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5. PALLADIUM AND PLATINUM

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CONTENTS

INTRODUCTION

This review covers the papers recorded in Chemical Abstracts during 1979 as well as those in the major journals during that period. It thus effectively covers the period mid-1978 to mid-1979 with some later references.

Undoubtedly the highlight of the year is the approval of *cis*-[Pt$(NH_3)_2Cl_2$] by the U.S. Food and Drug Association and the U.K. Department of Health and Social Security for use against tumours. In the U.S., the drug is marketed as Platinol and in the U.K. as Neoplatin (see Section 5.5.3.4). The discovery of the anti-cancer powers of this and other platinum compounds has led to a great deal of research into the biochemical activity of platinum and its neighbours in the Periodic Table, with particular emphasis on the interaction of platinum compounds with DNA (Section 5.5.3, especially 5.5.3.3). This work is now bearing fruit. Another active and fruitful area has been the synthesis and study of *quasi*-one-dimensional mixed oxidation state compounds (Section 5.3) which may be of use in solid state devices. A goal that is still some way off is the catalytic activation of hydrocarbons; however, the description of the ^1H and ^{13}C NMR spectra of the phenyl(hydrido)platinum(IV) species formed by oxidative-addition of benzene to $Na_2[PtCl_4]$ has greatly added to knowledge, as opposed to speculation, in this area (Section 5.5.5.4). Worthy of mention also are the novel hydrido-platinum(II) complexes being reported by several groups; these may well provide a rich source of new catalysts (Section 5.5.7).

On the debit side, although it was well established by the turn of the century that platinum bonds to most nitrogen and sulphur donors, there are still a very large number of papers being published that do nothing more than confirm the truth of this observation.

5.1 PALLADIUM(VI) AND (V), AND PLATINUM(VI) AND (V)

No papers describing either palladium(VI) or platinum(VI) chemistry have been published during this year.

The previously known compounds $[Xe_2F_3][PtF_6]$ and $[XeF][PtF_6]$ have been prepared by the interaction of XeF_2 with PtF_4. Thermal decomposition of $[XeF][PtF_6]$ yields highly pure XeF_4 which, together with routes involving platinum(IV) and palladium(IV) fluorides mentioned below, provides a good route for the conversion of XeF_2 to XeF_4 [1].

5.2 PALLADIUM(IV) AND PLATINUM(IV)

5.2.1 Complexes with Group (VII) donor ligands

In addition to the platinum(V) compounds mentioned above, $XePt_2F_{10}$ is formed by the reaction of XeF_2 with PtF_4. XeF_2 reacts with either PdF_4 or Pd_2F_6 to yield $XeF_2 \cdot PdF_4$ or $XePd_2F_{10}$, respectively [1]. Thermal decomposition of $XePd_2F_{10}$ yields pure XeF_4, providing an alternative route to that mentioned in Section 5.1 for the conversion of XeF_2 to XeF_4. $XePd_2F_{10}$ is structurally similar to $XePt_2F_{10}$; spectroscopic evidence suggests that both are salts of XeF^+ and a polymeric anion $[M_2F_9]_n^{n-}$. The syntheses of

$Y_2[PtCl_6]_3 \cdot 25\ H_2O$ and $Sm_2[PtCl_6] \cdot 12\ H_2O$ have been reported; on heating they decompose to yield successively H_2O, HCl, Cl_2, metallic platinum and either Y_2O_3 or SmOCl [2].

A solution of $Na_2[PtCl_6]$ in D_2O is stable for over a year. Since it gives a sharp band in its ^{195}Pt NMR spectrum, it has been put forward as a suitable reference for ^{195}Pt NMR spectra. It is recommended, in line with IUPAC conventions, that ^{195}Pt chemical shifts to higher frequency than $Na_2[PtCl_6]$ be recorded as positive [3]. On stepwise substitution of Cl^- in $[PtCl_6]^{2-}$ by Br^-, there is a low frequency shift of —287 p.p.m for each Cl^- substitution; each Br^- provides a further —12 p.p.m. Thus ^{195}Pt NMR chemical shift data can be used to determine the coordination sphere of the metal [3]. The oxidative-addition of chlorine to chloropalladium(II) species in dilute aqueous solution to yield $[PdCl_6]^{2-}$ occurs in two stages: firstly, oxidation of palladium(II) to palladium(IV), and secondly a slow substitution of any aqua ligands present by chloride ions [4]. $[pyH]_2[PtI_6]$ can be prepared by the reaction of platinum, iodine and pyridine in the presence of a small amount of hydriodic acid in dichloromethane. The product is copper-coloured due to I—I interactions between adjacent $[PtI_6]^{2-}$ octahedra. Within the $[PtI_6]^{2-}$ unit, the mean Pt—I bond length is 2.67 Å [5]. A study of the Raman spectrum of $Rb_2[PtI_6]$ has shown that the anharmonic Raman process is dominant but not to the total exclusion of the ordinary Raman process [6]. The dibenzotetrathiafulvalene (dttf) complexes $[dttf]_8[PtCl_6]_3$ and $[dttf]_3[PtBr_6]$ show high metallic conductivity in restricted temperature intervals [7].

Three papers have been concerned with platinum(IV) haloammine complexes. In the first, the structure of $[Pt(en)_2Br_2][C_4O_4] \cdot 2\ H_2O$ has shown Pt—N and Pt—Br distances of 2.05(3) and 2.459(2) Å, respectively [8]. The absorption spectra of a number of platinum(IV) chloroammine complexes have been recorded. All have three maxima: one at 380—415 nm (ϵ = 15—50 l mol^{-1} cm^{-1}) due to a singlet—triplet ligand field transition, the second at 305—350 nm (ϵ = 150—310 l mol^{-1} cm^{-1}) due to a singlet—singlet ligand field transition and the third between 245 and 277 nm (ϵ = 850—4500 l mol^{-1} cm^{-1}) due to a chlorine to platinum charge-transfer transition. The photochemical effects of irradiating such complexes have been investigated; absorption in the charge transfer region is relatively efficient and square—pyramidal platinum(III) intermediates are thought to be formed [9]. Unlike chlorination, fluorination of platinum(IV) chloroammine complexes does not yield chloro-amido-complexes, but rather complexes such as *trans*-$[Pt(NH_3)_4Cl_2][H_2F_3]_2$ in which the fluorine is present in the anion rather than the cation [10].

The kinetics of bromide anation of $[Pt(CN)_4Br(H_2O)]^-$ have been studied at higher bromide concentrations than previously. A two-term rate law is found, in which the first term involves a reversible first-order reduction of the ion-pair $[Br...BrPt(CN)_4H_2O]^{2-}$ and the second term involves a bromide-assisted reduction of the same ion-pair, suggesting an overall reductive-elimination/oxidative-addition mechanism [11].

An investigation of the uptake of platinum as $[NH_4]_2[PtCl_6]$ by tomato, corn and bean plants grown hydroponically showed that platinum is extensively taken up by the roots and transported to the tops of the plants. This latter is less true of palladium which was studied in the form of $Na_2[PdCl_4]$ [12].

5.2.2 Complexes with Group (VI) donor ligands

A series of mixtures of composition $M_{1-x}Rh_xSe_2$ (where M = Pt or Pd, and $x \geqslant 0.3$) have been prepared. At ambient pressure the palladium compound is a mixture of $PdSe_2$ and $RhSe_2$. On increasing the pressure to 50 kbar at 1000°C a single-phase, crystallising with the pyrites structure, is formed. When $0.3 \leqslant x \leqslant 0.4$, the platinum compound, at atmospheric pressure and 1000°C, yields a solid solution that crystallises with a CdI_2 structure; there is no high pressure phase transformation up to 50 kbar [13]. PtS_2 and $PtTe_2$ have been prepared in sealed tubes by reactions (1) and (2). The phosphorus and sulphur are essential in order to achieve platinum transport; chlorine helps but is not essential [14].

$$\mathrm{Pt} + 2\,\mathrm{S} \xrightarrow[\mathrm{Cl_2}\ (75\ \mathrm{torr})]{800^\circ\mathrm{C};\ \mathrm{P}} \mathrm{PtS_2} \tag{1}$$

$$\mathrm{Pt} + 2\,\mathrm{Te} \xrightarrow[\mathrm{Cl_2}\ (75\ \mathrm{torr})]{875^\circ\mathrm{C};\ \mathrm{P,\ S}} \mathrm{PtTe_2} \tag{2}$$

X-ray and neutron powder diffraction studies of $Na_2[Pt(OD)_6]$ have yielded bond lengths of 2.06(2) and 0.95(2) Å for Pt—O and O—D, respectively [15]. The electronic spectrum of $[Pt(OH)_6]^{2-}$ has been assigned with the aid of an extended Hückel calculation [16].

Sulphato-complexes of platinum(IV) are rare and their hydrolysis has not previously been studied. It has now been shown that alkaline hydrolysis of *trans*-$[Pt(NH_3)_4(OH)(SO_4)]^+$ is accompanied by isomerisation to yield a mixture of *cis*- and *trans*-$[Pt(NH_3)_4(OH)_2][SO_4]$, a type of behaviour not previously reported for platinum(IV) ammine complexes. The *cis*-isomer is only formed under very alkaline conditions, and is formed by hydrolysis of the conjugate base complex $[Pt(NH_3)_3(NH_2)(OH)(SO_4)]^{2-}$ probably by dissociative hydrolysis. No platinum(II) catalysis is involved [17].

A number of fluorosulphate complexes of palladium and platinum have been described {reactions (3)—(6)}. The fluorosulphate anion acts as a unidentate oxygen-donor ligand [18].

$$2\,\mathrm{CsCl} + \mathrm{Pd} + 2\,\mathrm{HSO_3F} \xrightarrow[\text{2. Addition of } \mathrm{S_2O_6F_2}]{\text{1. Removal of HCl on vacuum line}} \mathrm{Cs_2[Pd(SO_3F)_6]} + 2\,\mathrm{HCl} \tag{3}$$

$$\mathrm{Pt} + 2\,\mathrm{S_2O_6F_2} \xrightarrow[\mathrm{HSO_3F}]{100^\circ\mathrm{C}} [\mathrm{Pt(SO_3F)_4}] \tag{4}$$

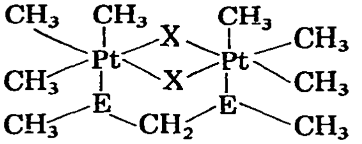
$$2\,\mathrm{Pd} + 3\,\mathrm{S_2O_6F_2} \xrightarrow[\mathrm{HSO_3F}]{100^\circ\mathrm{C}} \mathrm{Pd[Pd(SO_3F)_6]} \xrightarrow[130^\circ\mathrm{C}]{\text{heat}} [\mathrm{Pd(SO_3F)_2}] + 2\,\mathrm{S_2O_6F_2} \tag{5}$$

$$[Pd(SO_3F)_2] + [Pt(SO_3F)_4] \xrightarrow[HSO_3F,\ 3\ days]{80°C} Pd[Pt(SO_3F)_6] \qquad (6)$$

Heating *cis*-$[PtL_2Cl_4]$ (where L = Me_2S, Et_2S, thiophane or Me_2SO) in the solid state converts them to the thermodynamically more stable *trans*-isomers [19]. The difference in the total energy of *cis*- and *trans*-$[Pt(Me_2SO)_2Cl_4]$ is 8.4 kJ mol^{-1}.

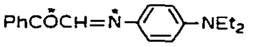
Tetrameric $[Pt(CH_3)_3(SMe)]_4$ has been prepared by reaction (7) [20]. An NMR study of $[Pt(CH_3)_3X_2(CH_3ECH_2ECH_3)]$, (1), has shown that the Group VI donors exchange platinum atoms. In addition, at higher temperatures, an intramolecular random cleavage of the halide bridges occurs giving short-lived five-coordinate species, so allowing all three platinum methyl environments to become completely averaged [21].

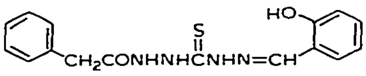
$$2[Pt(CH_3)_3]_2[SO_4] + 4\ Na[SMe] \xrightarrow{H_2O} [Pt(CH_3)_3(SMe)]_4 + 2\ Na_2[SO_4] \qquad (7)$$



(1) X = Cl or Br; E = S or Se

5.2.3 *Complexes with mixed Group (VI)/Group (V) donor ligands*

Platinum(IV) complexes $[Pt(sbts)_2Cl_2]Cl_2$ (sbts = 1-salicyl-4-benzylamidothiosemicarbazone (2)) and $[Pt(fbts)_2]Cl_2$ (fbts = 1-(α-)-furyl-4-benzylamidothiosemicarbazone (3)) have been prepared by reaction of the appropriate ligand with chloroplatinic acid in ethanol; fbts behaves as a tridentate *SNO* ligand whereas sbts bonds as a bidentate *SN* donor [22]. The Schiff base  forms $[PtL_2Cl_2]Cl_2$, in which it acts as a chelate ligand through the starred donor atoms [23]. A study of glycine ring formation in *trans*-$[Pt(en)NH_3(glyH)X_2]X_2$ (X = Cl or Br) showed that it was catalysed by the platinum(II) complex *cis*-$[Pt(en)NH_3(glyH)]^{2+}$ and increased in rate with increasing pH over the pH range 2—4 [24—26].



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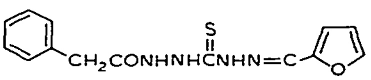
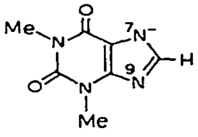


(3)

5.2.4 *Complexes with Group (V) donor ligands*

A study of the reaction of the theophillinate anion (4) with *fac*-$[PtMe_3(H_2O)_3]_2[SO_4]$ has been undertaken because this anion provides a useful

6-oxopurine model to mimic guanosine. The product is trimeric $[PtMe_3L]_3$, in which the theophillinate anion bridges two platinum atoms through N^7 and N^9. The N^7—Pt bond is the stronger since reaction of the trimer with



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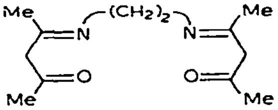
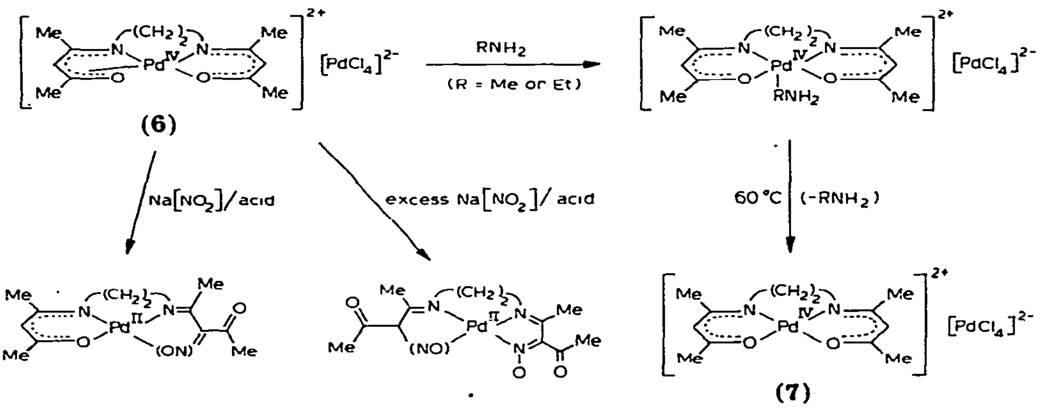


(5)

excess methylamine yields $[PtMe_3(MeNH_2)_2L]$ in which the ligand is bound only through N^7 [27]. A palladium(IV) complex, of the tetradentate Schiff base (5), which has oxo-π-allylic bonding on one side (6) has been prepared. It undergoes a number of interesting reactions, including the formation of the bond isomer (7), and nitrosation with concomitant reduction to palladium(II) (Scheme I) [28].



Scheme I

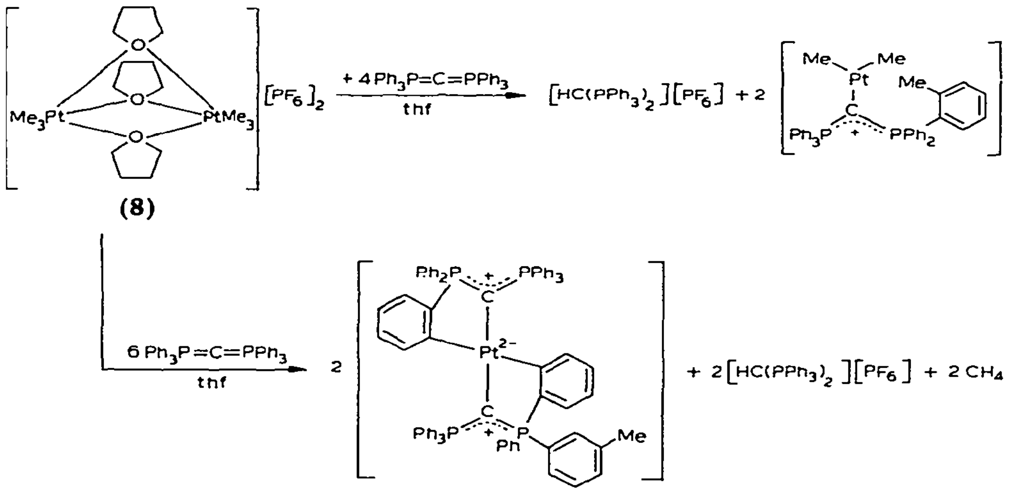
The synthesis of *trans*-$[Pt(dien)Cl(NO)_2NH_3]Cl_2$ has been reported [29]. An investigation of the acidic properties of a number of dinitro-platinum(IV) complexes showed that the *cis*- and *trans*-effects of the nitro-groups were less than those of Cl^-, in agreement with earlier work. It appeared that nitro-groups had a π-acceptor ability unless two nitro-groups were mutually *cis* [30]. The *N*,*N'*-dimethyl-1,2-diaminoethane complexes $[Pt(MeNHCH_2CH_2NHMe)Cl_2(py)NO_2]Cl$ and $[Pt(MeNHCH_2CH_2NHMe)Cl(py)(NO_2)_2]Cl$ do not react with chlorine or nitrosylation reagents, in contrast to the corresponding 1,2-diaminoethane complexes which form *N*-chlorinated or *N*-nitrosylated 1,2-diaminoethane, respectively [31]. The *N*-nitrosylated 1,2-diaminoethane complex $[Pt(ONNHCH_2CH_2NH_2)(py)(NO_2)_2Cl]$ can be denitrosylated by heating with hydrochloric acid {reaction (8)}. Both denitrosylation and nitrosylation of 1,2-diaminoethane occur without cleavage of

$$[Pt(ONNHCH_2CH_2NH_2)(py)(NO_2)_2Cl] \xrightarrow[HCl]{heat} [Pt(NHCH_2CH_2NH_2)(py)Cl_2(NO_2)] + [Pt(en)(py)Cl_2(NO_2)]Cl \qquad (8)$$

the Pt—N bond [32]. The circular dichroism and absolute configuration of $[Pt\{NH_2CH_2CH(Me)NHCH_2)_2\}Cl_2]$ have been determined [33].

5.2.5 Complexes with Group (IV) donor ligands

NMR studies suggest that trimethylplatinum hexafluorophosphate in tetrahydrofuran exists as (8). This solution reacts with hexaphenylcarbodiphosphorane to give novel products when both one and two equivalents of the bis(ylide) per platinum atom are used {reaction (9)} [34].



(9)

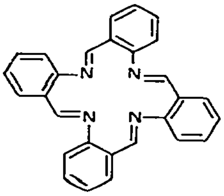
The compound $Cd[Pt(CN)_6]$ is remarkable in that it crystallises from water with a cage structure big enough to pick up water, but it is anhydrous. Thus the water molecules obviously prefer the hydrogen-bonded clusters of the solvent to the cavities of the lattice, which must therefore be regarded as hydrophobic. In agreement with this, the inclusion compounds $Cd[Pt(CN)_6] \cdot 1.046\ Kr$ and $Cd[Pt(CN)_6] \cdot 1.128\ Xe$ were grown in an autoclave at 64 bar. The former compound has a krypton density equivalent to gaseous krypton at 118 bar; if all the lattice cavities had been occupied, the density would have been equivalent to the gas at 216 bar. As a result, this type of compound, with a metal cheaper than platinum, could provide a technically interesting alternative to steel cylinders for the transfer of krypton and xenon [35].

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

A great deal of research has been conducted into mixed-valence compounds of platinum. The overall aim of the work is to understand and develop new superconductors, particularly one-dimensional conductors, that would be of value in the construction of solid state devices [36]. Particular emphasis has been given to compounds involving partially oxidised $Pt(CN)_4$ units, with the synthetic emphasis being directed to understanding how to make a controlled and pre-determined change to the lattice [37—48]. Besides the use of X-ray diffraction as a structural tool, IR and Raman spectroscopy have been studied extensively [49—52]. One paper has shown that an observation of the luminescence spectrum permits direct detection of the Peierls gap [52]. Mean field theory with arbitrary band filling has been used to calculate the Peierls transition temperature in $K_2Pt(CN)_4Br_{0.3} \cdot 3\ H_2O$ [53]. Reaction of one equivalent of $K_2[Pt(CN)_6]$ with two equivalents of $K_2[PtCl_4]$ in aqueous solution is reported to yield a mixture of $\{NC—Pt(CN)_4—CN—Pt(H_2O)_2\}_n$ and $[Cl(H_2O)_2Pt—NCPt(CN)_4—CN—Pt(H_2O)_2Cl]$ [54].

Further structural and spectroscopic studies on mixed valence diamine complexes, such as $[Pt(diamine)_2][Pt(diamine)_2X_2][ClO_4]_4$ have been reported [55—59]. The iodination of $[Pt(RNHCH_2CH_2NHR)(SCN)_2]$ in ethanol gives the complexes $[Pt(RNHCH_2CH_2NHR)(SCN)_2I]$, and provides a very simple route to a series of *quasi*-one-dimensional complexes which show extended *z*-axis interaction even with iso-propyl R groups present [60]. A detailed study of the products formed upon oxidation of *cis*-$[Pt(NH_3)_2X_2]$, *cis*-$[Pt(diamine)X_2]$ and $[Pt(diamine)_2]X_2$ (where X = halide) has shown: (i) the structure of the product obtained from *cis*-$[Pt(NH_3)_2X_2]$ depends very much on the reaction conditions and the other ions present; (ii) with diamines, the chance of isolating a characterisable mixed-valence system increases as the atomic weight of X increases, and that (iii) the Pt—Pt separation increases as X gets bigger due to the Pt^{IV}—X bond length increase (the Pt^{II}...X distances are nearly independent of X) [61]. Passing air through a suspension of Magnus' Green salt in dilute sulphuric acid results in its oxidation to a brown chloride-bridged chain polymer [62].

A number of *quasi*-one-dimensional palladium complexes have been described [63—65]. $[Pd(dpg)_2I]$ (dpg = diphenylglyoximate), prepared by treating $[Pd(dpg)_2]$ with iodine in 1,2-dichlorobenzene at 110°C, involves $Pd(dpg)_2$ units carrying a fractional +0.20 charge in vertical stacks with $[I_5]^-$. The $Pd(dpg)_2$ stacking interactions give rise to a band at 505 nm whilst a broad band at 675 nm is associated with the polyiodide chains [64]. Self-condensation of 2-aminobenzaldehyde yields a tetrazomacrocyclic ligand (**9**) which has been used to prepare $[PdL][I_3]_{2.7}$. This shows an unusually large pressure dependence in its conductivity, but the origin of this is not clear since its infrared spectra show no corresponding changes that might indicate structural changes [65].



(9)

Differential thermal analysis and thermogravimetric analysis have been used to study the thermal stability of mixed platinum(II)—platinum(IV)—chloro—pyridine complexes {reactions (10)—(12)} [66].

$$[\mathrm{Pt(py)_4}][\mathrm{PtCl_6}] \xrightarrow[\leqslant 190^\circ\mathrm{C}]{heat} cis\text{-}[\mathrm{Pt(py)_2Cl_4}] + trans\text{-}[\mathrm{Pt(py)_2Cl_2}] \qquad (10)$$

$$[\mathrm{Pt(py)_4Cl_2}][\mathrm{PtCl_4}] \xrightarrow[\leqslant 180^\circ\mathrm{C}]{\mathrm{heat}} [\mathrm{Pt(py)_4}][\mathrm{PtCl_6}] \qquad (11)$$

$$[\mathrm{Pt(py)_4Cl_2}][\mathrm{PtCl_6}] \xrightarrow[190\text{—}250^\circ\mathrm{C}]{\mathrm{heat}} 2[\mathrm{Pt(py)_2Cl_4}] \qquad (12)$$

5.4 PALLADIUM(III) AND PLATINUM(III)

The oxidation state (III) is very rare for both palladium and platinum. However, the preparation of platinum(III) ethanoate $[\mathrm{Pt_2(O_2CMe)_6}]$ has been described [67], together with the Raman spectra of a number of platinum(III) ethanamido-complexes $[\mathrm{Pt(CH_3CONH)_2X}]_n$, (X = Cl, Br, I, NCS, $\mathrm{NO_2}$ or $\mathrm{NO_3}$) [68]. The interaction of *cis*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ with tryptophan in aqueous solution yields paramagnetic species that can be detected by EPR spectroscopy after several hours reaction time. The spectra indicate that more than one paramagnetic species is present and are consistent with d^7 low spin platinum(III) [69].

The presence of a dimeric palladium(III) species has been postulated in the oxidative arylation of olefins promoted by $\mathrm{Na_2[Pd_2(O_2CMe)_6]}$ {reaction (13)}.

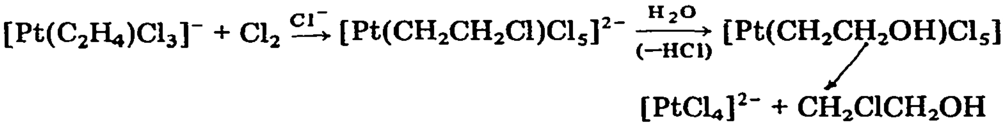
$$\mathrm{ArH + PhCH{=}CH_2} \xrightarrow[\mathrm{Na[O_2CMe]\ in\ HO_2CMe}]{\mathrm{Na_2[Pd_2(O_2CMe)_6]}} \mathrm{ArCH{=}CHPh + H^+} \qquad (13)$$

This suggestion accounts for the observed kinetic order of 0.5 in palladium(II) and avoids the need to postulate oxidative-addition of ArH to Pd(II) to form Ar—$\mathrm{Pd^{IV}}$—H, by postulating oxidative-addition of ArH to $\mathrm{Pd^{II}}$...$\mathrm{Pd^{II}}$ to form Ar—$\mathrm{Pd^{III}}$—$\mathrm{Pd^{III}}$—H which should result in a lower activation energy [70].

5.5 PALLADIUM(II) AND PLATINUM(II)

5.5.1 Complexes with Group (VII) donor ligands

Two papers have described the synthesis of halo-palladium(II) and platinum(II) complexes by aerial oxidation of metallic palladium or platinum in the presence of HX, CuX_2 and $[YH]^+$ or Z {where YH = pyH, $[Me_3NH]$, $[Et_4N]$, $\frac{1}{2}[bipyH_2]$ or $[Me_3S]$; Z = dmf, MeCN, Me_3NO or pyridine *N*-oxide}. The product formed {e.g. $[YH]_2[PdX_4]$, $[YH]_2[Pd_2X_6]$, $[YH]_2[PtX_6]$, $[Pd(py)_2X_2]$ or $[Pd(bipy)X_2]$} depends on both X and Y and the ratio of X : Y [71,72]. $[PtCl_4]^{2-}$ is formed as shown in reaction (14) when $[Pt(C_2H_4)Cl_3]^-$ is oxidised by chlorine in aqueous solution [73]. The equilibrium constants



$$\begin{array}{l} [Pt(C_2H_4)Cl_3]^- + Cl_2 \xrightarrow{Cl^-} [Pt(CH_2CH_2Cl)Cl_5]^{2-} \xrightarrow[(-HCl)]{H_2O} [Pt(CH_2CH_2OH)Cl_5]^{2-} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \swarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad [PtCl_4]^{2-} + CH_2ClCH_2OH \end{array} \qquad (14)$$

linking $[PdCl_4]^{2-}$ and ethene in 2 *M* and 3 *M* aqueous sodium perchlorate at 25°C {equilibria (15)—(17)} are $K_{15} = 19.6$, $K_{16} \sim 0.003$, $K_{17} = 0.012$ at $\mu = 2$ mol l^{-1} and $K_{15} = 11.0$, $K_{16} < 0.01$, $K_{17} = 0.006$ at $\mu = 3$ mol l^{-1}, respectively [74]. A cryoscopic study of the chloropalladium(II) ions formed suggested that at

$$[PdCl_4]^{2-} + C_2H_4 \overset{K_{15}}{\rightleftharpoons} [Pd(C_2H_4)Cl_3]^- + Cl^- \qquad (15)$$

$$[Pd(C_2H_4)Cl_3]^- + H_2O \overset{K_{16}}{\rightleftharpoons} [Pd(C_2H_4)(H_2O)Cl_2] + Cl^- \qquad (16)$$

$$[PdCl_4]^{2-} + H_2O \overset{K_{17}}{\rightleftharpoons} [PdCl_3(H_2O)]^- + Cl^- \qquad (17)$$

low chloride concentration the species were mainly mononuclear [75]. This is surprising, and the reverse of previous findings [76—78]. $Pd(OH)_2$ dissolves in 0.1 *M* NaCl—$Na[ClO_4]$ below pH 4.5 to form $[PdCl_3(H_2O)]^-$ ($K = 3.9 \times 10^{14}$) and $[PdCl_4]^{2-}$ ($K = 3.6 \times 10^{13}$). Between pH 5.6 and 6, penta- to hexa-meric hydrolysed palladium(II) species are formed, and above pH 11 $[Pd(OH)_n(H_2O)_{4-n}]^{2-n}$ (where $n = 3$ or 4) are formed [79].

Thermal studies of the system NaCl—$PdCl_2$ show only the formation of $Na_2[PdCl_4]$, which melts congruently at 430°C [80]. On heating $[NH_4]_2[PdCl_4]$ there is a phase transition at 132 K [81]. The resonance Raman spectrum of a mixture of $PdCl_2$—$AlCl_3$ in the vapour phase between 500 and 900 K at 30 atmospheres suggests that $[Cl_2AlCl_2PdCl_2AlCl_2]$, which has a centre of symmetry, is formed [82]. A study of the interaction of dioxygen with $PdCl_2$ and $CuCl_2$—$PdCl_2$ in aqueous solution between 20 and 85°C showed dioxygen interaction with $PdCl_2$ and aggregate $CuCl_2$—$PdCl_2$ complexes with large heats of adsorption; at high dioxygen concentrations, $CuCl_2$ itself interacts with dioxygen with a lower heat of adsorption [83].

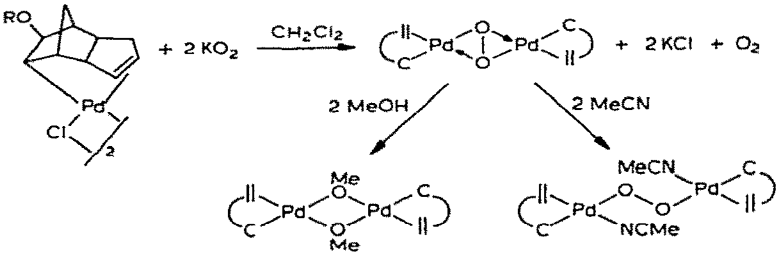
X-ray diffraction of $Rb_2[PtBr_4] \cdot H_2O$ has indicated a Pt—Br bond length of 2.435(6) Å [84]. Further investigations of the electronic spectra of $[MX_4]^{2-}$ ions (X = Cl, Br or SCN; M = Pd or Pt) have involved measuring the polarised crystal absorption spectra between 10 and 295 K. The spectra were assigned on the basis of ligand-field calculations including electron—electron interaction and spin—orbit coupling. The assignments are not in accord with previous work [85].

5.5.2 Complexes with Group (VI) donor ligands

5.5.2.1 Unidentate oxygen donors

The optical properties of PdO indicate a small energy band gap of 0.8 eV and a dielectric constant of 8.0 [86]. On heating, PdO decomposes between 780 and 850°C with an activation energy of 197 kJ mol^{-1} [87]. On heating PtO or PdO with alkali metal carbonates in the solid phase Na_2PtO_3, $Na_2Pd_3O_4$ or K_2PdO_2 are formed which have semiconductor properties [88]. On heating a 12 : 1 : 2.5 mixture of PbO : PbF_2 : PdO at 790°C for 140 hours, $PbPdO_2$ is formed, in which each Pd is in a square—planar environment and each Pb is at the apex of a PbO_4 square-pyramid [89].

A superoxide complex of palladium(II) has been prepared as in reaction (18). It reacts with methanol to give a methoxide bridged species and with ethanenitrile to yield a "linear" peroxide bridged complex [90]. Hydroxyl radicals react more readily with $[Pt(en)_2]^{2+}$ than with $[enH]^+$ or $[enH_2]^{2+}$ [91]. This reaction is of relevance to the interaction of the products of γ-radiation on the body with other possible cancer-therapy agents.



(18)

The minimum aqueous solubilities of $Pd(OH)_2$ and $Pt(OH)_2$ are $4.0 \times 10^{-6}\,M$ and $5.0 \times 10^{-6}\,M$, respectively [92]. When a solution of $[Pt\{P(CMe_2H)_3\}_3]$ in thf, where the major platinum species present is $[Pt\{P(CMe_2H)_3\}_2]$, is treated with water at room temperature *trans*-$[Pt\{P(CMe_2H)_3\}_2H(OH)]$ is formed as an extremely air-sensitive colourless compound [93]. Ligands such as $P(CMe_2H)_3$ or pyridine react with this hydroxo-compound to displace the hydroxo-ligand, so that dissolution of $[Pt\{P(CMe_2H)_3\}_3]$ in aqueous pyridine yields *trans*-$[Pt\{P(CMe_2H)_3\}_2(py)H][OH]$, which gives a very strongly basic solution. $[Pt(PEt_3)_3]$, which does not dissociate so readily, reacts with aqueous thf to form $[Pt(PEt_3)_3H][OH]$ which is an effective catalyst for H/D exchange of activated C—H groups (such as the α-hydrogen atoms of ketones, aldehydes, sulphones, sulphoxides and nitroalkanes) as well as for the hydration of unsaturated organic compounds {such as CH_3CN (to CH_3CONH_2) and $CH_2{=}CHCN$ (to a mixture of $CH_2{=}CHCONH_2$, $HOCH_2CH_2CN$, $O(CH_2CH_2CN)_2$ and $CH_2{=}C(CN)CH_2CH_2CN$)} [93].

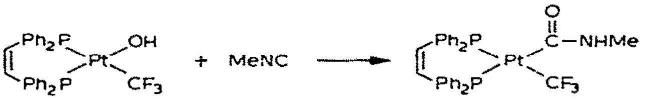
Iron(II) is rapidly oxidised by O_2 in acid solution in the presence of $[Pd(H_2O)_4][SO_4]$, through reactions (19)—(21) [94].

$$Pd^{2+} + Fe^{2+} + O_2 \rightarrow PdO_2^{+} + Fe^{3+} \qquad (19)$$

$$PdO_2^+ \rightarrow Pd^{2+} + O_2^- \tag{20}$$

$$4\ H^+ + O_2^- + 3\ Fe^{2+} \rightarrow 3\ Fe^{3+} + 2\ H_2O \tag{21}$$

The insertion of isocyanide into a number of M—E σ-bonds has been reported over the years. Isocyanide insertion into Pt—OH bonds yields carboxamido-complexes and its insertion into Pt—OMe bonds yields imidoyl complexes {reactions (22) and (23)} [95]. Other reagents that insert into Pt—OR bonds include CO, COS, CS_2 and SO_2. Weak acids HY (Y = SH, p-MeC_6H_4S, PhC≡C, CH_3CONH or PhMeN) react with alkoxy and hydroxy-platinum(II) complexes $[PtL_2(OH)R]$ to form the corresponding alcohol, or water, and $[PtL_2YR]$ [96].



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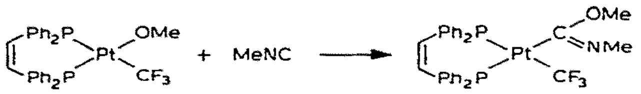
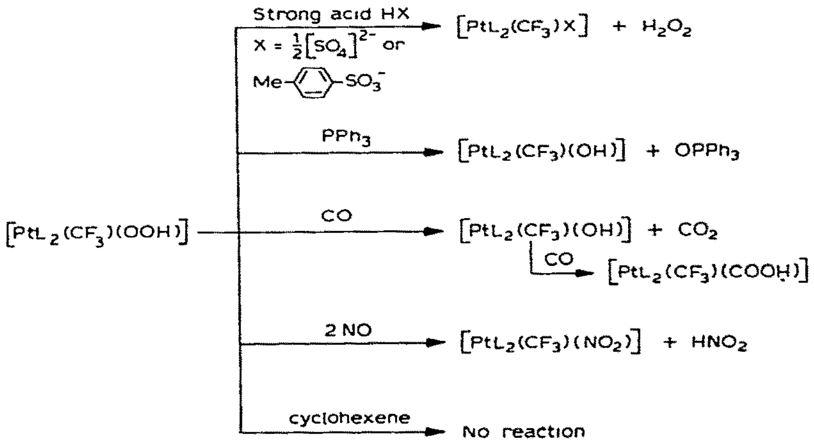


(23)

Platinum metal hydroperoxo-complexes have received increasing attention recently because they may be involved in the oxygenation of olefins catalysed by the platinum metals. However, the first hydroperoxo-complexes of platinum(II) were only isolated in 1979 by one of two routes {reactions (24) and (25)}; L_2 = 2 PPh_2Me gives *trans*-products; L_2 = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH{=}CHPPh_2$ gives *cis*-products. A number of reactions of these complexes have been investigated (Scheme II) [97].

$$[PtL_2(CF_3)OH] + H_2O_2 \rightarrow [PtL_2(CF_3)(OOH)] + H_2O \tag{24}$$

$$[PtL_2(CF_3)H] + H_2O_2 \rightarrow [PtL_2(CF_3)(OOH)] + H_2 \tag{25}$$



Scheme II

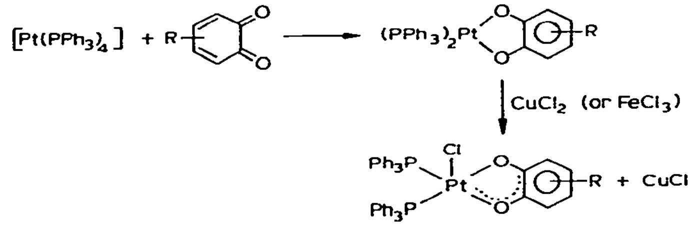
The inability of these hydroperoxo-complexes to react with cyclohexene demonstrates their limited oxygenation ability.

Nitrate ions do react with $[Pd(H_2O)_4]^{2+}$ to form $[Pd(H_2O)_3(NO_3)]^+$, although the equilibrium constant (1.2 ± 0.4 l mol^{-1} at pH 0) is too low to determine meaningfully. With perchlorate and 4-toluenesulphonate there is essentially no reaction in aqueous solution [98]. $[Pd(SO_3F)_2]$, prepared by heating $Pd[Pd(SO_3F)_6]$ at 130°C {see reaction (5)}, has a very similar spectrum in the d—d region to $Pd[Pd(SO_3F)_6]$, suggesting that the fluorosulphate anion behaves as a tridentate ligand giving palladium(II) in an octahedral geometry. If substantiated by a crystal structure, this will be one of the few octahedral palladium(II) complexes known [18].

$PdCl_2$ dissolves in dimethylformamide to form $[Pd(dmf)_4]Cl_2$ [99]. The chloride-bridged complexes $[Pt(am)Cl_2]_2$, am = pyridine, picoline or lutidine, dissolve in dimethylformamide to form $[Pt(am)(dmf)Cl_2]$; $\nu_{C=O}$ is lowered from 1668 in free dimethylformamide to between 1640 and 1625 cm^{-1} in the complexes. Oxygen donation is confirmed by this and the 0.2 p.p.m. upfield shift of the aldehyde proton in the NMR spectrum. This proton is coupled to ^{195}Pt with $J_{Pt-H} = 40$ Hz, whereas the protons of the methyl groups bound to nitrogen show no coupling to platinum-195 [100].

5.5.2.2 Bidentate oxygen donors

1,2-Quinones add oxidatively to $[Pt(PPh_3)_4]$ to form platinum(II) complexes which react further with copper(II) or iron(III) chloride to form paramagnetic complexes involving the semiquinone ligand $1,2\text{-}OC_6H_4O^-$ {reaction (26)} [101]. 1,2-Quinone complexes can be prepared by displacement of ethanoate from *cis*-$[Pt(Et_2S)_2(O_2CMe)_2]$ (see Section 5.5.2.7) {reaction (27)}



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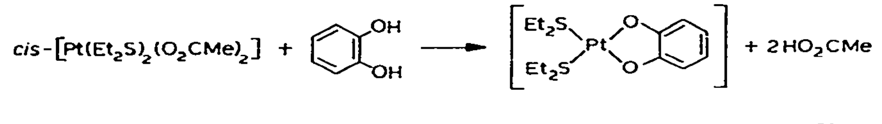
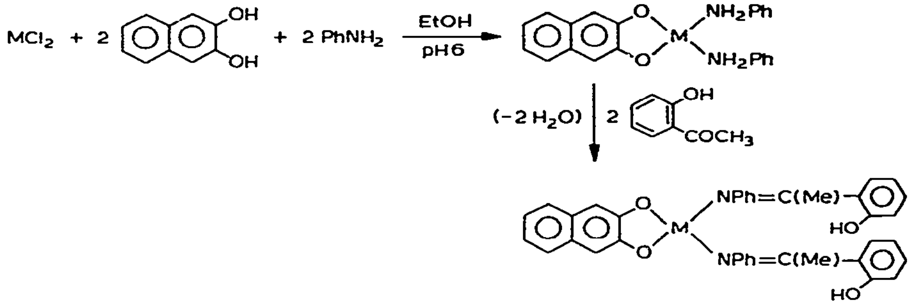


(27)

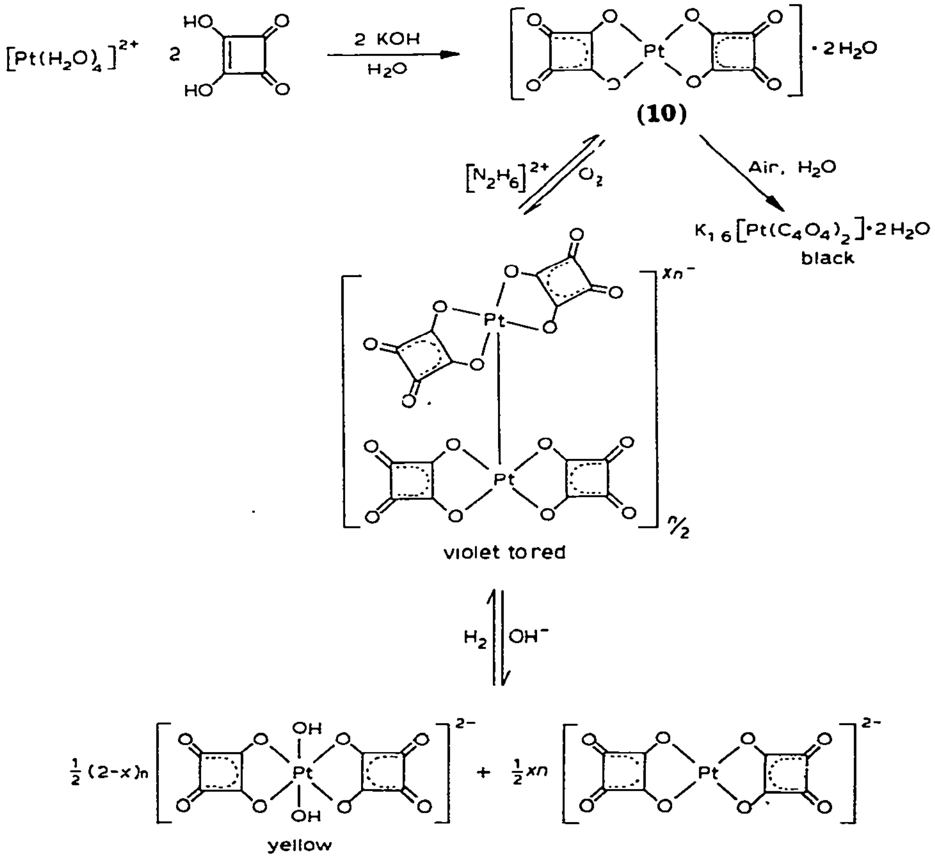
[102]. 1,2-Hydroxyacetophenone reacts with aniline coordinated to 1,2-naphthoquinone complexes of platinum(II) and palladium(II) to form Schiff base complexes {reaction (28)} [103]. 3,4-Dihydrocyclobutenedione, although it does not react with $Na_2[PtCl_4]$, reacts with $[Pt(H_2O)_4]^{2+}$ to give a yellow bis(squarate)complex, {(10), Scheme III}, $K_2[Pt(C_4O_4)_2] \cdot 2\,H_2O$ which on oxidation yields $K_{1.6}[Pt(C_4O_4)_2] \cdot 2\,H_2O$ with a Pt^{IV} : Pt^{II} ratio of 0.202 : 1 or a mean platinum oxidation state of 2.4. This latter complex shows



(28)

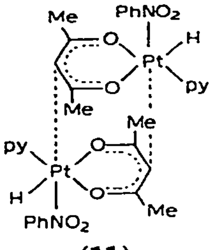
similar metallic properties to $K_{1.6}[Pt(oxalate)]_2$ [104].

The proceedings of an all-Soviet Union Seminar on the structure, properties and uses of metal-β-diketonates have been published [105]. $[Pd(acac)_2]$ in pyridine is a homogeneous catalyst for the reduction of nitrobenzene to aniline at 1 atmosphere H_2 pressure and room temperature. $[Pd(acac)H(PhNO_2)(py)]$, which appears to have structure (11) in the solid state, can be iso-



Scheme III

lated from the reaction medium. In solution, the bond from the γ-carbon to palladium is probably replaced by a molecule of solvent [106]. The palladium(II) and platinum(II) complexes of dibenzoylmethane react with ammonia to yield a Schiff base complex {reaction (29)} [107]. Palladium(II) com-



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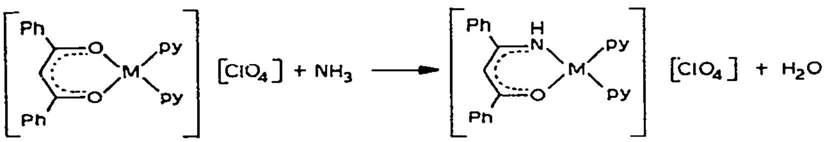
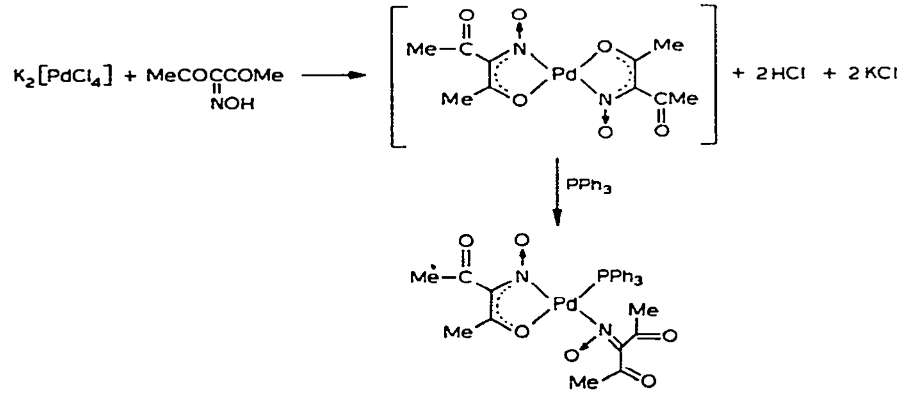


(29)

plexes of the isonitroso-β-diketone MeCOC(=NOH)COMe were prepared because the isonitroso group >C=NOH can function ambidentately. Two products could be prepared {reaction (30)}: in the first, the ligand was bonded in a bidentate fashion, but reaction with PPh_3, $AsPh_3$ or pyridine reduced one ligand to unidentate bonding through nitrogen [108]. 3-Hydroxy-2-methyl-4-pyrone forms both *cis*- and *trans*-biscomplexes with palladium(II) {**(12)** and **(13)**}. Although the ligand has a resemblance to pentane-2,4-dione, it is displaced from **(12)** and **(13)** by amines which acetylacetone is not [109]. When [M(acac)(γ-acac)(PPh_3)] is refluxed in toluene with another



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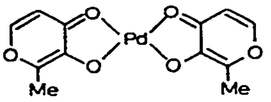

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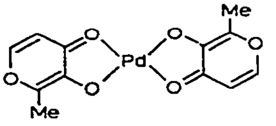
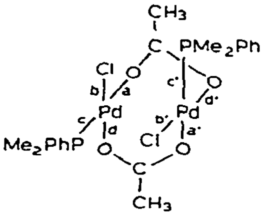


(13)

β-dicarbonyl compound one of three reactions may occur: (i) keto favouring β-dicarbonyls such as dimethylmalonate, methyl- and ethyl-acetoacetates replace only the γ-carbon bonded pentane-2,4-dionate ligand; (ii) enol favouring β-dicarbonyls such as dibenzoylmethane replace only the bidentate oxygen-bonded pentane-2,4-dionate ligand; (iii) benzoylacetone either replaces only the bidentate oxygen-bonded pentane-2,4-dionate ligand or both pentane-2,4-dionates [110].

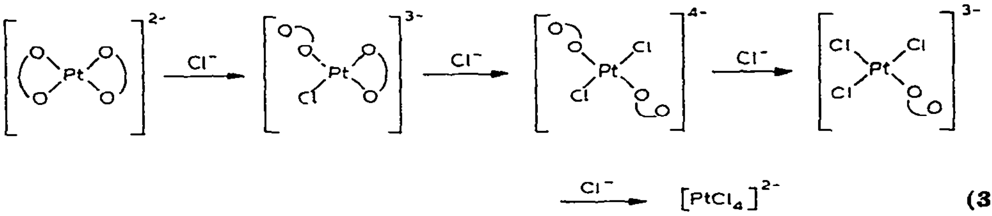
Ethanoate complexes are widely used as catalyst precursors. This has created a considerable interest in the structure and reactivity of platinum metal carboxylates. The bridging ability of carboxylates $RCOO^-$ falls off in the order $R{=}CH_3 > CH_2Cl > CH_2Br > CCl_3 > CF_3$ [111]. $[(PMe_2Ph)ClPd(\mu\text{-}O_2CMe)_2PdCl(PMe_2Ph)]$ has two ethanoate bridging groups approximately at right angles to each other, (14) [112]. $[Pt(OCMe_2)_2]_4$ involves a strong metal—metal bonded square of platinum atoms with Pt—Pt bonds in the range 2.493—2.501 Å. Of the eight bridging ethanoates, four lie approximately in the plane and the other four lie alternately above and below the plane; the Pt—O bonds perpendicular to the Pt_4 plane have normal lengths (mean 2.014 Å) whereas the eight coplanar Pt—O bonds are rather long (mean 2.157 Å) [113].



a = 2.110(9) Å; a' = 2.130(9) Å,
b = 2.260(4) Å, b' = 2.273(3) Å,
c = 2.212(4) Å, c' = 2.200(3) Å,
d = 2.04(1) Å; d' = 2.02(1) Å

(14)

The displacement of oxalate from $[Pt(ox)_2]^{2-}$ by chloride in the pH range 5.5—7.5 occurs sequentially as in reaction (31) [114].

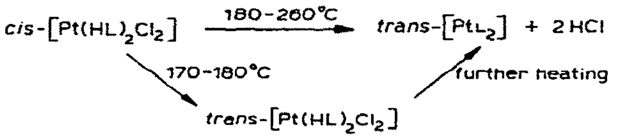


(31)

5.5.2.3 *Bidentate oxygen—nitrogen donor ligands*

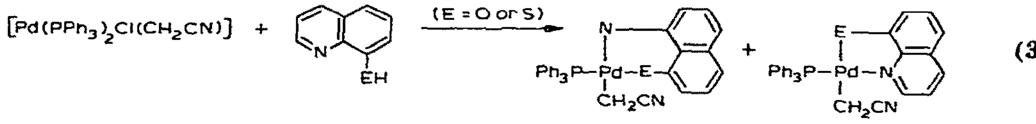
Chelate complexes of palladium(II) and platinum(II) with 8-hydroxyquinoline (HL) have been prepared thermally {reactions (32) and (33)}as well as by displacement of one neutral and one anionic ligand {reaction (34)} [115,116]. The 2-hydroxyazo dye (15) forms a 2 : 1 complex with palladium(II) (16) with log β_2 = 22.86 [117]. 2,4-dihydroxyvalerophenone is a useful gravimetric reagent for many metal ions that form 2 : 1 complexes with palla-

$$trans\text{-}[Pd(HL)_2Cl_2] \xrightarrow{165-260°C} trans\text{-}[PdL_2] + 2HCl \qquad (32)$$



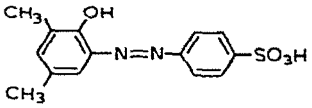
$$cis\text{-}[Pt(HL)_2Cl_2] \xrightarrow{180-260°C} trans\text{-}[PtL_2] + 2HCl \qquad (33)$$

$$cis\text{-}[Pt(HL)_2Cl_2] \xrightarrow{170-180°C} trans\text{-}[Pt(HL)_2Cl_2] \xrightarrow{\text{further heating}} trans\text{-}[PtL_2]$$



(34)

(sole product when E = S)



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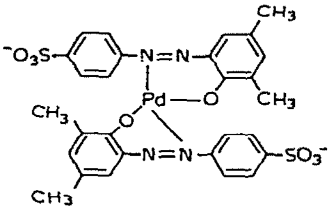
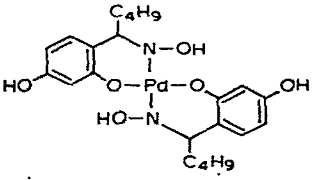


(16)

dium(II), (17) [118]. ^1H and ^{13}C NMR are very useful for distinguishing the two possible isomers, acolar and discolar, formed by 2,2′-dihydrazobenzenes (18) and (19) [119]. Pd—O and Pd—N stretching force constants have been determined for (20) following an IR spectral investigation between 77 and 298 K [120].



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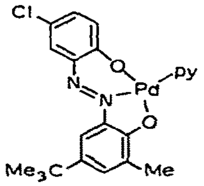
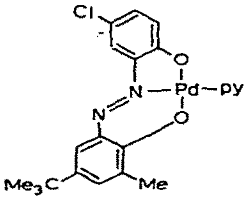
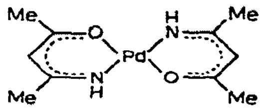


(18; acolar)



(19; discolar)

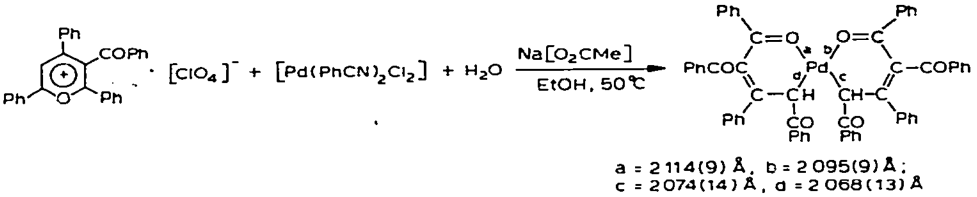


(20)

5.5.2.4 Bidentate oxygen—carbon donor ligands

2,4,6-triphenyl-3-benzoylpyrylium perchlorate reacts with $[Pd(PhCN)_2Cl_2]$

to form *cis*-bis(1,3,3-tribenzoyl-2-phenyl-σ-allyl)palladium(II) {reaction (35)}. Clearly the mode of coordination of this ligand depends very much on the reaction conditions since, with palladium(II) chloride in water, the 2,6-biphenyl analogue forms a π-allylic complex {reaction (36)} [121].



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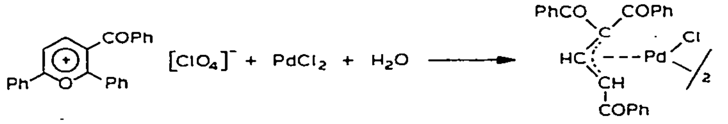


(36)

An X-ray diffraction study of [Pd(PPh$_3$)(py)(CH$_2$CO$_2$)] has shown the CH$_2$CO$_2$ ligand to be bidentate (Pd—C = 2.004(16) Å; Pd—C = 2.093(11) Å) [122].

5.5.2.5 *Ambidentate oxygen—sulphur donor ligands*

A vibrational analysis of a series of oxygen-bonded sulphoxide complexes showed that the S—O stretching force constant (F_{SO}) was related to the M—O stretching force constant by the relation (37). This implies a reduction of

$$F_{SO} = -(1.24 \pm 0.2)\,F_{MO} \pm (8.78 \pm 0.12)\ \text{mdyn Å}^{-1} \qquad (37)$$

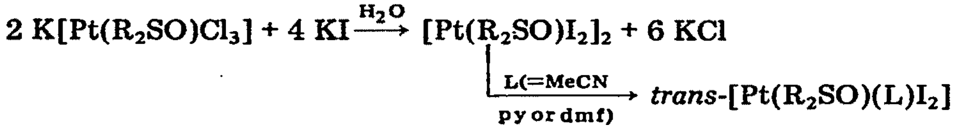
the $O_{p\pi} \rightarrow S_{d\pi}$ double-bond character as the M—O bond gets stronger. Of the metal ions studied, F_{MO} was greatest for Pt(II), next greatest for Pd(II) and weaker for all the rest; the greater the electronegativity of M the greater F_{MO} [123]. Cationic oxygen-bonded bis(dimethylsulphoxide) complexes have been prepared by reaction (38). The corresponding mono(dimethylsulphoxide)

$$[\mathrm{M(dppe)Cl_2}] + 2\,\mathrm{AgX} \xrightarrow[\mathrm{M = Pd,\ Pt;\ X = ClO_4, PF_6}]{\mathrm{CH_2Cl_2\text{-}Me_2SO}} [\mathrm{M(dppe)(Me_2SO)_2}]\,\mathrm{X_2} \qquad (38)$$

complexes {reaction (39)} are less stable. Although the platinum(II) complex is stable, the palladium(II) complex slowly loses dimethylsulphoxide. On standing in solution, slow deoxygenation of the dimethylsulphoxide occurs; this reaction is complete in 3 h for palladium(II) but incomplete even after a month with platinum(II) {reaction (39)} [124]. Although dialkylsulphoxides do not react with K$_2$[PtI$_4$], iodo-bridged complexes can be prepared from the chloro-complexes; these *S*-bonded dimethylsulphoxide complexes undergo

$$\begin{tikzcd}
{[\mathrm{M(dppe)Cl_2}] + \mathrm{AgX}} \arrow[rr, "\mathrm{CH_2Cl_2\text{-}Me_2SO}", "\substack{\mathrm{M = Pd,\ Pt;}\\ \mathrm{X = ClO_4,\ PF_6}}"'] & & {[\mathrm{M(dppe)(Me_2SO)Cl]X}} \arrow[dl] \arrow[d] \\
& {[\mathrm{M(dppe)(Me_2S)Cl]X}} \arrow[d, shift left] & {[\mathrm{M_2(dppe)_2Cl_2]X_2} + 2\,\mathrm{Me_2SO}} \\
& {\tfrac{1}{2}[\mathrm{M_2(dppe)_2Cl_2]X_2} + \mathrm{Me_2S}} \arrow[u, shift left] &
\end{tikzcd} \qquad (39)$$

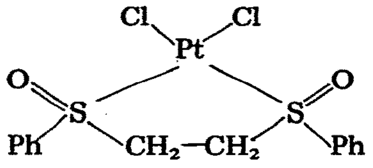
bridge cleavage with pyridine only {reaction (40)}, whereas the chloro- and bromo-bridged analogues are also cleaved by ethanenitrile and dimethylformamide [125]. $PhSOCH_2CH_2SOPh$ forms complexes with $PtCl_2$ in which both



$$2\ K[Pt(R_2SO)Cl_3] + 4\ KI \xrightarrow{H_2O} [Pt(R_2SO)I_2]_2 + 6\ KCl$$

$$[Pt(R_2SO)I_2]_2 \xrightarrow[\text{py or dmf)}]{\text{L(=MeCN}} trans\text{-}[Pt(R_2SO)(L)I_2] \qquad (40)$$

the *meso*- (21) and *rac*- (22) forms of the ligand are coordinated; in the *meso*-complex the platinum is slightly tetrahedrally distorted from square-planar whereas in the *rac*-complex it is close to square-planar [126].



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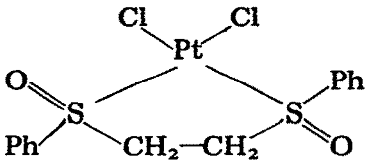


(22)

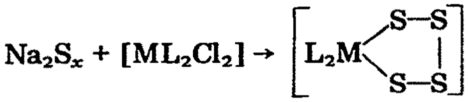
Passing SO_2 through a solution of palladium(II) ethanoate and styrene in glacial ethanoic acid at 20°C yields $[Pd(O_2CMe)(CH_2{=}CHPh)(HSO_3)]_2$ which contains *O*- and *S*-coordinated bisulphite bridges [127]. Heating 2,2,5,5-$Me_4C_6H_3OCS_2Me$ with $[Pt(PPh_3)_4]$ yields $[Pt(PPh_3)_2(S_2CO)]$, together with a series of olefins [128]. $PdCl_2$ reacts with sodium monothiobenzoate to form $[Pd(PhCSO)_2]$ which, IR spectroscopy suggests, involves virtually unidentate Pd—S bonding [129].

5.5.2.6 Bidentate oxygen—sulphur donor ligands

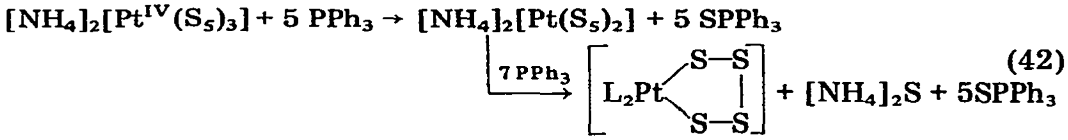
The monothio-β-diketones, $ArC(SH){=}CHCOCF_3$, react with palladium(II) and platinum(II) to form *cis*-complexes [130].

5.5.2.7 Unidentate sulphur donor ligands

PtS has a more open structure with internal channels than PdS; on increasing the pressure to 30 Kbar, PtS undergoes a phase transformation to a phase that is isomorphous with PdS. The ambient and high pressure phases of PtS are diamagnetic semiconductors with electrical band gaps of 0.32 and 0.19 eV, respectively [131]. The stabilization of palladium(II)-sulphur complexes appears to require a bidentate phosphine, whereas for platinum(II) monodentate phosphines are adequate. Thus, tetrasulphide complexes of palladium(II) ($L_2 = Ph_2PCH_2CH_2PPh_2$) and platinum(II) ($L_2 = 2\ PPh_3$) can be prepared from sodium polysulphide {reaction (41)} and by reduction of $[NH_4]_2[Pt^{IV}(S_5)_3]$ with PPh_3 {reaction (42)} [132,133]. Simple sulphide complexes can be prepared using sodium sulphide; again palladium(II) requires a bidentate



$$Na_2S_x + [ML_2Cl_2] \rightarrow \left[L_2M\begin{array}{l} S\!-\!S \\ \quad\ | \\ S\!-\!S \end{array}\right] \qquad (41)$$



$$[NH_4]_2[Pt^{IV}(S_5)_3] + 5\,PPh_3 \rightarrow [NH_4]_2[Pt(S_5)_2] + 5\,SPPh_3 \xrightarrow{7\,PPh_3} [L_2Pt(S_4)] + [NH_4]_2S + 5SPPh_3 \quad (42)$$

phosphine whereas platinum(II) does not {reaction (43)} [134]. HS^- and HSe^- complexes have been prepared following reactions (44) to (47)

$$[ML_2Cl_2] + 2\,Na_2S\cdot 9\,H_2O \xrightarrow[M\,=\,Pd,\ L_2\,=\,dppe;\ M\,=\,Pt,\ L\,=\,PPh_3]{EtOH} Na_2[PdL_2(S)_2] + 2\,NaCl + 9\,H_2O \quad (43)$$

[134,135]. The rôle of the bidentate phosphine for palladium(II) is probably

$$[Pt(PPh_3)_2Cl_2] + 2\,H_2S + K_2CO_3 \xrightarrow{CH_2Cl_2} [Pt(PPh_3)_2(SH)_2] + CO_2 + 2\,KCl + H_2O \quad (44)$$

$$[Pd(dppe)Cl_2] + 2\,H_2S + 2\,NEt_3 \xrightarrow{benzene} [Pd(dppe)(SH)_2] + 2[NEt_3H]Cl \quad (45)$$

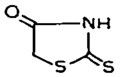
$$[Pt(PPh_3)_2Cl_2] + 2\,NaSeH \xrightarrow{EtOH/benzene} [Pt(PPh_3)_2(SeH)_2] + 2\,NaCl \quad (46)$$

$$[Pd(dppe)Cl_2] + 2\,NaSeH \xrightarrow{EtOH/benzene} [Pd(dppe)(SeH)_2] + 2\,NaCl \quad (47)$$

to stabilise the *cis*-geometry, since the platinum(II) products are all *cis*. The influence of the ionic medium ($HClO_4$, KOH or KNO_3) on the stability of platinum(II)–unithiol complexes has been shown to be considerable [136].

By comparing the $S_{2p_{3/2}}$ binding energies in the X-ray photoelectron spectra of cysteine, $HOOCH(NH_2)CH_2SH$, and penicillamine, $HOOCCH(NH_2)C(SH)Me_2$, and their palladium(II) and platinum(II) complexes, it is possible to distinguish sulphide (M—SR) and thioether ($M—SR_2$) coordination [137]. C_6F_5SH reacts with $K_2[PtCl_4]$ to form $[Pt(SC_6F_5)_4]^{2-}$ [138]. Stability constants for ligands *trans* to thiourea in platinum(II) have been determined at 25°C in 0.1 *M* KNO_3 {reaction (48)} [139]. Rhodamine (**23**) forms a series of complexes with palladium(II) and platinum(II) in which it bonds, either ter-

$$\begin{array}{c} trans\text{-}[Pt(NH_3)_2(\{NH_2\}_2CS)Cl]^+ \underset{Cl^-}{\overset{H_2O}{\rightleftharpoons}} trans\text{-}[Pt(NH_3)_2(\{NH_2\}_2CS)(H_2O)]^{2+} \\ {\scriptstyle +H^+}\Big\Updownarrow{\scriptstyle -H^+} \\ trans\text{-}[Pt(NH_3)_2(\{NH_2\}_2CS)(OH)]^+ \end{array} \quad (48)$$

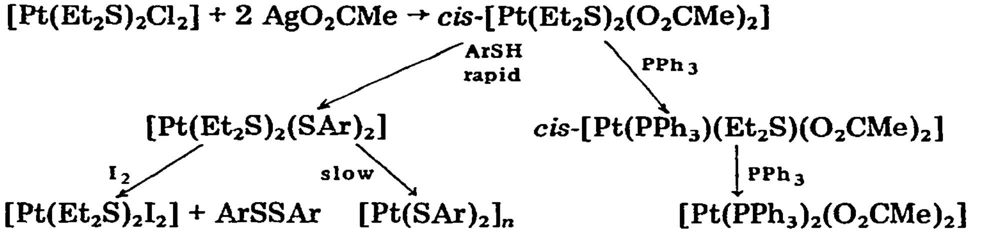


(**23**)

minally or as a bridging ligand, through the thiocarbonylic sulphur [140].

SCl_2 forms *trans*-$[PdCl_2(SCl_2)]_2$ [141]. On heating *trans*-[Pt-

$(\overline{SCH_2CH_2CH_2})_2Cl_2]$ it isomerises to the *cis*-complex [142]. *Cis*- and *trans*-isomers of $[Pt(Bu_2S)_2Cl_2]$ have been separated by thin layer chromatography [143]. *Cis*-$[Pt(Et_2S)_2(O_2CMe)_2]$ is a useful starting material because all four ligands are modest donors and can readily be displaced {reaction (49)} [102]. The reactions of {(but-3-enyl)butylsulphide}dichloropalladium(II) with tertiary phosphines have been studied {reaction (50)} in an attempt to prepare the, as yet non-existent, complex *cis*-$[Pt(PPh_3)_2Cl_2]$ [144]. *S*-bonded palladium(II) and platinum(II) complexes of ethylthioglycolic acid ($EtSCH_2COOH$) *trans*-$[M(EtSCH_2CO_2H)_2Cl_2]$ have been prepared starting from $K_2[MCl_4]$ [145]. Although thiamine (vitamin B_1) (24) prefers to bond to platinum(II) through N_1 of the pyrimidine ring, tetrahydrothiamine (25) bonds through the thioether donor [146].



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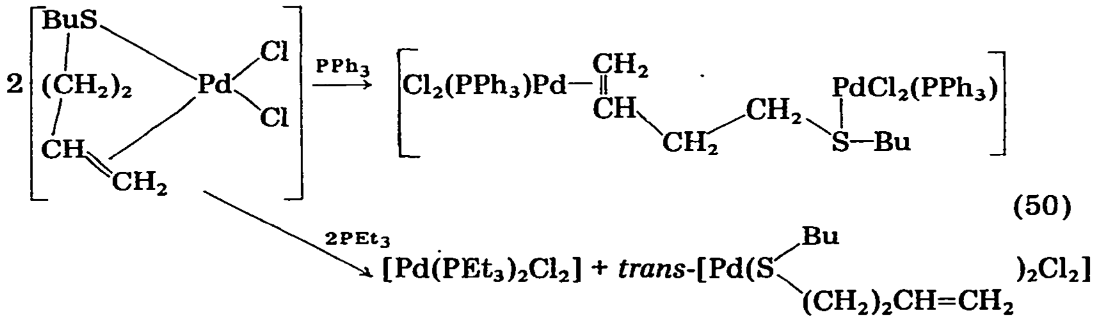

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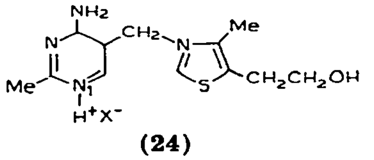

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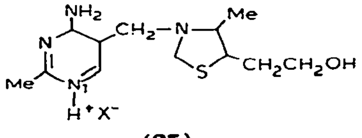
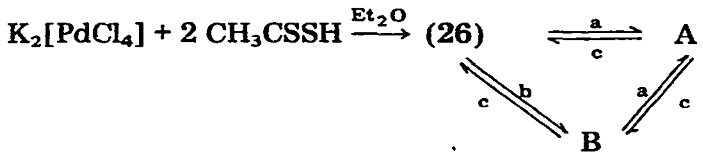


(25)

5.5.2.8 *Bidentate sulphur donor ligands*

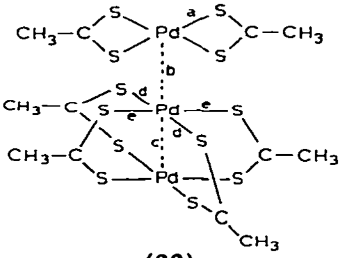
Thioacetic acid reacts with $K_2[PdCl_4]$ to give a series of complexes $[Pd(CH_3CS_2)_2]_n$ {reaction (51)}. X-ray diffraction shows (26) to have alternate mononuclear ($n = 1$) and binuclear ($n = 2$) units on an axis. In A, the binuclear units form linear chains of directly interacting palladium atoms through stacking in columns. The Pd—Pd distances are shorter than in (26), at 2.738(1) Å within the dimer and at 3.257(1) Å between dimers. Although the



(51)

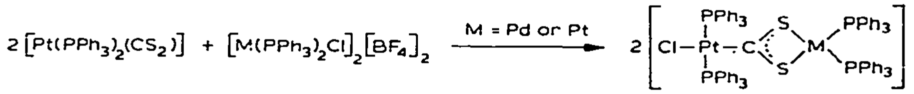
a, recrystallisation in the presence of CS_2
b, sublimation; c, recrystallisation from benzene

detailed structure of B is uncertain, it appears to be a mixture of monomeric and dimeric species. The monomeric and dimeric $[Pd(CH_3CS_2)_2]_n$ units coexist, not only in the solid state but also in solution and in the vapour phase, indicating that they have very similar stabilities [147]. A series of di- and trinuclear CS_2 complexes have been prepared by treating CS_2 complexes with palladium(II) or platinum(II) species {reactions (52) and (53)}. A variant of the basic metal—CS_2 interaction is provided by reaction (54), where a trithiocarbonate bridged complex is formed [148]. The electrochemical reduction



(26)

a = 2 331(5) Å;
b = 3 399(1) Å,
c = 2 754(1) Å,
d = 2 31 0(5) Å,
e = 2 324(6) Å



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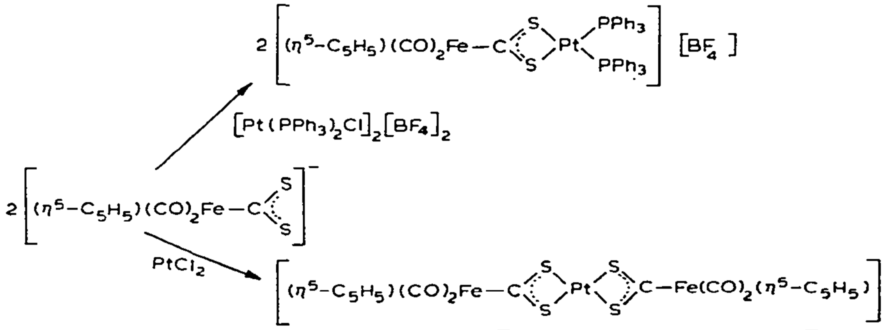

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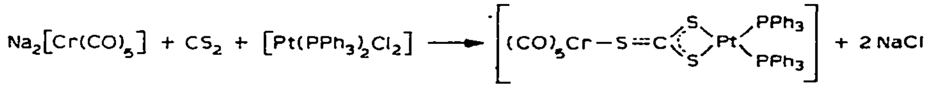
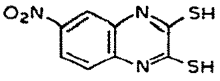


(54)

of $[M(M'S_4)_2]^{2-}$ (M = Pd(II) or Pt(II); M′ = Mo or W) leads to reversible formation of the formally monovalent (Pd) or zerovalent (Pd and Pt) products [149]. 3-Indoledithiocarboxylate forms 1 : 2 complexes with palladium(II) and platinum(II) [150].

Bifunctional mercaptans and selenomercaptans, $HE(CH_2)_3EH$ (E = S or Se), react with $[ML_2Cl_2]$ (M = Pd, L_2 = dppe; M = Pt, L = PPh_3) to form bidentate sulphide or selenide complexes $[ML_2\{S(CH_2)_3S\}]$ [151]. Similarly, 6-nitroquinoxaline-2,3-dithiol (27) and 2,3-dithiolobenzo(*g*)quinoxaline-5,10-dione form $(Et_4N)_2[PdL_2]$ [152]. A series of unsaturated cyclic five-membered disulphides react with $[Pt(PPh_3)_4]$ to give sulphide complexes {e.g. reaction (55)} [153].



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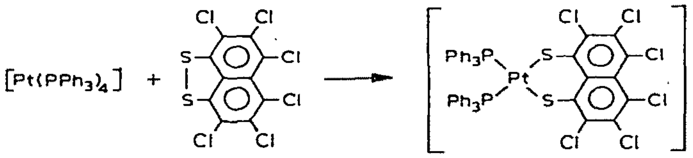


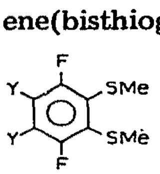
(55)

Multidentate thioethers such as $RSCH_2SCH_2SR$ react with $K_2[MCl_4]$ (M = Pd or Pt) to form $[MCl_2(RSCH_2SCH_2SR)]$, in which only the terminal sulphur donors coordinate [154]. Complete coordination of all four sulphur donors of a series of aliphatic and partially aromatic tetrathioethers has been accomplished by ensuring that no halide ligands are present, since this allows only bidentate coordination to any one metal atom {reaction (56)} [155]. A

$$[M(MeCN)_2Cl_2] + MeS(CH_2)_3S(CH_2)_2S(CH_2)_3SMe + 2\ Ag[ClO_4] \xrightarrow{MeCN}$$

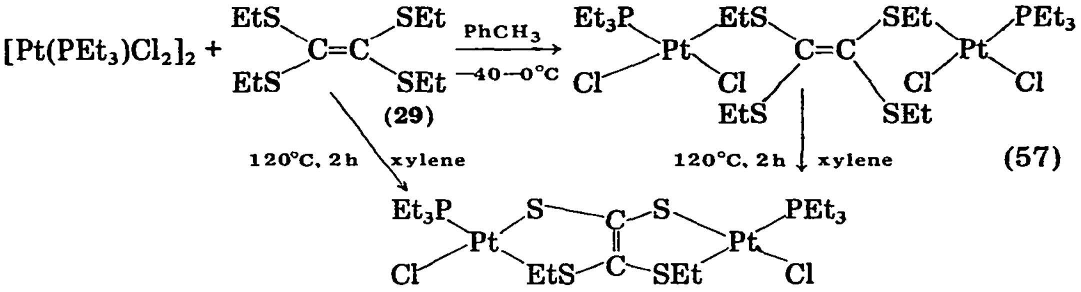
$$[M\{MeS(CH_2)_3S(CH_2)_2S(CH_2)_3SMe\}][ClO_4]_2 + 2\ AgCl + 2\ MeCN \qquad (56)$$

series of dithioether complexes of palladium(II) and platinum(II), *cis*-$[MLX_2]$ and $[ML_2][ClO_4]_2$ (with L = $RS(CH_2)_nSR$, R = Me or Ph; n = 2 or 3), have been prepared and their spectra reported. Variable temperature NMR studies show that the rate of inversion at coordinated sulphur is M = Pd > Pt and X = I > Br > Cl. $PhS(CH_2)_mSPh$ (m = 6 or 8) yield polymeric $[Pd(L)X_2]_n$ complexes whilst $PhS(CH_2)_{12}SPh$ forms monomeric *trans*-$[M(L)Cl_2]$ [156]. Other bidentate thioethers studied include (28) (Y = H, Br or SMe) [157] and ethylene(bisthioglycollic acid) [158], the latter forming water soluble palladium(II)



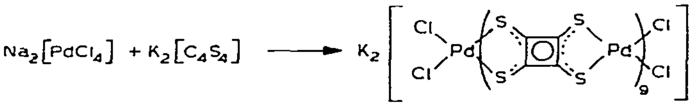
(28)

complexes whose stability constants have been determined. The electron rich tetrathioether (29) readily cleaves the chloride bridge of $[Pt(PEt_3)Cl_2]_2$, *S*-dealkylation occurring at high temperature {reaction (57)} [159].



(57)

Interest in metal di- and tetrathiolenes has been sustained because of their remarkable electrochemical and one-dimensional anisotropic conductivities and semiconductivities [160—163]. Complexes of the tetrathiosquarate anion $[C_4S_4]^{2-}$ have been investigated because of their potential as one-dimensional conductors {e.g. reaction (58)}. Their electrical properties including the temperature dependence of their semiconductivities are similar to those of the dithiolenes [164].



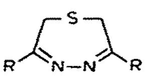
(58)

5.5.2.9 Ambidentate chalcogen—nitrogen donor ligands

^{13}C NMR spectroscopy is a valuable technique for determining the mode of coordination of SCN^- and $SeCN^-$ since the order of increasing ^{13}C shielding is M—NCS(Se) < NCS(Se) < M—S(Se)CN, although with OCN^- the order is NCO < M—NCO [165]. *Cis*-$[Pt(py)_2(SCN)_2]$ isomerises to the *trans*-product on heating to 90°C [166]. An X-ray diffraction study of *trans*-$[Pd(Te\{(CH_2)_3SiMe_3\}_2)_2(SCN)_2]$ has found a Pd—S distance of 2.310(3) Å, which is rather shorter than the sum of the covalent radii and implies the presence of some π-bonding between the filled p_z-orbitals of sulphur and the empty p_z-orbital of palladium [167]. A series of platinum(II) complexes $[Pt(PPh_3)_2L]$ (with L = S_2N_2, $S_2N_2H_2$ or S_4N_4) have been reported [168]. A normal coordinate analysis has been carried out on $[Pd(S_3N)_2]$ [169]. Of the thiobenzamide complexes $[Pd(PhCSNH_2)_2X_2]$, all involve Pd—S bonding; the chloride complex is *cis*- whereas the bromide and iodide complexes are *trans* [170,171].

5.5.2.10 Multidentate sulphur- or selenium—pnictogen donor ligands

When (30) is hydrolysed in the absence of metal ions (31) is formed,



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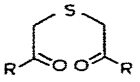

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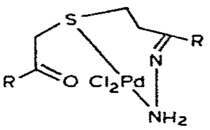
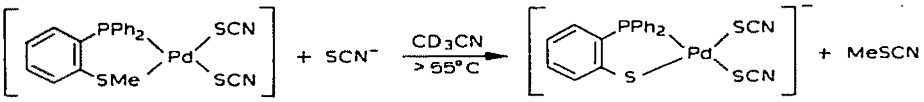


(32)

whereas in the presence of $PdCl_2$, (32) can be isolated [172]. Thiosemicarbazides, thiosemicarbazones and *sym*-dibenzylthiourea all form palladium(II) complexes in which they act as bidentate *S*/*N* donors [173—175]. The kinetics of ring closure by $(H_2NCH_2CH_2)_2S$ suggest that, compared to $(H_2NCH_2CH_2)_2NMe$, more strain is involved in reaching the transition states, with the second ring closure involving more steric strain than the first. The extra strain is ascribed to the greater Pt—S as opposed to Pt—N bond length [176].

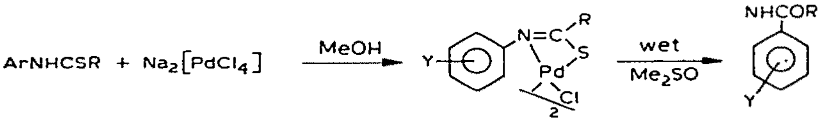
Earlier suggestions that the *S*-dealkylation of coordinated thioethers occurs in a manner similar to the Zeisel ether cleavage have received further support from the observation that, in addition to dimethylformamide, nucleophiles such as thiocyanate or iodide can promote *S*-dealkylation {reaction (59)}.



(59)

Only MeSCN, and not MeNCS, is formed suggesting that the reaction involves nucleophilic attack by NCS^- on the thioether sulphur atom [177].

Thioanilides react with $Na_2[PdCl_4]$ to form complexes which react with wet dimethylsulphoxide to yield amides {reaction (60)}. The net result is desulphurisation of the thioanilide, which can be made catalytic [178].



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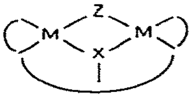
Attempts to prepare binuclear palladium(II) and platinum(II) complexes (33) in order to look for novel chemistry at the bridgehead *Z* position have

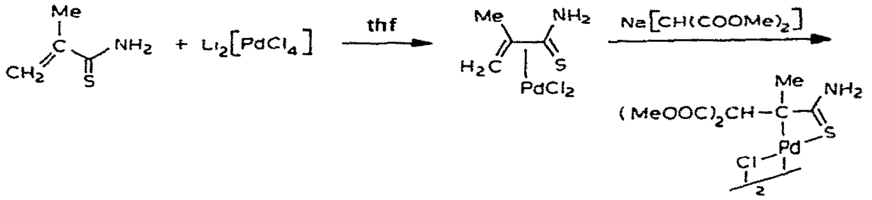


(33)

shown that if X = O, Z must be a good bridging ligand, although when X = S, weaker bridging ligands, Z (such as carboxylate) can be accepted [179—181].

5.5.2.11 Multidentate sulphur—carbon donor ligands

α,β-unsaturated thioamides react with $Li_2[PdCl_4]$ to form much stronger complexes than their oxo-analogues, suggesting strong coordination through sulphur is involved {reaction (61)} [182].



(61)

5.5.2.12 *Selenium donor ligands*

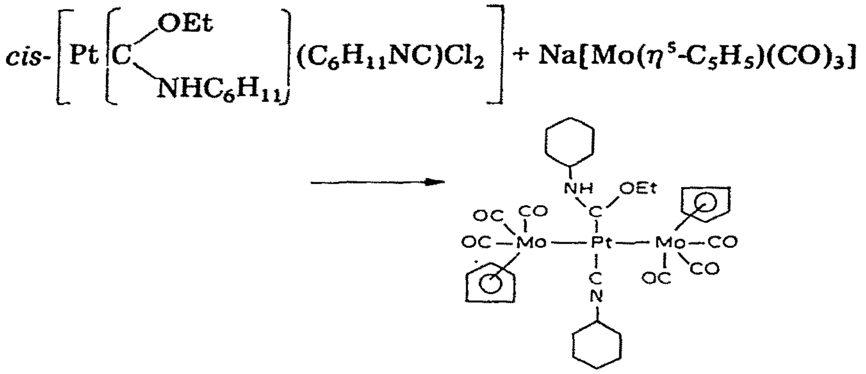
The fluorinated diselenoethers, $CF_3SeCH_2CH_2SeCF_3$ and $CH_3SeCF_2CF_2SeCH_3$, readily form $[M(Se^{\frown}Se)Cl_2]$ (M = Pd or Pt) whereas, of the sulphur analogues, only $CF_3SCH_2CH_2SCF_3$ forms a complex and that only with platinum(II). Thus in these fluorinated ligands Se is a better donor than S [183]. Diselenocarbamate complexes have been studied electrochemically [184], by ^{77}Se NMR spectroscopy (which shows conclusively that the NMR equivalence of the two diselenocarbamate ligands in $[Pt(\{Me_2CHCH_2\}(\{Me_2CHCH_2\}_2NCSe_2)_2(PR_3)]$ occurs by an intramolecular not an intermolecular mechanism) [185], and by X-ray diffraction (of $[Pt\text{-}(Et_2NCSe_2)])$ [186]. The last result shows that Pt—Se bonds are susceptible to weakening and lengthening by high *trans*-influence ligands such as methyl groups.

5.5.2.13 *Tellurium donor ligands*

A number of *trans*-$[Pd(TeR_2)_2X_2]$ (X = Cl or SCN) complexes have been prepared and characterised. An X-ray diffraction study of *trans*-$[Pd(Te\{(CH_2)_3SiMe_3\}_2)_2(SCN)_2]$ has shown that the configuration at tellurium is pyramidal, with a stereochemically active lone-pair of electrons at one corner of the tetrahedron. The Pd—Te bond length (2.606(1) Å) is only slightly shorter than the sum of the covalent radii (2.63 Å), suggesting little, if any, Pd—Te π-bonding [167].

5.5.2.14 *Molybdenum donor ligands*

An unusual platinum(II)-molybdenum complex has been prepared, by reaction (62), with fairly short Pt—Mo bonds (2.889(2) Å), which suggest strong Pt—Mo bonding [187]. The Pt—Mo stretching vibration is assigned to a band at 156 cm^{-1}.



$$cis\text{-}\left[Pt\left[C\begin{matrix}OEt\\NHC_6H_{11}\end{matrix}\right](C_6H_{11}NC)Cl_2\right] + Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$$

(62)

5.5.3 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. This follows from the discovery that *cis*-$[Pt(NH_3)_2Cl_2]$ is active against certain tumours. Since most biological molecules bind through *N*, *O* or *S* donor sites, it is appropriate to consider such molecules at this point.

5.5.3.1 Amino-acids

Platinum(II) complexes of both unidentate and bidentate β-alanine (AH), $K[Pt(NO_2)_2A]$ and $[Pt(NO_2)_2(AH)_2]$, that also contain nitro-groups, have been reported [188]. A thorough investigation of the complexing ability of methionine with palladium(II) has led to the synthesis of complexes in which methionine is unidentate (through S), or bidentate through either S and N or (under alkaline conditions) S and O [189]. Similarly, cysteine bonds to platinum(II) through O, S or N, the exact mode of coordination being critically dependent upon the pH [190]; *S*-methyl cysteine and glutathione have been shown to bond through S and N [191,192]. X-ray diffraction studies of [Pd(L-tyrosinate)$_2$], [Pd(L-serinate)$_2$] and [PdCl$_2$(DL-methionine)] have been reported [193—195]. Solution and solid-state circular dichroism studies of amino-acid complexes of palladium(II) [196] and platinum(II) [196, 197] show a fairly consistent pattern which is opposite to that of dipeptide complexes, although at present there is insufficient structural data to understand why this should be so. Stability constant studies have been reported for $[PdCl_4]^{2-}$ with glutathione [198,199], and for palladium(II) and platinum(II) with aspartic, glutamic, aminoadipic and aminopimelic acids [200]. The alkaline hydrolysis of glycine chelates of platinum(II), which occurs with ring opening, has shown the formation of stable hydroxo-complexes {reactions (63) and (64)} [201]. The kinetics of ring closure by serine and β-phenylalanine on platinum(II) have been studied [202,203].

$$[Pt(en)(gly)]^+\,Cl^- + OH^- \underset{40^\circ C;\ 0.1\,M\ KNO_3}{\overset{K = 3.4 \times 10^3}{\rightleftharpoons}} [Pt(en)(gly)OH] + Cl^- \tag{63}$$

$$cis\text{-}[Pt(gly)_2] \underset{40^\circ C;\ 0.1\,M\ KNO_3}{\overset{OH^-;\,K = 3.56 \times 10^3}{\rightleftharpoons}} [Pt(gly)_2(OH)]^- \overset{OH^-,\,K = 8.0 \times 10^5}{\rightleftharpoons} [Pt(gly)_2(OH)_2]^{2-} \tag{64}$$

The *cis* to *trans* isomerisation of *cis*-$[Pt(glycine)_2X_2]$, X = halide, occurs exothermally [204]. The thermal stabilities of a series of platinum(II)—glycine and —haloglycine complexes have been determined [205,206].

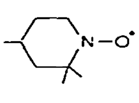
5.5.3.2 Peptides

Glycylglycine and glycyl-α-alanine bond to platinum(IV) as monodentate ligands through their—NH_2 groups [207]. Glycylmethionine and α-alanylmethionine react with *cis*-$[Pt(NH_3)_2Cl_2]$ and *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$ to form complexes in which the thioether moiety is coordinated to platinum

[208]. Cyclo-L-methionyl-L-methionine acts as a bidentate thioether ligand towards $PdCl_2$ and $PtCl_2$ [209]. ^1H NMR studies of the palladium(II) complexes of alanyltyrosine and D-leucyltyrosine have shown that the mode of coordination, which is pH dependent, plays an important part in determining the conformation of the dipeptide in solution [210].

5.5.3.3 *Nucleic acids and nucleosides*

The complexes formed between platinum(II) and DNA constituents have been reviewed [211]. The interaction of *cis*-$Pt^{II}(NH_3)_2$ with imidazole, pyrimidine, inosine and guanosine has been studied by ^{13}C NMR spectroscopy, for which water is a far superior solvent to dimethylsulphoxide because with the latter solvolysis and exchange effects significantly reduce the ^{13}C NMR resolution [212]. Although only one diastereoisomer of the guanosine complex is obtained in the crystal, two diastereoisomers which interconvert rapidly are present in solution [213]. Inosine-5′-monophosphate binds to *cis*-$Pt^{II}(NH_3)_2$ through N^7 [214], inosyl(3′-5′)inosine binds through N^7 in each ring, and adenylyl(3′—5′)adenosine binds through N^7 in only one ring [215]; adenine in *trans*-$[Pd(PBu_3)_2(adeninate)_2]$ is also bound through N^7 [216]. Equilibrium constants have been determined for the interaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with 1-methylguanosine, 7-methylguanosine and 1-methyladenosine [217]. The use of spin labelled complexes $[PtCl_2(NH_2Y)]$ (where Y = (34) or (35)) yields both quantitative and qualitative information about the site of platinum(II) interaction with deoxyguanosine [218]. Crystal structures have been reported for $[Pt(dien)(inosine)][NO_3]_2 \cdot H_2O$, $[Pt(dien)(guanosine)][ClO_4]_2$, and $[ThH][Pt(Th)Cl_3]$ (Th = theophylline = (36)) [219—221], as well as powder diffraction data for $[Pd(imidazole)_4]Cl_2$, $[Pd(N\text{-}Me\text{-}imidazole)_4][PdCl_4]$ and *cis*- and *trans*-$[PtCl_2(N\text{-}Me\text{-}imidazole)_2]$ [222,223].



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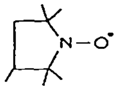

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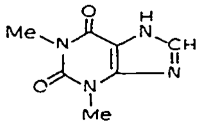

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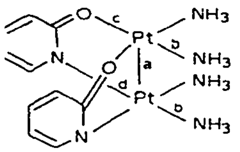
Circular dichroism has been used in studying the interaction of palladium(II) with gelatin; the nature of the donor groups involved depends on the pH [224]. Thyamine in "platinum-thymine blue" is probably bound through N^1, since the crystal structure of $[Pt(NH_3)_2(thymine)(1\text{-}methylcytosine)][ClO_4]$ shows such coordination. There is, however, evidence that thymine can also bind platinum through N^3 [225]. The "platinum blue" formed by 1-methylnicotinamide has been prepared, but its structure is unknown [226]. The degree of binding of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ to four homopolynucleotides has been studied spectrophotometrically [227].

^{15}N NMR spectroscopy yields ^{15}N chemical shifts and ^{195}Pt—^{15}N coupling constants that provide a potentially very useful technique for determining the mode of binding of nitrogen donors in cells to *cis*-$Pt(NH_3)_2$ [228]. Both *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ bind and produce cooperative changes in closed and nicked circular duplex DNA's. Covalent binding of both complexes to closed circular DNA alters the degree of supercoiling, presumably by disrupting and unwinding the double helix [229]. $[Pt(bipy)(H_2O)_2]^{2+}$ reacts with DNA to form an initial intercalation complex between the DNA bases and then, in a second step, coordinates to vertically-positioned nitrogen donors belonging to adjacent bases [230]. A similar effect occurs when $[Pt(2,2',2''\text{-}terpy)(SCH_2CH_2OH)]^+$ reacts with both deoxycytidyl(3',5')-deoxyguanosine [231] and polyadenylatepolyuridylate [232]. The introduction of bulky groups into platinum(II)-dipeptide complexes has been shown by ^1H and ^{13}C NMR spectroscopy to modify their coordinating ability towards ATP and ADP nucleotides [233,234]. During the course of studying the binding of *cis*-$[Pt(NH_3)_2Cl_2]$ to polynucleotides, it was found that "platinum blues" are formed with polyuridine, thymine and uracil, and that these "platinum pyrimidine blues" have high anti-tumour activity across a broad spectrum of tumours and low renal toxicity, as compared to that of *cis*-$[Pt(NH_3)_2Cl_2]$ [235]. Since their compositions were uncertain, a model complex with α-pyridone was prepared, $[Pt_2(C_5H_4NO)_2(NH_3)_4]_2[NO_3]_5 \cdot H_2O$, which involved $[Pt_2(NH_3)_4(C_5H_4NO)_2]$ units, (37); it was found that the amidate nitrogens



a = 2 2779 Å,
b = 2 06 Å,
c = 2 04 Å,
d = 2 05 Å.

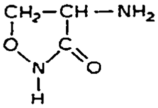
(37)

appeared to labilise the ammonia ligands *trans* to them, which suggests that the platinum(II) atom of *cis*-$[Pt(NH_3)_2Cl_2]$ may bind to DNA through four coordination sites rather than two as normally considered. This lability would be consistent with the ineffectiveness of *trans*-$[Pt(NH_3)_2Cl_2]$ where no labilization of ammonia would follow DNA binding [235].

5.5.3.4 Cancer therapy and related topics

Following the approval of *cis*-$[Pt(NH_3)_2Cl_2]$ for use in cancer therapy in both the U.S. and the U.K. [236], a large number of platinum(II) and palladium(II) complexes have been screened. Useful compounds include *cis*-$[Pt\{trans\text{-}1,2\text{-}cyclo\text{-}C_8H_{14}(NH_2)_2\}(BrCH_2CO_2)]$ [237], *cis*-$[Pt(histamine)Cl_2]$ [238], *cis*-$[Pt(2\text{-}aminomethylpiperidine)Cl_2]$ [239], and a number of palladium(II) amine complexes (although these appear to be less effective than their platinum(II) analogues); *cis*-$[Pd(NH_3)_2Cl_2]$ and $[NH_4]_2[PdCl_4]$ are effective antivirals [240].

Since it has been suggested that the antibiotic action of tetracyclines may be related to their ability to form complexes, the reaction of cycloserine (38)



(38)

with $K_2[MX_4]$ (M = Pd or Pt; X = Cl, Br or I) to yield $[ML_2Cl_2]$, $[ML_3Br_2]_2$ and $[ML_3I_2]_2$ has been studied. It is claimed that cycloserine always binds through the carbonyl oxygen [241].

5.5.4 Complexes with Group (V) donor ligands

5.5.4.1 Unidentate amines

Interest in $[Pt(NH_3)_4]^{2+}$ salts has continued with studies of the far IR and Raman spectra of Magnus' Green salt [242], a full normal-coordinate analysis of $[Pt(NH_3)_4]^{2+}$ [243], the thermal decomposition of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ [244] and the polarised crystal absorption spectrum of $[Pt(NH_3)_4][SO_4]$ [245]. Ammine complexes of platinum(II) have been prepared by displacement of aqua and chloride ligands [246,247]. The barriers to NH_3 torsions have been shown to be low by inelastic neutron scattering [248]. Solid phase thermal transformation of $[AmH]_2[PdBr_4]$ becomes easier the more basic the amine [249].

^{195}Pt—^{15}N coupling constants in *trans*-$[PtCl_2(^{15}NH_2C_6H_{13})L]$ have been recorded for a range of L ligands; they vary from 138 to 336 Hz, and correlate linearly with $^1J_{^{195}Pt-^{31}P}$ in *trans*-$[PtCl_2(PBu_3)L]$. The amine complexes were prepared by reaction (65). The initial product is usually the *trans*-isomer

$$[PtLCl_2]_2 + 2\ C_6H_{13}{}^{15}NH_2 \rightarrow 2[PtCl_2(C_6H_{13}{}^{15}NH_2)L] \qquad (65)$$

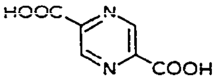
which is sometimes the only product, sometimes isomerises to the *cis*-isomer and, in the case of arsine ligands, disproportionates [250]. Pent-4-enylamines with methyl substituents on the 1, 2 or 3 carbon atoms cyclise in the presense of $[PtCl_4]^{2-}$ to yield the corresponding *cis*- and *trans*-dimethylpyrrolidine in a reaction that occurs with marked region- and stereoselectivity, as confirmed by X-ray determinations of the crystal structures [251].

A study of the kinetics and equilibria of the reversible redox reaction (66) has led to the suggestion that the reaction involves two successive one-electron transfer steps [252].

$$[Pt(NH_3)_4]^{2+} + 2\ Fe^{3+} + 2\ Br^- \rightleftharpoons trans\text{-}[Pt(NH_3)_4Br_2]^{2+} + 2\ Fe^{2+} \qquad (66)$$

5.5.4.2 Heterocyclic nitrogen compounds

Palladium(II) and platinum(II) complexes of pyrazine-2,5-dicarboxylic acid, (39), have been prepared as potential semiconductors; they have high resistivities [253]. 2,5-diphenylpyrazine, (40), forms a palladium(II) complex, which



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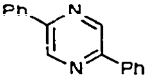

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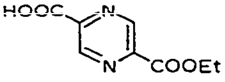
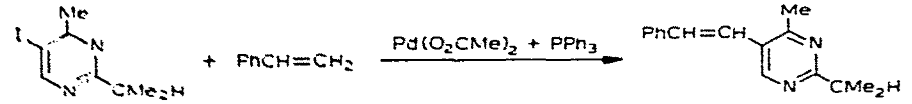


(41)

reacts with carbon monoxide in ethanol to yield (41) [254]. *Cis*-[PtL_2Cl_2] (where L is a pyrimidine) have been prepared and isomerised to the *trans*-products by heating in dimethylsulphoxide [255]. Olefins react with 5-iodopyrimidines, in the presence of [$Pd(O_2CMe)_2$] and triphenylphosphine, to give cross-coupled products; 2- and 4-iodopyrimidines, by contrast, couple together independent of the presence of olefin {reactions (67) and (68)} [256]. A series of palladium(II) and platinum(II) imidazole and benzimidazole complexes have also been described [257—260].



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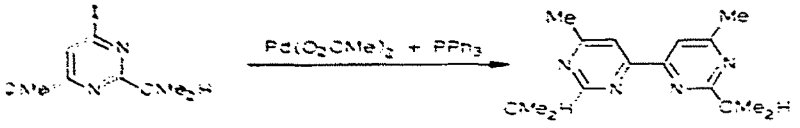
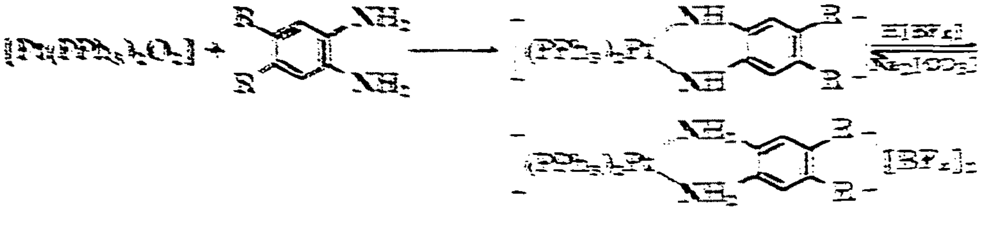


(68)

5.5.4.3 *Bidentate amines*

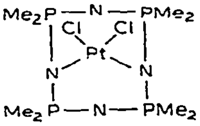
A wide range of complexes of bidentate amines have been described [261]. These include complexes of 2,6-diaminopyridine, of which the [$PtLCl_2$] complex shows high antimitogenic behaviour [262], $(HOOCCH_2NHCH_2)_2$ and edta [263,264], a series of optically active amines [265] including R,R- and R,S-$H_2NCH(Ph)CH_2CH(Ph)NH_2$ [266], R-$NH_2CH(Ph)CH_2NH_2$ [267], *N*-alkyl-substituted(S)-1,2-diaminopropanes [268], S,S-2,4-diaminopentane (for which both CD spectroscopy and X-ray diffraction have been used to study the bisdiamineplatinum(II) cation) [269], *cis*-3,5-diaminopiperidine (which failed to yield an octahedral palladium(II) complex) [270], $Me_2N(CH_2CH_2)_3N$ (which only coordinates to palladium(II) as a tridentate ligand) [271], 8-aminoquinoline [272], and $Me_2N(CH_2)_nNMe_2$ (n = 5, 7 or 10; which like $Me_2NN{=}CH(CH_2)_nCH{=}NNMe_2$ forms *trans*-[$PdCl_2$(diamine)$_2$]) [273,274]. 1,2-Diaminobenzenes react with [$Pt(PPh_3)_2O_2$] to yield imino complexes which can be reversibly protonated {reaction (69)} [275].



(69)

5.5.4.4 *Multidentate amines*

The circular dichroism spectra of [Pd{$NH_2CH(Me)CONH(CH_2)_nNHCOCH(Me)NH_2$}] (n = 2 or 3) have been determined [276]. The cyclic ligands $NH(CH_2)_2NH(CH_2)_2NH(CH_2)_x$ (x = 2 or 3) form [PdCl(cyclo-[illegible])][ClO_4], with the *N*-donor adjacent to $(CH_2)_r$ protonated; when $r = 6, 7, 8$ or 10, $[PdCl(\textit{cyclo}\text{-}N_3)][ClO_4]$ is formed, in which the ligand is tridentate with the $(CH_2)_r$ chain spanning two *trans*-sites [277]. Preparative details for the formation of $(Me_2NCH_2CH_2)_3N$, Me_5dien and $MeEt_4$dien complexes of the form [PdCl(polyamine)][PF_6] and an X-ray diffraction study of $[Pd(dien)Br]_2[PtBr_4]$ have been published [278,279]. The cyclophosphazene $(NPMe_2)_4$ forms a complex with platinum(II), (42), in which the ring is in a saddle conformation with σ- and π-type interactions between the platinum and the ring [280].

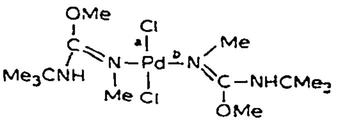


(42)

5.5.4.5 *Imines*

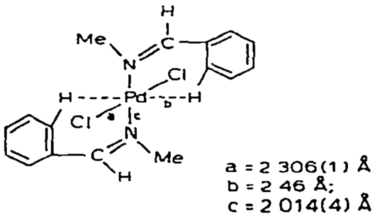
X-ray diffraction has shown that the methyl groups in $[Pd(\eta^3\text{-}C_3H_5)(8,8'\text{-dimethyl-}2,2'\text{-biquinoline})][ClO_4]$ would severely clash with the η^3-allyl ligand were it not for the palladium atom lying 1.10 Å out of the plane of the bidentate biquinoline ligand, which results in the nitrogen atoms being pyramidal [281]. It has been confirmed [282] that hydroxide attack on bis(2,2'-bipyridine)platinum(II) complexes occurs on the platinum atom, and not on the bipyridine ring, as suggested earlier [283,284]. Palladium(II) and platinum(II) complexes of the benzodiazepines librium, mogadon and valium have been characterised [285]

X-ray diffraction has been used to determine the structures of (43)—(45)



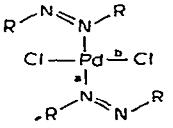
a = 2 307(3) Å
b = 2 017(5) Å

(43)



a = 2 306(1) Å,
b = 2 46 Å;
c = 2 014(4) Å

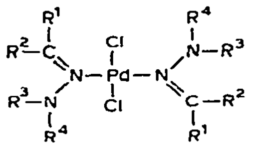
(44)



for R = $-C_6H_{11}$: a = 2 02 Å; b = 2 31 Å.
for R = $-CHMe_2$: a = 2 009 Å; b = 2 302 Å.

(45)

[286—288]. A number of papers have appeared concerning the structure of hydrazone complexes which have been shown to exist in two isomeric forms (46) and (47), which differ in the mutual orientation of the hydrazone



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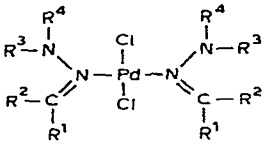
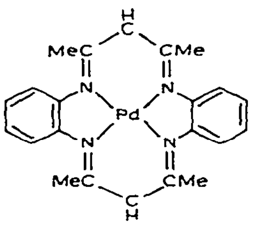


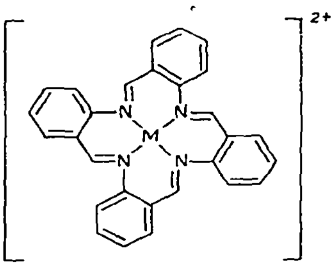
(47)

ligands [289—292]. The α-diimine skeleton in $Me_3CNCH{=}CHNCMe_3$ is very flexible, bonding in both the *trans*-form between two platinum(II) atoms and in the *cis*-form as a chelate ligand [293]. *N,N'*-diarylformamidines and 1,3-diaryltriazenes, RN=CH—NHR and RN=N—NHR, act as unidentate ligands in $[Pd(\eta^3\text{-}C_3H_5)Cl(L)]$ complexes, which are fluxional due to exchange between the two nitrogen donor sites [294]. Palladium(II) and platinum(II) complexes of the macrocyclic N_4 ligands (48)—(50) have been prepared [295—297]. The electronic properties of both palladium(II) and platinum(II) porphyrin and phthalocyanine complexes and their derivatives have been studied [298—300]. The amide ligand (51) reacts with $K_2[PdCl_4]$ to form a complex



Pd—N = 1.996(5) Å average

(48)



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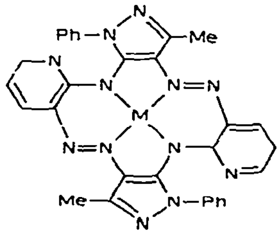
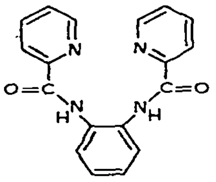


(50)



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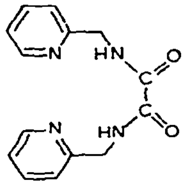
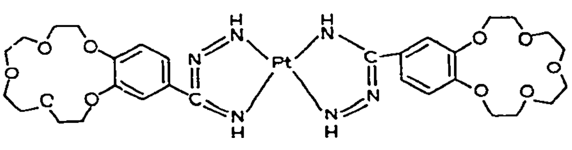


(52)

in which the amide groups are deprotonated and all four nitrogens bond to palladium(II) [301]. A similar complex is also formed by the oxamide (52), although this also forms complexes in which the amide nitrogens are protonated and only the pyridines bond to the metal [302].

Triazabutadiene and cyclopalladated oxime complexes (53) and (54), containing crown ethers, have been described [303]. X-ray diffraction and resonance Raman spectroscopy have been used to study the bis(dimethylglyoximate) complexes of palladium(II) and platinum(II) [304,305]. Other oximes studied include 4-chromanone oxime [306], 2,3,6,7-octanetetronetetraoxime (whose palladium(II) complex can reversibly take up carbon monoxide) [307], phenylazoacetaldoxime [308], 1,2-benzoquinonedioxime (which forms a completely delocalised π-electron system, and whose complexes on partial oxidation with iodine have "one-dimensional electrical conductances") [309,310], alkyl- and aryl-α,β-dionedioximes (whose complexes crystallise in columnar stacks) [311], and a tetradentate α-aminooxime [312]. Bis(isonitrosomethylacetoacetateimino)palladium(II) undergoes an interesting linkage isomerisation on heating {reaction (70)} [313].



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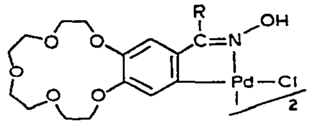

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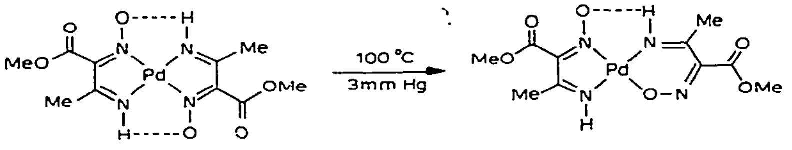


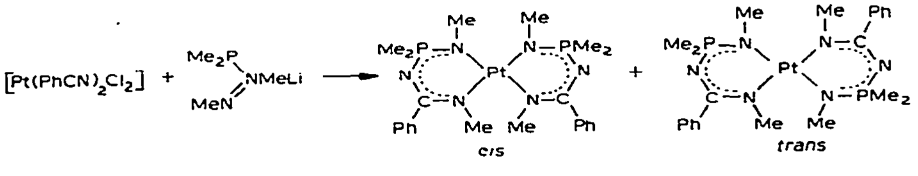
(70)

5.5.4.6 *Nitrosyl and nitro-complexes*

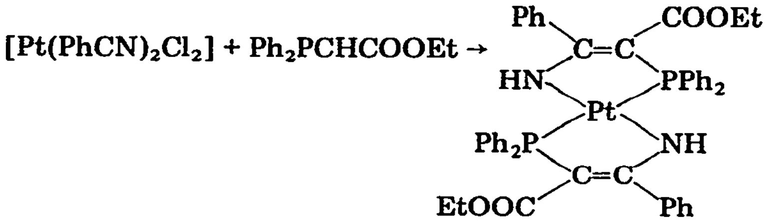
Nitrosylation of $[Pt(Me_2SO)Cl_3]^-$ yields $[Pt(Me_2SO)Cl_3(NO)]$ which, on storage, disproportionates to $[Pt(Me_2SO)_2Cl_2]$ and chloronitroplatinum(IV) complexes [314]. The *N*-bonded nitro-complex $[Pd(MeEt_4dien)(NO_2)]^+$ isomerises to be *O*-bonded nitrito-complex $[Pd(MeEt_4dien)(ONO)]^+$ on irradiation [315].

5.5.4.7 *Nitrile complexes*

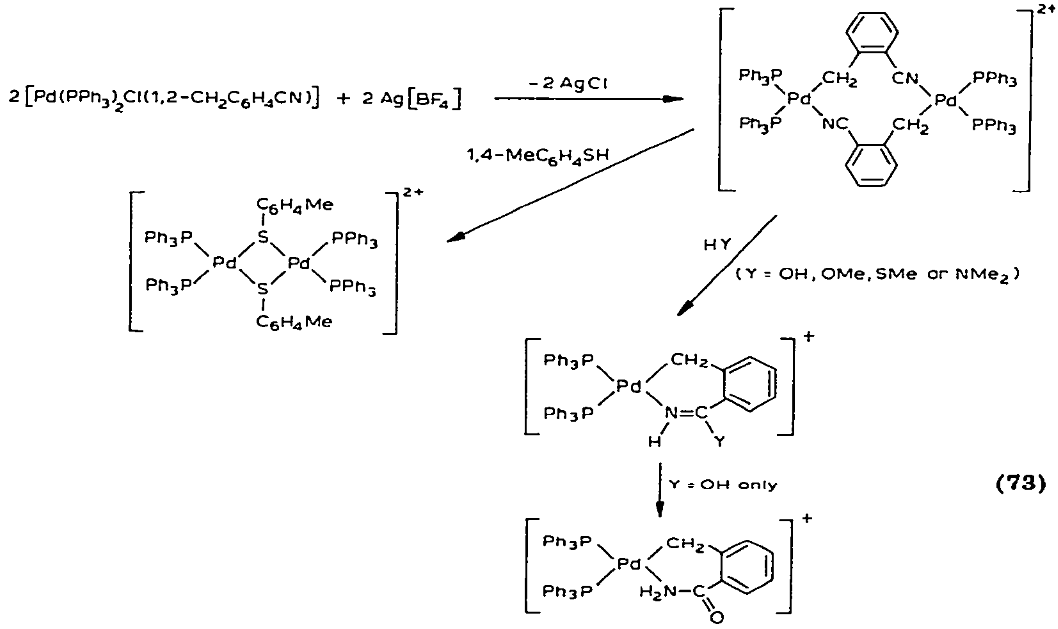
P,N-ylides and α-phosphinocarbanions insert into the benzonitrile-platinum bond {reactions (71) and (72)} [316,317].



(71)

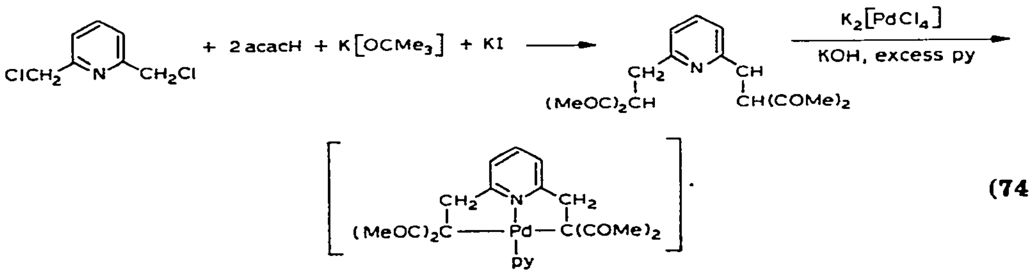

(72)

The 1,2-cyanobenzyl bridged dimers of palladium(II) undergo interesting reactions with weak acids {reaction (73)} [318].

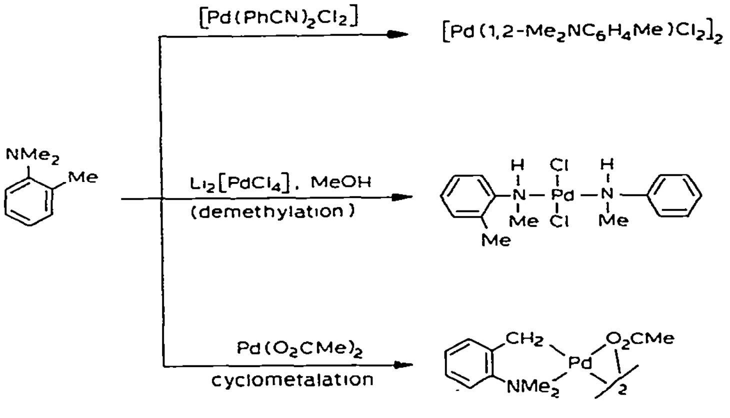

(73)

5.5.4.8 *Carbon—nitrogen donor ligands*

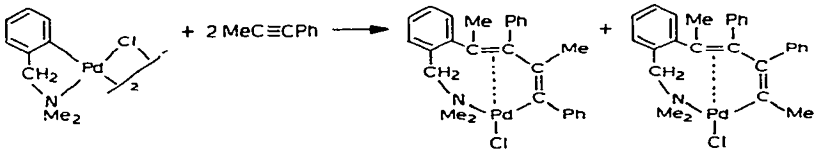
Cis-[Pt(PPh_3)(C_2H_4)Cl_2] reacts with dimethylamine to form the 4-membered ring complex [Pt($Me_2NCH_2CH_2$)(PPh_3)Cl]; this is unexpected and is probably due to the steric bulk of triphenylphosphine, since replacing it by dimethylsulphoxide results in the expected [Pt($CH_2CH_2NMe_2H$)(dmso)Cl_2] [319]. A CN_2 ligand has been prepared by reaction (74) [320]. 1,2-Methyldimethyl-


(74)

amine reacts with palladium(II) to give straightforward amine complexes as well as both demethylation at nitrogen and cyclometalation (Scheme IV) [321]. Other ligands that yield metalated products with palladium(II) include Me_2NCH_2-ruthenocene and the nitroxyl radical of imidazoline [322,323]. Two acetylene molecules insert into 1,2-metalated dimethylbenzylamine {reaction (75)} [324]; only one olefin inserts into this Pd—C bond {reaction (76)}, unless the aryl ring is activated with an —HgOMe substituent {reaction (77)} [325]. 1-$Me_2NCH(Me)$-ferrocene reacts with palladium(II) to form optically active chelate complexes, which on treatment with PhCOCH=CH_2 or CO yield optically active ferrocene derivatives through insertion reactions into the Pd—C bond [326].



Scheme IV



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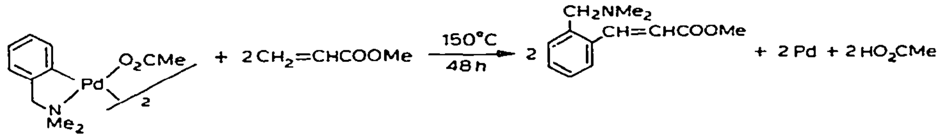

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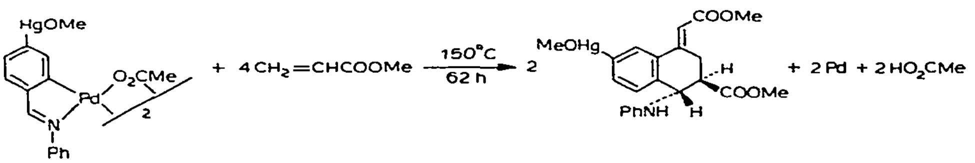


(77)

5.5.4.9 Monodentate tertiary phosphines

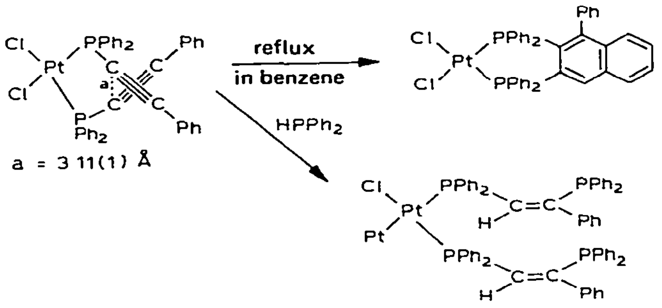
The reactions of $[Pt(PPh_3)_3Cl][Ti_3Cl_{11}]$ have been further studied; the two ions react independently [327]. *Cis*-$[Pd(PPh_3)_2Cl_2]$ has been reported several times in the literature [328]; although it has not in fact been isolated [144,329], it can be formed in solution [329]. PPh_2CH_2COOH forms a normal *trans*-complex (*trans*-$[PdBr_2(PPh_2CH_2COOH)_2]$) with Pd—P bonds of 2.322(2) Å and Pd—Br = 2.447(1) Å [330]; if the preparation is carried out using PPh_2CH_2COONa at a pH below 7, then $[Pd(PPh_2CH_2COO)_2]$, in which the phosphine also bonds through oxygen, is formed [331]. PPh_2CH_2CN, PPh_2CH_2COOEt and $P(NEt_2)_3$ form conventional phosphine complexes with palladium(II) and platinum(II) [332,333]. Thin layer chromatography on alumina, using benzene—dioxane as the mobile phase, is a useful way of separating palladium—phosphine complexes [334]. Reaction (78) has provided a clean route to the preparation of a number of chloride-bridged palladium(II) dimers; replacing $PdCl_2$ by $Na_2[PdCl_4]$ either yields complex products or no reaction at all [335]. When complexes such as *trans*-$[Pd(PPh_3)_2Br_2]$

$$[PdL_2(C_6F_5)_2] + PdCl_2 \xrightarrow[3\text{—}20\ h]{Me_2CO\ at\ reflux} [Pd(C_6F_5)(\mu\text{-}Cl)L]_2 \qquad (78)$$

(L = N, P, As, Sb or S-donor)

are heated in air, an inner-sphere oxidation occurs to yield $OPPh_3$ [336]. The photochemical conversion of norbornadiene to quadricyclane is a potential energy storage system; phosphinated polystyrene supported palladium(II) chloride has been examined as a catalyst for the release of the stored energy, but it is less effective than $[Pd(PPh_3)_2Cl_2]$ [337].

On mixing PPh_3, styrene and $Pd(O_2CMe)_2$ in ethanoic acid at room temperature, *trans*-stilbene and a mixture of $PhP(O)(OH)_2$, $Ph_2P(O)OH$ and Ph_3PO are formed; the P—C bond cleavage is initiated by nucleophilic attack by ethanoate on the phosphorus [338]. On treating $[Pd(PPh_3)_2Cl_2]$ with 4-tolyllithium, P—C bond cleavage occurs to yield all the possible dibenzenes and PPh_2(4-tolyl) [339]. Two papers have described unusual reactions of *cis*-complexes of $PPh_2C{\equiv}CPh$, in which the two acetylene groups are constrained close together {reaction (79)} [340,341].

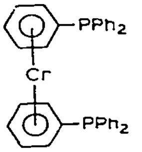


(79)

One of the rapidly developing techniques for studying metal—phosphine complexes is NMR spectroscopy. Two books have appeared [342,343], one exclusively on ^{31}P and ^{13}C NMR spectroscopy of transition metal—phosphine complexes [342]. Although most ^{31}P NMR spectra are recorded with proton decoupling, one paper has appeared describing both the effects of Nuclear Overhauser enhancement of the ^{31}P signals (which may develop when the protons are irradiated) and the ^{31}P spin—lattice relaxation time in metal—phosphine complexes [344]. The results show: (1) Nuclear Overhauser enhancements are small (0.8 to 1.2); (2) T_1 relaxation stems mostly, and in some cases exclusively, from ^{31}P—^{1}H dipole—dipole relaxation; (3) potential differences in Nuclear Overhauser enhancements must be considered when comparing integrals in $^{31}P\{^{1}H\}$-spectra; (4) both Nuclear Overhauser effects and T_1 values are solvent dependent; (5) T_1 decreases with decreasing temperature; (6) T_1 increases with increasing molecular weight of trialkylphosphines; (7) arylphosphines give larger T_1's than alkylphosphines due to the smaller number of protons at the first carbon atom and hence less efficient dipole—dipole relaxation [344]. Dynamic behaviour due to restricted rotation about P—C bonds has been confirmed in $[Pt(\eta^3\text{-allyl})(PCych_3)_2][PF_6]$ and *trans*-$[Pt\{P(C_6F_5)_3\}X_2L]$ ($L = P(C_6F_5)_3$, PPh_3, PMe_2Ph or $PMePh_2$) [345,346]. The ^{31}P NMR chemical shift progresses linearly to higher applied field whilst the energy of the lowest d—d band falls monotonically with increasing metallic charge in a series of d^8 isoelectronic and isostructural complexes [347]. *Cis*- and *trans*-isomers can be distinguished by their ^{195}Pt—^{31}P coupling constants, which depend mainly on the Pt—P bond lengths and are about 1000 Hz larger in *cis*- than *trans*-complexes [348]. An XPES study of Pd(0), Pd(I) and Pd(II) triphenylphosphine complexes has shown, as for the corresponding platinum complexes, that there are no well-defined boundaries between the separate oxidation states [349].

5.5.4.10 Bidentate tertiary phosphines

Complexes of a number of novel tertiary phosphines (55)—(57) have been described [350—352]. A number of potentially tridentate polyphosphines only coordinate in a bidentate fashion to *cis*-$PtMe_2$ and give rapid exchange between free and coordinated phosphorus [352]. The structure of $[Pt\{(CMe_3)_2P(CH_2)_3P(CMe_3)_2\}Cl_2]$ has been determined by X-ray diffraction [353]. The R,R and S,S forms of (58) have been separated through the 1,2-metalated palladium(II) complex of dimethyl(α-methylbenzyl)amine [354].



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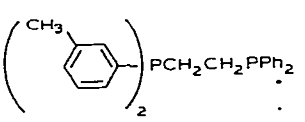
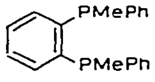


(56)

$Ph_2P(CH_2)_3PPh(CH_2CH_2CH{=}CH_2)$

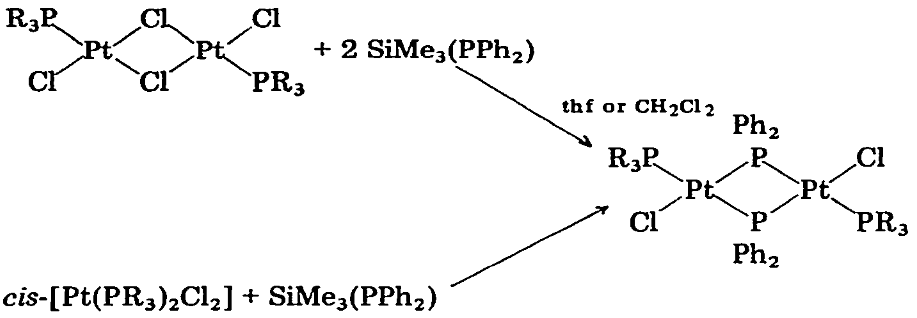
(57)



(58)

5.5.4.11 Phosphide ligands

Bridged diphenylphosphide complexes have been prepared by reactions (80) and (81) [355].



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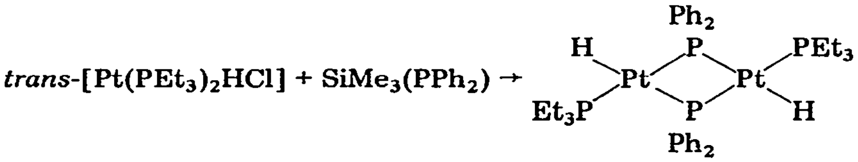


(81)

5.5.4.12 Ambidentate phosphorus—sulphur or phosphorus—oxygen ligands

[Pd(SPCy$_3$)Cl$_2$] is formed by reaction of K$_2$[PdCl$_4$] with SPCy$_3$ [356]. Trimethylphosphite reacts with K$_2$[PtCl$_4$] to give dimethylphosphite complexes {reaction (82)} [357]. X-ray diffraction has shown that [Pt(PEt$_3$)$_2$Cl(OPF$_2$)]$_2$

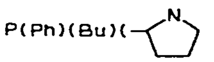
$$K_2[PtCl_4] + 4\,P(OMe)_3 + 4\,H_2O \rightarrow 2\,KCl + 4\,MeOH + 2\,HCl$$

$$\begin{tikzcd} & + [Pt\{OP(OMe)_2\}_2\{HOP(OMe_2)\}_2] \arrow[dl, "diars"'] \arrow[d, "cis\text{-}[Pt(PPh_3)_2Cl_2]"] \\ 2\,HOP(OMe)_2 + [Pt\{OP(OMe)_2\}_2(diars)] & 2[Pt(PPh_3)Cl\{OP(OMe)_2\}\{HOP(OMe)_2\}] \end{tikzcd}$$

(82)

involves one terminal and one bridging difluorophosphate ligand, with P—O bond lengths of 1.465 Å (terminal) and 1.498 Å (bridging) [358]. [Pt{(RO)$_2$PS$_2$}$_2$] and [Pd{R(R'O)PS$_2$}]$_n$ are reduced polarographically in one irreversible diffusion-controlled step in dimethylformamide [359].

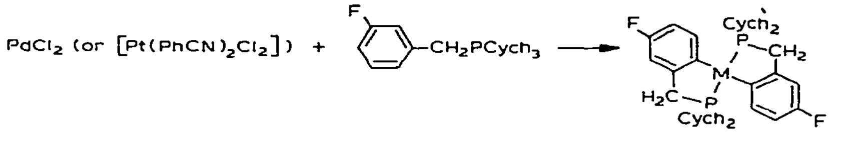
5.5.4.13 Bidentate phosphorus—nitrogen ligands



reacts with [Pd(MeCN)$_2$Cl$_2$] to form a pair of diastereoisomers in which the ligand is coordinated through both phosphorus and nitrogen. The diastereoisomers crystallised in different forms, needle and block, that were separated by hand-picking [360].

5.5.4.14 Multidentate phosphorus—carbon ligands

$PhCH_2PCych_2$ and its 1,3-fluoroderivative react with palladium(II) or platinum(II) to give 1,2-metalated derivatives with the metalation site *para* to fluorine {reaction (83)}. For palladium(II), this was taken to indicate a nucleophilic mechanism, although the long reaction times necessary with platinum(II) did not allow a radical mechanism to be completely excluded in that case [361]. An oxygen group accelerates metalation at an adjacent carbon atom, as shown by comparing the rates of platination of $P(CMe_3)_2(CH_2OMe)$ and $P(CMe_3)_2(OCH_2CH_3)$ [362]. The complex *trans*-$[Pt\{P(2\text{-tolyl})_3\}_2I_2]$ fails to undergo metalation which is ascribed to the very large bulk of the ligand, cone angle 183°, which prevents the necessary internal rotations occurring [363]. The diphosphines $(CMe_3)_2P(CH_2)_nP(CMe_3)_2$ react with $[Pd(PhCN)_2Cl_2]$ to form dimeric $[PdCl_2\{(CMe_3)_2P(CH_2)_nP(CMe_3)_2\}]_2$ (when $n = 5, 7$ or 8) and with $[Pt(PhCN)_2Cl_2]$ to form monomeric *trans*-$[PtCl_2\{(CMe_3)_2P(CH_2)_5P(CMe_3)_2\}]$ (when $n = 5$). $[Pd(PhCN)_2Cl_2]$ also forms the volatile cyclometalated complex (59) and an analogous complex is formed with platinum(II), contaminated by a very similar species that is possibly an η^3-allylic complex (60). When polymeric $[PtCl_2\{(CMe_3)_2P(CH_2)_6P(CMe_3)_2\}]_n$ is treated with 1,1,1-trifluoroethanoic acid pure $[Pt(CF_3COO)\{(CMe_3)_2P(CH_2)_3CH(CH_2)_2P(CMe_3)_2\}]$ is formed in almost quantitative yield; the pure halide complexes can be prepared from this by metathesis [364].



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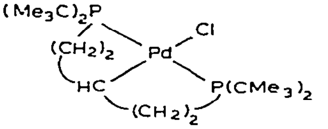
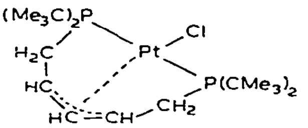


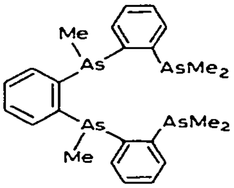
(59)



(60)

5.5.4.15 Arsine ligands.

There is "pseudo-octahedral" coordination about palladium in *trans*-$[Pd(AsPh_3)_2I_2]$ as a consequence of two hydrogen atoms from the phenyl ligands being 3.4 Å from the palladium [365]. A novel route has been described for the preparation of ditertiary arsine complexes $[Pt\{Ph_2As(CH_2)_nAsPh_2\}X_2]$ (X = Br, I or SCN) in which solid $K_2[PtCl_4]$ is treated with the ligand in chloroform; no reaction occurs until NaX is added. The advantage of the method is that chloroform only dissolves the ligand and the complex, which is therefore uncontaminated with NaX, a problem when ethanol, the more common solvent, is used [366]. Substitution reactions at square—pyramidal platinum(II) in $[Pt(RR,SS\text{-tpas})X]^+$, tpas = (61), follow a second-order rate



(61)

law and proceed through a transition state of enhanced coordination number. Since the ligand prevents any change of geometry occurring, it is suggested that nucleophilic attack occurs at the basal plane [367].

5.5.4.16 Stibine ligands

Trans-$[M\{(CMe_3)_3Sb\}Cl_2]_2$ (M = Pd or Pt) have been prepared by several routes, including reaction of $(CMe_3)_3Sb$ with $Na_2[PdCl_4]$, $PtCl_2$ or $[M(PhCN)_2Cl_2]$ [368].

5.5.5 Complexes with Group (IV) donor ligands

Clearly the majority of the complexes involving Group (IV) ligands are "organometallic complexes". These have been specifically excluded from this review unless it is believed that they have special or wide significance.

5.5.5.1 Carbonyl complexes

Good yields of *cis*-$[PtCl_2(CO)_2]$ can be obtained by heating $PtCl_4 \cdot 4\ H_2O$ in thionyl chloride solution at 110°C with carbon monoxide [369]; the use of thionyl chloride prevents hydrolytic side-reactions occurring. The rate of carbonylation of a series of dimeric palladium complexes $[LPdX_2]_2$, decreases in the order $L = Pr_2S \geqslant Pr_2Se > Me_2S \geqslant Me_2Se > Et_2Se > Et_2S$ [370]. Polymer supported carbonyl complexes have been prepared by displacing benzonitrile from $[Pd(polymer\text{-}PPh_2)(PhCN)Cl_2]$, a reaction that is analogous to reaction (84) [371]. A study of the force constants in *cis*-$[PtX_2(CO)_2]$ (X = Cl or Br) showed that the Pt—C stretching force constants are

$$[Pd(PhCN)_2Cl_2] + CO \xrightarrow[\text{room temp.}]{\text{benzene}} [Pd(PhCN)(CO)Cl_2] + PhCN \qquad (84)$$

proportionately more sensitive to the nature of the halide ligand than the C—O stretching force constants [372].

X-ray diffraction and ^{31}P NMR spectroscopy were used to study the products of reaction (85). It has previously been suggested that large $^{195}Pt—^{31}P$

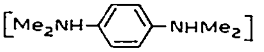
$$cis\text{-}[Pt(PMe_2Ph)Cl_2(CO)] + Et_2Hg \rightarrow cis\text{- and } trans\text{-}[Pt(PMe_2Ph)(\mu\text{-}Cl)(COEt)]_2 \qquad (85)$$

coupling constants are indicative of short Pt—P bonds [373]; however, the *trans*-isomer shows a large coupling constant and fairly typical bond lengths, suggesting that such a correlation breaks down when the complexes compared differ greatly [374]. In order to study the effects of the stereochemistry at platinum on the ability of alkyl groups to insert into Pt—CO bonds, all three isomers of $[Pt(PMePh_2)Cl(Ph)(CO)]$ were prepared; only the isomer with CO *trans* to $PMePh_2$ undergoes insertion to form the dimeric chloride-bridged acyl complexes, the other isomers merely eliminate CO. The ability of groups to promote insertion is $Et > Ph > Me > CH_2Ph(\approx 0)$ [375]. The reaction of *trans*-$[Pt(PPh_3)_2Cl(CO)][ClO_4]$ with a range of tin, lead, mercury and boron organoelement compounds results in replacement of the chloride ligand by an organic group in all cases; only with $Hg(4\text{-}MeC_6H_4)_2$ is even a small amount of the acyl complex formed [376]. Di-isopropylamine nucleophilically attacks a coordinated carbonyl ligand in *cis*-$[PtCl_2(CO)_2]$, to form the carbamoyl complex $[(CMe_2H)_2NH_2]_2[\textit{cis}\text{-}PtCl_2(CO)\{C(O)N(CMe_2H)_2\}]$, in which the carbamoyl ligand is planar and almost perpendicular (88.1°) to the platinum square—plane; thus both C and N are sp^2-hybridised [377].

5.5.5.2 Cyanide complexes

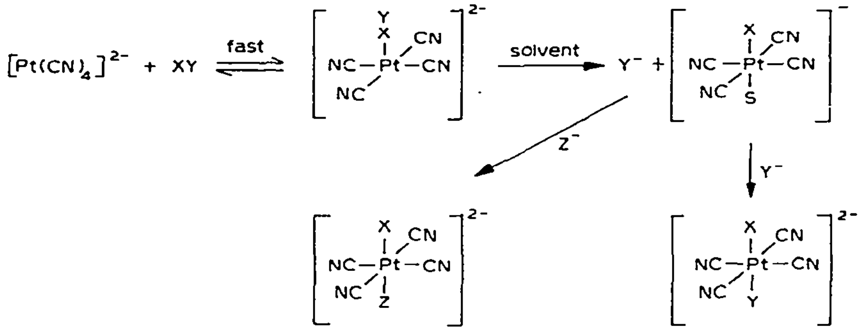
The electrochemical synthesis of $Ba[Pt(CN)_4] \cdot 4\,H_2O$, according to reaction (86), has been described [378], as have the crystal structures of

$$2\,Ba(CN)_2 + Pt_{\text{electrodes}} + 6\,H_2O \xrightarrow[15-20\,V]{a.c.,\ 5A} Ba[Pt(CN)_4] \cdot 4\,H_2O + Ba(OH)_2 + H_2 \qquad (86)$$

 $[Pt(CN)_4] \cdot H_2O$ and $Cs_2[Pd(CN)_4] \cdot H_2O$ [379,380].

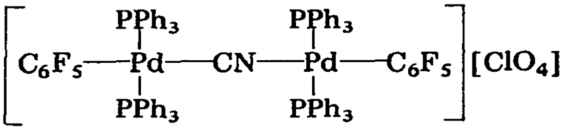
The integrated intensities of the C—N stretching vibrations in a number of cyanide complexes have been determined. They appear to give an indication of the extent of metal—cyanide π-bonding [381]. $Cs_2[Pt(CN)_4] \cdot H_2O$, although itself achiral, forms a helical vertical stack which conveys chirality. The circular dichroism spectrum of this complex in a chiral polymer (hydroxypropylcellulose) enabled the intramolecular charge transfer and exciton bands to be characterised. The effect on the optical properties of the phase changes that occur on heating, or subjecting to high pressure, a number of $[Pt(CN)_4]^{2-}$ salts have been studied [382—385]; it is possible to continuously tune to optical absorption between 3.3 and 1.35 eV by varying both the cation and the pressure [385].

The kinetics of the replacement of chloride by cyanide in $[PtCl_4]^{2-}$ indicate a typical two-term rate law [386]. A study of the oxidative-addition reactions of a number of reagents XY to $[Pt(CN)_4]^{2-}$ indicated the mechanism shown in reaction (87); when the reaction was carried out in the presence of an excess of a ligand Z^-, competition between Y and Z occurred [387]. Cyanide bridged palladium(II) complexes can be prepared by reactions (88) and (89) [388].



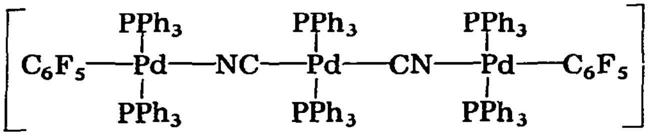
(87)

$[Pd(PPh_3)_2(CN)C_6F_5] + [Pd(PPh_3)_2(C_6F_5)(OClO_3)] \rightarrow$



$$\left[C_6F_5{-}\overset{PPh_3}{\underset{PPh_3}{Pd}}{-}CN{-}\overset{PPh_3}{\underset{PPh_3}{Pd}}{-}C_6F_5 \right][ClO_4] \qquad (88)$$

$[Pd(PPh_3)_2(CN)_2] + 2[Pd(PPh_3)_2(C_6F_5)(OClO_3)] \rightarrow$



$$\left[C_6F_5{-}\overset{PPh_3}{\underset{PPh_3}{Pd}}{-}NC{-}\overset{PPh_3}{\underset{PPh_3}{Pd}}{-}CN{-}\overset{PPh_3}{\underset{PPh_3}{Pd}}{-}C_6F_5 \right] \qquad (89)$$

5.5.5.3 Isonitrile and carbene complexes

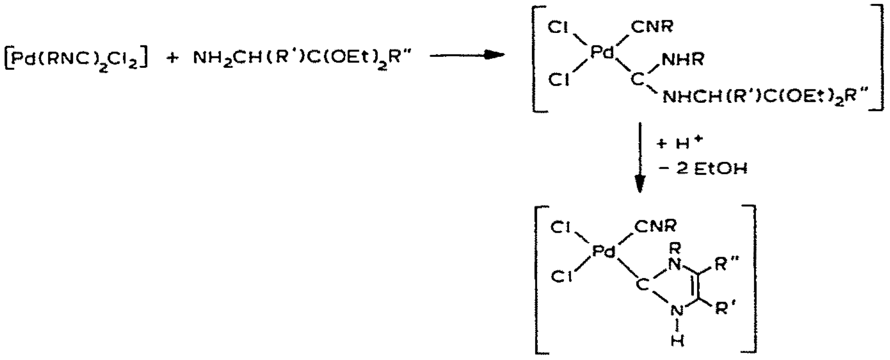
Trans-$[Pt(CNcyclohexyl)_2(SCN)_2]$ melts at 115°C and isomerises to the *cis*-isomer at 130°C indicating, together with previous results, that the *trans*-influence of cyclohexylisonitrile is greater than that of SCN^-, Cl^- and Br^-, but less than that of I^- [389]. Full preparative details for reactions (90)—(92) have been given [390]. α-Aminoacetals react with coordinated isocyanides to form diaminocarbene intermediates that can be isolated and characterised but which cyclise on protonation {reaction (93)} [391]. The electron-rich olefin, bis(1,3-diphenyl-2-imidazolidinylidene) (62) has been used to prepare the cyclopalladated carbene complex (63) [392].

$$trans\text{-}[Pt(PEt_3)Cl_2]_2 + 2\ RNC \xrightarrow{benzene} 2\ cis\text{-}[Pt(PEt_3)(RNC)Cl_2] \qquad (90)$$

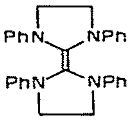
$$cis\text{-}[Pt(PEt_3)(RNC)Cl_2] + R'EH \xrightarrow[R'=alkyl\ or\ aryl]{E=O\ or\ NH} cis\text{-}[Pt(PEt_3)\{C(ER')(NHR)\}Cl_2] \qquad (91)$$

$$trans\text{-}[Pt(PEt_3)_2(PhNC)Cl][ClO_4] + EtNH_2 \rightarrow trans\text{-}[Pt(PEt_3)_2\{C(NHPh)(NHEt)\}Cl][ClO_4] \qquad (92)$$

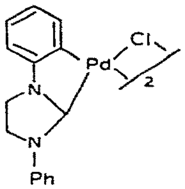
The synthesis of α-diazomethylpalladium(II) complexes has been achieved through reaction (94); an X-ray diffraction study of (64; R = COMe) suggests the CN_2 unit is a resonance hybrid of $>C{=}N^+{=}N^-$ and $>C^-{-}N^+{\equiv}N$ [393].



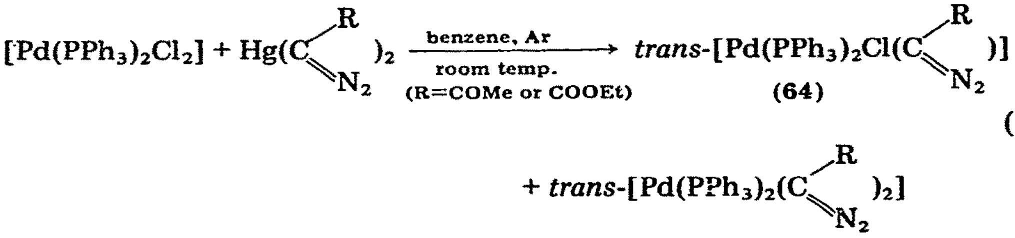
(93)



(62)



(63)



$$[Pd(PPh_3)_2Cl_2] + Hg(C{\overset{R}{\underset{N_2}{}}})_2 \xrightarrow[\text{room temp.}\ (R=COMe\ \text{or}\ COOEt)]{\text{benzene, Ar}} \textit{trans}\text{-}[Pd(PPh_3)_2Cl(C{\overset{R}{\underset{N_2}{}}})] \ (64) + \textit{trans}\text{-}[Pd(PPh_3)_2(C{\overset{R}{\underset{N_2}{}}})_2]$$

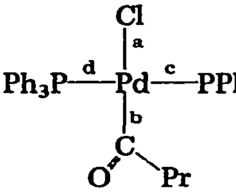
(94)

5.5.5.4 Alkyl and aryl complexes

^{1}H and ^{13}C NMR spectra have been recorded for the platinum(IV) complex formed by oxidative-addition of benzene to $Na_2[PtCl_4]$; this complex was previously thought to be an intermediate in the activation of benzene to H/D exchange by $Na_2[PtCl_4]$ [394]. Monohaloacyl complexes are of interest because they may lose carbon monoxide to form monohaloalkyl complexes, possible precursors of simple carbenes which are believed to be active olefin metathesis catalysts. Although some transition metals do form monochloroacetyl complexes, monochloroacetyl chloride reacts with $[Pt(PPh_3)_4]$ to yield $[Pt(PPh_3)_2Cl_2]$ and allene, probably through an initial oxidative-addition reaction [395]. The "non-bonded radius" of platinum(II) has been determined as 1.78 Å by measuring the angle Pt—C—Si in $[Pt(PPh_3)_2Cl(CH_2SiMe_3)]$ and assuming electronic effects tend to reduce this angle whilst steric effects increase it [396].

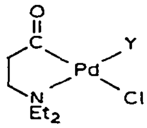
5.5.5.5 Acyl complexes

During the hydrocarboxylation of propene with carbon monoxide and butanol in the presence of $[Pd(PPh_3)_2Cl_2]$ and two equivalents of PPh_3, (65) was isolated [397]. The long Pd—Cl bonds in (65) and (66) are consistent with the Pd—O bond in (67) which is the longest known; both indicate the very large *trans*-influence of acyl ligands [397—399]. Two acyl complexes (68) and (69) have been prepared by cyclometalation of the corresponding aldehyde [400,401].



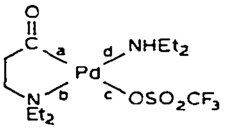
(65)

a = 2.449(3) Å;
b = 1.974(10) Å;
c = 2.342(2) Å;
d = 2.344(2) Å.



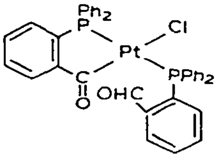
Pd—Cl = 2 446(4) Å, Y = Et_2NH;
Pd—Cl = 2 461(2) Å, Y = $C(NEt_2)NHMe$

(66)

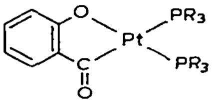


a = 1 938(11) Å,
b = 2 106(7) Å,
c = 2 271(7) Å,
d = 2 117(8) Å

(67)



(68)



(69)

5.5.5.6 *Tin ligands*

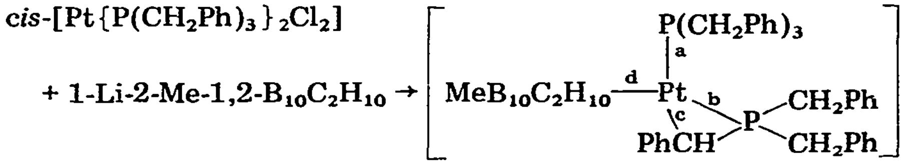
Complexes containing tin ligands have been prepared by reactions (95) and (96) [402,403]. When $SnPh_4$, $SnPh_3Cl$, $SnPh_2Cl_2$, $SnMe_4$ or $SnMe_3Cl$ react with zerovalent platinum phosphine complexes, platinum inserts into the Sn—C bond, whereas with $SnPhCl_3$, $SnMe_2Cl_2$, $SnMeCl_3$ or $SnCl_4$, it inserts into the Sn—Cl bond [404]. $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)(SnCl_3)]$ reacts with the heteropolytungsten anion $[W_{12}SiO_{40}]^{3-}$ to form $[Pd(\eta^3\text{-}C_3H_5)(SnW_{11}SiO_{39})_2]^{11-}$ [405].

$$[M(PF_3)_4] + 4\,Et_4NSnCl_3 \xrightarrow[\substack{\text{room temp.}\\ (M=Pd,\,Pt)}]{CH_2Cl_2} (NEt_4)_4[M(SnCl_3)_4] + 4\,PF_3 \tag{95}$$

$$[M\{P(OR)_3\}_2Cl_2] + SnCl_2 \xrightarrow[M=Pd,\,Pt]{} [M\{P(OR)_3\}_2(SnCl_3)Cl] + [M\{P(OR)_3\}_2(SnCl_3)_2] \tag{96}$$

5.5.6 Complexes with Group (III) donor ligands

NMR spectroscopy suggests that [M{$Ph_2P(CH_2)_2PPh_2$}$Cl(B_5H_8)$] (M = Pd or Pt) have a static metallo-*nido*-pentaborane structure [406]. Although the insertion of platinum(0) into small *closo*-carbaboranes is stereospecific, with 1,7-$C_2B_6H_8$ a mixture of *closo* and *nido* products is formed, and with 4,5-$C_2B_7H_9$ and 1,6-$C_2B_8H_{10}$ only the *nido* results [407]. A range of hydrido-platinum(II) complexes [$Pt(PEt_3)_2H$(*nido*-carbaborane)] have been prepared by oxidative-addition of the *nido*-carbaborane to [$Pt_2(PEt_3)_4(\mu$-cod)] [408]. Reaction (97) results in metalation of the phosphine to give a product which in many ways appears to have a  $\mathrm{Pt}-\overset{\mathrm{P}}{\underset{\mathrm{C}}{\|}}$ bond [409].



(97)

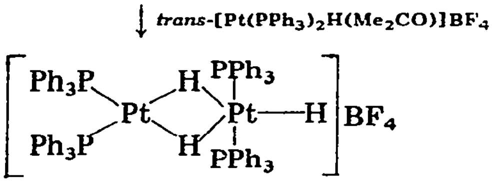
a = 2.302(4) Å;
b = 2.235(4) Å;
c = 2.15(1) Å;
d = 2.09(1) Å.

5.5.7 Hydride complexes

β-Face centred cubic $PdH_{0.60-0.92}$ and γ-$PdH_{1.18-1.20}$ have been characterised [410,411]. Semi-hydride bridged [$(\eta^5$-$C_5Ph_5)Pd(\mu$-$H)(\mu$-$Cl)Pd(\eta^5$-$C_5Ph_5)$] has been prepared by treating the product of the reaction of palladium(II) ethanoate and excess diphenylacetylene with hydrochloric acid [111]. *Trans*-[$Pt(PPh_3)_2HX$] (X = Cl, Br, $SnCl_3$ or $SnBr_3$) have been prepared [412], the $SnCl_3$ species is dynamic and must be cooled to between −50 and −70°C to record its NMR spectrum, which is consistent with the observation that the presence of $SnCl_3$ ligands promotes the insertion of olefins into *trans*-Pt—H bonds [413]. The high *trans*-influence of cyanoalkyl ligands also promotes this insertion [414]. *Trans*-[$Pt(PEt_3)_2H(NO_3)$] is an active hydrogenation catalyst for internal and terminal olefins; olefins with electron-withdrawing substitutents are polymerised unless excess nitrate ions are added when no reaction occurs [415]. *Trans*-[Pt{$P(CMe_3)_3$}$_2$HX] (X = Cl, Br or CF_3COO) undergo rapid intramolecular metalation with elimination of hydrogen in benzene solution under ambient conditions to form [Pd{$P(CMe_3)_2CMe_2CH_2$}-{$P(CMe_3)_3$}X] [416,417]. Carbon monoxide reacts under ambient conditions with [$Pt(PR_3)_2H_2$] (PR_3 = $PCych_3$, $P(CMe_2H)_3$, $P(CMe_3)_2(Bu)$ or $P(CMe_3)Ph_2$) to displace H_2 and one PR_3 ligand to yield trinuclear [$Pt(PR_3)$-$(CO)]_3$ clusters [418].

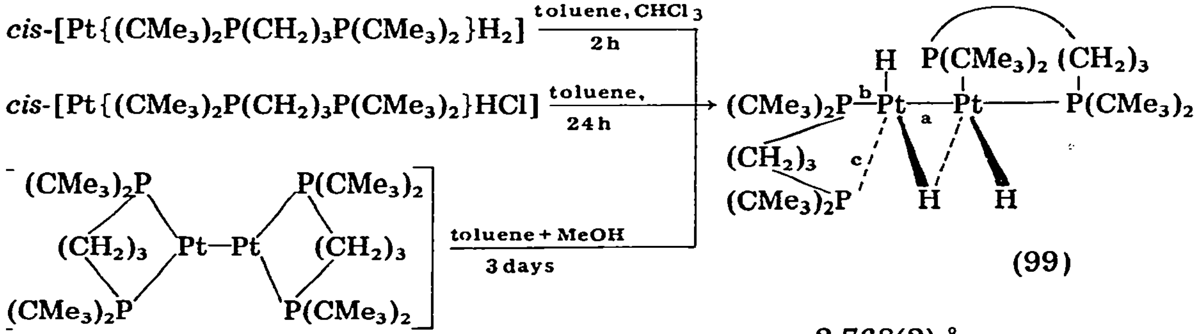
Two new binuclear trihydride complexes, **(70)** and **(72)** have been prepared {reactions (98) and (99)} [419,420]; **(72)** is of structural interest. Each platinum atom is approximately trigonal bipyramidal with phosphorus and platinum as the axial donors; the platinum—platinum bond length is virtually the same

$[Pt(cod)_2] + 2\ PPh_3 + H_2 \rightarrow$ "hydride intermediate"



(70)

(98)



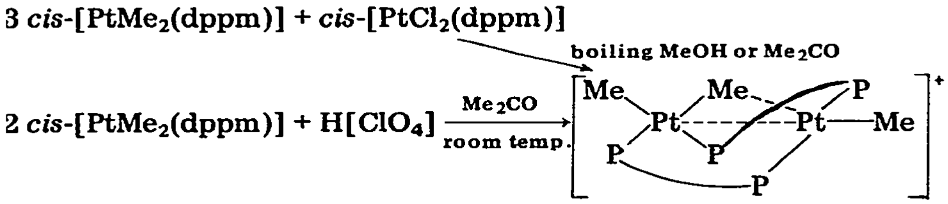
(71)

(99)

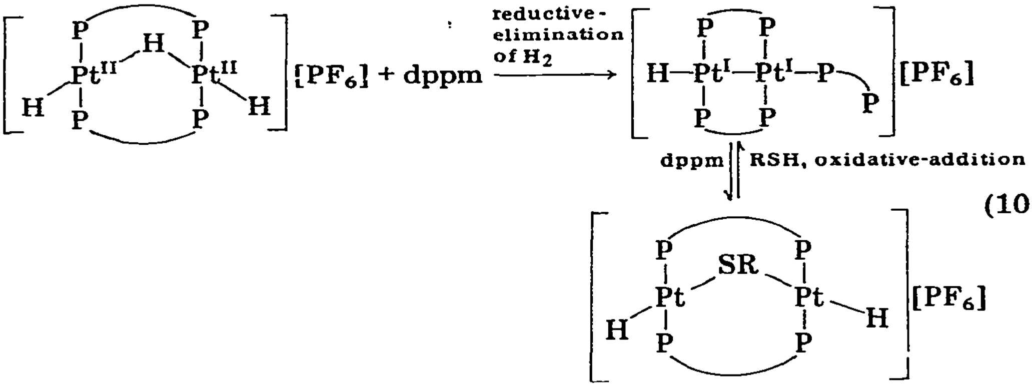
a = 2.768(2) Å;
b = 2.345(10) Å mean;
c = 2.262(8) Å mean.

(72)

as in **(71)** which is unusual, since all previous hydrido-bridging ligands have lengthened the M—M bond. It is possible that the steric demands in **(71)** give it an unusually long Pt—Pt bond [420]. In contrast to reaction (99), *trans*-dihydridoplatinum(II) hydrides react with chloroform to give *trans*-[Pt-$(PR_3)_2HCl$] exclusively [420]. The structure of **(70)** is significantly different to that of $[Pt_2Me_3(Ph_2PCH_2PPh_2)_2]^+$, prepared by reaction (100); both structures are based on spectroscopic data [421]. Some further reactions of an early binuclear trihydride have been described {reaction (101)} [422,423].



(100)



(101)

5.5.8 *Substitution reactions of complexes of the divalent metals*

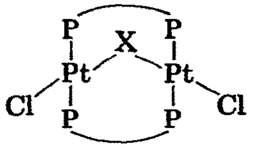
An LCAO—MO study of substitution in σ-bonded complexes including ML_4 has been given [424]. There has been particular interest in studying substitution reactions in mixed solvents [425—428]; although specific solvent effects are very important in the substitution reactions of square—planar complexes, studies this last year have highlighted the importance of non-specific effects as well [426,428]. In the reaction of *cis*-$[PtCl_2(4\text{-cyanopyridine})_2]$ with thiourea, initial state effects are more important than transition state effects [427].

A study of the temperature and pressure dependences of the rates of the substitution reactions of *cis*- and *trans*-$[Pt(PEt_3)_2(\text{mesityl})Br]$ with I^- and thiourea in methanol show negative volumes of activation. Division of these into intrinsic and solvation parts supports an associative mechanism, in contrast to previous workers' conclusions for this highly sterically crowded system. The *cis-trans*-isomerisation of the starting complexes also appeared to follow an associative route [429]. The pressure dependence of the second-order rate constant for the reaction of pyridine with *trans*-$[Pt(py)_2Cl(NO_2)]$ in nitromethane, methanol, ethanol and dichloromethane also supported an associative mechanism [430].

5.6 PALLADIUM(I) AND PLATINUM(I)

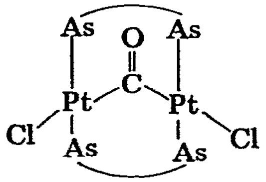
5.6.1 *Complexes with phosphines and arsines*

Interest in complexes of dppm and its arsenic analogue (dpam) has continued, and some of this work has been mentioned in Section 5.5.7. X-ray diffraction has been used to determine the structures of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [431], $[Pd_2Cl(SnCl_3)(\mu\text{-dppm})_2]$ [432], and $[Pt_2Cl(CO)(\mu\text{-dppm})_2][PF_6]$ [433]. Points to note include: (i) the Pt^I—Pt^I bond is generally shorter than both the Pt^0—Pt^0 and Pd^I—Pd^I bonds; (ii) replacement of Cl by CO shortens the $Pt^I—Pt^I$ bond by withdrawing some electron density from the π^*-orbitals of the $Pt^I—Pt^I$ bond; (iii) each Pt or Pd atom in these complexes is approximately square—planar with the square—planes at about 40° to each other to minimise anti-bonding interactions between filled interaxial d-orbitals. CH_2N_2, SO_2 and S_8 react with $[Pt_2Cl_2(\mu\text{-dppm})_2]$ to yield (73) [423]. An X-ray diffraction investigation of (74) has confirmed the structure, and shown that



(73)

(X = CH_2, SO_2 or S)



(74)

it is an exception to Cotton's rule that a bridging carbonyl group is always accompanied by a metal—metal bond [434]. The C—O stretching vibration in (74) (1635 cm^{-1}) lies well below the typical range for bridging carbon monoxide (1700—1850 cm^{-1}). The value of the $^{195}Pt—^{195}Pt$ coupling constant is very dependent upon the *trans*-ligand; as a result a large coupling constant is indicative of a Pt—Pt bond, but a small coupling constant is not diagnostic of its absence [435].

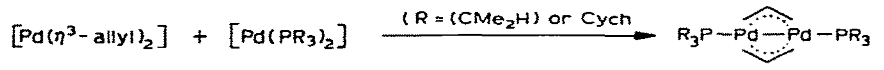
5.6.2 Isonitrile complexes

A review of previous redox-based routes to $[Pd_2(CNR)_6]^{2+}$ has been given. Reaction (102) can be used to prepare heteronuclear dimers essentially free of homonuclear dimers, indicating that the Pt—Pd bond must be strong [436]. The Pd—Pd bond in $[Pd_2(CNMe)_6][PF_6]_2$ gives an intense band in the Raman at 160 cm^{-1} [437].

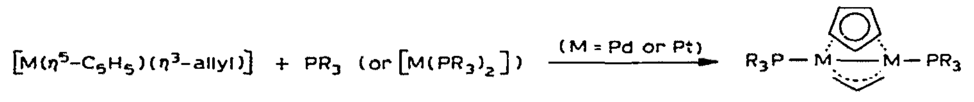
$$[Pt(CNMe)_4]^{2+} + [Pd(CNMe)_x] \rightarrow [PtPd(CNMe)_6]^{2+} \qquad (102)$$

5.6.3 Complexes with organic bridging ligands

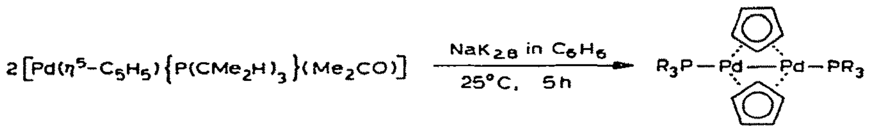
Bridged palladium(I) and platinum(I) dimeric complexes can be prepared by reactions (103)—(105) [438—440].



(103)



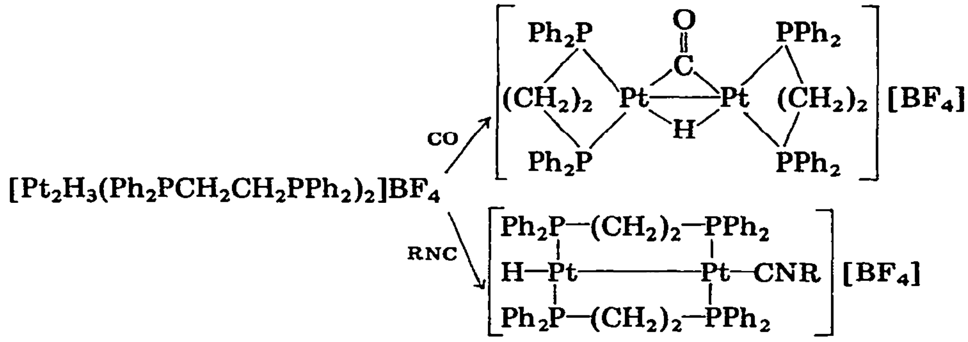
(104)



(105)

5.6.4 *Carbonyl complexes*

A bridged hydrido-carbonyl platinum(II) dimer and a terminal hydrido-isonitrile platinum(II) dimer have been synthesised from $[Pt_2H_3(Ph_2PCH_2CH_2PPh_2)][BF_4]$ {reaction (106)} [441].



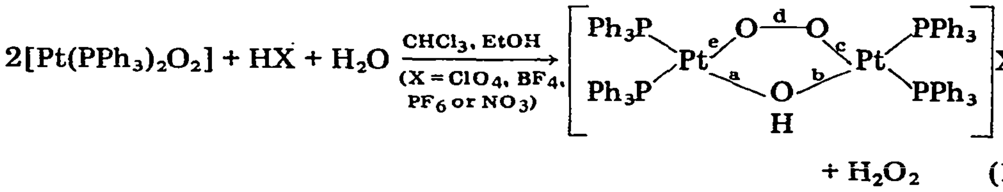
(106)

$[Pd(CO)Cl]_n$ + LiI (1 : 4 ratio) is an active olefin isomerisation and acetylene carbonylation catalyst; the catalyst precursors react together in aqueous hydrochloric acid to liberate carbon monoxide, traces of carbon dioxide and dihydrogen (from $CO + H_2O \rightarrow CO_2 + H_2$) and $LiPdI_2 \cdot 2\,H_2O$ [442].

5.7 PALLADIUM(0) AND PLATINUM(0)

5.7.1 *Complexes with Group (VI) donor ligands*

Protonation of $[Pt(PPh_3)_2O_2]$ yields a mixed oxygen/hydroxide bridged dimer {reaction (107)} [443]. Alloxan and diethyloxomalonate react with

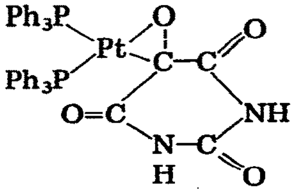


(107)

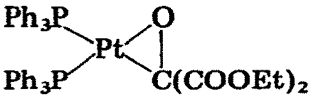
a = 2.08(2) Å;
b = 2.10(2) Å;
c = 1.99(2) Å;
d = 1.55(2) Å;
e = 2.01(2) Å.

zerovalent platinum phosphine complexes to yield side-bonded ketone complexes, (75) and (76) [444].

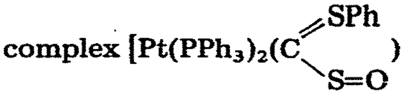
$[(\eta^5\text{-}C_5H_5)_2Ta(SMe)_2]$ acts as a bidentate sulphur donor towards platinum(0) in $[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}SMe)_2Pt(\mu\text{-}SMe)_2Ta(\eta^5\text{-}C_5H_5)_2]$ in which the tetrahedral

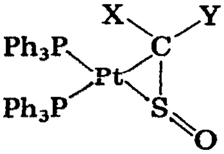


(75)

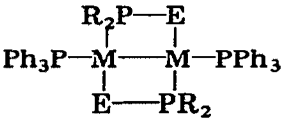


(76)

platinum atoms are 2.80 Å from the tantalum atoms [445]. Sulphines, XYC=S=O (X,Y = arylS, alkylS or Cl), react with $[Pt(PPh_3)_4]$ to yield (77), in a reaction in which the configuration of the sulphine is retained on coordination [446]. In chloroform, (77) with X=Y=SPh rearranges to the platinum(II) complex  $[Pt(PPh_3)_2(C(SPh){=}S{=}O)(SPh)]$, which is obtained as a mixture of

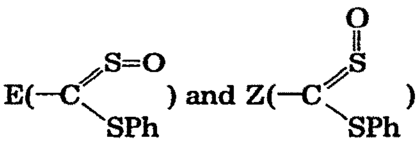


(77)



(E = S, Se)

(78)

 $E(-C(=S{=}O)SPh)$ and $Z(-C(=S{=}O)SPh)$ isomers [447]. $R_2P(S)H$ and $R_2P(Se)H$ react with $[M(PPh_3)_4]$ (M = Pd or Pt) to yield dimeric products (78) [448].

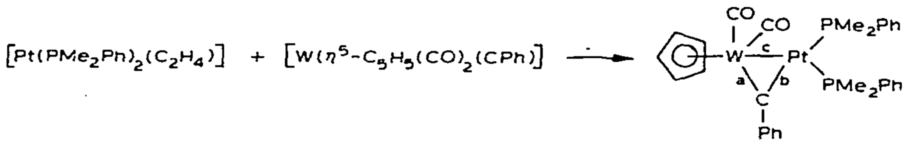
5.7.2 Complexes with tertiary phosphines

Detailed routes for the synthesis of $[PdL_2]$ $\{L = PPh(CMe_3)_2, PCych_3$ or $P(CMe_3)_3\}$ [449], $[PtL_2]$ $\{L = PPh(CMe_3)_2$ or $PCych_3\}$ [449], $[PtL_3]$ $\{L = PEt_3$ or $P(CMe_2H)_3\}$ [450] and $[Pt(PEt_3)_4]$ [451] have been described. The mechanism of the reaction of $[Pd(PPh_3)_4]$ with CF_3COOH, to yield dihydrogen and $[Pd(PPh_3)_2(CF_3COO)_2]$, and the importance of the mixture as a catalyst for the liquid-phase conversion of carbon monoxide have been reported [452].

Although no evidence was obtained for the formation of stable $[Pd(PF_2H)_4]$, by co-condensation of palladium vapour and F_2PH, the ready transport of palladium in the system and the formation of F_3PH_2 and dihydrogen indicate that some compound is formed [453].

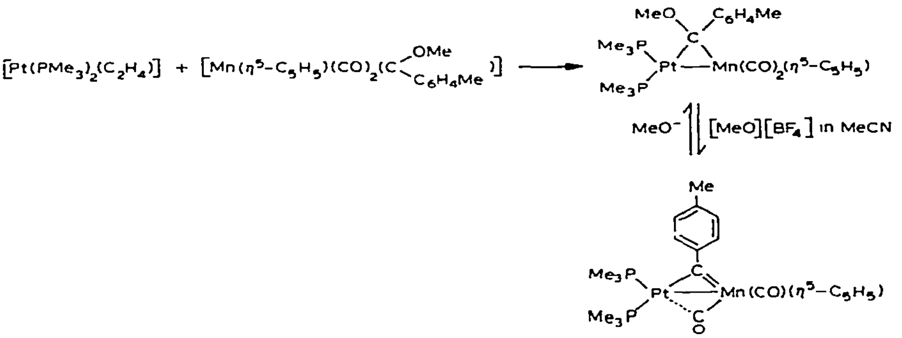
5.7.3 Complexes with carbon donor ligands

Platinum(0) adds to tungsten—and rhenium—carbyne [454,455] and manganese—carbene [455,456] complexes in reactions (108)—(110), whereas in reaction (111) it inserts into the chromium—or tungsten—carbene bond [457].

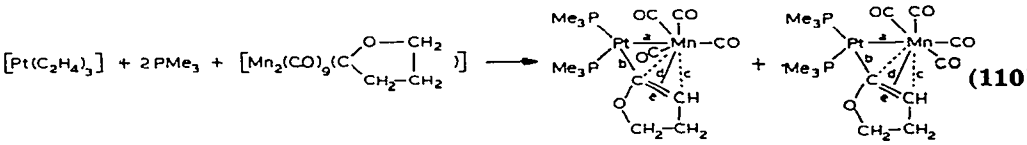


(108)

a = 1.96(2) Å,
b = 2.05(2) Å,
c = 2.273(1) Å



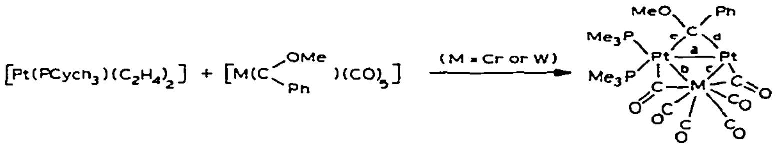
(109)



(110)

Yellow isomer a = 2.658(2) Å,
b = 1.98(1) Å,
c = 2.28(1) Å,
d = 2.22(1) Å,
e = 1.32(2) Å

Red isomer a = 2.693(1) Å,
b = 2.014(9) Å,
c = 2.253(1) Å,
d = 2.18(1) Å,
e = 1.37(1) Å



(111)

M = W, a = 2.628(1) Å;
b = 2.833(2) Å,
c = 2.830(2) Å,
d = 2.06(2) Å,
e = 2.09(3) Å

5.7.4 *Carbonyl complexes*

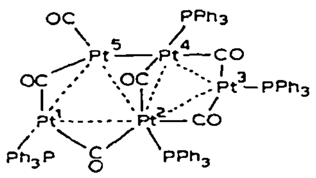
5.7.4.1 *Mononuclear carbonyls*

There is no general method for the synthesis of $[M(PPh_3)_2L_n]$ (L = PR_3, CO or olefin). However, reaction of $[M(PPh_3)_2Cl_2]$ (prepared in situ) with zinc dust in the presence of L (L = PPh_3 or CO) in tetrahydrofuran solution yields $[M(PPh_3)_3]$ or $[Pt(PPh_3)_2(CO)_2]$, although this route does not work when L = C_2H_4 [458]. Contrary to earlier reports, $[Pd(PPh_3)_3CO]$ can be prepared by simply bubbling carbon monoxide into a solution of $[Pd(PPh_3)_4]$ in benzene under ambient conditions [459].

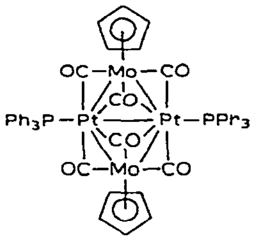
5.7.4.2 *Polynuclear carbonyls*

Carbon monoxide displaces hydrogen under ambient conditions from $[Pt(PR_3)_2H_2]$ (PR_3 = $PCych_3$, $P(CMe_2H)_3$, $P(CMe_3)_2$ Bu or $P(CMe_3)Ph_2$) to yield $[Pt(PR_3)CO]_3$ clusters [418]. The structures of cluster carbonyl anions $[Pt_3(CO)_6]_n{}^{2-}$ (*n* = 1—5) have been of interest; they are made up of approximately vertical stacks of $Pt_3(CO)_6$ units in which the Pt—Pt bond length is notably shorter (2.66 Å) than in metallic platinum itself (2.774 Å). This is ascribed to some of the platinum sp electron density being removed from the plane of the Pt_3 triangle into the inter-triangular region [460]. ^{195}Pt NMR data in deuteriochloroform suggests that, in solution, the $Pt_3(CO)_6$ triangles rotate about the 3-fold vertical axis [461]. Two attempts have been made to provide a uniform theory to describe the bonding in both clusters and bulk metals [460,462]. When $[Pt_9(CO)_{18}]^{2-}$ is heated under reflux in ethanenitrile, some of the carbonyl groups are driven off and $[Pt_{19}(CO)_{22}]^{4-}$ may be isolated in about 50 percent yield as its $[Bu_4N]^+$ salt [463]. This complex is of particular catalytic interest because it is much closer in stoicheiometry (CO : Pt ratio = 1.16) to a carbonylated metal surface (CO : M ratio ~0.75) than any previously reported metal carbonyl (previously CO : M $\geqslant$ 1.7), although its catalytic properties have not been reported so far. Its structure is based on a vertical eclipsed stack of three planar Pt_5 rings with two Pt atoms sandwiched between them and one above and one below this stack. There are twelve terminal carbonyls bound to the six platinum atoms on the top and the six on the bottom of the stack, together with ten bridging carbonyls that link the three planar Pt_5 rings together. Two platinum atoms are completely encapsulated in the centre of the complex, and have no adjacent carbonyl ligands [463].

Cis-$[Pt(PPh_3)_2Cl_2]$ is reduced by $Na[Mn(CO)_5]$, in tetrahydrofuran at room temperature, to $[Pt_5(CO)_6(PPh_3)_4]$ (79), in which two almost orthogonal triangles $Pt^1Pt^2Pt^5$ and $Pt^2Pt^3Pt^4$ share an apex, Pt^2, which has the highest coordination number (i.e. eight) ever found for a platinum atom [464]. With $Na[M(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W), *cis*-$[Pt(PPh_3)_2Cl_2]$ yields (80), in which the semi-triple bridging carbonyls lie one on either side of the Mo_2Pt_2 plane, largely over one Mo—Pt bond [465]. The bimetallic clusters $[Fe_2Pt(CO)_9(PPh_3)]$ and $[RuPt_2(CO)_5(PPh_3)_3]$ have been supported on phosphinated



(79)

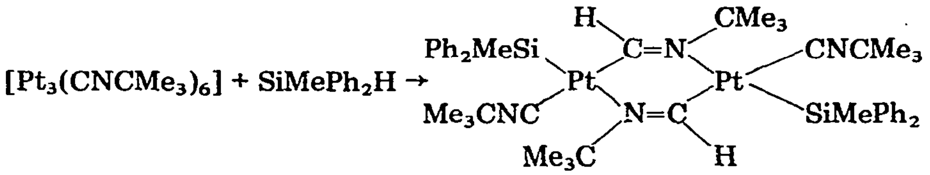


(80)

polystyrene and silica; they are olefin hydrogenation catalysts [466].

5.7.5 Isonitrile complexes

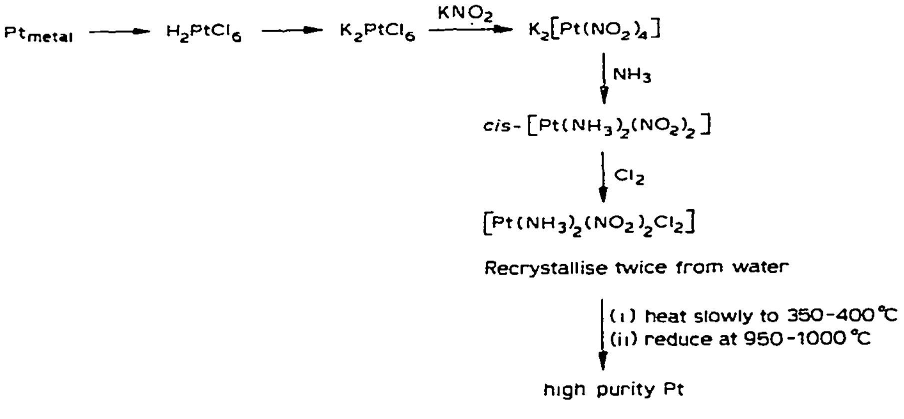
A polynuclear isonitrile $[Pt_7(2,6\text{-xylylNC})_{12}]$ has been prepared by reducing $[Pt(2,6\text{-xylylNC})_2Cl_2]$ with sodium amalgam in tetrahydrofuran. The cluster is a distorted trigonal bipyramid to which two extra platinum atoms have been added between one basal platinum and each apical platinum. The two Pt—Pt bonds on the edges having a bridging platinum atom are shorter than the others. There are six terminal isocyanides, five bridging two platinum atoms and one that bridges three platinum atoms [467]. $[Pt_3(Me_3CNC)_6]$ oxidatively adds SiR_3H, and then the isocyanide inserts into the Pt—H bond in reaction (112); $GeMe_3H$ reacts similarly [468].



(112)

5.8 PLATINUM METAL

Scheme V outlines a method for producing high purity platinum suitable for use in the electronic industry [469].

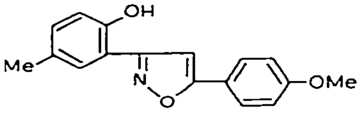


The mercury(I) wave can be exploited for the indirect polarographic determination of palladium(II), using a dropping mercury electrode, because reaction (113) is instantaneous and quantitative [470]. 3-(2-hydroxy-5-methylphenyl)-5-(4-methoxyphenyl)isoxazoline (81) is an effective reagent for the extraction and spectrophotometric determination of palladium(II).

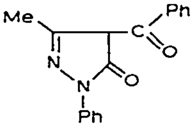
$$Pd^{2+} + 2\ Hg^0 \rightarrow Pd^0 + [Hg_2]^{2+} \qquad (113)$$

The extracted species is PdL_2 [471].

Trioctylamine, triisooctylamine and tetraoctylammonium perchlorate have been used to extract anionic halo- and oxalato-complexes of palladium(II) and platinum(II) out of aqueous solution [472—474]. Trioctylphosphine oxide, 2,2′-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline and (82) (which resembles pentane-2,4-dione) can all be used to extract palladium and platinum from aqueous hydrochloric or hydrobromic acid into benzene or chloroform[475—477].



(81)



(82)

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