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Table 3.24 NMR coupling constants for platinum amine complexes [156]

	$J(^{195}Pt-^{15}N)$ (Hz)
cis-PtL_2Cl_2	351
cis-PtL_2Cl_4	249
trans-PtL_2Cl_2	290
cis-PtL_2Br_2	334
cis-PtL_2Br_4	223
trans-PtL_2Br_2	279

$L = C_{12}H_{25}NH_2$

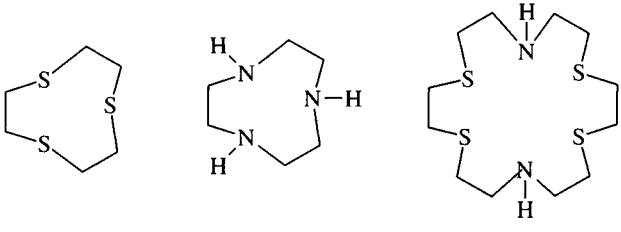
Support for this view is found in the $^{195}Pt-^{15}N$ coupling constants for dodecylamine complexes of platinum(II) and platinum(IV), where π-bonding cannot of course occur, which exhibit similar trends (Table 3.24) [156].

As already mentioned, a purely π-bonding mechanism cannot account for the position of hydride in *trans*-effect and *trans*-influence series. Overall, therefore, a major role (though not necessarily the only one) for σ-bonding is implied.

3.9 Palladium(III) and platinum(III) compounds

Mononuclear complexes of palladium and platinum in the +3 oxidation state have only recently been unequivocally characterized [157]. The major advance has come in complexes with macrocyclic ligands such as 1,4,7-trithiacyclononane (ttcn) and 1,4,7-triazacyclononane (tacn) (Figure 3.96).

Complexes of the divalent metals $[M(ttcn)_2]^{2+}$ undergo electrochemical oxidation to paramagnetic $[M(ttcn)_2]^{3+}$. Red $[Pd(ttcn)_2]^{3+}$ has a tetragonally distorted octahedral structure (d^7, Jahn–Teller distortion) with Pd–S 2.356–2.369 Å (equatorial) and 2.545 Å (axial) in keeping with the ESR spectrum ($g_\perp = 2.049$, $g_{||} = 2.009$) which also displays ^{105}Pd hfs. Similarly, electrochemical oxidation of the palladium(II) tacn complex (at a rather lower



ttcn ($9S_3$) tacn $18[ane]N_2S_4$

Figure 3.96 Macrocyclic ligands used to stabilize palladium(III) and platinum(III).

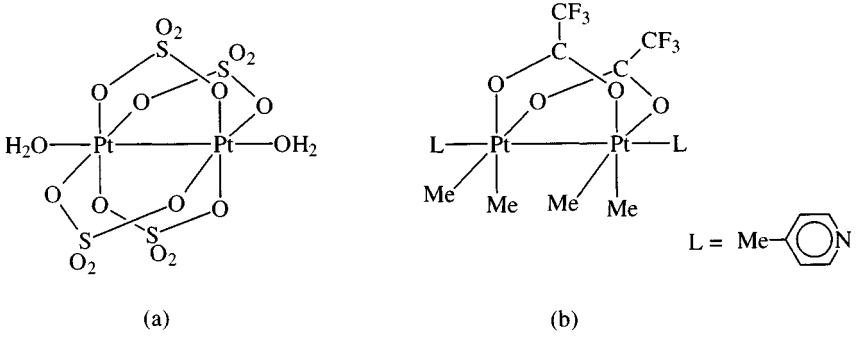


Figure 3.97 Dinuclear platinum(III) compounds.

potential than the ttcn complex) gives $[Pd(tacn)_2](PF_6)_3$, again with a tetragonally distorted octahedral structure (Pd–N (equatorial) 2.111–2.118 Å; Pd–N (axial) 2.180 Å). The palladium(III) complex of the N_2S_4 macrocycle ([18]ane N_2S_4) (Figure 3.96) has been synthesized by electrochemical oxidation and detected in solution by ESR.

Oxidation of $[Pt(C_6Cl_5)_4]^{2-}$ yields the unusual paramagnetic organometallic $[Pt(C_6Cl_5)]_4^-$ with square planar coordination of platinum

$$[Pt(C_6Cl_5)_4]^{2-} \xrightarrow{Cl_2} [Pt(C_6Cl_5)]_4^-$$

Rather more dinuclear platinum(III) compounds are known [158]; formally the Pt_2^{6+} unit is isoelectronic with Rh_2^{4+}. The first species to be characterized was $Pt_2(SO_4)_4(H_2O)_2^{2-}$ (Figure 3.97a):

$$Pt(NO_2)_4^{2-} \text{ or } Pt(NH_3)_2(NO_2)_2 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} [Pt_2(SO_4)_4(H_2O)_2]^{2-} + NO_x$$

Analogous compounds have been made with HPO_4^{2-} bridges; Pt–Pt distances in these compounds are 2.46–2.50 Å. Other dimers include $[Pt_2(\mu\text{-}O_2CMe)_4(H_2O)_2]^{2+}$ [158].

Binuclear platinum(III) methyls have been made, these complexes utilizing carboxylate bridges (Figure 3.97b)

$$PtCl_2(R_2S)_2 \xrightarrow{Me_2Mg} [PtMe_2(R_2S)]_2$$

$$\xrightarrow{AgO_2CR^1} Pt_2Me_4(O_2CR^1)_2(R_2S)_2$$

$$\downarrow \text{py}$$

$$Pt_2Me_4(O_2CR^1)_2py_2$$

while related structures have been made using 2-oxopyridine as the bridging ligand. The compounds with two instead of four such bridges tend to have longer Pt–Pt distances (2.54–2.58 Å) [159].

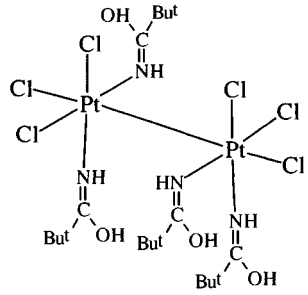


Figure 3.98 A dimeric platinum(III) complex with no bridging ligands.

The presence of bridging ligands is, however, not essential [160].

$$cis\text{-}PtCl_2\{2NCBu^t\} \xrightarrow[CH_2Cl_2]{1.\,KOH\quad 2.\,HCl} cis\text{-}PtCl_2\{NH{=}C(OH)Bu^t\}_2$$

$$\downarrow Cl_2$$

$$Pt_2Cl_6\{NH{=}C(OH)Bu^t\}_4$$

The long Pt–Pt bond (2.694 Å) follows the trend observed in rhodium dimers as the number of bridging ligands decreases (Figure 3.98).

As with the 'trihalides', some formally platinum(III) compounds are in fact mixed-valence species [161]. Thus:

$$cis\text{-}Pt(NH_3)_2(SCN)_2 \xrightarrow{I_2} Pt(NH_3)_2(SCN)_2I$$

the compound in fact being $[Pt^{II}(NH_3)_2(SCN)_2][Pt^{IV}(NH_3)_2(SCN)_2I_2]$ [152].

3.10 Complexes of platinum(IV)

Platinum(IV) forms complexes with a range of ligands [1, 2, 10, 11].

3.10.1 Complexes of N-donors

The full range of platinum(IV) ammines can readily be prepared [162].

Hexammines

$$(NH_4)_2PtX_6 \xrightarrow[-40°C]{\text{liq. } NH_3} [Pt(NH_3)_6]X_4 \qquad (X = Cl, Br, I)$$

The reaction is best carried out at −40°C, otherwise amide bridged species $[(NH_3)_4Pt(NH_2)_2Pt(NH_3)_4]Cl_6$ are obtained.

Pentammines

Introducing more than five molecules of ammonia is difficult (hence the use of liquid ammonia in the synthesis of the hexammine), but Chugaev's synthesis of the pentammine is facile:

$$K_2PtCl_6 \xrightarrow[\text{reflux, 10 min}]{NH_3/Na_2HPO_4} [Pt(NH_3)_5Cl]PO_4 \xrightarrow[HCl]{\text{conc.}} [Pt(NH_3)_5Cl]Cl_3$$

Tetrammines

The chloride and bromide can be made by oxidative addition.

$$[Pt(NH_3)_4]Cl_2 \xrightarrow[HCl\,(aq.)]{Cl_2} \textit{trans}\text{-}[Pt(NH_3)_4Cl_2]Cl_2$$

In the triflate salt, Pt–Cl is 2.302–2.309 Å, while Pt–N distances are in the range 2.049–2.059 Å [163].

$$[Pt(NH_3)_4](MeSO_3)_2 \xrightarrow{Br_2} \textit{trans}\text{-}[Pt(NH_3)_4Br_2](MeSO_3)_2$$

The Pt–Br distance is 2.447 Å while Pt–N distances are 2.065–2.068 Å [163].

The *cis*-dichloro complex can be made in a synthesis that makes use of the lability of a Pt–Cl bond *trans* to chloride.

$$\textit{mer}\text{-}[Pt(NH_3)_3Cl_3]^+Cl^- \xrightarrow{NH_3} \textit{cis}\text{-}[Pt(NH_3)_4Cl_2]Cl_2$$

Triammines

$$\textit{cis}\text{-}Pt(NH_3)_2Cl_2 \xrightarrow[2.\,HCl]{1.\,(NH_4)_2HPO_4/\text{reflux}} \textit{mer}\text{-}[Pt(NH_3)_3Cl_3]^+Cl^-$$

This reaction may involve ammoniolysis, followed by oxidative addition [164].

Diammines

$$\textit{cis}\text{-}Pt(NH_3)_2Cl_2 \xrightarrow[80°C]{Cl_2} \textit{cis}\text{-}Pt(NH_3)_2Cl_4$$

$$\textit{trans}\text{-}Pt(NH_3)_2Cl_2 \xrightarrow[100°C]{Cl_2} \textit{trans}\text{-}Pt(NH_3)_2Cl_4$$

These syntheses again involve the retention of configuration on oxidation. In the *cis*-isomer Pt–N is 2.059 Å and Pt–Cl is 2.318 Å (*trans* to N) and 2.322 Å (*trans* to Cl) [165].

Monoammine

$$K[Pt(NH_3)Cl_3] \xrightarrow{Cl_2} K[Pt(NH_3)Cl_5]$$

In this anion, Pt–N is 2.065 Å and Pt–Cl 2.314–2.331 Å (*cis*) and 2.313 Å (*trans*).

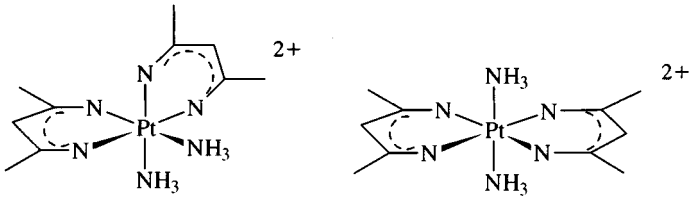


Figure 3.99 Platinum(IV) diimine complexes.

Vibrational spectra of these ammines indicate Pt–N stretching frequencies around 550 cm^{-1} (Raman) and 530 cm^{-1} (IR) [166].

Platinum(IV) ammines react with diketones to give diimmines, a reaction proceeding via deprotonation of one ammonia [167].

A second diimine group can be introduced, obtainable as *cis*- and *trans*-isomers (Figure 3.99).

The platinum(IV) ammines studied in most detail recently [168] have been hydroxy species (Figure 3.100).

The diisopropylamine complex (a) has undergone clinical trials as the drug 'iproplatin' (CHIP); the simple ammonia analogue (b) 'oxoplatin' has shown promising anti-tumour activity (see also section 3.10).

Their synthesis uses H_2O_2 to carry out oxidative addition to platinum(II) ammines

$$cis\text{-}Pt(RNH_2)_2Cl_2 \xrightarrow{H_2O_2} cis,cis,trans\text{-}Pt(RNH_2)_2Cl_2(OH)_2$$

(R = H, Me_2CH). They are obtained as H_2O_2 adducts (perhydrates) containing lattice H_2O_2. The perhydrate adducts cleave DNA but the unsolvated compounds do not.

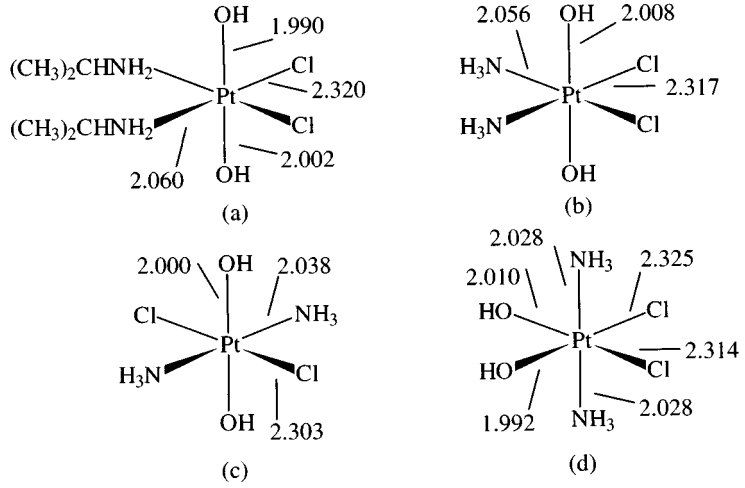


Figure 3.100 Bond lengths in platinum(IV) ammine hydroxy complexes.

Table 3.25 The structure of platinum(IV) en complexes

	Pt–N (Å)	Pt–X (Å)
cis-$Pt(en)_2Cl_2^{2+}$	2.045–2.068	2.30–2.31
trans-$Pt(en)_2Cl_2^{2+}$	2.074–2.087	2.313
trans-$Pt(en)_2Br_2^{2+}$	2.04–2.07	2.459
trans-$Pt(en)_2I_2^{2+}$	2.059–2.060	2.681

Oxidation of *trans*-$Pt(NH_3)_2Cl_2$ with H_2O_2 affords the all-*trans* isomer (Figure 3.100c); this isomerizes on recrystallization to give (d). Presumably (c) is the kinetic product while (d) is thermodynamically more stable.

trans-$[Pt(NH_3)_4(OH)_2]Cl_2$ has the expected octahedral coordination with Pt–N and Pt–O distances of 2.042 and 2.004 Å, respectively, distances very similar to those in the all-*trans*-isomer of $Pt(NH_3)_2(OH)_2Cl_2$ [169].

Several complexes with 1,2-diaminoethane have been studied in detail [170].

$$cis\text{-}PtenX_2 \xrightarrow{X_2} cis\text{-}PtenX_4 \qquad (X = Cl, Br)$$

$$(Pten_2)X_2 \xrightarrow{X_2} [trans\text{-}Pten_2X_2]X_2 \qquad (X = Cl, Br, I)$$

$$(Pten_2)Cl_2 + 2HCl \xrightarrow[HCl]{conc.} trans\text{-}[Pt(enHCl)_2Cl_2]$$

$$\xrightarrow[heat]{H_2O_2} cis\text{-}Pten_2Cl_2^{2+}Cl_2$$

$$H_2PtCl_6.6H_2O \xrightarrow[80°C]{en/EtOH} (Pten_3)Cl_4$$

The $Pten_3^{3+}$ and *cis*-$Pten_2Cl_2^{2+}$ ions have been resolved, the former by Werner.

Structures of several of these complexes have been determined: data are summarized in Table 3.25.

Another platinum(IV) ammine complex studied as a possible anti-tumour compound is shown in Figure 3.101 [171]; *cis*-(1,2-diaminocyclohexane)tetrachloroplatinum has undergone clinical trials but was found to be too neurotoxic.

Complexes of the more rigid 2,2′-bipyridyl and 1,10-phenanthroline are made:

$$cis\text{-}Pt(L{-}L)Cl_2 \xrightarrow{Cl_2} cis\text{-}Pt(L{-}L)Cl_4 \qquad (L{-}L = phen, bipy)$$

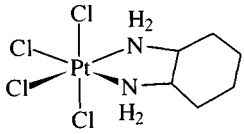


Figure 3.101 *cis*-(1,2-Diaminocyclohexane)tetrachloroplatinum.

Reaction of iodine with $Pt(phen)Cl_2$ gives compounds with the unusual stoichiometrics $Pt(phen)I_x$ ($x = 5, 6$); these contain $Pt(phen)I_4$ molecules and free iodine molecules in the lattice. $Pt(bipy)I_4$ has also been made [172].

Macrocyclic complexes of platinum(IV) are readily made by oxidation:

$$Pt(TPP) \xrightarrow[2.\,HCl]{1.\,H_2O_2/CH_3COOH} Pt(TPP)Cl_2$$

$$Pt[[14]aneN_4]Cl_2 \xrightarrow[O_2]{HCl(aq.)} [Pt[[14]aneN_4]Cl_2]Cl_2$$

Six-coordination is confirmed for the latter by X-ray diffraction (Pt–N 2.04 Å, Pt–Cl 2.307 Å) [173].

3.10.2 Tertiary phosphine complexes

The most important of the tertiary phosphine complexes of platinum(IV) are $Pt(QR_3)_2X_4$, generally prepared by halogen oxidation [174] of *cis*- or *trans*-$Pt(QR_3)_2X_2$ (Q = P, As, R = alkyl; Q = Sb, R = Me), since direct reaction of the platinum(IV) halides with the ligands leads to reduction. Once made, the platinum(IV) compounds are stable to reduction:

$$Pt(QR_3)_2X_2 + X_2 \rightarrow Pt(QR_3)_2X_4$$

Generally the configuration is retained on oxidation, though a certain amount of isomerization can take place. (Br_2 added *trans* to *trans*-$Pt(PEt_3)_2Cl_2$ in the dark, but scrambling was found in the light [175].) Anionic and cationic complexes can be made:

$$Pr_4N^+PtX_3L^- + X_2 \rightarrow Pr_4N^+PtX_5L^- \qquad (L, \text{e.g. } PMe_3;\ X = Cl, Br, I)$$

$$Pt(PMe_3)_3Cl^+BF_4^- + Cl_2 \rightarrow \textit{mer}\text{-}Pt(PMe_3)_3Cl_3^+BF_4^-$$

The structures of the *cis*- and *trans*-isomers of $Pt(PEt_3)_2Cl_4$ have been determined [176]. Table 3.26 shows the bond lengths depend slightly on the *trans*-ligand.

The *cis*-isomer shows slight deviation from regular octahedral symmetry (P–Pt–P 98.1°). The *cis*- and *trans*-isomers can be distinguished in various ways; the far-IR spectra [177] of the *cis*-isomers (*cis*-PtL_2X_4 has 'local' C_{2v} symmetry) has more bands owing to Pt–X stretching between *c.* 280 and 350 cm^{-1} than the *trans*-isomer (D_{4h} symmetry) (Figure 3.102).

Table 3.26 Bond lengths in $Pt(PEt_3)_2Cl_4$ (Å)

	trans-$Pt(PEt_3)_2Cl_4$	*cis*-$Pt(PEt_3)_2Cl_4$
Pt–P (*trans* to P)	2.393	
Pt–P (*trans* to Cl)		2.335
Pt–Cl (*trans* to Cl)	2.332	2.321
Pt–Cl (*trans* to P)		2.394

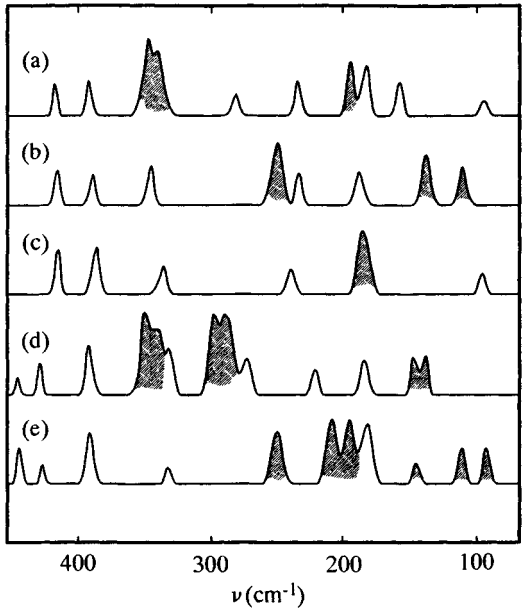


Figure 3.102 Far-IR spectra of (a) *trans*-$Pt(PEt_3)_2Cl_4$; (b) *trans*-$Pt(PEt_3)_2Br_4$; (c) *trans*-$Pt(PEt_3)_2I_4$; (d) *cis*-$Pt(PEt_3)_2Cl_4$; (e) *cis*-$Pt(PEt_3)_2Br_4$. Platinum–halogen vibrations are shaded. (Reproduced with permission from *J. Chem Soc. (A)*, 1967, 1009.)

In the ^{31}P NMR spectra, there is a significant difference in, for example, the ^{195}Pt–^{31}P coupling constant [155]. Therefore, for *cis*-$Pt(PBu_3)_2Cl_4$, $J = 2070$ Hz; *trans*-isomer, $J = 1462$ Hz).

Some platinum(IV) hydride complexes have been synthesized *in situ* (Figure 3.103).

Solid $PtH_2X_2(PEt_3)_2$ (X = Cl, Br) is isolated by removal of solvent at −20°C; the order of stability is Cl > Br > I and solutions decompose at room temperature, eliminating H_2. Monohydrides $PtHX_3(PR_3)_2$ are less stable [178].

Complexes are similarly formed by polydentate phosphine and arsine ligands; synthetic routes involve oxidation of the platinum(II) complex, either with the halogen or with nitric acid:

$$cis\text{-}Pt(L\text{–}L)X_2 \xrightarrow[CCl_4]{X_2} cis\text{-}Pt(L\text{–}L)X_4$$

(L–L, e.g. $Ph_2PCH_2CH_2PPh_2$, $Me_2As(CH_2)_3AsMe_2$, X = Cl, Br)

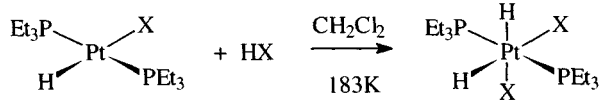


Figure 3.103 Synthesis of a platinum(IV) hydride complex.

$$trans\text{-}Pt[o\text{-}C_6H_4(QMe_2)_2]X_2 \xrightarrow{HNO_3} trans\text{-}Pt[C_6H_4(QMe_2)_2]_2X_2^{2+}$$

(Q = P, As; X = Cl, Br, I).

The structure of the iodo complex (Q = As) shows Pt–As 2.446–2.454 Å, Pt–I 2.669–2.672 Å [179].

3.10.3 *Complexes of S-donors*

The most interesting complexes with Pt–S bonds involve polysulphide rings [180]. The classically simple $[Pt(S_5)_3]^{2-}$ was first reported in 1903; more recently it has been resolved into its enantiomers using (+)-$[Ru(phen)_3]^{2+}$.

$$H_2PtCl_6 \xrightarrow{(NH_4)_2S_5} (NH_4)_2Pt(S_5)_3$$

This was only the third purely 'inorganic' ion (with no carbons) to be resolved [180b], the previous two being 'Werner's hexol' $Co[(\mu\text{-}OH)_2Co(NH_3)_4]_3^{6+}$ (*Chem. Ber.*, 1914, **47**, 3087) and F.G. Mann's *cis*-$[Rh(OH_2)_2[SO_2(NH_2)_2]_2]^-$ (*J. Chem. Soc.*, 1933, 412). The ammonium salt has quite regular octahedral (S–Pt–S 90.9–92.8°) coordination of platinum (Pt–S 2.365–2.428 Å); in the potassium salt, Pt–S distances are 2.332–2.479 Å.

Reaction of $Pt(S_5)_3^{2-}$ with concentrated HCl affords PtS_{17}^{2-}; on treatment with Ph_4P^+ and slow crystallization, disproportionation occurs:

$$3PtS_{17}^{2-} \rightarrow 2Pt(S_6)_3^{2-} + Pt(S_5)_3^{2-}$$

$(Ph_4P)_2Pt(S_6)_3$ again has octahedral coordination by sulphur (Pt–S 2.350–2.366 Å; S–Pt–S 98.4–100.7°) (Figure 3.104) [181].

The thiocyanate $K_2[Pt(SCN)_6].2H_2O$ contains octahedrally coordinated platinum, confirming the readiness of platinum(IV) to bind to a 'soft' donor atom like sulphur [182].

3.10.4 *Application of the* trans*-effect to synthesis of platinum(IV) complexes*

In addition to the methods already outlined for platinum(II) complexes, simultaneous crystallization can be used to prepare mixed complex halides (Figure 3.105).

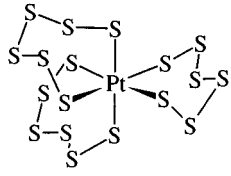


Figure 3.104 Structure of $[Pt(S_6)_3]^{2-}$.

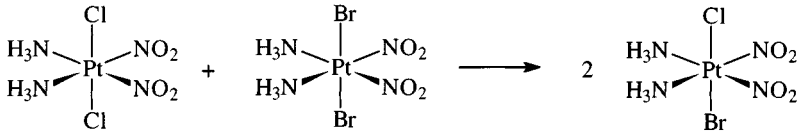


Figure 3.105 Synthesis of $PtBrCl(NH_3)_2(NO_2)_2$ by cocrystallization.

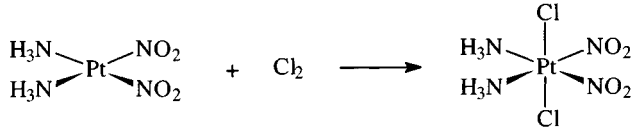


Figure 3.106 Synthesis of a platinum(IV) complex by *trans*-oxidative addition of a platinum(II) complex.

Halogen oxidation of platinum(II) complexes generally occurs *trans*, as does reaction with H_2O_2 to afford dihydroxy complexes (Figure 3.106).

The isomers of $[PtCl_2(NH_3)_4]Cl_2$ may be prepared as shown in Figure 3.107.

The last step is the synthesis of the *cis*-complex involving the *trans*-effect and the lability of Pt–Cl bonds.

The five isomeric forms of $PtBr_2Cl_2(NH_3)_2$ have been isolated by a variety of methods [183]. Isomer 1 is produced by the method shown in Figure 3.108.

The 'obvious' route by *trans*-addition of Br_2 was found to give the desired product contaminated by tri- and tetrabromo species because of substitution reactions (Figure 3.109).

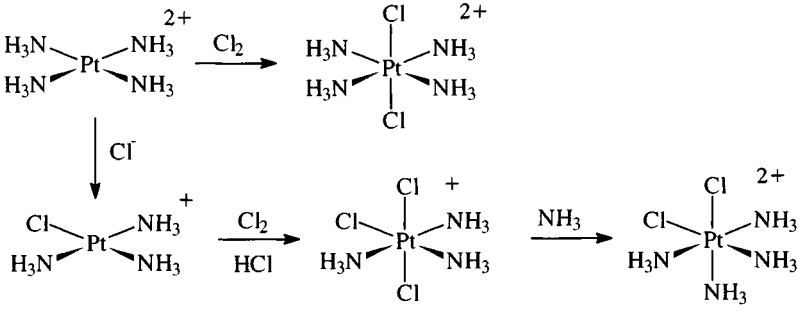


Figure 3.107 Synthesis of the isomers of $[PtCl_2(NH_3)_4]^{2+}$.

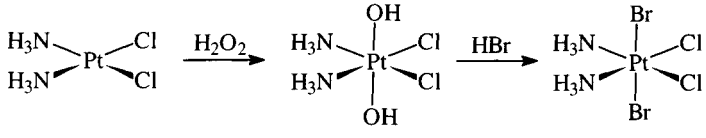
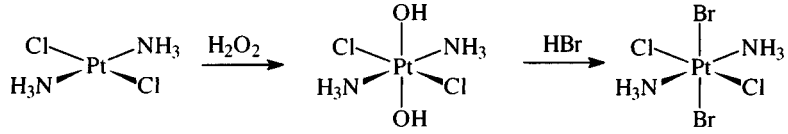
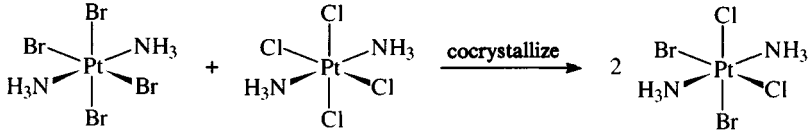


Figure 3.108 Synthesis of the *trans,cis,cis*-isomer (isomer 1) of $PtBr_2Cl_2(NH_3)_2$.

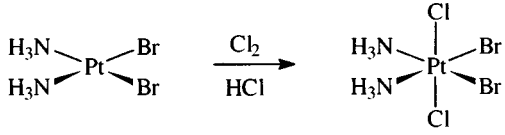
Isomer 2



Isomer 3



Isomer 4



Isomer 5

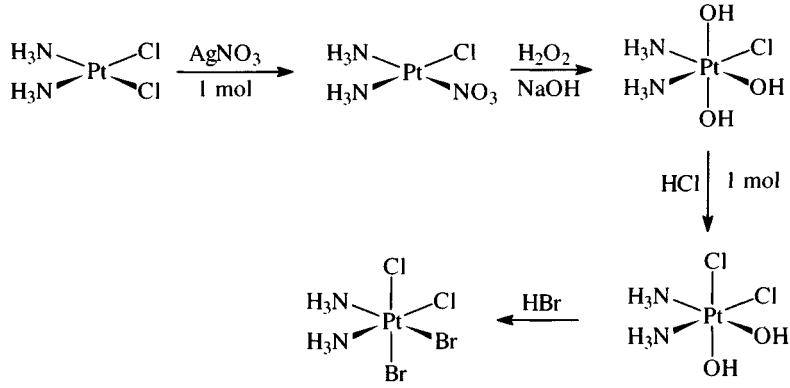


Figure 3.109 Synthesis of the other isomers of $PtBr_2Cl_2(NH_3)_2$.

Complexes of the form 'PtABCDEF' potentially have 15 isomeric forms, and a number of the isomers of $Pt(NH_3)py(NO_2)IBrCl$ have been made [184]. One such synthesis is shown in Figure 3.110.

3.10.5 The trans*-influence in some platinum(IV) complexes*

Table 3.27 shows bond lengths for a number of platinum(IV) and related platinum(II) complexes.

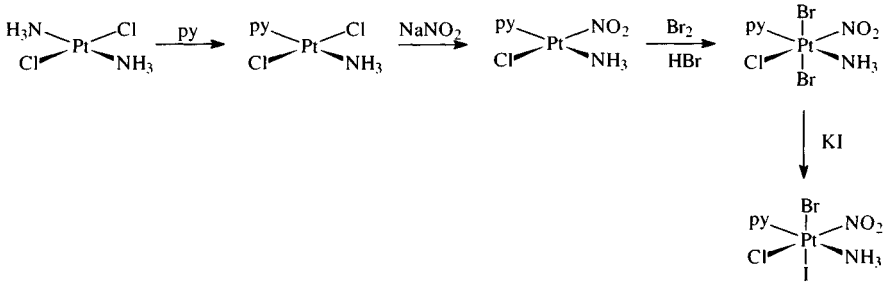


Figure 3.110 Synthesis of one PtABDEF isomer.

The Pt–Cl bond lengths in $PtCl_4^{2-}$ and $PtCl_6^{2-}$ are virtually identical [185], implying that the shortening in bond length consequent upon the increase in oxidation state from +2 to +4 is almost exactly cancelled out by the increase in bond length accompanying an increase in coordination number from 4 to 6. A comparison of *cis*-$Pt(PEt_3)_2Cl_2$ with *cis*-$Pt(PEt_3)_2Cl_4$ [186] indicates that the more 'ionic' Pt–Cl bond is less sensitive to the increase in oxidation state than is the Pt–P bond. Similar effects can be seen in the $PtLCl_x^-$ (L = PEt_3, py; $x = 3, 5$) ions [187].

As far as *trans*-influence is concerned, comparing *cis*- and *trans*-$Pt(PEt_3)_2Cl_4$ [186] shows a considerable *trans*-influence of the tertiary phosphine on the Pt–Cl bond lengths, also found in $Pt(PEt_3)Cl_5^-$. (The pronounced lengthening of the *trans*-Pt–C bond compared with the *cis* bond in $Pt(PEt_3)Cl_5^-$ is greater than that in $Pt(PEt_3)Cl_3^-$, implying the *trans*-influence of the phosphine is greater in the platinum(IV) compound.)

Table 3.27 Bond lengths in platinum(II) and platinum(IV) complexes (Å)

	Pt–Cl (*trans*-Cl)	Pt–Cl (*trans*-L)	Pt–L (*trans*-Cl)	Pt–L (*trans*-L)
$PtCl_4^{2-}$	2.310			
$PtCl_6^{2-}$	2.314			
$Pt(PEt_3)Cl_3^-$	2.300	2.382	2.215	
$Pt(PEt_3)Cl_5^-$	2.316	2.424	2.308	
$PtpyCl_3^-$	2.296[a]	2.305	2.018	
$PtpyCl_5^-$	2.319[a]	2.313	2.062	
cis-$Pt(PEt_3)_2Cl_2$	2.301		2.258	
cis-$Pt(PEt_3)_2Cl_4$	2.321	2.394	2.335	
trans-$Pt(PEt_3)_2Cl_4$	2.332			2.393

[a] Average value.

3.11 Complexes of palladium(IV)

Compared with the plethora of platinum(IV) compounds, the palladium(IV) complexes are as yet relatively few in number [10, 11]. When isolable, they tend to resemble the corresponding platinum compounds.

The PdX_6^{2-} (X = halogen) complexes are described in section 3.3.1. A limited range of complexes have been made by oxidation of palladium(II) species [188]:

$$trans\text{-}PdL_2Cl_2 \xrightarrow{Cl_2} trans\text{-}PdL_2Cl_4$$

(L = NH_3, py, PPr_3, $AsMe_2Ph$)

$$trans\text{-}Pd(Me_3N)_2Br_2 \xrightarrow{Br_2} trans\text{-}Pd(Me_3N)_2Br_2$$

$$R_4N^+PdX_3L^- \xrightarrow{X_2} R_4N^+PdX_5L^-$$

(X = Cl, L = $AsEt_3$, NMe_3, py, Me_2S, Me_2Se; X = Br, L = $AsEt_3$, PEt_2Ph, py, Me_2S, Me_2Se)

$$Pd(L{-}L)Cl_2 \xrightarrow[CCl_4]{Cl_2} Pd(L{-}L)Cl_4$$

(L–L = phen, bipy, $Me_2NC_2H_4NMe_2$).

The limited stability of these compounds is shown by the fact that other tertiary phosphines and arsines do not yield isolable products.

With chelating phosphine and arsine ligands, two types of complex have been isolated:

$$Pd(L{-}L)X_2 \xrightarrow{X_2} Pd(L{-}L)X_4$$

(L–L, e.g. $Me_2P(CH_2)_2PMe_2$, *o*-$C_6H_4(AsMe_2)_2$; X = Cl, Br)

$$Pd(L{-}L)_2Cl_2 \xrightarrow{Cl_2} Pd(L{-}L)Cl_4$$

(L–L = *o*-$C_6H_4(AsMe_2)_2$, $Ph_2QC_2H_4QPh_2$; Q = P, As)

$$Pd(L{-}L)_2X_2 \xrightarrow[HX,0°C]{\text{conc. } HNO_3} Pd(L{-}L)_2X_2^{2+}$$

(L–L = $Me_2P(C_2H_4)PMe_2$, *o*-$C_6H_4(QMe_3)_2$; Q = P, As).

Crystallography confirms structures for $Pd(bipy)Cl_4$ (Pd–N 2.037–2.044 Å; Pd–Cl *trans* to N 2.289–2.290 Å, Pd–Cl *trans* to Cl 2.302–2.310 Å) and $Pd[C_6H_4(AsMe_2)_2]_2Cl_2(ClO_4)_2$ (Pd–Cl 2.302 Å; Pd–As 2.452–2.455 Å) (Figure 3.111). Other compounds isolated include a complex of the tetradentate (N_4) macrocycle cyclam $[Pd(cyclam)Cl_2](NO_3)_2$, a tellerate $Na_8K_2H_4[Pd_2Te_4O_{24}H_2].20H_2O$, and some methyl palladium complexes such as *fac*-$PdMe_3(bipy)I$.

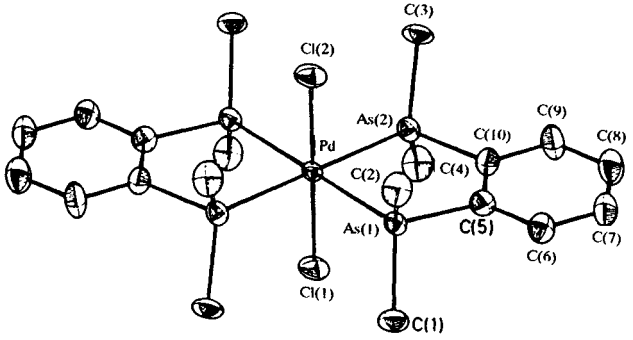


Figure 3.111 The structure of the cation in $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_2]ClO_4$. (Reproduced with permission from *J. Chem. Soc., Dalton Trans.*, 1983, 133.)

Just as many palladium(IV) complexes are produced by halogen oxidation of the corresponding palladium(II) complex, so the palladium(IV) compounds tend to decompose by the reverse process, usually on heating:

$$cis\text{-}Pd(bipy)Cl_4 \rightarrow Cl_2 + cis\text{-}Pd(bipy)Cl_2$$

3.12 The σ-bonded organometallics of palladium(IV) and platinum(IV)

Palladium and platinum form a wide range of very stable alkyls and aryls in the (+2) state (section 3.8.4) generally with 'supporting' ligands like tertiary phosphines [85, 189].

There is also a considerable chemistry, especially of platinum, in the +4 state, some of these being among the most stable σ-bonded organometallics known. The prototype compound $PtMe_3I$ was reported as long ago as 1907 (Pope and Peachey) and certain of its features have become clear particularly as a result of studies since the 1960s.

1. No homoleptic tetramethyl has been made, though $PtMe_6^{2-}$ and Lewis base adducts $PtMe_4L_2$ (L = PMe_2Ph, 1/2 bipy etc.) can be made.
2. Platinum(IV) exhibits an exceptionless preference for octahedral coordination in these complexes, using bridging ligands when necessary to achieve this.

Many of these compounds are trimethyls [190]. A selection of syntheses and structures are shown in Figures 3.112 and 3.113.

While $(Bu_4N)_2PtMe_6$ is only stable at room temperature under nitrogen, the trimethyls in particular are rather stable: bond energies of 160–210 kJ mol^{-1} have been estimated for Pt–Me bond energies in various platinum(IV) methyls [191].

The β-diketonates demonstrate that, like platinum(II), platinum(IV) can bond to both carbon and oxygen atoms in the diketonate ligand.

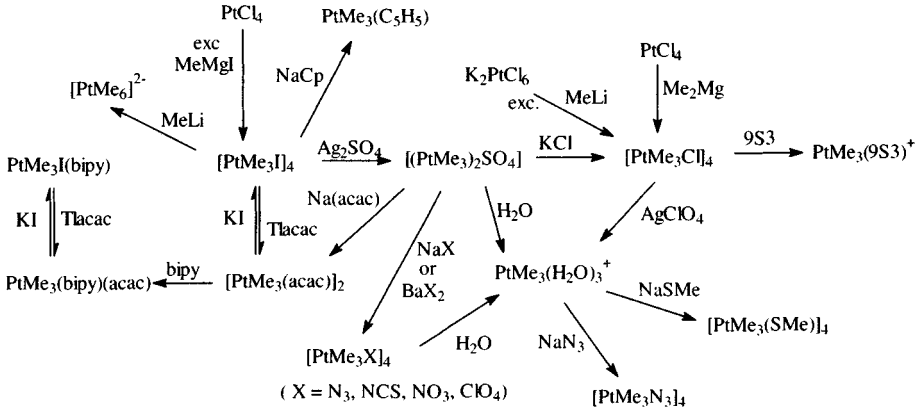


Figure 3.112 Syntheses and reactions of methylplatinum(IV) compounds.

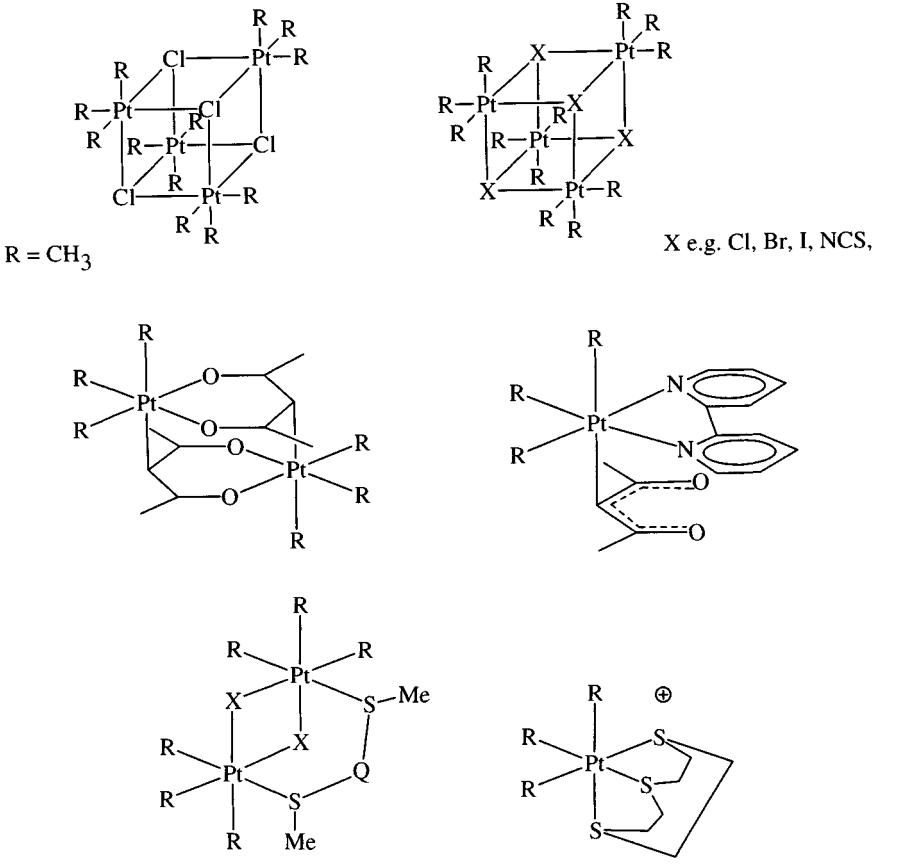


Figure 3.113 Structures of some methylplatinum(IV) compounds

Six-coordination is obtained in $[PtMe_3(acac)]_2$ by bidentate (O,O′) behaviour and by a bond to the γ-carbon, a situation maintained in solution at room temperature (on warming, the bond to the γ-carbon breaks). In the bipyridyl adduct, it is the bond to the γ-carbon that completes the octahedral coordination [192].

Complexes like $(PtMe_3X)_2MeQCH_2QMe$ (X = halogen; Q = S, Se) are rigid at low temperatures, but on warming, inversion occurs in the Pt–Q–CH_2–Q–Pt rings, then above 0°C the bridging dithioether (or selenoether) switches synchronously from one platinum to another. The thioether 1,4,7,10-tetrathiocyclododecane is only tridentate in *fac*-$PtMe_3(C_8H_{16}S_4)^+$ and in solution there is exchange between bound and unbound sulphur; this is in contrast to the complex of the tridentate 1,4,7-trithiacyclononane where all three sulphurs are simultaneously bound [193].

All the trimethylplatinum(IV) species have a *fac*-arrangement of the methyls; this is enforced in the $[PtMe_3X]_4$ oligomers, but nevertheless appears to reflect a genuine stereochemical preference (e.g. the isoelectronic *fac*-$Ir(PMe_2Ph)_3Me_3$, section 2.13.5).

The *trans*-influence can be monitored in $PtMe_3$ complexes by both NMR and IR spectra. The coupling constants between the platinum and the methyl hydrogens ($^2J(^{195}Pt-^1H)$) is sensitive to the other atoms bound to platinum, ranging from 81.7 Hz ($(PtMe_3Cl)_4$) to 60.8 Hz ($PtMe_3(CN)_3^-$), the order being CN < py < NH_3 < SCN < I < H_2O < Br < Cl [194].

A strong line is seen in the Raman spectra of these complexes that is assigned to ν(Pt–C); typical values are 600 cm^{-1} ($PtMe_3(H_2O)_3^+$), 581 cm^{-1} ($(PtMe_3Cl)_4$) and 553 cm^{-1} ($PtMe_3(CN)_3^-$); here the frequency order is CN < I < SCN < Br < py < Cl < NH_3 < H_2O, correlating better with other *trans*-influence series based on vibrational spectra.

Although they are η^5-organometallics, it is pertinent to mention compounds like $PtMe_3(\eta^5\text{-}C_5H_5)$; the cyclopentadienyl group can be thought of as occupying three coordination sites, so that the complexes may, again, be considered to involve octahedrally coordinated platinum(IV). With a volatility comparable to a metal carbonyl (b.p. 20°C at 0.01 mmHg) it decomposes to platinum metal and methane on heating (*c.* 165°C) or on irradiation; laser photolysis of complexes of this type is being actively studied as a way of depositing thin platinum films. Other trimethylplatinum(IV) species undergo photoemission with reductive elimination to platinum(II) species [195].

The only homoleptic organoplatinum(IV) compound synthesized so far is $Pt(C_6Cl_5)_4$, produced by electrochemical oxidation of the platinum(III) analogue or by chemical oxidation with Cl_2 in the presence of $AlCl_3$

$$[Pt(C_6Cl_5)_4]^- \xrightarrow{Cl_2} [Pt(C_6Cl_5)_4]$$

The diamagnetic orange compound is air and moisture-stable but eliminates C_6Cl_5–C_6Cl_5 on standing. The crystal structure shows that the octahedral

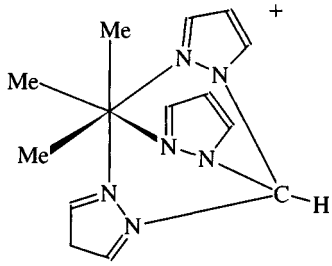


Figure 3.114 Structure of *fac*-$[PdMe_3(pz_3CH)]^+$.

coordination characteristic of Pt(IV) is attained by four Pt–C σ-bonds and two Pt–*o*-Cl interactions [196].

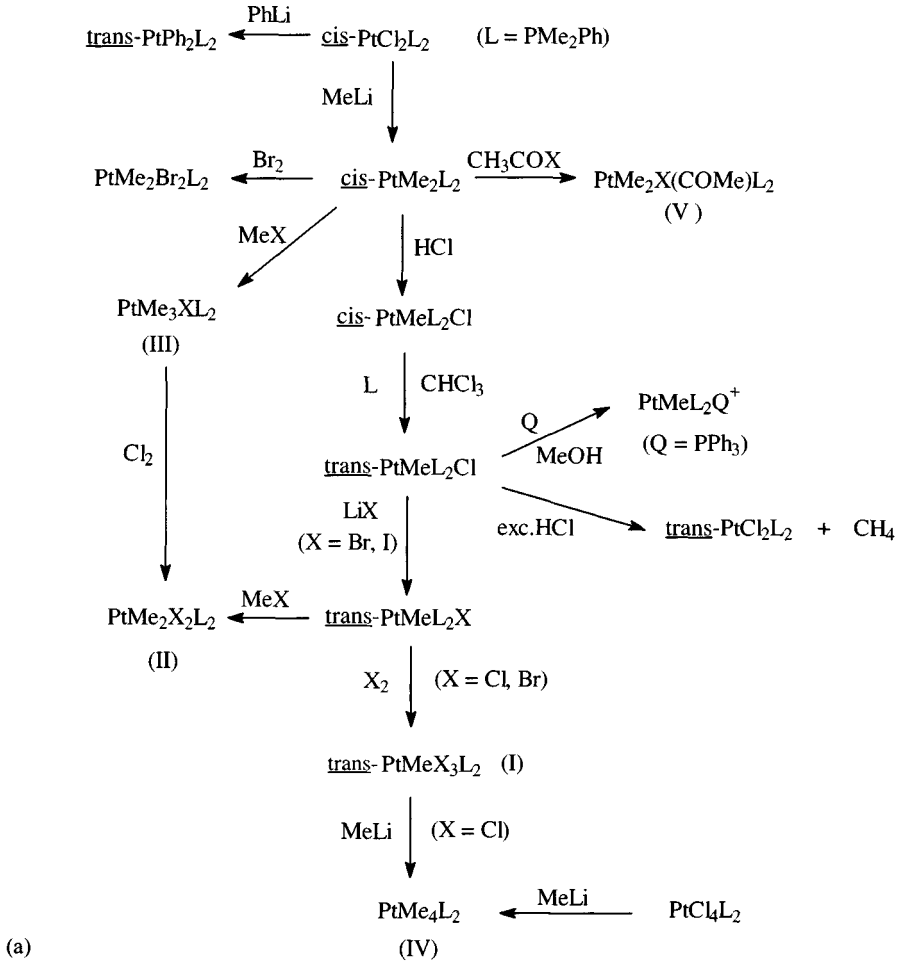
Very recently a significant organopalladium(IV) chemistry has begun to emerge [197], with isolable species like *fac*-$PdMe_3(bipy)I$ (stable at 20°C but decomposing in solution in 30–40 min at room temperature) and *fac*-$[PdMe_3(pz_3CH)]^+I^-$ (Figure 3.114) (isomorphous with the platinum analogue).

Methylplatinum phosphine complexes have been synthesized in both the +2 and +4 oxidation states (see also section 3.8.4). Syntheses for a number of these with the tertiary phosphine PMe_2Ph, which appear to be typical, are shown in Figure 3.115.

(The use of this phosphine facilitates assignment of configuration as 'virtual coupling' is observed when the phosphines are *trans* (section 2.9.5).) Syntheses follow established routes using methyllithium as an alkylating agent; the platinum(IV) complexes can be made by direct alkylation of platinum(IV) compounds or by oxidative addition to platinum(II) species.

Assignment of stereochemistry for these compounds follows from NMR spectra (also from electric dipole moments). Therefore, when *trans*-$PtMeX(PMe_2Ph)_2$ (dipole moments 3.8–3.95 Debye) adds X_2, the resulting $PtMeX_3(PMe_2Ph)_2$ is assigned configuration (I) in Figure 3.115b, as NMR shows the phosphines still to be *trans* while the dipole moment is virtually unchanged (4.3 Debye, X = Cl). When *trans*-$PtMeX(PMe_2Ph)_2$ adds MeX forming *cis,cis,trans*-$PtMe_2X_2(PMe_2Ph)_2$ (Figure 3.115b, II), the NMR spectrum shows the phosphines to remain *trans*; the complex can also be made by treating $PtMe_3Cl(PMe_2Ph)_2$ with Cl_2, causing loss of MeCl. NMR shows that $PtMe_4(PMe_2Ph)_2$ is *cis* (Figure 3.115b, IV) as the methyl resonances are a doublet rather than the 'virtual' 1 : 2 : 1 triplet for a *trans*-arrangement.

Addition of MeCOX to *cis*-$PtMe_2(PMe_2Ph)_2$ yields $PtMe_2X(COMe)(PMe_2Ph)_2$ (Figure 3.15b,V); here the acetyl group *cis* to the methyls doubtless assists the elimination of Me_2CO on pyrolysis, as will be seen in the next section [198].



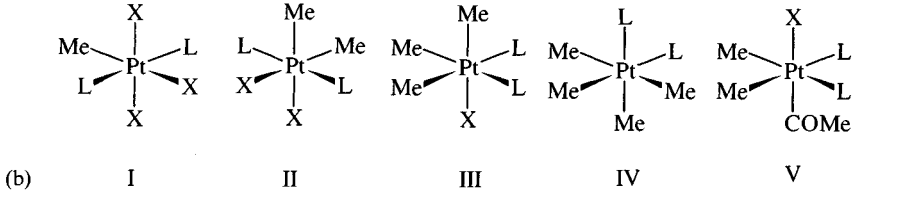


Figure 3.115 (a) Syntheses of organoplatinum phosphine complexes; (b) structures of methylplatinum phosphine complexes.

3.12.1 Reductive elimination reactions

Many platinum(IV) alkyls undergo this process on heating to 150–180°C, with the elimination of a small organic molecule and formation of a platinum(II) product [198, 199].

Reactions often proceed solely by one route:

$$PtMe_2(COMe)X(PMe_2Ph)_2 \xrightarrow{130°C} Me_2CO + \textit{trans}\text{-}PtMeX(PMe_2Ph)_2$$

$$\textit{cis}\text{-}PtMe_4(PMe_2Ph)_2 \xrightarrow{160°C} C_2H_6 + \textit{cis}\text{-}PtMe_2(PMe_2Ph)_2$$

$$\textit{fac}\text{-}PtMe_3I(PMe_2Ph)_2 \xrightarrow{165°C} C_2H_6 + \textit{trans}\text{-}PtMeI(PMe_2Ph)_2$$

Mixtures are, however, often obtained:

$$\textit{mer}\text{-}PtMeX_3(PMe_2Ph)_2 \rightarrow MeX + \textit{cis}\text{- and } \textit{trans}\text{-}PtX_2(PMe_2Ph)_2$$

(X = Cl, Br)

$$\textit{fac}\text{-}PtMe_3Cl(PMe_2Ph)_2 \rightarrow C_2H_6\,(90\%) + \textit{trans}\text{-}PtMeCl(PMe_2Ph)_2 + MeCl\,(10\%)$$

Compounds with N-donor ligands tend to be more stable and not to undergo reductive elimination:

$$PtMe_3Xpy_2 \xrightarrow{-py} [PtMe_3Xpy]_2 \xrightarrow{-py} [PtMe_3X]_4$$

The Pt–CF_3 bond is stronger than the Pt–Me bond so that the latter is preferentially broken

$$PtMe_2(CF_3)I(PMe_2Ph)_2 \xrightarrow{180°C} \textit{trans}\text{-}Pt(CF_3)I(PMe_2Ph)_2 + C_2H_6$$

$$PtMe(CF_3)I_2(PMe_2Ph)_2 \xrightarrow{225°C} \textit{trans}\text{-}Pt(CF_3)I(PMe_2Ph)_2 + MeI$$

A kinetic study of the reaction, retarded by excess phosphine [189],

$$\textit{fac}\text{-}PtMe_3X(PMe_2Ph)_2 \rightarrow C_2H_6 + \textit{trans}\text{-}PtMeX(PMe_2Ph)_2$$

indicates prior dissociation of a tertiary phosphine followed by an intramolecular elimination of C_2H_6. When the chelating diphosphine ($Ph_4PC_2H_4PPh_2$) analogue is decomposed, the elimination occurs without prior dissociation of the phosphine (the decomposition of *fac*-$PdMe_3I$(bipy) is first order and retarded by iodide, suggesting that here iodide loss is followed by decomposition of a 5-coordinate intermediate).

Study of the reductive elimination reactions of *fac*-$PtMe_3$(dppe)I leads to estimated Pt–Me and Pt–I bond energies of 132 and 196 kJ mol^{-1}, respectively [200].

$$\textit{fac}\text{-}PtMe_3(dppe)I \rightarrow \textit{cis}\text{-}PtMe_2(dppe) + MeI$$

and

$$\textit{cis}\text{-}PtMeI(dppe) + C_2H_6$$

A Pt–Si bond energy of 233 kJ mol^{-1} has been estimated from study of the process

$$PtMe_2I(SiMe_3)(bipy) \rightarrow Me_4Si + PtMeI(bipy)$$

Some reactions of $PtMe_4L_2$ systems do not involve reductive elimination; thus reaction of $PtMe_4(NN)$ (NN = phen, bipy) with organic acids yielding $PtMe_3A(NN)$ (A = formate, acetate, benzoate, salicylate) is first order in both reactants [201].

3.13 Anti-tumour activity of platinum complexes

The initial discovery of a potential anti-tumour activity of platinum complexes [202] was made in the 1960s by Barnett Rosenberg's research group, who were studying the effect of an electric current on the bacterium *Escherichia coli*: cell division was prevented although cell growth continued if platinum electrodes were used. The platinum had reacted with ammonium chloride buffer to form ammine complexes. Tests showed that *cis*-$Pt(NH_3)_2Cl_4$ and *cis*-$Pt(NH_3)_2Cl_2$ were active compounds.

Anti-tumour screening showed that *cis*-$Pt(NH_2)_2Cl_2$ (but not the *trans*-isomer) was a very active agent and clinical tests were started in 1971. A number of side-effects were experienced – kidney toxicity, neurotoxicity, nausea, vomiting, inner ear damage and loss of sensation in head and feet – combated by pre- and post-hydration treatment and forced diuresis with mannitol solutions. Used in conjunction with other drugs, intravenous *cis*-$Pt(NH_3)_2Cl_2$ (cisplatin) received Food & Drug Administration (FDA) approval in 1979 and has been found to give 90% long-term remission of testicular cancer, with good results for ovarian, bladder, head and neck tumours. Obviously there is a need for drugs to counter the more common cancers, those of the lung and breast for example. There has, therefore, been an intensive screening programme investigating many compounds (not just involving platinum) of which a number have been investigated clinically, but at the time of writing only two platinum complexes have received FDA approval.

It has been found that certain features are desirable, if not essential, in 'active' platinum complexes:

1. Two ammine groups (with at least one H per N) in a *cis*-configuration (or a bidentate ammine)
2. The presence of good leaving groups like chloride or carboxylate in a *cis*-configuration
3. An uncharged complex.

Palladium(II) complexes with these features are inactive, owing to their greater lability. Platinum(IV) complexes are often less toxic than their platinum(II) analogues, because of their stability to substitution, though it is believed that they undergo *in vivo* reduction to platinum(II).

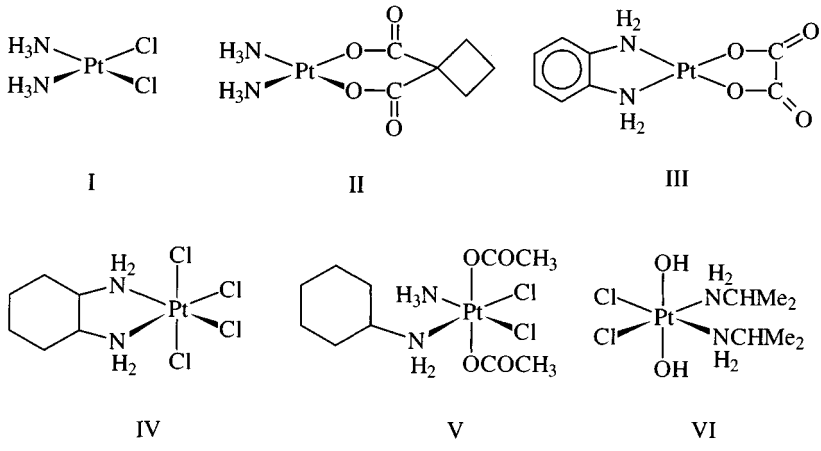


Figure 3.116 Platinum compounds studied for possible anti-tumour activity. I, *cis*-Dichlorodiammineplatinum(II); cisplatin, platinol; NSC 119875; neoplatin; platinex. II, *cis*-Diammine(1,1-cyclobutanedicarboxylato)platinum(II); JM-8; paraplatin; NSC 241240. III, Oxiplatin. IV, Tetraplatin. V, Amminediacetatodichloro(cyclohexylamine)platinum(IV). VI, *cis*-Dichloro-*trans*-dihydroxy-*cis*-bis(isopropylamine)platinum(IV); iproplatin; JM-19; CHIP; NSC 256927.

The platinum(IV) compound that has shown most promise is carboplatin (paraplatin), which received FDA approval in 1990. Features to note in its structure are the use of hydroxy and carboxylate groups to improve water solubility. As noted above, the ammine ligand has been found to need at least one hydrogen, possibly for hydrogen-bonding to phosphate groups in the DNA (Figure 3.116).

Carboplatin is less nephrotoxic than cisplatin and it also causes less nausea, though it does cause lowered platelet levels. It is being used to treat ovarian tumours. Interest in alternative methods of ingestion is leading to the study of compounds capable of being administered orally (Figure 3.117a) and that are reduced *in situ* to reactive platinum(II) species (Figure 3.117b). Compounds of this type are under review for activity [203], with JM-216 (bis(acetato-*O*)amminedichloro(cyclohexylamine)platinum(IV)) undergoing worldwide clinical trials.

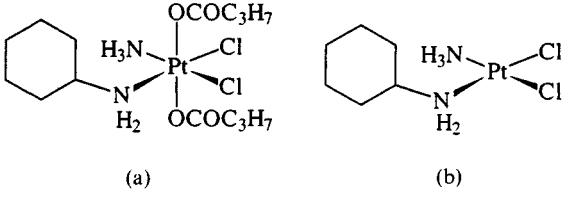


Figure 3.117 (a) JM-216, a platinum(IV) compound under clinical tests as an orally administered anti-tumour agent; (b) the platinum(II) product of *in vivo* reduction, likely to be the active species.

Dimeric complexes like $[Cl(NH_3)Pt\{H_2N(CH_2)_4NH_2\}Pt(NH_3)Cl]Cl_2$ are also being investigated as they bind to DNA in a different way to that involved in cisplatin binding and are active in cisplatin-resistant human tumour cells. They are more potent than cisplatin in lung cancer models *in vivo* and are likely to go on clinical trials in the near future [204].

How cisplatin works [202, 205]

Cisplatin cannot be taken orally owing to hydrolysis in gastric juice. In blood, some is bound to plasma protein and excreted venally, the rest is transported in the blood as uncharged $Pt(NH_3)_2Cl_2$ molecules, which pass unaltered through cell walls. Once through the cell walls, however, the cisplatin undergoes hydrolysis to *cis*-$[Pt(NH_3)_2Cl(H_2O)]^+$ and, more slowly, to *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$, owing to the lower intracellular Cl^- concentration (4 mM, compared with 100 mM outside)

$$cis\text{-}[Pt(NH_3)_2Cl_2] + H_2O \rightarrow Cl^- + cis\text{-}[Pt(NH_3)_2Cl(H_2O)]^+$$

$$cis\text{-}[Pt(NH_3)_2Cl(H_2O)]^+ + H_2O \rightarrow Cl^- + cis\text{-}[Pt(NH_3)_2(H_2O)_2]^{2+}$$

Loss of Cl^- makes the platinum complex more reactive, since water is better leaving group than Cl^-.

The ability of cisplatin to be toxic to tumour cells is believed to relate to its binding to DNA, but since *trans*-$[Pt(NH_3)_2Cl_2]$ also binds to DNA, the reason for the inactivity of the *trans*-form is more complex.

Cisplatin has been shown to form adducts with DNA mainly by forming intrastrand cross-links (Figure 3.118); it does so by binding to adjacent guanines (mainly) or adjacent guanine and adenine groups: these occupy the *cis*-positions originally filled by Cl^-, as seen in the model compound *cis*-$[Pt(NH_3)_2\{d(pGpG)\}]$ (Figure 3.119). This structure also shows an

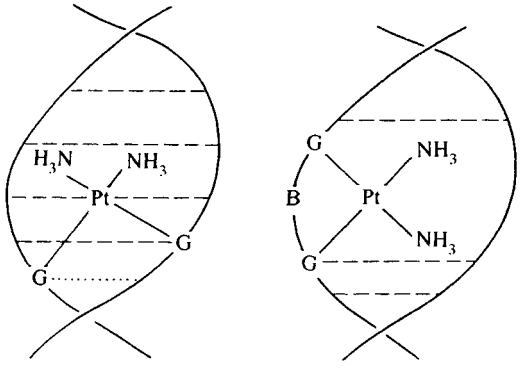


Figure 3.118 Possible modes of cisplatin binding to DNA strands. (Reproduced from J.J.R. Frausto da Silva and R.J.P. Williams, *The Biological Chemistry of the Elements*, 1994, p. 539, by permission of Oxford University Press.)

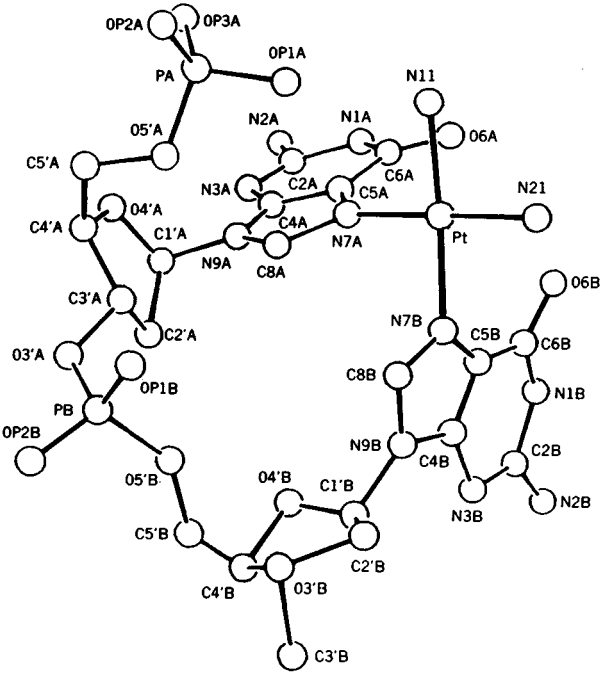


Figure 3.119 *cis*-$Pt(NH_3)_2$[d(pGpG)], model compound for the binding of cisplatin to DNA. (Reprinted with permission from *Science*, 1985, **230**, 430. Copyright (1985) American Association for the Advancement of Science.)

intramolecular hydrogen bond to a phosphate group, which probably explains the need for amine ligands with at least one hydrogen. The need to replace two Cl^- explains why species like $[Pt(dien)Cl]^+$, with only one labile Cl^-, are inactive. Because of the different geometry of *trans*-$Pt(NH_3)_2Cl_2$ molecules, they are unable to emulate cisplatin by forming intrastrand 1,2-d(GpG) or 1,2-d(ApG) cross-links with neighbouring guanines and adenines; instead they form *interstrand* cross-links or intrastrand 1,3-d(GpNpG) links (where N represents another, intervening, nucleotide base).

Binding of cisplatin to the neighbouring bases in the DNA disrupts the orderly stacking of the purine bases; when it forms a 1,2-intrastrand cross-link, it bends the DNA helix by some 34° towards the major groove and unwinds the helix by 13°. These cross-links are believed to block DNA replication.

Cisplatin-modified DNA specifically binds certain proteins, several of which are known to contain the high-mobility group (HMG) domain of 80 amino acids. It is thought that HMG-domain proteins recognize cisplatinated DNA adducts in the cancer cell and are diverted from their usual binding sites on the genome, thus shielding the point of cisplatin binding from the DNA repair enzymes. This maintains the ability of the bound

cisplatin to stop replication from happening and results in death of the tumour cell [205].

The body excretes platinum in various ways, mainly through urine; the complex Pt(L-methionine-SN)$_2$ is one of the few characterized products [206].

Table 3.28 Bond lengths for palladium and platinum congeners (Å)

	Bond	M		Ref.
		Pd	Pt	
$M(PBu^t_3)_2$	M–P	2.285	2.249	207(a)
$M(PBu^t_2Ph)_2$	M–P	2.285	2.252	207(b)
$M(Pcy_3)_2$	M–P	2.26	2.231	207(c)
$M(PPh_3)_3$	M–P	2.307–2.322	2.262–2.277	207(d)
trans-$MI_2(C_4H_8S)_2$	M–S	2.316–2.329	2.309–2.310	207(e)
	M–I	2.603–2.625	2.606–2.610	
cis-MCl_2 (bipy)	M–N	2.03	2.001	207(f)
	M–Cl	2.297	2.306	
cis-$M(Me_2)(PPh_2Me)_2$	M–P	2.323	2.284	207(g)
	M–C	2.090	2.120	
cis-$MCl_2(PMe_3)_2$	M–P	2.257	2.238	207(h)
	M–Cl	2.368	2.372	
MCl_4^{2-}	M–Cl	2.299	2.308	207(i)
MBr_4^{2-}	M–Br	2.438	2.445	207(j)
MF_6^{2-}	M–F	1.896	1.922	207(k)
MCl_6^{2-}	M–Cl	2.309	2.315	207(l)
MBr_6^{2-}	M–Br	2.466–2.470	2.481	207(m)
MCl_4(bipy)	M–N	2.307–2.044	2.038–2.044	207(n)
	M–Cl (*trans*-Cl)	2.302–2.310	2.316–2.320	
	M–Cl (*trans*-N)	2.289–2.290	2.306–2.307	
trans-$MCl_2(Pcy_3)_2$	M–P	2.363	2.337	207(o)
	M–Cl	2.301	2.317	
$M(PPh_3)_2C_{60}$	M–P	2.315–2.330	2.253–2.303	207(p)
	M–C	2.086–2.123	2.115–2.145	
$MMe_3[(pz)_3CH]^+$	M–C	2.039–2.060 (av. 2.048)	2.031–2.056 (av. 2.048)	207(q)
	M–N	2.191–2.225 (av. 2.208)	2.156–2.189 (av. 2.169)	
$M(DMSO)_4^{2+}$	M–S	2.240–2.249 (av. 2.245)	2.205–2.208 (av. 2.207)	207(r)
	M–O	2.061–2.065 (av. 2.063)	2.040–2.051 (av. 2.045)	
$M(PBu^t_2Ph)_2O_2$	M–P	2.357–2.360	2.290	207(s)
	M–O	2.05–2.06	2.02	
trans-M(P–P)Cl_2[a]	M–P	2.307	2.293	207(t)
	M–Cl	2.306	2.304	
MCl_2(dppe)	M–P	2.226–2.223 (av. 2.230)	2.208	207(u)
	M–Cl	2.357–2.361 (av. 2.359)	2.341–2.355 (av. 2.348)	
$[M(CNMe)_4](PF_6)_2$	M–C	1.981	1.990	207(v)

[a] P–P = 2,11-bis(diethylphosphinomethyl)benzo[c]phenanthrene.

3.14. Bond lengths in palladium and platinum analogues

Table 3.28 compares bond lengths for a series of congeners of platinum and palladium [207]. One fact that emerges is that bonds from a given atom to palladium and platinum have very similar lengths. There is, however, a pattern; *in general* for the more 'ionic' (e.g. metal–halogen) bonds; the bond to platinum is often slightly longer, whereas for the more 'covalent' bonds (e.g. metal–nitrogen or phosphorus) it is the bond to palladium that is slightly longer.