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1. PALLADIUM AND PLATINUM

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CONTENTS

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INTRODUCTION

This review covers mainly the papers recorded in Chemical Abstracts Volumes 102 and 103, as well as the 1985 issues of the main English language inorganic chemistry journals. Thus, although most of the papers covered were published in 1985, many from 1984 are also included, together with earlier work which was slow to reach Chemical Abstracts.

Once again the amount of published material has greatly increased, with particular areas of growth being studies of binary and ternary compounds, and biomedical applications of platinum complexes. In an attempt to control the explosive growth of the review's length, I have this year limited coverage of reactions catalysed by palladium and platinum complexes to papers in which the main intertest is in the coordination chemistry. For papers in which the primary interest is the organometallic chemistry, readers are referred to the annual surveys of the organometallic chemistry of nickel, palladium and platinum, published in the Journal of Organometallic Chemistry.

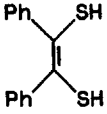
General reviews published this year have included accounts of the immunological, pharmacological and physiological effects of platinum salts exposure in primates [1], and the extraction of platinum group metals by aromatic amines [2]. A review of the inorganic chemistry of the platinum group metals stressed particularly X-ray studies of clusters and carbonyl complexes [3], and there has been an account of the advances reported in 1982-1983 in the study of clusters containing heteronuclear M-M' bonds. Platinum derivatives of Ph_2Ppy, cyclometallated complexes, and A-frame complexes were discussed in detail [4]. Two reviews of the use of transition metal complexes in organic synthesis, covering 1983, have been published [5,6]. A method for the determination of palladium in palladium based catalysts involved ignition of the sample followed by decomposition with *aqua regia*. After cooling and dilution the sample was titrated with potassium iodide [7].

1.1 PLATINUM(VI)

Kinetic constants for the species $[XF_6]$ were obtained on the basis of Wilson's group theory. These gave rise to a significant constant characteristic of the configuration of the molecules. Using these kinetic constants and the revised vibrational frequencies, unique sets of force constants were evaluated, and used to calculate the mean square amplitudes of vibration and centrifugal distortion constants of the molecules. $[PtF_6]$ was included in the discussion [8]. The general inertia defect of $[XF_6]$ type molecules (including $[PtF_6]$) was evaluated for the first time by applying the method suggested by Herschbach and Laurie [9].

1.2 PALLADIUM(V) AND PLATINUM(V)

The electronic structure and ionisation potential for $[PtF_6]^-$ was calculated using the non-relativistic spin-polarised version of the discrete variational X_α method [10]. The species $[PdF_6]^-$ was considered in calculations of the electronic structures of the first and second transition series [11]. In the oxidation of $[PtL_2]$ (H_2L = (1)) a cherry red platinum(V) species, $[PtL_2Cl]$, was identified by EPR spectroscopy [12].



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1.3 PALLADIUM(IV) AND PLATINUM(IV)

A solvent extraction procedure has been developed for the recovery of rhodium(III) from solutions containing palladium(IV), platinum(IV), rhodium(III) and iridium(III) [13]. There has been a study of a platinum on silica catalyst in the presence and absence of $Cd[SO_4]$. It was concluded that $Cd[SO_4]$ did not poison the catalyst for H_2O_2 decomposition. Poisoning was related to the amount of soluble Pt^{4+} present, which depended mainly on the method of catalyst preparation [14]. The binding of platinum(IV) and palladium(II) to rat liver metallothionein has been investigated [15].

1.3.1 Complexes with Group 17 donor ligands

The nephelauxetic effect in metal ion paramagnetic shielding of spin-paired d^6 transition metal complexes has been discussed; $[PtF_6]^{2-}$ and $[PtCl_6]^{2-}$ were considered [16]. Force field calculations for $[MF_6]^{2-}$ (M = Ru, Rh, Pd, Os, Ir or Pt) were undertaken on the basis of the theoretical analysis of vibrational frequencies. The data obtained were compared with the chloro, bromo and iodo analogues [17].

Ion-molecule equilibria in the saturated vapour of the PtF_2/MnF_3 system were studied by high temperature mass spectrometry. The electron affinity of PtF_4 was determined, and a number of complex equilibria studied [18].

Recent thermodynamic data were used to construct a scale of increments for the entropy of dissolution of many ions, including $[PtCl_6]^{2-}$ [19]. An aerosol of $Na_2[PtCl_6]$ was found not to stimulate the pulmonary irritant receptors in cynomolgus monkeys [20].

The $[PtCl_6]^{2-}$ ion has been used as the counter ion in a number of determinations of structure by X-ray diffraction techniques. In $[Me_2NH_2]_2[PtCl_6]$ the ion had a regular octahedral geometry and the cations were linked to the anions by hydrogen bonds [21]. An almost regular octahedral geometry was adopted in $[H_3N(CH_2)_3NH_3][PtCl_6]$, and again the crystal lattice was stabilised by hydrogen bonding between anions and cations [22]. $[HL]_2[PtCl_6]$ was prepared from L, 2-(4-methylphenyl)quinoline, and $H_2[PtCl_6]$, and was characterised by IR spectroscopy, thermal analysis and X-ray diffraction studies [23]. $[H_2tmen][PtCl_4]$ and $[H_2tmen][PtCl_6]$ were isolated as side products from the reaction of $[Pt(C_2H_4)Cl(tmen)]^+$ and conc. HCl, and were characterised by X-ray diffraction studies. The crystals were again stabilised by hydrogen bonding [24].

Two papers have reported EPR measurements on Re^{4+} in $[NH_4]_2[PtCl_6]$ at 10 and 34 GHz. A random distortion model was developed, which predicted significant line shifts and other effects in accord with the experimental results [25,26].

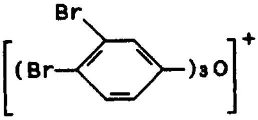
The complex $[(H_3O)^+18\text{-crown-}6]_2[PtCl_6]$ was studied by IR and Raman spectroscopy [27]. The effect of hydrogen bonding on the structure of $[Hhmta]_2[PtCl_6]$ was investigated using IR and laser Raman spectroscopy, and theoretical approaches [28].

The Pd L_{III} absorption spectra of $K_2[PdCl_6]$, $K_2[PdCl_4]$, $[NH_4]_2[PdCl_4]$ and *trans*-$[Pd(NH_3)_2Cl_2]$ were measured using a 50 cm bent quartz crystal vacuum spectrograph. Experimental data were interpreted in molecular orbital terms. The white line absorption of $K_2[PdCl_6]$ was some 2.0 eV to higher energy relative to $K_2[PdCl_4]$, due to the palladium oxidation state [29].

In a low temperature NMR spectroscopy experiment T_1 and $T_{1\rho}$ of protons in pure and partially deuterated $[NH_4]_2[MCl_6]$ (M = Pd or Pt) were measured. The data were explained on the basis of one- and two-phonon relaxation, due to low-temperature tunnelling [30].

$PtCl_4$ and $H_2[PtCl_6]$ doped polyacetylene was studied by XPES and TEM. It is thought that platinum doping involves charge transfer from the polymer chain to the platinum(IV), resulting in partial reduction to platinum(II). The TEM data indicated the existence of $PtCl_2$ clusters on the polymer surface [31]. The transport mechanism in $H_2[PtCl_6]$ doped polyacetylene was studied by EXAFS. The data also supported partial reduction to $PtCl_2$ [32].

$[PtCl_6]^{2-}$ was used as a counterion for the isolation of (2) [33]. The thermal behaviour of $[N\text{-alkylpy}]_2[PtCl_6]$ has been studied. At about 170 °C, HCl was lost to give [*N*-alkylpy][Pt(*N*-alkylpy-H)Cl_5], in which the pyridine ring had been metallated [34].



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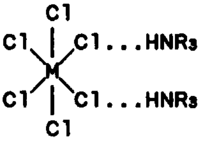
Dielectric constants and vapour pressure data for solutions of $[R_3NH]_2[MCl_6]$ (M = Pt, Ir, Os or Re; R = octyl) were used to calculate dipole moments and effective molecular weights. The degree of anion/cation association in non-polar solvents was determined. It was noted that the associated species could adopt *cis* or *trans* geometries, (3a) or (3b), with the *trans*-species predominating to the extent of about 65:35 [35]. Further association could also take place with the predominent initial process being dimerisation of the *cis*-isomer [36].



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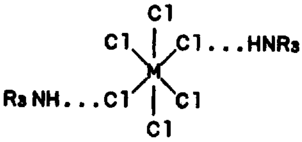


(3b)

A more efficient method for the preparation of $H_2[PtCl_6]$ by electrochemical dissolution of the metal in HCl, has been described. A higher quality product was obtained, and environmental pollution by nitrogen oxides avoided [37].

Platinum on titania catalysts were prepared by photoelectrochemical deposition of platinum from $H_2[PtCl_6]$. The rates of reaction under various conditions were determined [38]. The properties of the catalysts for CO and H_2 adsorption were measured [39]. There has been an X-ray electron study of core levels and valence regions of catalysts prepared by the deposition of 0.6 % (by weight) of platinum on L-zeolite in the potassium form, and also by simultaneous deposition of 0.6 % phosphorus and 1 % molybdenum. In the presence of molybdenum the platinum(IV) of the hexachloroplatinic acid was completely reduced by molecular hydrogen, but without molybdenum material containing both reduced and ionic metal was obtained [40]. $H_2[PtCl_6]$ on alumina or CaY zeolite was used to prepare chlorided platinum catalysts for *n*-butane isomerisation [41].

When an aqueous solution of $H_2[PtCl_6]$ was either hydrogenated or photolysed in the presence of a surfactant, a colloidal dispersion of platinum protected by the surfactant was obtained [42]. γ-Irradiation of an aqueous solution of $H_2[PtCl_6]$ containing *N*-methylolacrylamide, gave a catalyst solution for the photodecomposition of water [43]. [Zn(TPP)] as well as tetramethyldipyridylhexahydrotetrazine efficiently promoted the photogeneration of hydrogen from water containing the system $K_2[PtCl_6]/[Rh(bipy)_3]^{3+}$/triethanolamine [44].

The reactions of $H_2[MCl_6]$ (including M = Pt) with graphite in a stream of chlorine gas at high temperature gave graphite salts [45].

In the electrosynthesis of persulphuric acid, almost complete deposition of copper and platinum (from $H_2[PtCl_6]$) occurred at the graphite cathode [46]. In a vigourously mixed suspension of $[NH_4][PtCl_6]$ in anolyte, the electrodialytic dissolution of $[NH_4][PtCl_6]$ was limited by the transfer rate of $[NH_4]^+$ ions in the membrane [47]. There has been an extensive study of the redox behaviour of the 4d- and 5d-hexachlorometallates. The data suggested that it should be possible to oxidise $[PtCl_6]^{2-}$ to $[PtCl_6]^-$, and to study the product by electrochemical methods [48].

Gas adsorption chromatography of ethene on $PdCl_2$, $PtCl_2$ and $PtCl_4$ suggested that a chemical reaction was occurring at room temperature. On $PtCl_4$ chlorination occurred at room temperature, giving a chlorinated oligomer, *via* a radical mechanism [49]. Oxidation of secondary alcohols by molecular oxygen was photocatalysed by $H_2[PtCl_6]$ and $CuCl_2$. Photoreduction to platinum(II) occurred *via a* platinum(III) intermediate, and the oxidation was almost certainly of the radical type [50]. Kinetic data have been obtained for the dealkylation of methylcobalamine and related species by $[PtCl_6]^{2-}/H^+$. A mechanism involving a single electron transfer and a platinum(III) intermediate was proposed [51]. Transition metal complexes, including $H_2[PtCl_6]$, were combined with hydride donors to initiate the radical reduction of trichloromethyl compounds [52].

When the mass spectra of phthalocyanine complexes were measured in the presence of $K_2[PtCl_6]$, some of the hydrogen atoms of the rings were found to have been chloro-substituted [53]. A study of the preparative titration of precious metal halides against cetyl pyridinium chloride included investigations on $[MCl_6]^{2-}$ and $[MCl_4]^{2-}$ (M = Pd or Pt) [54].

The selectivity coefficients of nitrate and chloride ions, and of anionic chloro complexes of palladium(II) and platinum(IV), on Spheron DEAE in the chloride form, were determined by the dynamic methods [55]. Decreasing the pH resulted in decreased adsorption of $[PtCl_6]^{2-}$ on alumina, but depth penetration increased [56].

The heterogeneous equilibrium between platinum(IV), platinum(II) and platinum(0) at 152.5 °C in 1M H_2SO_4 was investigated. The disproportionation constant for $[PtCl_4]^{2-}$ was determined, as was the rate of aquation of $[PtCl_6]^{2-}$ [57].

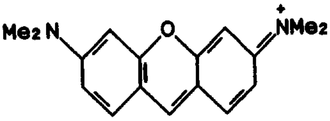
All the general quadratic force field potential constants of $K_2[PtCl_4Br_2]$ were evaluated using kinetic constants, and were then used to obtain other molecular constants. Some unassigned vibration frequencies were correctly predicted [58]. The exchange of bromide for chloride in $[PtCl_6]^{2-}$ adsorbed on alumina was studied by ^{195}Pt NMR spectroscopy, and compared with solution data [59]. The species $[Me_2NH_2]_2[PtX_6]$ (X = Cl or Br) were used to oxidise tetrathiofulvalene derivatives. With dibenzotetrathiofulvalene (dbttf), for example, a species of stoicheiometry $[dbttf]_8[PtCl_6]_3$ was obtained. An X-ray diffraction study indicated that the dbttf formed regular stacks with an interplanar distance of 3.49 Å [60].

A general quadratic valence force field was applied to $[MBr_6]^{2-}$ (M = Pd or Pt), using molecular kinetic constants and Wilson's FG matrix method to give a theoretical description of the IR and laser Raman spectra of the complexes [61]. The room temperature elastic constants of $A_2[PtBr_6]$ (A = K or $[NH_4]$) were measured by Brillouin scattering or ultrasonic pulse echo overlap. The elastic stiffness and Debye temperatures of the compounds were small compared with the alkaline earth fluorides, due to their larger lattice spacings and weaker Coulombic forces [62].

Neutron powder diffraction profiles were obtianed for $K_2[PtBr_6]$ at 296, 160, 141 and 120 K. Each corresponded to a different crystal structure, and space groups were assigned on the basis of the neutron diffraction data, and from bromine NQR spectroscopy. The data indicated that only two true phase transitions occur between 296 and 120 K [63]. XPES was used to study the interaction of $PtBr_4$ and a silica support. Bombardment with argon atoms gave $PtBr_2$ after one minute and a Pt(I)Br species after five minutes [64].

The preparations of $M_2[PtI_6]$ (M = K or Rb) were described using $[PtI_6]^{2-}$ and an excess of MI. X-ray diffraction data indicated that the potassium salt crystallised in a tetragonally distorted variant of the $K_2[PtCl_6]$ type. TGA and DTA data showed an exotherm at 398 K, assigned to a reversible phase transition with a transition enthalpy of 5 kJ mol^{-1}. X-ray powder data indicated that this was a transition from the tetragonally distorted variant to a true $K_2[PtCl_6]$ structure [65].

Platinum has been determined as the $[PtI_6]^{2-}$ salt of (4) in concentrations as low as 0.02 ppm [66]. The reaction of $[PtI_6]^{2-}$ with cyanide ion has been investigated by stopped-flow techniques. The reaction mechanism was determined, and some intermediates were observed by UV spectroscopy [67].



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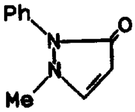
1.3.2 Complexes with Group 16 ligands

The preparation and thermolysis of the diamagnetic low spin complex, $[PtLL'_2Cl]Cl$, in which L = (5) and HL' = (6) have been described. IR spectroscopic data implied that coordination of $[L']^-$ involved the oxygen of the nitroso group and the adjacent phenolate [68].



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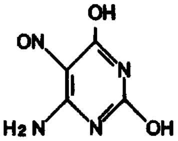

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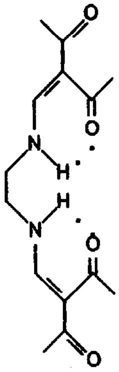
The reactions of $[PtCl_6]^{2-}$ with the mono potassium salt of $MeN(CH_2COOH)_2$ (K[HMida]) have been investigated, and were shown to give $K[Pt(Mida)Cl_3]$ in water at pH 5-6. Both kinetic factors and considerations of angle strain would suggest that the *fac*-isomer would be formed preferentially. It had earlier been claimed that $K_2[PtCl_4]$ reacted with this ligand to give K[Pt(mida)Cl].2HCl, but this reaction could not be repeated, and it was concluded that the previously reported products were in fact platinum(IV) complexes formed by air oxidation. $[Pt(ida)_2]$, assumed to be the *trans*-isomer, was prepared by H_2O_2 oxidation of the platinum(II) complex *trans*-$[Pt(Hida)_2]$ [69]

Platinum(IV) was determined spectrophotometrically with reasonable selectivity using 2-oximino-1-indanone; an *N,O*-chelated complex was postulated [70]. Reaction of (7) with platinum(IV) in the presence of chloride ion gave (8), M = $PtCl_2$ [71].

Electrochemical oxidation of (9) gave a palladium(IV) complex, (10), in which X = Br, Cl or OH, depending on the reaction conditions. The complex (10) oxidised alcohols to ketones in moderate yield, and could be reduced to (9) by CO or NH_2OH [72].



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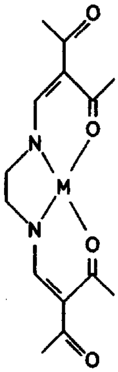

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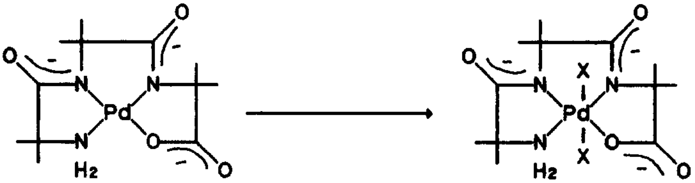


(9)

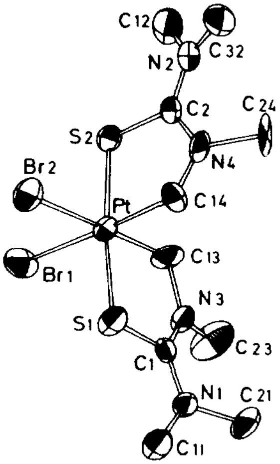
(10)

Both platinum(II) and platinum(IV) have been said to form stable complexes with thiophenol, and substituted thiophenols, and stability constants were determined in dilute solution. Some of the structures were probably oligomeric [73]. Reaction of $K_2[PtCl_6]$ with ammonium polysulphide gave a brick-red complex, $[NH_4]_2[Pt(S_5)_3]$, when crystallisation was carried out slowly. Rapid crystallisation or addition of conc. HCl gave a maroon species, $[NH_4]_2[PtS_{17}]$, which was much less water soluble. $[NH_4]_2[Pt(S_5)_3]$ crystallised as a racemate, which could be resolved using $[RuL_3]^{2+}$ (L = bipy or phen). The $[PtS_{17}]^{2-}$ ion underwent spontaneous resolution on crystallisation, and this represents the first spontaneous occurrence of optical activity in a purely inorganic salt. In $[Pt(S_5)_3]^{2-}$ there are three pentasulphido chelate rings, but for $[PtS_{17}]^{2-}$ structures corresponding to either $[Pt(S_5)_2(S_7)]^{2-}$ or $[Pt(S_5)(S_6)_2]^{2-}$ were proposed [74].

Acid dissociation constants were determined for $[PtL(H_2O)Cl_2]$, $[PtL(H_2O)_2Cl]^+$ and $[PtL(H_2O)_3]^{2+}$ (H_2L = $O{=}S(CH_2COOH)_2$). These aqua complexes were stronger acids than simple sulphoxide derivatives, though $[L]^{2-}$ did bind at sulphur in an analogous manner [75].

The platinum(IV) complex of the dianion of L-cysteine was shown to have a high stability constant [76]. The species [PtL$_2$X$_4$] (L = glyOEt, glyglyOEt or glyleuOEt or L$_2$ = metOEt; X = Cl or Br) were prepared by oxidative addition of X$_2$ to [PtL$_2$X$_2$]. ^{15}N NMR spectroscopic data were presented. In [Pt(metOEt)Cl$_4$], the amino acid acted as an *S,N*-bidentate ligand [77].

Reaction of tetramethylthiourea with K$_2$[PtBr$_4$] gave the known complex [{Pt(tmtu)Br$_2$}$_2$], in which tmtu acts as a bridge between the platinum atoms. Further addition of tmtu gave [Pt(tmtu-H)$_2$Br$_2$], (11), characterised by an X-ray diffraction study. The geometry of the complex was close to regular octahedral, and this is the first example reported of the cyclometallation of tmtu [78].



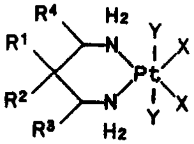
(11) (Reproduced with permission from [77])

1.3.3 Cancer Chemotherapy

The platinum(IV) species, *cis,cis,trans*-[Pt(NH$_3$)$_2$Cl$_2$(OH)$_2$] was shown to be ten times less toxic than *cis*-platin, and to have a longer duration of activity [79]. However, no evidence for its binding to PMe-DNA or cleavage of PM$_2$-DNA could be found, and the same observation was made for CHIP, *cis,cis,trans*-[Pt(H$_2$NCHMe$_2$)$_2$Cl$_2$(OH)$_2$] [80]. Pulse radiolysis of CHIP resulted in the initial formation of [Pt(III)(RNH$_2$)$_2$Cl$_2$(OH)$_2$]$^-$, followed by disproportionation to give a mixture of platinum(II) and platinum(IV) complexes [81]. CHIP was compared with *cis*-platin and CARBOPLATIN in the *N*-{4-(5-nitro-2-furyl)-2-thiazolyl}methanamide induced murine bladder tumour model [82].

A number of structures of platinum(IV) complexes with anti-tumour activity have been determined by X-ray diffraction methods, including *cis,cis,trans*-[Pt(3-MeOPrNH$_2$)$_2$Cl$_2$(OH)$_2$]. Oxidation of *cis*-[Pt(RNH$_2$)$_2$)X$_2$] with H$_2$O$_2$ gave *cis,cis,trans*-[Pt(RNH$_2$)$_2$X$_2$(OH)$_2$] for X$_2$ = propane dioate, and the propane dioate ring was shown to adopt a boat conformation by an X-ray diffraction study. The reactions of the complexes in which X$_2$ was either 2-ethyl propane dioate or cyclobutane-1,1-dicarboxylate were more complex, however, giving more than one product as monitored by ^{195}Pt nmr spectroscopy [83].

The complex [Pt(dach)Cl$_4$] was prepared from the ligand and K$_2$[PtCl$_4$] in water, followed by oxidation by molecular chlorine [84]. Species of the type (12) were generally prepared by addition of Y$_2$ to the corresponding platinum(II) complex. Most of the complexes had high activity and low renal toxicity [85].



(12)

The new complexes *cis,cis,trans*-[PtL$_2$Cl$_2$(OH)$_2$] and *cis*-[PtL$_2$Cl$_2$], in which L was a polychlorinated aniline, were prepared, and their anti-tumour activity investigated [86]. Both platinum(IV) and platinum(II) derivatives of adamantidine, A, including *cis,cis,trans*-[PtA$_2$X$_2$(OH)$_2$] and *cis*-[PtA$_2$X$_2$] showed activity against L-1210 in BDA/2 mice [87].

1.3.4 Complexes with Group 15 donor ligands

In the salt [Pt(NH$_3$)$_6$]$^{4+}$[Lasalocid A]$_4$ the structure was maintained by hydrogen bonding involving the ammine protons, but no unambiguos picture of the structure was established [880]. [Pt(NH$_3$)$_6$]$^{4+}$ was shown to inhibit the electron transfer reactions of plastocyanin [89].

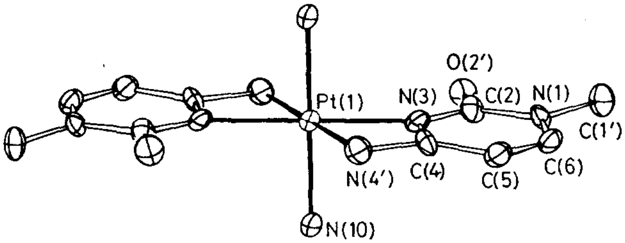
Microscale syntheses of *cis*-[^{191}PtL$_2$Cl$_2$] (L = NH$_3$ or cyclopropylamine) ^{191}Pt-CHIP and ^{191}Pt-CARBOPLATIN have been described [90]. The ^{195}Pt and ^{15}N NMR spectra of *mer*-[Pt(^{15}NH$_3$)$_3$(OH)$_2$Z]$^{n+}$ and [Pt(^{15}NH$_3$)$_2$(OH)$_2$Z$_2$]$^{m+}$ have been recorded. There was good agreement between experimental and predicted values. The changes in $^1J_{PtN}$ depended on the variation in the platinum 6s contribution to the Pt-N bond [91].

The quenching of the luminescence of [Ru(bipy)$_3$]Cl$_2$, and its photosensitised reaction with $[Pt(NH_3)_5X][ClO_4]_3$ (X = Cl or Br) have been studied. Electron transfer yielded a platinum(II) complex which readily disproportionated [92]. There has been a kinetic study of the solution photochemistry of the complexes *trans*-$[Pt(NH_3)_4X_2][ClO_4]_2$ (X = Cl or Br), which yields $[Pt(NH_3)_4(OH)X]^{2+}$. Photoaquation of the chloride proceeded from an excited state, by homolytic cleavage of the chloride to give a platinum(III) intermediate. Photoaquation of the bromide proceeded from the lower ligand field type excited electronic state, with heterolytic platinum-bromine cleavage. In all $[Ru(bipy)_3]^{2+}$ sensitised photolyses of these platinum(IV) complexes platinum(III) intermediates were formed [93]. The photochemistry and luminescence spectrsoscopic properties of polycrystalline *trans*-$[PtA_4X_2][ClO_4]_2$ (A = NH_3 or A_2 = en or pn; X = Cl or Br) have been investigated. In the complexes of en or pn, excitation in the region of ligand field bands resulted in photoreduction to mixed valence species. Paramagnetic platinum(III) complexes were observed as intermediates [94].

The solubilities of $[Pt(en)_3][Fe(CN)_6]$ in aqueous solutions of NaCl, NaBr $Na[NO_3]$ or Na[OOCH] were established at 295.15 K. It was demonstrated that platinum(IV) formed more stable associates than did Co(III), Rh(III) or Ir(III) [95]. 5-Nitroimidazole complexes of platinum(IV) and palladium(II) were shown to have fungicidal activity against *Pestalotia* and *Altenaria* [96].

A series of platinum(II) and platinum(IV) porphyrins were prepared and characterised. The kinetics of the reduction of the platinum(IV) derivatives by amines were established. In the reaction with piperidine, which gave pyridine, a unique 6-electron oxidation was proposed, and dihydro and tetrahydropyridine intermediates were responsible for the complex kinetics observed [97]. The reaction of adenine, adH, with $PtCl_4$ gave $[Pt(adH)_2Cl_4]$, which was insoluble in common organic solvents. A polymeric structure was proposed for the complex, with metal binding through N(9) and N(7) [98]. Hydrogen peroxide oxidation of *trans*-$[Pt(NH_3)_2(1\text{-Mecyt})_2]$ gave *trans,trans*-$[Pt(NH_3)_2(1\text{-Mecyt-H})_2][NO_3]_2.2H_2O$, (13), characterised by an X-ray diffraction study. This demonstrated that the deprotonated 1-methylcytosine was coordinated to the platinum(IV) through N(3) and N(4), forming an almost planar 4-membered chelate ring. This represents the first example of *N*(3),*N*(4) chelation of a metal to a cytosine nucleobase to be established by a diffraction study [99].

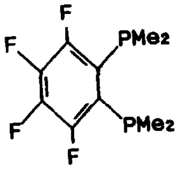
Photoreduction of $[Pt(NO_2)_{6-x}X_x]^{2-}$ (x = 0, 1, or 2; X = Cl or Br) gave the platinum(II) complex $[Pt(NO_2)_4]^{2-}$, irrespective of the initial composition. Quantum yields were established for the reaction, and it was shown that two intra-ligand CT states were the states responsible for the photochemical reactions [100]. The influence of single oriented layers on the electrode kinetics of unadsorbed, unchanged redox couples at smooth polycrystalline platinum electrodes in aqueous solutions was investigated by means of thin layer cyclic voltammetry. The redox couples investigated included $[Pt(NO_2)_2(NH_3)_2Cl_2]/[Pt(NO_2)_2(NH_3)_2]$ [101].



(13) (Reproduced with permission from [99])

Oxidation of $[Bu_4N]_2[Pt(N_3)_4]$ by X_2 (X = Br, I or [SCN]) gave *trans*-$[Bu_4N]_2[Pt(N_3)_4X_2]$. Some spectroscopic data for the new complexes were reported [102].

Oxidation of $[PdL_2]Cl_2$ (L = (14)) by $HNO_3/H[ClO_4]$ gave $[PdL_2Cl_2][ClO_4]_2$; the product stereochemistry was not specified [103]. The stability and ligand exchange reactions of $[PdL_2Cl_4]$ have been investigated by stopped-flow techniques [104].



(14)

1.3.5 Complexes with Group 14 donor ligands

The reduction of *trans*-$[Pt(CN)_4X_2]$ (X = Cl or Br), by $[SCN]^-$, $[S_2O_3]^{2-}$, $[CN]^-$ or $[SO_3]^{2-}$, in aqeuous solution, has been investigated; the product in all cases was $[Pt(CN)_4]^{2-}$. The results were interpreted in terms of a mechanism which involved transfer of X^+ from platinum to the reducing anion [105]. Transfer of Br^+ was also the key step in the hydrolysis of *trans*-$[Pt(CN)_4Br_2]^{2-}$ (reactions (1)-(5)) [106].

$$[Pt(CN)_4Br_2]^{2-} + [HO]^- \leftrightharpoons [Br...Pt(CN)_4...Br...OH]^{3-} \qquad (1)$$

$$[Br...Pt(CN)_4...Br...OH]^{3-} \leftrightharpoons [Pt(CN)_4]^{2-} + HOBr + Br^- \qquad (2)$$

$$HOBr + [HO]^- \leftrightharpoons H_2O + [BrO]^- \qquad (3)$$

$$H_2O + [Pt(CN)_4]^{2-} + HOBr \longrightarrow [H_2O\text{-}Pt(CN)_4Br]^- + [HO]^- \qquad (4)$$

$$[H_2O\text{-}Pt(CN)_4Br]^- + [HO]^- \longrightarrow [Pt(CN)_4Br(OH)]^{2-} + H_2O \qquad (5)$$

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

Thermolysis of PtI_4 at 300 °C under an 8 atmosphere pressure of iodine gave a species of stoicheiometry PtI_3, which was in fact a mixed valence compound. Single srystals could be grown from PtI_4 and aqueous solutions of KI/I_2 at 270 °C. An X-ray diffraction study revealed square planar $\{PtI_4\}$ units and octahedral $\{PtI_6\}$ units which were connected in chains by common edges [107].

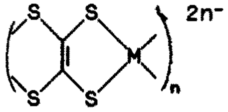
Structural evidence with respect to the one-dimensional oxalato platinates has been described for the existence in these sytems of a superstructure of electrons (or holes) which is totally commensurate with the underlying lattice, but statistically incommensurate along the chains [108]. $Ni_{0.84}[Pt(C_2O_4)_2].6H_2O$ was shown to undergo the same two phase transitions as had been previously observed for cobalt(II) and zinc(II) salts, but at higher temperatures. X-ray diffraction studies indicated that the crystals deteriorated at high temperatures due to loss of long-range order, but partially recovered on cooling [109]. The complexes $M_{0.8}[Pt(C_2O_4)_2].6H_2O$ (M = Ni, Co, Zn, Mg or Mn) were found to be isostructural at high temperatures, and were one-dimensional conductors with $\sigma = 2\text{-}200\ \Omega^{-1}\ cm^{-1}$. At low temperatures the values of σ suggested that a simple Peierls transition took place, but diffuse X-ray scattering experiments showed unexpected behaviour, ascribed to a second competing instability associated with cation ordering. The competition gives rise to metastable states which relax towards equilibrium in a stepwise fashion reminiscent of the devil's staircase [110]. The phase transition in $Mg_{0.8}[Pt(C_2O_4)_2].6H_2O$ was studied in more detail by a combination of electrical conductivity, DSC and X-ray techniques. Evidence for chaotic behaviour and long lifetime metastable states was presented [111].

Many papers again described features of $[Pt(mnt)_2]^{n-}$ complexes. The chemical composition of the lithium salt was discussed, and the platinum complexes were compared with those of nickel and palladium. The d_{xz} and d_{yz}

orbitals played a central role in delocalising the charge across the anion [112]. The $Li_{0.5}$ salt gave an irregular stack with metal-metal interactions, but the $Li_{0.82}$ derivative gave a more regular stack. The rubidium salt gave only a dimer. Related complexes of other transition metals gave dimers with metal-sulphur interactions [113]. The structure of $[H_3O]_{0.33}Li_{0.8}[Pt(mnt)_2].1.67H_2O$ was determined by X-ray diffraction techniques at 153 K and at room temperature. The anions were stacked face-to-face along the *c*-axis with Pt-Pt = 3.6 Å. The room temperature conductivity was 200 S cm^{-1}, and the compound underwent a metal insulator transition (Peierls transition) at 220 K. The conduction path through the ligand centred π-system was composed predominently of sulphur $3p_z$ orbitals [114]. The pressure dependence of the temperature at which the Peierls transition occurred has been measured for pressures up to 10 kbar. At high temperatures the metallic properties improved with pressure and it was concluded that the Peierls instability was gradually supressed by pressure because of an increase in interchain coupling [115].

Thermoelectric power and EPR data have been reported for $[perylene]_2[M(mnt)_2]$ (M = Au, Pd or Pt). EPR data suggested that the complexes did not undergo a simple Peierls transition, but that the nature of the anion was significant. The transitions had some spin-Peierls character [116]. The palladium and platinum complexes underwent clear metal insulator transitions at 28 and 6.5 K respectively. The electrons on the segregated perylene stacks were itinerant, but those on the dithiolate stacks appeared to be localised. A formulation with one unpaired electron per dithiolate and 0.5 holes per perylene was in agreement with both magnetic and conductivity data. Conductivity definitely involved the perylene stacks, with holes as the carriers [117,118]. The structure of $[perylene][Pt(mnt)_2]$, formed by oxidation of perylene by iodine in the presence of $[Bu_4N]_2[Pt(mnt)_2]$, was established by an X-ray diffraction study. It contained mixed cation anion stacks running parallel to the <011> direction, with the alternation of two cations and two anions [119].

The preparations and conduction properties of polymers based on transition metal complexes of 1,1,2,2-ethene tetrathiolate, (15), have been described. The nickel, copper and platinum complexes showed high conductivity, but cobalt and palladium derivatives gave poorer results [120]. $[Et_4N]_2[\{Pd(C_2S_4)_{4.5}\}(C_2S_4)]$ was prepared from $[Et_4N]_2[C_2S_4]$ and $PdCl_2$. The material was air stable and had σ = 1 S cm^{-1} [121]. The nature of the metal also played a predominent role in determining transport properties and structures of the complexes $[TTF][M(dmit)_2]_x$ (M = Ni or Pd, x = 2; M = Pt, x = 3; H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione). The palladium complex exhibited *quasi* metal-like conductivity at temperatures down to 220 K. Below this temperature the crystals underwent an irreversible metal insulator transition, and subsequently exhibited semiconductor behaviour. The platinum complex showed thermally activated conductivity. The structure consisted of non-uniform stacks of [PtL_2] comprising alternate monomer and dimer units, and uniform stacks of TTF, with large stacking distances [122].

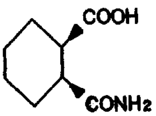


M^{2+}

(15)

There have again been several reports of the preparation and chemistry of mixed valence "platinum blue" and related complexes. EPR data on the blue complexes derived from 1-methylhydantoin and 5-methyl-2-pyrrolidone were in good agreement with calculations which asssumed that the hyperfine structure was attributable to the coupling of an unpaired electron with four platinum nuclei in a tetrameric structure [123]. The structure of *cis*-diammine α-pyrrolidone violet, $[Pt_4(NH_3)_8(C_4H_6NO)_4][PF_6]_2[NO_3]_{2.56}\cdot5H_2O$, has been established in an X-ray diffraction study. Each platinum atom was coordinated by two NH_3 ligand in a *cis*-relationship, and either two oxygens or two deprotonated nitrogens of the pyrrolidone. The platinum-platinum distances were found to be related to oxidation state, established by titration against cerium(IV) to be 2.14. The compound is in fact a non-stoicheiometric mixture of platinum pyrrolidine blue and platinum pyrrolidine yellow [124]. Reaction of *cis*-$[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$, *cis*-diammine platinum pyrrolidone tan, with an average oxidation state of 2.5, with water gave a dark blue species, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ (average oxidation state 2.5) and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$. In an aqueous solution under air a yellow platinum(III) complex was formed. It was concluded that the pyrrolidone tan was only stable in acidic solution, and in the dark [125].

Three new platinum blues have been prepared from the half amides of propanedioic acid, butanedioic acid, and (16). The complex derived from (16) had significant anti-tumour activity [126]. Reaction of either benzoic acid or phthalic acid with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ gave a blue precipitate, in which analytical data suggested that there was only one ammine ligand per platinum. Structures were not definitively established, and EPR spectroscopic data suggested an oxidation state close to 2.0, but oxidative titration gave a value of 2.56. The phthalate blue showed activity against the *Ascites* S180J tumour system in mice [127]. Reaction with (17) gave initially a platinum(II) complex, which was oxidised in air to give a paramagnetic blue product, the structure of which has not yet been established [128].



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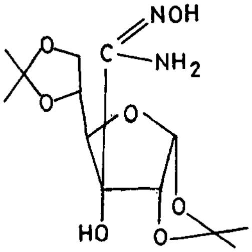


(17)

The structures of two crystalline modifications of $[Pt(en)_2][Pt(en)_2Br_2][ClO_4]_4$ have been established by X-ray diffraction studies. Both were typical Wolfram's salt analogues with infinite chains of $\{Pt(en)_2\}$ units bridged by bromide ions. Strong hydrogen bonds between the anions and cations imposed three dimensional ordering. Irradiation (Cu K_α) converted the monoclinic form to an orthorhombic modification [129]. The structure of the related palladium complex was also determined. On the basis of the Pd-Br distances (2.496(1) and 2.911(1) Å) it was concluded that the oxidation states were less localised than in the chloro analogue [130]. The structure was also determined by another group, who further noted thermally activated motion of the bromide ions in the direction of the infinite chains [131].

XPES data for $[Pd(en)_2][Pd(en)_2X_2][ClO_4]_2$ (X = Cl or Br) have been reported. The difference in the binding energies of the Pd 3d electrons between Pd(II) and Pd(IV) was smaller for the bromo than the chloro complex, confirming the lower oxidation state localisation in that complex [132]. In the XPES of $[Pd(en)_2][Pt(en)_2X_2][ClO_4]_2$ (X = Cl, Br or I), as the halogen changes from chlorine to iodine, the binding energies of the platinum(IV) 4f electrons were lowered, whilst those of the palladium(II) 3d electrons increased, with both gradually approaching the M(III) levels [133].

Absorption, luminescence and Raman spectra have been recorded under high pressure for Wolfram's red salt, $[Pt(EtNH_2)_4][Pt(EtNH_2)_4Cl_2][ClO_4]_4$. The data suggested that the *quasi* one-dimensional electron-phonon system was continuously changed by pressure from a moderate coupling state at atmospheric pressure to a weak coupling state, not by a decrease in the electron-phonon coupling energy but by increased energy transfer [134]. Raman spectroscopic data under high pressure suggested that the energy of the LO phonon which resonates most strongly with the CT excitation from Pt(IV) to Pt(II) shows several stages of change in response to pressure, but the microscopic mechanism of the changes remained uncertain [135].

The absorption spectra of $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$ (X = Cl, Br or I) and Wolfram's red salt have been measured. The reflectance spectra were obtained for the chloro and iodo complexes. The data could not be explained in terms of a simple band model [136,137]. When resonance Raman, IR, luminescence and absorption spectra were obtained for single crystals using polarised light at 2 K and room temperature, the results were in contrast to previous work on polcrystalline samples. In this case the incident photon energy dependence of the Raman cross-section due to the symmetrical Cl-Pt(IV)-Cl stretching mode had a resonance peak at the CT absorption edge, which was well explained using the 2-band model in a one-dimensional system [138].

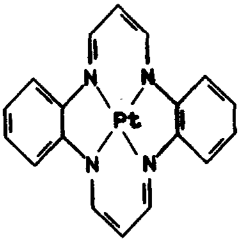
The syntheses of the neutral linear chain mixed valence compounds $[Pd(en)Cl_2][Pd(en)Cl_4]$, $[Pd(en)Br_2][Pd(en)Br_4]$, $[Pd(tn)Br_2][Pd(tn)Br_4]$ and $\{Pd(en)_2Br_3Cl_3\}$ (tn = 1,3-diaminopropane) have been described. Their electronic spectra showed intense broad intervalence bands, and their resonance Raman spectra showed the typical overtone progressions in the X-Pd(IV)-X symmetric stretching modes. Oxidation states were more delocalised than in the complexes of the +2 charge type, and these species were consequently better semiconductors [139]. Electronic, resonance Raman and IR spectroscopic data for $[Pd(LL)_2][Pt(LL)_2Cl_2][ClO_4]_4$ (LL = 1,2-diaminopropane or 1,3-diaminopropane) suggested that the metal-metal interactions in these cases were weaker, and oxidation states more localised that for Pd(II)/Pd(IV) or Pt(II)/Pt(IV) analogues [140].

The X-ray absorption near edge structure of mixed valence $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$ and $[Pd(en)_2][Pt(en)_2X_2][ClO_4]_4$ complexes was measured using synchrotron radiation with a high energy resolution. It was confirmed that the unoccupied level was formed from $d_{x^2-y^2}$ and d_{z^2}, and that the latter was the origin of the charge density wave [141].

Photolyis of $[Pt(en)_2X_2][[ClO_4]_2$ in the solid state gave the mixed valence species as the end product. The course of the reaction was followed by EPR spectrsocopy, indicating that the first step was formation of chlorine radicals and $[Pt(III)(en)_2Cl]$ [142]. The platinum(III) state was detected in single crystals of $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$ (X = Cl, Br or I) by EPR spectrsocopy. The defect density responsible for the Pt(III)Pt(II) states was 1 in 10^4 for the method of recrystallisation used [143].

Reaction of $K_2[Pt_2(pop)_4].2H_2O$ with $[Pt(en)_2X_2]X_2$ at 100 °C gave $[Pt(II)(en)_2][Pt(IV)(en)_2][Pt(III)_2(pop)_4X_2]$ as copper needles for X = Br and as green dichroic microcrystals for X = I. Spectroscopic evidence indicated that the complex should be formulated as a linear chain Pt(II)-X-Pt(IV) cation in association with a dimeric platinum(III) anion. The complex, unique in its three different oxidation states for platinum, is also unusual in that it is Class II in respect of the partly localised valence in the cation chains, but Class I in the localised valence interaction between the cation and anion chains. The X-Pt(III)-Pt(III)-X backbone lies parallel to the cation chain axis [144].

Conducting compounds based on phthalocyanine derivatives, including $[PcPt]I_x$, have been reviewed [145]. Oxidation of [Pt(dbtaa)], (18), with molecular iodine, gave a mixture of $[Pt(dbtaa)I_2]$, which was an insulator, and $[Pt(dbtaa)][I_3]_{0.67}$, which was highly conductive. Both complexes were fully characterised by X-ray diffraction studies, and other phases with varying iodine contents were also prepared [146].



(18)

The structure of $[Pt(dienH^+)(CN)_2]_2[Pt(CN)_6]$ has been established in an X-ray diffraction study. There were weak interactions between the nitrogen atoms of the cyano groups and the hydrogens of the ammonium ion [147].

A review has been published dealing with the one-dimensional conductor $K_2[Pt(CN)_4]Br_{0.3}$ (KCP) and related complexes [148]. A classroom experiment to determine the Pt-Pt distance using powder diffraction data has been described [149]. A number of papers have discussed a new pinning mechanism for KCP, based on the $2K_F$ quasi-modulated bromide ion distribution [150-152]. The pinning mechanism was used to calculate the far IR conductivity. Fair agreement with experimental data was obtained when the phason lifetime was included [153].

The low frequency regions of the Raman spectra of KCP and $Rb_2[Pt(CN)_4Cl_{0.3}]$ have been analysed. The A_1 mode associated with the $\{Pt(CN)_4\}$ units exhibited strong temperature dependent properties connected with interchain ordering. There was, however, no phase transition and the Peierls distortion persisted up to 273 K [154]. The Peierls instability has been compared for KCP and $Li_x[Pt(mnt)_2]$ [155].

EPR data obtained at 85 K for KCP have been simulated in terms of coupled platinum nuclear spins. The platinum hyperfine parameters and the degree of delocalisation were discussed [156]. Soliton formation was also studied by this technique [157]. Polarised absorption spectra of single crystals of $M_x[Pt(CN)_4].nH_2O$ (M = Na, Sr, Ca, Ba or Mg) have been recorded at 10 and 300 K. The energetic order of the low lying excited electronic states was established [158].

It was shown that crystals of $[Metal]_x[Pt(CN)_4].nH_2O$ (metal = Sr, Ca, Ba, Mg or Lu) could be partially photooxidised at 1.7 K. An exiton-exiton interaction within the polaron-like A'_{1u} state removes electrons from the anti-bonding orbitals of the platinum chain. The electrons could be trapped between the chains where they were coordinated by crystal water molecules. The nature of the partially oxidised species was discussed [159].

1.5 PALLADIUM(III) AND PLATINUM(III)

The papers published on platinum(III) complexes up to June 1984 have been reviewed. The article includes discussions of mono and binuclear species, platinum blues and mixed valence platinum(III)/platinum(IV) complexes [160]. Binuclear mixed dimers and organometallic derivatives of platinum(III) were also reviewed [161]. The EPR spectrum of Pd^{3+} in a single crystal of CaO at the X-band frequency showed an intermediate quadrupole interaction and a static Jahn-Teller effect [162].

Palladium(III) has been unambiguosly characterised in elpasolites, $A_2A'[PdF_6]$, where A and A' are alkali metals. $K_2Li[PdF_6]$ was shown to be cubic at room temperature, with the other complexes possessing tetragonal symmetry. The phase transition in the elpasolites was followed using low and high temperature X-ray diffraction studies; all the complexes underwent a tetragonal$\rightleftharpoons$cubic phase transition between 200 and 500 K. EPR spectroscopic data were characteristic of a doublet ground state, $t_{2g}{}^6e_g{}^1$, stabilised by an important Jahn Teller splitting of the ^2E_g state [163].

Further relativistic multiple scattering X_α calculations on $[PtCl_6]^{3-}$, $[PtCl_5]^{2-}$ and $[PtCl_4]^-$ have been undertaken. All of these species have been proposed as short lived transients generated by pulse radiolysis or flash photolysis of $[PtCl_6]^{2-}$ [164]. These and other species containing water or hydroxyl ligands were subjected to the same calculations, as models for the transients generated by pulse radiolysis of $[PtCl_4]^{2-}/H_2O$. The calculated structures and predicted spectra of these complexes were compared with experimental data, with the conclusion that the short-lived transient is either $[Pt(OH_2)(OH)Cl_4]^{2-}$ or $[Pt(OH)_2Cl_4]^{3-}$ [165].

A new preparation of $K_2[Pt_2(pop)_4]$ (pop = $[P_2O_5H_2]^{2-}$), without contamination by partially oxidised species, has been described. Oxidation of $[Pt_2(pop)_4]^{4-}$ by X_2 gave $[Pt_2(pop)_4X_2]^{4-}$ (X = Cl, Br, I, $[NO_2]$ or [SCN]). The influence of the ligands on the electronic structures was investigated by UV spectroscopy and XPES [166]. The structures of $[Bu_4N]_4[Pt_2(pop)_4Br_2]$, $K_4[Pt_2(pop)_4I_2]$ and $K_2[Bu_4N]_2[Pt_2(pop)_4I_2]$ were established. The Pt-Pt distances were shown to be in the order X = I > X = Br > X = Cl, in accord with the σ-donor ability of the halides. The Pt-X distances were long due to the high *trans*-influence of the Pt-Pt bond [167]. Oxidation of $[Pt_2(pop)_4]^{4-}$ by NO_2 gave $[Pt_2(pop)_4(NO_2)_2]^{4-}$, the structure of the sodium salt being established by an X-ray diffraction study. One of the NO_2 ligands was readily displaced by X^- to give mixed complexes [168].

Electronic, IR, Raman and resonance Raman spectra have been recorded for $K_4[Pt_2(pop)_4].2H_2O$, $K_4[Pt_2(pop)_4X_2].2H_2O$ and $K_4[Pt_2(pop)_4X].nH_2O$. The lowest transition in the $Pt(II)_2$ complex was confirmed to be $^1A_{1g} \rightarrow {}^1A_{2u}$. The resonance Raman spectrum of the $\{Pt(III)_2\}$ species consisted of long and nearly harmonic progressions in ν_1. In the mixed valence complex the electronic spectra were dominated by the Pt(II)→Pt(III) intervalence band. For X = Cl valences were shown to be highly localised, with very non-symmetric bridges, but the bromo and iodo derivatives showed more delocalisation [169]. MCD spectra were recorded for the $\{Pt(II)_2\}$ and $\{Pt(III)_2\}$ complexes; most of their features could be interpreted in molecular orbital terms [170].

Photolysis of $[Pt_2(pop)_4]^{4-}$ gave an excited species with a microsecond lifetime. The excited state $((d_{z^2})^2(d^*_{z^2})^1(p_z)^1)$ added ArBr or ArI to give the {platinum$(III)_2$} complex $[Pt_2(pop)_4ArX]^{4-}$ [171].

All the equilibrium and rate constants were determined for reaction (6). The substitution of the axial halides was some 10^4 times faster than in $[Pt_2(pop)_4X_2]^{4-}$, due to a strong metal-metal bond in the μ-hydrogen phosphate species, which has a high *trans*-effect [172]. The units $\{Pd_2\}^{6+}$ and $\{Pt_2\}^{6+}$ have a d^7d^7 net single bond. The synthesis of eight examples of $\{Pt_2\}^{6+}$ derivatives has been noted and six of these were characterised by X-ray diffraction studies [173].

$$[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-} + X^- \leftrightarrows [Pt_2(\mu\text{-}PO_4H)_4(H_2O)X]^{3-} \leftrightarrows [Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-} \tag{6}$$

The hydrolyses of tri- and pyrophosphate anions was accelerated by $[Pt(NH_3)_2(H_2O)_2]^{2+}$ and its conjugate bases. The reaction was subjected to a kinetic study using ^{31}P nmr spectroscopy. A very complex series of intermediates was proposed, including mixed valence platinum(III)/platinum(II) complexes [174]. ^{195}Pt NMR spectroscopic data were reported for $[Pt_2Z_4XY]^{n-}$ (Z = SO_4 or HPO_4; X,Y = ^{13}CN, $^{15}NO_2$, or $^{15}NH_3$). $^1J_{PtPt}$ was larger for the phosphate bridged complexes, although neither Raman spectroscopic data nor the Pt-Pt bond lengths determined by X-ray diffraction studies indicated a stronger bond. The observations were interpreted in terms of the rehybridisation of both platinum atoms when one is substituted [175].

The oxidation of the platinum pyridone blue, $[\{Pt_2(NH_3)_4(C_5H_4NO)_2\}_2][NO_3]_5.2H_2O$ with HNO_3 gave a platinum(III) dimer $[(NO_3)Pt(NH_3)_2Pt(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(H_2O)][NO_3]_3.3H_2O$, which was fully characterised by an X-ray diffraction study. The platinum-platinum distance was 2.540(1) Å. A similar species, but with two capping nitrate groups, was obtained by electrochemical oxidation of the related platinum(II) dimer. Other structural data for related platinum(III) dimers with different capping ligands were also reported [176].

1.6 PALLADIUM(II) AND PLATINUM(II)

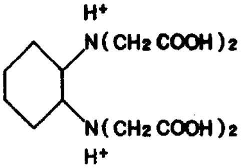
A review of complexes of nickel(II), palladium(II) and platinum(II) focussed on *cis/trans*-isomerism, magnetic properties and electronic structures [177]. Chromatography of eleven pairs of *cis*- and *trans*-complexes of palladium(II) and platinum(II) on silica in 28 solvent systems has been undertaken. In all single solvent systems the *trans*-complexes had higher R_f values [178]. IR spectroscopic data have been reported for 40 complexes of the type *cis*-$[PdL_2X_2]$ and 70 of the type *cis*-$[PtL_2X_2]$. The date were discussed in terms of the *trans*-influence of L [179].

The formation of metal particles during the thermal treatment *in vacuo* of stabilised HY zeolite exchanged with Pd^{2+} cations was assumed to arise by reduction of hydroxyl ions [180].

1.6.1 Complexes with Group 17 donor ligands

Fluorine bearing fluids were generated by the breakdown of PdF_2 in hydrothermal experiments. This allowed the addition of a fixed amount of fluorine without affecting the composition of the rest of the system. PdF_2 was found to be superior to the more generally used silver fluorides, since it is non-hygroscopic, and safe to handle [181]. Relations between the high pressure form of PdF_2 and other MX_2 and M_2X_4 structural types have been discussed. The anionic packing in hp-PdF_2 is intermediate between the fluorite type and the pyrite type [182].

The structures of the $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ salts of (19) were established in X-ray diffraction studies. (19) was not metal coordinated, but the crystal lattices were held together by extensive networks of anion-cation hydrogen bonding [183].



(19)

Derivation of the AOM Parametrization from the effective Hamiltonian for complexed transition metal ions was undertaken with application to tetragonal four-coordinate systems including $[MX_4]^{2-}$ (M = Pd or Pt, X = Cl or Br) [184]. Relativistic MS-X_α calculations were reported for $[PtCl_4]^{2-}$, and the data were in good agreement with the optical spectrum. The high intensity spectrum could clearly be interpreted in terms of Rydberg platinum 5d→6p transitions [185].

The electronic properties of $[PtLCl_3]^n$ (L = CN, CO, $[NO]^+$ or N_2) were calculated, and donor acceptor properties of the ligands were discussed in terms of MO populations [186]. *Ab initio* calculations using the effective core potential were reported for $\{Pd(Nu)_2\}$ (Nu = Me^-, H^-, Br^-, Cl^-, F^-, $[CH(CHO)_2]^-$, $[HOO]^-$, $[MeO]^-$ or $[HO]^-$). An analysis of the reactivity of coordinated nucleophiles was carried out on the basis of bond strength and the energy of the Pd-Nu bonding orbital. The ability of a nucleophile to migrate within the coordination sphere was found to be correlated with the metal-nucleophile bond strength [187].

Hooded Lister rates were sensitised to $[NH_4][PtCl_4]$ in a conjugated form with ovalbumin. There was significant cross-reaction with $[NH_4][PtCl_6]$ and other $[PtCl_4]^{2-}$ conjugates, but little with other platinum salts [188]. $PdCl_2$ caused elevation of the binding of ^3H-cimetidine to membrane from rat brain, apparently due to formation of a cimetidine palladium complex [189].

The electrorecovery of palladium from spent solutions used in electroplating, and containing $PdCl_2$, was accomplished by electrodeposition of palladium on graphite fibre cathodes [190]. The electrochemical detection and removal of copper from an ammine chloro palladium electroplating bath has been studied [191]. A cyclic voltammogram of $SnCl_2/PdCl_2$ sensitising solution was used to monitor concentrations of tin and palladium *in situ* [192].

A number of papers have reported the sorption of palladium halides onto various supports. The sorption of platinum(II) chloro complexes on $TiO_2.nH_2O$

and $SnO_2.nH_2O$, both modified by Sn^{2+}, was studied by Mössbauer spectrsocopy. Modification of the supports increased sorption. The mechanism of sorption was complex, including ion exchange, redox reaction and complex formation steps [193,194]. There were found to be three types of adsorption interactions between γ-alumina and $[Pd(H_2O)_2Cl_2]$, $[Pd(H_2O)Cl_3]^-$ or $[PdCl_4]^{2-}$ [195]. The activity of palladium catalysts formed by deposition of palladium from aqueous solutions of $M_2[PdCl_4]$ (M = H, $[NH_4]$, Na or K) for oxidation of carbon monoxide has been studied [196]. Low concentrations of H_2S and HCN could be removed from air at room temperature by oxidation on contact with a catalyst containing $PdCl_2$ and copper(II) on alumina [197].

The sorption of $PdCl_2$ or $[PdCl_4]^{2-}$ by silica immobilised 8-methylquinoline was studied by diffuse reflectance, electronic and IR spectroscopy. Structures detected included $[PdL_2]^{2+}$, $[PdLCl_2]$, and $[PdL_2][PdCl_4]$ [198]. The kinetics of palladium sorption from chloride containing solutions were studied on copolymers of *N*-ethenyl-3(5)-methylpyrazole with diethenylbenzene [199]. Modified PVA fibres were found to have a high sorption capacity for platinum metals [200].

Hydrogen generation by irradiation of aqueous solutions containing a photosensitiser, an electron donor, and $K_2[PtCl_4]$ as the catalyst, has been studied [201]. Quantum yields were determined for a range of systems [202]. Assignment of the IR and Raman spectra of $[MV][PdCl_4]$ was accomplished using deuterated species [203].

The X-ray dichroism observed at the L-absorption edges of platinum in $K_2[PtCl_4]$, and the anomalous scattering tensor for platinum, were measured in experiments with linearly polarised synchrotron radiation. The polarisation anisotropy of up to 10 electrons $atom^{-1}$ for f" is the largest yet reported for anomalous scattering [204]. The K-absorption-edge spectra of the chloro ligand in the square planar complexes *cis*-and *trans*-$[Pd(NH_3)_2Cl_2]$ and $[NH_4]_2[PdCl_4]$ were reported, and were dicussed in connection with data for $K_2[PtCl_4]$ and $K_2[PdCl_4]$ [205].

Changes in the ^{103}Pd radioactive decay probability were measured in solid $^{103}PdCl_2$, and in solution, giving $\Delta\lambda/\lambda = 0.0126\pm0.0012$. The reasons for such a large change in λ, and possible applications of the effect, were discussed [206].

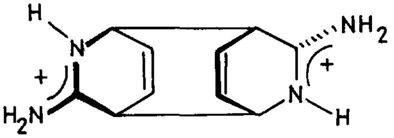
The transient absorption spectrum of $[PtCl_4]^{2-}$ in an ethane-1,2-diol/water matrix was recorded at 158 K. Excitation was at 347 nm with a pulsed ruby laser source, and the excited state absorption of $[PtCl_4]^{2-}$ in its lowest triplet state, was well structured between 16,500 and 33,000 cm^{-1}. The emitting state was significantly distorted along the totally symmetric stretching coordinate [207].

The temperature dependence of proton T_1 values at various Larmor frequencies was measured for $[guH]_2[PtCl_4]$, $[guH]_2[PtBr_4]$ and the palladium analogues ($[guH]^{2+} = [C(NH_2)_3]^{2+}$). The phase transition for $[guH]_2[PtCl_4]$ was at 359 K, and the high temperature phase was easily supercooled. Below room temperature the data for the chloro salts showed an unusual temperature dependence which was not easily explained by BPP theory [208].

A closed flow thermostable titration vessel was used for a study of the reaction of $Pd^{2+}{}_{aq}$ with iodide ion to give $[PdI]^+$ [209]. Palladium was determined in hydrogenation catalysts by conversion to $[PdI_4]^{2-}$, and measurement of the absorbance at 410 nm [210].

The equilibrium (7) was studied under *quasi*-equilibrium conditions. The existence of an intermediate, unstable phase, $[pyH][Pd(py)Cl_3]$, was established [211]. When *trans*-$[Pd(2\text{-aminopyridine})_2Cl_2]$ was allowed to stand in dmf containing HCl for several weeks, $[(20)][PdCl_4]_2$ was isolated and characterised by an X-ray diffraction study [212].

$$[pyH]_2[PtCl_4] \rightleftharpoons [Pt(py)_2Cl_2] + 2HCl + Pd \qquad (7)$$



(20)

The solid phase reaction of PdO with $[NH_4]Cl$ at temperatures above 250 °C gave $[Pd(NH_3)_2Cl_2]$. Further reaction with $[NH_4]Cl$ at a temperature between 250 and 300 °C gave $[NH_4]_2[PdCl_4]$, which decomposed to metallic palladium above 350 °C [213].

Reduction of palladium(II) chloro, bromo and sulphato aquo complexes by CO was accelerated by gaseous oxygen. The mechanism is shown in reactions (8)-(12) [214].

$$[PdX_4]^{2-} + O_2 \rightleftharpoons [Pd(O_2)X_3]^- + X^- \qquad (8)$$

$$[Pd(O_2)X_3]^- + CO \rightleftharpoons [Pd(CO)X_3]^- + O_2 \qquad (9)$$

$$[Pd(O_2)X_3]^- + CO \rightleftharpoons [Pd(CO)(O_2)X_2] + X^- \qquad (10)$$

$$[Pd(CO)X_3]^- + H_2O \longrightarrow \{Pd(0)\} + CO_2 + 3X^- + 2H^+ \qquad (11)$$

$$[Pd(CO)(O_2)X_2] + H_2O \longrightarrow \{Pd(0)\} + CO_2 + 2H^+ + 2X^- + O_2 \qquad (12)$$

Thin films of $Pd(OCOMe)_2$, $PdCl_2$ or $PdBr_2$ on polyimide substrates were irradiated by ion beams to give metallic films [215]. The kinetics of ozonation of palladium(II) in aqueous chloride containing solvents were studied. Two pathways were discerned, one of them chloride catalysed [216]. Chlorination of the Si-H bond of FcSiPhMeH was accomplished using $PdCl_2$ in C_6H_6/hexane [217].

The reactions of various halo platinum(II) complexes with $BF_3.Et_2O$ were investigated. $K_2[PtCl_4]$ gave β-$PtCl_2$, and $K[Pt(py)Cl_3]$ gave $[\{Pt(py)Cl_2\}_2]$ [218]. In complexes of stoichelometry $Na_2MCl_4(amide)_2$ (M = Pd or Pt; amide = dmf, methanamide or *N*-methylmethanamide, the carbonyl groups of the amides showed substantial changes in their IR spectra, but it was demonstrated that they acted only as solvating ligands [219].

1.6.2 Complexes with Group 16 donor ligands

1.6.2.1 Unidentate oxygen donor ligands

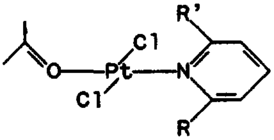
Very slow water exchange at $[Pt(H_2O)_4]^{2+}$ has been studied in the temperature range 273-334 K at pressure from 0.1-228 mPa by ^{17}O nmr spectroscopy. Exchange was much faster in the related palladium complex. The reaction between the palladium complex and dmso was studied by stopped-flow techniques, and the data were interpreted in terms of an associative activation mode [220]. The pressure and temperature dependence of the data for the platinum complex supported an I_a transition state [221].

The products of hydrolysis of $K_2[PdCl_4]$ sorbed on Y_2O_3, $Ca[CO_3]$ or $Ba[CO_3]$ were studied spectroscopically. $[Pd(OH)_4]^{2+}$ was observed on Y_2O_3 and $Ba[CO_3]$. On $Ca[CO_3]$ a polymer aquo hydroxo palladium complex was produced, and this could be converted to the tetraaquo species on boiling in the presence of $H[ClO_4]$ [222]. The kinetics of the reactions of MeI and BuI with Pd^{2+}/MeCOOH were studied. Only the species $[Pd(H_2O)_4]^{2+}$ and $[Pd(H_2O)_3(OCOMe)]^+$ appeared to be kinetically significant [223].

Reaction of $Na_2[Pd(OH)_4]$ with MOH (M = Sr or Ba) gave $M[Pd(OH)_4].H_2O$, characterised by IR spectroscopy, DTGA and X-ray studies [224].

The complexes $[P_2Pt(R_X)(OH)]$ (P_2 = basic monophosphine or biphosphine; R_X = activated alkyl or aryl group) were in equilibrium with $[P_2Pt(R_X)]^+$ and $[HO]^-$. The complexes were catalysts for the epoxidation of 1-alkenes by H_2O_2 [225]. It had been assumed that the oxidation of 1-hexene to 2-hexanone and 1-hexene-2-ol ethanoate, by Me_3COOH in the presence of $Pd(OCOMe)_2$, involved insertion of the alkene into {PdOOR} or {PdOCOMe} followed by a β-hydride shift or a β-hydride elimination. The reaction of Pd(OCOMe)$_2$ with H_2O_2, however, was shown to give a palladium superoxo complex, and in this case epoxides were the main reaction products [226]. Treatment of [Pt(dppe)Cl$_2$] with Na[OMe] in benzene/methanol gave the thermally unstable species [Pt(dppe)(OMe)$_2$], which decomposed in CD_2Cl_2 to give methanol, methanal and various oligomers. The reaction was slower in thf, suggesting that β-elimination from the methoxyl group required an open coordination site. Carbonylation of the dimethoxy compound gave [Pt(dppe)(COOMe)$_2$], stable at room temperature [227].

A range of mixed ligand complexes with oxygen and nitrogen donor ligands and containing at least one optically active ligand have been synthesised, and their MCD spectra recorded and interpreted [228]. The mobility of the propanone ligand in *trans*-[Pt(Me$_2$CO)(substituted pyridine)Cl$_2$] has been studied by ^{1}H and ^{13}C nmr spectroscopy. Only for symmetric ketones could the exchange between (21a) and (21b) be studied; non-symmetric ketones adopted a strongly preferred conformation [229].



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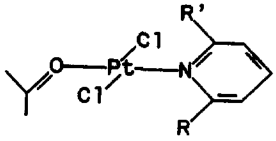


(21b)

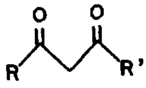
1.6.2.2 Bidentate and multidentate oxygen donor ligands

The IR and Raman spectra of [Pd(acac)$_2$] have been recorded and interpreted [230]. The synthesis of [Pd(Cl$_3$CCOCHCOCH$_3$)$_2$] has been described. When the mass spectrum of the complex was compared with that of the tfacac analogue, loss of {CCl$_2$} fragments suggested that a chlorine atom might be transferred to the metal [231].

Vapour pressures of metal complexes of tfacac have been determined in helium, and in helium containing the ligand vapour. The sublimation enthalpy for [Pd(tfacac)$_2$] was found to be 26.5±0.5 J mol^{-1}, but the data were not reproducible [232]. The dipole moment of [Pd(dbm)$_2$] both alone and in molecular complexes with iodine has been measured in various solvents. The data obtained demonstrated that the molecular interaction between polar solutes and non-polar aromatic moieties is governed by dipole induced dipole electrostatic interactions [233]. [Pt(acac)$_2$]/PEt$_3$, [Pd(acac)$_2$] and palladium(II) complexes of *N,N*-diethyldithiocarbamate were used to precipitate pastes of rather dubious compositions on glass or ceramic supports [234].

Preparation of derivatives of (22), L, [PdL$_2$] (R = 4-FC$_6$H$_4$, R' = Me, Et,

CF_3, C_2F_5 or 2,3,5,6-F_4C_6H) has been described. The authors were not able to separate *cis*- and *trans*-isomers [235]. [PdL'_2] (HL' = (23)) was prepared from $Pd(OCOMe)_2$ and HL' [236]. A copolymer of ethenylbenzene and 2-methyl-1,3-butadiene was prepared bearing 1.4 % acac groups attached to some of the ethenyl benzene units. The copolymer was cross-linked by chelation of the acac groups using $Pd(OCOMe)_2$ to form bis(acac) palladium species [237].



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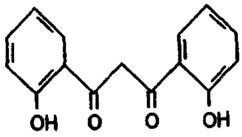
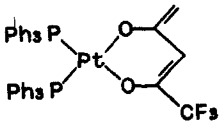


(23)

Reaction of [PdL_2] (HL = hfacac or tfacac) with L' (L' = 2-, 3-, or 4-methylpyridine or 2,6-dimethylpyridine) gave [PdL'_4][L]$_2$ [238]. Treatment of [$Pd(acac)_2$] with $BF_3.OEt_2$ yielded [Pd(acac)(μ-F)$_2$B(acac)]F, *via* [(acac)Pd(μ-F)$_2$B(acac)F], in which the boron atom was 5-coordinate. The reaction was monitored by IR and UV spectroscopy [239]. Deprotonation of [$Pt(PPh_3)_2$(hfacac)] gave initially (24), which rearranged readily to (25) [240].



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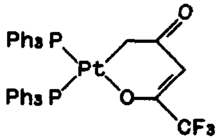
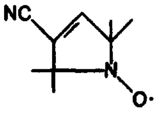


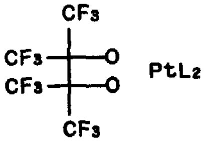
(25)

Cocrystallisation of [$Pd(hfacac)_2$] and (26) gave a species of stoicheiometry {$Pd(hfacac)_2L_2$}. There was no specific intermolecular interaction between the species, however [241].



(26)

Complexes of the type (27) were prepared for a wide range of ligands, L. NMR spectroscopic data allowed the static *trans*-influence of the fluorinated alkoxy group to lie between that for Cl^- and Br^-. A dynamic *trans*-effect was measured from the barrier to inversion in thioether complexes, and adjudged to be less than that for Cl^- [242].



(27)

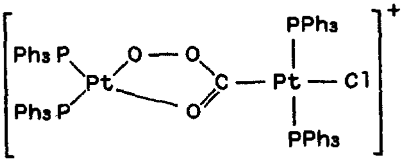
The structure of *cis*-$[Pt(NH_3)_2$(cyclobutane-1,1-dicarboxylate)] has been established in an X-ray diffraction study. Substantial dynamic puckering of the dicarboxylate chelate ring was deduced from substantial disorder in one of the carbon atoms [243]. Host-guest binding of the complex with α-cyclodextrin was studied by nmr spectroscopy and microcalorimetry. The dicarboxylate ligand was situated in the cyclodextrin cavity, and a 1:1 complex was readily isolated [244].

The structure of $[Pt(NH_3)_2$(propanedioate)] was established in a diffraction study. The chelate rings of the dicarboxylate ligand adopted a boat conformation, and the complex molecules were stacked along the *a*-axis with hydrogen bonds between adjacent molecules. $[Pt(NH_3)_2(C_2O_4)]$ was also stacked in the *a*-direction, with intercolumn hydrogen bonds in the *b*- and *c*-directions [245].

Photolysis of $[ML_2(C_2O_4)]$ (M = Pd or Pt; L = R_3P or SEt_2) gave CO_2 and $\{ML_2\}$. The latter fragment reacted readily with L' (alkenes, alkynes, or R_3P) to give $[ML_2L']$. $\{ML_2\}$ underwent oxidative addition with organic halides, and hydrogen [246]. The preparations of TTF and TSF derivatives of $[Pt(C_2O_4)_2]^{2-}$ and $[Pt(C_2O_4)Cl_2]^{2-}$ have been described. The partially oxidised salts (such as $[TTF]_{2.7}[Pt(C_2O_4)_2]$) contain neutral TTF as well as TTF radical cations. XPES implied that there was some transfer of electron density from TTF to the platinate. All the species prepared were semiconductors with resistivity between 10^2 and 10^4 Ωcm^{-1} [247].

The influence of steric factors on the lengths of metal-metal bonds has been studied using molecular models. Calculations for $\{Pd_2\}^{4+}$ (in a hypothetical species $\{Pd(OCOCH_3)_2\}_n$) in which no metal-metal bond was present accounted successfully for the metal-metal distances [248].

Reaction of $[Pt(PPh_3)_2(O_2)]$ with $[Pt(PPh_3)_2(CO)Cl]^+$ gave (28); further treatment with PPh_3 yielded (29) [249]. When $[Pt(PPh_3)_2(PhNO)]$ was reacted with CO_2, (30) was formed reversibly, and could be isolated and characterised. This is the first example of reversible CO_2 insertion into a metal-nitrogen bond. Insertion of other species, including CS_2, PhNCO and PhNCS, gave similar results. Further reactions of (30) were studied in detail [250]. Treatment of the related complex (31) with [NO][PF$_6$] gave (32), which could also be prepared by reaction of [Pt(PPh$_3$)$_2$Cl$_2$] with Ag[ON(R)NO] [251].



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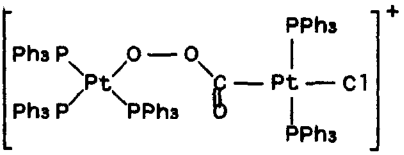

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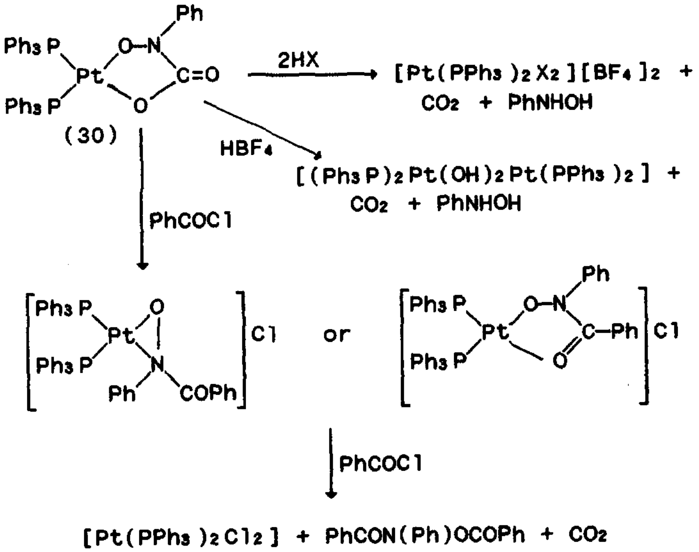

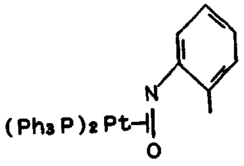

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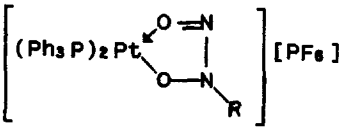


(32)

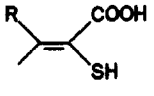
1.6.2.3 Ambidentate sulphur oxygen donor ligands

The structure of *cis*-[Pt(dmso)$_2$Cl$_2$] has been determined in an X-ray diffraction study. The coordination at platinum was square planar, and the dmso ligands was *S*-bonded to the metal [252]. Dmso was also *S*-bonded in *trans*-[Pt(NH$_3$)$_2$(dmso)Cl]Cl. The cations were stacked in columns parallel to the *a*-axis, and were linked within the columns by N-H...O hydrogen bonds. The columns were linked to each other by N-H...Cl hydrogen bonds [253]. An X-ray diffraction study of *cis*-[Pt(tetrahydrothiophene-*S*-oxide)$_2$Cl$_2$] revealed that the sulphoxide ligands were *S*-bonded [254].

The new complexes [Pt$_2$L$_2$(μ-Cl)$_2$Cl$_2$] (L = dmso or Et$_2$SO) were prepared from *cis*-[PtL$_2$Cl$_2$] and PtCl$_2$. IR spectroscopic data indicated that the ligands were *S*-bonded. Reaction of the dimers with further L gave *trans*-[PtL$_2$Cl$_2$], in equilibrium with the *cis*-isomers in CH$_2$Cl$_2$. The kinetics of the isomerisation reaction were investigated, and preliminary studies showed that ligand exchange was much faster in both isomers than was their interconversion. Two mechanisms were proposed for the isomerisation [255]. The *S*-bonded complexes [PdLL'$_2$Cl]Cl (L = dmso or tht-*S*-oxide; L' = cycloalkylamine) were prepared from [PdL$_2$Cl$_2$] and L'. Possible anti-tumour activity was investigated [256]. Reaction of dmso with K[Pt(C$_2$H$_4$)Cl$_3$] gave *trans*-[Pt(PCy$_3$)(dmso-*S*)Cl$_2$] which slowly interconverted with the *cis*-*S*-bonded isomer; at equilibrium 85 % of the *cis*-isomer was present. This is in contrast to the related PPh$_3$ complex, for which isomerisation was so fast that the *trans*-isomer could not be isolated. Dibenzylsulphoxide, however, reacted slowly to give the species *trans*-[Pt(PCy$_3$)(R$_2$SO-*O*)Cl$_2$]. Over a period of 8 months in CDCl$_3$ this isomerised to give 90 % of the *cis*-*S*-bonded complex [257].

1.6.2.4 Bidentate oxygen sulphur donor ligands

The ligand (33) was said to form palladium(II) complexes of the type (34), but these were not well characterised [258]. Chromatography of the chelate complexes of (35) including those of palladium(II) and platinum(II) has been studied [259]. Complexes of Rh(III), Ir(III), Pd(II) and Pt(II) could be determined simultaneously chromatographically, as complexes of the type (36) [260].



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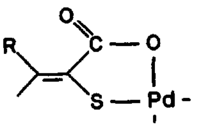
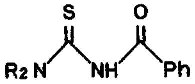


(34)

Halo derivatives of cobalt(III) dicarbollide in organic solvents containing nitrobenzene have a high extraction selectivity for palladium(II) bound in chelates containing ligands such as (37) [261]. Self-sensitised photooxidation of [Pt(bipy)(TSA)] (TSAH$_2$ = thiosalicylic acid) has been studied [262].



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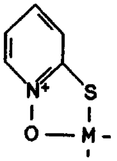

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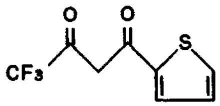
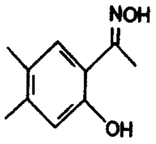


(37)

1.6.2.5 Ambidentate oxygen nitrogen donor ligands

Palladium(II) has been determined gravimetrically using (38), but there was no indication of the mode of binding in the complex isolated [263]. The trioxime, (39), was also used in both gravimetric and spectrophotometric analysis for palladium(II). The third oxime group enhanced water solubilty of the complex (40), which is closely related to dmg derivatives [264]. Spectrophotometric determination of palladium(II) has also employed 2,4-dihydroxy-3,5-dibromoacetophenone oxime, but the binding mode of the ligand was not established [265]. (41) was determined by potentiometric titration with $PdCl_2$ in Britton Robinson buffer at pH 6.83, using a silver indicator electrode [266].



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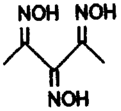

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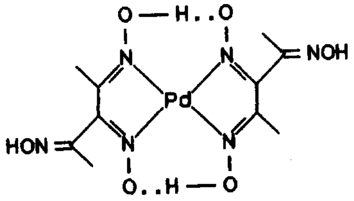

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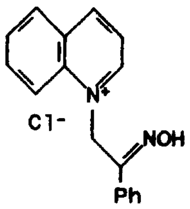
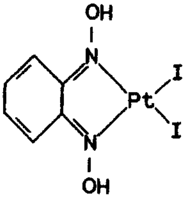


(41)

IR and Raman spectra of palladium(II) bis(salicylaldoximates) have been recorded between 4000 and 200 cm^{-1}. Most bands could be assigned [267].

The structure of (42) was established in an X-ray diffraction study. The molecules are planar and stacked [268]. The structure of (43), $[Pt(oaoH_2)(oaoH)]I$, was also established by a diffraction study. The cations exhibited substantial distortion from planarity, and the units formed a stack of dimers, clamped in pairs by hydrogen bonding [269]. In the related $[TCNQ]^-$ salt there were regular segregated stacks and the compound was a semiconductor. The structure of the 2:3 Pt:TCNQ complex, (44), was also established; it contained segregated acceptor stacks with half a negative charge per molecule. These ran perpendicular to mixed stacks of the type -donor-donor-acceptor-donor-donor-acceptor- with integral charges on both donor and acceptor [270,271].



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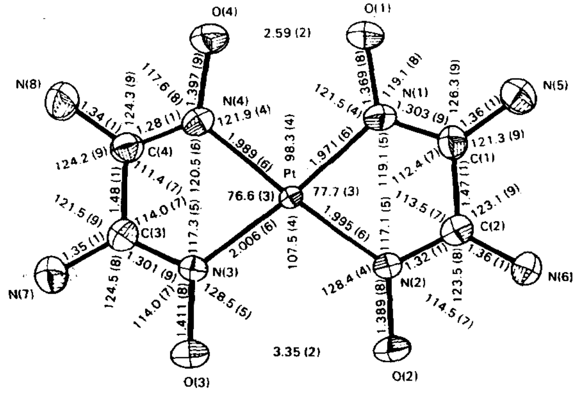
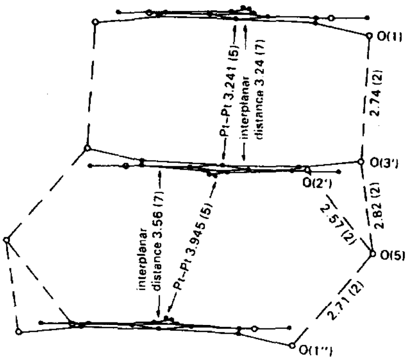


(43a) Reproduced with permission from [269]

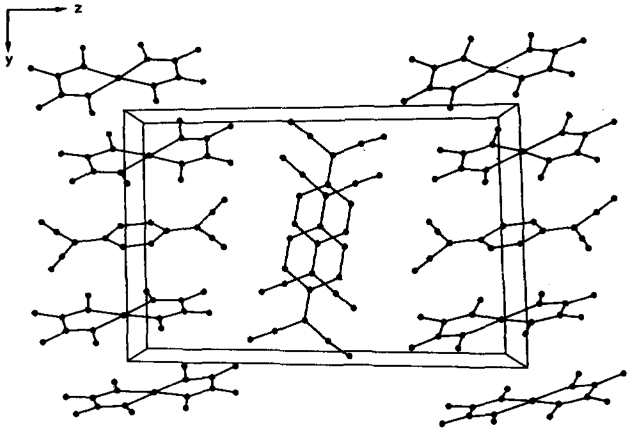
The $[Pt(oaoH)(oaoH_2)]^+$ complex cation with bond distances (Å) and angles (°).

Thermal contors are at 50 % probability.

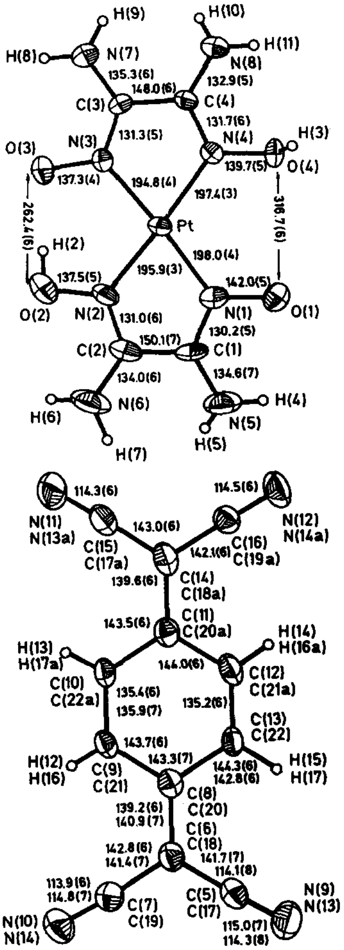
Reaction of $[Pd(HL)_2]$ (H_2L = (45) with chloranil gave $[PdL_2]$, in which the second deprotonation occurred at the nitrogen atom [272]. The preparation of (46), H_2L', has been detailed; this was easily converted to $[Pd(HL')_2]$ [273]. The reaction of chelating dioxime complexes with Me_3M' gave methane and species such as (47). The complex for which M = Pt and M' = Ga, (48), was investigated by a diffraction study; the complex was not planar and there were weak interactions between Ga(III) and Pt(II) [274].



(43b) Reproduced with permission from [269]
Section of a stack along *a* with relevant distances (Å). The complex cations are related in pairs by inversion centres, and the top and bottom molecules by a unit cell translation, *a*. Interplanar distances refer to the planes through the four oxime *N*-atoms

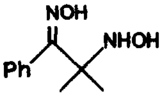


(44a) Reproduced with permission from [271].
Projection of the structure of $[Pt(oaoH)(oaoH_2)]_2\{(tcnq)_3\}^{2-}$ along the tcnq$^{\frac{1}{2}-}$ stack.

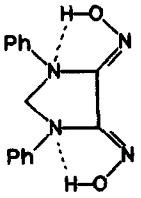


(44b) Reproduced with permission from [271]

Bond lengths in pm in the complex cation (top) and in the tcnq anions (bottom). In the case of the anions the upper value applies for the tcnq$^{1/2-}$ ion of the pure stack, the lower one for the tcnq$^-$ ion of the mixed stack.



(45)



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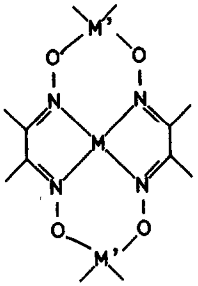

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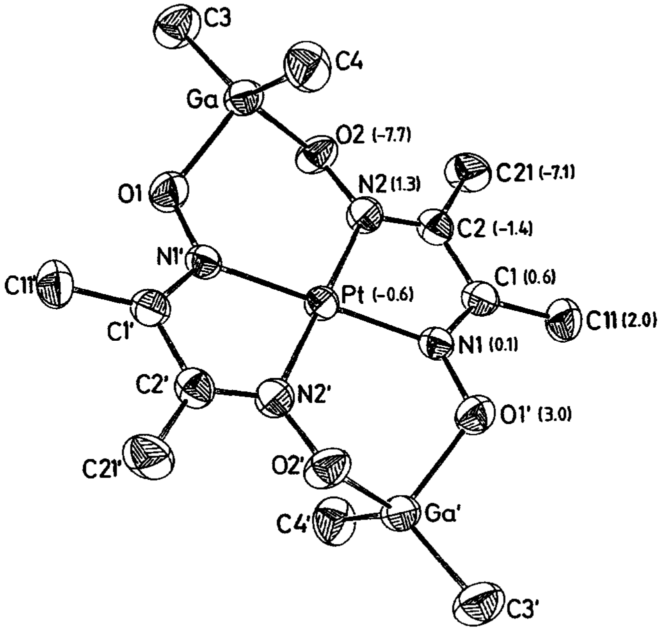
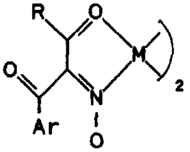


(48) (Reproduced with permission from [274])
ORTEP drawing with 50 % probability ellipsoids.

The synthesis and characterisation of transition metal complexes of 4,5-dimethyl-2-hydroxyacetophenone oxime have been described. Although IR and UV spectroscopic data were presented, the authors were unable to assign either binding mode, or complex stereochemistry, with any certainty [275]. The extraction of palladium(II) by cyclic secondary α-aminooximes has been described. *N,N*-bonding appeared to be the general rule [276].

Reaction of oximes with KO_2 in the presence of allyl palladium halide complexes in CH_2Cl_2 gave species of the type $(R^1R^2C{=}N{-}O)_2CH_2$; the *N*-bonded palladium complex formed with the oxime acted as a phase transfer agent to solubilise the KO_2 [277].

The compounds 4-chloro and 4-bromoisonitrosobenzoylpropanone were used as chromogenic reagents for palladium and ruthenium. The $[PdL_2]$ complex formed was postulated to have the structure (49) (*sic*), but it was not clear whether the *cis*- or the *trans*-isomer was formed [278].



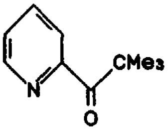
(49)

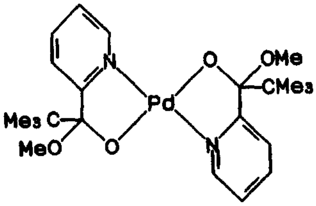
EPR spectroscopy of transition metal complexes of sulphamidate, $[H_2NSO_3]^-$, were recorded, and linkage isomerism could be deduced from the differences observed in the N_{1s} and S_{2p} binding energies. In the palladium complex, $[PdL_2]$, the ligand was *O*-bonded to the metal [279].

1.6.2.6 Bidentate and multidentate oxygen nitrogen donor ligands

Complexes of the type *trans*-$[Pt(LH)_2Cl_2]$, $[PtL_2]$ and $[Pt(LH)_2(SR)_2]$ for LH = $H_2NCMe_2CH_2OH$ or $H_2NC(CH_2OH)_2$ have been prepared. An X-ray diffraction study of *trans*-$[Pt(H_2NCMe_2CH_2OH)_2Cl_2]$ was described; in this complex the ligand is monodentate and *N*-bonded. The *N,O*-chelate complexes, $[PtL_2]$, reacted with HCl or RSH to give the species containing the monodentate ligand [280].

The palladium and platinum derivatives of 8-hydroxyquinoline could be separated using supercritical fluid chromatography [281]. The platinum complex shows suitable light absorption, redox, and excited state properties to decompose water under illumination by visible light [282]. Reaction of (50) with palladium ethanoate in the presence of methanol gave (51), albeit in rather low yield [283].



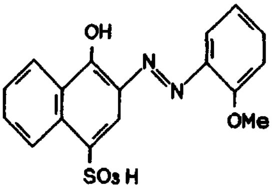


(50)

(51)

Various palladium(II) complexes of amido substituted arene carboxylic acids, including 2-(aminobenzoyl)benzoic acid have been prepared, and tested for anti-fungal activity. The structures of the complexes were not discussed, and did not seem to have been established [284]. The substitution kinetics of X in $[Pt(pyridine\text{-}2\text{-}carboxylate)LX]^-$ (L = Cl or NO_2; X = Cl) by Y^- (Y^- = Br^-, $[NO_2]^-$, $[N_3]^-$, $[NCS]^-$ or I^-) have been studied. The azide and thiocyanate nucleophiles were more effective than had been predicted [285].

Spectrophotometric methods were used to determine the stabilities of palladium(II) complexes with azoeosine, (52). The authors suggested that the metal was coordinated to the deprotonated phenol and π-coordinated to the nitrogen-nitrogen double bond, which seems a little unlikely [286]. A very sensitive detrmination of palladium(II) involved the use of 2-(2-hydroxyphenyl)iminomethyl phenol, but complex structures were not discussed [287]. IR spectroscopic data were used to assign the binding of (53) as being *via* the deprotonated phenol and the imino nitrogen atom. The geometry of the complex was not assigned [288].



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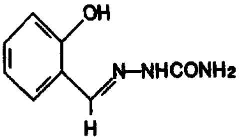
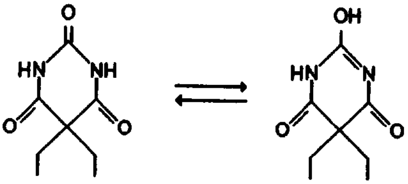


(53)

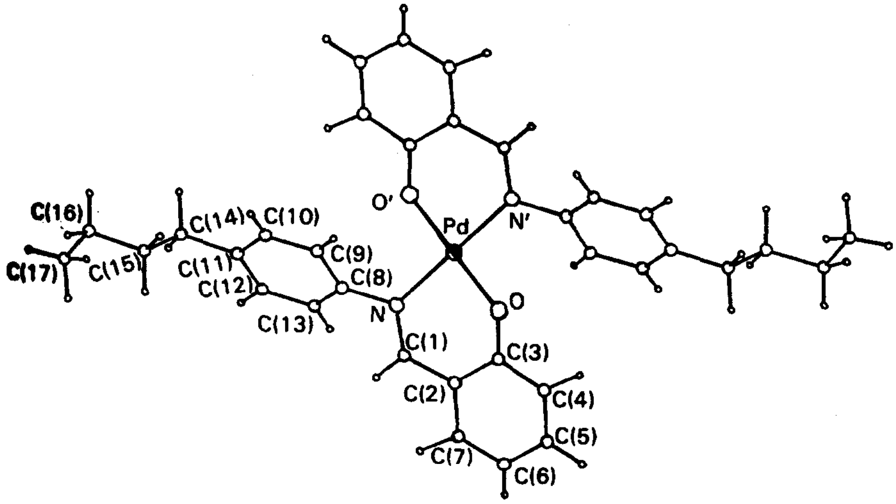
Two papers have reported the preparation of complexes of barbituric acid. With LH = 5,5-diethylbarbituric acid, (54), a complex of stoicheiometry $[PdL_2]$ was formed, with coordination of N(1) and O(2) in a lactim form in a *trans*-complex [289]. The coordination of the unsubstituted barbituric acid was postulated to be different, and may involve the CH_2 group in an enolised form [290].



(54)

O,N-Binding was proposed for coordination of 2-carboxamidopyridine in $[PdL_2]Cl_2$, with IR spectroscopic data indicating that only the amide group was involved in coordination. This seems to be unlikely, particularly in view of the fact that the 3- and 4-carboxamido isomers were monodentate ligands in $[PdL_2Cl_2]$, with coordination only through the pyridyl nitrogen atom [291].

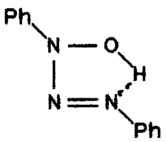
The structure of bis{*N*-(4-butylphenyl)salicylideneaminato}palladium(II), (55), has been determined in an X-ray diffraction study [292]. *trans*-Stereochemistry was deduced from a diffraction study on bis{*N*-(2-pyridyl)-1-imino-2-carboethoxy-3-oxo-butan-2-ido)palladium(II) [293].



(55) (Reproduced with permission from [292])

IR spectroscopic data indicated the importance of tautomerism and strong hydrogen bonding in 1,3-diphenyl-3-hydroxytriazine, (56). This was supported by data for the *trans*-complex, (57) [294]. Reaction of [MLL'] (M = Pd or Pt; L = (58), L' = acac) with NH_3 or RNH_2 (A) resulted in the formation of complexes of stoicheiometry [MLL'A] in which condensation of the amine with the aldehyde had occurred, and the initial *N,O*-chelate, (59), had been converted to an *N,N*-coordinated complex. The reaction with $HOCH_2CH_2NH_2$ gave the tridentate species, (60) [295]. Reaction of $[Pd(hfacac)_2]$ with (61) gave (62) in very low yield, *via* an unknown mechanism. The metal is bound in an η^2-manner to the reduced nitroxyl group [296].

Reaction of $K_2[PtCl_4]$ with $idaH_2$ gave $[Pt(idaH)_2]$, and the reaction was also successful for $midaH_2$, although it had been previously reported to fail. In base, $[Pt(idaH)_2]$ yielded $[Pt(ida)_2]^{2-}$, but bound and free ethanoate groups did not interconvert readily, only slowly in concentrated base. The *trans*-isomer was generally isolated, and was in very slow equilibrium with the *cis*-compound [69].



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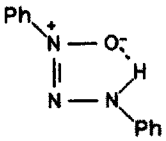
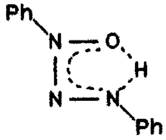


(56b)



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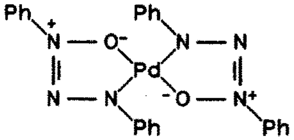

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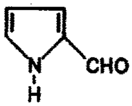

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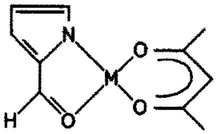

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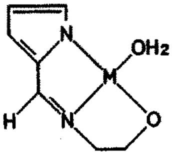

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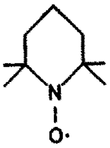
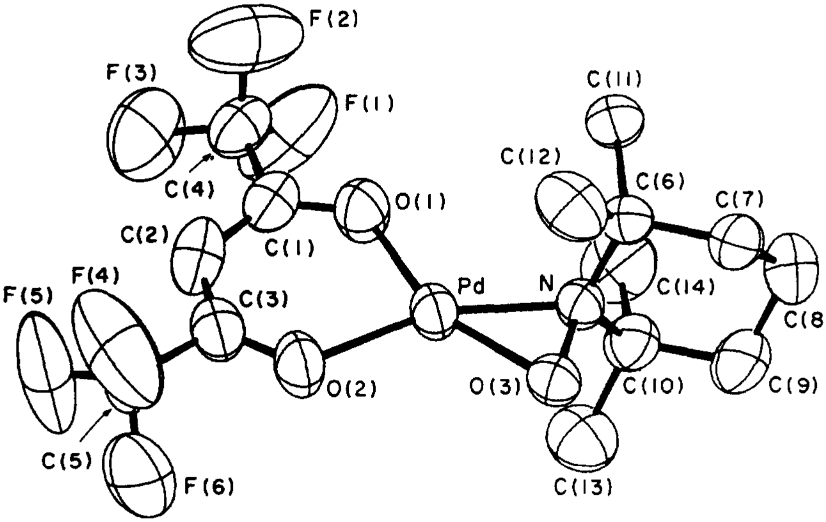


(61)

The mass spectra of [PdLCl], [PtLCl] and [PdL'Cl] (HL = (63), HL' = (64)) have been recorded. A structure involving coordinateion of the pyridyl nitrogen, deprotonated phenol and one of the azo nitrogen atoms was proposed [297]. (65) was characterised in an X-ray diffraction study; the six-membered {PdN_4C} ring adopted a shallow boat conformation [298]. A range of tridentate complexes of Schiff's bases, such as (66), have been prepared and characterised [299].

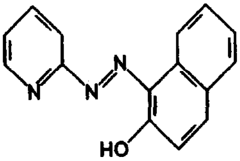
The structure of (67) was established in an X-ray diffraction study. The complex was isostructural with its copper and cobalt analogues [300].

A range of complexes, (68), with varying substituents X, Y and Z has been prepared and characterised [301]. Reaction of H_2L, (69), (R = Me or OEt) with $K_2[PtCl_4]$ gave [PtL], in which the metal was coordinated by an imine nitrogen and the oxygen of the {COR} group in the enolate tautomer [302].



(62) (Reproduced with permission from [296])

Thermal ellipsoids have been drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.



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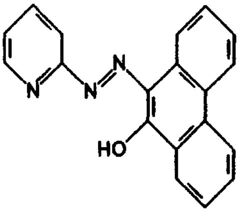
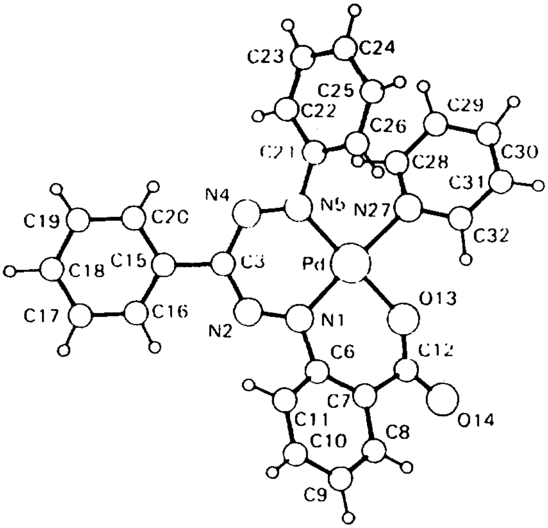


(64)

Palladium(II) was determined in Pd/C catalysts by conversion to (70) and measurement of the absorbance of the complex [303]. The Schiff base complex (71) has been prepared and characterised [304].

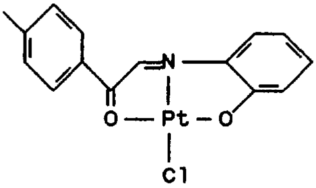
1.6.2.7 Multidentate oxygen nitrogen phosphorus donor ligands

The carbaldehyde substituted phosphine (72) reacted with (73) to give (74), which was characterised by an X-ray diffraction study [305]. It appears that the starting material had decomposed to give 2-aminobenzaldehyde, which condensed with (72) to give a Schiff base. The transformation was completed by oxidation.



(65) (Reproduced with permission from [298])

Projection of the molecule onto the plane of the formazan nucleus.



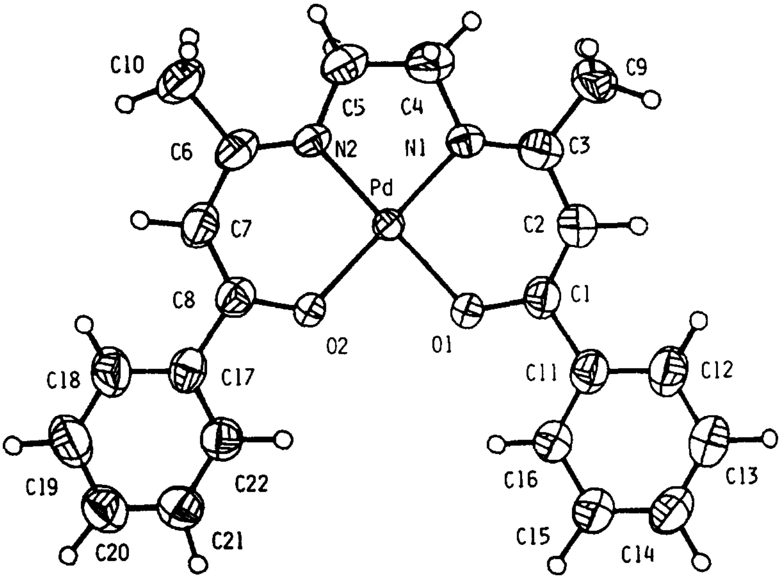
(66)

1.6.2.8 Bidentate oxygen phosphorus donor ligands

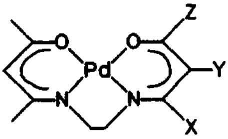
The complexes $[ML_2]$ (M = Pd or Pt) were prepared and characterised for HL = $Ph_2PCH_2C(CF_3)_2OH$. NMR spectroscopy indicated *cis*-coordination of the ligands as *O,P*-chelates [306].

1.6.2.9 Bidentate oxygen carbon donor ligands

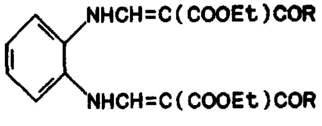
The reactions of the complex (75), the synthesis of which had been previously described, have been detailed. The palladium-oxygen bonds are rather more labile than palladium-nitrogen bonds in other cyclometallated species, and the carbon-palladium bonds also showed enhanced reactivity [307].



(67) (Reproduced with permission from [300])
The hydrogen atoms are represented by open circles of arbitrary radius, the other atoms by thermal ellipsoids of 50 % probability.



(68)



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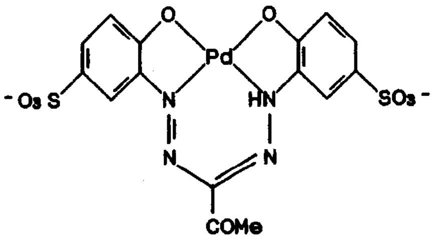

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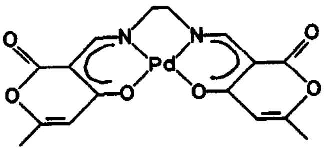

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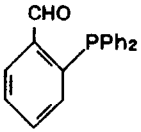

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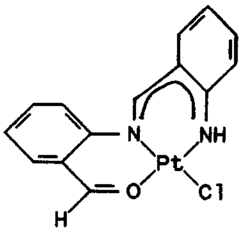

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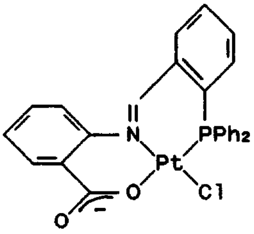


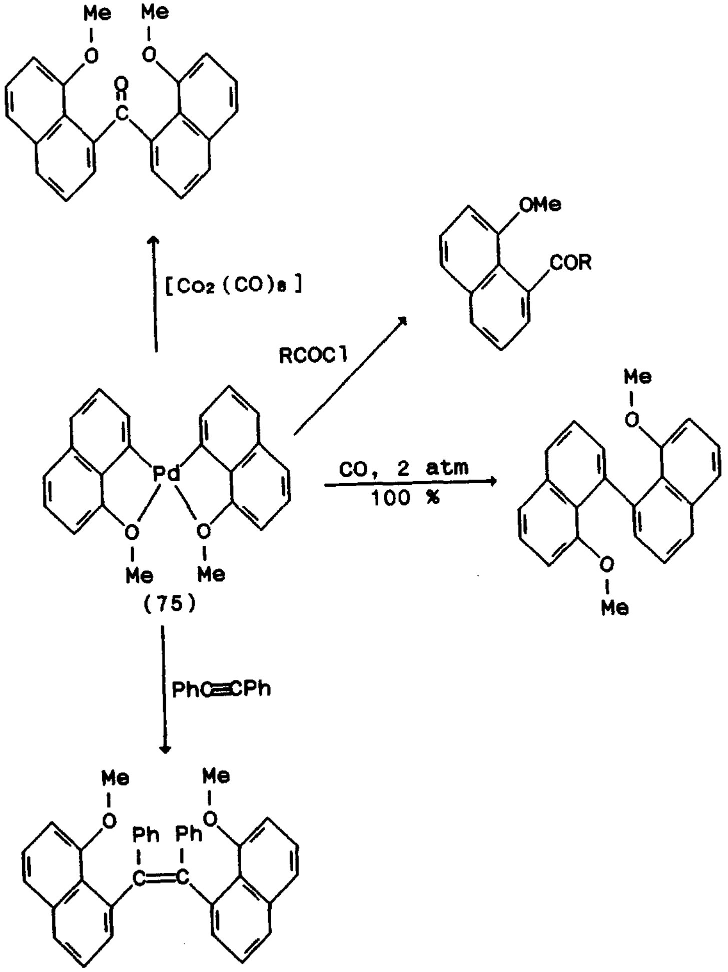
(74)

The structure of (76), prepared from sodium ascorbate and *cis*-[Pt(RNH$_2$)$_2$(OH$_2$)$_2$][NO$_3$]$_2$, has been determined in an X-ray diffraction study. This is the first example of a C(2)-O(5) coordinated ascorbate complex to be so characterised [308].

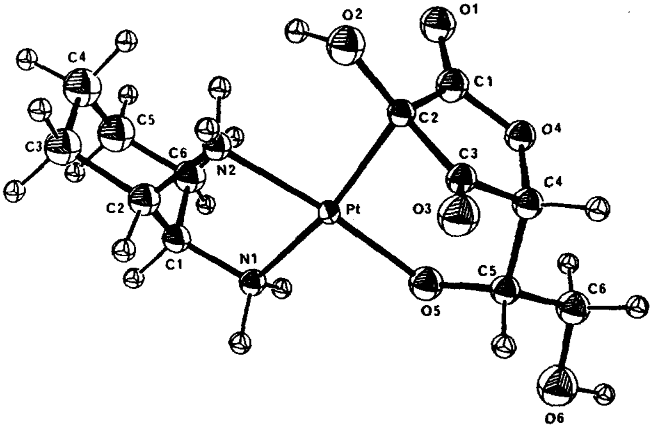
1.6.2.10 Unidentate sulphur donor ligands

Colourimetric determination of lincomycin as its palladium complex has been reported. Although the nature of the complex formed was not specified, a thioether group seems to be the most likely site of ligation [309]. Addition of an extracting agent with hard nucleophilic atoms (for example, tributyl phosphate) to the extraction mixture of palladium(II) with R$_2$S (or other soft groups) was shown to catalyse the extraction. The explanation of this phenomenon lay in the fact that the extraction agents with "hard" donor atoms were appreciably concentrated at the interface and reacted with the salts of the soft cations, when the phases were in contact, and transferred them to the organic phase as a solvate. They then reacted with the "soft" extraction agent to give the thermodynamically stable product [310].

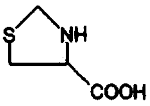
An Anderson rearrangement of a complex of 1-oxa-4-thiacyclohexane, thioxone, (to) has been reported. [pyH]$_2$[Pt$_2$(to)Cl$_6$], on thermolysis, yielded [Pt$_2$(py)$_2$(to)Cl$_4$] with the elimination of HCl, and the benzimidazole complex reacted similarly [311]. Cyclic voltammetry was used to study the mode of binding of 1,4-dithiacyclohexane-1-oxide to platinum(II). Model studies had shown that thioether complexes require more negative potentials for reduction than do those of the analogous sulphoxides. When the ligand reacted with $[Pt_2(PPh_3)_2(\mu\text{-}Cl)_2Cl_2]$, ligation occurred through the thioether rather than the sulphoxide, giving $[Pt(PPh_3)LCl_2]$ [312]. DRIFT was used to monitor functional group interconversions on modified silica surfaces, including the reaction of $\{SiO_2\}\text{-}CH_2SEt$ with $[Pt_2(PPh_3)_2(\mu\text{-}Cl)_2Cl_2]$ to give $\{SiO_2\}\text{-}CH_2SEtPt(PPh_3)Cl_2$ [313].



Reaction of palladium(II) with *N*-ethanoylthiaproline gave a complex in which the sulphur atom, but neither nitrogen nor carboxylate, was bound to palladium. The reaction with thiaproline, (77), was similar, with sulphur binding, but it was thought that some other group must be involved in binding in a polymeric structure [314].

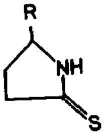


(76) (Reproduced with permission from [308])
40 % probability ellipsoids for all non-hydrogen atoms.



(77)

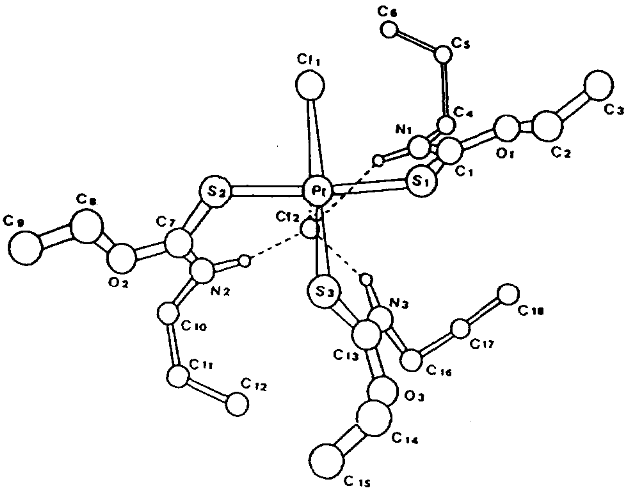
Substituted thiopyrrolidones, (78), reacted with MX_2 to give $[M(78)_2Cl_2]$ (M = Pd or Pt). All the complexes isolated had *trans*-stereochemistry and the ligand was *S*-coordinated. The complexes had moderate antiphage, antibacterial, and antifungal activities [315].



(78)

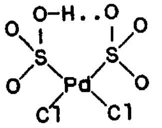
The complexes $[PtL_3X]X$ (L = *N*-ethyl-*O*-ethylthiocarbamate, ETC, or *N*-propyl-*O*-ethylthiocarbamate, PTC) have been prepared and characterised. The complex for which L = PTC, (79), was investigated by X-ray diffraction techniques [316]. In $[Pt(Me_2NCSSMe)_2I_2]$ the platinum was ligated by two halides and two thiocarbonyl groups in a *trans*-geometry. In the related complexes, $[PtLX_2]$, however, this and other dithiocarbamates acted as *S,S*-chelating ligands, and the complexes necessarily adopted *cis*-geometry

[317].



(79) (Reproduced with permission from [316])
Positions of the hydrogen atoms are not shown.

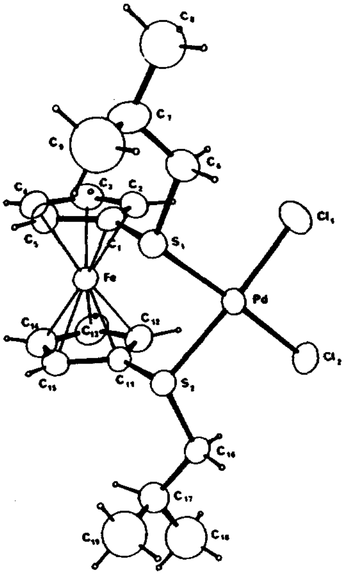
Reaction of $K_2[PdCl_6]$ with $K_2[CO_3]$ and SO_2 yielded $K_3[Pd\{(SO_3)_2H\}Cl_2]$, (80), characterised by an X-ray diffraction study. The O-H...O hydrogen bond was very short (2.396(4) Å), symmetry restricted, and close to linear [318].



(80)

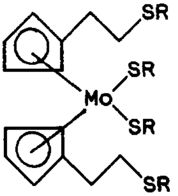
1.6.2.11 Bidentate and multidentate sulphur donor ligands

The polysulphides of platinum(II) have been reviewed [319]. The preparation of [M{1,1'-bis(thioalkyl)ferrocene}X_2] (M = Pd or Pt; X = Cl or Br; alkyl = Me, Ph, CH_2Ph, $CHMe_2$ or CH_2CHMe_2) has been described. The complexes were characterised by ^{1}H, ^{13}C and ^{195}Pt NMR spectroscopic studies, and for (81) by an X-ray diffraction study [320]. Variable temperature NMR spectroscopic studies were used to investigate the sterodynamics of the complexes, with particular reference to establishing the barrier to pyramidal inversion at the sulphur atoms [321].



(81) (Reproduced with permission from [320])

In the complex [MLX_2] (M = Pd or Pt, L = $EtS(CH_2)_{10}SEt$)) the chelating ligand occupies *trans*-positions in the coordination sphere. No association was noted either in the solid state or in solution [322]. The metal-based dithioether ligand, (82), was used in a preparation of (83) [323].



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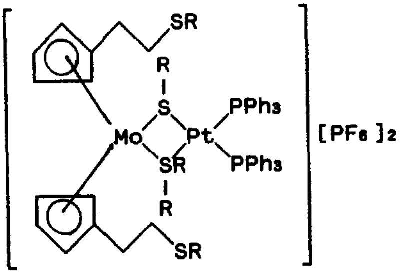
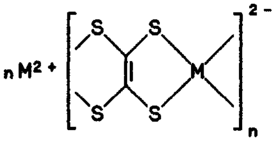


(83)

The conductivity properties of thiooxalate polymers such as (84) have been reviewed [324]. EPR data for dithiooxalate complexes, (85) (M = Pd or Pt) were reported; there was a linear relationship between binding energy and effective charge [325].



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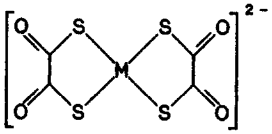
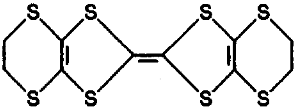


(85)

The electrocrystallisation of solutions of $[M(mnt)_2]^{2-}$ (M = Pd or Pt) gave semiconducting materials. Nickel, palladium and platinum complexes of (86) and (87) gave similar results [326]. The complexes $Cu[M(mnt)_2]$ (M = Pt, Pd, Ni or Cu) and $Cu[M(mnt)_2]_2$ (M = Pt, Ni or Cu) all exhibited compressed pellet conductivities in excess of 10^{-6} S cm^{-1} at room temperature. The monoanionic species were more conducting than either neutral or dianionic species. The particularly good results obtained with the copper salts may be related to involvement of a Cu(I)/Cu(II) redox couple [327]. Spectroscopic and electrochemical behaviour of mnt complexes of palladium and platinum was compared at platinum or transparent SnO_2 electrodes. For $[Pt(mnt)_2]^{2-}$ the main band corresponded to the MLCT excitation, and cathodic photocurrents were observed. In the palladium complex the corresponding band was assigned to LMCT, and no current was observed [328].



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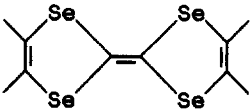
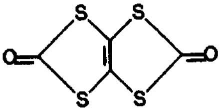
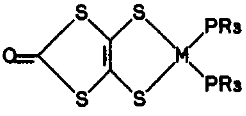


(87)

The reaction of (88) with methoxide ion gave a species of stoicheiometry $[C_3OS_4]^{2-}$ not $[C_3S_4]^{4-}$ as previously reported. Reaction of this product with $[M(PR_3)_2Cl_2]$ (M = Pd or Pt) gave (89) [329].



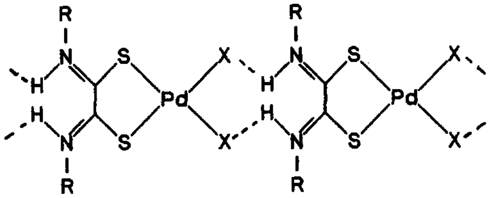
(88)



(89)

The oligomeric species (90) was formed from the ligand L, palladium(II) and HX. Thermolysis gave an intermediate $[\{PdL'\}_n]$, which was reasonably stable. Further heating resulted in the formation of palladium metal [330].

Thermolysis of the related species, (91) was also investigated [331].



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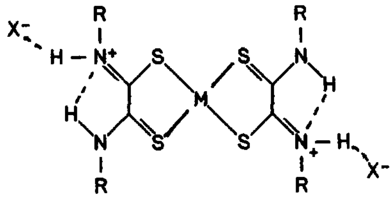
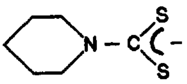


(91)

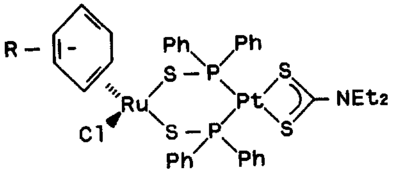
There continues to be considerable interest in dithiocarbamate complexes. Derivatives of diethyldithiocarbamate deactivated 3-4 moles ozone per mole of ligand, with rate constants in the region of 10^2-10^4 $M\ l^{-1}\ s^{-1}$. The mechanism of the reaction was discussed [332]. Complexes of palladium(II) with $[PhNHNCS_2]^-$ were determined by tlc [333]. Palladium(II) and platinum(II) were separated by glc as their bis(trifluoroethyl)dithiocarbamate chelates [334].

Complexes of the piperidine derived dithiocarbamate, (92), were prepared and characterised by IR and UV spectroscopy and by thermal analysis [335]. Reaction (13) was used to prepare the novel dithiocarbamate derivatives (93) [336]. When the structure of $[Co\{(\mu\text{-}Ph_2PO)_2Pt(\{C_5H_{10}\}_2NCS_2)\}_2]$ was initially determined [337] the space group was assigned as $P\bar{1}$, but it was later shown to possess higher symmetry, C2/c [338].



(92)

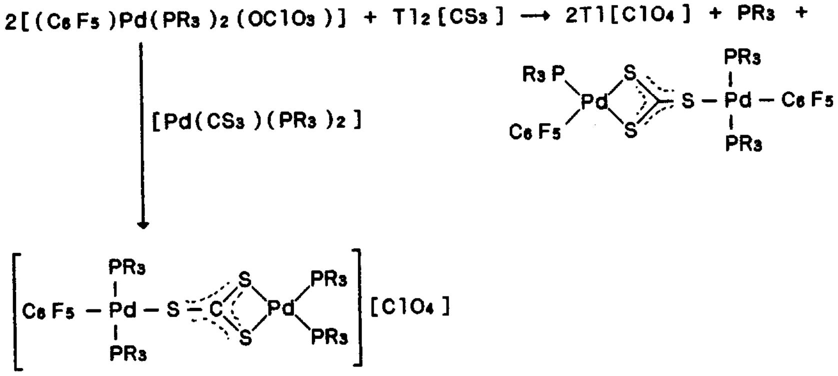
$[\{Ru(\eta\text{-arene})Cl_2\}_2] + [H_2NEt_2][Pt(S_2CNEt_2)(Ph_2PS)_2] \longrightarrow$



(13)

(93)

Some reactions of thiocarbonate derivatives have been described (Scheme 1) [339].



Scheme 1 Reaction of thiocarbonate derivatives [339]

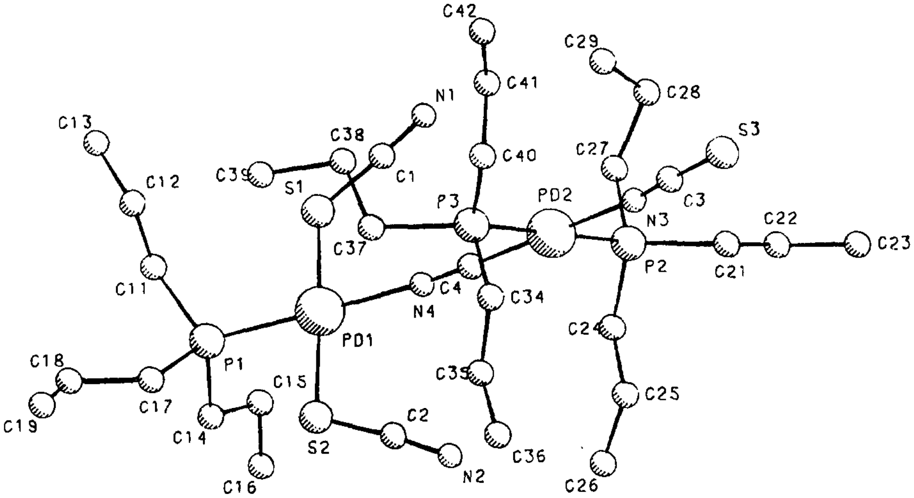
1.6.2.12 Ambidentate sulphur nitrogen donor ligands

IR spectra have been recorded for $[PdL_2(SCN)_2]$ (L = Ar_3P). Both these and powder diffraction data implied *S*-coordination of the SCN groups. However, in $[Pd\{PPh(C_6H_4OMe)_2\}_2(SCN)_2]$ the $[SCN]^-$ may act as a bridging ligand [340]. Palladium(II) has bveen determined as $[H(lobeline)][Pd(H_2O)(SCN)_3]$ by amperometric titration with $[SCN]^-$ in the presence of lobeline, with 0.1 M H_2SO_4 as a background electrolyte. IR data implied that the [SCN] groups were *S*-coordinated in the complex [341].

Thermolysis of $[bipyH_2][M(SCN)_4]$ (M = Pd or Pt) yielded $[M(bipy)(SCN)_2]$, and a similar reaction was observed with 2-(2'-pyridyl)benzimidazole, pyBAZ. In the complexes prepared in this way the [SCN] group was *N*-coordinated in $[M(bipy)(NCS)_2]$ and $[Pt(pyBAZ)(NCS)_2]$, but *S*-bonded in $[Pd(pyBAZ)(SCN)_2]$. When $[Pt(bipy)(SCN)_2]$ was prepared from $K_2[Pt(SCN)_4]$ and bipy, the *S*-bonded complex was formed, and was only isomerised to the *N*-coordinated species at 130 °C

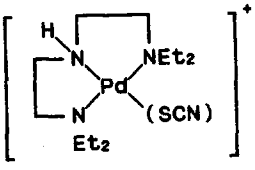
[342].

Photolysis of *trans*-$[Pd(PPr_3)_2(NCS)_2]$ in ethanenitrile gave (94), $[(Pr_3P)(SCN)_2Pd(\mu\text{-}N{\equiv}C)Pd(PPr_3)_2(NCS)]$, possibly *via* $[Pd(PPr_3)_2(SCN)_2]$. The modes of ligation in (94) suggests that both steric aand electronic effects are significant. No stable product was produced on photolysis in methanol, but the origin of the μ-CN was not definitively established [343].



(94) (Reproduced with permission from [343])

The influence of the conterion on the [SCN] bonding mode in (95) has been investigated. It had previously been stated that the $[BPh_4]$ salt contained the *S*-bonded ligand. Now it has been shown that this salt may exist in two forms. The unsolvated salt and the propoanone solvate contained the *N*-bonded ligand, whilst the methanol solvate was *S*-bonded, but unstable. The CH_2BrCl solvate was also *N*-bonded. It was concluded that the nature of the ligation was dictated by the crystal packing, and was not a direct consequence of the nature of the counterion [344].

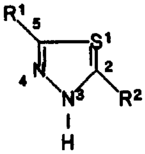


(95)

In the new complexes $[PtL_2Q_2]$ (L = NH_3, $MeNH_2$, Me_2NH, py or

2-amimopyrimidine; Q = methylated thiourea) the thiourea ligands were all *S*-bonded [345]. Palladium(II) forms both 1:1 and 1:4 complexes with thiourea; IR spectroscopic data imply that both contain the *S*-bonded ligand. A similar result was obtained for *N*-propenyl thiourea [346].

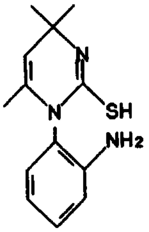
Palladium(II) complexes of variously substituted thiadiazoles, (96), have been prepared and characterised. The 2-mercapto-5-methylthiadiazole acts as an *S,N*-chelate, releasing halide, whereas the 2,5-dimethyl derivative acts as monodentate ligand, binding at the ring nitrogen atom. 2-Aminosubstituted ligands were bound at the amino function as monodentate ligands in most cases, but *N,N*-chelates were also formed in some complexes [347].



(96)

1.6.2.13 Bidentate and multidentate sulphur nitrogen donor ligands

2-Aminoethanethiol, HL, formed complexes of the type [PdL_2], which probably adopt *trans*-geometry [348]. Palladium(II) reacted with (97) to give a 1:2 complex, of unspecified structure, which was used for the spectrophotometric determination of palladium [349]. Complexes of stoicheiometry {$PtLCl_2$} in which L = (98) (R^1 = $(CH_2)_3NMe_2$ or $CH_2CH(Me)CH_2NMe_2$; R^2 = $COCHMe_2$ or OMe) were prepared from the ligand and $H_2[PtCl_6]$. Their insolubility suggested that the complexes were polymeric, and IR spectroscopic data indicated bonding through the sulphur atom and the tertiary nitrogen of the side chains [350]. Similar palladium complexes have also been reported [351].



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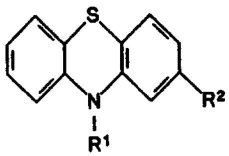
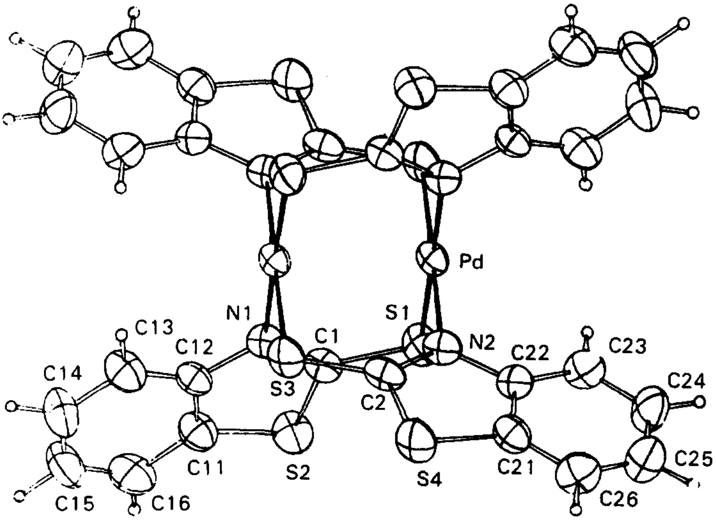


(98)

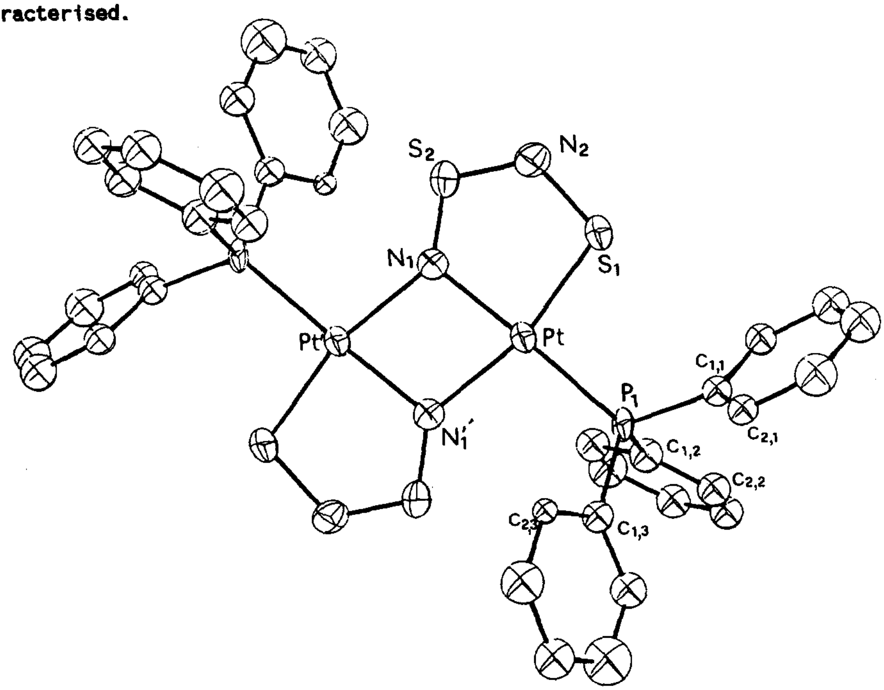
Palladium(II) could be extracted as [PdL_2] (the binding was assumed to be *via* the nitrogen of the heterocycle and the deproptonated mercapto group) using HL = 2-propyl-8-mercaptoquinoline [352]. Reaction of (99) (R = CH_2SEt or CH_2SPh) with $K_2[PtCl_4]$ at room temperature in water gave $[PtL_2][PtCl_4]$. However, if these or the ligands for which R = CH_2CH_2SMe or CH_2SMe were reacted with $K_2[PtCl_4]$ in dmf at 60 °C the product was $[PtLCl_2]$. The differences in the products with the reaction conditions were ascribed to differential solubilities [353]. Clear brick-like crystals of (100), tetrakis(*μ*-1,3-benzothiazole-2-thiolate-*N,S*)dipalladium(II), were obtained from the ligand and $K_2[PdCl_4]$. The palladium-palladium distance was determined to be 2.745(1) Å, less than that in palladium metal [354].

(99)



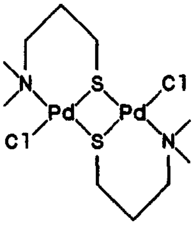
(100) (Reproduced with permission from [354].

Two groups have published the structure of (101) established in X-ray diffraction studies. In one case the platinum complex was prepared by reaction of $[Pt(PPh_3)_3]$ with S_4N_4, and the related palladium derivative using $[Pd(PPh_3)_4]$ [355], whilst in the other the complexes $[M(PPh_3)_2(C_2H_4)]$ were used as the precursors [356]. This is the first example of a binuclear platinum complex with inorganic sulphur nitrogen units to be thus characterised.



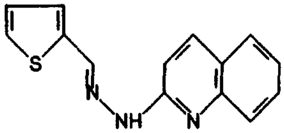
(101) (Reproduced with permission from [356])
Perspective view of $[(Ph_3P)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)]$. ORTEP drawing with 30 % probability ellipsoids.

The complex $[Pd_2L_2Cl_2]$, (102), in which L = $HS(CH_2)_3NMe_2$ was prepared and characterised. It was compared with the related nickel complexes [357].



(102)

For a reviewer who is attempting to be systematic, this area contains much material which is highly irritating, since a number of authors present data about new complexes without making very much attempt to prove their structures definitively. For example, Pd^{2+} is said to form a 1:1 complex with (103) at pH 1, but the paper gives no details of the structure, nor any data which might allow readers to draw their own conclusions [358]. Data concerning derivatives of thiosemicarbazones is often similarly lacking. (104) reacted with both palladium(II) and platinum(IV), but the mode of binding in the products was not proven [359]. IR spectroscopic data suggested binding at the imino nitrogen and the thiocarbonyl for $[PtLX_2]$, L = (105) [360]. UV spectroscopic data were reported for complexes of the type $[ML_2]$ (M = Pd or Pt; HL = $RR'C{=}NNHC({=}S)NH_2$), in which bonding through the imino nitrogen and deprotonated thiolate in the tautomeric form of the ligand occurs [361]. In neither these cases nor in the related complex of (106) was it clear whether *cis*- or *trans*-isomers had been formed [362].



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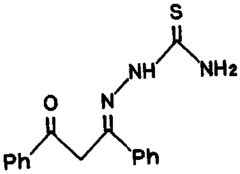

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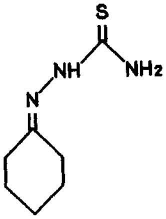

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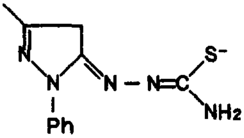
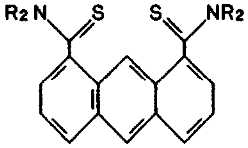


(106)

Reaction of the bis(thioamide), (107), with $[Pd(PhCN)_2Cl_2]$ gave a bis(palladium) derivative, with *N,S*-coordination [363]. Treatment of $[Pt(PPh_3)_2(C_2H_4)]$ with (108) resulted in a ring opening oxidative addition reaction to give (109), characterised by an X-ray diffraction study [364]. New complexes of the type (110) have been prepared and characterised [365].

A direct spectrophotometric method for the determination of *cis*-platin in urine was based on complexation with (111) [366].

Crown ether type ligand containing sulphur and nitrogen binding sites have been prepared. (112) reacted with $[Pd(PhCN)_2Cl_2]$ to give a bis(palladium) derivative, (113), characterised by microanalysis, IR spectroscopy and mass spectrometry. The related monopalladium derivatives of (114) and (115) were also prepared [367]. In the FAB mass spectrum of $[(113)]Cl_2$ the $\{LPd_2Cl_3\}^+$ fragment gave rise to a particularly intense signal [368]. Palladium(II) and platinum(II) complexes of 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane have been prepared [369].



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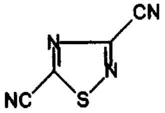

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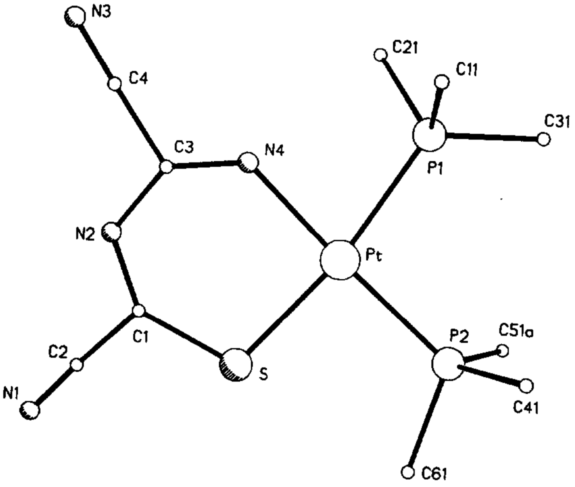
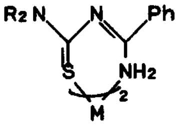


(109) (Reproduced with permission from [364])

For the sake of clarity only the first carbon atom of each phenyl ring is shown. The asymmetric unit contains 1.5 disordered molecules of dioxan, and one phenyl ring is disordered.



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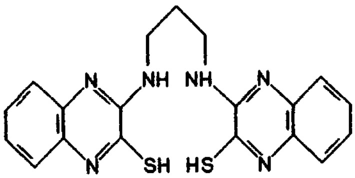

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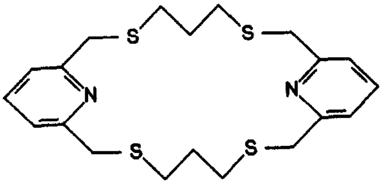

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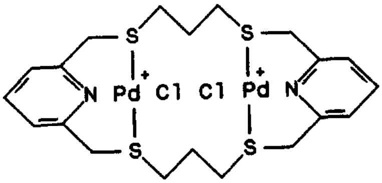

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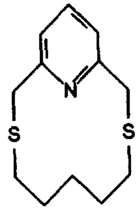

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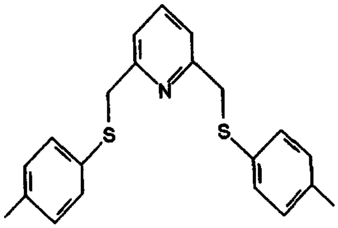
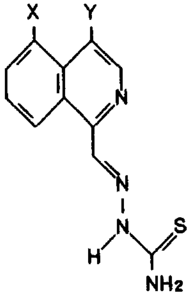


(115)

A series of heterocycle substituted thiosemicarbazones have provided tridentate ligands in complexes of the type [MLCl] (M = Pd or Pt). For example, (116) (X = H or NH_2; Y = H or Me) reacts with $K_2[PtCl_4]$ to give a species coordinated through the imine nitrogen, the ring nitrogen and the deprotonated thiol [370,371]. A similar derivative was prepared of (117), but all these complexes showed poor anti-tumour activity [372].



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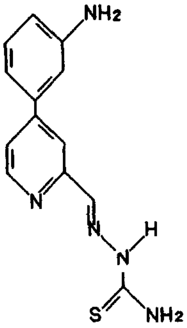
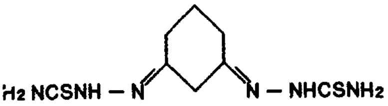


(117)

The potentially polydentate ligand (118) reacted with $PdCl_2$ to give [PdL]Cl. The structure proposed was (119), on the basis of IR and UV spectroscopic measurements and conductivity data [373]. The product obtained from the reaction of HL, PhCH(Me)NHC(=S)NRNR'R", with palladium(II) depended on the pH of the reaction solution. At low pH $[Pd(HL)_2]Cl_2$ was formed, but in less acidic solution the product was $[PdL_2]$, (120). Very detailed mass spectrometric studies were used to demonstrate that the complex was monomeric [374].



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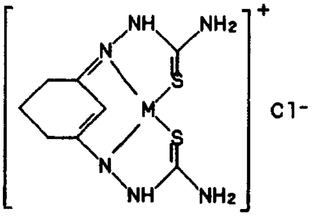
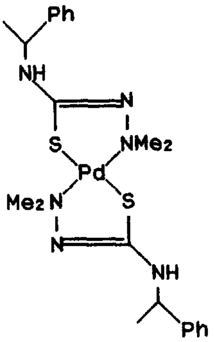


(119)

Square planar monomeric complexes of diphenylthiocarbazone, (121), H_2Dz, of stoicheiometry $[M(HDz)_2]$ could be prepared for M = Pd or Cu, but it was not deduced whether *cis-* or *trans-*isomers were formed. Resonance Raman spectroscopic data indicated *trans-*geometry. The species [MDz] probably have the structure (122) [375,376]. Palladium(II) has been extracted using (121)

[377].



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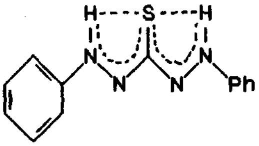

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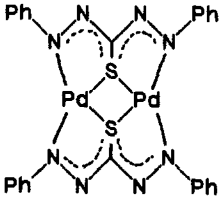


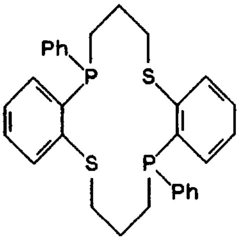
(122)

1.6.2.14 Bidentate and multidentate sulphur phosphorus donor ligands

Preparations of the complexes *trans*-$[ML_2][ClO_4]$ (M = Pd or Pt, L = $Ph_2P(CH_2)_2SR$) have been described. Monodentate species $[M(L\text{-}P)_2X_2]$ were also reported [378]. Many analogues of crown ethers containing sulphur and phosphine binding sites have been prepared. Reaction of (123) with $[Pt(cod)Cl_2]$ followed by treatment with $Ag[PF_6]$ gave $[PtL][PF_6]_2$, (124). The X-ray diffraction study established that the phenyl groups were *cis*, and that both the $\{SPtP(CH_2)_3\}$ rings adopted a chair conformation [379].

1.6.2.15 Bidentate sulphur carbon donor ligands

The product of the cyclometallation of (124) depended on the conditions of the reaction. The product, (126), was a mixture of dl and *meso* isomers, which could be resolved by addition of a chiral ligand in a bridge splitting reaction, and separation of the products [380,381].



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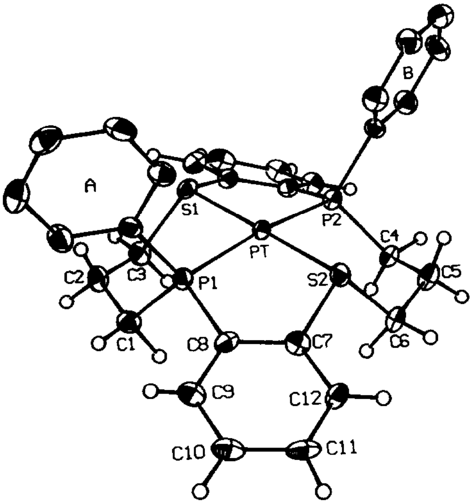


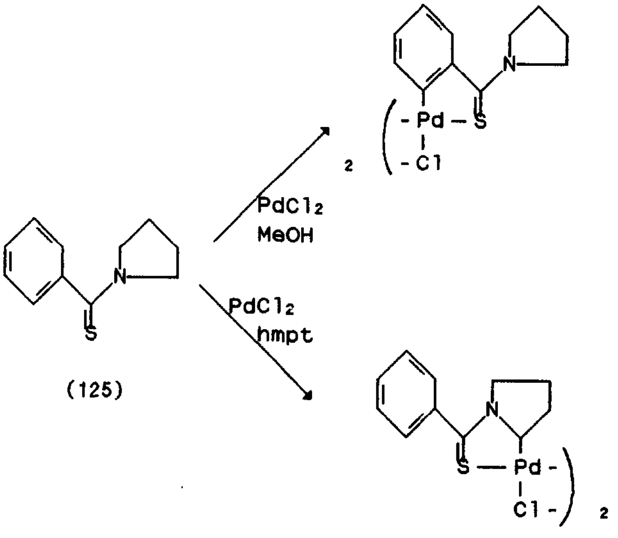
(124) (Reproduced with permission from [379])

ORTEP plot with non-hydrogen atoms represented as 30 % probability ellipsoids

1.6.2.16 Selenium donor ligands

Reaction of $[M(MeCN)_2X_2]$ (M = Pd or Pt; X = Cl, Br or I) with a range of bis(selenoethers), (L-L, including $MeSe(CH_2)_2SeMe$, $PhSe(CH_2)_2SePh$, Z-MeSeCH=CHSeMe and 1,2-bis(methylseleno)benzene), gave $[M(L\text{-}L)X_2]$. The complexes were characterised by microanalysis, UV, ^1H, ^{77}Se and ^{195}Pt NMR spectroscopy. The trends in $\delta(^{77}Se)$ and $^1J(PtSe)$ with the invertomer, chelate ring size and *trans*-halide were discussed [382]. The complexes $[M\{MeC(CH_2SeMe)_3\}Cl_2]$ (M = Pd or Pt) were prepared and characterised. the ligand was bidentate, and NMR spectroscopy was used to determine the rate of pyramidal inversion at selenium. Complexes of various other bis(selenoethers) were also prepared [383].

The complex (127) proved to be an effective anti-tumour agent, and a number of analogues were also prepared [384].



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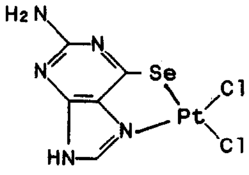


(127)

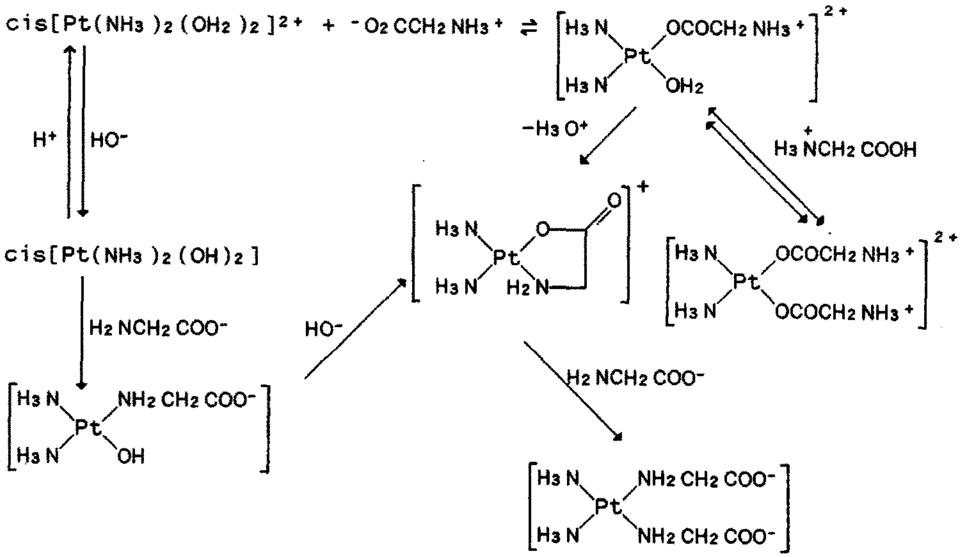
1.6.3 Complexes with amino acids, peptides and nucleic acids

Since most biologically important molecules bind to palladium and platinum through Group 16 and Group 15 donor atoms, the practice of considering them between ligands belonging to these two groups is continued.

1.6.3.1 Amino acids

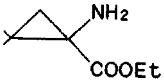
Palladium(II) complexes with amino acids and peptides have been reviewed [385].

The complexes *cis*-$K[Pt(NH_2CH_2COO)Cl_2]$ and *cis*-$Cs[Pt(L\text{-serinato})Cl_2]$ have been investigated with respect to their anti-tumour action; it was found to be significant, but lower than that of *cis*-platin [386]. The products of the reaction of *cis*-platin with glycine or histidine have been analysed by electrophoresis and ^1H and ^{13}C NMR spectrsocopy. Chelating complexes appeared to be the main products [387]. The reaction of $[Pt(H_2O)_4]^{2+}$ with glycine has been reinvestigated in considerable detail, by spectroscopic techniques. The monocarboxylate substituted complex, *cis*- and *trans*-disubstituted carboxylate complexes and the *cis*- and *trans*-chelating complexes were identified under appropriate conditions. The reactions with *cis*-platin were shown to be equally complex (Scheme 2). This is the first report of glycine complexes which involved only carboxylate binding [388].



Scheme 2 Reactions of *cis*-platin with glycine

The syntheses of the complexes *cis*-$[Pt(H_2NCMe_3)\{H_2NCH(R)COOH\}Cl_2]$ (R = H, Me, CH_2Ph, CH_2OH, $CH(OH)CH_3$ or $(CH_2)_4NH_2$) *via* $[Pt(H_2NCMe_3)Cl_3]^-$ have been described. The complexes had low anti-tumour activity [389]. The complex *trans*-$[ML_2Cl_2]$ (L = (128)) was prepared and characterised in an X-ray diffraction study; *O,N*-chelating complexes were formed from the free acid [390]. When $Li_2[PdCl_4]$ was reacted with $Me_2NCH(Ph)COOH$, HL, a *trans-O,N*-chelating complex was formed, and could be crystallised on addition of sodium ethanoate. Under the same conditions the related ethyl ester gave the cyclometallated complex (129) [391].



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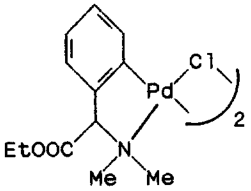
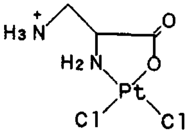


(129)

The reactions of $[PdCl_4]^{2-}$ with HL, $ArNHCH_2COOH$, gave chelated complexes $[PdL_2]$, which were suggested, on the basis of IR spectroscopy, to possess *trans*-geometry. Reaction with $[4\text{-}EtC_6H_4N(CH_2COOH)CH_2COO]Na$ also gave an *N,O*-chelate. On thermolysis the unbound carboxylate lost CO_2 fairly readily, with the bound carboxylate reacting only at much higher temperatures. By contrast, $2,6\text{-}Me_2C_6H_3N(CH_2COOH)_2$ gave an *O,O*-chelate, which underwent only a single decarboxylation [392].

When $H_2NCH_2CH(NH_2)COOH.HCl$, HL.HCl, was reacted with $K_2[PtCl_4]$, a mixture of *cis- and trans*-$[Pt(LHCl)_2Cl_2]$ was formed, in which only the carboxylate group was metal coordinated. On heating this was rapidly transformed to the *N,O*-chelate, (130), and longer heating gave (131) [393]. In a rather similar reaction sequence, L-2,4-diaminobutanoic acid reacted to give (132) as the initial product, which could be converted on heating to (133). Lysine and ornithine gave *N,O*-chelates, whilst 4,5-diaminopentanoic acid gave an *N,N*-chelated product, indicating that the size of the chelate ring formed is important in determining the nature of the product of this type of reaction [394].



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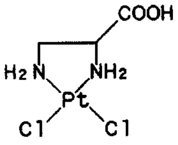

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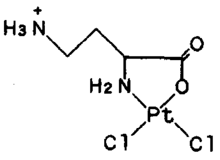

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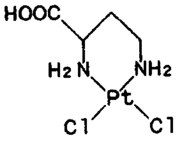
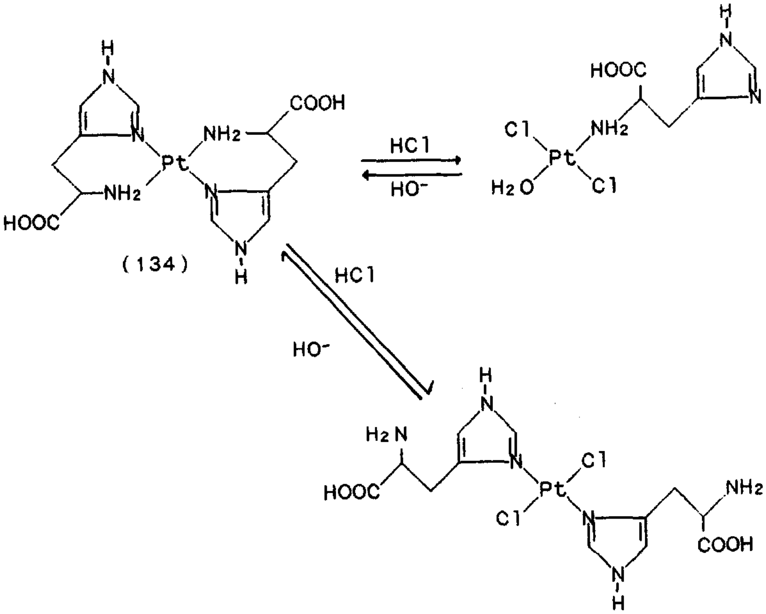


(133)

The reaction of $H_2[PtCl_4]$ with histidine has been reinvestigated. The initial product, (134) underwent various acid base transformations. Reaction with *cis*-platin gave a range of products; (135) was stable and could be isolated and purified, whilst the others (Scheme 3) were identified by electrophoresis [395].

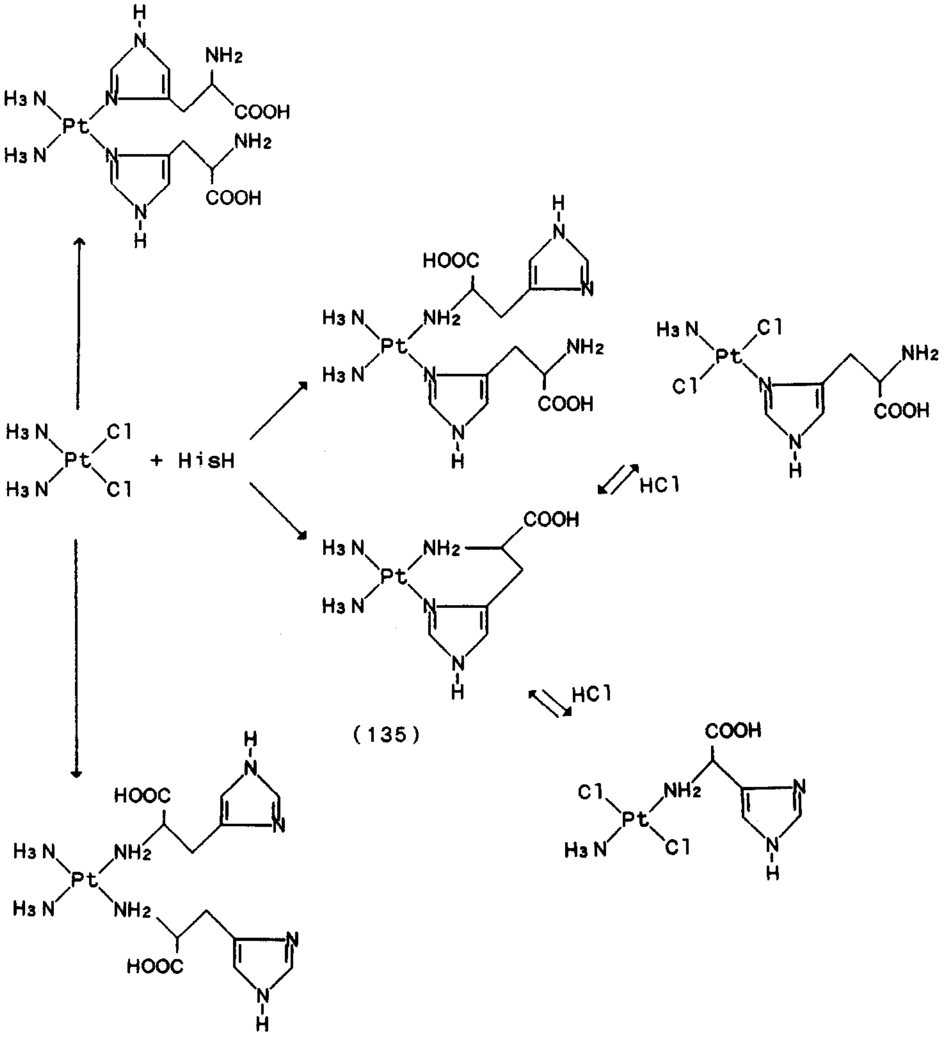


(134)

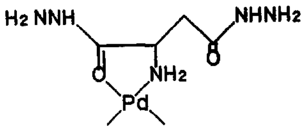
The synthesis of [Pt(pro)(pyrrolidine)Cl] has been described. The prolinato anion was shown to be *N,O*-chelated, and the nitrogen atoms to be *trans* in an X-ray diffraction study. The 5-membered ring of the proline ligand adopted an envelope conformation [396].

Reaction of $K_2[PtCl_4]$ with HL, *S*-alkyl cysteine, gave a series of complexes $[Pt(HL)Cl_2]$, $[Pt(HL)_2]Cl_2$ and $[PtL_2]$, in which the amino acid acted as an *S,N*-chelate. Two diastereomers of each complex were formed, due to the generation of a chiral centre at the sulpur atom. When $[Pt(HL)Cl_2]$ reacted with a nucleoside, such as guanosine or inosine, complexes of the stoicheiometry $[Pt(HL)(nucl)_2]$, in which the nucleoside was bound at N(7), were formed. The higher *trans*-influence of the sulphur ligand meant that the nucleoside *trans* to sulphur had a longer and weaker N-Pt bond [397]. $[Pt(HL)Cl_2]$ (HL = methionine) reacted with ammonia to give $[Pt(NH_3)_2L]Cl$ in which the amino acid anion was *S,O*-ligated. A similar type of binding was found in $[Pt(NH_3)(OH_2)Q]$ (H_2Q = cysteine), whilst in $[Pt(NH_3)_2(H_2O)Z]^-$ (H_3Z = glutathione) the glutathione moiety was *S*-bonded [398].

Various palladium and platinum complexes of D-cycloserine have been prepared and used in assays of the amino acid. The structures of the materials obtained were not, in general, established [399]. Reaction of $K_2[PdCl_4]$ with aspartic acid dihydrazide gave $[Pd_2L_2Cl_2]Cl_2$ or $[Pd_2L_2Cl_2][OH]_2$ depending on the reaction conditions. EPR, IR and UV spectra indicated that chloride ions bridged the dinuclear cations, and that the ligands were coordinated through amino nitrogen and carbonyl groups, (136) [400]. A more extensive study using both mono and dihydrazides of aspartic and glutamic acids, allowed the preparation of both mono and dinuclear complexes, and *N*,*N*- and *N*,*O*-chelates, the exact course of the reaction depending both on the ligand and the reaction conditions [401]. The complex (137) was prepared by reaction of the glycinato metal complex with an amide acetal. A related process occurred with $Me_2NCH(OR)_2$ [402].



Scheme 3 Reactions of histidine with *cis*-platin [395].



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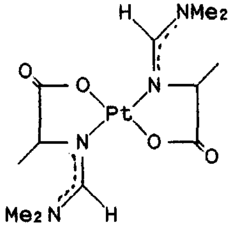
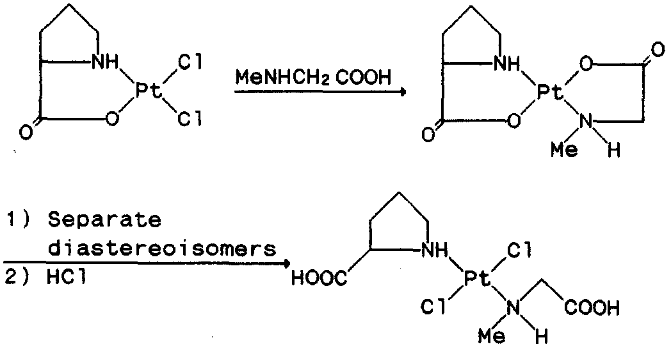


(137)

The structure of the novel complex *trans*-[Pt(hydroxyprolinate)$_2$].2H$_2$O was determined in an X-ray diffraction study. The five membered chelate rings adopted a flattened envelope conformation with the pyrrolidine rings gauche. UV and CD spectroscopic data were compared with those for *trans*-[Pt(hydoxyprolinate)(prolinate)] and *cis*- and *trans*-[Pt(prolinate)$_2$] [403]. In *trans*-[Pt(pro)(proH)X] (X = Cl or Br) the proline is a unidentate ligand, and the complex exists as a mixture of diastereoisomers due to the chiral centre at the nitrogen donor atom. For the diastereoisomer with the S-configuration at the bound nitrogen, conversion to the chelate complex [Pt(pro)$_2$], is very rapid, but the reaction was rather slow for the complex with the R-configuration at this position. In basic solution an equilibrium was established between the distereoisomers with the R-isomer very much more abundant [404]. In the complex *trans*-[Pt(proH)(sarH)Cl$_2$], prepared *via* reaction (14), the configuration at the proline nitrogen was R, but both configurations were found at nitrogen in the other ligand [405].



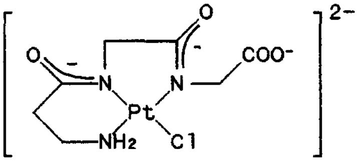
(14)

Complexes of the type [Pt(bipy)L]$^{n+}$ (HL = amino acid; n = 1 or 2) were shown to inhibit the growth of P388 lymphocytic leukaemic cells *in vitro* [406]. Reaction of *trans*-[Pt(H$_2$NCRR'COO)$_2$] with [NO][X] ([X] = [PF$_6$], [BF$_4$] or [SbF$_6$]) in ethane nitrile at -20 °C gave a blue complex {(ON)Pt(H$_2$NCRR'COO)$_2$}X, which could be converted to the platinum(IV) species, [Pt(H$_2$NCRR'COO)$_2$X$_2$], by X$_2$ or LiX. Nitrosation of the amino group did not occur [407].

1.6.3.2 Peptides

Chloro glycyl-L-methioninato platinum(II), prepared from $K_2[PtCl_4]$ and glycyl-L-met, has been used specifically to label methionine residues in collagen, and hence to discriminate collagen types [408]. This complex was also used to label histones, for scanning TEM [409].

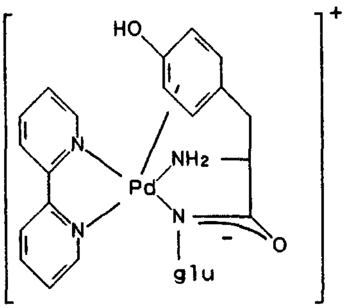
The reaction of $[PtCl_4]^{2-}$ with triglycine, $[H_2G_3]^-$, gave a mixture of the complexes $[Pt(G_3)Cl]^{2-}$, (138), $[Pt(G_3)]^-$ and $[Pt(G_3)(OH)]^{2-}$ identified by ^1H, ^{13}C and ^{195}Pt NMR spectroscopy. The value of the ^{195}Pt chemical shift was very high, indicating the high donor strength of the deprotonated nitrogen atom of the peptide. Some CD data for related alanyl complexes were presented [410]. The stability constants of palladium(II) glygly complexes with a series of aliphatic amines were logarithmically related to the pKa's of the amines [411].



(138)

Various platinum(II) complexes of glyalaH (gaH_2), *cis*- and *trans*-$[Pt(gaH_2)_2Cl_2]$, *cis*- and *trans*-$[Pt(NH_3)_2(gaH)_2]$, *cis*- and *trans*-$[Pt(NH_3)_2(gaH_2)_2]Cl_2$ have been prepared and characterised. The complexes closely resembled the related glygly complexes, and in all cases the peptide acted as a unidentate ligand, coordinated through the $-NH_2$ group [412]. Both *cis*- and *trans*-$[Pt(peptide\ ester)_2Cl_2]$ could be prepared by peptide synthesis at the free carboxyl group of an *N*-coordinated amino acid, using a water soluble carbodiimide as the coupling agent. The free peptide ester could be recovered using either dppe or molecular hydrogen, with little or no racemisation [413].

Rotamer populations in (139) and the related copper complex were investgated using ^1H NMR spectroscopy. The data indicated that there was stacking between the bipy ligand and the aromatic side chain of the peptide [414]. At acidic pH the growth modulating tripeptide, H-gly-his-lys-OH formed complexes (140) with $K_2[PdCl_4]$, involving the glycyl nitogen atom, and the α- and ring nitrogen atoms of the histidine [415].



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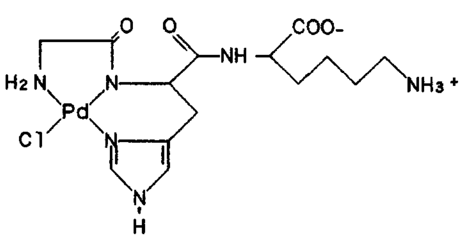
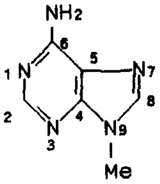


(140)

1.6.3.3 Nucleic acids and nucleosides

The FTIR spectra of nucleic acids and their metallated derivatives have been reviewed [416]. The interaction of *cis*-platin with DNA and model nucleobases has been discussed [417]. A Raman and CD spectroscopic study of the determination of the secondary structure of nucleic acids as a function of base composition and platination, revealed distinct differences between *cis*- and *trans*-platin, in both low and high salt conditions [418]. A review of reactive derivatives of nucleic acids as affinity reagents included a discussion of bifunctional platinum complexes [419].

Ion exchange chromatography was used to isolate mono platinated derivatives of adenine, guanosine and cytosine, but characterisation of the complexes was poor [420]. Platinum complexes of 9-methyladenine, (141) and 1-methylcytosine, (142), have been studied. Reaction of $[Pt(9\text{-}MeAH)Cl_3]$ with ammonia gave $[Pt(9\text{-}MeA)(NH_3)_3]^{2+}$. The structure of the $[ClO_4]^-$ salt was established in an X-ray diffraction study, coordination of 9-MeA being through N(7) [421]. A range of mixed complexes including the mononuclear species *cis*-$[Pt(NH_3)_2\{9\text{-}MeA\text{-}N(7)\}\{1\text{-}MeC\text{-}N(3)\}]^{2+}$, (143), *cis*-$[Pt(NH_3)_2\{9\text{-}MeA\text{-}N(1)\}\{1\text{-}MeC\text{-}N(3)\}]^{2+}$, and the related *trans*-$[Pt(NH_3)_2\{9\text{-}MeA\text{-}N(7)\}\{1\text{-}MeC\text{-}N(3)\}]^{2+}$, (144), and the binuclear complex, *cis*-$[(NH_3)_2\{1\text{-}MeC\text{-}N(3)\}Pt\{\mu\text{-}9\text{-}MeA\text{-}N(1),N(7)\}Pt\{1\text{-}MeC\text{-}N(3)\}(NH_3)_2]^{4+}$, were prepared and characterised. In (143) the two nucleobase planes are at right angles relative to the platinum coordination plane with a hydrogen bond between the exocyclic keto group of 1-MeC and the exocyclic amino group of 9-MeA, giving a 91.6 ^{o} angle between the two base planes. In (144) the nucleobases are close to coplanar, but perpendicular to the platinum coordination plane [422]. 1:1 Complexes of palladium(II) with adenosine 5'-monophosphate have been isolated, $[Pd(H_2AMP)Cl_2]$. Binding involved N(7) of the purine and the phosphate [423].



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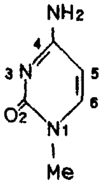

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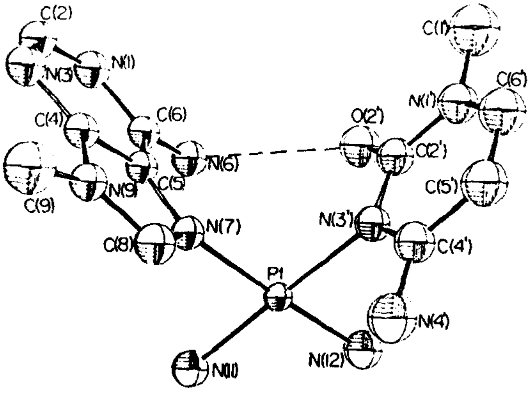
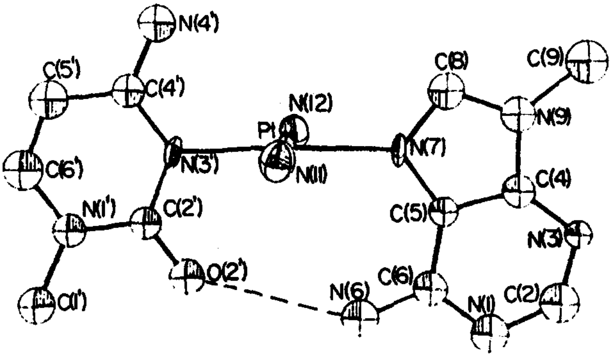


(143) (Reproduced with permission from [422])

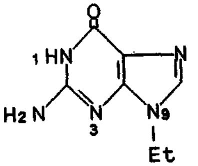


(144) (Reproduced with permission from [422])

Kinetic studies of the reaction of $[Pt(NH_3)_2(OH_2)_2]^{2+}$ with various nucleobases showed that guanosine reacted faster than adenosine, cytidine or thymidine. A monophosphate unit considerably enhanced the rate of reaction of guanosine [424]. The preparation of $Ca[Cu(5'\text{-}GMP)_2(en)(OH_2)_2].8H_2O$ has been reported, and the complex was characterised by an X-ray diffraction study.

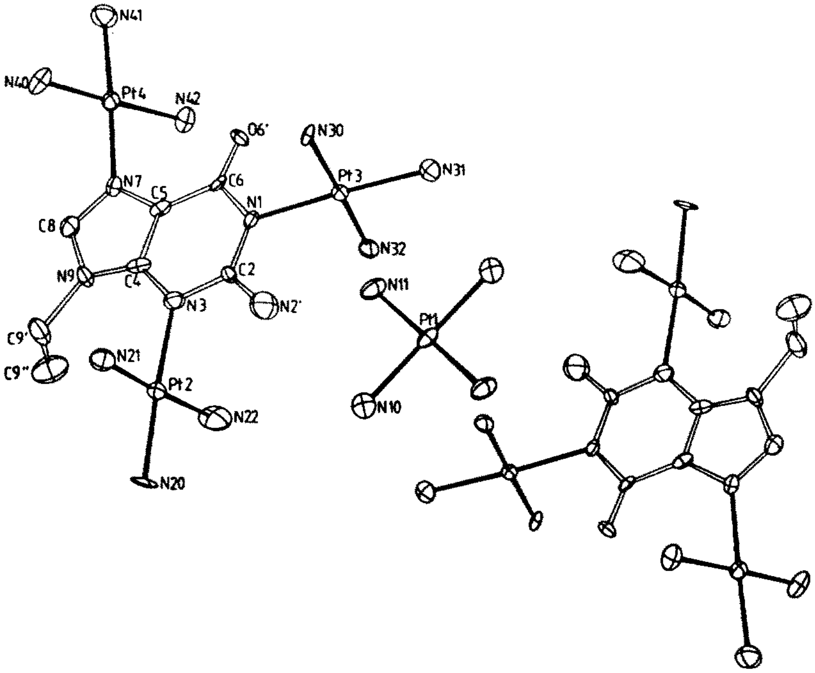
This is the first non-platinum complex in which the central metal ion shows coordination essentially identical to that of the analogous platinum complex, and suggests that copper might be a potential candidate for replacement of platinum in anti-tumour complexes [425].

The reaction of 9-ethylguanine, GH, (145), with $[Pt(NH_3)_3(H_2O)]^{2+}$ yielded $[Pt(NH_3)_3(GH)]^{2+}$ in which the GH was bound at N(7), $[(NH_3)_3Pt(\mu\text{-}G)Pt(NH_3)_3]^{3+}$, in which the deprotonated guanine was platinated at N(7) and N(1), and finally $[\{Pt(NH_3)_3\}_3(G)]^{5+}$ with guanine platinated at N(7), N(1) and N(3). The structure of $[\{Pt(NH_3)_3\}_3(G)][NO_3]_5.0.5[Pt(NH_3)_4][NO_3]_2.H_2O$, (146), was established in an X-ray diffraction study, this being the first example of an X-ray structure of a guanine complex with a site of platination other than N(7) [426]. In *cis*-$[Pt(NH_3)_2(GH)_2]X_2$ ($[X]^- = [NO_3]^-$, Cl^-, $[ClO_4]^-$, $0.5[SO_4]^{2-}$, or $0.5[Pt(CN)_4]^{2-}$) the 9-ethylguanine was coordinated to platinum at N(7). The structures of the sulphate and tetracyanoplatinate salts were determined by X-ray diffraction studies, and the guanines were shown to be head-to-head, as is the case in the previously studied chloride. However, the three complexes did show differences in dihedral angles between the guanine planes which led to variations in the interbase distances. The solid state Raman spectra of the complexes could be divided into three classes which differed in the degree of intramolecular base overlap [427].



(145)

The N(7)-O(6) chelate hypothesis for guanine binding to platinum has once again been receiving attention. Titration curves for *cis*-$[Pt(NH_3)_2(9\text{-ethylguanine})(OH_2)]^{2+}$ suggested that this is not significant. All the available data indicated that *cis,cis*-$[(NH_3)_2\{GH\text{-}N(7)\}Pt\{\mu\text{-}G\text{-}N(1),N(7)\}Pt(NH_3)_2(OH_2)]^{3+}$ was formed [428]. A range of mono and bis nucleobase complexes has been prepared, and their reactions with $[CN]^-$ investigated. Monodentate 9-ethylguanine or 9-methyladenine bound at N(7) were substituted rapidly, as was 1-methylcytosine bound at N(3), except in mixed complexes with deprotonated 1-methyluracil, (U), or deprotonated 1-methylthymine, (T). The kinetic stability of complexes containing U or T was general, and was due to the shielding of platinum by the exocyclic oxygen atoms close to the platinum coordination site. The first ligand substitution by $[CN]^-$ led to labilisation of both *cis* and *trans*-ligands, and eventually to the formation of $[Pt(CN)_4]^{2-}$ [429].



(146) (Reproduced with permission from [426])

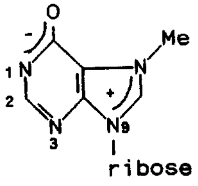
View consisting of a pair of centrosymmetrically arranged $[\{(NH_3)_3Pt\}_3(G)]^{5+}$ cations and a $[Pt(NH_3)_4]^{2+}$ cation in the centre of inversion between the two trinuclear species.

The six diastereomeric conformations of the chiral square planar complex $[Pt(N,N'-Me_2en)(guanosine)_2]$ have been investigated. Three sets arise from the configurations of the nitrogen atoms of the en ligand, and the ribose moieties of the guanosines break mirror symmetry in and between the stereoisomers. Rotation about the platinum guanosine bond, which was shown to be fast on the nmr spectroscopic timescale at 103 °C, causes exchange within each pair of diastereoisomers [430]. Model complexes *cis*-$[Pt(NH_3)_2(N)_2]Cl_2$ in which N was guanosine, inosine or xanthosine were prepared. Many spectroscopic data were reported, and it was shown that guanosine formed the strongest complex. The use of the complexes in the treatment of herpetic lesions was explored [431]. NMR spectroscopic and titration data have been presented for $[Pt(NH_3)_2L_2]Cl_2$

and $[Pt(NH_3)_2LL']Cl_2$ in which L = cytosine-N(1) or -N(3), or cytidine-N(3) and L' = guanosine-N(7) or inosine-N(7) [432]. Reaction of an excess of *cis*-platin with guanosine, guoH, in the presence of $[Cl]^-$ gave three products, *cis*-$[Pt(NH_3)_2(guo)_2]^{2+}$, *cis*-$[Pt(NH_3)_2(guo)Cl]^+$ and *cis,cis*-$[(NH_3)_2ClPt\{\mu\text{-guo-N(7),N(1)}\}Pt(NH_3)_2Cl]^+$, analogous to tthe products previously reported with GMP [433].

There has been a study of *cis*- and *trans*-$[Pt(NH_3)_2(5'GMP)_2]$ and the derivatives of the related desoxy ligand by ${}^1H$ NMR spectroscopy at 400 MHz. Whilst in all cases the platination was at N(7), the *cis*- and *trans*-complexes showed substantially different conformational changes in the nucleotide [434]. In particular, in the *cis*-complex, the ${}^3E \rightleftharpoons {}^2E$ equilibrium for the sugar was significantly shifted towards the 3'-*endo* conformers [435]. It was also clear that the purine ring was reorientated on N(7)-platination [436].

The reaction of 7-methylinosine, (147), with *cis*-$[Pt(dmso)_2Cl_2]$ was studied by NMR spectroscopy. The initial displacement was of a chloride ligand, and various equilibria were noted (Scheme 4). The inosine was bound to the metal at N(1), and similar results were obtained with 7-methyl-9-propyl hypoxanthine, (148). Cytidine derivatives were also studied, but complex formation was less favourable in these cases [437]. The kinetics of the substitution of halides ions in $[Pt(NH_3)_2LX]X$ (L = inosine or cytidine) by further inosine or cytidine have been studied. The substitution of X was slower using inosine as the incoming ligand, but the presence of inosine in the initial complex accelerated reaction, presumably due to its bulk [438].



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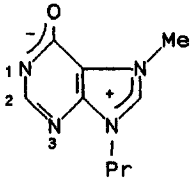
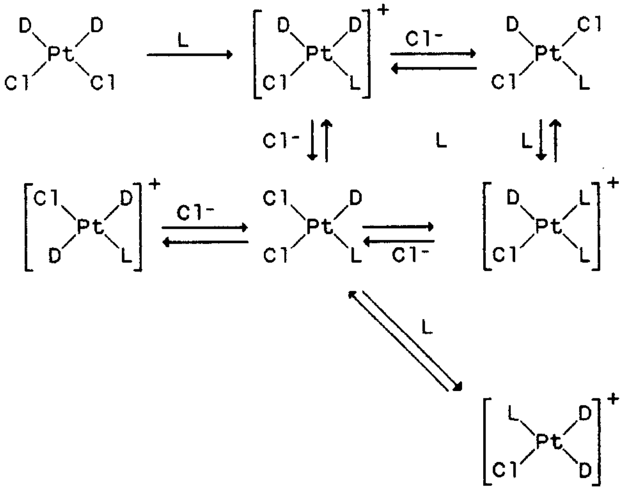
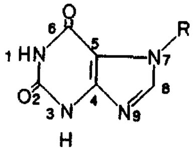


(148)

A wide range of complexes of substituted xanthines, (149), (XH), has been prepared, and their binding sites assigned by IR spectrsocopy. In $[Pd(1\text{-}MeX)_2(NH_3)_2]$ and $[Pd(NH_3)_2(7\text{-}MeX)_2]$ binding was at N(9), whilst in $[Pt(NH_3)_2(9\text{-}MeX)]Cl$ the xanthine acted as a chelating ligand bound at O(6) and N(7). In $[Pd(7\text{-}MeXH)_2]Cl_2$ chelation involved O(2) and either N(1) or N(3) [439]. In a study using 8-ethylxanthine, complexes of the type *trans*-$[PdL_2Cl_2]$ were prepared and characterised. In this case ${}^1H$ NMR spectroscopy was used to show that the ligand binding site was N(9) [440]. Thermochemistry of the complexes, as well as of the free ligands, has also been studied [441]. In the thermal decomposition of *trans*-$[Pt(NH_3)_2(3\text{-}MeX)_2]$ and *trans*-$[Pd(NH_3)_2(9\text{-}MeX)_2]$ the ammonia ligands were lost first, but this was followed by a rapid loss of the xanthine. The activation energy for the second process suggested that the pyrimidine was intially cleaved, and that this was closely followed by the loss of the remaining imidazole [442]. In the complex $[Pt(en)L]_2[PF_6]_2$ of L = (150), each platinum was coordinated to two non-linked hypoxanthine bases *via* N(7) [443].



Scheme 4 Equilibria in the reaction of 7-methylinosine, L, with *cis*-$[Pt(dmso)_2Cl_2]$ (D = dmso) [437].



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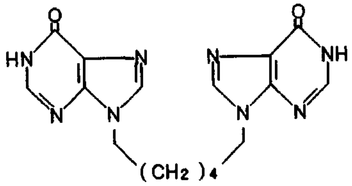
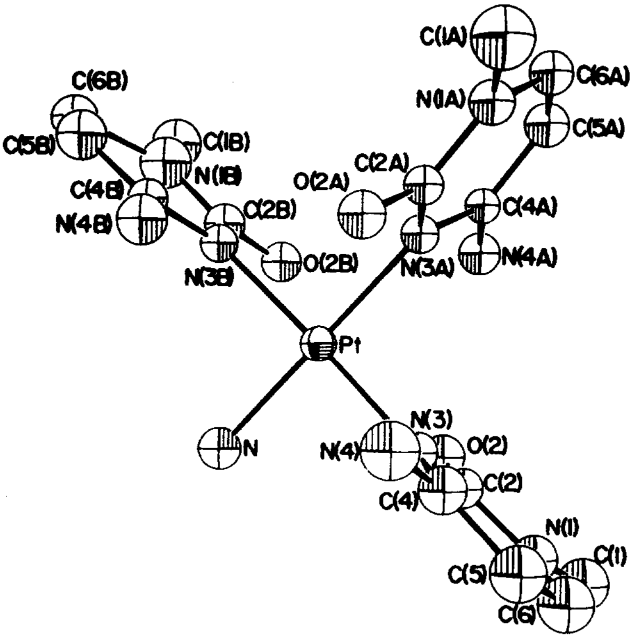


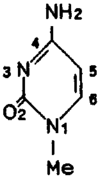
(150)

Complexes of theophylline, HL, $[ML_2].xH_2O$ (M = Pd or Pt; x = 2, 3 or 4) were prepared and poorly characterised by microanalysis, IR spectroscopy and TGA. It was suggested that bonding was through N(7) [444]. A poorly characterised series of mixed ligand complexes of 2,6-diaminopurine and 6-thioguanine was reported [445].

The tris(nucleobase) complex, $[Pt(NH_3)(1\text{-}MeC)_3][ClO_4]_2.H_2O$, (151), (1-MeC = 1-methylcytosine, (152)) was prepared and characterised by an X-ray diffraction study. The 1-MeC was bound to platinum at N(3) and the *trans*-cytosine ligands were roughly coplanar [446]. The structure of *cis*-$[Pt(NH_3)_2\{1\text{-methylthyminato-}N(3)\}Cl]$, (153), was also established; there were no intramolecular hydrogen bonds [447].



(151) (Reproduced with permission from [446])



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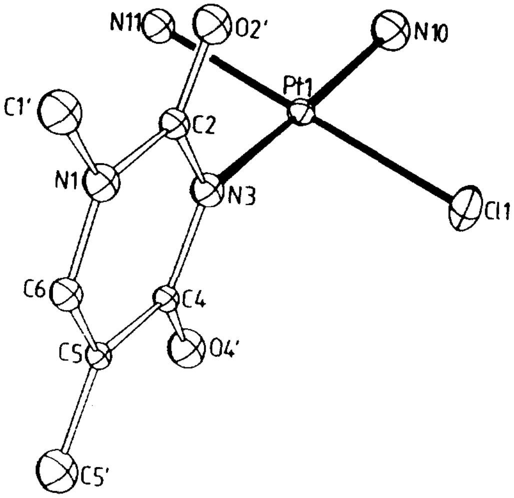
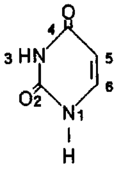


(153) (Reproduced with permission from [447])

Hydrazine derivatives of the anions of uracil, HU, (154) and 6-azathymine, ATH, (155), formed complexes of the type [{PtUCl}$_2$].nH$_2$O, which were prepared and characterised. The ligands acted as chelates bonded through N(3) and the hydrazine NH$_2$ group [448]. The anionic ligands 1-MeU and 1-methylthymine, (1-MeTH = (156)) are generally platinated at N(3). Reaction of *cis*-[Pt(NH$_3$)$_2$L$_2$] with simple metal salts gave species of the type (157) and (158) [436].



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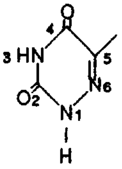

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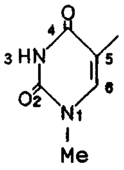

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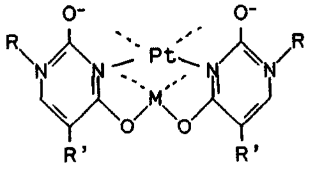

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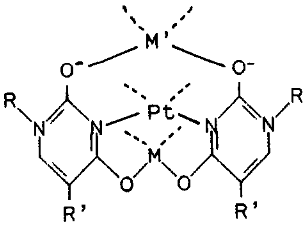
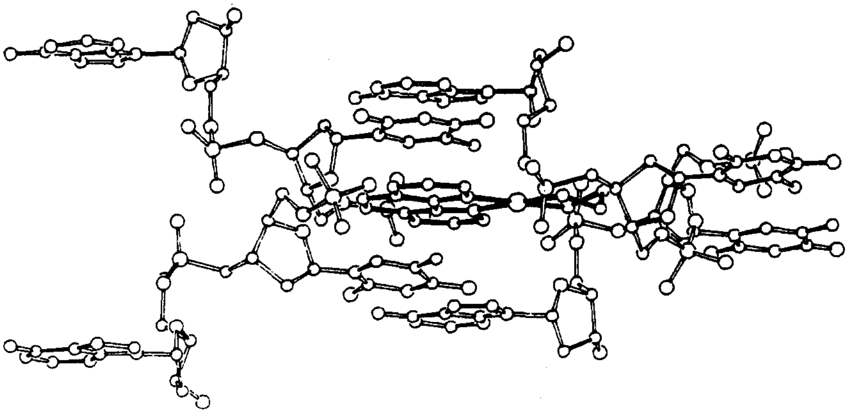


(158)

The ^{1}H and ^{31}P NMR spectra of *cis*-[Pt$(NH_3)_2${d(CpGpG)-N7(2),N7(3)}] together with pH profiles were interpreted in terms of stack ⇋ destack equilibria changes. d(CpGpG) adopts a normal B DNA-like single helical stucture, but in the platinated species the central sugar ring adopts an *N*-type conformation. Despite this, the C(1) residue stacks well on G(2), with normal backbone torsion angles [450]. The conformations of *cis*-[Pt(LL){d(GpCpG)-N7(1),N7(3)}] (LL = $(NH_3)_2$, en, tmen or 1,2-bis(aminomethyl)cyclohexane) were also studied by NMR spectroscopy. In all but the tmen derivative there was fast Pt-N(7) rotation on the NMR spectroscopic timescale, and a head-to-tail arrangement of the guanines at platinum. The tmen induced changes due to restricted rotation about the Pt-N(7) bonds, resulting in a preferred and rather rigid conformation [451].

The cation $[Pt(phen)(en)]^{2+}$ forms a 1:2 crystalline complex with the 5'-phosphorylthymidylyl-3'-5'deoxyadenosine ammonium salt, (159), characterised by an X-ray diffraction study. The complex molecules form sandwich-like stacks with the adenine/thymine hydrogen bonded pairs along the *a*-axis [452].

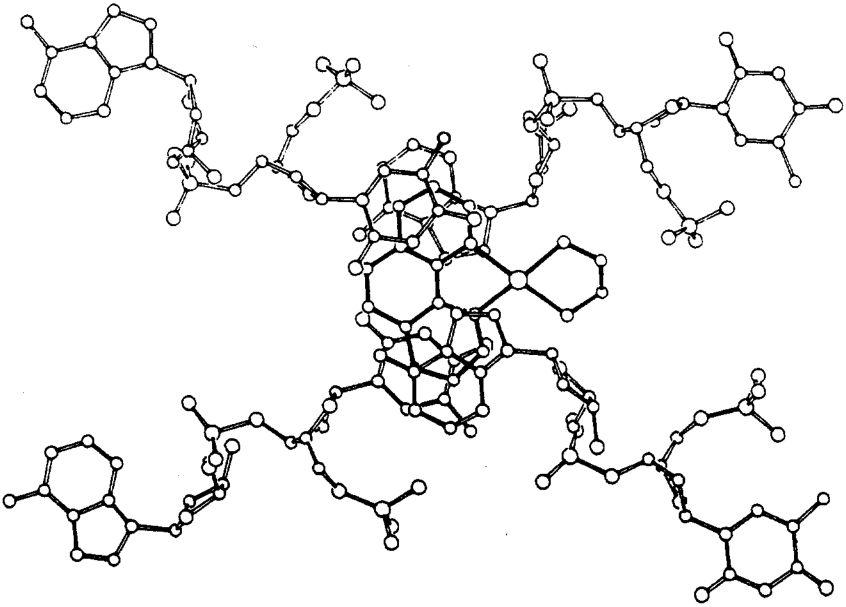
The complex *cis*-$[Pt(NH_3)_2Cl_2]$ was reacted with each of {5'-d(GpGpTpCpGpApCpC)-3'}$_2$ and {5'-d(CpGpGpApTpCpCpG)-3'}$_2$, and the products were then treated with the exonuclease, snake venom phosphodiesterase and/or calf spleen phosphodiesterase. Semiquantitative analysis by HPLC showed that, as expected, adjoining guanine bases have a specific binding affinity for *cis*-platin [453]. With a single strand undecanucleoside decaphosphate, *cis*-platin reacted to give a chelate complex at a d(GpTpG) site, bonded at N(7). The distortions of a double helix on platination resulted in the loss of two hydrogen bonds and a lowering of the duplex melting temperature by 26 °C. This distortion is considerably greater than that noted when *cis*-platin binds to adjacent guanines, so that although this lesion is relatively infrequent, it may be of considerable significance [454]. The structural distortion on platination of $[Pt(NH_3)_2\{d\text{-}(TpCpTpCpGpGpTpCpTpC)\text{-}N7(5),N7(6)\}]$ was studied by ^{31}P NMR spectroscopy. The position of the resonance of P(6), between the two guanines, was shifted to the greatest extent, and a similar result was noted for salmon sperm DNA [455].



(159a) (Reproduced with permission from [452])
A portion of the 1,10-phenanthroline-platinum(II)-ethylene diamine:d-pTpA structure viewed from a skewed direction.

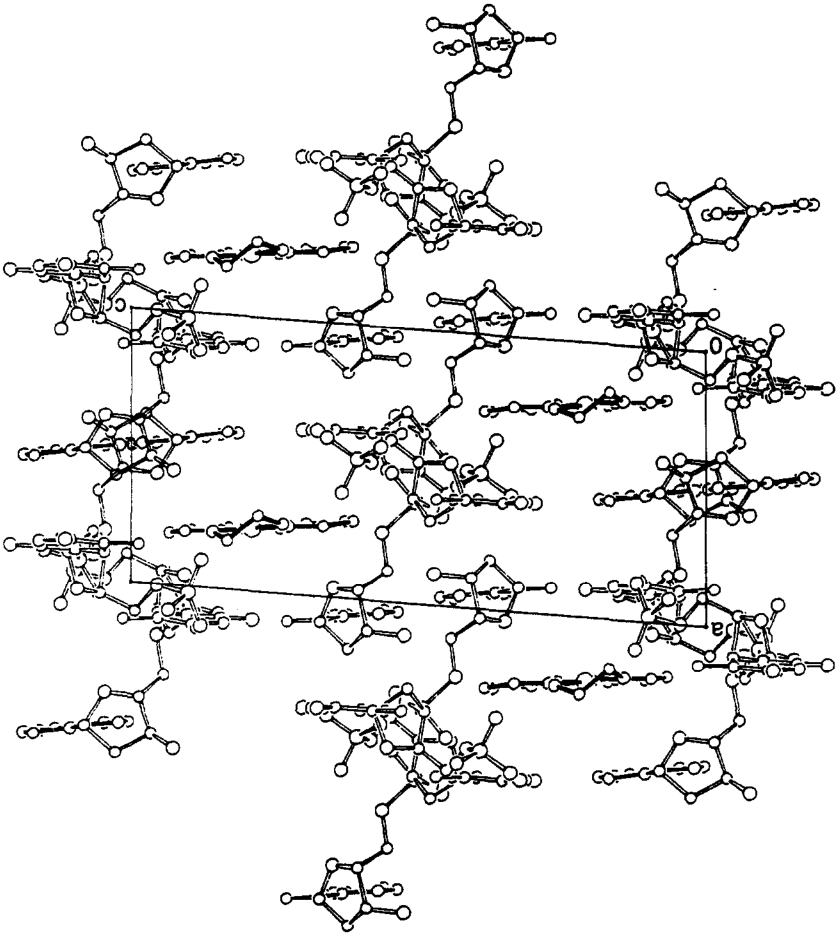
Molecular mechanics calculations have been undertaken for *cis*-$[Pt(NH_3)_2\{d(pGpG)\}]$ adducts in oligonucleotide complexes. The 5'-*endo* coordinated guanine is predicted to tilt out of the base stack, thus breaking one of the amino hydrogen bonds involved in GC base pairing, and weakening the imino hydrogen bond (A-DNA), or forming a weak bifurcated hydrogen bond (B-DNA). It was also predicted that a hydrogen bond would be formed between the ammine ligand at platinum and the 5'-phosphate of d(pGpG) in both A- and B-DNA, thus closing a ring in which the 5'-sugar is constrained into a twisted conformation. In B-DNA platination was predicted to switch the sugar pucker in the 5'-guanosine to C(3')*endo*, thus offering an explanation for the C(3')*endo* and C(2')*endo* sugar conformations previously detected by NMR spectroscopy in platinated species [456].

In the adduct of *cis*-platin with the guanine residues of *poly*(dGdC).*poly*(dGdC), alterations in the secondary structure of the polymer were investigated by electron microscopy. The extent of distortion increased with the drug:nucleotide ratio [457]. The results of the low temperature platination of *polyI*.*polyC* were investigated by NMR spectroscopy. In contrast to earlier reports, it was shown that the platinum was attached to two adjacent I residues *via* N(7), with essentially complete disruption of the duplex, for *cis*-platin and $[Pt(en)Cl_2]$. Little disruption of the duplex was noted using *trans*-platin or [Pt(dien)Cl]Cl [458]. The reaction of (160) (X = OH_2, Y = Br or OH) with oligonucleotides has been studied. Water was the most easily displaced ligand. Cytidine was platinated at N(3), inosine at N(1), and guanosine at N(7) [459].

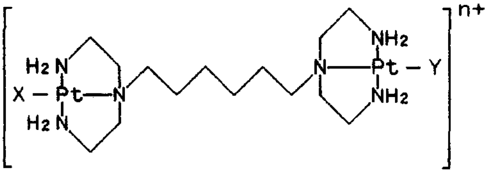


(159b) (Reproduced with permission from [452])
A portion of the 1,10-phenanthroline-platinum(II) ethylene diamine:d-pTpA structure viewed from a direction perpendicular to the drug molecule and base pairs.

The structural distortion of a single and double stranded decadeoxynucleotide on binding of *cis*-platin was studied by ^1H NMR spectrsocopy. Most of the signals of the selectively platinated derivative could be assigned, and the shifts could be rationalised in terms of the platinum binding causing a kink located at the G(5)G(6) base pair, characterised by a bend of 40-70 °, with a large change in helical winding. Platinum binding caused overall destabilisation, resulting in a decrease of 10-20 °C in the melting temperature, but CD spectroscopic data did not imply gross unwinding of the duplex, nor a complete loss of hydrogen bonding between opposite strands. Structural distortions around the phosphates were more severe in single than in double stranded material [460]. A solution of *cis*-platin was diffused into crystals of the pregrown B-DNA double helix dodecamer, C-G-C-G-A-A-T-T-C-G-C-G, and bound preferentially to the N(7) position of the guanines with an aquo bridge between platinum and the adjacent O(6) atom of the same guanine. The X-ray diffraction study of the platinated material shows that the entire guanine moiety moves slightly towards the platinum site, into the major groove. Only three of the eight potential binding sites were occupied, which could be explained in terms of the relative freedom of motion of the various guanines towards the major groove [461].



(159c) (Reproduced with permission from [452])
A portion of the 1,10-phenanthroline-platinum(II)-ethylene diamine:d-pTpA structure viewed from the *b*-axis. For clarity, water structure has been omitted.



(160)

The interaction of DNA and RNA with *cis*- and *trans*-platin has been studied by FTIR spectroscopy. A correlation between metal-base binding and conformational changes in the sugar pucker was established. DNA exhibited a B→Z transition on reaction with *trans*-platin [462]. The dependence of the conformation and flexibilty of DNA on base composition has been probed in solution by laser Raman scattering. Conformational changes on platination were probed, and again substantial changes in sugar pucker noted [463]. The interaction between ten different platinum complexes and salmon sperm DNA was investigated using UV and CD spectroscopy. Differences were noted between active and inactive complexes, which it was hoped would provide the basis of a useful assay [464].

^{31}P NMR spectroscopy was used to investigate the reactions of a range of platinum complexes with salmon sperm and calf thymus DNA. With complexes which have anti-tumour activity, a shoulder 1-2 ppm downfied of the signal for DNA was observed. No shoulder was noted with inactive complexes, again providing a possible assay [465]. The interaction of theophilline and cytidine complexes of platinum(II) and platinum(IV) with calf thymus DNA were followed by UV spectrsocopy and XPES. All the data were interpreted in terms of binding to the N(7) of a guanine residue, and a phosphate group [466].

Salmon sperm DNA was reacted with *cis*-platin, and the product was then enzymically degraded to oligonucleotides. The major aducts were of d(pGpG) and d(pApG), bonded in all cases at N(7); adducts of d(pGpA) were not detected [467]. The sensitivity of S1 nuclease to *cis*- and *trans*-platin modified DNA was examined as a function of the level of platination, the percentage of {G+C} in the DNA, and the DNA sequence. The extent of DNA digestion increased with platination and decreased with the percentage of {G+C}. The results were discussed in terms of the mode of platinum binding [468].

A theoretical model was developed for the binding of *cis*-platin to DNA. Quantum mechanical calculations indicated that the best binding site was N(7) of a guanine residue, but that binding to N(3) of cytidine might also be important [469]. Possible mechanisms for DNA shrinkage after platination have been considered. Calculations suggested the opening of a 3.4 nm segment of

DNA, and were compatible with experimental data [470].

The effective unwinding angle, Φ, for *cis* and *trans*-platin, was determined using high resolution gel electrophoresis and supercoiled ΦX174 RF DNA as substrate. The value of Φ was greatest at low levels of bound platinum and decreased with an increase in platination [471]. *cis*-Platin was twice as effective as the *trans*-isomer. *cis*-Platin binding to DNA was responsible for the effective inhibition of restriction endonuclease cleavage, and the topoisomerase 1 mediated unwinding, and inhibition of DNAase II was attributed to a direct inhibition in the vicinity of the cleavage site by bound platinum, but did not involve distortion of large region of the DNA structure [472].

The products of the reaction of salmon sperm DNA with *cis*-platin *in vitro* were purified and compared with model compounds. Kinetic studies suggested that binding was initailly at N(7) of a single guanine residue, but that most of these lesions rapidly chelated to another purine base, usually, but not exclusively, guanine. The remaining monofunctional lesions reacted slowly, mainly with adenine [473]. The interaction of *cis*-platin with phenylalanine tRNA from yeast was studied by X-ray diffraction. Two major sites of binding were noted, the N(7) positions of the guanine bases G(15) and G(18), and there were no intrastrand cross links [474].

The reactions of *cis*- and *trans*-platin with DNA or chromatin have been studied. For *cis*-platin, binding to two guanine residues was the major outcome in both cases, but *trans*-platin gave more monofunctional adducts. The *trans*-complex reacted preferentially with the chromosomal proteins in chromatin, resulting in lower level of DNA platination [475,476]. The rare interstand crosslinked adducts have now been studied in the reaction of *cis*-platin or [Pt(en)Cl_2] with DNA. In most cases these also involved two guanine residues [477].

Structural damage to DNA on binding to *cis*- or *trans*-platin, or to {Pt(dien)}, was probed using the peptide lys-trp-lys, which preferentially binds to single stranded structures. Phosphorescence lifetime measurements implied that platinum induced heavy atom effects were similar in all three peptide/DNA/Pt complexes, but fluorescence quenching depended on the nature of the platinum derivative. Quenching was therefore attributed to stacking interactions involving the tryptophan residue with the nucleic acid bases. Modification by *cis*-platin induced formation of strong stacking sites, implying the existence of locally opened DNA regions [478].

Immunochemical analysis was employed to investigate the cell cycle dependent protein-DNA cross-linking by *cis*-platin in HeLa-S_3 cells. Several antigens changed their DNA cross-linking pattern during the progression of HeLa cells through their reproductive cycle [479].

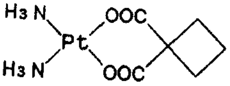
Treatment of primed phage M13 mp8 viral DNA templates with *cis*-platin, followed by second strand synthesis using large fragment DNA polymerase I, reveals that *cis*-platin forms an adduct which inhibits DNA synthesis *in vitro*. Inhibition occurred at all $(dG)_n$ sequences for $n \geqslant 2$ [480].

1.6.4 Cancer Chemotherapy

The coverage of papers concerning the use of platinum complexes as chemotherapeutic agents in this section is not comprehensive. The papers chosen are those with some chemical interest, and papers in which the principal interest is clinical, and particularly those in which a platinum drug is only one of a long list of chemotherapeutic agents considered, are largely excluded.

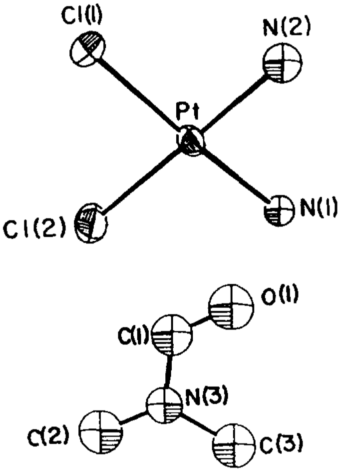
Reviews this year have addressed the general topic of platinum complexes in cancer chemotherapy [481-487], and others have focussed on *cis*-platin [488-495], with particular reference to its binding to DNA [496], its nephrotoxicity [497], radiopharmokinetics [498] or chemistry in a biochemical context [499]. The mechanism of action of the platinum drugs has been considered [500], and their uses in tumour radiosensitisation discussed [501,502]. Polymeric analogues of *cis*-platin have been reviewed [503].

Two reviews have discussed the use of hplc for the clinical monitoring of *cis*-platin in biological fluids [504,505]. *cis*-Platin in plasma ultrafiltrate was derivatised with sodium diethyldithiocarbamate and determined by hplc against $NiCl_2$ as an internal standard [506]. High performance tlc on a precoated SiO_2-60 plate with Me_2CO/H_2O (95:5) or $Me_2CO/PhMe/H_2O$ (76:20:4) as the mobile phase was used to separate *cis*- and *trans*-platin, and the aquo derivatives of *cis*-platin [507]. Liquid chromatography with electrochemical detection was applied to the determination of *cis*-platin, carboplatin, (161), and related complexes [508]. *cis*-Platin has also been determined by differential pulse polarography [509], and by a combustion method [510]. FTMS of *cis*-platin and related drugs has been reported; since relatively few ions are needed the technique is particularly useful for biological studies [511].



(161)

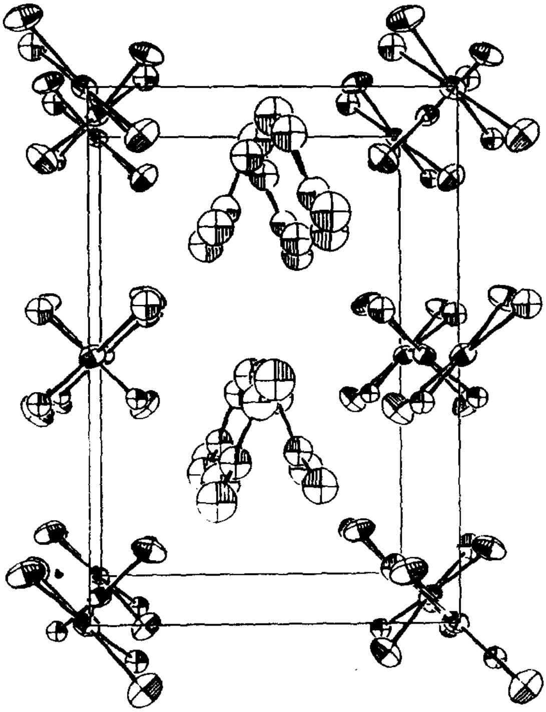
The purity of *cis*-platin is very important for its use in chemotherapy. The preparation of adducts of *cis*-$[Pt(NH_3)_2X_2]$ (X = Cl or I) with RR'NCHO was used as a method of purification, and the structure of (162) was established in an X-ray diffraction study [512]. The synthesis of ^{13}N labelled *cis*-platin has been described. It was used to asses drug delivery to primary and metastatic brain tumours [513].



(162a) (Reproduced with permission from [512])
The platinum complex and the solvate molecule showing atom numbering.

One of the main disdvantages of the use of *cis*-platin in chemotherapy is that it is extremely toxic, causing damage to both liver and kidney. There have been many further reports of substances which, when coadministered with *cis*-platin, reduce its toxicity. Diethyldithiocarbamate does not inhibit the anti-tumour effect of *cis*-platin, but does ameliorate nephrotoxicity. In an attempt to discover its mode of action, [Pt(NH$_3$)$_2$(guanosine)$_2$] was prepared as a model of platinated DNA, but this did not react with diethyldithiocarbamate [514]. The use of sodium thiosulphate as a protective against the nephrotoxic effect of *cis*-platin was studied in rabbits [515], and methylprednisolone and meloclopramide were also useful [516]. Fosfomycin had a preventative effect on renal and hematotopoietic toxicity, but not on hepatic toxicity [517,518]. Quinine and cyanine protected against the inhibition of renal cation and anion transport, and the renal lesions caused by *cis*-platin [519]. Phenobarbitol, when coadministered, increased liver oxidase activity, an indication of decreased *cis*-platin toxicity [520]. Pretreatment with Cu[SO$_4$], NaCl or [NH$_4$]Cl also offered considerable protection [521,522].

Squalene was shown to potentiate the cytotoxicity of *cis*-platin, against S180 *ascites* cells [523], whilst bestatin enhanced its effect against a syngenic solid tumour of colon adenocarcinoma 26 in BALB/c mice [524]. A single dose of *cis*-platin enhanced *in vivo* tumour killing by melphalan [525]. There was a synergistic effect between *cis*-platin and 3',5'-dichloromethotrexate in treatment of the human colon carcinoma cell line CT-8 [526].



(162b) (Reproduced with permission from [512])
Packing within the unit cell. *b* and *c* are parallel to the bottom and side of the page respectively, and the view is down *a*.

It was shown that *cis*-platin is embryotoxic, and causes a decrease in foetal weight and a decrease in the number per litter, but severe malformations were relatively rare [527].

The administration of *cis*-platin to ovarian rat tumours showed large necrosis in the central area, but did not seem to have a cytotoxic effect on the peripheral region of the tumour [528]. A proliferation inhibition study using *cis*-platin on a L1210 cell culture suggested a mechanism of action different from that of the previously studied copper complexes [529]. A combination of *cis*-platin and cytoxan was the most effective treatment in retarding tumour growth and metastatic spread in the murine bladder tumour model [530].

Proliferative lesions in inbred F 344 rat kidneys were studied at six and fifteen months after a single injection of 6 mg of *cis*-platin. Solid or cystic lesions developed from altered proximal tubular epithelial cells [531]. The effect of *cis*-platin on ATPase activity was determined *in vitro* and *in vivo* to investigate the correlation between nephrotoxicity and inhibition of ATPase activity. The highest concentration of platinum found in kidney tissue in Sprague Dawley rats was too low to inhibit the enzyme's activity *in vitro*, and it was concluded that the two were not connected [532]. In rats *cis*-platin inhibited the normal accumulation of Cu^{2+} and Zn^{2+} in the kidney. This may result from the inhibition of tubular reabsorption of copper and zinc, and/or the inhibition of the synthesis of metallothionen [533]. The effect may also be connected with the binding of platinum to cystolic proteins [534]. Binding of the drug to metallothionen in Ehrlich cells has been investigated. At concentrations which caused 60 % inhibition of cell proliferation most of the platinum is found in the cytosol, and of this 30 % was metallothionein bound. Isolated rat liver metallothionein reacted slowly with hydrolysed *cis*-platin, and it was concluded that this is a major site of platinum binding [535].

After *cis*-platin exposure dam-3 *E. coli* were more sensitive to the cytotoxic effect of the drug. Differences in the repair of DNA damage were thought to underlie this effect [536]. Protease deficient *recA431* mutants of *E. coli* are defective in their capacity for induction of SOS responses, and were intermediate in their sensitivity to UV light and *cis*-platin. Survival after treatment, determined as colony forming ability, was greater in rec^+ strains, and decreased in *recA13* mutants which are defective in both *recA* proteolitic and recombination capability [537]. Mutant human cells were found to be more sensitive to *cis*-platin than normals, and data presented suggested that induced interstrand crosslinks were an important and potentially lethal lesion [538].

The effects of *in vivo* treatment with *cis*-platin and/or cyclophosphamide on overall cellular cytoplasmic and mitochondrial protein synthesis in Zajdela hepatoma were examined. The rate of overall protein synthesis was decreased by 60-80 %, but the rate of the process in the mitochondria was affected only marginally [539]. There has been an EPR investigation of the effects of the drug on the iron sulphur centres of the mitochondrial membranes. Characteristic changes were produced in the electron transport chain in various organs [540].

The concentrations of platinum and other trace elements were measured exploiting a 50x50 μm proton beam for PIXE analysis. The lateral distribution of platinum in *cis*-platin treated human kidney and dog tissues was measured;

the highest concentrations of platinum were found in arterial walls, followed by glomeruli and tubules. Chronic kidney damage is related to this pattern of retention [541]. A physiological model has been developed to describe the disposition of platinum following IV dosing in female rats bearing Walker 256 carcinoma [542].

Following the IP injection of *cis*-platin into tumour bearing mice two immune responses were augmented. The total splenic plaque forming cells' response to sheep red blood cells, and the delayed hypersensitivity reaction to oxazolone were higher in treated animals [543].

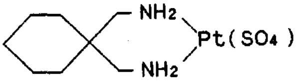
Treatment of rats with *cis*-platin for seven days caused a 70-80 % reduction in the microsomal cytochrome P450 levels in the testis. This was accompanied by a 70-80 % reduction in steroid 17α-hydroxylase activity and in plasma testosterone concentration. The effect was not related to deficiencies in the haem metabolic processes, and is was concluded that the anterior pituitary hormones control the factors involved, and that this process is interrupted by *cis*-platin [544].

The rate of inactivation of T4 phage by *cis*-platin, $[Pt(en)Cl_2]$ or $[Pt(en)(OH_2)_2][NO_3]_2$ at fixed pH was substantially reduced by phosphate buffer, and slightly by ethanoate buffer. The mechanism of the process was discussed [545].

Crosslinking and inactivation of the plasma protein α_2-macroglobulin by *cis*-platin was used to study the binding of platinum(II) to protein in the presence of other compounds. Diethyldithiocarbamate completely prevented crosslinking, whilst amino acids showed lower but still significant effects [546]. With polyclonal antibodies raised against *cis*-$[Pt(NH_3)_2(Guo)(GMP)]$ small quantities of specific platinum adducts could be detected in DNA from Chinese hamster ovary cells treated with *cis-platin*, after the DNA was digested with nucleases, and the degradation products separated by anion exchange chromatography. 35.9 % of the platinum was recovered as *cis*-$[Pt(NH_3)_2\{d(pGpG)\}]$ and 3.1 % as *cis*-$[Pt(NH_3)_2\{d(GMP)\}_2]$ [547].

The kinetics of a model reaction between *cis*-platin and the signal nucleotide diadenosine 5',5'''-P^1,P^4-tetraphosphate was studied using potentiometry and a chloride specific electrode. At least four steps in the reaction could be detected, and initial reaction was probably at a phosphate group [548].

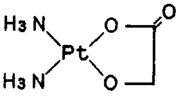
The drugs *cis*-platin, CHIP and carboplatin were tested for induction of chromosome aberrations and the formation of micronuclei, as well as for sister chromatid exchange [549]. Carboplatin was less effective than *cis*-platin in the treatment of pancreatic ductal adenocarcinomas [550]. However, DNA protein and DNA interstrand crosslinks were formed in cells exposed to either drug, although the rates of reaction were different [551]. The antitumour effects of *cis*-platin, carboplatin, CHIP, spiroplatin, (163), and JM40 were compared using MR1-H-207 [552].



(163)

Numerous new compounds have been prepared in a search for improved platinum anti-tumour drugs. Carboplatin was cytotoxic against the MGH-U1 human bladder carcinoma cell line [553]. Spiroplatin was more cytotoxic towrds the Lewis lung carcinoma line M1087 [554]. Aqueous solutions were shown to contain hydrolysed and oligomerised species, and the toxicity could be reduced if this hydrolysis was inhibited by $Na_2[SO_4]$ [555].

The preparation of (164) has been described; the complex is reasonably active against Sarcoma 180 [556]. A binuclear complex of stoicheiometry $[Pt_2(NH_3)_4(165)_2][SO_4]$ had similar activity [557]. A range of complexes of quinones such as (166) has also been tested for activity against leukaemia L1210 and Ehrlich ascites tumours grown *in vivo* [558,559].



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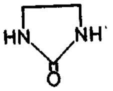

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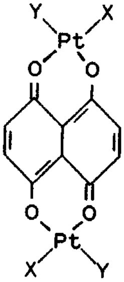
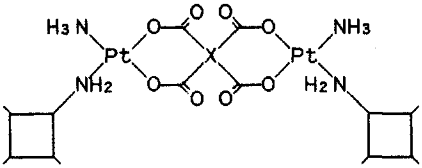


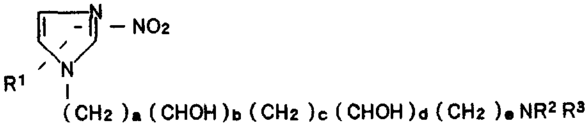
(166)

Complexes of the type $[Pt(NH_3)(L)Cl_2]$ in which L was a cycloalkylamine, have been prepared and shown to have significant anti-tumour activity, and low nephrotoxicity [560]. Related species, (167), in which the two carboxylate units are connected by a cycloalkyl ring or a benzene ring, have also been claimed [561]. Structure activity relationships have been determined for the series *cis*-[PtL_2X] and [$PtL_2(OH)_2X$] in which L was cyclohexylamine and $[X]^{2-}$ was the anion of a dicarboxylic acid. The platinum(II) complexes were more active than the platinum(IV) derivatives [562].



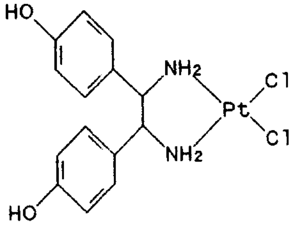
(167)

Complexes of the type [$Pt(L)(L')Cl_2$] in which L was an aminophenol and L' was a substituted pyridine were prepared by addition of the aminophenol to the bridged species [{PtL'Cl(μ-Cl)}$_2$]. In general, either the *cis* or the *trans*-isomer was obtained reasonably pure, depending on the steric demands of the ligands. The complexes were tested as inhibitors of the growth of murine leukaemic cells [563]. The complexes *cis*-[PtL_2X_2] and [$PtL_2(OH)_2X_2$] in which L was cyclohexylamine and X was the monoanion of a dithiocarbamic acid were also tested against mouse tumours [564]. Binuclear amine complexes with bridging water solubilising groups, and derivatives of (168) have been patented [565,566].



(168)

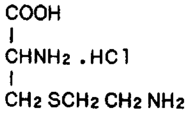
A number of papers have reported the activity of platinum complexes of substituted en ligands. For example, [$Pt(HOCH_2CH_2NHCH_2CH_2NH_2)Cl_2$] had good activity and low toxicity in treatment of Sarcoma 180 [567]. In (169) the R,R- or S,S-stereoisomers were more effective than the R,S for inhibition of estradiol receptor interactions, and there were only slight nephrotoxic and no myelotoxic effects [568]. Other en ligands with aromatic substituents have also been investigated [569].



(169)

Numerous complexes of 1,2-diaminocyclohexane, dach, have been prepared, characterised and tested. In some cases the stereochemistry was not specified, and in this group the anions used included isophthalic and homophthalic [570,571], nitrate and malonate derivatives [572], ascorbate and furandicarboxylate [573]. Both isomers of the bis(ascorbate) derivative had significant activity *in vitro* against L1210 leukaemia and were relatively non-nephrotoxic, but they did cause bone marrow and gastrointestinal toxicity [574]. Sugar derived dicarboxylate anions were used in complexes of both *cis*- and *trans*-geometry [575]. The complex [Pt(*trans*-dach)(oxalate)] was compared in its anti-tumour action to *cis*-platin. It inhibits RNA synthesis better, and was also more active against various mouse tumours [576,577].

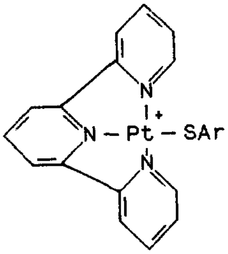
The radiosensitisation of EMT 6 cells by four platinum complexes has been studied. Ligands used included 2-nitroimidazole and 2-amino-5-nitrothiazole, and all the ligands have the potential to undergo a redox reaction with the platinum centre during irradiation [578]. Palladium(II) and platinum(II) complexes of (170), [PtLCl$_2$], contained *S,N*-chelate rings; the platinum complexes had good anti-tumour action, but the palladium complexes were inactive [579].



$$\begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CHNH_2\,.HCl} \\ | \\ \mathrm{CH_2SCH_2CH_2NH_2} \end{array}$$

(170)

A series of intercalating square planar platinum(II) complexes have been prepared, and had significant activity against murine leukaemia L1210 cells. The complex (171) was inhibitory in culture, and caused cell lysis at high concentrations [580]. The antitumour antibiotic daunomycin was *N*-acylated by symmetrical disulphide diacids and then reduced to thiols by dithioerythritol. Coupling to [Pt(terpy)(OH)][CF$_3$COO] using a derivative with a six carbon linkage gave a complex with sufficient flexibility to permit bis intercalation with DNA [581].



(171)

1.6.5 Complexes with Group 15 Donor Ligands

1.6.5.1 *Unidentate amine donor ligands*

A number of studies of the biological effects of *cis*-platin and related complexes have not been directly related to their anti-tumour activity. For example, African trypanosomiasis could be treated by the IP injection of *cis*-platin [582], and both *cis* and *trans*-platin had activity against the trypanosome *T. brucei gambiense* [583]. The *cis*-platin prolactin complex retains the capacity of native prolactin to bind to cell receptor membrane, and might be used to target *cis*-platin to cells with prolactin receptors [584].

The complex ions $[Pd(NH_3)_4]^{2+}$ penetrate into the channels of zeolite NH_4-ZSM and are probably stabilised close to $\{AlO_4\}^-$ tetrahedra. Vacuum treatment at 180-500 °C resulted in the destruction of the palladium ammine complex, and eventual reduction to palladium(0). The larger clusters of Pd(0) appearing on reduction in molecular hydrogen were capable of being redispersed in an oxygen atmosphere with the formation of Pd^{2+} in the zeolite structure [585]. Impregnation of Al_2O_3 or SiO_2/Al_2O_3 from an aqueous solution of $[Pd(NH_3)_4]Cl_2$ and/or $[Pt(NH_3)_4]Cl_2$, followed by ion exchange, and reduction, gave a catalyst powder carrying the noble metals. This was mixed with Al_2O_3 sol to give a paste, used in a detector for flammable gases [586].

The vibrational modes of $[Pt(NH_3)_4]^{2+}$ on Na-Y zeolite were directly probed *in situ* by far FTIR spectroscopy. The technique was also used to probe the dehydration/deamination processes which occur on *in situ* vacuum and thermal treatment, resulting in the reduction of Pt(II) to give highly dispersed platinum(0) clusters immobilised on the zeolite [587]. Ion exchange of $[Pt(NH_3)_4]^{2+}$ on ZSM-5 and ZSM-11 was studied in detail [588]. The dispersion of the platinum(0) on ZSM-5 was critically dependent on the temperature of calcination, when the calcination is conducted under a high air-flow, but temperature was less important when reduction was conducted in a nitrogen atmosphere [589]. Ion exchange reactions were studied for H-mordenite with $[Pt(NH_3)_4]^{2+}$ [590].

The oxidations of $[Pt(NH_3)_4][NO_3]_2$, $[Pt(NH_3)_3Cl][NO_3]$, *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$, $K[Pt(NH_3)Cl_3]$ and $K_2[PtCl_4]$ were studied at a platinum electrode against a background of 2M KCl and 2M $[ClO_4]^-$ [591]. In the anodic oxidation of $[Pt(NH_3)_4]^{2+}$ in HCl solution, the first wave was associated with the formation of $[Pt(NH_3)_4Cl_2]Cl_2$, and the second with the production of $[Pt(NH_3)(OH)Cl]X_2$ [592].

Isomeric energies and conformations for a range of platinum ammine complexes were calculated from *ab initio* MO theory using energy gradient methods. The trends in the metal-ligand bond distances obtained allowed the ordering of the ligand *trans*-influence. The hydroxyl group was predicted to occupy an anomalous position, and it was suggested that differences between theory and experiment arose from the importance of hydrogen bonding [593].

The concentration of $[Pt(NH_3)_4]^{2+}$ was determined by means of its redox reaction with $[IrCl_6]^{2-}$ [594].

The complex $[Pt(NH_3)_2Cl_2]$ was used to platinise Nafion film [595]. Anodic slipping voltammetry at a glassy carbon electrode was used for the determination of platinum species derived from *cis*-platin [596].

PdO may be prepared by the decomposition of $[Pd(NH_3)_2Cl_2]$ in oxygen at 500 °C. However, reaction of PdO with ammonia at 250 °C gave $[Pd(NH_3)_2Cl_2]$, and thermolysis of this complex at 300-340 °C yielded $[NH_4]_2[PdCl_4]$. Above 350 °C decomposition to palladium metal, ammonia, HCl and nitrogen occurred [597].

The complex *cis*-platin was purified by formation of an adduct with dmf at room temperature, followed by chilling at 3 °C for 15 h to recover crystals of the adduct. The dmf was removed by holding the complex at 2 °C and 1 μbar pressure [598]. Quenched biacetyl phosphorescence was used for the detection of platinum complexes such as *cis*-platin and carboplatin in HPLC [599].

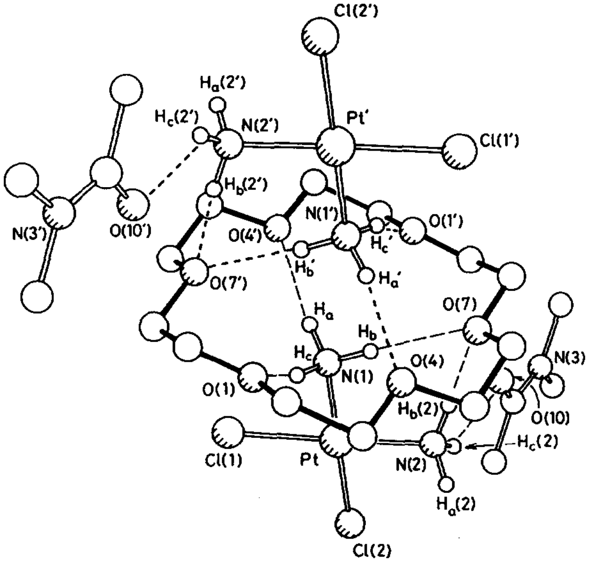
Potential energy surfaces were obtained for low lying electronically excited states of *cis*- and *trans*-platinum(II) complexes, and for the lowest singlet and triplet terms of tetrahedral isomers. The data were used for an analysis of the mechanism of intramolecular photoisomerism, suggesting a route involving twisting through tetrahedral intermediates. In cases in which the tetrahedral species was relatively stable, the *trans*-to-*cis* isomerisation was deduced to proceed through a triplet intermediate, and the *cis*-to-*trans* through a singlet species. The results were used to interpret experimental data for $[Pt(NH_3)_2Cl_2]$, $[Pt(py)_2Cl_2]$ and $[Pt(gly)_2]$ [600].

Solvolysis of *cis*-platin in dmso/H_2O has been investigated [601]. The kinetics of the hydrolysis of *cis*- and *trans*-platinum(II) ammine and amine complexes were monitored conductimetrically at 25 °C. Association of an ion-dipole type of chloride ion with the *cis*-, but not the *trans*-complexes, was established; the chloride then increases the hydrolysis rates [602]. The hydrolysis reaction of tri- and pyrophosphates was accelerated by $[Pt(NH_3)_2(OH_2)_2]^{2+}$. Kinetic data suggested the formation of $[Pt(NH_3)_2(H_2P_2O_7)(OH_2)]$ from pyrophosphate, but from the triphosphate, platinum blue complexes were obtained, especially in air. Very complex schemes for the reactions were proposed, and were to some extent justified by the observation of the reaction intermediates by NMR spectrsocopy [603].

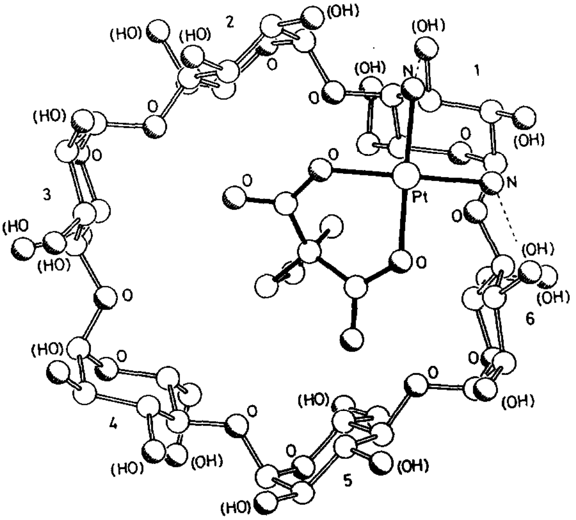
During crystallisation from aqueous solutions, a continuous series of *cis*-$[Pt(NH_3)_2Cl_nBr_{2-n}]$ (n = 0,1, or 2) solid solutions were obtained, and were characterised by powder diffraction data. A method for obtaining 95 % *cis*-$[Pt(NH_3)_2ClBr]$ was described [604-606].

Reaction of *cis*-platin with 18-crown-6 in the presence of dma gave a 1:2:2 complex (18-C-6:Pt:dma), (172), characterised by an X-ray diffraction study. Hydrogen bonding involves all three hydrogen atoms on both ammine ligands and all six oxgen atoms of the crown ether, as well as one chloride and the carbonyl group of dma [607]. Complexes of $[Pt(NH_3)_2(bipy)]^{2+}$ with dibenzo-30-crown-10 and dibenzo-24-crown-8 have been characterised by X-ray diffraction studies. As well as extensive hydrogen bonding, some stabilisation is also provided by stacking interactions and charge transfer between the bipy ligand and the benzene rings of the crown ether [608]. The α-cyclodextrin complex of carboplatin, (173), has been the subject of an X-ray diffraction study. The cyclobutane diacarboxylate ligand occupies the cyclodextrin cavity and there are two N-H...O hydrogen bonds between the ammine and the secondary hydroxyl group at C(3) on neighbouring glucose units. This provides a relatively rare example of a neutral metal guest molecule bound into a cyclodextrin [609].

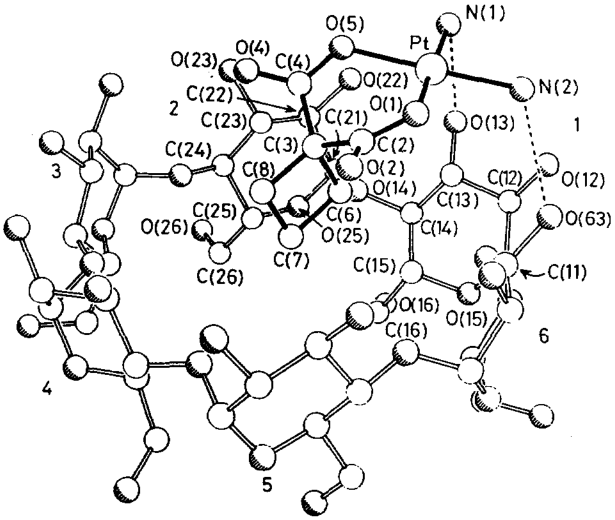
The structure of *trans*-$[Pd(4\text{-}FC_6H_4NH_2)_2Cl_2]$ has been determined in an X-ray diffraction study [610]. In (174) the crystal structure was stabilised by N-H...Cl intermolecular hydrogen bonds [611]. Reaction of $[\{Pt(SnCl_3)(PEt_3)(\mu\text{-}Cl)\}_2]$ with $4\text{-}XC_6H_4NH_2$ (X = Cl or Me) gave (175), shown in an X-ray diffraction study to possess approximately square planar coordination. The Pt-Cl distance of 2.331 Å suggested that the $SnCl_3$ group had a weak to moderate *trans*-influence, similar to that of an alkene [612].



(172) (Reproduced with permission from [607])
Crystal structure of $\{18\text{-crown-}6[\mathit{cis}\text{-PtCl}_2(NH_3)_2.MeCONMe_2]_2\}$.

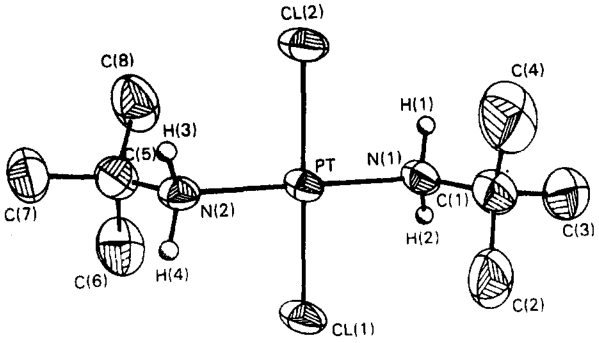


(173a) (Reproduced with permission from [609])
A plan view of the framework representation of $[Pt(NH_3)_2(CBDCA).\alpha\text{-CD}]$. Note that the α-D-glucopyranoside units are numbered 1 to 6 in an anticlockwise direction.



(173b) (Reproduced with permission from [609])

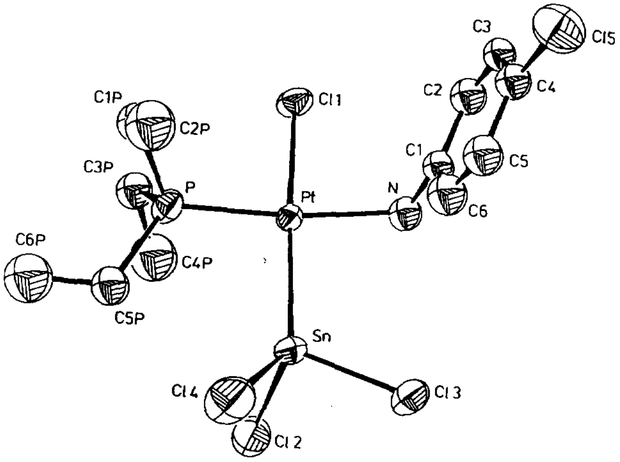
A side-on view of the framework representation of [Pt(NH_3)$_2$(CBDCA).α-CD], showing the atomic numbering scheme for the guest and two (1 and 2) of the α-D-glucopyranoside units in the host.



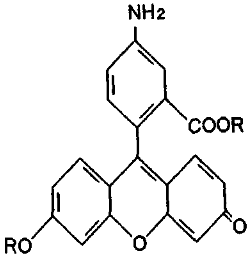
(174) (Reproduced with permission from [596])

The ellipsoids correspond to 50 % probability

Platinum complexes of fluoresceinamines such as (176) have been prepared, and used as low toxicity radiation sensitisers [613].



(175) (Reproduced with permission from [597])

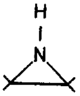


(176)

IR and NMR spectroscopic data have been presented for $[ML_2X_2]$ in which M = Pd or Pt, L = MeNHOH, and X = Cl, Br or I. The palladium complex adopted *trans*-geometry, whilst the platinum complex was *cis*. In both cases MeNHOH acted as a monodentate ligand coordinated through nitrogen. The stabilisation of various rotamers by hydrogen bonding was investigated [614]. Applications of UVPES and XPES in organometallic chemistry have been reviewed. The N_{1s} ionisation potentials were determined for palladium complexes such as $[Pd(NMe_3)Cl_3]^-$ and $[Pd(NMe_3)_2Cl_2]$, and supported analogues [615].

Single crystal polarized spectra were obtained for $[Pr_4N][Pt(NMe_3)Cl_3]$ at 10 K. Both spin-allowed and spin-forbidden ligand field transitions were assigned. The data were compared with those obtained at room temperature and for $[Pt(NH_3)Cl_3]^-$, Cossa's salt. Angular overlap parameters indicated that Me_3N is a strong σ-donor, and its influence on the d-orbitals of π-symmetry through a proposed electrostatic interaction is significant [616].

The complex *trans*-[PdL_2Cl_2], in which L = 2,6-dimethoxy-4-chloroaniline, has been prepared and characterised [617]. A range of derivatives of $CH_3CH_2CH_2NH_2$ has been prepared and characterised by IR and NMR spectroscopy, DTA and thermogravimetric techniques. Both [PtL_3Br]Br and [PtL_4]Br_2 yielded *trans*-[PtL_2Br_2] on themolysis [618]. IR spectroscopy and thermal analysis were used for the characterisation of palladium complexes of the strained cyclic amines (177) and (178) [619]. The complexes [Pd(hmta)$_2X_2$] (hmta = hexamethylene tetramine; X = Cl, [NO_2], [OCOMe] or [SCN]) have been claimed; they were apparently characterised only by microanalytical techniques [620]. Another paper from the same group reported that *trans*-[Pd(hmta)$_2Cl_2$] was formed on reaction of the ligand with K_2[$PdCl_4$] in dmf. When the substrate was [R_3NH]$_2$[$PdCl_4$] and the solvent was CCl_4, however, the species isolated was [Pd(hmta)$_2Cl_2$].2hmtaHCl, which appeared to be an inclusion complex [621].



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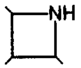
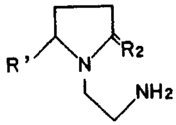


(178)

The *cis*⇋*trans* isomerisation of complexes [ML_2X_2] (M = Pd or Pt; L = (179); X = Cl or Br) has been studied. The ligand is monodentate in all the complexes, and is bonded through the NH_2 group. The palladium complexes were isomerised at lower temperatures than the platinum analogues, but in both cases DTA indicated that isomerisation occurred before further decomposition [622]. Amine functionalised polyethene was reacted with [Pd(PhCN)$_2Cl_2$] to give a complex which catalysed the hydrogenation of nitroarenes [623].



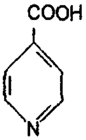
(179)

R' = Bu, i-C_5H_{11} or C_7H_{15}; R_2 = O or H_2

1.6.5.2 Unidentate heterocyclic nitrogen donor ligands

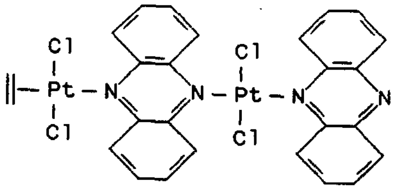
The solvent extraction and spectrophotometric determination of palladium(II) as pyridine thiocyanate complexes has been reported [624]. Relaxation parameters, T^1, in ^{13}C and ^{195}Pt NMR spectra have been compared in different solvent systems, and were used to obtain correlation times for rotation about the Pt-N bond in $[Bu_4N][Pt(py)Cl_3]$. The ion pair was shown to form aggregates or stacks in solvents of low dielectric constant [625].

The structure of *trans*-$[Pd(2\text{-aminopyridine})_2Cl_2]$ was determined in an X-ray diffraction study. The crystal packing was maintained by both intra and intermolecular N-H...Cl hydrogen bonds [626]. The complexes *cis*-$[PtL_2X_2]$ in which L = isonicotinic acid, (180), and the related amide, were prepared from the ligands and $K_2[PtCl_4]$. The *trans*-isomers could be obtained by treatment of $[PtL_4]^{2+}$ with HCl [627].

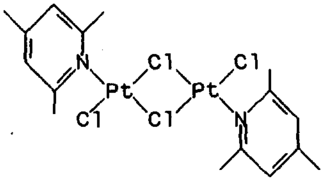


(180)

The kinetics of the reaction of *trans*-$[PtL(amine)Cl_2]$ with HCl to give $[PtLCl_3]^-$ and $[Hamine]^+$ were investigated for L = C_2H_4, CO, PMe_3 or substituted pyridines. Reactivity decreased as steric hindrance increased [628]. Complexes of the type *trans*-$[Pt(C_2H_4)LCl_2]$ were prepared by addition of the ligand L to $[Pt(C_2H_4)Cl_3]^-$. The ligands studied included phenazine, pyrazine, quinoxaline, and their substituted analogues. The phenazine complex was a hydrosilylation catalyst. Using phenazine as the ligand, binuclear species, such as (181), could also be prepared [629]. Reaction of 2 equivalents of 2,6-dimethylpyrazine with (182) gave (183), but with equal amounts of the two components, a mono chloro bridged species, (184), was formed, although it disproportionated rapidly above room temperature [630].

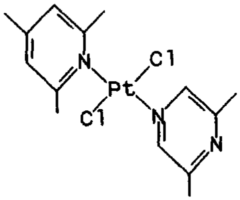


(181)

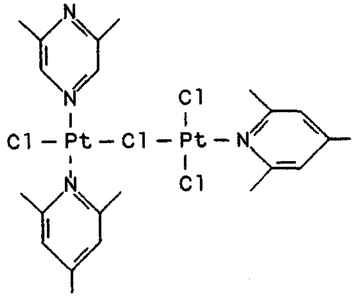


(182)

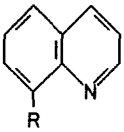
In the complexes *trans*-$[PtL(PEt_3)Cl_2]$, where L = 8-substituted quinoline, (185), the coupling constant between the proton of the R group (CHO, CH_3, $CHMe_2$ or $CHBr_2$) was rather large for a normal 5-bond coupling, and suggested a Pt...H-C interaction [631]. Reaction of $[Pd(PhCN)_2Cl_2]$ with *o,m*-$RCB_{10}H_{10}CCH_2NR'_2$ (*sic*) was said to yield a *B,N*-chelated chloro bridged dimer. The dimer could be opened with 4-methypyridine to give (186), and multiple insertions of alkynes were also noted [632].



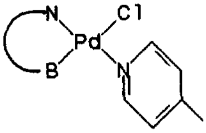
(183)



(184)

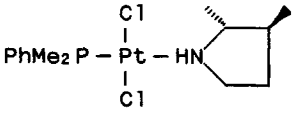


(185)



(186)

The structure of the complex (187) was established in an X-ray diffraction study. The methyl groups occupied equatorial positions in the puckered part of the five-membered ring in an envelope conformation [633].

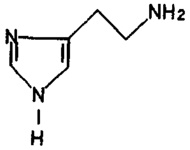


(187)

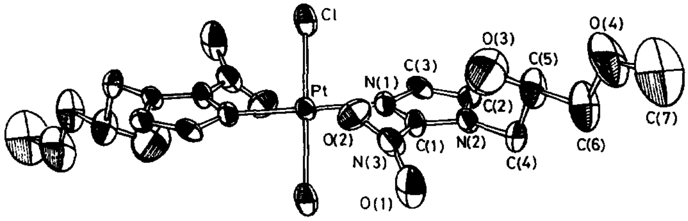
Reaction of $[Pd(PhCN)_2Cl_2]$ with $[(C_4H_4N)Mn(CO)_3]$ gave $[\{(C_4H_4N)Mn(CO)_3\}_2PdCl_2]$ in which the heterocyclic ring was coordinated to the palladium at nitrogen. $[(C_4H_4N)FeCp]$ reacted similarly, and the related platinum derivatives could be obtained from $K_2[PtCl_4]$ [634]. Phthalimide acted as an anionic ligand in the complexes $[M(PPh_3)_2(ptm)Cl]$ (M = Pd or Pt), which were prepared from $[M(PPh_3)_2Cl_2]$ [635].

The complex *trans*-[Pd(*N*-propylimidazole)$_2$Cl$_2$] was prepared by reaction of the ligand with $K_2[PdCl_4]$, and its structure was established in an X-ray diffraction study [636]. A range of complexes of imidazole and *N*-methylimidazole has been prepared and characterised, including

$[Pd(imidH)_4]Cl_2$, $[Pd(imidH)_4][PdCl_4]$ and *cis*- and *trans*-$[Pd(1\text{-}Meimid)_2Cl_2]$. When the ligand used was the related histamine, (188), analogous species were obtained, and spectroscopic data indicated that metal binding was at the ring nitrogen atom [637]. In preparing $[PtL_2Cl_2]$ where L is a substituted 5-nitroimidazole, the kinetic product, the *cis*-compound was formed, but with 2-nitroimidazoles the thermodynamic *trans*-products were obtained, as was verified in an X-ray diffraction study of *trans*-$[\{1\text{-}(2'\text{-hydroxy-}3'\text{methoxypropyl})\text{-}2\text{-nitroimidazole})\}_2PtCl_2]$, (189). Coordination to platinum was shown to lower the wavelength of the $\pi\rightarrow\pi^*$ absorption of the ligand, and to reduce its polarographic reduction potential by 0.15-0.2 V [638].



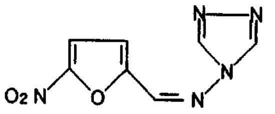
(188)



(189) (Reproduced with permission from [638])

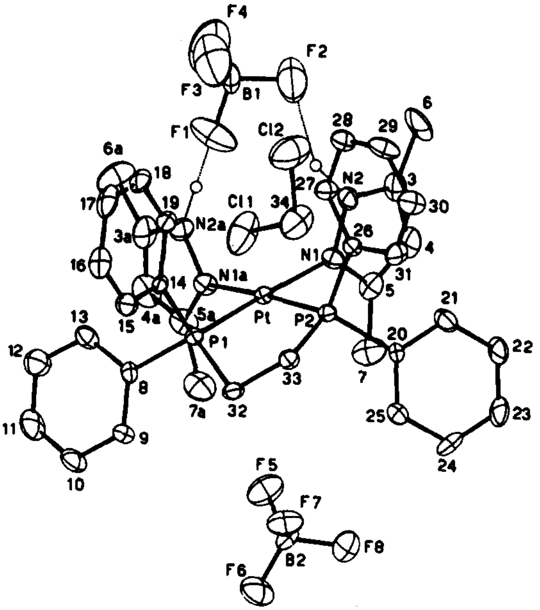
A number of complexes of the type $[PdL_2X_2]$ in which L is a 2-substituted benzimidazole have been claimed. The characterisation of the complexes was poor [639]. A palladium dichloride complex of polybenzimidazole was reduced by molecular hydrogen, under basic conditions, to give a stable polybenzimidazole palladium(0) derivative, which had high activity as a catalyst in the hydrogenation of nitroarenes, and considerable stability towards metal leaching [640].

Complexes *trans*-$[PdL_2Cl_2]$ in which L is 3-Me or 1,3-Me_2pyrazole, have been prepared and characterised by thermal analysis, diffuse reflectance spectroscopy and dipole moment studies. Both were rather toxic and had no antiviral activity [641]. In complexes prepared from 1-ethenylimidazole and related ligands, there was no coordination of the alkenyl double bond. Some polynuclear species in which the azole acted as a bridging ligand were also prepared [642]. Platinum and palladium complexes of (190) involved ligand bonding at a ring nitrogen atom, and had significant antibacterial, antiviral and fungicidal properties [643].



(190)

An X-ray diffraction study of [Pt(dppe)(3,5-Me_2pzlH)$_2$][BF_4]$_2$.CH_2Cl_2, (191), showed that the complex was unusual in that the pyrazoles are similarly oriented away from the coordination plane [644].



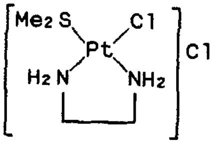
(191) (Reproduced with permission from [644])

ORTEP plot and numbering scheme of atoms, viewed down the *c*-axis of the cell. Thermal ellipsoids enclose 25 % of the electron density. Carbon atoms are indicated only by numbers. Hydrogen atoms are omitted for clarity, except those involved in hydrogen bonding.

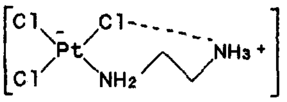
1.6.5.3 Bidentate and polydentate amine donor ligands

The structure of $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3].3H_2O$ was determined in conjunction with a study of the exchange of $^{18}OH_2$ in the anion [645]. The complexes of platinum(II) formed during sorption and separation of platinum metals using a macroporous hydrophilic glycidyl methacrylate polymer functionalised with en groups have been studied [646]. The dimerisation of $[Pt(en)(OH_2)_2]^{2+}$ was studied by ion pair HPLC at pH 2.5-10. Dimerisation to give a bis(μ-hydroxo) complex occurred betweem pH 4.9 and pH 8.5, but not in other pH ranges [647].

Reaction of (192) with HCl gave (193), in which the protonated en ligand adopted a gauche conformation with a hydrogen bond between the $-NH_3^+$ and the *cis*-chloride [648].

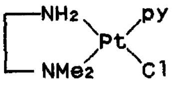


(192)



(193)

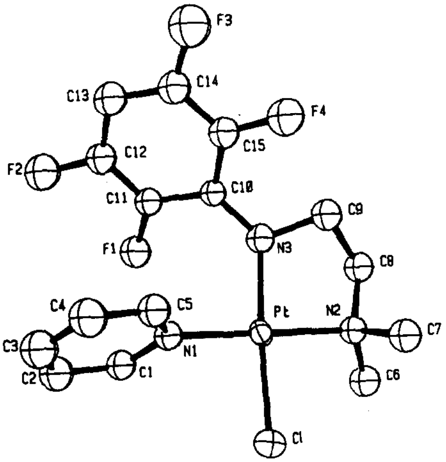
Treatement of (194) with C_6F_5COOTl in the presence of pyridine gave (195), characterised by an X-ray diffraction study. Only this stereoisomer was formed, and the mechanism of this unusual reaction is to be published elsewhere [649].



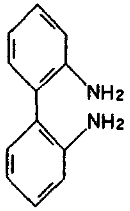
(194)

There has been a study of the conformations of dabp, (196), in complexes such as $[Pt(S\text{-}pn)(dabp)]Cl_2$ and $[Pt(\mathit{trans}\text{-}S,S\text{-}dach)(dabp)]Cl_2$ (pn = 1,2-diaminopropane, dach = 1,2-diaminocyclohexane). The dabp ligand adopted a δ-conformation in the S- and S,S-derivatives, and (197) was characterised in an X-ray diffraction study [650,651].

The structure of (198) was determined in an X-ray diffraction study; the O-Pt-O angle was only 80 °, substantially smaller than in related complexes. The electronic structure of the molecule was investigated by CNDO/2, and the relationship of the unusual bond angle to the anti-tumour effect of the complex was discussed [652]. The ligand (±)-2,3-diaminobutane (bn) reacted with (199), $[Pt(R\text{-dmdabp})Cl_2]$, in a stereospecific manner to give only $[Pt(R\text{-bn})(R\text{-dmdabp})]Cl_2$ [653].



(195) (Reproduced with permission from [649])

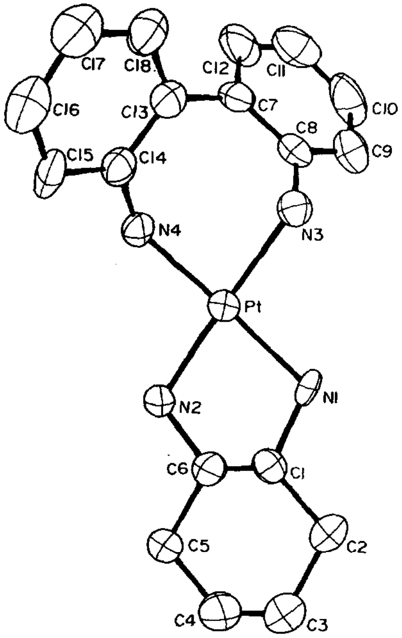


(196)

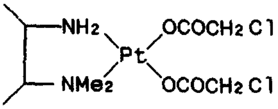
Reaction of $[PtLCl_2]$ ($L = ClCH_2CH_2NHCH_2CH_2NH_2$) with KOH gave (200) and its platinum complex [654].

The structure of racemic $[Pt($*trans*-dach$)(OCOMe)_2].H_2O$, (201), prepared from $[Pt($*trans*-dach$)Cl_2]$ and Ag[OCOMe], has been determined in an X-ray diffraction study. The molecules are stacked in pairs along the *b*-axis with the two molecules of each pair 180 ° apart about the stacking axis and forming N-H...O hydrogen bonds [655]. A range of water soluble salts $[Pt(dach)(RCO_2)_2]$, (R = cycloalkyl and cycloalkenyl) or related complexes with the anions of dicarboxylic acids, has been prepared. The water solubility appears to be important in the cytotoxic effects of the complexes [656]. Derivatives of {Pt(dach)} with arene carboxylic acids and dithiocarbamates have also been prepared and evaluated for their anti-tumour properties [657]. The ligand 1R,2S,3S-(202) has been resolved and its absolute configuration assigned on the basis of the Cotton effects in *trans*-$[Pt(NH_3)_2(202)]^{2+}$ and

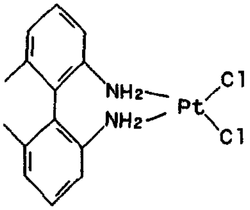
$[Pt(en)(202)]^{2+}$. The ligand backbone adopts a δ-configuration, mainly because of the preferred equatorial orientation of the C_2C_3 bond of the ring [658].



(197) (Reproduced with permission from [651])

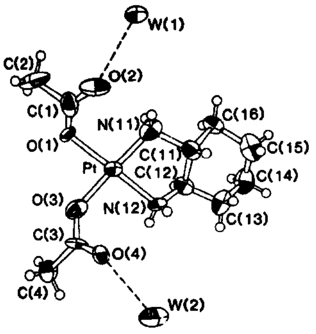


(198)



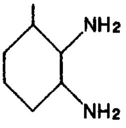
(199)

(200)



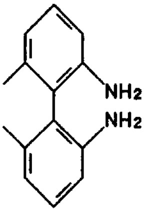
(201) (Reproduced with permission from [655])

View of the [Pt(dl-dach)(OCOMe)$_2$] molecule. Ellipsoids correspond to 50 % probability. Hydrogen atoms are represented by spheres of arbitrary size.

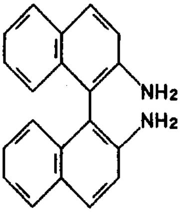


(202)

The ligand (203) was resolved *via* tartrate salts, and complexes of the resolved ligand, [PtLCl$_2$], were prepared and characterised. A δ-conformation was deduced for the S-ligand on the basis of CD data and a study of molecular models [659,660]. In a related study by the same authors, racemic *trans*-dach was reacted with [Pt{R-(204)}Cl$_2$] to give only [Pt{R-(204)}(R,R-dach)]Cl$_2$ in which both ligands adopted a λ-conformation [661].



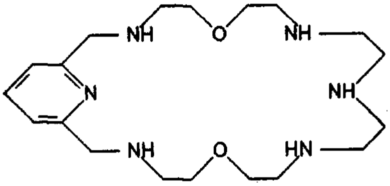
(203)



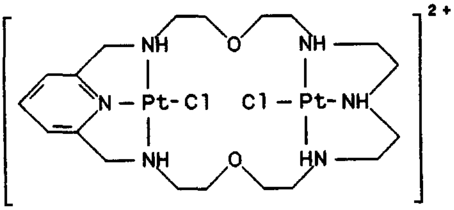
(204)

Reversed phase HPLC analysis was used for the estimation of spiroplatin and the products of its oligomerisation and hydrolysis. In aqueous solutions the sulphate was found to be in equilibrium with various aquo complexes and hydroxo bridged dimers [662].

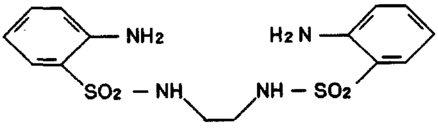
The preparation of the macrocyclic ligand (205) was described; reaction with $[Pt(RCN)_2Cl_2]$ gave (206), which was characterised by FAB-MS. Related palladium complexes were also prepared [663]. The formation of $[Pd(R_5dien)(OCO_2)]$ (R_5dien = 1,1,7,7-Me_4dien or 1,1,7,7,Et_4dien) was followed as a function of pH, carbonate concentration and temperature. The kinetic data suggested that the complex was not produced by CO_2 uptake, but by anation of an aquo complex by $[HCO_3]^-/[CO_3]^{2-}$. The complexes produced underwent acid catalysed aquation, and basic hydrolysis, and the activation parameters obtained suggested that the solvolysis was associative in character [664]. The complex $[M(LH_2)Cl_2]$ (LH_2 = (207)) has been prepared, and was characterised by conductivity measurements, TGA, powder diffraction data, UV, IR and NMR spectrsocopy. The data indicated that coordination involved the amino nitrogen groups in a *trans*-complex, which may be polymeric [665].



(205)



(206)

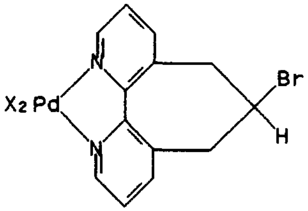


(207)

The chemisorption of palladium(II) onto silica modified by either bipy or phen has been investigated using IR and diffuse reflectance spectra [666]. Diffuse reflectance spectra and emission behaviour were used to characterise the lowest excited state of platinum(II) anionic and cationic species, including studies of complexes such as $[Pt(bipy)_2][PtCl_4]$, $[Pt(bipy)(4\text{-}Me,4'\text{-}heptylbipy)][PtCl_4]$ and the related $[Pt(CN)_4]^{2-}$ derivatives. Salts of $[PtCl_4]^{2-}$ have lowest excited states of the ligand field type [667].

The kinetics of the reaction of $[Pt(phen)_2]^{2+}$ with $[CN]^-$ to give $[Pt(phen)_2(CN)]^+$, and the reaction of $[Pt(phen)_2(CN)]^+$ to give $[Pt(phen)(CN)_2]^+$, have been studied. It was concluded that $[Pt(phen)_2(CN)]^+$ was not four- but five-coordinate [668].

Reaction of (208) (X = I) with iodide ion gave mainly substitution products, and the effect of the metal on the reaction rate was minimal. However, in (208) (X = OCOMe), using $[MeCOO]^-$, the rate of elimination was increased by a factor of 10^3 over that for the free ligand, due to conformational changes on complexation [669,670]. The preparation of palladium and platinum complexes of (209) has been reported. Their electronic spectra are rather different from those of the parent bipy complexes, which is attributed to a different degree of twist about the 2-2' bond [671].



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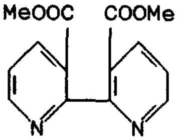
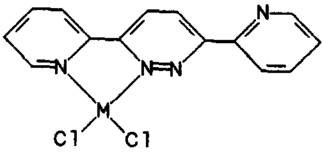


(209)

Complexes of 3,6-bis(2-pyridyl)pyridazine, dppn, have been studied. Both mono, (210) (M = Pd or Pt) and bis, (211) (M = Pd or Pt, M' = Pt, Ni, Cu or Co) complexes could be formed depending on the stoichiometry of the reactants. The electronic spectra and magnetic properties of the heterobinuclear species were studied, and indicated some magnetic interaction between the metals [672]. The complex (212) has also been described [673,674].

The synthesis of (213) has been described; reaction with $Pd(OCOMe)_2$ gave a bis(palladium) deivative [675]. $PdCl_2$ in MeCN reacted with 2- or 8-aminomethylquinoline, L, grafted on Aerosil to give the species $[PdLCl_2]$ and/or $[PdL_2][PdCl_4]$ [676]. The preparation of $K_2[PtL_2Cl_2]$ (L = (214)) has been described, and the structure of the product, (215), established in an

X-ray diffraction study. The synthesis of the binuclear species (216) was also noted [67].



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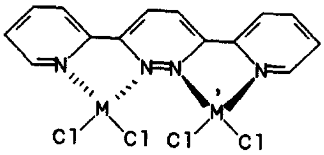

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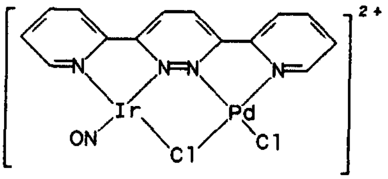

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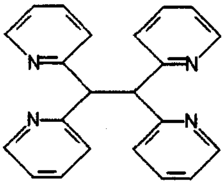

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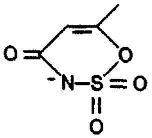

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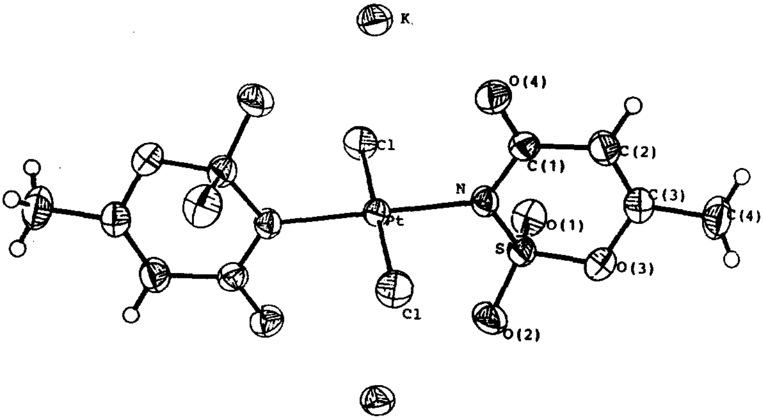
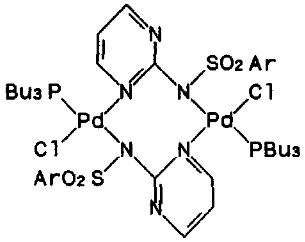


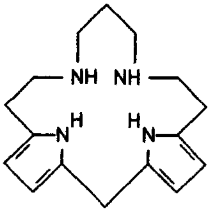
(215) (Reproduced with permission from [677])
Thermal ellipsoids correspond to 20 % probability



(216)

A sensitive and selective spectrophotometric method for the determination of palladium(II) was based on its reaction with 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene in sulphuric acid to give a violet-blue complex [678]. A method for analysis of palladium in ores has been developed, based on the reaction with 5-(3,5-dibromo-2-pyridylazo)-2,4-diaminotoluene. A 1:1 metal:ligand complex was formed [679,680]. In none of these papers was the structure of the complex formed described.

The complex (217) was formed when the dehydrogenation of (218) was attempted using PtO_2 [681]. Condensation of 1,2-diaminobenzene with (219) gave (220) [682].



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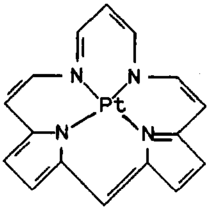
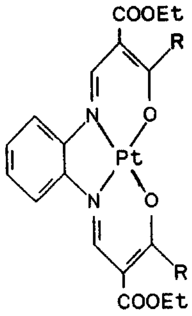


(218)

The reactions of $PdCl_2$ with a range of ligands, (221), has been investigated. In most cases monomeric species of the type (222) were formed, but in cases in which these would be very strained, dimers such as (223) were produced [683]. Related results were obtained for the series (224). With $R^1 = CH_2CH_2$ and $R^2 = Me$ both $[PdL]Cl_2$, (225), and $[PdL_2]Cl_2$, (226), could be formed. They were isolated by different work-up procedures and were characterised by X-ray diffraction studies [684].



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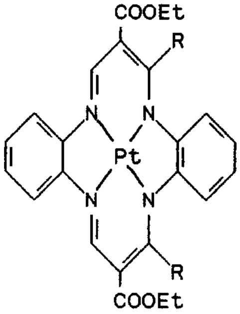

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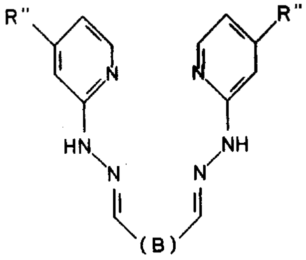

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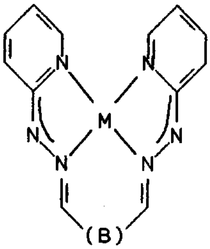

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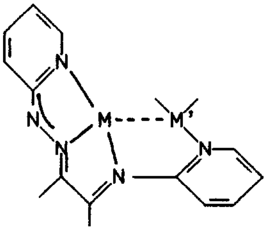

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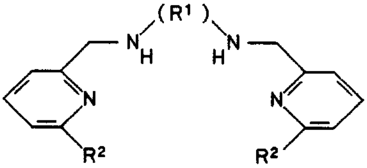

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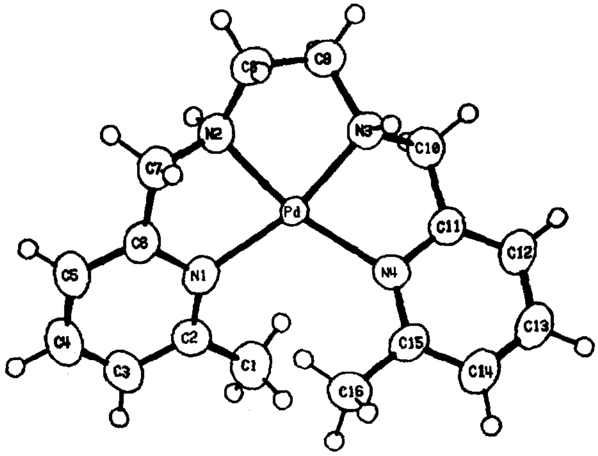
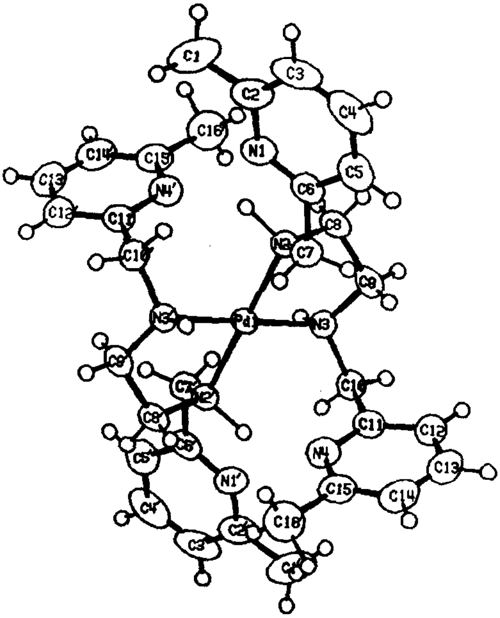


(225) (Reproduced with permission from [684])



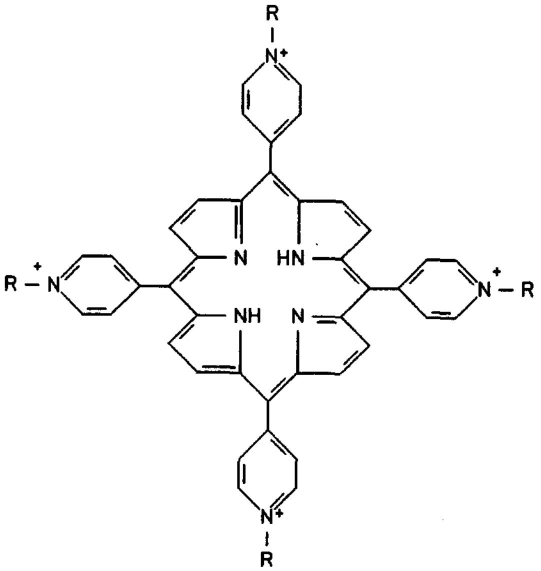
(226) (Reproduced with permission from [684])

1.6.5.4 Porphyrin and Phthalocyanine Complexes

The ^{1}H and ^{13}C nmr spectra of 2,3,4,8,12,13,17,18-octaethylporphyrin and *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin derivatives of platinum have been reported. Long range couplings between platinum and hydrogen involved Fermi contact through the π-system, but the couplings to carbon were through the σ-framework [685]. The ^1H and ^{13}C NMR spectra of the platinum complex of deuteroporphyrin IX dimethyl ester were reported, and were used in a study of aggregation phenomena [686].

Mass spectrometry of metal phthalocyanaine complexes, including derivatives of palladium and platinum, have been recorded [687]. FAB mass spectra of palladium corrinoids have also been described [688].

The effect of substituents at the periphery of a porphyrin ring on the $\pi \rightarrow \pi^*$ absorption was determined in a quantitative manner using a new approach based on the four orbital model. The UV/visible absoption spectra of Mg, Sn, Zn, Cu, Ni and Pt complexes with differently substituted porphyrins were systematically investigated [689]. The electronic spectra of metal complexes of *meso*-tetramethylporphine, and their methylene bridged dimers, have been recorded. The dimers showed an intense splitting of the Soret band, which was a result of the conformation of the exciton coupled porphine dimer [690]. The porphyrin derivative (227) was prepared with the intention that the amphoteric functional groups would improve aggregation properties and adsorption characteristics of its complexes. The Soret bands of the metal porphyrin complexes, including that of palladium(II) were reported [691].



(227)

R = $-CH_2COO^-$, $-CH_2CH_2COO^-$ or $-CH_2CH_2SO_3^-$

There has been a study of the dependence of the phosphorescence of the palladium(II) complex of etioporphyrin I on concentration and temperature [692]. Kinetic data on quenching in 10^{-8}-$6x10^{-4}$ M solutions in toluene was in agreement with a mechanism involving the formation of a complex between a molecule in the ground state and one in the triplet state. The Shock type complex was found to be more probable than the eximeric one [693].

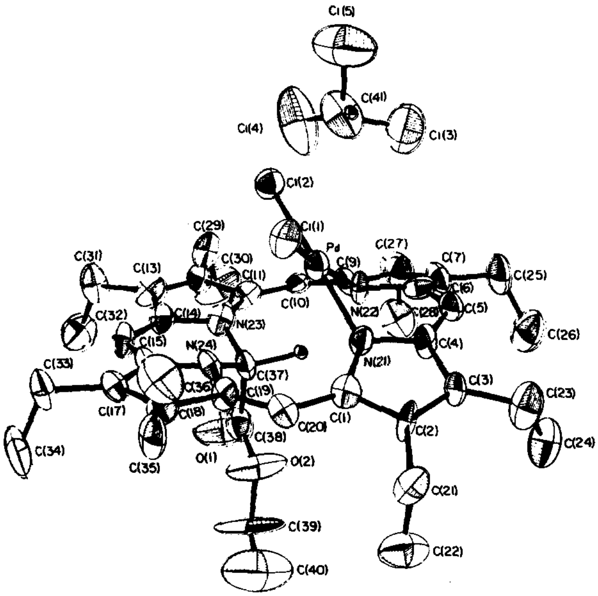
The Zeeman splitting in the lowest phosphorescent state of palladium phthalocyanine in Shpol'skii matrxes of mixed 1-chloronaphthalene and *n*-octane has been reported. This is the first study of a randomly oriented large molecular system investigated using Zeeman spectrsocopy, without reliance on photoselection [694]. Metal phthalocyanines were examined in thin film form on metal substrates by electron microscopy, UV/visible spectroscopy and electrochemical and photoelectrochemical techniques. The palladium and platinum derivatives had poor photoelectrochemical activity [695].

A method has been suggested to determine the mean degree of association in a solution of molecules which exhibit luminescence. In this way, the palladium(II) complex of tetra-6-*tert*-butyl-2,3-naphthalocyanaine was shown to form trimers in toluene [696]. The complex formed between platinum uroporphyrin I and methyl viologen has been investigated by resonance Raman difference spectrsocopy and UV/visible spectroscopy. It was deduced that the complex was a 2:1 π:π-species with a substantial contribution to the binding energy coming from electrostatic interactions [697]. Non-Stern-Volmer quenching of the triplet state was observed in a donor acceptor system comprising palladium octaethylchlorin as the donor, and ytterbium etioporphyrin as the quencher. The quenching mechanism involved direct and reversible energy transfer [698].

Metal complexes of 5,10,15,20-tetrakis(3-carboxyphenyl)porphine were tested for the chemiluminescence reaction of luminol and hydrogen peroxide. The iron derivative gave better results than either the palladium or the platinum complex [699].

The structure of (228) was determined in an X-ray diffraction study. This represents a rare example of 5-coordinate palladium, with the metal adopting coordination best described as square planar with a trigonal pyramidal distortion. The distortion arises from significant intramolecular Pd-H bonding [700].

Metal complexes of tetraarylporphyrins have been separated by reverse phase high-performance liquid chromatography [701]. However, even in polar solvents there were some problems in the separation of the nickel and palladium derivatives of the *meso*-tetrakis (4-methylphenyl)porphine [702].



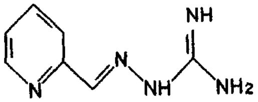
(228) (Reproduced with permission from [700]
Thermal ellipsoids are drawn at the 50 % probability level

The complex *meso*-tetrakis(4-*N*-methylpyridyl)porphine palladium(II) interacted strongly with mononucleotides and nucleosides in aqueous solution. The interactions involved stacking, with extensive overlap of the π-systems [703].

1.6.5.5 Imine donor ligands

Derivatives of (229) with 1:1 and 1:2 ligand:metal stoicheiometries were used for palladium analysis, but the structures of the complexes were not given [704]. Stability constants were determined for the reaction of (230) with palladium(II), but again the structure of the complexes formed were not given [705].

XPES of various imine complexes of platinum(II) such as (231) were compared with five coördinate species, [Pt(diimine)(alkene)Cl_2] [706]. Palladium and platinum complexes of a polyimide were studied by TG and difference TG [707].



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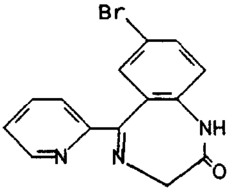

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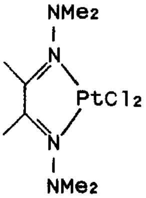


(231)

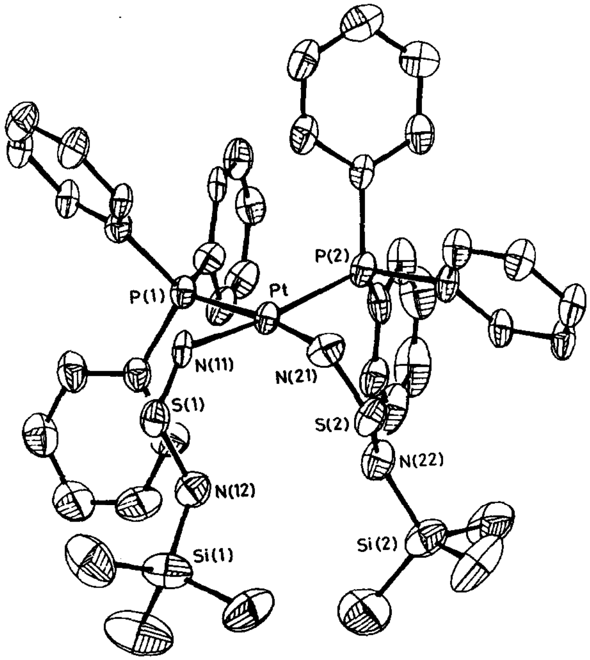
1.6.5.6 Nitro ligands

The complex anions $[M(NO_2)_4]^{2-}$ (M = Pd or Pt) were extracted by $[R_4N]^+$ as ion pairs, and $[R_4N]_2[M(NO_2)_4]$ could be isolated. Tha platinum complexes were more extensively associated than the palladium analogues [708]. The photolysis and isomerisation of *trans*-$[Pt(PPr_3)_2(NO_2)_2]$ has been investigated. Photolysis in the UV region gave a photostationary *trans/cis* equilibrium mixture, but in the dark the *cis*-isomer reverted to the *trans*-form. The pure *cis*-isomer could be isolated after photolysis in hexane, and was fully characterised. Crossover experiments indicated that the isomerisation was intramolecular, probably involving a twist mechanism [709].

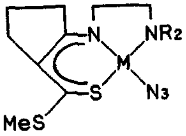
1.6.5.7 Other nitrogen ligands

Complexes of glycolphosphorous acid diethylamide have been studied [710]. The reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with $(Me_3SiN)_2S$ gave (232), which was characterised by an X-ray diffraction study [711].

The azide complex (233) underwent 1,3-dipolar cycloaddition reactions involving the azide ligand to give complexes such as (234). The cycloaddition reaction was also successful with RCN, CS_2, PhNCS or CH_2CHCN [712].



(232) (Reproduced with permission from [711])



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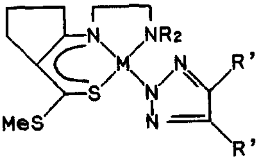
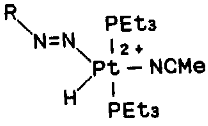


(234)

The kinetics of the reaction of *trans*-[HPt(PEt$_3$)$_2$Cl] with [ArN$_2$]$^+$ in MeCN have been investigated using the stopped flow technique. The initial reaction was replacement of the chloride by MeCN, to give *trans*-[HPt(MeCN)(PEt$_3$)$_2$]$^+$, followed by the formation of (235), (236), (237) and (238), the aryl diazine product. The electronic effect of the substituent at the 4-position in the aryl group was considerable. For Ar = 4-MeOC$_6$H$_4$, (237) lost nitrogen to give *trans*-[ArPt(PEt$_3$)$_2$Cl] [713].



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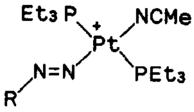

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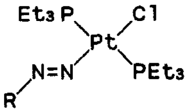

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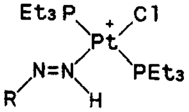
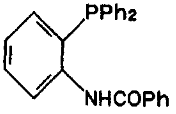


(238)

1.6.5.8 Bidentate and polydentate nitrogen phosphorous donor ligands

Reaction of the ligands (239) and (240) with $[MCl_4]^{2-}$ (M = Pd or Pt) gave initially *trans*-$[ML_2Cl_2]$ in which the ligands were monodentate, bound at phosphorus. Treatment with base resulted in activation of an N-H bond to give *cis*- and *trans*-$[M(L-H)_2]$, in which the ligands were bidentate. The process is analogous to orthometallation. Reaction of the chelate complexes with HCl gave *cis*-$[ML_2Cl_2]$ [714].



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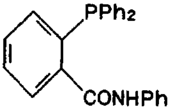
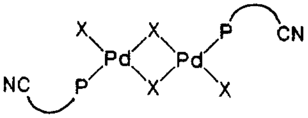


(240)

Reaction of $H_2[PdX_4]$ (X = Cl or Br) with an excess of $Ph_2PCH_2CH(CH_3)CN$ gave *trans*-$[PdL_2X_2]$. Similar results were obtained for $Ph_2PCH_2CH_2CN$ and 2-diphenylphosphinobenzonitrile. However, if the amount of ligand was reduced, $[\{LPdX_2\}_2]$ was formed. NMR spectrsocopic data indicated that in these complexes there was an equilibrium between halide bridged, (241), and ligand bridged forms, (242). Reaction of the dimers with an alcohol, ROH, gave the phosphine imidate complex, (243), *via* a facile attack on the coordinated nitrile [715].

Treatment of either $[Pt(PhCN)_2Cl_2]$ or $[Pt(dmso)_2Cl_2]$ with a mixture of the stereoisomers of (244) (shown as the S,S-form) gave two complexes. The complex derived from *meso*-(244), (245), was tetradentate with two amino and two phosphine ligands. However, the racemic complex, derived from R,R- and S,S-(244), (246), was tridentate, with two phosphine, one amine and one chloro ligand. This is the first demonstration of ionisation isomerism, from tridentate to tetradentate coordination, with racemic and *meso*-diastereoisomers [716].



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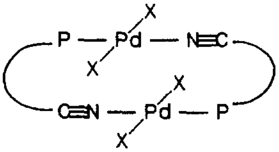

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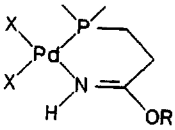

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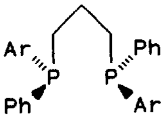

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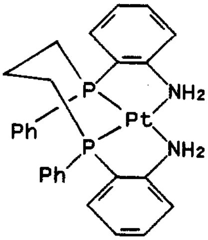


(245)

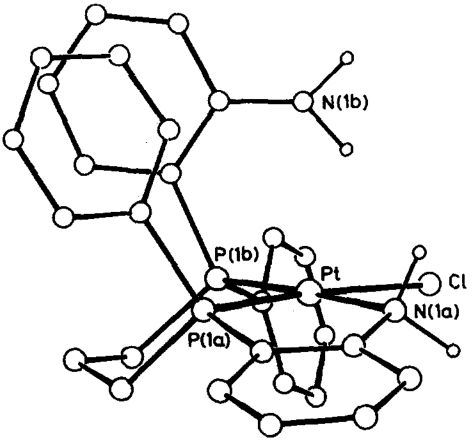
The reaction of $[Ni_2(PNNP)_2]$ (HPNNP = (247)) with $[PdCl_4]^{2-}$ gave (248) *via* an interesting metal transfer synthesis [717].

1.6.5.9 Bidentate nitrogen arsenic donor ligands

The two bidentate nitrogen arsenic donor ligands (249) (R = Me or Bu) were prepared and resolved *via* palladium cyclometallated complexes, (250). CD spectra were recorded for $[MLX_2]$ (M = Pd or Pt). The arsines were readily racemised by HCl, but their complexes were more stable [718].

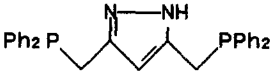
1.6.5.10 Bidentate and polydentate nitrogen carbon donor ligands

The reaction of $PhCH_2NH_2$, L, with $Pd(OCOMe)_2$ gave either $[PdL_2(OCOMe)_2]$ or $[PdL_4][OCOMe]_2$. A determination of the structure of $[PdL_4][OCOMe]Cl$ by X-ray diffraction showed that there was no interaction of the *ortho*-hydrogen atom with the metal. Similarly $PHCH_2NHMe$, L', gave $[PdL'_2(OCOMe)_2]$. However, the reaction with $PhCH_2NMe_2$ yielded the cyclometallated complex, presumably *via* initial formation of the simpler species [719]. Related cyclometallated species were obtained from (251). The kinetics were in this case studied with great care, and it was concluded that the cyclopalladation was not the rate-controlling step. Spectroscopic data also supported the initial formation of simple amine complexes [720]. The structures of the three regioisomers, (252) were determined in X-ray diffraction studies; all adopted *trans*-geometry [721]. For the first time, and somewhat surprisingly, cyclometallated complexes of primary and secondary benzylamines have been obtained (Scheme 5) (R^3 = H or alkyl, R^1, R^2 = OMe, H or OCH_2O) [704].



(246) (Reproduced with permission from [697])

The structure of $[Pt^{II}(rac\text{-}L)Cl]Cl.2H_2O$. An amino hydrogen atom on N(1a) is strongly hydrogen bonded to a water molecule with H...O 1.93 Å



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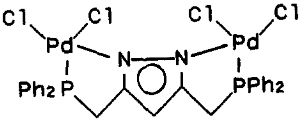

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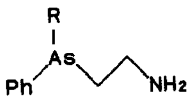

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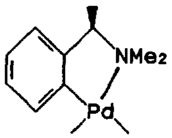

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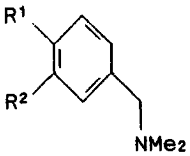

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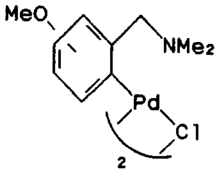

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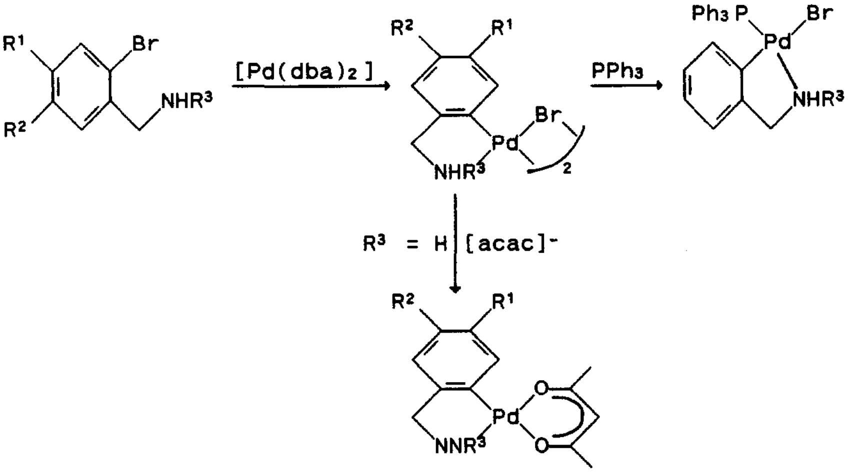
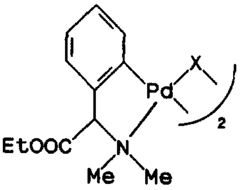


Scheme 5 Preparation of cyclometallated complexes of primary and secondary benzylamines [722]

Reaction of $PhCH(NMe_2)COOEt$ with $Li_2[PdCl_4]$ gave (253), whereas the related free acid gave an *N,O*-chelated complex [723]. Treatement of $Pd(OCOMe)_2$ with $Me_2NCH_2CMe_3$ yielded the cyclometallated species (254), which underwent the usual bridge-splitting reactions [724].



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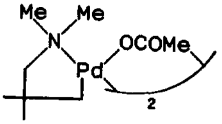
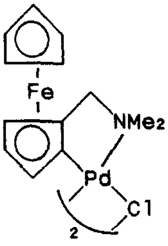


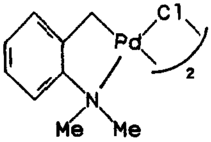
(254)

Reaction of dimethylaminomethylferrocene with $[PdCl_4]^{2-}$ in dioxan gave the complex *trans*-$[PdL_2Cl_2]$, but in methanol in the presence of sodium ethanoate the cyclometallated species (255) was formed; this underwent all the usual bridge splitting reactions [725]. Carbonylation of the optically active complex in the presence of $HOCH_2CH(OCH_2Ph)CH_2OH$ gave $HOCH_2CH(OCH_2Ph)CH_2OCOFc$ with 36 % asymmetric induction [726].



(255)

The reaction of either *cis* or *trans*-(256) with Ag[OCOMe] gave the ethanaote bridged dimer, which showed dynamic behaviour in its NMR spectrum. However, when 2,*N*,*N*-trimethylaniline was reacted with palladium ethanoate in ethanoic acid, the product was a trimer, (257) [727].



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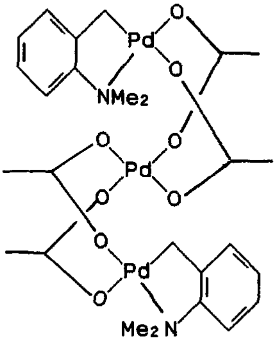
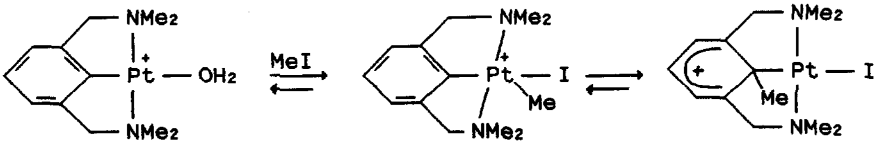


(257)

The reversible reaction of (258) with iodomethane has been further studied. The initial step is electrophilic reaction at platinum, followed by a reversible 1,2-alkyl shift along the platinum-carbon bond. In the reaction of (259), a single stereoisomer, (260) was formed [728].



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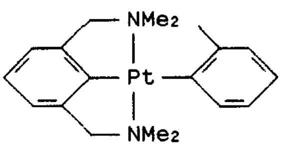

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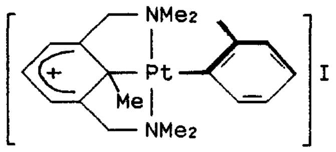
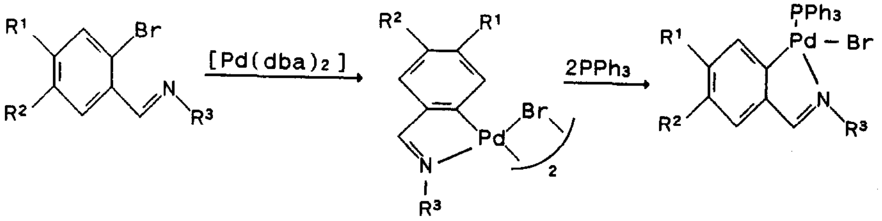


(260)

There has been continued interest in the cyclometallation reactions of imines. An improved method of preparation of the cyclometallated complexes was described (reaction (15)), and the usual bridge splitting reactions of the product investigated [729]. Most imine complexes, however, continue to be made by direct metallation of an aryl ring using Pd(OCOMe)$_2$. In reaction (16) the rate of metallation depended on the nature of Y; the process was slow when Y was an electron-withdrawing group [730]. Metallation of (261) seemed to occur at the 2-position of the naphthalene ring, but the structures of the product were not given in the paper [731]. The related reaction of (262) was assumed to occur at the unsubstituted ring, and some bridge splitting reactions were studied, but details again seemed to be rather lacking [732,733]. Reaction of the benzylamine derivative, (263), gave only the cyclometallated species containing a five-membered ring, and only the *trans*-dimeric form of the product (264) was observed [734].



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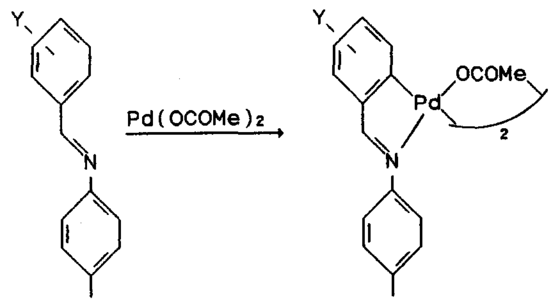
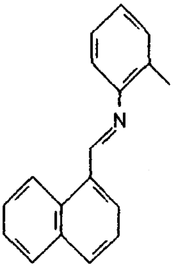


(16)



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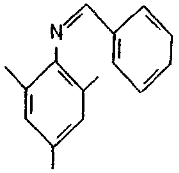

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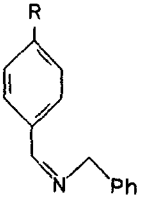

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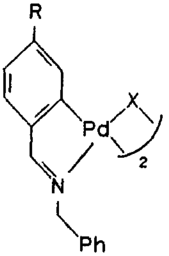
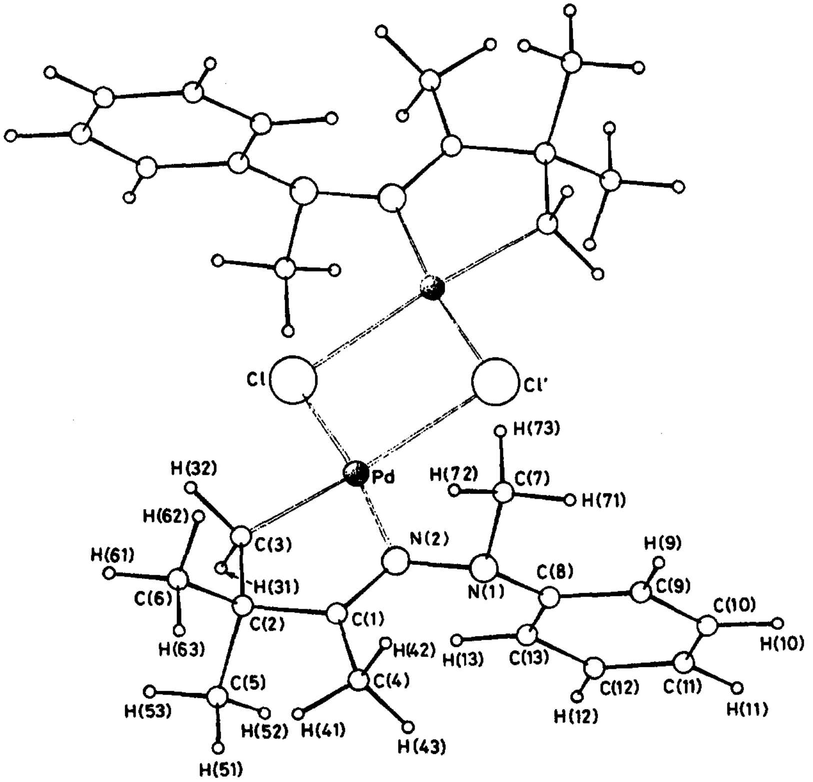


(264)

Metallation of the substituted hydrazone, $Me_3CC(Me)=NNMePh$, gave a mixture of (265) and (266) as previously described; these complexes have now been fully characterised by X-ray diffraction studies. Bridge splitting reactions were studied, and the temperature dependence of the NMR spectrum was interpreted in terms of *cis/trans*-isomerisation and restricted rotation about the N-N bond [735].

The regioselectivity of the metallation of non-symmetrically substituted azines such as (267) has been further studied. Palladation occurs preferentially in the ring with the higher electron density. The electronic spectra of both ligands and complexes were recorded, the low energy region being dominated by transitions localised on the azobenzene chromophore [736]. The azo compound (268) was reported not to react directly with $PdCl_2$, but with the copper complex, (269) was formed. Reactions of the related ligand bearing a carboxylic acid group at the 2-position were also studied, and cyclometallation reported to occur, but the characterisation of the palladium complexes left much to be desired [737]. It was known that benzalazines reacted with $PdCl_2$ to give oligomeric coordination complexes. However, when they were treated with $Pd(OCOMe)_2$ followed by $K_2[PtCl_4]$, the first mixed metal bis(cyclometallated) species, (270), was prepared. This was oligomeric, but reaction with PEt_3 gave the monomer (271) [738].

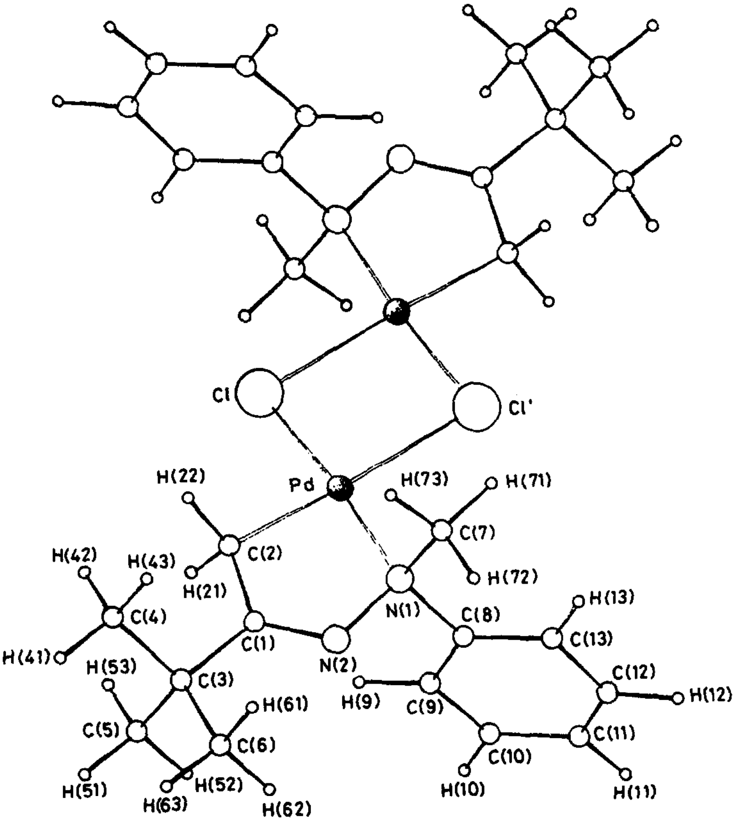


(265) (Reproduced with permission from [735])

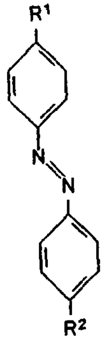
The structure of (272) was established in an X-ray diffraction study. The central 6-membered ring adopted a boat conformation, and at 3.165(3) Å the palladium-palladium distance was rather long for Pd-Pd bonding [739]. The preparation (from pyridyl substituted polymer, 2,6-bis(CH_2CHR_2)pyridine and $Na_2[PdCl_4]$), and characterisation of a cyclometallated polymer supported palladium complex, (273), has been described. When the polymer is generated at high temperatures the material exhibits significant catalysis for the hydrogenation of cinnamic acid [740].

Reaction of bipy with $Pd(OCOMe)_2$ gave a cyclometallated dimer (274). The usual bridge splitting and anion exchange reactions were reported, and it seems likely that cyclometallation of this ligand is a great deal more common than has previously been realised [741]. In similar vein, thermolysis of $[Ar_2Pt(bipy)]$ gave (275) with no significant coupling of the arenes. In the absence of a trapping agent this readily oligomerises, but in the presence of 4-Me_3CPy, (276) was formed, and characterised in an X-ray diffraction study

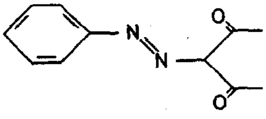
[742].



(266) (Reproduced with permission from [735])



(267)



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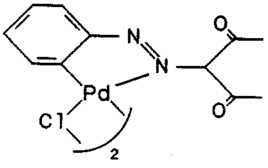

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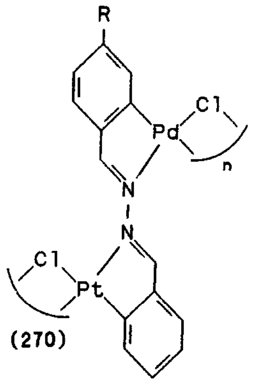

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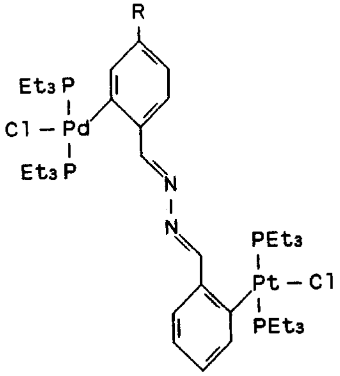

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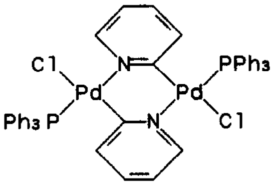

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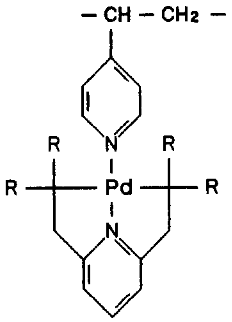

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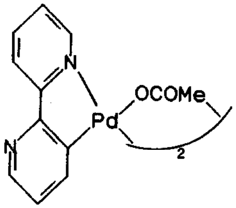

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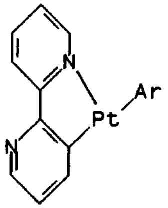
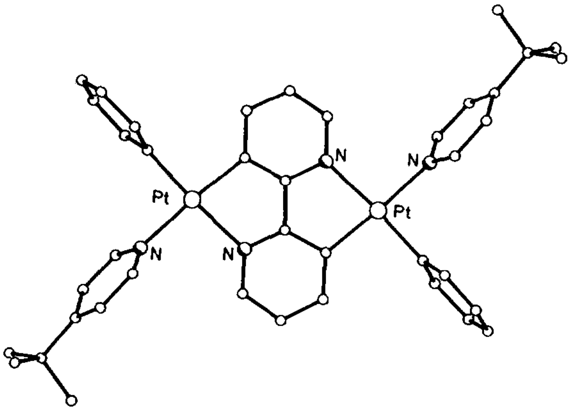
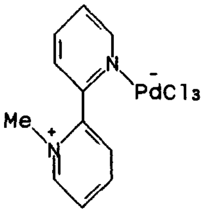


(275)



(276) (Reproduced with permission from [742])

Thermolysis of (277) in water gave a cyclometallated derivative, tentatively formulated as (278), although it was difficult to distinguish between this an a halo bridged dimer [743]. Reaction with bipy or py resulted in substitution of the chloride ligands [744]. When the substituted bipy palladium complex, (279) (R = COOEt), was treated with base, double cyclometallation occurred in two controllable stages. The structures of the mono and bis(metallated) derivatives, (280) and (281) were established in X-ray diffraction studies. The binding of the bis(cyclometallated) complex to phage PM2 DNA was investigated with rather inconclusive results [745].



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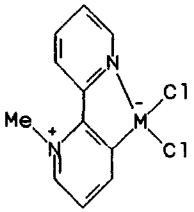
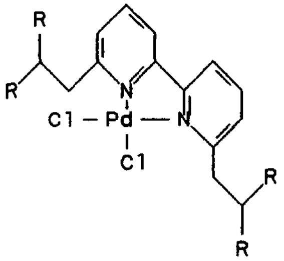


(278)

The treatment of *trans*-$[\{Pt(PEt_3)Cl(\mu\text{-}Cl)\}_2]$ with (282) at ambient temperature gave (283), characterised in an X-ray diffraction study. The distance between the platinum atom and the hydrogen atom of the aldehyde is relatively short (2.3 Å), suggesting that the metal might activate the C-H bond. This indeed proved to be the case, with ready conversion to (284), with loss of HCl [746].



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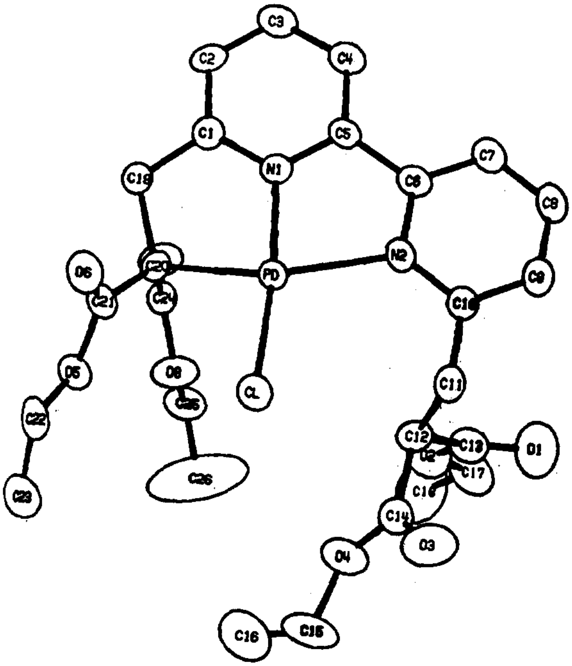
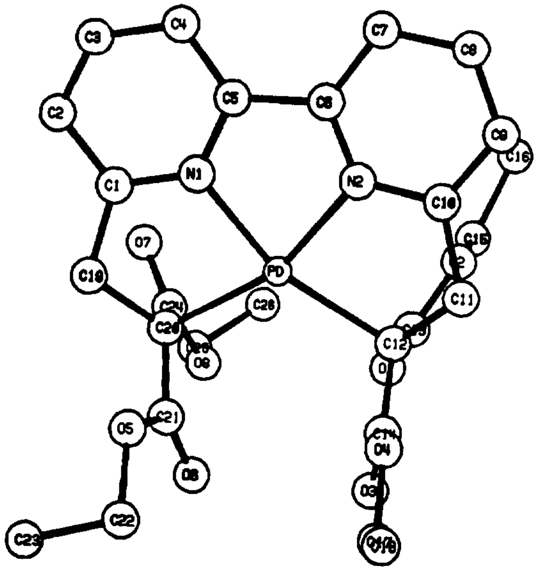
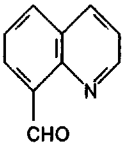


(280) (Reproduced with permission from [745])

The electrochemistry of the cyclometallated ylid complex, (285), has been ivestigated [747]. The bridged cyclometallated dimer, (286), was prepared from the ligand and $Pd(OCOMe)_2$ or $K_2[PdCl_4]$ [748].



(281) (Reproduced with permission from [745])



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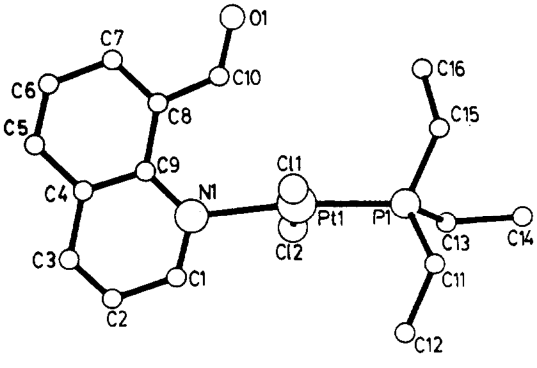
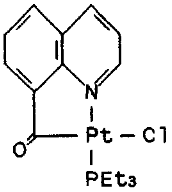


(283) (Reproduced with permission from [729])



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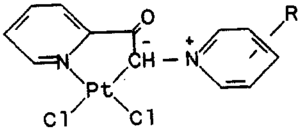

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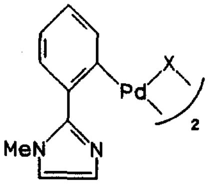
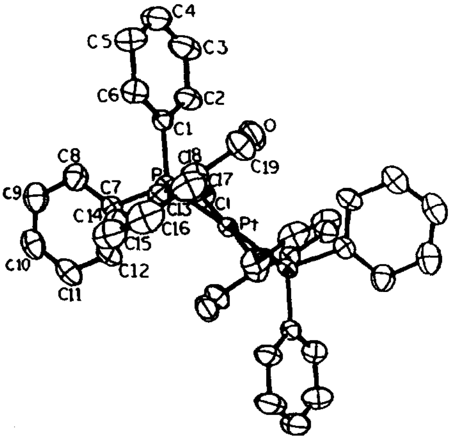


(286)

1.6.5.11 Unidentate phosphine donor ligands

The structure of *cis*-$[Pt(PPh_3)_2Cl_2]$ was determined in an X-ray diffraction study. Metal ligand bond lengths were rationalised in terms of the *trans*-effect [749]. Reaction of 2-diphenylphosphinobenzaldehyde with $K_2[PtCl_4]$ gave *trans*-$[PtL_2Cl_2]$, (287), in which the aldehyde was not metal coordinated. In fact the oxygen of the aldehyde was more closely associated with the phosphorus atom (P...O = 2.92(8) Å) than the metal [750].

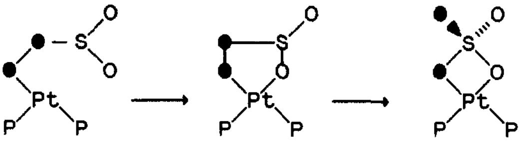


(287) (Reproduced with permission from [750])

FAB mass spectrometry has been used to observe platinum(II) complexes of

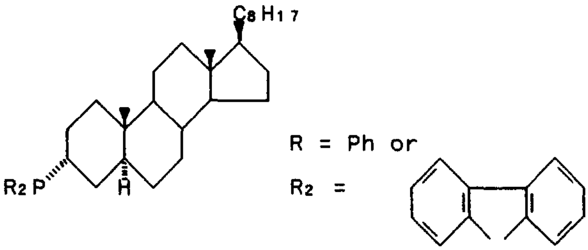
Et_3P in solution, and has allowed the identification of species in complex equilibria. In dilute H_2SO_4 solution a good spectrum was obtained for $[Pt(PEt_3)_3X]^+$ showing fragementations corresponding to the loss of each of the ligands. In a solution containing *cis*-$[Pt(PEt_3)_2Cl_2]$, PEt_3 and $Ag[ClO_4]$ both $[Pt(PEt_3)_3(OH_2)]^+$ and $[Pt(PEt_3)_3(ClO_4)]^+$ were identified from the FABMS [751].

The binding of phosphinidines, H_2P-P:, to transition metal fragments has been studied theoretically; $[PtCl_3]^+$ was among the fragments investigated and had a weak bonding interaction with the ligand [752]. Calculations on the mechanism of the reaction of $[Pt(PPh_3)_2(O_2)]$ with SO_2 have been undertaken, showing that the first step is coordination of the SO_2 with one oxygen atom of the complex, followed by M-O bond scission and reorientation to give (288). This rearranges rapidly to bidentate coordinated sulphate [753].



(288)

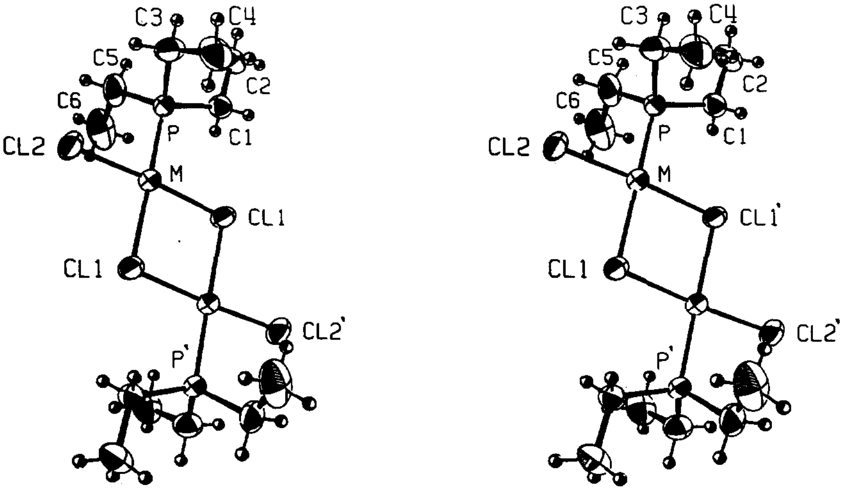
The complexes *trans*-$[PdL_2Cl_2]$ (L = (289)) have been prepared by reaction of the ligands with $[Pd(PhCN)_2Cl_2]$ [754].



(289)

The *trans*→*cis* isomerisation of $[Pt\{PPh(CF_3)_2\}_2Cl_2]$ at 125-130 °C was studied by DTA and IR spectroscopic analysis [755]. There has been further discussion about the reported electrochemical data for $[Pt(PR_3)_2Cl_2]$. One group has commented that the reduction potentials for the *cis*- and *trans*-isomers are necessarily equal since the two are in a catalysed equilibrium under the reaction conditions [756]. This suggestion is disputed by the authors of the original study [757].

The reaction of *trans*-$[Pt(PR_3)_2Cl_2]$ with $PdCl_2$ or *trans*-$[Pd(PR_3)_2Cl_2]$ with $PtCl_2$ gave the bridged species *trans*-$[Cl(R_3P)Pd(\mu\text{-}Cl)_2Pt(PR_3)Cl]$. The mixed metal bridged complex was in equilibrium with the homometallic dimers, the position of the equilibrium being dependent on the [Pd]:[Pt] ratio but not on temperature. ^{31}P and ^{195}Pt NMR spectra were reported, and the structure of (290) was established in an X-ray diffraction study. The dimers reacted with $SnCl_2$ by insertion into the terminal metal-chloride bonds [758]. The kinetics of the reactions of *cis* or *trans*-$[Pt(PPh_3)LCl_2]_{solid}$ (L is a nitogen or sulphur donor ligand) to give gaseous L and *trans*-$[Pt_2(PPh_3)_2(\mu\text{-}Cl)_2Cl_2]$ have been studied by a non-thermal method, based on analysis of the gas liberation curves. A dissociative mechanism seemed the most likely [759].



(290) (Reproduced with permission from [758])
Stereoview of a molecule of the centrosymmetric complex. M represents the disordered Pd/Pt atom.

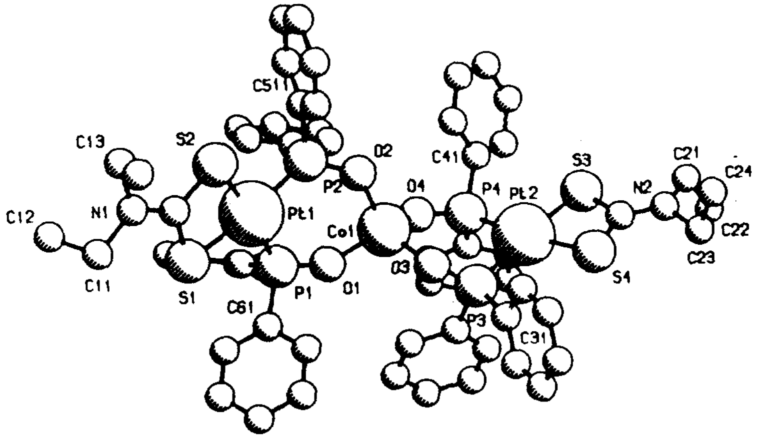
The substitution reactions of $[Pt(PEt_3)_2Cl_2]$ by X^- have been studied by mass spectrometry. Negative CI showed peaks due to $[Pt(PEt_3)_2Cl_2I]^-$, $[Pt(PEt_3)_2Cl_3]^-$ and $[Pt(PEt_3)_2ClI]^-$, suggesting that there is a true five-coordinate intermediate in the substitution reaction, with a lifetime in excess of 10^{-5} sec [760].

Treatment of *cis*-$[Pt(PMe_3)_2Cl_2]$ with sodium naphthalide under a hydrogen atmosphere gave *trans*-$[HPt(PMe_3)_2Cl]$, and this is further converted to *cis*- and *trans*-$[H_2Pt(PMe_3)_2]$. The *trans*-isomer was crystallised in the presence of naphthalene, the material being stable only in a hydrogen atmosphere [761].

1.6.5.12 Other unidentate phosphorus donor ligands

Reaction of montmorillonite with Ph_2PCl, followed by treatment with $[Pd(PhCN)_2Cl_2]$, gave a montmorillonite with palladium(II) phosphite units truly anchored in the interlamellars. The material was characterised by powder X-ray diffraction studies [762].

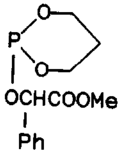
When the complex $[Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}]$ was treated with $[Co(acac)_2]$, the cobalt replaced the hydrogen of the hydrogen bond to give (291), $[Co\{(\mu\text{-}OPPh_2)_2Pt(SCNEt_2)\}_2]$, characterised in an X-ray diffraction study [763].



(291) (Reproduced with permission from [763])

General view of the molecule showing the coordination of the platinum and cobalt atoms. The $CHCl_3$ solvate molecule and the hydrogen atoms have been omitted for clarity.

Coordination of $PhOPCl_2$ to platinum(II) was accomplished by reaction with *cis*-$[Pt(PhCN)_2Cl_2]$. Reaction of the ligand within the coordination sphere successively with 4-methylphenol and 4-chlorophenol resulted in displacement of the two chlorides from phosphorus, and the preparation of the complex of the chiral phosphite, $PhOP(OC_6H_4\text{-}4\text{-}Me)OC_6H_4\text{-}4\text{-}Cl$. The complex could be resolved using *cis*-$[Pt\{(+)\text{-}(292)\}_2I_2]$, which reacted to yield diastereomeric mixed ligand complexes, which were then separated by chromatography. The chiral phosphite ligand was recovered by decomposition of the separated complexes with $[CN]^-$, but racemised slowly over a period of weeks [764]. The reactions of *cis*-$[M\{(RO)_3P\}_2(SCN)_2]$ with phosphite ligands have been studied. Partially hydrolysed products were said to be obtained, but characterisation was poor [765].



(292)

1.6.5.13 Bidentate and multidentate phosphorus donor ligands

The structures of the complexes $[Pd(dppe)_2]Cl_2$ and $[Pt(dppe)_2]Cl_2$ have been established in X-ray diffraction studies [766]. The preparations of derivatives of the non symmetric phosphines $Ar_2PCH_2CH_2PPh_2$ (Ar = 3- or 4-MeC_6H_4), $[MLCl_2]$ (M = Pd or Pt), have been described. Reaction with Na[HS] gave $[ML(SH)_2]$ [767]. The cationic complex $[Pd(dppe)(ROH)_2][ClO_4]_2$ was shown to promote the alcoholysis of silanes R_3SiH to R_3SiOR' *via* reactions (17)-(19) [768].

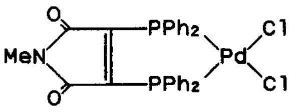
$$2[Pd(dppe)(ROH)_2][ClO_4]_2 + 2Ph_3SiH + H[ClO_4] \longrightarrow [Pd_2(dppe)_2][ClO_4]_2 + H_2 + 2Ph_3SiOClO_3 \qquad (17)$$

$$Ph_3SiOClO_3 + ROH \longrightarrow Ph_3SiOR + HClO_4 \qquad (18)$$

$$Ph_3SiH + H[ClO_4] \xrightarrow{[Pd(dppe)_2][ClO_4]_2} H_2 + Ph_3SiOClO_3 \qquad (19)$$

When $(HOOCCH_2)_2PCH_2CH_2P(CH_2COOH)_2$ reacted with $[MCl_4]^{2-}$ (M = Pd or Pt), a 1:2 complex was formed, with the ligand acting as a *P,P*-donor to the metal. The soft metal centre shows a preference for the soft site in the ligand [769]. In complexes $[MLX_2]$ of $Ph_2P(CH_2)_nPPh_2$ (*n* = 8, 10 or 16) the chelate occupied *trans*-positions in the coordination sphere, and the complexes are monomeric [322].

Reaction of (293) with $[Pd(PPh_3)_4]$ gave (294), characterised in an X-ray diffraction study. Further reactions of the product were discussed [770].



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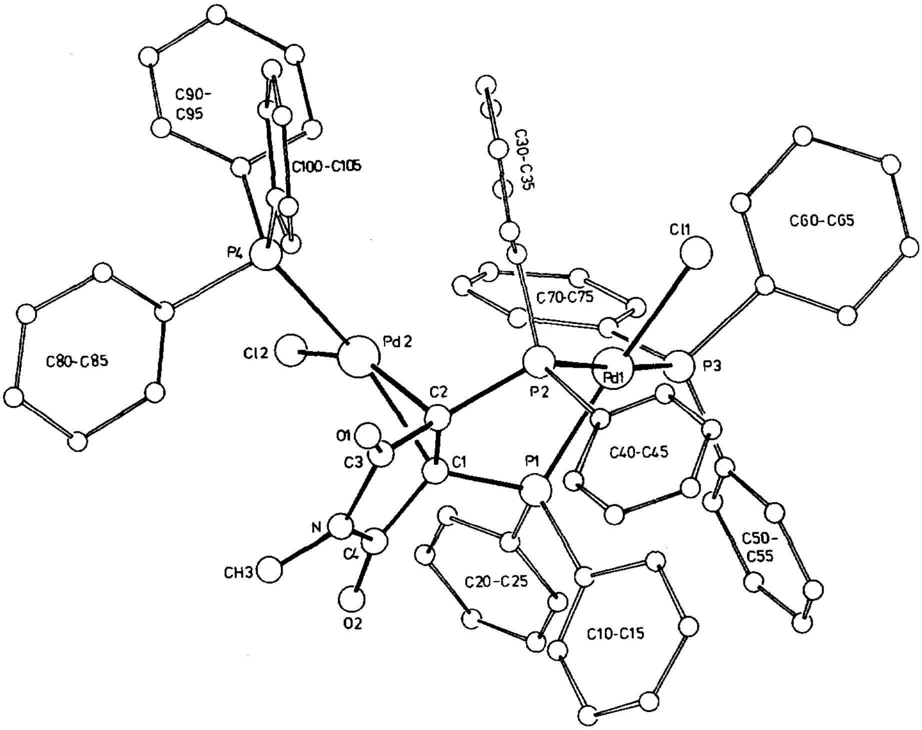
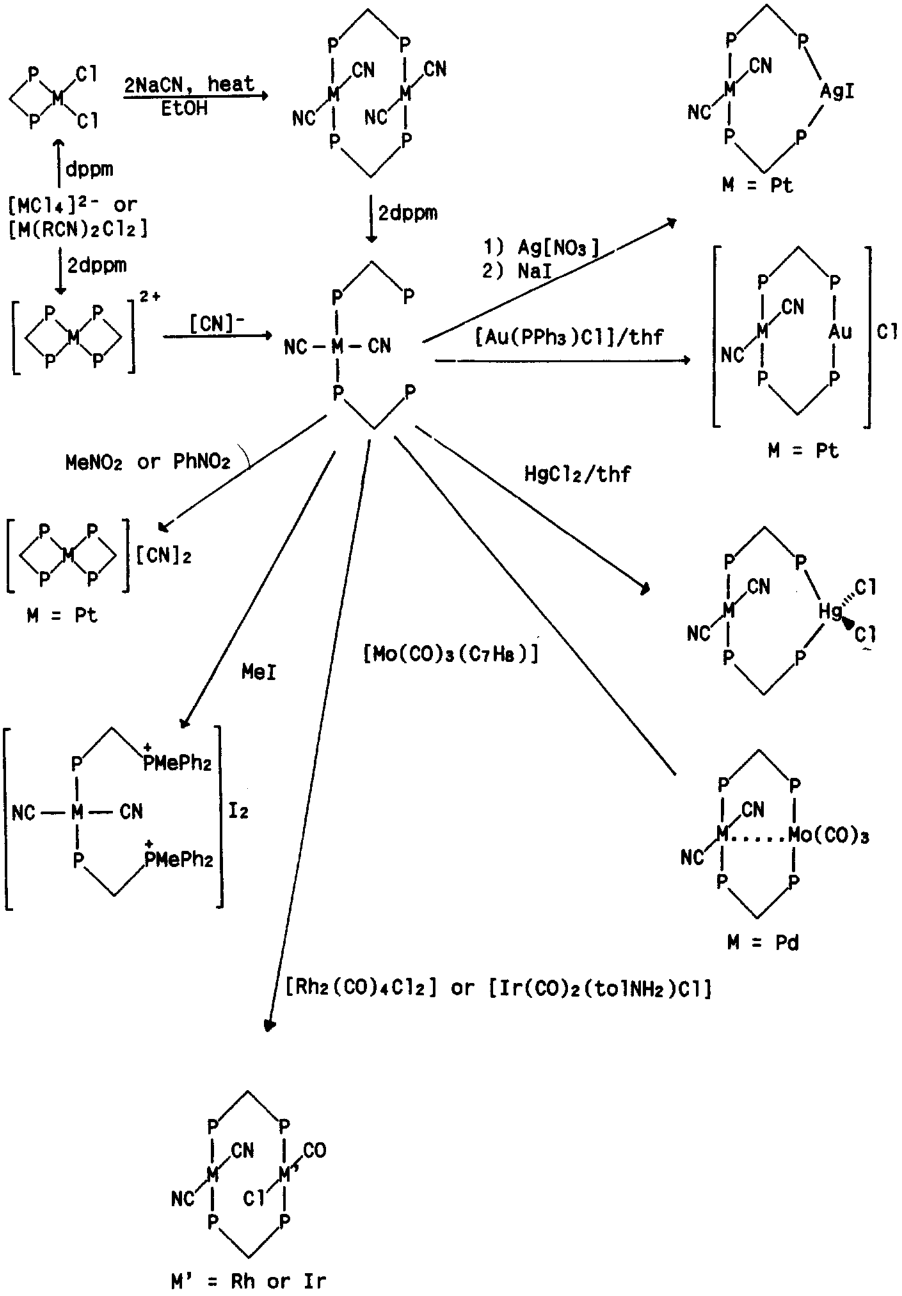


(294) (Reproduced with permission from [770])

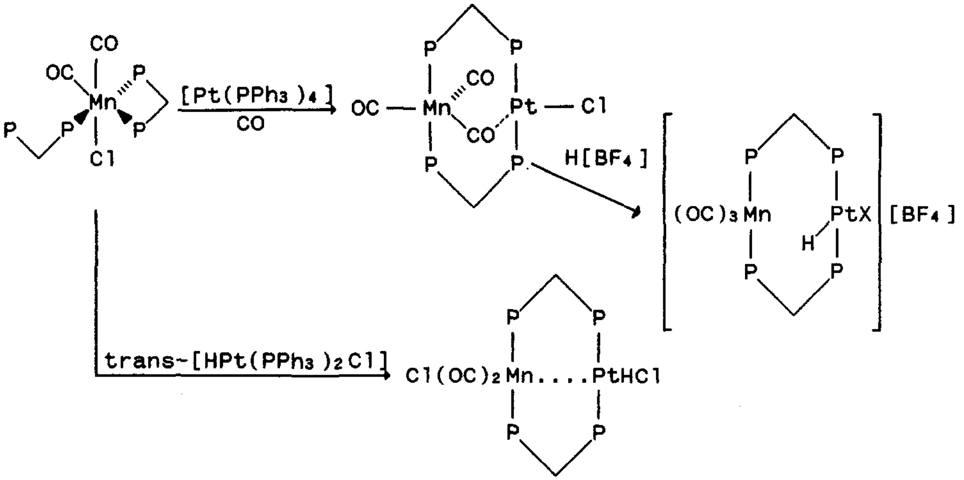
A substantial full paper detailing reactions of mono and binuclear palladium and platinum derivatives of dppm has been published (Scheme 6) [771]. Binuclear derivatives with manganese carbonyls have also been studied (Scheme 7) [772].

Treatment of $[Pt(SMe_2)_2Cl_2]$ with $Et_2PCH_2PEt_2$, depm, gave $[Pt(depm)Cl_2]$ A similar reaction occurred with $(Me_2CH)_2PCH_2P(CHMe_2)_2$, but with dmpm an oligomer, possibly *cis*-$[Pt_2(\mu\text{-dmpm})_2Cl_4]$, was formed. The dimeric species formed with $(Me_3C)HPCH_2PH(CMe_3)$ was characterised by an X-ray diffraction study, and it was concluded that steric effects are of primary importance in determining product nuclearity [773].

When a mixture of isotropic liquid crystalline guests is equilibrated in a host capable of forming a clathrate phase, the mole ratio of the guests in the clathrate differs from that in the coexisting liquid. A preference for C_6H_6 over C_6D_6 in $[Pt(Ph_2PCHPPh_2)_2]$ (separation factor = 0.95) was attributed to a tight fit of the guest in the host lattice, although vapour pressure may also be important [774].



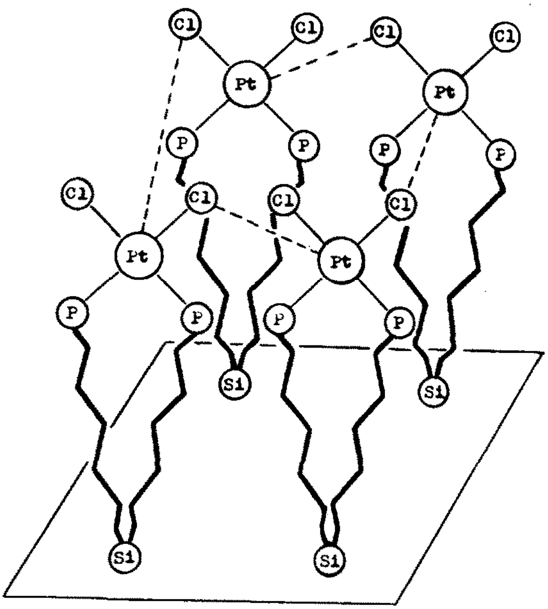
Scheme 6 Reactions of palladium and platinum complexes of dppm (M = Pd or Pt) [771]



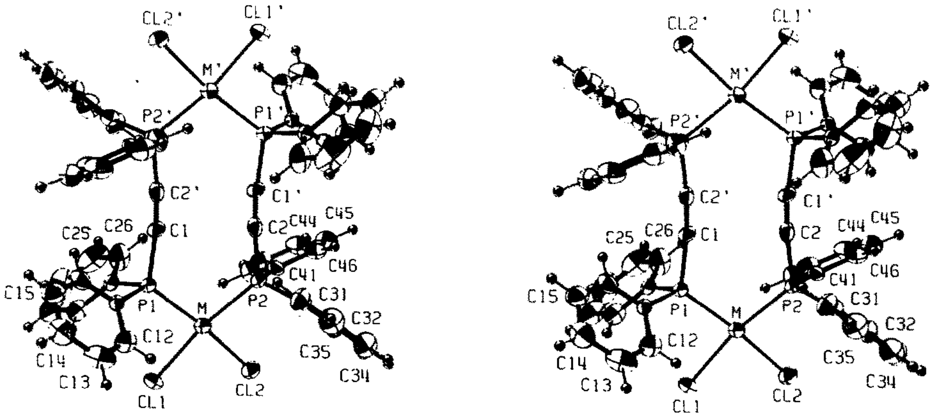
Scheme 7 Reactions of binuclear manganese platinum dppm complexes [772]

The structure of [(dppf)$PdCl_2$] was established in a diffraction study; the cyclopentadienyl rings adopted a staggered arrangement. Derivatives of various related non-symmetrical diphosphinoferrocenes were also prepared by reaction of the ligand with [Pd(cod)Cl_2], [Pd$(PhCN)_2Cl_2$] or $K_2[PdCl_4]$ [775]. Phosphinated silica was prepared by treating SiO_2 with $(EtO)_2Si\{(CH_2)_3PCy_2\}_2$, and the product was converted to the platinum derivative with [Pt$(PhCN)_2Cl_2$]. The complex, (295), was studied using high resolution electron microscopy, and showed aggregates of 5-6 platinum atoms, not on the surface, but on stems which were uniformly distributed on the support [776].

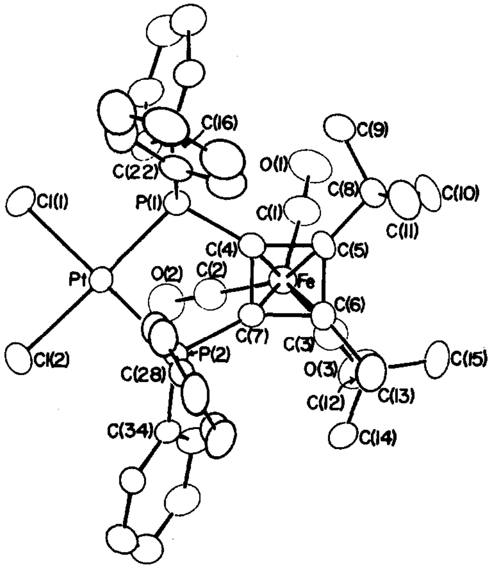
Reaction of [$(Me_2PhP)ClPd(\mu\text{-}Cl)_2PtCl(PMe_2Ph)$] with $Ph_2P\text{-}C{\equiv}C\text{-}PPh_2$ gave (296) in equilibrium with the $\{Pt_2\}$ and $\{Pd_2\}$ species. The ten-membered ring is not planar, with some bowing of the $\{PC{\equiv}CP\}$ moiety [777]. When *cis*-[$Pt(Ph_2PC{\equiv}CCMe_3)_2Cl_2$] was treated with [$Fe_2(CO)_9$], (297) was produced. The alkynes are forced close together in the coordination sphere of platinum and interact readily. A similar derivative was formed on photolysis with [$cpCo(CO)_2$]. However, when *cis*-[$Pt(Ph_2PC{\equiv}CPh)Cl_2$] was used as the starting material, the reaction with [$Fe_2(CO)_9$] gave the cyclopentadienone derivative, (298), also characterised in an X-ray diffraction study [778]. It has long been known that when the complexes [PdL_2Cl_2] and [PdL'_2Cl_2] are mixed, there is a strong tendency to form [$PdLL'Cl_2$]. When L = 1-phenyl-3,4-dimethylphosphole and L' = $R_2PCH{=}CH_2$, in the mixed complex a diene and dienophile, suitable for a Diels Alder reaction, are forced close together in the coordination sphere. In practice the intermediate mixed complex was not observed, and the product of cycloaddition, (299) was isolated as a single diastereoisomer. The platinum analogue reacted similarly [779].



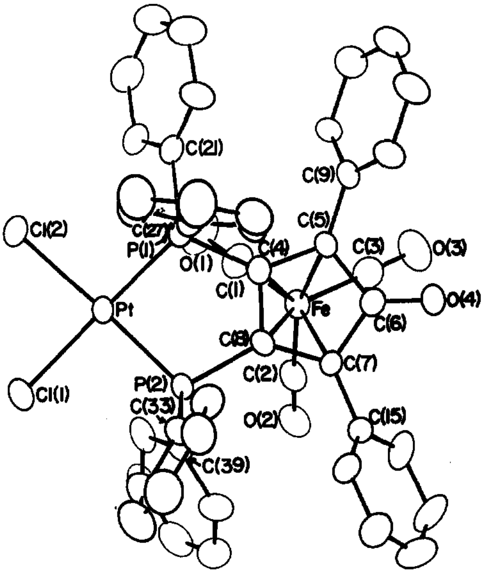
(295) (Reproduced with permission from [776])
A model for aggregates of anchored platinum complexes. $Si-P = Si-OSi(CH_2)_3PR_2$.



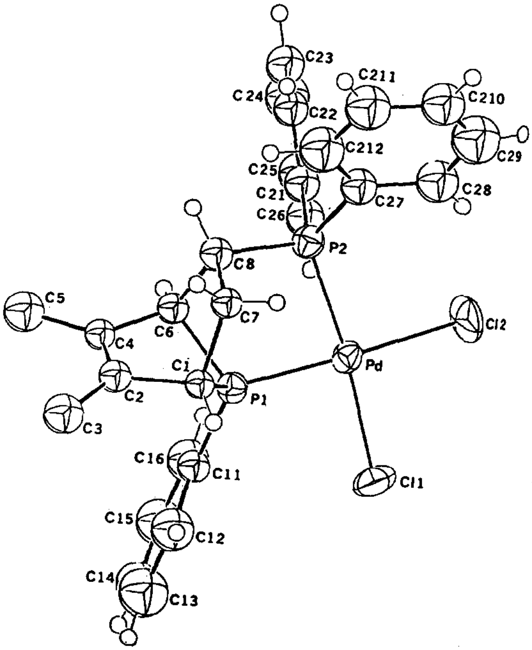
(296) (Reproduced with permission from [777])
Stereoview with the crystallographic numbering scheme. The ellipsoids are shown at the 50 % probability level; the hydrogen atoms are spheres with an arbitrary radius.



(297) (Reproduced with permission from [778])

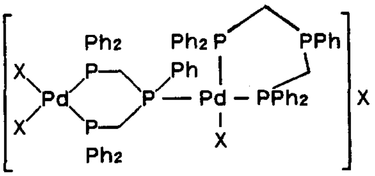


(298) (Reproduced with permission from [778])



(299) (Reproduced with permission from [779])
Structure of dichloro
5-(diphenylphosphino)-2,3-dimethyl-7-phenylphosphabicyclo[2.2.1]heptene
palladium(II) showing the 50 % probability ellipsoids.

The coordination chemistry of $Ph_2PCH_2P(Ph)CH_2PPh_2$, dpmp, has been further studied. In $[M(dpmp)X_2]$ (M = Pt, X = Me or CN, or M = Pd, X = Cl, Br or I) the internal phosphorus atom was uncoordinated. However, in solution at low temperatures, a monomer dimer equilibrium was observed in the palladium series, involving the formation of (300). Mixed metal complexes such as (301) were also prepared [786].



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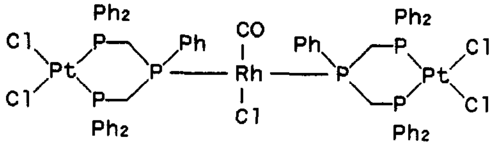


(301)

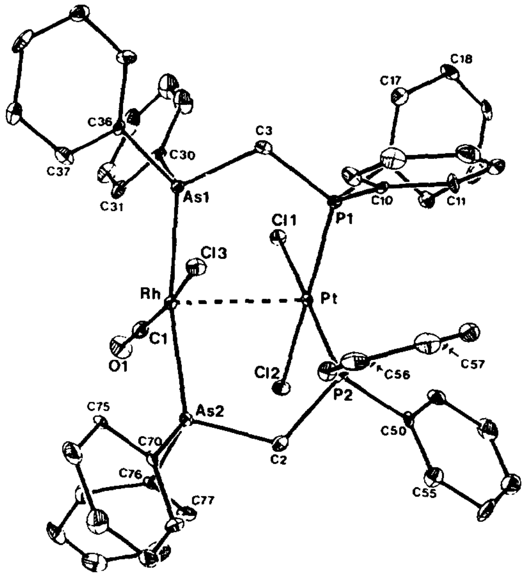
The phosphorescence spectra from the individual triplet spin levels of $K_4[Pt_2(pop)_4]$ have been obtained (pop = $P_2O_5H_2$). The spectrum from the upper degenerate component (E_u representation in the D'_{4h} double group) was well structured and had a long progression due to the Pt-Pt stretching vibration. The spectrum from the lower component (A_u representation in the D'_{4h} double group) was, however, broad and structureless, and was shifted to the red by about 300 cm^{-1} compared with the E_u spectrum. This shift was attributed to the 50 cm^{-1} zero field splitting and 250 cm^{-1} non-totally symmetric vibration responsible for vibronic coupling [781]. Reexamination of the phosphorescence of $Ba_2[Pt_2(pop)_4]$ revealed that the 10 K spectrum was a superposition of two electronic transitions, $[^3A_{2u}(E_u,A_{1u}) \rightarrow A_{1g}]$ separated by $\approx$40 cm^{-1}. Each band displayed a prominent vibrational progression. Franck-Condon analysis suggested an 0.25 Å distortion of the Pt-Pt bond in the excited state, interpreted as a contraction [782].

The effects of a magnetic field of 0-1.0 T on the luminescence lifetime and spectrum of microcrystalline $K_4[Pt_2(pop)_4]$ at 2 K has been described. The decay lifetime decreases in the presence of the magnetic field, and the decay becomes non-exponential. The magnetic field also produces a blue shift in the luminescence peak wavelength, which is accompanied by an increase in the peak intensity of the spectrum. The results were explained using the spin-orbit model previously proposed, with the addition of a vibrational level above the ground state [783]. In addition to the characterisation of luminescence in aqueous and non-aqueous solvents, energy and electron transfer processes involving the lowest triplet excited state of $[Pt(pop)_4]^{4-}$ have been studied. Effeicent transfer of excitation energy from the excited triplet occurred to various acceptors, including naphthalene and $[Ru(bipy)_3]^{2+}$. Direct evidence for the formation of redox products was also presented both for reductive and oxidative quenching [784].

1.6.5.14 Bidentate phosphorus arsenic donor ligands

Reaction of $Ph_2AsCH_2PPh_2$, dapm, with $[Pt(cod)X_2]$ (X = Cl, Br or I) gave $[Pt(dapm)X_2]$ or *cis*-$[Pt(dapm\text{-}P)_2X_2]$ depending on the reaction stoicheiometry.

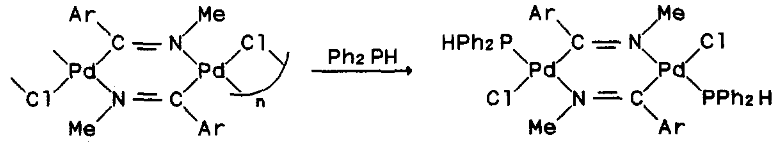
The latter complex was in equilibrium with [Pt(dapm)(dapm-*P*)X]X and [Pt(dapm)$_2$]X$_2$, the degree of ionisation depending on the nature of X and the solvent. Reaction of [Pt(dapm-*P*)$_2$Cl$_2$] with [Rh$_2$(CO)$_4$(μ-Cl)$_2$] gave [Rh(CO)Cl(μ-dapm)$_2$PtCl$_2$], (302), characterised by an X-ray diffraction study. The platinum retains *cis*-geometry and phosphine coordination, and the rhodium adopts *trans*-geometry and is ligated by arsenic [785].



(302) (Reproduced with permission from [785])

1.6.5.15 Bidentate phosphorus carbon donor ligands

Reaction of the oligomeric complex (303) (Ar = C$_6$F$_5$) with Ph$_2$PH in benzene resulted in simple bridge splitting to give a dimeric complex. However when the reaction was carried out in the presence of KOH in propanone, (304) was formed, in which a phosphorus carbon bond has been formed at the expense of a carbon-fluorine bond. (304) underwent a bridge splitting reaction with PPh$_3$ to give (305) [786].



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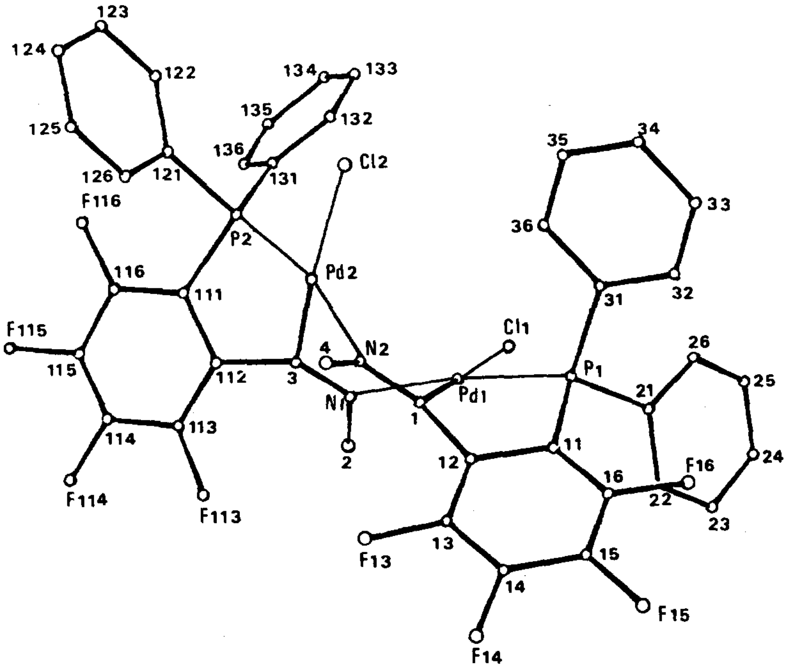
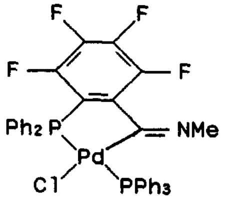
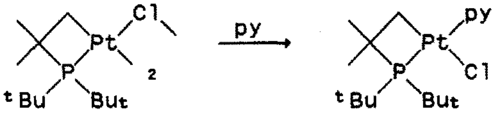


(304) (Reproduced with permission from [786])



(305)

A number of bridge splitting reactions have been reported for (306) [787]. The decomposition of (307) (L = PPh_3) to give (308) was followed in solution; this is the first reported example of the platinum(II) induced cleavage of the phosphorus-carbon bond of $P(CMe_3)_3$ under mild conditions [788].



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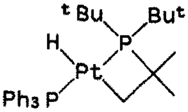

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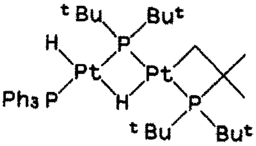
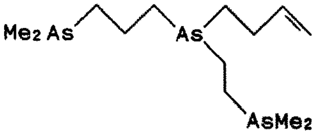


(308)

1.6.5.16 Arsenic donor ligands

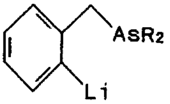
Reaction of $[Me_2Pt(cod)]$ with $Ph_2AsCH_2AsPh_2$, dpam, gave $[Me_2Pt(\mu\text{-dpam})_2PtMe_2]$ rather than the monomeric chelating complex formed in the analogous reaction of dppm. This implies that dpam is a poorer chelating ligand than dppm. However, a chelated complex, $[Pt(dpam)Cl_2]$, was formed from $[Pt(MeCN)_2Cl_2]$ at 80 °C. Reaction with further dpam at 40 °C gave *trans*-$[Pt(dpam)_2Cl_2]$ [789].

The preparation of the polydentate arsenic donor ligand tasol, (309), has been described. Reaction with $[PdX_4]^{2-}$ gave a species of stoicheiometry $\{Pd(tasol)X_2\}$. Solution data implied that this was in fact $[Pd(tasol)X]X$, and the behaviour of the platinum complex was similar. In the solid state, however, palladium was coordinated by three arsenic and two halide donors, but the platinum complex involved coordination by three arsenic donors, the alkene and a single halide [790].



(309)

The lithium derivative, (310) was prepared by metal halogen exchange on the corresponding bromide. This reacted with $[M(SEt_2)_2Cl_2]$ (M = Pd or Pt) to give (311). Mixed cyclometallated complexes were produced by its reaction with (312) [791].



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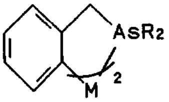

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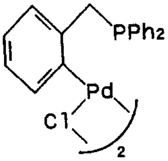


(312)

1.6.6 Complexes with Group 14 donor ligands

Many of the complexes of Group 14 donor ligands are organometallics, and as such fall outside the scope of this review. The interested reader is referred to the annual surveys of the organometallic chemistry of nickel, palladium and platinum published in the Journal of Organometallic Chemistry.

1.6.6.1 Carbonyl complexes

Equilibrium geometries and harmonic frequencies of {PtXY} (XY = CO, N_2, $[CN]^-$ or $[NO]^+$) in the $^1\Sigma^+$ state were calculated using the *ab initio* SCF method, with gradients using the appropriate effective core potentials. The calculated results for {PtCO} and {PtN_2} were compared with the experimental IR spectra from the matrix isolated species [792].

The structure and properties of platinum films obtained by thermal dissociation of $[Pt(CO)_2Cl_2]$ on amorphous alumina, single crystal KCl, or glass ceramics have been studied [793].

Cocondensation of platinum atoms with oxalyl chloride gave *cis*-$[Pt(CO)_2Cl_2]$ as colourless crystals [794]. A study of the vibrational spectra of $[Pt(CO)_2Cl_2]$ and $[Pt(CO)_2Br_2]$ indicated a planar *cis*-configuration in the solid state. However, in the gas phase or in solution in hydrocarbons, the geometry was deduced as tetrahedral [795,796].

The carbonylation of $PhNO_2$ to give PhNCO was catalysed by the palladium(II) carbonyl complex $[Bu_4N][Pd(CO)Cl_3]$, the palladium(I) derivative $[Bu_4N]_2[Pd_2(CO)_2Cl_4]$, and $[Bu_4N]_2[Pd_2Cl_6]$ [797].

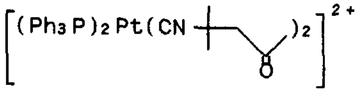
1.6.6.2 Cyanide complexes

Both unsolvated $H_2[Pt(CN)_4]$ and a range of alcohol solvates have been isolated. Neither the unsolvated material nor the glycine solvate had a columnar structure, but the other complexes did. For example, $[PrOH_2]_2[Pt(CN)_4]$ was colourless and had a Pt-Pt distance of 3.65 Å. Shorter interplatinum distances were associated with deepening colour, with $[glyH][H_3O][Pt(CN)_4]$ having Pt-Pt = 3.17 Å and being dark red. Anodic oxidation of these materials led to the formation of partially oxidised phases with smaller repeat distances [798]. The solvent dependence of the sorptive ability of the clathrate $[Cd(en)Pd(CN)_4.2C_6H_6]$ has been studied [799].

Triboluminescence spectra and photoluminescence spectra of single crystals, and of powders, have been recorded at atmospheric pressure, and high pressure photoluminescence spectra have also been recorded for $KLi[Pt(CN)_4].2H_2O$, $KNa[Pt(CN)_4].3H_2O$, $Cs_2Ca[Pt(CN)_4]_2.nH_2O$ and $Cs_2[Pt(CN)_4].H_2O$. There were large pressure dependent shifts in the luminescence maxima under hydrostatic high pressure conditions. This was used as a sensitive probe of the pressure at the crystal sites giving rise to triboluminescence, indicating that this was in fact only 1 atm. Thus triboluminescence takes place at sites where stress is relaxed, not at the tips of cracks [800]. Polarised single crystal absorption spectra of $Ba[Pt_{1-x}M_x(CN)_4].4H_2O$ (M = Pd or Ni; $0<x<1$: T = 80 K) were recorded. The structures of the spectra depended on x [801].

Oxidation of $[Pt(CN)_4]^{2-}$ by molecular chlorine in water has been studied by the stopped-flow technique. At pH<7 there were two reaction paths, with Cl_2 and HOCl as the oxidants. In unbuffered $H[ClO_4]$, the slow HOCl path predominated, but in weak acid buffered by HCl, oxidation occurred involving molecular Cl_2, this path being some 10^5 times more rapid. The primary product in acidic solution was *trans*-$[Pt(CN)_4Cl(H_2O)]^-$, which reacted slowly with Cl^- to give *trans*-$[Pt(CN)_4Cl_2]^{2-}$. In weak alkali at pH 11 oxidation by $[ClO]^-$ gave *trans*-$[Pt(CN)_4(OH)_2]^{2-}$. Oxidation by either $[ClO]^-$ or HCOl is an inner sphere two electron transfer process with the oxygen of the hypochlorite acting as the bridge [802]. Thermolysis of $[Ni(en)_3][Pt(CN)_4].H_2O$ was followed by TGA measurements, and investigation of the structure and morphology of the sample. The first two steps involved loss of water and en to give $[Ni(en)_2][Pt(CN)_4]$, which was postulated to have a chain structure with the nitrogen atom of cyanides, which were bound at carbon to platinum, coordinated to nickel. Successive losses of two further en ligands followed [803]. Reaction of $[M(CN)_4]^{2-}$ (M = Pd or Pt) with $[Co(H_2O)_2(NH_3)_4]^{3+}$ gave $[(H_2O)(NH_3)_4CoNC\text{-}M(CN)_3]^+$. The rates of the reactions and the stability of the products were strongly pH dependent [804].

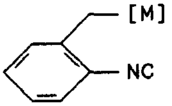
The reaction of *trans*-$[PtL_2I_2]$ (L = $PhCH_2NH_2$, $EtNH_2$ or 2,4,6-$Me_3C_6H_2NH_2$) with $Ag[BF_4]$/MeCN, followed by $[Et_4N][CN]$, gave *trans*-$[PtL_2(CN)_2]$. Treatment of anhydrous $Pt(CN)_2$ with RNH_2 gave *cis*-$[Pt(RNH_2)_2(CN)_2]$ [805]. When the platinum complex of protonated cyanide, $[Pt(PPh_3)_2(CNH)_2]^{2+}$, reacted with 4-methyl-3-pentene-2-one, (313) was formed by attack of the nitrogen on the protonated enone, and was fully characterised [806].



(313)

1.6.6.3 Isonitrile complexes

The treatment of (314) ([M] = $CpMo(CO)_3$, $CpW(CO)_3$ or $Mn(CO)_5$) with $[Pt(cod)Cl_2]$ gave *cis*-$[PtL_2Cl_2]$ in which (314) was bonded to platinum at the isonitrile carbon atom. Similar results were obtained using $[Pd(MeCN)_2Cl_2]$. When the tungsten derivative was reacted with *trans*-$[HPt(PPh_3)_2Cl]$, (315) was obtained [807].



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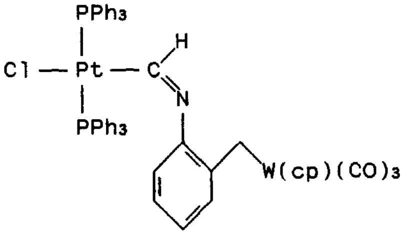
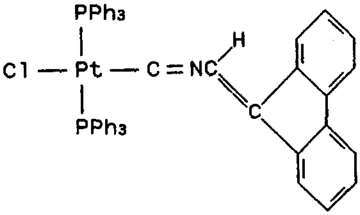


(315)

The preparation of $[Ph_3PNNC]$ has been described in detail. It was converted to a range of complexes including *cis*-$[Pt(PPh_3)_2(CNNPPh_3)Cl][BF_4]$ and *trans*-$[Pt(PPh_3)_2(CNNPPh_3)_2][BF_4]_2$ [808]. Treatment of *trans*-$[Pt(PPh_3)_2(CNCH_2PPh_3)Cl][BF_4]_2$ with fluorenone gave (316) [809]. Formation of $[PdL_2X_2]$ was also reported for L = (317) [810].



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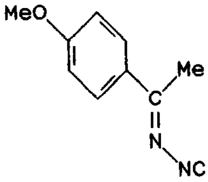


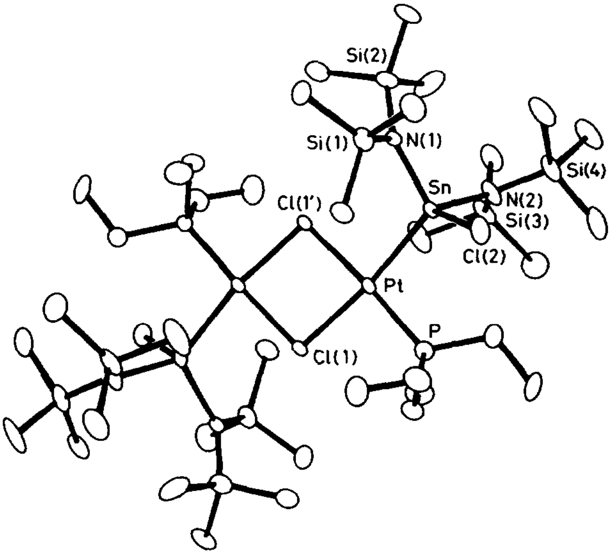
(317)

1.6.6.4 Tin donor ligands

The geometry of $[Et_4N]_2[Pt(SnCl_3)_2Cl_2]$ has been established in an X-ray diffraction study to be *cis*, and coordination was shown to be square planar.

The electronic structure of the complex was calculated using the MO LCAO method and compared with $[Pd(SnCl_3)Cl_3]^-$ [811]. In another study, the electronic structure of the $[SnCl_3]^-$ ligand and of $[Pt(SnCl_3)Cl_3]^-$ was calculated using CNDO and Mulliken-Wolfsberg-Helholtz methods. The donor-acceptor nature of the Pt-Sn bond was discussed [812]. The average square amplitudes of vibration of the tin atom in various platinum containing anions have been determined as a function of temperature [813].

Reaction of $M'(NR_2)_2$ (M' = Sn, Ge or Pb, R = $SiMe_3$) with *trans*-$[Pt(PEt_3)_2(\mu\text{-}Cl)_2Cl_2]$ resulted in insertion of the $M'(NR_2)_2$ into the terminal Pt-Cl bonds only. This is in contrast to the reaction of the more stongly nucleophilic $Sn\{CH(SiMe_3)_2\}_2$, which caused bridge splitting as well as insertion [814]. The product, (318), was characterised in an X-ray diffraction study, and a more detailed investigation indicated that substantial amounts of the *cis*-isomer were also formed [815].



(318) (reproduced with permission from [815])

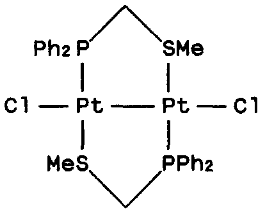
1.6.7 Hydride complexes

Reaction of platinum metal with NaH in an atmosphere of hydrogen at 280-310 °C yielded $Na_2[PtH_4]$, characterised by a neutron diffraction study on $Na_2[PtD_4]$. The $[PtH_4]^{2-}$ anion was planar and diamagnetic, and its structure was compared with that of $[PtCl_4]^{2-}$ [816]. A study of the T_1 values of metal hydrides complexes has been undertaken, and $[HPt(PEt_3)_3][BF_4]$ was among the complexes chosen for study. It was concluded that the relaxation of hydrides may be anomalous, but anomalies occur in either direction, so that it is difficult to draw firm conclusions [817].

1.7 PALLADIUM(I) AND PLATINUM(I)

Electrochemical reduction of $[Pd(SacSac)_2]$ gave the palladium(I) species $[Pd(SacSac)_2]^-$, the EPR spectrum of which was recorded. Although there was less anisotropy than in the analogous nickel complex, the coupling to the protons was larger, these results being consistent with a π-type singly occupied molecular orbital [818].

The structure of $[Pd(\mu\text{-}Ph_2PS)_2(CNMe_2)_2].CHCl_3$ was determined in an X-ray diffraction study; the two palladium(I) atoms were directly bonded. The structure of $[Pt_2(\mu\text{-}Ph_2PS)_2(PPh_2)_2(PPh_3)_2]$ was similar, and in both these cases the $\{M_2P_2S_2\}$ framework was planar. In the platinum(II) dimer, $[Pt_2(\mu\text{-}Ph_2PS)_2\{P(CMe_3)_3\}_2H_2]$, however, the six-membered ring adopted a boat conformation and there was no metal-metal interaction [819,820]. The coordination chemistry of Ph_2PCH_2SMe has been further investigated. Reaction of either *cis* or *trans*-$[Pt(Ph_2PCH_2SMe\text{-}P)_2Cl_2]$ with $[Pt(dba)_2]$ gave (319). The related reaction in the palladium series gave a mixture of head-to-head and head-to-tail dimers. Carbonylation of (319) yielded (320) [821].



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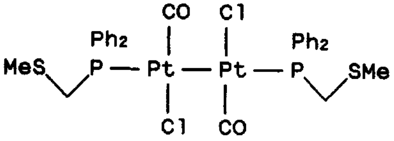
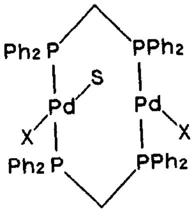


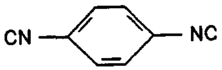
(320)

As always, there have been numerous studies of the complexes of dppm and related ligands. The reaction of $[Pt_2(\mu\text{-dppm})_2Cl_2]$ with PPh_3 gave $[Pt_2(\mu\text{-dppm})_2(PPh_3)Cl]Cl$, the latter species also being formed on reaction of halide with $[Pt_2(\mu\text{-dppm})_2(PPh_3)_2]^{2+}$ [822]. An irreversible reaction occurred between $[Pd_2(\mu\text{-dppm})_2X_2]$ and H_2S to give (321) at a rate which depended on the nature of X (X = Cl >> Br >I). Oxidation of (321) with peracid gave the starting material and SO_2; the intermediate bridging SO_2 complex could be isolated if H_2O_2 was used as an oxidant [823].



(321)

Insertion of (322) into the palladium-palladium bonds of two molecules of $[Pd_2(\mu\text{-dppm})_2X_2]$ gave $[\{Pd_2(\mu\text{-dppm})_2X_2\}_2(\mu,\mu'\text{-}CNC_6H_4\text{-}4\text{-}NC)]$, with a wide range of groups X. When X = Cl or C_6F_5 one of the X ligands could be displaced by another isonitrile, RNC [824]. Insertion of (323) into $[Pd_2(\mu\text{-dppm})_2Cl_2]$ gave the expected isonitrile bridged complex. However, an attempted X-ray diffraction study of this molecule proved rather unsatisfactory; the COOMe group could not be unambiguously located as it extends into a channel in the structure, and hence has rather high thermal motion [825].



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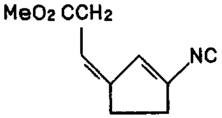
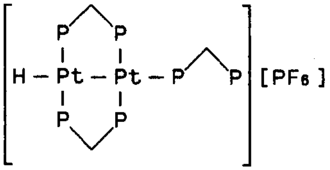


(323)

Treatment of $[Pt_2(\mu\text{-dppm})_3]$ with $[NH_4][PF_6]$ gave (324) (groups on phosphorus are omitted for clarity), but the results with analogous ligands were more varied. The phosphite complex $[Pt_2\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_3(PPh_3)_2]$ yielded (325); this is probably fluxional on the NMR spectroscopic timescale, since all the phosphorus atoms are equivalent. Products with the skeleton (326) were obtained from both $[Pt_2(\mu\text{-}Me_2PCH_2PMe_2)_3(PPh_3)]$ and $[Pt_2(\mu\text{-}Et_2PCH_2PEt_2)_3]$, and (327) was characterised by an X-ray diffraction study. It was concluded that diprotonation was possible only for complexes with relatively low steric requirements [826].

Reaction of $Pd(OCOMe)_2$, dppm and CO in the presence of an excess of CF_3COOH gave $[Pd_3(\mu_2\text{-dppm})_3(\mu_3\text{-}CO)]$. The route proposed for the formation of the cluster involved initial reaction to give $[Pd(dppm)X_2]$, which was reduced to {Pd(dppm)}. The latter species combined with $[Pd(dppm)X_2]$ to give the known binuclear complex, $[Pd(\mu\text{-dppm})_2X_2]$, which was then carbonylated. Reaction of {Pd(dppm)} with $[Pd(\mu\text{-dppm})_2(\mu\text{-}CO)X_2]$ completes the sequence. Spectroscopic evidence was provided for some of the intermediates [827].



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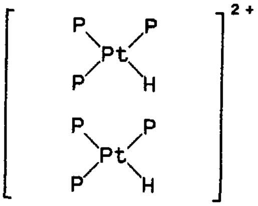

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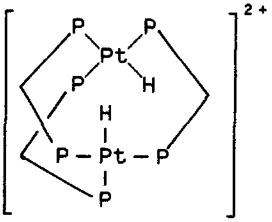

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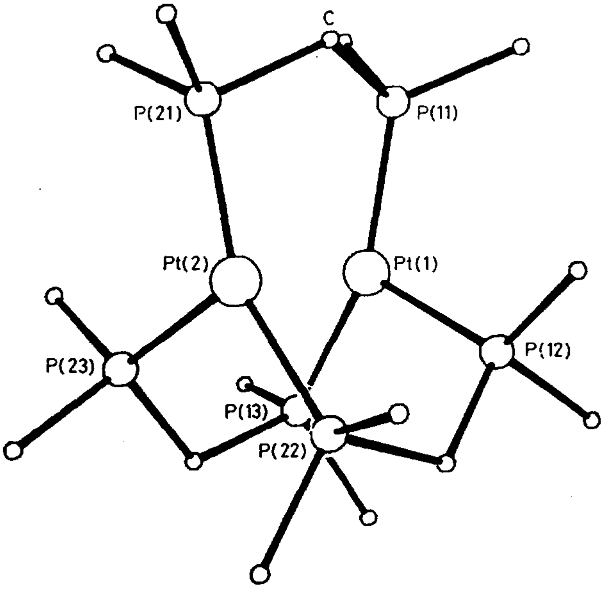
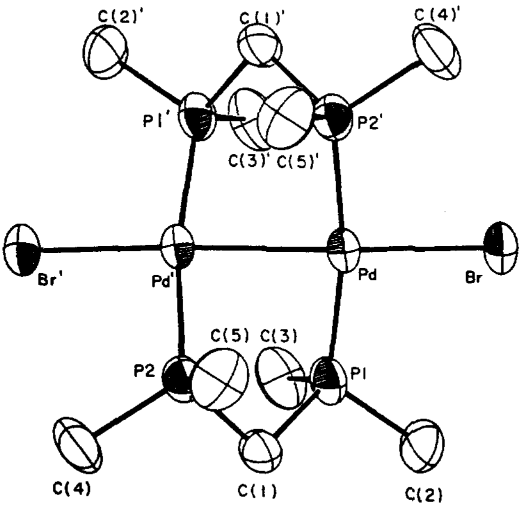


(327) (Reproduced with permission from [826])
Ths structure of $[H_2Pt_2(\mu\text{-depm})_3]^{2+}$ with the hydrogen atoms and the methyl carbon atoms omitted for clarity.

The bis palladium(I) complex, $[Pd_2(\mu\text{-dmpm})_2Cl_2]$, was prepared from dmpm and $[\{Pd(CO)Cl\}_n]$. The structure of the related bromide, (328) (produced by exchange), was established in an X-ray diffraction study. The palladium-palladium distance of 2.603 Å was consistent with the existence of a palladium-palladium bond [828].

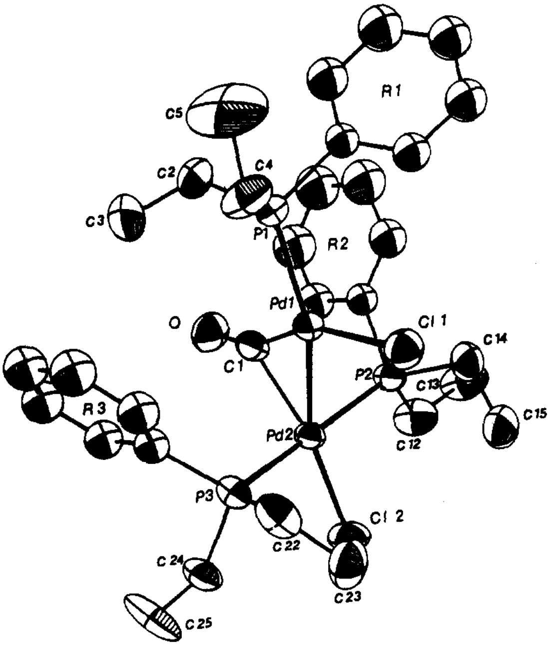


(328) (Reproduced with permission from [828])
ORTEP drawing of the $[Pd_2(dmpm)_2Br_2]$ molecule viewed down the 2-fold rotation axis. Primed atoms are generated by the 2-fold axis.

Treatment of either $[Pd(PEt_2Ph)_2(NO_2)_2]$ or $[Pd(PEt_2Ph)_2(NO_2)Cl]$ with carbon monoxide in CH_2Cl_2 gave the palladium(I) dimer, (329), in which the carbonyl group is semi-bridging [829].

Oxidation of the mixed phosphine palladium complexes such as $[Pd(Ph_2PC_6H_4\text{-}4\text{-}F)_2(PPh_3)]$ gave species shown to be paramagnetic by EPR spectroscopy and XPES, and these were tentatively characterised as palladium(I) adducts of $\{O_2\}^-$. Slow decomposition to phosphine oxide and unidentified palladium dimers occurred [830].

Potentiostatic one electron reduction of *cis*-$[Pt(RNC)_2Cl_2]$ at a mercury pool electrode gave $[\{Pt(RNC)_2Cl\}_2]$, the structure of which, (330), was established in an X-ray diffraction study. Two electron reduction yielded clusters (*vide infra*) [831]. The structure of the analogous species $[\{Pd(CNCMe_3)_2Cl\}_2]$ was very similar, the complex this time being prepared from $[Pd_2(dba)_3]$ and $[Pd(RNC)_2Cl_2]$. Photolysis cleaved the metal-metal bond to give *trans*-$[Pd(Me_3CNC)_2Cl_2]$ [832]. The photochemistry of $[MM'(CNMe)_6]^{2+}$ (M = M' = Pd or Pt or M = Pd, M' = Pt) has also been investigated. Initially the 15-electron species, $[M(CNMe)_3]^{+\cdot}$. was formed; this reacted with CX_4 (X = Cl or Br) to give $[M(CNMe)_3X]^+$. The rate of halide abstraction was greater for platinum than for palladium, this result being explained in terms of excited state decay channels [833].



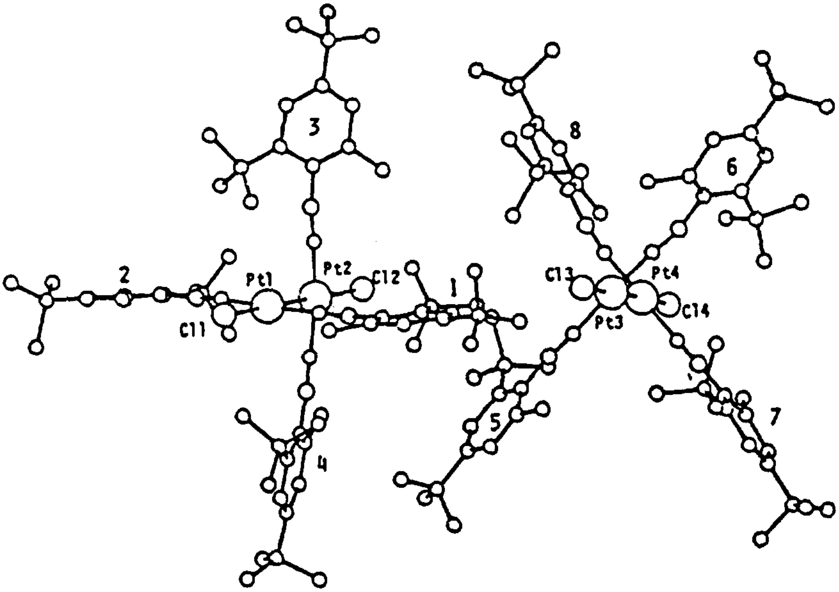
(329) (Reproduced with permission from [829])
The hydrogen atoms are omitted for clarity.

1.8 PALLADIUM(0) AND PLATINUM(0)

1.8.1 Complexes with Group 16 donor ligands

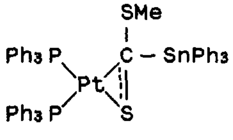
There has been a study on the interaction of 54 aromatic and quinonoid compounds with platinum thin layer electrodes, to establish the surface coordination chemistry of polycrystalline platinum with these species in solution. Attachment of thiophenols was at sulphur [834]. The electrocatalytic hydrogenation of sulphur bonded pentafluorothiophenol was also studied [835].

Hartree Fock Slater calculations have been reported on bonding energies for complexes of O_2 with $\{M(PH_3)_2\}$ (M = Ni, Pd or Pt). The bonding energies were found to be in the order 3d > 5d > 4d, and back donation of charge from metal to oxygen was calculated to be more important than donation from the ligand to the metal [836]. Reaction of $[M(PPh_3)_2(O_2)]$ with RCOOH gave successively *cis*-[M(PPh_3)$_2$(OOH)(OOCR)] and *cis*-[M(PPh_3)$_2$(OCOR)$_2$] and H_2O_2. This casts some light on the earlier observation that the reaction of [Pt(PPh_3)$_4$] with RCOOH to give the latter complex was successful only in air; it proceeds *via* [Pt(PPh_3)$_2$(O_2)] [837].



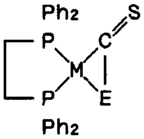
(330) (Reproduced with permission from [831])

A review of the chemistry of stannane dithiocarboxylates has been published, including the complex (331) [838].



(331)

The reaction of (332) (M = Pd or Pt, E = S or Se) with [Pt(PPh_3)$_2$L] (L = C_2H_4 or (PPh_3)$_2$) gave (333). The structure of the related complex, (334), was established in an X-ray diffraction study [839]. The reactions of [PdL$_n$], where L is a bulky phosphine, with CS_2 have been investigated. With L = PCy_3 or P(CMe_3)Ph_2, [L_2Pd(η^2-CS_2)] was precipitated, whereas with L = P(CMe_3)$_3$ or P(CMe_3)$_2$Ph the dimeric complex [L_2Pd_2(μ-CS_2)$_2$] was obtained. The dimers were also obtained by treatment of $[Pd_3L_3(CO)_3]$ with CS_2, and (335) was characterised by an X-ray diffraction study [840].



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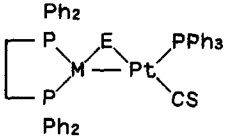

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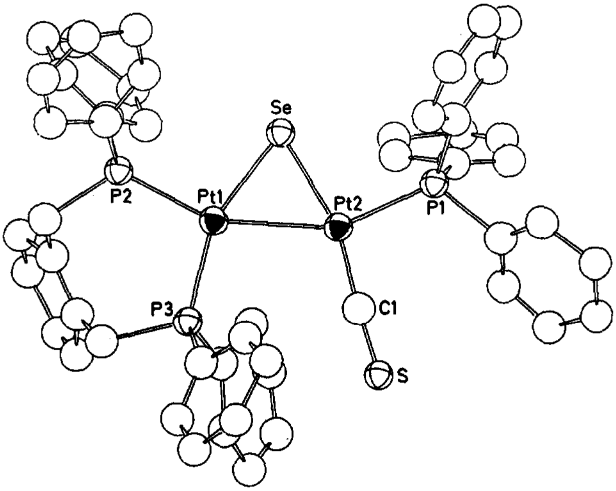
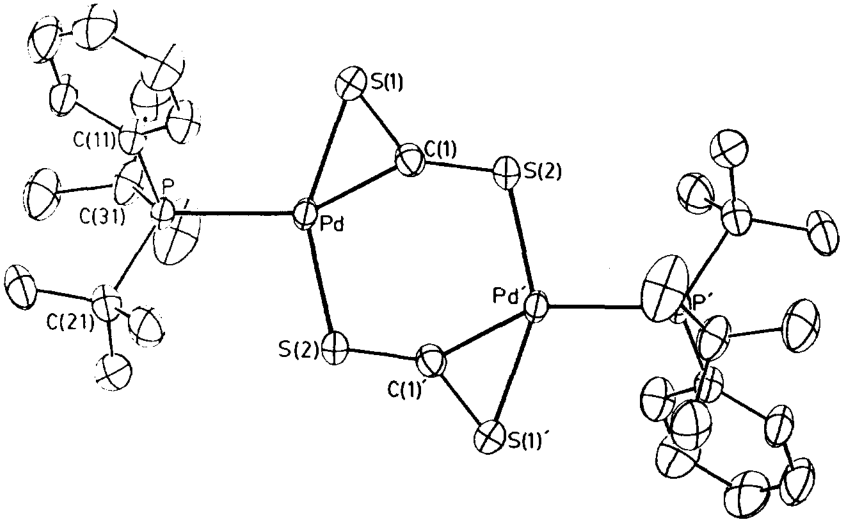


(334) (Reproduced with permission from [839])

A major full paper has been published detailing reactions and interconversions of mono and binuclear platinum(0) complexes of CS_2 (Scheme 8). The mechanisms of the reactions are discussed in detail, and several of the complexes were characterised by X-ray diffraction studies [841].

1.8.2 Complexes with Group 15 donor ligands

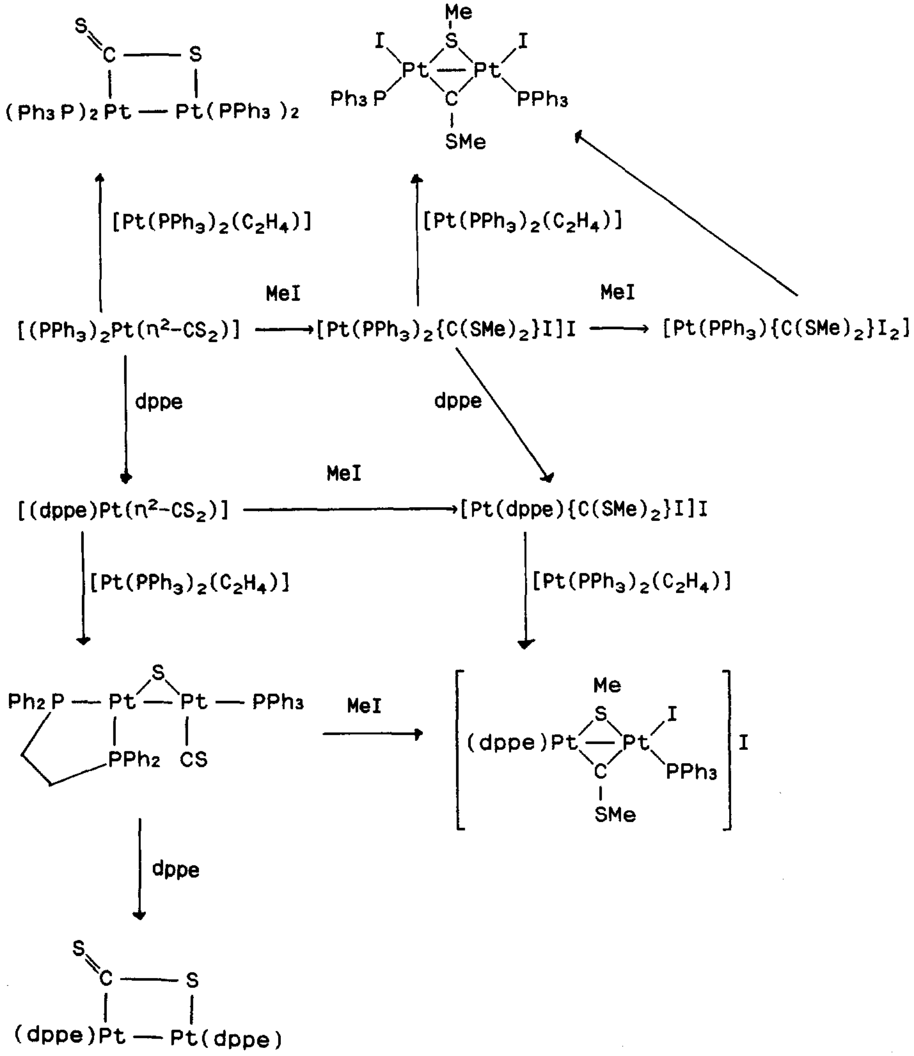
Reaction of $PdCl_2$ and PPh_3 in the presence of (336) as reductant gave $[Pd(PPh_3)_4]$ [842]. A range of complexes $[PtL_4]$ (L = $P(OBu)_3$, $AsBu_3$ or $SbBu_3$) was prepared from $[Pt(cod)_2]$ and an excess of the ligand. In some cases both tri- and tetracoordinate derivatives were produced [843].



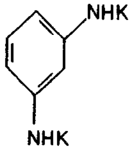
(335) (Reproduced with permission from [840])

Platinum films have been formed on quartz and graphite by UV laser induced deposition during the dissociation of $[Pt(PF_3)_4]$ [844].

There has been a study of the ^{195}Pt NMR spectra of the complexes $[Pt(PR_3)_n]$. The values of the spin lattice relaxation time for platinum were strongly dependent on the coordination number, over several orders of magnitude. In $[PtL_2]$ relaxation was dominated by CSA effects, but in $[PtL_3]$ and $[PtL_4]$ there was also a contribution from spin rotation [845]. The absorption and emission spectra for $[Pd(PR_3)_4]$, $[Pt(PPh_3)_4]$, $[Pd_2(dppm)_3]$ and $[Pd_2(dpam)_3]$ have been recorded in thf solution. On the basis of the data obtained, it was concluded that the observed solution luminescence arose from part dissociated species which are three-coordinate in both the ground and excited states. The radiative decay rates indicated that the electronic transitions responsible are only weakly allowed. Organic triplet quenchers quench the emissive excited states of $[Pd(PR_3)_4]$ and $[Pd_2(dppm)_3]$ at rates which depend systematically on the organic triplet energy, suggesting that emission from the d^{10} complexes originates from a low-lying triplet state. The insensitivity of the effect to the nature of the ligand implies that the excited state is mainly metal localised, in agreement with Huckel calculations. Possible applications to photocatalysis were discussed [846].



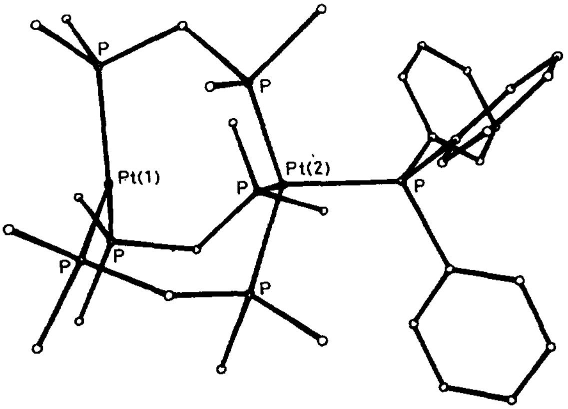
Scheme 8 Reactions of platinum(0) CS_2 complexes [841]



(336)

It has been proposed that the initial stages of activation of $[PdL_2L']$ by molecular oxygen to give a cluster which is an active hydrogenation catalyst, involve inner sphere oxidation of the aryl phopshines to give, initially, phosphine oxides and $[\{PdL'_2\}_2]$ or $[\{PdL'\}_2]$. This may well be true, but little evidence is presented [847].

The dimeric complex (337) has been prepared by the reaction of $[Pt(PPh_3)_3]$ with dmpm. Its stucture was determined in an X-ray diffraction study, and the molecule has approximately C_3 symmetry with one platinum atom adopting approximately trigonal planar coordination, and the other having distorted tetrahedral geometry. The platinum-platinum distance was 3.3 Å, compared with 3.023 Å in $[Pt_2(\mu\text{-dppm})_3]$, reflecting the greater degree of steric crowding. When the chelating ligand added was $(EtO)_2PCH_2P(OEt)_2$, which has lower steric demands, $[Pt_2\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_3(PPh_3)_2]$ was produced. Fluxional behaviour was detected in the complexes by NMR spectrsocopy at room temperature [848].



(337) (Reproduced with permission from [848])

CNDO calculations have been undertaken for $[Pd_2(PPh_3)_2]$, to study the rôle of intramolecular Pd...Ph coordination in stabilising the complex. It was shown that the stability arose from a donor-acceptor interaction of the weakly populated 5s and 5p atomic orbitals of palladium with the filled orbitals of the aryl rings [849].

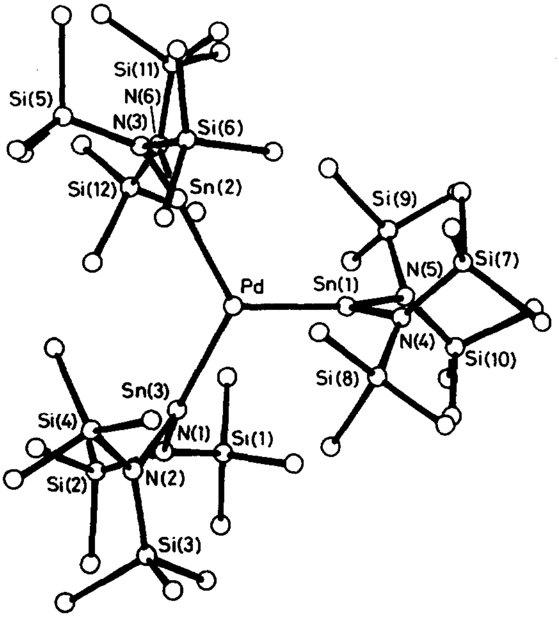
Platinum complexes of phosphaalkynes have been reviewed [850]. The diphosphaallene, Ar-P=C=P-Ar (Ar = 2,4,6-$(Me_3C)_3C_6H_2$), reacted with $[Pt(PPh_3)_2(C_2H_4)]$ to give an η^2-complex, formed by simple displacement of the ethene. Although the ^{31}P NMR spectrum was broad at room temperature, this was thought to be due to PPh_3 exchange rather than any fluxional behaviour in the phosphaallene [851]. Solid state ^{31}P NMR spectrsocopy of $[Pt(PPh_3)_2\{Ph_2C{=}P(2,4,6\text{-}Me_3C_6H_2)\}]$ showed that the phosphaalkyne was

η^1-ccordinated in the solid state, the spectrum being quite distinct from that of the η^2-complex seen in solution [852].

1.8.3 Complexes with Group 14 donor ligands

The electronic structure of {Pd(CO)} was studied by means of effective core potential calculations, including configuration interaction. A study of the $^3\Sigma^+$ and $^1\Sigma^+$ states showed that their low spin states are bound and their high spin states repulsive [853]. Similar calculations were used to determine SCF equilibrium geometries and the properties of both mono and tetracarbonyls of nickel, palladium and platinum. As predicted, the relative stability based on M-CO bond energy is in the order Ni > Pt > Pt, as observed experimentally [854]. Hartree-Fock-Slater calculations have been reported on protonation energies for $[M(CO)_4]$ (M = Ni, Pd or Pt) [855].

The preparation of homoleptic complexes $[M\{M'(NR_2)_2\}_3]$ (M = Pd or Pt, M' = Ge or Sn, R = $SiMe_3$) has been described, using $[Pd(cod)Cl_2]$ or $[Pt(cod)_2]$ as the precursors. Carbonylation gave clusters $[(M\{\mu\text{-}M'(NR_2)_2\}CO)_3]$, one of which, (338), was characterised in an X-ray diffraction study [856].



(338) (Reproduced with permission from [856])

The molecular structure and atom numbering scheme for $[Pd\{Sn(NR_2)_2\}_3]$. The Pd, Sn and N Atoms are all trigonally planar coordinated. The SnN_2 planes are at *ca.* 90 ° to the $PdSn_3$ plane.

1.9 PALLADIUM AND PLATINUM CLUSTERS

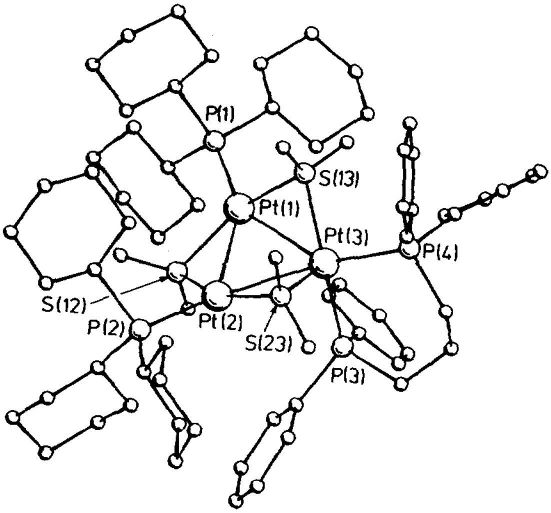
The SCF-X_{α} (Dirac scattered wave) method has been used in the calculation of the electronic energy levels of $\{Pt_n\}$ (n = 2-13) and $\{Pd_m\}$ (m = 3-13) [857]. A general topological electron counting rule has been proposed for polyhedral transition metal clusters. Among those considered were $[Pt_6(CO)_{12}]^{2-}$ and $[Pd_2(PPh_3)_2L_2]^+$ (L = $CH_3C(CH_2PPh_2)_3$) [858]. Platinum clusters interacting with hydrocarbons in a molecular beam cause dehydrogenation to a C:H ratio close to unity, and exhibit a cluster-size dependent extent of chemisorption. Benzene is dehydrogenated on $\{Pt_3\}$ and larger clusters, these having activity comparable to a platinum <111> surface [859].

1.9.1 Trimeric clusters

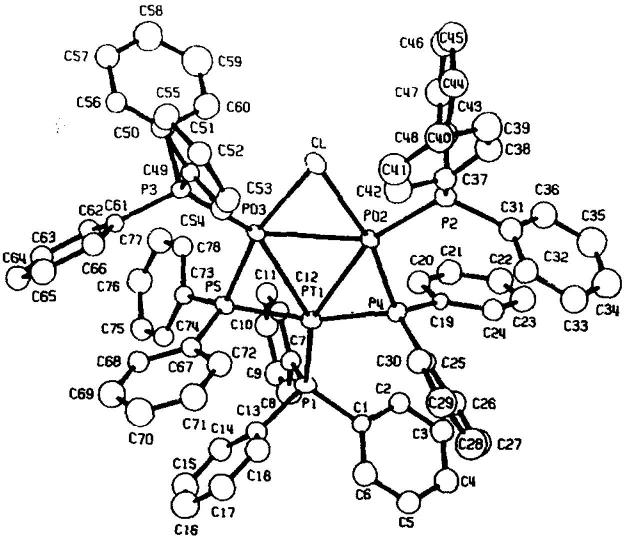
In the presence of $[Pd_3(OCOMe)_6]$, $H[ClO_4]$ is reduced by CO to HCl, this being the first example of the reduction of a dilute solution under mild conditions. The only identifiable palladium intermediate seemed to be $[\{Pd(CO)Cl\}_n]$, but this was shown not to be the catalyst. It seems likely that the active species was $[Pd_3(OCOMe)_5]^+$, formed on cluster protonation. The reduction of HNO_3 successively to NO_2 and NO was also studied. Although $[Pd_4(OCOMe)_4(CO)_4].2MeCOOH$ was the material isolated at the end of the reaction, it was not a part of the catalytic cycle, and in fact inhibited reduction [860].

Reaction of $[Pt_3(\mu\text{-}X)_3(PCy_3)_3]$ (X = SO_2 or CO) with a bidentate chelating phosphine yielded $[Pt_3(\mu\text{-}X)_3(PCy_3)_2\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 2 or 3). The chelating biphosphine adopts a low symmetry conformation with respect to the $\{Pt_3\}$ plane so that the other two phosphines are inequivalent at low temperature in the ^{31}P NMR spectrum. The structure of (339) was established in an X-ray diffraction study [861].

The reaction of $[Pd(PPh_3)_3Cl][BF_4]$ with $[Pt(PPh_3)_3Cl][BF_4]$ yielded $[PtPd_2(\mu\text{-}PPh_2)_2(PPh_3)_3Cl][BF_4]$, the first example of a mixed palladium platinum cluster. Its structure, (340), was successfully established in an X-ray diffraction study, despite the fact that the crystals obtained contained 19 % $[Pd_3(\mu\text{-}PPh_2)_2(PPh_3)_3Cl][BF_4]$. The structure of the $\{Pd_3\}$ analogue was determined independently, as was that of $[Pd_3(PPh_2)_2(PEt_3)_3Cl][BF_4]$. The Pd-Pt distance in (340), 2.92 Å, is relatively long, but still bonding [862]. When $[Pt(PPh_3)_2(C_2H_4)]$ is reacted with P_4S_3, platinum is inserted into a P-P bond, and the trinuclear structure $[\{Pt(\mu\text{-}P_4S_3)(PPh_3)\}_3]C_6H_6$, (341), is formed by sharing one of the phosphorus atoms from such a bond between two platinum atoms [863].

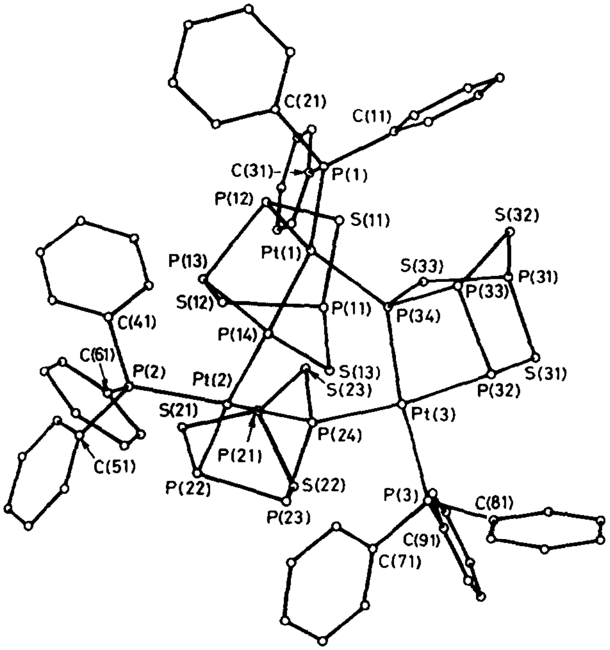


(339) (Reproduced with permission from [861])



(340) (Reproduced with permission from [862])

ORTEP plot of the cation $[PtPd_2Cl(PPh_2)_2(PPh_3)_3]^+$

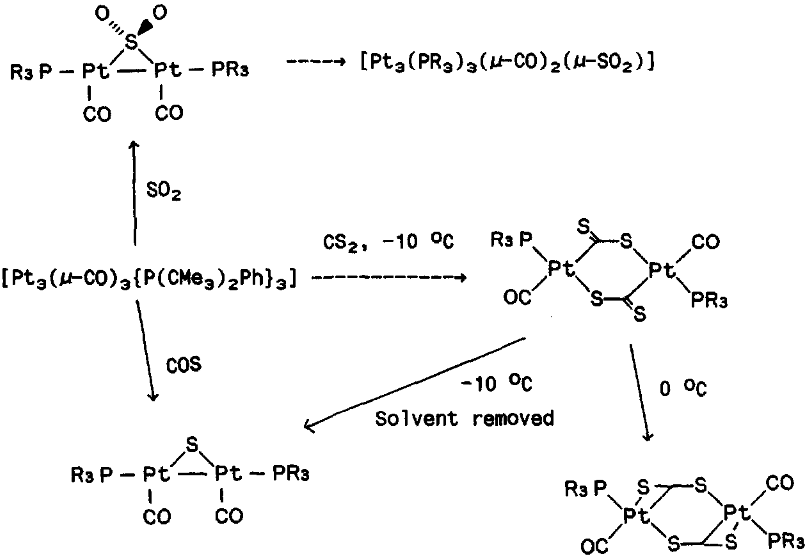


(341) (Reproduced with permission from [863])
A view of the $[\{Pt(\mu\text{-}P_4S)(PPh_3)\}_3]$ molecule. Only the first carbon atom of each phenyl group is labelled.

The bonding in triangular clusters of the type $[M_3L_6]^n$ has been discussed, with particular reference to all-terminal or terminal plus bridging arrangements of the ligands. $[Pt_3(CO)_6]^{2-}$ is a classic example of a 44e "unsupported-bridged" structure [864]. The calculations of the electronic structures of $[\{M_3(CO)_6\}_n]^{2-}$ (M = Ni or Pt, n = 1, 2 or 3) show that the highest occupied state in these diamagnetic anions is a low-lying molecular orbital from the $2\pi_z$ CO system. The unoccupied molecular orbitals of $2\pi_z$ origin are at least 0.7 eV higher in energy. The data were used to discuss the different configurations of the nickel and platinum complexes, and the absence of a related palladium series [865].

The reaction of $[Pd_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)]^{2+}$ with an anion, X^-, yielded $[Pd_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)(\mu_3\text{-}X)]^+$ (X = Cl, Br, I or $[CF_3COO]$). Equilibrium constants for the formation of the adduct were in the order I > Br > Cl > $[CF_3COO]$, as might be expected for a covalent interaction with a soft palladium acceptor. The structures of the adducts with chloride and bromide were established in X-ray diffraction studies. The Pd-Cl (2.741 Å) and

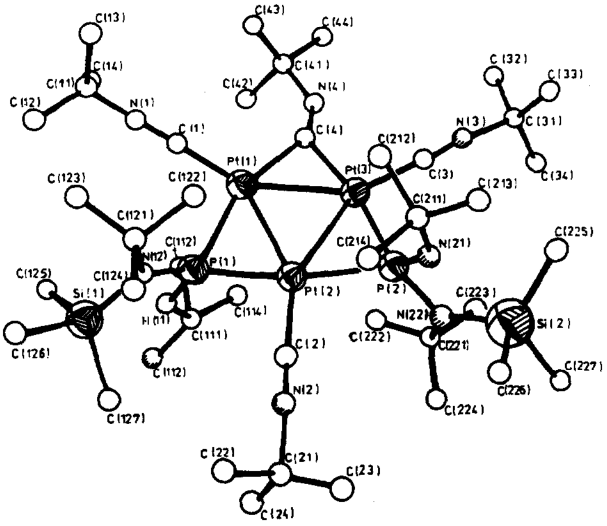
Pd-Br (3.161 Å) distances are too long for ordinary covalent bonding [866]. Treatment of $[Pt_3(\mu\text{-}CO)_3L_3]$ with a different ligand L' (L, L' are bulky phosphines) resulted in the replacement only of L, and not of the carbonyl groups. It seems likely that the mechanism of the substitution is associative, with the $\{Pt_3\}$ triangular unit remaining intact. Carbon monoxide scrambles between clusters in a much slower reaction. When $[Pt_3(\mu\text{-}CO)_3\{P(CMe_3)_2Ph\}_3]$ was treated with CS_2, COS or SO_2 dimeric complexes were formed (Scheme 9) [867].



Scheme 9 Some reactions of $[Pt_3(\mu\text{-}CO)_3\{P(CMe_3)_2Ph\}_3]$ [867].

Reduction of $[Pt_3(\mu\text{-}dppm)_3(\mu\text{-}CO)_3]^{2+}$ with $Na[BH_4]$ gave $[Pt_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)(\mu_3\text{-}H)]^+$, which lost CO relatively easily, and reversibly. $[Pt_3(\mu\text{-}dppm)_3(\mu_3\text{-}H)]^+$ was also obtained when the tricarbonyl cluster was reduced by sodium amalgam. The structures of the reduction products were established in NMR spectroscopic studies; both showed fluxional behaviour [868].

Treatment of $[PtL_3]$ ($L = R^1R^2N\text{-}P\text{=}NR^3$) with Me_3CNC gave the trimeric cluster $[Pt_3(CNCMe_3)_3(\mu\text{-}L)_2(\mu\text{-}CNCMe_3)]$, (342), which was also formed by the reaction of L with $[Pt_3(\mu\text{-}CNCMe_3)_3(CNCMe_3)_3]$. Carbonylation of $[PtL_3]$ gave $[Pt_3(\mu\text{-}L)_3(CO)_3]$, (343). The complexes (342) and (343) were characterised in X-ray diffraction studies [869]. Reaction of $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ with three molar equivalents of $2,6\text{-}Me_2C_6H_4NC$ yielded $[Pt_3(\mu\text{-}CO)(\mu\text{-}CNR)_2(CNR)(PCy_3)_2]$, (344), whereas with five molar equivalents, $[Pt_3(\mu\text{-}CNR)_2(CNR)_2(PCy_3)]$, (345), was formed. Both the new complexes were characterised in diffraction studies, and NMR spectroscopy indicated that the solid state structures persisted in solution. The bridging isonitriles were severely bent about nitrogen, and it seems that their steric reqirements are not compatible with the presence of the bulky PCy_3 ligand on both of the metal atoms that they are bridging. Thus the replacement of a bridging CO ligand by RNC labilises the adjacent terminal PCy_3 ligand to substitution. Reduction of $[Pt(CO)(PCy_3)Cl_2]$ with sodium amalgam in the presence of RNC also gave (345) [870].

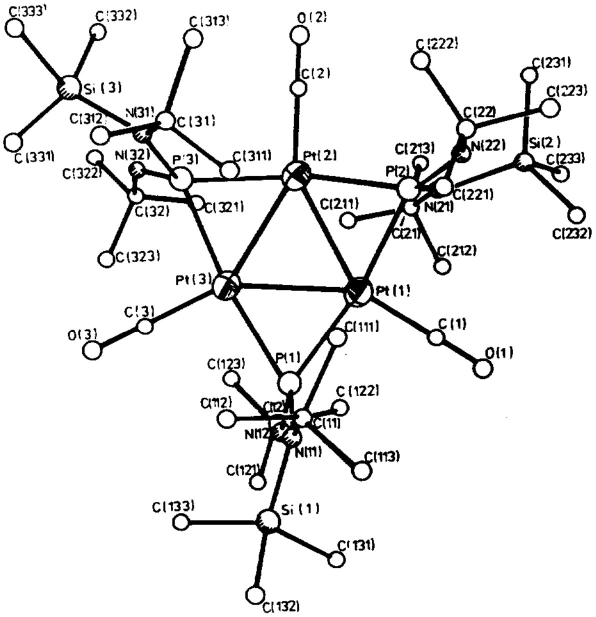


(342) (Reproduced with permission from [869])

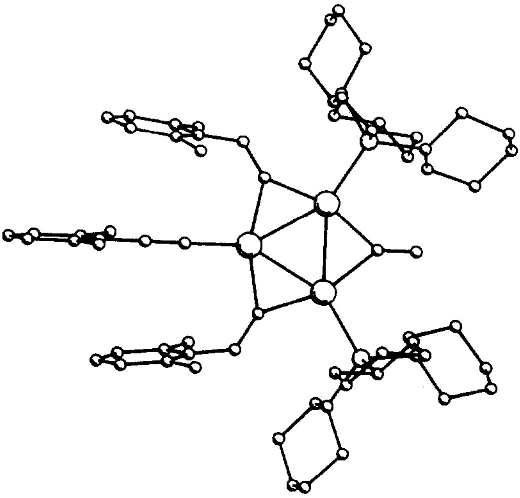
1.9.2 Tetrameric clusters

Reaction of $K_2[Pt(OH)_6]$ with MeCOOH and HCOOH yielded the tetrameric cluster $[Pt_4(OCOMe)_{10}(OH)_2]$, which could be partially hydrolysed to $[Pt_4(OCOMe)_4(OH)_8(OH_2)_2]$. The structures suggested were (346) and (347) on the basis of EXAFS data [871].

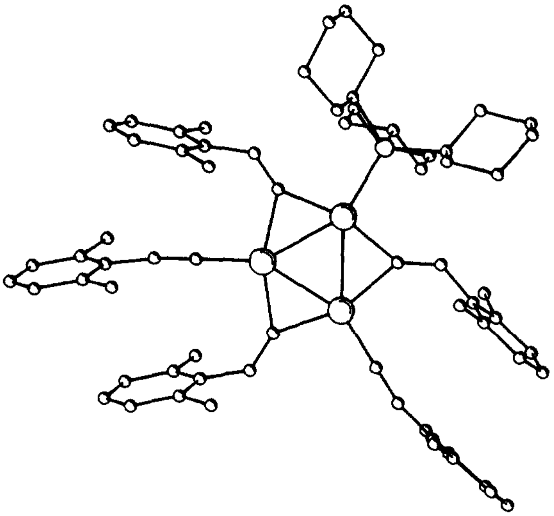
The structure of $[Pt_4(CO)_5(PEt_3)_4]$ has been established; the four platinum atoms form a tetrahedral framework with edge bridging carbonyl groups and a PEt_3 ligand on each platinum atom [872]. When the cluster $[Pd_4(CO)_4(PPh_3)_4]$ was treated with a mixture of CO and O_2, $[Pd_{10}(CO)_{12}(PPh_3)_6]$, Ph_3PO and CO_2 were produced. The same cluster was obtained from $[Pd(PPh_3)_4]$ under these conditions. Thus, oxidative removal of phosphine and CO ligands is a general method to increase cluster nuclearity [873].



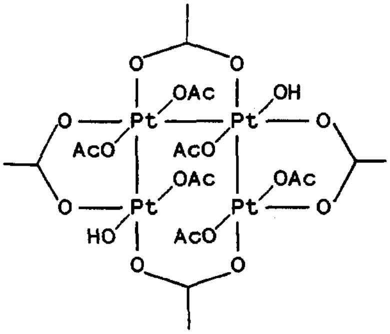
(343) (Reproduced with permission from [869])



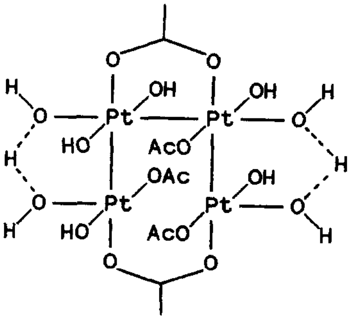
(344) (Reproduced with permission from [870])



(345) (Reproduced with permission from [870])



(346)



(347)

1.9.3 Higher Nuclearity Clusters

There has been a mathematical derivation of the preferred values of nuclearity (the magic numbers) corresponding to various symmetrical close-packed polygons and polyhedra. A simple general formula for various numbers of atoms was obtained. The application of these atom counting results to electron counting in close packed high nuclearity clusters was illustrated for (among other complexes) $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$ and $[Pt_{38}(CO)_{44}H_x]^{2-}$ [874]. It has been suggested that bonding in high nuclearity clusters with close-packed arrangements is dependent primarily on radial interactions between the surface and the interstitial atoms. Clusters were characterised by having $12n_s + \Delta_i$ valence electrons, where n_s is the number of surface atoms and Δ_i is a characteristic of the interstitial group of atoms. It was thus shown how radial bonding interactions predominate in $[Pt_{19}(CO)_{22}]^{4-}$ and $[Pt_{26}(CO)_{32}]^{2-}$, but in $[Pt_{24}(CO)_{30}]^{2-}$ tangential bonding interactions make a partial contribution [875].

In $[\{Pt_3(\mu_2\text{-}CO)_3(CO)_3\}_n]^{2-}$ (n = 2,3,4,5,6 or 10) the longer platinum chains were predicted to adopt a simple stack with a three fold axis and D_{3h} symmetry. For n = 2 there is a departure from ideality in that the two $\{Pt_3\}$ triangles are laterally slipped, whilst the trimer has a helical twist of 13 ° from one unit to the next. In the pentamer the angular distortion is confined to the middle three platinum triangles of the cluster. $[Pt_3(CO)_3\{Fe(CO)_4\}_3]$ was also discussed [876].

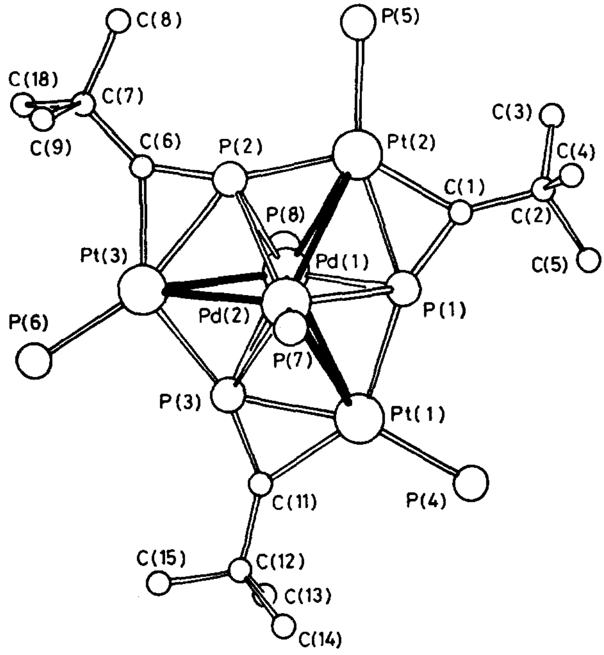
Reaction of $[Pt(PPh_3)_2(\eta^2\text{-}Me_3CC{\equiv}P)]$ with $[Pd(PPh_3)_4]$ gave $[Pd_2Pt_3(PPh_3)_5(Me_3CCP)_3]$, (348), which was characterised by an X-ray diffraction study. The $\{Pd_5\}$ and $\{Pt_5\}$ species were isomorphous. The metals adopt a trigonal bipyramidal arrangement with palladium axial and platinum equatorial, and each metal bears one PPh_3 ligand. The phosphalkynes bridge two metals. The structure is in accord with predictions based on the cluster condensation generalisation [877].

The hydrogenation of $Pd(OCOMe)_2$ in the presence of either bipy or phen, followed by treatment of the product with oxygen gave a palladium containing material which was studied by high resolution electron microscopy. This was a spherical palladium particle 26 Å in diameter with 570±30 palladium atoms, which was formulated as $[\{Pd_9(L)(O)_3(OCOMe)_3\}_n]$. The cluster is active for the oxidation of ethene to ethenyl ethanoate [878]. $[Pd_{10}(CO)_{12}(PR_3)_4]$ was among the clusters which could be prepared, yet again, from $Pd(OCOMe)_2$, CO and PR_3 under various conditions [879]. Chlorided γ-alumina was impregnated with $[Et_4N]_2[Pt_{15}(CO)_{30}]$ and $[Re_2(CO)_{10}]$, and was then reduced and sulphided, to give a catalyst for the reformation of heptane [880].

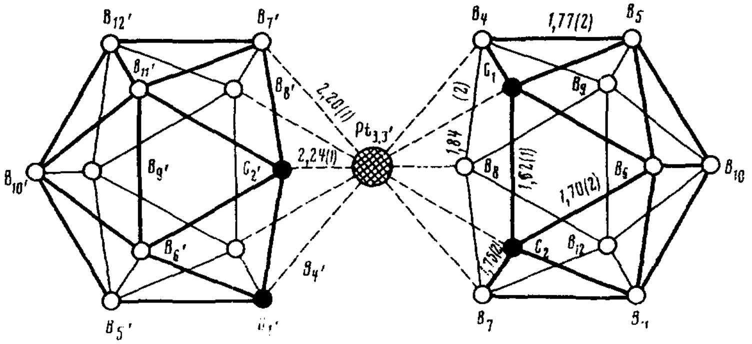
1.9.4 Heteronuclear clusters

The cluster $[3,3'\text{-}Pt(1,2\text{-}C_2B_9H_{11})_2]$, (349), was characterised by an X-ray diffraction study, and has been used as a catalyst for alkene hydrosilylation, having particularly good activity for alkenes bearing nucleophilic groups [881]. The structure of *nido*-$[9\text{-}(PPh_3)_2Pt\text{-}6\text{-}CB_8H_{12}]$, (350), prepared from *arachno*-$[4\text{-}CB_8H_{14}]$ and $[Pt(PPh_3)_4]$, has also been established; the platinum atom is coordinated by two phosphine ligands and a triatomic π-allyl-like $\{B_3\}$

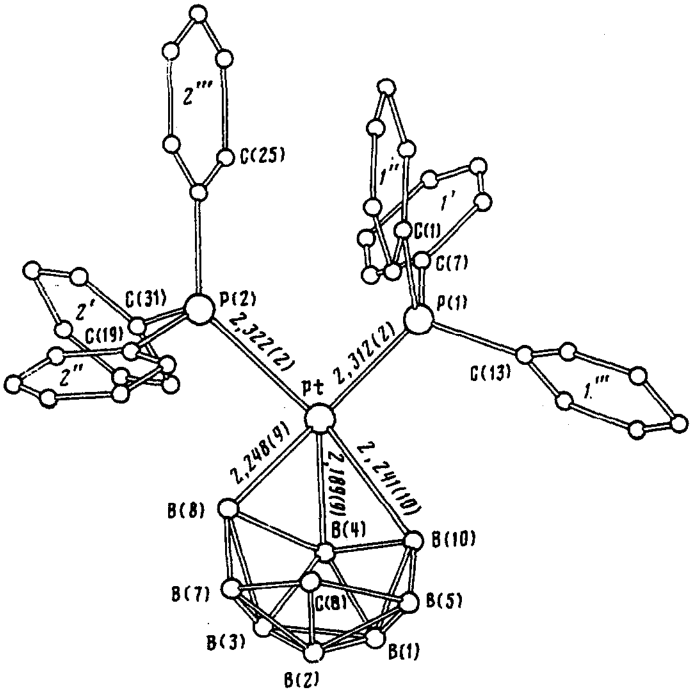
fragment in the carborane [882]. The product of the thermolysis of [9-$(PPh_3)_2Pt$-6-CB_8H_{12}] was characterised by a diffraction study. The structural change noted in (351) involved the attachment of the carborane ligand to two phenyl groups of the PPh_3 ligands [883].



(348) (Reproduced with permission from [877])

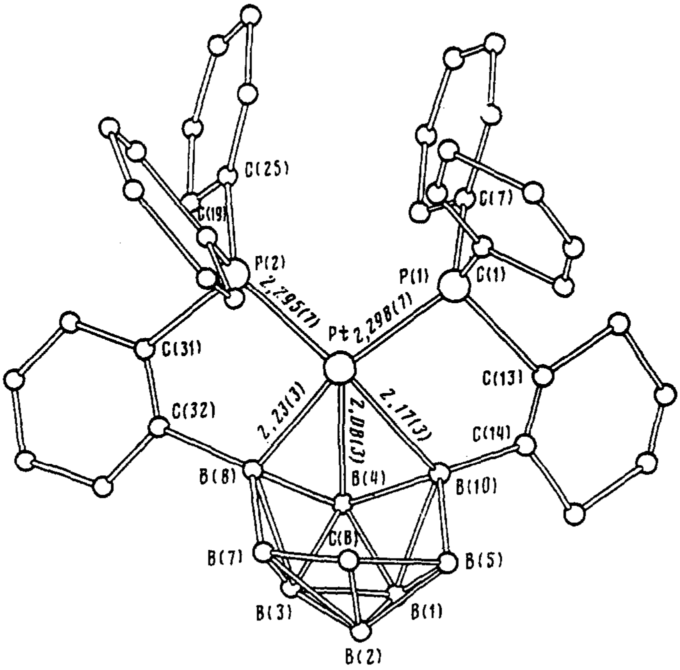


(349) (Reproduced with permission from [881])

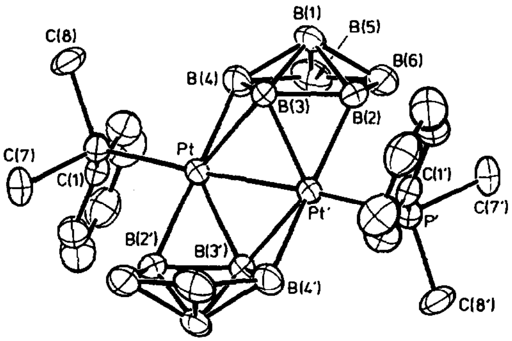


(350) (Reproduced with permission from [882])
Hydrogen atoms have been omitted for clarity

The addition of two molar equivalents of PMe_2Ph to $[(Me_2PhP)_2PtB_{10}H_{12}]$ resulted in the formation of $[(Me_2PhP)_4Pt_2B_{10}H_{10}]$ and $[B_{10}H_8(PMe_2Ph)_2]$. Yields were low, and the complexes could have been more thoroughly characterised [884]. The reaction of *cis*-$[PtL_2Cl_2]$ with 6-$B_{10}H_{13}OH$ or $[6,6'-(B_{10}H_{13})_2O]$ gave *arachno*-$[L_2PtB_8H_{12}]$, *nido*-$[L_2PtB_{10}H_{12}]$ and $[Pt_2(\mu,\eta^3-B_6H_9)_2L_2]$, (352). (352) is a centrosymmetric, fourteen vertex *arachno*-diplatinaborane in which two $\{B_6H_9\}$ clusters are bonded above and below a linear {P-Pt-Pt-P} unit. In the palladium series, reaction of *cis*-$[PdL_2Cl_2]$ with $[6,6'-(B_{10}H_{13})_2)]$ gave phosphinated boranes and *arachno*-$[L_2PdB_8H_{12}]$. When *arachno*-$[(Me_2PhP)_2PtB_8H_{12}]$ was treated with KH, followed by *cis*-$[Pd(PMe_2Ph)_2Cl_2]$, *arachno*-$[(PhMe_2P)_4PdPtB_{10}H_{10}]$ was produced, the first metalloborane to contain metals from different periods. When (352) was treated with *cis*-$[Pt(PMe_2Ph)_2Cl_2]$, a fifteen vertex species, $[Pt_2(\mu-\eta^3-B_6H_9)(\mu-\{\eta^3-B_6H_8-\eta^2-PtH(PMe_2Ph)_2\}(PMe_2Ph)_2]$, (353), was formed, and was characterised by X-ray diffraction and NMR spectroscopy [885].

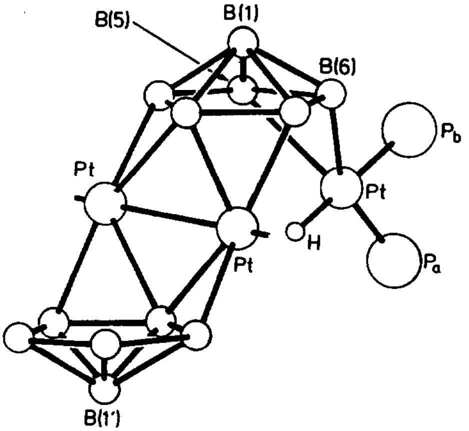


(351) (Reproduced with permission from [883])



(352) (Reproduced with permission from [885])

ORTEP drawing of the molecular structure of $[Pt_2(\mu\text{-}\eta^3\text{-}B_6H_9)_2(PMe_2Ph)_2]$. Hydrogen atoms were not located in the diffraction analysis, but NMR spectroscopy shows that each boron atom has an *exo*-terminal hydrogen bound to it, and that there are bridging hydrogen atoms at borane cluster sites (2,6), (4,5), and (5,6). Peaks corresponding to these positions appeared in the final difference maps.

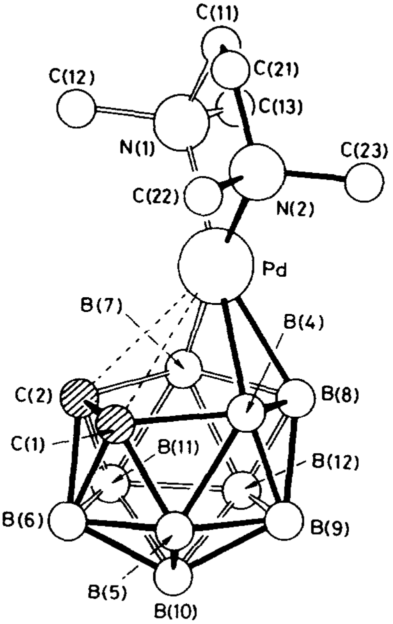


(353) (Reproduced with permission from [885])
Schematic representation of the $\{Pt_2(B_6H_9)(B_6H_8\{Pt(PMe_2Ph)_2H\})\}$ unit of $[Pt_2(\mu\text{-}\eta^3\text{-}B_6H_9)\{\mu\text{-}(\eta^3\text{-}B_6H_8\text{-}\eta^2\text{-}\{PtH\text{-}cis\text{-}(PMe_2Ph)_2\})\}(PMe_2Ph)_2]$ with borane H-atoms and *P*-organo groups omitted for clarity.

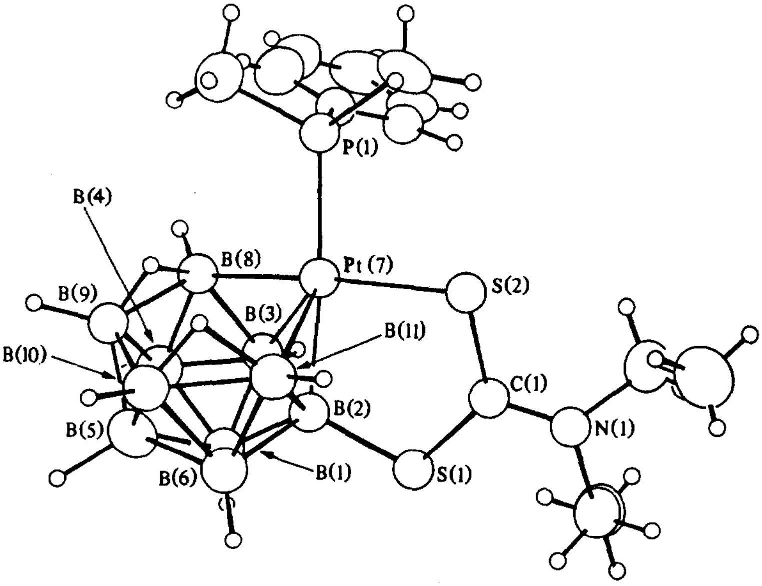
The reaction of $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ with $[(tmen)PdCl_2]$ gave $[3\text{-}(tmen)\text{-}3,1,2\text{-}PdC_2B_9H_{11}]$, (354), which was shown in an X-ray diffraction study to have a slipped structure. The tmen ligand could be displaced by two moles of Me_3P; the product, $[3,3\text{-}(Me_3P)_2\text{-}3,1,2\text{-}PdC_2B_9H_{11}]$, had a more symmetric structure, suggesting that the distortion should be attributed to electronic effects [886]. When [7,7-$(PMe_2Ph)_2$-*nido*-7-$PtB_{10}H_{12}$] was reacted with $[Au(SCNEt_2)Br_2]$, ligand exchange occurred yielding [μ-2,7-(S_2CNEt_2)-7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{11}$], (355), in which the dithiocarbamate is bridging the Pt(7) and B(2) positions. The tetrahapto platinum boron bonding has a considerable twist distortion relative to other *nido*-7-platinaundecaboranes which do not possess this cyclic feature [887].

Reaction of *trans*-$[HPt(PEt_3)_2Cl]$ with $Na[Mn(CO)_5]$ gave $[(Et_3P)_2Pt(\mu\text{-}H)(\mu\text{-}CO)Mn(CO)_4]$, characterised in an x-ray diffraction study. ^1H NMR spectrsocopy revealed an interesting, and strictly intramolecular, fluxional process in which the $\{Pt(PEt_3)_2\}$ unit rotates about the Mn-H bond [888]. The $\{Pt(PPh_3)_2\}$ unit from $[Pt(PPh_3)_2(C_2H_4)]$ undergoes oxidative addition of a P-H bond of $[Cp(CO)(NO)Re(PCy_2H)]^+$ to give (356), as the initial product. This slowly loses CO to give successively (357) and (358). Various other transformations were investigated (Scheme 10) [889]. A similar initial step may be postulated for the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with $[CpM(CO)_3(PPh_2H)][PF_6]$ (M = Mo or W) to give (359) and $[HPt(PPh_3)_3][PF_6]$.

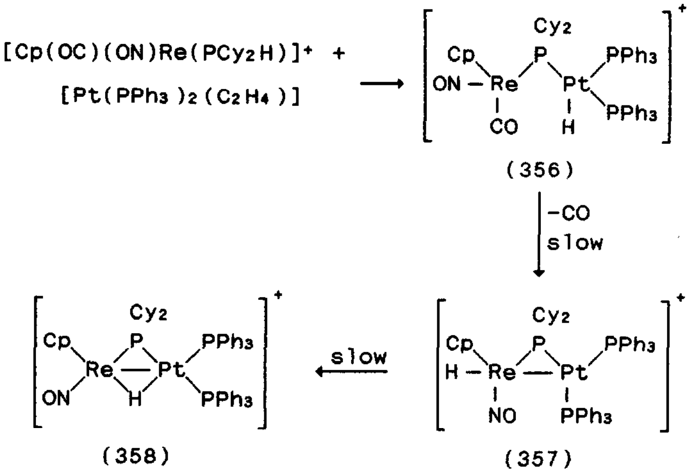
Reactions of (359) were investigated (Scheme 11) [890].



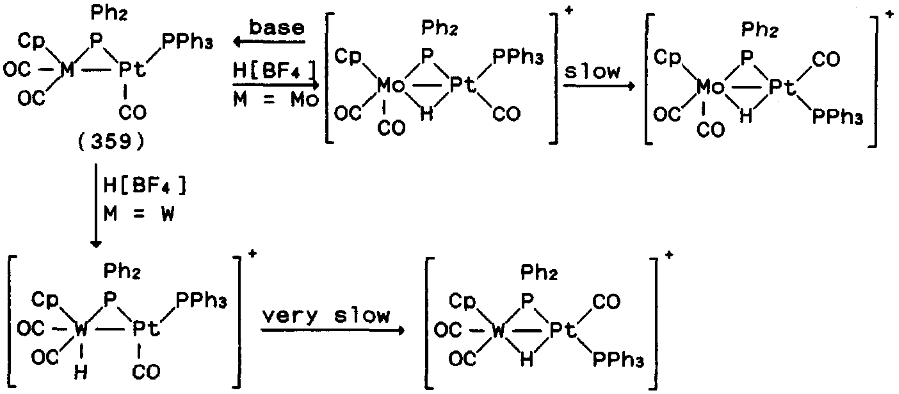
(354) (Reproduced with permission from [886])
Hydrogen atoms are omitted for clarity



(355) (Reproduced with permission from [887])

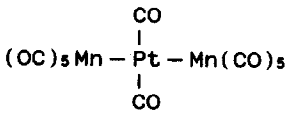


Scheme 10 Reactions of $[Cp(NO)(CO)Re(\mu\text{-}PCy_2)Pt(H)(PPh_3)_2]^+$ [889]



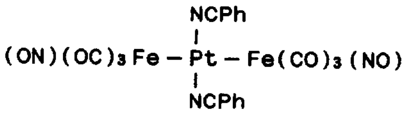
Scheme 11 Reactions of $[Cp(CO)_2M(\mu\text{-}PPh_2)Pt(CO)(PPh_3)]$ [890]

The structures of the square planar complexes (360) [891] and (361) [892] were established in diffraction studies. Reaction of $[Pt(PPh_3)_n]$ (n = 3 or 4) with $[\{(CF_3)_3Ge\}_2Hg]$ resulted in the insertion of $\{Pt(PPh_3)_2\}$ into each of the mercury-germanium bonds to give (362). Hydrogenation of (362) gave $[(CF_3)_3GePt(PPh_3)_2H]$, whilst reaction with $[R_2Hg]$ yielded either $[RHgPt(PPh_3)_2R]$ or $[R_2Pt(PPh_3)_2]$ [893].



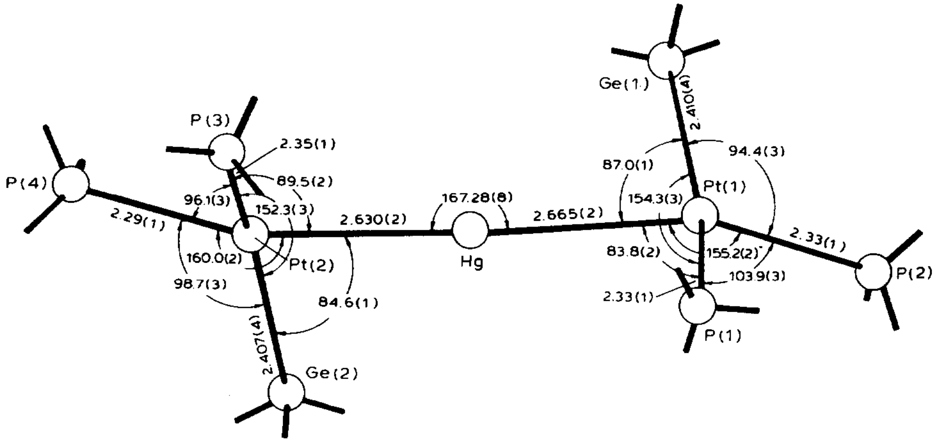
$$(OC)_5Mn-\overset{\overset{\displaystyle CO}{|}}{\underset{\underset{\displaystyle CO}{|}}{Pt}}-Mn(CO)_5$$

(360)



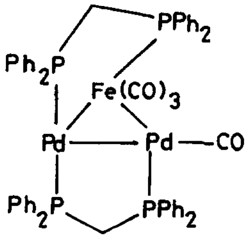
$$(ON)(OC)_3Fe-\overset{\overset{\displaystyle NCPh}{|}}{\underset{\underset{\displaystyle NCPh}{|}}{Pt}}-Fe(CO)_3(NO)$$

(361)



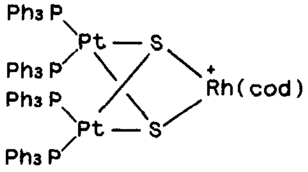
(362) Reproduced with permission from [893]
Polymetallic chain of $[\{(CF_3)_3GePtL_2\}_2Hg]$

When $[Pd_2(\mu\text{-dppm})_2Cl_2]$ reacted with $Na_2[Fe(CO)_4]$ the product was (363), formed by insertion into a Pd-P bond. This complex catalysed the carbonylation of nitroarenes. When a mixed {PtPd} precursor was used, both of the possible products of insertion were obtained, and were not readily separable [894].

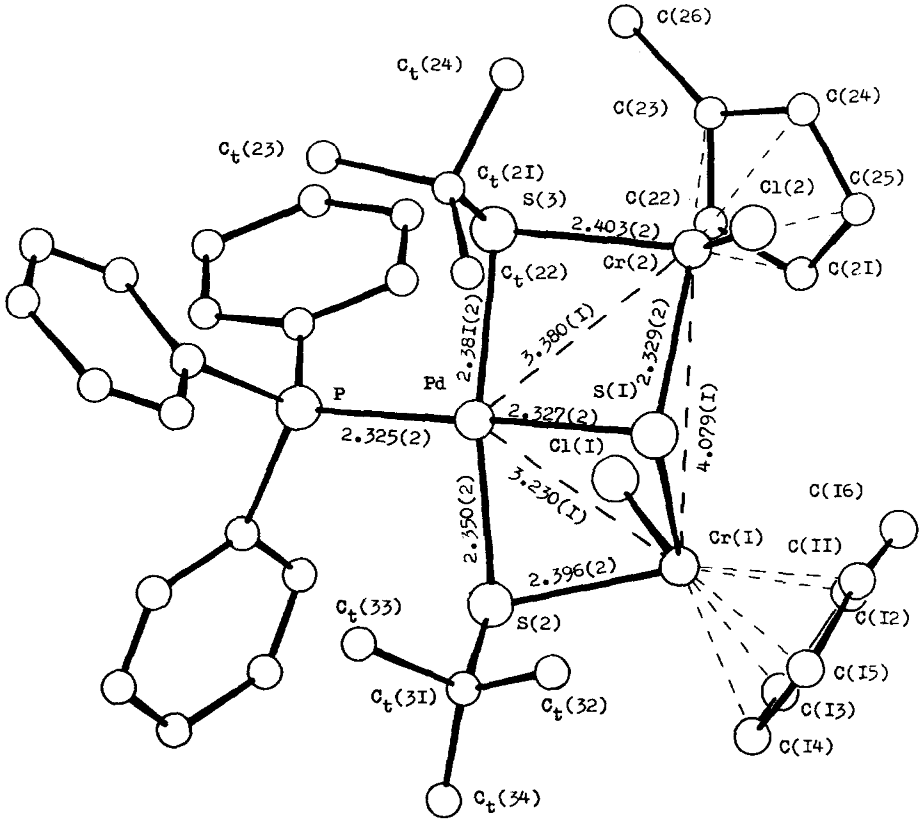


(363)

In the complex $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ the sulphur atoms retain coordination ability, and on treatment with [{Rh(cod)Cl}$_2$], the cationic complex, (364), was formed, in which each metal adopted approximately square planar geometry [895]. A similar situation obtains in the reaction of [(Cp)$_2$Cr$_2$(μ-SCMe$_3$)$_2$(μ-S)] with [Pd(PhCN)$_2$Cl$_2$] to give (365) [896].



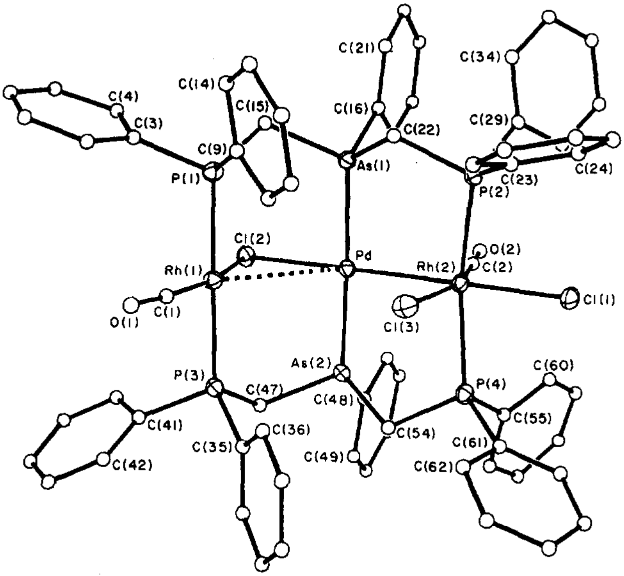
(364)



(365) (Reproduced with permission from [896])

When [Rh$_2$(CO)$_2$(μ-dpma)$_2$Cl$_2$] (dpma = Ph$_2$PCH$_2$As(Ph)CH$_2$PPh$_2$) is reacted with

$[Pd(PhCN)_2Cl_2]$, the palladium becomes bound to the uncoordinated arsenic centre in (366). The iridium complex reacted similarly [897].



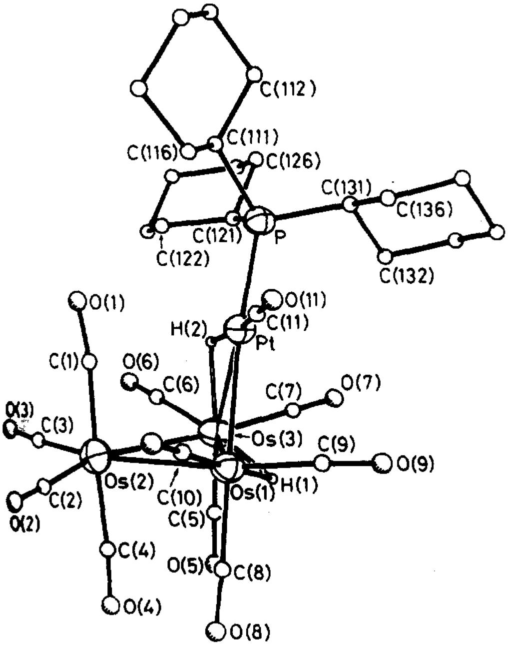
(366) (Reproduced with permission from [897])
Perspective drawing of the cation $[Rh_2Pd(CO)_2Cl_3(\mu\text{-dmpa})_2]^+$.

The preparation and characterisation of $[(M\{\mu_2\text{-}M'(NR_2)_2\}(CO))_3]$ (M = Pd or Pt, M' = Ge or Sn, R = $SiMe_3$) have been described. All the complexes undergo reversible one electron reduction in thf at -1.2 V, to give products which could be characterised by EPR spectrsocopy [898].

The tetrametallic complexes $[M^1_2M^2_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PR_3)_2]$ (M^1 = Pd or Pt; M^2 = Cr, Mo or W; R = Me, Et, Bu or Ph) have been investigated electrochemically in dmf or 1,2-dichloroethane. A two electron reduction was noted, but led to decomposition. Two distinct one electron oxidations were observed, with only the second leading to decomposition. A scheme was proposed for each process, and it was noted that the cluster radical cations appeared to be fairly stable [899].

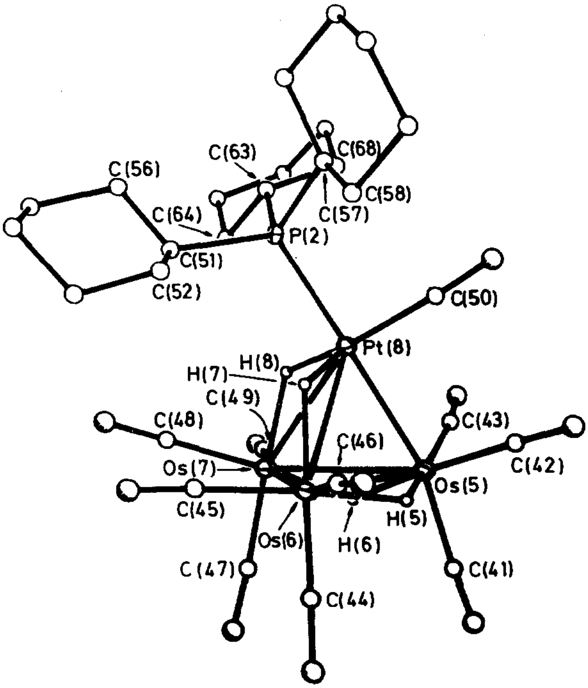
The reactions of the unsaturated cluster $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)]$ with small molecules have been investigated. The product of carbonylation, $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}(PCy_3)]$, (367), had been previously prepared, but has now been fully structurally characterised. The metal skeleton is of the butterfly type, with the platinum atom at the wingtip. One hydride bridges the Os-Os vector of the "body", and one the Os-Pt vector. The platinum is ligated by

PCy_3 and CO. The osmium atom at the wingtip bears four carbonyl ligands and the others three. By contrast, $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}(PCy_3)]$, (368), formed on hydrogenation, has a *closo* tetrahedral metal core. The hydride ligands occupy edge bridging sites on two Os-Pt and two Os-Os bonds. The metal core has D_{2d} symmetry with two unbridged shorter edges, and four bridged longer ones. The reaction with diazomethane yielded $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}(PCy_3)]$, (369), which was formed as an equilibrium mixture of two isomers, one giving orange-yellow and one red crystals. In both cases the metal core was a distorted *closo*-tetrahedron, with the carbene bridging the Os-Os edge cisoid to the PCy_3 on platinum in the orange-yellow form, and transoid to it in the red form. NMR spectrsocopy suggested that these structures were maintained in solution [900].



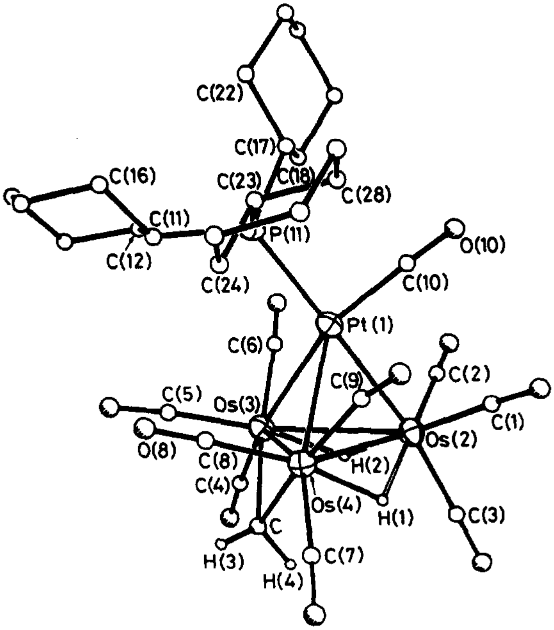
(367) (Reproduced with permission from [900])

When $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ was reacted with $[Pt(C_2H_4)_2(PCy_3)]$, the tetrameric cluster $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}(PCy_3)]$, (370), and the pentametal species $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9(PCy_3)_2]$, (371), were formed. In (370) the osmium atoms form a triangle with the platinum atom bonded to them. The carbide is irregularly bonded to all four metal atoms. Hydrides bridge Os-Os vectors. In (371) two platinum and two osmium atoms form a square plane with the third osmium atom bridging an Os-Os edge. The carbide is approximately equidistant from all of the five metal atoms, and again the hydrides bridge Os-Os bonds. NMR spectroscopic data in solution are in accord with the solid state structure. A related reaction was that of $[Pt(C_2H_4)_2(PCy_3)]$ with $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ to give $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9(PCy_3)_2]$, (372). This is an unusual process in that a carbide containing species is generated from a non-carbide precursor. Two platinum and two osmium atoms form a buckled square plane and the third osmium is bonded only to Os(1). The distances from the carbide to the metal atoms are approximately equal. The bridging carbonyl is asymmetrically disposed on the Pt-Pt edge and the hydride bridges the shorter Pt-Os edge [901].



(368) (Reproduced with permission from [900])

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

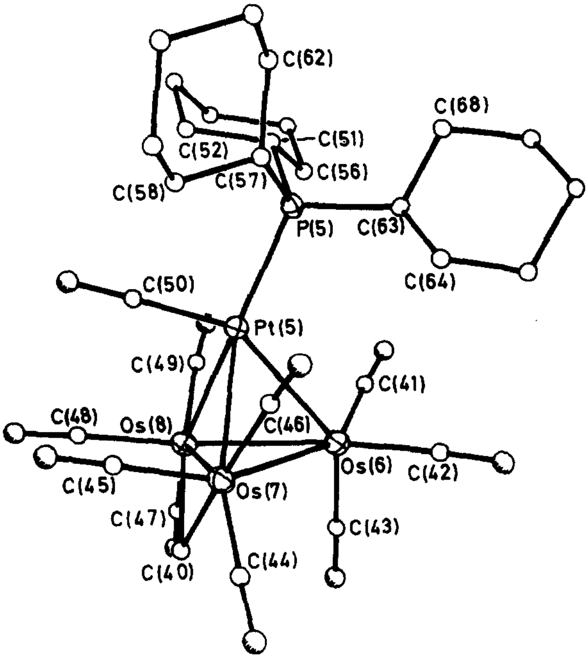


(369a) (Reproduced with permission from [900])
Molecular structure of the complex $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}(PCy_3)]$ (yellow isomer).

The cluster $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ reacted with $[Pt(PMe_2Ph)_4]$, under an atmosphere of carbon monoxide, to give $[Os_3Pt(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2]$, (373). This was shown to be an open triangular cluster of osmium atoms with the $\{Pt(PMe_2Ph)_2\}$ unit bridging an Os-Os bond. The NMR spectra of the complex showed dynamic behaviour [902].

The reaction of $[Os_6(CO)_{20}]$ with $[Pt(cod)_2]$, under an ethene atmosphere, gave $[Os_6Pt_2(CO)_{17}(cod)_2]$, (374). The cod ligands in (374) were readily displaced by dppe [903]. Treatment of $[Et_4N]_2[Fe_5C(CO)_{14}]$ with $[Pt(PPh_3)_4]$ gave $[Et_4N]_2[Fe_5PtC(CO)_{14}(PPh_3)]$, but the structure of the new carbide complex was not established [904].

In the reaction of $[Pt(C_2H_4)_3]$ with $[Cp^*Ir(CO)_2]$, ethene was displaced to yield $[Cp^*{}_3Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3]$, (375), in quantitative yield. The dynamic behaviour of the complex was investigated by NMR spectroscopic studies [905].

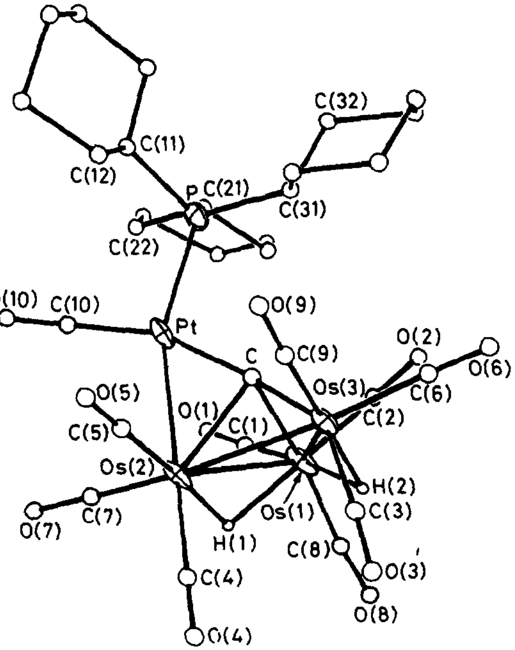


(369b) (Reproduced with permission from [900])

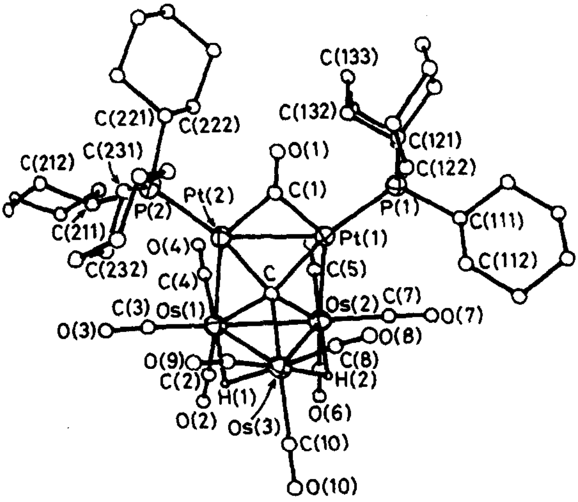
Molecular structure of the complex $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}(PCy_3)]$ (red isomer) showing one of the two crystallographically independent molecules and the atom mumbering scheme.

When $Ag[O_3SCF_3]$ reacted with $[Pt_3(CO)_3(PCHMe_2)_3]$ the bridged species $[Ag\{Pt_3(\mu_2\text{-}CO)_3\{P(CHMe_2)_3\}_2]$, (376), was produced. A silver atom links two staggered platinum triangles, but these triangles rotate fast on the NMR spectroscopic timescale [906]. A two electron reduction of *cis*-$[Pt(CNR)_2Cl_2]$ (R = 2,4,6-$(CMe_3)_3C_6H_2$) at a mercury pool electrode yielded $[Hg\{Pt_3(CNR)_6\}_2]$ as the initial product, but this decomposed to give $[Pt_3(CNR)_3]$ [831].

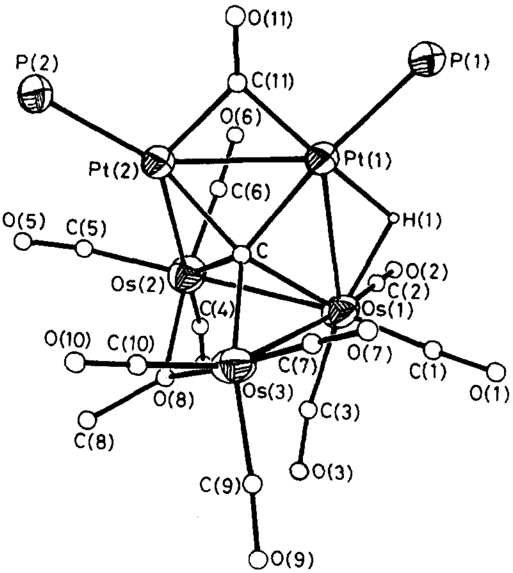
The high nuclearity mixed clusters $[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$ (n = 3,4,5 or 6) were prepared from $[Ni_6(CO)_{12}]^{2-}$ and either $PtCl_2$ or $K_2[PtCl_4]$ under a variety of conditions. The structure of $[Ph_4As]_2[H_2Pt_6Ni_{38}(CO)_{48}]$ was established in an X-ray diffraction study. The metal core consisted of an inner octahedron of platinum atoms fully encapsulated by a ν_3 octahedron of 38 nickel atoms. The metal cluster has the same structure as a fragment of a ccp metal lattice, and is closely related to the homonuclear cluster ion $[H_4Pt_{38}(CO)_{44}]^{2-}$. Preliminary measurements indicated unusual magnetic behaviour [907].



(370) (Reproduced with permission from [901])



(371) (Reproduced with permission from [901])



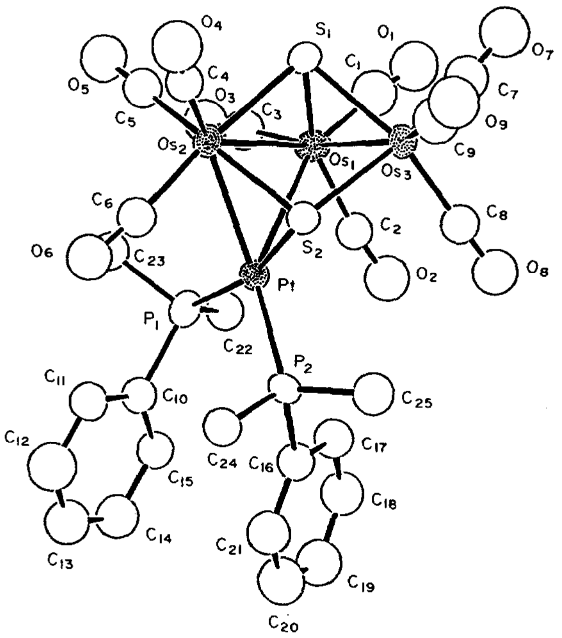
(372) (Reproduced with permission from [901])

The molecular structure of $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9(PCy_3)_2]$ showing the crystallographic numbering, but with the cyclohexyl groups omitted for clarity.

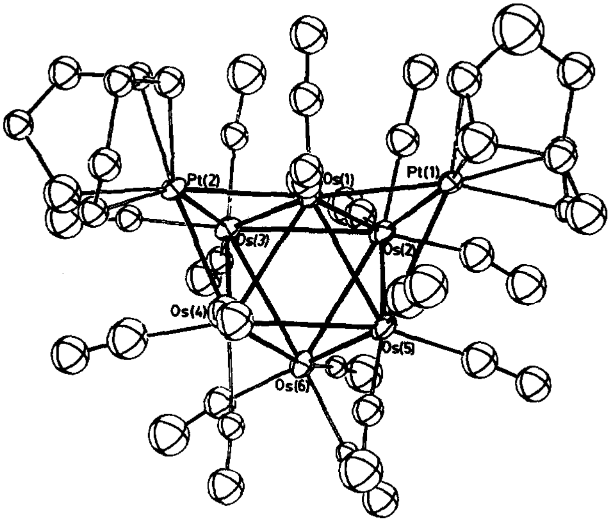
1.10 CATALYSIS BY PALLADIUM AND PLATINUM COMPLEXES

In view of the limitations of space, many of the reactions formerly detailed in this section have been reserved for the reviews of the organometallic chemistry of nickel, palladium and platinum published in the Journal of Organometallic Chemistry. Only reactions which are not of a strictly organometallic type are discussed here.

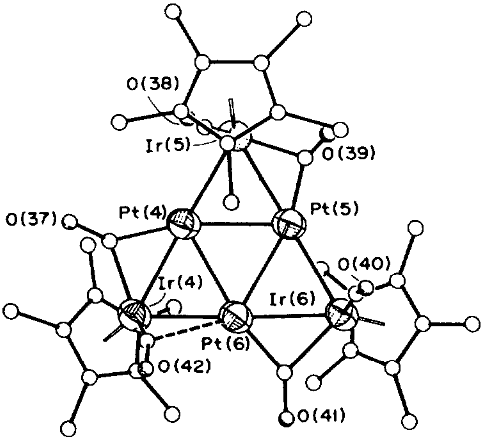
The preparation of very active palladium and platinum powders for catalysis, by reduction of salts with alkali metals has been described [908]. The formation, structure, and properties of supported palladium catalysts has been investigated [909]. For platinum complexes the relationships between the coordination sphere and catalytic properties has been reviewed [910].



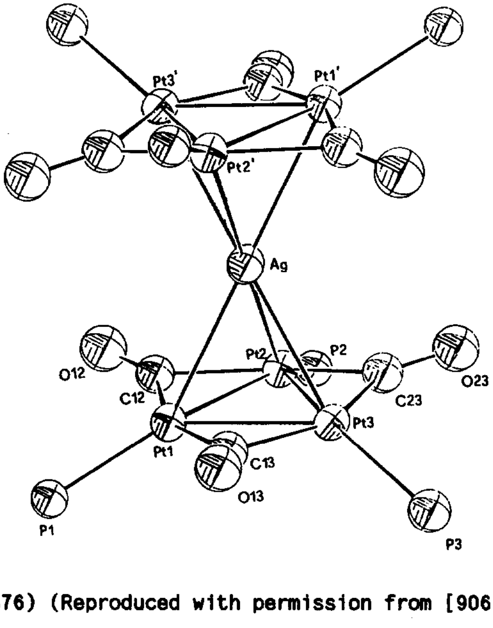
(373) (Reproduced with permission from [902])
Perspective ORTEP drawing of [$Os_3Pt(CO)_9(PMe_2Ph)(\mu_3\text{-}S)_2$] showing 50 % probability ellipsoids.



(374) (Reproduced with permission from [903])



(375) (Reproduced with permission from [905])
Molecular structure of one of the two crystallographically independent molecules of $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ showing the atom numbering scheme.



(376) (Reproduced with permission from [906])
ORTEP diagram of the structure of the cation $[Ag\{Pt_3(\mu_2\text{-}CO)_3(P\{CHMe_2\}_3)_3\}_2]^+$; phosphorus atom substituents are omitted for clarity.

$PdCl_2$ on alumina has been used as a catalyst for the oxidation of carbon monoxide by air [911]. In the oxidation of CO in the presence of

Pd(II)/Fe(III)/Na[NO_2], the presence of bromide ion increased the rate 3-4 fold. The iron(III) acts as the oxidising agent, and is itself reoxidised, in oxygen-free solution, by $[NO_2]^-$ [912]. The kinetics of CO oxidation in the presence of palladium(II) aquo complexes, $[VO_2]^+$, Fe(III) and heteropoly acids have been studied. A species with the stoicheiometry $\{Pd_2(CO)\}^{2+}$ was suggested as an intermediate [913]. Various palladium aquo carbonyl intermediates were proposed as intermediates in the oxidation by Ce(IV) or $[Cr_2O_7]^{2-}$ in the presence of palladium(II) [914].

Reaction of carbon monoxide with $[M(ArNO)_2Cl_2]$ (M = Pd or Pt), above the melting point of the complex yielded CO_2, though it is not clear that this reaction is strictly catalytic [915].

A patent has described the oxidation of CO using O_2/BuONO/BuOH, in the presence of $PdCl_2$, to give $(BuO)_2CO$, with excellent selectivity [916]. Palladium(II) also catalyses the oxidation of CO to carbonate by $[S_2O_8]^{2-}$. Two complex mechanistic pathways were proposed, involving Pd(IV), Pd(II) and Pd(0) intermediates [917].

Hydrogenation of carbon monoxide and carbon dioxide has been studied using catalysts prepared by the decomposition of $[Pd(acac)_2]$ on γ-alumina [918]. Copper metal was produced by reduction of copper(II) in basic solutions by carbon monoxide in the presence of $Li_2[PdCl_4]/[CH_3COO]Na$ [919].

Two patents have described the reaction of nitroarenes with CO to give isocyanates in the presence of $[Pt_{15}(CO)_{30}]^{2-}$ [920,921]. A $PdCl_2$/py catalyst system was promoted by a wide range of additives, including $PhNH_2$, H_2O, $[NH_4]Cl$ or PhNHCOMe [922]. For the conversion of azo compounds to isocyanates, the catalyst system was promoted by Lewis acids, and inhibited by organic bases [923]. Reduction of $ArNO_2$ to $ArNH_2$ by CO was accomplished in the presence of $[Pt(PPh_3)_2Cl_2]/SnCl_4/PPh_3/Et_3N$; the mechanism proposed involved carbonylation to ArNCO, hydration to ArNHCOOH, and decarboxylation [924].

Catalysts of reduced and non-reduced $PdCl_2$ with hydrazine, deposited on polyaminochloroquinones, were used for the reduction of styrene to ethylbenzene [925]. The reaction of an aldehyde with $ArNO_2$ in the presence of hydrogen to give $ArNHCH_2R$, *via* reduction and reductive amination, was catalysed under mild conditions by palladium(II) supported on an anion exchange resin [926]. The effect of the nature of supports and solvents on the catalysis of the reduction of $ArNO_2$, in the presence of $[Pd(3\text{-aminocoumarin})_2Cl_2]$, was examined [927].

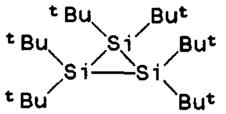
Kinetic data for the hydrogenation of 1-alkenes on palladium sulphide in the presence of various arenes, indicated that the arenes inhibit the reaction by displacing the alkenes from the catalytic sites. The measured deuterium isotope effects suggested that hydrogen participates in the rate controlling steps of both hydrogenation and isomerisation [928]. Hydroisomerisation of 1,3,5-trimethylcyclohexane at 440 °C on PdS/Al_2O_3 gave arenes, cyclohexane and cyclopentane, the reaction being kinetically controlled [929].

Blue tungsten oxides were produced in $H_2[SO_4]/[NH_4]_2[SO_4]$ solutions of tungstates in the presence of $PdCl_2/H_2$ at high temperatures and pressures. Palladium(II) was reduced to metallic palladium, and the reaction may have been heterogeneous [930]. Similar reactions were studied for molybdates [931].

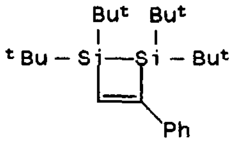
The ion pair complexes $[Bu_4N]Cl/Pd(OCOMe)_2$ and $[Bu_4P]Cl/Pd(OCOMe)_2$ were used as catalysts for the autoxidation of butanal under mild conditions in a radical reaction. Kinetic data indicated that $[Pd_2(OCOMe)_4Cl_2]^{2-}$ was responsible for the initiation reaction [932].

Disproportionation of H_2SiCl_2 over active carbon and $[Pd(PPh_3)_4]$ gave SiH_4 and H_3SiCl [933]. Chlorination of $Me_3SiOSiH_2OSiMe_3$ by $PdCl_2/CCl_4$ gave $Me_3SiOSiHClOSiMe_3$ in 89 % yield, with only a small amount of dichlorinated product [934].

Reaction of the trisilacyclopropane (377) with $[Pd(PPh_3)_2Cl_2]$ gave the silicon equivalent of a carbene and $(Me_3C)_2Si{=}Si(CMe_3)_2$. The disilaalkene reacted with $PhC{\equiv}CH$ to give (378) [935].



(377)



(378)

Platinum(II) bromide is known to promote cage growth and dehydrocoupling reactions between diborane and small polyhedral boranes and carboranes, to give larger single cage compounds or bridge substituted polyhedral carborane/borane complexes. The reactions of diborane with $[1,5\text{-}C_2B_3H_5]$, $[1,6\text{-}C_2B_4H_6]$ and $[B_5H_9]$, gave, respectively, *arachno*-$[5,6\text{-}C_2B_6H_{12}]$, $2{:}1'2'\text{-}[1,6\text{-}C_2B_4H_5][B_2H_5]$ and $2{:}1'2'\text{-}[B_5H_8][B_2H_5]$ [936].

1.11 NON-STOICHEIOMETRIC, BINARY AND TERNARY COMPOUNDS

This year has seen an explosive growth in the literature to be reviewed in this section, particularly in the area of superconducting intermetallic compounds and metal silicides. The author pretends to no expertise in these areas, and this section is designed to be a record of the literature, rather than a critical review.

1.11.1 Compounds with Group 17 elements

Reaction of $PdCl_2$ with two molar equivalents of $[NH_4]Cl$ at 300 ^oC gave $[NH_4]_2[PdCl_4]$, and the temperature of formation and stability of this species were determined. Above 300 ^oC it decomposed to palladium metal, $[NH_4]Cl$, and HCl. A low melting eutectic of $PdCl_2$ and $[NH_4]_2[PdCl_4]$ was formed at a 3:1 molar ratio, and melted at 265 ^oC [937]. $PdCl_2$ was studied using tight-binding band structure computations on the crystal lattice, and MO calculations on fragments out of the lattice. It was concluded that the demands of local angular geometry of the anion and the cation were most important in determining the details of the crystal structure, but the energetics of the anionic matrix were also important [938].

Using the X-ray absorption near edge structure technique, the palladium L-edge absorption spectra of $PdCl_2$ and $PdAl_3$ were studied. The palladium 4d population was depleted relative to palladium metal in both compounds. This was discussed in terms of the MO approximation for $PdCl_2$, and a charge compensation model for $PdAl_3$ [939].

The $PdCl_2/BiCl_3$ system has a eutectic at 228 ^oC and 3 % $PdCl_2$. There is a monotectic region above 329 ^oC from 11-51 % $PdCl_2$. $PdCl_2$ and $NiCl_2$ form a eutectic at 639 ^oC and 98 % $PdCl_2$ [940]. DTA and X-ray phase analysis showed that the $PdCl_2/ZnCl_2$ system is of the eutectic type, and there is a monotectic region from 55-95 % $ZnCl_2$ at temperatures above 310 ^oC. The compound $PdCl_2.2ZnCl_2$ was formed below 160 ^oC [941]. The $PdCl_2/AlCl_3$ system was shown to contain the compound $PdCl_2.2AlCl_3$, which melts congruently at 136 ^oC. The system was studied by DTA, DTGA, isothermal saturation, X-ray diffraction and IR spectroscopy [942]. In the $TlCl/PdCl_2$ system, DTA, X-ray phase analysis and IR spectroscopy showed the formation of $Tl_2[PdCl_4]$ and $TlCl.3PdCl_2$, which melted incongruently at 359 ^oC and 352 ^oC respectively. $Tl_2[PdCl_4]$ was polymorphic with a tetragonal low temperature modification [943]. The equilibrium potentials of platinum in melts based on the ternary eutectic NaCl(KCl)CsCl have been measured [944].

1.11.2 Compounds with Group 16 elements

The percentage thermal expansion of PdO has been derived from regression analysis of published data [945]. Both literature data and calculational methods were used to establish heat capacity of PdO. Its thermal decomposition was also discussed [946].

Mulliken population analyses for several metal oxides, including PdO, gave a value of ~0.7 e for the negative charge at oxygen [947]. The shift in binding energy of the core electrons due to chemical combination may be calculated using the valence shell potential model. The calculations were correlated with the chemical shifts of X-ray absorption edges observed experimentally. Compounds considered included PtO and PtS [948].

A gas detector has been constructed using a sintered compound containing Fe_2O_3, SnO_2, PdO and/or PtO_2. It had increased sensitivity for methane, but reduced sensitivity for hydrogen [949]. Coating with PdO/TiO_2 was shown to be useful for corrosion prevention on titanium [950].

Far IR reflection spectra have been recorded for PdO, PdS, PtS and PdSe. From Kramers-Kronig analysis the TO and LO-phonon frequencies were determined for PdO, PdS and PtS. Strong temperature-dependent free-carrier contributions to the reflection spectrum were observed for PdSe, and their relationship to the near zero band gap of the compound discussed [951].

The amount of PdO which does not dissolve in dilute HCl was determined as a function of its content in palladium catalysts which have been calcined in air. The dispersivity variations were correlated with the solubility of the supported (on alumina) PdO before reduction [952]. The oxidation state of palladium was determined as a function of its treatment, by temperature progression reduction and fromits dispersion. Dispersion occurs only after complete oxidation. Palladium crystallites are oxidised at 600 °C, but dispersion is still low at this temperature. Considerable redispersion occurs from 700-800 °C [953]. The surface of a palladium crystallite oxidised in oxygen at 900 K was analysed by XPS, showing that a thick and uniform layer of PdO had been formed. PdO decomposed in ultra high vacuum in two distinct steps at 420 K and 750-800 K. In the intervening temperature range XPS showed the presence of both metal and oxide. Similar results were noted with other noble metals, and were interpreted in terms of the formation of a cluster oxide phase, which could consist either of small metal clusters in an oxide matrix, or oxide clsuters enclosed in reduced metal [954].

The adsorption of methanoic acid, propenal or propenoic acid on SnO_2/PdO has been studied by transmission IR spectroscopy. At low temperature the acids are bound to the surface *via* the carboxylate groups, and can be removed by evacuation at high temperature. Propenal gave a surface coordinated complex at low temperature, but at higher temperature, bound propenoate was observed [955]. In a study of propene adsorption, it was shown that if the sample was outgassed at ambient temperature, the chemisorbed species were ethanoate and propenoate, but at 570 °C only the ethanoate was observed. The process involves electrophilic addition of surface acidic -OH groups to the carbon-carbon double bond to give surface 2-propoxide, which undergoes oxidation to ethanoate *via* surface bound propanone. The propenoate is formed *via* palladium induced C-H bond fission of the methyl group of propene, generating a surface bound propeneoxide species, which is subsequently oxidised [956]. Adsorption of ethane and ethene onto SnO_2/PdO at various pretreatment temperatures in the range 320-740 K was also studied by transmission IR spectroscopy. In all cases the ultimate surface product was ethanoate, *via* oxidation of surface ethoxide [957].

A pH electrode was constructed consisting of a palladium coated glass substrate coated with a stoicheiometric sputter film of PdO [958].

TGA, differential TGA and DTA studies have been undertaken of PdO alone and of $PdO/M_2[S_2O_8]$ mixtures. PdO catalytically lowers the T_i values of decomposition of $M_2[S_2O_8]$ by 20 ^{o}. In the absence of water, at 80 ^{o}C, PdO reacted with $Na_2[S_2O_8]$ to give $Na_4[PdO(SO_4)]_2$, stable below 155 ^{o}C. At higher temperatures the reaction gave $Pd[SO_4]$. The eutectics $Pd[SO_4].M_2[S_2O_7]$ (M = Na or K) were identified [959].

A platinum electrode was anodically polarised at 3 V *vs* the SHE in 0.5M H_2SO_4, or in 1M Na[OH] at 3 V *vs* an Ag/AgCl reference. The oxide coating formed in acid was $Pt(OH)_4$, whilst in base, $PtO(OH)_2$ was produced [960]. The nature of the product of the basic reaction was confirmed by XPES. $PtO(OH)_2$ decomposed at 400 ^{o}C to various oxides and hydroxides of platinum(II) and platinum(IV), and to platinum metal [961]. The surface chemistry of Pt<111> single crystal electrodes in 0.5 M H_2SO_4 was studied in the potential range 0-4 V by XPES and cyclic voltammetry [962]. The dependence of oxygen surface covering on potential was shown to have several distinct regions, each corresponding to the formation of a specific compound [963].

Monolayer and multilayer oxide films on palladium metal electrodes were studied as a function of pH. The potential for the onset of oxidation increased with increasing pH, though less markedly than for platinum. The initially formed anionic species underwent exchange type reactions to give a more neutral deposit, and finally thick hydrous oxide films [964].

Oxidation of a platinum foil surface in K[OH] was examined by PES and Auger spectrsocopy. PtO and PtO_2 were detected at the surface and $[Pt(OH)_6]^{2-}$ in solution [965]. Square wave hydrodynamically modulated voltammetry was used to study anodic reactions electrocatalysed by surface oxides at platinum electrodes. In particular, the anodic formation of {PtOH} in acidic media catalyses the oxidation of I^- to $[IO_3]^-$ [966].

The reactions of MgO with Pd or Pt metal have been studied; the products were not very well-defined [967]. A $Pb_2[V_2O_7]/V_2O_5$ melt dissolves platinum from a sealed crucible [968].

Single crystals of the hitherto unknown $BaNd_2PtO_5$ were studied by X-ray diffraction; platinum(II) adopted square planar coordination [969].

$Ba(Sn_{1-x})In_x)O_3$ perovskites exhibit a maximum of solid solution for $x = 0.4$. At this composition they also have maximum activity for propene oxidation, this activity being increased by the presence of traces of ionic platinum [970].

The electronic structures of $[MO_4]^{n-}$ (including M = Pd) have been calculated by the DV-X_α method. In most cases their electron affinities were in excess of 3.5 eV, and they were classed as superhalogens [971].

The bulk photoluminescence of Schottky diodes constructed from palladium and *n*-type CdS is sensitive to molecular hydrogen, providing a method for the optically coupled sensing of H_2 [972].

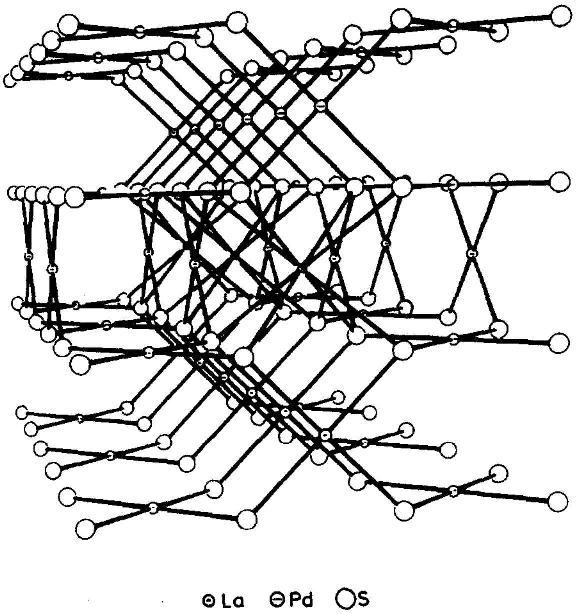
Laser-pulse transient measurements were performed at single crystalline *n*-PtS_2 electrodes, with the aim of understanding light induced hydroxide, oxide, and oxygen formation. There were distinct changes in the reaction products with time, since surface oxidation gave rise to a large number of different surface states. Thus oxygen was evolved only when a rather large electrode biasing potential was applied [973].

Sulphur pressures in the Pd/S system were measured for liquid mattes and PdS/liquid matte mixtures. Standard free energies for the formation of solid and liquid Pd_4S, Pd_3S, and $Pd_{16}S_7$, and solid PdS were derived. The results for Pd_4S were substantially different from those previously accepted [974]. DTA, SEM, X-ray diffraction and electron microprobe analysis were used to study the liquid solid equilibrium in the Pt/PtS system. A nonvarient eutectic equilibrium at 9.2 % sulphur and 1240 °C was found [975].

The extended Zintl principle was discussed for framework structures of ternary metal chalcogenides, pnictides and hydrides, including A_2PdX_2, $A_2Pd_3X_4$, A_2PtX_2 and $A_2Pt_3X_4$ [976].

The synthesis of MPd_3S_4 (M = rare earth) from a stoicheiometric mixture of the elements at 1125 K for three weeks has been reported. $LaPd_3S_4$, (379), had the ideal $NaPt_3O_4$ structure, as shown by X-ray and neutron diffraction. Magnetic measurements on the compound were discussed in detail. Neutron diffraction data and conductivity measurements were consistent with a partially reduced nature for the sulphides [977].

Polycrystalline samples of the CdI_2-type mixed crystals, $PtS_{2-x}Se_x$, $PtS_{2-x}Te_x$ and $Pt_{2-x}Te_x$, were prepared and characterised by far IR spectroscopy and X-ray diffraction measurements. A change in the behaviour of the *c/a* ratio, and in in the *x*-dependence of the plasma resonance frequency of the free carriers present, was observed in $PtS_{2-x}Se_x$ near $PtS_{0.6}Se_{1.4}$. This was interpreted in terms of a critcal composition for p,d band overlap [978].

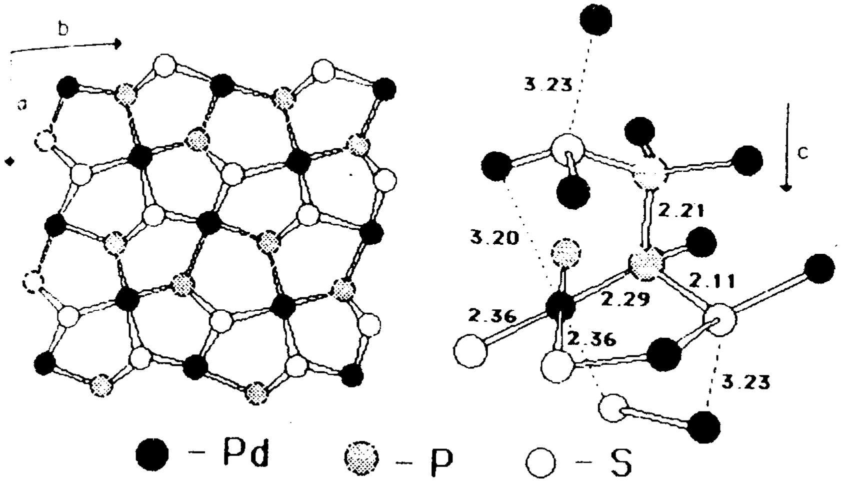


(379) (Reproduced with permission from [977])
Drawing of the $LaPd_3S_4$ structure. The eight-coordinate lanthanum atoms are in the centre of the figure.

Crystals of the layered material *n*-PdPS, (380), have been prepared. This is an *n*-type semiconductor with an indirect band gap of 1.45 eV, and a direct band gap of 1.66 eV. The photoresponse of the crystals was tested in a variety of redox electrolytes; only ferrocyanide supported large photocurrents, and was not associated with photocorrosion. Topographic photoresponse, studied by an *in situ* laser scanning technique, revealed that higher quantum yields were associated with non van der Waals crystal surfaces. The interaction of the ferrocyanide with the reactive edge sites of the PdPS crystal, resulting in a stable surface trap and an interfacial charge mediator, was proposed [979].

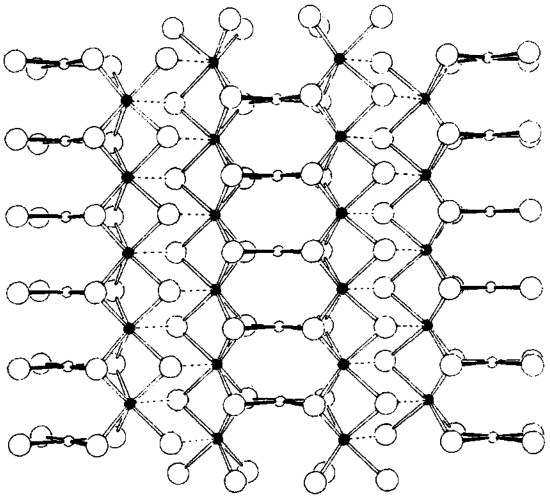
One dimensional ML_2 chains with edge sharing tetrahedral or square planar coordination were subjected to theoretical analysis, and the band structures of the materials were examined in detail. The compounds considered included Na_2MS_2 (M = Pd ot Pt), K_2PtS_2, Rb_2PtS_2 and α-$PdCl_2$ [980].

The compounds M_2PdE_6 (M = Ta or Nb, E = S or Se) were prepared from their elements. The tantalum derivatives, (381), were characterised by single crystal X-ray diffraction studies, and were isostructural. In this novel laminar structural type, each layer consists of collocated units, $\{M_2PdE_6\}$, composed of ME_3 face-sharing trigonal prismatic chains bridged by palladium atoms in a square planar environment of E atoms. Conductivity measurements indicated a formulation of $Ta^{V}Pd^{II}S^{-II}$ [981].



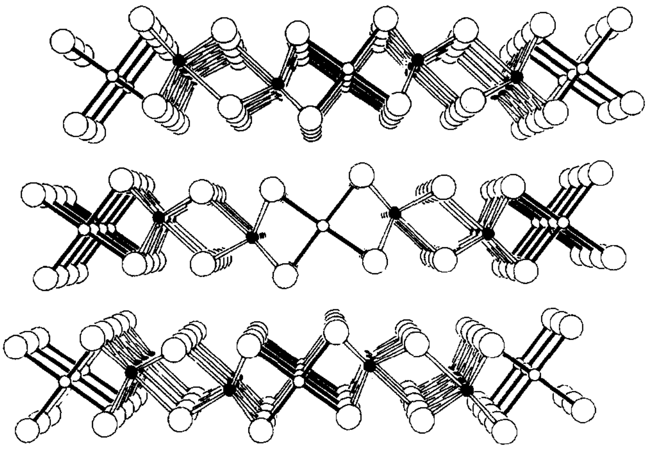
(380) (Reproduced with permission from [979])

Top view of the net making up the cleavage planes of PdPs (left), and the local geometry and bond distances through a layer (right). The long (3.23 Å) distances are interlayer, while the intralayer Pd-Pd distance is 3.20 Å.



(381a) (Reproduced with permission from [981])

Drawing of an individual layer of $^{2}_{\infty}[Ta_2PdSe_6]$ as viewed orthogonal to <101>. Ta atoms are small filled circles, Pd atoms are small open circles, and Se atoms are large open circles.

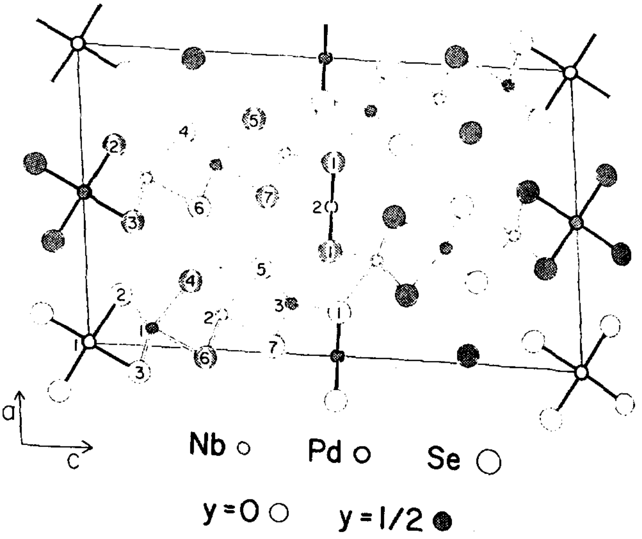


(381b) (Reproduced with permission from [981])
Perspective view of Ta_2PdSe_6 along <010>.

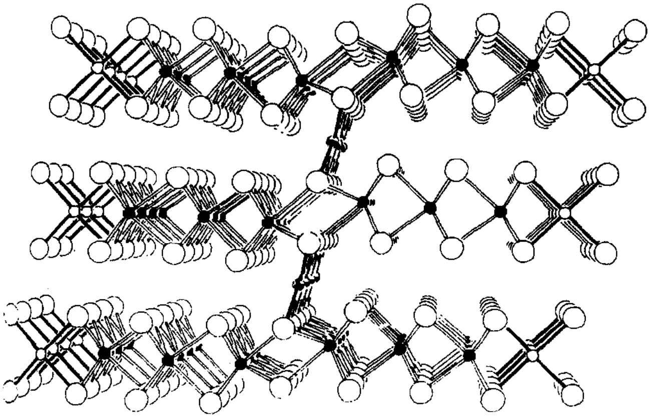
High purity synthetic $PdSe_2$ was roasted at 300-900 ^{o}C, and then added to a copper electrolysis slime to prepare a feed containing copper (30 %), nickel (20 %), palladium (2 %), and an excess of sulphuric acid, for a study of the recovery of palladium and selenium [982].

The new compound $Ta_2Pd_3Se_8$ was prepared in a similar manner to the known $Nb_2Pd_3Se_8$, and was shown to be isostructural with it. $Co_2Ta_4PdSe_{12}$ was derived from an attempt to substitute cobalt for five-coordinate palladium in $Ta_2Pd_3Se_3$. The structure of the mixed compound is of a new laminar type with five-coordinate cöbalt atoms. $Nb_2Pd_{0.71}Se_5$, which showed metallic conductivity, resulted from a different starting composition in the Nb/Pd/Se system [983]. $Nb_3Pd_{0.72}Se_7$ was also prepared by the reaction of the elements, and its structure, (382), established by single crystal X-ray measurements. The structure is another new laminar type with layers of the formula $^{2}_{\infty}[Nb_6PdSe_{14}]$. Between the layers, palladium atoms occupy statistically 43 % of rhombic sites. A general model was proposed for the electronic structure of ternary phases containing niobium, palladium and selenium atoms [984].

Tl_2PdSe_2 was prepared from TlSe and palladium metal at 1100 K. Palladium and selenium form infinite linear chains of edge sharing {$PdSe_4$} rectangles separated by thallium atoms. Thallium is coordinated by eight selenium atoms in a distinctly polar configuration, with one palladium neighbour at 2.92 Å. The lone pair of electrons on thallium plays a decisive rôle in determining structure [985].



(382a) (Reproduced with permission from [984])
Projection of the structure of the phase $Nb_3Pd_{0.72}Se_7$ onto the *a*-*c* plane.



(382b) (Reproduced with permission from [984])
Perspective drawing of the phase $Nb_3Pd_{0.72}Se_7$ along the direction <010>. Nb atoms are small filled circles, Pd atoms are small open circles, and Se atoms are large open circles.

1.11.3 Compounds with Group 15 elements

Far IR reflectance spectra of hot-pressed samples of PtY_2 (Y = P, As or Sb) have been recorded from 40-700 cm^{-1}. The spectra show five reststrahlen bands, and more or less free carrier contributions to deviations from stoicheiometry. The phonon frequencies were determined and reflect the increase in bond strengths from P to As to Sb [986].

Hole sizes and intersite dimensions were calculated for all types of interstices in $Pd_3P_{1-x}H_n$, which has the structure of cementite (Fe_3C). In $Pd_3P_{0.8}D_{0.15}$, the radii of the holes range from 0.87-0.43 Å [987]. The geometric model was used to rationalise the observed site occupation; only one type of interstice, associated with a vacant phosphorus site, is actually used [988].

The ternary compound, $EuPd_2P_2$, has been classified as a mixed valent species from lattice volume anomaly data, but Mössbauer isomer shifts and magnetic measurements suggest divalent $4f^7$ europium. The Eu L_{III}-edge X-ray absorption spectrum is double peaked, as expected for a mixed valence material. The explanation suggested is a partly extended 4f radius [989]. It has also been proposed that final state configuration interaction affects the L_{III}-edge spectrum, and that there is significant 4f covalent bonding [990]. Valence band photoemission of the 4f shell is consistent with a divalent nature for europium, but white photoemission from the 3d deep core level suggested mixed valence [991].

New compounds A_2BX_2 (A = K or Ru, B = Ni, Pd or Pt, X = P or As) with the orthorhombic K_2PdP_2 structure, and the space group *Cmcm*, have been prepared from the elements. Their structures are characterised by BX_2 zigzag ribbons surrounded by channel like arrangements of alkali metal atoms [992].

The axial *c/a* ratio, unit cell volume, valence electron density average, and Madelung constants have been determined for the metastable phases of Pd_5As, $Pd_{0.4}Tl_{0.1}As_{0.5}$, $PdPb_{0.2}As_{0.8}$ and $Pd_{25}Si_{4.5}Sn_{4.5}$, and were compared with the values for the stable phases [993]. Intermetallic resistors have been formed by reacting to completion a 300 Å film of platinum with underlying GaAs. PtAs, PtGa and $PtGa_2$ phases were identified after reaction at 450-550 °C [994].

The reactions of palladium on <100> and <110> GaAs surfaces at 20-500 °C has been studied by TEM. Two new Pd-Ga-As phases were identified for the first time. Below 250 °C, $PdGa_{0.3}As_{0.2}$ was formed, with a hexagonal structure similar to that of Pd_2Ge or Pd_2Si. Between 350 °C and 500 °C, in a high vacuum environment, only PdGa was produced, but at 500 °C, in a gas ambient, the hexagonal phase $PdGa_{0.6}As_{0.4}$ was formed. It was concluded that the reaction of palladium with gallium arsenide is very sensitive to ambient conditions, but not particularly to surface cleanliness or substrate orientation [995].

Fifteen ternary compounds $M_2Pd_2Pn_2$ (M = alkaline earth or rare earth, Pn = As, Sb or Bi) have been prepared. Guinier powder patterns showed that the arsenides crystallise in the $ThCr_2Si_2$ structure, and the bismuth and antimony derivatives have structures related to $CaBe_2Ge_2$ [996]. Ellipsometry measurements on polycrystalline samples of PtMnSb at room temperature under high vacuum conditions have been reported. The measured optical conductivities are in reasonable agreement with those calculated from the band structures. The band gap for the minority spin direction is clearly observed, and can be brought into agreement with the band structure calculations by consideration of spin orbit coupling [997].

1.11.4 Intermetallic compounds

1.11.4.1 Compounds with silicon

Thin films of Pd_2Si and PtSi were formed by short duration incoherent light exposure of evaporated palladium or platinum films on <111> or <100> silicon single crystals. After processing for 15 sec at temperatures of 500-800 K the silicides were characterised by their sheet resistivities [998]. Annealing at 200 °C of palladium films less than 10 Å thick on silicon gave a polycrystalline film of Pd_2Si, *via* the formation of flat Pd_2Si islands which grow epitaxially to the substrate. For thicker films annealing results in silicon segregation over the silicide surface [999]. Pd_2Si has also been produced on monocrystalline silicon substrates by rapid thermal annealing at 350-450 °C for 1-60 secs. The results obtained were similar to those from annealing at a lower temperature for a longer time [1000]. The effects of impurities on the growth of the Pd_2Si layer, on thermal annealing of a palladium film on <100> and amorphous silicon substrates, has been investigated. Both nitrogen and oxygen retard silicide growth, if initially present in the silicon, but not if present in the palladium. By using nitrogen implanted into silicon as a marker, palladium and silicon can be induced to trade roles as the moving species, when the silicide front reaches the nitrogen rich region [1001]. Thermal annealing of palladium on SiC was studied by X-ray diffraction and MeV backscattering spectrometry. Initially Pd_3Si is formed, followed by Pd_2Si at higher temperatures. The reaction temperatures for Pd/SiC are higher than those for Pd/Si, but carbon containing compounds were not detected [1002].

The reactions at the interface of <111> Si and palladium have been investigated as a function of the thickness of palladium coverage in the range 5-50 Å. Surface conditions were monitored by Auger spectroscopy, and the structural interactions by Raman spectroscopy. With a 5 Å coverage Auger data indicated strong Si-Pd bonding, but Raman spectra gave no evidence fpr the formation of a crystalline silicide until the depth was 10 Å. The effect was attributed to the need for critical cluster sizes to form stable nuclei [1003]. The kinetics of the growth of epitaxial Pd_2Si films on <111>Si substrates were studied by X-ray diffraction in the temperature range 160-222 ^oC [1004]. The kinetics were also compared for as-deposited and high dose H-implanted films. The growth rate increased, and the activation energy for silicide formation fell, in the implanted samples [1005]. The growth of the Pd_2Si phase was also studied using MeV-^{4}He ion backscattering, and TEM [1006]. Palladium was deposited on <100> and <111> Si, and on polycrystalline silicon, and cross-sectional samples for TEM were prepared and heated *in situ* [1007]. Interfacial reactions were studied between amorphous silican and 1, 5, 50 or 200 nm palladium films in the as-deposited state, and after annealing at 200-500 ^oC. An amorphous phase was observed in the as-deposited state in samples of 1 nm palladium on α-Si, but Pd_2Si was formed from both as deposited and annealed states in thicker films. The growth of Pd_2Si at 200-224 ^oC was shown to be diffusion controlled with E_a = 1.25 eV [1008].

Various transition metal silicides were prepared by vacuum thermal annealing of 20 nm metal layers on silicon substrates. The samples were then argon sputtered at 2 keV in an ultrahigh vacuum Auger system until the silicide/silicon interface was reached. The interface was irradiated with electrons, and the Auger spectra recorded at regular time intervals. Metal atoms which had diffused into the silicon move to the surface under electron bombardment, and a surface silicide layer 1-2 nm thick was formed by these migrating metal atoms. The electron induced migration of metal atoms was stronger for the Pd_2Si/Si interface than for the Pt_2Si/Si interface [1009]. The effect of a platinum concentration in palladium films on nucleation and growth of PdSi and $Pd_xPt_{1-x}Si$ was investigated by TEM. A low concentration of platinum (10 %) enhances the formation of PdSi at lower than normal temperatures, by triggering nucleation. A high concentration (55 %) of platinum lowers the temperature of the phase transition from metal rich silicide to $Pd_xPt_{1-x}Si$ [1010].

The thermal and ion-induced formation of Pd_2Si in a Pd-Si system with an interfacial silica layer was studied. The blocking of the thermal silicide formation by the silica is partially removed by pre-irradiation with ions, inducing a quadratic laterally non-uniform thermal growth of the silicide [1011]. Silicide formation with palladium on hydrogenated amorphous silicon substrates was studied with Rutherford back scattering spectrometry and forward recoil spectrometry. The activation energy for silicide formation was the same as on single crystal substrates. During silicide formation hydrogen is released from the silicides, and presumably outdiffuses into a vacuum without interfacial accumulation. Thus, barrier formation does not occur, and the hydrogen has no effect on silicide growth [1012].

Evaporated tungsten and silver were used as markers in growth studies of silicides formed both by annealing and by ion mixing in the Pd/Si system. In annealing both palladium and silicon move, with the palladium moving faster. Using ion irradiation, the silicon is the faster moving species [1013]. A titanium marker was used to investigate the moving species during Pd_2Si formation on <111> and <100> Si substrates. This work led to the conclusion that silicon was generally the mobile species, but palladium participated in mass transport when silicon motion was obstructed [1014]. A multilayer film structure, $Pd/Pd_2Si/Ge$, in which germanium served as a sink for palladium, was used to monitor the flux of palladium through Pd_2Si. The silicon flux was measured similarly using $Si/Pd_2Si/Cr$, with the chromium acting as the silicon sink. There was good agreement between the palladium mobility and the existing parabolic growth constant for the growth of Pd_2Si at 200 ^oC. The mobility of the silicon was orders of magnitude lower [1015]. Palladium was also identified as the dominant moving species in a study using a sample of configuration Si<111>/single crystal Pd_2Si/polycrystalline Pd_2Si/Pd [1016].

The kinetics and mechanism of the oxidation of Pd_xSi on amorphous silicon at 900-1100 ^oC in wet oxygen have been studied. The silicide dissociates on the surface, and both palladium and silicon diffuse through the silicide to the substrate. Only silicon is oxidised, to SiO_2 [1017]. Room temperature oxidation of M_2Si (M = Ni, Pd or Pt) was studied by core-valence-valence Auger line measurements, before and after oxygen treatment. $PdSi_2$ was oxidised more rapidly than silicon, and gave SiO_x, $x < 2$, whilst Pt_2Si reactd at a rate similar to that for pure silicon [1018].

Inverse photoemisison was used as a new probe for unoccupied electronic states, and the density of unoccupied antibonding states was determined for Pd_2Si [1019]. X-ray absorption spectroscopy was used to investigate the near L-edge structure of palladium in the pure metal and in bulk Pd_2Si and PdSi. Possible many body effects were used to explain the apparent discrepancy between the occurrence of $L_{2,3}$ white lines and the 4d hole filling in the palladium silicides. The interpretations of the extended fine structures, and of the near edge features, were correlated to find common support for a dynamical relaxation model for the $L_{2,3}$ deep core holes of palladium silicides [1020].

Deep level transient spectroscopy, current-voltage and Rutherford back-scattering spectrometry measurements of nickel, palladium and platinum silicide barriers on *n*-Si annealed at 300-800 K have been reported. Reversed-bias leakage currents increased with an increase in the annealing temperature. Degradation of PtSi was negligible at temperatures at which nickel and palladium silicide barriers had become very leaky [1021]. Phase transformations in a number of ion-implanted and subsequently annealed silicides have been investigated. The electrical resistance change as a function of $^{28}Si^+$ ion implantation has been found to correlate with the presence of a disordered state in the silicide. Implantaion of an 1860 Å Pd_2Si layer on <111>Si with 250 keV $^{28}Si^+$ ions, at liquid nitrogen temperature, yields no apparent diffuse halo in electron diffraction (TEM) experiments for doses up to $2x10^6$ $^{28}Si^+$ cm^{-2}. Pd_2Si layers show no saturation in resistance for doses up to $2x10^{16}$ $^{28}Si^+$ cm^{-2}, with the resistance increasing by a factor of less than four [1022].

A new platinum silicide formation method has been described, using the reaction between a platinum film and silane at 250-400 ^{o}C. This process was less influenced by oxygen contamination than the platinum silicon reaction [1023]. In general, when platinum silicides are formed in an oxygen atmosphere, or the platinum film contains significant oxygen, the rate of silicide formation is reduced. In the latter case an oxide layer is formed between the surface platinum and the Pt_2Si and PtSi phases. Molecular oxygen diffuses from the ambient into the platinum during the Pt_2Si formation stage, and an oxide layer is formed under the surface when the front of the Pt_2Si phase meets the oxygen in the metal film. This hinders further growth of the Pt_2Si phase. Subsequent formation of the PtSi phase proceeds until it meets the oxide layer, and is then hindered from further growth. The oxide layer has, however, little effect on the bulk growth of the two silicides, and other mechanisms are needed to account for the reduced growth rate [1024].

High intensity quartz halogen lamps have been used to form platinum silicide films. Platinum films of 42 and 52 nm were evaporated on single crystal silicon, and subsequently processed in a roughing vacuum for periods from 5-20 sec. The electrical characteristics and the microstructure of the silicide films were studied by four point probe measurements, X-ray diffraction, AES, and Rutherford backscattering spectrometry. The dominant phase formed was PtSi, together with a small amount of Pt_2Si [1025]. The growth of the Pt_2Si phase under conditions of thermal annealing was shown to be a diffusion controlled process. Penetrating Xe ions did not induce silicide growth [1026]. Layers of mixed platinum and silicon were formed on p^+-n junction silicon crystal wafers by depositing platinum on the p^+-Si surface followed by heating to 320-350 °C. XPES data implied that PtSi (or PtSi and Pt_2Si) was formed when a 3.5 nm thick platinum layer on silicon was heated, whereas a non-stoicheiometric Pt-Si intermixed layer was formed from an ultrathin platinum layer [1027].

An interfacial silicon nitride layer, 30-60 Å thick, could be produced by sputter etching of a silicon substrate with pure nitrogen, before platinum deposition. When the layers were annealed at >500 °C the platinum reacted locally with the silicon to form disc-shaped clusters, the cluster radius increasing with an increase in annealing time. The growth rate was inversely proportional to the thickness of the nitride layer. The silicide growth was explained by diffusion of platinum through the nitride layer in the locally stressed region of the growth front [1028]. Interfacial melting at near eutectic compositions has been observed for Pt/Si using pulsed ion beam irradiation. In all cases the reaction occurred at a temperature below the melting point of either platinum or silicon [1029]. The moving species during the formation of Pt_2Si by both ion mixing with 300-600 keV Xe ions, and by thermal annealing, have been identified using inert markers and backscattering spectrometry. The thermal annealing data indicated a predominant motion of platinum, but in the ion mixing process, movement of silicon was marginally favoured [1030].

The current transport mechanism was studied for Pt_2Si and PtSi contacts on *n*-silicon [1031].

All the compounds predicted by the Si-Pt phase diagram have been observed by depositing thin layers of platinum on silicon in known quantities and ratios to each other. The new binary compounds Pt_6Si_5 and $Pt_{12}Si_5$ were identified experimentally for the first time in a planar film reaction. The materials were analysed using $^4He^+$ backscattering and X-ray diffraction [1032]. The interface structure beteen PtSi and <111>Si was studied on an atomic scale with a 1 MV high resolution electron microscope. At the interface the transition is abrupt, without the presence of any other phase. Lattice fringe images show that the interface is heavily undulated, and has atomic steps [1033].

Optical microscopy, X-ray diffraction and microhardness were used to study the interaction of the silicide phases in the Pd-Mo-Si system. Pd_2Si was shown to be the most thermodynamically stable of the palladium silicides, and therefore the molybdenum silicides interacted only with this [1034]. The interaction of aluminium with Pd/W alloys deposited on silicon, or on silica, has been studied using Auger-electron spectroscopy, Rutherford back-scattering spectrometry, X-ray diffraction and forward current-voltage measurement of the Schottky-barrier height. For the bilayers on single crystal silicon, annealing shows extraction of palladium to both sides of the alloy, forming $PdSi_2$ at the silicon side and Al-Pd intermetallic compounds at the aluminium side. In the bilayer films on silica, the palladium reacts with the aluminium to give aluminium rich Al-Pd intermetallic compounds [1035]. It has been suggested that the reaction of silicon with alloys may be regarded as a phase transformation of the alloy under the influence of a reactive substrate. At high temperatures an Er-Pt alloy reacted with silicon to give ErPt, $ErSi_2$ and PtSi [1036].

The magnetic properties of polycrystalline $Pd_{1.5}Mn_{0.5}Si$, $Pd_{1.5}Mn_{0.5}Ge$ and PdMnGe have been investigated using magnetometric measurements. All showed ferromagnetic properties at low temperature. The values obtained for the magnetic moment in the saturated state were discussed in terms of Pauling's valence concept [1037].

There have been numerous studies of the mixed valence compound $EuPd_2Si_2$ and related species. The mean valence of europium was determined by L_{III}-edge X-ray absorption and ^{151}Eu Mössbauer isomer shift measurements in the temperature range 1.7-300 K. $EuPd_2Si_2$ exhibits the steepest temperature induced valence transition among europium based mixed valence systems [1038]. A quantative correlation of these two valence sensitive spectroscopies was made over the range of the thermally induced valence change [1039]. In $EuPd_2Si_2$, $EuPd_6B_4$ and $Eu_2Ni_2P_2$ the linewidth of the ^{151}Eu Mössbauer resonance attains a maximum value when the isomer shift varies most strongly with temperature [1040]. Intra-configurational spin-orbit split (J) multiplet excitations were observed in $EuPd_2Si_2$ and $CePd_3$. The temperature dependence of the interconfigurational excitation energy and the fluctuation temperature were obtained from Raman peak positions and widths respectively. The spectroscopic data provide the first direct proof of the ionic interconfigurational fluctuation model [1041].

Mössbauer spectra and magnetisation have been measured for $EuPd_{2-x-y}Rh_xRu_ySi_{2-z}Ge_z$ ($0 \leqslant x + y \leqslant 2$; $0 \leqslant z \leqslant 2$) in the temperature range 4.1-295 K. In $EuPd_{2-x}Rh_xSi_2$, the valence electron transition temperature, T_V, decreased as x increased. However, in $EuPd_{2-y}Ru_ySi_2$, the europium ions were predominently divalent, and T_V was low. Only for $y \geqslant 1.5$ was the Eu trivalent component again dominant [1042]. L_3 XANES and EXAFS studies of M in MPd_2Si_2 (M = Sm, Gd or Tm), prepared by arc melting, have been reported. The results indicated that the d states in MPd_2Si_2 are rather localised, and EXAFS features are governed by the nearest neighbours of the absorbing M ion [1043]. Other L_3 XANES studies of R in RPd_2X_2 (R = Nd, Sm, Gd, Tm or Yb; X = Si or Ge) have also been reported [1044]. Electrical field gradient measurement on ^{170}Yb in $YbPd_2Si_2$ were interpreted within the interconfigurational model, and provide clear evidence of the persistence of crystal field effects in the intermediate valence state [1045].

The structures of $CePt_2Si_2$ and $CePt_2Si_2$ were determined by X-ray diffraction studies on single crystals. Both crystallise in the tetragonal $CaBe_2Ge_2$ structure, space group *P4/nmm*. The cerium was trivalent at room temperature but seems to approach a non-magnetic ground state at low temperatures. No superconducting transition was detected down to 20 mK [1046]. The compounds MPt_2Si_2 (M = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Tm, Yb, Lu, U or Th) are isotypic, and crystallise with the primitive tetragonal $CePt_2Si_2$ type structures. Their magnetic properties were investigated. At temperatures below 40 K, antiferromagentic ordering was found for the compounds of Gd, Tb or U. For the Dy, Ho, Er and Tm compounds the onset of ferromagnetism occurred below 4 K [1047]. In another study, 27 ternary intermetallic compounds with either $ThCr_2Si_2$ or $CaBe_2Ge_2$ type structures were investigated for their superconducting properties. Superconductivity was consistently favoured for the primitive tetragonal $CaBe_2Ge_2$-type structures, rather than the $ThCr_2Si_2$ type. None of the latter showed superconductivity avove 1.1 K. $ThPt_2Si_2$, $ThPt_2Ge_2$ and $LaPt_2Si_2$ were among the compounds with the $CaBe_2Ge_2$ type structure studied. Examples of $ThCr_2Si_2$ type structures investigated included YPd_2Si_2, $ThPd_2Si_2$ and $ThPd_2Ge_2$ [1048].

1.11.4.2 Compunds with other Main Group Metals

The electronic structure and reactivity of PdLi have been reported, and non-empirical pseudopotential CI calculations were performed on it [1049]. $LiPt_7$ was prepared by the reaction of $Li_2[CO_3]$ with platinum metal under a hydrogen atmosphere at 1260 K. It adopts a cubic space group, $Fm\bar{3}m$ [1050].

The relaxation times for electron scattering and concentration dependence of extremal cross-sectional areas, A, of the Fermi surface of dilute PdB_x ($0 < x < 0.002$) have been established [1051]. At 900 °C, the high platinum single phase $PtAl_2$ was more resistant to corrosion under acidic fluxing conditions than the low platinum two phase $PtAl_2$-NiAl system [1052]. X-ray absorption spectra (XAS) were obtained with synchrotron radiation at the Pd $L_{2,3}$ edges of Pd-Al alloys, and Bremsstrahlung Isochromat Spectra (BIS) at 1486.6 eV of these alloys and of Pd_2Si. The XAS and BIS results were similar for the alloys, but BIS resilts for Pd_2Si showed differences attributed to more localised bonds [1053].

A rapid increase of the yield stress with increasing temperature, often observed in $L1_2$ ordered alloys, is commonly called "anomalous flow behaviour". It is believed to be due to thermally activated transformations of the core of

1/2<110> screw dislocations from a glissile form to a sessile form, at high temperatures. It has now been shown that another classs of $L1_2$ alloys exists, in which these two forms of screw dislocation are not available, These are the alloys in which the APB on {111} planes is not stable, and the atomistic studies of screw dislocations in such alloys show that their cores are always sessile. The yield stress of these alloys increases as the temperature decreases. The theory was used to predict the behaviour of Pt_3Al, giving good agreement with experimental observations [1054].

Single crystals of $PdSn_4$ and $PtSn_4$ were grown by fast cooling of a molten mixture of the pure metals, containing an excess of tin. In contrast to $AuSn_4$, no superstructure was observed [1055]. Room temperature elastic constants of tetragonal $PdPb_2$ were measured, and the Debye temperature derived. This was compared with the value obtained from low temperature electrical resistivity measurements [1056].

PtFeSn is hexagonal, with space group $P6_3/mmc$. The crystal structure is based on the NiAs unit cell, the iron atoms being equally distributed over the 2*a* and 2*c* sites. The same structure was found for PtXSn, X = Ni, Co or Cr. PtFeSn has a saturation moment at 4.2 K of 2.21/formula unit. The Curie temperature is comparatively high (T_C = 1010 K) and only slightly below that of natural iron. Mössbauer data showed that only 56 % of the iron atoms were magnetic; the magnetic moment of these was ≈ 2.7 μB/Fe, and a small magnetic moment of 0.7 μB/Pt was also ascribed to platinum [1057].

1.11.4.3 Compounds with Transition Metals

The heats of formation of A_5BH_X, A_2BH_X, ABH_X, AB_2H_X and AB_5H_X in which, amongst others A = Pd, and B is a transition metal, were calculated by a semi-empirical model based on the electronic structure of the host alloy. Only 44 out of the 1380 systems tested were predicted to react with hydrogen with ΔH_{form} between -12 and -25 kJ mol^{-1}, and hence to have potential for hydrogen storage. Among these were Pd_2Sc, $PtHf_2$, PdTa and PdNb [1058].

The phases Ti_3Pt, TiPt and $TiPt_3$ were detected in contacts of platinum and titanium across a weld zone [1059]. An energetically favourable bonding type was found for Ti_3Pt, TiPt, Ti_3Pt_5 and $TiPt_{2.9}$, by using a binding analysis based on the plural correlation model [1060]. Analysis of X-ray diffraction studies on a 70 % palladium, 30 % titanium alloy indicated that the main phase present was PdTi, with small amounts of Pd_5Ti_3. At a 50:50 composition, $PdTi_2$ was the main component, together with some PdTi. The amounts of the minor phases depend on the heat treatment of the sample [1061].

The thermal stability of α-Zr_2Pd was studied. It undergoes two-step crystallisation, with the initial formation of a disordered bcc phase, followed by formation of a tetragonal Zr_2Pd phase with a c11b structure [1062]. The effect of hydrogen on its electronic properties was investigated. The electronic density of states decreases steadily with increasing hydrogen content, and T_C is constant for $H:Zr > 0.5$. Results of mass density, electrical resistivity, thermoelectric power, T_C, and upper critical field measurements could all be interpreted in terms of two different binding states for hydrogen at low and high hydrogen concentrations [1063]. The hydrogenation and isomerisation of 1-hexene over Zr_2PdH, has been described [1064].

Experiments conducted with bilayers of elements chosen to maximise chemical, and minimise physical, differences, demonstrated the importance of chemistry in determining the amount of interaction which results from ion mixing experiments. Thus, ion bombardment of Pd/Hf bilayers gave Pd_3Hf, and the existence of such compounds was not detected in other bilayers of similar elements [1065].

New superconducting ternary transition metal compounds with fcc $E9_3$ structure type phases have been reported. Details of structural studies were also reported for Ti_4Pt_2O, $Zr_{4.2}Pt_{1.8}O_{0.9}$, $Zr_{4.2}Pd_{1.8}N_{0.7}$ and $Zr_{4.3}Pt_{1.7}N_{0.9}$, and T_C values ranged from 1.34 to 2.51 K [1066].

The electric quadrupole interaction of ^{181}Ta impurity nuclei in Hf_2Pd was investigated by a time differential perturbed angular correlation experiment at 77, 295, 873 and 1023 K. The temperature dependence of the quadrupole frequency was described by a $T^{3/2}$ law [1067].

Local spin density functional calculations were performed for VPd_3 and VPt_3. These are non-magnetic in the $TiAl_3$ structure, but ferromagnetic in the Cu_3Au structure, which has a calculated total energy/fomula unit 0.25 eV higher than the $TiAl_3$ structure. The calculations were compared with experimental results [1068]. The electron configuration and X-ray photoemission spectra of VPd_3 with the Cu_3Au-type structure were calculated using the self-consistent LMTO method. The Stoner parameter of 1.04 may indicate that this material is a weak itinerant ferromagnet [1069]. Pt_3V quenched from above the ordering temperature shows short range ordering which can most conveniently be observed along a cubic zone pattern as lines of diffuse intensity along $h = 2n + 1$ and $k = 2m + 1$. These correspond to the existence of tetrahedra of nearest neighbours with a 3:1 composition in the $L1_2$ structure as well as in the DO_{22} structure [1070].

The synthesis of Pd_xCr_y catalysts was studied by XPS and EXAFS. The test reaction with ^{13}C labelled hexanes shows the influence of metal loading, temperature, and time of treatment in air [1071].

Inelastic scattering of polarised neutrons was used to study the nature of the magnetic response in the vicinity of the Curie temperature (T_C = 493 K) for the imtermetallic ferromagnet Pt_3Mn. The measurements were taken on the HB-1 triple axis spectrometer at ORNL, in a field of 10 koe, applied along the scattering vector Q. For $0.9\ T_C < T < 1.2\ T_C$ undamped magnons were observed, not only with the conventional (+) spin-wave polarisation, but also with the "forbidden" (-) polarisation, with an intensity difference I(+)-I(-) approximately proportional to the magnetisation. Both observations are in accord with the slowly fluctuating spin density theory of itinerant ferromagnetism [1072].

The electronic structures of Pd_3Mn and Pd_3Mo in the paramagnetic phase were calculated using the method of orthogonalised LCAOs. The Stoner criterion was applied to predict magnetic ordering in these compounds. The magnetic ordering predicted for Pd_3Mn was in agreement with the observed antiferromagnetic phase transition in this compound. The Stoner criterion was not satisfied for Pd_3Mo, and no experimental data are available for the ordered phase [1073]. Paramagnetic scattering from the localised metallic ferromagnet Pd_2MnSn was characterised for the entire range of energy and momentum space for a temperature range between T_C (193 K) and room temperature. The scattering function could be well described by a simple double Lorentzian [1074].

The structures of Pd_3Fe and PdFe were determined after deformation to 75-90 %, and annealing at 200-1000 ^{o}C. The as-deformed specimens showed a disordered structure, but long range order was present in Pd_3Fe after annealing at 400-500 ^{o}C [1075]. Magnetisation and ^{57}Fe Mössbauer data were recorded for $Pd_3FeH_{0.7}$; the strong ferromagnetic coupling noted for Pd_3Fe was altered in the hydride. The magnetic moment was reduced, and there was a 46 % decrease in the magnetic transition temperature. Anisotropic antiferromagnetic coupling dominates in the hydride [1076]. The structures of $Y(Pd,Fe)_2$ and $Y_2(Pd,Fe)_{17}$ were studied in amorphous and crystalline states by X-ray diffractometry and Mössbauer spectroscopy. Palladium appears to stabilise a disordered distribution of iron [1077].

The formation of an amorphous structure in equiatomic Co-Pd films was considered. The microcrystalline structure containing bcc and fcc phases was transformed into a new fcc phase by either the conventional mechanism of nucleation and growth, or favourable nucleation in the residual glassy phase. On heating to a temperature above 470 ^{o}C the new fcc phase was transformed into a face-centred tetragonal phase [1078]. A photoemission technique was used to study the surface composition of PtPd, PtRu and PtIr alloys over a wide range of bulk compositions. The alloys were submitted to *in situ* oxygen exposure at 1 atm pressure and 200-600 ^{o}C. The platinum based alloys were oxidised if the impurity surface concentration was >13-20 %, and PtO, α-PtO_2

and β-PtO_2 were detected. In the low impurity range neither component was oxidised [1079].

^{60}Co irradiation of $Cu[SO_4]/PdCl_2$/2-propanol/PVA gave a dark green colloid of stoicheiometry Cu_3Pd. The diffraction patters obtained for the solid implied some ordering [1080].

1.11.4.4 Compounds with Lanthanides

Based on a new method of chemical bond parameter computerised pattern recognition, a list of unknown intermetallic compounds was presented. It was predicted that $LaPd_5$ would have the $CaCu_5$ structure [1081]. By using a spectrum subtraction method it was possible to show directly the $4f^{n}\to 4f^{n+1}$ shakedown satellite near the L_{III} edge in $LaPd_3$, $PrPd_3$ and $NdPd_3$. Such shakedown effects are sufficiently small that they may be ignored in (mixed) valence determinations based on the L_{III} method [1082]. A joint analysis of the palladium and rare earth (R) L_{III} XANES of RPd_3 (R = La, Ce, Pr, Nd or Sm) intermetallic compounds made it possible to discriminate experimentally between the interactive hybridisation of 4f↔(5d,6s) orbitals, and the interactive mixing of the R 4f orbitals with the palladium 4d orbitals [1083]. Magnetisation and susceptibility were measured as a function of magnetic field and temperature for R_7Pt_3 (R = La, Ce, Pr or Gd), R_2Pt (R = Gd, Tb, Dy, Er or Ho) and R_5Pt_3 (R = Gd, Tb, Dy or Ho). The magnetic properties were due almost entirely to localised f electrons. The inability of the Runderman-Kille-Kasuya-Yoshida theory to account for the paramagnetic Curie and magnetic ordering temperatures was attributed to magnetocrystalline anisotropy [1084].

Many papers concerning the properties of $CePd_3$ continue to be published. The magnetic susceptibility of some cerium intermetallic compounds including $CePd_3$ and $CePt_2$ was measured at temperatures up to 1200 K. Fluctuation temperatures were calculated using the susceptibility data and the valence derived from L_{III} X-ray absorption measurements [1085]. A neutron scattering investigation of the high energy magnetic response in α-Ce and $CePd_3$ has been reported. For $CePd_3$ the magnetic response has a peak at 60 meV, which is attributed to the energy difference between magnetic and non-magnetic configurations [1086]. Polarised neutron scattering with polarisation analysis on α-Ce and $CePd_3$ has also been reported. In $CePd_3$ the magnetic response is essentially inelastic, and reveals a characteristic excitation at 65 meV. The data were discussed in terms of the theories of intermediate valence [1087].

The electrical resistivity of $CePd_3$ was measured at temperatures from 1.5-300 K under hydrostatic pressures greater than 20 kbar. The temperature for maximum resistivity increased with pressure [1088]. Anomalies in the temperature and pressure dependence of the electrical resistivity of $CePd_3$ have been discussed. The effects were said to demonstrate the existence of an energy scale T_{coh} (related to the single-ion spin fluctuation scale T_{sf} by a factor of $1/(2J + 1)$), over which coherence develops among spin fluctuations on different sites [1089].

Point contact measurements on $CePd_3$ have been reported. Point contact theory applicable to valence fluctuating compounds is still lacking, but the results were discussed in terms of bulk resistivity and thermopower *via* the classical heating model [1090]. This type of spectroscopy was also used as a tool to obtain information on anomalies in the electron density of states near E_F, and on the quasiparticle density of states. A peak at E_F in the electronic density of states was found with 14 meV width. In related measurements on $ThPd_3$ no anomalies were observed in the electron density of states, but the phonon density of states was obtained [1091].

The far IR absorptivity of $CePd_3$ was measured at temperatures between 4.2 and 300 K, over a photon energy range an order of magnitude larger than previously reported. Together with earlier data, these results map out the entire region of the low temperature $CePd_3$ absortivity, which is larger and extends to larger energies than extrapolation from earlier cavity measurements would suggest. The anomaly is too large to be compatible with simple conduction electron scattering off a resonant level near the Fermi energy [1092].

The thermal expansion and specific heat of $CePd_3$ and YbInPd have been measured in the temperature range 1.5-400 K. Both properties were strongly influenced by the mixing of the two integral valence states [1093].

The Hall coefficients for $CePd_3$ and $Ce(Pd_{0.88}Ag_{0.12})_3$ have been measured from 4.2-300 K [1094]. It has been proposed that the large anomalous Hall constants of mixed-valence and Kondo-lattice systems can be understood in terms of a simple resonant-level Fermi-liquid model. Splitting of a narrow, orbitally unquenched, spin-orbit split, f-resonance in a magnetic field leads to a strong skew scattering of band electrons. Both the anomalous signs and the strong temperature dependence of the Hall mobilities in $CePd_3$ were explained in terms of this theory [1095].

An extensive investigation of the XANES of palladium 3d, 2p and 2s levels, and of the rare earth 4p, 2p and 2s core levels was carried out at the Frascati synchrotron radiation facility, with the X-ray and the soft X-rays grasshopper beam lines. In $CePd_3$ the 4f-5d hybridisation is the dominant effect determining valence fluctuations [1096].

Photoemission studies revealed two peaks in the 4f spectral weight of cerium based systems, and in their Pr and Nd homologues. The results suggested a new microscopic description for the mixed valent state in $CePd_3$ [1097]. The lineshape of the peak near E_F has been analysed [1098].

In $CePd_3$, the intraionic $J = 5/2 \rightarrow J = 7/2$ excitation of the $4f^1$ (^2F_J) configuration, and the interconfigurational $4f^1 \rightarrow 4f^0 + e^-$ excitation energy, were observed near 256 and 325 meV respectively, by means of electronic Raman scattering [1099]. An amorphous film analogue of $CePd_3$ was prepared by sputter deposition onto cryogenic substrates using intermetallic targets. L_{III} measurements on the new film were reported. The valence was determined as 3.29, close to the saturated upper valence for cerium, and the film was chemically more dense than the bulk crystalline material. The film crystallised slowly over several months, but seemed to retain the near saturated cerium valence [1100].

A cumulant expansion theory starting from the atomic limit has been presented for intermediate valence compounds. The IR conductivity calculated was in good agreement with the experimental results for $CePd_3$ [1101]. Valence fluctuation and the Kondo effect have been discussed for the non-cubic compounds of the Ce-Pt systems [1102]. Some debate has arisen concerning the two energy scales in $CePd_3$ [1103,1104].

The crystal structure of the $CePd_5$ phase has been analysed by X-ray diffraction and electron micrsocopy. Two phases were observed, one stable at high and one at low temperatures. The low temperature phase was identified as a kind of long period antiphase structure with fcc fundamental cells [1105].

The EPR spectra of Gd^{3+} and Mn^{2+} impurities in $CePd_3$ have been recorded. The spectra can be explained within the phenomenological models of hybridisation and covalent magnetism [1106]. The first example of a resolved hyperfine structure of the manganese EPR spectrum was reported for 150 ppm manganese in $CePd_3$. The linewidth of each of the six hyperfine components increased in a linear manner with temperature ($1.5 < T < 4$ K) [1107].

CF parameters of diluted rare earth ions in $CePd_3$ were derived from inelastic neutron scattering spectra [1108]. The specific heat, susceptibility, and resistivity of thorium diluted $CePd_3$ was measured. As expected, dilution by thorium lowered the f level with respect to the Fermi level, driving the cerium to the +3 state. This more than offset any positive lattice pressure effects that are present when the thorium compound has a smaller lattice constant than its cerium counterpart [1109].

Bulk susceptibility and ^{11}B NMR spectroscopic data for $CePd_3B_x$ have been analysed. Cerium becomes trivalent for $x = 3$ [1110]. In a survey of rare earth/transition metal ternary borides it was noted that compounds were typically found at a few unique compositions, including RT_3B_2, RT_4B_4, RT_2B_2, R_2TB_6 or RTB_4 [1111].

Mixed valence and Kondo lattice systems exhibit large anomalous Hall coefficients with a striking change in sign at low temperatures in several systems. A study of the Hall effect for $Ce_{1-x}Y_xPd_3$ was carried out. In this compound the substitution of small amounts of yttrium for cerium prevents the development of coherence at low temperature. The Hall coefficient does not change sign at low temperature, and the data can be well understood in terms of the one impurity model of Ramakrishnan, Coleman and Anderson. This suggests that the change in sign of the Hall coefficient in $CePd_3$ is an effect of coherence [1112]. The results of the alloying behaviour of the low temperature constant susceptibility, χ_0, and the linear coefficient, γ, of the specific heat has been reported for $Ce_{1-x}Y_xPd_3$. The correlation between χ_0 and γ, known to exist for intervalence compounds, was shown to apply to this series, implying a $2J + 1 = 6$ ground state degeneracy [1113].

Specific heat data for the system $Ce(Rh_{1-y}Pt_y)_2$ system support earlier resistivity and susceptibility measurements, which were interpreted in terms of a mixed valence regime for $y < 0.5$ [1114]. There have been reported magnetic measurements under hydrostatic pressures up to 6 kbar on orthorhombic $CeNi_xPt_{1-x}$ dense Kondo ferromagnets with $x = 0.0$, 0.5 or 0.8. For all the compounds there is a decrease in the cerium magnetic moment. The reduction is weak for CePt, but about 35 % for $x = 0.8$. The pressure effect on the Curie temperature is similar to an increase in nickel content. The results confirm the Kondo lattice model, which predicts that T_C passes through a maximum, but the Kondo effect always increases [1115]. The increase in the 4f-conduction electron hybridisation, as determined from deep-core photoemission studies, is compared with the increase in the mixed valence across the archetypal continuously variable valence system $Ce(Pd_{1-x}T_x)$ (T = Ag or Rh). No anomaly was observed in the hybridisation near $x_{Rh} = 0.2$, where the mixed valence abruptly saturates. There was, however, a linear relationship between f-d hybridisation and the volume of the unit cell. The data were consistent with a recent model which explains the valence saturation in terms of thermodynamics [1116].

Magnetisation measurements on single crystal $PrPd_3$ in the temperature range 2-100 K, and for magnetic fields up to 8 T, have been discussed. Specific heat measurements for polycrystalline material in magnetic fields up to 7.5 T, in the temperature range 4-16 K, were also reported. The experimental data were interpreted in terms of a Crystalline Electric Field (CEF), and were compared with existing CEF parameters [1117].

$EuPd_3$ has been studied using X-ray excited photoelectron spectroscopy and

BIS. Due to the very small contribution from empty palladium d states, BIS gives a clearer view of the Eu 4f state than XPS valence electron spectra. In the BIS, a contribution from a divalent surface layer as well as core level spectra were observed. It was concluded that there is a substantial surface disproportionation of the compounds, with an increase in the europium concentration at the surface [1118].

The alloying of boron with RPd_3 gives RPd_3B_x ($0 < x < 1$). RPd_3 crystallises in the cubic $AuCu_3$ type structure, and addition of boron does not change the structure, but does expand the lattice, suggesting that boron occupies the vacant body centred position. Some susceptibility measurements of the compounds were reported, and it was noted that $GdPd_3$ orders antiferromagnetically with T_N = 6 K, but $GdPd_3B$ does not order magnetically above 4.2 K [1119]. The changes in magnetic properties and ^{155}Gd hyperfine field parameters was studied in several GdM compounds (M = Rh, Pd, Cu, Ag or Au) when these materials were charged with hydrogen gas. The changes comprise increases in the asymptotic Curie temperature as high as 107 K, and increases in the ^{155}Gd hyperfine fields as high as 35 T [1120]. There has been a report of volume effects of the Mössbauer isomer shift in intermetallic compounds of gadolinium, including GdM_3, GdM_2 (M = Pd or Pt), GdPd, Gd_3Pt, Gd_2Pt,- Gd_3Pt_4, and $GdPt_5$ [1121].

Among the Heusler alloys, Pd_2RSn, (R = Tb-Lu, Sc or Y) the compunds of Yb, Tm, Lu, Sc and Y were superconducting. Structural studies showed that none of the superconducting alloys showed a structural transformation. Structural transformations were observed for the derivatives of Tb and Dy. The transformation temperature was decreased by 50 K on going from stoicheiometric Pd_2TbSn to $Pd_2Tb_{0.85}Sn$, and the transformation was completely supressed in $Pd_2Dy_{0.95}Sn$ [1122]. Magnetic susceptibilty and ^{119}Sn Mössbauer studies on this series were also reported. The magnetic susceptibility of Pd_2TmSn and Pd_2YbSn deviates from Curie-Weiss behaviour at low temperatures, indicating that crystalline electric field effects are appreciable. The Tb and Dy compounds order antiferromagnetically, whilst the Er and Ho derivatives are paramagnets down to 1.4 K [1123]. The compounds RGa_2Pd (R = Y, Tb, Dy, Ho, Er, Tm, Yb or Lu) have been prepared by direct interaction of the elements. The structures were shown to be isotypic, and cell parameters are reported [1124].

A revised phase diagram for Pd/Y has been discussed and related to electronic properties. None of the ordered compounds showed magnetic ordering [1125].

By using neutron diffraction, the magnetic structure of the Er_2Pt antiferromagnet (T_N = 9 K) was investigated [1126].

Specific heat, thermal expansion and electrical resistivity measurements were used to investigate YbPd. It undergoes four phase transitions at 0.5, 1.9, 105 and 125 K. Magnetic susceptibilty measurements show that the transition at 0.5 K is magnetic. The quasielastic magnetic linewidth is, as usual for mixed valence compounds, large, but decreases with temperature, and is everywhere less than k_BT. The magnetic ordering of YbPd occurs at a fractional Yb valence of $\nu = 2.8$ (measured by L_{III} absorption), near the configurational crossover of $4f^{13}$ and $4f^{14}$ [1127]. Resistivity, specific heat, and magnetic susceptibility measurements were used to investigate the magnetic ordering of Yb_3Pd_4. A magnetic phase transition at 3 K was noted [1128].

Magnetic and superconducting properties of the Heusler alloy, Pd_2YbSn, were investigated by heat capacity, resistivity, and magnetic susceptibility measurements. It undergoes a superconducting transition at 2.46 K and a magnetic transition at 0.23 K. The absence of reentrant behaviour implies that the magnetically ordered state is coexistent with the superconductivity [1129]. The thermodynamic and physical properties (crystal structure, thermal expansion, magnetic properties and heat contents) of YbPdIn and MPdIn (M = Ca, Sr, Er or Eu) were measured in the temperature range 100-1000 K, to explain the anomalous behaviour of YbPdIn. The results led to the detection of three previously unknown compounds (Ca, Sr or Eu)PdIn, which crystallise in the TiNiSi structure. The anomalous behaviour of YbPdIn depends on the instability of the valence of Yb, which shows an amost regular change from divalency to trivalency with increasing temperature. All the measurements converged to a room temperature value of the valence of 2.1-2.2, at variance with earlier data from X-ray absorption spectroscopy. The valence increased with temperature, reaching 2.55 at 1000 K. From the heat capacity measurements, the energy required was 0.11 eV, in good agreement with the results from other mixed valence compounds [1130].

1.11.4.5 Compounds with Actinides

Phase equilibria and structures were studied in the palladium rich region of the Pd-Th system. Incongruent-type peritectic reactions occurred at 1145 ^{o}C to form the α-phase, at 1215 ^{o}C to form the δ-phase (probably as Th_3Pd_{13}) and at 1340 ^{o}C to give the ϵ-phase [1131].

Spin fluctuations and superconductivity have been reviewed in UPt_3 [1132,1133]. Superconductivity, spin fluctuation and magnetic order under high pressure, were reviewed for this material, and for a series of (nearly) ferromagnetic compounds, UM_2, including UPt_2 [1134]. UPt_3 was amongst the heavy fermion uranium intermetallic compounds considered in a review of their physical properties, including crystal structure, electrical resistance, superconductivity, magnetic moments and heat capacity [1135].

It has been shown that the spin fluctuation temperature for UPt_3 increases with pressure [1136]. The strength of the spin fluctuation spectrum has been found, using neutron scattering, to decrease dramatically with temperature on approach to the superconducting transition. The spin fluctuations are antiferromagnetic, and their thermally activated intensity is consistent with the existence of a gap-like structure in the normal phase. This seems to indicated that spin fluctuations take part in the formation of the superconducting state [1137].

The thermal expansion and elastic constants of single crystalline UPt_3 have been measured [1138]. Thermal expansion of the polycrystalline compounds UPt_2, UPt_3, and UPt_5 was measured in the temperature range 1.4-80 K. The thermal expansion of UPt_3 reveals a large anomalous contribution below 50 K. This appears as a low temperature upturn in a plot of α/T *versus* T^2, and is associated with spin fluctuation. A similar, but less pronounced upturn was noted for UPt_2 and UPt_5 [1139].

Specific heat, resistivity, thermal conductivity and thermoelectric power measurements have been reported for the normal and for the superconducting regimes of UPt_3 [1140]. UPt_3 shows a strongly enhanced linear contribution to the specific heat. A self-consistent, fully relativistic, band structure calculation for this material within the local density approximation was described, and the implications of the results for the properties of the material discussed [1141]. Heat capacity measurements in an 11 T magnetic field showed that, above approximately 7 K, UPt_3 behaves like the spin fluctuation compounds UAl_2 and $TbBe_2$ [1142]. Specific heat, electrical resistivity and ac susceptibilty measurements on Czochralski-grown single crystalline UPt_3 revealed the transition into the superconducting states below 0.48 K. For the temperature dependence of the upper critical field, dBc^2/dT, a value of -4.4 T/K was found. A numerical analysis of the normal-state specific heat data below 20 K results in a large $T^3\ln(T/T^*)$ contribution, indicating pronounced spin fluctuation effects [1143].

Measurements have been made of the ultrasound attenuation and sound velocity as a function of temperature, through the superconducting transition temperature of UPt_3. The attenuation varied as T^2 at low temperatures, and was inconsistent with the indentification of UPt_3 as a singlet superconductor. Below T_C the sound velocity varies as T^3, and above T_C as T^2, implying that UPt_3 is an anisotropic (triplet) superconductor in a polar-like state [1144]. From the ultrasound attenuation below T_C, a quasiparticle density of states linear in energy is deduced, which is also interpreted in these terms. The attenuation in the normal state gives the electron-phonon interaction strength, and the product of the deformation potential times the effective mass is found to be the same as for ordinary "light" fermion systems [1145].

Magnetic and resistivity measurements were performed on polycrystalline UPt_3 at temperatures well below its superconducting transition temperature T_C. T_C varied linearly with H over a wide range of magnetic fields [1146]. Magnetic susceptibily measurements were made in zero and finite magnetic fields [1147]. The differential susceptibilities of UPt_3 were measured at low temperatures as a function of magnetic field up to 40 T. A systematic relationship was observed between the signs of the second derivative with respect to field and temperature. Low temperature anomalies indicated spin fluctuation phenomena [1148]. The effect was determined of hydrostatic pressure on the susceptibility, the T^2 dependence of the spin-fluctuation resistivity, and on superconductivity in UPt_3. T_C and the initial slope of the upper critical field decreased under pressure [1149]. Experiments on the normal phase of UPt_3 showed a large positive magnetoresistivity, almost temperature independent and linear in field, and a positive thermoelectric power, which is not linear in temparature as $T \to 0$ K. The superconducting phase is characterised by a high thermal conductivity, with a strong T^2 term, by a coherence length smaller than the mean free path, and by lower and upper critical fields [1150].

Photoemission and Bremsstrahlung Isochromat Spectroscopic data have been reported for various 5f electron systems, including UPt_3 [1151]. The 5f spectral weights in the heavy fermion materials, UAl_2 and UPt_3, were measured by electron spectrsocopy, and were compared with those from density-functional calculations. The calculated one-electron 5f widths are too large to account for the enhanced values of the specific heat coefficient, γ, and too small to account for the measured widths. In the Anderson Hamiltonian both discrepancies arise from the 5f Coulomb interaction [1152].

An attempt has been made to determine the electronic structure of UBe_{13} and UPt_3. The UPt_3 electronic system was determined using the semi-relativistic LMTO method, and the electronic structure of both systems was determied self-consistently for the observed crystal structure at zero pressure. The electronic structure in both cases effectively separated into uranium and non-uranium bands. The inter-uranium separations are large, and the system does not exhibit local moment magnetism; with these large separations it is unusual to observe superconductivity [1153].

No Josephson effect was found between UPt_3 and Al, Nb or UPt_3 as counterelectrodes, in accord with a possible anisotropic ($L \geqslant 1$, $S = 0$ or 1) pairing in UPt_3. For this material, the thermal conductivity in the superconducting state approaches an asymptotic $K_S = \alpha T^2$ law as T approaches zero, with $\alpha = 32$ mWcm^{-1}K^3. The thermopower above T_C shows a temperature dependence similar to that of the spin-fluctuation system UAl_2 [1154].

Recent results on the magnetic and electric properties of UPt under high pressure, and results of neutron diffraction and neutron depolarisation studies, have been presented. The experiments suggest that there are two different magnetic phases in UPt, with ordering temperatures of 19 and 27 K respectively. Internal stresses and oxide content determine the amount of each of these phases in a particular sample. The magnetic phase with the ordering temperature of 27 K exhibits a ferro to antiferromagnetic transition at 4 kbar. This antiferromagnetic phase is characterised at 4.2 K by a metamagnetic transition at a field of 3 T [1155].

Measurements of the low temperature resistivity, and specific heat, of $U(Pt_{0.8}Pd_{0.2})_3$ have been reported. It was concluded that spin fluctuation was totally supressed, suggesting that spin fluctuation in UPt_3 depends critically on the hybridisation of the uranium electrons [1156]. Measurements of the temperature dependent electrical resistivity, and the superconducting transition temperature of the "nearly heavy fermion" compound, U_2PtC_2, under hydrostatic pressure, indicated that the superconductivity arises within a strongly pressure dependent, highly correlated electron system [1157]. The 5f electronic structure of UPt_4Ir was investigated by XPES and BIS. The hybridisation between the 5f and ligand metal d states is large, giving rise to configuration fluctuation [1158].

The thermodynamic properties and sublimation behaviour have been investigated for a range of Pu-Pt compounds ($PuPt_5$, $PuPt_4$, $PuPt_3$, and $PuPt_2$). Vapour pressure was measured by Knudsen effusion using target collection and mass spectrometry. Sublimation gave mainly plutonium gas [1159].

Polonium vapour was noticeably absorbed by palladium at 340-350 ^{o}C to give the intermetallic compounds PdPo, Pd_2Po and Pd_3Po. These dissociate with the separation of elememtary polonium, and pressures and heats of dissociation were measured [1160].

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