation of $[PtLCl_2].2H_2O$ (L = hexamethylenetetramine) is

reported. Despite its apparent stoicheiometry, IR spectroscopic evidence strongly implies that the platinum is interacting directly with a single nitrogen atom of the ligand [334].

Reaction of *cis*-$[PtL_2Cl_2]$ (L = PEt_3 or PMe_2Ph) with $Na[NPh_2]$ yields *cis*-$[PtL_2(NPh_2)Cl]$, which was characterised by X-ray diffraction. Bis-substitution occurs with the sterically less demanding nucleophile, sodium pyrollidinate [335].

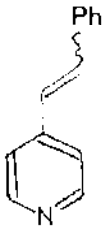
Extraction of palladium(II) from 0.25 - 0.5 M sulphuric acid may be achieved using chloroform or toluene solutions of 4-octyl aniline, L. The organic phase contains $[L_2Pd(SO_4)]$, in which $[SO_4]^{2-}$ acts as a bidentate ligand [336].

cis- and *trans*-$[Pt(NH_2OH)_2(NO_2)_2]$ and *trans*-$[Pt(NH_2OH)_2(NO_2)Cl]$, in which both NH_2OH and NO_2 are *N*-bonded, have been subjected to normal vibrational analysis [337, 338].

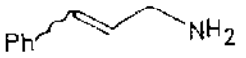
1.5.4.2 Unidentate heterocyclic donor ligands

Luminescecence, electronic absorption and magnetic CD spectroscopic measurements on the *cis*- and *trans*-isomers of $[Pt(py)_2Cl_2]$ allowed the conclusion that for the *cis*-compound the LUMO is a metal d-orbital [339]. IR and Raman spectra were analysed to give metal-ligand bond strengths [340]. DTA and IR measurements on the solid *cis*-isomer show that it is converted to the *trans*-complex at 115 °C. The *cis* to *trans* transformation of the dibromide occurs at 96 °C [341].

The photochemistry of *trans*-$[PtL^1L^2Cl_2]$, where L^1 is a methylpyridine and L^2 is **(152)** or **(153)**, has been investigated. The complexes undergo *cis/trans* isomerisation of L^2 as the only important photoreaction [342]. The kinetics of the reaction of $[PdCl_4]^{2-}$ with pyridoxol, pyridoxal and pyridoxamine are complex. Coordination occurs through the pyridine nitrogen atom in $[PdL_2Cl_2]$ for pyridoxal and pyridoxol, but under acidic conditions pyridoxamine forms a salt [343].



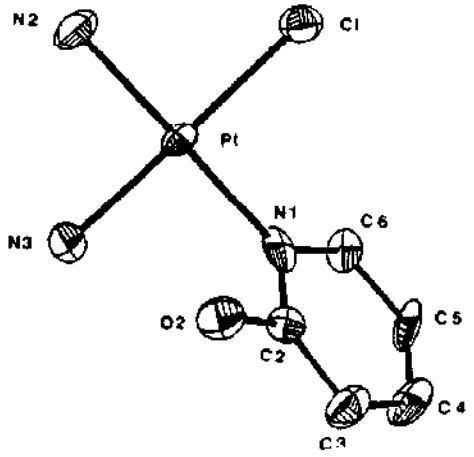
(152)



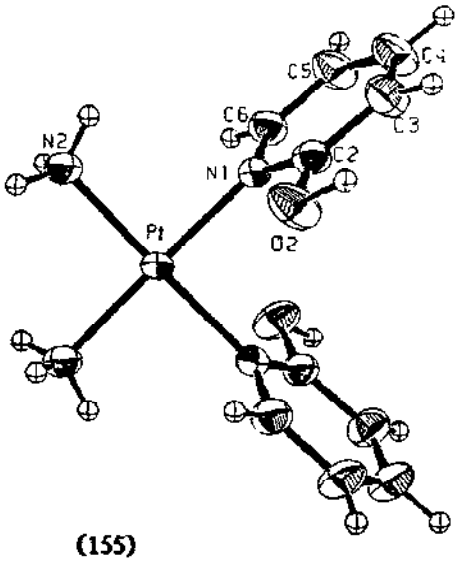
(153)

The complexes *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl][NO_3]$, (154), and *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$, (155), of 2-hydroxypyridine have been characterised by X-ray crystallography. Only the pyridine nitrogen atom is metal bound in each case and in the bis-compound the two heterocycles are oriented in an *anti* rotational conformation. Treatment of (154) with chlorine yields *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$; deprotonation of the ligand is promoted by the high Lewis acidity of platinum(IV) [344].

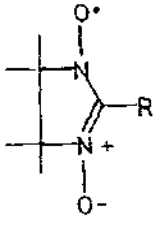
2-Substituted 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxides, (156), have been converted to palladium and platinum complexes, $[ML_2Cl_2]$, with binding through the pyridine nitrogen atom. There is no interaction between the unpaired electron and the metal [345].



(154)



(155)



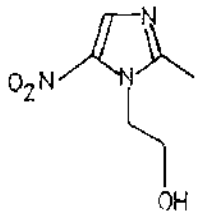
R = 2-pyridyl, 3-pyridyl or 4-pyridyl

(156)

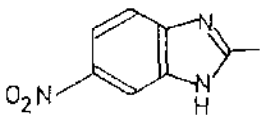
The salts, $[LH]_2[PtCl_4]$, on heating in the solid state yield *cis*-$[PtL_2Cl_2]$. Among the heterocyclic ligands, L, investigated were 2-aminopyridine, benzothizole and benzotriazole; the presence in the ligand of an additional proton acceptor leads to an increase in the temperature of the Anderson rearrangement [346].

As usual there are many reports of imidazole complexes. Reaction of PdX_2 with L in a 2:1 ratio (L = 2-methyl-, 2-ethyl-, 2-*iso*-propyl-, 4-methyl-, 1-methyl-, 1-vinyl-, 1-vinyl-2-methyl-, 4-methyl-, 1,2-dimethyl- or 2-ethyl-4(5)-methyl-imidazole) gives $[PdL_2X_2]$ (X = Cl or Br). With an excess of the imidazole ligand the product is $[PdL_4]X_2$. The stereochemistry of the compounds prepared by this route is unfortunately not given [347, 348]. X-ray

diffraction studies of *trans*-Pd(1-methylimidazole)$_2$Cl$_2$] [349] and *trans*-[Pd(2-methylimidazole)$_2$Cl$_2$] [350] are reported. Complexes [PtL$_2$X$_2$ (L = metronidazole, **(157)** or 2-methyl-5-nitrobenzimidazole, **(158)**; X = Cl or I) were deduced to have *cis*-geometry on the basis of IR data [351].



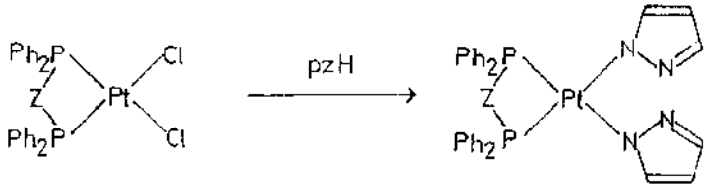
(157)



(158)

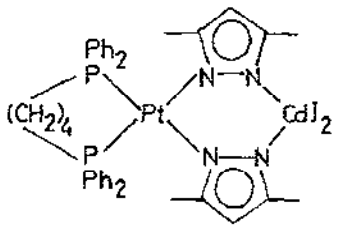
New pyrazolato derivatives of platinum(II) have been prepared (reaction (38)). Treatment of **(159)**, Z = $(CH_2)_2$ with H[BF$_4$] gives the known species [(dppe)Pt(μ-pz-N,N')$_2$Pt(dppe)][BF$_4$]$_2$. The complex of dimethylpyrazole for which Z = $(CH_2)_4$ reacts with cadmium iodide to yield (160) [352]. Both methyl trifluoromethyl pyrazole, (161), and 2H-indazole, (162), react with [Pt$_2$(μ-Cl)$_2$(PEt$_3$)$_4$][BF$_4$]$_2$ to yield each a single isomer of *cis*-[Pt(PEt$_3$)$_2$LCl][BF$_4$], in both solution and the solid state. X-ray diffraction studies confirm that (161) binds through N(2) and (162) through N(1), both in accord with theoretical predictions [353].

Treatment of [Pd(PhCN)$_2$Cl$_2$] with 3-diethylamino-2,2-dimethyl-2-H-azirine (L, (163)) yields a complex of stoicheiometry *trans*-[PdL$_2$Cl$_2$]. With Pd(OCOCH$_3$)$_2$ and the *N,N*-dimethyl analogue, Q, [PdQ(OCOCH$_3$)$_2$] is formed.

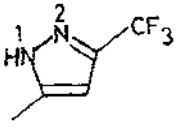


(38)

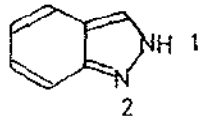
(159)



(160)



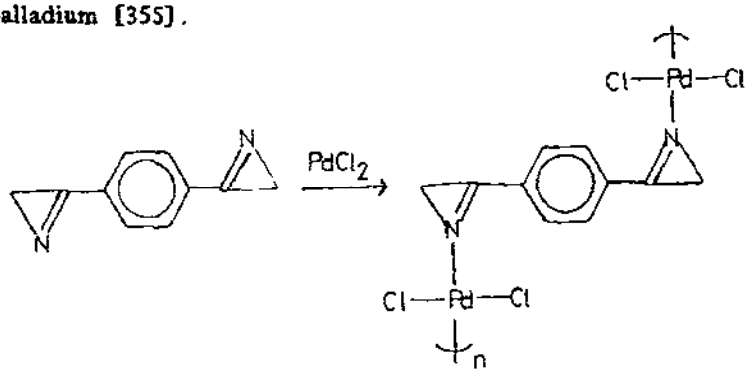
(161)



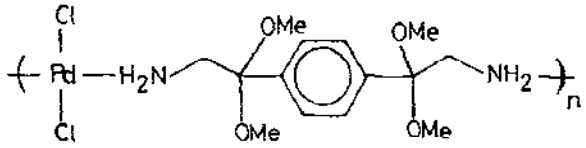
(162)

In neither case was the structure of the complex firmly established [354]. Reaction of (164) with $PdCl_2$ gives a *trans*-polymer, (165). Treatment with methanol opens the three-membered rings to yield (166) but it is not easy to liberate the ligand from palladium [355].

(163)



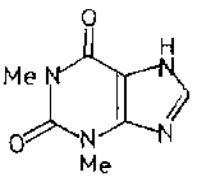
(164) (165)



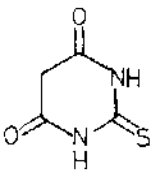
(166)

A range of complexes, $[PtL_2Cl_2]$ and $[PtL'Cl_2]$, where L and L' are mono and bidentate nitrogen donors respectively, were studied by XPES. The platinum $4f_{7/2}$ binding energies showed 1,8-diaminonaphthalene to be the best donor. Interaction between *cis*-$[PtL_2Cl_2]$ (L = theophylline, (167)) and calf thymus DNA resulted in a loss of base stacking due to the N(7)-O(6) binding of

guanine [356]. In both platinum and palladium complexes of thiobarbituric acid, (168), sulphur is not metal coordinated, but some interaction with oxygen may occur as well as the usual binding at nitrogen [357].



(167)

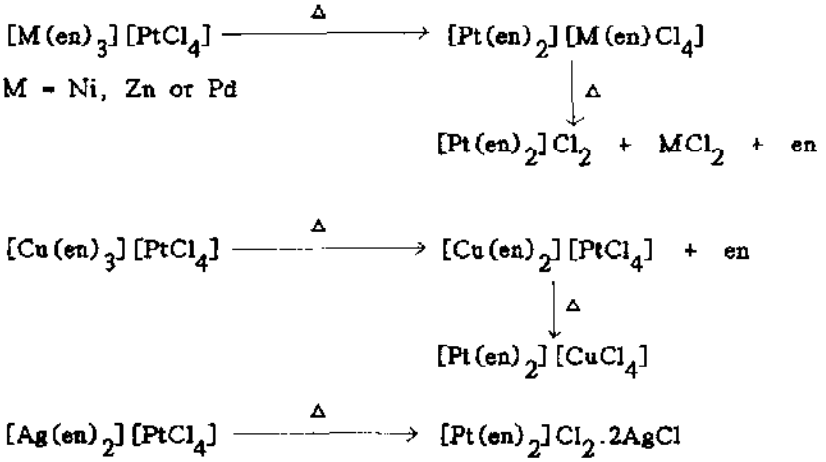


(168)

1.5.4.3 Bidentate and polydentate amine donor ligands

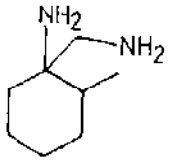
Polarised single crystal specular reflection spectroscopy studies of $[M(en)Cl_2]$ (M = Pd or Pt) are reported. There is a strong out-of-plane absorption which is shifted to a lower energy on going from solution to the solid state. Strong in-plane bands are associated with ligand to metal CT transitions [358]. The structure of the anti-tumour agent, [Pt(en)(malonate)] has been established by X-ray diffraction. The malonate ligand adopts a boat conformation [359].

Thermolysis of various $[M(en)_n][PtCl_4]$ salts has been studied; the pathway followed depends on the metal, M (Scheme 6) [360].



Scheme 6 Reactions of $[M(en)_n][PtCl_4]$ [360]

The conformations of the chelate six-membered rings in $[Pt(bipy)L]^{2+}$ and $[Pt(NH_3)_2L]^{2+}$ (L = *meso* or *dl*-2,4-diaminopentane, 1,3-diaminobutane, 2-methyl-2,4-diaminopentane or 1,3-diaminopropane) have been studied by NMR spectroscopy. For *meso*-2,4-diaminopentane a chair conformation with both methyl groups equatorial predominates, whereas for the *dl*-isomer one methyl is axial and the other equatorial in the major chair conformer. In the latter case the skew boat conformation is also sigificantly populated [361]. In analogous complexes of 1R,2S-(169) CD measurements imply that the five-membered chelate is mainly in the λ-conformation [362]. Complexes $[PtL(CO_3)]$ of 1,10-phen and 1,2-diaminocyclohexane have been characterised [363].

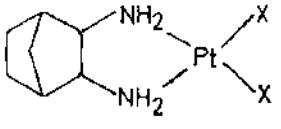


(169)

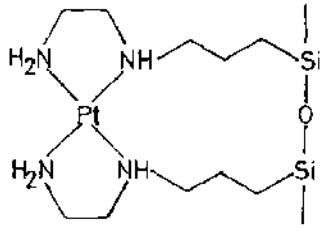
In (170), the alkene ligand is strongly activated towards nucleophilic attack and further reports of its reactivity have been published (Scheme 7) [364].

Several of the complexes (171), prepared from the diamine, $K_2[PtCl_4]$ and an appropriate anion, showed powerful anti-leukaemic activity in mice [365].

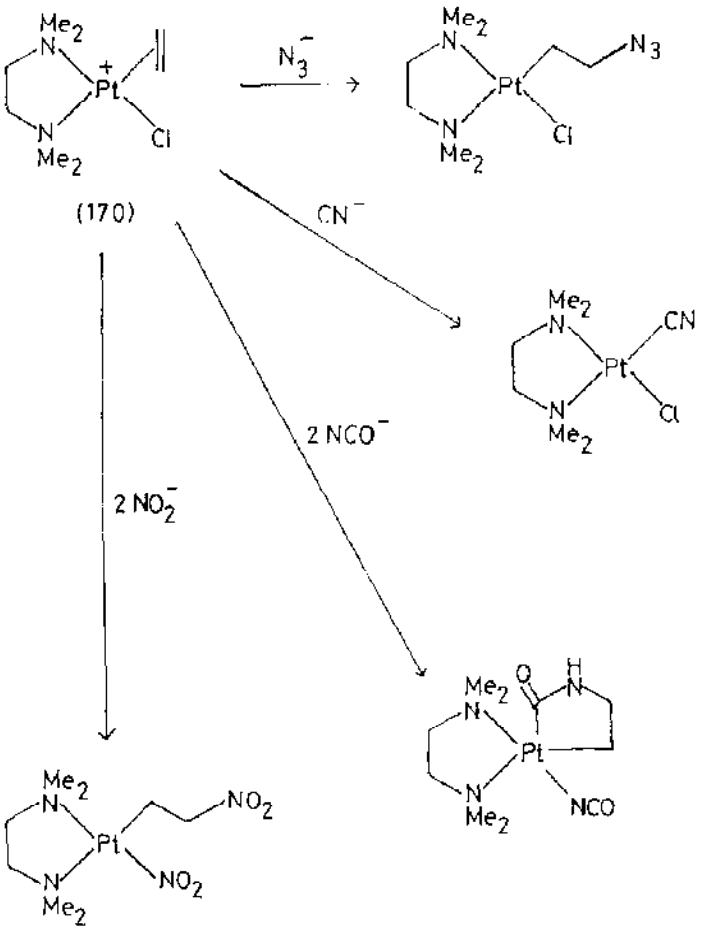
Platinum(II) attatched to aminated silica was studied by ^{13}C NMR spectroscopy both in suspension and in the solid state. Peaks assignable to the bis chelate **(172)** were detected [366].



(171)

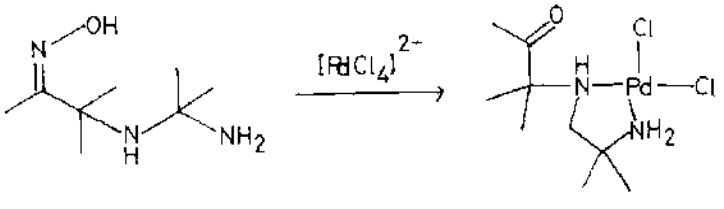


(172)



Scheme 7 Reactions of **(170)** with nucleophiles [364]

When the oxime, (173), a potentially tridentate ligand, reacts with $[PdCl_4]^{2-}$ the product formed is (174), in which the oxime has been hydrolysed. The structure of (174) was established by X-ray diffraction [367].



(173) **(174)**

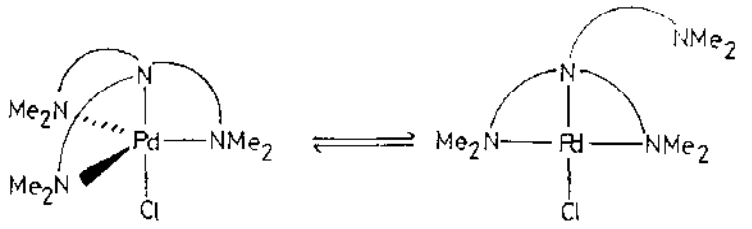
Two X-ray diffraction studies refer to complexes of dien. [Pt(dien)Cl]Cl is isostructural with the dibromide and $[Pt(dien)(NO_3)][NO_3]$ is similar. Crystal packing in both cases is determined by hydrogen bonding [368]. In $[Pt(dien)(CN)]_2[Pt(CN)_4].H_2O$, both platinum atoms have approximately square planar coordination [369]. The rather well studied anation reaction (39) was interpreted in terms of an associative mechanism [370]. A study of the reactions of complexes of alkylated dien showed that kinetic behaviour was dependent on the size of the substituents, again indicating an associative pathway [371].

$$[Pt(dien)(H_2O)]^{2+} + Cl^- \longrightarrow [Pt(dien)Cl]^+ + H_2O \qquad (39)$$

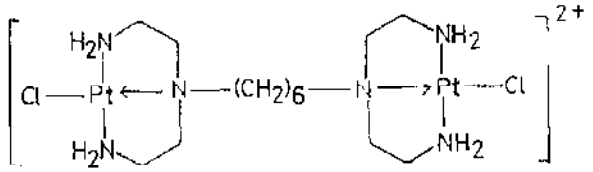
It had previously been reported that the reaction of [Pt(dien)X]X with KNH_2 and CH_3I resulted in methylation on the central nitrogen atom, *trans* to coordinated X. A new study, involving the synthesis of $H_2NCH_2CH_2N(CH_3)CH_2CH_2NH_2$, demonstrates that the original conclusion was wrong and that methylation of dien occurs at the terminal nitrogen, as would be expected from theoretical considerations [372].

Complexes of the type $[Pd(trenMe_6)X]Y$ ($trenMe_6 = (Me_2NCH_2CH_2)_3N$; X = Y = Cl, Br, I or SCN; X = Cl, Br, I or SCN, Y = PF_6 or BPh_4) have been prepared and characterised. In both protic and aprotic solvents, there is a rapid intramolecular rearrangement between four and five coordinated metal centres (reaction (40)). At low temperature the rate of interconversion is slowed and the equilibrium is shifted to the right. $[Pd(trenMe_6)(NCS)]^+$ is isolated in the solid state but in solution is in equilibrium with its linkage isomer [373]. Procedures for the synthesis of $trenMe_6$ complexes, as well as those of the tetradentate ligand $Me_2N(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2NMe_2$, have been described in detail [374].

Reaction of $(H_2NCH_2CH_2)_2N(CH_2)_6N(CH_2CH_2NH_2)_2$, L, with three molar equivalents of $K_2[PtCl_4]$ yields $[Pt_2LCl_2][PtCl_4]$, which on reaction with $[Pt(NH_3)_4][PtCl_4]$ gives $[Pt_2LCl_2]Cl_2$, (175) [375].



(40)

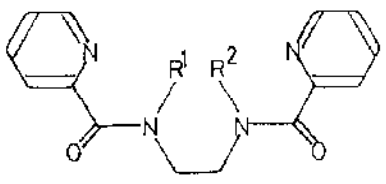


(175)

Complexes $[PtLX_2]$ (L = 1,2-bis(3,5-dioxopiperazin-1-yl)ethane or 1,2-bis(3,5-dioxopiperazin-1-yl)propane; X = Cl or Br) have been tested for their anti-tumour activity [376].

Polyhedral borane ions have been used to stabilise palladium and platinum complexes $[ML_2][B_nX_n]$ (L = bipy or phen; n = 10 or 12; X = H, Cl or Br) against thermal decomposition [377].

Further complexes of the potentially tetradentate ligands **(176a)** - **(176c)** have been investigated. [Pd(bpenMe)Cl] is synthesised from $K_2[PdCl_4]$ and **(176b)**. NMR spectroscopic studies and X-ray diffraction established that both the pyridine nitrogens and the deprotonated NH are metal coordinated, but the tertiary nitrogen is not [378]. In the analogous complex of $bpenMe_2$ only the pyridine nitrogen atoms are bound, in a *trans* arrangement with an eleven membered chelate ring [379].



(176)

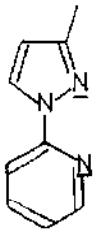
a $R^1 = R^2 = H$; $bpenH_2$

b $R^1 = H$ $R^2 = Me$; bpenMeH

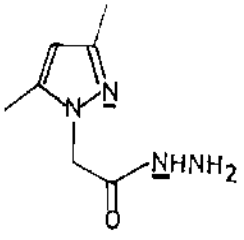
c $R^1 = R^2 = Me$; $bpenMe_2$

$[Pt_2(\mu\text{-}Cl)_2\{(2\text{-amino-}4,6\text{-dimethyl})pyridine\}_2]$ has been prepared and is an excellent catalyst for homogeneous hydrogenation and hydrosilylation of carbon-carbon double bonds [380].

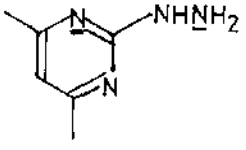
The detection of trace levels of palladium(II) relies on the extraction of the purple red tridentate Pd(II) complex of biethanoyl monooxime 2-pyridyl hydrazone complex from aqueous acid into $CHCl_3$ [381]. In $[Pt(HL)Cl_2]$ (HL = $PhC(NHR)\text{=}NNH_2$) the ligand is coordinated through the NH_2 and NHR groups. *cis*- and *trans*-$[PtL_2]$ may be prepared by the reaction of $[NH_4]_2[PtCl_4]$ with HL; the mode of coordination of L is the same as for HL but the NH_2 group is deprotonated [382]. Complexes of the ligands **(177)**, **(178)** and **(179)**, $[MLCl_2]$ (M = Pd or Pt) have been prepared and characterised. The ligating atoms were assumed but not proven to be as shown [383].



(177)

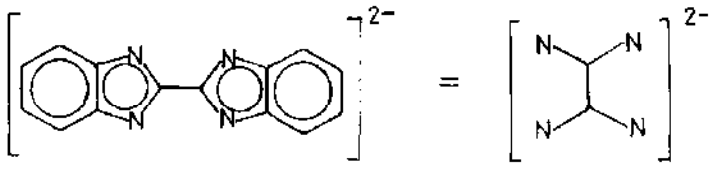


(178)

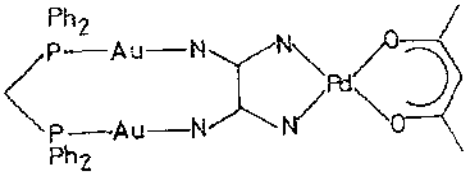


(179)

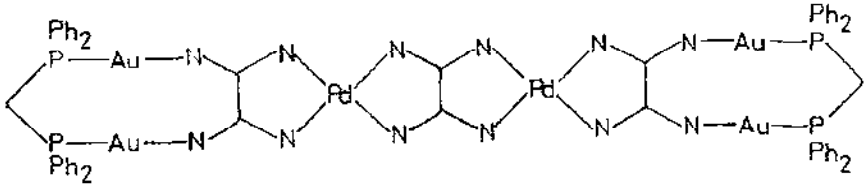
The bis(benzimidazole) ligand, **(180)**, has been used to bridge two metal centres in a wide range of complexes. For example, $[\{(dppm)Au\}_2\{\mu\text{-}(180)\}]$ reacts with $[Bu_4N]_2[Pd(\mu\text{-}X)_2Ar_4]$ to give $[\{(dppm)Au\}_2\{\mu\text{-}(180)\}PdAr_2]$ and **(181)** and **(182)** were also characterised [384].



(180)

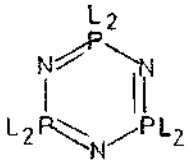


(181)



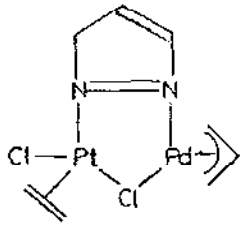
(182)

The extremely ornate ligands, (183), where L = pyrazolyl, have been prepared and their complexation with palladium and platinum investigated. In complexes such as $[N_3P_3(Me_2pz)_6(MCl_2)_2]$ (M = Pd or Pt) and *gem*-$[N_3P_3(Me_2pz)_2Ph_4(PdCl_2)]$, bidentate coordination occurs through two pyrazolyl groups attatched to the same phosphorus atom [385].

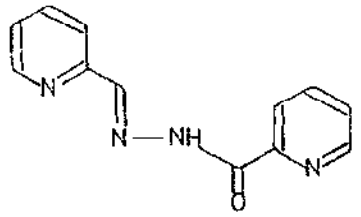


(183)

The bimetallic compound, **(184)**, was obtained from *trans*-$[PtCl_2(pz)(C_2H_4)]^-$, generated *in situ* by deprotonation of the pyrazolyl adduct of Zeise's salt [386].



(184)

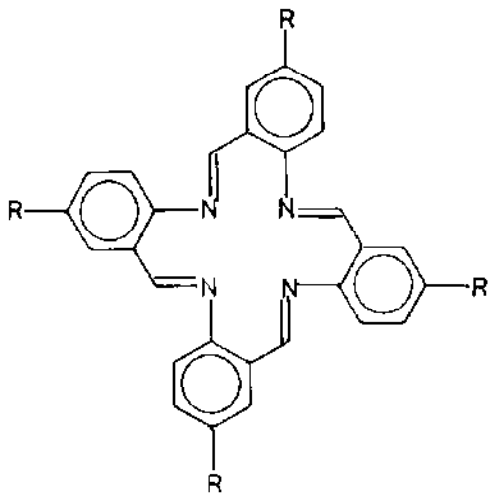


(185)

(185) is said to coordinate to palladium through the imino and pyridyl nitrogen atoms; the authors seem to be in some doubt as to the geometry of the resulting five-coordinate $[PdLCl_2]$ complex [387].

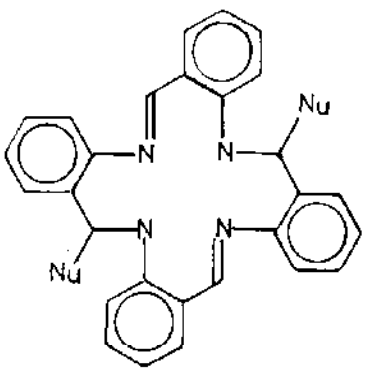
1,4,7-triazacyclononane, L, reacts with $[PtCl_4]^{2-}$ to give, after treatment with bromide ions, $[PtL_2]Br_2$ in which L was shown to be bidentate by an X-ray diffraction study. The acid-base behaviour of this and analogous complexes was investigated, and they may be readily oxidised to Pt(IV) species [388].

Tetradentate tetraaza macrocycles, both synthetic and naturally occurring, have received much additional attention this year. XPES gives data on bonding energies of deep electrons in $[LPd]^{2+}$ complexes of this type. These may be related to the degree of donor acceptor electron transfer from nitrogen to palladium [389,390]. Tetrabenzo-1,5,9,13-tetraazacyclohexadeca-1,5,9,13-tetraene, **(186)**, has been converted to **[(186)**Pd$][ClO_4]_2$ and the stability constant of its adducts with pyridine, 3-methylpyridine, dmf and ethanol determined [391]. The complex reacts with nucleophiles to give (188) (R = NH_2, OH or NEt_2) [392]. Complexes of **(187)** seem to be somewhat flatter than those of **(186)** [393].



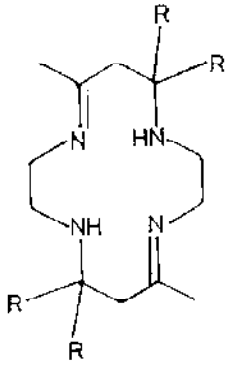
(186) R = H

(187) R = Me

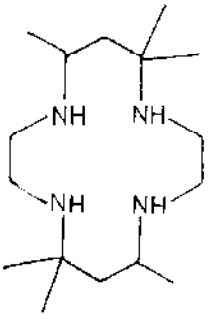


(188)

Complexes of **(189)** (R = H or Me) and **(190)**, $[PdL][ClO_4]_2$, were prepared from the ligand and $Na_2[PdCl_4]/Na[ClO_4]$ [394]. Both palladium(II) and platinum(IV) complexes of **(190)** are reported by Chinese workers [395].



(189)



(190)

Studies of palladium and platinum porphyrin complexes have mainly involved their photochemistry and photophysics. The low temperature fluorescence of palladium porphine derivatives was studied during selective laser excitation [396]. Picosecond laser spectroscopy was used in a study of palladium(II) octaethylporphyrin, time-resolved excited spectra being recorded from the time of photoexcitation for 5 ns. The initial excited state, S_1, decays in <15 ps, but a second excited state, T_1, survives for >50 ns [397]. When a metalloporphine is excited to its lowest ^3E_u state in a crystalline environment of low symmetry, the orbital degeneracy is removed, as evidenced by phosphorescence Zeeman and EPR experiments on a platinum porphyrin complex in the A-site of decane [398]. Iterative extended Huckel calculations have led to a better understanding of spectroscopic data for palladium(II) octaethyl- and tetraphenyl-porphyrins and Pd(II) and Pt(II) etioporphyrins [399].

The photophysics of water soluble diamagnetic metalloporphyrins containing Zn(II), Pd(II) or Sn(IV) were studied in dilute aqueous solution. All undergo efficient intersystem crossing to give long lived triplet excited states that can participate in electron-transfer reactions. Thus, with an

appropriate acceptor metal, porphyrin radical cations are formed in high yield. Although powerful oxidants they may not be used for photooxidation of water, since they undergo secondary reactions to π-dications and isoporphyrins [400].

Redox reactions of tetra(4-hydroxy-3,5-di-*tert*-butylphenyl)porphyrin metal complexes in the presence of $K_3[Fe(CN)_6]$ have been investigated. Quinoid, mono and biradical complexes are successively formed, but at least in the case of the palladium complex, there is little conjugation between the radical and the porphyrin [401]. Unlike zinc, cadmium and magnesium analogues, palladium tetraphenylporphyrins do not give adducts with $[O_2]^-$ from $K[O_2]$ [402]. Palladium tetraphenylporphyrin trisulphonate has been demonstrated to be an effective photosensitiser for the photoreduction of viologen dyes [403].

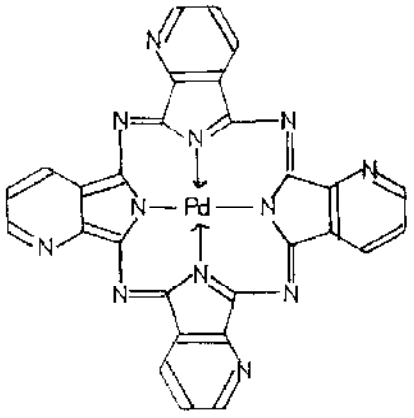
The preparation of palladium haematoporphyrins has been achieved in good yield from *N*-methylhaematoporphyrin in dmso. The reaction proceeds *via* formation of the metal *N*-methyl complexes, followed by rate-determining demethylation [404].

The palladium(II) complex, (191), of tetra-2,3-pyridine porphyrazine has been prepared and its acid dissociation constants measured spectrophotometrically [405]. The kinetics of oxidative decomposition of this complex and its analogues with other metals, were measured in the presence of H_2O_2. Not only is the palladium complex the most stable of the series (rates fall in the order [CuL] > H_2L > [CoL] >> [NiL] > [PdL]) but complexes of this ligand are up to a hundred-fold more stable than those of the phthalocyanines [406].

The formation of stable associations between molecules of metal pheophytin complexes was studied in aqueous binary solutions of dioxan, thf, morpholine and ethanol. The ability of the metal atoms to participate in long range interactions is in the order Zn > Mg > Cd > Cu > Pd [407].

The basicity of copper, nickel and palladium complexes of tetra(*tert*-butyl)tetraazaporphine, tetra(6-*tert*-butyl)-2,3-naphthalocyanine

and tetra(4-*tert*-butyl)phthalocyanine has been studied by electronic spectroscopy. Basicity is determined by the extent of the delocalisation of the π-system and the acceptor capacity of the metal [408].



(191)

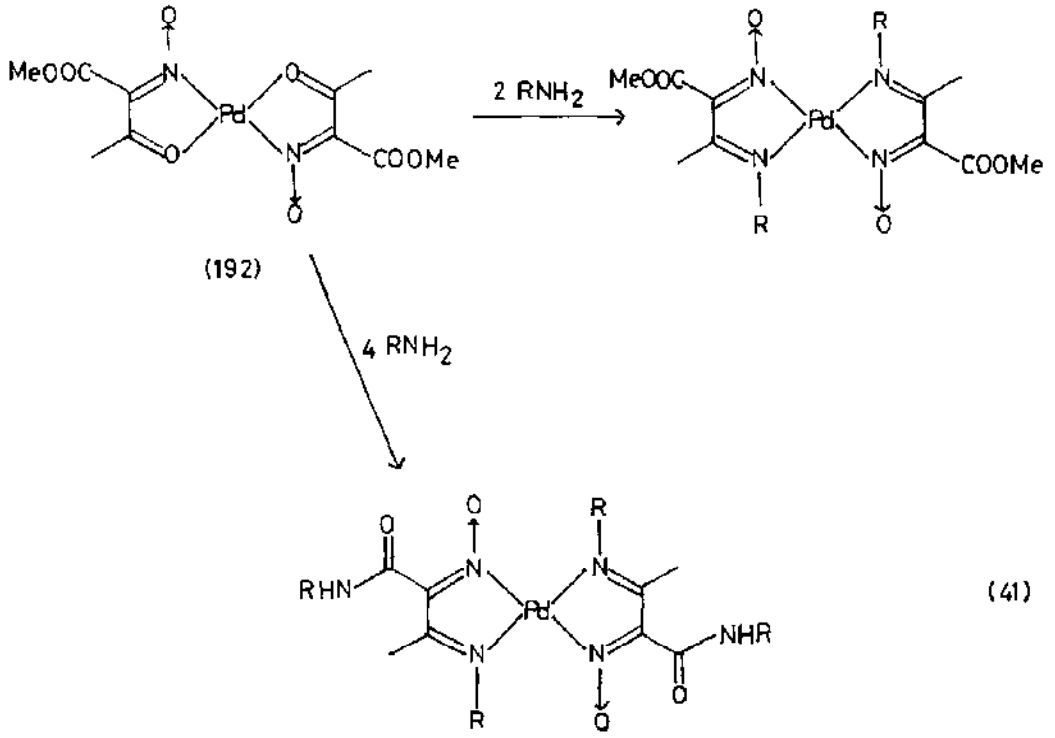
The epitaxial growth of molecular crystals of platinum phthalocyanines is noted [409].

1.5.4.4 Imine donor ligands

The reaction of bis(*t*-nitrosomethylacetoacetato)palladium(II), (192), with amines has been investigated (reaction (41)) and the product complexes characterised [410].

Thermal decomposition of the oddly formulated species $[Pd(LH_2)_2I_2].1.5HI$ (LH_2 = *N,N'*-dimethyldithiooximide) yields $[Pd(LH_2)I_2]$, LH_2 and HI, whereas $[Pd(LH_2)Cl_2]$ gives $[(PdL)_n]$ [411].

The complexes $[PdL_4]Cl_2$ and $[PdL_4][NO_3]_2.3H_2O$, where L is the Schiff base derived from terephthaldehyde and cycloserine, have been characterised [412].



(41)

1.5.4.5 Nitro complexes

^{195}Pt NMR spectroscopic studies of $[^{15}NO_2]^-$ labelled complexes are reported. The ^{195}Pt signal in $Na_2[Pt(^{15}NO_2)_4]$ is a quintet, whereas $[Pt(^{15}NO_2)_3(OH_2)]^-$ and $[Pt(^{15}NO_2)_3(OH)]^{2-}$ give doublets of triplets. The effect of the *trans*-ligand on $^1J_{Pt-N}$ is in the order $[NO_2]^- < [OH]^- < H_2O < [C_2O_4]^{2-}$ [413].

Thermolysis of $[LH]_2[Pt(NO_2)_4]$ according to reaction (42) (LH = benzimidazole, 1,2-dimethylbenzimidazole or 5,6-dimethylbenzimidazole) occurs at a lower temperature than for the corresponding $[PtBr_4]^{2-}$ or $[PtCl_4]^{2-}$ salts. *cis*-$[LH]_2[Pt(NO_2)_2X_2]$ (X = Cl or Br) gives *cis*-$[PtL_2X_2]$, since the more basic ligand is lost more easily [414].

$$[LH]_2[Pt(NO_2)_4] \xrightarrow{\Delta} cis\text{-}[PtL_2(NO_2)_2] \qquad (42)$$

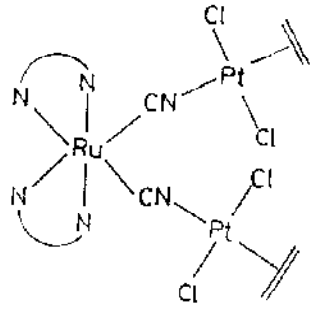
Trans-$Na[Pd(NO_2)(NH_3)Cl_2]$ acts as a stoicheiometric oxidant for ethene, yielding ethanal. $[NO_2]^-$ is converted to $[NO]^+$ and the reaction proceeds more

rapidly if HCl is present to protonate the nitro group [415].

1.5.4.6 Nitrile ligands

cis- and *trans*-$[Pt(PhCN)_2Cl_2]$ were prepared from $PtCl_2$ and were characterised by IR and Raman spectroscopy and X-ray diffraction [416].

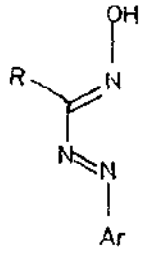
cis-$[Ru(bipy)(CN)_2]$ reacts with $K[Pt(C_2H_4)Cl_3]$ to give 1:1 and 1:2 adducts such as **(193)**. In the adducts, there are blue shifts in both the absorption and emission spectra, with an enhancement of emission intensity and an increase in lifetime [417].



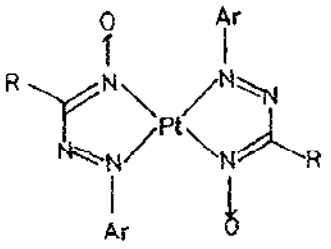
(193)

1.5.4.7 Diazine, triazine and tetrazadiene ligands

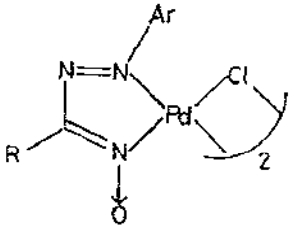
The reaction of $K_2[PtCl_4]$ with (194), HL, gives two isomers of $[PtL_2]$, depending on the conditions. The compound formed under basic conditions is simply *trans*-$[PtL_2]$, (195). Under acidic conditions *cis*-$[PtL_2]$ is formed; the structure was shown to be dimeric by X-ray diffraction. Both isomers readily add Cl_2 to give a Pt(IV) complex [418]. The analogous reaction with $K_2[PdCl_4]$ gives a chloro-bridged dimer, **(196)**. Amines cause bridge splitting to give **(197)** and an analogous species is formed with one mole of PPh_3. With an excess of phosphine this is in equilibrium with **(198)**, the nature of R affecting the stability of the complex [419].



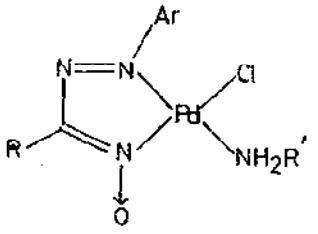
(194)



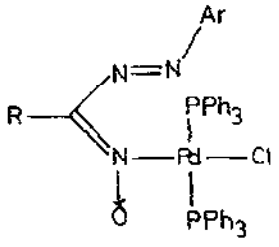
(195)



(196)



(197)

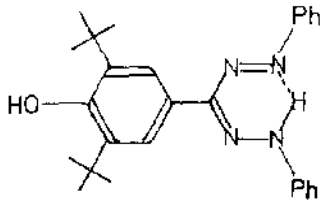


(198)

(199), HLOH, forms complexes $[Pd(LOH)_2]$ with $Na_2[PdCl_4]$. When the benzene solutions of the complexes are oxidised with $K_3[Fe(CN)_6]$, an EPR signal is observed, and the starting material is regenerated by dithionite. $[M(LOH)_2]$ reacts with $[M(LO^{\cdot})_2]$ to give $[M(LOH)(LO^{\cdot})]$, isolable as dark green crystals [420].

The term "coligand isomers" has been proposed to describe the pair of compounds in which one is formed by the reaction of the ligands in the central

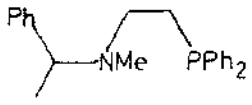
atom coordination sphere of the other. $[(Ph_3P)_2Pt(N_3)(4\text{-}CN\text{-}C_6H_4)]$ is thus converted to the coligand isomer, the tetraazolate complex [421].



(199)

1.5.4.8 Bidentate nitrogen phosphorus donor ligands

Complexes of the chiral ligand **S-(200)**, $[PtLCl_2]$ and $[PdLCl_2]$, have been prepared [422].

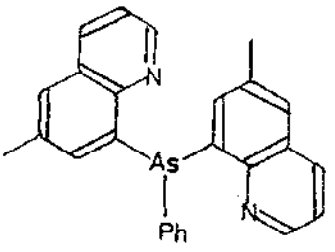


(200)

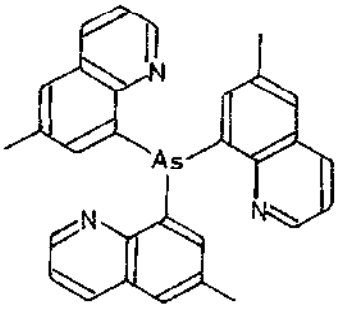
$Ph_2PCH_2SiMe_2N(Li)SiMe_2CH_2PPh_2$ reacts with $[Pd(PhCN)_2Cl_2]$ or $K[Pt(C_2H_4)Cl_3]$ to give $[MCl\{N(SiMe_2CH_2PPh_2)_2\}]$ in which the ligand is tridentate. The structure of the palladium complex was established by X-ray diffraction; the phosphine groups are *trans* and there is no puckering of the ligand backbone [423].

1.5.4.9 Bidentate nitrogen arsenic donor ligands

The ligands **(201)**, AsN_2, and **(202)**, AsN_3, form bidentate complexes $[PdLX_2]$. X-ray diffraction shows *pseudo* square-planar coordination with no interaction with the other nitrogen atom(s) [424].



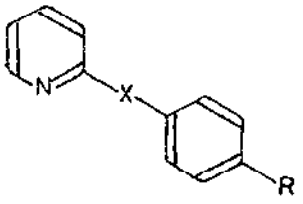
(201)



(202)

1.5.4.10 Bidentate nitrogen carbon donor ligands

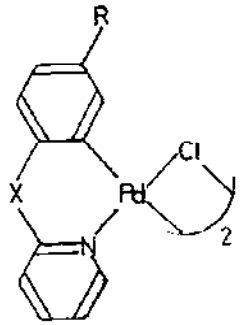
Reaction of $PdCl_2$ with (203), HL, gives *trans*-$[Pd(HL)_2Cl_2]$ in which HL is coordinated through the pyridine nitogen atom. Using a 1:1 molar ratio cyclopalladation to **(204)** occurs [425].



R = H, Me or Cl

X = NH, CH_2, O or *S*

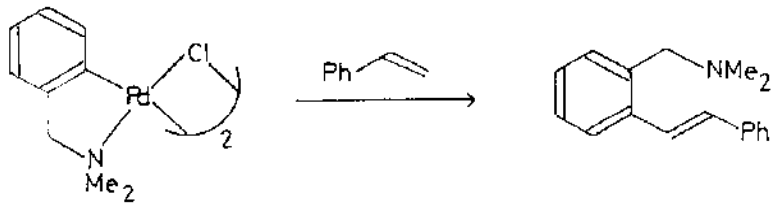
(203)



(204)

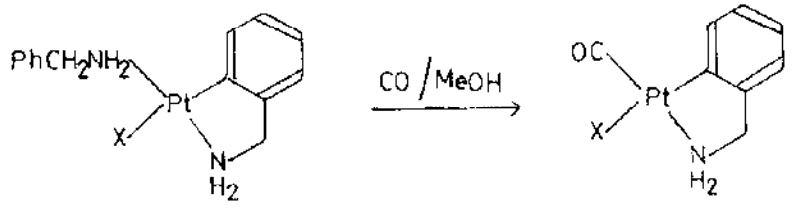
The cyclopalladated dimer, (205), inserts styrene to give (206) [426].

Similar insertions of $CF_3C{\equiv}CCF_3$ are also reported [427].



(205) (206)

Treatment of $[Pd(PhCH_2NH_2)_2I_2]$ with two molar equivalents of $Ag[BF_4]$ followed by KX yields **(207)**, which is readily converted to **(208)** in the presence of CO. The structure of **(208)** (X = I) was established by X-ray diffraction. Metallation is proposed to involve electrophilic attack of the metal on the aryl ring [428].

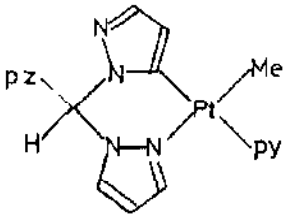


(207) **(208)**

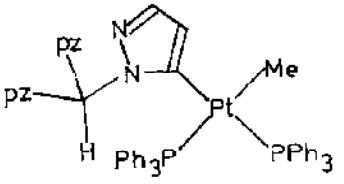
Reaction of *N*-(2-thienyl)pyrazole (H-2-tpz) or the 3-thienyl isomer (H-3-tpz) with $PdCl_2$ in a 2:1 molar ratio gives *trans*-$[PdL_2Cl_2]$. However, in a 1:1 molar ratio, two isomers of $[\{Pd(3\text{-tpz})Cl\}_2]$ are formed, the major and minor species being identified as **(209)** and **(210)** by NMR spectroscopy [429].

(209) **(210)**

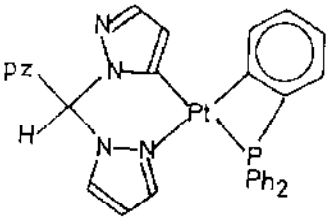
Tripyrazolylmethane, tpzm, reacts with $[Me_2Pt(cod)]$ in refluxing benzene to yield a species of stoicheiometry $[Me_2Pt(tpzm)]$. In the presence of donor ligands methane is lost with metallation of the ring to give complexes such as **(211)**, **(212)** and **(213)**. The structures of **(211)** and **(212)** were established by X-ray diffraction; there is no weak axial interaction with the other nitrogen atom(s) [430].



(211)



(212)



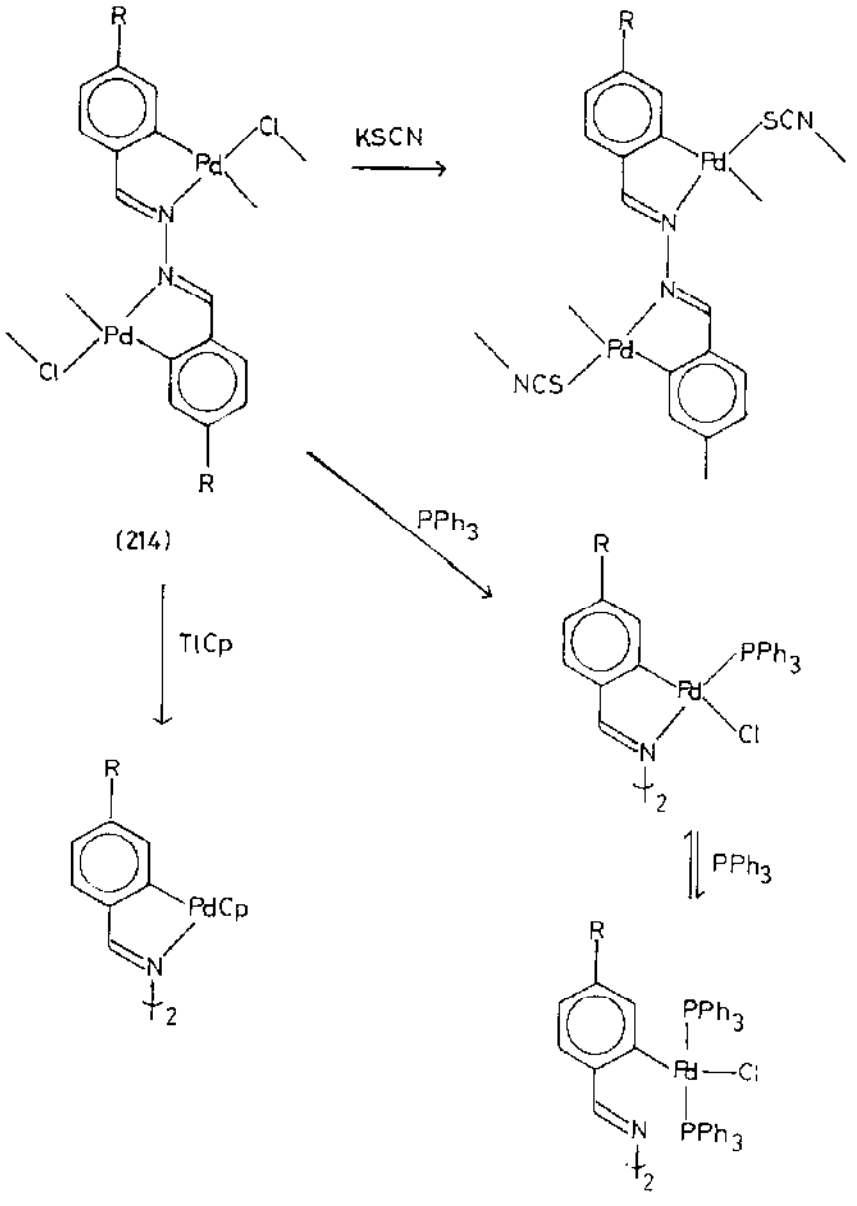
(213)

Phenylazophenyl (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)palladium(II) hexafluoroacetoacetate may be grown in solution in either a red or a yellow polymorphic form. Heating the yellow form gives the red polymorph with a sudden discontinuous crystal expansion. The packing patterns from X-ray diffraction show that the interconversion is a slip mechanism similar to a martensitic transformation. The colour change and expansion are not synchronous, the colour change being due to rotation of the exocyclic phenyl group into the plane of the phenylazo group [431,432].

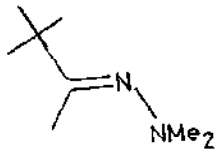
Reaction of benzalazines, ArCH=N-N=CHAr with $PdCl_2$ gives a cyclometallated polymer, **(214)**, some reactions of which are shown in Scheme 8 [433].

Two papers detail cyclometallations of methyl groups. Treatment of (215) with $[Pd(RCN)_2Cl_2]$ yields (216), in a reaction which is accelerated by base. With the analogous compound in which the nitrogen atom bears one methyl and one phenyl group, cyclometallation is disfavoured and $[PdL'_2Cl_2]$ may be isolated. Treatment with base then gives **(217)** in a slow reaction. It is

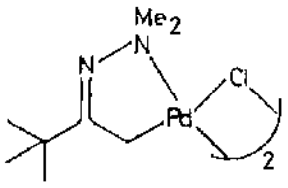
noteworthy that the usual mode of hydrazone coordination is through N-1 rather than N-2, N-2 binding being induced in (216) only by steric hindrance [434]. Treatment of (218) with $Pd(OCOCH_3)_2$ yields (219) and its stereoisomer. LiCl yields a chloro bridged dimer of the familiar type, with donor ligands then able to cause bridge splitting [435].



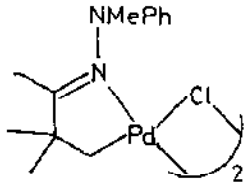
Scheme 8 Reactions of the cyclometallated polymer, (214) [433].



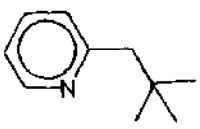
(215)



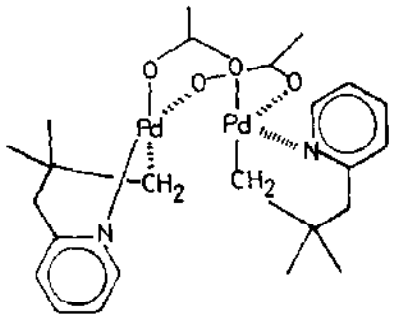
(216)



(217)

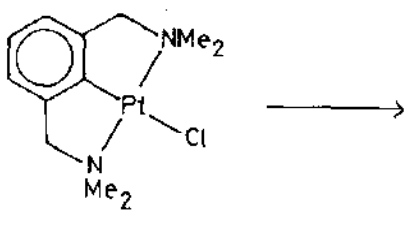


(218)

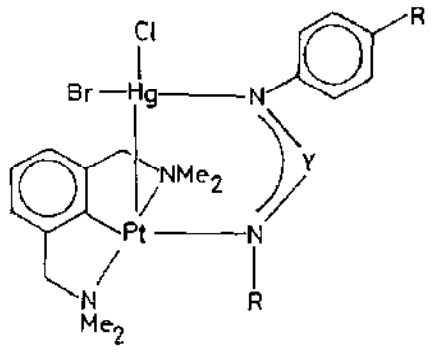


(219)

Further studies of the adduct (221) formed from (220) and [Hg(4-methylphenylNYNR)Cl] (Y = CH or N; R = Me, Et or $CH(CH_3)_2$) are reported. The structure proposed involves a platinum-to-mercury donor bond and further electron transfer is inhibited by the tridentate ligand [436].



(220)

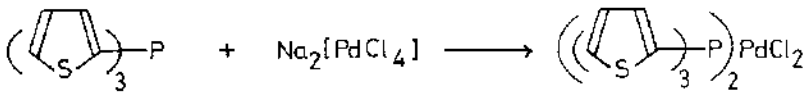


(221)

1.5.4.11 Unidentate phosphine donor ligands

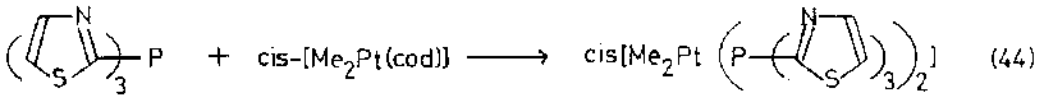
Diffraction studies of *trans*-$[Pd(PPh_3)_2Cl_2]$ [437], *cis*-$[Pt(PPh_3)_2Cl_2]$ [438] and *cis*-$[Pt\{P(CH_2Ph)_2Ph\}_2Cl_2]$ [439] are reported. In the last of these there is a significant degree of overcrowding with the angle P-Pt-P equal to 103 °.

A number of heteroaryl substituted phosphines have been converted to their palladium or platinum complexes, for example in reactions (43) [440] and (44) [441]. The structure of (222) was determined by X-ray diffraction, and in all cases the phosphines act as monodentate ligands with only the phosphorus atom metal coordinated.



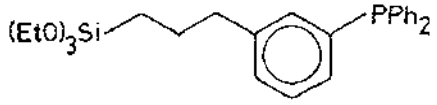
(43)

(222)

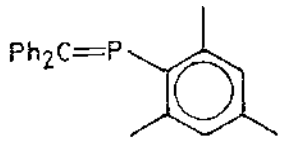


(44)

The complexes, *trans*-$[PdL_2Cl_2]$, where L is $PhP\{(CH_2)_3OR\}_2$, $P\{(CH_2)_3OR\}_3$ (R = Me or CH_2CH_2OMe) or $P\{CHMeCH_2CH_2OR'\}_3$ (R' = Me, CH_2CH_2OMe or $CH_2CH_2OCH_2CH_2OMe$) have been synthesised and have potential as phase transfer catalysts. For example, reduction of bromobenzene to benzene by sodium hydride occurs in up to 93% yield in the presence of such species [442]. Two series of phosphines, R_3P (R = $C_{10}H_{22}$ - $C_{19}H_{39}$ or R = 4-R'C_6H_4, R' = C_2H_5 - C_9H_{19}) were synthesised with a view to the preparation of extremely soluble transition metal complexes. The preparation, stereochemistry and reactivity of such complexes including *cis*-$[PtL_2Cl_2]$, *trans*-$[PdL_2Cl_2]$, *trans*-$[PtL_2HCl]$ and $[PtL_4]$ have been reviewed [443]. The complex prepared by treatment of **(223)** immobilised on silica with $Na_2[PdCl_4]$ is useful as a catalyst for alkene hydrogenation, and may be recovered and reused with little loss of activity [444].



(223)



(224)

The unusual ligand (224) reacts with $[Pt_2(PEt_3)_2Cl_4]$ to give a mixture of *cis*- and *trans*-$[Pt\{(224)\}(PEt_3)Cl_2]$. NMR spectroscopic studies allowed stereochemical assignment, and the structure of the *cis*-isomer was determined by X-ray diffraction. *cis*-$[Pt\{(224)\}_2Cl_2]$ is produced on reaction of the ligand with $[Pt(cod)Cl_2]$. In all cases (224) is coordinated to platinum through the sp^2 phosphorus atom [445]. Further reactions of Pd(II) and Pt(II) halides with $\{(CH_3)_3C\}_3E$ (E = P or As) including cyclometallation, carbonylation and cluster formation are reported [446].

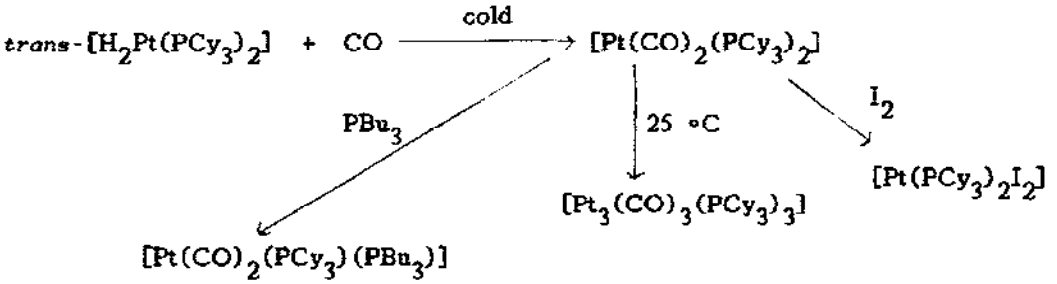
Soviet workers have been particularly interested in the electrochemistry of palladium(II) phosphine complexes. Both oxidation and reduction of $[PdL_2X_2]$ (L = PPh_3 or $P(OPh)_3$; X = Cl or [SCN]) occur irreversibly on a platinum microelectrode in dmf. Substitution of PPh_3 by $P(OPh)_3$ leads to difficulty in the electroreduction of the Pd(IV) complex formed, but facilitates the reduction of Pd(II) to Pd(0) [447,448]. In oxygenated solutions of $[PdL_2X_2]$ (L = PPh_3, $P(OPh)_3$ or $P(OCH\{CH_3\}_2)_3$; X = Cl or [SCN]) palladium(II) is reduced to palladium(0), which reacts with O_2 in a solution layer next to the electrode [449,450]. Cyclic voltammograms of solutions of $[HPt(PEt_3)_3]^+$ in phosphate buffer at mercury electrodes show large reduction waves on all forward and reverse scans except for the first negative scan, which is interpreted in terms of catalytic hydrogen production [451].

Photolysis of $[PdL_2(O_2)]$ (L = PPh_3 or PPh_2Me) in the presence of an excess of ligand and an alkyl halide, RX, gives phosphine oxide and *trans*-$[PdL_2X_2]$. By contrast, using an aryl halide and L = PPh_3, $[Ph_4P]X$ is isolated. The photochemical interconversion of the *cis*- and *trans*-isomers

of the complex is discussed in relation to their luminescence spectra [452].

Platinum(0) complexes, $[PtL_n]$ (L = PEt_3, n = 3 or L = $P\{CH(CH_3)_2\}_3$, n = 2 or 3) are very powerful nucleophiles and react with water to yield $[PtL_mH(OH)]$ which, from conductance measurements, exists as an ion pair and is a strong base. The system $[PtL_n]/H_2O$ serves as a catalyst for the hydration of acrylonitrile and for H/D exchange α to carbonyl, sulphonyl or nitro groups [453].

The complexes $[HML(PCy_3)_2]$ and *trans*-$[HPt(O_2CR)(PCy_3)_2]$ (M = Ni or Pd; HL = succinimide; R = $C(CH_3)=CH_2$ or $CH_2CH=CH_2$) were prepared by oxidative addition of HL or RCOOH to the $[(Cy_3P)_2M(0)]$ complex [454]. A series of reactions of platinum complexes of PCy_3 was established and is shown in Scheme 9 [455].



Scheme 9 Reactions of platinum complexes of tricyclohexyl phosphine [455]

cis-$[HPt(PPh_3)_2(CH_2CF_3)]$ is prepared by successive treatment of *cis*-$[Pt(PPh_3)_2(CH_2CF_3)I]$ with Ag^+ and $Na[BH_4]$. CH_3CF_3 is produced slowly just above room temperature, the kinetic data being consistent with a concerted unimolecular reductive elimination [456].

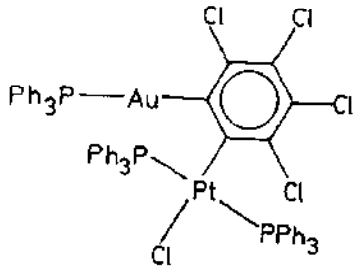
The replacement of Cl^- in $[Pt(PR_3)(en)Cl]^+$ (R = Me, Et, Bu or OMe) by nucleophiles has been investigated. The second order rate constant is related to the nucleophilicity of the attacking species, and the rates are also sensitive to steric hindrance from the *cis*-ligand [457]. Intermolecular exchange of ligands in *trans*-$[M(C_6Cl_5)(PMe_2Ph)_2X]$ (M = Ni, Pt or Pd; X = Cl, Br or I) has been studied. When chloride and iodide are exchanged

between nickel and palladium the equilibrium is strongly in favour of Ni-Cl and Pd-I bond formation, as would be expected on thermodynamic grounds [458].

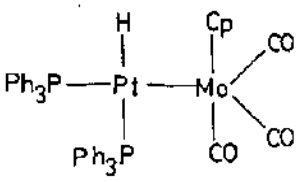
cis-$[Pt(PPh_3)_2Cl_2]/SnCl_2$ is an extremely active catalyst for alkene hydroformylation. It reacts with CO and propene in ethanol to yield *trans*-$[Pt(COPr)(PPh_3)_2Cl]$, whilst from the reaction mixture $[Pt(COPr)(PPh_3)_2(SnCl_3)]$ is isolated. The structures of both complexes were established by X-ray diffraction [459]. *cis*-$[Pt(PPh_3)_2Cl_2]$, *cis*-$[Pt(CO)(PPh_3)Cl_2]$ and *trans*-$[HPt(PPh_3)_2X]$ (X = Cl, Br or I) were prepared and studied by IR and NMR spectroscopy and DTA. The structures were related to the catalytic activity of the complexes in oxidative chlorination of pentane [460].

closo-Borate anions have been further exploited in stabilisation of unusual coordination compounds. *closo*-$[Pd_2(PPh_3)_4Cl_2][B_nX_n]$ and $[Pd(PPh_3)_3Cl]_2[B_nX_n]$ (n = 10 or 12; X = Cl or Br) are catalysts for the oxidation of Ph_3P to Ph_3PO and ethanol to ethanal [461].

Several new bimetallic phosphine complexes are reported. X-ray diffraction shows that in (225) coordination about gold is distorted linear and that about platinum roughly square planar with no metal π-interactions [462]. Oxidative addition of $[R_2Hg]$ to $[Pt(PPh_3)_3]$ gives $[(Ph_3P)_2Pt(R)(HgR)]$, **(226)** (R = chlorinated phenyl). **(226)** reacts with tfaH to give $[(Ph_3P)_2Pt(R)(OCOCF_3)]$ and may be thermolysed to yield $[(Ph_3P)_2PtR_2]$ and mercury metal [463]. Reaction of $[HPt(PPh_3)_2Cl]$ with $Na[Mo(CO)_3(cp)]$ gives **(227)**, the structure of which was established by X-ray diffraction [464].



(225)



(227)

Reduction of $[(Ph_3P)Pd(OCOCH_3)_2]$ with molecular hydrogen proceeds *via* reactions (45)-(49) [465].

$$[(Ph_3P)Pd(OCOCH_3)_2] + H_2 \longrightarrow [Ph_3P\text{-}Pd\text{-}Pd\text{-}PPh_3] + 2CH_3COOH \quad (45)$$

(228)

$$[Ph_3P\text{-}Pd\text{-}Pd\text{-}PPh_3] + H_2 \longrightarrow [(Ph_3P)_2Pd_2H_2] \quad (46)$$

$$[Ph_3P\text{-}Pd\text{-}Pd\text{-}PPh_3] + 2(228) \longrightarrow 2\ Ph_3P\text{-}Pd\ \text{(229)}\ Pd\text{-}PPh_3 + 2H^+ \quad (47)$$

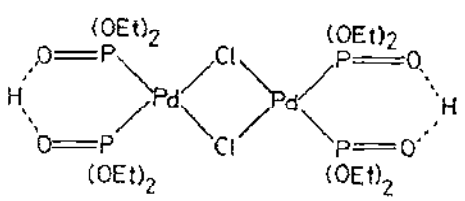
(229)

$$[(Ph_3P)_2Pd_2H_2] + (228) \longrightarrow (229) + [Ph_3P\text{-}Pd\text{-}Pd\text{-}PPh_3] + 2CH_3COOH \quad (48)$$

$$\textbf{(229)} + [(Ph_3P)_2Pd_2H_2] \longrightarrow 2[Ph_3P\text{-}Pd\text{-}Pd\text{-}PPh_3] + 2CH_3COOH \quad (49)$$

1.5.4.12 Other unidentate phosphorus donor ligands

$K_2[PtCl_4]$ reacts with $EtOP(NEt_2)_2$, L, to give $[PtL_4][PtCl_4]$ which, on treatment with HCl yields $[PtL_2Cl_2]$; coordination is through phosphorus. An unidentified crystalline material is obtained with $Et_2NP(OEt)_2$; this is hydrolysed by aqueous HCl to give $[Pt\{P(OH)_2NEt_2\}_2\{P(OH)O(NEt_2)_2\}]$ [466]. When the allyl palladium chloride dimer reacts with $(RO)_2P(H)=O$, LH, $[Pd_2(LH)_2L_2(\mu\text{-}Cl)_2]$ is obtained (R = Me, Et, Ph, $CH(CH_3)_2$ or $CH_2CH(CH_3)_2$). The structure of (230) was determined by X-ray diffraction [467].

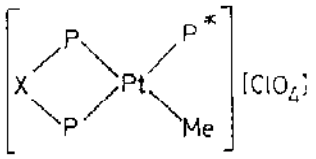


(230)

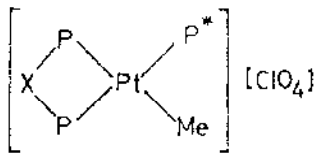
1.5.4.13 Bidentate phosphorus donor ligands

$[(dppe)PtCl_2]$ has been prepared and its structure determined to be distorted square planar by X-ray diffraction [468]. The preparation of nickel, palladium and platinum dichloro complexes of R-1,2-bis(diphenylphospino)propane, 2S,3S-2,3-bis(diphenylphosphino)butane and R-1,2-bis(diphenylphosphino)-1-phenylethane has been reported. Their CD, IR and ^1H and ^{31}P nmr spectra were recorded and compared [469]. Bidentate chelate complexes of $Cy_2P(CH_2)_3PHPh$ and $Ph_2P(CH_2)_3PHPh$, (PPH), $[MLCl_2]$ (M = Pd or Pt) have been prepared. Treatment of $[M(PPH)Cl_2]$ with base and $[M(PPH)_2]Cl_2$ yields $[\{MCl(\mu\text{-}PP)\}_2]$, which is phosphido bridged, the acidity of the P-H group being enhanced by coordination [470].

Several papers have reported strategies for the resolution and the determination of the optical purity of chiral phosphines. In complexes such as (231), where PXP is dppe, S,S-CHIRAPHOS, S-*N*,*N*-bis(diphenylphosphino)-1-phenylethylamine or (+)-DIOP and P^* is a chiral monodentate phosphine, differing degrees of stereoselective binding are noted and partial resolution of the monophosphines is achieved [471]. Analogous behaviour is noted for monodentate chiral amines, and diastereomer ratios, measured by ^{31}P NMR spectroscopy, are highest for complexes of S,S-CHIRAPHOS. The structure of [MePt(DIOP)Cl] was determined by X-ray diffraction; the seven membered chelate adopts a twist chair conformation [472]. X-ray diffraction and NMR spectroscopic studies of **(232)**, where X is a 4-substituted pyridine or R_3P, have established the steric and electronic effects of the ligand on structure. The cationic pyridine complexes show a correlation between ρ_{para} and ^{31}P chemical shifts and coupling constants [473].

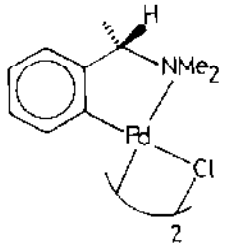


(231)

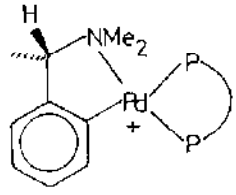


(232)

Reaction of the cyclopalladated species **(233)** with chelating biphosphines yields **(234)**. Diastereomers are obtained with chiral phosphines and ^{31}P NMR can detect 3 % of a minor diastereomer, providing an extremely sensitive test of optical purity [474].



(233)

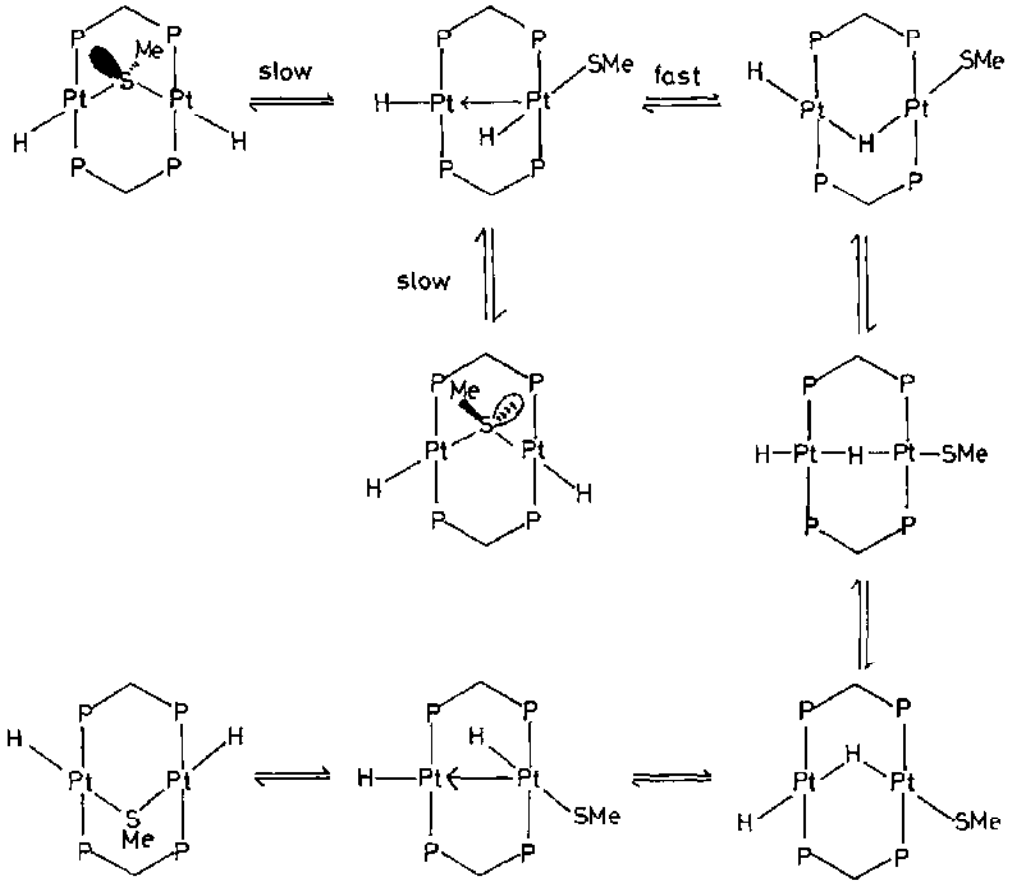


(234)

Reaction of $K_2[PtCl_4]$ with dppm in the presence of KOH yields $[Pt(Ph_2PCHPPh_2)_2]$, the first homoleptic complex in which the ligand is chelating. X-ray diffraction demonstrated that coordination about platinum was square planar. Reaction with H^+ gives the known $[Pt(dppm)_2]^{2+}$ [475]. Deprotonation of dppm is also achieved on treatment of $[Pt(dppm)I_2]$ with $LiN(SiMe_3)_2$, and the anion may be readily alkylated [476].

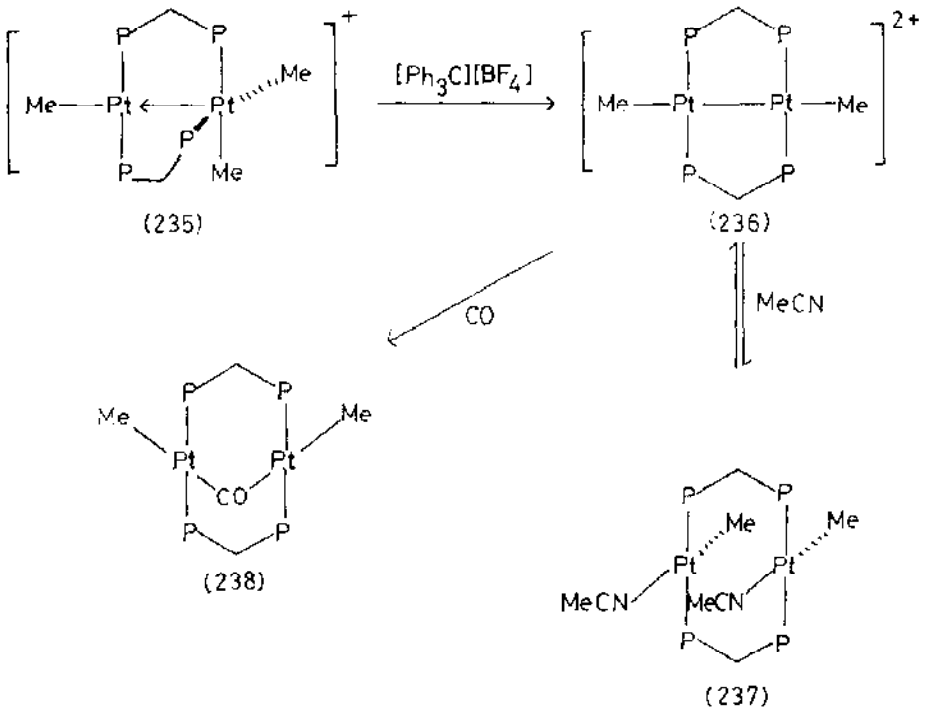
A mechanism has been proposed which accounts for all the known examples of "A-frame" inversion for complexes $[Pt_2(\mu\text{-dppm})_2(\mu\text{-Y})X_2]^{n+}$ (n = 0 or 1). For Y = H, the reaction is believed to proceed *via* a linear M-H-M arrangement. It was noted that all the known inversions occur in complexes with a bridging

hydride or in species which may be readily rearranged to a complex with a bridging hydride. Thus, although $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2]$ shows an "A-frame" inversion, sulphur inversion occurs at the same rate, implying the mechanism of Scheme 10 [477].



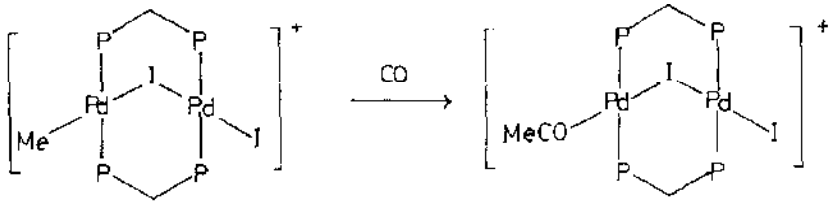
Scheme 10 Mechanism of "A-frame" inversion [477]

(235) is demethylated by trityl tetrafluoroborate to give (236). (236) reacts reversibly with MeCN to give the *cis*-species, (237), and with CO to give a new "A-frame" complex, (238). (238) is formed very rapidly and equilibrates over about 5 min with the CO analogue of (237) [478].



(235) (236) (238) (237)

Addition of carbon monoxide to $[Me_2Pd_2(\mu\text{-}X)(\mu\text{-dppm})_2]X$ (X = Br or I) leads to the bis(ethanoyl) complex $[(MeCO)_2Pd_2(\mu\text{-}X)(\mu\text{-dppm})_2]X$ which may be isolated and characterised. Oxidation of this product (X = I) yields $[Pd_2I_2(\mu\text{-dppm})_2]$ and acetic anhydride. Reactions of **(239)** were also studied; **(240)**, obtained on carbonylation, and $[Pd_2(\mu\text{-dppm})_2(\mu\text{-MeC=NMe})(CNMe)_2]^{3+}$, from treatment with MeNCO, have weak metal metal bonds [479].

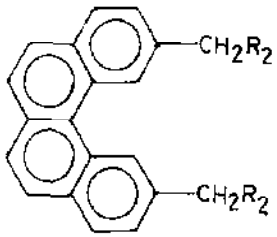


(239) **(240)**

Treatment of $[Pt(dppm\text{-}P,P)Cl_2]$ with RC≡C-Li yields the face to face

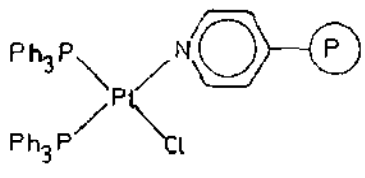
isomer of $[Pt_2(C{\equiv}C\text{-}R)_4(\mu\text{-dppm})_2]$. If the reaction is performed in the presence of dppm, or if dppm is added to the product, *trans*-$[Pt(C{\equiv}C\text{-}R)_2(dppm\text{-}P)_2]$ is formed. This is a fluxional molecule and the uncoordinated phosphine may be readily oxidised or alkylated. In a related process, treatment of $[Pt(dppm\text{-}P,P)_2]Cl_2$ with $[Hg(C{\equiv}C\text{-}R)_2]$ gives the bimetallic compound $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ in excellent yield [480].

$o\text{-}Ph_2PCB_{10}H_{10}CPPh_2$ and the closely related compound, $o\text{-}Ph_2PCB_{10}H_{10}CP(NMe_2)_2$, act as *cis* chelating ligands towards palladium in $[PdLCl_2]$ [481]. (241), on the other hand, is a *trans* chelating ligand (R = Ph, $3\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $3\text{-}CF_3C_6H_4$, C_6H_{11} or Me_3C). NMR spectroscopy of palladium and platinum complexes of the *tert*-butyl substituted ligand show two distinct dynamic processes, with four non-equivalent *tert*-butyl groups at low temperature [482].

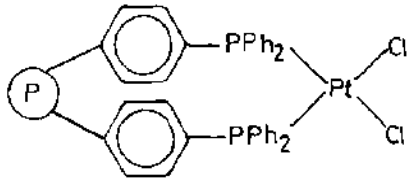


(241)

Polymer supported complexes such as (242) and (243) have been investigated by ^{31}P NMR spectroscopy in the solid state [483,484].



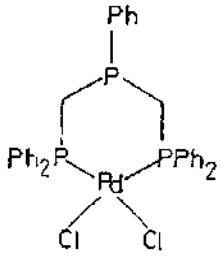
(242)



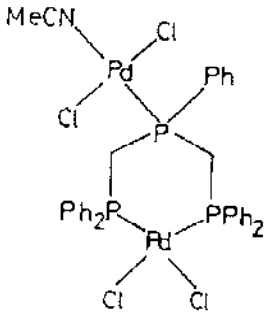
(243)

The coordination chemistry of $Ph_2PCH_2PPhCH_2PPh_2$ has been investigated.

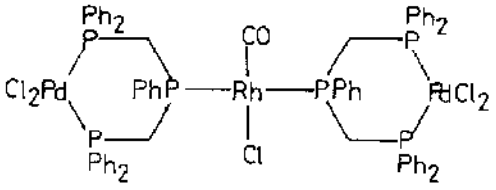
Reaction with $[Pd(PhCN)_2Cl_2]$ gives **(244)**, in contrast to the process with $[Rh_2(CO)_4Cl_2]$, which yields a trinuclear bridged species [485]. X-ray diffraction studies of both **(244)** and **(245)** are reported. The six-membered ring in **(245)** has a skew boat conformation. Reaction of **(244)** with $[Rh_2(CO)_4Cl_2]$ gives an adduct **(246)** [486].



(244)

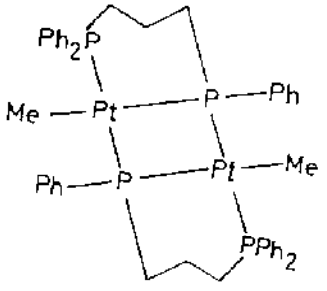


(245)



(246)

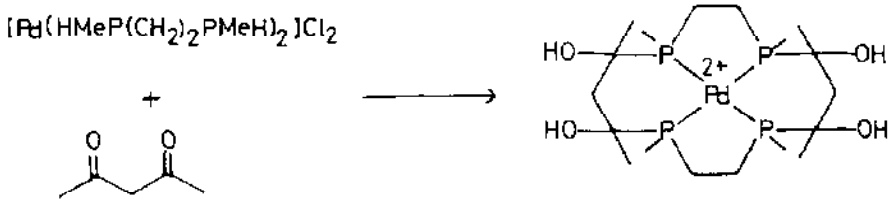
Reaction of $[Me_2Pt(cod)]$ with $R_2P(CH_2)_3PHPh$ gives both displacement of cod and cyclisation, to yield **(247)** [487].



(247)

Square planar complexes of nickel(II) and palladium(II) with 14-membered macrocyclic tetradentate phosphine ligands had been synthesised by the one step template ring closure reaction (50), and details are now reported in a

full paper. Two isomers of **(248)** are formed and their structures were determined by X-ray diffraction. In the **RSSR**-form, palladium is a square planar diacation as shown, but the **RSRS**-diastereomer has square pyramidal coordination with chlorine occupying the fifth site [488].

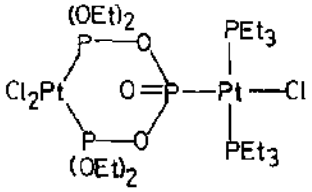


(50)

(248)

Resonance Raman spectra of $[Pt_2(pop)_4]^{4-}$ have been studied as a probe of the metal-metal interaction. The change in the Pt-Pt vibration from 118 cm^{-1} ($^1A_{1g}$, $(d\sigma^*)^2$) to 156 cm^{-1} ($^3A_{2u}$, $d\sigma^*$ $p\sigma^*$) implies an increase by a factor of 1.8 in restoring force in the excited state relative to the ground state [489]. Low temperature electronic absorption and emission spectra of single crystals show absorption systems in the 450 nm and 360 nm regions, attributable to transitions to the $^3A_{2u}$ and $^1A_{2u}$ excited states respectively [490].

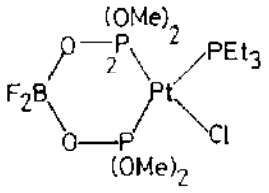
Reaction of $(EtO)_2POP(OEt)_2$ with *trans*-$[Pt_2(PEt_3)_2Cl_4]$ yields **(249)**, the structure of which was established by X-ray diffraction. Rather romantically, the six-membered ring is described as possessing a chaise longue conformation. The same complex is obtained from HCl/H_2O/propanone hydrolysis of *cis*-$[Pt\{PCl(OEt)_2\}(PEt_3)Cl_2]$ [491].



(249)

The structure of **(250)** has been established by X-ray diffraction, being

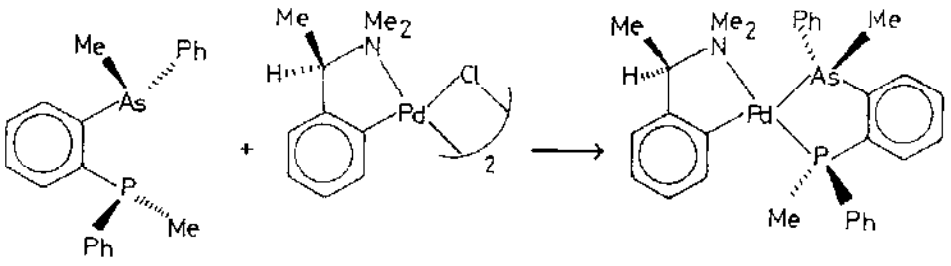
the first determined of a complexed phosphinito or secondary phosphito ring. The Pt-P2 distance is short, as chlorine has a low *trans*-influence [492].



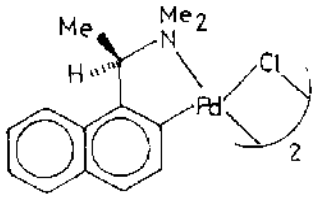
(250)

1.5.4.14 Bidentate phosphorus arsenic donor ligands

(251) and its stereoisomers have been prepared, and the RR/SS diastereomer resolved *via* diastereoisomeric salts such as (252). Phosphine and nitrogen are *trans*, and there was no evidence for the presence of regioisomers. The RS/SR diastereomer was resolved using (253) [493].



(251) (252)



(253)

1.5.4.15 Arsenic donor ligands

The complexes $[Pd\{As(CH_2Ph)_3\}_2X_2]$ (X = Cl, Br, I or NO_2), $[Pd_2(AsPh_3)_2Cl_4]$ and $[Pd(AsPh_3)(py)Cl_2]$ have been

prepared and characterised [494].

The syntheses of the bidentate ligands $Ph_2As(CH_2)_nAsPh_2$ (n = 6-12 and 16) is described. These form square-planar complexes $PdLX_2$ (X = Cl, Br, I or [SCN]; n = 6, 8, 10, 12 or 16) and $PdLCl_2$ (n = 7, 9 or 11), which were characterised by IR, electronic, solid state reflectance and ^1H NMR spectroscopy. The *trans*-isomer is the sole product when $n > 9$ and the major one for $n < 9$. The molecular weight of the complexes is a function of chain length, with polymeric complexes of short chain ligands, and monomeric ones with longer chain analogues [495,496].

1.5.5 Complexes with Group IV donor ligands

Many of the complexes of Group IV donor ligands are strictly "organometallic" and thus fall outside the scope of this review.

1.5.5.1 Carbonyl complexes

Molecular orbital calculations were performed on all the possible isomers of $[Pd_2(CO)_2Cl_4]^{2-}$ and $[Pd_2(CO)_2Cl_4]$. It was concluded that the choice of bridging groups was dependent on the relative energies of the bridging ligands and the HOMO for the Pd(I) complex, but the LUMO for the Pd(II) compound [497]. Reaction of $[Pt(CO)_2Cl_2]$ and $[Pt_2(CO)_2Cl_4]$ in the melt gives a phase of composition $Pt_2(CO)_3Cl_4$, but X-ray analysis demonstrated that this was a eutectic and not a true compound [498].

A scheme has been devised to describe the reduction of Fe(III) to Fe(II) by CO in the presence of Pd(II) (reactions (51)-(55)) [499].

$$Pd(II) + CO \longrightarrow Pd(II)(CO) \quad (51)$$

$$Pd(II)(CO) + H_2O + CO \longrightarrow Pd(0)(CO) + 2H^+ + CO_2 \quad (52)$$

$$Pd(0)(CO) + Pd(II) + CO \longrightarrow 2Pd(I)(CO) \quad (53)$$

$$Pd(I)(CO) + 2Fe(III) + H_2O \longrightarrow Pd(II) + CO_2 + 2Fe(II) + 2H^+ \quad (54)$$

$$Pd(I)(CO) + Fe(III) \longrightarrow Pd(II)(CO) + Fe(II) \qquad (55)$$

A species of stoicheiometry $[(Ph_3P)_2Ir(CO)_2PdCl_2]$ of unspecified structure is formed on reaction of $[(Ph_3P)_2Ir(CO)_2(COOMe)]$ with *cis*-$[Pd(PhCN)_2Cl_2]$ [500].

1.5.5.2 Cyanide complexes

$[NH_4]_2[Pd(CN)_4]$ has been prepared from $Pd(CN)_2$ and $[NH_4][CN]$ in non-aqueous solvents [501].

Further spectroscopic studies of the one-dimensional salt, $Ba[Pt(CN)_4]$, are reported this year. Luminescence and absorption studies were used to identify localised and delocalised electronic states [502]. Two studies report data on $Ba[Pt(CN)_4]$ doped with $[Ni(CN)_4]^{2-}$. Luminescence and optical emission results were explained by assuming two types of $[Pt(CN)_4]^{2-}$ species within a linear system of *quasi*-localised states [503]. Emission decay curves and time resolved emission spectra were interpreted somewhat differently, with a three level model including radiationless passage from the lowest excited state of $[Pt(CN)_4]^{2-}$ to $[Ni(CN)_4]^{2-}$ [504].

In $Ln_2[Pt(CN)_4]_3.yH_2O$, the optical properties of the compound depend systematically on the intra-columnar Pt-Pt distance. Some modification of the emitting states of the platinum occurs due to the Ln^{3+} cations and this is explained by a mixing of the emitting A'_{1u} state with a CT state ($Pt(5d_{z^2})$-$Ln(4f)$), the energy of which depends on the lanthanide [505].

A study of the optical properties of $[enH]_2[Pt(CN)_4]$ crystals represents the first example of an investigation of a complex with an organic counter ion. A very large pressure induced red shift (360 cm^{-1} $kbar^{-1}$) is noted and the emission is profoundly affected by the magnetic field, being shifted by 220 cm^{-1} and increased in intensity by a factor of ten between 0 and 5 Tesla. The role of the organic cation is restricted to its effect on the Pt-Pt distance [506].

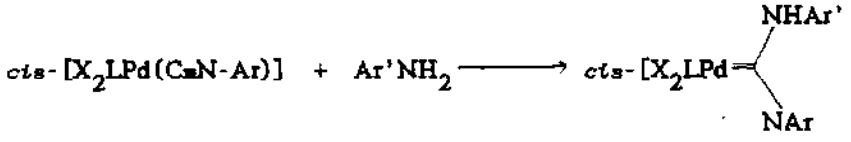
Raman scattering from $[Pt(CN)_4]^{2-}$ adsorbed on platinum colloids has been compared with that in free solution [507].

The ions $[M(CN)_4]^{2-}$ (M = Pd or Pt) have been compared with other $[M(CN)_4]^{n-}$ species in terms of their rates of exchange of $[CN]^-$. The kinetics of exchange were studied by ^{13}C NMR spectroscopy and the rate expression shown to be of the form $k_2[M(CN)_4][CN]$, with no cyanide independent term. The order of substitution rate, which is similar to the for ligand replacement in other square planar complexes, is Ni >> Au > Pd > Pt. The anomalous reactivity of nickel is due to the stability of $[Ni(CN)_5]^{3-}$, which resembles the intermediate or an I_a transition state [508].

Cyclic voltammetry of cyanide melts with platinum metals indicated that palladium was dissolved at potentials < 1.9 V and that M(II), M(I) and M(0) (M = Pd or Pt) could be produced in the melt [509].

1.5.5.3 Isonitrile complexes

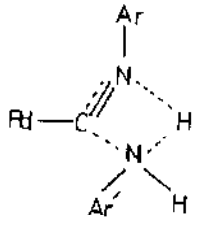
Further papers this year have discussed the reactions of coordinated isonitriles with nucleophiles. From nucleophilic attack of amines on isonitriles in square-planar palladium(II) species, amino carbene complexes are the main products (reaction (56)) *via* a four centre transition state (254). A general mechanism is formulated for reactions with secondary anilines, in which a second mole of aniline is used to assist proton transfer in (255) [510].



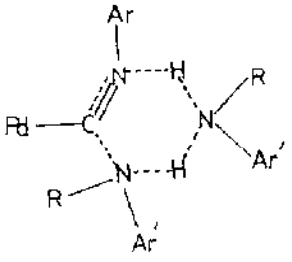
(56)

Both palladium and platinum complexes $[ML_2X_2]$ X = Cl, Br or I; L = $CNCH_2SO_2C_6H_4$-4-Me, $CNCH_2Ph$ or $CNCHPh_2$) have been prepared and treated with a wide range of nucleophiles. As before, amines (including methyl glycinate) give diamino carbene complexes, and the anion of RCH_2CN yields

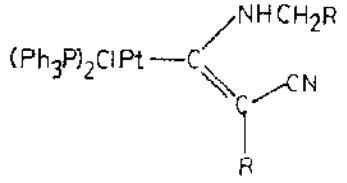
(256) after proton transfer. Stronger nucleophiles cause displacement of the isonitrile. The dipolar nature of the isonitrile complexes is shown in their reactions (for example, (57)) with dipolarophiles such as PhNCO [511].



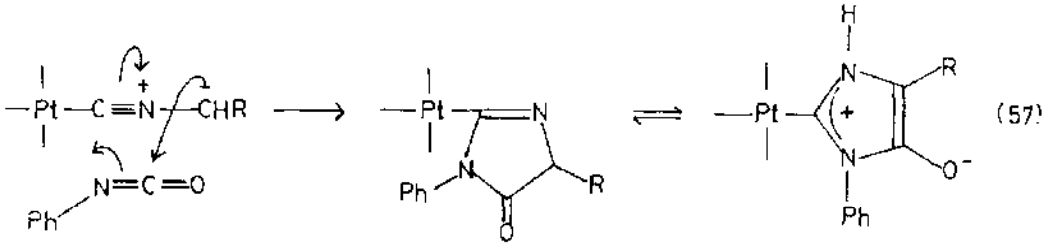
(254)



(255)



(256)



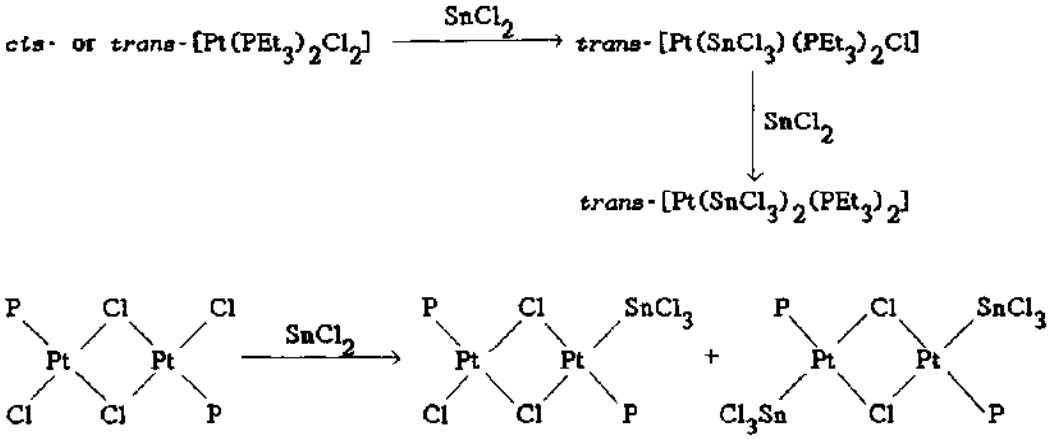
(57)

1.5.5.4 Tin donor ligands

Reaction of $K_2[PtCl_4]$ with $SnCl_2$ in the presence of $[Me_4N]Cl$ gives a variety of products, the ratios of which depend on reaction conditions. These include $[Me_4N]_2[Pt(SnCl_3)_2Cl_2]$, $[Me_4N]_3[Pt(SnCl_3)_5]$, $[Me_4N]_6[Pt_3(SnCl_3)_8]$ and $[Me_4N]_4[Pt_3(SnCl_3)_5]$. With high Cl:Pt ratios and an excess of $SnCl_2$, $[Pt(SnCl_3)_5]^{3-}$ is the main product, but at lower molar ratios clusters predominate [512]. A closely related series of bromo compounds results from the reaction of $K_2[PtBr_4]$ with $SnBr_2$ [513]. Similar species seem to result from the treatment of $PdCl_2$ with $SnCl_2$, though oxidation states are rather randomly assigned by the authors, and evidence for the structures of the complexes is lacking [514]. Reaction of $K_2[PtCl_4]$ with $SnCl_2$/HF yields

$K_3[Pt(SnF_3)_5].4H_2O$, which is presumed to have a trigonal bipyramidal structure [515].

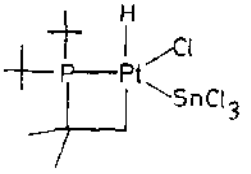
Much of the study of tin complexes of platinum has been motivated by the importance of $SnCl_2$ as a cocatalyst with $[PtL_2Cl_2]$ and analogues in hydrogenation and hydroformylation processes. ^{31}P, ^{119}Sn and ^{195}Pt NMR spectroscopy has been used to identify the products of the reaction of $SnCl_2$ with platinum(II) phosphine complexes. These processes have been reviewed (Scheme 11) [516].



Scheme 11 Reactions of $SnCl_2$ with platinum(II) complexes [516]

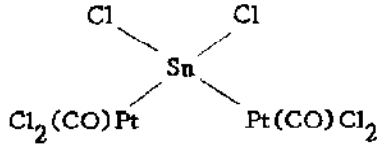
An entirely analogous process is reported for $[PtL_2Cl_2]$, where L is 4-methylpyridine [517]. However, the reaction with *cis*-$[Pt(AsR_3)_2Cl_2]$ (R = Me or Et) is somewhat different, at least when carried out in propanone in the presence of $[(Ph_3P)_2N]^+$. The main product is $[Pt(SnCl_3)_3(AsR_3)_2]^-$ in which platinum adopts trigonal bipyramidal geometry with the arsine ligands axial [518]. Spectroscopic data for these and related species are reported [519].

The reaction of *trans*-$[HPt(PR_3)_2Cl]$ with $SnCl_2$ has been investigated. The product is *trans*-$[HPt(PR_3)_2(SnCl_3)]$ and the species with R = *tert*-butyl carbometallates to give **(257)** [520]. A study of solvent effects suggests that unsolvated SnX_2 inserts into Pd-X, bonds but solvated SnX_2 gives substitution *via* a pentacoordinated intermediate [521].



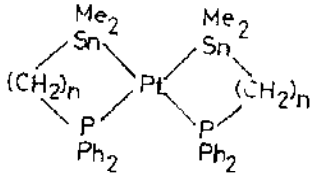
(257)

Propanone solutions of *cis*-$[Pt(PPh_3)(CO)Cl_2]/SnCl_2$ are active catalysts for alkene hydroformylation. The species $[Pt(PPh_3)_2(CO)Cl]^+$, $[Pt(SnCl_3)_5]^{3-}$, *trans*-$[Pt(CO)(SnCl_3)_2Cl]^-$ and ultimately *trans*-$[Pt(PPh_3)(SnCl_3)_2Cl]^-$ are formed in a complex series of rearrangements, and could be identified spectroscopically [522]. However, in $CHCl_3$ as solvent, a single insertion of $SnCl_2$ occurs [523]. Reaction of $[R_4N]_2[Pt_2(CO)_2Cl_4]$ with $SnCl_2$ gives insertion of $SnCl_2$ between the platinum atoms in **(258)** [524]. $[Pt(SnCl_3)_2Cl_2]^{2-}$ is also formed by reaction of $H_2[PtCl_6]$ or $PtCl_4$ with $SnCl_2$ in $(CH_3)_2CHOH$ [525].



(258)

The synthesis and characterisation of **(259)** and its *trans*-isomer is reported [526].



(259) n = 2 or 3

1.5.5.5 Germanium donor ligands

Reaction of $[M(PPh_3)_n]$ (M = Pd, Pt or Ni; n = 3 or 4) with $[(Ph_3Ge)_2M']$ (M' = Cd or Hg) yields $[(Ph_3P)_2M(M'GePh_3)(GePh_3)]$ by oxidative addition. The complexes are crystalline solids, which are readily oxidised in air [527].

1.5.5.6 Lead donor ligands

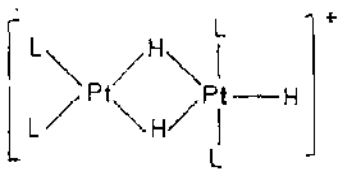
The complexes *cis*-$[(Ph_3P)_2Pt(R)(PbR_2R')]$ and *trans*-$[(Bu_3P)_2Pt(PbR_3)_2]$ (R = aryl; R' = R, Br or I) have been prepared and characterised. In the NMR spectrum, second order coupling effects between ^{195}Pt and ^{207}Pb have been observed for the first time [528].

1.5.6 Hydride complexes

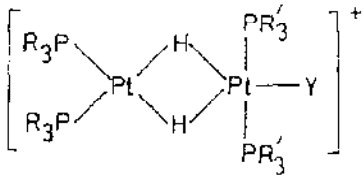
trans-$[HPt(PPh_3)_2X]$ (X = Br, I, $[NO_3]$ or $[ClO_4]$) is prepared by substitution of chlorine in *trans*-$[HPt(PPh_3)_2Cl]$. The perchlorate is readily converted to *trans*-$[HPt(PPh_3)_2L][ClO_4]$ on addition of L = C_2H_4, C_3H_6, CO, PPh_3, $SbPh_3$ or py [529].

Further studies of bridged hydride complexes are reported. Photolysis of $[Pt(PEt_3)_2(C_2O_4)]$ in a stream of hydrogen yields **(260)**, which is also obtained on addition of $[H_2Pt(PEt_3)_2]$ to $[HPt(solvent)(PEt_3)_2]^+$. Using $[D_2PtL_2]$ deuterium is incorporated specifically into the bridging position. The solution chemistry of **(260)** depends on the counter ion. With methanoate, C_2H_4 yields $[PtL_2(C_2H_4)]$, but no reaction occurs with the analogous tetraphenylborate salt [530]. A general synthetic route to (261) is described by another group, using $[H_2Pt(PR_3)_2]$, formed *in situ* from $[Pt(cod)_2]$, PR_3 and H_2, and *trans*-$[Pt(PR'_3)_2(Me_2CO)Y][BF_4]$. The hydride **(260)** is more easily prepared from $[HPt(PR_3)_2Cl]$ and $Na[BH_4]$. ^1H, ^{31}P and ^{195}Pt NMR spectroscopic data confirmed the bridging nature of two hydrides in all cases and an X-ray diffraction study of $[(Et_3P)_2Pt(\mu\text{-}H)_2Pt(PEt_3)_2Y][BPh_4]$ (Y = H or Ph) shows that one platinum is four- and the other five-coordinate

[531].



(260) L = Et_3P



(261)

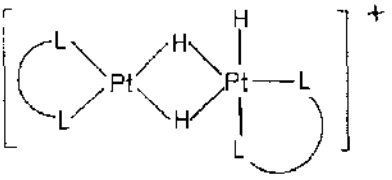
Analogous complexes of chelating biphosphines $[Pt_2H_3(L\text{-}L)_2]X$ (L-L = dppe, dppp, dppb, *cis*-$Ph_2PCH{=}CHPPh_2$ or $Ph_2PCH_2CH_2AsPh_2$; X = $[BF_4]$, I, $[NO_3]$ or $[BPh_4]$) were synthesised according to Scheme 12. Whilst NMR data imply fluxional behaviour, an X-ray crystallographic study shows bridging hydrides in (262) [532]. Reaction of (262) with L' (CO or RNC) yields $[Pt_2HL'(L\text{-}L)_2]^+$, the IR spectrum of which is consistent with bridging CO or RNC. Again NMR spectroscopic data imply fluxionality, but X-ray data from the complex in which L' = CO and L-L = dppe shows that both the hydride and CO are bridging. Possible mechanisms for the reaction are shown in Scheme 13 [533].

$$[Pt(pz)_2(L\text{-}L)] + 2H[BF_4] \xrightarrow{MeOH} [Pt(pzH)_2(L\text{-}L)][BF_4]_2$$

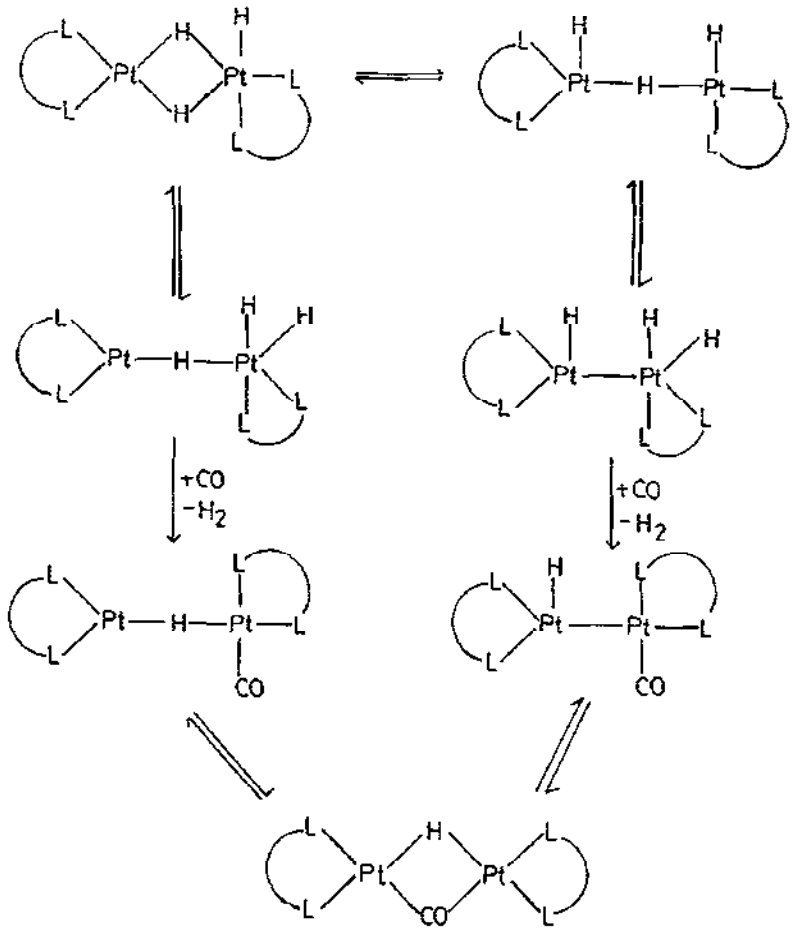
$$[Pt(pzH)_2(L\text{-}L)][BF_4]_2 \xrightarrow{K[BH_4]/MeOH} [Pt_2H_3(L\text{-}L)_2][BF_4]$$

$$[Pt(L\text{-}L)Cl_2] + Ag[BF_4] \xrightarrow{MeOH} \text{"X"} \xrightarrow{K[BH_4]/MeOH} [Pt_2H_3(L\text{-}L)_2][BF_4]$$

Scheme 12 Synthesis of platinum complexes of chelating biphosphines with bridging hydrides [532]



(262)



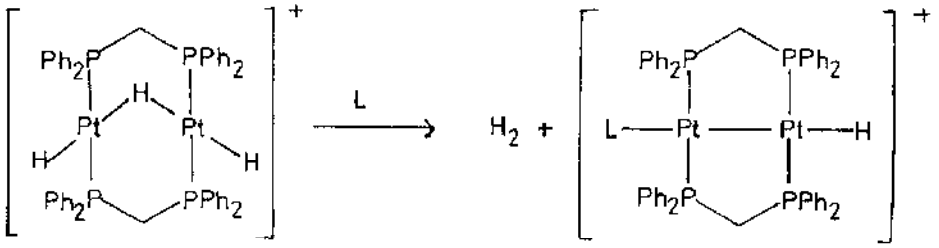
Scheme 13 Mechanism of reaction of bridging hydride complexes with CO [533]

1.6 PALLADIUM(I) AND PLATINUM(I)

An excellent preparation of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ from $[Pd(PhCN)_2Cl_2]$ or $[Pd_2(dba)_3]$ is reported [534]. New syntheses of $[M^1M^2(\mu\text{-dppm})_2X_2]$ (M^1, M^2 = Pd or Pt; X = Cl, Br, I or [SCN]) are also described, and the regiochemistry of the insertion of CS_2 and other small molecules to yield "A-frame" complexes investigated [535]. Reaction of $[Pt_2(\mu\text{-dppm})_2Cl_2]$ with $SnCl_2$ yields $[Pt_2(\mu\text{-dppm})_2(SnCl_3)Cl]$ and $[Pt_2(\mu\text{-dppm})_2(SnCl_3)_2]$. In the

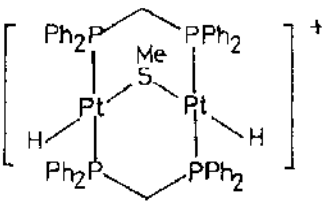
NMR spectrum of the latter species $^{3}J(^{117}Sn^{119}Sn)$ is 24,300 Hz, the largest three-bond coupling thus far recorded [536].

Ligand exchange and insertion into $[Pt_2(\mu\text{-dppm})_2Cl_2]$ has been reviewed. Reaction of $[Pt(dppm)Cl_2]$ with $Na[BH_4]$ gives (263), isolable as the crystalline $[PF_6]^-$ salt. NMR spectroscopy shows fluxional behaviour in the hydrogens only at high temperatures [537]. Treatment of (263) with a variety of ligands, L, results in loss of H_2 and formation of (264). Deuterium labelling and ligand studies imply that the mechanism is that shown in Scheme 14, in which rate determining reductive elimination occurs from the platinum centre remote from L [538].

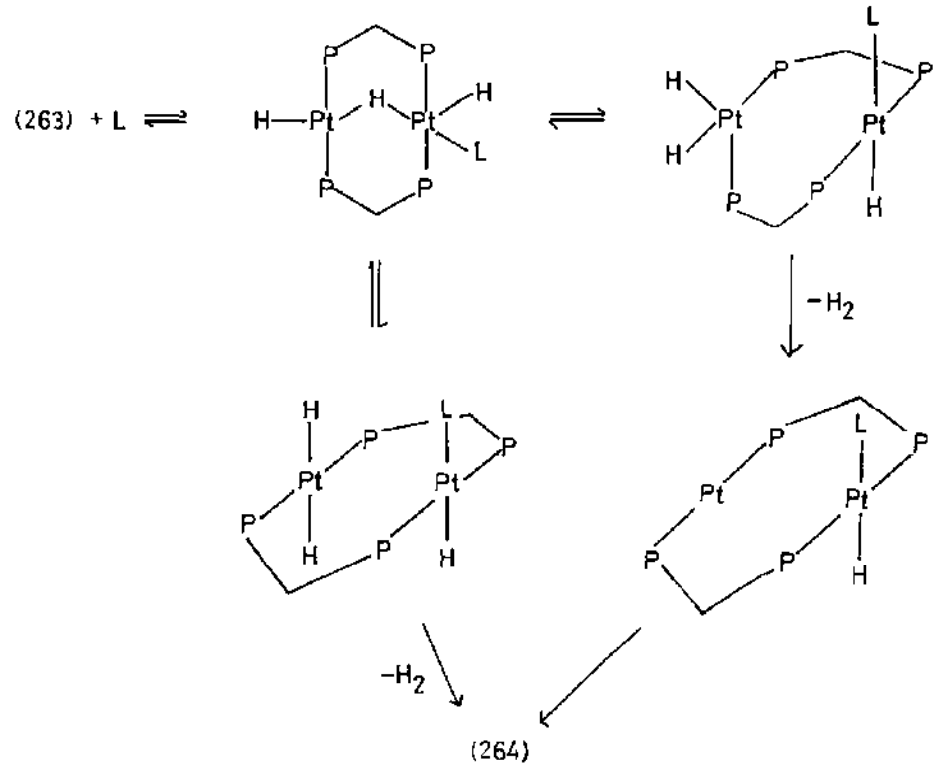


(263) (264)

Reaction of (263) with CO yields (264) (L = CO), which may also be obtained by treatment of $[Pt_2(\mu\text{-dppm})_2(CO)_2][PF_6]_2$ with hydroxyl ion. $[Pt_2(\mu\text{-dppm})_2(CO)_2][PF_6]_2$ was fully characterised by X-ray diffraction. CO may be replaced by other ligands such as PMe_2Ph, but reaction with MeSH proceeds *via* binuclear oxidative addition to yield **(265)** [539].



(265)



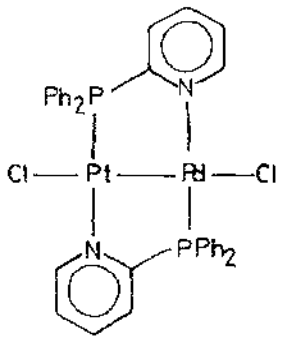
Scheme 14 Mechanism of reaction of **(263)** with ligands [538]

$[Pd_2(\mu\text{-dppm})X_2]$ and $[Pd_2(\mu\text{-dpam})_2X_2]$ (X = Cl, Br or I) only react with alkynes bearing electron withdrawing groups to give $[Pd_2(\mu\text{-alkyne})(\mu\text{-dppm})_2X_2]$ [540].

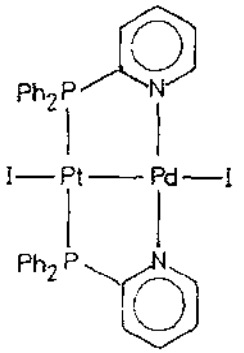
The kinetics of methylene insertion in reaction of CH_2N_2 with $[Pt_2(\mu\text{-dppm})_2X_2]$ have been investigated. The data suggest that the rate-determining step in "A-frame" formation is transfer of an electron pair from the Pt-Pt bond to the methylene group of diazomethane [541]. Reactions of $[Pd_2(\mu\text{-dppm})_2XY]$ and $[Pd_2(\mu\text{-dppm})_2(\mu\text{-}O_2)XY]$ with X_2 have been investigated [542].

Further studies of the coordination chemistry of $Ph_2P(2\text{-py})$ are reported. Reaction between $[Pt(PPh_2\text{-}2\text{-py})_2Cl_2]$ and $[M_2(dba)_3]$ (dba =

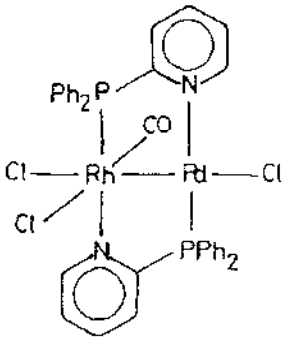
1,5-diphenyl-penta-1,4-diene-3-one) yields $[PtM(\mu\text{-}PPh_2\text{-}2\text{-}py)_2Cl_2]$ (M = Pd or Pt) in which both metals are in the +1 oxidation state. Extensive ^{31}P and ^{195}Pt NMR spectroscopic studies established that these are head-to-tail isomers such as **(266)**. However, with the analogue $[Pt(PPh_2\text{-}2\text{-}py)_2I_2]$, the head-to-head isomer, **(267)**, is formed. On heating, **(267)** is converted to the more stable head-to-tail isomer [543]. The head-to-tail complex, **(268)**, may be synthesised from $[Rh(PPh_2\text{-}2\text{-}py)_2(CO)Cl]$ and $[Pd(cod)Cl_2]$ or $[Pd(PPh_2\text{-}2\text{-}py)_2Cl_2]$ and $[Rh_2(CO)_4(\mu\text{-}Cl)_2]$. In either case, rhodium has undergone oxidative addition of a Pd-Cl bond. The structure was confirmed by X-ray diffraction; the M-M bond has a strong *trans*-effect, as evidenced by the long axial Rh-Cl and Pd-Cl bonds. The head-to-head isomer was also prepared, but is less stable than **(268)** [544].



(266)

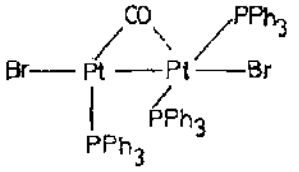


(267)

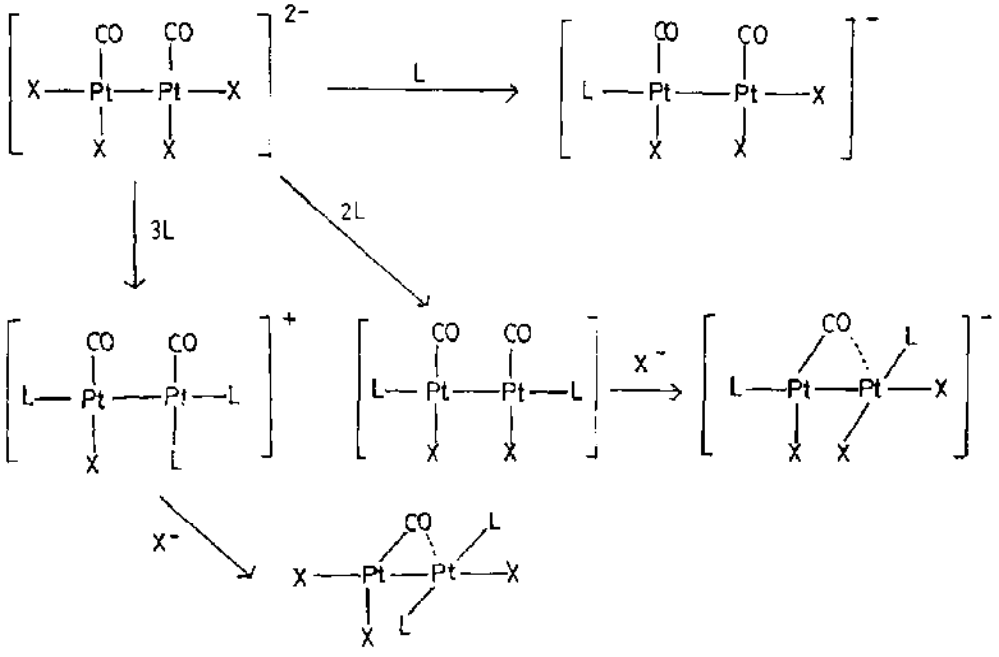


(268)

A new structural type for a Pt(I) dimer was established by X-ray diffraction of **(269)**; the $\{PtL_3\}$ fragments are close to planarity. A complex series of reactions was investigated (Scheme 15) [545].



(269)

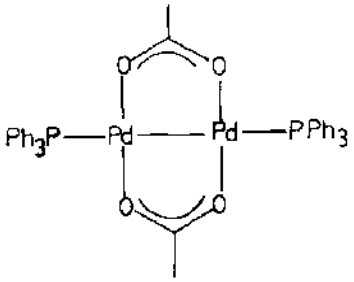


Scheme 15 Reactions of **(269)** (L = phosphine, X = halide) [545]

By contrast, in two slightly vague papers, Soviet workers reported the formation of $[\{Pd(PR_3)Cl\}_2(CO)]$ from PR_3 and $[H_2Pd_2(CO)_2Cl_4]$. Infrared data suggested a semibridging carbonyl, with electrochemical measurement confirming that the complex is still of Pd(I). The species disproportionates quite readily [546,547].

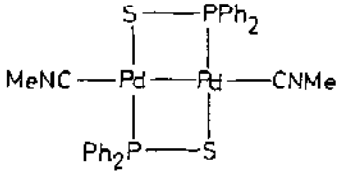
$[Pt(CO)X_3]^-$ (X = Cl, Br or I) reacts with methanoic acid and trialkylamines to yield $[Pt_2(CO)_2X_4]^{2-}$, the species being identified by ^{13}C and ^{195}Pt NMR spectroscopic studies. At 300 K there is exchange of CO between the platinum atoms [548].

Reduction of $[Pd_2(PPh_3)_2(OCOCH_3)_4]$ or $[Pd_2(PPh_3)_2Cl_2]$ with H_2 or Na/Hg gives $[Pd_2(PPh_3)_2]$ in equilibrium with $[H_2Pd_2(PPh_3)_2]$. $[Pd_2(PPh_3)_2]$ reacts with further $[Pd_2(PPh_3)_2(OCOCH_3)_4]$ to give **(270)**, a palladium(I) dimer. Although H_2 does not normally undergo oxidative addition to Pd(0) or Pd(II), the binuclear Pd(I) complex reacts readily, giving further $[Pd_2(PPh_3)_2]$ [549]. Treatment of $[\{H_2Pt_2(OH)_8(H_2O)_2\}_2]$ with an excess of dmso at 100 °C yields $[Pt_2(OH)_2(H_2O)_2(dmso)_4]$, which is indicated by XPES data to be a Pt(I) dimer. $[Pt_2(dmso)_2(OCOCH_3)_2]$ and $[Pt_2(dmso)_4(OCOCH_3)_2]$ were also somewhat vaguely characterised [99].



(270)

X-ray diffraction studies of **(271)** indicate that the complex is a Pd(I) dimer with a direct metal metal bond. **(271)** is synthesised by ligand exchange from the analogue with terminal phosphines; none of the species RNC, CO, S_8 or SO_2 insert into the metal metal bond [550].



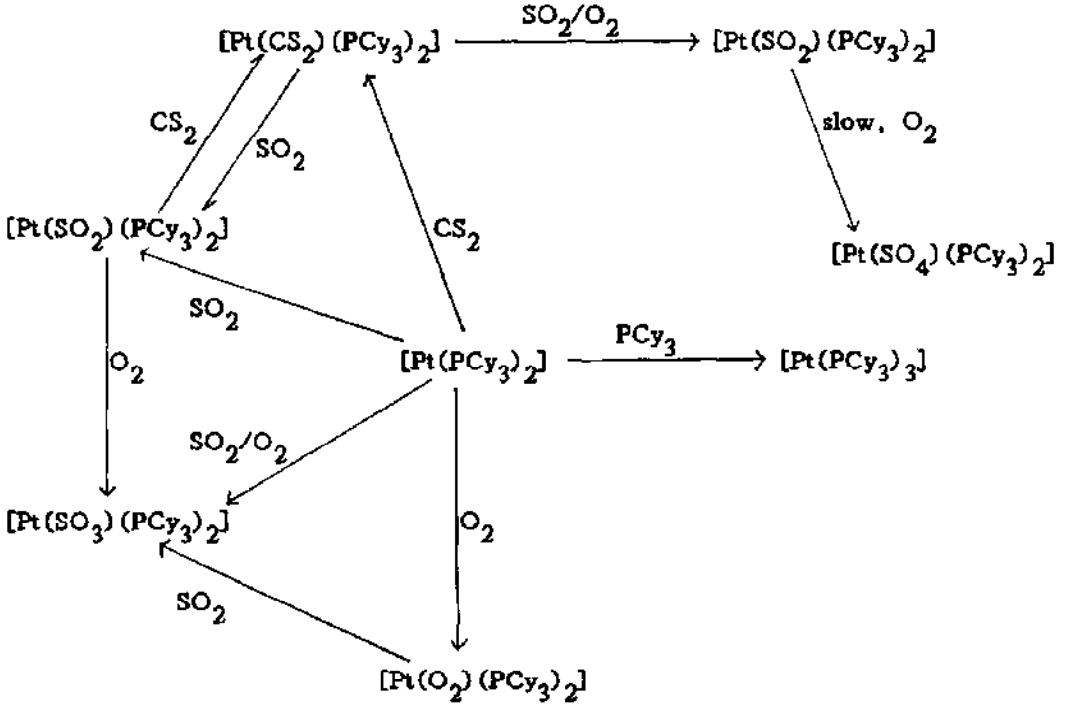
(271)

1.7 PALLADIUM (0) AND PLATINUM (0)

The thermochemistry of the oxidative addition of species AB to platinum(0) has been reviewed [551].

1.7.1 Complexes with Group VI donor ligands

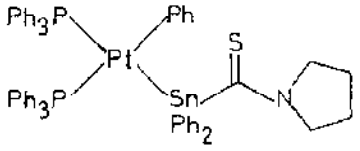
X-ray diffraction data are reported for $[Pt(SO_2)(PCy_3)_2]$, the first for a stable tricoordinate zerovalent platinum complex of this type. SO_2 is η^1 coordinated, with pyramidal geometry. Reactions of this (Scheme 16) and its $P(CMe_3)_3$ analogue were studied; the latter is less reactive, presumably due to the steric bulk and the low compressibility of the ligand [552].



Scheme 16 Reactions of platinum complexes of tricyclohexylphosphine [552]

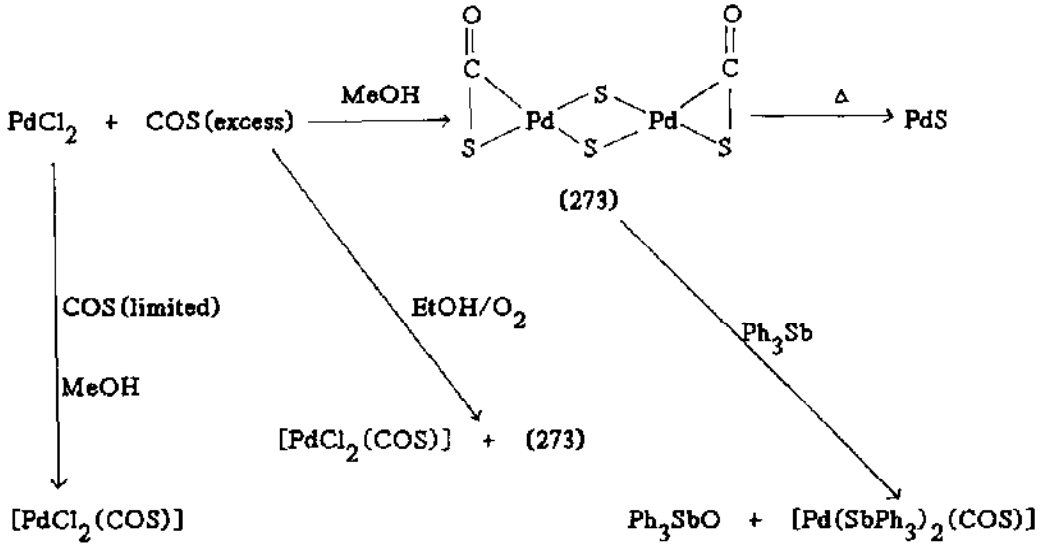
Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with Ph_3SnCS_2R (R = CH_3, CH_2Ph or 2-propenyl) leads to displacement of ethene and formation of

$[Pt(PPh_3)_2(Ph_3SnCS_2R)]$. X-ray diffraction studies indicate η^2 coordination of C=S, with the other sulphur atom uncoordinated. The initial product of a similar reaction of the thioamide is analogous and η^2-C=S coordinated, but this undergoes internal oxidative additon to yield **(272)** [553].



(272)

The very complex reactions of COS with $PdCl_2$, $[Pd(PPh_3)_4]$ and $[Pd(PPh_3)_2(O_2)]$ have been further investigated. The characteristic mode of binding is η^2-C-S as previously noted (Scheme 17) [554].

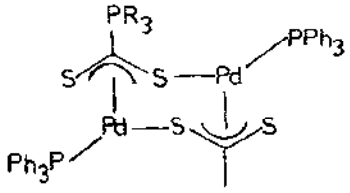


(273) + Ph_3As ⟶ Ph_3AsS + $[Pd(AsPh_3)_2(COS)]$

Scheme 17 Reactions of palladium complexes with COS [554]

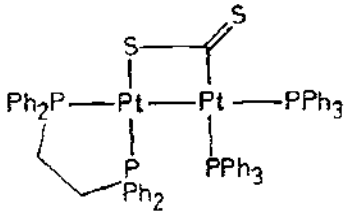
As previously shown, CS_2 also binds in the η^2 manner; the new compounds

$[Pd(PR_3)_2(CS_2)]$ (R_3 = $(Me_2CH)_3$ or $MePh_2$) have been characterised, formed from CS_2 and $[Pd(PR_3)_n]$. However, when $[Pd(PMe_3)_4]$ or $[Pd(PMe_2Ph)_4]$ react with CS_2, the product has the stoicheiometry $[\{Pd(PR_3)(S_2CPR_3)\}_2]$. The structure seems likely to be **(274)**, but this was not rigorously proven [555].

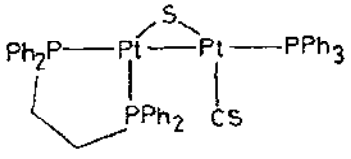


(274)

$[Pt(dppe)(\eta^2\text{-}CS_2)]$ reacts with $[Pt(C_2H_4)(PPh_3)_2]$ to give (275) as an intermediate. This is not isolable, unlike its PPh_3 analogue, but rearranges to **(276)**, the thiocarbonyl fragment having been transferred to the other platinum atom [556].



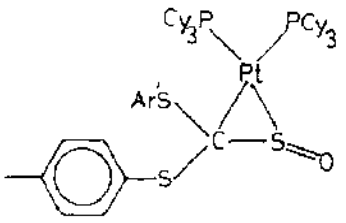
(275)



(276)

Palladium(0) phosphine complexes, $[Pd(PR_3)_n]$ react with R'NCS (R' = Ph or Me) to yield $[Pd(PR_3)_2(\eta^2\text{-}SCNR')]$. For R' = Ph, further reaction yields the dithiocarbamate complex [557].

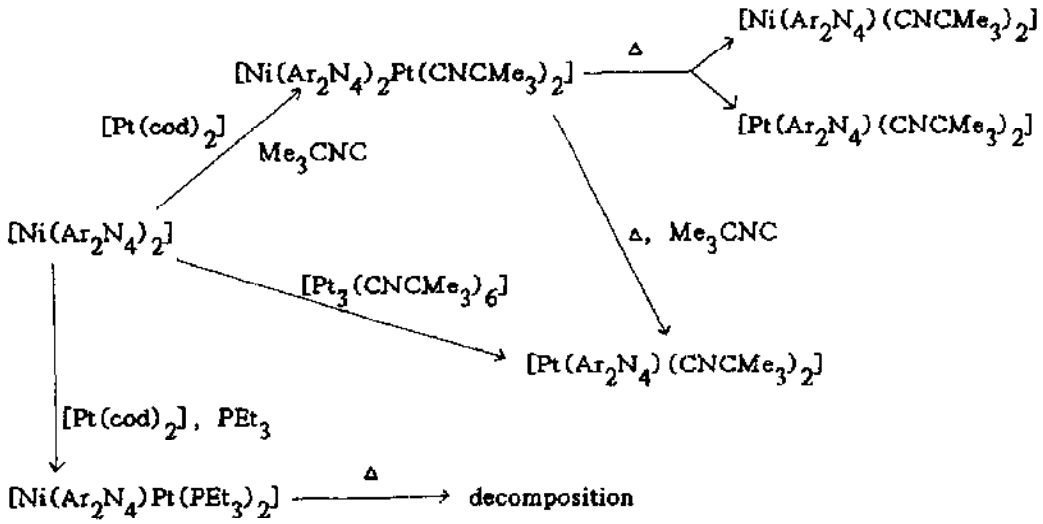
Sulphine coordination chemistry has been further investigated, with the aim of synthesising unstable sulphines in the metal coordination sphere. Thus the Pt(0) complex, $[(Cy_3P)_2Pt\{E\text{-}(4\text{-}MeC_6H_4S)\text{-}ClCSO\}]$ undergoes oxidative addition to yield *cis*-**E**-$[PtCl(4\text{-}MeC_6H_4SCSO)(PCy_3)_2]$. Reaction with [Ar'S]K then gives **(277)** as a mixture of **Z**- and **E**-isomers. Whilst this does represent a formal sulphine synthesis, it is less efficient than the conventional routes [266].



(277)

1.7.2 Complexes with Group V donor ligands

Tetraazadiene complexes of nickel react with a variety of platinum(0) complexes, with transfer of the complete azadiene ligand from one metal to the other (Scheme 18). The formulations of several possible intermediates were in accord with the limited spectral data available [558].



Scheme 18 Transfer of tetraazadienes from nickel to platinum [558]

Several routes to mixed-ligand palladium(0) and platinum(0) complexes have been more firmly established this year. Reduction of $[Pd(PPh_3)_2Cl_2]$ by $K[BH_4]$ in the presence of L yields, somewhat surprisingly, $[Pd(PPh_3)L_2]$ (L = $Ph_2PC_6H_4$-4-X; X = F, Cl, CH_3, OCH_3 or COOH). The complexes have been characterised by IR, electronic and NMR spectroscopy, cyclic voltammetry

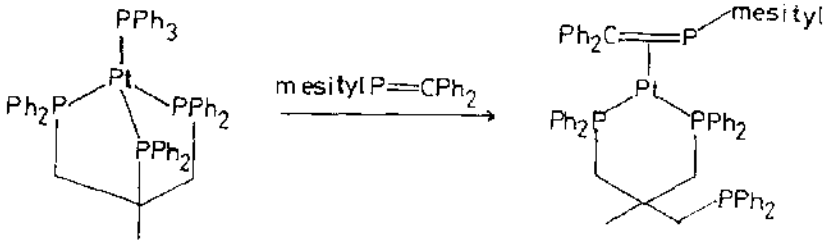
NMR spectroscopy, cyclic voltammetry and DTA [559,560]. Thermal stability decreases in the order X = Cl > OCH_3 F > COOH > CH_3 [561]. Photolysis of $[Pt(PEt_3)_2(C_2O_4)]$ in the presence of L yields CO_2 and $[Pt(PEt_3)_2L_n]$ (L = PEt_3 or CO, n = 2; L = C_2H_4 or C_2F_4, n = 1). Using XY (MeOH, $HSiEt_3$ or CH_3Cl), which is capable of oxidative addition, *cis*- or *trans*-$[Pt(PEt_3)_2XY]$ is obtained, the intermediate in all cases being $[Pt(PEt_3)_2]$ [562].

IR and Raman spectra of $[Pt(PPh_3)_4]$, $[Pt(PPh_3)_2(O_2)]$ and $[Pt(PPh_3)_2(C_2H_4)]$ have been studied [563]. The lifetime of homogeneous metal(0) phosphine complexes, such as $[Pd(PPh_3)_4]$, used in cyanation of aryl chlorides, may be increased several fold by application of a reducing potential [564].

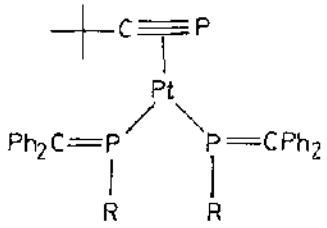
Reaction of $[PdL_4]$ (L = Me_3P or $MePh_2P$) with HCl yields, *via* oxidative addition, *trans*-$[HPdL_2Cl]$. Reaction of this product (L = Me_3P) with $Na[BPh_4]$ in the presence of an excess of Me_3P gives $[HPd(PMe_3)_3]$, formally a Pd(I) species. Oxidative addition of $PhCH_2Br$ to $[PdL_4]$ results in the formation of $[PhCH_2PdL_2Br]$ [565].

Treatment of (278) with (mesityl)P=CPh_2 yields (279), in which the η^2-coordination of the ligand was established spectroscopically. This is in contrast to the reaction with $[Pt(PPh_3)_2(C_2H_4)]$, reported last year, and that with $[Pt(cod)_2]$, both of which result in the formation of η^1-species. $Me_3CC{\equiv}P$ also reacts with **(278)** to give an η^2-product. The preference of the triple bond for η^2 coordination is shown in the formation of **(280)** from a mixture of ligands and $[Pt(cod)_2]$ [566]. He I PE spectra of $Me_3CC{\equiv}P$ have been assigned by comparison with other related species. It was shown that there is greater separation of π and n levels in C≡P than in C≡N, in accord with the observation that the phosphorus lone pair is not the sole binding site for any complex of this ligand [567].

The preparation of $[Pt_2(\mu\text{-dppm})_3]$ by three different routes has been reported [568]. A simpler synthesis of $[Pd(dppm)_2]$ is achieved by reduction of $[Pd(PhCN)_2Cl_2]$ by $Na[BH_4]$ in the presence of dppm [569].

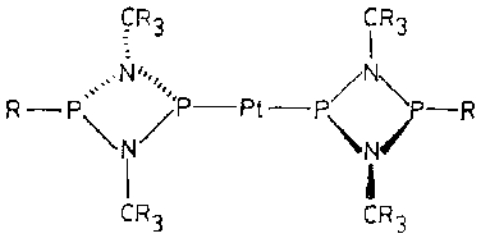


(278) (279)



(280) R = mesityl

The structure of $[PtL_3]$ (L = $Me_3C(Me_3Si)NP{=}NCMe_3$), the preparation of which was reported last year, has been determined by X-ray diffraction [570]. Reaction of $[Pt(cod)_2]$ with *cis*-$[(RPNCR_3)_2]$, diazaphosphetidine, yields $[PtL_2]$, (281). In benzene, disproportionation to [L-Pt-L-Pt-L] and L is significant [571].



(281)

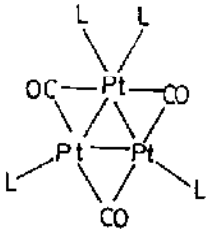
Diphenylphosphonylazide, $(PhO)_2P(=O)N_3$, reacts with $[Pt(PPh_3)_3]$ to yield $[Pt(PPh_3)_2N_3(O{=}P(OPh)_2)]$, characterised by IR spectroscopy [572].

1.8 PALLADIUM AND PLATINUM CLUSTERS

The orbital interactions of platinum clusters with CO have been studied [573]. Other hydrido platinum carbonyl clusters have been investigated [574].

1.8.1 Trimeric clusters

In the clusters $[Pt_3(\mu\text{-}CO)_3L_4]$ (L = PEt_3, PMe_2Ph, $PMePh_2$, $PEt_2t\text{-}Bu$ or $P(CH_2Ph)Ph_2$), ^{31}P and ^{195}Pt NMR spectroscopic measurements show non-equivalent phosphines and two types of platinum atoms, leading to a postulate of (282) for the structure [575]. The complex with L = PPh_3, when impregnated onto inorganic supports for catalysis or chromatography, yields $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$, a fact which is significant in terms of the use of such systems in catalysis [576].

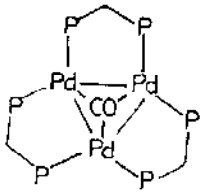


(282)

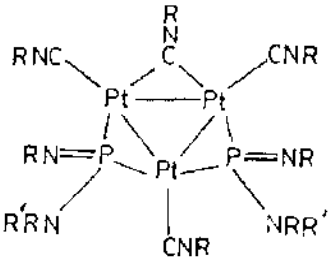
Two other papers report the preparation of proven triangular clusters. Reaction of $Pd(OCOCH_3)_2$ with dppm, CO and tfaH yields $[(283)]^{2+}$; X-ray diffraction studies indicate that the $\{Pd_3P_6\}$ unit is roughly planar [577]. Treatment of $[PtL_3]$ {L = $Me_3C(Me_3Si)NP{=}NCMe_3$} with Me_3CNC or CO gives respectively **(284)** and **(285)**. These structures, confirmed by X-ray diffraction, represent the first examples of clusters containing a bridging phosphazene ligand [578].

Both X-ray data and ^{31}P NMR spectroscopic studies imply that the cyano

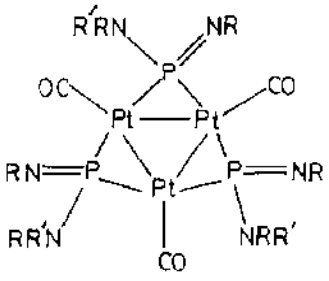
bridges in $[Pd_3(dppe)_3(\mu\text{-}CN)_3][ClO_4]_3$ are significantly non-linear [579].



(283)



(284)



(285)

The reaction of the $Pd(OCOCH_3)_2$ trimer with CO has been investigated, the pathway proposed being shown in Scheme 19. Whilst kinetic measurements and studies of intermediates have clearly been useful, a number of the steps are still less than well-defined [580,581].

$$[\{Pd(OCOCH_3)_2\}_3] + CO \longrightarrow [\{Pd(OCOCH_3)_2\}_3CO] \longrightarrow$$

$$[Pd_3(OCOCH_3)_5(COOCOCH_3)] \longrightarrow [Pd_3(OCOCH_3)_5(COCH_3)] + CO_2 \rightarrow$$

$$trans\text{-}[Pd_2(CO)_2(OCOCH_3)_2(\mu\text{-}OCOCH_3)_2] \longrightarrow [\{Pd(CO)(OCOCH_3)\}_4]$$

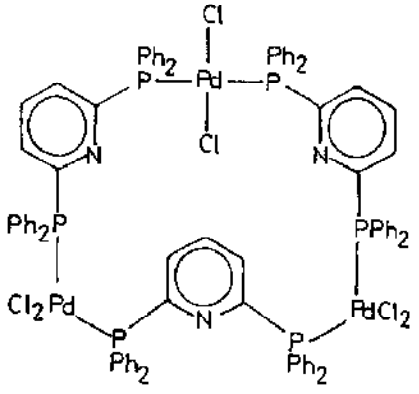
$$\downarrow [CH_3COO]Na/CH_3COOH$$

$$Pd(0) + 2CO + 2CO_2 + 2CH_3COOCOCH_3$$

Scheme 19 Reaction of palladium ethanoate trimer with carbon monoxide [580,581]

Treatment of $[Pd(PPh_3)_2Cl_2]$ or $[Pd_2(PPh_3)_2Cl_4]$ with dihydrogen and an amine yields $[Pd_3(PPh_3)_3(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)]Cl$, in which XPES suggests an oxidation state close to +1 for palladium. Various mechanisms are proposed for formation of the cluster and the reaction is related to that of the ethanoates [582]. The same cluster is among several products formed by reduction of $[Pd(acac)_2]$ with molecular H_2 in the presence of PPh_3 [583].

A somewhat different type of trimer, **(286)**, is formed on reaction of 2,6-bis(diphenylphosphino)pyridine with $[Pd(cod)Cl_2]$. X-ray diffraction shows a non-symmetric structure with two *cis*- and one *trans*-coordinated palladium [584].



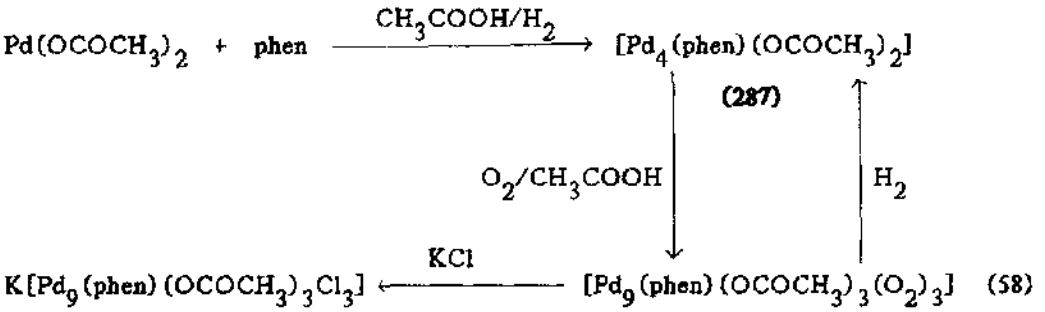
(286)

Reaction of $PdCl_2$ with $K^+/SnCl_2/HF$ is reported to yield $K_8[Pd_3Sn_8F_{24}].10H_2O$ as the major product [515].

1.8.2 Tetrameric clusters

Molecular orbital calculations on phosphine substituted clusters of the platinum metals indicate how they may be encompassed within the framework of the polyhedral skeletal electron pair theory. Both the butterfly cluster $[Pt_4(CO)_5(PR_3)_4]$ and the edge bridged tetrahedron $[Pt_5(CO)_6(PR_3)_4]$ are considered in detail [585]. The butterfly structure was assumed by groups synthesising $[Pd_4(CO)_5(PBu_3)_4]$ from $[Pd_{10}(CO)_{12}(PBu_3)_6]$, CO and PBu_3

[586], and $[Pd_4(CO)_5(PMePh_2)_4]$ from $[Pd(PMePh_2)_2(NO_2)]$ and CO [587]. No attempt was made to define the structure of the diamagnetic species **(287)** formed in reaction (58) [588].



1.8.3 Higher nuclearity clusters

The stoicheiometries and geometries of $[M_n(PR_3)_n]^{x+}$ (n = 3,4,5 or 6; M = Au or Pt) were analysed using extended Huckel calculations. The isolobal nature of the $\{M(PH_3)\}$ fragment depends critically on the nature of M and may be used to provide a basis for predicting cluster structure [589].

$[Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)]$ reacts with CO in toluene at -30 °C to give $[Pd_7(CO)_7(PMe_3)_7]$. X-ray diffraction established that the structure is a face-capped octahedron of Pd atoms with one PMe_3 attatched to each. Four of the CO molecules bridge faces of the octahedron and the other three bridge edges to the unique palladium [590].

Treatment of $Pd(OCOCH_3)_2$ with $CO/R_3P/CH_3COOH$ in propanone gives a mixture of $[Pd_{10}(CO)_{12}(PR_3)_6]$, $[Pd_{10}(CO)_{14}(PR_3)_4]$ and the tetrameric cluster, $[Pd_4(CO)_5(PR_3)_4]$ (R = Bu or Et), the ratio of the products depending on the molar ratio of the reactants. Solvent is also important. The Pd_{10} compound with R = Bu is a 10-vertex polyhedron, an octahedron with four unsymmetrically centred palladium atoms on non-adjacent faces. The PBu_3 ligands are coordinated to the apical palladium atoms, and the capping atoms [591,592].

A careful investigation of commercially available $PdCl_2$ has been performed. It appears to be very similar to "β-$PdCl_2$", which is also formed from $[Pd_3(OCOCH_3)_6]$, CO and HCl. Mass spectral data suggest a Pd_6Cl_{12} formulation with two $\{Pd_3Cl_3\}$ units linked by chlorine bridges [593]. $[Pt_{12}(CO)_{24}]^{2-}$ catalyses the reaction between water and benzoquinone to give oxygen and 1,4-dihydroxybenzene. $\{Pt_3\}$ units seem to be the important reacting species [594].

Two salts of the supercuneane dianion, $[Pt_{24}(CO)_{22}(\mu\text{-}CO)_8]^{2-}$, have been isolated. The cubic close-packed $\{Pt_{24}\}$ unit is related to two ten atom Pt(111) faces, and the structure may be considered as a model for absorption of CO on metallic platinum [595].

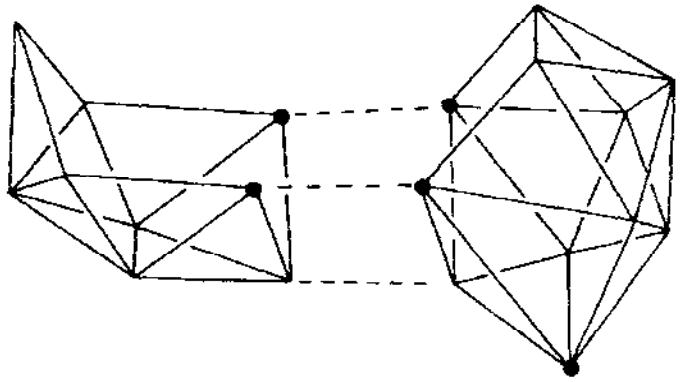
1.8.4 Heteronuclear clusters

Whilst structural studies continue to dominate reports of heteronuclear clusters, reactivity is becoming more significant to many authors.

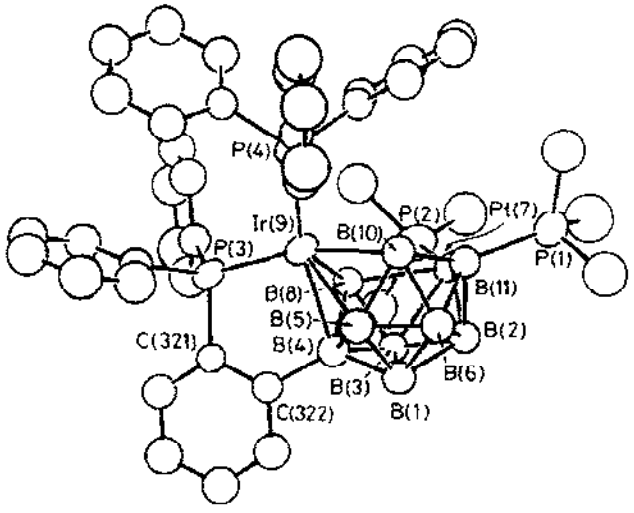
Extended Hückel molecular orbital calculations have been performed on the *closo*-platinaboranes $[L_2M(B_{11}H_{11})]^{2-}$ and $[L_2M(B_6H_6)]^{2-}$ and the *closo*-platinacarboranes $[L_2M(C_2B_9H_{11})]$ and $[L_2M(C_2B_4H_6)]$ $\{L_2M = (H_3P)_2Pt\}$. These chiefly relate to the orientation and slip distortion of the $\{ML_2\}$ fragment relative to the polyhedron [596].

The clusters of this type which are being synthesised are becoming more complicated. The 17-vertex macropolyhedral trimetalloborane, $[(PhMe_2P)_4Pt_3B_{14}H_{16}]$, (288), may be interpreted as a formal pentadecahapto complex of a 7,7'-bi(*arachno*-heptaboranyl) type ligand coordinated η^4,η^5,η^6 to three metal centres, or a *ntdo* type 2,7,10-trimetallaundecaborane cluster conjoined to an *iso-arachno*-6,8-dimetallanonaborane cluster with three adjacent vertices, Pt-B-Pt, in common [597]. The first *ntdo* 11-vertex dimetallaborane cluster, $7,7\text{-}(Me_3P)_2\text{-}9\text{-}(PPh_3)\text{-}9\text{-}(Ph_2P\text{-}2'\text{-}C_6H_4)\text{-}9\text{-}H\text{-}ntdo\text{-}7,9\text{-}PtIrB_9H_{10}\text{-}4]$, (289),

has been characterised by X-ray diffraction. The complex is prepared from an iridadecaborane and *cis*-$[Pt(PMe_3)_2Cl_2]$, and the metal atoms are in non-adjacent positions on the open face [598].



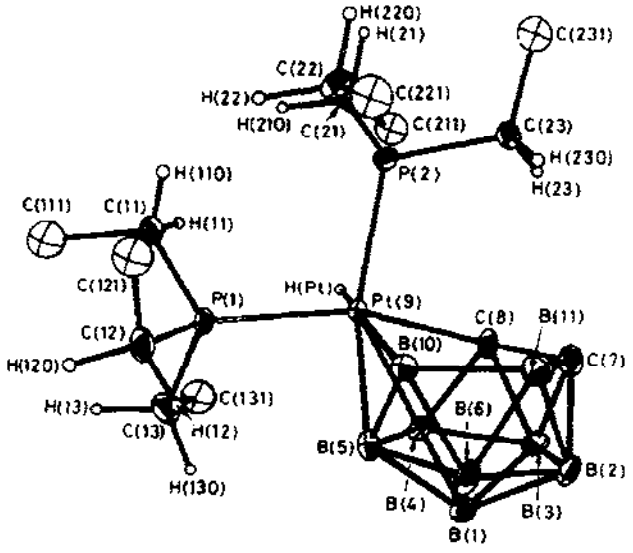
(288)



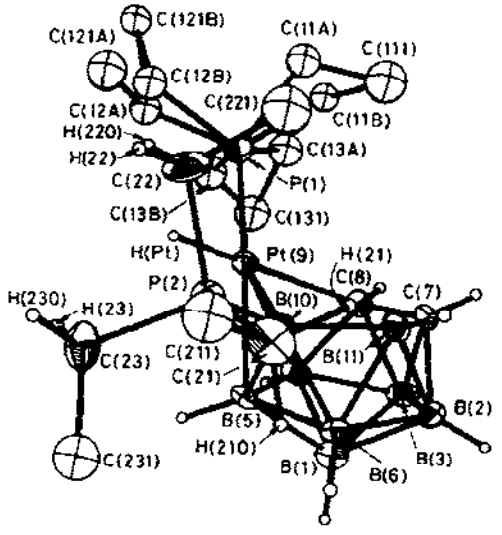
(289)

Reaction of $[Pt_2(PEt_3)_4(\mu\text{-cod})]$ with *nido*-$5,6\text{-}C_2B_6H_{12}$ yields $[9\text{-H-}9,9\text{-}(Et_3P)_2\text{-}(\mu_{10,11}\text{-H})\text{-}7,8,9\text{-}C_2PtB_8H_{10}]$, (290), characterised by X-ray diffraction. It is formed by oxidative insertion of the $\{P_2Pt\}$ fragment into a

μ-BHB function followed by interaction of Pt(II) with the cage. The structure approximates to a *nido* icosohedron with a CCPtBB open face. On heating molecular hydrogen is evolved; the μ-H is lost and one PEt_3 ligand is transferred from platinum to boron to give $[9\text{-H-}9,10\text{-}(Et_3P)_2\text{-}7,8,9\text{-}C_2PtB_8H_9]$, **(291)** [599].



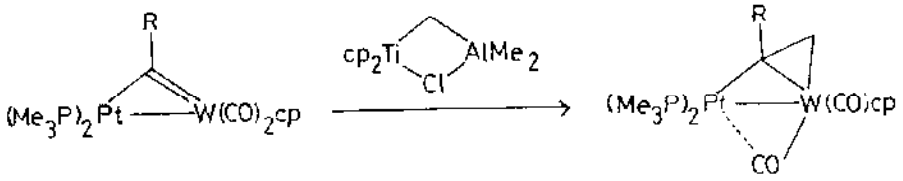
(290)



(291)

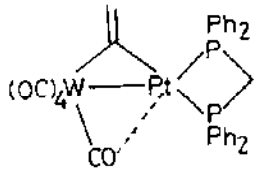
Reaction of $[Pt(PPh_3)_4]$ with $K_4[Pb_9]$ in the presence of en yields a species which shows a triplet in the ^{207}Pb NMR spectrum ($J_{Pt\text{-}Pb}$ = 4122 Hz), allowing the assignment of a formula $[Pb_xPtL_y]^{q-}$. An analogous species is proposed from $K_4[Sn_9]$/en. The structure predicted is related to *ntdo*-$B_{10}H_{14}$, with platinum occupying one of the open positions [600].

Some further reactions of bimetallic W-Pt compounds have been reported this year, and two extensive full papers published. When **(292)** is treated with the Tebbe reagent, **(293)** is isolated and characterised by X-ray diffraction [601]. Treatment of $[PtW(\mu\text{-}C\{OMe\}R)(CO)_5(cod)]$ with dppm yields $[Pt_3(CO)_3(\mu\text{-}C\{OMe\}R)_3]$, $[PtW(\mu\text{-}C\{OMe\}R)(\mu\text{-dppm})(dppm\text{-}P)(CO)_4]$ and, as the major product, $[PtW(\mu\text{-}C\{OMe\}R)(\mu\text{-dppm})(CO)_5]$, **(294)**, this latter being characterised by X-ray diffraction. The platinum atom has roughly square planar coordination with one coordinated carbon monoxide ligand. Treatment with $H[BF_4]$ yields species with bridging carbyne ligands [602]. Under carefully controlled conditions, **(295)**, an intermediate in the formation of **(294)**, may be isolated. Chromatography on basic alumina yields **(296)**, characterised by X-ray diffraction [603].



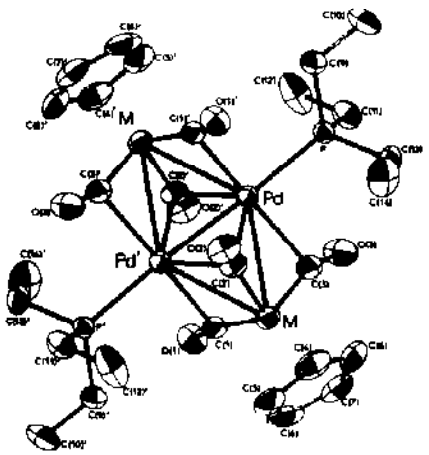
(292) **(293)**

(294) **(295)**



(296)

Two routes to the first family of heterotetrametallic palladium clusters $[Pd_2M_2(cp)_2(CO)_6(PR_3)_2]$, (297) (M = Cr, Mo or W; PR_3 = PMe_3, PEt_3, PBu_3, PMe_2Ph or PPh_3), have been described {reactions (59) and (60)}. The X-ray diffraction studies of (297) showed several notable features. PEt_3 is coordinated to palladium and the four metal atoms are coplanar in a triangulated parallelogram. The eighteen electron $\{M(cp)(CO)_3\}^-$ fragments act as $4e^-$ donors towards the L-Pd(I)-Pd(I)-L unit. Two of the CO ligands are semi triply bridged on the heterotrimetallic face M-Pd-Pd', with M-CO shorter than Pd-CO. All the metal metal contacts are short, but at 2.578 A for Pd-Pd', this is the shortest reported for this bond type, shorter even than in the bulk metal [604]. The clusters, which have also been prepared for platinum, exhibit an unexpected irreversible two-electron reduction leading to rupture of the metallic core [605]. Adsorbed on alumina, (297) (M = Mo; PR_3 = PPh_3) is an active catalyst for carbonylation of $PhNO_2$ to PhNCO in high yield [606].



(297)

$$Na[M(CO)_3(cp)] + [Pd(PPh_3)_2Cl_2] \longrightarrow \textbf{(297)} + [M_2(CO)_5(PR_3)(cp)_2] \quad (59)$$

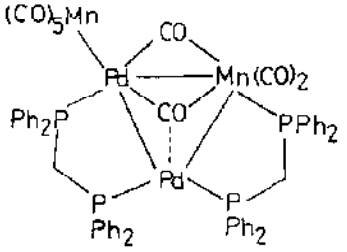
M = Mo or W

$$Na[M(CO)_3(cp)] + [Pd(PhCN)_2Cl_2] \longrightarrow [(cp)(CO)_3M\text{-}Pd(PhCN)_2\text{-}M(CO)_3(cp)]$$

$$\downarrow R_3P$$

$$\textbf{(297)} \ (90\ \%) \quad (60)$$

Nucleophilic attack of $Na[Mn(CO)_5]$ on $[Pd_2(\mu\text{-dppm})_2Cl_2]$ gives the non-symmetric tetrametallic species **(298)** in 23 % yield, as well as 18 % of $[PdCl(\mu\text{-dppm})_2Mn(CO)_3]$ [607]. In a closely related reaction, $Na[Co(CO)_4]$ yields $[Pd_2Co_2(CO)_7(dppm)_2]$, again characterised crystallographically [608].



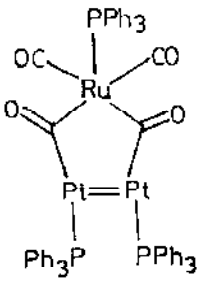
(298)

Roussin's red salt, $Na_2[Fe_2(\mu\text{-}S)_2(NO)_4]$, reacts with *cis*-$[Pt(PPh_3)_2Cl_2]$ in thf to yield $[(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(NO)_4]$, which is also obtained by displacement of CO by NO in $[(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6]$. The complex was characterised by X-ray diffraction, and the planar $\{S_2Fe_2\}$ rhombus of the initial salt is folded in the platinum adduct, with both linear and bent nitrosyls on each iron atom [609]. $[PtFe_2Te_2(CO)_6(PPh_3)_2]$, like $[Fe_3Te_2(CO)_9]$, is a fifty-electron cluster. However, since Pt(II) prefers a sixteen-electron system, the $\{(Ph_3P)_2Pt\}$ fragment is effectively equivalent to $\{Fe(CO)_4\}$ or $\{Co(CO)(cp)\}$. Thus although a *nido*-structure would be expected purely on the grounds of the electron count, the ^{125}Te NMR signal observed is more typical

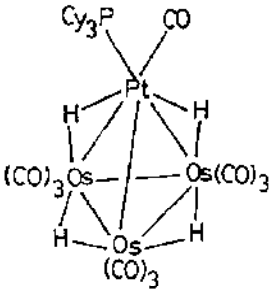
of an *arachno* compound [610]. Chiral octahedral complexes, containing three different types of metal atom in the polyhedron, were formed in reaction (61) [611].

$$[Et_4N]_2[Fe_5C(CO)_{14}] + RhCl_3 \xrightarrow{\text{diglyme}} [Et_4N][Fe_4RhC(CO)_{14}] \xrightarrow{[\{(\eta^3\text{-allyl})PdCl\}_2]} [Et_4N][Fe_4RhPdC(CO)_{15}] \quad (61)$$

The unstable crimson cluster **(299)** is obtained from $[Ru_3(CO)_{11}(CNCMe_3)]$ and $[Pt(PPh_3)_2(C_2H_4)]$ at -30 °C. At room temperature it decomposes rapidly, yielding trimetallic species $[Ru_2Pt(CO)_7(PPh_3)_3]$, $[RuPt_2(CO)_5(PPh_3)_3]$ and $[RuPt_2(CO)_6(CNCMe_3)(PPh_3)]$ as well as the tetrametallic cluster, $[Ru_2Pt_2(CO)_9(CNCMe_3)(PPh_3)]$ as the major platinum containing species. $[RuPt_2(CO)_5(PPh_3)_3]$ becomes the major product in the presence of CO, and was characterised crystallographically. Reactions of **(299)** with Me_3CNC, Me_3P and $(MeO)_3P$ were also studied [612].



(299)



(300)

An unsaturated osmium platinum cluster $[Os_3Pt(\mu\text{-}H)(CO)_{10}(PCy_3)]$, reacts with molecular hydrogen at 200 atm pressure to give **(300)**, the reaction being reversed if dihydrogen is removed. CO may also be reversibly added to the compound, yielding $[Os_3Pt(\mu\text{-}H)(CO)_{11}(PCy_3)]$ [613].

In the presence of MCl_2 (M = Pd or Pt), $[Rh_2(cp)_2(\mu\text{-}CO)(CO)_2]$

is converted to $[\{Rh(cp)(\mu\text{-}CO)\}_3]$. $[Rh_2(cp)_2(CO)_2(\mu\text{-}MCl_2)]$ is formed as an intermediate and decomposes to give [Rh(cp)(CO)], which readily trimerises [614]. $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ and $[PtRh_{12}(CO)_{24}]^{4-}$ were obtained from the controlled pyrolysis of $[PtRh_5(CO)_{15}]^-$. The platinum atom lies inside a twelve metal atom shell, and there are twelve bridging and twelve terminal CO ligands [615].

Structures of neutral and cationic complexes with bridging Cl and CN ligands have been investigated. The bent MClM and MCNM bridges in oligomers suggest that chlorides will normally be dimeric, whereas cyanides prefer a tetrameric structure [616].

1.9 CATALYSIS BY PALLADIUM AND PLATINUM COMPLEXES

Synthetic and catalytic reactions involving Pd(II) and Pt(II) complexes have been reviewed [617]. Complexes with Pd-Pd bonds are active catalysts for hydrogenation, carbonylation, oligomerisation, hydration and oxidative acetylation of alkenes [618].

1.9.1 Hydrogenation

Again this year, many reports refer to the use of palladium complexes immobilised on polymer supports for "homogeneous" hydrogenation. As noted previously, XPES identifies the active species as an *O,N*-bonded chelate when the catalyst is a polyvinylpyrrolidone palladium complex supported on silica. In addition to the previous studies with alkenes, this species has now been used for reduction of nitrobenzene to aniline with H_2 (1 atm, 25 °C) [619]. An analogous catalyst bound to a crosslinked polystyrene backbone is also reported [620]. High activities in alkene reduction are noted for poly(oxa-7-diphenylphosphino-6-hydroxyheptyl)siloxane [621] and poly{γ-(3 or 4-diphenylphosphino)phenylpropyl}siloxane palladium complexes on

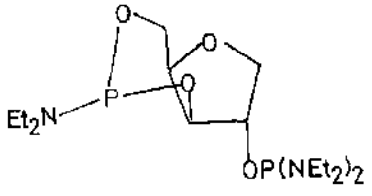
silica [622,623]. The latter two catalysts are readily reusable without loss of activity. Polystyrene bearing NMe_2 groups, complexed to $PdCl_2$, gives a catalyst for alkene hydrogenation which is sensitive to steric hindrance in the substrate. The catalyst is air stable, and again reusable without loss of activity [624]. Polyphenyl quinoxaline palladium complexes supported on silica [625] and chelates of palladium with poly(3- or 4-hydroxyphenylbenzoxazole)terephthalimides as fibres [626] have also been used as catalysts.

$[Pt(PPh_3)_4]$ has been used for preparation of Pt/C and Pt/Al_2O_3 catalysts for hydrogenation; this complex gives catalysts of higher activity than those obtained using $[Pt(NH_3)_4]Cl_2$ [627]. The mechanism of selective hydrogenation and isomerisation of hexenes in the presence of aromatic hydrocarbons on a palladium sulphide catalyst has been investigated [628].

$PdCl_2$, with or without $Na[BH_4]$, in polyethylene glycol is an excellent and selective catalyst for reduction of alkynes to *cis*-alkenes. Under more forcing conditions, alkanes are obtained [629-631].

$[Pd_2(PPh_3)_2Cl_4]$ has been used as a catalyst for reduction of $ArNO_2$, the aniline being the sole product under elevated H_2 pressure. The reaction intermediate $[Pd(PPh_3)(PhNO_2)Cl_2]$ was isolated and characterised, and a mechanism accounting for all the observed products proposed [632]. Using *trans*-$[Pd(py)_2Cl_2]$ as catalyst, 60-90 % $ArNH_2$ is obtained from $ArNO_2$ at 1 atm H_2, but the yield is increased at higher pressure [633].

Chiral carboxylate derived ligands such as (301) form complexes $[(\eta^3\text{-allyl})PdLCl]$ with the allyl palladium chloride dimer. On treatment with $Na[BH_4]$, a catalyst for enantioselective reduction of itaconic acid is obtained, but optical yields are low [634].



(301)

Pd(II) catalyses the decomposition of methanoic acid to H_2 and CO_2, an important step in the use of HCOOH as a reducing agent [635].

The activity of $[Pt(H_2O)_nCl_{4-n}]^{n-2}$ (n = 0, 1, 2, 3 or 4) in catalysing H/D exchange in alkanes is related to the distortion energy of the complex [636]. $K_2[PtCl_4]$ is reported to be generally the best catalyst for H/D exchange of hydrocarbons and heterocycles by D_2O, but $[Pt(en)_2]Cl_2$ is recommended for sulphur containing heterocycles [637, 638].

1.9.2 Carbon monoxide reactions

$[Pt(PPh_3)_2Cl_2]/SnCl_2$ is a well established catalyst for alkene hydroformylation. Addition of chelating diphosphines alters the reaction rate; dppe is an inhibitor and the best rate is obtained with dppb, which also gives enhanced selectivity for aldehydes. It seems that a chelating phosphine in which one phosphine is relatively readily decoordinated is the ideal ligand [639]. The precatalytic reactions of $[Pt(PR_3)LCl_2]$ (L = R_2S or CO; R = Ar) with $SnCl_2$ have been investigated [640].

Hydroformylation of 1-pentene in the presence of $[Pt(PhCN)_2Cl_2]$/dppf/$SnCl_2$ at 100 °C and 100 atm gives 60 % aldehydes, of which 97 % are straight chain [641]. $Pd(OCOCH_3)_2/R_3P$/maleic anhydride is a useful catalysts system for dimerisation/carbonylation of butadiene to yield octadienoate esters [642].

The rather spectacular enantiomer excess (95 %) reported in asymmetric hydroformylation of styrene in the presence of $[\{(-)\text{-DBPDIOP}\}PtCl_2]$ has now been revised to 73 %, a result which is, by any standards, still impressive [643].

Reaction of 1-nonene with CO/H_2O in the presence of polymer supported Pd(II) yields decanoic acid and its isomers. The best yield and selectivity is obtained using $PdCl_2$ on chlorinated poly(vinylchloride) [644]. α-Methyl

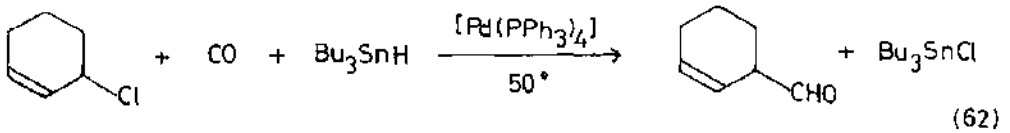
carboxylic acids are the main products when 1-alkenes are treated with CO/H_2O in the presence of $PdCl_2/CuCl_2/O_2/HCl$ [645].

Carbonylation of halides, RX, in the presence of $[Pd(PhCN)_2Cl_2]/R'_3P$ yields RCOOH. Rates are in the order R = alkyl < Ph < $PhCH_2$ and X = Cl < Br < I [646]. Acids are also obtained using $[Pd(PPh_3)_4]$ as catalyst under phase transfer conditions. The nature of the palladium complex employed is critical in this case; $[Pd_2(dba)_3]$ (dba = 1,5-diphenyl-penta-1,4-diene-3-one) catalyses reduction and coupling of the halides, whereas $[Pd(dppe)_2]$ gives acids under "normal" conditions, but esters under phase transfer conditions [647]. Esters, ArCOOR, are also obtained from $[Ar_2I]X$ in the presence of $PdCl_2$ or $Pd(OCOCH_3)_2$ [648].

Carbonylation of alkyl substituted 3-bromo-but-3-ene-1-ols in the presence of $[Pd(PPh_3)_4]$ yields α-methylene lactones [649].

In the presence of amines, one might expect to obtain amides as the products of halide carbonylation, and many intramolecular reactions of this type are known. However, using $[Pd(PMePh_2)_2Cl_2]$ or $[Pd(dppb)Cl_2]$ as catalysts, the main product is $RCOCONR'_2$ from RX, CO and R'_2NH. Selectivity is up to 98 % for R = Ph, R' = Et [650,651].

Halides may be converted to aldehydes by a combination of carbonylation and hydrogenolysis (reaction (62)) [652].



(62)

Carbonylation of 1,3-dinitrobenzene in the presence of $[Pd(py)_2Cl_2]$ or $[Pd(quin)_2Cl_2]$ gives the bis(isocyanate) [653]. However, in the presence of ethanol and using $VCl_3/PdCl_2$ as catalyst, ArNHCOOEt is obtained from $ArNO_2$, with a selectivity which depends on the nature of Ar [654].

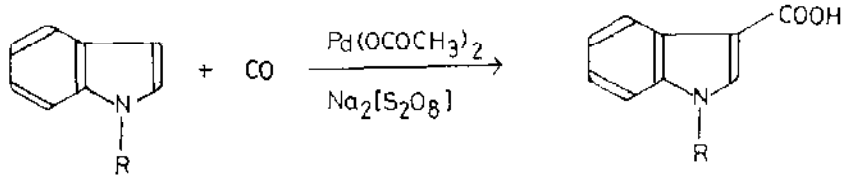
Reduction of CO by molecular hydrogen over platinum metal carbonyl

cluster catalysts gives ethanol as the major product [655].

Oxidative coupling and carbonylation of ROH in the presence of stoicheiometric benzoquinone and catalytic $[Pd(PPh_3)_2(OCOCH_3)_2]$ gives 60-95 % of oxalate esters [656].

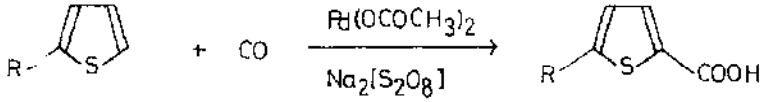
Reaction of ethyne with CO in the presence of $FeCl_3$, $HgCl_2$, LiCl, $PdCl_2$ and HCl yields *trans*-3-chloropropenoic acid, *via* vinyl mercury and vinyl palladium compounds [657].

Site specific oxidative carbonylation of indole and its derivatives takes place in the presence of $Pd(OCOCH_3)_2/Na_2[S_2O_8]$ (reaction (63)) [658]. Thiophene derivatives, such as **(302)** react similarly [659].



(63)

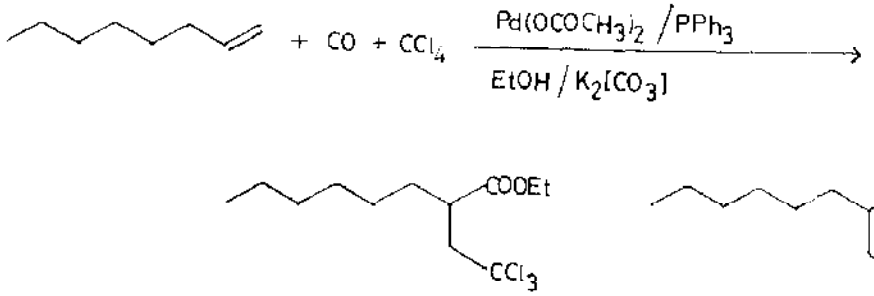
R = COOMe, COPh or H



(302)

R = H, Me, Cl or Br

Finally, CO and CCl_4 may be added simultaneously to an alkene under palladium catalysis (reaction (64)) [660].



60 40 (64)

1.9.3 Oxidation

$K_2[PtCl_4]$ supported on alumina is active for the oxidative chlorination of CH_4 by HCl/O_2 mixtures [661].

The effect of hydrophilic solvents on the palladium catalysed reactions of alkenes has been investigated. Mechanistic implications for isomerisation and oxidation to ketones were discussed [662].

Again this year, many papers concerning the Wacker oxidation refer to little more than minor improvements in technique or reaction conditions or more detailed kinetic studies [663-665]. Further details of the study of reaction (65) are reported; ^{17}O NMR spectroscopy implies that the oxygen atom from $Li[NO_3]$ becomes the carbonyl oxygen [666].

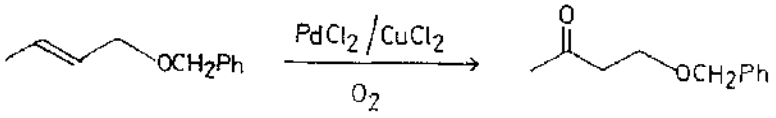
$$C_2H_4 + O_2 \xrightarrow{CH_3COOH,\ Pd(OCOCH_3)_2,\ Li[NO_3]} CH_3CHO \qquad (65)$$

A long series of papers from a Soviet group details kinetic studies, effects of catalyst and additives, and proposed mechanisms of the various versions of the palladium catalysed oxidation of ethene to $CH_3COOCH_2CH_2OCOCH_3$ or $CH_3COOCH_2CH_2OH$ [667-672].

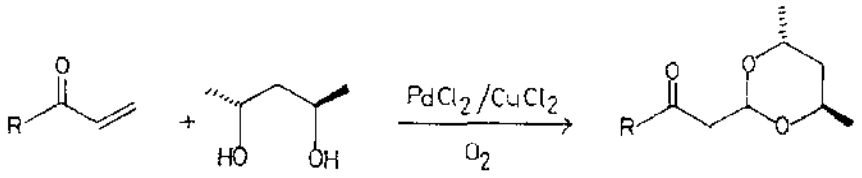
Numerous other oxidations of 1-alkenes in the presence of $PdCl_2/Cu_2Cl_2$ have been investigated. The kinetics of butene oxidation have been studied and imply a binuclear $[Pd_2(butene)_2Cl_2]$ intermediate [673,674]. ω-Unsaturated esters have also been oxidised, the presence of quaternary ammonium salts giving increased yields [675]. $Na_2[Pd(Ph_2PC_6H_4SO_3)_2Cl_2]$ [676] and $[Pd(MeCN)_2(NO_2)Cl]$ [677], in the presence of $CuCl_2$, have also been used as catalysts. XPES studies of palladium black samples and $[Pd_{10}(phen)_4(OCOCH_3)_2(O_2)_3]$ have been related to their catalytic activity in propene oxidation [678].

Whilst the palladium catalysed oxidation of internal alkenes is relatively uncommon, allyl benzyl ethers are converted to ketones with good

regioselectivity (reaction (66)) [679]. If the reaction of enones is performed in the presence of a diol, an aldehyde acetal is obtained, again with good selectivity (reaction (67)) [680].

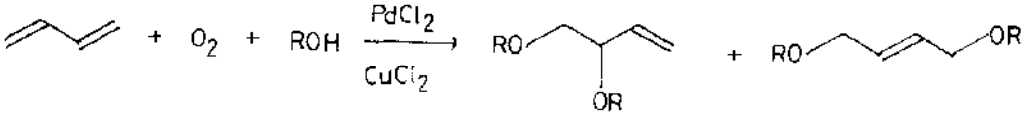


(66)



(67)

When the catalyst system used is $Pd(OCOCH_3)_2/LiCl/Li[NO_3]/CH_3COOH$, the major products of 1-alkene oxidation are mono- and di-ethanoates [681]. Both 1,2- and 1,4-oxidative addition products are obtained from butadiene and ROH (reaction (68)) [682].

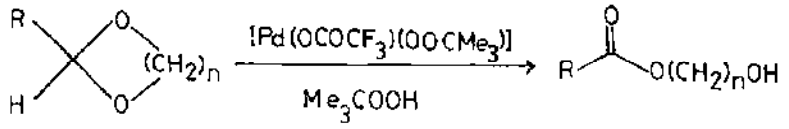


(68)

Other catalytic systems promote allylic oxidation of alkenes. For example, propene is converted to allyl ethanoate in the presence of a phen or bipy Pd(0) cluster [683]. Cyclopentene gives cyclopentenyl ethanoate as the main product using Me_3COOH as oxidant and a catalyst system formed from $PdCl_2/TeO_2/AgOCOCH_3$ in CH_3COOH. The mechanism is thought to involve acetoxypalladation followed by dehydropalladation [684]. Both enones (from allylic oxidation) and methyl ketones are obtained by photolysis of 1-alkenes in the presence of O_2 and $Pd(O_2CCF_3)_2$ [685].

Thiocyanates, RNCS, are oxidised to RNCO by molecular oxygen in the presence of $PdCl_2$ [686].

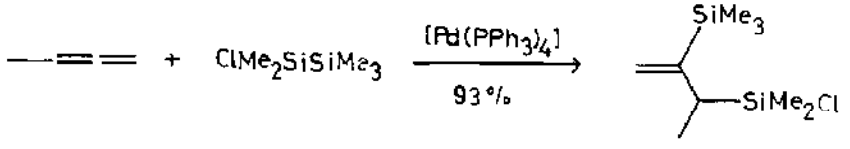
Aldehyde acetals may be opened to yield hydroxyesters by Me_3COOH, using $[Pd(OCOCF_3)(OOCMe_3)]$ as catalyst (reaction (69)); $PdCl_2$ and $[Pd(MeCN)_2Cl_2]$ are also effective but yields are lower [687].



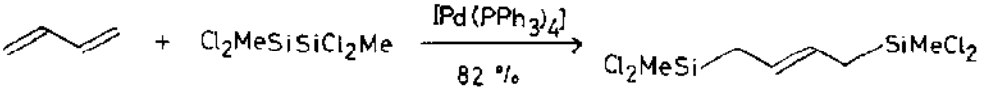
(69)

1.9.4 Other additions to alkenes and alkynes

This year's reactions have provided some novel processes in hydrosilylation chemistry. 4-Halophenylpropyltrichlorosilane and 4-halophenylpropylalkyldichlorosilanes form useful copolymers with $[Si(OEt)_4]$. Both may be prepared in good yield and selectivity by hydrosilylation of the appropriate allybenzene in the presence of $H_2[PtCl_6]$ [688]. There have been two reports of rather regioselective addition of disilanes catalysed by $[Pd(PPh_3)_4]$ (reactions (70) and (71)) [689,690].



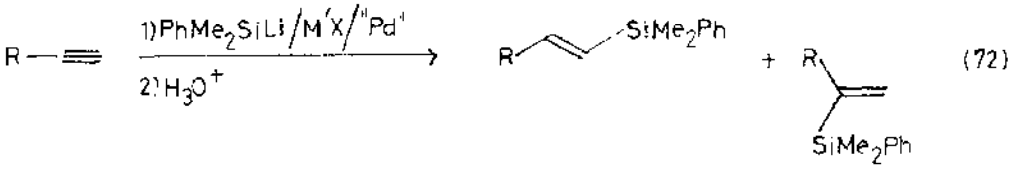
(70)



(71)

Two other, somewhat more curious, addition reactions also yield silanes as the ultimate product. Reaction of alkynyltrimethylsilanes with allylic chlorides in the presence of $[Pd(PhCN)_2Cl_2]$ generates

E-4-trimethylsilyl-5-chloro-1,4-dienes with good regio- and stereo-selectivity, being the product of formal *trans*-addition of the allyl chloride across the triple bond [691]. Silylmetalation of alkynes occurs in the presence of $[ML_2Cl_2]$ (M = Pd or Pt; L = R_3P) (reaction (72)). Regioselectivity depends on M'X and L. **(303)** is favoured by more than 99:1 with M'X = MeMgX and *cis*-$[Pt(PBu_3)_2Cl_2]$, but (304) is the major product (85 %) with M'X = Et_2AlCl and $[Pd\{P(2\text{-}MeC_6H_4)_3\}_2Cl_2]$ as catalyst [692].

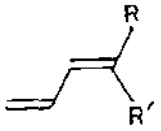


(72)

(303) (304)

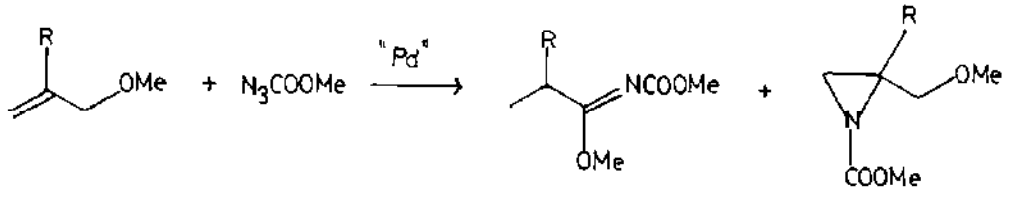
The strictly *cis*-addition of DCN to alkenes in the presence of $[Pd(DIOP)_2]$ may be contrasted with the reaction in the presence of $[Ni\{P(OPh)_3\}_4]/ZnCl_2$, in which rearrangement and isotopic exchange occur [693]. Asymmetric addition of HCN to norbornene using $[Pd(DIOP)_2]$ gives an optical yield up to 24 %, but catalysts derived from diphosphine ligands forming five-membered chelate rings are inactive [694].

Stereoselectivity in the reaction of ethyl diazoacetate with styrene catalysed by $Pd(OCOCH_3)_2$ is only 2:1 in favour of the *cis*-cyclopropane [695]. Numerous catalysts were tested for the reaction of diene (305) with $N_2CHCOOEt$. Regioselectivity was very poor when $[Pd(PhCN)_2Cl_2]$ was employed [696]. New this year are two reports of palladium catalysed reactions of nitrenes, derived from N_3CO_2R (R = Me or Et). N_3CO_2Me reacts with (306) to give **(307)** and **(308)**. The best catalyst for the formation of **(307)** is $[Pt(PhCN)_2Cl_2]$, giving 95 % of the desired material. Up to 24 % of the aziridine is obtained with $[Pd(PPh_3)_4]$ [697,698].



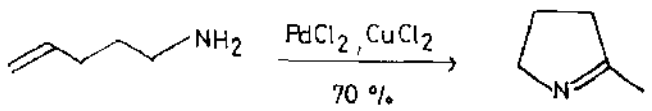
(305) R = H, R' = Me, Ph, Cl or OMe

R = Me, Ph, Cl or OMe, R' = H



(306) R = H or Me (307) (308)

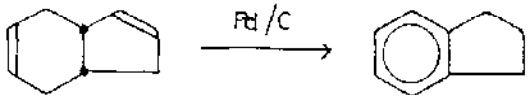
Some palladium catalysed additions involve attack of a nucleophile on a palladium alkene complex formed *in situ*. Cyclisation of (309) is an example of such a process, proceeding in 70 % yield [699].



(309)

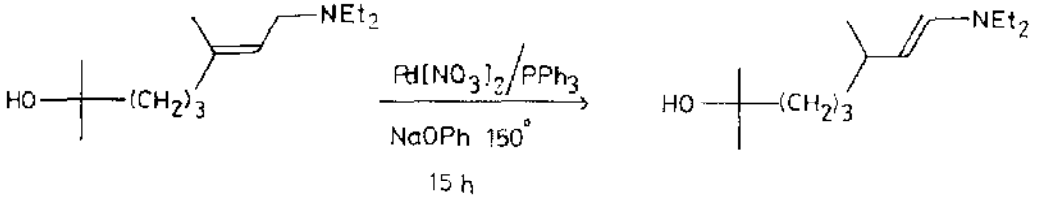
1.9.5 Isomerisation

$PdCl_2$, supported on various grafted copolymers, treated with $Na[BH_4]$/MeOH, has been tested for activity in isomerisation and reduction of allyl benzene. Activity depends strongly on the electron donor properties of the grafted group [700]. Palladium on carbon gives only (311) on isomerisation/dehydrogenation of (310), in contrast to other catalysts [701].



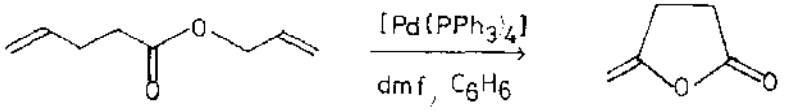
(310) (311)

Isomerisation of the allylamine (312) to the enamine (313) is achieved in the presence of $Pd[NO_3]_2/PPh_3$, the product being used in a synthesis of 7-hydroxycitronellal [702].



(312) (313)

The allyl ester (314) is readily converted to (315) *via* cleavage of the C-O bond to form an allyl, attack of carboxylate on coordinated alkene and loss of {HPd(allyl)} [703].

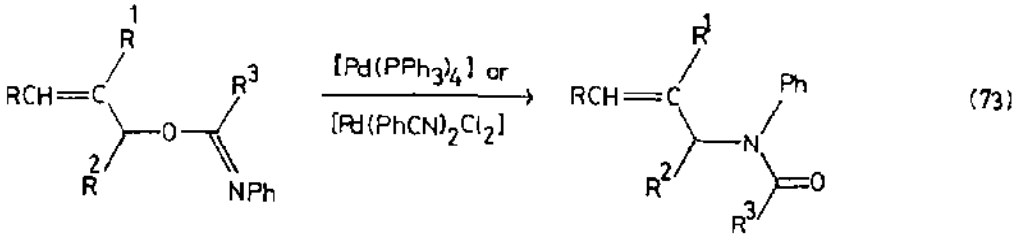


(314) (315)

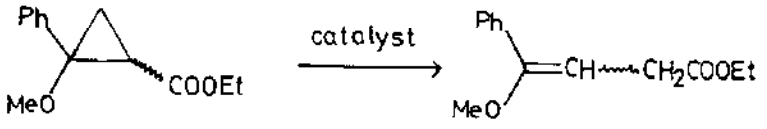
Reaction (73) involves a similar process, with attack on the intermediate allyl by the more nucleophilic nitrogen atom [704].

$[M(PhCN)_2Cl_2]$ (M = Pd or Pt), among many other species, catalyse the opening of (316) to (317) in good yield. It is thought that the ester group

participates in the reaction, since the analogous alcohol gives a poor result, with a mixture of products in low yields [705].

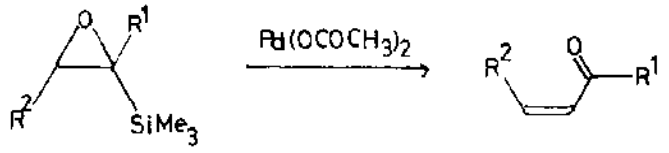


(73)



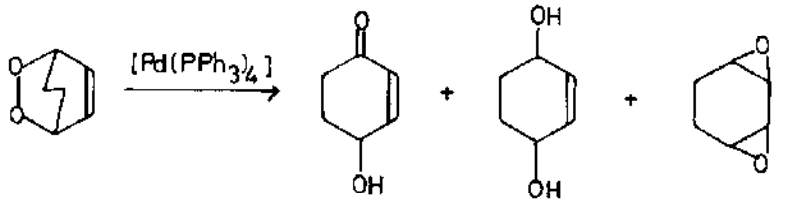
(316) (317)

Reaction (74), of a silylated epoxide, gives an enone in good yield, ring opening being accompanied by desilylation [706].



(74)

The ring opening of epiperoxides, such as (318), gives a mixture of products. Several pathways are proposed to account for this, some involving Pd(I) and some Pd(II) [707].



(318)

39 % trace 8 %

1.9.6 Hydrogenolysis

Pt(II) catalyses the acidic hydrogenolysis of alkyl halides and alcohols in the presence of NaI (reactions (75)-(78)) [708,709]. Na[HCOO] may also act as a reductant for ArBr in the presence of $[Pd(PPh_3)_2Cl_2]$ and a phase transfer catalyst [710].

$$ROH \underset{I^-}{\overset{H^+}{\rightleftharpoons}} RI \qquad (75)$$

$$RI + Pt(II) \longrightarrow RPt(IV)I \qquad (76)$$

$$RPt(IV)I + I^- \longrightarrow [RPt(II)]^- + I_2 \qquad (77)$$

$$[RPt(II)]^- + H^+ \longrightarrow RH + Pt(II) \qquad (78)$$

Hydride is the source of the new hydrogen atom in the hydrogenolysis of allyl derivatives, reactions (79) and (80) probably proceeding *via* π-allyl complexes [711,712].

$$ArCH{=}CH\text{-}\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}\text{-}R \xrightarrow[[Pd(PPh_3)_4]]{Bu_3SnH} ArCH{=}CHCH_2R \qquad (79)$$

R = H, CN or Ph

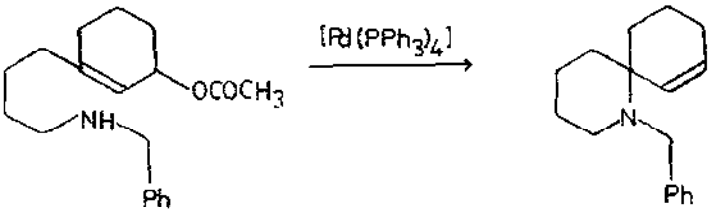
$$E\text{-}CH_3(CH_2)_6CH{=}CHCH_2OPh \xrightarrow[[Pd(PPh_3)_4]]{Li[BHEt_3]} \underset{\text{mainly E}}{CH_3(CH_2)_6CH{=}CHCH_3} \qquad (80)$$

1.9.7 Allylic substitution

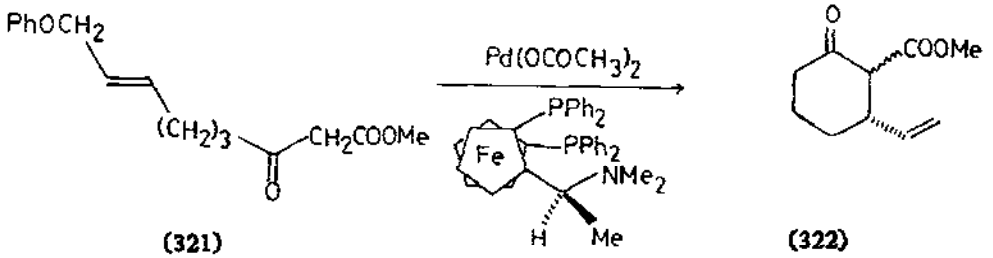
Once again the uses of the palladium(0) catalysed nucleophilic substitution of allyl derivatives have been prominent in synthetic reactions. A timely review focusses particularly on the factors determining regioselectivity of attack on the palladium allyl intermediates [713]. In the

presence of $[Pd(PPh_3)_4]$ the anion of 1-methyl-1-nitroethane reacts with various allyl derivatives, $CH_2{=}CHCH_2X$, reactivities being in the order X = OPh > $OCOCH_3$ > OH [714,715].

Two cyclisation reactions are worthy of note. (319) cyclises to the spiro compound, (320), a precursor of dehydrohistrionicotoxin [716]. Cyclisation of (321), in the presence of a chiral palladium complex, gives the six-membered ring (322) (in contrast to many earlier reactions which gave predominently eight-membered ring products) in up to 48 % enantiomer excess [717].

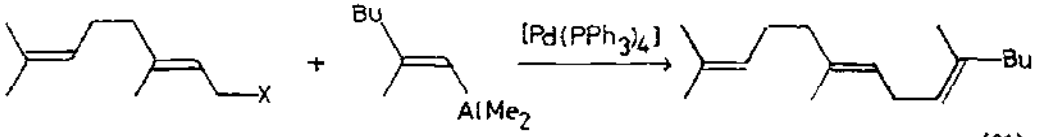


(319) (320)



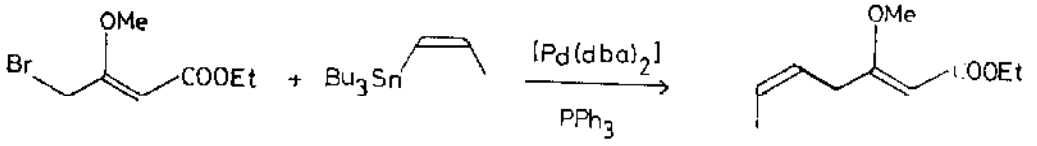
(321) (322)

Organometallic nucleophiles have also been prominent; both reactions (81) [718] and (82) [719] proceed with excellent stereoselectivity. With an epoxide as the substrate the stereochemical integrity of the nucleophile is maintained, but both product regioisomers were formed in reaction (83) [720].

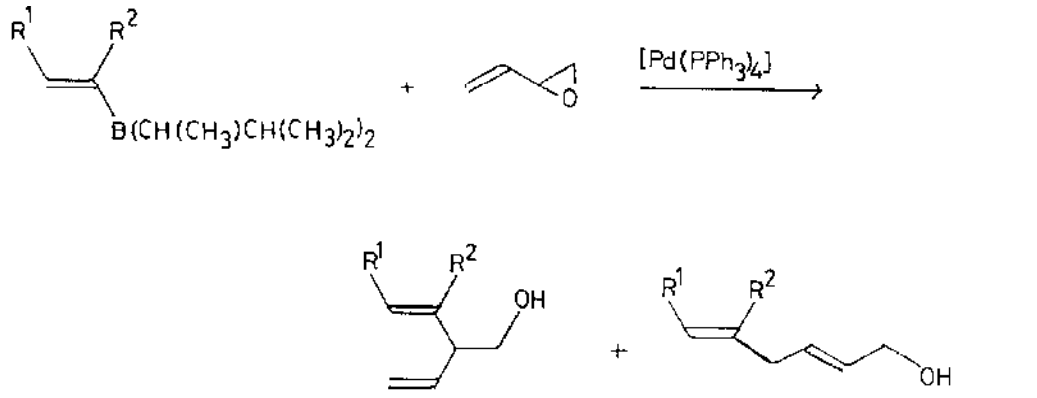


(81)

X = Cl, $OCOCH_3$, $OAlMe_2$, $OPO(OEt)_2$, $OSiMe_3$ or $OSiMe_2CMe_3$

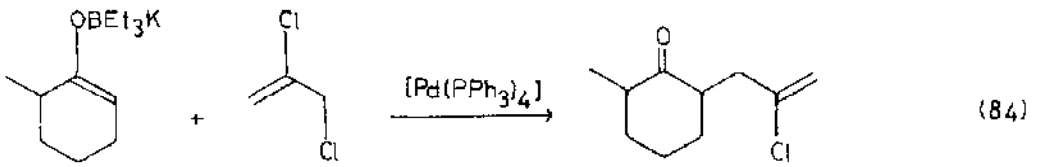


(82)



(83)

Reaction of potassium enoxyborates (from potassium enolates and Et_3B) with allyl derivatives gives α-allylated ketones with retention of enolate regiochemistry and allyl geometry (reaction (84)) [721].



(84)

Allyl silanes may act as precursors to allyl complexes, the reaction being enantiospecific for chiral silanes [722].

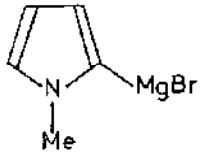
1.9.8 Oxidative coupling of hydrocarbons

Oxidative coupling of hydrocarbons in the presence of palladium(II) has been reviewed [723]. Both 2,2'- and 2,3'-isomers of bis(thiophene) are obtained *via* electrophilic addition of Pd(II) to the heterocyclic ring [724].

Palladium(II) catalysed oxidation of arenes by $Tl(OCOCF_3)_3$ gives high selectivity for *para*-coupling [725] and $Na_2[S_2O_8]/O_2$ may also be used as an oxidant [726].

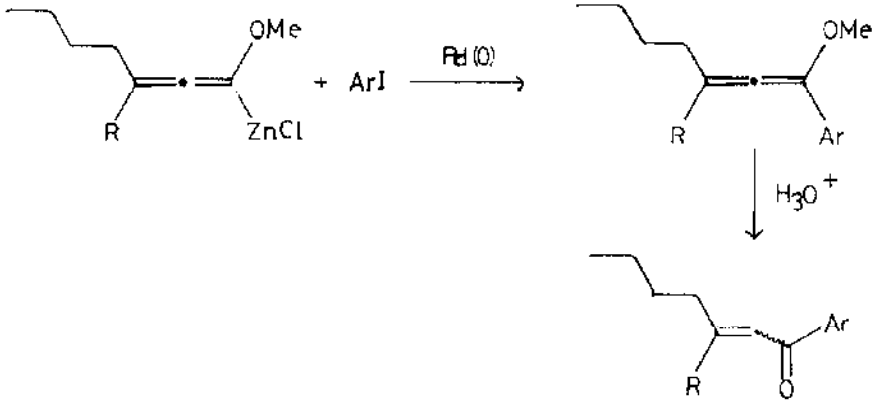
1.9.9 Coupling of carbanions with halides

Again this year the range of organometals and substrates used in palladium catalysed couplings has been wide. Heteroaromatic halides are substituted by (323) in excellent yield in the presence of $[Pd(dppb)Cl_2]$ [727] and vinyl iodides react readily with Me_3SiCH_2MgCl or Me_3SiCH_2ZnCl using $[Pd(PPh_3)_4]$ as catalyst [728]. Vinyl tellurides are also substituted, but maintenance of stereochemistry is somewhat variable [729]. Asymmetric coupling of both Grignard reagents and organozinc compounds with vinyl halides in the presence of palladium complexes of ferrocenyl aminophosphines has been reviewed [730].

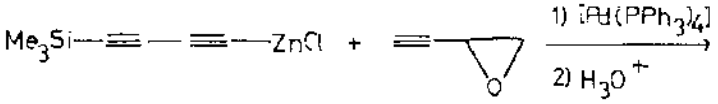


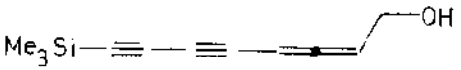
(323)

Reactions of zinc derivatives of enol ethers were reported previously, and this process has now been extended to use allenic compounds (reaction (85)) [731]. The catalysed reaction of zinc compounds with acyl halides has been extended to include Reformatsky reagents [732]. Allenes are obtained in reaction (86) from organozinc halides and epoxides bearing an acetylenic group; the product is used in a synthesis of a metabolite from the fungus *Cortinellus berkeleyanus* [733].



(85)

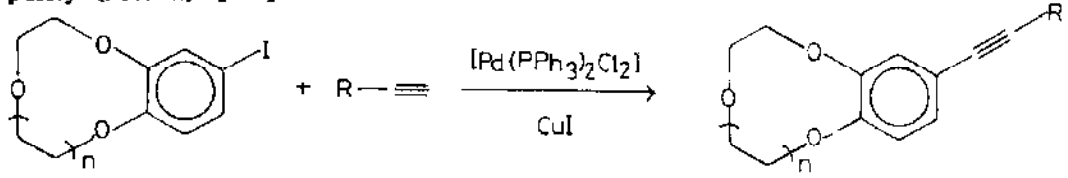




(86)

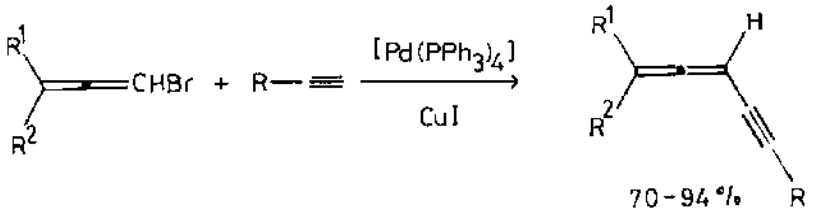
The range of tin containing nucleophiles has been extended to include Bu_3SnNEt_2, an NEt_2 group being transferred in coupling with ArBr in the presence of $[Pd\{P(2\text{-methylphenyl})_3\}_2Cl_2]$ [734].

Two reactions of alkynyl copper compounds formed *in situ* are reported. In one the substrate is an aryl halide (reaction (87)) [735], whilst the other, more unusually, employs an allenyl bromide which reacts without rearrangement (reaction (88)) [736]. A vinyl copper compound is coupled to a vinyl iodide (reaction (89)) to give a product with excellent stereoisomeric purity (98.9 %) [737].

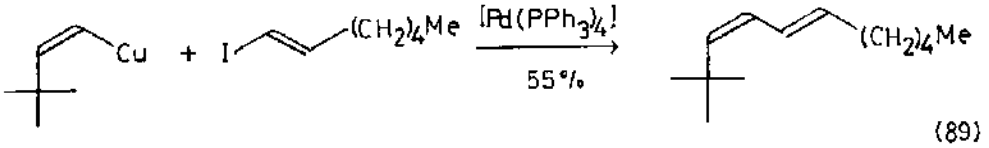


(87)

n = 3 or 4



(88)



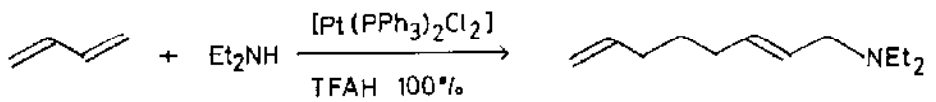
(89)

1.9.10 Oligomerisation and telomerisation

Both $[Pd(dmso)_2Cl_2]$ and $K[Pd(dmso)Cl_3]$ supported on silica catalyse ethene dimerisation [738]. Propene dimerisation was also studied [739]. $Na_2[Pd(4\text{-}Ph_2PC_6H_4SO_3)_2Cl_2]$ catalyses chloroprene emulsion polymerisation to give soluble *trans*-1,4-polychloroprene [740].

Oligomerisation of butadiene in the presence of $Pd(OCOCH_3)_2/Et_3N/Et_3P/HCOOH$ gives 1,7-octadiene and 1,6-octadiene in the ratio 93:6. The highest selectivity is obtained for $R_3P:Pd > 1$ for R = alkyl [741].

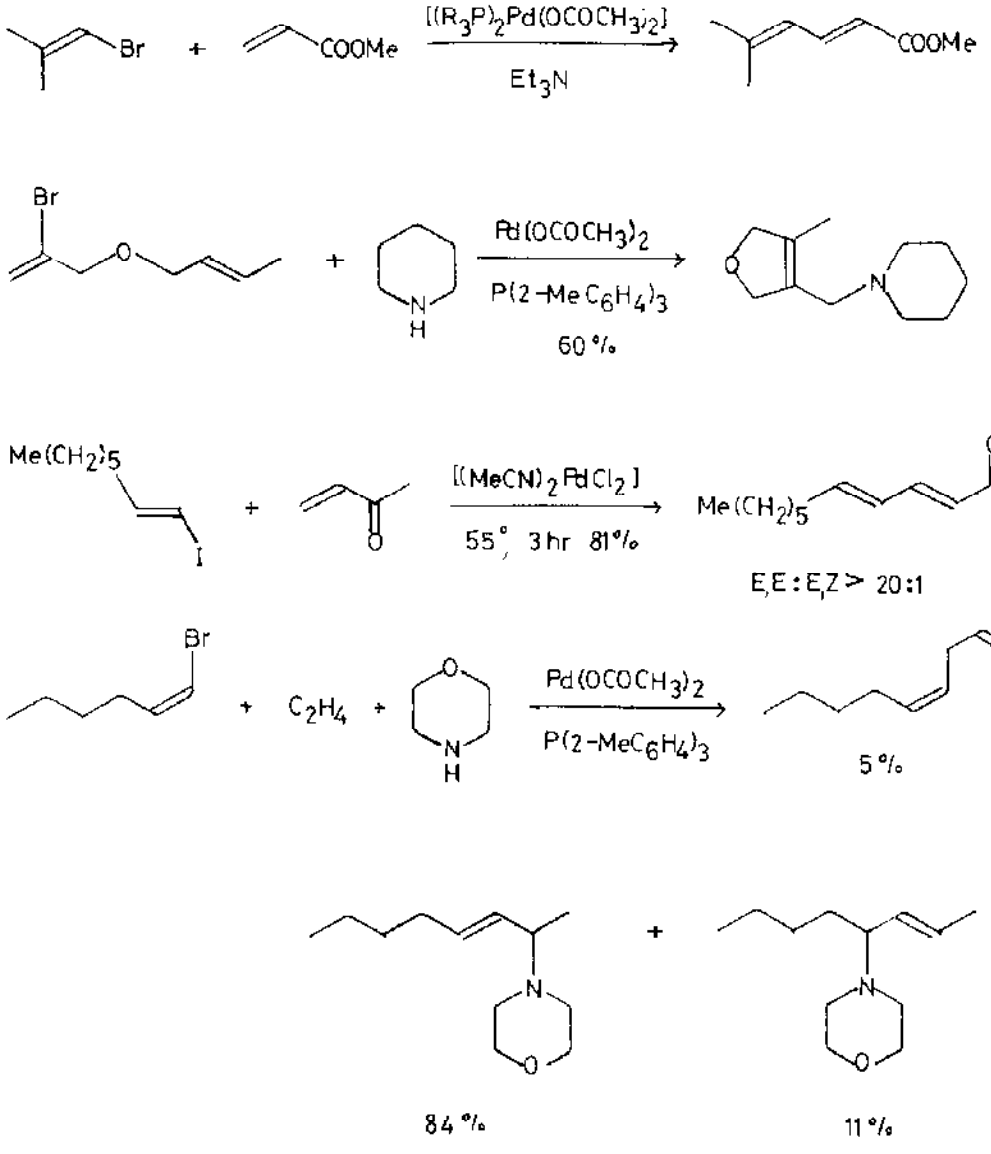
Reaction of butadiene with Et_2NH in the presence of $[Pt(PPh_3)_2Cl_2]$/Tfah gives the linear octadienylamine in quantitative yield (reaction (90)). $[Pd(PPh_3)_4]$ is a less satisfactory catalyst, giving a lower yield and a mixture of butenylamine products [742]. Telomerisation of isoprene with phenol [743] or amines [744] gives a complex mixture of products in the presence of palladium complexes.



(90)

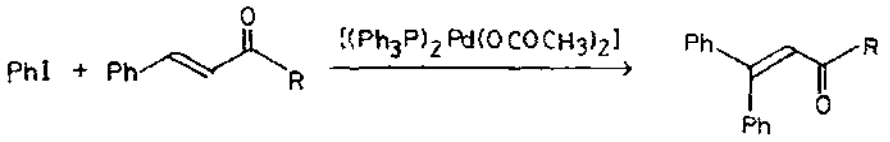
1.9.11 Other coupling reactions

Once again, the work of Heck's group has been prominent in adding to the range of coupling reactions of vinyl halides catalysed by palladium complexes. Some applications, both from these workers and others, are shown in Scheme 20 [745-748].



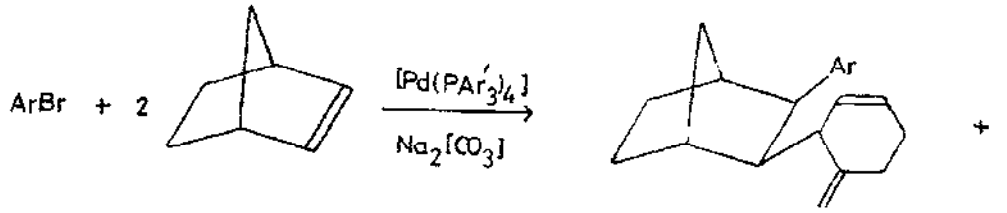
Scheme 20 Heck reactions of vinyl halides [745-748]

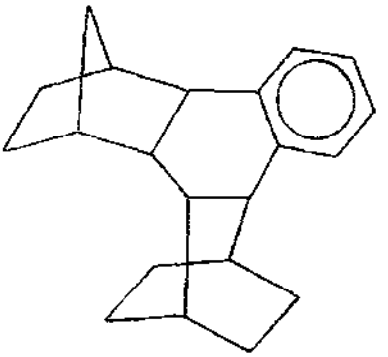
Some related reactions involve coupling of aryl halides with alkenes, for example (91). The mechanism involves formation of ArPdX, followed by addition across the carbon-carbon double bond and HPdX elimination [749].



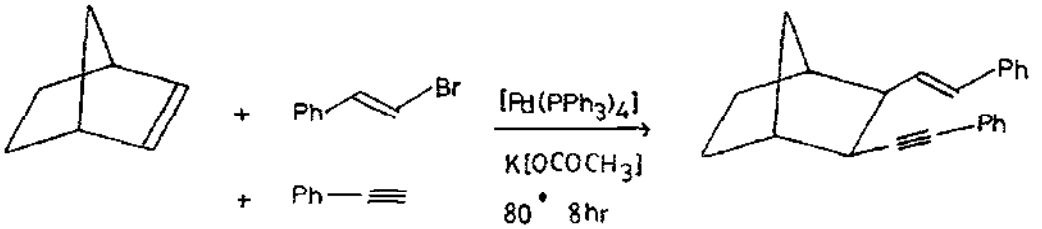
(91)

An analogous initial step is invoked in reactions (92) and (93) [750,751].





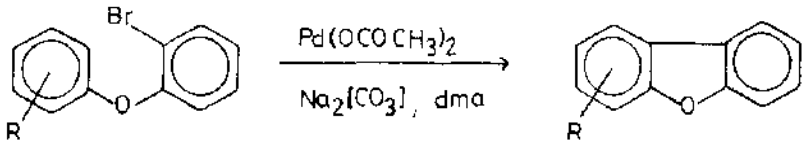
(92)



(93)

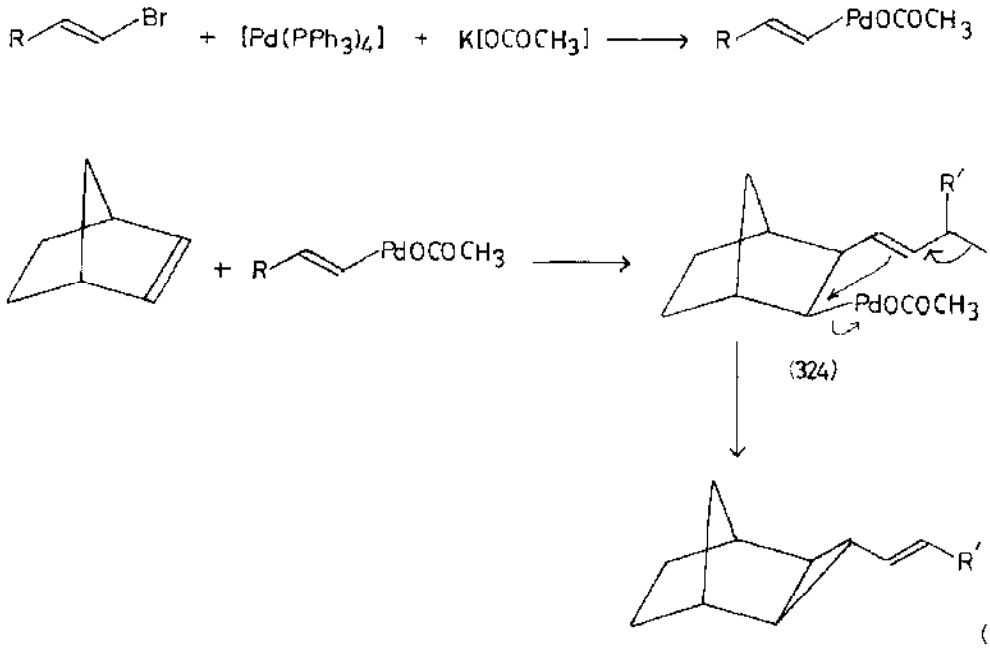
Intramolecular coupling of an aryl halide to an arene occurs in reaction (94) [752]. If one regards silicon as a metal, coupling of

vinyltrimethylsilane with aryl halides to yield styrene has features in common with the reactions of Grignard reagents, but the two are probably not mechanistically related [753].

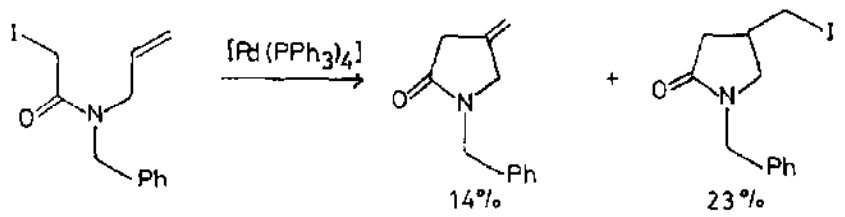


(94)

The coupling of reaction (95) follows a somewhat unusual course, yielding a cyclopropane. In the intermediate, (324), stereoelectronic considerations do not allow any easy β-hydride elimination [754]. Another unusual reaction involves (325); yields are low but the process requires the addition of a C-I bond, activated only by an adjacent carbonyl, to Pd(0) [755].

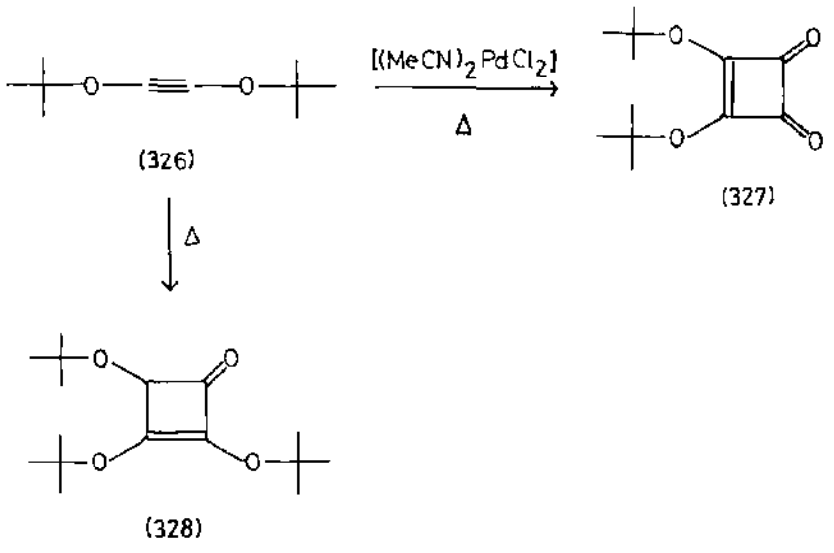


(95)



(325)

Some further data on the reaction of palladium trimethylene methane complexes with alkenes bearing electron withdrawing groups are reported [756]. An apparent $2\pi + 2\pi$ cycloaddition in the presence of $[Pd(MeCN)_2Cl_2]$ followed by loss of Me_3COH yields (327) from (326). Thermolysis in the absence of catalyst yields only (328) [757].



(326) (327) (328)

Other reports of couplings are more scattered and less general. Treatment of terminal allenes, $R^1R^2C{=}C{=}CH_2$, with BuLi presumably gives a metallated derivative, which reacts with vinyl halides, R^3X, in the presence of Pd(0) to give $R^1R^2C{=}C{=}CHR^3$ [758]. Ferrocenyl mercury compounds are oxidatively coupled with acrylonitrile in the presence of $Li_2[PdCl_4]$ [759].

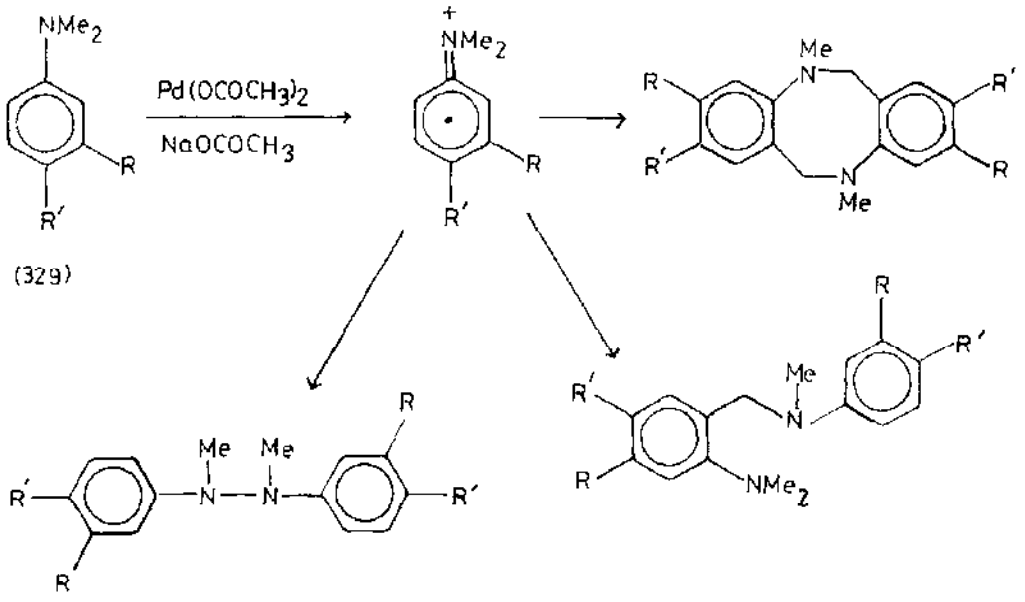
Diaryliodonium salts, $[(RC_6H_4)_2I]X$, give biaryls in the presence of

Zn/[Pd(acac)$_2$], yields being excellent [760]. Treatment of $ArCHCl_2$ with [$(ClMe_2Si)_2$] gives reactions (96) or (97) depending on the molar ratios [761].

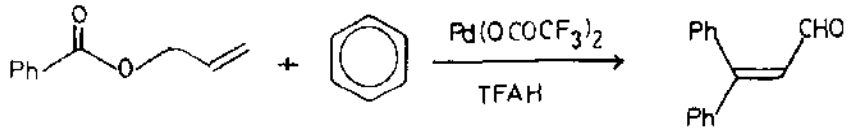
$$ArCHCl_2 + [(ClMe_2Si)_2] \xrightarrow{[Pd(PPh_3)_4]} 1/2ArCH{=}CHAr + 2Me_2SiCl_2 \quad (96)$$

$$ArCHCl_2 + 1/2[(ClMe_2Si)_2] \xrightarrow{[Pd(PPh_3)_4]} 1/2ArCHClCHClAr + Me_2SiCl_2 \quad (97)$$

Treatment of **(329)** with Pd(OCOCH$_3$)$_2$ under N_2 gives a range of products, all of which derive from a single electron transfer from palladium to give an aryl radical cation, which dimerises with varying regioselectivity [762].



Reaction of ethene with aroyl halides gives both decarbonylation and coupling to give styrenes (18-60 %) and stilbenes (~45 %) [763]. Acyl oxygen fission and phenylation of **(330)** gives **(331)** as the main product. Addition of Na[OCOCH$_3$] increases the yield, and if benzoquinone is added as a reoxidant, the reaction becomes catalytic in palladium [764].



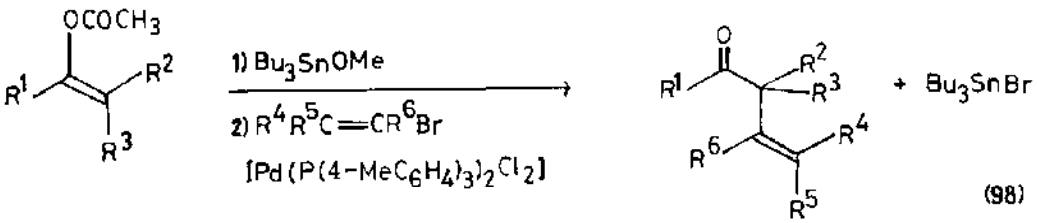
(330) **(331)**

1.9.12 Other reactions catalysed by palladium and platinum complexes.

Dehydrogenation of *N*-hydroxy compounds $R^1CH_2NR(OH)R^2$ to $R^1CH{=}N^+(R^2){-}O^-$ occurs in the presence of palladium complexes, and R^1NHOH is coupled, with H_2 and H_2O loss, to $R^1N^+(O^-){=}NR^1$ [765].

Photolysis of hexane in the presence of $H_2[PtCl_6]$ yields a platinum(II) hexene complex, formed *via* a σ-hexyl Pt(IV) intermediate [766]. Dehydrodimerisation of B_5H_9 in the presence of $PtBr_2$ gives [1:2'-$(B_5H_8)_2$] in 92 % yield without 1:1'- or 2:2'-isomers; the reaction mechanism is unknown [767]. Dehydrohalogenation of chloroalkenes occurs in the presence of supported palladium complex catalysts [768].

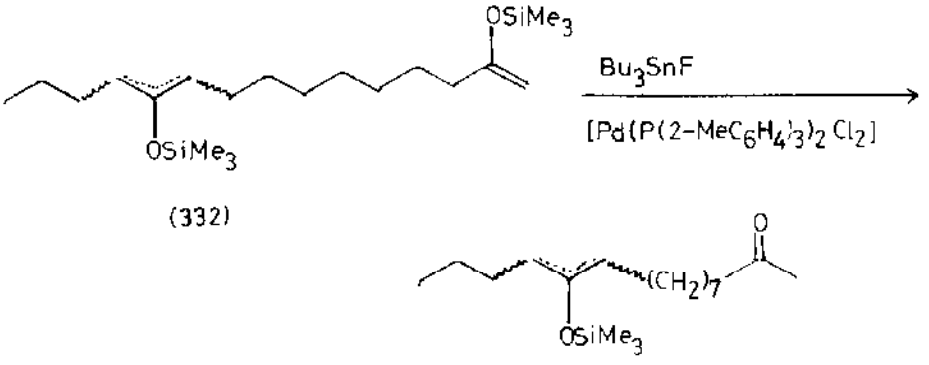
Reactions of tributyltin enolates (formed *in situ* from enol ethanoates and Bu_3SnOMe) with vinyl halides are catalysed by $[Pd\{P(2\text{-methylphenyl})_3\}_2Cl_2]$, yielding allyl ketones in moderate yields (reaction (98)) [769]. Coupling also occurs with aryl halides, providing a route for efficient α-phenylation of ketones [770].



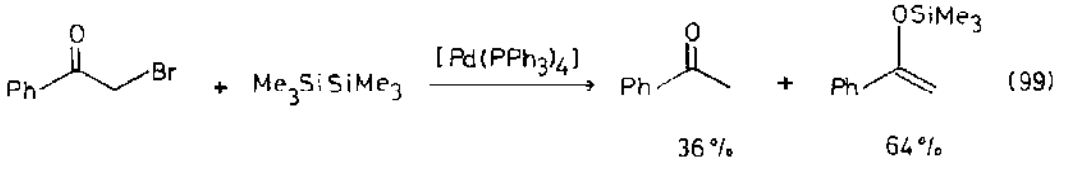
(98)

Fluoride ion is known to have a high affinity for silicon, and is often used for the regeneration of enolates from silyl enol ethers. Treatment of

(332) with Bu_3SnF gives desilylation, but the presence of $[Pd\{P(2\text{-methylphenyl})_3\}_2Cl_2]$ considerably accelerates the reaction, which is very selective for the unhindered site [771]. Silyl enol ethers are among the products of reaction (99), which proceeds *via* palladium oxallyls [772].

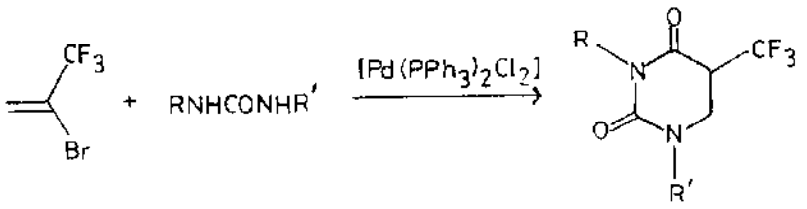


(332)



Substitution of heterocyclic halides by $[CN]^-$ is facilitated by the presence of $[Pd(PPh_3)_4]$ [773].

The synthesis of trifluoromethyl substituted dihydrouracils such as **(333)** is catalysed in rather variable yield by $[Pd(PPh_3)_2Cl_2]$ [774]. *N,N*-Dimethyl uracil is readily nitrated by $Na[NO_2]$ in the presence of $Pd(OCOCH_3)_2$ [775].



(333)

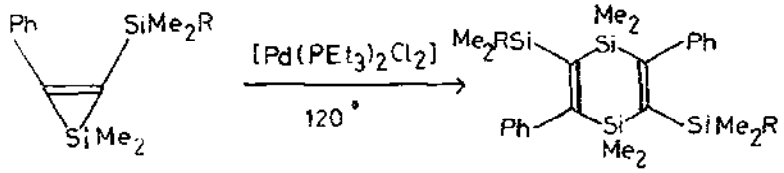
Reaction of diethylzinc with benzaldehyde in the presence of chiral

palladium complexes of camphorquinone dioxime gives 1-phenyl-1-propanol in 40-60 % enantiomer excess [776].

A significant paper from Baeckvall's group gives further details of the palladium(II) catalysed acetoxylation of dienes. Both *cis*- and *trans*-1,4-diethanoates may be obtained from cyclic dienes by altering Cl^- and $[CH_3COO]^-$ concentrations. With moderately increased chloride ion concentration *cis*-1,4-chloroethanoates are formed [777].

The reaction between Ph_3P and styrene in the presence of $Pd(OCOCH_3)_2$ is a complex one, yielding stilbene, $PhCH{=}CHOCOCH_3$, Ph_2POOH, $PhPO(OH)_2$, H_3PO_4 and $Ph_3P{=}O$. A new mechanism is proposed for this process, involving a cyclic mechanism for C-P cleavage in the coordination sphere of palladium [778].

The role of palladium in the curious conversion of (334) to (335) is unknown [779].



(334) (335)

Finally, palladium complexes of dppm are more active than their Ph_3P or dppe analogues in catalysis of the reaction of CO_2 and EtOH in the presence of Et_3N to yield CH_4 and HCOOEt [571].

1.10 NON STOICHEIOMETRIC, BINARY AND TERNARY COMPOUNDS

Pd_6P dissolves hydrogen to from an interstitial solution with composition $Pd_6PH_{0.15}$ at 1 atm., 298 K. The hydrogen solubility follows Sieverts's Law at low H_2 concentration, showing that H_2 dissociates in the lattice [780].

The mixed valence compounds, MPt_3O_6 (M = Mn, Co, Zn or Mg) are isostructural, containing a rigid framework of planar $\{PtO_4\}$ and octahedral $\{PtO_6\}$ groups with disordered cations. The $\{PtO_4\}$ units are stacked with one-dimensional Pt-Pt interactions; $NiPt_3O_6$ is more distorted [781]. Bulk magnetic susceptibility measurements show magnetic coupling along the linear arrays. Electrical conductivity is also along the $\{PtO_4\}$ stacks [782].

$LaPd_3S_4$ is prepared from its elements at 1125 K. X-ray powder and neutron powder data suggest that it conforms with the ideal $NaPt_3O_4$ structural type. A model involving [Rare earth(III)$Pd(II)_3S_4 + e^-$] is invoked to explain the observation of metallic conductivity for the pressed powder of this first example of a metallic platinum bronze [783].

The structure of ternary alloys $MPdS_n$ (M = rare earth) have been studied. Those with M = Ho, Er, Tm, Lu and Sc all have the Fe_2P structure [784].

The compounds $PrPt_2$ and other PrX_2 species all crystallise in the $MgCu_2$ structure. There are eight Pr^{3+} ions per unit cell, occupying cubic sites in a diamond lattice surrounded by platinum tetrahedra [785].

Stellae quadrangulae is the term proposed for a tetrahedron with a cap on every face, or a central tetrahedron sharing all faces with tetrahedra. X-ray data on $Ge_8Na_6Pt_8$ show that platinum atoms occupy the capping sites [786].

The spillover of isocyanate surface species on Pt/SiO_2 was studied by IR spectroscopy, showing that NCO migrates from Pt to Si [787].

ACKNOWLEDGEMENTS

I am grateful for permission to reproduce the following items:-

(11) Reprinted with permission from K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem.*, 22 (1983) 4066. Copyright (1983) American Chemical Society.

REFERENCES

1. Yu.N. Kukushkin, *Russ. J. Inorg. Chem.*, 28 (1983) 1081.
2. M.G.H. Wallbridge and J.G. Taylor, *Ann. Rep. Prog. Chem., Sect A: Inorg. Chem.*, 78A (1981) (Pub. 1982) 251.
3. J.C. Bailar, *J. Indian Chem. Soc.*, 59 (1982) 1214.
4. W. Beck, *Transition Met. Chem., Proc. Workshop*, 1980 (Pub. 1981) 307 [*Chem. Abstr.*, 98 (1983) 64551m].
5. A.A. Timakov, V.N. Prusakov and Yu.V. Drobyshevskii, *Zh. Neorg. Khim.*, 27 (1982) 3007.
6. A.V. Dzhalavyan, E.G. Rakov and A.S. Dudin, *Russ. Chem. Rev.*, 52 (1983) 960.
7. D.J. Gulliver and W. Levason, *Coord. Chem. Rev.*, 46 (1982) 1.
8. V.E. Mironov and A.K. Pyartman, *Russ. Chem. Rev.*, 52 (1983) 837.
9. G. Marcu and C. Nascu, *Rev. Chim. (Bucharest)*, 33 (1982) 374 [*Chem. Abstr.*, 97 (1982) 192185m].
10. V.M. Mit'kin, Yu.I. Mironov, S.U. Zemskov, B.D. Zil'berman and S.P. Gabuda, *Sov. J. Coord. Chem.*, 9 (1983) 18.
11. S. Mohan and A. Mukunthan, *Acta Cienc. Indica, [Ser.] Phys.*, 8 (1982) 9.
12. V.V. Vasil'ev, K.P. Balashov and G.A. Shagisultanova, *Opt. Spetrosk.*, 54 (1983) 876 [*Chem. Abstr.*, 99 (1983) 79403j].
13. V.V. Vasil'ev, K.P. Balashov and G.A. Shagisultanova, *Russ. J. Phys. Chem.*, 57 (1983) 461.
14. C. Sugiura and M. Ohashi, *J. Chem. Phys.*, 78 (1983) 88.
15. A. Goursot, E. Penigault and H. Chermette, *Chem. Phys. Lett.*, 97 (1983) 215.
16. M. Krupski, *Phys. Status Solidi A*, 78 (1983) 751.
17. M. Prager, A.M. Raaen and I. Svare, *J. Phys. C*, 16 (1983) L181.
18. I.A. Khartonik, G.G. Novitskii and T.M. Buslaeva *Deposited Doc.*, (1982) VINITI 1974 - 82 [*Chem. Abstr.*, 99 (1983) 61073s].
19. G.A. Kitaev and E.I. Stepanovskikh, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 25 (1982) 1201 [*Chem. Abstr.*, 98 (1983) 60575z].
20. E.A. Golubova, G.V. Volkova and G.A. Ryzhko, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, (1982) 50 [*Chem. Abstr.*, 96 (1982) 149863y].
21. A.A. Castro, O.A. Scelza, E.R. Benvenuto, G.T. Baronetti, S.R. De Miguel and J.M. Parera, *Stud. Surf. Sci. Catal.*, 16 (Prep. Catal. 3) (1983) 47.
22. Yu.N. Kukushkin and V.N. Demidov, *Zh. Neorg. Khim.*, 27 (1982) 2590.
23. N.L. Kovalenko, G.A. Kozhukhovskaya and G.D. Mal'chikov, *Deposited Doc.*, (1981) SPSTL 966 Khp-D81 [*Chem. Abstr.*, 98 (1983) 96583q].
24. J. Chen, Z. Yang and N. Cui, *Jinshu Xuebao (Acta Metalurgica Sinica)* 18 (1982) 235.
25. W. Preetz and G. Rimkus, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 38B (1983) 442.
26. P.S. Pregosin, M. Kretschmer, W. Preetz and G. Rimkus, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 37B (1982) 1422.
27. R. Kuroda, S. Neidle, I.M. Ismail and P.J. Sadler, *Inorg. Chem.*, 22 (1983) 3620.
28. S. Sato, R. Ikeda and D. Nakamura, *Ber. Bunsenges. Phys. Chem.*, 86 (1982) 936.
29. G. Theile, C. Mrozek, D. Kammerer and K. Wittmann, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 39B (1983) 905.
30. G. Theile and K. Wittmann, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 38B (1983) 674.
31. U. Lee, A. Kobayashi and Y. Sasaki, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C39 (1983) 817.
32. N.U. Venkovskii, B.N. Ivanov-Emin and I.V. Lin'ko, *Zh. Neorg. Khim.*, 28 (1983) 1065.
33. N.E. Dixon, G.A. Lawrance, P.A. Lay and A.M. Sargeson, *Inorg. Chem.*, 22 (1983) 846.

34. P.C. Srivastava and C. Aravindakshan, *Z. Phys. Chem., (Leipzig)*, 264 (1983) 61.
35. G. Rimkus and W. Preetz, *Z. Anorg. Allg. Chem.*, 502 (1983) 73.
36. G.I. Zharkova, I.G. Igumenov and S.V. Zemskov, *Koord. Khim.*, 9 (1983) 845.
37. K.C. Koshy and G.M. Harris, *Inorg. Chem.*, 22 (1983) 2947.
38. K. Banerjee and S. Raychaudhury, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3621.
39. V.V. Vasil'ev, I.A. Konovalova and G.A. Shagisultanova, *Koord. Khim.*, 9 (1983) 1110.
40. S.A. Simanova, G.S. Krylova and Yu. N. Kukushkin, *J. Appl. Chem. USSR*, 55 (1982) 2110.
41. R.A. Krause, A.W. Kozlowski and J.L. Cronin, *Inorg. Synth.*, 21 (1982) 12.
42. E.W. Abel, K.G. Orrell and A.W.G. Platt, *J. Chem. Soc., Dalton Trans.*, (1983) 2345.
43. D.J. Gulliver, A.L. Hale, W. Levason and S.G. Murray, *Inorg. Chim. Acta*, 69 (1983) 25.
44. V.K. Sinha, M.N. Srivastava and H.L. Nigam, *Indian J. Chem., Sect. A*, 22A (1983) 348.
45. N.N. Zheligovskaya and S.V. Al Ansari, *Koord. Khim.*, 9 (1983) 962.
46. N.N. Zheligovskaya and S.V. Al Ansari, *Koord. Khim.*, 9 (1983) 255.
47. H.S. Gowda and R. Janardhan, *Proc.-Indian Acad. Sci., [Ser.]: Chem. Sci.*, 91 (1982) 339.
48. K.C. Mathur, G.S. Saharia, H.R. Sharma and R.C. Saxena, *Chem. Era*, 18 (1982) 255.
49. A. Syamal and B.K. Gupta, *Transition Met. Chem. (Weiheim, Ger.)*, 8 (1983) 36.
50. R. Kuroda, S. Neidle, I.M. Ismail and P.J. Sadler, *J. Chem. Soc., Dalton Trans.*, (1983) 823.
51. A. Vogler and J. Hlavatsch, *Angew. Chem.*, 95 (1983) 153.
52. M. Kretschmer and L. Heck, *Z. Anorg. Allg. Chem.*, 490 (1982) 205.
53. V.A. Palkin, T.A. Kuzina, N.N. Kuz'mina and R.N. Shchelokov, *Zh. Neorg. Khim.*, 28 (1983) 1267.
54. V.V. Lapkin, E.F. Shubochkina and L.K. Subochkin, *Sov. J. Coord. Chem.*, 9 (1983) 548.
55. W. Tang, R. Shao, Y. Guan, A. Zhou, A. Dai, X. Ji and J. Wan, *Kexue Tongbao*, 27 (1982) 607 [*Chem. Abstr.*, 97 (1983) 207122q].
56. N.N. Zheligovskaya, P.S. Al Ansari, I.P. Feranidi and V.I. Spitsyn, *Koord. Khim.*, 9 (1983) 560.
57. D. Atamanov and N.N. Zheligovskaya, *Koord. Khim.*, 8 (1982) 1121.
58. N.N. Zheligovskaya, P.L. Al Ansari and V.I. Spitsyn, *Koord. Khim.*, 9 (1983) 675.
59. E.S. Domnina, V.N. Voropaev, G.G. Skvortsova, S.M. Minakova and V.A. Chernov, *Khim.-Farm. Zh.*, 17 (1983) 700 [*Chem. Abstr.*, 99 (1983) 114957s].
60. E.S. Domina, V.N. Voropaev, G.G. Skvortsova, M.V. Sigalov, T.K. Voropaeva and G.S. Muraveiskaya, *Koord. Khim.*, 9 (1983) 1101.
61. D.G. Craciunescu, A. Doadrio, A. Furlani and V. Scarcia, *Inorg. Chim. Acta*, 67 (1982) L11.
62. L.N. Kolobova, A.K. Pyartman, L.A. Obozova and V.E. Mironov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 26 (1983) 191 [*Chem. Abstr.*, 98 (1983) 186590u].
63. L.N. Kolobova, A.K. Pyartman and V.E. Mironov, *Koord. Khim.*, 8 (1982) 1393.
64. L.R. Gray, D.J. Gulliver, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1983) 133.
65. G. Ferguson, M. Parvez, P.K. Monaghan and R.J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, (1983) 267.
66. H.A. Boucher, G.A. Lawrence, P.A. Lay, A.M. Sargeson, A.M. Bond, D.F. Sangster and J.C. Sullivan, *J. Am. Chem. Soc.*, 105 (1983) 4652.

67. A. Harriman and D. Williams, *J. Electroanal. Chem. Interfacial Electrochem.*, 139 (1982) 413.
68. R. Sambathu and K.G. Srinivasacharya, *Ind. J. Pure Appl. Phys.*, 20 (1982) 834.
69. A.V. Babkov, M.N. Kuznetsova and N.P. Nikolaeva, *Koord. Khim.*, 9 (1983) 130.
70. W.K. Wilmarth, Y.T. Fanchiang and J.E. Byrd, *Coord. Chem. Rev.*, 51 (1983) 141.
71. W.K. Wilmarth, R. Dooly and J.E. Byrd, *Coord. Chem. Rev.*, 51 (1983) 125.
72. M. Tanaka, I. Tsujikawa, K. Toriumi and T. Ito, *Acta Crystallogr., Sect. B: Struct. Sci.*, B38 (1982) 2793.
73. M. Cannas, M.B. Lucchesini and G. Marongiu, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C39 (1983) 1514.
74. R.J.H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, (1983) 761.
75. R.J.H. Clark, M. Kurmoo, A.M.R. Galas and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1983) 1583.
76. M. Yamashita, H. Ito, K. Toriumi and T. Ito, *Inorg. Chem.*, 22 (1983) 1566.
77. G.C. Papavassiliou and D. Layek, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 37B (1982) 1406.
78. C-M. Che, F.H. Herbstein, W.P. Schaefer, R.E. Marsh and H.B. Gray, *J. Am. Chem. Soc.*, 105 (1983) 4604.
79. J.M. Williams, *Inorg. Synth.*, 21 (1982) 141.
80. H. Kobayashi and A. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 81 (1982) 197.
81. G.S.V. Coles, A.E. Underhill, J.M. Williams and A.J. Schultz, *J. Chem. Soc., Dalton Trans.*, (1983) 2529.
82. G.S.V. Coles, A.E. Underhill and K. Carneiro, *J. Chem. Soc., Dalton Trans.*, (1983) 1411.
83. C.A. Bignozzi, C. Bartocci, A. Maldotti and V. Carassiti, *Inorg. Chim. Acta*, 62 (1982) 187.
84. J. Kovacova and J. Gazo, *Zb. Pr. Chemickotechnol. Fak. SVST*, (1981) 35 [*Chem. Abstr.*, 96 (1982) 227972z].
85. J.M. Bret, P. Castan, G. Commenges and J.P. Laurent, *Polyhedron*, 2 (1983) 901.
86. J-M. Bret, P. Castan and J-P. Laurent, *Transition Met. Chem. (Weinheim, Ger.)*, 8 (1983) 218.
87. J-M. Bret, P. Castan, G. Commenges, J-P. Laurent and D. Muller, *J. Chem. Soc., Chem. Commun.*, (1983) 1273.
88. A. Tressaud, S. Khairoun, J.M. Dance, J. Grannec, G. Demazeau and P. Hagenmuller, *C. R. Seances Acad. Sci., Ser. 2*, 295 (1982) 183.
89. B.Ya. Brach and I. Piir, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 19 (1983) 1219 [*Chem. Abstr.*, 99 (1983) 114859m].
90. S.A. Vinogradov, K.P. Balashev and G.A. Shagisultanova, *Koord. Khim.*, 9 (1983) 949.
91. M.L. Conder, F.A. Cotton, L.R. Falvello, S. Han and R.A. Walton, *Inorg. Chem.*, 22 (1983) 1887.
92. L.S. Hollis, M.M. Roberts and S.J. Lippard, *Inorg. Chem.*, 22 (1983) 3637.
93. L.S. Hollis and S.J. Lippard, *Inorg. Chem.*, 22 (1983) 2605.
94. C. Bellitto, A. Flamini, L. Gastaldi and L. Scaramuzza, *Inorg. Chem.*, 22 (1983) 444.
95. T.G. Appleton, J.R. Hall, D.W. Neale and S.F. Ralph, *Inorg. Chem. Acta*, 77 (1983) L149.
96. P. Stein, M.K. Dickson and D.M. Roundhill, *J. Am. Chem. Soc.*, 105 (1983) 3489.
97. K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem.*, 22 (1983) 4086.
98. S. Durand, G. Jugie and J-P. Laurent, *Transition Met. Chem (Weinheim, Ger.)*, 7 (1982) 310.
99. R.I. Rudyi, N.V. Cherkashina, Ya.V. Salyn and I.I. Moiseev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 32 (1983) 1691.

100. D.V. Bamburov, B.D. Vasin, A.S. Kazakov and S.P. Raspopin, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, (1983) 56 [*Chem. Abstr.*, 99 (1983) 130756f].
101. V.V. Safonov and V.A. Mireev, *Russ. J. Inorg. Chem.*, 28 (1983) 1004.
102. M. Geissler, *Z. Chem.*, 22 (1982) 341.
103. J.M. Mestre, X. Montagut, M. Ruiz and L. Victori, *Afinidad*, 39 (1982) 484.
104. K.M. Neiman, A.V. Kondratenko, L.N. Mazalov, E.A. Kravtsova, L.V. Molchanova and V.A. Nasluzov, *Zh. Strukt. Khim.*, 24 (1983) 106.
105. S. Ohba, S. Sato, Y. Saito, K. Ohshima and J. Harada, *Acta Crystallogr., Sect. B: Struct. Sci.*, B38 (1983) 49.
106. Yu.N. Kukushkin and V.N. Demidov, *Zh. Neorg. Khim.*, 27 (1982) 2839.
107. H. Hagemann and H. Bill, *Chem. Phys. Lett.*, 90 (1982) 282.
108. B.G. Mueller, *Z. Anorg. Allg. Chem.*, 491 (1982) 245.
109. L.G. Kuz'mina and Yu. T. Struchkov, *Sov. J. Coord. Chem.*, 9 (1983) 407.
110. O.V. Sizova, N.V. Ivanova and V.I. Baranovskii, *Sov. J. Coord. Chem.*, 8 (1982) 872.
111. J. Mink and P.L. Goggin, *Kem. Kozl.*, 58 (1982) 215 [*Chem. Abstr.*, 99 (1983) 12876x].
112. I.A. Selezneva. S.N. Ivanova and L.M. Gindin, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (1982) 107 [*Chem. Abstr.*, 98 (1983) 60702p].
113. S.I. Pechenyuk, *Deposited Doc.*, (1981) VINITI 5186-81 [*Chem. Abstr.*, 98 (1983) 8473a].
114. V.V. Zamashchikov, E.S. Rudakov and A.P.Yaroshenko, *React. Kinet. Catal. Lett.*, 22 (1983) 39.
115. Z. Xiang and L. Dai, *Jiegou Huaxue*, 1 (1982) 51 [*Chem. Abstr.*, 98 (1983) 188560h].
116. R.F. Gur'eva, S.B. Savvin, L.M. Trutneva and N.N. Chalisova, *Zh. Anal. Khim.*, 38 (1983) 881.
117. U. Sassenberg and R. Scullman, *Phys. Scr.*, 28 (1983) 139.
118. V.A. Levitskii, P.B. Narchuk, M.L. Kovba and Yu.Ya. Skolis, *Zh. Fiz. Khim.*, 56 (1982) 2405.
119. N.A. Shorokhov, A.A. Vashman, V.E. Samsonov, R.N. Chuklinov and V.S. Shmidt, *Zh. Neorg. Khim.*, 27 (1982) 3137.
120. G. Strukul, R.A. Michelin, J.D. Orbell and L. Randaccio, *Inorg. Chem.*, 22 (1983) 3706.
121. E.S. Rudakov, A.I. Lutsyk and A.P. Yaroshenko, *Ukr. Khim. Zh., (Russ. Ed.)*, 49 (1983) 1083 [*Chem. Abstr.*, 99 (1983) 194215m].
122. V.L. Lebedev, A.A. Bagatur'yants, G.M. Zhidomirov and V.B. Kazanskii, *Zh. Fiz. Khim.*, 57 (1983) 1057.
123. D.T. Haworth, M.R. Pitluck, B.D. Pollard and M. Das, *Synth. React. Inorg. Met.-Org. Chem.*, 13 (1983) 601.
124. G.D. Fallon and B.M. Gatehouse, *Cryst Struct. Commun.*, 11 (1982) 1317.
125. E.W. Berg, N.M. Herrera and C.L. Modenbach, *Inorg. Chem.*, 22 (1983) 1991.
126. M. Das, *Inorg. Chim. Acta*, 76 (1983) L111.
127. B.K. Sahu and B.K. Mohapatra, *J. Indian Chem. Soc.*, 59 (1982) 723.
128. B.K. Sahu and B.K. Mohapatra, *Indian J. Chem., Sect. A*, 21A (1982) 730.
129. S. Okeya, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1460.
130. A.R. Siedle, R.A. Newmark and L.H. Pignolet, *Inorg. Chem.*, 22 (1983) 2281.
131. B.K. Sahu, S.B. Misra and B.K. Mohapatra, *Indian J. Chem., Sect. A*, 21A (1982) 823.
132. B.K. Sahu, S.B. Misra and B.K. Mohapatra, *Curr. Sci.*, 51 (1982) 193.
133. S. Ooi, T. Matsushita, K. Nishimoto, Y. Nakamura and S. Kawaguchi, *Inorg. Chim. Acta*, 76 (1983) L55.
134. S. Okeya, Y. Nakamura, S. Kawaguchi and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 55 (1982) 477.

135. Y. Otani, Y. Nakamura, S. Kawaguchi, S. Okeya and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1467.
136. S. Okeya, Y. Kawakita, S. Matsumoto, Y. Nakamura, S. Kawaguchi, N. Kanehisa, K. Miki and N. Kasai, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2134.
137. B. Vlckova, B. Strauch and M. Ebert, *Proc. Conf. Coord. Chem.*, (1983) 9th, 455 [*Chem. Abstr.*, 99 (1983) 79271q].
138. L.A. Il'yukevich and L.N. Neokladnova, *Khim. Vys. Energ.*, 16 (1982) 471 [*Chem. Abstr.*, 97 (1982) 227336r].
139. S.N. Mal'chenko, G.A. Branitskii, V.I. Grigorenko and V.V. Sviridov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 26 (1983) 656 [*Chem. Abstr.*, 99 (1983) 113641x].
140. G. Al-Takhin, G. Pilcher, J. Bickerton and A.A. Zaki, *J. Chem. Soc., Dalton Trans.*, (1983) 2657.
141. M.V. Capparelli, D.M.L. Goodgame, R.T. Riley and A.C. Scapski, *Inorg. Chim. Acta*, 67 (1982) L9.
142. J. Kuduk-Jaworska and B. Jezowska-Trzebiatowska, *Pol. J. Chem.*, 55 (1981) 1143.
143. O. Gandolfi and J. Blum, *Inorg. Chim. Acta*, 80 (1983) 103.
144. J.S. Jessup, E.N. Duesler and R.T. Paine, *Inorg. Chim. Acta*, 73 (1983) 261.
145. A.V. Fedin and M.Z. Yampol'skii, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 26 (1983) 62 [*Chem. Abstr.*, 98 (1983) 114120t].
146. L.K. Bell, J. Mason, D.M.P. Mingos and D.G. Tew, *Inorg. Chem.*, 22 (1983) 3497.
147. U. Casellato, S. Tamburini, P.A. Vigato, A. De Stefani, M. Vidali and D.E. Fenton, *Inorg. Chim. Acta*, 69, (1983) 45.
148. J.F. Endicott and R.L. Lintvedt, *Report* 1982 DOE/ER/04685-2 [*Chem. Abstr.*, 99 (1983) 186360q].
149. H.M. Colquhoun, D.F. Lewis, J.F. Stoddart and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, (1983) 607.
150. G. Bruno, G. Bombieri, G. Alibrandi, S. Lanza and R. Romeo, *Cryst. Struct. Commun.*, 11 (1982) 1369.
151. Yu.N. Kukushkin and V.N. Demidov, *J. Gen. Chem. USSR*, 53 (1983) 1286.
152. G. Annibale, L. Cattalini, L. Canovese, G. Michelon, G. Marangoni and M.L. Tobe, *Inorg. Chem.*, 22 (1983) 975.
153. L. Canovese, L. Cattalini, G. Marangoni, G. Michelon, M. Nicolini and M.L. Tobe, *J. Coord. Chem.*, 12 (1983) 63.
154. T. Hoover and A.P. Zipp, *Inorg. Chim. Acta*, 63 (1982) 9.
155. S. Lanza, D. Minniti, R. Romeo and M.L. Tobe, *Inorg. Chem.*, 22 (1983) 2006.
156. V.I. Vshivtsev, N.N. Patrusheva and E.P. Mironova, *Deposited Doc.*, (1982) SPSTL 85 Khp-D82 [*Chem. Abstr.*, 98 (1983) 136558u].
157. D.K. Breitinger, G. Petrikowski and G. Bauer, *Acta Crystallogr., Sect. B*, B38 (1982) 2997.
158. J. Howard, J. Tomkinson, J. Eckert, J.A. Goldstone and A.D. Taylor, *J. Chem. Phys.*, 78 (1983) 3150.
159. D.T. Haworth and M. Das, *J. Inorg. Nucl. Chem.*, 43 (1981) 3015.
160. S.V. Kovalenko and G.D. Mal'chikov, *Zh. Neorg. Khim.*, 27 (1982) 3125.
161. J.L. Davidson, P.N. Preston and M.V. Russo, *J. Chem. Soc., Dalton Trans.*, (1983) 783.
162. E. Fritsch, B. Gorski, M. Beer, J. Beger and R. Jacobi, *Z. Chem.*, 23 (1983) 193.
163. H. Elias, *Proc. Conf. Coord. Chem.*, 1983, 9th, 79 [*Chem. Abstr.*, 99 (1983) 77564p].
164. K. Isa and Y. Yamada, *Shitsuryo Bunseki*, 31 (1983) 55 [*Chem. Abstr.*, 99 (1983) 81572q].
165. J.B. Westmore and D.K.C. Fung, *Inorg. Chem.*, 22 (1983) 902.
166. A. Gul and O. Bekaroglu, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 889.
167. T.J. Kistenmacher and R. Destro, *Inorg. Chem.*, 22 (1983) 2104.

168. A.G. Constable, W.S. McDonald, B. Odell and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1983) 2509.
169. C. Natarajan and A.N. Hussain, *Transition Met. Chem. (Weinheim, Ger.)*, 7 (1982) 252.
170. A. Gül and O. Bekâroğlu, *J. Chem. Soc., Dalton Trans.*, (1983) 2537.
171. M. Massacesi, R. Pinna, M. Biddau, G. Ponticelli and I.A. Zakharova, *Inorg. Chim. Acta*, 80 (1983) 151.
172. A.T. Hutton, D.M. McEwan, B.L. Shaw and S.W. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1983) 2011.
173. A. Syamal, B.K. Gupta and S. Ahmed, *Curr. Sci.*, 51 (1982) 1153.
174. M.S. Masoud and A.F.A. Elmoneim, *Izv. Khim.*, 14 (1981) 399 [*Chem. Abstr.*, 98 (1983) 23050d].
175. A.I. Stetsenko, L.I. Shigina, A.I. Mokhov and L.S. Tikhonova, *Zh. Neorg. Khim.*, 27 (1982) 2834.
176. J. Kragten and L.G. Decnop-Weever, *Talanta*, 30 (1983) 449.
177. V.I. Kornev, V.A. Valyaeva and L.N. Churakova, *Koord. Khim.*, 9 (1983) 1264.
178. F.G. Vilchez, J.M.L. Alaca and M.G. Basallote, *Thermochim. Acta*, 58 (1982) 317.
179. M.C. Martos, F.G. Vilchez and E.R. Carrasco, *Thermochim. Acta*, 60 (1983) 131.
180. L.S. Hollis and S.J. Lippard, *Inorg. Chem.*, 22 (1983) 2600.
181. T.V. O'Halloran and S.J. Lippard, *J. Amer. Chem. Soc.*, 105 (1983) 3341.
182. L.S. Hollis and S.J. Lippard, *J. Amer. Chem. Soc.*, 105 (1983) 3494.
183. W. Clegg, C.D. Garner, L. Akhter and M.H. Al-Samman, *Inorg. Chem.*, 22 (1983) 2466.
184. H. Elias, E. Hilms and H. Paulus, *Z. Naturforsch., B; Anorg. Chem., Org. Chem.*, 37B (1983) 1266.
185. K. Lal and S.R. Malhotra, *An. Quim., Ser. B*, 79 (1983) 56.
186. M. Mittal, K. Lal and S.P. Gupta, *J. Indian Chem. Soc.*, 60 (1983) 188.
187. S. Srihari and N.A. Raju, *J. Indian Inst. Sci.*, 64 (1983) 45 [*Chem. Abstr.*, 99 (1983) 186342k].
188. G.N. Gorbunova and V.M. Ivanov, *Deposited Doc.*, 1980 VINITI 2843-80 [*Chem. Abstr.*, 96 (1982) 92411t].
189. M.J. Ruedas and J.L.P. Gonzalez, *Bol. Soc. Quim. Peru*, 48 (1982) 26 [*Chem. Abstr.*, 98 (1983) 190559h].
190. M.R. Mahmoud, F.A. Adam, K. Yousef and M.T. El-Haty, *Bull. Soc. Chim. Belg.*, 92 (1983) 13.
191. P.K. Biswas, M.K. Dasgupta, S. Mitra and R. Chaudhur, *J. Coord. Chem.*, 11 (1982) 225.
192. J.R. Lusty and P. Pollet, *Inorg. Chim. Acta*, 78 (1983) L7.
193. J.M. Tsangaris and T.A. Kabanos, *Monatsh. Chem.*, 113 (1982) 1393.
194. K. Hiraki, M. Onishi, M. Hayashida and K. Kurita, *Bull. Chem. Soc. Jpn.*, 56 (1983) 1410.
195. V.J. Babar and V.M. Shinde, *Indian J. Chem., Sect. A*, 22A (1983) 447.
196. G.P. Pokhariyal, *J. Indian Chem. Soc.*, 60 (1983) 132.
197. R. Robson, *Inorg. Chim. Acta*, 57 (1982) 71.
198. R.P. Mathur, P. Mathur and R.K. Mehta, *Curr. Sci.*, 52 (1983) 481.
199. G. Read, M. Urgelles, A.M.R. Galas and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1983) 911.
200. M. Tubino and A.E. Merbach, *Inorg. Chim. Acta*, 71 (1983) 149.
201. M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M.L. Tobe, *Inorg. Chem.*, 22 (1983) 902.
202. E.A. Andronov, A.L. Ryazanov, Yu.V. Murashkin and A.K. Pyartman, *Deposited Doc.*, (1981) SPSTL 648 Khp-D81 [*Chem. Abstr.*, 98 (1983) 41409g].
203. O.A. Bozhenova, V.G. Kharchenko and A.D. Shebaldova, *Koord. Khim.*, 9 (1983) 1096.
204. R.L. Batstone-Cunningham, H.W. Dodgen, J.P. Hunt and D.M. Roundhill, *J. Chem. Soc., Dalton Trans.*, (1983) 1473.

205. P.H. Bird, U. Siriwardane, R.D. Lai and A.Shaver, *Canad. J. Chem.*, 60 (1982) 2075.
206. K. Ogura, T. Aizawa, K. Uchiyama and H. Iida, *Bull. Chem. Soc. Jpn.*, 56 (1983) 953.
207. P.N. D'yachkov and A.A. Levin, *Zh. Neorg. Khim.*, 28 (1983) 275.
208. V.V. Sibirskaya, N.V. Vorob'ev-Desyatovskii, A.I. Petrov and V.V. Strukov, *J. Gen. Chem. USSR*, 53 (1983) 780.
209. V.M. Kiseleva, M.I. Gel'fman and T.A. Mel'nikova, *Deposited Doc.*, (1982) SPSTL 657 Khp-D82 [*Chem. Abstr.*, 100 (1984) 180781v].
210. A. Furlani, V. Scarcia, G. Faraglia, L. Sindellari and B. Zarli, *Inorg. Chim. Acta*, 67 (1982) L41.
211. G. Faraglia, L. Sindellari, L. Chiavegato and S. Sitran, *Inorg. Chim. Acta*, 76 (1983) L103.
212. T.S. Lobana and K. Sharma, *Transition Met. Chem. (Weinheim, Ger.)*, 7 (1982) 333.
213. C.E. Briant, T.S.A. Hor, N.D. Howells and D.M.P. Mingos, *J. Chem. Soc., Chem. Commun.*, (1983) 1118.
214. A.A. Pasynskii, I.L. Eremenko, O.G. Ellert, V.M. Novotortsev, Yu.V. Rakitin, V.T. Kalinnikov, V.E. Shklover, Yu.T. Struchkov, G.Sh. Gasanov and T.Kh. Kurbanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 31 (1982) 2325.
215. D. Seyferth, B.W. Hames, T.G. Rucker, M. Cowie and R.S. Dickson, *Organometallics*, 2 (1983) 472.
216. C.E. Briant, M.J. Calhorda, T.S.A. Hor, N.D. Howells and D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.*, (1983) 1325.
217. M.I. Gel'fman and V.V. Solomentsev, *Deposited Doc.*, (1980) SPSTL 885 Khp-D80, 12 [*Chem. Abstr.*, 97 (1982) 84074r].
218. M.H. Torrens, *Rev. Soc. Quim. Mex.*, 26 (1982) 118 [*Chem. Abstr.*, 98 (1983) 10591f].
219. L.R. Gray, D.J. Gulliver, W. Levason and M. Webster, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C39 (1983) 877.
220. L.R. Gray, D.J. Gulliver, W. Levason and M. Webster, *Inorg. Chem.*, 22 (1983) 2362.
221. P. Shao, C. Chao, M. Gui and W. Gan, *Gaodeng Xuexiao Huaxue Xuebao*, 4 (1983) 189 [*Chem. Abstr.*, 99 (1983) 77720m].
222. E.W. Abel, S.K. Bhargava, K. Kite, K.G. Orrell, V. Sik and B.L. Williams, *Polyhedron*, 1 (1982) 289.
223. E.W. Abel, K. Kite and B.L. Williams, *J. Chem. Soc., Dalton Trans.*, (1983) 1017.
224. G. Dessy, V. Fares, C. Bellitto and A. Flamini, *Cryst. Struct. Commun.*, 11 (1982) 1743.
225. G.A. Bowmaker, P.D.W. Boyd and G.K. Campbell, *Inorg. Chem.*, 22 (1983) 1208.
226. G.A. Heath and J.H. Leslie, *J. Chem. Soc., Dalton Trans.*, (1983) 1587.
227. M.M. Ahmad and A.E. Underhill, *J. Chem. Soc., Dalton Trans.*, (1983) 165.
228. C.E. Johnson, R. Eisenberg, T.R. Evans and M.S. Burberry, *J. Am. Chem. Soc.*, 105 (1983) 1795.
229. R.D. Lai, Ph. D. Thesis, McGill University, Montreal, *Diss. Abstr. Int. B*, 43 (1982) 1094.
230. S.A. Bryan and D.M. Roundhill, *Acta Crystallogr., Sect. C*, C39, (1983) 184.
231. V.P. Vozdvizhenskii, Kh.K. Ospanov, U.I. Sholtyreva, N.Kh. Ospanova and Yu.Ya. Kharitonov, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, (1983) 1 [*Chem. Abstr.*, 99 (1983) 184201q].
232. D. Troy and J.P. Legros, *Phosphorus Sulphur*, 14 (1983) 377.
233. J.P. Legros and D. Troy, *Acta Crystallogr., Sect. B: Struct. Sci.*, B39 (1983) 337.
234. H.S. Sangari, N.K. Kaushik and R.P. Singh, *Therm. Anal., Proc. Int. Conf., 7th*, 1 (1981) 402 [*Chem. Abstr.*, 99 (1983) 186313b].

235. N.K. Kaushik, G.R. Chhatwal and A.K. Sharma, *Thermochim. Acta*, 58 (1982) 231.
236. M. Moriyasu, Y. Hashimoto and M. Endo, *Bull. Chem. Soc. Jpn.*, 56 (1983) 1972.
237. H.B. Singh, S. Maheshwari and H. Tomer, *Thermochim. Acta*, 64 (1983) 47.
238. A.B. Goel, S. Goel, D. Van Derveer and C.G. Brinkley, *Inorg. Chim. Acta*, 64 (1982) L173.
239. R. Schierl and W. Beck, *Chem. Ber.*, 115 (1982) 1665.
240. B.K. Nefedov, V.I. Manov-Yuvenskii, V.A. Semikolenov, V.A. Likholobov and Yu.I. Ermakov, *Kinet. Katal.*, 23 (1982) 1001.
241. L. Maijs, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, (1983) 374 [*Chem. Abstr.*, 99 (1983) 93927q].
242. G. Mezaraupe, E. Jansons, V. Zvirbule and A. Krismane, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, (1983) 118 [*Chem. Abstr.*, 98 (1983) 197714p].
243. D.H. Farrar, R. Taylor and A. Walker, *Inorg. Chim. Acta*, 64 (1982) L195.
244. H. Werner, W. Bertleff, B. Zimmer-Gasser and U. Schubert, *Chem. Ber.*, 115 (1982) 1004.
245. J.J. MacDougall, J.H. Nelson, W.C. Fultz, J.L. Burmeister, E.M. Holt and N.W. Alcock, *Inorg. Chim. Acta*, 63 (1982) 75.
246. B.G. Sodnomov, V.K. Polovnyak and A.D. Troitskaya, *Deposited Doc.*, (1980) SPSTL 80 Khp-D80 [*Chem. Abstr.*, 96 (1982) 92662a].
247. M. Mares, D.A. Palmer and H. Kelm, *Inorg. Chim. Acta*, 60 (1982) 123.
248. E.A. Andronov, A.L. Ryazanov, Yu.V. Murashkin, A.K. Pyartman and M.S. Kuznetsov, *Deposited Doc.*, (1981) SPSTL 647 Khp-081 [*Chem. Abstr.*, 98 (1982) 114446d].
249. S.J. Al-Bazi and A. Chow, *Talanta*, 30 (1983) 487.
250. R. Uson, J. Fornies, A. Laguna and J.I. Valenzuela, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 935.
251. I.V. Zhakova, A.D. Garnovskii, Yu.V. Kolodyazhnyi and L.Yu. Ukhin, *Koord. Khim.*, 9 (1983) 1143.
252. A. Syamal and B.K. Gupta, *Rev. Chim. Miner.*, 20 (1983) 123.
253. I. Kinoshita, Y. Yasuba, K. Matsumoto and S. Ooi, *Inorg. Chim. Acta*, 80 (1983) L13.
254. C.R. Saha and N.K. Roy, *J. Coord. Chem.*, 12 (1983) 163.
255. K. Chakrabarty and S.P. Sen Gupta, *Indian J. Phys., A*, 57A (1983) 205.
256. V. Muresan and N. Muresan, *An. Univ. Craiova, [Ser.]: Mat., Fiz.-Chim.*, 8 (1980) 97 [*Chem. Abstr.*, 97 (1982) 229011e].
257. M. Friese, F. Dietze, R. Szargan, E. Hoyer and H.U. Kibbel, *Z. Chem.*, 22 (1982) 455.
258. S. Chandra, *Synth. React. Inorg. Met.-Org. Chem.*, 13 (1983) 89.
259. A.A. Dobrov and N.V. Gerbeleu, *Zh. Neorg. Khim.*, 28 (1983) 1764.
260. A. El-Toukhy, M. El-Essawi, M. Tawfik, L. El-Sayed and M.F. Iskander, *Transition Met. Chem. (Weinheim, Ger.)*, 8 (1983) 116.
261. D. Miernik and B.B. Kedzia, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 30 (1982) 71 [*Chem. Abstr.*, 99 (1983) 166118p].
262. R.Roy, S.K. Mondal and K. Nag, *J. Chem. Soc., Dalton Trans.*, (1983) 1935.
263. G. Ferguson, R. McCrindle, A.J. McAlees, M. Parvez and D.K. Stephenson, *J. Chem. Soc., Dalton Trans.*, (1983) 1865.
264. J. Browning, G.W. Bushnell, K.R. Dixon and A. Pidcock, *Inorg. Chem.*, 22 (1983) 2226.
265. G. Ferguson, R. McCrindle and M. Parvez, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C39 (1983) 993.
266. J.W. Gosselink, F. Paap and G. Van Koten, *Inorg. Chim. Acta*, 59 (1982) 155.
267. W.H. Pan and J.P. Fackler, *Inorg. Synth.*, 21 (1982) 6.
268. E. Matczak-Jon and H. Kozlowski, *Wiad. Chem.*, 36 (1982) 177 [*Chem. Abstr.*, 98 (1983) 154120z].
269. T.G. Appleton and J.R. Hall, *J. Chem. Soc., Chem. Commun.*, (1983) 911.

270. A.L. Kaufman, R.G. Golovchanskaya and V.P. Nikolaev, *Tr.-Mosk. Khim.-Tekhnol. Inst. im. D. I. Mendeleeva*, 121 (1982) 158 [*Chem. Abstr.*, 98 (1983) 133099j].
271. Yu.Ya. Kharitonov, H. Bissinger, E. Ambach and W. Beck, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 37B (1982) 1034.
272. E. Ambach, U. Nagel and W. Beck, *Chem. Ber.*, 116 (1983) 659.
273. M-C. Lin, *J. Chem. Soc., Dalton Trans.*, (1983) 1675.
274. W. Tang, K. Yan and A. Dai, *Huaxue Xuebao*, 41 (1983) 111 [*Chem. Abstr.*, 99 (1983) 114877r].
275. Q. Yang, Y. Tang, W. Tang and K. Yan, *Wuli Xuebao*, 31 (1982) 1550 [*Chem. Abstr.*, 98 (1983) 81797p].
276. X. Xu, G. Zhou, Y. Tang, W. Tang, K. Yan and A. Dai, *Sci. Sin., Ser. B (Engl. Ed.)*, 26 (1983) 689 [*Chem. Abstr.*, 99 (1983) 131603].
277. O.P. Slyudkin, *Russ. J. Inorg. Chem.*, 28 (1983) 550.
278. O.P. Slyudkin and B.J.F. Norden, *Inorg. Chem.*, 22 (1983) 2637.
279. K.M. Trusova and N.N. Chemova, *Zh. Neorg. Khim.*, 27 (1982) 2847.
280. L. Kumar, N.R. Kandasamy and T.S. Srivastava, *Inorg. Chim. Acta*, 67 (1982) 139.
281. L.E. Erickson, T.E. Ferrett and L.F. Buhse, *Inorg. Chem.*, 22 (1983) 1461.
282. V.S. Kravchenko, G.D. Zegzhda, V.P. Morozov and Z.I. Sour, *Russ. J. Inorg. Chem.*, 28 (1983) 852.
283. V.S. Kravchenko, G.D. Zegzhda and V.P. Morozov, *Zh. Neorg. Khim.*, 28 (1983) 1760.
284. D. Dalietos, A. Furst and D. Theodoropoulos, *Biol. Trace Elem. Res.*, 4 (1982) 331.
285. H. Kozlowski, B. Decock-Le Reverend, J.L. Delaruelle, C. Loucheux and B. Ancian, *Inorg. Chim. Acta*, 78 (1983) 31.
286. S. Xu, X. Liu, G. Sun and K. Wang, *Fenxi Kexue Xuebao*, 2 (1982) 19 [*Chem. Abstr.*, 98 (1983) 60708v].
287. T. Kowalik, H. Kozlowski and B. Decock-Le Reverend, *Inorg. Chim. Acta*, 67 (1982) L39.
288. H. Kozlowski and E. Matczak-Jon, *Pol. J. Chem.*, 55 (1983) 2243.
289. N. Ueyama, K. Sasaki, M. Nakata and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2364.
290. L.J. Lijk, K.H. Kalk, N.P. Brandenburg and W.G.J. Hol, *Biochemistry*, 22 (1983) 2952.
291. R.G. Bhattacharyya and I. Bhadhuri, *J. Indian Chem. Soc.*, 59 (1982) 919.
292. U.K. Haring and R.B. Martin, *Inorg. Chim. Acta*, 80 (1983) 1.
293. A. Skauge and P.I. Vestues, *Acta Chem. Scand., Ser. A*, A37 (1983) 47.
294. G. Pneumatikakis, *Inorg. Chim. Acta*, 80 (1983) 89.
295. B.T. Khan, G.N. Goud and S.V. Kumari, *Inorg. Chim. Acta*, 80 (1983) 145.
296. W. Kadima and M. Zador, *Inorg. Chim. Acta*, 78 (1983) 97.
297. N. Hadjiliadis, G. Pnuematikakis and S. Paraskevas, *Chem. Chron.*, 11 (1982) 11.
298. L. Kumar and T.S. Srivastava, *Inorg. Chim. Acta*, 80 (1983) 47.
299. A.T.M. Marcelis, J.L. Van der Veer, J.C.M. Zwetsloot and J. Reedijk, *Inorg. Chim. Acta*, 78 (1983) 195.
300. A. Terzis and D. Mentzafos, *Inorg. Chem.*, 22 (1983) 1140.
301. S.A. D'yachenko, D.N. Bochkov, N.A. Smorygo, A.I. Stetsenko, E.P. Studentsov, V.I. Danevich and B.A. Ivin, *Koord. Khim.*, 9 (1983) 410.
302. B. Lippert, D. Neugebauer and G. Raudaschl, *Inorg. Chim. Acta*, 78 (1983) 161.
303. A.A. Zaki, C.A. McAuliffe, M.E. Friedman, W.E. Hill and H.H. Kohl, *Inorg. Chim. Acta*, 69 (1983) 93.
304. U.K. Haring and R.B. Martin, *Inorg. Chim. Acta*, 78 (1983) 259.
305. B. Jezowska-Trzebiatowska and S. Wolowiec, *Biochim. Biophys. Acta*, 708 (1982) 12.

306. M. Sabat, K.A. Satyshur and M. Sundaralingam, *J. Am. Chem. Soc.*, 105 (1983) 976.
307. D. Neugebauer and B. Lippert, *Inorg. Chim. Acta*, 67 (1982) 151.
308. A. Adeyemo, A. Shamin, A. Turner and K. Akinade, *Inorg. Chim. Acta*, 78 (1983) 191.
309. A. Adeyemo, A. Shamin and A. Turner, *Inorg. Chim. Acta*, 78 (1983) L23.
310. K. Inagaki and Y. Kidani, *Inorg. Chim. Acta*, 80 (1983) 171.
311. J.H.J. Den Hartog, C. Altona, J.H. Van Boom, A.T.M. Marcelis, G.A. Van der Marel, L.J. Rinkel, G. Wille-Hazeleger and J. Reedijk, *Eur. J. Biochem.*, 134 (1983) 485.
312. A.T.M. Marcelis, J.H.J. Den Hartog, G.A. Van der Marel, G. Wille and J. Reedijk, *Eur. J. Biochem.*, 135 (1983) 343.
313. M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, J.G. Haasnnot and J. Reedijk, *Inorg. Chim. Acta*, 72 (1983) 81.
314. W. Tang, R. Shao, Y. Guan, A. Zhou, A. Che, A. Dai, A. Tai, K. Ji and J. Wan, *Kexue Tongbao*, 28 (1983) 54 [*Chem. Abstr.*, 99 (1983) 32213g].
315. T. Solin, K. Matsumoto and K. Fuwa, *Inorg. Chim. Acta*, 65 (1982) L171.
316. J.R. Bales, C.J. Coulson, D.W. Gilmour, M.A. Mazid, S. Neidle, R. Kuroda, B.J. Peart, C.A. Ramsden and P.J. Sadler, *J. Chem. Soc., Chem. Commun.*, (1983) 432.
317. A. Pasini, E. Bersanetti, F. Zunino and G. Savi, *Inorg. Chim. Acta*, 80 (1983) 99.
318. N.P. Johnson, J.P. Macquet, J.L. Weibers and B. Monsarrat, *Nucleic Acids Res.*, 10 (1982) 5255.
319. L. Zhu, Y. Chu and W. Tang, *Kexue Tongbao*, 27 (1982) 1491 [*Chem. Abstr.*, 99 (1983) 11048s].
320. I.V. Lipnitskii, N.L. Rogalevich, I.K. Skutov, L.N. Neokladnova and N.M. Ksenofontova, *Deposited Doc.*, (1982) VINITI 186-82, 23 [*Chem. Abstr.*, 98 (1983) 80765q].
321. N.N. Zheligovskaya, N.A. Chernova, R.G. Kiselev and V.I. Spitsyn, *Soviet J. Coord. Chem.*, 9 (1983) 380.
322. C.A. Bignozzi, C. Bartocci, C. Chiorboli and V. Carassiti, *Inorg. Chim. Acta*, 70 (1983) 87.
323. Y-T. Fanchiang, G.T. Bratt and H.P.C. Hogenkamp, *J. Chem. Soc., Dalton Trans.*, (1983), 1929.
324. R.N. Shelkov, A.Yu. Tsivadze, T.V. Paatashvili and T.N. Leonova, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 19 (1983) 1391 [*Chem. Abstr.*, 99 (1983) 168424j].
325. R.N. Shchelokov, A.Yu. Tsivadze, T.V. Paatashvili and T.N. Leonova, *Zh. Neorg. Khim.*, 28 (1983) 1888.
326. G. Al Takhin, H.A. Skinner and A.A. Zaki, *J. Chem. Soc., Dalton Trans.*, (1983) 2323.
327. A.V. Babkov, A.L. Vorontsov and A.B. Golovkin, *Koord. Khim.*, 8 (1982) 1523.
328. L. Guczi and F. Till, *Mater. Sci. Monogr.*, 10 (React. Solids, v 2) (1982) 908 [*Chem. Abstr.*, 98 (1983) 150184a].
329. M.I. Gel'fman, L.A. Ezhova and Yu. A. Makashev, *Deposited Doc.*, (1981) VINITI 664-82 [*Chem. Abstr.*, 98 (1983) 171898b].
330. R. Gosling and M.L. Tobe, *Inorg. Chem.*, 22 (1983) 1235.
331. A. Peloso, *J. Chem. Soc., Dalton Trans.*, (1983), 1285.
332. V.I. Bystrenina, A.D. Shebaldova, T.G. Nikolaeva, A.P. Krivenk'ko, L.K. Kulikova, E.I. Boreko, L.V. Korobchenko and G.V. Vladyko, *Khim.-Farm. Zh.*, 17 (1983) 173 [*Chem. Abstr.*, 98 (1983) 171952q].
333. V.I. Kornev, V.A. Valyaeva, T.I. Volkova and R.G. Killeev, *Oktsitt.-vosstanov. i Adsorbtion. Protessy na Poverkhnosti Tverd. Met., Izhevsk*, (1980) 171 [*Chem. Abstr.*, 97 (1982) 61896w].
334. N. Katsaros, J.M. Tsangaris and G.M. Tsangaris, *Monatsh. Chem.*, 114 (1983) 27.
335. D.T. Eadie, A. Pidcock, S.R. Stobart, E.T. Brennan and T.S. Cameron, *Inorg. Chim. Acta*, 65 (1982) L111.

336. V.V. Belova and A.A. Vasil'eva, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, (1982) 87 [*Chem. Abstr.*, 98, (1983) 41586n].
337. M.A. Sarukhanov, Sh.M. Mridkha and Yu.Ya. Kharitonov, *Sov. J. Coord. Chem.*, 8 (1982) 677.
338. M.A. Sarukhanov, M.Sh. Mridkha, Yu.Ya. Kharitanov, N.D. Mitkinova and T.G. Abzaeva, *Russ. J. Inorg. Chem.*, 28 (1983) 1158.
339. M. Martin, M-B. Krogh-Jespersen, M. Hsu, J. Tewksbury, M. Laurent, K. Viswanath and H. Patterson *Inorg. Chem.*, 22 (1983) 647.
340. V.I. Berezin, V.V. Ganin, A.B. Kovikov, I.V. Lipnitskii and N.L. Rogalevich, *Zh. Prikl. Spectrosk.*, 38 (1983) 434 [*Chem. Abstr.*, 98 (1983) 169608p].
341. Yu.N. Kukushkin and R.A. Vlasova, *Zh. Obshch. Khim.*, 53 (1983) 948.
342. R. Rumin and P. Courtot, *J. Photochem.*, 20 (1982) 107.
343. M.S. El-Ezaby and H.M. Abu-Soud, *Inorg. Chim. Acta*, 67 (1982) 121.
344. L.S. Hollis and S.J. Lippard, *Inorg. Chem.*, 22 (1983) 2708.
345. K.E. Schwarzhans and A. Stuefer, *Monatsh. Chem.*, 114 (1983) 137.
346. Yu.N. Kukushkin, G.Kh. Khamnuev and K.A. Davarskii, *Zh. Neorg. Chem.*, 27 (1982) 2688.
347. T.N. Hazarika and T. Bora, *Indian J. Chem., Sect. A*, 22A (1983) 439.
348. T.N. Hazarika and T. Bora, *Transition Met. Chem. (Weinheim, Ger.)*, 7 (1982) 210.
349. M.C. Navarro-Ranninger, S. Martinez-Carrera and S. Garcia-Blanco, *Acta Crystallogr., Sect. C*, C39 (1983) 186.
350. M.C. Navarro-Ranninger, S. Martinez-Carrera and S. Garcia-Blanco, *Acta Crystallogr., Sect. C*, C39 (1983) 188.
351. V. Callaghan, D.M.L. Goodgame and R.P. Tooze, *Inorg. Chim. Acta*, 78 (1983) L1.
352. G. Banditelli, A.L. Bandini, F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, 60 (1982) 93.
353. J.L. Atwood, K.R. Dixon, D.T. Eadie, S.R. Stobart and M.J. Zaworotko, *Inorg. Chem.*, 22 (1983) 774.
354. P.P. Dos Santos Filho, L.A. Ortella do Zelada and U. Schuchardt, *Quim. Nova*, 6 (1983) 69 [*Chem. Abstr.*, 99 (1983) 98176d].
355. U. Schuchardt and P.F. Dos Santos Filho, *J. Chem. Res., Synop.*, (1983) 122.
356. P. Umpathy and R.A. Harnesswala, *Polyhedron*, 2 (1983) 129.
357. K.S. Siddiqi, P. Khan, S. Khan and S.A.A. Zaidi, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 681.
358. B.G. Anex and W.P. Peltier, *Inorg. Chem.*, 22 (1983) 643.
359. S.D. Cutbush, R. Kuroda, S. Neidle and A.B. Robins, *J. Inorg. Biochem.*, 18 (1983) 213.
360. Yu.N. Kukushkin, E.N. Kalyukova and V.F. Yustratova, *Koord. Khim.*, 9 (1983) 1107.
361. C.J. Hawkins, R.H. Holm, J.A. Palmer and D.D. Traficante, *Aust. J. Chem.*, 35 (1982) 1815.
362. R. Saito and Y. Kidani, *Bull. Chem. Soc. Jpn.*, 56 (1983) 449.
363. G. Garzon, C. Rosas and C. Marina de Rivas, *Rev. Colomb. Quim.*, 11 (1982) 9 [*Chem. Abstr.*, 99 (1983) 114917d].
364. L. Maresca and G. Natile, *J. Chem. Soc., Chem. Commun.*, (1983) 40.
365. T. Totani and K. Yamaguchi, Fr. Demande FR (1981) 2,481,696 [*Chem. Abstr.*, 96 (1982) 162946x].
366. S. Shinoda and Y. Saito, *Inorg. Chim. Acta*, 63 (1982) 23.
367. E.O. Schlemper, R.K. Murmann and J. Pal, *Transition Met. Chem. (Weinheim, Ger.)*, 8 (1983) 204.
368. J.F. Britten, C.J.L. Lock and W.M.C. Pratt, *Acta Crystallogr., Sect. B*, B38 (1982) 2148.
369. A.I. Akhmedov, A.I. Yanovskii, A.V. Babkov and Yu.T. Struchkov, *Koord. Khim.*, 9 (1983) 1138.
370. J.K. Beattie, *Inorg. Chim. Acta*, 76 (1983) L69.

371. L. Canovese, M. Cusumano and A. Giannetto, *J. Chem. Soc., Dalton Trans.*, (1983) 195.
372. I. Mochida and J.C. Bailar, *Inorg. Chem.*, 22 (1983) 1834.
373. S.N. Bhattacharya and C.V. Senoff, *Inorg. Chem.*, 22 (1983) 1607.
374. F.S. Walker, S.N. Bhattacharya and C.V. Senoff, *Inorg. Synth.*, 21 (1982) 129.
375. V.V. Vlasov, S.A. Kazakov and V.G. Misovets, *Dokl. Chem.*, 266 (1982) 349.
376. I.A. Zakharova, A.P. Kurbakova, N.A. Ivanova and M.M. Kaganskii, *Proc. Conf. Coord. Chem., (1983) 9th*, 475 [*Chem. Abstr.*, 99 (1983) 98171y].
377. Yu.L. Gaft, N.T. Kuznetsov and L.M. Sukova, *Russ. J. Inorg. Chem.*, 28 (1983) 89.
378. M. Mulqi, F.S. Stephens ans R.S. Vagg, *Inorg. Chim. Acta*, 62 (1982) 215, 221.
379. M.W. Mulqi, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, 63 (1982) 197.
380. R. Rusin, *J. Organomet. Chem.*, 247 (1983) 351.
381. A.G. Asuero, M.J. Navas, J.M. Bautista and D. Rosales, *Microchem. J.*, 28 (1983) 183.
382. R. Pelova, G.P. Syrtsova, N.V. Gerbeleu, A.N. Shishkov, A.P. Gulya and V.N. Shafranskii, *Zh. Neorg. Khim.*, 28 (1983) 1506.
383. N. Saha, D. Bhattacharya and S.K. Kar, *Inorg. Chim. Acta*, 67 (1982) L37.
384. R. Uson, J. Gimeno, J. Fornies, F. Martinez and C. Fernandez, *Inorg. Chim. Acta*, 63 (1982) 91.
385. K.D. Gallicano and N.L. Paddock, *Canad. J. Chem.*, 60 (1982) 521.
386. W.C. Deese and D.A. Johnson, *J. Orgnanomet. Chem.*, 232 (1982) 325.
387. F. Salinas, J. Gimenez Plaza, J.M. Bocanegra Garces and J.I. Marcos, *An. Quim., Ser. B*, 78 (1982) 291.
388. K. Wieghardt, M. Köppen, W. Swiridoff and J. Weiss, *J. Chem. Soc., Dalton Trans.*, (1983) 1869.
389. K.B. Yatsimirskii, L.P. Kazanskii, A.N. Boiko and V.V. Pavlishchuk, *Teor. Eksp. Khim.*, 18 (1982) 490.
390. K.B. Yatsimirskii, A.N. Boiko and L.P. Kazanskii, *Russ. J. Inorg. Chem.*, 28 (1983) 1155.
391. K.B. Yatsimirskii, A.N. Boiko and V.A. Bidzilya, *Russ. J. Inorg. Chem.*, 27 (1982) 1313.
392. K.B. Yatsimirskii, A.N. Boiko, V.A. Bidzilya and L.P. Kazanskii, *Zh. Neorg. Khim.*, 27 (1982) 2586.
393. A.J. Jircitano, R.I. Sheldon and K.B. Mertes, *J. Am. Chem. Soc.*, 105 (1983) 3022.
394. A.N. Boiko, K.B. Yatsimirskii and V.A. Bidzilya, *Koord. Khim.*, 9 (1983) 555.
395. Z. Yang and M. Wang, *Huarue Tongbao*, (1983) 17 [*Chem. Abstr.*, 99 (1983) 132653u].
396. K.N. Solov'ev, I.V. Stanishevskii, A.S. Starukhin and A.M. Shul'ga, *Izv. Akad., Nauk SSSR, Ser. Fiz.*, 47 (1983) 1399.
397. G. Ponterini, N. Serpone, M.A. Bergkamp and T.L. Netzel, *J. Am. Chem. Soc.*, 105 (1983) 4639.
398. W.A.J.A. Van der Poel, A.M. Nuijs, M. Noort and J.H. Van der Waals, *J. Phys. Chem.*, 86 (1982) 5191.
399. A. Antipas and M. Gouterman, *J. Am. Chem. Soc.*, 105 (1983), 4896.
400. A. Harriman, G. Porter and P. Walters, *J. Chem. Soc., Faraday Trans. I*, 79 (1983) 1335.
401. A.V. Melezhik, D.N. Vovk and V.D. Pokhodenko. *J. Gen. Chem. USSR*, 53 (1983) 1442.
402. T. Ozawa and A. Hanaki, *Inorg. Chim. Acta*, 80 (1983) 33.
403. I. Okura, S. Aono, M. Takeuchi and S. Kusunoki, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3637.
404. J.D. Doi, Ph. D. Thesis, City Univ., New York, 1982, *Diss. Abstr. Int. B*, 43 (1982) 1485.

405. A.S. Akopov, V.V. Bykova and B.D. Berezin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 25 (1982) 1068 [*Chem. Abstr.*, 97 (1982) 109002u].
406. A.S. Akopov, V.V. Bykova and B.D. Berezin, *J. Org. Chem. USSR*, 19 (1983) 512.
407. E.I. Zen'kevich, M.V. Sarzhevskaya and T.V. Vitovtseva, *Zh. Prikl. Spektrosk.*, 37 (1982) 818.
408. S.S. Iodko, O.L. Kaliya, M.G. Gal'pern, V.N. Kopranenkov, O.L. Lebedev and E.A. Luk'yanets, *Sov. J. Coord. Chem.*, 8 (1982) 552.
409. M. Ashida, *Kobunshi Kako*, 31 (1982) 211 [*Chem. Abstr.*, 97 (1982) 227638r].
410. B. Sudha, N. Dixit, N.S. Dixit and C.C. Patel, *Indian J. Chem., Sect. A*, 21A (1982) 970.
411. H. Hofmans, H.O. Desseyn, A.J. Aartsen and M.A. Herman, *Therm. Anal., Proc. Int. Conf., 7th*, 1 (1982) 457 [*Chem. Abstr.*, 99 (1983) 151075y].
412. C. Preti, L. Tassi, G. Tosi, P.Zannini and A.F. Zanoli, *J. Coord. Chem.*, 12 (1983) 177.
413. F.E. Wood and A.L. Balch, *Inorg. Chim. Acta*, 76 (1983) L63.
414. Yu.N. Kukushkin, G. Kh. Khamnuev, N.P. Fedyanin and V.I. Lobadyuk, *Zh. Neorg. Khim.*, 28 (1983) 2312.
415. Z.M. Zavorokhina and L.V. Levchenko, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, (1983) 63 [*Chem. Abstr.*, 99 (1983) 205094z].
416. H.H. Eysel, E. Guggolz, M. Kopp and M.L. Ziegler, *Z. Anorg. Allg. Chem.*, 499 (1983) 31.
417. C. Bartocci, C.A. Bignozzi, F. Scandola, R. Rumin and P. Courtot, *Inorg. Chim. Acta*, 76 (1983) L119.
418. D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, F.A. Cotton and L.R. Falvello, *Inorg. Chem.*, 22 (1983) 1315.
419. K.C. Kalia, M. Singla and A. Kumar, *Transition Met. Chem. (Weinheim, Ger.)*, 7 (1982) 151.
420. V.D. Pokhodenko, A.V. Melezhik and D.N. Vovk, *Sov. J. Coord. Chem.*, 8 (1982) 667.
421. M. Hvastijova, J. Kohout and J. Gazo, *Proc. Conf. Coord. Chem., 1983, 9th*, 121 [*Chem. Abstr.*, 99 (1983) 98217t].
422. A. De Renzi, G. Morelli and M. Scalone, *Inorg. Chim. Acta*, 65 (1983) L119.
423. M.D. Fryzuk, P.A. MacNeil, S.J. Rettig, A.S. Secco and J. Trotter, *Organometallics*, 1 (1982) 918.
424. G.L. Roberts, B.W. Skelton, A.H. White and S.B. Wild, *Aust. J. Chem.*, 35 (1982) 2193.
425. M. Nonoyama, *Transition Met. Chem. (Weinheim, Ger.)*, 7 (1982) 281.
426. A.K. Yatsimirskii, A.D. Ryabov, I.K. Sakadynskaya and I.V. Berezin, *Dokl. Akad. Nauk SSSR*, 270 (1983) 150 [Phys. Chem.].
427. C. Arlen, M. Pfeffer, O. Bars and D. Grandjean, *J. Chem. Soc., Dalton Trans.*, (1983) 1535.
428. A. Avshu, R.D. O'Sullivan, A.W. Parkins, N.W. Alcock and R.M. Countryman, *J. Chem. Soc., Dalton Trans.*, (1983) 1619.
429. M. Nonoyama, *J. Organomet. Chem.*, 229 (1982) 287.
430. A.J. Canty, N.J. Minchin, J.M. Patrick and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1983) 1253.
431. M.C. Etter and A.R. Siedle, *J. Am. Chem. Soc.*, 105 (1983) 641.
432. M.C. Etter and A.R. Siedle, *Mol. Cryst. Liq. Cryst.*, 96 (1983) 35.
433. J. Granell, J. Sales, J. Vilarrasa, J.P. Declercq, G. Germain, C. Miravitlles and X. Solans, *J. Chem. Soc., Dalton Trans.*, (1983) 2441.
434. B. Galli, F. Gasparrini, L. Maresca, G. Natile and G. Palmieri, *J. Chem. Soc., Dalton Trans.*, (1983) 1483.
435. Y. Fuchita, K. Hiraki and T. Uchiyama, *J. Chem. Soc., Dalton Trans.*, (1983) 897.
436. A.F.M.J. Van der Ploeg, G. Van Koten and K. Vrieze, *J. Organomet. Chem.*, 226 (1982) 93.

437. G. Ferguson, R. McCrindle, A.J.McAlees and M. Parvez, *Acta Crystallogr., Sect. B*, B38 (1982) 2679.
438. G.K. Anderson, H.C. Clark, J.A. Davies, G. Ferguson and M. Parvez, *J. Crystallogr. Spectrosc. Res.*, 12 (1982) 449.
439. N.W. Alcock and J.H. Nelson, *Acta Crystallogr., Sect. B*, B38 (1982) 2463.
440. Ya.L. Gol'dfarb, A.A. Dudinov, V.P. Litvinov, D.S. Yufit and Yu.T. Struchkov, *Khim. Geterotsikl. Soedin*, (1982) 1326 [*Chem. Abstr.*, 98 (1983) 89625b].
441. S.S. Moore and G.M. Whitesides, *J. Org. Chem.*, 47 (1982) 1489.
442. T. Okano, M. Yamamoto, T. Noguchi, H. Konishi and J. Kiji, *Chem. Lett.*, (1982) 977.
443. S. Franks, F.R. Hartley and J.R. Chipperfield, *Adv. Chem. Ser.*, 196 (Catal. Aspects Met. Phosphine Complexes) (1982) 273.
444. Y. Chen, J. Liu, Y. Lin, J. Ni, C. Xiao and Y. Wan, *Wuhan Daxue Xuebao, Ziran Kexueban*, (1982) 41 [*Chem. Abstr.*, 97 (1982) 61687d].
445. H.W. Kroto, J.F. Nixon, M.J. Taylor, A.A. Frew and K.W. Muir, *Polyhedron*, 1 (1982) 89.
446. W.O. Ogini, Ph. D. Thesis, Univ. Guelph, 1982, *Diss. Abstr. Int. B*, 43 (1982) 720.
447. K.K. Gazizov, D.M. Yukhnovich, G.K. Budnikov, V.K. Polovnyak and N.S. Akhmetov, *Zh. Neorg. Khim.*, 27 (1982) 2983.
448. K.K. Gazizov, D.M. Yukhnovich, G.K. Budnikov, V.K. Polovnyak and N.S. Akhmetov, *Deposited Doc.*, (1982) SPSTL 39 Khp-D82 [*Chem. Abstr.*, 98 (1983) 115635b].
449. K.K. Gazizov, D.M. Yukhnovich, G.K. Budnikov, V.K. Polovnyak and N.S. Akhmetov, *Zh. Neorg. Khim.*, 27 (1982) 3205.
450. K.K. Gazizov, D.M. Yukhnovich, G.K. Budnikov, V.K. Polovnyak and N.S. Akhmetov, *Deposited Doc.*, (1982) SPSTL 40 Khp-D82 [*Chem. Abstr.*, 98 (1983) 97911g].
451. J.R. Fisher, R.G. Compton and D.J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, (1983) 555.
452. D.B. Deal, Ph. D. Thesis UCLA, 1982, *Diss. Abstr. Int. B*, 43 (1982) 1093.
453. T. Yoshida and S. Otsuka, *Adv. Chem. Ser.*, 196 (Catal. Aspects Met. Phosphine Complexes) (1982) 135.
454. T. Yamamoto, K. Sano and A. Yamamoto, *Chem. Lett.*, (1982) 907.
455. G.K. Anderson, H.C. Clark and J.A. Davies, *Organometallics*, 1 (1982) 550.
456. R.A. Michelin, S. Faglia and P. Uguagliati, *Inorg. Chem.*, 22 (1983) 1831.
457. G. Annibale, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M.L. Tobe, *J. Chem. Soc., Dalton Trans.*, (1983) 775.
458. M. Wada and K. Nishiwaki, *J. Chem. Soc., Dalton Trans.*, (1983) 1841.
459. R. Bardi, A.M. Piazzesi, G. Cavinato, P. Cavoli and L. Toniolo, *J. Organomet. Chem.*, 224 (1982) 407.
460. Y. Wang, *Cuihua Xuebao*, 3 (1982) 147 [*Chem. Abstr.*, 97 (1982) 110177y].
461. M.E. Vol'pin, M.Yu. Tuvin, Yu.L. Gaft and I.A. Zakharova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 31 (1982) 1927.
462. X. Solans, C. Miravitlles, J.M. Arrieta, G. Germain and J.P. Declercq, *Acta Crystallogr., Sect. B*, B38 (1982) 1812.
463. O. Rossell, J. Sales and M. Seco, *J. Organomet. Chem.*, 236 (1982) 415.
464. O. Bars and P. Braunstein, *Angew. Chem.*, 94 (1982) 319.
465. A.S. Berenblum, A.A. Grigor'ev, E.A. Katsman, A.G. Knizhnik, S.L. Mund and I.I. Moiseev, *Kinet. Katal.*, 23 (1982) 1494.
466. A.D. Troitskaya, K.S. Knirik, R.A. Konoval'chuk, P.A. Gurevich, I.G. Martynova, T.E. Busygina and V.V. Senlemov, *J. Gen. Chem. USSR*, 52 (1982) 2470.
467. E.E. Nifant'ev, T.S. Kukhareva, M.Yu. Antipin and Yu.T. Struchkov, *J. Gen. Chem. USSR*, 52 (1982) 2413.

468. D.H. Farrar and G. Ferguson, *J. Crystallogr. Spectrosc. Res.*, 12 (1982) 465.
469. F. Morandini, G. Consiglio and O. Piccolo, *Inorg. Chim. Acta*, 57 (1982) 15.
470. R.D. Waid, Ph. D. Thesis, Ohio State Univ., *Diss. Abstr.*, 43 (1983) 2551.
471. N.C. Payne and D.W. Stephan, *J. Organomet. Chem.*, 221 (1981) 223.
472. N.C. Payne and D.W. Stephan, *J. Organomet. Chem.*, 228 (1982) 203.
473. N.C. Payne and D.W. Stephan, *J. Organomet. Chem.*, 221 (1981) 203.
474. E.P. Kyba and S.P. Rines, *J. Org. Chem.*, 47 (1982) 4800.
475. M.P. Brown, A. Yavari, L. Manojlovic-Muir, K.W. Muir, R.P. Moulding and K.R. Seddon, *J. Organomet. Chem.*, 236 (1982) C33.
476. S. Al-Jibori and B.L. Shaw, *Inorg. Chim. Acta*, 65 (1982) L123.
477. R.J. Puddephatt, K.A. Azam, R.H. Hill, M.P. Brown, C.D. Nelson, R.P. Moulding, K.R. Seddon and M.C. Grossel, *J. Am. Chem. Soc.*, 105 (1983) 5642.
478. A.T. Hutton, B. Shabanzadeh and B.L. Shaw, *J. Chem. Soc., Chem. Commun.*, (1983) 1053.
479. C-L. Lee, C.T. Hunt and A.L. Balch, *Organometallics*, 1 (1982) 824.
480. C.R. Langrick, D.M. McEwan, P.G. Pringle and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1983) 2487.
481. M.E. Solis, M.S. Trivino and J.G. Contreras, *Bol. Soc. Chil. Quim.*, 27 (1982) 88.
482. P.N. Kapoor. P.S. Pregosin and L.M. Venanzi, *Helv. Chim. Acta*, 65 (1982) 654.
483. H.C. Clark, J.A. Davies, C.A.Fyfe, P.J. Hayes and R.E. Wasylishen, *Organometallics*, 2 (1983) 177.
484. C.A. Fyfe, H.C. Clark, J.A. Davies, P.J. Hayes and R.E. Wasylishen, *J. Am. Chem. Soc.*, 105 (1983) 6577.
485. R.R. Guimerans, M.M. Olmstead and A.L. Balch, *J. Am. Chem. Soc.*, 105 (1983) 1677.
486. R.R. Guimerans, M.M. Olmstead and A.L. Balch, *Inorg. Chem.*, 22 (1983) 3223.
487. D.W. Meek, R. Waid, K.D. Tau, R.M. Kirchner and C.N. Morimoto, *Inorg. Chim. Acta*, 64 (1982) L221.
488. R. Bartsch, S. Hietkamp, S. Morton, H. Peters and O. Stelzer, *Inorg. Chem.*, 22 (1983) 3624.
489. C-M. Che, L.G. Butler, H.B. Gray, R.M. Crooks and W.H. Woodruff, *J. Am. Chem. Soc.*, 105 (1983) 5492.
490. S.F. Rice and H.B. Gray, *J. Am. Chem. Soc.*, 105 (1983) 4571.
491. D.E. Berry, G.W. Bushnell, K.R. Dixon and A. Pidcock, *Inorg. Chem.*, 22 (1983) 1961.
492. S.G.N. Roundhill and D.M. Roundhill, *Acta Crystallogr., Sect. B.*, B38 (1982) 2479.
493. G. Salem and S.B. Wild, *Inorg. Chem.*, 22 (1983) 4049.
494. V. Serban and I. Serban, *Bul. Inst. Politeh. "Gheorghe Gheorghiu-Dej" Bucuresti, Ser. Chim.-Metal.*, 44 (1982) 73 [*Chem. Abstr.*, 98 (1983) 64602d].
495. W.E. Hill, D.M.A. Minahan and C.A. McAuliffe, *Inorg. Chem.*, 22 (1983) 3382.
496. D.M.A. Minahan, Ph. D. Thesis, Auburn Univ., 1982, *Diss. Abstr. Int. B*, 42 (1982) 4785.
497. N.M. Kostić and R.F. Fenske, *Inorg. Chem.*, 22 (1983) 666.
498. L.D. Polyachenok, S.V. Yasinetskaya, V.P. Bochin and O.G. Polyachenok, *Zh. Neorg. Khim.*, 28 (1983) 2149.
499. V.A. Golodov, N.G. Glubokovskikh and G.V. Taneeva, *React. Kinet. Catal. Lett.*, 22 (1983) 101.
500. Y. Jaued, T.V. Lysyak, I.S. Kolomnikov and Yu.A. Kharitonov, *Koord. Khim.*, 8 (1982) 260.

501. O.I. Kuntyi, D.I. Semenishin and K.N. Mikhalevich, *Ukr. Khim. Zh. (Russ. Ed.)*, 49 (1983) 121.
502. A.K. Viswanath, J. Vetuskey, R. Leighton, M.B. Krogh-Jesperson and H.H. Patterson, *Mol. Phys.*, 48 (1982) 567.
503. R. Schultheiss, I. Hidvegi and G. Gliemann, *J. Chem. Phys.*, 79 (1983) 4167.
504. S. Clark, P. Day, D.J. Huddart and C.N. Ironside, *J. Chem. Soc., Faraday Trans. 2*, 79 (1983) 65.
505. W. Von Ammon and G. Gliemann, *J. Chem. Phys.*, 77 (1982) 2266.
506. R. Dillinger, G. Gliemann, H.P. Pfleger and K. Krogmann, *Inorg. Chem.*, 22 (1983) 1366.
507. R.E. Benner, K.U. Von Raben, K.C. Lee, J.F. Owen, R.K. Chang and B.L. Laube, *Chem. Phys. Lett.*, 96 (1983) 65.
508. J.J. Pesek and W.R. Mason, *Inorg. Chem.*, 22 (1983) 2958.
509. J.H.F. Notton, *Platinum Met. Rev.*, 27 (1983) 26.
510. U. Belluco, B. Crociani, R. Michelin and P. Uguagliati, *Pure Appl. Chem.*, 55 (1983) 47.
511. W.P. Fehlhammer, K. Bartel, A. Voelkl and D. Achatz, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 37B, (1982) 1044.
512. P.G. Antonov, Yu.N. Kukushkin, V.G. Shtrele, Yu.P. Kostikov and F.K. Egorov, *Zh. Neorg. Khim.*, 27 (1982) 3130.
513. P.G. Antonov, Yu.N. Kukushkin, F.K. Egorov, Yu.P. Kostikikov and V. Strele, *J. Gen. Chem. USSR*, 52 (1982) 1911.
514. P.G. Antonov, Yu.N. Kukushkin, R.Kh. Karymova, V. Strele and Yu.P. Kostikov, *Zh. Obshch. Khim.*, 53 (1983) 858.
515. P.G. Antonov, Yu.N. Kukushkin, R.Kh. Karymova and V.G. Shtrele, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 25 (1982) 918 [*Chem. Abstr.*, 98 (1983) 45770r].
516. K.A.O. Starzewski and P.S. Pregosin, *Adv. Chem. Ser.*, 196 (Catal. Aspects Met. Phosphine Complexes) (1982) 23.
517. K.R. Koch, *S. Afr. J. Chem.*, 36 (1983) 89.
518. A.Albinati, R. Naegeli, H. Rueggar and P.S. Pregosin, *Angew. Chem.*, 94 (1982) 310.
519. K.H.A. Ostoja Starzewski, P.S. Pregosin and H. Ruegger, *Helv. Chim. Acta*, 65 (1982) 785.
520. A.B. Goel and S. Goel, *Indian J. Chem., Sect. A*, 21A (1982) 980.
521. V.I. Bogdashkina, A.B. Permin, V.S. Petrosyan, V.I. Pol'shakov and O.A. Reutov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 31 (1982) 917.
522. G.K. Anderson, H.C. Clark and J.A. Davies, *Inorg. Chem.*, 22 (1983) 427.
523. G.K. Anderson, H.C. Clark and J.A. Davies, *Inorg. Chem.*, 22 (1983) 434.
524. R.J. Goodfellow and I.R. Herbert, *Inorg. Chim. Acta*, 65 (1982) L161.
525. V.I. Perevalova, A.S. Belyi, L.Ya. Al't and V.K. Duplyakin, *Koord. Khim.*, 9 (1983) 280.
526. H. Weichmann, *J. Organomet. Chem.*, 238 (1982) C49.
527. S.N. Titova, V.T. Bychov, G.A. Domrachev, Yu.A. Sorokin, T.N. Konkina and G.A. Razuvaev, *J. Gen. Chem. USSR*, 52 (1982) 1396.
528. S. Carr, R. Colton and D. Dakternieks, *J. Organomet. Chem.*, 240 (1982) 143.
529. I.V. Gavrilova, *Deposited Doc.*, (1980) SPSTL 885 Khp-D80, 18 [*Chem. Abstr.*, 97 (1982) 84075s].
530. R.S. Paonessa and W.C. Trogler, *Inorg. Chem.*, 22 (1983) 1038.
531. F. Bachechi, G. Bracher, D.M. Grove, B. Kellenberger, P.S. Pregosin, L.M. Venanzi and L. Zambonelli, *Inorg. Chem.*, 22 (1983) 1031.
532. C.B. Knobler, H.D. Kaesz, G. Minghetti, A.L. Bandini, G. Banditelli and F. Bonati, *Inorg. Chem.*, 22 (1983) 2324.
533. G. Minghetti, A.L. Bandini, G. Banditelli, F. Bonati, R. Szostak, C.E. Strouse, C.B. Knobler and H.D. Kaesz, *Inorg. Chem.*, 22 (1983) 2332.
534. A.L. Balch and L.S. Benner, *Inorg. Synth.*, 21 (1982) 47.
535. P.G. Pringle and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1983) 889.

536. M. Grossel, R.P. Moulding and K.R. Seddon, *Inorg. Chim. Acta*, 64 (1982) L275.
537. M.P. Brown, J.R. Fisher, S.J. Franklin, R.J. Puddephatt and M.A. Thompson, *Adv. Chem. Ser.*, 196 (Catal. Aspects Met. Phsophine Complexes) (1982) 231.
538. R.H. Hill and R.J. Puddephatt, *J. Am. Chem. Soc.*, 105 (1983) 5797.
539. J.R. Fisher, A.J. Mills, S. Sumner, M.P. Brown, M.A. Thompson, R.J. Puddephatt, A.A. Frew, L. Manojlović-Muir and K.W. Muir, *Organometallics*, 1 (1982) 1421.
540. C.L. Lee, Ph. D. Thesis, Univ. California, Davis, 1981, *Diss. Abstr. Int. B*, 43 (1983) 2203.
541. S. Muralidharan and J.H. Espenson, *Inorg. Chem.*, 22 (1983) 2786.
542. C.T. Hunt, Ph. D. Thesis, Univ. California, Davis, 1981, *Diss. Abstr. Int. B*, 42 (1982) 3679.
543. J.P. Farr, F.E. Wood and A.L. Balch, *Inorg. Chem.*, 22 (1983) 3387.
544. J.P. Farr, M.M. Olmstead and A.L. Balch, *Inorg. Chem.*, 22 (1983) 1229.
545. R.J. Goodfellow, I.R. Herbert and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1983) 1386.
546. V.P. Linev, O.N. Temkin, V.K. Polovnyak, L.G. Bruk and G.V. Romanov, *J. Gen. Chem. USSR*, 51 (1981) 2187.
547. V.K. Polovnyak, V.P. Linev, O.N. Temkin and N.S. Akhmetov, *Deposited Doc.*, (1981) SPSTL 687 Khp-D81 [*Chem. Abstr.*, (1983) 167731z].
548. N.M. Boag, P.L. Goggin, R.J. Goodfellow and I.R. Herbert, *J. Chem. Soc., Dalton Trans.*, (1983) 1101.
549. A.S. Berenblyum, A.G. Knizhnik, S.L. Mund and I.I. Moiseev, *J. Organomet. Chem.*, 234 (1982) 219.
550. B. Messbauer, H. Meyer, B. Walther, M.J. Heeg, A.F.M. Rahman and J.P. Oliver, *Inorg. Chem.*, 22 (1983) 272.
551. J.U. Mondal and D.M. Blake, *Coord. Chem. Rev.*, 47 (1982) 205.
552. J.M. Ritchey, D.C. Moody and R.R. Ryan, *Inorg. Chem.*, 22 (1983) 2276.
553. S.W. Carr, R. Colton, D. Dakternieks, B.P. Hoskins and R.J. Steen, *Inorg. Chem.*, 22 (1983) 3700.
554. S. Datta and U.C. Agarwala, *Indian J. Chem., Sect. A*, 20A (1981) 1190.
555. W. Bertleff and H. Werner, *Z. Naturforsh., B: Anorg. Chem., Org. Chem.*, 37B (1982) 1294.
556. W.M. Hawling, A. Walker and M.A. Woitzik, *J. Chem. Soc., Chem. Commun.*, (1983) 11.
557. W. Bertleff and H. Werner, *Chem. Ber.*, 115 (1982) 1012.
558. P. Oberbosch and G. Van Koten, *J. Organomet. Chem.*, 229 (1982) 193.
559. V.Sh. Slobodina, V.K. Polovnyak, N.S. Akhmetov, *Deposited Doc.*, (1981) SPSTL 902 Khp-D81 [*Chem. Abstr.*, 98 (1983) 45899q].
560. V.K. Polovnyak, V.Sh. Slobodina, V.V. Kormachev and N.S. Akhmetov, *Zh. Neorg. Khim.*, 28 (1983) 168.
561. V.Sh. Slobodina, V.K. Polovnyak and N.S. Akhmetov, *Deposited Doc.*, (1982) SPSTL 137 Khp-D82 [*Chem. Abstr.*, 98 (1983) 118551g].
562. R.S. Poanessa and W.C. Trogler, *Organometallics*, 1 (1982) 768.
563. J.A. Crayston and G. Davidson, *Raman Spectrosc., Proc. Int. Conf., 8th* (1982) 627 [*Chem. Abstr.*, 99 (1983) 148765t].
564. J.B. Davison, P.J. Peerce-Landers and R.J. Jasinski, *J. Electrochem. Soc.*, 130 (1983) 1862.
565. H. Werner and W. Bertleff, *Chem. Ber.*, 116 (1983) 823.
566. S.I. Al-Resayes, S.I. Klein, H.W. Kroto, M.F. Meidine and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1983) 930.
567. J.C.T.R. Burckett-St. Laurent, M.A. King, H.W. Kroto, J.F. Nixon and R.J. Suffolk, *J. Chem. Soc., Dalton Trans.*, (1983) 755.
568. M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding and K.R. Seddon, *J. Organomet. Chem.*, 232 (1982) C13.
569. B. Denise and R.P.A. Sneeden, *J. Organomet. Chem.*, 221 (1981) 111.
570. O.J. Scherer, R. Konrad, C. Krueger and Y.H. Tsang, *Chem. Ber.*, 115 (1982) 141.

571. O.J. Scherer and K.D. Krieger, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 37B (1982) 1041.
572. K. Bartel, K. Von Werner and W. Beck, *J. Organomet. Chem.*, 243 (1983) 79.
573. R. Chen and H. Wang, *Cuthua Xuebao*, 4 (1983) 1 [*Chem. Abstr.*, 98 (1983) 204900b].
574. R. Szostak, Ph. D. Thesis, UCLA, 1982, *Diss. Abstr. Int. B*, 43 (1982) 1097.
575. A. Moor, P.S. Pregosin and L.M. Venanzi, *Inorg. Chim. Acta*, 61 (1982) 135.
576. R. Bender and P. Braunstein, *J. Chem. Soc., Chem. Commun.*, (1983) 334.
577. L. Manojlović-Muir, K.W. Muir, B.R. Lloyd and R.J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, (1983) 1336.
578. O.J. Scherer, R. Konrad, E. Guggolz and M.L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 21 (1982) 297.
579. J.A. Davies, F.R. Hartley, S.G. Murray and M.A. Pierce-Butler, *J. Chem. Soc., Dalton Trans.*, (1983) 1305.
580. M.N. Vargaftik, T.A. Stromnova, G.Ya. Mazo and I.I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1254.
581. T.A. Stromnova, M.N. Vargaftik and I.I. Moiseev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 32 (1983) 21.
582. A.S. Berenblyum, A.P. Aseeva, L.I. Lakhman and I.I. Moiseev, *J. Organomet. Chem.*, 234 (1982) 237.
583. T.I. Bakunina, L.V. Mironova, V.A. Khutoryanskii, S.V. Zinchenko, A.Sh. Bikbaeva and F.K. Shmidt, *Koord. Khim.*, 8 (1982) 1431.
584. P.E. Wood, M.M. Olmstead and A.L. Balch, *J. Am. Chem. Soc.*, 105 (1983) 6332.
585. D.G. Evans and D.M.P. Mingos, *J. Organomet. Chem.*, 240 (1982) 321.
586. E.G. Mednikov and N.K. Eremenko, *Izv. Akad. Nauk SSSR., Ser. Khim.*, (1982) 2540.
587. J.C. Simondsen, Ph. D. Thesis, Univ. Arizona, 1982, *Diss. Abstr. Int. B*, 43 (1982) 1488.
588. M.N. Vargaftik, V.P. Zagorodnikov and I.I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 1209.
589. D.G. Evans and D.M.P. Mingos, *J. Organomet. Chem.*, 232 (1982) 171.
590. R. Goddard, P.W. Jolly, C. Krüger, K.-P. Schick and G. Wilke, *Organometallics*, 1 (1982) 1709.
591. E.G. Mednikov and N.K. Eremenko, *Koord. Khim.*, 9 (1983) 243.
592. E.G. Mednikov, N.K. Eremenko, S.P. Gubin, Yu.L. Slovokhotov and Yu.A. Struchkov, *J. Organomet. Chem.*, 239 (1982) 401.
593. A. Yatsimirskii and R. Ugo, *Inorg. Chem.*, 22 (1983) 1395.
594. S. Bhadhuri and K.R. Sharma, *J. Chem. Soc., Chem. Commun.*, (1983) 1412.
595. R.A. Montag, Ph. D. Thesis, Univ. Wisconsin, 1982, *Diss. Abstr. Int. B*, 43 (1983) 3235.
596. M.J. Calhorda, D.M.P. Mingos and A.J. Welch, *J. Organomet. Chem.*, 228 (1982) 309.
597. M.A. Beckett, J.E. Crook, N.N. Greenwood and J.D. Kennedy, *J. Chem. Soc., Chem. Commun.*, (1983), 1228.
598. J. Bould, J.E. Crook, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1983) 949.
599. G.K. Barker, M. Green, F.G.A. Stone, W.C. Wolsey and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1983) 2063.
600. F. Teixidor, M.L. Luetkens and R.W. Rudolph, *J. Am. Chem. Soc.*, 105 (1983) 149.
601. R.D. Barr, M. Green, J.A.K. Howard, T.B. Marder, I. Moore and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1983) 746.
602. K.A. Mead, I. Moore, F.G.A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1983) 2083.
603. M.R. Awang, J.C. Jeffery and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*,(1983) 2091.

604. R. Bender, P. Braunstein, J-M. Jud and Y. Dusausoy, *Inorg. Chem.*, 22 (1983) 3394.
605. R. Jund, P. Lemoine, M. Gross, R. Bender and P. Braunstein, *J. Chem. Soc., Chem. Commun.*, (1983) 86.
606. P. Braunstein, R. Bender and J. Kervennal, *Organometallics*, 1 (1982) 1236.
607. P. Braunstein, J-M. Jud and J. Fischer, *J. Chem. Soc., Chem. Commun.*, (1983) 5.
608. P. Braunstein, J.M. Jud, Y. Dusausoy and J. Fischer, *Organometallics*, 2 (1983) 180.
609. A.M. Mazany, J.P. Fackler, M.K. Gallagher and D. Seyferth, *Inorg. Chem.*, 22 (1983) 2593.
610. D.A. Lesch and T.B. Rauchfuss, *Inorg. Chem.*, 22 (1983) 1854.
611. V.E. Lopatin, N.M. Mikova and S.P. Gubin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 32 (1983) 1962.
612. M.I. Bruce, J.G. Matisons, B.W. Skelton and A.H. White, *Aust. J. Chem.*, 35 (1982) 687.
613. L.J. Farrugia, M. Green, D.R. Hankey, A.G. Orpen and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1983) 310.
614. F. Faraone, S. Lo Schiavo, G. Bruno, P. Piraino and G. Bombieri, *J. Chem. Soc., Dalton Trans.*, (1983), 1813.
615. A. Pumagalli, S. Martinengo and G. Ciani, *J. Chem. Soc., Chem. Commun.*, (1983) 1381.
616. J.A. Davies and J.F. Liebman, *J. Chem. Soc., Dalton Trans.*, (1983) 1793.
617. F.R. Hartley and J.A. Davies, *Rev. Inorg. Chem.*, 4 (1982) 27.
618. I.I. Moiseev, *Sov. Sci. Rev., Sect. B*, 4 (1982) 139.
619. Y.J. Li and Y.Y. Jiang, *J. Mol. Catal.*, 19 (1983) 277.
620. H. Liu, *Cuihua Xuebao*, 3 (1982) 315 [*Chem. Abstr.*, 98 (1983) 125157m].
621. Y. Chen, J. Liu, Y. Lin, C. Xiao and C. Mai, *Wuhan Daxue Xuebao, Ziran Kexueban*, (1982) 29 [*Chem. Abstr.*, 98 (1983) 82741c].
622. Y. Chen, J. Liu, Y. Lin, J. Ni, C. Xiao and Y. Wang, *Wuhan Daxue Xuebao, Ziran Kexueban*, (1982) 42 [*Chem. Abstr.*, 97 (1982) 183562e].
623. Y. Lin, J. Liu, J. Ni, Y. Chen, C. Xiao and Y. Wang, *Cuihua Xuebao*, 3 (1982) 220 [*Chem. Abstr.*, 97 (1982) 215076t].
624. P. Feng and S. Shen, *Zhongguo Kexue Jishu Daxue Xuebao*, 13 (1983) 188 [*Chem. Abstr.*, 99 (1983) 201132n].
625. Z. Guo and H. Liu, *Cuihua Xuebao*, 3 (1982) 311 [*Chem. Abstr.*, 98 (1983) 125473m].
626. V.N. Kolot, M.V. Lyubomilova, E.F. Litvin, G.I. Kudryavtsev, L.Kh. Freidlin and S.L. Davydova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 31 (1982) 1267.
627. V. Machek, V. Ruzicka, M. Sourkova, J. Kunz and L. Janacek, *React. Kinet. Catal. Lett.*, 21 (1982) 13.
628. T.M. Matveeva, N.V. Nekrasov and S.L. Kiperman, *Mekhanizm Katalit. Reaktsii. Materialy 3 Vses. Konf., Novosibirsk*, (1982) 112 [*Chem. Abstr.*, 98 (1983) 34074r].
629. N. Suzuki, Y. Ayaguchi, T. Tsukanaka and Y. Izawa, *Bull. Chem. Soc. Jpn.*, 56 (1983) 353.
630. N. Suzuki, Y. Ayaguchi and Y. Izawa, *Chem. Ind. (London)*, (1983) 166.
631. N. Suzuki, T. Tsukanaka, T. Nomoto, Y. Ayaguchi and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, (1983) 515.
632. T.K. Banerjee and D. Sen, *J. Chem. Technol. Biotechnol.*, 31 (1981) 676.
633. S. Bhattacharya, P. Khandual and C.R. Saha, *Chem. Ind. (London)*, (1982) 600.
634. E.E. Nifant'ev, S.A. Rumyantseva, M.P. Koroteev, E.M. Abbasov, A.T. Teleshev, V.A. Pavlov and E.I. Kalbunovskii, *Phophorus Sulphur*, 12 (1981) 27.
635. K. Holze, Z. Li, B. Oser, M. Kelm and W.D. Deckwer, *Chem.-Ing.-Tech.*, 55 (1983) 650 [*Chem. Abstr.*, 99 (1983) 130108w].
636. A.F. Shestakov and S.M. Vinogradova, *Koord. Khim.*, 9 (1983) 248.

637. A.G. Dedov, T.Yu. Filippova, E.B. Neimerovets, L.V. Popov, I.P. Stepanova and E.A. Karakhanov. *Khim. Geterotsikl. Soedin.*, (1983) 912 [*Chem. Abstr.*, 99 (1983) 122210h].
638. E.A. Karakhanov, A.G. Dedov, A.S. Loktev, L.V. Popov, P.A. Sharbatyan and I.V. Arkhangel'skii, *Khim. Geterotsikl. Soedin.*, (1983) 754 [*Chem. Abstr.*, 99 (1983) 87587n].
639. Y. Kawabata, T. Hayashi, T. Isoyama and I. Ogata, *Fundam. Res. Organomet. Chem., Proc. China-Jpn.-U.S. Trilateral Semin., Organomet. Chem., 1st*, (1980) (Pub. 1982) 781 [*Chem. Abstr.*, 97 (1982) 109276y].
640. G.K. Anderson, C. Billard, H.C. Clark, J.A. Davies and C.S. Wong, *Inorg. Chem.*, 22 (1983) 439.
641. Agency of Industrial Sciences and Technology, Jpn. Kokai Tokkyo Koho JP 82,131,734 (1982) [*Chem. Abstr.*, 97 (1982) 215550t].
642. J. Kiji, T. Okano, K. Odagiri, N. Ueshima and H. Konishi, *J. Mol. Catal.*, 18 (1983) 109.
643. G. Consiglio, P. Pino, L.I. Flowers and C.U. Pittman, *J. Chem. Soc., Chem. Commun.*, (1983) 612.
644. M.R. Popchenko, M.N. Manakov and T.I. Tarasova, *Neftepererab. Neftekhim. (Moscow)*, (1982) 37 [*Chem. Abstr.*, 97 (1982) 181677x].
645. H. Alper, J.B. Woell, B. Despeyroux and D.J.H. Smith, *J. Chem. Soc., Chem. Commun.*, (1983) 1270.
646. A.I. Min'kov and G.V. Savchenko, *Kinet. Katal.*, 23 (1982) 634.
647. H. Alper, K. Hashem and J. Heveling, *Organometallics*, 1 (1982) 775.
648. M. Uchiyama, T. Suzuki and Y. Yamazaki, *Nippon Kagaku Kaishi*, (1982) 236 [*Chem. Abstr.*, 96 (1982) 217396a].
649. L.D. Martin and J.K. Stille, *J. Org. Chem.*, 47 (1982) 3630.
650. T. Kobayashi and M. Tanaka, *J. Organomet. Chem.*, 233 (1982) C64.
651. F. Ozawa, H. Soyama, T. Yamamoto and A. Yamamoto, *Tetrahedron Lett.*, 23 (1982) 3386.
652. V.P. Baillargeon and J.K. Stille, *J. Am. Chem. Soc.*, 105 (1983) 7175.
653. Mitsui Toatsu Chemicals Inc., Jpn. Kokai Tokkyo Koho JP 82 07,456 (1982) [*Chem. Abstr.*, 96 (1982) 218394k].
654. V.I. Manov-Yuvenskii, B.K. Nefedov and Kh.O. Khoshdurdyev, *Izv. Akad. Nauk USSR, Ser. Khim.*, (1982) 1320.
655. M. Ichikawa, *CHEMTECH*, 12 (1982) 674.
656. S.P. Current, *J. Org. Chem.*, 48 (1983) 1779.
657. S.M. Brailovskii, O.N. Temkin and V.S. Shestakova, *Kinet. Katal.*, 24 (1983) 326.
658. T. Itahara, *Chem. Lett.*, (1982) 1151.
659. T. Itahara, *Chem. Lett.*, (1983) 127.
660. J. Tsuji, K. Sato and H. Nagashima, *Tetrahedron Lett.*, 23 (1982) 893.
661. V.P. Tret'yakov and A.N. Osetskii, *Kinet. Katal.*, 23 (1982) 1126.
662. A. Kaszongi, J. Vojtko and M. Hrusovsky, *Collect. Czech. Chem. Commun.*, 47 (1982) 2128.
663. N.I. Kuznetsova, V.A. Likholobov, M.A. Fedotov and Yu.I. Ermakov, *Zh. Khim.*, (1982) Abstr. No. 2281045 [*Chem. Abstr.*, 98 (1983) 71277e].
664. Kh.M. Minachev, N.Ya. Usachev, A.P. Rodin and Ya.I. Isakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1975.
665. L.V. Levchenko and Z.M. Zavorkhina, *Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR*, 57 (1982) 168 [*Chem. Abstr.*, 98 (1983) 178320t].
666. N.I. Kuznetsova, V.A. Likholobov, M.A. Fedotov and Yu.I. Ermakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 2799.
667. M.G. Volkhonskii, V.A. Likholobov and Yu.I. Ermakov, *React. Kinet. Catal. Lett.*, 21 (1982) 213.
668. M.G. Volkhonskii, V.A. Likholobov and Yu.I. Ermakov, *Kinet. Katal.*, 24 (1983) 578.
669. N.I. Kuznetsova, V.A. Likholobov and Yu.I. Ermakov, *React. Kinet. Catal. Lett.*, 22 (1983) 139.
670. M.G. Volkhonskii, V.A. Likholobov, L.I. Shtokalo and Yu.I. Ermakov, *React. Kinet. Catal. Lett.*, 21 (1982) 225.

671. M.G. Volkhonskii, V.A. Likholobov, E.P. Talzi and Yu. I. Ermakov, *React. Kinet. Catal. Lett.*, 21 (1982) 205.
672. M.G. Volkhonskii, V.A. Likholobov and Yu.I. Ermakov, *Kinet. Catal.*, 24 (1983) 289.
673. M. Iriuchijima, *Sekiyu Gakkaishi*, 25 (1982) 349 [*Chem. Abstr.*, 98 (1983) 53134b].
674. M. Iriuchijima, *Sekiyu Gakkaishi*, 26 (1983) 8 [*Chem. Abstr.*, 98 (1983) 197389m].
675. G.A. Dzhemileva, V.N. Odinokov, U.M. Dzhemilev and G.A. Tolstikov, *Izv. Akad. Nauk SSSR. Ser. Khim.*, (1983) 343.
676. G.A. Chukhadzhyan, V.P. Kukolev, N.A. Balyushina and L.N. Melkonyan, *Arm. Khim. Zh.*, 35 (1982) 367 [*Chem. Abstr.*, 98 (1983) 4361q].
677. A. Heumann, P. Chauvet and B. Waegell, *Tetrahedron Lett.*, 23 (1982) 2767.
678. Ya.V.Salyn, M.K. Starchevskii, I.P. Stolyarov, M.N. Vargaftic, V.I. Nefedov and I.I. Moiseev, *Kinet. Catal.*, 24 (1983) 631.
679. J. Tsuji, H. Nagashima and K. Hori, *Tetrahedron Lett.*, 23 (1982) 2679.
680. T. Hosokawa, T. Ohta and S-I. Murahashi, *J. Chem. Soc., Chem. Commun.*, (1983) 848.
681. E.J. Mistrik and A. Mateides, *Chem. Tech. (Leipzig)*, 35 (1983) 90.
682. S.M. Brailovskii, L. Elfteriu, O.N. Chernysheva and A.P. Belov, *Kinet. Katal.*, 23 (1982) 54.
683. I.P. Stolyarov, M.N. Vargaftik, O.M. Nefedov and I.I. Moiseev, *Kinet. Catal.*, 23 (1982) 313.
684. S. Uemura, S. Fukuzawa, A. Toshimitsu and M. Okano, *Tetrahedron Lett.*, 23 (1982) 87.
685. J. Muzart, P. Pale and J.P. Pete, *Tetrahedron Lett.*, 23 (1982) 3577.
686. S.M. Paraskewas and A.A. Danopoulos, *Synthesis*, (1983) 638.
687. T. Hosokawa, Y. Imada and S-I. Murahashi, *J. Chem. Soc., Chem. Commun.*, (1983) 1245.
688. Y. Chen, J. Liu, Y. Lin, J. Ni, J. You, C. Xiao and Y. Wang, *Wuhan Daxue Xuebao, Ziran Kexueban*, (1981) 61 [*Chem. Abstr.*, 97 (1982) 7147q].
689. H. Watanabe, M. Saito, N. Sutou, K. Kishimoto, J. Inose and Y. Nagai, *J. Organomet. Chem.*, 225 (1982) 343.
690. Toshiba Silicone Co., Ltd., Jpn Kokai Tokkyo Koho JP 81,122,387 (1981) [*Chem. Abstr.*, 96 (1982) 162931p].
691. R. Yamaguchi, H. Kawasaki, T. Yoshitome and M. Kawanisi, *Chem. Lett.*, (1982) 1485.
692. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima and H. Nozaki, *J. Am. Chem. Soc.*, 105 (1983) 4491.
693. W.R. Jackson and C.G. Lovel, *Aust. J. Chem.*, 35 (1982) 2053.
694. P.S. Elmes and W.R. Jackson, *Aust. J. Chem.*, 35 (1982) 2041.
695. M.W. Majchrzak, A. Kotelko and J.B. Lambert, *Synthesis* (1983) 469.
696. M.P. Doyle, R.L. Dorow, W.H. Tamblyn and W.H. Buhro, *Tetrahedron Lett.*, 23 (1982) 2261.
697. T. Migita, M. Chiba, K. Takahashi, N. Saitoh, S. Nakaido and M. Kosugi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3943.
698. T. Migita, N. Saitoh, H. Iizuka, C. Ogyo, M. Kosugi and S. Nakaido, *Chem. Lett.*, (1982) 1015.
699. B. Pugin and L.M. Venanzi, *J. Am. Chem. Soc.*, 105 (1983) 6877.
700. L.N. Sukhobok, G.P. Potapov, V.G. Luksha, V.N. Krutii and B.D. Polkovnikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 31 (1982) 2030.
701. T. Kagayama, S. Okabayashi, Y. Amaike, Y. Matsukawa, Y. Ishii and M. Ogawa, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2297.
702. S. Akatuagawa and T. Taketomi, Brit. UK Pat. Appl. GB 2,088, 355 (1982) [*Chem. Abstr.*, 97 (1982) 198413f].
703. T. Tsuda, Y. Chujo and T. Saegusa, *Synth. Commun.*, 11 (1981) 775.
704. T. Ikariya, Y. Ishikawa, K. Hirai and S. Yoshikawa, *Chem. Lett.*, (1982) 1815.
705. M.P. Doyle and D. Van Leusen, *J. Org. Chem.*, 47 (1982) 5326.

706. T. Hirao, N. Yamada, Y. Ohshiro and T. Agawa, *Chem. Lett.*, (1982) 1997.
707. M. Suzuki, Y. Oda and R. Noyori, *Tetrahedron Lett.*, 22 (1981) 4413.
708. V.V. Zamashchikov, E.S. Rudakov and S.A. Mitchenko, *React. Kinet. Catal. Lett.*, 21 (1982) 141.
709. V.V. Zamashchikov, E.S. Rudakov, M.A. Mitchenko and S.L. Litvinenko, *J. Gen. Chem. USSR*, 52 (1982) 2096.
710. R. Bar, Y. Sasson and J. Blum, *J. Mol. Catal.*, 16 (1982) 175.
711. E. Keinan and N. Greenspoon, *Tetrahedron Lett.*, 23 (1982) 241.
712. R.O. Hutchins and K. Learn, *J. Org. Chem.*, 47 (1982) 4380.
713. J. Tsuji, *Pure Appl. Chem.*, 54 (1982) 197.
714. P. Aleksandrowicz, H. Poitrowska and W. Sas, *Monatsh. Chem.*, 113 (1982) 1221.
715. P. Aleksandrowicz, H. Piotrowska and W. Sas, *Tetrahedron*, 38 (1982) 1321.
716. W. Carruthers and S.A. Cumming, *J. Chem. Soc., Chem. Commun.*, (1983) 360.
717. K. Yamamoto and J. Tsuji, *Tetrahedron Lett.*, 23 (1982) 3089.
718. E. Negishi, S. Chatterjee and H. Matsushita, *Tetrahedron Lett.*, 22 (1981) 3737.
719. P.K. Sheffy and J.K. Stille, *J. Am. Chem. Soc.*, 105 (1983) 7173.
720. N. Miyaura, Y. Tanabe, H. Suginome and A. Suzuki, *J. Organomet. Chem.*, 233 (1982) C13.
721. E. Negishi, H. Matsushita, S. Chatterjee and R.A. John, *J. Org. Chem.*, 47 (1982) 3188.
722. T. Hayashi, M. Konishi and M. Kumada, *J. Chem. Soc., Chem. Commun.*, (1983) 736.
723. I.V. Kozhevnikov, *Usp. Khim.*, 52 (1983) 244.
724. E.S. Rudakov and V.M. Ignatenko, *React. Kinet. Catal. Lett.*, 22 (1983) 75.
725. S.A. Deiko, A.D. Ryabov, A.K. Yatsimirskii and I.V. Berezin *Dokl. Akad. Nauk SSSR*, 266 (1982) 874 [Chem.].
726. T. Itahara, *Chem. Ind. (London)*, (1982) 599.
727. A. Minato, K. Tamao, T. Hayashi, K. Suzuki and M. Kumada, *Tetrahedron Lett.*, 22 (1981) 5319.
728. E. Negishi, F-T. Luo and C.L. Rand, *Tetrahedron Lett.*, 23 (1982) 27.
729. S. Uemura, S. Fukuzawa and S.R. Patil, *J. Organomet. Chem.*, 243 (1983) 9.
730. T. Hayashi, *ACS Symp. Ser.*, 185 (Asymmetric React. Processes Chem.) (1982) 177.
731. C.E. Russell and L.S. Hegedus, *J. Am. Chem. Soc.*, 105 (1983) 943.
732. T. Sato, T. Itoh and T. Fujisawa, *Chem. Lett.*, (1982) 1559.
733. H. Kleijn, J. Meijer, G.C. Overbeek and P. Vermeer, *Recl.: J. R. Neth. Chem. Soc.*, 101 (1982) 97.
734. M. Kosugi, M. Kameyama and T. Migita, *Chem. Lett.*, (1983) 927.
735. K. Kikukawa, A. Abe, F. Wada and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 56 (1983) 961.
736. T. Jeffrey-Luong and G. Linstrumelle, *Synthesis*, (1983) 32.
737. N. Jabri, A. Alexakis and J.F. Normant, *Tetrahedron Lett.*, 23 (1982) 1589.
738. Yu.N. Usov, E.D. Chekurovskaya and N.I. Kuvshinova, *Deposited Doc.*, (1980) SPSTL 898 Khp-D80 [*Chem. Abstr.*, 97 (1982) 91661h].
739. F.K. Shmidt, V.S. Tkach, L.V. Mironova and N.D. Malakhova, *Ref. Zh. Khim.*, (1982) Abstr. No 23B1061 [*Chem. Abstr.*, 98 (1982) 88747f].
740. G.A. Chukhadzhyan, L.I. Sagradyan, T.S. Elbakyan and V.A. Matosyan, *Arm. Khim. Zh.*, 36 (1983) 478 [*Chem. Abstr.*, 99 (1983) 196361e].
741. C.U. Pittman, R.M. Hanes and J.J. Yang, *J. Mol. Catal.*, 15 (1982) 377.
742. H. Watanabe, A. Nagai, M. Saito, H. Tanaka and Y. Nagai, *Kenkyu Hohoku-Asahi Garasu Kogyo Gijutsu Shoreikai*, 38 (1981) 111 [*Chem. Abstr.*, 97 (1982) 181653m].

743. L.I. Zakharkin, V.N. Medvedkov and E.A. Petrushkina, *J. Gen. Chem. USSR*, 52 (1982) 1886.
744. L.I. Zakharkin, E.A. Petrushkina and L.S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 886.
745. R.F. Heck, *Pure Appl. Chem.*, 53 (1981) 2323.
746. L. Shi, C.K. Narula, K.T. Mak, L. Kao, Y. Xu and R.F. Heck, *J. Org. Chem.*, 48 (1983) 3894.
747. F.E. Zeigler, U.R. Chakraborty and R.B. Weisenfeld, *Tetrahedron*, 37 (1981) 4035.
748. R.F. Heck, *Adv. Chem. Ser.*, 196 (Catal. Aspects Met. Phosphine Complexes) (1982) 213.
749. S. Cacchi and A. Arcadi, *J. Org. Chem.*, 48 (1983) 4236.
750. M. Catellani and G.P. Chiusoli, *J. Organomet. Chem.*, 247 (1983) C59.
751. M. Catellani and G.P. Chiusoli, *Tetrahedron Lett.*, 23 (1982) 4517.
752. D.E. Ames and A. Opalko, *Synthesis*, (1983) 234.
753. A. Hallberg and C. Westerlund, *Chem. Lett.*, (1982) 1993.
754. M. Catellani and G.P. Chiusoli, *J. Organomet. Chem.*, 233 (1982) C21.
755. M. Mori, I. Oda and Y. ban, *Tetrahedron Lett.*, 23 (1982) 5315.
756. B.M. Trost and D.M.T. Chan, *J. Am. Chem. Soc.*, 105 (1983) 2315.
757. A. Bou, M.A. Pericas and F. Serratosa, *Tetrahedron Lett.*, 23 (1982) 361.
758. T. Jeffery-Luong and G. Linstrumelle, *Synthesis*, (1982) 738.
759. P.M. Henry, N.A. Lewis and H. Taube, *Canad. J. Chem.*, 60 (1982) 1143.
760. M. Uchiyama, T. Suzuki and Y. Yamazaki, *Chem. Lett.*, (1983) 1165.
761. T. Nakano, M. Takahashi, T. Ashizawa, T. Arai, S. Seki, H. Matsumoto and Y. Nagai, *Chem. Lett.*, (1982) 613.
762. T. Sakakibara and T. Hamakawa, *Chem. Lett.*, (1982) 1823.
763. A. Spencer, *J. Organomet. Chem.*, 247 (1983) 117.
764. Y. Fujiwara, M. Yoshidomi, H. Kuromaru and H. Taniguchi, *J. Organomet. Chem.*, 226 (1982) C36.
765. S. Murahasi, H. Mitsui, T. Watanabe and S. Zenki, *Tetrahedron Lett.*, 24 (1983) 1049.
766. G.B. Shul'pin, G.V. Nizova and A.E. Shilov, *J. Chem. Soc., Chem. Commun.*, (1983) 671.
767. E.W. Corcoran and L.G. Sneddon, *Inorg. Chem.*, 22 (1983) 182.
768. Yu.N.Unusov, E.D. Chekurovskaya, T.G. Vaistub and A.N. Akimov, *Mekhanizm Katalit. Reaktsii. Materialy 3 Vses. Konf., Novostbirsk* (1982) 194 [*Chem. Abstr.*, 98 (1983) 34000p].
769. M. Kosugi, I. Hagiwara and T. Migita, *Chem. Lett.*, (1983) 839.
770. M. Kosugi, I. Hagiwari, T. Sumiya and T. Migita, *J. Chem. Soc., Chem. Commun.*, (1983) 344.
771. H. Urabe, Y. Takano and I. Kuwajima, *J. Am. Chem. Soc.*, 105 (1983) 5703.
772. H. Urata, H. Suzuki, Y. Moro-Oka and T. Ikawa, *J. Organomet. Chem.*, 234 (1982) 367.
773. Y. Akita, M. Shimazaki and A. Ohta, *Synthesis*, (1981) 974.
774. T. Fuchikami and I. Ojima, *Tetrahedron Lett.*, 23 (1982) 4099.
775. T. Itahara, R. Ebihara and K. Kawasaki, *Bull. Chem. Soc. Jpn.*, 56 (1983) 2171.
776. N. Oguni, T. Omi and Y. Yamamoto, *Chem. Lett.*, (1983) 841.
777. J.E. Baeckvall, R.E. Nordberg and J.E. Nystrom, *Tetrahedron Lett.*, 23 (1982) 1617.
778. K. Kikukawa and T. Matsuda, *J. Organomet. Chem.*, 235 (1982) 243.
779. M. Ishikawa, H. Sugisawa, M. Kumada, T. Higuchi, K. Matsui and K. Hirotsu, *Organometallics*, 1 (1982) 1473.
780. T.B. Flanagan, B.S. Bowerman, S. Rundqvist and Y. Andersson, *J. Chem. Soc., Faraday Trans. 1*, 79 (1983) 1605.
781. K.B. Schwartz, J.B. Parise, C.T. Prewitt and R.D. Shannon, *Acta Crystallogr., Sect. B: Struct. Sci.*, B39 (1983) 217.
782. K.B. Schwartz and J.B. Parise, *J. Phys. Chem. Solids*, 43 (1982) 911.
783. D.A. Keszler and J.A. Ibers, *Inorg. Chem.*, 22 (1983) 3366.
784. A.E. Dwight, *J. Less-Common Met.*, 93 (1983) 411.

785. F.J.A.M. Greidanus, L.J. De Jongh, W.J. Huiskamp, A. Furrer and K.H.J Buschow, *Physica B + C (Amsterdam)*, 115 (1983) 137.
786. H. Nyman, *Acta Crystallogr., Sect. B, Struct. Sci.*, B39 (1983) 529.
787. T. Bansagi, J. Rasko and F. Solymosi, *Stud. Surf. Sci. Catal.*, 17 (Spillover Adsorbed Species) (1983) 109.