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1. PALLADIUM AND PLATINUM

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CONTENTS

INTRODUCTION

This review covers the papers recorded in Chemical Abstracts between Volume 93 Number 19 and Volume 94 Number 24, as well as issues of the major English language inorganic chemistry journals received in England by

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One of the most pressing problems of the eighties is undoubtedly energy and platinum and palladium are continuing to demonstrate their importance in this field. Whilst their major contribution is in the field of catalysis and lies outside the scope of this review, the ability of platinum hydrosols to catalyse the photo-induced liberation of hydrogen from water, as well as the development of a fuel cell using porous platinum electrodes that enables the energy of the oxidation of ammonia to nitric acid to be converted directly into electricity, are considered in Section 1.9. Another exciting development in this field is the discovery that the far uv-irradiation of $[M(PEt_3)_3]$ (M = Pd or Pt) in aqueous sulphuric acid solution liberates hydrogen (see Section 1.5.7). This is an important development which involves intermediate hydride complex formation, a subject that is attracting increasing attention.

Some of the most significant developments of the past year have come in the significant strides made in understanding the complexity of the "simple" chemistry of palladium(II) and platinum(II). A significant contribution in this field has been the preparation and characterisation of complexes of weak donor ligands such as simple alcohols, ketones and other oxygen donors including perchlorate ions. These complexes are very active as catalysts for organic transformations because of their enhanced ability to interact with the organic substrate (see Section 1.5.2.1). Another basic area, in which 1981 has marked great progress, is the preparation and characterisation of the various isomers of the divalent tertiary phosphine complexes, discussed in Section 1.5.4.10. Developments have included both simpler synthetic routes as well as the synthesis of unexpected isomers. The synthesis of tertiary phosphine complexes with unusual solubility properties, both very high solubilities in non-polar solvents and solubility in aqueous solution should further enhance the contributions that palladium(II) and platinum(II) can make in the field of homogeneous catalysis (see Section 1.5.4.10).

A particularly exciting development, mentioned in Section 1.5.4.13, is the discovery that the *P,O*-bidentate ligand $PPh_2(CH{=}COOEt)^-$, when coordinated to palladium(II), can reversibly react with carbon dioxide through the formation of a C-C bond. The study of the interaction of palladium(II) and especially platinum(II) with nucleic acids and nucleosides (Section 1.5.3.2) has continued. A number of crystal structures have been determined which help in the interpretation of the very complex data obtained from solution studies, for example using NMR spectroscopy. As a result, understanding of the interaction of platinum complexes with DNA, which is essential to an understanding of the mechanism of the action of platinum drugs in the chemotherapy of cancer, is becoming clearer.

1.1 PALLADIUM(VI) AND PLATINUM(VI)

The electron affinity of PtF_6 has been found to be 8.0±0.3 eV using the effusion method to study the charge exchange reactions between PtF_6 and PtF_4 [1]. Non-relativistic, overlapping spheres, Xα-multiple scattering calculations have been used to give a consistent interpretation of the ionisation potentials, electron affinities and charge transfer electronic absorption bands of 5*d* element hexafluorides, including PtF_6 [2].

No papers on palladium(VI), palladium(V) or platinum(V) have appeared during the past year.

1.2 PALLADIUM(IV) AND PLATINUM(IV)

1.2.1 Complexes with Group VII donor ligands

Heating PdF_4 gives very high purity fluorine [3]. $K_2[PtF_6]$, $K_2[PtF_5Br]$ and K_2*cis*-$[PtF_4Br_2]$ can be prepared by treating $K_2[PtBr_6]$ with bromine trifluoride in the presence of freon [4]. DTA shows that PtF_4 reacts with bromine trifluoride to form $[BrF_2]_2[PtF_6]$, which was shown to be ionic using ^{19}F NMR spectroscopy, as well as $PtF_4.7BrF_3$ [5]. X-ray diffraction indicates a Pt-F bond length of 1.933 Å in $K_2[PtF_6]$ [6]. Pt-F and Pt-Cl bond energies in $[PtF_6]^{2-}$ and $[PtCl_6]^{2-}$ have been determined from reactions (1) and (2) and a study of equilibrium (3) [7]. A neutron diffraction study of the structural phase transitions in the antifluorites $Rb_2[PtI_6]$ below 65 K and $[NH_4]_2[PtBr_6]$ below 50 K shows that both become tetragonal, with no evidence for rotation of the octahedra, whereas the 258 K transition in $[NH_4]_2[PtI_6]$ is antiferro-rotative, with octahedra in successive planes rotated in opposite senses, accompanied by a tetragonal distortion; the transition at 100 K involves a further ferro-rotation [8]. The ^{35}Cl NQR signals in $Na_2[PtCl_6].6H_2O$ steadily broaden as the water is removed by heating, until no signal is observed at all for anhydrous $Na_2[PtCl_6]$ [9].

$$Na_2[PtF_6](s) + 2H_2(g) \rightarrow 2NaF(s) + Pt^{0}(s) + 4HF(g) \quad \Delta H = -160\pm3\ kJ.mol^{-1} \qquad (1)$$

$$Na_2[PtF_6](s) \xrightarrow{H_2O} 2Na^{+}.aq + [PtF_6]^{2-}.aq \quad \Delta H = -9.2\pm0.8\ kJ.mol^{-1} \qquad (2)$$

$$[PtF_6]^{2-}.aq + 6Cl^{-}.aq \rightleftharpoons [PtCl_6]^{2-}.aq + 6F^{-}.aq \qquad (3)$$

The reaction of metallic platinum with chlorine or bromine is inhibited by surface halide formation. Addition of aluminium halide accelerates the reaction by removal of the surface layers [10].

A new method for the separation of the platinum metals, involving liquid-liquid extraction, has been developed and installed in Johnson-Matthey's Royston refinery [11]. The method reduces both the number of refining stages and the time required, whilst increasing purity and allowing increased automation to be used. $[PtCl_6]^{2-}$ is extracted from the aqueous phase using tri-*n*-octylamine, whereas palladium is extracted with oximes in the presence of accelerating additives based on organic amines [12].

The effect of the nature of ligands on the Pt^{II}/Pt^{IV} redox potential has been reviewed [13]. The effects of ligands on the rates of reductions of *trans*-$[Pt(en)Z_2X_2]$ (X = *trans*-ligand = Cl or Br; Z = Cl, Br, SCN or NO_2) by $[Fe(CN)_6]^{4-}$ (outer-sphere), Fe^{2+} (inner-sphere) and $[Pt(NH_3)_4]^{2+}$ (inner-sphere), show that, for the inner-sphere reactions, the *trans*-dibromo-complexes react 11 to 28 times faster than the *trans*-dichloro complexes. The *cis*-bonded Z-groups affect the reactivity in the order Br < Cl < SCN ∿ NO_2, which applies to both inner- and outer-sphere reductions and is probably related to the σ-donor/π-acceptor abilities of these groups [14]. *Trans*-$[Pt(PEt_3)_2Cl_4]$ reacts with *trans*-$[M(PEt_3)_2(CO)Cl]$ (M = Rh or Ir) to form *trans*-$[Pt(PEt_3)_2Cl_2]$ and $[M(PEt_3)_2(CO)Cl_3]$ [15].

A study of the substitution of fluoride in *trans*-$[Pt(NH_3)_4F_2]^{2+}$ by chloride and bromide showed that the stability of *trans*-$[Pt(NH_3)_4X_2]^{2+}$ increases as X is altered in the order F < Cl < Br < I [16].

1.2.2 Complexes with Group VI donor ligands

Poorly crystallised PdS_2 and PtS_2, prepared by the reaction of $[MCl_6]^{2-}$ with hydrogen sulphide, are diamagnetic; on annealing, PdS_2 crystallises with an orthorhombic, distorted pyrite structure and PtS_2 crystallises in the hexagonal CdI_2 structure [17]. The Pt-O bond length in $H_2[Pt(OH)_6]$ is 2.00(3) Å [18]. The electronic structures of $K_2[PtCl_{6-n}(OH)_n]$ (n = 0-6) have been calculated on the basis of their optical spectra [19]. When KO_x (x = 1.55 or 1.88) and platinum powder are heated, black metallic crystals of $K_3Pt_2O_4$, in which each platinum is surrounded by 4 oxygens, are formed [20]. The interacting bond method has been used to estimate the acid dissociation constants of platinum(IV) and platinum(II) aqua complexes [21].

Tributylphosphate can be used to extract the platinum metals from hydrochloric acid solution; the extractability order is Ir(IV) ∿ Pt(IV) > Pd(IV) > Pd(II) ∿ Pt(II) >> Rh(III) ∿ Ir(III) [22]. Addition of sulphuric acid increases the degree of separation during this extraction [23]. Triphenylphosphine oxide has been used similarly to separate platinum and palladium [23a]. Complexes of platinum(IV) chlorides with tri(2-, 3- or 4-tolyl)phosphine sulphide have been prepared and characterised [24]. When the sulphoxide complexes *cis*-$[PtL_2Cl_4]$ (L = Et_2SO, tetramethylene sulphoxide, or thioxane) are heated in the solid state, they isomerise to the thermodynamically more stable *trans*-isomers [25].

The complexes DL-$[(PtXMe_3)_2(MeEEMe)]$ and DL-$[(PtXMe_3)_2(MeECHREMe)]$ (E = S or Se; X = Cl, Br or I; R = H or Me) are fluxional undergoing:

(i) ring reversal, where the energy barrier is 4-10 kJ mol^{-1} less for the selenium than the sulphur heterocycles;

(ii) chalcogen inversion, which involves about 10 kJ mol^{-1} more energy than ring reversal; selenium inversion has a higher activation energy than sulphur inversion, although the actual difference does not vary in a clearly defined way;

(iii) ligand switching and platinum-methyl scrambling, which involves about 20 kJ mol^{-1} more energy than pyramidal inversion; the sulphur complexes have lower activation energies for methyl scrambling than the selenium complexes [26,27].

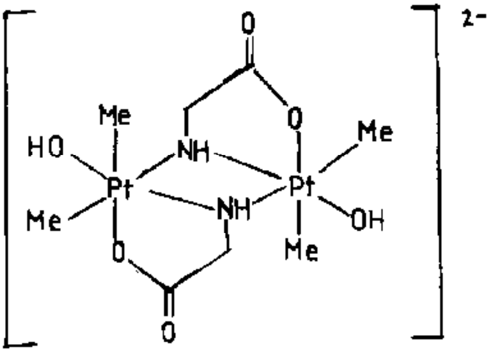
$[(PtXMe_3)_2(SCHRSCHRECHR)]$ (E = S or CH_2; R = H or Me; X = Cl, Br or I) are also fluxional [28,29], undergoing a series of 60° pivots of the cyclic ligand about individual S-Pt bonds, and a higher energy process associated with ligand dissociation-recombination.

1.2.3 Complexes with mixed Group VI and Group V donor ligands

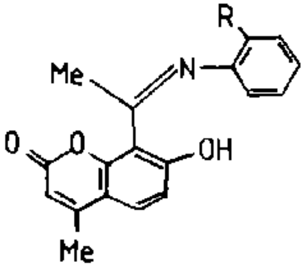
Heating $[PtMe_2Br(OH)(NH_2CH_2COO)]^-$ (N *trans* to Br) in alkali yields the dimer (*1*), which, upon acidification, undergoes hydroxide protonation to yield the aqua complex; this is followed by slow decomposition to $[PtMe_2(NH_2CH_2COO)(H_2O)_2]^+$ (N *trans* to H_2O) [30]. Octahedral complexes, PtL_2, have been prepared with H_2L = (*2*) [31]. Ligands containing the thioamide-group -CS-NH- or the -NHCSNH- group react with H_2PtCl_6, in a 3:1 ratio to form $[PtL_4][PtCl_6]$ and, in a 1:3 ratio, to form $[PtL_2Cl_2][PtL_2Cl_4]$ [32]. The 1,4,7-thiazodiazomine, (*3*), reacts with $PtCl_4$ to form $[PtCl_3L]Cl.nH_2O$, in which the ligand binds through both nitrogens and the sulphur in a tridentate manner [33]. The diantipyrylthiourea, (*4*), extracts platinum(IV) from weakly acid, neutral, and alkaline solution as a dithizonate complex [34].

1.2.4 Complexes with Group V donor ligands

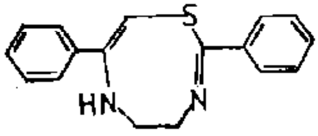
Replacement of the anions in $[Pt(en)_3]Cl_4$ and $[(NH_3)_4Pt(NH_2)_2Pt(NH_3)_4]$-$[ClO_4]_6$ by hydroxide using a strongly basic anion-exchange resin gave $[Pt(en\text{-}H)_2(en\text{-}2H)]$ and $[(NH_3)_2(NH_2)_2Pt(NH_2)_2Pt(NH_2)_2(NH_3)_2]$, respectively [34a]. The Pt-Cl (2.315(3)-2.332(4) Å and Pt-N (2.05(1)-2.08(1) Å) bond lengths in



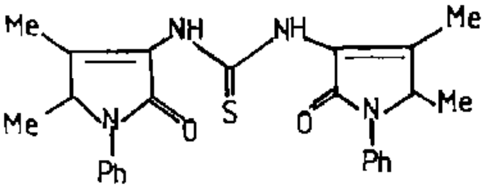
(1)



(2; R = COOH or H)



(3)



(4)

fac-$[\mathrm{Pt(dien)Cl_3]Cl.H_2O}$ are normal; the crystals are held together by extensive hydrogen-bonding [35]. Platinum(IV) complexes $[\mathrm{Pt}(\widehat{\mathrm{L\ L}})\mathrm{X_4}]$ of the bidentate ligands $(\widehat{\mathrm{L\ L}})$ = $\mathrm{Me_2N(CH_2)_2NMe_2}$, $\mathrm{Ph_2P(CH_2)PPh_2}$, *cis*-$\mathrm{Ph_2ECH{=}CHEPh_2}$ (E = P or As), $\mathrm{Me_2As(CH_2)_2AsMe_2}$, 2-$\mathrm{C_6H_4(ER_2)_2}$ ($\mathrm{ER_2}$ = $\mathrm{AsMe_2}$, $\mathrm{AsPh_2}$ or $\mathrm{SbPh_2}$), $\mathrm{Me_2Sb(CH_2)_3SbMe_2}$ and $\mathrm{(SbMe_3)_2}$, have all been prepared by halogen oxidation of the platinum(II) complexes $[\mathrm{Pt}(\widehat{\mathrm{L\ L}})\mathrm{X_2}]$. The amine, phosphine, and arsine complexes are very stable both thermally and in solution, but the stibines decompose slowly at ambient temperature and immediately in solution. Several unstable $[\mathrm{Pt}(\widehat{\mathrm{L\ L}})\mathrm{I_4}]$ complexes which lose iodine readily have been prepared [36].

1.2.5 *Complexes with Group IV donor ligands*

The displacement of iodide in $[\mathrm{Pt(CN)_5I}]^{2-}$ by cyanide is photostimulated; about 3% of the starting complex is reduced to $[\mathrm{Pt(CN)_4}]^{2-}$ [37].

The germanes GeH_3X (X = F, Cl or I) react with $[Pt(PEt_3)_3H][BPh_4]$ to form $[Pt(PEt_3)_2H_2(GeH_2X)]^+[BPh_4]^-$ which were identified by NMR spectroscopy at 213 K; on warming, decomposition occurs forming $[PEt_3H]^+[BPh_4]^-$ and *trans*-$[Pt(PEt_3)_2H(GeH_2X)]$ [38]. $[PtBr_2Me_2]$ and $[Pt(OH)_2Me_2].1.5H_2O$ have been prepared by the reaction (4) [39].

$$[PtIMe_3] + Br_2 \xrightarrow{-MeI} [PtBr_2Me_2] \xrightarrow[-2NaBr]{4NaOH} Na_2[Pt(OH)_4Me_2] \xrightarrow{H_3O^+} [Pt(OH)_2Me_2].1.5H_2O \qquad (4)$$

Although these reviews largely exclude organometallic compounds, the further characterisation of organoplatinum(IV) compounds formed by direct interaction of organic compounds with H_2PtCl_6 have important implications for C-H bond activation. A methyl-platinum(IV) complex has been characterised by ^1H NMR spectroscopy, following the interaction of methane with a mixture of H_2PtCl_6 and H_2PtCl_4 in trifluoroacetic acid [40]. Platinum(IV)-aryl complexes have been prepared similarly and characterised for nitrobenzene, 2-nitrotoluene, benzoic acid, acetophenone, diphenyl, fluorobenzene, 2- and 3-chlorofluorobenzene [41,42]. By refluxing aromatic compounds with H_2PtCl_6 in aqueous trifluoroacetic acid for a few minutes, in the case of alkylated benzenes and anisole, and for a few days in the case of chlorobenzene, followed by column chromatography on ammoniated silica gel, $[NH_4]$*trans*-$[PtCl_4(NH_3)Ar]$ (Ar = aryl) have been isolated [43]. Single crystal X-ray diffraction of the bis-acetone adducts have shown that naphthalene forms only the β-naphthyl product (Pt-C = 2.05(3) Å, Pt-N = 2.21(3) Å and Pt-Cl = 2.310(7)-2.341(7) Å) and 2-nitrotoluene forms only the 4-product (Pt-C = 2.06(2) Å, Pt-N = 2.20(3) Å and Pt-Cl = 2.316(6)-2.319(6) Å) [44].

Mechanical spectroscopy, in which a sample is subjected to a sinusoidal mechanical stress at a fixed frequency and then the energy dissipation of the sample measured as a function of temperature, has been used to measure the energy of η^5-cyclopentadienyl ring rotation in a series of η^5-$CpPt^{IV}$ complexes as a function of the other ligands present [45].

1.2.6 Complexes with Transition Metal ligands

A platinum(IV) pentaammine containing silver amide in the inner coordination sphere, $[Pt(NH_3)_4(NH_2Ag)Cl]$, has been prepared by mixing a saturated solution of $[Pt(NH_3)_4(NH_2)Cl][NO_3]_2$ with silver nitrate [46].

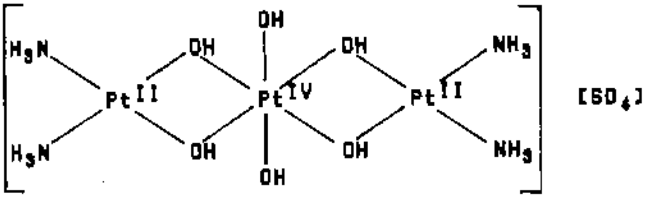
1.3 PALLADIUM AND PLATINUM COMPLEXES WITH MIXED (IV/II) OXIDATION STATES

Surveys of the progress in mixed valence chemistry over the past ten years [47] and of one-dimensional metallic complexes [48] have been published. The crystal structure of *trans*-$[Pt(NH_3)_2Br_2]$ *trans*-$[Pt(NH_3)_2Br_4]$ has been reinvestigated because the earlier structure was inconsistent with resonance Raman spectral results. The present work shows two platinum sites rather than the single site of the earlier work; Pt^{IV}-Br and Pt^{II}-Br distances are 2.485(4) Å and 3.068(4) Å, respectively [49]. Successful refinement of the structure of $[Pt_2(NH_2CH(CH_3)CH_2NH_2)_2Br_6]$ requires all the Pt-Br distances to be 2.673(1) Å [50]. Resonance Raman spectroscopy has been used extensively to study these mixed valence complexes. Polarised single crystal spectra of $[Pt_2(\overset{\frown}{L\,L})_4X_2]Y$ ($\overset{\frown}{L\,L}$ = $2NH_3$ or en; X = Cl, Br or I; Y = HSO_4, ½SO_4, ClO_4 or ½$PtCl_4$) show anisotropic character and the presence of $\cdots Pt^{II}\cdots X—Pt^{IV}—X\cdots$ chains [51]. In $[Pt_2(H_2NCH_2CHRNH_2)_2Br_6]$ (R = H, Me, Et or *n*-Pr), the wavenumber of the totally symmetric $\nu(Br-Pt^{IV}-Br)$ mode is independent of R, averaging 171.2 ± 0.6 cm^{-1}, indicating the highly one-dimensional nature of these complexes, in which the chain mode is effectively decoupled from the equatorial modes [52]. The resonance Raman spectra of $[Pt_2\{NH_2(CH_2)_3NH_2\}_4X_2]Y_4$ (X = Cl, Br or I when Y = ClO_4; X = Br when Y = BF_4 or ½Cu_3Br_5; and X = Cl or Br when Y = CuX_4) are characterised by the intense progression $V_1\nu(X-Pt^{IV}-X)$, where V_1 ranges from 4 to 18 [53,54]. A similar progression reaching to between 7 and 9 $\nu(I-Pt^{IV}-I)$ is observed in $[Pt_2(NH_3)_4(SCN)_4I_2]$, $[Pt_2(en)_2I_6]$ and $[Pt_2(en)_4I_2][ClO_4]_4$ [55,56]. The band gaps and stabilities of the chains in $[Pt_2(NH_3)_8X_2]^{4+}$ (X = Cl or Br) were examined as a function of distortion in their unit cell geometries; the results lead to the prediction that, under high pressure, Pt^{IV}-X bond lengthening may accompany Pt^{II}-X bond shortening, leading to an increasing similarity of the two, that is an approach to Pt^{III} [57]. The electrical conductivities (σ) of $[MA_2][MA_2X_2]Y_4$ (M = Pd or Pt; A = en or 1,3-pn; X = Cl, Br or I; Y = ClO_4 or BF_4) followed equation (5),

$$\sigma = \sigma_o e^{-E/kT} \tag{5}$$

with the activation energy E decreasing as the ratio of the Pt^{IV}-X/Pt^{II}-X bond lengths approached zero. This suggests that, not only is the conduction electrical in origin but also that it is dominantly characterised by a band type carrier excitation [58].

Irradiation of *cis*-$[Pt(NH_3)_2(H_2O)_2][SO_4]$ at 254 nm gives a blue platinum compound which is a mixed valence compound, probably (*5*) [59]. Treatment of H_2PtX_6 with thiourea and other thioamido-ligands, such as thiocaprolactam,



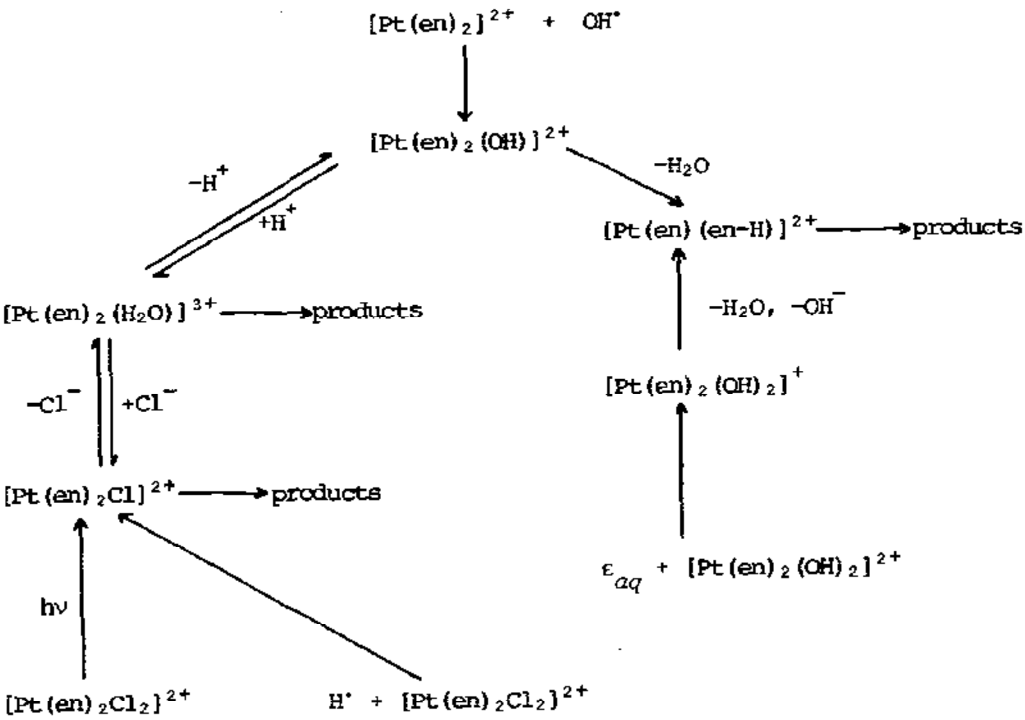
(5)

pyrimidine-2-thione, tetrahydropyrimidine-2-thione and 2-imidazolidinethione, in ethanol yield the mixed valence $[Pt_2L_4X_6]$ (X = Cl or Br) complexes. For all of the ligands excepting thiourea, the nature of the product, $[PtL_4][PtX_6]$ or $[PtL_2X_2][PtL_2X_4]$, depends critically on the preparative method [60,61]. Preparative methods have been reported in Inorganic Syntheses for $Rb_3[Pt(CN)_4][SO_4\text{-}H\text{-}O_4S]_{0.46}.H_2O$ [62], $Rb_2[Pt(CN)_4][FHF]_{0.29}.1.67H_2O$ [63], $Rb_2[Pt(CN)_4][FHF]_{0.38}$ [64], $Cs_2[Pt(CN)_4][FHF]_{0.23}$ [65], $Cs_2[Pt(CN)_4][FHF]_{0.38}$ [66], and $Cs_2[Pt(CN)_4]F_{0.19}$ [67].

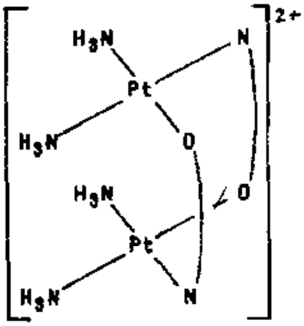
1.4 PALLADIUM(III) AND PLATINUM(III)

Formic acid reduction of $H_2[Pt(OH)_6]$ in acetic acid yields $H_2[Pt_2(OH)_4(H_2O)_2]$ which has a Pt-Pt bond and reacts with trifluoroacetic acid, to form $[Pt_2(O_2CCF_3)_6].4H_2O$, and, with hydrochloric acid, to give a mixture of $H_2[PtCl_4]$ and $H_2[PtCl_6]$ [68]. Solid $[Pt_2(OAc)_6]$ reacts with trifluoroacetic acid on heating to form $[Pt_2(OAc)_3(O_2CCF_3)_3]$ [68]. $[Pt(en)_2][ClO_4]_2$ reacts in aqueous solution with hydroxyl radicals generated by pulse radiolysis to form the platinum(III) complex ion $[Pt(en)_2(OH)]^{2+}$, which then reacts as in Scheme 1 to give two series of products, one based on the formally five-coordinate complex $[Pt(en)_2X]^{n+}$ (X = OH, H_2O or Cl; n = 2 or 3) and one based on the four-coordinate complex $[Pt(en)(NH_2CH_2CH_2NH)]^{2+}$ [69].

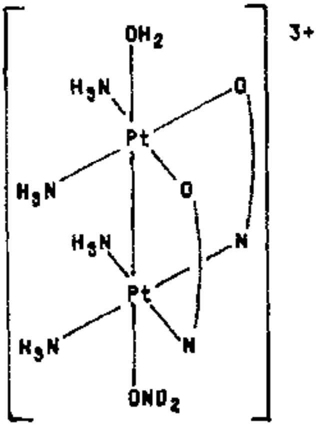
Treatment of *cis*-$[Pt(NH_3)_2(NO_3)_2]$ with α-pyridone yields both a yellow head to tail dimer, (*6*), and *cis*-$[Pt(NH_3)_2(\alpha\text{-pyridonate})]_4[NO_3]_{10}.2H_2O$, a platinum blue, which is a head to tail tetrameric compound that formally contains 3 platinum(II) and 1 platinum(III) atoms. On treatment with nitric acid, it is oxidised to a metal-metal bonded orange-red platinum(III) dimer, (*7*) [71,71]. A Fourier analysis of the X-ray diffraction pattern of platinum acetamide blue indicates that it contains a partially oxidised platinum chain (Pt-Pt bond length = 2.76 Å) with chains of 4 or 5 platinum atoms [72]. A new class of mixed valence platinum blue has been prepared from *cis*-$[Pt(NH_3)_2Cl_2]$ and potassium phthalimide; different average platinum oxidation states can be obtained by altering the ratios of the reactants.



Scheme 1: The reaction of $[Pt(en)_2]^{2+}$ with ·OH [69].



(6; $\widehat{\mathrm{N\,O}}$ = py-2-O)



(7; $\widehat{\mathrm{N\,O}}$ = py-2-O)

All of these blues are either borderline class II-class III or delocalised class III mixed-valent compounds, according to Robin and Day's classification [73]. Platinum oxamic acid blue can be prepared from $K_2[Pt(NO_2)_4]$ [74].

1.5 PALLADIUM(II) AND PLATINUM(II)

1.5.1 Complexes with Group VII donor ligands

The structure of the high pressure form of PdF_2, as determined by neutron diffraction, is derived from a fluorite structure by a rhombohedral distortion of the cubic environment of palladium, in which the six Pd-P distances are about 2.18 Å. Below 190 K PdF_2 is antiferromagnetic [75]. The β-α transition of $PtCl_2$ occurs between 300 and 600 °C and involves the intermediate formation of unstable phases [76]. The elastic constants of $K_2[PtCl_4]$ have been determined by the ultrasonic pulse superposition method [77], whilst the vibronic structure in the single crystal polarised luminescence spectra of $K_2[PtCl_4]$ and $K_2[PtBr_4]$ has been analysed by Franck-Condon calculations [78]. The relatively complicated pattern of d^8 states, that give rise to the ligand field spectra of square-planar palladium(II) and platinum(II) complexes, can be rationalised by introducing an extra parameter σ_{sd} into the simple orbital method, where σ_{sd} determines the energy of the $a_{1g}(d_{z^2})$ orbital; it arises from the $nd_{z^2}/(n+1)s$ interaction which is impossible in octahedral or tetrahedral fields [79]. The ^{35}Cl NQR spectra of $PdSe_2Cl_6$, $PtSe_2Cl_8$, $PtSe_2Cl_{12}$, $PtTe_2Cl_{12}$, and $(PtCl_2)_n$ have been reported [80].

The thermal transformations of $[LH]_2[PtX_4]$ complexes into hydrogen halide and $[PtL_2X_2]$ have been studied for thiuronium [81], ammonium, piperidinium, pyridinium, and quinolinium [82,83], and imidazolium [84] cations. The initial product is the *cis*-isomer but in most cases this isomerises subsequently to form *trans*-$[PtL_2Cl_2]$. Thermolysis of the imidazolium complexes $[LH]_2[Pt(PhSO_2)Cl_3]$ also yields *trans*-$[PdL_2Cl_2]$, together with HCl and $PhSO_2H$ [85]. The action of heat on $[PtL_4][PtX_4]$ to yield, initially, *cis*-$[PtL_2X_2]$ has been studied for L = tetramethylthiourea (X = Cl or Br) [86] and for L = $PPhMe_2$ (X = Cl or Br), $PPhBu_2$ (X = Cl) and PBu_3 (X = Cl or I) [87]; only the last undergoes subsequent *cis* to *trans*-isomerisation and, in this case, only when X = Cl.

The heat capacities of the green and rose forms of $[Pt(NH_3)_4][PtCl_4]$ have been measured between 55 and 305 K. Enthalpies, entropies, and free energies of formation have been calculated for both forms [88].

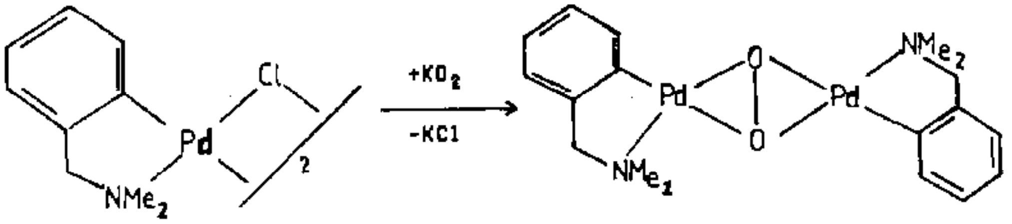
The mechanism of the electroreduction of $[PtBr_4]^{2-}$ to Pt on a platinum electrode has been studied [89].

1.5.2 Complexes with Group VI donor ligands

1.5.2.1 Unidentate oxygen donor ligands

The kinetics of the decomposition of PdO have been studied [90]. La_4PdO_7

and $La_2Pd_2O_6$ have been obtained by heating La_2O_3, $La_2(C_2O_4)_3$, or $La(OH)_3$ with PdO, $[Pd(dmg)_2]$, or $[Pd(NH_3)_4][PdCl_4]$ [91], whilst heating a 1:1 mixture of $Pd[NO_3]_2.2H_2O$ and B_2O_3 at 800 °C and 40 kbar yielded PdB_2O_4 [92]. Peroxide bridged complexes have been prepared by reaction (6); reaction of the peroxide bridged complex with methanol gave the methoxide bridged complex $[Pd(C_6H_4CH_2NMe_2)(\mu\text{-}OMe)]_2$ [93].



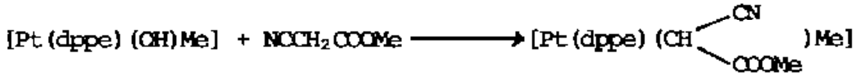
(6)

Acid dissociation constants of platinum(II)-aqua complexes have been calculated using the interacting bond method [21]. Bis-solvento-complexes of palladium(II), $[Pd(dppe)(S_2)][ClO_4]_2$ ($S = H_2O$, Me_2CO, dmf) have been isolated and characterised; the analogous complexes with S = MeOH, EtOH, and thf are stable in solution but, on attempted isolation, the ethanol complex deposits palladium metal whilst the methanol and thf complexes lose solvent to form the bis-perchlorato-complex $[Pd(dppe)(OClO_3)_2]$. All of these complexes should be handled WITH GREAT CARE [94]. These solvento-complexes have an unusually high ability to activate olefins, $[Pd(dppe)(Me_2CO)_2][ClO_4]_2$ catalyses the hydrogenation of olefins at ambient temperatures and pressures [95]. Solvento-complexes of palladium(II) and platinum(II) have been reviewed [96]. Reaction of C_6F_5MgBr with $K_2[PdCl_4]$ in thf, followed by addition of 1,4-dioxane (diox), yields $[Pd(C_6F_5)(diox)(\mu\text{-}Cl)]_2$, *cis*-$[Pd(C_6F_5)_2(\mu\text{-}diox)]_2$, and *trans*-$[Pd(C_6F_5)_2(diox)_n]$ (n = 2 or 3), the precise product depending upon the ratio of the reactants; addition of different ligands to these displaces dioxane and yields *cis*-$[PdL_2(C_6F_5)_2]$ from the *cis*-complex and *trans*-$[PdL_2(C_6F_5)_2]$ from the *trans*-complex [96*a*].

ClO_3 reacts with $PdCl_2$ to form $Pd(ClO_4)_2$ and $ClO_2Pd(ClO_4)_3$ [97]. A series of complexes, $[Pt(PR_3)_2(OH)R']$ (R' = Me or Ph), prepared by treating the corresponding chloride complexes in acetone with silver(I) followed by potassium hydroxide, have been reported. All have a *trans* geometry except $[Pt(PMe_2Ph)_2(OH)Ph]$ which was obtained as a *cis/trans* mixture. On reaction with nitromethane, acetone, acetamide, or 4-cresol, the hydroxide ligand is displaced as water and $[Pt(PR_3)_2R'Z]$ ($Z = CH_2NO_2$, CH_2COCH_3, $NHCOCH_3$ or

$OC_6H_4CH_3$-4, respectively) is formed. Both the hydroxo- and acetamido-complexes catalyse the hydration of acetonitrile to acetamide, the reactivity decreasing in the order $PR_3 = PEt_3 > P^tBuMe_2 > PPh_3 \sim PMe_2Ph > P^tBu_2Me \gg PCych$ and $R' = Ph > Me$. Methylcyanoacetate reacts with phenylhydroxo-complexes to form an *N*-bonded product but with methylhydroxo-complexes to form a *C*-bonded product (reactions (7) and (8)) [98].

$$[PtL_2(OH)Ph] + NCCH_2COOMe \xrightarrow[P^tBu_2Me]{L = PEt_3} [PtL_2(N{=}C{=}CHCOOMe)(Ph)] \qquad (7)$$



$$[Pt(dppe)(OH)Me] + NCCH_2COOMe \longrightarrow [Pt(dppe)(CH(CN)(COOMe))Me] \qquad (8)$$

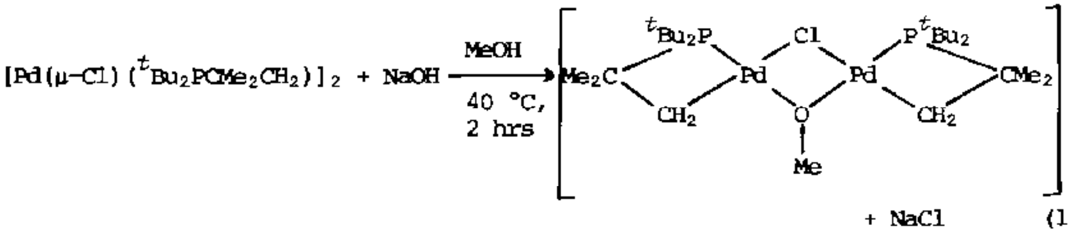
Methoxo-complexes of platinum(II) readily undergo β-hydrogen elimination which can provide a convenient route to hydrido-complexes (reaction (9)) [99].

$$\left.\begin{array}{l} trans\text{-}[Pt(PR_3)_2X(R')] \\ \qquad X = Cl,\ OH \text{ or } NHCOMe \\ \qquad R' = Me \text{ or } Ph \\ trans\text{-}[Pt(PR_3)_2(MeOH)R'] \end{array}\right] \xrightarrow[\text{or } NaBH_4]{+\ NaOH \text{ in } MeOH} trans\text{-}[Pt(PR_3)_2H(R')] \qquad (9)$$

A similar β-hydrogen elimination occurs from formate complexes (reaction (10)) [99]. Methoxo-bridged complexes can conveniently be prepared by treating

$$\begin{tikzcd}
{[Pt(dppe)Me(OH)]} \arrow[r, "+\ HCOOH", "\text{or } NaHCOO"'] & {[Pt(dppe)Me(OOCH)]} \arrow[r, "> -20\ ^\circ C \text{ in solution}", "> \text{room temperature in solid state}"'] & {[Pt(dppe)HMe]} \arrow[d, "\text{room temperature}"'] \\
 & & \text{Decomposition to 'Pt(dppe)' cluster compounds} + CH_4
\end{tikzcd} \qquad (10)$$

chloro-complexes with alkaline methanol (reactions (9) and (11)) [99,100]. An alternative route to methoxo-bridged complexes involving removal of chloride with silver(I), illustrated in reaction (12), led to the formation of $[Pt(C_8H_{12}OMe)(\mu\text{-}OMe)_2]$, for which X-ray diffraction showed Pt–O bond lengths of



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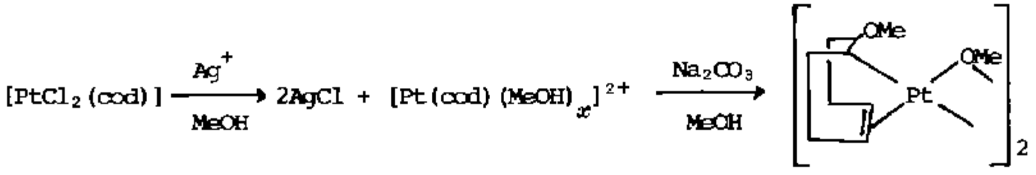


(12)

2.034(3) Å *trans* to olefin and 2.153(3) Å *trans* to σ-carbon [101,102]. Like halide bridges, methoxo-bridges are readily cleaved by tertiary phosphines to yield monomeric methoxo-complexes [100,101].

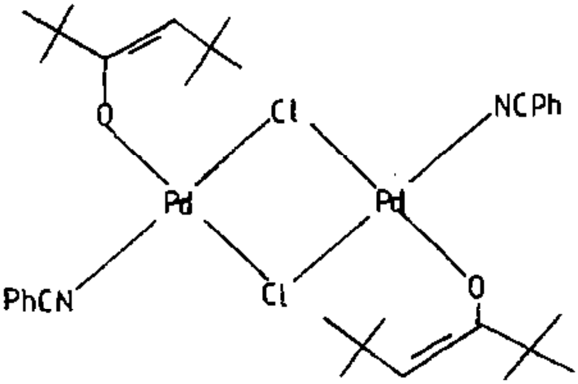
Amides, such as acetamide, reversibly displace water from platinum(II) (reaction (13)) to form complexes that form platinum blues on subsequent

$$[Pt(NH_3)_2(H_2O)_2]^{2+} + MeCONH_2 \longrightarrow [Pt(NH_3)_2(H_2O)(O{=}C(CH_3)NH_2)]^{2+} + H_2O \qquad (13)$$

oxidation; the amide is bound through the carbonyl oxygen [103]. *O*-bonded palladium(II) enolate complexes, (*8*), have been prepared by reaction of $[Pd(PhCN)_2Cl_2]$ with trimethylsilylenol ethers ($^tBuC(OSiMe_3){=}CH^tBu$) [104]. Tetrameric *t*-butylperoxide palladium(II) carboxylate complexes, (*9*), which selectively oxidise terminal olefins to methylketones can be prepared by treating palladium(II) carboxylates with *t*-butylperoxide [105]; the $Pd\text{-}O_{peroxide}$ and $Pd\text{-}O_{carboxylate}$ bond lengths average 1.994(3) Å and 2.039(5) Å, whilst the Pd-Pd bond lengths (2.912(1) and 2.923(1) Å) are too long for direct Pd-Pd interaction. The stability constants for the interaction of palladium(II) with the naphthoquinone, (*10*), have been reported [106].

The major product from the reaction of S_4N_4 with $[Pt(PPh_3)_4]$ in acetone has been shown to be (*11*) by X-ray diffraction [107]. The competitive insertion of SO_2 into alkyl- and aryl-platinum(II) complexes has been studied and the insertion occurs exclusively into the Pt-alkyl bond, with retention of stereochemistry (reaction (14)); since this is the exact reverse of the situation with main group metals, it appears that in the present case SO_2 is not acting simply as an electrophile [108].

$$cis\text{-}[Pt(PMePh_2)_2Me(Ph)] + SO_2 \xrightarrow{CH_2Cl_2} cis\text{-}[Pt(PMePh_2)_2(O_2SMe)(Ph)] \qquad (14)$$



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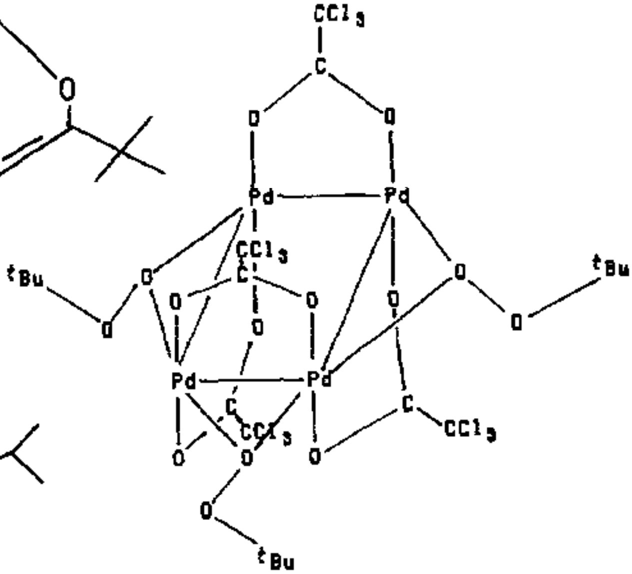

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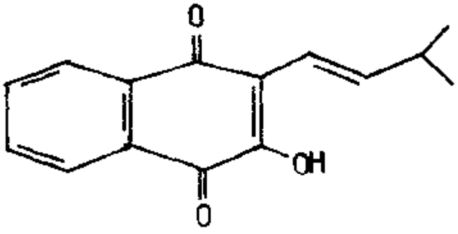

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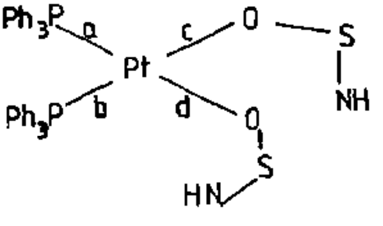


(11)

a	2.288(4) Å
b	2.264(4) Å
c	2.088(12) Å
d	2.173(11) Å

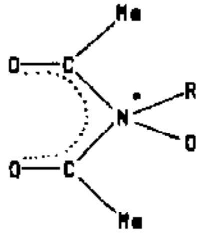
1.5.2.2 Bidentate oxygen donor ligands

An examination of the structure of palladium(II) acetate complexes on phosphinated polystyrene has shown that both mono- and bi-nuclear complexes are formed [109].

Preparations of [Pt(acac)$_2$], [Pt(tfacac)$_2$], and [Pt(hfacac)$_2$] have been described in Inorganic Syntheses [110]. Palladium(II)-β-diketonate complexes have been obtained by reaction (15), in which oxygen is transferred from

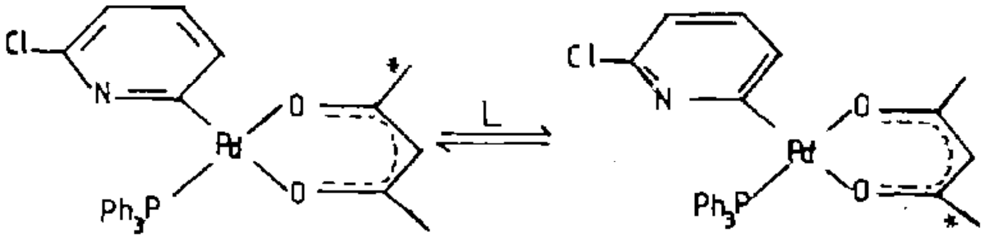
$$3PdCl_2 + 3Na_2CO_3{}^{18} + 2RCH{=}CHCOR' \xrightarrow{\text{thf-}O^{16}} [Pd(O^{18}CRCHCR'O^{16})_2] + 2Pd_{metal} + 3CO_2 + 6NaCl + H_2O \qquad (15)$$

carbonate to an αβ-unsaturated ketone [111]. Hfacac can be transferred from $[Pd(hfacac)_2]$ to ruthenium in place of a hydride and phosphine ligand, although the yields are low and the reaction is accompanied by deposition of palladium metal [112]. The ligand, (*12*), has been coordinated to palladium(II) and



(*12*; R = CMe_3 or CF_3)

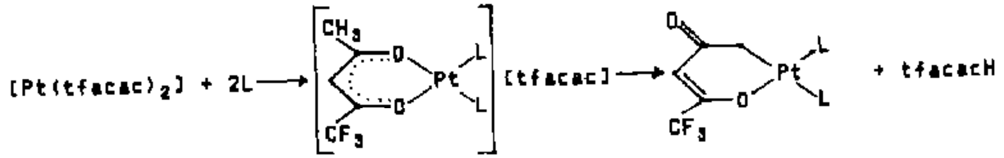
platinum(II) to obtain spin-labelled β-diketonate complexes [113]. The crystal structure of $[Pt(acac)_2].C_6H_6$ shows Pt-O bonds of 2.008(15) and 1.979(14) Å. The ESCA spectrum of $[Pd(acac)_2]$ has been measured [115]. The unsymmetrical acetylacetonate complex, (*13*), exhibits two methyl signals which, in the presence of added ligand L, become equivalent (reaction (16)); L may be one of



(16)

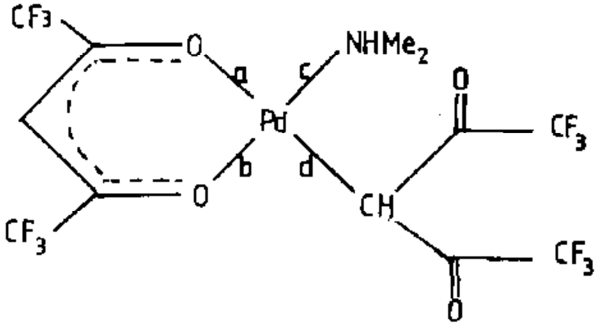
(*13*)

a range of ligands including solvents, whose effectiveness decreases in the order L = PPh_2 >> pyr > hmpa (109.5) > dmso (78.0) > MeOH (30.3) ∿ MeCN (29.8) ∿ dmf (29.1) > $MeNO_2$ (8.8) > Me_2CO (4.9) [116]. Variable temperature ^{19}F NMR spectroscopy shows that rapid exchange occurs between the ionic and coordinated hfacac groups in $[PdL_2(hfacac)](hfacac)$ [117]. Displacement of tfacac from $[Pt(tfacac)_2]$ by triphenyl-phosphine or -arsine leads to formation of the neutral C,O-bonded β-diketonate complex (reaction (17)) [118]. When $[Pd(hfacac)_2]$ is treated with only one equivalent of Lewis base, one diketonate ligand is



(17)

converted to a unidentate ligand; this may be either *O*-bonded, as in [Pd(hfacac-O)(hfacac-O,O)(PhCH$_2$NMe$_2$)], or *C*-bonded, as confirmed by an X-ray diffraction study of (*14*) [119,120]. When 2,2'-bipyridyl in



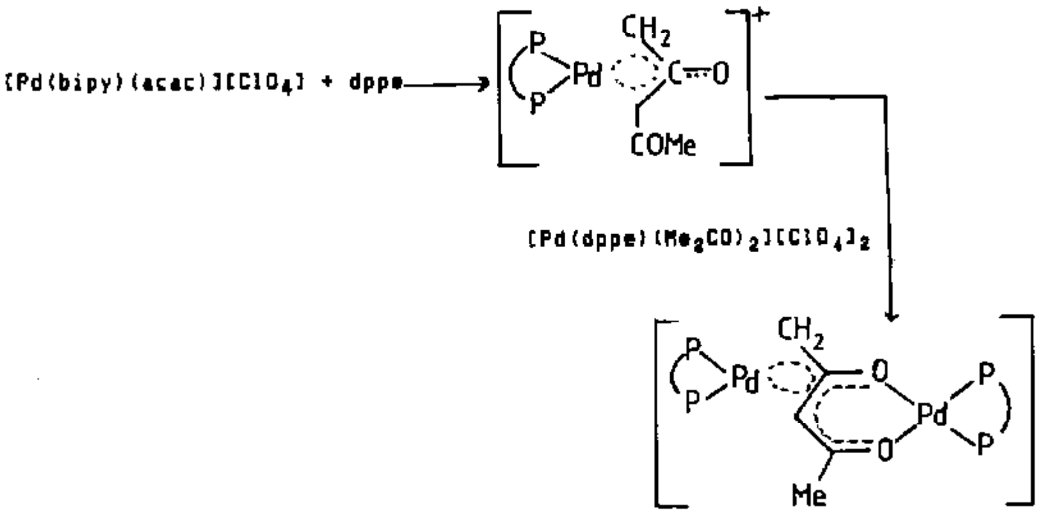
a	2.059(5) Å
b	2.002(4) Å
c	2.101(7) Å
d	2.028(6) Å

(14)

[Pd(bipy)(β-dik)][ClO$_4$] (β-dik = acac or ethylacetoacetate) is replaced by a diphosphine, an η^3-bonded β-diketonate complex is formed which reacts with a further palladium(II) complex to give a remarkable β-diketonate-bridged dimer (reaction (18)) [121]. The tridentate phosphine Ph$_2$P(CH$_2$)$_2$PPh(CH$_2$)$_2$PPh$_2$ reacts with [Pd(hfacac)$_2$] to form an interesting product in which hfacac is "semi-chelating", with one long and one short Pd-O bond, (*15*) 122. Not only is the coordinated hfacac in (*15*) fluxional ($\Delta H^{*} = 33.9 \pm 4.2$ kJ mol^{-1}) but also (*15*) provides an attractive model for the transition states in some substitution and isomerisation reactions of metal β-diketonate complexes.

The partition equilibria of [Pt(acac)$_2$], between dodecane and water in the presence and absence of added dmso and ethyleneglycol, have been studied [123]. 'Pd(acac)$_2$' has been bonded on to silica by reacting γ-aminopropyl-aerosil with bis(3-bromoacetylacetonate)palladium(II) [124], whereas [Pd(hfacac)$_2$] has been incorporated onto alumina by direct reaction in which the alumina acts as a bidentate Lewis base in place of one hfacac ligand [125].

Chelate complexes of palladium(II) and platinum(II) with 2-catechol and



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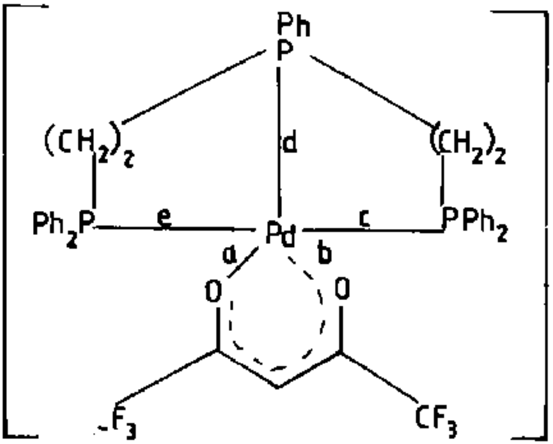
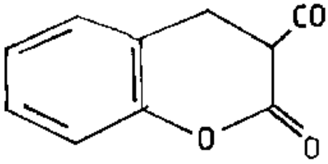


(*15*)

a	2.110 Å
b	2.653 Å
c	2.321 Å
d	2.209 Å
e	2.343 Å

substituted 2-catechols [126–128], 3-carboxycoumarin, (*16*) [129], and *N*-(4-methyl-7-hydroxy-8-acetocoumarinylidene)-2-aminophenyl, (*17*) [130] have been described. The reaction of salicylaldehyde with chloroplatinum(II) complexes requires the presence of dmso, no products are formed when dmf or chloroform are used instead (reaction (19)) [131]. 2,4-Dinitroresorcinol-6-sulphonate, (*18*), binds as a unidentate and bidentate (through the 2-nitroso oxygen and 3-hydroxy oxygen atoms) ligand towards palladium(II) [132].



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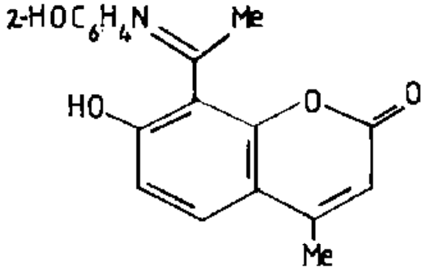

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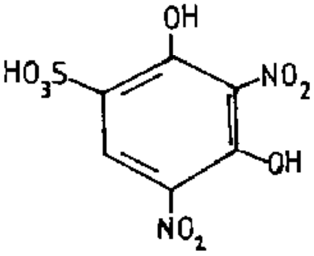

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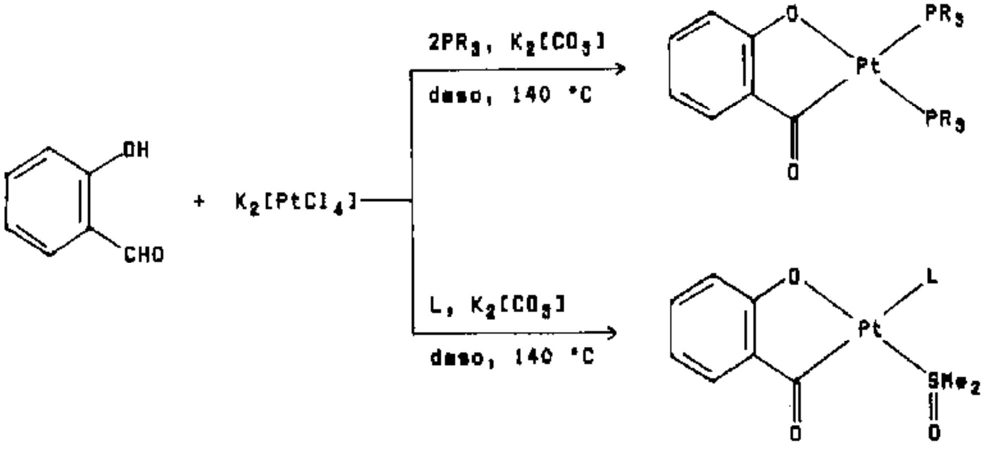


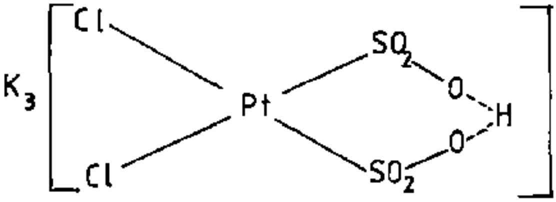
(19)

(L = picoline or $NH_2C_6H_{13}$)

1.5.2.3 Ambidentate oxygen–sulphur donor ligands

A major review on transition metal sulphoxides includes a very good discussion of the preparation, characterisation, and bonding in palladium(II) and platinum(II) sulphoxide complexes [133]. $[Pd(dmso)_4][BF_4]_2.dmso$ has a *cis*-geometry with two *S*-bonded (Pd–S = 2.245 Å (mean)) and two *O*-bonded (Pd–O = 2.063 Å (mean)) dmso ligands [134]. In *cis*-$[Pt(dmso)_2Ph_2]$, the two Pt–S bonds are considerably lengthened (Pt–S = 2.315(2) and 2.324(2) Å) relative to those in *cis*-$[Pt(dmso)_2Cl_2]$ [135]. Heating *trans*-$[PtL(NH_2CH_2CH_2OH)Cl_2]$ (L = tetramethylenesulphoxide) yields the *cis*-isomer, whereas replacement of chloride by iodide using potassium iodide yields *cis*-$[Pt(NH_2CH_2CH_2OH)I_2]$ which, on heating, isomerises to the *trans*-isomer [136]. The *S*-bonded dmso complexes, *cis*-[Pt(dmso)$_2$R$_2$] and *cis*-[Pt(dmso)$_2$RCl] (R = aryl or Me), are readily obtained by treating K$_2$[PtCl$_4$] with SnMe$_3$R in dmso at 70–90 °C; the dmso ligands may be displaced by tertiary phosphines but replacing the chloride ligand in *cis*-[Pt(dmso)$_2$PhCl] with bromide, iodide or thiocyanate yields the dimeric [Pt(dmso)(Ph(μ-X)]$_2$ (X = Br, I or SCN) complex [137]. The kinetics of ring opening of *cis*-[Pt(*meso*- and *rac*-PhSOCH$_2$CH$_2$SOPh)Cl$_2$] by amines has been studied, in order to gain insight into the absolute reactivity, nucleophilic discrimination, and steric retardation effects in asymmetric complexes [138]. The use of sulphoxides in forming extractable solvates of platinum(II) have been studied [139].

The potentially ambidentate sulphite ion binds through sulphur in [Pd(SO$_3$)(NH$_3$)$_3$] and [Pt(SO$_3$)$_4$]$^{6-}$ [140]. K$_3$[Pt{(SO$_3$)$_2$H}Cl$_2$], (*19*), has a very short O---H---O bond (2.386(2) Å) and rather short Pt-S bonds (2.247(2) Å) [141].



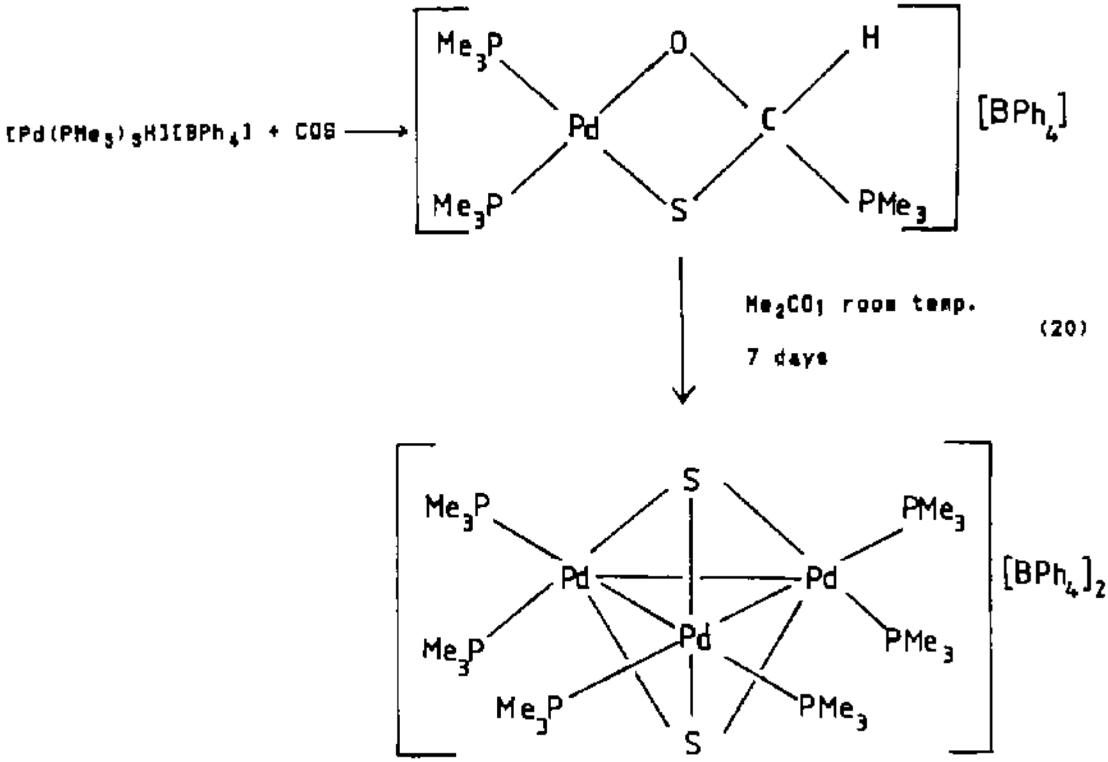
(*19*)

1.5.2.4 Bidentate oxygen-sulphur donor ligands

The dipole moments of [Pd{RC(S)=CHC(O)R'}$_2$], in which R' is a fluoroalkyl ligand, demonstrate a *cis*-geometry [142].

1.5.2.5 Unidentate sulphur donor ligands

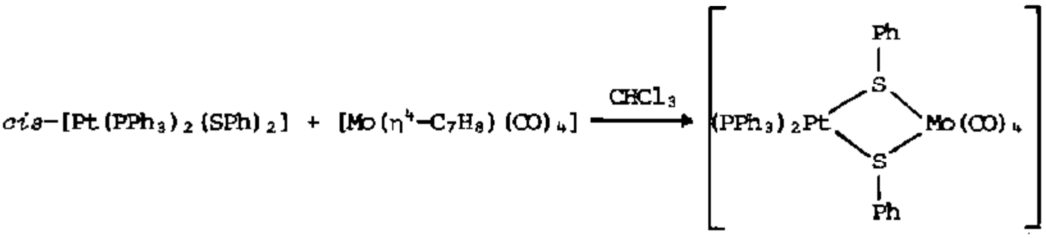
Quantitative precipitation of PdS$_2$ from [PdCl$_4$]$^{2-}$ can be achieved by using a controlled amount of Na$_2$S [143]. Triply bridging sulphide ligands are found in [Pd$_3$(PMe$_3$)$_6$(μ-S)$_2$][BPh$_4$]$_2$, in which a Pd$_3$ triangle has one triply bridging sulphide ligand above and one below the distorted Pd$_3$ triangle (Pd-S = 2.336(6) Å; Pd-Pd = 3.011, 3.178, and 3.144 Å). The complex is made by COS insertion into the Pd-H and one Pd-P bond of [Pd(PMe$_3$)$_3$H][BPh$_4$], followed by standing in acetone under dinitrogen at room temperature for a week (reaction (20)); an alternative synthesis is given in reaction (21) [144]. Treatment of [Pt(PPh$_3$)$_2$O$_2$] with RSH (R = H, Me, *n*-Bu or Ph) in chloroform yields *cis*-[Pt(PPh$_3$)$_2$(SR)$_2$] and hydrogen peroxide; X-ray diffraction of the complex with R = H shows Pt-S and Pt-P bond lengths of 2.350 (mean) and 2.283 Å (mean). These complexes can act as ligands to other transition metals (reactions (22)



(20)

$$[Pd(MeCN)_4][BF_4]_2 + H_2S + PR_3 \xrightarrow[PR_3 = PMe_3,\ PMePh_2]{Na[BPh_4]} [Pd_3(PR_3)_6(\mu\text{-}S)_2][BPh_4]_2 \quad (21)$$

and (23)) [145]. An alternative preparation of sulphide complexes involves the use of triethylamine to remove chloride from the dichloroplatinum(II) starting materials (reaction (24)). Only the alkylsulphide complexes are *cis* and these isomerise on exposure to air [146].



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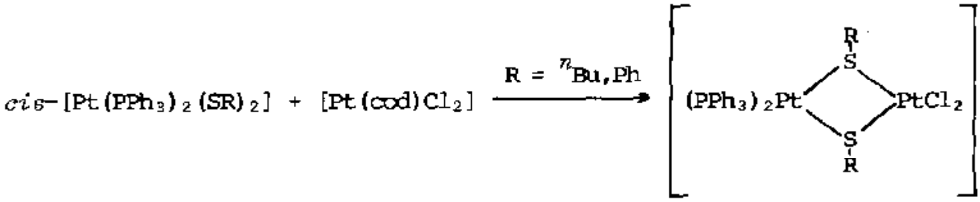

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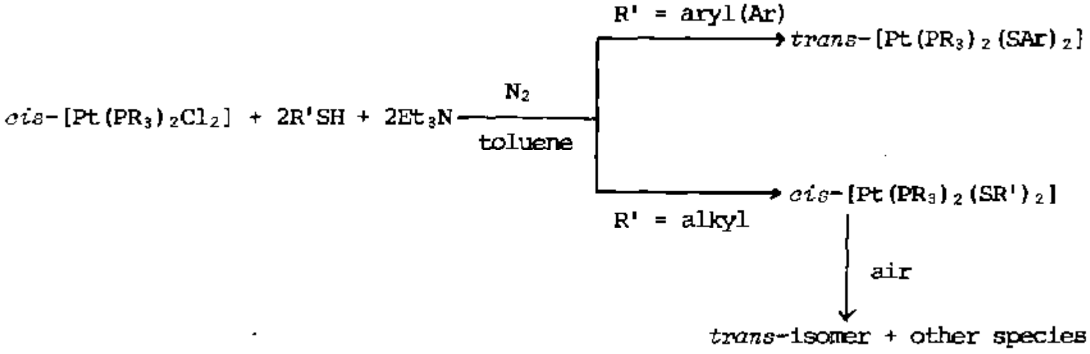
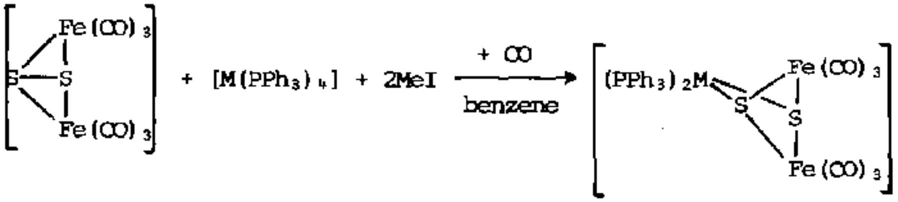


(24)

A study of the UV photoelectron and IR spectra of *cis*-[MCl_2L] (L = ($C_6F_5SCH_2)_2$, $C_6F_5SCH_2$-2-py), and *trans*-[$Pt(C_6F_5SEt)_2Cl_2$] shows that the fluorocarbon weakens the M–S σ-bond but reinforces the π-backbond just sufficiently to compensate for σ-bond weakening, indicating that thioethers are electronically very adaptable ligands [147]. Self-consistent MO LCAO calculations in the CNDO approximation have been attempted on [$PtLCl_3]^-$ complexes with a number of ligands, including sulphur donors [148].

$M(PPh_3)_2$ units (where M = Pd or Pt) have been complexed with '$Fe_2(\mu\text{-}S)_2$' ligands using reactions (25), (26) and (27), of which the latter only works for platinum [149–151].



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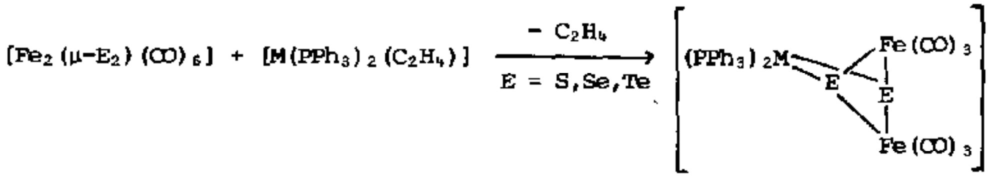

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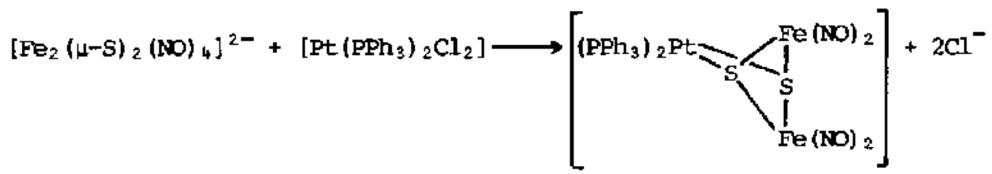


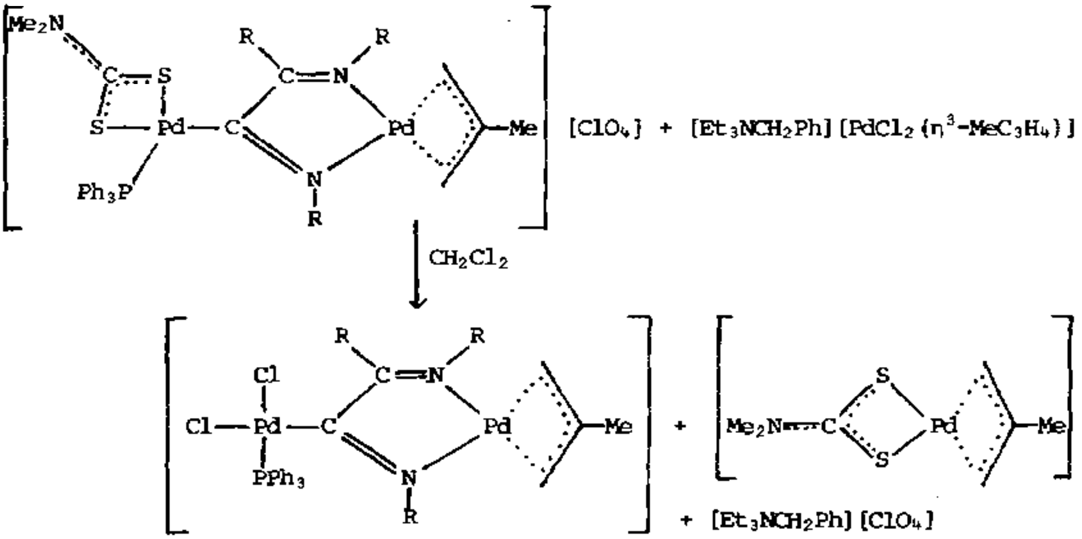
(27)

Tris(2-, 3- and 4-tolyl)phosphine sulphide form *S*-bonded complexes with palladium(II) [24].

1.5.2.6 Bidentate sulphur donor ligands

A comprehensive review of the coordination chemistry of thioethers, selenoethers, and telluroethers in transition-metal complexes includes a detailed account of the preparation, structure, bonding, and reactions of palladium(II) and platinum(II) complexes of bidentate thioethers [152]. $PhSCH_2SPh$ coordinates too weakly to palladium(II) and platinum(II) to overcome the strain of chelation; it thus acts only as a monodentate ligand, whereas $MeSCH_2SMe$ binds in a bidentate fashion [153], as do a series of quinoxaline-2,3-dithiols [154]. $^tBuS(CH_2)_5S^tBu$ forms $[M_2Cl_4(^tBuS(CH_2)_5S^tBu)_2]$ (M = Pd or Pt) which has a 16-membered ring in a 'barge' conformation [155]. The polyfluoroalkyldithioethanes $CF_3S(CH_2)_2SCF_3$, $CF_3SCHMeCH_2SCF_3$, and $PhS(CH_2)_2SPh$ form $[MX_2L]$ complexes which are fluxional with rapid ring conformational changes but slow inversion at sulphur; $[PtI_2(MeSCHCF_3CHCF_3SMe)]$ shows a sufficiently high energy barrier to ring conformational changes as to be measurable [156]. A mass-spectrometric study of the chloro-complexes showed successive loss of the chlorine and of the substituents bound to sulphur [157]. Cationic $[Pd(MeSCHMeCH_2SMe)_2]I_2$ exists as several diastereoisomers in solution [158].

$[Pt_2(Me_2CHCS_2)_4]$ can be crystallised in two forms, a deep purple form which is strongly dichroic in plane-polarised light and has Pt-Pt distances of 2.795 Å within the dimers and 3.081 Å between dimers, and a green form with corresponding distances of 2.85 and 3.40 Å, respectively [159]. The electronic structures of monomeric $[Pd(MeCS_2)_2]$ and dimeric $[Pd(MeCS_2)_2]_2$ have been investigated by the LCAO-MO-SCF method; the total energy of the monomer is almost exactly half that of the dimer, in agreement with the coexistence of both forms in solution. The Pd-Pd interactions are bonding in character and involve the $4d_{z^2}$ and $5p_z$ Pd orbitals [160]. $[Pt(MeCS_2)_2]_2$ is dimeric with a Pt-Pt distance of 2.767(1) Å; the angle of 28° between dimeric units and long intermolecular Pt-Pt distance (∿ 3.8 Å) do not suggest any significant stabilization of the stack through bonding interactions [161]. The transfer of $Me_2NCS_2^-$ from one palladium(II) to η^3-methallylpalladium(II), in reaction (28), occurs *via* an associative mechanism involving a trinuclear intermediate [162].



(28)

The isodithiobiuret 4-ClC$_6$H$_4$NHC(SH)=N–C(SCH$_2$Ph)=NPh, H$_2$L, forms [Pd(HL)$_2$] in which it acts as a bidentate ligand [163]. Addition of alkali to solutions of [Pd(ethylenedithioglycolic acid)] results in a complex with 4 axial sulphur atoms and a deprotonated carboxylate group at the apex of a square pyramid [164].

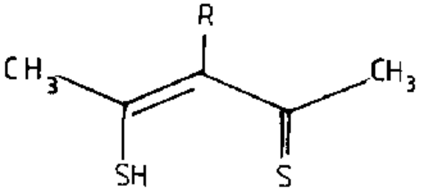
Trans-[M{S$_2$P(OEt)Ph}$_2$], Pd–S = 2.341(2), 2.343(2) Å and Pt–S = 2.341(3) and 2.333(3) Å, undergo isomerisation to produce essentially equal amounts of *cis*- and *trans*-isomers in solution [165]. [Pr$_4$N]$_2$(M(M'OS$_3$)$_2$] and [Pr$_4$N][M(M'S$_4$)(S$_2$CNEt$_2$)], (M = Pd or Pt; M' = Mo or W) in which M is surrounded by four sulphur atoms have been prepared; their electrochemical reduction is being studied [166].

Interest in dithiolate complexes continues. A new synthesis based on Me$_2$Snmnt has been described [167]. Slow aerial oxidation of a 50% aqueous acetone solution of H$_2$[Pt(mnt)$_2$] and LiCl yields black needles of Li$_x$[Pt(mnt)$_2$].2H$_2$O, $x \sim 0.75$, which have a room temperature conductance of between 30 and 200 Ω^{-1} cm^{-1} and a conductance temperature dependence similar to that of one-dimensional partially oxidised "Pt(CN)$_4$" complexes [168]. Planar dithiooxamide complexes, [M(LH)$_2$], are formed by solid state deprotonation of [M(LH$_2$)$_2$X$_2$] when pressed with sodium fluoride (reaction (29)) [169]. The methane enhanced negative ion mass spectra of [Pt(C$_2$S$_2$Me$_2$)$_2$] and [Pt(C$_2$S$_2$Ph$_2$)$_2$]

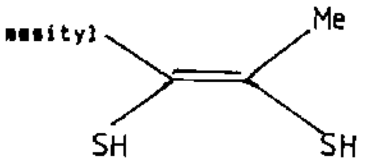
$$[\mathrm{M(RHNCSCSNHR)_2X_2}] + 4\mathrm{NaF} \xrightarrow[\text{disc}]{\text{press in}} [\mathrm{M(RHNCSCSNR)_2}] + 2\mathrm{NaX} + 2\mathrm{NaHF_2} \qquad (29)$$

are characterised by a stable M^- ion; the latter also has an $(M + CH_3)^-$ ion at 80% abundance [170]. Photooxidation of [Pt(bipy)(tdt)] (tdt = 3,4-toluenedithiolate) in chloroform yields $[Pt(bipy)(tdt)]^+Cl^-$ and $\dot{C}HCl_2$ radicals, following an initial dithiolate to bipyridyl charge transfer excitation [171].

Examination of the evidence for electron delocalisation in the cyclic complexes $[ML_2]$ and $[ML'_2]^{2-}$ of the "odd-ligand" (*20a*), HL, and the "even-ligand" (*20b*), H_2L', showed that the merits of Schrauzer's "odd/even" distinction lie in the clear and correct topological differentiation of these two types of complexes, but these differences only manifest themselves in properties which directly depend on the symmetry characteristics of the entire molecule [172].



(20a)



(20b)

1.5.2.7 Ambidentate oxygen-nitrogen donor ligands

The force constants in *cis*-$[Pt(NH_2OH)_2(NO_2)_2]$ have been determined by normal vibrational analysis of the IR and Raman spectra [173]. *Trans*-$[ML_2(NO_2)_2]$ (M = Pd or Pt; L = PEt_2Ph or PEt_3) react with carbon monoxide to form $[ML_2(CO)_2]$ and higher clusters, except for $[Pt(PEt_3)_2(NO_2)_2]$ where evidence for the formation of $[Pt(PEt_3)_2(NO)(NO_2)]$ and $[Pt(PEt_3)_2(NCO)(NO_2)]$ has been observed [174]. $[Pt(PPh_3)_4]$ reacts with N_2O_4 to form $[Pt(PPh_3)_2(NO)(NO_3)]$, which rearranges to $[Pt(PPh_3)_2(NO_2)_2]$ in the absence of dioxygen but forms $[Pt(PPh_3)_2(NO_3)_2]$ in the presence of dioxygen [174].

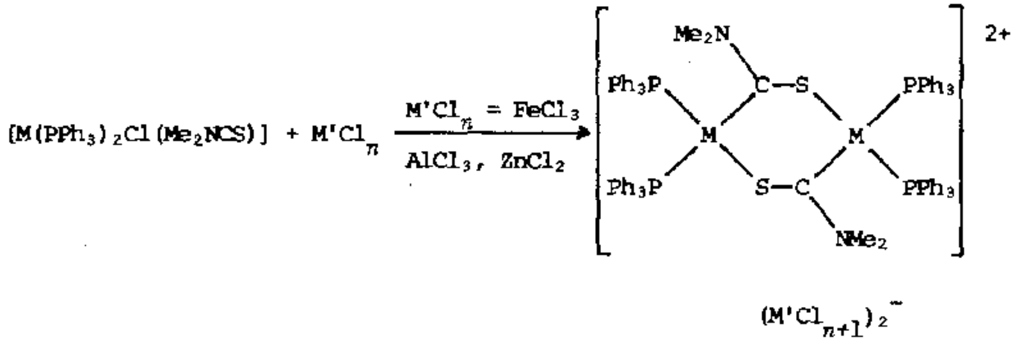
Benzaldehydesemicarbazone [175], isonitrosoacetophenone [176], phenylazobenzaldoxime [177], 1-tetralone oximes [178] and arylazo-bis(acetaldoximes) [179] all form bidentate *N,O*-complexes with palladium(II). Bromination of $[Pd(dpg)_2]$ produces $Pd(dpg)_2Br_{1.1}$, in which palladium is formally in the +2.2 oxidation state since resonance Raman spectroscopy shows the predominant bromine species is Br_5^-. The electrical conductivity of $Pd(dpg)_2Br_{1.1}$ is very similar to that of $Pd(dpg)_2I$ which is unexpected if halogen chains are the major charge carriers [180].

1.5.2.8 Ambidentate sulphur-nitrogen donor ligands

Yellow [Pd(5-NO_2phen)$(NCS)_2$] is obtained by reacting $K_2[Pd(SCN)_4]$ with 5-NO_2phen in dimethylformamide, whereas the orange *S*-bonded isomer is formed when the reaction is carried out in ethanol; on heating in the solid state the *N*-bonded isomer isomerises to the *S*-bonded form, whereas the *S*-bonded form is unaltered [181]. The thermal decomposition of $[Pd(PPh_3)_2(NCS)_2]$ to PdS and of $[Pd(PEt_3)_2(NCS)_2]$ to PdS_2 have been studied thermogravimetrically and by DTA [182]. Reduction of the Pt-S distance on subjecting $K_2[Pt(SCN)_4]$ to 57 kbar results in a blue-shift of about 10 cm^{-1}/kbar in the single crystal luminescence spectrum [183].

X-ray diffraction studies of *cis*- and *trans*-$[Pt\{Me_2NCS(OEt)\}_2Cl_2]$ show Pt-S bond lengths of 2.288(4) Å (mean *cis*) and 2.310(1) Å (*trans*) [184,185]. In *trans*-$[Pd\{Me_2NCS(OEt)\}_2Br_2]$ the Pd-S bond is 2.327(1) Å [186]; all three are significantly less than the sum of the covalent radii (2.35 Å), suggesting some multiple bonding. MeHNC(S)OEt coordinates as a sulphur donor in the anti-form in $[Pd\{MeHNC(S)OEt\}_2X_2]$ (X = Cl, Br or SCN), with a Pd-$S_{thiocarbamate}$ bond length of 2.331(2) Å in the thiocyanate complex [187,188].

The reactions of $[M(PPh_3)_2Cl(Me_2NCS)]$ (M = Pd or Pt) with metal chlorides have been investigated (reactions (30-32)). An X-ray diffraction study showed considerable asymmetry in the bridge of the dimeric palladium(II) complex (*21*) [189].



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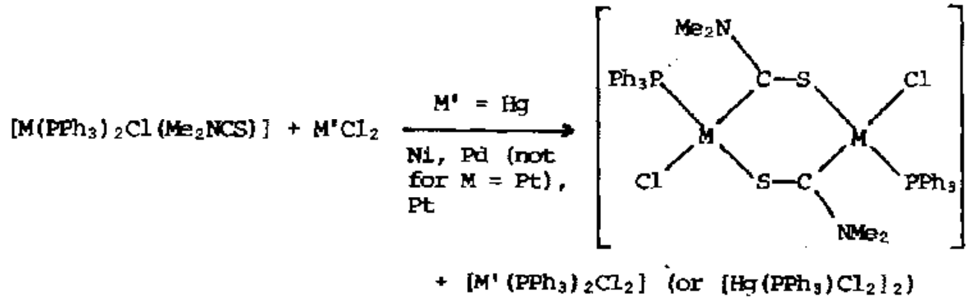

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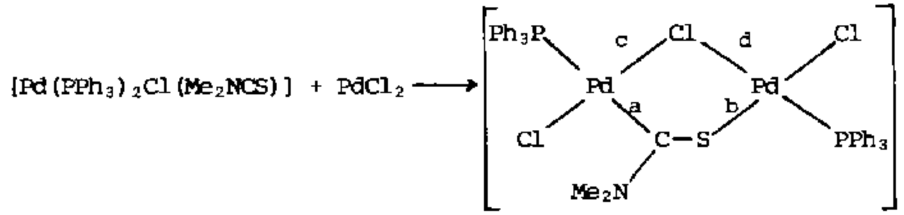


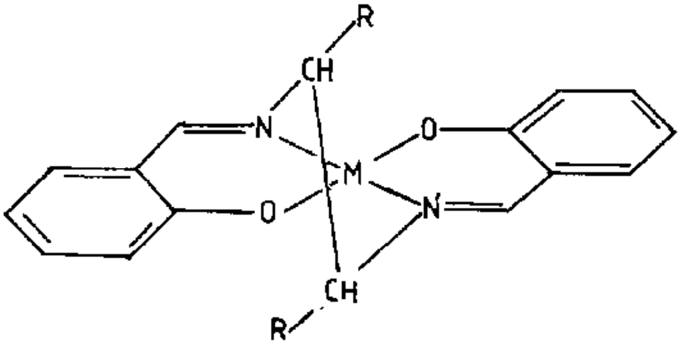
(32)

a	1.963(8) Å		c	2.453(2) Å
b	2.294(2) Å		d	2.495(2) Å

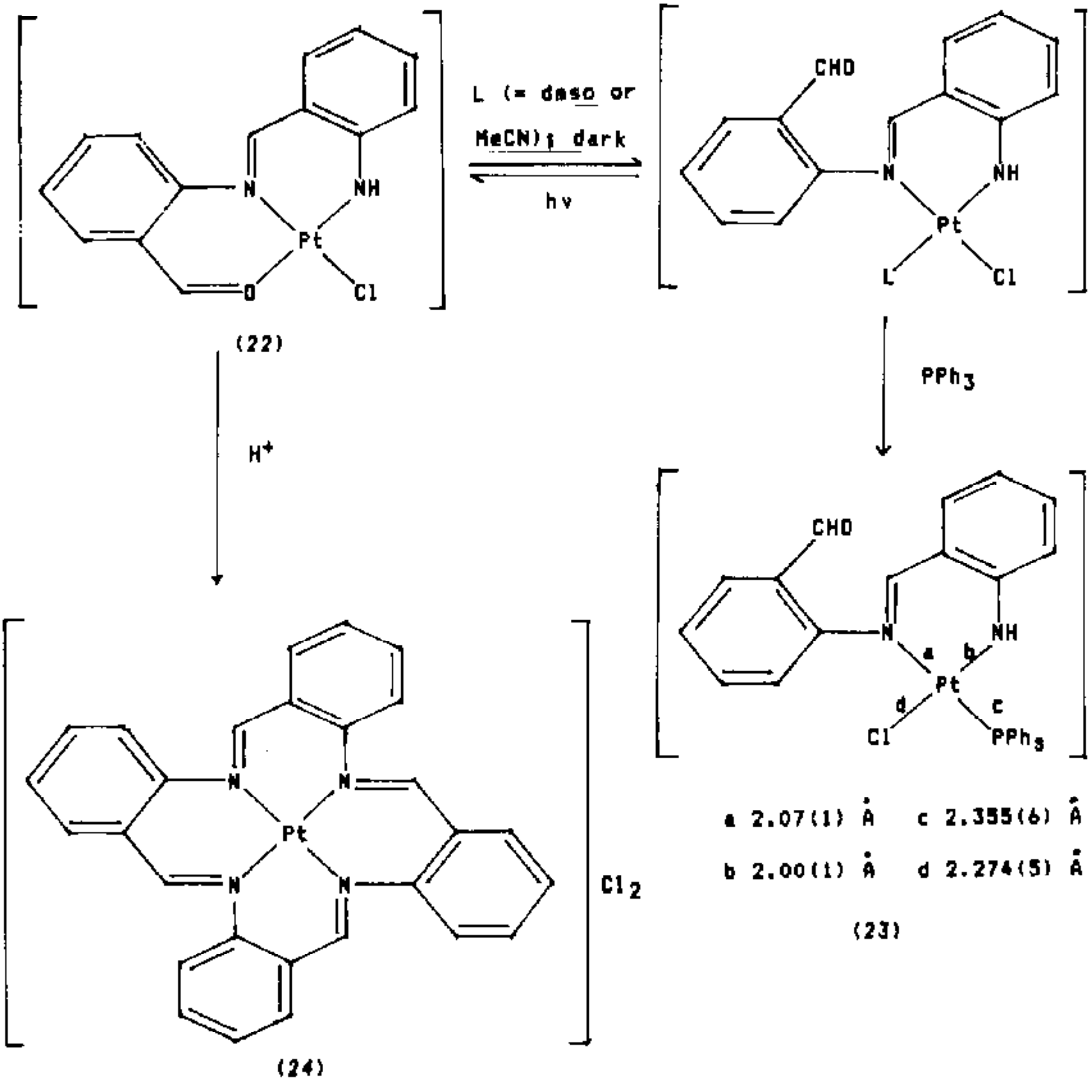
(*21*)

1.5.2.9 Bidentate oxygen-nitrogen donor ligands

Oxamic acid, $H_2NCOCOOH$, acts as a bidentate anionic ligand towards palladium(II) and platinum(II) [190]. The long wavelength bands in [Pd(8-HS-quin)$_2$] and [Pd(8-H_2N-quin)$_2$] arise from $\pi \rightarrow \pi^*$ transitions in the quinoline ligand, in contrast to the situation in [Pd(8-HO-quin)$_2$] [191]. The complexes of palladium(II) and platinum(II) with a number of Schiff bases have been studied. 2-$HOC_6H_4CH{=}NC_6H_4OH$-2 and 2-$HOC_6H_4CH{=}NCH_2CH_2OH$ bond in a tridentate *O,N,O* fashion to platinum(II) [192]. The coordinated formyl group in (*22*) is displaced by dmso or MeCN but can be replaced on irradiation (Scheme 2); an X-ray diffraction study of (*23*) shows that, on dissociation of the formyl group, the benzaldehyde ring rotates through 90° so that the oxygen is poised above the imine nitrogen [193,193*a*]. Protonation of (*22*) results in a template condensation to yield the tetraaza macrocyclic complex (*24*) [194]. The syntheses, structures and conformations of the palladium(II) and platinum(II) complexes of quadridentate Schiff bases, (*25*), have been reported [195].

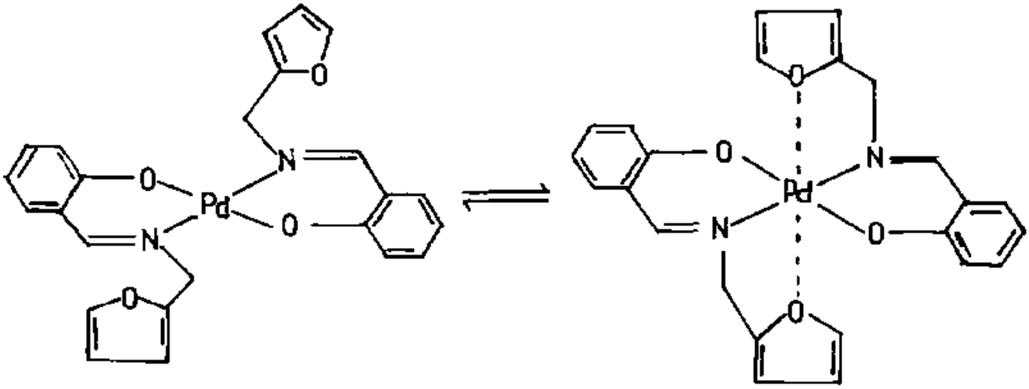


(*25*)



Scheme 2: Photochemically induced Schiff-base formation.

N-Furfurylsalicylaldimine forms a 4-coordinate complex with platinum(II), in which the furfuryl oxygen is not involved, whereas for the corresponding palladium(II) system, weak axial interaction may also occur (equilibrium (34)) [196]. Aroylhydrazines are deprotonated on reaction with $[Pt(PPh_3)_2O_2]$ to form hydrogen peroxide and products in which X-ray diffraction shows the presence of a $\underbracket{\mathrm{Pt^{II}\text{-}NH\text{-}N{=}CR\text{-}O}}$ ring, rather than a $\underbracket{\mathrm{Pt^{0}\text{-}NH{=}N\text{-}CR{=}O}}$ ring [197]. Furan-2-aldoxime [198], isonitrosobenzoylacetone [199] and 1-(2-hydroxyphenyl)-3,5-diphenylformazan (through a six-membered ring) [100] act as bidentate *N,O*-ligands towards palladium(II), as do the



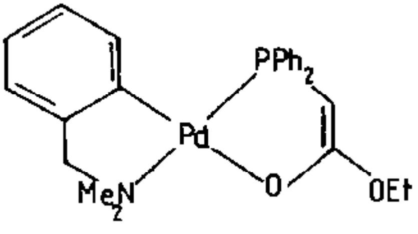
(34)

cis-s-*cis*-enaminones, formed by condensation of aniline with β-diketones [201].

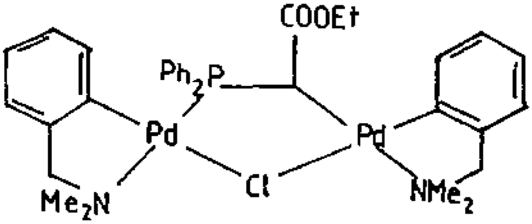
Palladium(II) polyimide films, which exhibit surface and volume resistivities 10^{10} times lower than of the polymer alone, have been prepared [202].

1.5.2.10 Bidentate oxygen-phosphorus donor ligands

$Ph_2PCHCOOEt^-$ acts as a bidentate *O,P*-donor ligand in (*26*) and as a bridging ligand in (*27*) (see also section 1.5.4.13) [203].



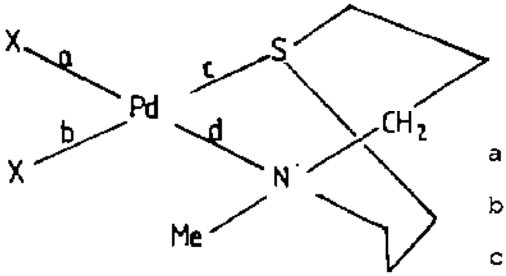
(*26*)



(*27*)

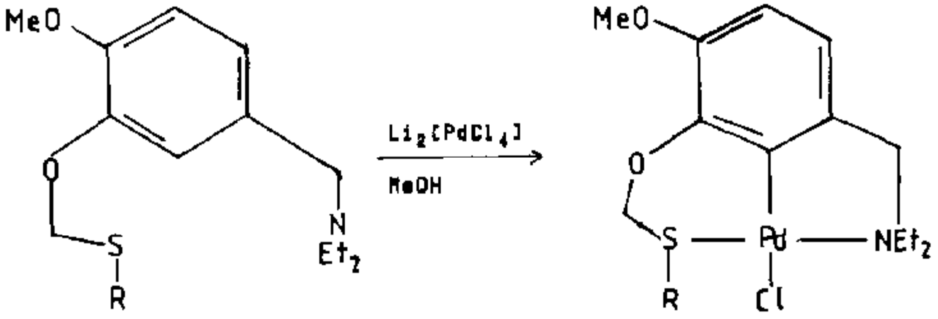
1.5.2.11 Bidentate sulphur-nitrogen donor ligands

5-Methyl-1-thia-5-azacyclooctane reacts with $PdCl_2$ to give (*28*) (X = Cl), which does not dissociate in solution or exhibit inversion at sulphur or nitrogen [204]. The *S,N*-bidentate ligand, (*29*), reacts with $Li_2[PdCl_4]$ to form a complex in which the ligand acts as a *trans* *S,N*-bidentate ligand that then metallates (reaction (35)); a number of bis-thioether analogues have also



(28)

	X = Cl	X = I
a	2.305(1) Å	2.601(2) Å
b	2.330(1) Å	2.624(2) Å
c	2.104(3) Å	2.14(2) Å
d	2.268(1) Å	2.323(7) Å

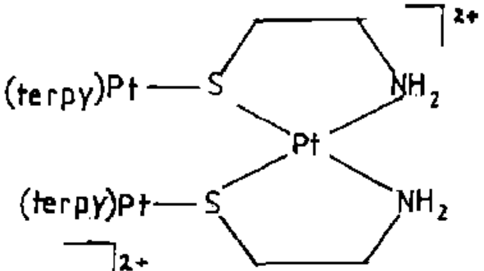


(29)

(35)

(R = Me or Ph)

been studied, but in these cases metallation of the phenyl group is catalysed by silica gel [205]. *S*-Dealkylation of $[Ph_3CS(CH_2)_2NH_2(CH_2)_3NH_2(CH_2)_2SCPh_3][Br]_2$ occurs when this ligand is treated with palladium acetate in methanol; the product is trimeric (*30*) [206]. When $[Pt(terpy)(SCH_2CH_2NH_3)]^{2+}$ is treated with deoxymethyl-pTpA (A = adenine, T = thymine) it yields (*31*), in which the two Pt(terpy) units are above one



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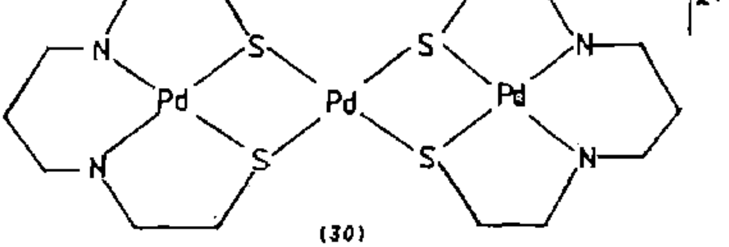
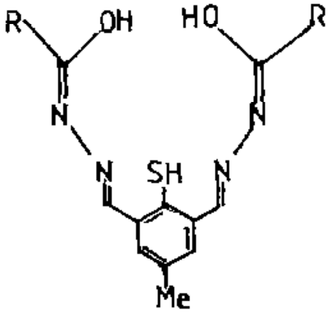


(30)

another and the third platinum is perpendicular to this [207]. In the deoxymethyl-pTpA, (*31*), adduct, the A-T base pairs are stacked on either side of (*31*) but do not form a miniature double helix; indeed, models show that base-pair displacement in the DNA double helix would be necessary to accommodate intercalative binding of a bis-terpyridylplatinum(II) reagent, which may therefore be useful to identify base substitution mutations [207].

Cyclic voltammetry and controlled potential coulometry of $[Pd\{(sacac)_2en\}]$ ($(sacac)_2en$ = $(CH_3CSCHCMe{=}NCH_2)_2$) shows that reduction gives successively the unstable uninegative and dinegative anion species, whereas oxidation gives the dipositive cation from which the starting complex can be regenerated [208]. The binucleating ligands, (*32*) (R = Ph or cych) formed binuclear complexes of the type $[Pd_2L(\mu\text{-}Z)]$, where L = (*32*) acting as *O,N,S* donors to each palladium [209]. (*33*) (E = O or S) did not form the expected binuclear complexes but tetranuclear complexes such as $[Pd_4L(OAc)]$ which were not fully characterised [210].



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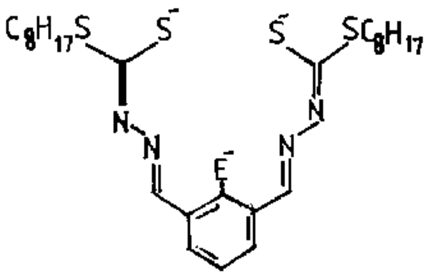

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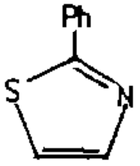
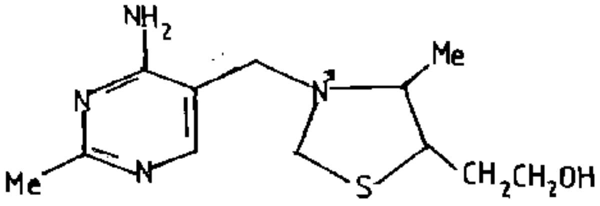


(34)

2-Mercaptopyridine and 2-thiouracil have been shown to act as unidentate *N*-donors towards platinum(II) [211]. 2-Phenylthiazole, (*34*), reacts with palladium(II) acetate to form [Pd(OAc)L], in which the thiazole, instead of acting as an *S,N*-donor, acts as a *C,N*-bidentate ligand [212]. The hydrogenated thiamine derivatives, (*35*) and (*36*), bond to platinum through either N^3 or *S*



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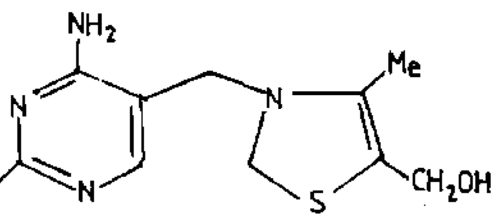
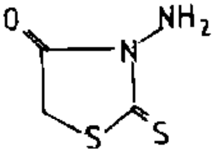


(36)

[212*a*]. (*37*) and (*38*) both act as *S*,*N*-chelating ligands towards palladium(II) and platinum(II) [213,214] whilst, in $[Pd(SNSNH)_2]$, the bidentate *S*,*N*-ligands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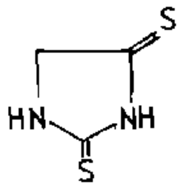
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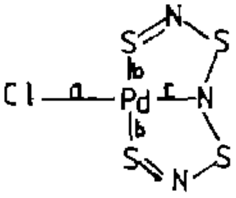


(39)

a 2.294(10) Å
b 2.242(7) Å
c 1.963(25) Å

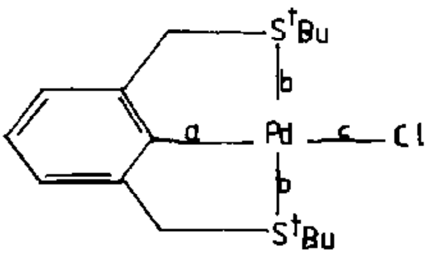
bond in a *cis* arrangement [215]. $S_4N_4H_4$ reacts, unexpectedly, with $K_2[PtCl_4]$ in aqueous acetone to form $[Pt(\mathit{O}SNH)_2(\mathit{S}NHS\mathit{N}H)]$ (donor atoms italicised) [216], whilst S_4N_4 reacts with *cis*-$[Pt(PhCN)_2Cl_2]$ to form a square planar complex in which the S_4N_4 ligand retains its identity and bonds in a tridentate fashion, (*39*) [217].

1.5.2.12 Bidentate sulphur-phosphorus donor ligands

$[Pd(Ph_2PC_6H_4SMe\text{-}2)X_2]$ (X = SCN or I) undergo demethylation on reaction with halide ion to form $[Pd(Ph_2PC_6H_4S\text{-}2)X_2]^-$, which can be remethylated by alkyl halide 50 times faster than demethylation [218].

1.5.2.13 Bidentate sulphur-carbon donor ligands

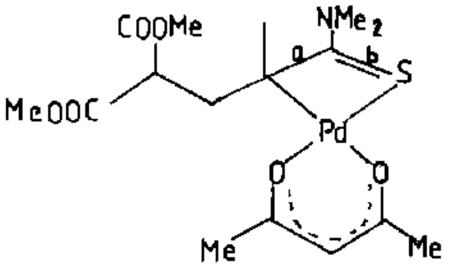
An X-ray diffraction study of [Pd(acac)(CH$_2$NMeC(Ph)S)] shows that the Pd-O bond lengths are influenced by the *trans*-donor, since Pd-O$_{trans}$ to C = 2.106(3) Å whereas Pd-O$_{trans}$ to S = 2.054(3) Å [219]. 1,3-$(BuSCH_2)_2C_6H_4$ readily metallates at the 2-position to form (*40*) which, on reaction with triphenylphosphine, suffers Pd-S but not Pd-C bond cleavage to yield



a 1.988(11) Å
b 2.308(2) Å
c 2.406(3) Å

(40)

$[Pd(PPh_3)_2\{C_6H_3(CH_2SBu)_2\text{-}1,3\}Cl]$ [220]. The thiaallyl complex, (*41*), prepared previously [221], has been shown to involve two η^1-bonds and not an η^3-bond [222].



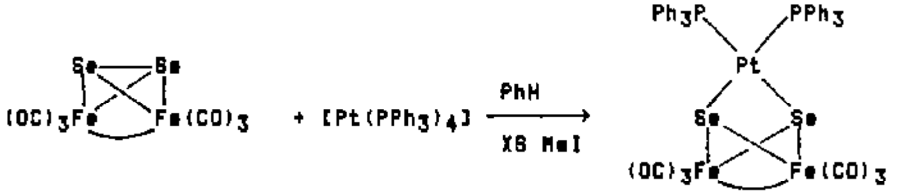
a 2.058(3) Å

b 2.262(1) Å

(41)

1.5.2.14 *Bidentate selenium donor ligands*

$[Fe(CO)_3(\mu\text{-}Se)_2Fe(CO)_3]$ can act as a bidentate selenium donor towards platinum, as in reaction (36)) [223]. A convenient small scale synthesis of



(36)

CSe_2, which can then be used to prepare dialkylselenocarbamates, has been described [224]. The structure of $[Pt(Se_2CN^{i}Bu_2)_2]$ is the same as in the sulphur analogue, with Pt–Se = 2.427(3) Å (average) [224].

1.5.2.15 *Tellurium donor ligands*

$ArTeEPh_3$ (E = Ge or Sn) react with $[Pd(PhCN)_2Cl_2]$ to form aryltelluride bridged polymers $[Pd(ArTe)_2]_n$ [225]. $Te(CH_2CH_2Ph)_2$ prepared by alkylation of Na_2Te forms $[M\{Te(CH_2CH_2Ph)_2\}_2Cl_2]$; when M = Pd the complex has a *cis*-geometry but the platinum complex forms a mixture of *cis*- and *trans*-isomers in solution, as shown by ^{125}Te NMR spectroscopy [226].

1.5.3 *Complexes with amino-acids, peptides, nucleic acids, and other biologically important molecules*

Since most biologically important molecules bond through Group VI and

Group V donor atoms, the previous practice of considering them between ligands belonging to these two groups is continued.

1.5.3.1 Amino-acids and peptides

The X-ray crystal structure of Ba*cis*-$[Pd(NH_2CH_2COO)Cl_2].H_2O$ shows Pd-Cl, Pd-N and Pd-O bonds of 2.303, 2.03 and 2.015 Å, respectively [227,228]. A study of the kinetics of glycine ring formation in [Pt(en)(gly)Br]Br has shown that intrasphere bromide substitution predominates under pH conditions that favour the non-protonated form [229]. DL-Phenylglycine and its esters coordinate to palladium(II) and platinum(II) as unidentate nitrogen donors [230]. The hydrolysis of the glycinate, α-alaninate, β-phenylalaninate and picolinate complexes $[Pd(en)(NH_2CHRCOOR')]^{2+}$ shows substantial acceleration under basic conditions, whereas this is less marked in the cysteinate and histidinate complexes [231]. A study of the ligand-ligand interactions in [PdAB], where A is a deprotonated acidic amino acid and B is a protonated basic amino acid, shows stereoselectivity in the palladium(II) coordination plane due to ligand-ligand interaction [232].

$[Ag_8Pd_6L_{12}Cl]^{5-}$, where L = $^{-}SCMe_2CH(NH_2)COO^{-}$, involves a central chloride with a cube of silver(I) ions surrounded by an octahedron of palladium(II) atoms, each of which has 2 penicillamine ligands attached to it [233]. A series of platinum(II) complexes of L-α,γ-diaminobutyric acid and L-ornithine have been prepared [234]. The IR spectra of *trans*-$[M(L\text{-alaninate})_2]$ (M = Pd or Pt) have been assigned with the aid of ^{18}O and ^{15}N isotopic labelling [235]. The band signs in the CD spectra of *cis*- and *trans*-$[Pt(ZH)_2Cl_2]$ (ZH = L-alanine, L-valine, L-isoleucine, L-norvaline, or D-leucine) are determined both by the absolute configuration of the ligand and the geometric configuration of the complex [236]. *Cis*-$[Pd(L\text{-serinate})_2]$ has been prepared from $K_2[PtCl_4]$ and L-serine by deionisation by passage down an ion-exchange resin column [237]. Although the neutral -OH group in ethanolamine coordinates to palladium(II) on reaction with $[Pd(en)(H_2O)_2]^{2+}$, the neutral -OH groups in L-serine, L-threonine, and L-homoserine do not, although coordination does occur on deprotonation of the -OH; for L-hydroxyproline neither the neutral -OH group nor the deprotonated alkoxy-group coordinate [238].

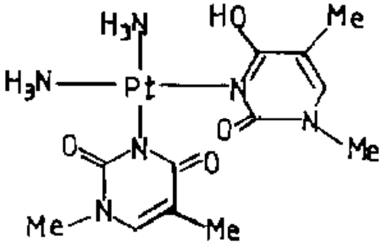
X-ray and NMR studies confirm the *S*,*N* coordination of *S*-methyl-L-cysteinemethyl ester in its dichloropalladium(II) complex [239]. The *S*,*S*-*cis*-chelation of the cysteine tetrapeptides cys-ala-ala-cys, in contrast to the lack of chelation of the cys-val-val-cys peptide on treatment with $Na_2[PdCl_4]$, confirmed the importance of the steric effects of the two intermediate amino acid residues in determining conformational fitness, which is important for understanding the cys-A-B-cys sequence involved in the active sites of some metalloenzymes [240].

1.5.3.2 Nucleic acids and nucleosides

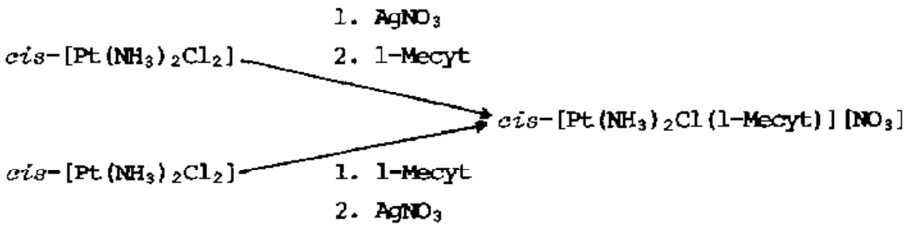
The adenosine phosphates ADP and ATP mainly coordinate to palladium(II) and platinum(II) through the N^1 and N^7 purine *N*-donors which have nearly equal coordination abilities [241-246]; the presence of the 5-phosphate group enhances N^7 over N^1 coordination [247]. By using palladium(II) compounds as a thermodynamic reference for reactions of analogous platinum(II) compounds at equilibrium, it appears that in some previous platinum(II) studies equilibrium was not achieved and the reported stability constants for platinum(II)-nucleoside complexes are too low. At pH 7 the order of $Pd(dien)^{2+}$ binding strengths is N^7 of GMP > N^3 of TMP > N^3 of CMP > N^7 of AMP > N^1 of AMP [247]. The solution isotropic absorption, CD, and stretched film CD spectra of the complexes of adenosine with *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ above about 250 nm have been interpreted in terms of two relatively close vibronic (π^*,π) transitions [248]. An upper limit of 217 kJ mol^{-1} has been derived for the Pt-N^7 bond strength in $[PtCl_3(9\text{-methyladeninium})]$ [249]. *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ shows complete selectivity for AMP and GMP when $0 > r_t$ (total metal:total phosphate) $\leqslant 0.3$; *trans*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ shows less affinity for AMP and $[Pd(en)(H_2O)_2]^{2+}$ and *trans*-$[Pd(NH_3)_2(H_2O)_2]^{2+}$ show intermediate behaviour [250]. Raman and ^{13}C NMR spectroscopy has been used to study the interaction of *cis*-$[Pt(dmso)_2Cl_2]$ with adenosine, uridine, and cytidine in dmso [251].

X-ray diffraction has been used to study the purine complexes $[Pt(dien)L][PF_6]$ (L = 7,9-dimethylguanine and 7,9-dimethylhypoxanthine), both of which involve Pt-N^1 coordination (Pt-N^1 bond lengths being 2.044(5) and 2.051(6) Å, respectively) [252]. 9-Ethylguanine coordinates to platinum(II) at N^7 and this facilitates deprotonation at N^1, as well as altering the hydrogen bonding of guanine to other bases and hence its selectivity for cytidine [253]. Deprotonated guanosine acts as an *N,O*-chelate ligand towards (en)Pt [254]. The homodinucleotides GpG, ApA and IpI react with *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$ to give N^7 - N^7 chelation of the metal, whereas GpC and ApC give mixtures of several complexes in which cytosine appears to have more affinity for platinum than guanine and adenine [255]. An X-ray diffraction study of $[Pt(1,3\text{-pn})(Me\text{-}5'\text{-GMP})_2]$ shows N^7 coordination as well as highly significant intracomplex base-base interactions dominated by O^6 ... imidazole ring contacts, which will cause large local distortions in DNA structure since the base-base overlap in the platinum(II) complex is very different to that postulated for the various forms of DNA [256]. Bis-nucleotides show the same enhanced CD spectra as polynucleotides with *cis*- but not *trans*-platinum(II) complexes and so may provide valuable information on Pt^{II}-DNA binding [257]. Previous work, suggesting that *cis*-$[Pt(NH_3)_2Cl_2]$ binds in a sequence specific manner to DNA, has been supported by showing that it binds in a unique fashion to $(dG)_n.(dC)_n$ for $n > 2$ [258].

Laser Raman spectroscopy has been shown to be useful for differentiating the tautomers of uracil and thymine in solution and coordinated to platinum(II) [259]. *cis*-[Pt$(NH_3)_2$(1-methylthyminate)$_2$], in which thymine is bound to platinum through N^3, reacts with one equivalent of $MnCl_2.4H_2O$ to form Mn[Pt$(NH_3)_2$(1-methylthyminate)$_2$]$_2Cl_2.10H_2O$, in which a square-planar manganese(II) ion is coordinated by four oxygens (O^4) of the thymines [260]. Protonation of *cis*-[Pt$(NH_3)_2$(1-methylthyminate)$_2$] yields (*42*), in which one thymine ligand is in the iminol form [250*a*]. *cis*-[Pt$(NH_3)_2$Cl(1-Mecyt)][NO_3] (1-Mecyt = 1-methylcytosine) can be prepared in two different ways (reaction (37)) and in each case two types of crystals, needles and roughly cubic parallepipeds are formed; the temperature and rate of recrystallisation determine which form predominates. The cations are similar in both materials, the structural differences derive from the relation between the cations and nitrate ions [261]. In aqueous solution one of the ammine ligands in *cis*-[Pt$(NH_3)_2$Cl(1-Mecyt)]Cl, which are generally considered inert, is labilised to form *trans*-[Pt$(NH_3)Cl_2$(1-Mecyt)], in which all the bond lengths are normal but the pyrimidine ring is at 64° to the square-plane. This product reacts with further 1-methylcytosine to yield *trans*-[Pt$(NH_3)_2$(1-Mecyt)$_2$]$^{2+}$ which has been isolated as its nitrate salt; in this complex, the pyrimidine square-plane



(*42*)



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dihedral angle is 78° [262]. The crystal structure of *cis*-$[Pt(NH_3)_2(1\text{-}Mecyt)_2][NO_3]_2.1\text{-}Mecyt$ shows that the two *cis*-bases lie perpendicular to the plane such that the exocyclic $=O$ and $-NH_2$ match up [263,264]; similarly, in *cis*-$[Pt(NH_3)_2(NO_2)(1\text{-}Mecyt)]_2$ and *cis*-$[Pt(NH_3)_2(1\text{-}Mecyt)(\text{thyminate})][ClO_4]$ has the pyrimidine groups arranged so that the $=O$ and $-NH_2$ groups can hydrogen-bond together [264,265].

The above observation, that *cis*-$[Pt(NH_3)_2Cl(1\text{-}Mecyt)]Cl$ can be converted to *trans*-$[Pt(NH_3)Cl_2(1\text{-}Mecyt)]$ under mild conditions in aqueous solution at room temperature, opens up an interesting alternative to the generally accepted bifunctional attack of *cis*-$[Pt(NH_3)_2Cl_2]$ with replacement of both chloride ligands, since *trans*-$[Pt(NH_3)Cl_2L]$ could coordinate a second biomolecule hence giving inter- and intra-strand linking of DNA and/or bidentate DNA plus protein crosslinking (reaction (38)). However, loss of ammonia inside the cell is unlikely as $[Cl^-]$ is too low; this could occur in the plasma to yield *trans*-$[Pt(NH_3)Cl_2X]$ (X = plasma component), which could then be taken up by the cell [266].

$$\begin{tikzcd} & {[Pt(NH_3)(1\text{-}Mecyt)_3][ClO_4]_2} \\ trans\text{-}[Pt(NH_3)Cl_2(1\text{-}Mecyt)] + 2AgClO_4 \arrow[ur, "2 \times 1\text{-}Mecyt"] \arrow[dr, "2 \times 9\text{-}Etguanine"'] & \\ & {[Pt(NH_3)(1\text{-}Mecyt)(9\text{-}Etguanine)_2][ClO_4]_2} \end{tikzcd} \tag{38}$$

Cytidine (Cytn) coordinates to platinum(II) through N^3, as in $[Pt(O\text{-}Mecysteine)(Cytn)Cl]$ [246,247]. Reaction of $[Pt_2(NH_3)_4(\mu\text{-}OH)_2]^{2+}$ with 1-methyluracil (1-Meur) yields *cis*-$[(NH_3)_2Pt(\mu\text{-}1\text{-}Meur\text{-}N^3,O^4)_2Pt(NH_3)_2]\text{-}[NO_3]_2.3H_2O$, in which the uracil ligands bridge (N^3,O^4) in head to tail fashion two *cis*-$[Pt(NH_3)_2$ units which lie above each other [268]. The formation constants of uracil, uridine, and thymidine complexes with $[Pd(dien)(H_2O)]^{2+}$ and $[Pd(en)(H_2O)_2]^{2+}$ have been determined potentiometrically [269]. 6-Methyl-2-thiouracil (HL) forms $[PtL_2]$ on reaction with *cis*-$[Pt(NH_3)_2Cl_2]$ and $[PdL_2]$ on reaction with *trans*-$[Pd(NH_3)_2(NO_2)_2]$; in both complexes the ligand is bound via the S and the heterocyclic N atoms [270].

Premelting conformational changes may have considerable biological significance in DNA recombination, transcription, and replication processes, since DNA functions *in vivo* far below the temperature of melting. It is significant that *cis*-$[Pt(NH_3)_2Cl_2]$ causes DNA premelting at low Pt:DNA doses, whereas *trans*-$[Pt(NH_3)_2Cl_2]$, which has no anti-tumour activity, does not cause this premelting [271]. Evidence has been obtained that the *cis*-$[Pt(NH_3)_2Cl_2]$ recognition site on DNA is intrastrand cross-linking of nearest neighbour guanine or cytosine bases, since *cis*-[Pt$(NH_3)_2Cl_2$] binds selectively to the $(dG)_n(dC)_n$, $n \leqslant 4$ sequence in DNA [272]. A study of the Raman spectrum in aqueous solution has shown that *cis*-[Pt$(NH_3)_2Cl_2$] perturbs the guanine carbonyl region of salmon sperm DNA; both the *cis*- and *trans*-isomers interact with N^7-guanine sites but in clearly different ways [273]. The interaction of $K_2[MCl_4]$ (M = Pd or Pt), and the 5-sulpho-8-mercaptoquinolinates of platinum and palladium with membrane-bound Ca^{2+}- and Mg^{2+}-ATPase of sarcoplasmic reticulum has been studied by spectrofluorimetry; interaction is with the tryptophan residues [274,275].

1.5.3.3 Cancer therapy and related topics

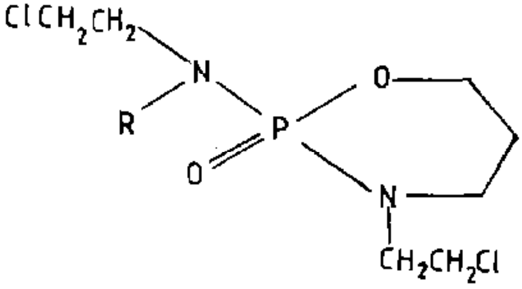
The biological interest in *cis*-[Pt$(NH_3)_2Cl_2$] has been reviewed [276]. The significant factors in the mechanism of the anti-tumour action of *cis*-[Pt$(NH_3)_2Cl_2$] are [277]:

(i) *cis*-[Pt$(NH_3)_2Cl_2$] loses chloride ions slowly in water and the resulting aqua ions are deprotonated to form a variety of hydroxy-species,

(ii) *cis*-[Pt$(NH_3)_2Cl_2$] appears to bind to DNA preventing replication,

(iii) one particular DNA site, O^6 of guanosine, has been linked with both carcinogenesis and the mechanism of the anti-tumour action of platinum complexes.

The optical resolution of two anti-tumour drugs, (*43*) (R = H and CH_2CH_2Cl) have been achieved through their diastereomeric *cis*-platinum(II) complexes with (S)-(+)-(*44*) [278].



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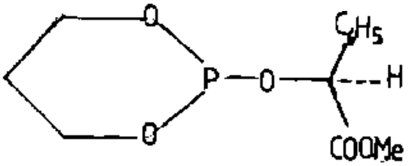

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1.5.4 Complexes with Group V donor ligands

1.5.4.1 Unidentate nitrogen donor ligands

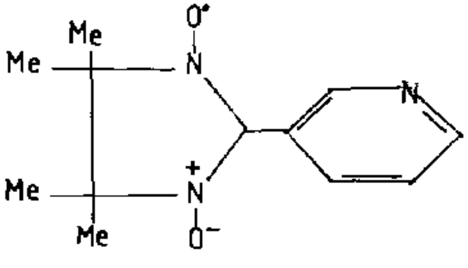
Luminescence, absorption, magnetic circular dichroism, and ^{35}Cl NQR experiments, together with extended Hückel MO calculations on *cis*- and *trans*-[Pt$(NH_3)_2Cl_2$] indicate that, whilst the relative energies of the *d*-orbitals are the same in both isomers ($d_{x^2-y^2} > d_{xy} > d_{xz} > d_{yz} > d_{z^2}$) the Pt-Cl bond is more covalent in the *trans*- than in the *cis*-isomer [279]. The barrier to ammonia rotation in *trans*-[Pt$(NH_3)_2Br_2$] is less than in the *cis*-isomer, so that the *trans*-isomer has the higher heat capacity at low temperatures [280]. *cis*-[Pd$(NH_3)_2Cl_2$] decomposes to NH_3, Cl_2 and palladium metal, some of which is oxidised to PdO, between 240 and 300 °C; between 380 and 400 °C the remaining palladium is oxidised to PdO and then between 800 and 860° the PdO decomposes [281].

Solutions of *cis*- and *trans*-[Pt$(NH_3)_2Cl_2$] can be quantitatively analysed by measuring their optical absorbances before and after controlled reaction with allyl alcohol [282]. MO calculations have been carried out on *cis*- and *trans*-[M$(NH_3)_2X_2$] (X = halide or H_2O; M = Pd [283] or Pt [284,285]). Crown ethers, such as 18-crown-6 and dibenzo-18-crown-6, hydrogen-bond to the ammine ligands in *trans*-[Pt$(NH_3)LCl_2$] (L = PMe_3, PEt_3 or NH_3) [286].

Cyclobutylamine reacts with $K_2[PtCl_4]$ in aqueous solution to give yellow [PtL_2Cl_2] which forms *cis*-[PtL_2Cl_2] on recrystallisation from dmf containing HCl but yields *trans*-[PtL_2Cl_2] on recrystallisation from acetone; Pt-N and Pt-Cl both lengths in the two isomers are similar [287]. The crystal structures of *cis*-[PtL_2Cl_2] (L = cyclohexylamine) and *trans*-[PtL_2Cl_2] (L = cycloheptylamine) also show typical Pt-N and Pt-Cl bond lengths [288,289]; the latter was prepared by the route previously reported to yield the *cis*-isomer but recrystallised from acetone which clearly promotes *cis* to *trans* isomerisation in these complexes. The presence of excess amines, such as aniline or nicotinamide, also promotes formation of the *trans* isomer, whereas exactly 2 equivalents may yield a mixture of *cis*- and *trans*-[Pt(amine)$_2Cl_2$] [290]. The acid dissociation constants of *cis*- and *trans*-[Pt$(NH_2OH)_2Cl_2$] and *cis*- and *trans*-[Pt$(NH_2OH)(NH_3)Cl_2$] have been determined in acetone; [Pt$(NH_3)_2Cl_2$] shows no acidic properties for the ammine ligands in dmf [291]. The kinetics of aquation of *cis*-[PtL_2Cl_2] (L = NH_3, NH_2OH or NH_2OMe) show that oxygen-containing ligands give significantly higher activation energies of aquation than ammonia itself [292]. The water soluble primary amine $H_2NC(CH_2OH)_3$ forms *trans*-[PtL_2Cl_2] on reaction with $Na_2[PtCl_4]$ [293].

cis-bis-organopalladium(II) complexes are rare; however, [NBu_4]*cis*-[PdLCl$(C_6F_5)_2$] and *cis*-[$PdL_2(C_6F_5)_2$] (L = N, P, As or Sb donor ligand) have been prepared by chloride bridge cleavage of $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ [294]. *cis*- and *trans*-[Pt(py)LCl_2] (L = 4-nitroaniline) have been prepared; the *cis*-isomer was obtained by reaction of K[Pt(py)Cl_3] with L, whereas the *trans*-isomer was obtained by reaction with K[$PtLCl_3$] [295]. Similarly, whilst *cis*-[Pt$(PhNH_2)_2Cl_2$] is formed by reaction of aniline with K[Pt$(PhNH_2)Cl_3$] in aqueous solution, excess aniline reacts with $K_2[PtCl_4]$ in aqueous alcohol to yield *trans*-[Pt(PhNH$_2$)$_2$Cl$_2$] [295]. 3-Aminocoumarin, however, reacts with K$_2$[PtCl$_4$] to yield *N*-bonded *cis*-[PtL$_2$Cl$_2$] [296]. The explosive thermal decomposition of [Pd(4-ONC$_6$H$_4$NMe$_2$)$_2$Cl$_2$] occurs at 190 °C [297]. 2-Alkylsubstituted anilines react with [Pd(PhCN)$_2$Cl$_2$] in dichloromethane to give simple aniline complexes [Pd(2-R'C$_6$H$_4$NR$_2$)Cl$_2$]$_2$, whereas, with Li$_2$[PdCl$_4$] in methanol, *N*-dealkylation occurs to yield *trans*-[Pd(2-R'(C$_6$H$_4$NHR)$_2$Cl$_2$] and with palladium(II) acetate in glacial acetic acid metallation of 2-methyl groups occurs, to yield [{Pd(2-CH$_2$C$_6$H$_4$NR$_2$)(μ-Cl)}$_2$] [298].

Single crystal X-ray diffraction studies have been reported for [Pt(2,6-lutidine)Cl$_2$]$_2$ (Pt-N = 2.020(10) Å) [299], *trans*-[Pt(pyrimidine)$_2$X$_2$] (X = Cl, Pt-N = 2.008(5) Å); X = Br, Pt-N = 2.014(7) Å [300], *trans*-[Pt(PEt$_3$)LCl$_2$] (L = pyrrolidine or 2,5-dimethylpyrrolidine) [301], *trans*-[Pt(4-EtOOcpy)Cl$_2$] (Pt-N = 1.991(11) Å) [302] and [PPh$_3$Me][Pt(caffeine)Cl$_3$] (Pt-N^9 = 2.021(5) Å) [303]. 2,4-dimethyl-6-hydroxypyrimidine reacts with K$_2$[MCl$_4$] to form [ML$_2$Cl$_2$] (M = Pd or Pt), in which the ligand coordinates through N^1 [304], whereas 4-amino-2,6-dimethylpyrimidine and pyridine-2,6-dicarboxylic acid form only 1:1 complexes [305,306]. 2-Aminopyrimidine coordinates to platinum(II) through the heterocyclic nitrogen [307]. 2-, 3-, and 4-bromopyridine (LH) undergo oxidative-addition to [Pd(PPh$_3$)$_4$] to yield [{Pd(PPh$_3$)LBr}$_2$] which, with excess PEt$_3$, forms [Pd(PEt$_3$)$_2$LBr]; all three of these complexes have been studied by X-ray diffraction. The pK$_a$ of pyridine (4.47) is altered to 5.38, 5.01, and 7.44 when the "Pd(PEt$_3$)$_2$Br" group is at the 4-, 3-, and 2-positions, respectively, indicating that all of the complexes are stronger bases than pyridine itself [308]. The stable free radical, (*45*), forms *cis*-[ML$_2$Cl$_2$] (M = Pd or Pt), in which the L ligands are bound through the pyridyl nitrogen atom and the nitroxide radicals, show considerable interaction with each other [309].



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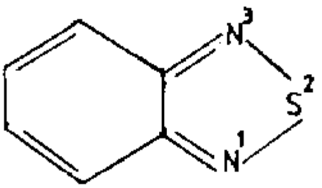
A very convenient way to prepare [{Pt(C$_2$H$_4$)Cl$_2$}$_2$] is to pour a solution of *trans*-[Pt(C$_2$H$_4$)(py)Cl$_2$] down a sulphonated cation exchange resin and remove pyridine as the pyridinium ion [310]. On UV irradiation *cis*-[Pt(C_2H_4)(4-Mepy)Cl_2] undergoes photoisomerisation to the *trans*-isomer, through a low-energy *d*-*d* excited state, photosubstitution, and photodissociation of the Pt-C_2H_4 bond when irradiated in the $Pt_{5d} \rightarrow C_2H_{4\pi*}$ band [311].

The crystal structure of [(C_2H_4)ClPt(μ-Cl)(μ-pyrazolide)PtCl(C_2H_4)] shows that the complex is almost planar, except for the ethylene ligands which lie at 85(1)° and 92(1)° to the plane [312]. In *cis*-[Pt(PEt_3)$_2$ClL] (L = pyrazole) the two phosphorus atoms are inequivalent; they become equivalent in the palladium complex by a mechanism in which pyrazole dissociation is the rate-determining step [313]. Pyrazolate and imidazolate ligands in [Pt(dppe)L_2] complexes can coordinate to rhodium(I) on reaction with [Rh(cod)(Me_2CO)$_x$][ClO_4] to give pyrazolate bridged dinuclear and imidazolate bridged tetranuclear complexes [314]. [Pt(1,2-dimethylimidazolate)$_4$][I_3]$_2$ has Pt-N^3 bonds of between 2.009(8) and 2.014(5) Å and a very low solubility in aqueous solution, in contrast to other [PtL_4]X_2 (X = Cl, Br, I or ClO_4) species [315]. Thiadiazoles, (*46*), bond to palladium(II) through N^1 [316], whereas pentamethyltetrazole, (*47*), probably bonds to both palladium(II) and platinum(II) through N^4 [317].



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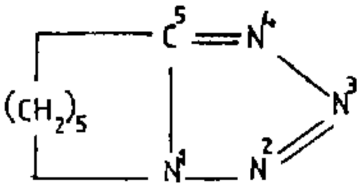

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1.5.4.2 *Bidentate nitrogen donor ligands*

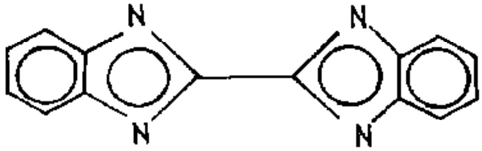
Single crystal X-ray diffraction studies have been reported for *cis*-[Pt{1,2-(NH_2)$_2$cych}$_2X_2$] (X = Cl or Br) [318], [Pd(*S*-$R_2NCHMeCH_2NH_2$)Cl_2] (R = Me in which the molecules are held together by strong hydrogen bonds between Cl and -NH_2, and R = Et where the hydrogen-bonding is somewhat hindered), where the Pt-NH_2 bonds are shorter than the Pt-NR_2 bonds [319] and [Pd(*R*-$NH_2CHMeCH_2NH_2$)Cl_2] which exists in two crystalline forms, monoclinic and triclinic, which have essentially the same structure, except that one has a chelate ring of λ-conformation with an equatorial methyl group whilst the other has a δ-conformation with an axial methyl group [320]. ^{13}C and ^1H NMR has been used to study the conformation of aliphatic 1,3-diamines coordinated to platinum(II) [321], whilst low temperature IR and Raman spectra have been used to study the correlation coupling that occurs between closely spaced hydrogen bonded pairs of *cis*-$[M(meso\text{-}2,3\text{-diaminobutane})Cl_2]$ (M = Pd or Pt) molecules [322].

$H_2[PtLCl_2]$ and $[PtL'Cl_2]$ (H_2L = *meso*-1,2-diaminosuccinic acid, 2,3-diaminopropionic acid and L' = ethylester of HL) have been examined for anti-tumour activity; only the neutral ester complexes have any activity; the inactivity of $H_2[PtLCl_2]$ is ascribed to their reduced ability to permeate into cells and their lower reactivity with DNA [323]. $[Pd(edta)X_2]$ (X^- = Cl^-, Br^-, I^-, SCN^-, NO_2^-, OH^-, SO_3^{2-} or $S_2O_3^{2-}$), in which $edta^{4-}$ acts as a bidentate nitrogen donor, have been studied [324]. The reaction of ethylenediamine with $[Pd(\overset{\frown}{L\,L})Cl_2]$ ($\overset{\frown}{L\,L}$ = dppe, diars, en, phen, bipy or $PhS(CH_2)_2SPh$) occurs in two stages, forming $[Pd(\overset{\frown}{L\,L})en]Cl_2$ as the intermediate stage except when $\overset{\frown}{L\,L}$ is $PhS(CH_2)_2SPh$ when the intermediate is $[Pd(en)Cl_2]$ [325]. An X-ray diffraction investigation showed that $[Pt(en)_2.18\text{-crown-}6]_n[PF_6]_{2n}$ involves dications sandwiched between two crown ether molecules that are displaced laterally, such that each ethylenediamine ligand is involved in only two hydrogen-bonds to ether oxygen atoms and each crown ether ring is involved in only four hydrogen-bonds [326].

The structures of $[Pd(phen)_2]X_2$ (X = Cl or ClO_4) both involve tetrahedral distortion of the PdN_4 framework to relieve overcrowding ($\angle PdN_2/PdN_2$ = 18.7(2)° for X = ClO_4 and 20.9(5)° for X = Cl [327,328]. Pyridylsubstituted benzenesulphonamide ligands, such as $2\text{-py}(CH_2)_2NHSO_2Ph$, act as bidentate ligands towards platinum(II) [329]. The planar molecules of $[\{Pd(\text{oxamide oxine})(\text{oxamide oximato})Pd\}_2][SO_4].H_2O$ form dimers, with two independent molecules linked by hydrogen bonding through water and sulphate ions; the dimers are arranged in vertical stacks [330].

2,2'-Bibenzimidazolate, *(48)*, can bridge two palladium(II) atoms or a palladium(II) and a gold(I) atom bonding in bidentate fashion to each [331,332]. Higher concentrations of $[Pt(\overset{\frown}{L\,L})Cl_2]$ ($\overset{\frown}{L\,L}$ = *(49)* or *(50)* (R = Me)) than *cis*-$[Pt(NH_3)_2Cl_2]$ are required to inhibit L1210 mouse leukemia cells, although, for L = *(50)* (R = H), the same concentration is required [333]. The potentially tridentate ligand, *(51)*, forms [PdLX] (X = Cl, Br, I, SCN or OAc) complexes where it is tridentate, as well as $[PdL_2]$ and $[Pd_3L_2X_4]$ (X = Cl or OAc) in which it is bidentate [334]; in $[PdL_2]$ the ligand undergoes rapid isomerisation about the imine bond [335].

6-Alkylpyridine-2-carbaldehyde imine forms trigonal bipyramidal platinum(II)-η^2-olefin complexes in which, as expected [336], both carbons of the olefin and the bidentate nitrogen donor lie in the plane, *(52)* [337]; $[PdCl_2(\eta^2\text{-olefin})(\overset{\frown}{L\,L})]$ (L = RN=CHCR'=NR or $RNHCH_2CH_2NHR$) have the same structure [338] and the olefin, α-diimine and halogen atoms can all be replaced with retention of the trigonal bipyramidal structure [339]. α-Diimines react



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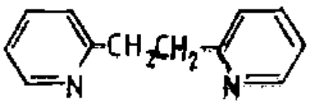

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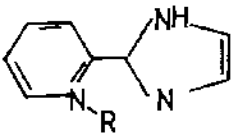

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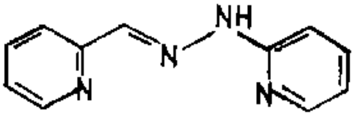

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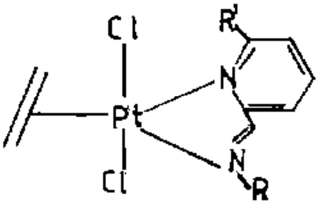
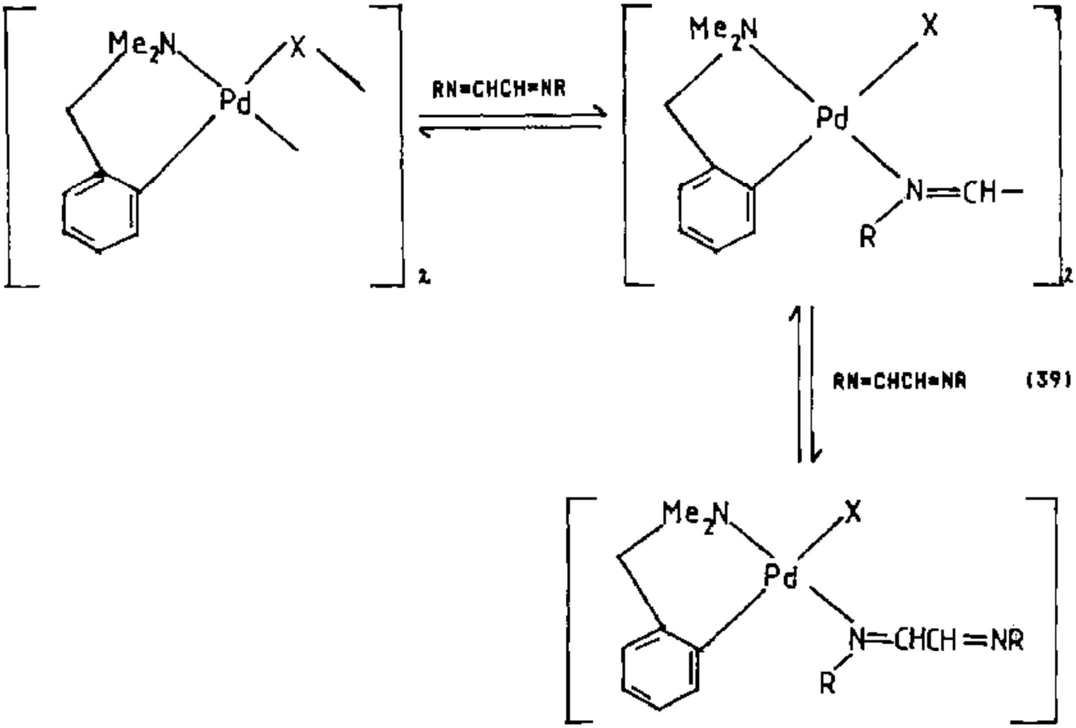


(52)

with cyclometallated palladium(II) complexes to form dinuclear and mononuclear species (reaction (39)); the latter is fluxional due to rapid head to tail exchange of the α-diimine nitrogen donors [340]. α-Diimines also displace chloride from $[\{Pd(\eta^3\text{-allyl})Cl\}_2]$ and $[\{PtCl(allyl)\}_4]$ to form $[M(\alpha\text{-diimine})(\eta^3\text{-allyl})]^+$ salts (M = Pd or Pt) [341].

Arylazooximes form bis-complexes with palladium(II) which undergo selective Pd-N_{oxime} cleavage with hydrogen chloride and Pd-N_{azo} cleavage with tertiary phosphines or a large excess of a unidentate amine (reaction (40)) [342].

$P(NSiMe_3)_3$ reacts with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ to form (*53*) in which the phosphine coordinated through two nitrogen atoms [343]. The thiosemicarbazones $H_2NCSNHN{=}CMeC({=}NOH)CONHAr$ (HL) form $[PdL_2]$ complexes, in which the ligands coordinate through N^1 of the thiosemicarbazone moiety and the deprotonated hydroximino-nitrogen [343*a*].



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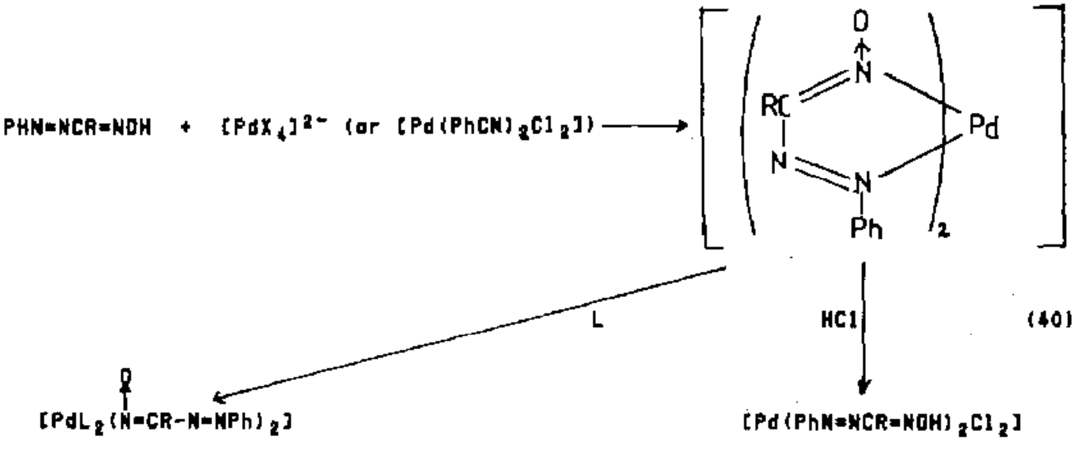
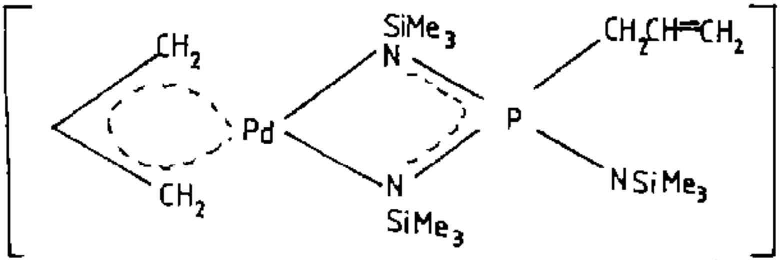


(40)

(L = PPh_3 or amine)

The crystal structure of [Pt(Et_4dien)I] shows that the central Pt-N bond (1.98(2) Å) is significantly shorter than the other two (Pt-N = 2.09(2) Å), as is also observed in the nitrite and azide but not in the bromide complex [344]. The influence of the ligand X on the equilibrium constants of the substitution reaction (equilibrium (41)) and the dimerisation reaction (equilibrium (42)) are very similar, K_{41} increasing as X^- varies in the order $Cl^- < Br^- < I^- < SCN^- < OH^-$ and K_{42} increasing in the order



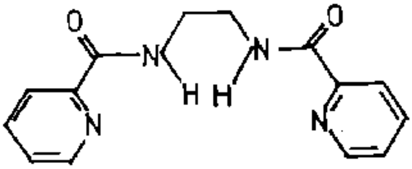
(53)

$$[Pd(dien)H_2O]^{2+} + X^- \overset{K_{41}}{\rightleftharpoons} [Pd(dien)X]^+ + H_2O \tag{41}$$

$$2[Pd(dien)H_2O]^{2+} + X^- \overset{K_{42}}{\rightleftharpoons} [Pd_2(dien)_2X]^{3+} + 2H_2O \tag{42}$$

$X^- = I^- \ll OH^- < SCN^-$ [345]; the same relative orders apply when dien is replaced by Et_4dien and Me_5dien [345]. The syntheses of the metallointercalation reagents $[Pt(terpy)X]Y$ ($X = Cl$, $Y = Cl$; $X = SCH_2CH_2OH$, $SCH_2CH_2NH_3$, $Y = NO_3$) have been described in detail [346].

Palladium(II) and platinum(II) complexes of tetradentate tetraaza[14]annulenes (Pd^{II} only) [347], (*54*) and (*55*), which coordinate in the



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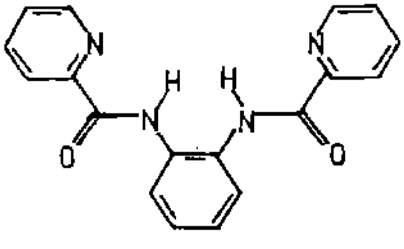
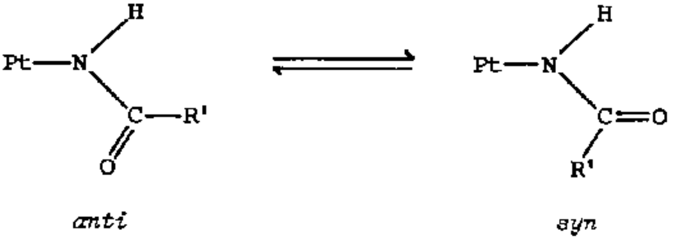


(55)

deprotonated form [348-350], have been characterised; in the deprotonated form (*54*) and (*55*) behave as *trans*-bidentate ligands [350]. The effects of solvents on the excitation profile of platinum phthalocyanine as well as its soft X-ray and photoelectron emission spectra have been reported [351,352]. The mechanism of phosphorescence quenching and Zeeman effects in palladium porphyrin have been studied [353,354]. Excitation of the resonance Raman spectra of platinum hematoporphyrin complexes in the Soret region mainly enhances the totally symmetric vibrational modes, whereas excitation in the α and β absorption region enhances primarily the non-totally symmetric modes [355]. Three of the resonance Raman frequencies in palladium(II) and platinum(II) tetraphenylporphyrins exhibit a linear correlation with porphyrin core size [356]. The photovoltaic properties of palladium tetraphenylporphyrin on *n*-doped transparent SnO_2 electrodes have been studied [357].

1.5.4.3 *Amide donor ligands*

When $[PtL_2R(R'CN)][BF_4]$ (L = PMe_2Ph, $PMePh_2$ or PPh_3; R = Me or Ph; R' = Me, CH_2=CH or Ph) are treated with potassium hydroxide the amide complexes $[PtL_2(R)(NHCOR')]$ are formed, in which the amide ligand is *N*-bonded. NMR spectroscopy showed solvent- and temperature-dependent equilibria between the *syn*- and *anti*-isomers arising from restricted rotation about the N$\overset{\cdot\cdot\cdot}{-}$C bond of the carboxamido-group (equilibrium (43)). The *anti*-isomer is favoured by non-polar solvents and increasingly bulky tertiary phosphines [358]. Multidentate amides that only coordinate in the deprotonated form ((*54*) and (*55*)) have been described in section 1.5.4.2 above.



(43)

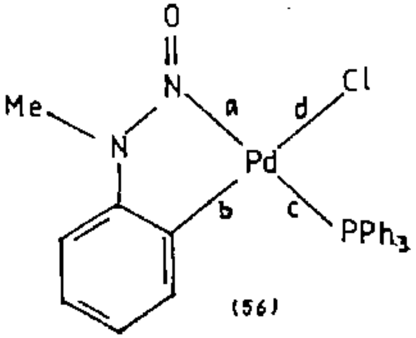
1.5.4.4 *Nitrosyl complexes*

$(Ph_3PCH_2Ph)_2[Pd_2X_4(NO)_2]$ (X = Cl or Br), formed by reaction of $[PdX(NO)]_n$ with $(Ph_3PCH_2Ph)X$, react with dioxygen in acetone solution to form $[Ph_3PCH_2Ph]_2[Pd_2X_4(NO_2)_2]$ [359]. Dimeric $[Pd_2(NO)(OAc)_3]$ is precipitated when nitric oxide is bubbled into a solution of palladium(II) acetate and lithium nitrate in acetic acid [360].

Although Me_2NCH_2Ph is readily cyclopalladated, $MeNHCH_2Ph$ and NH_2CH_2Ph are not. Since secondary amines are readily converted into *N*-nitroso derivatives the reactions of $PhCH_2N(NO)Me$ and $PhN(NO)Me$ with $Na_2[PdCl_4]$ have been studied; the former is not cyclopalladated whereas the aniline derivative is, as confirmed by an X-ray diffraction structure of (*56*), which reacts with two moles of triphenylphosphine to cleave the Pd-NO bond and yield (*57*) [361].

1.5.4.5 *Nitrile complexes*

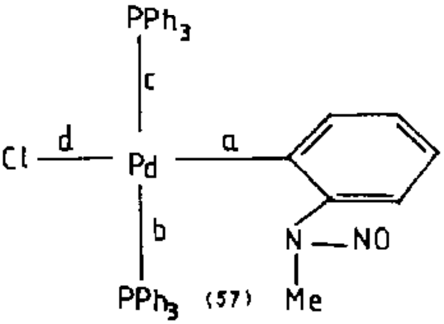
$[Pd(MeCN)_4][BF_4]_2$, prepared by the action of $NO[BF_4]$ on palladium metal in acetonitrile solution, is an air-sensitive yellow solid which catalyses the



(56)

a 2.088(12) Å c 2.263(3) Å

b 2.031(15) Å d 2.371(4) Å



(57)

a 1.989(11) Å c 2.395(3) Å

b 2.312(3) Å d 2.328(3) Å

oligomerisation of ethylene and the polymerisation of styrene; with triphenylphosphine it yields air-stable, green $[Pd(PPh_3)_3(MeCN)][BF_4]_2$ [362]. The reaction of $PtCl_2$ with neat benzonitrile yields a mixture of *cis*- and *trans*-$[Pt(PhCN)_2Cl_2]$ in variable proportions depending on the temperature. The isomers have been separated chromatographically and identified by IR and ^{13}C NMR spectroscopy. In benzonitrile the *cis*-isomer predominates at room temperature and the *trans* at higher temperature whereas, in chloroform, the *trans*-isomer dominates at 25 °C [363]. *cis*-$[Pd(PhCN)_2Cl_2]$ reacts with $[\{CpFe(CO)_2\}_2]$ to give a product containing the $Fe(\mu\text{-}CO)_2Fe$ group but no coordinated benzonitrile [364]. $[Pt(PEt_3)_2H(NCCH{=}CH_2)][BF_4]$, prepared by treating *trans*-$[Pt(PEt_3)_2HCl]$ with $AgBF_4$ followed by acrylonitrile, involves *N*-bonded acrylonitrile rather than coordination of the olefin group [358].

1.5.4.6 Azide complexes

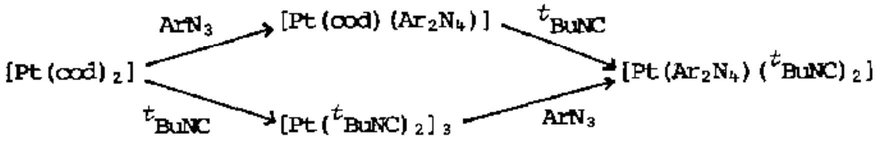
Photolysis of *cis*-$[Pt(PPh_3)_2(N_3)_2]$ at 77 K in ethanol or thf at 280 nm appears to yield yellow hexaazobenzene (N_6) and $[Pt(PPh_3)_2]$. On warming to room temperature, hexaazobenzene decomposes to dinitrogen because its resonance energy is compensated by repulsion between the lone pairs of electron on nitrogen. $[Pt(PPh_3)_2]$ dimerises on warming to room temperature [365].

1.5.4.7 Diazonium and tetraazadiene ligands

Treatment of $[Pd(PPh_3)_4]$ with ArN_2Y (Ar = Ph, 4-tolyl, 4-fluorophenyl or 2,4,6-trichlorophenyl; Y = PF_6 or BF_4) yields a mixture of the diazonium and aryl complexes, $[Pd(PPh_3)_3(N_2Ar)]Y$ and $[Pd(PPh_3)_3Ar]Y$; where Ar = 4-methoxyphenyl, only the diazonium complex is formed. The elimination of nitrogen from the diazonium complex to form the aryl complex occurs at room temperature and is promoted by UV irradiation [366].

Tetraazadiene complexes of platinum(II) can be formed either by transfer of the tetraazadiene ligand from nickel (reaction (44)) or by treating a platinum(0) complex with arylazide (reaction (45)) [367].

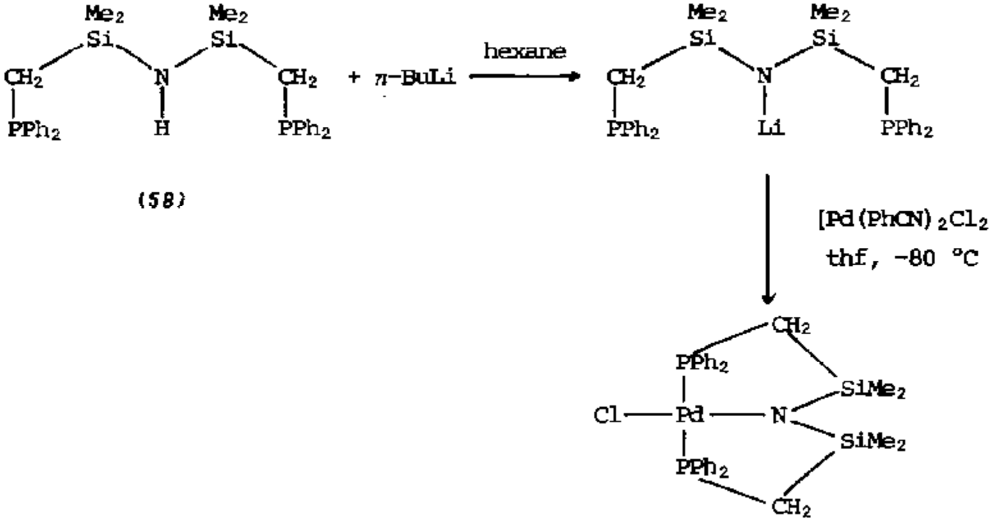
$$[\mathrm{Ni(Ar_2N_4)_2}] + [\mathrm{Pt(}^t\mathrm{BuNC)_2]_3} \longrightarrow [\mathrm{Pt(Ar_2N_4)(}^t\mathrm{BuNC)_2}] \tag{44}$$



(45)

1.5.4.8 Bidentate nitrogen-phosphorus donor ligands

When (*58*) is treated with *n*-BuLi in hexane, followed by $[\mathrm{Pd(PhCN)_2Cl_2}]$ in thf at -80 °C, the amide complex (*59*) is formed (reaction (46)) [368].



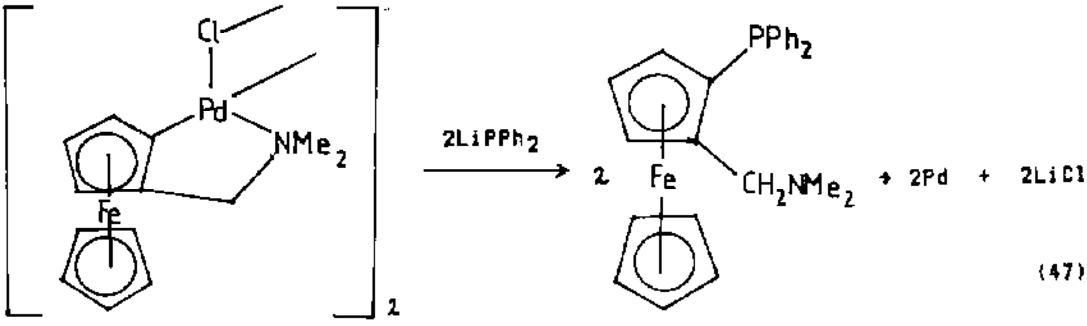
(*58*)

(46)

(*59*)

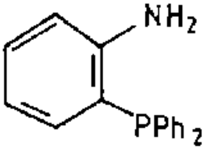
$\mathrm{NH_2CH_2CH_2P(Bu)Ph}$ has been resolved into its enantiomers using $(+)_D$-$[\mathrm{Pd_2(\mu\text{-}Cl)_2}\{(S)\text{-}N,N\text{-dimethyl-1-}\alpha\text{-methylbenzylamine-}2C,N\}_2]$ [369]. Bidentate palladium(II) and platinum(II) complexes $[\mathrm{MLCl_2}]$, as well as unidentate $[\mathrm{ML_2Cl_2}]$ and $[\mathrm{ML_4}]\mathrm{X_2}$ (X = Cl or $\mathrm{BPh_4}$) have been prepared from 2-$\mathrm{pyCH_2CH_2P(H)Ph}$, $\mathrm{NH_2(CH_2)_3PPh_2}$ and $\mathrm{PhCH{=}N(CH_2)_3PPh_2}$ [370]. Reaction (47) provides a convenient one-step synthesis to (*60*) which is an important ligand in asymmetric catalysis [371].

$\widehat{\mathrm{P\ N}}\mathrm{H_2}$, (*61*), reacts with $\mathrm{PtCl_2}$ in dmf at 130 °C to form $[\mathrm{Pt(\widehat{P\ N}H_2)Cl_2}]$ which reacts with a further mole of $\widehat{\mathrm{P\ N}}\mathrm{H_2}$ in chloroform in the presence of



(47)

(60)

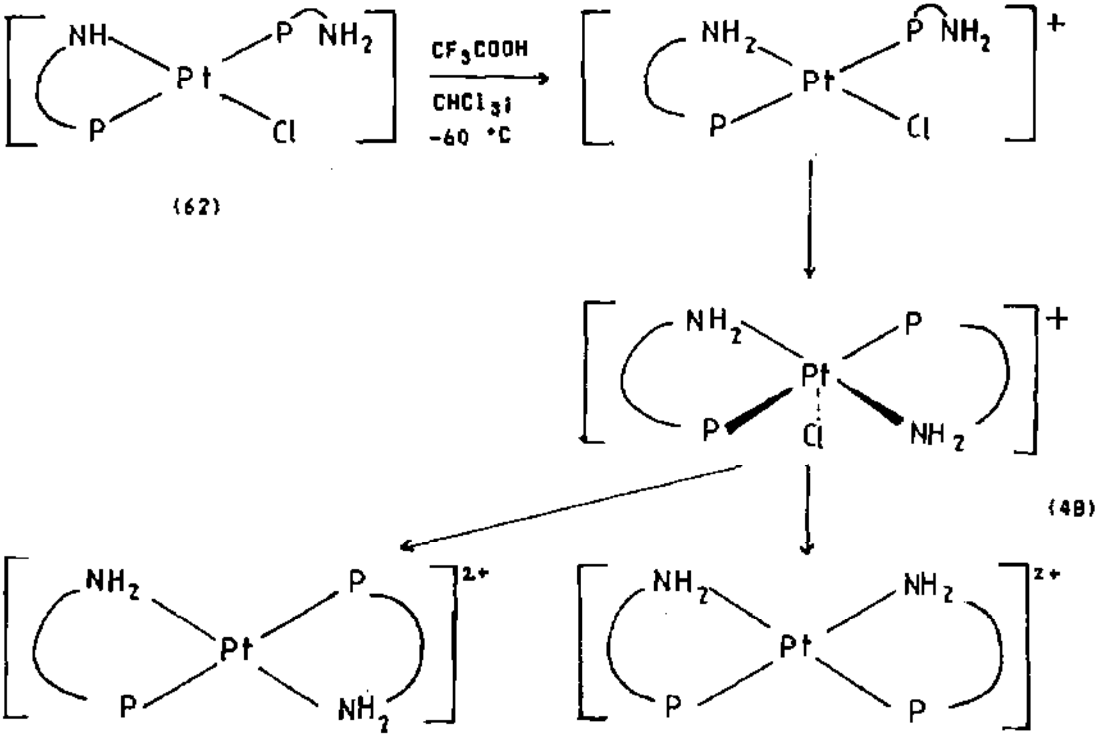


(61)

triethylamine to form $[Pt(\overset{\frown}{P\,NH})(\overset{\frown}{P\,NH_2})Cl]$, (*62*) [372]. On treatment with trifluoroacetic acid (*62*) undergoes ring-closure without retention of stereochemistry (reaction (48)), thus providing the first direct evidence for pseudo-rotation in a 5-coordinate platinum(II) complex [372]. 2-Diphenylphosphinopyridine forms phosphorus bonded *cis*- and *trans*-$[Pd(2\text{-}pyPPh_2)_2Cl_2]$ which with $[M_2(dba)_3]$ forms (*63*) (M = Pd or Pt) which are not as reactive as $[M_2(dppm)_2Cl_2]$, due to the ease with which the pyridyl nitrogen is displaced and the limited flexibility of the ligand, although with carbon monoxide, (*64*) is formed [373]. $Ph_2\overset{\frown}{P\,CN}$ ($\frown$ = CH_2, $(CH_2)_3$ or 2-C_6H_4) have been synthesised; all form phosphorus bonded unidentate complexes with palladium(II) [374,374*a*]. In addition, Ph_2PCH_2CN can act as a bidentate ligand.

1.5.4.9 Bidentate nitrogen-carbon donor ligands

Whilst (*65*)-(*67*) all react with PtX_2 (X = Cl or Br) to form $[PtLX_2]$ complexes, in which the ligands are coordinated through both amine and olefin groups, (*68*) does not coordinate to platinum(II) at all in contrast to its phosphorus and arsenic analogues PPh_3 and $AsPh_3$ [375]. The chloride bridge in (*69*) is split by treatment with excess lithium chloride in acetic acid, to yield



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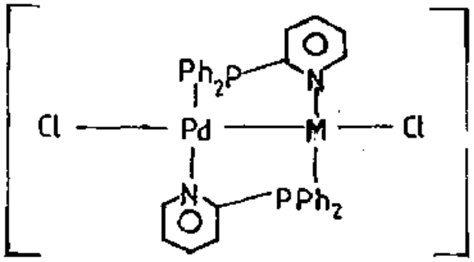

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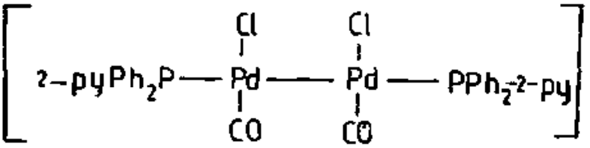
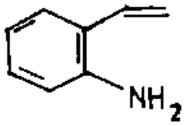


(64)

the first anionic palladium(II) complex of *N,N*-dimethylbenzylamine (reaction (49)) [376]. By contrast, (*70*) yields [{Pd(PPh$_3$)Cl$_2$}$_2$], due to the high *trans*-influence which labilises the Pd-N bond (reaction (50)) [376]. When *N,N*-dimethylanilines with electron-donating *para*-substituents are treated with palladium(II) acetate in benzene/acetic acid, cyclodimerisation products, (*71*), are formed [377]. Cyclopalladated dimethylaminoethylferrocene, (*72*), has been resolved into optically pure enantiomers through its (S)-proline derivatives [378].

An X-ray diffraction study of the 2-pyridyl complex (*73*) shows each



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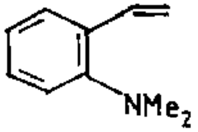

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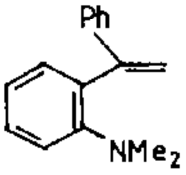

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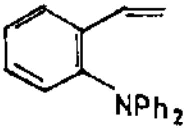

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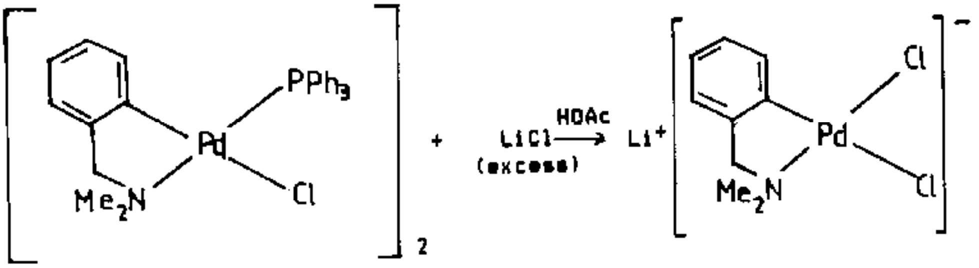

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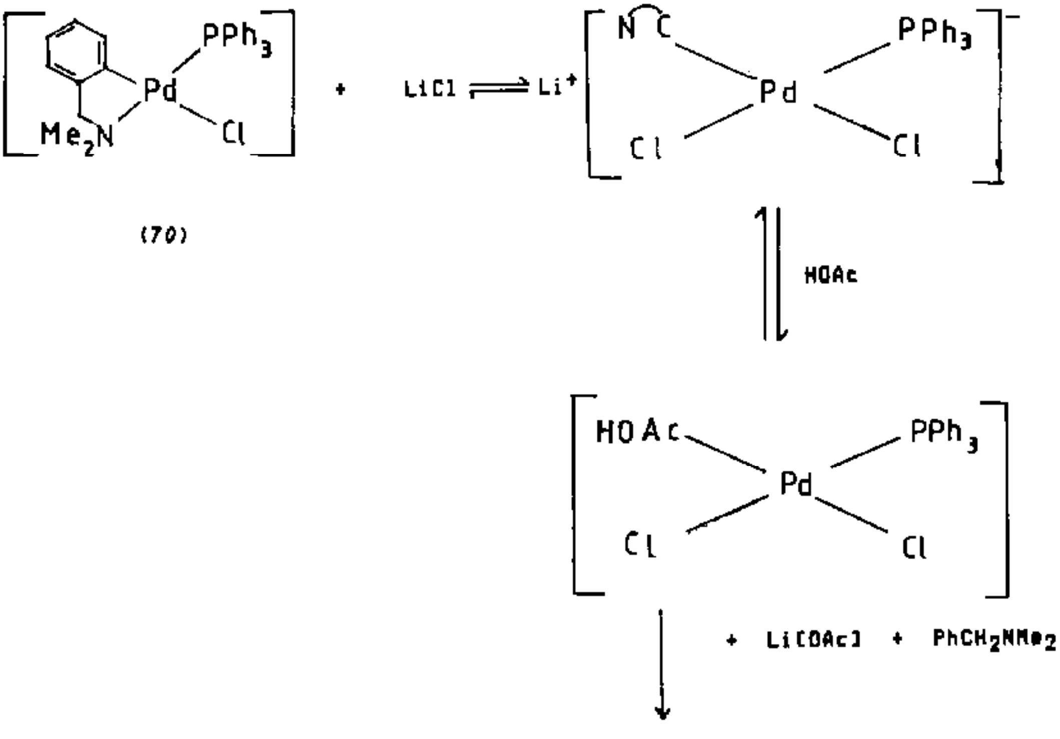
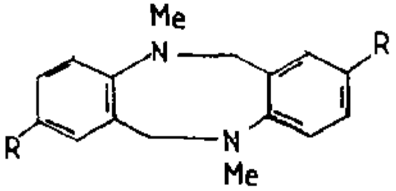


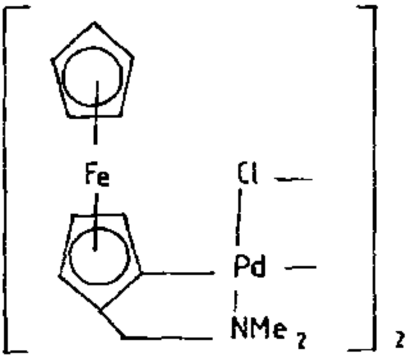
(70)

$\frac{1}{2}$[Pd$_2$(PPh$_3$)$_2$Cl$_4$]

(50)



(71; R = OMe, Me or Cl)



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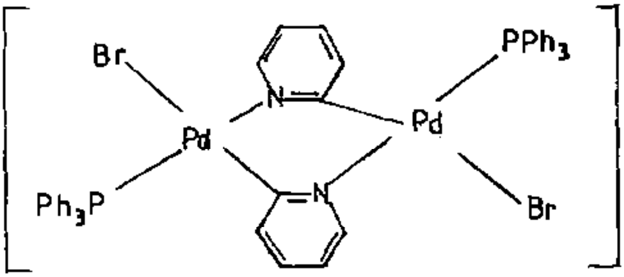
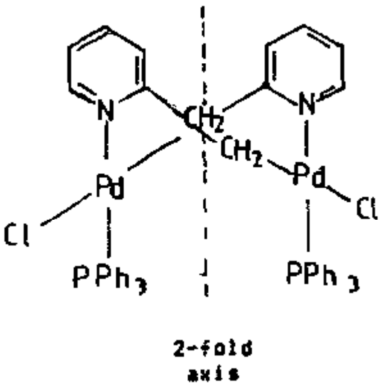


(73)

palladium is in a square-planar environment with the PdNCPdNC unit folded along the Pd---Pd axis to give a 6-membered boat [379]. The picolyl-bridged complex, (74), formed by oxidative-addition of picolyl chloride to $[Pd(PPh_3)_4]$, also has a boat-like 8-membered $PdNC_2PdNC_2$ ring, with the palladium(II) planes lying at 63° to each other and a two-fold axis between them [380]. (75) and (76) have also been studied by X-ray diffraction [381]; (75) (R = EtOOC) has the ability to nick supercoiled DNA at low concentrations [382]. The cyclometallation of



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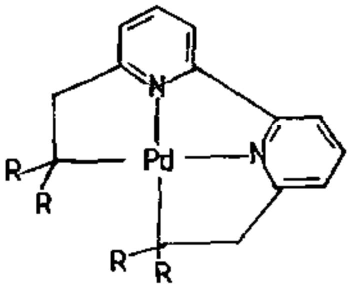
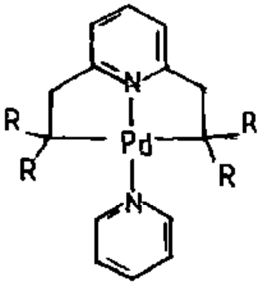
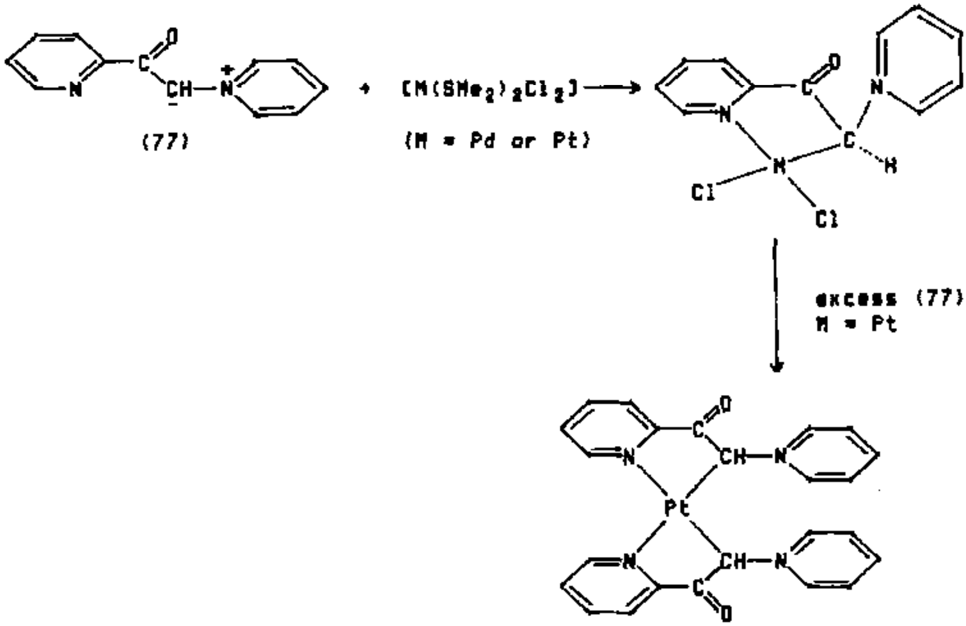


(75)



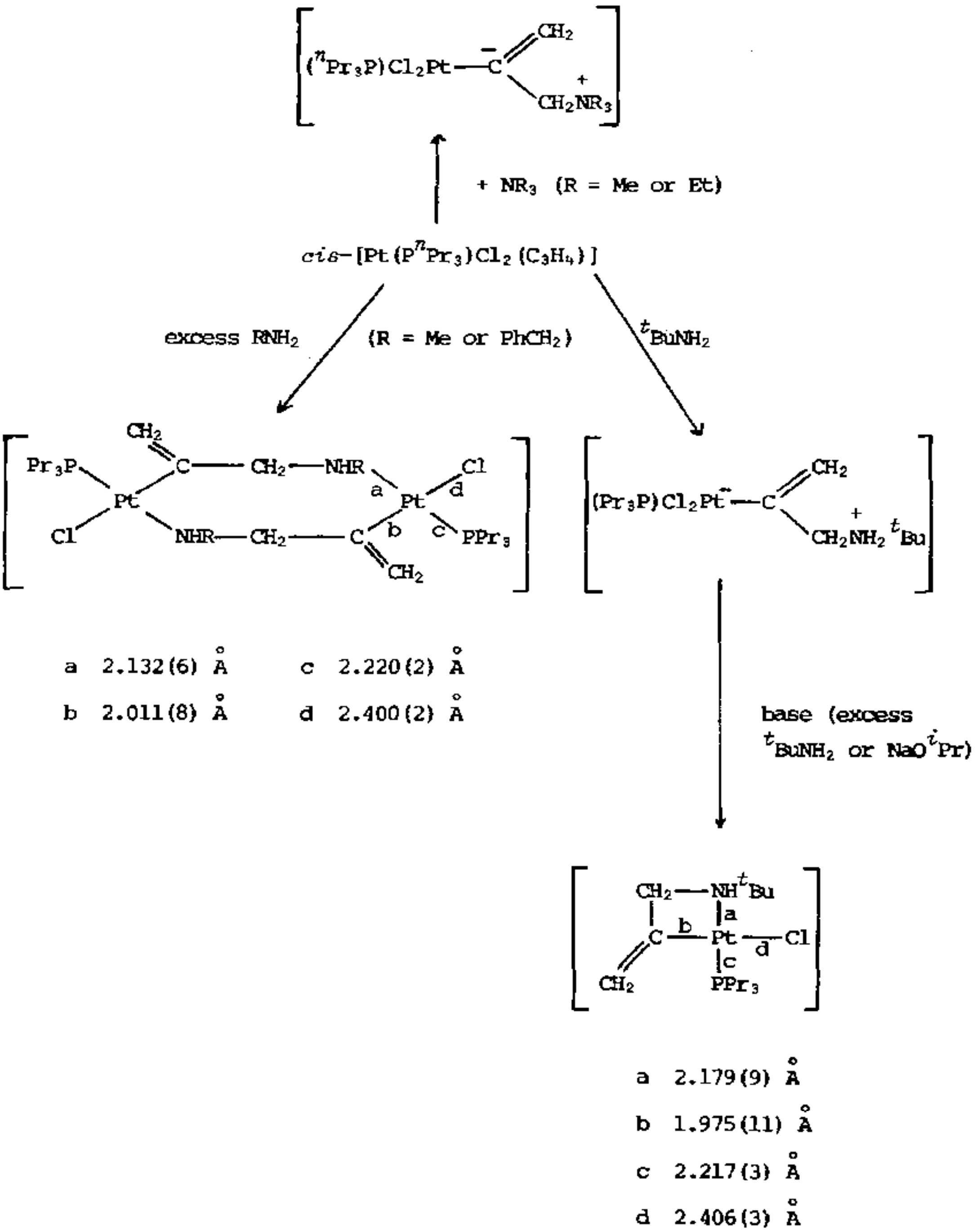
(76)

2-arylpyridines occurs more readily with palladium(II) acetate than palladium(II) chloride and the resulting acetato-bridged dimers are more soluble in organic solvents; by studying the effect of varying the substituents on the aryl nucleus, the reaction appears to involve electrophilic-attack by the palladium on the aryl nucleus after initial nitrogen coordination [383]. The chelate yields (*77*), forms bidentate *N*,*C* complexes with platinum(II) (reaction (51)) [384].



(51)

Amines react with the allene complex *cis*-[Pt(P^{n}Pr$_3$)Cl$_2$(C$_3$H$_4$)] to give *C*,*N*-chelated complexes and carbene complexes (Scheme 3) [385]. The fact that ^{t}BuNH$_2$ gives a 4-membered $\overline{\text{Pt–CC–N}}$ ring, whereas the less bulky MeNH$_2$ and PhCH$_2$NH$_2$ give 8-membered $\overline{\text{PtC}_2\text{NPtC}_2\text{N}}$ ring, is considered to be a further example of the Thorpe-Ingold effect. A four-membered ring is also formed when dimethylamine attacks 1,1-dimethylallene coordinated to platinum(II) (reaction (52)) [386]; carbon monoxide readily inserts into the 4-membered ring and, if this is followed by treatment with hydrogen peroxide and later hydrogen chloride, free β-amino acids can be obtained (reaction (53)).



a 2.132(6) Å c 2.220(2) Å

b 2.011(8) Å d 2.400(2) Å

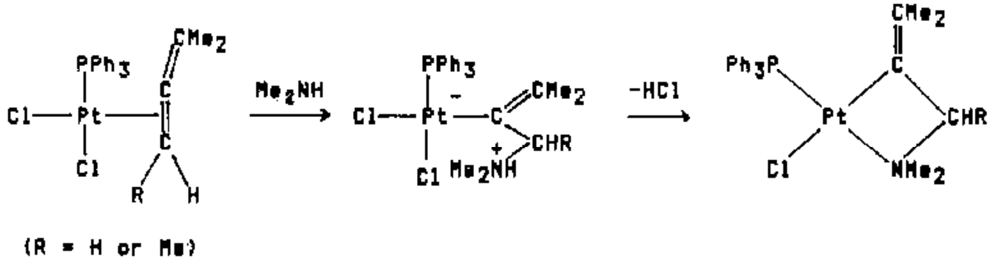
a 2.179(9) Å

b 1.975(11) Å

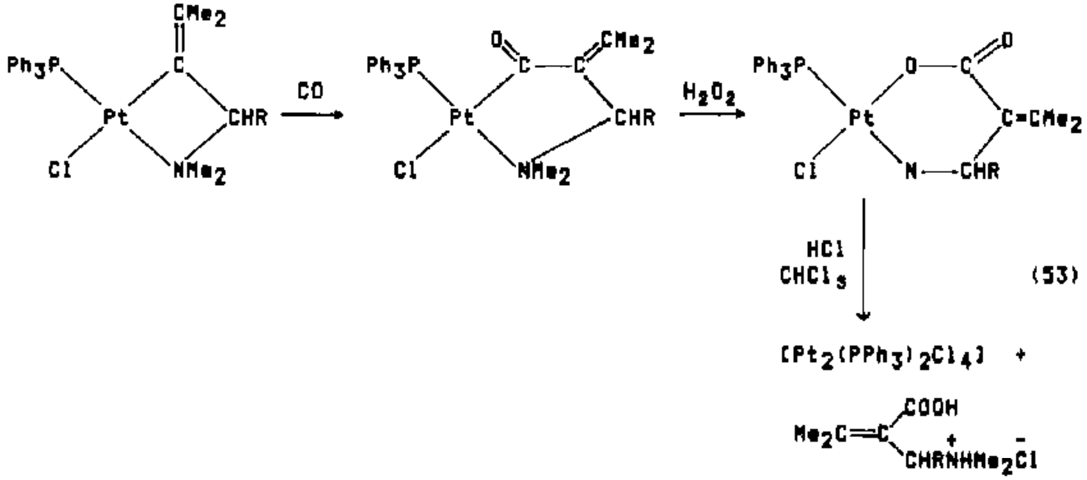
c 2.217(3) Å

d 2.406(3) Å

Scheme 3: Reaction of a platinum(II) allene complex with amines [385].



(52)



(53)

1.5.4.10 Unidentate tertiary phosphines

Some very convenient syntheses of tertiary phosphine platinum(II) complexes starting with chloroplatinic acid have been described. Reactions (54) and (55) yield *cis*- and *trans*-$[Pt(PPh_3)_2Cl_2]$, respectively; reactions (56) and (57) are

$$H_2PtCl_6.6H_2O + \underset{(4.4\ \text{equivs})}{PPh_3} \xrightarrow[\text{1 hour}]{\text{reflux in EtOH}} \textit{cis}\text{-}[Pt(PPh_3)_2Cl_2] \qquad (54)$$

$$H_2PtCl_6.6H_2O + \underset{(4.4\ \text{equivs})}{PPh_3} \xrightarrow[\substack{\text{reflux in EtOH,}\\ \text{1 hour}}]{+\ 40\%\ HCHO\ \text{in}\ H_2O} \textit{trans}\text{-}[Pt(PPh_3)_2Cl_2] \qquad (55)$$

carried out in an autoclave that has first been "washed" with carbon monoxide [387]. Halide bridge cleavage of platinum(II) dimers is often used for synthetic purposes; it is usually assumed that the geometry of the products

$$H_2PtCl_6.6H_2O + \underset{(4.4\ \text{equivs})}{PPh_3} + \underset{(100\ \text{atm}\ 1:1)}{CO/H_2} \xrightarrow[\substack{100\ °C \\ 4\ \text{hours}}]{EtOH} \textit{trans}\text{-}[Pt(PPh_3)_2HCl] \qquad (56)$$

$$H_2PtCl_6.6H_2O + \underset{(4.4\ \text{equivs})}{PPh_3} + \underset{(110\ \text{atm}\ 10:1)}{CO/\text{propene}} \xrightarrow[\substack{100\ °C \\ 4\ \text{hours}}]{EtOH} \textit{trans}\text{-}[Pt(PPh_3)_2(CO^nPr)Cl] \qquad (57)$$

depends on the relative *trans*-effects of the ligands, although the initial products sometimes undergo subsequent disproportionation or isomerisation. However, whilst PMe_2Ph reacts with $[\{Pt(PMe_2Ph)Cl_2\}_2]$ in chloroform at room temperature to form a 1:1 mixture of *cis*- and *trans*-$[Pt(PMe_2Ph)_2Cl_2]$, at -60 °C 85% of the products are ionic $[Pt(PMe_2Ph)_3Cl]^+$ and $[Pt(PMe_2Ph)Cl_3]^-$ which, on warming, yield the corresponding neutral complexes. Careful experiments with high local concentrations of phosphine showed that the initial product is $[(PMe_2Ph)_2ClPt(\mu\text{-}Cl)PtCl_2(PMe_2Ph)]$ which reacts with more phosphine to form either *trans*-$[Pt(PMe_2Ph)_2Cl_2]$ or $[Pt(PMe_2Ph)_3Cl]^+[Pt(PMe_2Ph)Cl_3]^-$. The cation forms *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ exclusively by Cl^- attack, whereas phosphine attack on the anion yields *trans*-$[Pt(PMe_2Ph)_2Cl_2]$. The formation of ionic intermediates is critically dependent on the phosphine, none being formed at all with tributylphosphine [388,389]. The *trans*-effect and the chelate effect can be combined to prepare otherwise inaccessible complexes. Thus, *cis*-$[Pt(PR_3)(CO)Cl_2]$ can be prepared by treating $[Pt(cod)Cl_2]$ with a tertiary phosphine and carbon monoxide; the phosphine can be a bulky phosphine such as $P(cych)_3$ for which the halide-bridged dimer is unknown. The reaction is believed to involve substitution of one end of the diolefin by phosphine followed by CO substitution once the chelating effect has been broken [390].

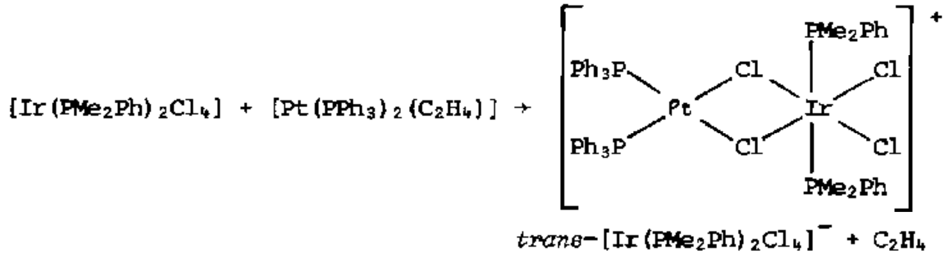
The chemical shifts of the 2- as opposed to 3- and 4-protons in the ^1H NMR spectra of bis-complexes of PPh_3, $AsPh_3$ and $BiPh_3$ shift by more than 0.5 ppm in *trans*-complexes but less than 0.5 ppm in *cis*-complexes in C_6D_6 solution [391]. The ^{31}P NMR spectra of dichloromethane solutions of $[Pd(PMe_3)_2X_2]$ show that, if a trace of PMe_3 is added, more than 99% of the complex is the *cis*-isomer when $X = Cl$, but more than 99% is the *trans*-isomer when $X = Br$ or I; when 1 equivalent of PMe_3 is added, more than 99% of the complex is present as trigonal bipyramidal $[Pd(PMe_3)_3X_2]$ with axial PMe_3 ligands ($X = Cl$, Br or I) and when two equivalents of PMe_3 are added more than 99% of the complex is present as square-pyramidal $[Pd(PMe_3)_4X]^+X^-$ with axial X ($X = Cl$, Br or I) [392].

In a review of recent work on sterically demanding phosphines, it was concluded that non-bonding interactions are very important [393]. The hitherto unknown compound $[\{Pt(Pcych_3)Cl_2\}_2]$ can be prepared by the slow addition of $Pcych_3$ in high dilution to $K[Pt(C_2H_4)Cl_3]$; if high dilution is not used, *trans*-$[Pt(Pcych_3)_2Cl_2]$ is formed as are the analogous complexes of PEt_3 and PPh_3 under all dilution conditions. Treatment of $[Pt(Pcych_3)Cl_2]_2$ with phosphine gives bridge cleavage at a rate inversely dependent on the bulk of the phosphine. Carbon monoxide cleaves $[\{Pt(Pcych_3)Cl_2\}_2]$ to form *trans*-$[Pt(Pcych_3)(CO)Cl_2]$ which is very stable showing little tendency to isomerise to the thermodynamically preferred *cis*-isomer; Me_2S, py, $AsPh_3$ and $^{t}BuNC$ also all give the *trans*-product, in contrast to the *cis*/*trans* mixture formed when the less bulky PEt_3 is present [394]. UV irradiation of *trans*-$[Pt(PR_3)_2Cl_2]$ (R = Et, ^{n}Bu or ^{n}Pr) in nitromethane gives up to 70% of the labile *cis*-form which can be isolated as a crystalline solid; use of mixtures of complexes shows that the reaction is predominantly intramolecular. The crystal structure of *cis*-$[Pt(P^{n}Pr_3)_2Cl_2]$ shows considerable overcrowding with short Pd-P bonds (2.322 Å mean) and long Pd-Cl bonds (2.407 Å mean) [395].

A series of complexes of the long alkyl chain tertiary phosphine ligands $P(C_nH_{2n+1})_3$ (n = 10-19) and $P(C_6H_4C_mH_{2m+1}-4)$ (m = 2-9), including *cis*-$[PtL_2Cl_2]$, *trans*-$[PdL_2Cl_2]$, and *trans*-$[PtL_2HCl]$ have been prepared and characterised. As expected, these complexes are extremely soluble in hydrocarbon and chlorinated solvents, so that "clean" preparative routes with either volatile or easily removed side products should be used [396]. The Pt-P coupling constants in a series of tris(4-substituted phenyl)phosphine complexes *trans*-$[Pt(^{t}Bu_2PCMe_2CH_2)\{P(C_6H_4X-4)_3\}Cl]$ indicated that the *trans*-influence of the phosphine increased as the 4-substituent X was altered, in the order $Cl < F < H < CH_3 < CH_3O < (CH_3)_2N$ [397]. When a racemic mixture of $PPhR^1R^2$ was reacted with $[Pt(\overset{\frown}{P\ P})(CH_3)(Me_2CO)][ClO_4]$ ($\overset{\frown}{P\ P}$ = dppe or chiral bidentate phosphine) varying degrees of stereoselective binding of the asymmetric phosphine were observed but never more than 2:1. The ability to coordinate one enantiomer preferentially was very sensitive to small changes in steric size and shape, a result which does not augur well for the synthesis of general purpose catalysts; rather careful tailoring of the chiral ligand and substrate would seem to be essential [398].

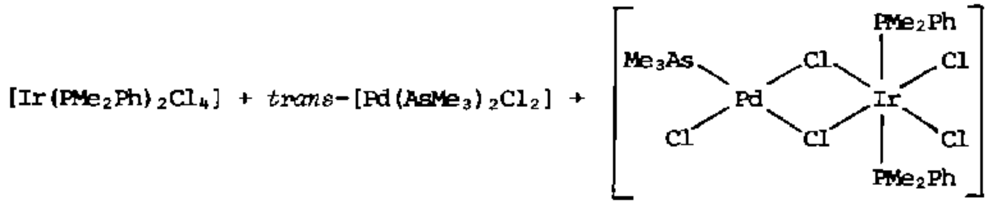
It has been suggested that the ^{31}P NMR chemical shifts of tertiary phosphine oxides provide a good basis for predicting phosphine basicity [399]. The UV spectra of *cis*- and *trans*-$[Pt(PEt_3)_2YZ]$ complexes show strong Pt5d → P3d transitions which, for the *cis*-complexes, follow the YZ order $YZ = Et_2 < Me_2 < MeX < X_2$ (X = Cl or Br), whereas the *trans*-complexes follow the order $HX < EtX < MeX < X_2$, suggesting that the platinum oxidation state decreases in the order $X > Me > Et > H$ [400]. By studying the kinetics of ligand substitution in $[PdL_2(SCN)_2]$, a *trans* activation effect order for L of $L = P(OEt)_3 > PPh_3 > PEt_3 > P(OPh)_3$ was observed [401].

Mixed palladium(II)- or platinum(II)-iridium(III) complexes have been prepared by reactions (58a) and (58b) [402].



$$[\mathrm{Ir(PMe_2Ph)_2Cl_4}] + [\mathrm{Pt(PPh_3)_2(C_2H_4)}] \rightarrow [(\mathrm{Ph_3P})_2\mathrm{Pt}(\mu\text{-}\mathrm{Cl})_2\mathrm{Ir(PMe_2Ph)_2Cl_2}]^+ \; trans\text{-}[\mathrm{Ir(PMe_2Ph)_2Cl_4}]^- + \mathrm{C_2H_4}$$

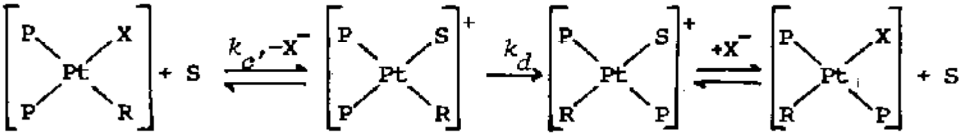
(58a)



$$[\mathrm{Ir(PMe_2Ph)_2Cl_4}] + trans\text{-}[\mathrm{Pd(AsMe_3)_2Cl_2}] \rightarrow [(\mathrm{Me_3As})\mathrm{ClPd}(\mu\text{-}\mathrm{Cl})_2\mathrm{Ir(PMe_2Ph)_2Cl_2}]$$

(58b)

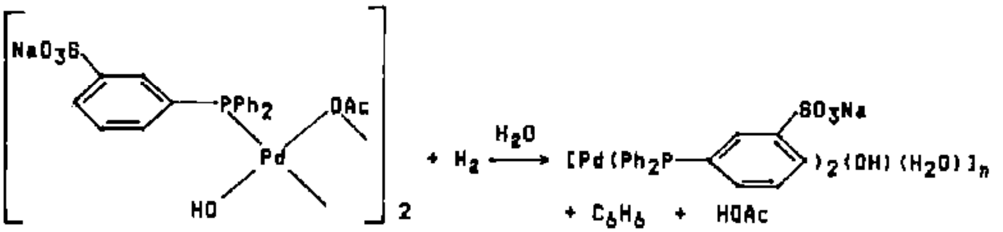
The isomerisation of square-planar complexes has become a rewarding field of study, revealing many mechanistic variations; the processes are much more subtle than once thought [403]. Previous evidence for a dissociative mechanism in methanol involving a 3-coordinate intermediate [404] has received further support from studies of the spontaneous isomerisation of *cis*-$[\mathrm{Pt(PEt_3)_2(C_6H_4Me\text{-}}m\mathrm{)Cl}]$ in a variety of hydroxylic solvents, as well as acetonitrile [405]. However, such a mechanism has been criticised on the grounds that definitive evidence cannot be obtained in good donor solvents [404], that the activation volumes of methanol solvolyses as well as isomerisation indicate an associative mechanism [406,407], and that mechanism (59) can explain all the available data, if a switch in the rate-determining step from k_c to k_d occurs on going from a more to a less crowded R group [408,409]. Autocatalysis *via* dimerisation has been shown to be a mechanism available for isomerisation, since dimerisation of $[\mathrm{PtL_2X_2}]$ yields $[\{\mathrm{PtLX_2}\}_2]$, together with free ligand that can catalyse isomerisation by forming 5-coordinate complexes which can undergo pseudo-rotation [410]. The photochemical *cis* → *trans* isomerisation of $[\mathrm{Pt(PEt_3)_2(Ph)Cl}]$ in acetonitrile appears to proceed through an intramolecular twisting from a low lying ligand field state, whereas the



(59)

trans → *cis* conversion appears to involve a dissociative path from a charge-transfer state [411]. The fact that *trans* → *cis* photoisomerisation of $[Pd(P^nPr_3)_2X_2]$ occurs with high efficiency, whereas the *cis* → *trans* photoisomerisation does not, suggests that the thermally equilibrated excited state responsible for isomerisation, although probably slightly tetrahedral in geometry, is distorted towards a *cis*-configuration [412].

$[\{Pd(PPh_3)Cl_2\}_2]$ reacts autocatalytically with hydrogen in aniline or toluidines to form $[Pd_3(PPh_3)_3(PPh_2)_2Cl]Cl$ and benzene [413] which is similar to the reaction of $[\{Pd(PPh_2C_6H_4SO_3\text{-}3)(OH)(\mu\text{-}OAc)\}_2]$ with hydrogen in water to yield benzene and acetic acid (reaction (60)) [414]. On heating $[M(PPh_3)_2Cl_2]$ (M = Pd or Pt) with organic compounds, such as pyrrolidine or 2-propanol, the triphenylphosphine ligands are extensively hydrogenolysed to benzene and phosphine [415].



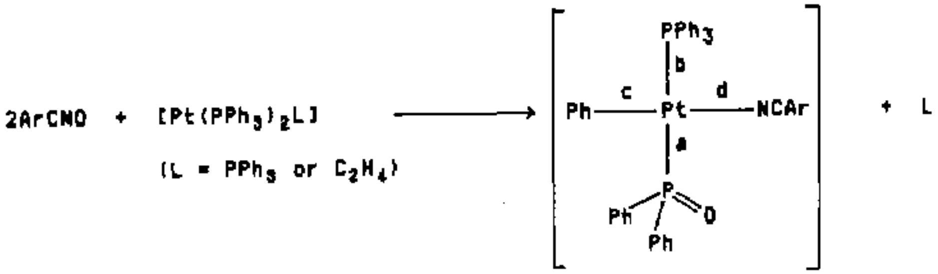
(60)

1.5.4.11 Other unidentate phosphorus donor ligands

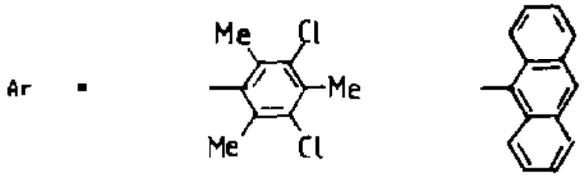
A detailed description of the reaction of trimethylphosphite with palladium(II) chloride in the presence of sodium tetraphenylborate to yield $[Pd\{P(OMe)_3\}_5][BPh_4]_2$ has been published in Inorganic Syntheses [416]. Nitrile oxides cleave the P-C bond of triphenylphosphine coordinated to platinum(0) (reaction (61)), the crystal structures of the products reveal long Pt-PPh$_3$ bonds, which indicate that the OPPh$_2$ ligand has a large *trans*-influence [417].

Although coordination of PPh$_2$Cl stabilises the P-Cl bond against hydrolysis, prolonged exposure of *cis*-$[Pd(PPh_2Cl)_2Cl_2]$ to aqueous acetone yields (*78*) [418] and not *cis*-$[Pd(PPh_2OH)_2Cl_2]$ as previously reported [419]. The crystal structure of *cis*-$[Pd\{P(OMe)Ph_2\}_2Cl_2]$ shows Pd-P and Pd-Cl bond lengths of 2.237(7) and 2.354(8) Å, respectively [420].

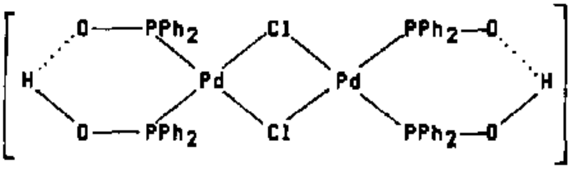
Palladium(II) and platinum(II) complexes of the fluorophosphines (L) PF$_3$, PF$_2$(OPh), PF(OPh)$_2$, and 2-fluoro-1,3,2-benzodioxaphosphole, of the type $[ML_2X_2]$ and $[MLX_3]^-$ (X = halide) have been prepared and characterised spectroscopically [421-423]. Hydrolysis of $[Pt(PF_3)_2X_2]$ (X = Cl or Br) by atmospheric moisture gives *cis*-$[Pt(PF_3)(PF_2O)X_2]^-$ as the initial product [421]. PF$_2$H(Y)



(61)



a	2.316(5) Å	2.324(2) Å
b	2.347(6) Å	2.354(2) Å
c	2.03(2) Å	2.05(1) Å
d	1.98(2) Å	2.01(1) Å

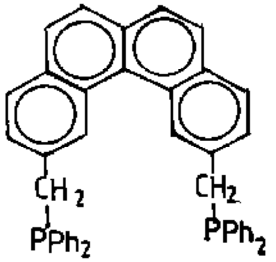


(78)

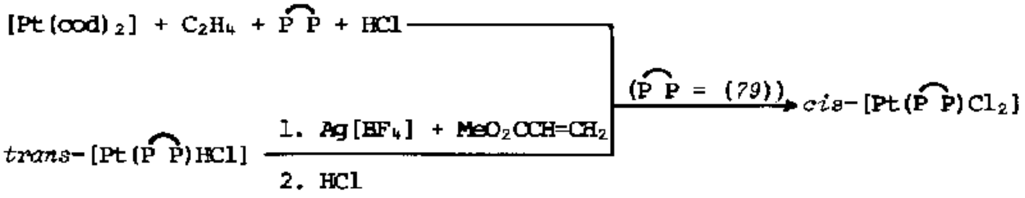
(Y = S or Se) react with *trans*-[Pt(PEt$_3$)$_2$HX] (X = Cl, Br or I) to form [Pt(PEt$_3$)$_2$(PF$_2$Y)X], through the intermediate formation of [Pt(PEt$_3$)$_2$(PF$_2$Y)H$_2$X] and [Pt(PEt$_3$)$_2$(PF$_2$Y)H]; the Pt-PF$_2$S bond length in *trans*-[Pt(PEt$_3$)$_2$(PF$_2$S)Cl] (2.213(5) Å) is intermediate between Pt-PF$_3$ and Pt-PEt$_3$ in *cis*-[Pt(PEt$_3$)(PF$_3$)Cl$_2$], indicating a PF$_2$S π-acceptor ability between PF$_3$ and PEt$_3$ [424].

1.5.4.12 Bidentate phosphorus donor ligands

The bidentate ligand, (*79*), although designed to span *trans*-positions can also form *cis*-complexes, as in reaction (62) where the product has Pt-P bond lengths of 2.253(2) and 2.256(2) Å and Pt-Cl bond lengths of 2.358(3) and



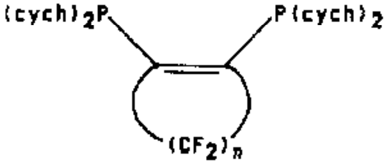
(*79*; $\overset{\frown}{P\ P}$)



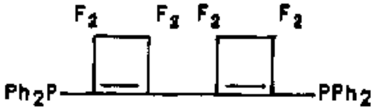
(62)

2.347(2) Å [425]. Similarly, treatment of *trans*-[Pt($\overset{\frown}{P\ P}$)H(Me$_2$CO)][BF$_4$] ($\overset{\frown}{P\ P}$ = (*79*)) with triphenylphosphine yields *trans*-[Pt($\overset{\frown}{P\ P}$)(PPh$_3$)H][BF$_4$], which isomerises to the *cis*-isomer in dichloromethane at room temperature in the presence of a trace of triphenylphosphine [425]. (*79*) has been of value in studying the mechanism of 1,1-reductive-elimination from [Pd($\overset{\frown}{P\ P}$)R$_2$], which has shown that the 1,1-reductive-elimination of R-R requires a *cis*-complex, does not require coordinative unsaturation on palladium, but does require loss of phosphine when R = Ph in contrast to reductive-elimination of Ph-Ph from *cis*-[Pt(PR$_3$)$_2$Ph$_2$] [426].

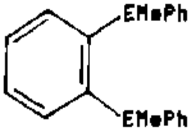
The reactions of the fluorinated bidentate phosphines, (*80*) and (*81*), with Na$_2$[MCl$_4$] (M = Pd or Pt) have been reported [427]. Whereas the square-planar [M($\overset{\frown}{E\ E}$)$_2$]$^{2+}$ (M = Pd or Pt; $\overset{\frown}{E\ E}$ = (*82*), E = P or As) complexes are kinetically stable and retain their structural identity in solution, the corresponding square-pyramidal [M($\overset{\frown}{E\ E}$)$_2$Cl]$^+$ complexes undergo rapid chloride ligand site exchange from above to below the plane, redistribution of the di(tertiary arsine) ligands in the palladium(II) complex, and intramolecular isomerisation of the chelate rings occurs for both metals [428]. Complexes of RN(PPh$_2$)$_2$ (R = PhCH(Me) or EtOCOCH(Me)), [Pt{RN(PPh$_2$)$_2$}MeCl] and



(80; n = 2 or 3)



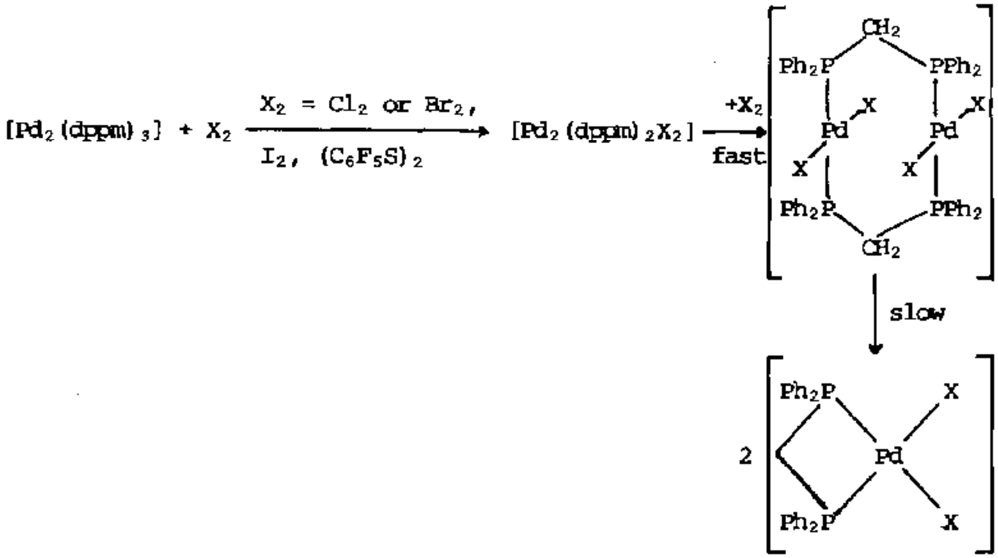
(81)



(82; E = P or As)

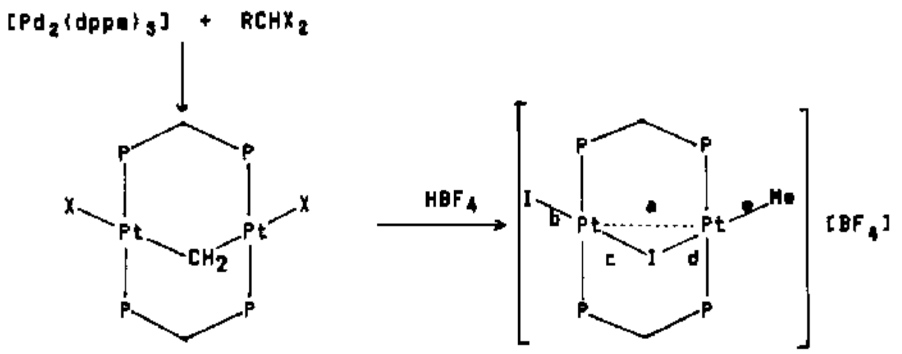
$[Pt(RN(PPh_2)_2\}Me(X)][ClO_4]$ (X = Me_2CO, 4-substituted pyridine, ER_3 (E = P, As or Sb), in which an asymmetric centre is present, have been prepared [429].

Halogens react with $[Pd_2(dppm)_3]$ to give binuclear palladium(II) complexes which slowly isomerise to the mononuclear product (reaction (63)) [430].



(63)

Dihalomethanes $RCHX_2$ (R = H or Me; X = Cl, Br or I) add to $[Pd_2(dppm)_3]$ to form methylene bridged A-frame palladium(II) complexes [431] which, on treatment with fluoroboric acid, undergo conversion of the bridging methylene group to a terminal methyl group (reaction (64)), as confirmed by an X-ray diffraction study which indicates a dative Pd-Pd bond with the cation being the palladium bearing the methyl group [432]. *(83)* is fluxional with iodide exchange between terminal and bridging positions [432]. $[Pt(dppm)Cl_2]$ reacts with methyllithium to form $[Pt(dppm)Me_2]$ which, with hydrogen chloride, forms



(64)

(83)

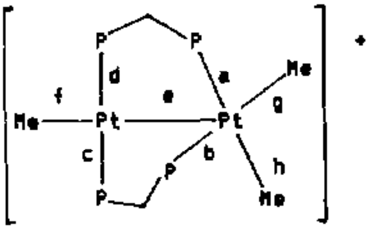
a 2.976(6) Å   d 2.648(5) Å
b 2.28(4) Å   e 2.577(6) Å
c 2.740(5) Å

$[Pt(dppm)(Me)Cl]$ together with the A-frame complex $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ previously thought to be a non-ionic trimer [433]. The same two products are formed when $[Pt(cod)MeCl]$ is treated with dppm, whereas dppm reacts with $[Pt(cod)(COPh)Cl]$ to give only the A-frame complex $[Pt_2(COPh)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ [434]. $[Pt(dppm)Me_2]$ can be formed by heating the thermodynamically less stable phosphine bridged dimer $[Me_2Pt(\mu\text{-}dppm)_2PtMe_2]$ in benzene at 60°, which is asymmetric with a twist-saddle conformation [435]. $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$, (*84*), which like (*83*) has a dative metal-metal bond [435a,436] can be prepared by reactions (65) and (66), of which the latter is reminiscent of Venanzi's

$$[Pt(dppm)Me_2] + [Pt(dppm)Cl_2] \rightarrow 2[Pt(dppm)MeCl] \xrightarrow{+\ 2[Pt(dppm)Me_2]} 2[Pt_2Me_3(\mu\text{-}dppm)_2]^+ + 2Cl^- \qquad (65)$$

$$2[Pt(dppm)Me_2] + HX \xrightarrow[X\ =\ PF_6,\ SbF_6\ \text{or}\ ClO_4]{\text{reflux}} [Pt_2Me_3(\mu\text{-}dppm)_2]^+X^- + CH_4 \qquad (66)$$

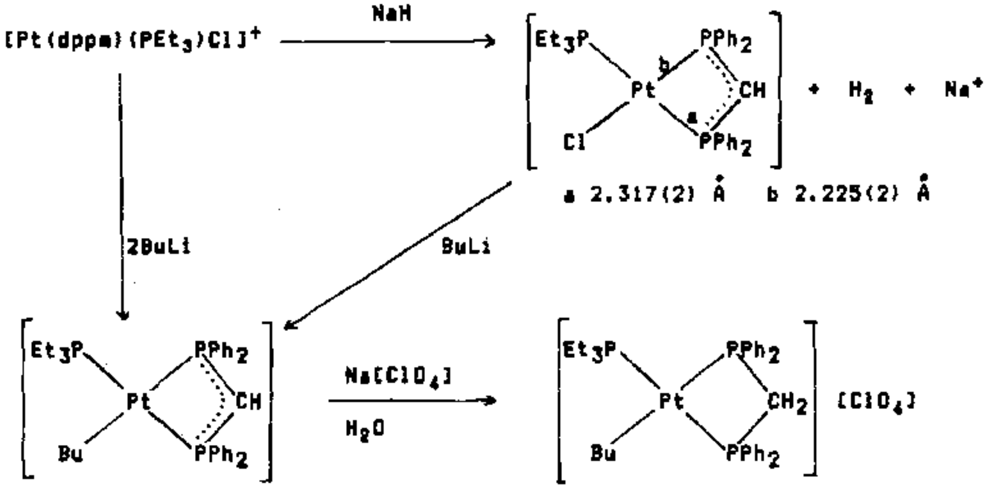
route for converting $[Pt(PR_3)_2H_2]$ into $[Pt_2(PR_3)_4H(\mu\text{-}H)_2]^+$ [436]. The electronic structures of these and other A-frame complexes have been discussed; once ambiguities in electron counting in these complexes have been clarified it is possible to obtain a consistent picture of their bonding [437]. Deprotonation of dppm in platinum(II) complexes using *n*-butyl lithium gives



(84; P⌒P = dppm)

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

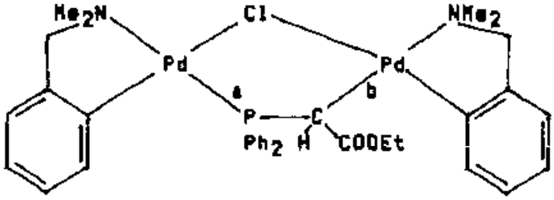
[Pt(PEt$_3$)(Ph$_2$PCHPPh$_2$)Bu] which has a virtually planar PtPCP 4-membered ring with multiple P$\cdots$C bonding (P—C = 1.72 Å) (reaction (67)) [438].



(67)

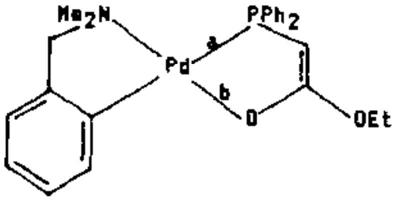
1.5.4.13 *Bidentate phosphorus-carbon donor ligands*

The carbanion Ph$_2$P$\tilde{C}$HCOOEt (L$^-$) reacts with [{Pd(Me$_2$NCH$_2$C$_6$H$_4$-2)Cl}$_2$] in a Pd:L$^-$ ratio of 2:1 to form (*85*) whereas, when a 1:1 ratio is used, (*86*) is formed [203,374a]. (*86*) reacts with further [Pd(Me$_2$NCH$_2$C$_6$H$_4$-2)Cl]$_2$ to yield (*85*), hence showing the nucleophilic character of the carbon atom α to the phosphorus. This is further shown by the reaction of (*86*) with carbon dioxide in thf under ambient conditions to form the insertion product (*87*), in which a new C–C bond has been created. Since the carbon dioxide can be liberated in thf solution by bubbling in argon, (*86*) provides the first example of a carbon dioxide carrier that involves reversible C–C bond formation [374a].



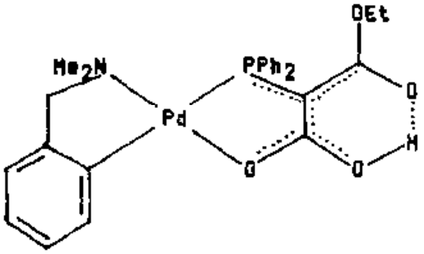
a 2.23X(6) Å b 2.01(2) Å

(85)



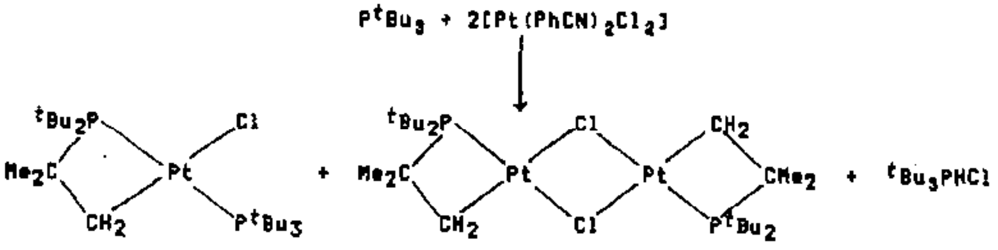
a 2.242(2) Å b 2.117(5) Å

(86)



(87)

The crystal structures of the metallated P^tBu_3 complexes $[\{M(^tBu_2PCMe_2CH_2)Cl\}_2]$ (M = Pd or Pt) show non-planar 4-membered rings which, in the palladium complex, become time-averaged to a planar geometry in solution [439]. P^tBu_3 reacts with $[\{Pt(^tBu_2PCMe_2CH_2)Cl\}_2]$ to cleave the chloride bridge and form (*88*) which is also formed in reaction (68); when reaction (68) is carried out with only a 1:1 ratio of phosphine and platinum

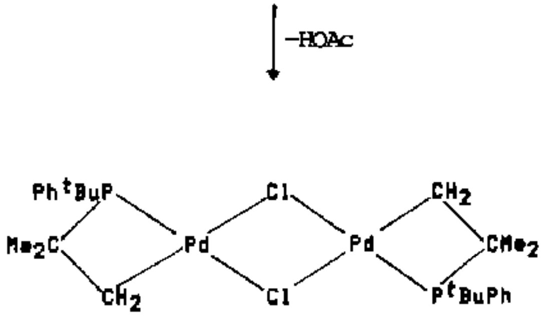


(68)

(88)

$[Pt(P^{t}Bu_3)(PhCN)Cl_2]$ is formed [440]. $P^{t}Bu_2Ph$ undergoes ready palladation in the presence of acetate (reaction (69)); $P^{t}Bu_3$ reacts in the same way even more readily [441]. Thus, in addition to HCl and H_2 elimination, metallation may also be achieved by HOAc elimination.

$$2[Pt(P^{t}Bu_2Ph)_2Cl_2] + 2AgOAc \rightarrow [\{Pd(P^{t}Bu_2Ph)Cl(\mu\text{-}OAc)\}_2]$$



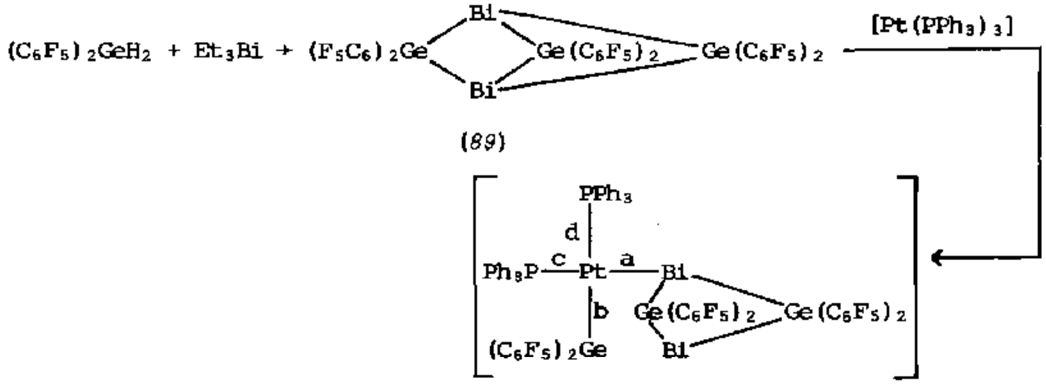
(69)

1.5.4.14 *Stibine donor ligands*

The stibine ligands $SbRMe_2$ (R = (2-pyridyl)methyl or 8-quinolinyl) have been prepared together with their bis-complexes $[ML_2X_2]$ (M = Pd or Pt; X = Cl, Br, I or SCN) [442].

1.5.4.15 *Bismuth donor ligands*

The bis-bismuth ligand, (*89*), and its platinum(II) complex have been prepared and characterised (reaction (70)) [443].



(*89*)

(70)

a 2.759(3) Å   c 2.32(1) Å

b 2.466(5) Å   d 2.37(1) Å

1.5.5 *Complexes with Group IV donor ligands*

Clearly the majority of the complexes involving Group IV ligands are "organometallic complexes" which have been specifically excluded from this review. The use of ^{13}C NMR spectroscopy in the structural analysis of platinum(II) complexes has been reviewed [444].

1.5.5.1 *Carbonyl complexes*

$[Pd(cod)R_2]$ (R = Me or Ph) react with carbon monoxide to form $[Pt(CO)_2R_2]$, due to the *trans*-effect of the R group facilitating loss of diolefin. Spontaneous insertion of carbon monoxide into the Pt–R bond does not occur, nor can it be promoted by addition of a nucleophile. However, [Pt(cod)RCl] does undergo carbon monoxide insertion to yield [Pt(cod)(COR)Cl] [390]. Halocarbonyl complexes of palladium(II) are rare and have not been well characterised. However, a convenient preparation of *trans*- $[\{Pd(CO)Cl_2\}_2]$ in about 60% yield can be obtained by treating $PdCl_2$ with carbon monoxide (50 atmospheres) in thionyl chloride at 120 °C. The single ν_{CO} absorption at 2167 cm^{-1} in Nujol is higher than that in the platinum(II) analogue, due to less π-back donation, which is why palladium(II) is reluctant to form carbonyls. Attempts to cleave the chloride bridge with triphenylphosphine result in carbon monoxide displacement to yield $[\{Pd(PPh_3)Cl_2\}_2]$ (Pd:PPh_3 = 1:1), or *trans*-$[Pd(PPh_3)_2Cl_2]$ if two equivalents of triphenylphosphine are used [445].

The syntheses and photochemistry of a number of platinum(II) alkoxycarbonyl complexes have been described [446]. The ^{195}Pt-^{13}C coupling constants *trans* to tertiary phosphines, as in *trans*-$[Pt(PR_3)(CO)Cl_2]$ or *trans* to halide or aryl groups, are positive; the *cis* two bond ^{31}P-Pt-^{13}C coupling is small and negative, whereas the *trans* ^{31}P-Pt-^{13}C coupling is large and positive [447].

The reaction of CO and NO to give CO_2 and N_2O is promoted by solutions of palladium(II) in aqueous hydrochloric acid; addition of copper(II) prevents deposition of palladium metal [448]. The carbon monoxide reduction of palladium(II) chloride in aqueous solution is autocatalysed by the $[Pd(CO)Cl_3]^-$ anion which can be isolated as its caesium salt [449].

1.5.5.2 *Cyanide complexes*

$[Pd(C_6F_5)_n(CN)_{4-n}]^{2-}$ (n = 1, 2 (*cis* and *trans*) or 3) have been prepared by reactions (71)-(74) as their ammonium or phosphonium salts; tetrameric $[\{Pd(\eta^3-C_3H_5)(\mu-CN)\}_4]$ forms monomeric $[Pd(\eta^3-C_5H_5)(CN)_2]^-$ on reaction with excess cyanide [450]. The structure of polycrystalline $Tl_4[Pt(CN)_4](CO_3)$ has been determined by time of flight neutron powder diffraction, in order to develop the technique for use with samples for which large enough crystals for

$$[Pd(C_6F_5)_3(tht)]^- + CN^- \rightarrow [Pd(C_6F_5)_3(CN)]^{2-} + tht \tag{71}$$

(tht = tetrahydrothiophen)

$$[\{Pd(C_6F_5)_2(\mu\text{-}Br)\}_2]^{2-} + 4CN^- \rightarrow 2\mathit{cis}\text{-}[Pd(C_6F_5)_2(CN)_2]^{2-} + 2Br^- \tag{72}$$

$$\mathit{trans}\text{-}[Pd(C_6F_5)_2(tht)_2] + 2CN^- \rightarrow \mathit{trans}\text{-}[Pd(C_6F_5)_2(CN)_2]^{2-} + tht \tag{73}$$

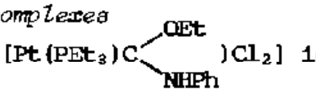
$$[\{Pd(C_6F_5)(tht)(\mu\text{-}Cl)\}_2] + 6CN^- \rightarrow 2[Pd(C_6F_5)(CN)_3]^{2-} + 2Cl^- + tht \tag{74}$$

single crystal neutron diffraction cannot be obtained; the structure involves perfectly linear chains with Pt-Pt separations of 3.245(3) Å [451].

Laser-excited luminescence studies of $[Pd(CN)_4]^{2-}$ ions doped in sodium chloride crystals have demonstrated the existence of $[Pd(CN)_4]^{2-}$ clusters with luminescence similar to that from single crystals of $Ba[Pd(CN)_4].4H_2O$ [452], which itself involves a short-lived component (< 10 ns) centred at about 26,000 cm^{-1} and a long-lived (2 ms at 5 K) component at about 19,000 cm^{-1}. The 26,000 cm^{-1} transition shows a strong temperature dependence due to the changing Pd-Pd separation [453]. Doping of $[Ni(CN)_4]^{2-}$ complexes into $Ba[Pd(CN)_4].4H_2O$ single crystals quenches selectively the host emission by a phonon-assisted hopping process towards a quenching region with a subsequent isotropic radiationless energy transfer to the quencher [454].

Hydrogen atoms generated by γ-radiolysis of aqueous sulphuric acid matrices at 77 K add to $[Pt(CN)_4]^{2-}$ to form $[H\text{-}Pt(CN)_4]^{2-}$ ions in which the unpaired electron is in a σ orbital confined to hydrogen (∿ 35%) and platinum; electron addition followed by proton addition in methanol matrices forms the same complex [455].

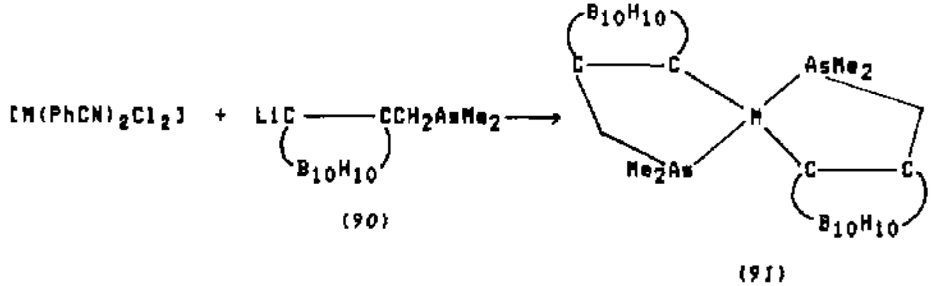
1.5.5.3 Isonitrile and carbene complexes

The platinum(II) carbene complex  $[Pt(PEt_3)C\begin{smallmatrix}OEt\\NHPh\end{smallmatrix})Cl_2]$ is converted into a carbonyl complex $[Pt(PEt_3)(CO)Cl_2]$, by loss of PhNHEt on treatment with $COCl_2$ and NEt_3, and into an isonitrile complex $[Pt(PEt_3)(PhNC)Cl_2]$ by loss of ethanol on treatment with $AlCl_3$ and NEt_3 [456]. *trans*-$[Pt(PR_3)(R'NC)Cl_2]$ may be prepared by treating $[Pt(PR_3)Cl_2]_2$ with isonitriles at low temperatures (at room temperature only the *cis*-isomer is obtained). Treatment of *trans*-$[Pt(P^tBu_2{}^nPr)(CNC_6H_4Me\text{-}4)Cl_2]$ with 4-toluidine at 20 °C gives *trans*-$[Pt(P^tBu_2{}^nPr)\{C(NHC_6H_4Me\text{-}4)_2\}Cl_2]$, the first example of a *trans*-complex not involving a cyclic carbene formed by fission of an electron-rich olefin [457].

Electroreduction of *cis*- and *trans*-$[Pt(RNC)_2X_2]$ occurs by two irreversible one-electron steps [458].

1.5.5.4 Carborane ligands

Treatment of $[M(PhCN)_2Cl_2]$ (M = Pd or Pt) with the arsinocarborane (*90*) yields (*91*) (reaction (75)) [459]. Treatment of $[Pt(PPh_3)_2Cl_2]$ with $Na_2C_2B_8H_{10}$ in thf yields $[Pt(PPh_3)_2(C_2B_8H_{10})]$, in which both the carbon atoms of the carborane coordinate to platinum(II) [460].



(75)

1.5.5.5 Silicon and germanium donor ligands

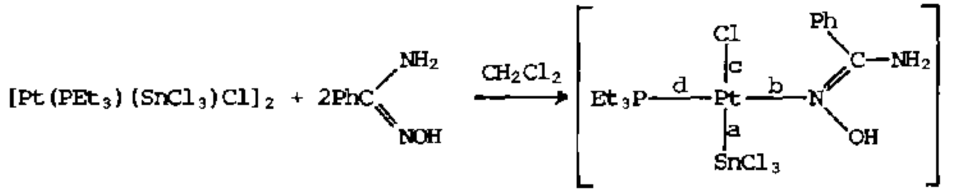
$Ph_2PCH_2CH_2SiHR^1R^2$ (R^1,R^2 = H, Me or Ph) undergo rapid oxidative-addition with $[Pt(cod)_2]$ in ether at room temperature to form *cis*-$[Pt(PPh_2CH_2CH_2SiR^1R^2)_2]$, in which the Pt-Si and Pt-P bond lengths ($R^1 = R^2$ = Me) are 2.342(8)/2.368(6) Å and 2.374(6)/2.317(6) Å, respectively. When $R^1 \neq R^2$, racemic and meso-diastereoisomers are formed in varying ratios, consistent with asymmetric induction during the stepwise chelation to give the racemic complex as the preferred isomer [461].

$[Pt(PEt_3)_3H]BPh_4$ react with EH_3X (E = Si or Ge; X = H, F, Cl, Br or I) to give initial platinum(IV) complexes at 213 K, which decompose to *trans*-$[Pt(PEt_3)_2(EH_2X)H]$ on warming; with SiH_4 and SiH_3Cl, no platinum(IV) intermediate could be detected; GeH_4 and SiH_3F did not react at all [38].

1.5.5.6 Tin donor ligands

$SnMe_3Ar$ complexes react with $[Pt(PPh_3)_2(C_2H_4)]$ to form a mixture of *cis*-$[Pt(PPh_3)_2(SnMe_3)Ar]$ and *cis*-$[Pt(PPh_3)_2(SnMe_2Ar)Me]$; when Ar = Ph, the mixture catalyses the redistribution of $SnMe_3Ph$ to $SnMe_4$ and $SnMe_2Ph_2$ [462]. Oxidative-addition of $SnAr_3H$ to $[Pt\{P(OPh)_3\}_4]$ forms *trans*-$[Pt\{P(OPh)_3\}_2(SnAr_3)_2]$, which is also formed when oxalate is displaced from $[Pt\{P(OPh)_3\}_2(C_2O_4)]$ by $SnAr_3H$ [463].

Single crystal X-ray diffraction shows a Pd-Sn bond length of 2.473(6) Å in $[PPh_4]_2[Pd(SnCl_3)Cl_3]$ [464]. An interest in making $[PtLL^1L^2L^3]$ (because they would be useful in: (i) *trans*-effect studies of ligands with variable electronic and steric parameters, (ii) asymmetric syntheses, and (iii) homogeneous hydrogenation and polymerisation catalysis) led to the isolation of [Pt(PEt$_3$){PhC(NH$_2$)=NOH}(SnCl$_3$)Cl] by reaction (76) [465].



(76)

a 2.501(1) Å   c 2.325(3) Å

b 2.097(7) Å   d 2.242(3) Å

A comparison of [Pt(PPh$_3$)$_2$(SnPh$_3$)Cl] and [Pt(PPh$_3$)$_2$(SnCl$_3$)Cl], in respect of the isomerisation of 1,5-cod, showed that, in the presence of excess of the cocatalyst SnPh$_3$Cl or SnCl$_2$, the SnCl$_3^-$ complex catalysed isomerisation and hydrogenation whereas the SnPh$_3^-$ complex gave almost exclusively isomerisation [466]. Similarly, [Me$_4$N]$_4$[Pt(SnCl$_3$)$_5$Cl] catalyses both the hydrogenation and isomerisation of olefins [467].

trans-[Pt(PPh$_3$)$_2$HX] (X = Cl, Br or I) reacts with SnX$_2$ in chloroform or acetone to give *trans*-[Pt(PPh$_3$)$_2$H(SnX$_3$)] which, with excess SnX$_2$ in acetone, forms [Pt(PPh$_3$)$_2$H(SnX$_3$)(SnX$_2$)].Me$_2$CO. Addition of LiX in acetone or addition of dmf to *trans*-[Pt(PPh$_3$)$_2$H(SnX$_3$)] regenerates *trans*-[Pt(PPh$_3$)$_2$HX] [468].

1.5.6 Complexes with Group III donor ligands

The complete NMR spectrum of the B$_{10}$H$_{12}$$^{2-}$ ligand in [Pt(PMe$_2$Ph)$_2$(B$_{10}$H$_{12}$)] has been recorded by ^{1}H{^{11}B} and ^{11}B{^{1}H} NMR spectroscopies and assigned [469]. Reaction of *cis*-[Pt(PMe$_2$Ph)$_2$Cl$_2$] with excess B$_9$H$_{14}^-$ yields [Pt(PMe$_2$Ph)$_2$(*arachno*-B$_8$H$_{12}$)] in which the B$_8$ unit is trihapto bonded to platinum(II), as well as [Pt$_2$(PMe$_2$Ph)$_2$(B$_6$H$_9$)$_2$]. When [Pt(PMe$_2$Ph)$_2$(*arachno*-B$_8$H$_{12}$)] is treated with potassium hydride, followed by *cis*-[Pt(PMe$_2$Ph)$_2$Cl$_2$], [(PMe$_2$Ph)$_2$Pt(μ-*arachno*-B$_8$H$_{10}$)Pt(PMe$_2$Ph)$_2$] is obtained, in which the borane bonds to both platinum(II) atoms in a trihapto manner [470]. Treatment of 4-XB$_8$H$_{12}$ (X = CH$_2$, NH or S) with [Pt(PPh$_3$)$_4$] gives [Pt(PPh$_3$)$_2$(XB$_8$H$_{10}$)], which are isoelectronic with *nido*-6-CB$_9$H$_{13}$ [471].

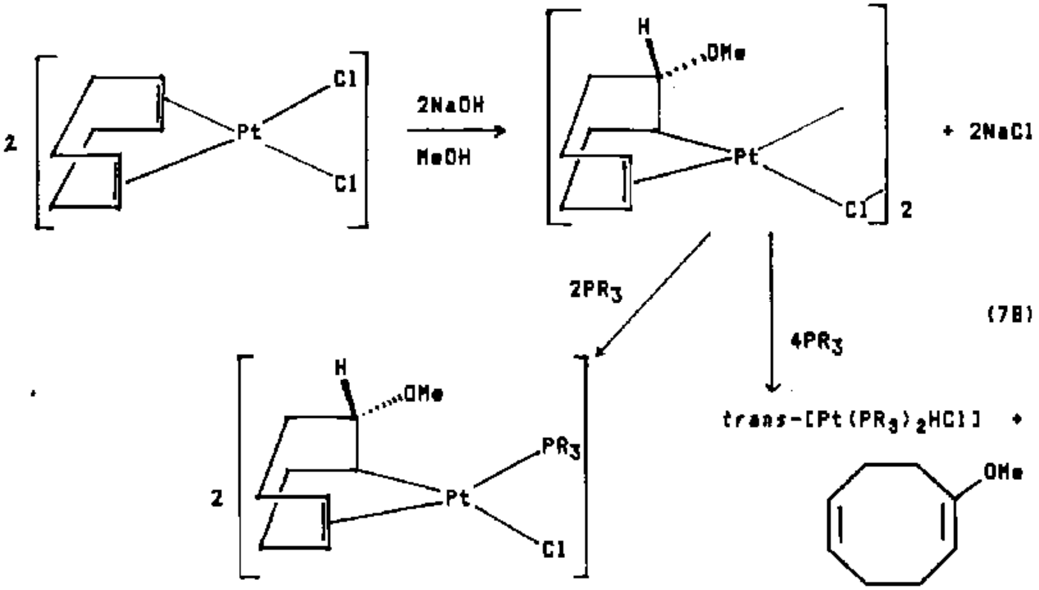
1.5.7 Hydride complexes

H.C. Clark has reviewed his interest in platinum(II)-hydride complexes [472]. A simple route for the preparation of platinum(II)-hydride complexes under mild conditions and free of byproducts, uses dihydrogen as the source of hydride ligand (reaction (77)); after precipitation of Me_4NSnCl_3, only the

$$\textit{cis}\text{-}[Pt\{P(C_6H_4X\text{-}\textit{p})_3\}_2Cl_2] + 2SnCl_2 \xrightarrow[CHCl_3,\ room\ temp.]{\substack{1.\ H_2 \\ 2.\ Me_2NCl}} \textit{trans}\text{-}[Pt\{P(C_6H_4X\text{-}\textit{p})_3\}HCl] + Me_4NSnCl_3 \qquad (77)$$

(X = OMe, Me, H, F or Cl)

starting material, which is sometimes a *cis*/*trans* mixture, and the product are present suggesting that a series of equilibria are set up [473]. An alternative route to hydride complexes that is particularly suitable when bulky phosphines are present is given in reaction (78); the yield of hydride is negligible if benzene or hexane are substituted for methanol [474].



(78)

Thermally stable *trans*-$[PtL_2H(R)]$ (L = PMe_3, PEt_3, PPh_3, P^iPr_3, P^tBuMe_2, or P^tBu_2Me; R = Me or Ph) can be obtained in good yield from thermally unstable methoxy (reaction (79)) or formate (reaction (80)) complexes [99].

$$\left.\begin{array}{l} \textit{trans}\text{-}[PtL_2XR]\ \ (X = Cl,\ OH\ \text{or}\ NHCOMe) \\ \\ \textit{trans}\text{-}[PtL_2(MeOH)R][BF_4] \end{array}\right] \xrightarrow[\text{in MeOH}]{+\ \text{NaOH or NaBH}_4} \textit{trans}\text{-}[PtL_2H(R)] \qquad (79)$$

$$[Pt(\overset{\frown}{L\ L})Me(OH)] + HCOOH \xrightarrow[\text{dppp}]{\overset{\frown}{L\ L} = \text{dppe}} [Pt(\overset{\frown}{L\ L})Me(OOCH)] \xrightarrow[\substack{\text{room temperature} \\ \text{in solid state}}]{> -20\ ^{\circ}C\ \text{in solution}} [Pt(\overset{\frown}{L\ L})Me(H)] + CO_2 \qquad (80)$$

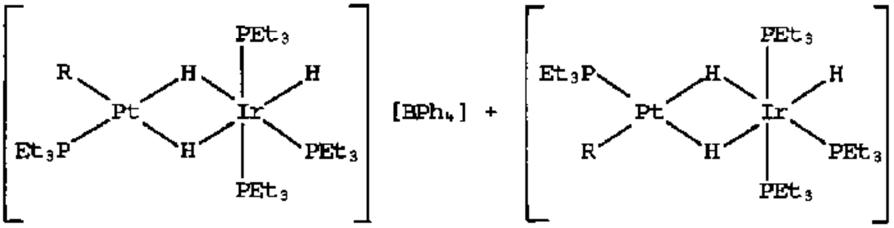
Treatment of *trans*-$[Pt(P^tBu_3)_2HCl]$ with $Ag[PF_6]$ in methanol or acetone yields three-coordinate $[Pt(P^tBu_3)_2H][PF_6]$ which reacts with carbon monoxide, acetonitrile, or water to form *trans*-$[Pt(P^tBu_3)_2HL][PF_6]$ (L = CO, MeCN or H_2O) whereas, with P^tBu_3, $Pcych_3$, or ammonia, $[Pt(P^tBu_3)_2]$ is formed [475]. $[Pt(P^tBu_2Ph)(C_2H_4)_2]$ reacts with dihydrogen (300 atmospheres) at 15 °C in light petroleum over a period of 5 days to form $[Pt_5(P^tBu_2Ph)_5H_8]$, which has a distorted trigonal bipyramid of platinum atoms with a phosphine bound to the three platinum atoms in the trigonal plane, a phosphine and a terminal hydride bound to the axial platinum atoms, and six hydride bridges linking the axial and trigonal plane platinum atoms; in solution the complex has time-averaged D_{3h} symmetry [476]. When the same reaction is carried out using $[Pt(P^tBu_3)(C_2H_4)_2]$, large yellow crystals of $[Pt_3(P^tBu_3)_3H_6]$ are formed after 16 hours, with a trigonal planar arrangement of platinum atoms each bound to a terminal hydride and a phosphine with the Pt-Pt bonds bridged by hydrides. Treatment of a toluene solution of $[Pt_3(P^tBu_3)_3H_6]$ with ethylene yields ethane and $[Pt_4(P^tBu_3)_4H_2]$; the latter involves a tetrahedral cluster of platinum atoms; the hydride ligands (ν_{Pt-H} = 1800, 1650 cm^{-1}) were not located by X-ray diffraction and are fluxional in solution [477]. The nature of the product is clearly critically dependent on the phosphine, since $[Pt(P^iPr_2Ph)(C_2H_4)_2]$ on treatment with dihydrogen (300 atmospheres) in light petroleum at 15 °C for 16 hours yields $[Pt_4(P^iPr_2Ph)_4H_8]$ (ν_{Pt-H} = 2100, 1550 cm^{-1}) which has a tetrahedral arrangement of platinum atoms and is fluxional under ambient conditions [477].

A thermogravimetric study of *trans*-$[Pt(PPh_3)_2HCl]$ shows loss of benzene and formation of $[\{Pt(PPh_3)(PPPh_2)Cl\}_2]$ at 230 °C [478]. 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU) is a commercially available dehydrochlorinating agent that enables *trans*-$[Pt(PPh_3)_2HCl]$ to be used as a source of "$Pt^0(PPh_3)_2$" (reaction (81)) [479].

$$\textit{trans}\text{-}[Pt(PPh_3)_2HCl] + DBU + PhC{\equiv}CPh \xrightarrow[\text{or MeOH, reflux}]{C_6H_6\text{, room temp.}} [Pt(PPh_3)_2(PhC{\equiv}CPh)] + DBU.HCl \qquad (81)$$

Reaction (82) has been used to prepare hydride bridged platinum-iridium complexes [480].

$$\textit{trans}\text{-}[Pt(PEt_3)_2R(MeOH)]^+ + [Ir(PEt_3)_2H_5] \xrightarrow[\text{R = Me or Ph}]{\text{+ Na[BPh}_4\text{],}}$$



(82)

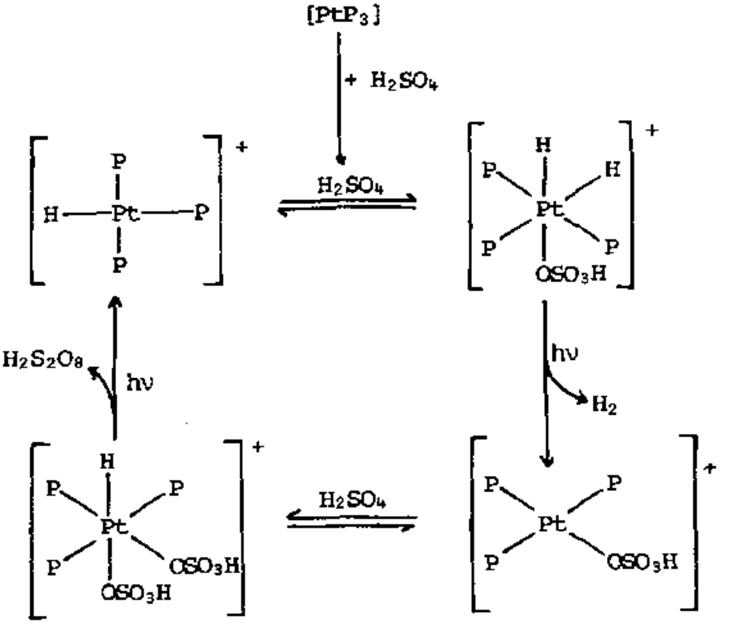
Far UV irradiation of $[M(PEt_3)_3]$ (M = Pd or Pt) in aqueous acid solutions yields hydrogen and $[M(PEt_3)_3(H_2O)]^{2+}$ [481]. When M = Pt, at pH 2.5 in dilute sulphuric acid persulphate is also formed, giving a net reaction as in reaction (83); ^{31}P NMR spectroscopic data suggest that $[Pt(PEt_3)_3(H_2O)]^{2+}$, $[Pt(PEt_3)_3(SO_4H)]^+$, and $[\{Pt(PEt_3)_3\}_2SO_4]$ are all present in solution and are

$$2H_2SO_4 \xrightarrow{h\nu,\ [Pt(PEt_3)_3]} H_2 + H_2S_2O_8 \qquad (83)$$

linked by complex equilibria. Scheme 4 represents the catalytic cycle, which can be entered using $[Pt(PEt_3)_3]$, $[Pt(PEt_3)_3H]^+$, or $[Pt(PEt_3)_3(OSO_3H)]^+$ [482].

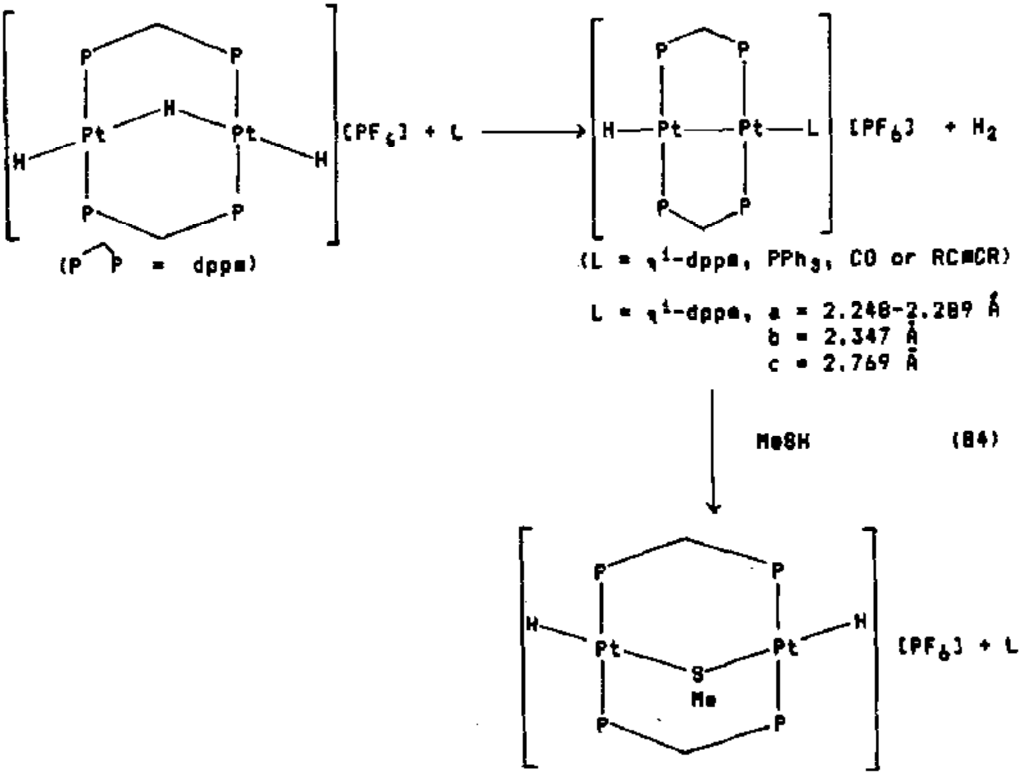
An *ab initio* MO calculation has indicated that, in the oxidative-addition of dihydrogen to $[Pt(PH_3)_2]$, the transition state involves bending the P-Pt-P angle to 150° and only a 4% extension of the H-H bond. The initial product is *cis*-$[Pt(PH_3)_2H_2]$ which is calculated to be between 4 and 12 kJ mol^{-1} less stable than the *trans*-isomer [483,484].

The reductive-elimination of dihydrogen from $[Pt_2(dppm)_2H_3][PF_6]$ (reaction (84)) is intramolecular, since a mixture of the H_3 and D_3 complexes gives almost exclusively H_2 and D_2, and involves an initial bimolecular reaction between $[Pt_2(dppm)_2H_3][PF_6]$ and the entering phosphine [485-487a]; methanethiol regenerates an A-frame complex, although refluxing $[Pt(dppm)_2(L)H][PF_6]$ with NaOH in methanol or treatment with $Li[AlH_4]$ or $Na[BH_4]$ gives no reaction [486]. $Na[BH_4]$ reacts with the bridging ligand in $[Pt_2(dppm)_2Me_2(\mu\text{-}Me)][PF_6]$ and $[Pt_2(dppm)_2Me_2(\mu\text{-}Cl)][PF_6]$ to form $[Pt_2(dppm)_2Me_2(\mu\text{-}H)][PF_6]$, in which the dihedral angle between the platinum



(P = PEt$_3$; for convenience the [HSO$_4$]$^-$ counterion is not shown).

Scheme 4: Photolysis of sulphuric acid [482].



(84)

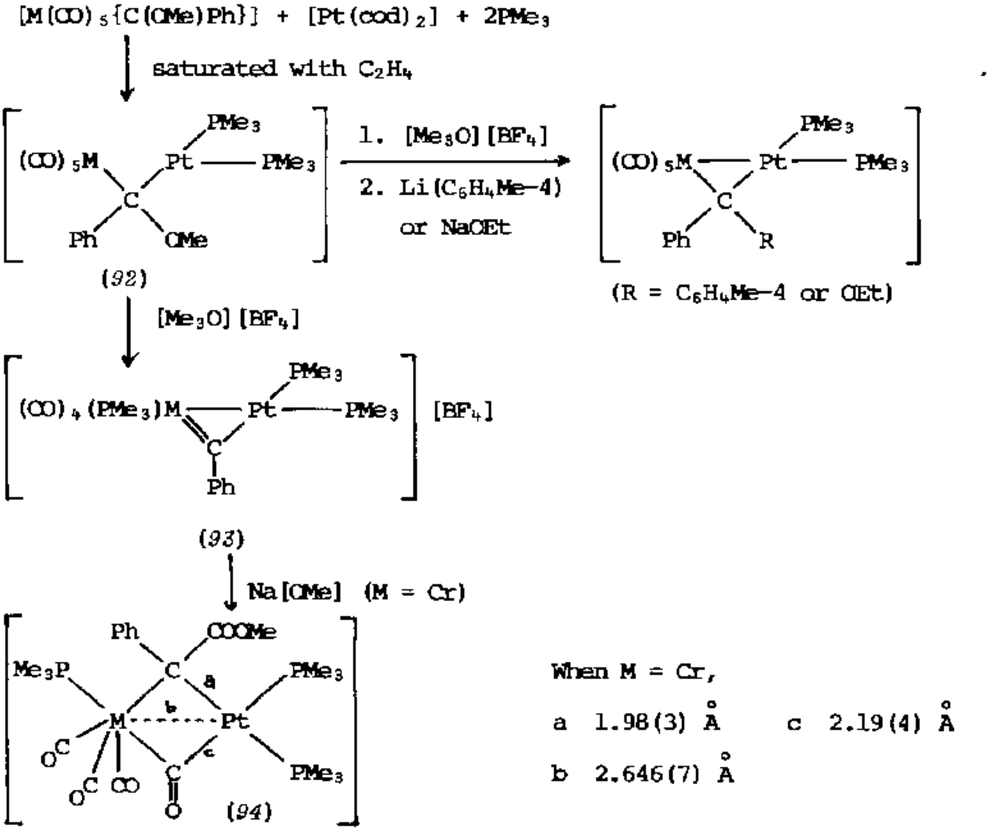
square-planes is 31°; the Pt-H-Pt bond is a bent electron-deficient three-centre, two-electron bond (Pt-Pt = 2.933(1) Å) [488].

A review of the heterolytic activation of dihydrogen has shown that the palladium(II)-salen system and the enzyme hydrogenase are the only cases when heterolytic activation has been fully established [489].

1.5.8 Complexes with direct bonds to other transition metals

Although previously these have been included in section 1.8 under zerovalent complexes because many complexes of palladium and platinum have, in the past, been prepared from zerovalent starting materials, some of these complexes are better considered as derivatives of the divalent metals. These are therefore discussed here in section 1.5 this year; the remainder are in section 1.8.6.

The chromium- and tungsten-platinum complexes with bridging carbene ligands, (*92*), can be prepared as shown in Scheme 5 [490]. They react with $[Me_3O][BF_4]$ to form bridged carbyne complexes, (*93*), which react with sodium methoxide to form (*94*) which has a semi-bridging carbonyl ligand (Scheme 5),



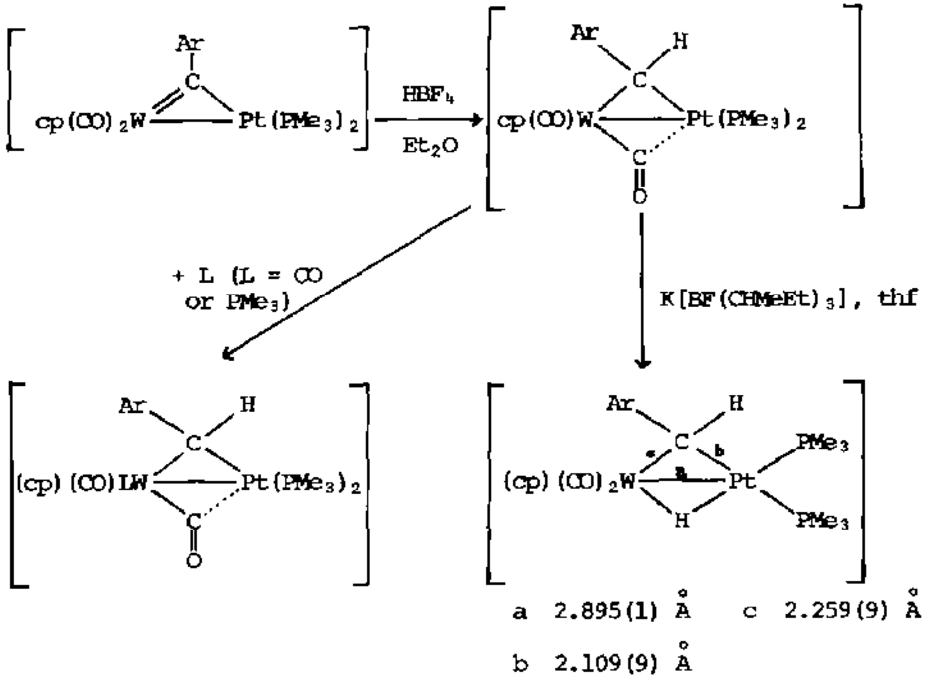
When M = Cr,

a 1.98(3) Å c 2.19(4) Å

b 2.646(7) Å

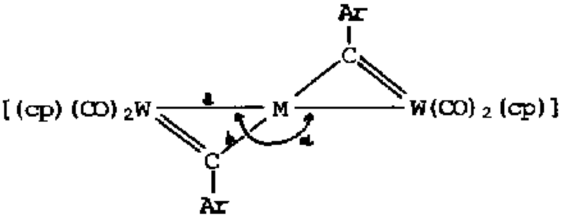
Scheme 5: Synthesis of {Pt-M} complexes (M = Cr or W) [490,491].

although the tungsten analogue $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(PMe_3)_3]$, which has a Pt-W bond of 2.825(1) Å and an asymmetrically bridging carbene group (C-W = 2.37(1) Å; C-Pt = 2.03(1) Å) has no semi-bridging carbonyl [490,491]. The presence of the phosphine ligand on the tungsten and the chromium of (*94*) enhances the stability of these complexes, in comparison to their purely carbonyl analogues. Treatment of the alkylidyne complex $[W(cp)(CO)_2(CC_6H_4Me\text{-}4)]$ with 2-equivalents of $[Pt(C_2H_4)_3]$ or $[Pd(C_7H_{10})_3]$ yields the non-linear trimetal species (*95*) [492]; with 1-equivalent of $[Pt(PMe_3)_2(C_2H_4)]$, $[cp(CO)_2W(\mu\text{-}CC_6H_4Me\text{-}4)Pt(PMe_3)_2]$ is formed [493] which is readily protonated (Scheme 6) [494]. The manganese-carbene complex (*96*) reacts with $[Pt(PMe_3)_2(C_2H_4)]$ to form a carbene bridged complex, which is deprotonated with $[Me_3O][BF_4]$ to form a carbyne bridged complex (*97*) (reaction (85)) [491]; the analogous rhenium complexes have also been prepared [491].



Scheme 6: Interconversion of some {Pt-W} complexes (Ar = $4\text{-}MeC_6H_4$) [494].

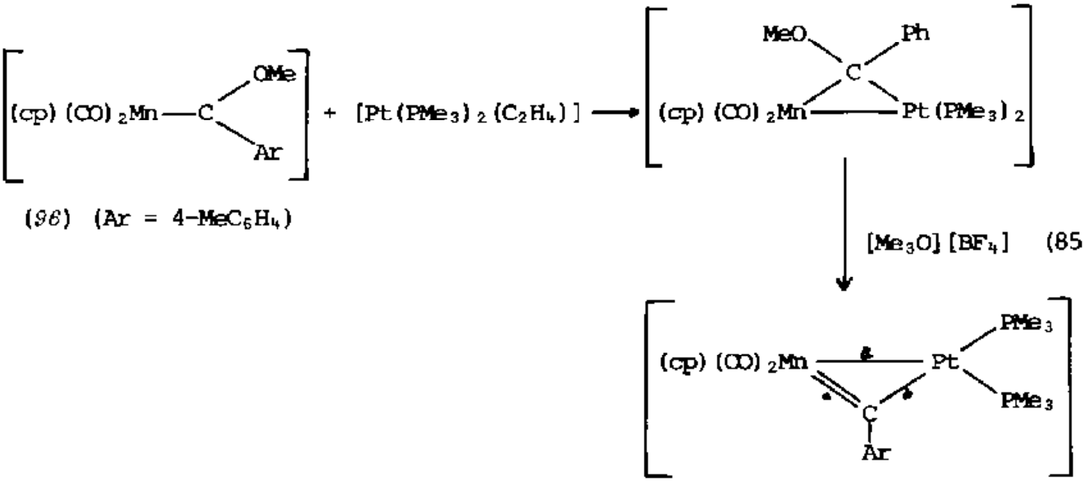
Dimeric Pd_2^{II} complexes in which molybdenum, iron, and cobalt carbonyl moieties act as bridging three-electron donor ligands have been prepared as in Scheme 7 [495]. When a 3:1 ratio of $[Fe_3(CO)_{11}]^{2-}$ and a metal(II) salt (MCl_2, $K_2[MCl_4]$, $[M(PhCN)_2Cl_2]$, or $[M(SEt_2)_2Cl_2]$ (M = Pd or Pt)) are mixed together $[Fe_4M(CO)_{16}]^{2-}$, (*98*), is formed, together with Fe^{2+} and carbon monoxide. The



M = Pt, a = 2.713(1) Å

b = 2.02(1) Å, α = 165°

(*95*) (Ar = 4-MeC$_6$H$_4$)



(*96*) (Ar = 4-MeC$_6$H$_4$)

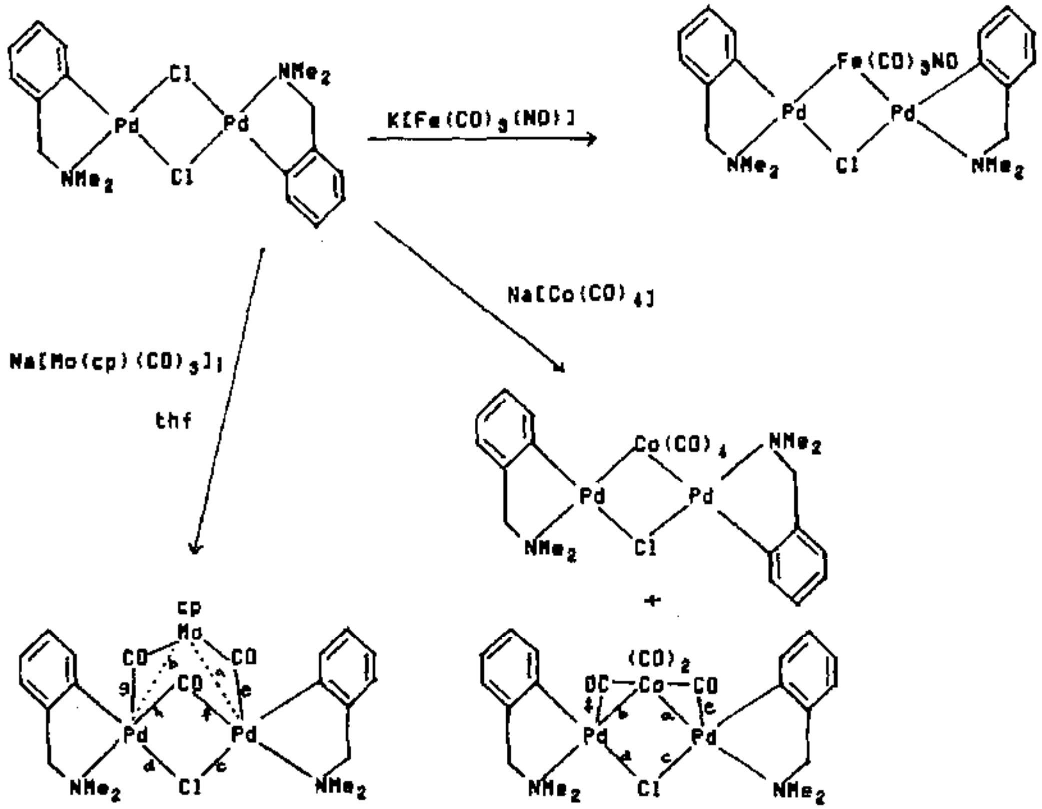
[Me$_3$O][BF$_4$] (85)

a 2.628(1) Å c 1.829(8) Å

b 1.968(1) Å

(*97*)

stoichiometry of this reaction is rather critical and if more platinum(II) is added the initially formed (*98*) is rapidly converted into the more oxidised anions $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_4Pt_6(CO)_{22}]^{2-}$, whereas excess palladium(II) oxidised (*98*) to $[Fe(CO)_5]$ and palladium metal [496]. Slow reaction over 5-10 days of $(TMBA)_2[Fe_4(CO)_{13}]$ (TMBA = $Me_3(PhCH_2)N^+$) with one equivalent of $K_2[PdCl_4]$ affords mainly $[Fe(CO)_5]$, $[Fe_4(CO)_{13}H]$, $[Fe_4Pd(CO)_{16}]^{2-}$ and small amounts of precipitated (*99*) and (*100*), which are linked by equilibrium (86); (*99*) has a trigonal prismatic array of 6 palladium atoms with the 6 lateral faces each capped by an iron atom carrying two terminal carbonyl ligands;



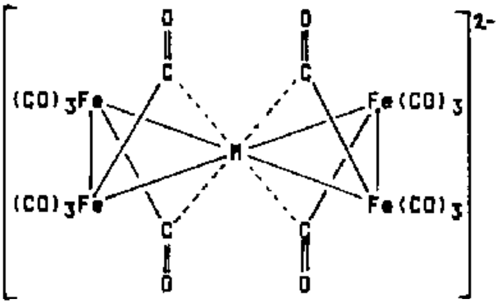
a	2.832(1) Å	e	2.28(1) Å	a	2.597(1) Å	d	2.434(2) Å
b	2.788(1) Å	f	2.39(1) Å	b	2.595(1) Å	e	2.170(8) Å
c	2.470(3) Å	g	2.20(1) Å	c	2.434(2) Å	f	2.138(9) Å
d	2.454(3) Å	h	2.37(1) Å				

Scheme 7: Syntheses of $\{Pd_2M\}$ complexes (M = Fe, Mo or Co) [495].

6 carbonyls doubly bridge the 6 Fe–Pd bonds connecting the two quasi-planar Fe_3Pd_3 units, and 6 triply bridge the 6 $FePd_2$ triangles [496].

$[Pt(RNC)_2M_2]$ (R = ^{t}Bu or cych; M = $cpM'(CO)_3$, M' = Cr, Mo or W; M = $Mn(CO)_5$, $Fe(CO)_3NO$ or $Co(CO)_4$) are reduced in non-aqueous solution by irreversible one-electron reduction that involves rupture of one Pt–M bond [497].

$[Rh(Ph_2P\text{-}2\text{-}py)_2(CO)Cl]$ reacts with $[Pd(cod)Cl_2]$ to form the Pd–Rh bonded complex (*101*), by oxidative-addition of d^8 palladium(II) to an isoelectronic d^8 rhodium(I) – a reaction that is otherwise unknown; it presumably occurs because the $Ph_2P(2\text{-}py)$ ligand brings the two metal atoms very close together

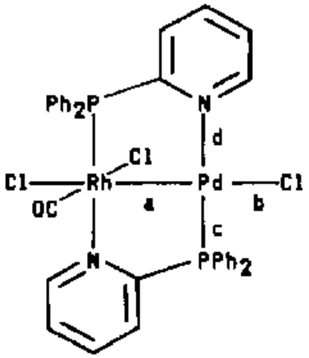


(*98*) Fe–Pd = 2.599 Å average
Fe–Pt = 2.601 Å average

$$[\mathrm{TMBA}]_3[\mathrm{Fe_6Pd_6(CO)_{24}H}] \underset{\mathrm{MeCN}}{\overset{\mathrm{Me_2SO}}{\rightleftharpoons}} [\mathrm{TMBA}]_3\mathrm{H}[\mathrm{Fe_6Pd_6(CO)_{24}}] \qquad (86)$$

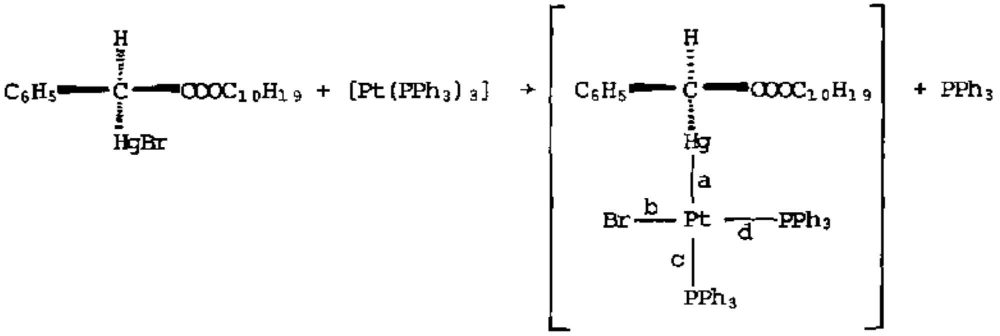
(*99*) (*100*)

[498]. [Pt(PPh$_3$)$_3$] inserts into the Au^{I}–C bond in [Au(PPh$_3$)R] (R = CH$_3$ or C$_6$Cl$_5$) to form [Pt(AuPPh$_3$)(PPh$_3$)$_2$R]; when R = C$_6$Cl$_5$, the product is recovered unchanged from boiling xylene after two hours whereas the methyl compound decomposes. Thus the stability of the Pt–Au bond is enhanced by the greater size and electronegativity of the C$_6$Cl$_5$ ligand, as found with other Pt–M bonds [499]. A similar insertion into an Hg^{II}–C bond is shown in reaction (87) [500].



a 2.594(1) Å c 2.220(4) Å
b 2.393(4) Å d 2.13(1) Å

(*101*)



(87)

a 2.499(2) Å c 2.30 Å

b 2.36 Å d 2.31 Å

1.5.9 Substitution reactions of complexes of the divalent metals

A study of the substitution of X in the rigid platinum(II) complexes [Pt(Fo)X] (H_2Fo = 1-(2-hydroxyphenyl)-3,5-diphenylformazan; X = NH_3 or py) by thiourea, triphenylphosphine, and thiocyanate has shown that the reactions occur by an associative mechanism in which steric effects are important [501]. A number of substitution reactions on complexes with bulky ligands have been shown to occur by an associative mechanism, in spite of the presence of bulky ligands; these include chloride anation of $[Pd(1,1,7,7\text{-}Et_4(dien)(H_2O)]^{2+}$ and $[Pd(1,1,4\text{-}Et_3dien)(H_2O)]^{2+}$ (by volume of activation measurements) [502], replacement of Cl^- by NCS^- in *trans*-$[Pt(PPh_3)_2Cl(R)]$ (R = 2-substituted polychlorophenyl) [503], and the replacement of Br^- by thiourea in *trans*-$[Pt(PEt_3)_2Br(mesityl)]$ in ethanol, dmso, and benzene [504].

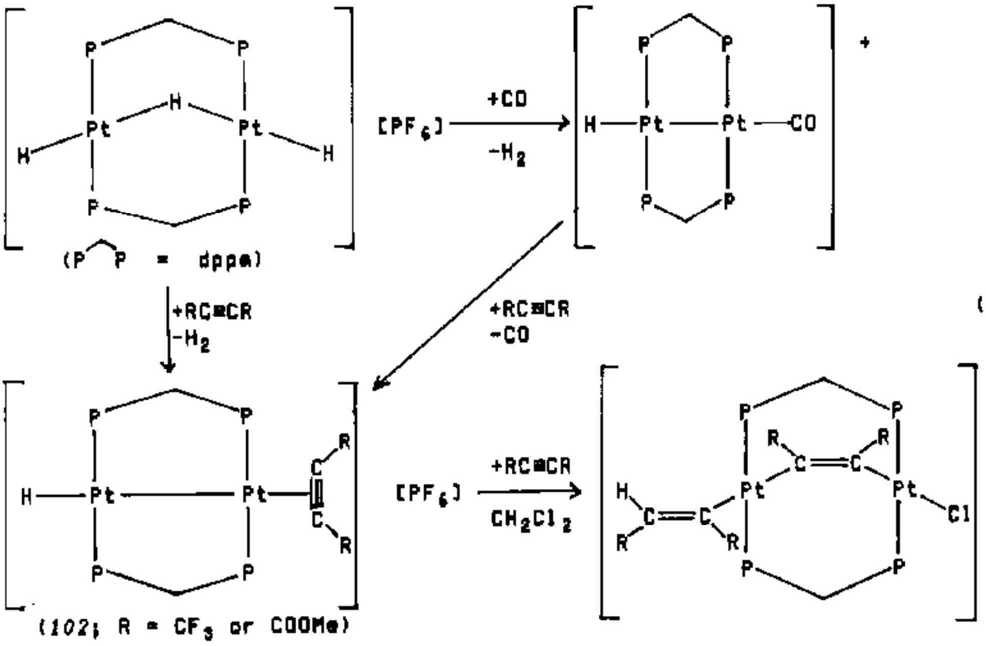
The replacement of aqua or dmso ligands in $[Pt(dien)L]^{2+}$ (L = H_2O or dmso) by the biphilic reagents $SeCN^-$ and thiourea and, to a lesser extent, SCN^- occur more slowly with these 2+ charged cations than expected on the basis of the n°_{Pt} scale; for these cations the nucleophilicity scale is $Cl^- < N_3^- < Br^- <$ thiourea $< SCN^- < I^- < SeCN^- < S_2O_3^{2-}$; dmso is a more discriminating leaving group than water [505].

A series of papers have attempted to quantitatively predict the kinetics of substitution at square-planar metal complexes, based on the properties of the entering and departing ligands [506-509].

1.6 PALLADIUM(I) AND PLATINUM(I)

1.6.1 Complexes with tertiary phosphines

The crystal structure of $[HPt(\mu\text{-}dppm)_2Pt(\eta^1\text{-}dppm)]$ has already been noted in section 1.5.7 (equation (84)) [487a]. The platinum(I)-hydride (*102*), formed by reductive-elimination of dihydrogen from $[Pt_2(dppm)_2H_3][PF_6]$ undergoes oxidative-addition with ethyne (reaction (88)) [487]. This latter reaction is similar to reaction (89), in which ethyne derivatives add oxidatively to palladium(I) [510]. CS_2 undergoes a similar oxidative-addition (reaction (90)) [511].

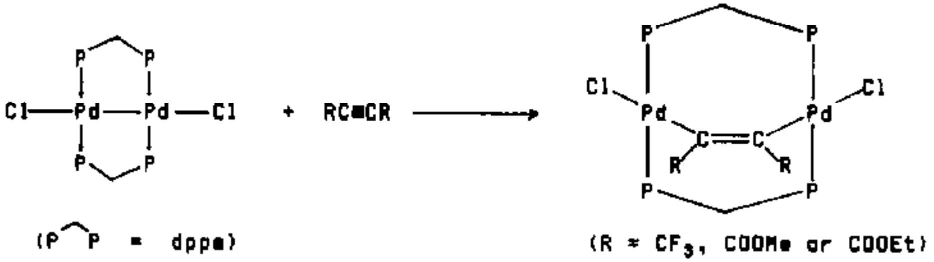


(88)

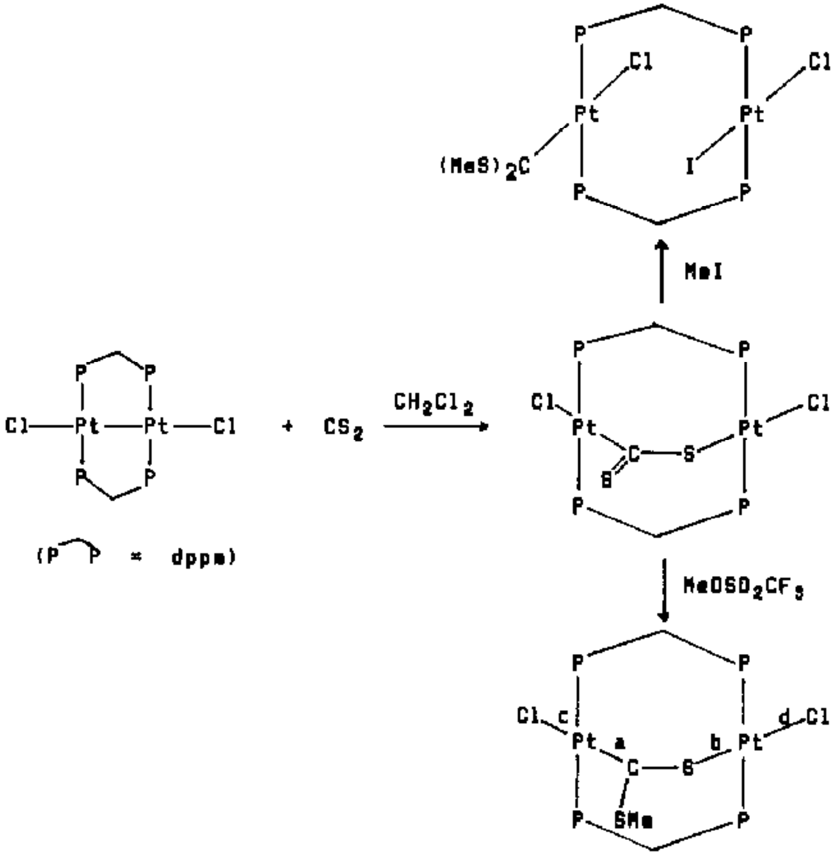
An ESCA study of $[Pt_2(dppm)Cl_2]$ and $[Pt_2(dppm)HL][PF_6]$ (L = η^1-dppm, CO or PPh_3) has established the Pt $4f_{7/2}$ energy levels in these platinum(I) complexes. This enabled the formulation of $[Pt(dppm)_2Me_3]$, (*84*), with a $Me_2Pt^{II} \rightarrow Pt^{II}Me$ dative bond as opposed to the alternative $MePt^{I} - Pt^{III}Me_2$, to be confirmed [435a].

A number of palladium(I) complexes of di- and tri-phosphines have been prepared from $[Pd_2(CNMe)_6][PF_6]_2$ (reactions (91) and (92)); the two palladium square-planes in the products are twisted at 90° to each other. Neither of these palladium(I) dimers show any tendency to insert carbon monoxide or methyl isocyanide into the Pd-Pd bond [512].

The value of selective population transfer experiments in identifying resonances in the NMR spectrum of a single isotopomer and, consequently, in facilitating spectral analysis has been demonstrated by a study of the $^{31}P\{^1H\}$ NMR spectrum of $[(PPh_3)_2Pt(\mu\text{-}S)Pt(PPh_3)CO]$ [513].



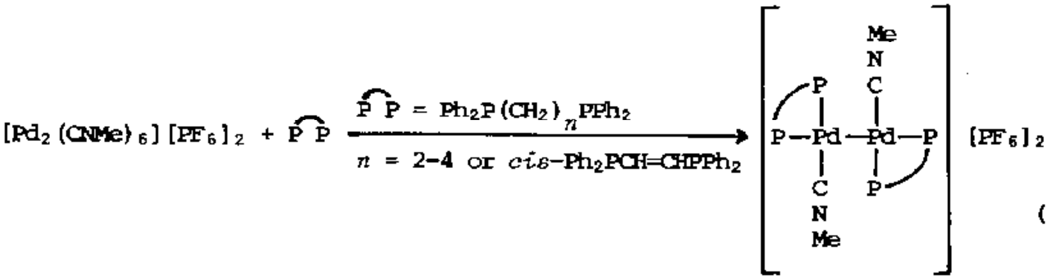
(89)



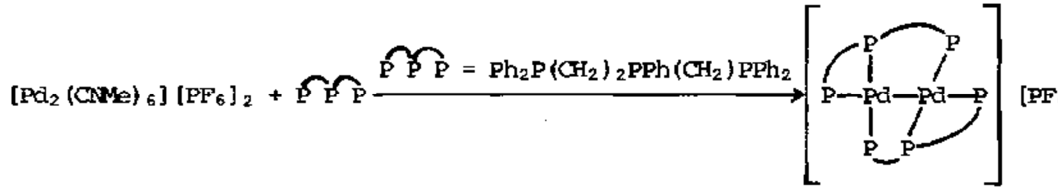
(90)

a 2.175 Å c 2.427 Å

b 2.305 Å d 2.363 Å



(91)



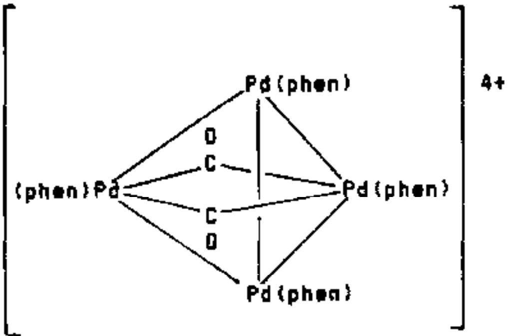
(92)

1.6.2 *Acetonitrile complexes*

The vibrational spectra of $[M_2(MeCN)_6][PF_6]_2$ (M = Pd or Pt) and $[PtPd(MeCN)_6]]PF_6]_2$ have been analysed and the M-M force constant shown to decrease in the order Pt-Pt (1.30 mdyn/Å) > Pt-Pd (1.03 mdyn/Å) > Pd-Pd (0.80 mdyn/Å). The axial M-N bonds (Pt-N = 2.4 mdyn/Å; Pd-N = 1.2 mdyn/Å) are stronger than the equatorial bonds (Pt-N = 3.4 mdyn/Å; Pd-N = 2.4 mdyn/Å) with the bonds to platinum being stronger than to palladium [514].

1.6.3 *Carbonyl complexes*

Iodine reacts with $[\{Pt(P^tBu_3)(\mu\text{-}CO)\}_3]$ to form $[\{Pt(P^tBu_3)(CO)(\mu\text{-}I)\}_2]$ which undergoes intramolecular metallation in the presence of excess iodine to give $[\{Pt(P^tBu_2CMe_2CH_2)(\mu\text{-}I)\}_2]$ [515]. $[Pd_4(CO)_4(O_2CMe)_4]$ reacts with 1,10-phenanthroline to form $[Pd_4(CO)_2(phen)_4][O_2CMe]_4$, (*103*), which is also formed when palladium(II) ethanoate is treated with 1,10-phenanthroline in ethanoic acid at 50 °C in the presence of carbon monoxide [516,517].



(*103*)

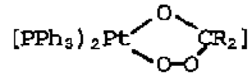
1.7 PALLADIUM HYDRIDE

Since the assignment of an oxidation state to palladium in its hydrides is meaningless, palladium hydride species are described in a section of their own this year. *Ab initio* SCF calculations have been performed on PdH which demonstrate involvement of the Pd 4*d* electrons in the bonding [518]. γ'-Pd_3H_4

forms cubic crystals [519]. In tetragonal Pd_3H_4 the palladium atoms are octahedrally sited with Pd–Pd separations of 2.64 Å [520].

1.8 PALLADIUM(0) AND PLATINUM(0)

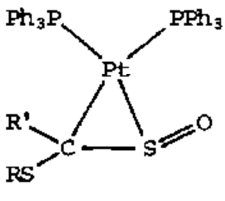
1.8.1 Complexes with Group VI donor ligands

The nucleophilic character of oxygen in $[Pt(PPh_3)_2O_2]$ has been reviewed [521]. Insertion of ketones into $[Pd(PPh_3)_2O_2]$ occurs by a dual pathway mechanism; the major pathway involves precoordination of the ketone to the vacant axial site, followed by insertion to yield  $[(PPh_3)_2Pt\langle O, O{-}O\rangle CR_2]$. The minor pathway involves prior activation of dioxygen, perhaps as $(PPh_3)_2Pt-\overset{\delta+}{O}{=}\overset{\delta-}{O}$ [522]. Although no reaction occurs when $[Pt(PPh_3)_2O_2]$ is irradiated above 300 nm in dioxygen saturated chloroform, in the absence of dioxygen, "$Pt(PPh_3)_2$" and singlet oxygen are the primary photoproducts formed [523]. $[Pd_{10}(phen)_4(O_2)_3(OAc)_2]$ is formed when palladium(II) acetate is treated with 1,10-phenanthroline and dihydrogen, followed by exposure to air [524].

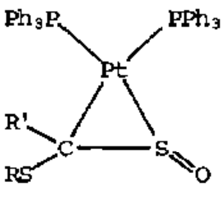
Sulphines, XYC=S=O, can be divided into four groups according to their reactivity with $[Pt(PPh_3)_4]$ [525]:

(i) $Ph_2C{=}S{=}O$ form stable η^2–CS coordinated $[Pt(PPh_3)_2(Ph_2CSO)]$ complexes [525,526].

(ii) Sulphines with one C–S side bond, (RS)R'C=S=O give rise to stereoisomeric coordination complexes, (*104*) and (*105*), in which η^2–CS bonding is present. These coordination stereoisomers are present in equilibrium with the oxidative-addition stereoisomers (*106*) and (*107*) [525,527]. This oxidative-addition is more difficult when PPh_3 is replaced by $Pcych_3$ [526].

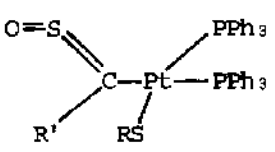


(*104*; E)

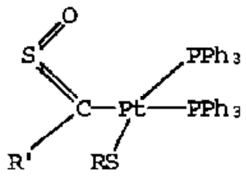


(*105*; Z)

(iii) After forming an η^2–CS bonded complex $[Pt(PPh_3)_2\{(RS)_2C{=}S{=}O\}]$, sulphines with two C–S side bonds undergo oxidative-addition to yield the stereoisomers *cis*-(E) and *cis*-(Z)-$[Pt(PPh_3)_2(RS)(RSCSO)]$, which again is



(*106*; E)

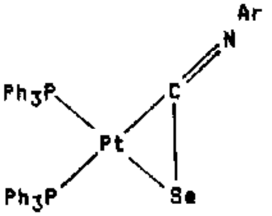


(*107*; Z)

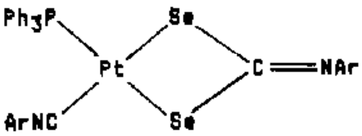
more difficult with $Pcych_3$ than with PPh_3 [525,526]. Complexes $[Pt(PPh_3)_2\{X(RS)C{=}S{=}O\}]$ containing a C-S side bond *syn* to the S=O group are unstable in chloroform, relative to their corresponding oxidative-addition products, while those without such a *syn* C-S group have almost the same thermodynamic stability as their oxidative-addition products.

(iv) Sulphines with a C-Cl side bond form η^2-CS bonded complexes which undergo very rapid oxidative-addition to yield *cis*-(E)-, *cis*-(Z)-, *trans*-(E)- and *trans*-(Z)-$[Pt(PPh_3)_2(RSCSO)Cl]$ [525].

$[Pt(PPh_3)_2(C_2H_4)]$ reacts with 4-tolylisoselenocyanate to form an η^2-bonded C-Se complex, (*108*), which is alkylated by methyl iodide at selenium rather than nitrogen to yield $[Pt(PPh_3)(CN4\text{-}tolyl)I_2]$ as the final product. In dichloromethane, $[Pt(PPh_3)_2(C_2H_4)]$ reacts with 4-tolylisoselenocyanate to give selenium abstraction and formation of (*109*) which is not alkylated by methyl iodide [528].



(*108*; Ar = C_6H_4-4-Me)



(*109*; Ar = C_6H_4-4-Me)

1.8.2 Complexes with Group V donor ligands

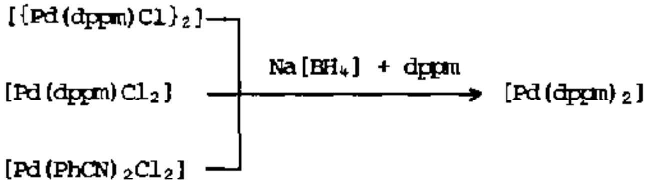
Complexes of the type $[Pd(^tBuN{=}CHCH{=}N^tBu)(ol)]$ (ol = tcne, maleic anhydride, dimethylfumarate or dimethylmaleate) have been prepared from

[Pd(dba)$_2$], [Pd$_2$(dba)$_3$].CHCl$_3$, and [Pd$_3$(ttaa)$_3$] (ttaa = tritoluidineacetylacetone). The advantage of ttaa is that it is only sparingly soluble in methanol, so that it can be easily removed [529].

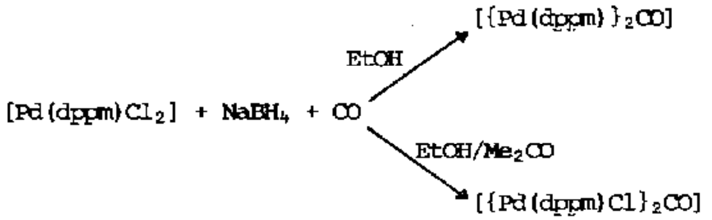
Otsuka has reviewed his work on [PtL$_2$] complexes in which L are bulky phosphines [530]. $J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ in [Pt(PF$_3$)$_4$] (6480 Hz) is larger than in [Pt(PR$_3$)$_4$] or [Pt{P(OR)$_3$}$_4$] because the strongly electronegative fluorine increases the *s*-character of the phosphorus lone-pair on PF$_3$, relative to the other phosphines [531]. The luminescence of [Pt(PPh$_3$)$_2$L] (L = C$_2$H$_4$, tcne, fumaronitrile, or tetracyanocyclopropane) is ligand-centred, but has a life-time affected by the heavy atom [532].

The oxidative-addition of methyl iodide to aged solutions of [Pt(PR$_3$)$_2$] and [Pt(PR$_3$)$_3$] occurs in two steps for phosphines other than PPh$_3$. These two steps are rapid reaction of [Pt(PR$_3$)$_2$] followed by slower reaction of [Pt(PR$_3$)$_3$]. The rate of oxidative-addition varies with R in the order R = C$_6$H$_4$Et-4 < C$_6$H$_4$Me-4 < *n*-C$_{16}$H$_{33}$ < *n*-C$_8$H$_{17}$ [533]. Oxidative-addition of dihalomethanes, CHRXY (CH$_2$I$_2$, CH$_2$Br$_2$, CH$_2$BrCl, CH$_2$BrI, CH$_2$ClI, or CHBr$_3$) to [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] yields *trans*- and usually also *cis*-[Pt(PPh$_3$)$_2$(CHRX)Y], of which the structure of *cis*-[Pt(PPh$_3$)$_2$(CH$_2$I)I] has been determined by X-ray diffraction ($\text{Pt-P}_{\textit{trans}\ \text{to C}}$ = 2.355(7) Å; $\text{Pt-P}_{\textit{trans}\ \text{to I}}$ = 2.228(6) Å). By contrast, diiodomethane reacts with [Pt(PEt$_3$)$_3$] to form *trans*-[Pt(PEt$_3$)$_2$(CH$_2$PEt$_3$)I]I [534]. CH$_2$Cl$_2$ can add oxidatively to [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] either in the presence of light or on addition of the double ylide (Me$_3$Si)$_2$NP(=NSiMe$_3$)$_2$ which reacts with HCl; in both cases the products are *cis*- and *trans*-[Pt(PPh$_3$)$_2$(CH$_2$Cl)Cl] and *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] [535]. N$_2$O$_3$ reacts with [M(PPh$_3$)$_4$] (M = Pd or Pt) to form [M(PPh$_3$)$_2$(NO$_2$)$_2$], if the reaction is carried out under dinitrogen, and [M(PPh$_3$)$_2$(NO$_2$)(NO$_3$)] if dioxygen is present [536].

[Pd(dppm)$_2$] has been prepared using Na[BH$_4$] reduction of palladium(II) complexes (reaction (93)). If carbon monoxide is present, the nature of the product depends on the solvent (reaction (94)). All of these palladium-dppm complexes catalyse the hydrocondensation of dihydrogen with carbon dioxide; [Pd(dppm)$_2$] was the most effective, giving CH$_4$ (40 µmol), HCOOEt (400 µmol) and (COOEt)$_2$ (0.4 µmol) [537].



$$\left.\begin{array}{l}[\{\mathrm{Pd(dppm)Cl}\}_2]\\ [\mathrm{Pd(dppm)Cl_2}]\\ [\mathrm{Pd(PhCN)_2Cl_2}]\end{array}\right\}\xrightarrow{\mathrm{Na[BH_4]\ +\ dppm}}[\mathrm{Pd(dppm)_2}] \qquad (93)$$



$$[Pd(dppm)Cl_2] + NaBH_4 + CO \begin{cases} \xrightarrow{EtOH} [\{Pd(dppm)\}_2CO] \\ \xrightarrow{EtOH/Me_2CO} [\{Pd(dppm)Cl\}_2CO] \end{cases} \qquad (94)$$

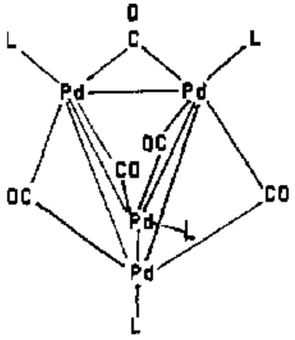
$[Pd(diop)_2]$ is dynamic with an activation energy (41.2 kJ mol^{-1}), rather lower than that of $[Pt(diop)_2]$ (48 kJ mol^{-1}) [538].

1.8.3 Carbonyl complexes

Reviews of cluster chemistry and of Chini's work on large carbonyl clusters have been published [539,540]. The effects of size on the electronic properties of clusters of up to 79 atoms have been examined. The adsorption energies of hydrogen, C_2, or oxygen molecules on different clusters show a widely varying size dependence, which can be related to the electronic properties of the cluster [541]. By treating a cluster as a perturbed spherical shell or an assembly of concentric spherical shells, electron-counting rules for cluster compounds have been developed, which explain the common preference for triangulated polyhedral structures, as well as showing how departures from such structures can arise [542].

The field desorption mass spectra of $[Pt_3(CO)_3(PPh_3)_4]$, $[Pt_4(CO)_5(PPh_3)_4]$, and $[Pt_5(CO)_6(PEt_3)_4]$ show molecular ion and $[M{-}CO)_x]^{\cdot+}$ peaks [543]. The nuclearity of platinum-carbonyl-phosphine clusters in solution can be determined by ^{31}P NMR spectroscopy using the multiplicity data in the ^{195}Pt satellites. $^2J_{^{195}Pt-^{31}P}$ and $^3J_{^{31}P-^{31}P}$ can be useful indicators for the presence of Pt-Pt bonds, being rather large (419-488 and 56-63 Hz, respectively) when a Pt-Pt bond is present [544].

A new high yield synthesis of $[Pt_5(CO)_6(PPh_3)_4]$ has been described [545]. Thermal decomposition of $[Pt_3(CO)_6]_n^{\ 2-}$ (n = 2 or 3) in acetonitrile yields $[Pt_{19}(CO)_{22}]^{4-}$ and $[Pt_{13}(CO)_{17}]^{4-}$, which react with acids to form $[Pt_{38}(CO)_{44}H_4]^{2-}$ and $[Pt_{26}(CO)_{32}H_2]^{2-}$, respectively [546]. $[Pd(PPh_2Me)_2(NO_2)_2]$ reacts with carbon monoxide to form $[Pd_4(CO)_5(PPh_2Me)_4]$, *(110)*, (Pd-Pd = 2.750(2) Å mean; Pd-P = 2.315(4) Å mean; Pd-C = 2.085(16) Å mean), CO_2, N_2O and other unidentified products [547]. Palladium(II) ethanoate reacts with carbon monoxide in the presence of P^nBu_3 in dioxane to form $[Pd_{10}(CO)_{12}(PBu_3)_6]$ and $[Pd_{10}(CO)_{14}(PBu_3)_4]$ which are precipitated on addition of acetone. $[Pd_{10}(CO)_{12}(PBu_3)_6]$ involves a tetracapped octahedral of palladium atoms with "slightly opened" caps; the slight opening may be due to the fact that the

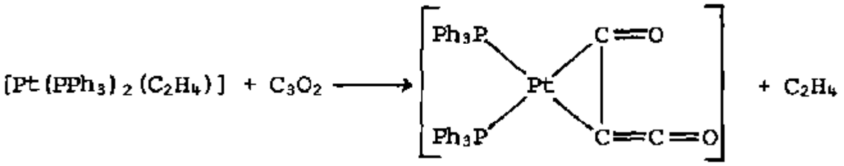


(*110*; L = PPh_2Me)

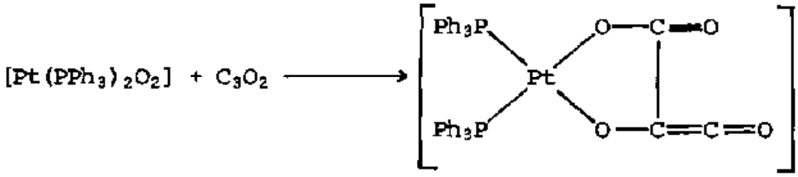
16 skeletal electrons are more than Wade's rules require for an octahedron [548]. When the reaction between palladium(II) ethanoate and carbon monoxide is performed in aqueous ethanoic acid containing trifluoroacetic acid, Pd_{12} clusters, $[Pd_{12}(CO)_{15}(PR_3)_7]$ (R = ^{n}Bu or Et) and $[Pd_{12}(CO)_{17}(PBu_3)_5]$ are obtained [549] whereas, if R_2S (R = Me, Et, Pr or Bu) are present, $[Pd(R_2S)_3(CO)]$ are formed which react with PPh_3 to form $[Pd(PPh_3)_4]$ [550].

1.8.4 Reactions of C_3O_2 with platinum(0) complexes

C_3O_2 reacts with platinum(0) complexes as shown in reactions (95) and (96) [551].



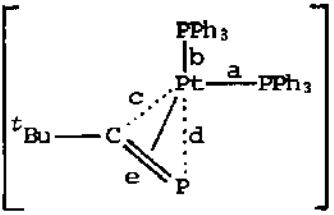
(95)



(96)

1.8.5 η^2-C≡P ligands

Excess ^{t}BuC≡P displaces ethylene from $[Pt(PPh_3)_2(C_2H_4)]$ to form (*111*), in which the ligand is η^2-bonded with no significant interaction between the phosphorus lone-pair and platinum(0) [552].



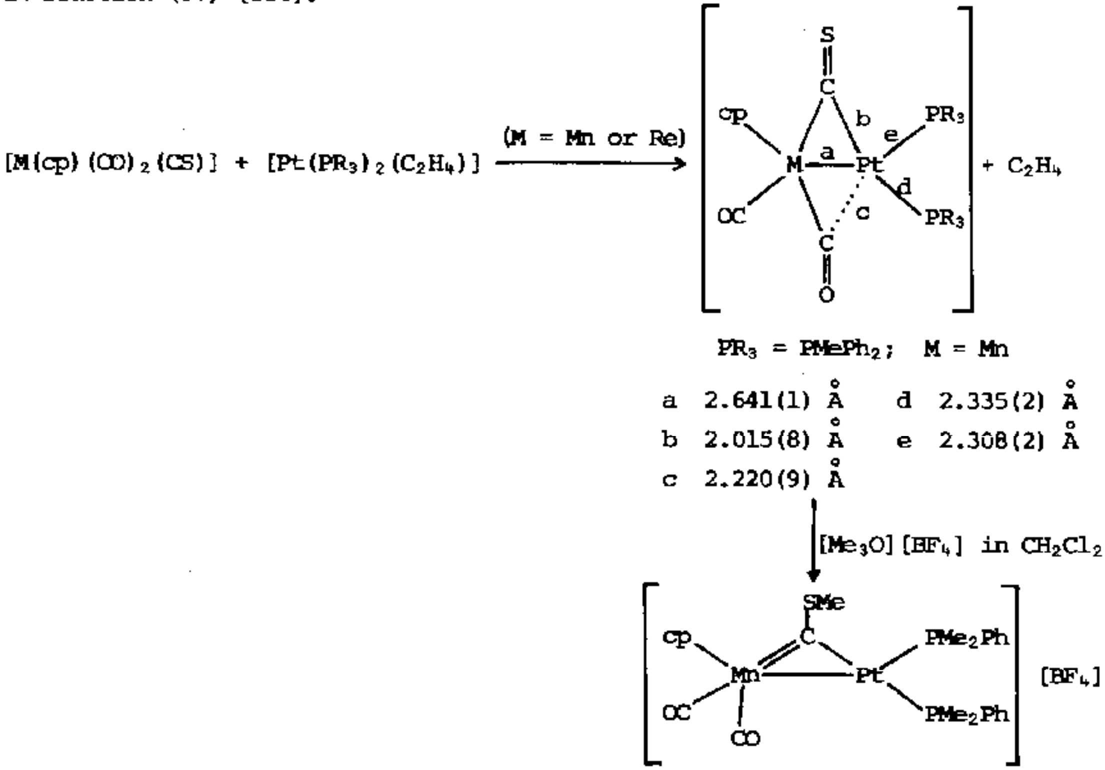
(111)

a 2.292(5) Å
b 2.285(5) Å
c 1.973(21) Å
d 2.320(6) Å
e 1.672(17) Å

∠ between PtP$_2$ and PtPC planes = 6.7°

1.8.6 Complexes with other transition metals

The use of $[Pt(C_2H_4)_3]$, $[Pt(PR_3)_{3-n}(C_2H_4)_n]$ (n = 1 or 2), and [Pt(cod)$_2$] in the preparation of multinuclear complexes with Pt-M bonds has been reviewed [553]. Interest in the resulting products lies in: (i) activation of small organic ligands bonded to more than one metal centre; (ii) the core geometries of small clusters in relation to the number of valence electrons present; (iii) the properties of heteronuclear in comparison to homonuclear metal-metal bonds; (iv) dynamic behaviour of the peripheral ligands. Platinum-manganese and platinum-rhenium complexes with bridging CS ligands have been prepared as in reaction (97) [554].



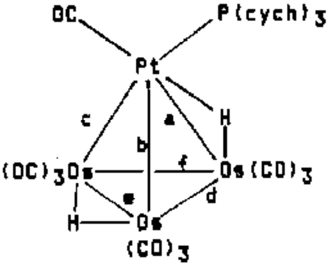
PR$_3$ = PMePh$_2$; M = Mn

a 2.641(1) Å
b 2.015(8) Å
c 2.220(9) Å
d 2.335(2) Å
e 2.308(2) Å

(97)

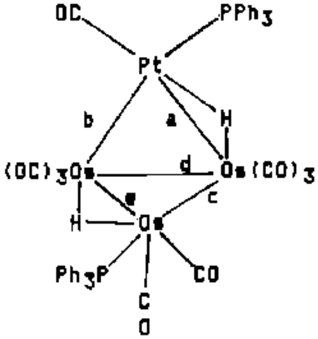
$[Fe_3Pt_3(CO)_{15}]^{2-}$ can be prepared by: (i) redox condensation between $[Pt_3(CO)_6]^{2-}$ and $[Fe(CO)_5]$; (ii) reaction of $[Fe_3(CO)_{11}]^{2-}$ with $K_2[PtCl_4]$ in a 2:3 molar ratio, during which the IR spectrum indicates intermediate formation of $[Fe_4Pt(CO)_{16}]^{2-}$, and (iii) reaction of $[Fe_4Pt(CO)_{16}]^{2-}$ in a 1:1 molar ratio with $K_2[PtCl_4]$. Controlled oxidation of $[Fe_3Pt_3(CO)_{15}]^{2-}$ by iodine, phosphoric or sulphuric acids in dichloromethane, or thf yields $[Fe_3Pt_3(CO)_{15}]^{-}$, which can be reduced back to the dinegative anion by treatment with methanolic alkali hydroxide [555]. The crystal structures of $[PhCH_2NMe_3][Fe_3Pt_3(CO)_{15}]$ and the dianion both involve essentially planar arrangements of Pt_3, each platinum carrying a terminal carbonyl ligand and the Pt-Pt bonds bridged by $Fe(CO)_4$ units [555]. The EPR spectrum of essentially planar $[Fe_3Pt_3(CO)_{15}]^{-}$ suggests that the unpaired electron is mainly located in a non-degenerate MO on the Pt_3 system which, under idealised D_{3h} symmetry may be primarily the $a_2{}^{1*}$ combination of three d_{xz} platinum orbitals. The stability of the cluster probably derives from the unpaired electron being localised mainly on the platinum atoms, together with the steric properties of the bridging $Fe(CO)_4$ groups which hinder spin-pairing by dimerisation [556]. $[Fe_3Pt_3(CO)_{15}]^{-}$ slowly decomposes to $[Fe_4Pt_6(CO)_{22}]^{-}$, apparently by loss of an $Fe(CO)_4$ group and orthogonal condensation along the pseudo-C_2 axes of two resulting trapezoidal $Fe_2Pt_3(CO)_{11}{}^{2-}$ units to give a tetrahedral Pt_4 core [555]. $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]^{-}$ reacts with $[Pt(PPh_3)(C_2H_4)_2]$ in thf to form $[Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]^{-}$. The structure of the $[N(PPh_3)_2]^{+}$ salt shows an Fe_2Pt triangle, edge-bridged by three CO ligands and capped by a Pt atom carrying a terminal CO and PPh_3 ligand; the hydride bridges an Fe-Pt bond [557]. Protonation of this complex yields $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, in which an Fe_2Pt_2 tetrahedral core has bridging hydride ligands on the longest Fe-Pt edges; each iron has 3 terminal CO ligands and each platinum a CO and a PPh_3 ligand [557]. $[Pt(PPh_3)(C_2H_4)_2]$ and $[Pt(cod)(C_8H_{13})][BF_4]$ both react with $[NEt_3H][Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]$ to form $[NEt_3H][Fe_3Pt(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}(PPh_3)]$ and $[Fe_2Pt(CO)_8(cod)]$, respectively, the latter having a triangular Fe_2Pt core with 4 terminal CO ligands on each iron and cod η^4-bonded to platinum [557].

$[Pt(PR_3)(C_2H_4)_2]$ (PR_3 = $Pcych_3$, PPh_3 or P^tBu_2Me) react with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to form $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$, *(112)*, a 58-electron dynamic species with site exchange by bridging hydrides [558]. *(112)* reacts with donor ligands, L, (L = CO, PPh_3, or $AsPh_3$) to form $[Os_3Pt(\mu\text{-}H)_2(CO)_{12}(PR_3)L]$, *(113)*, in which the 4 metal atoms adopt a butterfly as opposed to tetrahedral arrangement. With ethynes, *(112)* forms 5 polynuclear species none of which contain the Os_3Pt cluster which is obviously fairly easily degraded; one of these is $[OsPt_2(CO)_5(PPh_3)_2(\mu\text{-}MeC{\equiv}CMe)]$, *(114)* [559]. With $[OsH_2(CO)_4]$, $[Pt(PR_3)_2(C_2H_4)]$ (R = Me, Ph or cych) reacts to form $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PR_3)_2]$



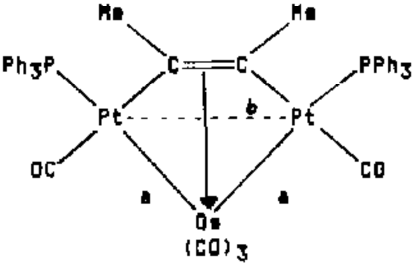
a	2.863(1) Å	d	2.277(1) Å
b	2.791(1) Å	e	2.789(1) Å
c	2.832(1) Å	f	2.741(1) Å

(*112*)



a	2.848(2) Å	d	2.773(2) Å
b	2.717(1) Å	e	3.043(2) Å
c	2.914(2) Å		

(*113*)



a	2.662(2) Å mean
b	3.033(2) Å

(*114*)

which has a butterfly arrangement of metal atoms with 2 osmium atoms at the hinge and 2 platinum atoms at the wingtips [560].

$[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ reacts with $[Co_2(CO)_8]$ to form $[PtCo_2(CO)_8(PPh_3)]$ and $[Pt_2Co_2(CO)_8(PPh_3)_2]$ [545]; the latter may also be formed by electrochemical reduction of the former in an aprotic medium [561], and on a support affords a stable hydrogenation catalyst [545].

Crystals of $[PtRh_4(\mu\text{-}CO)_4(cpMe_5)_4]$, prepared by reaction (98), are monoclinic at 293 K but, on cooling to 200 K and rewarming to room temperature, undergo a non-reversible phase change to orthorhombic. In the orthorhombic form, the $PtRh_4$ core has an angle of 90° between the two $PtRh_2$ planes, whereas in the monoclinic form this is 100°. In the monoclinic form the $cpMe_5$ rings

$$[\mathrm{Pt(C_2H_4)_3}] + [\mathrm{Rh_2(\mu\text{-}CO)_2(cpMe_5)_2}] \xrightarrow[0\ ^\circ\mathrm{C}]{\text{toluene}} [\mathrm{PtRh_4(\mu\text{-}CO)_4(cpMe_5)_4}] \tag{98}$$

are staggered with respect to the Rh-Rh vectors, whereas in the orthorhombic form the pair related by a mirror plane are eclipsed, whilst those lying astride the mirror are staggered [562].

1.9 PALLADIUM AND PLATINUM METAL

A chemist's view of the platinum metals has been put forward which demonstrates how vague is the stage at which in the construction of a metallic lattice starting from a single atom metallic properties emerge [563]. The bond dissociation energy for Pt_2 in the gas phase has been determined as 358±15 kJ mol^{-1} using Knudsen cell mass spectrometry [564].

A fuel cell for the oxidation of ammonia to nitric acid, with the generation of electricity rather than heat, has been developed using porous platinum electrodes [565]. Platinum hydrosols, prepared by reducing $H_2[PtCl_6]$ with sodium borohydride in basic solution and then buffering to pH 5-6 in the presence of 0.5% polyethyleneglycol, catalyse dihydrogen evolution from water with nearly 100% efficiency, in the light-induced redox reaction using the $[Ru(bipy)_3]^{2+}$-methylviologen-edta system [566]. An alternative system uses a hydrosol prepared from $H_2[PtCl_6]$ and sodium citrate, together with methylviologen and sodium dithionite [567]. The water-gas shift reaction is catalysed by platinised TiO_2 under UV illumination [568].

A palladium-hydrogen electrode, incorporated in a probe that also contains reference and auxiliary electrodes (the PallapHode electrode system) has been developed for determining pH under adverse environments in both aqueous and non-aqueous media up to 250 °C [569].

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