

3 Palladium and platinum

3.1 Introduction

Palladium and platinum are the longest known and most studied of the six platinum metals [1–11], a reflection of their abundance and consequent availability. Platinum occurs naturally as the element, generally with small amounts of the other platinum metals. It was used as a silver substitute by Colombian Indians and first observed there by Ulloa (1736), who called it *platina del Pinto* ('little silver of the Pinto river') but the first sample was actually brought to Europe in 1741 by Charles Wood, Assay Master of Jamaica. Palladium was isolated in 1803 by W.H. Wollaston, who was studying the aqua regia-soluble portion of platinum ores (he announced his discovery by an anonymous leaflet advertising its sale through a shop in Soho) and named it after the newly discovered asteroid Pallas [12].

These two metals resemble each other more closely than any of the other 'pairs' in this book. Their chemistry is largely that of the +2 and +4 oxidation states, though there are a few, formally, +1 and +3 compounds and there is an important group of zero valent tertiary phosphine complexes though no stable carbonyl comparable to $\text{Ni}(\text{CO})_4$. Unlike nickel(II), where there are large numbers of tetrahedral complexes, these metals adopt almost exclusively square planar geometries in this oxidation state. As expected, they form more compounds in high oxidation states than nickel, partly a consequence of the lower ionization energies (Table 3.1).

Significant differences include:

1. The +4 oxidation state is more stable for platinum.
2. Platinum complexes are usually less labile.
3. There are many more examples of *cis*- and *trans*-isomers for platinum (a consequence of (2)).

Platinum in particular forms numbers of stable σ -bonded alkyls and aryls in both the +2 and +4 states.

3.2 The elements and uses

Both palladium and platinum are shiny, silvery metals (with ccp structures), easily drawn and worked when pure. Palladium has the lower melting and boiling points (1552 and 3141°C, respectively); the corresponding figures

Table 3.1 Ionization energies (kJ mol^{-1})

	Ni	Pd	Pt
I_1	736.7	805	870
I_2	1753	1875	1791
I_3	3393	3174	(2800)
I_4	5300	(4100)	(3900)

Values in parentheses are estimated.

for platinum are 1772 and 3825°C. Palladium is the more reactive, attacked by air at 700°C and by moist halogens at 20°C; it dissolves in hot oxidizing mineral acids whereas platinum is only dissolved by aqua regia. Both are attacked by molten caustic alkali.

Uses

The main uses of palladium [13] are in the electronics and electrical industries, in circuitry and in dental alloys. It finds many catalytic applications in industry, as well as in diffusion cells for the synthesis of hydrogen, and in automobile catalysts. Jewellery and 'three way' auto-catalysts are the principal uses of platinum, which fulfils a wide range of roles in the chemical industry.

The 'three way' catalysts are a major present day use for platinum and rhodium, and a lesser one for palladium; their role in minimizing exhaust emissions (while maximizing energy release) from petrol engines entails complete combustion of hydrocarbons, conversion of CO into CO₂ and also removal of nitrogen oxides as N₂ (reduction of NO_x). Platinum metal catalysts are thermally stable and operate at relatively low temperatures. They are prepared by dispersing a mixture of these three metals and alumina, together with certain additives like ceria, over a ceramic or metal matrix to obtain a large surface area. Platinum is the best alkane (and CO) oxidation catalyst while palladium is superior for alkenes. The role of the CeO₂ lies partly in the ability of cerium to switch oxidation states and thus act as a local oxygen store.

Fuel cells essentially reverse the electrolytic process. Two separated platinum electrodes immersed in an electrolyte generate a voltage when hydrogen is passed over one and oxygen over the other (forming H₃O⁺ and OH⁻, respectively). Ruthenium complexes are used as catalysts for the electrolytic breakdown of water using solar energy (section 1.8.1).

3.2.1 Extraction

The principal countries where platinum and palladium are extracted (along with nickel) are South Africa, Canada and the former USSR, though significant amounts come from Colombia, China and Western Australia [14]. The

ores include all six platinum metals, with palladium and platinum most abundant; relative amounts vary, with the Merensky reef (South Africa) richer in platinum, roughly equal amounts in Sudbury (Ontario), and the Noril'sk deposits (Siberia) richer in palladium. They tend to occur along with nickel and copper ores, e.g. cooperite (PtS), braggite (MS) and sperrylite (PtAs₂).

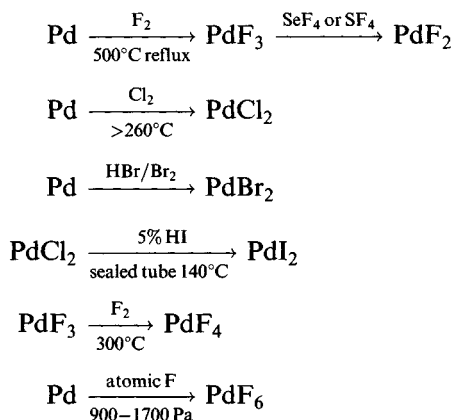
The metals are obtained from the metallic phase of the sulphide matte or the anode slime from electrolytic refining of nickel. In the traditional process for the platinum metals, their separation was facilitated by their solubility in aqua regia and convertibility into PdCl₄²⁻ or PtCl₆²⁻ salts. Nowadays, substantial amounts are obtained using solvent extraction.

3.3 Halides

As expected, the heavier metal favours higher oxidation states (Table 3.2): the MX₃ compounds are not genuine M³⁺ species but are diamagnetic, with equal amounts of M²⁺ and M⁴⁺. PtF₅, however, is a platinum(V) compound.

3.3.1 Palladium halides

Syntheses of palladium halides often involve direct reaction with a halogen:



PdF₂ is that rare substance, a paramagnetic palladium compound, explicable in terms of (distorted) octahedral coordination of palladium with octahedra sharing corners [15]. It exists in two forms, both having $\mu_{\text{eff}} \sim 2.0 \mu_{\text{B}}$, rather below the spin only value for two unpaired electrons. Bond lengths are Pd–F 2.172 Å (two) and 2.143 Å (four) in the tetragonal form (rutile structure).

The other palladium(II) halides are all diamagnetic. PdCl₂ exists in well defined α - and β -forms [16] (as well as a γ -form); the former has a PdCl₄/2

Table 3.2 Characteristics of palladium and platinum halides

	Palladium				Platinum			
	F	Cl	Br	I	F	Cl	Br	I
MX ₂	Pale violet solid	Red solid, dec. >600°C	Brown solid	Black (α), deep red (β), black (γ), dec. >350°C		Black–brown solid	Brown solid	Black solid, dec. >500°C
MX ₃	Black solid					Green–black solid	Black–green crystal	Black solid
MX ₄	Brick red solid, rapid dec. >350°C				Yellow–brown solid	Red–brown crystal, dec. >350°C	Dark red solid, dec. >180°C	Black crystal, slow dec. RT
MX ₅					Red solid, m.p. 80°C			
MX ₆	Dark red solid, dec. ~0°C				Dark red solid, m.p. 61.3°C			

M, palladium or platinum; X, halide.

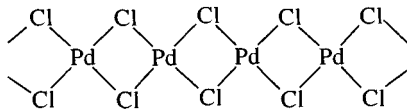


Figure 3.1 The chain structure of α -PdCl₂.

chain structure (Figure 3.1) while the β -form, synthesized by subliming the α form at 430–460°C) is Pd₆Cl₁₂, similar to the platinum analogue.

PdBr₂ also has a chain structure, but puckered, unlike α -PdCl₂, with planar coordination (somewhat irregular: Pd–Br 2.34, 2.57 Å). PdI₂ has three modifications, all made starting from the black γ -form precipitated from aqueous PdCl₂ reacting with HI at 140°C; it is traditionally used, because of its insolubility, in the gravimetric determination of palladium. The α -form of PdI₂ has a structure with tetragonal PdI₄ units forming side-by-side chains (Pd–I 2.60 Å) while in the β -form there are planar Pd₂I₆ units (Pd–I 2.61–2.62 Å) cross-linked with two distant iodines (3.29, 3.49 Å) to give distorted 6-coordination.

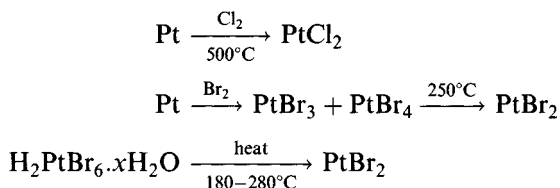
PdF₃ is really Pd²⁺PdF₆²⁻; both palladiums have an octahedral environment (Pd²⁺–F 2.17 Å; Pd⁴⁺–F 1.90 Å); like PdF₂, it is paramagnetic with a magnetic moment of 1.75 μ_B per palladium. It is possible that application of pressure causes the Pd–F bonds to even out, so that at high pressures the compound could become PdF₃ (genuine alkali metal salts of PdF₆³⁻ do exist) [17].

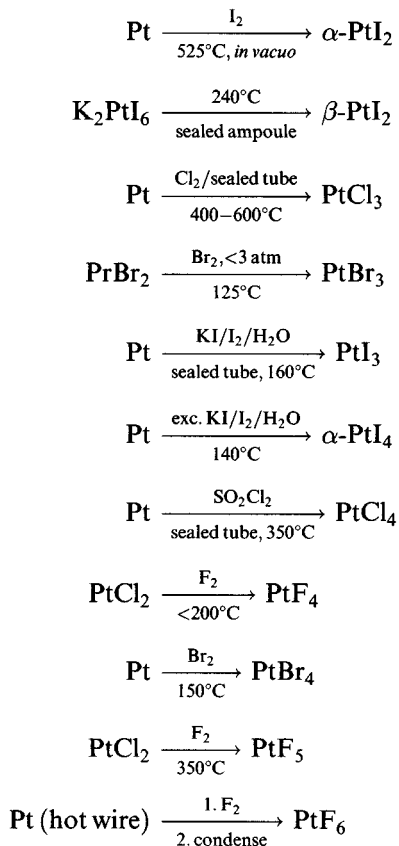
PdF₄ is the only stable palladium(IV) halide [18] (testimony to the oxidizing nature of palladium(IV)) and is a very moisture-sensitive diamagnetic red solid; the structure is based on Pd₆F₂₄ hexameric units linked three-dimensionally. It has octahedrally coordinated palladium with two terminal (*cis*) fluorines and four bridging ones. Despite the absence of other tetrahalides, the complete series of PdX₆²⁻ exist (cf. Ir).

PdF₆ has been reported [19] (but not confirmed) to result from the reaction of powdered palladium with atomic fluorine under pressure (900–1700 Pa) as a dark red solid, unstable at 0°C that oxidizes both oxygen and water. An IR band at 711 cm⁻¹ has been assigned as ν (Pd–F). There are unsubstantiated claims for PdF₅.

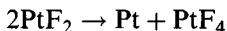
3.3.2 Platinum halides

Syntheses of platinum halides [20] include





PtF_2 is unknown, presumably unstable with respect to the disproportionation



This would occur as a consequence of the stability of the low spin d^6 platinum(IV) state and of the oxidizing power of fluorine. PtCl_2 , like the other platinum dihalides, is insoluble in water. It has two crystalline forms: the β -form is similar to $\beta\text{-PdCl}_2$ (Figure 3.2; Pt—Cl 2.34–2.39 Å, Pt—Pt 3.32–3.40 Å). This transforms to the α -form at 500°C ; this form has square planar coordination of platinum (Pt—Cl 2.299–2.310 Å) in a chain structure [21]. PtBr_2 is isomorphous with $\beta\text{-PtCl}_2$, and thus believed to be $\text{Pt}_6\text{Br}_{12}$, while $\beta\text{-PtI}_2$ is isomorphous with $\beta\text{-PdI}_2$ [20].

All the trihalides are mixed valence compounds. PtF_3 is isostructural with $\text{PdF}_3 \cdot \text{PtX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) cannot be made by straightforward thermal decomposition of PtX_4 [22] under open conditions but by routes involving continuous decomposition and formation under closed, equilibrium conditions.

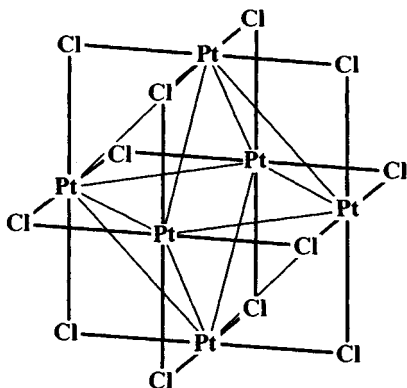


Figure 3.2 The structure of β - $\text{PtCl}_2(\text{Pt}_6\text{Cl}_{12})$. (Reproduced with permission from S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan Press Ltd, 1975, p. 109.)

PtCl_3 and PtBr_3 (Figure 3.3) are isomorphous and contain both Pt_6X_{12} clusters and $[\text{PtX}_2\text{X}_{4/2}]_\infty$ chains, thus representing a 'half way' stage in decomposing PtX_4 [20].

PtF_4 prepared by various routes, including fluorination (BrF_3) of PtCl_4 or heating PtF_6 , is isostructural with PdF_4 (Pt–F (terminal) 1.818 Å, Pt–F (bridge) 2.048 Å) [23]. The other tetrahalides similarly have chain structures (Figure 3.4) with two *cis*-terminal halides.

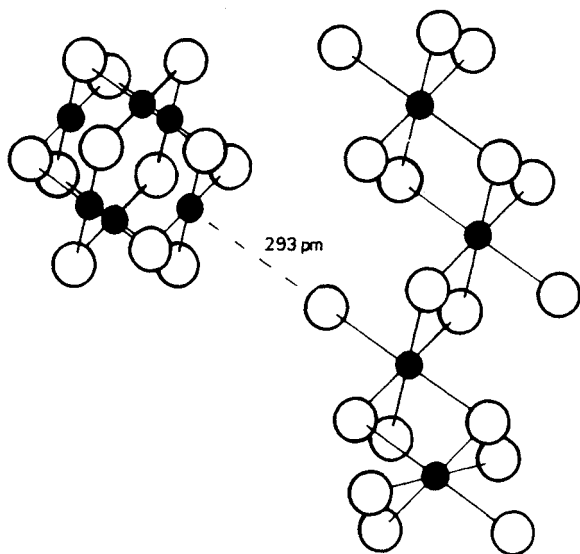


Figure 3.3 The structure of PtBr_3 , showing the $\text{Pt}_6\text{Br}_{12}$ and $[\text{PtBr}_2\text{Br}_{4/2}]_\infty$ structural units. (Reproduced with permission from *Transit. Met. Chem.*, 1975/6, 1, 45.)

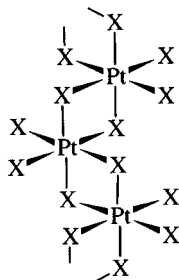


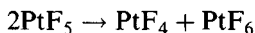
Figure 3.4 The chain structure adopted by PtX_4 in the solid state.

The iodide is polymorphic, with the α - and γ -forms known to have this structure (bond lengths are 2.65–2.72 Å (γ - PtI_4), 2.62–2.78 Å (α - PtI_4) 2.41–2.54 Å (PtBr_4).

On heating, PtCl_4 and PtBr_4 give PtX_2 but PtI_4 first yields PtI_3 or Pt_3I_8 , depending on conditions [24].

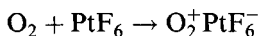
Evaporation of solutions of platinum in aqua regia gives yellow crystals of the hydrates *trans*- $[\text{PtCl}_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ and *fac*- $[\text{PtCl}_3(\text{H}_2\text{O})_3]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ [25].

PtF_5 , made by fluorination of PtCl_2 at 350°C disproportionates above its m.p.



Its structure is not known but it may be a tetramer, like RhF_5 .

The original synthesis of PtF_6 [26] involves electrical ignition of a platinum wire in a fluorine atmosphere then rapidly cooling the vapour (liquid nitrogen); it is also reported to result from the reaction of the elements under pressure at 200°C. It has a molecular structure ($\text{Pt}-\text{F}$ 1.839 Å) and is intensely reactive, forming PtF_5 and PtF_4 on heating, vigorously decomposing water to O_2 , and even attacking dry glass. It also is readily reduced:



3.3.3 Halide complexes

An extensive range of mono- and binuclear halide complexes of platinum and palladium exist. Of the tetrahalometallate(II) ions, some like PtF_4^{2-} and PdI_4^{2-} are elusive, the latter only having been characterized in solution.

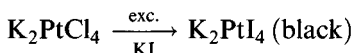
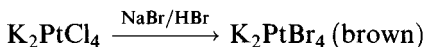
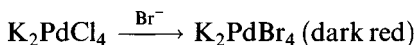
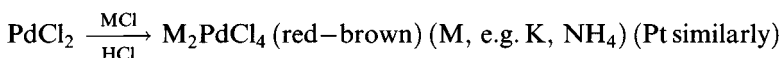


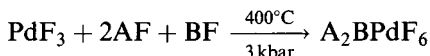
Table 3.3 Bond lengths in MX_4^{2-} together with M–X stretching frequencies (cm^{-1})

Ion	Cation	M–X (Å)	Ion	$\nu_1(\text{A}_{1g})$	$\nu_2(\text{B}_{1g})$	$\nu_6(\text{E}_u)$
PdCl_4^{2-}	NH_4^+	2.299	K	310	275	336
PtCl_4^{2-}	K^+	2.308	Bu_4N	330	312	317
PdBr_4^{2-}	K^+	2.438	(aq.)	188	172	225
PtBr_4^{2-}	K^+	2.445	–	208	194	243
PtI_4^{2-}	(in $(\text{MeNH}_3)_4\text{Pt}_3\text{I}_{11}$)	2.625	(aq.)	155	142	–

They have square planar structures; corresponding bond lengths and vibrational frequencies are given in Table 3.3.

PtI_4^{2-} has been identified in the unusual $(\text{MeNH}_3)_4\text{Pt}_3\text{I}_{11}$, a mixed-valence compound with PtI_4^{2-} , PtI_6^{2-} and $\text{Pt}_2\text{I}_6^{2-}$ ions all present (K_2PtI_4 has not definitely been confirmed) [27].

Genuine palladium(III) fluoroferrates have been made [28]



(A = K, Rb, Cs; B = Li, Na, K).

The beige to green solids have the elpasolite structure. Magnetic measurements confirm the $t_{2g}^6 e_g^1$ configuration; they give strong ESR signals (Na_3PdF_6 $g_{\perp} = 2.312$, $g_{\parallel} = 2.025$) and exhibit a peak in the photoelectron spectra intermediate between those for palladium(II) and palladium(IV). K_2NaPdF_6 has been shown (X-ray) to have Jahn–Teller-distorted PdF_6^{3-} octahedra with Pd–F = 1.95 Å (four) and 2.14 Å (two).

‘Chloroplatinic acid’, $(\text{H}_3\text{O})_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ($x \sim 2$), is obtained as brown-red crystals by dissolving platinum in aqua regia, followed by one or two evaporations with hydrochloric acid; it is a very useful starting material. Thermogravimetric data show that, after initial dehydration (up to 125°C), PtCl_4 is formed at 220°C and $\beta\text{-PtCl}_2$ at 350°C , before final decomposition to platinum around 500°C [29]. The Pt–Cl bond length is 2.323 Å in $(\text{H}_3\text{O})_2\text{PtCl}_6$ [30].

All eight possible octahedral MX_6^{2-} (X = F, Cl, Br, I) have been made [31]:

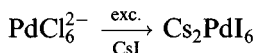
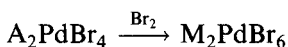
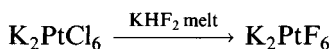
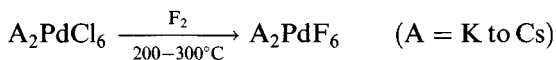
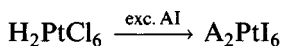
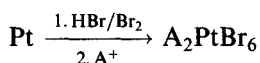
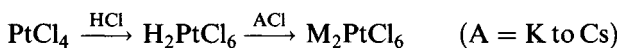


Table 3.4 Bond lengths in MX_6^{2-} (Å)

Pd complexes	Counter-ion	M-X	Pt complexes	Counter-ion	M-X
PdF_6^{2-}	XeF_5^+	1.893	PtF_6^{2-}	NH_4^+	1.942
	K^+	1.896		K^+	1.922
$PdCl_6^{2-}$	NH_4^+	2.300	$PtCl_6^{2-}$	K^+	2.315-2.316
	K^+	2.309			
	Me_4N^+	2.312			
$PdBr_6^{2-}$	$(en)H_2^{2+}$	2.466-2.470	$PtBr_6^{2-}$	K^+	2.481
			PtI_6^{2-}	pyH^+	2.661-2.670
				Cs^+	2.673



The palladium compounds are generally, as expected, less stable. Therefore, PdF_6^{2-} is decomposed by water while PtF_6^{2-} can be synthesized in aqueous solution. The M_2PdCl_6 salts decompose on heating to 200°C. Bond lengths for a selection of the MX_6^{2-} ions are given in Table 3.4 and the structure of K_2PtCl_6 is shown in Figure 3.5 (based on the fluorite structure with K^+ in the fluoride positions and $PtCl_6^{2-}$ taking the place of the potassium) [32].

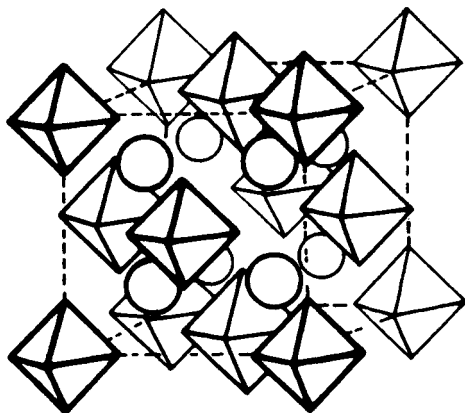


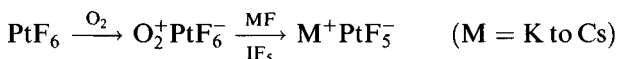
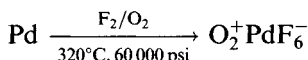
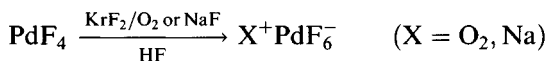
Figure 3.5 The crystal structure of K_2PtCl_6 . (Reproduced from A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, 1975, p. 387, by permission of Oxford University Press.)

Table 3.5 Comparing bond lengths in MF_6^- (Å)

	M-F
PtF_6	1.839
KPtF_6	1.886
K_2PtF_6	1.926
K_2PdF_6	1.896
K_2NaPdF_6	1.95–2.14 ^a

^a Jahn-Teller distorted.

Synthesis for the octahedral MF_6^- ions include [33]

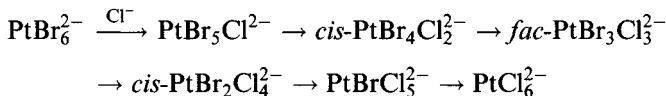


The magnetic moment for PtF_6^- (K^+ salt) is $0.87 \mu_{\text{B}}$ (t_{2g}^5). The bond lengths for this ion are, as expected, intermediate between PtF_6 and PtF_6^{2-} (Table 3.5).

Both these ions are strong oxidizing agents; PtF_6^- will, unlike PtF_6^{2-} , oxidize water to O_2 and O_3 . Vibrational data for a number of MX_6^- species are listed in Tables 3.6 and 3.7.

As expected, there is a shift to lower frequency as the oxidation state of the metal decreases and as the mass of the halogen increases.

Mixed haloplatinate(IV) ions have been synthesized [34] by use of substitution reactions on PtCl_6^{2-} and PtBr_6^{2-} ; using the stronger *trans*-influence of Br, the *cis*-isomers can be made by treating PtBr_6^{2-} with Cl^- (in the presence of Br_2):

**Table 3.6** Vibrational frequencies in MX_6^{2-} (M = Pd, Pt; X = F, Cl, Br, I)

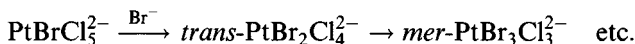
	PdF_6^{2-}	PdCl_6^{2-}	PdBr_6^{2-}	PtF_6^{2-}	PtCl_6^{2-}	PtBr_6^{2-}	PtI_6^{2-}
Counter-ion	NO^+	K^+	K^+	Cs^+	K^+	K^+	(aq.)
ν_1	573	317	198	591	351	218.5	150
ν_2	554	292	176	566	321	195.5	131
ν_3	602	357	253	571	345	244.5	186
ν_4	—	175	130	281	184		
ν_5	246	164	100	221	174	114.5	69.5

Data from: Y.M. Bosworth and R.J.H. Clark (1974) *J. Chem. Soc., Dalton Trans.*, 1749; M.P. Laurent *et al.* (1981) *Inorg. Chem.* **20**, 372; D.M. Adams *et al.* (1981) *J. Chem. Phys.* **74**, 2800; W. Preetz and G. Rimkus (1982) *Z. Naturforsch., Teil B*, **37**, 579.

Table 3.7 Comparative vibrational data for MF_6^{2-} (cm^{-1})

	PdF_6	PdF_6^-	PdF_6^{2-}	PtF_6	PtF_6^-	PtF_6^{2-}
ν_1		643	573	656	647	591
ν_2		570	554	601	590/572	566
ν_3	711		602	705	630	571
ν_4				273		281
ν_5			246	242	249/236	221
ν_6				211		

The *trans*-isomers can be made by substitution of Br^-



Reaction mixtures can be separated by chromatography. Individual isomers can be identified by their vibrational spectra.

In the case of $\text{PtF}_n\text{Cl}_{6-n}^{2-}$, it has even been possible to synthesize isotopically labelled species using isotopically labelled HCl (Figure 3.6).

Spectra of *trans*- $\text{Pt}^{35}\text{Cl}_2\text{F}_4^{2-}$ and the *cis*-isomer show the simpler spectra expected from the *trans*-isomer (three Pt–F and two Pt–Cl stretches) compared with the *cis*-isomer (four Pt–F and two Pt–Cl stretches). The complexity of the spectrum of the *cis*-isomer is also the result of the lack of a centre of symmetry in the *cis*-form; the selection rules allow all bands to be seen in both the IR and the Raman spectra (in theory, at least).

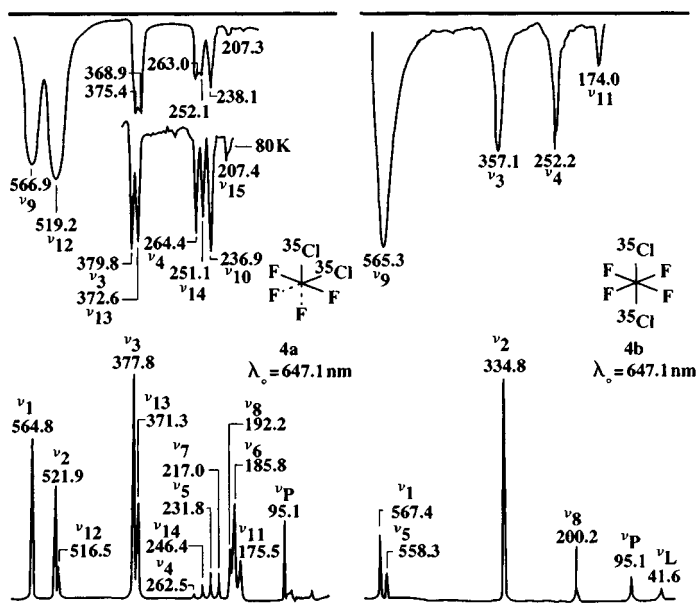


Figure 3.6 IR (upper) and Raman (lower) spectra of $\text{Cs}_2[\text{Pt}^{35}\text{Cl}_2\text{F}_4]$: *cis*-isomer on the left; *trans*-isomer on the right. (Reproduced with permission from *Z. Naturforsch., Teil B*, 1989, **44**, 619.)

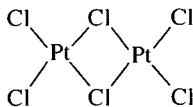
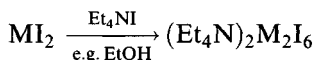
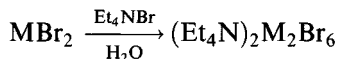
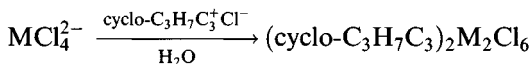
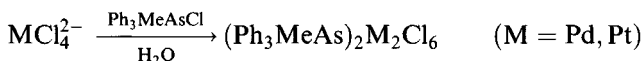


Figure 3.7 The dimeric structure of $[\text{Pt}_2\text{Cl}_6]^{2-}$.

The structures of *fac*-(py_2CH_2)[PtF_3Cl_3] and *mer*-(py_2CH_2)[PtF_3Cl_3] show the greater *trans*-influence of chloride. The Pt–F bonds are 1.950–1.995 Å in the *fac*-isomer and 1.936–1.937 Å (*trans* to F) and 1.972 Å (*trans* to Cl) in the *mer*-isomer; similarly Pt–Cl is 2.265–2.285 Å in the *fac*-isomer and 2.271 Å (*trans* to F) and 2.292–2.303 Å (*trans* to Cl) in the *mer*-isomer [35].

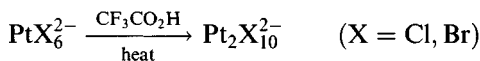
The $\text{M}_2\text{X}_6^{2-}$ salts are the simplest binuclear complexes [36]



They have di- μ -halogen bridged structures and are planar (Figure 3.7).

Typical bond lengths in $\text{Pd}_2\text{Cl}_6^{2-}$ are Pd–Cl 2.27 Å (terminal) and 2.32 Å (bridge) with Pd–Pd 3.41 Å and in $\text{Pd}_2\text{Br}_6^{2-}$ Pd–Br 2.398–2.405 Å (terminal) and 2.445–2.452 Å (bridge).

Dinuclear platinum(IV) complexes have recently been reported:



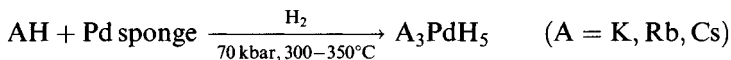
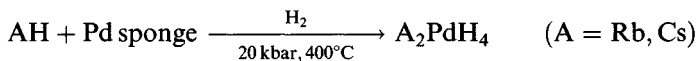
They have edge-sharing bioctahedral structures [37].

3.4 Other binary complexes

Palladium is notable for its ability to absorb (and desorb) hydrogen; diffusion through thin palladium films can be used to separate hydrogen from other gases. At 300 K, the Pd/H phase diagram shows an α -phase up to $\text{PdH}_{0.03}$, a two-phase region up to $\text{PdH}_{0.56}$ after which the β -phase becomes the sole species. The greatest H: Pd ratio obtainable is $\sim 0.83:1$ (at 195 K). The hydride reportedly has a defect NaCl structure.

The ability of palladium and platinum to catalyse hydrogenation reactions is of considerable industrial importance.

Tertiary hydrides can be made [38, 39]



Na_2PdH_4 , A_2PtH_4 ($\text{M} = \text{Na, K}$) and K_2PtH_6 are similarly made, only K_2PtH_6 requiring any high hydrogen pressure.

All A_2MH_4 contain square planar MH_4^{2-} units, but at high temperatures the A_2MH_4 salts adopt the K_2PtCl_6 structure with hydrogens able to move between different square planar orientations. M_2PdH_2 ($\text{M} = \text{Li, Na}$) compounds have metallic lustre and display metallic conductivity [40].

Palladium and platinum combine on heating with the group V (15) and VI (16) elements [41].

The important oxides are black PdO and brown PtO_2 . The former can be made by heating palladium in oxygen; other methods include heating PdCl_2 in an NaNO_3 melt at 520°C . A hydrated form precipitates from aqueous solution, e.g. when $\text{Pd}(\text{NO}_3)_2$ solution is boiled. It has 4-coordinate square planar palladium (Figure 3.8).

Black PdO_2 (rutile structure) is claimed to result from heating PdO with KClO_3 under pressure at 950°C , then rapidly cooling to room temperature. PtO_2 , however, is well authenticated; it is made in hydrated form by hydrolysis (with Na_2CO_3) of boiling PtCl_6^{2-} solution. It dehydrates on heating.

PtS (PdO structure) and PdS (similar) are prepared from $\text{M}^{2+}(\text{aq.})$ and H_2S or Li_2S . They have square planar coordination of M^{2+} (Figure 3.9).

On heating with sulphur, MS_2 result. PtS_2 has the 6-coordinate CdI_2 structure whereas PtS_2 is $\text{Pd}^{2+}(\text{S}_2^{2-})$ in a distorted pyrite structure (4-coordinate $\text{PdPd-S } 2.30 \text{ \AA}$) confirming the preference for the divalent state for

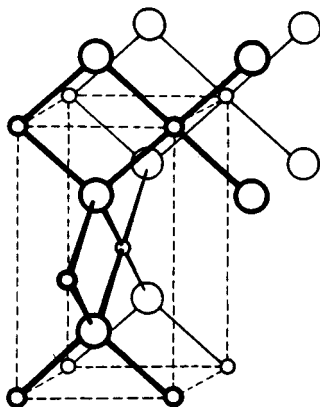


Figure 3.8 The structure of PdO and PtO . (Reproduced from A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, 1975, p. 446, by permission of Oxford University Press.)

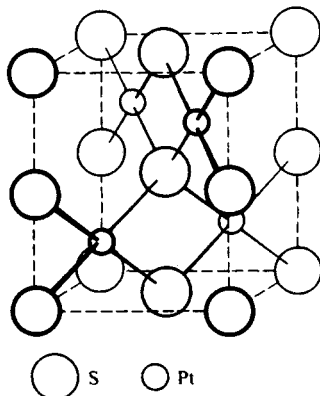


Figure 3.9 The structure of PtS. (Reproduced from A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, 1975, p. 661, by permission of Oxford University Press.)

palladium. Other phases like $\text{Pd}_{2.2}\text{S}$, Pd_3S and Pd_4S (the last two both alloy like) exist. The former is a superconductor below 1.63 K.

The tellurides MTe reportedly have the NiAs structure.

The pyrites structure is exhibited by several pnictides: MAS_2 and MSb_2 ($\text{M} = \text{Pd}, \text{Pt}$) and PtP_2 (Figure 3.10).

PdP_2 , however, contains continuous chains of phosphorus atoms (with, as expected, planar 4-coordinate Pd) while PdP_3 has the CoAs_3 structure (P_4 rings).

3.5 Aqua ions

Syntheses of palladium and platinum aqua ions [42] include

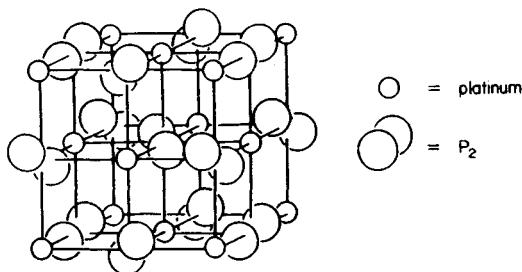
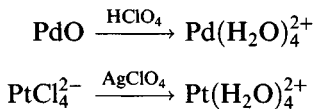


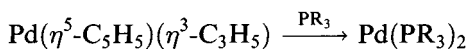
Figure 3.10 The structure of PtP_2 . (Reproduced with permission from S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan Press Ltd, 1975, p. 111.)

Hydrated palladium perchlorate has been isolated as brown needles of $\text{Pd}(\text{H}_2\text{O})_4(\text{ClO}_4)_2$ by first dissolving palladium sponge in concentrated HNO_3 , adding 72% HClO_4 , evaporating until it fumes strongly and then crystallizing. $\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2$ is made by the reaction of palladium with nitric acid; it is also brown.

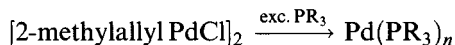
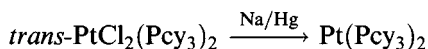
3.6 Palladium(0) and platinum(0) compounds

3.6.1 Tertiary phosphine complexes

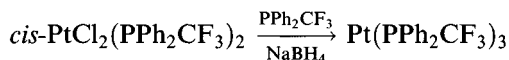
The tertiary phosphine complexes are the most important zerovalent compounds. They are frequently prepared by reductive methods, often using the phosphine as the reducing agent [43], e.g.



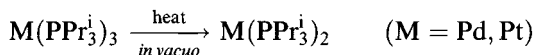
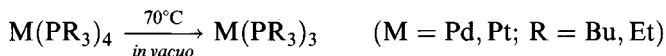
($\text{R} = \text{Bu}^t$, cy; $\text{PR}_3 = \text{PPhBu}_2^t$)



($\text{PR}_3 = \text{PMe}_3$, PMe_2Ph , PBU_3^n ($n = 4$); $\text{PR}_3 = \text{Pcy}_3$, PPr_3^i , Pbz_3 ($n = 3$); $\text{PR}_3 = \text{PBU}_2^t\text{Ph}$ ($n = 2$))



Compounds with high coordination numbers sometimes eliminate a molecule of phosphine on heating:



Tetrahedral structures have been established for $\text{Pd}(\text{PPh}_3)_4$ (rather long Pd-P bonds at 2.443 Å), $\text{Pd}[\text{P}(\text{CH}_2\text{OH})_3]_4$ (Pd-P 2.321 to 2.326 Å), $\text{Pt}(\text{PF}_3)_4$ (electron diffraction: Pt-P 2.229 Å), $\text{Pd}[\text{P}(\text{C}\equiv\text{CPh})_3]_4$, $\text{Pt}(\text{PEt}_3)_4$ and $\text{Pt}(\text{PMe}_2\text{Ph})_4$ [44]. Trigonal planar structures are found for $\text{Pt}(\text{Pcy}_3)_3$, $\text{Pd}(\text{PPh}_3)_3$ (Pd-P 2.307–2.322 Å) and $\text{Pt}(\text{PPh}_3)_3$ (Pt-P 2.262–2.271 Å) [45] and essentially linear 2-coordination for $\text{M}(\text{PBU}_2^t\text{Ph})_2$ ($\text{M} = \text{Pd, Pt}$; M-P 2.285 and 2.252 Å, respectively), $\text{M}(\text{Pcy}_3)_2$ (Pd-P 2.26 Å, Pt-P 2.231 Å) and $\text{Pd}(\text{PBU}_3^t)_2$ (Pd-P 2.285 Å). The last named has a P-Pd-P angle of 180° while the PBU_2^tPh complexes are virtually linear but with some short metal *ortho*-hydrogen contacts. Curiously, the Pcy_3 complexes have

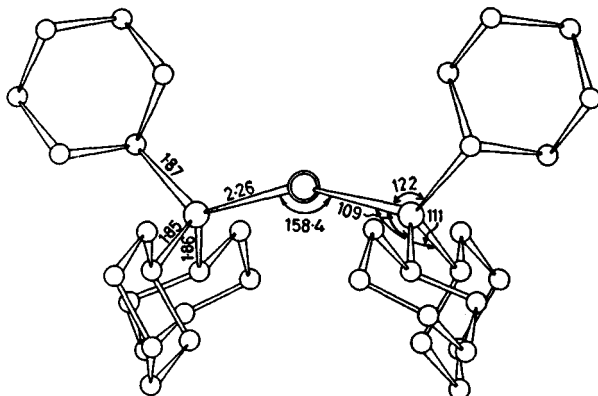


Figure 3.11 The structure of $\text{Pd}(\text{Pcy}_3)_2$. (Reproduced with permission from *J. Chem. Soc., Chem. Commun.*, 1974, 400.)

significantly 'bent' P–M–P bonds (158.4° M = Pd; 160.5° M = Pt) (Figure 3.11). $\text{Pd}(\text{P}(o\text{-tolyl})_3)_2$ has linear P–Pd–P coordination [46].

As expected, the Pt–P bond increases from 2.231 \AA in the 2-coordinate $\text{Pt}(\text{Pcy}_3)_2$ to 2.303 \AA in 3-coordinate $\text{Pt}(\text{Pcy}_3)_3$. (Similarly in $\text{Pd}(\text{PPh}_3)_n$ ($n = 3, 4$), from 2.31 \AA ($n = 3$) to 2.443 \AA ($n = 4$).

Most of these compounds are solids (though a few such as $\text{Pt}(\text{PEt}_3)_3$, $\text{Pt}(\text{PBu}_3)_3$ and $\text{Pt}(\text{PF}_3)_4$ are oils at room temperature). Their stoichiometry in solution has been studied, most particularly by ^{31}P NMR at low temperatures, to determine which species are present [47]. Table 3.8 shows that the coordination number is principally determined by the bulk of the ligand

Table 3.8 $\text{M}(\text{PR}_3)_n$ complexes isolated in the solid state (S) and detected in solution (✓)

PR_3	Cone angle ($^\circ$)	PtL_4	PtL_3	PtL_2	PdL_4	PdL_3	PdL_2
PF_3	104	S					
$\text{P}(\text{OEt})_3$	109	S✓	X				
PMe_3	118	S✓	X		S✓	X	
PMe_2Ph	122	S✓			S✓	X	
PEt_3	132	S✓	S✓	X	S✓	✓	
PBu_3^n	132	S✓	S✓		S✓	✓	
PMePh_2	136	S✓			S✓		
PPh_3	145	S	S✓		S✓	S✓	S
$\text{P}(o\text{-tolyl})_3$	145	X	S✓				S✓
PPr_3^i	160		S✓	S✓		✓	✓
$\text{P}(O\text{-}o\text{-tolyl})_3$	141		S✓	X			
Pbz_3	165		S✓	X		✓	
PBu_2^iPh	170		X	S✓		X	S✓
Pcy_3	170		S✓	S✓		✓	S✓
PBu_3^t	182			S✓			S✓

(conveniently measured in terms of its cone angle), i.e. the bulkier the ligand, the lower the coordination number of the complex isolated.

Steric requirements also affect the stability of compounds; therefore, for the complexes $\text{Pt}(\text{PR}_3)_4$, the PET_3 complex (cone angle 132°) loses 1 mol phosphine *in vacuo* at 50°C , but the PMe_3 complex (cone angle 118°) is unaffected.

Steric factors are not the only ones to affect stability; $\text{Ni}(\text{Pcy}_3)_3$ does not dissociate, while $\text{M}(\text{Pcy}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) is stable, the reverse of what would be expected on steric grounds. Similarly with $\text{P}(o\text{-tolyl})_3$, nickel forms NiL_4 while platinum forms PtL_3 . Such discrepancies may be accounted for by taking into account the electron-donating power (basicity) of the phosphine and the electronic properties of the metal; thus electron-donating phosphines like PPR_3^i can satisfy the electron demand of the metal better than aryl phosphines such as $\text{P}(O\text{-}o\text{-tolyl})_3$ [48]. Compression of the cone angle or meshing of the ligands may also be important [45c]. Tricyclohexylphosphine has a cone angle of 170° yet meshing of the ligands leads to the isolability of $\text{Pt}(\text{Pcy}_3)_3$ from solution at -15°C (only $\text{Pt}(\text{Pcy}_3)_2$ is detected in solution above 0°C). Corresponding palladium and platinum complexes generally resemble each other closely, but there are differences; $\text{Pd}(\text{PPh}_2\text{Me})_4$ does not dissociate while the platinum analogue does. $\text{Pd}(\text{PBu}_2^t\text{Ph})_2$ binds oxygen reversibly, the platinum analogue binds irreversibly; PtL_2 ($\text{L} = \text{PPR}_3^i, \text{Pcy}_3, \text{PBu}_2^t\text{Ph}$) adds hydrogen reversibly whereas the palladium analogues do not.

In these compounds, compared with the palladium and platinum complexes, nickel generally exhibits higher coordination numbers, an effect similar to that seen with copper and silver compared with gold (section 4.1). Consideration of the d-s and s-p separations (Table 3.9) suggests that 2-coordination may be favoured for large s-p or small d-s separations (while relativistic effects may be significant for platinum, the general similarity between platinum and palladium suggests that it is not an important factor).

In addition to the tertiary phosphine complexes, a few others such as $\text{Pt}(\text{QBu}_3)_4$ ($\text{Q} = \text{As}, \text{Sb}$) and $\text{Pt}(\text{QPh}_3)_4$ have been made, but they have been the subjects of few studies.

Compounds $\text{M}(\text{PPh}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) have been postulated as kinetic intermediates but controversy has surrounded their isolation. It seems some ' $\text{M}(\text{PPh}_3)_2$ ' species reported could have been $\text{M}(\text{PPh}_3)_2\text{L}$ (L , e.g. H_2 ,

Table 3.9 Values for d-s and s-p separations (eV)

	$d^{10}-d^9_s$	$d^9_s-d^9_p$	$d^{10}-d^9_p^1$
Ni	-1.8	3.52	1.72
Pd	0.81	3.42	4.23
Pt	0.76	4.04	3.28

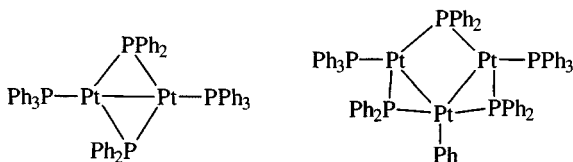
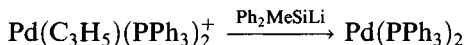


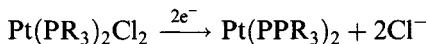
Figure 3.12 Complexes produced by refluxing solutions of $\text{Pt}(\text{PPh}_3)_4$.

N_2 , C_2H_4) or internally metallated species. Reactions such as extended refluxing of $\text{Pt}(\text{PPh}_3)_4$ in benzene yields clusters [49] (Figure 3.12).

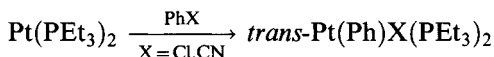
Recently, however, $\text{Pd}(\text{PPh}_3)_2$ has been reported to result from reduction of palladium(II) complexes as a very reactive yellow solid [50]:



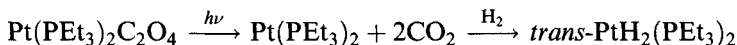
Electrochemical reduction of *cis*- $\text{PtCl}_2(\text{PR}_3)_2$ ($\text{R} = \text{Ph}, \text{Et}$) generates very reactive $\text{Pt}(\text{PR}_3)_2$ species [51] (though it has been suggested that corresponding palladium compounds may be anionic, e.g. $\text{Pd}(\text{PR}_3)_2\text{Cl}_2^{2-}$)



They can be trapped by reactive molecules



UV irradiation of $\text{Pt}(\text{PEt}_3)_2(\text{C}_2\text{O}_4)$ under a dihydrogen atmosphere yields a hydride by trapping [52]:



Thermolysis of *cis*- $\text{PtH}(\text{CH}_2\text{CMe}_3)(\text{cy}_2\text{PCH}_2\text{CH}_2\text{Pcy}_2)$ at $45\text{--}80^\circ\text{C}$ yields a bent platinum(0) complex (Figure 3.13) that is intensely reactive to a whole range of unactivated C–H bonds in saturated and unsaturated hydrocarbons.

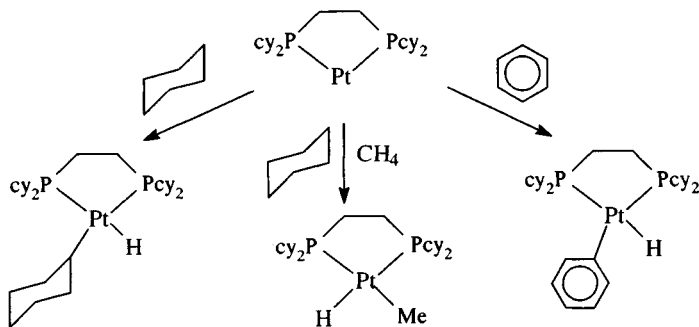


Figure 3.13 Addition reactions of $\text{Pt}(\text{cy}_2\text{PCH}_2\text{CH}_2\text{Pcy}_2)$.

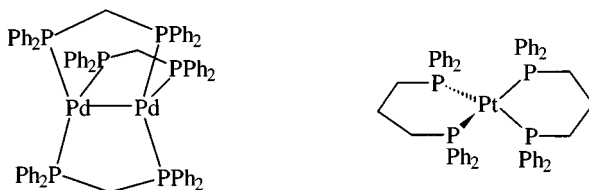
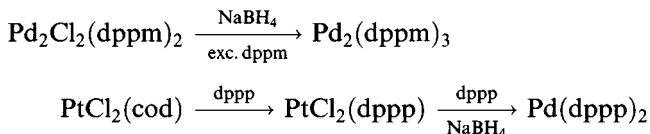


Figure 3.14 Zerovalent complexes of polydentate phosphines.

Zerovalent complexes are also obtained with polydentate phosphines [53]:



Their structures are shown in Figure 3.14.

3.6.2 Reactions of $\text{Pt}(\text{PPh}_3)_n$ and related species

$\text{Pt}(\text{PPh}_3)_n$ ($n = 3, 4$) species [54] have been studied with profit for many years; they undergo a wide range of addition reactions with attendant loss of phosphine, the kinetically active species probably being $\text{Pt}(\text{PPh}_3)_2$. (The palladium analogues generally behave similarly but are much less studied.)

Though many of the products shown in Figure 3.15 are clearly platinum(II) species, some are formally platinum(0).

However, it seems that these are best viewed as platinum(II) species too, so that two-electron metal-to-ligand transfer has been effected. The structures of $\text{Pt}(\text{PPh}_3)_2\text{Z}$ ($\text{Z} = \eta^2\text{-O}_2, \eta^2\text{-C}_3\text{H}_4, \eta^2\text{-CS}_2$) (Figure 3.16) all involve 'square planar' coordination as expected for platinum(II) rather than the tetrahedral 4-coordination anticipated for platinum(0).

Similarly, ESCA data show the platinum $4f_{7/2}$ binding energy in $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ (73.2 eV) to be nearer to that in $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ (73.4 eV) rather than $\text{Pt}(\text{PPh}_3)_4$ (71.7 eV) or platinum metal (71.2 eV) [55]. Like many of the rhodium and iridium dioxygen adducts (section 2.11) adduct formation with O_2 is irreversible (though that with SO_2 is reversed on heating). With unsaturated compounds (alkenes, alkynes, benzene) η^2 -coordination is the rule. Reactions with alkyl and some aryl halides affords a route to mono alkyls and aryls. The reactions with halogens gives a route to *cis*- $\text{Pt}(\text{PPh}_3)_2\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$); if an excess of halogen is used and the reaction stopped after a few minutes (to prevent oxidation to platinum(IV)) the initial *trans*-product is isolated (the halogen oxidizes liberated PPh_3 and prevents it catalysing, as occurs so often with platinum(II), the *trans*-*cis* isomerization). Other reactions can involve coupling (NO) and decoupling (C_2N_2).

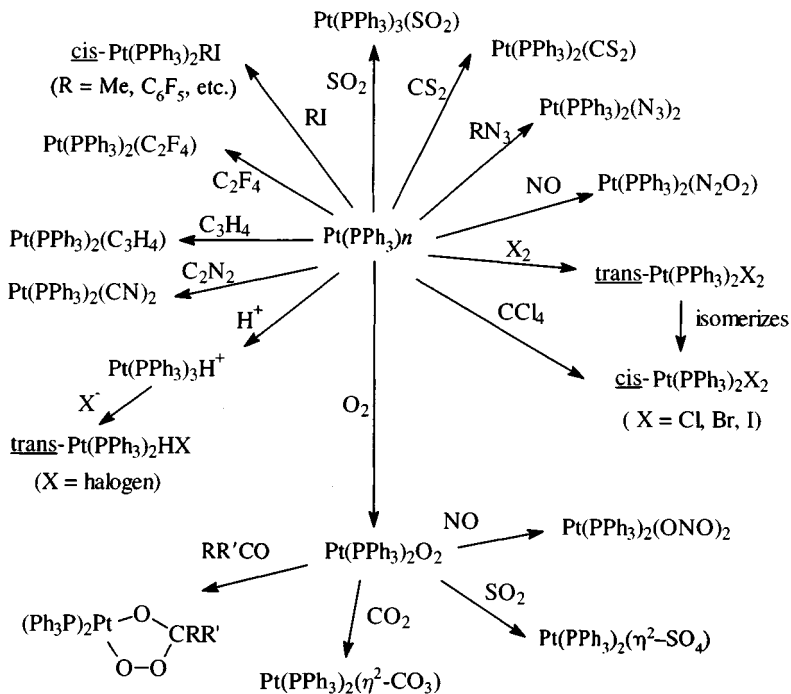


Figure 3.15 Reactions of $[Pt(PPh_3)_n]$.

The O_2 adduct has a rich chemistry of its own (Figure 3.15) reacting with small electrophiles in processes involving oxidation of the substrate. Thus NO couples to give nitrite and N_2O_4 nitrate; SO_2 is turned into sulphate and CO_2 into carbonate. In several cases, as with aldehydes and ketones, a peroxochelate ring results.

Other zerovalent phosphine complexes sometimes exhibit different reactions. $Pt(PPh_3)_3$ does not react with dihydrogen but $Pt(PEt_3)_3$ forms $Pt(PEt_3)_3H_2$. $Pt(PR_3)_3$ ($R = Et, Pr^i$) adds H_2O to form hydroxybases $[Pt(PEt_3)_3H^+OH]^-$ and $[Pt(PPr_3)_2H(solvent)]^+OH^-$. $Pd(Pcy_3)_2$ reacts with the strong acid HBF_4 to give $trans-[Pd(Pcy_3)_2H(H_2O)]^+BF_4^-$ and with carboxylic acids to form $[Pd(Pcy_3)_2H(OCOR)]$; with phenols it gives $[Pd(Pcy_3)_2H(OC_6X_5)]$

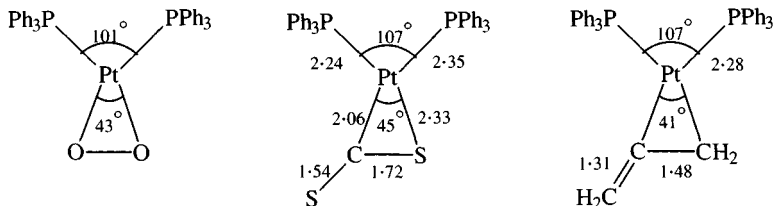


Figure 3.16 Structures of $Pt(PPh_3)_2Z$ ($Z = O_2, CS_2, C_3H_4$).

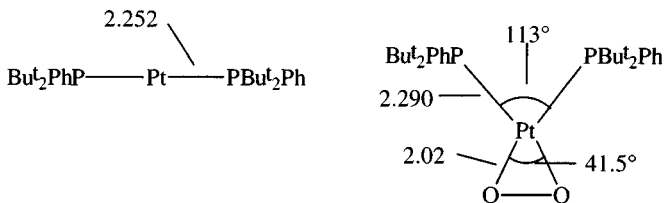


Figure 3.17 A comparison between the geometries of $[\text{Pt}(\text{P}(\text{Bu}_2\text{Ph})_2)_2]$ and $[\text{Pt}(\text{P}(\text{Bu}_2\text{Ph})_2)_2(\text{O}_2)]$.

(X = H, F). The platinum analogue behaves similarly, and it also reacts with H_2 to form *trans*- $\text{Pt}(\text{Pcy}_3)_2\text{H}_2$.

Both $\text{M}(\text{PPh}_2)_2$ compounds (M = Pd, Pt) add O_2 , the former reversibly. They are nearly isostructural, with a slightly longer O-O bond in the platinum compound (1.43 Å) than in the palladium analogue (1.37 Å). Compared with the parent platinum compound (Figure 3.17) the Pt-P bonds are some 0.04 Å longer in the dioxygen compound, but though the P-Pt-P angle has closed from 180° to 113.1°, this is a good deal larger than the value in the PPh_3 analogue (101°) and suggests steric crowding.

The adoption of a planar structure in these adducts, rather than the sterically more favourable tetrahedral one, is in keeping with a platinum(II) oxidation state. The side-on bonding of the O_2 molecule is believed to involve two components, as in Zeise's salt (Figure 3.18).

There is (a) σ -donation from a filled oxygen orbital to an empty platinum orbital and (b) π back-bonding from a filled metal d orbital into an empty oxygen π^* -anti-bonding orbital.

There has been considerable study of reactivity patterns and reaction mechanisms for oxidative additions of $\text{Pt}(\text{PR}_3)_n$ species. Reactivity is determined by (a) steric factors, thus complexes like $\text{Pt}(\text{Pcy}_3)_2$ are very reactive and (b) the basicity of the phosphine. The more basic the phosphine, the more facile is oxidative addition; therefore $\text{Pt}(\text{PEt}_3)_3$ will add PhCl and PhCN while the less nucleophilic $\text{Pt}(\text{PPh}_3)_3$ will not. It is thought that many of these reactions involve initial dissociation of a phosphine, as in the addition of benzyl halides to $\text{Pd}(\text{PPh}_3)_4$, proceeding generally by inversion through a $\text{S}_{\text{N}}2$ mechanism. Either ionic or radical mechanisms are possible. Radical pathways can be detected in three ways:

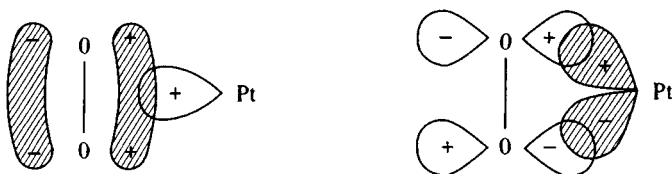
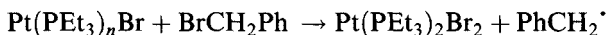
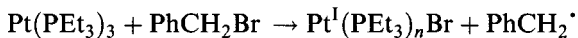


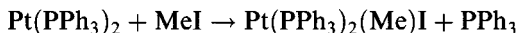
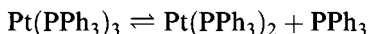
Figure 3.18 Metal-dioxygen bonding in platinum-dioxygen complexes.

1. Addition of radical inhibitors (e.g. duroquinone, galvinoxyl), which will slow up any pathway involving radicals.
2. Adding a radical trap like Bu^tNO to the reaction mixture; this reacts with radicals (R^\cdot) forming nitroxide radicals $\text{Bu}^t(\text{R}^\cdot)\text{NO}$ that can be detected by ESR.
3. Observation of CIDNP effects in the resonances of either reactant or product species in the NMR spectrum of the reaction mixture.

In the case of the reaction of PhCH_2Br with $\text{Pt}(\text{PEt}_3)_3$, it is thought that $\text{Pt}(\text{PEt}_3)_2(\text{PhCH}_2)\text{Br}$ is formed via a $\text{S}_{\text{N}}2$ route where the platinum forms a cationic complex that undergoes immediate attack by Br^- while some $\text{Pt}(\text{PEt}_3)_2\text{Br}_2$ is formed in a very rapid reaction unaffected by radical scavengers.



This is in contrast with the reaction of $\text{Pt}(\text{PEt}_3)_3$ with $\text{Me}_3\text{CCH}_2\text{Br}$, which is affected by radical scavengers like galvinoxyl, where the radicals are sufficiently long lived to undergo side reactions with the solvent – in toluene, some $\text{Pt}(\text{PEt}_3)_2(\text{PhCH}_2)\text{Br}$ is formed – giving credence to a radical chain mechanism. In the reactions of alkyl halides (EtI , MeI , PhCH_2Br) to $\text{Pt}(\text{PPh}_3)_3$, believed to proceed by a non-chain radical process, addition of radical traps results in the formation of ESR-active radicals. This reaction is very solvent dependent; in benzene MeI adds to give solely $\text{Pt}(\text{PPh}_3)_2\text{MeI}$ while in THF $\text{Pt}(\text{PPh}_3)_2\text{I}_2$ is the main product [56]. A detailed study of this reaction in benzene shows that the most important steps are



Undissociated $\text{Pt}(\text{PPh}_3)_3$ is much less reactive.

Addition of RX to a $\text{Pt}(\text{PR}_3)_n$ species may occur by two main pathways:

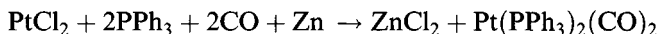
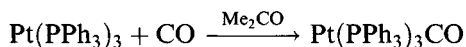
1. $\text{S}_{\text{N}}2$ attack of the electron-rich platinum(0) on the alkyl halide to give the $\text{Pt}^{\text{II}}(\text{R})\text{X}$ species directly, possibly via an ionic intermediate.
2. Platinum removes a halogen atom from the halide, causing homolytic fission of the C–halogen bond. The resulting $\text{Pt}^{\text{I}}\text{–XR}$ radical pair can either react to form $\text{Pt}^{\text{II}}(\text{R})\text{X}$ or separate, with subsequent reaction with RX leading to either PtX_2 or PtRX species or reaction with solvent molecules.

3.6.3 Carbonyl complexes

$\text{Ni}(\text{CO})_4$ is a most important nickel carbonyl compound and can even be prepared directly from its constituents yet the corresponding palladium

and platinum compounds do not exist (at least, at room temperature). If platinum (or palladium) is vaporized from a hot rod (around 1800°C) to produce gaseous platinum atoms, and co-condensed with CO in an argon matrix, IR spectra indicate the presence of metal carbonyl species $M(\text{CO})_x$ ($x = 1-4$). On controlled warming, diffusion takes place with successive CO addition taking place to yield $M(\text{CO})_4$ as the stablest product ($\nu(\text{C}-\text{O})$ 2052, 2070, 2053 cm^{-1} for nickel, palladium and platinum tetracarbonyls, respectively). Analysis of spectra leads to metal-carbon force constants of 1.80, 0.82 and 1.28 mdyn \AA^{-1} for nickel, palladium and platinum tetracarbonyls, respectively. This indicates the weakness of the Pd-C and Pt-C bonds; they decompose if the matrices are warmed above *c.* 80 K [57, 58].

The M-CO bond is stabilized by the presence of tertiary phosphines



Both $\text{Pt}(\text{PPh}_3)_3\text{CO}$ and $\text{Pt}(\text{PPh}_2\text{Et})_2(\text{CO})_2$ have essentially tetrahedral coordination of platinum.

The reason for the greater stability of $M(\text{PR}_3)_n$ over $M(\text{CO})_4$ must lie in the difference in donor characteristics of the two kinds of ligand. CO is a poor σ -donor but a strong π -acceptor, while tertiary phosphines are much better σ -donors.

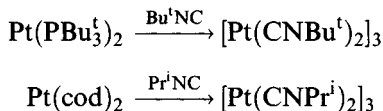
In a binary carbonyl both σ - and π -components are important in the metal-carbon bond: a σ -bond owing to $M \leftarrow C$ donation and a π -bond owing to back-bonding from filled metal d orbitals to empty CO π^* -orbitals. The relative energies of the metal d orbitals are in the order of $4d(\text{Pd}) > 5d(\text{Pt}) > 3d(\text{Ni})$ so that the strength of the σ -component would be in the order of $\text{Pd} < \text{Pt} < \text{Ni}$ (this also correlates with the electronegativities of the metals). The ability of the metal to donate electrons may correlate with the ionization energies; I_1 values are 737 (Ni), 805 (Pd) and 870 (Pt) kJ mol^{-1} , giving a π -bonding order $\text{Pt} < \text{Pd} \ll \text{Ni}$. Therefore, on both grounds the Ni-C bond is predicted to be the strongest.

3.6.4 Carbonyl clusters

Apart from the mixed phosphine/carbonyl species $\text{Pt}(\text{PPh}_3)_{4-n}(\text{CO})_n$ ($n = 1, 2$), there are polynuclear species $\text{Pt}_3\text{L}_n(\text{CO})_3$ ($n = 3, 4$; $\text{L} = \text{PR}_3$), and additionally some remarkable anionic binary carbonyl clusters, formed by reductive carbonylation of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with general formulae $[\text{Pt}_3(\text{CO})_6]_n^{2-}$. These contain $\text{Pt}_3(\text{CO})_3(\mu^2\text{-CO})_3$ clusters stacked along a three-fold axis but with a twist or sliding minimizing repulsions in adjacent layers [59].

3.6.5 Isocyanide complexes

A few isocyanides of palladium and platinum are known in the zerovalent oxidation state. The best characterized compounds involve triangular M_3 clusters with $M-M$ bonds.



The palladium compound $[\text{Pd}(\text{CNcy})_2]_3$ has been made by metal vapour synthesis, from Pd atoms and a solution of cyNC at 160 K. It has an analogous structure $[\text{Pd}_3(\text{CNcy})_3(\mu^2\text{-CNcy})_3]$ [60].

3.7 Palladium(I) and platinum(I) compounds

A limited chemistry of the +1 oxidation state of palladium and platinum has developed since the 1970s, mainly involving metal-metal bonded dinuclear complexes [61].

3.7.1 Phosphine complexes

Phosphine complexes can be synthesized by reduction or reproporationation. Complexes of dppm are the most important and can undergo both substitution reactions and insertions (Figure 3.19).

Using a 2-diphenylphosphinopyridine as the bridging ligand (with a similar 'bite' to dppm) leads to a similar dimer (Figure 3.20).

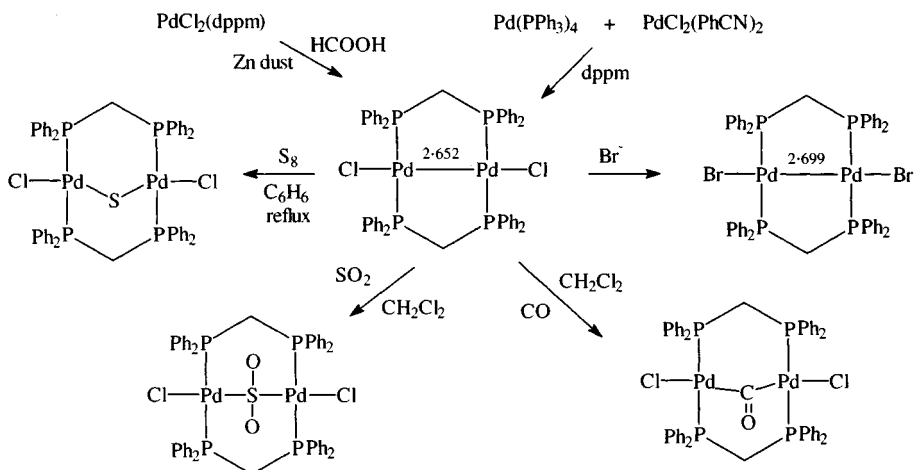


Figure 3.19 Synthesis and reactions of palladium(I) bis(diphenylphosphino)methane complexes.

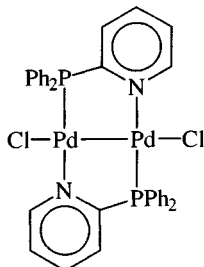


Figure 3.20 A palladium(I) 2-diphenylphosphinopyridine complex.

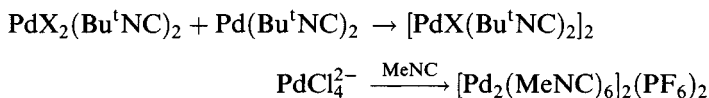
Hydrogen reduction of $(dppp)Pd(CF_3SO_3)_2(dppp)Ph_2P(CH_2)_3PPh_2$ affords $[dpppPd]_2(CF_3SO_3)_2$, which has agonistic Pd–phenyl interactions as well as normal Pd–P coordination and a Pd–Pd bond (2.701 Å) (Figure 3.21).

Several *cis*-platinum(II) dihydrides lose H_2 reversibly in solution, forming dinuclear platinum(I) hydrides $[(diphosphine)PtH]_2$ [62].

Isocyanide complexes can also be made by reproporationation.

3.7.2 Isocyanide complexes

Isocyanide complexes can be synthesized by:



The methylisocyanide complex has a dimeric structure with a direct metal–metal bond (2.531 Å) and only terminal isocyanides, in a staggered configuration (Figure 3.22).

The platinum analogue is similarly made.

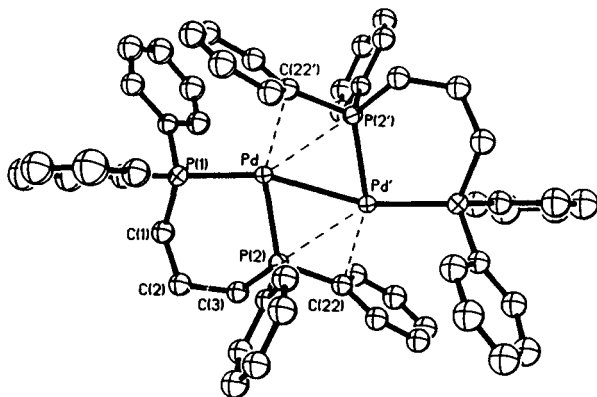


Figure 3.21 Structure of the dimeric palladium(I) complex $[(dppp)Pd]_2(CF_3SO_3)_2$. (Reprinted with permission from *Organometallics*, 1992, **11**, 23. Copyright (1992) American Chemical Society.)

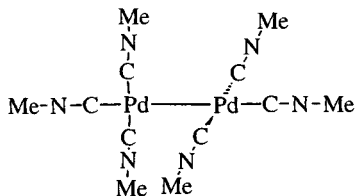


Figure 3.22 The staggered structure of $[\text{Pd}_2(\text{MeNC})_6]^{2+}$.

3.8 Complexes of palladium(II) and platinum(II)

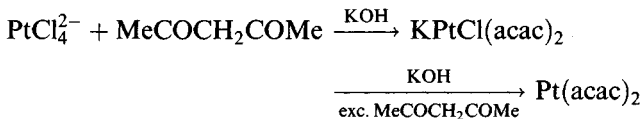
A wide variety of complexes are formed by both metals in the +2 oxidation state; indeed, it is the most important one for palladium. The complexes can be cationic, neutral or anionic. Both Pd^{2+} and Pt^{2+} are 'soft' acids so that many stable complexes are formed with S or P as donor atoms but few with O-donors, though there are important amines. There are pronounced similarities between corresponding palladium and platinum complexes; the latter are more studied (and less labile).

3.8.1 Complexes of O-donors

Complexes of O-donors are relatively rare, explicable by the 'soft' nature of the divalent ions. A telling indication is that sulphoxide ligands will only bind through O if steric effects make S-bonding impractical. The most important complexes are diketonates and carboxylates (for the aqua ions see section 3.5).

Diketonates

Two kinds of platinum diketonate may be made



$\text{Pt}(\text{acac})_2$ has the expected square planar coordination by oxygen ($\text{Pt}-\text{O}$ 1.979–2.008 Å) with bidentate diketonates; this has also been confirmed for $\text{Pd}(\text{PhCOCHCOMe})_2$, which is obtainable as *cis*- and *trans*-isomers that can be crystallized and separated manually (Figure 3.23).

In $[\text{PtCl}(\text{acac})_2]^-$, 4-coordination is possible because one of the diketonates is C-bonded (Figure 3.24).

The diketonates can form Lewis base adducts such as 5-coordinate $\text{Pd}[\text{p-tolyl}]_3(\text{CF}_3\text{COCHCOCF}_3)_2$ (Figure 3.25), though with acetylacetonate square planar adducts of the type $\text{M}(\text{acac})_2(\text{PR}_3)_2$ are usually obtained, where the diketone is monodentate O-bonded [63].