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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 Volume 99, issues 25 and 26 and Volumes 100 and 101, as well as the 1984 issues of the major English language inorganic chemistry journals. Thus, although most of the papers covered were published in 1984, many from 1983 are also included, together with earlier work slow to reach Chemical Abstracts.

Once again the number of references has increased, the areas of greatest expansion being catalytic reactions, the chemistry of the metal silicides and biomedical applications of platinum complexes. The section on cancer chemotherapy has been considerably expanded.

General reviews published this year have included an account of all the platinum group metals by Taylor and Wallbridge [1], a discussion of complexes of paramagnetic ligands [2], and a review of the industrial toxicology of the platinum group metals [3].

1.1 PALLADIUM(VI) AND PLATINUM(VI)

The ease of preparation of the species $[MF_6]$, including $[PtF_6]$, has been studied in terms of correlation between heats of vapourisation and fusion and their boiling and melting points [4]. $[PtF_6]$ has been used as an oxidative fluorinator towards NF_3 in the presence of fluorine (reaction (1)) and ClF_5 (reaction (2)). The mechanism proposed involved electron transfer [5]. Deposits of platinum metal catalysts have been formed on alumina or quartz from $[PtF_6]$ or $[Pt(PF_3)_4]$ [6]. Whilst it has been claimed that $[PtCl_6]$ was used as a catalyst for polymerisation of 2-propene-1-ol, this unlikely remark seems to arise from the authors' inability to distinguish $[PtCl_6]$ and $H_2[PtCl_6]$, the latter presumably being the catalyst actually used [7].

$$2[NF_3] + F_2 + 2[PtF_6] \xrightarrow{\qquad} 2[NF_4][PtF_6] \qquad (1)$$

$$2[ClF_5] + 2[PtF_6] \xrightarrow{HF,\ 25\ ^\circ C} [ClF_4][PtF_6] + [ClF_6][PtF_6] \qquad (2)$$

The electronic structure of $[PdO_4]^-$ was calculated and the electron affinity of the neutral species estimated [8]. Compounds of radioactive platinum formed in air at 725 ± 25 °C were isolated on a quartz chromothermographic column. PtO_3 was adsorbed at high temperature, as evidenced by mass spectrometric data, and species of the type $[PtO_2(OH)_2]$ and $[PtO_3(OH)]$ were also postulated [9].

1.2 PALLADIUM(V) AND PLATINUM(V)

Two papers have reported calculations of the electronic structures of $[MF_6]^-$ (M = Pd or Pt among others) using the discrete variational X_α method within an extended basis of numerical Hartree-Fock functions [10,11].

1.3 PALLADIUM(IV) AND PLATINUM(IV)

Metal ion chemical shifts in platinum(IV) complexes have been parametrised into metal and ligand contributions. An analysis of the ligand parameters gave a magnetochemical series [12]. Trace quantities of platinum(IV) and platinum(II) have been determined by their catalysis of the periodate oxidation of chlorophyll a and chlorophyll b. The optimum conditions for the chemiluminescence reactions in alkaline media were determined [13]. The use of catalytic polarographic currents in determining trace concentrations of platinum(IV) in the presence of platinum(II) has been reviewed [14].

1.3.1 Complexes with Group 17 donor ligands

Gaseous $[PtF_2]$ and $[PtF_4]$ were generated under equilibrium conditions by admitting gaseous fluorine into a platinum effusion cell, or by addition of solid MnF_3. Kinetic data for the reaction of platinum metal with fluorine and data on flash desorption of fluorine from platinum were accounted for on thermodynamic grounds [15]. Analysis of the enthalpy of reaction (3) yielded standard enthalpies of formation of PdF_2 (−495 kJ mol^{-1}), $K_2[PdF_6]$ (−2040 kJ mol^{-1}), $[PtF_4]$ (−681 kJ mol^{-1}) and $K_2[PtF_6]$ (−2055 kJ mol^{-1}) [16].

$$2K_2[MF_6] \longrightarrow MF_2 + 2KF + F_2 \qquad (3)$$

Data on the toxicology and hygenic rating of $H_2[PtCl_6]$ and $PdCl_2$ have been reviewed [17]. Cellular resistances to the toxic effects of $K_2[PtCl_6]$ and $Pt[SO_4]_2$ were induced in Chinese hamster ovary cells by continuous exposure to the compounds for four and five months respectively. The two cell lines then had resistant phenotypes which were stable for at least fifty-five population doublings. Whilst each resistance was specific, some cross-resistance to other platinum complexes was conferred [18]. $H_2[PtCl_6]$ and $[Pt(NH_3)_2Cl_2]$ were examined for their *in vitro* inhibition of human renal microsomal ATPase. The inhibition by $H_2[PtCl_6]$ was reduced by cysteine, glutathione and ascorbic acid. Since the inhibition of ATPase may be associated with tubular damage, such data are relevant to studies of platinum toxicity [19].

The chlorine K absorption spectra of $M_2[PtCl_6]$ (M = K or $[NH_4]$) have been measured and explained by MO theory. The intense white line at the threshold was ascribed to an electronic transition from a chlorine 1s orbital to the lowest unoccupied antibonding orbital, $e_g\sigma^*$ [20]. The diffuse reflectance spectrum of $K_2[PtCl_6]$ at 90 K has been determined and several new transitions localised [21]. X-ray emission spectroscopic data for the dibenzotetrathiofulvalene ion radical salts with $[PtCl_6]^{2-}$ and $[Pt(CN)_4Br_2]^{2-}$ have led to a determination of their electronic structure [22]. The pressure dependence of ground state tunnel splitting and the energy of transition to the first excited librational state of $[NH_4]^+$, in $[NH_4]_2[PdCl_6]$, was measured by inelastic neutron scattering [23].

The first direct nmr spectroscopic observation of the ^{105}Pd nucleus in solution has been reported for $H_2[PdCl_6]/HCl/Cl_2/H[NO_3]$. The linewidth was 1200 Hz and it is likely that chemical applications of this technique will be limited to very symmetric palladium(IV) complexes with solution concentrations greater than 1 molar [24]. ^{195}Pt nmr spectroscopic measurements on a mixture of $Na_2[PtCl_6]$ and $Na_2[Pt(OH)_6]$ in aqueous base have allowed the observation of signals due to mixed species [25].

An attempt was made to fix the unique force fields of some $\{XY_6\}$ type ions through the parametric representation method of Strey. Species considered included $[PdCl_6]^{2-}$ and $[PtCl_6]^{2-}$ [26]. A new programme for ligand field theory calculations was used for consideration of Re^{4+} ions in $K_2[PtCl_6]$ [27].

An X-ray diffraction study of $K_2[PtCl_6]$ has revealed the electron density distribution in the anion. X-X synthesis showed a peak of 0.5(2) $e\AA^{-3}$ in the <111> direction at 0.5 Å from platinum. This is thought to be the non-bonding 5d electrons in a t_{2g} orbital [28]. The salts $[R_3NH]_2[PtCl_6]$ (R_3N = amphetamine, cocaine or ephedrine) were prepared and characterised by infra-red spectroscopy and X-ray diffraction techniques. The complexes proved useful for amine analysis in forensic chemistry [29]. $[HL]_2[PtCl_6]$ (L = 4-azafluorene or 2,3-benzo-4-azafluorene) were characterised by infra-red and electronic spectroscopy and X-ray phase analysis [30].

Extraction of $H_2[PtCl_6]$ and $PdCl_2$ by N_{1923} was shown to be near quantitative at low acidity [31]. Palladium and platinum could be recovered from these solutions by reduction with $Na[BH_4]$ at pH 4-10 in the presence of $K[MnO_4]$. Manganese dioxide served as the collector for the metals [32]. Platinum was determined by reaction of $[PtCl_6]^{2-}$ with thallium(I) (produced by electrochemical reduction of thallium(III)) with deposition of $Tl_2[PtCl_6]$

on the electrode for gravimetric determination [33]. The process was amenable to mathematical analysis [34].

Impregnation of γ-alumina with $H_2[PtCl_6]$ has been studied by reflectance spectroscopy [35]. In the deposition of a mixture of HCl, $H_2[PtCl_6]$ and $H[ReO_4]$ on γ-alumina all three components competed for the same surface sites and the adsorbate-support interactions were not strong [36]. A high dispersion of platinum + rhenium or platinum + iridium metal catalysts on alumina supports was obtained by drying acidic solutions of $H_2[PtCl_6]$ containing either $H[ReO_4]$ or $H_2[IrCl_6]$ on alumina after adsorbing carbon dioxide on to it. The material was then calcined in air and reduced in hydrogen, resulting in increased activity for carbon monoxide chemisorption [37]. The effect of the conditions of preparation on the valence state of platinum and the catalytic activity of platinum on various supports was studied. $[NH_4]_2[PtCl_6]$ and $[NH_4]_2[PtCl_4]$ on Al_2O_3, SiO_2 or MgO were particularly considered [38].

In the sorption of $[PtCl_6]^{2-}$on hydrated zirconium dioxide static sorption capacity increased with increasing platinum concentration and solution temperature, and decreased with increasing pH [39]. In a study of the chemisorption of $[MCl_6]^{2-}$ on hydrated oxides of cerium and lutetium, in general the metal was said to be adsorbed and the chloride to remain in solution. However, it is claimed that platinum was an exception, with two chloride ions adsorbed per platinum atom [40]. A method for preparation of metal catalysts with controlled properties consists of dissolving the metal complex in an aqueous solution containing a suspension of a photoconductor and a mono or polyfunctional alcohol or thiol, and exposing the mixture to light of wavelength greater than the bandgap. Thus a titania suspension in aqueous ethanol containing $H_2[PtCl_6]$ was irradiated with a mercury lamp to form a Pt-TiO_2 catalyst [41]. XPES of the platinum species deposited implied that from a buffer free deposition both platinum(IV) and platinum(II) were present, whilst in the presence of a buffer platinum(II) predominated. With an excess of buffer platinum(0) was the major species [42].

Electroless platinum was deposited on silica coated doped silicon from an acid bath containing $PtCl_4$, PtF_4 or $H_2[PtCl_6]$ and HF. The coating was sintered at 400-600 °C to form an electrical contact between the platinum coating and the silicon substrate for solar cells, field-effect transitors and other semiconductors [43]. $[PtCl_6]^{2-}$ was used as a scavenger for conduction band electrons in a system in which aqueous dispersions of cadmium sulphide loaded with noble metal oxides evolve oxygen under illumination with visible light [44]. Platinum colloidal solutions of very high stability and low polydispersivity were produced by radiolysis of aqueous solutions of

$H_2[PtCl_6]$ and acrylamide or *N*-methylolacrylamide (NMAM). The catalytic effectiveness of the platinum supported on poly-NMAM for light induced hydrogen generation from water was investigated using the $[Ru(bipy)_3]^{2+}/MV^{2+}/edtaH_4$ system. Specific activity was low [45]. An electrode film was formed on an ion exchanging membrane by allowing an alkaline solution on one side of the membrane to penetrate the membrane in contact with a plating bath containing $H_2[PtCl_6]$ and hydrazine at pH 5-6 [46].

The sorption of aqueous $H_2[PtCl_6]$ by poly(ethenemonosulphide) at 30-80 °C occurred by first order kinetics. The sorption mechanism was ligand substitution of the hydrolysed acid complexes [47]. Microaggregates of platinum were produced by γ-irradiation of an aqueous solution of $H_2[PtCl_6]$. Electron micrographs of the aggregates indicated an aggregation number of 30-50 atoms [48].

Hydrogen was generated from aqueous acidic $TiCl_3/K_2[PtCl_6]$ on irradiation. As the reaction proceeded the $TiCl_3$ was consumed and the reduction rate fell [49,50]. The reaction could be accomplished in neutral solutions with Ti^{3+}, La^{3+} or Fe^{3+} as a sacrificial electron donor [51].

$H_2[PtCl_6]$ was shown to act as a chain transfer agent in the copolymerisation of acrylonitrile and 2-propene-1-ol [52]. Polyethyne doped with $PtCl_4$ or $H_2[PtCl_6]$ formed an electrically conducting material. XPES implied that doping was accompanied by a partial reduction to platinum(II) [53]. $PtCl_4$ was said to be an excellent nucleating agent for the growth of titanium carbide whiskers on a hot graphite substrate [54].

The entropies of polyatomic gaseous ions have been reviewed; species discussed included $[PdCl_6]^{2-}$ and $[PtCl_6]^{2-}$ [55]. Empirically calculated effective atomic charges were used for the estimation of ΔH_f for complexes including $[PdCl_6]^{2-}$, $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ [56]. Diffusion coefficients of $H_2[PtCl_6]$ and $PdCl_2$ in aqueous, propanone and ethanol solutions were measured [57]. Thermolysis of a range of platinum complexes was examined using TGA and DTGA techniques; $H_2[PtCl_6]$ decomposed according to reaction (4) [58].

$$H_2[PtCl_6].6H_2O \longrightarrow H_2O + HCl + PtCl_4 \longrightarrow Cl_2 + PtCl_2 \longrightarrow Pt \qquad (4)$$

The kinetics and products of heterogeneous hydrolysis of platinum group halides on $M[CO_3]$ (M = Ca, Sr or Ba) were studied. $[PtCl_6]^{2-}$ was extremely slow to react [59]. Pyrolysis of $K_2[PtCl_6]/KOH/K_2[CO_3]/KO_2CC_6H_4CO_2K$ gave a product containing 3.66 % by weight of platinum [60].

Reaction of $H_2[PtCl_6]$ with hexamthylenetetramine (HMTA) gave a species of composition $[HMTAH_2][PtCl_6]$; the anion and cation were connected by N-H--Cl hydrogen bonds [61]. The species $[RPCl_3]_2[PtCl_6]$ (R = Me_3C, Cy or Ph_3C) have been prepared and characterised [62].

1.3.2 Complexes with Group 16 donor ligands

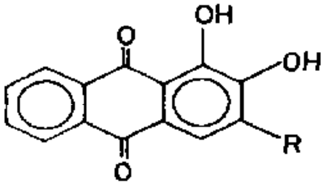
X-ray powder photographs of $Na_2[Pd(OH)_6]$ and $K_2[Pd(OH)_6]$ were compared with those of their platinum analogues [63]. XPES and electron energy loss spectroscopy indicated that the species formed on the surface of a platinum electrode anodically oxidised in 0.5 M $H_2[SO_4]$ was $[Pt(OH)_4]$ rather than platinum oxide [64].

A simple synthetic route to pure $\{Pt(SO_3F)_4\}$ has been described. This was an excellent acceptor of SO_3F, yielding $[Pt(SO_3F)_6]^{2-}$. $\{Pt(SO_3F)_4\}$ was shown to have a polymeric structure with oxygen oxygen bridging. Several equilibria (for example, reactions (5) and (6)) were studied, and $Cs[Pt(SO_3F)_5]$ shown to contain both mono and bidentate $\{SO_3F\}$ groups [65]. Facile routes to trifluoromethylsulphonate complexes have also been reported, including one for $[Pt(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_3$. Trifluoromethylsulphonate is an excellent leaving group and such species were useful in preparing a range of complexes of neutral ligands [66].

$$H_2[Pt(SO_3F)_6] + HSO_3F \rightleftharpoons \{H[Pt(SO_3F)_6]\}^- + [H_2SO_3F]^+ \qquad (5)$$

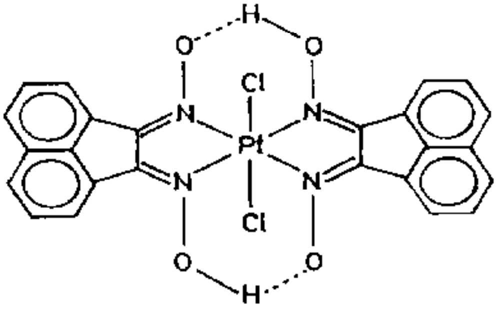
$$\{H[Pt(SO_3F)_6]\}^- + HSO_3F \rightleftharpoons [Pt(SO_3F)_6]^{2-} + [H_2SO_3F]^+ \qquad (6)$$

Complexes of **(1)** and **(2)** with platinum(IV) have been synthesised but their structures were not specified [67].



(1) R = H

(2) R = SO_3Na

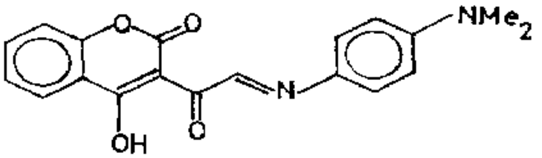


(3)

The oximes of 2-butanone and 4-heptanone have been used to extract platinum in µg quantities as $[PtL_2Cl_4]$ and $[PtL_2Cl_2]$ [68]. The preparation of

(3) has been described [69].

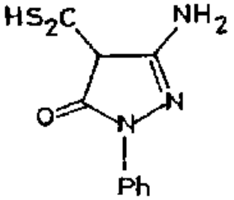
Reaction of $H_2[PtX_6]$ (X = Cl or Br) with caprolactam, L, gave $[PtL_4X_2]X_2$. Infra-red spectroscopic data suggested that the lactam were coordinated through the carbonyl oxygen atom, but the authors seemed unclear as to whether the amide nitrogen atom was also involved [70]. A complex of stoicheiometry $[PtL_2].3H_2O$ (H_2L = **(4)**) was prepared from the ligand and $H_2[PtCl_6]$. On the basis of little evidence, the authors claim that coordination was through a deprotonated OH group, a carbonyl oxygen and the imino nitrogen atom [71]. Further reactions of $HN(CH_2COOH)_2$ with platinum(IV) complexes have been noted [72].



(4)

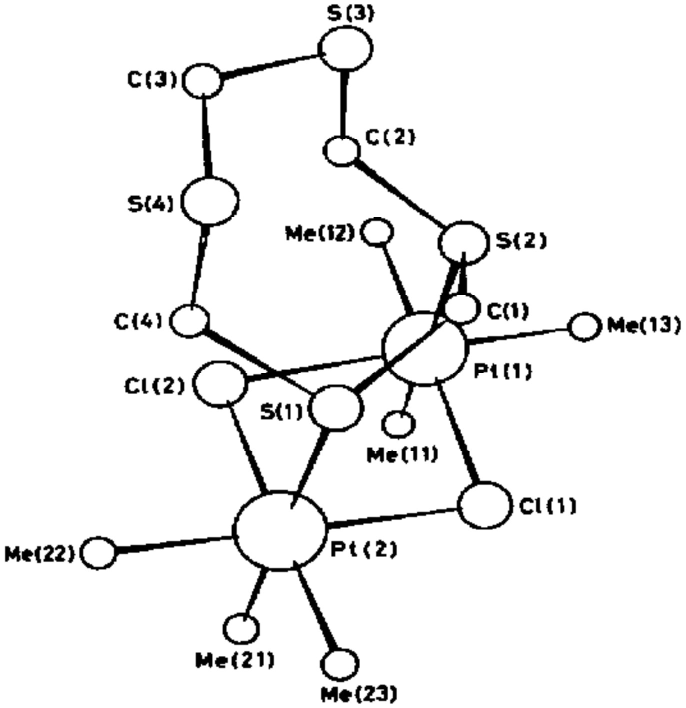
When [Pt(dmso)(en)Cl]Cl reacted with HCl an inner sphere redox reaction occurred giving $[Pt(enH)(Me_2S)Cl_4]Cl$. Over a more protracted period this complex lost dimethyl sulphide to give $[Pt(enH)Cl_5]$, characterised by X-ray diffraction [73].

The species $[PtCl_4(ECl_2)_2]$ and $[PtCl_4(E'Cl_4)_2]$ (E = S or Se, E' = Se or Te) were prepared from the corresponding halides in non-aqueous solution, and characterised by IR and Raman spectroscopy and ^{35}Cl NQR spectroscopy. The complexes appear to have tetragonally distorted octahedral geometry [74]. A somewhat dubious species $[PtL_4]$ (HL = **(5)**) has been reported. The authors suggest a metal-sulphur π-bond (!) and also claim the species $[PdL_2]$ and $[PtL_2]$ [75].



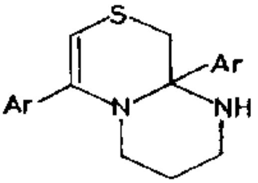
(5)

The complex $[Me_3PtX(MeSCH_2SCH_2SMe)]$ was prepared and studied by nmr spectroscopy. The separate energy barriers associated with pyramidal inversion of the sulphur, methyl scrambling and chelate ring rotation were established by complete band shape analysis [76]. In **(6)**, prepared from $[\{Me_3PtCl\}_4]$ and $\overline{\mathrm{SCH_2SCH_2SCH_2SC}}\mathrm{H_2}$, the metal pivot and Pt-Me intramolecular rearrangements were shown to be different manifestations of one transition state rather than independent rearrangements [77]. X-ray diffraction data on $[Pt(dmtp)_4][Pt(SCN)_6]$ showed that the thiocyanates were *S*-bonded (dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-a]-pyrimidine) [78].



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

Thiocaprolactam was said to form 1:1 complexes with $[PtX_6]^{2-}$ (X = Cl, Br, I or SCN). However, rather confusingly, the only species which appeared to be formally identified by the authors had the formula $[Pt(C_5H_{11}SN)_2X_2]$. The structure suggested involved *S,N*-coordination of the enolised and deprotonated ligand with *cis-S,S cis-N,N* and *trans-Cl,Cl* coordination in an octahedral geometry [79]. Octahedral platinum(IV) derivatives of **(7)** have been claimed, on the basis of IR spectroscopic data, to involve coordination of sulphur and the NH group [80]. The complex of **(8)**, $[PtL]Cl_4$, was not structurally characterised [81]. Platinum(IV) complexes of methionine, metH, including *cis*-$[Pt(metH_2Cl_2]Cl_2$ and $[Pt(metH)_3]Cl_4$ have been prepared; in the latter complex the sulphur atoms of the *S,N*-chelate occupied meridianal positions [82].



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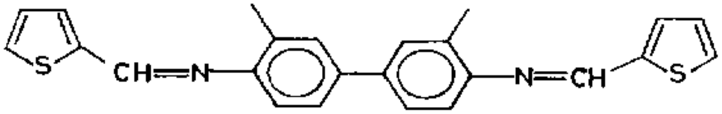


(8)

1.3.3 Cancer Chemotherapy

Reaction of *cis*-[Pt$(NH_3)_2Cl_2$], *cis*-platin, with X_2 (X_2 = H_2O_2, Br_2 or Cl_2) gave *cis,cis,trans*-[Pt$(NH_3)_2Cl_2X_2$]. The complexes were characterised by microanalysis, IR and ^{195}Pt nmr spectroscopy. Their anti-tumour activity was thought to be due either to direct binding of platinum(IV) or *in vivo* reduction to platinum(II) [83]. One of the isomers (unspecified) of [Pt$(NH_3)_2Cl_2(OH)_2$] was noted to be less toxic than *cis*-platin [84]. The *cis,cis,trans*-isomer could be determined by HPLC [85]. In a redetermination of the crystal structure of three of the isomers of this formula, new data indicated that the *cis,cis,trans*-isomer should be assigned to the space group $P4_2/nmc$ rather than $P4_2/n$ [86]. The species *cis,cis,trans*-[Pt$(NH_3)_2Cl_2(OH)_2$].$3H_2O_2$ could also be obtained from the reaction of *cis*-platin with hydrogen peroxide. X-ray diffraction showed that the H_2O_2 molecules bridged the platinum complexes by hydrogen bonding to oxygen. Although this species could cause breaks in PM2-DNA, this was entirely as a result of breakdown of H_2O_2 to give radicals [87].

CHIP, *cis,cis,trans*-[Pt$(H_2NCHMe_2)_2Cl_2(OH)_2$], has been reviewed as a chemotherapeutic agent [88]. Preclinical studies in mice, rats and dogs of CHIP have been reported; it was shown to be as active as *cis*-platin against hemopoietic step cells but less active against the mouse tumours, leukaemia L1210 and osteosarcoma C22LR [89]. A microscale synthesis of [^{195m}Pt] CHIP was described; its concentration/time profile in blood showed an initial rapid decline followed by a slowed decline [90]. Both CHIP and the platinum(II) complex, *cis*-[Pt(metronidazole)$_2Cl_2$] (FLAP) induced sister chromatic exchange in CHO cells *in vitro*, CHIP being more potent than FLAP [91]. Neither CHIP nor *cis,cis,trans*-[Pt$(NH_3)_2Cl_2(OH)_2$] interacted directly with PM2-DNA *in vitro*. However, in the presence of Fe$[ClO_4]_2$ or ascorbic acid as reductant, *cis*-[Pt$(H_2NCHMe_2)_2Cl_2$] and *cis*-platin, both of which were active, were obtained, suggesting that platinum(IV) antitumour complexes must be reduced *in vivo* [92]. X-ray diffraction data for [CHIP].$0.5H_2O_2$, [CHIP].CH_3CONMe_2 and [CHIP].H_2O have been reported [93].

Compounds such as *cis,trans*-$[Pt(H_2NCH_2CR^1R^2CH_2NH_2)Cl_2Y_2]$ (Y = halide or OH) [94] and platinum(IV) and platinum(II) complexes of nitropyrazoles [95] have also been used for chemotherapy. A simple biochemical λ-prophage induction assay was used to study the effect of structural variations in platinum complexes on their anti-tumour action. Seven complexes of the fifty-three tested were more active than *cis*-platin, and others were less toxic. The test was most reliable for compounds showing very high or very low activity [96].

1.3.4 Complexes with Group 15 donor ligands

The radiolysis and photochemistry of $[Pt(NH_3)_4]^{2+}$ and $[Pt(NH_3)_4(OH)_2]^{2+}$ have been studied. The short-lived intermediates formed on pulse radiolysis or flash photolysis were platinum(III) or platinum(I) complexes [97]. The reaction volume at infinite dilution for reaction (7) was determined. The results were consistent with theories of electrorestriction effects [98]. $[Pt(NH_3)_6]^{4+}$ was used as an oxidant for cytochrome b_5 at 25 °C in a kinetic study. It was concluded that a binding site of charge −3 or −4 was involved [99].

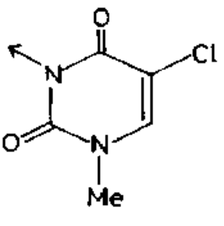
$$[Pt(NH_3)_6]^{4+} + [HO]^- \longrightarrow [Pt(NH_3)_5(NH_2)]^{3+} + H_2O \qquad (7)$$

The potential barrier to internal rotation of the NH_3 groups in $[Pt(NH_3)_4I_2]I_2$ was calculated by a quantum statistical method in the quasi-harmonic approximation, and was essentially shown to be free. The related chloride appeared to differ in having higher barriers and stronger hydrogen bonds [100]. Experimental heat capacity determinations on *trans*-$[Pt(NH_3)_4I_2]I_2$ confirmed this view [101]. The heat capacity of *cis*-$[Pt(NH_3)_4Cl_2]Cl_2$ was measured calorimetrically over the range 55-299 K. The potential barrier to ammine rotation was determined to be 14.7 kJ mol^{-1}, insufficient to suggest very strong hydrogen bonds [102]. However, in the related *trans*-complex two λ-type anomalies due to phase transitions were observed. The phase changes were shown to correspond to the formation of N-H--Cl hydrogen bonds for two of the four ammine ligands [103]. A value of 25.2 kJ mol^{-1} for the barrier to ammine rotation in *trans*-$[Pt(NH_3)_4Cl_2][NO_3]_2$ was taken to indicate rather stronger hydrogen bonds between anion and cation [104]. The structure of the complex has been determined by X-ray crystallography, the existence of the hydrogen bonds being clearly demonstrated [105].

The complexes *cis*-$[Pt(NH_3)_2L_2Cl_2][NO_3]_2$ (L = NH_3, $MeNH_2$, $EtNH_2$, Me_3CNH_2, Me_2NH, Et_2NH, Me_3N, Et_3N or py) were prepared from *cis*-$[Pt(NH_3)_2Cl_2(NO_3)_2]$ and L, and were characterised by thermal analysis [106]. The reaction of $[Pt(NH_3)_2(NO_2)_2]$ with phosphoric acid (reaction (8), *sic*) has been studied [107].

$$[Pt(NH_3)_2(NO_2)_2] \xrightarrow{H_3PO_4} X \underset{+H_3PO_4}{\overset{-H_2O}{\rightleftharpoons}} \textit{trans}\text{-}[Pt(NH_3)_2(NO_2)(NO)(H_2PO_4)(H_3PO_4)] \qquad (8)$$

Complexes $[PtL_2X_4]$ (X = Cl or Br; L = alkyl substituted imidazole) have been prepared by two groups. In all cases, even for alkenyl substituted species, L acted as a monodentate ligand bound through N(3) [108,109]. Either *cis* or *trans*-$[Pt(RNH_2)_2Cl_4]$ or $[Pt(EtNH_2)_4][ClO_4]_2$ was reduced by $[Cp_2Fe]$ or NaI at rates which depended inversely on the σ-donor ability of R and directly on its bulk [110]. Species of stoicheiometry $[PtL_2Cl_4]$ (L = $H_n(CH_2CH_2OH)_{3-n}$; n = 0, 1 or 2) and $[PtLCl_4]$ (n = 0 or 1) have been prepared and characterised by IR spectroscopy and pKa measurements. The paper gave little indication of the geometries of the complexes or of the extent of oxygen binding [111]. The first examples of an octahedral platinum(IV) complex of 1-methyluracil bound through N(3) have been prepared. *cis*-$[Pt(NH_3)_2(1\text{-}MeU)Cl].H_2O$ reacted with HOCl to give *mer*-$[Pt(NH_3)_2(1\text{-}MeU)Cl_3]$. Molecular chlorine gave mixtures of *mer*-$[Pt(NH_3)_2(L)Cl_3]$ and *mer*-$[Pt(NH_3)_2(L')Cl_3]$ (L = **(9)**, L' = **(10)**). Both were characterised by X-ray diffraction techniques and both had a strong intramolecular hydrogen bond between one of the exocyclic oxygen atoms and an ammonia ligand [112].



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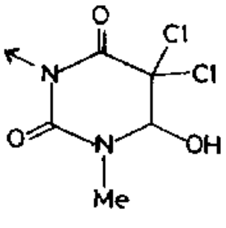


(10)

The structure of the product formed on reaction of poly(2,2'-1,4-phenylene)-6,6'-oxybis(3-phenylquinolaline)] and $H_2[PtCl_6]$ was investigated by XPES. It was concluded that a lone pair of the nitrogen heterocycle was acting as a donor towards platinum(IV) [113]

The complex *cis*-$K_2[Pt(NO_2)_2Cl_4]$ was prepared by the sequence of reaction

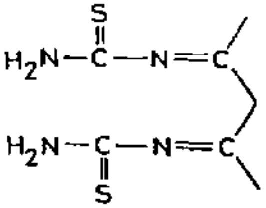
(9), and its structure proven by X-ray diffraction measurements. The previously reported synthesis of the complex was shown to give the *trans*-isomer [114].

$$K_2[Pt(NO_2)_4] + H_2[SO_4] \xrightarrow{100\ ^\circ C} cis\text{-}K_2[Pt(NO_2)_2(SO_4)_2] \xrightarrow{\text{anion exchange resin}} cis\text{-}K_2[Pt(NO_2)_2Cl_4] \qquad (9)$$

Reaction of [Pt(dmso)(en)Cl]Cl with concentrated hydrochloric acid and chloride ion gave the platinum(IV) complex $[Pt(Hen)Cl_5].nH_2O$. The structure of the product was determined by X-ray diffraction; the Hen ligand was monodentate and adopted an extended conformation [115]. The solubility of $[Pt(phen)_2(en)][Fe(CN)_6]$ in NaX (X = ½$[ClO_4]$, I, Br or Cl) containing aqueous solution at 298 K and ionic strengths varying between 0.1 and 0.75 was investigated. Outer sphere association constants were calculated for $\{Pt(phen)_2(en)X_n\}^{(4-n)+}$ (n = 1 or 2) and extrapolated to zero ionic strength. There was shown to be a linear correlation between the first association constants and the reciprocals of the crystallographic radii and heats of hydration of the outer sphere ligands [116].

The species *trans*-$[Pt(edtaH_4)LX_2]X_2$ (L = en, 1,2-pn, 1,3-pn, bipy or phen) were prepared by oxidative addition of X_2 to $[Pt(edtaH_4)L]X_2$ [117]. $[PtACl_4]$ in which A is 1,2-pn or aminomethylpyrrolidine were synthesised. An X-ray diffraction study of the pyrrolidine derivative revealed that the coordinated nitrogen of the ring was a new chiral centre and was formed essentially stereospecifically [118]. A number of platinum(II) and platinum(IV) complexes of 2,3-dimethyl-2,3-diaminobutane have been prepared and were tested for their anti-tumour activity [119].

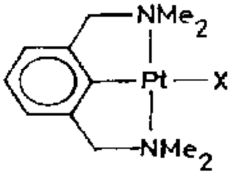
The ligand (11) was prepared from urea and acacH. In $[PtLCl_4]$ coordination was stated to be through the amino nitrogen groups only, and no comment was passed on the unfavourable ten-membered ring which would thus be formed [120].



(11)

The adsorption changes and kinetic behaviour produced by excitation of $[Pt(TPP)Cl_2]$ with 35ps flashes at 355 nm and 532 nm have been studied. The absorption changes decay rapidly with a time constant 45±10 ps. A low-lying ligand to metal charge transfer state was predicted theoretically [121].

Oxidative addition of X_2 (from the element or from CuX_2 ; X = Cl, Br or I) to **(12)** gave (13), characterised as an approximately octahedral complex by X-ray diffraction [122].



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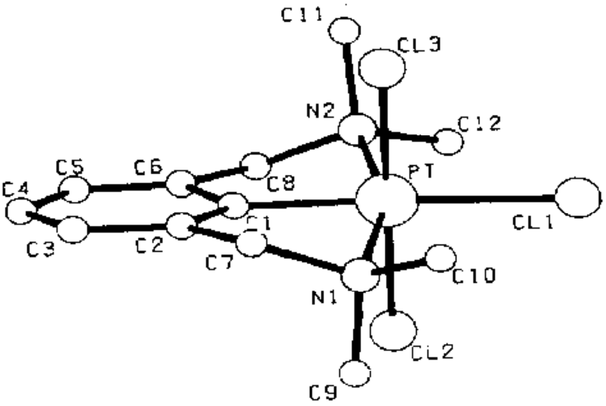


(13) (Reproduced with permission from [122])

Complexes of stoicheiometry $[PdL_2Cl_4]$ (L = triaryl phosphine) have been prepared and their thermolysis was studied. Chlorine was lost below 200 °C [123]. Elsewhere the reaction was noted to give *cis*-products and an analogous process was described for $[L(MeCOO)Pd(\mu\text{-}OCOMe)_2Pd(OCOMe)L]$, although the account provided was rather confusing [124].

1.3.5 Complexes with Group 14 donor ligands

The reaction of $H_2[PtCl_6]$ with $SnCl_2$ in propanone has been studied by Mössbauer and by ^{195}Pt and ^{119}Sn nmr spectroscopy. Numerous species could be identified, but it was generally clear that the major process involved reduction to platinum(II) complexes [125-127].

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

The chemistry of one-dimensionally ordered mixed valence compounds has continued to be widely studied and a review has been published [128]. Theoretical studies have addressed the problem of complex classification from resonance Raman spectroscopic data; this method is very effective in distinguishing class II linear chain complexes, in which structural changes on excitation are confined to a single coordinate, from complexes near to the classII/III borderline, in which only small structural changes occur along each of several totally symmetric normal coordinates [129]. The wavenumber of the symmetric chain stretching mode of such X-bridged complexes increased as the wavenumber of the excitation line increased, whereas those of the equatorial modes did not [130]. Other electronic and vibrational spectroscopic data were discussed with particular reference to size effects [131]. A method to derive LCAO bases has been adapted to the symmetry of quasi 1-dimensional crystals [132].

The excitation spectrum of Wolfram's red salt, $\{Pt(EtNH_2)Cl_3\}$, has been subjected to theoretical analysis. Since the ground state of the dimerised chain possesses two-fold degeneracy, elementary excitations corresponding to topological solitons or propagating domain walls are obtained. Such domain wall motions govern the charge lattice relaxation process at low temperatures [133]. The luminescence of this complex has also been considered in detail [134]. The intense Gaussian like Raman band observed from this salt is consistent with the electronic Raman band predicted by the PKS vibronic coupling model for a strongly localised symmetric mixed valence system, although some discrepancies between theory and experiment remain [135]. EXAFS and XANES measurements detected the locally distorted structure of the linear chain and allowed direct confirmation of the presence of platinum(II) and platinum(IV) species [136].

X-ray diffraction data for the species $[Pt(3\text{-}pn)_2][Pt(3\text{-}pn)_2X_2][Y]_2$ (X = Cl, Y = $[BF_4]$ or X = Br, Y = $[BF_4]$ or $[ClO_4]$) were insufficient to allow a distinction between platinum(II) and platinum(IV) centres to be made; the chelate rings adopted a chair conformation [137,138]. Crystal structures were also reported for related derivatives of en and 2-pn [139,140]. Electronic, infra-red and resonance Raman spectra of the related palladium complexes have been analysed. The palladium complexes had lower intervalence band maxima and band excitation profile maxima than the platinum analogues. This would suggest that the palladium containing species have more delocalised valencies [141]. Simple equations obtained for calculating dimensionless shifts and relative intensities of overtones in resonance Raman spectra of linear chain species were applied to $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$, with results in good agreement with the spectra measured at 80 K [142].

The species $\{M_2PtI_5\}.2H_2O$ (M = K, Rb or $[NH_4]$) were obtained from

$H_2[PtCl_4]$ and a ten-fold excess of MI in aqueous solution. Thermolysis yielded $M_2[PtI_6]$, MI and PtI_2. X-ray diffraction studies of the potassium and rubidium salts indicated a structure related to Wolfram's salt with well distinguished Pt-I distances (2.715(2) and 3.205(2) for the potassium salt) [143].

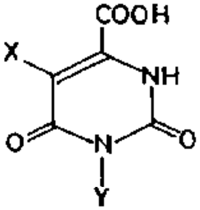
The preparation and properties of partially oxidised (electrolytically) $[R_4N]_2[Pt(C_2O_4)_2]$ have now been described in a full paper. Electrical conduction properties could be related to the value of the Fermi wave vector determined from X-ray diffuse scattering experiments [144]. Crystals of $[H_2en]_{0.82}[Pt(C_2O_4)_2].2H_2O$ suitable for X-ray diffraction were prepared from $H_{1.6}[Pt(C_2O_4)_2]$ and $[Cu(en)][NO_3]_2$ by slow diffusion [145].

An X-ray diffraction study of $Li_{0.5}[Pt(mnt)_2].2H_2O$ revealed that the $[Pt(mnt)_2]^{0.5-}$ anions were stacked face-to-face along the *a*-axis to form a platinum chain with four-fold symmetry. In contrast to the regular chain in the metallic compound $Li_{0.8}[Pt(mnt)_2]$ the four-fold symmetric structure could be regarded as a Peierls insulating species [146]. $Li_{0.82}[Pt(mnt)_2].2H_2O$ underwent a simple Peierls transition (T_C = 215 K) which was not influenced by cation ordering [147]. Optical absorption, reflectance and resonance Raman spectra of the dimercaptodithiolene type complexes, $[Bu_4N]_x[M(C_3X_5)_2]$ ($x = 1$ or 2 or $0<x<1$; X = S or Se; M = Ni, Pd or Pt) have been reported [148]. The preparation of $Rb[Pt(mnt)_2].2H_2O$ was described. An X-ray diffraction study revealed planar anions in a dimeric eclipsed configuration in a columnar stacked structure. Along the platinum axis room temperature conductivity was $2.5x10^{-5}$ $\Omega^{-1}cm^{-1}$ [149]. The related 3,7-bis(dimethylamino)phenothiazan salts were also semiconductors at room temperature [150].

Many papers again report the preparation and chemistry of mixed valence "platinum blue" complexes. For example, the X-ray diffraction data, magnetic properties and visible spectroscopy of $[Pt_4(en)_4(C_5H_4NO)_4][NO_3]_5.H_2O$ and $[Pt_2(en)_2(C_5H_4NO)_4(NO_2)(NO_3)][NO_3]_2.\frac{1}{2}H_2O$ have been described. SCF X_α calculations on the related ammine complexes (with which they are essentially isomorphous) provided assignments for the optical spectra. The colour of the complexes derives from intervalence M-M charge transfer bands, which vary predictably in energy with intermetallic distance [151]. The X-ray diffraction data for $[Pt_4(NH_3)_8(1\text{-}MeU)_4][NO_3]_5$ have also been reported; this is the first pyrimidine blue to be fully structurally and magnetically characterised [152]. The related species $[X(NH_3)_2Pt(\mu\text{-}1\text{-}MeU)_2Pt(NH_3)_2X][NO_2]_y.nH_2O$ (X = NO_2 $y = 2$, $n = 3$; X = H_2O, $y = 3$, $n = 5$; X = NO_3, $y = 2$, n = 4.5) have also been prepared [153]. The crystal structure of *cis*-diammine α-pyrrolidone violet, $[Pt_4(NH_4)_8(C_4H_6NO)_4][PF_6]_2[NO_3]_{2.56}$, has also been noted [154]. *cis*-Diammine α-pyrrolidone green has been shown to be a non-stoicheiometric mixture of the pyrrolidone blue and pyrrolidone tan structures. X-ray diffraction data indicated that the Pt-Pt bond length decreased as the platinum oxidation state increased (over the range 2.25 to 2.5) [155].

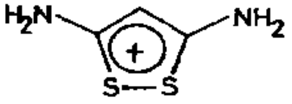
The electronic structure and optical spectrum of *cis*-diammine platinum α-pyridone blue was probed by SCF-X_α-SW calculations. It was concluded that the HOMO was almost entirely platinum localised and that two quite different platinum-platinum interactions existed. These data together with XPES and epr measurements suggested that this was a Robin-Day class IIIA compound [156].

A wide range of platinum blues has been obtained by treating a large excess of various amides with $K_2[PtCl_4]$. The amides used included $H_2NC(=O)(CH_2)_nCOOH$ (n = 0, 1, 2 or 3), *cis*- and *trans*-cyclohexane 1,2-dicarboxamide and $H_2N(C=O)CH_2CR_2CH_2COOH$ (R = Me or Ph). ^{13}C nmr data suggested that the amide was coordinated and the carboxyl free. Redox titrations suggested oxidation states for platinum between 2.3 and 2.8. The authors inferred that the function of the carboxyl group was to anchor the ligand whilst formation of the "blue" complex proceded [157]. 1,4-Butanedioic acid monoamide and 1,4-butanedioic acid imide gave similar results. Again the amide oxygen appeared to be the coordination site with a mean platinum oxidation state of 2.5 [158]. In platinum blues formed from substituted orotic acids, **(14)**, complexation occurred at N(1), and in some cases at the carboxylate group. The epr spectra of these species closely resembled those of pyridone blue, and the mean oxidation state of the platinum was between 2.20 and 2.42 [159]. Slow oxidation of $[Pt(NH_3)_2(HL')][NO_3]_2$ or $[Pt(NH_3)_2L'][NO_3]$ (L' = guanosine) gave the first true guanosine platinum blue [160].



(14a) X = Me, Y = H

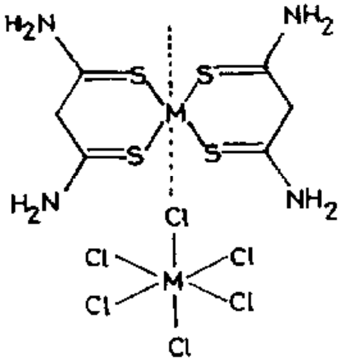
(14b) X = H, Y = NO_2



(15)

"Dithiomalonamide", HL, **(15)** reacted with $[MX_6]^{2-}$ to give $[M(II)(HL)_2][MX_6]$, **(16)**, or $[M(HL)_2][M(HL)_2X_2]X_4$, **(17)**, (M = Pd or Pt). In **(16)** the ligand acted as an *S,S*-donor, whilst in **(17)** there was a *trans*-array of sulphur and nitrogen donors [161]. The species $[Pt(H_2L)Cl_2][PtCl_6]$ and $[Pt(H_2Q)Cl_2][PtCl_6]$ (H_2L = *N,N'*-bis(2-aminobenzoyl)ethane-1,2-diamine;

H_2Q = *N*,*N*'-bis(2-(2-hydroxybenzaldimino)benzoyl)ethane-1,2-diamine) have been prepared and characterised [162].



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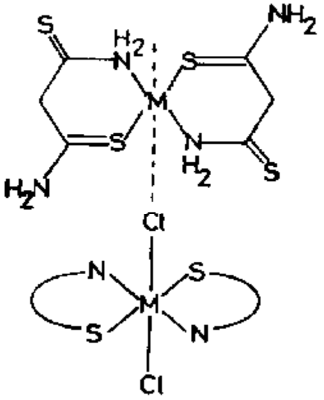


(17)

1.5 PALLADIUM(III) AND PLATINUM(III)

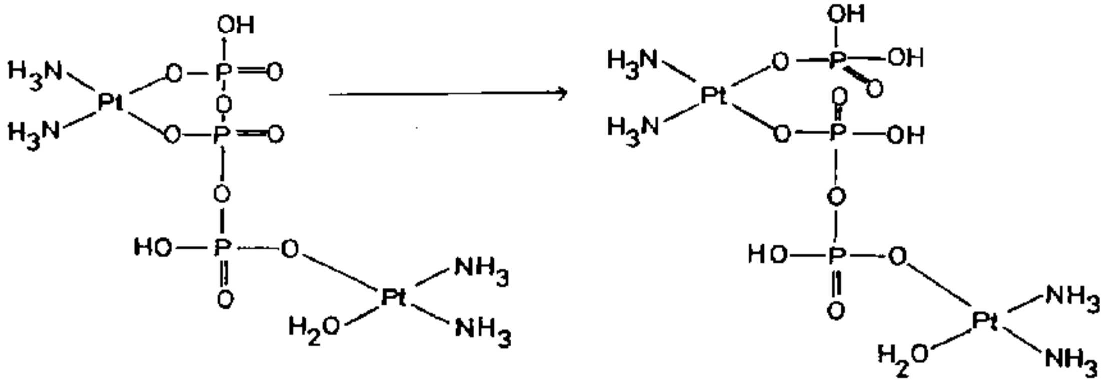
Palladium and platinum M(III)-M(III) dimers have been the subject of an excellent review [163]. New $K_2Li[MF_6]$ phases, including that for which M = Pd(III) have been studied. The temperature dependence of the reciprocal magnetic susceptibility of $K_2Li[PdF_6]$ deviated from the Curie Weiss law only at low temperatures. This was associated with exchange couplings between the trivalent species along the diagonal face of the cube [164]. In $K_2Na[PdF_6]$ crystal structural data indicated a tetragonal structure at 25 °C with a transition to the cubic form with the elpasolite $K_2Na[AlF_6]$ structure at 105 °C. $4d^7$ low spin palladium was characterised by magnetic measurements and epr spectroscopy. The data indicated that the strong axial distortion of the $\{PdF_6\}$ octahedra characteristic of elpasolite permits the stabilisation of palladium(III) [165].

Relativistic MS-X_α calculations have been performed for the species $[PtCl_6]^{3-}$, $[PtCl_4]^-$ and $[PtCl_5]^{2-}$. All of these have been proposed as models for the short-lived transients generated by pulse radiolysis or flash photolysis of $[PtCl_6]^{2-}$. Comparison with experimental UV spectroscopic data implied that $[PtCl_4]^-$ was the best representation of the species generated, possibly with weak coordination in the apical positions. Thus, the primary event on photoexcitation of $[PtCl_6]^{2-}$ was direct homolysis of a platinum-chlorine bond, and trigonal pyramidal $[PtCl_3]^-$ was not formed [166]. Sensitised photolysis of $[PtX_6]^{2-}$ (X = Cl, Br or [SCN]) in a system containing [Ru(bipy)$_3$}$^{2+}$ or osmium(II) also gave [PtX$_4$]$^-$, which led to a chain aquation process. The efficiency of [PtX$_4$]$^-$ in propagation of chain aquation was in the order X = Br > Cl > [SCN], which could in turn be related to the different abilities of the ligands to form intermediates of the type [X$_4$Pt--X--PtX$_5$]$^{3-}$ [167].

Further {Pt$_2$}$^{6+}$ units have been characterised by X-ray diffraction techniques, the results being summarised below [168,169]. In all cases the {Pt$_2$(O$_2$XO$_2$)$_4$} arrangement had the Pt$_2$O$_2$X rings all bent in the same direction to give C_{4h} symmetry.

Complex	r(Pt-Pt)/Å
$K_2[Pt_2(SO_4)_4(H_2O)_2]$	2.461
$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$	2.485, 2.487
$[C_5H_5NH]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2].H_2O$	2.529
$[3,4\text{-}Me_2C_5H_3NH]_2[Pt_2(HPO_4)_4(3,4\text{-}Me_2C_5H_3NH)_2]$	2.494

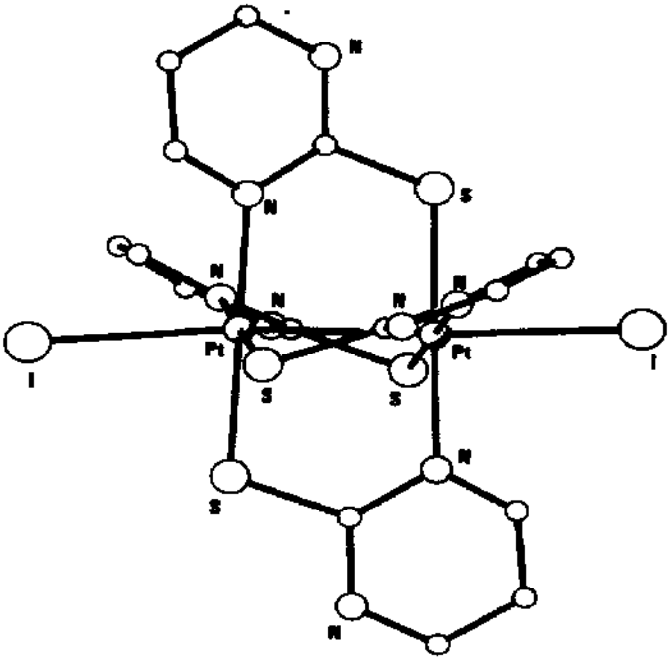
In the reaction of *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ with [PO$_4$]$^{3-}$ at pH 1-4 the dimerisation of the platinum complex, as monitored by ^{31}P nmr spectroscopy, was slow. **(18)** was formed initially but rearranged to **(19)**. The blue coloured complex then formed had an average platinum oxidation state of 2.3, suggesting that it might be composed of two units of (19) with one platinum(III) and three platinum(II) centres [170].



(18) **(19)**

Treatment of [Pt$_2$L$_4$] (HL = Me$_2$CHCS$_2$H) with iodine yielded the platinum(III) dimer, [Pt$_2$L$_4$I$_2$], characterised by ^{1}H and ^{13}C nmr spectroscopy, XPES and X-ray diffraction [171]. Reaction of pyrimidine-2-thione (PymS) with

$[PtI_4]^{2-}$ in the air gave the platinum(III) bridged dimer, **(20)**, identified by X-ray diffraction. The intermediate $[Pt(PymS)_2]$ could be isolated in the absence of air. This is the first example of the formation of a platinum(III) dimer formed by direct reaction of a ligand with a platinum(II) complex. The platinum-platinum distance (2.554 Å) lay between the values for dimers quadruply bridged by *O,O*-donors and those found in *P,P* bridged species such as pop derivatives [172].



(20) (Reproduced with permission from [172])

A detailed study of the reactions of $[Pt(NH_3)_2(NO_2)_2]$ with phosphoric acid proposed the species $[NH_4]_2[Pt_2(HPO_4)_2(H_2O)_2]$ to be formed, though there appears to be a misprint in the text at this point [107]. Another paper on the same subject claimed the intermediates $[H_7Pt^{(III)}(NH_3)_2(NO_2)(NO)(PO_4)_3]$ and $[NH_4]_2[H_4Pt_2(\mu\text{-}PO_4)_4(H_2O)_2]$, the characterisation of these species being somewhat unclear [173].

Reaction of $[Pt_2(pop)_4]^{4-}$ with MeI (pop = $[P_2O_5H_2]^{2-}$) gave $[MePt(pop)_4PtI]^{4-}$, characterised by X-ray diffraction. The Pt-Pt distance of 2.782 Å is shorter than in $[Pt_2(pop)_4]^{4-}$, but exceeds that in the related $[Pt(pop)_4Cl_2]^{4-}$ complex (2.695 Å). The strong *trans*-influence of the methyl and iodide ligands was evidenced by the red shift of the $d_\sigma \rightarrow d_{\sigma^*}$ transition relative to $[Pt_2(pop)_4Cl_2]^{4-}$ [174]. The photochemistry of $[Pt_2(pop)_4X_2]^{4-}$ has been investigated. $[Pt_2(pop)_4XY]^{4-}$ could be prepared by photochemically accelerated halogen substitution [175].

The first mononuclear platinum(III) species to be characterised by X-ray diffraction was (21), prepared by reaction (10). It was a stable deep blue paramagnetic complex without platinum-platinum bonding [176].

$$[Bu_4N]_2[Pt(C_6Cl_5)_4] \xrightarrow{X_2 \text{ or } TlCl_3} [Bu_4N][Pt(C_6Cl_5)_4] \qquad (10)$$

(21)

1.6 PALLADIUM(II) AND PLATINUM(II)

The relative stabilities of *cis*- and *trans*-isomers of $[PtL_2Cl_2]$ was studied using perturbation theory [177]. The separation of polarographic waves in solutions containing more than one type of metal ion with close $E_{½}$ values is difficult and the problem was tackled by differential complexation [178].

1.6.1 Complexes with Group 17 donor ligands

The photoexcitation of chloro derivatives of platinum(II) and the consequent changes in their geometry may be related to their biological properties [179]. Reaction of a glowing platinum filament with molecular chlorine under equilibrium conditions at 1300 K gave $PtCl_2$ [180]. The absorption and reflection spectra of a crystal of the chain compound $PdCl_2$ have been measured at 1-11 eV at low temperature. The structures found in the spectra and their anisotropies were related to D_{2h} MO states of a d^8 metal ion in a rhombic planar ligand field [181]. In X-ray absorption near edge structure (XANES) studies, the L-edge absorption spectra of $PdCl_2$ were obtained with synchrotron radiation and the results compared with those for metallic palladium. $PdCl_2$ was shown to have a higher and narrower density of unoccupied states than palladium metal [182]. The heat capacity of α-$PdCl_2$ was measured by DSC at 301-620 K to determine the transition temperature of 390±5 °C and the heat of transition as 167±17 $Jmol^{-1}$ [183].

The effect of chloride ion concentration on the adsorption of $PdCl_2$ on alumina from solutions containing $PdCl_2$ or $PdCl_2/AlCl_3$ was investigated [184]. Active carbon on silica was treated with a solution containing $PdCl_2/HCl$, dried and retained in a porous container for use as a carbon monoxide filter [185]. The distribution behaviour of $PdBr_2$ between the immiscible liquid phases in the $AlBr_3/HBr$ system was studied. $[PdBr_4]^{2-}$ was the predominant palladium containing species in both phases [186].

The reduction of $PdCl_2$ in aqueous dmf gave highly disperse palladium with good catalytic activity. Kinetic studies at 70-90 °C and spectrophotometry suggested that the species reduced was $[Pd(dmf)_2Cl_2]$, with an activation energy for reduction of 110 kJ mol^{-1}. An intermediate unstable palladium carbonyl complex was postulated [187]. An aqueous solution for the activation of non-conducting surfaces for electroless deposition of metals contained $PdCl_2/HCl/MeC(OH)(PO_3H)_2/SnCl_2$ [188]. Insulating systems could also be coated with metals by pretreatment with a dry catalytically active powder followed by $PdCl_2/SnCl_2$ catalysis of deposition [189]. The use of $PdCl_2/SnCl_4$ in alkaline solution for the catalytic deposition of metal conductor patterns for printed circuits has been reviewed [190].

PtI_2 was synthesised by reaction of $H_2[PtCl_6]$ with molecular iodine in aqueous ethanol [191]. The crystal and molecular structure of $[Bu_4N]_2[Pt_2I_6]$ has been determined by X-ray diffraction; the iodo bridged anion was planar [192].

The adsorption of $[PdCl_4]^{2-}$ on alumina fibres and η-alumina pellets has been described [193]. The sorption of $K_2[PdCl_4]$ and $K_2[PtCl_4]$ on hydrated zirconia was investigated. The platinum complex could be eluted using 0.1 M Na[OH] and 0.1 M NaCl, with palladium eluted later with 2M HCl [194].

The electronic absorption and magnetic CD spectra for $[PtCl_4]^{2-}$ in methanol or ethanenitrile and $[PtBr_4]^{2-}$ in methanol, have been measured and largely assigned [195]. Comparison of data for $[PdCl_4]^{2-}$ suggested that the separation of the $\Gamma_1(^1A_{2g})$ and $\Gamma_5(^1E_g)$ excited states was greater for platinum than for palladium [196]. The electronic spectra of these species were analysed by quantum chemical methods in order to explain the difference in reactivity between the complexes [197]. The temperature dependence of the ^{35}Cl NQR spectra, and the ^1H nmr T_1 values for $[(H_2N)_3C]_2[MCl_4]$ (M = Pd or Pt) has been reported. The changes may be attributed to the reorientation of the cations with breaking and reformation of N-H--Cl hydrogen bonds [198]. An XPES study of $[Ph_4P]_2[MX_4]$ (M = Pd or Pt; X = $[C(CN)_3]$, $[N(CN)_2]$, $[ONC(CN)_2]$, Cl, [SCN] or [NCO]) suggested that the pseudohalides withdrew electron density most effectively from the metal centre [199].

X-ray diffraction data for the salt $[PhCH_2CH(COOEt)NH_3]_2[PtCl_4]$ showed hydrogen bonding between the NH_3^+ group and the chlorine of $[PtCl_4]^{2-}$ [200]. Analogous structures were proposed for $[HMTAH_2][PtCl_4]$ (HMTA = hexamethylene tetrammine) [61]. A related complex of palladium was prepared, as well as $[HMTAH]_2[Pd_2Cl_6]$ [201].

Microgram quantities of palladium could be determined by extraction of acridine orange tetrabromopalladate from dilute $H_2[SO_4]$ into 3-methylbutyl ethanoate/propanone, and measurement of the fluorescence at 530 nm [202]. Imipramine tetrahalopalladate salts were also used for spectrophotometric determination of palladium [203] as was $[PhCH_2N(Ph)Me_2][PdI_4]$ [204].

The complexes $[KL]_2[PdCl_4]$ (L = crown ether) were prepared and characterised by IR spectroscopy [205]. $[LH_2]_2[PdCl_4]$ (L = theophilline or theobromine) have also been isolated and studied by IR and ^1H nmr spectroscopy, DSC and TGA [206]. $[NH_4]_2[PtCl_4]$ was used in free and conjugated forms with ovalbumin-Pt to elicit a specific antibody directed against free platinum or the platinum moiety of ovalbumin conjugates in the hooded rat [207]. The reactions of iodomethane and iodoethanoic acid with $[PtCl_4]^{2-}$ were studied; the products of oxidative addition were characterised [208].

The interactions of methyl cobalamin, MeB_{12}, with $[PtCl_4]^{2-}$, $[Pt(CN)_4]^{2-}$ and $[Pt(SCN)_4]^{2-}$ have been studied by ^1H nmr and UV spectroscopy in solution. Three platinum binding sites could be identified [209]. The quantum yield for hydrogen production from the catalytic photoreduction of water was measured in the $[Ru(bipy)_3Cl_2]/[Rh(bipy)_3Cl_3]/N(CH_2CH_2OH)_3/K_2[PtCl_4]$ system using a $[Fe(C_2O_4)_3]^{3-}$ actinometer [210]. The radiation induced reduction of 5-bromo-6-hydroxythymine to give thymine was promoted by transition metal salts including $K_2[PtCl_4]$. An electron transfer pathway was assumed to operate [211].

1.6.2 Complexes with Group 16 donor ligands

1.6.2.1 Unidentate oxygen donor ligands

Thermochemical data for gaseous monoxides, including PdO and PtO, have been derived from experimental data from the literature [212].

Water exchange in $[Pd(H_2O)_4]^{2+}$ was studied as a function of temperature and pressure by measurement of the linewidth of the signal in the ^{17}O nmr spectrum. The thermodynamic parameters thus derived implied an associative mechanism for the exchange. The exchange rate was 1.4×10^6 times faster than that for the platinum analogue [213]. Anation of $[Pt(H_2O)_4]^{2+}$ (reaction (11)) has been investigated ($A^{m-} = Cl^-$, $n = 1,2,3$ or 4; $A^{m-} = [ONO_2]^-$, $n = 1,2$ or 3; $A^{m-} = [OSO_3]^{2-}$, $n = 1$ or 2; $A^{m-} = [OPO_3H_2]^-$, $n = 1,2,3$ or 4; $A^{m-} = [OCOCH_3]^-$, $n = 1$). The products were characterised by ^{195}Pt nmr spectroscopy [214].

$$[Pt(H_2O)_4]^{2+} + nA^{m-} \longrightarrow [Pt(A)_n(H_2O)_{4-n}]^{(2-mn)+} \qquad (11)$$

The hydrolysis of Pd^{2+} in aqueous media has been studied electrochemically. At a specified pH hydrolysis increased with the concentration of Pd^{2+} and decreased with an increase in the concentration of NaCl [215]. The electronic structures of $\{M^{n+}-OH_2---OH_2\}$ complexes (including that of Pt^{2+}) were calculated by the CNDO approximation by using double-zeta contracted GTO basis sets. The effect of the charge and the composition of the first coordination sphere on the hydrogen bonds as well as the $M^{n+}-OH_2$ bond were analysed [216].

$M[Pd(OH)_4]$ (M = Ba or Sr) was prepared from $Na_2[Pd(OH)_4]$ and $M(OH)_2$. X-ray diffraction powder data implied that these complexes were orthorhombic and isostructural. Thermolysis gave successively $MPdO(OH)_2$ and $MPdO_2$ [217].

Anation of the complex *cis*-$[Pt(^{15}NH_3)_2(OH_2)_2][ClO_4]_2$ to give *cis*-$[Pt(^{15}NH_3)_2A(OH_2)]^{(2-m)+}$ was studied by ^{195}Pt, ^{15}N and, for A^{m-} = $[H_2PO_4]^-$, ^{31}P nmr spectroscopy. Reaction with $[NO_3]^-$ gave successively *cis*-$[Pt(NH_3)_2(OH_2)(ONO_2)]^+$ and *cis*-$[Pt(NH_3)_2(ONO_2)_2]$, both of which could be identified spectroscopically. $[SO_4]^{2-}$ gave a unidentate sulphate complex. Both ethanoate and phosphate gave anion bridged dimers which were converted on oxidation to platinum blues [218].

Palladium(II) could be extracted by trioctylamine, or better by tetraoctylammonium nitrate, as respectively $[R_3NH]_2[Pd(NO_3)_4]$ or $[R_4N]_2[Pd(NO_3)_4]$ [219]. Other amines and ammonium salts have also been used, and the extracted complexes characterised by IR and electronic spectroscopy and thermal analysis methods [220]. A spectrophotometric study of palladium(II) in $H_2[SO_4]$ revealed the presence of $[Pd(H_2O)_3(HSO_4)]^+$ [221].

Palladium ethanoate could be synthesised by oxidation of palladium metal by nitric oxide in a mixture of nitric and ethanoic acids [222]. The structure of $[\{Pd(OCOMe)_2\}_3]$ as crystallised from benzene was determined by an X-ray diffraction study. The $\{Pd_3\}$ unit consisted of an isosceles triangle of palladium atoms with two ethanoate bridges between each pair of palladium atoms, but no palladium-palladium bonding [223]. Palladium and platinum salts of 7,13-abietadiene-18-oic acid were used for the preparation of electrically conducting coatings on insulators such as glass [224].

1.6.2.2 Bidentate and multidentate oxygen donor ligands

A platinum film was laser deposited on a quartz plate by using photodissociation of $[Pd(hfacac)_2]$ [225]. Metal complexes of diones and dithiones related to acacH were used for stabilisation of photographic image colours [226]. Polyvinyl alcohol was removed from waste water by adding $Na_2[B_4O_7]$, $Na_2[SO_4]$ and $[M(acac)_2]$ (M = Ni, Pd or Pt) [227].

The enthalpy of sublimation of a range of transition metal complexes has been determined. These included $[Pd(acac)_2]$ ($\Delta H_{sub}{}^{298}$ = 132±17 kJ mol^{-1}) and

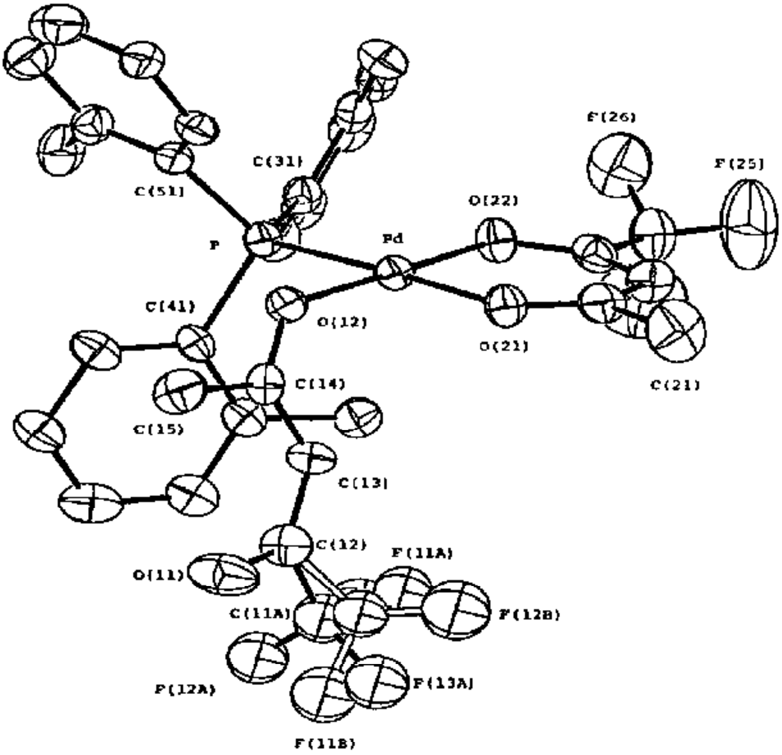
$[Pt(acac)_2]$ (ΔH_{sub}^{298} = 133±9 kJ mol^{-1}). 8-Hydroxyquinolinate complexes were also discussed [228]. The partition coefficients of $[Pd(acac)_2]$ between water and dodecane, tetrachloromethane and/or benzene were determined. The major factor determining these was cavity formation energy, but hydration was also important [229].

The FTIR spectra of $[ML_2]$ (M = Cu, Pd or Pt; L = β-diketonato) were recorded. For $[PtL_2]$ ν(M-O) could be correlated with $\delta(^{195}Pt)$ in the nmr spectrum [230]. The ^{195}Pt spin-lattice relaxation time and the shielding anisotropy were analysed as a function of temperature (295-353 K) and field strength (4.7 and 9.4 Tesla). The relaxation was dominated by CSA at both field strengths. A shielding anisotropy for ^{195}Pt of *ca.* 10.000 ppm was calculated from the correlation time derived from ^{13}C relaxation data [231].

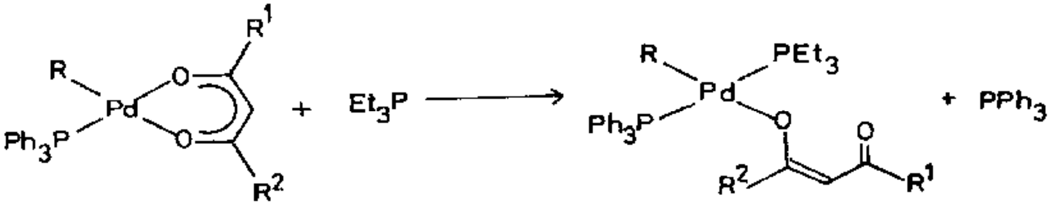
The reaction of $[Pd(tfacac)_2]$ with $(2\text{-}MeC_6H_4)_3P$ gave only $[Pd(tfacac)(tfacac\text{-}O)\{P(C_6H_4\text{-}2\text{-}Me)_3\}]$. The reaction proceeded no further because of the steric bulk of the ligands. **(22)** was characterised by X-ray diffraction; this is the first unidentate tfacac platinum complex to be so identified. In solution two isomers could be observed spectroscopically but **(22)** predominated to the extent of more than 80 % [232]. Reaction of the σ-aryl species, **(23)**, with an excess of Et_3P (R = 2-, 3- or 4-pyridyl) gave **(24)**. It was considered that the σ-aryl ligand might favour *O*-bonding Reactions (12) and (13) confirmed that the $Pd\text{-}PEt_3$ bond was stronger than the $Pd\text{-}PPh_3$ bond. The spectra and fluxional behaviour of the products was discussed [233]. Halide substitution (reaction (14)) in a related system was also investigated [234]. $[Pd(Ha)_2]$ (HaH = **(25)**) reacted with a variety of ligands, B, to give [Pd(Ha){Ha-*C(3)*}B], **(26)**, although the evidence for the stereochemistry of the product was rather tenuous [235].

The reaction of Et_3Al with $[Pd(acac)_2]$ (and related complexes of other metals) resulted in the transfer of the acac ligand to aluminium according to Scheme 1 [236]. The reactions of a species curiously described as $\{Pd_3(tribenzylideneacac)_3\}$ with phosphorus and arsenic containing ligands was said to reflect the electron acceptor properties of the ligand and to proceed *via* an associative pathway [237].

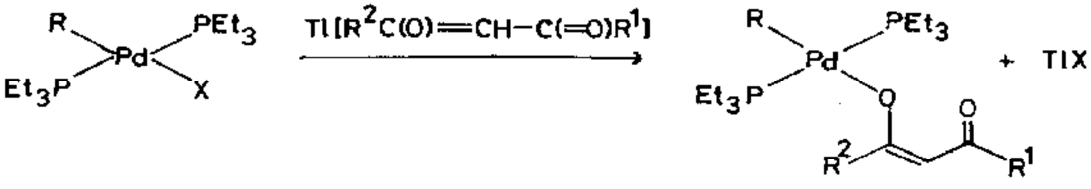
The palladium(II) complex with **(27)**, $[PdL_2]$, was studied by pHmetric titrations and IR spectroscopy; a chelate structure was assumed [238]. The related complexes **(28)** and **(29)** were also prepared [239]. **(28)** was shown to form charge transfer complexes with the $ArNO_2$ acceptor molecules, which are its substrates for catalytic hydrogenation. The method for characterisation was static quenching of first order luminescence in a matrix at 77 K. The quenching constants and the electron affinity of the acceptors were systematically related, and it sould thus be inferred that molecular complexes were formed [240]. A polymeric structure was proposed for metal complexes of Arnebin I, **(30)** [241]. The stability constants of palladium(II) derivatives of **(31)** in 1:1 and 1:2 stoicheiometries were determined [242].



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



(23) **(24)**



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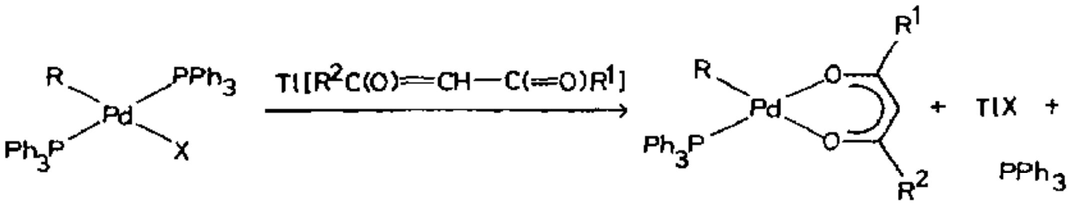

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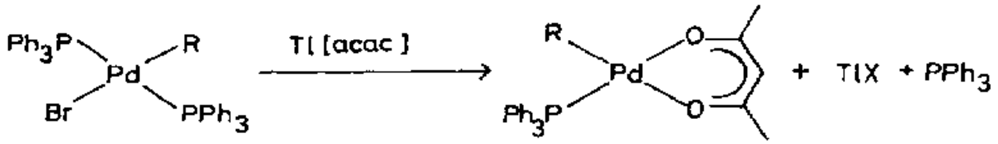

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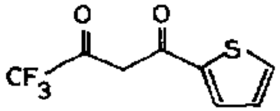

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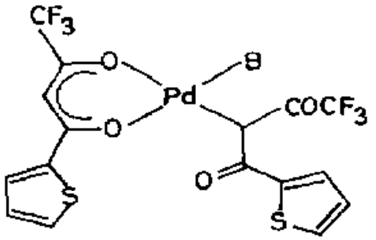

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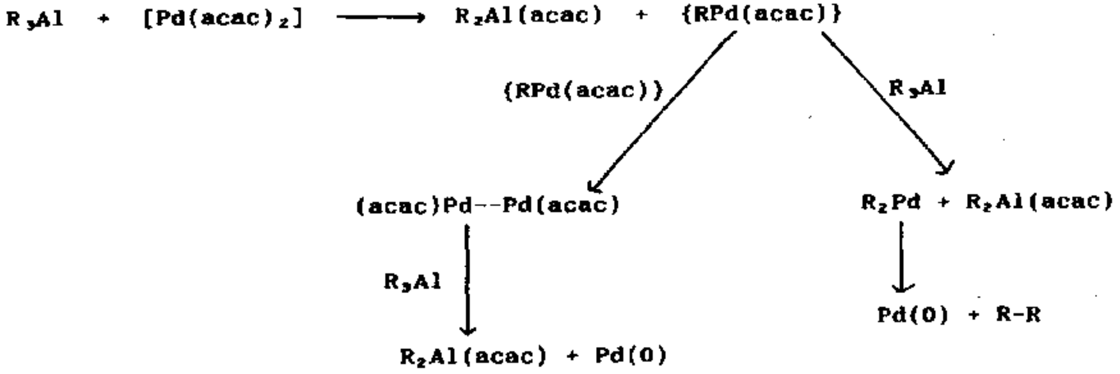
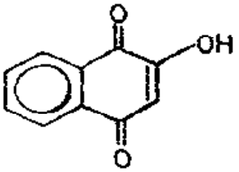


Scheme 1 Reactions of [Pd(acac)$_2$] with alkyl alanes [236].



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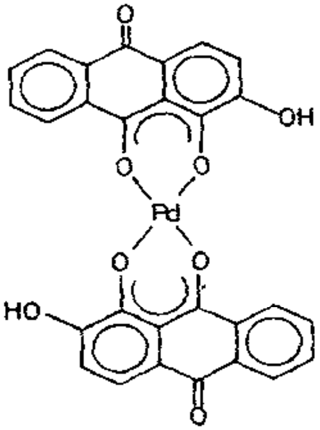

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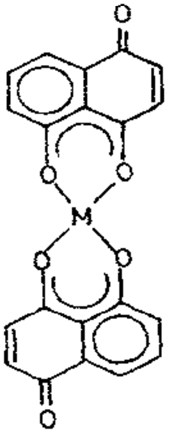

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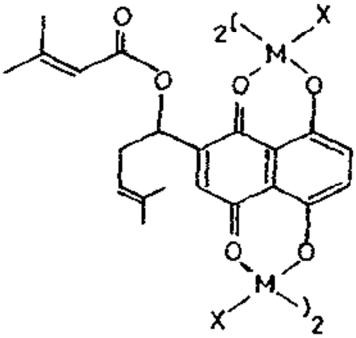

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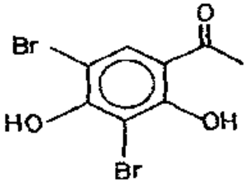


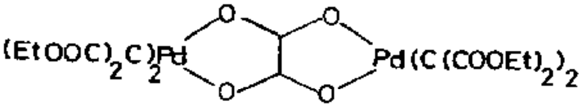
(31)

$[Pt(C_2O_4)_2]^{2-}$ and $[Pd(C_2O_4)_2]^{2-}$ were separated from other chelates using supercritical fluid chromatography [243]. $K_2[Pd(C_2O_4)_2]$ was used in the preparation of a photoimaging layer [244].

$K_2[Pt(C_2O_4)_2]$ inactivated carboxypeptidase; binding occurred at a single site close to the Zn^{2+} cofactor within the enzyme active site. This was in considerable contrast to the reactions of $K_2[PtCl_4]$, the derivative of which was non-isomorphic. It was thought that four distinct binding sites were occupied in this case [245].

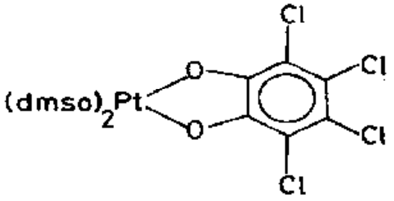
$[NH_4]_2[Pd(C_2O_4)_2]$ yielded, on photolysis or thermolysis, palladium metal, ammonia and CO_2. Under thermal conditions the Pd-N bond was the first one broken, but under a photochemical regime the Pd-O bond was first cleaved [246].

Reaction of $(EtO_2C)_2CH_2$ with $[PdCl_4]^{2-}$ in basic solution gave **(32)**, among other compounds, the structure of the complex being elucidated by X-ray diffraction [247].



(32)

Reaction of 3,4,5,6-tetrachloro dihydroxybenzene with $[\{Pt(OCOMe)(OH)_2(H_2O)\}_4]$ in dmso gave **(33)**, in which the dmso ligands were *S*-bonded [248]. The structure was determined by X-ray diffraction techniques [249]. New steroidal platinum dihydroxyarene complexes such as **(34)** have been prepared. Their biological effect on the human breast tumour cell line MCF-7 was similar to that of *cis*-platin [250].



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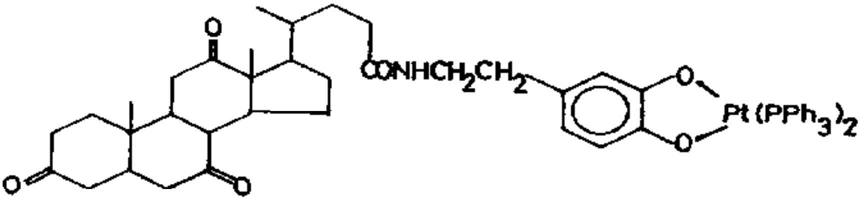
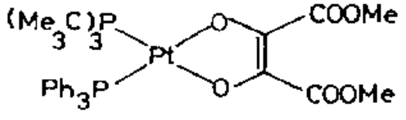


(34)

A series of [Pt(bipy)L] complexes (H_2L = 4-Me_3C-1,2-dihydroxybenzene, benzene-1,2-dicarboxylic acid, 2-hydroxybenzoic acid or 2-mercaptobenzoic acid) were prepared by treatment of $[Pt(bipy)Cl_2]$ with Na_2L, with or without $Ag[NO_3]$. Their UV spectra showed CT bands from a platinum d orbital to the π^* antibonding orbital of the bipy ligand, as well as ligand to ligand CT bands [251].

Reaction of $[H_2Pt(PPh_3)\{P(CMe_3)_3\}]$ with molecular oxygen gave $[Pt(PPh_3)\{P(CMe_3)_3\}(O_2)]$. $MeO_2CC\equiv CCO_2Me$ could be inserted into the O_2 ligand to give **(35)**, though the mechanism of the process was unclear. A curious observation, not commented on by the authors, was that the ^{31}P nmr spectrum of **(35)** and its precursor apparently showed phosphorus-platinum but not phosphorus-phosphorus coupling, despite the obvious inequivalence of the phosphines [252]. Treatment of $[Pt(PPh_3)_2O_2]$ with $MeO_2CCH_2COCH_2CO_2Me$ gave the expected product (36) by reaction at the carbonyl group. A detailed mechanism for the reaction was proposed [253].



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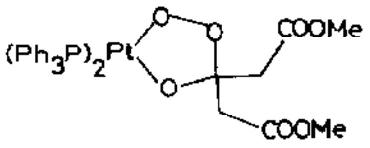
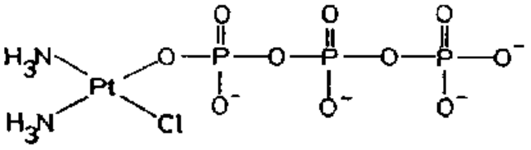


(36)

A detailed study of the reaction of *cis*-$[Pt(NH_3)_2Cl_2]$ with orthophosphate, pyrophosphate and triphosphate anions has been undertaken using ^{31}P nmr spectroscopy. Monodentate phosphate containing products such as (37) were initially formed, with subsequent cyclisation to **(38)** and **(39)**. Orthophosphate also gave a platinum blue complex. Such reactions are important as models of metal activation of phosphate hydrolysis and of the mechanisms of binding to DNA [254].



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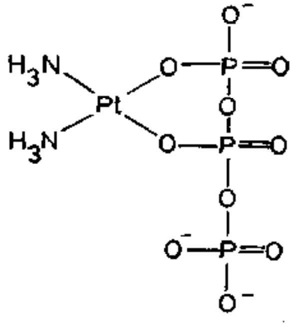

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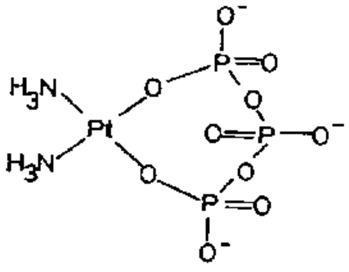


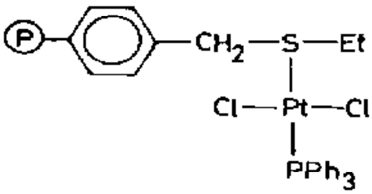
(39)

1.6.2.3 Ambidentate sulphur oxygen donor ligands

The exchange of free and bound dmso and the replacement of dmso by chelating ligands LL in $[Ph_2Pt(dmso)_2]$ has been investigated. The reaction mechanism involved a true dissociation to give initially $[Ph_2Pt(dmso)]$ in which the dmso was η^2-bonded, followed by competition for the intermediate between dmso and LL [255,256]. The kinetics of the reaction between $[PtCl_4]^{2-}$ and R^1R^2SO to give $[Pt(R^1R^2SO)Cl_3]^-$ have been studied in methanol at 25 °C. The rate was not very sensitive to electronic effects but decreased with increasing sulphoxide bulk. This was consistent with an asynchronous associative intimate mechanism with oxygen as the attacking atom in the rate controlling step [257].

An X-ray diffraction study of *trans*-$[Pt(H_2NCHMe_2)(dmso)Cl_2]$ showed that the dmso was *S*-bonded, the crystal being stabilised by intermolecular hydrogen bonds [258]. In $[Pt(en)(dmso)_2][PF_6]_2$.dmso two dmso molecules were *S*-coordinated to platinum and the third was solvent of crystallisation. The kinetics of dmso replacement were studied. There appears to be a mutual labilisation effect between the two dmso ligands, which could not be readily accounted for by *cis*- or *trans*-effects, but which made dmso replacement in $[Pt(en)(dmso)]^{2+}$ much easier than in $[Pt(en)(dmso)(H_2O)]^{2+}$ [259].

Oxidation of polymer bound sulphide complexes such as **(40)** gave only *S*-bonded *cis*-dichlorosulphoxide complexes [260]. The complexes *trans*-$[PtLL'Cl_2]$ (L,L' = dmso, Et_2SO, Pr_2SO or $OS(CH_2)_4$) were prepared from $[\{PtLCl(\mu-Cl)\}_2]$ and L'. In solution isomerisation to a *cis/trans*-mixture occurred at a rate which diminished with sulphoxide bulk, supporting an associative mechanism [261].



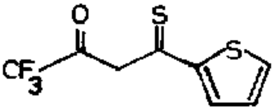
(40)

The nature of the bridges in the previously prepared complexes $[\{PtL^1(OH)X\}_2]$ and $H_2[\{PtL^2(O)Cl\}_2]$ was investigated by far IR spectroscopy (L^1 = Et_2SO, L^2 = dmso, X = Cl or Br). It was concluded that the hydroxy groups were bridging in the L^1 complex and oxygen atoms bridged in the L^2 species [262]. Acidity constants have been determined for $[Pt(en)L(H_2O)]^{2+}$ and $[Pt(1,2-pn)L(H_2O)]^{2+}$ (L = R_2S, R_2SO or R_2Se; R = Me, Et or Pr). The sulphoxides exerted a stronger *cis*-effect on the dissociation constants than either sulphides or selenides. [263].

1.6.2.4 Bidentate oxygen sulphur donor ligands

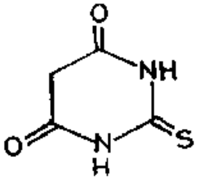
Palladium(II) complexes of **(41)** sublimed particularly easily and without decomposition, providing a useful method for purification [264].

Thiocarbamide complexes $[M(RNHC(=S)NHC(=O)Ph)Q_2]$ (M = Pd or Pt, R = substituted aryl, HQ = benzene-1,2-dicarboxylic acid imide) were prepared and characterised. IR spectroscopic data indicated *S,O*-coordination for the thiocarbamides [265].



(41)

The precipitation and extraction of the metal chelates of 1-hydroxy-2-pyridine thione and its derivatives have been investigated. When compared with the related *O,O*-chelates the pH dependent precipitation was shifted to lower pH values [266]. Palladium(II) formed 2:3 and 1:3 complexes with thiobarbituric acid, **(42)**. Ir spectroscopy implied sulphur and possibly also oxygen coordination [267].

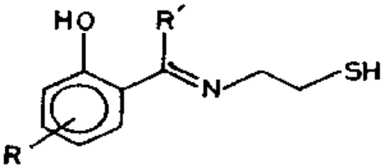


(42)

The complex $[PtL_2]$ (HL = $H_2NC(=S)NHN=C(Me)COOH$) was prepared from $[NH_4]_2[PtCl_6]$. The ligand acted as an *S,O*-chelate and the geometry was *trans*. The complex exhibited some antibacterial activity, but this was lower than that of the free ligand [268].

1.6.2.5 Multidentate oxygen sulphur nitrogen donor ligands

Reaction of $PdCl_2$ with H_2L, **(43)**, gave $[PdL(H_2O)]$ in which $[L]^{2-}$ acted as a tridentate *O,S,N*-donor [269]. Ligands acting as N_2O_2-donors or N_2S_2-donors are quite well known and numerous complexes have been prepared. The new compound, **(44)**, represents an intermediate type [270].



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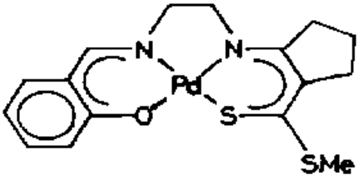
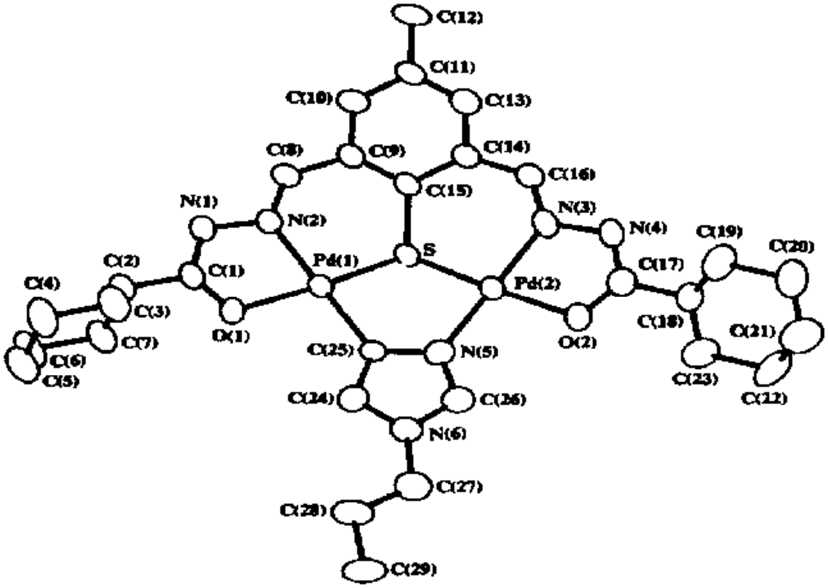
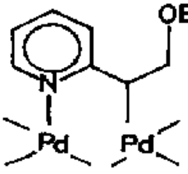


(44)

Complexes of a quinquidentate species such as **(45)** have been further studied. In **(45)**, characterised by X-ray diffraction, an unusual and unprecedented N(3),C(4) binding of the propyl imidazole bridge was established [271]. When $[PhN^2=N^1-O]^-$ was used in place of the imidazole as the bridging ligand the most likely coordination was said to be through the two nitrogen atoms for the *syn*-isomer and through N^2 and O^- for the product derived from the *anti*-isomer [272]. The formation of the *N,C*-bridged derivative, **(46)** occurred when [LPd$_2$(μ-OCOMe)] was treated with 2-ethylpyridine and ethanol. This and related complexes showed interesting dynamic behaviour in their nmr spectra [273].



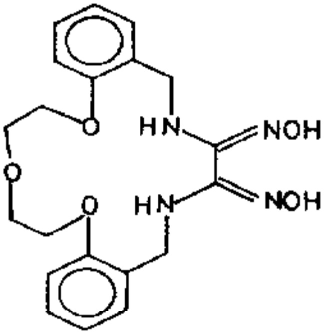
(45) (Reproduced with permission from [271])



(46)

1.6.2.6 Ambidentate oxygen nitrogen donor ligands

The complexes of nickel, copper and palladium with dimethylglyoxime and salicylaldoxime have been reviewed [274]. The preparation of **(47)** was described; palladium(II) formed a complex bound at the oxime nitrogen atoms and could also be coordinated inside the macrocycle [275]. Similar results were obtained with (48) [276].



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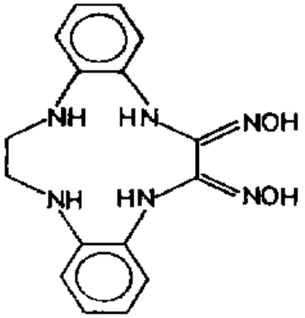
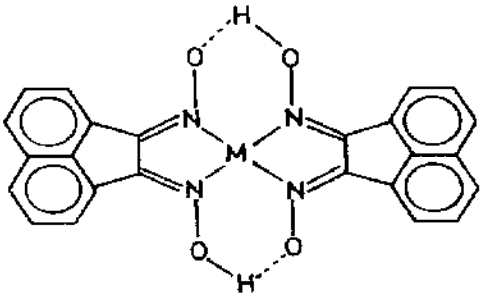


(48)

A quantum chemical study of intermolecular interactions in $[\{M(RC\{=NO)C\{=NOH\}R')_2)_2]$ (R,R' = H, Me or Et) was undertaken taking into consideration different types of packing and the possibility of M–O interactions [277]. The complexes $[ML_2]$, (49), were also prepared [69].

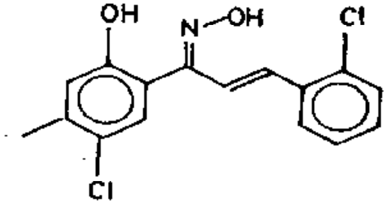


(49)

Complexes $[ML_2]$, (HL = **(50)**) were reported; there is little indication of their structure but the deprotonated phenolic oxygen and the oxime nitrogen seem to be involved [278]. Stability constants for the complexes of **(51)** with palladium(II) have been determined; again the structures were not specified [279]. $[Pd(MeCN)_2Cl_2]$ reacted with $PhCH_2N{=}C(Me)C(R){=}NOH$, HL, to give $[PdL_2]$. Binding in this case was through the deprotonated oxime and the imine nitrogen atom [280]. Complexes of the *syn*-oxime, **(52)**, with platinum have been prepared; in **(53)** coordination was through the oxime nitrogen and the pyridyl nitrogen atoms [281].

The ligand **(54)** was used for the determination of palladium(II) but the mode of binding was not specified [282]. The complexes $[M(TP)_2]$ and $[M(CPT)_2]$

M = Pd or Pt; TPH = **(55)**, CPTH = **(56)**) have been prepared. The authors suggested that TP was bonded through the urea oxygen and the NH group (it was not clear where they believed deprotonation to have occurred) and that **(56)** was bound through the amide carbonyl and the NH group in a polymeric structure. This seems unlikely in view of earlier data [265,283].



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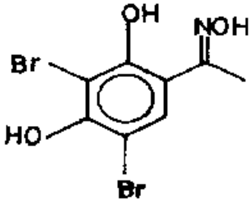

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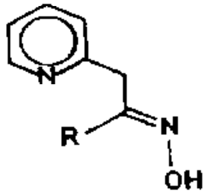

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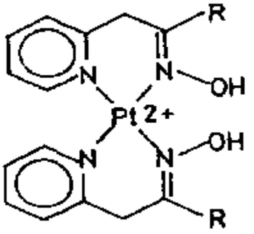

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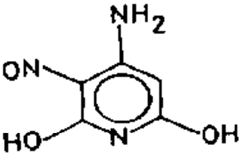

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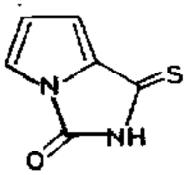

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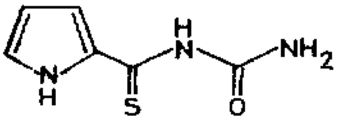


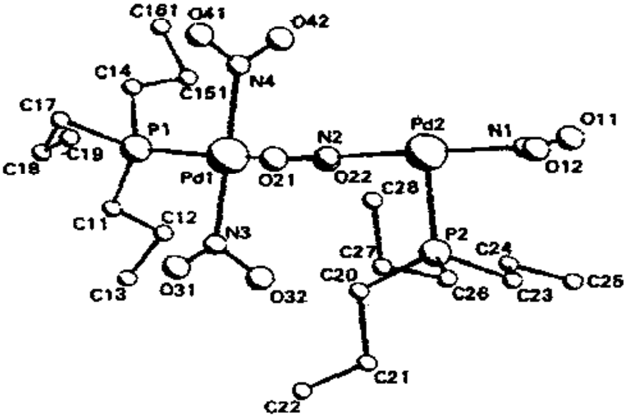
(56)

An X-ray diffraction study of $[Pd_4(NO_2)_4(\mu\text{-}ONO)_4(PPr_3)_4]$, **(57)**, prepared from $[Pd_2(PPr_3)_2Cl_4]$ and $Na[NO_2]$ in methanol, indicated Pd-O-N(O)-Pd bridges [284].

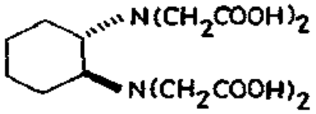
1.6.2.7 Bidentate and multidentate oxygen nitrogen donor ligands

The preparation and characterisation of [PtLL'] (L = 1,2-diaminobenzene, 2-aminophenol or 2-aminoethanol; H_2L' = HOOCCOOH or $HO_2CCH_2CO_2H$) has been described [285]. Complex formation between palladium(II) and $HO_2CCH_2N(CH_2COOH)_2$ has been investigated [286]. Palladium and platinum complexes of $RR^1NCH_2CH_2NR^2R^3$ ($R = R^2 = H$, $R^1 = R^3 = CH_2COOH$; $R = R^1 = H$,

$R^2 = R^3 = CH_2COOH$; $R = R^1 = R^2 = R^3 = CH_2COOH$) have been characterised. Metal ligand binding was exclusively through nitrogen in halo complexes but *N,O*-chelates were formed in the absence of halides [287]. The thermal decomposition of $[Pd(H_2L)]$ (H_4L = **(58)**) was investigated by DTA and thermogravimetry. The first process observed was loss of uncoordinated carboxyl groups. In $[Pd(H_4L)Cl_2].2HCl.2H_2O$ the initial loss was of water and subsequently of CO_2. H_4L was initially *N,N*-coordinated but after HCl loss it became tetradentate with binding also through deprotonated carboxylate groups [288]. Complexes of $(HOOCCH_2)_2NCH(CH_3)CH_2N(CH_2COOH)_2$ were also investigated; this ligand gave complexes analogous to those of edtaH_4 [289]. Equilibrium constants were determined for the reactions of $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$ with Pd^{2+} were determined but the structures of the species formed were not elucidated [290].

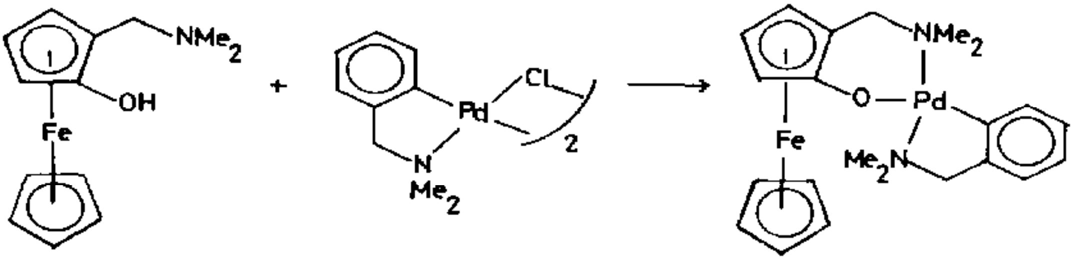


(57) (Reproduced with permission from [284])

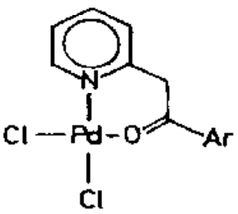


(58)

The reaction of the ferrocene derivative, **(59)**, with **(60)** gave **(61)** [291]. Extraction equilibria of palladium by trichloromethane solutions of 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol from aqueous chloride solutions showed that the extracted species was a simple chelate, $[ML_2]$, [292].


(59) **(60)** **(61)**

Palladium(II) complexes of 2-(substituted pyridyl)-1-phenyl ethanones and propanones have been prepared and characterised. Species such as [PdLCl$_2$}, **(62)**, [PdL$'_2$X$_2$], **(63)**, and [PdL$_2$], **(64)**, were described [293,294].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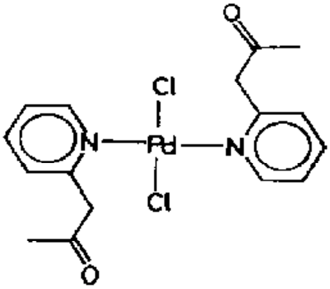
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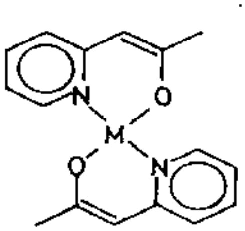
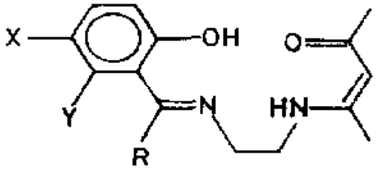

(64)

A range of *O,N*-chelating ligands involving an imine nitrogen atom and a deprotonated phenolic OH group have been studied. Interesting examples were provided by the ligands **(65)** [295] and **(66)** [296]. It was hoped to make molecular complexes of chelated species such as (67) and 1,3,5-trinitrobenzene. An X-ray diffraction study of the adduct showed that there were indeed π-π-molecular interactions between alternately stacked donors and acceptors [297]. A further study of the structures of α-bis(*N*-methyl-2-hydroxybenzaldiminato) metal complexes (M = Ni, Cu or Pd) has been reported. For the palladium complex only a commensurate monoclinic phase was found, but for the copper and nickel complexes there was also an incommensurate modulated phase [298].

Further complexes of 4-(2-pyridylazo)-1,3-dihydroxybenzene, H$_2$L, **(68)**, have been studied. Complexes of 1:1 and 3:2 stoicheiometry with palladium(II) were formed, depending on pH [299,300]. Soviet authors proposed a species involving coordination of the pyridine nitrogen atom, deprotonated OH and the N=N π-bond. Although the structure proposed was unlikely, these species supported on alumina were useful catalysts for nitrobenzene hydrogenation

[301,302]. Palladium complexes of 5-sulpho-2,2',4'-trihydroxyazobenzene and 3-sulpho-5-nitro-2,2',4'-trihydroxyazobenzene have been reported, but they were not simple 1:1 species, and the authors did not know which atoms were metal bound [303].



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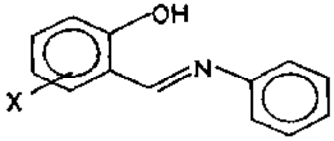

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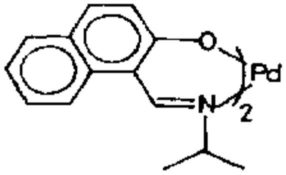

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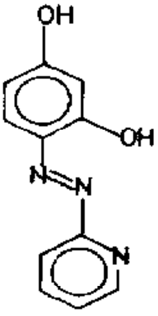
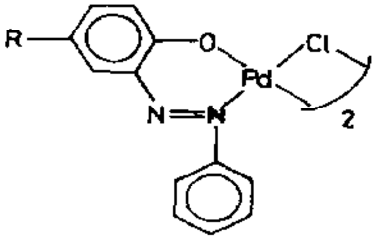


(68)

(69) could be synthesised from reaction of the ligand with $PdCl_2$ or by peracid oxidation of **(70)** [304]. In the reaction of **(71)** with palladium(II) three 1:1 complexes could be identified, the product formed depending almost entirely on the pH at which the reaction was conducted [305]. **(72)** was used in analysis of palladium(II) [306].

On the basis of ^1H nmr and IR spectroscopic data HL, RC(=O)C(=NNPh)C=O)R', exists as the hydrazone tautomer. In the complex $[PdL_2]$ an *N,O*-chelate was clearly formed and was equally clearly inaccurately represented [307]. In the (chroman-3-alkanoyl)hydrazone complexes $[MLCl_2]$ (M = Pd or Pt; R = Ph or Me), the structures **(73)** were proposed from IR spectroscopic data [308]. The series of complexes, **(74)**, were isolated and characterised [309]. Palladium(II) complexes of (75) (X = O or S) were coordinated through the amide and X^- functions, whilst those of **(76)** were carboxylate and N-H bound [310]. Numerous complexes of quinazoline-(3H)-4-ones, **(77)**, of stoicheiometry [PdL_2Cl_2] were prepared. In (77a) and (77b) the amino nitrogen atom was metal bonded whilst in **(77c)** and (77d) the NH group was said to be involved. In **(77e)** and **(77f)** the pyridyl nitrogen atom participated, whilst with **(77g)** and **(77h)** *O,O*-chelates were formed [311].



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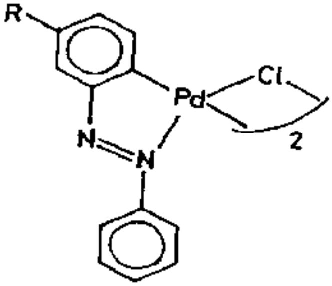

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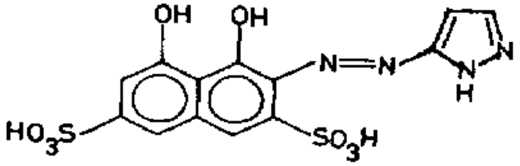

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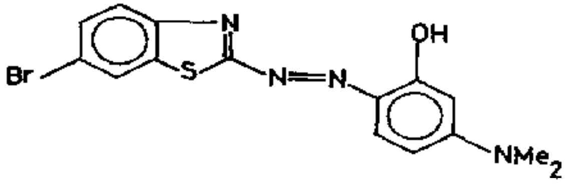

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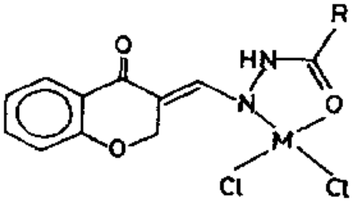

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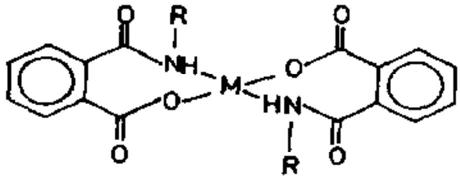

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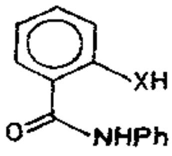

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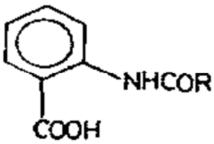

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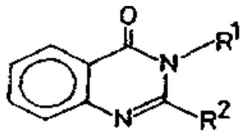
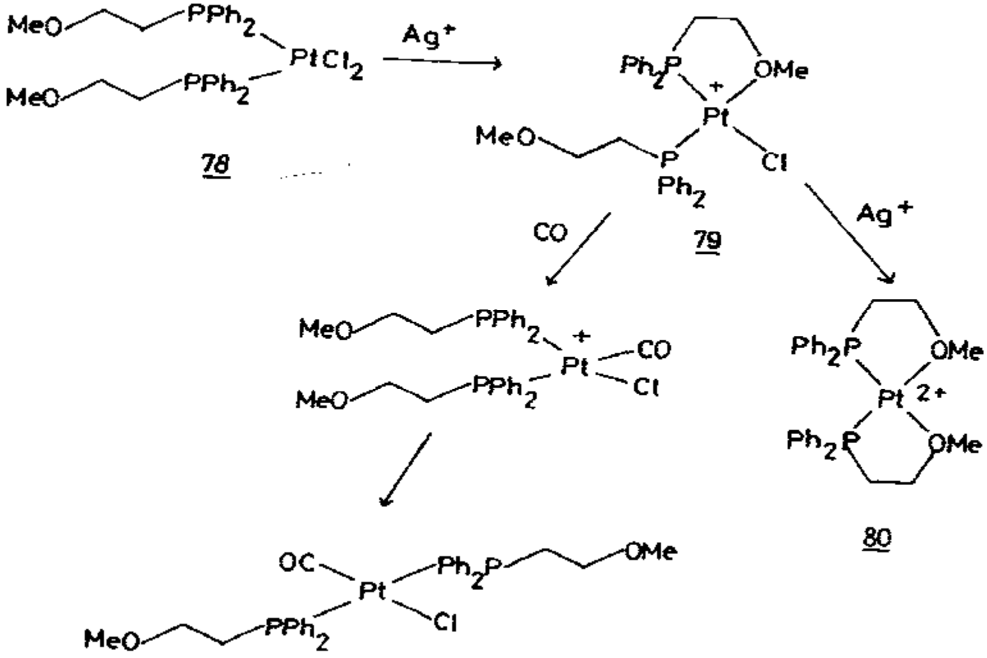


	R^1	R^2
(77a)	NH_2	Me
(77b)	NH_2	Ph
(77c)	NHPh	Me
(77d)	NHPh	Ph
(77e)	2-pyridyl	Me
(77f)	2-pyridyl	Ph
(77g)	OH	Me
(77h)	OH	Ph

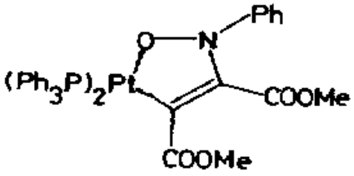
1.6.2.8 Bidentate oxygen phosphorus donor ligands

The reaction of $Ph_2P(CH_2)OMe$ with $[Pt(cod)X_2]$ was studied. The tendency of the ligand to form chelating complexes depended on the nature of the other ligands and the chelate size. For example, **(78)** was converted to **(80)** in the presence of Ag^+. The intermediate, (79) reacted readily with carbon monoxide [312].



1.6.2.9 Bidentate oxygen carbon donor ligands

$[Pt(PPh_3)_2(\eta^2\text{-}PhNO)]$ reacted with $MeOOCC\equiv CCOOMe$ to give **(81)**, characterised by X-ray diffraction [313].



(81)

1.6.2.10 Unidentate sulphur donor ligands

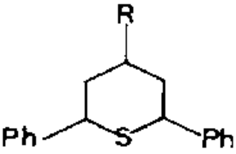
A range of complexes of *N*-methylpiperidine-4-thiol (HRS) including species of formula $[M(HRS)X_2].nH_2O$, $[Pd(HRS)_2][Y]_2.2H_2O$ and $[M(RS)_2]$ were prepared (M = Pd or Pt, X = Cl, Br or I; $[Y] = [NO_3]$ or $[ClO_4]$). IR spectroscopic data implied that only the sulphur atoms were metal coordinated, and all the complexes appeared to be polymeric [314].

Reliable syntheses of $[\{Pt(Me_2S)Cl_2\}_2]$, $[Bu_4N][Pt(Me_2S)Cl_3]$ and $[Pt(Me_2S)_3Cl][BF_4]$ have been published [315,316]. In basic solution the ammine ligands in *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ were displaced by hydroxyl ion in two stages. A mechanism involving an octahedral diaquated complex was proposed [317]. Reactions of other nucleophiles were also studied. The high *trans*-effect of the Me_2S ligand meant that the first leaving group was ammonia, with rate constants for the incoming nucleophile in the order $Cl^- < [NO_2]^- < [N_3]^- < Br^- < [SCN]^- < I^-$. Further displacement of ammonia occurred when the nucleophile was a halide, but with the other species Me_2S was the favoured leaving group [318].

Trans-$[PtL_2Br_2]$ (L = **(82)**, R = H, Me or Ph) was prepared from *trans*-$[PdL_2Cl_2]$ and KBr in aqueous propanone. The complexes proved to have moderate antimicrobial but low antifungal activity [319]. Treatment of $[Pt(NH_3)_2X_2]$ with 4-thiahepta-1,6-diene, L, gave initially *trans*-$[Pt(NH_3)_2(OH)L]^+$ for X = Cl, but little reaction when X = $[NO_2]$. A sulphur bridged polymer was formed by reaction with the starting material. With the *cis*-isomer, *cis*-$[Pt(NH_3)_2L_2]$ was formed. In all cases the sulphide was coordinated at sulphur with no apparent interaction with the carbon-carbon double bonds [320,321].

Polarographic reduction of $[Pt(NH_3)_2(tu)Cl]Cl$ was shown to be a two electron process [322].

The complexes $[M(PPh_3)_2L_2]$ (M = Pd or Pt, HL = $PhNHCS_2Et$) were prepared and characterised; they appeared to involve monodentate *S*-coordination of the ligand [323]. Complexes of *N,N*-dimethyl-*O*-ethylthiocarbamate (DMTC), *cis*-[Pt(DMTC)$_2$Cl$_2$], were shown to increase mitochondrial oxygen consumption, to inhibit Co(II) accumulation and to induce release of accumulated calcium(II) in rat liver mitochondria. The corresponding *trans*-complex had little effect. The *cis*-isomer also reduced the transmembrane potential and inhibited the ATPase activity of submitochondrial particles; again the *trans*-complex had a lesser effect [324].



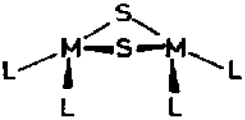
(82)

When *trans*-[(C$_6$F$_5$)M(PR$_3$)$_2$(OClO$_3$)] was treated with $[R'_3PCS_2]^-$, *trans*-[(C$_6$F$_5$)M(PR$_3$)$_2$(S$_2$CPR$'_3$)][ClO$_4$] was formed (M = Pd, R$_3$ = R$'_3$ = Et$_3$, Bu$_3$ or Et$_2$Ph or R = Bu, R' = Cy or R = Ph, R' = Et or Cy; M = Pt, R = R' = Et or Bu). The related bipy complexes were also prepared and the structure of *trans*-[(C$_6$F$_5$)Pt(PEt$_3$)$_2$(S$_2$CPEt$_3$)][ClO$_4$] was established by X-ray diffraction [325].

Reaction of 1-methyl imidazoline-2(3H)-thione (Mimt) with PdCl$_2$ in the presence of HCl gave an orange-red complex [Pd(Mimt)$_4$]Cl$_2$.2H$_2$O. All the ligands were *S*-bonded [326]. [Pd(ECl$_2$)Cl$_2$] (E = S or Se) was prepared from PdCl$_2$ in non-aqueous solution and was characterised (E = S) by X-ray diffraction. The sulphur atom was directly coordinated to the palladium [74].

1.6.2.11 Bidentate and multidentate sulphur donor ligands

XPES data were reported for [(Ph$_3$P)$_2$Pt(μ-S)$_2$Pt(PPh$_3$)$_2$], [(Ph$_3$P)$_2$Pt(μ-S)(μ-SMe)Pt(PPh$_3$)$_2$] and [{Pt$_2$(μ-S)$_2$L$_4$}$_2$Hg][BPh$_4$]$_2$. These indicated that the phosphines were σ-coordinated to platinum with only a small degree of metal to ligand back donation [327]. Both this type of complex and [{Pt(PPh$_3$)(μ-SMe)}$_2$] adopted a square planar geometry, **(83)**. Reaction of [{Pt(PPh$_3$)(μ-SMe)}$_2$] with NO gave **(84)**, identified by X-ray diffraction [328].



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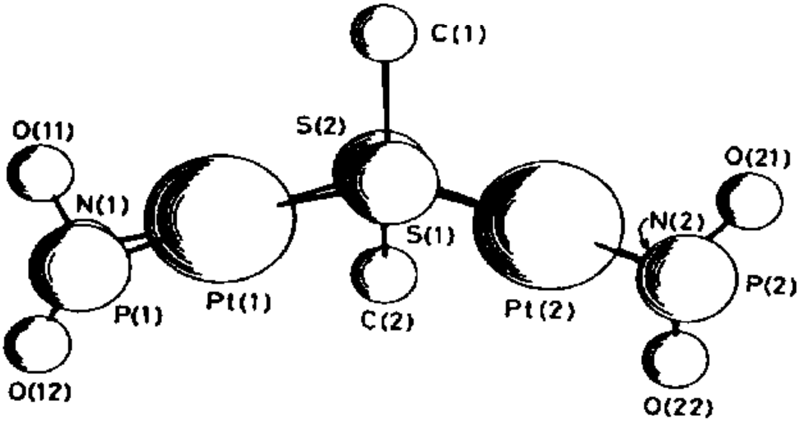
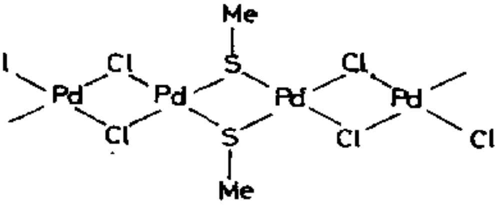


(84) (Reproduced with permission from [328])

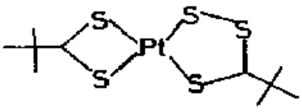
For reasons of clarity the phenyl rings have not been shown.

Progressive heating from 350-550 °C of [Pd(metH)(NH$_3$)$_2$][PdCl$_4$] in air or in an inert atmosphere gave the polymer (85) [329].



(85)

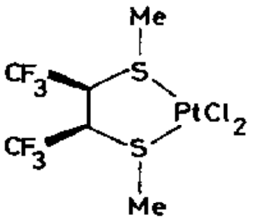
The reaction of 2-hydroxydithiobenzoic acid, HL, with [MCl$_4$]$^{2-}$ gave [ML$_2$] (M = Pd or Pt). The mode of binding of the ligand was not entirely clear [330]. The structure of **(86)** was determined by X-ray diffraction [331].



(86)

X-ray diffraction data for (87) and (88) have been reported. In **(87)** the *S*-methyl groups were *syn* and lay on the opposite side of the chelate ring to the trifluoromethyl substituents. This corresponds to the main solution conformation [332]. The *S*-methyl groups in **(88)** were also mutually *syn*

[333]. Tetraalkyl ammonium salts of **(89)** have been used in the production of high density optical recording media [334]. In a designed synthesis of novel one-dimensional materials with a *pseudo*$(SN)_x$ bundle structure a 1:1 complex of $[Pt(dept)_2]^{2-}$ and bis(benzildioxime)copper was prepared (H_2dept = **(90)**). Epr measurements in the solid state and in solution revealed that $\{PtS_4\}$ and $\{CuN_4\}$ units alternated in the stack [335].



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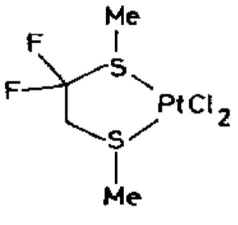

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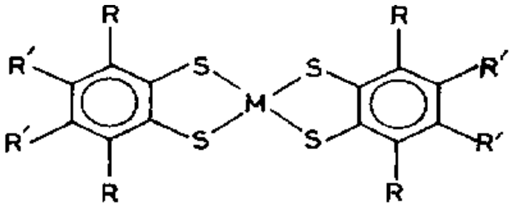

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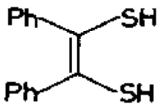
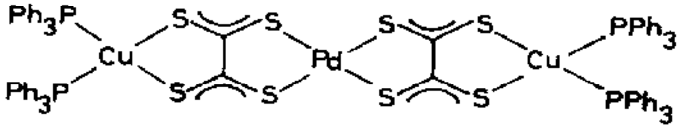


(90)

The synthesis of mixed metal dithiooxalate complexes such as **(91)** has been described [336]. The related polymers, **(92)** and **(93)** have also been prepared [337]. Bimetallic one-dimensional compounds with dithiooxalate ($[S_2C_2O_2]^{2-}$) bridges of formula $[AMn(S_2C_2O_2)_2(H_2O)_3].4.5H_2O$ (A = Cu, Ni, Pd or Pt) have been prepared. X-ray diffraction data for the copper, nickel and platinum complexes revealed that they were isostructural, **(94)**, with extended zig-zag chains. The A atoms formed a stack coordinated to four sulphur atoms and the manganese (II) atoms bridged the stacks, coordinated by six oxygen atoms [338].



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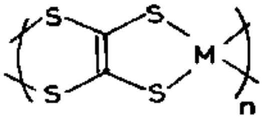

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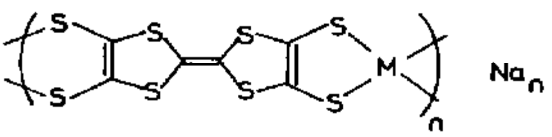

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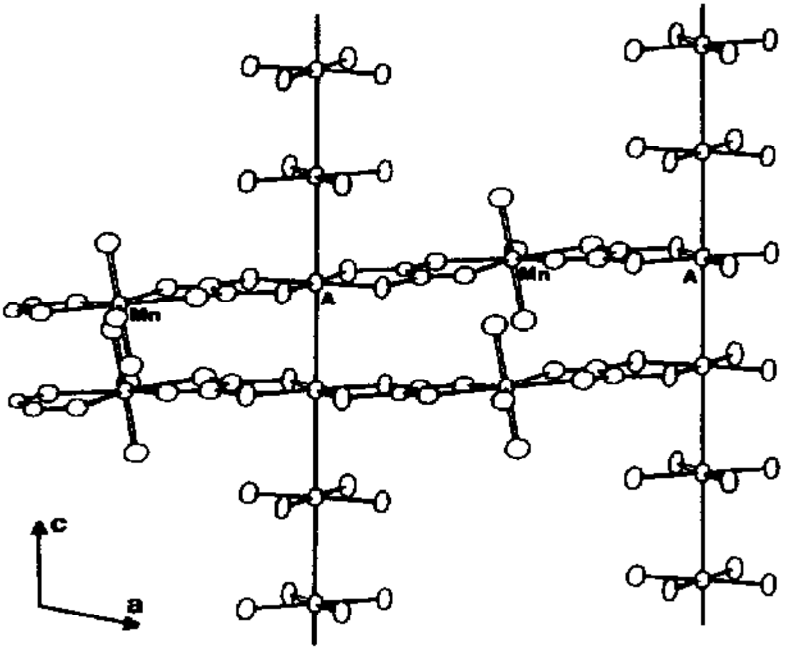


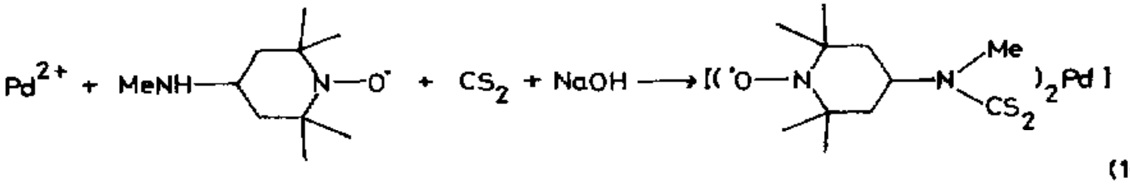
(94) (Reproduced with permission from [338])
Partial view down the *b*-axis of stacked ...A-($S_2C_2O_2$)-Mn(H_2O)$_3$-($O_2C_2S_2$)... chains, emphasising the columnar stucture generated by the AS_4 fragments.

Kinetic data for reaction (15) (L = [mnt], L' = isomaleonitrile diselenate) have been determined [339]. Liquid chromatographic separation of $[mnt]^{2-}$ complexes of palladium(II) and platinum(II) has been established using a reversed phase ion pair technique. This procedure was used for the spectrophotometric determination of $[Pd(mnt)_2]^{2-}$ and $[Pt(mnt)_2]^{2-}$ [340].

$$[CuL_2]^{2-} + [PdL'_2] \rightleftharpoons [CuLL']^{2-} + [PdLL']^{2-} \qquad (15)$$

Interest in dithiocarbamate complexes has continued. The species $[ML_2]$ (M = Co, Ni, Pd or Pt; HL = Ar_2NCS_2H, Ar = 2-, 3- or 4-ClC_6H_4) were prepared and characterised [341]. He I and He II PES of $[M(S_2CNEt_2)_2]$ (M = Zn, Ni, Pd or Pt) were reported. The assignment of the bands was based on experimental criteria and considerations of symmetry and overlap. Metal and chromophore based levels could be clearly identified and an estimate of the perturbations on the chromophore of complexation derived. The data indicated an increase in π-bonding capability from nickel to palladium to platinum [342]. The complexes $[Pd(S_2CNR_2)_2]$ (R = Pr, Bu, CH_2CHMe_2 or CF_3CH_2) were prepared and studied by X-ray diffraction, IR spectroscopic and thermogravimetric techniques [343]. ΔS^* values for redox reactions of dithiocarbamato complexes have been determined in non-aqueous solvents. The differences between the experimental data and those predicted theoretically were largely due to solvation effects [344].

Complexes of spin labelled dithiocarbamato ligands were prepared according to reaction (16) [345]. A simple, rapid and sensitive HPLC assay for *cis*-platin in human plasma ultrafiltrate and urine has been described. The drug was first chelated by exchange with diethyl dithiocarbamate and then extracted into trichloromethane [346]. Insoluble polyethenedithiocarbamate on an inert support has been used to recover palladium(II) from aqueous $Na_2[PdCl_4]$ [347]. The species $[ML_2$ (M = Pd or Pt, HL = $(HOCH_2CH_2)_2NCS_2H$) were prepared, and their interactions with $[CuL_2]$ studied [348].

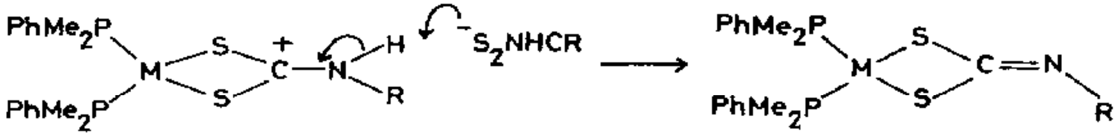


(16)

Mixed phosphine dithiocarbamate complexes could be prepared by several routes. Reaction of a bis(dithiocarbamate), $[M(S_2CNHR)_2]$, with R'_3P gave initially $[M(S_2CHNR)_2(PR'_3)]$. In the presence of iodine $[M(S_2CHNR)(PR'_3)I]$ was formed (M = Pd or Pt), and for M = Pt this could be converted to $[Pt(SnCl_2I)(S_2CNHR)(PR'_3)]$ by $SnCl_2$ [349]. However, with R'_3P = PMe_2Ph or ½[dppe], and in the absence of further reactants, one dithiocarbamate ligand was lost and subsequently effected deprotonation of the complex to give **(95)** [350]. Species of the type **(95)** could also be prepared by reaction of $[M(PR_3)_2Cl_2]$ with $R'NH_2/CS_2$ [351]. Treatment of $[Pt(S_2CNR_2)\{(Ph_2PO)_2H\}]$ with $[M(acac)_n]$ (R = $CHMe_2$ or Et; M = VO, Co, Cu or Ni, n = 2 or M = Mn, n = 3) gave the mixed species (96) [352,353].

The infra-red spectra of *O*-ethylmethyldithiophosphonate complexes, $[Pd(S_2P(OEt)Me)_2]$, were compared with those of related species [354]. ^{195}Pt nmr spectroscopy of $[Pt(LL)_2]$ where LL = $[S_2PR_2]^-$, $[S_2P(OR)_2]^-$ and $[S_2CNR_2]^-$ gave platinum signals over a very large range of frequencies.

Reaction of $[Pt(S_2PR_2)_2]$ (R = Me or Ph) with a phosphine, R'_3P, occurred in two distinct steps (reaction (17)). In the intermediate, **(97)**, there was fast exchange between the mono and bidentate ligands. The reaction with the complex of $[S_2P(OR)_2]^-$ was, however, more complex (Scheme 2) [355].



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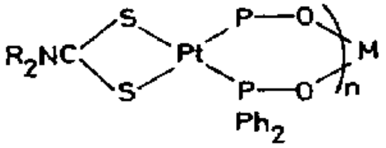


(96)

$$[Pt(S_2PR_2)_2] \;+\; R'_3P \longrightarrow [(R_2PS_2)Pt(R_2PS_2\text{-}S)(PR'_3)]$$

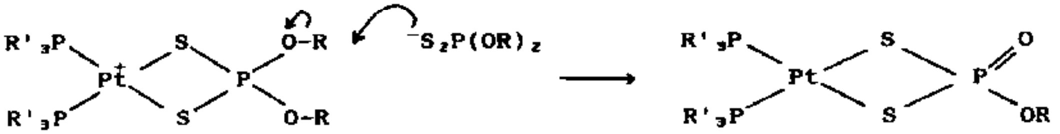
(97)

$$\downarrow\uparrow \quad R'_3P$$

$$[(R_2PS_2)Pt(PR'_3)_2]^+ \qquad (17)$$

$$[Pt\{S_2P(OR)_2\}_2] + R'_3P \longrightarrow [P(S_2P(OR)_2)(PR'_3)_2][S_2P(OR)_2]$$

(98)

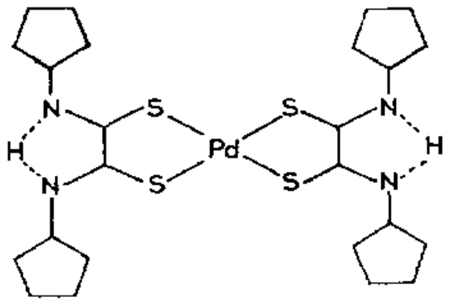


(98)

$+\ (RO)_2PS_2R$

Scheme 2 Reaction of $[Pt\{S_2P(OR)_2\}_2]$ with phosphines [355].

Treatment of $[Pd(dppe)Cl_2]$ with $[HL']^-$ gave $[Pd(dppe)L']$ where H_2L' = $(HSCH_2)_2Se$ or $(HSeCH_2)_2Se$. The complexes were characterised by IR and nmr spectroscopy [356]. Bidentate *S,S*-chelation was established by an X-ray diffraction study in **(99)** [357]. Palladium and platinum complexes of the ionophore, **(100)**, $[MLCl_2]$, acted as anion exchangers. It was not entirely clear how the metals were bound, but an *S,S*-coordination mode seemed the most likely [358].



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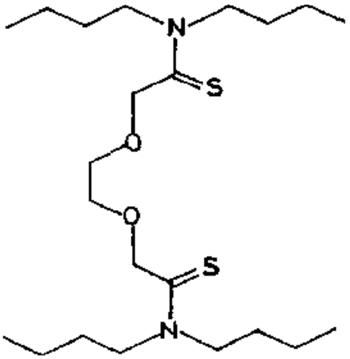
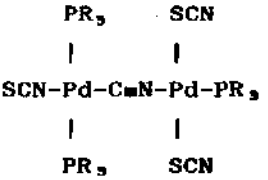


(100)

1.6.2.12 Ambidentate sulphur nitrogen donor ligands

Thiocyanate could be determined in the presence of bromide by precipitation with palladium chloride as $[Pd(SCN)_2]$ [359]. A long-standing controversy as to linkage isomerism in palladium thiocyanate complexes of phen derivatives appears to have been resolved. When the 5-nitrophen complex was prepared in dmf and isolated by pouring into cold ethanol the di *N*-coordinated isomer was formed. However, preparation in ethanol at 60 °C gave the di-*S*-bonded complex. Heating the *N*-coordinated isomer in the solid state gave the *S*-bonded species, which appeared to be the thermodynamic product [360]. UV irradiation of *trans*-$[Pd(PPr_3)_2(NCS)_2]$ gave a stepwise reaction resulting ultimately in the formation of **(101)**, characterised by X-ray diffraction. It seems likely that the first step in the process was the formation of a linkage isomer [361].



$$\begin{array}{ccccc} & PR_3 & & SCN & \\ & | & & | & \\ SCN- & Pd & -C{\equiv}N- & Pd & -PR_3 \\ & | & & | & \\ & PR_3 & & SCN & \end{array}$$

(101)

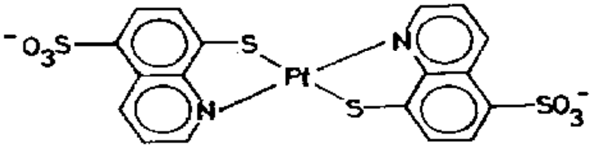
Excitation of aqueous acidic $[Pt(SCN)_4]^{2-}$ in a ligand field band gave $[Pt(SCN)_3(H_2O)]^-$. However, excitation in the ligand to metal CT band yielded $[Pt(SCN)_2(H_2O)_2]$ *via* a chain reaction of a radical pair [362].

An X-ray crystallographic determination of the structure of *cis*-[Pd(SNNMe$_2$)(AsPh$_3$)Cl$_2$] demonstrated that the *N*-thionitrosodimethylamine ligand was *S*-bonded to palladium. The palladium-sulphur bond was very short (2.249(1) Å) A number of other complexes of this ligand were also prepared, all *S*-coordinated [363]. A polarographic study of [Pt(NH$_3$)$_2$(tu)Cl]Cl has been reported, as have its reactions with a range of anions [364]. Palladium(II) formed 1:1, 1:2 and 1:4 complexes with PhSO$_2$NHCSPh. Stability constants and reaction rates were determined, but modes of binding were not [365].

1.6.2.13 Bidentate and multidentate sulphur nitrogen donor ligands

The tlc of metal chelates of several derivatives of the ligands 8-mercapto-1,2,3,4-tetrahydroquinoline, 2-mercaptoaniline and *N,N*-dimethyl-2-mercaptoaniline has been studied. Both palladium(II) and platinum(II) formed simple [ML$_2$] complexes with the deprotonated thiol and amino groups metal coordinated [366]. A related range of 8- and 2-substituted quinoline and quinoline-*N*-oxide derivatives was also investigated. The complexes with *S,N*- or *S,O*-coordination gave satisfactory results on chromatography, but *N,O*- and *O,O*-chelates were adsorbed irreversibly or showed strong tailing [367].

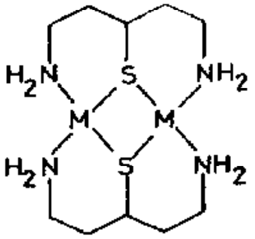
The dependence of the rates of ATP hydrolysis by Ca^{2+} and Mg^{2+} activated ATPase, and Ca^{2+} transport through sarcoplasmic reticulum (SR) membrane modified by synthetic phospholipids and other manufactured triglycerides was studied as a function of triglyceride structure. Platinum 5-sulpho-8-mercaptoqinolinate, (102), was shown to inhibit the ATPase of lipid modified SR more than it did before modification [368].



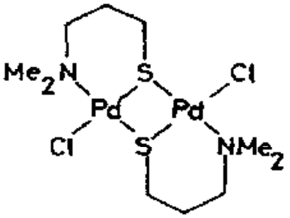
(102)

The ligands H$_2$NCH$_2$CH$_2$CH(SH)CH$_2$CH$_2$NH$_2$ and H$_2$NCH$_2$CH$_2$CH(OH)CH$_2$CH$_2$NH$_2$ both formed similar binuclear complexes such as [(**103**)][ClO$_4$]$_2$ (M = Pd or Pt), the structure of the complexes being maintained in solution [369]. The structure of the related species, (**104**), was determined by X-ray diffraction techniques. Despite a somewhat disordered structure it was clear that the palladium-sulphur bonds were abnormally short [370].

The structure of [Pt{H$_2$N(CH$_2$)$_3$S(=O)Me}Cl$_2$] was determined by X-ray diffraction. The sulphur and nitrogen atoms of the amino sulphoxide were platinum coordinated and the six-membered chelate ring adopted a chair conformation [371].

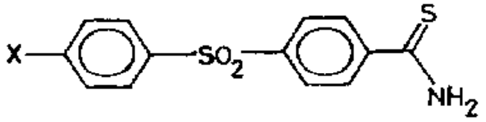


(103)



(104)

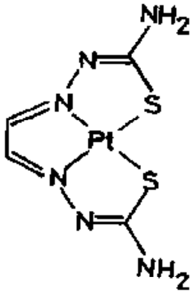
Further thioamide complexes have been prepared. In derivatives of **(105)**, HL, such as $[Pt(HL)Cl_2]$, (105) was coordinated *via* the thiocarbonyl and the amino group. In $[PtL_2]$ the amino group was said to be deprotonated in a *trans*-complex [372]. Palladium analogues were also synthesised [373]. However, other workers proposed structures involving thiol and thiolate tautomers on the basis of IR and UV spectroscopic evidence [374].



(105)

The electronic spectra of the complexes $[MLCl_2]$ and $[ML_2Cl_2]$ (M = Ni or Pd; L = thiosemicarbazide, 1-phenylthiosemicarbazide or 4-phenylthiosemicarbazide) have been recorded [375]. [Pt(glyoxal bisthiosemicarbazone)], (106), and $[PtL'_2]$ ($HL' = H_2NC(=S)NHN{=}C(CH_3)COOH$) were investigated for their (rather limited) antibacterial properties [268]. The electrochemical behaviour of the palladium(II) complexes of **(107)** was investigated, unfortunately after little attempt to establish their structures conclusively [376]. Diphenylthiocarbazone complexes of stoicheiometry $[PdL_2]$ were also studied [377].

Complexes of dithiocarbazic acid esters, H_2NNHCS_2Me (L) and $PhNHNHCS_2Me$ (PhL) were prepared. In $[PtL_2]Cl_2$ the ligands were coordinated as the ammonium salts, (108), whilst in $[Pt(PhL)_2Cl_2]$, PhL acted as a unidentate ligand, coordinated through the thiocarbonyl group. Both *cis*- and *trans*-isomers could be isolated. In the species $[Pt(L\text{-}H)_2]$, $[Pt(L\text{-}2H)_2]$, $[Pt(PhL\text{-}H)(PhL)Cl]$, $[Pt(PhL\text{-}H)_2]$ and $[Pt(PhL\text{-}2H)_2]$ XPES indicated that the platinum atom was still in the +2 oxidation state, the ligand having been oxidised. Structures such as (109) were proposed for $[Pt(L-H)_2]$, which existed as a *cis/trans*-mixture in slow equilibrium in solution [378].



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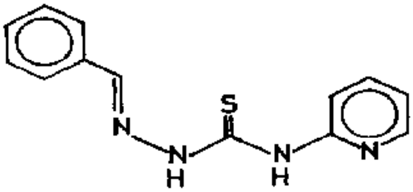
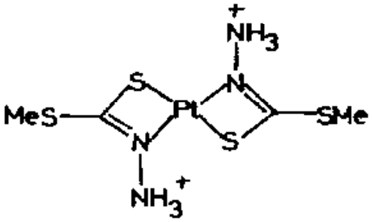


(107)



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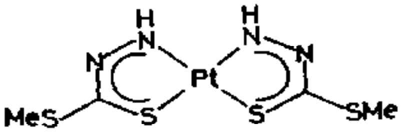
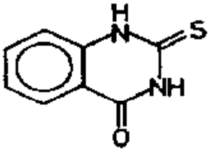


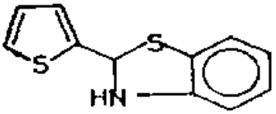
(109)

Milligram quantities of platinum(II) could be extracted using 2-mercaptobenzthiazole (HL) in chlorinated solvents. The species extracted was $[ML_2]$, which precedent suggests should be an *S,N*-chelate [379]. 2-Thio-4-oxo-1,2,3,4-tetrahydroquinazoline, **(110)**, formed a 1:1 complex with palladium(II); this could be used for determination of the ligand [380].



(110)

Reaction of 2-mercaptoaniline with thiophene-2-carbaldehyde gave **(111)**. On reaction with $[Pd(PhCN)_2Cl_2]$ this gave a red complex of stoicheiometry [PdLCl]. Although the data provided was not definitive, the most likely structure appeared to be **(112)** in which the thiazoline ring had been opened [381].



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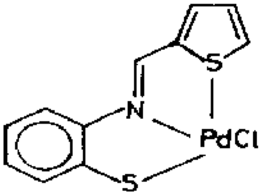
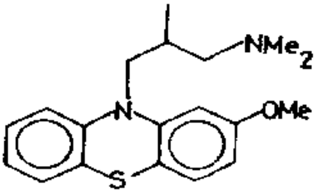
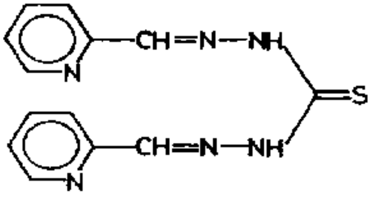


(112)

A range of complexes, $[PdLCl_2]$, of *N*-alkylphenothiazines such as **(113)** were prepared. IR spectroscopic data suggested that both the sulphur atom and the NMe_2 group were metal bound, and it seems likely that the complexes are polymeric [382]. Palladium(II) complexes of **(7)** were also prepared, with little effort at proper structural characterisation [80]. The complex $[Pd(\mathbf{114})_2]$ was said to involve *N,S*-coordination of the thiourea, but little evidence was presented [383].

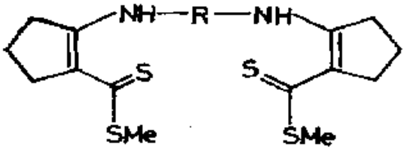


(113)



(114)

Several complexes of the tetradentate ligand, **(115)**, (H_2L), have been prepared (R = $CH_2CH(CH_3)$, $(CH_2)_3$ or $CH_2CH_2NHCH_2CH_2$). In [PdL], S_2N_2-coordination obtained, whilst in [Pd(HL)X] the donor unit was N_2S. Structure (116) was proposed for the derivative of **(115)** (R = $CH_2CH_2NHCH_2CH_2$) [384]. (117), related to **(45)**, was characterised by X-ray diffraction techniques. Both palladium atoms adopted square planar coordination and the palladium-palladium distance was the longest recorded (3.66 Å) for such atoms bridged by an ethanoate group [385].



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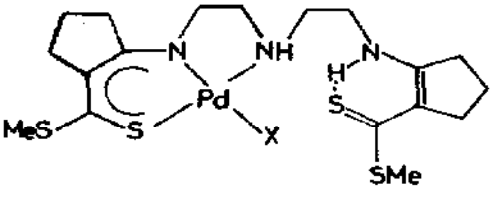
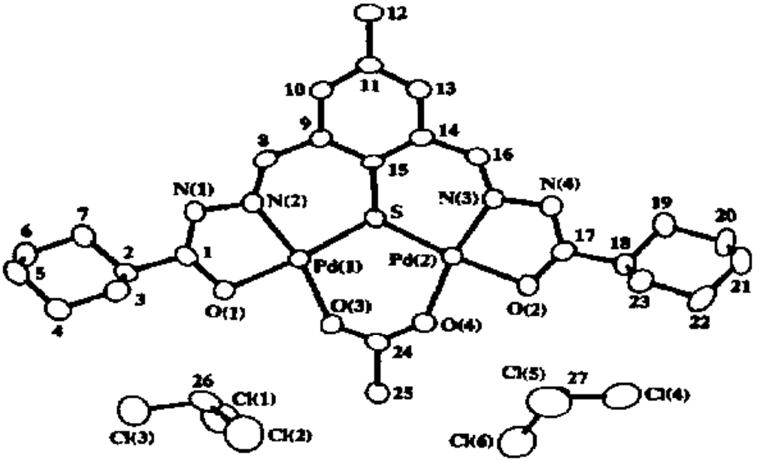


(116)

1.6.2.14 Bidentate and multidentate sulphur phosphorus donor ligands

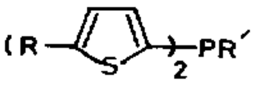
$[Cy_2PCS_2]^-$ acted as a *P,S*-chelate in the complexes $[PdL_2]$ and $[PtL_2]$.

both of which were shown to possess *trans*-geometry by an X-ray diffraction study [386].



(117) (Reproduced with permission from [385])

The thiophene substituted phosphines, **(118)** (R = H or Me; R' = Et or Ph) were said to act as *P*,*S*-chelates in [PdLCl$_2$]; the evidence presented was limited [387]. Reaction of Ph$_2$P(CH$_2$)$_n$SPh with [Pd(PhCN)$_2$Cl$_2$] gave [Pd{Ph$_2$P(CH$_2$)$_2$SPh}Cl$_2$], a predictable *S*,*P*-chelate, from the ligand for which *n* = 2, but a tetramer, **(119)**, when *n* = 1. With an excess of either ligand *cis*-[PtL$_2$Cl$_2$] was formed, but the palladium complex produced possessed *trans*-geometry. Reaction of *trans*-[Pd{Ph$_2$P(CH$_2$)$_2$SPh}$_2$Cl$_2$] with Na[BPh$_4$] gave successively [Pd{Ph$_2$P(CH$_2$)$_2$SPh-*S*,*P*}{Ph$_2$P(CH$_2$)$_2$SPh-*P*}Cl][BPh$_4$] and [Pd{Ph$_2$P(CH$_2$)$_2$SPh-*S*,*P*}$_2$][BPh$_4$]$_2$. In the mixed complex, ^{31}P nmr spectroscopy demonstrated that the bound phosphines were mutually *cis* [388]. Reaction of [Pt(cod)X$_2$] (X = Cl or Br) with Ph$_2$PCH$_2$CH$_2$SMe gave initially the chelated complex [Pt(Ph$_2$PCH$_2$CH$_2$SMe)X$_2$], with *cis*-[Pt(Ph$_2$PCH$_2$CH$_2$SMe)$_2$] formed in the presence of an excess of the ligand and Ag[BF$_4$] [312].



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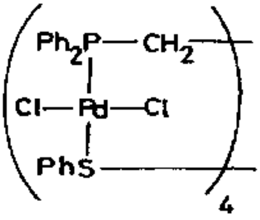
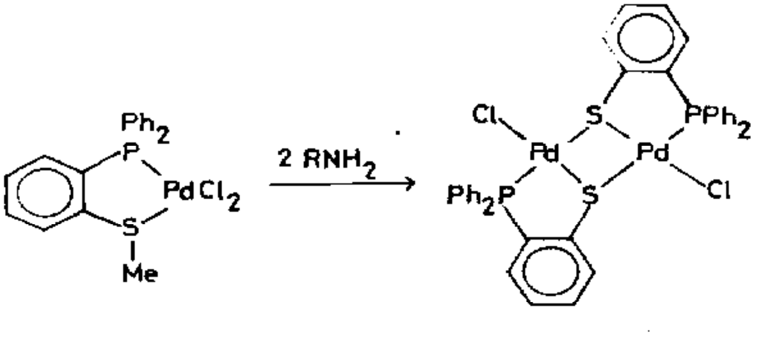


(119)

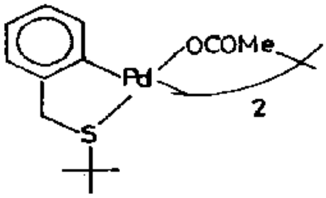
Reaction of **(120)** with RNH$_2$ gave the demethylated binuclear complex, (121). Demethylation of $[Pd\{2-MeS(C_6H_4)PPh_2\}_2]^{2+}$ also occurred, with isomerisation of the *cis*-starting material to a *trans*-product. The mechanism proposed involved the amine in nucleophilic attack by an SN_2 Menschutkin type reaction at the methyl group of the thioether [389].

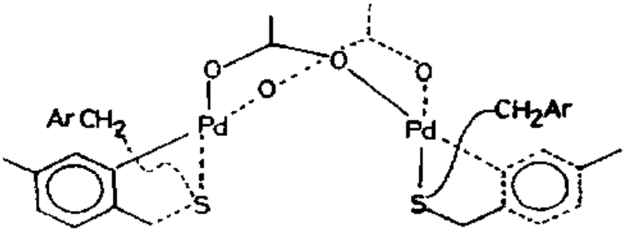


(120) **(121)**

1.6.2.15 Bidentate sulphur carbon donor ligands

Reaction of palladium chloride with Me_3CSCH_2Ph gave a thiol bridged polymer, $[\{Pd_2(\mu-SCH_2Ph)_2Cl_2\}_n]$ by cleavage of a sulphur carbon bond. However, with palladium ethanoate the first product was $[Pd\{S(CH_2Ph)CMe_3\}_2(OCOMe)_2]$, which on heating in methanol gave a cyclometallated ethanoate bridged complex, (122). This underwent the expected substitution and bridge splitting reactions [390]. Reaction of $4-MeC_6H_4CH_2SCH_2C_6H_4-4-NO_2$ with palladium ethanoate gave a single isomer of the cyclometallated complex, (123), in which metallation had taken place only at the electron rich ring [391].





(122) **(123)**

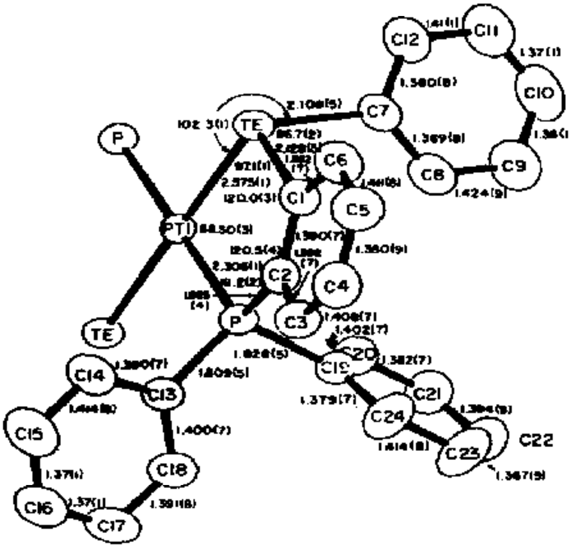
1.6.2.16 Selenium donor ligands

The epr spectra and ion impact mass spectra of the selenothiocarbamate complexes $[M\{Se(S)CNEt_2\}_2]$ (M = Cu, Ni, Pd or Pt) have been reported. At high temperatures irreversible rearrangement to $[M\{Se(S)CNEt_2\}(Se_2CNEt_2)]$ and

$[M\{Se(S)CNEt_2\}\{S_2CNEt_2\}]$ occurred, at a rate determined by temperature, metal and solvent [392].

1.6.2.17 Tellurium donor ligands

Reaction of $K_2[PtSCN)_4]$ with $2\text{-}(PhTe)C_6H_4PPh_2$ (tep) yielded $[Pt(tep)_2][Pt(SCN)_4]$. The structure, **(124)**, was determined by X-ray diffraction and represents the first example of a structurally characterised $[Pt(SCN)_4]^{2-}$ complex other than $K_2[Pt(SCN)_4]$ [393].



(124a) (Reproduced with permission from [393])

Bond lengths and selected angles in the $[Pt(tep)_2]^{2+}$ cation

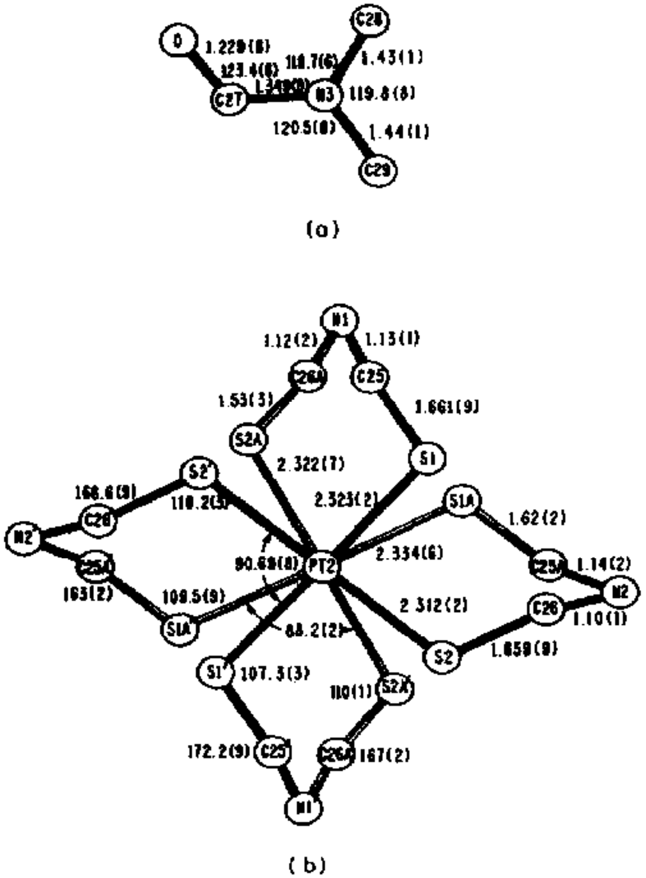
1.6.3 Complexes with amino acids, peptides and nucleic acids

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

New methods for electroless deposition of palladium and alloy contacts for semiconductor devices have been developed. For example, palladium Schottky contacts with silicon were prepared by reductive deposition with $H_2[PdCl_4]$ in baths containing amino acids, amino alcohols, $Na[H_2PO_2]$ or hydrazine [394].

The structure of *cis*-$[Pt(py)(H_2NCH_2COOH)Cl_2]$ was determined by X-ray diffraction techniques. The glycine was bonded through the NH_2 group, and there were intermolecular hydrogen bonds involving the carboxylate groups [395]. Complete thermolysis of $[Pt(NH_3)_3(glyH)]Cl_2$ yielded $[NH_4]Cl$, HCl, glyH and platinum amides. However, heating to only 150 °C gave a colour change from white to yellow, purportedly associated with the displacement of glycine from the coordination sphere [396]. Reaction of $[Pd(gly)_2]$ with thionyl chloride gave a mixture of *cis*- and *trans*-$[Pd_2(H_2NCH_2COCl)_2Cl_4]$ [397].

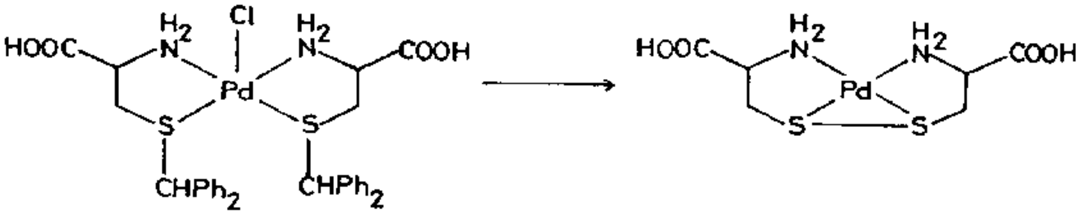


(124b) (Reproduced with permission from [293])

Bond lengths and angles for dmf (a) and $[Pt(SCN)_4]^{2-}$ (b). The anion was disordered involving alternate positions for the sulphur and carbon atoms labelled S1A, S2A, C25A and C26A.

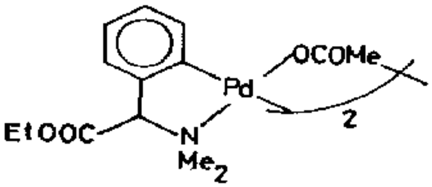
FAB, FD and desorption CI mass spectrometric techniques have been used for analysis of the species *cis*-$[Pt(\text{amino acid anion})Cl_2]^-$ and of dipeptide complexes. Desorption CI was only useful for non-ionic species, but FD could be used for both ionic and non-ionic complexes [398]. Nmr spectroscopic data for palladium methionine complexes have been reported [399]. A rather poorly defined complex of palladium(II) with L-arginine was studied polarometrically. A quasi-reversible reduction with a two electron wave was described [400].

Treatment of $K[PdLCl_2]$ with a four molar excess of HL' (HL = alaH, HL' = glyH, valH or proH; HL = proH, HL' = valH) gave the mixed complex [PdLL']. Reaction of this successively with HCl, NH_3 and a further equivalent of $K_2[PdCl_4]$ yielded $[Pd(HL)(HL')(NH_3)_2][PdCl_4]$. The new complexes were characterised by IR spectroscopy and thermogravimetric measurements [401]. The reactions of $PdCl_2$ with an amino acid derivative could be shown to yield $[PdL_2Cl_2]$ (L = L-serine methyl ester), $[PdL'_2Cl_2]$ (HL' = *S*-Me_3C-L-cysteine or *S*-ethanamidomethyl-L-cysteine) or $[PdL^2_2]$ (HL^2 = *O*-benzyl-L-serine). L acted as an *O*,*N*-chelate and L' as an *S*,*N*-chelate. When *S*-diphenylmethyl-L-cysteine was used as the reactant the initial product was **(125)** which was rapidly converted to (126) [402].



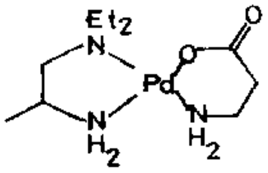
(125) **(126)**

The complexes *trans*-$[Pd(HL)_2Cl_2]$ in which HL was an amino acid, amino acid ester, dipeptide or dipeptide ester were generally prepared by addition of HCl to $[PdL_2]$. The structure of *trans*-$[Pd(NH_2CH_2COOEt)_2Cl_2]$ was established by X-ray diffraction techniques; the amino acid ester was *N*-coordinated [403]. Reaction of 2-phenylglycine (PhglyH) with palladium ethanoate gave a mixture of $[Pd(PhglyH)_2(OCOMe)_2]$ and $[\{Pd(PhglyH)(OCOMe)_2\}_2]$, the proportions of the products depending on the molar ratio of the starting materials. However, with $Me_2NCH(Ph)COOEt$, cyclometallation occurred to give (127) [404].

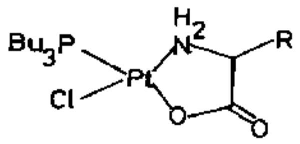


(127)

A wide range of synthetic techniques was developed to make mixed palladium complexes with oxygen and nitrogen ligands including many of amino acids with amines (for example **(128)**). In all cases at least one of the ligands was optically active and the influence of the achiral ligands on the CD spectra was investigated [405]. The reaction of *trans*-[Pt(SR_2)(**R**,**S**-valOMe)Cl_2] with **R**- or **S**-PhCH(NH_2)Me proceeded *via* a trigonal bipyramidal transition state. The stereoselectivity of the reaction (diastereomer excess 6-10 %) was determined by nmr spectroscopy in S-(+)-$CF_3CH(Ph)OH$ [406]. Reaction of *trans*-[$Pt_2(PBu_3)_2Cl_2(\mu\text{-}Cl)_2$] with an amino acid anion gave **(129)** (R = H, Me or $CHMe_2$). Further reactions of such species were investigated (reactions (18)-(20)) [407].



(128)



(129a) R = H
(129b) R = Me
(129c) R = $CHMe_2$

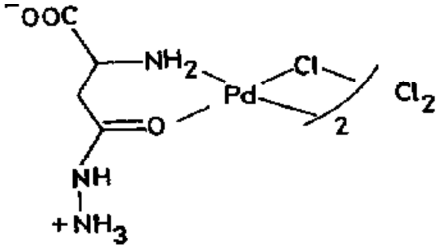
$$\textbf{(129a)} \xrightarrow{SOCl_2} cis\text{-}[Pt(NH_2CH_2COCl)(PBu_3)Cl_2] \xrightarrow{MeOH} cis\text{-}[Pt(NH_2CH_2COOMe)(PBu_3)Cl_2] \qquad (18)$$

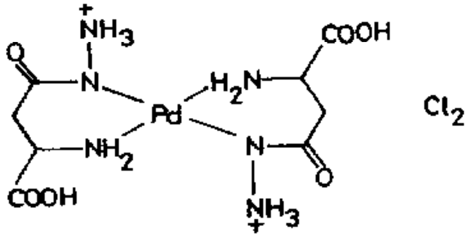
$$\textbf{(129a)} \xrightarrow{CH_3COCl} cis\text{-}[Pt\{NH_2CH_2C(=O)OC(=O)Me\}] \qquad (19)$$

$$\textbf{(129c)} \xrightarrow{PCl_5} trans\text{-}[Pt\{NH_2CH(CHMe_2)COCl\}(PBu_3)Cl_4] \qquad (20)$$

Intramolecular ligand-ligand interactions in ternary mixed ligand palladium(II) complexes have been studied. In complexes of two different amino acids fractional rotamer populations could be calculated from nmr spectroscopic data. It was concluded that only hydrogen bonding and electrostatic interactions were influential in determining the conformations of the complexes [408].

The complexes [$Pd_2(LH)_2Cl_2]X_2$ (LH = aspartic acid hydrazide or glutamic acid hydrazide; X = Cl or OH) were prepared and characterised. The related species, [$Pd(LH)_2Cl_2$] and [PdL_2] could also be isolated; their preparations are shown in reactions (21) and (22) [409].

$K_2[PdCl_4] + HL \xrightarrow{\text{cold, } H_2O}$  (21)

$PdCl_2 + HL \xrightarrow{\text{HCl, propanone}}$  (22)

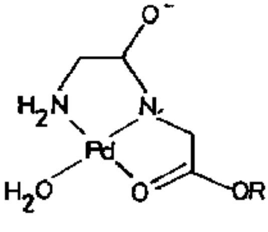
A CD spectroscopic study of palladium(II) complexes with polymer bound *S*-methyl-L-cysteine has been reported [410]. A combination of $K_2[PdCl_4]$ and L-serine caused elongation of some cells and interior clumping of ribosomes in *E. coli B*, whilst *cis*-Cs[Pd(L-serinato)Cl_2] induced pronounced filamentous growth but no surface changes in the cells. Inside the cells clumping of the cytoplasm was noted and there were also significant effects on the nucleoplasm [411].

1.6.3.2 Peptides

An nmr spectroscopic study of non covalent ligand-metal and ligand-ligand interactions in tridentate dipeptide palladium(II) complexes was undertaken. Im [Pd(glygly)Cl] the peptide was tridentate with binding through amine, amide and carboxylate oxygen. Stability constants for complexes of a range of amines were found to be directly related to amine basicity. However, those amines containing aryl rings showed an additional favourable interaction with the metal atom. In more substituted peptides side chain conformations were discussed in detail [412].

A kinetic study of the palladium(II) promoted hydrolysis of methyl and methylethyl glycylglycinate has been undertaken. The mechanism proposed was attack of external hydroxyl ion on **(130)** at the coordinated carbonyl group [413].

The effect of *cis*-[Pt(glyglyOEt)$_2$Cl$_2$] and *cis*-platin on the protein biosynthesis in Walker 25 carcinosarcoma was confirmed to arise from an inhibition of the aminoacylation of t-RNA and the biosynthesis of polyphenylalanine [415]. [PtA$_2$Cl$_2$] (A = peptide ester) and ten known anti-tumour compounds were compared in three bacteriological tests. Prophage induction in *E. coli* K12 (λ) was found to correlate with neoplasm inhibiting activity [416]. Platinum derivatives of the leucine binding protein of *E. coli* were prepared by treatment of the protein with four different platinum complexes [417].



(130)

1.6.3.3 Nucleic acids and nucleosides

Complexation of the platinum metals with Schiff bases and nucleotides has been reviewed [418]. The binding of *cis*-platin and related compounds to DNA has been discussed [419,420]. Binding of palladium(II) and platinum(II) to DNA was studied using bacterial strains with defective repair systems; the results could be related to the antibacterial, antineoplastic and mutagenic properties of the complexes [421].

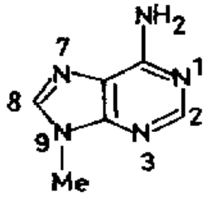
Raman spectroscopy has been used to study the interaction of heavy metals with nucleotides, especially using *cis*-platin [422]. A simple polarographic assay for platinum determination in *cis*-platin DNA complexes has been developed [423].

Derivatives of therapeutically active platinum complexes reacted at 40 °C with nucleic bases to produce soluble complexes which were active catalysts for the decomposition of hydrogen peroxide (especially the cytosine derivative). *Trans*-platin, however, gave species lacking this activity. This suggested to the authors that a redox reaction might be involved in the chemotherapeutic activity of *cis*-platin [424].

Plots of stability constants against pKa for $\{Pd(dien)\}^{2+}$ binding to a variety of nitrogen heterocycles have been established. The points for binding at a pyridine-like purine nitrogen atom, or at a pyrimidine N(3) site in nucleosides and 5'-mononucleotides fell on a single straight line. However, binding at imidazole-like purine N(7) nitrogen atoms was stronger and N(7) binding to purine bases bearing a 6-oxo group was still better [425].

The products of reaction between 9-methyladenine, **(131)**, and [Pt(dien)Cl] were separated chromatographically. The species identified included N(1) and N(7) bound adducts as well as a dimer, $[Pt_2(dien)_2\{\mu\text{-9-Me-adenine-N(1),N(7)}\}]$

[426]. The complexes, $K[Pt(AMP)Cl_3]$, $[Pt(AMP)_2Cl_2]$ and $[Pt(AMP)_3]Cl$ (AMP = 5'-adenosine monophosphate) were studied by FTIR spectroscopy. In all cases N(7) was metal bound and in the related species *cis*- and *trans*-$[Pt(NH_3)_2(AMP)_2]Cl_2$ the ammonia ligands were hydrogen bonded to the phosphate groups [427]. The preparations of *trans*-$[Pt(NH_3)_2LCl]Cl$ (L = adenosine or inosine) and *cis*-$[Pt(NH_3)_2LCl]Cl$ (L = adenosine, cytosine or inosine) have been described, and their hydrolysis constants determined [428].

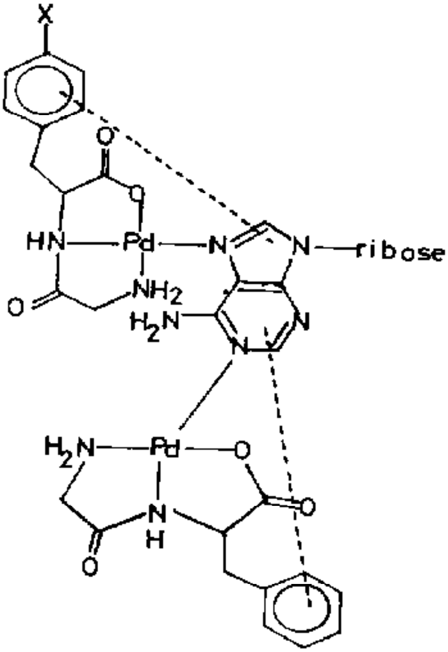


(131)

The adducts resulting from the reactions of *cis*-platin with d-adenosine or d-guanosine were separated on Sephadex G-25. With d-adenosine both 1:1 and 2:1 complexes bound at N(7) were formed [429]. The reactions of *cis*-platin, $[Pt(en)Cl_2]$ and $[Pt(1,2\text{-}pn)Cl_2]$ with adenosine and guanosine were studied by UV spectroscopy and HPLC. It was demonstrated that the reaction with guanosine was complete, and that with adenosine in a steady state, after ten hours [430]. The reactions of *trans*-platin with 5'-AMP, guanosine, cytidine or thymidine were investigated by ^{13}C nmr spectroscopy. Guanosine and 5'-AMP were bound to the metal at N(7) [431].

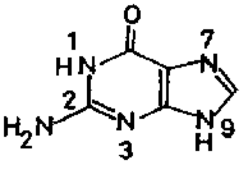
Mixed amino acid nucleotide complexes were formed by reaction of [Pd(glygly)X] with ATP or GMP. With ATP both N(1) and N(7) bound complexes were formed. The result for GMP was similar, with the N(1) bound species predominating at pH 11.9. Peptide complexes of glytyr or glyphe gave mainly N(1),N(7) bridged complexes such as **(132)**, stabilised by interactions between the aromatic rings [432]. Treatment of $PdCl_2$ with L-proH gave $[Pd_2(pro)_2(\mu\text{-}Cl)_2]$. On reaction with either purine or pyrimidine nucleosides a mixed species [Pd(pro)(Nucl)Cl] was produced. Adenosine and inosine gave N(1) or N(7) adducts, with guanosine binding at N(7) and cytidine at N(3) [433].

The structure of $[Pt(NH_3)_2(9\text{-ethylguanine})_2Cl_2].3H_2O$ was determined by X-ray diffraction techniques. Platinum binding was at N(7) with no interaction with O(6). The geometry about platinum was essentially normal but there were large angles between the purine ligand and the platinum coordination planes. There was also a hydrogen bond between O(6) and one of the ammine ligands at platinum [434]. The FTIR spectrum of *cis*-$[Pt(NH_3)_2(5'\text{-}GMP)_2]Cl_2.6H_2O$ has been recorded [435].



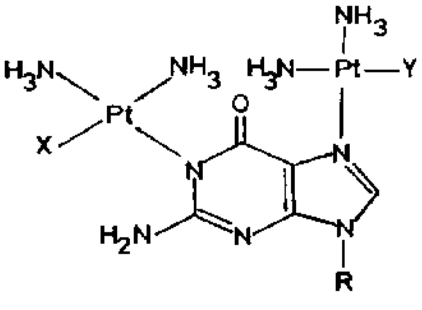
(132)

The reactions of derivatives of guanine, (133), with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ have been investigated. Guanine, 1-, 7- or 9-methyl guanine each yielded more than eight products, separated by HPLC. The structures formed involved all of the available nitrogen atoms, but not O(6) [436]. Reaction of $K_2[PtCl_4]$ with guanine, L, in the presence of 1M HCl at 60 °C gave *cis*-$[PtL(H_2O)Cl_2].2H_2O$. The structure of the complex was determined from IR and ^1H nmr spectroscopy, and thermal analysis [437].



(133)

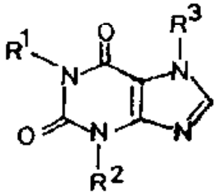
The complexes *cis*-$[Pt(NH_3)_2L_2]$, *cis*-$[Pt(NH_3)_2LCl]$, *cis*-$[Pt(NH_3)_2(H_2O)L]$ and *cis*-$[Pt(NH_3)_2LL']$ (L, L' = 3'- or 5'-GMP or IMP) were prepared and characterised. Related species prepared from dien and $H_2NCH_2CMe_2CH_2NMe_2$ derivatives were also isolated. Some interesting observations as to the relative rates of reactions of these nucleosides with platinum complexes were made [438]. The species $K[Pt(GMP)Cl_3]4H_2O$, $[Pt(GMP)_2Cl_2].6H_2O$, $[Pt(GMP)_3Cl]Cl.6H_2O$, $[Pt(GMP)_4]Cl_2$ and *cis*- and *trans*-$[Pt(NH_3)_2(GMP)_2]Cl_2.6H_2O$ were characterised by another research group. Hydrogen bonding to the phosphates was inferred, in some but not all of the complexes from IR spectroscopic data [439,440]. The reaction of 5'-GMP with *cis*-platin was studied in considerable detail. The species *cis*-$[Pt(NH_3)_2(GMP)_2]$ and *cis*-$[Pt(NH_3)_2(GMP)(H_2O)]^+$ were the primary products reported. After prolonged heating at 80 °C, however, new species were formed, which had previously been described as N(7)-O(6) chelates. More careful investigation led to the assignment of the structure as **(134)** which corresponds to a known derivative of AMP. No evidence was found for the previously postulated chelates, or for slow rotation on the nmr spectroscopic timescale [441]. When the incubations of *cis*-platin with guanosine in the presence and absence of cysteine were compared it was found, rather unsurprisingly, that the presence of cysteine limited the production of the bis(guanosine) adduct [442]. The ^1H nmr spectra of *cis*- and *trans*-$[Pt(NH_3)_2(\text{9-ethylguanidine})X]$ and $[Pt(NH_3)(\text{9-ethylguanidine})ClX]$ ($X = D_2O$, Cl, I, NH_3, dmso or 9-ethylguanidine) have been studied. There are significant *cis*- and *trans*-influences of X on $^3J(^{195}Pt\text{-}H(8))$ [443]. {Pd(glygly)} bound cytidine through N(3) and guanosine through N(7). With a cytidine/guanosine mixture the major binding site was N(7) of the guanosine. However, $PdCl_2$ reacted with the cytidine-guanosine pair at N(1) of guanosine and N(3) of cytidine to give a ternary complex [444].



(134)

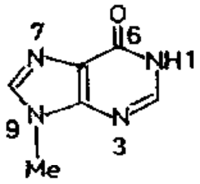
The reaction of the disodium salt of inosine 5'-monophosphate (IMP) with *cis*- or *trans*-platin gave *cis*- or *trans*-$[Pt(NH_3)_2(IMPNa_2)_nCl_2]$ (n = 1 or 2). In the 1:2 complexes the ligand was bound only at N(7) in a bridged structure. In the 1:1 complex the authors claimed binding through N(7) and O(6) [445].

The complexes $[PdL_2Cl_2]$ (L = xanthine, **(135)**, theophylline, theobromine, 3,8-dimethylxanthine, caffeine, **(136)**, or 1,3,8-trimethylxanthine) were prepared in acidic solution. Their structures were established by IR and nmr spectroscopy; all were coordinated to palladium *via* N(9) [446]. IR spectroscopy established the structure of $[Pt(NH_3)_2(9\text{-methylxanthine})]Cl$ to involve N(7)-O(6) chelate coordination [447]. Caffeine was shown to potentiate the lethal and chromosome damaging effects of *cis*-platin in Chinese hamster cells. This was probably due to enhancement of DNA lesions by inhibition of a process permitting replication past the lesions. The species $[Pt(caffeine)_2Cl_2]$ and $K[Pt(caffeine)Cl_3]$ were prepared. The structure of the bis-complex was established by an X-ray diffraction study; the caffeine moieties were N(9)-coordinated to platinum in a *cis*-arrangement [448]. $K[Pt(caffeine)Cl_3]$ was somewhat unstable in water due to a redox reaction, but could be stabilised by nucleosides in species such as $[Pt(caffeine)(adenosine)Cl_2]$ [449]. Numerous complexes of xanthosine 5'-monophosphate have been prepared. FTIR spectroscopy implied that binding was through N(7) of the imidazole ring and there was no direct metal-O(6) interaction [450]. The reaction products from 9-methylhypoxanthine, **(137)**, with *cis*-platin or [Pt(dien)Cl]Cl were separated by ion exchange chromatography. Both N(1)- and N(7)-bound species as well as μ-N(1),N(7) dimers were isolated, the proportions of the products depending on pH [451].



(135) $R^1 = R^2 = R^3 = H$

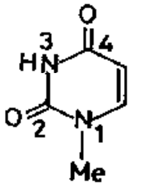
(136) $R^1 = R^2 = R^3 = Me$



(137)

Some further complexes of 1-methyluracil (1-MeUH, **(138)**) and 1-methylcytosine (1-MeC, **(139)**) have been studied. Thus *cis*-$[(NH_3)_2Pt(1\text{-MeC-N}(3))(1\text{-MeU-N}(3))][NO_3].2H_2O$ was prepared and characterised by ^1H nmr, IR and Raman spectroscopic studies. In acidic solution the 1-MeU ligand was protonated (pKa $\sim$ 0.9) and 1-MeUH was slowly released. The reaction with copper(II) was described to give *cis*-$[\{(NH_3)_2Pt(\mu\text{-1-MeU-N}(3),O(4))(\mu\text{-1-MeC-N}(3),O(2))\}_2Cu][NO_3]_4.6H_2O$, **(140)**. Platinum was bound to the N(3) sites of 1-MeU and 1-MeC, and copper(II) to O(4) of 1-MeU and O(2) of 1-MeC. Epr spectroscopy indicated that the copper atom was in a tetragonally elongated ligand field [452].

The reactions of *cis*-$[Pt(NH_3)_2(1\text{-MeU-N}(3))(H_2O)]^+$ and the head-to-tail isomer of *cis*-$[\{Pt(NH_3)_2(\mu\text{-}1\text{-}MeU\text{-}N(3),O(4))\}_2]^{2+}$ with Ag^+ were studied. The structure of the product from the head-to-tail dimer, *cis*-$[Pt_2(NH_3)_4(1\text{-}MeU)_2Ag_2](NO_3)_4.2H_2O$, (141), was determined by X-ray diffraction. Each 1-MeU ligand bridged two *cis*-$\{Pt(NH_3)_2\}$ units, bonded through N(3) and O(4), with bonding to silver through O(2). A related polymer from *trans*-platin was also prepared [453,454].



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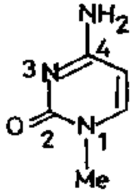

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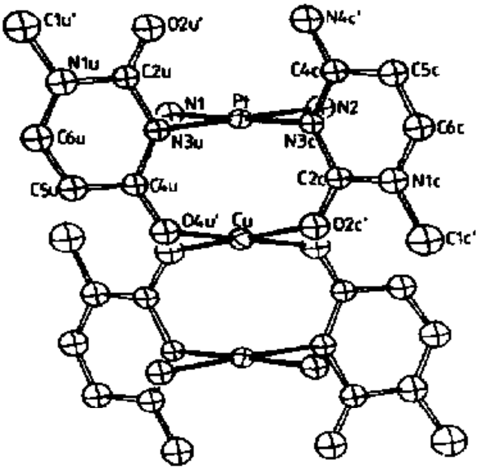
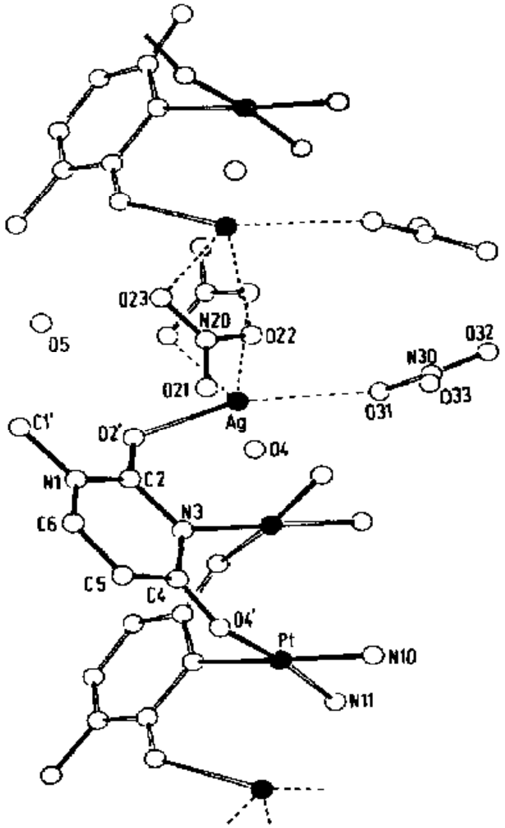


(140) (Reproduced with permission from [452])

In the numbering scheme 1MeC atoms are indicated by C and 1MeU atoms by U. The copper atom occupies an inversion centre.

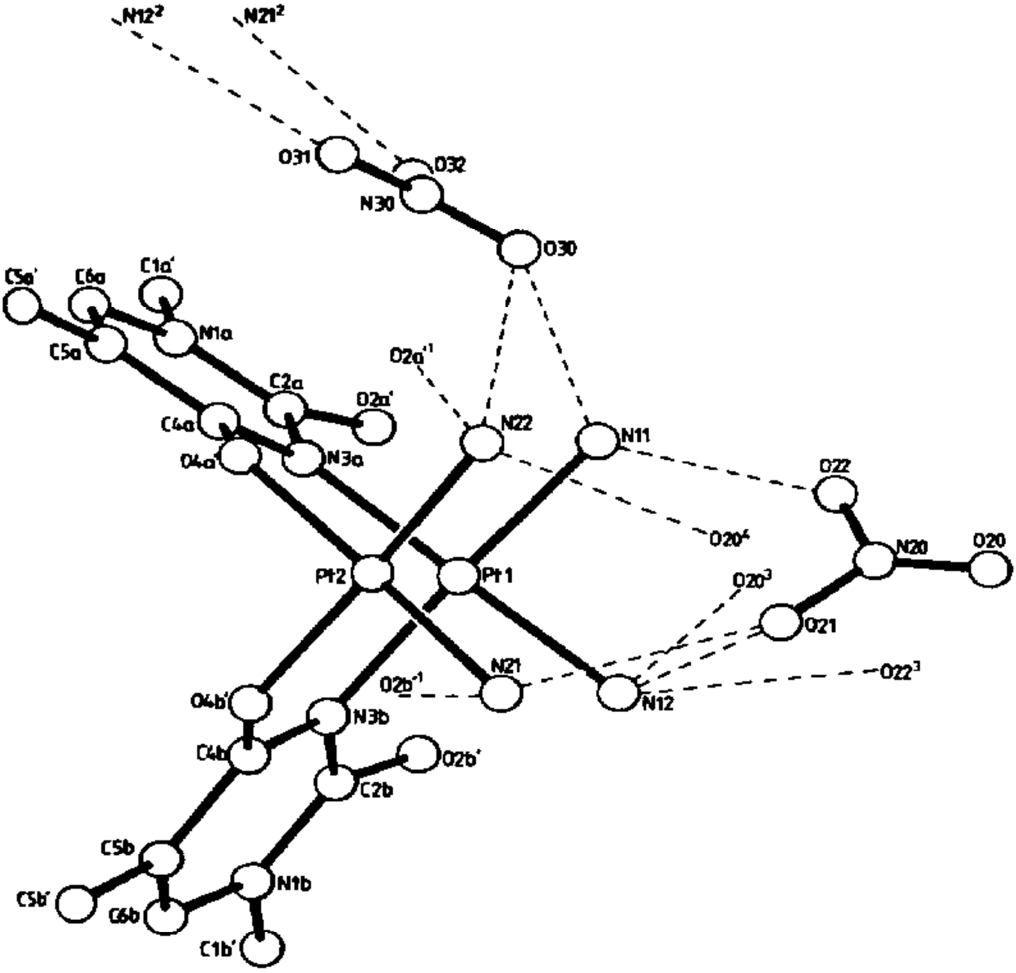
The complex *cis*-$[Pt(NH_3)_2Cl_2]$ was treated with a range of 5-substituted uracils in dmso to give $[Pt(NH_3)_2(dmso)L]^+$, and for the 5-fluoro and 5-bromo ligands, $[Pt(NH_3)_2L_2]$. The 5-nitrouracil was N(1) coordinated with the other ligands N(3) bonded [455]. The complexes $[ML_2]$ (M = Pd or Pt, HL = dithiouracil) have been isolated. Neither IR spectroscopy nor XPES could distinguish *trans-N(3),S(4)* from *trans-N(3),S(2)* binding [456].

The structure of head-to-head $[\{$*cis*-$Pt(NH_3)_2\}_2(\mu\text{-}1\text{-}MeT)_2][NO_3]_2$, (142), (1-MeT = (143)) has been established by X-ray diffraction. One of the two platinum atoms is N_4-coordinated, the other N_2O_2-bound. Both of the platinum atoms adopted square planar coordination with the two coordination planes almost eclipsed and tilted towards each other. The relation of the platinum-platinum tilt angle and twist angle conformed to trends seen in the α-pyridone dimers [457].

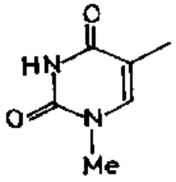


(141) (Reproduced with permission from [453]
Section of the crystal structure of *cis*-$[(NH_3)_2Pt(1MeU)Ag]_2[NO_3]_4.2H_2O$
projected along the *x*-axis.

The equilibrium constants for the reactions of $[PdCl_4]^{2-}$ and $[Pd(en)Cl_2]$ with cytidine have been determined. Intramolecular hydrogen bonding and steric interactions of exocyclic substituents *ortho* to the cytidine binding site do not contribute greatly to stability [458]. The kinetics and equilibria of the reactions of $[Pd(dien)Cl]^+$ with cytidine (C) and cytidine 5'-monophosphate (CMP) were studied by spectrophotometry and stopped-flow techniques. $[Pd(dien)(H_2O)]^{2+}$ was an intermediate. With CMP initial coordination was *via* phosphate, before rearrangement to the stable N(3)-bonded complexes [459].



(142) (Reproduced with permission from [457])
Possible hydrogen bonds between the ammine ligands and the surrounding nitrate groups are indicated.

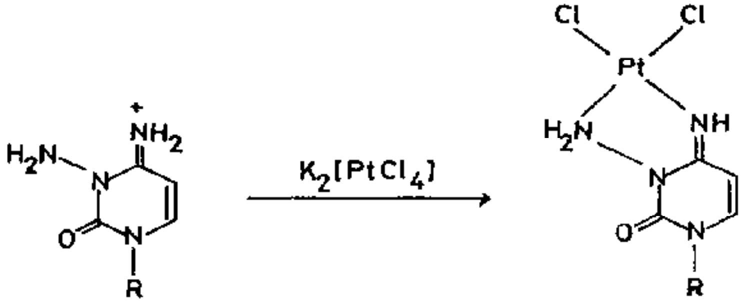


(143)

[Pt(phen)(en)]$^{2+}$ formed a crystalline complex with cytidine 3'-phosphate

(3'-CMP), characterised by X-ray diffraction techniques. 3'-CMP was hemiprotonated and formed hydrogen bonded pairs which stacked above and below the platinum(II) drug molecule. This was an end product of the hydrolytic cleavage of the dinucleoside monophosphate, CpG, by the intercalator. The intercalator seemed to be specific for the RNA dinucleoside monophosphate fragment, since d(CpG) and other deoxyribonucleotides were not cleaved [460].

Complexes of 2,4-dioxopyrimidines with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ were prepared and tested for anti-tumour, antiviral and anti-bacterial activity. In general they had good activity and low renal toxicity [461]. Reaction of $K_2[PtCl_4]$ with **(144)** gave **(145)**; this and related species had good activity against L1210 *in vitro* and in mice, and very low nephrotoxicity [462]. Orotic acid and its derivatives formed a wide range of complexes with $[PdCl_4]^{2-}$, $[Pd(en)Cl_2]$ and $[Pd(NH_3)_4]^{2+}$ [463].



(144) **(145)**

The complex $[BrPt\{dien(CH_2)_6dien\}Pt(H_2O)]^{3+}$ was proposed as a useful starting material for the preparation of complementary addressed reagents to form reactive derivatives of oligonucleotides and polynucleotides, since the two "ends" would be expected to react at different rates. This was especially useful for directed damage of nucleic acid sequences *in vivo* [464].

CpG and d(pCpG) reacted with *cis*-platin or *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$ to give a C-N(3)-G-N(7) chelate complex. Very careful nmr spectroscopic studies indicated that there was an equilibrium between C-*anti*-G-*anti* and C-*syn*-G-*anti* conformations (approximately 20:80). In the CpG adduct the cytidine ribose adopted an N-type conformation with C(3') *endo*, whereas the guanine ribose had an S-type conformation with C(2') *endo*. The C-*anti*-G-*anti* conformer represented an important perturbation leading to a zigzag left-handed pseudohelical conformation [465].

The oligonucleotides d(ApTpGpG) and d(CpCpApTpGpG) were reacted with *cis*-platin or *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$ to give, in each case, a single monomeric complex with one platinum atom per oligonucleotide. ^1H nmr spectroscopy implied that platinum was in all cases chelated by the N(7) sites of adjacent guanines [466]. The conformations of d(ATGG) and the d(ATGG)/*cis*-platin complex were investigated by ^1H nmr spectroscopy at 500 MHz. In d(ATGG) all the sugar residues adopted an S(C(2')-*endo*) conformation. In the platinum complex the N(C(3')-*endo*) conformer predominated for the internal dG. Substantial changes in conformation with temperature were observed [467]. Ap_4A, an intracellular regulatory nucleotide, reacted with *cis*-platin to give a single N(7),N(7)-chelated complex. The two adenines adopted a head-to-tail arrangement with a very considerable decrease in flexibility [468].

The site(s) of platination of oligonucleotides have been established by digestion with various enzymes. For example, platinum modified 5'-d(CpCpGpG)-3' and 5'-d(GpGpCpC)-3' were digested by *endo*-and *exo*-nuclease and the products identified by HPLC. R,R-1,2-diaminocyclohexane platinum(II) was thus shown to bind selectively to N(7) sites of guanine residues to form intrastrand cross-links [469]. Related N(7)-guanine-N(7)-guanine cross-links were similarly established for the reaction of *cis*-platin with d(GpCpGpC) [470]. The products of reaction of *cis*-platin with the self-complementary deoxyribotetranucleoside tetraphosphates $d[(pGpGpCpC)]_2$ and $d[(pCpCpGpG)]_2$ were digested with snake venom phosphodiesterase and calf spleen phosphodiesterase. From both starting materials the product after digestion was *cis*-$[Pt(NH_3)_2\{d(GpG)\}]$ [471].

The d(GpG) platinum adduct of the oligonucleotide, d(GATCCGGC) gave a duplex with the complementary decanucleotide d(GCCGGATCGC). The melting temperature of the duplex was 30 °C, implying that eight imino protons were involved in hydrogen bonding. This suggested that platinum chelation may not in this case induce a large distortion of the DNA duplex. The distortion may only be a "kink" or a region of systematically bent B DNA, and this raises the question of the detection of the lesion by repair enzymes [472]. The guanine N(7)-guanine N(7) *cis*-platin chelate in the decamer double helix d(TCTCGGTCTC)/d(GAGACCGAGA) was also studied [473].

The complexes *cis*-platin, *trans*-platin and [Pt(dien)Cl]Cl were all shown to fix on N(7) of inosine in poly(I).poly(C). The effect of the products on interferon induction activity was investigated. The destabilisation of the duplex by *cis*-platin decreased interferon induction and increased RNAase sensitivity. The "sandwich" stabilisation by {Pt(dien)} at low binding ratios was manifested by an increased interferon induction and a high resistance towards RNAase degradation. By contrast, *trans*-platin had little effect on interferon induction or RNAase sensitivity [474]. A more detailed study of the reaction of *trans*-platin revealed three types of reaction depending on concentration and binding ratio. At $r_b < 0.1$, coordination to the poly(I) strand caused some destabilisation of the double strand which was established by UV and CD spectroscopy, and an observed decrease in T_m. At a higher value of r_b and a lower polynucleotide concentration the free cytidine bases reacted with platinum bound to the complementary strand producing interstrand crosslinks which restabilised the double strand. At high r_b values and high platinum concentration intermolecular crosslinks predominated. No separation of the strands occurred under any of the conditions used [475,476]. Fixation of {Pt(dien)} on poly(I).poly(C) led to only minor changes in UV and CD spectra at ambient temperatures. However, the melting profile showed two steps. At 80 °C nmr spectra indicated that the platinum amino groups were hydrogen bonded to the N(7) site of adjacent hypoxanthine bases. The hydrogen bonds were thought to be disrupted in the second melting step [477].

Conformational changes induced by the binding of *cis*-platin to poly(dGdC).poly(dGdC) were studied by CD and ^{31}P nmr spectroscopy, and reaction with specific antibodies. Unplatinated regions were shown to have B or Z conformations depending on experimental conditions, whereas platinated regions were unable to adopt the canonical Z conformation and the presence of left-handed helices was suggested [478]. For poly(dAdT).poly(dAdT) CD spectroscopic data were interpreted in terms of a dimer helix to single hairpin helix transition induced by the metal [479].

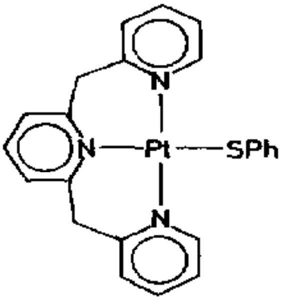
The complex formed between acridine orange and poly(C) has been investigated. The kinetics of the reaction of this complex with {Pt(dien)} were studied by stopped-flow methods. The complex was shown to dissociate on fixation of palladium(II) to N(3) of the cytidine [480]. *Cis*-platin formed interstrand crosslinks in poly(dG).poly(dC). Initially binding was to the poly(dG) strand, and poly(dC) alone was reluctant to react [481]. The nature of the adducts and the conformational changes produced in poly(dGm^{5}dC).poly(dGm^{5}dC) by *cis*-platin were studied. CD spectroscopy of the platinated adduct implied that it adopted a distorted Z-DNA conformation [482].

SERS has been used to study the interaction of DNA with platinum complexes. *Cis*-platin was said to give an "inner" complex, with platinum coordinated inside the DNA helix. {Pt(dien)}, which is inactive in chemotherapy, however, gave an outer complex [483,484].

The conformational changes in double stranded calf thymus DNA induced by different types of platinum complexes were investigated by CD spectroscopy and differential pulse polarography. Both *cis*-platin and *cis*-[Pt(NH_3)$_2$(cyclobutane-1,1-dicarboxylate)], the CARBOPLATIN derivative, induced changes corresponding to the formation of "premelted" but still double stranded DNA. *Trans*-platin yielded single stranded denatured DNA, whilst [Pt(dien)Cl]Cl had little effect [485].

Monoclinic crystals of yeast tRNA^{Phe} were sealed in a solution containing the hydrolysis products of *cis*-platin. Drug binding resulted in crystal deterioration and a loss of the diffraction pattern beyond a resolution of 6 Å. The most probable interpretation is that *cis*-$\{Pt(NH_3)_2\}^{2+}$ reacted to give intrastrand crosslinks at GG and AG sites, giving local distortion [486]. However, other workers interpreted their data in terms of monodentate ligation to N(7) of guanine in non-helical regions, with no intrastrand crosslinks [487]. Calf thymus DNA was reacted to completion with varying amounts of ^{195m}Pt-*cis*-platin. The platinated species was then hydrolysed in methanoic acid and the fragments separated chromatographically. Most of the radiolabel was found in a bifunctional homo adduct between platinum and two guanine moieties, and a bifunctional hetero adduct between platinum, adenine and guanine [488]. The effect of inorganic salts on the binding of *cis*-platin to salmon sperm DNA was studied [489].

This year there has been a new report of a platinum(II) complex acting as an intercalating agent towards DNA. For example in the interaction of $[Pt(terpy)(SPh)]^+$, **(146)**, with nucleic acids there was evidence both for intercalation and non-intercalated externally bound platinum [490].



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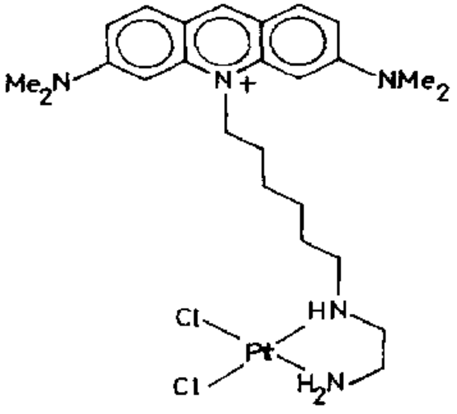
The presence of ethidium bromide during DNA platination reduced the duplex shortening effect. Whilst the duplex unwinding effect of *cis*-platin was unaffected, that of *trans*-platin was considerably reduced. The results were interpreted in terms of a model in which ethidium bromide blocked intermediate and long-range platinum DNA crosslinks. Whilst the *cis*-complex could still make short range crosslinks, *trans*-platin does not normally make such links [491]. A new platinum complex of the substituted acridine orange, **(147)**, has been prepared, and a study of CPK models suggested that with platinum bound to DNA the acridine would be able to intercalate one or two base pairs away. This appeared to be the case in practice and some extra duplex unwinding was caused. Like acridine orange itself, **(147)** could nick DNA in the presence of light, and may therefore be able to act as an internal photoactivated scissors to map platinum binding sites [492].



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1.6.3.4 Cancer chemotherapy

Reviews this year have addressed the general topic of platinum complexes in cancer chemotherapy [493-503], and others have focussed on *cis*-platin [504] with particular reference to its pharmacology [505,506] and nephrotoxicity [507,508]. The nomenclature of platinum chemotherapeutic agents has been considered [509] and a range of platinum complexes has been examined for their emetic potential [510]. Structure activity relationships and the clinical pharmacology of platinum anti-tumour agents were reviewed [511].

Methods for the detection of *cis*-platin in body fluids have been reviewed [512]. Selective and convenient HPLC assays for [Pt(en)(malonate)], JM40 and *cis*platin in plasma ultrafiltrate and urine have been developed [513,514]. Trace analysis using dual electrode operation in HPLC was described for drugs such as *cis*-platin, CHIP and CARBOPLATIN [515]. A post-column reaction detector sensitive for platinum(II) complexes was developed using sodium hydrogen sulphite as a derivatising agent and potassium dichromate as an activator. The system was used to monitor the kinetics of aquation of *cis*-platin and to determine quantitatively the rate of *cis*-platin degradation in plasma [516]. Differential pulse polarography was used in an assay of *cis*-platin analogues after oxidative acidic hydrolysis of biological samples [517]. The development of sensitive analytical methodology for determination of levels of platinum containing neoplasm inhibitors in tissue samples was described in relation to the evaluation of *cis*-platin metabolism in humans and in laboratory animals [518].

Laser microprobe mass analysis (LAMMA) was used to detect platinum in the renal proximal tubular cells of a dog which had been administered *cis*-platin intravenously. No definite subcellular localisation of the heavy metal was obtained [519]. The determination of platinum distribution in adenocarcinoma in black mice was achieved using neutron activation analysis. It was found that the tumour tissues concentrated more platinum if the *cis*-platin was administered with prednisolone [520]. After multiple intraperitoneal injection of *cis*-platin into rats, the liver DNA contained several ppm of platinum as measured by atomic absorption spectrometry [521].

Cis-platin has been used in a parenteral solution as an anti-tumour agent [522]. Cells from human colon carcinoma were cultured in soft agar; *cis*-platin was then found to be very cytotoxic *in vitro*, in contrast to earlier results [523]. The metabolites of *cis*-platin in rats were found to be more nephrotoxic and to have lower anti-tumour activity than *cis*-platin itself [524].

A number of compounds, when coadministered, have been shown to reduce *cis*-platin nephrotoxicity. These have included the diuretic acetazolamide [525,526], selenium, usually as sodium selenite [527,528], and diethyldithiocarbamic acid [529]. The mechanism of sodium thiosulphate inhibition of *cis*-platin toxicity was shown to involve formation of $[Pt(S_2O_3)_4]^{6-}$ in the extracellular fluid; cell entry and binding to macromolecules was thus prevented [530]. Diethyl dithiocarbamate reduced both *cis*-platin nephrotoxicity and local gastrointestinal toxicity in the mouse, the rat and the dog. Beneficial effects on nausea and vomiting were also noted, and there was no inhibition of anti-tumour activity [531].

The mechanism of the nephrotoxic effect of *cis*-platin has been studied. An earlier physiological impairment than previously noted, and reduced glutathione synthesis were established [532]. The pharmokinetics of free and total platinum species after short term infusion of *cis*-platin were investigated. the curves showed a rapid initial phase and a prolonged terminal phase separated by a phase with secondary peaks attributed to the existence of an enterohepatic recirculation [533]. The pharmokinetics of *cis*-platin and CARBOPLATIN were compared in experimental animals in order to elucidate the differences in nephrotoxicity of the two compounds. It was shown that whilst renal levels of the two complexes were similar, the excretion of *cis*-platin was half that of CARBOPLATIN. CARBOPLATIN was accumulated to a greater extent than *cis*-platin in red blood cells [534]. The renal handling of *cis*-platin was investigated; the secretion by the kidney was improved by administration of probenicid [535]. In a study of renal pathology it was shown that *cis*-platin caused selective necrosis of proximal tubules in the deep cortex, which extended to subcapsular tubules with increasing doses. The mechanism of tubular changes appeared to be disturbance of regeneration due to damage to the intracellular respiratory system. Adequate hydration and furosemide administration reduced nephrotoxicity [536].

Other compounds, when coadministered with *cis*-platin, synergistically enhanced its anti-tumour activity. These included spirogermanium [537], and interferon [538,539]. A combination with mytomycin C was the most effective regimen for xenografted human mesothelioma [540], whilst the highest selective activity against Ascitic Zajdela hepatoma in rats used *cis*-platin and methotrexate [541]. By combining 5-fluorouracil and *cis*-platin, at drug levels which were ineffective alone, and using a low γ-ray dose, L1210 leukaemia in mice was cured in a single session [542]. The encapsulation of *cis*-platin in neutral liposomes (egg lecithin-cholesterol) was used to enhance the activity of the drug on Ehrlich ascites carcinoma in mice [543]. In an attempt to optimise the treatment of mouse tumour sarcoma 180, liposomes containing *cis*-platin and having transition temperatures a few degrees higher that the rectal temperature of the mice were used in combination with local hyperthermia [544]. Step-down heating had little effect on the cytotoxicity of *cis*-platin [545].

It was shown that *cis*-platin did not significantly alter intracellular ATP levels in leukaemic cells [546]. In a study of the effect of *cis*-platin on the developing neocortex of NMRI mouse embryos or fetuses the teratogenic efficiency depended on the ability of the drug to pass the placental barrier [547].

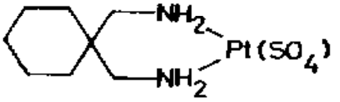
Guinea pigs were pretreated with *cis*-platin at various times before intravenous administration of [^{195m}Pt] labelled *cis*-platin. The concentration of [^{195m}Pt] was greater in the tissues of the pretreated than of the control animals. It was concluded that urinary excretion of platinum was decreased in pretreated animals due to kidney damage [548]. *Cis*-platin was administered to rodent and canine models of the osmotic blood-brain barrier modification to evaluate the relationship between drug concentration in the brain and the physiological and neuropathological effects of the drug. Even without the osmotic procedure, intracarotid administration of *cis*-platin produced modification of the blood-brain barrier with resultant severe neurotoxicity [549].

Guinea pigs treated with *cis*-platin showed a 60-70 % outer hair cell loss in the basal turn of the cochlea, and a decrease in the auditory brain stem response waveform and amplitude. When *cis*-platin was combined with kanamycin the outer hair cell loss rose to 90-100 % and marked cortical medullary tubular necrosis and interstitial nephritis were noted [550].

Cis-platin was shown to be both recombinagenic and mutagenic in the wild type diploid strain D7 of yeast. Both the cytotoxicity and the genotoxicity were considerably reduced if the *cis*-platin was dissolved in a phosphate buffer rather than in simple aqueous solution. The diploid strain (D7 rad 3), deficient in an ability to excise UV-induced pyrimidine dimers or similar adducts, was shown to be hypersensitive to *cis*-platin, as was the diploid strain, (rad 52/rad 52), blocked in the repair of DNA double strand breaks. The results were discussed in terms of *cis*-platin induced cell death and genotoxicity [551].

The effect of *in vivo* administered *cis*-platin on mitochondrial and overall cellular protein synthesis in hepatocytes from regenerating rat liver and Zajdela hepatoma was examined. In both types of cells the overall cellular protein synthesis was inhibited to the extent of 50 %. Protein synthesis in the mitochondria of Zajdela hepatoma was unaffected, but normal rat liver mitochondrial protein synthesis was inhibited to the same extent as overall cellular protein synthesis. This resulted from a lower binding of *cis*-platin to tumour mitochondria [552].

The *in vivo* binding of *cis*-platin to metallothionein in rat tissues after the injection of *cis*- or *trans*-platin was shown to depend on the availability of -SH groups [553]. Preclinical studies in mice, rats and dogs of *cis*-platin, CARBOPLATIN and TNO-6, **(148)**, were conducted. The other complexes had lower renal toxicity than *cis*-platin, and were as active as *cis*-platin against hemopoietic step cells. They were, however, less active against the mouse tumours, leukaemia L1210 and osteosarcoma C22LR [89].



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Cross-linking of chromosomal non-histone proteins to DNA in isolated nuclei or intact HeLa cells exposed to *cis*- or *trans*-platin was studied. Both platinum complexes cross-linked considerable numbers of chromosomal non-histone proteins to DNA, and the action of both could be reversed and/or blocked by thiourea or 2-mercaptoethanol [554]. Calf thymus nucleosomes containing histones H1 were treated with *cis*- or *trans*-platin at low binding ratios. A change in the electrophoretic mobility of the extranucleosomal DNA was observed after treatment with *cis*- but not *trans*-platin. Thermal melting behaviour of the nucleosomal DNA was also affected more by *cis*-platin, and a destabilisation of the DNA helix was observed [555].

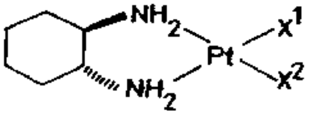
Numerous new platinum complexes continue to be prepared in a search for more effective and less toxic anti-tumour agents. Forty new water stable derivatives of 1,2-diaminohexane platinum were assayed against P388 tumours and/or KB cell bearing mice [556]. Thirty-five complexes were evaluated for their anti-tumour activity in mice bearing leukaemia L1210. An *in vitro* clonogenic assay with L1210 cells gave eighteen true positive, fifteen true negative and two false negative results [557].

Twenty-six ant-tumour platinum ammine complexes induced the formation of polyploid nuclei in plasmodia of *Physarum polycephalum* at drug concentrations one third that required to block plasmoidal growth. Platinum complexes without anti-tumour activity did not have this effect. Since DNA replication was normal in all cases it was concluded that activity might be connected with inhibition of mitosis rather than gross inhibition of DNA synthesis [558,559].

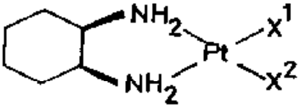
TNO-6 was shown to have similar anti-tumour activity and lower nephrotoxicity when compared with *cis*-platin [560]. The dose limiting toxicity in patients with a variety of solid tumours was determined; the toxicity derived from mylosuppresion and renal failure [561]. The reaction with human plasma was studied by HPLC; most of the platinum was initially bound to protein [562]. Other complexes of the platinum diamine unit of TNO-6 with halides and dicarboxylates were also active against lymphoid L1210 leukaemia in mice [563].

Cis-$[Pt(NH_3)_2(ascorbate)]$ and other platinum amine ascorbate complexes were active against S-180a ascites and leukaemia L1210 in mice [564]. $[PtLL^1L^2L^3]$ in which L and L^1 were NH_3 or amines, L^2 was a phosphatidyl group with a negative charge and fatty acid substituents, and L^3 was a biologically compatible negative ion, were prepared. Encapsulated in egg phosphatidylcholine vesicles these were also active against L1210 in mice [565]. The complexes $[Pt(RNH_2)(R'NH_2)XX'\}$ (R,R' - selenium containing alkyl or aryl groups, or selenium containing amino acid derivatives; X,X' = Cl, $[NO_3]$, $\frac{1}{2}[SO_3]$ or $\frac{1}{2}[SO_4]$) were useful neoplasm inhibitors [566].

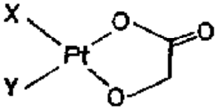
Numerous derivatives of 1,2-diaminocyclohexane have been described. These have included (149)-(154) [567,568,569]. In **(150)**, **(152)** and **(153)** the effect in *Crepis capillans* was found to be stereochemically dependent, with the (+)-isomer more active than the (-)-species [570]. The *cis*-complexes, **(155)**, were also used as neoplasm inhibitors [571]. The isocitrate derivative was active against L1210 leukaemia, and was less mutagenic and nephrotoxic than *cis*-platin, but the stereochemistry was not specified [572]. The stereochemistry was also not specified in the related species, **(156)** [573].



(149) X^1 = [RCO_2] (R = alkyl or $C_mH_mO_{m-1}OH$), X^2 = OH
(150) X^1 = X^2 = Cl
(151) X^1 = X^2 = OH_2
(152) X^1X^2 = [SO_4]
(153) X^1 = X^2 = [NO_2]
(154) X^1 = halide, X^2 = glucuronic acid residue



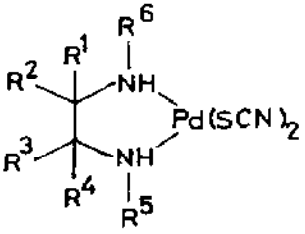
(155) X^1X^2 = [SO_4], [NO_3]$_2$ or [carboxylate]$_2$



(156) X,Y = RNH_2, en or 1,2-diaminohexane

1R,2S-[Pt(1,2-diaminocyclopentane)Cl_2] was thought to adopt the λ-gauche conformation; this was more active than the **1S,2S**-complex which had a δ-gauche conformation [574]. Bis(pyruvate) platinum 1,2-diaminobenzene was active against a range of human malignancies and human tumour xenografts in nude mice. Unlike *cis*-platin it was not particularly nephrotoxic, and bone marrow suppression was expected to prove dose limiting [575].

Complexes of the type **(157)** were prepared and were active against S180 ascites in mice; the thiocyanate anion was said to be essential [576]. **(158)**, in which X = [NO_3] or X_2 = [SO_4] or glucuronate had a high anti-tumour action. The interaction of calf thymus DNA with the sulphate was investigated by CD spectrometry [577]. The *meso*-isomer of (158) was found to be less active than the chiral complex in treatment of the human breast cancer cell line MDA-MB231 and rat leukaemia L52222 [578]. However, other workers have concluded that in chiral *cis*-platin analogues, [Pt(diamine)Cl_2], the activity against P388 leukaemia in mice was essentially unaffected by the configuration of the amine [579].



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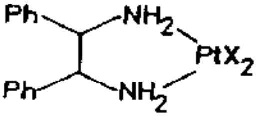

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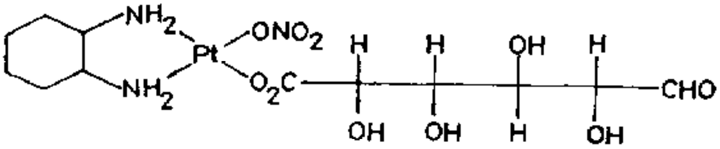
The sugar derivative, **(159)**, preferentially inhibited RNA synthesis in the presence of S-II, a regulatory protein of transcription [580]. *Cis*-dichloroaquoguanositin platinum(II) monoethanol was said to have anti-tumour activity [581]. The chelated complexes, **(160)** (R = H or Me; Y^1,Y^2 = X, [NO_3], [R'COO] *etc.*), have also been tested [582]. Anti-tumour platinum compounds complexed directly or *via* dextranamine moieties to a tumour specific Ig were less toxic and more effective than platinum anti-tumour compounds alone, because they allowed targeting of the drug to the site of the tumour. For example, the YAC specific lymphoma Ig coupled to $K_2[PtCl_4]$ was twenty times as effective as the platinum complex alone [583].



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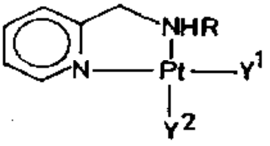
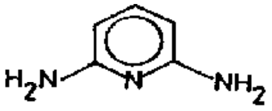


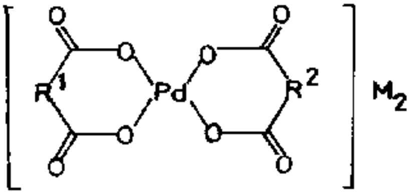
(160)

A number of platinum complexes of polymers have been used successfully in chemotherapy. For example, the platinum complex of a vinylamine/vinylsuphonate copolymer gave results comparable with those of related monomers [584]. Polyhydroxylated amines and diamines were useful in conferring water solubility on platinum anti-tumour agents [585]. *Cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$ was treated with the sodium salt of poly(L-glutamic acid) and the product dialised to give species with anti-tumour and anti-trypanosomal activity [586]. Polyamines such as **(161)** were converted to platinum(II) polymeric complexes and used as anti-tumour agents [587].

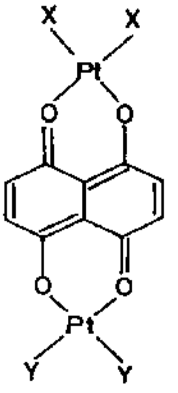


(161)

The activities of *cis*-[Pt(amino acid or amino acid ester)$_2$Cl$_2$] complexes were tested against the mammary tumour cell line MDA-MB231. Only *cis*-[Pt(GlyOBu)$_2$Cl$_2$] and *cis*-[Pt(GlyOCMe$_3$)$_2$Cl$_2$] inhibited incorporation of ^{3}H thymidine. However, *in vivo* these complexes did not influence tumour growth of ADJ/PC6 plasmacytoma [588]. **(162)** [589], **(163)** and **(164)** [590] also had anti-tumour activity.



(162) R^1,R^2 = alkylene, alkylidene, cycloalkylene or phenylene



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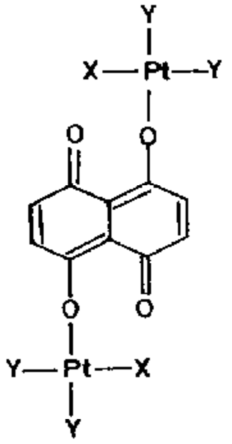


(164)

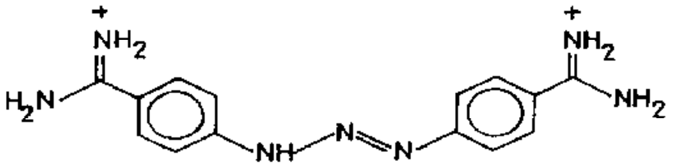
X,Y = NH$_3$, RNH$_2$, Cl, OH
Br, NO$_2$ CN or SCN

A number of anti-tumour platinum complexes related to *cis*-platin showed trypanocidal activity against *Trypsosoma rhodesiense in vitro* but not *in vivo*. Complexes of Berenil, (165), were also prepared (Scheme 3) [591].

1.6.4 Complexes with Group 15 donor ligands

1.6.4.1 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 effects. In particular a number of enzymes including β-lactamase [592], dihydropteridine reductase, and dihydrofolate reductase [593] were inhibited. Both malate dehydrogenase and fumarase could distinguish *cis*- and *trans*-platin. The inhibition of fumarase was dominated by interaction with the SMe group of an essential methionine at the active site, whilst that of malate dehydrogenase was caused by reaction with two thiol groups near the enzyme binding site [594,595].



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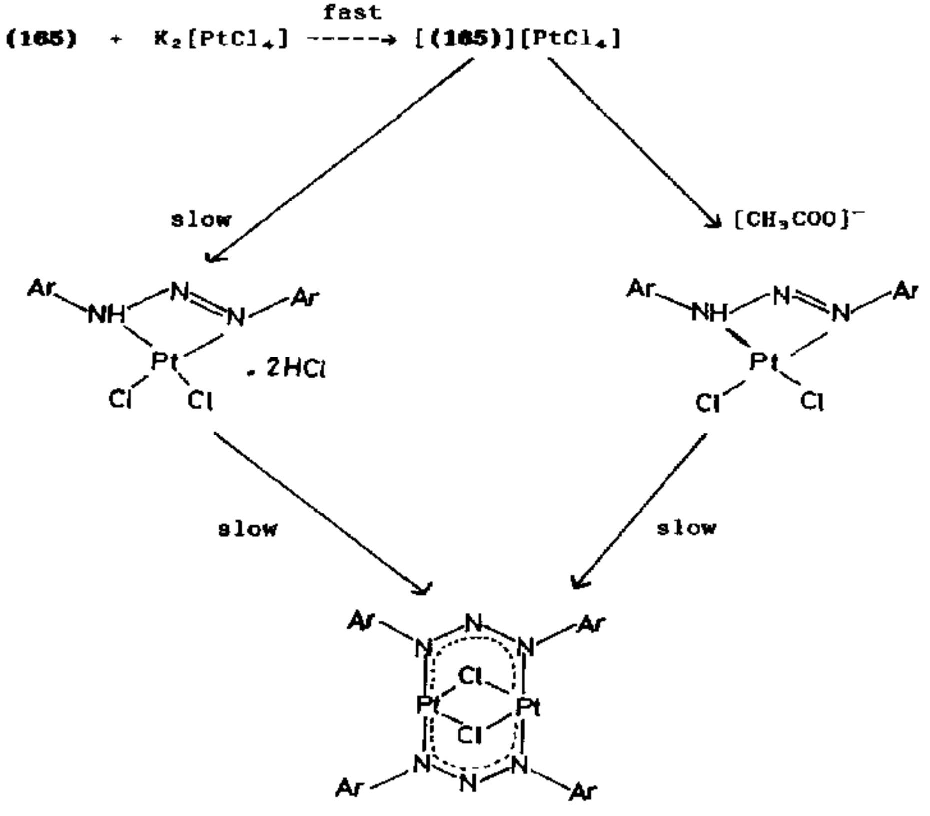


Scheme 3 Reactions of Berenil with $K_2[PtCl_4]$ [591]

Cis-platin worsened the healing of enterostomies in rats, the reasons being reduced induction of connective tissue proliferation, inhibition of proliferation of fibroblasts and endothelial cells, and retardation of vessel proliferation [596]. Treatment of human peripheral leucocyte microcultures with *cis*-platin for 24-72 hours produced enough cytogenic damage markedly to increase the micronucleus indices of the cultures. Caffeine enhanced the mutagenic action [597]. Vaccines could be prepared by the interaction of non-enveloped viruses with *cis*-platin in the presence of a detergent. The viruses inactivated included the Bluetongue, orbi- and double stranded RNA containing species. The effectiveness of the treatment of viremia in sheep was demonstrated [598].

In human transformed cells in culture (W1-98-VAD) grown in the presence of *cis*-platin, the platinum was found to be concentrated in the nucleolar region [599]. An EELS study of the distribution of platinum after *cis*-platin administration revealed that it was concentrated in the chromatin and chromosomes, nucleoli and lysosymes of the cricket testis [600]. *Cis*-platin in blood serum could be quantified voltammetrically by its chloride assisted oxidation at platinum electrodes [601]. *Cis*-and *trans*-platin could be determined by classical or differential pulse polarography with a detection limit of 10^{-6} mol l^{-1} [602,603].

A *cis*-diammine platinum(II) complex of polyglutamic acid was shown to have a substantial trypanocidal activity in mice infected with *Trypanosoma congolense*. A high therapeutic ratio was noted and *cis*-platin was ineffective [604]. Complexes of the type *cis*-[Pt(amine)LCl$_2$] (L = strong *trans*-labilising ligand) were neither toxic nor mutagenic towards *Salmonella typhimurium* in dmso, but were toxic to most bacteria in propanone. *Cis*-[Pt(amine)$_2$Cl$_2$] was less toxic, but was mutagenic. Complexes of some amines including BuNH$_2$ and PhCH(Me)NH$_2$ were mutagenic only towards strains deficient in excision repair mechanisms, implying that they caused specific and repairable damage [605].

The entropies of polyatomic gaseous ions have been reviewed, including discussions of $[M(NH_3)_4]^{2+}$ (M = Pd or Pt) [55]. The effect of the geometric configuration of square planar metal complexes on R_f in paper chromatography was discussed; among the species considered were *cis*- and *trans*-$[Pt(RNH_2)_2X_2]$; the R_f value for the *cis*-isomers was greater than that for the *trans*-analogues [606].

The heat capacity of $[Pt(NH_3)_4]Cl_2$ was measured over the range 87-267 K, indicating a phase transition at 146.6 K. The potential barrier to rotation of the ammine ligands in both phases was determined. The phase transition was of type I, which usually involves a change of crystal structure [607]. The solid phase *cis* $\rightleftharpoons$ *trans*-transformations of $[Pt(NH_3)_2X_2]$ have been studied

[608].

The decomposition of $[Pt(NH_3)_4]Cl_2$ at 1 atm began at 204 °C to give $[Pt(NH_3)_2Cl_2]$, but at 7 mm Hg decomposition was initiated at 193 °C. In contrast, the *trans* to *cis* isomerisation of $[Pt(dmso)(NH_3)Cl_2]$ and $[Pt(dmso)(py)Cl_2]$ occurred on melting, and the temperature was not pressure dependent, implying an inner sphere mechanism [609]. Another study of the decomposition of $[Pt(NH_3)_4]Cl_2$ involved heating in oxygen or hydrogen and an investigation of the effect of mixing with rhenium salts [610]. The thermal decomposition reactions of $[Pt(NH_3)_4][NO_3]_2$ and $[Pt(NH_3)_2(NO_2)_2]$ have also been studied [58]. Thermal decomposition of *trans*-$[Pt(NH_3)_2Cl_2]$ gave $PdCl_2$ then Pd metal or PdO [611]. Both this and $[Pd(NH_3)_4]Cl_2$ catalysed the thermal decomposition of aminoguanidine hydrogen carbonate or cyanuric acid, by a mechanism which was not entirely elucidated [612].

Polarographic studies of *cis*-$[Pt(NH_3)_2X_2]$ (X = [SCN] or $[NO_2]$), *trans*-$[Pt(NH_3)_2X_2]$ (X = $[NO_2]$, [SCN] or [CN]) and *cis*-$[Pt(MeNH_2)_2Cl_2]$ have been described [613,614]. Electrochemical oxidation of $[Pt(NH_3)_xCl_y]^{n-}$ ($x = 0-4$, $y = 0-4$, $n = -2-+2$) have been undertaken [615].

An excellent synthesis of $[Pt(NH_3)_3Cl]Cl$ in three steps (reactions (23)-(25)) has been described in detail [616]. Reaction of *trans*-$[Pt(NH_3)_2Cl_2]$ with thiourea, tu, gave *trans*-$[Pt(NH_3)_2(tu)Cl]Cl$, and the kinetics of the reaction were investigated [617].

$$\textit{trans}\text{-}[Pt(NH_3)_2Cl_2] + KI \xrightarrow{\qquad} \textit{trans}\text{-}[Pt(NH_3)_2ClI] \qquad (23)$$

$$\textit{trans}\text{-}[Pt(NH_3)_2ClI] \xrightarrow{Ag[NO_3],\ H_2O} \textit{trans}\text{-}[Pt(NH_3)_2(H_2O)Cl][NO_3] \qquad (24)$$

$$\textit{trans}\text{-}[Pt(NH_3)_2(H_2O)Cl]^+ \xrightarrow{HCl,\ [NH_4][OH]} [Pt(NH_3)_3Cl]Cl \qquad (25)$$

The outer sphere association constants of $[Pt(NH_3)_4]Cl_2$ (curiously described as *cis* and *trans*) and $[Pt(en)_2Cl_2]$ (*sic !*) with Cl^-, Br^- and $[SeO_3]^{2-}$ were determined [618]. The activation volumes for the first acid hydrolysis of *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(en)Cl_2]$ were determined from a study of the effect of pressure on the aquation velocity. A hexacoordinate transition state with two $Pt-OH_2$ bonds was inferred by comparison with analogues [619].

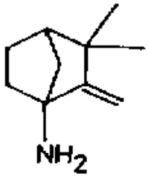
The reaction of $[Pt(NH_3)_2(NO_2)_2]$ with phosphoric acid under a range of conditions has been studied. This was extremely complex, and few of the products were properly characterised [107,173].

$[Pt(NH_3)_4]Cl_2$ was trapped in vesicles and reduced to platinum metal to give a catalyst for the photocatalytic reduction of water to hydrogen [620]. The exchange of $[Pt(NH_3)_4]^{2+}$ and H^+ on α-zirconium phosphate was studied.

This was found to be easier than the related reaction with $[Co(NH_3)_6]^{3+}$ [621]. $[Pd(NH_3)_4][BPh_4]_2$ exhibited photothermographic properties and could be used in a photoimaging system [622]. An electrically conductive support comprising a poly(ethene terephthalate), a subbing layer and a cermet layer was coated with $[Pd(NH_3)_4]Cl_2$, and a surfactant, and combined with an element containing a layer of a lead(II) oxide photoconductor on an electrically conductive support to give an electrically activated recording element [623]. The preparation of an ion exchanging membrane and catalyst-electrode composite useful for water electrolysis involved as its first step the impregnation of an ion exchanging membrane with $[Pt(NH_3)_2Cl_2]$ [624].

N-Butyl aniline in trichloromethane was used to extract palladium from 1-2 M HCl media. This proved especially useful for the extraction of submicro, micro and milligram quantities of palladium in the presence of other platinum group metals [625].

A number of complexes of the type $[ML_2X_2]$ (M = Pd or Pt; X = halide) of monoamines have been described. Among the primary aliphatic amine complexes synthesised were those of 1-aminohexane [626], with $[ML_2X_2]$, $[ML_3X]X$ and $[ML_4]X_2$ being prepared [627]. Both *cis*- and *trans*-isomers of $[PtL_2Cl_2]$ (L = 1-aminocamphene, (166)) were prepared and characterised; the *cis*-compound displayed weak activity against the ospovaccinia virus [628]. When an amino sugar was used as the ligand, the iodo complexes had *cis*-geometry, but Kurnakov's test suggested that the chloro complexes adopted *trans*-geometry [629].

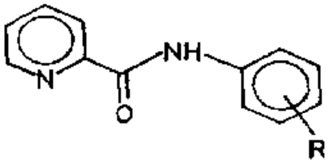


(166)

Thermolysis of $PdCl_2$ in $(Me_2N)_3PO$ at 80-85 °C gave *trans*-$[Pd(Me_2NH)_2Cl_2]$ which was characterised by X-ray diffraction. Since the reaction was not successful under strictly anhydrous conditions it was presumed that the mechanism involved hydrolytic cleavage of $(Me_2N)_3PO$ to Me_2NH [630]. The complexes *cis*-$[M(pyrrolidine)_2X_2]$ (M = Pd or Pt; X = Cl, Br, I, $[NO_2]$ or $[SCN]$) were prepared and characterised by IR and electronic spectroscopy [631]. In the complex $[PtLBr_2].2H_2O$ in which L was hexamethylene tetramine, the structure was not fully defined, but it may well be polymeric [632].

In an X-ray diffraction study of *cis*-$K_2[Pt(NH_2CH_2CH_2SO_3)_2Cl_2].3H_2O$ the anions were shown to be packed into the crystal in columns with significantly different platinum-platinum distances (3.22 and 4.70 Å) [633].

The preparation of 2-aminopyridine complexes, $[PdL_4]Cl_2$, and *trans*-$[PdL_2Cl_2]$ has been described. The species were characterised by IR spectroscopy, DTA and TG measurements, but the authors did not indicate which nitrogen atom was metal bound [634]. In *cis*- and *trans*-$[ML_2X_2]$, in which L was 2-, 3-, or 4-aminobenzonitrile, the ligand was bonded through the amino group [635]. **(167)** and **(168)** were also bonded to platinum through the $-NH_2$ groups [636].



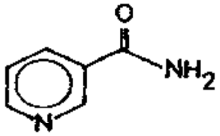
(167) R = 2-NH_2
(168) R = 3-NH_2

The complex *cis*-$[Pt(BuNH_2)_2I_2]$ was converted to the *trans*-isomer on thermolysis, the reaction being followed by ^{127}I NQR spectroscopy. Similar processes were observed for related bromides, the reaction being monitored by $^{79,81}Br$ NQR spectroscopy [637]. Some of the species formed by reaction of $PdCl_2$ with RNH_2 were poorly characterised, but could be used as catalysts for hydrogenation of dienes to monoenes [638].

1.6.4.2 Unidentate heterocyclic nitrogen donor ligands

The complexes *cis*-$[PtL_2Q_2]^{2+}$ (L = thiourea, Q = py, 2-Mepy or imidazole) were prepared from $[PtL_4]^{2+}$ and the neutral amine. Related derivatives of methylthiourea were also reported [639]. The reaction of *cis*-$[Pt(4\text{-NCpy})_2Cl_2]$ with tu was subjected to a kinetic study in the presence of added salts [640]. A simple complex, *cis*-$[PtL_2Cl_2]$, could be prepared from 2,6-dimethylpyrazine (coordinated at N(4)) but the 2,3-dimethyl and 2,5-dimethyl ligands gave only polymeric complexes [641]. Complexes *cis*-$[PtL_2X_2]$, *cis*- and *trans*-$[PtL_2(NH_3)_2]Cl_2$ and $[PtL_4]Cl_2$ of nicotinamide, **(169)**, have been prepared. IR spectroscopic data indicated that binding involved the pyridine nitrogen atom in all cases, although the amide group was involved in extensive hydrogen bonding [642].

Trans-$[Pt(1\text{-ethenyl-3-methylpyrazole})_2Cl_2]$ was prepared from $PdCl_2$ and the ligand in propanone. X-ray diffraction data showed the ligand, **(170)**, was coordinated *via* the sp^2 nitrogen atom, N(2) [643]. A similar study was performed on the complex of (171), which was also N(2) coordinated. The nmr spectra were analysed in great detail [644]. The structure of *trans*-$[Pt(pzl)_2(PPh_3)_2]$, **(172)**, was also reported [645]. Reaction of $[Pt(dppe)(pzl)_2]$ with $[CpRu(PPh_3)_2(MeOH)]^+$ did not give the desired complex $[(dppe)Pt(\mu\text{-}pzl)_2Ru(PPh_3)Cp][BPh_4]$, but instead the complex underwent disproportionation yielding the known compounds $[Pt_2(\mu\text{-}pzl)_2(dppe)_2]^{2+}$ and $[CpRu(pzl)(PPh_3)_3]$ [646].



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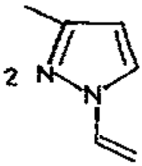
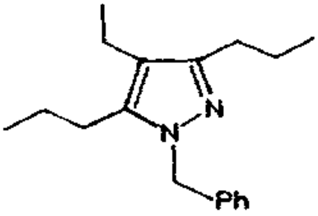
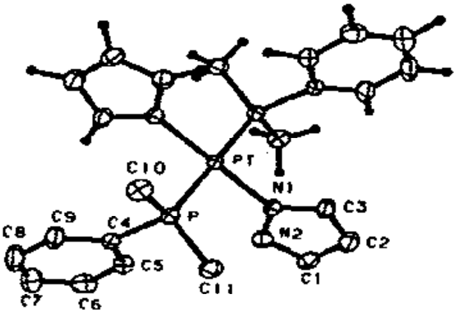


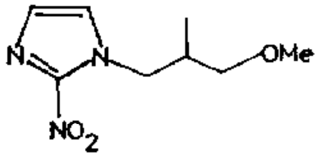


(170) **(171)**



(172) (Reproduced with permission from [645])

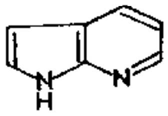
Reaction of 1-propylimidazole, L, with $K_2[PtCl_4]$ and KI gave *cis*-$[PtL_2I_2]$, characterised by IR spectroscopy and conductivity measurements [647]. Other workers reported related *cis*-complexes of palladium. These were found to be less good inhibitors than oxazole complexes of membrane bonded calcium and magnesium dependent ATPase [648]. A range of complexes of nitrated imidazoles has been prepared. In *trans*-$[Pt(misonidazole)_2Cl_2]$ ((173) = misonidazole) an X-ray diffraction study established N(1) as the site of metal coordination. All the complexes were moderate radiosensitisers with low toxicity [649].



(173)

IR, Raman and ^{1}H nmr spectroscopy were used to investigate the structure and bonding in *cis*- and *trans*-[Pt(oxazole)$_2$Cl$_2$]. The nitrogen atom was platinum bound [650]. A range of palladium complexes, (Pd(oxalate)L$_n$), (n = 1, L = isoxazole, 3,5-Me$_2$isoxazole, 2-Mebenzoxazole or 2,5-Me$_2$benzoxazole) were characterised as sparingly soluble dimers. Other related complexes (n = 2, L = *N*-Me-, *N*-Et- or *N*-Pr-imidazole or 3-amino-5-Me-isoxazole) were monomeric [651].

Tocicity data and preliminary anti-tumour tests have been reported for the 7-azaindole complexes, *cis*-[Pt(**174**)$_2$X$_2$] (X = Cl or I or X$_2$ = oxalate). Coordination was *via* N(7), and although toxicity varied considerably, there was little or no anti-tumour action [652]. The structure of [Pt(dmtp)$_4$][Pt(SCN)$_6$] was established by X-ray diffraction (dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine, (**175**)). The [SCN] ligands were *S*-bonded, and dmtp acted as a monodentate ligand binding through the triazole nitrogen corresponding to the N(9)-nitrogen of a purine fused ring system. It thus resembled guanine rather than adenine or hypoxanthine [78]. Benzotriazole (BTAH), (**176**), was N(3)-coordinated in [Pd(BTAH)$_2$Cl$_2$] [653]. The fog in a black and white silver halide radiographic film was reduced without a decrease in photographic sensitivity by addition of [Pd(**177**)$_4$]Cl$_2$ to the developer [654].



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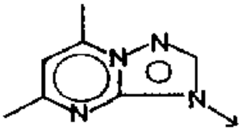

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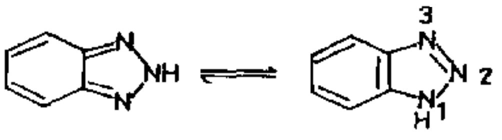

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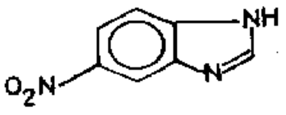
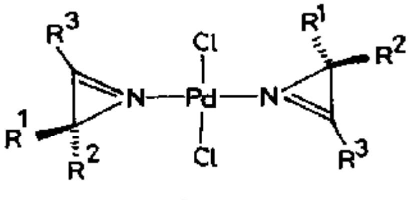


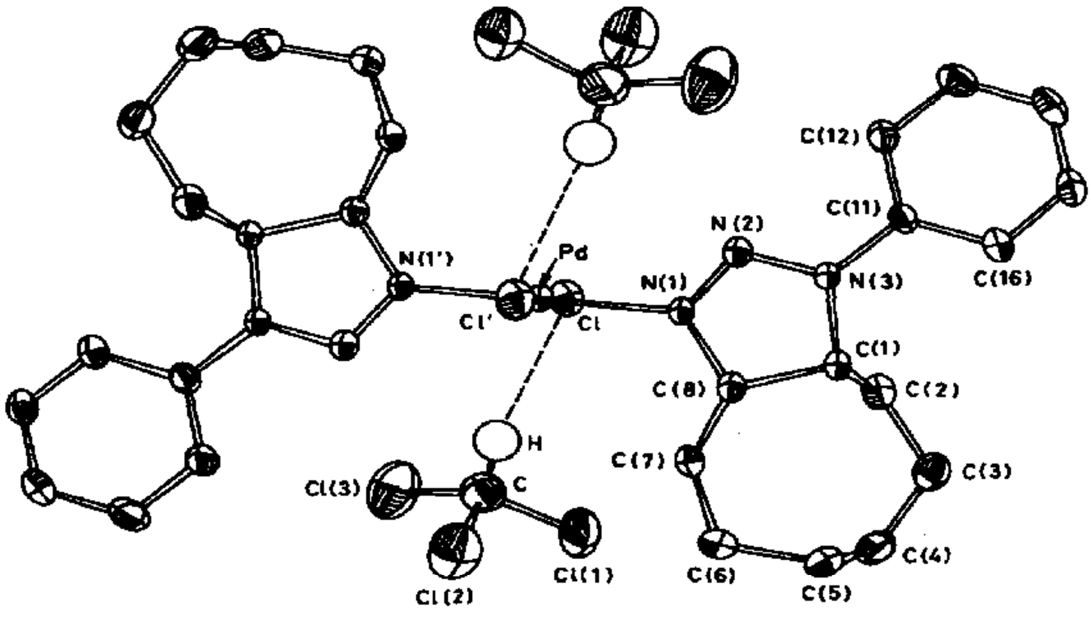
(177)

Palladium complexes of the type **(178)** have been investigated. The rate of ring opening depended on the substituents, with the C-N single bond being ruptured in all cases [655].



(178)

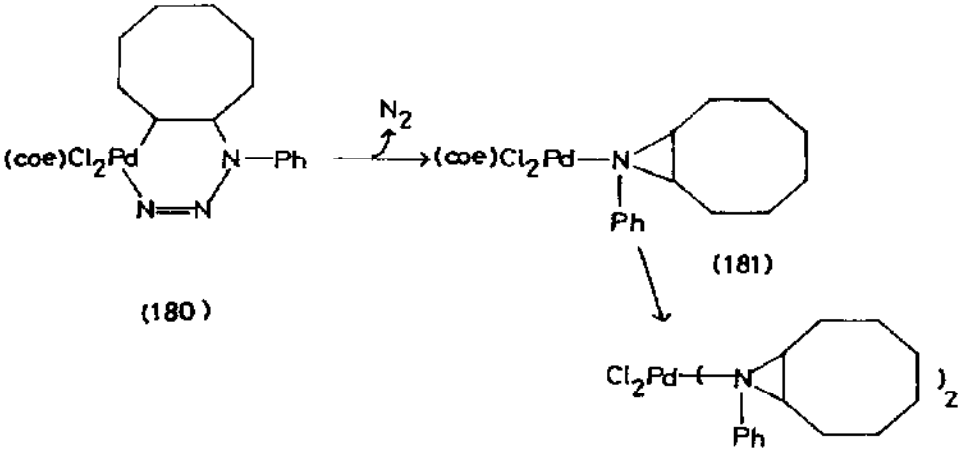
Reaction of $PdCl_2$ and PhN_3 with cyclooctene gave **(179)**, characterised by X-ray diffraction. This was presumed to be formed *via* the triazole ligand, formed from cyclooctene and the azide. However, with $[Pd(cyclooctene)_2Cl_2]$ and PhN_3, reaction took place in the coordination sphere, yielding sucessively **(180)**, **(181)** and **(182)** [656].



(179) (Reproduced with permission from [656])

1.6.4.3 Bidentate and polydentate amine donor ligands

A method for determining the total platinum content in urine, blood plasma and tissues of patients or experimental animals receiving *cis*-platin has been developed. This was based on drying and combustion in a muffle furnace, followed by dissolution in aqua regia/HCl/en. This gave a platinum complex of 1,2-diaminoethane, which could be detected by pulse polaraography [657].



(180)

(181)

(182)

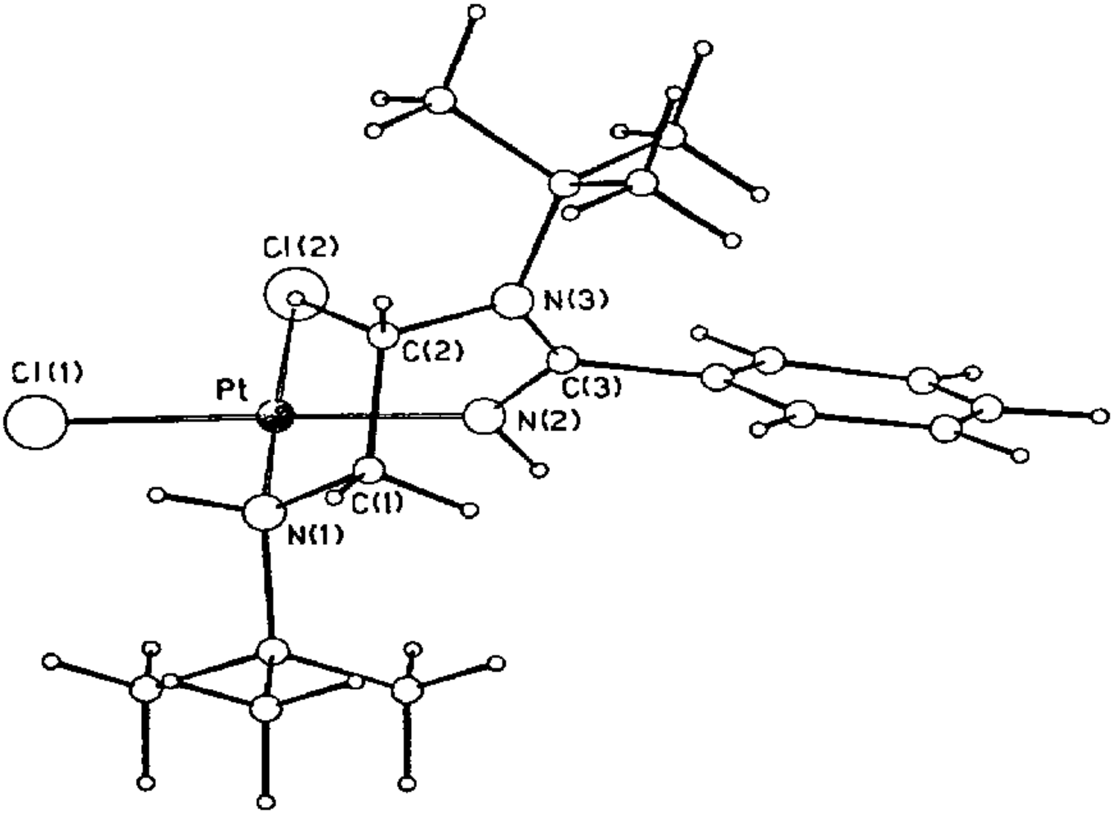
The electronic configurations of a range of platinum diamine complexes were calculated by the CNDO/2-SCF method. Electron indices were correlated with anti-tumour activity, LD_{50} and therapeutic indices [658].

A range of complexes $[PdLCl_2]$ in which L = en, 1,3-pn, 1,2-pn, $H_2NCH_2CH_2NMe_2$, $HMeNCH_2CH_2NHMe$, $Et_2NCH_2CH_2NH_2$ or $Me_2N(CH_2)_3NMe_2$ were prepared. Electronic absorption and magnetic CD spectra were measured. These implied that the pattern of the metal d orbitals was similar to that for $[PdCl_4]^{2-}$. However, for the related species *trans*-$[PdL_2Cl_2]$ (L = monodentate amine) the d_{xz} and d_{yz} to $d_{x^2-y^2}$ band was split to give two spin allowed dd bands [659].

Reaction of *cis*-$[Pt(PhCN)_2Cl_2]$ with $Me_3CNHCH_2CH_2NHCMe_3$, L, gave species of stoicheiometry $[Pt(PhCN)(L)Cl_2]$, $[Pt_3(PhCN)_4(L)_4Cl_4]$ and $[Pt_2(PhCN)_3(L)_3Cl_2]$. IR spectroscopic data implied that the amine had reacted with the coordinated nitrile to give an imine complex, the structure of the mononuclear species, (183), being established by X-ray diffraction [660]. Complexes of the gross structure **(184)** (R = H or Bu) were synthesised in *meso*, **RR**, **SS** and {RR+SS} forms. The SS-form with R = H had the best effect on the growth of the hormone dependent human MCF 7 breast cancer cell line [661]. Treatment of $[Pt(H_2L)Cl_2]$ (H_2L = **(185)**) with $Tl[OOCC_6H_5]$ in hot pyridine gave $[Pt(py)_2L]$ *via* $[Pt(H_2L)(py)_2][OOCC_6F_5]$. The structure of the product was established by X-ray diffraction [662].

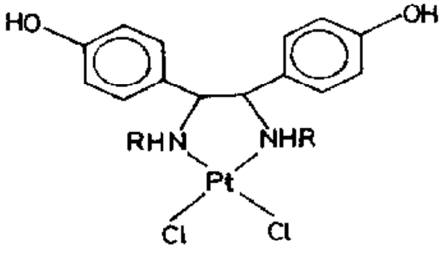
The ligand 1,3-pn was described to be a useful complexing agent for palladium in electroplating; $[Pd(1,3\text{-}pn)Cl_2]$ was readily soluble both in water and in typical electroplating baths [663]. A range of complexes (186)

(R^1, R^2, R^3, R^4 = H, alkyl, cycloalkyl or arylalkyl; X = Cl or X_2 = [$O_2CCH_2CO_2$]) was prepared and characterised; the complexes showed some anti-tumour effect in mice [664]. Although the structure given for a new anti-leukaemic compound was **(187)** (X = halide or [NO_3] or X_2 = glycolate or pyruvate) it was described as an aminomethyl piperidine derivative; the interested (and linguistically adept) reader would be well-advised to consult the original paper in Japanese [665]. Reaction of $K_2[MX_4]$ (M = Pd or Pt; X = Cl or Br) with **(188)** gave a mixture of [M**(188)**X_2] and [M**(188)**$_2$]X_2. [M(188)X_2] was shown to be polymeric with **(188)** acting as a bridge, but the other complex was probably monomeric [666].



(183) (Reproduced with permission from [660])

1,2-Diaminocyclohexane has been a popular ligand this year. The structures of [Pt(R,R-1,2-diaminocyclohexane)X] (X = oxalate or [$OOCCH_2COO$]) have been determined by X-ray diffraction. Both were useful anti-tumour compounds [667,668]. The related bis(pyruvate) derivative was shown to act as an immunosuppressant, and inhibited the transformation of human peripheral blood lymphocytes by phytohaemaglutinin, pokeweed mitogen or concanavalin-A [669]. An X-ray diffraction study of **(189)** showed that the achiral biphenyl derived ligand was coordinated entirely stereospecifically in a λ-chiral configuration [670]. Electronic absorption and CD spectra of $[PtLCl_2]$, $[PtL(NH_3)_2][PtCl_4]$ and $[PtL(NH_3)_2][PdCl_4]$ (L = R,R-1,2-diaminocyclohexane) in the region of singlet dd transitions of the chiral species showed very strong bands induced by intermolecular and interionic interactions in the solid state. Optical activity was also induced in the dd transitions of the anions [671].



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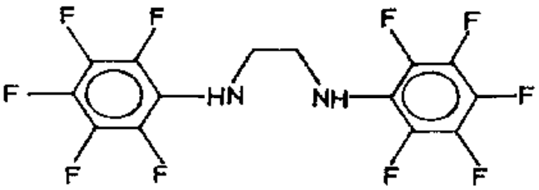

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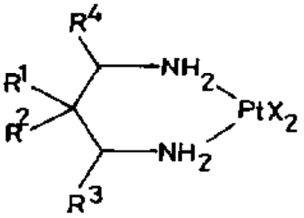

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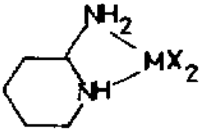

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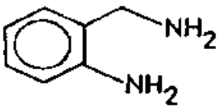
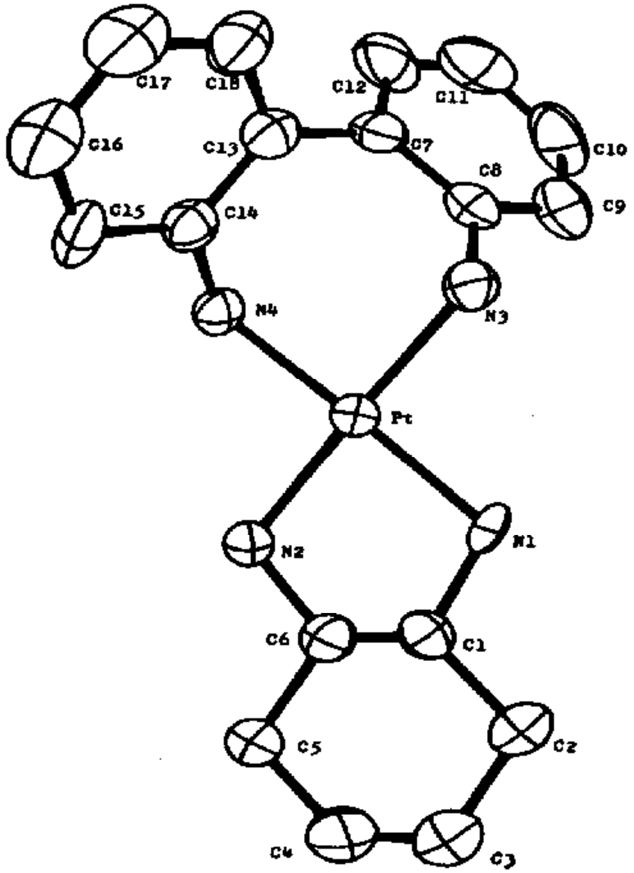


(188)

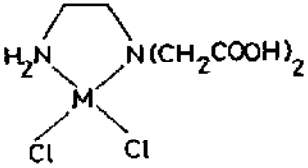
$Edta H_4$ was shown to inhibit vitamin C oxidation in an aqueous solution of palladium(II) [672]. Two methods for the determination of palladium in electroplating baths were based on chelation with $[edtaNa_2]^{2-}$ at pH 10, and back titration of the excess of $edtaH_4$ with 0.1 M $Zn[SO_4]$ [673]. The reaction of *cis*-$[Pt(edtaH_4)Cl_2]$ with L (L = en, 1,3-pn, bipy or phen) gave $[Pt(edtaH_4)L]Cl_2$, characterised by IR and UV spectrsocopy and conductance measurements [674]. The complexes **(190)** and **(191)** (M = Pd or Pt) have been prepared [675].

A number of palladium and platinum derivatives of polymeric amines and related species have been described. For example, polyetheneimine was reacted with $K_2[PtCl_4]$ to give species with a platinum loading of 40-50 %. The use of such complexes may reduce the toxic effects of platinum chemotherapy and may also have some targeting value [676]. Square planar platinum(II) derivatives of poly(*N*-ethenylpyrrolidone) and poly(*N*-ethenyl-5-methyl-2-oxazolidone) proved useful as hydrogenation catalysts and anti-bacterial agents [677]. A study of the complexation of $PdCl_2$ on the surface of dien modified Aerosil A175 led to the conclusion that **(192)** had been formed. However, there was also evidence for bis(diamine) chelated species [678]. **(193)** was synthesised as a polymer of good thermal stability with a molecular weight of 10^5-10^6, from $K_2[PtCl_4]$ and $RNHNH_2$. It showed some activity against tumoural cell lines [679].



(189) (Reproduced with permission from [670])

Organometallic polymers were prepared from $K_2[PtCl_4]$ and 1,6-diaminohexane or urea, or from $K_2[PdCl_4]$ and 1,6-diaminohexane or 1,4-diaminobenzene. Mass spectrometry was used for characterisation of the materials [680]. Related complexes were tested for antibacterial activity [681].



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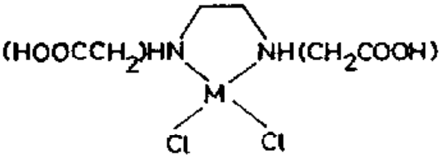

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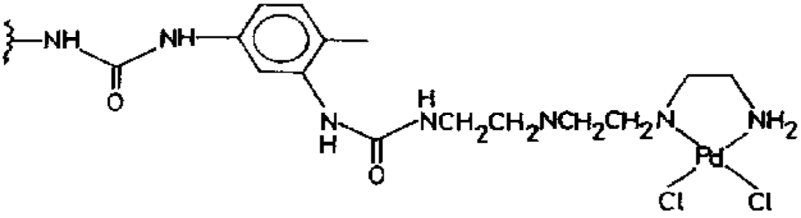

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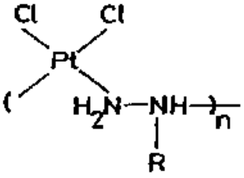


(193)

There have been more reports of the kinetics of substitution of dien complexes. Anation reactions of the type (26) (L = 1,4,7-Et_3dien, 1,1,7,7-Me_4dien or 1,1,4,7,7-Me_5dien) were subjected to kinetic analysis. For a given L the second order rate cosntants were in the order X = Cl < Br < I < $[N_3]$. ΔH^*, ΔS^* and ΔV^* values were consistent with a mechanism in which the aquo complex was the only reactive species, but deviations occurred above pH 9 due to the intervention of hydroxo and/or conjugate base containing species [683]. The kinetics of the spontaneous solvolysis of $[Pd(R_5dien)X]^{2-n+}$ (R = H, Me or Et; X^{n-} = Cl^-, Br^-, I^- or py) were studied spectrophotometrically. The aquation and reverse anation rates depended strongly on the nature of the R groups, but the equilibrium constants were almost independent of substitution [684]. The kinetics of substitution of $[PdLCl]^+$ (L = 1,4,7-Me_3dien, 1,1,7,7-Me_4dien or 1,1,4,7,7-Me_5dien) by hydroxyl or iodide ion were studied as a function of nucleophile, temperature and pressure. The rate constants decreased as steric hindrance in the substrate increased. There was very strong evidence in the

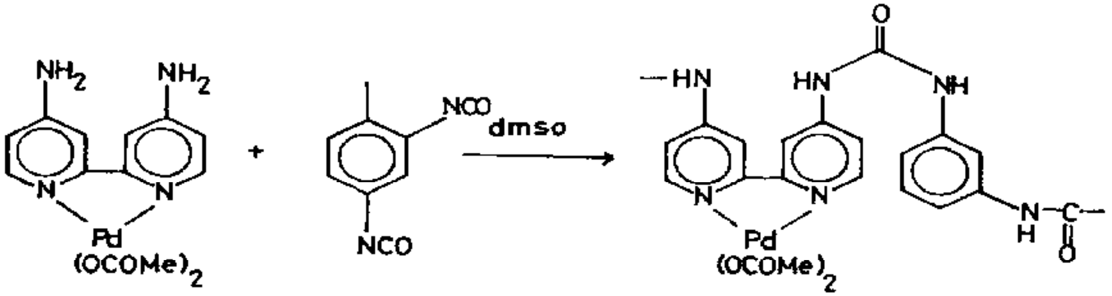
$\Delta V^{\ddagger}$ values for an associative reaction mechanism [685]. Related ethyl substituted dien derivatives were also investigated; again the reaction mechanism was associative for most nucleophiles. However, with the hydroxyl ion a conjugate base mechanism was also important [686].

$$[PdL(H_2O)]^{2+} \; + \; X^- \longrightarrow [PdLX]^+ \; + \; H_2O \qquad (26)$$

The photophysical and redox properties of two newly prepared cyano bridged complexes $[(CN)(bipy)_2Ru(CN)Pt(dien)][ClO_4]_2$ and $[(dien)Pt(NC)\{Ru(bipy)_2\}(CN)Pt(dien)][ClO_4]_4$, synthesised from $[Pt(dien)Br]Br$, were investigated [687]. Since the added platinum moiety was essentially inert from a redox point of view this functionalisation did not destroy the original excited state properties of the ruthenium chromophore. Its effect was limited to slight modifications to the lifetime, energy and redox properties of the excited state [688].

The liquid extraction of palladium(II) by cobalt dicarbolide hexachloride ($[(C_2B_9H_8Cl_3)_2Co]$ = $[BCl_6]$) in the presence of bipy was very effective, the major species in the organic phase being $[Pd(bipy)_2][BCl_6]_2$ [689].

The kinetics of the nucleophilic substitution of chloride in $[Pt(bipy)(am)Cl]^+$ (am = $EtNH_2$ or $HOCH_2CH_2NH_2$) were studied. It was shown that solvent controlled anchimeric assistance to the departing chlorine was important in the aprotic solvent ethanenitrile but not in methanol [690]. Reaction of the substituted bipy complex, **(194)**, with the diisocyanate, **(195)**, gave the polymeric species, **(196)**. Reduction of **(196)** with $Li[AlH_4]$ gave a palladium(0) complex which was a good catalyst for alkene hydrogenation [691].

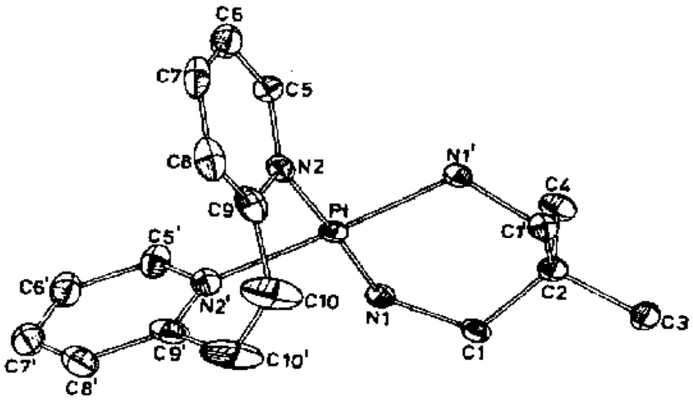


(194) **(195)** **(196)**

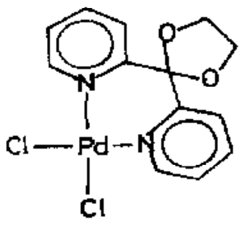
Reaction of $[Pd(5\text{-}NO_2phen)_2][ClO_4]_2$ with 1-aminopropane or piperidine gave a red species which was unstable both thermodynamically and kinetically.

Attack of the amine occurred at the coordinated phenanthroline [692]. Treatment of the related complex [Pd(5-NO_2phen)Cl_2] with en gave, ultimately [Pd(en)$_2$]Cl_2. In this case the diamine attacked both directly at palladium and at the 5-NO_2phen ligand to give a Meisenheimer complex [693].

The complex [({1,2-bis(pyridin-2-yl)-ethane-*N*,*N'*}-2,2-dimethyl-1,3-diaminopropane-N^1,N^3)PtCl_2].H_2O, **(197)**, was prepared and studied by X-ray diffraction techniques. Even at -115 °C the -CH_2CH_2- bridge showed crystallographic disorder, and the interconverison of the two possible chair forms was still fast on the nmr spectroscopic timescale at -90 °C [694]. (198) was synthesised from PdCl_2 and the ligand, and its structure was elucidated by an X-ray diffraction study. The coordination at platinum was tetrahedrally distorted square planar, and the six-membered chelate ring adopted a boat conformation. The complex is a precursor to a series of *C*-bonded propane dioate complexes [695].

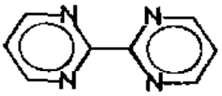


(197) (Reproduced with permission from [694])



(198)

Reaction of *cis*-[Ph_2Pt(dmso)$_2$] with bipym, **(199)**, gave [Ph_2Pt(bipym)], which could be converted to a series of bimetallic species, **(200)** in which {MX_2} was {HgCl_2}, {MnCl_2} or {PtPh_2} [696].



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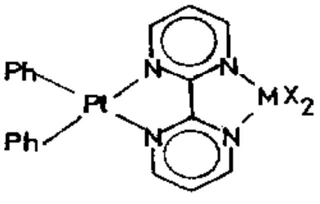
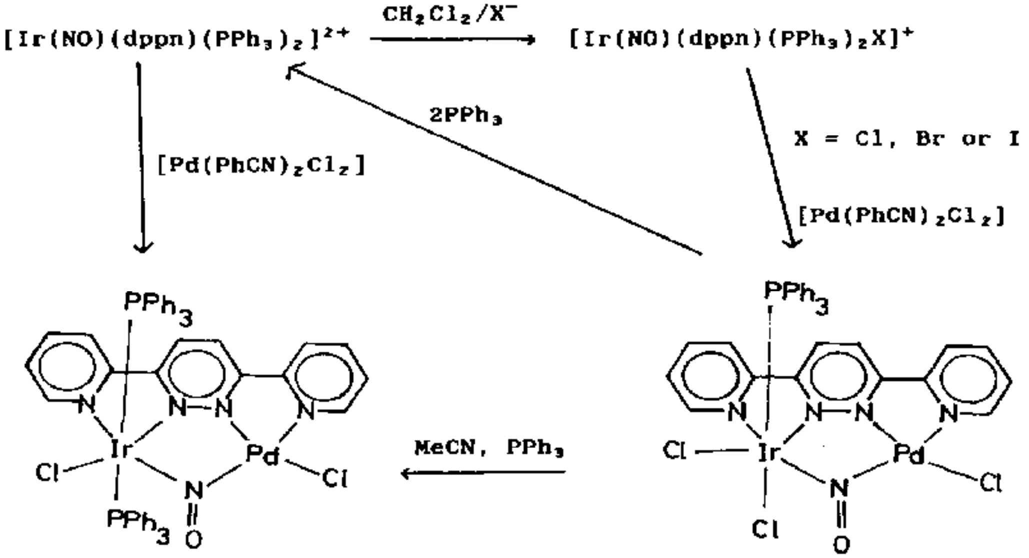


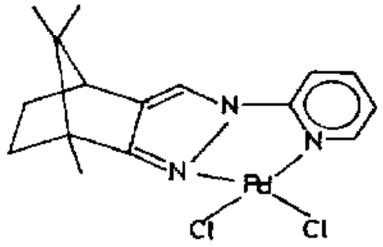
(200)

Interesting bimetallic complexes could also be obtained using the ligand 3,6-bis(2-pyridyl)pyridazine (dppn) (Scheme 4) [697].

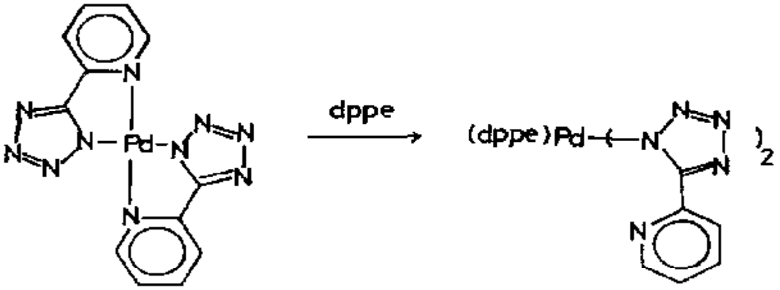


Scheme 4 Preparation and interconversions of bimetallic complexes of 3,6-bis(2-pyridyl)pyridazine (dppn) [697]

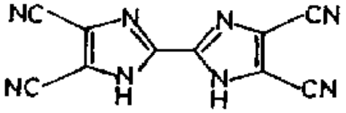
The structure of **(201)**, prepared by the reaction of $PdCl_2$ with the ligand, was established by X-ray diffraction techniques. The coordination at palladium was essentially planar, suggesting that the ligand shows little steric resistance to coordination and may therefore be useful as a chiral auxiliary [698]. Reaction of $[Pd(PPh_3)_2(N_3)_2]$ with 2-cyanopyridine gave **(202)**, which was transformed to (203) by addition of dppe [699]. The preparation of $K_2[PdL(CN)_2]$ and $M_2[PtL(CN)_2]$ (H_2L = **(204)**; M = K, $[NH_4]$ or $[Bu_4N]$) has been described. The aim was to use the 4,4',5,5'-tetracyano-2,2'-biimidazole ligand as an alternative to two cyanides, since its donor ability might be expected to be comparable. An X-ray diffraction study of $[Bu_4N]_2[PtL(CN)_2]$ showed distorted square planar geometry at platinum and a platinum-carbon bond distance shorter than in the tetracyanoplatinates. This indicates a slightly lower π-acceptor capacity for L than for [CN]. The size of the cation prevented the stacking of the planar anions, and partially oxidised compounds were not obtained on treatment with molecular chlorine [700].



(201)



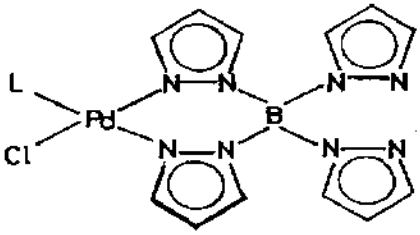
(202) **(203)**



(204)

Reaction of *trans*-[{PdLCl(μ-Cl)}$_2$] with Na[Bpzl$_4$] gave **(205)** for L = PEt$_3$ or P(OEt)$_3$ and **(206)** for L = Et$_2$S. An analogue of **(205)** was prepared from [Pd(en)Cl$_2$]. All these complexes showed interesting dynamic behaviour on the nmr spectroscopic timescale [701].

(207) proved to be a sensitive and selective reagent for the spectrophotometric determination of palladium(II), with which it formed a 1:1 complex in HCl solution. Although it was not made clear, binding through an amino group and an azo nitrogen atom seems probable [702]. The ligand **(208)** reacted with PdCl$_2$ to give **(209)** but the precise course of the reaction was not delineated [703]. Complexes of stoicheiometry [PtL(HL)]Cl and [PtL$_2$] were formed from LH = *syn*- or *anti*-**(210)** (R = Ph or Me). Although the mode of bonding was discussed and it seemed certain that both nitrogen atoms were used, the structures were not fully established [704]. In the complexes [PdLCl] of both **(211)** and **(212)** (LH) the ligand was tridentate. Deprotonation of the amido NH was promoted by metal coordination to the other nitrogen atoms, thus altering the more usual *O*-ligation of amides [705].



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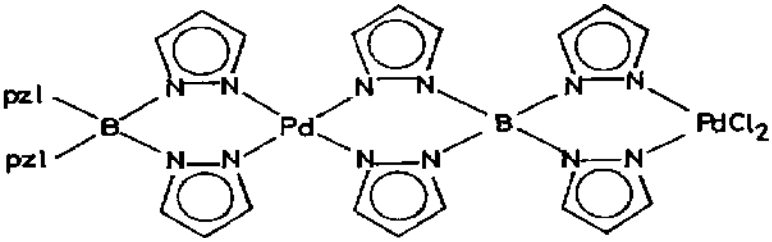

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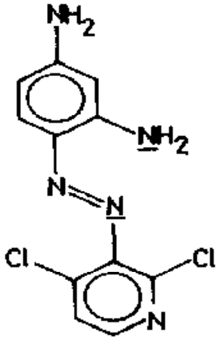
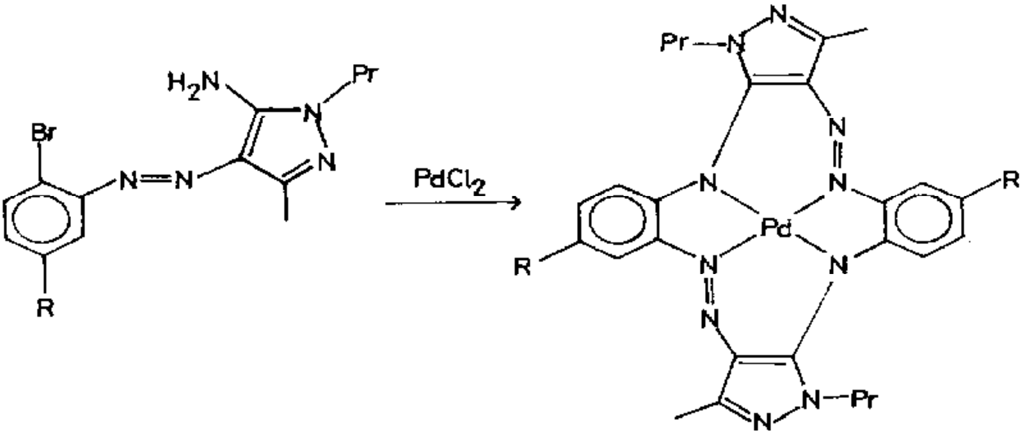
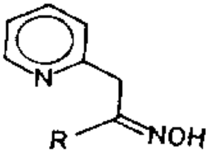


(207)

More complexes of tetraaza tetradentate macrocycles have been reported, including the derivatives of **(213)**. Pyridine derivatives gave association complexes studied by UV spectroscopy. There was a linear correlation between the pKa of the ligand and the stablity constant of the complex. In the palladium complex of **(213)** the palladium atom was postulated to occupy a position above the plane of the ring. It was thus easy to form a five-coordinate complex, but association of a sixth ligand was more difficult [706].



(208) **(209)**



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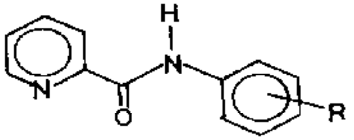
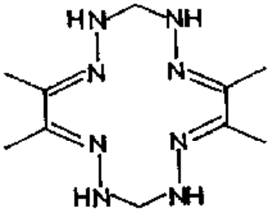


(211) R = 2-NH_2
(212) R = 3-NH_2



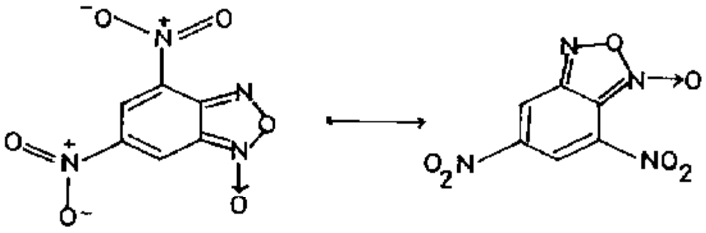
(213)

1.6.4.4 Porphyrin and Phthalocyanine Complexes

An increased number of studies of palladium(II) and platinum(II) porphyrin complexes has been published, with many again dealing with photochemistry and photophysics. The ^{1}H and ^{13}C nmr spectra of [Pd(TPP)] and [Pt(TPP)] have been determined. In [Pt(TPP)] there was coupling between ^{195}Pt and the β-hydrogen and β-carbon nuclei of the pyrrole rings, with some evidence of coupling to the α-carbon centres [707]. The migration behaviour of metal complexes of tetrakis(4-methyphenyl)porphyrin in HPTLC has been investigated; the palladium derivative was included in the study [708]. The structure of [Pt(TPP)] was determined by X-ray diffraction, and it was shown to be isomorphous with the iron, cobalt, nickel, copper and palladium complexes. The porphine nucleus was ruffled with the nitrogen donors alternately above and below the mean plane of the complex [709].

The electronic structures of metal derivatives of uroporhyrin I have been investigated by UV spectroscopy. Dimerisation caused shifts in the orbital energies which led to a change in the transition dipoles of the $\pi \rightarrow \pi^*$ transitions that give rise to the α- and Soret bands [710]. Monomeric and aggregated forms of both the palladium and platinum derivatives in aqueous solution were studied using absorption and resonance Raman difference spectroscopy [711].

[Pt(TPP)] (and TPP derivatives of other metals) forms 1:1 molecular complexes with 4,6-dinitrobenzofuroxane, (214). The association could be described in terms of a π-π interaction, with the porphyrin complex as the donor. Association constants were determined from optical absorption and ^{1}H nmr spectroscopic data. Epr spectroscopic data suggested that π-complexation resulted in changes to the electronic structure of the central metal atom which were reflected in the Pd-N σ-bonding [712]. Similar data were obtained for [Pd(TPP)] and (215) [713].



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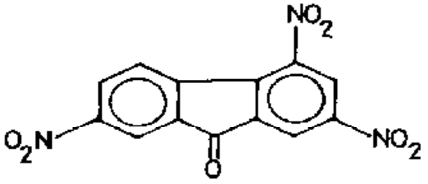


(215)

The redox chemistry of water soluble metalloporphyrins has been studied by electrochemical and pulse radiolytic techniques. The palladium derivatives of TPPSH$_6$ and tetrakis *N*-methyl-4-pyridyl porphyrin were investigated. Under both electrochemical and radiolytic conditions unstable π-radical cations were formed [714]. Voltammetric and epr spectroscopic methods were used to study the electrochemical behaviour of free radical derivatives of tetrakis(4-hydroxo-3,5-bis(1,1-dimethylethyl)phenyl)porphyrin and its palladium complex. The presence of the radical led to a decrease in the redox potential of the complex, implying that the odd electron could be coupled with the porphyrin π-system [715].

Kinetic data for the dealkylation reaction of *N*-methyl-5,10,15,20-tetraphenylporphyrin by palladium(II) in MeCN, dmso or dmf have been reported. These were consistent with a mechanism involving ion-dipole association of a solvated palladium porphyrin complex with the free base *N*-methylporphyrin, followed by a series of ligand dissociation and bond formation equilibria, and a final step invoving nucleophilic displacement of the *N*-methyl group. Whilst kinetic details were solvent dependent, the final product in all cases was [Pd(TPP)] [716].

The formation of dimers of $TPPSH_6$ and its zinc(II) and palladium(II) complexes was studied using optical and triplet epr spectroscopy [717]. The epr study showed a strong effect of dimerisation on the values of the zero field splitting parameters of the triplets [718].

Quantum yields for the formation of singlet oxygen were measured in neutral aqueous solution for several palladium complexes of water soluble porphyrins [719].

Fine structure fluorescence spectra of palladium porphyrin complexes in different organic solvents and films of polyethylenebutyral were obtained using selective laser excitation at 4.2 K [720]. Phosphorescence and polarization spectra of the lowest ^3E_u state of a platinum porphyrin derivative in a glass at 1.3 K and 77 K were obtained. The decay of the ^3E_u state to the $^1A_{1g}$ state in the emission spectrum was confirmed [721]. Correlations between core size and the wavelength of the α-band in the Raman spectra of palladium and platinum porphyrin complexes were found. This method allowed the authors to relate porphyrin geometry directly to the energetics of the porphyrin π-system [722].

The FAB mass spectrometric technique allowed the observation of molecular ions (and also of protonated molecules) from palladium and platinum complexes of 2,9(10),16(17),23(24)-tetrakis(4-(1-phenyl)-1-methylethyl)phenoxy)phthalocyanines with little or no fragmentation. This provided a facile method to obtain the molecular weights of these otherwise rather intractable complexes [723].

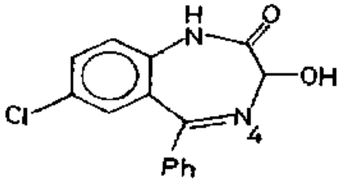
Fluorescence from the first and second excited singlet states of [Pd(TPP)] and [Pd(Pc)] was studied in various solvents [724].

The syntheses, association in solution, and Langmuir-Blodgett monomolecular layer formation of palladium and platinum (and various other metal) complexes of phthalocyanines substituted with 4-(1-phenyl-1-methylethyl)phenoxy groups have been reported. The highest degree of association was found for the platinum complex, which formed a tetramer. It was noted that complexes which showed a high degree of association also gave a a larger area per phthalocyanine moiety in the monolayers [725].

Resonance Raman, fluorescence and phosphorescence spectra were obtained for [Pd(Pc)] in Shpol'skii matrices at 4.2 K. The degenerate states of the first excited singlet and triplet were lifted 67±2 cm^{-1} by a CF stabilised Jahn Teller effect [726]. The effect of three different mixed solvent Shpol'skii matrices at 4.2 K on site formation and vibronic progressions of [Pd(Pc)] has been investigated [727].

1.6.4.5 Imine donor ligands

Complexes $[ML_2X_2].2H_2O$ and $[ML_4]I_2$ (M = Pd or Pt, X = Cl or Br) of the oxazepam, **(216)**, have been synthesised and characterised by IR, ^1H nmr and UV spectroscopy. The ligand was invariably coordinated *via* N(4) [728]. The first transition metal complex of an iminoaziridine, **(217)**, has been prepared and characterised [729].



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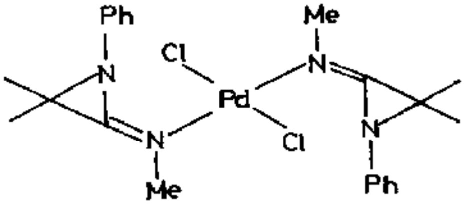
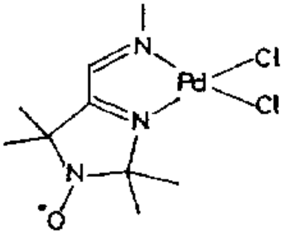


(217)

A number of the *N*,*N*-chelating ligands studied this year have included an imine function as at least one of the two nitrogen donor atoms. For example, the preparation of the interesting radical complex **(218)** was described [730], and **(219)** acted as a tridentate donor towards palladium in $[PdLCl][ClO_4]$ [731]. Pd^{2+} reacted with **(220)**, HL, to give a *trans*-complex, $[PdL_2]$, in which coordination was *via* the imine nitrogen and the deprotonated pyrrole nitrogen atom [732].

Reaction of $[Pd(PhCN)_2Cl_2]$ with **(221)**, $[Ni\beta_2]$, gave a coordination polymer of composition $\{PdCl_2(Ni\beta_2)_{0.25}\}$. Coordination of $Ni\beta_2$ to palladium was through the imine nitrogen atom and the nitrile in a *trans*-arrangement [733]. Another chelate involving an imine nitrogen was **(223)** and its geometric isomer, prepared from the carbene complex, **(222)**. The imino portions of the carbene ligand in **(222)** could also act as an *N,N*-chelate donor towards {Pd(acac)} or {$PtCl_2$} [734].



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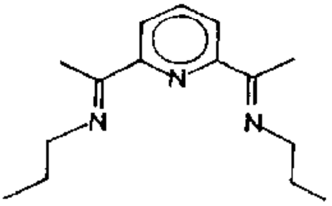

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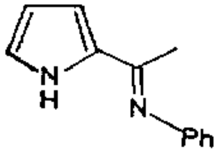

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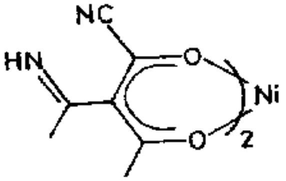

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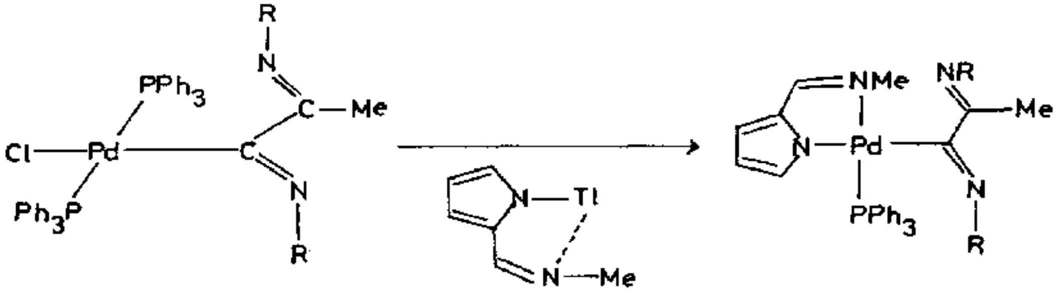


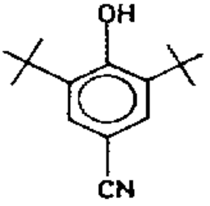
(222) **(223)**

1.6.4.6 Nitro complexes

$K_2[M(NO_2)_4]$ (M = Pd and/or Pt) was used in platinum or platinum-palladium alloy electroless coating baths [735].

1.6.4.7 Nitrile ligands

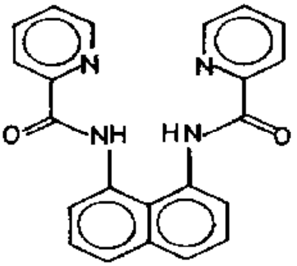
The structure of *cis*-$[Pt(MeCN)_2Cl_2]$ was determined by an X-ray diffraction study. The platinum-chlorine bonds (2.264 Å) were relatively short, due to the low *trans*-influence of the nitriles [736]. Exchange of PhCN in $[Pd(PhCN)_2Cl_2]$ for other aryl nitrile ligands including **(224)** has been described. The related radical complex was studied by epr spectroscopy [737].



(224)

1.6.4.8 Amides and related ligands

The nitrogen atoms of amides are rather rarely metal coordinated and examples are found usually only in ligands with strong geometric constraints. For example, **(225)**, H_2Q, acted as a tetradentate ligand towards both palladium and platinum in [MQ] [636]. The imide nitrogen atoms of **(226)** were also deprotonated before coordination in complexes of stoicheiometry $M_2[PdL_4].nH_2O$ [738].



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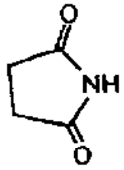


(226)

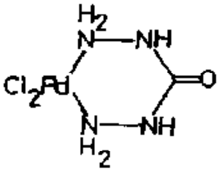
Complexes of carbohydrazide, $H_2NNHCONHNH_2$, L, were prepared including $[PdL_2(C_2O_4)]$, $[PdLCl_2]$, **(227)**, $[ML_2X_2]$ (M = Pd or Pt, X = Cl or Br) and the *N,O*-chelate, (228) [739]. A novel factor contributing to the stability of nitrogen containing ylide complexes was clarified by IR and XPES measurements on aminimide palladium complexes such as **(229)**. An interaction through the σ-bond between the quaternary nitrogen and the anionic nitrogen was observed in the ylide and could be termed an electron displacement effect [740].

1.6.4.9 Diazine, triazine and tetraazadiene ligands

The structure of *trans*-$[Pd(PPh_3)(Me_3CN{=}CH{-}CH{=}NCMe_3)Cl_2]$ was determined by an X-ray diffraction study. The diazabutadiene acted as a monodentate ligand with the chain extended [741].

The chemistry of arylazooximate complexes has been reviewed. Both *cis*-

and *trans*-platinum complexes are known and stack in the solid state [742]. In particular, reaction of **(230)**, (LH), with $K_2[PtCl_4]$ gave the *cis*-isomer, **(231)**, which was fully characterised by X-ray diffraction. The structure is a loose stack with a platinum-platinum distance of 3.151 Å. Under basic conditions the *trans*-isomer was obtained and was also fully characterised. However, *trans*-$[PdL_2]$ did not stack and showed a large and unexpected distortion towards tetrahedral geometry [743]. The reaction of [Pd(L)BCl] (B = Ar_3P, PMe_2Ph, $PMePh_2$ or PCy_3) with an excess of B gave *trans*-$[Pd(L)B_2Cl]$ in which L was monodentate. The equilibrium between the species depended on the steric demand of B [744].



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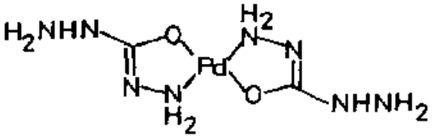

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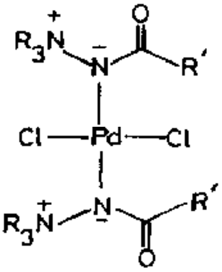

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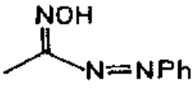

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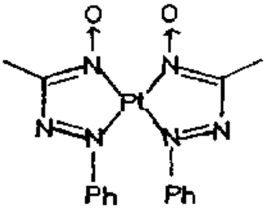
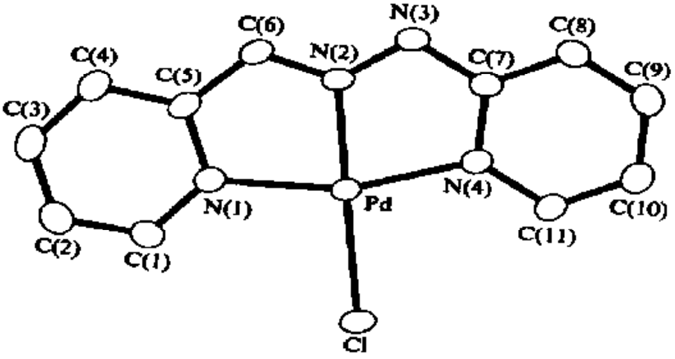


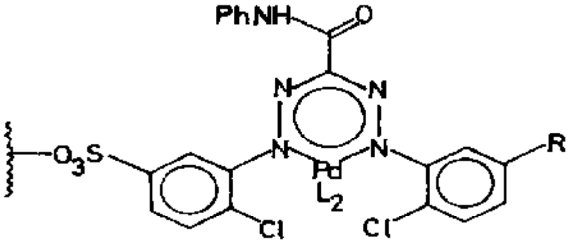
(231)

The structure of the complex **(232)** of E-pyridine-2-carbaldehyde pyridin-2-ylhydrazine was elucidated by X-ray diffraction [745].

Formazans have been used as the functional groups of chelating ion exchangers; palladium(II) was readily coordinated to the terminal nitrogen atoms in **(233)** [746].



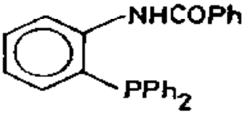
(232) (Reproduced with permission from [745])



(233)

1.6.4.10 Bidentate nitrogen phosphorus donor ligands

Reaction of $K_2[PtCl_4]$ with PNH, **(234)**, gave *trans*-$[Pt(PNH\text{-}P)_2Cl_2]$. Treatment with triethylamine gave the *cis*-chelate, $[Pt(PNP\text{-}P,N)_2]Cl_2$, which underwent cyclometallation on heating yielding **(235)**, characterised by X-ray diffraction. The mechanism for formation of **(235)** involved CH oxidative addition followed by NH reductive elimination [747].



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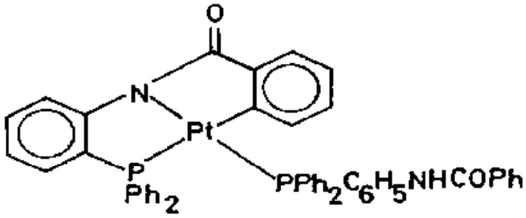
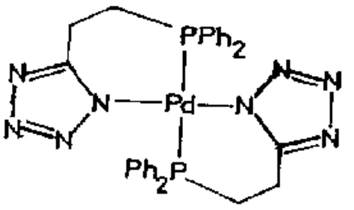


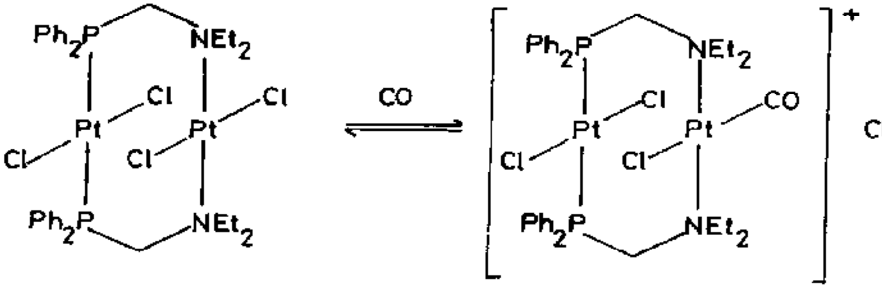
(235)

Treatment of $[Pt(cod)X_2]$ with $Ph_2P(CH_2)_3NMe_2$ gave initially a complex in which the ligand was phosphorus coordinated. Reaction with Ag$^+$ yielded [Pt{Ph$_2$P(CH$_2$)$_3$NMe$_2$-*N,P*}{Ph$_2$P(CH$_2$)$_3$NMe$_2$-*P*}Cl]Cl [312]. Reaction of [Pd(PPh$_3$)$_2$(N$_3$)$_2$] with Ph$_2$PCH$_2$CH$_2$CN gave **(236)** [699].



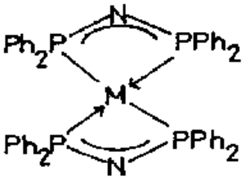
(236)

Carbonylation of **(237)** gave **(238)** reversibly; the equlibrium could be shifted to the right using [BPh$_4$] as counter ion [748].



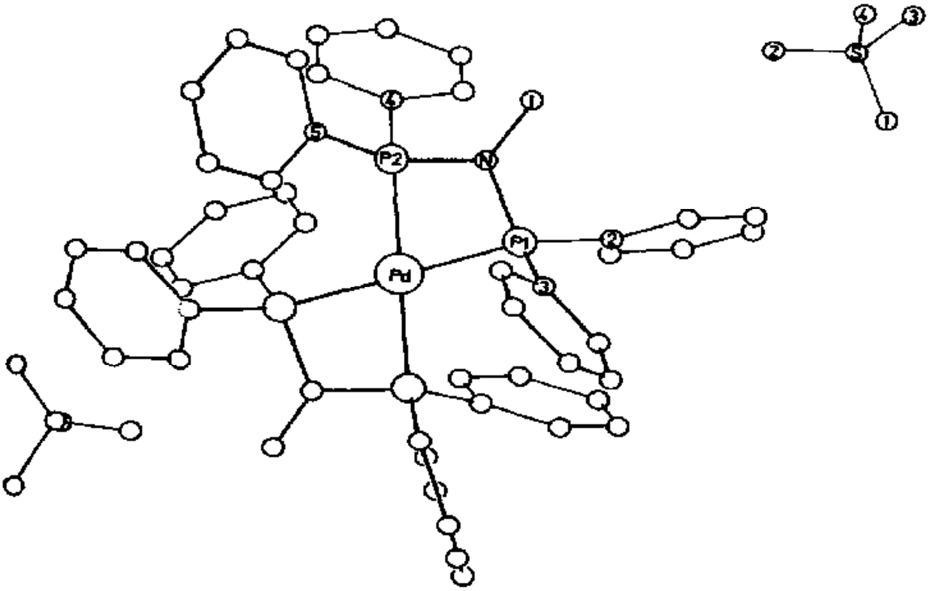
(237) **(238)**

Treatment of K$_2$[PtCl$_4$] or PdCl$_2$ with [(Ph$_2$P)$_2$N]Li gave the homoleptic complexes, **(239)**, characterised spectroscopically. Reaction of **(239)** with MeOSO$_2$F gave a product methylated on nitrogen. The structure of the palladium complex, **(240)**, was established by X-ray diffraction [749].

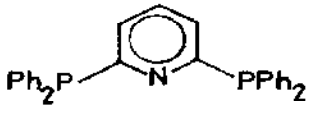


(239)

Reaction of [M(cod)Cl$_2$] (M = Pd) with **(241)** gave *cis,cis,trans*-[Pd$_3${μ-(2-Ph$_2$P)$_2$py}$_3$Cl$_6$], **(242)**, which was rather stable with respect to conversion to other isomers or to polymer. However, with M = Pt a complex mixture was obtained including the complexes *cis,cis*-[$Pt_2\{\mu-(2-Ph_2P)_2py\}_2Cl_4$], **(243)**, and *trans*-[$Pt_2\{\mu-(2-Ph_2P)_2py\}_2I_4$], **(244)**, both of which were identified by X-ray diffraction. It is clear that solubility was important in determining which complex was actually isolated [750].



(240) (Reproduced with permission from [749])



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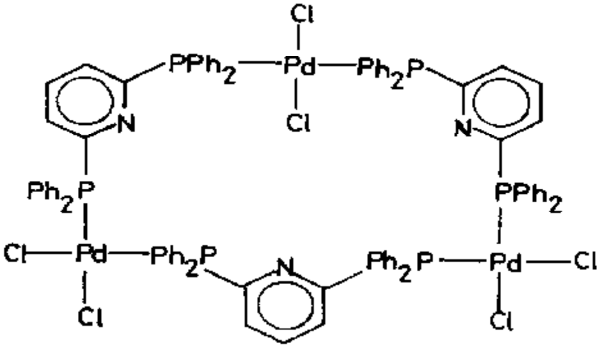
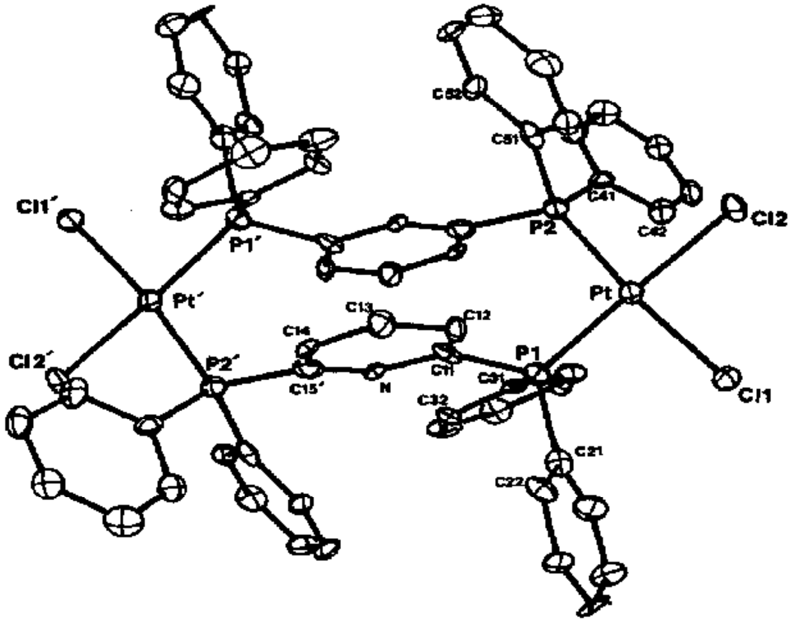
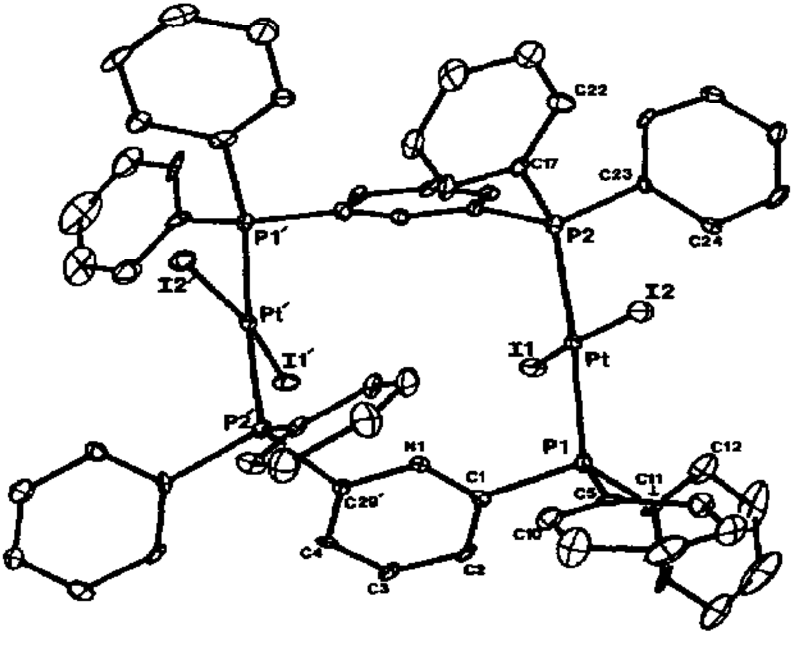


(242)

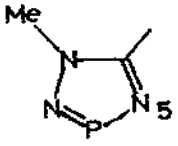
Trans-[$\{Pt(PEt_3)Cl_2\}_2$], when reacted with **(245)**, L, yielded [$Pt(PEt_3)_2L_2]Cl_2$, which reacted with methanol to give (246) by attack of the alcohol on an intermediate in which **(245)** was coordinated *via* N(5). Loss of chloromethane gave **(247)**, characterised by X-ray diffraction. In similar reactions of the related ligand, (248), an intermediate *trans*-[M(**248**)(PEt$_3$)Cl$_2$] was initially produced. For M = Pt, **(248)** was *P*-bonded, but for M = Pd *N*-coordination was dominant. Reaction with methanol again gave ring opening, this time to **(249)** [751].



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



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



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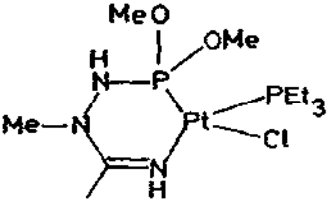
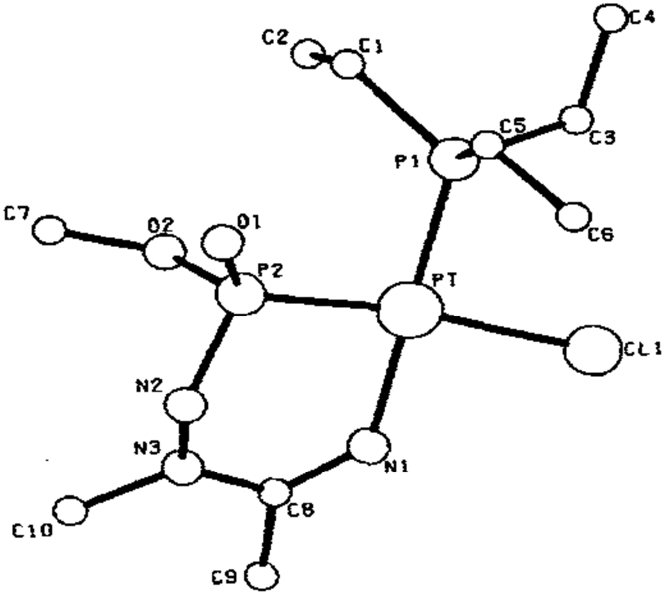
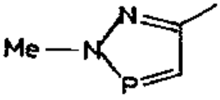


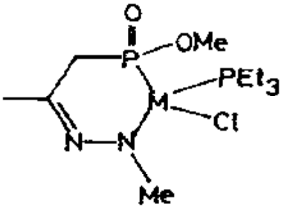
(246)



(247) (Reproduced with permision from [751])



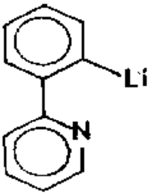
(248)



(249)

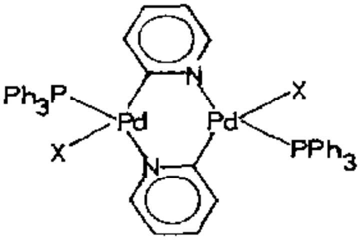
1.6.4.11 Bidentate nitrogen carbon donor ligands

Pure *cis*-[bis(2-phenylpyridine)platinum(II) was prepared from **(250)** and *trans*-[Pt(SEt$_2$)$_2$Cl$_2$]. The X-ray diffraction study of the compound revealed bow-like distortions of the ligands and a solid state association in dimers, with the Pt-Pt distance 3.53 Å. However, there did not seem to be any significant association in solution. Cyclic voltammetry revealed an almost reversible one electron reduction at −1.94 V involving a ligand to radical anion transformation, but oxidation (at +0.46 V) was irreversible [752]. The crystalline material showed a very strong emission at room temperature under UV irradiation [753].

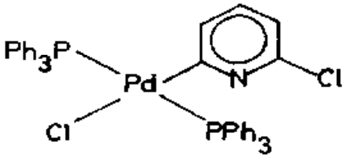


(250)

The protonation and methylation of **(251)** has been investigated. Electrophilic attack involved only the 2-pyridyl nitrogen, without cleavage of the N–C bond [754]. Treatment of **(252)** with $Ag[ClO_4]$ gave a cyclometallated dimer, **(253)** [234]. Other cyclometallated 2,6-dichloropyridine derivatives have been studied [755].



(251)



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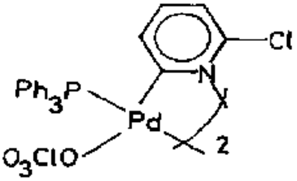
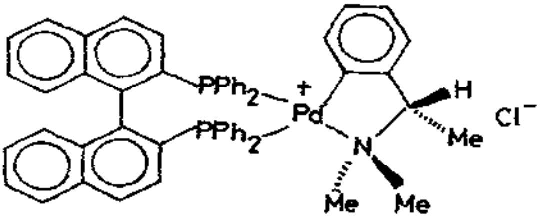
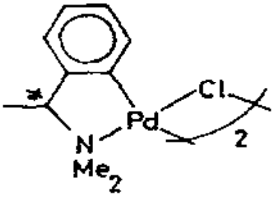


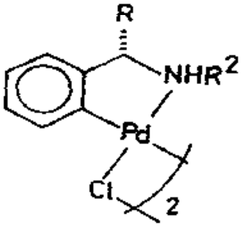
(253)

The optical purity of new chiral binaphthyl biphosphine ligands has been checked by complexation as **(254)** [756]. Enantioselective reduction of Δ^2-oxazoline-5-one was studied using a system formed from $PdCl_2$/chiral 1-phenylethylamine. It was concluded that **(255)** was the precursor of the active catalyst [757]. Chiral complexes, (256), have been prepared and characterised [758]. Asymmetric bidentate ligands, (257) (E = P or As) could be resolved by fractional crystallisation of diastereomeric palladium(II) complexes of cyclometallated chiral 1-phenylethylamine. Only the complexes with nitrogen *trans* to phosphorus or arsenic were obtained [759]. Stereoselective formation of a chiral centre in **(258)** has been studied [760]. The selection of an appropriate base when reacting the ligand with $Li_2[PdCl_4]$ proved important [761].

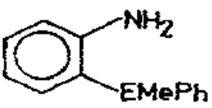


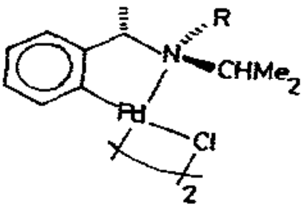
(254)





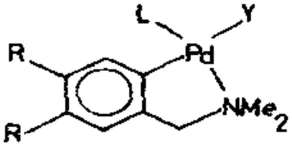
(255) **(256)**





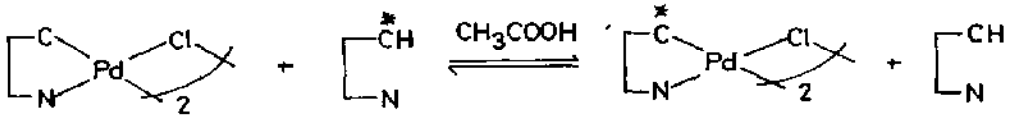
(257) **(258)**

^{13}C nmr spectra have been recorded for **(259)** (L = PPh_3 or $AsPh_3$, X = Cl or Br, R = OMe or H). No quadrupolar broadening due to coupling to ^{105}Pd was observed [762].



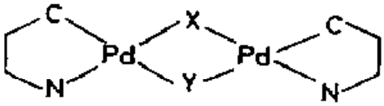
(259)

Exchange of one cyclometallated ligand for another (reaction (27)) has been studied. The reaction was useful not only as an example of ligand exchange, but also as route to the cyclopalladation of reluctant substrates such as 4-diethylaminomethyl nitrobenzene, which would not cyclometallate directly, but would exchange [763]. It was also shown that solution conformation was extremely important in determining the ease of cyclometallation [764].

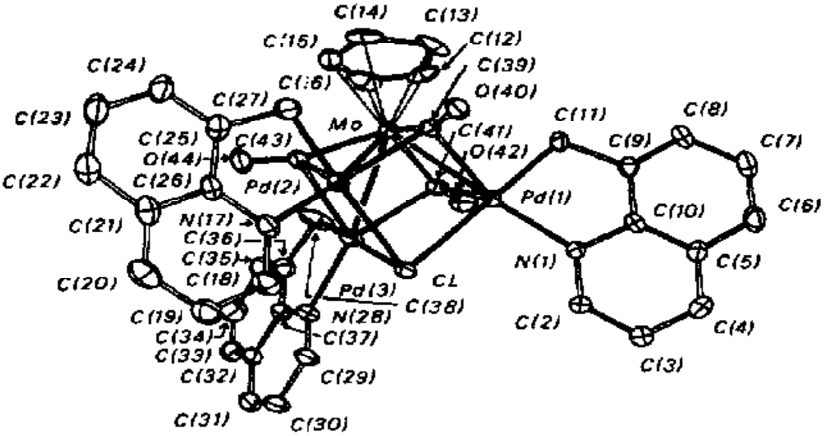


(27)

The preparation of a wide range of bridged cyclometallated complexes, (260), with {μ_3-(Ph$_2$PCHCOOEt)} and {(μ_3-Mo(CO)$_3$Cp)(μ_3-Cl)} ligands has been described. The structure of (261) was determined by X-ray diffraction [765].



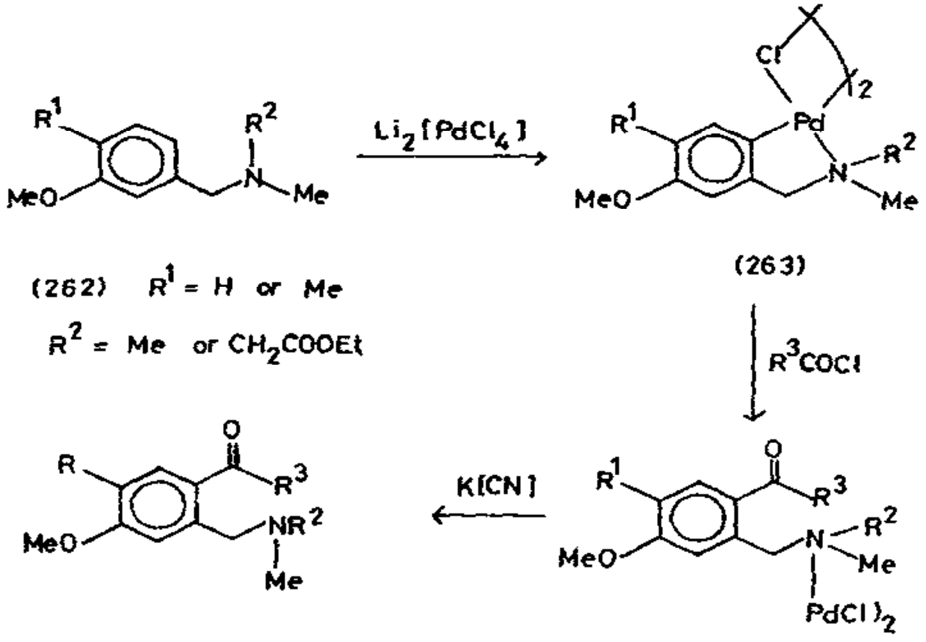
(260)



(261) (Reproduced with permission from [765])
Structure of [{Pd(8-mq)}$_3$(μ_3-Mo(CO)$_3$Cp)(μ_3-Cl)][BF$_4$]

Reaction of Li$_2$[PdCl$_4$] with (262) gave (263), which could be reacted with R^{3}COCl to give (264) [766].

Cyclometallation of (265) occurred regiospecifically giving (266). (267) was formed on treatment with 3-butene-2-one. (266) also underwent the usual bridge splitting reactions [767].

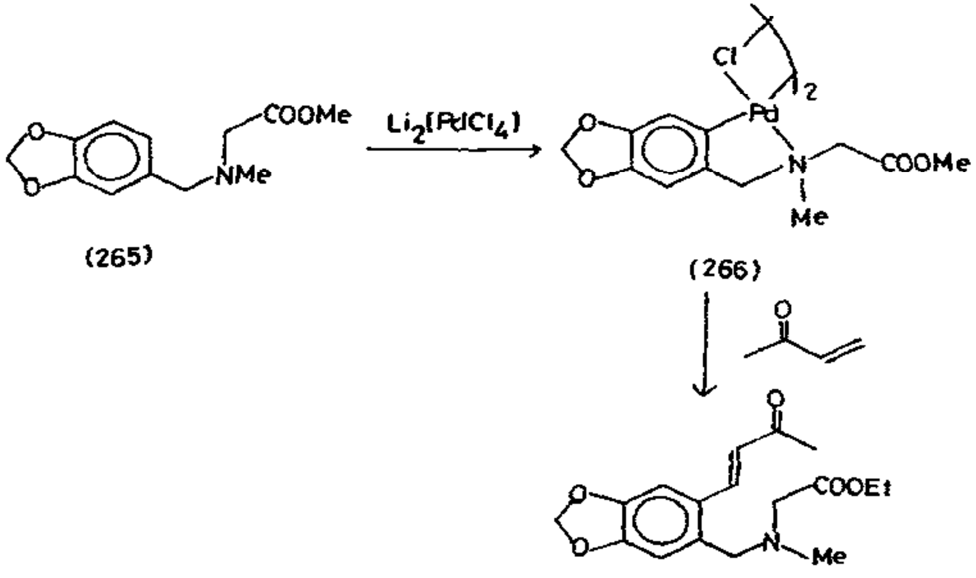


(262) R^1 = H or Me

R^2 = Me or CH_2COOEt

(263)

(264)

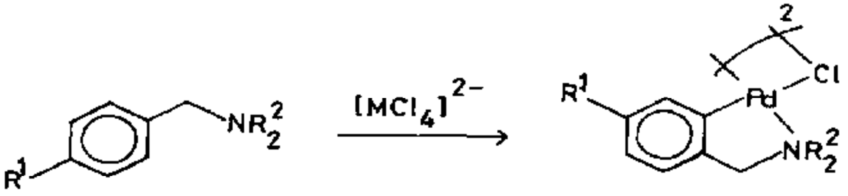


(265)

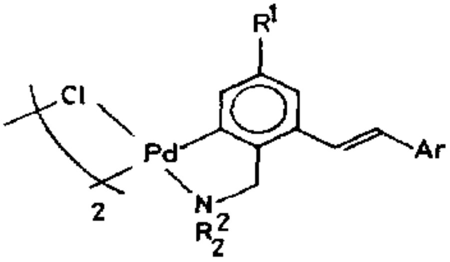
(266)

(267)

Reaction of (268) with $[MCl_4]^{2-}$ gave the expected derivatives. ([illegible]). Treatment with phenyl ethene, however, did not give an obvious insertion product, but more unusually, **(270)** [768]. A kinetic study of the reaction suggested that this was a complex process (Scheme 5) [769].



(268) **(269)**

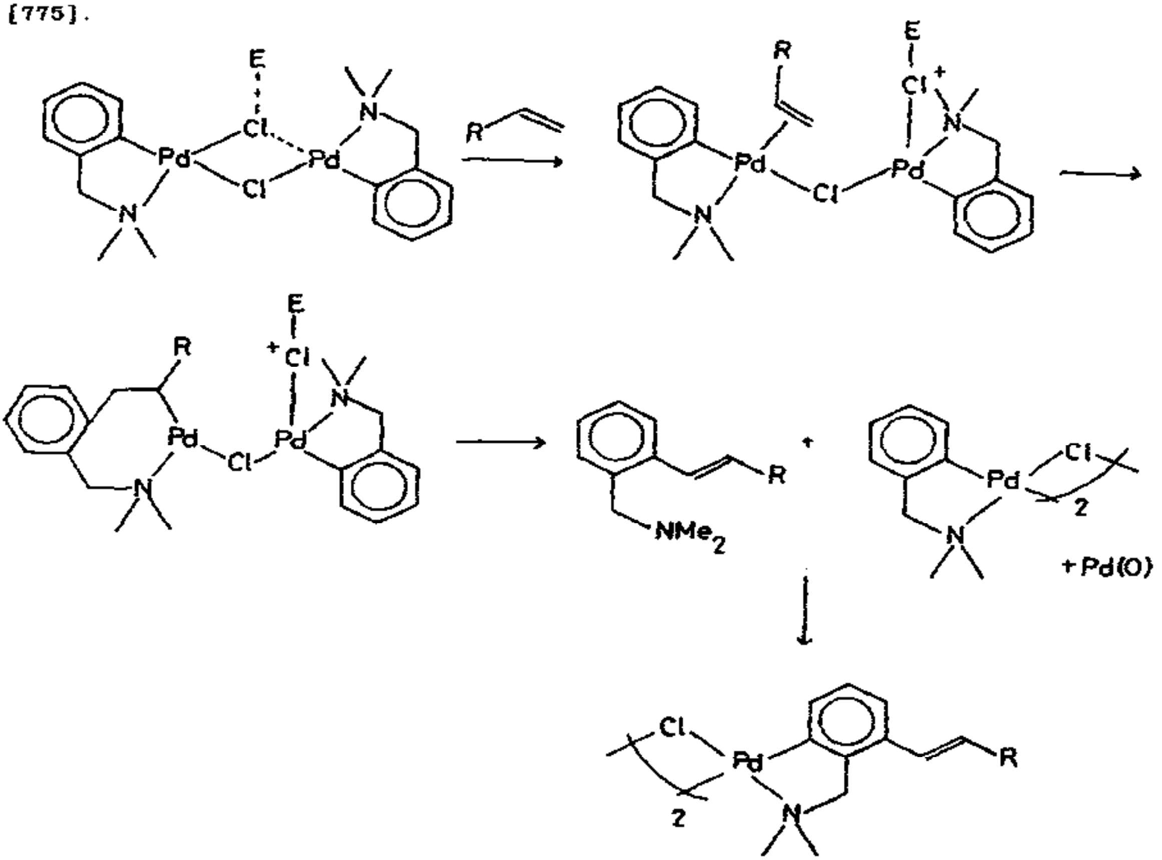


(270)

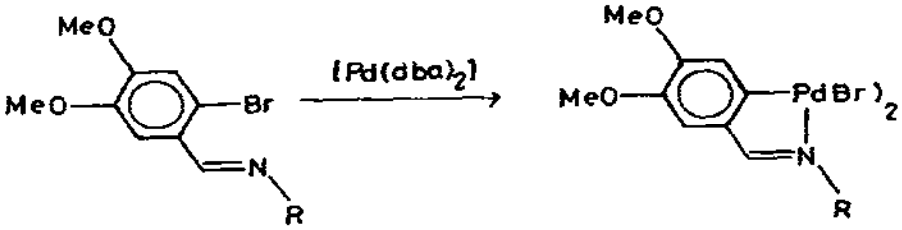
Reaction of **(271)** with [Pd(dba)$_2$] gave the cyclometallated dimer **(272)**, and a number of related processes were also described [770]. The bis cyclometallated diimine polymer, (273), underwent all the expected depolymerisation bridge splitting reactions on treatment with phosphine ligands, and the products were characterised in greater detail this year [771].

Further cyclometallated azoarenes have been prepared this year. Reaction of 4,4'-dimethoxyazobenzene gave a cyclometallated bridged dimer on reaction with K$_2$[PdCl$_4$]. This reacted with 8-hydroxyquinoline to give **(274)**, characterised by X-ray diffraction. Neither complex had a thermotropic mesophase, in contrast to the free ligand [772]. The non-symmetric azobenzene in **(275)** appears to have undergone rather regioselective metallation; the usual bridge splitting reactions with pyridine, aniline and quinoline were noted, giving complexes in which the incoming ligand was *trans* to carbon. In **(275)** the existence of a strongly birefringent and fluid nematic mesophase between 190 °C and 205 °C was confirmed by miscibility measurements. The adducts with pyridine and quinoline were shown to be new mononuclear liquid crystals in which a layered smectic phase was present [773].

Some unusual reactions of **(276)** (X = OCOMe) have been noted. With PPh$_3$ and [Bu$_4$N][CN] a conventional bridge splitting and substitution occurred to give **(277)**, but using dppe as the ligand the 3-aminobenzo[g]indazole, **(278)**, was formed. Reaction with CyNC gave the insertion product, **(279)**, for X = OCOMe but the more conventional bridge split complex, **(280)**, without PPh_3 and when X = Cl [774]. When **(281)** was treated with $[PdCl_4]^{2-}$ metallation occurred regiospecifically at the aryl ring. **(282)** was then converted to (283), which on attempted metallation gave **(284)** possibly *via* **(285)** and **(286)** [775].



Scheme 5 Mechanism of phenyl ethene insertion into a cyclometallated dimer [769]



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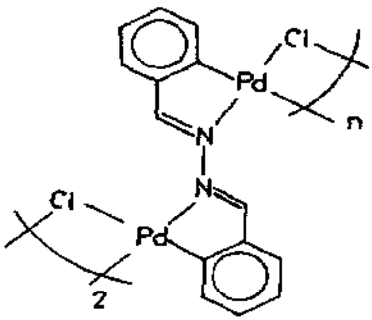

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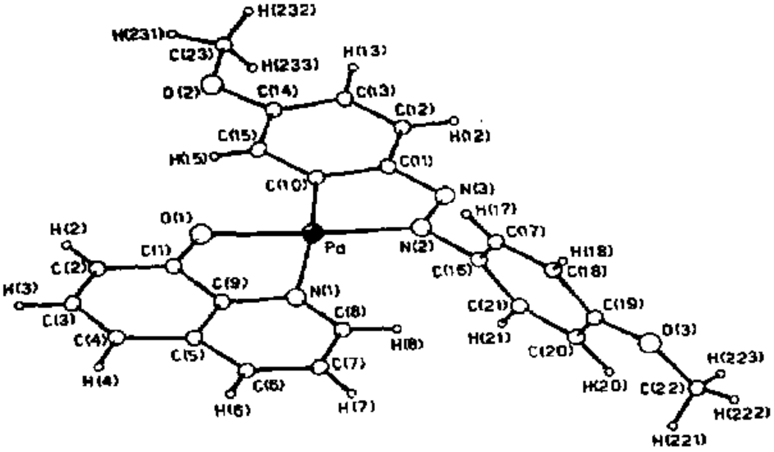
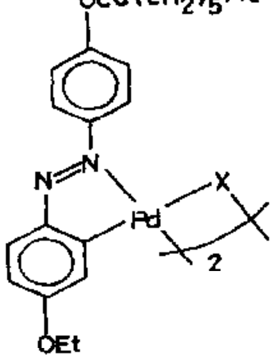


(274) (Reproduced with permission from [772])



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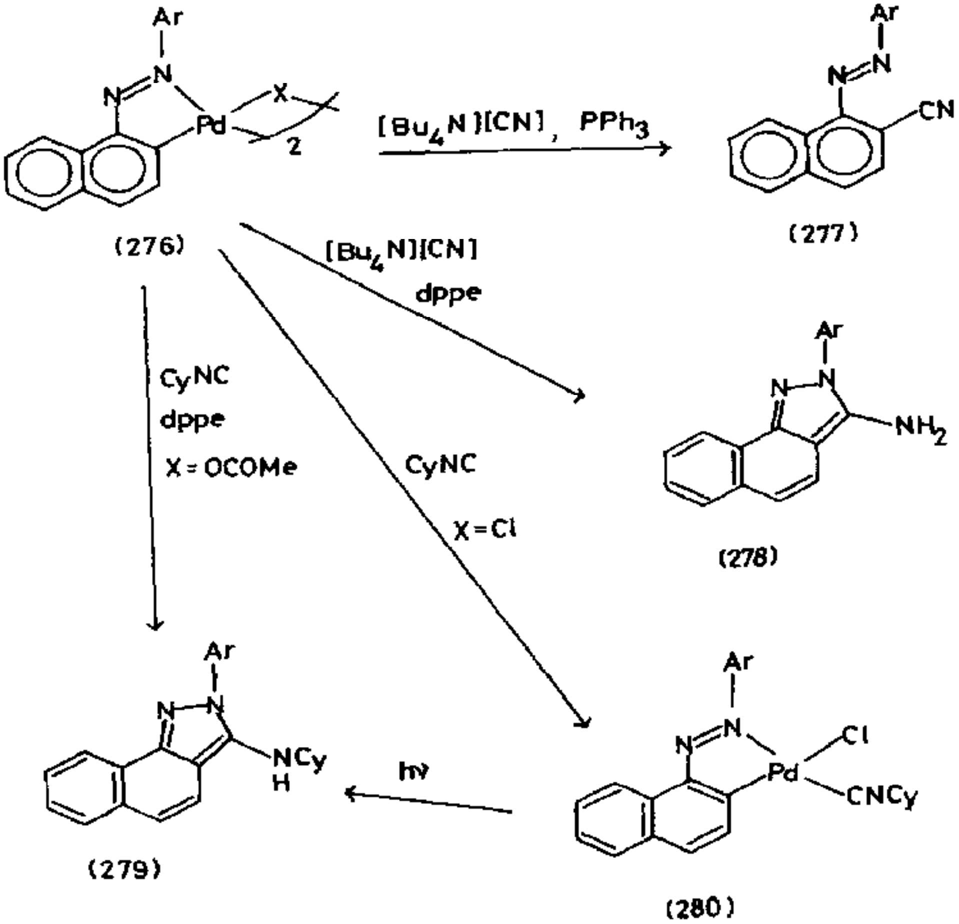
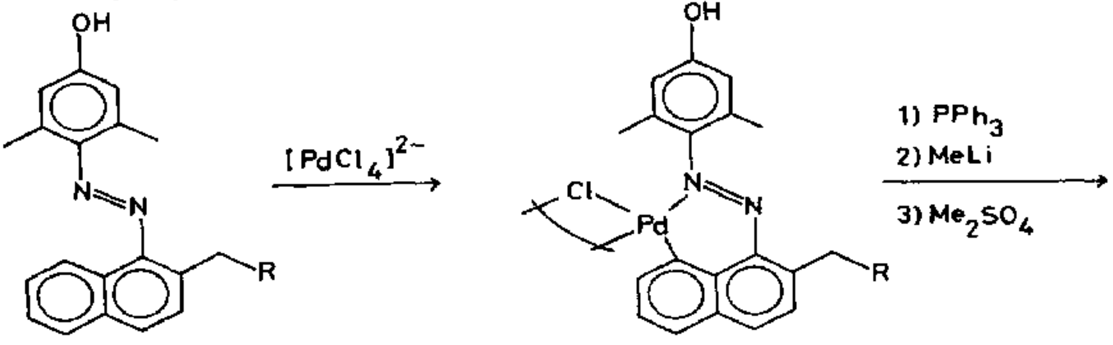


Metallation of 5-membered rings has also been noted. Reaction of 2-(1-pyrrolyl)pyridine with $Li_2[PdCl_4]$ gave **(287)**, which was subjected to the usual bridge splitting reactions [776]. Cyclometallation of a ferrocene derivative to yield **(288)** was an early step in a rather novel prostaglandin synthesis [777].

The complex **(289)**, in which metallation had occurred on a methyl group, reacted with amines to give (290). The abstract of this paper describes **(289)** as doubly charged, which I assume to be a misprint [778]. A related reaction was described for (291). A kinetic study suggested that bridge splitting occurred initially to give **(292)** and that the rate controlling step was nucleophilic attack of the amine *via* a rather curious four-membered transition state [779]. A similar mechanism was invoked to explain the same reaction of the analogous platinum complex [780].

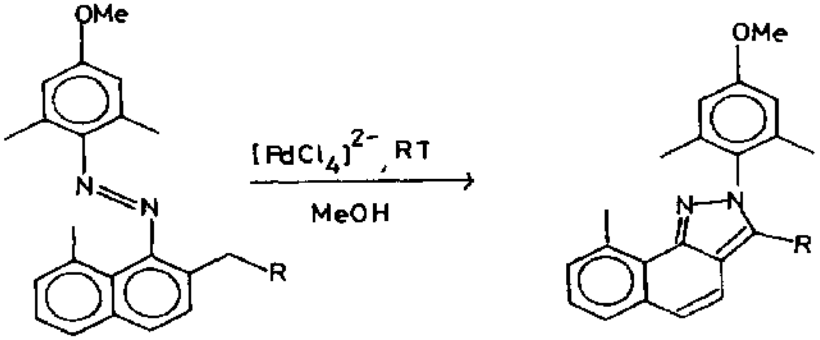
When (293) was reacted with LiCl in ethanoic acid the intermediate **(294)** could be observed spectroscopically. Thermolysis gave $PhCH_2NR_2$ and

[{Pd(PPh$_3$)Cl(μ-Cl)}$_2$]. Numerous other cyclometallated complexes behaved similarly [781].



(281) R=H or Me

(282)



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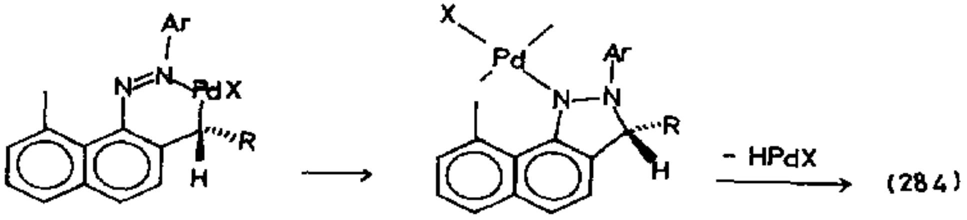

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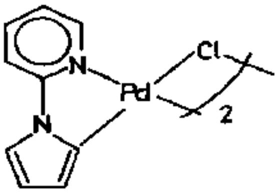

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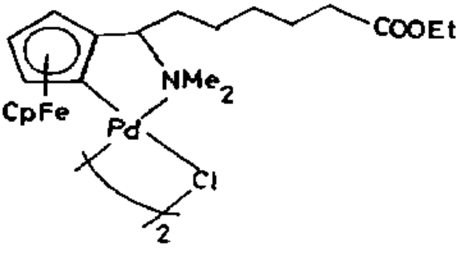

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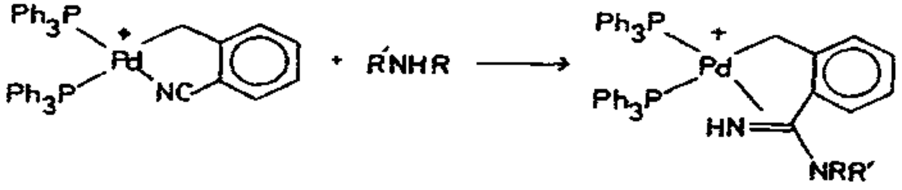
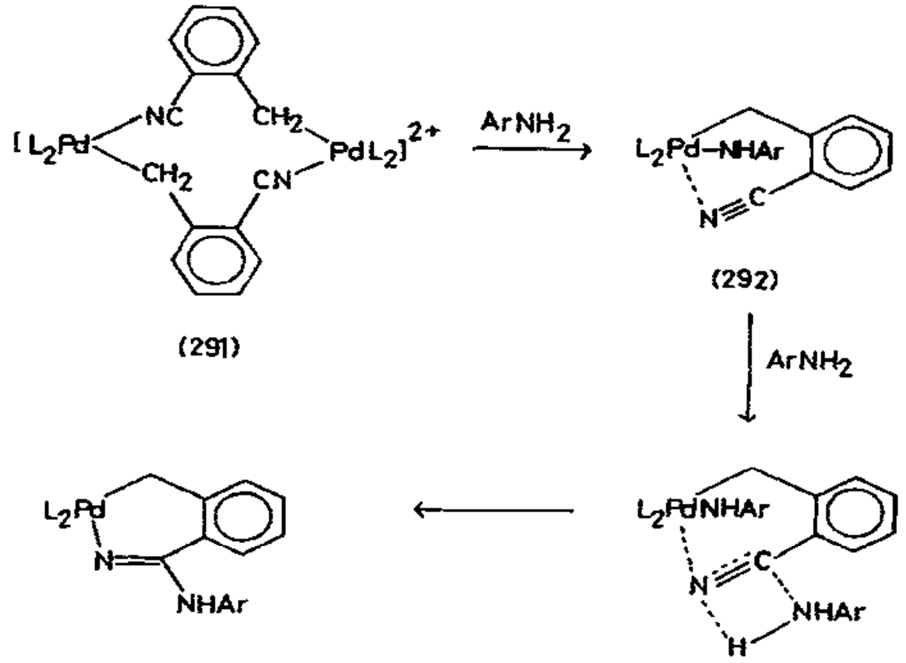
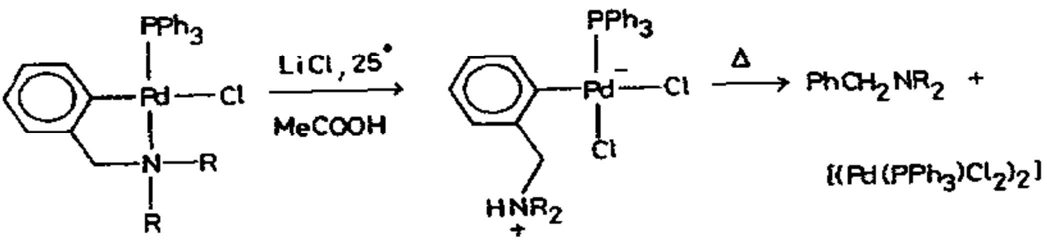


(289) **(290)**

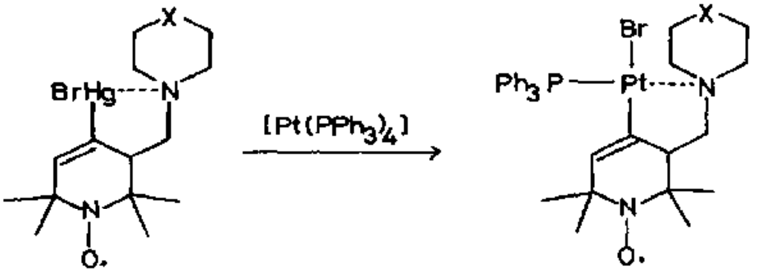


(291) (292)



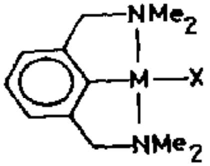
(293) **(294)**

A rather unusual way to prepare cyclometallated complexes is the metal exchange reaction of (295). Epr measurements were performed on the product [782].



(295)

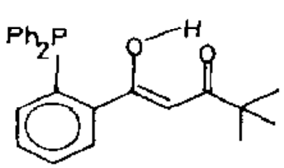
In **(296)** (M = Ni or Pt, X = Cl, Br or I; M = Pd, X = Br) UVPES provided strong evidence for a π-interaction of the phenyl ring with the metal orbitals [783].



(296)

1.6.4.12 Unidentate phosphine donor ligands

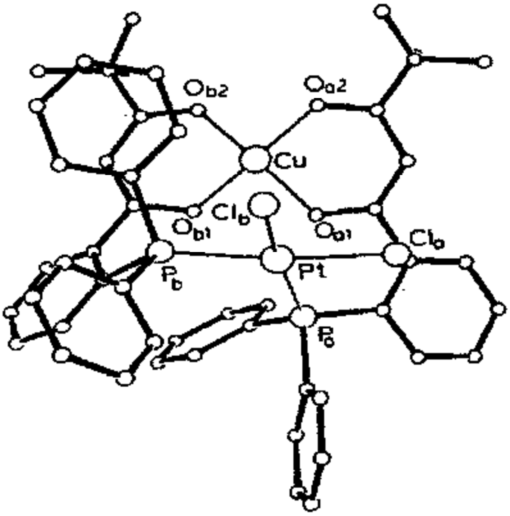
Trans-$[Pd(PPh_3)_2Cl_2]$ reacted with 4-chloro-2-butanone to give $[Ph_3PCH_2CH_2COCH_3][Pd(PPh_3)Cl_3]$, characterised by X-ray diffraction [784]. **(297)** was used to make a number of simple and heterobimetallic complexes including *cis*-$[ML_2Cl_2]$ (M = Pd or Pt), *cis*-$[Pt(TiL_2Cl_2)Cl_2]$ and **(298)**, the structure of which was determined by X-ray diffraction [785]. Microcalorimetric measurements of enthalpies of decomposition of complexes such as $[M(PR_3)_2Cl_2]$ (M = Pd or Pt, R = Et, Cy, Ph or $CHMe_2$) have been made and used in derivations of bond energies [786].



(297)

The He I and He II PES of *trans*-$[Pd(PEt_3)_2X_2]$ have been recorded. Some assignments were made [787]. The nmr spectra of *cis*- and *trans*-$[Pt(PAr_3)_2Cl_2]$ were studied as a function of the varying electronic character of Ar.

$^1J(Pt-P)$ was found to be an unambiguous criterion for distinguishing the isomers and could also be correlated with the σ values for the aryl groups [788]. The *trans*-effect of ligands on calculated dipole moments for $[Pt(PEt_3)_2ClX]$ was studied (X = H, Me or Ph). Experimental data were in reasonable agreement with theoretical predictions [789].

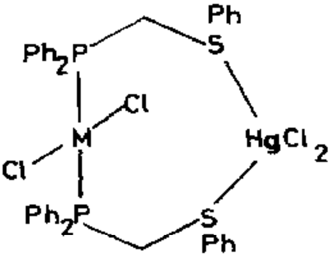


(298) (Reproduced with permission from [785])

Jahn-Teller effect theory was used for the analysis of the photoisomerisation of $[Pt(PEt_3)_2Cl_2]$ and was found to agree well with experiment. In the *trans→cis* process photoexcitation gave a long lived triplet with $\tau \geqslant 10$ µsec, whereas in the *cis→trans* reaction a short lived singlet with $\tau \leqslant 0.1$ µsec was formed. Addition of triplet quenchers suppressed the *trans→cis* process to the level of the reverse reaction [790].

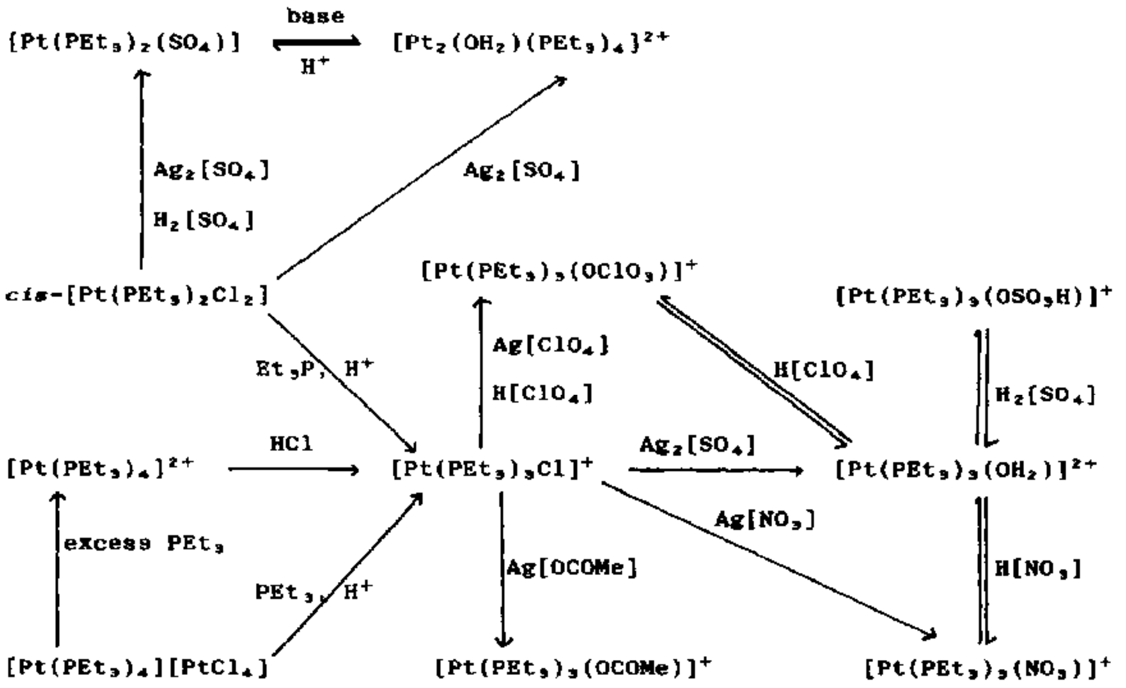
The triphenylphosphine catalysed equilibration of *cis*- and *trans*-$[Pt(PPh_3)_2Cl_2]$ was studied using cyclic voltammetry. An intermediate, $[Pt(PPh_3)_3Cl]$, was identified [791]. There has been a report of an electrochemical study of $[PdL_2X_2]$ (L = PBu_3, PPh_3, $P(OPh)_3$, X = Cl or {CNS]) and $[Pd(PhCN)(PPh_3)Cl_2]$. Redox potentials in dmf ranged from zero to -0.35 V. A two electron reversible reduction of the complexes to palladium(0) was associated with autoinhibition of the electrode process by electrolysis products [792,793].

$[Pt(PPh_3)_2Cl_2]$ was prepared by a new method from $K_2[PtCl_6]$ and PPh_3. Ph_3PO was identified as a by-product implying that PPh_3 acted both as a ligand and as a reducing agent [794]. The complexes $[Pd\{P(CH_2CH_2CN)_3\}_2(SCN)_2]$ and $[Pt\{P(CH_2CH_2CN)_3\}_2(NCS)_2]$ were prepared, indicating that linkage isomerism is very sensitive to steric effects [795]. Reaction of *trans*-$[M(Ph_2PCH_2SPh\text{-}P)_2Cl_2]$ (M = Pd or Pt) with $HgCl_2$ gave the bimetallic species (299) [796].



(299)

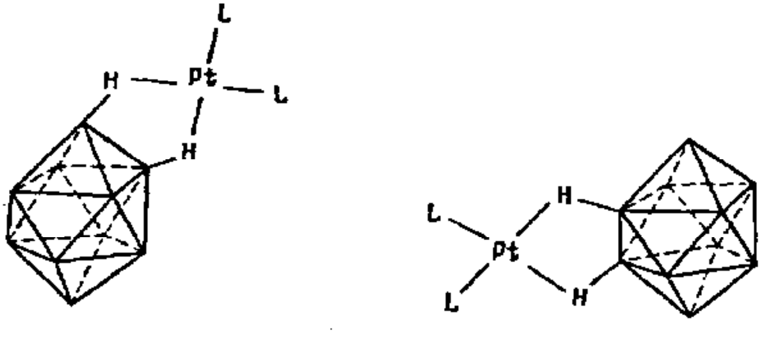
The synthesis and transformations of $[Pt(PEt_3)_3Cl]^+$ have been explored in detail (Scheme 6) [797].



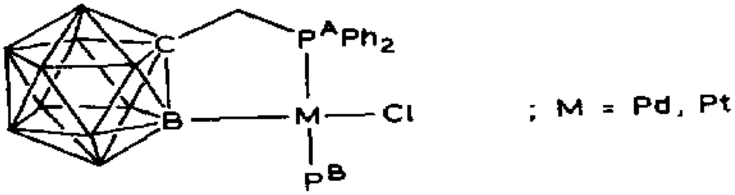
Scheme 6 Preparation and reactions of $[Pt(PEt_3)_3Cl]^+$ [797]

Reaction of *cis*- or *trans*-$[Pt(PPh_3)_2I_2]$ with $M_2[B_{10}H_{10}]$ (M = K or Ag) gave *cis*-$[Pt(PPh_3)_2(B_{10}H_{10})]$ and $[HPt(PPh_3)_2I]$. Spectroscopic data suggested two possible structures (300a) and (300b) with Pt-H-B bonds [798]. The phosphine *o*-$HCB_{10}H_{10}CCH_2PPh_2$ formed conventional complexes *trans*-$[ML_2Cl_2]$

with $[MCl_4]^{2-}$ (M = Pd or Pt). Thermolysis resulted in cyclometallation to give a five-membered ring metallocycle, **(301)** [799].



(300) (Reproduced with permission from [798])
Probable structures of the complex *cis*-$[Pt(PPh_3)_2(B_{10}H_{10})]$



(301) (Reproduced with permission from [799])

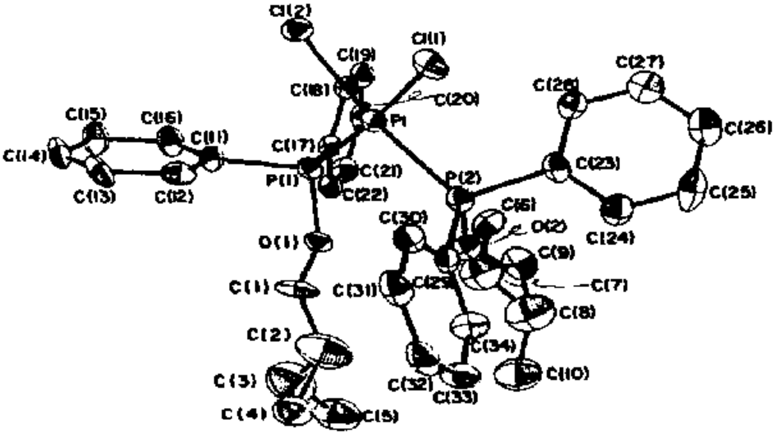
Cis-$[Pt(PPh_3)_2Cl_2]$ reacted with alkynes in 30 % aqueous ammonia solution to give a series of σ-alkynyl complexes [800]. Hydrogen was produced catalytically on photolysis of an aqueous solution of $[HPd(PEt_3)_3]^+/[Ru(bipy)_3]^{2+}$ and ascorbic acid. Kinetic studies implied that photolysis gave initially $[Ru(bipy)_3]^+$ which transferred an electron to the palladium complex to give a palladium(I) radical, $[HPd(PR_3)_3]^{\cdot}$, this decomposing rapidly in protic solution to yield molecular hydrogen [801].

1.6.4.13 Other unidentate phosphorus donor ligands

$[Me_2NH_2][Pd(P(OPh)_3)Br_3]$ was prepared from $PdBr_2$ and $P(OPh)_3$ in butanol containing HBr and LiBr. An X-ray diffraction study indicated that the bromine was hydrogen bonded to an NH of the cation [802]. The structure of (302) was also determined by diffraction techniques; the $\bar{P}PtP$ angle was widened to 97 °, presumably due to steric crowding [803].

Platinum(II) phosphite complexes were formed from platinum(0) complexes in reactions (28) and (29) [804].

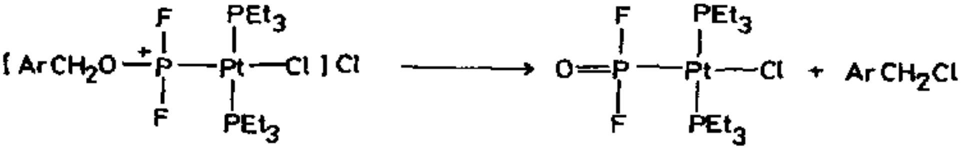
Treatment of $[Pt(P(OMe)_3)_2Cl_2]$ with $Na[BH_4]$ gave *trans*-$[HPt(P(OMe)_3)_2Cl]$, which was stable in solution. $[HPt\{MeP(OMe)_2\}_2Cl]$ was prepared similarly. Both inserted methyl propenoate readily and regiospecifically to give *cis*-$[PtL_2\{CH(CH_3)COOMe\}Cl]$ [805]. An alkyldifluorophosphite, $ArCH_2OPF_2$, reacted with *trans*-$[Pt(PEt_3)_2Cl_2]$ to give **(303)** which eliminated $ArCH_2Cl$. Variation of the aryl group caused no change in the reaction. $[Pt(PPh_3)_2Cl_2]$ reacted with $ArCH_2OPF_2$ to give $[ArCH_2PPh_3][Pt(POF_2)_4]$ in most cases. However, with $4\text{-}MeOC_6H_4CH_2OPF_2$, *trans*-$[Pt(POF_2)(PPh_3)_2Cl]$ was formed [806].



(302) (Reproduced with permission from [803])

$$[Pt\{P(OEt)_3\}_4] + O_2 \xrightarrow{HCl} [Pt\{P(OH)(OEt)_2\}_2\{P(O)(OEt)_2\}_2] \qquad (28)$$

$$[Pt\{P(OEt)_3\}_4] + O_2 \xrightarrow{H[ClO_4]} [Pt\{P(OEt)_3\}_4]^{2+} \qquad (29)$$



$$[ArCH_2O-\overset{+}{P}F_2-Pt(PEt_3)_2-Cl]Cl \longrightarrow O=PF_2-Pt(PEt_3)_2-Cl + ArCH_2Cl$$

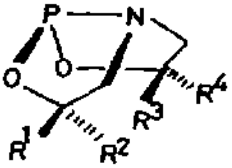
(303)

A mixed metal complex with bridging ligands was formed in reaction (30) [807]. **(304)** acted as a phosphorus donor towards platinum(II) in *cis*-$[PtL_2Cl_2]$ [808].

$$2[(OC)_5Mo(Ph_2POPPh_2)] + [Pd(PhCN)_2Cl_2] \longrightarrow trans\text{-}[Pd\{(Ph_2POPPh_2)Mo(CO)_5\}_2Cl_2] \qquad (30)$$

1.6.4.14 Bidentate and multidentate phosphorus donor ligands

Solution absorption and magnetic CD spectra have been reported for $[M(dppe)_2]X_2$ (M = Pd, Pt or Ni, X = $[PF_6]$ or $[ClO_4]$) as well as other phosphine and phosphite complexes. Each complex showed several UV bands assigned to metal to ligand CT bands. Detailed assignments were made in terms of a model including spin-orbit coupling in excited MLCT states [809].



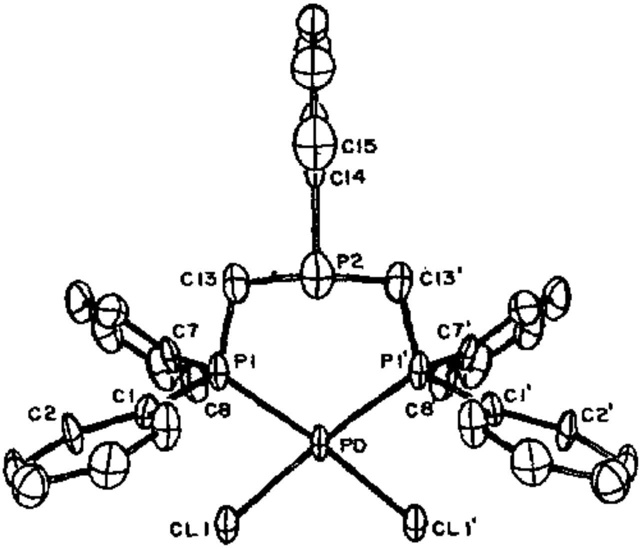
(304)

The dynamic behaviour of metal complexes of diop, including $[Pd(diop)Cl_2]$, has been ivestigated by nmr spectroscopy [810]. The *cis*-chelating ligands, $Ph_2P(B_{10}H_{10}C_2)PRR'$ (R = R' = Ph, NMe_2 or F or R = NMe_2, R' = F) and $(Me_2N)_2P(B_{10}H_{10}C_2)PRR'$ (R = R' = C_6F_5 or R = NMe_2, R' = F), gave complexes $[PtLCl_2]$. These were characterised by ^1H, ^{19}F and ^{31}P nmr spectroscopy [811]. Reaction of $[Pd(PhCN)_2Cl_2]$ with $Ph_2PCH_2P(Ph)CH_2PPh_2$ gave (305), characterised by X-ray diffraction. Addition of an excess of the benzonitrile complex yielded a species of stoicheiometry $[Pd_3L_2Cl_6]$, probably with the structure, **(306)**. **(307)** was also prepared and characterised by X-ray diffraction. In all the complexes dynamic behaviour was observed by ^{31}P nmr spectroscopy [812].

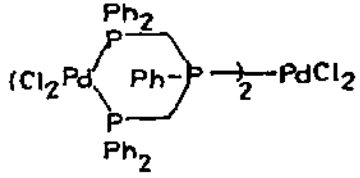
Reaction of **(308)** (R = CMe_3) with $[Fe_2(CO)_9]$ gave **(309)**, characterised by X-ray diffraction. With R = Ph, Cy or $SiMe_3$, however, **(310)** was formed [813]. Treatment of **(311)** with $[CpPd(\eta^3-C_3H_5)]$ gave **(312)** which reacted with iodine to give (313), characterised by X-ray diffraction [814].

Phosphinated polymers of the type **(314)** reacted readily with $[Pd(PhCN)_2Cl_2]$ to give 1:1 and 1:2 complexes [815].

$[Pt(SMe_2)_2Cl_2]$ has been converted to $[\{Pt(\mu-dmpm)Cl_2\}_n]$ and to $[Pt(dmpm)Cl_2]$ as well as to various σ-alkyl complexes (dmpm = $Me_2PCH_2PMe_2$) but the paper describing these reactions is rather irritating in that it does not give details of the reagents used [816]. Reaction of $[Pt(dppm)X_2]$ with $Li[N(SiMe_3)_2]$ followed by RX gave $[Pt(Ph_2PCHRPPh_2)X_2]$, and full experimental details of this process have now been published [817]. Treatment of $[Mn(CO)_5X]$ with $[Pd(dba)_2]$ in the presence of dppm gave (315), characterised by X-ray diffraction for X = Br. Two of the carbonyl groups showed some interaction with palladium [818].



(305) (Reproduced with permission from [812])



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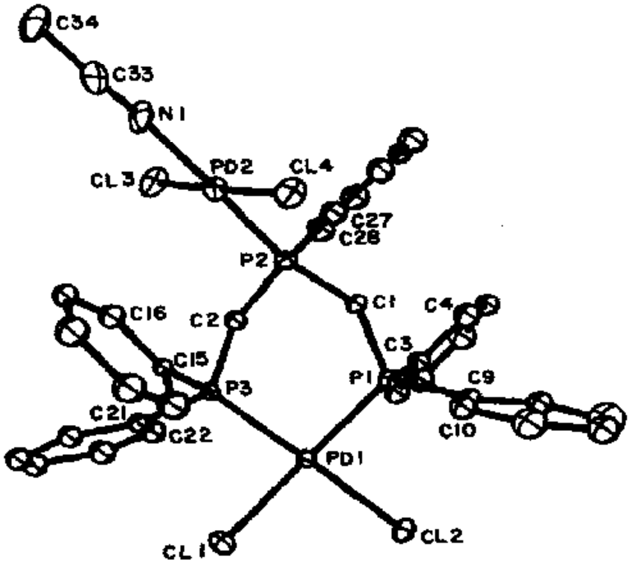

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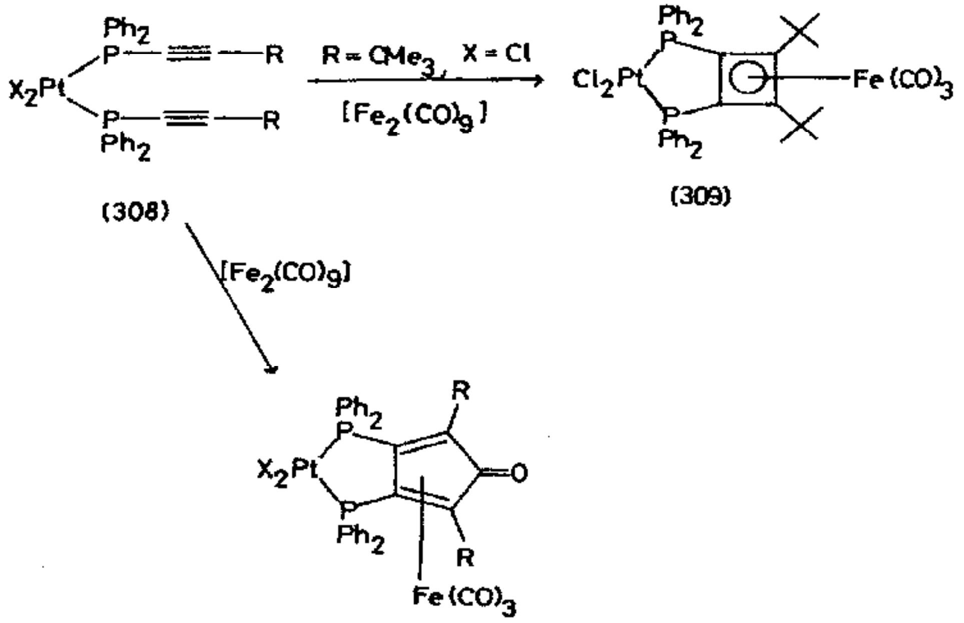

(308) (309)

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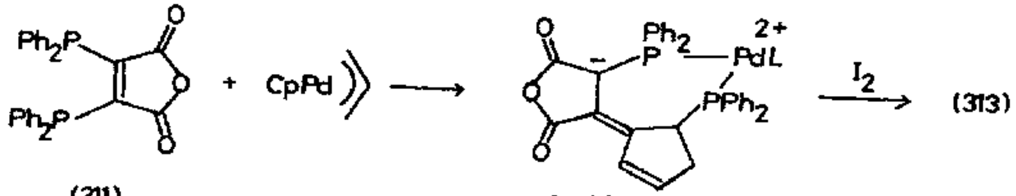
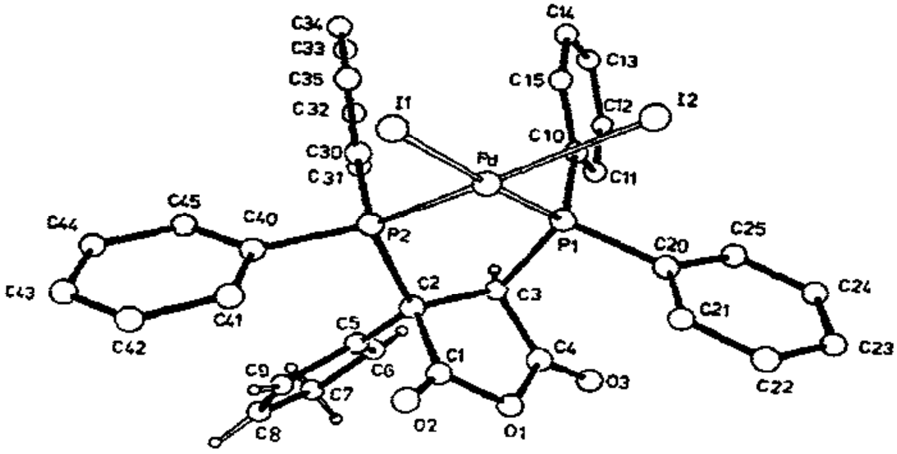


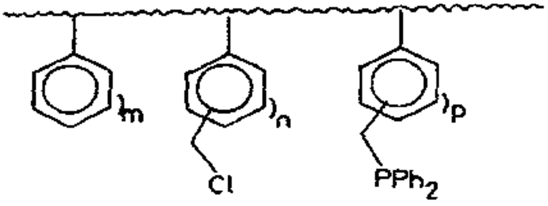
(311) (312)

Treatment of $[Pt(Ph(H)P(CH_2)_3PCy_2)_2Cl_2]$ with Et_3N gave $[\{Pt(PhP(CH_2)_3PCy_2Cl\}_2]$. X-ray diffraction studies indicated that platinum adopted square planar coordination and that the six-membered rings had a chair conformation. The diastereomers **(316)** and **(317)** could be separated, and both were fully characterised by X-ray diffraction. The *meso*-complex, **(317)** had a planar $\{M_2P_2\}$ core but **(316)** had a bent arrangement for the $\{Pt_2P_2\}$ unit [819,820].

The chelating unsymmetrical triphosphine ligands $R_2P(CH_2)_3P(Ph)(CH_2)_nPR'_2$, ($R = R' = Ph$ or Cy or $R = Cy$, $R' = Ph$, $n = 1$ or 2) were synthesised rapidly on platinum by triethylamine catalysed condensation of a second phosphine unit with a coordinated secondary phosphine (reaction (31)). The resulting [Pt(triphos)Cl]Cl complexes were characterised by microanalysis, ^{1}H, ^{31}P and ^{195}Pt nmr spectroscopy [821]. Tetradentate phosphines were also synthesised in a metal coordination sphere *via* reaction (32) (M = Ni, Pd, Pt or Zn; X = Cl or Br; R^1 = H or Me; R^2 = C_2H_4; *m* = 2 or 3; *n* = 2 or 3). Careful analysis of nmr spectroscopic data revealed the diastereoselectivity of the reaction, which was generally better for the formation of the small ring complexes.

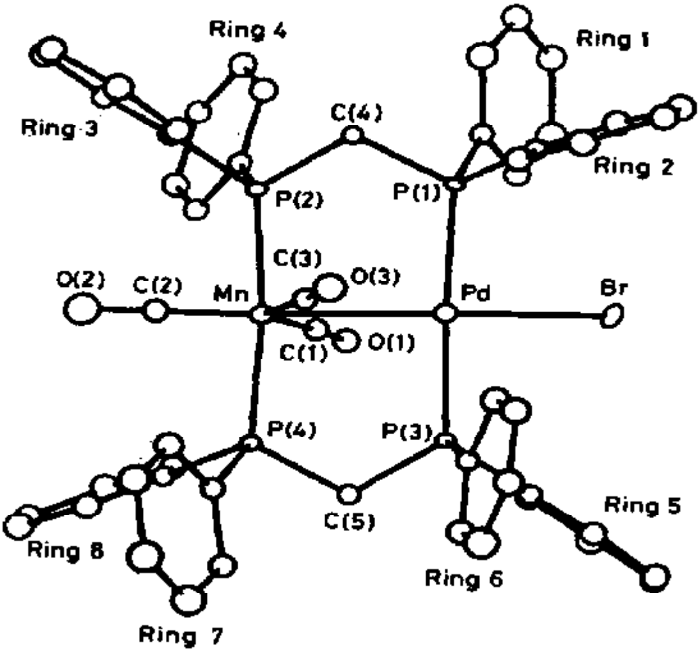


(313) (Reproduced with permission from [814])

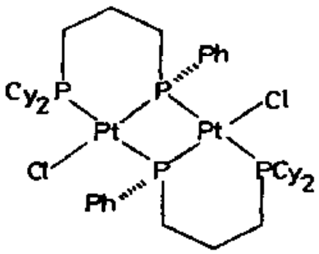


(314)

Assignment of the lower electronic states of $K_4[Pt_2(P_2O_5H_2)_4]$ ($K_4[Pt_2(pop)_4]$) was achieved on the basis of calculations of the spin-orbit coupling. All the absorption bands below 43,000 cm^{-1} were assigned to 5d→6p transitions except for a weak absorption at 32,500 cm^{-1} asigned to a 5d→5d transition. The phosphorscence observed was emission from the lowest E_u state which is mainly composed of the $^3A_{2u}$ zero order state, whilst fluorescence was emission from the lowest A_{2u} state mainly composed of the $^1A_{2u}$ zero order state [823]. Symmetry assignments of the excited states of $[Pt_2(pop)_4]^{2-}$ were made using data from linear polarization ratios [824]. The influence of magnetic fields on the polarized phosphorescence of $Ba_2[Pt_2(pop)_4]$ single crystals has been reported. When the magnetic field was raised from zero to 4 Tesla, the low temperature ($T\leq4.2$ K) phosphorescence was blue-shifted by 280 cm^{-1}, and at 10 K a striking change of the vibrational structure was noted. The results could be explained within the symmetry of the complex. The symmetry of the lowest excited state was confirmed as $^1A_{2u}$ and that of the emitting triplet as E_u [825]. The phosphorescence emission intensity at 517 nm from $[Pt_2(pop)_4]^{4-}$ was quenched by addition of sulphur dioxide. That SO_2 coordinated at the axial Pt(II) sites in an η^1-manner was supported by data from ^{31}P nmr and Raman spectroscopy. The binding constant could be estimated from the electronic spectra [826].



(315) (Reproduced with permission from [818])



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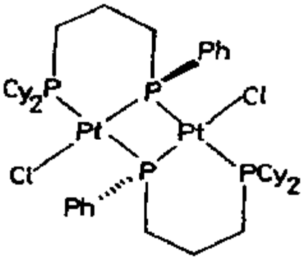

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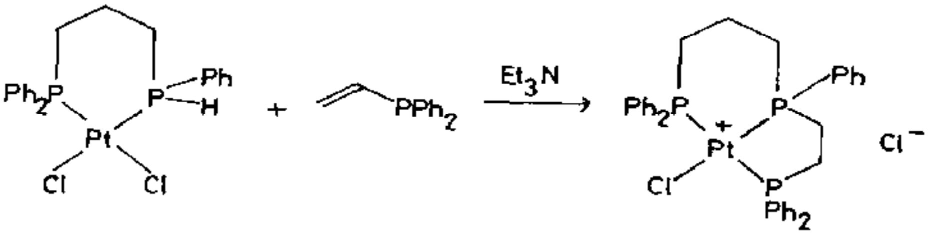

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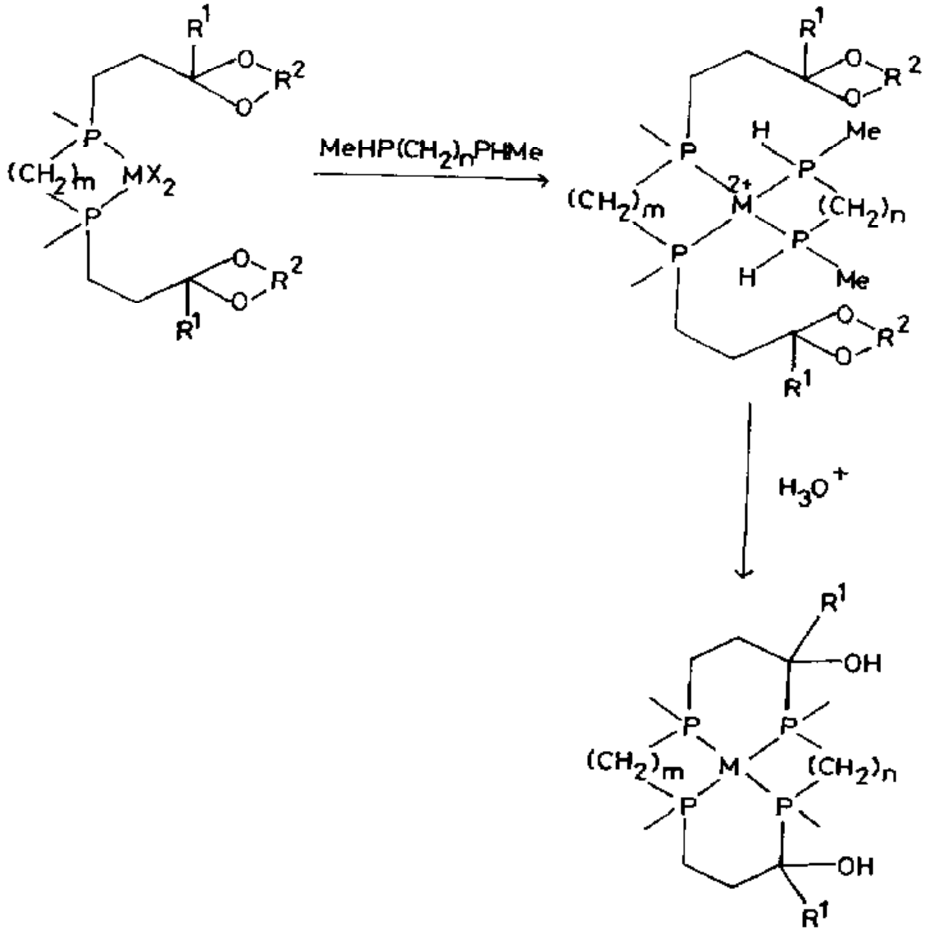
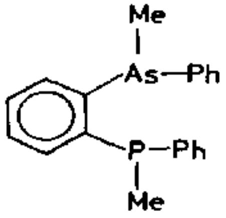


(32)

The electroluminescence of $[Pt_2(pop)_4]^{4-}$ has been investigated [827]. Its triplet excited state was reduced to $[Pt_2(pop)_4]^{5-}$ by a series of aromatic amine quenchers including 1,4-bis(dimethylamino)benzene, suggesting that the complex might have some promise as a photoredox catalyst [828]. Pulse radiolysis of $[Pt_2(pop)_4]^{4-}$ gave $[Pt_2(pop)_4]^{5-}$, of which the transient absorption spectrum was recorded. The absorption was attributed to the allowed $d\sigma^* \rightarrow p\sigma$ transition. $[Pt(pop)_4]^{5-}$ has a $^2A_{1g}$ ground state with a formal $\frac{1}{2}p\sigma$ bond [829].

1.6.4.15 Bidentate phosphorus arsenic donor ligands

The ligand (318), phas, exists in four stereoisomeric forms and complexes of these, $[MLCl_2]$, (M = Pd or Pt) were prepared. Reaction with further phas in ethanol gave species of stoicheiometry $[ML_2]Cl_2$. In CH_2Cl_2 these were shown to be univalent electrolytes adopting square pyramidal geometry as $[ML_2Cl]Cl$; the axial chlorine was in fast exchange on the nmr spectroscopic timescale at temperatures as low as 178 K. In water, however, $[ML_2]Cl_2$ was a diunivalent electrolyte. *Cis*- and *trans*-isomers of $[ML_2][PF_6]_2$ were prepared and characterised by ^1H and ^{31}P nmr spectroscopy. Both were stable and were not readily interconverted. Reaction of ±[M(*R,R*-phas)Cl_2] with ±*R,R*-phas gave only the *meso* complex, although the racemic species was of comparable stability [830].

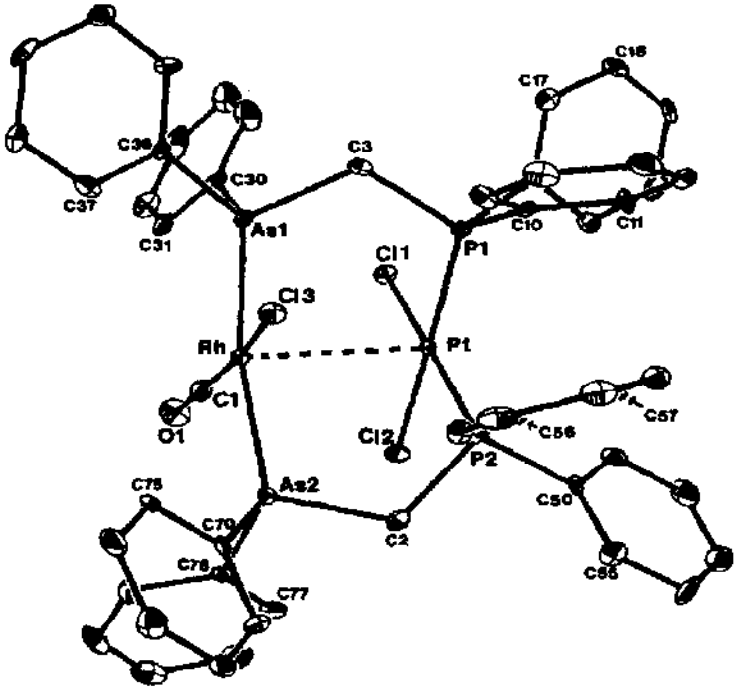


(318)

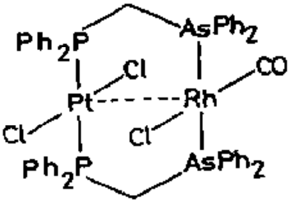
Reaction of $[Pt(cod)Cl_2]$ with $Ph_2AsCH_2PPh_2$ (dapm) gave *cis*-[Pt(dapm-*P*)$_2$Cl$_2$]. When this was treated with $[Rh_2(CO)_4(\mu\text{-}Cl)_2]$, **(319)** was formed, characterised by X-ray diffraction. (319) was converted to the more stable *trans*-isomer, **(320)** under dapm catalysis, but no head-head to head-tail isomerisation was noted [831].

1.6.4.16 Bidentate phosphorus carbon donor ligands

Reaction of $[Pt(Me_3CCN)_2Cl_2]$ with $Ph_2PCH_2CHMe_2$, L', gave only $[PtL'_2Cl_2]$, with no cyclometallation occurring even on prolonged heating. However, with $\{P(CMe_3)_2(CH_2CHMe_2)\}$, L, both (321) and its *trans*-isomer were formed. Bridge splitting with phosphines or acacH occurred in a similar manner to that well known for cyclometallated amine complexes [832]. Cyclometallation of $P(CMe_3)_3$ has been known for some time, and some new reactions of the dimer $[Pt_2Cl_2\{(Me_3C)_2PCMe_2CH_2\}_2]$ have been observed this year. Bridge splitting occurred with phosphines and the products could be reacted with $SnCl_2$ to give (322) (L = Ph_3As, Ph_3Sb, CO, Ph_2PMe or PCy_3). Many nmr spectroscopic data were reported [833]. However, with the pyrazole as addend, bridge splitting did not occur and the new bridged complex **(323)** was formed [834].



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



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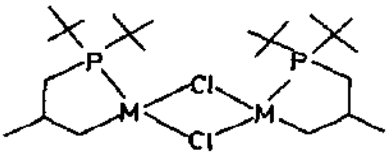

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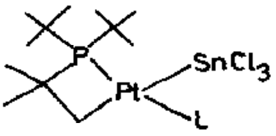

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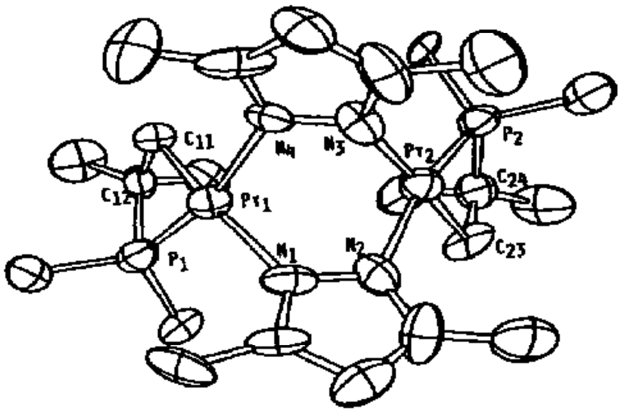
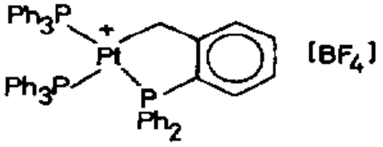


(323) (Reproduced with permission from [834])

(The methyl carbons of the non metallated CMe_3 groups are omitted for clarity)

Treatment of $[Pt(PPh_3)_2(C_2H_4)]$ with CH_2XX' gave *cis*- and/or *trans*-$[Pt(PPh_3)_2(CH_2X')X]$ ($X = X' = I$, $X = Br$, $X' = Cl$ or $X = I$ $X' = Cl$). In the presence of $Ag[BF_4]$ the *trans*-isomers reacted with triphenylphosphine to give **(324)**. Without added PPh_3 and in an appropriately coordinating solvent, S, (325) was formed. It was considered that the breaking of the M-X bond was the initial step in the reaction [835].



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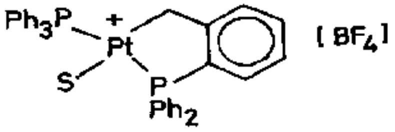
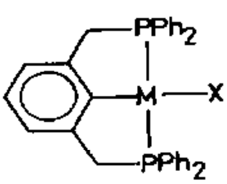


(325)

1,3-Bis(diphenylphosphino)methyl benzene reacted with palladium(II) or platinum(II) to give **(326)** (X = halogen). X may be replaced by hydride using $Na[BH_4]$ for M = platinum but with M = palladium decomposition occurred [836]. Reaction with $Ag[CF_3SO_3]$ in propanone gave (326) (X = propanone), which on treatment with [HCOO]Na yielded **(327)**, which was surprisingly stable [837].

1.6.4.17 Arsenic donor ligands

Cis- and *trans*-isomers of $[PtLCl_2]$ $L = Ph_2As(CH_2)_nAsPh_2$ (n = 6-12 or 16) were prepared by reactions (33) and (34). For n = 10 or 12 the *cis*-complexes were shown to be dimeric [838].



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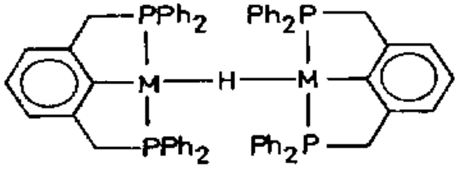


(327)

$$K[Pt(C_2H_4)Cl_3] + L \xrightarrow{\text{propanone/toluene}} trans\text{-}[PtLCl_2] \tag{33}$$

$$K_2[PtCl_4] + L \xrightarrow{\Delta\text{/ethanol}} cis\text{-}[\{PtLCl_2\}_2] \tag{34}$$

1.6.5 Complexes with Group 14 donor ligands

Many of the complexes of Group 14 donor ligands are organometallics and thus fall outside the scope of this review. The history of organometallic compounds, beginning with Zeise's salt, has been discussed [839].

1.6.5.1 Carbonyl complexes

A semi-empirical method was proposed for the calculation of the electronic structure of complex molecules. It was based on a linear combination of valence MO's of the fragments, and was tested on $[Pt(CO)Cl_3]^-$ [840]. The preparation of $[Pd_2(CO)_2Cl_4]$ from $PdCl_2$ and CO in $SOCl_2$ was studied as a function of temperature and CO pressure. The data were used to deduce a value of 101 kJ mol^{-1} for the Pd-CO bond energy. Comparison with the Pd(I) species, $[Pd_2(CO)_2Cl_4]^{2-}$, suggested that the Pd(II)-CO bond was "normal" in strength and that bonding decreased with a decrease in the palladium oxidation state [841]. However, this bond is weaker than those in related nickel and platinum complexes, largely due to poor back bonding. This fact may be used to explain the fact that there is no analogue of reaction (35) for the related palladium complex [842].

$$[Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2] + 2CO \rightleftharpoons 2trans\text{-}[Pt(CO)_2Cl_2] \xrightarrow{\text{fast}} cis\text{-}[Pt(CO)_2Cl_2] \tag{35}$$

1.6.5.2 Cyanide complexes

The complexes $[Ph_2I]_2[M(CN)_4]$ (M = Pd or Pt) were prepared from $K_2[M(CN)_4]$ and Ph_2ICl [843]. The species $[R_3S]_2[Pd(CN)_4]$ (R = Me or Ph) were also synthesised [844]. Reaction of $[CN]^-$ with $[Pt(dien)X]^+$ gave successively $[Pt(dien)(CN)]^+$, $[Pt(dien)(CN)_2]$ and $[Pt(CN)_4]^{2-}$. The NH group of the dien was the first ligating species to be replaced by the cyanide [845].

The effects of magnetic fields on the luminescence of $Ln_2[Pt(CN)_4]_3.H_2O$ single crystals at 1.9 K have been studied [846]. A multiple-scattering generalised partitioning molecular cluster model was used to calculate the electronic states of the $[Pt(CN)_4]^{2-}$ dimer units. The mechanism which places the d_{z^2} like band at the Fermi level in the $K_2[Pt(CN)_4]$ quasi one-dimensional conducting solid was analysed [847].

A study of the ligand substitution of $[Pt(H_2O)I_3]^-$ by $[CN]^-$ to give $[Pt(CN)_4]^{2-}$ revealed that the *trans*-effect of the $[CN]^-$ was weaker than that of iodide [848].

Trans-$[Cr(H_2O)(1,2\text{-}pn)_2F][ClO_4]$ reacted with $[M(CN)_4]^{2-}$ (M = Ni, Pd or Pt) to give *cis*-$[(1,2\text{-}pn)_2FCr\text{-}(NC)\text{-}M(CN)_3].H_2O$. IR spectroscopic data established the presence of terminal and bridging cyano groups. As with the related en complexes the platinum derivative showed some unique behaviour, involving platinum-platinum interactions [849]. When *cis*-$[CrX(H_2O)(en)_2][M(CN)_4]$ M = Ni, Pd or Pt) was allowed to stand in a desiccator $[(en)_2XCr\text{-}(NC)\text{-}M(CN)_3]$ was formed [850].

The solid phase thermal deaquation anation of *trans*-$[CrF(H_2O)(en)_2][M(CN)_4]$ (M = Ni, Pd or Pt) to give $[(en)_2FCr\text{-}N{\equiv}C\text{-}M(CN)_3]$ was studied by DSC and isothermal and non-isothermal TG. The activation energies derived implied an SN_1 process *via* a square pyramidal activated complex, which was explained in terms of Frenkel defect formation by water elimination. Water slips into an interstitial position and escapes, the rate of the reaction depending on the size of the holes in the lattice [851].

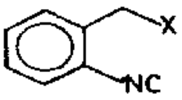
The new complexes, $[Co(H_2O)(NH_3)_5]_2[M(CN)_4]_3$ (M = Ni, Pd or Pt) were prepared and the solid sate kinetic parameters for deaquation anation determined. The activation energy for the platinum complex was substantially lower than that for the nickel or palladium analogues, the difference being attributed to platinum-platinum association in the crystal lattice which caused distortion and allowed the water molecules to escape readily [852]. Reaction of $[Ru(bipy)_2(CN)_2]$ with *cis*-$[Pt(C_2H_4)(4\text{-}Mepy)Cl_2]$ occurred by a first order process to give 1:1 and 2:1 species. A range of related bridging complexes were investigated [853].

1.6.5.3 Isonitrile complexes

The aryl isonitriles, (328), formed simple complexes, *cis*-$[PtL_2Cl_2]$, on reaction with $[Pt(cod)Cl_2]$ [854,855].

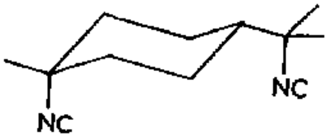
The complexes *trans*-$[Pt(PPh_3)_2LCl]Cl$ ($L = C{\equiv}N\text{-}C(R){=}C(R')\text{-}NR''_2$) were prepared from *cis*-$[Pt(PPh_3)_2Cl_2]$ and L. Thermolysis gave *cis*-$[Pt(PPh_3)LCl_2]$.

The isonitrile complexes reacted readily with amines to give diaminocarbene derivatives [856].



(328)

Reaction of dmb, **(329)** with Pd(II) in protic solvents gave $[Pd_2(dmb)_4]^{4+}$. A bromide or chloride ion could be encapsulated between the metal atoms in $[Pd_2(dmb)_4X]^{3+}$ [857].



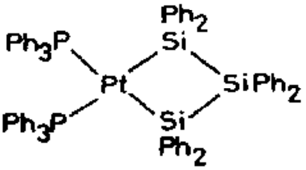
(329)

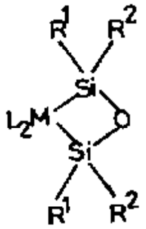
Treatment of $[Pt(dppm)Cl_2]$ with Me_3CNC gave *cis*-$[Pt_2(\mu\text{-dppm})_2(CNCMe_3)_4]^{4+}$. Transfer of RNC from [Ag(CNR)Cl] occurred in reaction (36) (M = Pd or Pt) [858].

$$[M(dppm)_2]Cl_2 + [Ag(CNR)Cl] \longrightarrow [(RNC)M(\mu\text{-dppm})_2AgCl]Cl_2 \qquad (36)$$

1.6.5.4 Silicon donor ligands

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $HSiPh_2SiPh_2SiPh_2H$ gave **(330)** [859]. Tetraalkyl disiloxanes reacted similarly to give **(331)** (M = Pd or Pt), this complex being a catalyst for siloxane oligomerisation and redistribution [860].





(330) **(331)**

1.6.5.5 Tin donor ligands

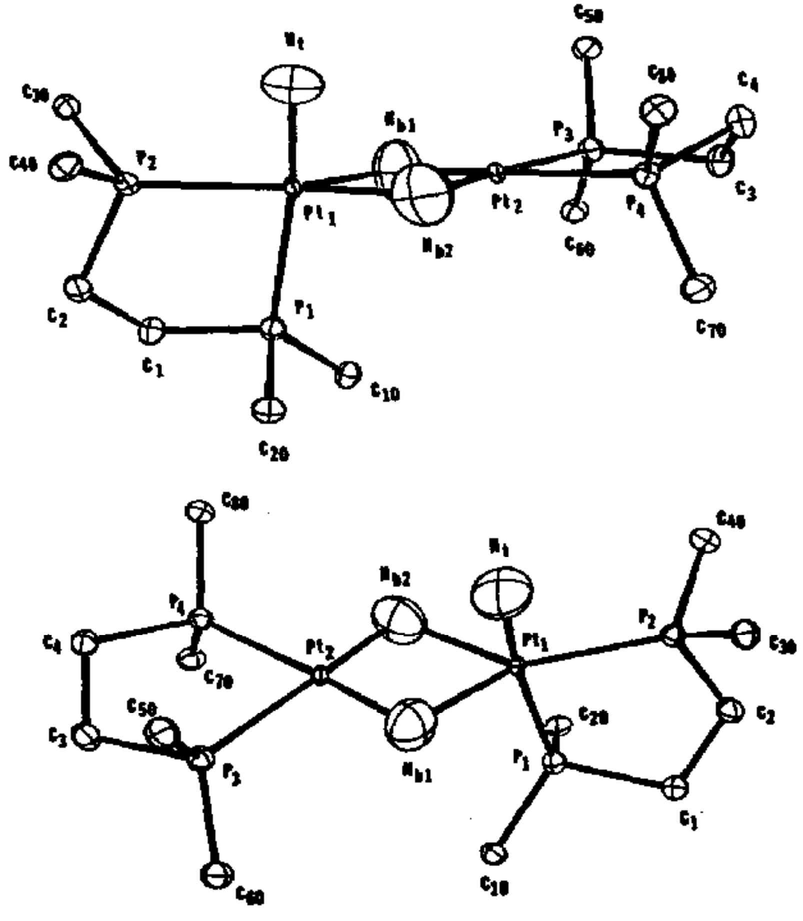
The reactions of *cis*-$[Pt(SnCl_3)_2Cl_2]^{2-}$ with $P(OPh)_3$ have been studied. A wide range of complexes was identified by ^{195}Pt, ^{119}Sn and ^{31}P nmr spectroscopy. The importance of such species in catalysis was discussed [861]. ^{119}Sn and ^{195}Pt nmr spectroscopic data were reported for the range of complexes $[Pt(SnCl_3)Cl_3]^{2-}$, $[Pt(SnCl_3)_2Cl_2]^{2-}$, $[Pt(SnCl_3)_3Cl]^{2-}$, $[Pt(SnCl_3)_4]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$, which were formed successively on addition of $SnCl_2$ to $[PtCl_4]^{2-}$. An increase in the number of coordinated $SnCl_3$ groups resulted in the deshielding of ^{119}Sn and the shielding of ^{195}Pt. Reaction of $[\{PtL(\mu-Cl)Cl\}_2]$ with $SnCl_2$ gave $[Pt_2L_2(\mu-Cl)_2(SnCl_3)Cl]$ and *trans*-$[Pt_2L_2(\mu-Cl)_2(SnCl_3)_2]$. This was in contrast to the reactions of Group 15 donor ligands which cause bridge splitting [862]. An ^{119}Sn Mössbauer study of these species has also been reported [863].

When $[PtL_2Cl_2]$ (L = 1-alkyl-3,4-dimethylphosphole) was reacted with $SnCl_2$ the initial product was $[PtL_2(solvent)(SnCl_3)Cl]$. The addition of $SnCl_2$ labilised the phosphole complexes towards ligand exchange yielding several species in solution [864]. Treatment of $[Pt(\eta^3-C_3H_5)Cl_2]$ with $SnCl_2$ gave a bright red solution in which 1:1, 1:2 and 1:5 complexes were identified [865]. $[Pd(SnCl_3)_4]^{2-}$ fixed on AV-17-8 anion exchange resin catalysed double bond isomerisation in hexene [866].

1.6.6 Hydride complexes

A theoretical study of the reaction of $[Pt(PH_3)_2]$ with molecular hydrogen to give $[H_2Pt(PH_3)_2]$ suggested that the hydrogen molecule remained intact up to the transition state and that the reaction was exothermic by 66.8 kJ mol^{-1}, with an activation energy of 9.7 kJ mol^{-1}. The rôle of the platinum s^1d^9 and d^{10} states was discussed [867]. Other workers favoured an early transition state on the basis of *ab initio* calculations [868]. Concerted additions of hydrogen to the naked palladium atom and to $\{Pd(H_2O)_2\}$ were studied using multireference CI calculations. Whilst it was found that stable complexes were formed in both cases with binding energies of about 22 kJ mol^{-1}, the equilibrium bonding and geometries were different in the two cases. The d^{10} ground state of the palladium atom caused only a slight increase in the H-H bond distance, and palladium hydrogen bonding was hardly reflected in the wave function. The addition of water ligands lowered the energy of the s^1d^9 configuration and facilitated sd hybridisation. This resulted in the formation of covalent palladium hydrogen bonds and the total rupture of the hydrogen-hydrogen bond [869].

A neutron diffraction study of $[H_3Pt_2(dppe)_2][BPh_4]$, **(332)**, allowed the accurate location of the hydrogen atoms. One platinum atom was four coordinate and the other five coordinate. A noticeable feature of the structure was that the bridging hydrides were in very unsymmetrical positions. This is suggestive of a donor acceptor complex in which the neutral sixteen electron fragment, $\{H_2Pt(dppe)\}$, acts as a donor through two Pt-H bonds to a cationic fourteen electron $\{HPt(dppe)\}^+$ unit [870]



(332) (Reproduced with permission from [870])
Two views of the central core of the $[H_3Pt_2(dppe)_2]^+$ cation. Only the *ipso* carbons of the phenyl rings are shown, for clarity.

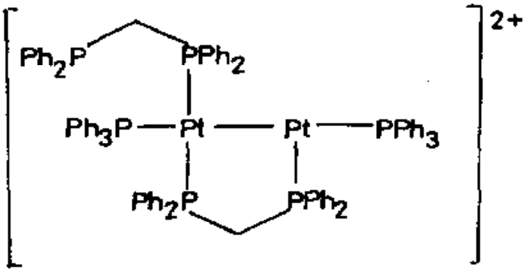
Despite the fact that the hydrogen atom in *trans*-$[HPt(PPh_3)_2Cl]$ is not protic in character, reaction of this complex with *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ gave ammonia after alkaline hydrolysis [871]. Hydrogen was reductively eliminated from $[H_2Pt\{R_2P(CH_2)_nPR_2\}]$ on photolysis. The $\{Pt(R_2P(CH_2)_nPR_2)\}$ fragment produced reacted readily with allyl derivatives or alkenes, or, in the absence of other reagents, yielded bridged dimers [872].

1.7 PALLADIUM(I) AND PLATINUM(I)

An excellent review of metal(I)-metal(I) dimers has been published [163]. In a reduced and thermoevacuated palladium on MgO catalyst epr signals due to Pd^{+} ions were observed. Absorption of oxygen at 20 °C on reduced samples increased the concentration of Pd^{+} as O_2 radical anions were formed [873]. The reaction of a glowing platinum filament with molecular bromine at 1900 K gave PtBr [180].

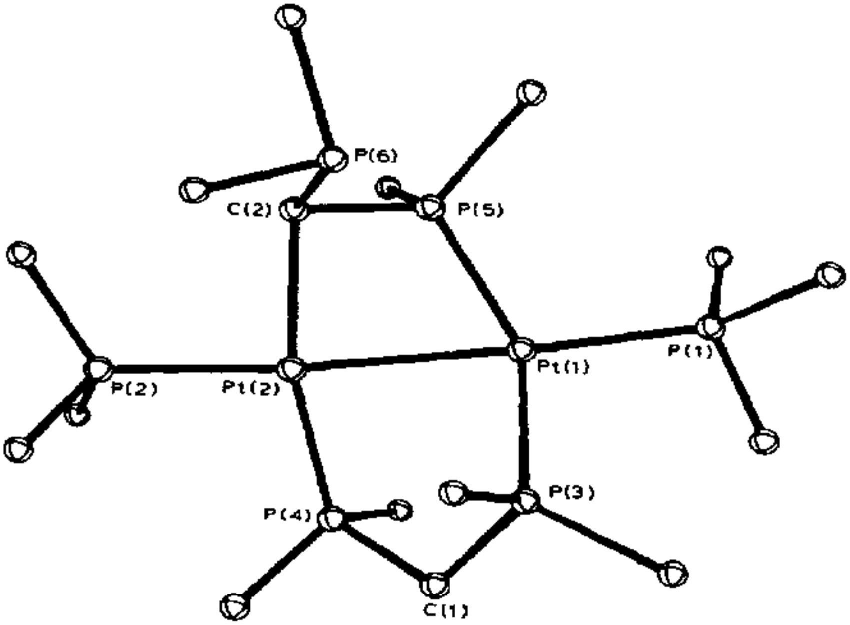
^{31}P and ^{195}Pt nmr spectra of $[Pt_2(\mu\text{-}SPR_2)_2L_2]$ were recorded. $\delta(^{31}P)$ and J(Pt-Pt) were strongly influenced by the π-acceptor character of L. Some of the coupling constants showed an unusually high temperature dependence [874].

$[Pt_2(PPh_3)_2(\mu\text{-}dppm)_2]^{2+}$ reacted with species X (X = CO, CH_2N_2, SO_2 or S_8) to give $[Pt_2(PPh_3)_2(\mu\text{-}Y)(\mu\text{-}dppm)_2]$ (Y = CO, CH_2, SO_2 or S). Kinetic data implied that the starting material underwent a dissociative reaction, probably giving (333) before insertion [875]. The halide exchange reaction of $[Pt_2(\mu\text{-}dppm)_2Br_2]$ with $[Et_4N]Cl$ to give $[Pt_2(\mu\text{-}dppm)_2Cl_2]$ was much more rapid than related substitutions at platinum(II). An explanation for the accelerated rate might lie in the large *trans*-effect of the metal-metal bond [876]. When $[Pt_2(PPh_3)_2(\mu\text{-}dppm)_2][PF_6]_2$ was reacted with K[OH] in ethaonol the derivative of bis(diphenylphosphino)methanide, $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCHPPh_2)(\mu\text{-}dppm)][PF_6]$, (334), was formed. The platinum-platinum bond was 2.658(2) Å long, which is not inconsistent with a Pt(I)-Pt(I) formulation. However, this could also be described as a Pt(0)→Pt(II) donor bond, which would also explain the observed tetrahedral distortion at Pt(1) [887].



(333)

The reversible carbonylation of $[Pd_2(\mu\text{-}dppm)_2X_2]$ (X = Cl, Br or [NCO]) to give the A-frame complex $[Pd_2(\mu\text{-}dppm)_2(\mu\text{-}CO)X_2]$ was investigated. CO insertion occurred because the process was exothermic, despite an unfavourable ΔS term. It appeared to be one-stage process, not involving halide dissociation [878]. The related complex, $[Pd_2(\mu\text{-}dmpm)_2Cl_2]$ (dmpm = $Me_2PCH_2PMe_2$), prepared from dmpm and $[\{Pd(CO)Cl\}_n]$ at -78 °C, also reacted with CO to give an A-frame species, $[Pd_2(\mu\text{-dmpm})_2(\mu\text{-CO})Cl_2]$, characterised by X-ray diffraction. $[Pd_2(\mu\text{-dmpm})_2(OH)_2]$ reacted similarly but with $[Pd_2(\mu\text{-dmpm})_2(OPh)_2]$ CO was inserted into both the Pd-Pd and Pd-OPh bonds to give $[Pd_2(\mu\text{-dmpm})_2(\mu\text{-CO})_2(COPh)_2]$. Thermolysis of this bis(acyl) species gave CO_2, among other products [879].

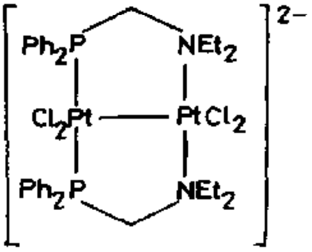


(334) (Reproduced with permission from [877])

A perspective view of the metal coordination polyhedra in the $[Pt_2(PPh_3)_2(Ph_2PCHPPh_2)(Ph_2PCH_2PPh_2)]^+$ cation. For clarity each of the fourteen phenyl rings is represented by its *ipso* carbon only.

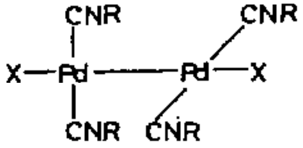
Isonitriles also inserted into $[Pt(\mu\text{-dppm})_2X_2]$ (X = Cl or I) in the presence of $Na[PF_6]$ to give various substitution and insertion products such as $[Pt_2(\mu\text{-dppm})_2(\mu\text{-CNR})X_2]$, $[Pt_2(\mu\text{-dppm})_2(CNR)X]^+$, $[Pt_2(\mu\text{-dppm})_2(CNR)_2]^{2+}$ and/or $[Pt_2(\mu\text{-dppm})_2(\mu\text{-CNR})(CNR)_2]^{2+}$, the product ratios depending on the exact ratios of reactants used. Protonation or alkylation gave μ-aminocarbyne complexes [880]. Analogous insertions were observed for $[Pd(\mu\text{-dppm})_2(C_6F_5)X]$ (X = Cl, Br, I, [CNO] or $\{C_6F_5\}$) [881].

Platinum(I) dimers of $Ph_2PCH_2NEt_2$, ddpa, (335), were prepared by addition of the ligand to $[Pt_2(CO)_2Cl_4]^{2-}$. The complex was readily carbonylated to give a μ-carbonyl derivative [748]. $[Pt(cod)Cl_2]$ reacted with dapm, $Ph_2AsCH_2PPh_2$, to give *cis*-$[Pt(dapm\text{-}P)_2Cl_2]$. This reacted with $[Pt(dba)_2]$ to give $[Pt_2(\mu\text{-dapm})_2Cl_2]$ as an inseparable mixture of head-to-head and head-to-tail isomers [882].



(335) Data did not distinguish between this structure and the isomeric head-to-tail species

[$Pd_2(CNMe)_4I_2$] was prepared from [$Pd(CNR)_4$] and [$Pt(CNR)_4$]X_2. Although IR spectroscopic data initially suggested that the complex was a halo bridged dimer, X-ray diffraction showed a rare unbridged structure, **(336)**, in accord with theoretical predictions. The palladium-palladium distance (2.533 Å) was similar to that in other Pd(I)-Pd(I) dimers. The terminal palladium-iodine bonds were rather long (2.697 and 2.699 Å) in accord with the high *trans*-effect of the metal-metal bond [883].

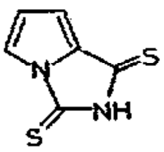


(336)

1.8 PALLADIUM(0) AND PLATINUM(0)

1.8.1 Complexes with Group 16 donor ligands

The complexes [$M(PPh_3)_2L$] (M = Pd or Pt; L = (337)) have been described. Although the authors "assume" the complexes to be tetrahedral, they present no convincing evidence for the mode of binding of **(337)** [884]. Treatment of [$Pt(C_2H_4)L_2$] with RR'N-P(=X)=NR (R = Me_3C, R' = Me_3Si, X = S or Se) gave (338). The structure of the complex for which X = S, **(338a)**, was established by X-ray diffraction. Nmr spectroscopy suggested that in solution structures involving a pentacoordinate silicon atom, **(339)**, were favoured, and this observation was supported by the structure determination, which showed a weak donor acceptor bond between nitrogen and silicon [885].



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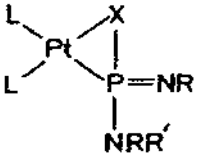

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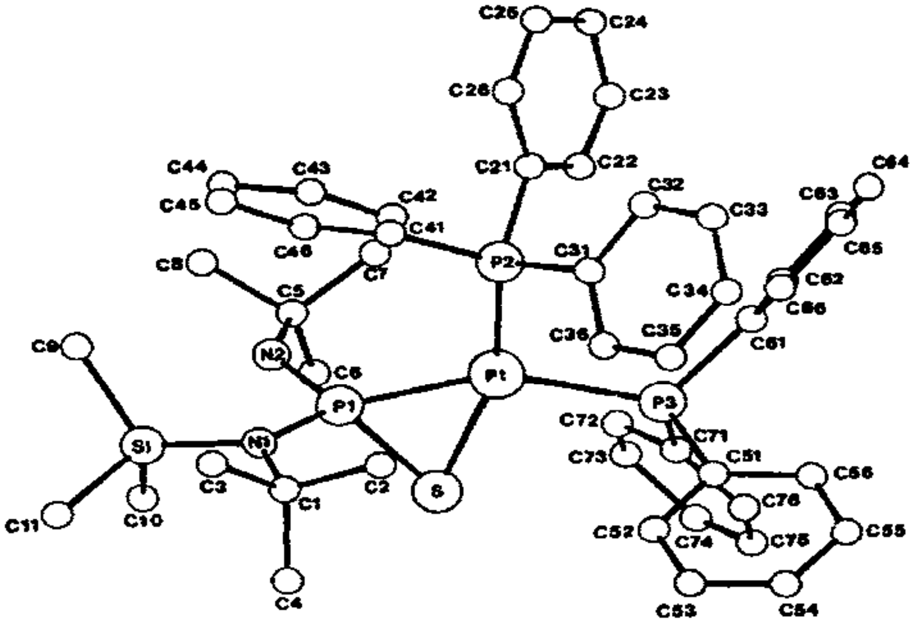
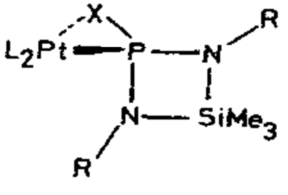


(338a) (Reproduced with permission from [885])



(339)

The reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $R_2P(=S)-C(=S)SR'$ (R = Ph or Cy, R' = Me or CH_2Ph) has been studied. The data were consistent with η^2-*C,S*-coordination. Rearrangement to platinum(II) hydrides occurred fairly readily, *via* a complex mechanism involving *P,S- and S,S*-coordinated intermediates [886].

Treatment of $[Pd(PCy_3)_2(\eta^2-CS_2)]$ with an excess of CS_2 gave $[Pd(PCy_3)(CS_2)]$ and the zwitterion $[Cy_3PCS_2]$. Species of the stoicheiometry $[PdL(CS_2)]$ were also produced by reactions (37) and (38). On the basis of IR spectroscopic data, and with their insolubility in mind, it seems likley that these complexes were polymeric [887,888].

$$[(C_6F_5)Pd(OCOMe)(bipy)] + [PdL_2(\eta^2\text{-}CS_2)] \xrightarrow{Me_2CO/CS_2} \{PdL(CS_2)\} + [(C_6F_5)Pd(bipy)][OCOMe] \quad (37)$$

$$[(C_6F_5)Pd(propanone)(bipy)][ClO_4] + [PdL_2(\eta^2\text{-}CS_2)] \xrightarrow{Me_2CO/CS_2} \{PdL(CS_2)\} + [(C_6F_5)Pd(bipy)L][ClO_4] \quad (38)$$

Reaction of $[Pt(PPh_3)_4]$ with ethene thiourea (etu) was reported to give tetrahedral $[Pt(PPh_3)(etu)_3]$ or octahedral $[Pt(PPh_3)(etu)_5]$ or $[Pt(PPh_3)(etu)(OH_2)_4]$. The data seemed unconvincing [889].

Treatment of $[Pt(PPh_3)_4]$ with CSe_2 gave $[Pd(PPh_3)_2(\eta^2\text{-}CSe_2)]$. Addition of dppe or 1,2-bis(diphenylphosphinomethyl)benzene caused replacement of the triphenylphosphine ligands by the chelating biphosphines. In related reactions of CSSe IR spectroscopic data favoured η^2-*C*,*Se*-coordination [890].

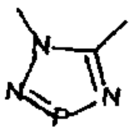
1.8.2 Complexes with Group 15 donor ligands

PhN=S=O was reported to act as a monodentate ligand, through nitrogen, to palladium(0) [891].

Two new preparations of $[Pd(PPh_3)_4]$ have been noted [892,893]. A range of complexes $[Pd(PPh_3)L'_2]$ ($L' = Ph_2PC_6H_4\text{-}4\text{-}X$; X = Cl, F, COOH or Me) have been prepared and their stabilities studied. They were readily oxidised in solution at rates which depended on L' [894,895]. Kinetic studies indicated autocatalytic behaviour [896]. $[Pt(PPh_3)_3L]$ and $[Pt(PPh_3)_2L_2]$ (L = **(340)** or **(341)**) were prepared by reactions (39) and (40). That **(340)** was σ-bonded *via* the phosphorus atom was established by an X-ray diffraction study [897].

$$[Pt(PPh_3)_3] + L \longrightarrow [Pt(PPh_3)_3L] \quad (39)$$

$$[Pt(C_2H_4)(PPh_3)_2] + 2L \longrightarrow [Pt(PPh_3)_2L_2] \quad (40)$$



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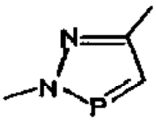


(341)

Low temperature ^{31}P nmr spectroascopy on the products of addition of

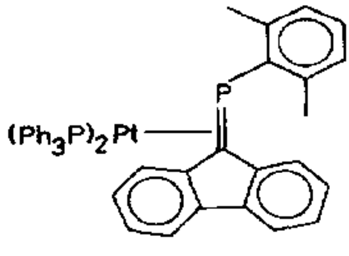
Ph_2MeP or Et_3P to {$Pd(PPh_3)_2$} or {$Pd(P(OPh)_3)_2$} indicated the formation of four coordinate complexes with C_{3v} symmetry, for example $[Pd(PPh_3)(PMePh_2)_3]$, as the major, but not exclusive products. Rapid exchange occurred on the nmr spectroscopic timescale at room temperature [898]. ^{195}Pt nmr spectra for $[Pt(PR_3)_n]$ have been recorded [899].

Cyclic voltammetry was used to study the electrochemical behaviour of $[PdLL'_2]$ (L = PPh_3, L' = $Ph_2PC_6H_4$-4-Cl, $Ph_2PC_6H_4$-4-F, $PhP(C_6H_4\text{-}4\text{-}OMe)_2$ or Ph_2PMe) [900].

A new and more reliable procedure for the preparation of platinum(0) phosphite complexes has been published (reaction (41)) [804].

$$[PtCl_4]^{2-} + 5P(OR)_3 + 2[OH]^- \longrightarrow [Pt\{P(OR)_3\}_4] + 4Cl^- + (RO)_3P{=}O + H_2 \qquad (41)$$

The complex $[Pt(PPh_3)_2(Ph_2C{=}P\text{-}C_6H_2\text{-}2,4,6\text{-}Me_3)]$ was shown by nmr spectroscopy to be in equilibrium between η^1- and η^2-forms in solution, although an X-ray diffraction study implied an exclusively η^1-structure in the solid state [901]. Although an η^1- form of **(342)** could not be detected by nmr spectroscopy, a red colour, indicative of η^1-coordination, was noted [902]. Both $Ph_2C{=}P(C_6H_2\text{-}2,4,6\text{-}Me_3)$ and $Me_3CC{\equiv}P$ formed η^2-complexes such as **(343)** on reaction with [Pt(PPh_3)(triphos)]. The phosphaalkene reacted with $[Pt(cod)_2]$ to give $[Pt(Ph_2{=}PC_6H_2\text{-}2,4,6\text{-}Me_3)_3]$, in which all the ligands were η^1-coordinated. With a mixture of phosphaalkene and phosphaalkyne, $[Pt(\eta^2\text{-}Me_3CC{\equiv}P)(\eta^1\text{-}Ph_2C{=}PC_6H_2\text{-}2,4,6\text{-}Me_3)_2]$ was formed [903]. Treatment of *cis*-$[ML_2Cl_2]$ (L_2 = dppe or L = PPh_3; M = Pd or Pt) with $Li_2[PhP{=}PPh]$ gave $[M(PhP{=}PPh)L_2]$, characterised by X-ray diffraction [904].



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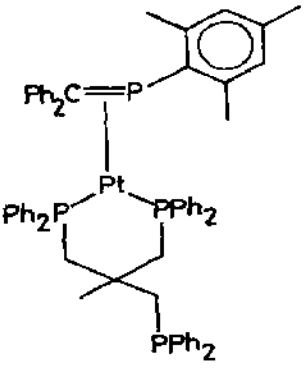
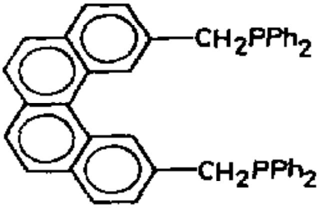


(343)

Numerous mixed complexes in which L and L' were chelating biphosphines were prepared by reaction (42) [905]. The dynamic behaviour of the seven-membered chelate rings in diop complexes, including $[Pd(diop)_2]$, was studied by nmr spectroscopy [810].

$$[PtLCl_2] + L' \xrightarrow{Na[BH_4]/EtOH} [PtLL'] + [PtL_2] + [PtL'_2] \qquad (42)$$

Reaction of **(344)** with $[Pt(cod)_2]$ gave a rather insoluble orange material which could not be readily characterised. With $[Pt(C_2H_4)_3]$, however, $[\{Pt(344)(C_2H_4)\}_n]$ was formed (n = 1 or 2), and this could be reacted with other ligands, L, (L = CO, alkynes or PPh_3) to give [Pt**(344)**L] [906].



(344)

Reaction of $[Co(triphos)(E_2S)][BF_4]$ (E = P or As) with $[Pt(C_2H_4)(PPh_3)_2]$ gave **(345)**, characterised by X-ray diffraction, in which the platinum has inserted into the S-As edge of the SAs_2 ring [907]. $[M\{N(CH_2CH_2PPh_2)_3\}]$ ($[M(np_3)]$; M = Ni or Pd) reacted with P_4X_3 (X = S or Se) to give **(346)**. The nickel complex was characterised by X-ray diffraction and the palladium complex was assumed to adopt a similar structure [908].

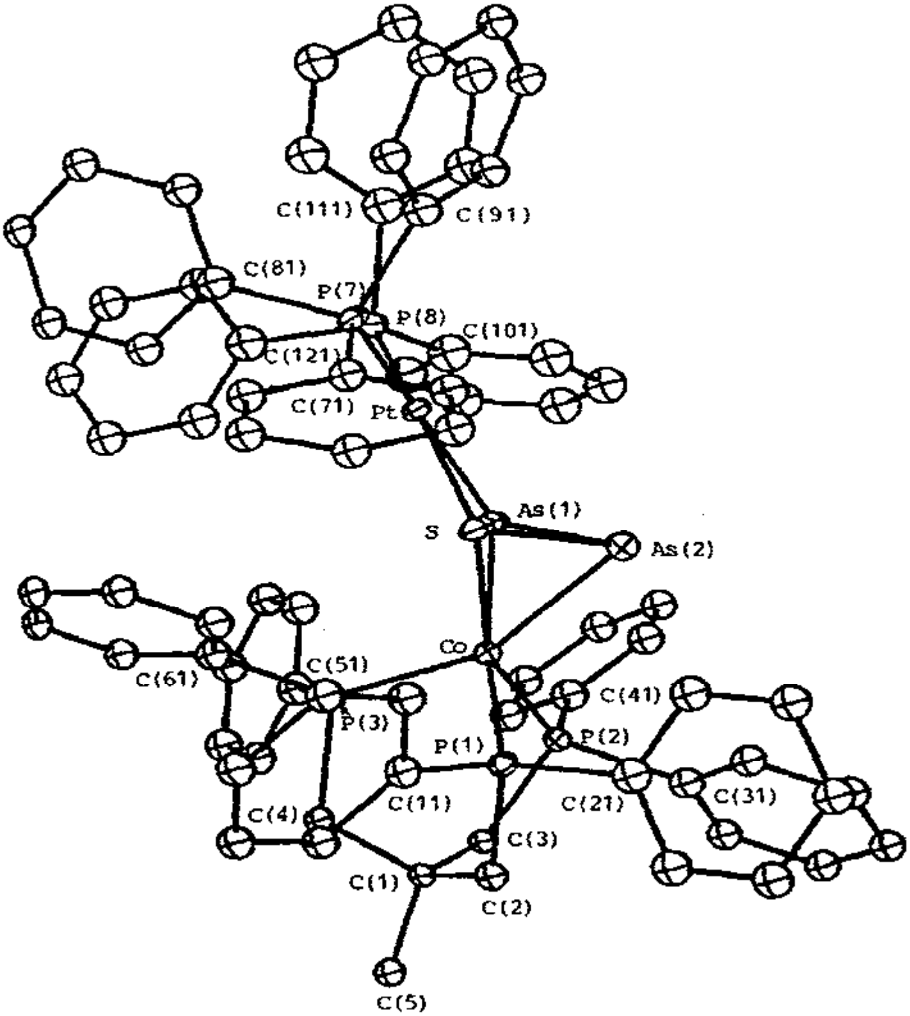
1.8.3 Complexes with Group 14 donor ligands

The concept of absolute electronegativity was used to show that transition metals act as Lewis bases, and carbon monoxide as a Lewis acid in neutral carbonyl complexes. This would imply that π-bonding was dominant with some σ-bonding being induced. It was predicted that electron density would be transferred from the metal to the carbonyl in proportion to the mean bond strength. The known instabilities of $[Pt(CO)_4]$ and $[Pd(CO)_4]$ were predicted [909]. The introduction of the transition state into the semiconductor method for calculation of ionisation potentials and electronic transition energies of multielectron complex systems was studied. $[Pd(CO)_4]$ was considered [910].

$[NH_4][CN]$ acted as an oxidising agent towards $K_2[Pd(CN)_2]$, yielding $K_2[Pd(CN)_4]$ [911].

1.9 PALLADIUM AND PLATINUM CLUSTERS

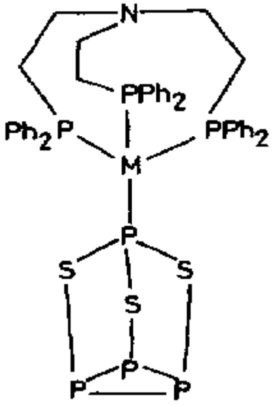
Accounts have been published of carbonyl phosphine clusters of palladium and platinum [912], and of palladium clusters as catalysts in hydrogen transfer reactions [913]. An excellent review of platinum clusters in catalysis considered syntheses of homo and heteronuclear clusters, structure and bonding, chemical reactivity, and uses in catalysis [914].



(345) (Reproduced with permission from [907])
The occupancies of the sites in the As$_2$S ring are As(1) (0.56 As, 0.44 S) As(2) (1.00 As, 0.00 S) S (0.44 As, 0.56 S)

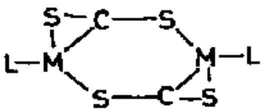
1.9.1 Trimeric clusters

A new topological electron counting theory based on Euler's theorem and the effective atomic number rule has been developed to predict the electron counts of a large number of polyhedral metal clusters including $[\{Pt_3(CO)_6\}_n]^{2-}$ [915].



(346)

$[Pt(C_2H_4)_2(PCy_3)]$ reacted with SO_2 to give $[Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3]$, which could also be obtained from $[Pt_3(CO)_3(PCy_3)_3]$. $[Pt_3(CS_2)_3(PCy_3)_3]$ was similarly prepared [916]. The species $[M_2(CS_2)_2L_2]$ were, however, formed from $[M_3(CO)_3L_3]$ (M = Pt, L = $PPh(CMe_3)_2$ or M = Pd, L = $PPh(CMe_3)_2$ or $P(CMe_3)_3$). An X-ray diffraction study of the platinum complex revealed the structure (347) [917]. A new synthesis of $[Pt_3(\mu_3\text{-}S)_2(PMe_2Ph)_2][BEt_4]_2$ from Li_2S and *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ has been described. An X-ray diffraction study showed that the platinum-platinum distances were too long for formal bonding, but were within interaction range. The sulphur atoms capped each face of the $\{Pt_3\}$ triangle [918].

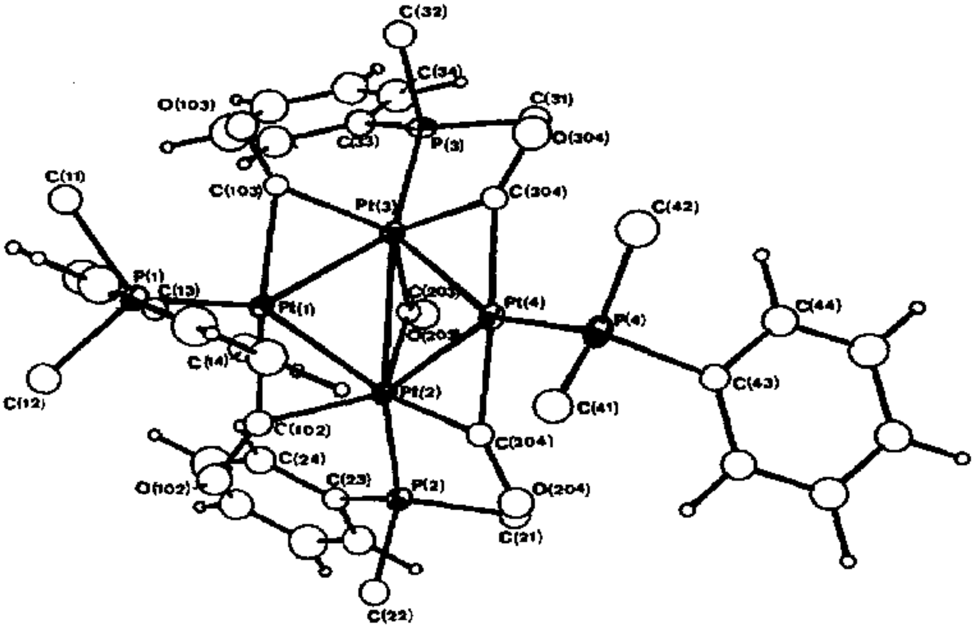


(347)

Relatively few palladium isonitrile clusters have previously been characterised. Palladium vapour reacted with CyNC to give $[Pd_3(CNCy)_6]$ as the sole product. This was rather similar to $[Pt_3(CNCMe_3)_6]$ with three terminal and three bridging CNCy ligands [919]. $[Pd_3(CNR)_6]$ (R = 2,6-$Me_2C_6H_3$) was formed by reaction of the ligand with $[Pd(dba)_2]$ or $[Pd_2(dba)_3.CHCl_3]$ [920].

1.9.2 Tetrameric clusters

The clusters $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (L = PEt_3, PEt_2CMe_3 or $PMePh_2$) were prepared from $[Pt(cod)_2]$, L, C_2H_4 and CO, and their ^{195}Pt and ^{31}P nmr spectra were recorded. The structure of the purple monoclinic modification of the PMe_2Ph complex, **(348)**, was determined; the $\{Pt_4\}$ unit was a distorted edge-opened tetrahedron with five edge-bridging carbonyl groups and four terminal phosphine ligands [921]. A similar technique was used to prepare $[Pt_4(CO)_5(PEt_3)_4]$; ^{31}P and ^{195}Pt nmr spectra were said to demonstrate a tetrahedral arrangement of platinum atoms in solution [922].

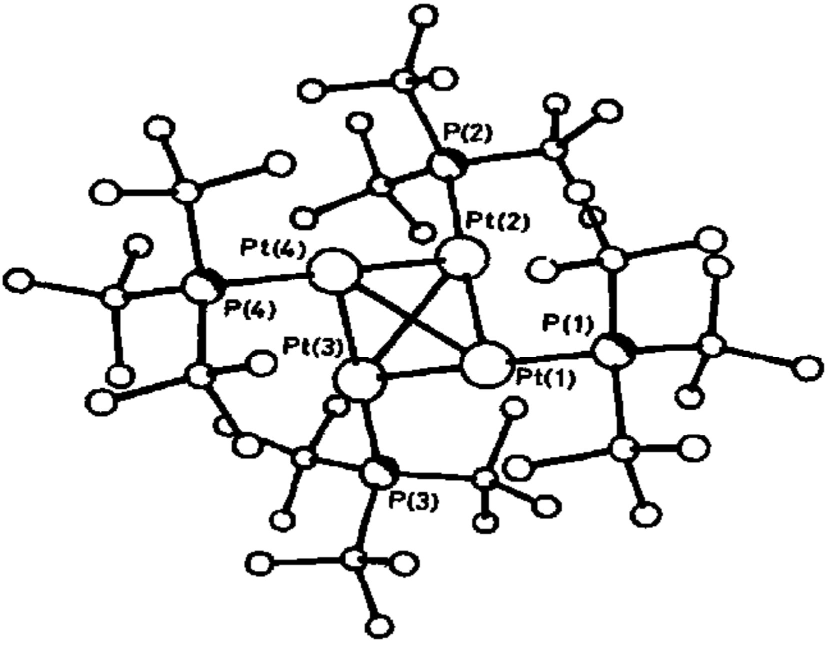


(348) (Reproduced with permission from [921])

Protonation of $[H_2Pt_4\{P(CMe_3)_3\}_4]$ with $H[BF_4]$ gave $[H_2Pt_4\{P(CMe_3)_3\}_4][BF_4]_2\cdot[HBF_4]_2$, **(349)**, characterised by X-ray diffraction. The cluster adopted a flattened tetrahedral structure similar to that of $[H_8Pt_4\{PPh(CHMe_2)_2\}_4]$. Reaction with hydrogen gave **(350)**, again characterised by a diffraction study. This was a butterfly type structure with a distinct head and tail. In both cases the hydrides were very mobile, migrating fast over all the available sites on the nmr timescale [923].

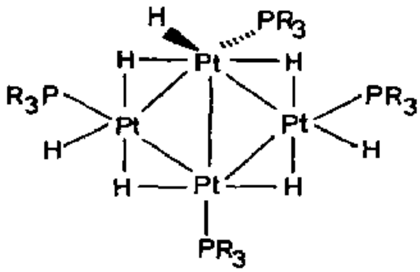
1.9.3 Higher nuclearity clusters

The topological electron counting theory developed in [915] was applied to a wide range of transition metal clusters including $[Pt_6(CO)_{12}]^{2-}$, $[Pt_9(CO)_{18}]^{2-}$, $[Pt_{15}(CO)_{30}]^{2-}$ and $[Pt_{19}(CO)_{22}]^{2-}$ [924]. The rate parameters for the conversion of water to oxygen by $[Pt_{12}(CO)_{24}]^{2-}$ were determined. Quinone could be reduced to hydroquinone using water or hydrogen in the presence of a platinum cluster [925]. Thermolysis of $[Pt_{15}(CO)_{30}]^{2-}$ under nitrogen gave $[Pt_{24}(CO)_{30}]^{2-}$. An X-ray diffraction study revealed that the $\{Pt_{24}\}$ core was a fragment of a cubic close packed structure. Using a limited amount of a phosphine ligand, L, $[Pt_{24}(CO)_{29}L]^{2-}$ was isolated, but with an excess of L, $[Pt(CO)L_3]$ was obtained [926]. Layered compounds suitable for ion exchangers, and exhaust gas and hydrocarbon conversion catalysts, were prepared having the formula, $[A_x^{2+}B_y^{3+}(OH)_{2x+3y-n}(D)_3^{n-}].tH_2O$, in which A and B were metals and D was a polyanion, $x,y,z,t > 0$, $n = 1\text{-}10$, and $0.5 \leqslant x/y < 10$. The species D included $[Pt_{18}(CO)_{36}]^{2-}$ [927].



(350) (Reproduced with permission from [923])

Carbonylation of $[Pd_{10}(CO)_{12}(PBu_3)_6]$ gave $[Pd_{10}(CO)_{14}(PBu_3)_4]$, **(351)**. The $\{Pd_{10}\}$ polyhedron was a four-capped octahedron with unsymmetrical caps [928].



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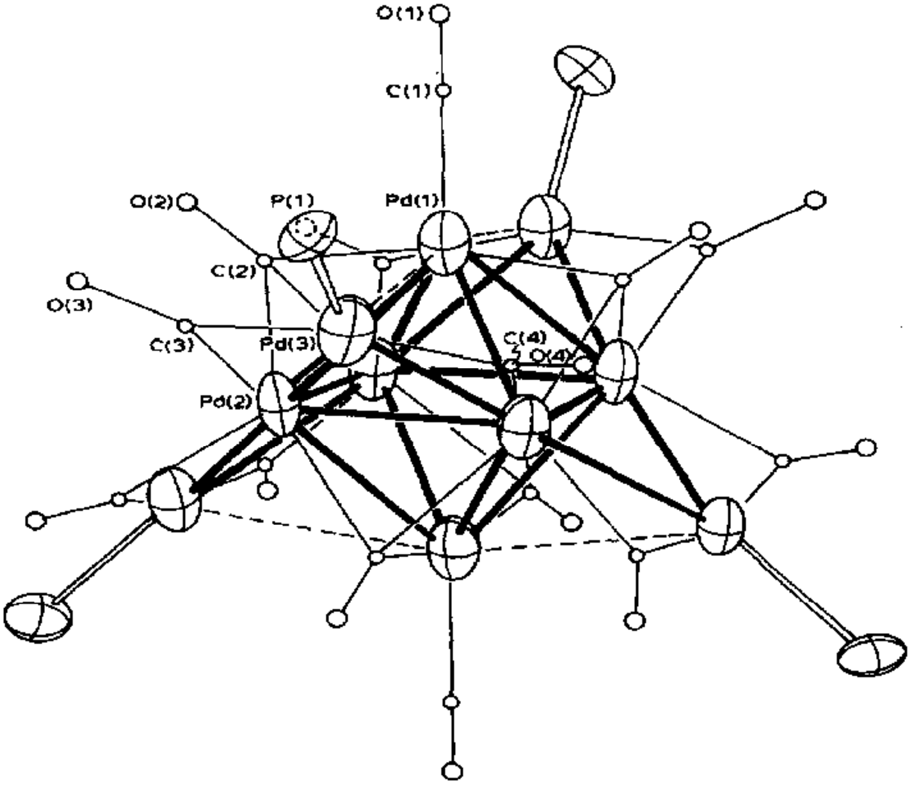
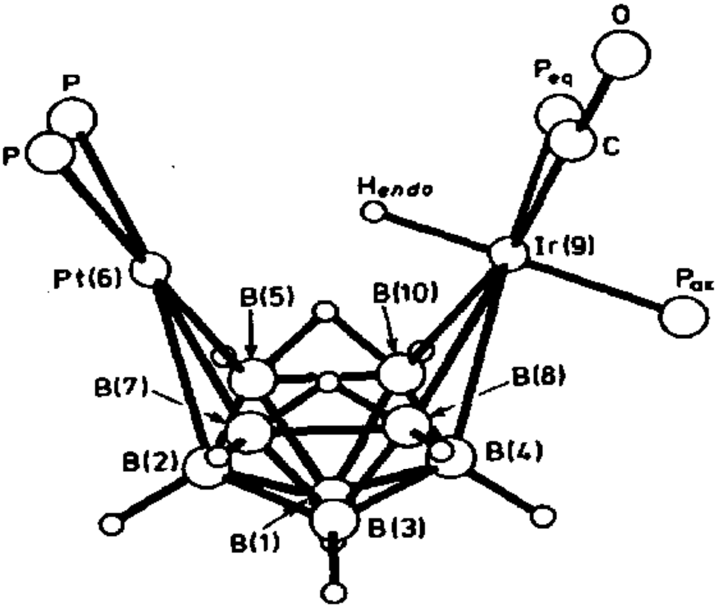


(351)(Reproduced with permission from [928])
Butyl substituents omitted

1.9.4 Heteronuclear clusters

A review of novel cluster interactions in metalloboranes discussed platinaboranes in considerable detail [929]. Reaction of *arachno*–[(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] with KH and [Pt(PMe$_3$)$_2$Cl$_2$] gave, in a

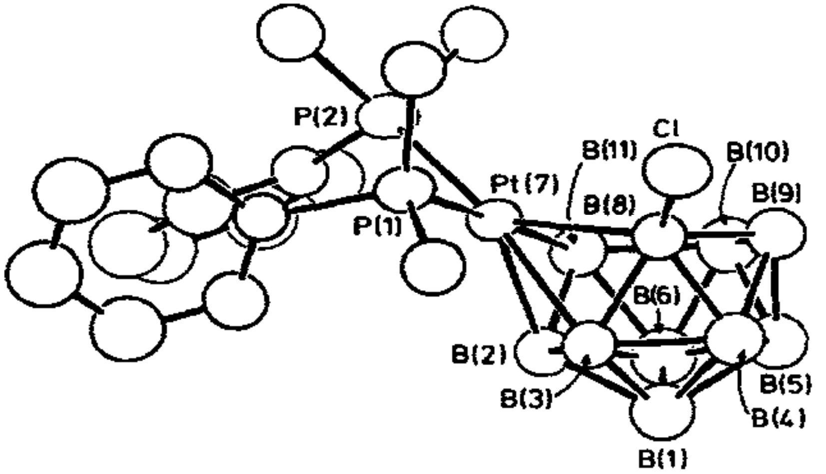
12 % yield, 6,6-(PMe$_3$)$_2$-*asym*-9,9,9,9-(CO)-*endo*-H-*cis*(PMe$_3$)$_2$-*arachno*-6,9-platinairidadecaborane, **(352)**. Although an X-ray diffraction study failed, the structure could be assigned using nmr spectroscopic data in comparison with related species [930]. Reaction of *arachno*-6,9-$X_2B_{10}H_{12}$ (X = Me_2S or MeCN) with *cis*-[Pt(PMe$_2$Ph)$_2$Cl$_2$] gave *nido*-[8-Cl-7,7-(PMe$_2$Ph)$_2$-7-PtB$_{10}$H$_{11}$], (353), together with 6 % *nido*-[7,7-(PMe$_2$Ph)$_2$-7-PtB$_{10}$H$_{12}$] [931].



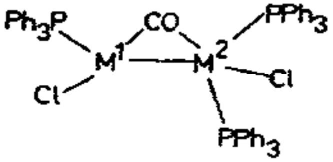
(352) (Reproduced with permission from [930])

Representation of the proposed molecular structure of *arachno*-[(Me$_3$P)$_2$PtB$_8$H$_{10}$IrH(PMe$_3$)$_2$(CO)]. Nmr spectroscopic evidence suggested that the bonding and stereochemistry about Pt(6) and Ir(9) are essentially the same as about the metal atoms in [(Me$_2$PhP)$_2$PtB$_8$H$_{12}$] and [(OC)(Me$_3$P)$_2$HIrB$_8$H$_{11}$Cl] respectively.

Reaction of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] with RHgCl gave [(Ph$_3$P)$_2$ClPt-HgR] in which R was an aryl group bearing chlorine atoms at the 2- and 6-positions and at at least one other site on the ring. Many spectroscopic data were provided [932]. Treatment of [M^1(PPh$_3$)$_3$(CO)] with [M^2(PhCN)$_2$Cl$_2$] (M^1, M^2 = Pd or Pt) gave **(354)**. The complex with M^1 = M^2 = Pd reacted with Na[W(CO)$_3$(Cp)] to give the known tetranuclear species [{PdW(Cp)(μ_3-CO)(μ-CO)$_2$(PPh$_3$)}$_2$] [933]. The cyclometallated species **(355)** reacted with Na[M] to give (356) (M = [Co(CO)$_4$], [Mo(CO)$_3$(Cp)] or [Fe(CO)$_3$(NO)]). Chromium and tungsten complexes could also be prepared and one metal could be replaced by another [934].



(353) (Reproduced with permission from [931])



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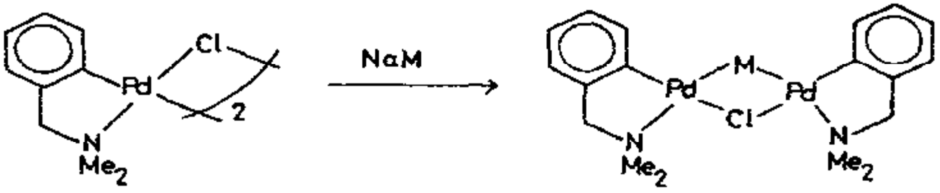
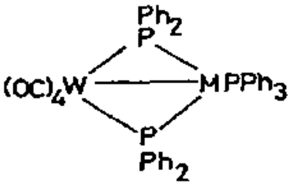
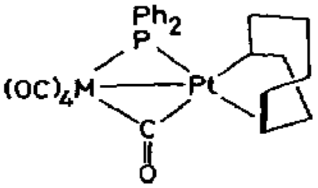


(355) **(356)**

Treatment of $[M(PPh_3)_2X_2]$ (M = Ni, Pd or Pt) with $Li_2[W(CO)_4(PPh_2)_2]$ gave **(357)**; the complex for which M = Pt was characterised by X-ray diffraction [935]. Oxidative addition of $[(OC)_5M(PPh_2H)]$ (M = Cr, Mo or W) to platinum(0) also gave μ-phosphido complexes such as $[(OC)_5M(\mu\text{-}PPh_2)Pt(cod)H]$, which rearranged readily to **(358)**. Similarly, $[Pt(C_2H_4)(PPh_3)_2]$ yielded $[(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]$, since the initially formed adduct, $[(OC)_5M(\mu\text{-}PPh_2)Pt(H)(PPh_3)_2]$ also rearranged easily [936].

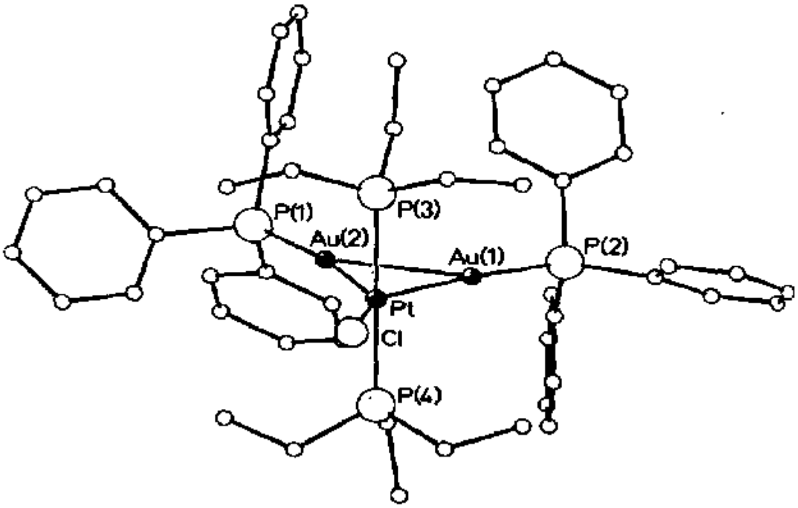


(357)



(358)

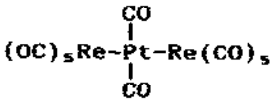
Trans-[HPt(PEt$_3$)$_2$Cl] reacted with two equivalents of [Au(PPh$_3$)(thf)][CF$_3$SO$_3$] to give **(359)**, the first fully characterised compound with a platinum-gold bond [937].



(359) (Reproduced with permission from [937])

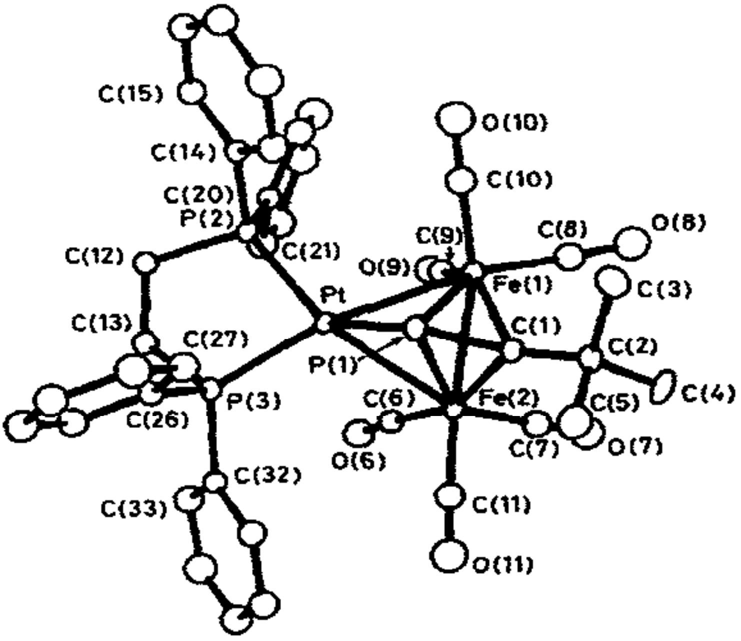
[Me$_2$Pt(cod)] reacted with an excess of [HM(CO)$_5$] (M = Mn or Re) under a carbon monoxide atmosphere to give [M$_2$Pt(CO)$_{12}$]. [M$_2$(CO)$_{10}$] was a by-product, suggesting that the reaction involved a radical pathway. [Re$_2$Pt(CO)$_{12}$], **(360)**, was shown by X-ray diffraction to have D_{2h} symmetry with octahedral geometry at rhenium and a square planar arrangement at platinum [938,939]. More generally in *trans*-[M(M')$_2$L$_2$] (M' = {Mn(CO)$_5$}, {Co(CO)$_4$} or {W(CO)$_3$(Cp)}; L = py) the M-M' bond strengths increased in the order M = Pd < Pt < Au < Hg [940].

A phosphaalkyne, RC$\equiv$P, may act as 2-, 4- or 6-electron donor towards transition metals. Treatment of [Pt(dppe)(Me$_3$CC$\equiv$P)] (in which the phosphaalkyne is η^2-bonded) with [Fe$_2$(CO)$_9$] or [Fe$_3$(CO)$_{12}$] gave [Fe$_2$Pt(dppe)(CO)$_6$(Me$_3$CC$\equiv$P)], **(361)**, characterised by X-ray diffraction; the phosphorus atom of the phosphaalkyne was coordinated to all three metal atoms in an unprecedented new cluster type [941]. The use of organic peracids for the oxidation of coordinated chalcogens has been examined. Thus $[Fe_2Pt(\mu_3\text{-}E)_2(CO)_6(PPh_3)_2]$ (E = S, Se or Te) was converted to $[Fe_2Pt(\mu_3\text{-}EO)(\mu_3\text{-}E)(CO)_6(PPh_3)_2]$, for example, (362) [942].

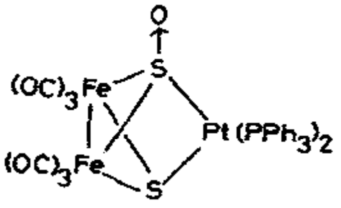


$$(OC)_5Re\text{-}\underset{\displaystyle CO}{\overset{\displaystyle CO}{Pt}}\text{-}Re(CO)_5$$

(360)

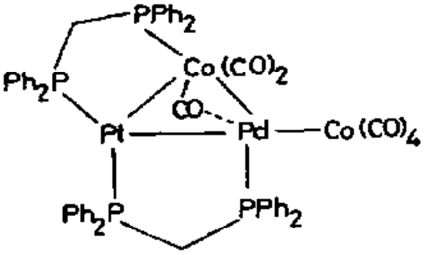


(361) (Reproduced with permission from [941])



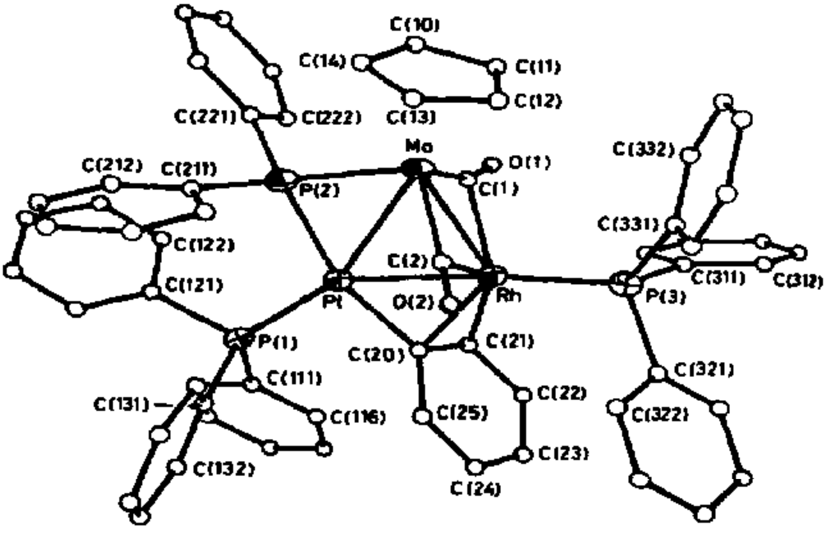
(362)

Metal carbonyl anions were shown to insert into the palladium-phosphorus bond of $[\mathrm{PdPt}(\mu\text{-dppm})_2\mathrm{Cl}_2]$ to give, for example, (363). $\mathrm{Na}[\mathrm{Mn}(\mathrm{CO})_5]$ reacted similarly, again with excellent regioselectivity [943].



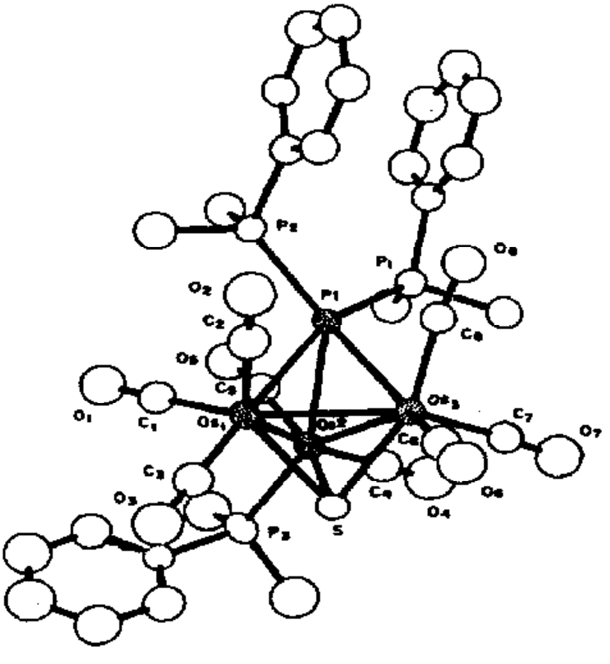
(363)

The bimetallic complex, $[\mathrm{MoRh}(\mu\text{-CO})_2(\mathrm{CO})(\mathrm{PPh}_3)_2(\mathrm{Cp})]$, reacted with $[\mathrm{Pt}(\mathrm{C}_2\mathrm{H}_4)(\mathrm{PPh}_3)_2]$ to give $[\mathrm{MoPt}(\mu\text{-PPh}_2)(\mathrm{CO})_2(\mathrm{PPh}_3)_2(\mathrm{Cp})]$ and the trimetallic species $[\mathrm{MoRhPt}(\mu\text{-CO})_2(\mu\text{-PPh}_2)(\mu\text{-1-}\sigma\text{:1-2-}\eta\text{-C}_6\mathrm{H}_5)(\mathrm{PPh}_3)_2(\mathrm{Cp})]$, **(364)**, characterised by X-ray diffraction. The Mo-Rh bond was bridged by two CO ligands, the Mo-Pt bond by PPh_2 and the Rh-Pt bond by a benzene ring, σ-bonded to platinum and η^2-coordinated to rhodium [944].



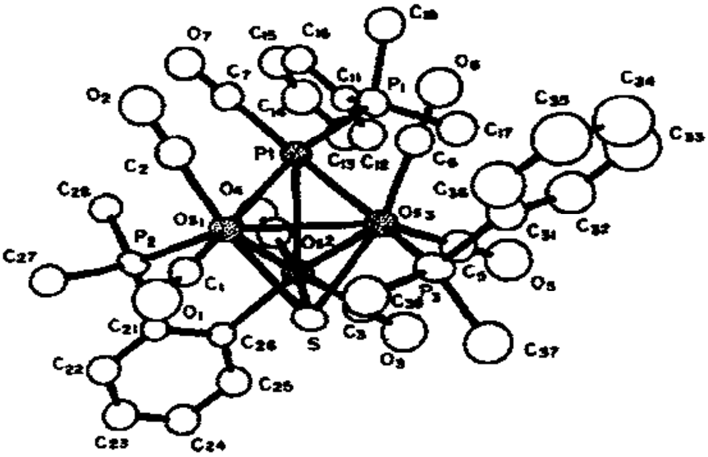
(364) (Reproduced with permission from [944])

Further work on $\{\mathrm{PtOs}_3\}$ clusters has been reported this year. $[\mathrm{PtOs}_3(\mathrm{CO})_8(\mathrm{PMe}_2\mathrm{Ph})_3(\mu_3\text{-S})]$, **(365)**, was prepared from $[\mathrm{Os}_3(\mathrm{CO})_{10}(\mu_3\text{-S})]$ and $[\mathrm{Pt}(\mathrm{PMe}_2\mathrm{Ph})_4]$, and was characterised by diffraction techniques. The $\{\mathrm{PtOs}_3\}$ core was a distorted tetrahedron with the platinum atom unsymmetrically bound to the three osmium atoms. The sulphur bridged the three osmium atoms, and one carbonyl was semi-bridging [945]. A more thorough study showed that several other products were also formed including $[PtOs_3(CO)_9)(PMe_2Ph)_3(\mu_3\text{-}S)]$, $[PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)]$ and $[PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)]$. In the last of these species X-ray diffraction indicated that sulphur bridged the $\{PtOs_2\}$ triangular face. Photolysis of $[PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)]$ gave $[PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)]$ and $[HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)]$, **(366)**, characterised by X-ray diffraction. The formation of these species was in contrast to the reaction of $[Os_3(CO)_{12}]$ with $[Pt(PR_3)_4]$, which gave no mixed clusters; the sulphur is thought to coordinate first to platinum to initiate reaction [946]. Reaction of $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ with $[Pt(C_2H_4)(PPh_3)_2]$ under nitrogen gave $[PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2]$ and $[PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2]$. Under carbon monoxide, the decacarbonyl was the major product and both complexes were characterised by X-ray diffraction. They were triangular clusters of one platinum and two osmium atoms with a third osmium linked to one of the others *via* a metal-metal bond and a bridging sulphide [947].

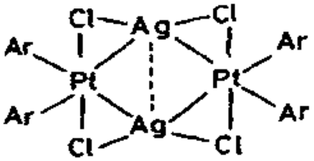


(365) (Reproduced with permission from [945])

Reaction of $Ag[NO_3]$ with *trans*-$[Bu_4N]_2[(C_6F_5)_2PtCl_2]$ gave the bis tetrabutyl ammonium salt of (367) in which each silver had one close and one longer platinum-silver contact distance. The silver-silver distance was rather too long to be considered bonding [948]. A similar metal skeleton with a flattened butterfly structure was established for (368), prepared from $[Pt(C_2H_4)((PPh_3)_2]$ and $[Au(CN\text{-}2,6\text{-}Me_2C_6H_3)_2]^+$. The gold-gold distance was 2.59 Å [949].



(366) (Reproduced with permission from [946])



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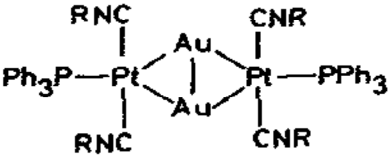


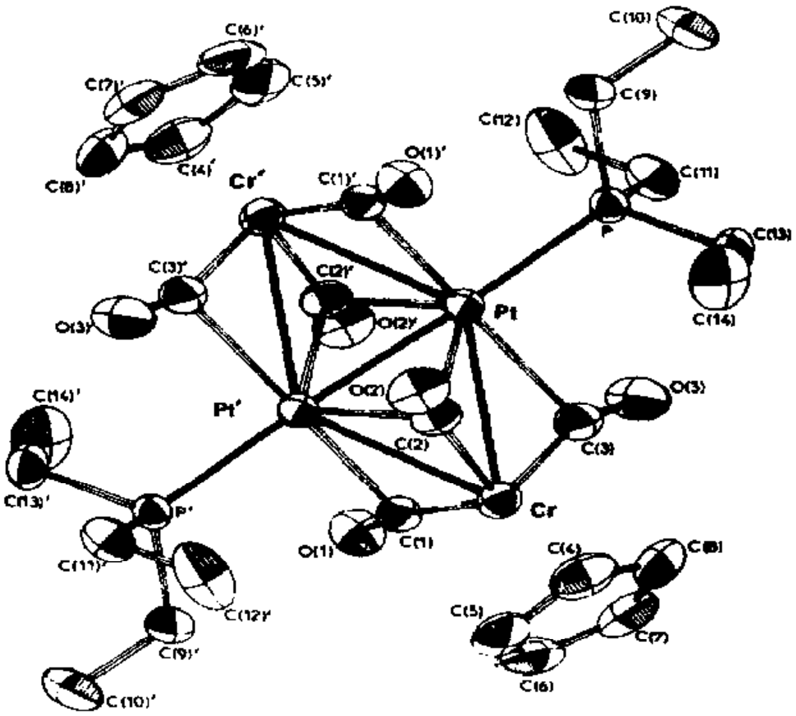
(368)

New strategies for the preparation of mixed metal clusters of the type (Pt_2M_2) (M = Cr, Mo or W) have been developed. Whilst $[PtL_2Cl_2]$ (L = PhCN or RNC) reacted with Na[M] ([M] = $[Cr(Cp)(CO)_3]$, $[Mo(Cp)(CO)_3]$, $[W(Cp)(CO)_3]$ or $[Mn(CO)_5]$) to give *trans*-$[PtM_2L_2]$, the complexes for which L = PR_3 reacted with $[M(Cp)(CO)_3]^-$ to give $[Pt_2M_2(Cp)_2(CO)_6(PR_3)_2]$. An alternative preparation was the reaction of *trans*-$[Pt\{M(Cp)(CO)_3\}_2(PhCN)_2]$ with PR_3. Many new complexes were isolated and characterised; all possessed a planar traingulated parallelogram for the metal core. In the 58-electron clusters the $[M(Cp)(CO)_3]^-$ bridged the L-Pt(I)-Pt(I)-L unit as in **(369)** [950].

Reaction of $[Pt_{12}(CO)_{24}]^{2-}$ with $[Ir(CO)(PPh_3)_2Cl]$ gave $[Pt_2Ir_2(CO)_7(PPh_3)_3]$, which had a butterfly structure with iridium atoms at the hinge and platinum at the wingtips. As might be expected from its open structure the complex was a catalyst for alkene hydrogenation [951].

The triangular platinum species $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ reacted with $[Au(PCy_3)Cl]$ to give $[Pt_3Au(\mu_2\text{-}CO)_3(PCy_3)_4][PF_6]$, (370), in which the

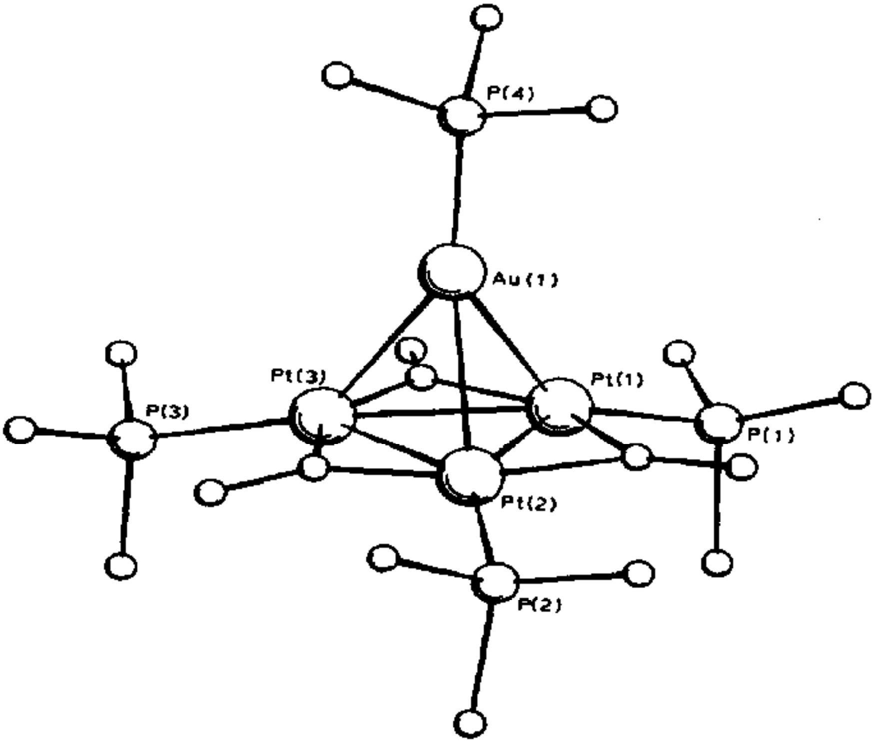
{Au(PCy$_3$)} fragment occupied an apical site above the (Pt$_3$) triangle [952]. The dimercurated carborane, **(371)**, reacted with [PtL$_3$] to give **(372)** [953].



(369) (Reproduced with permission from [950])

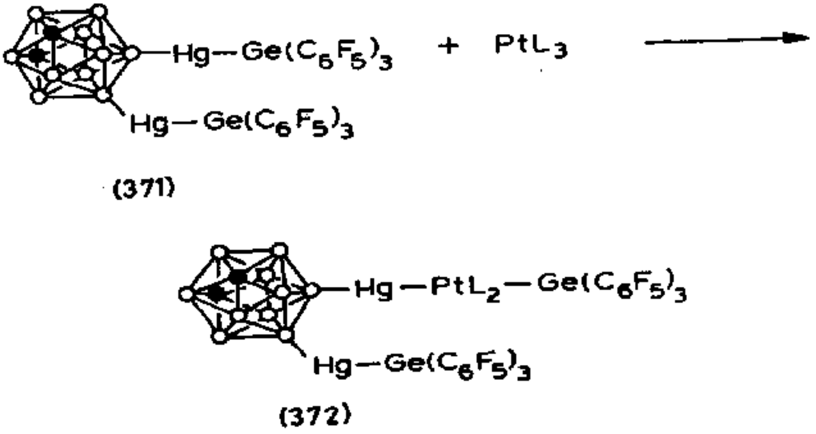
The topological electron counting theory developed in [915] was applied to heteronuclear complexes including $[PtRh_4(CO)_{14}]^{2-}$, $[PtRh_4(CO)_{12}]^{2-}$ and $[HPd_6Fe_6(CO)_{24}]^{3-}$ [924]. Reaction of $Na_2[PtCl_6]$ with $RhCl_3$ under a carbon monoxide atmosphere in the presence of a strong base yielded $[PtRh_5(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^-$. The latter species was in equilibrium with $[PtRh_4(CO)_{12}]^{2-}$, with an increased pressure of carbon monoxide favouring the $\{PtRh_4(CO)_{14}]^-$ cluster. This is the first example of a facile interconversion of two trigonal bipyramidal clusters with 76 and 72 cluster valence electrons. The platinum site, however, was not the same in both species, and solution structures and fluxional behaviour were studied by ^{13}C, ^{103}Rh and ^{195}Pt nmr spectroscopy [954]. Controlled pyrolysis of $\{PtRh_5(CO)_{15}]^-$ allowed the isolation of $[Pt_2Rh_{11}(CO)_{24}]^{3-}$, **(373)**, $[PtRh_{12}(CO)_{24}]^{4-}$, **(374)**, and a little $[Pt_2Rh_9(CO)_{22}]^{3-}$, **(375)**. This latter species was also obtained from $[PtRh_5(CO)_{15}]^-$ and $[PtRh_4(CO)_{12}]^{2-}$. The $\{M_{13}\}$ clusters **(373)** and **(374)** had similar structures with metallic coordination analogous to a hcp arrangement and a platinum atom in the centre. $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ reacted with

$[Rh(CO)_2(MeCN)_2]^+$ to give $[Pt_2Rh_{12}(CO)_{26}]^{2-}$, (376), and on protonation *via* a multistep process, $[PtRh_{13}(CO)_{25}]^{3-}$, (377) [955].



(370) (Reproduced with permission from [952])

For reasons of clarity the cyclohexyl rings have been omitted except for the *ipso* carbon atoms



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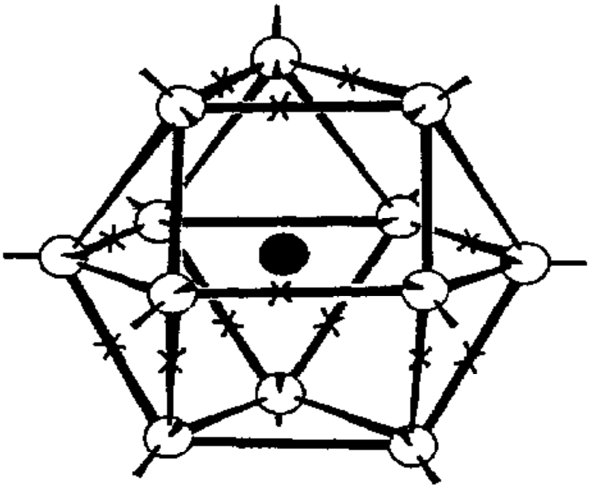
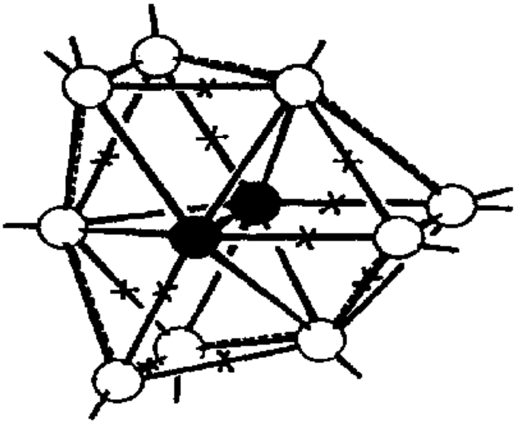


(373), **(374)** (Reproduced with permission from [955])

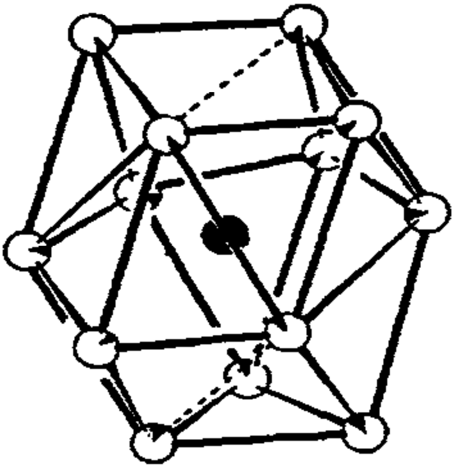
Each surface metal atom bears one terminal CO ligand and is connected to two bridging carbonyls (X-bridged edges). The second platinum atom in **(373)** was found to be disordered on the outer shell, without any evidence of a prefered location.



(375) (Reproduced with permission from [955])

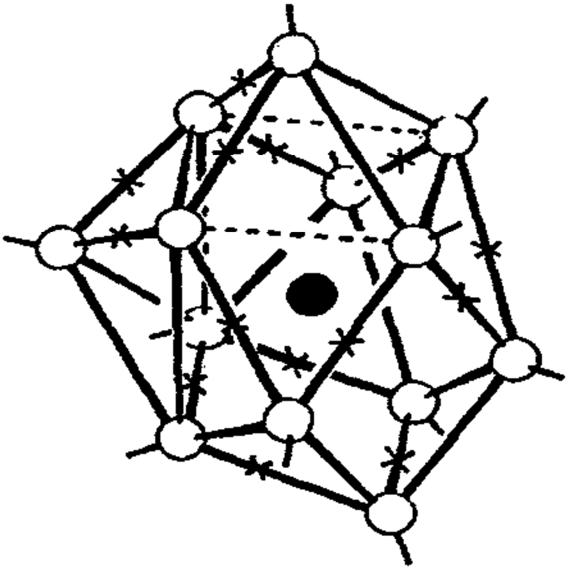
The structure consists of three condensed octahedra with a common edge (Pt-Pt, coincident with the ideal threefold axis). X represents the bridged edges

The fragment $(Pt_2(\mu_2\text{-}S)_2(PPh_3)_4)$ acted as a bidentate ligand towards silver in (378); the intersulphur distance was 3.1 Å [956].



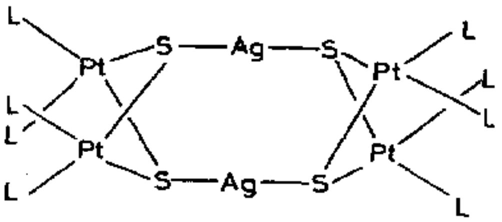
(376) (Reproduced with permission from [955])

Only the metal array could be established in a poor diffraction study.



(377) (Reproduced with permission from [955])

The metallic skeleton is intermediate between closest packing and bcc. The central platinum atom exhibits nine short metal-metal bonds (2-64-2.73 Å), two longer bonds (mean 2.98 Å) and two very long interactions (3.28 and 3.49 Å). X represents the bridged edges.



(378)

Reaction of the carbide cluster $[Fe_4C(CO)_{12}]^{2-}$ with platinum salts gave $[Fe_5PtC(CO)_{15}]^{2-}$ in which the carbide occupied the centre of the octahedron of metal atoms [957].

Transition metals could be incorporated into a homonuclear main group metal cluster, if bonded to the appropriate ligand. Thus reactions (43) and (44) were studied by ^{119}Sn nmr spectroscopy [958].

$$\begin{tikzcd}
{[Pt(PPh_3)_4] + [Sn_9]^{4-}} \arrow[r, "en"] & {[L_2PtSn_9]^{4-}} & (43) \\
{[Pt(PPh_3)_4] + [Sn_8Tl]^{5-}} \arrow[r, "en"] & {[L_2PtTlSn_8]^{5-}} \arrow[u, "\text{``Sn''}"'] & (44)
\end{tikzcd}$$

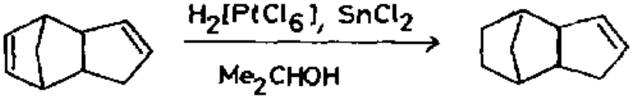
1.10 CATALYSIS BY PALLADIUM AND PLATINUM COMPLEXES

A review of the use of complexes of the platinum metals in catalysis has been published [959]. There have also been accounts of reactions using complexes with a palladium-palladium bond [960] or complexes of palladium(II) or platinum (II) with pyridine monocarboxylic acids as catalysts [961].

1.10.1 Hydrogenation and hydrogenolysis

The rate of hydrogenation of C_6-C_9 alkenes over palladium sulphide was decreased by the presence of aromatic hydrocarbons, which seemed able to dislodge the alkenes from the catalytic site [962]. Palladium phthalocyanine catalysed the reduction of alkenes, carbon-nitrogen double bonds and nitroarenes [963]. A catalyst formed from $H_2[PtCl_6]/SnCl_2/Me_2CHOH$ was useful for the highly selective reduction of (379) [964].

Unsaturated aldehydes were reduced to the saturated analogues in the presence of palladium complexes of nitrogen containing ligands including 1-(2-pyridylazo)-2-naphthol, β-naphthol orange and 3-aminocoumarin derivatives [965]. A comparison between homogeneous and heterogeneous palladium catalysts for reduction of methyl-2,4-hexadieneoate revealed that [Pd(acac)$_2$] was a rather selective catalyst, yielding mainly methyl 2-hexenoate [966]. Benzothiophene was reduced to (380) with a maximum selectivity of 77 %; to prevent hydrogenolysis and to maximise selectivity the reaction was generally terminated before conversion was complete [967]. Palladium(0) complexes of sulphonated alizarin were used to hydrogenate fatty acids in order to cold acclimatise *Anacystis nidulanes* [968].

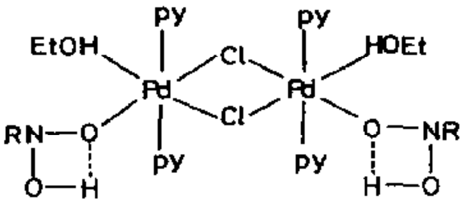


(379)

(380)

Palladium complexes containing primary amines were active catalysts for the reduction of alkynes to alkenes; selectivity was 98-99 % at 95 % conversion, since 1-alkenes were isomerised to internal alkenes which were not readily reduced [969]. Treatment of PdCl$_2$ with chiral 1-phenylethylamine and hydrogen gave a dark brown solution which catalysed enantioselective reduction of azlactones. Although the catalytically active species was poorly defined, it semms likely that a cyclometallated intermediate was involved [970]. The complexes *trans*-[Pd(py)$_2$X$_2$] catalysed reduction of ArNO$_2$ to ArNH$_2$. An intermediate, probably (381), was isolated, but its structure was not fully elucidated [971]. Hydrogenation of the 2-, 3- and 4-isomers of **(382)** to dihydroxylamines was catalysed by PdCl$_2$/trioctylamine [972].

Numerous catalysts described this year have been polymer bound complexes. Crosslinked polystyrene was functionalised with [Pd(bipy)Cl$_2$] and the product used as a catalyst for the selective reduction of 1,5-cod [973]. Pd(OCOMe)$_2$ anchored to polystyrylbipy was a useful catalyst for alkene reduction at atmospheric pressure. Rates were dependent on steric hindrance and there was little competing isomerisation [974]. 4,4'-Diamino-2,2'-bipy was prepared, converted to its complex with Pd(OCOMe)$_2$, and polymerised with 2,4-diisocyanatotoluene to give a polyurea. On reduction with Li[AlH$_4$] a good catalyst for alkene hydrogenation was obtained [975]. The anthranilic acid functionalised polystyrene, (383), was used in reduction of $ArNO_2$ to $ArNH_2$; the catalyst was very active, and had a long lifetime and excellent stability [976].



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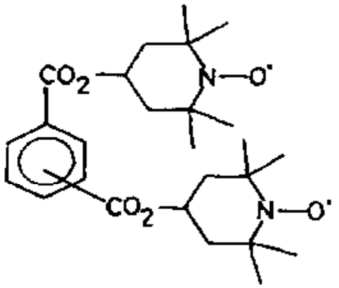

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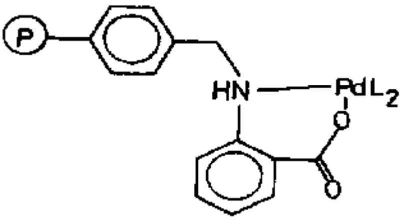
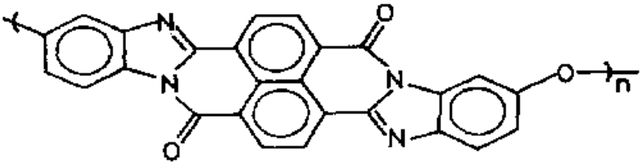


(383)

A soluble homogeneous reduction catalyst was obtained from polyvinylpyrrolidone, $PdCl_2$ and Et_3N [977]. This material has also been supported on silica and used for nitroarene hydrogenation [978]. Silica supported polymethacrylic acid palladium and platinum complexes were used in reduction of RNO_2, $ArNO_2$, alkenes, aldehydes and ketones [979]. The species produced on treatment of polyethyleneimine/$PdCl_2$ with $Na[BH_4]$ was a selective catalyst for reduction of 1,4-cyclohexadiene to cyclohexene [980]. A catalyst system for alkene reduction was prepared by impregnating **(384)** with $Na_2[PdCl_4]$. On reduction, palladium clusters of diameter 35±10 Å were formed [981].

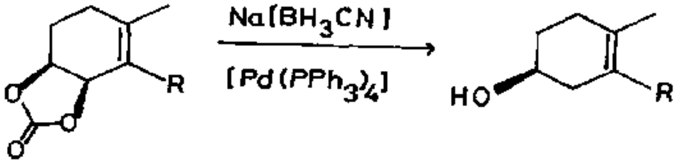


(384)

It has been known for some time that palladium complexes of silica modified by γ-aminopropyl groups catalysed reduction of alkenes, alkynes, imines and nitro compounds. The hydrogenation/isomerisation of $PhCH_2CH{=}CH_2$ has now been studied. The reaction rate depended on the structure of the modifying amine, with ammonium salts giving slower reactions than tertiary amines [982]. Aldehydes and ketones could also be reduced under ambient conditions [983]. A platinum complex of silica supported poly(3-diphenylphosphinopropyl)siloxane was a reduction catalyst and has been studied by XPES [984].

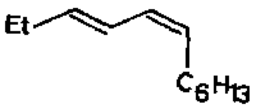
The grafting of palladium chloride with tertiary amines on to microporous and macroporous zeolites, and macroporous adsorbants was studied. The preactivation of the grafted catalysts enhanced the rate of hydrocarbon hydrogenation [985]. $PdCl_2/R_3N$ supported on inorganic oxides provided useful catalysts for the reduction of alkynes to *cis*-alkenes [986]. XPES studies of palladium complexes have been related to their catalytic activity [987].

Hydrogenolysis of allyl derivatives has this year been accomplished using a variety of hydrogen sources. For example, $Na[BH_3CN]$ was used in the catalytic hydrogenolysis and decarboxylation of **(385)** [988], whilst allyl halides were reduced to 1-alkenes using $Pd(0)/PBu_3/[HCOO]^-$ [989].



(385)

Hydrogenolysis of alkenyl sulphones was accomplished using $BuMgX/[ML_n]$ ($[ML_n]$ = $[Pd(acac)_2]$, $[Pd(acac)_2]/PBu_3$ or $[Ni(acac)_2]/L$). Whilst yields were modest, selectivity was high and **(386)** was thus prepared for use in the synthesis of the pheromone of *spodoptera littoralis* [990,991]. Electrochemical hydrogenolysis of allyl ethanoates has also been noted; an allyl anion, able to react with electrophiles, was the first product [992]. Hydrogenolysis of benzyl esters was achieved in the presence of $PdCl_2/Et_3SiH/Et_3N$ [993].



(386)

Catalytic oxidation and H/D exchange of alkanes in the presence of platinum group metal complexes has been reviewed [994]. The activation of methane by *trans*-$[Pt(H_2O)_2Cl_2]$ was studied theoretically. As the reactants approached, repulsion energy was decreased by distortion of the platinum complex, and then by H-C-H deformation in the methane, and finally by C-H stretching [995]. Kinetic studies were also discussed [996], as was the effect of chloride ion concentration [997]. H/D exchange in acidic methylene groups using D_2O was reported in the presence of $[Pd(PR_3)_n]$ (n = 3 or 4; $PR_3 = PBu_3 > PMePh_2 > PPh_3$), but the reaction rate was not simply related to pKa, since pentane-2,4-dione did not exchange at all. A reaction mechanism was proposed [998].

Reaction of phenylglycine with D_2O or T_2O in the presence of $K_2[PtCl_4]$ led to deuteration of the aryl ring [999]. Using $ArCH_2CH(NH_2)COOH$ as substrate, electron donors in the 4-position accelerated the reaction, whilst electron withdrawing groups retarded it [1000].

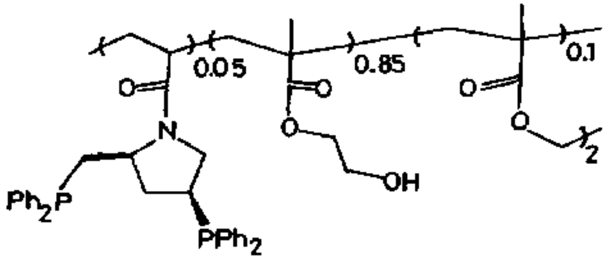
1.10.2 Carbon monoxide reactions

The cyclocarbonylation of alkenes and alkynes using $[Ni(CO)_4]$ or palladium complexes as carbonylating agents and/or catalysts has been reviewed [1001]. Hydroformylation of propene occurred in the presence of *trans*-1,2-bis(diphenylphosphino)cyclobutane platinum(II) dichloride to give butanal and 2-methyl propanal in the ratio of 9.3:1 [1002].

The rates of palladium catalysed carbomethoxylation of alkenes increased when a perfluoroalkyl sulphonic acid or powdered Nafion was added in place of HCl or $H_2[SO_4]$ [1003,1004]. Decene yielded mainly methyl 2-methyldecanaote in the presence of $PdCl_2/CuCl_2/HCl/CO/MeOH$ [1005]. Branched esters were also obtained selectively from 1-alkenes with the $PdCl_2/CuCl_2/CO/O_2/HCl/ROH$ system, and this catalyst was also active for carbomethoxylation of cyclic and internal alkenes [1006]. Using $[Pd(PR_3)_2Cl_2]/SnCl_2$ as the catalyst, however, linear esters were the major products, and the reaction was achieved under rather mild conditions [1007]. 4-(2-Methypropyl)-1-ethenylbenzne reacted using $[Pd(PPh_3)_2Cl_2]/CO/H_2O/HCl/3\text{-}ClC_6H_4CO_3H$ to give mainly a linear acid in 90 % yield. Without the peracid only a 67 % yield was obtained [1008]. When ethane-1,2-diol was used as the added alcohol in the reaction of $RCH{=}CH_2$ with $PdCl_2/CuCl_2/CO/O_2/HCl$ the major product was $RCH(Me)CO_2CH_2CH_2OH$, obtained in about 70 % yield at 1 atm pressure and 25 °C, using 1-decene as substrate [1009].

Enatioselective hydroformylation of ethenyl benzene was reported to occur in 78 % enantiomer excess using $[Pt\{(-)\text{-DBPDIOP}\}Cl_2]$ as catalyst. Optimisation was achieved by systematic variation of the reaction parameters

[1010]. Platinum chloride supported on **(387)** gave similar optical yields, the best so far reported for a polymer supported catalyst [1011]. Hydrocarboxylation of **(388)** and **(389)** gave good chemical but poor optical yields using [Pd(diop)Cl_2] [1012].



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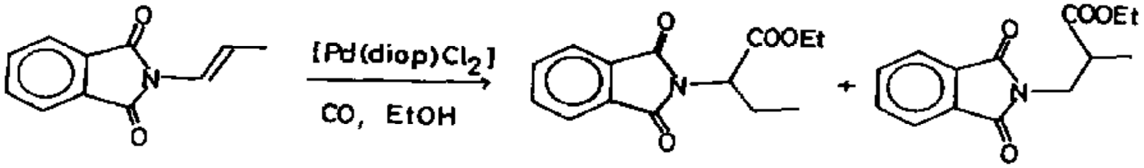

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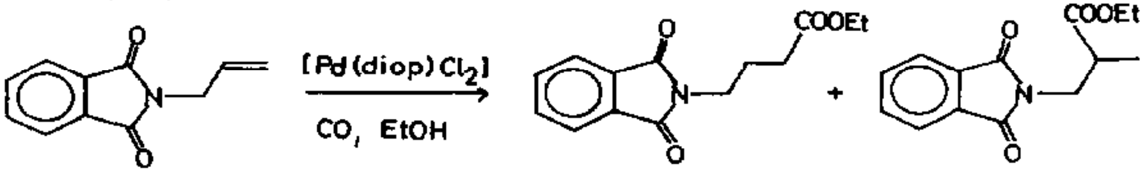
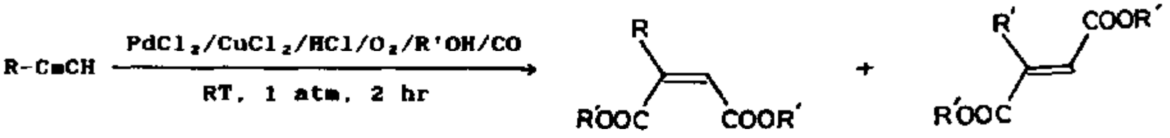
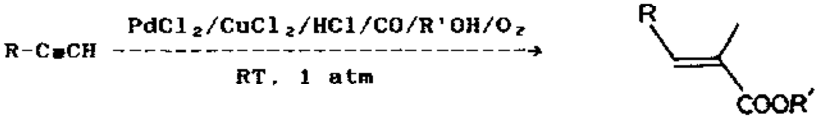


(389)

Oxidative hydrocarboxylation of 1-alkynes gave **(390)** and **(391)**, the former being the major product and usually being obtained in good yield. However, with 2-alkynes only a mono ester, **(392)** was obtained, again with good selectivity [1013]. Reaction of the α,ω-diyne, **(393)**, gave **(394)** and **(395)** in similar quantities (2:1-1.26:1); a mechanism for the process was proposed [1014]. Hydrocarboxylation of butadiene using $PdCl_2/CO/HCl/H_2O/[Bu_4N]Cl$ gave a complex mixture of saturated and unsaturated carboxylic acids and some butenes, the major product being *E*-3-pentenoic acid [1015].



(390) **(391)**



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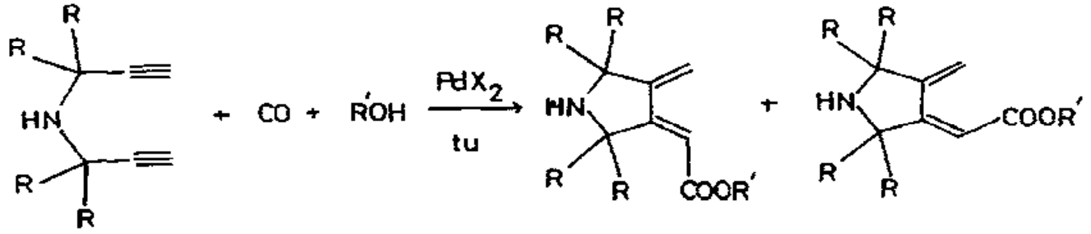


(393) **(394)** **(395)**

Reaction of ethene, carbon monoxide and hydrogen in the presence of $[Pd(PPh_3)_2Cl_2]$, PPh_3 and tfaH gave 3-pentanone with 95-99 % selectivity. The mechanism of reactions (45)-(51) was proposed [1016].

$$[PdL_2X_2] + 2L + H_2O + CO \longrightarrow [PdL_4] + CO_2 + 2HX \qquad (45)$$

$$[PdL_4] + HX \rightleftharpoons [HPdL_mX] \qquad (46)$$

$$[PdL_2X_2] + H_2 \longrightarrow [HPdL_mX] + HX \qquad (47)$$

$$[HPdL_mX] + C_2H_4 \longrightarrow [EtPdL_mX] \qquad (48)$$

$$[EtPdL_mX] + CO \longrightarrow [EtCOPdL_mX] \qquad (49)$$

$$[EtCOPdL_mX] + C_2H_4 \longrightarrow [EtCOCH_2CH_2PdL_mX] \qquad (50)$$

$$[EtCOCH_2CH_2PdL_mX] + HX + PPh_3 \longrightarrow EtCOEt + [PdL_2X_2] \qquad (51)$$

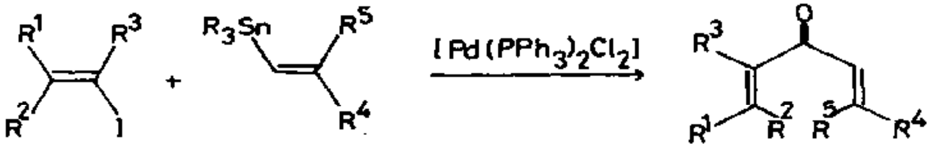
A number of patents have reported carbonylation of aryl halides in the presence of palladium catalysts. For example, using $CO/H_2/[Pd(PPh_3)_2Cl_2]/PPh_3/Bu_3N$, bromobenzene was converted to benzaldehydes in 88 % yield [1017]. 2-Bromo-6-phenoxy pyridine reacted similarly [1018]. Poly(methylhydrosiloxane) could also be used as the hydrogen donor and $[Pd(PPh_3)_4]$ as the catalyst [1019]. In the presence of an alcohol [1020] or phenol [1021] benzoic acid esters were produced.

Alkenyl halides reacted similarly. Thus 2-bromopropene was converted to methyl 2-methylpropenoate in the presence of $[Pd(PPh_3)_2Cl_2]/CO/(MeO)_2CO$ at

150 °C [1022], and $CH_2=C(CF_3)X$ could be analogously transformed to $CH_2=C(CF_3)COOH$ [1023]. However, *E*-PhCH=CHBr reacted with CO in the presence of $[Pd(dppe)_2]$/benzene/NaOH/H_2O under phase transfer conditions to give Ar-C≡C-C≡C-Ar. $RCH=CBr_2$ yielded *E*-RCH=CHCOOH. Although reaction mechanisms may be readily proposed, none was definitively demonstrated [1024].

Allylic halides such as $MeC(R)=CHCH_2X$ were carbonylated to the aldehydes $MeC(R)=CHCH_2CHO$ using $H_2/CO/[Pd(PPh_3)_2Br_2]$ [1025]. Carboxylation of $ArCH_2X$ to $ArCH_2COOH$ was achieved in the presence of $[M\{R_2P(CH_2)_nPR_2\}X_2]$ (M = Ni or Pd, $n \leqslant 3$, X = halogen) [1026].

Carbonylative coupling (for example, reactions (52) and (53)) was shown to occur between allylic or alkenyl halides and alkenyl or aryl tin compounds. In both cases the true catalyst was a palladium(0) complex, formed *in situ* [1027,1028]. Allyl tin compounds reacted similarly (reaction (54)) [1029] and alkenyl trifluoromethylsulphonates (ROTf) were also useful substrates (reaction (55)). **(396)** was used in a synthesis of $(\pm)$-$\Delta^{9(12)}$-capnellene [1030]. A related process, reaction (56), involved cross-coupling of an aryl and an alkyl halide. The dialkylzinc compound, R_2Zn, was thought to be formed *in situ* [1031]. Alanes, also formed *in situ*, reacted similarly (reaction (57)) [1032].



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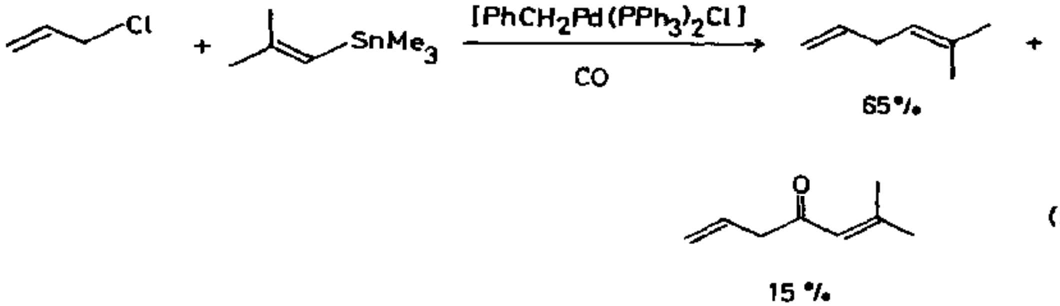

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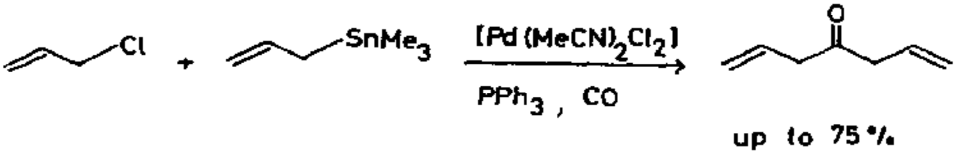

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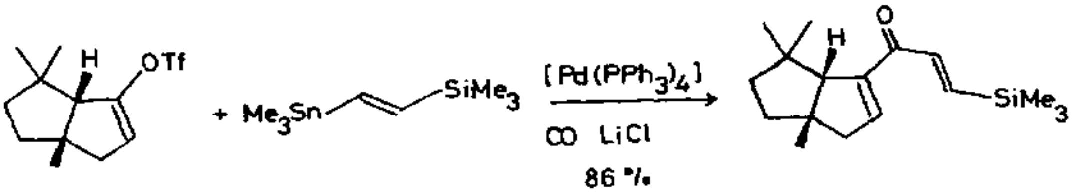


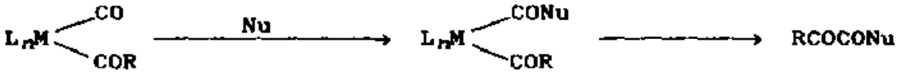
(55)

(396)

$$ArX + RX \xrightarrow[\text{1 atm, thf}]{[Pd(PPh_3)_4]/CO/Zn/Cu} \underset{\text{80-90 \%}}{ArCOR + ArR + ArH + ArAr} \qquad (56)$$

$$RBr + CO + Al(OR')_3 \xrightarrow{[Pd(PPh_3)_4]} RCOOR' + AlBr_3 \qquad (57)$$

A range of double carbonylations of halides has been reported this year. Thus iodobenzene reacted with CO/Et_2NH in the presence of $PdCl_2$ to give $PhCOCONEt_2$ (80.5 %) and $PhCONEt_2$ (9.6 %), although the use of $[PhPd(PPh_3)_2I]$ as catalyst gave approximately equal yields of the two products [1033]. The use of $PdCl_2/Cy_2P(CH_2)_2PCy_2$ as catalyst increased selectivity towards $PhCOCONEt_2$ to 98 % [1034]. Other amines and alkyl or benzilic halides also gave useful results [1035]. An investigation of the reaction mechanism, including a ^{13}C labelling study, established that $L_nMCOCOR$ was <u>not</u> an intermediate in the reaction, which almost certainly proceeded *via* **(397)** and **(398)** [1036]. Reaction of iodobenzene with CO and Me_3CNH_2 in the presence of $PdCl_2$ gave, as well as the expected $PhCOCONHCMe_3$ (93 %), 7 % of the imine derivative, $PhC(=NCMe_3)CONHCMe_3$ [1037]. The imine became the major product using $CyNH_2$ [1038]. A mixture of Ar_2CO (38-68 %) and ArCOCOAr (4-20 %) was obtained by treating the iodonium salt, $[Ar_2I]X$, with carbon monoxide in the presence of palladium salts. Increasing the pressure of CO resulted in the formation of an increased proportion of ArCOCOAr [1039].

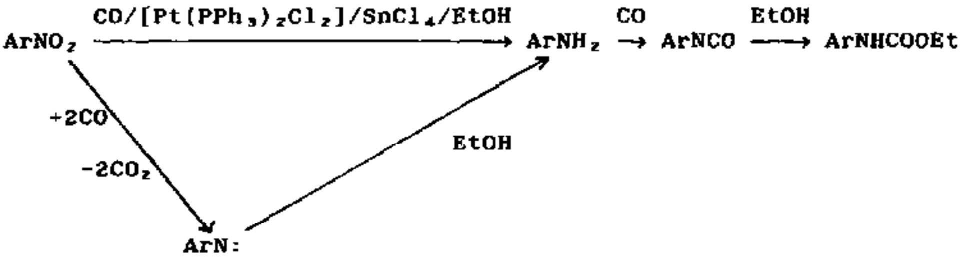


(397) (398)

Reaction of nitrobenzene with CO to give the isocyanate, PhNCO, has again been studied, and new catalysts systems including $[Pd(py)_2Cl_2]$ [1040], $[Pd(py)_2Cl_2]/[pyH]_3[Fe_2Cl_9]$ [1041], and $V_2O_5/PdCl_2/Al_2O_3$ [1043] described. Very high slectivity for formation of the bis(isocyanate) from

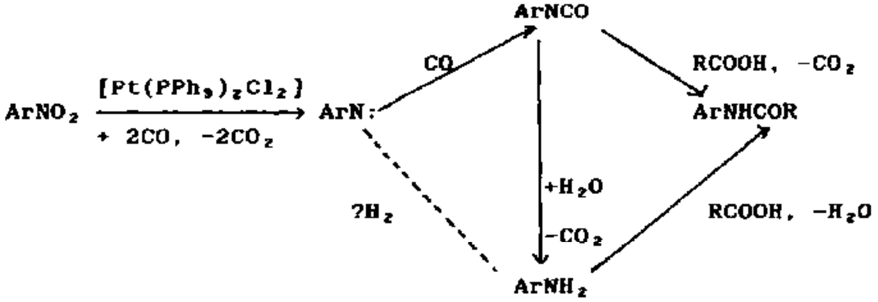
2,4-dinitrotoluene was favoured by low pressures and catalysts concentrations, and a short contact time [1043]. In the presence of alcohols, the urethane was usually obtained using $PdCl_2/py/V_2O_5$ as catalyst [1044]. The mechanism of the reaction was studied by two groups but the catalyst systems they used were different and the mechanisms they proposed quite distinct (reactions (58) and (59)) [1045,1046].

$$ArNO_2 + CO \xrightarrow{PdCl_2/NaX/FeX_3} ArN(-O)=NAr \longrightarrow ArN=NAr \xrightarrow{CO/EtOH} ArNHCOOEt \qquad (58)$$



(59)

Again using $[Pt(PPh_3)_2Cl_2]/SnCl_4$ as catalyst but with a carboxylic acid rather than an alcohol as the nucleophile, ArNHCOR was obtained with selectivities up to 91 % (reaction (60) [1047]. The course of the reaction could be altered to give the arylamine as the principal product by the use of CO/H_2O as reagent. Any carbamic acid formed would readily decarboxylate under the reaction conditions [1048].

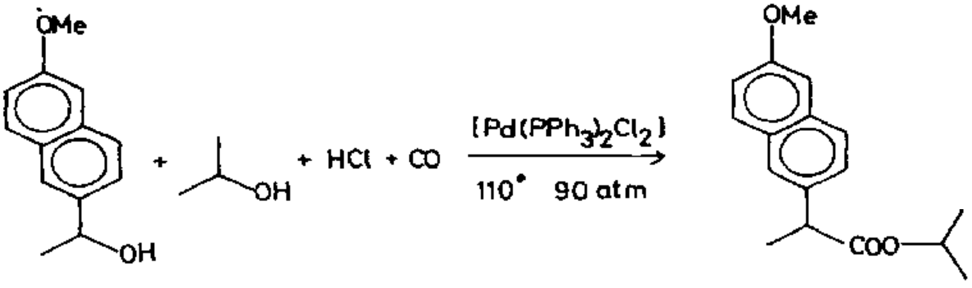


(60)

Carbonylation of methanol has again received some attention in the patent literature. Ethanol was formed with 73 % selectivity using CO and H_2 in a 1:1 ratio in the presence of $[Co_2(CO)_8]/PdCl_2/Bu_3P$ [1049]. However, with $PtCl_2/Co(OCOMe)_2/LiI$ as the catalyst system the major product was MeOCOMe [1050]. A similar reaction was observed for higher alcohols in the presence of $K_2[PdCl_4]/CuBr/K[OCOMe]$ or $Pd(OCOMe)_2/CuCl/K[OCOMe]$ [1051]. **(399)** was converted to **(400)** [1052].

Oxidative carbonylation of methanol to yield MeOOCCOOMe was reported to occur in the presence of $[\{Pd(CO)Cl\}_n]/LiCl/quinone/MeOH/CO/O_2$. Bimetallic

(PdCOOMe)-containing intermediates were proposed [1053] and the kinetics of the reaction interpreted in terms of both palladium(I) and palladium(II) species [1054].



(399) **(400)**

Oxidative carbonylation of benzene using CO and a peroxide yielded benzoic acid in the presence of $Pd(OCOMe)_2$ [1055]. Carboxylation could be achieved using $Pd(OCOMe)_2$ or, under more severe conditions, with $Pd[NO_3]_2$. The yield was increased by addition of $Fe[NO_3]_3$ as cocatlyst [1056]. Reaction of CO with ROH in the presence of $PdX_2/CuCl_2/Na_5H_2PMo_8V_4O_{40}$ gave carbonates and oxalates [1057].

Carbonylation of methyl ethanoate was reported in patents to yield MeCHO and MeCOOH (1:1.5) in the presence of $PdCl_2/RhCl_3/MeI/K[OCOMe]$ [1058], but mainly ethanoic anhydride using $PdCl_2/VCl_3/MeI/[MePBu_3]Cl$ [1059]. Ethanal was formed using the catalyst system $PdCl_2/RhCl_3/K[OCOMe]$/active carbon/MeI [1060]. Carbonylation of $Me_3COOCMe_3$ in the presence of $[Pd(acac)_2]/MeOH/py/CuCl$ was said to give dimethyl oxalate and dimethyl carbonate. Using propanone in place of methanol purported to give the unlikely compound $Me_3CO_2CCCO_2CMe_3$ (*sic*) [1061].

The Fischer Tropsch reaction between hydrogen and carbon monoxide yielded C_2-C_6 alcohols over Cu, Co or Al oxide/PdO/alkali metal oxide [1062]. By contrast the bimetallic homogeneous systen, $[Ru_3(CO)_{12}]/K_2[PtCl_4]/[C_7H_{15}PPh_3]Br/SnCl_2$ gave ethanal as the major product [1063], whilst [TPPFe]/polyvinylpyrrolidine/platinum/1,2-dimethylimidazole promoted the formation of methanol [1064]. Among useful catalyst systems for the water gas shift were $[PtCl_4]^{2-}/SnCl_4/SnCl_2$, *trans*-$[Pt(SnCl_3)_2Cl_2]^{2-}$, $PtCl_2/4PbCl_2$ and $[Pt(C_2H_4Cl]^-$ [1065].

The reaction of CO with molecular chlorine to give phosgene was catalysed by $[M(CO)Cl_3]^-$, the palladium complex being more effective than the platinum analogue [1066]. A study of the kinetics of CO oxidation in the presence of palladium(II), copper(II) and copper(I) suggested the mechanism of reactions (61)-(66) [1067]. Oxidation of carbon monoxide was also catalysed by $PdCl_2$ or

$Pd[SO_4]$ with $Na_5H_2PMo_8V_4O_{40}$ in alcohol [1068].

$$CuCl + CO \rightleftharpoons \{Cu(CO)Cl\} \tag{61}$$

$$\{Cu(CO)Cl\} + [PdCl_4]^{2-} \longrightarrow \{Pd(CO)Cl_3\}^- + Cl^- + CuCl \tag{62}$$

$$[Pd(CO)Cl_3]^- + CuCl_2 + CO + 2H_2O \rightarrow \{Pd(I)(CO)\} + CuCl + CO_2 + 2H^+ + 4Cl^- \tag{63}$$

$$\{Pd(I)(CO)\} + CuCl_2 \longrightarrow \{Pd(II)(CO)Cl\} + CuCl \tag{64}$$

$$\{Pd(II)(CO)Cl\} + H_2O \longrightarrow \{Pd(0)\} + CO_2 + HCl + H^+ \tag{65}$$

$$\{Pd(0)\} + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl \tag{66}$$

Oxidative carbonylation of methanal in the presence of $Me(CH_2)_4ONO$ and $[Pd(PPh_3)_2Br_2]/SnCl_2/[Bu_4N]Cl$ as catalyst gave $CH_2\{COO(CH_2)_4Me\}_2$ in 86.5 % yield. The yield was lower in the absence of the quaternary ammonium salt [1069]. A similar reaction on diketene using $MeONO/CO/MeOH/PdCl_2$ yielded $MeO_2CCH_2COCH_2COOMe$ by an unknown mechanism [1070].

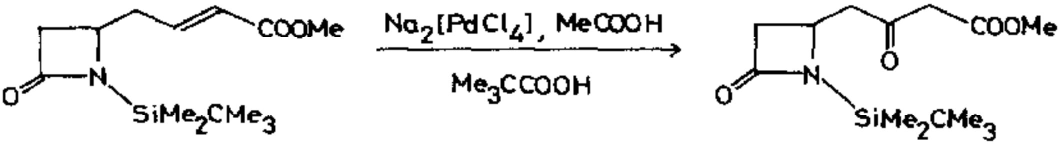
1.10.3 Oxidation

The catalytic oxidation of methane by molecular oxygen was noted to occur in solutions containing platinum salts and heteropolyacids [1071].

Palladium catalysed oxidation of alkenes to ketones has been reviewed [1072]. A method for recycling a Wacker type oxidation catalyst containing palladium(II), a heteropolyacid (HPA) and surfactant was described [1073]. Numerous oxidations of 1-alkenes to methyl ketones have again been reported. Catalyst systems employed have included $Pd[SO_4]/HPA$ [1074], $PdCl_2/HPA/H_2O$/decane/CTAB/perfluorodecalin [1075,1076], $PdCl_2/CuCl_2/[RNMe_3]Cl/H_2O/PhH$ [1077], $PdCl_2/CuCl_2/CuCl/MeCOOH/Zn(OCOMe)_2/H_2O$ [1078], and $PdCl_2/CuCl_2/H_2O/$*N*-methylpyrrolidone [1079]. The effect on the reaction course of quaternary ammonium salts was studied in some detail [1080]. When $Pd[SO_4]/VO[SO_4]/H_2SO_4$ adsorbed on carbon was used as the catalyst, ethanal, ethanoic acid and butane-2,3-dione were obtained from oxidation of 1-butene, as well as the expected butanone [1081]. The use of a nitro compound rather than molecular oxygen as an oxidising agent has been reported [1082].

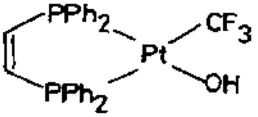
Whilst internal alkenes are less readily oxidised than 1-alkenes under Wacker conditions, a number of examples of this reaction have been reported.

Cyclopentene was oxidised to cyclopentanone with 83 % selectivity in the presence of $PdCl_2/CuCl_2$ [1083], and $Pd[SO_4]$/HPA/*N*-methylmethanamide was said to be a useful catalyst system for cyclohexene oxidation [1084]. Oxidation of the unsaturated ester, **(401)** proceeded with excellent regioselectivity [1085].



(401)

Epoxidation of alkenes by dilute hydrogen peroxide was catalysed by **(402)**; 1-octene gave the epoxide with 99 % selectivity [1086]. A stoicheiometric epoxidation of norbornene was accomplished using *cis*-$[Pd(NO_2)(MeCN)_2Cl]$; the reaction became catalytic under an oxygen atmosphere [1087].

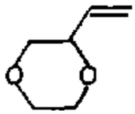


(402)

Allylic oxidation of cyclohexene to 2-cyclohexenyl ethanoate occurred in the presence of $Pd(OCOMe)_2/MnO_2$/MeCOOH/quinone, but the mechanism remained undefined [1088]. Although *cis*-$[Pd(NO_2)(MeCN)_2Cl]$ reacted with bicyclic alkenes to give epoxides, with cycloalkenes as substrates, allylic alcohols were the major products. A mechanistic scheme could be proposed to account for the observed selectivity [1089].

The conversion of ethene to ethane-1,2-diol monoethanaote in the presence of $PdCl_2/Fe[NO_3]_2$/MeCOOH has been modelled mathematically, and the optimal conditions predicted [1090]. In the presence of $PdCl_2/CuCl_2/HOCH_2CH_2OH$, butadiene was converted to **(403)** with 92 % selectivity; the reaction mechanism probably involves a π-allyl complex, and 1,4-dichloro-2-butene and 3,4-dichloro-1-butene were also detected in the reaction mixture [1091].

A kinetic study of the oxidation of toluene to $PhCH_2OCOMe$ in the presence of $Pd(OCOMe)_2/Sn(OCOMe)_2$/K[OCOMe] was said to show three distinct stages, and to involve formation of palladium(0) clusters. The data presented could, however, have been interpreted in several ways [1092]. Oxidation of fluorene in the presence of palladium phthalocyanine complexes gave fluorenone and 9-hydroxy fluorene [1093]. Hydrogen peroxide oxidation of 2,3,6-trimethyl phenol yielded the quinone; the best catalysts were iron or ruthenium salts, but in the presence of palladium chloride conversion was 23 % and the yield 29 % [1094]. Oxidation of **(404)** by molecular oxygen gave **(405)** in the presence of $[PdL_2Cl_2]$, $[PdCuL_2Cl_2]$ or $[PdNiL_2Cl_2]$ (L = methionylmethionine). The nature of the catalytic species in solution was not clear [1095].



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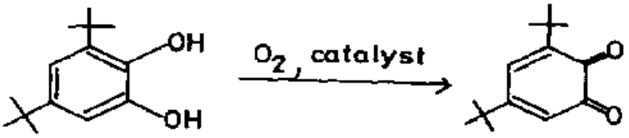
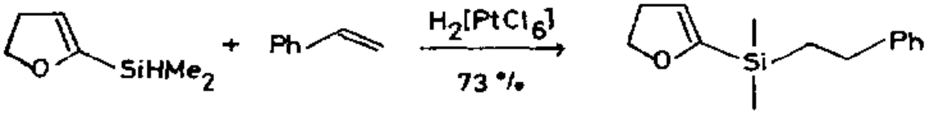


(404) (405)

1.10.4 Other additions to alkenes and alkynes

Numerous examples of hydrosilylations catalysed by palladium and platinum complexes have been reported this year [1096,1097]. Thus, $MeHSiCl_2$ reacted with with 1-octadecene in the presence of $H_2[PtCl_6]/Me_2CHOH$ to give 83 % $C_{18}H_{37}SiMeCl_2$ [1098], and trialkyl silanes showed similar selectivity in their conversions to linear silanes [1099]. 3-Phenylpropene was hydrosilylated to $Ph(CH_2)_3SiR_3$ in good yield and with little isomerisation in the presence of $H_2[PtCl_6]/PR_3$ [1100]. Linear silanes were also obtained from phenylethene and **(406)** [1101], and from $Me_3SiNHCH_2CH{=}CH_2$ and $HMeSi(OSiMe_3)_2$ [1102]. In the reaction of **(407)** both the alkene and the trifluoromethyl ketone reacted, the latter giving a silyl enol ether [1103]. However, in a most unusual reaction 3,3,3-trifluoropropene reacted with $HSiMeCl_2$ in the presence of $[Pd(PhCN)_2Cl_2]/2PPh_3$ to give $CF_3CH(CH_3)SiMeCl_2$ as the sole product, this being a useful monomer for the preparation of new fluorosilicones. Other catalysts including $H_2[PtF_6]$, and radical initiators gave only $CF_3CH_2CH_2SiMeCl_2$. The result is doubly unusual in that trichlorosilane, under all conditions, gave only $CF_3CH_2CH_2SiCl_3$ [1104].



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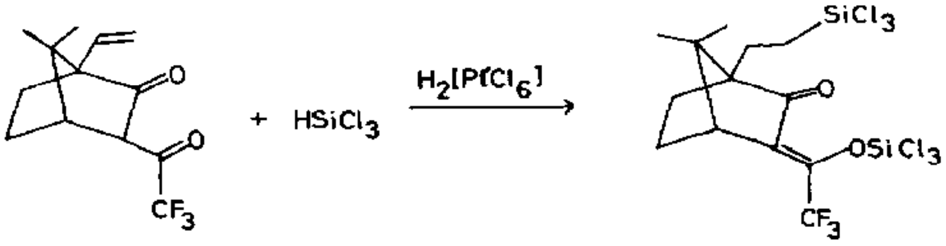


(407)

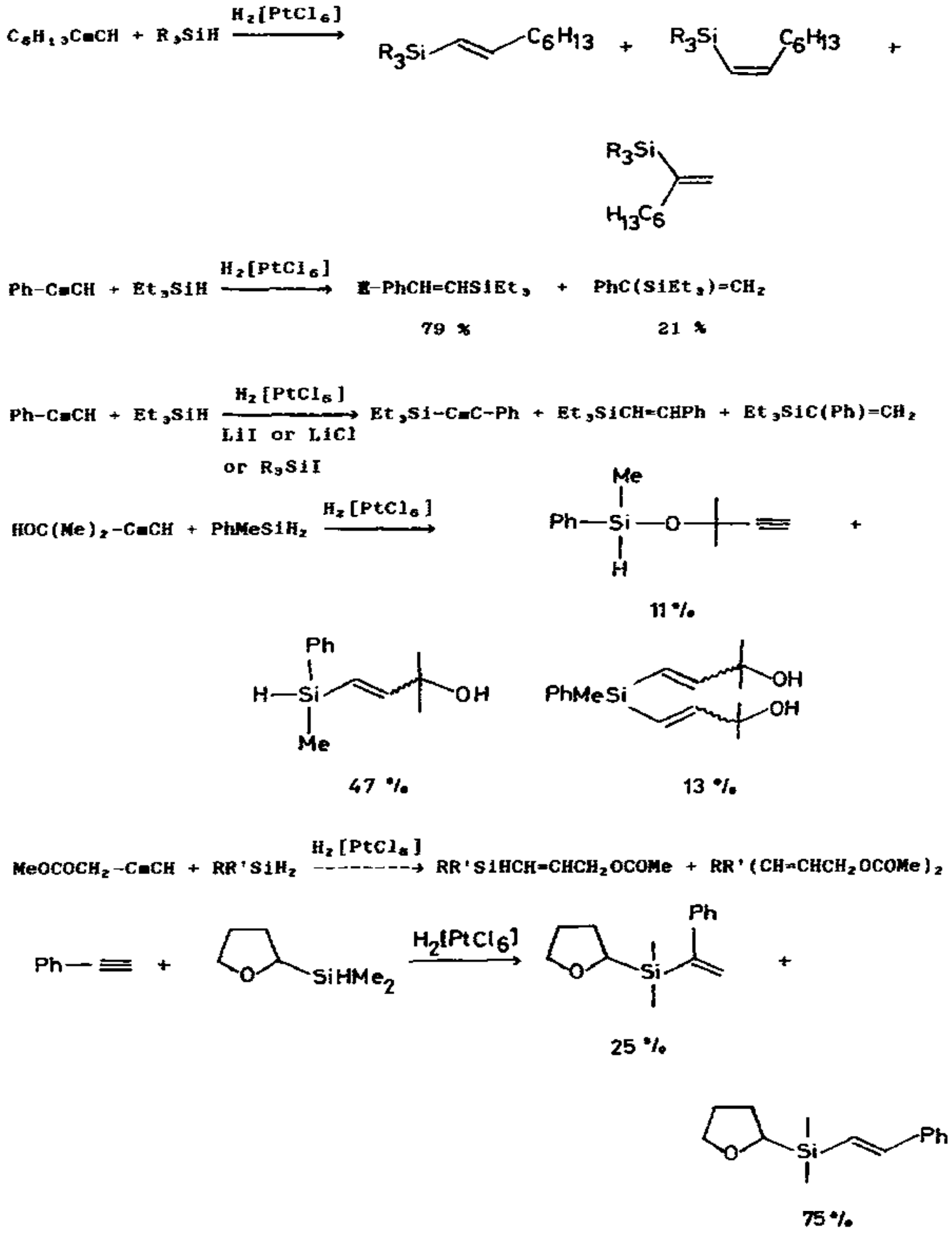
Hydrosilylation of monosubstituted alkyne derviatives in the presence of boron containing palladium and platinum complexes has been reported [1105]. Hydrosilylation of 1-alkynes generally gives a mixture of α- and β-adducts with varying stereoselectivity and further examples have been noted (Scheme 7) [1099,1101,1106-1109].

That alkynes are hydrosilylated more readily than alkenes was again demonstrated by the reaction of **(408)** [1110]. Hydrosilylation of 1-silyl substituted alkynes, $R\text{-}C\equiv C\text{-}SiMe_3$, in the presence of $H_2[PtCl_6]$ gave **(409)**, used in the synthesis of α-silyl ketones [1111]. The reaction of $Me_3Si\text{-}C\equiv C\text{-}COR$ was reasonably regioselective giving moderate yields of **(410)** and **(411)** in the ratio 5:1 [1112].

Hydrogermylation of 1-alkynes in the presence of $H_2[PtCl_6]$ followed an essentially similar course to that of hydrosilylation gaiving mainly $E\text{-}C_{10}H_{21}CH{=}CHGeR_3$ from $C_{10}H_{21}C\equiv CH$ [1113].

It was known that $RC\equiv CH$ reacted with Me_6Sn_2 in the presence of $[Pd(PPh_3)_4]$ to give $Z\text{-}RC(SnMe_3){=}CHSnMe_3$. The related reactions of allenes have now been studied; kinetic addition to **(412)** gave **(413)**, but its formation was reversible and **(414)** and **(415)** were the thermodynamic products [1114]. Stannylmetallation of alkynes using $Bu_3Sn\text{-}Zn(SnBu_3)_2$ and a palladium complex as catalyst gave, after work-up, a mixture of **(416)** and **(417)**, the proprtions depending on R and the catalyst. **(416)** predominated using aryl alkynes and (417) with alkyl substituted substrates [1115].

Numerous patents have reported the use of platinum catalysed hydrosilylation reactions in the preparation and cross-linking of siloxane polymers [1116-1126].



$C_6H_{13}C\equiv CH + R_3SiH \xrightarrow{H_2[PtCl_6]}$

$Ph-C\equiv CH + Et_3SiH \xrightarrow{H_2[PtCl_6]} E-PhCH=CHSiEt_3 + PhC(SiEt_3)=CH_2$

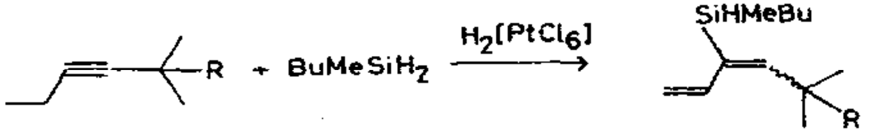
79 % 21 %

$Ph-C\equiv CH + Et_3SiH \xrightarrow[\text{LiI or LiCl or } R_3SiI]{H_2[PtCl_6]} Et_3Si-C\equiv C-Ph + Et_3SiCH=CHPh + Et_3SiC(Ph)=CH_2$

$HOC(Me)_2-C\equiv CH + PhMeSiH_2 \xrightarrow{H_2[PtCl_6]}$

$MeOCOCH_2-C\equiv CH + RR'SiH_2 \dashrightarrow RR'SiHCH=CHCH_2OCOMe + RR'(CH=CHCH_2OCOMe)_2$

Scheme 7 Hydrosilylation of 1-alkynes in the presence of $H_2[PtCl_6]$



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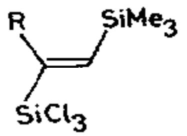

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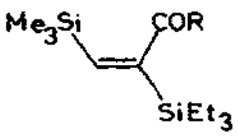

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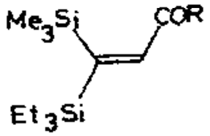

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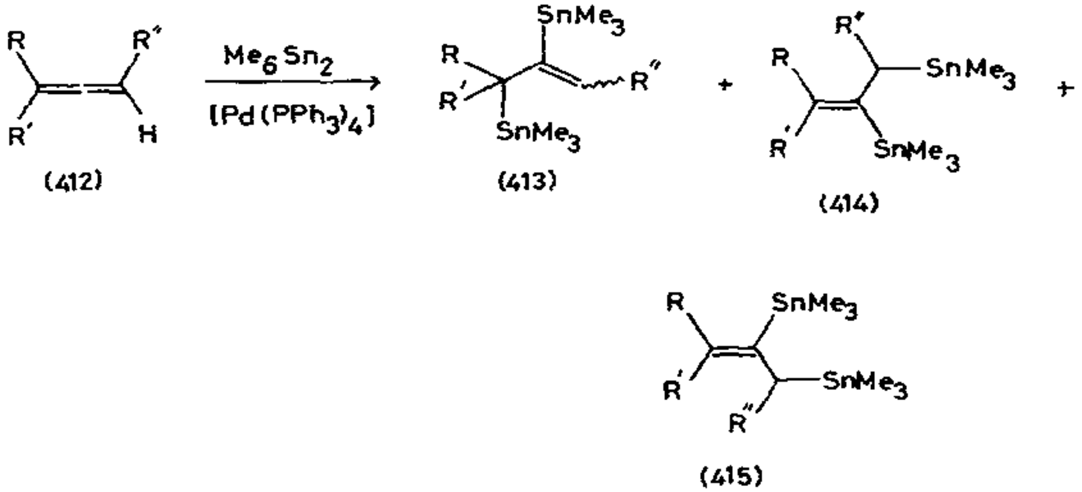


(412) (413) (414) (415)

$$\text{R-C}\equiv\text{CH} \xrightarrow[\text{2) } H_3O^+]{\text{1) } Bu_3Sn\text{-}Zn(SnBu_3)_2/\text{"Pd"}} Z\text{-}RCH{=}CHSnBu_3 + RC(SnBu_3){=}CH_2$$

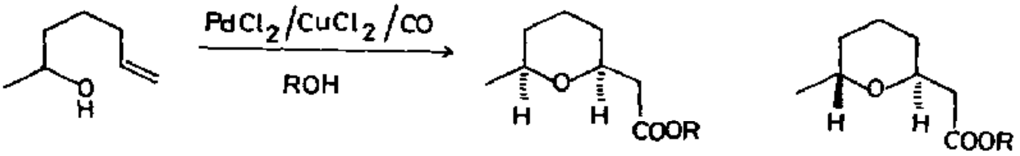
(416) **(417)**

Addition of HCl to ethyne in the presence of $PdCl_2/FeCl_3$ gave chloroethene, 1-chlorobutadiene and products of oxidative oligomerisation [1127]. The complex $[Pd(cod)Cl_2]$ catalysed addition of an alcohol across $CH_2{=}C(Me)OCH_2Ph$ to give the protected species $Me_2C(OR)OCH_2Ph$. Deprotection was achieved by hydrogenolysis [1128].

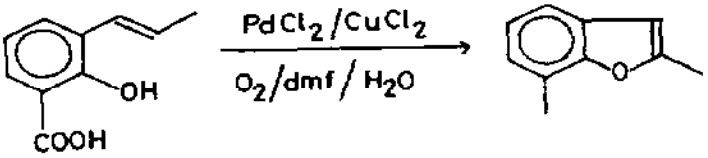
Cyclopropanation of strained alkenes such as norbornene and norbornadiene by diazomethane occurred in the presence of a range of palladium complexes.

Under related conditions 4-ethenylcyclohexene reacted mainly at the monosubstituted double bond [1129]. A range of catalysts for the reaction of $N_2CHCOOEt$ with $R^1R^2C{=}CR^3H$ was investigated. $[Pd(PhCN)_2Cl_2]$ proved less useful than $[Rh_2(OCOMe)_4]$ or $[Cu\{P(OCHMe_2)_3Cl\}]$, giving low yields and low *trans:cis* ratios in the products [1130].

Some palladium catalysed additions involve attack of a nucleophile on a palladium alkene complex formed *in situ*. Thus **(418)** gave mainly **(419)**, the explanation given involving a six-membered chair-like transition state [1131]. The reaction of **(420)** proceeded similarly [1132].



(418) **(419)**



(420)

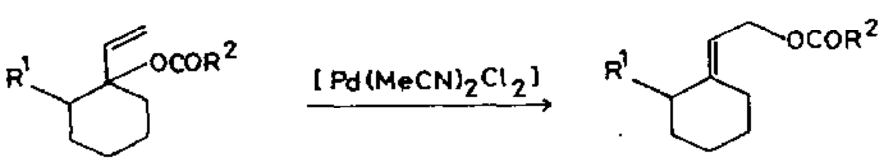
1.10.5 Isomerisation

Cis,trans-1,5-cyclododecadiene was isomerised to the *cis,cis*-1,6-isomer in the presence of $PdCl_2/CuCl$ [1133]. Both $[Pd(PhCN)_2Cl_2]$ and $[Pd(nbd)Cl_2]$ have been used to catalyse the isomerisation of quadricyclane to bicyclo[3.3.1]hepta-1,3-diene. The mechanism postulated involved radical intermediates [1134].

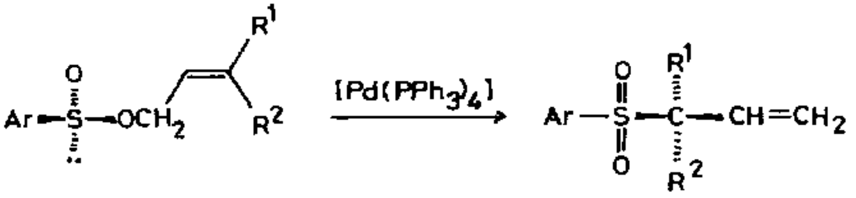
(421) was converted to **(422)** rather stereospecifically; the reaction involved cleavage of the C-O bond to form an allyl complex followed by attack of the carboxylate at the less hindered site [1135]. A similar process was involved in a sulphinate→sulphone rearrangement (reaction (67)), which was accomplished with almost complete transfer of chirality [1136]. The rearrangement of a vinyl epoxide (reaction (68)) was used in synthesis of pentenomycin [1137].

Palladium(II) catalysed [3,3]-sigmatropic rearrangements have been reviewed [1138], and mechanisms for chirality transfer in such reactions discussed [1139]. The Cope rearrangement of **(423)** in the presence of $PdCl_2$

gave E- and Z-isomers of **(424)** in comparable amounts [1140].



(421) **(422)**



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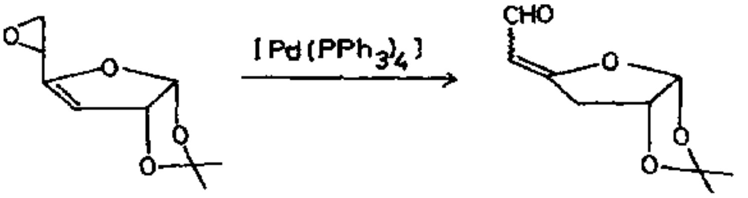

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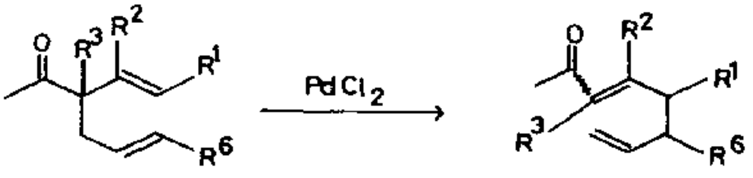
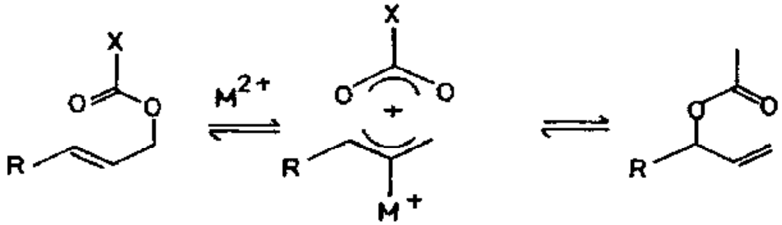
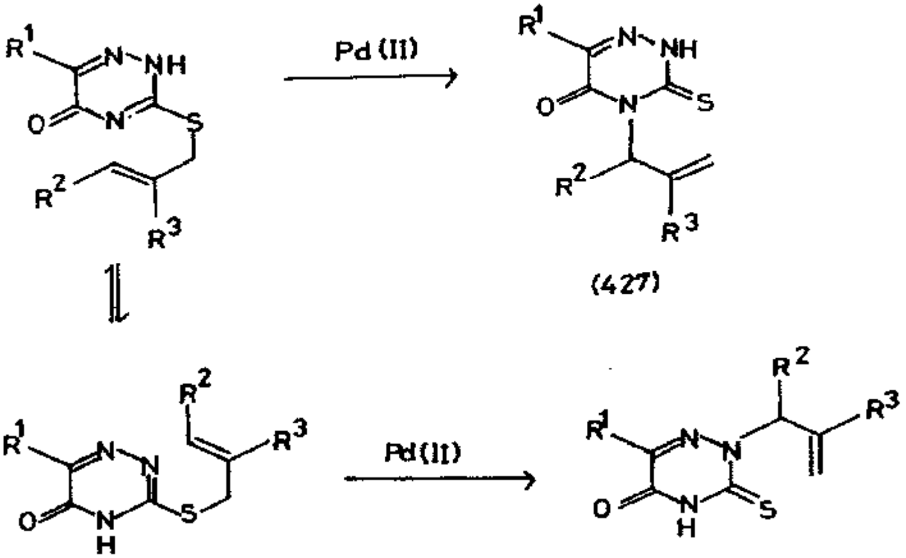


(423) **(424)**

The rearrangement of **(425)** (X = Me or NMe_2) in the presence of $[Pd(MeCN)_2Cl_2]$ was postulated to involve **(426)** as an intermediate. The Z-isomers reacted much more slowly than the E-analogues, indicating a considerable stereochemical bias in the six-membered transition state [1141]. The hetero Claisen rearrangement, (69), was catalysed by $[Pd(PhCN)_2Cl_2]$. The ratio of **(427)**:**(428)** obtained was 88:12 for R^1 = H or Me, R^2, R^3 = H and 30:70 for R^1 = H or Ph, R^2 = Me or R^3 = H [1142]. Reaction (70) was the first example of a [3,3]-sigmatropic rearrangement of a 1,5-eneyne in organophosphorus chemistry [1143].



(425) (426)



(427)

(428)

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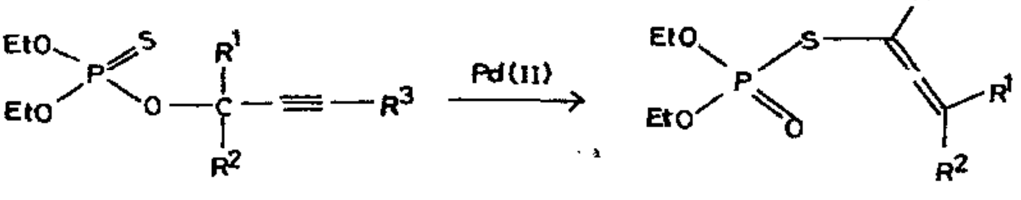
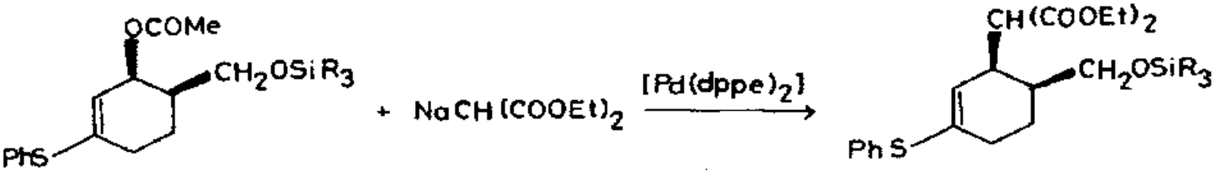


(70)

1.10.6 Allylic substitution

The use of palladium catalysed nucleophilic substitution of allyl derivatives in organic synthesis has again been widespread. Asymmetric allylation using palladium or nickel complexes as catalysts has been reviewed. A mechanism for the reaction involving palladium(II) and palladium(IV) intermediates, rather than the more conventionally described process involving palladium(0) and palladium(II), has been proposed. Whilst the arguement is quite convincing in terms of the system examined, the theory has not yet gained much general currency [1145].

$PhCH_2ZnBr$ reacted with allyl ethanoate in the presence of $[Pd(acac)_2]/PPh_3$ to give $PhCH_2CH_2CH=CH_2$; other allyl derivatives also gave acceptable results [1146]. The relative reactivities of various organometallics and various allyl derivatives were examined [1147]. Organoaluminium compounds, R_3Al, reacted with $PhSO_2CH_2CH=CH_2$ in the presence of $[Pd(acac)_2]$, but yields were generally low and copper salts were more suitable catalysts [1148]. The conversion of **(429)** to **(430)** was fairly stereospecific *via* the well known double inversion mechanism [1149]. The reaction of **(431)** was 83 % stereoselective [1150].



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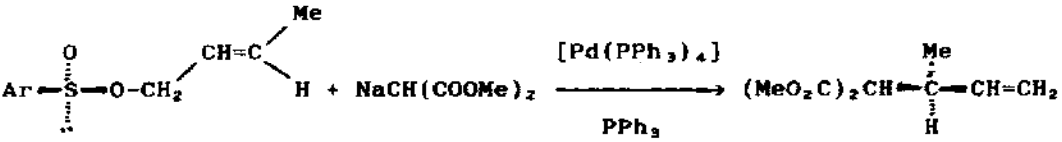


$$\mathrm{Ar{-}\overset{O}{S}{-}O{-}CH_2CH{=}C(Me)H + NaCH(COOMe)_2 \xrightarrow[PPh_3]{[Pd(PPh_3)_4]} (MeO_2C)_2CH{-}\overset{Me}{\underset{H}{C}}{-}CH{=}CH_2}$$

(431)

83 %, 50 % chirality transfer

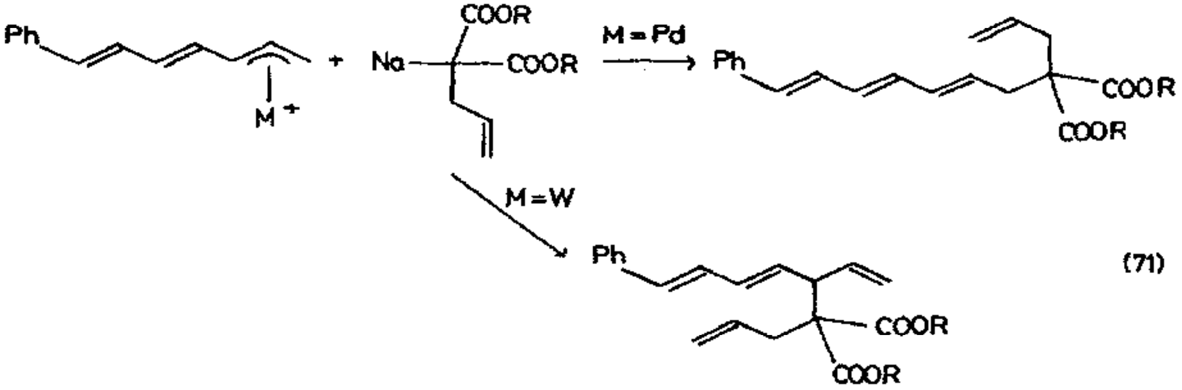
+ $MeCH=CHCH_2CH(COOMe)_2$
50 %

The regiochemistry of allylic alkylation catalysed by $[Pd(PPh_3)_4]$ has been studied. Reaction generally occurs at the less hindered terminus of the intermediate π-allyl complex. This is in contrast to the analogous reactions using tungsten based catalysts, which are dominated by electronic factors and generally yield the more highly substituted products (reaction (71)) [1151,1152].

Tin enolates such as **(432)** have proved to be useful nucleophiles towards allyl derivatives, generally reacting with good regioselectivity [1153]. The enolate of **(433)** (R = Me, allyl or $CH_2CH=CMe_2$; Z = O or H_2; *n* = 1 or 2) was generated *in situ* [1154]

Silicon substitution in an allyl derivative was achieved using $Me_3SiSiMe_3$; the yields of reaction (72) depended on the catalyst, R^1 and R^2

[1155]. Although reaction (73) is technically an allylic substitution its mechanism is unknown. Intramolecular allylic substitution (reaction (74)) was a key step in the synthesis of depentylhistrionicotoxin [1157].



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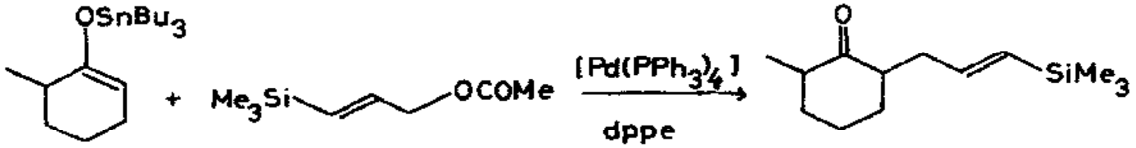

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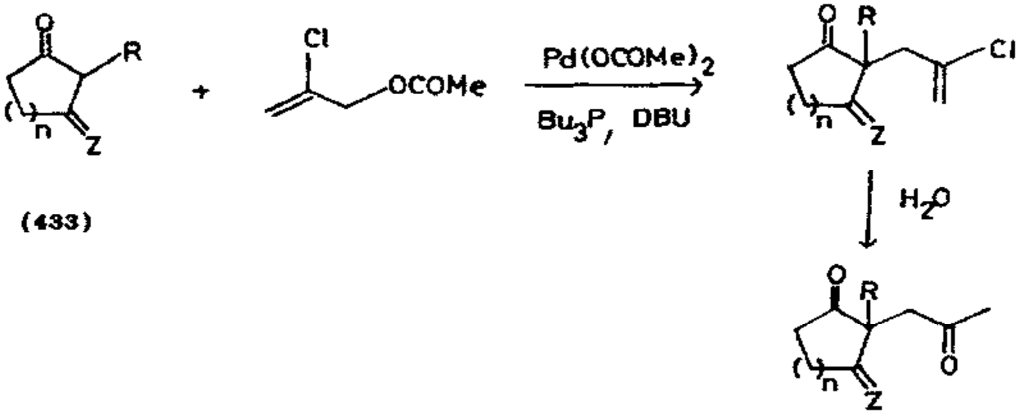
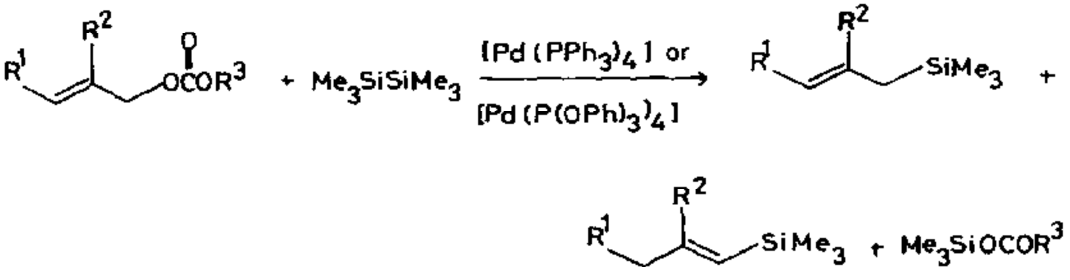


(433)

The reaction of E-$PhCH{=}CHCH_2OCOMe$ with alkynyltributyl tin gave a mixture of E-$PhCH{=}CHCH_2CH_2C{\equiv}CH$ and E-$PhCH{=}CHCH_2CH{=}C{=}CH_2$. More generally the regioselectivity of the reaction depended on the substituents on the allyl substrate [1158].



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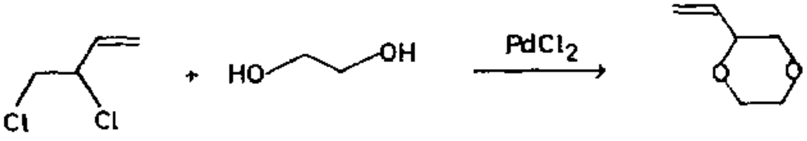

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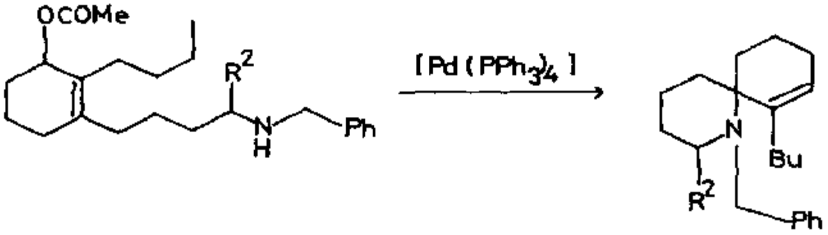


(74)

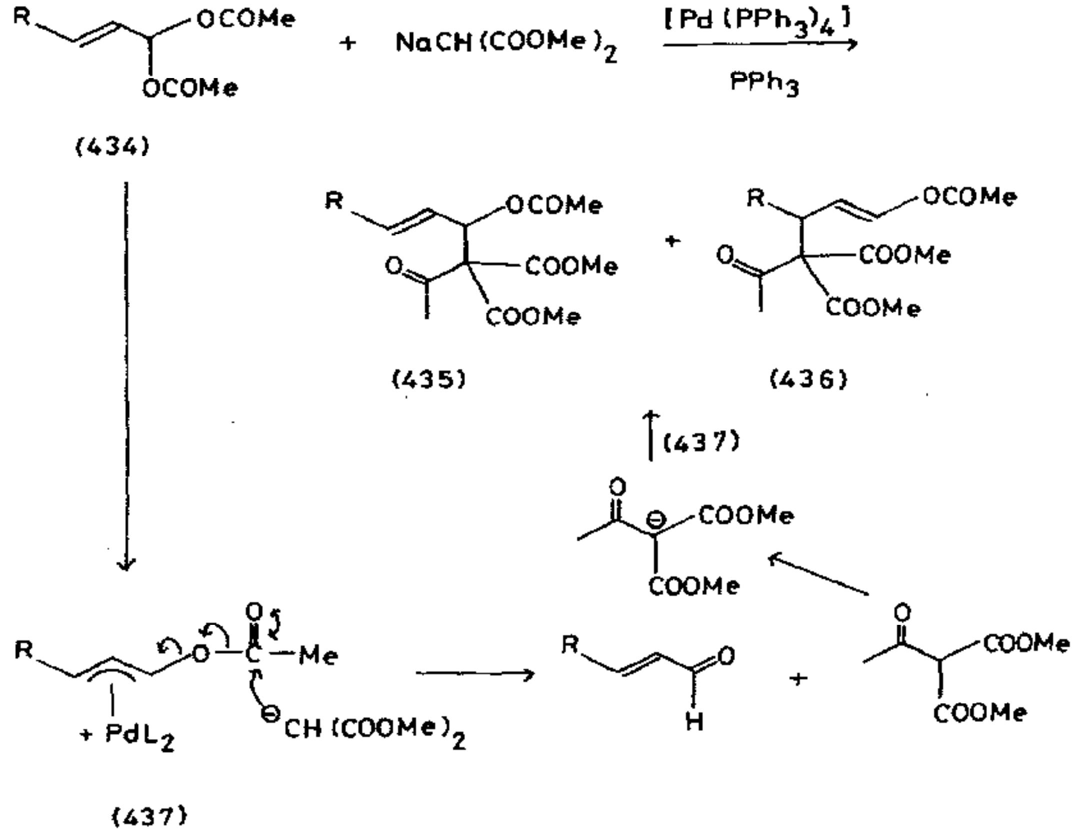
Treatment of the disubstituted allyl derivative, **(434)**, with a carbanion gave a mixture of **(435)** and **(436)**. The proposed reaction mechanism is shown in Scheme 8 [1159].

Diketene has proved a suitable substrate for allylic substitution in the presence of $[Pd(PPh_3)_2Cl_2]$/dibaH, reacting readily with E-$RCH{=}CHAl(CH_2CHMe_2)_2$, $R{-}C{\equiv}C{-}ZnCl$ or ArZnCl to give, for example, **(438)** [1160]. Allenyl derivatives such as (439) were also readily substituted [1161] as were propargyl halides (440) [1162].

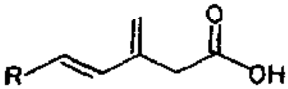
1.10.7 Coupling of carbanions with halides

Numerous reactions of this type have again been discussed this year and two reviews published [1163,1164]. Aryl halides were efficiently substituted by K[CN] in the presence of $[Pd(PPh_3)_4]$ and 18-crown-6. Alkenyl halides reacted similarly and stereospecifically [1165]. Substitution by $Na[CH(CN)_2]$

was also very successful [1166]. [Pd(dppf)Cl$_2$] was the optimum catalyst for the reaction of aryl or alkenyl halides with $CH_3CH_2CH(MgBr)CH_3$ [1167].



Scheme 8 Mechanism of reaction of allyl diethanoates with carbanions [1159]



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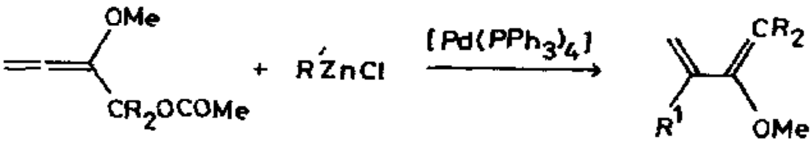

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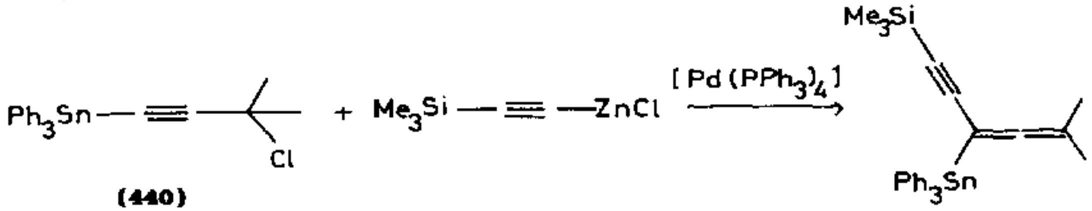
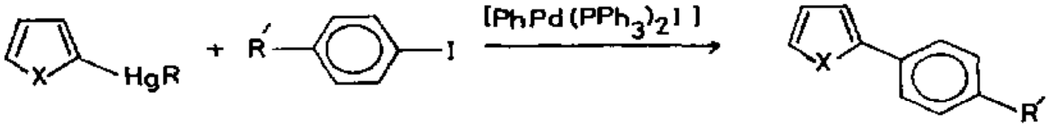


(440)

Tin derivatives have been popular nucleophiles. Facile substitution of $4\text{-}XC_6H_4I$ (X = NO_2, CN, Cl, COMe or COOMe) occurred using $RSnMe_3$/[$Pd(MeCN)_2Cl_2$] in which R was aryl, alkenyl or alkynyl [1168]. $Alkyl_3SnNu$ (Nu = OMe, NEt_2 or SPh) was also reactive, the catalyst of choice being [$PhPd(PPh_3)_2I$] [1169]. Treatment of an aryl bromide with $MeOCH_2SnBu_3$ in the presence of [$Pd(PPh_3)_2Cl_2$] gave $ArCH_2OMe$ in good yield [1170]. In a related process the tin itself was substituted on to the aryl ring (reaction (75)): this was successful only with arenes bearing electron withdrawing groups, and was conducted under rather mild conditions to avoid cross-coupling of $ArSnBu_3$ with the starting material to give Ar-Ar, this reaction also being palladium catalysed [1171].

$$Bu_3SnSnBu_3 + ArX \xrightarrow{[Pd(PPh_3)_4],\ 60\ ^\circ C} ArSnBu_3 + Bu_3SnX \qquad (75)$$

Dialkyl mercury compounds, R_2Hg, were coupled with aryl halides in the presence of [$PhPd(PPh_3)_2I$]/I^-; the halide ion suppressed the formation of R-R. The reaction was especially useful for hindered aryl halides [1172]. The predictable reactions of (441) and (442) (X = S or O; R = Br, Cl or 2-thienyl) were noted [1173,1174].



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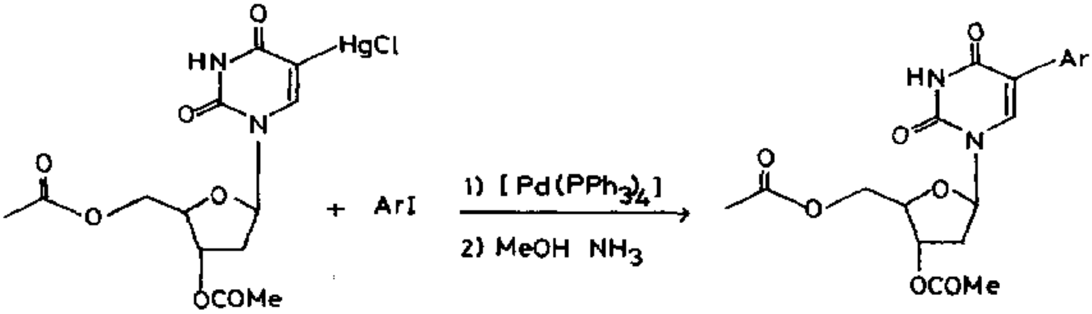
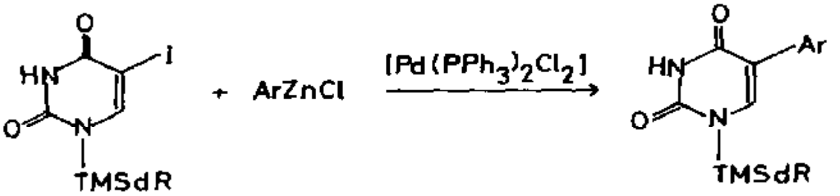


(442)

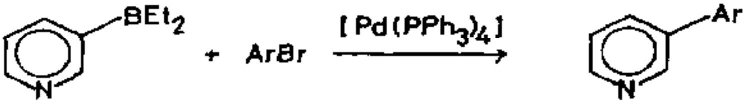
Nucleosides substituted at C-5 by a carbocycle or heterocycle could also be obtained in low yield by reaction (76) (TMSdR = *O*-triemthylsilyl-3',5'-deoxy-2'-ribose) [1175].



(76)

[2,4,6-TrimethylphenylCuI]⁻ reacted with aryl iodides using [PhPd(PPh$_3$)$_2$I] as catalyst under phase transfer conditions to give 2,4,6-Me$_3$C$_6$H$_2$Ar. Aryl halides bearing either electron donating or electron withdrawing groups were good substrates, although very strong donors retarded the reaction [1176].

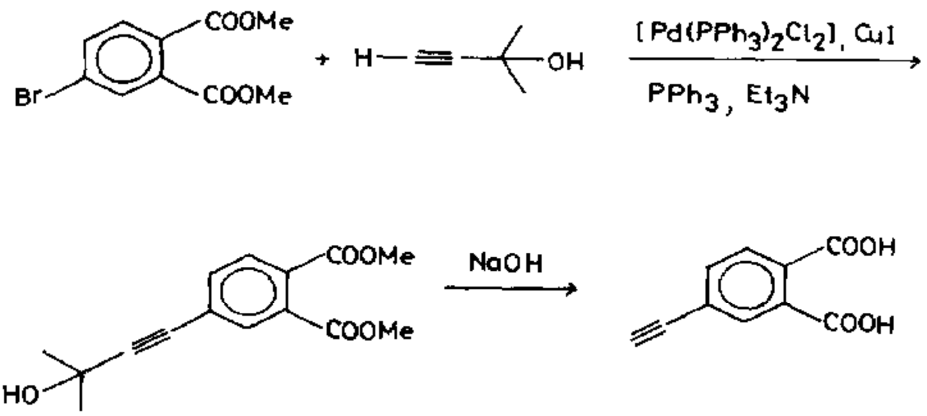
Organoborane nucleophiles have this year been shown to react with aryl halides without the need for conversion to ate complexes (reactions (77) and (78)) [1177,1178]. Heteroaryl halides have reacted similarly; several new reactions of bromothiophenes with {B(OH)$_2$} substituted thiophenes were reported [1179,1180]. Bromothiophenes also reacted readily with Grignard reagents in the presence of [Pd(dppb)Cl$_2$] [1181].



(77)

$$\mathrm{ArB(OH)_2 + Ar'Br \xrightarrow{[Pd(PPh_3)_4]} ArAr'} \qquad (78)$$

A number of reactions of alkynyl copper compounds formed *in situ* have been reported. A coupling in the presence of [Pt(PPh$_3$)$_2$Cl$_2$]/CuCl was used in a synthesis of carboranes [1182], whilst the reaction of 1,4-C$_6$H$_4$X$_2$ with HC≡C-C$_6$H$_4$-4-C≡CH was employed in a polymer synthesis [1183]. 1,4-Diiodobenzene also reacted with HC≡CCH$_2$OH using [Pd(PPh$_3$)$_2$Cl$_2$]/CuI/Et$_2$NH as the catalyst sytem [1184]. Ethyne itself is not a very suitable substrate for the reaction, but HOCMe$_2$C≡CH may be employed instead, deprotection being acieved using base (reaction (79)) [1185]. Alternatively the initial product, ArC≡CCMe$_2$OH, may react with a second equivalent of aryl halide to give Ar^1-C≡C-Ar^2 in a one-pot process [1186]. A somewhat more unusual reaction occurred using the bis iodinated biphenyl, **(443)**, as the substrate. The mechanism of Scheme 9 was proposed [1187].



(79)

Numerous alkenyl halides have also proved useful substrates reacting with heteroaryl Grignard reagents in the presence of $[Pd(dppb)Cl_2]$ [1181]. Good stereospcificity was noted in the reaction of chloroalkenes with Grignard reagents in the presence of $[Pd(PPh_3)_4]$ [1188], and **(444)** also gave a very selective reaction [1189].

Alkynylzinc reagents reacted with iodo or bromoalkenes in the presence of $[Pd(PPh_3)_4]$ to give enynes in good yield. That chloroalkenes were rather unreactive was demonstrated by reaction (80) [1190]

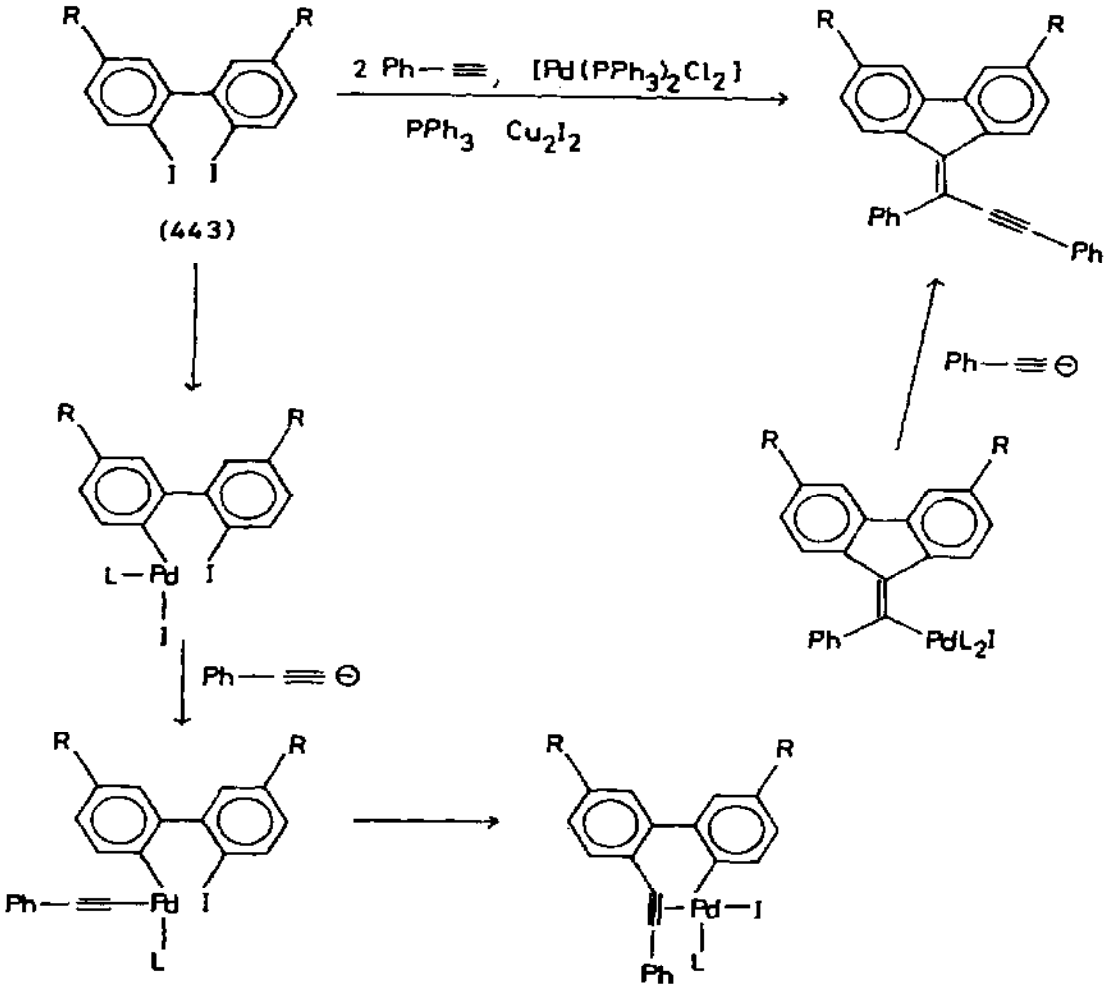
$$E\text{-}ICH{=}CHCl + RC{\equiv}CZnX \xrightarrow{[Pd(PPh_3)_4]} E\text{-}ClCH{=}CH\text{-}C{\equiv}CR \qquad (80)$$

$(Me_3Si)_3Al$ reacted with E- or Z-$C_5H_{11}CH{=}CHI$ to give E- or Z-$Me_3SiCH{=}CHC_5H_{11}$ respectively using $[Pd(PPh_3)_4]$ as catalyst; little loss of stereochemistry was observed [1191].

Two lengthy articles from Normant's group have described numerous applications of the cross-coupling of alkenylcopper compounds with alkenyl halides in the presence of palladium complexes. Stereoselectivity was generally excellent [1192,1193].

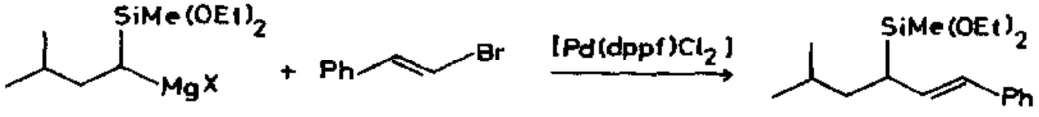
The coupling of alkenyltin compounds with alkenyl trifluoromethyl sulpphonates (OTf) has been applied to a short synthesis of Pteraplysillin-1, **(445)** [1194].

In the reaction of **(446)** with nucleophiles in the presence of a palladium complex two outcomes could be envisaged, *viz.* allylic substitution or substitution of the haloalkene. In practice, using $[PhC{\equiv}C]^-$ as nucleophile, only the halide substitution occurred, giving **(447)** in good yield [1195].



(443)

Scheme 9 Mechanism of palladium catalysed coupling of a diiodobiphenyl with a 1-alkyne [1187].



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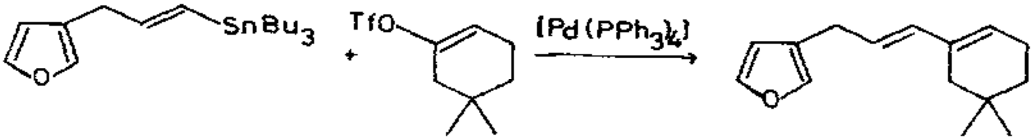
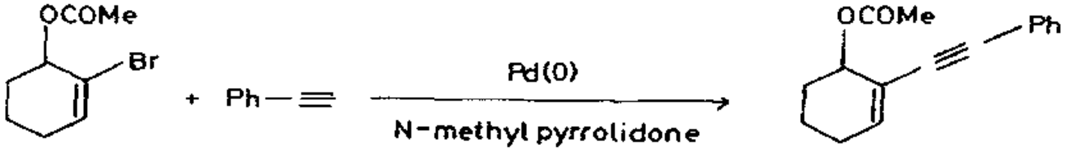
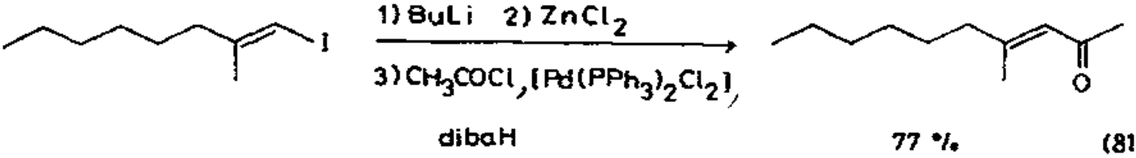


(445)



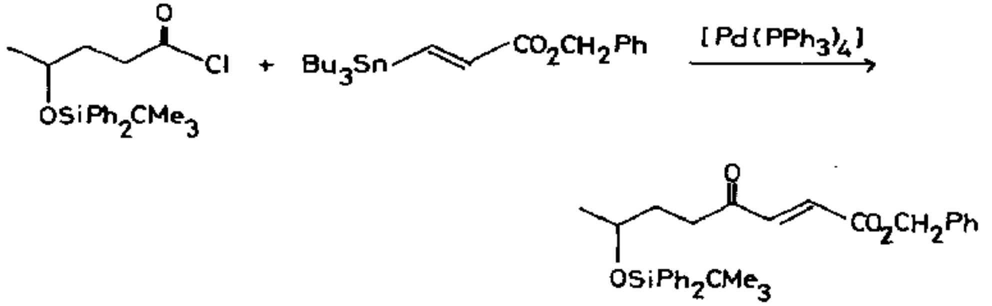
(446) **(447)**

Reaction of acyl halides with organometallics, particularly derivatives of the less electropositive metals, are not invariably rapid in the absence of the catalyst. Thus the reaction of R'ZnX with RCOCl was accelerated by $[Pd(PPh_3)_4]$ or $[PhCH_2Pd(PPh_3)_2Cl]$ [1196], whilst in reaction (81) the organozinc nucleophile was generated *in situ* [1197]. $RR'C{=}CCu.MgX_2$ behaved similarly [1198]. In this context tin containing nucleophiles have proved particularly useful, since they do not react readily with other sensitive functional groups. A precursor of pyrenophorin was synthesised in reaction (82) [1199]. Although only the allyl group was transferred from allyltrialkyltins in these processes, substantial allylic transposition could occur, depending on the reaction conditions (reaction (83)) [1200].

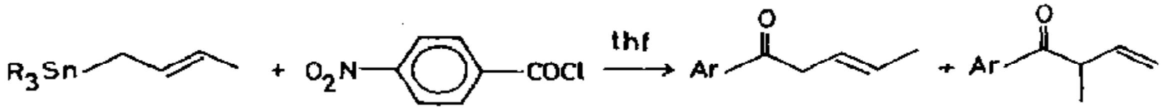


(81)

Although α-haloketones are not particularly reactive towards oxidative addition to palladium(0), they do couple with tin enolates under appropriate conditions (reaction (84)). The reaction failed for bromopropanone and α-haloaldehydes since the tin nucleophile attacked directly at the carbonyl group [1201]. However, other authors reported quite a different process (reaction (85), n = 0, 1 or 2, R^4 = Bu, R^3 = allyl or $-CH_2COCH_3$) [1202] and it is not immediately clear that the two observations can be readily reconciled.

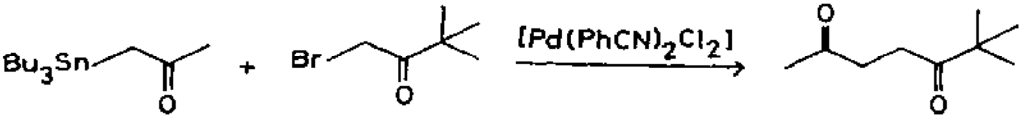


(82)



R = Me,	$[Pd(PPh_3)_4]$, 65 °	50	50
R = Bu,	$[PhCH_2Pd(PPh_3)_2Cl]$, 65 °	30	70
R = Bu,	$[PhCH_2Pd(PPh_3)_2Cl]$, 50 °	17	83

(83)



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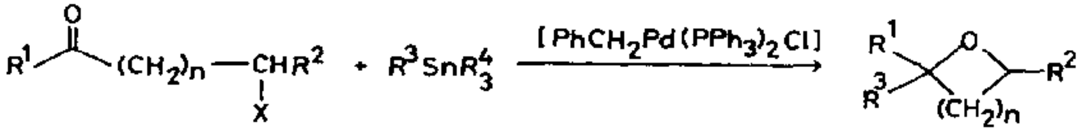


(85)

In the presence of $[Pd(PPh_3)_4]$ only a trace yield of PhBu was obtained from the cross-coupling of PhYbI and BuI; PhPh was the major product in this case, although the use of copper salts as catalysts resulted in more cross-coupling [1203]. $[Pd(PPh_3)_2Cl_2]$ was employed as a catalyst for the coupling of iodocarboranes with Grignard reagents [1204].

The reaction of $ArCHCl_2$ with R_3SiSiR_3 in the presence of palladium(0) gave $ArCHClSiR_3$ as the initial product (reactions (86)-(88)). This could undergo further coupling, and an alternative coupling pathway was also proposed (reactions (89)-(94)), the course of which depended on the substituents [1205].

$$[PdL_4] + ArCHCl_2 \longrightarrow [Pd(CHClAr)L_2Cl] \qquad (86)$$

$$[Pd(CHClAr)L_2Cl] + R_6Si_2 \longrightarrow [Pd(CHClAr)(SiR_3)L_2] + R_3SiCl \qquad (87)$$

$$[Pd(CHClAr)(SiR_3)L_2] \longrightarrow \{PdL_2\} + ArCHClSiR_3 \qquad (88)$$

$$[Pd(CHClAr)L_2Cl] + ArCHClSiR_3 \longrightarrow [Pd(CHClAr)_2L_2] + R_3SiCl \qquad (89)$$

$$[Pd(CHClAr)_2L_2] \longrightarrow ArCHClCHClAr + \{PdL_2\} \qquad (90)$$

$$ArCHClCHClAr + [PdL_4] \longrightarrow [ArCHCHCH(Ar)PdL_2Cl] \qquad (91)$$

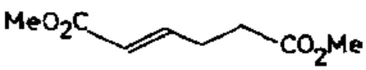
$$[ArCHClCH(Ar)PdL_2Cl] + R_6Si_2 \longrightarrow [ArCHClCH(Ar)PdL_2(SiR_3)] + R_3SiCl \qquad (92)$$

$$[ArCHClCH(Ar)PdL_2(SiR_3)] \longrightarrow ArCHClCH(SiR_3)Ar + \{PdL_2\} \qquad (93)$$

$$ArCHClCH(SiR_3)Ar \xrightarrow{\Delta} E\text{-}ArCH{=}CHAr \qquad (94)$$

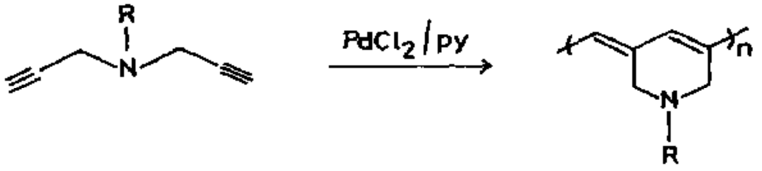
1.10.8 Oligomerisation, telomerisation and polymerisation

Dimerisation of ethene over heterogenised $PdCl_2$ [1206] and propene on heterogenised $Pd(CN)_2$ have been reported. The propene gave approximately 73 % linear dimers [1207]. The polymerisations of phenylethene, 1,3-cyclohexadiene and bicyclo[3.3.1]heptene were catalysed by $[Pd(MeCN)_4]^{2+}$, by a carbocation mechanism. Related phosphine complexes catalysed coplymerisation of alkenes with carbon monoxide to give an alternating copolymer under very mild conditions [1208,1209]. The same catalyst was used in the dimerisation of methyl propenoate to give **(448)** with 93-96 % selectivity [1210,1211].



(448)

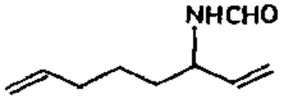
Dimerisation of 1-alkynes, $RC{\equiv}CH$, to give $RC{\equiv}C\text{-}C(R){=}CH_2$ together with some higher oligomers, occurred in the presence of $[Pd(acac)_2]/L/Et_3N$ [1212]. However, with phenylethyne and $[Pd(PPh_3)_2Cl_2]/PPh_3/CuI/Et_3N/MeI$, polyphenylethyne was obtained [1213]. Buteneyne was readily cyclodimerised to give ethenylbenzene: although the reaction proceeds thermally, yields were increased in the presence of $[Pd(acac)_2]/PPh_3/Et_3Al$ [1214]. Polymerisation of **(449)** in boiling pyridine or dmf with $PdCl_2$ as a catalyst yielded the soluble product **(450)** [1215].



(449) **(450)**

Telomerisation of butadiene with butane-1,4-diol in the presence of $[Pd(acac)_2]/PPh_3$ gave octadienyl ethers, which were used in surfactant synthesis [1216]. The 2-, 3- and 4-aminopyridines gave mixtures of mono and dioctadienyl amines using $[Pd(acac)_2]/PPh_3/Et_3Al$ as the catalyst system. Yields were excellent and the ratio of the products could be controlled by the ratio between the starting materials [1217]. Methanamide yielded a mixture of **(451)** and **(452)** under these conditions, but in dmso it decomposed to ammonia and carbon monoxide, and the ammonia telomer, **(453)**, was also formed [1218].

(451)

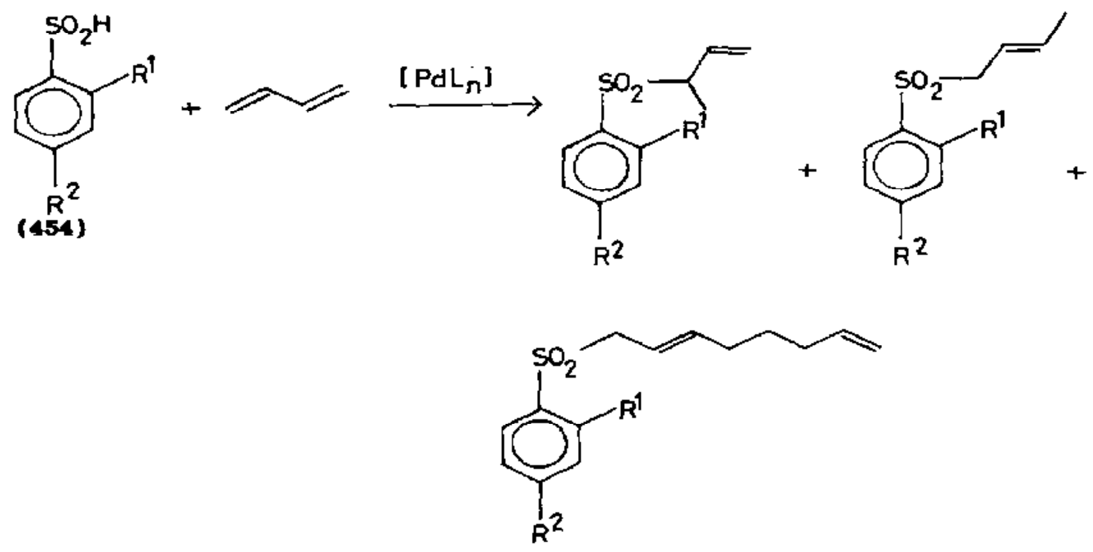


(452)

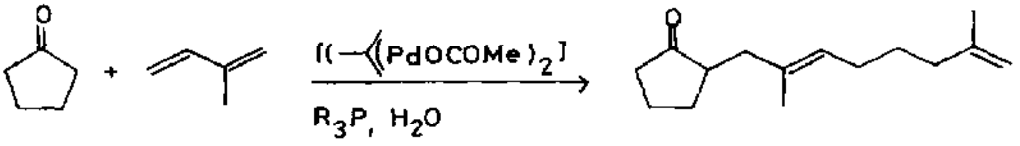
(453)

Reaction of butadiene with arylsulphinic acids, (454), gave mixtures of products, depending on the exact reaction conditions [1219].

Telomerisation of butadiene with the enolate ions from cyclic ketones gave α-octadienyl ketones. Little of any branched product was formed, but up to 30 % of the 2,2-bis(octadienyl) product was produced in some cases. The product ratio depended primarily on the bulk of the phosphine [1220]. When the same reaction was considered for isoprene, **(455)**, the tail-to-tail telomer, was the major product. In both cases the active catalyst was considered to be $[HPdL_3][OH]$ [1221].

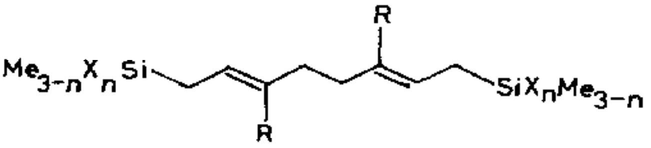


(454)



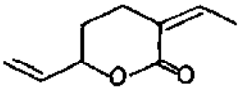
(455)

In a novel and unusual process $Me_{3-n}X_nSiSiX_nMe_{3-n}$ reacted with butadiene or isoprene to give **(456)** (R = H or Me) using $Pd(OCOMe)_2$ or $[Pd(PhCN)_2Cl_2]$ as catalyst. (456) (R = H) was used in a short synthesis of muscone [1222].



(456)

A complex mechanism explained the formation of products **(457)**-**(461)** from carbon dioxide and butadiene. Up to 95 % of **(457)** could be obtained using the palladium(0) complex of a bulky phosphine of high basicity such as PCy_3. The use of complexes of PEt_3 or PBu_3 gave **(460)** or **(461)** [1223]. The reaction of methylene cyclopropane with CO_2 in the presence of $[PdL_4]$ has also been investigated. Lactones were the invariable products, and although **(462)** could be produced in up to 80 % selectivity by judicious choice of conditions, a complex mixture of products more generally resulted [1224].



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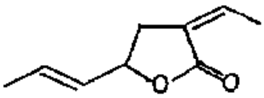

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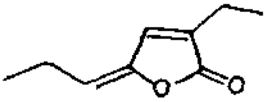

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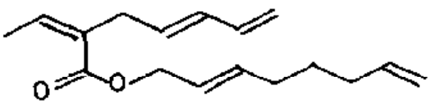
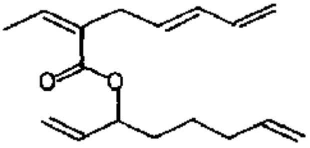


(460)



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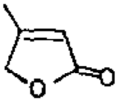
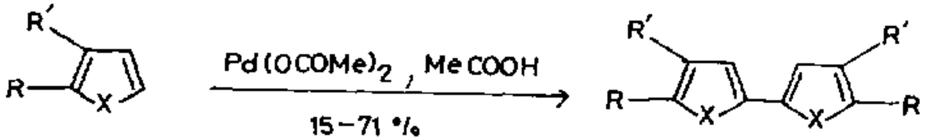


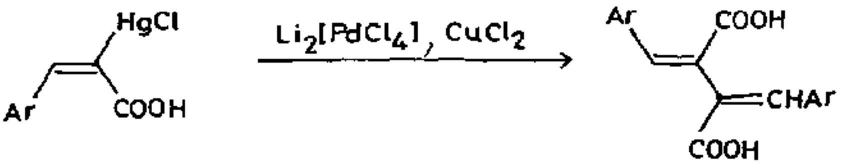
(462)

Oxidative dimerisation of toluene using $Pd[SO_4]/H_2[SO_4]$ has been studied. Routes involving palladium(I) and palladium(II) intermediates could be distinguished [1225]. In the oxidative oligomerisation of benzene the rate-controlling step was said to be formation of the aryl palladium intermediate. The reaction yielded 2-, 3- and 4-terphenyls [1226]. Oxidative dimerisation of furans and thiophenes, **(463)** (X = O or S, R = MeCO, CHO, NO_2, R' = H or Me), was achieved using $Pd(OCOMe)_2$, but the reaction was not strictly catalytic [1227].



(463)

Treatment of 4-bromothiophenol with $[Pd(PPh_3)_4]$ in a mixture of BuOH and Me_3COH gave *para*-polyphenylenethioether [1228]. Oxidative dimerisation of **(464)** gave **(465)** as a mixture of E,Z- and Z,Z-isomers. The Stobbe condensation gave only the **E,E**-product [1229].



(464) **(465)**

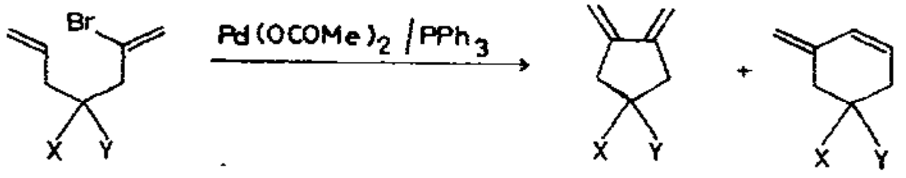
Platinum(II) bromide was shown to be a general dehydrodimerisation catalyst for boron hydrides and carboranes leading to the formation of boron-boron linked polyhedral cage compounds in good yields and selectivities under mild conditions (for example, reactions (95) and (96)). The reaction mechanism is not known with any certainty but since the site of the coupling was found to depend on the electron density, an initial electrophilic attack was proposed [1230].

$$2B_5H_9 \xrightarrow{PtBr_2,\ 25\ ^\circ C} 1{:}2'(B_5H_8)_2 \qquad (95)$$

$$2B_4H_{10} \xrightarrow{PtBr_2,\ 25\ ^\circ C} 1{:}1'(B_4H_9)_2 \qquad (96)$$

1.10.9 Other coupling reactions

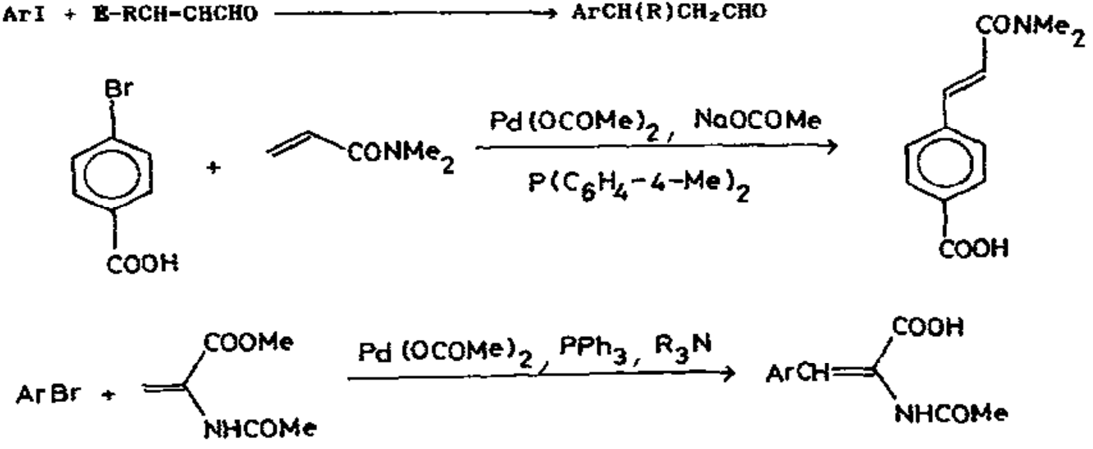
Again the Heck reaction and related processes have been widely used in synthesis this year (for example, reaction (97)) [1231]. Reports of couplings of aryl halides have, however, been much more numerous, some examples being shown in Scheme 10 [1232-1237]. The first reports of coupling reactions of aryl chlorides have been published using phenylethene or $CH_2{=}CHCN$ as the other reagent, but yields were in all cases low [1238-1240]



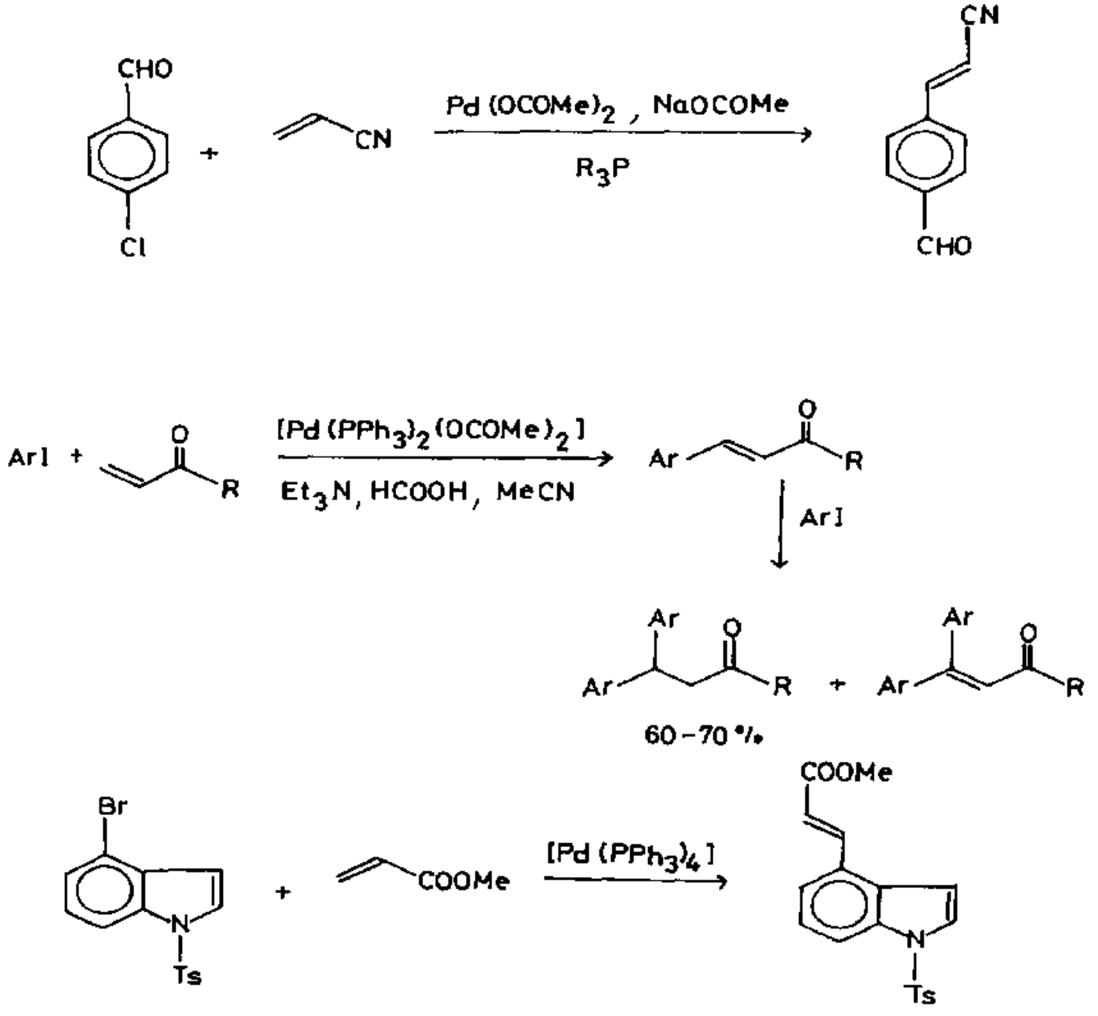
(97)

$$PhI + CH_2{=}CHCOOMe \xrightarrow{Pd(OCOMe)_2/Na[HCO_3]/[Bu_4N]Cl} E\text{-}PhCH{=}CHCOOMe$$

$$ArI + E\text{-}RCH{=}CHCHO \xrightarrow{[Pd(OCOMe)_2(PPh_3)_2]} ArCH(R)CH_2CHO$$

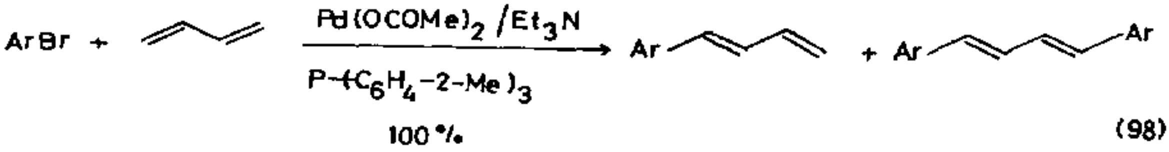


Scheme 10 Heck reactions of aryl halides [1231-1237]



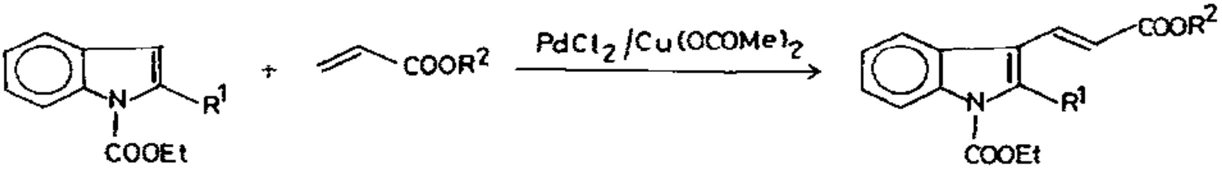
Scheme 10 cntd.

Coupling of aryl halides with dienes has also been reported (reaction (98)). Many examples were given and it was noted that whilst arenes bearing electron withdrawing groups gave significant amounts of diarylated dienes those bearing electron donors rarely did so [1241].



(98)

Several papers have reported the oxidative coupling of indole derivatives with alkyl propenoates. For **(466)** coupling occurred at the 3-position (R = H or alkyl) but if this site was blocked, as in **(467)**, substitution took place at the 2-position [1242,1243]. Furfural reacted at the 5-position under similar conditions [1244]



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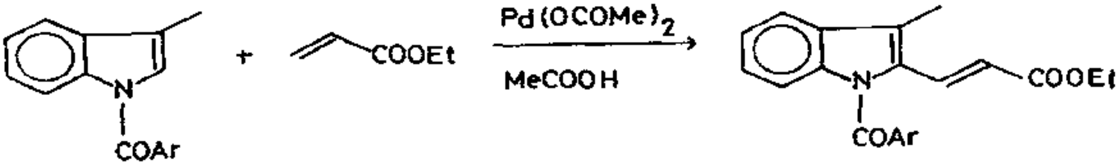


(467)

Diphenylethyne reacted with iodobenzene in the presence of $[Pd(PPh_3)_2(OCOMe)_2]/HCOOH/Et_3N/MeCN$ to give triphenylethene. The reaction mechanism was thought to involve oxidative addition of the aryl halide followed by alkyne insertion [1245].

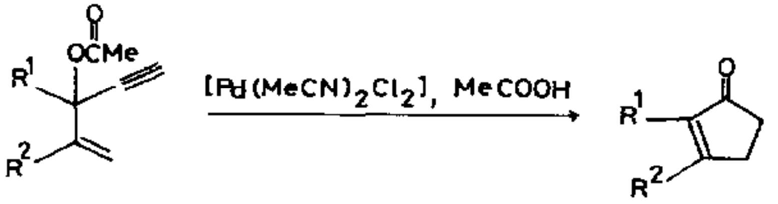
Addition of an organozinc compound, formed *in situ*, to an aldehyde was catalysed by $[Pd(PPh_3)_2Cl_2]$ (reaction (99) $R = (CF_2)_nCF_3$, $n = 0,1,3,5$ or 7; $R' = Ph$, $PhCH{=}CH-$, C_6H_{13} or C_5H_{11}) [1246]. Organotin compounds do not in general react with aldehydes, but may be induced to couple with ArCHO (Ar bears an electron withdrawing group) using $[PdL_2Cl_2]$ as catalyst (reaction (100)). When L was a chiral phosphine a rather low optical yield was obtained for this process [1247].

$$RI + R'CHO \xrightarrow{Zn,\ [Pd(PPh_3)_2Cl_2]} RCH(R')CHO \tag{99}$$

$$Bu_3SnCH_2CN + ArCHO \xrightarrow{[PdL_2Cl_2]} ArCH(OH)CH_2CN \tag{100}$$

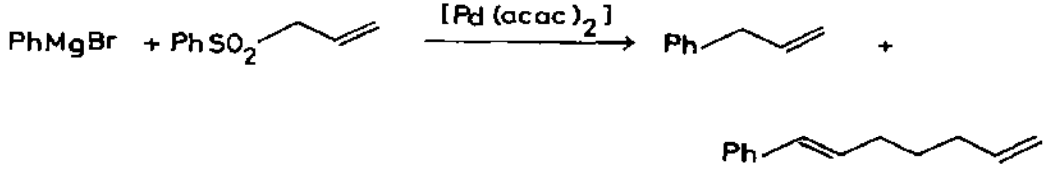
The reductive coupling of organic halides using hydrazine or an aryl hydrazine occurred in the presence of $PdCl_2$ or $PdCl_2/HgCl_2$ [1248]. Using zinc metal and a palladium complex as catalyst the salts $[R^1R^2I]X$ yielded a complex mixture of R^1R^1, R^2R^2, R^1R^2, R^1I and R^2I [1249].

Cyclisation of the enyne, **(468)**, occurred in the presence of $[Pd(MeCN)_2Cl_2]/MeCOOH$. The mechanism of the reaction was not fully defined but palladium(II) and palladium(IV) intermediates could be postulated [1250,1251].



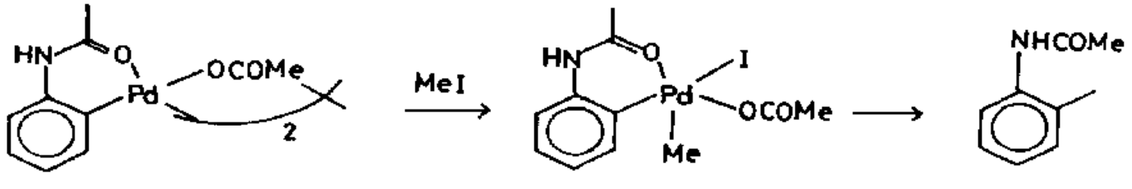
(468)

Reaction of aryl Grignard reagents with substituted dienes using $[Pd(PhCN)_2Cl_2]$ as the catalyst gave complex mixtures with low yields of arylated alkenes and dienes, as well as a substantial amount of biaryls [1252]. Low yields were also obtained in reaction (101) [1253]. The enol ethanoate, $CH_3C(OCOMe)=CH_2$, reacted with Bu_3SnOMe in the presence of $[Pd(P(2\text{-}MeC_6H_4)_3)_2Cl_2]$ to give Bu_3SnCH_2COMe, which was coupled with aryl halides to give $ArCH_2COMe$ in modest yields [1254].



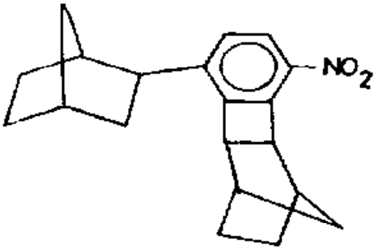
(101)

Two new methylations of aryl rings involving palladium catalysed reactions have been reported. In the presence of Amberlite supported $PdCl_2$ 2,6-bis(1,1-dimethylethyl) phenol reacted with methanal/H_2 to give 2,6-bis(1,1-dimethylethyl)-4-methylphenol with 93 % selectivity [1255]. Cyclometallation of $PhNHCOCH_3$ with palladium ethanoate gave **(469)** which reacted with methyl iodide to give a palladium(IV) intermediate, **(470)**, which collapsed to (471) [1256].

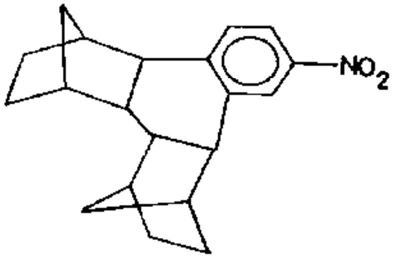


(469) **(470)** **(471)**

Coupling of 4-bromonitrobenzene with bicyclo[3.3.1]heptene in the presence of $[Pd(PPh_3)_4]$ gave a mixture of (472) and (473), characterised by X-ray diffraction. The mechanism was not defined, but was thought to involve an aryne intermediate [1257]. Bicyclo[3.3.1]heptene also reacted with dialkyl alkynes *via* the mechanism of Scheme 11 to give cyclopropanes [1258].



(472)



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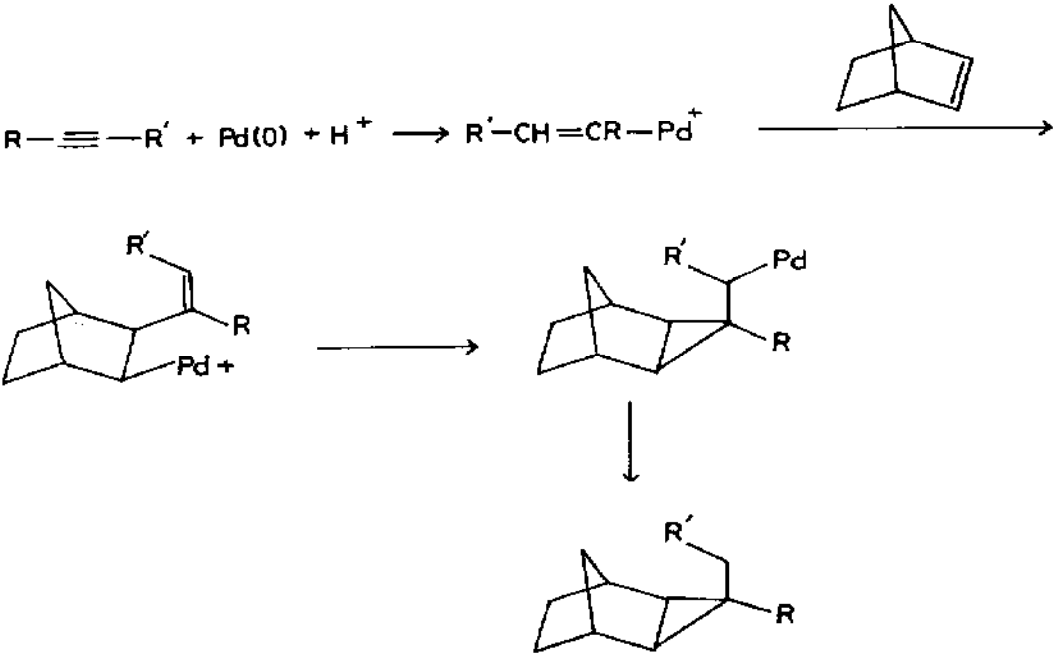


Scheme 11 Palladium catalysed cyclopropanation of bicyclo[3.3.1]heptene [1258].

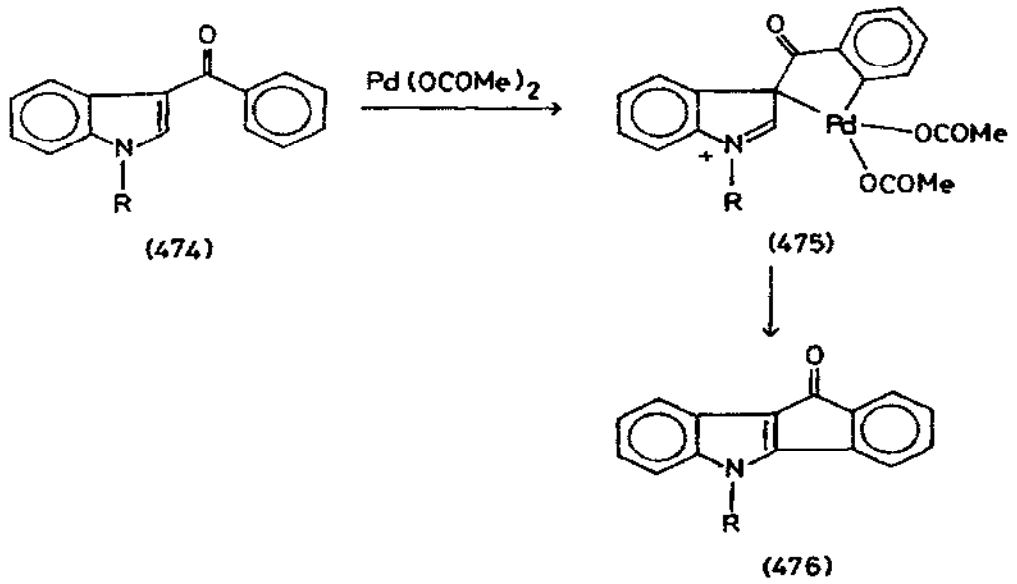
Electrophilic substitution and cyclometallation of **(474)** with palladium ethanoate gave **(475)**. **(476)** was formed *via* a palladium shift [1259].

Indoles were synthesised by reaction (102) [1260].

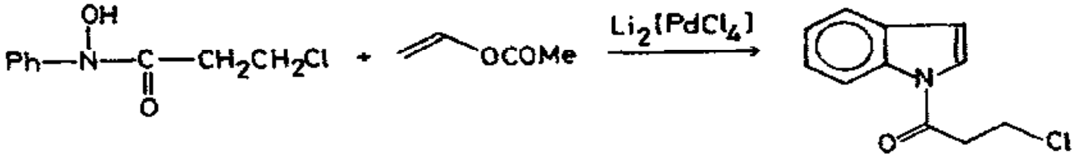
1.10.10 Other reactions catalysed by palladium and platinum complexes

Hexaalkyl ditin compounds were prepared by reactions (103) and (104) and could be converted to $R'SnR_3$ in reaction (105) [1261]. Hydrolysis of $ArSiMe_3$

to give $Me_3SiOSiMe_3$ and ArH was catalysed by $Li_2[PdCl_4]$. The kinetics and mechanism of the reaction were investigated, and it was concluded that the key step was electrophilic substitution of the aryl ring by palladium [1262]. Treatment of tetraalkyl silanes with trichlorosilane in the presence of $H_2[PtCl_6]$ gave R_3SiCl and $RSiHCl_2$. In mixed silanes the least hindered groups migrated the most easily, and selectivity was generally good [1263].



(474) (475) (476)



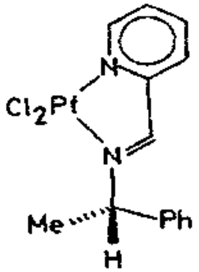
(102)

$$R_3SnCl \xrightarrow[2)\ H_2O]{1)\ Li[AlH_4]/Et_2O} R_3SnH \qquad (103)$$

$$R_3SnH + Pd(0) \longrightarrow R_3SnPdH \longrightarrow R_6Sn_2 + H_2 + Pd(0) \qquad (104)$$

$$R'X + R_6Sn_2 \xrightarrow{[Pd(MeCN)_2Cl_2]/hmpa} R'SnR_3 + R_3SnX \qquad (105)$$

Hydrosilylation of ketones occurred in the presence of $K[Pt(C_2H_4)Cl_3]$ with added amine chelate ligands, and also using isolated complexes such as **(477)**. Enantiomer excesses were modest in most cases [1264]. Condensation of alkyl silanes, $RSiH_3$, with 1,3,5-trihydroxybenzene to give **(478)** was catalysed by $[Pt(PPh_3)_2Cl_2]$ or $H_2[PtCl_6]$, but better yields were obtained using [Rh(PPh_3)$_3$Cl] [1265]. Reaction of α-haloketones with $Bu_3SnSiMe_3$ in the presence of [Pd(PPh_3)$_4$] gave silyl enol ethers and dehalogenated ketones (reaction (106)) the ratio between the products depending on the catalyst and conditions [1266].



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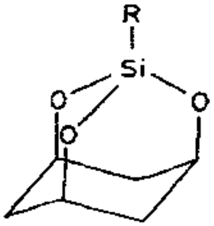
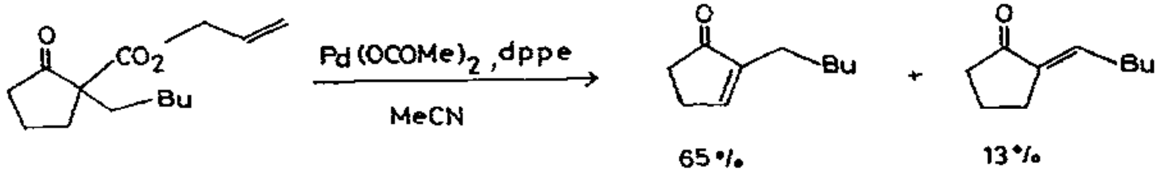


(478)

$$Bu_3SnSiMe_3 + BrCH_2COPh \xrightarrow{[Pd(PPh_3)_4]} PhC(OSiMe_3){=}CH_2 + PhCOMe \qquad (106)$$

A patent has reported the catalytic conversion of an allyl carbonate to an ester in the presence of carbon monoxide (reaction (107)). The process was presumed to involve carbonylation of a π-allyl palladium intermediate [1267]. Allyl complex formation and decarboxylation to give an enolate was involved in reaction (108) [1268].

$$CH_2{=}CHCH_2OCOOMe \xrightarrow{Pd(OCOMe)_2/PPh_3/CO} CH_2{=}CHCH_2COOMe \qquad (107)$$



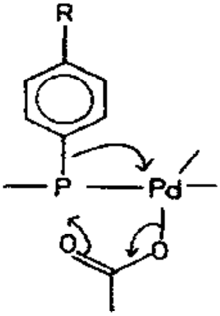
(108)

Alkenyl esters of carboxylic acids could be prepared by palladium catalysed transesterification with ethenyl ethanoate (reaction (109)) [1269]. In the presence of $[PtX_6]^{2-}$, $[PtX_4]^{2-}$ or *trans*-[Pt(py)$_2$X$_2$] ethanol reacted with molecular iodine to give ethyl ethanoate [1270]. Conversion of methanol to carbon monoxide and hydrogen occurred in the presence of $H_2[PtCl_6]$ supported on Al_2O_3/CeO_2 [1271].

$$EtCOOH + CH_2CH{=}OCOMe \xrightarrow[K[OCOMe],\ KBr,\ 48\ hr,\ 60^{\circ}C]{Pd(OCOMe)_2,\ Cu(OCOMe)_2} EtCO_2CH{=}CH_2 \qquad (109)$$

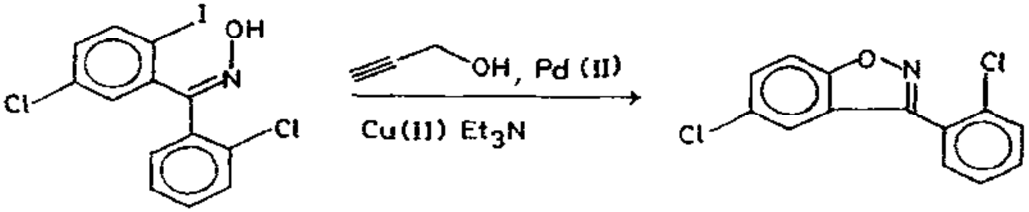
Quaternisation of triarylphosphines with aryl halides was catalysed by

$[Pd(PPh_3)_4]$ or $Pd(OCOMe)_2$; the reaction was quite sensitive to steric hindrance [1272]. Cleavage of triaryl phosphines or stibines occurred slowly using palladium(II) ethanoate in toluene. The reaction was thought to involve migration of an aryl group from phosphorus to palladium, **(479)** [1273].

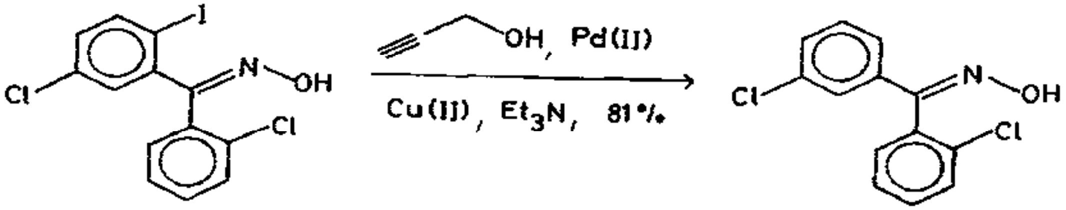


(479)

Intramolecular substitution of an aryl iodide by oxygen occurred in reaction (110). However, the isomeric substrate, (480), which is prevented from cyclisation by geometric factors, underwent hydrogenolysis, the propargyl alcohol probably acting as the reductant [1274]. The palladium catalysed cyclisation of (481) was used in a synthesis of lavendamycin [1275].



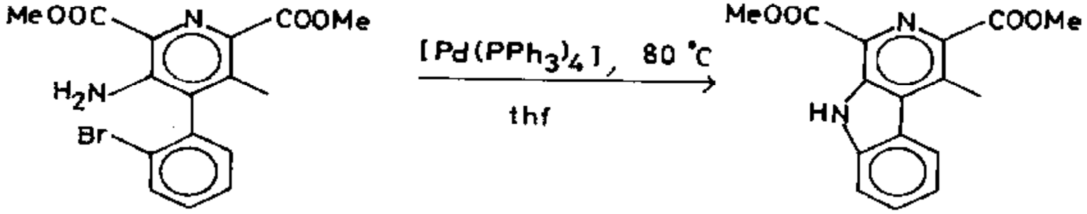
(110)



(480)

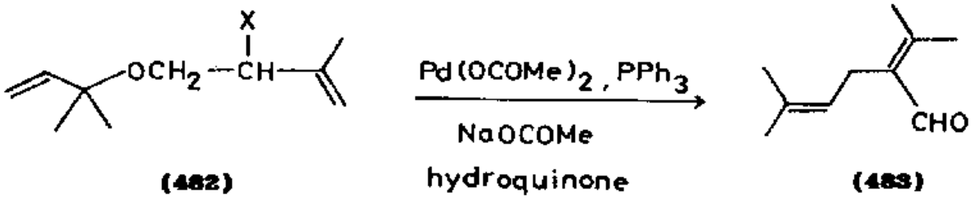
Treatment of a primary amine, RNH_2, with $[PtL_2Cl_2]/SnCl_2$ (L = PPh_3 or PhCN) at 180 °C for 5 hours gave R_2NH by an unknown mechanism [1276].

Reaction of Na[OMe]/MeOH with isoprene in the presence of $[\{(\eta^3\text{-allyl})PdCl\}_2]/Bu_3P$ gave up to 46 % methoxy isoprenes [1277].



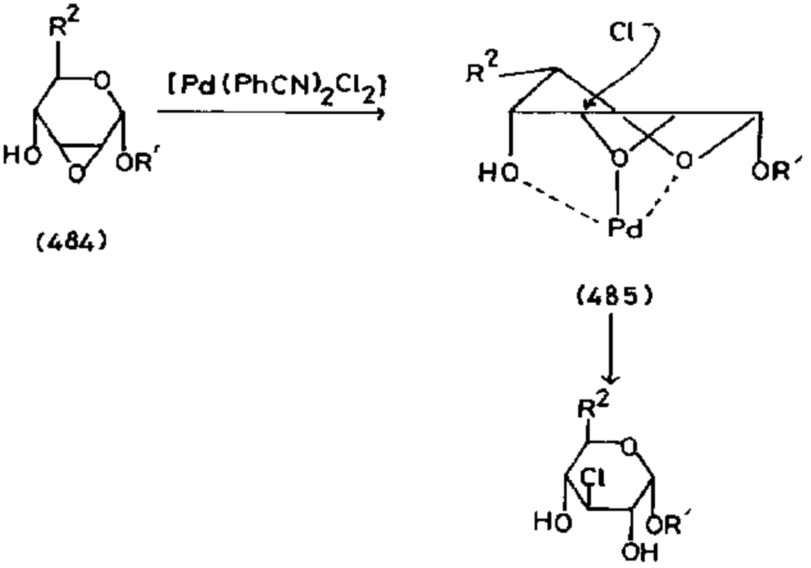
(481)

Treatment of **(482)** (X = Cl or OCOMe) with $Pd(OCOMe)_2/PPh_3/Na[OCOMe]$/hydroquinone gave **(483)**; the reaction mechanism was not studied [1278]. Dehydrogenation of RCH_2CH_2CHO to $RCH{=}CHCHO$ was accomplished using $Ag[OSO_2CF_3]/[Pd(PhCN)_2Cl_2]$; the reaction was not strictly catalytic [1279]



(482) **(483)**

The opening of the epoxide, **(484)**, was rather regioselective, leading to an effective synthesis of chlorodeoxy sugars. The product was derived from the more stable conformer of the intermediate, **(485)** [1280].



(484)

(485)

$K_2[PdCl_4]$ supported on Dowex 1, Amberlyst-27 or a polystyrene-divinylbenzene copolymer, catalysed conversion of cyclohexyl hydroperoxide to cyclohexanone and cyclohexanol together with a small amount of $CH_3CH_2CH_2CH{=}CHCHO$ [1281].

1.11 NON-STOICHEIOMETRIC, BINARY AND TERNARY COMPOUNDS

1.11.1 Compounds with Group 17 elements

Mass spectrometric measurements on Pd_6Cl_{12}, Pt_6Cl_{12} and their solid solution showed fragmentation at 50 eV. At decreased ionisation energy the species $[Pd_6Cl_{12}]^+$, $[Pt_6Cl_{12}]^+$ and $[Pd_xPt_{6-x}Cl_{12}]^+$ were observed [1282]. $Rb_2[PdCl_4]$ and tetragonal $Cs_2[PdCl_4]$ were shown to melt congruently. Phase diagrams were constructed from DTA, thermogravimetric and X-ray phase analytical data. New phases with the composition $MCl.3PdCl_2$ were observed. $RbCl.3PdCl_2$ decomposed above 340 °C in the subsolidus region, and $CsCl.3PdCl_2$ melted incongruently at 361 °C [1283]. Phase diagrams were also constructed for the $PdCl_2/LiCl/NdCl_5$ system. $LiCl/PdCl_2$ is of the Roozeboom Type V and contained $Li_2[PdCl_4]$ in the solid phase below 351 °C. $NbCl_5/PdCl_2$ is of the eutectic type with a eutectic at 96.5 mole % $NbCl_5$ at 197 °C [1284].

The interaction of a palladium containing NaCl/CsCl melt (35:65) with liquid bismuth or zinc was studied in the temperature range 791-1073 K. The redox reactions (111) and (112) resulted in the complete transfer of palladium to the metallic melt [1285].

$$2Bi + 3Pd^{2+} \longrightarrow 2Bi^{3+} + 3Pd \qquad (111)$$

$$Zn + Pd^{2+} \longrightarrow Zn^{2+} + Pd \qquad (112)$$

Studies by LEED, Auger spectroscopy and electrochemistry showed that platinum <100> monocrystal surfaces, which had been deliberately disordered by electrochemical oxidation and reduction, were restored to an ordered state by programmed heating under an argon atmosphere containing iodine vapour. A near hexagonal centred adlattice of iodine atoms was formed, containing three iodines and five platinums per surface unit cell. Programmed heating of the adlattice gave stepwise iodine desorption and a series of related adlattices [1286].

1.11.2 Compounds with Group 16 elements

The structural and electronic properties of binary and ternary platinum oxides have been reviewed [1287]. The standard free energy of formation of solid PdO was determined electrochemically [1288]. The electronic and electrochemical propoerties of vapour grown single crystals of PdO have been reported. This PdO was a p-type semiconductor with a band gap of approximately 0.8 eV, corresponding to a strongly forbidden d-d transition. A higher energy transition with a threshold near 2.2 eV was assigned to an O(2p)-Pd(4d) charge transfer [1289].

The electronic structure of PdO has been studied. Soviet workers used calculations on a $[Pd_6O_6]^{4-}$ cluster model within the X_α scattered wave method with finite boundary conditions. The results were compared with experimental XPES data and it was concluded that the electronic structure could not be interpreted by simple crystal Field theory [1290].

XPES was used to study $PdO.nH_2O$ on various supports, produced by different impregnation treatments. The interaction with the support was generally found to be weak, but the nature of the species obtained did depend on the activity of the support. It was also noted that $PdO.nH_2O$ was not very different in terms of Pd $3d_{5/2}$ binding energy from anhydrous PdO [1291]. XANES using synchrotron radiation was also used to study PdO catalysts supported on inert and quasi-inert substrates. The white line in the PdO XANES spectrum was found to be an excitonic state with 0.8 eV binding energy. From the joint analysis of the L_3 and L_1 edges the "p-like" and "d-like" local unoccupied electronic states were determined. The local structures of the PdO catalysts differed from PdO crystals. Evidence for structural disorder in these catalysts, and for PdO.substrate interactions was reported [1292]. The dissolution of PdO suppoorted by alumina in 0.2–0.6 M HCl was studied to detrmine quantitatively the dispersion of the PdO catalyst on the support [1293].

Reaction of a glowing filament of platinum with molecular oxygen gave PtO_2 under equilibrium conditions [180]. Treatment of α-PtO_2 with $H[ClO_3]$ or BaO_2 gave a new modification of β'-PtO_2 with the rutile structure at 40-60 kbar pressure and 500 °C [1294]. X-ray absorption measurements on the platinum L_{II} and L_{III} edges have been made in α- and β-PtO_2, $Na_2[Pt(OH)_6]$, and $Li_{0.6}Pt_3O_4$. In α-PtO_2 each platinum was shown to have six oxygen near neighbours at 2.05 Å, consistent with the CdI_2 structure. Data for β-PtO_2 and $Li_{0.6}Pt_3O_4$ were also consistent with the known structures of these compounds. In Adam's catalyst the platinum had six oxygen neighbours at 2.06 Å and an edge structure similar to that of α-PtO_2. It was concluded that this was a highly disorded form of α-PtO_2 [1295].

Single crystals of Sr_4PtO_6 were obtained from the reaction of SrO and platinum metal at 1150 °C. X-ray diffraction analysis revealed a structure of rhombohedral symmetry in the space group $R\bar{3}c$(167). Single crystals were found to be more resistant to hydrolysis than a powder sample [1296]. In firing a powdered mixture of In_2O_3 (25–30 %), SnO (75–50 %) and PdO (0.06–5 %) to form a detector for combustible gases, a raw material having a specific surface area greater than 25 m^2g^{-1} was obtained [1297].

The heteropolyanion derivative, $K_6Na_2[PtW_6O_{24}].12H_2O$ was obtained at pH 7.5 from $K_2[WO_4].2H_2O/K_2[Pt(OH)_6]/Na^+/H[NO_3]$. An X-ray diffraction study showed that the heteropolyanion had an ideal Anderson type structure with D_{3d} symmetry [1298]. The compounds $K_{3.5}[\alpha\text{-}H_{4.5}PtMo_6O_{24}].3H_2O$ and $[NH_4]_4[\beta\text{-}H_4PtMo_6O_{24}].1.5H_2O$ were subjected to X-ray diffraction analysis. $[PtMo_6O_{24}]^{8-}$ was shown to have two geometrical isomers, one having the Anderson structure, **(486)**, and the other with the same framework as the heptamolybdate ion and 2mm(C_{2v}) symmetry, **(487)** [1299].

A Pt/PtS electrode was prepared and its behaviour was examined in different media. ΔG°, ΔH° and ΔS° were determined for the equilibrium (113) [1300].

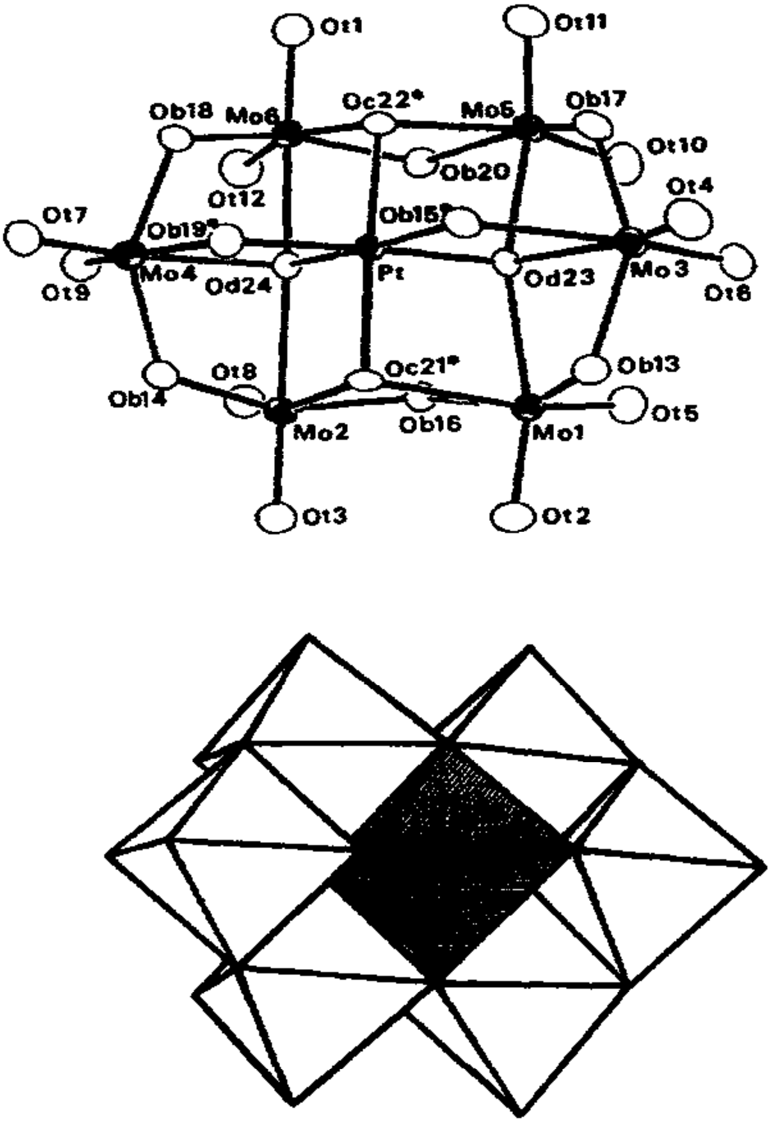
$$Pt_{(s)} + S^{2-}_{(aq)} \rightleftharpoons PtS_{(s)} + 2e^- \qquad (113)$$

The species $PtSe_2Cl_8$, $PtSe_2Cl_{12}$ and $PtTe_2Cl_{12}$ were studied by X-ray powder diffraction. All were rather unstable towards halogen loss [1301]. Polarisation curves for PdSe in sodium hydroxide solution were plotted on a potentiostat under potentiodynamic conditions. Electrochemical decomposition of PdSe in such solutions occurred rapidly and completely under conditions in which oxidation occurred [1302].

A study of the Nb/Pd/Se system showed the existence of a new phase, $Nb_2Pd_3Se_8$. X-ray diffraction analysis revealed two chains of edge-sharing selenium trigonal prisms centred by niobium. The chains conjoined through two types of palladium atoms, one with square planar and one with square pyramidal coordination. "Tunnels" along the *c*-direction resulted and the phase was a metallic semiconductor [1303].

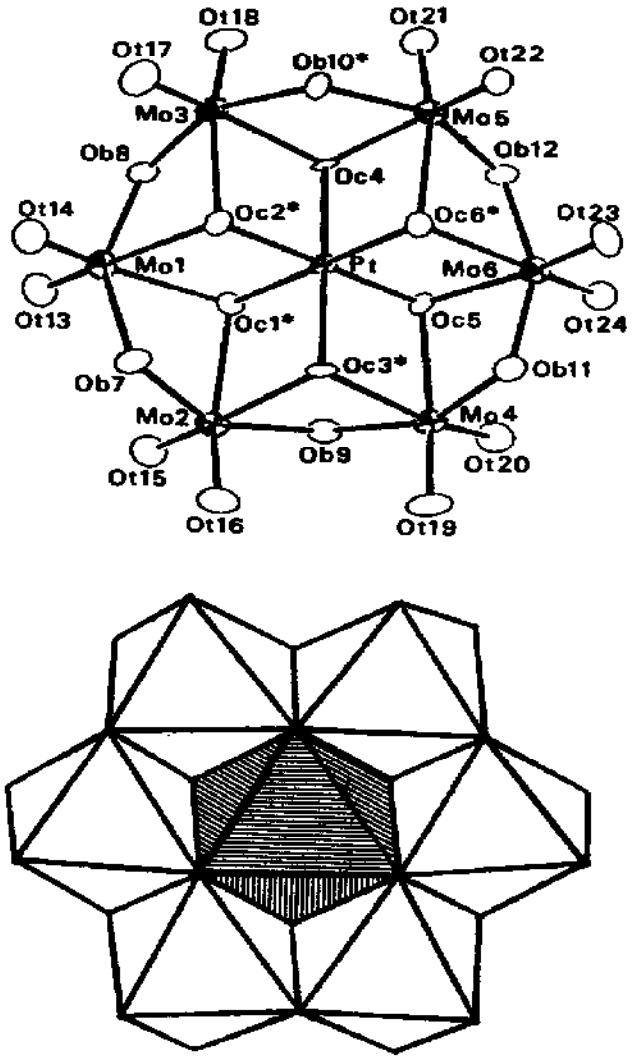
1.11.3 Compounds with Group 15 elements

The structures of the species A_2MX_2 (A = K, Na or Rb; M = Pd or Pt; X = P, As or S) have been studied. In K_2PdAs_2 and K_2PdP_2 the As–As and P–P distances were typical of single bonds, whilst the Pd–Pd distance of 3.01 Å implied some interaction, but fell short of a full bond. This was explained in terms of a puckered one-dimensional chain structure. K_2PtS_7 contains planar PtS_2 chains. The band structure of these species was calculated and analysed in terms of the increased stability afforded by the bending of the planar chain into a zig-zag ribbon [1304].



(496) (Reproduced with permission from [1299])

Structure of $[\beta\text{-}H_4PtMo_6O_{24}]^{4-}$ anion (H atoms not shown) and its polyhedral model. * - protonated oxygen atom.



(487) (Reproduced with permission from [1299])
Structure of $[\alpha\text{-}H_{4.5}PtMoO_{24}]^{3.5-}$ anion (H atoms not shown) and its polyhedral model. * = protonated oxygen atom.

The compounds MPd_2P_2 (M = Ca, Sr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Yb), $La_6Pd_6P_{17}$ and $Ce_6Pd_6P_{17}$ have been prepared by reaction of the elements. Guinier powder patterns indicated $ThCr_2Si_2$ and $La_6Ni_6P_{17}$ structures respectively [1305]. However, $BaPd_2P_2$ and $BaPd_2As_2$ crystallised in the $CeMgSi_2$ type structure but had tetragonal symmetry. Some crystals of $BaPd_2As_2$ showed structural elements of the $CaBe_2Ge_2$ type [1306]. $EuPd_2P_2$ was previously classed as an intermediate valence compound on the basis of a unit cell volume anomaly. Mössbauer isomer shifts and magnetic susceptibility measurement have now proved that it is a europium(II) derivative and the anomalies may be attributed to strong chemical bonding between Eu(II) and the ligands [1307].

New data on the X-ray absorption near-in structure of the $(Ni_{0.5}Pt_{0.5})_{75}P_{25}$ systems have been published. The number of 5d holes per platinum site was shown to be greater than for pure platinum [1308]. At 500 °C $Pd_{1.5}Cu_{2.5}P$ was in equilibrium with PdP. It was also isotypic with Pd_4Se, and its valence electron composition and atomic sites permitted UU2 binding compatible with that of related phases [1309]. Comparison of neutron diffraction structural data for $Pd_3P_{0.8}H_{0.17}$ and $Pd_6PH_{0.33}$ with previous neutron diffraction data for $Pd_3P_{0.8}$, $Pd_3P_{0.8}D_{0.15}$, Pd_6P and $Pd_6PD_{0.26}$ have confirmed the supposition that hydrogen and deuterium occupy the same crystallographic positions when dissolved in $Pd_3P_{0.8}$. For solutions in Pd_6P the two sites occupied by deuterium were also occupied by hydrogen, and hydrogen occupied one additional site [1310].

In the $NiPd_mAs_{m'}$ alloy system three classes of phase could be distinguished. The first was a brass-like phase with valence electron concentrations between $N_b^{\ell A}$ = 1 and 2, and the second a post brass-like phase with $N_b^{\ell A}$ = 2 to 3. The final phase was silicon like with $N_b^{\ell A}$ = 3 to 5 [1311]. The effect was investigated of thermal treatment on the physicochemical reaction at the metal-semiconductor interface, and on the electrical characteristics of contacts produced by successive electrochemical deposition of thin layers of gallium or arsenic followed by palladium layers on the epitaxial structure of n-n^+ GaAs. X-ray phase analysis and SIMS were used to study the process of palladium and gallium interdiffusion and the formation of intermetallic compounds Pd_2Ga, $PdAs_2$ and PdGa under thermal treatment in a hydrogen atmosphere [1312].

1.11.4 Compounds with silicon

The use of Pd_2Si and PtSi in Schottky barrier IR charge coupled devices has been reviewed [1313].

The synthesis of Pd_2Si films *via* dual source sputtering has been investigated [1314]. The formation of Pd_2Si by rapid thermal annealing of palladium layers has been studied as a function of annealing time, and the growth rate was found to be diffusion limited. A silicide resistivity of 30–40 Ω cm^{-1} was obtained for 200–400 nm thick Pd_2Si layers formed at 400 °C over a few seconds [1315]. The process was studied by mass spectrometry, and isotope separation was observed for silicon during silicide formation. Epitaxial growth was noted at 300 °C [1316]. Pd_2Si formed at room temperature became epitaxial after annealing at 200 °C. Surface segregation of silicon was observed above 400 °C [1317]. Various coverages of palladium were deposited on substrates formed from a few layers of copper on a silicon <111> face at room temperature. Photoemission results showed that formation of Pd_2Si was strongly inhibited by the presence of the Cu/Si interlayer [1318].

At 1.3-50 K ultrathin films of Pd/Pd_2Si (6-55 Å) showed a positive anisotropic magnetoresistance which was logarithmic in field at high magnetic fields, this phenomenon being characteristic of two-dimensional localisation with strong (three-dimensional) spin-orbit scattering. At lower temperatures the magnetoresistance saturated to a field independent value. The change was due to a crossover of spin-orbit scattering from its bulk value to a form characteristic of a two-dimensional film [1319]. The electronic and morphological interactions which occur at the interface between silicon and a variety of metals have been investigated by synchrotron radiation photo-emission studies of the bulk silicides, and by calculations [1320]. Interdiffusion in the Si<100>/Pd_2Si/NiSi<111>/Pd_2Si/Ni thin film systems was studied using Rutherford back scattering spectrometry (RBS). Nickel was shown to diffuse along the grain boundaries of polycrystalline Pd_2Si, upon which it accumulated at the Si<100>/Pd_2Si interface [1321].

PES and EELS were used to observe the formation and oxidation of the Pd/SiC interface. The interface was reactive at room temperature, and intermixing gave a surface phase consisting of palladium silicide and some dissolved carbon. The $Si(L_{2,3}VV)$ lineshape dependence on palladium coverage and annealing time implied the presence of Pd_3Si and Pd_4Si rather than Pd_2Si. On oxidation adsorption occurred preferentially at the silicon sites [1322]. The growth of oxide films by room temperature oxidation of Pd_4Si, Pd_2Si, PdSi, Pt_2Si and PtSi was studied by PES. Growth proceeded by chemisorption at the silicon atoms with formation of $Si(Si_3O)$, $Si(Si_2O_2)$, $Si(SiO_3)$ and SiO_4 (*sic*). The degree of oxidation and film thickness increased with the amount of metal in the initial silicide [1323].

Silicide formation in the Ni-Pt-Si system as a function of heat treatment was investigated using MeV backscattering spectrometry, glancing-angle X-ray diffraction and Auger electron spectroscopy (AES). Schottky barrier values were used to identify the metals present at the silicide/silicon interface. It was shown that the reaction starts with formation of Ni_2Si or Pt_2Si, depending on the metal in contact with silicon, until all the contact metal has been used up. Subsequently the other metal diffuses [1324]. Formation of Pt/Ni silicide was studied by sputter depositing a 600 Å $Pt_{0.4}Ni_{0.6}$ alloy layer on to <111> n-type silicon and annealing for 20 minutes in nitrogen at 300-750 °C. RBS, AES and cross-sectional STEM/EDS were used for characterisation. The ternary silicide developed as a two or three layer structure, and only at high temperatures did a uniform $Pt_{0.4}Ni_{0.6}Si$ layer result. The silicide growth mechanism could be understood in terms of metal atom diffusion, with the preferential bonding of silicon to platinum leaving nickel to diffuse deeper into the silicon substrate [1325].

A platinum film was sputter deposited on clean n-type oriented single crystal silicon. Thin films of Pt_2Si and PtSi were formed and analysed by X-ray diffraction. The isotope separation noted for the mobile species in the reactions was consistent only with a growth mechanism involving grain-boundary diffusion [1326]. Solid state reactions in ultra-thin films of "as deposited" platinum on silicon in the thickness range 10-60 Å were studied using transmission electron diffraction (TED) for structural and phase identification, and AES for depth profiling, and to obtain chemical bonding information. An amorphous glassy layer was formed at the interface and was stable for platinum film thicknesses less than 35 Å. With thicker films this phase was unstable with respect to nucleation of crystalline phases. TED measurements on silicon substrates with 40 Å platinum films showed patterns due to the α-Pt_2Si phase and other patterns due to mixtures of Pt and α-Pt_2Si phases in the interface [1327]. Lateral diffusion couples formed by depositing platinum islands on silicon layers on alumina were used in conjunction with scanning electron microprobe measurements to investigate the growth of platinum silicides over the temperature range 400-700 °C. The Pt_2Si phase was shown to grow over a length of 4-30 µm with a rate proportional to $(time)^{½}$ and an activation energy of 1.3 eV [1328].

Raman spectroscopy has been used to identify PtSi formed on the Si<100> and Pt<111> surfaces [1329]. Etching characteristics of PtSi were described using the chemically assisted ion beam etching (AIBE) technique [1330]. The effect of ion bombardment on the composition of PtSi and Pt_2Si films was studied by AES; platinum enrichment of the film was observed [1331].

The atomic structure and composition of silicide layers grown on a platinum surface were studied in a field ion microscope. The layers near the platinum interface had the composition Pt_2Si. Beyond the relatively sharp interface a few silicon atoms were still found tens of atomic layers within the platinum matrix [1332]. The crystalline perfection of epitaxial PtSi thin films and the microstructure of the PtSi/Si interface were examined using tunnelling electron microscopy (TEM) including lattice image techniques. It was found that epitaxial PtSi layers grow with domains which have three different positions on a <111> silicon substrate. Inside a domain the crystalline perfection was high and at the domain boundary no intermediate region was observed. The undulation of the PtSi/Si interface was larger than that of other epitaxial silicide/Si interfaces. Despite the large undulation a cross-sectional lattice image showed that the epitaxial layer extended to the abrupt interface [1333]. In a related paper other workers descibed similar studies of "as-deposited" platinum on silicon <100>. On annealing at 250-350 °C, PtSi together with a little Pt_2Si was formed. Pt_2Si persisted to 400 °C. At 600 °C the PtSi showed an epitaxial relationship with its *c*-axis perpendicular to the silicon <100> surface. The silicide structure showed a multidiffraction pattern with three-fold symmetry reflecting the three equivalent but strained epitaxial orientations [1334].

The high temperature stability of PtSi formed by metal reaction with silicon or cosputtering was studied. Film properties were examined as a function of annealing temperature using a resistance measuring technique, RBS, Auger and X-ray analyses, TEM and SEM techniques, and by measuring forward current volatge characteristics of silicide n-Si Schottky diodes. PtSi was found to dissolve increasing amounts of silicon on high temperature (700-1000 °C) treatments, causing considerable degredation of its properties [1335].

Thin platinum layers sputter deposited on silicon <100> wafers were irradiated in air by one pulse from a Nd-glass laser for 1 ms. White frontside irradiation gave multiphase systems but backside irradiation gave single phase silicides in a sequence similar to furnace annealing [1336]

The thermal expansion coefficients of glassy PdSiCu and many other disordered solids were studied [1337].

Bulk and surface valence states of ytterbium in $YbPd_2Si_2$ were determined by measuring χ susceptibility, L_{III} edge X-ray absorption and valence band photoemission. This was shown to be a homogeneously mixed valence system with a mean valence at room temperature close to the high temperature limiting value given by the ionic ICF model [1338]. These results were consistent with Mössbauer effect data for $TmPd_2Si_2$ and $YbPd_2Si_2$ [1339].

1.11.5 Other compounds

The orthogonalised LCAO method was used to study the electronic structure of $Pd_{41}Zr_{59}$ glass [1340]. Hyperfine interactions and Mössbauer parameters of Pd_6Sn in iron were studied as functions of temperature and pressure [1341]. Crystal structures of Pt_5Am and Pt_5Cm thin layers were investigated. Pt_5Am possessed the hexagonal Cu_5Ca type structure, but Pt_5Cm underwent rapid X-ray amorphisation as a result of self-irradiation at room temperature [1342].

Values or limits have been provided for the Gibbs free energy of formation of a wide range of intermetallic compounds A_nB_m including $LiPt_7$, $BePt_{15}$, $MgPt_3$, Ca_2Pt_7, $SrPt_2$, $SrPt_3$, $SrPt_5$, AlPd, Al_3Pt_2, Al_3Pt_5, $ScPt_3$, $BaPt_5$ and many others [1343].

The species LnMAl (Ln = Sm, Gd, Tb, Y, Dy, Ho, Er or Tm, M = Pd or Pt; Ln = Lu, M = Pt) were prepared from their elements by arc melting on a copper hearth, and were characterised by X-ray techniques. TbPtAl had the TiNiSi structure. Whilst the radius ratios were favourable for the formation of a Laves phase, the electron concentration factor favouring the TiNiSi structure was more important [1344]. The results obtained with superconducting U_2PtC_2 placed it intermediate between heavy fermion (UBe_{13} or UPt_3) and less anomalous (U_6Fe or α-U) superconductors [1345].

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