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6. PALLADIUM AND PLATINUM

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CONTENTS

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INTRODUCTION

This review covers the papers recorded in Chemical Abstracts during 1980 up to and including Volume 93 Number 18. It thus effectively covers the period from mid-1979 to mid-1980 with one or two earlier papers that were slow to appear in Chemical Abstracts.

The highlights of the year have included continual developments of our understanding of the interaction of platinum(II) complexes with polypeptides and nucleic acids as well as a study of the factors involved in the liberation of histamine by platinum(II) complexes used in the course of cancer therapy which gives rise to "platinosis" (Section 6.5.3). Many platinum and palladium compounds are still being tested as potential drugs for cancer therapy, although many of the ligands involved are themselves so much more toxic than ammonia and chloride that most are clearly unlikely to be successors to *cis*-$[Pt(NH_3)_2Cl_2]$ even if activity were significantly greater with respect to certain tumours.

Palladium(I) and platinum(I) chemistry has been developed significantly during the year. Although still very much in its infancy, our knowledge and understanding of this area is beginning to open up and catalytically interesting species can be anticipated soon (see Section 6.6). A similar comment applies to platinum(0)-carbonyl chemistry, where our understanding of the chemistry of the polynuclear carbonyl anions $[Pt_3(CO)_6]_n^{2-}$ has taken a significant step forward. The preparation of $[Pt_{19}(CO)_{22}]^{4-}$ takes us a long way towards a molecular species with less than one carbonyl ligand per metal atom as found on metal surfaces during heterogeneous catalysis (see Section 6.7.3). The systematic synthesis of heteropolynuclear complexes containing platinum and other transition metal atoms linked through carbene and carbyne bridges will almost certainly yield exciting new catalytically active species (see Section 6.7.5).

6.1 PLATINUM(VI)

PtF_6 has been prepared by heating thoroughly-dried Pt sponge in an atmosphere of fluorine ($Pt:F_2 = 1:15$) at 200 °C for several hours [1]. The thermal decomposition of PtF_6 is a useful method for preparing PtF_4 [1].

6.2 PALLADIUM(IV) AND PLATINUM(IV)

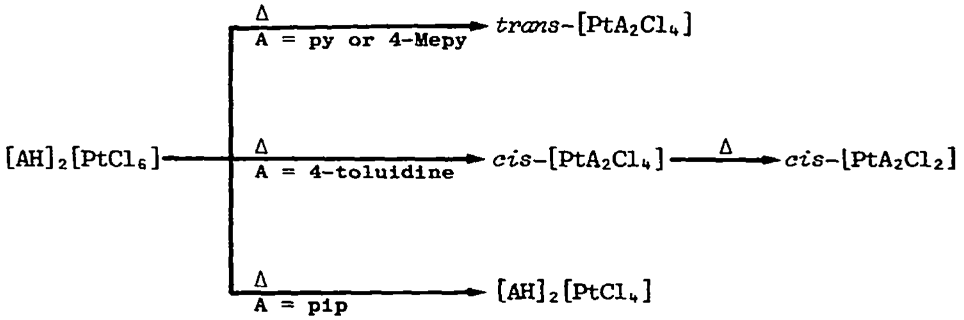
6.2.1 Complexes with Group VIIB Donor Ligands

Nitrosyl salts of $[PdF_6]^{2-}$ and $[PtF_6]^{2-}$ have been prepared by either treating the metals with NOF and fluorine, or the metal fluorides with nitric oxide [2]. An X-ray diffraction study of $[NH_4]_2[PtF_6]$ showed it to have the $K_2[PtCl_6]$ antifluorite structure with Pt-F bonds of 1.742(8) Å [3]. A study of the electronic structures of $K_2[PdX_6]$ (X = F, Cl or Br) by XPES showed that substitution of F by Cl led to a decrease in the ionisation potential of all molecular electron levels in the complex; this effect was smaller on replacing Cl by Br [4]. The enthalpy of formation of PtF_4 is 40±40 kJ mol^{-1} and the dissociation energy of reaction (1) is 326±40 kJ mol^{-1} [5]. The electron

$$PtF_4 \longrightarrow PtF_2 + F_2 \qquad (1)$$

affinity of PtF_4 is 5.11 eV [6]. XeF_2 oxidises $[Pt(NH_3)_4]Cl_2$ to *trans*-$[Pt(NH_3)_4F_2]Cl_2$ in the solid phase, but on dissolving the product in ethanenitrile it rearranges to *trans*-$[Pt(NH_3)_4Cl_2]F_2$, which on dissolving in water is claimed to form $[Pt(NH_3)_4(OH)_2]Cl_2$ [7].

When $PtCl_4$ is prepared from platinum sheet or platinum black through H_2PtCl_6, the rate at which the platinum dissolves is markedly accelerated if the etching solution is saturated with chlorine. The optimum chlorination temperature is 265 °C; $PtCl_4.1.48\ H_2O$ initially formed is fully dehydrated by heating at 220 °C. $PtCl_4$ itself starts to decompose above 290 °C forming $PtCl_2$, which then decomposes above 490 °C to platinum metal [8]. The heats of formation of platinum chlorides [9] and the heat capacity of $K_2[PtCl_6]$ at low temperatures [10] have been reported. The synthesis and study of the action of heat on a series of $[AH]_2[PtCl_6]$ (A = amine) complexes showed that the result of the action of heat depends upon the cation, reactions (2)-(4) [11,12]. Three series of

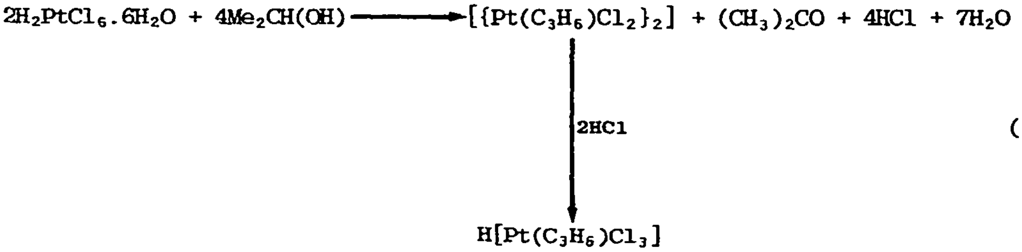


$$[AH]_2[PtCl_6] \xrightarrow[\text{A = py or 4-Mepy}]{\Delta} trans\text{-}[PtA_2Cl_4] \qquad (2)$$

$$[AH]_2[PtCl_6] \xrightarrow[\text{A = 4-toluidine}]{\Delta} cis\text{-}[PtA_2Cl_4] \xrightarrow{\Delta} cis\text{-}[PtA_2Cl_2] \qquad (3)$$

$$[AH]_2[PtCl_6] \xrightarrow[\text{A = pip}]{\Delta} [AH]_2[PtCl_4] \qquad (4)$$

solid solutions $K_2[(Pt/M)Cl_6]$ (M = Re, Os or Ir) have been prepared and their spectroscopic and magnetic properties investigated [13]. A Franck-Condon analysis has been applied to platinum(IV) spectra [14]. ^{35}Cl, ^{37}Cl and ^{79}Br, ^{81}Br isotope shifts of 0.167 ppm per chlorine and 0.028 ppm per bromine isotope substitution are clearly resolved in the 86 MHz ^{195}Pt NMR spectra of $Na_2[PtCl_6]$ and $Na_2[PtBr_6]$ as well as in the mixed chloro-bromo complexes. This enables the number of chlorine and bromine ligands in mixed complexes to be counted from the multiplet splitting patterns [15]. When $[NH_4]_2[PtCl_6]$ is irradiated at 254 nm, $PtCl_4$ is the sole platinum-containing product [16]. Speier's catalyst is used as a catalyst for the hydrosilylation of alkenes. It is prepared by dissolving $H_2PtCl_6.6H_2O$ in isopropanol and has now been shown to contain $H[Pt(C_3H_6)Cl_3]$, formed by reaction (5), as the active hydrosilylation catalyst [17].



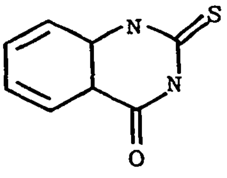
$$\begin{tikzcd}
2H_2PtCl_6.6H_2O + 4Me_2CH(OH) \arrow[r] & {[\{Pt(C_3H_6)Cl_2\}_2]} + (CH_3)_2CO + 4HCl + 7H_2O \arrow[d, "2HCl"] \\
 & H[Pt(C_3H_6)Cl_3]
\end{tikzcd} \qquad (5)$$

The low frequency vibrational spectra of $A_2[PtBr_6]$ (A = K, $[NMe_4]$ or $[N(CD_3)_4]$) show new, and in some cases sharp, bands being formed at low temperature due to phase transitions breaking the antifluorite $K_2[PtCl_6]$-type symmetry [18]. The literature ambiguity in the assignment of the ν_4 mode of $[PtBr_6]^{2-}$ is resolved, placing it at *ca.* 130 cm^{-1} [18]. Measurement of the ^{127}I NQR resonance frequency for the $\frac{3}{2}$ to $\frac{1}{2}$ transition in the antifluorite crystal $[NH_4]_2[PtI_6]$ revealed the presence of a previously unknown structural phase transition in which the crystal symmetry is reduced from cubic to orthorhombic [19].

6.2.2 Complexes with Group VIB Donor Ligands

The preparation, structure and uses of the platinum group metal oxides have been reviewed [20]. Divalent transition metal and alkaline-earth metal (M) hydroxides of the type $M[Pt(OH)_6]$ have been prepared, and used to prepare $MPtO_3$ by heating; however, heating above 600 °C gives the metal oxide together with platinum metal [21]. Single crystals of $Pd_{0.5}Pd_3O_4$ and $Na_xPt_3O_4$ have been prepared and investigated by X-ray diffraction [22]. Thin films of PtO and PtO_2 have been prepared by reactive sputtering. By adjusting the deposition rate a new phase intermediate between PtO and PtO_2 can be formed [23].

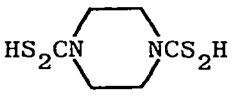
$Na_2[Pd(OH)_6]$ prepared by treating $Na_2[PdCl_6]$ with a 50% excess of sodium hydroxide, has been fully characterised and shown to be isostructural with $K_2[Pt(OH)_6]$ [24]. Decomposition begins on heating at 170 °C and is complete at 254 °C, yielding Na_2PdO_3 [24]. A vibrational study of $K_2[PtCl_5\{O(H/D)\}]$ has enabled force fields to be calculated [25]. Acid-dissociation constants of a range of platinum(IV) amino-halo-aqua complexes have been reported [26,27]. X-ray diffraction and differential thermal analysis have been used to study a series of $[\{PtMe_3L\}_2]$ and $[PtMe_3LL']$ (L = acac, benzac, 4-imino-2-pentanone, hfacac or pivaloyltrifluoroacetone; L' = H_2O or py) complexes [28]. Quinazoline-2-thione-4-one (1; HQ) is reported to form $[PdQ_2(H_2O)_2]Cl_2$, in which the ligand



(1)

is bound through nitrogen and sulphur to palladium(IV), and $[Pt(QH)_6]Cl_4$ in which it is bound through oxygen [29].

Platinum(IV)-5-pyrazolone complexes with thiocyanate ligands involve Pt^{IV}-S bonding [30]. $[\{PtMe_3(SMe)\}_4]$, prepared from $[PtMe_3]_2[SO_4]$ and Na[SMe], is tetrameric in chloroform solution and in the vapour phase; the totally symmetric Pt-S stretching vibration is observed at 126 cm^{-1} [31]. $[PtMe_3X]$ (X = Cl, Br or I) react with $MeE(CH_2)_nEMe$ (E = S or Se) to form mononuclear $[PtXMe_3\{MeE(CH_2)_nEMe\}]$ (n = 2 or 3) or dinuclear $[\{PtXMe_3\}_2(MeECH_2EMe)]$ (n = 1), in which $MeECH_2EMe$ and the two halides bridge between the two $\{PtMe_3\}$ groups [32]. These preparations require heating under reflux in benzene or chloroform when E = S, but take place at room temperature when E = Se. Dynamic NMR studies have yielded accurate energy data for sulphur and selenium pyramidal inversion in $[PtXMe_3\{MeE(CH_2)_nEMe\}]$ (n = 2 or 3). The energy of the intramolecular inversion, in which $^{195}Pt-^{1}H$ coupling is retained, is 9-12 kJ mol^{-1} higher at selenium than at sulphur [33]. The main reason for this is thought to be the increase in *s*-character of the lone pair of electrons on the chalcogen. There is no obvious dependence on halide, suggesting that the *cis*-influence of the halide is not pronounced. Oxidation of palladium(IV) dithiolene complexes, $[Pd(S_2C_2R_2)_2]$ (R = CMe_2H, Ph or C_6H_4-4-OMe), yields ESR evidence for a palladium(V) species [34]. Piperazinebis(dithiocarbamate) (2) complexes of platinum(IV), PtL_4, with two bidentate and two monodentate ligands, have been prepared; palladium forms palladium(II) complexes only [35]. Substituted thiosemicarbazide and thiosemicarbazone complexes of palladium(IV) and 3,4,5-pyridazinetrithiol complexes of platinum(IV) have been reported [36,37]. Tetramethylthiourea (3) reacts with $[PtCl_6]^{2-}$ to form a platinum(IV) derivative; less substituted thioureas, $Me_nH_{4-n}N_2CS$ (n = 0-3), form initial platinum(IV) complexes which are then reduced to platinum(II) at the expense of the thiourea which is oxidised to formamidine disulphide (4) or its corresponding methyl derivatives [38].



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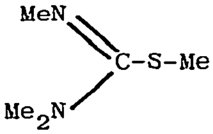

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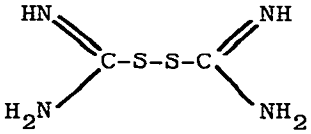
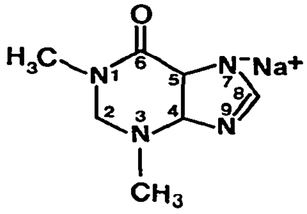


(4)

High pressure phase transition studies of $Pd_{1-x}M_xSe_2$ (M = Ni, Co or Ru) have been reported [39].

6.2.3 Complexes with Group VB Donor Ligands

Fac-$[PtMe_3(H_2O)_3]_2[SO_4]$ reacts with sodium theophyllinate, Na[thp] (5) to give $[\{PtMe_3(thp)\}_3]$ after dehydration. This has a cyclic structure with Pt-N(7), N(9)-Pt bridges and weak direct O(6)-Pt bonds [40]. The three geometric isomers of $[PtMe_2X(gly)H_2O]$ with the two methyls and the halide in a *facial* arrangement have all been prepared [41]. Their reactions with sodium



(5)

hydroxide, sodium bromide and 3,5-Me_2py are largely controlled by the high *trans*-effects of the methyl ligands, although slower reactions *cis* to the methyl groups also occur [41]. The three isomers react with sodium glycinate to form *bis*- and *tris*-glycinate complexes according to the following rules [42]:

(i) H_2O *trans* to methyl is displaced by glycinate *N*.

(ii) If excess glycinate is used the glycinate *O* coordinated *trans* to methyl in a chelate ring may be displaced by glycinate *N*.

(iii) Groups coordinated *cis* to methyl are not displaced at room temperature.

(iv) Glycinate *O* coordinated *trans* to methyl in $[PtMe_2(gly)_2]$ is susceptible to attack by hydroxide ions or glycinate *N*.

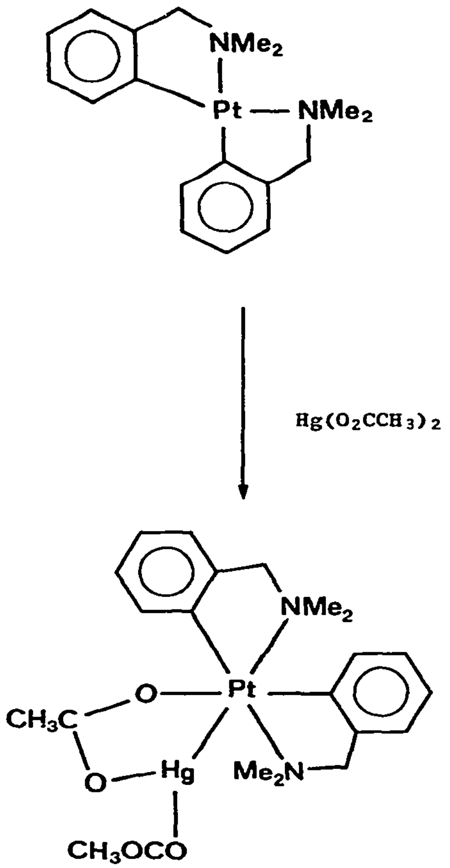
The l- and dl-methionine (HL) complexes $[Pt(HL)Cl_4].H_2O$ and $[PtLCl_3]$, prepared by reactions (6) and (7) involve bidentate *N*,*S* and tridentate coordination

$$[Pt(HL)Cl_2] \xrightarrow[(2)\ HCl]{(1)\ aq.K[MnO_4]} [Pt(HL)Cl_4].H_2O \qquad (6)$$

$$[Pt(HL)Cl_4].H_2O + NaOH \longrightarrow [PtLCl_3]^{\cdot} + NaCl + 2H_2O \qquad (7).$$

through *N*,*S* and carboxylate, respectively [43]. 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine and 2,2'-biquinoline form 1:1 complexes on reaction with $[PtCl_6]^{2-}$ [44]. Oxidation of [Pt(TTP)] with H_2O_2 in acidic solution followed by treatment with HCl yields $[Pt(TTP)Cl_2]$ which is thermally stable up to 200 °C. Electrochemical reduction yields [Pt(TTP)] in a two-electron step. The platinum to porphine π-back donation decreases on oxidation from platinum(II), but does not completely disappear [45].

A platinum(IV) complex, thought to be an intermediate in transmetallation reactions between platinum(II) and mercury(II), has been isolated using reaction (8). It has been characterised by X-ray diffraction, which shows a Pt^{IV}-Hg bond length of 2.513(1) Å [46]. When the *trans*-platinum(II) starting complex is used, an unstable platinum(IV)-mercury intermediate is formed which eliminates mercury metal to form a mixture of *cis*-C,*trans*-N- and *trans*-C,*cis*-N-$[Pt(2\text{-}C_6H_4CH_2NMe_2)_2(O_2CMe)_2]$ [46]. Platinum(IV) complexes of the pentacoordinated



(8)

2,6-dipicolinic acid hydrazide and *N*,*N*'-dibenzylidene dipicolinic acid hydrazide [47], as well as of a number of substituted indazoles [48], have been characterised. The acidic properties of *trans*-tetraamine and pentaamine complexes of platinum(IV) with 1,2-diaminoethane, pyridine or ammonia ligands have been determined and shown to support Grinberg's hypothesis of amine dissociation [49]. The rate of oxidation of $[PtL_4]^{2+}$ (L = ½en or RNH_2; R = H, Me, Et or Pr) by iron(III), which involves two successive one-electron oxidations, decreases in the presence of iron(II) [50].

$K_2[PdAs_2]$, which has been prepared from its elements, forms infinite $PdAs_2$ zig-zag ribbons and conforms to a filament [51].

6.2.4 Complexes with Group IVB Donor Ligands

A platinum(IV)-naphthalene complex has been prepared by treating H_2PtCl_6 with naphthalene in aqueous trifluoroethanoic acid [52]. The crystal structure shows that $[H_3O][Pt(C_{10}H_7)Cl_4(H_2O)]$ contains a platinum-carbon σ-bond. This type of compound is believed to be an intermediate in H/D exchange for aromatic compounds, catalysed by H_2PtCl_6. A scanning laser has been used to react electron-beam-deposited palladium and platinum thin films with single-crystal silicon substrates [53]. A single laser scan reacts 1300 Å of palladium with silicon to form either Pd_2Si or PdSi, depending on the laser power; platinum forms superconducting Pt_2Si_3. Pt_2Si and PtSi films on silicon have been prepared by depositing thin platinum films under ultra-high vacuum in the complete absence of oxygen [54].

6.3 PALLADIUM AND PLATINUM COMPLEXES WITH MIXED (IV/II) OXIDATION STATES

The crystal and molecular structures of a number of complexes containing linear chains of alternating platinum(IV) and platinum(II) have been determined and the results are summarised below $\{\rho = r(Pt^{IV}\text{-}X)/r(Pt^{II}\text{-}X)\}$:

$[Pt(en)_2][Pt(en)_2Cl_2][CuCl_4]_4$	[55]	$r(Pt^{IV}\text{-}Cl)$	2.328(8) Å
		$r(Pt^{II}\text{-}Cl)$	2.937(9) Å
		ρ	0.80
$[Pt(en)_2][Pt(en)_2Br_2][ClO_4]_4$	[56]	$r(Pt^{IV}\text{-}Br)$	2.71(2) Å
		$r(Pt^{II}\text{-}Br)$	2.76(2) Å
		ρ	0.98
$[Pt(1,2\text{-}pn)_2][Pt(1,2\text{-}pn)_2I_2]I_4$	[56]	$r(Pt^{IV}\text{-}I)$	2.815(2) Å
		$r(Pt^{II}\text{-}I)$	2.995(2) Å
		ρ	0.94
$[Pt(1,3\text{-}pn)_2][Pt(1,3\text{-}pn)_2Cl_2][BF_4]_4$	[57]	$r(Pt^{II}\text{-}Cl)$	2.299(6) Å
		$r(Pt^{IV}\text{-}Cl)$	3.096(6) Å
		ρ	0.74
$[Pt(1,3\text{-}pn)_2][Pt(1,3\text{-}pn)_2Br_2][ClO_4]_4$	[57]	$r(Pt^{II}\text{-}Br)$	2.546(7) Å
		$r(Pt^{IV}\text{-}Br)$	2.955(7) Å
		ρ	0.86
$[Pt(1,3\text{-}pn)_2][Pt(1,3\text{-}pn)_2Br_2][BF_4]_4$	[57]	$r(Pt^{II}\text{-}Br)$	2.541(5) Å
		$r(Pt^{IV}\text{-}Br)$	2.921(5) Å
		ρ	0.87

Since ρ would have a value of unity if the platinum atoms both had the same oxidation states, it is apparent that the oxidation states are least different with the highly polarisable iodide ligands, and are most different when chloride ligands are present. $[Pt(EtNH_2)_4][Pt(EtNH_2)_4Br_2]Br_4$ has a $Pt^{II}...Br-Pt^{IV}$ chain with two half-occupied bromide positions. The bromides are ordered one-dimensionally but disordered three dimensionally, in that neighbouring chains have alternate Pt-Br distances of Pt^{IV}-Br 2.284(7) and 2.684(6) Å, and Pt^{II}-Br 3.811(7) Å and 3.411(6) Å [58]. Polarised Raman and resonance Raman studies of $[M(en)_2][M(en)_2X_2][ClO_4]_4$ (M = Pd or Pt; X = Cl or Br), $M'_2[MLX_3][MLX_5]$ (M' = K or $[NH_4]$; M = Pd or Pt; L = NH_3 or pyr; X = Cl, Br or I) and $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$ show a strong resonance enhancement of the $X-M^{IV}-X$ symmetric stretching vibration in the chain. Analysis shows the metals are coupled through electron-transfer *via* the halide ions from the d_{z^2} orbitals of the lower to the higher oxidation state metal ions [59-62]. Treatment of $[Pt(NH_3)_4]Cl_2$ with $K_2[PtCl_6]$ yields the Magnus' Green salt extrinsically doped with about 0.5 mol per cent of Pt^{3+}, which are charge compensated by interstitial chloride ions and give rise to semi-conducting properties [63].

Pulsed ^{195}Pt NMR has been used to determine the spin-spin (T_2) and spin-lattice (T_1) relaxation times in $K_2[Pt(CN)_4Br_{0.30}].3.2H_2O$ between 4 and 130 K [64]. A "spin-lattice" model that emphasises the importance of site II water molecules lying between bromide and $[Pt(CN)_4]^{2-}$ ions has been proposed to solve the puzzling problem of the apparent complete softening of shear modulus C_{66} in $K_2[Pt(CN)_4Br_{0.30}].3.2H_2O$, without any structural phase transition at low temperatures [65]. The products obtained by recrystallising $M_2[Pt(CN)_4Cl_{0.3}].3H_2O$ (M = NH_4 or K) from acidic chloride solutions are isomorphous with the original compounds, but contain extra chloride ions and protons in the lattice; these extra ions result in only small changes in the electrical conduction properties [66]. The EPR linewidth in $K_2[Pt(CN)_4Br_{0.30}].3H_2O$ is proportional to the cube of the absolute temperature in the range 100-219 K, and has an anisotropy with a minimum nearly at an angle of the magnetic field of 50° from the *c*-axis [67]. These results have been interpreted as a superposition of the spin-phonon and spin-spin relaxation component in a *quasi*-one-dimensional conductor, within the framework of the mixed-valence model. The crystal structures of $K_{1.75}[Pt(CN)_4].1.5H_2O$ and $K_{1.6}[Pt(C_2O_4)_2].1.2H_2O$ have been reported [68].

6.4 PALLADIUM(III) AND PLATINUM(III)

Platinum(III) ethanoate, $[Pt_2(O_2CMe)_6]$, which has a Pt-Pt bond, is formed in 50% yield when $K_2[Pt(OH)_6]$ is treated with 85% methanoic acid in hot glacial ethanoic acid [69]. Use of excess methanoic acid gave $[Pt_2(O_2CMe)_5]$. The peroxo-bridged platinum(III) complex $[Pt_2(O_2)_2(OH)_2].nK[HSO_4]$ can be prepared by heating $K_2[Pt(NO_2)_4]$ in sulphuric acid at 100-120 °C. After removing the precipitate of $K_2[H_3O][Pt_2(SO_4)_4(OH)(H_2O)]$, the solution is evaporated until sulphuric acid vapour appears, and the residue then dissolved in propanone to yield $[Pt_2(O_2)_2(OH)_2].nKHSO_4$ [70]. Platinum(III) phosphates have been reported. Thus, when *cis*- or *trans*-$[Pt(NH_3)_2(NO_2)_2]$ are treated with phosphoric acid at 100 °C, brown, green and blue precipitates with compositions close to $[NH_4]_2[H_4\{Pt_2(PO_4)_4(H_2O)_2\}]$ are formed, which contain Pt^{III}-Pt^{III} bonds [71].

Photolysis of Pd^{II}-doped silver bromide single crystals at liquid nitrogen temperatures produces a trapped-hole centre, $[PdBr_6]^{3-}$, and a trapped-electron centre, $[PdBr_6]^{5-}$ [72].

A range of "platinum blues" have been investigated. Platinum blues formed by reaction of oxamic acid (H_2L; $HOOCCONH_2$) with $K_2[PtCl_4]$ or $K_2[Pt(NO_2)_4]$ have formulae $K_2[PtLCl_3]$, involving one platinum(III), and $K_7Pt_4L_3(HL)_2(OH)_4(NO_2)_4$, with three platinum(II) and one platinum(III) atoms [73]. The platinum blue formed by reaction between $K_2[PtCl_4]$ and acetamide in water has the formula $[Pt(MeCONH)_2Cl]$ [74,74a]. Platinum blues involving pyrimidine nucleotides, trimethylacetamide, thymine, cytidine, cytosine and oxamic acid have been reported [75-80]. Many of these are oligomeric compounds of variable chain length, in which some platinum atoms are in the +3 oxidation state.

6.5 PALLADIUM(II) AND PLATINUM(II)

6.5.1 Complexes with Group VIIB Donor Ligands

High pressure cubic PdF_2 is stable at 60 kbar and metastable at normal pressure; it is antiferromagnetic with weak overlapped ferromagnetism [81]. A fluorite-type form of PdF_2 with a Pd-F distance of 2.16 Å can be obtained from the rutile-type at 25 °C and 50 kbar followed by quenching at room conditions; the change in volume is 11% relative to the rutile form [82]. Fluorite-type PdF_2 has a resistivity of 10^5 Ω.cm under room conditions, 10^5 lower than the rutile form. The enthalpy of formation of PtF_2 is 80±40 kJ mol^{-1}, and the dissociation energy with formation of platinum metal and fluorine is 644±40 kJ mol^{-1} [5].

A large scale laboratory preparation of 99.9% purity $PtCl_2$ from platinum involves the intermediate formation of $PtCl_2$ and its reduction with hydrazine [83]. $[(MeCONMe_2)_2H]_2[Pd_2Cl_6]$ is formed when palladium and copper powders are heated in the presence of dma and carbon tetrachloride for 8 h at 50 °C [84]. When palladium or platinum are treated with S_2Cl_2, both chlorides and sulphides are formed initially. The sulphides are converted to the chlorides under the action of S_2Cl_2 in the later stages [85].

A study of the chloropalladium(II) species present in aqueous solutions over a range of Pd:Cl ratios showed that only monomeric species were present [86]. A reevaluation of the four stepwise palladium(II)-chloride stability constants in aqueous perchlorate solution at 25 °C agreed with previous literature values to within 0.1 log units [87]. A study [88] of the effect of temperature on the standard potential of the Pd^{2+}/Pd_k system in 1 *M* perchloric acid showed that $E^\circ_{Pd^{2+}/Pd_k}$ is described by equation (9), and that the formation constants for

$$E^\circ_{Pd^{2+}/Pd_k} = 0.932 - 0.00028(T - 298)\ \text{volts} \tag{9}$$

$$Pd^{2+} + 4Cl^- \rightleftharpoons [PdCl_4]^{2-},\ \log K = 5.68 + 1245.90/T \tag{10}$$

$$Pd^{2+} + 4Br^- \rightleftharpoons [PdBr_4]^{2-},\ \log K = 3.56 + 2863.39/T \tag{11}$$

$[PdCl_4]^{2-}$ and $[PdBr_4]^{2-}$ are given by equations (10) and (11), respectively.

A single crystal X-ray diffraction structure of $[dienH_3]_2[PdCl_4]Cl_4$ showed that bond distances were normal [89]. An SCF-Xα calculation yielded binding energies that gave a reasonable interpretation of the XPES spectrum of $[PtCl_4]^{2-}$; the relative energies of the *d*-orbitals were $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ [90]. The resonance Raman spectra of $PdAl_2Cl_8$ and $PdAl_2Br_8$ showed three high-intensity, polarised bands which were attributed to the vibrational modes of the complex associated with the palladium atom [91].

The photochemistry of transition metal complexes has been reviewed [92]. Irradiation of $[NH_4]_2[PtCl_4]$ yields both $PtCl_2$ and $[Pt(NH_3)_4]Cl_2$ [16]. The electronic structures of the excited states involved in the photochemical substitution of $[PtCl_4]^{2-}$ and $[Pt(C_2H_4)Cl_3]^-$ with water, calculated by Adamson's method, agree well with the experimental results [93]. Both $K[Pt(C_2H_4)Cl_3]$ and $K[Pt(dmso)Cl_3]$ catalyse the aquation of $[PtCl_4]^{2-}$; reactions (12)-(14) are believed to describe the mechanism for this [94]:

$$[PtLCl_3]^- + H_2O \underset{\text{dmso)}}{\overset{\text{(L = }C_2H_4\text{ or}}{\rightleftharpoons}} [PtLCl_2(H_2O)] + Cl^- \tag{12}$$

$$[PtLCl_2(H_2O)] + [PtCl_4]^{2-} \rightleftharpoons [LCl_2PtClPtCl_3]^{2-} + H_2O \tag{13}$$

$$[LCl_2PtClPtCl_3]^{2-} \rightleftharpoons [PtLCl_3]^- + [Pt(H_2O)Cl_3]^- \tag{14}$$

The ^{129}I Mössbauer spectra of a number of palladium(II) and platinum(II) complexes have been recorded [95]. The spectra suggest that the *cis*-influence is of comparable magnitude but opposite direction to the *trans*-influence, but neither effect in Mössbauer spectroscopy is directly related to conventional *cis*- and *trans*-influences. In Mössbauer spectroscopy, the effect is related to the charge on the iodide ligand and as such gives a measure of polarising effects, which is useful in homogeneous catalysis since substrate polarisation can influence the availability of low energy reaction pathways [95]. The thermal isomerisation of palladium(II) and platinum(II) is claimed to occur in such a direction as to place a neutral, low *trans*-effect 'indicator' ligand opposite the other ligand with the least *trans*-effect [96]. ^{127}I NQR has been used to following the thermal isomerisation of $[Pt(amine)_2I_2]$ complexes [97].

Trilaurylamine, triphenylphosphine, trioctylphosphine oxide and tetramethyldiamide heptylphosphate have been used to extract palladium from aqueous hydrochloric acid solutions [98–101].

6.5.2 Complexes with Group VIB Donor Ligands

6.5.2.1 Complexes with Unidentate Oxygen Donors

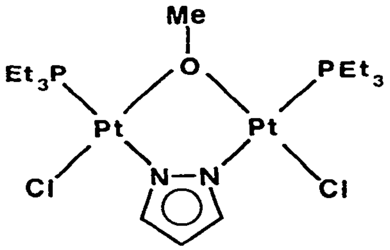
The electronic structure of PdO has been investigated using XPES and UVPES photoemission studies [102]. Treatment of $[M(dppe)Cl_2]$ (M = Pd or Pt) with one equivalent of silver(I) perchlorate in dmf yields oxygen-bonded $[M(dppe)(dmf)Cl][ClO_4]$; weaker oxygen-donors such as alcohols, ethers and propanone result in dimeric $[\{M(dppe)Cl\}_2][ClO_4]_2$ being formed [103]. Treatment of $[Pd(dppe)Cl_2]$ with two equivalents of silver(I) perchlorate in the presence of oxygen donor solvents led to the isolation of $[Pd(dppe)(solvent)_2][ClO_4]_2$ (where solvent = propanone or water) [104]. When the solvent is MeOH, EtOH or thf, the $[Pd(dppe)(solvent)_2]^{2+}$ complexes are stable in solution, but on attempted isolation the ethanol complex decomposes to give palladium metal and acetaldehyde, whereas the methanol and tetrahydrofuran complexes lose solvent to form the *bis*-perchlorato complex $[Pd(dppe)(OClO_3)_2]$. This latter complex is formed directly if the reaction is performed in dichloromethane-benzene solution. The perchlorate ligands are readily displaced by solvent ligands to form $[Pd(dppe)(solvent)_2][ClO_4]_2$ in more donor solvents. The propanone complex $[Pd(dppe)(Me_2CO)_2][ClO_4]_2$ is very sensitive to moisture, readily forming the *bis*-aqua complex [104]. A study of equilibrium (15) showed that, with

$$[Pt_2Cl_4(PPr_3)_2] + 2\text{solvent} \rightleftharpoons 2\textit{trans}\text{-}[PtCl_2(PPr_3)(\text{solvent})] \qquad (15)$$

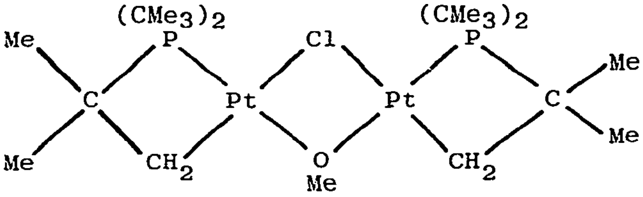
oxygen donor solvents, the position of the equilibrium lay increasingly to the left as the solvent was varied in the order H_2O < MeOH < cyclopentanone < Me_2CO << MeCHO, PhCHO < PhCOPh [105]. Acid dissociation constants of aqua ligands in $[M(H_2O)_2(NO_2)_2]$, $[M(H_2O)_2(NO_2)_3]^-$ (M = Pd or Pt) and $[Pt(NH_3)_2L(H_2O)]^{2+}$ (L = Et_2SO, Pr_2SO, $(CH_2)_4SO$, thiophane or thioxane) have been reported [106,107].

In addition to the perchlorato complex mentioned above $[Ph(PPh_3)_2(OClO_3)(C_6Cl_5)]$ has been prepared by chloride abstraction with silver(I) perchlorate in benzene [108]; the perchlorato ligand is readily displaced by many ligands including ethanoate. Perchlorate and hexafluorophosphate bridged dinuclear complexes $[\{Pd(PPh_3)X(L)\}_2]$ (X = ClO_4 or PF_6; L = 2,4-Cl_2py), have been characterised [109]. When *trans*-$[Pd(NH_3)_2(NO_2)_2]$ is heated in 84% phosphoric acid until the solution becomes deep green, then cooled to room temperature and a 5.7 fold excess of ethanol added, green $H_7[Pd_4(PO_4)_5(NH_3)_6]$ is precipitated; if addition of ethanol is preceeded by cooling to 0 °C, the precipitate obtained is yellow $H_7[Pd_4(PO_4)_5(NH_3)_6]$ which has a different degree of polymerisation [110]. When *trans*-$[Pd(NH_3)_2(NO_2)_2]$ is heated at 40-50 °C in aqueous sulphuric acid until loss of nitrogen oxides has ceased, $[H_3O][NH_4][(SO_4)Pd(NH_3)_2(SO_4)Pd(NH_3)_2(SO_4)Pd(NH_3)_2(SO_4)]^{2+}$ with two bridging and two terminal sulphates is formed [111].

Peroxidation of $[PtL_2(CF_3)(OH)]$ with H_2O_2 yields $[PtL_2(CF_3)(OOH)]$, (L = ½dppe, ½$Ph_2PCH{=}CHPPh_2$ or PPh_2Me) [112]. The methoxy-bridged complexes (6) and (7),



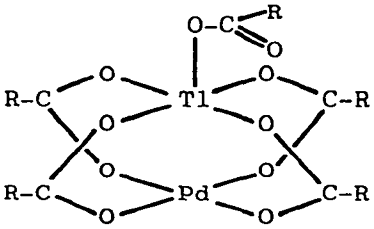
(6)



(7)

have been prepared by treating the corresponding chloride-bridged complexes with methanolic sodium hydroxide [113,114]. Na[OR] (R = H or CH_3) reacts with $[PtL_2ClR']$ (L = ½dppe, PPh_3; R' = CH_2CN, CF_3 or CH_2CF_3) to form *cis*- and *trans*-$[PtL_2(OR)R']$, which undergo facile insertion of CO, COS, CS_2 or SO_2 into the Pt-O bonds [115]. The hydroxo complexes react with a variety of acids, including fairly weak carbon or nitrogen acids, such as phenylethyne, acetamide and methylaniline to give the corresponding condensation complexes. In the activation of molecular hydrogen by $[Pd(PH_3)_2XY]$ (X, Y = O_2CMe, OH or Cl) coordination of dihydrogen is realised by electron density transfer from the 1σ MO of hydrogen to the $5p_z$ orbital of palladium. The H-H bond becomes polarised by interaction with the coordinated acidato ligands, more so in oxygen-containing than in chloride complexes, so that the former are more effective at promoting H-H bond cleavage [116].

Carboxylate bridged palladium(II)-thallium(III) complexes, (8), are formed in reactions (16) and (17) [117]. *Trans*-$[Pd(PPh_3)(O_2CMe)(COOMe)]$ has a unidentate ethanoate ligand, with a Pd-O bond length of 2.116(3) Å [118].



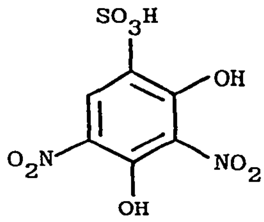
(8)

$$\tfrac{1}{3}[\{Pd(O_2CR)_2\}_3] + Tl(O_2CR')_3 \longrightarrow [PdTl(O_2CR)_2(O_2CR')_3] \qquad (16)$$

$$[PdTl(O_2CMe)_5] + \underset{\text{(excess)}}{5RCOOH} \longrightarrow [PdTl(O_2CR)_5] + 5MeCOOH \qquad (17)$$

Reaction of $[Pd(PR_3)_2Me_2]$ with carbon dioxide in the presence of amines yields the carbamatopalladium(II) complexes $[Pd(PR_3)_2Me(O_2CNR'R'')]$, (R', R'' = H, alkyl or phenyl). When $[Pd(PPh_3)_2Me(O_2CNH_2)]$ is heated in toluene solution, the bridged carbonate palladium(II) complex $[Pd_2(PPh_3)_3Me_2(\mu\text{-}CO_3)]$ is formed [119].

$K_2[PtCl_4]$ reacts with sodium phenylsulphonate and pyridine to form $[Pt(PhSO_2)_2(py)_2]$ which, when dissolved in sulphuric acid solution, slowly precipitates $[Pt(PhSO_2)_2(H_2O)_2]$. During potentiometric titration of $[M(PhSO_2)_2(H_2O)_2]$ (M = Pd or Pt), polymerisation occurs with formation of $K_2[\{M(PhSO_2)_2(\mu\text{-}OH)\}_2]$ [120]. The aqua ligands in $[M(PhSO_2)_2(H_2O)_2]$ have been replaced by the bidentate thioether ligands, $(CH_2SCH_2COOH)_2$ and $EtSCH_2CH_2SCH_2COOH$ [121]. (9; H_3L) reacts with palladium(II) complexes to form $Na[PdCl_2(H_2O)(H_2L)].H_2O$ and $Na_2[Pd(HL)_2].H_2O$ [122]. The reaction of $[Pt(PPh_3)_4]$ with tetrasulphur tetraimide in propanone-benzene solution has now been shown [123] to yield

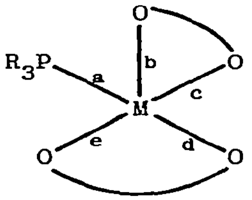


(9)

cis-$[Pt(PPh_3)_2(OSNH)_2]$, with Pt–O bonds of 2.088(12) and 2.173(11) Å, and not $[Pt(PPh_3)_2(S_2N_2H_2)]$ as first thought [124].

6.5.2.2 Complexes with Multidentate Oxygen Donors

X-ray diffraction studies of $[Pt(acac)_2]$ and $[Pd(acac)_2]$.tetrathiafulvalene have yielded Pt–O and Pd–O bond lengths of 1.991(8) and 1.98 Å respectively [125,126]. The crystal structure of $[Pd(acac)(EtNH_2)_2][acac]$ shows Pd–O and Pd-N bond lengths of 2.000(3) and 2.044(3) Å respectively [127]. $[M(hfacac)_2]$ (M = Pd or Pt) react with tertiary phosphines in hexane solution at room temperature to form air-stable square-pyramidal $[M(PR_3)(hfacac)_2]$ complexes. Crystal structures of two of these complexes, (10), have been determined and

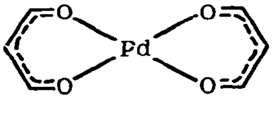


(10)

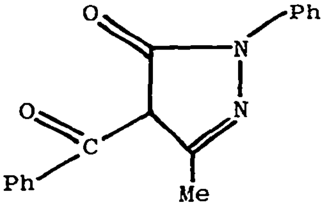
	(M = Pd, R = 2-tolyl)	(M = Pt, R = cych)
a	2.253(2) Å	2.230(4) Å
b	2.797(6) Å	2.794(13) Å
c	2.017(5) Å	1.988(9) Å
d	2.084(6) Å	2.098(10) Å
e	2.001(6) Å	1.984(10) Å

they reveal that the apical oxygen is only very weakly bonded. Consistent with this, the complexes are stereochemically non-rigid in solution. In the platinum complex, site exchange between the oxygen *trans* to phosphorus and the apical oxygen occurs by a twist mechanism, whereas for the palladium complex it is the oxygen *cis* to phosphorus that exchanges with the apical oxygen, again by a twist mechanism [128]. $[M(acac)(\gamma\text{-acac})(PPh_3)]$, (M = Pd or Pt), react with β-dicarbonyl compounds, Hdik, to give one of three types of compound. Dimethylmalonate or methyl or ethylacetoacetate yield $[M(acac)(\gamma\text{-dik})(PPh_3)]$ exclusively, whereas dibenzoylmethane yields $[M(dik)(\gamma\text{-acac})(PPh_3)]$ exclusively, and benzoylacetone yields a mixture of $[M(dik)(\gamma\text{-dik})(PPh_3)]$ and $[M(dik)(\gamma\text{-acac})(PPh_3)]$. The selectivity depends on the keto-enol character of the β-dicarbonyl compounds

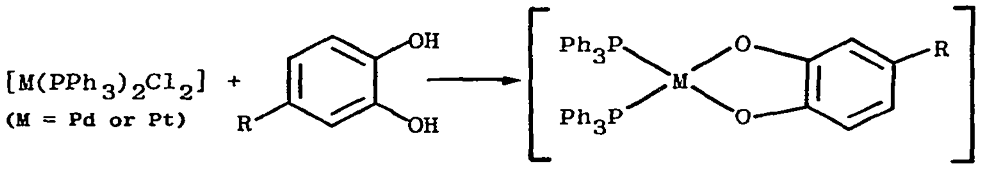
[129]. The photoelectron spectra of $[M(acac)_2]$ and $[M(Me_3COCH_2COCMe_3)_2]$ (M = Pd or Pt) confirm the covalent nature of the M–O bonding [130]. Complexes of palladium(II) and platinum(II) with malonaldehyde or dithiomalonaldehyde $[M\{CH_2(CHE)_2\}_2]$, (E = O or S) have been prepared; thus hydrolysis of $(EtO)_2CHCH_2CH(OEt)_2$ in aqueous hydrochloric acid, neutralisation and treatment with $PdCl_2$ yielded (11) in 50% yield [131]. A photothermographic study of palladium(II) malonato complexes shows them to be less sensitive than the corresponding oxalate compounds [132]. The stability constants of complex formation of palladium(II) with biuret, $NH_2CONHCONH_2$, have been determined by pH titration [133]. A palladium pyrazolonate complex in which the ligand, (12), is bound through two Pd–O bonds is formed when palladium(II) is extracted from aqueous $PdCl_2$ solution with 1-phenyl-3-methyl-4-benzoyl-pyrazolen-5-one [134]. (13) and (14) react with palladium(II) and platinum(II) to form complexes in which the two hydroxyl groups act as the donor groups reactions (18) and (19); formally the palladium in (15) is in the +3 oxidation state [135,136]. 2,5-dihydrobenzoic acid, HL, forms PdL_2 [137]. An efficient route for preparing



(11)

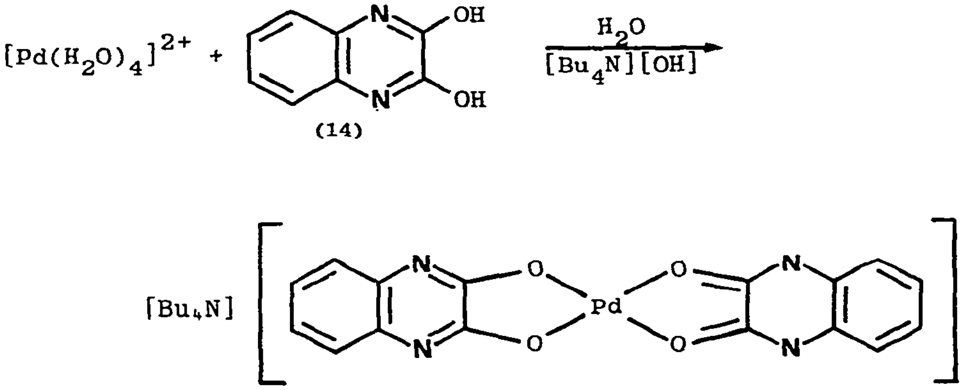


(12)



(18)

(13; R = COOH, CH_2COOH, CH_2CH_2COOH)

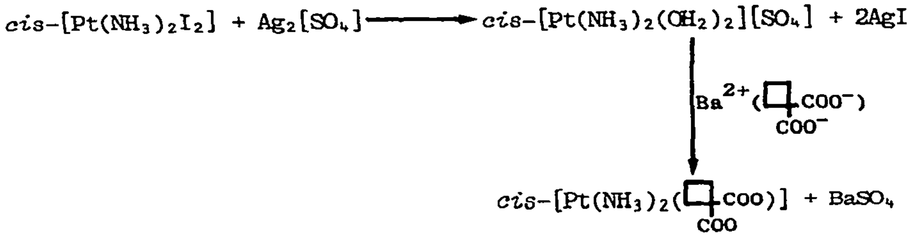


(14)

(19)

(15)

highly soluble anti-tumour platinum(II) complexes, reaction (20), uses silver sulphate as a reagent to remove halide ligands; previously the nitrate has been



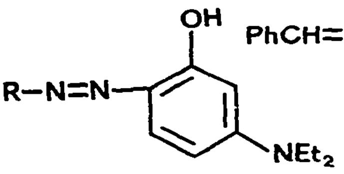
$$cis\text{-}[Pt(NH_3)_2I_2] + Ag_2[SO_4] \longrightarrow cis\text{-}[Pt(NH_3)_2(OH_2)_2][SO_4] + 2AgI \xrightarrow{Ba^{2+}(\square(COO^-)_2)} cis\text{-}[Pt(NH_3)_2(\square(COO)_2)] + BaSO_4$$

(20)

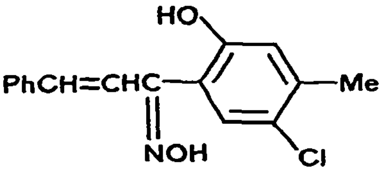
used but this gives subsequent separation problems [138].

6.5.2.3 *Complexes with Multidentate Oxygen-Nitrogen Donor Ligands*

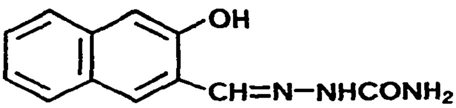
The complexes formed by a number of bidentate and multidentate oxygen-nitrogen donor ligands, (16)-(23) have been investigated [139-145]. In (21; R = Ph),



(16; R = 2-pyridyl or 2-thiazolyl)



(17)



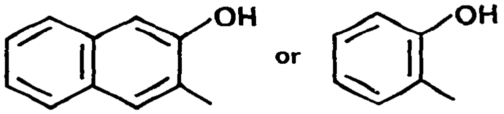
(18)

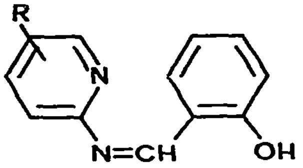
conjugation with the aromatic ring results in the palladium complex, (24), having a ketoamine structure rather than the normal Schiff base form, (25), that is found for (21; R = H or Me) [143]. A complex related to (25) has been prepared,

RCH=NNHCONH=CHR'

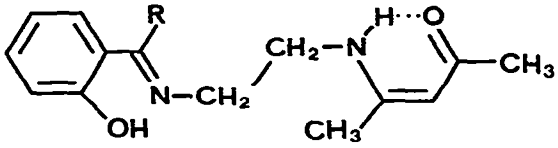
(19)

R,R' =

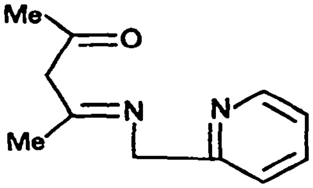




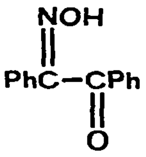
(20)



(21)

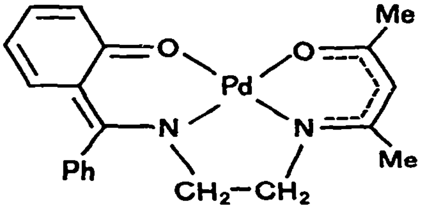


(22)

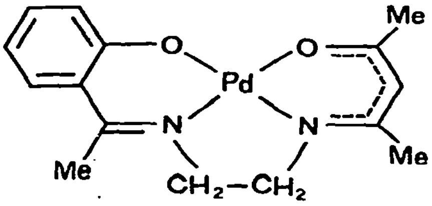


$PhC(=NOH)-C(=O)Ph$

(23)

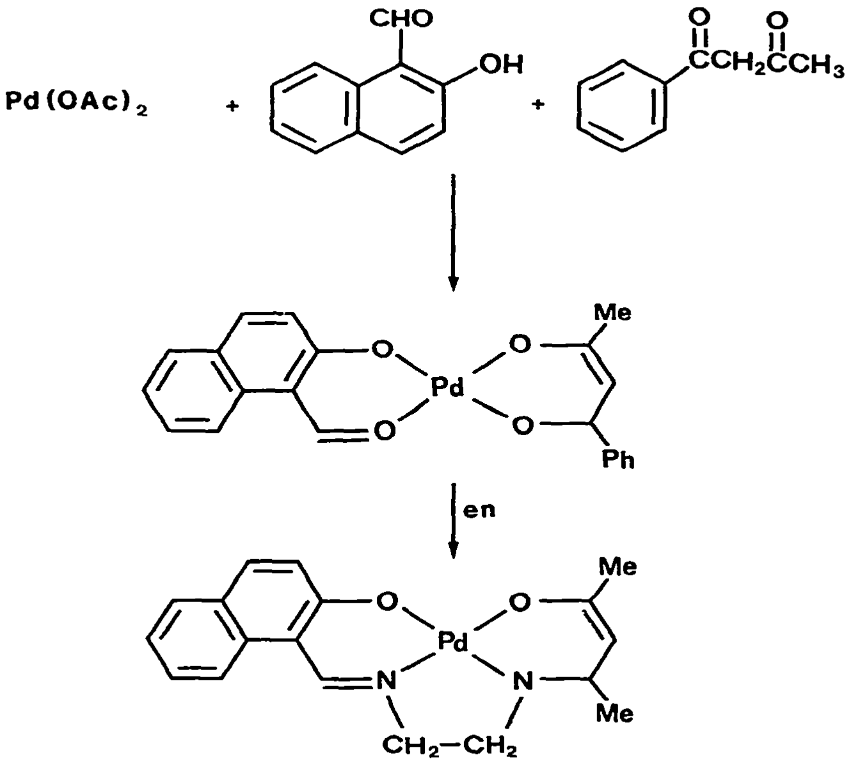


(24)

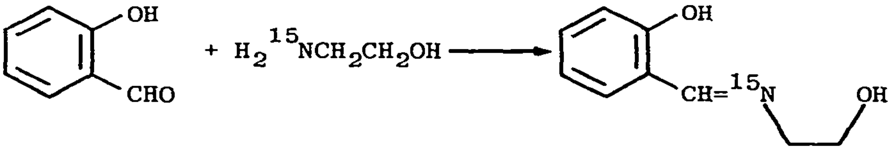


(25)

as shown in reaction (21) [146]. The $\{O^{\frown 15}N^{\frown}O\}$ tridentate ligand, (26), was synthesised as in reaction (22) and used to prepare a series of platinum(II) complexes by reaction (23). Values of $J(^{195}Pt-{}^{15}N)$ increase and $\delta\ {}^{15}N$ decrease as the *trans*-influence of the *trans*-ligand L decreases in the order py > aliphatic amine > dmso > AsR_3 > PR_3 [147]. A series of palladium(II) complexes of $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$ or *trans*-1,2-cyclohexanediaminetetraacetic acid (H_4L) have been prepared, the latter according to Scheme I [148,149]. An X-ray structure has confirmed the tridentate coordination of β-hydroxyethyliminodiacetic acid in (27) [150]. The M-N σ- and π-bonds in *bis*(8-hydroxyquinoline) palladium(II) and platinum(II) complexes are stronger than in the *bis*-8-mercaptoquinoline complexes; the M-S bonds are stronger than the M-O bonds [151]. The ground state absorption of $[Pt(8\text{-hydroxyquinolato})_2]$ is very solvent dependent, whereas the solvent dependence of the luminescent lifetime is small [152].

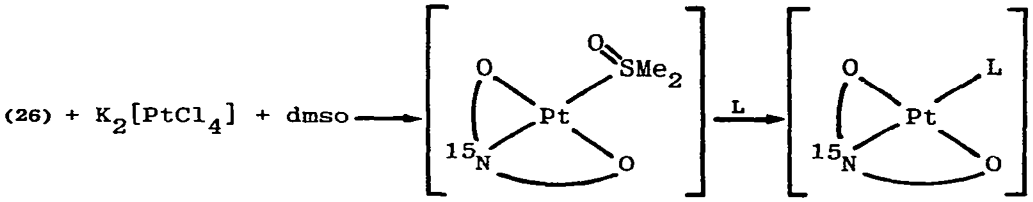

Pd(OAc)₂
CHO
OH
O O
CCH₂CCH₃
Pd
Me
Ph
en
N
CH₂—CH₂

(21)

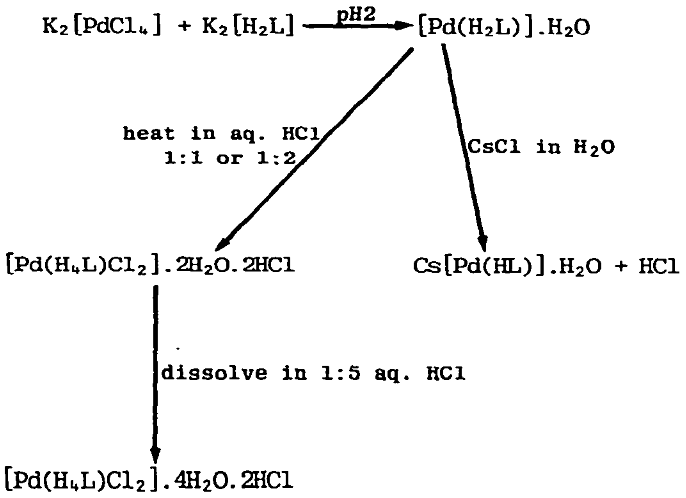

OH
CHO
+ H₂¹⁵NCH₂CH₂OH
CH=¹⁵N
OH

(22)

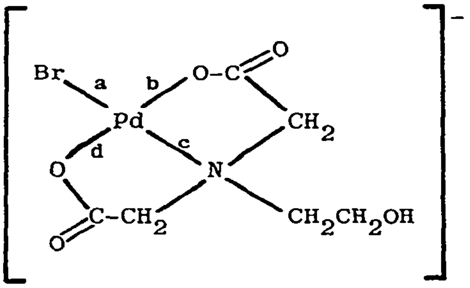
(26)


(26) + K₂[PtCl₄] + dmso
O
SMe₂
Pt
¹⁵N
L

(23)



SCHEME I

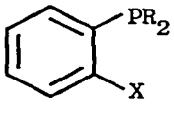


(27)

a	2.434(2) Å
b	2.023(6) Å
c	2.003(7) Å
d	2.004(7) Å

6.5.2.4 Complexes with Bidentate Oxygen-Phosphorus Donor Ligands

The complexes formed by potentially bidentate oxygen-phosphorus donor ligands, (28), have been reviewed [153]. $P(CMe_3)_2(CH_2COR)$ prepared as in



(28; X = COOH, CHO, OCH_3 or OH)

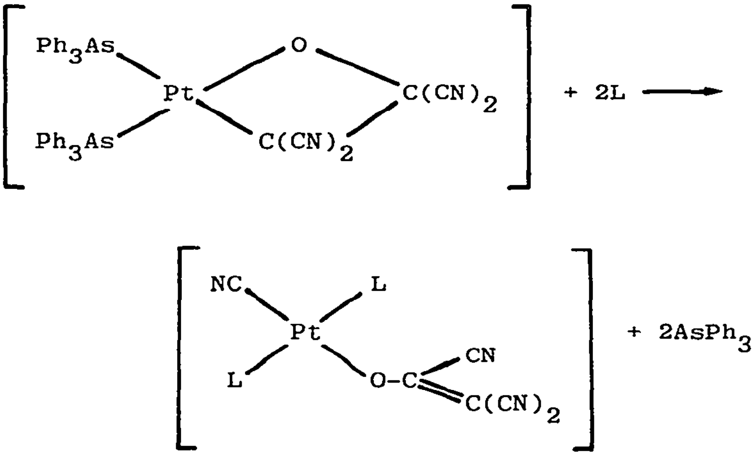
reaction (24) forms *trans*-$[MCl_2\{P(CMe_3)_2(CH_2COR)\}_2]$ (M = Pd or Pt) in which the phosphine is monodentate. However treatment with sodium 2-methoxyethoxide results in ring closure and formation of *trans*-$[\overline{M\{(CMe_3)_2PCH=CO}R\}_2]$ [154]. An

$$BrCH_2COR + P(CMe_3)_2H \xrightarrow{Me_2CO} [P(CMe_3)_2(CH_2COR)H]Br \xrightarrow{Na[O_2CMe]} P(CMe_3)_2(CH_2COR) \quad (24)$$

X-ray study of *cis*-[Pd(Ph$_2$PCH$_2$COO)$_2$] has confirmed the *cis*-geometry and indicated Pd-P and Pd-O bond lengths of 2.235(2) and 2.076(5) Å respectively [155].

6.5.2.5 Complexes with Bidentate Oxygen-Carbon Donor Ligands

[Pt(AsPh$_3$)$_2${OC$_2$(CN)$_4$}] reacts with phosphine ligands to give ring opening {reaction (25)} [156].

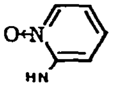


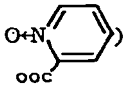
(25)

(L = PMe$_2$Ph, PMePh$_2$, PEt$_3$ or PEt$_2$Ph)

6.5.2.6 Complexes with Ambidentate Sulphur/Oxygen Ligands

The kinetics of replacement of chloride ligands in [Pt(en)ClL]$^+$ (L = Me$_2$SO or NH$_3$) showed the *cis*-effect of dimethylsulphoxide to be at least an order of magnitude greater than that of ammonia, due to the greater nucleophilic discrimination factor in the dimethylsulphoxide complex [157]. A series of dialkylsulphoxide halogen-bridged dimers [{Pt(R$_2$SO)X$_2$}$_2$] (R = Me, Et, Pr, Bu or ½(CH$_2$)$_4$; X = Cl, Br or I) have been prepared. On reaction with ethanenitrile and dimethylformamide in chloroform, the halide bridge is split to form [Pt(Me$_2$SO)LCl$_2$] (L = MeCN or dmf) in which the dmso is *S*-bonded [158].

[Pt(Me$_2$SO)LCl] (where L = 

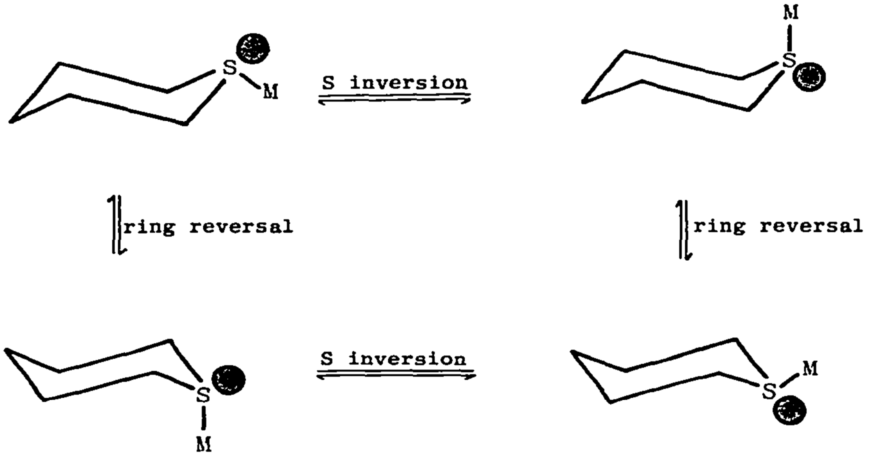
and 

) have been prepared [159]; with the former ligand dmso is *cis* to the oxygen at room temperature, but on heating to 140–170 °C the complex isomerises to a *trans*-arrangement. *Trans*-[Pt(Me$_2$SO)(py)Cl$_2$] has two independent molecules in the unit cell with almost identical bond lengths and angles {$\bar{r}$(Pt-Cl) = 2.294(2) Å; $\bar{r}$(Pt-S) = 2.225(2) Å;

$\bar{r}$(Pt-N) = 2.057(8) Å} [160].

6.5.2.7 *Complexes with Unidentate Sulphur Donor Ligands*

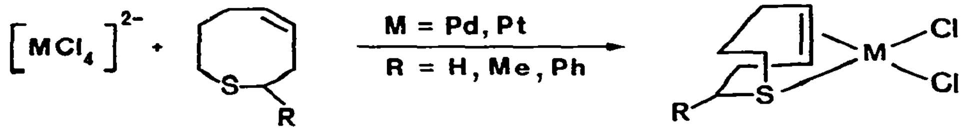
The interaction of palladium chloro complexes with thioethers has been studied polarographically [161]. The *cis-trans* equilibrium of $[PtBr_2(tht)_2]$ is shifted towards the *cis*-isomer in the solid state at 95 °C, and towards the *trans*-isomer in aqueous potassium bromide solution [162]. The energy barrier to pyramidal inversion at sulphur in $[MX_2\{S(CR_2)_n\}]$ (M = Pd or Pt; X = Cl, Br or I; n = 2-5) depends on the halide (in the order Cl > Br > I) and the ring size. When n = 4 or 5, the energy barrier is comparable to that in linear thioethers; when n = 3 the energy barrier is much greater, and when n = 2 no inversion is detectable before decomposition occurs because in the transition state for inversion it is necessary to open up the SCS angle to 120°, which is severely restricted in 3-membered rings [163]. For complexes in which n = 6, the temperature dependent ^1H and ^{13}C NMR spectra were analysed using total band-shape fitting methods to determine the energy barriers for ligand ring reversal and inversion at sulphur {reaction (26)} [164]. The energy barriers for ring reversal were found to be similar to those in the uncoordinated ligands, whereas the barriers for inversion at sulphur were similar to those for non-cyclic ligands. The power of the ^{13}C dynamic NMR spectral analysis was demonstrated by the fact that no simplifications in the conformational analyses were needed to account for the ^{13}C spectral line changes. This was in marked contrast to the ^1H NMR spectra which, in order for their analyses to be possible, had to be attributed to the conformations of either six-membered heterocyclic ring rather than to the total conformational structures of the complexes. A comparison of the *trans*-effects of Me_2S and Et_2S in promoting chloride substitution by amine in $[Pt(R_2S)Cl_3]^-$, and



(26)

3-chloropyridine substitution by chloride in $[Pt(R_2S)(3\text{-}Clpy)Cl_2]$ showed that Et_2S complexes were generally more reactive than Me_2S complexes [165].

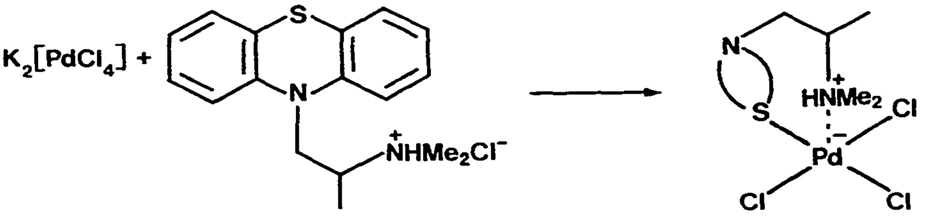
The unsaturated cyclic thioethers, (29), form palladium(II) and platinum(II)



(29)

(27)

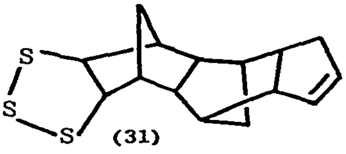
complexes in which both the sulphur and the alkene function are coordinated {reaction (27)}, as confirmed by an X-ray structure determination on the methyl substituted complex [166]. When the *trans*-methyl substituted (29) coordinates to platinum(II), *trans* to *cis*-isomerisation occurs prior to coordination. The phenothiazine heterocyclic ligand, (30), forms a palladium(II) complex {reaction (28)} that has a "scorpion-like" conformation with a direct Pd–S bond



(30)

(28)

and electrostatic interaction between the quaternary nitrogen atom on the side chain and the $\{PdCl_3\}^-$ unit, with a Pd-N distance of 3.17 Å [167]. $[Pt(PPh_3)LCl_2]$ (L = thioether or amine) are more effective catalysts for the hydrogenation of styrene in the presence of tin(II) chloride than either $[Pt(PPh_3)_2Cl_2]$ or $[PtL_2Cl_2]$ [168]. This is attributed to the ability of the L ligand to function as a leaving group in the catalytic hydrogenation cycle. Platinum(II) complexes of $\{(2\text{-pyridyl})CH_2NHCOCH_2\}_2S$, and palladium(II) and platinum(II) complexes of $(CHMe_2O)_2S$ or (31)–(34) have been prepared and characterised [169–171]. Although (31)–(34) react with palladium(II) salts to form RS_3 complexes, with $[Pd(PPh_3)_4]$ desulphurisation occurs with formation of $[Pd(PPh_3)(RS_2)]$ [171].



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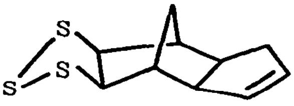
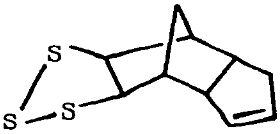
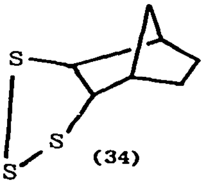


(32; exo)



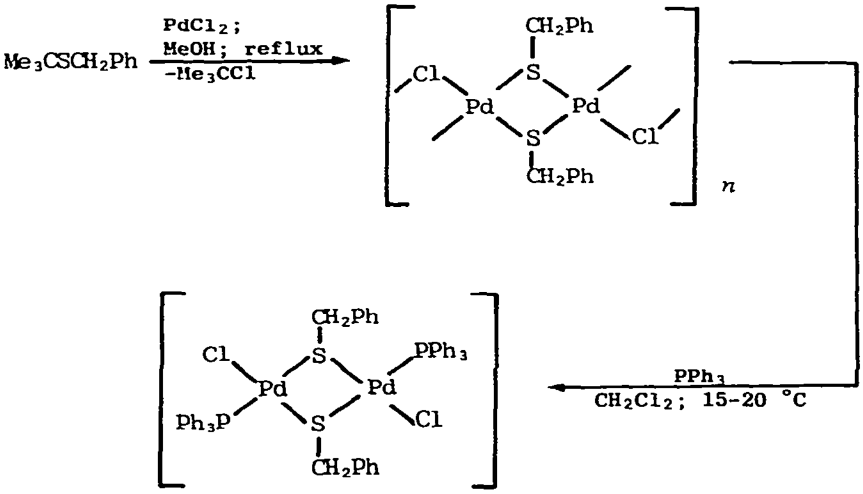
(33; endo)



(34)

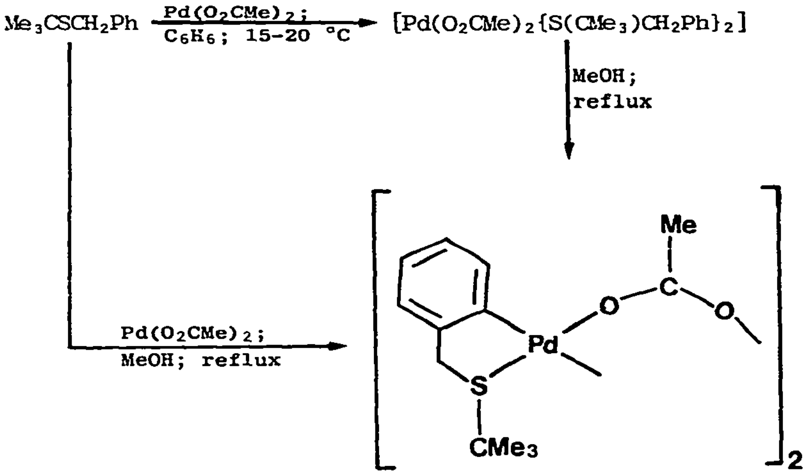
$[Pt(PPh_3)_2(EH)_2]$ (E = S or Se) have been prepared and shown to react with sodium ethoxide to form bridged binuclear $[\{Pt(PPh_3)_2(\mu\text{-}E)\}_2]$, and with S_8 in chloroform to form $[Pt(PPh_3)_2(ESSE)]$ [172]. Pentafluorophenyl sulphide complexes of palladium(II) have been prepared by reaction (29) [173]. Carbon-sulphur bond cleavage occurs during the reaction of benzyl-*t*-butylthioether with palladium(II) chloride {reaction (30)}, but not with palladium(II) ethanoate {reaction (31)} [174]. The difference arises because the weaker basicity of chloride ion enables it to capture the CMe_3 group, whereas the greater basicity of ethanoate leads to preferential capture of an *ortho*-proton of the benzyl group.

$$[Pd(PPh_3)Cl_2]_2 + [C_6F_5S]^- \longrightarrow [\{Pd(PPh_3)(SC_6F_5)Cl\}_2] + Cl^- \qquad (29)$$



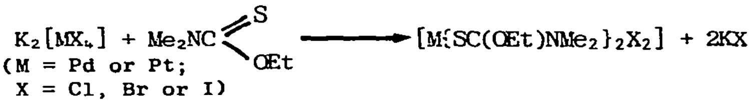
(30)

N,*N*-dimethyl-*O*-ethylthiocarbamate complexes of palladium(II) and platinum(II) have been prepared by reaction (32) [175]. The ligand is *S*-bonded and the complexes are normally *trans*, although with M = Pt and X = Cl or Br, *cis* complexes



(31)

may be isolated which slowly isomerise in solution. An X-ray diffraction study of *trans*-[Pd{SC(OEt)NMe$_2$}$_2$Cl$_2$] showed *r*(Pd-S) = 2.330(1) Å and *r*(Pd-Cl) = 2.313(1) Å [176]. When *N*,*N*'-di(4-tolylthiomethyl)ethylenethiourea reacts with

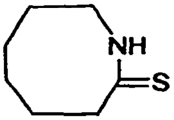


$$K_2[MX_4] + Me_2NC(=S)OEt \longrightarrow [M\{SC(OEt)NMe_2\}_2X_2] + 2KX$$

(M = Pd or Pt;
X = Cl, Br or I)

(32)

palladium(II), the ligand decomposes leaving the thiolate fragment coordinated to palladium [177]. (35)-(37) react with PtCl$_2$ or K$_2$[PtCl$_4$] to form a series



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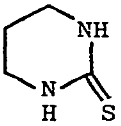

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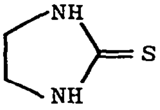


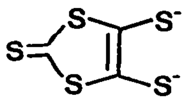
(37)

of complexes [PtL$_4$]Cl$_2$, [{PtLCl$_2$}$_2$] and [PtL$_2$Cl$_2$] [178].

6.5.2.8 *Complexes with Bidentate Sulphur Donor Ligands*

PhS(CH$_2$)$_n$SPh forms *cis*-palladium(II) complexes on reaction with [Pd(PhCN)$_2$Cl$_2$] when *n* = 2 or 3, but *trans* ligand-bridged complexes when *n* = 1, 4-6 or 8 [179]. [Pd(PhSCH$_2$CH$_2$SPh)Cl$_2$] exists in different forms which have significantly different IR spectra, as observed previously for *cis*-[Pt(SMe$_2$)$_2$Cl$_2$] [180]. The S-alkylated dithiolene ligands *S*-ethyl-ethene-1,2-dithiolate form *bis*-complexes with palladium(II) and platinum(II) which have Pd-S bonds of 2.278(6) and

2.403(6) Å, and Pt-S bonds of 2.280(6) Å [181]. Mesomorphic dithiene complexes of palladium(II) and platinum(II) have been reported [182] as well as complexes of (38) and (39) [183]. The kinetics of the exchange of maleonitriledithiolate, isomaleonitrilediselenate and diethyldiselenocarbaminate [184], and the vibrational spectra of palladium(II) and platinum(II) dithiooxamide and dithiobiuret complexes [185,186] have been studied. The selectivity of the resonance Raman effect in $[Fe(\alpha\text{-diimine})_3][M(dithiooxalate)_2]$ (M = Ni or Pt), which contains two chromophores, was studied as a function of the distance between the absorption maxima [187]. When the two electronic absorptions overlap, the resonance Raman spectrum is dominated by bands originating in the chromorphoric group with the larger absorptivity, the bands of the other species being suppressed (as expected from theory). Tetrasulphurtetranitride reacts with palladium(II) and platinum(II) complexes to form a mixture of three products which must be separated by preparative TLC {reaction (33)} [188].



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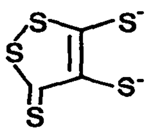
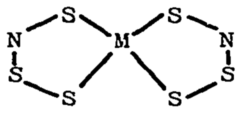


(39)

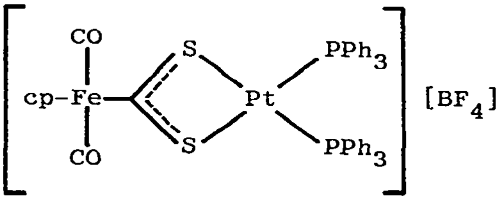
$$\left.\begin{array}{l} N_4S_4 + PdCl_2 + 2[NH_4]Cl \\ \\ \\ N_4S_4 + Na_2[PtCl_4] + Na_2[S_2O_4] \end{array}\right] \xrightarrow[\text{2. Prep. TLC}]{\text{1. MeOH reflux}} \begin{array}{l} [M(S_2N_2H)_2] + \\ [M(S_2N_2H)(S_3N)] + \\ [M(S_3N)_2] \end{array} \qquad (33)$$

The IR spectra of $[M(S_3N)_2]$ support the *cis*-structure, (40).



(40)

An XPES study of trithiocarbonate, *N*-cyanodithiocarbamate, maleonitriledithiolate and 1-nitroethylene-2,2-dithiolate complexes showed that the charge on the metal decreased, Ni > Pd > Pt [189]. $[Pd(PEt_3)_2(S_2CNEt_2)]X$ and $[Pd(PR_3)X(S_2CNEt_2)]$ (X = Cl, Br or I) have been characterised spectroscopically [190]. In $[Pd(S_2COCH_2CF_3)_2]$ the average Pd-S bond length is 2.331 Å [191]. (41) was prepared by a 1:1 reaction of $Na[Fe(cp)(CO)_2(CS_2)]$ with



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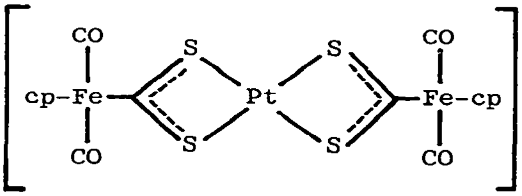

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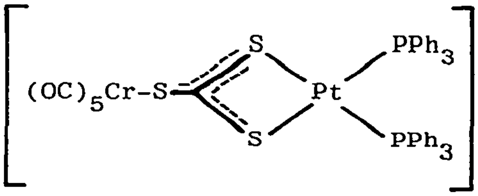


(43)

$[\{Pt(PPh_3)_2Cl\}_2][BF_4]_2$, (42) by a 2:1 reaction of $Na[Fe(cp)(CO)_2(CS_2)]$ with $PtCl_2$, and (43) from $[Cr(CO)_5(CS_2)]$ [192]. CS_2 inserts into the Pd-Me bond of *trans*-$[Pd(PMe_3)_2MeI]$ {reaction (34)}, but into the Pd-P bonds of *trans*-$[Pd(PMe_3)_2(COMe)I]$ and $[Pd(PMe_3)_3R][BPh_4]$, (R = Me, COMe or Ph) {reactions (35) and (36)} [193]. With $[Pd(PR_3)_3H][BPh_4]$ (R = Me or Et), CS_2 insertion

$$trans\text{-}[Pd(PMe_3)_2MeI] + CS_2 \longrightarrow trans\text{-}[Pd(PMe_3)_2(S_2CMe)I] \quad (34)$$

$$trans\text{-}[Pd(PMe_3)_2(COMe)I] + CS_2 \longrightarrow [Pd(PMe_3)(S_2CPMe_3)(COMe)I] \quad (35)$$

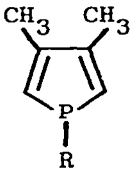
$$[Pd(PMe_3)_3R][BPh_4] + CS_2 \longrightarrow [Pd(PMe_3)_2(S_2CPMe_3)R][BPh_4] \quad (36)$$

(R = Me, COMe, Ph)

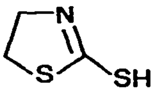
is followed by ligand migration to give $[Pd(PR_3)_2(S_2CHPR_3)][BPh_4]$ with a bidentate sulphur ligand. $[M(RR'PS_2)_2]$ (M = Pd or Pt) have been prepared and shown to be an equimolar mixture of *cis*- and *trans*-isomers [194]. Thiomolybdate and thiotungstate complexes $[R_4N]_2[M(M'S_4)_2]$ (M = Pd or Pt; M' = Mo or W) have been prepared in good yields using aqueous ethanenitrile as solvent [195]. $[Pt(PPh_3)_2(S_3OW)]$ involves $Pt(\mu\text{-}S)_2W$ bonding and in $[Pt(PPh_3)_2(S_4W)]$ the two Pt-S bond lengths are 2.352(3) and 2.388(3) Å [196]. The sulphides in $[Pt(PPh_3)_2(SR)_2]$ (R = Ph or $CHMe_2$) and in $[Pd(dppe)(SPh)_2]$ can act as bidentate ligands to nickel(II) forming $[(PR_3)_2M(\mu\text{-}SR)_2Ni(\mu\text{-}SR)_2M(PR_3)_2]$ (M = Pd or Pt) [197].

6.5.2.9 *Complexes with Ambidentate Sulphur/Nitrogen Ligands*

Pyrazolones, PPh_3, $P(OPh)_3$ and edta yield *S*-bonded thiocyanate complexes, $[ML_2(SCN)_2]$ (M = Pd or Pt) whereas $PPh(OEt)_2$ or $P(OEt)_3$ form *N*-bonded $[PdL_2(NCS)_2]$ [30,198-201], although $[Pt\{P(OEt)_3\}_2(NCS)_2]$ forms thiocyanate bridged $[\{Pd\{P(OEt_3\}(SCN)_2\}_2]$ on standing unless a high concentration of $P(OEt)_3$ is present [202]. ^{15}N NMR can be used to diagnose *N*- or *S*-bonding in thiocyanate complexes: *N*-bonding gives a large upfield chemical shift, whereas *S*-bonding gives a moderate downfield shift [203]. Since large upfield ^{15}N shifts have also been found for imine and azo complexes of platinum, this may be a general phenomenon for sp^2-*N* bound to metals. ^{195}Pt, and to a lesser extent ^{31}P, NMR are also diagnostic of the mode of thiocyanate coordination: ^{195}Pt chemical shifts move to higher field with *S*- than with *N*-bonding [203]. On heating $[PtL_4][Pt(SCN)_4]$ (L = NH_3 or py) in the solid state, $[Pt_2L_3(SCN)_4]$ are formed [204]. A study of seven $[PdL_2(CNS)_2]$ (L = PMe_nPh_{3-n}, PBz_nPh_{3-n} or (44)) complexes showed no trend to *S*- or *N*-bonding based on steric or electronic effects alone, supporting an earlier contention that very small changes in electronic and steric effects play a large rôle in determining both the nature of the linkage isomer, and the *cis* or *trans* geometry of the complex [205,206]. 2-Mercaptothiazoline, (45), is deprotonated on coordination to platinum(II); the thiazoline ring is distorted and appears thionic (>C=S) rather than thiolic (-SH), with a Pt-S bond length of 2.315(7) Å [207]. 2-(4-tolyl)benzthiazole and 2-(4-tolyl)benzoxazole, (46), both react with $Pd(O_2CMe)_2$ to form ethanoate bridged dimers $[\{PdL(\mu\text{-}O_2CMe)\}_2]$ with Pd-C (to the *ortho*-carbon of the tolyl group) and Pd-N bonding {r(Pd-N) = 2.020(8) (E = S) or 2.037(1) Å (E = O)} [208].



(44; R = Me, CMe_3, Ph or $PhCH_2$)



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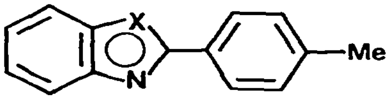


(46; X = O or S)

6.5.2.10 Complexes with Multidentate Sulphur-Nitrogen Donor Ligands

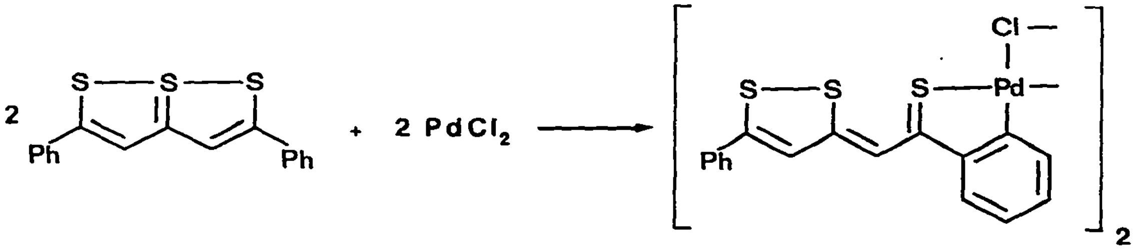
Palladium(II) and platinum(II) complexes of 8-mercaptoquinoline [151] and 4-quinolinethiocarboxylic acid [209] of the type $[ML_2]$ have been prepared and characterised. The mechanism whereby bis(5-sulpho-8-mercaptoquinoline) complexes of palladium(II) and platinum(II) effectively inhibit calcium ion-dependent ATPase from sarcoplasmic reticulum has been investigated [210]. The vibrational and XPES studies upon *cis*-$[M(SNSNH)_2]$ (M = Pd or Pt) have been reported [211, 212]. A series of palladium(II) and platinum(II) complexes of several aminoalkylmercaptans have been prepared using the aminoalkyl thiosulphates, which decompose to thiols in acid or alkaline solution [213]. Palladium(II) complexes of vanillin thiocarbohydrazone and bidentate Schiff bases derived from hydrazine-*S*-methyldithiocarboxylate and thiosemicarbazide have also been characterised [214,215].

6.5.2.11 Complexes with Bidentate Sulphur- or Selenium-Phosphorus Ligands

$[Pd(2\text{-}MeEC_6H_4PPh_2)X_2]$ (E = S or Se; X = SCN or I) react with thiocyanate or iodide ions reversibly to form demethylated $[Pd(2\text{-}EC_6H_4PPh_2)X_2]^-$. The reaction involves nucleophilic attack by the anion at the methyl group [216].

6.5.2.12 Complexes with Bidentate Sulphur-Carbon Ligands

Reaction of (47) with $PdCl_2$ gives the metallated product, (48) {reaction (37)} [217].



(47) (48) + 2HCl (37)

6.5.2.13 Complexes with Unidentate Selenium Ligands

Trans-$[M\{SeP(NMe_2)_2\}_2Cl_2]$ (M = Pd or Pt) have been prepared and tested for biological activity. In solution the complexes lose one phosphine-selenide ligand to form $[M\{SeP(NMe_2)_2\}Cl_2]_2$ [218]. Heating $[Pt(Se_2CNEt_2)_2]$ with $[Pt(PPh_3)_2Me_2]$ in ethanol at reflux gives $[Pt(Se_2CNEt_2)(CH_3)PPh_3]$ which has asymmetric platinum-selenium bonding $\{r(\text{Pt-Se})_{trans\ \text{to methyl}} = 2.491(3)$ Å; $r(\text{Pt-Se})_{trans\ \text{to}\ PPh_3} = 2.462(4)$ Å$\}$ [219]. The vibrational spectra of selenourea complexes of palladium(II) and platinum(II) have also been reported [220].

6.5.2.14 Complexes with Bidentate Selenium-Nitrogen Ligands

The vibrational spectra of $[M(selenosemicarbazide)_2]Cl_2$ (M = Pd or Pt) complexes have been analysed in detail [221]. 5-Chloromethyl-4-selenohexahydropyrimidine-2-thione complexes have been characterised in solution [222].

6.5.2.15 Complexes with Unidentate Tellurium Ligands

In PdTe, the *d*-bands of platinum are completely occupied so that the bands near the Fermi level possess the *p*-character of tellurium [223]. $[Pd\{Te(C_6F_5)_2\}Cl_2]$ has been studied as a photosensitive compound of palladium that can be used to produce an image of developable palladium nuclei [224]. ArCOTeAr' react with $[Pd(PhCN)_2Cl_2]$ to form polymeric $\{Pd(TeAr')_2\}_n$, suggesting that ArCOTeAr' may be a useful precursor for $[TeAr']^-$ ligands for transition metal substrates [225].

6.5.3 Complexes with Amino-Acids, Peptides, Nucleic Acids and Other Biologically Important Molecules

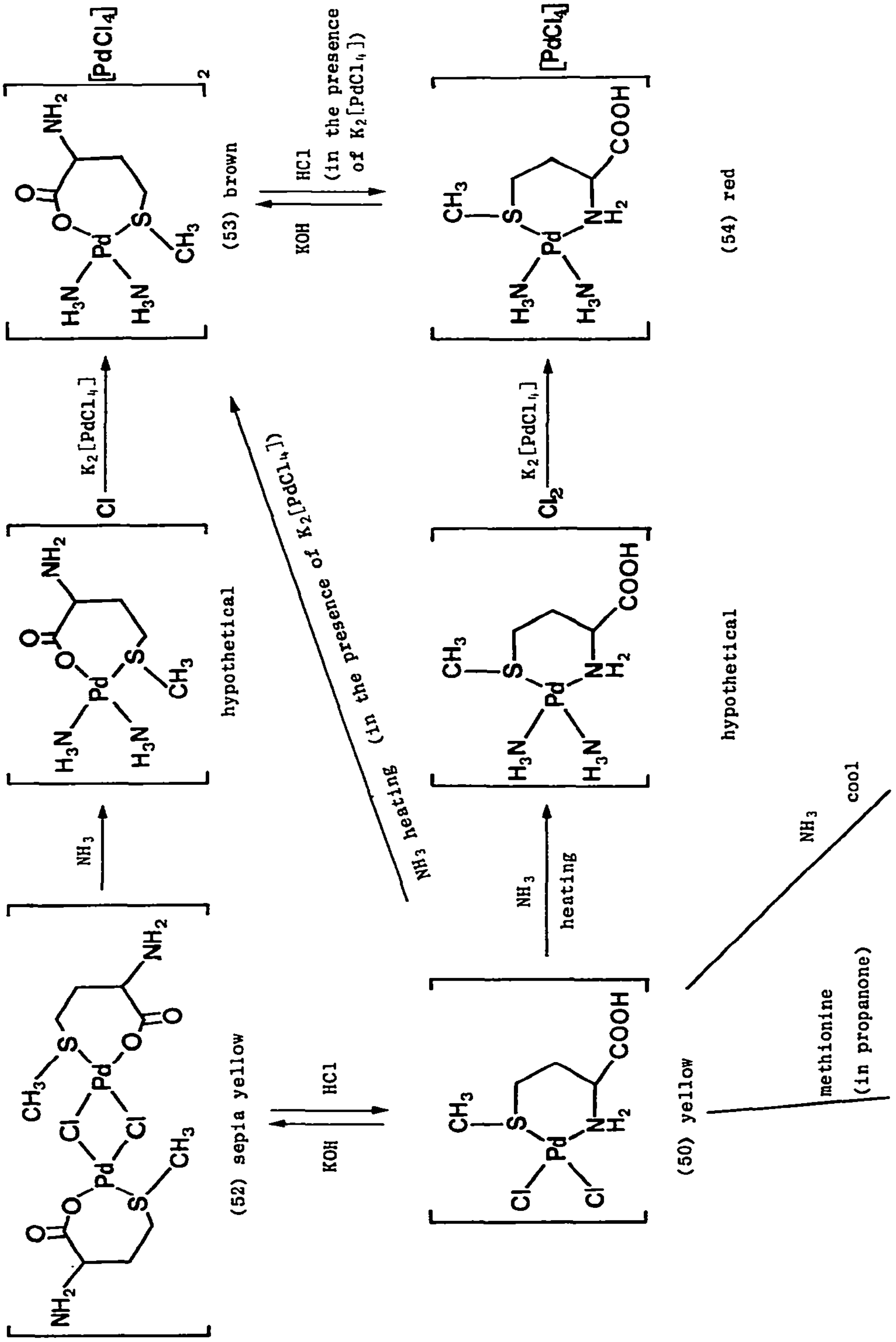
There is an increasing interest in the interaction of platinum(II) and palladium(II) complexes with biologically important molecules. Since most biological molecules bind through *N*, *O* or *S* donor sites, it is appropriate to consider such molecules at this point.

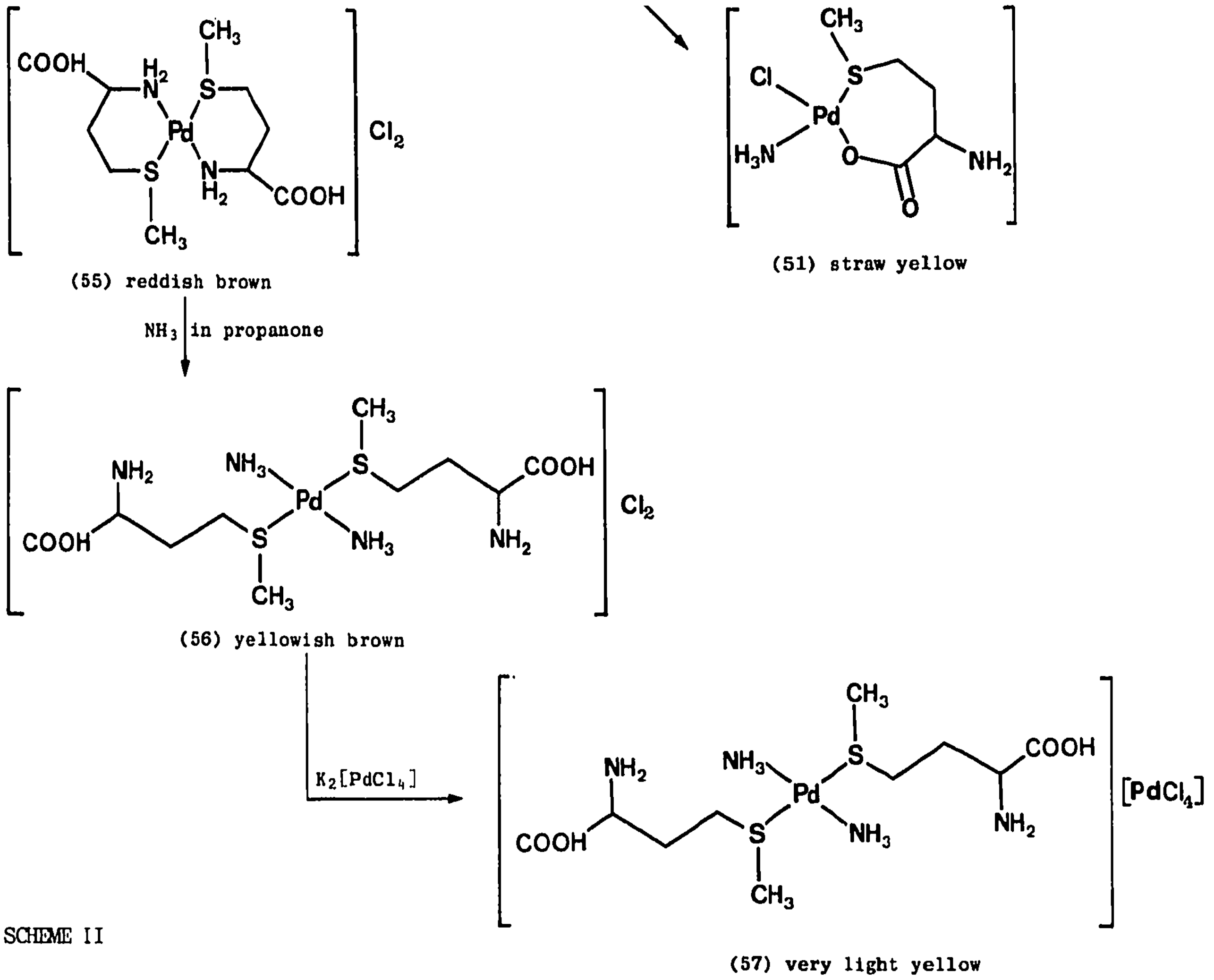
6.5.3.1 Amino-Acids and Peptides

X-ray diffraction studies have been reported on *cis*-$[PtCl_2(NH_3)(NH_2CH_2COOH)]$ $\{r(Pt\text{-}N)_{glycine} = 2.10$ Å$\}$, $[PtCl(NH_3)(NH_2CH_2COO)]$ $\{r(Pt\text{-}N)_{glycine} = 2.08$ Å; $r(Pt\text{-}O) = 2.04$ Å$\}$ [226,227], *cis*-$[PtCl_2(py)(NH_2CH_2COOH)]$ $\{r(Pt\text{-}N)_{glycine} = 1.97(3)$ Å$\}$ [228], and 2*cis*-$[Pt(NH_2CH_2COO)_2].H_2C_2O_4.2H_2O$ $\{r(Pt\text{-}N) = 2.013$ Å$\}$ [229]. On heating a mixture of solid $PtCl_2$ and solid glycine, the zwitterion of glycine $^-OOCCH_2NH_3^+$ intrudes into the inner coordination sphere of platinum, and subsequently the glycine chelate ring closes [230].

Methionine, glycylmethionine and α-alanylmethionine (L) react in a 2:1 molar ratio with $[Pt(en)Cl_2]$ to form $[Pt(en)L_2]Cl_2$ [231]. Seven new palladium(II) methionine complexes **(50)**-**(57)** have been prepared by the reactions shown in Scheme II; further complexes may be formed but are too soluble to isolate [232]. X-ray and fluorescence spectra of platinum(II) complexes of methione and methionine-containing peptides have been recorded [233]. The base hydrolysis of bis(ethylcysteinato)palladium(II) occurs in two stages, both stages involving a base dependent and a base independent route [234]. S-methyl-L-cysteine forms two diastereoisomeric 1:1 complexes with palladium(II) which differ in the chiral centre at sulphur, **(49a)** and **(49b)** [235].

The sulphonate group of L-cysteate interacts with the hydroxyl group of


(52) sepia yellow
HCl
KOH
NH3
hypothetical
Cl
K2[PdCl4]
(53) brown
HCl (in the presence of K2[PdCl4])
KOH
NH3 heating (in the presence of K2[PdCl4])
(50) yellow
NH3 heating
Cl2
K2[PdCl4]
hypothetical
(54) red
methionine (in propanone)
NH3 cool



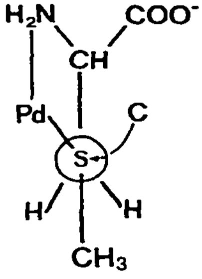
(55) reddish brown

(51) straw yellow

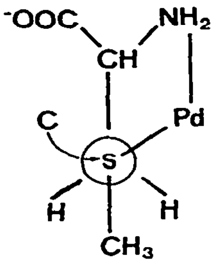
(56) yellowish brown

(57) very light yellow

SCHEME II



(49a)



(49b)

(49a) and (49b) are represented in a view down the S-C bond.

L-threoninate in the palladium(II)-L-cysteate-L-threoninate complex [236].

S-Methyl-L-cysteinesulphoxide forms two palladium(II) and platinum(II) diastereoisomers which, like (49a) and (49b) differ in the conformation at sulphur [237]. An interesting difference arises when the palladium(II) and platinum(II) complexes are dissolved in water. With palladium(II), the ^{1}H NMR spectra of dissolved crystals are exactly the same as for a freshly prepared 1:1 mixture of palladium(II) and ligand whereas the crystals of the platinum(II) complex on dissolution showed only one isomer present. The spectrum of the second isomer appeared after three days, due to inversion at sulphur. In the dichloroplatinum(II) complex, the Pt-S distance of 2.182(3) Å is the shortest Pt-S distance ever reported [238].

The synthesis and optical activity of the proline (HL) complexes *trans*-$[Pt(HL)(NH_3)_2X]X$ and $[PtL(HL)Br]$ have been reported [239-241]. Histidine (HL) reacts with palladium(II) to form $[PdL_2]$ in which it is bidentate, and $[Pt(H_2L)_2Cl_2]Cl_2$ in which it is monodentate and bound through nitrogen [242]. One of the phenolic rings of tyrosine in *cis*-[Pd(L-tyrosinato)$_2$] is approximately parallel to the basal plane of the complex, whilst the other is directed away from the palladium atom [243]. Platinum(II) complexes with L-norvaline, L-isoleucine [244], palladium(II) and platinum(II) complexes with aspartic, glutamic, aminoadipic and aminopimelic acids [245], platinum(II) complexes with L-alanine dipeptide esters [246] and palladium(II) complexes of tri- and tetra-peptides containing ala-ala-cys sequences [247] have been studied.

6.5.3.2 Nucleic Acids and Nucleosides

A review has been given of palladium(II) and platinum(II) compounds related to nucleic acids [248]. X-ray structures of $[H_5O_2][Pt(en)Cl\{uracilato\text{-}N(1)\}]Cl$ $\{r(Pt\text{-}N^1)_{uracil} = 2.04(1)$ Å$\}$, [Pt(en)Cl{thyminato-N(1)}] $\{r(Pt\text{-}N^1)_{thymine} = 2.036(5)$ Å$\}$ [248a] and $[\{Pt(NH_3)_2[1\text{-methylthyminato-}N(3)]\}_2]$ [249] have been determined, principally to confirm the mode of coordination. *Cis*-$[Pt(NH_3)_2\{1\text{-methylthymine-}N(3)\}_2]$ can coordinate as a bidentate ligand to silver(I) through the carbonyl oxygen atoms [250]. X-ray diffraction has shown that because of the *anti*-orientation of the two guanosine ligands, the platinum centre in *cis*-$[Pt(NH_3)_2(guanosine)_2]Cl_{1.5}[ClO_4]_{0.5}.7H_2O$ is chiral; this complex and its inosine and xanthosine analogues have a small but significant anti-tumour activity [251]. The ^1H and ^{13}C NMR spectra of *cis*-$[Pt(NH_3)_2L_2]^{2+}$ (L is a substituted imidazole) complexes have been studied in water and dmso solution; water is far superior as a solvent, yielding narrower resonances and hence the possibility of observing smaller coupling constants [252]. A circular dichroism study of the interaction of palladium(II) with gelatin shows two carboxylate bonded complexes at acid pH; at about pH 4.5, palladium(II) is bound by imidazole and amino-groups, and at alkaline pH all the carboxyl, imidazole and amino groups are involved in coordination [253].

^1H and ^{13}C NMR spectra suggest that palladium(II) interacts with the N^3 of cytidine and the N^7 of guanosine monophosphate [254]. An X-ray diffraction study of $Cs_{0.5}H_{1.5}$[*cis*-$Pt(NH_3)_2$(cytidine-3'-monophosphate)] confirms the N^3 bonding {$r(Pt{-}N^3) = 2.16(3)$ Å} [255]. In the inosine-platinum(II) complexes, $K[Pt(ino)Cl_3]$ and $[Pt(ino)_2Cl_2]$, bonding is through N^7 [256]. 7,9-dimethylhypoxanthine, L, has been shown to coordinate to platinum(II) through N^1 in $[Pt(dien)L][PF_6]_2$ {$r(Pt{-}N^1) = 2.051(6)$ Å} and $[Pt(en)L_2][PF_6]_2$ {$r(Pt{-}N^1) = 2.021(8)$ Å} [257]. An NMR study of the interaction of [Pd(dien)Cl]Cl with some nucleosides and nucleotides showed guanosine, guanosinemonophosphoric acid, xanthosine and inosine all coordinated through N^7, cytidine through N^3, and adenosinemonophosphate as a bidentate ligand to two different palladium atoms through N^1 and N^7 [258]; the structure of $[Pd(dien)(guanosine)][ClO_4]_2$ was confirmed by X-ray diffraction. An HPLC study showed the order of reactivity of deoxynucleosides with *cis*-$[Pt(NH_3)_2Cl_2]$ was thymidine (no reaction) << deoxyadenosine < deoxycytidine < deoxyguanosine [259].

Cis-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ forms adducts with adenosylcobalamin and alkylcobalamins in which the N^3 of the 5,6-dimethylbenzimidazole moiety is coordinated to platinum(II), and not to the cobalt(III) [260].

A study of nucleoside complexes of platinum(II) as well as $[Pt(PBu_3)_2Cl_2]$ and $[\{Pt(PBu_3)Cl_2\}_2]$ showed that a dominant chemical shift anisotropy relaxation mechanism can account, at high magnetic fields, for the disappearance of some of the ^{195}Pt-^1H and ^{195}Pt- ^{13}C coupling constants, and the line broadening observed in the ^{195}Pt NMR spectra of these complexes [261].

A UV difference spectral study of the interaction of platinum(II) complexes with DNA showed anti-tumour active compounds gave a bigger change in the secondary structure of DNA than inactive compounds [262]. Active compounds showed a preference for binding to guanine residues. The intercalative binding of $[Pt(terpy)(2\text{-hydroxyethanethiolate})]^+$, $[Pt(bipy)(en)]^{2+}$ and $[Pt(phen)(en)]^{2+}$ with calf thymus DNA depends on base composition, the platinum(II) complex, and the ionic strength of the medium [263].

6.5.3.3 Cancer Therapy

The effects of $K_2[PtCl_4]$, *cis*-$[Pt(NH_3)_2Cl_2]$ and *trans*-$[Pt(NH_3)_2Cl_2]$ on the activities of seven enzymes have been studied. Three of the enzymes, which are thought to have essential thiol groups, were significantly inhibited, whilst the other four were largely unaffected. Of the three complexes, *cis*-$[Pt(NH_3)_2Cl_2]$ was the least effective inhibitor [264].

The use of platinum(II) complexes as *anti*-tumour drugs often results in "platinosis", which manifests itself in the form of dermatitides and asthmoid conditions due to the histamine liberating action of platinum complexes. Histamine liberation has been found to increase as the energy of the Pt_{4f} or Pd_{3d} energy levels increase [265].

6.5.4 Complexes with Group VB Donor Ligands

6.5.4.1 Complexes with Unidentate Amines

The EPR spectra of linear structures derived from the Magnus' Green salt, $[Pt(NH_3)_4][PtCl_4]$, were attributed to the interaction of a Pt^{3+} ion, with $S = \frac{1}{2}$ in the d_{z^2} orbital, with four ^{195}Pt nuclei [266]. $[Pt(NH_3)_4][ReO_4]_2$ was prepared by treating the dichloride in aqueous solution with $Ag[ReO_4]$ [267]. The standard enthalpy and free energy of formation of $[Pt(NH_3)_4]I_2$ at 25 °C are -538.1 kJ mol^{-1} and -233.17 kJ mol^{-1}, respectively; the free energy of decomposition to *trans*-$[Pt(NH_3)_2I_2]$ and gaseous ammonia at 151 °C is -31.25 kJ mol^{-1} [268]. ^1H chemical shifts and $^{195}Pt-^1H$ coupling constants of the ammonia protons in *trans*-$[Pt(NH_3)_2(amine)_2]^{2+}$ do not depend on the donor properties of the amines; the $^{195}Pt-^1H$ coupling constants to the amine protons are larger than to the ammonia protons [269]. The heat capacities of $[Pt(NH_3)_4]Cl_2.0.92H_2O$ and $[Pt(NH_3)_4]Br_2.0.76H_2O$ have been reported [270,271]. The thermal disproportionation of $[M(NH_3)_4][MCl_4]$ into $[M(NH_3)_2Cl_2]$ (M = Pd or Pt) is exothermic [272]. The vibrational spectra of $[Pt(NH_3)_4Cl_2].X_2O$ in X_2O (X = H or D) have confirmed that when X = H, ν_{sym}(Pd-N) is at 507 cm^{-1} in the solid state and at 504 cm^{-1} in aqueous solution, whilst ν_{asym}(Pd-N) is at 471 cm^{-1} in the solid state and at 468 cm^{-1} in solution [273]. A normal coordinate analysis of $[Pd(NH_3)_4]^{2+}$ has been described [274].

Studies of the heat capacities of *cis*- and *trans*-$[Pt(NH_3)_2I_2]$ have allowed the free energy of *cis-trans* isomerisation to be determined [275]. From the temperature dependence of the specific heat, the energy barriers to internal rotation of ammonia are 2510 (*cis*) and 1255 J mol^{-1} (*trans*) [276]. An SCF-Xα method has been applied to the electronic structures of *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ [277], and an INDO method has been applied to $[PdCl_{4-n}(NH_3)_n]^{n-2}$

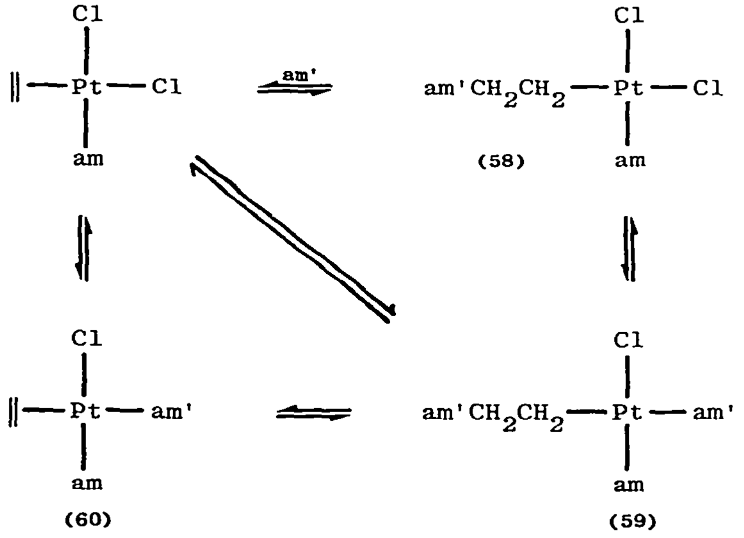
[278]. The increase in the rate constant for quenching the luminescence of Tb^{3+} ions in aqueous solution by $[PtCl_{4-n}(NH_3)_n]^{n-2}$ (n = 0-4) or $[Pt(CN)_4]^{2-}$ correlates with the increase in the oxidation capability of the platinum(II) complexes [279]. The uptake of platinum salts on electro-oxidised carbon fibre paper follows the sequence $[Pt(NH_3)_2(NO_2)_2] > [Pt(NH_3)_4][OH]_2 > [Pt(NH_3)_4]Cl_2 > H_2[PtCl_6]$, as expected on the basis of their relative acidities [280]. The *cis-* and *trans-*isomers of $[PtCl_2(RNH_2)_2]$ (R = H, OH or OCH_3) and $[PtCl_2(NH_3)(NO_2)]$ each give distinct polarographic waves allowing the two isomers to be readily distinguished; in the presence of thiourea the difference between isomers becomes even more pronounced [281,282]. A number of reactions of platinum(II)-ammine complexes with triphenylphosphine have been reported {reactions (38)-(40)} [283].

$$[Pt(NH_3)_3Cl][NO_3] + PPh_3 \xrightarrow{aq.EtOH} [Pt(NH_3)_2(PPh_3)Cl][NO_3] + NH_3 \qquad (38)$$

$$cis\text{- and } trans\text{-}[Pt(NH_3)_2Cl_2] + 2PPh_3 \longrightarrow cis\text{-}[Pt(PPh_3)_2Cl_2] + 2NH_3 \qquad (39)$$

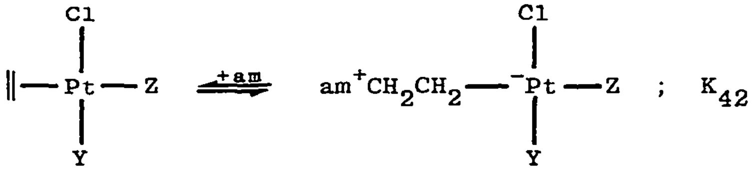
$$[NH_4][Pt(NH_3)Cl_3] + PPh_3 \longrightarrow [Pt(NH_3)(PPh_3)Cl_2] \xrightarrow{PPh_3} cis\text{-}[Pt(PPh_3)_2Cl_2] \qquad (40)$$

An X-ray diffraction study of *trans*-[Pt(cyclohexylamine)$_2$Br$_2$] showed r(Pt-Br) = 2.388(2) Å and r(Pt-N) = 2.06(1) Å [284]. $K_2[PtCl_4]$ reacts with RNH_2 (R = 2-FC_6H_4, 3-FC_6H_4, 3-$CF_3C_6H_4$, 2,4-$F_2C_6H_3$ or $CH_2C_6H_4F$-2) in the presence of $[RNH_3]Cl$ to form *cis*-$[Pt(RNH_2)_2Cl_2]$, which have no value as *anti*-cancer drugs [285]. 3-Nitroaniline (L) reacts with $K[PtLCl_3]$ to form *trans*-$[PtL_2Cl_2]$, which is also obtained from the reaction of $K_2[PtCl_4]$ with L in a 1:6 molar ratio; when the reaction is carried out in the presence of KCl, *cis*-$[PtL_2Cl_2]$ is formed [286].



(41)

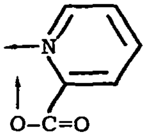
X-ray diffraction studies of *cis*-[$PtCl_2(\eta^2-C_2H_4)$(2,6-dimethylpiperidine)] showed the *trans*-influence of ethene to be greater than that of the amine, {$r(Pt-Cl)_{trans\ to\ C_2H_4}$ = 2.337(6) Å, whereas $r(Pt-Cl)_{trans\ to\ N}$ = 2.285(6) Å; $r(Pt-N)$ = 2.111(17) Å [287]. ^{195}Pt NMR of *trans*-[$PtCl_2(\eta^2-C_2H_4)$(substituted pyridine)] complexes have been reported [288]. When *cis*-[$PtCl_2(\eta^2-C_2H_4)$(amine)] is attacked by further amine (am') three products (58)-(60) can be formed in principle, however only (58) and (59) are certainly formed; (60) is probably not formed {reaction (41)} [289]. The 2-ammonioethanide complexes, (62), are not particularly stable compared to (61), so that with Y = Cl and Z = amine, K_{42} is



$$\|-Pt(Cl)(Y)-Z \underset{}{\overset{+am}{\rightleftharpoons}} am^+CH_2CH_2-{}^-Pt(Cl)(Y)-Z \quad ; \quad K_{42} \qquad (42)$$

(61) (62)

rarely greater than 30. However a conjugated π-accepting bidentate Y-Z ligand, such as (63)-(65), increases the relative stability of (62), because the η^1-alkyl



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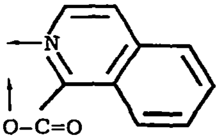

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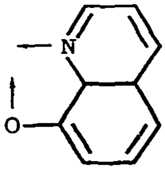
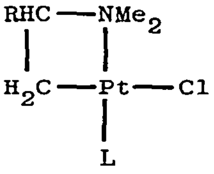


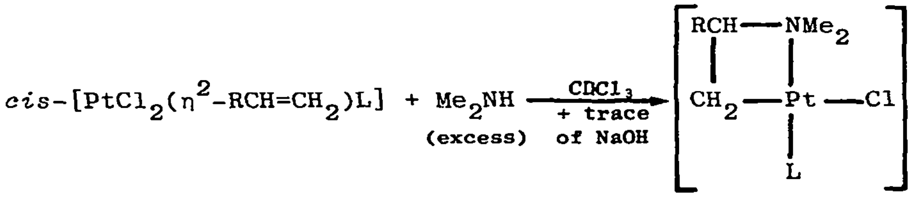
(65)

is a σ-donor that does not compete with the π-accepting Z in the way that $\eta^2-C_2H_4$ does in (61) [290]. A number of cyclic σ-ammonioethanide complexes, (66; L = PPh_3,



(66)

Me_2SO or Me_2NH) have been formed by reaction (43) [291,292]. ^{15}N-labelled (58) has been prepared and NMR studies used to show that $^+NHMe_2(CH_2)_2$ exerts a smaller *trans*-influence than $\eta^2-C_2H_4$ [293]. The lability of the N-H bond in



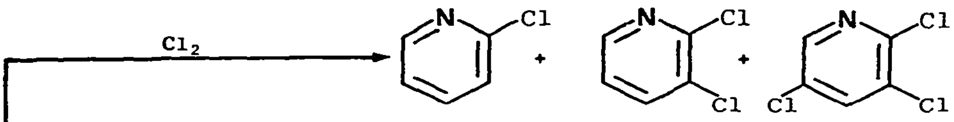
(43)

trans-[$PtCl_2L(NHEt_2)$] (L = alkene, carbonyl, ethanide or phosphine) has been compared to that of the Pt-amine link, using ^1H NMR spectroscopy [294].

Free pyridine does not exchange with coordinated pyridine in [$M(py)_4$]$^{2+}$ (M = Pd or Pt); broadening of pyridine protons in the NMR spectra is due to reaction (44) [295]. *Trans*-[Pt(substituted pyridine)$_2X_2$] can be prepared from

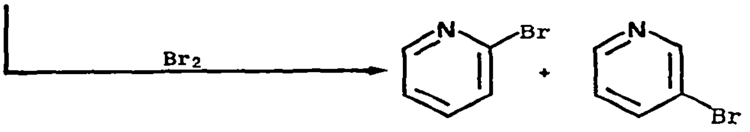
$$\text{pyH}^+ + \text{py}^* \rightleftharpoons \text{py} + \text{py}^*\text{H}^+ \qquad (44)$$

[Pt(substituted pyridine)$_4$]X_2 (X = Cl, Br or NCS), either in aqueous solution or by heating [Pt(substituted pyridine)$_4$]X_2 in the solid state [296]. X-ray diffraction of *trans*-[$PtCl_2$(dmf)(2,6-Me_2py)] shows that the lutidine ring is perpendicular to the platinum square plane; dimethylformamide is bound through oxygen [297]. In [$Pt(NH_3)_4$][$PtCl_3$(2,6-Me_2py)], $r(\text{Pt-N})_{\text{lutidine}}$ = 2.024(5) Å, and the lutidine ligand has the same *trans*-influence as chloride [298]. A series of amino-substituted pyridine complexes, [PtL_2X_2].nH_2O (X = Cl or I),



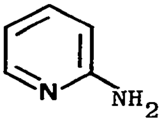
0–5 °C	90%	0%	0%
25 °C	51%	10%	3.5%
50 °C	12%	57%	4.5%
75 °C	9%	62%	4.5%

trans-[$Pt(py)_2Cl_2$] (45)



0–5 °C	86%	9–10%
25 °C	82%	12%
50 °C	49%	49%
75 °C	32%	66%

$[\{Pt(NH_3)_2Cl\}_2L]^{2+}$, $[\{Pt(en)Cl\}_2L]^{2+}$ {L = (67)}, $[Pt_3L'_2X_6].6H_2O$ (X = Cl or I), $[Pt_2L'_3Cl_3(OH)]$, $[Pt_3L'_4I_5(OH)]$ or $[PtL'_3Cl_4].4H_2O$ {L' = (68)} have been prepared



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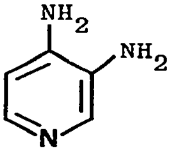
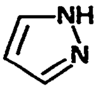


(68)

[299,300]. 1,2- and 1,4-diaminobenzenes form $[PtLX_2]$, where both nitrogens are coordinated [299]. A polymer supported palladium(II) complex, prepared by reacting $[Pd(py)_2Cl_2]$ with phosphinated polystyrene, catalyses the hydrogenation of soybean oil under the mild conditions of one atmosphere of dihydrogen, and 80–140 °C [301]. The chlorination and bromination of *trans*-$[Pd(py)_2Cl_2]$ yields chlorinated and brominated pyridines {reaction (45)} [302].

6.5.4.2 Complexes with Pyrazole, Oxazole and Imidazole Ligands

Cis-$[Pt(pyrazole)_2Cl_2]$ has been prepared by reaction of $K_2[PtCl_4]$ with pyrazole, (69), in water adjusted to pH 1.5 with 2 *M* HCl [303]. *Trans*-$[Pd(oxazole)_2Cl_2]$ involves planar oxazole (70) rings lying at 33° to the



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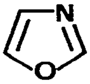
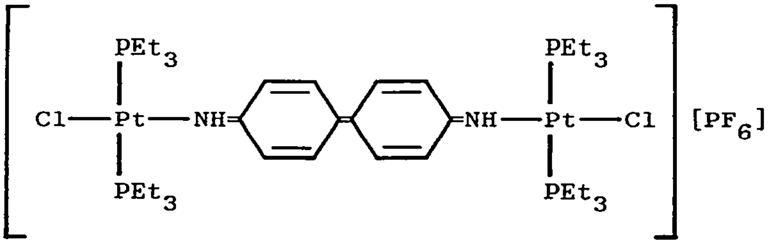


(70)

palladium(II) square plane {r(Pd-N) = 2.016(2) Å, r(Pd-Cl) = 2.293(1) Å} [304]. Treatment of $[Pt(PEt_3)_2(PhNH)Cl]$ with $Ag[PF_6]$ in propanone gives oxidative dimerisation, with formation of weakly paramagnetic *trans*-$[\{Pt(PEt_3)_2Cl\}_2(\mu\text{-}C_{12}H_{11}N_2)]$, which itself undergoes reversible deprotonation to (71). The X-ray structure of (71) indicates that the benzidine ligand has

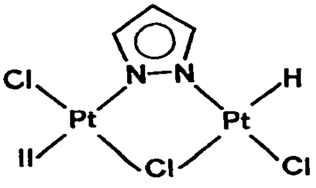


(71)

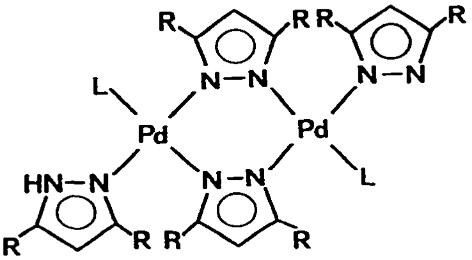
marked quinonoid character {r(Pt-N) = 2.003(4) Å; r(Pt-Cl) = 2.319(1) Å and r(Pt-P) = 2.309(1) Å} [305].

Thermolysis of the imidazolinium salts $[AH]_2[PdX_4]$ (A = imidazole, benzimidazole, 5,6-dimethylbenzimidazole or 6-nitrobenzimidazole; X = Cl or Br) yields *trans*-$[PdA_2X_2]$ [306]. A series of imidazole (imidH) platinum(II) complexes, *cis*- and *trans*-$[Pt(imidH)_2X_2]$ and $[Pt(imidH)_4]X_2$ (X = Cl, Br or I), have been prepared [307]. $[Pt^{II}$(N-methylimidazole)$_4][Pt^{IV}Cl_6]$ has a chain type structure, but there is no charge transfer due to the long Pt^{II}-Pt^{IV} distance of 5.588 Å {r(Pt-N) = 1.986-2.012(14) Å} [308].

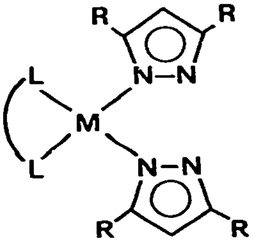
Pyrazole may act as a unidentate ligand and as a bridging ligand, as in (72), (73) and (74) [309-312]. (74; L-L = dppe) suffers pyrazolate displacement on reaction with hydrochloric acid or iodine {reaction (46)}; fluoroboric acid gives reaction (47) [312]. *Trans*-$[PdCl_2$(1-benzyl-3,5-dipropyl-4-ethylpyrazole)$_2]$ has Pd-N bond lengths of 2.014 Å and Pd-Cl of 2.300 Å [313].



(72)



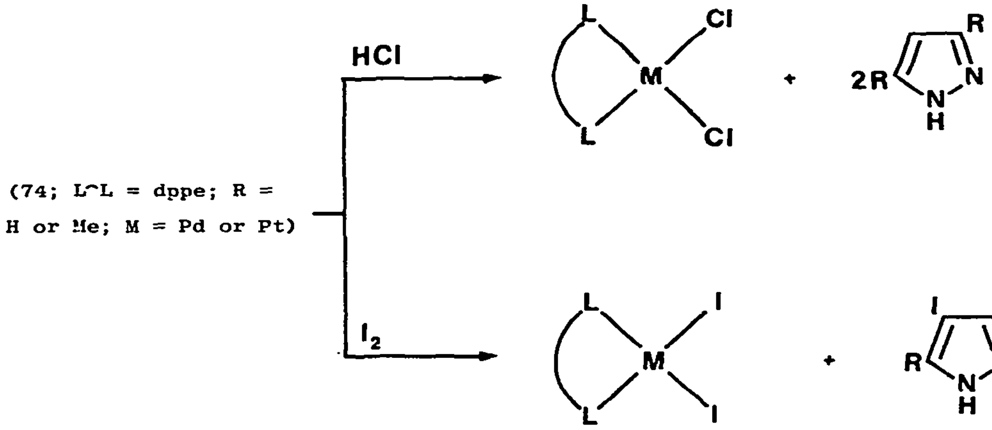
(73; R = H, Me or Ph; L = $MeCO_2$, Br_3CCO_2, $ClCH_2CO_2$, Cl_2CHCO_2, Cl_3CCO_2, F_3CCO_2 or $PhCO_2$)



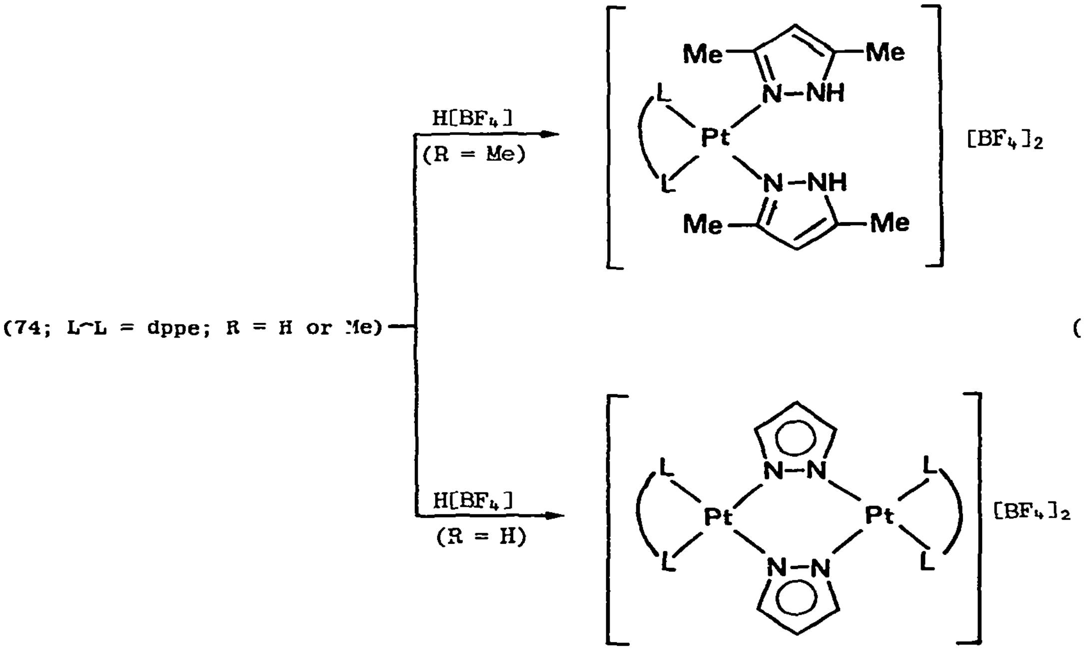
(74; L⌒L = dppe, dpae, bipy or cod; R = H or Me; M = Pd or Pt)

6.5.4.3 Complexes with Bidentate Amines

$[Pt$(2,2-dimethyl-1,3-pn)$_2$(malonate)$]$ has a layer structure with Pt-N bonds of 2.022(4) Å and Pt-O bonds of 2.029(4) Å [314]. The absolute configurations


(74; L⌒L = dppe; R = H or Me; M = Pd or Pt)
HCl
L
L
M
Cl
Cl
+
2R
R
N
N
H
I2
L
L
M
I
I
+
I
R
R
N
N
H

(46)


(74; L⌒L = dppe; R = H or Me)
H[BF4]
(R = Me)
Me
Me
N–NH
L
Pt
L
N–NH
Me
Me
[BF4]2
H[BF4]
(R = H)
N–N
L
L
Pt
Pt
L
L
N–N
[BF4]2

(47)

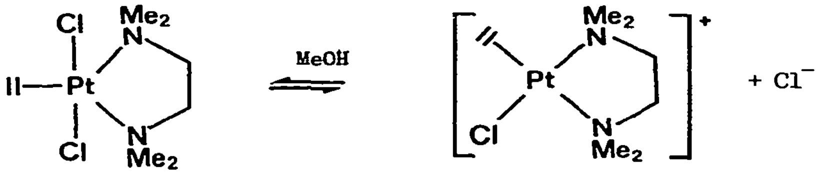
and CD spectra of $[\mathrm{Pt(en)(Me_2en)}]^{2+}$, $[\mathrm{Pt(R\text{-}pn)(Me_3en)}]^{2+}$ and $[\mathrm{Pt(NH_3)_2(Me_3en)}]^{2+}$ have been determined [315]. In contrast to $[\mathrm{Pt(en)Cl_2}]$, the polarised electronic spectrum of $[\mathrm{Pd(en)Cl_2}]$ shows no intensity enhancement in the stacking direction of the molecules [316]. Five coordinate η^2-alkene complexes of platinum(II) with chiral diamines, prepared by reaction (48), have axial chloride ligands. The alkene lies in the trigonal plane $\{r(\mathrm{Pt\text{-}C})_{\mathrm{C_2H_4}} = 2.087(24)$ Å; $r(\mathrm{Pt\text{-}C})_{\mathrm{C_3H_6}} = 2.148(29)$ Å$\}$. The two prochiral nitrogen atoms in R,R-mben (R,R-PhCHMe-NMe-$\mathrm{CH_2CH_2}$-NMe-CHPhMe) have equal absolute configurations, identical to that of the asymmetric carbon atoms [317].

$$\begin{tikzcd}
\mathrm{K[PtCl_3(C_2H_4)]} + \mathrm{R,R\text{-}mben} \arrow[r] & \mathrm{[PtCl_2(R,R\text{-}mben)(C_2H_4)]} \arrow[d, "\begin{array}{l}+\ \text{alkene (alkene = acrolein,}\\ \text{acrylonitrile, fumarodi-}\\ \text{nitrile, maleic anhydride,}\\ \text{maleimide or propene)}\end{array}"] \\
& \mathrm{[PtCl_2(R,R\text{-}mben)(alkene)]}
\end{tikzcd} \qquad (48)$$

Rate constants for the displacement of $\mathrm{Cl^-}$ in $[\mathrm{Pd(5\text{-}Rphen)Cl_2}]$ by $\mathrm{Br^-}$, $\mathrm{I^-}$, $[\mathrm{SCN}]^-$ or thiourea in dmf at 25 °C increase, as does the discriminating ability of the complex, with decreasing $\mathrm{p}K_\mathrm{a}$ of the phenanthroline [318]. $[\mathrm{Pt(phen)_2}]^{2+}$ rapidly adds cyanide in aqueous solution; ^{13}C NMR spectra in water and ethanenitrile show the product to be a fluxional five-coordinate complex with $[\mathrm{CN}]^-$ bonded to the Pt. In the solid state the complex is square-pyramidal with cyanide in the square plane; hydroxide and hydrosulphide react similarly to cyanide. These results argue strongly against the pseudo-base mechanism [319]. Axial, greater than four-coordination, is important in the photolysis of $\mathrm{Na_2[PdCl_4]}$, $[\mathrm{Pd(phen)(NH_3)_2}][\mathrm{ClO_4}]_2$ and $[\mathrm{Pd(phen)(OH)_2}]$ [320].

$[\mathrm{Pt(L\text{-}L)X_2}]$ $\{$L-L = 1,2-$\mathrm{(H_2N)_2C_6H_3R}$-4; R = Me, OMe, H, Cl, COOH, $\mathrm{NO_2}$ or $\mathrm{SO_3H}\}$ have been prepared and tested for *anti*-tumour activity against P-388 leukemia; the activity is related to the Pt-N stretching frequency [321]. $[\mathrm{PdLCl_2}]$ and $[\mathrm{PtL_2Cl_2}]$ (L = 2,6-diaminopyridine, 4-methoxy- or 4-ethoxy-2,6-diaminopyridine) have been studied similarly [322]. $[\mathrm{Pt(2\text{-}aminomethylpyridine)_2}]\mathrm{Cl_2.H_2O}$ possesses deformed chelate rings, due to the considerable ring strain imposed by chelation [323]. A series of 2-aminopyrimidine (L) complexes, including *cis*-$[\mathrm{Pt(NH_3)_2L_2}]\mathrm{Cl_2}$, $[\mathrm{Pt(en)L_2}]\mathrm{Cl_2}$, *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2L_2}]\mathrm{(NO_3)_2}$ and $[\mathrm{PtL_2Cl_2}]$, have been prepared. In all these complexes, the ligand coordinates in a unidentate fashion through the N^1 hetero atom [324].

Five-coordinate $[\mathrm{PtCl_2(\eta^2\text{-}C_2H_4)(tmen)}]$, (75), loses chloride ions {reaction



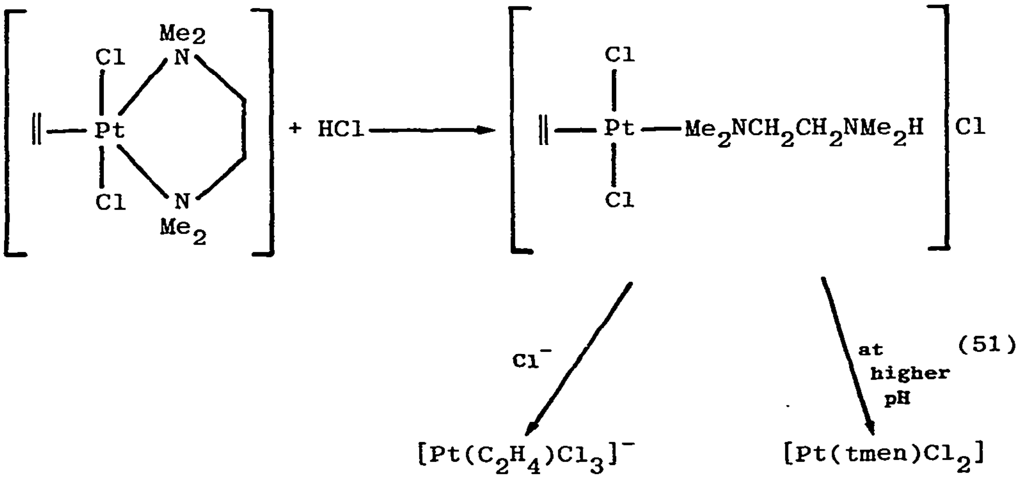
(75) (76) (49)

(49)} in methanol solution to form $[PtCl(\eta^2\text{-}C_2H_4)(tmen)]^+$, (76), which reacts with further tmen to form binuclear (77), which can regenerate (75) on treatment

$$\begin{tikzcd}
2[PtCl(\eta^2\text{-}C_2H_4)(tmen)]^+ + tmen \arrow[r] & {[(tmen)ClPtCH_2CH_2NMe_2CH_2CH_2NMe_2\text{-}CH_2CH_2PtCl(tmen)]^{2+}} \arrow[d, "HCl"] \\
 & {[PtCl_2(\eta^2\text{-}C_2H_4)(tmen)]}
\end{tikzcd} \quad (50)$$

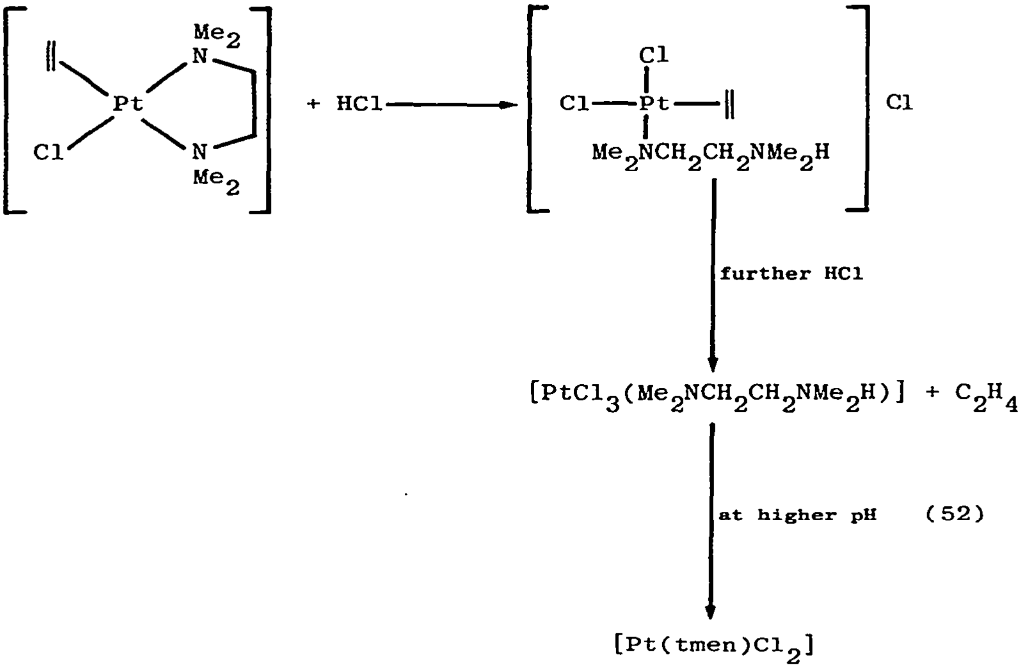
(77)

with aqueous mineral acid reaction (50) [325]. The acidolyses of five-coordinate (75) and four-coordinate (76) occur as shown in equations (51) and



(51)

(52) [326]. A structural study of five-coordinate $[PtCl_2(\eta^2\text{-}alkene)\{PhCHMeN(Me)CH_2CH_2N(Me)CHMePh\}]$ (alkene = C_2H_4, C_3H_6 or (E)-NCCH=CHCN) showed that only one absolute configuration is achieved by the prochiral nitrogen



(52)

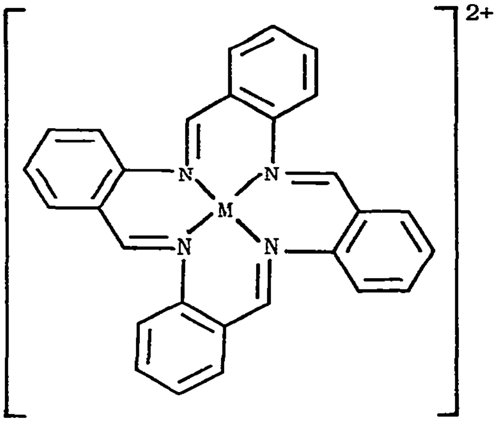
atoms upon coordination [327].

6.5.4.4 *Complexes with Other Bidentate Nitrogen Ligands*

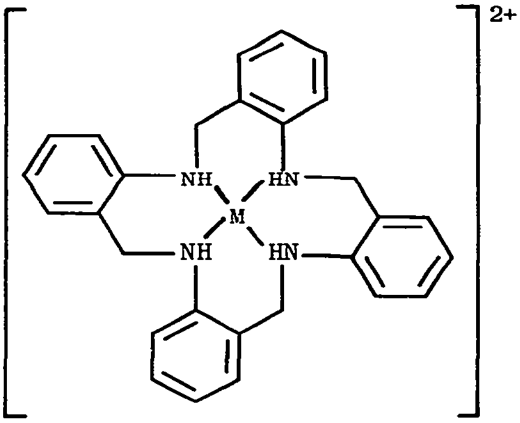
The coordination behaviour of *N*-phenylcarbamoylpyrrole-2-thiocarboxamide and 4-nitrosodimethylaniline have been reported [328,329].

6.5.4.5 *Complexes with Multidentate Amines*

$[Pd(tren)X]Y$ (X = Cl, Br, I or SCN; Y = Cl, Br, I, [SCN], $[ClO_4]$ or $[BPh_4]$) exist as four-coordinate complexes in the solid state but in equilibrium with a five-coordinate form in solution. When Y = $[ClO_4]$, $[Pd(tren)(NCS)][ClO_4]$ reacts with perchloric acid to form $[Pd(trenH)(NCS)][ClO_4]_2$. $[Pd(tren)(NCS)]^+$ undergoes *N* → *S* isomerisation when the anion is changed from $[SCN]^-$ to $[BPh_4]^-$ [330]. The intercalation of $[Pt(terpy)(SCH_2CH_2OH)]^+$ with salmon sperm DNA has been studied [331]. $[Pd(2\text{-}py\text{-}CH_2NH(CH_2)_3NHCH_2\text{-}2\text{-}py)][ClO_4]_2$ has two independent palladium cations in the unit cell; in both the terminal pyridyl rings are twisted away from each other to minimise 6- and 6'-hydrogen atom interactions [332]. The macrocyclic complexes, (78; M = Pd or Pt), are prepared by template condensation of 2-aminobenzaldehyde in the presence of palladium(II) or platinum(II) salts [333]. Saturated macrocyclic complexes, (79), with both palladium(II) and platinum(II) have four nitrogens situated on a saddle-shaped surface around the metal. The tetrafluoroborate complexes react with iodine to form the mixed-valence complexes $[M(L)][I_3]_{2\cdot 7}$, where $[M(L)]$ = (79), which have



(78)

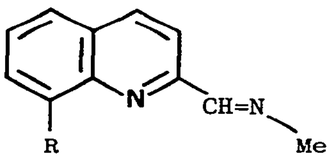


(79)

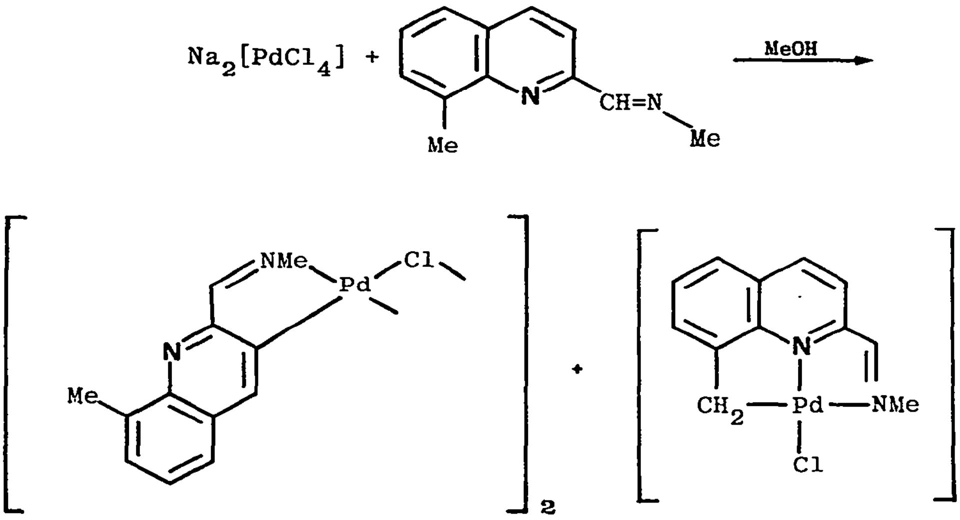
unusual pressure dependent conductances [333a]. Tetrabenzoporphyrin (TBPH$_2$) complexes of palladium(II) and platinum(II), [M(TBP)], exhibit phosphorescence from the lowest triplet of the TBP ligand [334]. Photochemical studies of other porphyrins have also been reported [335,336].

6.5.4.5 Complexes with Imines

X-ray diffraction has been used to determine the structures of the following imine complexes: *trans*-[PdCl$_2$(1,3-dimethyl-1,4,5,6-tetrahydropyridazine)$_2$] [337], [{Pt(PBu$^i_3$)Cl$_2$}$_2${Me$_3$CN=CHCH=NCMe$_3$}] [338,339], trigonal bipyramidal [PtCl$_2$(PhCH=CH$_2$)(Me$_3$CN=CHCH=NCMe$_3$)] with axial chloride ligands [338], [Pd(η^3-C$_3$H$_5$){2-(MeN=CH)-8-CHMe$_2$-quinoline}] [340] and [Pd(1,3,5-tri-4-tolylformazan)$_2$] [340a]. The reactions of 1,4-diazo-3-methylbutadien-2-yl complexes of palladium(II) with rhodium(I) complexes, in which ligand exchange between palladium(II) and rhodium(I) occurs, have been described [341]. *Trans*-[Pd(Me$_2$C=NNMePh)$_2$X$_2$] (X = Cl or Br) consist of two rotational isomers differing in the mutual orientations of the imine ligands [342]. Cyclopalladation of (80) occurs by in-plane interaction of palladium(II) with the hydrocarbon group, assisted by chelation [343]. When R = Me, the reaction depends upon the other ligands present {as shown in reactions (53) and (54)}: when R = Et or CHMe$_2$,



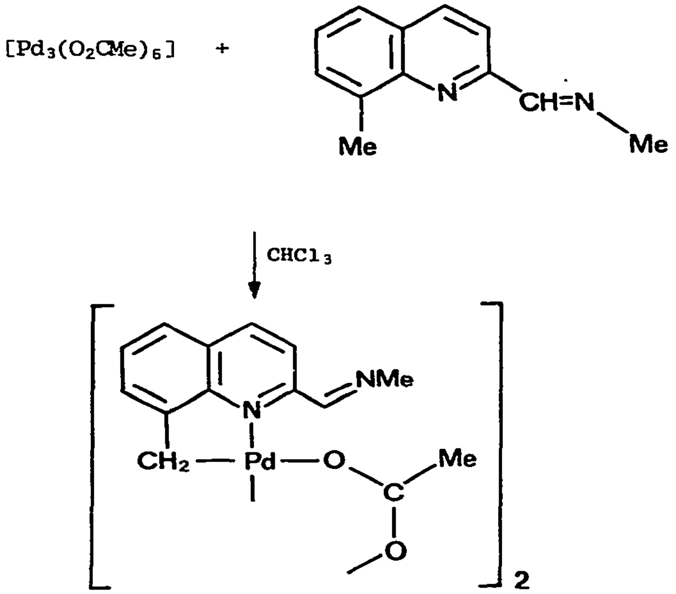
(80)



(81)

(53)

only the analogue of (81) involving metallation at the 3-position is formed [340]. In [Pd(RCH=NN=CHR)$_2$Cl$_2$] (R = furanyl or thienyl) the ligands bind through the azomethine nitrogen [344].



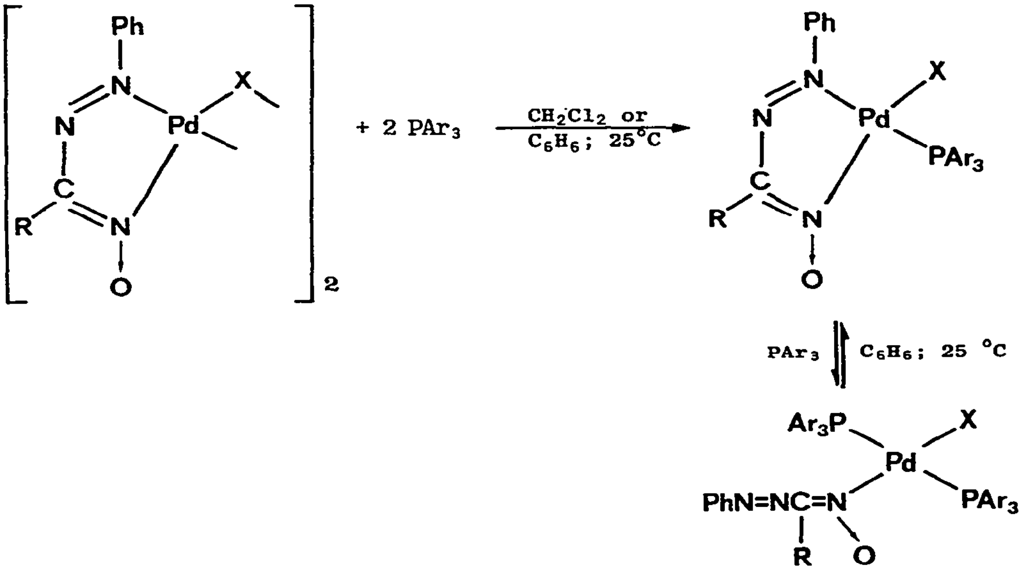
(54)

Palladium(II) complexes of Ph$_3$P=NH have been prepared by the *in situ* alcoholysis of Ph$_3$P=NSiMe$_3$ [345]. 1,4-Benzoquinonediimine, L, forms [PdL$_2$Cl$_2$].2H$_2$O and a polynuclear complex of platinum(II) [346]. Irradiation of chloroform solutions of $[Pt\{1,2\text{-}C_6H_4(NH)_2\}_2]$ below 350 nm decolourises it, and reduces it smoothly to $[Pt\{1,2\text{-}C_6H_4(NH_2)_2\}_2]^{2+}$ [347]. α-Diimines react in a 1:1 ratio with $[Pd(PhCN)_2X_2]$ to form *cis*-$[Pd(RN{=}CHCH{=}NR)X_2]$ (R = alkyl) in which both nitrogens are bound to palladium(II); with more diimine, the complexes $[Pd(RN{=}CHCH{=}NR)_2X_2]$ are formed with two unidentate diimine ligands, each in an *anti*-configuration with the C-C and Pd-N bonds mutually *cis* [348]. $[\{MLCl_2\}_2]$ (M = Pd or Pt; L = phosphine or arsine: M = Pt; L = C_2H_4) react with α-diimines to form *trans*-$[M(RN{=}CHCH{=}NR)LCl_2]$ in which the diimine is monodentate but fluxional with L = phosphine or arsine, but bidentate giving a trigonal bipyramidal complex with axial chloride ligands when L = ethene [348,349].

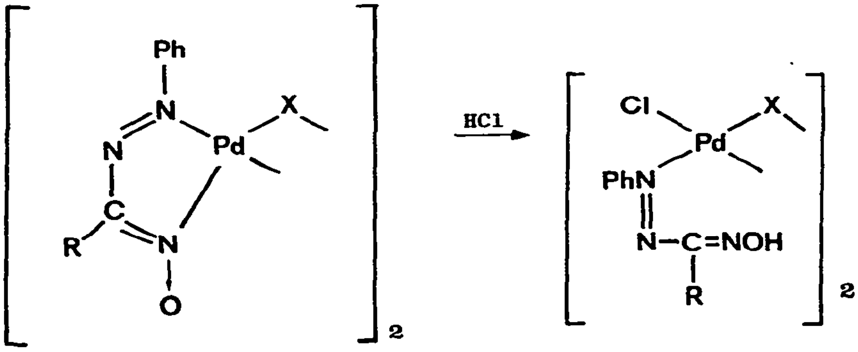
Complexes of 2-(*N*-α-pyrrolylmethyleneamino)benzenesulphonic acid with Pd(II), 2-(2-pyrrolylmethyleneimino)benzoic acid with Pd(II) and Pt(II), 3-(2-pyrrolylmethyleneimino)propanoic acid with Pd(II) and Pt(II), and resorcinaldehyde-aminoguanidine with Pd(II) have been described [350-352].

6.5.4.7 Complexes with Oximes

X-ray diffraction has been used to study a number of bis(oxamide oximato)platinum(II) adducts in which the platinum complex molecules form vertical stacks [353-356]. The selective cleavage of the two palladium(II)-nitrogen bonds in arylazo-oximato palladium(II) complexes, by tertiary phosphines, involves initial halide bridge cleavage followed by a bidentate to unidentate transformation {reaction (55)} [357-359]. Hydrochloric acid results in oxime protonation {reaction (56)} [357]. Negative ion mass spectrometry of $[M(dmg)_2]$ (M = Ni, Pd or Pt) gives $P^{\dot{-}}$, $[P\text{-}H_2O]^{\dot{-}}$ (which is the major peak for M = Pd or Pt) and $[P\text{-}CH_4O]^{\dot{-}}$, where P is the parent molecular ion [360]. The

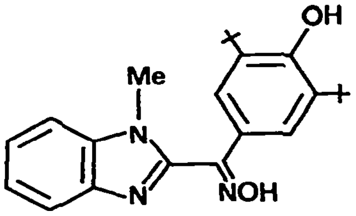


(55)

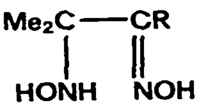


(56)

UV-VIS spectra of $[M(dmg)_2]$ (M = Ni, Pd or Pt) have been analysed by a semi-empirical LCAO-MO method [361]. Complexes of (82) and (83) have been described [362,363].



(82)



$$\begin{matrix} Me_2C & \text{—} & CR \\ | & & \| \\ HONH & & NOH \end{matrix}$$

(83; R = H, Me or Ph)

6.5.4.8 *Nitrosyl and Nitro-Complexes*

The nitro or nitrito coordination in $K_2[Pt(ONO)_n(NO_2)_{n-4}]$, $K_2[Pt_3O(NO_2)_3(ONO)_3]$ and $K_2[Pt_2O_2(NO_2)_6]$ has been determined [364], and "$[Pt(PH_3)_2(N_2O_2)]$" has been the subject of EHMO calculations [365]. Sulphur dioxide reacts with $[Pt(PPh_3)_2(N_2O_2)]$ to form $[Pt(PPh_3)_2(NO_2)_2]$, whereas nitrogen oxide reacts with $[Pt(PPh_3)_2(SO_2)]$ to form $[Pt(PPh_3)_2(SO_3)]$ and $[\overline{Pt(PPh_3)_2(SO_2ONNO)}]$ [366].

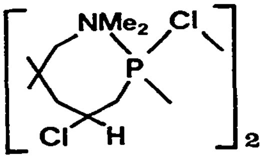
6.5.4.9 *Complexes with Nitriles*

Although $[Pt(PhCN)_2Cl_2]$ had been thought to exist solely as the *cis*-isomer, it has now been shown that reaction of $PtCl_2$ with neat benzonitrile affords a mixture of *cis*- and *trans*-isomers in varying proportions depending on the temperature. In chloroform at 25 °C, the *trans*-isomer is favoured since $k_{cis \rightarrow trans} = 3.8 \times 10^{-6}\ s^{-1}$ and $k_{trans \rightarrow cis} = 2.9 \times 10^{-7}\ s^{-1}$ [367]. The chelating nitrile $\{1,2\text{-}(NC)C_6H_4OCH_2\}_2$ displaces benzonitrile from $[Pt(PhCN)_2Cl_2]$ [368]. $[Pt(PhCN)_2Cl_2]$ reacts with Tl[acac] to give three products, one of which is the fine yellow crystalline *trans*-$[Pt(MeCOCN{=}CPhCH_2COMe)_2]$, formed by nucleophilic attack on coordinated benzonitrile [369].

6.5.4.10 Complexes with Bidentate Nitrogen-Carbon Donor Ligands

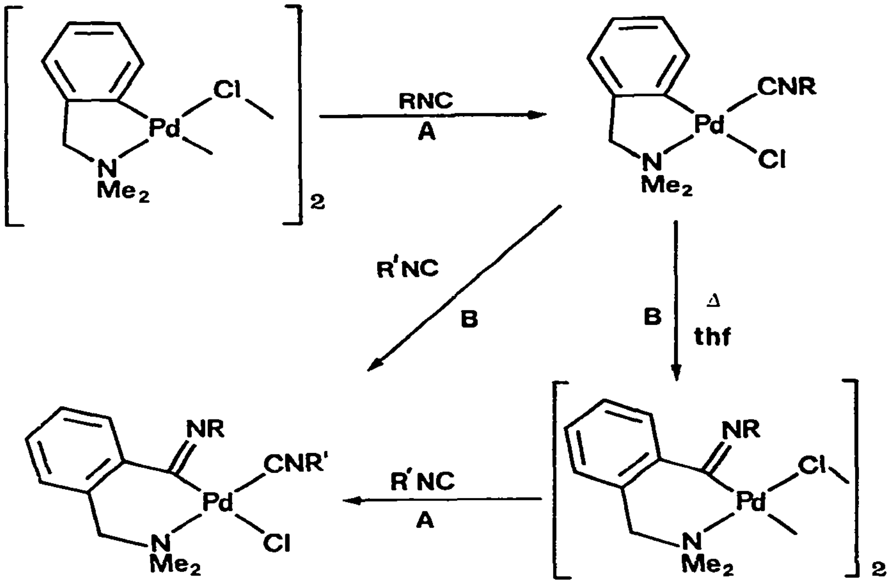
$Me_2NCH_2CMe_2CH_2CH{=}CH_2$ reacts with $[Pd(PhCN)_2Cl_2]$ to give a bidentate *N-C* ligand in which the olefin has inserted into the Pd-Cl bond {reaction (57)} [370]. In contrast $MeSCH_2CMe_2CH_2CH{=}CH_2$ forms a sulphur-alkene complex after

$[Pd(PhCN)_2Cl_2] + CH_2{=}CHCH_2CMe_2CH_2NMe_2 \longrightarrow$



(57)

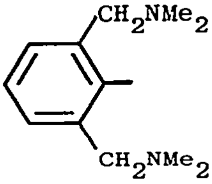
a 1,2-shift of the double bond. The reactions of *N,N*-dimethylbenzylamine complexes of palladium(II) with isocyanides follow Scheme III [371]. The



(A = halide bridge cleavage; B = insertion into Pd-C bond)

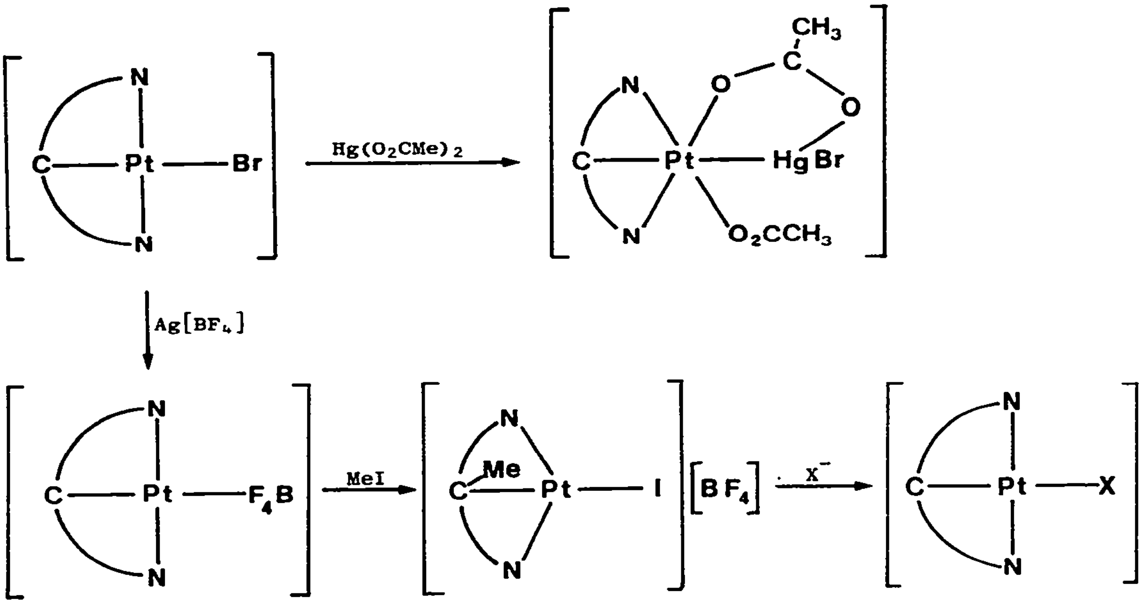
SCHEME III

palladation of azobenzene is catalysed by $[CH_3CO_2]^-$, $[ClCH_2CO\ ]^-$, $[OH]^-$ or Et_3N; the catalytic activity is independent of the nature and concentration of the catalyst, but increases in the presence of chloride ions [372]. A comparison of structural studies upon azobenzene derivatives indicates that the coordinating ability of the azo group, and the palladocycle ring size, depends on the steric, not electronic, effects of the substituents [373]. The reactions of the platinum(II) complexes of the tridentate *N-C-N* ligand, (84),



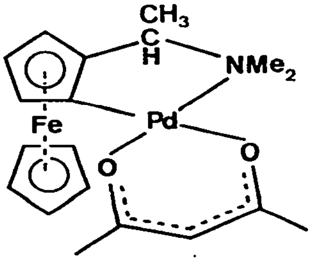
(84)

are shown in Scheme IV. Of particular interest is the addition of methyl iodide



SCHEME IV

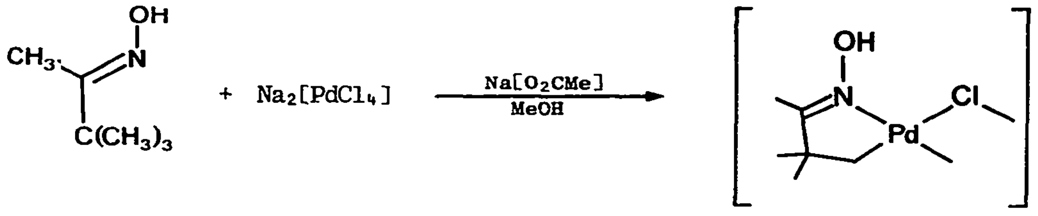
to (85) to form (86), in which the methyl group bonds to the phenyl group, which still remains coordinated to platinum [374]. The palladated ferrocene, (87), has been shown by X-ray diffraction to have an R-configuration at the chiral



(87)

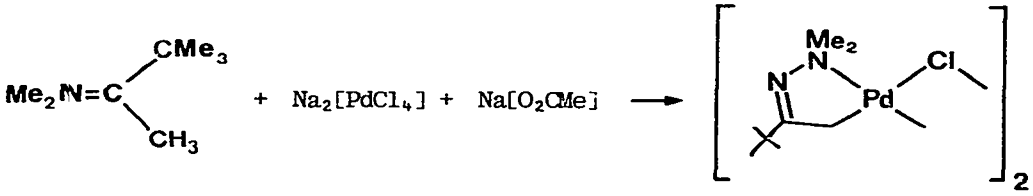
carbon, and an S-configuration at the substituted ferrocene moiety [375]. Cyclopalladated complexes of 1-ethyl-2-phenylimidazole have also been described [376].

Oximes are widely used as protecting groups in organic chemistry which can be reconverted, after chemically modifying the molecule elsewhere, to the original carbonyl compounds. Accordingly, the cyclopalladation of oximes was studied [377]. E-R-*t*-butylketoximes (R = Me, Et or Ph) are regiospecifically cyclopalladated, according to reaction (58). Ketoximes less sterically hindered than



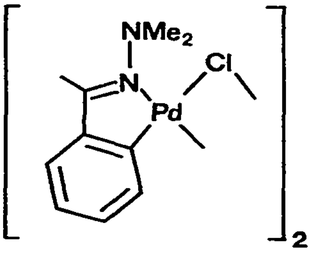
(58)

methyl-*t*-butylketoxime (such as oximes of trimethylacetaldehyde, methylisopropylketone, diisopropylketone, methylethylketone or 2-methylcyclohexanone) do not give cyclopalladation, but dark intractable products. Hydrazones were studied next, as they have a lower energy barrier to rotation about the >C=N- bond [377]. Methyl-*t*-butyl-*N*,*N*-dimethylhydrazone cyclopalladates regiospecifically on a single methyl group {reaction (59)}, whereas less hindered hydrazones do



(59)

not cyclopalladate. Acetophenone-*N*,*N*-dimethylhydrazone cyclopalladates specifically at the 2-position of the phenyl ring, and not on the methyl group (88). Methyl-*t*-butylketazine cyclopalladates on the *t*-butyl methyl group, (89).



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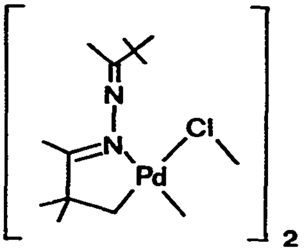
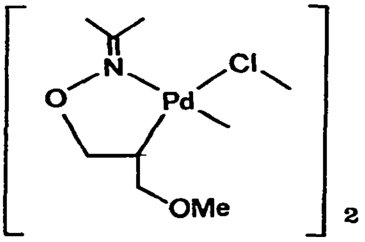


(89)

Acetoxime *O*-allyl ether in methanol cyclopalladates with concomitant attack of methoxide to give (90) [377].



(90)

6.5.4.11 *Complexes with Monodentate Tertiary Phosphines*

Normally only the *trans* isomer of $[Pd\{P(alkyl)_3\}_2Cl_2]$ can be prepared. However, xenon arc irradiation of *trans*-$[Pd(PBu_3)_2Cl_2]$ in nitromethane at room temperature gives a mixture of *cis* (75%) and *trans* (25%) isomers, from which the *cis*-isomer can be isolated by evaporation in a stream of dinitrogen, followed by addition of ether to precipitate the *cis*-isomer (leaving the *trans*-isomer in solution) [378]. Alternatively photolysis of *trans*-$[Pd(PBu_3)_2Cl_2]$ in hexane at 0 °C precipitates the *cis*-isomer, which has Pd-P and Pd-Cl bond lengths of 2.239(2) and 2.417(2) Å respectively, and a $P\widehat{Pd}P$ angle of $105.75(5)^\circ$ indicative of considerable steric crowding [378]. An X-ray study of *trans*-$[Pt\{P(cych)_3\}_2Cl_2]$ shows that the Pd-P bonds (2.337(2) Å) are 0.034 Å shorter than in the corresponding iodide complex, where steric crowding is greater [379]. X-ray studies of $[Pt(PEt_3)_3X]Y$ ($X = H$, $Y = [PF_6]$; $X = F$ or Cl, $Y = [BF_4]$) show that Pt-P bond lengths *trans* to X follow the expected *trans*-influence order of X; H (2.335(4) Å) > F (2.239(3) Å) > Cl (2.251(3) Å). Pt-P bonds *cis* to X decrease as the size of X decreases in the order; Cl (2.353(3) Å) > F (2.337(4) Å) > H (2.300(3) Å) [380]. *Cis*-$[Pt\{P(CMe_3)_2Ph\}_2Cl_2]$ is a very distorted square-planar complex, with $P\widehat{Pt}P = 107.3(4)^\circ$ and $r(Pt\text{-}P) = 2.358(6)$ Å. The stability of this complex in spite of the *cis*-relation of the bulky phosphines is due to inter-meshing of the phosphines [381]. In *trans*-$[Pt\{P(CMe_3)_3\}_2H_2]$, the mutual repulsion between the phosphines leads to $Pt\widehat{P}C$ (mean = 110.8°) greater than tetrahedral values, and $C\widehat{P}C$ (mean = 108.1°) less than tetrahedral values. The maximum cone angle of the $P(CMe_3)_3$ moiety is 184°, which is less than found in uncrowded $P(CMe_3)_3$ complexes [382].

A ^{19}F and ^{31}P dynamic NMR study of $[Pt\{P(C_6F_5)_3\}(PR_3)XY]$ ($R = C_6F_5$, $X = Y =$ Cl or I; R = Ph, X = Y = Cl; $PR_3 = PPhMe_2$, X = Y = Br; $PR_3 = PMePh_2$, X = Ph, Y = Cl) demonstrated restricted rotation at low temperatures about the Pt-P and P-C bonds, with a preferred conformation in which none of the P-C bonds lie in the platinum square-plane. The mechanism of helicity reversal of the propeller-shaped $P(C_6F_5)_3$ ligand is a two ring flip [383]. A ^{31}P NMR study of several

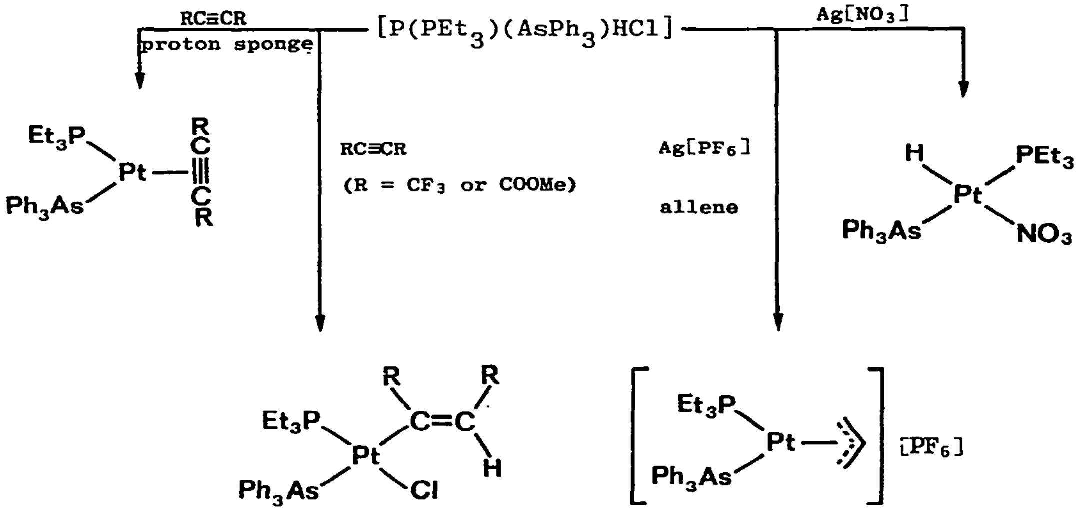
4-substituted triarylphosphines has provided further evidence against a simple dependence of ^{195}Pt-^{31}P coupling constants on the basicity of the phosphine [384]. Multinuclear NMR studies of $[Pt(PPh_3)_3R]^+$ (R = CH_2X; X = H, Me, CF_3, Ph, CN, CH_2CN, CH_2CH_2CN, 2-C_6H_4CN, NO_2 or $COCH_3$) found changes in $^1J_{^{195}Pt\text{-}cis\text{-}^{31}P}$ are as large as changes in $J_{^{195}Pt\text{-}trans\text{-}^{31}P}$, with a rough inverse correlation of the two. An X-ray diffraction study of $[Pt(PMe_2Ph)_3(CH_2CN)][PF_6]$ found $r(Pt\text{-}P)_{(trans\ to\ C)}$ = 2.395(5) Å, the longest bond of this type yet observed, whereas r(Pt-C) was 2.023(16) Å, one of the shortest yet found; $r(Pt\text{-}P)_{(cis\ to\ C)}$ at 2.339(4) and 2.302(5) Å are not unusually long [385].

Cis-$[M(Ph_2PC{\equiv}CR)_2Cl_2]$ (M = Pd, Pt; R = CF_3, Ph or CMe_3) undergo a facile 1:1 reaction with secondary phosphines (PR'R''H; R' = R'' = Ph, C_2H_4CN; R' = Et, R'' = Ph) to give stereospecifically *cis*-$[M\{Ph_2PCH{=}C(R)PR'R''\text{-}cis\}Cl_2]$ [386]. Reaction (60) provides a simple synthetic route to [PtLL'XY] complexes, which unexpectedly

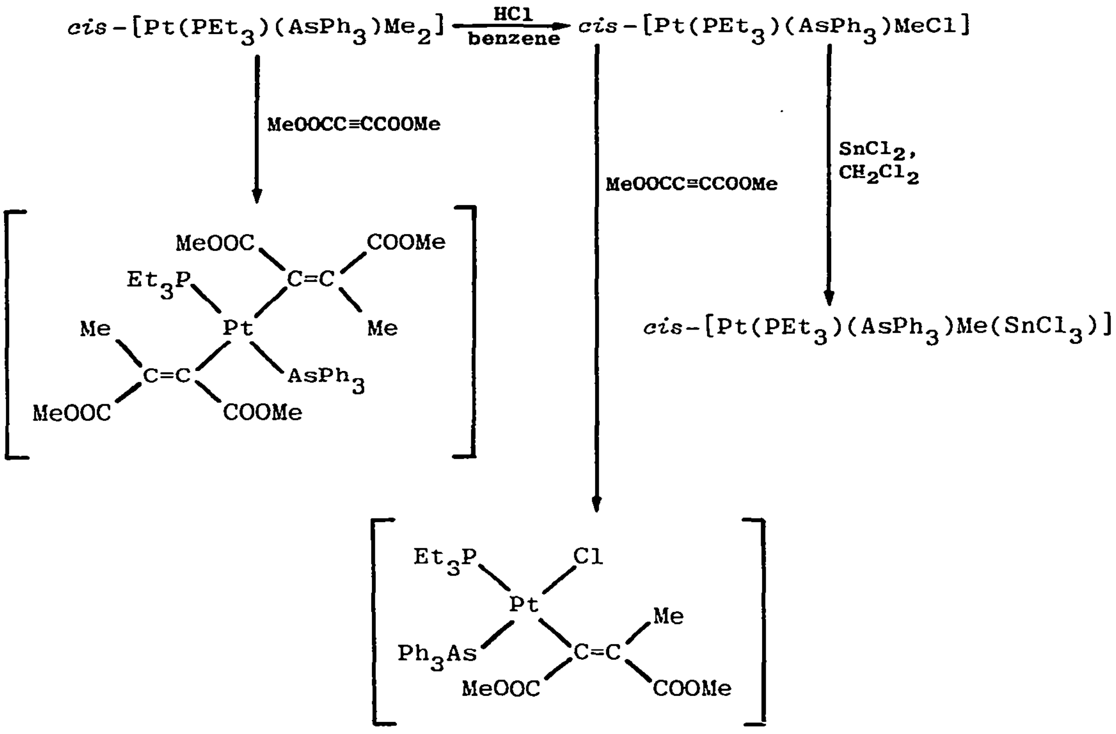
$$cis\text{-}[PtL(PEt_3)Cl_2] \xrightarrow[2.\ HCl]{1.\ Na[BH_4]} [PtL(PEt_3)HCl] + [Pt(PEt_3)_2HCl] + [PtL_2HCl]$$

L = PPh_2Me	2	:	1	:	1	(60)
L = PPh_3	4	:	1	:	1	
L = $AsPh_3$	sole product					

display an extensive chemistry without disproportionation, although some scrambling does occur. This depends on L and L'; the less alike they are the less scrambling occurs. The reactions in Schemes V and VI indicate that low



SCHEME V



SCHEME VI

symmetry mixed ligand complexes can be preserved through a wide range of reactions [387].

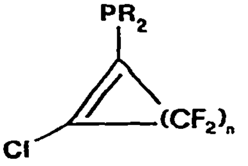
The chemistry of $[Pt(PPh_3)_3Cl][Ti_3Cl_{11}]$ has been investigated [388]. The hydrolytic decomposition of $Na_2\{(PPh_2C_6H_4SO_3)(OH)Pd(\mu\text{-}O_2CMe)\}_2]$ yields at first mononuclear $Na[Pd(PPh_2C_6H_4SO_3)(OH)_2(H_2O)]$, with subsequent formation of $Pd(OH)_2$ and free phosphine [389]. The acid dissociation constants of $[Pt(PR_3)L(H_2O)_2]^{2+}$ (PR_3 = PBu_3 or PEt_2Ph; L = Me_2SO or thiodiglycol) have been determined [390,391].

The *cis-trans* isomerisation of bisphosphine complexes of palladium(II) and platinum(II) has been widely studied [392-395]. A study of the pressure dependence of the isomerisation of $[Pt(PEt_3)_2RX]$ (R = alkyl, X = halide) suggested that the first step must be associative rather than dissociative as previously suggested; $[Pt(PEt_3)_2R(solvent)]X$ is suggested as the product of the first stage [393]. Dichloromethane solutions of $[PtL_2X_2]$ with added L {L = PMe_3, PEt_3, PBu_3, $P(4\text{-tolyl})_3$} contain *cis*- and *trans*-$[PtL_2X_2]$, $[PtL_3X]^+$ (when X = Cl or Br) and square-pyramidal $[PtL_4X]^+$ (when X = Cl, Br or I) with apical halide [394]. The only five-coordinate species observed that contained three phosphines was $[Pt(PMe_3)_3I_2]$. ^{31}P NMR studies show there is intramolecular

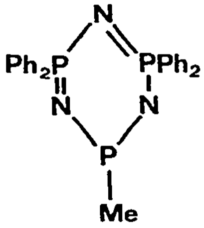
PMe_3 exchange between $[PtL_3Cl]^+$, $[PtL_4Cl]^+$, $[PtL_3I_2]$ and free PMe_3. The isomerisation of $[PtL_2X_2]$ in dichloromethane appears to involve rapid displacement of X by L, followed by slow displacement of L by X, and not *pseudo*-rotation of a five-coordinate intermediate. X-ray diffraction shows Pt-P bond lengths in $[Pt(PMe_3)_3Cl]Cl$ of 2.242(3) Å *trans* to Cl, and 2.338(2) Å *cis* to Cl, with the anionic chloride not located in an axial position corresponding to a fifth coordination site [394].

Bis(1-substituted-3,4-dimethylphosphole)palladium(II) dihalide complexes are all *cis* in the solid state [395,396]. In solution, solvents of increasing dipole moment tend to favour the *cis*-isomer. A plot of ΔS against ΔH for the *cis-trans* equilibrium is linear, with phosphines fitting on the same plot. Thus although palladium(II)-phosphole bonding is stronger than palladium(II)-phosphine bonding [395], the *cis-trans* differences for phosphole and phosphine complexes are about the same [395]. A conductance study suggested that *cis-trans* isomerisation of $[Pd(phosphole)_2X_2]$ in chloroform occurs by *pseudo*-rotation in a five-coordinate complex, whereas in nitromethane formation of $[PdL_3X]^+X^-$ followed by displacement of L by X^- occurs [396].

The tertiary phosphines (91) coordinate to palladium(II) and platinum(II) through phosphorus only [397]. Cyclotri-λ^5-phosphazenes, (92), form *cis*- and *trans*-$[PdL_2X_2]$ complexes, but only *trans* complexes with platinum(II) in ethanenitrile [398].



(91; R = Ph or cych;
n = 2, 3 or 4)



(92)

6.5.4.12 *Complexes with Other Unidentate Phosphorus Ligands*

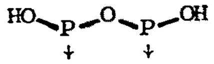
The stability of $[PdL_2(SCN)_2]$ varies with phosphorus ligand in ethanol in the order of L = $PEt(OPh)_2 > PPh_2(OEt) > PEt_2(OPh) > PEt_3$, and in ethanenitrile in the order $PPh_2(OEt) > PEt(OPh)_2 > PEt_2(OPh) > PEt_3$ [399]. $K_2[PtI_4]$ reacts with $PPh(OEt)_2$ to form *trans*-$[Pt\{PPh(OEt)_2\}_2I_2]$ which on heating to between 115 and 140 °C gives the *cis*-isomer [400]. ^{31}P NMR parameters for trialkylphosphite complexes of palladium(II) and platinum(II) have been reported [401]. Reactions (61)-(63) have been used to prepare palladium(II) and platinum(II) complexes of $(MeO)_2PO$ [402]. $[Pt(S_2CNR_2)(Ph_2PO)_2H]$ reacts with $BF_3.Et_2O$ to replace the hydrogen by BF_2 {reaction (64)} [403]. Reaction of $K_2[PtCl_4]$ with

$$[M(PPh_3)_n] + Hg\{OP(OMe)_2\}_2 \xrightarrow[\substack{M\,=\,Pt,\ n\,=\,3\\ \text{benzene}}]{M\,=\,Pd,\ n\,=\,4;} [M(PPh_3)_2\{OP(OMe)_2\}_2] \qquad (61)$$

$$[M(PPh_3)_n] + ClHgOP(OMe)_2 \xrightarrow[M\,=\,Pt,\ n\,=\,3]{M\,=\,Pd,\ n\,=\,4;} [M(PPh_3)_2Cl\{OP(OMe)_2\}] \qquad (62)$$

$$[Pt(PPh_3)_3] + Hg\{OP(OR)_2\}_2 \xrightarrow[R\,=\,Me\text{ or }Et]{PhCH_3\text{ at }-22\ ^\circ C} [\{(RO)_2PO\}HgPt(PPh_3)_2\{OP(OR)_2\}] \qquad (63)$$

$$Pt(S_2CNR_2)(Ph_2PO)_2H] \xrightarrow[(R\,=\,Et\text{ or }CHMe_2)]{BF_3.Et_2O} [Pt(S_2CNR_2)\{(Ph_2PO)_2BF_2\}] \qquad (64)$$

phosphorous acid yields a mixture of $\{PtP_4\}$, $\{PtP_3Cl\}$ and *cis*-$\{PtP_2Cl_2\}$ (where P represents a phosphorous acid ligand in an undetermined state of ionisation). Careful evaporation of this aqueous solution gives evolution of hydrochloric acid, with concomitant formation of green or purple solids. Recrystallisation of the purple solid from water yields dark green prismatic needles of $K_4[Pt_2H_8P_8O_{20}].2H_2O$ in which two platinum atoms surrounded by four phosphorus atoms are bridged by four  groups to give a Pt-Pt separation of 2.925 Å [404]. Fluorophosphonate complexes are formed by reactions (65) and (66)

$$(CH_2{=}CHCH_2O)PF_2 + [M(PhCN)_2Cl_2] + PR_3 \xrightarrow{M\,=\,Pd\text{ or }Pt} [M(PR_3)_2(F_2P{=}O)Cl] \qquad (65)$$

$$(BuO)_2PF + [Pt(PhCN)_2Cl_2] + PPh_3 \longrightarrow \begin{array}{l} trans\text{-}[Pt(PPh_3)_2(F_2P{=}O)Cl] + \\ trans\text{-}[Pt(PPh_3)_2\{(BuO)PF{=}O\}Cl] \end{array} \qquad (66)$$

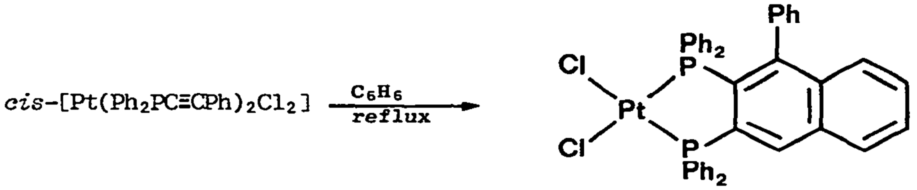
[405]. A series of platinum(II) complexes of dihalodiazadiphosphetidine $(PXNR)_2$ ring systems have been prepared [406].

6.5.4.13 *Complexes with Bidentate Phosphines*

Long chain bidentate phosphines $(Me_3C)_2P(CH_2)_nP(CMe_3)_2$ (n = 5-8), $(Me_3C)_2P(CH_2)_2CHMe(CH_2)_2P(CMe_3)_2$ or $Ph_2P(CH_2)_nPPh_2$ (n = 5,6,8,10 or 12) react with $[M(PhCN)_2Cl_2]$ (M = Pd or Pt) to form complexes of the type $[\{MCl_2(P\text{-}P)\}_2]$ in which rectangular rings are formed with bulky $P(CMe_3)_2$ or PPh_2 groups located at the corners [407-410]. The importance of non-bonded interactions between bulky groups in promoting large ring formation has been stressed [407, 411]; this effect is variously known as the Thorpe-Ingold effect or stereopopulation control. In addition to the formation of $[\{MCl_2(P\text{-}P)\}_2]$, $(Me_3C)_2P(CH_2)_5P(CMe_3)_2$ reacts with $[M(PhCN)_2Cl_2]$ to form monomeric $[MCl\{(Me_3C)_2PCH_2CH_2CHCH_2CH_2P(CMe_3)_2\}]$ (M = Pd or Pt), in which the central carbon of $(Me_3C)_2P(CH_2)_5P(CMe_3)_2$ has been metallated [407]. Platinum also metallates the central carbon of $(Me_3C)_2P(CH_2)_2CHMe(CH_2)_2P(CMe_3)_2$ whereas palladium(II) does not [409]. Trifluoroethanoic acid reacts with $[\{Pt((Me_3C)_2P(CH_2)_2CHMe(CH_2)_2P(CMe_3)_2)Cl_2\}_2]$ to form cycloplatinated $[Pt\{(Me_3C)_2P(CH_2)_2CMe(CH_2)_2P(CMe_3)_2\}(OOCCF_3)]$ [409].

Both $[Pd((-)\text{-diop})Cl_2]$ and $[Pt((-)\text{-diop})Cl_2]$, which are isostructural, have two non-equivalent molecules in their unit cells with different conformations of the seven-membered rings; the two molecules are roughly related by a centre of symmetry [412]. These results do not provide an explanation for the high efficiency of the chiral ligand diop in promoting asymmetric reactions. However different conformations of $[Pt(diop)_2]$ are known to occur in solution, the energy barrier for their interconversion being rather low ($\Delta G^{\ddagger}_{250}$ = 48 kJ mol^{-1}) [413]. A conformational adaptability of the ligand with respect to the substrate in the catalyst-substrate complex could well be an important factor in determining asymmetric induction by diop [414].

The presence of proximate acetylenic groups in *cis*-$[M(Ph_2PC{\equiv}CPh)_2Cl_2]$ (M = Pd or Pt) gives rise to some unusual coupling reactions {reaction (67)} [415].

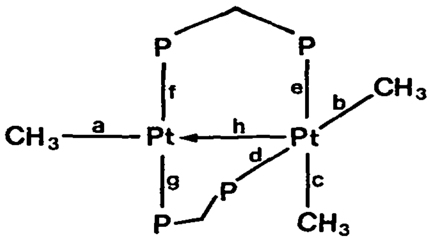


(67)

The crystal structure of $[Pt(cis\text{-}Ph_2PCH{=}CHPPh_2)(CF_3)Cl]$ shows $r(\text{Pt-P})_{trans\ \text{to}\ CF_3}$ = 2.275(4) Å, $r(\text{Pt-P})_{trans\ \text{to}\ Cl}$ = 2.236(4) Å, r(Pt-Cl) = 2.346(4) Å and r(Pt-C) = 2.188(8) Å [416]. $K_2[PtCl_4]$ reacts with $(Ph_2P)_2NH$ to form $[Pt(Ph_2PNHPPh_2)_2]Cl_2$ [417]. When $[Pt(Ph_2PCH{=}CHPPh_2)X_2]$ (X = Cl, Br or I) is heated, the phosphine undergoes inner-sphere oxidation, whereas with $[Pd(dppe)X_2]$ no such reaction takes place [418]. Molar conductance measurements in ethanenitrile are a useful way of determining the charge on a complex ion. A survey of a range of metal complexes including many palladium(II) and platinum(II) complexes of bidentate phosphines indicated that typical values of the slope of a plot of $(\Lambda_o-\Lambda_E)$ against $c^{\frac{1}{2}}$ {where Λ_E is the conductance at concentration c (equiv l^{-1}), and Λ_o is the conductance at infinite dilution} are in the ranges 300-500 (1:1), 600-1100 (2:1) and about 1300 Ω^{-1} l$^{\frac{1}{2}}$ equiv$^{-\frac{1}{2}}$ for 3:1 electrolytes in ethanenitrile [419].

A single crystal X-ray diffraction study of $[Pt_2(\mu\text{-dppm})_2Me_3]PF_6$ (93) shows the presence of a platinum(II) d_{z^2} → platinum(II) $d_{x^2-y^2}$ donor → acceptor metal-metal bond [420].

6.5.4.14 Complexes with Multidentate Phosphines

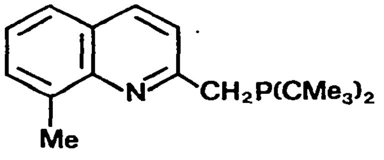


a	2.06(4) Å	e	2.338(7) Å
b	2.10(3) Å	f	2.293(7) Å
c	2.08(3) Å	g	2.263(7) Å
d	2.314(7) Å	h	2.769(1) Å

(93; P^P = dppm)

$[Pt(P\text{-}P\text{-}P)X]^+$ and $[Pt(P\text{-}P\text{-}P)Y]^{2+}$ (P-P-P = $PhP\{(CH_2)_3PPh_2\}_2$; X = Cl, NCS, NO_2, H, CH_3, CH_2CN, COOMe, C_3H_5 or Ph; Y = $P(OMe)_3$ or PEt_3) have been prepared and characterised. ^{31}P NMR studies indicate that σ-donor ligands that exert a large *trans*-influence (such as methyl or σ-allyl) display a small *cis*-influence, whereas ligands that exert a small *trans*-influence (such as chloride) exert a relatively large *cis*-influence [421], contrary to earlier predictions [422]. The *trans*-influence decreased in the order $Ph^- \sim \sigma\text{-}C_3H_5^- > COOMe^- > CH_3^- > H^- > CH_2CN^- > PEt_3 > P(OMe)_3 > NO_2^- > NCS^- > Cl^-$, and the *cis*-influence decreased in the order $P(OMe)_3 > NCS^- > Cl^- > PEt_3 > NO_2^- > CH_2CN^- > COOMe^- > H^- > CH_3^- > Ph^- > \sigma\text{-}C_3H_5^-$ [421]. The addition of $R_n(Me_2CHO)_{2-n}P(O)CH_2CH{=}CH_2$ to $R'PH(CH_2)_3PHR'$ gave $CH_2\{CH_2PR'(CH_2)_3P(O)(OCHMe_2)_{2-n}R_n\}_2$, which on hydrogenation with $Li[AlH_4]$ gave $H_{2-n}R_nP(CH_2)_3PR'(CH_2)_3PR'(CH_2)_3PR_nH_{2-n}$ (where R,R' = Me or Ph; n = 0 or 1). These ligands, L, complex with MCl_2 to form $[ML]Cl_2$ (M = Pd or Pt) [423].

6.5.4.15 Complexes with Bidentate Phosphorus-Nitrogen Ligands



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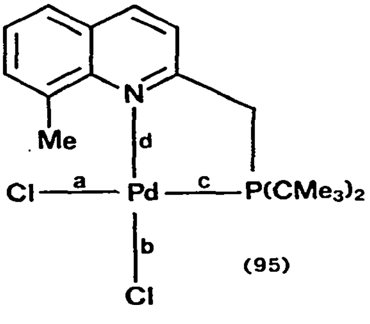


(95)

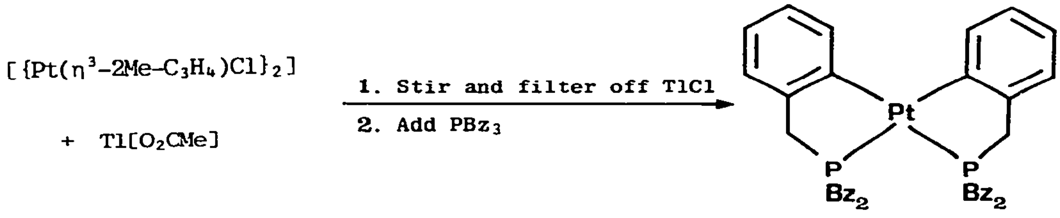
a	2.393(1) Å
b	2.294(1) Å
c	2.229(1) Å
d	2.078(4) Å

Two equivalents of (94), L, react with $Na_2[PdCl_4]$ in methanol to form *trans*-$[PdL_2Cl_2]$ in which only the phosphorus is coordinated. When only one equivalent is used, (95) is formed, in which distortions are present that drastically reduce the 8-Me .... Pd and 8-Me .... Cl interactions: the chloride *trans* to phosphorus is 0.66 Å out of the PdNPCl plane. In view of the strain in (95), it is not surprising that it readily reacts with pyridine to form

[PtL(py)Cl_2], in which (94) reverts to a unidentate phosphorus donor [424].

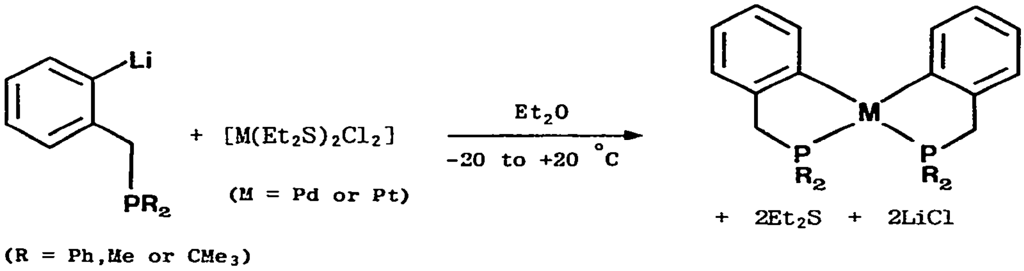
6.5.4.16 *Complexes with Bidentate Phosphorus-Carbon Ligands*

An X-ray analysis of the product of reaction (68) shows Pt-P bonds of



(68)

2.277(2) Å and Pt-C bonds of 2.067(7) Å [425]. This is believed to be the first *cis*-dimetallated complex, although similar *cis*-dimetallated complexes are also formed in reaction (69): some reactions of these complexes have been



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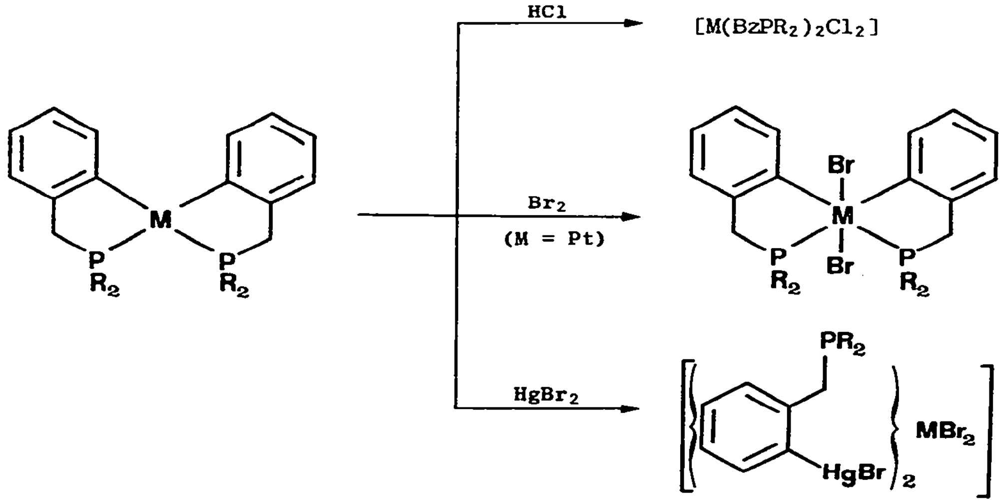
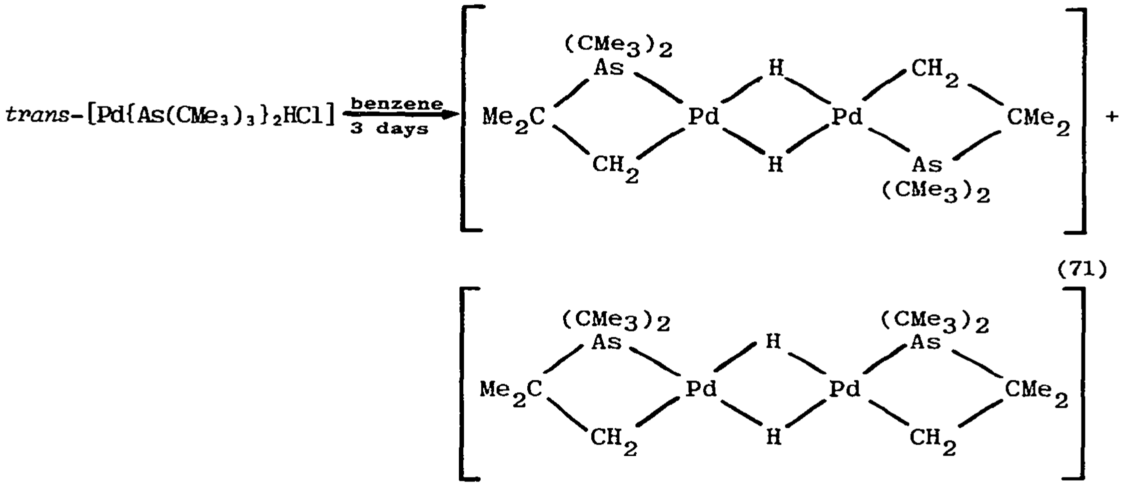


(70)

investigated {reaction (70)} [426].

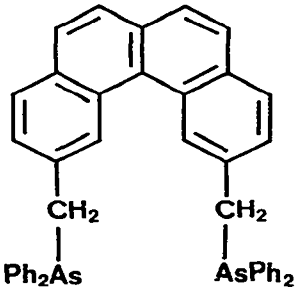
6.5.4.17 Complexes with Arsines

$Na_2[PdCl_4]$ reacts with $As(CMe_3)_3$ in absolute ethanol at room temperature to form *trans*-$[Pd\{As(CMe_3)_3\}_2HCl]$, which is stable at room temperature as a solid for several months. On dissolving in benzene, it slowly cyclometallates {reaction (71)} to form hydride bridged dimers [427], in contrast to



(71)

trans-$[Pd\{P(CMe_3)_3\}_2HCl]$ which cyclometallates with Pd-H bond cleavage [428]. (96) reacts with $[M(PhCN)_2Cl_2]$, $Na_2[PdBr_4]$, $PtBr_2$ or $[NEt_3Me][M_2I_6]$ to form



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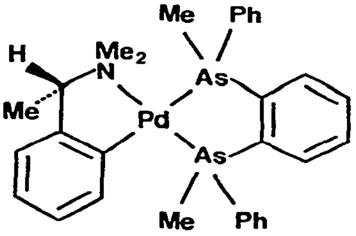
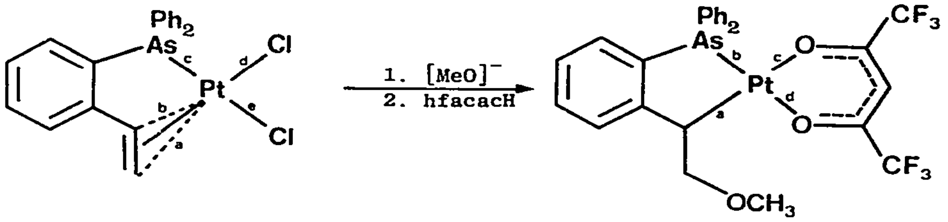


(97)

trans-$[MLX_2]$ (M = Pd or Pt; X = Cl, Br or I). An X-ray study of the *trans*-$[PtLCl_2]$ L = (96) showed Pt-As bonds of 2.380(1) and 2.370(1) Å and Pt-Cl bonds of 2.304(2) and 2.308(2) Å, as well as confirming the *trans*-bidentate coordination of the ligand [429]. (RR,SS)-1,2-$(PhMeAs)_2C_6H_4$ has been resolved into its enantiomers by fractionally recrystallising the internally diastereoisomeric palladium(II) complex, (97), in a procedure which constitutes the first satisfactory route to optically active tertiary arsines [430]. X-ray diffraction was used to determine the absolute configuration of the arsine in (97), as well as to show that the Pd-As bond *trans* to carbon was very long (2.462(2) Å), whilst that *trans* to nitrogen was very short (2.339(2) Å) [431]. The X-ray determined structures of *meso*-[Pd{RR,SS-1,2-(PhMeAs)$_2$C$_6$H$_4$}$_2$]X$_2$ (X = Cl or I) were also reported [431]. ClCH$_2$CH$_2$As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$, As-As-As, forms [Pd(As-As-As)Cl]Cl [432]. The X-ray structures of (98) and (99) show that arsines have a strong



(72)

a 2.12(2) Å d 2.274(4) Å
b 2.19(2) Å e 2.318(4) Å
c 2.317(1) Å
The alkene lies at 83.6° to the square plane

(98)

a 2.05(2) Å c 2.11(1) Å
b 2.275(2) Å d 2.06(1) Å

(99)

trans-influence relative to alkenes and chloride ions (the latter by comparison of (99) with [PtCl(γ-acac)(acac)]$^-$) [433].

6.5.5 Complexes with Group IVB Donor Ligands

Clearly the majority of the complexes involving Group IVB ligands are "organometallic complexes", and therefore have been specifically excluded from this review.

6.5.5.1 Carbonyl Complexes

The synthesis and properties of palladium-carbonyl complexes [434] and the photochemistry of transition metal carbonyl complexes have been reviewed [435]. The ^{13}C NMR chemical shifts in [Pt(PR$_3$)(CO)Cl(Ph)] and [Pt(PR$_3$)(CO)X(R')] (R = alkyl or aryl) and the ^{195}Pt-^{13}C coupling constants are markedly affected by changes in the *cis*-ligands, as well as those *trans* to CO, whilst (contrary to previous reports) the electronic charge on the complex does not exert a dominating influence on these parameters [436]. It is normally assumed that the product of the reaction of [{PtLX$_2$}$_2$] (L = PR$_3$ or AsR$_3$) is *cis*-[PtL(CO)X$_2$], but in fact the initial product is the *trans*-isomer [437,438]. *Trans* → *cis* isomerisation is rapid and can be complete in less than one hour in the presence of carbon monoxide, although if the excess carbon monoxide is removed isomerisation is slower, taking one to three days. This enables *trans*-isomers to be isolated and stored in the dark at -10 °C for a few days. The isomerisation is catalysed by UV light, and some $[\{PtLX_2\}_2]$ is also produced [437,438].

Coordinated carbon monoxide in $[Pt(PEt_3)_2Cl(CO)]^+$ reacts reversibly with water according to reaction (73) [439]. The product, (100), is air stable for

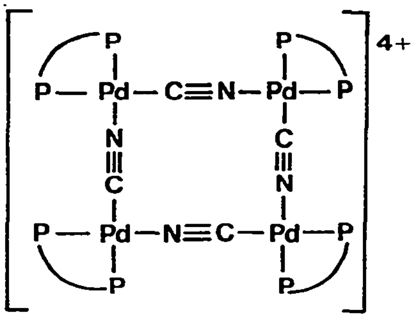
$$[Pt(PEt_3)_2Cl(CO)]BF_4 + H_2O \xrightleftharpoons{\text{propanone}} \underset{(100)}{[Pt(PEt_3)_2Cl(COOH)]} + HBF_4 \qquad (73)$$

several hours at room temperature, but decomposes on prolonged standing, or *in vacuo*, or on heating at 170 °C for 15 minutes, to give $[Pt(PEt_3)_2HCl]$ and carbon dioxide. Extraction of $K[Pt(CO)Br_3]$ by dibutylsulphide in benzene is rapid and complete, with formation of $[Pt(Bu_2S)(CO)Br_2]$ [440].

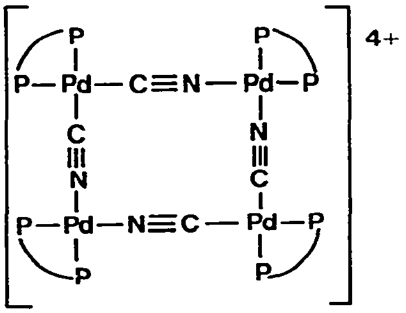
The catalytic properties of $[\{Pt(CO)Cl_2\}_2]$ in hydrochloric acid solution [441], and the binding and activation of CO, CO_2 and NO and their homogenously catalysed reactions [442] have been reviewed. The rate of oxidation of carbon monoxide in a solution of $PdCl_2$ containing KBr, HCl and traces of Fe(III) or Cu(II) is proportional to the concentrations of palladium(II) and carbon monoxide [443].

6.5.5.2 Cyanide Complexes

$Ba[Pd(CN)_4].4H_2O$, $Ba[Pt(CN)_4].4H_2O$ and crystals containing both species have been studied by polarised reflection spectroscopy. A UV-VIS absorption band is found in the solid state spectra, associated with a highly delocalised excited state [444]. The kinetics of the thermal decomposition of clathrates of the type $[Cd(NH_3)_2][Pd(CN)_4].2G$ and $[Cd(en)][Pd(CN)_4].2G$ (G = PhOH, C_6H_6, thiophene or pyrrole) have been studied [445]. The thermal decomposition of $[Ph_2I]_2[M(CN)_4]$ (M = Pd or Pt) involves formation of a mixture of iodobenzene and benzonitrile below 400 °C, and cyanogen above 400 °C [446]. Extraction of one cyanide ligand from $[Pd(dppe)(CN)_2]$ with silver perchlorate yields a mixture of two compounds, believed to be the tetramers (101) and (102) [447].



(101; P-P = dppe)

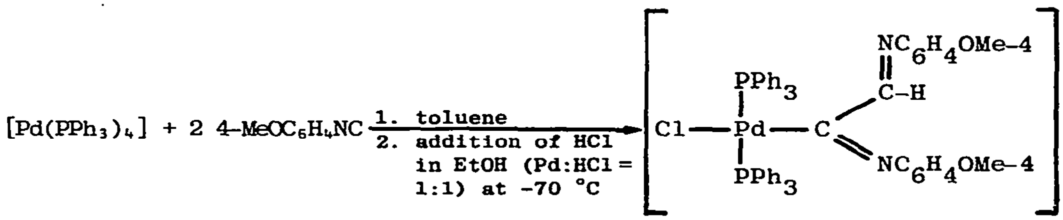


(102; P-P = dppe)

6.5.5.3 Isocyanide Complexes

The crystallographic parameters of $[Pt(CNEt)_4][Pt(CN)_4]$ have been determined from X-ray powder data [448]. Polymeric $\{Pd(CNR)_2\}_n$, with bridging and terminal isocyanide ligands, is formed when palladium is vapourised into an RNC matrix (R = Me or C_6H_{11}) [449]. A study of the electrochemical behaviour of *cis*-$[M(PR_3)(ArNC)Cl_2]$ indicates that, when M = Pt, Pt(II) is reduced to Pt(0), whereas, although at room temperature Pd(II) is reduced to Pd(0), at 0 °C Pd(II) is only reduced to Pd(I) [450]. *Trans*-$[Pt(PR_3)(ArNC)_2Cl]^+$ are oxidised electrochemically to platinum(IV) in a two-electron process, but reduced to platinum(0) in two successive one-electron processes [451].

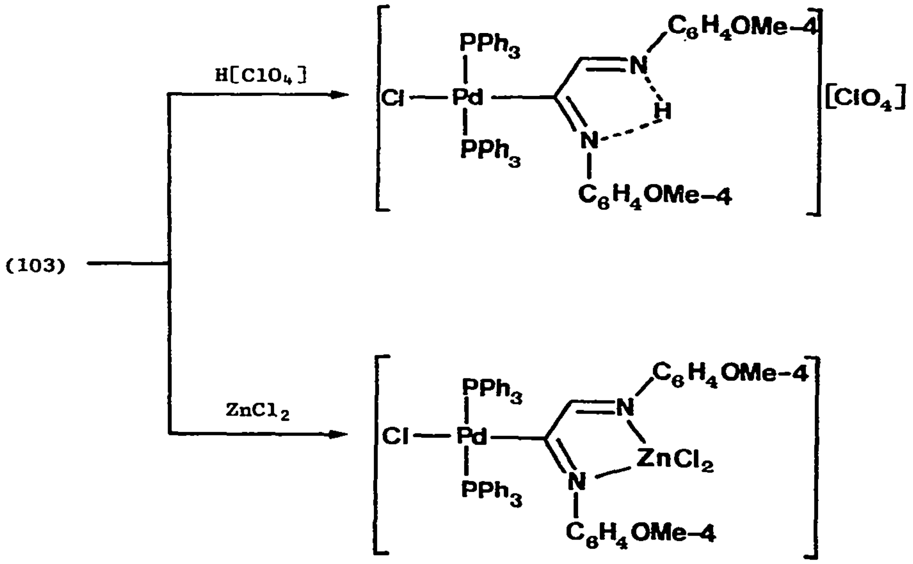
Treatment of $[Pd(PPh_3)_4]$ in toluene with two equivalents of an isocyanide, followed by addition of ethanolic hydrogen chloride, yields (103) by reaction (74),



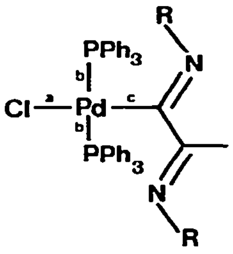
(74)

(103)

through an initial palladium(0) isocyanide complex, oxidative-addition of hydrogen chloride and subsequent isocyanide insertion into the Pd-H bond [452]. (103) reacts with Lewis acids to form five-membered ring compounds {reaction (75)}. An X-ray diffraction study has shown that the N=C-C=N group in (104)

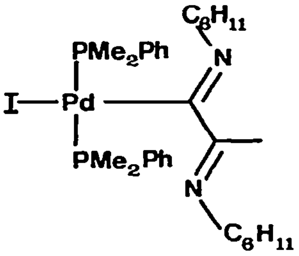


(75)



a 2.41(1) Å
b 2.34(1) Å
c 1.98(1) Å

(104; R = C_6H_4-4-OMe)



(105)

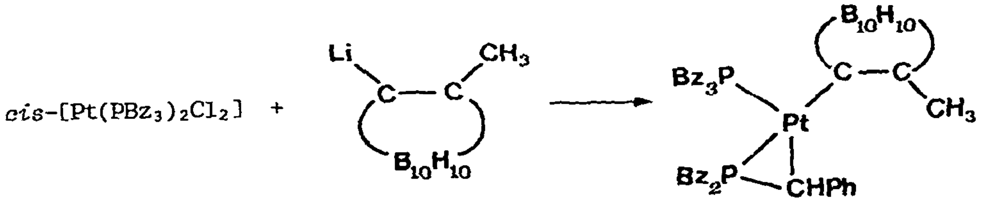
is *trans*, virtually planar and nearly normal to the palladium(II) coordination plane [453]. Sterically hindered rotation about the Pd–C bond accounts for the inequivalence of the phosphine methyl groups in (105) [453].

6.5.5.4 *Diazomethyl Complexes*

$[Pd(PPh_3)_2Cl(CN_2R)]$ (R = COOEt or $MeCO_2$) have been prepared from $[Pd(PPh_3)_2Cl_2]$ and $Hg(CN_2R)_2$. $[Pd(PPh_3)_2(CN_2R)_2]$ (R = COOEt, $MeCO_2$ or Ph) can be prepared either by reaction of $[Pd(PPh_3)_2Cl_2]$ with $LiCN_2R$ or by oxidative-addition of $Hg(CN_2R)_2$ to $[Pd(PPh_3)_4]$ [454].

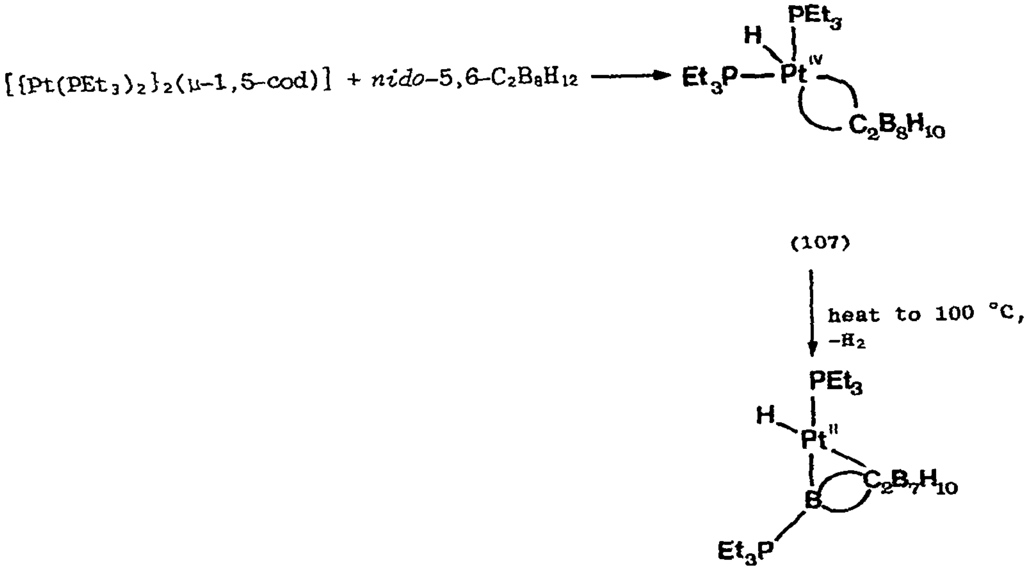
6.5.5.5 *Carborane Complexes*

$[M(PhCN)_2Cl_2]$ (M = Pd or Pt) and $[Pt(Et_2S)_2Cl_2]$ react with 1-lithio-2-dialkylamino-methyl-*o*-carboranes to form complexes in which $C(B_{10}H_{10})CCH_2NEt_2$ acts as a bidentate *N–C* ligand [455]. The structures of (106), (107) and (108), prepared by reactions (76) and (77), have been determined by X-ray diffraction [456,457]. When (109) is recrystallised from benzene, chloroform, dichloromethane or propanone, (110) is formed by insertion of platinum into a B–H bond [458]. EHMO calculations on the trigonal prismatic platinoboranes and carbaplatinaboranes, $[B_8\{Pt(PH_3)_2\}H_8]^{2-}$ and $[B_6C_2\{Pt(PH_3)_2\}H_8]$, have enabled the observed conformations of these molecules to be accounted for in terms of the nodal characteristics of the frontier orbitals of the constituent $Pt(PH_3)_2$ and borane or carbaborane fragments [459]. Sealed tube pyrolysis of



(76)

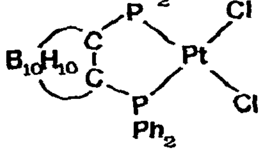
(106)



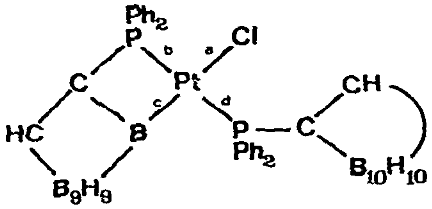
(107)

(77)

(108)



(109)



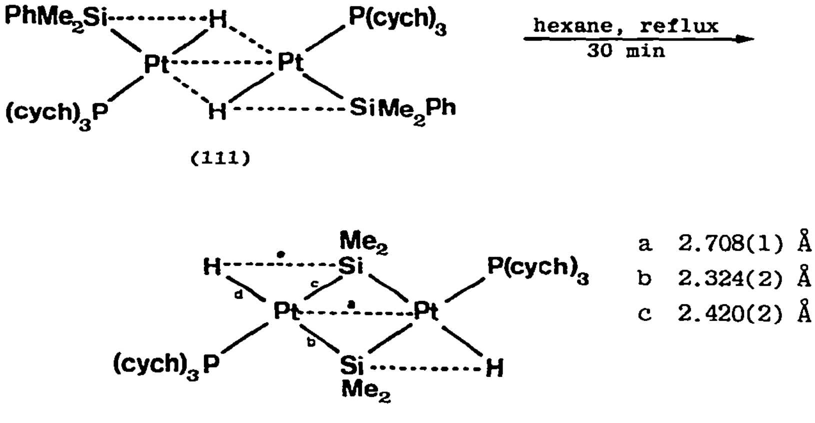
a 2.415(3) Å
b 2.279(3) Å
c 2.073(9) Å
d 2.305(2) Å

(110)

[*nido*-$\mu_{4,5}$-{*trans*-$Pt(PEt_3)_2H$}-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$] affords the *closo*-carbametallaborane [1,1-$(PEt_3)_2$-2,3-Me_2-1,2,3-$PtC_2B_4H_4$], together with loss of a molecule of hydrogen. By contrast pyrolysis of [*nido*-$\mu_{4,5}$-{*trans*-$Pt(PEt_3)_2H$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$] loses hydrogen and gives separation of the cage carbon atoms on pyrolysis, forming [*closo*-1,1-$(PEt_3)_2$-1,2,4-$PtC_2B_4H_6$] [460].

6.5.5.6 Complexes with Silicon Donor Ligands

The kinetics of the cleavage of the aryl-silicon bond in $Me_3SiC_6H_4R$ (R = H, 3- or 4-Me, -Cl, -OMe), in the presence of $Li_2[PdCl_4]$, are first-order with respect to arysilane except for the 4-methoxy derivative, where a second-order dependence is found [461]. The preparation and electronic absorption spectrum of $[Pt(PPh_3)_2\{Si(C_6F_5)_3\}\{HgSi(C_6F_5)_3\}]$ have been reported [462]. Reports of the effectiveness of $[\{Pt(P(cych)_3)(SiR_3)(\mu\text{-}H)\}_2]$, (111), as a hydrosilylation catalyst for alkynes and α,β-unsaturated aldehydes and ketones have appeared [463,464]. On heating (111) under reflux in hexane for thirty minutes, the phenyl groups of the $SiMe_2Ph$ groups are lost to yield (112), which shows no hydridic ^1H NMR resonance above 0 δ, and exhibits ν(PtH) at 1650 cm^{-1}, indicative of a three-centre two-electron PtHSi bond [465]. (112) can also be prepared by reaction (79).



(111)

(112)

a	2.708(1) Å	d	1.78 Å	
b	2.324(2) Å	e	1.72 Å	(78)
c	2.420(2) Å			

$$[Pt(P(cych)_3)(C_2H_4)] + Me_2SiH_2 \longrightarrow (112) \qquad (79)$$

6.5.5.7 Complexes with Germanium Donor Ligands

A number of platinum(II)-germyl complexes have been prepared by reactions

(80)-(82) [466]. $[Pt(PPh_3)_2\{HgGe(C_6F_5)_3\}\{Sn(C_6F_5)_3\}]$, prepared by the reaction of $[Pt(PPh_3)_2]$ with $(C_6F_5)_3GeHgSn(C_6F_5)_3$, has a *cis*-structure with

$$[Pt(PPh_3)_3] + Ge(C_6F_5)_3H \longrightarrow [Pt(PPh_3)_2H\{Ge(C_6F_5)_2H\}] + PPh_3 \qquad (80)$$

$$\begin{tikzcd}[Pt(PPh_3)_3] + (C_6F_5)_2HGeGeH(C_6F_5)_2 \arrow[r] & {[Pt(PPh_3)_2H\{Ge(C_6F_5)_2Ge(C_6F_5)_2H\}] + PPh_3} \arrow[d, "{[Pt(PPh_3)_2]}"] \\ & {[\{Pt(PPh_3)_2H\}\{Ge(C_6F_5)_2Ge(C_6F_5)_2\}\{Pt(PPh_3)_2H\}] + PPh_3}\end{tikzcd} \qquad (81)$$

$$[Pt(PPh_3)_3] + Ge(C_6F_5)_3EX \xrightarrow{(E = S \text{ or } Se)} [Pt(PPh_3)_2H\{EGe(C_6F_5)_3\}] + PPh_3 \qquad (82)$$

r(Pt-Sn) = 2.518(2) Å and r(Hg-Pt) = 2.617(1) Å: in solution a slow *cis-trans*-isomerisation occurs [467].

6.5.5.8 Complexes with Tin Ligands

NMR studies show that *cis*- and *trans*-$[PtL_2Cl_2]$ (L = PBu_3, PEt_2Ph, $PEtPh_2$ or PMe_2Ph) react with $SnCl_2$ in a range of solvents to form *trans*-$[PtL_2Cl(SnCl_3)]$ in a reaction that depends only slightly on the solvent; in some solvents *trans*-$[PtL_2(SnCl_3)_2]$ is also formed [468]. ^{195}Pt-^{119}Sn NMR couplings provide the largest one-bond spin-spin couplings ever observed: $[Pt(SnCl_3)_5]^{3-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$ have $J(^{195}Pt\text{-}^{119}Sn)$ = 27640 Hz [469]; and *trans*-$[Pt(PEt_3)_2(SnCl_3)Y]$ have $J(^{195}Pt\text{-}^{119}Sn)$ = 28954 (Y = Cl), 20410 (Y = $SnCl_3$) and 9067 Hz (Y = H) [470,471]. These very large couplings are due to the relatively large gyromagnetic ratios of the nuclei, combined with the high mutual polarisability of the s-orbitals on platinum and tin and the high s-character of the Pt-Sn bond, giving large values of $|\Psi(0)|^2$. The observation of a full spectrum when such large spin couplings are present can afford some difficulty, and a caveat is given. In cases where there is no check on the basis of gyromagnetic constants, the centre of the signal should be offset from the centre of the spectral window to see if peak separations within the apparent multiplet remain invariant. With this caveat, ^{195}Pt NMR spectroscopy is a valuable and sensitive probe for the structure of these catalytically valuable complexes. The ^{31}P NMR spectra of *trans*-$[Pt(PEt_3)_2(SnCl_3)_nCl_{2-n}]$ (n = 1 or 2) in propanone at room temperature show no ^{31}P-^{119}Sn coupling, suggesting fast Pt-Sn bond-breaking on the NMR time scale [471]. Equilibria (83) have been observed by NMR spectroscopy [401]. A mixture of $[Pt\{Ph_2P(CH_2)_4PPh_2\}Cl_2]$ and $SnCl_2$ is an active and

$$[\mathrm{M}\{\mathrm{P(OR)_3}\}_2\mathrm{Cl_2}] \xrightarrow{\mathrm{SnCl_2}} [\mathrm{M}\{\mathrm{P(OR)_3}\}_2\mathrm{Cl(SnCl_3)}] \xrightarrow{\mathrm{SnCl_2}} [\mathrm{M}\{\mathrm{P(OR)_3}\}_2\mathrm{(SnCl_3)_2}] \qquad (83)$$

(M = Pd or Pt; R = Et or $CHMe_2$)

selective alkene hydroformylation catalyst that gives a straight:branched chain ratio of aldehydes of 99:1 [472].

Trans-[$PtL_2H(SnR_3)$] with bulky tertiary phosphines have been prepared by various routes [473]:

(i) When L = $P(cych)_3$, $P(CHMe_2)_3$, $P(CMe_3)Ph_2$ or $P(CHMeEt)_2Me$, they are formed by equimolar reaction of $HSnR_3$ with *trans*-[PtL_2H_2].

(ii) When L = $P(CHMe_2)_3$ or $P(CMe_3)Ph_2$, they are formed by oxidative-addition of [PtL_2] with $HSnPh_3$.

(iii) When L = $P(CHMe_2)_3$, $P(CMe_3)Ph_2$, they are also formed by reaction of *trans*-[PtL_2H_2] with $ClSnR_3$ (R = Me or Bu) in the presence of pyridine in benzene.

(iv) Finally, they are formed by sodium borohydride reduction of *trans*-[PtL_2HCl] and $ClSnPh_3$ in tetrahydrofuran, which occurs by reactions (84)-(86).

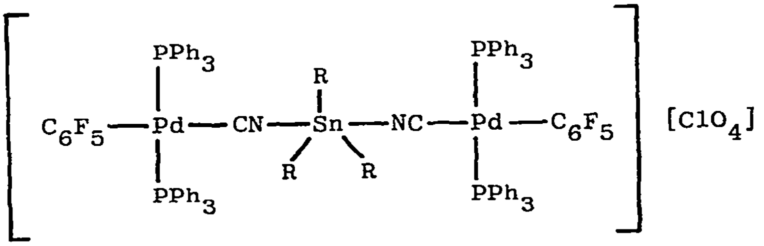
$$trans\text{-}[\mathrm{PtL_2HCl}] + \mathrm{Na[BH_4]} \longrightarrow trans\text{-}[\mathrm{PtL_2H_2}] + \mathrm{NaCl} \qquad (84)$$

$$\mathrm{ClSnPh_3} + \mathrm{NaBH_4} \longrightarrow \mathrm{HSnPh_3} + \mathrm{NaCl} \qquad (85)$$

$$trans\text{-}[\mathrm{PtL_2H_2}] + \mathrm{HSnPh_3} \longrightarrow trans\text{-}[\mathrm{PtL_2H(SnPh_3)}] \qquad (86)$$

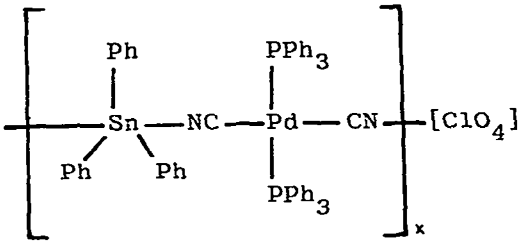
Reactions between [$Pt(PPh_3)_2(C_2H_4)$] and organotinhalides have been investigated. Whereas with $SnPh_2Cl_2$ platinum inserts into the Sn-Ph bond to form *cis*-[$Pt(PPh_3)_2Ph(SnPhCl_2)$], and with Me_3SnCl it inserts into the Sn-Me bond to form *cis*-[$Pt(PPh_3)_2Me(SnMe_2Cl)$], it inserts into the Sn-Cl bond of $SnMe_2Cl_2$, $SnPhCl_3$, $SnMeCl_3$ and $SnCl_4$ to form *cis* and *trans*-[$Pt(PPh_3)_2Cl(SnCl_nR_{3-n})$] [474,475]. Competitive experiments indicated an order of reactivity in the oxidative-addition reaction of $SnMe_4 < SnPh_4 < SnMe_3Cl < SnPh_3Cl$, $SnMe_2Cl_2 < SnPh_2Cl_2$, $SnMeCl_3 < SnPhCl_3 < SnCl_4$; no radicals were detectable during these reactions [474]. Coupling products are obtained in good yields from the reaction of tetraorganotin compounds or Grignard reagents with [$Pd(PR_3)_2R'X$], provided that a benzyl bromide is present [476]. The first step of reaction of [$Pd(PPh_3)_2(CH_2Ph)X$] with $SnMe_4$ or MeMgBr is methathesis of the benzyl ligand, rather than the halogen. The reactions of SnR_3X compounds with mono-, di- and tetra-cyano complexes of palladium(II) have been investigated {reactions (87)-(89)} [477].

$2[Pd(PPh_3)_2(CN)(C_6F_5)] + R_3Sn(O_2ClO_2) \longrightarrow$



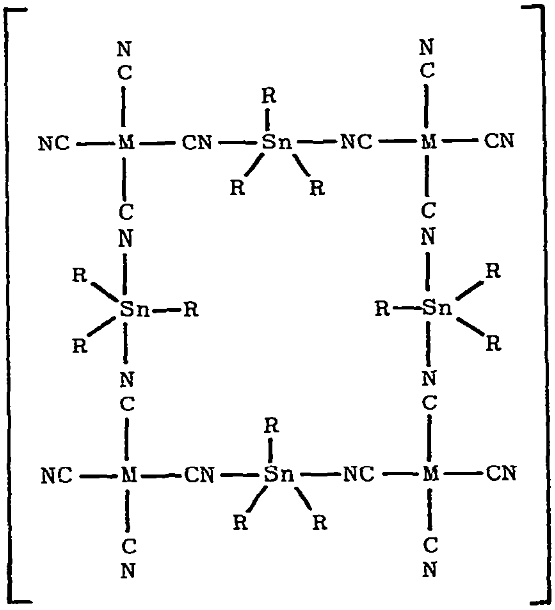
(87)

$[Pd(PPh_3)_2(CN)_2] + Ph_3Sn(O_2ClO_2) \longrightarrow$



(88)

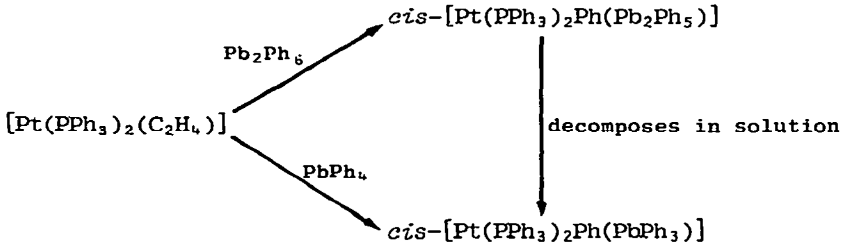
$K_2[M(CN)_4] + 2[SnR_3S_2]ClO_4 \longrightarrow$



$+ 2KClO_4 + 4S$ (89)

6.5.5.9 Complexes with Lead Donor Ligands

Pb_2Ph_6, $PbPh_4$, $PbPhMe_3$ and $PbPh_3Br$ react with $[Pt(PPh_3)_2(C_2H_4)]$ to give insertion into the Pb-Ph bond according to reaction (90) [478]. In contrast, $[Pt(PPh_3)_2(C_2H_4)]$ inserts into the Pb-Cl bond of $PbMe_3Cl$ to give *cis*- and *trans*-$[Pt(PPh_3)_2Cl(PbMe_3)]$.



(90)

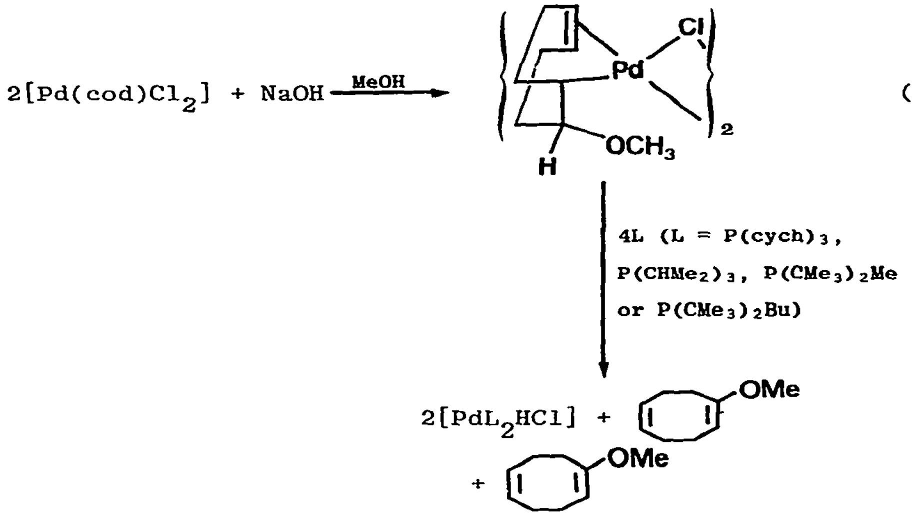
6.5.6 Complexes with Group III Donor Ligands

The preparation, properties and structures of $[6\text{-}X\text{-}9\text{-}Pt(PPh_3)_2(B_8H_{10})]$ (X = CH_2, NH or S) have been described [479]. $PdCl_2$ reacts with $H_2B_{10}X_{10}$ or $H_2B_{12}X_{12}$ (X = Cl or Br) on heating in aqueous solution, followed by the addition of triphenylphosphine in ethanol, to form $\{Pd(PPh_3)_2Cl\}_2Y$ or $2\{Pd(PPh_3)_3Cl\}Y$ (where Y = $[B_{10}X_{10}]$ or $[B_{12}X_{12}]$), respectively [480]. One of the products of reaction of *nido*-decaboranyloxide, 6,6'-$(B_{10}H_{13})_2O$, with *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ is $[\{Pt(\mu\text{-}\eta^3\text{-}B_6H_9)(PMe_2Ph)\}_2]$, which has a Pt-Pt bond (2.644 Å) bridged by two η^3-*nido*-hexaboranate ligands [481].

6.5.7 Hydride Complexes

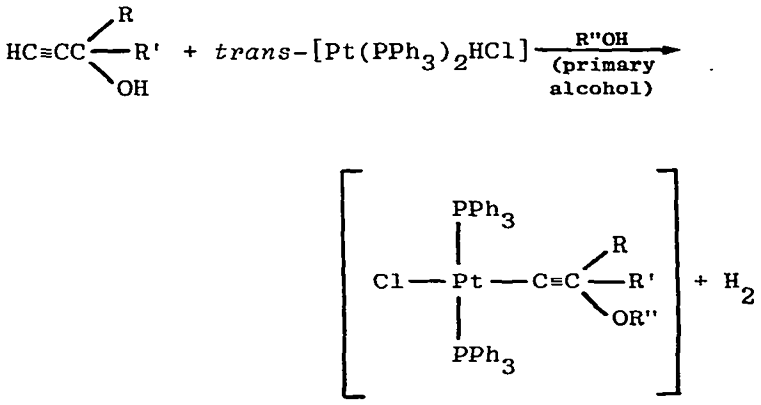
The effect of palladium hydride transformations on the formation of supported palladium catalysts formed by hydrogen reduction has been investigated [482], and novel platinum-hydride complexes have been described [483]. *Trans*-$[Pt\{As(CMe_3)_3\}_2H_2]$ can be prepared in good yield by the facile reaction of $K_2[PtCl_4]$ with $As(CMe_3)_3$ in alkaline ethanol [484]. With trifluoroethanoic acid or hydrogen chloride, *trans*-$[Pt\{As(CMe_3)_3\}_2HX]$ (X = CF_3COO or Cl) is formed in almost quantitative yield from the dihydride. The preparation of *trans*-$[PtL_2H(SnR_3)]$ with bulky tertiary phosphine ligands was described above (in Section 6.5.5.7). *Trans*-$[PdL_2HCl]$ with bulky phosphines may be prepared by reaction (91). When the phosphine is $P(CMe_3)_3$, the initially formed $[Pt\{P(CMe_3)_3\}HCl]$ loses $[P(CMe_3)_3H]Cl$ to form the metallated complex $[\{PdCl[(CMe_3)_2PCMe_2CH_2]\}_2]$ [485].

An X-ray diffraction study of *trans*-$[Pt(PPh_3)_2H(CH_2CN)]$ shows r(Pt-H) = 1.5 Å, r(Pt-P) = 2.274(4) Å and r(Pt-C) = 2.16(1) Å, which is the longest Pt-C bond reported so far [486]. The NMR spectra of *trans*-$[Pt(PR_3)_2H(SnCl_3)]$ (PR_3 = PPh_3 or $PPh(CH_2Ph)_2$) show the largest two-bond Sn-H couplings recorded so far. These



(91)

extreme values stem in part from the *trans*-arrangement of these ligands and in part from the presence of three strongly electron-withdrawing chlorines on the tin [487].



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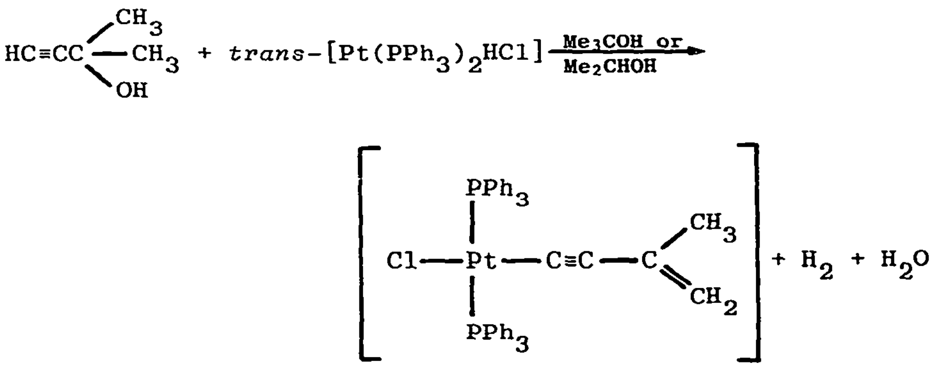
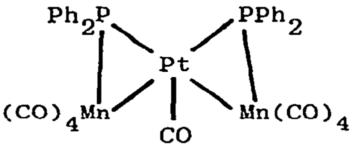


(93)

The electronic structures of *trans*-$[Pd(PH_3)_2XY]$ (X, Y = H, Cl, OH or O_2CMe) complexes have been calculated by the CNDO method because of the value of these complexes in the activation of dihydrogen [488]. In the reactions between tertiary acetylenic alcohols and *trans*-$[PtL_2HCl]$, no insertion into the Pt-H bond occurs. In the presence of primary alcohols, alkynyl ethers are formed by reaction (92), whereas in the presence of secondary alcohols intramolecular dehydration occurs {reaction (93)} [489].

6.5.8 Complexes with Transition Metals

$Na[Mn(CO)_5]$ reacts with *cis*-$[Pt(PPh_3)_2Cl_2]$ in tetrahydrofuran to form 3% of $[Pt(CO)_2\{Mn(CO)_5\}_2]$ and 11% of (113) [490].



(113)

6.5.9 Substitution Reactions of Complexes of the Divalent Metals

The first order rate constants of the reaction of $[Pd(Et_4dien)Cl]^+$ with MBr in water decrease with increasing salt concentration; the magnitude of the decrease depends upon M^+ in the order $[NBu_4]^+ > [NPr_4]^+ > [NEt_4]^+ > [NMe_4]^+ > K^+ \sim Na^+$ [491]. The pressure dependence of the rates of solvolysis of $[Pt(dien)X]^+$ in water, and of $[Pd(Et_4dien)I]^+$ in a series of solvents, all support an associative interchange mechanism in all the solvents studied [492, 493]. Pressure dependence studies also support an associative interchange mechanism for the reaction of $[Pd(Et_4dien)X]^+$ with Cl^-, Br^-, N_3^-, I^-, $[SCN]^-$ or NH_3 entering ligands [494].

A reinvestigation of the reaction of nucleophiles with $[Pd(dien)(H_2O)]^{2+}$ showed that only a k_2 term is present, decreasing in the order $I^- > [SCN]^- > (CH_3)_2CS > Br^- > NO_2^- > Cl^-$ [495]; previous reports of a k_1 term are in error [496]. The kinetics of solvolysis of $[PtCl_4]^{2-}$ in HCl-H$[ClO_4]$ mixture in aqueous methanol or Me_3COH have been studied at 308.2 K [497]. A study of the kinetics of the reaction of ethene with $[PtCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0–4), including the *cis*- and *trans*-isomers when n = 2, showed that [498]:

(i) In *trans*-$[PtCl_2(H_2O)_2]$, both chloride and aqua ligands are substituted by ethene in two parallel paths, differing in rate by a factor of only 1.5, with chloride loss being the faster.

(ii) Ethene is an inefficient entering ligand, like dmso. When water is the leaving group, the entering group efficiencies for chloro-aqua-platinum(II) complexes are $H_2O(\sim 10^{-3}) < \text{dmso}(0.3) \sim C_2H_4(0.4) \sim Cl^-(1) < Br^-(4) < [SCN]^-(40) < I^-(100)$.

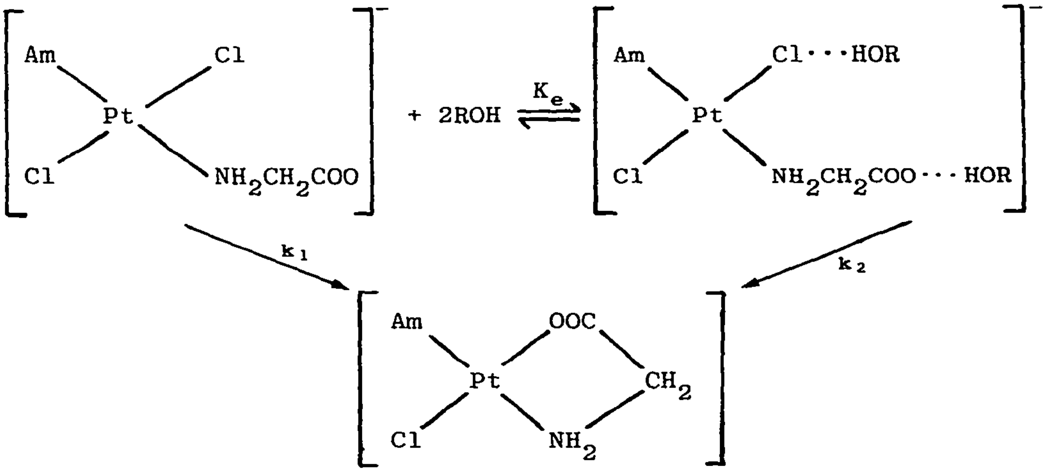
(iii) The relative *trans*-effects of chloride as opposed to aqua ligands for the replacement of H_2O by L are $Cl^-(350) > Br^-(200) \sim [SCN]^-(200) > I^-(80) > \text{dmso}(50) > C_2H_4(10)$.

(iv) Milburn and Venanzi's [499] observation of no solvento-path was a consequence of having a large concentration of the leaving chloride group present, not to the non-reactivity of $[PtCl_3(H_2O)]^-$.

The substitution of nitro-ligands in $[Pt(NO_2)_4]^{2-}$ by cyanide occurs practically irreversibly, with no appreciable amounts of intermediate substitution products, in a reaction that is first-order in both cyanide and $[Pt(NO_2)_4]^{2-}$ [500]. A study of the kinetics of the substitution reactions of *cis*-$[Pt(4\text{-NC-py})_2Cl_2]$ with thiourea, $[SCN]^-$ or I^- in 50% aqueous methanol showed that initial-state effects are more important than transition states effects [501]. The reaction of $[Pd(acac)_2]$ with amines to form $[Pd(acac)(amine)_2][acac]$ does not involve intermediate formation of $[Pd(acac)(\gamma\text{-acac})(amine)]$; indeed $[Pd(acac)(amine)_2][acac]$ is an intermediate in the formation of $[Pd(acac)(\gamma\text{-acac})(amine)]$ [502].

The kinetics of ring closure in $K[Pt(amine)Cl_2(NH_2CH_2COO)]$ in aqueous organic solvents followed the rate law (94), which was interpreted in terms of

$$k_{obs} = k_1k_2K_3[ROH]^2 \tag{94}$$



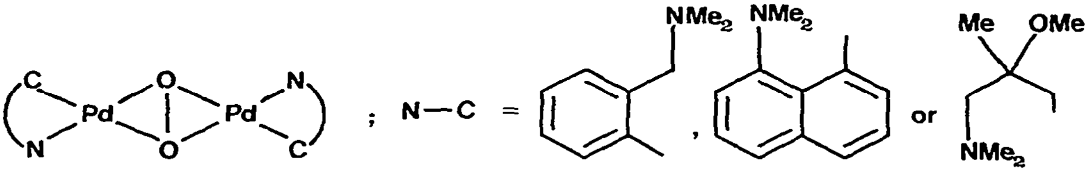
(95)

mechanism (95) [503]. The substitutions of palladium(II) and platinum(II) ethylxanthate and dithiophosphate complexes by dithiocarbamate ion followed second-order kinetics [504].

6.6 PALLADIUM(I) AND PLATINUM(I)

6.6.1 Complexes with Group VIB Donor Ligands

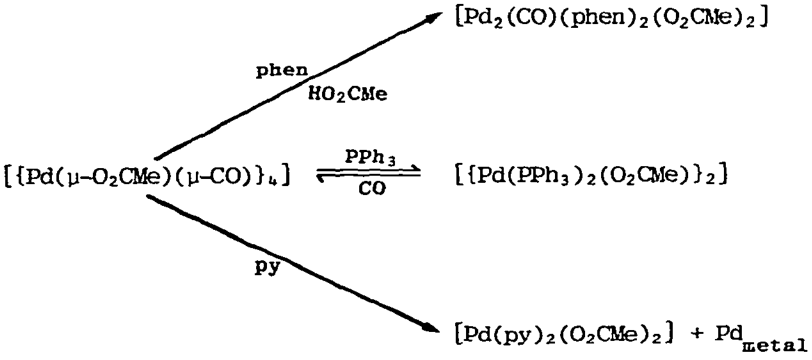
A series of dioxygen-bridged palladium(I) complexes, (114), have been prepared by anion exchange, using superoxide as the source of dioxygen [505].



(114)

These complexes react with alcohols, acids and various active methylene compounds to form hydrogen peroxide.

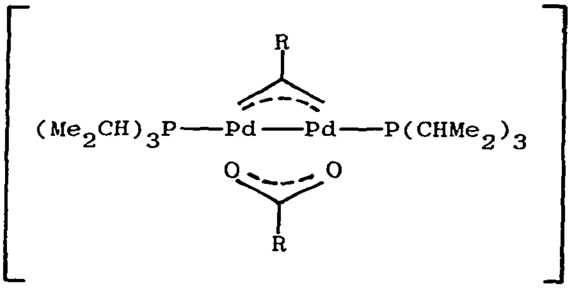
The palladium(I) ethanoate-bridged complex $[\{Pd(\mu\text{-}O_2CMe)(\mu\text{-}CO)\}_4]$ contains tetranuclear clusters with a parallelogram of palladium atoms with Pd-Pd distances of 2.663(1) and 2.909(1) Å, and $Pd\hat{P}dPd$ angles of 96.64 and 83.36°. Two sides of the parallelogram have bridging ethanoate groups, and two sides have bridging carbonyl groups [506]. A number of reactions of $[\{Pd(\mu\text{-}O_2CMe)(\mu\text{-}CO)\}_4]$ have been described {reactions (96)} [507]. When



(96)

$[\{Pd(PPh_3)(O_2CMe)_2\}_2]$ in dichloromethane is treated with dihydrogen, purged with argon, and then treated with more $[\{Pd(PPh_3)(O_2CMe)_2\}_2]$, $[Pd(PPh_3)(O_2CMe)]$, which has a Pd-Pd bond, is formed [508]. Palladium(I) complexes with bridging carboxylate ligands have also been prepared by reactions (97) and (98) [509].

$[Pd(\eta^3\text{-}2RC_3H_4)(O_2CR')] + [Pd\{P(CHMe_2)_3\}_2] \xrightarrow[R' = Me,\ Ph\ or\ CF_3)]{(R = H,\ Me,\ CHMe_2\ or\ CMe_3;}$



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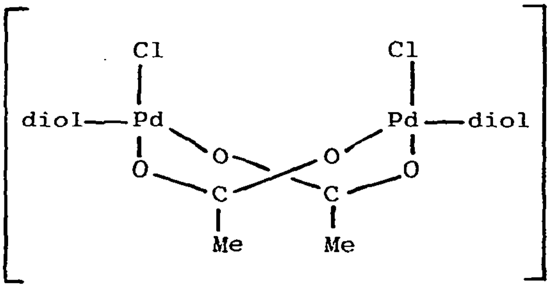
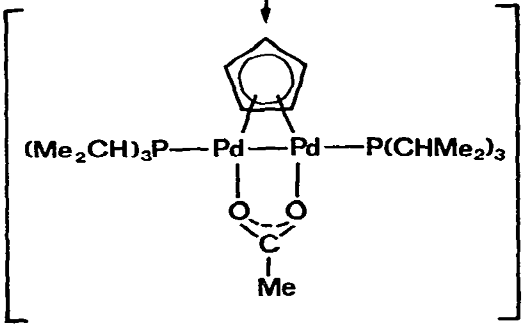


(diol = 1,3-cyclohexadiene or
1,3-cycloheptadiene)

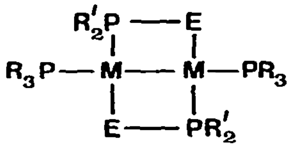
$+ Tl[C_5H_5] \longrightarrow [Pd(diol)(C_5H_5)(O_2CMe)]$ (98)

$\downarrow [Pd\{P(CHMe_2)_3\}_2]$



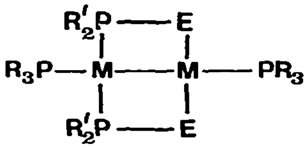
6.6.2 Complexes with Phosphorus and Either Sulphur or Selenium Donors

An XPES study of $[M_2(PR_3)_2(\mu\text{-}EPR'_2)]$ (M = Pd or Pt; E = S or Se) suggests that the metals are in the +1 oxidation state, the complexes being a mixture of (115) and (116) [510].



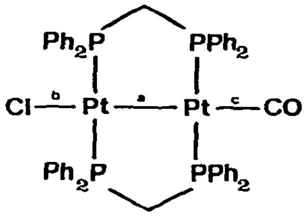
(115)

$\rightleftharpoons$



(116)

$[Pt_2Cl_2(\mu\text{-dppm})_2]$ reacts with ligands L (L = PMe_2Ph, $PMePh_2$, PPh_3, NH_3 or py) in the presence of $[PF_6]^-$ to give $[Pt_2L_2(\mu\text{-dppm})_2][PF_6]_2$. $[Pt_2(NH_3)_2(\mu\text{-dppm})_2][PF_6]_2$ reacts with carbon monoxide to give $[Pt_2(CO)_2(\mu\text{-dppm})_2][PF_6]_2$; unsymmetrical $[Pt_2(CO)(NH_3)(\mu\text{-dppm})_2][PF_6]_2$ was also prepared [511]. The structure of $[Pt_2Cl(CO)(\mu\text{-dppm})_2][PF_6]_2$, (117), shows two square-planar platinum atoms with a dihedral angle of 40.1° between the two coordination planes [512]. XPES studies of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-dpam})_2]$, and their products following insertion of CO, MeNC, SO_2 or S into the Pd-Pd bond, show either no change or only a modest change in the $Pd_{3d_{5/2}}$ binding energy; where observable, the binding energies of the inserting atoms decrease, sometimes substantially [513]. The structures of the SO_2 (two molecules distinguishable in crystal) and S insertion products are shown in (118); the sulphur insertion product arises from reaction of either cyclic S_8 or propylene sulphide with $[Pd_2Cl_2(\mu\text{-dppm})_2]$ [514]. The Pd-Pd bond has been cleaved during insertion and replaced by two Pd-S bonds, so that it is perhaps not surprising that the photoelectron spectra show only small changes in the $Pd_{3d_{5/2}}$ binding energies. The similarity of the



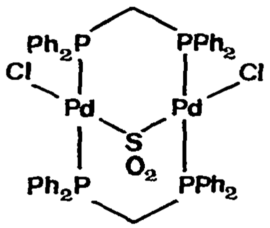
(117)

a 2.623(1) Å

b 2.384(5) Å

c 1.89(3) Å

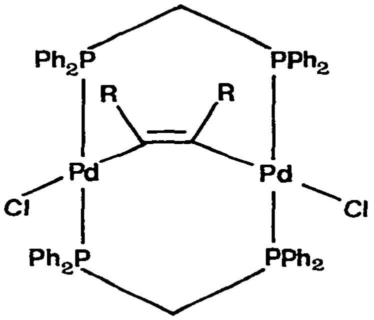
$r(\text{Pt-P}) = 2.291(5)\text{-}2.308(5)$ Å



(118)

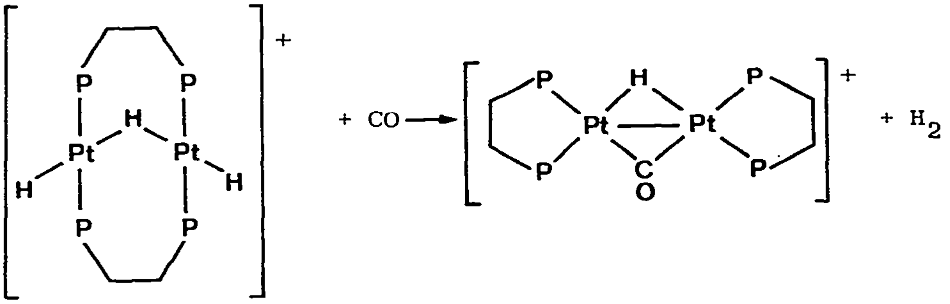
	SO_2 product		
	Molecule A	Molecule B	S product
r(Pd-Pd)	3.383(4) Å	3.220(4) Å	3.258(2) Å
r(Pd-Cl)	2.381(4) Å	2.381(4) Å	2.360(5), 2.383(5) Å
r(Pd-S)	2.234(4) Å	2.241(4) Å	2.298(5) Å
r(Pd-P)	2.344(4) Å 2.343(4) Å	2.372(4) Å 2.345(4) Å	2.327(5) Å 2.300(5) Å
r(S-O)	1.48(1) Å	1.45(1) Å	–
Pd$\hat{S}$Pd	98.4(4)°	91.9(4)°	90.3(2)°

μ-S and μ-SO_2 products accounts for the fact that $[Pd_2Cl_2(\mu\text{-dppm})_2(\mu\text{-S})]$ is oxidised by 3-chloroperbenzoic acid to the μ-SO_2 product, the first report of oxidation of a coordinated sulphide [514]. The alkynes RC≡CR (R = COOMe or CF_3) insert into the Pd-Pd bond of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ to form a *cis*-dimetallated alkene product, (119), with *r*(C=C) = 1.338(16) Å [515]. Although reaction (99),



(119)

with bridging dppe ligands, is not reversible [516], reaction (100) with bridging dppm is [517]. The different structures of the products of reactions (99) and (100) reflect the greater bridging ability of dppm.



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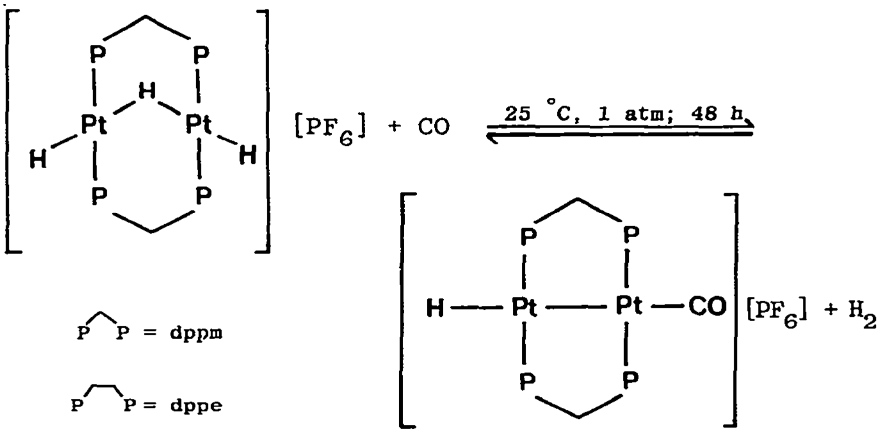
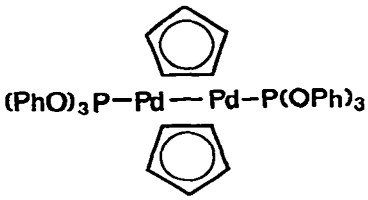


(100)

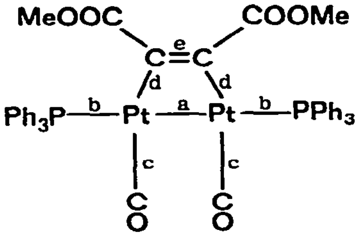
6.6.4 *Complexes with Group IVB Donor Ligands*

The resonance Raman spectra of $[Pd_3(CNMe)_6(PPh_3)_2][PF_6]_2$ and $[Pd_3(CNMe)_8][PF_6]_2$

show that, for the latter, vibrations excited at the wavelength of the lowest allowed transition (411 nm) are those arising from the four a_g-type skeletal stretching modes. Those excited at 473 nm, the lowest allowed transition in $[Pd_3(CNMe)_6(PPh_3)_2][PF_6]_2$, are the four skeletal stretching modes together with two arising from phenyl group modes [518]. Sodium cyclopentadienide reacts with $[\{PdCl_2\{P(OPh)_3\}\}_2]$ in tetrahydrofuran at 0 °C to yield the palladium(I) complex (120) [519]. The platinum(I) *cis*-dimetallated alkene complex, (121),



(120)



a 2.6354(8) Å
b 2.320(3) Å
c 1.85(1) Å
d 2.07(1) Å
e 1.34(2) Å
PtPtP = 169.4(1)°

(121)

is formed when $[Pt(PPh_3)_2(CO)_2]$ is treated with MeOOCC≡CCOOMe, and also when $[Pt(PPh_3)_2(MeOOCC{\equiv}CCOOMe)]$ is treated with carbon monoxide [520].

6.6.5 *Hydride Complexes*

The novel dinuclear platinum(I) hydrides $[Pt_2(dppe)_2LH]X$ (L = CO or RNC; X = $[BF_4]$ or I) are obtained by reaction of $[Pt_2(dppe)_2H_3]X$ with carbon monoxide or isocyanides [521].

6.7 PALLADIUM(0) AND PLATINUM(0)

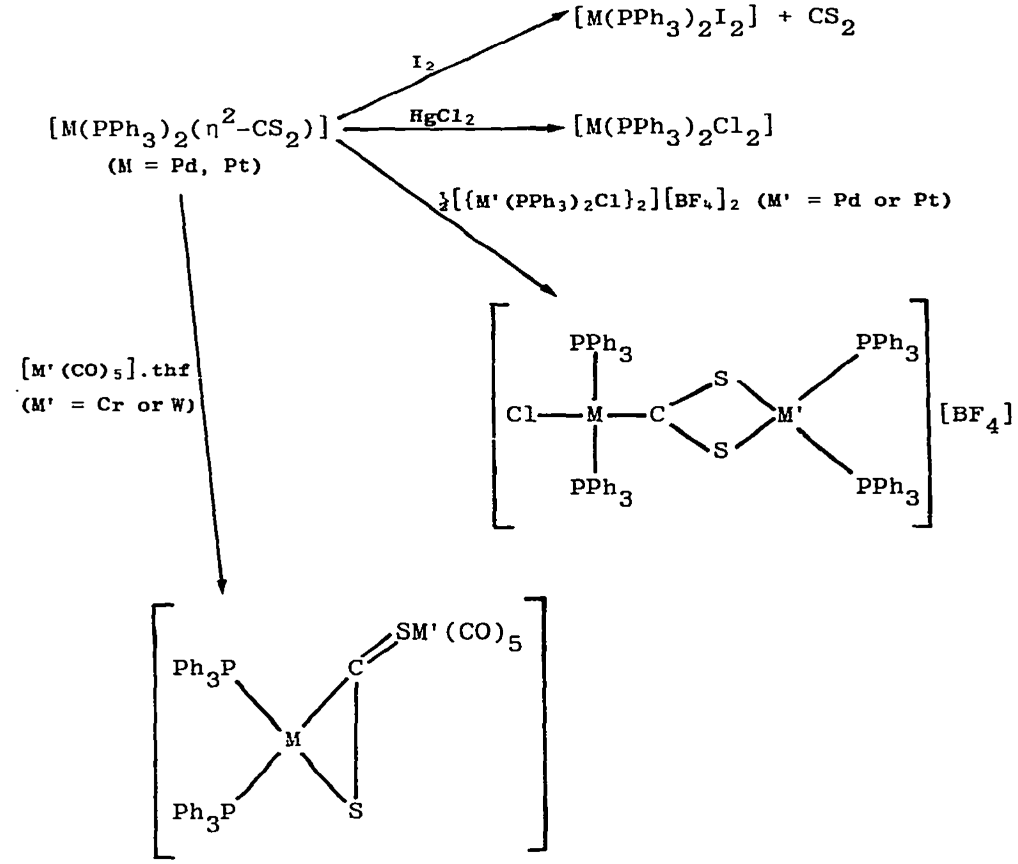
A theoretical model for the electrochemical synthesis of transition metal complexes in low oxidation states has been developed on the basis of the principle of Hard and Soft Acids and Bases [522].

6.7.1 *Complexes with Group VIB Donor Ligands*

The synthesis and catalytic properties of palladium(0) complexes of dialkylsulphides have been reported [523]. The reactions of $[M(PPh_3)_2(\eta^2\text{-}CS_2)]$ (M = Pd or Pt) are shown in Scheme VII [524].

6.7.2 *Complexes with Tertiary Phosphines*

The low temperature chemistry of $[Pt(PPh_3)_3]$ is significantly different to



SCHEME VII

that at room temperature [525]. Thus at −100 °C, equilibrium (101) lies far

$$[Pt(PPh_3)_3] + PPh_3 \overset{K_{101}}{\rightleftharpoons} [Pt(PPh_3)_4] \qquad (101)$$

to the right in contrast to the situation at room temperature; at −80 °C, $K_{101} = 3 \times 10^4\ M^{-1}$. At −80 °C, reaction (102) goes virtually to completion, whereas at 25 °C, equilibrium (103) has $K_{103} = 0.12$; the driving force of the

$$2[Pt(PPh_3)_3] + C_2H_4 \longrightarrow [Pt(PPh_3)_4] + [Pt(PPh_3)_2(C_2H_4)] \qquad (102)$$

$$[Pt(PPh_3)_3] + C_2H_4 \overset{K_{103}}{\rightleftharpoons} [Pt(PPh_3)_2(C_2H_4)] + PPh_3 \qquad (103)$$

−80 °C reaction is at least in part scavenging of PPh_3 by $[Pt(PPh_3)_3]$. Dioxygen does not react with $[Pt(PPh_3)_3]$ in toluene below −70 °C; at −70 °C, it reacts in the same way as ethene {reaction (102)}, and at -45 °C it follows reaction (104). At -80 °C, carbon monoxide reacts with $[Pt(PPh_3)_3]$ to give

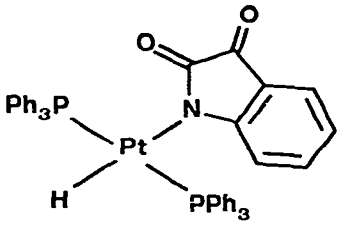
$$[Pt(PPh_3)_4] + O_2 \longrightarrow [Pt(PPh_3)_2O_2] + 2PPh_3 \qquad (104)$$

$[Pt(PPh_3)_3(CO)]$, which on warming to -65 °C reacts with a further molecule of carbon monoxide to give $[Pt(PPh_3)_2(CO)_2]$ [525].

A series of $[Pt(PR_3)_n]$ complexes have been prepared, including $n = 4$; $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PEt_3 or PBu_3: $n = 3$; PEt_3, PBu_3, $P(p\text{-tolyl})_3$, $P(CH_2Ph)_3$, $P(CHMe_2)_3$ or $P(cych)_3$: and $n = 2$; $PR_3 = P(CHMe_2)_3$, $P(cych)_3$ or $P(CMe_3)_2Ph$ [526]. Equilibria between $[Pt(PR_3)_4]$ and $[Pt(PR_3)_3]$ depend strongly on the bulk of the phosphine, and slightly on the solvent. $[Pt(PR_3)_4]$ undergo phosphine exchange by a dissociative route, whereas $[Pt(PR_3)_2]$ exchange phosphines through an associative route; $[Pt(PR_3)_3]$ use both routes. The destabilization of the complexes of bulky phosphines by steric interaction is a purely entropy effect, with no enthalpy contribution [526]. $[Pd_2(PPh_3)_2]$ reacts with palladium(II) ethanoate in dimethylformamide under dihydrogen to give $[Pd_5(PPh)_2]$, which catalyses the oxidative dehydrogenation of cyclohexane, and the hydrogenation of aldehydes in alcohols, and of dienes, monoenes, alkynes, nitro-compounds, nitroso-compounds, azo-compounds, Schiff bases, organic peroxides and quinones in dimethylformamide solution [527].

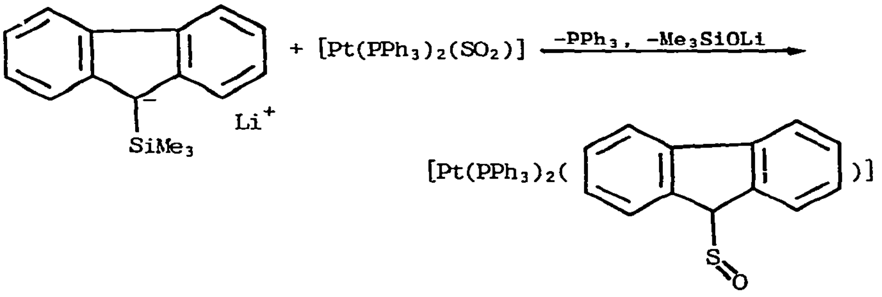
An improvement on earlier routes to $[M(PPh_3)_3]$ (M = Pd or Pt) involves the 1:3 reaction of MCl_2 with PPh_3 and zinc dust, to form $ZnCl_2$ and 65-80% $[M(PPh_3)_3]$; $[Pt(CO)_2(PPh_3)_2]$ is formed when two equivalents of triphenylphosphine in the presence of carbon monoxide are used [528]. The signs and magnitudes of coupling constants in $[M\{P(OMe)_3\}_4]$ are $^3J(^{31}P-^1H) = +11.4(Pd)$, $+12.1$ Hz(Pt) and $^2J(^{31}P-^{31}P) = +22(Pd)$, $+81$ Hz(Pt) [529].

The crystal and molecular structures of the dioxygen-reversible $[Pd\{P(CMe_3)_2Ph\}_2O_2]$ and the dioxygen-irreversible $[Pt\{P(CMe_3)_2Ph\}_2O_2]$ showed mean M-O distances of 2.05(1) Å (M = Pd) and 2.02(1) Å (M = Pt); the dihedral angles between the MP_2 and MO_2 planes are 6.8° (M = Pd) and 2.7° (M = Pt), and the O-O bond lengths differ significantly at 1.37(2) (M = Pd) and 1.43(2) Å (M = Pt), as do the $P\hat{M}P$ angles at 115.4(2)° (M = Pd) and 113.1(2)° (M = Pt). This geometrical difference appears to be an important factor in governing the $M-O_2$ bond strength [530]. Side-bonded ketone complexes $[Pt(PPh_3)_2(\eta^2\text{-ketone})]$ have been prepared by displacing *trans*-stilbene or diphenylacetylene from platinum(0) with alloxan or diethyloxomalonate; isatin reacts with $[Pt(PPh_3)_4]$ to give the *N*-bonded platinum(II) complex, (122) [531]. Sulphines XYC=S=O (X,Y = aryl, *S*-alkyl, *S*-aryl or Cl) react with $[M(PPh_3)_4]$ (M = Pd or Pt) to yield $[M(PPh_3)_2(\eta^2\text{-XYCSO})]$, in which the sulphine retains its configuration and is coordinated side-on through the C=S π-bond [532,533]. $[Pt(PPh_3)_2(\eta^2\text{-XYCSO})]$



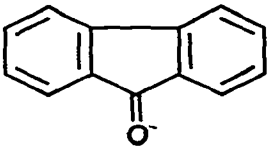
(122)

complexes that contain reactive C-X and/or C-Y bonds rearrange in solution to [$Pt(PPh_3)_2X(YCSO)$]. Sulphine complexes can also be prepared by reaction (105)

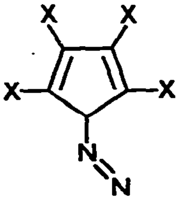


(105)

[533]. Oxidation of the product of reaction (105) with 3-chloroperbenzoic acid or [$Pt(PPh_3)_2O_2$] yields [$Pt(PPh_3)_2(SO_4)$] and (123). Ethene is displaced from



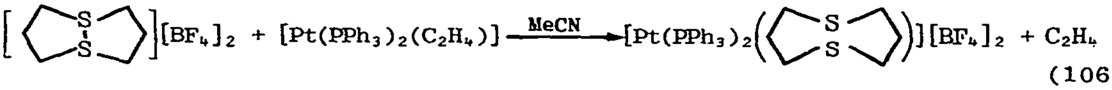
(123)



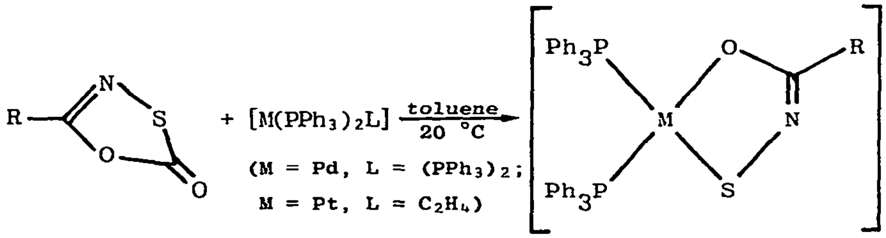
(124; X = Cl or Br)

[$Pt(PPh_3)_2(C_2H_4)$] by $Me_3Si(CMe_3)NP(S){=}NCMe_3$ or (124), L, to form [$Pt(PPh_3)_2L$] in which the former is η^2-bonded to platinum through the P=S double-bond [534] and the latter is η^2-bonded through the N=N bond [535].

The dithioether (124) and oxathiazoles both add oxidatively to platinum(0) by reactions (106) and (107) [536,537].



(106)



(107)

6.7.3 *Carbonyl Complexes*

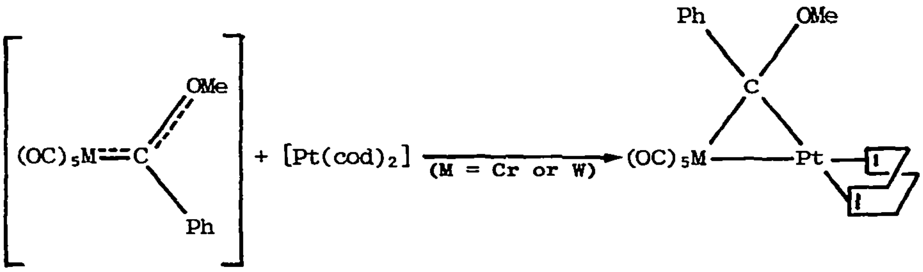
When $[Pt_9(CO)_{18}]^{2-}$ is heated under reflux in ethanenitrile, a lot of the carbonyl groups are driven off and $[Pt_{19}(CO)_{22}]^{4-}$ can be isolated in about 50% yield as its $[Bu_4N]$ salt [538]. This complex is of particular catalytic interest because it is much closer in stoicheiometry (CO:Pt ratio = 1.16:1) to a carbonylated metal surface (CO:Pt ratio ~ 0.75:1) than any previously reported carbonyl (previously CO:M > 1.7:1), although its catalytic properties have not been reported to date. Its structure is based on a *pseudo*-fivefold principal axis. The cylindrically-shaped Pt_{19} core, surrounded by 12 terminal and 10 bridging carbonyl ligands, may be envisioned as arising from head-to-tail fusion of three eclipsed pentagonal bipyramidal platinum units at two common axial platinum atoms. These axial platinum atoms are completely encapsulated within the Pt_{17} frame. The electronic structures of $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 1 or 2) have been calculated; the main electronic interactions involve platinum *s*- and *d*-orbitals and the lone pair 5σ MO's of the carbonyl ligands [539]. It is noteworthy that the Pt-Pt bonds in the $[\{Pt_3(CO)_6\}_n]^{2-}$ cluster anions (2.66 Å) are shorter than in platinum metal itself (2.774 Å). This is achieved by some of the platinum *sp* electron density, which is repulsive in character, being removed from the plane of the Pt_3 triangle into the inter-triangular region [540]. ^{195}Pt NMR data in deuteriochloroform solution for $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 1-5) suggest that in solution the two outer Pt_3 triangles rotate with respect to the central one about the vertical three-fold axis [541].

6.7.4 *Isocyanide Complexes*

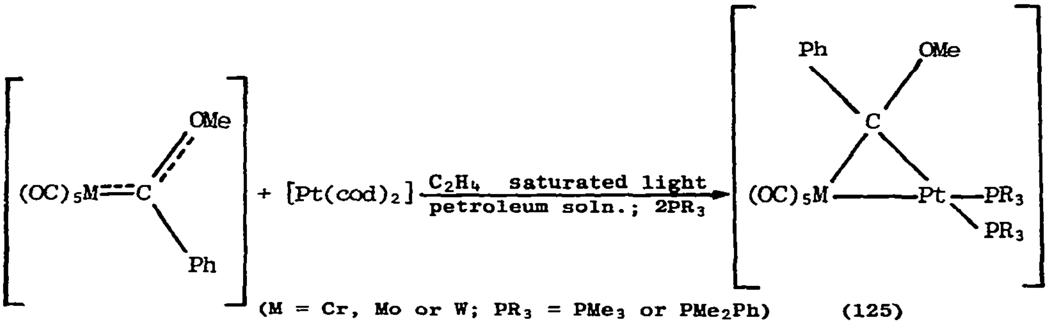
Zerovalent metal isocyanide complexes have been reviewed [542]. R_3SiH and Me_3GeH react with $[Pt_3(CNCMe_3)_6]$ to form $[\{Pt(CH{=}NCMe_3)(ER_3)(CNCMe_3)\}_2]$ (E = Si or Ge) by insertion of Me_3CNC into a Pt-H bond formed in the initial oxidative-addition step [543].

6.7.5 Complexes with Other Transition Metals

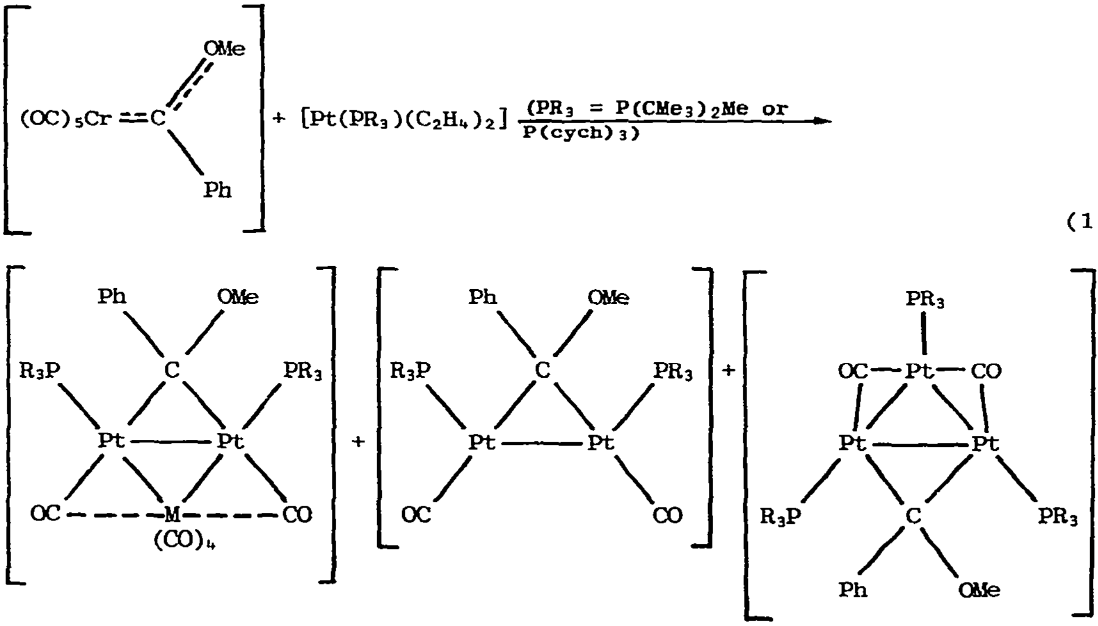
Platinum(0) complexes of chromium, molybdenum or tungsten with bridging carbene or carbyne ligands have been prepared by reactions (108)-(112) [544-546].



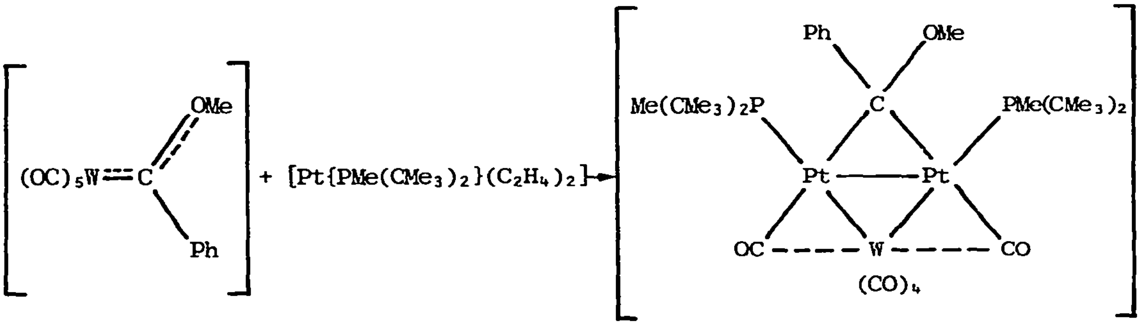
(108)



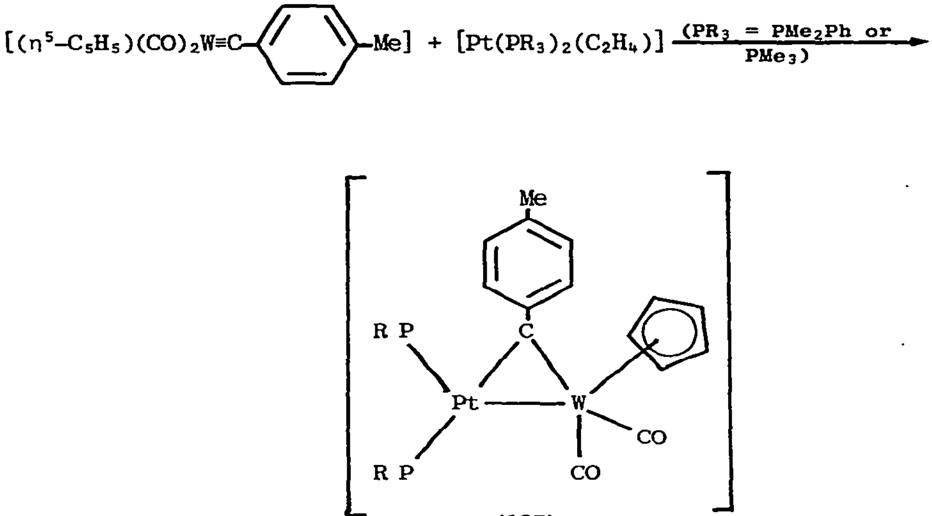
(109)



(110)



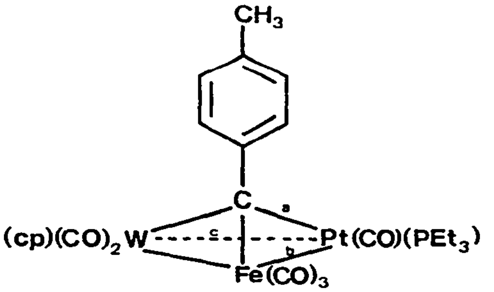
(126) (111)



(127)

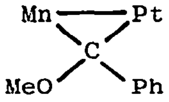
(112)

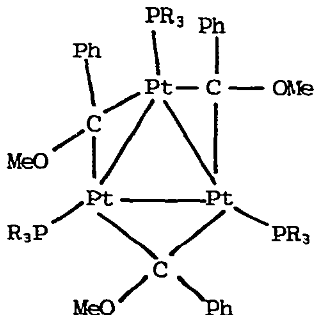
X-ray diffraction of (125; M = W, R = Me) showed the carbene bridge to be very asymmetric {r(W–C) = 2.48(1) Å, r(Pt–C) = 2.04(1) Å}, with the Pt–P bond *trans* to carbene = 2.335(3) Å significantly longer than the Pt–P bond *trans* to tungsten (2.253(3) Å), and r(Pt–W) = 2.861(1) Å [544]. (126) has a Pt–Pt bond of 2.627(1) Å, a symmetric carbene bridge {r(Pt–C) = 2.05(2) Å} with the plane of the carbene at 90° to the Pt_2W plane, Pt–W bonds of 2.830(2) Å (mean) (close to the sum of their covalent radii) and Pt–P bonds of 2.350(7) Å which is at the upper end of the Pt–P range of bond lengths [545]. (127) has Pt–W bonds of 2.751(1) Å, only slight asymmetry in the carbyne bridge {r(Pt–C) = 1.997(9) Å, r(W–C) = 1.967(6) Å} with the phenyl plane virtually perpendicular to the PtWC plane, and a Pt–P bond *trans* to carbyne of 2.325(2) Å, which is significantly longer than that *trans* to tungsten (2.258(2) Å) [546]. The inherent "unsaturation" of the novel dimetallocycopropene ring in (127) should lead to an extensive chemistry, and in support of this (127) reacts with $[Fe_2(CO)_9]$ to give the trimetallic cluster (128) together with $[Fe(CO)_4(PEt_3)]$ (formed because the platinum has lost a triethylphosphine ligand and gained a carbonyl ligand) [547]. Thus a rational synthesis of complexes in which an alkylidene group caps a metal triangle involves reaction of a mononuclear metal-alkylidyne complex with either two different low-valent metal compounds in sequence, or with a reactive dimetal species.



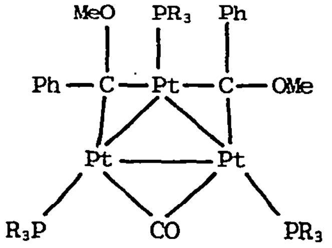
a	2.23(2) Å
b	2.542(3) Å
c	2.775(1) Å

(128)

The ease of transfer of a carbene group from a mononuclear metal carbene to platinum is reflected in the reaction of $[Mn(\{C(OMe)Ph\}(CO)_2(\eta^5\text{-}C_5H_5)]$ with $[Pt(PR_3)(C_2H_4)]$, from which no manganese-platinum compounds were obtained. Instead (129) and (130) were formed, probably through an initial  system, since (125; M = Cr; PR_3 = PMe_3) decomposes at 80 °C in toluene to give (129) and (130) [545]. Platinum-manganese carbene bridged complexes can be prepared by reactions (113)-(118) [548,549]. The two forms of (131) differ mainly in the relative orientations of some least-squares planes, as well as in the Mn-Pt distance [548].



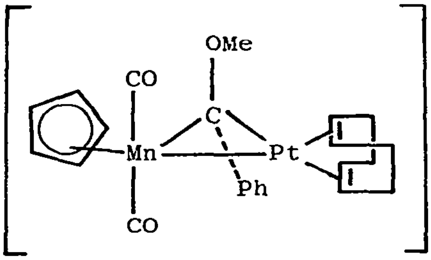
(129)



(130)

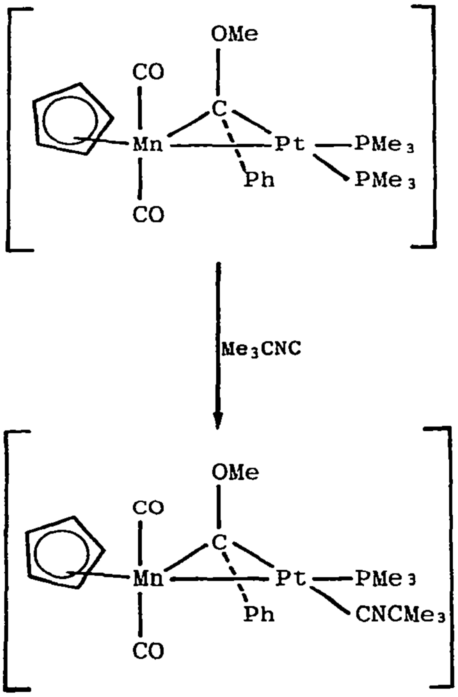
(134), which has a Rh=Rh double-bond, reacts with a variety of metal fragments

$$[Pt(cod)_2] + [Mn\{C(OMe)Ph\}(CO)_2(\eta^5\text{-}C_5H_5)] \xrightarrow[\text{petroleum; 0 °C}]{\text{light}}$$

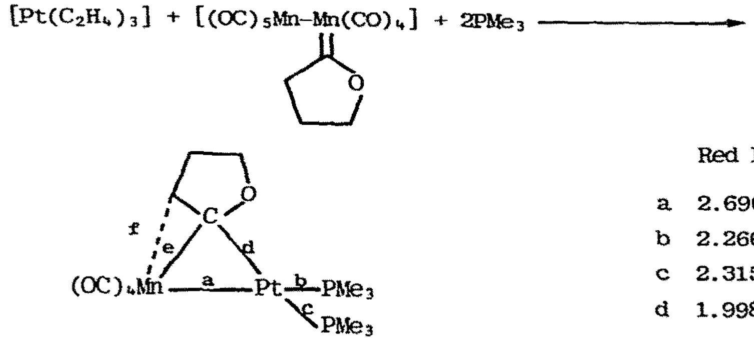


(113)

$$[Pt(C_2H_4)_3] \text{ or } [Pt(dba)_2] + [Mn\{C(OMe)Ph\}(CO)_2(\eta^5\text{-}C_5H_5)] \xrightarrow{2PMe_3}$$



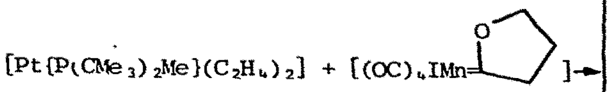
(114)

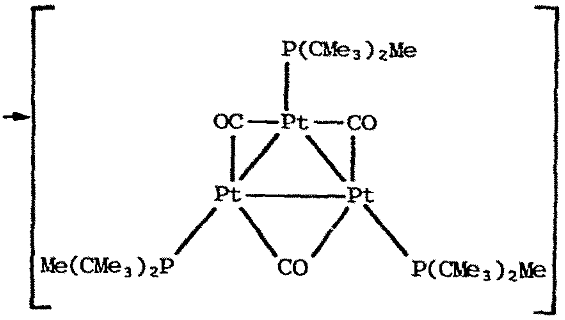


(131)

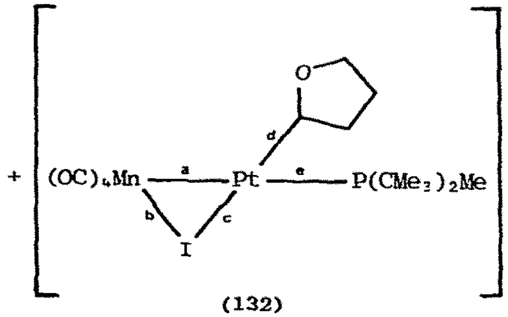
	Red Form	Yellow Form
a	2.6909(7) Å	2.659(2) Å
b	2.266(1) Å	2.265(4) Å
c	2.315(1) Å	2.301(4) Å
d	1.998(5) Å	1.996(12) Å
e	2.197(5) Å	2.275(15) Å
f	2.251(5) Å	2.292(17) Å

(115)



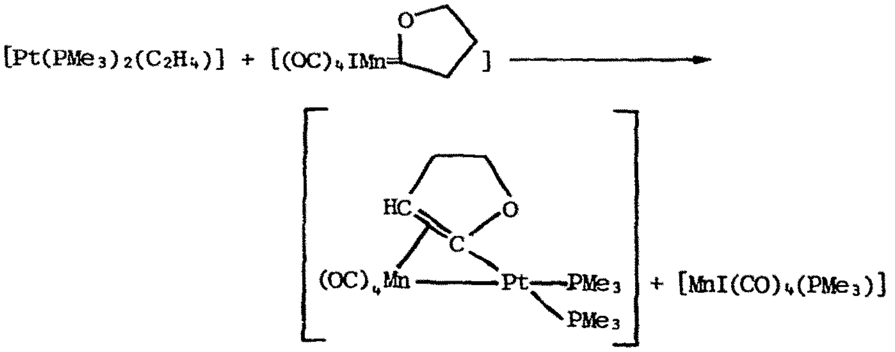


(116)



(132)

a 2.603(1) Å
b 2.689(2) Å
c 2.662(1) Å
d 1.889(8) Å
e 2.310(2) Å

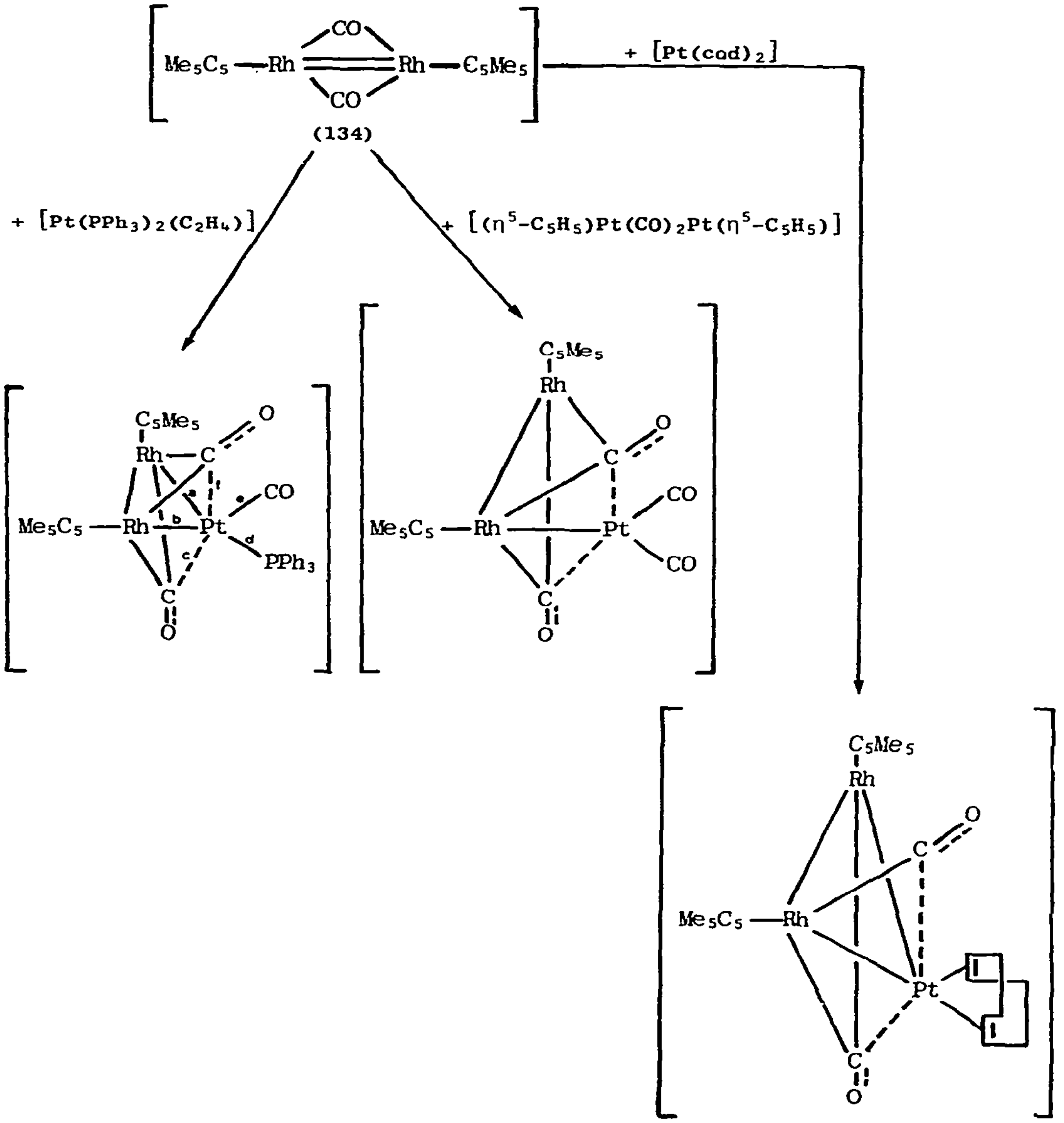


(117)

(133)

$$(132) + PMe_3(excess) \longrightarrow (133) + [MnI(CO)_3(PMe_3)_2] \qquad (118)$$

in the same way as other M=M and C=M species (Scheme VIII) [550].



a	2.617(1) Å	d	2.284(4) Å
b	2.683(1) Å	e	1.830(18) Å
c	1.998(14) Å	f	2.001(18) Å

SCHEME VIII

6.8 PALLADIUM AND PLATINUM METAL

Two reviews have been concerned with firstly the history, properties, origins and methods for producing ore concentrates [551], and secondly the refining and uses [552] of the platinum group metals. The corrosion of platinum black in 1 *M* KOH solution occurs through the intermediate formation of surface oxides, both through discharge of water molecules and through reaction with molecular oxygen. It is not clear, however, whether it is the formation of surface oxides or their subsequent dissolution that is the slow step [553].

There has been great interest for some years on the photocatalytic production of hydrogen from water or methanol at TiO_2 surfaces. Mixing TiO_2 powder with platinum metal, palladium metal or a mixture of platinum metal and RuO_2 gave efficient production of dihydrogen from 1:1 aqueous methanol on irradiation at 380 nm with quantum yields of 40, 19 or 44%, respectively [554].

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