Chemistry of Precious Metals

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BLACKIE ACADEMIC & PROFESSIONAL
An Imprint of Chapman & Hall
London · Weinheim · New York · Tokyo · Melbourne · Madras

Published by Blackie Academic and Professional,
an imprint of Chapman & Hall, 2–6 Boundary Row, London SE1 8HN, UK

Chapman & Hall, 2–6 Boundary Row, London SE1 8HN, UK

Chapman & Hall GmbH, Pappelallee 3, 69469 Weinheim, Germany

Chapman & Hall USA, 115 Fifth Avenue, New York, NY 10003, USA

Chapman & Hall Japan, ITP-Japan, Kyowa Building, 3F, 2-2-1 Hirakawacho,
Chiyoda-ku, Tokyo 102, Japan

DA Book (Aust.) Pty Ltd, 648 Whitehorse Road, Mitcham 3132, Victoria,
Australia

Chapman & Hall India, R. Seshadri, 32 Second Main Road, CIT East, Madras
600 035, India

First edition 1997

Typeset in 10/12pt Times by Academic & Technical Typesetting, Bristol

Printed in Great Britain by T. J. International Ltd.

ISBN 0 7514 0413 6

A catalogue record for this book is available from the British Library

Library of Congress Catalog Card Number: 97–70446

∞ Printed on acid-free text paper, manufactured in accordance with ANSI/NISO Z39.48-1992 (Permanence of Paper).

Preface

Some 20 years ago, I was privileged to share in writing a book on the descriptive chemistry of the 4d, 5d, 4f and 5f metals that included these eight elements within its compass (S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan, 1975). This volume shares the same aim of covering the descriptive chemistry of silver, gold and the six platinum metals in some detail at a level suitable for advanced undergraduate and postgraduate study.

It does not attempt to be a comprehensive treatise on the chemistry of these metals. It attempts to fill a slot between the general text and the in-depth review or monograph. The organometallic chemistry is confined to σ-bonded compounds in normal oxidation states; compounds with π-bonding ligands are generally excluded. Their inclusion would have increased the length of the book considerably and, moreover, their recent chemistry has been extensively and expertly reviewed in the new *Comprehensive Organometallic Chemistry*, *II*, eds G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, Oxford, 1995.

I have concentrated upon providing information on 'essential' binary compounds and complexes of these elements – oxides, halides, aqua complexes, ammines and tertiary phosphine complexes, for example – and highlighting key areas of study rather than giving comprehensive coverage (impossible outside a monograph). It is easy to be seduced by the 'latest thing' in research to the detriment of more fundamental, if prosaic, topics (in any case, there are other texts that provide up to the moment coverage of all research developments). There is still a lot of basic research waiting to be done out there and we have all heard the horror stories of students who can produce *ab initio* MO calculations at the drop of a hat yet think that sodium chloride is a green gas. The data are intended to illustrate trends in the chemistry and not to replace it; theories explain facts and not vice versa. I make no apology for this approach; a sound factual understanding is fundamental to any scientific discipline.

My first priority has, therefore, been to try to provide 'the facts' (and I hope that I have got (most of) them right) but I have tried to write the book with the needs of the teacher in mind, by providing plenty of bond lengths and also spectroscopic data (mainly vibrational, with a little NMR and ESR) that can be used as a teaching tool by hard-pressed lecturers or tutors who have not time to look up the information themselves.

The bibliography is intended to give key references (particularly to structures), not just to the recent literature (which can be hard to find because they are not yet in compilations) but in some cases to relevant older work (which can also be hard to find because everyone assumes that you know them); it begins for each chapter with a listing of the relevant sections of Gmelin and of the various 'Comprehensive Chemistries' and monographs. I have attempted to follow the literature received up to March 1996.

Some readers may feel that I have been unduly optimistic (or just plain presumptuous) in writing this book, when I am not actually carrying out research on any of these metals. They may well be right, though I would point out that the spectator does get a different view of events on the sports fields to that obtained by the player.

Producing a book like this is impossible without access to the primary literature, for which I am mainly indebted to the Chemistry Department of the University of Cambridge, and to Mrs Cheryl Cook in particular.

Much of the background reading, especially for osmium and gold, as well as work on the bibliography was done in the course of visits to l'Abbaye N-D du Bec-Hellouin; it is again a pleasure to give thanks to Dom Philibert Zobel O.S.B., Abbot of Bec, and to the monastic community for the shelter of their roof and a calm and sympathetic environment.

I should like to take the opportunity to thank all those who have supplied information, answered questions or discussed points with me, including the late Sir Geoffrey Wilkinson; Professors S. Ahrland, K.G. Caulton, F.A. Cotton, W.P. Griffith, D.M.P. Mingos, J.D. Woollins and R.K. Pomeroy; and Drs A.J. Blake, P.R. Raithby, S.D. Robinson and P. Thornton. They are not, of course, responsible for the use I have made of the information.

I am particularly grateful to Dr John Burgess for reading the whole manuscript in (a very rough) draft and making many helpful suggestions for improvement, some of which I have been wise enough to adopt. John has also been an invaluable sounding board for ideas. I must also thank three (anonymous) reviewers for drawing my attention to a number of omissions, mistakes and ambiguities, which I hope have now been resolved.

I should finally like to thank Patricia Morrison for her encouragement in the earlier part of the project and Louise Crawford for patient, sympathetic and accurate typing.

Simon Cotton
Uppingham
December 1996

Abbreviations

acac	acetylacetonate, $CH_3COCHCOCH_3$
Ar	aryl
bipy	bipyridyl (usually 2,2′-bipyridyl)
Bu or Bu^n	*n*-butyl, $CH_3CH_2CH_2CH_2$
Bu^t	*t*-butyl, $(CH_3)_3C$
bz	benzyl
cod	cycloocta-1,5-diene
cy	cyclohexyl, cyclo-C_6H_{11}
cyclam	1,4,8,11-tetraazaacyclotetracane
depe	bis(diethylphosphino)ethane
diars	*o*-phenylenebis(dimethylarsine), $C_6H_4(AsMe_2)_2$
dien	diethylenetriamine, $HN[(CH_2)_2NH_2)]_2$
dimphen	2,9-dimethylphenanthroline
dme	1,2-dimethoxyethane, glyme
DMF	*N*,*N*-dimethylformamide
dmg	dimethylglyoximate
dmpe	bis(dimethylphosphino)ethane
DMSO	dimethylsulphoxide, Me_2SO
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2(CH_2)_2Ph_2$
dppm	1,2-bis(diphenylphophino)methane, $Ph_2(CH_2)Ph_2$
dppp	1,2-bis(diphenylphosphino)propane, $Ph_2(CH_2)_3Ph_2$
dppz	bis(diphenylphospino)benzene
EDTA	ethylenediamine tetracetate (4-)
en	1,2-diaminoethane, ethylenediamine
equ	2-ethyl-8-quinolinate
Et	ethyl
Et_4dien	*N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine, $HN[(CH_2)_2NEt_2]_2$
im	imidazole
M-CPBA	*m*-chloroperoxybenzoic acid
Me	methyl
mes	mesityl, 2,4,6-trimethylphenyl
MNTS	*N*-methyl-*N*-nitrosotoluene sulphonamide
ncs	*N*-chlorosuccinamide
np	naphthyl
OEP	octaethylporphyrin
Ph	phenyl
phen	1,10-phenanthroline

PP	2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene
Pr	propyl, $CH_3CH_2CH_2$
Pr^i	isopropyl, $(CH_3)_2CH$
py	pyridine, C_5H_5N
py_2CH_2	dipyridiniomethane, $(C_5H_5N)_2CH_2$
pz	pyrazole
tacn	1,4,7-triazacyclononane, $[9]aneN_3$
terpy	2,2′:6,2″-terpyridyl
thf	tetrahydrofuran
tht	tetrahydrothiophene
TMP	tetramesitylporphyrin
tmpp	tris(2,4,6-trimethoxyphenyl)phosphine
tmu	tetramethylthiourea
TPP	tetraphenylporphyrin
trien	triethylenetetramine, $N[(CH_2)_2NH_2)]_3$
ttcn	1,4,7-trithiacyclononane, $9S_3$
tu	thiourea, $(H_2N)_2CS$
$9S_3$	1,4,7-trithiacyclononane
$10S_3$	1,4,7-trithiacyclodecane
$14[ane]N_4$	1,4,8,11-tetraazaacyclotetracane, cyclam
$14S_4$	1,4,8,11-tetrathiacyclotetradecane
$18S_6$	1,4,8,11,14,17-hexathiacyclooctadecane

All bond lengths given in ångström units (1 Å = 0.1nm)

Contents

1 Ruthenium and osmium

1.1 Introduction

Ruthenium and osmium are the first pair of 'platinum metals' [1–13]. They exhibit oxidation states up to +8, the highest observed for any element, as in MO_4 (M = Ru, Os) though this requires the use of the most electronegative elements, fluorine and oxygen, for stability. Generally, the +2 and +3 states are the most important, along with +4 for osmium; however, there is a considerable chemistry of the MO_2^{2+} ('osmyl' and 'ruthenyl') and $M{\equiv}N^{3+}$groups, as well as the 'classical' hydride complexes $OsH_6(PR_3)_2$, which also involve osmium(VI).

1.2 The elements and uses

Along with iridium, osmium was discovered in 1803 by Smithson Tennant. He took the insoluble residue from the digestion of platinum ores with aqua regia and heated it with sodium carbonate to give soluble yellow $OsO_4(OH)_2^{2-}$. On acidification, distillable OsO_4 formed. Noting the smell of the (very toxic) tetroxide, Tennant gave the element its name from the Greek *osme* (*οσμη* = smell); he also noted that it stained the skin, prefiguring a future use.

The last of the metals described in this book to be discovered was ruthenium. As with osmium, it was extracted from the aqua regia-insoluble residue from concentrated platinum ores and was first claimed in 1826 by G.W. Osann but definitely characterized by K.K. Klaus (1844), who oxidized the residue with KOH/KNO_3, acidified and distilled off the OsO_4 then reacted the residue with NH_4Cl. (Aqua regia is a 3 : 1 mixture of concentrated HCl/HNO_3 (containing some chlorine).) Thermal decomposition of the resulting $(NH_4)_2RuCl_6$ in an inert atmosphere gave ruthenium, taking its name from *ruthenia*, the Latin name for Russia.

Both of these elements are silver–white lustrous metals with high melting (ruthenium 2310°C, osmium 3900°C) and boiling (3900 and 5510°C, respectively) points. As usual, the 5d metal is much more dense (ruthenium 12.45, osmium 22.59 $g\,cm^{-3}$); both adopt hcp structures; osmium is the densest metal known. The metals are unreactive, insoluble in all acids, even aqua regia. Ruthenium tends to form a protective coating of the dioxide and is not attacked by oxygen below 600°C nor by chlorine or fluorine below

300°C. Powdered osmium is slowly attacked by oxygen at room temperature, yielding OsO_4 (though not below 400°C if in bulk). Osmium reacts with fluorine and chlorine at about 100°C. Both metals are attacked by molten alkalis and oxidizing fluxes.

Ruthenium nowadays finds many uses in the electronics industry, particularly for making resistor tracks. It is used as an ingredient in various catalysts and, importantly, in electrode materials, e.g. RuO_2-coated titanium elements in the chloralkali industry. Osmium tetroxide is a very useful organic oxidant and, classically, is used as a tissue stain. Both elements are employed in making certain platinum alloys.

1.2.1 Extraction

Extraction of ruthenium and osmium is done by solvent extraction [1, 2, 5, 14]. Following the traditional route, however, aqua regia-insoluble residues or anode slimes from nickel refining undergo bisulphate oxidation to remove rhodium, then on alkaline fusion ruthenium and osmium are stabilized as Na_2RuO_4 and $Na_2OsO_2(OH)_4$. The ruthenium(VI) can be reduced (alcohol) to RuO_2, which is then converted into $(NH_4)_3RuCl_6$, giving ruthenium metal in a flow of hydrogen at 100°C. Osmium can be precipitated and stored as $K_2OsO_2(OH)_4$ or first converted into OsO_4 (by distillation of the osmate with HNO_3) which is then reduced with hydrogen or turned into $(NH_4)_2OsCl_6$, reduced in the same manner as the ruthenium analogue.

In the solvent-extraction process, the platinum metal concentrate is solubilized in acid using chlorine oxidant. Ruthenium and osmium are separated by turning them into the volatile tetroxides.

1.3 Halides

1.3.1 Ruthenium halides

Ruthenium forms the whole range of trihalides but only fluorides in higher states.

RuF_3 can be made by iodine reduction of RuF_5. It is obtained as a dark brown powder that contains corner-shared RuF_6 octahedra [15]. $RuCl_3$ exists in α- and β-phases:

$$Ru_3(CO)_{12} \xrightarrow[360^\circ C]{Cl_2/N_2} \beta\text{-}RuCl_3 \text{ (brown solid)}$$

$$\beta\text{-}RuCl_3 \xrightarrow[360^\circ C]{Cl_2} \alpha\text{-}RuCl_3 \text{ (black crystals)}$$

The α-form has the α-$TiCl_3$ structure with 6-coordinate ruthenium and a rather long Ru–Ru distance (3.46 Å) compared with the β-form where there are one-dimensional chains, again with octahedrally coordinated ruthenium (Ru–Ru 2.83 Å). The β-form transforms irreversibly to the α-form above 450°C. Both these forms are insoluble in water though β-$RuCl_3$ dissolves in ethanol [16].

Commercial 'ruthenium trichloride' purporting to be $RuCl_3.xH_2O$ is an ill-defined mixture of oxochloro and hydroxychloro species of more than one oxidation state. Obtained by dissolving RuO_4 in hydrochloric acid, it can be purified by repeatedly evaporating to dryness with concentrated HCl. $RuBr_3$ is usually made by brominating the metal while several routes to RuI_3 are open

$$Ru \xrightarrow[450°C,\,20\,atm]{Br_2} RuBr_3$$

$$RuO_4 \xrightarrow{HI\,(aq.)} RuI_3$$

$$Ru(NH_3)_5I_3 \xrightarrow{heat} RuI_3$$

Black–brown $RuBr_3$ has roughly octahedral coordination of ruthenium (Ru–Br 2.46–2.54 Å) with short Ru–Ru contacts (2.73 Å) [17]. Black RuI_3 has a similar structure. Neither is particularly soluble in water.

RuF_4 can be made as a deep pink solid:

$$K_2RuF_6 \xrightarrow{AsF_5/HF} RuF_4$$

It has a VF_4 type puckered sheet structure with 6-coordinated ruthenium; four fluorines bridge, two non-bridging ones are *trans* with the terminal distances shorter as expected (Table 1.1). It is paramagnetic ($\mu_{eff} = 3.04\,\mu_B$ at room temperature).

Green RuF_5, sublimeable *in vacuo* (65°C, 10^{-8} torr (1.33×10^{-6} Pa)) can be made by fluorination

$$Ru \xrightarrow{F_2} RuF_5$$

$$Ru \xrightarrow{BrF_3} BrF_2^+RuF_6^- \xrightarrow{120°C} BrF_3 + RuF_5$$

It melts at 86.5°C and boils at 227°C. The tetrameric structure (Figure 1.1) is one adopted by a number of pentafluorides with *cis*-bridges completing the 6-coordination.

Table 1.1 Bond lengths (Å) in ruthenium fluorides

	Ru–F (terminal)	Ru–F (bridge)
RuF_3	–	1.982
RuF_4	1.82	2.00
RuF_5	1.795–1.824	1.995–2.007
RuF_6	1.824	–

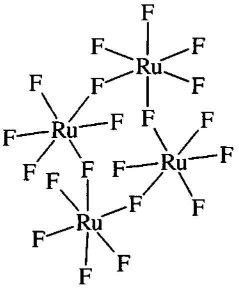

Figure 1.1 The tetrameric structure of RuF_5.

A second, red form has recently been reported; from mass spectral evidence, it may be a trimer. In the gas phase at 120°C, it consists mainly of a trimer (with octahedrally coordinated Ru) [18].

RuF_6 is made by fluorination of RuF_5 under forcing conditions:

$$RuF_5 \xrightarrow[50\,\text{atm},\,230^\circ\text{C}]{F_5} RuF_6$$

It is an extremely moisture-sensitive dark brown solid (m.p. 54°C); bond lengths have been obtained from an EXAFS study [19].

There is some evidence that $RuCl_3$ reacts with chlorine in the gas phase above 400°C to form $RuCl_4$ but $RuCl_4$ has not been authenticated as a solid, neither has RuF_8, which is claimed to exist at low temperatures.

1.3.2 Osmium halides

Unlike ruthenium (and other platinum metals) osmium forms chlorides and bromides in a range of oxidation states [11, 12].

There are no convincing reports of halides in oxidation states below III: early reports of OsI and OsI_2 seem to result from oxide contaminations. Neither is there OsF_3, evidence of the greater stability of the +4 state compared with that of ruthenium.

Dark grey $OsCl_3$ has the 6-coordinate α-$RuCl_3$ structure

$$OsCl_4 \xrightarrow[Cl_2,\,100-500\,\text{torr}]{470^\circ\text{C}} OsCl_3$$

Black $OsBr_3$ and OsI_3 ($\mu = 1.8\,\mu_B$) are also prepared by thermal methods

$$OsBr_4 \xrightarrow[\text{sealed tube}]{300-400^\circ\text{C}} OsBr_3$$

$$(H_3O)_2OsI_6 \xrightarrow[N_2/\text{sealed tube}]{250^\circ\text{C}} OsI_3$$

There is evidence for $OsX_{3.5}$ (X = Cl, Br).

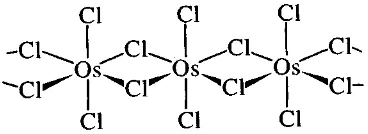

Figure 1.2 The structure adopted by $OsCl_4$.

OsF_4, a yellow–brown solid that distills as a viscous liquid, is made by reduction of solutions of OsF_5

$$OsF_5 \xrightarrow[UV]{H_2/Pt\ gauze} OsF_4$$

It is isomorphous with MF_4 (M = Pd, Pt, Ir, Rh).

Black $OsCl_4$ exists in two forms. A high-temperature form is made by reaction of the elements

$$Os \xrightarrow[700°C]{Cl_2} OsCl_4$$

It has 6-coordinate osmium in a structure (Figure 1.2) regarded as being made from a hexagonally packed array of chlorides with osmiums occupying half the holes in alternate layers; Os–Cl bond lengths are 2.261 Å (terminal) and 2.378 Å (bridge) [20].

The low-temperature form is made using thionyl chloride as the chlorinating agent.

$$OsO_4 \xrightarrow[reflux]{SOCl_2} OsCl_4$$

Black $OsBr_4$ (PtX_4 structure) has 6-coordinate osmium [21]

$$OsCl_4 \xrightarrow[330°C/120\,atm]{Br_2} OsBr_4$$

$$Os \xrightarrow[10\,atm,\ 470°C]{Br_2} OsBr_4$$

A second form can be made by refluxing OsO_4 with ethanolic HBr, then drying the product.

The green–blue pentafluoride (m.p. 70°C, b.p. 226°C) is thermochromic, becoming bright blue at its boiling point (the vapour is colourless). It is synthesized by reducing OsF_6: it has the tetrameric structure adopted by RuF_5 (Os–F = 1.84 Å (terminal) 2.03 Å (bridge)) in the solid state [18c].

$$OsF_6 \xrightarrow[55°C]{I_2/IF_5} OsF_5$$

Like RuF_5, it is mainly a trimer $(OsF_5)_3$ in the gas phase.

In contrast to this, very moisture-sensitive black $OsCl_5$, prepared by chlorinating OsF_6 using BCl_3 as the chlorinating agent, has the dimeric

$ReCl_5$ structure (Os–Cl = 2.24 Å (terminal) 2.42 Å (bridge)). Its magnetic moment is 2.54 μ_B

$$OsF_6 \xrightarrow[RT]{BCl_3} OsCl_5$$

Like several other heavy metals, osmium forms a volatile (bright yellow) hexafluoride (m.p. 33.2°C, b.p. 47°C)

$$Os + 3F_2 \xrightarrow[1\,atm]{250-300^\circ C} OsF_6$$

The solid is polymorphic, with a cubic structure above 1.4°C. A bond length of 1.816 Å has been obtained from EXAFS measurements at 10 K, while vapour phase measurements give Os–F of 1.831 Å [22].

There is uncertainty about the heptafluoride, claimed to be formed as a yellow solid from fluorination under very high pressure

$$Os \xrightarrow[600^\circ C/450\,atm]{F_2} OsF_7$$

Material with the same IR spectrum has been obtained by fluorination of OsO_3F_2 at 180°C (50 atm). OsF_7 is said to decompose at −100°C (1 atm fluorine pressure) [23].

As osmium forms a tetroxide, OsF_8 might possibly exist, especially in view of the existence of the osmium(VIII) oxyfluorides, but MO calculations indicate the Os–F bond would be weaker in the binary fluoride. It is also likely that non-bonding repulsions between eight fluorines would make an octafluoride unstable [23b].

1.3.3 Oxyhalides

Much less is known about ruthenium oxyhalides than about the osmium compounds. The only compound definitely characterized [24] is $RuOF_4$, synthesized by fluorination of RuO_2, condensing the product at −196°C. It loses oxygen slowly at room temperature, rapidly at 70°C.

$$RuO_2 + 2F_2 \xrightarrow{300-400^\circ C} RuOF_4 + \tfrac{1}{2}O_2$$

It has also been made by passing RuF_5 vapour down a hot glass tube:

$$RuF_5 + SiO_2 \longrightarrow RuOF_4 + SiF_4$$

It gives the parent ion in the mass spectrum and has a simple IR spectrum (ν(Ru=O) 1040 cm^{-1} and (ν(Ru–F) 720 cm^{-1}) similar to that of the vapour (1060, 710, 675 cm^{-1}), implying a monomeric structure. Chlorides $RuOCl_2$ and Ru_2OCl_x ($x = 5, 6$) have been claimed; various oxo complexes $Ru_2OX_{10}^{4-}$ are well defined.

Although no OsF_8 has been described, there are oxofluorides in the +8 state.

Table 1.2 Vibrational frequencies[a] for osmium oxyhalides

	State[b]	Vibrational frequencies (cm^{-1})		
		Os=O	Os–F (term)	Os–F (bridge)
cis-OsO_2F_4				
Raman		942, 932	672, 579, 571	
IR		940, 930	675, 588, 570	
OsO_3F_2		954 (947, 942)		
	Matrix	931	646	
$OsOF_5$		960	710, 700, 640	
	Matrix	966.5	713, 638.5	
	Vapour	964	717, 700, 645	
OsO_2F_3		995, 955	720	480–580 (broad)
	Matrix	907	655	
$OsOF_4$		1018	735, 705, 657, 648	529, 423
	Matrix	1079.5	685	
$OsOCl_4$		1028	392 (Os–Cl)	
	Matrix	1032	395	
	Gas	1028	397	

[a] Only IR except for OsO_2F_4; [b] solid unless otherwise stated.

Deep red OsO_2F_4 (m.p. 89°C) has recently been made [25]

$$OsO_4 \xrightarrow[-196^\circ C]{HF/KrF_2} cis\text{-}OsO_2F_4$$

It is thermally stable but instantly hydrolysed in air (like osmium oxyhalides in general); it has a simple vibrational spectrum (ν(Os=O) 940 cm^{-1}; ν(Os–F) 680, 590, 570 cm^{-1}) (Table 1.2) and a *cis*-octahedral structure has been confirmed by an electron diffraction study (Os=O 1.674 Å, Os–F 1.843–1.883 Å).

Several syntheses have been reported for orange–yellow diamagnetic OsO_3F_2 (m.p. 172–173°C) [26]:

$$OsO_4 \xrightarrow[300^\circ C]{F_2} OsO_3F_2$$

$$OsO_4 \xrightarrow[RT]{ClF_3} OsO_3F_2$$

OsO_3F_2 is a monomer in the gas phase, to which a monomeric D_{3h} structure has been assigned. EXAFS and X-ray diffraction measurements show a 6-coordinate solid-state structure with *cis*-fluorine bridges (Figure 1.3) (Os=O 1.678–1.727 Å, Os–F 1.879 Å (terminal), 2.108–2.126 Å (bridge)).

The other possible osmium(VIII) oxyfluoride $OsOF_6$ has so far eluded synthesis and recent *ab initio* MO calculations indicate it is unlikely to exist.

Emerald green $OsOF_5$ (m.p. 59.5°C; b.p. 100.6°C) has an octahedral structure like OsF_6 but is rather less volatile (Os=O 1.74 Å, Os–F 1.72 Å (*trans*) 1.76–1.80 Å (*cis*)) [27]. It is paramagnetic ($\mu_{eff} = 1.47\ \mu_B$ at 298 K) and ESR

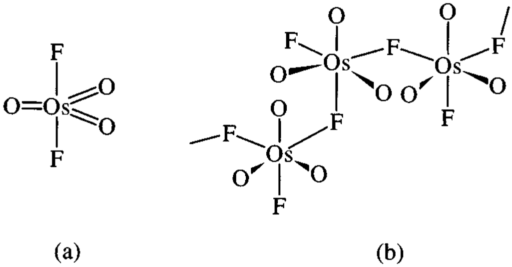

Figure 1.3 The structure of OsO_3F_2 in (a) the gas phase and (b) the solid state.

studies in low-temperature matrices indicate delocalization of the unpaired electron 11.5% from the osmium $5d_{xy}$ orbital to each equational fluorine. Syntheses include

$$OsO_3F_2 \xrightarrow[180°C]{exc.\ F_2} OsOF_5$$

On heating a 3 : 1 OsF_6/OsO_4 mixture at 150–200°C, a mixture of $OsOF_5$ and OsO_4 is obtained that can be separated by using the greater volatility of $OsOF_5$.

OsO_2F_3 is a yellow–green solid, disproportionating at 60°C to OsO_3F_2 and $OsOF_4$, from which it may be made:

$$OsOF_4 + OsO_3F_2 \xrightarrow[12\,h]{100°C} 2OsO_2F_3$$

$$OsO_4 + OsF_6 \xrightarrow[17\,h]{150°C} 2OsO_2F_3$$

Matrix isolation studies suggest isolated D_{3h} molecules, but the pure solid has a more complicated IR spectrum indicating both bridging and terminal fluorines [28].

Blue–green $OsOF_4$ (m.p. 80°C) is a byproduct in the synthesis of $OsOF_5$ and can also be made in small quantities by reduction of $OsOF_5$ on a hot tungsten wire. In the gas phase it has a C_{4v} pyramidal structure (Os=O 1.624 Å, Os–F 1.835 Å); crystallography suggests a solid-state structure similar to tetrameric OsF_5; the more complex IR spectrum of the solid is in keeping with this [29].

Oxychlorides are less prolific, apart from the red–brown $OsOCl_4$ (m.p. 32°C). This probably has a molecular structure in the solid state as the IR spectra of the solid, matrix-isolated and gas-phase molecules are very similar, and the volatility is consonant with this [30]. Syntheses include heating osmium in a stream of oxygen/chlorine ('oxychlorination') and by:

$$OsO_4 \xrightarrow{BCl_3} OsOCl_4$$

Table 1.3 Bond lengths in MX_6^{n-} (Å)

n	RuF_6	$RuCl_6$	$RuBr_6$	OsF_6	$OsCl_6$	$OsBr_6$
0	1.824 (EX)			1.816 (EX) 1.831 (ED)		
1	1.845 (EX) 1.85 (X)			1.882 (EX)	2.284 (X) 2.303 (X)	
2	1.916 (EX)	2.29 (X) 2.318 (X)		1.927 (EX)	2.332 (X) 2.336 (X)	~2.5 (X)
3		2.375 (X)	2.514 (X)			

ED, electron diffraction; X, X-ray; EX = EXAFS.

Electron diffraction measurements on the vapour indicate a C_{4v} square pyramidal structure (Os=O 1.663 Å, Os–Cl 2.258 Å; O–Os–Cl 108.3° Cl–Os–Cl 84.4°) with osmium 0.709 Å above the basal plane.

$OsOCl_2$ can be made as dark olive green needles from heating $OsCl_4$ in oxygen [31]. There are also reports of $OsO_{0.5}Cl_3$ (probably Os_2OCl_6) and a corresponding bromide [32].

1.3.4 Halide complexes

The complexes of ruthenium and osmium in the same oxidation state are generally similar and are, therefore, treated together; the structural (Table 1.3) and vibrational data (Table 1.4) have been set out in some detail to demonstrate halogen-dependent trends.

No complexes have at present been authenticated in oxidation states greater than +6, whereas oxyhalide complexes exist where the +8 state is known; this parallels trends in the halides and oxyhalides.

Oxidation state +6

Reaction of NOF with OsF_6 produces $NO^+OsF_7^-$, along with some $NO^+OsF_6^-$.

Table 1.4 Vibrational frequencies in MX_6^{n-} species (cm^{-1}) (M = Ru, Os; X = halogen)

n	RuF_6	$RuCl_6$	$RuBr_6$	RuI_6	OsF_6	$OsCl_6$	$OsBr_6$	OsI_6
0	675, 735				731, 720			
1	660, 630				688, 616 (XeF_5^+)	375, 325 (Et_4N)		
2	609, 581	328, 327 (Cs)	209, 248 (K)		608, 547 (Cs)	344, 313 (Cs)	211, 227 (K)	152, 170 (Bu_4N)
3		–, 310 (K)	184, 236 ($PhNH_3^+$)			313, 294 ($Co(en)_3$)	201, 200 ($Co(en)_3$)	144, 140 ($Co(en)_3$)

The first figure given for each species is ν_1 (A_{1g}), the second is ν_3 ($T_{1\mu}$).
Data are for ions in solution except where a counter-ion is indicated.

Oxidation state +5

Fluorination of a mixture of alkali metal halide and an appropriate ruthenium or osmium halide affords cream $MRuF_6$ (M = alkali metal, Ag; $\mu_{eff} = 3.5–3.8\,\mu_B$) or white $MOsF_6$:

$$RuCl_3 \text{ or } OsF_4 \xrightarrow[BrF_3 \text{ or } F_2]{MCl} MRuF_6 \text{ or } MOsF_6$$

They contain octahedral MF_6^- (Table 1.3) [33]; in $XeF^+RuF_6^-$ the attraction of XeF^+ distorts the octahedron by pulling one fluorine towards it, so that there is one long Ru–F distance of 1.919 Å compared with the others of 1.778–1.835 Å (EXAFS measurements indicate $KRuF_6$ has regular octahedral coordination (Ru–F 1.845 Å)) [19].

Magnetic moments are as expected for d^3 ions. Disproportionation occurs on hydrolysis:

$$MF_6^- \xrightarrow{H_2O} MO_4 + MF_6^{2-}$$

Octahedral $OsCl_6^-$ has been isolated as Ph_4As, Ph_4P and Ph_4N salts (μ_{eff} values of 3.21 and 3.03 μ_B have been reported) [34]:

$$OsCl_5 + Ph_4AsCl \xrightarrow{CCl_3CF_3} Ph_4AsOsCl_6$$

$$Os(CO)_2X_4^- \xrightarrow[120°C]{Cl_2} Et_4NOsCl_6 \qquad (X = Br, I)$$

$OsCl_6^-$ is reduced to $OsCl_6^{2-}$ in contact with most solvents (e.g. CH_2Cl_2); the redox potential for $OsCl_6^-/OsCl_6^{2-}$ is 0.8 V and for $OsBr_6^-/OsBr_6^{2-}$ it is 1.20 V. PbO_2 can be used to form a transient $OsBr_6^-$ ion by oxidizing $OsBr_6^{2-}$; it will also oxidize $OsCl_6^{2-}$ to $OsCl_6^-$.

Cation size can affect bond lengths in $OsCl_6^-$; Os–Cl is 2.284 Å and 2.303 Å in the Ph_4P and Bu_4N salts, respectively. Oxidation, however, has a more significant effect, so that Os–Cl in $(Ph_4P)_2OsCl_6$ is 2.332 Å.

Oxidation state +4

All MX_6^{2-} have been isolated except RuI_6^{2-}. MF_6^{2-} can be made by hydrolysis of MF_6^-, as already mentioned, but other methods are available:

$$RuCl_3 + BaCl_2 \xrightarrow{F_2} BaRuF_6$$

Yellow Na_2RuF_6 has the Na_2SiF_6 structure while M_2RuF_6 adopts the K_2GeF_6 structure (M = K to Cs). EXAFS indicates Ru–F is 1.934 Å in K_2RuF_6 while in K_2OsF_6 Os–F is 1.927 Å [35]. Magnetic moments are as expected for a low spin d^4 ion (K_2RuF_6 2.86 μ_B, Cs_2RuF_6 2.98 μ_B, K_2OsF_6 1.30 μ_B, Cs_2OsF_6 1.50 μ_B); the lower values for the osmium compounds are a consequence of the stronger spin-orbit coupling for the 5d metal.

Various routes are available for the chlorides [36]:

$$\text{Ru or Os} \xrightarrow[\text{MCl}]{\text{Cl}_2} \text{M}_2\text{RuCl}_6 \text{ or } \text{M}_2\text{OsCl}_6$$

$$\text{M}_2\text{RuCl}_5(\text{OH}_2) \xrightarrow[\text{HCl (aq.)}]{\text{Cl}_2} \text{M}_2\text{RuCl}_6$$

$$\text{OsO}_4 \xrightarrow[\text{EtOH}]{\text{conc. HCl/MCl}} \text{M}_2\text{OsCl}_6$$

The last synthesis uses ethanol as the reducing agent. Soluble Na_2OsCl_6 has been used to make the less soluble salts of other alkali metals by metathesis.

Typical colours are red–brown to black (Ru) and orange to dark red (Os). K_2RuCl_6 has the K_2PtCl_6 structure. Magnetic moments for the ruthenium compounds are 2.7–3.0 μ_B; the osmium compounds have substantially lower moments (1.51 μ_B for K_2OsCl_6) but on doping into K_2PtCl_6 the moment of $OsCl_6^{2-}$ rises to 2.1 μ_B, 'superexchange' causing a lowered value in the undiluted salts.

Bromides and iodides can be made (except X = I for Ru).

$$\text{RuBr}_5(\text{H}_2\text{O})^{2-} \xrightarrow[\text{Br}_2]{\text{HBr(aq.)}} \text{RuBr}_6^{2-}$$

$$\text{K}_2\text{RuCl}_6 \xrightarrow{\text{Br}_2} \text{K}_2\text{RuBr}_6$$

$$\text{OsO}_4 \xrightarrow[\text{M}^+]{\text{HBr(aq.)}} \text{M}_2\text{OsBr}_6 \qquad (\text{M} = \text{alkali metal})$$

$$\text{OsO}_4 \xrightarrow[\text{M}^+]{\text{HI(aq.)}} \text{M}_2\text{OsI}_6$$

These compounds tend to be black in colour. Magnetic moments of 2.84 and 1.65 μ_B have been reported for K_2RuBr_6 and K_2OsI_6, respectively.

$OsCl_6^{2-}$ is a useful starting material for the synthesis of a range of osmium complexes (Figure 1.4).

The mixed halide species $OsX_{6-n}Y_n^{2-}$ or $OsX_aY_bZ_c^{2-}$ $(a + b + c = 6)$ have been studied in considerable detail [37].

Reaction of $OsCl_6^{2-}$ with BrF_3 affords stepwise substitution

$$\text{OsCl}_6^{2-} \rightarrow \text{OsCl}_5\text{F}^{2-} \rightarrow cis\text{-OsCl}_4\text{F}_2^{2-} \rightarrow fac\text{-OsCl}_3\text{F}_3^{2-} \rightarrow$$

$$cis\text{-OsCl}_2\text{F}_4^{2-} \rightarrow \text{OsClF}_5^{2-} \rightarrow \text{OsF}_6^{2-}$$

with the stronger *trans*-effect of chloride directing the position of substitution. This can likewise be utilized to synthesize the *trans*- and *mer*-isomers, for example

$$cis\text{-OsCl}_2\text{F}_4^{2-} \xrightarrow{\text{Cl}^-} mer\text{-OsCl}_3\text{F}_3^{2-}$$

The isomer(s) obtained depend on the reaction time; thus reaction of K_2OsCl_6 with BrF_3 at 20°C affords 90% cis-$OsF_4Cl_2^{2-}$ after 20 min whereas

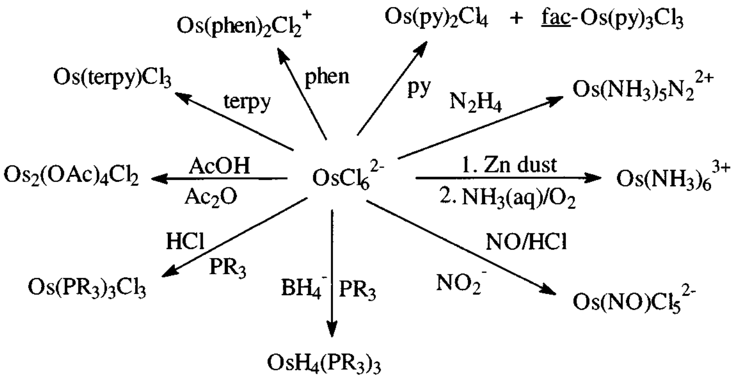

Figure 1.4 Reactions of $OsCl_6^{2-}$.

after 10 h the mixture contains 30% *cis*-$OsF_4Cl_2^{2-}$, 40% OsF_5Cl^{2-} and 30% OsF_6^{2-}. Mixtures can be separated by chromatography or ionophoresis; within this series, the *cis*-isomers are eluted before the *trans* (on diethylaminoethyl cellulose) whereas in ionophoresis, the *trans*-isomers move 3–5% faster.

Such octahedral anions are, of course, amenable to study by vibrational spectroscopy; as the anion symmetry descends from $O_h(MX_6^{2-})$, the number of bands increases as the degeneracy of vibrations is removed. Pairs of isomers can be distinguished; thus for $OsF_2Cl_4^{2-}$, the more symmetric *trans*-isomer (D_{4h}) gives rise to fewer stretching vibrations (5) than the *cis*-isomer (C_{2v}), which has 6. Moreover the centre of symmetry in the *trans*-isomer means there are no IR/Raman coincidences. The Os–F vibrations can be associated with bands in the 490–560 cm^{-1} region and Os–Cl stretching vibrations in the 300–360 cm^{-1} region (Figure 1.5).

Other series of mixed hexahalide complexes have been made. Thus from K_2OsI_6 and concentrated HBr:

$$OsI_6^{2-} \rightarrow OsBrI_5^{2-} \rightarrow cis\text{-}OsBr_2I_4^{2-} \rightarrow fac\text{-}OsBr_3I_3^{2-} \rightarrow$$

$$cis\text{-}OsBr_4I_2^{2-} \rightarrow OsBr_5I^{2-} \rightarrow OsBr_6^{2-}$$

As before the *trans*-isomers can be obtained using $OsBr_6^{2-}$ and concentrated HI; similarly, starting from $OsCl_6^{2-}$ and concentrated HI, the sequence $OsCl_5I^{2-}$, *trans*-$OsCl_4I_2^{2-}$, *mer*-$OsCl_3I_3^{2-}$, *trans*-$OsCl_2I_4^{2-}$, $OsClI_5^{2-}$ and OsI_6^{2-} is obtained. A more drastic synthesis of this type has been achieved by taking mixed crystals K_2OsBr_6/K_2SnCl_6 and using the nuclear process $^{190}Os(n, \gamma)^{191}Os$, when all the mixed species $^{191}OsCl_nBr_{6-n}^{2-}$ were obtained.

Mixed species with three different halogens have been made

$$OsF_5Cl^{2-} \xrightarrow[50°C,\,30\,min]{conc.\ HBr} trans\text{-}OsF_4ClBr^{2-}$$

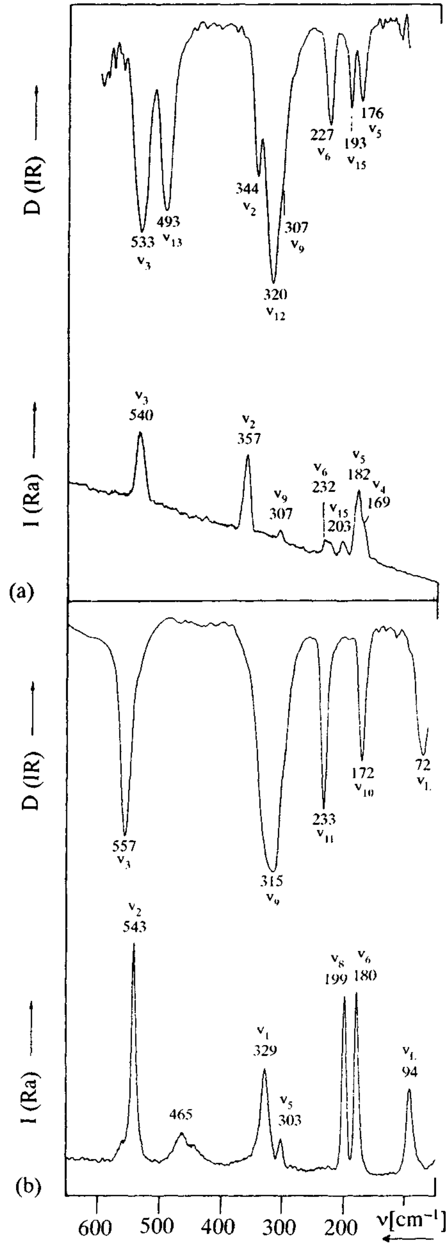

Figure 1.5 The vibrational spectra of the *cis* (a) and *trans* (b) isomers of $[OsCl_2F_4]^{2-}$ in their caesium salts. (Reproduced with permission from *Z. Naturforsch.*, Teil B, 1984, **39**, 1100.)

Table 1.5 Bond lengths (Å) in dipyridinio methane salts

	OsF_5Cl^{2-}	*fac*-$OsF_3Cl_3^{2-}$	*mer*-$OsF_3Cl_3^{2-}$	*cis*-$OsF_2Cl_4^{2-}$	*trans*-$OsF_2Cl_4^{2-}$
Os–F					
trans to F	1.918		1.944		1.926
trans to Cl	1.959	1.948	1.976	1.948	
Os–Cl					
trans to F	2.329	2.320	2.278	2.316	
trans to Cl			2.307	2.338	2.337

The crystal structure of the caesium salt shows Os–F, Os–Cl and Os–Br bonds of 1.94, 2.43 and 2.49 Å, respectively. The complex exhibits strong IR bands at 552, 320 and 222 cm^{-1}, assigned to Os–F, Os–Cl and Os–Br stretching, respectively (compare ν_3 of OsX_6^{2-} at 547 cm^{-1} (F), 313 cm^{-1} (Cl) and 227 cm^{-1} (Br)) [38].

Bond lengths in the dipyridinio methane salts $[(C_5H_5N)_2CH_2][OsF_5Cl]$, *fac*- and *mer*-$[(C_5H_5N)_2CH_2][OsF_3Cl_3]$ and *cis*- and *trans*-$[(C_5H_5)_2CH_2][OsF_2Cl_4]$ show the mutual *trans*-influence of chlorine and fluorine; thus Os–Cl bonds *trans* to fluorine are shorter than those *trans* to chlorine, while Os–F bonds *trans* to chlorine are longer than those *trans* to fluorine (Table 1.5) [38c].

Oxidation state +3

Halide complex ions of ruthenium and osmium in the +3 state are known for all except OsF_6^{3-} [39]. Syntheses include:

$$RuCl_3 \xrightarrow[\text{fuse}]{KHF_2} K_3RuF_6 \qquad (\mu = 1.25\,\mu_B)$$

$$K_2RuCl_5(H_2O) \xrightarrow{HCl(g)} K_3RuCl_6$$

$$RuX_3 \xrightarrow[\text{conc. } HX/N_2]{[C_6H_5NH_3]^+X^-} (C_6H_5NH_3)_3RuX_6 \qquad (\mu = 2.09\,\mu_B,\ X = Br)$$

A general synthesis for the osmium compounds is

$$OsX_6^{2-} \xrightarrow{\text{conc. } HX/N_2} (Coen_3)^{3+}OsX_6 \qquad (X = Cl, Br, I)$$

Magnetic moments reported for the OsX_6^{3-} salts are 1.70, 1.67 and 1.61 μ_B for $X = Cl$, Br and I, respectively, consonant with the low-spin d^5 configuration.

A number of dinuclear complexes have been synthesized [40]

$$Os_2(OCOMe)_4Cl_2 \xrightarrow[EtOH]{HCl(g)} Os_2Cl_8^{2-}$$

$$Os_2Cl_8^{2-} \xrightarrow[Me_2CO]{NaI} Os_2I_8^{2-}$$

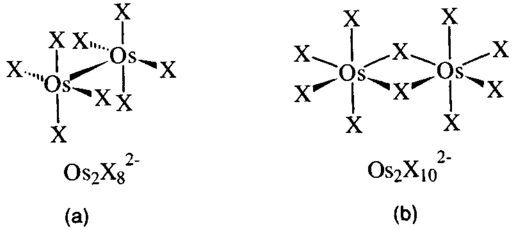

Figure 1.6 The structures of the diosmate ions $Os_2X_8^{2-}$(a) and $Os_2X_{10}^{2-}$(b).

Oxidation with halogens gives the decahalogenodiosmate (IV) (2−) ions (Figure 1.6):

$$Os_2X_8^{2-} \xrightarrow[CH_2Cl_2]{X_2} Os_2X_{10}^{2-} \qquad (X = Cl, Br)$$

The short Os−Os bonds in $Os_2X_8^{2-}$ correspond to triple bonds and give rise to stretching vibrations associated with bands around 280 cm^{-1} in the Raman spectrum (Table 1.6).

The $Os_2X_8^{2-}$ ions participate in various redox processes: at 235 K $Os_2Cl_8^{2-}$ undergoes reversible oxidation to $Os_2Cl_8^{n-}$ ($n = 1, 0$), the bromide behaves similarly. At high temperatures, the Os−Os bond is broken and $OsCl_6^-$ is formed. $Os_2Cl_8^{2-}$ can also be cleaved with Bu^{t}NC to form *trans*-$OsCl_4(CNBu^t)_2^-$ [41].

In addition to the doubly bridged $Os_2X_{10}^{2-}$, triply bridged $Os_2Br_9^-$ can be made (Figure 1.7):

$$OsBr_6^{2-} \xrightarrow[40°C]{CF_3CO_2H} Os_2Br_{10}^{2-} \xrightarrow[110°C]{CF_3CO_2H} Os_2Br_9^-$$

It can be reduced electrochemically to $Os_2Br_9^{n-}$ ($n = 2, 3$), with $Os_2Br_{10}^{n-}$ ($n = 3, 4$) similarly accessible. $Rb_3Os_2Br_9$ has Os−Os 2.799 Å [42].

Table 1.6 Characteristics of $Os_2X_8^{2-}$

	Counter-ion	Os−Os (Å)	ν_{sym} (Os−Os) (cm^{-1})
$Os_2Cl_8^{2-}$	Bu_4N	2.182	285
$Os_2Br_8^{2-}$	Bu_4N	2.196	287
$Os_2I_8^{2-}$	$(Ph_3P)_2N$	2.212	270

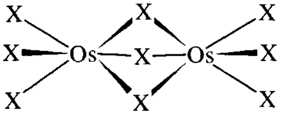

Figure 1.7 The structures of the diosmate ions $Os_2X_9^{3-}$.

In the case of ruthenium, the Ru_2X_9 system with confacial octahedra is important

$$M_2RuCl_5(H_2O) \xrightarrow[in\ vacuo]{250°C} M_3Ru_2Cl_9 \qquad (M = \text{alkali metal})$$

$$RuCl_6^{3-} \xrightarrow{HBr} Ru_2Br_9^{3-}$$

These evidently have some Ru–Ru bonding with Ru–Ru distances of 2.73 and 2.87 Å in $Cs_3Ru_2Cl_9$ and (1-methyl-3-ethylimidazolinium)$_3Ru_2Br_9$, respectively; the magnetic moments of $(Bu_4N)_3Ru_2X_9$ of $0.86\,\mu_B$ (Cl) and $1.18\,\mu_B$ (Br) are lower than expected for low spin d^5 and indicate some metal–metal interaction. $Ru_2X_9^{3-}$ again forms part of a redox-related series $Ru_2X_9^{n-}$ ($n = 1$–4) obtainable in solution by low-temperature electrochemistry [42].

1.3.5 'Ruthenium blues' [43]

It has long been known (Claus, 1846) that reduction (e.g. Zn, H_2 with Pt catalyst) of some ruthenium salts gives a blue solution, which on treatment with HCl or oxidation turns green. Various claims have been made for the species present: $RuCl_4^{2-}$, $Ru_2Cl_3^{2+}$, $Ru_2Cl_4^{+}$ and $Ru_5Cl_{12}^{2-}$. A cluster $(Cl_3Ru(\mu\text{-}Cl)_3Ru(\mu\text{-}Cl)_3RuCl_3)^{4-}$ has been isolated and characterized from such a solution [44]. At present it seems likely that the compound in solution is a cluster, that the ruthenium valency is between 2 and 2.5 and that more than one species is present.

The blue solutions have been found to catalyse alkene isomerization and hydrogenation and have very considerable synthetic utility (Figure 1.8).

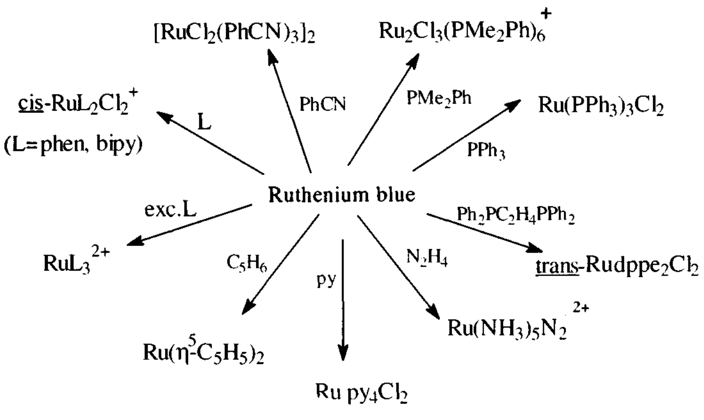

Figure 1.8 Syntheses using 'Ruthenium blue'.

1.3.6 *Oxyhalide complexes*

Various anionic complexes have been made [26a]:

$$OsO_3F_2 + KF \xrightarrow{\text{heat}} K[OsO_3F_3]$$

$$OsO_4 \xrightarrow{\text{CsF(aq.)}} Cs_2[OsO_4F_2]$$

EXAFS measurements on $KOsO_3F_3$ indicate the presence of *fac*-$OsO_3F_3^-$ with Os=O 1.70 Å, Os–F 1.92 Å; in $Cs_2OsO_4F_2$, *cis*-$OsO_4F_2^{2-}$ has Os=O 1.70 Å and Os–F 2.05 Å.

Reaction of Ph_4PCl with OsO_4 gives $Ph_4P^+OsO_4Cl^-$, the anion having a tbp structure with a very long equatorial Os–Cl bond (2.76 Å) [45].

Both ruthenium and osmium form *trans*-$MO_2X_4^{2-}$ species (X = Cl, Br), for example

$$RuO_4 \xrightarrow[\text{HCl}]{\text{MCl}} M_2RuO_2Cl_4 \qquad (M = Rb, Cs)$$

$$K_2[OsO_2(OH)_4] \xrightarrow{\text{HCl}} K_2OsO_2Cl_4$$

Typical bond lengths are M=O 1.709 Å (Ru) 1.750 Å (Os) and M–Cl 2.388–2.394 Å (Ru) 2.379 Å (Os) in $[(Ph_3P)_2N]RuO_2Cl_4$ and $K_2OsO_2Cl_4$, respectively. Characteristic ν(M=O) bands can be seen in the vibrational spectra owing to both the symmetric and asymmetric stretches: for $OsO_2X_4^{2-}$ the symmetric stretch is at 904 (X = Cl) and 900 (X = Br) cm^{-1}, with corresponding values for the asymmetric stretch of 837 and 842 cm^{-1} (in the potassium salts).

In solution $[(Ph_3P)_2N]_2$ RuO_2Cl_4 loses chloride to form $[(Ph_3P)_2N]$ RuO_2Cl_3, which has a tbp structure with two axial chlorines (Ru–Cl 2.37–2.39 Å); the equatorial bond lengths are 1.66–1.69 Å (Ru–O) and 2.13 Å (Ru–Cl) [46].

The dimeric $M_2OCl_{10}^{4-}$ ions contain linear M–O–M units (Figure 1.9); in $Cs_4Os_2OCl_{10}$ the Os–O–Os stretching vibration is at 852 cm^{-1} in the IR spectrum [47] while its crystal structure reveals Os=O 1.778 Å, Os–Cl 2.367–2.377 Å (*cis* to O) and 2.433 Å (*trans* to O). In $K_4Ru_2OCl_{10}$, Ru=O is 1.801 Å, Ru–Cl is 2.363 (*cis*) and 2.317 Å (*trans*). The shortness of the M–O bridge bonds is explained by the formation of two M–O–M three-centre MOs. Figure 1.10 shows the formation of one of these by overlap of

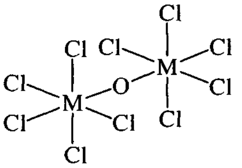

Figure 1.9 The dimeric $[M_2OCl_{10}]^{4-}$ ions (M = Ru, Os).

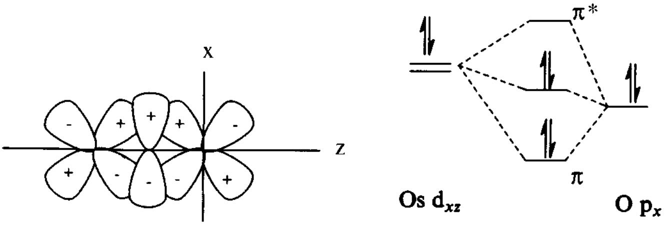

Figure 1.10 The three-centre molecular orbitals in $[Os_2OCl_{10}]^{4-}$.

osmium 5d and oxygen 2p orbitals; each MO contains two osmium electrons and two from the oxygen occupying the bonding and non-bonding MOs. These two MOs account for two of the four electrons belonging to each Os^{4+} ion (d^4); the remaining two occupy the d_{xy} orbital (unused in the MO scheme) explaining the diamagnetism of these M^{IV} compounds.

1.4 Oxides and related anions

The oxides are dominated by the very volatile and toxic tetroxides. Yellow RuO_4 (m.p. 25.4°C, b.p. 40°C) is isomorphous with OsO_4; electron diffraction measurements indicate that it is tetrahedral in the gas phase (Ru–O 1.706 Å) [48a]. It is light sensitive and thermodynamically unstable with respect to RuO_2 (from which, however, it can be made) and can be explosive. Because of the lesser stability of ruthenium(VIII) compared with osmium (VIII), RuO_4 is a stronger oxidizing agent than OsO_4 (and therefore less selective); solutions in CCl_4 are stable [48b]. A convenient synthesis involves periodate oxidation of $RuCl_3$ or RuO_2:

$$RuCl_3 \text{ or } RuO_2 \xrightarrow{NaIO_4} RuO_4$$

RuO_4 reacts with pyridine to form $RuO_3(py)$, probably a dimer $Py_2(O)_2Ru(\mu\text{-}O)_2Ru(O)_2Py_2$, an aerobically assisted oxidant [48c].

RuO_2 can be made by high-temperature oxidation of ruthenium. It has the rutile structure (Ru–O 1.942 Å and 1.984 Å) and forms blue–black crystals [49b].

Recently RuO_3 has been made as a brown solid by photolysis:

$$RuO_4 \xrightarrow[370-440\,\text{nm}]{h\nu} RuO_3$$

In matrices, RuO_2 is bent (149°) while RuO_3 is trigonal planar.

Copper-coloured OsO_2 also has the rutile structure: it can be made from the metal and NO at 650°C.

OsO_4 is obtained on oxidation of any osmium compound or by direct synthesis at 300–800°C from the elements [50]. Its solubility in CCl_4 and volatility make it easy to purify; it forms pale yellow crystals (m.p. 40.46°C, b.p. 131°C). Like RuO_4 it forms tetrahedral molecules with Os–O 1.684–1.710 Å, O–Os–O 106.7–110.7° in the solid state; Os–O 1.711 Å in the gas phase [51]. It is soluble in water as well as in CCl_4 and is very toxic (TLV 2.5 ppm), affecting the eyes. (Its use as a biological stain involves its reaction with tissue.)

Gas-phase vibrational data for OsO_4 are $\nu_1 = 965.2$, $\nu_2 = 333.1$, $\nu_3 = 960.1$ and $\nu_4 = 322.7\,\text{cm}^{-1}$.

Photoelectron spectra have been interpreted with a MO scheme, shown in Figure 1.11 [52].

OsO_4 will add to C=C bonds but will only attack the most reactive aromatic bonds; thus benzene is inert, but it will attack the 9,10 bond in phenanthrene and will convert anthracene to 1,2,3,4-tetrahydroxytetrahydroanthracene. It can be used catalytically in the presence of oxidizing agents such as $NaClO_3$ or H_2O_2 [53].

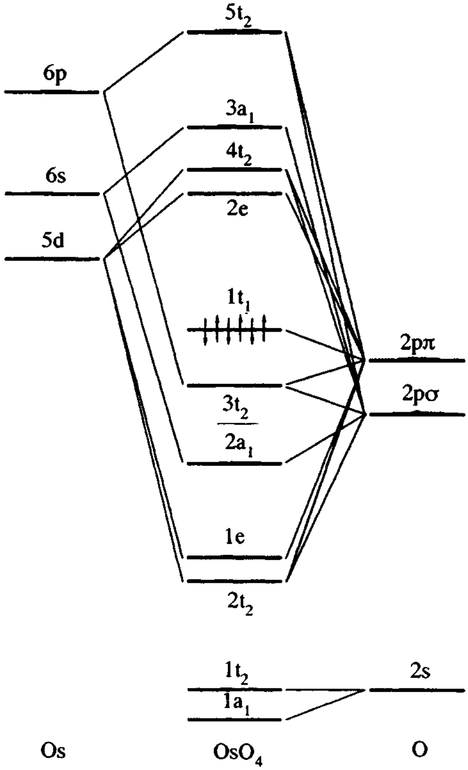

Figure 1.11 A molecular orbital diagram for OsO_4. (Reprinted with permission from *Inorg. Chem.*, 1992, **31**, 1588. Copyright American Chemical Society.)

1.4.1 Anions

Alkalis reduce RuO_4 to RuO_4^-; various salts have been prepared

$$RuCl_3.xH_2O \xrightarrow{NaIO_4} RuO_4 \xrightarrow[K_2CO_3]{Pr_4NOH} Pr_4NRuO_4$$

On heating it decomposes in a similar manner to $KMnO_4$:

$$2KRuO_4 \rightarrow K_2RuO_4 + RuO_2 + O_2$$

The anion in $KRuO_4$ has a slightly flattened tetrahedral structure (Ru–O 1.73 Å). Organic-soluble salts like Pr_4NRuO_4 are selective mild oxidants that will oxidize alcohols to carbonyl compounds but will not affect double bonds [54a]. ESR indicates that RuO_4^- ($g_x = 1.93$; $g_y = 1.98$; $g_z = 2.06$) has a compressed tetrahedral geometry with the electron in d_{z^2} [54b].

RuO_4^{2-}, which is believed to be tetrahedral in solution, is formed from RuO_4 and excess concentrated aqueous KOH, isolable as black crystals of $K_2RuO_4.H_2O$, which is actually $K_2[RuO_3(OH)_2]$. The anion has a tbp structure with axial OH groups (Ru=O 1.741–1.763 Å, Ru–OH 2.028–2.040 Å) [55].

In contrast to ruthenium, osmium exists in alkaline solution as $OsO_4(OH)_2^{2-}$, believed to be *cis* and isolable as crystalline salts:

$$OsO_4 + 2KOH \rightarrow K_2OsO_4(OH)_2$$

Similarly, instead of forming OsO_4^{2-}, reduction of OsO_4 with ethanolic KOH yields $K_2[OsO_2(OH)_4]$.

The osmiamate ion, OsO_3N^-, is isoelectronic with OsO_4. The yellow potassium salt is the most convenient one to prepare; other, less soluble, salts, can be made by metathesis:

$$OsO_4 + NH_3 \xrightarrow{KOH} KOsO_3N$$

The crystallographic study of the potassium salt is complicated by disorder but in $CsOsO_3N$ Os≡N is 1.676 Å and Os=O 1.739–1.741 Å. Assignments of the vibrational spectrum of OsO_3N^- is assisted by isotopic substitution: the higher frequency absorption is shifted significantly on ^{15}N substitution whereas the band just below 900 cm^{-1} is scarcely affected (Table 1.7); conversely the latter band is shifted by some 50 cm^{-1} on replacing ^{16}O by ^{18}O [56].

Nitrido salts are discussed later (section 1.12.2).

Table 1.7 Vibrational data for osmiamate ions (in cm^{-1})

	ν_1 (Os≡N)	ν_2 (Os=O)
OsO_3N^-	1029	898
$OsO_3{}^{15}N^-$	998	896
$K[Os^{18}O_3N]^-$	1024	844

1.5 Other binary compounds

Ruthenium and osmium form no stable binary hydrides, but very recently heating mixtures of the metals with alkaline earth metal hydrides under pressure in a hydrogen atmosphere have been shown to give oxygen- and moisture-sensitive hydrides M_2RuH_6 (M = Mg, Ba), M_2OsH_6 (M = Mg to Ba) and Li_4OsH_6. These contain MH_6^{4-} (K_2PtCl_6 structure) with Ru–D 1.673 and Os–D 1.682 Å in the corresponding deuterides [57]. $LiMg_2RuH_7$ has RuH_6^{2-} with Ru–D 1.704 Å in the deuteride.

The mineral laurite is the mixed sulphide $(Ru,Os)S_2$; this and RuS_2 and OsS_2 have the pyrite structure as does RuQ_2 (Q = Se, Te). These can be made from the reaction of the chalcogen with the metals, while $RuCl_3$ will also react with Se and Te.

MP_2, MAs_2 and MSb_2 all have a compressed form of the marcasite structure, while the carbides MC have trigonal prismatic coordination in the WC structure. Several borides are known: MB_2 has nets of boron atoms. $Ru_{11}B_8$ has branched chains while Ru_7B_3 has isolated borons.

1.6 Aqua ions [58]

Diamagnetic, low-spin d^6 $Ru(H_2O)_6^{2+}$ has been made by reduction of RuO_4 with activated Pb (or Sn) followed by ion-exchange purification. The pink tosylate salt contains octahedral $Ru(H_2O)_6^{2+}$ (Ru–O 2.122 Å); though the solid is air stable, it is readily oxidized in solution by oxygen and ClO_4^-. The hexaqua ions also occur in the red diamagnetic Tutton salts $M_2Ru(H_2O)_6(SO_4)_2$ (M = NH_4, Rb)

$$RuO_4 \xrightarrow[H^+]{Pb/Hg} Ru(H_2O)_6^{2+} \xrightarrow{(NH_4)_2SO_4} (NH_4)_2Ru(H_2O)_6(SO_4)_2$$

Ru $(H_2O)_6(BF_4)_2$ has been isolated but decomposes on standing.

Aerial oxidation of $Ru(H_2O)_6^{2+}$ produces lemon-yellow $Ru(H_2O)_6^{3+}$ (Ru–O 2.029 Å in the tosylate salt)

$$Ru(H_2O)_6^{2+} \rightarrow Ru(H_2O)_6^{3+} + e^- \qquad E^\ominus = -0.205\,V$$

The yellow alum $CsRu(H_2O)_6(SO_4)_2.6H_2O$ has also been synthesized with $\mu_{eff} = 2.20\,\mu_B$ at 300 K; the Ru–O distance is 2.010 Å.

Vibrational spectra of octahedral $Ru(H_2O)_6^{n+}$ ($n = 2$, $\nu_1 = 424\,cm^{-1}$, $\nu_3 = 426\,cm^{-1}$; $n = 3$, $\nu_1 = 532\,cm^{-1}$, $\nu_3 = 529\,cm^{-1}$) have been interpreted in terms of the force constants 1.91 mdyn $Å^{-1}$ ($n = 2$) and 2.98 mdyn $Å^{-1}$ ($n = 3$), showing a stronger bond for the ruthenium(III) species.

The ruthenium(II) aqua ion reacts with nitrogen at room temperature under high pressure (200 bar) forming yellow–brown $[Ru(H_2O)_5N_2]^{2+}$, isolated as a tosylate salt, showing $\nu(N{\equiv}N)$ at 2141 cm^{-1} in its IR spectrum [59].

The ruthenium(IV) aqua ion, best made by electrochemical oxidation of $Ru(H_2O)_6^{2+}$, but also made by the reaction of RuO_4 with $H_2O_2/HClO_4$, is tetranuclear, formulated as $[Ru_4O_6(H_2O)_{12}]^{4+}$, though this may be protonated [60]. FAB mass spectra of a pyrazolylborate complex show Ru_4O_6-containing fragments.

No simple osmium aqua ion has been definitely isolated and characterized, though in alkaline solution (and the solid state) the osmium(VIII) species $OsO_4(OH)_2^{2-}$ is well characterized (sections 1.4.1 and 1.12.1).

Osmium(II) is probably too reducing to exist as $Os(H_2O)_6^{2+}$, but $Os(H_2O)_6^{3+}$ and a polynuclear Os_4^+(aq.) species are likely.

1.7 Compounds of ruthenium(0)

Apart from $Ru(CO)_5$ and other carbonyls, there are mixed carbonyl–phosphine species and a few simple phosphine complexes like $Ru(PF_3)_5$ and $Ru[P(OMe)_3]_5$ [61a].

Photochemistry of $Ru(CO)_3(PMe_3)_2$ and the ruthenium(II) compound $Ru(CO)_2(PMe_3)_2H_2$ in low-temperature matrices affords $[Ru(CO)_2(PMe_3)_2 \cdots S]$ ($S = Ar$, Xe, CH_4) [61b]. These monomers all have 18-electron tbp structures.

The phosphine complex $Ru(dmpe)_2$ has been studied in matrices [62]. $Ru(diphos)_2$ (diphos = depe, dppe, $(C_2F_5)_2P(CH_2)_2P(C_2F_5)_2$) has similarly been formed by photolysis of $Ru(diphos)_2H_2$ in low-temperature matrices. They probably have square planar structures and undergo oxidative addition with cobalt, C_2H_4 and hydrogen [63].

Additionally a number of nitrosyls such as $Ru(NO)_2(PPh_3)_2$ (section 1.8.5) exist.

1.8 Complexes of ruthenium(II and III)

Because of the relationship between compounds in the adjacent oxidation states +2 and +3, they are grouped together here; the section is subdivided by ligand, concentrating on some classes of complex important in their diversity and in current research interest.

1.8.1 Ammine complexes

Orange $Ru(NH_3)_6^{2+}$ can be obtained by various routes (see Figure 1.12).

As expected for the +2 state of a heavy metal, it is reducing:

$$Ru(NH_3)_6^{2+} \rightarrow Ru(NH_3)_6^{3+} + e^- \qquad E^\ominus = +0.214\,V$$

Historically, the most important ruthenium(II) ammine species is $[Ru(NH_3)_5N_2]^{2+}$, the first stable dinitrogen complex to be isolated (1965). It was initially obtained by refluxing $RuCl_3$ in hydrazine solution (but many

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2 Rhodium and iridium

2.1 Introduction

Rhodium and iridium were discovered independently in the same year and also share many resemblances in their chemistry [1–10]. They form a wide range of conventional complexes as well as those of π-bonding ligands. Both metals exhibit an extensive chemistry, principally in the +3 oxidation state, with +1 also being important, and a significant chemistry of iridium +4 existing. Few compounds are known in the +2 state, in contrast to the situation for cobalt, their lighter homologue (factors responsible include the increased stability of the +3 state consequent upon the greater stabilization of the low spin d^6 configuration as 10 Dq increases).

Rhodium was discovered in 1803 by the eminent Norfolk scientist W.H. Wollaston; he dissolved platinum metal concentrates in aqua regia and found that on removing platinum and palladium he was left with a red solution. From this he obtained the salt Na_3RhCl_6, which yielded the metal on reduction with hydrogen. The rose-red colour (Greek rhodon) of many rhodium salts gave the element its name.

In the same year, Smithson Tennant was studying the black aqua regia-insoluble portion of platinum ores and found that, after fusion with soda and extraction with water, the black residue gave a blue solution in hydrochloric acid that went red when heated. The red crystals thus obtained yielded the metal on heating. Tennant gave iridium its name from the Greek iris (rainbow) 'from the striking variety of colours which it gives'.

2.2 The elements and uses

Both rhodium (m.p. 1976°C, b.p. 3730°C) and iridium (m.p. 2410°C, b.p. 4130°C) are unreactive silvery metals, iridium being considerably more dense ($22.65\,g\,cm^{-3}$) than rhodium ($12.41\,g\,cm^{-3}$), the densest element known apart from osmium. Both form fcc (ccp) lattices and, like the other platinum metals, are ductile and malleable. Neither is affected by aqua regia and they only react with oxygen and the halogens at red heat.

The main use of rhodium is with platinum in catalysts for oxidation of automobile exhaust emissions. In the chemical industry, it is used in catalysts for the manufacture of ethanoic acid, in hydroformylation of alkenes and the synthesis of nitric acid from ammonia. Many applications of iridium rely on its inertness (e.g. high temperature crucibles, electrode coatings, thermocouples); it is speculated that applications include defence, nuclear and aerospace industries. The inert alloy with osmium is traditionally used in pen nibs.

2.2.1 Extraction

Rhodium and iridium are obtained from the aqua regia-insoluble residues by first smelting with PbO or $PbCO_3$ then treating the product with nitric acid to remove silver along with the lead [11]. The residue is smelted with $NaHSO_4$ which converts the rhodium into soluble $Rh_2(SO_4)_3$, while peroxide fusion of the residues leaves an insoluble residue of IrO_2. Traditionally these products were purified in several stages involving repeated precipitation and solution, ultimately affording the pure salts $(NH_4)_3MCl_6$ (M = Rh, Ir), which then yielded the metal on hydrogen reduction at 1000°C. A more up to date process uses solvent extraction to give a more efficient and rapid separation.

2.3 Halides and halide complexes [3b, 4]

2.3.1 Rhodium halides

Rhodium halides occur mainly in the +3 state. In some cases where a 'soluble' and 'insoluble' form have been reported, the former may be a hydrate.

RhF_3 [12] can be conveniently made by fluorination

$$RhCl_3 \xrightarrow[500^\circ C]{F_2} RhF_3$$

It has the VF_3 structure (Rh–F 1.961 Å) having a hcp array of fluorines with rhodium occupying 1/3 of the octahedral holes. Various hydrates have been reported

$$Rh(NO_2)_6^{3-} \xrightarrow{\text{conc. HF}} RhF_3.9H_2O$$

Insoluble red $RhCl_3$ is made by direct combination, with similar routes for the other trihalides

$$Rh \xrightarrow[800^\circ C]{Cl_2} RhCl_3$$

$$Rh \xrightarrow[\text{then } Br_2\ 400^\circ C]{45\%\ HBr/Br_2,\ \text{heat}} RhBr_3\ \text{(red)}$$

$$Rh \xrightarrow[400^\circ C]{I_2} RhI_3\ \text{(black)}$$

All of these probably have the $AlCl_3$ structure (unconfirmed for RhI_3) with bond lengths (EXAFS) of 2.337 Å (Rh–Cl) [13] and 2.48 Å (Rh–Br) [14]. 'Soluble' chlorides and bromides are made by dissolving the oxide in the appropriate acid.

Rhodium trihalides (and complexes like K_3RhBr_6) are frequently added to photographic emulsions in trace quantities to improve the gradation of the emulsion (the 'rhodium effect') [15].

Only fluorides are known in higher oxidation states with tetra-, penta- and hexafluorides isolated.

$$RhBr_3 \xrightarrow{BrF_3} RhF_4.2BrF_3 \xrightarrow{heat} RhF_4$$

$$Rh \xrightarrow[400°C,\,6\,atm]{F_2} RhF_5$$

$$RhF_3 \xrightarrow[400°C]{F_2} RhF_5$$

$$RhF_5 \xrightarrow[250°C,\,30\,atm]{F_2} RhF_6$$

Little is known about the structure of purple paramagnetic RhF_4 ($\mu_{eff} = 1.1\,\mu_B$) but it may be similar to PdF_4 [16]. RhF_5 has a tetrameric structure [17] similar to RuF_5 and OsF_5 (section 1.3.4); the terminal Rh–F bonds are 1.808 Å and the bridges 2.01 Å. The ruby red solid (m.p. 95.5°C) has $\mu_{eff} = 2.39\,\mu_B$. Rhodium hexafluoride is a very reactive black solid (attacking glass at room temperature) vaporizing to a deep brown gas (triple point *c.* 70°C). EXAFS measurements indicate a Rh–F bond length of 1.838 Å [18].

Various ill-defined binary halides have been reported but not characterized, such as RhI_2.

2.3.2 *Iridium halides*

The pattern of iridium halides resembles rhodium, with the higher oxidation states only represented by fluorides. The instability of iridium(IV) halides, compared with stable complexes $IrCl_4L_2$ and the ions IrX_6^{2-} (X = Cl, Br, I), though unexpected, finds parallels with other metals, such as plutonium.

Preparations of the halides include [19]

$$IrF_4 \xrightarrow{400°C} IrF_3 \text{ (black)}$$

$$IrF_5 + SF_4 \xrightarrow{400°C} IrF_3 + SF_6$$

$$Ir \xrightarrow[600°C]{Cl_2} \alpha\text{-}IrCl_3 \text{ (brown)} \xrightarrow[vacuum]{750°C} \beta\text{-}IrCl_3 \text{ (deep red)}$$

$$\mathrm{Ir} \xrightarrow[540^\circ\mathrm{C},\, 8-9\,\mathrm{atm}]{\mathrm{Br_2\ (sealed\ tube)}} \mathrm{IrBr_3\ (yellow)}$$

$$\mathrm{Ir(OH)_3} \xrightarrow[2.\ \mathrm{heat},\ 400^\circ\mathrm{C}]{1.\ \mathrm{HI}\ 20^\circ\mathrm{C}} \mathrm{IrI_3\ (black)}$$

$$\mathrm{Ir + 2IrF_6} \xrightarrow{1\ \mathrm{to}\ 15\ \mathrm{torr}} \mathrm{3IrF_4\ (red{-}brown)}\ [20]$$

$$\mathrm{2Ir + 5F_2} \xrightarrow{350-380^\circ\mathrm{C}} \mathrm{2IrF_5\ (yellow{-}green)}$$

$$\mathrm{Ir + 3F_2} \xrightarrow{240^\circ\mathrm{C}} \mathrm{IrF_6\ (yellow)}$$

All the trihalides are known to have 6-coordinate iridium (except the unknown structure of IrI_3). IrF_3 has the PdF_3 structure; α-$IrCl_3$ and $IrBr_3$ have structures of the $AlCl_3$ type (Ir–Cl 2.30–2.39 Å in the former).

IrF_5 (until 1965 thought to be IrF_4) is paramagnetic ($\mu = 1.32\,\mu_B$) and has the same tetrameric structure as RhF_5; it has a slightly higher m.p. (104°C) than IrF_6, in keeping with the larger molecular units [21]. Like RhF_6, IrF_6 is very reactive, attacking most glass and undergoing slow photolysis to IrF_5. IrF_6 has a regular octahedral structure in the vapour (Ir–F 1.83 Å) and in the solid state (Ir–F 1.822 Å, EXAFS). It is paramagnetic with $\mu \sim 3\,\mu_B$; vibrational frequencies of the octahedral molecule have been assigned to bands at 719 cm^{-1} (T_{1u}), 701.7 cm^{-1} (A_{1g}) and 645 cm^{-1} (E_g) [18, 22].

2.3.3 Halometallates

A wide range of MX_6^{n-} species exist, typical preparations appear below.

$$\mathrm{RhF_3} \xrightarrow[550^\circ\mathrm{C}]{\mathrm{KF,\,CsF}} \mathrm{Cs_2KRhF_6\ (pink)}$$

$$\mathrm{RhCl_3.3H_2O} \xrightarrow[3\mathrm{M\ HCl}]{\mathrm{ACl}} \mathrm{A_3RhCl_6.H_2O} \xrightarrow{\mathrm{heat}} \mathrm{A_3RhCl_6\ (red)\ (A = K, Rb, Cs)}$$

$$\mathrm{Rh(OH)_3} \xrightarrow[\mathrm{KBr}]{\mathrm{HBr}} \mathrm{K_3RhBr_6}$$

$$\mathrm{RhF_3} \xrightarrow[\mathrm{NaCl}]{\mathrm{BrF_3}} \mathrm{Na_2RhF_6\ (yellow)}$$

$$\mathrm{RhF_6} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{NOF}} \mathrm{(NO)_2RhF_6\ (yellow)}$$

$$\mathrm{Cs_3RhCl_6} \xrightarrow{\mathrm{Cl_2\ or\ Ce^{4+}}} \mathrm{Cs_2RhCl_6\ (dark\ green)}$$

$$\mathrm{RhF_5} \xrightarrow[\mathrm{HF\ or\ IF_5},\ 20^\circ\mathrm{C}]{\mathrm{MF}} \mathrm{MRhF_6\ (yellow{-}ochre)\ (M = K, Cs)}$$

$$\mathrm{M_2IrF_6} \xrightarrow[\mathrm{MF}]{\mathrm{N_2H_4}} \mathrm{M_3IrF_6\ (M = K, Rb, Cs)}$$

$$\mathrm{Ir} \xrightarrow[\mathrm{KCl}]{\mathrm{Cl_2}} \mathrm{K_2IrCl_6} \xrightarrow[80^\circ\mathrm{C}]{\mathrm{C_2O_4^{2-}}} \mathrm{K_3IrCl_6.H_2O}\ (\text{yellow})$$

$$\mathrm{M_3IrCl_6} \xrightarrow[\mathrm{H_2O}]{\mathrm{HBr}} \mathrm{M_3IrBr_6.H_2O}\ (\text{green})$$

$$\mathrm{Cs_3IrBr_6} \xrightarrow[160^\circ\mathrm{C}]{\mathrm{NaI}} \mathrm{Cs_3IrI_6}\ (\text{brown})$$

$$\mathrm{MIrF_6} \xrightarrow{\mathrm{H_2O}} \mathrm{M_2IrF_6} + \mathrm{IrO_2} + \mathrm{O_2}\ (\mathrm{M} = \text{alkali metal})$$

$$\mathrm{IrO_2}.n\mathrm{H_2O} \xrightarrow[\mathrm{HBr}]{\mathrm{MBr}} \mathrm{M_2IrBr_6}\ (\text{purple})$$

$$\mathrm{IrBr_3} \xrightarrow[\mathrm{BrF_3}]{\mathrm{KBr}} \mathrm{KIrF_6}\ (\text{white})$$

$$\mathrm{IrF_6} \xrightarrow{\mathrm{NOF/F_2}} \mathrm{NO^+IrF_6^-}$$

IrI_6^{2-} does not exist: Ir^{4+} is too strongly oxidizing to coexist with the reducing I^-.

Points to note in these syntheses include the use of BrF_3 as an oxidizing agent, and the stability of IrX_6^{2-}, also used as a source of IrX_6^{3-}.

Structural data [23] (Table 2.1) confirm the presence of the hexahaloanions in these states; M_2RhF_7 (M = Sr, Pb) contain RhX_6^{3-} octahedra too, as do salts like $(MeNH_3)_4RhX_7$ (X = Cl, Br) and $(enH_2)_2RhX_7$.

Many of the compounds in higher oxidation states are reactive, and for moisture-sensitive solids that cannot be crystallized, some of the bond lengths quoted in Table 2.1 are from EXAFS measurements [24]. Raman spectroscopy is likewise well suited to studying such reactive compounds, and vibrational data for halometallates are given in Table 2.2; trends illustrated include the decrease in frequency as the oxidation state of the metal decreases, and similarly a decrease in vibrational frequency, for a given oxidation state, with increasing mass of the halogen.

Table 2.1 Bond lengths in hexahalometallate ions and related species

Rhodium	Rh–X (Å)	Iridium	Ir–X (Å)
RhF_6	1.838	IrF_6	1.822
RhF_6^-	1.855	IrF_6^-	1.910
RhF_6^{2-}	1.934	IrF_6^{2-}	1.928
RhF_6^{3-}	1.969		
$RhCl_6^{2-}$	2.313	$IrCl_6^{2-}$	2.332
$RhCl_6^{3-}$	2.330–2.354	$IrCl_6^{3-}$	2.327–2.387
		$IrBr_6^{2-}$	2.515–2.549
$RhBr_6^{3-}$	2.465–2.485	$IrBr_6^{3-}$	2.486–2.512

Table 2.2 Vibrational fundamentals in MX_6^{n-} species (cm^{-1}) (M = Rh, Ir; X = F, Cl, Br, I; $n = 0$–3)

	$\nu_1(A_{1g})$	$\nu_3(T_{1u})$		$\nu_1(A_{1g})$	$\nu_3(T_{1u})$
RhF_6			IrF_6	702	719
RhF_6^-	632	655	IrF_6^-	671	
RhF_6^{2-}	592		IrF_6^{2-}	603–610	554
RhF_6^{3-}			IrF_6^{3-}		
$RhCl_6^{2-}$	320	335	$IrCl_6^{2-}$	345–346	313–321
$RhCl_6^{3-}$	302–308	312	$IrCl_6^{3-}$	330	296
			$IrBr_6^{2-}$	215	221
$RhBr_6^{3-}$	187–190	244-260	$IrBr_6^{3-}$	198	209
			IrI_6^{3-}	149	175

The hexahalometallate(III) ions are reasonably stable, except for IrI_6^{3-}; water-sensitive Cs_3IrI_6 was made by tempering pellets of Cs_3IrBr_6 and NaI at 160°C for some days [25]. As expected for low-spin d^6 systems, these are diamagnetic, but the MX_6^{2-} species are paramagnetic with one unpaired electron [26]. Thus Cs_2RhCl_6 has $\mu_{eff} = 1.7\,\mu_B$ and various RhF_6^{2-} salts have moments of *c.* $2.0\,\mu_B$; moments in this range have been reported for IrX_6^{2-} (X = F, Cl, Br).

Salts of $IrCl_6^{2-}$ were used in the classic first ESR experiments to demonstrate delocalization of unpaired electrons onto the chloride ligand (Figure 2.1); the unpaired electron spends 30% or more of its time in ligand orbitals in this case [27].

Na_2IrCl_6 is a convenient starting material in the synthesis of iridium compounds.

$NaRhF_6$ is reported to have $\mu = 2.8\,\mu_B$.

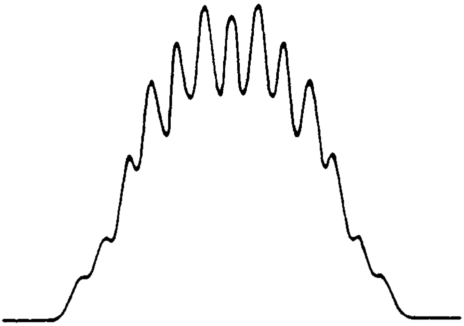


Figure 2.1 Ligand hyperfine structure in the ESR spectrum of $Na_2[(Ir, Pt)Cl_6].6H_2O$. (Reproduced with permission from *Proc. R. Soc., London, Ser. A*, 1953, **219**, 526.)

Mixed halometallates [28] can be synthesized: $RhCl_6Br^{3-}_{6-x}$ from the reaction of $RhCl_6^{3-}$ with HBr, or $RhBr_6^{3-}$ with HCl. Individual isomers have been identified in solution by ^{103}Rh NMR, which can even distinguish between stereoisomers (Figure 2.2) and shows isotopic splitting (Figure 2.3).

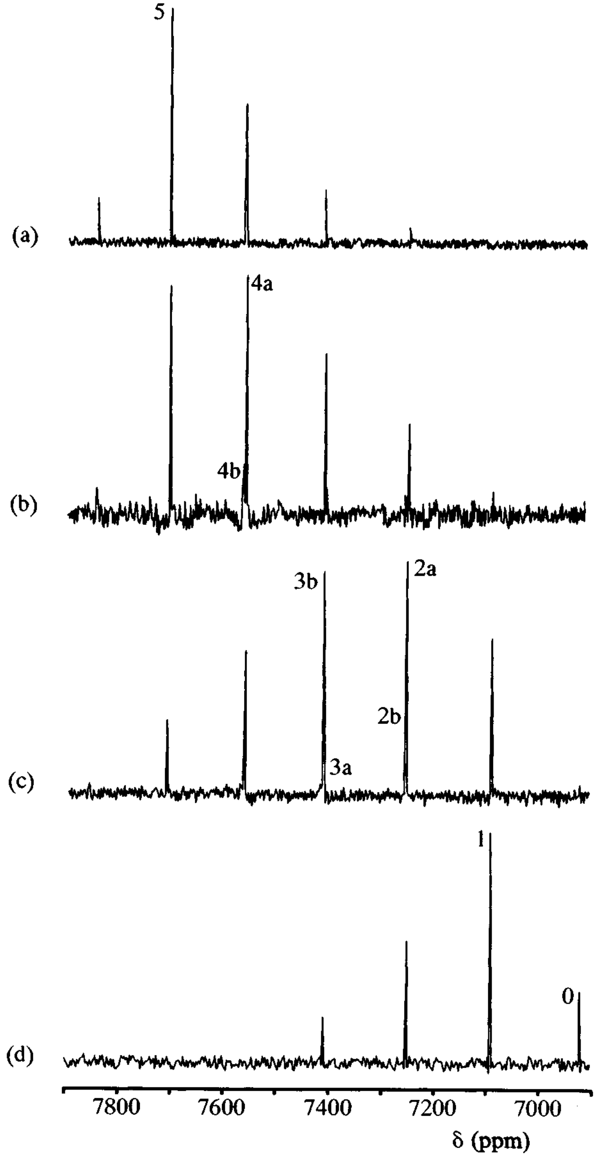


Figure 2.2 ^{103}Rh NMR spectrum of mixtures of $[RhCl_nBr_{6-n}]^{3-}$ species ($n = 0$–6; a denotes *cis,fac*-isomer, b denotes *trans,mer*-isomer). (a–d) are varying Cl : Br ratios in the starting material. (Reproduced with permission from *Z. Naturforsch., Teil B*, 1989, **44**, 1402.)

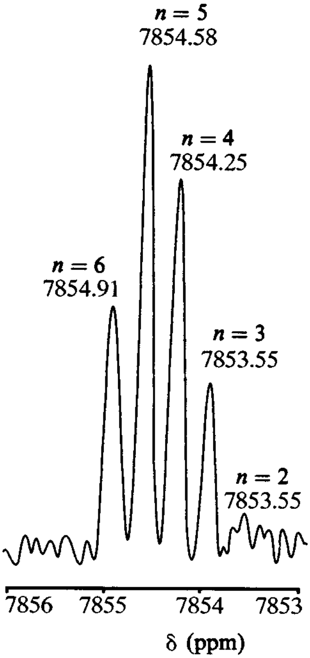


Figure 2.3 ^{103}Rh NMR spectrum of mixtures of $[Rh^{35}Cl_n^{37}Cl_{6-n}]^{3-}$ species ($n = 2$–6). (Reproduced with permission from *Z. Naturforsch., Teil B*, 1989, **44**, 1402.)

The series $[IrX_{6-x}Cl_x]^{2-}$ have likewise been made, as have the free acids $(H_3O)_2IrX_6$ (X = Cl, Br).

Various dinuclear complexes exist

$$A_3RhCl_6 \xrightarrow{H_2O} A_2RhCl_5(H_2O) \xrightarrow{\text{heat}} A_3Rh_2Cl_9$$

(A = alkali metal)

$$2RhX_6^{3-} + 6Bu_4N^+ \xrightarrow[(X=Cl,\,Br)]{CH_2Cl_2} (Bu_4N)_3Rh_2X_9 + 3Bu_4NX$$

In the latter example, the ligand abstraction is favoured by the non-polar solvent CH_2Cl_2. IR spectra distinguish between the bridging and terminal groups; thus in $Cs_3Rh_2X_9$, terminal Rh–X stretching vibrations occur in the regions 342–361 cm^{-1} (X = Cl) and 252–272 cm^{-1} (X = Br) with bridging Rh–X vibrations in the regions 267–302 cm^{-1} (X = Cl) and 171–195 cm^{-1} (X = Br) [29].

2.4 Oxides, hydrides and other binary compounds

Both rhodium and iridium form the oxides M_2O_3 and MO_2 [30]. Heating rhodium in air or oxygen (300–1000°C) yields brown Rh_2O_3, also obtained by heating rhodium nitrate at 730°C.

$$4Rh(NO_3)_3.6H_2O \rightarrow 2Rh_2O_3 + 12NO_2 + 3O_2 + 24H_2O$$

It exists in two stable forms, of which the α-form has the corundum (α-Al_2O_3) structure with octahedrally coordinated rhodium (Rh–O 2.03–2.07 Å); the β-form and a high-temperature form also have octahedral coordination. Black RhO_2 has the rutile structure (Rh–O 1.95–1.97 Å) and is best made by heating rhodium or Rh_2O_3 at 400–900°C under oxygen pressures up to 3500 atm.

Ir_2O_3 can be made by heating K_2IrCl_6 with Na_2CO_3; it is a (impure) brown solid about which little is known. Like RhO_2, IrO_2 also has the rutile structure. It is obtained by heating the metal in oxygen or by dehydrating the hydrated oxide precipitated on hydrolysis of Ir^{4+}(aq.)

The oxides decompose on heating:

$$2Ir_2O_3 \xrightarrow{500°C} Ir + 3IrO_2$$

$$IrO_2 \xrightarrow{1100°C} Ir + O_2$$

$$4RhO_2 \xrightarrow{680°C} 2Rh_2O_3 + O_2.2Rh_2O_3 \xrightarrow{1050°C} 4Rh + 3O_2$$

Rhodium(III) hydroxide is an ill-defined compound $Rh(OH)_3.nH_2O$ ($n \sim 3$) obtained as a yellow precipitate by careful addition of alkali to Na_3RhCl_6. Addition of imidazole solution to suitable aqua ions leads to the precipitation of 'active' rhodium(III) hydroxides formulated as $Rh(OH)_3(H_2O)_3$, $Rh_2(\mu\text{-}OH)_2(OH)_4(H_2O)_4$ and $Rh_3(\mu\text{-}OH)_4(OH)_5(H_2O)_5$ [31]. Hydrated iridium(III) hydroxide is obtained as a yellow precipitate from Ir^{3+} (aq.) at pH 8.

The metals form the usual wide range of binary compounds. Therefore, a range of sulphides and selenides are known, including MX_2 (M = Rh, Ir; X = S, Se, Te), M_3X_8 (X = S, Se), M_2S_3 and IrS_3. Of these, M_2S_3 is isostructural, containing pairs of face-sharing octahedra linked into a three-dimensional array by further sharing of sulphur. $RhSe_2$ and IrX_2 (X = S, Se) contain a special variety of the pyrite structure and are probably both represented as $M^{3+}X^{-1.5}(X_2^{3-})_{1/2}$ [32].

Other binary compounds include MAs_3 (M = Rh, Ir), which has the skutterudite ($CoAs_3$) structure [33] containing As_4 rectangular units and octahedrally coordinated M. The corresponding antimonides are similar. M_2P (M = Rh, Ir) has the anti-fluorite structure while MP_3 has the $CoAs_3$ structure. In another compound of this stoichiometry, $IrSi_3$, 9-coordination exists for iridium.

No binary hydrides have been characterized, but reactions of the metal powders with alkali metal hydrides in a hydrogen atmosphere lead to Li_3RhH_4 (planar RhH_4^{3-}) and M_3MH_6 (M = Li, Na; M = Rh, Ir) with octahedral MH_6^{3-} [34].

2.5 Aqua ions and simple salts

Aqua ions and simple salts have been thoroughly investigated recently [35]. Rhodium perchlorate, $Rh(ClO_4)_3.6H_2O$, can be made as yellow crystals by dissolving rhodium hydroxide in perchloric acid or alternatively by repeatedly heating hydrated rhodium chloride with perchloric acid. (Equilibrium is only slowly established and oligomers persist in quite acid solutions.) It contains slightly distorted $Rh(H_2O)_6^{3+}$ octahedra (Rh–O 2.128–2.136 Å); the Rh–O bonds may be lengthened slightly compared with the alum by hydrogen bonding to perchlorate ions. Solutions of iridium(III) perchlorate have been made by hydrolysis of $(NH_4)_2IrCl_6$, reacting the hydrolysis product with $HClO_4$ and then removing polymeric species by ion exchange. The alums also contain the hexaqua ion:

$$M(OH)_3 \xrightarrow{H_2SO_4} M_2(SO_4)_3(aq.) \xrightarrow{Cs_2SO_4} CsM(SO_4)_2.12H_2O$$

M–O bond lengths are 2.016 Å (Rh) and 2.041 Å (Ir), the former corresponds well to the value of 2.04 Å deduced from X-ray studies on aqueous solutions of $Rh(H_2O)_6^{3+}$ [36].

$Rh(H_2O)_6^{3+}$ is quite acidic ($pK_a = 3.4$ at 25°C). Spectroscopic study of crystals of the alums at 80 K leads to the assignment of ν_1 (A_{1g}) in $M(OH_2)_6^{3+}$ to bands at 548 cm^{-1} (Rh) and 553 cm^{-1} (Ir); in solution at room temperature they are found at 529 and 536 cm^{-1}, respectively.

Brown rhodium nitrate is reportedly formed from the reaction of RhI_3 with boiling nitric acid; it forms a hexahydrate.

The rhodium(II) aqua ion is not yet completely characterized. Cr^{2+} reduction of $Rh(H_2O)_5Cl^{2+}$ gives a diamagnetic species believed to be Rh_2^{4+} (aq.) [37], which may have the structure $(H_2O)_4Rh(\mu\text{-}OH_2)_2Rh(H_2O)_4^{4+}$.

In addition to the aqua ion, a range of mixed aquo–halo complexes are known [38], including all 10 isomers of $Rh(H_2O)_{6-x}Cl_x^{(3-x)+}$. Synthetic entry into the series is possible from either end, the determining factor being the labilizing effect of chloride:

$$Rh(H_2O)_6^{3+} \xrightarrow{Cl^-} RhCl(H_2O)_5^{2+} \xrightarrow{Cl^-} trans\text{-}RhCl_2(H_2O)_4^{+}$$
$$\xrightarrow{Cl^-} mer\text{-}RhCl_3(H_2O)_3$$

$$RhCl_6^{3-} \xrightarrow{H_2O} RhCl_5(H_2O)^{2-} \xrightarrow{H_2O} cis\text{-}RhCl_4(H_2O)^{-}$$
$$\xrightarrow{H_2O} fac\text{-}RhCl_3(H_2O)_3$$

This affects both the position of substitution and the rate; thus $RhCl(H_2O)_5^{2+}$ substitutes more than an order of magnitude faster than $Rh(H_2O)_6^{3+}$. These substitutions are all believed to follow a dissociative (S_N1) reaction. Particular compounds can sometimes be obtained under specific conditions;

thus recrystallizing a $RhCl_6^{3-}$ salt generally affords the corresponding $RhCl_5(H_2O)^{2-}$ species. Usually a mixture is formed, needing to be separated by ion-exchange: on refluxing $Rh(H_2O)_6(ClO_4)_3$ in 0.5 M HCl for 6–8 h, *mer*-$RhCl_3(H_2O)_3$ is the dominant product, while 15 min reflux of K_3RhCl_6 in dilute $HClO_4$ gives principally *fac*-$RhCl_3(H_2O)_3$. Individual species afford separate peaks in their electronic and vibrational spectra but in a mixture these will tend to overlap. However, separate signals can be seen in the ^{103}Rh NMR spectrum of such a mixture, it is even possible to discern isotopic splitting (see also Figure 2.3) [39].

Similar studies have been carried out on the corresponding bromides. Some structures have been determined; in Me_4N^+ [*trans*-$RhCl_4(H_2O)_2]^-$, Rh–O is 2.032 Å while Rh–Cl distances average 2.33 Å. $(NH_4)_2RhCl_5(H_2O)$ has Rh–O of 2.090 Å, *cis*-Rh–Cl distances average 2.347 Å while Rh–Cl *trans* to O is 2.304 Å (*trans*-influence of Cl); in the corresponding Cs salt, these distances are 2.096, 2.337 and 2.300 Å, respectively [40]. In *trans*-$[Ir(H_2O)_4Cl_2]^+$, Ir–Cl is 2.350 Å and Ir–O 2.039–2.048 Å.

2.6 Compounds of rhodium(0)

The best defined rhodium(0) compound [41] is diamagnetic $Rh_2(PF_3)_8$

$$RhCl_3 \xrightarrow[150°C,\,250\,atm]{PF_3/Cu} Rh_2(PF_3)_8$$

It is believed to be metal–metal bonded $(PF_3)_4Rh-Rh(PF_3)_4$ and readily reacts with hydrogen

$$Rh_2(PF_3)_8 + H_2 \rightarrow 2RhH(PF_3)_4$$

Electrochemical reduction in MeCN of various $RhCl(R_3P)_3$ complexes give the diamagnetic $Rh(R_3P)_4$ ($R_3P = Ph_3P$, Me_2PhP), which are probably analogous to the PF_3 complex.

2.7 Compounds of rhodium(I)

Many important compounds are found in the +1 oxidation state [42], though unlike rhodium(III) it has no aqueous chemistry. Rhodium(I) generally forms 4-coordinate square planar and 5-coordinate species, the latter being the highest CN expected for the d^8 configuration under the 18-electron rule. (An octahedral rhodium(I) complex would involve putting two electrons in an anti-bonding orbital, as well as more steric crowding.)

2.7.1 *Tertiary phosphine complexes*

Tertiary phosphine complexes [42] are the most important rhodium(I) compounds. $RhCl(PPh_3)_3$ ('Wilkinson's compound'), a hydrogenation catalyst, is the most important, but they exist in a range of stoichiometries.

Synthesis follows several routes:

1. Substitution in rhodium(I) alkene complexes

$$RhCl_3.3H_2O \xrightarrow{C_2H_4} [RhCl(C_2H_4)_2]_2 \xrightarrow{PR_3} RhCl(PR_3)_3 \quad (R = \text{alkyl})$$

$$RhF(C_8H_{12})_2 \xrightarrow{Pcy_3} RhF(Pcy_3)_2 \xrightarrow{NaX} RhX(Pcy_3)_2$$

$$[RhCl(C_8H_{12})_2]_2 \xrightarrow{P(OMe)_3} [RhCl\{P(OMe)_3\}_2]_2$$

2. Displacement of CO, only possible with strong π-acids

$$[RhCl(CO)_2]_2 \xrightarrow{PF_3} [RhCl(PF_3)_2]_2$$

3. Substitution of other phosphines

$$RhCl(PPh_3)_3 \xrightarrow[PMe_3]{exc.} [Rh(PMe_3)_4]^+Cl^-$$

4. Reduction using certain arylphosphines as reducing agents

$$RhCl_3.3H_2O \xrightarrow[EtOH/boil]{exc.\ PPh_3} RhCl(PPh_3)_3$$

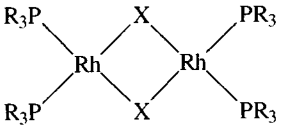
2 : 1 complexes

The intensely reactive $RhX(Pcy_3)_2$ complexes are probably monomers; they bind both N_2 and SO_2 [43a], but most $RhX(PR_3)_2$ systems are dimers ($R = Ph$, $X = Cl$, OH; X-ray [43b]) (Figure 2.4)

$$[RhCl(PPr^i_3)_2]_2 + 2L \rightarrow 2RhClL(PPr^i_3)_2 \qquad (L = H_2, CO, Bu^tNC)$$

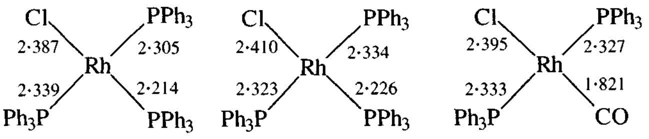
where the bridge can be cleaved

$$[RhCl(PPh_3)_2]_2 + 2PPh_3 \rightarrow 2RhCl(PPh_3)_3$$



X	Rh–X	Rh–P	Rh–Rh
Cl	2.40	2.200–2.213	3.662
OH	2.06	2.185–2.207	3.278

Figure 2.4 Bond lengths in $[Rh(PPh_3)_2X]_2$ dimers.



Red form Orange form

Figure 2.5 Bond lengths in $Rh(X)Cl(PPh_3)_2$ (X = CO, PPh_3).

3 : 1 complexes

A wide range of $RhX(QR_3)_3$ complexes exist (QR_3, e.g. PMe_3, PMe_2Ph, PPh_3, $AsPh_3$, etc.), generally made by replacing alkenes. Red $RhCl(PPh_3)_3$ [44] is made by an unusual route

$$RhCl_3 + 4PPh_3 \xrightarrow[\text{EtOH}]{\text{reflux}} RhCl(PPh_3)_3 + Ph_3PO$$

The ability of triphenylphosphine to act as a reducing agent probably involves initial formation of Ph_3PCl_2, which then undergoes solvolysis. If the synthesis is carried out using a small volume of ethanol, an orange polymorph is formed [45].

The crystal structures of both forms of $RhCl(PPh_3)_3$ show square planar coordination geometry (with a slight tetrahedral distortion). The mutually *trans* Rh–P bonds are similar to those in the less congested $RhCl(CO)(PPh_3)_2$, suggesting that steric crowding is not responsible for this distortion, which is also found in $RhCl(PMe_3)_3$ (Figure 2.5).

There are, however, short Rh–H contacts (2.77–2.84 Å) to *ortho*-hydrogens in phenyl groups. The Rh–P bond *trans* to Cl is some 0.1 Å shorter than the others, evidence of the weak *trans*-influence of chloride [46].

The ^{31}P NMR spectrum in solution [47] is in accordance with a square planar structure (Figure 2.6).

It shows a doublet of doublets owing to the pair of equivalent phosphorus nuclei, the signal being split by coupling to ^{103}Rh ($I = \frac{1}{2}$) and to the unique phosphorus; similarly the resonance owing to the third phosphorus shows coupling to two equivalent phosphorus nuclei, the resulting triplet being

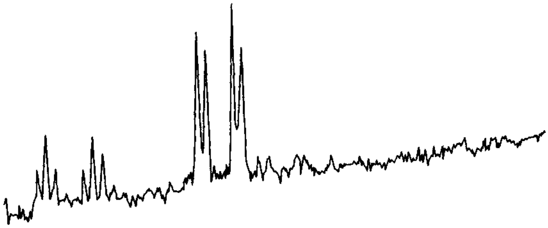


Figure 2.6 The ^{31}P NMR spectrum of $RhCl(PPh_3)_3$ at 30°C in C_6H_6 solution. (Reprinted with permission from *J. Am. Chem. Soc.*, 1972, **94**, 340. Copyright (1972) American Chemical Society.)

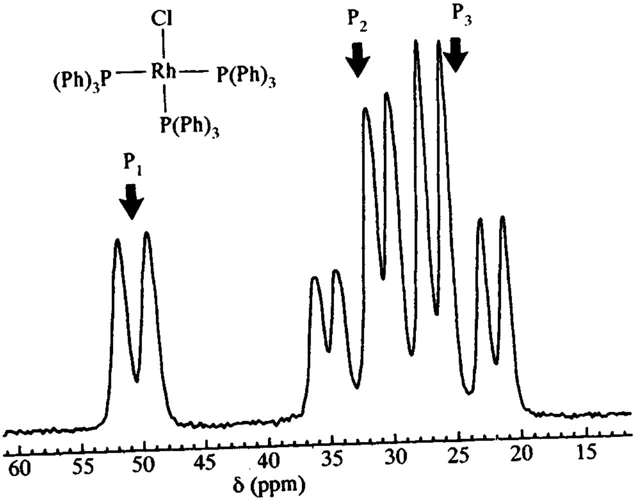


Figure 2.7 The solid-state ^{31}P NMR spectrum of $RhCl(PPh_3)_3$. (Reprinted with permission from *Organometallics*, 1992, **11**, 3240. Copyright (1992) American Chemical Society.)

split by coupling to rhodium. The solid-state ^{31}P NMR spectrum (Figure 2.7) is composed of a low-field cluster owing to the unique phosphorus split by coupling with rhodium (*cis*-P–P coupling is too small to be resolved); the multiplet has been analysed as the AB part of an ABX system, showing the two *trans*-phosphines are non-equivalent in the solid state.

$RhCl(PPh_3)_3$ is an air-stable solid (m.p. 157°C) soluble in a wide range of organic solvents with little dissociation of ligands. It does react readily with dioxygen in solution [48] forming a number of O_2 adducts (Figure 2.8); the consequent dissociation of PPh_3 is probably the reason why molecular weight measurements in incompletely deoxygenated solvents have implied

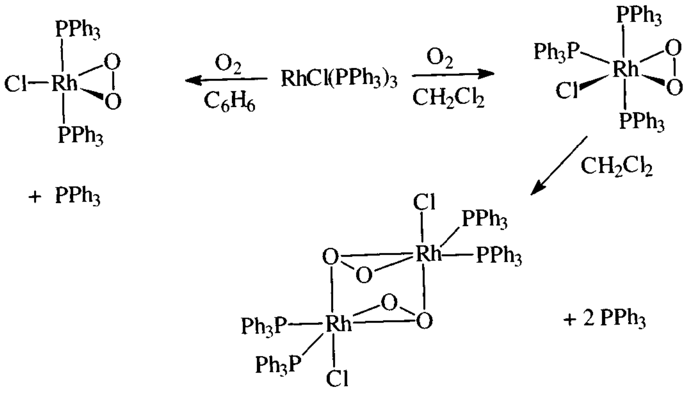


Figure 2.8 Rhodium dioxygen complexes.

dissociation for $RhCl(PPh_3)_3$. (It is notable that the isoelectronic 16-electron $Pt(PPh_3)_3$ shows no significant dissociation in solution.)

$RhCl(PPh_3)_3$ is a very active homogenous hydrogenation catalyst, because of its readiness to engage in oxidative addition reactions with molecules like H_2, forming Rh–H bonds of moderate strength that can subsequently be broken to allow hydride transfer to the alkene substrate. A further factor is the lability of the bulky triphenylphosphines that creates coordinative unsaturation necessary to bind the substrate molecules [44].

Reactions of $RhCl(PPh_3)_3$ can be divided into three classes (Figure 2.9)

1. oxidative addition (usually involving partial loss of PPh_3)
2. halide substitution
3. substitution of PPh_3 ligands (whole or partial).

In class (1), a range of small molecules adds to rhodium, usually with the loss of one PPh_3, thus maintaining the 16-electron configuration, rather than an 18-electron species unable to bind a substrate.

The reversible addition of hydrogen is the most significant of these reactions. In the presence of excess PPh_3, $RhH_2Cl(PPh_3)_3$ is formed, but generally the 5-coordinate $RhHCl_2(PPh_3)_2$ is obtained. Chlorine and HCl likewise add with fission of the X–Cl bond and loss of one PPh_3; $RhHCl_2(PPh_3)_2$ will insert ethene to form an ethyl complex.

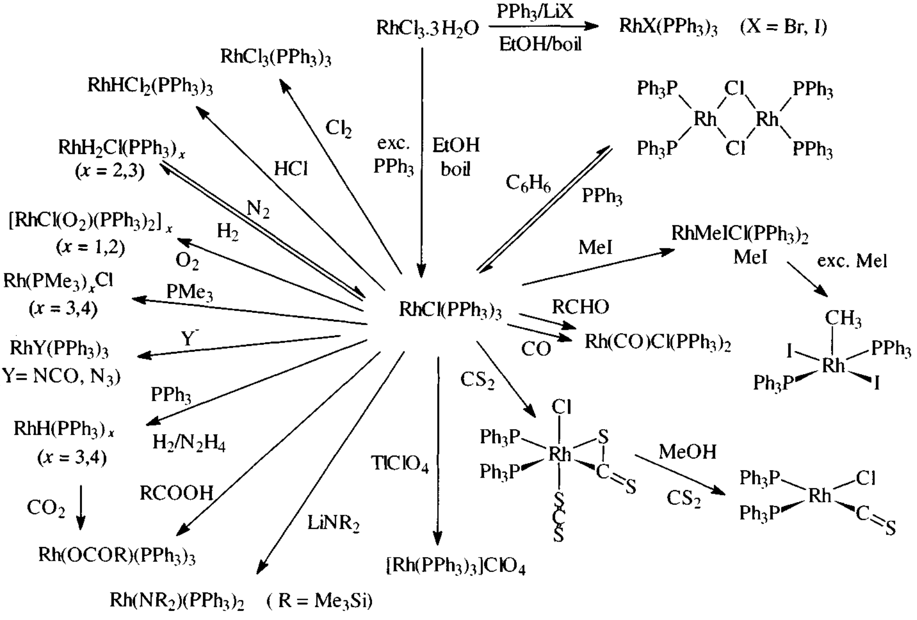


Figure 2.9 Synthesis and reactions of $RhCl(PPh_3)_3$.

The reaction with MeI proceeds in two stages. Initial reaction is oxidative addition to give a rhodium(III) species, isolated as a MeI adduct

$$RhCl(PPh_3)_3 + 2MeI \rightarrow RhClIMe(PPh_3)_2MeI + PPh_3$$

This then eliminates MeCl on recrystallization from benzene

$$RhClIMe(PPh_3)_2(MeI) \rightarrow MeCl + RhI_2(Me)(PPh_3)_2$$

Replacement reactions frequently involve a simple substitution of halide by an anionic ligand (e.g. N_3, NCO, S_2CNR_2). While chloride can be replaced by bis(trimethylsilyl)amide, $N(SiMe_3)_2$, most alkylamides are unstable to α-hydride elimination, forming the hydride $RhH(PPh_3)_3$ [49] (which is also obtained in the attempted preparation of $Rh(CH_2CH_2Me)((PPh_3)_3)$. The hydride ligand can be identified in the ^1H NMR spectrum of $RhH(PPh_3)_3$ by its high-field line (doublet, $\delta = -8.3$ ppm, J(Rh–H) = 12.4 Hz). The ^{31}P NMR spectrum at room temperature is a doublet (J(Rh–P) 164 Hz) but on cooling a fluxional process slows down and the spectrum converts into a double doublet and a double triplet (Figure 2.10) that overlap slightly.

The double triplet results from the unique phosphorus, split into a triplet by interaction with two equivalent phosphorus atoms (J(P–P) 25 Hz) then split into a doublet by rhodium (J(Rh–P) 145 Hz).

The double doublet corresponds to P_B, with splitting owing to phosphorus A (*cis*) (J(P–P) 25 Hz) and rhodium (J(Rh–P) 172 Hz). The fluxional behaviour is consistent with a rapidly rearranging (at room temperature) square planar structure rather than a tetrahedral one (Figure 2.11).

Determination of this crystal structure of the complex did not locate the hydride ligand but its position can be deduced from the distortion from

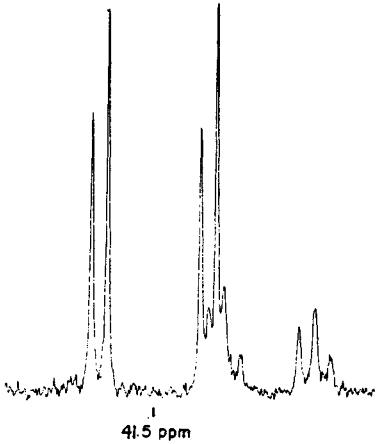


Figure 2.10 ^{31}P NMR spectrum of $RhH(PPh_3)_3$. (Reprinted with permission *Inorg. Chem.*, 1978, 17, 3066. Copyright (1978) American Chemical Society.)

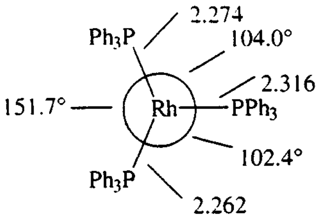


Figure 2.11 Bond lengths in $RhH(PPh_3)_3$ (hydride not shown).

regular trigonal geometry and the lengthened Rh–P bond *trans* to hydride. ($RhH(PPh_3)_4$, however, has a regular RhP_4 core so that here hydride has no stereochemical influence.)

Alkylation of $RhCl(PPh_3)_3$ yields unstable alkyls that undergo CO_2 insertion; $Rh(OCOPh)(PPh_3)_3$ has monodentate benzoate (X-ray).

Halide abstraction in donor solvents (with e.g. $TlClO_4$) affords [50] pseudo-tetrahedral $[Rh(solvent)(PPh_3)_3]^+$ ions (solvent, e.g. MeCN, Me_2CO, ROH) (Figure 2.12), which on recrystallization from CH_2Cl_2 gives $Rh(PPh_3)_3^+ClO_4^-$ (Figure 2.13) [51].

This has a distorted trigonal planar (nearly T-shaped) geometry with weak Rh–C and Rh–H interactions owing to the close approach of a phenyl group (Rh–H 2.56 Å, Rh–C 2.48 Å) supplementing the three Rh–P bonds in what is formally a 14-electron species. This ion is also formed by protonation of $RhH(PPh_3)_4$ (note the hydride ligand behaving as H^-).

$$RhH(PPh_3)_4 \xrightarrow{H_2C(SO_2CF_3)_2} [Rh(PPh_3)_3]^+HC(SO_2CF_3)_2^- + H_2 + PPh_3$$

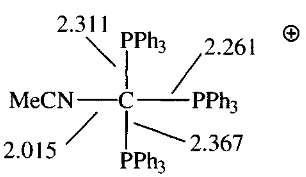


Figure 2.12 Bond lengths in $[Rh(MeCN)(PPh_3)_3]^+$.

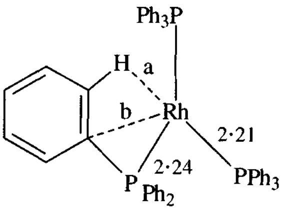


Figure 2.13 Bond lengths in $[Rh(PPh_3)_3]^+ClO_4^-$ showing short Rh–H and R–C contacts. a = 2.56 Å; b = 2.48 Å.

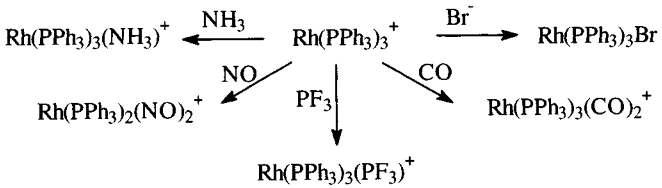


Figure 2.14 Reactions of $[Rh(PPh_3)_3]^+$.

^{31}P NMR spectra indicate the T-shape geometry is retained in solution at −30°C but that the molecule is fluxional at room temperature. $Rh(PPh_3)_3^+$ undergoes a range of addition reactions with Lewis bases (CO, PF_3, NH_3) to afford various 16- and 18-electron species (Figure 2.14).

Substitution reactions of $RhCl(PPh_3)_3$ where PPh_3 is completely displaced are relatively rare, though this is achieved with PMe_3, affording $Rh(PMe_3)_3Cl$ and $Rh(PMe_3)_4^+Cl^-$. More usually, as with CO, DMSO and C_2H_4, one phosphine is displaced; indeed the stability of *trans*-$RhCl(CO)(PPh_3)_2$ is such that aldehydes are decarbonylated by $RhCl(PPh_3)_3$. The reaction with CS_2 to give the analogous $RhCl(CS)(PPh_3)_2$ is more complicated than was first believed. If the reaction is carried out in neat CS_2, an intermediate species $RhCl(\eta^1\text{-}SCS)(\eta^2\text{-}CS_2)(PPh_3)_2$ is isolated, which readily decomposes in more polar solvents ($CHCl_3$, MeOH) forming $RhCl(CS)(PPh_3)_2$ (for its structure, see section 2.7.2).

$RhCl(PPh_3)_3$ as a homogenous hydrogenation catalyst [44, 45, 52]. The mechanism of this reaction has been the source of controversy for many years. One interpretation of the catalytic cycle is shown in Figure 2.15; this concentrates on a route where hydride coordination occurs first, rather than alkene coordination, and in which dimeric species are unimportant. (Recent NMR study indicates the presence of binuclear dihydrides in low amount in the catalyst system [47].)

The initial catalytic step involves reversible binding of H_2 to afford a rather crowded 18-electron species $RhH_2Cl(PPh_3)_3$. The ^{31}P NMR spectrum at −25°C it consists of a doublet of doublets owing to the *trans* phosphorus atoms (P_A) and a doublet of triplets owing to the unique phosphorus (P_B) (Figure 2.15) [47]. On warming to room temperature, broadening occurs as a result of phosphine ligand exchange; the loss of the couplings involving P_B shows that this is the phosphine dissociating, forming a 16-electron species $RhH_2Cl(PPh_3)_2$ that can bind an alkene (again affording an 18-electron species). This dihydride can now transfer the hydrogens to the unsaturated linkage (any alkyl intermediate is presumably shortlived as spectroscopic measurements have failed to detect them); addition is stereospecifically *cis*. Once the alkane is eliminated, the resulting coordinatively unsaturated 14-electron $RhCl(PPh_3)_2$ can rapidly undergo oxidative addition with H_2 to regenerate the dihydride intermediate.

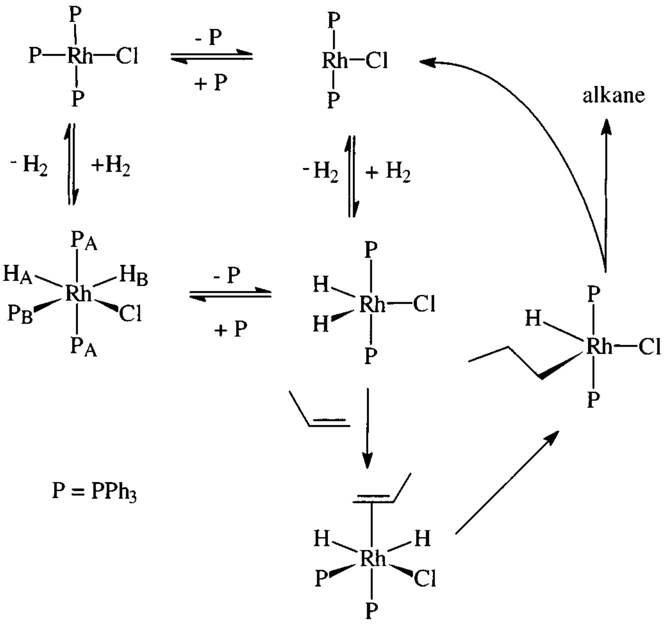


Figure 2.15 Cycle for the hydrogenation of alkenes catalysed by $RhCl(PPh_3)_3$.

Because the unsaturated hydrocarbon has to bind to rhodium in the presence of bulky PPh_3 groups, the catalyst favours unsubstituted double bonds ($RCH{=}CH_2$ rather than $RR^IC{=}CR^{II}R^{III}$). Since the alkyl intermediate is shortlived, there is little tendency to β-elimination with concomitant alkene isomerization. Although both alkene and alkyne functions are reduced, in general carbonyl or carboxylic groups and benzene rings are not, though aldehydes are frequently decarbonylated. Peroxides tend to oxidize and thus destroy the catalyst, so that substrates need to be purified carefully before use.

An example of a rhodium(I) complex with a tridentate phosphine is shown in Figure 2.16; it is formed by the usual route, reaction of the phosphine with [RhCl(cycloocta-1.5-diene)]$_2$.

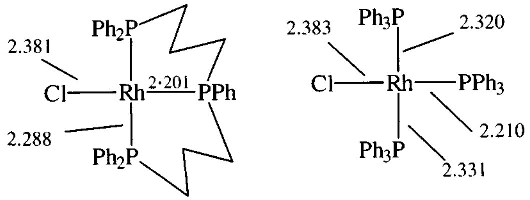


Figure 2.16 Bond lengths in a rhodium(I) complex of a tridentate phosphine compared with those in $RhCl(PPh_3)_3$.

It has an approximately square planar geometry, with bond lengths very similar to $RhCl(PPh_3)_3$ (Figure 2.5); like the latter, it undergoes a range of addition reactions, some involving no formal change in oxidation state, others a change to rhodium(III) species (Figure 2.17).

These are generally analogous to those of Wilkinson's compound, with the important difference that ligand dissociation cannot occur, so that the product of oxidative addition with H_2 cannot have a vacant site to bind an alkene and will thus not act as a hydrogenation catalyst [53].

4 : 1 complexes

The 4 : 1 complexes tend to be formed only by less bulky phosphines and even then tend to be coordinatively saturated.

$$RhCl(PPh_3)_3 \xrightarrow[X^-]{PR_3} Rh(PR_3)_4^+X^- \quad (X, \text{e.g.}\ PF_6, BF_4;\ PR_3 = PMe_3, PHPh_2)$$

Related compounds occur with bidentate phosphines

$$[RhCl(cod)]_2 \xrightarrow[X^-]{\text{diphos}} Rh(diphos)_2^+X^-$$

(cod = cycloocta-1.5-diene; diphos = $Ph_2P(CH_2)_2PPh_2$, $Me_2P(CH_2)_2PMe_2$).

$Rh(Ph_2P(CH_2)_2PPh_2)_2^+ClO_4^-$ has essentially square planar coordination of rhodium (Rh–P 2.289–2.313 Å) [54].

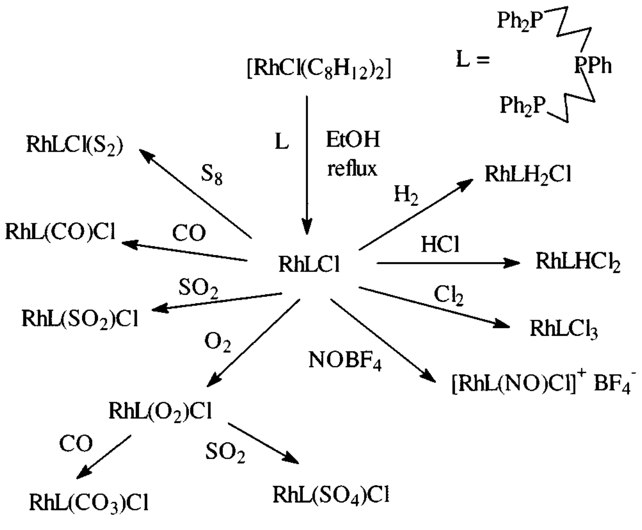


Figure 2.17 Reactions of the rhodium(I) complex of a tridentate phosphine.

5 : 1 complexes

Few of the 5:1 complexes [55] have been prepared, all with trialkylphosphites

$$[RhCl(cod)]_2 \xrightarrow{P(OR)_3} \{Rh[P(OR)_3]_5\}^+X^-$$

($X = BPh_4, PF_6$; R = Me, Et, Bu).

2.7.2 Carbonyl complexes

Three of the rhodium(I) carbonyl complexes are particularly important and are selected for special study.

$[RhCl(CO)_2]_2$

Reduction of hydrated $RhCl_3$ with CO at 100°C (best results are with CO saturated with methanol or ethanol) yields volatile red crystals of the dimer

$$RhCl_3.3H_2O \xrightarrow[100°C]{CO} [RhCl(CO)_2]_2$$

This has been shown to have an unusual dimeric structure (Figure 2.18) in which the two planar units are at an angle of 124° [56a].

The Rh–Rh distance is 3.12 Å, long compared with Rh–Rh single bonds (2.624 Å in $Rh_2(MeCN)_{10}^{4+}$, 2.73 Å in $Rh_4(CO)_{12}$); there is a weaker (3.31 Å) intermolecular attraction. Dipole moment and IR studies indicate that the structure is retained in solution and is, therefore, a consequence of electronic rather than solid-state packing effects. Furthermore, it is found for some other (but not all) $[RhCl(alkene)_2]_2$ and $[RhCl(CO)(PR_3)]_2$ systems. SCF MO calculations indicate that bending favours a Rh–Cl bonding interaction which also includes a contribution from Rh–Rh bonding [56b].

$[RhCl(CO)_2]_2$ undergoes a range of reactions (Figure 2.19) generally involving bridge cleavage and is, therefore, a useful starting material.

$RhH(CO)(PPh_3)_3$

$RhH(CO)(PPh_3)_3$ [57] is most conveniently prepared by

$$RhCl(CO)(PPh_3)_2 \xrightarrow[EtOH]{N_2H_4} RhH(CO)(PPh_3)_3$$

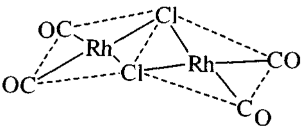


Figure 2.18 The structure of $[RhCl(CO)_2]_2$.

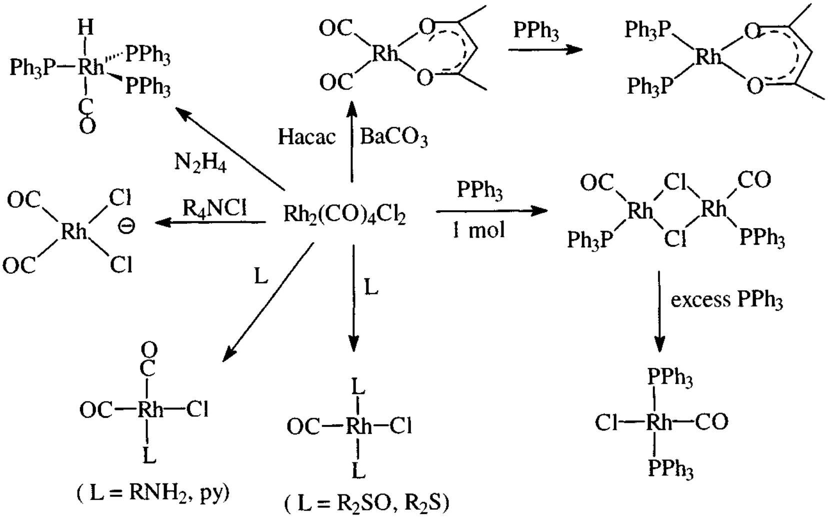


Figure 2.19 Reactions of $[RhCl(CO)_2]_2$.

It shows ν(Rh–H) and ν(C–O) at 2041 and 1918 cm^{-1}, respectively, in the IR spectrum (Nujol) and the low-frequency hydride resonance at $\delta = -9.30$ ppm in the ^1H NMR spectrum. It has a tbp structure (Figure 2.20) with the rhodium displaced out of the P_3 plane by 0.36 Å towards the CO.

It is an 18-electron species but in solution it tends to lose one PPh_3 to give $RhH(CO)(PPh_3)_2$, an active catalyst for hydroformylation and, to a lesser extent, hydrogenation of alkenes. (Evidence for the dissociation includes the fact that in the presence of other phosphines, mixed species $RhH(CO)(PPh_3)_2(PR_3)$ are formed by scrambling.) Initial coordination of the alkene is, in the absence of added CO, followed by hydrogenation (presumably via coordination of H_2 and an alkyl (intermediate)). Under a pressure of CO, hydroformylation occurs, with a high stereoselectivity in favour of straight-chain aldehydes, especially in the presence of added PPh_3. This supports the involvement of a crowded species (Figure 2.21) as the intermediate [58].

This process has been used commercially at the 100 kilotonne per year level running at around 100°C/20 atm.

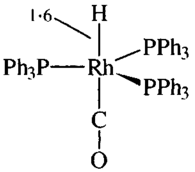


Figure 2.20 The structure of $RhH(CO)(PPh_3)_3$.

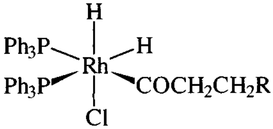


Figure 2.21 Probable structure of the intermediate in alkene hydroformylation catalysed by $RhH(CO)(PPh_3)_3$.

trans-$RhCl(CO)(PPh_3)_2$ and related compounds

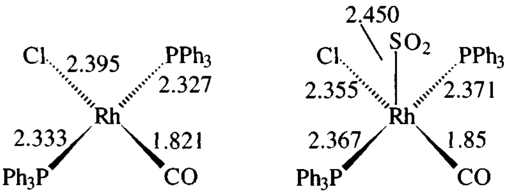
trans-$RhCl(CO)(PPh_3)_2$ [59] is the rhodium analogue of 'Vaska's compound' (section 2.10.2) and undergoes analogous oxidative addition reactions. It is a yellow solid (IR ν(C–O) 1980 cm^{-1} ($CHCl_3$)) conveniently obtained by the following route using methanal as the source of the carbonyl group.

$$RhCl_3 \xrightarrow[\text{EtOH reflux}]{PPh_3/HCHO} RhCl(CO)(PPh_3)_2$$

The *trans*-geometry (confirmed by X-ray) keeps the bulky PPh_3 groups as far apart as possible (Figure 2.22).

Other $RhX(CO)(PPh_3)_2$ compounds can be made as shown in Figure 2.23; metathesis with an alkali metal halide or pseudohalide is often convenient, but the most versatile route, as with the iridium analogues, is a two-stage process in which the fluoro complex is first prepared, the fluorine then being readily displaced.

Attempted synthesis of $RhY(CO)(PPh_3)_2$ in undried solvents (Y = a weakly coordinating anion, e.g. BF_4, ClO_4, SO_3CF_3) leads to $[Rh(H_2O)(CO)(PPh_3)_2]^+Y^-$. The water molecule is bound sufficiently strongly not to be displaced by alkenes (ethene, phenylethanol) but is removed by pyridine or CO (at 1 atm) yielding $Rh(CO)_3(PPh_3)_2^+$.



(X = Cl; Q = Ph)

X	Q	*n*	Rh–P	Rh–X	Rh–C
Cl	O	0	2.327–2.33	2.395	1.821
I	O	0	2.316–2.336	2.683	1.81
SH	O	0	2.314	2.416	1.767
Cl	S	0	2.335–2.337	2.386	1.787
OH_2	O	1	2.351	2.122	1.792

Figure 2.22 Bond lengths in $RhCl(CO)(PPh_3)_2$, $RhX(CQ)(PPh_3)_2]$ and $[Rh(OH_2)(CO)(PPh_3)_2]^+$ as well as in the SO_2 adduct.

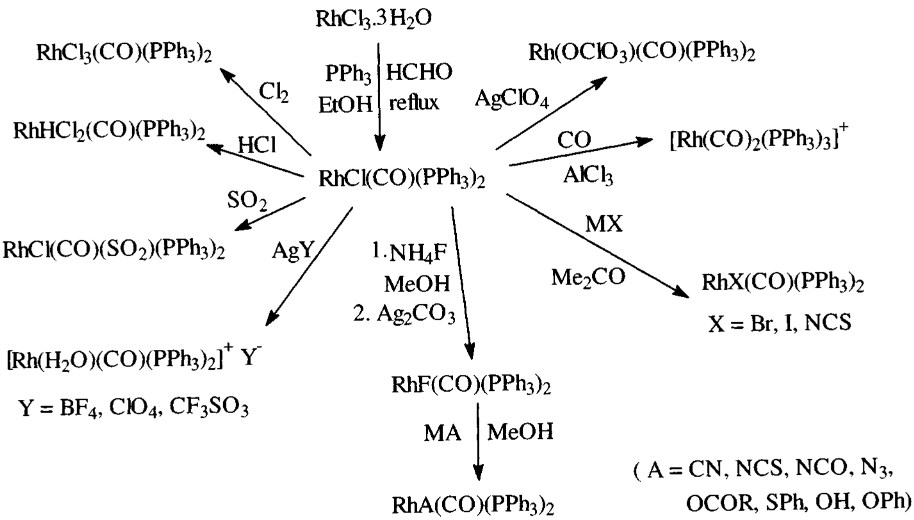


Figure 2.23 Reactions of $RhCl(CO)(PPh_3)_2$.

The mercapto complex $Rh(SH)(CO)(PPh_3)_2$ can be made by an unusual route [60] involving COS, where an intermediate with CS bound COS has been suggested.

$$RhH(PPh_3)_4 + COS \xrightarrow{\text{toluene}} Rh(\eta^2\text{-}COS)H(PPh_3)_3$$
$$\rightarrow Rh(SH)(CO)(PPh_3)_2 + 2PPh_3$$

The ^1H NMR spectrum of $Rh(SH)(CO)(PPh_3)_2$ in the mercaptide region (Figure 2.24) shows a 1:2:1 triplet owing to coupling to two equivalent (mutually *trans*) phosphines (J(P–H) 18.1 Hz), each line split into a doublet by a weaker coupling to ^{103}Rh (J(Rh–H) 1.6 Hz).

Structures have been determined for a number of these compounds, showing that the Rh–P bonds are little affected by the *cis*-ligands (Figure 2.22). The shorter Rh–C distance in the thiocarbonyl is probably a result of greater Rh=C back-bonding. Addition of SO_2 results in the formation of a 5-coordinate (sp) adduct with the expected lengthening in all bonds.

Other $RhCl(CO)(PR_3)_2$ compounds ($PR_3 = PEt_3$, PBu_3, $Palkyl_2Ph$, $PalkylPh_2$, $P(OR)_3$, PBu^t_2 alkyl) have been synthesized by the general route

$$[Rh(CO)_2Cl]_2 + 4PR_3 \xrightarrow{\text{MeOH}} 2RhCl(CO)(PR_3)_2 + 2CO$$

Structures have been determined for $PR_3 = PMe_2Ph$ and PBu^t_3 [61]. In the former, the square planar geometry is retained (with slightly shorter Rh–P bonds (2.316 Å) than for $PR_3 = PPh_3$), but in the latter, there is pronounced lengthening of the Rh–P bonds (Rh–Cl 2.395 Å, Rh–P 2.425-2.430 Å, Rh–C 1.784 Å) and a distortion towards a tetrahedral structure (P–Rh–P

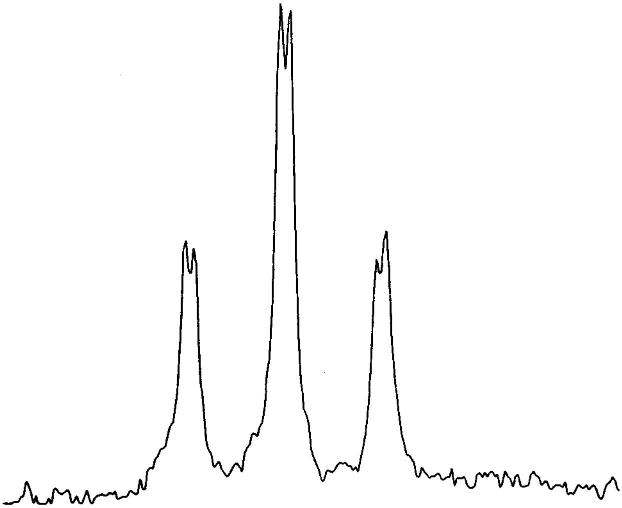


Figure 2.24 NMR spectrum of $Rh(SH)(CO)(PPh_3)_2$ in the mercaptide region. (Reprinted with permission from *Inorg. Chem.*, 1982, **21**, 2858. Copyright (1982) American Chemical Society.)

162.5°, C–Rh–Cl 150.7°) and some bending of the Rh–C–O bond (162.3°). Some short O–H and Cl–H intramolecular contacts may be responsible for the distortion though it has been suggested that in a distorted tetrahedral environment there may be an interaction between Rh d_{xz} electrons and the CO π^*-orbital causing bending.

Further evidence of steric crowding owing to bulky phosphines is found in $RhCl(CO)(PBu^t_2\ alkyl)_2$. Study of the ^{31}P NMR spectra at low temperature, 'freezing in' the rotational conformers shows separate signals for each (Figure 2.25) [62].

$RhCl(CO)(PR_3)_2$ (R = Et, Me, Ph) and the corresponding iridium systems undergo UV photolysis with the loss of CO, generating short-lived $RhCl(PR_3)_2$ species that act as catalysts for alkane carbonylation. Thus photolysis for 16.5 h under 1 atm CO using $RhCl(CO)(PMe_3)_2$ in pentane gives 2725% hexanal with high regioselectivity (45 : 1 hexanal to 2-methylpentanal) [63].

The complexes $[RhCl(CO)(PR_3)]_2$ can exist as *cis*- and *trans*-isomers (Figure 2.26).

The *cis*-structure (like $[Rh(CO)_2Cl]_2$ folded, with an angle of 123°) has been confirmed for PMe_2Ph (X-ray) whereas the $P(NMe_2)_3$ analogue is *trans* (IR). Comparison of solid-state and solution IR spectra indicates that both isomers are present in solution ($PR_3 = PMe_3$, PMe_2Ph, $P(NMe_2)_3$) [64].

Anionic carbonyl complexes of both rhodium(I) and (III) are synthesized by decarbonylation of formic acid, with reduction to rhodium(I) occurring

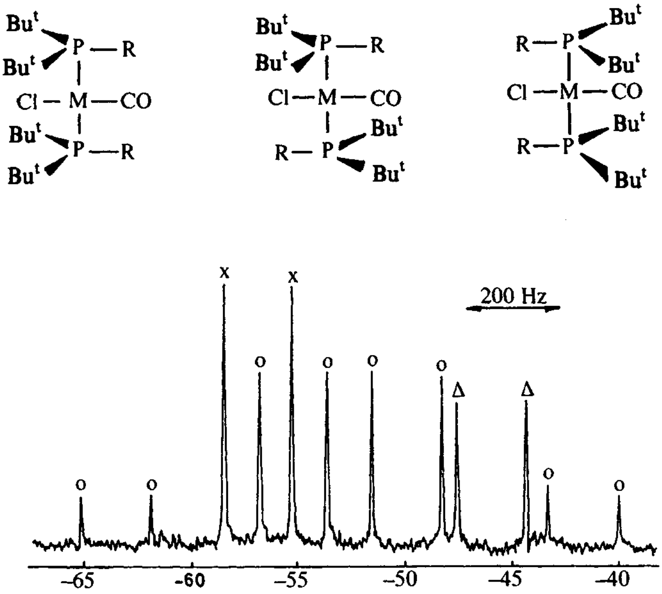


Figure 2.25 ^{31}P NMR spectrum of *trans*-RhCl(CO)(PBu$^t_2$Et)$_2$ at −60°C. The patterns ×, ○, △ correspond to the three conformers. (Reproduced with permission from *Chem. Comm.*, 1971, 1103.)

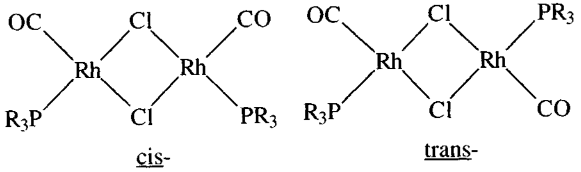
on extended reflux

$$\mathrm{RhX_3} \xrightarrow[\text{MX reflux}]{\text{HCOOH}} \mathrm{Rh(CO)X_5^{2-}} \xrightarrow[\text{reflux}]{\text{HCOOH}} \mathrm{Rh(CO)_2X_2^-}$$

Such a complex, *cis*-Rh(CO)$_2$I$_2^-$, is the active species in the Monsanto process for low-pressure carbonylation of methanol to ethanoic acid. The reaction is first order in iodomethane and in the rhodium catalyst; the rate-determining step is oxidative addition between these followed by

$$\mathrm{Rh(CO)_2I_2^- + MeI \Leftrightarrow Rh(CO)_2(Me)I_3^-}$$

methyl migration generating (MeCO)Rh(CO)I$_3^-$. This can then add CO, eliminate MeCOI (subsequently hydrolysed to the acid) and regenerate Rh(CO)$_2$I$_2^-$.



cis-

trans-

Figure 2.26 Isomers of [RhCl(CO)(PR$_3$)]$_2$.

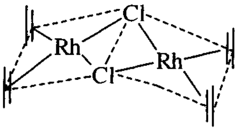


Figure 2.27 The structure of $[RhCl(C_2H_4)_2]_2$.

2.7.3 Alkene complexes

If ethene is bubbled through a methanolic solution of $RhCl_3.3H_2O$, red–orange crystals of $[RhCl(C_2H_4)_2]_2$ precipitate in a redox reaction.

$$2RhCl_3 + 6C_2H_4 + 2H_2O \rightarrow [RhCl(C_2H_4)_2]_2 + 2MeCHO + 4HCl$$

This has a 'folded' structure (Figure 2.27) similar to that of rhodium carbonyl chloride (Figure 2.18) with ethene acting as a two-electron donor, but ethene is more weakly held and readily displaced by CO and certain alkenes (e.g. cycloocta-1,5-diene).

Reaction under controlled conditions with tertiary phosphines leads to partial displacement of alkene retaining the dimeric structure [65].

Reaction of the dimer with Na(acac) leads to cleavage of the bridge giving yellow crystals of $Rh(alkene)_2(acac)$:

$$[RhCl(C_2H_4)_2]_2 + 2Na(acac) \rightarrow 2NaCl + 2(C_2H_5)Rh(acac)$$

C_2F_4 displaces one ethene to give $Rh(C_2H_4)(C_2F_4)(acac)$, as does hexafluorodewarbenzene, whereas other alkenes (e.g. propene, styrene, vinyl chloride) displace both ethenes. Comparison of the structures of two complexes (Figure 2.28) shows that the Rh–C bonds are shorter to tetrafluoroethene, because C_2F_4 is a better π-acceptor, with concomitant strengthening of the Rh–C bond.

NMR spectra show the ethene molecules to undergo a 'propeller' type rotation about the metal–alkene axis: the fluxionality is removed on cooling; such rotation is not observed with coordinated C_2F_4, indicating a higher barrier to rotation, in keeping with the stronger Rh–C bonds [66].

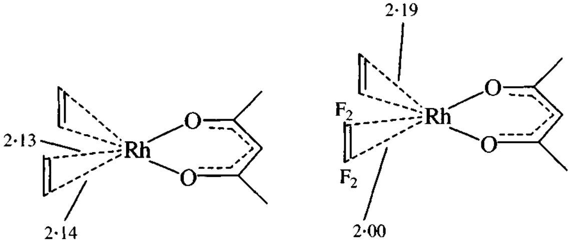


Figure 2.28 The structures of $Rh(acac)(C_2H_4)_2$ and $Rh(acac)(C_2H_4)(C_2F_4)$.

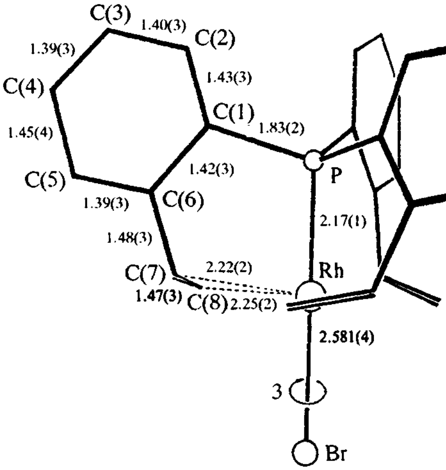


Figure 2.29 The structure of RhBr((*o*-vinylphenyl)$_3$P). (Reproduced with permission from *J. Chem. Soc., Dalton Trans.*, 1973, 2202.)

A number of tertiary phosphine ligands have been synthesized that also contain an alkene linkage capable of coordinating to a metal. A good example of this kind of coordination is formed in the complex of (tri-*o*-vinylphenyl)phosphine (Figure 2.29); with each alkene acting as a two-electron donor, a noble gas configuration is achieved [67].

2.7.4 Isocyanide complexes

Isocyanide complexes [68] can readily be prepared using excess isocyanide as the reducing agent:

$$[RhCl(CO)_2]_2 \xrightarrow[RNC]{exc.} Rh(RNC)_4^+ \xleftarrow[RNC]{exc.} RhCl_3.3H_2O$$

(R, e.g. alkyl, Ph)

In solution the compounds exhibit solvent-dependent colours; in dilute solution in non-polar solvents, planar monomers are present but in more concentrated solutions oligomerization occurs. In the solid state a dimeric structure has been identified (X-ray, Figure 2.30); with R = Ph there is a staggered configuration (Rh–Rh 3.193 Å) but with other isocyanides (R = 4-FC$_6$H$_4$) the configuration is eclipsed.

The weak Rh–Rh bond is taken to occur by d_{z^2}-d_{z^2} overlap.

Like other planar rhodium(I) complexes, Rh(RNC)$_4^+$ undergoes oxidative addition with halogens to form 18-electron rhodium(III) species and also add other small molecules (SO$_2$, NO$^+$) (Figure 2.31).

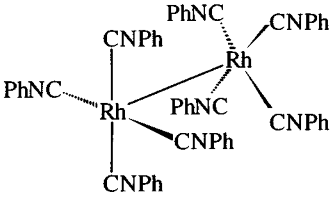


Figure 2.30 The dimeric structure of $[Rh_2(PhNC)_8]^{2+}$ in the solid state.

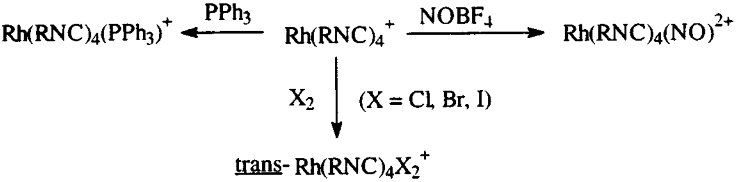


Figure 2.31 Reactions of $[Rh(RNC)_4]^+$.

2.8 Rhodium(II) complexes

Until recently, well-authenticated cases of the rhodium(II) oxidation state were rare, with the exception of the dinuclear carboxylates. They fall into two main classes, although there are other rhodium(II) complexes:

1. paramagnetic complexes ($4d^7$) with bulky phosphines, usually of the type $Rh(PR_3)_2X_2$
2. diamagnetic dinuclear carboxylates, and related dimers.

2.8.1 Phosphine complexes

Reaction of $RhCl_3.3H_2O$ with bulky tertiary phosphines at room temperature or below generally leads to reduction to rhodium(II).

$$RhCl_3.3H_2O \xrightarrow[0-25^\circ C]{PR_3} trans\text{-}RhCl_2(PR_3)_2$$

($PR_3 = P(o\text{-tolyl})_3$, Pcy_3, PBu^t_2R' ($R' = Me, Et, Pr^n$ etc.).

Oxidative cleavage may be used

$$[RhX(Pcy_3)_2]_2 \xrightarrow{X_2} trans\text{-}RhX_2(Pcy_3)_2 \qquad (X = Cl, Br)$$

(Other syntheses are mentioned in section 2.9.5.)

These compounds are paramagnetic ($PR_3 = P(o\text{-tolyl})_3$, $\mu_{eff} = 2.3\,\mu_B$; $PR_3 = Pcy_3$, $\mu = 2.24\,\mu_B$), deeply coloured (usually blue–green) and have IR spectra resembling those of *trans*-$PdCl_2(PR_3)_2$ systems. The structure has been determined for $PR_3 = PPr^i_3$ (Rh–P 2.366 Å, Rh–Cl 2.298 Å) [69].

A more unusual complex is formed by the very bulky tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) [70].

$$[\mathrm{Rh_2(MeCN)_{10}}](\mathrm{BF_4})_4 \xrightarrow{\text{tmpp}} 2[\mathrm{Rh(tmmp)_2}]^{2+} + 4\mathrm{BF_4^-}$$

The complex ion (Figure 2.32) contains Rh_2^+ bound *cis* to two phosphorus atoms (2.216 Å) and more distantly to four oxygens (2.201–2.398 Å), exhibiting a distortion ascribed to the Jahn–Teller effect; it is paramagnetic ($\mu = 1.80\,\mu_B$) and exhibits an ESR spectrum (Figure 2.33) showing rhodium hyperfine coupling as the doublet for $g_{||}$.

The complex reacts with CO reversibly via a series of redox reactions. $\mathrm{Rh(TMPP)_2^{2+}}$ forms adducts with bulky isocyanides RNC (R = $\mathrm{Bu^t}$, $\mathrm{Pr^i}$), retaining the +2 state but changing to a *trans*-geometry (Figure 2.34) with monodentate phosphines (and uncoordinated ethers) (R = $\mathrm{Bu^t}$, $\mu_{\mathrm{eff}} = 2.04\,\mu_B$; $g_\perp = 2.45$, $g_{||} = 1.96$).

2.8.2 Dimers

The second class of rhodium(II) complexes is the dimers [71]. The dimeric

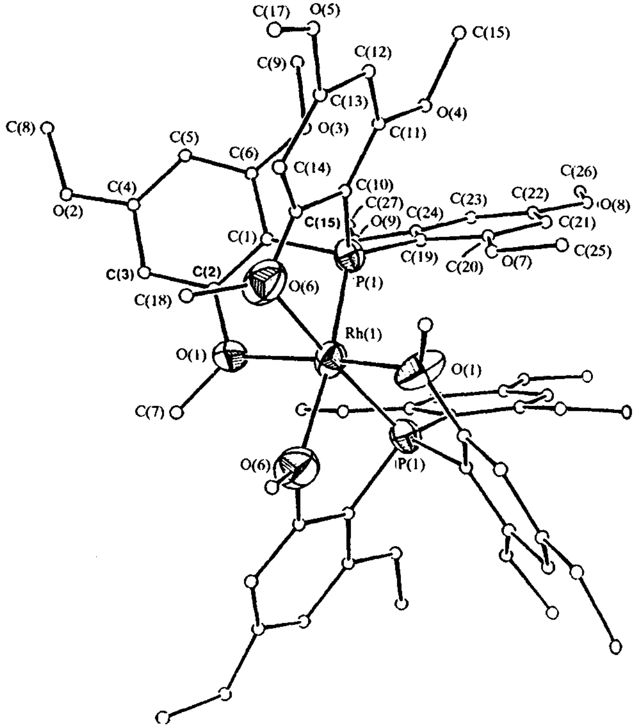


Figure 2.32 The structure of $[\mathrm{Rh(tmpp)_2}]^{2+}$. (Reprinted with permission from *J. Am. Chem. Soc.*, 1991, **111**, 5504. Copyright (1991) American Chemical Society.)

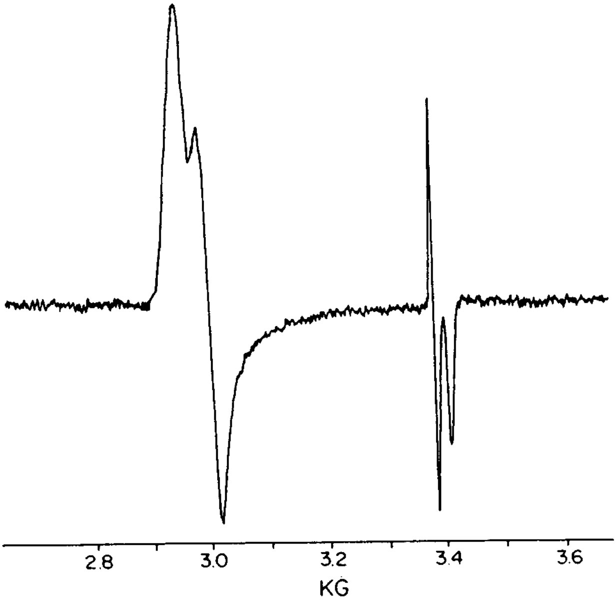


Figure 2.33 The ESR spectrum of $[Rh(tmpp)_2]^{2+}$ in CH_2Cl_2/toluene at 8 K. (Reprinted with permission from *J. Am. Chem. Soc.*, 1991, **111**, 5504. Copyright (1991) American Chemical Society.)

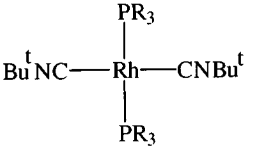
acetate can conveniently be prepared as a green methanol solvate:

$$RhCl_3.xH_2O \xrightarrow[\text{MeCH reflux}]{\text{MeCOOH/MeCOONa}} Rh_2(OCOMe)_4.2MeOH$$

The methanol can be removed by heating gently *in vacuo*. Similar compounds can be made with other carboxylate groups, either by using this method or by heating the acetate with excess carboxylic acid. Treatment of the anhydrous carboxylate with various neutral ligands (L) or anionic donors (X^-) forms $Rh_2(OCOR)_4L_2$ and $[Rh_2(OCOR)_4X_2]^{2-}$, respectively. The colour of the adduct depends on the donor atom in L (or X):

blue to green: oxygen
pink to red: nitrogen
orange to brown–red: phosphorus or sulphur.

These compounds all have the 'lantern' structure shown in Figure 2.35.



$R = 2,4,6\text{-}(MeO)_3C_6H_2$

Figure 2.34 Isocyanide adducts of $[Rh(tmpp)_2]^{2+}$.

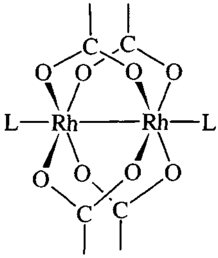


Figure 2.35 The 'lantern' structure adopted by dimeric rhodium(II) carboxylates.

Structural data for many carboxylates (Table 2.3) consistently show the presence of a metal–metal bond around 2.4 Å, shorter than that in rhodium metal (2.7 Å).

There is a slight dependence on the nature of the carboxylate group and upon the axial ligand, but they are not imposed by the steric requirements of the carboxylates. Some points are germane to this:

1. Adducts are formed with hard and soft donors, including π-acids such as CO, PF_3 and PPh_3. DMSO bonds through S for R = Me and Et, but through O when R = CF_3.

Table 2.3 Bond lengths in rhodium(II) carboxylates (Å)

(a) $Rh_2(OCOMe)_4L_2$

L	Rh–Rh	Rh–L
MeOH	2.377	2.286
MeCN	2.384	2.254
H_2O	2.3855	2.310
py	2.399	2.227
Me_2SO	2.406	2.451
$P(OMe)_3$	2.4556	2.437
$P(OPh)_3$	2.445	2.418
PPh_3	2.4505	2.477
PF_3	2.4215	2.340
CO	2.4193	2.091
Cl^-	2.3959	2.585
PhSH	2.4024	2.548
$AsPh_3$	2.427	2.576

(b) $Rh_2(OCOR)_4(H_2O)_2$

R	Rh–Rh	$Rh–OH_2$
Me	2.3855	2.310
CMe_3	2.371	2.295
CF_3	2.394	2.243

2. The long Rh–P bonds in the tertiary phosphine adducts show little dependence upon the tertiary phosphine and are interpreted in terms of a largely σ-component in the Rh–P bond; they are also affected by the strong *trans*-influence of the Rh–Rh bond.
3. ESCA data support a rhodium(II) oxidation state in these compounds. Therefore, the Rh $3d_{5/2}$ binding energy is *c.* 309.2 eV in simple carboxylates, midway between those in typical rhodium(I) complexes (*c.* 308.5 eV) and rhodium(III) complexes (*c.* 310.7 eV) [72].
4. The diamagnetism of all these rhodium(II) compounds indicates spin pairing via a metal–metal bond.
5. The lantern structure is quite stable, unlike certain other Rh_2 dimers. Protonation was formerly claimed to give 'Rh_2^{4+}' aqua ions, but they are believed now to be $[Rh_2(OCOMe)_3]^+$ (aq.) and $[Rh_2(OCOMe)_2]^{2+}$ (aq.) [73].
6. One-electron oxidation to $[Rh_2(OCOMe)_4(H_2O)_2]^+$ leads to an ion (violet to orange, depending on solvent) with a shorter Rh–Rh bond (2.317 Å) than that in the neutral molecule (2.385 Å), suggesting the electron has been removed from an orbital with anti-bonding character.

Unsolvated $[Rh_2(OCOR)_4]_2$ can be obtained by sublimation. The 'lantern' structure is retained with the axial position occupied by oxygens from neighbouring dimer units. The presence of axial ligands has little effect on the Rh–Rh bond; therefore, in $[Rh_2(OCOCF_3)_4]$ Rh–Rh is 2.382 Å compared with 2.394 Å in $[Rh_2(OCOCF_3)_4(H_2O_2)]$ and 2.418 Å in $Rh_2(OCOCF_3)_4(MeCN)_2$ [74].

The assignment of the Rh–Rh stretching frequency in the vibrational spectra of these compounds has been controversial for some 20 years, with ν(Rh–Rh) assigned variously to bands in the 150–170 and 280–350 cm^{-1} regions. Recent resonance Raman studies (Figure 2.36) exciting the metal-based $\sigma \rightarrow \sigma^*$ transition in $Rh_2(OCOMe)_4(PPh_3)_2$ showed enhancement of the symmetric stretching mode, at 289 cm^{-1}.

Isotopic (^2H, ^{18}O) labelling of the carboxylate groups has virtually no effect, as expected, on this band but produces shifts of 6–14 cm^{-1} in bands at 321 and 338 cm^{-1}, showing them to arise from Rh–O stretching [75].

Complexes of thiocarboxylic acids, $Rh_2(SCOR)_4L_2$, similarly adopt the 'lantern' structure. Rh–Rh distances are significantly greater than in the analogous carboxylates ($R = Me_3C$, $L = py$, Rh–Rh 2.514 Å; $R = Ph$, $L = py$, Rh–Rh 2.521 Å; $R = Me_3C$, $L = PPh_3$, Rh–Rh 2.584 Å). Raman studies on $Rh_2(SCOMe)_4L_2$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$, MeCOSH) assign ν(Rh–Rh) to bands in the region of 226–251 cm^{-1}, significantly lower than in the carboxylates, consistent with the longer and weaker Rh–Rh bond [76].

Part of the upsurge in interest in rhodium(II) carboxylates since the early 1970s results from the discovery that they have potential as anti-tumour

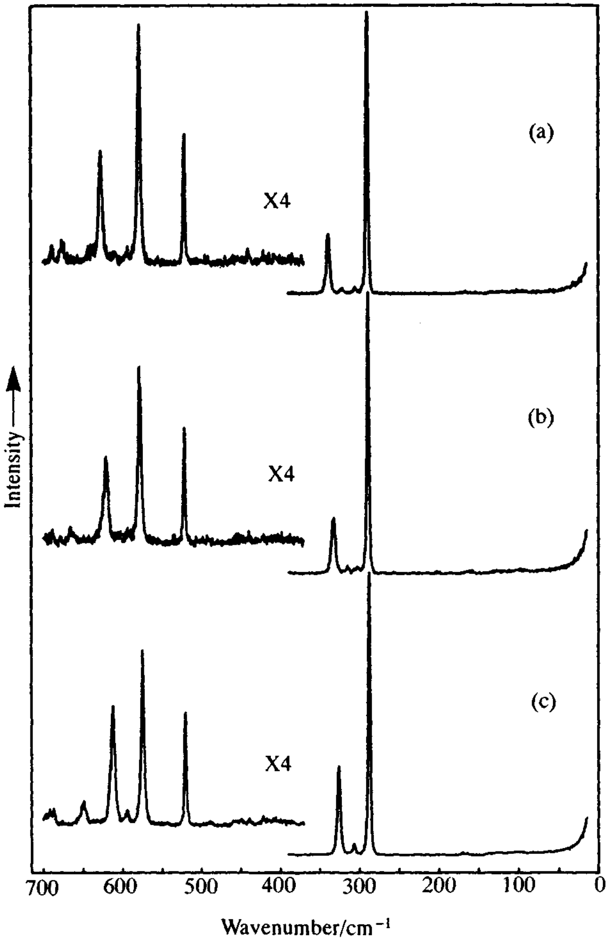


Figure 2.36 Resonance Raman spectra of (a) $Rh_2(^{16}O_2)CMe_4(PPh_3)_2$; (b) $Rh_2(^{18}O_2)CMe_4(PPh_3)_2$; (c) $Rh_2(^{16}O_2)C(CD_3)_4(PPh_3)_2$. Recorded as KCl discs at 80 K, L = 363.8 nm. (Reprinted with permission from *J. Am. Chem. Soc.*, 1986, **108**, 518. Copyright (1986) American Chemical Society.)

agents. The dimers form adducts with many biologically important N-donors but react irreversibly with some compounds containing SH groups. It seems that they may inhibit DNA synthesis by deactivating sulphydryl-containing enzymes [77].

Bonding in the dimers

Several MO schemes are suggested, most with a single bond but differing to some extent on the ordering of the energy levels [78] (Figures 2.37 and 2.38). The most recent results indicate the highest occupied MO (HOMO) is of σ-symmetry, consistent with ESR results on $[Rh_2(OCOR)_4(PR_3)_2]^+$.

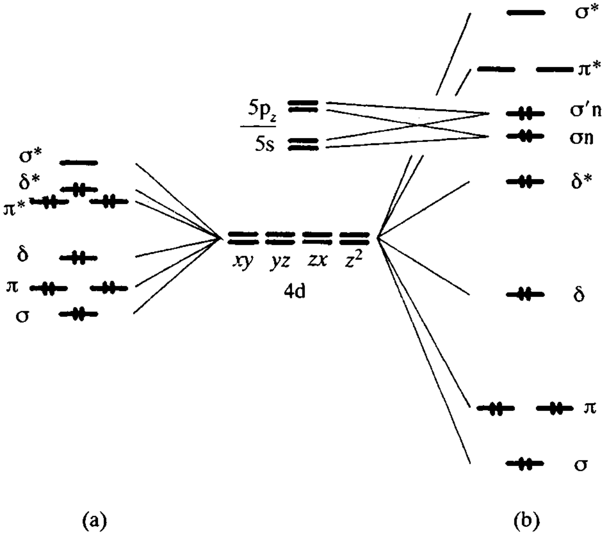


Figure 2.37 Models for the metal–metal bonding in $Rh_2(O_2CR)_4$. (a) corresponds to a single-bond; (b) corresponds to a triple-bond model in which there is a greater interaction between the rhodium 4d orbitals than between the 4d and 5s, 5p manifolds. (Reprinted with permission from *J. Am. Chem. Soc.*, 1981, **103**, 364. Copyright (1981) American Chemical Society.)

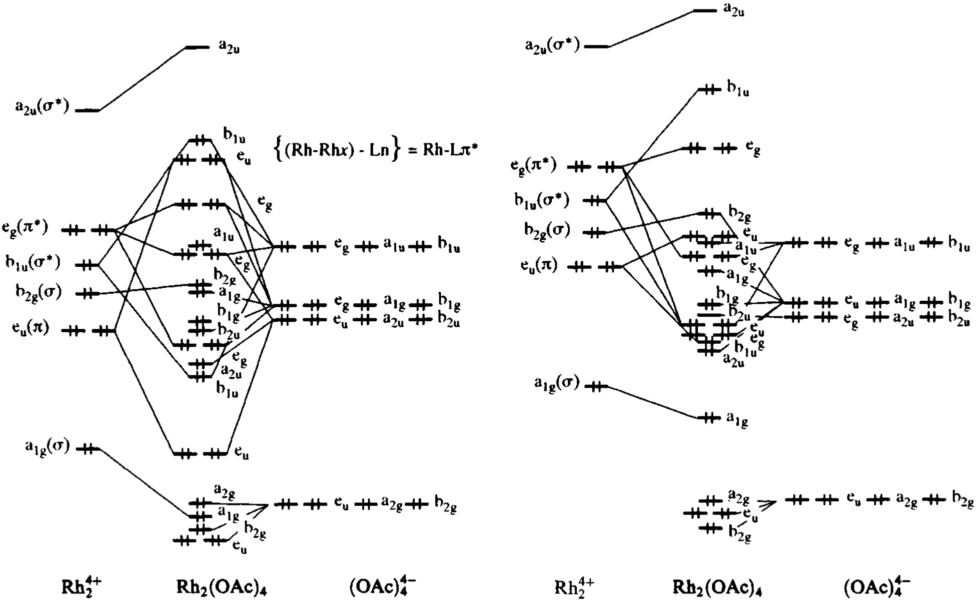


Figure 2.38 The effect of varying the relative energies of the metal and ligand orbitals upon the final molecular orbital scheme for a dimeric rhodium carboxylate. (Reprinted from *Coord. Chem. Rev.*, **50**, 109, 1983, with kind permission from Elsevier Science S.A., P.O. Box 564, 1001 Lausanne, Switzerland.)

In the MO scheme the rhodium atoms use their $d_{x^2-y^2}$ orbitals to form the Rh–O bonds, the remaining 4d orbitals are used to form four pairs of bonding and anti-bonding MOs (σ, δ and π) (Figure 2.37a).

The ligands interact with the two orbitals of σ-symmetry modifying the ordering somewhat (Figure 2.37b). As has been pointed out, altering the relative positions of the metal orbitals relative to those of the carboxylates affects the final scheme considerably (Figure 2.38).

Other compounds with the lantern structure include the acetamidates $Rh_2(MeCONH)_4L_2$ and the mixed-valence anilinopyridinate $Rh_2(ap)_4Cl$ (Figure 2.39), which has an unusual ESR spectrum in that the electron is localized on one rhodium [79].

Bridging ligands are not essential for the stability of dimers. Reduction of $[Rh(H_2O)_5Cl]^{2+}$ is believed to give a dimer $[Rh_2(H_2O)_{10}]^{2+}$.

Extended reflux of a MeCN solution of $Rh_2(OCOMe)_4$ with excess $Et_3O^+BF_4^-$ leads to successive replacement of the acetates [80]:

$$Rh_2(OCOMe)_4 \rightarrow [Rh_2(OCOMe)_2(MeCN)_6]^{2+} \rightarrow [Rh_2(MeCN)_{10}]^{4+}$$

$[Rh_2(MeCN)_{10}]^{4+}$ has a staggered structure (minimizing inter-ligand repulsions) with a Rh–Rh distance of 2.624 Å (presumably corresponding to a Rh–Rh single bond uninfluenced by bridging ligands (Figure 2.40).

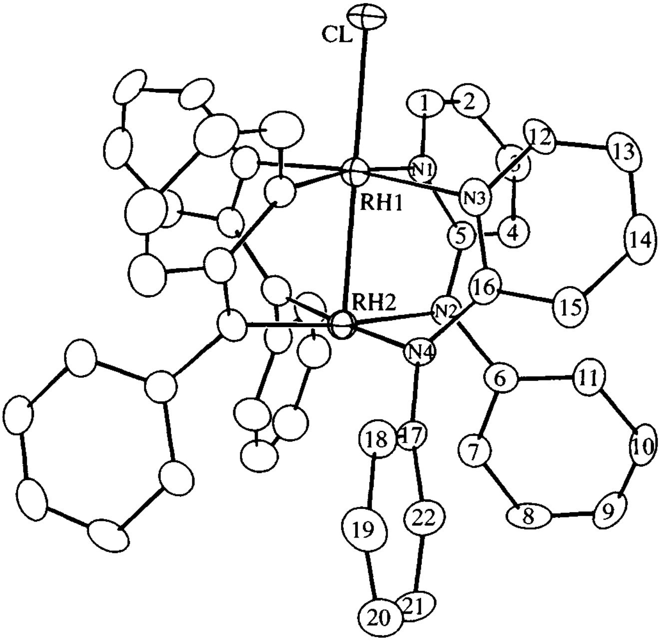


Figure 2.39 The 'lantern' structure of the dimeric rhodium antipyrine complex $Rh_2(ap)_4Cl$. (Reprinted with permission from *Inorg. Chem.*, 1988, **27**, 3783. Copyright (1988) American Chemical Society.)

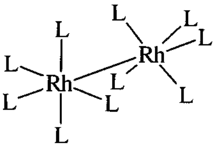


Figure 2.40 The staggered structure of the dimeric ion $[Rh_2(MeCN)_{10}]^{2+}$.

Reaction of $Rh_2(OCOR)_4$ with dimethylglyoxime leads to a non-bridged dimer [81].

$$Rh_2(OCOMe)_4 \xrightarrow{DMGH} Rh_2(DMG)_4$$

The bis(PPh_3) adduct has a long Rh–Rh bond of 2.936 Å, whereas in the 'mixed' dimer $Rh_2(OCOMe)_2(DMG)_2(PPh_3)_2$ where only two acetates bridge, Rh–Rh is 2.618 Å (Figure 2.41).

2.8.3 *Other complexes*

Photolysis of the rhodium(III) complex of octaethylporphyrin gives a rhodium(II) dimer that readily undergoes addition reactions to afford rhodium(III) species (Figure 2.42).

With more bulky porphyrins like TMP, a stable low-spin monomer Rh(TMP) can be isolated ($g_\perp = 2.65$, $g_{||} = 1.915$), which forms a paramagnetic CO adduct.

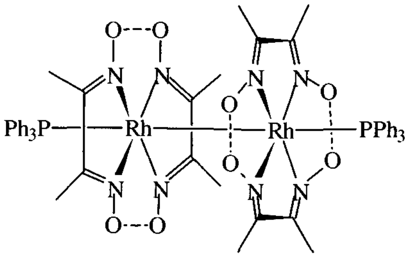


Figure 2.41 A dimeric non-bridged rhodium dimethylglyoxime complex (for clarity the hydrogen atoms in the hydrogen bonds are not shown).

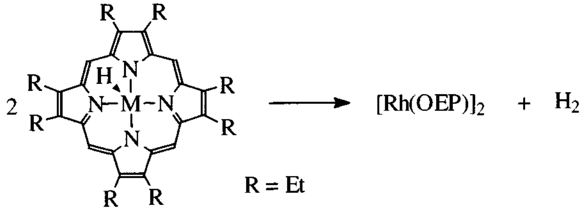


Figure 2.42 Synthesis of a dimeric rhodium(II) octaethylporphyrin complex.

A number of rhodium(III) complexes of thiacrown ligands can be reduced to give rhodium(II) species identifiable in solution. Thus controlled potential electrolysis of $Rh(9S_3)_2^{3+}$ ($9S_3$ = 1,4,7-trithiacyclononane) gives $Rh(9S_3)_2^{2+}$ ($g_1 = 2.085$, $g_2 = 2.042$, $g_3 = 2.009$) [82].

2.9 Rhodium(III) complexes

A considerable number of rhodium(III) complexes exist. Their stability and inertness are as expected for a low-spin d^6 ion; any substitution leads to a considerable loss of ligand-field stabilization.

2.9.1 *Complexes of O-donors*

The yellow acetylacetonate contains octahedrally coordinated rhodium (Rh–O 1.992 Å; O–Rh–O 95.3°) [83].

$$Rh(NO_3)_3 \xrightarrow[\text{pH 7}]{\text{acac}^-} Rh(acac)_3$$

The corresponding tri- and hexa-fluoroacetylacetonates may be similarly prepared. The stability of the acetylacetonate is such that not only can it be resolved on passage through a column of D-lactose, but the enantiomers retain their integrity on nitration or bromination.

Extended refluxing of hydrated $RhCl_3$ with excess oxalate leads to the tris complex, the potassium salt crystallizing as orange–red crystals with Rh–O 2.000–2.046 Å.

$$RhCl_3.3H_2O \xrightarrow[\text{reflux, 6 h}]{\text{aq. } K_2C_2O_4 \text{ (6 mol)}} K_3Rh(C_2O_4)_3.4\tfrac{1}{2}H_2O$$

$Rh(C_2O_4)_3^{3-}$ was resolved by Werner as the strychnine salt but other ions, such as $Coen_3^{3+}$ and $Niphen_3^{3+}$, have been used more regularly for this [84].

The dinuclear rhodium(II) acetate is described in section 2.8.2; the dinuclear structure is retained on one-electron oxidation, but when ozone is used as the oxidant, a compound with a trinuclear Rh_3O core is formed, analogous to those formed by Fe, Cr, Mn and Ru. (It can also be made directly from $RhCl_3$.)

$$RhCl_3.3H_2O \xrightarrow[\text{2. } ClO_4^-]{\text{1. MeCOOAg}} [Rh_3O(O_2CMe)_6(H_2O)_3]^+ClO_4^-$$

$$Rh_2(O_2CMe)_4 \xrightarrow[\text{2. } ClO_4^-]{\text{1. } O_3\text{/boiling MeCOOH}} [Rh_3O(O_2CMe)_6(H_2O)_3]^+ClO_4^-$$

Rhodium forms an EDTA complex isomorphous with the corresponding ones of Ru, Fe, Ga and Cr. In $Rh(EDTAH)(H_2O)$ one carboxylate is protonated and thus the acid is pentadentate, the water molecule completing the octahedron (Figure 2.43).

Next Page

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 $Ni(CO)_4$. 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 CO_2 and also removal of nitrogen oxides as N_2 (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 CeO_2 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 H_3O^+ 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 ($PtAs_2$).

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 $PdCl_4^{2-}$ or $PtCl_6^{2-}$ 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 MX_3 compounds are not genuine M^{3+} species but are diamagnetic, with equal amounts of M^{2+} and M^{4+}. PtF_5, however, is a platinum(V) compound.

3.3.1 Palladium halides

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

$$Pd \xrightarrow[500^\circ C\ \text{reflux}]{F_2} PdF_3 \xrightarrow{SeF_4\ \text{or}\ SF_4} PdF_2$$

$$Pd \xrightarrow[>260^\circ C]{Cl_2} PdCl_2$$

$$Pd \xrightarrow{HBr/Br_2} PdBr_2$$

$$PdCl_2 \xrightarrow[\text{sealed tube } 140^\circ C]{5\%\ HI} PdI_2$$

$$PdF_3 \xrightarrow[300^\circ C]{F_2} PdF_4$$

$$Pd \xrightarrow[900-1700\ Pa]{\text{atomic F}} PdF_6$$

PdF_2 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 $\mu_{eff} \sim 2.0\,\mu_B$, 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. $PdCl_2$ exists in well defined α- and β-forms [16] (as well as a γ-form); the former has a $PdCl_{4/2}$

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.

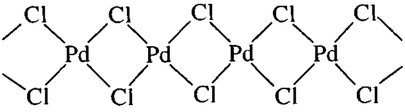


Figure 3.1 The chain structure of α-$PdCl_2$.

chain structure (Figure 3.1) while the β-form, synthesized by subliming the α form at 430–460°C) is Pd_6Cl_{12}, similar to the platinum analogue.

$PdBr_2$ also has a chain structure, but puckered, unlike α-$PdCl_2$, with planar coordination (somewhat irregular: Pd–Br 2.34, 2.57 Å). PdI_2 has three modifications, all made starting from the black γ-form precipitated from aqueous $PdCl_2$ reacting with HI at 140°C; it is traditionally used, because of its insolubility, in the gravimetric determination of palladium. The α-form of PdI_2 has a structure with tetragonal PdI_4 units forming side-by-side chains (Pd–I 2.60 Å) while in the β-form there are planar Pd_2I_6 units (Pd–I 2.61–2.62 Å) cross-linked with two distant iodines (3.29, 3.49 Å) to give distorted 6-coordination.

PdF_3 is really $Pd^{2+}PdF_6^{2-}$; both palladiums have an octahedral environment (Pd^{2+}–F 2.17 Å; Pd^{4+}–F 1.90 Å); like PdF_2, 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 PdF_3 (genuine alkali metal salts of PdF_6^{3-} do exist) [17].

PdF_4 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 Pd_6F_{24} 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 PdX_6^{2-} exist (cf. Ir).

PdF_6 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 PdF_5.

3.3.2 *Platinum halides*

Syntheses of platinum halides [20] include

$$Pt \xrightarrow[500^\circ C]{Cl_2} PtCl_2$$

$$Pt \xrightarrow{Br_2} PtBr_3 + PtBr_4 \xrightarrow{250^\circ C} PtBr_2$$

$$H_2PtBr_6.xH_2O \xrightarrow[180-280^\circ C]{heat} PtBr_2$$

$$\mathrm{Pt} \xrightarrow[525^\circ\mathrm{C},\ \textit{in vacuo}]{\mathrm{I_2}} \alpha\text{-}\mathrm{PtI_2}$$

$$\mathrm{K_2PtI_6} \xrightarrow[\text{sealed ampoule}]{240^\circ\mathrm{C}} \beta\text{-}\mathrm{PtI_2}$$

$$\mathrm{Pt} \xrightarrow[400-600^\circ\mathrm{C}]{\mathrm{Cl_2}/\text{sealed tube}} \mathrm{PtCl_3}$$

$$\mathrm{PrBr_2} \xrightarrow[125^\circ\mathrm{C}]{\mathrm{Br_2},<3\ \text{atm}} \mathrm{PtBr_3}$$

$$\mathrm{Pt} \xrightarrow[\text{sealed tube, }160^\circ\mathrm{C}]{\mathrm{KI/I_2/H_2O}} \mathrm{PtI_3}$$

$$\mathrm{Pt} \xrightarrow[140^\circ\mathrm{C}]{\text{exc. }\mathrm{KI/I_2/H_2O}} \alpha\text{-}\mathrm{PtI_4}$$

$$\mathrm{Pt} \xrightarrow[\text{sealed tube, }350^\circ\mathrm{C}]{\mathrm{SO_2Cl_2}} \mathrm{PtCl_4}$$

$$\mathrm{PtCl_2} \xrightarrow[<200^\circ\mathrm{C}]{\mathrm{F_2}} \mathrm{PtF_4}$$

$$\mathrm{Pt} \xrightarrow[150^\circ\mathrm{C}]{\mathrm{Br_2}} \mathrm{PtBr_4}$$

$$\mathrm{PtCl_2} \xrightarrow[350^\circ\mathrm{C}]{\mathrm{F_2}} \mathrm{PtF_5}$$

$$\mathrm{Pt\ (hot\ wire)} \xrightarrow[\text{2. condense}]{\text{1. }\mathrm{F_2}} \mathrm{PtF_6}$$

PtF_2 is unknown, presumably unstable with respect to the disproportionation

$$2\mathrm{PtF_2} \rightarrow \mathrm{Pt} + \mathrm{PtF_4}$$

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 β-$PdCl_2$ (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 β-$PtCl_2$, and thus believed to be Pt_6Br_{12}, while β-PtI_2 is isomorphous with β-PdI_2 [20].

All the trihalides are mixed valence compounds. PtF_3 is isostructural with PdF_3· PtX_3 (X = Cl, Br, 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.

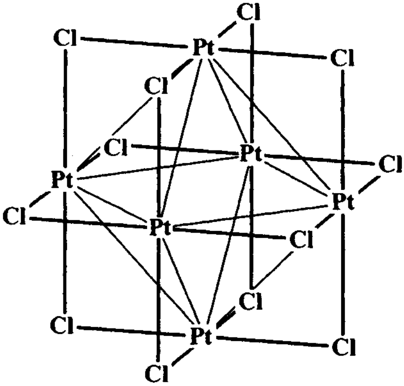


Figure 3.2 The structure of β-$PtCl_2(Pt_6Cl_{12})$. (Reproduced with permission from S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan Press Ltd, 1975, p. 109.)

$PtCl_3$ and $PtBr_3$ (Figure 3.3) are isomorphous and contain both Pt_6X_{12} clusters and $[PtX_2X_{4/2}]_\infty$ 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.

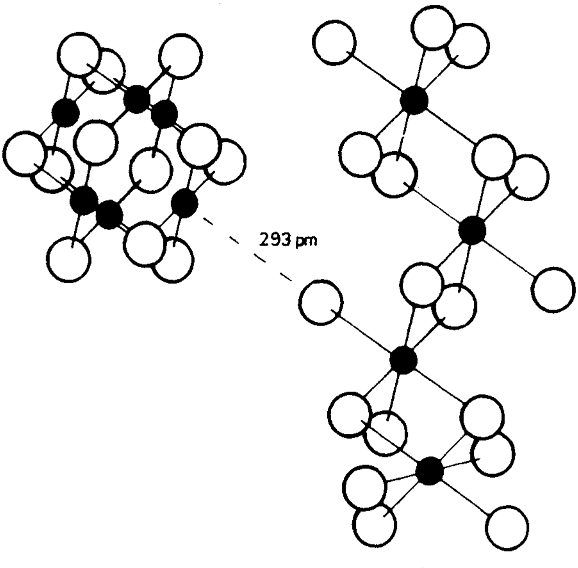


Figure 3.3 The structure of $PtBr_3$, showing the Pt_6Br_{12} and ${}^1_\infty[PtBr_2Br_{4/2}]$ structural units. (Reproduced with permission from *Transit. Met. Chem.*, 1975/6, **1**, 45.)

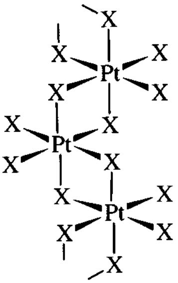


Figure 3.4 The chain structure adopted by PtX_4 in the solid state.

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*-$[PtCl_4(H_2O)_2].3H_2O$ and *fac*-$[PtCl_3(H_2O)_3]Cl.\frac{1}{2}H_2O$ [25].

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

$$2PtF_5 \rightarrow PtF_4 + PtF_6$$

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 (Pt–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:

$$O_2 + PtF_6 \rightarrow O_2^+PtF_6^-$$

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.

$$PdCl_2 \xrightarrow[HCl]{MCl} M_2PdCl_4 \text{ (red–brown) (M, e.g. K, NH}_4\text{) (Pt similarly)}$$

$$K_2PdCl_4 \xrightarrow{Br^-} K_2PdBr_4 \text{ (dark red)}$$

$$K_2PtCl_4 \xrightarrow{NaBr/HBr} K_2PtBr_4 \text{ (brown)}$$

$$K_2PtCl_4 \xrightarrow[KI]{exc.} K_2PtI_4 \text{ (black)}$$

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

Ion	Cation	M–X (Å)	Ion	$\nu_1(A_{1g})$	$\nu_2(B_{1g})$	$\nu_6(E_u)$
$PdCl_4^{2-}$	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 $(MeNH_3)_4Pt_3I_{11}$)	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 $(MeNH_3)_4Pt_3I_{11}$, a mixed-valence compound with PtI_4^{2-}, PtI_6^{2-} and $Pt_2I_6^{2-}$ ions all present (K_2PtI_4 has not definitely been confirmed) [27].

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

$$PdF_3 + 2AF + BF \xrightarrow[3\,\text{kbar}]{400^\circ\text{C}} A_2BPdF_6$$

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

The beige to green solids have the elpasolite structure. Magnetic measurements confirm the $t_{2g}^6e_g^1$ 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', $(H_3O)_2PtCl_6.xH_2O$ ($x \sim 2$), 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 β-$PtCl_2$ at 350°C, before final decomposition to platinum around 500°C [29]. The Pt–Cl bond length is 2.323 Å in $(H_3O)_2PtCl_6$ [30].

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

$$A_2PdCl_6 \xrightarrow[200-300^\circ\text{C}]{F_2} A_2PdF_6 \qquad (A = \text{K to Cs})$$

$$M \xrightarrow[2.\,\text{ACl}]{1.\,\text{aqua regia}} A_2MCl_6 \qquad (M = \text{Pd, Pt})$$

$$K_2PtCl_6 \xrightarrow{KHF_2\,\text{melt}} K_2PtF_6$$

$$A_2PdBr_4 \xrightarrow{Br_2} M_2PdBr_6$$

$$PdCl_6^{2-} \xrightarrow[\text{CsI}]{\text{exc.}} Cs_2PdI_6$$

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

$$PtCl_4 \xrightarrow{HCl} H_2PtCl_6 \xrightarrow{ACl} M_2PtCl_6 \qquad (A = K \text{ to } Cs)$$

$$Pt \xrightarrow[2.\ A^+]{1.\ HBr/Br_2} A_2PtBr_6$$

$$H_2PtCl_6 \xrightarrow{exc.\ AI} A_2PtI_6$$

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].

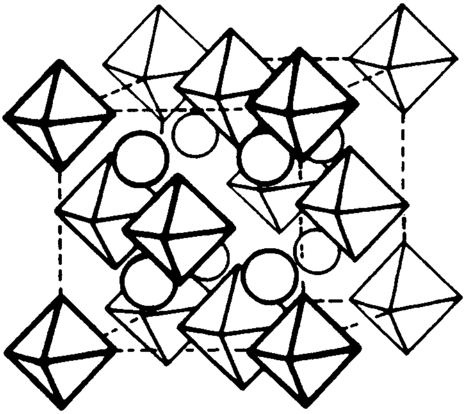


Figure 3.5 The crystal structure of K_2PtCl_6. (Reproduced from A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, 1975, p. 387, by permission of Oxford University Press.)

Table 3.5 Comparing bond lengths in MF_6^{n-} (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]

$$PdF_4 \xrightarrow[HF]{KrF_2/O_2 \text{ or } NaF} X^+PdF_6^- \qquad (X = O_2, Na)$$

$$Pd \xrightarrow[320°C, 60\,000 \text{ psi}]{F_2/O_2} O_2^+PdF_6^-$$

$$PtF_6 \xrightarrow{O_2} O_2^+PtF_6^- \xrightarrow[IF_5]{MF} M^+PtF_5^- \qquad (M = K \text{ to } Cs)$$

The magnetic moment for PtF_6^- (K^+ salt) is 0.87 μ_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^{n-} 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):

$$PtBr_6^{2-} \xrightarrow{Cl^-} PtBr_5Cl^{2-} \rightarrow cis\text{-}PtBr_4Cl_2^{2-} \rightarrow fac\text{-}PtBr_3Cl_3^{2-}$$

$$\rightarrow cis\text{-}PtBr_2Cl_4^{2-} \rightarrow PtBrCl_5^{2-} \rightarrow PtCl_6^{2-}$$

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^{n-} (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^-

$$PtBrCl_5^{2-} \xrightarrow{Br^-} trans\text{-}PtBr_2Cl_4^{2-} \rightarrow mer\text{-}PtBr_3Cl_3^{2-} \quad \text{etc.}$$

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

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

Spectra of *trans*-$Pt^{35}Cl_2F_4^{2-}$ 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).

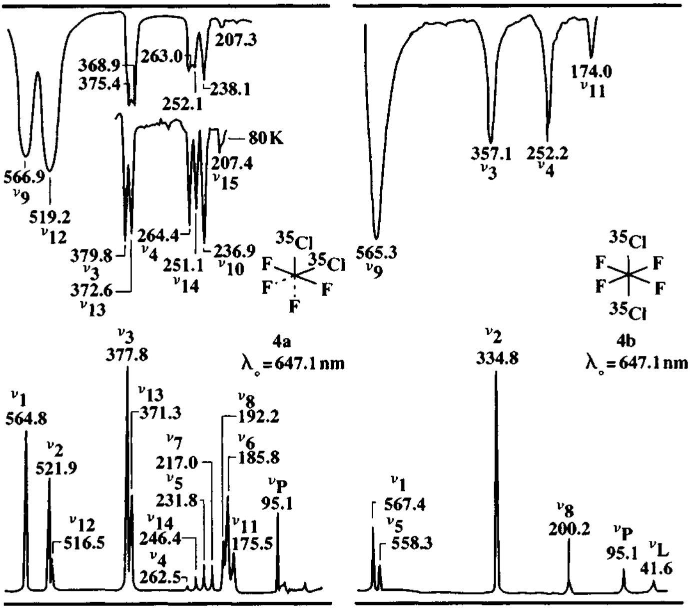


Figure 3.6 IR (upper) and Raman (lower) spectra of $Cs_2[Pt^{35}Cl_2F_4]$: *cis*-isomer on the left; *trans*-isomer on the right. (Reproduced with permission from *Z. Naturforsch., Teil B,* 1989, **44**, 619.)

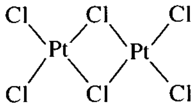


Figure 3.7 The dimeric structure of $[Pt_2Cl_6]^{2-}$.

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 (*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 (*trans* to F) and 2.292–2.303 Å (*trans* to Cl) in the *mer*-isomer [35].

The $M_2X_6^{2-}$ salts are the simplest binuclear complexes [36]

$$MCl_4^{2-} \xrightarrow[H_2O]{Ph_3MeAsCl} (Ph_3MeAs)_2M_2Cl_6 \qquad (M = Pd, Pt)$$

$$MCl_4^{2-} \xrightarrow[H_2O]{cyclo\text{-}C_3H_7C_3^+Cl^-} (cyclo\text{-}C_3H_7C_3)_2M_2Cl_6$$

$$MBr_2 \xrightarrow[H_2O]{Et_4NBr} (Et_4N)_2M_2Br_6$$

$$MI_2 \xrightarrow[\text{e.g. EtOH}]{Et_4NI} (Et_4N)_2M_2I_6$$

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

Typical bond lengths in $Pd_2Cl_6^{2-}$ are Pd–Cl 2.27 Å (terminal) and 2.32 Å (bridge) with Pd–Pd 3.41 Å and in $Pd_2Br_6^{2-}$ Pd–Br 2.398–2.405 Å (terminal) and 2.445–2.452 Å (bridge).

Dinuclear platinum(IV) complexes have recently been reported:

$$PtX_6^{2-} \xrightarrow[\text{heat}]{CF_3CO_2H} Pt_2X_{10}^{2-} \qquad (X = Cl, Br)$$

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 $PdH_{0.03}$, a two-phase region up to $PdH_{0.56}$ after which the β-phase becomes the sole species. The greatest H : Pd ratio obtainable is ~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]

$$\mathrm{AH + Pd\,sponge} \xrightarrow[20\,\mathrm{kbar},\,400^\circ\mathrm{C}]{\mathrm{H_2}} \mathrm{A_2PdH_4} \qquad (\mathrm{A = Rb, Cs})$$

$$\mathrm{AH + Pd\,sponge} \xrightarrow[70\,\mathrm{kbar},\,300-350^\circ\mathrm{C}]{\mathrm{H_2}} \mathrm{A_3PdH_5} \qquad (\mathrm{A = K, Rb, Cs})$$

Na_2PdH_4, A_2PtH_4 (M = 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 (M = 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 $Pd(NO_3)_2$ 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 M^{2+}(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 $Pd^{2+}(S_2^{2-})$ in a distorted pyrite structure (4-coordinate PdPd–S 2.30 Å) confirming the preference for the divalent state for

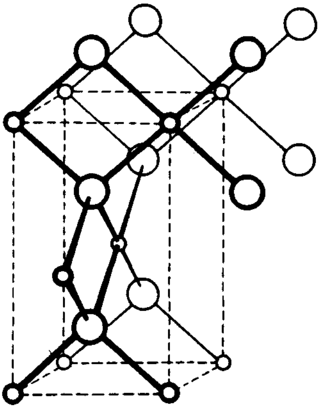


Figure 3.8 The structure of PdO and PtO. (Reproduced from A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, 1975, p. 446, by permission of Oxford University Press.)

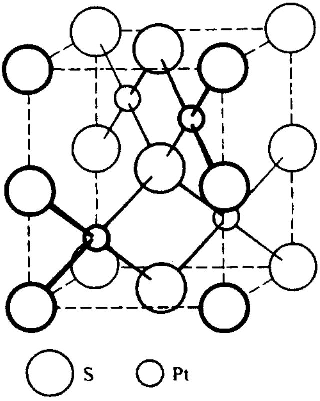


Figure 3.9 The structure of PtS. (Reproduced from A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, 1975, p. 661, by permission of Oxford University Press.)

palladium. Other phases like $Pd_{2.2}S$, 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 (M = Pd, 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

$$PdO \xrightarrow{HClO_4} Pd(H_2O)_4^{2+}$$

$$PtCl_4^{2-} \xrightarrow{AgClO_4} Pt(H_2O)_4^{2+}$$

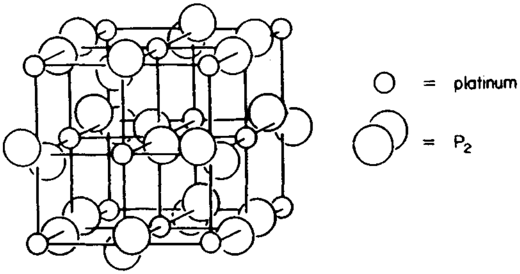


Figure 3.10 The structure of PtP_2. (Reproduced with permission from S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan Press Ltd, 1975, p. 111.)

Hydrated palladium perchlorate has been isolated as brown needles of $Pd(H_2O)_4(ClO_4)_2$ by first dissolving palladium sponge in concentrated HNO_3, adding 72% $HClO_4$, evaporating until it fumes strongly and then crystallizing. $Pd(NO_3)_2(H_2O)_2$ 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.

$$Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5) \xrightarrow{PR_3} Pd(PR_3)_2$$

($R = Bu^t$, cy; $PR_3 = PPhBu^t_2$)

$$trans\text{-}PtCl_2(Pcy_3)_2 \xrightarrow{Na/Hg} Pt(Pcy_3)_2$$

$$[\text{2-methylallyl}\,PdCl]_2 \xrightarrow{\text{exc.}\,PR_3} Pd(PR_3)_n$$

($PR_3 = PMe_3$, PMe_2Ph, PBu^n_3 ($n = 4$); $PR_3 = Pcy_3$, PPr^i_3, Pbz_3 ($n = 3$); $PR_3 = PBu^t_2Ph$ ($n = 2$))

$$cis\text{-}PtCl_2(PPh_2CF_3)_2 \xrightarrow[NaBH_4]{PPh_2CF_3} Pt(PPh_2CF_3)_3$$

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

$$M(PR_3)_4 \xrightarrow[in\ vacuo]{70^\circ C} M(PR_3)_3 \qquad (M = Pd, Pt;\ R = Bu, Et)$$

$$M(PPr^i_3)_3 \xrightarrow[in\ vacuo]{heat} M(PPr^i_3)_2 \qquad (M = Pd, Pt)$$

Tetrahedral structures have been established for $Pd(PPh_3)_4$ (rather long Pd–P bonds at 2.443 Å), $Pd[P(CH_2OH)_3]_4$ (Pd–P 2.321 to 2.326 Å), $Pt(PF_3)_4$ (electron diffraction: Pt–P 2.229 Å), $Pd[P(C{\equiv}CPh)_3]_4$, $Pt(PEt_3)_4$ and $Pt(PMe_2Ph)_4$ [44]. Trigonal planar structures are found for $Pt(Pcy_3)_3$, $Pd(PPh_3)_3$ (Pd–P 2.307–2.322 Å) and $Pt(PPh_3)_3$ (Pt–P 2.262–2.271 Å) [45] and essentially linear 2-coordination for $M(PBu^t_2Ph)_2$ (M = Pd, Pt; M–P 2.285 and 2.252 Å, respectively), $M(Pcy_3)_2$ (Pd–P 2.26 Å, Pt–P 2.231 Å) and $Pd(PBu^t_3)_2$ (Pd–P 2.285 Å). The last named has a P–Pd–P angle of 180° while the PBu^t_2Ph complexes are virtually linear but with some short metal *ortho*-hydrogen contacts. Curiously, the Pcy_3 complexes have

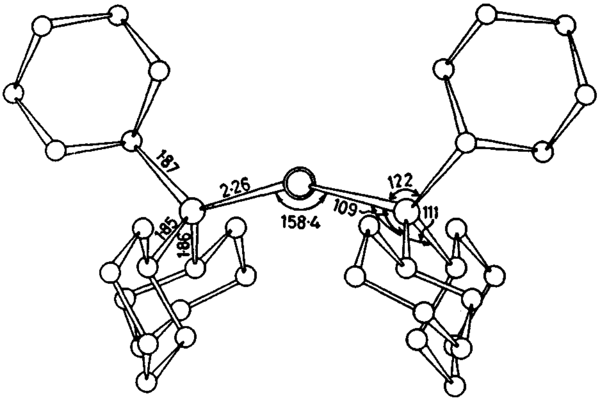


Figure 3.11 The structure of $Pd(Pcy_3)_2$. (Reproduced with permission from *J. Chem. Soc., Chem. Commun.*, 1974, 400.)

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

As expected, the Pt–P bond increases from 2.231 Å in the 2-coordinate $Pt(Pcy_3)_2$ to 2.303 Å in 3-coordinate $Pt(Pcy_3)_3$. (Similarly in $Pd(PPh_3)_n$ ($n = 3, 4$), from 2.31 Å ($n = 3$) to 2.443 Å ($n = 4$).)

Most of these compounds are solids (though a few such as $Pt(PEt_3)_3$, $Pt(PBu^n_3)_3$ and $Pt(PF_3)_4$ 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 $M(PR_3)_n$ complexes isolated in the solid state (S) and detected in solution (✓)

PR_3	Cone angle (°)	PtL_4	PtL_3	PtL_2	PdL_4	PdL_3	PdL_2
PF_3	104	S					
$P(OEt)_3$	109	S✓	X				
PMe_3	118	S✓	X		S✓	X	
PMe_2Ph	122	S✓			S✓	X	
PEt_3	132	S✓	S✓	X	S✓	✓	
PBu^n_3	132	S✓	S✓		S✓	✓	
$PMePh_2$	136	S✓			S✓		
PPh_3	145	S	S✓		S✓	S✓	S
$P(o\text{-tolyl})_3$	145	X	S✓				S✓
PPr^i_3	160		S✓	S✓		✓	✓
$P(O\text{-}o\text{-tolyl})_3$	141		S✓	X			
Pbz_3	165		S✓	X		✓	
PBu^t_2Ph	170		X	S✓		X	S✓
Pcy_3	170		S✓	S✓		✓	S✓
PBu^t_3	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 $Pt(PR_3)_4$, 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; $Ni(Pcy_3)_3$ does not dissociate, while $M(Pcy_3)_2$ (M = Pd, Pt) is stable, the reverse of what would be expected on steric grounds. Similarly with P(*o*-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^i_3 can satisfy the electron demand of the metal better than aryl phosphines such as P(O-*o*-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 $Pt(Pcy_3)_3$ from solution at −15°C (only $Pt(Pcy_3)_2$ is detected in solution above 0°C). Corresponding palladium and platinum complexes generally resemble each other closely, but there are differences; $Pd(PPh_2Me)_4$ does not dissociate while the platinum analogue does. $Pd(PBu^t_2Ph)_2$ binds oxygen reversibly, the platinum analogue binds irreversibly; PtL_2 (L = PPr^i_3, Pcy_3, PBu^t_2Ph) 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 $Pt(QBu_3)_4$ (Q = As, Sb) and $Pt(QPh_3)_4$ have been made, but they have been the subjects of few studies.

Compounds $M(PPh_3)_2$ (M = Pd, Pt) have been postulated as kinetic intermediates but controversy has surrounded their isolation. It seems some '$M(PPh_3)_2$' species reported could have been $M(PPh_3)_2L$ (L, e.g. H_2,

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

	d^{10}–d^9s	d^9s–d^9p	d^{10}–d^9p^1
Ni	−1.8	3.52	1.72
Pd	0.81	3.42	4.23
Pt	0.76	4.04	3.28

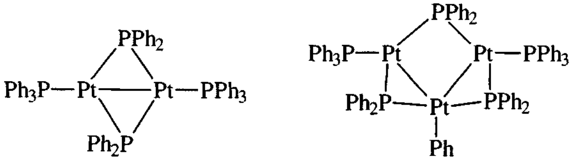


Figure 3.12 Complexes produced by refluxing solutions of $Pt(PPh_3)_4$.

N_2, C_2H_4) or internally metallated species. Reactions such as extended refluxing of $Pt(PPh_3)_4$ in benzene yields clusters [49] (Figure 3.12).

Recently, however, $Pd(PPh_3)_2$ has been reported to result from reduction of palladium(II) complexes as a very reactive yellow solid [50]:

$$Pd(C_3H_5)(PPh_3)_2^+ \xrightarrow{Ph_2MeSiLi} Pd(PPh_3)_2$$

Electrochemical reduction of *cis*-$PtCl_2(PR_3)_2$ (R = Ph, Et) generates very reactive $Pt(PR_3)_2$ species [51] (though it has been suggested that corresponding palladium compounds may be anionic, e.g. $Pd(PR_3)_2Cl_2^{2-}$)

$$Pt(PR_3)_2Cl_2 \xrightarrow{2e^-} Pt(PPR_3)_2 + 2Cl^-$$

They can be trapped by reactive molecules

$$Pt(PEt_3)_2 \xrightarrow[X=Cl,CN]{PhX} trans\text{-}Pt(Ph)X(PEt_3)_2$$

UV irradiation of $Pt(PEt_3)_2(C_2O_4)$ under a dihydrogen atmosphere yields a hydride by trapping [52]:

$$Pt(PEt_3)_2C_2O_4 \xrightarrow{h\nu} Pt(PEt_3)_2 + 2CO_2 \xrightarrow{H_2} trans\text{-}PtH_2(PEt_3)_2$$

Thermolysis of *cis*-$PtH(CH_2CMe_3)(cy_2PC_2H_2Pcy_2)$ at 45–80°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.

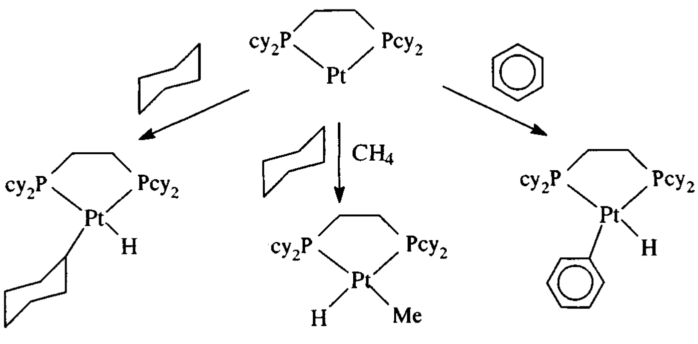


Figure 3.13 Addition reactions of $Pt(cy_2PCH_2CH_2Pcy_2)$.

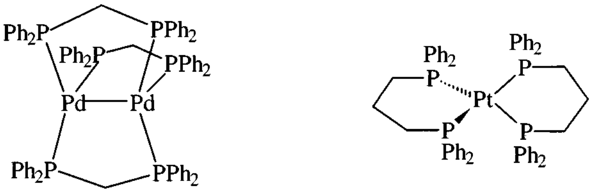


Figure 3.14 Zerovalent complexes of polydentate phosphines.

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

$$Pd_2Cl_2(dppm)_2 \xrightarrow[\text{exc. dppm}]{NaBH_4} Pd_2(dppm)_3$$

$$PtCl_2(cod) \xrightarrow{\text{dppp}} PtCl_2(dppp) \xrightarrow[NaBH_4]{\text{dppp}} Pd(dppp)_2$$

Their structures are shown in Figure 3.14.

3.6.2 Reactions of $Pt(PPh_3)_n$ and related species

$Pt(PPh_3)_n$ ($n = 3$, 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 $Pt(PPh_3)_2$. (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 $Pt(PPh_3)_2Z$ ($Z = \eta^2\text{-}O_2$, $\eta^2\text{-}C_3H_4$, $\eta^2\text{-}CS_2$) (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 $Pt(PPh_3)_2O_2$ (73.2 eV) to be nearer to that in $Pt(PPh_3)_2Cl_2$ (73.4 eV) rather than $Pt(PPh_3)_4$ (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*-$Pt(PPh_3)_2X_2$ ($X = Br$, 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).

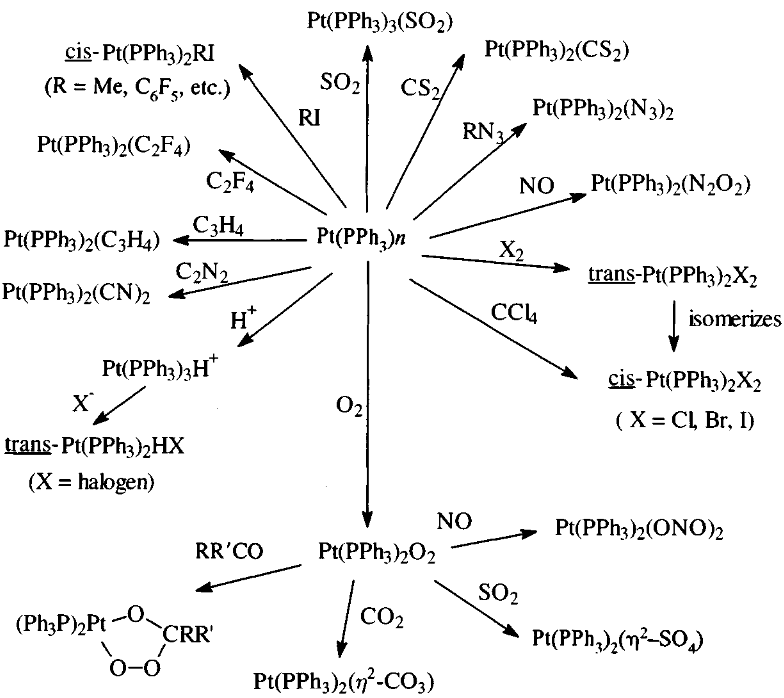


Figure 3.15 Reactions of $[Pt(PPh_3)_n]$.

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 peroxychelate 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 $[Pt(PPr^i_3)_2H(solvent)]^+OH^-$. $Pd(Pcy_3)_2$ 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 $[Pd(Pcy_3)_2H(OC_6X_5)]$

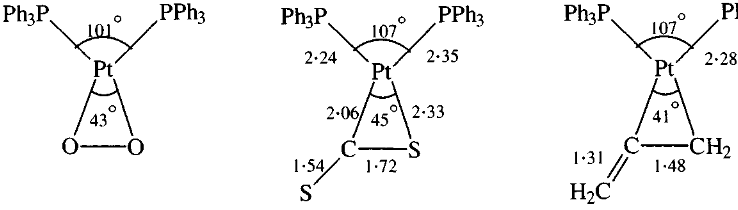


Figure 3.16 Structures of $Pt(PPh_3)_2Z$ ($Z = O_2, CS_2, C_3H_4$).

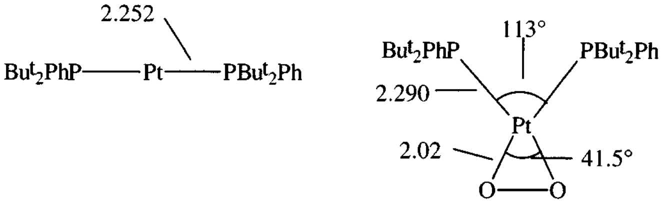


Figure 3.17 A comparison between the geometeries of $[Pt(PBu^t_2Ph)_2]$ and $[Pt(PBu^t_2Ph)_2(O_2)]$.

(X = H, F). The platinum analogue behaves similarly, and it also reacts with H_2 to form *trans*-$Pt(Pcy_3)_2H_2$.

Both $M(PPhBu^t_2)_2$ 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 $Pt(PR_3)_n$ species. Reactivity is determined by (a) steric factors, thus complexes like $Pt(Pcy_3)_2$ are very reactive and (b) the basicity of the phosphine. The more basic the phosphine, the more facile is oxidative addition; therefore $Pt(PEt_3)_3$ will add PhCl and PhCN while the less nucleophilic $Pt(PPh_3)_3$ will not. It is thought that many of these reactions involve initial dissociation of a phosphine, as in the addition of benzyl halides to $Pd(PPh_3)_4$, proceeding generally by inversion through a S_N2 mechanism. Either ionic or radical mechanisms are possible. Radical pathways can be detected in three ways:

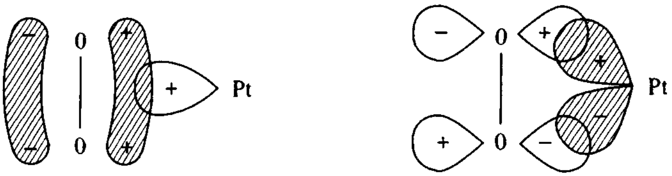


Figure 3.18 Metal–dioxygen bonding in platinum–dioxygen complexes.

1. Addition of radical inhibitors (e.g. duroquinone, galvinoxyl), which will slow up any pathway involving radicals.
2. Adding a radical trap like $\mathrm{Bu^tNO}$ to the reaction mixture; this reacts with radicals ($\mathrm{R^{\bullet}}$) forming nitroxide radicals $\mathrm{Bu^t(R^{\bullet})NO}$ 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 $\mathrm{PhCH_2Br}$ with $\mathrm{Pt(PEt_3)_3}$, it is thought that $\mathrm{Pt(PEt_3)_2(PhCH_2)Br}$ is formed via a $\mathrm{S_N2}$ route where the platinum forms a cationic complex that undergoes immediate attack by $\mathrm{Br^-}$ while some $\mathrm{Pt(PEt_3)_2Br_2}$ is formed in a very rapid reaction unaffected by radical scavengers.

$$\mathrm{Pt(PEt_3)_3 + PhCH_2Br \rightarrow Pt^I(PEt_3)_{\mathit{n}}Br + PhCH_2^{\bullet}}$$

$$\mathrm{Pt(PEt_3)_{\mathit{n}}Br + BrCH_2Ph \rightarrow Pt(PEt_3)_2Br_2 + PhCH_2^{\bullet}}$$

This is in contrast with the reaction of $\mathrm{Pt(PEt_3)_3}$ with $\mathrm{Me_3CCH_2Br}$, 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 $\mathrm{Pt(PEt_3)_2(PhCH_2)Br}$ is formed – giving credence to a radical chain mechanism. In the reactions of alkyl halides (EtI, MeI, $\mathrm{PhCH_2Br}$) to $\mathrm{Pt(PPh_3)_3}$, 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 $\mathrm{Pt(PPh_3)_2MeI}$ while in THF $\mathrm{Pt(PPh_3)_2I_2}$ is the main product [56]. A detailed study of this reaction in benzene shows that the most important steps are

$$\mathrm{Pt(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_2 + PPh_3}$$

$$\mathrm{Pt(PPh_3)_2 + MeI \rightarrow Pt(PPh_3)_2(Me)I + PPh_3}$$

Undissociated $\mathrm{Pt(PPh_3)_3}$ is much less reactive.

Addition of RX to a $\mathrm{Pt(PR_3)_{\mathit{n}}}$ species may occur by two main pathways:

1. $\mathrm{S_N2}$ attack of the electron-rich platinum(0) on the alkyl halide to give the $\mathrm{Pt^{II}(R)X}$ 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 $\mathrm{Pt^I{-}XR}$ radical pair can either react to form $\mathrm{Pt^{II}(R)X}$ or separate, with subsequent reaction with RX leading to either $\mathrm{PtX_2}$ or PtRX species or reaction with solvent molecules.

3.6.3 Carbonyl complexes

$\mathrm{Ni(CO)_4}$ 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 $M(CO)_x$ ($x = 1$–4). On controlled warming, diffusion takes place with successive CO addition taking place to yield $M(CO)_4$ as the stablest product (ν(C–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 $Å^{-1}$ 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

$$Pt(PPh_3)_3 + CO \xrightarrow{Me_2CO} Pt(PPh_3)_3CO$$

$$PtCl_2 + 2PPh_3 + 2CO + Zn \rightarrow ZnCl_2 + Pt(PPh_3)_2(CO)_2$$

Both $Pt(PPh_3)_3CO$ and $Pt(PPh_2Et)_2(CO)_2$ have essentially tetrahedral coordination of platinum.

The reason for the greater stability of $M(PR_3)_n$ over $M(CO)_4$ 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 (Pd) > 5d (Pt) > 3d (Ni) so that the strength of the σ-component would be in the order of Pd < Pt < 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 Pt < Pd $\ll$ 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 $Pt(PPh_3)_{4-n}(CO)_n$ ($n = 1, 2$), there are polynuclear species $Pt_3L_n(CO)_3$ ($n = 3, 4$; $L = PR_3$), and additionally some remarkable anionic binary carbonyl clusters, formed by reductive carbonylation of $Na_2PtCl_6.6H_2O$ with general formulae $[Pt_3(CO)_6]_n^{2-}$. These contain $Pt_3(CO)_3(\mu^2\text{-}CO)_3$ 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.

$$Pt(PBu^t_3)_2 \xrightarrow{Bu^tNC} [Pt(CNBu^t)_2]_3$$

$$Pt(cod)_2 \xrightarrow{Pr^iNC} [Pt(CNPr^i)_2]_3$$

The palladium compound $[Pd(CNcy)_2]_3$ has been made by metal vapour synthesis, from Pd atoms and a solution of cyNC at 160 K. It has an analogous structure $[Pd_3(CNcy)_3(\mu^2\text{-}CNcy)_3]$ [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 reproportionation. 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).

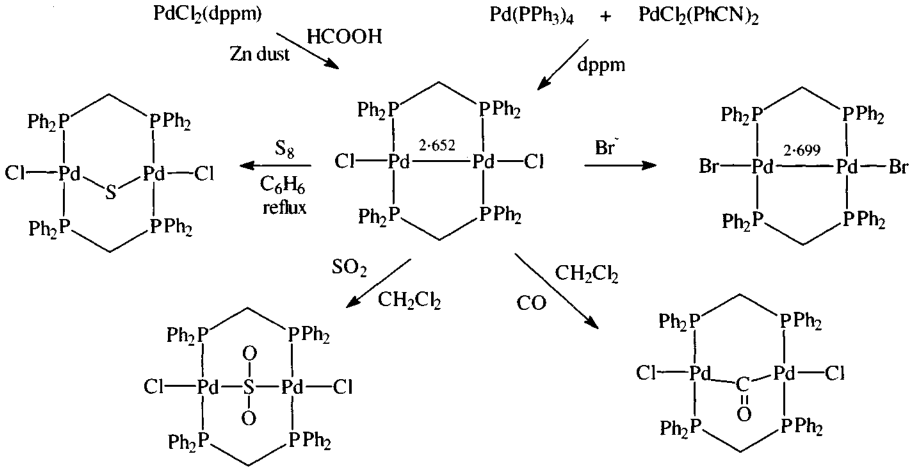


Figure 3.19 Synthesis and reactions of palladium(I) bis(diphenylphosphino)methane complexes.

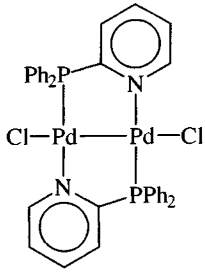


Figure 3.20 A palladium(I) 2-diphenylphosphinopyridine complex.

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 $[(\text{diphosphine})PtH]_2$ [62].

Isocyanide complexes can also be made by reproportionation.

3.7.2 *Isocyanide complexes*

Isocyanide complexes can be synthesized by:

$$PdX_2(Bu^tNC)_2 + Pd(Bu^tNC)_2 \rightarrow [PdX(Bu^tNC)_2]_2$$

$$PdCl_4^{2-} \xrightarrow{MeNC} [Pd_2(MeNC)_6]_2(PF_6)_2$$

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.

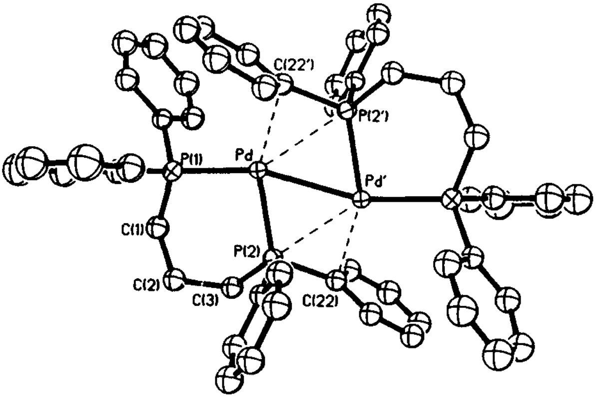


Figure 3.21 Structure of the dimeric palladium(I) complex $[(dppp)Pd]_2(CF_3SO_3)_2$. (Reprinted with permission from *Organometallics*, 1992, **11**, 23. Copyright (1992) American Chemical Society.)

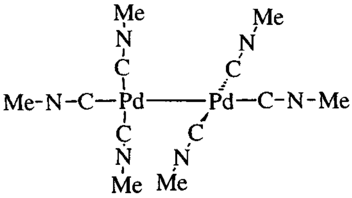


Figure 3.22 The staggered structure of $[Pd_2(MeNC)_6]^{2+}$.

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 ammines. 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

$$PtCl_4^{2-} + MeCOCH_2COMe \xrightarrow{KOH} KPtCl(acac)_2$$

$$\xrightarrow[\text{exc. }MeCOCH_2COMe]{KOH} Pt(acac)_2$$

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

In $[PtCl(acac)_2]^-$, 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 $Pd[P(o\text{-}tolyl)_3](CF_3COCHCOCF_3)_2$ (Figure 3.25), though with acetylacetone square planar adducts of the type $M(acac)_2(PR_3)_2$ are usually obtained, where the diketone is monodentate O-bonded [63].

Next Page

4 Silver and gold

4.1 Introduction

For many years, the chemistry of silver and gold was believed to be more similar than is now known to be the case [1–10]. In the Cu–Ag–Au triad, the stability of oxidation states does not follow the usual trend of increasingly stable high oxidation state on descending the group; for copper, the +2 state is the most important, for silver it is the +1 state and, though oxidation states between −1 and +7 are claimed, for gold it is the +1 and +3 states that dominate its chemistry. The types of compound are summarized in Table 4.1.

A plausible reason (or one of the reasons) for the relative stabilities of the oxidation states lies in the ionization energies (Table 4.2) [11]. The value of I_1 is lower for silver than for copper, as would be expected, but I_2 is higher for silver (this electron is removed from a 4d orbital, where the electrons are farther apart and repelled less, than in 3d orbitals); I_3 is again lower for silver, correlating with the increased stability of silver(III) and the tendency of silver(II) to disproportionate. The high I_1 value for gold results from the relativistic contraction of the 6s shell (from which this electron is removed) while the low I_3 value is in keeping with the stability of the +3 state, reinforced by the large ligand field splitting for the $5d^8$ ion. The preference of gold for the +3 state has been attributed to relativistic effects, according to Hartree–Fock calculations [12].

All three M^+ ions are known to form compounds with the unusual digonal linear coordination (see also section 4.9.7), though this is most common for gold. As a result, complexes R_3PMX of copper and silver are normally di- and tetranuclear species with 3- or 4-coordinate metals, while the gold analogues are 2-coordinate monomers. This is the reverse of what would be expected on steric grounds [13, 14].

Mixing of gold $5d_{z^2}$ and 6s orbitals, facilitated by the small d^{10}–d^9s separation (and also the large d^9s–d^9p separation, Table 4.3) gives rise to two orbitals Ψ_1 and Ψ_2 (Figure 4.1). The electron pair initially in $5d_{z^2}$ occupies Ψ_1, away from the two ligands (considered to lie along the z axis). The orbital Ψ_2 can mix further with $6p_z$, to afford two orbitals Ψ_3 and Ψ_4, which have (empty) lobes pointing along the z axis that can accept electron pairs from the two ligands (Figure 4.1). Recent Hartree–Fock calculations do indicate significant 5d involvement.

Table 4.1 Compounds of copper, silver and gold

Oxidation state	Copper	Silver	Gold
−1			With very electropositive metal (e.g. Cs^+Au^-)
+1	Stable if insoluble or complexed; usually 4-coordinate	Found with variety of ligands, e.g. NH_3, PR_3, Cl; usually 4-coordinate	Occurs with wide range of ligands; most often 2-coordinate
+2	Stable in aq. solution; found with wide variety of ligands, 4–6-coordinate	Usually found with N-, O-, F-donors; 4–6-coordinate	Rare, stabilized by 'suspect' ligands
+3	Rare, usually stabilized by F	Most often found bound to N, O, F; 4- and 6-coordinate	Common with wide range of ligands; usually square planar
+4			One example with a 'suspect' ligand
+5			Fluorine as ligand 6-coordinate
+7			Not confirmed, F as ligand

4.2 The elements and uses

Both silver (m.p. 962°C, b.p. 2212°C) and gold (m.p. 1065°C, b.p. 2807°C) have characteristic brilliant white and yellow colours in bulk but when finely divided are black or, in the case of gold, can be purple, ruby red or blue. Thus reduction of gold compounds by $SnCl_2$ gives the colloid known as 'Purple of Cassius', which is used as a ceramic colorant.

Table 4.2 Ionization energies ($kJ\,mol^{-1}$)

	Cu	Ag	Au
I_1	745	731	890
I_2	1958	2073	1978
I_3	3554	3361	(2900)
I_4	5326	(5000)	(4200)

Estimated values in parentheses.

Table 4.3 Energy separations (eV)

	Cu^+	Ag^+	Au^+
d^{10}–d^9s	2.72	4.86	1.86
d^9s–d^9p	5.72	5.07	5.96
d^{10}–d^9p	8.44	9.93	7.82

Neither metal is attacked by oxygen, but silver reacts with H_2S in town air forming a black tarnish of Ag_2S. Both dissolve in cyanide under oxidizing conditions. Non-oxidizing acids have no effect, but silver dissolves in concentrated HNO_3 and gold in aqua regia. Both silver and gold react with the halogens, and gold can, therefore, be dissolved in mixtures of halogens and ionic halides in a polar solvent (e.g. $Cl_2/Et_4NCl/MeCN$ or $I_2/KI/MeOH$) [15].

Like copper, both gold and silver have fcc (ccp) lattices (Au–Au 2.88 Å, Ag–Ag 2.889 Å) in which the metals are 12-coordinate.

4.2.1 *Extraction* [16]

Although silver does not often occur native, principal ores are AgCl ('horn silver') and Ag_2S (argentite), sometimes associated with copper ores; main ore-containing countries are Mexico, Canada, Peru, Australia, the USA, the former USSR and Poland. Gold is largely formed as the metal (USA, former USSR, South Africa, Canada) deposited in quartz, though erosion can lead to veins in rocks or deposits in rivers; it is sometimes found in sulphide minerals like pyrites and chalcopyrite ($CuFeS_2$) or arsenopyrite (FeAsS). Bacteria have been implicated in the accumulation of gold while various complexes like $AuCl_2^-$ and $Au(SH)_2^-$ are thought to also be responsible for gold transport and accumulation.

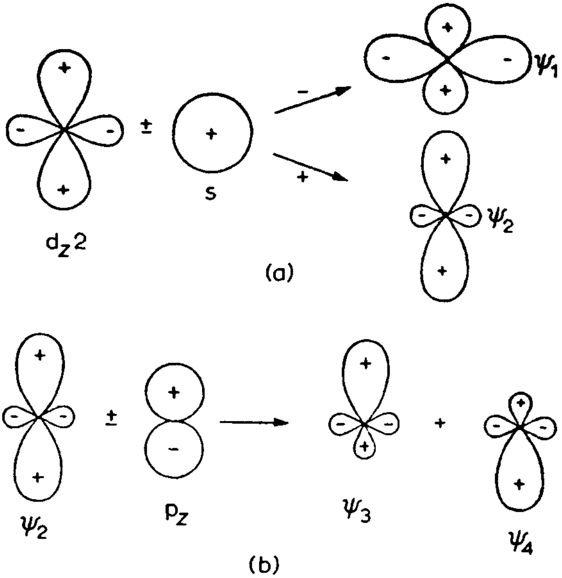


Figure 4.1 Mixing of atomic orbitals to give hybrid orbitals capable of generating digonal 2-coordination. (From J.E. Huheey, *Inorganic Chemistry*, Harper and Row, London, 1975. Reprinted by permission of Addison-Wesley Educational Publishers Inc.)

Silver was formerly extracted by cyanide solution of Ag_2S, the resulting $Ag(CN)_2^-$ being treated with zinc to afford the metal; roasted ores could also be extracted with mercury to give silver amalgam. Presently much silver is extracted by workup of the anode slime from the preparation of non-ferrous metals (Pb, Cu); pure silver is obtained by electrolysis of $AgNO_3$.

Gold ores can be concentrated by froth flotation, the resulting concentrate being roasted at 600–800°C to oxidize off sulphur and arsenic as their oxides. The product is extracted with cyanide under oxidizing conditions (using either peroxide or air itself) before displacement with powdered zinc. More reactive metals (silver etc.) can be removed by chlorination of molten gold.

An alternative route increasingly investigated is bio-oxidation using bacteria to oxidize pyrite or arsenopyrites at 45°C.

Final purification can be done by electrolysis using $HAuCl_4$ electrolyte.

4.2.2 Gold plating and other methods of gold deposition

Electrolysis of solutions containing $Au(CN)_2^-$ is widely used to recover gold from solution (electrowinning) [17]. The process is also used to deposit gold coverings for electrons (e.g. printed circuit boards, electrical connectors) and most recently for hip and shoulder joint replacement surgery.

Where insulated surfaces are to be joined, two other processes are employed: the ‘immersion’ and ‘electroless’ methods. Immersion gold plating is based on displacement reactions, where a copper or nickel object is coated with a thin film of gold from a solution of gold complex, usually in slightly acid solution (about 90°C); the process is self-terminating when a film of *c.* 0.2 μm is attained. Electroless processes use a reducing agent ($NaBH_4$, dimethylaminoborane, sodium hypophosphite) usually in hot alkaline solution (70–90°C) to reduce a gold complex such as $Au(CN)_2^-$.

4.3 Halides

The halides of silver and gold are listed in Table 4.4; as expected gold has more in higher oxidation states [18c].

4.3.1 Silver halides

The subfluoride Ag_2F can be prepared by reaction of silver with aqueous AgF or by electrolysis of AgF in HF:

$$Ag + AgF \rightarrow Ag_2F$$

It has the anti-CdI_2 structure, with alternating double layers of silver and intercalated fluorides. It is a metallic conductor.

Table 4.4 Characteristics of silver and gold halides

	Silver				Gold			
	F	Cl	Br	I	F	Cl	Br	I
M_2X	Bronze							
MX	Colourless, m.p. 435°C	Colourless, m.p. 455°C	Cream, m.p. 432°C	Yellow, m.p. 558°C		Yellow-white, dec. 170°C	Light yellow, dec. 115°C	Lemon, dec. 120°C
MX_2	Black					Black[a]		
MX_3	Bright red[b]				Gold-yellow, dec. 500°C[b]	Red, dec. 254°C	Dark brown, dec. 97°C	
MX_5					Yellow-brown			
MX_7					Pale yellow			

M, silver or gold; X, halide.

[a] $AuCl_2$ is, in fact, Au_4Cl_8, containing Au(I) and (III); [b] Ag_3F_8 and Au_2F_5 are also obtained.

Anhydrous AgF is best made by fluorination of finely divided silver at room temperature; alternatively it can be made by dissolving silver(II) oxide in hydrofluoric acid and crystallizing:

$$\mathrm{Ag} \xrightarrow{F_2/N_2\,(1:10)} \mathrm{AgF}$$

As expected from the similarity of ionic radii between Ag^+ (1.15 Å) and Na^+ (1.01 Å), one form has the NaCl structure (it is trimorphic) with other forms having the CsCl and inverse NiAs structures. Unlike the other silver(I) halides, it is very soluble in water (up to 14 M) and forms di- and tetrahydrates; it is decomposed by UV rather than visible light and melts unchanged at 435°C.

The other silver(I) halides are traditionally prepared by ionic precipitation, on account of their insolubility:

$$\mathrm{Ag^+(aq.) + X^-(aq.) \rightarrow AgX(s)} \qquad (\mathrm{X = Cl, Br, I})$$

which increases in the order Cl < Br < I, just as their covalent character increases and their colour deepens (as the energy of the charge transfer process $Ag^+X^- \rightarrow AgX$ decreases) [19]. AgCl and AgBr also have the 6-coordinate NaCl structure but the repulsion between I^- in a NaCl-type lattice is such that the stable (γ) form at room temperature of AgI has the 4-coordinate ZnS structure. Comparison between experimental lattice energies (derived from Born–Haber cycle calculations) and values calculated using the Kaputinskii equation show increasing discrepancy in the order F < Cl < Br < I, demonstrating increasing divergence from an ionic model as the larger halide ion becomes more polarizable by Ag^+ (this contributes to the lattice energy being greater than predicted on an ionic model, which in turn leads to a more positive enthalpy of solution, sufficient to ensure their insolubility rather than the solubility predicted from the similarity in size between Ag^+ and Na^+). Silver iodide also exists with the hexagonal ZnO structure (136–146°); above 146°C, it passes into the α-form which has a rigid bcc structure in which there is a fixed array of I^-, but the Ag^+ can move almost at will through the structure. This causes α-AgI to have the highest conductivity of any ionic solid: interest has centred on creating ionic conductors with high conductivities at room temperature [20].

The silver(I) halides are, of course, important in the photographic process, AgBr being most commonly used; in this process a photon causes an electron to be lost from a halide ion and gained by a silver ion, thus forming silver atoms. Subsequent development with hydroquinone intensifies the image by reducing those AgBr grains containing silver atoms, followed by 'fixing' the image, a process in which thiosulphate removes unreacted AgBr as the complex ion $Ag(S_2O_3)_2^{3-}$. Since the light-sensitive AgBr has been removed, the image is now stable.

Silver(II) fluoride AgF_2 is a genuine silver(II) compound exhibiting Jahn–Teller tetragonal distortion (4F at 2.07 Å; 2F at 2.59 Å); it exhibits a low magnetic moment (1.07 μ_B) owing to anti-ferromagnetic coupling. In the absence of excess fluorine, it decomposes at 150–200°C but under a fluorine atmosphere melts at ~620°C. It is prepared from the elements at 200°C and is quite a strong fluorinating agent.

AgF_3 has recently been characterized [21] as a red diamagnetic solid, isostructural with AuF_3; it is best made by adding a fluoroacid (BF_3, PF_5) to solutions of AgF_4^- salts in anhydrous HF

$$AgF_4^- + BF_3 \rightarrow AgF_3 + BF_4^-$$

The elongated octahedral coordination of silver has Ag–F 1.863 Å (×2) 1.990 Å (×2) and 2.540 Å (×2). When dry, it is stable for some weeks at room temperature, though it loses fluorine on standing in HF to form Ag_3F_8 and is a strong fluorinating agent. Ag_3F_8 is $Ag^{II}Ag_2^{III}F_8$ ($\mu_{eff} = 1.92\,\mu_B$); Ag_2F_5 ($Ag^{II}Ag^{III}F_5$) has also been made.

4.3.2 Gold halides

Only AuF of the gold(I) halides is unknown in the solid state; its stability can be examined by means of a Born–Haber cycle, assuming that it would have an ionic lattice like AgF. (AuF has been generated in the gas phase from Au^+ and CH_3COF [22].)

			ΔH (kJ mol^{-1})
Au(s)	→	Au(g)	343.1
Au(g)	→	$Au^+(g) + e^-$	890.1
$\frac{1}{2}F_2(g)$	→	F(g)	79.0
$F(g) + e^-$	→	$F^-(g)$	−322
$Au^+(g) + F^-(g)$	→	AuF(s)	−778
$Au(s) + \frac{1}{2}F_2(g)$	→	AuF(s)	+212.2

Its instability relative to its constituent elements is the result of the high value of I_1 of gold and to its large enthalpy of atomization, which are not compensated for by the small lattice energy.

AuCl, AuBr and AuI are all prepared by cautious heating of Au_2X_6 (X = Cl, Br) or, in the case of AuI, direct synthesis

$$Au_2Cl_6 \xrightarrow{150^\circ C} 2Cl_2 + 2AuCl \xrightarrow{200^\circ C} 2Au + Cl_2$$

$$Au_2Br_6 \xrightarrow{250^\circ C} 2Br_2 + 2AuBr \xrightarrow{250^\circ C} 2Au + Br_2$$

$$2Au + I_2 \longrightarrow 2AuI$$

$$AuCl_4^-(aq.) \xrightarrow{I_2} AuI$$

Table 4.5 Energy values[a] for gold halides

		F	Cl	Br	I	Ref.[b]
AuX	ΔH	(+75)	−35	−19	1.7	1
	ΔG		−16	−15	−3.3	1
	ΔH	+212[c]	−34.7	−13.8	0	2
AuX_3	ΔH	−360	−121	−67.3		1
	ΔG		−54	−36		1
	ΔH	−363.6	−117.6	(−49.3)		2
				(+62.8)		

[a] All values in kJ mol^{-1}; estimated values in parentheses.
[b] Data taken from:

1. R.J. Puddephatt (1978) *The Chemistry of Gold*, Elsevier, Oxford.
2. M.W.M. Hisham and S.W. Benson (1987) *J. Phys. Chem.*, **91**, 3631.

[c] This book.

Other methods are available, especially for AuCl, such as the decomposition of Au(CO)Cl. AuCl tends to disproportionate slowly at room temperature as predicted from the data in Table 4.5.

$$6AuCl \rightarrow 2AuCl_3 + 4Au \qquad \Delta G = -12\,\mathrm{kJ\,mol^{-1}}$$

Decomposition is rapid in solution, so that AuCl needs to be stored in an anhydrous state. All three gold(I) halides have a zig-zag chain structure (Figure 4.2) with linear coordination of gold; AuCl has a 'wide' Au–X–Au angle (93°) and AuI a narrower angle (72°), while AuBr exists in both crystalline forms.

Bond lengths are Au–Cl 2.36 Å, Au–Br 2.40–2.44 Å, Au–I 2.62 Å [23].

A compound $AuCl_2$ is, as might be expected from its black colour, the mixed valence $Au^{I}_{2}Au^{III}_{2}Cl_8$; it is prepared from the reaction of CO with excess $AuCl_3$ in $SOCl_2$:

$$2AuCl_3 + CO \rightarrow 2AuCl_2 + COCl_2$$

The gold(I) atoms have linear coordination (Figure 4.3) and the gold(III) atoms square planar coordination [24].

There are various routes for the synthesis of the trihalides:

$$Au + BrF_3 \rightarrow AuF_3.BrF_3 \xrightarrow[\textit{in vacuo}]{300^\circ C} AuF_3 \xrightarrow{500^\circ C} Au + F_2$$

$$Au \xrightarrow[1000^\circ C,\ 15\,\mathrm{bar}]{F_2} AuF_3 \quad [26]$$

$$2Au + 3Cl_2 \xrightarrow{240^\circ C} Au_2Cl_6$$

$$2Au + 3Br_2 \rightarrow Au_2Br_6$$

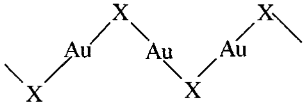


Figure 4.2 The structure of gold(I) halides in the solid state.

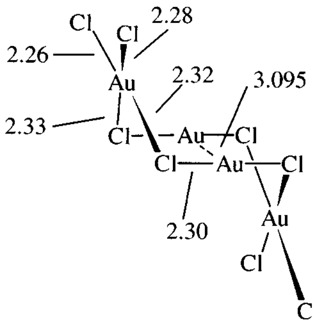


Figure 4.3 The structure of $AuCl_2$.

Two structures are exhibited, both involving 4-coordinate gold, giving rise to the diamagnetism expected for square planar d^8 systems. Like AgF_3, AuF_3 has [26] a fluorine-bridged helical structure (Figure 4.4) and is a strong fluorinating agent too.

The chloride [12] and bromide [27] are dimeric Au_2X_6 (Figure 4.5) with Au–Cl 2.243–2.249 Å (terminal) and 2.334 Å (bridge); some ligands break the bridges to form adducts $AuX_3.L$ while others reduce them to gold(I) species.

Gold(III) iodide has not been definitely characterized in the solid state; substances with this formula in the solid state are probably gold(I) polyiodides $Au^+I_3^-$; AuI_3 has also been detected in the gas phase (mass spectra).

The higher fluorides of gold, AuF_5 and AuF_7, have been reported; the former is well characterized [28]:

$$\mathrm{Au} \xrightarrow[350-380^\circ\mathrm{C}]{\mathrm{O_2/F_2}\,(1:4)} \mathrm{O_2^+AuF_6^-} \xrightarrow[160-200^\circ\mathrm{C}]{\text{sublime}} \mathrm{AuF_5 + O_2 + \tfrac{1}{2}F_2}$$

$$\mathrm{Au} \xrightarrow[0-20^\circ\mathrm{C}]{\mathrm{KrF_2/HF}} \mathrm{KrF^+AuF_6^-} \xrightarrow[\textit{in vacuo}]{40-60^\circ\mathrm{C}} \mathrm{AuF_5}$$

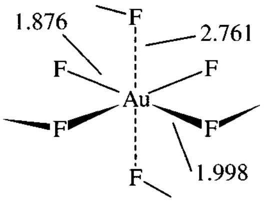


Figure 4.4 The structure of AuF_3.

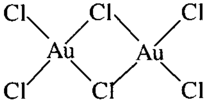


Figure 4.5 The structure of Au_2Cl_6.

It is an intensely reactive and hygoscopic yellow–brown substance (m.p. 75–78°C); its volatility suggests a low molecular mass; Mössbauer spectra indicate 6-coordinate gold while the Raman spectrum is interpreted in terms of *cis*-bridged octahedral units. In the gas phase at 170°C, it comprises dimers and trimers [29] (electron diffraction).

AuF_7 is reported to result from the reaction of fluorine atoms (produced in a high-voltage plasma) with AuF_5 at 120–130°C, being condensed out at -196°C as a very reactive and volatile pale yellow solid (vapour pressure >30 mmHg at room temperature) with an intense IR band at $734\,cm^{-1}$ (vapour). It decomposes to AuF_5 above 100°C and affords Au_2O_3 and Au on hydrolysis [18].

4.4 Oxides and other binary compounds

The main silver oxides are Ag_2O and AgO. The former is obtained as a dark brown precipitate when OH^- are added to solutions of Ag^+ salts; it tends to retain traces of water and alkali, even on drying. It is basic, giving slightly alkaline solutions in water (it is a convenient mild alkali in organic chemistry) and reacting with atmospheric CO_2. On heating to 160°C, it forms silver. Isostructural with Cu_2O, it has tetrahedral coordination of silver. When fused with alkali metal oxides, mixed oxides like KAgO are formed that have $Ag_4O_4^{4-}$ units with 2-coordinate silver. Analogous gold compounds are known (but not Au_2O) [30].

Black AgO is prepared by oxidation of silver salts with O_3, $S_2O_8^{2-}$ and, most recently, SO_2/air mixtures, as well as by anodic oxidation [31]. Neutron diffraction shows it to be $Ag^IAg^{III}O_2$ with 2-coordinate Ag^I and square planar Ag^{III} sites. It is stable to around 100°C and gives solutions of Ag^{2+} when dissolved in dilute acid. Treatment with alkaline periodate retains the disproportionation

$$4AgO + 6OH^- + 4IO_4^- \rightarrow 2Ag(IO_6)_2^{7-} + Ag_2O + H_2O + 4H^+$$

It finds important applications in batteries.

Less important oxides are Ag_2O_3, obtained impure by extended anodic oxidation of silver, and Ag_3O, obtained hydrothermally from Ag/AgO at 80°C, 4000 bar, which is a metallic conductor with the anti-BiI_3 structure containing an hcp array of silvers with oxide ions occupying 2/3 of the octahedral holes [32].

The only important gold oxide is brown Au_2O_3, obtained hydrated by alkaline precipitation of Au^{3+}(aq.); single (ruby) crystals have been produced by hydrothermal crystallization at 235–275°C (from $HClO_4/KClO_4$). It has a polymeric structure [33] with square planar Au^{3+} (Au–O 1.93–2.07 Å) though with four more distant oxygens (at 2.81–3.19 Å). It decomposes to the elements on gentle heating and dissolves in strong alkali as

$Au(OH)_4^-$. There have been claims for an AuO_2, which may have been impure Au_2O_3.

The ternary oxides M_3AuO (M = Rb, Cs) contain Au^-, however [34].

Other binary compounds include the very insoluble black Ag_2S ($k_{sp} \sim 10^{-51}$) and Au_2S. The latter has the cuprite structure while Ag_2S has three polymorphs; 2- and 3-coordination is found in the low-temperature form while at high temperatures Ag_2S is a conductor owing to movement of silver atoms between the framework of sulphurs. AuS and AuSe are, as would be expected, $Au^IAu^{III}X_2$ with digonal gold(I) and square planar gold(III) [35]; little is known about Au_2X_3 (X = S, Se, Te). $AuTe_2$ 'calverite' has 4 + 2-coordination of gold by tellurium [36]. Various polyanions such as $Au_2S_8^{2-}$, AuS_9^- and $Au_{12}S_8^{4-}$ have been made; the first two have rings with linear coordination of gold (as in $Au_2Se_5^{2-}$ and $Au_2Se_6^{2-}$) while the latter has a cube of sulphurs with golds at the middle of each edge [37]. Selenide complexes of silver [38] and gold [39] have been studied lately. Silver selenide complexes show dependence in structure on counter-ion as in $[Ph_4PAg(Se_4)]_n$, $[Me_4NAg(Se_5)]_n$, $[Et_4NAg(Se_4)]_4$ and $(Pr_4N)_2[Ag_4(Se_4)_3]$.

Gold forms no simple phosphide; Au_2P_3 is $Au^I_4(P_6^{4-})$ with P–Au–P angles of 171 and 180°.

4.5 Aqua ions

Only Ag^+ and Au^{3+} are stable in aqueous solution, the latter always being complexed. The relevant potentials (in acid solution) are:

$$Ag^+(aq.) + e^- \rightarrow Ag(s) \qquad E^0 = +0.799\,V$$

$$Ag^{2+}(aq.) + e^- \rightarrow Ag^+(aq.) \qquad E^0 = +1.980\,V$$

$$Au^+(aq.) + e^- \rightarrow Au(s) \qquad E^0 = +1.83\,V$$

$$Au^{3+}(aq.) + 2e^- \rightarrow Au^+(aq.) \qquad E^0 = -1.36\,V$$

From the Ag^+/Ag^{2+} potential, it is seen that the silver(II) ion is a strong oxidizing agent and is only fairly stable in strong acid; it may be prepared by ozone oxidation of Ag^+ or by reproportionation of AgO (section 4.4).

Ag^+ is stable to disproportionation in aqueous solution

$$2Ag^+(aq.) \rightarrow Ag^{2+}(aq.) + Ag(s) \qquad E^0 = -1.18\,V$$

though the potential is affected by complexation and certain silver(I) macrocyclic complexes disproportionate in solution (section 4.7).

Table 4.6 Selected electrode potentials for gold(I) and gold(III) complexes $[Au(L^{n-})_2]^{(1-2n)+}$ and $[Au(L^{n-})_4]^{(3-4n)+}$

L	Gold(I) E^0 (V)	Gold(III) E^0 (V)
H_2O	−1.83	−1.52
Cl^-	−1.15	−1.00
Br^-	−0.96	−0.85
I^-	−0.66	–
SCN^-	−0.58	−0.64
NH_3	−0.56	−0.33
CN^-	+0.61	+0.20

In the case of gold, study of the above potentials predicts correctly the disproportionation of Au^+ in aqueous solution

$$3Au^+(aq.) \rightarrow Au^{3+}(aq.) + 2Au(s) \qquad E^0 = 0.47\,V$$

For example, AuCl immediately decomposes into gold and gold(III) chloride, though some gold(I) halide complexes such as AuI_2^- are quite stable, while $Au(CN)_2^-$ is formed by oxidation of gold in the presence of CN^-:

$$Au + 2CN^- \rightarrow Au(CN)_2^- + e^- \qquad E^0 = +0.61\,V$$

Table 4.6 shows the potentials to be ligand dependent.

X-ray scattering data on solutions of Ag^+ indicate the presence of $Ag(H_2O)_4^+$ with Ag–O about 2.4 Å [40]. Soluble silver(I) salts include $AgNO_3$, $AgClO_4$ (the periodate is insoluble), $AgBF_4$, $AgClO_3$ and AgF (all other halides are insoluble). There is no evidence for perchlorate coordination in aqueous solution. Silver nitrate is prepared from the reaction of silver with concentrated nitric acid as colourless crystals m.p. 212°C. It decomposes above 350°C to silver, oxygen, nitrogen and oxides of nitrogen. Insoluble salts of silver include the bright yellow Ag_3PO_4 and (in contrast to the chlorate) the bromate and iodate. Little is known concerning gold(III) salts such as $Au(NO_3)_3$.

The oxidizing power of Ag^{2+} (aqueous) is being utilized in electrochemical cells for disposal of organic wastes; solutions of Ag^{2+} in HNO_3 were originally found to be efficient oxidants for organic nuclear waste (tributyl phosphate kerosene from solvent extraction processes) but the scope has been expanded to include rubber, certain polymers, hydraulic and lubricating oils, aromatic and aliphatic hydrocarbons, organo-phosphorus, sulphur and chloro compounds (including PCBs, notoriously difficult to oxidize) [41].

4.6 Silver(I) complexes

4.6.1 *Complexes of O-donors*

The aqua ion as a ligand is discussed in section 4.5. Silver forms a range of light-sensitive, insoluble carboxylates that find application in the synthesis of, for example, alkyl halides and esters. The benzoate, trifluoroacetate and perfluorobutyrate have dimeric structures; others are polymers (Figure 4.6).

Commercially, the most important complexes of O-donors are the thiosulphates, implicated in photographic 'fixing'; of several known, in $NaAgS_2O_3.H_2O$ each silver is tetrahedrally bound to three sulphurs and one oxygen while $(NH_4)_7Ag(S_2O_3)_4$ also has silver tetrahedrally bound by sulphur. Unlike other 'soft' metal ions, Ag^+ binds to Me_2SO via oxygen in $Ag(DMSO)_2ClO_4$ rather than by sulphur.

4.6.2 *Complexes of N-donors*

Dissolution of Ag_2O in aqueous ammonia lends to the formation of $Ag(NH_3)_2^+$ (Ag–N 2.110 Å in $Ag(NH_3)_2SO_4$); its reduction by aldehydes and reducing sugars is the basis of its use as Tollens' reagent, the 'silver mirror' test. In liquid ammonia, the tetrahedral $Ag(NH_3)_4^+$ is formed (Ag–N 2.31 Å), isolable as a perchlorate (which loses NH_3 on keeping); silver nitrate forms $[Ag(NH_3)_3]^+NO_3^-$ with a trigonally coordinated silver (Ag–N 2.281 Å) [42]. Linear coordination is formed in $Ag(pyridine)_2^+NO_3^-.H_2O$ (Ag–N 2.26 Å, bond angle 173°; four distant contacts to oxygens Ag–O *c.* 2.9 Å); an unstable $Ag(py)_4^+$ has similarly been characterized. $Ag(im)_2^+$ is linear in the nitrate, but in the perchlorate, $Ag(im)_2^+$ is associated in pairs (further grouped into triangular units). $Ag(pyrazine)NO_3$ has silver similarly bound to two nitrogens but nitrate coordination is stronger than in the pyridine complex as the chains are kinked (N–Ag–N 159°) (Figure 4.7).

An exception to the above types of structure is the cubane cluster in $(AgIpiperidine)_4$ [43].

Less study has been made of complexes with polydentate ligands. Ag–N linkages have been studied in relation to polynucleotide bases and the Ag–DNA interaction could be important in the use of the silver–sulphadiazine complex in burn treatment. Ethylenediamine is a bridging ligand in $AgenClO_4$ (2-coordinate silver) but essentially planar 5-coordination

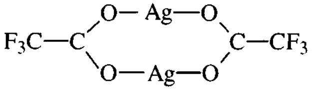


Figure 4.6 The dimeric structure adopted by some silver carboxylates such as silver trifluoroacetate.

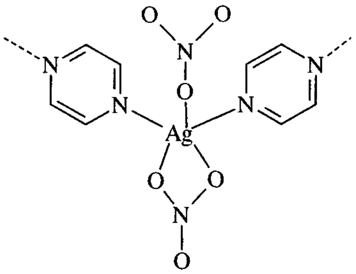


Figure 4.7 The environment of silver in Ag(pyrazine)NO_3.

occurs in Ag(quinquepyridine)PF_6; $[Ag(PPh_3)_2(terpy)]ClO_4$ has trigonal bipyramidal coordination [44].

Ag(4,4′-bipy)NO_3 has a three-dimensional structure with silver ions diagonally coordinated by two bipy ligands (N–Ag–N 173.7°) in extended infinite chains, the chains being cross-linked by Ag–Ag bonds (2.970 Å) [45].

4.6.3 *Tertiary phosphine and arsine complexes*

The 1 : 1 phosphine complexes resemble those of copper rather than gold (Figure 4.8) [46].

More bulky phosphines favour the chair structure; $[(R_3P)AgX]_4$ (R = Et, Ph; X = Cl, Br, I) all adopt the cubane form but a second form of $[(Ph_3P)AgI]_4$ has the chair structure in which some silver atoms are 3-coordinate. Some of these clusters may dissociate into dimers in solution. In contrast to the linear gold analogue, $[(Ag(O_2CMe)(PPh_3)]_4$ has a tetrameric structure featuring 3- (1P, 2O) and 4- (1P, 3O) coordinate silver while a second form is dimeric $[(Ph_3P)Ag(\mu\text{-}O_2CMe)Ag(PPh_3)]$ with 3-coordinate silver [47]; Ag(SCN)(PPr^n_3) has a chain structure where 4-coordination is attained with cross-linking of Ag–S–Ag–S-units. $(Ph_3P)_2AgX$ (X = Cl, Br, I, SCN) are X-bridged dimers [48] and $(Ph_3P)_3AgCl$ also features tetrahedral coordination; four tertiary phosphites, though not phosphines, can bind to one silver. Four-coordination is found in monomeric and dimeric

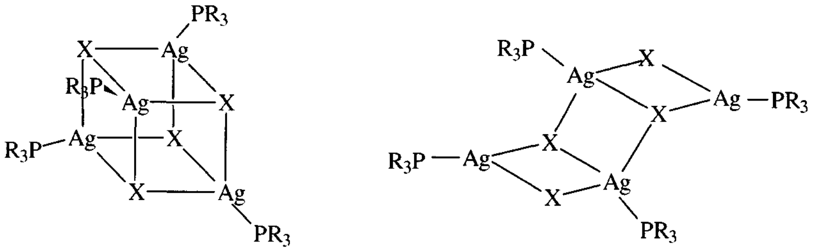


Figure 4.8 Cubane and chair structures adopted by complexes $(R_3P)AgX$.

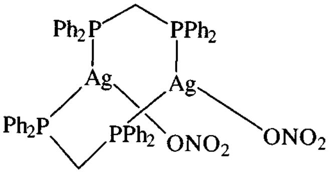


Figure 4.9 The dimeric structure adopted by $(Ph_2PCH_2PPh_2)AgNO_3$.

$(Ph_3P)_2AgNO_3$. $[(Ph_3P)_2Ag(O_2CH)]$ has 4-coordinate silver with a symmetrically bidentate formate ligand [49]. Two-coordination has been established for bulky phosphines, for $[(mesityl)_3P]_2Ag^+PF_6^-$ and probably for $(Bu^t_3P)_2Ag^+X^-$ ($X = PF_6$, BF_4, ClO_4). Among complexes of bidentate ligands, $(Ph_2PCH_2PPh_2)AgNO_3$ is a dimer with 3-coordinate silver (Figure 4.9).

The series M(PP)Cl (PP = 2,11-bis(diphenylphosphinomethyl)benzo[c]-phenanthrene; M = Cu, Ag, Au) is interesting in showing group trends (Table 4.7) where the silver and copper complexes have trigonal coordination and the gold member is linear [50].

Linear coordination is also found in Ag(tmpp)X (X = Cl, Br). Bond lengths are Ag–P 2.379 and Ag–Cl 2.342 Å in the chloride; Ag–P 2.374 and Ag–Br 2.448 Å in the bromide [51a]. The 3-coordinate monomers $Ag(PR_3)(CF_3COCHCOCF_3)$ (the diketonate chelates through the two oxygens; R = Me, Et) are volatile and thermally stable to over 100°C; they have been suggested as CVD precursors [51b]. Four-coordination occurs in $[Ag(S_2CAr)(PPh_3)_2]$ [52].

4.6.4 *Complexes of halogen-donors*

Silver halides dissolve in excess halide (e.g. AgCl is a hundred times more soluble in 1 M HCl than in water) forming complex ions AgX_2^- and AgX_3^{2-} [53]. These isolated anions are not often found in the solid state; thus M_2AgI_3 ($M = K$, Rb, NH_4) have corner linked tetrahedra (Figure 4.10), though $Au(S_2CNBu^n_2)_2^+AgBr_2^-$ does have digonally coordinated silver (Ag–Br 2.45 Å).

MAg_4I_5 (M = Rb, K) compounds are iodide-based solid electrolytes with high conductivities; the structures are based on packing of I^-, the ion Ag^+

Table 4.7 Structure of M(PP)Cl

M	M–P average (Å)	M–Cl (Å)	P–M–P (°)
Cu	2.237	2.222	131.9
Ag	2.434	2.514	140.7
Au	2.308	2.818	175.5

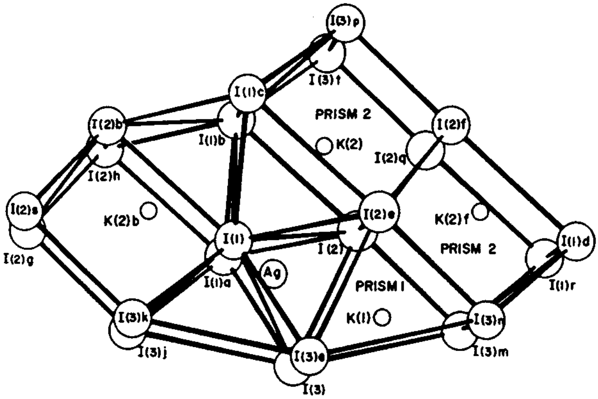


Figure 4.10 The structure of K_2AgI_3. (Reproduced with permission from *Acta Crystallogr. Sect. B*, 1975, **31**, 2339.)

(but not M^+) being mobile at room temperature, moving from one position to another with a relatively small energy barrier [54].

Trigonal coordination is also found in M(dibenzo-18-crown-6)AgX_3 (M = K, Rb; X = Cl, Br) with Ag–X bond lengths of 2.447 Å (X = Cl) and 2.550 Å (X = Br) in the rubidium salts. With the larger K(crypt-2,2,2)$^+$ counter-ion, it is possible to isolate individual ions as $AgCl_2^-$. In $(PPh_3Me)^+AgI_2^-$, Ag–I is 2.742–2.755 Å; $(Pr_4N)_4[Ag_4I_8]$, however, has cubane-type clusters [55].

4.6.5 *Complexes of C-donors*

The most important complexes with C-donors, other than organometallics, are cyanides. AgCN has a structure with Ag–C–N–Ag bonding in linear polymeric chains; it dissolves in excess KCN forming $K^+Ag(CN)_2^-$ (digonal with Ag–C 2.13 Å, ν(C≡N) 2135–2139 cm^{-1}), $Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$ [56].

4.6.6 *Complexes of S-donors*

Like gold, silver readily forms insoluble (yellow) thiolates $[Ag(SR)]_n$; primary alkylthiolates are thought to have non-molecular structures but with bulky tertiary alkyls ($n = \sim 8$), probably having a cyclic structure. Addition of excess thiolate leads to the formation of clusters like $Ag_6(SPh)_8^{2-}$, $Ag_5(SPh)_7^{2-}$ and $Ag_5(SBu^t)_6^-$ (phosphine adducts are known, too).

Octahedral silver clusters are also found in dithioacid complexes $[Ag(S_2CNR_2)]_6$ (R = Pr, Et) and $[Ag(S_2C{=}C(CN)_2)]_6^{6-}$, while $[Ag_8(S_2C{=}C(CN)_2)_6]^{4-}$ has a cube of silvers (Figure 4.11) [57].

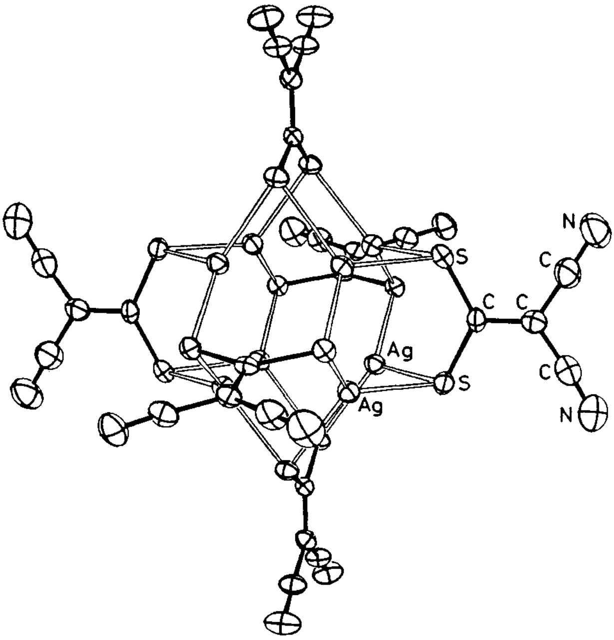


Figure 4.11 The structure of $[Ag_8\{S_2C{=}C(CN)_2\}_6]^{4-}$. (Reproduced with permission from *J. Chem. Soc., Chem. Commun.*, 1981, 323.)

A number of thiourea complexes of silver have shown the tendency to bind up to four ligands, in contrast to gold. Thus $Agtu_2X$ (X = Cl, NCS) have essentially 3-coordinate silver (one distant fourth atom); $Agtu_3ClO_4$ is a 4-coordinate dimer (Figure 4.12) [58].

Various thioether complexes have been synthesized: for example, 6-coordination is found in $[Ag(18S_6)]^+$ and $[Ag(9S_3)_2]^+$ but in $[Ag(16S_6)]^+$, tetrahedral coordination occurs, with two unused donor atoms in the ligand [59].

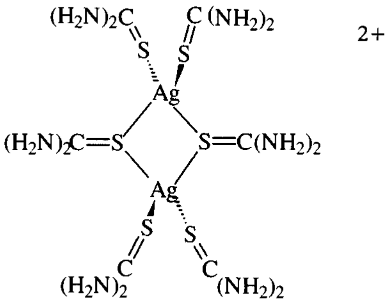


Figure 4.12 The structure of dimeric $[Ag_2(tu)_6]^{2+}$ in $Ag(tu)_3ClO_4$.

4.7 Silver(II) complexes

Stable compounds of silver(II) are found with N, O and F as donor atoms; macrocycles are, as elsewhere, able to support the higher oxidation state. As a d^9 system, Ag^{2+} imitates Cu^{2+} in displaying Jahn–Teller distortion.

Violet fluoro complexes like $BaAgF_4$ and Cs_2AgF_4 can be made by fluorination

$$BaCO_3 + Ag_2SO_4 \xrightarrow[800°C]{F_2} BaAgF_4 \qquad (\mu = 1.9\,\mu_B)$$

and have square planar silver (Ag–F 2.05 Å). $MAgF_3$ (M = K, Rb, Cs) and $CsAgMF_6$ (M = Tl, In, Sc, Fe) have also been made; $KAgF_3$ has distorted 6-coordination (perovskite structure) and $CsAgFeF_6$ has a compressed octahedral geometry [60].

Complexes of N-donor ligands have been made by chemical (ozone or persulphate) or electrochemical oxidation, such as $Agpy_4S_2O_8$, $Ag(bipy)_2(S_2O_8)$ and $Ag(bipy)_2(NO_3)_2.H_2O$. Solid $Ag(bipy)_2(S_2O_8)$ has $\mu_{eff} = 1.82\,\mu_B$; $g_\perp = 2.032$, $g_\parallel = 2.134$ (in frozen solution, hyperfine structure from both silver and nitrogen are seen). $Ag(bipy)_2(NO_3)_2.H_2O$ has distorted octahedral coordination (bidentate bipy, bridging nitrate). The value of E^0 for $Agbipy_2^+/Agbipy_2^{2+}$ is 1.453 V, compared with 2.0 V for the aqua ion, demonstrating the ability of these ligands to stabilize higher oxidation states [61].

Picolinate and pyridine-2,6-carboxylate give stable complexes, with 4- and 6-coordination. Macrocycles like porphyrins afford silver(II) derivatives; most remarkable is the reaction of the macrocycle *meso*-Me_6[14]ane (Figure 4.13).

It forms a stable silver(I) complex in acetonitrile, in keeping with the ability of MeCN to solvate Ag^+; in the presence of water, disproportionation occurs [62].

$$AgClO_4 + L \xrightarrow{MeCN} [AgL]^+ClO_4^- \xrightarrow{H_2O} [AgL]^{2+}(ClO_4)_2 + Ag + L$$

Silver has square planar coordination in Ag[*meso*-Me_6[14]ane]$(NO_3)_2$ (Ag–N 2.16 Å) with distant axial oxygens (Ag–O 2.81 Å); the complex has

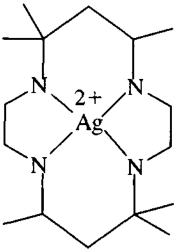


Figure 4.13 The structure of the silver(II) complex of the macrocycle *meso*-Me_6[14]ane.

$\mu_{eff} = 2.2\,\mu_B$; $g_{||} = 2.11$, $g_{\perp} = 2.058$. Similar complexes can be obtained with other ligands [63]; some can be oxidized, chemically or electrochemically, to silver(III) complexes.

4.8 Silver(III) complexes

As mentioned in the previous section, oxidation (with $NOClO_4$) of a silver(II) complex yields the yellow diamagnetic Ag[*meso*-Me_6[14]ane]$(ClO_4)_3$; other complexes such as $AgOEPClO_4$ can be made; the Ag^{3+}/Ag^{2+} potential is 0.44 V [64].

Fluoride complexes of silver(III) are exemplified by the purple–red Cs_2KAgF_6 (elpasolite structure, octahedral Ag^{3+}; paramagnetic with $\mu = 2.6\,\mu_B$). Yellow $MAgF_4$ (M = Na, Rb, K) and $XeF_5^+AgF_4^-$ are diamagnetic and probably square planar [65].

Yellow $Ag(OH)_4^-$, synthesized by anodic oxidation of silver in strong alkali, is said to be stable for 2 h at 25°C in 1.2 M NaOH but decomposes to AgO and O_2 at pH 11 in 1–2 min [66].

The longest established silver(III) complexes are the red to brown biguanides, like the ethylene bis(biguanide) shown in Figure 4.14; persulphate oxidation of Ag^+ in the presence of this ligand gives a silver(III) complex with essentially square planar coordination.

4.9 Gold(–I) complexes

Gold has a high electron affinity (223 kJ mol^{-1}, compare with that for I of 295 kJ mol^{-1}) to fill the 6s subshell, because of relativistic contraction (see section 4.18). It, therefore, forms 1 : 1 compounds MAu with group I metals; of these Cs^+Au^- and Rb^+Au^- are ionic semi-conductors [67] with the CsCl structure ('normal' alloys of gold like those with the lighter alkali metals are metallic conductors). Au^- is also formed when gold dissolves in liquid ammonia in the presence of Cs and other alkali metals. Au^- is also found in $K_{18}Tl_{20}Au_3$, which contains $[Tl_9Au_2]^{9-}$, $[Tl_{11}]^{7-}$ and Au^-.

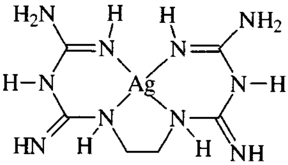


Figure 4.14 The coordination geometry of silver in the silver(III) ethylenebis(biguanide) complex.

4.10 Gold(I) complexes

4.10.1 Complexes of O-donors

Few studies have been made of these ligands; most complexes reported involve other supporting ligands as in $Au(OSiMe_3)(PPh_3)$ and $Au(OCOR)(PPh_3)$, though an important Au–O bond is formed in $[(Ph_3P)Au]_3O^+$ (section 4.17) [68]. Some air- and heat-stable alkoxides $Au(OR')(PR_3)$ ($R = Ph$ or cy; $R' = CH_2CF_3$ or $CH(CF_3)_2$) have been reported [69].

4.10.2 Complexes of N-donors

The 'soft' Au^+ forms relatively few complexes compared with those of phosphines. Complexes with ammines, nitriles and diazoles like $Au(NH_3)_2^+$ and $Au(RCN)_2^+$ are known but little studied. In linear $Au(NH_3)_2^+$, Au–N is 2.01–2.03 Å [70a]. $[Au(NCPh)_2]^+$ has been used as a labile source of other gold complexes [70b]. AuCl(piperidine) is a monomer with weak tetrameric association; in contrast AuX(py) (X = Cl, Br, I) are $[Aupy_2]^+[AuX_2]^-$ with a chain structure in the solid state (and Au–Au interactions), suggesting a close balance between factors for 'molecular' and ionic structures [70c] (note also the tetrahydrothiophene complexes in section 4.10.6).

4.10.3 Tertiary phosphine and arsine complexes

The phosphine and arsine complexes of gold(I) have been intensively studied since the early 1970s. The possibilities of coordination numbers between 2 and 4 have been explored, though the use of bulky ligands is less essential than with the isoelectronic $M(PR_3)_2$ (M = Pd, Pt) compounds and the coordination numbers depend on both steric and electronic factors [71].

The usual starting material is $AuCl_4^-$, which can be reduced with the tertiary phosphine

$$AuCl_4^- + 2R_3P \rightarrow R_3P.Au.Cl + R_3PCl_2 + Cl^-$$

or more cheaply, *in situ* with 2,2′-thiodiethanol, (bis-2-hydroxyethylsulphide)

$$AuCl_4^- + 2(HOCH_2CH_2)_2S$$
$$\rightarrow AuCl[S(CH_2CH_2OH)_2] + (HOCH_2CH_2)_2SO + Cl^- + 2HCl$$

or via an isolable complex with a weakly bound ligand like tht, the intermediate being reacted with the tertiary phosphine (or arsine)

$$AuCl_4^- + 2R_2S + H_2O \rightarrow AuCl(R_2S) + R_2SO + 2HCl + Cl^-$$

1 : 1 complexes

X-ray diffraction shows linear coordination in $(Ph_3P)AuX$ (X = Cl, Br, I, NO_3, SCN [72], Ph [73], SR [74], CN, Me, CF_3 [75] OCOMe [76],

Table 4.8 Au–P bond lengths in the 2-coordinate complexes $(Ph_3P)AuX$

Donor atom	X	Au–P (Å)
O	NO_3	2.199
	OCOMe	2.207
	$OCOCF_3$	2.208
	$OCOCHCl_2$	2.210
	$OCOPr^i$	2.213
	SO_4	2.216
	OCOCH(OH)Me	2.219
N	NCO	2.222
	NMe_3	2.231 (ClO_4 salt)
Cl	Cl	2.235
Br	Br	2.252
I	I	2.249
S	SCN	2.252
	SPh	2.259
	S_2COEt	2.260
	S_2COMe	2.261
	S_2CPh	2.263–2.269
C	CNO	2.274
	C_6F_5	2.27
	$C{\equiv}CC_6F_5$	2.274
	Me	2.279
	CN	2.278
	$(2,6\text{-}MeO)_2Ph$	2.284
	CF_3	2.285
	Ph	2.296
P	PPh_3	2.295 ($C(CN)_3$ salt)
	PPh_3	2.311 (NO_3 salt)
	PPh_3	2.312 (PF_6 salt)
	PPh_3	2.325 (solution)

$OCOCF_3$, S_2CNEt_2, S_2COMe [77], OCOPh, NMe_3 [78], etc.), R_3PAuCl [79] (R_3 = cy_3, $Phcy_2$, Me_3P, Et_3P, Cl_3P, $(PhO)_3P$ and $(tolyl)_3P$), $Pr_3PAuC_5H_5$ and Ph_3AsAuX (X = Cl, Br). In all of these the ligand X is monodentate (note the monodentate nitrate and dithio ligands, as well as the monohapto-cyclopentadienyl). Table 4.8 shows the *trans*-influence of the ligand X on the Au–P bond length in some of these compounds; it depends on the donor atom in X rather than X itself, the bond lengths following a trend in agreement with *trans*-effect orders.

Complexes other than the chloride are prepared by a variety of reactions, including metathesis and re-distribution:

$$Ph_3PAuCl \xrightarrow{NaXCN} Ph_3PAuXCN \qquad (X = S, Se)$$

$$Ph_3PAuCl \xrightarrow{AgOAc} Ph_3PAuOAc$$

$$(Ph_3P)_2Au^+ + Au(CNO)_2^- \rightarrow (Ph_3P)Au(CNO)$$

Table 4.9 Structure and spectroscopic data for AuX(tmpp)

X	Au–P (Å)	Au–X (Å)	ν(Au–X) (cm^{-1})
Cl	2.253	2.303	313
Br	2.255	2.413	218
I	2.239	2.586	183

PF_3AuCl, prepared from Au_2Cl_6 and PF_3 in $SOCl_2$ has a vapour pressure of 10^{-4} mbar at room temperature and has been suggested as a laser CVD precursor [80].

The series AuX (tmpp) shows clear patterns [81] in structure and spectroscopic parameters (Table 4.9) (X = Cl, Br, I).

Complexes with more than one phosphine

The 2 : 1, 3 : 1 and 4 : 1 complexes have been prepared by altering the stoichiometry of the reaction mixture; the complex formed in solution depends on the cone angle of the phosphine (as with $M(PR_3)_n$ (M = Pd, Pt)) [71]. Thus PBu^t_3 and Pcy_3 form only 2 : 1 complexes (three Pcy_3 can bind to the larger Pt) whereas PBu^n_3 forms 3 : 1 complexes and with PEt_3, up to 4 : 1 complexes can be obtained. The stoichemetry of the complex isolated in the solid state depends on factors such as the coordinating power of the anion present and upon the balance between cation and anion size. Thus $(PPh_3)_2AuSCN$ is 3-coordinate, but because of the bulk of tricyclohexylphosphine, $(cy_3P)_2Au^+SCN^-$ is 2-coordinate [82].

Many structures have been determined including $(PPh_3)_2Au^{2+}X^-$ (X^-, e.g. NO_3, PF_6, $C(CN)_3$) [83], $(Pcy_3)_2Au^+X^-$ (X = NCS, PF_6, Cl) [79], $(PPh_2Me)_2Au^+PF_6^-$, $(Bu_3P)_2Au^+BPh_4$ [84] (all are linear, 2-coordinate); $(PPh_3)_2AuX$ (X = Cl, Br, I, NCS) and $(PPh_3)_3Au^+X^-$ (X = BPh_4) are 3-coordinate and $(PPh_3)_3AuX$ (X = Cl, SCN), $(PPh_2Me)_4Au^+PF_6^-$, $(PPh_3)_4Au^+BPh_4^-$ and $(SbPh_3)_4Au^+ClO_4^-$ [85] are 4-coordinate. The 3-coordinate complexes are essentially trigonal when all the ligands are the same, or slightly distorted in $(PPh_3)_2AuX$, where steric effects force the P–Au–P angle to exceed 120° [86]. The 4:1 complexes are distorted tetrahedra [85]. 'Mixed' 3-coordinate complexes like $[(PPh_3)Au(bipy)]^+$ have been made [87], with very asymmetric bidentate coordination (Figure 4.15).

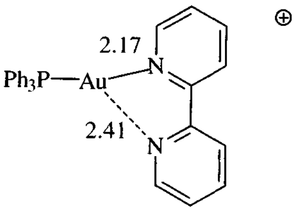


Figure 4.15 The asymmetric coordination geometry in $[(Ph_3P)Au(bipy)]^+$.

Table 4.10 Bond lengths (Å) in the complexes $(PPh_3)_nAuX$ and $(PPh_3)_2AuX$

$(PPh_3)_nAuCl$			$(PPh_3)_nAuSCN$			$(PPh_3)_2AuX$		
n	Au–P	Au–Cl	n	Au–P	Au–S	X	Au–P	Au–X
1	2.235	2.279	1	2.252	2.304	Cl	2.27	2.533
2	2.27	2.533	2	2.348	2.469	Br	2.323	2.625
3	2.41	2.71	3	2.396	2.86	I	2.333	2.754

Trends in Au–X and Au–P bond lengths in complexes $(PPh_3)_nAuX$ should be noted (Table 4.10); the Au–Cl bond length varies more with changes in coordination number than does the Au–P bond and is, therefore, more sensitive to the decrease in s character as the hybrid orbitals used by gold change from sp to sp^3.

Luminescence has been noted [88] in numerous gold phosphine complexes.

Rather fewer complexes with polydentate ligands have been studied [89]. Interest in possible use of $Au(dppe)_2^+$ in cancer therapy has led to the determination of the structures of $(AuCl)_2dppe$ and $Au(dppe)_2^+X^-$ (X = Cl, SbF_6). The former has the diphosphine acting as a bridging ligand while the latter has a tetrahedral cation as in $[Au(1,2\text{-}(Me_2As)_2C_6H_4)_2]^+$. The compound [Au(PP)]Cl has already been referred to in section 4.4 as an example of the preference of gold for 2-coordination [50].

The tridentate $MeC(CH_2PPh_2)_3$ gives $MeC(CH_2PPh_2AuCl)_3$.

4.10.4 *Complexes of halogen-donors*

The ions AuX_2^- (X = Cl, Br, I) are well known; the chloride and bromide are particularly unstable in water unless excess halide ion is present. Although AuF does not exist as a solid (section 4.3.2), it has been suggested that the unknown AuF_2^- could be stabilized by ions such as Ph_4As^+ to prevent the disproportionation:

$$3AuF_2^- \rightarrow AuF_4^- + 2Au + 2F^-$$

The series Bu_4NAuX_2 have been prepared by reactions like

$$2R_4NAuCl_4 + PhNHNH_2HCl \rightarrow R_4NAuCl_2 + R_4NPhAuCl_3 + N_2 + 4HCl$$

$$AuBr_4^- + MeCOMe \rightarrow AuBr_2^- + CH_2BrCOMe + HBr$$

$$AuBr_2^- \xrightarrow[I^-]{\text{exc.}} AuI_2^-$$

Au–X bond lengths in the series are 2.257 Å (Cl), 2.376 Å (Br) and 2.529 Å (I); they are affected by counter ions, Au–Cl being 2.281 Å in $Cs_2AuCl_2AuCl_4$. AuX_2^- exhibits Au–X stretching vibrations in the IR at 350, 254 and 210 cm^{-1} (X = Cl, Br, I, respectively, in the Bu_4N salts) and in Raman spectra at 329, 209 and 158 cm^{-1}, respectively [90].

Ions of the type AuX_2^- are found as counter ions in other complexes like $Aupy_2^+AuCl_2^-$, $Au(Bu_2NCS_2)_2^+AuBr_2^-$ and $Au(tht)_2^+AuI_2^-$.

4.10.5 Complexes of C-donors

AuCN has a similar structure to AgCN and likewise dissolves in excess cyanide to form $Au(CN)_2^-$; this is important in the extraction of gold. It has been characterized as various salts (Tl, K, Bu_4N, Cs) with Au–C 1.964 Å (Bu_4N salt [91]). The thallium salt has short Au–Au (3.10 Å) and Au–Tl (3.50 Å) interactions; extended-Hückel calculations indicate the importance of relativistic effects in these covalent interactions. Isocyanides form stable complexes:

$$AuCl(SMe_2) + MeNC \rightarrow AuCl(MeNC) + Me_2S$$

$$AuCl_4^- \xrightarrow[EtOH]{\text{exc. Bu}^t\text{NC}} AuCl(Bu^tNC)$$

The latter is linear with a short Au–C bond (1.92 Å); excess isocyanide lends to $Au(RNC)_2^+$ and possibly $Au(RNC)_4^+$. An unusual synthesis is

$$Ph_4AsAu(CN)_2^- \xrightarrow{MeI} MeNCAuCN$$

The linear Au(CO)Cl (ν(C–O) 2153 cm^{-1}), useful as a synthetic intermediate, is prepared by [92]

$$HAuCl_4 \xrightarrow[SOCl_2]{\text{exc. CO}} Au(CO)Cl + COCl_2$$

Au(CO)Br has been obtained in solution (only)

$$2Au_2Br_6 + 4CO \rightarrow 4Au(CO)Br + 4Br_2$$

while $Au(CO)_2^+$ has been isolated in various salts (section 4.16.1).

4.10.6 Complexes of S-donors

The most important complexes of S-donors are thiolates, simply regarded as $[Au(SR)]_n$, long used for treatment of rheumatoid arthritis (section 4.20). Little is known about their structures: it has been remarked that their clinical use would be unlikely to be sanctioned were they currently undergoing trial. EXAFS and Mössbauer measurements indicate that they have digonal coordination of gold (Au–S ~ 2.30 Å) and are, therefore, thiolate-bridged polymers [93a]. Hexameric structures have been suggested for some complexes with long alkyl groups that are soluble in organic solvents and have been established crystallographically for R = 2,4,6-$Pr^i_3C_6H_2$, which has a 12-membered Au_6S_6 ring in a chair configuration [93b]. Linear $Au(SH)_2^-$ is obtained from $Au(acac)_2^-$ and H_2S (Au–S 2.277–2.297 Å) [94]. Reaction with phosphines affords monomeric R_3PAuSR (e.g. auranofin);

the anion in $Ph_4As^+Au(SPh)_2^-$ [95] contains digonally coordinated gold (Au–S 2.262–2.271 Å) while in $Au(SR)_2^-$ ($R = 2,4,6\text{-}Pr^i_3C_6H_2$) Au–S is 2.288 Å [93].

Linear S–Au–S (but non-linear Au–S–C) is found in $PhAs^+Au(SCN)_2^-$ [96]; related phosphine complexes $(R_3P)_nAuSCN$ have been made (section 4.10.3). Sulphate and thiosulphate bind through sulphur; $Na_3Au(S_2O_3)_2.2H_2O$ has linear 2-coordinate gold in contrast to tetrahedral coordination of silver by sulphur and oxygen.

Among neutral ligands, thioethers form important complexes $AuCl(SR_2)$ (SR_2, e.g. Me_2S, Et_2S, $S(CH_2CH_2OH)_2$) that are synthetically useful since the sulphide is readily replaced by strong donors (e.g. tertiary phosphines) (sections 4.10.3 and 4.10.5). AuX(tht) (X = Cl, I) have been made. The iodide is $Au(tht)_2^+AuI_2^-$, but the chloride and bromide are neutral AuX(tht). The iodide remarkably can be synthesized at room temperature [97]:

$$2Au + I_2 \xrightarrow{tht} 2AuI(tht)$$

Essentially linear coordination is found in thiourea complexes $AuBr(S{=}C(NR_2)_2)$ (R = H, Me) and

$$[Au(S{=}C\text{–}\underbrace{NH\text{–}CH_2\text{–}CH_2\text{–}NH}_{})_2]^+Cl^-$$

Bidentate dithiolate ligands afford complexes like $Au(S_2CNR_2)$ (R = Et, Pr, Bu) and $Au(S_2PR_2)$ (R = Pr), which have dimeric structures based on 8-membered rings with linear S–Au–S coordination and short Au–Au distances. These in turn are associated into chains (Figure 4.16) (Au–Au *c*. 3.0–3.4 Å) [99].

The dithioacetate is a tetramer, still with digonally coordinated gold [100]. Though long known, the gold complexes of terpenethiolates ('liquid gold')

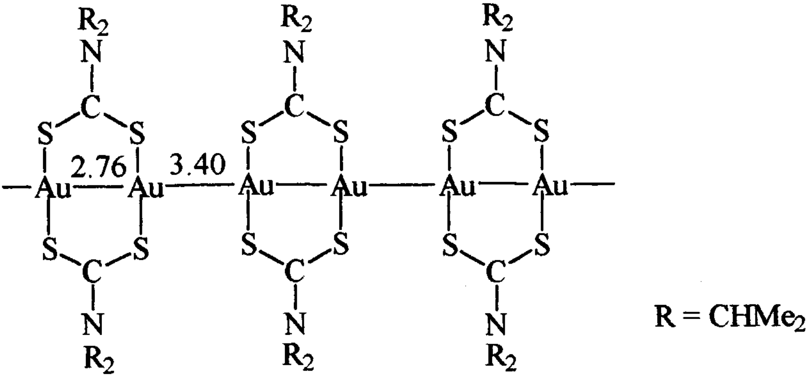


Figure 4.16 The structure of $Au(S_2CNPr^i_2)$ showing the association of dimeric units into chains.

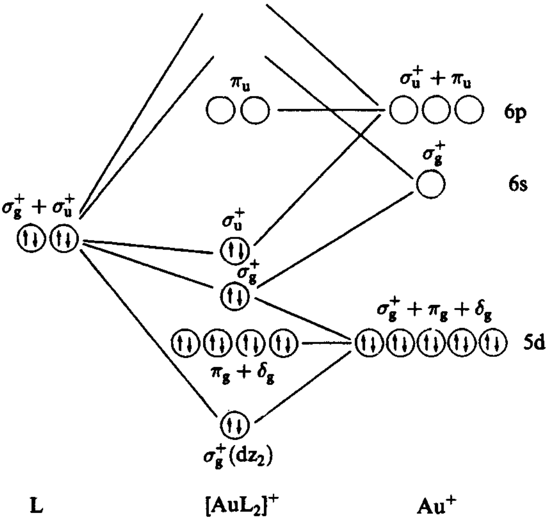


Figure 4.17 A qualitative molecular orbital scheme for a σ-bonded complex ion $[AuL_2]^+$. (Reprinted with permission from *Inorg. Chem.*, 1982, **21**, 2946. Copyright (1982) American Chemical Society.)

have, as yet, unknown structures; when painted on to pottery, then fired, they decompose to give a gold film.

4.10.7 MO schemes for 2-coordinate gold(I) complexes

A typical scheme [101] for a complex AuL_2^+ is shown in Figure 4.17.

A simple crystal field treatment predicts

$$5d_{z^2}(\sigma) > 5d_{xz,yz}(\pi) > 5d_{xy}, d_{x^2-y^2}(\delta),$$

the latter expected to be essentially non-bonding, but the relative energies will be ligand dependent, with electronegative ligands increasing d orbital participation and more electropositive ligands increasing s/p participation. There will also be gold 6s and 6p mixing into the highest ligand-field orbitals. Analysis of the spectra of $Au(CN)_2^-$ gave the ordering $d_{z^2}(\sigma) > d_{xy}$, $d_{x^2-y^2}(\delta) > d_{xz}$, $d_{yz}(\pi)$ whereas the PE spectrum of $(Me_3P)AuMe$ was interpreted in terms of $d_\pi \sim d_\delta > d_\sigma$. MO calculations for AuX_2^- (X = F to I) have recently indicated $d_\delta > d_\pi > d_\sigma$ [96].

4.11 Gold(II) complexes

Unstable dithiocarbamates $Au(S_2CNR_2)_2$ have been detected in solution by ESR but the square planar $Au(S_2C_2(CN)_2)_2^{2-}$ has been isolated as a green Bu_4N^+ salt; the gold(II) state appears to be stabilized by delocalization of

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This index is divided by element into eight parts. Each part is subdivided into sections devoted to each oxidation state, preceded by a general section. Thus if you want to find out about phosphine complexes of Rhodium, there is a general entry to phosphine complexes as well as separate references to phosphine complexes under the headings of Rhodium(0), (I), (II) and (III).

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