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5. PALLADIUM AND PLATINUM

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CONTENTS

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INTRODUCTION

Whilst being essentially a continuation of the series of reviews of palladium and platinum coordination chemistry written by Professor Hartley, there must be a certain change of style and emphasis as a result of the change of author. In particular, a new section is devoted to the applications of palladium and platinum complexes in catalytic reactions.

The review covers mainly the papers recorded in Chemical Abstracts between Volume 95, issue 19 and Volume 97, issue 20, as well as the 1982 issues of the major English language inorganic chemistry journals. Thus, although most of the papers covered were published in 1982, many from 1981 are also included, together with some earlier work which has been slow to reach Chemical Abstracts. It is encouraging and interesting to note the increasing number of reports emerging from laboratories in the People's Republic of China, and it is to be hoped that translations will become available so as to make this material more accessible to Western readers.

During the period covered two reviews of the inorganic chemistry of the platinum group metals have appeared [1,2] and oxidative addition in the coordination chemistry of these elements has also been comprehensively discussed [3].

5.1 PALLADIUM(VI)

A phase of composition $Pd(PdF_6)$ is formed on treatment of Pd_3U with fluorine, the reaction being used in a determination of the standard heat of formation of Pd_3U [4]. No papers on platinum(VI), palladium(V) or platinum(V) have appeared in the last year.

5.2 PALLADIUM(IV) AND PLATINUM(IV)

5.2.1 Complexes with Group VII donor ligands

The structures of the complexes $Cs_2[PtF_6]$ and $Rb_2[PtF_6]$ have been determined by X-ray crystallography [5]. Ligand field absorption and emission bands due to the $t_{2g} - e_g$ transitions for $[PtF_6]^{2-}$ and analogues have been reviewed [6].

The $[PtCl_6]^{2-}$ anion has been shown to be a regular octahedron in the X-ray crystallographic determination of the structure of $[Ph_4As]_2[PtCl_6]$ [7].

The temperature dependence of the ^{35}Cl NQR spectrum of $[Me_4N]_2[PtCl_6]$ shows the phase transitions previously discerned by DTA [8]. Proton T_1s show similar effects, with four phases clearly discriminated. The phase changes are related to the freezing of the rotational or reorientational freedom of $[Me_4N]^+$ [9].

The IR and Raman spectra of $[PhNH_3]_2[PtCl_6]$ and $[PhCH_2NH_3]_2[PtCl_6]$ are describable as the sum of two fragments [10]. The frequencies, widths and integral intensities of the IR bands of $K_2[PtCl_{6-n}Br_n]$ in an inert polyethylene matrix have been determined [11], and $[PdCl_6]^{2-}$ and $[PdBr_6]^{2-}$ are included in a theoretical study of vibrational modes [12]. The frequencies and normal vibration shapes have been calculated for *cis*- and *trans*-isomers of $[PtCl_2(OH)_4]^{2-}$, $[PtCl_4(OH)_2]^{2-}$ and $[PtCl_3(OH)_3]^{2-}$ and deuterated analogues [13]. The X-ray crystallographic structure and vibrational spectra of *cis,cis,trans*-$[Pt(NH_3)_2(OH)_2Cl_2]$ have been determined [14].

The two photon excitation spectra of a d–d transition in a transition metal complex has been measured for the first time on a single crystal of $K_2[PtCl_6]$; the data suggest alternative assignments for the one photon results [15]. The electronic structure of $[PtCl_{6-n}Br_n]^{2-}$ as determined by the MO-LCAO method is in agreement with experimental absorption spectral data [16]. The EPR spectrum of Re^{4+} in single crystals of $[NH_4]_2[PtCl_6]$ at frequencies near

10 GHz was reported [17].

The complexes $[PtCl_{6-n}Br_n]^{2-}$ (n = 1–5) may be separated by ion exchange chromatography on diethylaminoethyl cellulose, but separation of stereoisomers for n = 2,3 or 4 was not possible. The *trans*-effect of bromine allows the synthesis of pure *cis*- and *trans*-isomers with better stereoselectivity than for Re, Os or Ir analogues [18]. The heterogeneous reaction of $[PtCl_6]^{2-}$ with $Ln_2O_3.2H_2O$ has been studied [19]. Various aspects of the solution chemistry of palladium(IV) and platinum(IV) chloro complexes have been reviewed [20–22].

The temperature dependence of the heat capacity and the halogen NQR spectrum in $K_2[PtBr_6]$ have been measured. An anomaly in the heat capacity is noted at the transition point at 169 K [23]. The bromine NQR of the cubic phase provides indirect evidence for the formation of dynamic clusters of the low symmetry phase, before the rotative type phase transitions to tetragonal structures [24]. The species $Cs_2[MI_6]$ (M = Pd or Pt) are prepared by heating acidic solutions of $[MCl_6]^{2-}$ with an excess of CsI. Both crystallise in the cubic $K_2[PtCl_6]$ structure and full X-ray data are available for $Cs_2[PtI_6]$ [25].

5.2.2 Complexes with Group VI donor ligands

The structures of the complexes $[NH_4]_2[Pt(OH)_6]$ and $K_2[Pt(OH)_6]$ are similar but $[NH_4]^+$ is hydrogen bonded to three oxygen nearest neighbours whilst potassium is nine-coordinated by oxygen [26]. $M[Pd(OH)_6]$ (M = Ca, Sr or Ba) may be prepared from $Na_2[Pd(OH)_6]$ and MX_2. They were characterised by IR spectroscopy and thermal decomposition to $MPdO_3$ [27].

The complex *cis,trans*-$[Pt(NH_3)_2(OH)_2(CH_2(COO)_2)]$ may be prepared either from $K_2[PtCl_4]$ and the disodium salt of malonic acid, or by analogous treatment of *cis*-$[(NH_3)_2Pt(NO_3)_2]$. In both this and the 1,2-diaminoethane analogue the platinum has octahedral coordination and the three-dimensional structure is maintained by hydrogen bonding [28,29].

The ^{195}Pt chemical shift anisotropy in the solid complexes $[(Me_3Pt(acac))_2]$ and $[(Me_3Pt)_2][SO_4]$ has been measured; ^{195}Pt relaxation parameters are strongly field dependent [30]. ^{195}Pt NMR spectroscopy was also used to determine the barrier to ring inversion (51 kJ mol^{-1}) in $[NH_4]_2[Pt(S_5)_3]$ [31].

Platinum(IV) may be reduced by phosphorus(I) according to reactions (1-5), the initial product being a platinum(III) species [32].

$$HP(OH)O^- + [PtCl_5(OH)]^{2-} \longrightarrow [HP(O^-)\text{-}O\text{-}PtCl_5]^{3-} \qquad (1)$$

$$[HP(O^-)\text{-}O\text{-}PtCl15]^{3-} \xrightarrow[\text{slow}]{HO^-} \dot{H}P(O^-){=}O + [PtCl_5(OH)]^{3-} \qquad (2)$$

$$\dot{H}P(O^-){=}O \xrightarrow{[PtCl_5(OH)]^{2-}} \overset{+}{H}P(O^-){=}O + [PtCl_5(OH)]^{3-} \qquad (3)$$

$$\overset{+}{H}P(O^-){=}O \xrightarrow{HO^-} HPO_3H \qquad (4)$$

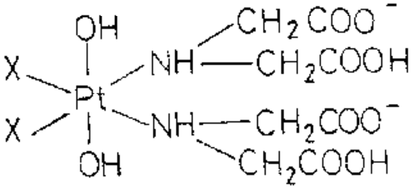
$$[PtCl_5(OH)]^{3-} \longrightarrow [PtCl_5(OH)]^{4-} + [PtCl_5(OH)]^{2-} \qquad (5)$$

5.2.3 Complexes with mixed Group VI/Group V donor ligands

The solid state reaction between $M_2[PtCl_4]$ (M = K or NH_4) and glycine is different from the solution reaction. The products identified were $[Pt(H^+L^-)_2(HL)_2Cl_2]Cl_2$, (1) ($H^+L^-$ is the glycine zwitterion and HL is the neutral molecule) and $[Pt(H^+L^-)(HL)_2(L^-)Cl]Cl_2$, (2) ($L^-$ is the glycine anion) of unspecified stereochemistry. On heating, (1) loses HCl to give (2) by ring closure [33].

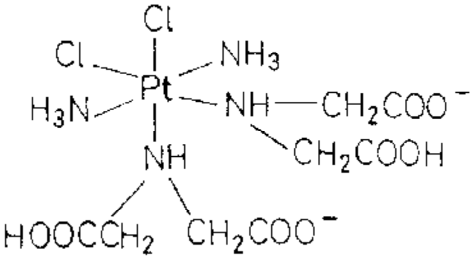
A number of platinum(IV) complexes of iminodiacetic acid (H_2L) have been reported. Reaction of H_2L with $K_2[PtCl_6]$ gives $K[PtLCl_3]$ in which L is tridentate and the coordinated carboxyl groups are *trans* in an octahedral complex. $K_2[PtCl_4(OH)_2]$ yields (3) and $[Pt(NH_3)_2Cl_2(OH)_2]$ gives (4). In a similar manner $[Pt(NH_3)_2Cl_2(NO_3)_2]$ is converted to (5). The structures of

(3), **(4)** and **(5)** were assigned on the basis of their IR spectra and potentiometric titrations [34].



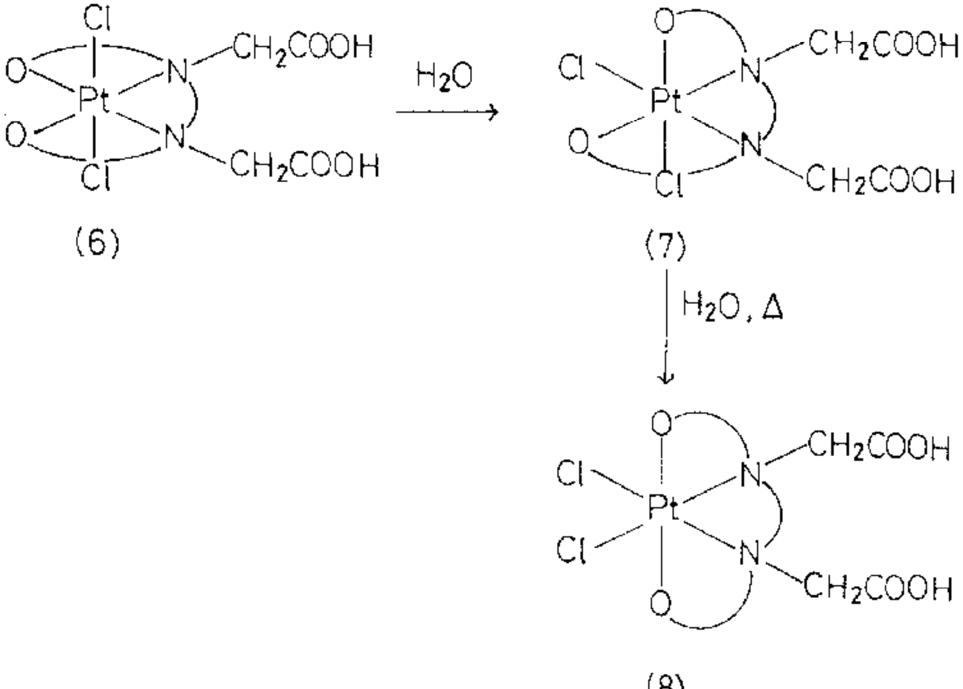
(3; X = Cl)

(4; X = NH_3)



(5)

Whilst the $edtaH_4$ complexes of platinum(II) are well known those of platinum(IV) had been less thoroughly studied. Oxidation of $[Pt^{II}(edtaH_2)]$ with molecular chlorine gives a pale yellow precipitate of $[Pt(edtaH_2)Cl_2]$. This initially formed isomer, **(6)**, is converted on standing to **(7)** and on heating in water to **(8)**. $[Pt(edtaH_4)Cl_2]$ is oxidised by H_2O_2 to **(9)** which undergoes two successive ring closures to give **(8)** [35].



(6)

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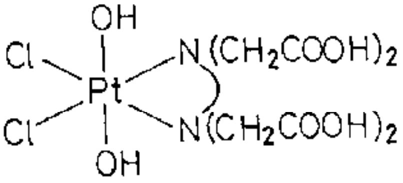
(8)



(9)

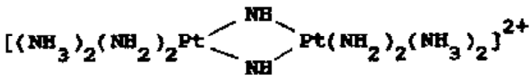
N,N′-Ethylenediaminediacetic acid forms both bi- and tridentate complexes with platinum(IV). Bi- and tridentate binding could be distinguished by IR spectroscopy and potentiometric titration, but coordination geometry is not specified [36,37]

Octahedral complexes, $[PtL_2Cl_2]$, have been prepared with HL = *N*-4-methylphenacylidene anthranilic acid and *N*-4-methylphenacylidene-2-aminophenol; coordination of L is through the azomethine nitrogen and deprotonated phenol [38].

Oxidation of $[Pt(LH_2)Cl_2]$ or $[Pt(LH)Cl]$ (LH = glycylmethionine or alanylmethionine) gave $[Pt(LH_2)Cl_4]$ and $[Pt(LH)Cl_3]$. In the latter complex LH acts as a tridentate ligand, bonding through amino and peptide nitrogens and sulphur [39].

5.2.4 Complexes with Group V donor ligands

The structure of $[(NH_3)_4Pt(\mu\text{-}NH_2)_2Pt(NH_3)_4]Cl_6$ has been determined in the solid state and by ^{15}N NMR spectroscopy in solution. Deprotonation gives successively $[(NH_3)_4Pt(\mu\text{-}NH_2)(\mu\text{-}NH)Pt(NH_3)_4]^{5+}$, $[(NH_3)_4Pt(\mu\text{-}NH)_2Pt(NH_3)_4]^{4+}$ and finally, (10). With KNH_2 this dicationic



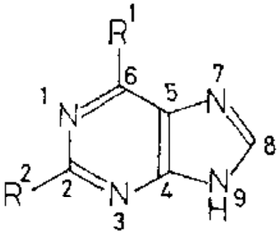
$$[(NH_3)_2(NH_2)_2Pt\genfrac{}{}{0pt}{}{NH}{NH}Pt(NH_2)_2(NH_3)_2]^{2+}$$

(10)

complex yields $K_2[(NH_3)(NH_2)_3Pt(\mu\text{-}NH)_2Pt(NH_2)_3(NH_3)]$ [40]. Heating the complexes *trans*-$[Pt(NH_3)_2L_2Cl_2]$ (L = primary or secondary amine) gives $[PtL'_2Cl_2]$ (L' = L or NH_3), the ligand lost depending on the strength of the platinum nitrogen bond [41]. Thermolysis of $[imidH]_2[PtX_6]$ gives $[Pt(imid)_2X_4]$ (X = Cl or Br) and an analogous reaction is observed for BzimidH (X = Cl or Br), 6-nitrobenzimidazole (X = Cl), 1,2-dimethylbenzimidazole or 5,6-dimethylbenzimidazole (X = Br). However, the 6-nitrobenzimidazole salt (X = Br) and the dimethyl compounds (X = Cl) yield $[PtL_2X_2]$ [42].

cis-$[Me_2Pt(PEt_3)_2]$ reacts with nitrogen oxide to yield $[Me_2Pt(NO_2)_2(PEt_3)_2]$ and N_2O. The product was characterised by X-ray diffraction showing *trans*-phosphines, *cis*-methyls and *cis*-NO_2 groups [43]. The system $[PtCl_6]^{2-}/Br^-/NO_2^-$ was studied by ^{195}Pt NMR spectroscopy. A total of 56 species are possible and all but 9 were observed. $\delta(^{195}Pt)$ for the unknowns may be predicted and $^1J_{Pt-N}$ is strongly dependent on the *trans*-ligand [44].

Platinum(IV) complexes of adenine (**11**) and guanine (**12**) have been synthesised. $[Pt(adenine)_3Cl_3]Cl.5H_2O$ and $[Pt(guanine)_3Cl_3]Cl$ have the nucleoside bonded through N(7) and the chlorines are *mer*. Neither the NH_2 nor the OH group is involved in bonding. In $[Pt_2(adenine\text{-}H)(H_2O)_2Cl_7].H_2O$, deprotonated adenine bridges two platinum(IV) centres, bonding through N(3) and N(9), whilst in $[Pt(guanineH^+)Cl_5].H_2O$ guanine is protonated at N(1) and bonded through N(7) [45].



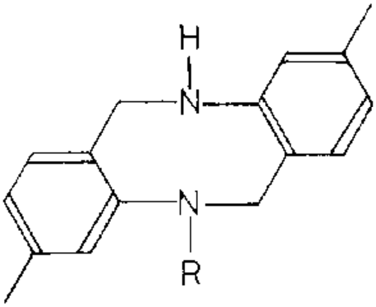
(**11**; R^1 = NH_2, R^2 = H)

(**12**; R^1 = OH, R^2 = NH_2)

$[Pt(en)_2I_2]_2[Ag_2I_6]$ has been shown to have *trans*-iodides in an octahedral cation [46]. Factor analysis may be used to resolve the overlapping XPES data obtained in the X-ray induced transformation of $[Pt(en)_2(OH)_2]Cl_2$ to

$[Pt(en)_2Cl_2]$ [47].

Complexes of the type $[L][PtCl_3X_2]$ (L is a monoprotonated diamine such as nicotine, 3-aminomethylpyridine or 3-aminoquinuclidene; X = Cl or OH) were formed by oxidation of $[L][PtCl_3]$, and tested for their effect against murine leukemic cells, L1210 [48]. Complexes of (13a) and (13b) were characterised by NMR spectroscopy and TGA [49]. The tetradentate ligand, ethylene dibiguanide



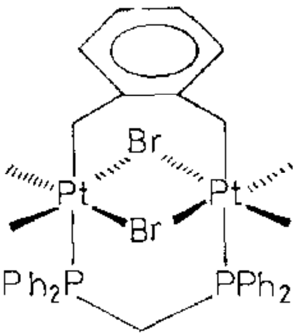
(13a; R = H)

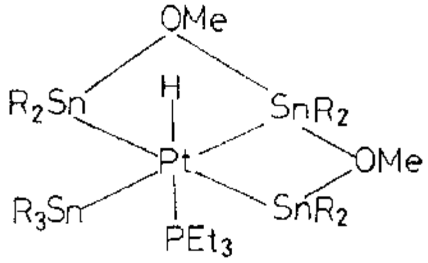
(13b; R = Me)

(H_4B), forms a complex of formula $[Pt(H_4B)Cl_2]Cl_4$, presumably with *trans*-halides [50]. The synthesis of $[Pt(TBP)X_2]$ is reported, but unlike the platinum(II) analogue it does not show strong phosphorescence [51].

Oxidation of $[R_4N][PdLX_3]$ by halogens gives $[R_4N][PdLX_5]$; ligands, L, included py, Me_3N, Pr_3P, Et_2PhP, Et_3As, Me_2S and Me_2Se. Similarly, *trans*-$[PdL_2X_2]$ gives *trans*-$[PdL_2X_4]$. Few palladium(IV) complexes of neutral unidentate ligands have previously been reported and they are generally less stable than platinum(IV) analogues as a consequence of the greater ionisation potential [52]. (14) was prepared by successive treatment of *cis*-$[PtMe_2L_2]$ (L = $AsMe_2Ph$) with xylylene dibromide and dppm and was characterised by X-ray diffraction [53].

K_2PdP_2 and K_2PtAs_2 are prepared from the elements and are isotypic with K_2PdAs_2 [54].





(14) **(15)**

5.2.5 Complexes with Group IV donor ligands

$[Pt(CN)_6]^{2-}$ may be prepared in high yield by ultra-violet irradiation of solutions containing cyanide ion and $[PtX_6]^{2-}$ (X = Cl, Br, I, SCN or OH) [55]. Oxidation of *trans*-$[Pt(CN)_2(R_2NH)_2]$ with Cl_2 or Br_2 gives *trans,trans,trans*-$[Pt(CN)_2(R_2NH)_2X_2]$. Hydrogen peroxide gives an analogous reaction yielding *trans,trans,trans*-$[Pt(CN)_2(R_2NH)_2(OH)_2]$. The platinum(IV) halide complexes are reduced to platinum(II) species on irradiation but the hydroxide reacts with water to yield $[Pt(CN)_2(H_2O)_2(R_2NH)_2]^{2+}$ [56]. A range of platinum(II) complexes has been oxidised by ICN to give species such as $[Pt(NH_3)_2(CN)_3I]$ and $[Pt(MeNH_2)_4(CN)I]Cl_2$ [57].

The oxidation of $[Pt(CO)Cl_3]^-$ to $[Pt(CO)Cl_5]^-$ has previously been reported. If the oxidation is carried out in $SOCl_2$, $[(Me_2CH)_2NH_2][Pt(CO)Cl_5]$ may be isolated; the carbonyl stretching frequency, 2191 cm^{-1}, is the highest so far recorded [58]. Addition of R_3SnH in methanol to $[Pt(CO_3)(SEt_2)(PEt_3)]$ gives a platinum(IV) complex, the structure, **(15)**, of which was determined crystallographically [59].

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

Reviews of mixed valence chemistry and one-dimensionally ordered metallic complexes have been published [60–62]. The products of oxidation of $[Pt(NH_3)_4][PtCl_4]$ (Magnus Green) with molecular oxygen in H_2SO_4 have long been controversial. Treatment of the products with KBr gives $[Pt(NH_3)_4][Pt(NH_3)_4Br_2][HSO_4]_4$, an analogue of Reihlen's Green. Both this [63] and $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$ [64–66] were characterised in detail. The Pt(IV)–Br distance is short compared with anionic linear chain compounds and the ammine groups attatched to successive platinums are eclipsed. Resonance Raman spectra have been important in studies of these and many analogous species [65]; the spectra are characterised by long progressions in ν_1, the totally symmetrical axial stretching mode. The electronic, Raman and Resonance Raman spectra of $M_2[PtLX_3][PtLX_5]$ (M = K or NH_4; L = NH_3 or py; X = Cl, Br or I) are reported and it is concluded that metal ion valences are slightly more delocalised in anionic chain complexes than in cationic ones [67]. The structure of $K_2[Pt(py)Br_3][Pt(py)Br_5].2H_2O$ has been determined [68].

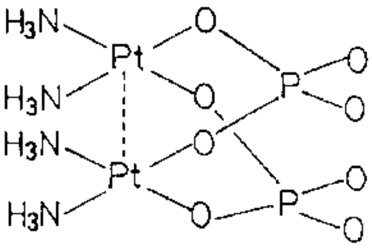
Resonance Raman spectra have also played an important part in the study of $[Pt(diamine)_2][Pt(diamine)_2Br_2]Br_2$ (diamine = $H_2N(CH_2)_nNH_2$, where n = 2,3,4 or 5). Analogous complexes are formed by 1,2-diaminocyclohexane and 1,2-diaminocyclopentane; the conformational isomers have different intervalence band maxima, and the Pt(II)–Pt(IV) distance is affected by steric factors associated with the amine ligands [69]. A new type of one-dimensional compound of formula $[Pt(en)(py)_2][Pt(en)(py)Cl_3]Cl_3.3.5H_2O$ is synthesised on treatment of *mer*-$[Pt(en)(py)Cl_3]Cl$ with an excess of pyridine [70]. Further extension of the range of such compounds is provided by the thioamide complexes $[Pt_2L_4Cl_6]$ (L = tu, thiocaprolactam, pyrimidine-2-thione or 2-imidazoline thione) [71,72]. X-ray diffraction studies of $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$ also show one-dimensional ordering with non-symmetric chlorine bridges [73].

XPES has established the presence of Pt(IV) in $K_2[Pt(CN)_4(Br)_{0.3}].3H_2O$ at 153 K; a ground state model with 0.85 Pt(II) + 0.15 Pt(IV) is proposed with Pt(III) being important in the excited state [74]. Crystals of $K_2[Pt(CN)_6]$ doped with $[Pt(CN)_4]^{2-}$ show an absorption band at 337 nm assigned to the mixed valence transition from Pt(II) to Pt(IV) [75]. In a similar system, the room temperature polarized reflectance spectrum of the potassium deficient chain, $K_{1.75}[Pt(CN)_4].1.5H_2O$ was studied [76].

The planar anions in $Li_{0.75}[Pt(mnt)_2]$ have been shown to stack face to face along the *c*-axis with direct eclipsing [77]. The electrical conduction properties of the complex have been studied in detail and the conduction pathway cannot be formed solely by the overlap of the $5d_{z^2}$ orbitals of platinum [78]. By contrast, the oxalate ligands in $Ni_{0.85}[Pt(C_2O_4)_2].6H_2O$, $Mg_{0.82}[Pt(C_2O_4)_2].5.3H_2O$ and $Co_{0.83}[Pt(C_2O_4)_2].6H_2O$ are staggered by about 55° [79].

More reports on platinum blues have appeared. *Cis*-$[Pt(NH_3)_2Cl_2]$ in phosphate buffer is oxidised to a "phosphate blue" which is similar to the amide blues. Two structures, **(16)** and **(17)**, were proposed for the blue paramagnetic solid, $H_n[Pt(NH_3)_2(PO_4)].0.5H_2O$ ($n < 1$), and from concentrated solutions a white solid, $H[Pt(NH_3)_2(PO_4)]$, was also obtained [80].

Cis-diammine platinum α-pyrrolidone tan is a structural analogue of the platinum blues; the average oxidation state of platinum is 2.25 compared with 2.0 in the related green complex $[Pt_4(NH_3)_8(C_4H_8NO)_4]^{4+}$, and the Pt-Pt distance in these complexes is largely dependent on the oxidation state [81]. Detailed study of the preparation of platinum thymine blue reveals that more than one blue compound is formed and that white compounds account for 10-30% of the total products. One of the white compounds is *cis*-$[Pt(NH_3)_2$(thymine monoanion)$_2]$ where one thymine monoanion is coordinated through N(1) and the other through N(3) [82]. Reaction of L-glutamine with $K_2[PtCl_4]$ gives a blue complex or a green/white complex, both of which give analyses close to PtL_2 (L is glutamine monoanion). The blue complex is paramagnetic and the green/white



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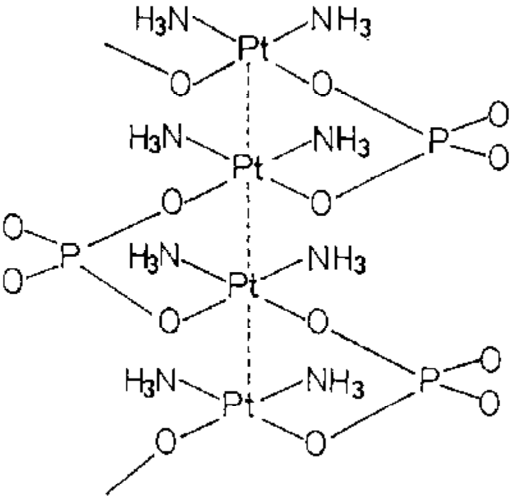
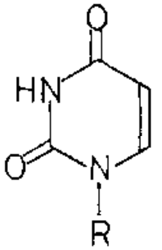


(17)

one is diamagnetic. In both, IR spectroscopy indicates that the carboxylate anion is metal coordinated [83]. Platinum blues have also been prepared containing uracil (18) and 1-methyluracil, (19) [84,85]



(18) R = H

(19) R = Me

Reaction of $H_2[PtCl_6]$ with $[Pd(NH_3)_4]Cl_2$ gives the complex $[Pt(NH_3)_4Cl_2][PdCl_4]$ [86]. Thermolysis of $[Pd(NH_3)_4][PtCl_6]$ yields *trans,trans*-$[Pd(NH_3)_2Cl_2][Pt(NH_3)_2Cl_4]$ and further heating gives *trans*-$[Pd(NH_3)_2Cl_2]$ and *trans*-$[Pt(NH_3)_2Cl_4]$ [87].

5.4 PALLADIUM(III) AND PLATINUM(III)

A range of $[Pt_2]^{6+}$ units have now been fully characterised by X-ray crystallography, and the results are summarised below.

Complex	r(Pt-Pt)/(Å)	Ref.
$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$	2.486	[88]
$K_2[Pt_2(SO_4)_4(dmso)_2]$	2.481	[89]
$K_4[Pt_2(P_2O_5H_2)_4Cl_2]$	2.69	[90]
$[X(NH_3)_2Pt(C_4H_4NO)_2Pt(NH_3)_2X][NO_3]_2$	2.603 (X = NO_2)	[91]
	2.575 (X = NO_3)	[91]

Electronic considerations suggest that Pt(III)-Pt(III) should be shorter than Pt(II)-Pt(II), and complexes with four bridging ligands have shorter metal metal bonds than those with only two. Some additional studies are reported involving the dioxygen complexes, $K_2[Pt(O_2)_2(SO_4)_2(H_2O)_2]$ and $K[Pt_2(O_2)_2(SO_4)(OH)(H_2O)_3]$ [92]. EPR studies of the blue complex formed by successive treatment of $K_2[PtCl_4]$ with 1-methylnicotinamide and guanosine suggests that its structure involves one Pt(III) and three or four Pt(II) centres [93].

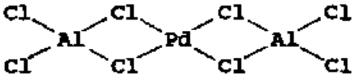
Photolysis of $M_2[PtCl_6]$ in the charge transfer or ligand field band region gives a Pt(III) complex as the primary product. The fate of this transient depends on the solvent, with reversion to starting material or further reduction to Pt(II) being the major pathways. For example, $[Pt(MeOH)Cl_5]^{2-}$ gives $[PtCl_4]^{2-}$ and $^{\cdot}CH_2OH$, the further reactions of which were studied [94,95].

Reaction of $[Pt(NH_3)_4]^{2+}$ with hydroxyl radical, generated by pulse irradiation with high energy electrons, gives the Pt(III) complex, $[Pt(NH_3)_4(H_2O)(OH)]^{2+}$, the fate of which depends on the pH of the solution. The mechanisms of the subsequent reactions are very similar to those reported last year for $[Pt(en)_2(OH)]^{2+}$ [96]. Photolysis of $[M(mnt)_2]^{2-}$ (M = Ni, Pd, Pt, Co or Cu) gives a metal(III) complex [97].

5.5 PALLADIUM(II) AND PLATINUM(II)

5.5.1 Complexes with Group VII donor ligands

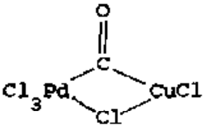
Solutions of palladium(II) in a eutectic mixture of sodium and caesium chlorides have been studied [98]. The best resolution in the electronic spectrum is obtained at low temperature [99,100]. Phase diagrams have been constructed for the systems $SeOCl_2/PdCl_2$ [101] and $AgCl/PdCl_2$ [102]. $CaPdF_4$ is diamagnetic with a tetragonal structure whilst $CdPdF_4$ has a cubic CaF_2 structure and is antiferromagnetic. The high pressure form of PdF_2 is isotypic with $HgPdF_4$ [103]. $[PdAl_2X_8]$ (X = Cl, Br or I) is synthesised from PdX_2 and Al_2X_6 [104] and the structure of the chloride (20) has been determined [105].



(20)

Theoretical studies involving $[PtCl_4]^{2-}$ have been published. The vibronic theory of static mutual influence of ligands was reviewed [106] and the mutual ligand effect in $[PtCl_3L]^{n-}$ (L = Cl, NH_3, CO, H_2O or CN) was treated by perturbation theory and the CNDO method [107]. Oscillator strengths of the symmetry forbidden transitions of $[PdCl_4]^{2-}$ were calculated by a method based on evaluation of the molecular orbitals of the distorted ion [108]. The relaxation energy, E_R, during ionisation of the valence electrons of $[PdL_4]$ was also calculated, and used to interpret X-ray emission spectra [109].

The kinetics of $[PtCl_4]^{2-}$ aquation have shown the reaction to be mainly a dissociative process, and solvent and nucleophile effects were studied [110]. The reaction of $PdCl_2$ with trimethylamine yields $[Me_3NH]_2[PdCl_4][Me_3NH]Cl$ [111]. The reduction of $[PdCl_4]^{2-}$ by carbon monoxide is accelerated by the presence of Cu(I), the critical species being the bridged complex **(21)** [112].



(21)

The electronic spectrum of $K_2[PtCl_4]$ in powder form has been investigated [113].

The effect of palladium complexes $[Pd(dmf)_2Cl_2]$ and $K_2[PdX_4]$ on the catalytic deposition of copper on plastic surfaces has been studied [114].

5.5.2 Complexes with Group VI donor ligands

5.5.2.1 Unidentate oxygen donor ligands

The electronic structures of PdO, PtO, PdS and PtS have been calculated [115]. PdO dissolves in the TiO_2 lattice, and X-ray phase analysis, DTA, EPR and conductivity studies all indicate a palladium–titanium interaction [116].

Further studies of the reaction of $La_2(C_2O_4)_3$ with $[Pd(dmg)_2]$ in dioxygen have lead to the isolation of La_2PdO_4, as well as the known La_4PdO_7 and La_2PdO_5 [117]. PdB_2O_4 has a structure isotypical with CuB_2O_4 [118]. A new high-yielding synthesis of a wide range of platinum bronzes, $M_xPt_3O_4$, (M = Li, Na, Mg, Ca, Zn, Cd, Co or Ni) from PtO_2 and metal nitrates or fluorides is reported, and XPES confirms that platinum is in oxidation state +2 [119]. $KPdO_4$, of cubic structure, is obtained from $PdCl_2$ and K_3PO_4 in a potassium chloride melt at 800 °C [120]. The solid solution Pd_2CdTeO_6/Ba_2MgTeO_6 has been studied [121].

Hydroxo complexes of the platinum metals have been reviewed with particular reference to the factors affecting bridging and polymerisation [122]. A method of preparation of a stock solution of $[Pt(H_2O)_4]^{2+}$ is reported

[123]; ^{195}Pt NMR spectroscopy of the ^{18}O labelled ion shows that all four water molecules exchange slowly [124]. Reaction of palladium metal with 12M nitric acid gives solid $[Pd(NO_3)_2(H_2O)_2]$ which "ages" in air by stepwise hydrolysis and loss of nitric acid [125].

$[Pt(OOCCF_3)_2(OOCMe_3)(HOOCMe_3)_2]$ is prepared from $[(nbd)Pt(OOCCF_3)_2]$ and is used for selective oxidation of 1-alkenes to methyl ketones [126]. An analogous family of complexes, $[(R_3P)_2M(R_x)OOR']$, where the metal is palladium or platinum, R' is H or CMe_3 and R_x is an activated alkyl such as CF_3CH_2, are prepared by reaction of $[(R_3P)_2M(R_x)OH]$ with R'OOH. They act as oxygen transfer agents to Ph_3P, benzaldehyde, carbon monoxide and nitrogen oxide [127]. Zerovalent complexes such as $[Pt(PPh_3)_4]$ react with $PhCO_3CMe_3$ to give $[Pt(PPh_3)_2(OCOPh)_2]$; $[Pt(PPh_3)_2(OCMe_3)(OCOPh)]$ is the intermediate proposed but definitive evidence for its presence is lacking [128].

Extraction of palladium(II) from nitrate solutions is accomplished by tributyl phosphate, the complexes extracted being $[Pd(NO_3)_2(OH_2)_2(OP(OBu)_3)_2]$ in tetrachlorometahane, and $[Pd(NO_3)_2(OP(OBu)_3)_2]$ in decane [129,130]. Platinum and iridium are separated by extraction from 0.5-1 M hydrochloric acid by 2-nonylpyridine-*N*-oxide [131]. Other complexes of platinum(II) with aromatic *N*-oxides are reported [132].

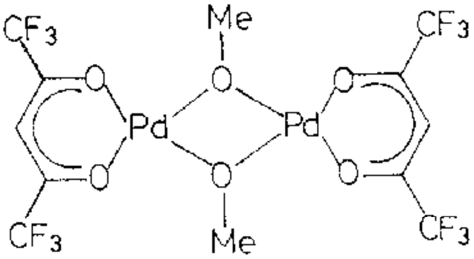
Reaction of $(CF_3)_2N{-}O^{\cdot}$ with $[Pt(PPh_3)_4]$ yields $[(Ph_3P)_2Pt(ON(CF_3)_2)_2]$ and analogous species are obtained from *cis*-$[PtL_2Cl_2]$ and $Hg(ON(CF_3)_2)_2$ [133].

Molecular bromine acts as reductant towards $Cs_2[Pd(SO_3F)_6]$, yielding $Cs_2[Pd(SO_3F)_4]$ and $BrSO_3F$. In contrast to other reported palladium(II) fluorosulphato derivatives, which are six coordinate with SO_3F behaving as a waek field ligand, this product has square planar geometry and is diamagnetic. Treatment with HSO_3F gives $Pd(SO_3F)_2$ [134].

5.5.2.2 Bidentate and multidentate oxygen donor ligands

Further studies of the reactions of bis(β-diketonato) complexes with nucleophiles are reported. With methanol and $Pd(hfacac)_2$ the bridged complex

(22) is formed, its structure being determined by X-ray diffraction [135]. The same complex gives $[PdL_4][hfacac]_2$ with a range of Lewis bases, L, and the structure of $[Pd(4\text{-chloropyridine})_4][hfacac]_2$ was determined. The PdN_4 core is square planar with oxygen atoms from hfacac in the axial sites [136]. Anilines react to give $[Pd(hfacac)(hfacac\text{-}C_3)L]$, $[Pd(hfacac)L_2][hfacac]$ and/or $[PdL_4][hfacac]_2$ depending on the molar ratio. The ease of displacement of β-diketonates to the outer sphere depends on their basicity, with the less basic ones being displaced most easily. Complexes such as (23) were also prepared in *syn*- and *anti*-forms [137]. Treatment of $[Pd(acac)_2]$ with one equivalent of Et_2NH gives (24) as confirmed by an X-ray diffraction study [138]. Comparable species are reported with 3- and 4-picoline [139].



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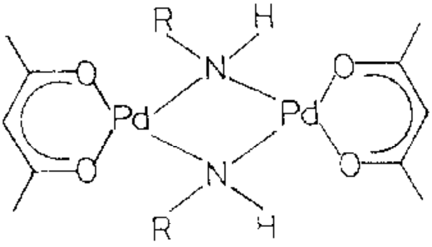

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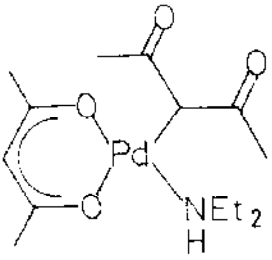


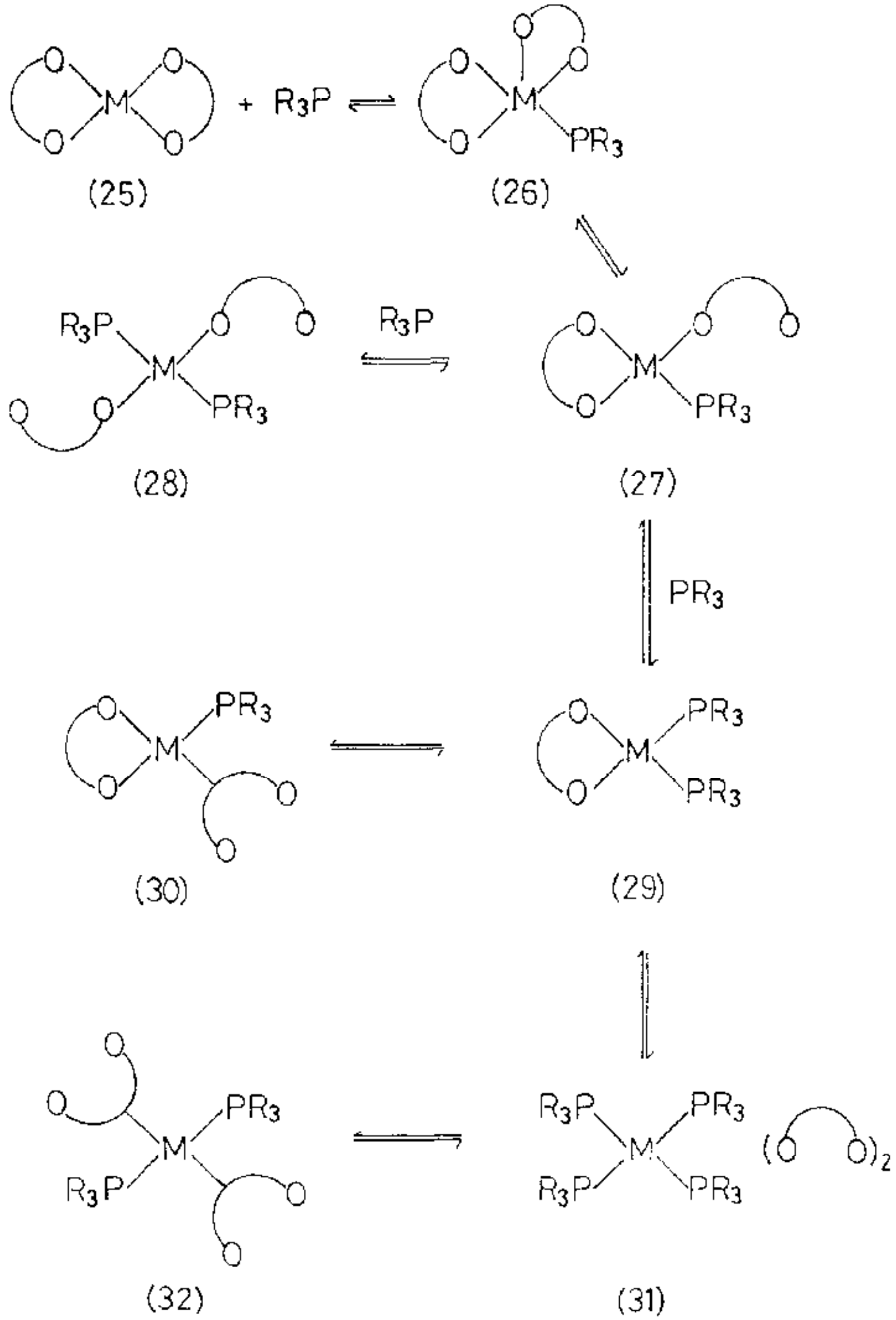
(24)

Bis{1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionate}palladium(II) ([Pd(thttfac)$_2$]) also reacts with nitrogen bases to give complexes of the type [Pd(thttfac)(bipy)][thttfac] and [Pd(4-ethylpyridine)$_4$][thttfac]$_2$ [140].

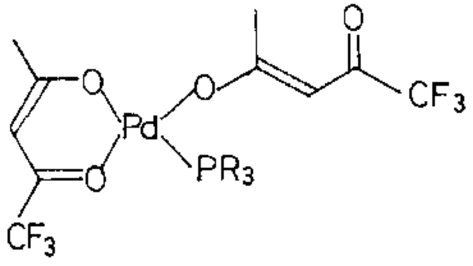
Reactions of β-diketonato complexes with phosphines provide a similar wealth of products with differing coordination modes, and a particularly thorough study is reported this year (Scheme 1). In contrast to the analogous reactions with amines, **(27)** is sufficiently stable to be characterised. The effect of metal, phosphine, and β-diketonate are discussed. Formation of **(30)**is favoured for palladium whereas **(27)** and **(28)** are more commonly found in the platinum series. Less basic β-diketones such as [tfacac]$^-$ and [hfacac]$^-$ stabilise *O*-unidentate complexes whilst carbon bonding is favoured for [acac]$^-$. The steric bulk of the phosphine is crucial; P(2-tolyl)$_3$ with a cone angle of 194°, gives only **(27)**, PPh$_3$ (cone angle 145°) gives (27), (29) and **(30)** and PMe$_2$Ph and dppe (cone angles 122° and 125°) give the fully substituted (31) [141]. Examples of the class of adducts (27) formed from Pd(hfacac)$_2$ and PAr$_3$ show fluxional behaviour in their NMR spectra; all the CF$_3$ groups become equivalent at a rate which depends on the phosphine bulk. The solid state structure is a distorted square pyramid with one of the β-diketonate groups "semi-chelating" [142].

Unsymmetrical β-diketonates present more complex possibilities. [Pd(tfacac)$_2$] was previously reported to have *trans*-stereochemistry but is actually a 3:1 *trans:cis* mixture. Reaction with P(2-tolyl)$_3$ gives [Pd(tfacac)(tfacac-*O*)(P(2-tolyl)$_3$)] as a 5:1 mixture of (33) and (34) [143]. The presence of *cis*- and *trans*-isomers in the β-diketonato complexes formed on reaction of K$_2$[PtF$_6$] with HL (HL = tfacacH, (CH$_3$)$_3$CCOCH$_2$COCF$_3$, PhCOCH$_2$COCH$_3$ or PhCOCH$_2$COCF$_3$) was confirmed [144]. The ^{195}Pt NMR spectrum of [Pt(acac)$_2$] in the presence of [Pr(fod)$_3$] was reported [145].

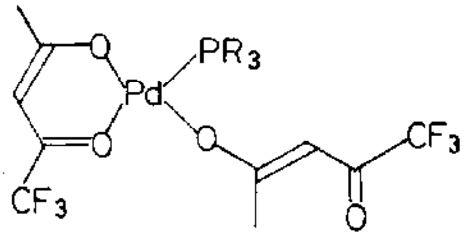
Both palladium and platinum complexes of Alizarin red S, (35), have been isolated. They are efficient catalysts for hydrogenation of alkenes, alkynes and nitroarenes [146], and for reductive amination of aldehydes [147].



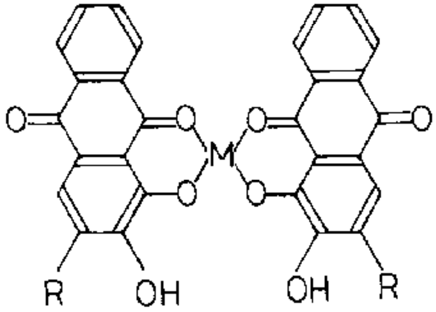
Scheme 1 Reaction of bis(β-diketonato) complexes with phosphines [141]


Pd
PR3
CF3
CF3

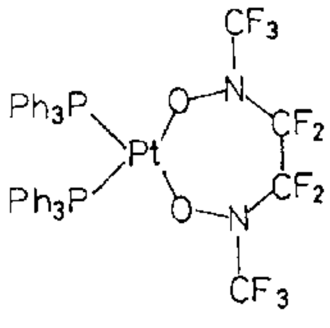
(33)


Pd
PR3
CF3
CF3

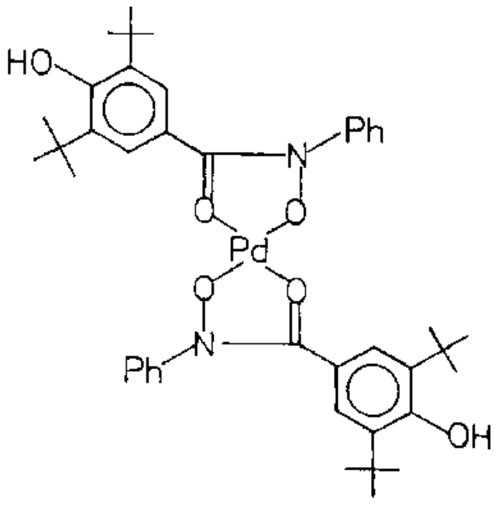
(34)


M
R
OH
OH
R

(35)

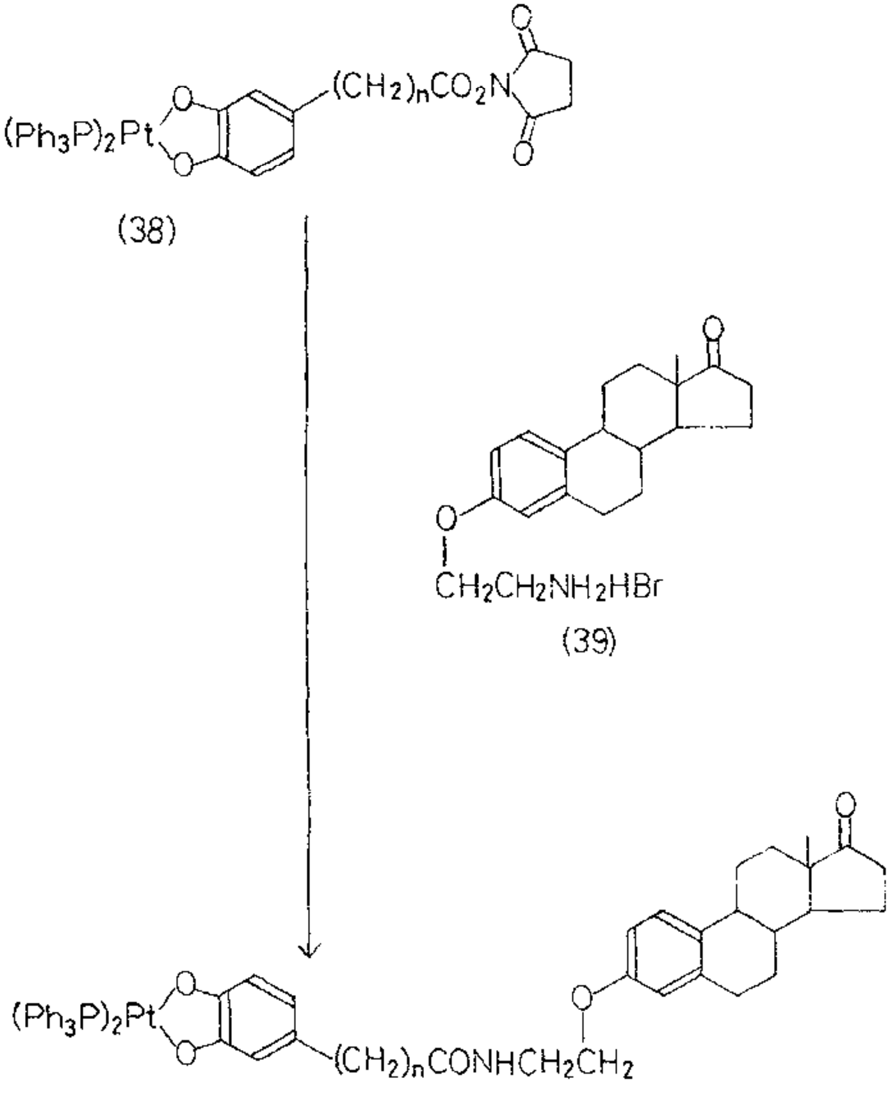

Ph3P
Ph3P
Pt
N
N
CF3
CF2
CF2
CF3

(36)


HO
Ph
Pd
Ph
OH

(37)

Oxidation of $[Pt(PPh_3)_4]$ with a bis(nitroso) compound yields the platinum(II) complex, (36), which shows fluxional behaviour in its NMR spectrum [148]. The chelate complex (37) is synthesised in analogous manner and may be reversibly oxidised to the stable mono- and diphenoxy radicals [149].



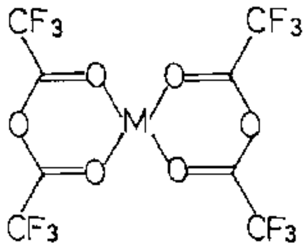
(38)

(39)

(40)

Platinum catechol complexes (38) react with amino substituted steroids to give species such as (40); these are chemically rather stable and may be useful for cancer chemotherapeutic studies [150]. Palladium(II) gives a highly coloured 1:1 complex of unspecified structure with 5,5'-methylene disalicylic acid, which may be used to determine palladium(II) in concentrations as low as 2-9 ppm [151].

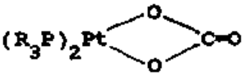
Dioxygen complexes of the platinum metals have been reviewed [152]. $[(Ph_3P)_2Pt(O_2)]$ reacts with benzil and benzoic anhydride by oxygen insertion to give, respectively, benzoic anhydride and dibenzoyl peroxide [153]. Trifluoroethanoic anhydride reacts with palladium metal at low temperature to give an anhydride complex (41) which, on warming, yields $Pd(OCOCF_3)_2$ [154].



(41)

$M_2PdP_2O_7$ (M = Li or Na), synthesised from $PdCl_2$ or PdO with MH_2PO_4 at 650 °C, contain the ion $[P_2O_7]^{4-}$, but diffraction studies failed to confirm any similarity to $K_2NiP_2O_7$, $K_2CdP_2O_7$ or $K_2CaP_2O_7$ [155].

$[Pt(PR_3)_2(OH_2)Cl][BF_4]$ and $[(Pt(PR_3)_2(O_3SCF_3)Cl]$ are prepared by abstraction of chloride ion from $[(R_3P)_2PtCl_2]$ with HBF_4 or CF_3SO_3H respectively. The tetrafluoroborate reacts with the hydrogencarbonate ion to give (42) [156].



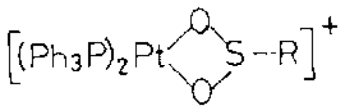
(42)

5.5.2.3 Ambidentate oxygen-sulphur donor ligands

In $[Pt(dmso)_4]^{2+}$, two sulphur and two oxygen atoms are normally metal bound, but the ratio between *O*- and *S*-bonding is solvent dependent. Addition of 1,2-diaminocyclohexane (dac) gives *cis*-$[Pt(dac)(dmso)_2]^{2+}$ in which both dmso molecules are *S*-bonded. It is more water soluble and less toxic than $[(NH_3)_2PtCl_2]$ and has similar therapeutic activity [157]. Treating $[\{Pt(CO)Cl_2\}_2]$ with dmso or diethylsulphoxide gives *cis*-$[Pt(CO)(sulphoxide)Cl_2]$ [158]. The *cis*-effect of the sulphoxide ligand on the rate of substitution of halide in [Pt(en)LX] (X = Cl or Br) was found to be in the order L = dmso > Me_2S > Et_2SO > Et_2S > Pr_2SO > Pr_2S [159].

[(*Cis*-{*rac*-*cis*-1,2-bis(phenylsulphinyl)}ethene)$PtCl_2$] is synthesised by treatment of $K_2[PtCl_4]$ with the ligand [160]; X-ray diffraction confirms that only sulphur is metal bound and that there is no interaction of platinum with the π-bond [161].

Trans-$[Pt(PPh_3)_2(O_2SR)Cl]$ has sulphur bonded to platinum and is desulphonated only at high temperature. Treatment with Ag^+ does not lead to migration of R to platinum but to formation of **(43)** [162].



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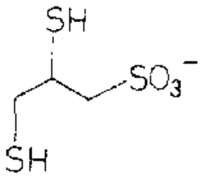
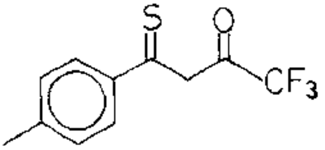


(44)

The kinetics of the reaction of platinum(II) with unithiol, **(44)**, were studied but the structure of the product was not reported [163].

5.5.2.4 Bidentate oxygen-sulphur donor ligands

Chelating monothio-β-diketonato complexes, $[ML_2]$, have been prepared for a range of ligands including **(45)**, **(46)** and **(47)** [164-166]. For the complexes



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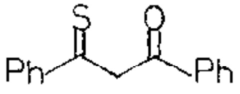

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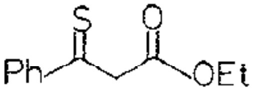
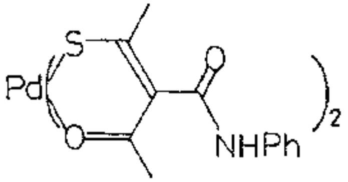


(47)

of (46) dipole moment measurements indicate a *cis*-geometry. $[(CH_3C(S)=CHC(O)CH_3)_2Pd]$ reacts with phenyl isocyanate to give complexes such as (48) [167].



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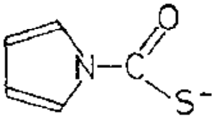
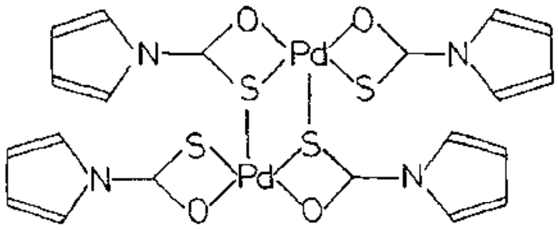


(49)

Reaction of monothiocarboxylate (49) with $PdBr_2$ gives a complex the structure of which is postulated to be (50) [168]. The complexes $[PtL_2(OH)_2]$, $[PtL_2Cl_2]$, $[PdL_2Cl_4]$ and $[PdL_2]$ where L is (51) have been reported. They exist as *cis/trans* mixtures in solution [169]. Calculations have been performed on the vibration frequencies of (52) and its *trans*-isomer [170].



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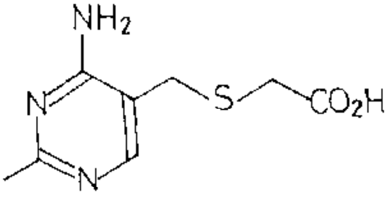

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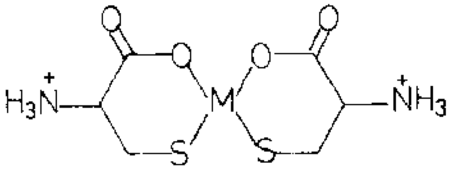


(52)

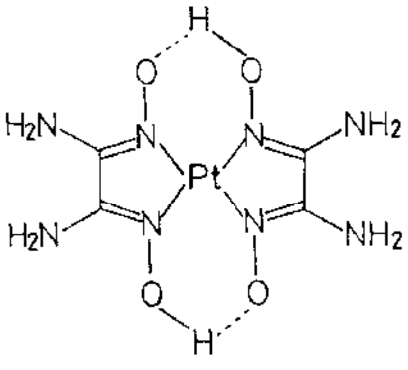
5.5.2.5 Ambidentate oxygen-nitrogen donor ligands

A range of bis(oxamide oxime) complexes of platinum with varying degrees of deprotonation are reported. (53) and (54) are centrosymmetric, whereas (55) is not, but all crystallise in a stacked structure. The adduct of (54) with 7,7,8,8-tetracyanoquinodimethanide has cations and anions forming separate, regular, parallel stacks with hydrogen bonds between them [171]. The oxalyl chloride oxime analogue (56) has also been studied by X-ray diffraction; the interplatinum distance in the stacks is smaller in this case [172].

Reaction of [Pd(dmg)$_2$] with [Al(O-CHMe$_2$)$_3$] yields (57) and the analogous complexes of 2-hydroxyacetophenone oxime derivatives give (58). Both products are extremely moisture sensitive and easily hydrolysed [173]. The spectra of some simple bis(α-dioxime) complexes of nickel, palladium and platinum have been studied [174].

Although oximes are formally ambidentate ligands, coordination to palladium or platinum through oxygen is, in practice, uncommon. An example is provided by the palladium complex, PdL$_2$ where HL is (59)(R = H). In this species one of the ligands is coordinated through the imine nitrogen and the oximo oxygen whilst the other binds through the imine nitrogen and the nitrogen of the nitroso tautomer. For R = alkyl, binding follows the more conventional form, involving the nitrogen atoms of both oxime and imine [175].

Complexes of palladium(II) with gallacetophenone oxime are reported to be unusually stable [176]. Platinum(II) complexes of MeONH$_2$ and MeNHOH were studied by ^1H NMR spectroscopy [177].



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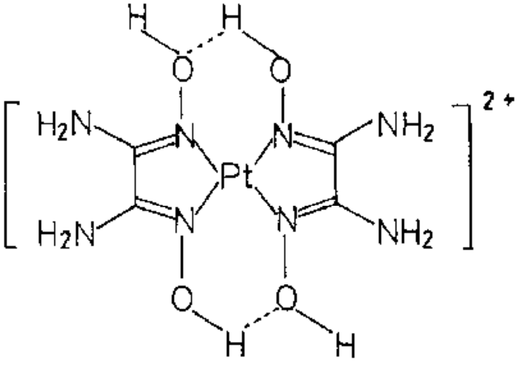

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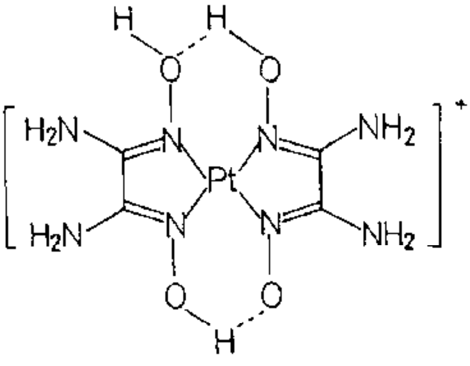

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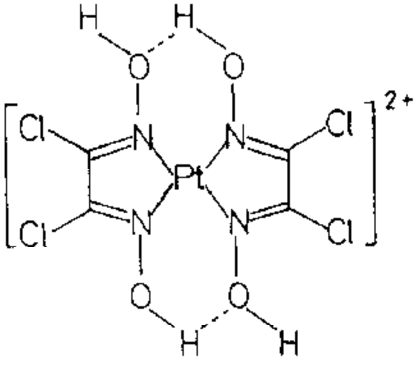

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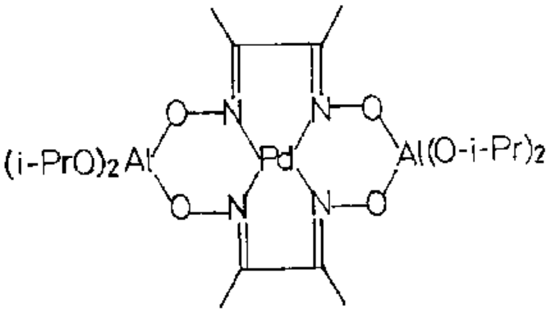

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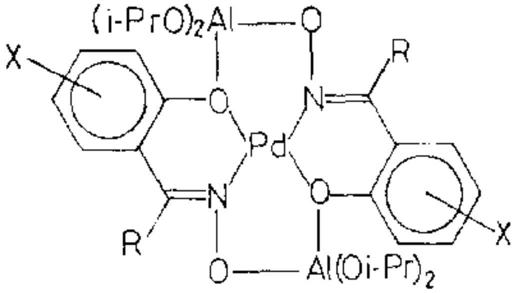

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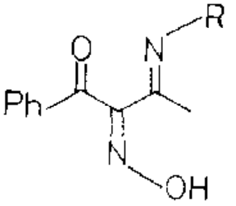
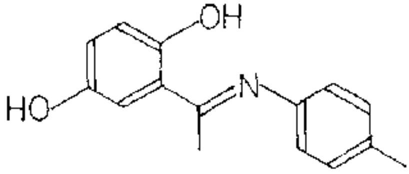


(59)

5.5.2.6 Bidentate and multidentate oxygen-nitrogen donor ligands

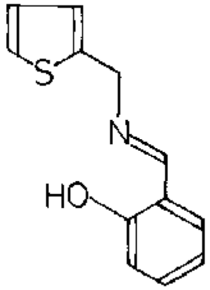
Treatment of $[Pt(H_2NC(CH_2OH)_3)_2Cl_2]$ with hydroxyl ion induces cyclisation to a bis(*N-O* chelated) compound. With weaker bases cyclisation is unsuccessful [178]. An X-ray diffraction study of $K[Pd(HOCH_2CH_2N(CH_2COO)_2)Br]$ shows that palladium has square planar coordination with nitrogen *trans* to bromine and two ionised carboxyl groups also coordinated [179].

A range of Schiff base complexes have also been studied. A 1:2 palladium complex is formed from **(60)**, with coordination through the imino nitrogen and the deprotonated phenolic OH [180]. Analogous palladium chelates of



(60)

N-(sulphophenyl)salicylaldimines are active for oligomerisation of 2-methyl-3-butyn-2-ol in the presence of triphenyl phosphine [181]. The two tautomers (61) and (62) are not separable, but their complexes with palladium may be separated by their differential solubility in benzene. The complex of (61) exists as the dimer (63), whilst (64) is in equilibrium with a six-coordinated form (64a); this closely parallels the behaviour previously noted for the furan analogue [182].



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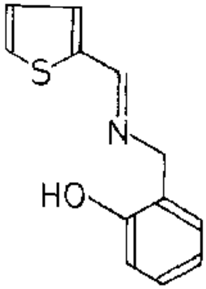

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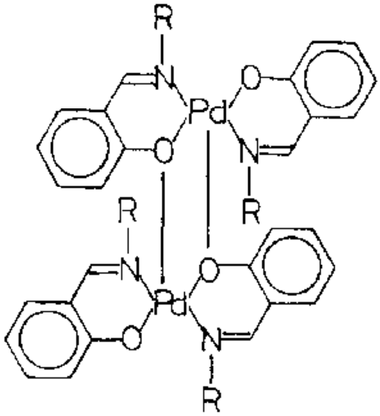

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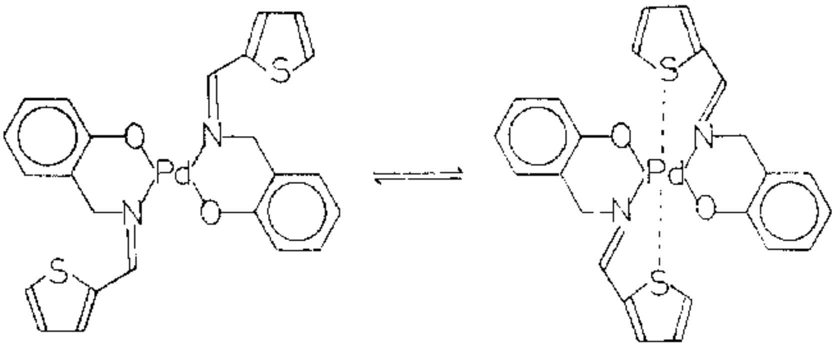
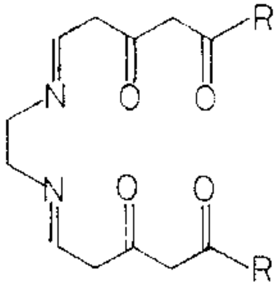


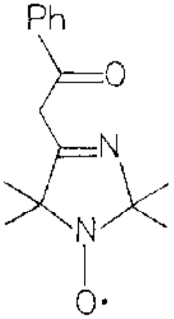
(64) (64a)

The palladium coordination chemistry of **(65a)** reveals a strong preference for N_2O_2 over O_4 coordination, although both isomers may be isolated. With **(65b)** only the N_2O_2 coordinated isomer is formed [183]. The thermal stability and volatility of complexes of tetradentate Schiff bases of this type is higher than that of bidentate analogues [184]. The stereochemistry of the four coordinate palladium complex of **(66)** is unknown [185].



(65a; R = Ph)

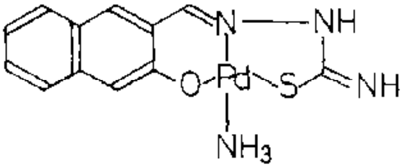
(**65b**; R = CMe_3)



(66)

The reaction of $PdCl_2$ with semicarbazide (HL) gives $[PdL_2]$; binding is probably through NH_2 and the deprotonated oxygen of the imino tautomer. The absence of a dipole moment suggests *trans*-stereochemistry [186].

Other ligands capable of multidentate coordination continue to be developed. The thiosemicarbazide of 3-hydroxy-2-naphthaldehyde acts as a tridentate ligand towards platinum in (67) [187], whilst five donor sites are used to coordinate to two palladium atoms in (68) [188].



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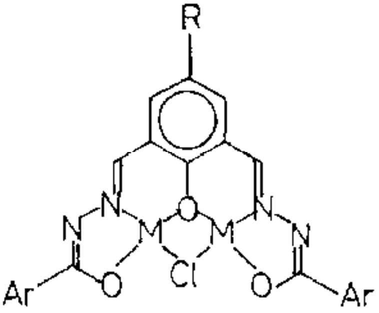
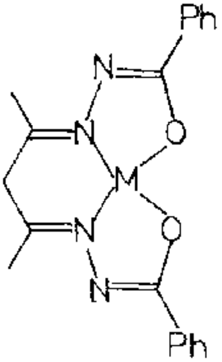


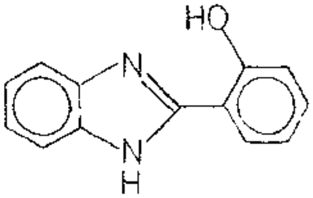
(68)

N,N'-bis(benzamido)acetylacetonediimine acts as a tetradentate ligand, giving a complex assigned the structure, (69) [189]. Tetradentate bis(salicylidene)1,2-diaminoethane palladium and platinum complexes are formed on heating the salts $[H_4L][MCl_4]$ at 175-185 °C [190].

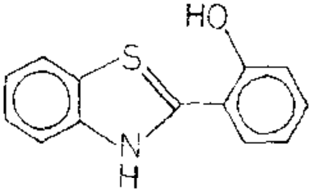


(69)

A number of bidentate *N,O*-donor ligands are provided by heterocyclic amines bearing a suitably positioned phenolic OH group. Both (70) and (71) bind as *N,O*-chelates to palladium(II) and platinum(II), but the stereochemistry of the complexes is not reported [191,192]. The sodium salt of 6-methyl-2-hydroxypyridine (mhpNa) reacts with palladium acetate to give $Na_2[Pd(mhp)_3OAc]$ which, in methanol, is converted to $[Pd_2(mhp)_4]$. X-ray diffraction shows that each palladium has *trans*-square planar coordination and that the Pd_2 unit is tetra-bridged by the mhp ligands. The Pd-Pd distance is short but there is no direct Pd-Pd bond; in $[Pd_2]^{4+}$ both bonding and antibonding orbitals are completely filled and the complex is diamagnetic [193].

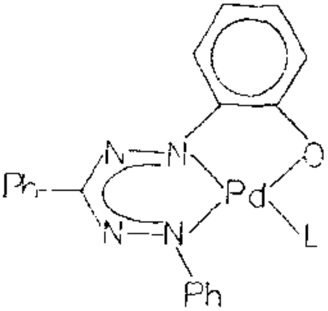


(70)



(71)

3-(3-tolyl)azoacetoacetone is reported to form two complexes, $[PdL_2]$ and $[PdL_3]$. These have differing crystalline form, and in the case of $[PdL_3]$, a somewhat dubious oxidation state [194]. The kinetics of substitution at 1-(2-hydroxyphenyl)-3,5-diphenylformazanato palladium(II) complexes, **(72)**, are reported; pyridine is a better leaving group than ammonia, due to difference in base strength, and the results are very similar to those reported for the platinum analogue [195].

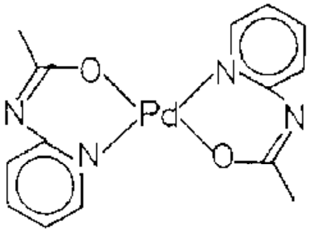


(72; L = py or NH_3)

2,5-Diphenyloxazole generally binds through nitrogen whilst 2,5-dimethylbenzoxazole (Me_2BO) is usually a monodentate oxygen ligand. However, in $[Pd(Me_2BO)(SCN)_2]_2$ both the nitrogen and the oxygen of the ligand are palladium bound as it acts as a bridge between the two palladium atoms

[196].

X-ray diffraction studies show that in bis(2-acetamidopyridine)palladium (73) coordination is through the pyridine nitrogen and oxygen, with the amide nitrogen deprotonated but not metal bound [197]. Reaction of $[(NH_3)_2PtCl_2]$ with 1-methylhydantoin gives $[Pt_2(NH_3)_4(\text{1-methylhydantoin})_2]_2[NO_3]_4$, the structure of which was determined crystallographically. The bridging hydantoins are bound in a head to tail manner with a Pt-Pt distance considerably longer than in the α-pyridone analogue. Treatment with H_2O_2 gives a blue-green paramagnetic species, a mixed valence platinum blue [198].



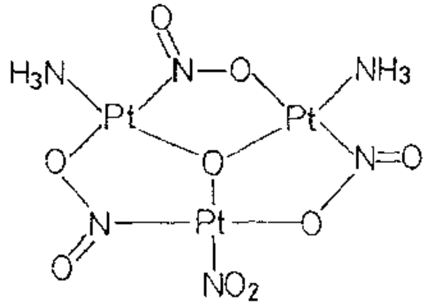
(73)

Reaction of $[Pd(OH)_2]$ with hydrazine-*N,N*-diacetic acid (H_2L) gives *trans*-$[Pd(HL)_2].4H_2O$ in which HL is coordinated through the amino group and the deprotonated carboxylate. However, treatment with $K_2[MX_4]$ (M = Pd or Pt; X = Cl or Br) yields *trans*-$[M(H_2L)_2X_2].2H_2O$ in which only the amino group is metal bound. The acidity of H_2L is increased on coordination [199].

Treatment of *cis*-$[(NH_3)_2Pt(NO_3)_2]$ with perchloric acid gives the trimer (74), which may be compared with the analogue in which the NH_3 groups are replaced by NO_2 [200]. X-ray diffraction shows distorted square planar coordination about palladium in (75) [201].

5.5.2.7 Bidentate oxygen-phosphorus donor ligands

$[PhPCH_2COO]^-$ acts as a bidentate *O,P*-donor ligand in (76); the molecules are linked into chains by hydrogen bonds between ethanoic acid and ethanoate ligands [202].



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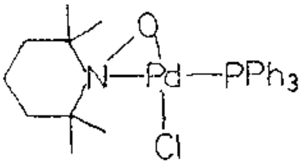

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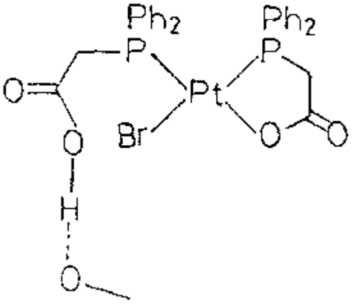


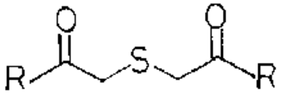
(76)

5.5.2.8 Unidentate sulphur donor ligands

Treatment of $Ba[Pt(CN)_4].2H_2O$ with H_2S gives $BaPt_2S_3$; X-ray diffraction shows that each platinum is coordinated by four sulphur atoms, with two edges and one corner of the sulphur tetrahedra shared [203].

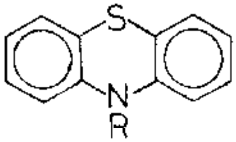
Palladium(II) is extracted successfully from HCl solution by Pr_2S and dihexyl sulphide [204]. The acid base properties of $[Pd(OH_2)_2(SR_2)_2]$ have been studied [205]. The electronic structures of $[PtCl_2(OH_2)L]$ (L = Me_2S, dmso, tu or NH_3) have been investigated by CNDO methods, again with reference to their acidities [206]. *Cis*- and *trans*-forms of $[Pt(NH_3)_2LCl]^+$ (L = Me_2S, dmso or C_2H_4) may be distinguished by their polarographic behaviour [207].

The tendency of palladium and platinum to bind to the soft sulphur centre in potentially ambidentate ligands is further demonstrated by the coordination chemistry of (77). 1:1 and 2:1 complexes were characterised, and there was no evidence for oxygen binding [208]. A wide range of complexes



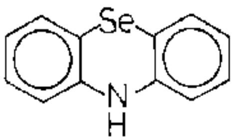
(77)

$[L_2MX_2]$ of phenothiazine, (78), and analogues such as (79) and (80), has been synthesised, though the reports are somewhat at variance as to the stereochemistry of the products. All the ligands are bound through sulphur (or



(78; R = H)

(81; R = $CH_2CH(Me)NHMe_2Cl$)



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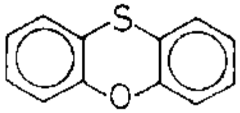


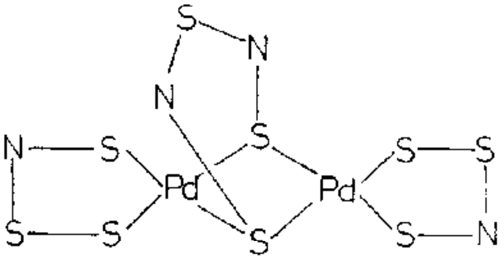
(80)

selenium) and unambiguous structural data are available for *cis*-$[Pt(79)_2Cl_2]$.MeCN and $[Pd(81)Cl_3]$, which has a hydrogen bond between coordinated chlorine and the side chain NMe_2 group [209]. Oxidation of *trans*-$[(phenothiazine)_2PtCl_2]$ with molecular iodine gives *trans*-$[phenothiazine]_2[PtCl_2I_4]$; XPES shows that this is best characterised as platinum(IV) derivative and that the ligand has been oxidised to the corresponding cation radical [210].

Binding of $[PtCl_4]^{2-}$ and *cis*-$[(NH_3)_2PtCl_2]$ to methionine-65 of tuna cytochrome C was investigated by ^1H NMR spectroscopy. Only a small local modification occurs on binding, in contrast to carboxymethylation, which involves far reaching structural changes [211]. Both palladium and platinum complexes inhibit the Ca^{2+}/Mg^{2+} dependent ATPase of rabbit skeletal muscle sarcoplasmic reticulum by interacting with a thiol group on the enzyme. The effect is enhanced by the presence of albumen [212].

5.5.2.9 Bidentate and multidentate sulphur donor ligands

Reports of complexes of bidentate thioethers have been somewhat more sparse than in previous years. $PdCl_2$ reacts with 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane, L, to give $[PdLCl_2]$, in which the ligand coordinates only through the sulphur atoms [213]. Reaction of $[NH_4]_2[Pt(S_5)_3]$ with triphenylphosphine gives $[(Ph_3P)_2PtS_4]$. The first X-ray diffraction study on a complex of this type showed that there was no alternation in S-S bond lengths, in contrast to MoS_4 or WS_4 rings [214]. When $PdCl_2$ reacts with S_4N_4, (82) is obtained among other products; the Pd-Pd distance (2.921 Å) is rather short [215].

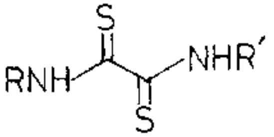


(82)

Interest in dithiolate complexes has been maintained. The photochemistry of $[M(S_2C_2R_2)_2]^z$ (M = Ni, Pd or Pt, R = CN, z = 2- and M = Ni or Pt, R = Ph, z = 0) has been studied. Oxidation of the ligands rather than the metal occurs on irradiation between 300 and 350 nm in chloroform [216]. The EPR of Co(II) doped in $[(1,4\text{-bis(dimethylamino)benzene})^+]_2[Pt(mnt)_2]$ shows well resolved hyperfine structure [217].

A number of complexes of dithiooxamide derivatives (LH_2, (83)) have been characterised. $[M(LH)_2]$ (M = Ni, Pd or Pt) was obtained from M^{2+} and LH_2 in alcohol [218, 219]. In acidic solution $[M(LH_2)_2]X_2$, (84), was the stable product [220]. $[Pd(RCSNHCSNHR')_2]$ has also been characterised [221].

Bis(8-quinoline dithiocarboxylates) and bis(2-methyl-3-indole dithiocarboxylates) of palladium and platinum have been characterised [222, 223].



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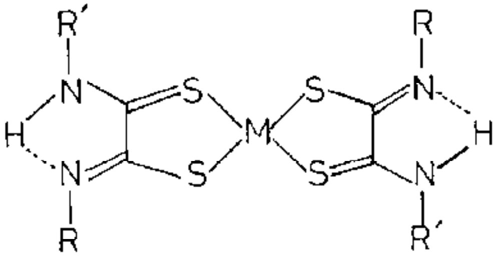
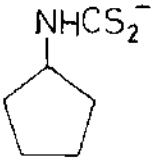


(84)

Interest in dithiocarboxamide complexes has also continued. $[Pd(S_2CNEt_2)(PR_3)Cl]$ and $[Pt(S_2CNEt_2)(PR_3)Cl]$ are monomeric and square planar. Solution NMR spectra imply that there is a substantial barrier to C–N rotation [224]. There is, however, no sign of *cis/trans*-isomerism in complexes of (85) [225]. An extensive study of the reactions of $[Pt(S_2CNR_2)_2]$ with phosphine oxides and sulphides is reported. Oxidative addition of $Ph_2P(S)H$ gives (86) which loses R_2NCS_2H to give the solvent complex, (87). In pure, dry methanol the sole product is (88), which was characterised by X-ray diffraction, and in which the counterion is derived from decomposition of R_2NCS_2H. Excess $Ph_2P(S)H$ or less pure solvents give more varied products. Under these conditions $[Pd(S_2CNEt_2)_2]$ gives a mixture of $[Pd(S_2NCEt_2)(SPPh_2)]_2$ (60%) and $[Et_2NH_2][Pd(S_2CNEt_2)(SPPh_2)_2]$ (20%), whilst reaction of $Ph_2P(Se)H$ with the platinum complex gives only (89), in good yield [226]. Treatment with trialkyl phosphines gives a new class of compounds, exemplified by (90), in which X-ray



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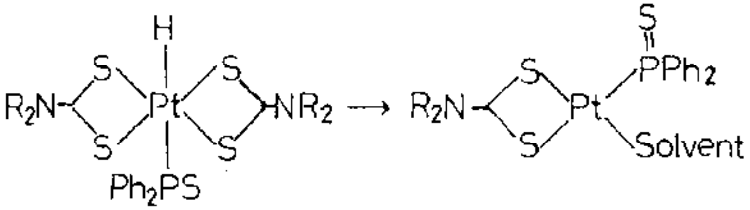
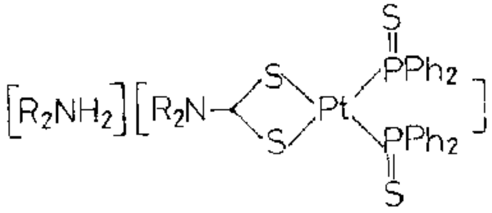


(86) **(87)**

diffraction shows one of the sulphur containing ligands to be semi-chelating. Addition of further phosphine gives an equilibrium involving species such as (91) and (92) [227].



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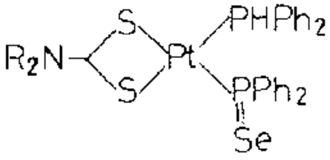

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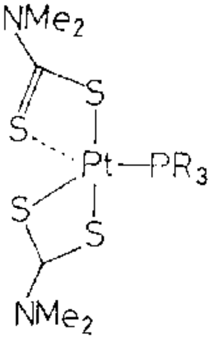

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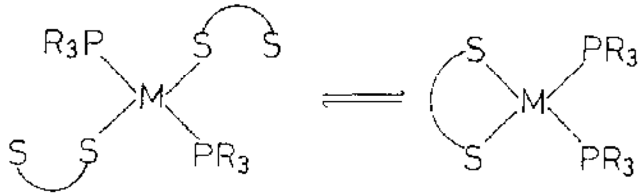
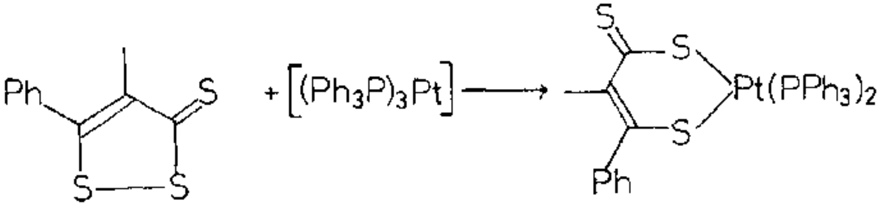


(91) (92)

Complexes of $[PhP(OEt)S_2]^-$ with bivalent nickel, palladium and platinum crystallise as *trans*-products with square planar S_4 coordination, but isomerise in solution to give roughly equal amounts of *cis*- and *trans*-isomers. The isomerisation mechanism involves solvent assisted M-S dissociation [228]. An X-ray diffraction study of $[Pt(S_2P(OCHMe_2)_2)_2]$ is reported [229]. $[Pd(S_2C_2O_2)_2]^{2-}$ forms 1:1 and 2:1 adducts with stannic chloride; the EPR of the one electron reduction product is reported. $[Pt(S_2C_2O_2)_2]^{2-}$ shows no reduction above -2 V but in the presence of one equivalent of $SnCl_4$ there is a reversible reduction at -1.5 V, and with two equivalents reversible reductions at -.15 and -.54 V [230].

$[Pt(PPh_3)_3]$ reacts with (93) by cleaving the sulphur sulphur bond to yield (94), which is also synthesised from $K_2[PtCl_4]$ and the dianion of $PhC(S)CHMeCS_2H$ [231].

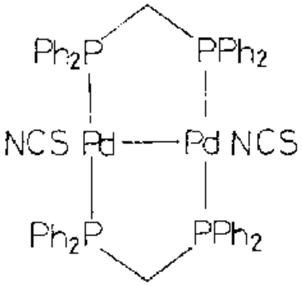


(93) (94)

5.5.2.10 Ambidentate sulphur-nitrogen donor ligands

Earlier reports on the linkage isomerism in $[Pd(5\text{-nitro-}1,10\text{-phen})(SCN)_2]$ were contradictory, with one group implying two nitrogen donors and another one nitrogen and one sulphur. Careful studies have now shown that if the complex is prepared in dmf at room temperature and isolated by pouring into cold ethanol, the yellow di-*N*-bonded isomer is formed (ν_{CN} = 2093 cm^{-1}). However, a preparation in ethanol at 60 °C gives the orange di-*S*-bonded isomer (ν_{CN} = 2122 cm^{-1}). Heating the *N*-bonded isomer in the solid state gives irreversible isomerisation to the *S*-bonded compound [232].

Thermolysis of $[Pt(dppe)_2][Pt(SCN)_4]$ yields $[Pt(dppe)(SCN)_2]$ in which thiocyanate is *S*-bonded. An analogous result is obtained with the $[Pt(EtSCH_2CH_2NH_2)_2]^{2+}$ salt. However, with ligands with a weaker *trans*-effect, such as ammonia or pyridine, $[Pt_2L_3(SCN)_4]$ is obtained, in which SCN is bridging [233]. Reaction of *cis*-$[(1\text{-phenyl-}3,4\text{-dimethylphosphole})_2PdCl_2]$ with SCN^- gives a bis(thiocyanate) which, in the solid state, has one *S*- and one *N*-bonded thiocyanate. The P-Pd bond *trans* to nitrogen is significantly shorter than the one *trans* to sulphur. The authors conclude that the binding site is determined by electronic effects, unless steric effects are very large [234]. The distribution of linkage isomers in the complexes $[(Ph_2P(CH_2)_nPPh_2)Pd(SCN)_2]$ (*n* = 1-3), $[(Ph_2PCH{=}CHPPh_2)Pd(SCN)_2]$ and **(95)** was studied by ^{31}P NMR spectroscopy. In contrast to the complexes of monophosphines, the isomers are in rapid exchange at room temperature [235].



(95)

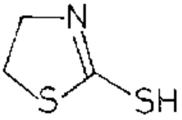
The kinetics of the reaction between $[Pd(SCN)_4]^{2-}$ and phosphorus ligands were studied, and the stability constants of the mixed complexes calculated [236]. $[NH_4][SCN]$ is effective in extracting Pd(II) from nitrate solution [237].

Complexes of thiourea and its derivatives have been the subject of revived interest. The kinetics of the reaction between $[Pd(tu)_4]Cl_2$ and heterocyclic amines have been studied spectrophotometrically and potentiometrically [238]. Sulphur coordination was proven by X-ray diffraction studies of tetrakis(1-methyl-4-imidazoline-2-thione)palladium dichloride; bonding through nitrogen had previously been postulated [239,240]. IR spectroscopy also implies *S*-bonding in palladium and platinum complexes of quinazoline-2-thione-4-one [241]. This makes the postulated all *N*-bonded structure for $[Pd_2(\mu\text{-}L)_4Cl_4]$ (L = *N,N'*-dicyclohexylthiourea) somewhat surprising [242].

A number of platinum complexes of *N*-methyl-*O*-ethyl thiocarbamate (mtc) including *cis*- and *trans*-$[Pt(mtc)_2X_2]$, $[Pt(mtc)_3X_2]$ and $[Pt(mtc)_4X_2]$ have been prepared. In all cases the ligand is *S*-coordinated. Both *cis*- and *trans*-$[Pt(mtc)_2X_2]$ give a multispecies equilibrium in benzene (reaction (6)) [243].

$$2[Pt(mtc)_2Cl_2] \rightleftharpoons [Pt(mtc)_3Cl_2] + [Pt(mtc)Cl_2] \qquad (6)$$

The thionic (C=S) rather than thiolic (CS-H) coordination of 2-mercaptothiazoline **(96)** to palladium is similar to that reported earlier for platinum [244]. 2-Mercaptobenzothiazole may be used in extraction of platinum(II) into chloroform from 1 M HCl; the structure of the 1:2 extracted complex is not reported but is presumably similar to those of mercaptothiazole [245].

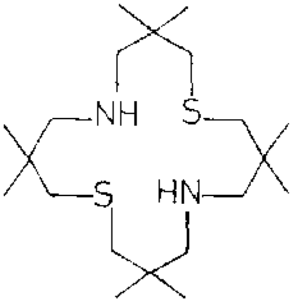


(96)

5.5.2.11 Bidentate and multidentate sulphur nitrogen donor ligands

The sulphur nitrogen macrocycle (97) acts as a tetradentate ligand towards palladium. In solution two major stereoisomers are observed, differing in configuration at nitrogen, but only one isomer is present in the solid state [246].

Thiosemicarbazides bind to palladium and platinum through sulphur and nitrogen donor atoms, forming 5-membered chelate rings (98) [247,248]. The one report of *N,N*-bidentate binding is at variance with the IR spectra of the complexes [249]. The contribution of thiono and thiolo tautomers seems to vary with the ligand [250], and in only one group of complexes, *trans*-$[M(NH_2NHC(S)NH_2)X_2]$ (M = Pd or Pt; X = Cl, Br or I) was the stereochemistry assigned [251]. Complexes of thiohydrazides such as [Pd(NH$_2$NHC(S)Ph)$_2$], appear to have a related structure. Somewhat surprisingly, using 2-hydroxyphenylthiohydrazide, the hydroxyl group plays no part in metal coordination [252,253].



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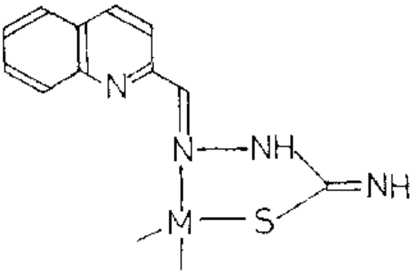
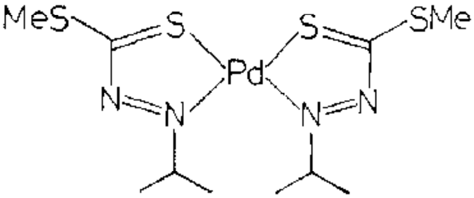


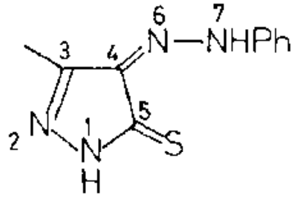
(98)

The preference for the formation of 5-membered chelate rings is also shown in dithiocarbazato complexes. The pseudo-planar coordination about palladium in (99) is considerably less distorted than in its nickel analogue [254]. Palladium complexes of tetradentate bis(dithiocarbazates) formed by reaction of R^{1}COCOR^2 and NH$_2$NHCS$_2$Me have also been studied [255].



(99)

Palladium(II) and platinum(II) acetates react with L, 1 phenyl 3 methyl-4-phenylazopyrazole-5-thione (100), to give [ML$_2$] in which the ligand is bound through sulphur and N(7) [256,257]. Complexes of 4-amino-3,5-dimercapto-1,2,4-triazole (101) were thought to be polymeric with binding through NH_2 and deprotonated SH [258].



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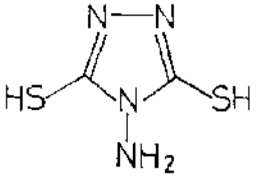

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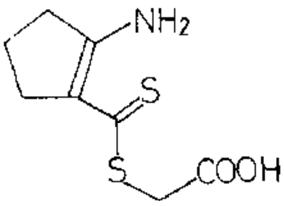


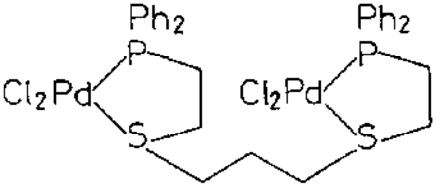
(102)

2-Aminocyclopentene dithiocarboxylate reacts with chloroacetic acid to give (102), which acts as an *N,S*-donor towards palladium in a complex of unknown stereochemistry, containing a 6-membered chelate ring [259].

Bridged derivatives of isothiourea are synthesised from $[Pt(en)(SCN)_2]$; under analogous conditions species derived from monodentate amines give complex polymers [260].

5.5.2.12 Bidentate sulphur-phosphorus donor ligands

Palladium(II) and platinum(II) complexes of $Ph_2PCH_2CH_2SEt$ and $Ph_2PCH_2CH_2SPh$ undergo irreversible two electron reduction [261]. $Ph_2PCH_2CH_2S(CH_2)_3SCH_2CH_2PPh_2$ forms a bis(palladium) complex (103); Pd–Cl bond lengths show a stronger *trans*-influence for phosphorus than for sulphur [262]. The ligand (104), with a variety of potential binding sites, reacts with $[(PhCN)_2PdCl_2]$ to give a complex bound through sulphur and phosphorus [263].



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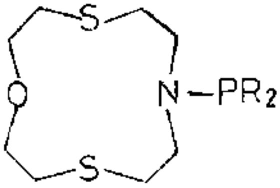

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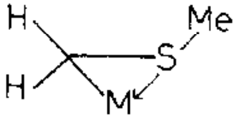
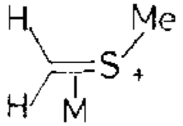
5.5.2.13 Bidentate sulphur-carbon donor ligands

The ligand CH_2SMe has three possible coordination modes **(105a–c)**. X-ray diffraction studies of $[Pd(PPh_3)_2(CH_2SMe)][PF_6]$ show it to belong to the class of **(105a)**, whilst the perchlorate, which is a less strong ion pair, has the **(105b)** structure [264].



(105a)

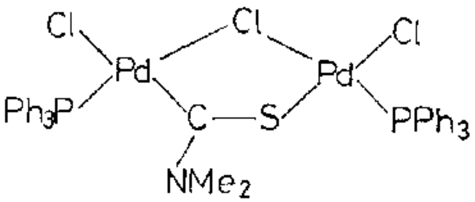


(105b)

MCH_2SMe

(105c)

Ligation of $R_2N{=}C{=}S$ may occur through carbon in an η^1 mode, or through carbon and sulphur (η^2). However, there is quite a strong preference for a bridging mode, and this is found in **(106)**, the product of the reaction of $[Pd(PPh_3)_2(SCNMe_2)Cl]$ with $PdCl_2$ [265].



(106)

5.5.2.14 Selenium donor ligands

Reaction of $PdCl_2$ with RSeCN in MeOH/NaOAc gives a complex of stoicheiometry $[Pd(RSeCN)Cl_2]$, which is probably dimeric or polymeric. In CH_2Cl_2 monomeric $[Pd(RSeCN)_2Cl_2]$ is obtained [266].

5.5.3 Complexes with amino acids, peptides and nucleic acids

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

5.5.3.1 Amino acids

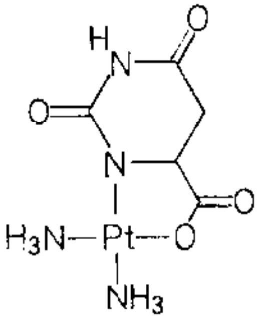
Thermal analysis curves for a number of known palladium glycine complexes are reported [267]. $[Pt(en)(NH_2CH_2COOH)Cl]Cl$ and $[Pt(en)(NH_2CH_2COO^-)]Cl$ were prepared and characterised, and the ring closure reaction studied potentiometrically [268]. Reaction of $[Pd(bipy)(OH_2)_2]^{2+}$ with an amino acid ester gives essentially complete formation of a chelate complex. A substantial (10^5-10^6-fold) acceleration is found for aqueous hydrolysis in these complexes, in contrast to the reactions of the methyl-L-cysteinate and histidinate complexes in which the carboxyl group is not metal coordinated. The results are compared with the previously reported data on $[Pd(en)(H_2NCHRCOOR')]^{2+}$, showing a small but measureable enhancement obtained using the bipy ligand, which is able to act as a π-acceptor [269].

The effect of electrostatic interactions and hydrogen bonding on selectivity in formation and side chain motion in ternary bis(amino acid) palladium complexes has been studied by CD and ^{13}C NMR measurements [270].

Bis(4-hydroxy-L-prolinato)palladium(II) has *cis*-square-planar coordination on the basis of X-ray diffraction measurements [271]. The platinum atom in $Cs[Pt($*N*-methyl-L-hydroxyprolinato$)Cl_2]$ is also coordinated by nitrogen and carboxylate [272]. Reaction of $[Pt(NH_3)_2(OH_2)_2]^{2+}$ with orotic acid gives three products as yellow needles, green needles and blue microcrystals. The yellow and green needles appear to be essentially identical and to have the structure **(107)** [273].

Detailed NMR spectroscopic and X-ray studies of *cis*-$[Pt($*S*-ethylcysteine$)Cl_2]$ confirm the existence of two isomers differing in chirality at sulphur, in both the solid state and solution. The *S,N*-chelate is in the λ-conformation, as found in other metal cysteine complexes [274]. CD spectra of palladium(II) complexes of D-cysteine may be used as a test for racemisation in a range of reactions [275]. Palladium and platinum complexes, $[LMCl_2]$, of *S*-2-aminoethyl-L-cysteine and *S*-2-aminoethyl-D,L-penicillamine hydrochloride have been prepared. Coordination is through sulphur and the amino acid NH_2, but some interaction with the carboxylate group is also indicated [276]. Coordination of NH_2 and carboxylate is proposed for cysteine complexes with Pd(phen) and Pd(bipy) but evidence for this unusual binding mode is weak [277].

$K_2[PdCl_4]$ reacts with (108) to give $[PdLCl_2]$, in which (108) is coordinated only through the NH_2 group [278].



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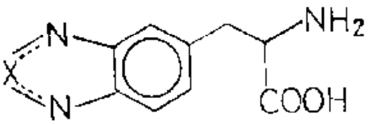
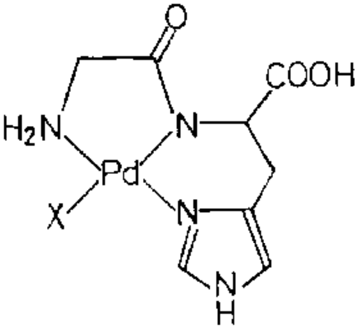


(108; X = S or Se)

5.5.3.2 *Peptides*

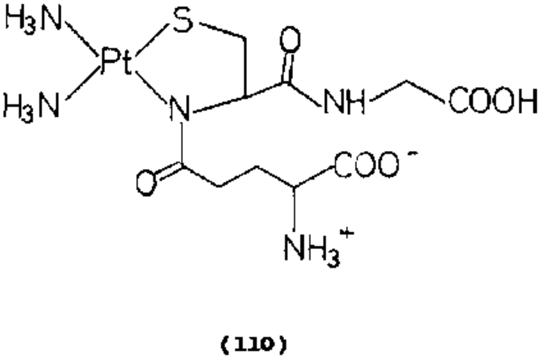
When palladium(II) reacts with gly-gly, initial coordination is thought to be through the amino group. Ionisation of the amido NH is metal induced and a tridentate peptide complex bound through amino, deprotonated amido, and carboxylate groups is formed. Some deviations from this established pattern are emerging. At low pH, gly-his forms (109), since the imidazole ring provides an excellent binding site [279]. In *trans*-[Pt(gly-gly)$_2$Cl$_2$)] the



(109)

peptide is monodentate, coordinating through the free amine. Judicious changes of pH may lead to formation of *N,N*- and *N,O*-chelates [280]. Thermolysis of *trans*-[Pt(NH$_2$CHRCONHCH(CH$_3$)COOEt)$_2$] gives *trans*-[Pt(NH$_2$CHRCONH)$_2$] as well as ligand degradation and decarboxylation [281].

The interaction of [(NH$_3$)$_2$PtCl$_2$] with cysteine gives a yellow product of unknown structure, which contains a sulphur platinum bond. The analogous reaction with glutathione is a model for protein binding and yields (110). A *trans*-bis complex may be obtained with excess ligand [282]. The interaction of



(110)

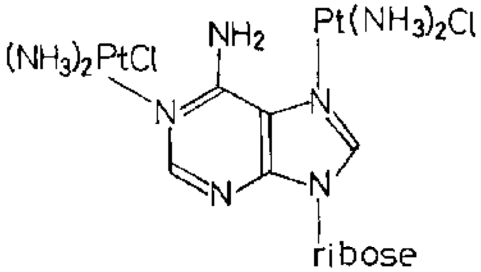
palladium(II) with peptides containing *S*-methylcysteine gives complexes bound through NH_2, deprotonated amide and SMe donors. Binding of the sulphur atom gives a new chiral centre, and inversion at sulphur is slow at pH < 9. Two diastereomers may consequently be distinguished [283].

Platinum peptide complexes, $[Pt(NH_2CHRCONHCHR'COOEt)_2X_2]$ may be synthesised by three distinct routes. The first involves treatment of $[PtX_4]^{2-}$ with the peptide ester, whilst the second uses carbodiimide to couple $[Pt(NH_2CHRCOOH)_2Cl_2]$ with $H_2NCHR'COOEt$. A good yield is also obtained on treating the bis-chelate, *cis*-$[Pt(NH_2CHRCO_2)_2]$ with acidic ethanol [284]. Ternary complexes of inosine with palladium peptide derivatives were studied by ^1H NMR spectroscopy. Rotamer fractions changed significantly on binding of the inosine to gly-phe and gly-asp complexes [285].

5.5.3.3 Nucleic acids and nucleosides

The electronic structures of 3-methyl and 9-methyl adenine (3-MeA, 9-MeA) were explored by INDO. Binding of the 3-methyl compound is, as the theory predicts, through N(7), as shown in an X-ray diffraction study of *cis*-$[Pt(NH_3)_2(3\text{-MeA})_2]^{2+}$ [286]. Reaction of *cis*-$[Pt(NH_3)_2(1\text{-methylthyminato})Cl]$ with $Ag[ClO_4]$ and then 9-MeA gives four products, two of which can be isolated in a pure state. As predicted by theory N(1) and N(7) are of similar basicity, and the products include N(1) and N(7) bound monomers and an N(1)-N(7) adenine bridged dimer [287]. The preparations of $[Pt(AdH+)Cl_3]$ and $[Pt(Ad)(OH_2)Cl_2]H_2O$ (Ad = adenine, (11)) are reported; in both cases adenine is N(7) coordinated [45]. The kinetics of the reaction of 5'AMP with $[(NH_3)_2PtCl_2]$ have been studied by ^1H NMR spectroscopy. Two pathways are involved as either N(1) or N(7) is initially coordinated to the metal, with subsequent reaction giving the N(1)-N(7) bridged dimer (111). By contrast 5'GMP gives two rapidly interconverting rotamers with platinum bound to N(7) [288].

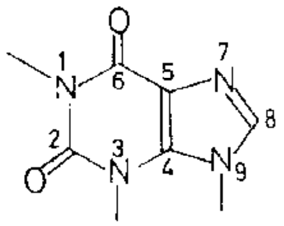
$K_2[PtCl_4]$ reacts with GMP to give $[Pt(GMP)Cl_3]^-$ and $[Pt(GMP)_2Cl_2]$, with binding at the favoured N(7) position. ^1H NMR spectroscopic studies indicate that the conformation of the sugar ring is altered on binding to platinum [289]. X-ray diffraction studies are reported on bis(guanosine) derivatives



(111)

of chelating diamine platinum complexes [290] and *cis*-$[Pt(NH_3)_2(N^2,N^2\text{-dimethyl-9-methylguanine})Cl][PF_6]$ [291]. In a considerable range of mixed nucleobase complexes such as cis-$[Pt(NH_3)_2(\text{9-ethylguanine})(\text{1-methylcytosine})][ClO_4]_2$ the three dimensional structure is maintained by intra and intermolecular H-bonds [292]. Mixed complexes containing 9-ethylguanine and 1-methylthymine anion (N(3) bound) also show N(7) binding [287]. In $[Pt(\text{guanineH}^+)Cl_3].MeOH$ the binding is similar, but for $[Pt(\text{guanine-H})_2Cl_2].7H_2O$ guanine binds as a bidentate ligand through N(7) and the C(6) oxygen, with chloride bridges [45]. Participation of the C(6) oxygen is excluded in $[Pd(NH_3)_2(dmso)(nucl)]Cl_2$ for nucl = inosine, guanosine or cytidine [293]. Further evidence for the kinetic binding of *cis*-$[(NH_3)_2PtCl_2]$ to DNA at N(7) of guanine with the formation of intrastrand dGpG crosslinks is accumulating [294,295].

The DNA crosslink G[N(7)]-Pt-G[N(7)] may be modelled in complexes of 1,3,9-trimethylxanthine (1,3,9-tmx) (**112**). *Cis*-$[Pt(en)(1,3,9\text{-tmx})_2]^{2+}$ was characterised by X-ray diffraction; N(7) is Pt-coordinated but there is no participation of the 6-oxo group [296]. In the Pt(en) complex of 7,9-dimethylhypoxanthine, platinum is coordinated to N(1) of the ligand (**113**); O(6) is not coordinated but is hydrogen bonded to the nitrogen of



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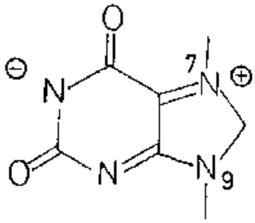
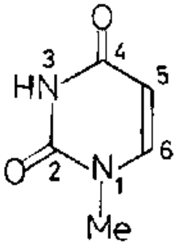


(113)

en [297]. The corresponding bis(ammine) complex may be compared, and is proposed as a model for a 5'-IMP[(N(1)]-Pt-[N(1)]5'-IMP interaction. In this case N(1) is bonded as before, with the ligands in a head-to-tail arrangement. However, the Pt-O(6) distance, 3.086 Å, implies a small but significant interaction with oxygen in the axial direction [298]. A head-to-tail arrangement of ligands is also found in *cis*[(bis{pyridin-2-yl}ethane)Pt(9-methylhypoxanthine)$_2$][NO_3]$_2$. Rotation about the Pt-N(7) bond is slow on the NMR time scale, with $\Delta G^{\ddagger} \sim 50$ kJ mol^{-1} [299].

Further studies of the coordination of the tautomers of uracil and thymine to platinum(II) are reported. The binding modes may be distinguished by a combination of IR and Raman spectroscopy. *Trans*-[Pt(NH_3)$_2$(dmf)Cl][NO_3] reacts with potassium thyminate (KHT) to give two isomers of *trans*-[Pt(NH_3)$_2$(HT)Cl], bonded through N(1) and N(3) respectively. The N(1) and N(3) bound isomers of [Pt(NH_3)$_3$(HT)]X and [Pt(NH_3)$_3$(T)] are similarly differentiated. A bridged N(1)-N(3) dimer and platinum thymine blue were also studied [300]. Full X-ray structural data are reported for [{*cis*-(Pt{NH_3}$_2$)$_2$(μ-1-methylthyminato)$_2$}MnCl_2].10H_2O [301].

X-ray diffraction data are reported for *cis*-[Pt(NH_3)$_2$(1-methyluracil)$_2$].4H_2O, (1-methyluracil = 1-MeU) in which N(3) of **(114)** is bonded to platinum. Reaction of this complex with copper(II) gives platinum-copper species of 1:1 and 2:1 stoicheiometry. In the 1:1 species, *cis*-$[Pt(NH_3)_2(1\text{-}MeU)_2Cu(H_2O)_2][SO_4]$, both metals are square planar and N(3) of the ligand is bound to platinum, whilst O(4) is bonded to copper [302]. Treatment of the head-to-tail dimer *cis*-$[Pt_2(NH_3)_4(1\text{-}MeU)_2][NO_3]_2$ with $Ag[NO_3]$ gives $[Pt_4(NH_3)_8(1\text{-}MeU)_4Ag]^{5+}$. X-ray diffraction studies show that this contains two dimer units, bridged by a silver atom which is coordinated to the four O(2) atoms of 1-MeU [85]. A range of complexes of 1-methylcytosine ((115), 1-MeCyt) with $\{(NH_3)_2Pt\}$ is reported. As well as the previously described 1:1 complexes, *cis*-$[(NH_3)_2Pt(OH_2)]^{2+}$ gives dimeric, N(3)–N(4) bonded, complexes with deprotonated 1-MeCyt, and with excess ligand $[Pt(NH_3)(1\text{-}MeCyt)_3]^{2+}$ is formed. In the latter, two of the ligands are bound to platinum through N(3) in a head-to-tail arrangement, allowing intramolacular hydrogen bonding between O(2) and N(4) of the nucleosides [303,304]. N(3) bonding is also demonstrated in the analogous perchlorate salt [305].



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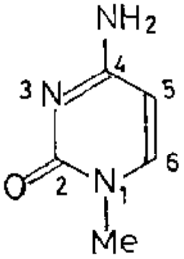
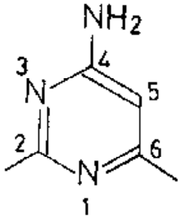


(115)

The stereochemistry of the complexes, $[PdL_2X_2]$, formed from $K_2[PdCl_4]$ and a wide range of pyrimidine bases, has been studied. With the exception of the cytosine complex, the initially formed *cis*-isomer could not be isolated. Both *cis*- and *trans*-$[Pd(cytosine)_2Cl_2]$ react with thiourea to give $[Pd(tu)_4Cl_2]$, rendering doubtful stereochemical arguments based on Kurnakov's test [306].

Treatment of $[(amino\ acid)PtCl_3]^-$ complexes with purine and pyrimidine bases gives *cis*-$[(amino\ acid)(nucleotide)PtCl_2]$ complexes. Adenine and guanine bind through N(7), cytosine and uracil through N(3), whilst hypoxanthine forms dimers of stoicheiometry $[Pt_2(alaH)(hypoxanthine)Cl_4]$, bridging through N(3) and N(9) [307].

4-Amino-2,5-dimethylpyrimidine, (admpy, **(116)**), reacts with $K_2[PdCl_4]$ to yield $[Pd(admpy)_2Cl_2]$. NMR spectroscopic data are consistent with binding only at N(1) in this complex, and also in $[Pt(admpy)Cl_3]^-$ and $[Pd(admpy)Cl_3]^-$, despite the steric hindrance of the methyl groups [308,309]. The preferred metal binding site of vitamin B1 (Th, **(117)**) is N(1'), but IIB metals, especially mercury, may bind at N(3') leaving N(1') available. Reaction of $Hg(Th)Cl_4$ with palladium(II) gives $[HgPd(Th)Cl_3]$ *via* $[HgCl_2Pd(Th)Cl_3]$, but evidence for the precise mode of binding is not available [310].



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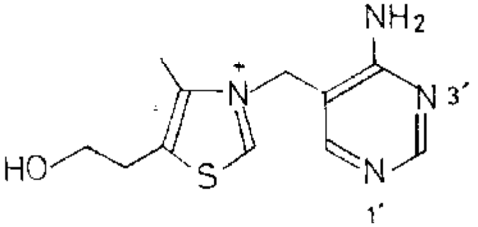
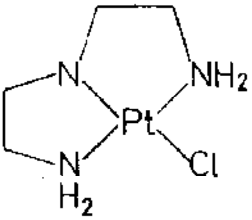


(117)

The complex **(118)** binds to N(7) of deoxyguanosine in poly-dG-dC and poly-dG-dC; having only one available binding site is cannot form crosslinks. With binding to < 10% of the nucleotide bases the amount of ethanol needed to bring about the B-Z conformational transformation is considerably reduced. Although **(118)** does not bind any more effectively to the Z form, it is thought to stabilise it through electronic and hydrogen bonding interactions [311].

5.5.3.4 Cancer chemotherapy

Further studies on the nature of the products of aquation of *cis*-$[(NH_3)_2PtCl_2]$ are reported [312]. The formation of $[(NH_3)_2Pt(\mu\text{-}OH)_2Pt(NH_3)_2]^{2+}$, (119), is proposed to occur before interaction with DNA. EXAFS spectroscopy above the Pt L_3 edge was used to study the platinum environment in the complex formed from (119) and calf thymus DNA. The most definitive observation was that a short Pt-Pt distance exists in the Pt-DNA complex [313].



(118)

A new range of complexes of general formula $[Pt(NXNH^+)Cl_3]$, where NXN is nicotine, 3-amimomethylpyridine, 1,2-bis(4-pyridyl)ethane or piperazine, has been tested against murine leukaemic cells L1210, which are resistant to $[(NH_3)_2PtCl_2]$ [48]. *Cis*-$[(NH_3)_2PtCl_2]$ causes immediate and long lasting decreases of mitotic acyivity of Ehlich tumour cells [314].

5.5.4 Complexes with Group V donor ligands

5.5.4.1 Unidentate amine donor ligands

Treatment of $[Pd(NH_3)_4]Cl_2$ with potassium iodide gives $[Pd(NH_3)_4]I_8$, in which coordination about palladium remains strictly square planar [315]. Reaction of $[Pt(NH_3)_4]^{2+}$ with a hydrated electron gives the transitory platinum(I) species, $[Pt(NH_3)_4]^+$, which releases ammonia in two steps giving $[Pt(NH_3)_2(OH_2)_2]^+$ and subsequently colloidal platinum [316].

The thermal stability of *cis*-$[Pd(NH_3)_2Cl_2]$ has been further investigated. Isomerisation to the *trans*-complex is the first process observed, followed, at 250 °C, by the irreversible formation of a new crystalline modification β-*trans*-$[Pd(NH_3)_2Cl_2]$ [317]. *Cis*-$[Pt(NH_3)_2XY]$ (X = Cl, Br, I or NO_2; Y = NO_2 or Cl) is less stable to γ-irradiation than the *trans*-isomer, though both eventually decompose to platinum metal, ammonia and halogen [318]. Kinetic [319] and theoretical [320] studies of $[M(NH_3)_2Cl_2]$ (M = Pd or Pt) have also been reported.

The hydroxo bridged complex $[(NH_3)_2Pt(\mu\text{-}OH)_2Pt(NH_3)_2]^{2+}$, has been studied from several viewpoints. A full normal coordinate analysis was performed [321], and the laser Raman spectrum of this and ^{18}O and D-labelled analogues recorded [322]. ^{195}Pt NMR studies of *cis*-$[Pt(ND_3)_2(OD)_2]$, $[(D_3{}^{15}N)_2Pt(\mu\text{-}OD)_2Pt({}^{15}ND_3)_2]^{2+}$ and the hydroxo bridged trimer, $[Pt_3({}^{15}ND_3)_6(\mu\text{-}OD)_3]^{3+}$, show that changes in $^{15}N\text{-}Pt$ coupling constants are related to *trans*-effects [323].

cis-$[Pt(NH_3)_2(NO_2)_2]$ reacts with phosphoric acid to give a complex mixture of intermediates (A), the fate of which depends on the reaction conditions (Scheme 2). **(120)** and **(122)** are thought to be polymeric with bridging phosphate ligands [324].

$$\begin{tikzcd}
\text{cis-}[Pt(NH_3)_2(NO_2)_2] \arrow[r, "H_3PO_4"] & A \arrow[dl, "\text{cool, } H_2O"'] \arrow[dr, "130\text{–}140\ ^\circ C"] & \\
{[Pt(NH_3)_2(NO_2)_{1.875}(H_2PO_4)_{.125}(H_3PO_4)]H_2O} & & {[Pt(NH_3)_2(NO_2)(H_2PO_4)]} \\
\mathbf{(120)} & & \mathbf{(121)}
\end{tikzcd}$$

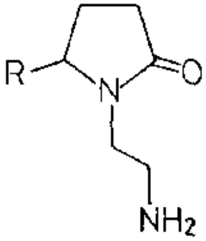
$$A \xrightarrow{100\text{–}105\ ^\circ C \text{ then } H_2O,\ 40\text{–}50\ ^\circ C} [Pt(NH_3)_2(NO_2)_{1.875}(H_3PO_4)_{.125}]$$

(122)

Scheme 2 Reactions of *cis*-$[Pt(NH_3)_2(NO_2)_2]$ with phosphoric acid [324].

$[Pt(NH_3)_2(bipy)]^{2+}$ forms 1:1 complexes with a range of crown ethers *via* NH_3-polyether-O hydrogen bonds, the polyether being in the second coordination sphere. There is a charge transfer exchange between the phenyl rings of dibenzo-18-crown-6 and the aromatic rings of the bipy ligand [325].

Cyclopropylamine reacts with $K_2[PtCl_4]$ under carefully controlled conditions to give *cis*-$[PtL_2Cl_2]$, the structure of which was defined by X-ray diffraction [326]. Analogous *cis*-complexes of 5-alkyl-N-β-aminoethyl-2-pyrrolidone , (123), all coordinate through the amino NH_2 and are weak antibacterials [327].



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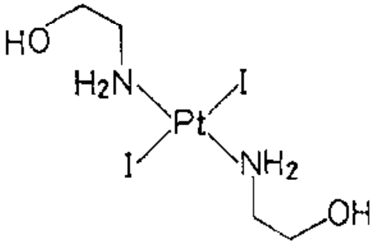


(124)

A ^1H NMR study of *trans*-$[Pt(H_2NMe)(\eta^2\text{-alkene})Cl_2]$ complexes was reported [328].

X-ray diffraction studies of (124) show a structure stabilised by intermolecular hydrogen bonds between OH groups [329]. Hydrogen bonding is also important in *trans*-bis(iminodiacetamide)$Pd^{II}Br_2$. $HN(CH_2CONH_2)_2$ acts as a terdentate ligand towards copper and nickel, but with palladium(II) the NH is bound to the metal and is hydrogen bonded to both the carbonyl groups in the same ligand [330].

The complexes *cis*-$[M(3\text{-aminocoumarin})_2X_2]$ (M = Pd or Pt; X = Br, I or SCN) are converted to the *trans*-isomers between 105 and 240 °C. The chloro compounds isomerise and decompose at a higher temperature [331].

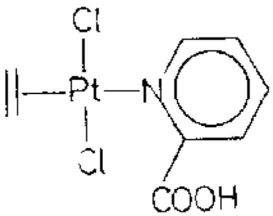
IR spectroscopic studies of *cis*- and *trans*-$[Pt(NH_2Ph)_2Cl_2]$, *cis*-$[Pt(NH_2Ph)_2Br_2]$ and D and ^{15}N labelled analogues allows the assignment of

Pt-N and Pt-X frequencies [332,333]. The stereochemical purity of *cis*- and *trans*-$[PtL_2Cl_2]$ complexes is very important in the search for active chemotherapeutic agents. Treatment of $K[Pt(NH_2Ph)Cl_3]$ with $PhNH_2$ gives pure *cis*-isomers. The *trans*-compound is formed on dissolution in dmf. Isomers were identified from their IR spectra, as Kurnakov's test proved unreliable [334].

Reaction of $K_2[MCl_4]$ (M = Pd or Pt) with fluorinated anilines, L, gives $[ML_2Cl_2]$ of unspecified stereochemistry [335].

5.5.4.2 Unidentate heterocyclic nitrogen donor ligands

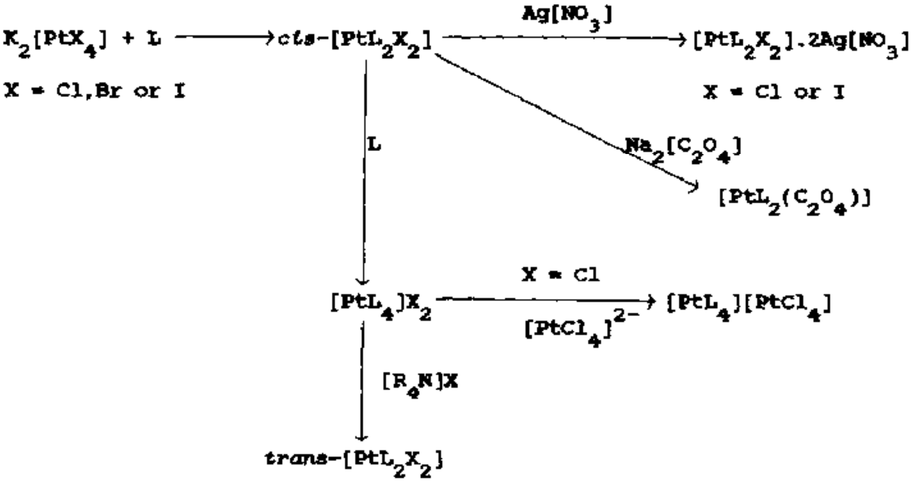
Reaction of $[Pt(py)_2(OH)_2]$ with a carboxylic acid gives *trans*-$[Pt(py)_2(O_2CR)_2]$, which decarboxylates on heating to $[R_2Pt(py)_2]$. The same products are obtained on heating $K_2[PtCl_4]$ with thallium carboxylates in the presence of pyridine [336]. The complexes $[PdL_2Cl_2]$ with L = 2-octylaminopyridine or 4-vinylpyridine both have ligand coordination only through the pyridine nitrogen [337,338]. *Cis*-$[Pt(nicotinic\ acid)_2Cl_2]$ decomposes on heating to give a binuclear complex, without decarboxylation [339]. Broadening of ^{195}Pt satellites in the ^1H NMR spectrum of (**125**) arises from ^{195}Pt relaxation *via* chemical shift anisotropy [340].



(125)

The IR spectra of *cis*- and *trans*-bis(pyrazine)platinum dihalides are reported [341]. Both 2,2'-thienylpyridine and thieno[2,3-b]pyridine complex with palladium only through the pyridine nitrogen, with no evidence for sulphur binding [342]. In *trans*-bis(2,4-dimethyl-6-hydroxypyrimidine)palladium(II) and platinum(II) chlorides it is proposed that the OH groups interact weakly with the metal, which is not possible with the *cis*-isomers [343].

Assignments of ν_{Pt-N} and ν_{Pt-X} in *cis*- and *trans*-$[Pt(imidH)_2X_2]$ complexes have been accomplished by comparison with deuterated derivatives [344]. The redox potentials of these and substituted imidazole complexes are rather similar to pyridine analogues [345]. In the presence of KI, $[Pt(1\text{-Meimid})_4]^{2+}$ gives $[Pt(1\text{-Meimid})_4][I_3]_2$, the structure of which was established by X-ray diffraction [346]. A series of complexes of 1-vinylimidazole, L, was prepared (Scheme 3) [347].



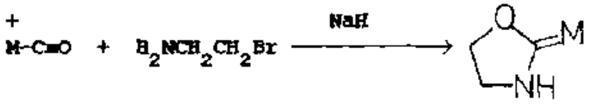
Scheme 3 Synthesis of complexes of 1-vinylimidazole [347].

The solid phase transformations of bis(benzimidazolium) tetrachloroplatinate(II) and palladate(II), $[LH]_2[MCl_4]$, differ somewhat. $[LH]_2[PtCl_4]$ gives $[PtL_2Cl_2]$ by an Anderson rearrangement between 155 and 190 °C, whereas $[LH]_2[PdCl_4]$ gives initially $[LH][PdLCl_3]$ which, on further heating, gives $PdCl_2$ [348]. Solid phase thermolysis of *cis*-$[PtL_2(SCN)_2].2H_2O$ gives loss of water at 105 °C and isomerisation to *trans*-$[PtL_2(SCN)_2]$ at

145 °C. The *cis/trans* isomerisation temperature differs little from that for *cis*-$[Pt(imidH)_2(SCN)_2]$ [349].

The crystal structure of *trans*-$[Pt(C_2H_4)(pyrazole)Cl_2]$ shows that the complex is almost planar, and the IR spectrum implies H-bonding between the pyrazole NH and chlorine [350].

The electrophilic carbonyl ligands in metal complexes may be converted (reaction (7)) to cyclic aminoxy or dioxocarbene ligands.



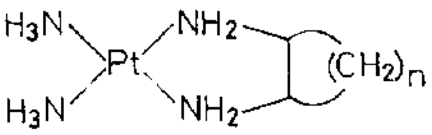
(7)

$[(cp)Fe(CO)_2(\overline{COCH_2CH_2N})]$is prepared in this way and reacts with $[(MeCN)_2PdCl_2]$ to give *sym,trans*-$[\{(cp)Fe(CO)_2(\overline{COCH_2CH_2N})Pd(\mu\text{-}Cl)Cl\}_2]$, where palladium is coordinated to the nitrogen atom [351].

5.5.4.3 Bidentate and polydentate amine donor ligands

The reactions of $H_2N(CH_2)_nNH_2$ (n = 2-6) with $[Pt(dmso)Cl_3]^-$ depend on the length of the carbon chain. For n = 2 or 3, only the chelate $[Pt\{H_2N(CH_2)_nNH_2\}(dmso)Cl]^+$ is isolated. However, for $n \geq 5$, monodentate amine complexes $[Pt\{H_2N(CH_2)_nNH_2\}(dmso)Cl_2]$ are isolable and entry of a second amine is favoured over ring closure. For n = 4 ring closure and the second substitution compete [352]. The kinetics of ring closure in *trans*-$[Pt(NH_3)\{H_2N(CH_2)_nNH_3\}Cl_2]^+$ also depend on n. The differences in the rate constant on changing ring size derive from changes in $\Delta H^\ddagger$ rather than $\Delta S^\ddagger$, in contrast to purely organic systems [353]. Similar observations were made for $[Pt\{Me_2N(CH_2)_nNMe_2\}Cl_3]^-$ (n = 2 or 3); the five membered ring is formed 183 times faster than the six membered analogue, and the methyl groups engender a 50-100 fold Thorpe-Ingold rate enhancement compared with primary amines [354].

Chelate complexes of 3,3-dimethyl-1,2-diaminobutane (dmbn) are restricted to the conformation in which the *tert*-butyl group is equatorial. Conformations of diamine, 5-membered, chelate rings have been studied by ^{1}H and ^{13}C NMR spectroscopy [355], and CD measurements [356]. It was concluded that in $[Pt(NH_3)_2(S\text{-}1,2\text{-}pn)]^{2+}$ the chelate ring is 70% δ, in accord with earlier reports. Quantitative CD and electronic spectral measurements may be made on microcrystalline $[Pt(S\text{-}1,2\text{-}pn)Cl_2$ in an alkali halide matrix [357]. X-ray diffraction studies on a six membered diamine chelate ring in $[Pt(bipy)\{(\pm)\text{-}2\text{-methyl-}2,4\text{-diaminopentane}\}][NO_3]_2.H_2O$ show it to adopt an unsymmetrical boat conformation, in accord with strain energy minimisation calculations. ^{1}H and ^{13}C NMR data indicate that the chair is the major solution conformation, but that the boat is also significantly populated [358]. The cytotoxic properties of platinum complexes of 1,2-diaminohexane, L, are different from those of $[(NH_3)_2PtCl_2]$. The formation of $[PtL(OH)_2]^{2+}$, $[LPt(\mu\text{-}OH)_2PtL]^{2+}$ and $[Pt_3L_3(\mu\text{-}OH)_3]^{3+}$ are pH dependent, the dimer and the trimer being less toxic than the monomer [359]. $^{2}J_{Pt-C}$ and $^{3}J_{Pt-C}$ for **(126a—e)** have been shown to vary considerably, increasing with ring strain. The relationship $^{3}J_{Pt-C} = 54\cos^{2}\phi$, where ϕ is the Pt-N-C-C dihedral angle, was established [360].

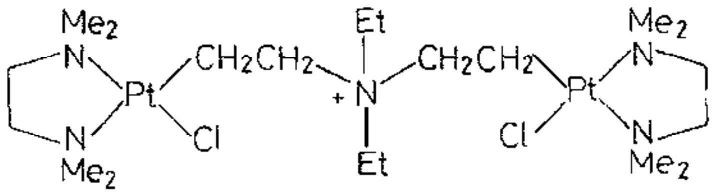


(126a) *cis*, *n* = 3 **(126b)** *trans*, *n* = 3

(126c) *cis*, *n* = 4 **(126d)** *trans*, *n* = 4

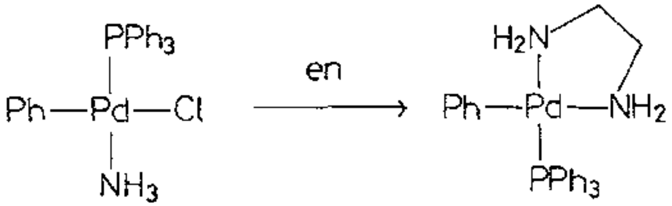
(126e) *trans*, *n* = 2

The ethene ligand in $[Pt\{Me_2N(CH_2)_2NMe_2\}(C_2H_4)Cl]^{+}$ is very reactive towards nucleophilic substitution and reacts with Et_2NH to give **(127)**. X-ray diffraction reveals roughly square planar coordination of platinum [361].



(127)

A range of substitution reactions involving chelating diamines have been examined. Typical examples are given by reactions (8) and (9). Treatment of (128) with en, however, gives (130), where metal promoted transamination as well as bridge splitting has occurred [362].



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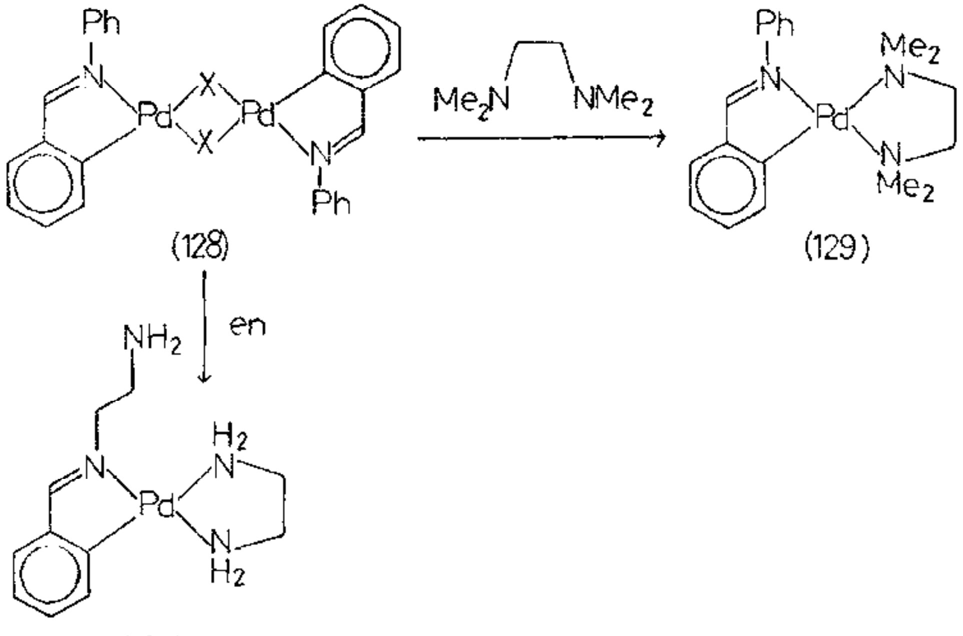


(9)

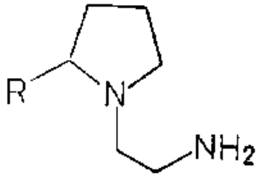
(128)

(129)

(130)

Both rates and equilibrium constants for the reactions of $[Pd(dien)X]^+$ with nucleophiles depend on X, and vary sensibly with changes in solvent, which principally affects leaving group ability [363]. The pressure dependence of anation of $[Pd(1,1,7,7\text{-}Et_4dien)(OH_2)]^{2+}$ by chloride was studied in a high pressure stopped flow system. Comparison with data for dien, Et_3dien and 4-methyl-1,1,7,7-Et_4dien complexes shows that rates decrease as steric hindrance increases. An interchange mechanism is indicated with high pressure data favouring I_a [364].

Both nitrogen atoms are metal coordinated in $[MLX_2]$ complexes of (131) (M = Pd or Pt; X = Cl, Br or I), prepared by treatment of $K_2[MX_4]$ with the ligand. These species function as effective fungicides and bacteriocides [365].

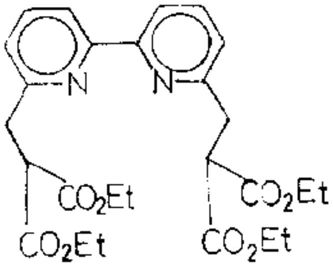


(131)

Palladium(II) and platinum(II) complexes of (13a) and (13b) have been characterised by NMR spectroscopy and DTA studies, but precise details of the structures are not well defined [49]. Further platinum(II) complexes of *N,N'*-ethylenediaminediacetic acid are reported; the ligand may be bi- or tridentate [37].

Studies of the electronic spectra of platinum(II) bipy complexes have been reported [366].

An X-ray diffraction study of the palladium(II) chloride complex of (132) shows that coordination about the metal is distorted towards the pyramidal, and the best plane of the four donor atoms surrounding the metal is bent by 40° out of the best plane for bipy [367]. Ligands such as (133) might be expected to experience considerable steric problems in becoming coordinated to palladium in a [Pd*N*$_4$] arrangement. However, preparation of [Pd{(133)}].H_2O proved relatively facile [368].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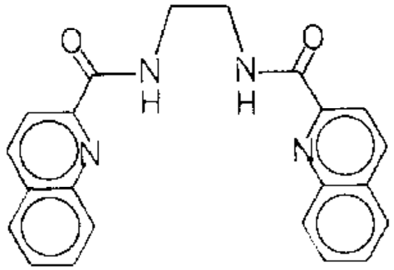
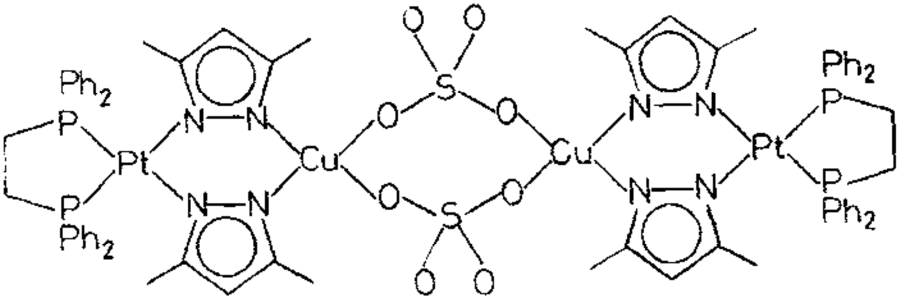

(133)

[(3,5-dimethylpyrazolyl)$_2$Pt(dppe)] reacts with copper(II) sulphate to form a 1:1 adduct. EPR studies restrict the possible structures for the adduct to (134) and (135) [369].

4,4',5,5'-tetracyano-2,2'biimidazole (L, (136)), which is a poor σ-donor but a strong π-acceptor reacts with $K_2[M(CN)_4]$ (M = Pd or Pt) to give $K_2[ML(CN)_2]$ [370]. 1:2 complexes of unspecified structure are formed between (137) and palladium(II) [371].

Palladium(II) complexes of the tetradentate tetraaza macrocycles, (138) and (139), have been characterised as models for corrin and porphyrin complexes [372,373]. [(TBP)Pt(II)] shows a strong phosphorescence at 745 nm, with a quantum yield of 0.18±0.04 [51]. The crystal structure of *N,N'*({benzyloxy}methylene)tetraphenylporphyrin-*N",N"'*-dibromopalladium(II), (140) shows the porphyrin ring to be highly distorted. The complex is proposed as a model for the intermediates in the synthesis of porphyrin complexes [374].



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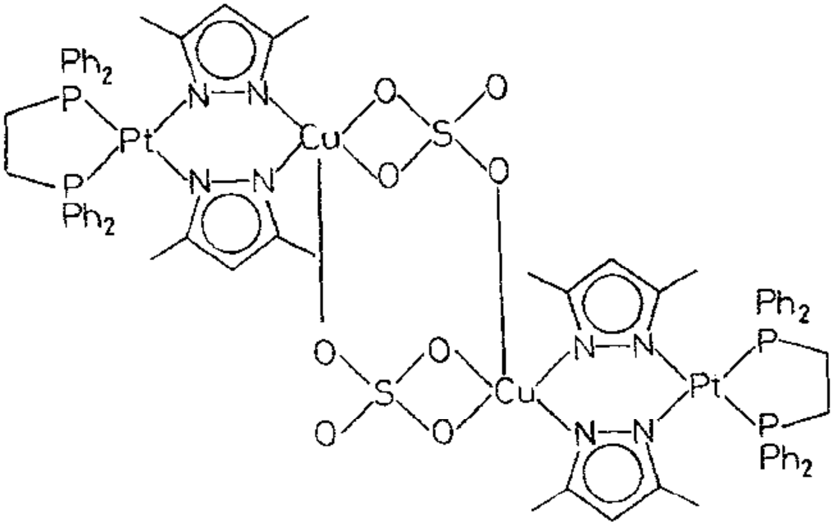

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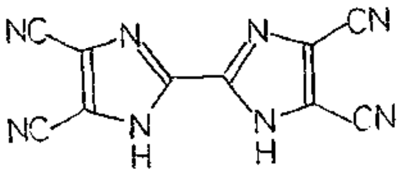

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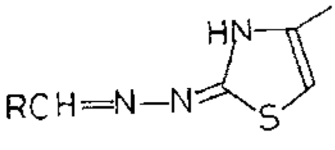

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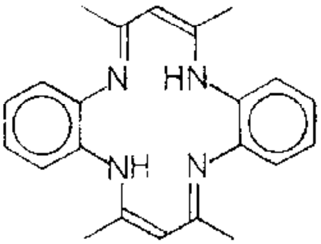

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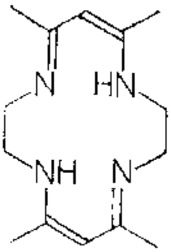

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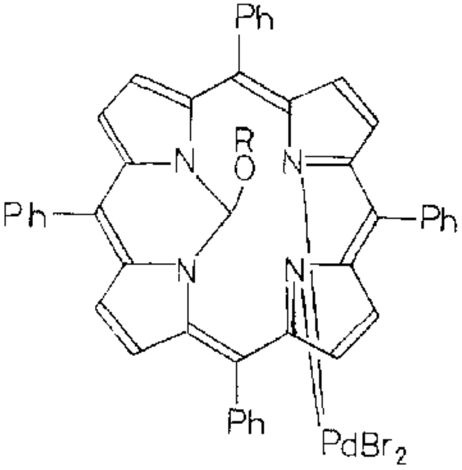


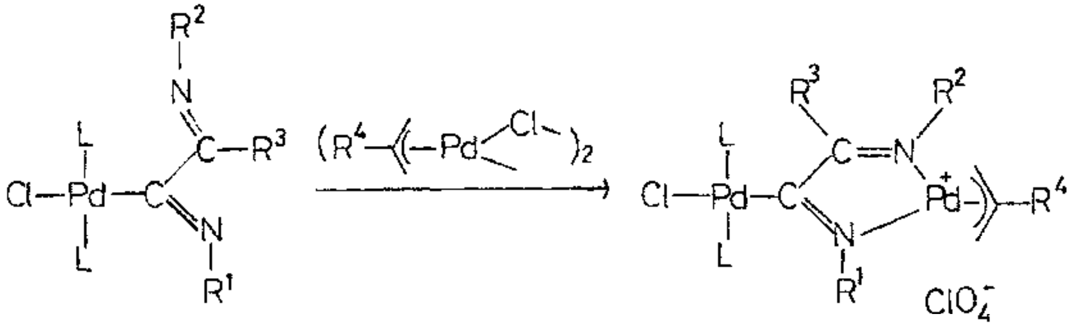
(140)

5.5.4.4 Imine donor ligands

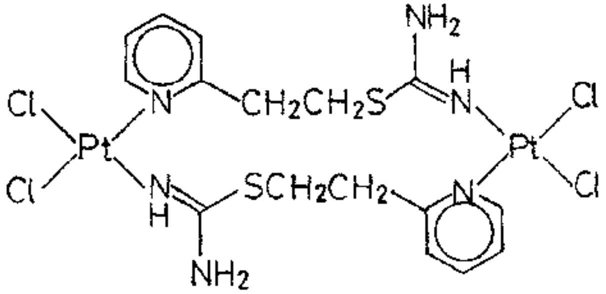
Treatment of the carbon bonded complex **(141)** with $[\{Pd(\eta^3\text{-}2\text{-}R^4\text{-}C_3H_4)Cl\}_2]$ in the presence of $Na[ClO_4]$, yields the chelating bis(imine) complex, **(142)** [375,376].

$Et_2NHCH_2CH_2SC(NH)NH_2$ coordinates in a monodentate manner *via* the imino nitrogen atom in $[Pt\{Et_2NHCH_2CH_2SC(NH)NH_2\}Cl_3]^-$, whereas pyridine α-ethylthiuramine acts as a bridge in the head to tail dimer **(143)** [377].

Spin exchange is realised by an indirect mechanism in a range of complexes such as **(144)** [378].



(141) **(142)**



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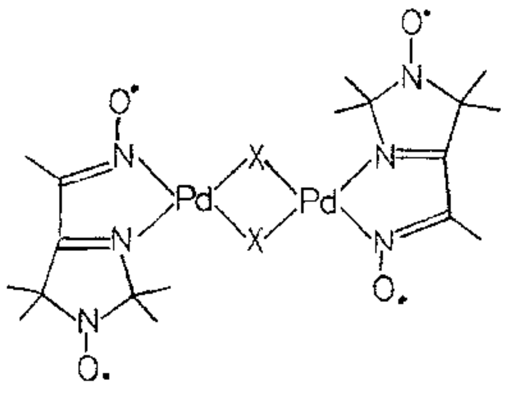
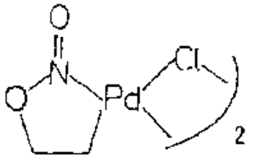


(144)

5.5.4.5 Nitro complexes

^{195}Pt NMR studies of the system $[PtCl_4]^{2-}/[NO_2]^-/Br^-$ are reported [44]. $[(MeCN)_2Pd(NO_2)Cl]$ reacts with ethene to give ketones *via* (145) [379].



(145)

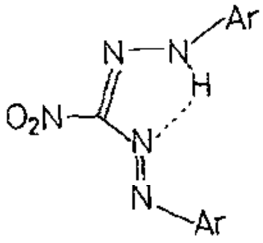
5.5.4.6 *Diazine, triazine and tetraazadiene ligands*

Diarytriazines, ArN=N-NHAr, may act as mono- or bidentate ligands. *Cis*- and *trans*-$[Pd(PR_3)_2Cl_2]$ both react to give *trans*-$[Pd(PR_3)_2(ArN-N=N-Ar)Cl]$. At room temperature these undergo an intramolecular dynamic process with rapid exchange of N(1) and N(3). Intermolecular exchange occurs but is much slower [380]. Reaction of $K_2[PtCl_4]$ with Ar-N=N-NHMe gives *cis*-$[Pt(Ar-N=N-NHMe)_2Cl_2]$, in which the triazine is monodentate. These have cytotoxic properties [381]. The extraction of palladium(II) with 1-(4-nitrophenyl)-3-(4'-azobenzene)triazine is reported [382].

Two palladium complexes are formed from 3-nitroformazan, **(146)**. The violet complex is a chloro bridged dimer, whilst the green species, formed in the presence of Ag^+ and an excess of ligand, has $[PdL_2]$ stoicheiometry. Both are said to contain an N(1)-N(3) five membered chelate ring, analogous to the corresponding nickel(II) complex [383]. Quite a different structure was assumed by Russian workers in **(147)**, a complex of 3-(4-oxo-3,5-di-*tert*-butylphenyl)-1,5-diphenylformazan, which is of interest in its radical form [384]. In neither paper was the evidence presented for the structures particularly convincing.

Tetraazadiene complexes of platinum(II) react with azide ions to give various exchange and rearrangement processes. For example, the 4-nitrophenyl compound **(148)** gives a mixture of products (Scheme 4) but the 4-chloro analogue is unreactive [385]. More complete details of the synthesis of tetraazadiene complexes from $[Pt(cod)_2]$ and $[Pt_3(tert\text{-}BuNC)_6]$ are reported.

$[Pt(Ar_2N_4)(cod)]$ reacts with Et_3P to give the bright blue compound $[Pt\{1,4\text{-}(4\text{-nitrophenyl})_2N_4\}\{\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH}_2\}(PEt_3)\}$, (149). X-ray diffraction showed roughly trigonal bipyramidal coordination with the PEt_3 and σ-bonded carbon axial and the π-acceptors, azadiene and η^2-alkene, equatorial [386].



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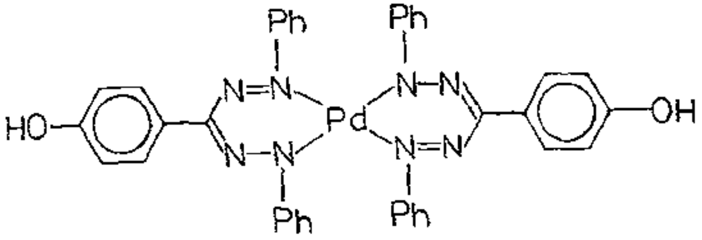

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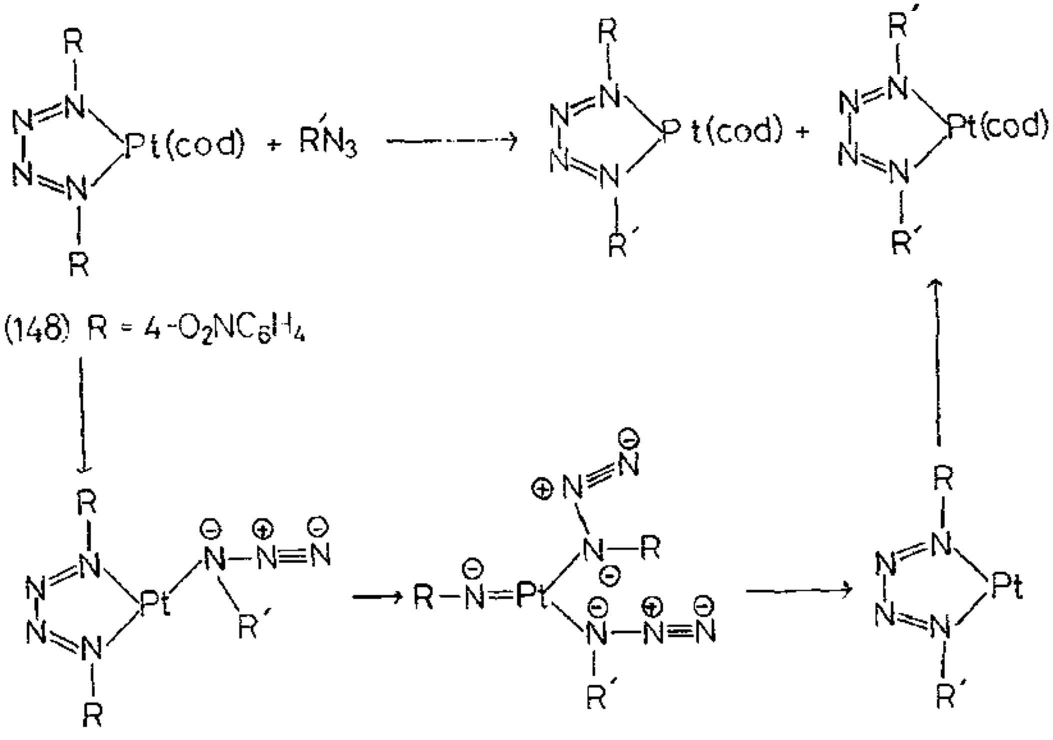
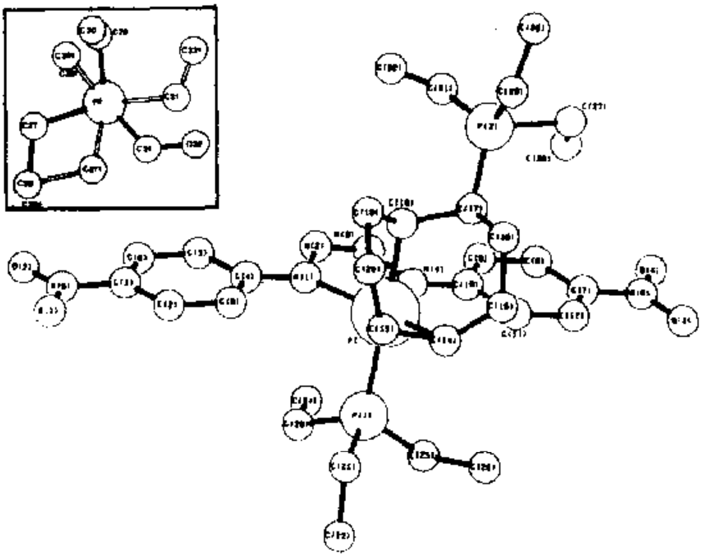


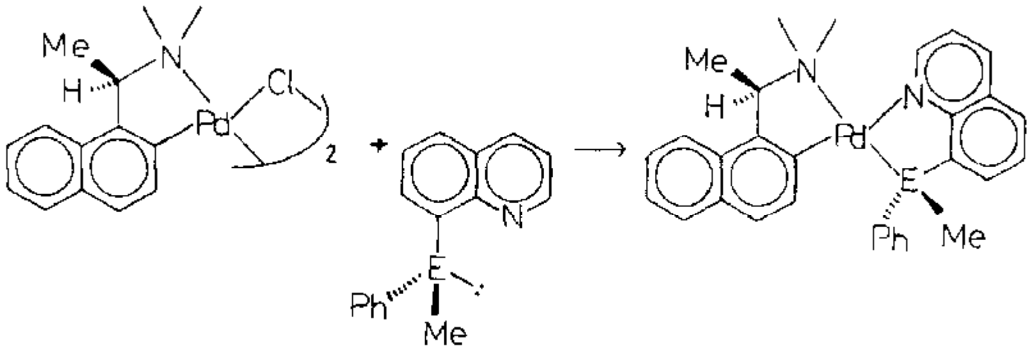
Scheme 4 Reactions of azide ion with tetraazadiene complexes [385].



(149)

5.5.4.7 *Bidentate nitrogen-phosphorus donor ligands*

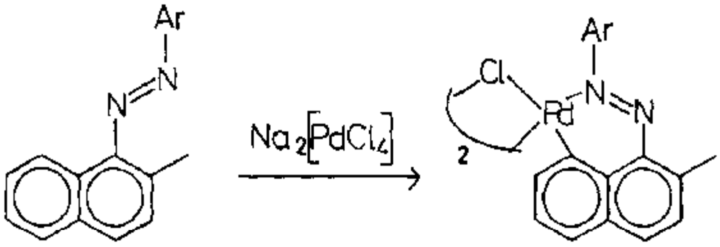
When (150) is treated with (151) (E = P or As), diastereomeric complexes (152) are produced and may be easily separated [387].



(150) (151) (152)

5.5.4.8 *Bidentate nitrogen-carbon donor ligands*

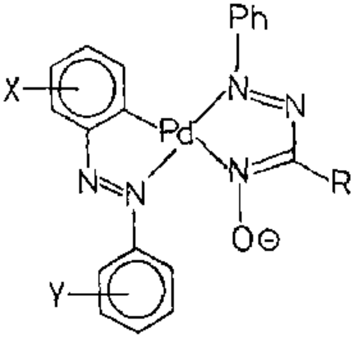
Cyclopalladation of (153) was studied by ^{15}N NMR spectroscopy; the six-membered rather than the five-membered product is formed (reaction (10)) [388]. About twenty complexes of the type (155) have been synthesised and



(10)

(153) (154)

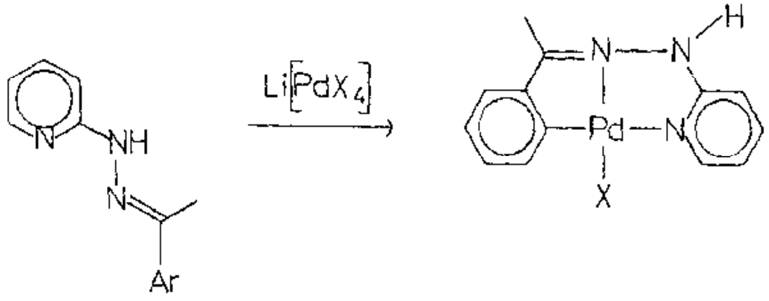
their electrochemistry studied; three cyclic voltammetric waves are found, the first two corresponding to reversible reduction of the azo ligand [389].



(155)

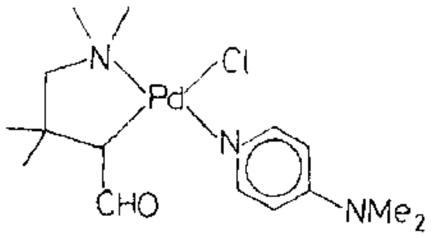
Reaction of lithium tetrachloropalladate(II) with the hydrazone (156) gives cyclopalladation (reaction (11)). It is interesting to note that cyclopalladation competes successfully with hydrazone deprotonation [390].

Cyclometallated products are also formed in the reactions of 2- and 3-thienylpyridine and 2-arylpyridines with $Li[PdCl_4]$ [391,392]. In (158) X-ray diffraction shows a somewhat distorted square-planar coordination of palladium with some interaction between the metal and the aldehyde [393].



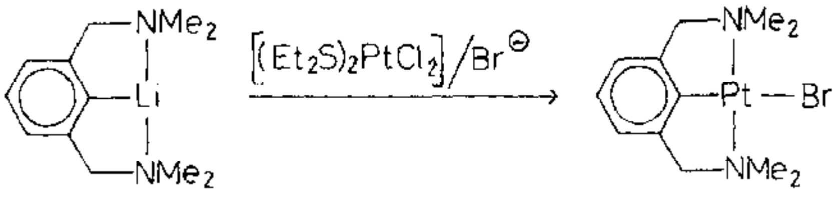
(11)

(156) **(157)**



(158)

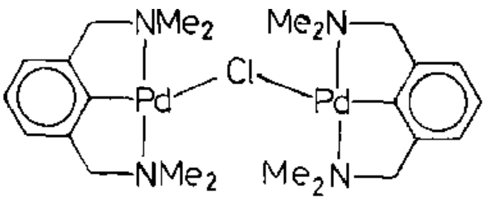
The carbon lithiated diamine ligand **(159)** reacts with $[Pt(SEt_2)_2Cl_2]$ in the presence of Br^- to give **(160)** (reaction (12)). The corresponding palladium



(12)

(159) **(160)**

complex is synthesised from $[Pd(cod)Br_2]$. Treatment with $Ag[BF_4]$ removes halide, to give the aqua compounds, which are stable both in the solid state and in solution [394]. On mixing the halo and the aqua complexes, homo and heteronuclear bridged dimers are formed; the structure of **(161)** was determined by X-ray diffraction [395]. Replacement of bromide by ethanoate occurs on treatment of (160) with silver ethanoate, but Ag[RNXNR'] (X = CH or N) gives the bimetallic compound **(162)**, indicating that formamidino and triazenido ligands have greater stabilising influence on the platinum-silver bond than the isoelectronic carboxylates. For R ≠ R' two isomers are formed in proportions depending on both electronic and steric factors [396]. The presence of a direct platinum to silver bond was confirmed, and $^1J_{Ag-Pt}$ measured using the INEPT technique in the ^{109}Ag NMR spectrum [397]. An analogous mercury complex, $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt(\mu\text{-}4\text{-}CH_3C_6H_4NC(H)NCHMe_2\}HgBrCl]$, was studied crystallographically, showing that the coordination about platinum is approximately square pyramidal. A low value for $^1J_{Hg-Pt}$ is consistent with the bond from platinum to mercury involving a molecular orbital with high d_{z^2} character [398].



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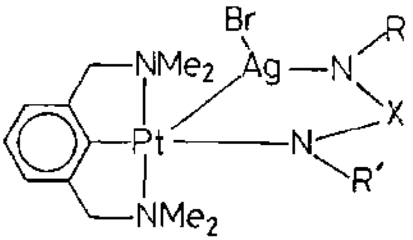
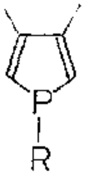


(162)

5.5.4.9 Unidentate phosphine donor ligands

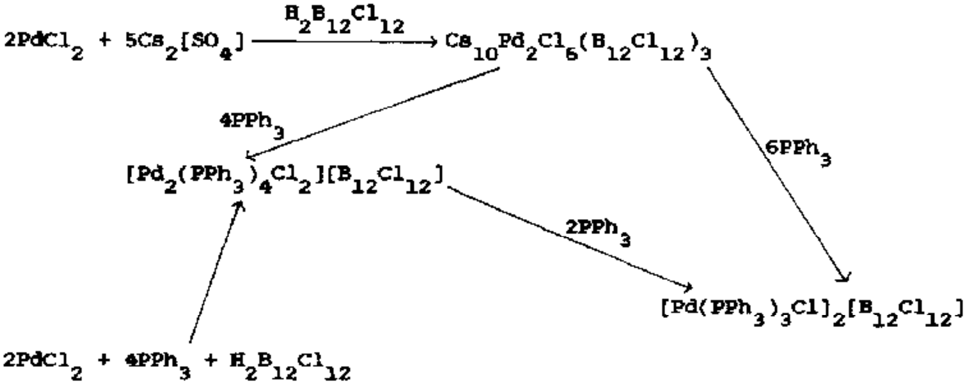
The published data on the isomerisation of palladium(II) and platinum(II) square planar complexes have been reviewed, with specific reference to $[PhPt(PEt_3)_2Cl]$; it is concluded that the *trans*-effect of the inner sphere ligands controls the direction of isomerisation [399]. Carbon monoxide induces *cis/trans* isomerisation of $[Pt(PR_3)_2Cl_2]$ *via* a pseudorotating five-coordinate intermediate [400]. A similar mechanism is invoked to explain the isomerisation of $[PtL_2Cl_2]$ in the presence of an excess of phosphole ligand **(163)** [401].



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

X-ray diffraction studies are reported for *trans*-$[Pd(P\{CH_2Ph\}_3)_2(N_3)_2]$ and *trans*-$[Pd(P\{CH_2Ph\}_3)_2(CN)_2]$. Only the *trans*-isomers may be isolated because of the steric bulk of the tribenzylphosphine ligands. The ligand cone angle measured in the azide is 200°, rising to 232° in the cyanide. Cyanide exerts a stronger *cis*-influence than azide [402]. *trans*-Geometry is also preferred for complexes of the bulky tri*iso*propylphosphine; in *trans*-$[Pt(P\{CHMe_2\}_3)_2Cl_2]$ and *trans*-$[Pt(P\{CHMe_2\}_3)_2HCl]$ the interactions between the phosphine substituents are important in determining Pt-P distances [403]. Diffraction studies of two crystalline modifications of *cis*-$[Pt(PMePh_2)_2Cl_2]$ are reported; both show small tetrahedral deformations from strictly square planar geometry [404].

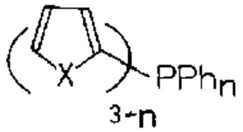
The use of *closo*-borate anions as a means of stabilising unusual coordination compounds has been reviewed. For example, it is difficult to make the tetrafluoroborate salt of $[Pd_2(PPh_3)_4(\mu\text{-}Cl)_2]^{2+}$ but the $[B_nX_n]^{2-}$ (n = 10 or 12; X = Cl or Br) salts are stable. Other useful transformations are shown in Scheme 5 [405]. A new preparation of $[Pt(PPh_3)_2)Cl_2]$ is reported; it is claimed that the product is in some way "different" from that produced in the past, an assertion for which little evidence is provided [406].



Scheme 5 Stabilisation of unusual palladium cations using *closo*-borate anions [405].

Ab initio MO calculations of the structures and relative energies of $[Pt(PH_3)_2XY]$ (X,Y = H,Cl) show that the *trans*-isomer should be more stable than the *cis* in each case. Available experimental data are in good agreement with the calculated values for bond lengths, bond angles and vibrational frequencies [407]. Self consistent field X_α-SW calculations for the related species $[Pt(PH_3)_2H_2]$, $[Pt(PH_3)_2HMe]$, $[Pt(PH_3)_2Me_2]$ and $[Pd(PH_3)_2Me_2]$ correctly predict the relative rates of reductive elimination from such complexes [408].

The ^{31}P NMR spectrum of solid *cis*-$[Pt(PR_3)_2Cl_2]$ may be resolved by magic angle techniques. The complexes with $R_3P = Ph_2PCH_2CH_2Si(OEt)_3$ may be immobilised on silica or glass and relatively well resolved spectra were still obtained [409,410]. ^{31}P NMR spectra of *cis*-$[Pt(PR_3)_2Cl_2]$, where R_3P = (164), show the effects of the ligand on chemical shifts and platinum phosphorus coupling constants [411].



(164; X = O or S; n = 0,1 or 2)

Reaction of $[Pd(PPh_3)_4]$ with trityl fluoroborate yields $[Pd(PPh_3)_4][BF_4]_2$ *via* one of the alternative pathways shown in Scheme 6. A similar result is obtained using $[Pd(P(OPh)_3)_4]$ and trityl hexafluorophosphate. In the presence of other suitable ligands mixed complexes, including $[Pd(PPh_3)(phen)_2][BF_4]_2$, are obtained [412]. Trityl cation acts towards *trans*-$[Pt(PPh_3)_3HCl]$ as a hydride abstractor giving Ph_3CH [413].

$$[Pd(PPh_3)_4] \rightleftharpoons [Pd(PPh_3)_3] + PPh_3$$

$$[Pd(PPh_3)_3] \xrightarrow{[Ph_3C]^+} [Pd(PPh_3)_3CPh_3]^+$$

$$[Pd(PPh_3)_3CPh_3]^+ \xrightarrow{[Ph_3C]^+} [Pd(PPh_3)_3(CPh_3)_2]^{2+}$$

$$[Pd(PPh_3)_3(CPh_3)_2]^{2+} \xrightarrow{PPh_3} [Pd(PPh_3)_4]^{2+} + 2[Ph_3C]^{\cdot}$$

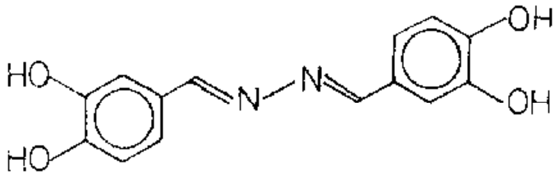
or

$$[Pd(PPh_3)_3] + [Ph_3C]^+ \longrightarrow [Pd(PPh_3)_3]^+ + [Ph_3C]^{\cdot}$$

$$[Pd(PPh_3)_3]^+ + [Ph_3C]^+ \xrightarrow{PPh_3} [Pd(PPh_3)_4]^{2+} + [Ph_3C]^{\cdot}$$

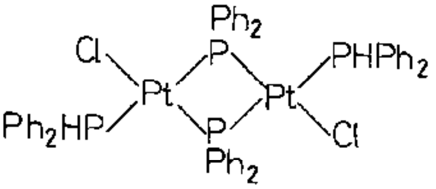
Scheme 6 Reactions of $[Pd(PPh_3)_4]$ with trityl cation [413].

$[Pt(PPh_3)_2Cl_2]$ acts as a bifunctional electrophile in a reaction with $[Fe_2(\mu\text{-}S)_2(NO)_4]^{2-}$ giving $[(Ph_3P)_2PtS_2Fe_2(NO)_4]$ of unknown structure [414]. The ligand H_4L (165) also gives displacement of halide from $[M(PPh_3)_2X_2]$ (M = Pd or Pt) to give complexes of stoicheiometry $[(M(PPh_3)_2)_2L]$ [415].



(165)

X-ray diffraction studies of (166) show that the (Pt_2P_2) ring is strictly planar. The Pt-P-Pt angle of 103° is at the top of the reported range for M-P-M, in agreement with the high field ^{31}P NMR signal for the bridging phosphide [416].



(166)

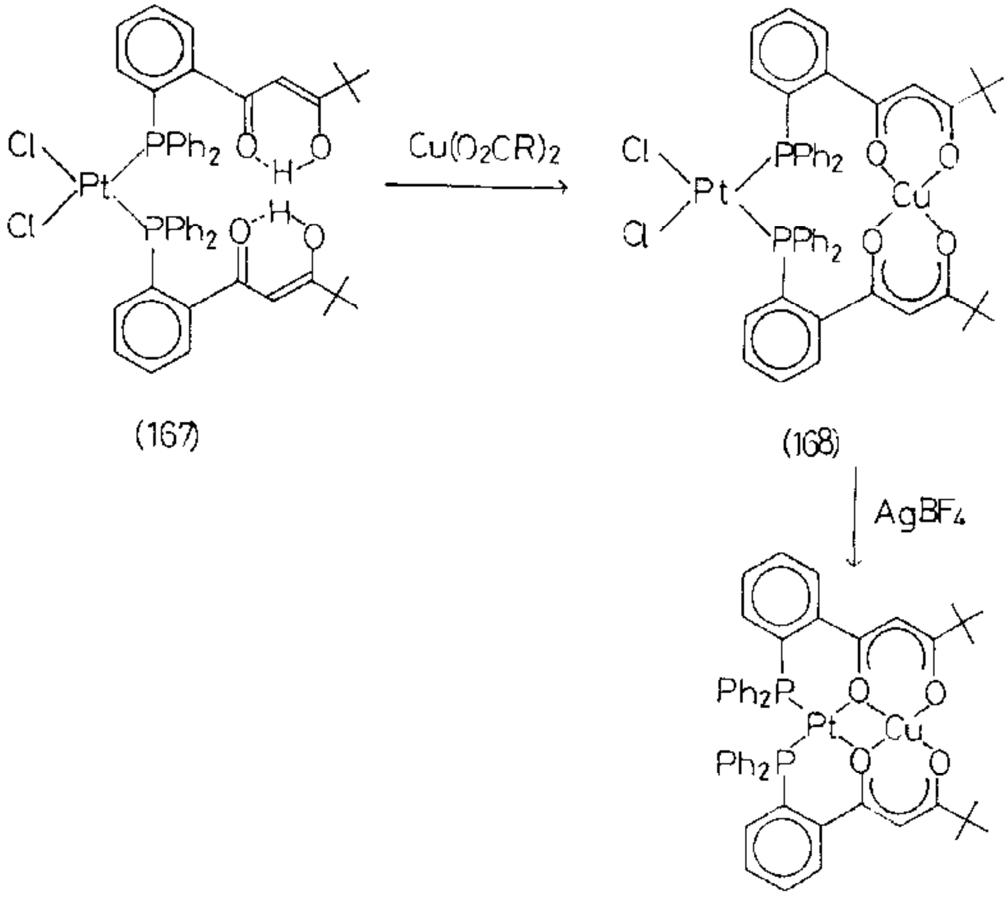
Reaction of the complex (167) with a copper carboxylate gives the emerald green paramagnetic species (168), the structure of which was confirmed crystallographically. (168) reacts with $Ag[BF_4]$ to give lime green (169) [417].

The solid state strucures of the propanone, ethanonitrile and benzene solvates of *trans*-$[Pd(PPh_3)_2(CH_2CN)Cl]$ show no obvious features capable of explaining the photochromicity of the compound [418].

5.5.4.10 Other unidentate phosphorus donor ligands

Reaction of $K_2[PtCl_4]$ with trimethyl phosphite yields $[Pt(\{P(OMe)_2O\}_2H)_2]$. The bridging hydrogen atoms may be replaced by BF_2 on treatment with $BF_3.Et_2O$, and X-ray diffraction shows that the six membered chelate ring in (170) adopts a distorted chair conformation [419]. The ^{31}P T_1 values in platinum(II) phosphine diphenylphosphinato and dimethylphosphito complexes were recorded. The ^{31}P NMR spectrum of (171) is concentration dependent with a monomer dimer equilibrium [420]. Reaction of $[(\eta^5-cp)Pd(\eta^3-(CH_2C(Me)CH_2))]$ with $HPO(OR)_2$ gives the hydrogen bonded product (172). IR spectroscopy implies that the hydrogen bond is symmetrical and the proton may be replaced by BF_2 or thallium [421].

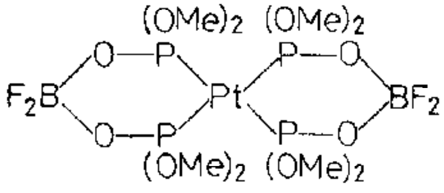
The stability constants and thermodynamic parameters for palladium bis(thiocyanate) complexes of phosphines and phosphites have been measured [422].



(167)

(168)

(169)



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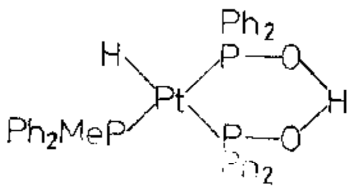

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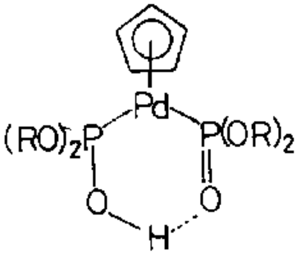


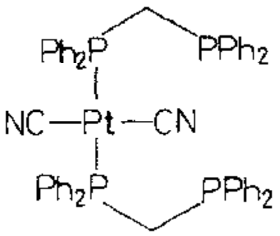
(172)

5.5.4.11 Bidentate phosphorus donor ligands

A range of *trans*-chelated platinum(II) complexes of $Ph_2P(CH_2)_nPPh_2$ (n = 6,7,8,9,10,11,12 or 16) have been synthesised, the degree of oligomerisation depending on the length of the carbon backbone [423]. Reaction of the biphosphines with $K_2[PtCl_4]$ gives *cis*-complexes which are isomerised to *trans*-analogues in the presence of excess phosphine. $K[Pt(C_2H_4)Cl_3]$ gives *trans*-isomers directly. Monomeric *trans*-complexes may be obtained only for $n \geq 7$ [424]. $Ph_2P(CH_2)_6PEtPh$ gives a *cis*-polymeric complex on reaction with $K_2[PtCl_4]$, but yields a mixture of *cis*-polymer and a soluble *trans*-isomer with $[(PhCN)_2PtCl_2]$. Zeise's salt also gives the less stable *trans*-isomer [425]. In contrast, $Ph_2P(CH_2)_5PPh_2$ reacts with $K_2[PtCl_4]$ to give a *cis*-chelated monomeric complex rather than a macrocyclic product [426].

Exchange reactions of $[Pd(dppm)X_2]$ and $[Pd(dppm)Y_2]$ to give $[Pd(dppm)XY]$ are easily monitored by ^{31}P or ^{1}H NMR spectroscopy. Equilibrium is established within 5 minutes both for this reaction and the analogous one of $[Pd_2(dppm)_2X_2]$ [427].

The strained complex $[Pt(dppm)_2]^{2+}$ reacts readily with cyanide ion to give **(173)**, in which the strong bonding of the CN^- stabilises the monodentate mode of coordination. **(173)** may also be obtained from treatment of $[Pd_2(CN)_4(\mu\text{-dppm})_2]$ with an excess of dppm [428]. (173) reacts with $[Rh_2(\mu\text{-Cl})_2(CO)_4]$, $HgCl_2$ and $Ag[NO_3]$ to give heterobimetallic complexes **(174)**.



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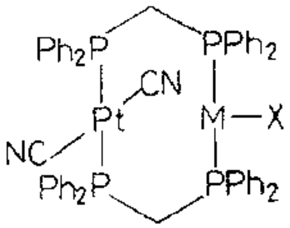
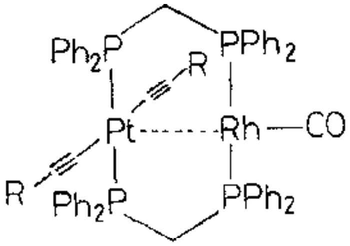


(174)

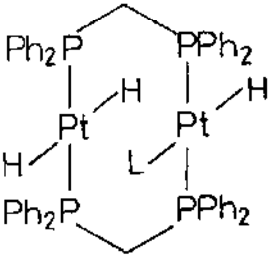
Trans-$[Pt(C\equiv CR)_2(\eta^1\text{-dppm})_2]$ reacts similarly with $Ag[NO_3]$, $[Au(PPh_3)Cl]$, $HgCl_2$ and $CdCl_2$ [429]. The mercury complex is also obtained from $[Pt(\eta^2\text{-dppm})_2]Cl_2$ and bis(alkynyl) mercury compounds [430]. In **(175)**, synthesised by treatment of *trans*-$[Pt(C\equiv CR)_2(\eta^1\text{-dppm})_2]$ with $[Rh_2(\mu\text{-Cl})_2(CO)_4]$, the rhodium-platinum bond is a donor-acceptor interaction. $[Ir_2(\mu\text{-Cl})_2(C_8H_{14})_4]$ gives the corresponding chloroiridium complex, which is able to undergo oxidative addition of dihydrogen. *fac*-$[W(CO)_3(MeCN)_3]$ gives *trans*-$[Pt(C\equiv CR)_2(\mu\text{-dppm})_2W(CO)_3]$ [431].



(175)

Addition of phosphine ligands to $[Pt_2H_3(\mu\text{-dppm})_2][PF_6]$ induces reductive elimination of molecular hydrogen. Deuterium labelling suggests that the rate controlling step is addition of the ligand, with bridge splitting, to give **(176)** [432]. The A-frame complex $[MePt(\mu\text{-H})(\mu\text{-dppm})_2PtMe]^+$ is prepared by reduction of $[Me_3Pt_2(\mu\text{-dppm})_2][PF_6]$ or $[Me_2Pt(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$, and is stable in the solid state. X-ray diffraction shows that there is a weak interaction between the metal atoms [433].

$[Pd(MeHPCH_2CH_2PHMe)_2]Cl_2$, formed by treatment of $K_2[PdCl_4]$ with the phosphine, reacts with pentane-2,4-dione to give **RSSR** and **RSRS** forms of (177) [434].



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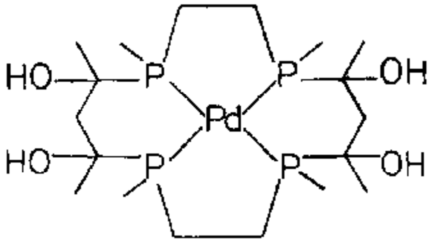


(177)

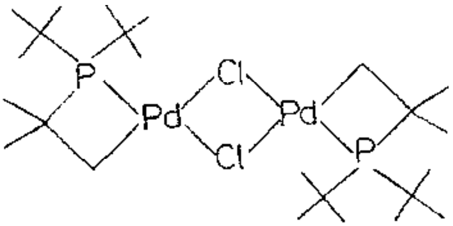
The curious ligand η^3-P_3 forms a series of complexes $[LM^1(\eta^3\text{-}P_3)M^2L]^{n+}$ with M^1 and M^2 being Co, Ni, Rh, Ir or Pd. η^3-P_3 behaves as a 3π-donor and L was $CH_3C(CH_2PPh_2)_3$ or $N(CH_2PPh_2)_3$. P_4, an intact tetrahedron of phosphorus atoms, may be σ-bonded to palladium [435].

When the synthesis of $K_4[Pt_2(pop)_4]$ is carried out at 170 °C rather than 100 °C, the reaction proceeds further to give a green compound, which reverts to $K_4[Pt_2(pop)_4]$ on standing in solution. Spectroscopic studies suggest a Pt_4 complex of $[HOP(O^-)OP(O^-)OP(O^-)OP(O^-)OH]^{4-}$ or, more likely, a Pt_3 complex of $[HOP(O^-)OP(O^-)OP(O^-)OH]^{3-}$ [436].

Polydentate phosphine ligand complexes of nickel, palladium and platinum have been investigated [437].

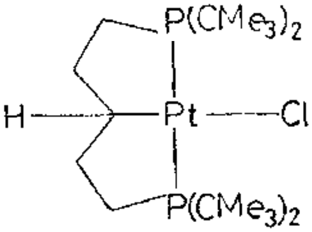
5.5.4.12 Bidentate phosphorus-carbon donor ligands

Further details of the metallation of $(Me_3C)_3P$ are reported, this year using $[(PhCN)_2PdCl_2]$, to give only the binuclear complex (178). Although the coordination about palladium is roughly square-planar, the four-membered ring is considerably puckered with a P-Pd-C angle of 70° [438].



(178)

Reaction of $[Pt(CNCMe_3)_2Cl_2]$ with $(Me_3C)_2P(CH_2)_5P(CMe_3)_2$ gives the metallated complex **(179)** together with an unidentified species. Cl may be substituted by CO, MeNC or Me_3CNC in the presence of $Na[BPh_4]$. X-ray diffraction showed the unidentified compound to be **(180)**, with a disordered double bond. It may be deduced that it is formed directly since dehydrogenation of **(179)** is difficult [439]. The behaviour of $(Me_3C)_2PCH_2CH(Me)(CH_2)_3P(CMe_3)_2$ differs when reacted with labile palladium(II) and platinum(II) complexes. $[(PhCN)_2PdCl_2]$ gives the analogue of **(179)** with the methyl group in a pseudoequatorial position, whilst $[(PhCN)_2PtCl_2]$ gives a complex mixture of sixteen-membered ring chelates, *trans*-$[Pt_2L_2Cl_4]$. This mixture may be converted into the analogue of **(179)** by treatment with tfaH followed by lithium chloride [440].



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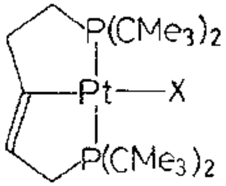

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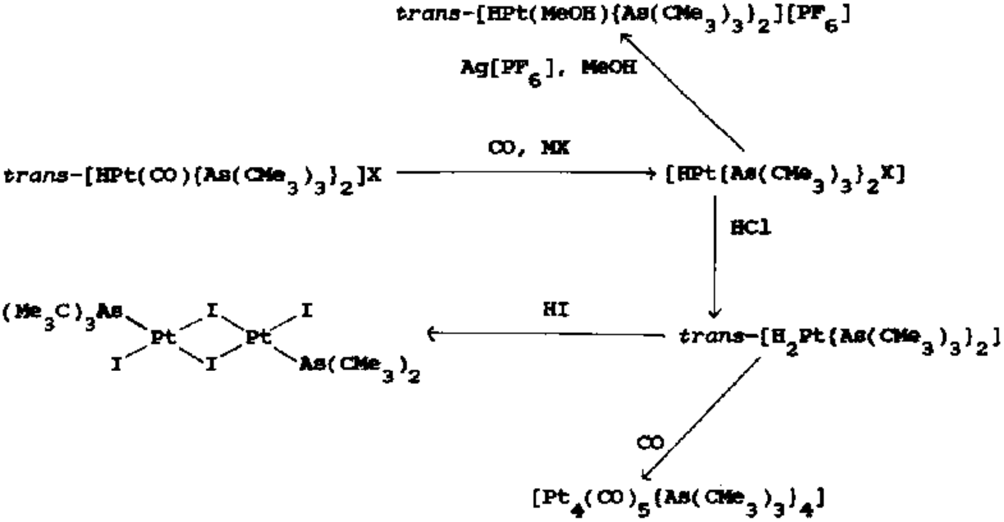
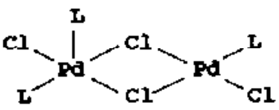
5.5.4.13 Arsenic donor ligands

In contrast to $(Me_3C)_3P$, $(Me_3C)_3As$ is not readily metallated and reacts with $K_2[PtCl_4]$ to give *trans*-$[H_2Pt\{As(CMe_3)_3\}_2]$. Several reactions of this complex are reported (Scheme 7) [441].



Scheme 7 Reactions of *trans*-$[H_2Pt\{As(CMe_3)_3\}_2]$ [441].

Some unusual coordination geometries are obtained with the ligands 1,2-bis(diphenylarsino)benzene and 1,2-bis(di-4-methlphenylarsino)benzene. The species $[PtLX_2]$ and $[PtL_2]X_2$ have conventional square-planar coordination but $[PtL_2(OH_2)_2][ClO_4]_2$ adopts distorted octahedral geometry and $[PtL_2X][ClO_4]$ (X = I or Br) are five coordinate [442]. A number of complexes of 1-arylarsolanes have been reported and characterised; those of stoicheiometry $[PtL_2Cl_2]$ are probably *cis*. Again some unusual coordination modes are postulated. $[PtL_3Br_2]$ is five coordinate and structures **(181a)** or **(181b)** are postulated for $[Pd_2\{1\text{-}(4\text{-methylphenyl})arsolane\}_3Cl_4]$. Thiocyanate counterions are *S*-bonded in



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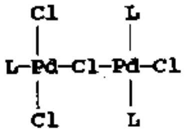


(181b)

most cases but in [Pt{1-(2-methylphenyl)arsolane}$_2$(*S*CN)(*N*CS)] one is *N*-bonded, and in [{Pd(1-{2-methylphenyl}arsolane)(SCN)}$_2$] both *S*-bonded and bridging coordination are indicated by the IR spectrum [443].

5.5.4.14 Antimony donor ligands

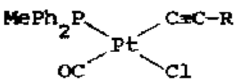
The structure of [Pd(η^5-cp)(SbPh$_3$)$_2$][PF$_6$] has been determined by X-ray diffraction and the synthesis of a wide range of analogous complexes of phosphines and arsines was reported [444].

5.5.5 Complexes of Group IV donor ligands

Many of the complexes of Group IV donor ligands are "organometallic complexes" and are thus excluded from this review. The organometallic chemistry of nickel, palladium and platinum, reported in 1979, has been reviewed [445].

5.5.5.1 Carbonyl complexes

Trans-[Pt(CO)$_2$Cl$_2$] may be synthesised from platinum atoms and oxalyl chloride [446]. Catalytic synthesis of phosgene from chlorine and carbon monoxide occurs in the presence of [Pt(CO)Cl$_3$]$^-$ and [Pd(CO)Cl$_3$]$^-$. In a study of the reaction mechanism it was shown that whilst *cis*-[Pt(CO)$_2$Cl$_2$] does not react with chlorine, [Pt(CO)Cl$_3$]$^-$ reacts in thionyl chloride to give [Pt(CO)Cl$_5$]$^-$. The corresponding palladium complex is unreactive since the +4 oxidation state is somewhat less accessible [447]. *Cis*-[Pt(CO)(PMePh$_2$)Cl$_2$] reacts with bis(alkynyl)mercury compunds to give (182) *via* an oxidative addition, reductive elimination sequence [448].



(182)

5.5.5.2 Cyanide complexes

A detailed study of the UV spectrum of $K_2[Pt(CN)_4]$ and $Ba[Pt(CN)_4]$ allows a more definitive set of excited state assignments than has previously been possible. Concentration dependent quenching and lifetime studies of the room temperature emission allow a distinction between fluorescence and phosphorescence, and a probable assignment of the oligomers responsible [449,450]. The phosphorescence of $([Pt(CN)_4]^{2-})_n$ is quenched by dioxygen and NO_2, and by some reducible species. Triplet state oligomers undergo excitation energy transfer if the acceptor has a triplet excited state below 2 V in energy [451]. Polarised emission measurements on single crystals of $Sm_2[Pt(CN)_4]_3.18H_2O$ exhibit a radiationless energy transfer from the lowest excited state of the linear $[Pt(CN)_4]^{2-}$ stacks to the Sm^{3+} cations [452]. The E⊥c polarised emission of $M_x[Pt(CN)_4]_y.H_2O$ is profoundly affected by magnetic fields, being blue shifted by 270 cm^{-1} between zero and six Tesla. This is explained within the D_{4h} symmetry of a single $[Pt(CN)_4]^{2-}$ group, assuming that the lowest emitting state is A'_{1u} [453]. The E⊥c absorption spectrum varies considerably with temperature both in frequency and in intensity [454]. The influence of electron-hole and electron-phonon interaction on the lowest excited states of $[Pt(CN)_4]^{2-}$ has been estimated [455].

Reaction of $Tl_2[Pt(CN)_4]$ with thallium(I) carbonate yields a green lustrous compound of formula $Tl_4[Pt(CN)_4][CO_3]$ which is definitely not a partially oxidised tetracyanoplatinate salt. A neutron diffraction study shows that the platinum atoms in the linear chain are 3.245 Å apart, considerably further than the 2.8-2.96 Å typical of oxidised salts [456]. $Y_2[Pt(CN)_4]_3$ undergoes a pressure induced phase change in the course of which the interplatinum distance decreases [457].

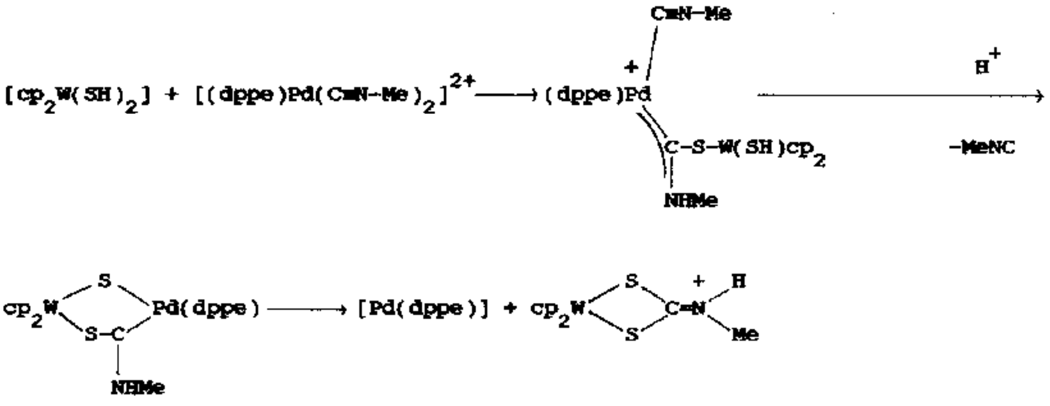
^{15}N chemical shifts and $^1J_{CN}$ coupling constants were measured for the ions $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$. $^1J_{CN}$ is larger in the complexes than for the free cyanide ion [458]. DTA of diphenyliodonium palladium and platinum tetracyanoplatinates(II) show that decomposition yields iodobenzene, benzonitrile, phenyl isocyanide and cyanogen [459].

Thermolysis of *trans*-[CrF(OH$_2$)(1,3-pn)$_2$][M(CN)$_4$] (M = Ni, Pd or Pt) yields [(1,3-pn)$_2$FCr(μ-CN)M(CN)$_3$]. The platinum complex is somewhat different from the other two analogues with a platinum-platinum interaction both in the solid state and in solution [460,461].

5.5.5.3 *Isonitrile complexes*

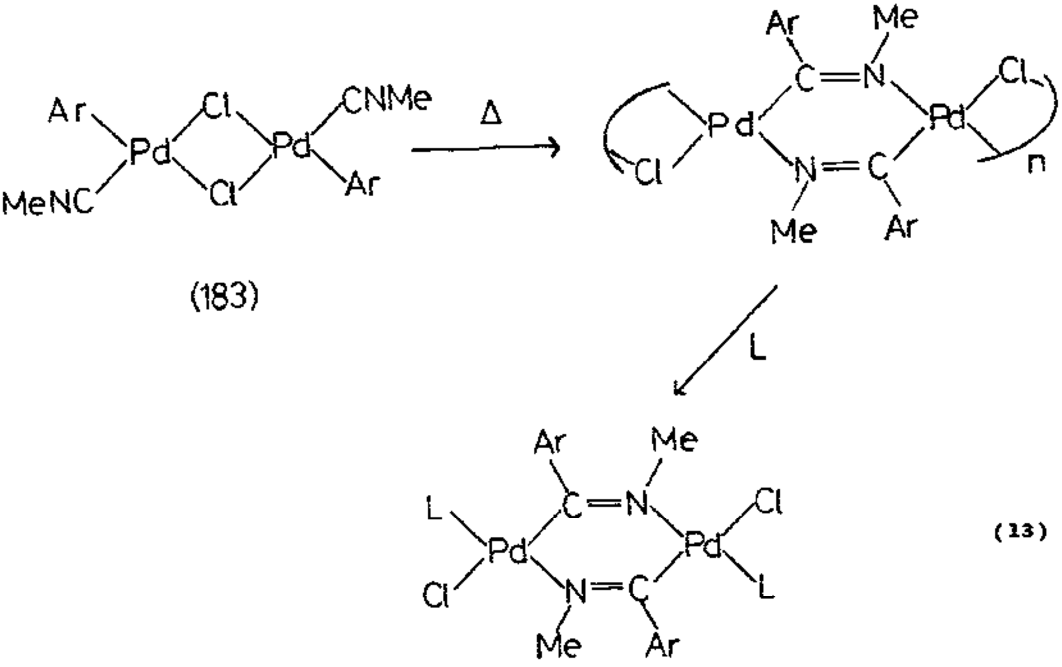
Two papers report the crystal structure of *cis*-[Pd(CNcych)$_2$Cl$_2$], prepared from PdCl$_2$ and cychNC. One isonitrile occupies an axial site on the cyclohexane ring whilst the other is equatorial [462,463].

The carbon-nitrogen bond of isonitriles is susceptible to attack by nucleophiles and this was used in the rather curious conversions of Scheme 8 [464].



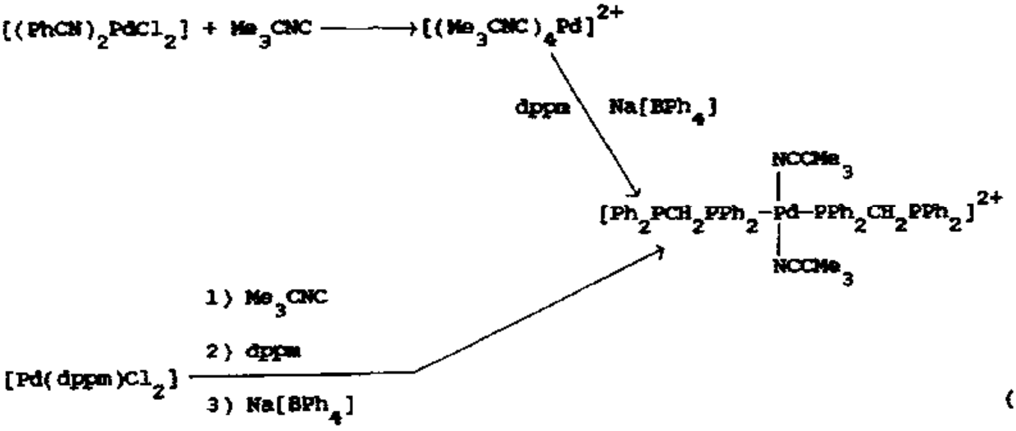
Scheme 8 Reactions of isonitrile complexes with nucleophiles [464].

Both *cis*- and *trans*-[Ar$_2$Pd(CNMe)$_2$] (Ar = C$_6$H$_5$) give (183) on treatment with PdCl$_2$. Thermolysis involves aryl ransfer and yields a bridged polymer (reaction (13)) which may be converted to a monomer using a variety of ligands, L. The structure of the complex for L = tht was established by X-ray diffraction [465]. The complex *trans*-[Pd(η^1-dppm)$_2$(Me$_3$CNC)$_2$]$^{2+}$ may be synthesised by the routes shown in reaction (14) [466].



(183)

(13)



$$[(PhCN)_2PdCl_2] + Me_3CNC \longrightarrow [(Me_3CNC)_4Pd]^{2+} \xrightarrow[\text{Na[BPh}_4]]{\text{dppm}} [Ph_2PCH_2PPh_2{-}\overset{NCCMe_3}{\underset{NCCMe_3}{Pd}}{-}PPh_2CH_2PPh_2]^{2+}$$

$$[Pd(dppm)Cl_2] \xrightarrow[\text{3) Na[BPh}_4]]{\text{1) Me}_3\text{CNC} \;\; \text{2) dppm}} [Ph_2PCH_2PPh_2{-}\overset{NCCMe_3}{\underset{NCCMe_3}{Pd}}{-}PPh_2CH_2PPh_2]^{2+}$$

(14)

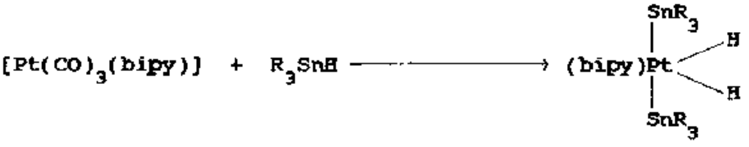
5.5.5.4 *Silicon donor ligands*

Cis-$[Pt(PPh_3)_2(SiR_3)(H)]$ undergoes a temperature dependent dynamic process in which the two phosphorus atoms become equivalent. Retention of $^1J_{PtH}$ and $^1J_{PtP}$ rules out H-Pt or P-Pt bond cleavage. Ph_3PO, R_3SiH and solvent have no effect on the rate, implying that association followed by pseudorotation is not involved. The authors were forced to conclude that a direct geometry change ocurred [467].

5.5.5.5 *Tin donor ligands*

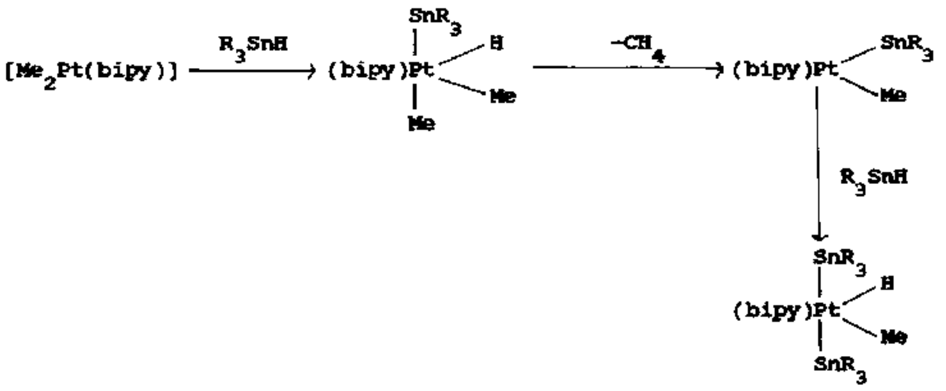
Although the axial and equatorial bonds in the trigonal bipyramidal anion $[Pt(SnCl_3)_5]^{3-}$ are not equivalent (despite earlier reports) the structure is less distorted than that of $[Pt(GeCl_3)_5]^{3-}$. In contrast to $[Pt(P(OMe)_3)_5]$, the anion is non rigid on the NMR time scale, even at 183 K, with exchange of axial and equatorial sites by Berry pseudorotation [468]. Single crystal X-ray diffraction studies of $[MePh_3P]_2$ *cis*-$[Pt(SnCl_3)_2Cl_2]$ and $[(PhCH_2)Ph_3P]_2[Pt(SnCl_3)_2Cl_2]$ show a Pt–Sn bond significantly shorter than that in $[Pt(SnCl_3)_5]^{2-}$. This is consistent with the much larger $^1J(^{195}Pt^{119}Sn)$ measured for this complex, and implies that Pt–Sn π-bonding is more important in four-coordinate than five-coordinate complexes [469].

The reaction between tetrakis phosphine and phosphite platinum(0) complexes and R_3SnH is rather complex. Phosphine complexes yield $[H_2Pt(SnR_3)_2(PR_3)_2]$ by a double oxidative addition, but $[Pt(P(OAr)_3)_4]$ gives *trans*-$[Pt(SnR_3)_2(P(OAr)_3)_2]$, presumably by reductive elimination of H_2 from the less stable platinum(IV) species. With bipy as the other ligand, the platinum(IV) complexes, **(184)**, show no tendency to lose hydrogen (reaction (15)). Treatment of $[Me_2Pt(bipy)]$, however, gives $[HPtMe(bipy)(SnR_3)_2]$ by the mechanism of reaction (16) [470].



$$[Pt(CO)_3(bipy)] + R_3SnH \longrightarrow (bipy)Pt(SnR_3)_2H_2 \qquad (15)$$

(184)



(16)

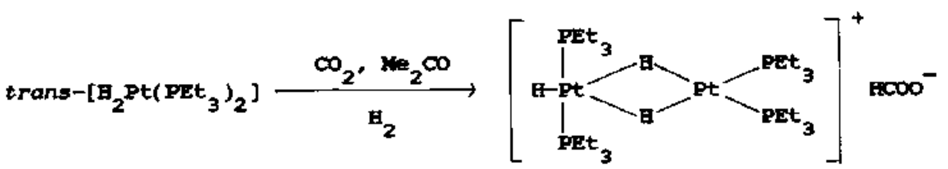
5.5.6 *Hydride complexes*

Treatment of $[Pt(PR_3)_2(C_2H_4)]$ with molecular hydrogen gives $[H_2Pt(PR_3)_2]$ and ethene with no trace of ethane detected. *Cis-* and *trans*-isomers of the product equilibrate in solution with the proportion of *cis*-isomer increasing in polar solvents. π-Acceptors including CO, C_2H_4 and C_2F_4 displace dihydrogen to give $[Pt(PR_3)_2L_n]$ ($n = 1$ or 2). Reaction of the triethylphosphine complex with methyl iodide gives methane (reaction (17)) presumably *via* oxidative

$$\textit{trans}\text{-}[H_2Pt(PEt_3)_2] + MeI \longrightarrow \textit{trans}\text{-}[HPt(PEt_3)_2I] + CH_4 \qquad (17)$$

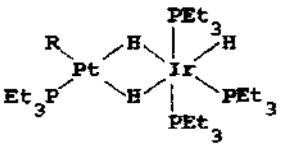
addition and reductive elimination [471]. The same complex reacts reversibly with CO_2 in toluene (reaction (18)), the equilibrium constant being about 2 atm^{-1} at 25 °C. In more polar solvents such as propanone or ethanonitrile the charge separated species is stabilised (reaction (19)) but the process may still be reversed by hydrogen pressure [472].

$$\textit{trans}\text{-}[H_2Pt(PEt_3)_2] + CO_2 \xrightarrow{\text{toluene}} \textit{trans}\text{-}[HPt(OCHO)(PEt_3)_2] \qquad (18)$$



(19)

Reaction of *trans*-$[RPt(MeOH)(PEt_3)_2]^+$ (R = H or Ph) with $[H_5Ir(PEt_3)_2]$ yields **(185)** the stucture of which was determined by X-ray diffraction. In solution isomerisation gives **(186)**. For the analogous complex **(187)** different solution behaviour is observed with exchange of terminal and bridging hydrides *via* a bridge splitting process [473].



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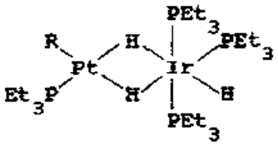

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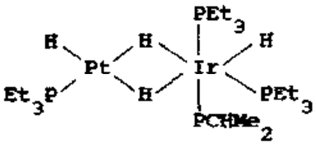
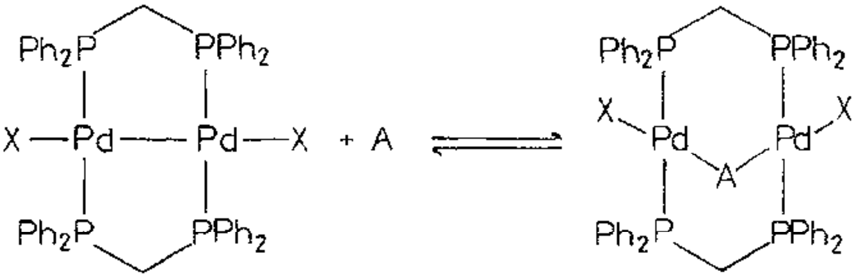


(187)

5.6 PALLADIUM(I) AND PLATINUM(I)

$[Pd_2(\mu\text{-dppm})_2X_2]$ inserts a variety of small molecules (reaction (20)), some of the processes being reversible; XPES implies that there is little change in oxidation state on adduct formation [474]. A new synthesis of (188) (X = Cl) from $[Pd(PPh_3)_4]$, $[(PhCN)_2PdCl_2]$ and dppm is reported. Using $[(Me_3CCN)_2PtCl_2]$ gives the mixed palladium-platinum complex, which is very stable towards disproportionation [475].

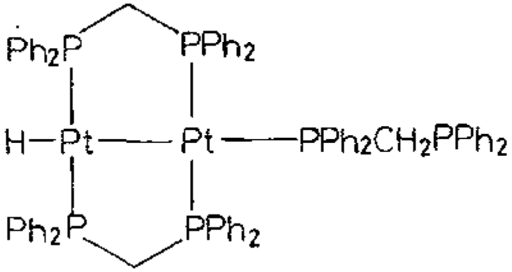


(20)

(188)

(189; A = CO, RNC, S, SO_2, RC≡CR' or PhN_2^+)

The first crystal structure of a complex containing monodentate dppm is provided by a study on (190), which may be regarded as a protonated form of $[Pt_2(\mu\text{-dppm})_3]$. The covalent platinum-platinum σ-bond is quite long [476]. Diazomethane reacts with (191) (L = CO or Me_2PhP) to insert CH_2 into the metal metal bond [477]. A careful study of the previously reported reductive elimination of molecular hydrogen from $[H_2Pt(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ by photolysis in the presence of various ligands has established its strictly intramolecular nature. Whilst the precise mechanism is still uncertain, the reaction probably occurs from the first singlet excited state [478].



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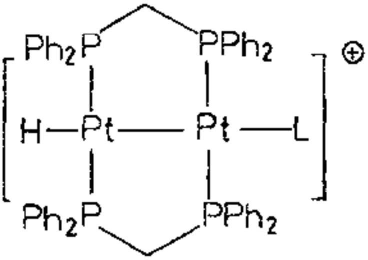
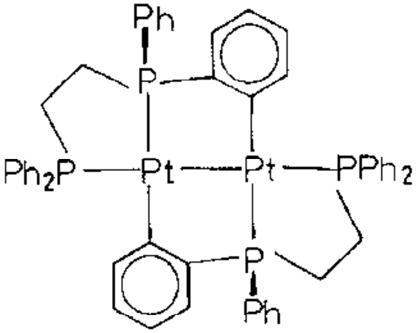


(191)

Thermolysis of [MePt(dppe)(OH)] gives a complex of stoicheiometry $[Pt_2(dppe)_2]$. X-ray diffraction studies of (192) shows that the only diastereomer formed is that with all four phenyl groups on the same side of the average coordination plane [479].

A palladium(I) dimer was an accidental product of the reaction between $[Ru(PPh_2py)_2(CO)_3]$ and $[(cod)PdCl_2]$. The complex, which is formed in 38% yield, probably has the head-to-tail structure (193). Two minor products of the reaction could be prepared in better yield from $[Ru(PPh_2py)_2(CO)_2Cl_2]$ and $[Pd_2(dba)_3]$. They are stereoisomers and interconvert in solution. In the solid state the structure of one isomer was established to be (194) with both palladium and ruthenium in oxidation state +1 [480].



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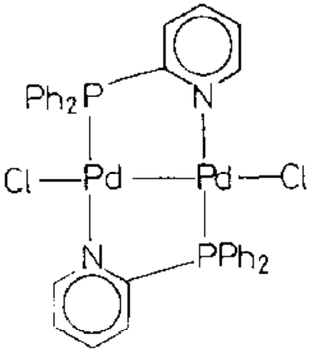

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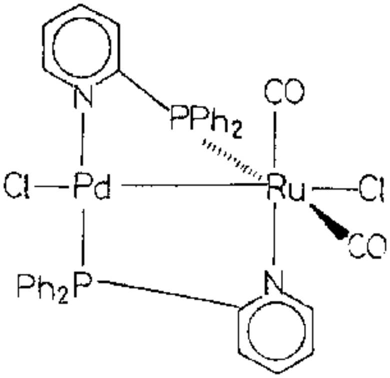
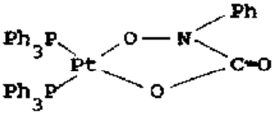


(194)

5.7 PALLADIUM(O) AND PLATINUM(O)

5.7.1 Complexes with Group VI donor ligands

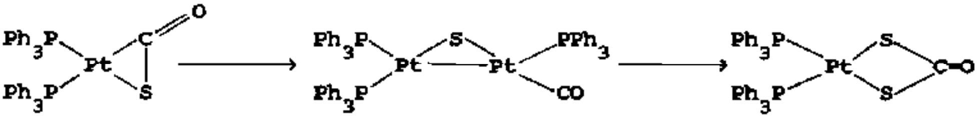
$[Pt(PPh_3)_2(PhNO)]$ forms 1:1 adducts with CO_2, CS_2, C_2H_4 and $MeO_2CC{\equiv}CCO_2Me$. The crystal structure of the CO_2 adduct (195) shows that this is the first example of the insertion of CO_2 into a metal nitrogen bond [481].



(195)

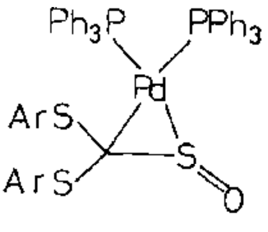
Mixed d^4d^{10} bimetallic compounds are formed when $[Pd(CNCMe_3)_2]$ is treated with $[Mo(SCMe_3)_4]$. In $[(Me_3CNC)_4Mo(\mu\text{-}SCMe_3)_2Pd(CNCMe_3)]$ the metals are bridged by two S–CMe_3 groups [482].

The reactions of CO_2, CS_2 and COS with platinum(II) and platinum(0) complexes have been studied by several groups. Photolysis of $PdCl_2$ in the presence of COS and Ph_3X (X = P or As) provides an alternative synthesis of $[(Ph_3X)_2Pd(\eta^2\text{-}COS)]$, which is also formed in the thermal reaction [483]. The same type of complex is formed by treating $[Pt(PPh_3)_3]$ with a limited amount of COS at low temperatures. The platinum complex is more stable than palladium analogues but still decomposes at $\geq$-20°C in solution (reaction (21)). This is somewhat at variance with the previous report of the isolation of $[(Ph_3P)_2Pd(COS)]$ at room temperature [484]. Carbon disulphide complexes, $[L_2Pd(\eta^2\text{-}CS_2)]$, are formed from $[Pd_2(dba)_3]$, L and CS_2 [485].



(21)

Last year it was reported that $[(Ph_3P)_2Pt(\eta^2\text{-}(PhS)_2C{=}S{=}O)]$ undergoes oxidative addition to give $[(Ph_3P)_2Pt(SPh)\{C(SPh){=}S{=}O\}]$. By contrast, $[Pd(PPh_3)_4]$ reacts with $(4\text{-methylphenyl-}S)_2C{=}S{=}O$ to give an η^2-coordinated sulphine complex **(196)**. This decomposes slowly in solution but does not undergo C–S oxidative addition. Similarly E-(4-methylphenyl-S)C(Cl)=S=O gives an η^2-C–S palladium(0) complex, with only a small amount of oxidative addition product, whereas the platinum analogue undergoes very rapid oxidative addition [486].



(196)

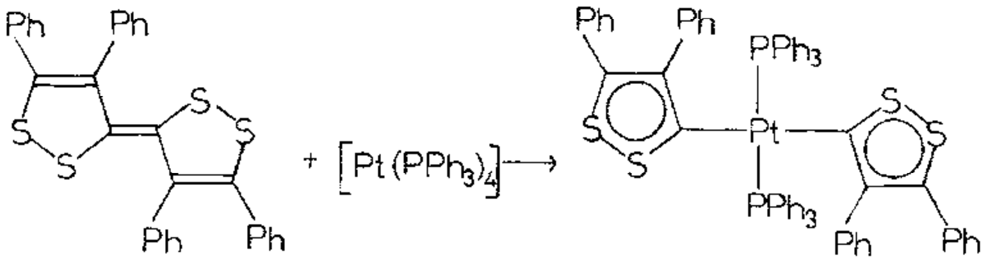
5.7.2 Complexes with Group V donor ligands

Studies of the reactions of palladium(0) and platinum(0) phosphine complexes have been largely theoretical. An *ab initio* treatment of $[Pt(PH_3)_2]/H_2$ suggests that the activation energy for the forward reaction is 71 kJ mol^{-1}. Dihydride formation is exothermic by 29 kJ mol^{-1}, implying a barrier of 100 kJ mol^{-1} to reductive elimination [487]. The SCF-MO-LCAO method within the valence CNDO approximation was used in studying $[Pd(PH_3)_n]$ (n = 1, 2 or 3) [488]. Other studies suggest that a bridging hydrogen complex such as **(197)** might be particularly stable [489].

(197)

A new synthesis of $[Pt(PR_3)_2(C_2H_4)]$ is reported and its transformations were extensively studied (Scheme 9). The most unusual of these involves decomposition of the (η^2-CH_2O) complex, postulated to occur *via* a hydride transfer [490].

$[(C_6Cl_5)Au(PPh_3)]$ reacts with $[Pt(PPh_3)_3]$ to yield (198). X-ray diffraction showed that this does not contain a platinum-gold bond. The attachment of an $\{Au(PPh_3)\}$ group activates the carbon-chlorine bond towards oxidative addition [491]. The mechanism of carbon-carbon bond cleavage in reaction (22) invites speculation [492].



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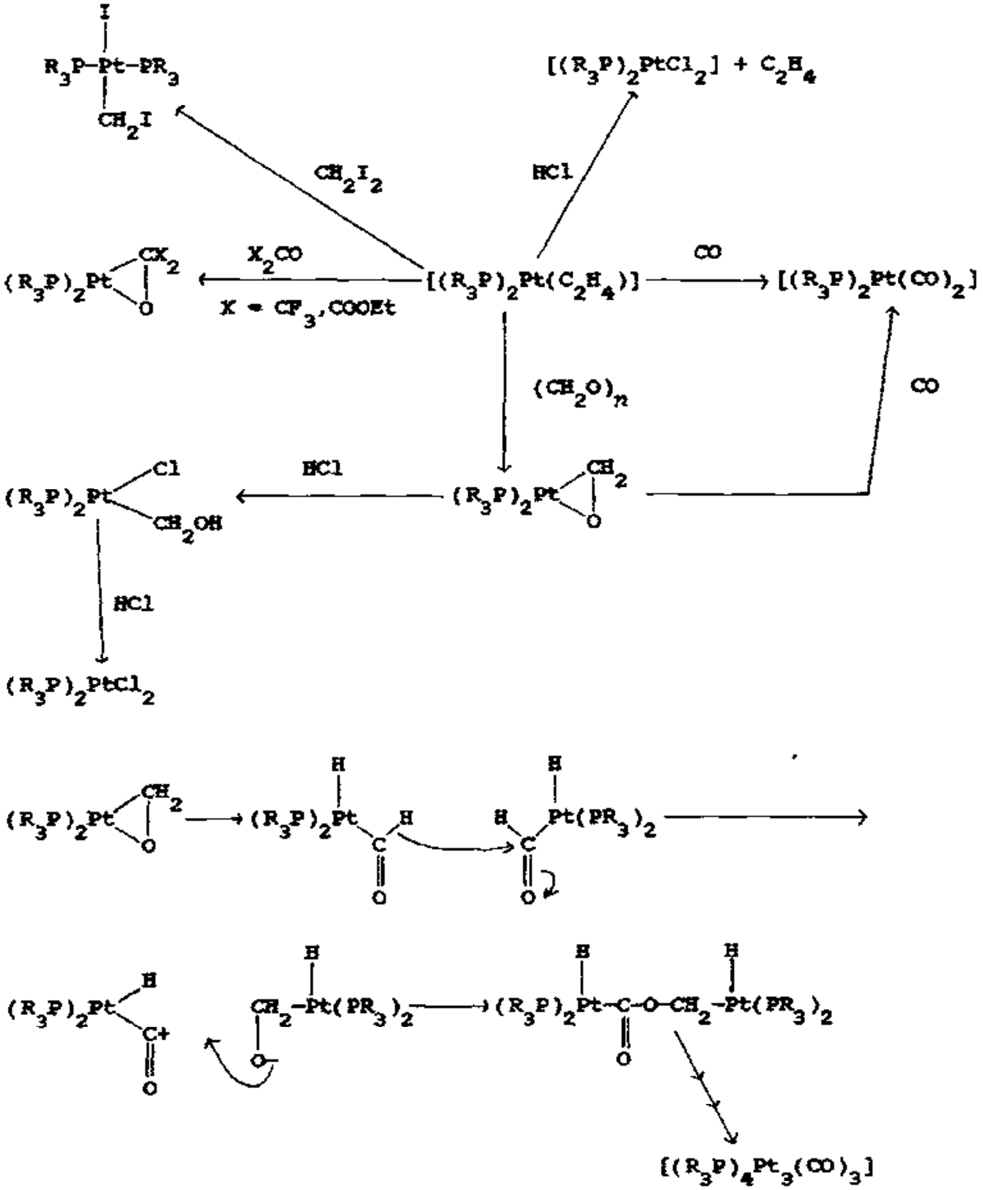
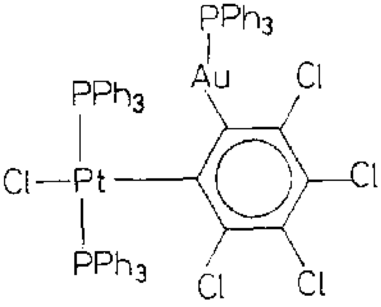
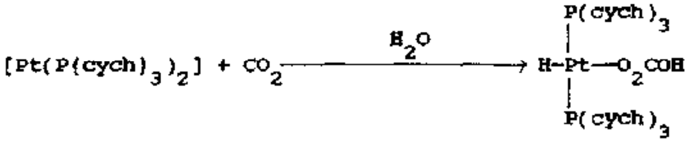


Scheme 9 Transformations of $[(R_3P)_2Pt(C_2H_4)]$ [490].



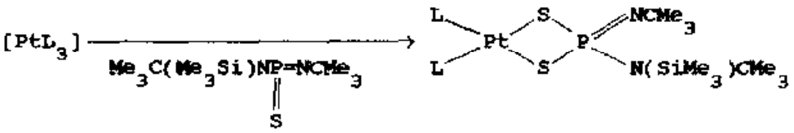
(198)

Neither palladium(0) nor platinum(0) bis(tricyclohexylphosphine) complexes react with pure CO_2. However, in the presence of a trace of water reaction (23) occurs, presumably by CO_2 attack on $[HPt(OH)(P\{cych\}_3)_2]$, formed by oxidative addition of water [493].



$$[Pt(P\{cych\}_3)_2] + CO_2 \xrightarrow{H_2O} H\text{-}\overset{P(cych)_3}{\underset{P(cych)_3}{Pt}}\text{—}O_2COH \qquad (23)$$

The preparation and reactions of complexes of the unusual ligand $Me_3C(Me_3Si)NP{=}NCMe_3$ have been reviewed. $[PtL_3]$ is prepared from $[Pt(cod)_2]$, and molecules of L may be displaced by addition of Ph_3P. In $[PtL_3]$ a dynamic process observed in the NMR spectrum at room temperature involves the 1,3-shift of the trimethylsilyl group. Ligand replacement is much easier than in analogous Ph_3P complexes (reactions (24) and (25)) [494].



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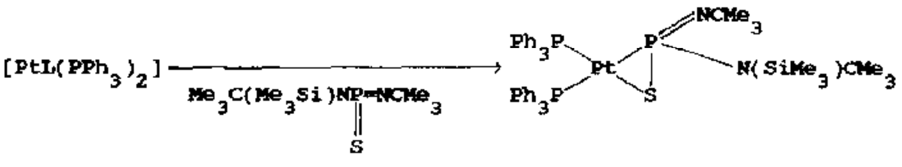


(25)

Another ligand with an sp^2 phosphorus lone pair is (mesityl)P=CPh_2, which reacts with $[Pt(PPh_3)_2(C_2H_4)]$ to displace ethene and yield the mixed-ligand complex. In the solid state X-ray diffraction indicates η^1-coordination, but in solution the ^{31}P NMR implies a dynamic process involving η^2-binding [495].

Reaction of $Li_2[PhP{=}PPh]$ with *cis*-$[ML_2Cl_2]$ (L_2 = $(PPh_3)_2$ or dppe; M = Pd or Pt) yields $[M(PhP{=}PPh)L_2]$. With this ligand X-ray diffraction shows η^2-coordination and $^1J_{PPt}$ for the diphosphene is only 280 Hz, compared with the 3000–4000 Hz typical for platinum(0) complexes of triaryl phosphines [496].

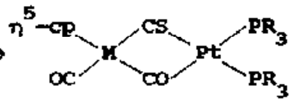
X-ray crystallography was also used to show that $[Pt_2(\mu\text{-dppm})_3]$ has a manxane structure, with trigonal planar coordination of platinum and approximately C_{3h} symmetry; the platinum-platinum distance is outside the range of Pt(0)–Pt(0) bonding interactions [497].

Finally it is reported that electroreduction of $[(dppe)PdCl_2]$ in the presence of an excess of dppe yields $[Pd(dppe)_2]$ [498].

5.7.3 Complexes of Group IV donor ligands

The ease of displacement of ethene from $[Pt(PR_3)_2(C_2H_4)]$ has been used in the synthesis of bridged bimetallic compounds (reaction (26)). The

$[M(CO)_2(CS)(\eta^5\text{-cp})] + [Pt(PR_3)_2(C_2H_4)] \longrightarrow$



(26)

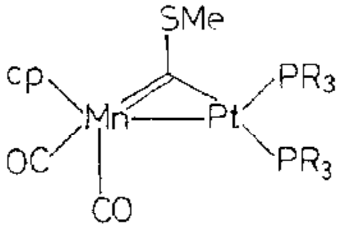
(**199**; M = Mn, PR_3 = $PPhMe_2$)

(**200**; M = Mn, PR_3 = PPh_2Me)

(**201**; M = Re, PR_3 = $PPhMe_2$)

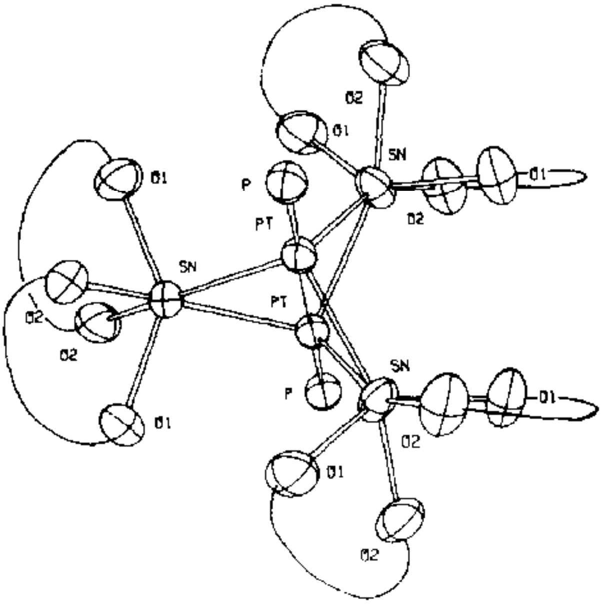
structure of (**199**) was determined by X-ray diffraction; the CS is bridging but the CO is semi-bridging, and the dynamic process observed in solution is interpreted in terms of site exchange of CO. Reaction of (**199**) with

$[Me_3O][BF_4]$ yields (202), the first example of a heteronuclear bimetallic complex with a bridging thiocarbyne ligand [499].



(202)

Reaction of $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(PPh_3)_4]$ with $[Sn(acac)_2]$ yields yellow orange crystals formulated as $[Pt(PPh_3)_2(Sn\{acac\}_2)_2]$ The value of $^1J_{PtP}$ confirms that this is a tetrahedral platinum(0) complex. Heating in toluene or treatment of $[Pt(PPh_3)_2(C_2H_4)]$ with an excess of $[Sn(acac)_2]$ yields the cluster $[Pt_2(PPh_3)_2(\mu\text{-}Sn\{acac\}_2)_3]$ (203). X-ray diffraction reveals very high molecular symmetry, with the platinum atoms within bonding distance {r(Pt-Pt) = 2.593 Å}. The bonding in the complex involves interaction between three orbitals on platinum with one orbital from each tin. Platinum(0) retains its d^{10} configuration and the tin(II) atoms each contribute two electrons to fill the three delocalised bonding molecular orbitals [500].



(203)

5.8 PALLADIUM AND PLATINUM CLUSTERS

5.8.1 Trimeric clusters

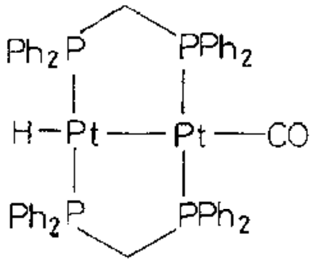
Photolysis of $[\mathrm{Pt(PPh_3)_2(C_2O_4)}]$ under a dihydrogen atmosphere followed by precipitation with $\mathrm{Na[BF_4]}$, gives $[\mathrm{Pt_3(PPh_3)_3}(\mu\text{-}\mathrm{PPh_2})_2(\mu\text{-}\mathrm{H})][\mathrm{BF_4}]$. The presence of the bridging hydride was established spectroscopically, and the rest of the structure determined by X-ray diffraction [501]. The CO bridges in clusters of various nuclearities including $[\mathrm{Pt_3}(\mu\text{-}\mathrm{CO})_3(\mathrm{PPh_3})_4]$, $[\mathrm{Pt_4}(\mu\text{-}\mathrm{CO})_5(\mathrm{PMe_2Ph})_4]$ and $[\mathrm{Pt_5}(\mu\text{-}\mathrm{CO})_5(\mathrm{CO})(\mathrm{PPh_3})_4]$ may be readily replaced by $\mathrm{SO_2}$; CO and $\mathrm{SO_2}$ are comparable as bridges. The $\{\mathrm{Pt_5}\}$ cluster gives $[\mathrm{Pt_5}(\mu\text{-}\mathrm{CO})_2(\mu\text{-}\mathrm{SO_2})_3(\mathrm{CO})(\mathrm{PPh_3})_4]$, the structure of which was determined crystallographically [502].

Formation and isolation of $[\mathrm{H}_n\mathrm{Pt_3(dppe)_3}]^+$ by treatment of the $[\mathrm{Pt(dppe)(3,5\text{-}dimethylpyrazole)}]^{2+}$ dication with $\mathrm{K[BH_4]}$ relies on the leaving group ability of the pyrazole. The same complex is also formed by $\mathrm{K[BH_4]}$ treatment of $[\mathrm{(dppe)Pt}(\mu\text{-}\mathrm{OH})_2\mathrm{Pt(dppe)}]^{2+}$ or $[\mathrm{H_3Pt_2(dppe)_2}]\mathrm{B[Ph_4]}$. $^1\mathrm{H}$ NMR spectroscopy suggests that the hydrides are mobile; n is probably 5, giving a formal oxidation state of +2 to platinum [503].

Polynuclear complexes of palladium with phosphine modified silica were studied by XPES. As the number of palladium atoms in the clusters $\textcircled{\scriptsize P}\!-\!\mathrm{Pd}_n\mathrm{X}_2$ increases from 1 to 10 the palladium oxidation state is reduced [504]. $[\mathrm{Pt_3}(\mu\text{-}\mathrm{CO})_3(\mathrm{PEt_3})_4]$ deposited on alumina is a hydrocracking catalyst [505].

5.8.2 Tetrameric clusters

The two tetrameric clusters reported this year both have the butterfly or open tetrahedron structure. Reaction of $\mathrm{Pd(OAc)_2}$ with CO and $\mathrm{R_3P}$ in the presence of NaOAc/HOAc gives $[\mathrm{Pd_4(CO)_5(PR_3)_4}]$, in contrast to the reaction without excess ethanoate which yields $[\mathrm{Pd_{10}(CO)_{12}(PR_3)_6}]$ [506]. Yet another report on this reaction, this time conducted in tfaH/propanone yields [$Pd_{12}(CO)_{15}(PR_3)_7$], [$Pd_{12}(CO)_{17}(PR_3)_5$] and the higher nuclearity species, [$Pd_{13}(CO)_{19}(PR_3)_5$] and [$Pd_{15}(CO)_{19}(PR_3)_9$], the proportions depending on the Pd:P ratios. The structures of the clusters are not specified but all show both terminal and bridging CO stretching frequencies [507]. [$H_2Pt_2(\mu$-H)(μ-dppm)$_2$][PF_6] is a precursor of a very active catalyst for the water gas shift reaction. The carbonyl hydride (204) is formed on treatment with CO and undergoes facile oxidative dimerisation to (205), the butterfly structure of which was established crystallographically [508].



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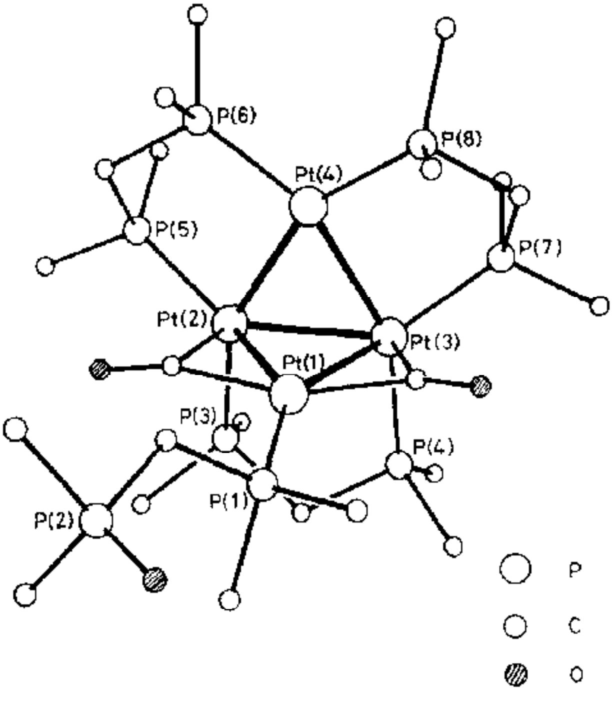


(205)

5.8.3 Higher nuclearity clusters

Hydrogenation of alkenes in the presence of $Pd(OAc)_2$ or [$Pd(PPh_3)(OAc)_2$]$_2$ and their derivatives is ineffective if dioxygen is rigorously excluded. The effect of the dioxygen is in generating the "true active species" which is normally a $\{Pd_5\}$ cluster of unspecified structure. One of the rather imaginative pathways proposed is shown in reaction (27) [509,510].

$$\begin{aligned}&Pd(OAc)_2 + phen \xrightarrow{H_2} [\{Pd_5(phen)_2(OAc)\}_n] \xrightarrow{O_2} \\ &[Pd_{10}(phen)_4(O_2)_3][OAc]_2 \xrightarrow{H_2} [\{Pd_5(phen)_2(OAc)\}_n] \qquad (27)\end{aligned}$$

Hydrogenation of aldehydes, ketones, alkenes and nitriles in the presence of $[Bu_4N]_2[\{Pt_3(CO)_6\}_{10}]$ was studied by IR spectroscopy. Reduction of the cluster yields, through several stages, $[\{Pt_3(CO)_6\}_3]^{2-}$, which subsequently adds molecular hydrogen [511].

5.8.4 Heteronuclear clusters

Interest in palladium and platinum containing heteronuclear clusters has increased considerably this year, with structural studies still dominating the published reports. In particular, the range of platinum containing boranes and carboranes has been considerably extended. Reaction of *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ with 4-Me_2S-7-MeO-*arachno*-B_9H_{12} yields the expected *arachno*-platinanonaborane $[(Me_2PhP)_2PtB_8H_{11}OMe]$, together with a small amount of $[(Me_2PhPPt)_2B_8H_{14}]$. The latter compound, characterised by X-ray diffraction, consists of four-vertex and eight-vertex subclusters $\{Pt_2B_2\}$ and $\{Pt_2B_6\}$ joined at the Pt-Pt bond, and can be regarded as an *iso*-*arachno*-diplatinadecaborane [512]. More unexpected products were isolated from the reaction of $[Pt(PMe_2Ph)_2Cl_2]$ with the deprotonated *anti*-isomer of $B_{18}H_{22}$. As well as $[(Me_2PhP)_2Pt$-η^4-*anti*-$B_{18}H_{20}]$, two further products were formed. One of these is a novel μ,η^1,η^2-isomer in which $\{Pt(PMe_2Ph)_2\}$ bridges two edge linked $\{B_{10}\}$-clusters, and the other a more compact green compound. By X-ray diffraction the latter, of formula $[(Me_2PhP)_4Pt_2B_{18}H_{16}]$, was shown to possess the novel confacial *conjuncto*-borane unit, $\{B_{18}H_{16}\}$, η^4-bonded to one $\{Pt(PMe_2Ph)_2\}$ unit and

η^4,η^2- to the other. Use of *syn*-[$B_{18}H_{22}$] yields a third isomer of [$(Me_2PhP)_2PtB_{18}H_{20}$] [513]. The first example of a contiguous seventeen-vertex cluster species is formed by reaction (28). The product involves a *nido* eight-vertex (PtB_7) subunit and a *nido*-(PtB_{10}) cluster conjoined with a Pt-B vector as the common edge [514].

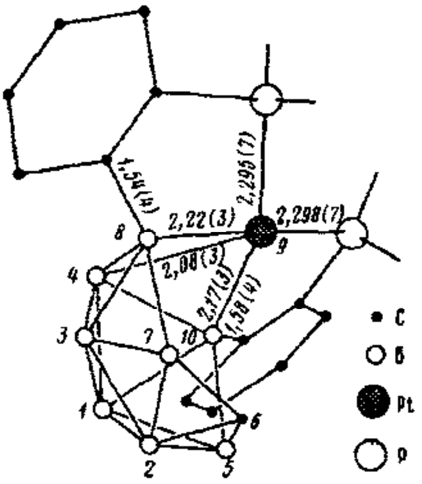
$$\textit{Arachno}\text{-}[(Me_2PhP)_2PtB_8H_{12}] \xrightarrow{\Delta} [7\text{-}(Me_2PhP)\{7\text{-}PtB_{16}H_{18}\text{-}9'\text{-}(PMe_2Ph)\}] \qquad (28)$$

Carboranes are also reactive, yielding carbaplatinaboranes; reaction (29) involves the double insertion of a platinum nucleophile into a *closo*-carborane [515]. *Nido*-[$9,6\text{-}(Ph_3P)_2PtCB_8H_{12}$], formed from

$$\begin{aligned}&[Pt_2(\mu\text{-cod})(PEt_3)_4] \;+\; \textit{closo}\text{-}[2,4\text{-}Me_2\text{-}2,4\text{-}C_2B_5H_5] \longrightarrow \\ &[4,4\text{-}(Et_3P)_2\text{-}1,7\text{-}Me_2\text{-}1,4,7\text{-}CPtCB_5H_5] \;+ \\ &\qquad\qquad [1,1,6,6,\text{-}(Et_3P)_4\text{-}4,5\text{-}Me_2\text{-}1,4,5,6\text{-}PtC_2PtB_5H_5] \qquad (29)\end{aligned}$$

arachno-[$4\text{-}CB_8H_{14}$] and [$Pt(PPh_3)_4$] undergoes insertion of boron into a CH bond to yield **(206)** [516]. Potentially still more complex are the reactions of metallocarboranes. Insertion of {$Pt(PEt_3)_2$} into [$H_2Fe(2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_2)_2$] yields **(207)**. This is an area capable of considerable development in future years; few mechanisms are defined with any certainty and there are few systematic guidelines for predicting the outcome of specific reactions [517].

Bridged bimetallic W-Pt complexes have again provided the source for a wide range of new bimetallic and trimetallic compounds. Carbonylation of **(208)** gives a mixture, the composition of which depends on PR_3 (reaction (30)). When $R_3P = Ph_2MeP$, only the trinuclear complex is produced but all three products are formed with Me_3P. **(210)** has a butterfly structure in the solid state and is related by the isolobal analogy to [$L_4Pt_2(\mu\text{-}RC{\equiv}CR)$] [518].



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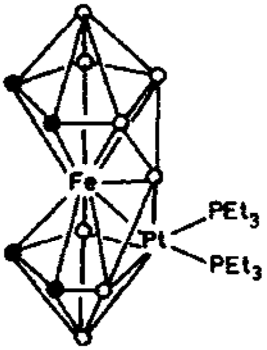
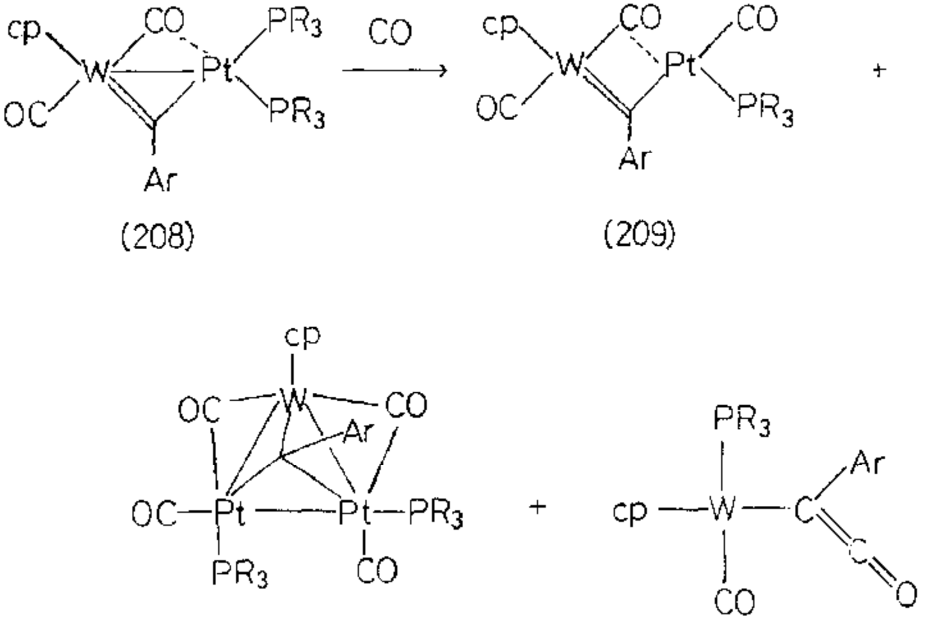


(207)

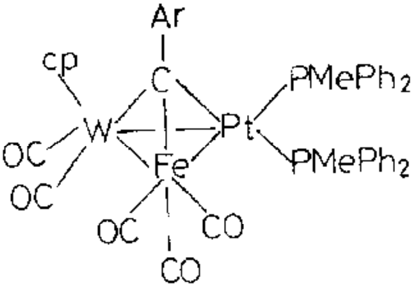
Reaction of (208) with $[Fe_2(CO)_9]$ gave a mixture of the three related clusters $[FePtW(\mu_3\text{-}CAr)(\mu\text{-}CO)(CO)_5(PR_3)_2cp]$, $[FePtW(\mu_3\text{-}CAr)(CO)_6(PR_3)cp]$ and $[FePtW(\mu_3\text{-}CAr)(CO)_5(PR_3)_2cp]$. The longest recorded Pt–W distance (2.883 A) was determined in $[FePtW(\mu_3\text{-}CAr)(CO)_5(PMePh_2)_2cp]$ **(212)** [519]. The bridging carbene complex **(213)** reacts with σ–donors (PMe_3 or dppe) to replace cod, but with π–acceptors such as CO or Me_3CNC, metal–metal fission occurs and the products isolated are stereoisomers of $[Pt_3\{\mu\text{-}C(OMe)Ar\}_3L_3]$ (reaction (31)). For L = CO the isomers are separable and the non-symmetric compound was studied by X-ray diffraction [520].



(208) (209)

(210) (211)

(30)



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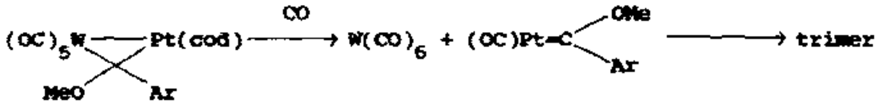
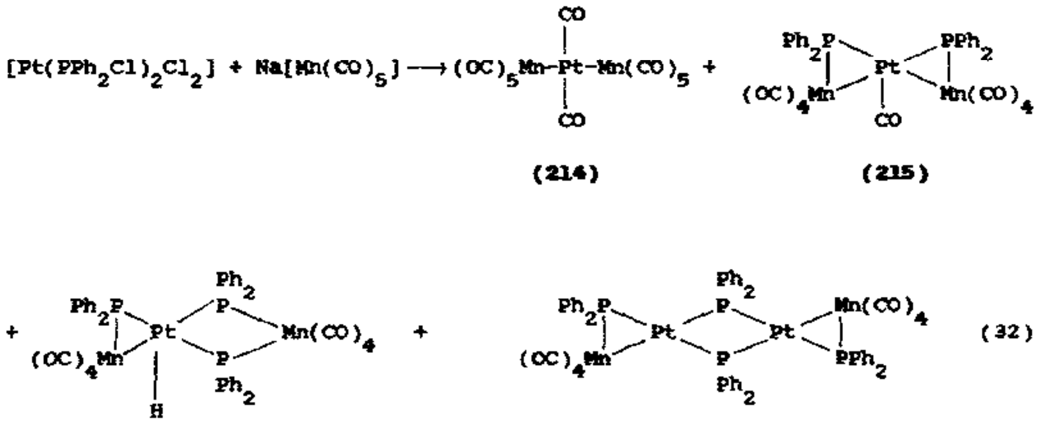
 (31)

(213)

$[Pt(PPh_2Cl)_2Cl_2]$ reacts with $Na[Mn(CO)_5]$ to give a range of products (reaction (32)). X-ray crystallography of **(215)**, **(216)** and **(217)** shows that platinum is pentacoordinate in an approximately square-pyramidal environment [521].

 (32)

(214) **(215)**

(216) (217)

The lability of ethene in $[Pt(PPh_3)(C_2H_4)_2]$ is utilised in its reaction with $[Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ to give the distorted tetrahedral $[Fe_3Pt(\mu_3\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}(PPh_3)]$. In this cluster COMe bridges $\{Fe_3\}$ and hydride bridges the $\{Fe_2Pt\}$ face [523]. A platinum insertion also occurs when $[R_2Pt(dppe)]$ (R = Ph or Me) reacts with $[Os_4H_4(CO)_{12}]$ to give $[Os_4H_2(CO)_{12}Pt(dppe)]$. The structure of the product is not known [522].

The requirement for an open cluster framework in catalysis was highlighted in a comparison of polymer-supported $[Co_2Pt_2(CO)_8]$ and $[H_2PtOs_3(CO)_{10}]$. The former has an open butterfly structure and is active for ethene reduction at 1 atm/<100 °C, but the closed $\{PtOs_3\}$ tetrahedron is quite inactive [524].

Ethene is more readily displaced from platinum(0) than cod as shown in the reactions (33) and (34) with $[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2]$. The structure of **(218)** (Figure 1) shows D_{2d} symmetry as predicted by degenerate perturbation theory, the rhodium atoms forming a pseudotetrahedron [525]. Reaction with

$$[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2] \xrightarrow{[Pt(C_2H_4)_3]} [PtRh_4(\mu\text{-}CO)_4(\eta^5\text{-}C_5Me_5)_4] \qquad (33)$$

(218)

$$[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2] \xrightarrow{[Pt(cod)_2]} [PtRh_2(\mu^3\text{-}CO)_2(cod)(\eta^5C_5Me_5)_2] \qquad (34)$$

(219)

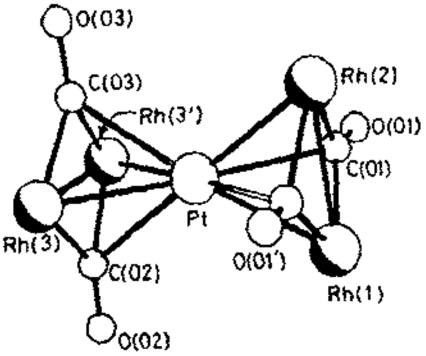
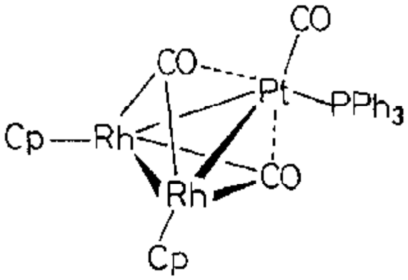


Figure 1 Crystal structure of $[PtRh_4(\mu\text{-}CO)_4(\eta^5\text{-}C_5Me_5)_4]$ [526]

$[Pt(PPh_3)_2(C_2H_4)]$ gives a complex mixture of which the main component is (220), structurally analogous to (219). (220) is also formed, in much better yield, in the reaction with $[Pt(PPh_3)(C_2H_4)_2]$, which also produces small amounts of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$. Carbonylation of **(220)** leads to metal-metal fission and the formation of $\{Pt_3\}$ and $\{Pt_5\}$ clusters [526]. Both **(219)** and **(220)** are protonated by $H[BF_4]$ along a Pt-Rh edge to give **(221)**. At low temperatures and in the solid state the structure is non-symmetric as shown, but at room temperature the hydrogen shifts from one platinum-rhodium bond to the other with an activation energy ranging from 49.3 kJ mol^{-1} for **(221a)** to 58.1 kJ mol^{-1} for **(221c)**. Since $^1J_{PtH}$ is temperature independent it is proposed that the dynamic process involves rotation of the $\{Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)\}$ fragment about an axis from platinum to the midpoint of the Rh-Rh bond [527].



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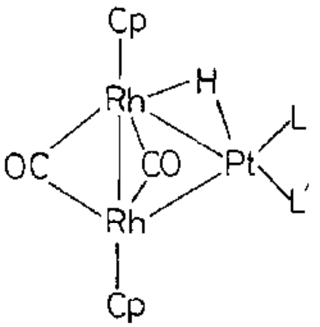


(221a; L,L' = CO)

(221b; L = CO, L' = PPh_3)

(221c; L,L' = cod)

(Cp = $\eta^5C_5Me_5$)

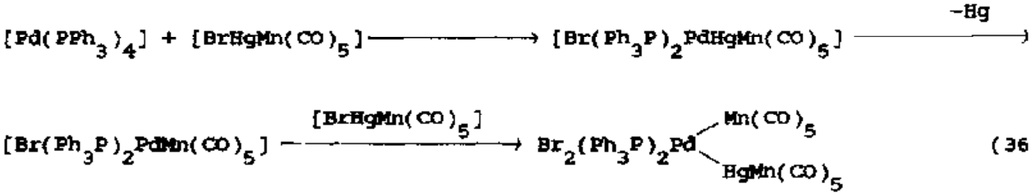
The cluster $[PtRh_{10}N(\mu\text{-}CO)_{10}(CO)_{11}]^{3-}$, prepared from $[Rh_6N(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^{2-}$, has the highest known metal to interstitial atom ratio [528].

Treatment of $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ with metallic mercury gives $[\{Pt_3Hg(\mu\text{-}CO)_3(PR_3)_3\}_2]$, in which the two triangular $\{Pt_3\}$ units are each capped by a mercury atom. The $\{Hg_2\}^{2+}$ unit has a long, weak, metal-metal bond. The binding in such species derives from a linear combination of one empty σ-type orbital of each $\{Pt_3\}$ fragment and the filled Hg 6s orbital. This gives one strongly and one weakly bonding molecular orbital, both filled. The weak Hg-Hg interaction arises from the non-bonding character of the HOMO between these two atoms [529]. Reduction of *cis*-$[Pt(CNR)_2Cl_2]$ by sodium amalgam in the presence of an excess of isocyanide gives three products (reaction (35)). The

$$cis\text{-}[Pt(CNR)_2Cl_2] + RNC \xrightarrow{Na/Hg} [HgPt_6(CNR)_{12}] + [Pt_7(CNR)_{12}] + [Pt(CNR)_5] \quad (35)$$

structure of $[HgPt_6(CNR)_{12}]$ was shown to involve two triangular $\{Pt_3\}$ units each with three bridging and three terminal isonitriles, joined by mercury. The two trangular units are nearly but not quite eclipsed. Heating in toluene gives $[Pt_3(CNR)_6]$ and mercury metal [530].

$[Pt(PPh_3)_3]$ undergoes oxidative addition of $[BrHgRe(CO)_5]$ to give $[Br(Ph_3P)_2PtHgRe(CO)_5]$. With the analogous manganese species, mercury is readily lost to yield the bimetallic species $[Br(Ph_3P)_2PtMn(CO)_5]$ and Hg metal. With $[Pd(PPh_3)_4]$ a second oxidative addition is possible yielding a palladium(IV) species as the final product (reaction (36)) [531].



$$[Pd(PPh_3)_4] + [BrHgMn(CO)_5] \longrightarrow [Br(Ph_3P)_2PdHgMn(CO)_5] \xrightarrow{-Hg}$$
$$[Br(Ph_3P)_2PdMn(CO)_5] \xrightarrow{[BrHgMn(CO)_5]} Br_2(Ph_3P)_2Pd\begin{matrix} Mn(CO)_5 \\ HgMn(CO)_5 \end{matrix} \quad (36)$$

5.9 CATALYSIS BY PALLADIUM AND PLATINUM COMPLEXES

5.9.1 Hydrogenation

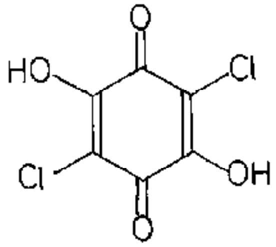
Palladium and platinum complexes were among those studied by Vaska in an extensive survey of dihydrogen addition. Reversible formation of an MH_2 intermediate is diagnosed by the abilty to interconvert *ortho*- and *para*-hydrogen. $[Pt(PPh_3)_4]$, $[(Ph_3P)_2Pt(O_2)]$ and $[Pt(PBu_3)_2Cl_2]$ were all active but $[Pt(dppe)_2]$ and $[Pt(Ph_2PCH{=}CHPPh_2)]$ were not. The formation of a $\{P_2Pt\}$ species is crucial for dihydrogen addition and the chelating biphosphines do not dissociate easily. Reaction (37) is mechanistically more demanding, requiring the ability to activate two dihydrogen molecules at the same centre; only $[Pt(PPh_3)_3]$ and $[(Ph_3P)_2Pt(O_2)]$ were able to catalyse this process [532].

$$H_2 + D_2 \rightleftharpoons 2HD \qquad (37)$$

Many of this year's reports on alkene hydrogenation relate to the activity and stability of catalysts immobilised on polymer supports. Silica supported poly(vinylpyrrolidone)palladium(II) is an active and selective catalyst for alkene reduction at 25 °C/1 atm. XPES shows that palladium is chelated by nitrogen and oxygen [533,534]. Phosphine-modified silicas loaded with palladium and platinum are similarly active [535,536]. Other active species include $PdCl_2$/polyaminochloroquinone and $PdCl_2$/polystyrene [537,538].

The species formed from $PdCl_2$ and trialkylamines contain Pd-N bonds and catalyse reduction of alkenes to alkanes. Reduction of diphenylethyne gives 95% *cis-* and 5% *trans*-stilbenes [539]. Arenes inhibit reduction of 1-hexene in the presence of PdS by displacing adsorbed substrate [540].

Non-empirical pseudopotential calculations for $[HPd(C_2H_4)Cl_3]^{2-}$ suggest that the mechanism of reduction involves collapse to planar $[C_2H_5PdCl_3]^{2-}$ [541].



(222)

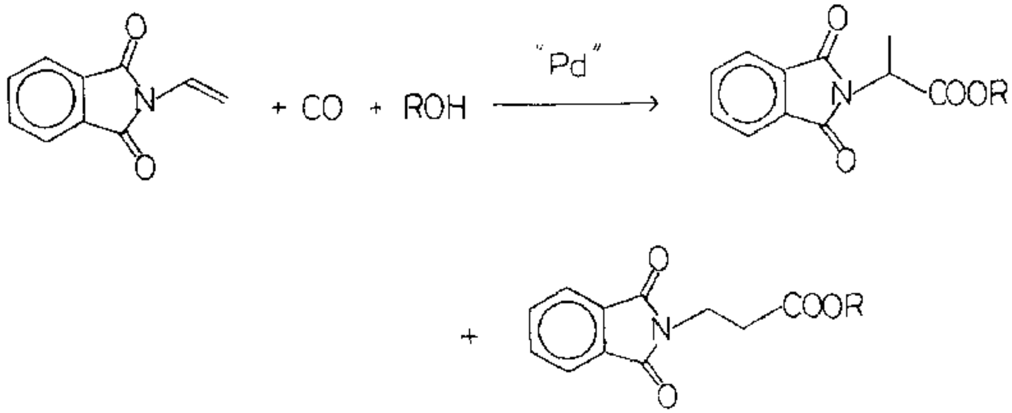
Palladium and platinum complexes on supported (222) catalyse reductive amination, yielding RCH_2NHPh from RCHO and nitrobenzene [542]. $[Pt(dmso)_2Cl_2]$ and $[(2\text{-methyl-3-hydroxy-4-pyrone})_2Pt]$ are also active catalysts for the reduction of nitroarenes [543].

Various palladium complexes supported on silica are active for the reduction of sulpholene and thiophene [544]. Polyamide-66 treated with $H_2[PtCl_6]$, $K_2[PdCl_6]$ or $RhCl_3$ at 100 °C for 30 minutes and then reduced by H_2 at 160 °C gives a species in which the metals are present as small crystallites on the polymer. This provides a catalyst for fairly selective reduction of benzene to cyclohexene, the latter being very weakly adsorbed [545].

A low conversion of dihydrogen and dioxygen to H_2O_2 is achieved in the presence of $[Pd(P(C_6F_5)_3)_2Cl_2]$ [546].

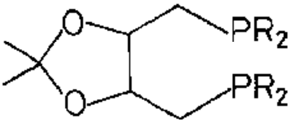
5.9.2 Carbon monoxide reactions

Selectivity has been the watchword in studies of alkene hydroformylation and hydrocarboxylation. *N*-vinylphthalimide gives an *n:iso* ratio up to 83.6:16.5 in the presence of $[Pd(PPh_3)_2Cl_2]/SnCl_2$ (reaction (38)). When dibenzophosphole replaces PPh_3, 98.5% of the product is linear, though



(38)

conversion is low [547]. Up to 99% linear aldehyde is obtained by hydroformylation of 1-alkenes in the presence of $PtCl_2/SnCl_2$/chelating biphosphine [548]. A combination of alkene isomerisation and hydroformylation gives linear aldehydes from internal alkenes in the presence of $[Pt(PR_3)_2(CO)Cl]^+/SnCl_2$ [549]. Quite spectacular enantiomer excesses were reported for the hydroformylation of styrene in the presence of $PtCl_2/SnCl_2$/(223) (subsequent more detailed studies have shown these to be somewhat exaggerated) [550]. Oxidative hydrocarboxylation of styrene yields methyl cinnamate and 1-phenyl dimethylsuccinate [551]. Somewhat unselective hydrocarboxylation of ethene to propanoate occurs in the presence of $[Pd(PPh_3)_2Cl_2]$ [552]. In the presence of $PdCl_2/CuCl_2/PPh_3$, $HC{\equiv}CCH_2CH_2OH$ is converted to the corresponding α-methylene lactone in excellent yield. Under the same conditions $HC{\equiv}CCH_2OH$ gives a polymer *via* intermolecular reactions [553].

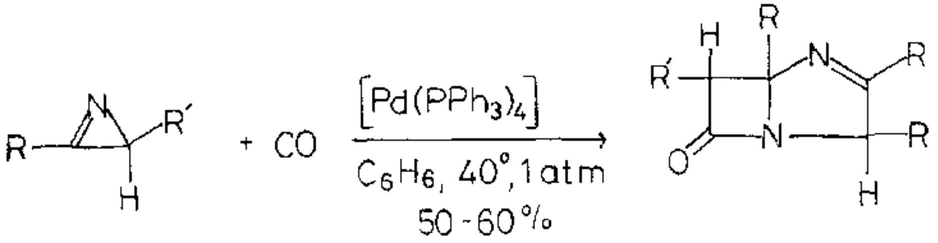


(223; R = Ph or R_2 = dibenzophosphole)

Carbonylation of 2,4-dinitrotoluene in the presence of $[Pd(py)_2Cl_2]/H_4SiMo_{12}O_4$ gives the bis(isocyanate) in modest yield [554]. When nitroarene carbonylation is carried out in the presence of ethanol and the catalyst is $[Pt(PPh_3)_2Cl_2]/SnCl_4$, the product is ArNHCOOEt. In contrast to alkene carbonylations Sn(IV) compounds are much better cocatalysts than Sn(II) species [555]. A useful alternative to the Friedel-Crafts reaction for deactivated arenes is provided by reaction (39) [556].

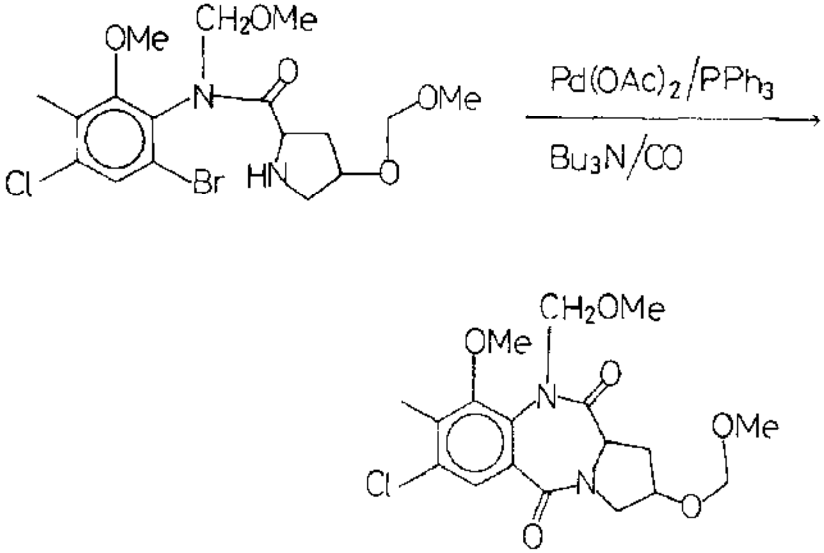
$$ArN_2X + CO + R_4Sn \xrightarrow[55-90\%]{Pd(OAc)_2} ArCOR \qquad (39)$$

Palladium catalysed carbonylation of azirine (224) gives the intriguing dimerisation to a β-lactam (225). The mechanism proposed involves ring opening followed by CO insertion, but is clearly still somewhat speculative [557].



(224) (225)

Carbon monoxide insertion combined with amine attack has provided precursors to both anthramycin (reaction (40)) and diazepam [558,559].



(40)

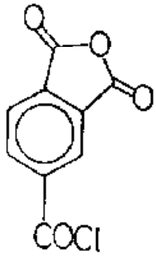
Copolymerisation of ethyne and carbon monoxide occurs in the presence of $[Pd(PPh_3)_3(MeCN)][BF_4]_2$, under much milder conditions than those previously reported [560]. Both carbonylation and polymerisation are said to occur using $PdBr_2/(PhO)_3P/ROH/HX$ as catalyst system, but selectivities are unpredictable

[561].

Reaction of RHgCl with carbon monoxide in the presence of $[PhPd(PPh_3)_2I]$ gives up to 99% yields of R_2CO [562].

Platinum-ruthenium bimetallic clusters supported on silica are prepared *in situ* from $H_2[PtCl_6]$ and $RuCl_3$. They act as methanation catalysts, but the turnover decreases as the proportion of platinum increases, implying that a Pt-Ru site is not as efficient as the Ru-Ru site [563].

Decarbonylation of (226) is catalysed at high temperatures by $[Pd(PPh_3)_4]$ or $PdCl_2$ [564].



(226)

5.9.3 *Oxidation*

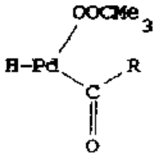
The oxidation of saturated hydrocarbons in the presence of $PdSO_4/H_2SO_4/[NO_2]^+$ in 50% H_2SO_4 has been reviewed [565]. Potential applications of the Pd(II)/Pd(IV) couple in catalysis of oxidation have been discussed [566].

Most of the reports on the Wacker oxidation of ethene to ethanal give only minor refinements to the conditions used [567-569]. A study of the mechanism of reaction (41) shows that oxygen is transferred from nitrate to the carbonyl group [570]. Further oxidations of 1-alkenes to methyl ketones

$$3C_2H_4 + 5HOAc + 2LiNO_3 \xrightarrow{Pd(OAc)_2} 3HOCH_2CH_2OAc + 2LiOAc + 2NO + H_2O \qquad (41)$$

using $PdCl_2/CuCl_2/O_2$/dmf have been reported [571-574]. Butadiene is oxidised to furan in the presence of $PdCl_2/TeO_2/NH_4VO_3/Al_2O_3$ or $PdCl_2$/heteropolyacid [575,576].

Two papers report oxidation of 1-alkenes using Me_3COOH. Some of the methyl ketone is formed but the major products are esters or acids. Oxidative addition of Me_3COOH yields species of the type (227) which undergo reductive elimination to esters [577].



(227)

Both palladium(I) clusters and palladium(0) complexes participate in arene oxidation catalysed by $PdSO_4$ [578]. The ion pair complex is the active catalyst in oxidation of cyclohexanol in the presence of $Pd(OAc)_2/Cl^-/K^+$/18-crown-6 [579]. Oxidative dehydrogenation of cyclohexanone in the presence of $[Pd(O_2CCF_3)_2]$ yields cyclohexenone [580].

5.9.4 Other additions to alkenes and alkynes

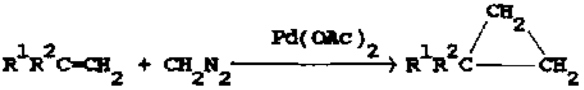
Platinum complexes have provided many catalysts for hydrosilylation; two new examples are shown in reactions (42) and (43) [581,582].

$$CH_2{=}CHCH_2Cl + HSiCl_3 \xrightarrow[100\ ^\circ C,\ 8h,\ 82\%]{[Pt(PPh_3)_2Cl_2]} Cl_3Si(CH_2)_3Cl \qquad (42)$$

$$CH_3(CH_2)_3CH{=}CH_2 + HSi(OEt)_3 \xrightarrow[100\%]{\enclose{circle}{SiO_2}-(CH_2)_3NH_2/H_2[PtCl_6]} (EtO)_3Si(CH_2)_5CH_3 \qquad (43)$$

Addition of DCN to terminal and cyclic alkenes in the presence of palladium(0) complexes of chiral phosphines has been shown to be stereospecifically *cis* [583].

New carbon-carbon bonds are produced in addition of CH_2N_2 to alkenes catalysed by $Pd(OAc)_2$ (reaction (44)) [584] and in addition of Cl_3CX (reaction (45)) [585].

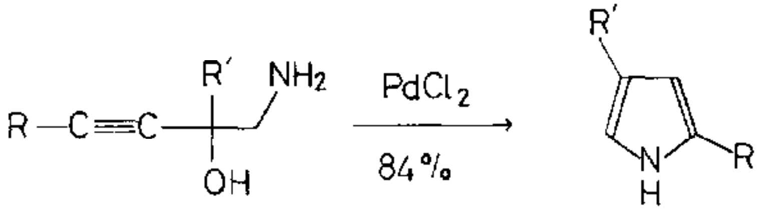


$$R^1R^2C{=}CH_2 + CH_2N_2 \xrightarrow{Pd(OAc)_2} R^1R^2C\overset{CH_2}{\text{———}}CH_2 \qquad (44)$$

$$R^1CH(OH)C(R^2){=}CH_2 + Cl_3CX \xrightarrow[(2\text{-methylphenyl})_3P/\text{base}]{Pd(OAc)_2} R^1COCH(R^2)CH_2CCl_3 \qquad (45)$$

A number of palladium catalysed addition reactions involve attack of a nucleophile on a palladium alkene complex formed *in situ*. Examples reported this year include oxygen [586], sulphur (reaction (46)) [587] and inter- [588] and intra-molecular reactions of amines (reaction (47)) [589,590]. Both ring opening and attack of amine occur in reaction (48) [591].

$$CH_2{=}CH{-}CH{=}CH_2 + BuSH \xrightarrow[95\%,\ thf]{[Pd(acac)_2]/Ph_3P/Et_3Al} \underset{70\%}{BuSCH_2CH{=}CHCH_3} + \underset{30\%}{BuSCH(CH_3)CH{=}CH_2} \qquad (46)$$



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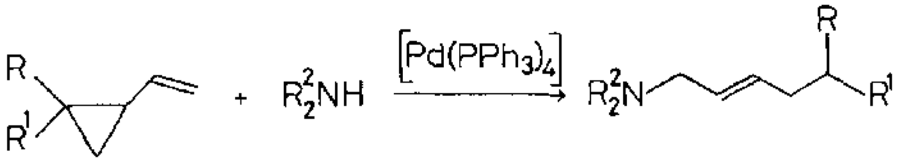
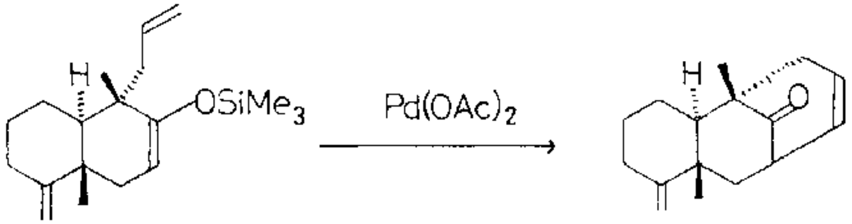


(48)

Carbanions are also suitable nucleophiles and benzylmagnesium bromide reacts with *N*-vinylacetamide to give, after reduction, *N*-acetylamphetamine [592]. Enolate anions, usually formed *in situ*, give similar reactions (for example, (49)) [593-595].



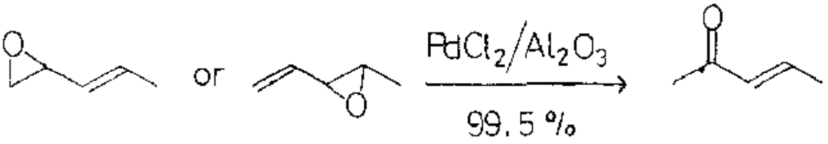
(49)

Hydrochlorination of ethyne occurs in the presence of Pd(II) and Hg(II) [596].

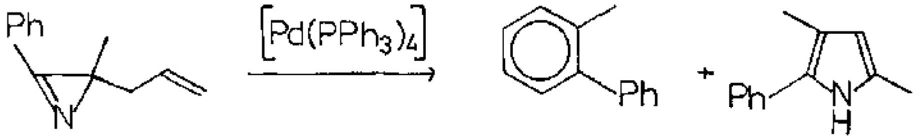
5.9.5 *Isomerisation*

1-Alkenes are isomerised mainly to *trans*-2-alkenes in the presence of $PdCl_2$ [597], whilst the use of $[HPt(PPh_3)_3][ClO_4]$ gives a predominence of *cis*-alkenes [598].

Opening of the three membered rings and formation of a π-allyl complex is the first step in reactions of (228) and (229), both of which yield (230) in excellent selectivity in the presence of $PdCl_2/Al_2O_3$ [599]. The mechanism of reaction (50) is not understood in detail [600]. Cyclopropane rings may also be opened under mild conditions where this leads to the formation of a π-allyl complex [601].

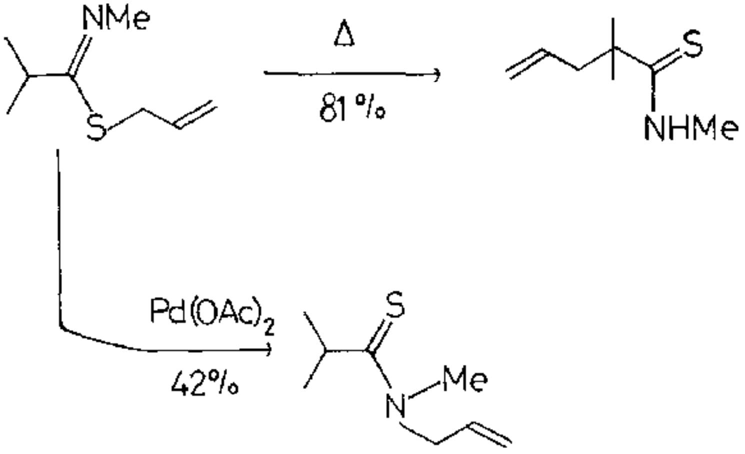


(228) (229) (230)



(50)

Thermolysis of *S*-allylthioimidates gives sulphur to carbon rearrangement, but in the presence of Pd(OAc)$_2$ the allyl group migrates from sulphur to nitrogen (reaction (51)) [602]. Almost complete chirality transfer occurs in the Cope rearrangement of (231) in the presence of [(MeCN)$_2$PdCl$_2$], the sense of the asymmetric induction being the same as that in the thermal reaction [603].



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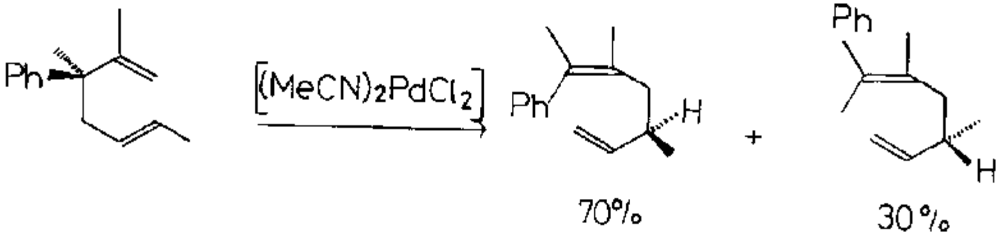
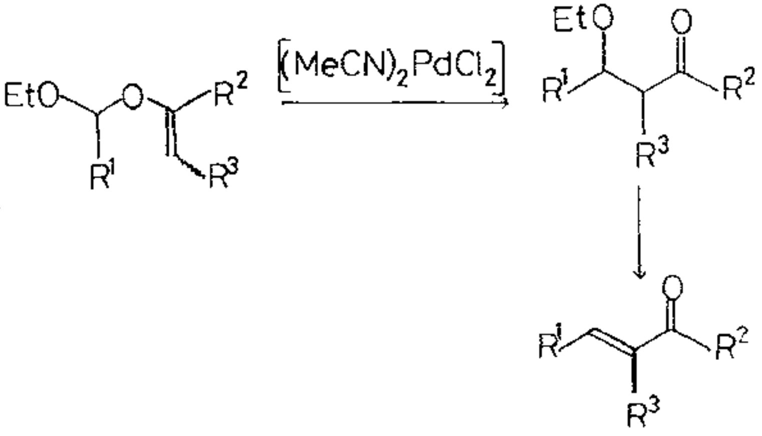


(231)

1,3-Alkyl migration of 1-alkenyl ethyl acetals occurs in the presence of [$(MeCN)_2PdCl_2$] and [$(diene)PdCl_2$] (reaction (52)) [604]. 1,3-Migration of ethanoate in (232) proceeds with retention of chirality, yielding a key intermediate for the preparation of 12-hydroxyprostaglandins (reaction (53)) [605].



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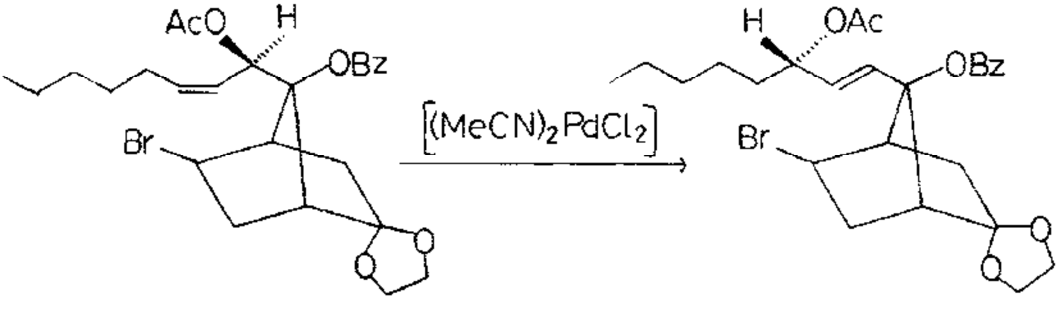
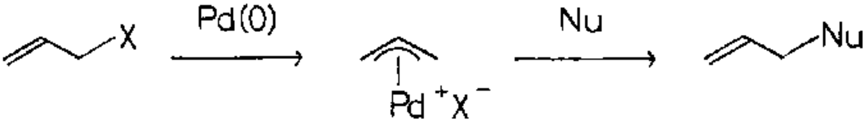


(53)

(232)

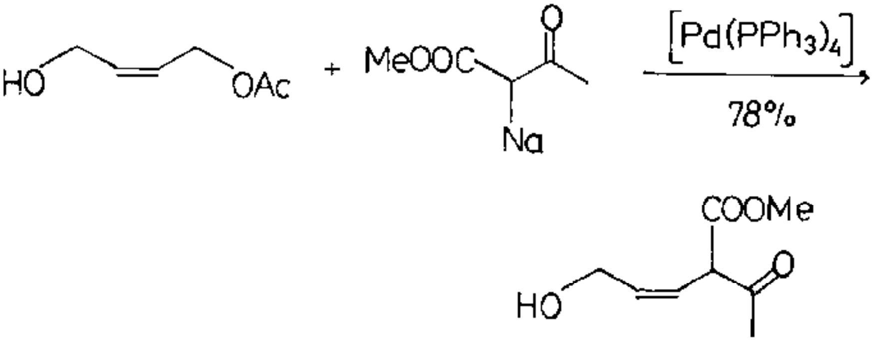
5.9.6 *Allylic substitution*

There continue to be very many reports of the nucleophilic substitution of allyl derivatives in the presence of palladium(0) complexes. These proceed *via* the formation of palladium allyl complexes (reaction (54)). Simple substitutions of this type have included β-dicarbonyl anions, amines, alkyl tin compounds and α-nitro anions as nucleophiles, and ethanoate, nitro and hydroxyl leaving groups [606-612].



(54)

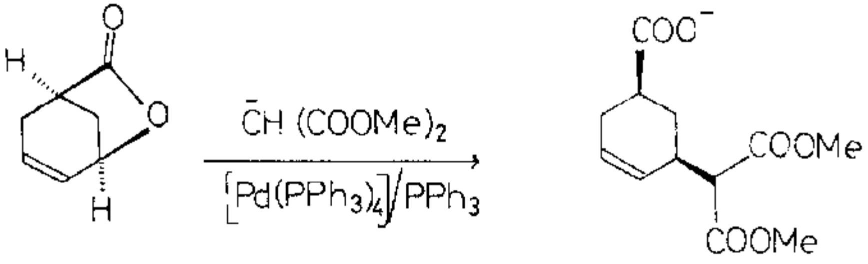
Much attention has been focused on various aspects of selectivity which may be achieved in this type of reaction [613]. Ethanoate is considerably easier to displace than hydroxyl and reaction (55) is also stereoselective, giving 75% Z product from Z starting material [614].



(55)

The usual stereochemistry of substitution using stabilised enolates is retention, *via* a double inversion (reaction (56)) [615]. However, with an alkenyl alane as nucleophile the first example of inversion (up to 95%) was noted, possibly *via* transmetallation [616].

Regioselectivity has been studied by other groups. In reaction (57) the branched product is formed under conditions of kinetic control with (233) as the major product from thermodynamic control [617]. In general, since the allyl complex may be formed from two isomeric allyl derivatives, both of these give quite similar results on substitution [618–620].



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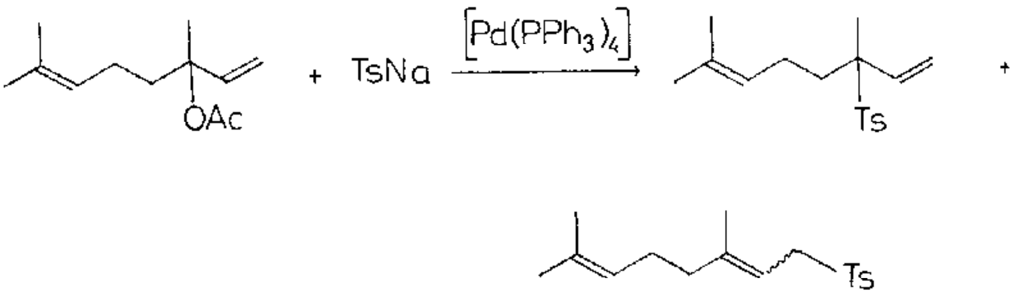
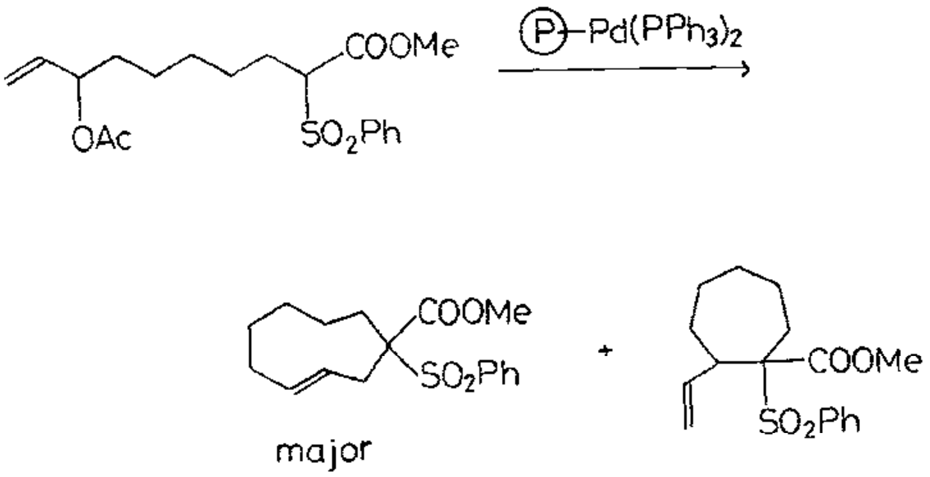


(233)

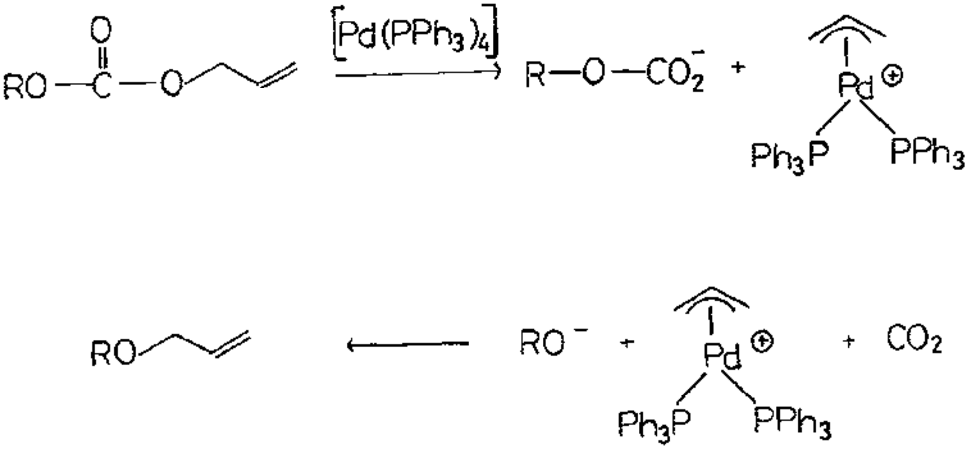
(57)

The regiochemistry of intramolecular allylic substitution is particularly intriguing, with a general tendency to form the larger and less thermodynamically favourable of two possible rings (reaction (58)) [621,622].

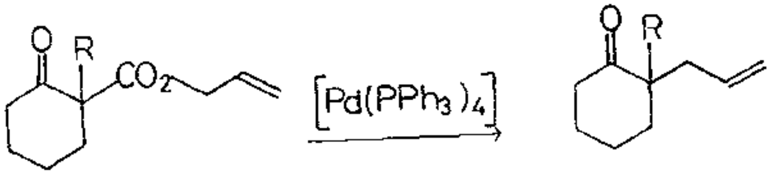
Allyl carbonates also yield allyl complexes on treatment with $[Pd(PPh_3)_4]$. Decarboxylation occurs readily and the alkoxide couples to the allyl complex (reaction (59)) [623]. β-Keto allyl esters decarboxylate by a similar route, and the enolate anion then attacks the palladium allyl complex (reaction (60)) [624,625]. The ease of palladium catalysed cleavage of allyl esters, carbonates and carbamates has lead to the use of the allyl group to


COOMe
OAc
SO₂Ph
Ⓟ-Pd(PPh₃)₂
COOMe
SO₂Ph
major
+
COOMe
SO₂Ph

(58)


RO
O
C
O
[Pd(PPh₃)₄]
R—O—CO₂⁻
+
Pd⊕
Ph₃P
PPh₃
RO
RO⁻
+
Pd⊕
Ph₃P
PPh₃
+
CO₂

(59)


O
R
CO₂
[Pd(PPh₃)₄]
O
R

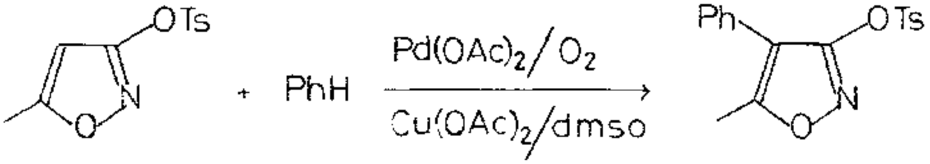
(60)

protect acids, alcohols and amines [626].

Reactions of iminoesters such as $Ph_2C=NCH_2COOEt$ have also been reported [627].

5.9.7 Oxidative coupling of arenes

Publications reporting palladium catalysed oxidative coupling of arenes continue, differing only in their selectivities (which are largely predictable and determined by the rate controlling step of ArPdX formation) and the oxidising agent used. Perchloric acid [628] and $[Tl(O_2CCF_3)_3]$ [629] have been used as oxidants. The cross coupling of reaction (61) was used in an approach to the total synthesis of muscimol [630].



(61)

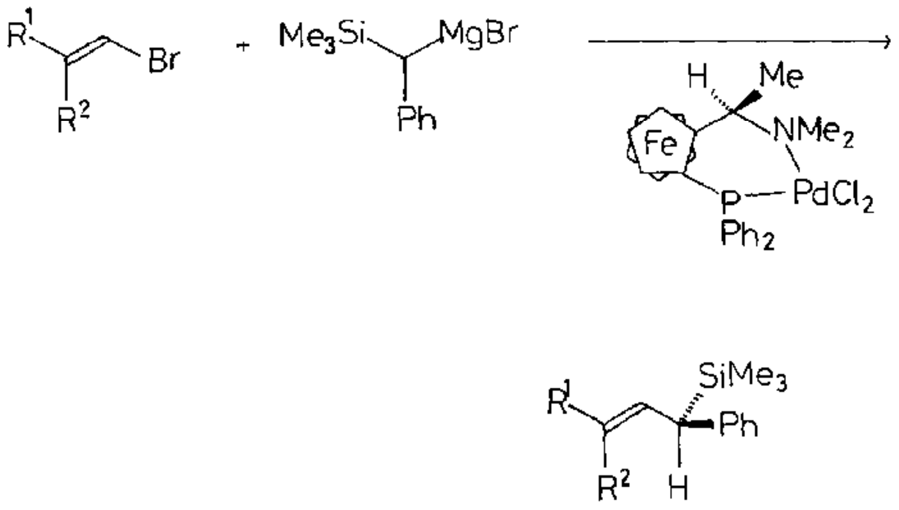
5.9.8 Coupling of carbanions with halides

The range both of organometals and substrates for the general reaction (62) has been much increased this year. Grignard reagents couple to aryl

$$R\text{-}M \ + \ R'X \xrightarrow{\text{"Pd"}} RR' \ + \ MX \qquad (62)$$

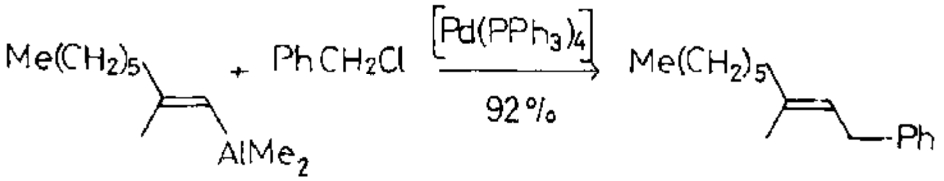
halides in the presence of $[Pd(PPh_3)_4]$ [631]. Halide and $[SPh]^-$ are successively substituted with good stereochemical control in reaction (63) [632], and vinyl phosphonates are also suitable substrates [633]. Optical yields in asymmetric coupling reactions continue to increase [634] and the first direct synthesis of chiral silanes in good enantiomer excess is exemplified by reaction (64) [635].

$$\mathrm{Br{-}CH{=}CH{-}SPh} \xrightarrow[\mathrm{[Pd(PPh_3)_2Cl_2]}]{\mathrm{R^1MgX}} \mathrm{R^1CH{=}CH{-}SPh} \xrightarrow[\mathrm{[Ni(dppe)Cl_2]}]{\mathrm{R^2MgX}} \mathrm{R^1CH{=}CHR^2} \qquad (63)$$



(64)

Aryl zinc halides react with RX in the presence of $[Pd(PPh_3)_4]$ to give ArR, where R is aryl, vinyl or heteroaryl [636]. Acyl halides are also reactive in the presence of $[Pd(PPh_3)_2Cl_2]$, the reaction in non-polar solvents in the absence of catalyst being extremely sluggish [637]. $[Pd(PPh_3)_4]$ is superior to its nickel analogue in catalysing the stereoselective coupling of vinyl alanes with benzyl halides (reaction (65)) [638].

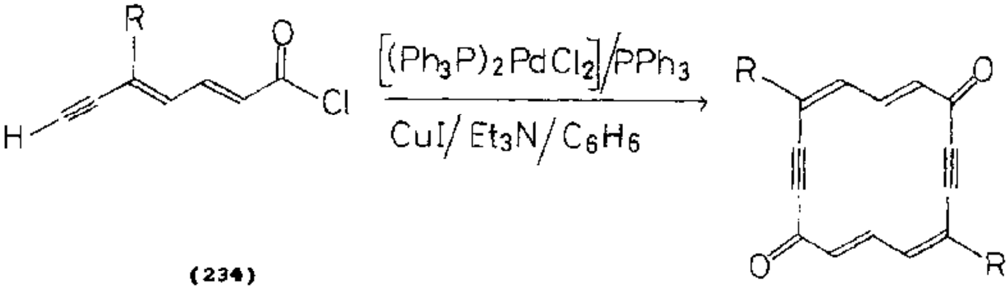


(65)

Organotin nucleophiles have become increasingly popular in several areas of organic synthesis, and coupling reactions are no exception. Tin enolates react with aryl halides (reaction (66)) [639]. Bu_3SnH gives a clean, high yielding hydrogenolysis of acyl halides in the presence of $[Pd(PPh_3)_4]$ [640]. Dialkyl mercury compounds, R_2Hg, react with R'X in the presence of $[PhPd(PPh_3)_2I]$ to give R-R' in excellent yield; without the catalyst homo coupling to R-R is extensive [641].

$$Bu_3SnCH_2COCH_3 + ArBr \xrightarrow{[Pd(\{2\text{-methylphenyl}\}_3P)_2Cl_2]} ArCH_2COCH_3 \qquad (66)$$

Alkynyl copper compounds to be used in coupling reactions are usually formed from 1-alkynes *in situ*. R'-C≡C-Cu is coupled with RX (R = vinyl or aryl) in the presence of $[PhPd(PPh_3)_2I]$ or $[Pd(PPh_3)_4]$ and a quaternary ammonium salt to give R'-C≡C-R. The reaction is very stereoselective with vinyl halides. Without the quaternary ammonium salt the diyne R'-C≡C-C≡C-R' is the major product [642,643]. Head-to-tail coupling of the dienynoyl chloride **(234)** occurs in the presence of $[Pd(PPh_3)_2Cl_2]/CuI/PPh_3/Et_3N$ (reaction (67)) [644].



(234)

(67)

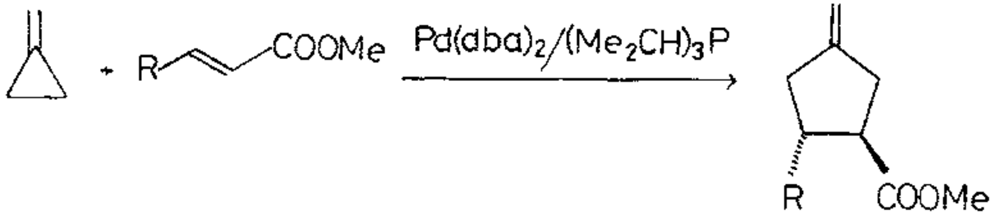
Organoboranes may be regarded as derivatives of metalloids and, as expected, react with aryl, alkynyl, vinyl, allyl and benzyl halides in the presence of $[Pd(PPh_3)_4]$ (reaction (68)) [645–647].

$$(EtOCH{=}CH)_3B \; + \; ArX \xrightarrow{[Pd(PPh_3)_4]} ArCH{=}CHOEt \qquad (68)$$

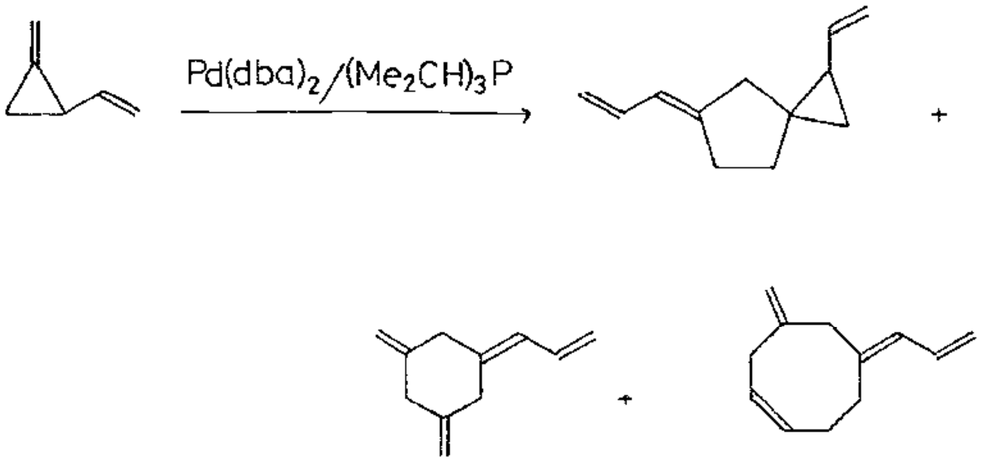
5.9.9 Other coupling reactions

The studies of Heck and his coworkers continue to add to the range of coupling reactions of unsaturated compounds catalysed by palladium complexes. Scheme 10 shows a few of the many processes reported or extended this year [648-650].

Two more cycloaddition reactions involving methylene cyclopropane have been reported by Binger's group (reactions (69) and (70)). Precedent suggests that palladium trimethylene methane complexes are the intermediates [651,652].



(69)



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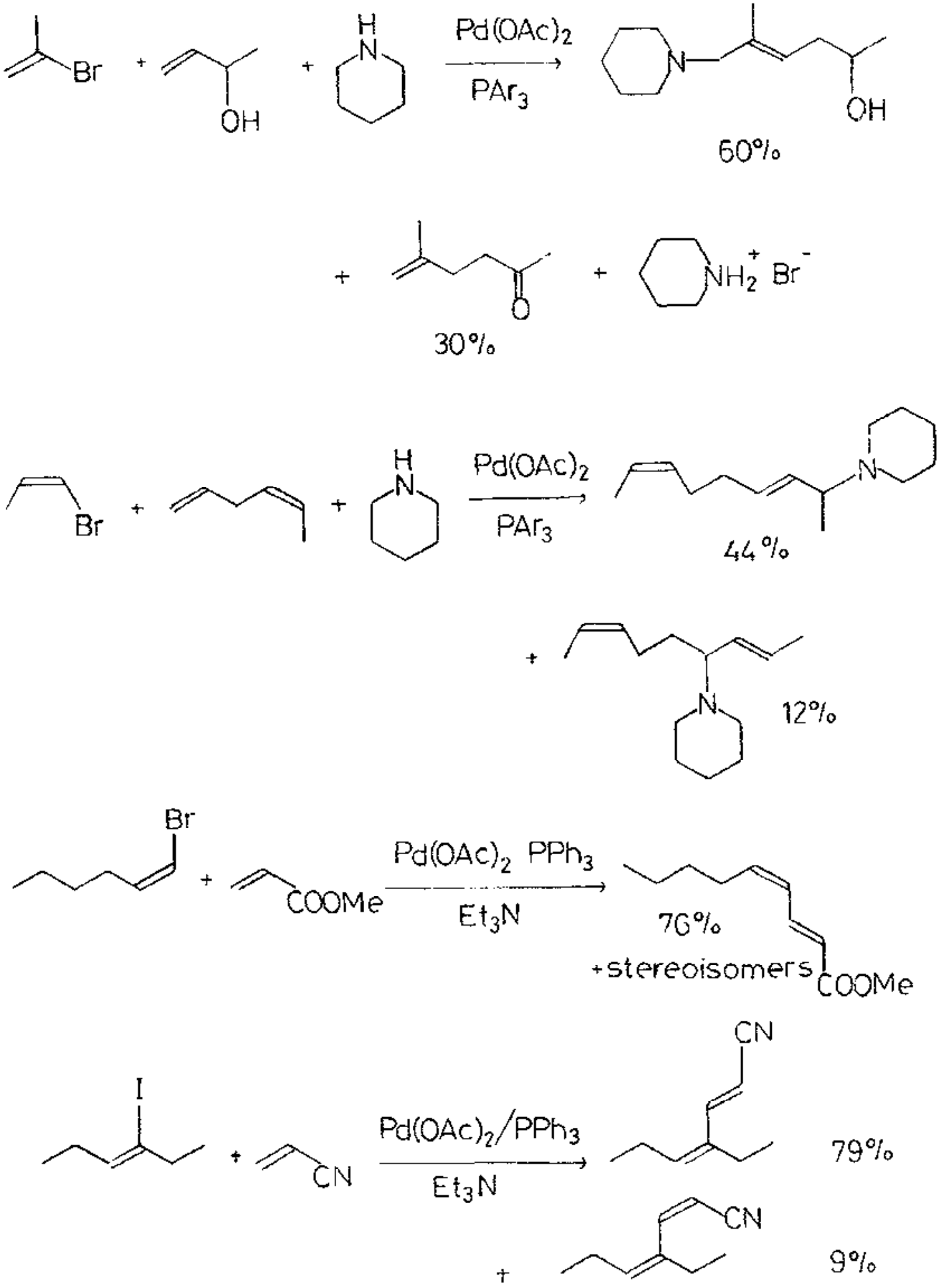
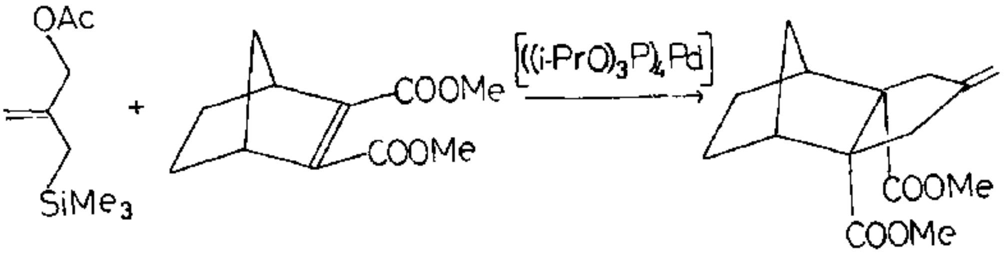


Scheme 10 Couplings of unsaturated compounds in the presence of palladium complexes [648-650].

A trimethylene methane complex is also involved in reaction (71); the product is converted to the cyclopentanoid natural product, albene [653].



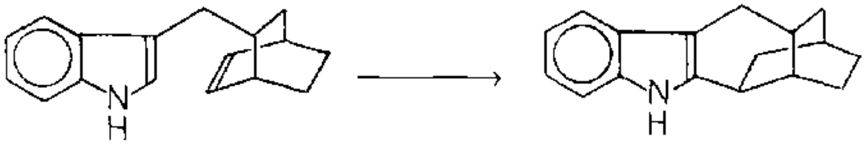
(71)

Homo coupling of arenes has been achieved using two rather different reactions. In the presence of $Pd(OAc)_2$, $PhB(OH)_2$ gives a good yield of biphenyl *via* PhPd(OAc) [654], whilst aryl iodides are reductively coupled by $Pd(II)/N_2H_4$ (reactions (72) and (73)). Yields are low but may be improved by the use of substituted hydrazines as reductants [655,656].

$$2ArI + Pd(0) \longrightarrow Ar\text{-}Ar + PdI_2 \qquad (72)$$

$$PdI_2 + N_2H_4 \longrightarrow Pd(0) + 2HI + N_2 + H_2 \qquad (73)$$

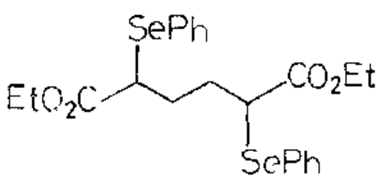
Coupling of benzene with ethene to yield styrene occurs in the presence of $Pd(OAc)_2$; the rate controlling step involves conversion of a π-aryl to a σ-aryl [657]. Cyclisation of (235) to (236) takes place in the presence of $PdCl_2/Ag[BF_4]/Et_3N$, but the role of the catalyst is not defined [658].



(235) (236)

Reaction of ethyl acrylate with PhSeBr in the presence of

$PdCl_2/PPh_3/Na[OAc]$ gives a mixture of **(237)** and **(238)** [659]. Aroyl halides yield cinnamates under these conditions. The mechanism is thought to involve oxidative addition of the acyl halide, decarbonylation, insertion of the acrylate and β-hydride elimination (Scheme 11) [660].



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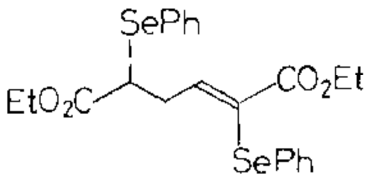

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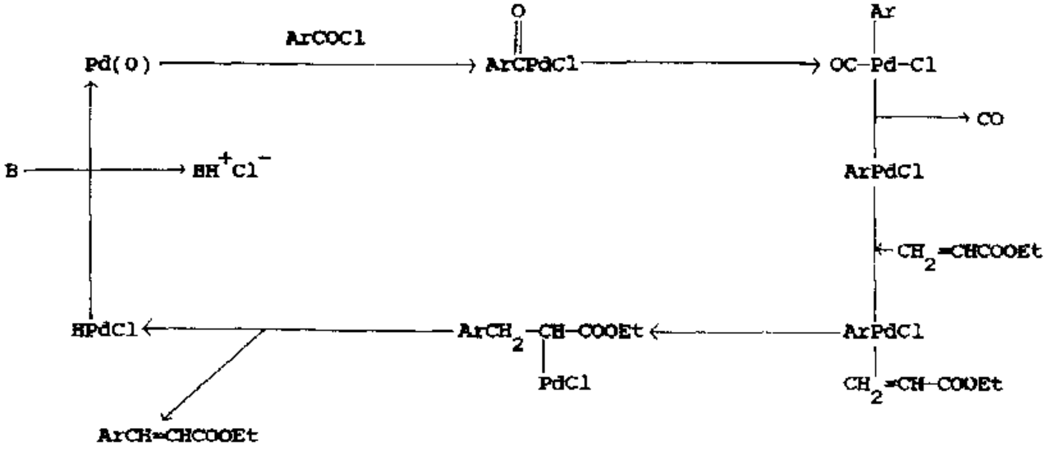
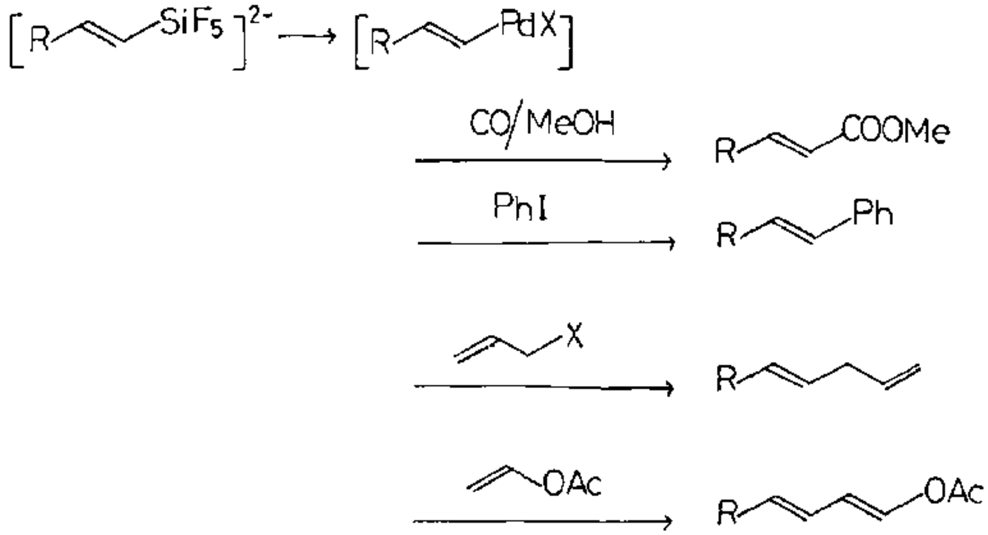


Scheme 11 Palladium catalysed coupling of aroyl halides and ethyl acrylate [660]

Other reports of coupling reactions have been scattered and lacking in generality. Aryl mercury halides react in a Michael fashion with enones in the presence of $PdCl_2/HCl/[R_4N]Cl$ [661]. $K_2[RSiF_5]$ in the presence of $PdCl_2$ yields RPdX and a range of useful conversions has been studied (Scheme 12) [662].

$[Pd(MeCN)_4][BF_4]_2$ catalyses cationic polymerisation of alkynes to high molecular weight polyalkynes which are highly coloured and have mainly *trans*-stereochemistry [663].



Scheme 12 Coupling reactions of $[RCH{=}CHSiF_5]^{2-}$ [662].

5.9.10 Other reactions catalysed by palladium and platinum complexes

Palladium and platinum catalysed reactions have been prominent in a number of other areas. A range of platinum complexes including $[Pt(PPh_3)_2Cl_2]$, $K_2[PtCl_4]$, $[HPt(PPh_3)_2Cl]$ and $K_2[PtCl_6]$ are catalysts for the chlorination of pentane [664], whilst isomerisation and dehydrogenation of alkenes occurs using $H_4[Pt_3(SnCl_2)_8Cl_4]$, or tetraalkylammonium salts of $[Pt(SnCl_3)_5]^{3-}$ and $[Pt(SnCl_3)_2Cl_2]^{2-}$ fixed on alumina [665]. A mixture of platinum and chromium polyphthalocyanines is also a catalyst for hexane dehydrogenation [666]. H/D exchange in hexane is catalysed in Pt(II)/Pt(IV) chloride solutions, probably *via* a platinum(II) alkane complex with a pentacoordinated carbon atom [667].

Hydrogenolysis of chlorinated heterocycles is achieved in excellent yield using HCOONa as reductant and $[Pd(PPh_3)_4]$ as catalyst [668]. Hydrolysis of ethanonitrile to ethanamide is accelerated by [Pd(bipy)(OH)Cl], the mechanism involving intramolecular attack of hydroxyl ion on coordinated nitrile [669].

Carboxylation of methylene cyclopropanes in the presence of $[Pd(PPh_3)_4]$ gives lactones in good yield *via* trimethylene methane complexes [670].

Finally in the rather curious reactions (74) and (75), cyclic, allylic and benzylic ethers are cleaved in the presence of $[PhCH_2Pd(PPh_3)_2Cl]$ and then coupled to acyl halides [671].

$$\text{thf} + RCOCl \xrightarrow[R'_3SnX]{[PhCH_2Pd(PPh_3)_2Cl]} RCOO(CH_2)_4Cl \qquad (74)$$

$$PhCH_2OR + CH_3COCl \xrightarrow[R'_3SnX]{[PhCH_2Pd(PPh_3)_2Cl]} PhCH_2Cl + CH_3COOR \qquad (75)$$

5.10 NON STOICHEIOMETRIC AND TERNARY COMPOUNDS

Systematic syntheses for the mixed oxides $Ba_3MPt_{0.5}Ru_{1.5}O_9$ and $Ba_3MPt_{0.75}Ru_{1.25}O_9$ (M = La, Pr, Nd, Sm-Lu, Sc or Y) are achieved by heating stoicheiometric mixtures of $BaCO_3$, M_2O_3 or M_4O_7, Pt and Ru in air. X-ray diffraction reveals the solid state structures to be closely related to that of hexagonal $BaTiO_3$. The catalytic activity of $Ba_3YbPt_{0.5}Ru_{1.5}O_9$ and $Ba_3MPtRuO_9$ (M = Sm, Y or Yb) for oxidation of CO and reduction of NO_x was determined [672]. The structures of two barium platinum titanates were determined. $BaTi_{0.88}Pt_{0.12}O_3$ is hexagonal and $Ba_4Ti_{1.81}Pt_{0.19}PtO_{10}$ is orthorhombic but both can be described as a close packed array of Ba and O atoms with titanium and platinum in the octahedral voids [673]. The structures of $Li_{0.64}Pt_3O_4$ and $Co_{0.37}Na_{0.14}Pt_3O_4$ were determined by neutron powder diffraction studies and are comparable with that of the prototype $NaPt_3O_4$ [674].

The ternary germanide PdMnGe has the Fe_2P structure [675], whilst MPtSi (M = La, Ce, Pr, Nd, Sm or Gd) adopts the ordered $ThSi_2$ structure with Pt replacing half the silicon atoms [676].

The compounds Pd_3M (M = Pu, Am or Cm) are prepared by reduction of the metal oxides by dihydrogen in the presence of palladium metal. All three are cubic with the Cu_3Au structure [677]. The rare earth complexes with this stoicheiometry adopt the same structure. When RPd_3 (R = rare earth) is melted together with boron, a single phase RPd_3B_x (x = 0-1) is formed with the boron body centered in the lattice. The structure is unchanged but the lattice is expanded and the valence state of the rare earth altered [678].

Neutron diffraction studies of Pr_2Pt show a single $MgCu_2$ type Laves phase system and no deviation from simple ferromagnetic ordering was detected [679]. Neutron powder diffraction was used to determine the structure of Pd_6P. Pd_6 forms triangular prisms, half of which are filled by phosphorus [680].

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