

The ruthenium(IV) aqua ion, best made by electrochemical oxidation of $\text{Ru}(\text{H}_2\text{O})_6^{2+}$, but also made by the reaction of RuO_4 with $\text{H}_2\text{O}_2/\text{HClO}_4$, is tetranuclear, formulated as $[\text{Ru}_4\text{O}_6(\text{H}_2\text{O})_{12}]^{4+}$, 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 $\text{OsO}_4(\text{OH})_2^{2-}$ is well characterized (sections 1.4.1 and 1.12.1).

Osmium(II) is probably too reducing to exist as $\text{Os}(\text{H}_2\text{O})_6^{2+}$, but $\text{Os}(\text{H}_2\text{O})_6^{3+}$ and a polynuclear $\text{Os}_4^+(\text{aq.})$ species are likely.

1.7 Compounds of ruthenium(0)

Apart from $\text{Ru}(\text{CO})_5$ and other carbonyls, there are mixed carbonyl-phosphine species and a few simple phosphine complexes like $\text{Ru}(\text{PF}_3)_5$ and $\text{Ru}[\text{P}(\text{OMe})_3]_5$ [61a].

Photochemistry of $\text{Ru}(\text{CO})_3(\text{PMe}_3)_2$ and the ruthenium(II) compound $\text{Ru}(\text{CO})_2(\text{PMe}_3)_2\text{H}_2$ in low-temperature matrices affords $[\text{Ru}(\text{CO})_2(\text{PMe}_3)_2\cdots\text{S}]$ ($\text{S} = \text{Ar}, \text{Xe}, \text{CH}_4$) [61b]. These monomers all have 18-electron tbp structures.

The phosphine complex $\text{Ru}(\text{dmpe})_2$ has been studied in matrices [62]. $\text{Ru}(\text{diphos})_2$ (diphos = depe, dppe, $(\text{C}_2\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_2\text{F}_5)_2$) has similarly been formed by photolysis of $\text{Ru}(\text{diphos})_2\text{H}_2$ 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 $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ (section 1.8.5) exist.

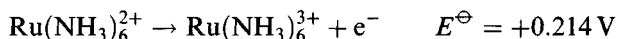
1.8 Complexes of ruthenium(II and III)

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 $\text{Ru}(\text{NH}_3)_6^{2+}$ can be obtained by various routes (see Figure 1.12).

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



Historically, the most important ruthenium(II) ammine species is $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$, the first stable dinitrogen complex to be isolated (1965). It was initially obtained by refluxing RuCl_3 in hydrazine solution (but many

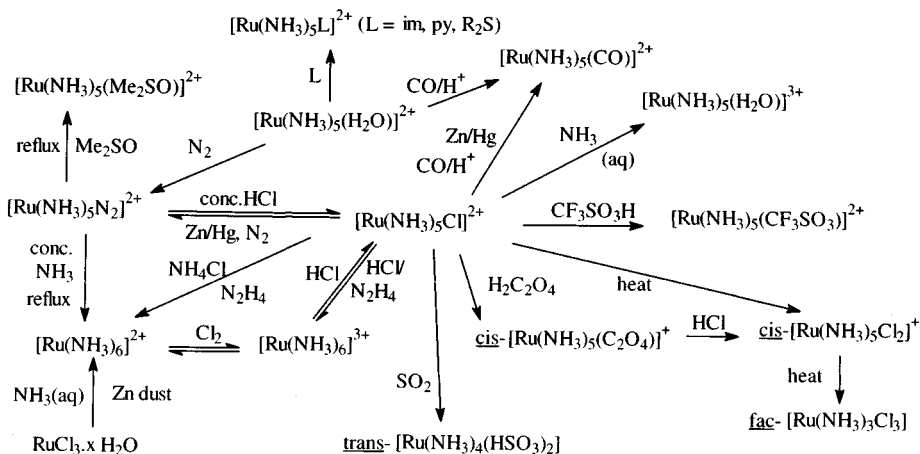


Figure 1.12 Ammine complexes of ruthenium.

other routes are available); it seems that the N₂ ligand may result from the oxidation of coordinated N₂H₄. Another synthesis [64] involves attack by NO on a coordinated NH₃ in [Ru(NH₃)₆]³⁺ (confirmed by using isotopically labelled ¹⁵NO), while the reaction of N₂ with [Ru(NH₃)₅(H₂O)]²⁺ is a simple substitution (Figure 1.13).

X-ray diffraction confirms the terminal N₂ geometry, with slight lengthening of the N–N bond (1.12 Å) compared to gaseous N₂ (1.09 Å) with concomitant lengthening shown by the change in ν(N≡N) in the IR spectrum (2110 cm⁻¹, compared with 2331 cm⁻¹ in nitrogen gas) [65].

The N₂ ligand is displaced by other ligands (e.g. py) and attempted oxidation to [Ru(NH₃)₅N₂]³⁺ results in the loss of N₂.

The colourless paramagnetic [Ru(NH₃)₆]³⁺ is readily synthesized by oxidation of [Ru(NH₃)₆]²⁺. Its magnetic moment is as expected for a low-spin d⁵ ion (2.17 μ_B for Ru(NH₃)₆Br₃ at 292 K).

The pentammine aqua ion [Ru(NH₃)₅(H₂O)]²⁺, best made by zinc amalgam reduction and aquation of [Ru(NH₃)₅Cl]²⁺, undergoes extensively studied substitution reactions first order in both the ruthenium complex and the incoming ligand (e.g. NH₃, py) and is a convenient source of other

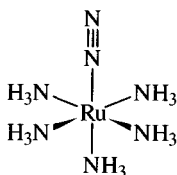


Figure 1.13 [Ru(NH₃)₅(N₂)]²⁺.

pentammines. The corresponding ruthenium(III) species $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ can be made by aquation of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ or the triflate $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)]^{2+}$. Heating solid $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ gives $[\text{Ru}(\text{NH}_3)_5\text{X}]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$) [66].

Structures determined include octahedral $\text{Ru}(\text{NH}_3)_6^{3+}$ in the tetrafluoroborate ($\text{Ru}-\text{N}$ 2.104 Å) and thiocyanate (2.105–2.113 Å), while in $[\text{Ru}(\text{NH}_3)_6]\text{BrSO}_4$ $\text{Ru}-\text{N}$ is 2.107 Å. In $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{SO}_4 \cdot 4\text{H}_2\text{O}$, $\text{Ru}-\text{Cl}$ is 2.374 Å while $\text{Ru}-\text{N}$ distances fall in the range 2.096–2.113 Å.

Among ruthenium(II) complexes, $\text{Ru}(\text{NH}_3)_6\text{I}_2$ has $\text{Ru}-\text{N}$ of 2.144 Å; $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ has $\text{Ru}-\text{N}(\text{NH}_3)$ and $\text{Ru}-\text{N}(\text{N}_2)$ 2.11 Å; and $[\text{Ru}(\text{NH}_3)_5(\text{Me}_2\text{SO})]^{2+}$ has $\text{Ru}-\text{N}$ (*cis*) of 2.169 Å, $\text{Ru}-\text{N}$ (*trans*) 2.209 Å and $\text{Ru}-\text{S}$ 2.188 Å. The $\text{Ru}-\text{N}$ bonds are, therefore, shorter in the ruthenium(III) complexes, as expected on electrostatic grounds [67].

The ESR spectra of $t_{2g}^5\text{Ru}(\text{NH}_3)_6^{3+}$ on cubic sites in $[\text{Ru}(\text{NH}_3)_6]\text{BrSO}_4$ show an isotropic g value of 1.926 while in $[\text{Ru}(\text{NH}_3)_6](\text{NCS})_3$ the g values are 2.357, 1.929 and 1.468 ($g_{\text{av}} = 1.918$) in a low symmetry field. The results have been interpreted in a crystal field model with an orbital reduction factor of 0.94 [67].

Binuclear ammine complexes

Two binuclear ammine complexes are of particular interest.

The Creutz-Taube compound (named after its discoverers), $[(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5]^{5+}$ is the middle member of a redox-related series, formally containing one ruthenium(II) and one ruthenium(III) (Figure 1.14); the interest lying in whether the two ruthenium centres are identical, whether the valencies are 'trapped' or whether there is partial delocalization.

The mixed-valence ion has an intervalence charge transfer band at 1562 nm not present in the spectra of the +4 and +6 ions. Similar ions have been isolated with other bridging ligands, the choice of which has a big effect on the position and intensity of the charge-transfer band (e.g. $\text{L} = \text{bipy}$, 830 nm).

The structural data (Table 1.8) and spectroscopic information indicate that the 5+ ion has considerable delocalization with rapid electron transfer between the two centres ($\sim 10^{12} \text{ s}^{-1}$) [68].

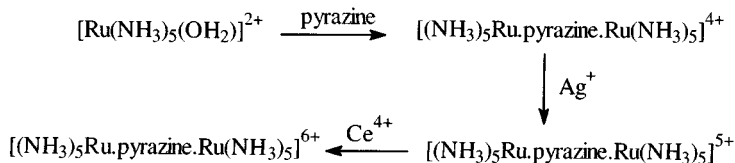
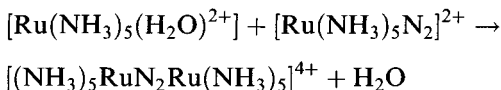


Figure 1.14 Dimeric pyrazine complexes of ruthenium.

Table 1.8 Bond lengths (Å) in $(\text{NH}_3)_5\text{RuN}$ (pyrazine) $\text{NRu}(\text{NH}_3)_5^{n+}$

n	4	5	6
$\text{Ru}-\text{NH}_3$ (<i>trans</i>)	2.149	2.134	2.089
$\text{Ru}-\text{NH}_3$ (<i>cis</i>)	2.132	2.111	2.101
$\text{Ru}-\text{N}$ (pyrazine)	2.013	2.002	2.115

A dimeric dinitrogen complex can be made by several routes, including



It has a symmetric eclipsed structure with a linear $\text{Ru}-\text{N}-\text{N}-\text{Ru}$ geometry (178.3°) (Figure 1.15).

Because of the symmetric structure, a strong $\nu(\text{N}\equiv\text{N})$ band is seen in the Raman spectrum at 2100 cm^{-1} , but not in the IR spectrum. It can be oxidized to the unstable $5+$ ion chemically and to the $6+$ ion electrochemically [69].

'Ruthenium red' and 'ruthenium brown'

Air oxidizes ammoniacal ruthenium chloride to a red solution, which on workup gives 'ruthenium red', brown diamagnetic $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]\text{Cl}_6$, formally containing two Ru^{3+} and one Ru^{4+} . Oxidation of this (Ce^{4+} , HNO_3) gives $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{7+}$, 'ruthenium brown' [70]. These are oxo-bridged species (the IR spectrum of the red shows a band at 805 cm^{-1} owing to $\text{Ru}-\text{O}-\text{Ru}$ stretching, which is shifted to 820 cm^{-1} in 'ruthenium brown'). The structure of the thiosulphate salt of 'ruthenium red' has been determined (Figure 1.16) and confirms the trinuclear $\text{Ru}-\text{N}$ bonds are eclipsed with the $\text{Ru}-\text{N}$ bonds at one end but 31° away from the eclipsed position with the $\text{Ru}-\text{N}$ bonds at the other end, so that the ion is non-centrosymmetric.

Reaction of 'ruthenium red' with ethylenediamine at 45°C yields a red-green analogue with chelating ethylenediamines bound to the central ruthenium $[(\text{NH}_3)_5\text{RuORu}(\text{en})_2\text{ORu}(\text{NH}_3)_5]^{6+}$ (Figure 1.17).

Here the $\text{Ru}-\text{NH}_3$ bonds at each end are eclipsed, with the $\text{Ru}-\text{N}(\text{en})$ bonds staggered.

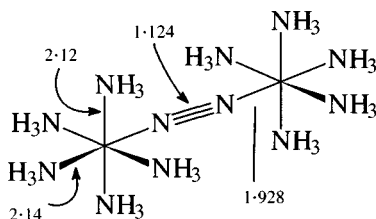


Figure 1.15 Bond lengths in the dimeric ion $[(\text{NH}_3)_5\text{RuN}_2\text{Ru}(\text{NH}_3)_5]^{4+}$.

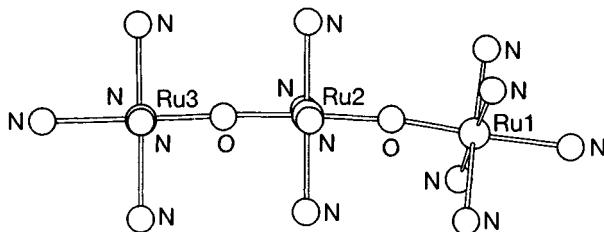


Figure 1.16 The structure of $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+}$, Ruthenium red. (Reprinted from *Biochim. Biophys. Acta*, **627**, 332, 1980, with kind permission of Elsevier Science – NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

Complexes of bi- and polydentate amines

There has been intense study of the complexes of bi- and polydentate amines since the mid-1970s, driven by interest in the catalytic photodecomposition of water using the excited states of $\text{Ru}(\text{bipy})_6^{n+}$ ($n = 2, 3$) and related systems (Figure 1.18) [5, 7, 8, 71].

The most important complexes are tris systems $\text{Ru}(\text{L-L})_3^{2+}$, traditionally prepared by fusing RuCl_3 with the molten ligand (L-L, e.g. phen, bipy). The ruthenium(II) compounds can be oxidized to the ruthenium(III) analogues by various chemical oxidizing agents (e.g. Ce^{4+} , PbO_2), though the products are somewhat unstable. X-ray diffraction shows the complexions to have approximately D_3 symmetry (the highest possible for an $\text{M}(\text{chelate})_3$ system). Ru–N bond lengths in $[\text{Ru}(\text{bipy})_3]^{n+}(\text{PF}_6)_n$ are 2.053 Å ($n = 2$) and 2.057 Å ($n = 3$) with N–Ru–N ‘bite’ angles of *c.* 77°. The relatively short Ru–N bonds, compared with the amines, suggest some π -bonding [72]. These cations exist in enantiomeric forms, of course; $\text{Ru}(\text{bipy})_3^{2+}$ was first resolved by Burstall (1936) and $\text{Ru}(\text{bipy})_3^{3+}$ by Dwyer (1949).

The virtual identity of the Ru–N bonds and coordination geometries in the ruthenium(II and III) complexes is noteworthy and accounts for the

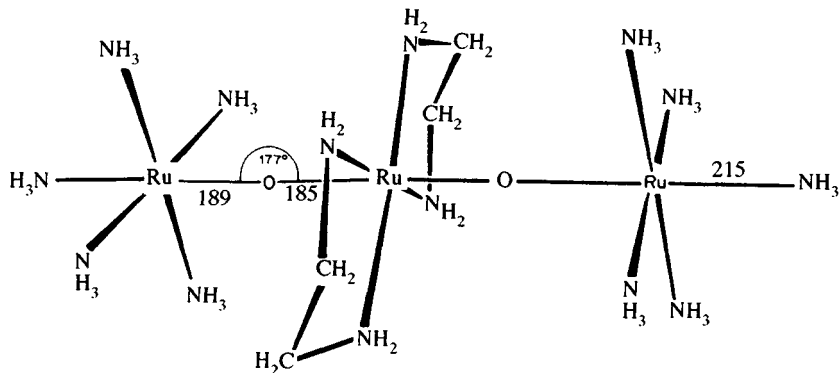


Figure 1.17 The structure of $[\text{Ru}_3\text{O}_2(\text{en})_2(\text{NH}_3)_{10}]^{6+}$. (Reproduced with permission from S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan Press Ltd, 1975, p. 62.)

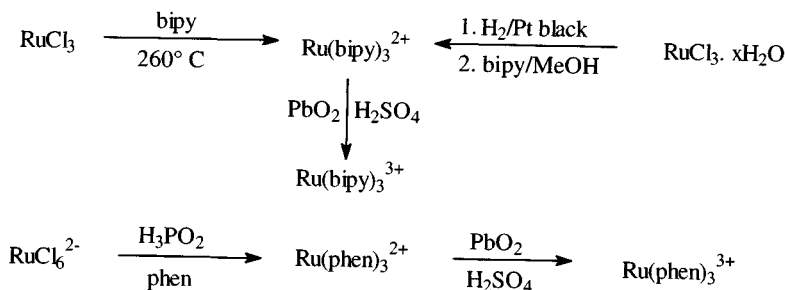
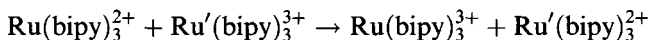


Figure 1.18 Syntheses of ruthenium tris complexes of 1,10-phenanthroline and Δ,Δ -bipyridyl.

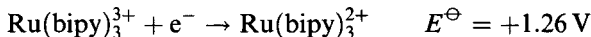
rapidity of the electron exchange.



for which $K = 4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ as virtually no molecular reorganization is needed on electron transfer [72b].

Mixed complexes $[\text{Ru}(\text{bipy})_2\text{L}](\text{ClO}_4)_2$ ($\text{L} = \text{phen}$, 5-methyl(phen)) have virtually identical Ru–N (phen) and Ru–N (bipy) distances.

The UV-visible spectrum of $\text{Ru}(\text{bipy})_3^{2+}$ has a strong absorption at 454 nm ($E = 14\,600$) owing to a $t_{2g} \rightarrow \pi^*$ charge-transfer transition. This triplet-state excited complex $^*\text{Ru}(\text{bipy})_3^{2+}$ can lose an electron by luminescence or by donating it to a suitable acceptor (quencher) producing ground-state $\text{Ru}(\text{bipy})_3^{3+}$, a very strongly oxidizing species



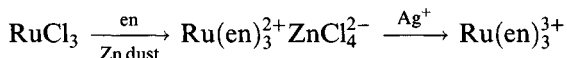
capable of oxidizing water or OH^- to O_2 (it may be germane to this that hydrated $\text{Ru}(\text{L}-\text{L})_3^{3+}$ salts are less stable than the anhydrous salts in general).

The emission can also be quenched by electron donors causing reduction of the ruthenium complex ion.

Although $\text{Ru}(\text{bipy})_3^{2+}$ alone will not split water into hydrogen and oxygen, it has been accomplished with $\text{Ru}(\text{bipy})_3^{2+}$ using various catalysts or radical carriers. Perhaps the most studied system for the photoreduction of water involves using methyl viologen as the quencher, EDTA as an electron donor (decomposed in the reaction) and colloidal platinum as a redox catalyst (Figure 1.19).

Systems for the photo-oxidation of water have used $\text{Ru}(\text{bipy})_3^{2+}$ with $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ as the electron donor and RuO_2 as catalyst.

Besides the tris ruthenium complexes, other complexes can be made (Figure 1.20), while ethylenediamine (en) complexes exist:



The optical isomers can be resolved again, for example with one enantiomer of $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ [73]. Again there is a contraction in Ru–N on passing from

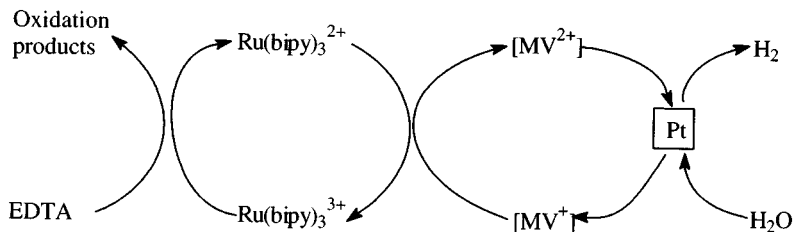
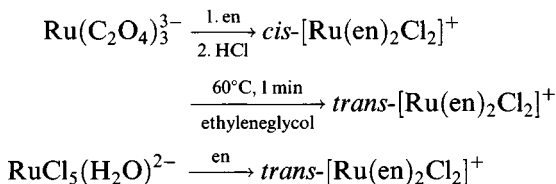


Figure 1.19 Cycles involved in a ruthenium-based system for the reduction of water.

the 2+ ion (2.132 Å) to the 3+ ion (2.11 Å) [74]



The *trans*-dichloro complex can be converted into an unusual complex with bound azide and dinitrogen (Figure 1.21) with linear Ru–N≡N, as in other dinitrogen complexes ($\nu(\text{N}\equiv\text{N})$ 2103 cm^{-1}) [75].

The *cis*-isomer can also be obtained ($\nu(\text{N}\equiv\text{N})$ 2130 cm^{-1} , $\nu(\text{N}_3)$ 2050 cm^{-1}). On oxidation it loses both azide and dinitrogen

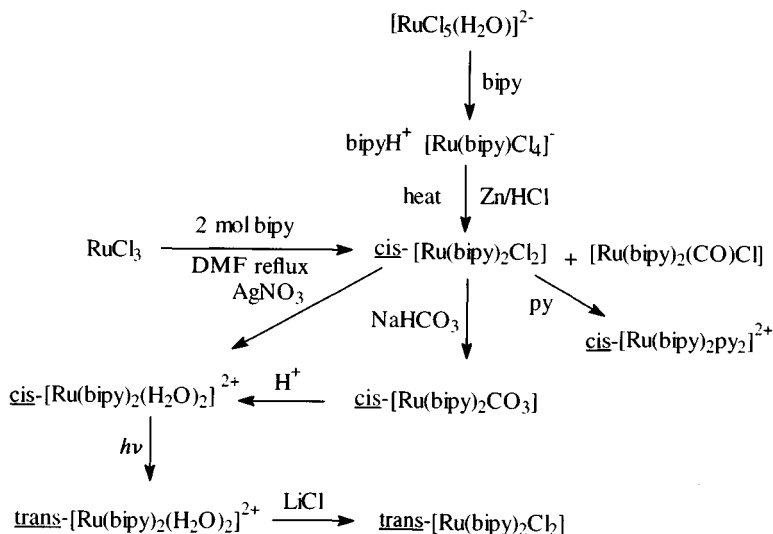
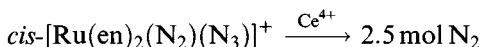


Figure 1.20 Syntheses of ruthenium 2,2'-bipyridyl complexes.

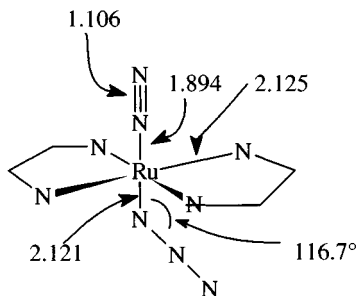


Figure 1.21 Bond lengths in $[\text{Ru}(\text{en})_2(\text{N}_2)(\text{N}_3)]^+$.

The terdentate ligand terpyridyl affords a range of complexes: fusion of RuCl_3 with terpy gives $\text{Ru}(\text{terpy})_2^{2+}$, while refluxing RuCl_3 with an ethanolic solution of the ligand yields $\text{RuCl}_3(\text{terpy})$. Both of these are doubtless 6-coordinate. Ruthenium bis(terpyridine) complexes are also attracting attention as photosensitizers [76].

mer- $[\text{Ru}(\text{terpy})\text{Cl}_3]$ is an active cystostatic agent in leukaemia cells, forming interstrand cross-links in DNA [77].

1.8.2 Tertiary phosphine complexes

Tertiary phosphine complexes have been studied intensively since the 1960s. The bulk of the work has been with phosphines, but corresponding arsine complexes are broadly similar.

The reactions of monodentate phosphines have been studied in most depth [58b]. The products of the reaction of a tertiary phosphine with RuCl_3 depends on both the phosphine concerned (size and reducing power) and upon the reaction conditions (Figure 1.22).

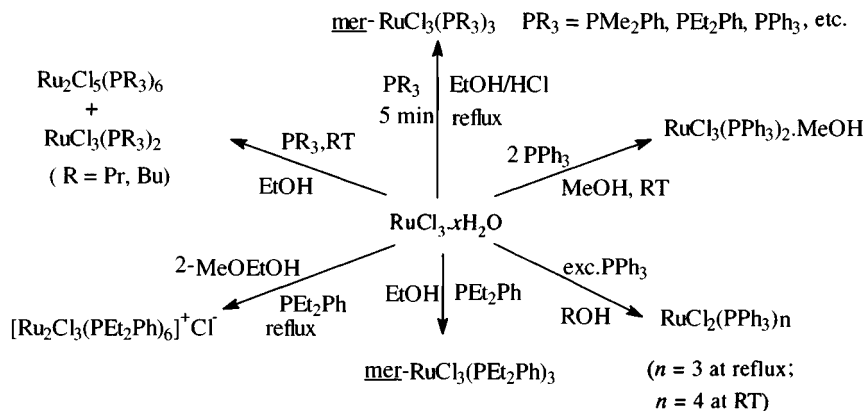


Figure 1.22 Syntheses of tertiary phosphine complexes of ruthenium.

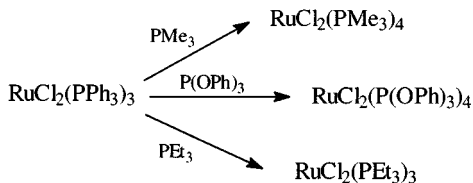


Figure 1.23 Syntheses of complexes of other tertiary phosphines by metathesis of $\text{RuCl}_2(\text{PPh}_3)_3$.

Initial reaction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with the tertiary phosphine in ethanol/concentrated HCl leads to *mer*- $\text{RuCl}_3(\text{PR}_3)_3$ or $[\text{RuCl}_3(\text{PR}_3)_2]$. (Omission of the HCl can lead to faster reduction and the formation of carbonyl complexes, particularly in solvents like 2-methoxyethanol.) Extended reaction times or using excess phosphine lead to reduction to $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$ or mixed-valence complexes, $\text{Ru}_2\text{Cl}_5(\text{PR}_3)_6$ being typical. Triphenylphosphine, the most studied phosphine (on account of its ease of handling as an air-stable solid) is atypical in forming monomers $\text{RuCl}_2(\text{PPh}_3)_3$, which are conveniently metathesized into $\text{RuCl}_2(\text{PR}_3)_n$ with other tertiary phosphines in hexane (use of ethanol or dichloromethane and refluxing leads to the ionic dimer $\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6^+\text{Cl}^-$) (Figure 1.23). Alkyl phosphines in general tend to be weaker complexing agents and are more strongly reducing.

$\text{RuCl}_2(\text{PPh}_3)_3$ has been studied in considerable detail [79]. Synthetic routes to it and some of its reactions are shown in Figure 1.24. It is important as a source of $\text{RuHCl}(\text{PPh}_3)_3$, a very active hydrogenation catalyst specific for alk-1-enes. Unlike $\text{RhCl}(\text{PPh}_3)_3$, it is not active in hydroformylation. $\text{RuCl}_2(\text{PPh}_3)_3$ has a distorted square pyramidal structure (Figure 1.25) with ruthenium in some 0.45 Å above the basal plane [80]. The sixth coordination position is blocked by an *ortho*-hydrogen from a phenyl ring ($\text{Ru}-\text{H}$ 2.59 Å). $\text{RuCl}_2(\text{PPh}_3)_4$ is probably $\text{RuCl}_2(\text{PPh}_3)_3\text{PPh}_3$ since NMR shows that the fourth phosphine is certainly not bound in solution; the

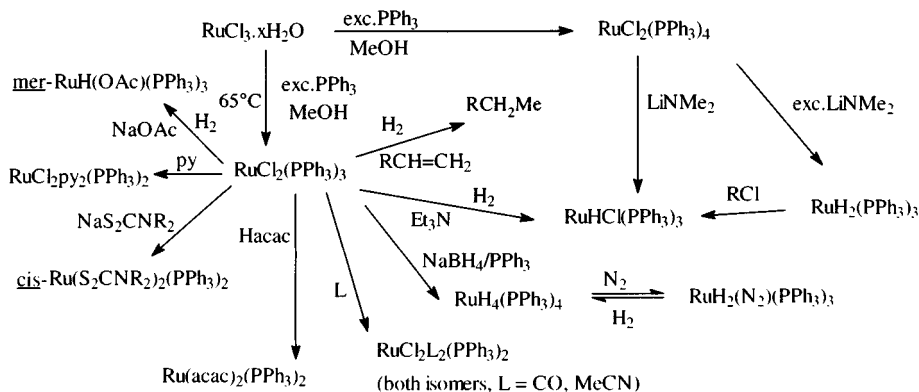


Figure 1.24 Reactions of $\text{RuCl}_2(\text{PPh}_3)_3$.

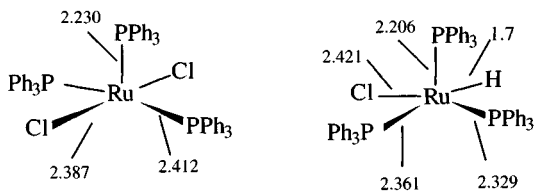


Figure 1.25 A comparison of bond lengths in the complexes $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$.

non-existence of the 18-electron 6-coordinate complex is probably a result of steric repulsion between the tertiary phosphine ligands, while 16-electron $\text{RuCl}_2(\text{PPh}_3)_3$ dissociates in solution affording dimeric $[\text{Cl}(\text{PPh}_3)_2\text{Ru}(\mu\text{-Cl})_2\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ (NMR evidence at low temperatures). $\text{RuCl}_2(\text{SbPh}_3)_4$ does exist (X-ray [81]).

Therefore, one reaction frequently observed involves displacement of a tertiary phosphine, either wholly (e.g. PMe_3 in hexane to form $\text{RuCl}_2(\text{PMe}_3)_4$) or partly (e.g. with pyridine $\text{RuCl}_2\text{py}_2(\text{PPh}_3)_2$ being formed); both are 18-electron species. The former reaction is a very convenient way of making monomeric alkyl phosphine complexes of ruthenium(II) as already noted [78]. Reactions with nitriles and CO are solvent and temperature dependent, with *cis*- and *trans*-isomers of $\text{RuCl}_2\text{L}_2(\text{PPh}_3)_2$ obtained depending upon conditions.

A second type of reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ involves substitution of the chloride ligands; this can be achieved using hydride, to give $\text{RuH}_2(\text{PPh}_3)_4$ (via $\text{RuHCl}(\text{PPh}_3)_3$), and other representative ligands such as dithiocarbamates and diketonates. As mentioned above, $\text{RuCl}_2(\text{PPh}_3)_3$ is a hydrogenation catalyst [82] (doubtless $\text{RuHCl}(\text{PPh}_3)_3$ is the active species (Figure 1.26)) where initially a π -alkene complex is formed, followed by hydride transfer [82] to give an alkyl.

$\text{RuHCl}(\text{PPh}_3)_3$ itself has a distorted square pyramidal structure (Figure 1.25) but the hydride ligand has less steric effect and the structure has been described as a capped tetrahedron ($\text{Ru}-\text{P}$ 1.7 Å, $\text{Ru}-\text{Cl}$ 2.421 Å, $\text{Ru}-\text{P}$ 2.206–2.329 Å; $\nu(\text{Ru}-\text{H})$ 2020 cm^{-1}) [83]. The $\text{Ru}-\text{Cl}$ stretching frequency in the IR spectrum of $\text{RuHCl}(\text{PPh}_3)_3$ is at 282 cm^{-1} , compared with 315 cm^{-1} in $\text{RuCl}_2(\text{PPh}_3)_3$, the weakening reflecting the *trans*-influence of hydride.

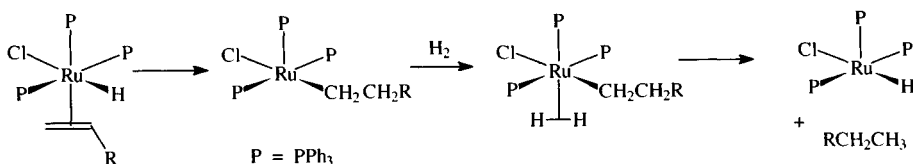


Figure 1.26 Abbreviated mechanism for the catalytic hydrogenation of a terminal alkene using $\text{RuHCl}(\text{PPh}_3)_3$.

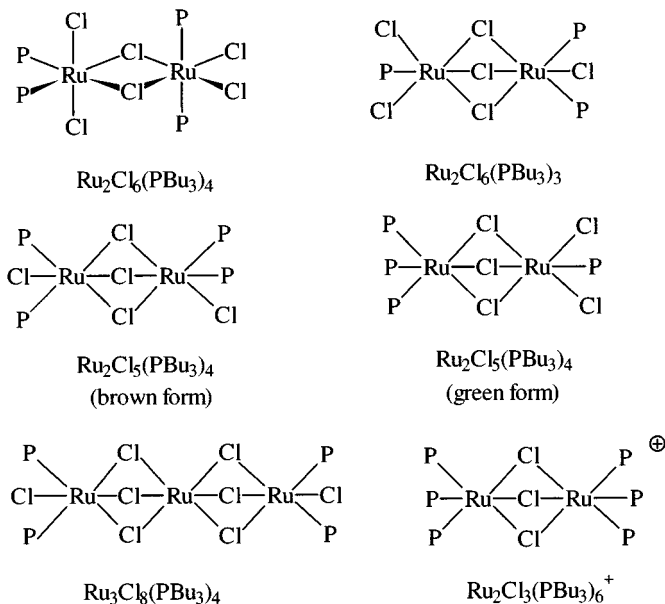


Figure 1.27 Ruthenium complexes of tributylphosphine ($\text{P} = \text{PBu}_3$).

Tributylphosphine complexes have been investigated in detail [84] and have revealed a bewildering variety of complexes. Reaction of RuCl_3 with tributylphosphine on brief reflux in ethanol/concentrated HCl gives monomeric *mer*- $\text{RuCl}_3(\text{PBu}_3)_3$. Otherwise di- and trimeric species are obtained. Reaction with the phosphine in ethanol at room temperature affords two kinds of diruthenium(III, III) dimers: edge-shared $\text{Ru}_2\text{Cl}_6(\text{PBu}_3)_4$ and face-shared $\text{Ru}_2\text{Cl}_6(\text{PBu}_3)_3$ (Figure 1.27).

The former has a long $\text{Ru}-\text{Ru}$ distance (3.733 Å) while in the latter the rutheniums are drawn closer (3.176 Å). In addition, reduction yields two isomers of $\text{Ru}_2\text{Cl}_5(\text{PBu}_3)_4$ and $\text{Ru}_3\text{Cl}_8(\text{PBu}_3)_4$, as well as the 'ionic' $\text{Ru}_3\text{Cl}_6(\text{PBu}_3)_6^+[\text{RuCl}_4(\text{PBu}_3)_2]^-$, all of which contain both ruthenium(II) and ruthenium(III). The classic diruthenium(II, III) cation $[\text{Ru}_2\text{Cl}_3(\text{PBu}_3)_6]^+$ has also been isolated.

In general, the dimers have three chlorine bridges, and $\text{Ru}_3\text{Cl}_8(\text{PBu}_3)_4$ resembles the mixed-valence chloro complex $\text{Ru}_3\text{Cl}_{12}^{4-}$. A similar, but less extensively studied, pattern of behaviour has been found with other alkyl phosphines.

The mixed valence compounds only have one unpaired electron per dimer unit. Their $\text{Ru}-\text{Ru}$ distances vary from 2.854 Å in $\text{Ru}_3\text{Cl}_8(\text{PBu}_3)_4$ through 3.115 Å in brown $\text{Ru}_2\text{Cl}_5(\text{PBu}_3)_4$ to 3.279 Å in green $\text{Ru}_2\text{Cl}_5(\text{PBu}_3)_4$ with a move to 'trapped' valences. In the $\text{Ru}_2\text{Cl}_6(\text{PR}_3)_4$ dimers, the two ruthenium sites behave independently; the ESR spectrum of $\text{Ru}_2\text{Cl}_6(\text{PET}_3)_4$ gives separate signals, one characterized by $g_{\perp} = 2.49$ and $g_{\parallel} = 1.65$, the second having $g_1 = 2.31$, $g_2 = 2.06$, $g_3 = 1.80$ (Figure 1.28).

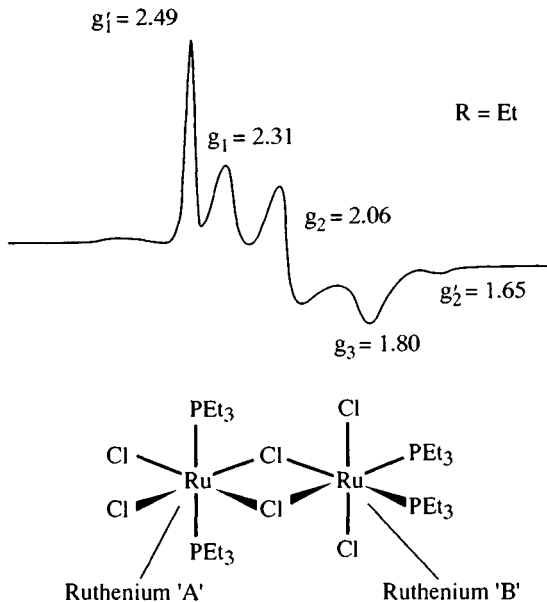
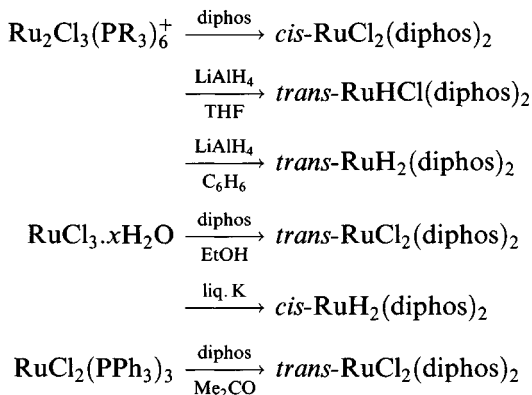


Figure 1.28 ESR spectra of $\text{Ru}_2\text{Cl}_6(\text{PEt}_3)_4$. (Reprinted with permission from *Inorg. Chem.*, 1991, 30, 4393. Copyright (1991) American Chemical Society.)

The axial resonance is assigned to ruthenium 'A' with its D_{4h} local symmetry (compare $g_{\perp} = 2.51$, $g_{\parallel} = 1.64$ in $\text{trans-RuCl}_4(\text{PEt}_3)_2^-$) while the 'rhombic' signal is assigned to ruthenium 'B', where the 'local' symmetry is D_{2h} and three different components of the g-tensor are expected.

Complexes of bidentate phosphines

The bidentate phosphine complexes were among the earliest ruthenium phosphine complexes to be made [85]; often displacement is a convenient route:



(Diphos typically is $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.)

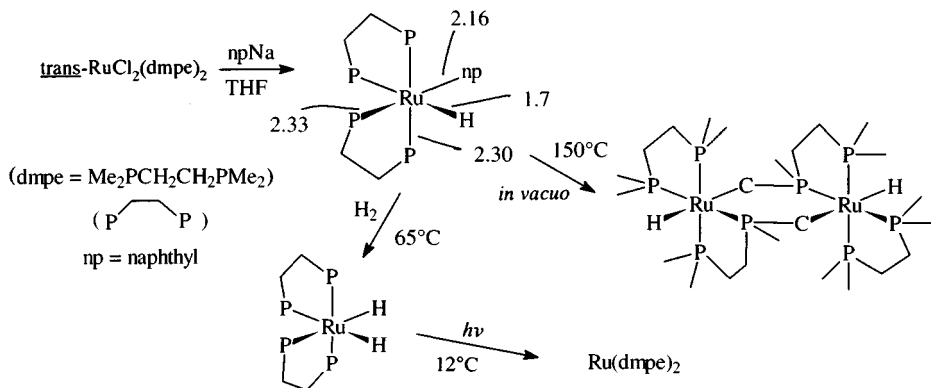


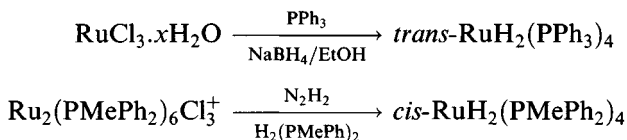
Figure 1.29 Synthesis of ruthenium complexes of the chelating ligand bis(dimethylphosphino)ethane (dmpe).

The halide groups can be replaced by other substituents like hydride or alkyl [86]. When the naphthyl (np) $\text{RuHnp}(\text{dmpe})_2$ is heated, the ligand undergoes an internal metallation to afford a dimer [87] (it was originally believed to be a monomer), though $\text{Ru}(\text{dmpe})_2$ has been isolated by photolysis of its dihydride, in matrixes at 12 K (Figure 1.29) [88].

Five coordination is not unknown (Figure 1.30) [89].

Hydridophosphine complexes

All the compounds of the type $\text{RuH}_2(\text{PR}_3)_4$ seem to be classical hydrides



Both *cis*- and *trans*-structures are possible: $\text{RuH}_2(\text{PMe}_3)_4$ is *cis* (Ru–H 1.507, 1.659 Å, Ru–P 2.276–2.306 Å) [90] while spectra show that $\text{RuH}_2(\text{PF}_3)_4$ and others have this configuration. $\text{RuH}_2[\text{PPh}(\text{OEt})_2]_4$ is definitely *trans* (X-ray) with Ru–H 1.6 Å, Ru–P 2.272 Å. Many diphosphines form dihydrides. $\text{Ru}(\text{dmpe})_2\text{H}_2$ has been a useful starting material for the synthesis of thiolate complexes [91] such as *trans*- $\text{Ru}(\text{SPh})_2(\text{dmpe})_2$.

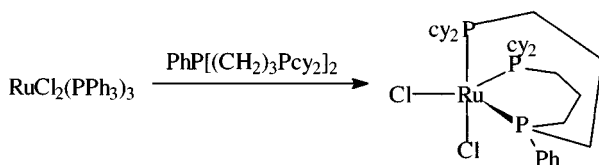


Figure 1.30 A 5-coordinate complex of a tridentate phosphine.

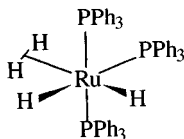
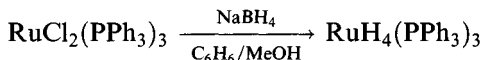


Figure 1.31 The probable structure of $\text{RuH}_4(\text{PPh}_3)_3$.

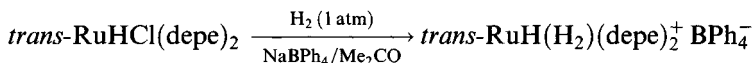
Many of the $\text{RuH}_4(\text{PR}_3)_3$ and $\text{RuH}_6(\text{PR}_3)_2$ systems have, however, η^2 -dihydrogen groups. Therefore, $\text{RuH}_4(\text{PPh}_3)_3$ prepared by:



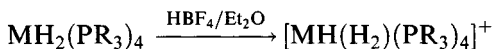
is believed to have the structure shown in Figure 1.31, like $\text{Fe}(\text{H})_2(\eta^2\text{-H}_2)\text{-}(\text{PEtPh}_2)_3$ (confirmed by neutron diffraction) while the osmium analogues are 'classical' hydrides.

MO calculations on $\text{MH}_4(\text{PPh}_3)_3$ indicate that the dihydrogen complex is most stable for iron and ruthenium, while the osmium compound is a classical hydride, owing to relativistic effects [92]. The IR spectrum of $\text{RuH}_4(\text{PPh}_3)_3$ shows an Ru-H absorption at 1950 cm^{-1} (shifting to 1400 cm^{-1} on deuteration): no Ru-H_2 absorption was seen and a low-frequency NMR resonance was seen at approximately 7.1 ppm. Relaxation time measurements, however, indicate a short t_1 (38 ms) characteristic of η^2 -bound hydrogen [93]. The dihydrogen ligand is displaced by N_2 , forming $\text{Ru}(\text{H})_2\text{N}_2(\text{PPh}_3)_3$ and, reversibly, by PPh_3 to form $\text{RuH}_2(\text{PPh}_3)_4$. $\text{RuH}_6(\text{Pcy}_3)_2$ is similarly $\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{Pcy}_3)_2$.

Cationic hydrides have been important in studying dihydrogen complexes [94]



($\text{depe} = \text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2$). In this reaction, the labile chloride is displaced. Protonation can be employed:



($\text{PR} = \text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$, etc.; $\text{M} = \text{Fe}$, Ru , Os).

Study of the high-field resonances in the ^1H NMR spectrum at 220 K of $\text{RuH}(\text{H}_2)(\text{depe})_2^+$ shows a broad singlet (-6.4 ppm) owing to bound H_2 with a very short t_1 (11 ms) and a resonance with a much longer relaxation time (270 ms) at -11.3 ppm associated with the terminal hydride. A large H-D coupling constant is another way to show the presence of a $\eta^2\text{-H}_2$ ligand: $J(\text{H-D})$ is 32 Hz in $\text{RuD}(\text{HD})(\text{depe})_2$ compared with 43.2 Hz in HD gas, showing the persistence of the H-D bond.

A few anionic hydrides exist, the best characterized being $\text{RuH}_3(\text{PPh}_3)_3^-$



The crystal structure of the K(18-crown-6) salt shows a *fac*-octahedral structure (Ru–H 1.59–1.71 Å, Ru–P 2.312–2.331 Å) with a large distortion from regular octahedral geometry (H–Ru–H 70–88°; P–Ru–P 102–111°) owing to the disparate steric demands of the hydride and tertiary phosphine ligands [95].

In general, ruthenium forms more dihydrogen complexes than osmium. When a hydrogen molecule joins to a metal, there is a balance between the energy lost when the H–H bond is broken and the energy gained in forming M–H bonds; osmium forms stronger ‘classical’ M–H bonds so is less likely to form dihydrogen complexes [93].

1.8.3 Carboxylate complexes

Ruthenium forms four significant families of carboxylate complexes.

Class 1

Refluxing $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with ethanoic acid/ethanoic anhydride mixtures, particularly in the presence of LiCl, gives a green solution and crystals of the dimeric $\text{Ru}_2(\text{OAc})_4\text{Cl}$, an unusual ‘mixed-valence’ compound with a ‘lantern’ structure (Figure 1.32) where the dimer units are linked into continuous chains by axial bridging chlorides (the bridges are sometimes kinked, sometimes linear) [96].

The complexes are 1 : 1 electrolytes in solution. Other such complexes can be made by a similar route or by halide (or carboxylate) exchange. The first monomeric system $\text{Ru}_2\text{Cl}(\text{O}_2\text{C}\cdot\text{C}_4\text{H}_4\text{N})_4(\text{thf})$, where the ruthenium at one end of the ‘lantern’ is bound to a thf and the other to a chloride, has recently been made [97]. $[\text{Ru}_2\text{Cl}(\text{O}_2\text{C}\text{Bu}^t)_4(\text{H}_2\text{O})]$ and $[\text{Ru}_2\text{Cl}(\text{O}_2\text{CPr}^i)_4(\text{thf})]$ are also monomeric [98].

These mixed-valence compounds have magnetic moments around $4\mu_{\text{B}}$, indicating an $S = 3/2$ (quartet) ground state, in keeping with their ESR spectra, which resemble those of Cr^{3+} compounds with a big zero-field splitting ($g_{\perp} = 4, g_{\parallel} = 2$) [99].

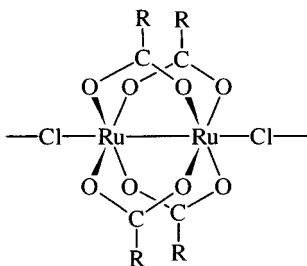


Figure 1.32 The ‘lantern’ structure adopted by $\text{Ru}_2(\text{OAc})_4\text{Cl}$ and other similar compounds.

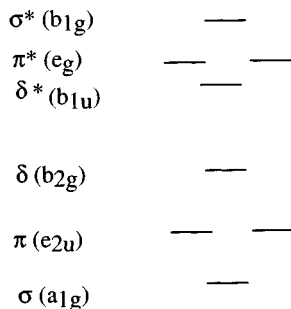


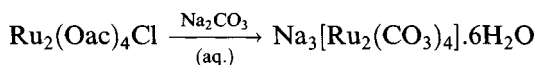
Figure 1.33 A possible orbital sequence for dinuclear ruthenium carboxylates.

The analogous diruthenium(II, II) compounds can be made starting from the blue solution of reduced RuCl_3 in ethanol (section 1.3.5) on extended refluxing with sodium acetate, whereupon the solvate $\text{Ru}_2(\text{OAc})_4(\text{MeOH})_2$ separates. This loses methanol readily on drying; the resulting anhydrous acetate will form weak adducts $\text{Ru}_2(\text{OAc})_4\text{L}_2$ (L, e.g. H_2O , thf). These are all paramagnetic with two unpaired electrons [100].

A bonding scheme for the dinuclear carboxylates can be constructed as follows [101]. Assuming the Ru–Ru axis to be the z axis, each ruthenium uses its 5_{px} , 5_{py} , $5s$ and $4d_{x^2-y^2}$ orbitals to form four σ -bonds to the carboxylate oxygens (lying along the x and y axes). The $4d_z$ orbitals from each ruthenium form an Ru–Ru σ -bond, d_{xz} and d_{yz} overlap to form two Ru–Ru π -bonds and the d_{xy} orbitals form a σ -bond, shown in an energy level diagram like Figure 1.33. (The p_z orbitals are available to bond to the ligands bridging dimers or in terminal positions.)

In $\text{Ru}_2(\text{OAc})_4\text{Cl}$, one ruthenium(II) supplies six electrons, the ruthenium(III) five electrons, giving rise to a $\sigma^2\pi^4\delta^2\pi^*2\delta^*1$ configuration (provided δ^* and π^* are close enough together) with three unpaired electrons. A diruthenium(II,II) dimer would have the configuration $\sigma^2\pi^4\delta^2\pi^*3\delta^*1$ with two unpaired electrons. (It should be recognized that the ordering of the orbitals can be changed by altering the terminal/bridging ligands.)

Apart from carboxylates, other groups such as carbonate and triazenate ($\text{R}-\text{NNN}-\text{R}$; $\text{R} = \text{Ph}$, p -tolyl, etc.) can fulfil the role of bridging ligands in the ‘lantern’ [102].



Class 2

The green solution mentioned in class 1 resulting from the reaction of RuCl_3 with $\text{RCOOH}/(\text{RCO})_2\text{O}$ mixtures contains a trinuclear species with an $\text{Ru}_3\text{O}(\text{OAc})_6$ core. Refluxing RuCl_3 with ethanoic acid and sodium acetate

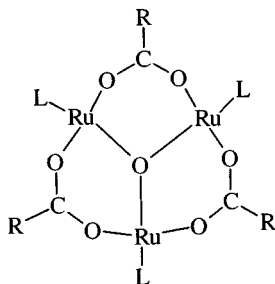


Figure 1.34 The structure of trinuclear oxo-centred ruthenium carboxylates. For clarity, only one of each pair of bridging carboxylates is shown.

in ethanol gives the complex $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}$ in which all the ruthenium is present in the +3 state (Figure 1.34).

This is paramagnetic (one unpaired electron: $\mu = 1.77 \mu_{\text{B}}$). A similar benzoate $[\text{Ru}_3\text{O}(\text{OCOPh})_6\text{py}_3]\text{PF}_6$ has been characterized by X-ray diffraction (the central Ru—O distance is short, at 1.935 Å). The structure of $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{ClO}_4$ is similar [103].

The aqua ion $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$ undergoes a one-electron reduction to form the pale green neutral species; either of these reacts with PPh_3 to form the neutral diamagnetic complex $\text{Ru}_3\text{O}(\text{OAc})_6(\text{PPh}_3)_3$ (which cannot be oxidized) that formally contains one ruthenium(II) and two ruthenium(III) centres [104]. The neutral aqua complex will undergo a further two-electron reduction to give a yellow air-sensitive species thought to be $\text{Ru}_3(\text{OAc})_6(\text{H}_2\text{O})_3$, a ruthenium molecule lacking the central oxygen.

The bonding in these Ru_3O carboxylates can be explained by the usual MO scheme for these systems. A σ -bonding framework involves using six orbitals from each ruthenium (one s, three p, two d) to form bonds to the central O, four carboxylate oxygens and the terminal ligand ($\text{PPh}_3\text{H}_2\text{O}$, etc.).

There are, therefore, three unused d orbitals per ruthenium one of which is used to form a π -bond with an unused oxygen p orbital (it has already used the 2s and 2p orbitals in the σ -bonds to the three rutheniums).

Complexes $[\text{Ru}_3\text{O}(\text{OAc})_6\text{L}_3]^{n+}$ ($\text{L} = \text{H}_2\text{O}$, PPh_3) have been found to be catalysts for the oxidation of primary and secondary alcohols to aldehydes and ketones under fairly mild conditions (65°C, 3 atm O_2) with high catalytic turnovers [104].

Class 3

Dinuclear complexes with an oxo-bridge have latterly achieved better characterization. When $\text{Ru}_3\text{O}(\text{OAc})_6(\text{PPh}_3)_3$ is reduced by hydrogen on heating, a dinuclear species is obtained that on oxidative workup affords diamagnetic oxo-bridged $[\text{Ru}_2\text{O}(\text{OAc})_4(\text{PPh}_3)_2]$ (Figure 1.35) [104c, 105].

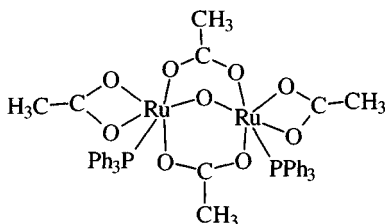


Figure 1.35 The structure of the oxo-bridged dimer $\text{Ru}_2\text{O}(\text{OAc})_4(\text{PPh}_3)_2$.

Class 4

Some important mononuclear complexes exist such as *mer*- $\text{RuH}(\text{OAc})-(\text{PPh}_3)_3$, a very efficient catalyst for the selective hydrogenation of alk-1-enes (Figure 1.36).

It has 6-coordination with a chelating acetate [106] and may be converted (reversibly) into $\text{Ru}(\text{OAc})_2(\text{PPh}_3)_3$, which has the *fac*-configuration with one monodentate and one bidentate acetate. It is fluxional at room temperature but at -70°C the phosphines are non-equivalent on the NMR timescale [107].

1.8.4 Sulphide and sulphoxide complexes

Sulphide and sulphoxide complexes have been extensively studied since *cis*- $\text{RuCl}_2(\text{DMSO})_4$ (DMSO, dimethyl sulphoxide, $(\text{Me})_2\text{SO}$) was found to have anti-tumour properties and to be a precursor for radiosensitizing agents. Such complexes can act as catalysts for the oxidation of sulphides with molecular oxygen.

The best characterized complexes are those of ruthenium(II); it is likely that several reports of ruthenium(III) complexes have, until very recently,

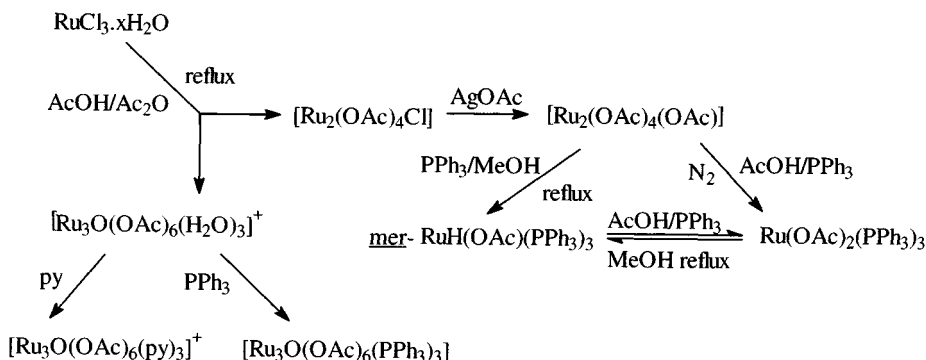


Figure 1.36 Syntheses of ruthenium carboxylate complexes.

been inaccurately describing either ruthenium(II) complexes or ruthenium(III) sulphide complexes formed by redox reaction.

Apart from DMSO complexes, others including those with tetramethylene sulphoxide have been increasingly examined, but the account here focuses on DMSO.

The best understood compounds are *cis*- and *trans*- $\text{RuX}_2(\text{DMSO})_4$ ($\text{X} = \text{Cl}, \text{Br}$). The *trans*-isomers are thermodynamically less stable and isomerize in DMSO solution to the *cis*-isomer, with first-order kinetics, probably via a dissociative mechanism. The reverse process, *cis* to *trans*, is catalysed by light. Syntheses for these and other DMSO complexes are shown in Figure 1.37 [108].

DMSO is an ambidentate ligand, capable of coordinating via either S or O. The *cis*-isomers have three S-bound and one O-bound ligand while in the *trans*-isomers all are S-bonded; IR spectra show the presence of both S- and O-bound DMSO in the *cis*-isomers with absorption owing to $\nu(\text{S}-\text{O})$ around 1100 cm^{-1} (S-bonded) and 930 cm^{-1} (O-bonded), while the *trans*-isomers only have $\nu(\text{S}-\text{O})$ around 1100 cm^{-1} (Figure 1.38).

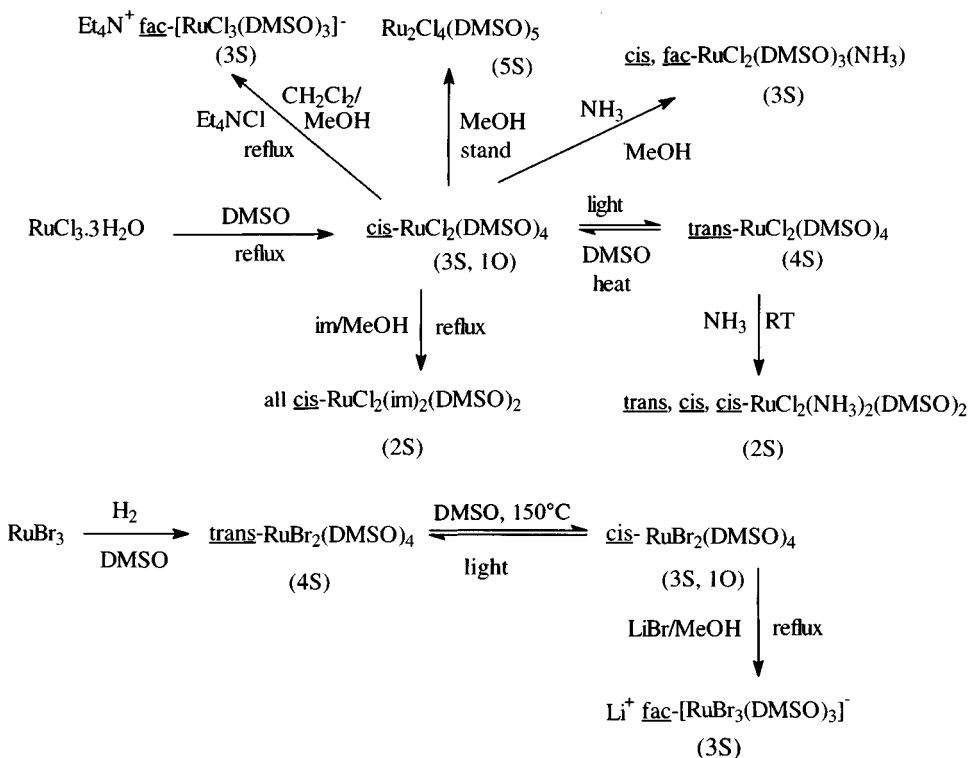


Figure 1.37 Syntheses of ruthenium complexes of dimethylsulphoxide (DMSO).

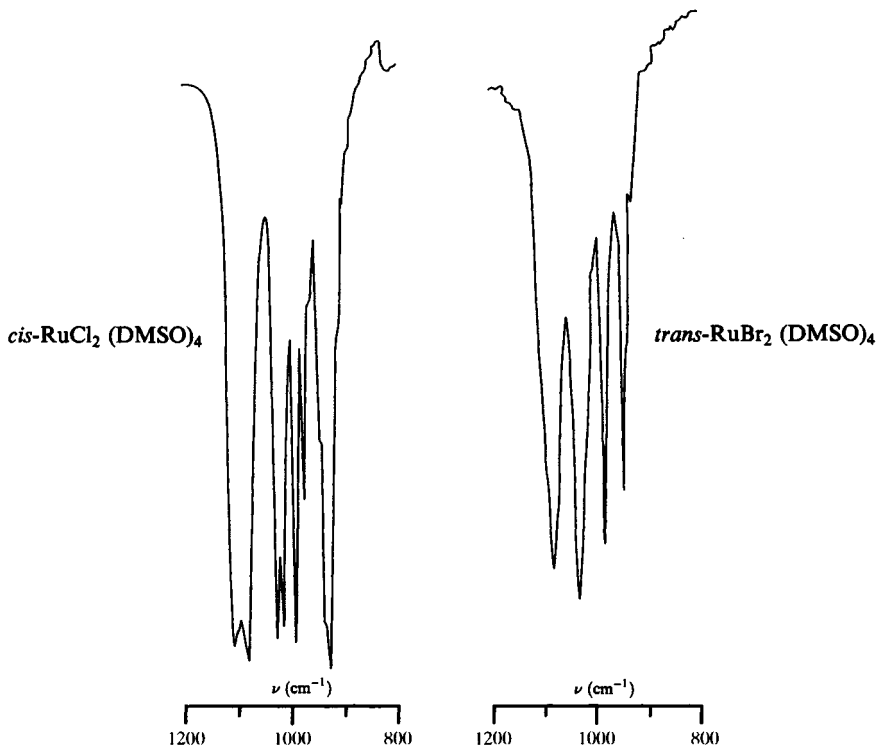


Figure 1.38 IR spectra of DMSO complexes of ruthenium. (Reprinted with permission from *Inorg. Chem.*, 1984, 23, 157. Copyright (1984) American Chemical Society.)

Ru–S bond lengths in the *cis*- and *trans*-isomers (Figure 1.39) indicate an order of *trans*-influence $O < Cl < Br < S$.

The O-bonded DMSO ligand in the *cis*-isomers is rather more labile than the S-bonded DMSO and, therefore, it can be replaced by NH_3 or imidazole [109]. Some syntheses using *cis*- $RuCl_2(DMSO)_4$ are shown in Figure 1.40.

When *cis*- $RuCl_2(DMSO)_4$ is stirred in methanol containing traces of water (to catalyse the formation of intermediate aqua species) $Ru_2Cl_4(DMSO)_5$ is formed; this has the unsymmetrical structure $(DMSO)_2ClRu(\mu-Cl)_3Ru(DMSO)_3$ based on face-sharing octahedra [110].

Ruthenium(III) sulphoxide complexes were less well authenticated until recently [111]; some syntheses are found in Figure 1.41.

Again both S- and O-bonded sulphoxides are found. *mer*- $[RuCl_3(Ph_2SO)_3]$ has one S-bonded sulphoxide and two O-bonded sulphoxides (one *trans* to Cl, one *trans* to S) [112]. The imidazole-substituted complexes are being studied as possible radiosensitizers and for anti-tumour activity.

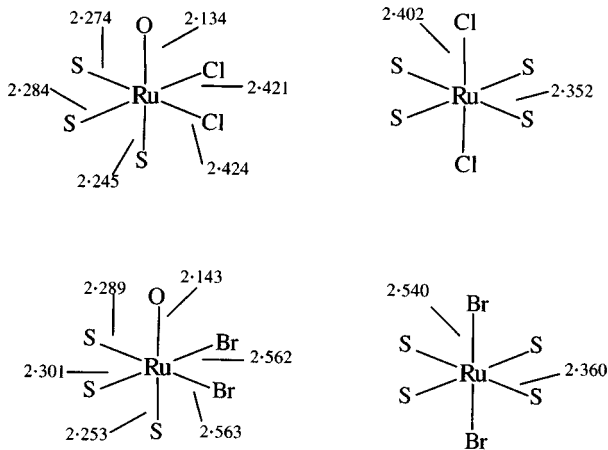


Figure 1.39 Bond lengths in the coordination spheres of *cis*- and *trans*-[RuX₂(DMSO)₄] (X = Cl, Br).

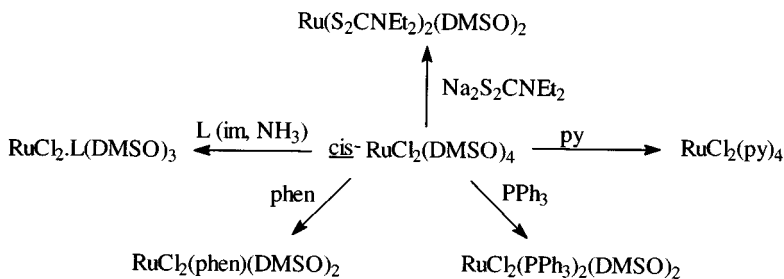


Figure 1.40 Syntheses using $\text{RuCl}_2(\text{DMSO})_4$.

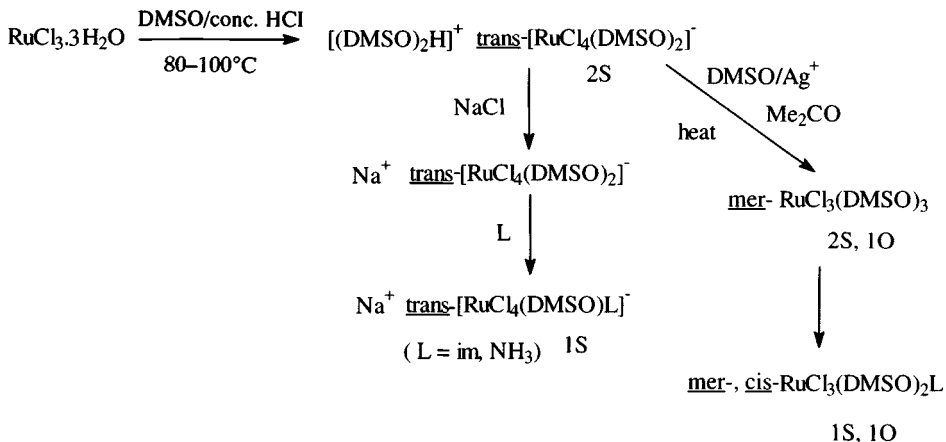
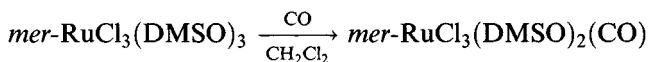
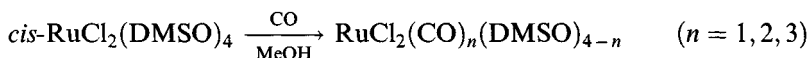
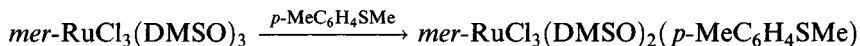


Figure 1.41 Ruthenium(III) sulphoxide complexes.

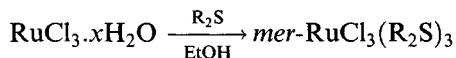
Carbonyl derivatives of ruthenium sulphoxide complexes have been made [113].



$\text{RuCl}_3(\text{DMSO})_3$ reacts with sulphides to form mixed sulphide/sulphoxide complexes that are catalysts for oxidation of thioethers to sulphoxides [114a]:

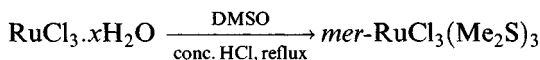


Alkyl sulphide complexes can be synthesized from RuCl_3 and R_2S in ethanol at reflux [114b,c]:



($\text{R}_2\text{S} = \text{Me}_2\text{S}, \text{PhSMe}, \text{PhSBu}$, etc.).

Another method involves refluxing acidified solutions of RuCl_3 in dimethylsulphoxide for extended periods



The structure of the last has been confirmed by X-ray diffraction.

1.8.5 Nitrosyl complexes

Ruthenium probably forms more nitrosyl complexes [115] than any other metal. Many are octahedral $\text{Ru}(\text{NO})\text{X}_5$ systems, where X_5 can represent a combination of neutral and anionic ligands; these contain a linear (or very nearly) $\text{Ru}-\text{NO}$ grouping and are regarded as complexes of ruthenium(II). They are often referred to as $\{\text{Ru}(\text{NO})\}^6$ systems.

Two types of NO coordination to ruthenium are known: linear $\text{Ru}-\text{N}-\text{O} \sim 180^\circ$ and bent, $\text{Ru}-\text{N}-\text{O} \sim 120^\circ$. Since NO^+ is isoelectronic with CO, linear $\text{Ru}-\text{N}-\text{O}$ bonding is generally treated as coordination of NO^+ , with bent coordination corresponding to NO^- ; thus, in the former an electron has initially been donated from NO to Ru, as well as the donation of the lone pair, whereas in the latter an electron is donated from the ruthenium to NO (making it NO^-) followed by donation of the lone pair from N. Though an oversimplification, this view allows a rationale of metal-nitrogen bond lengths, as with the $\text{Ru}-\text{NO}^+$ model π -donation is important and a shorter $\text{Ru}-\text{NO}$ bond is predicted – and, in fact, observed.

Diagnosing the mode of NO coordination, without resort to crystallographic study, can potentially be achieved using the position of $\nu(\text{N}-\text{O})$

in the IR spectrum. Removing the π^* -electron from NO forming NO^+ strengthens the N–O bond, reflected in a change in $\nu(\text{N–O})$ from 1877 cm^{-1} (NO) to $2200\text{--}2300\text{ cm}^{-1}$ (NO^+ salts). Coordination as NO^+ would involve stronger back-bonding than with NO^- , so that a higher frequency is expected for a linear arrangement; in fact a considerable overlap region exists. ^{15}N NMR spectra have, however, been utilized diagnostically, as bent nitrosyls give rise to resonances at much higher frequency.

A preparative entry to the area of nitrosyls is possible with the oligomeric $\text{Ru}(\text{NO})\text{X}_3$ [116] ($\text{X} = \text{halogen}$) (Figure 1.42).

This will add halide ions or tertiary phosphines to give octahedral $\text{Ru}(\text{NO})\text{X}_5^{2-}$ or $\text{Ru}(\text{NO})\text{X}_3(\text{PR}_3)_2$, respectively, all of these having the linear Ru–N–O geometries characteristic of $\{\text{Ru}(\text{NO})\}_6^6$ systems. The preference for octahedral coordination is such that in $\text{Ru}(\text{NO})(\text{S}_2\text{CNEt}_2)_3$, one dithiocarbamate ligand is monodentate (Figure 1.43) [117].

The NO ligand can be supplied by nitric oxide itself, but there are many other sources such as nitrite, nitrate or nitric acid, nitrosonium salts or *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (MNTS). The introduction of a nitrosyl group into a ruthenium complex is an ever-present possibility.

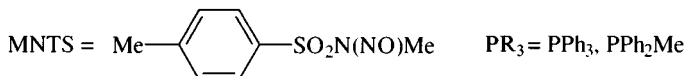
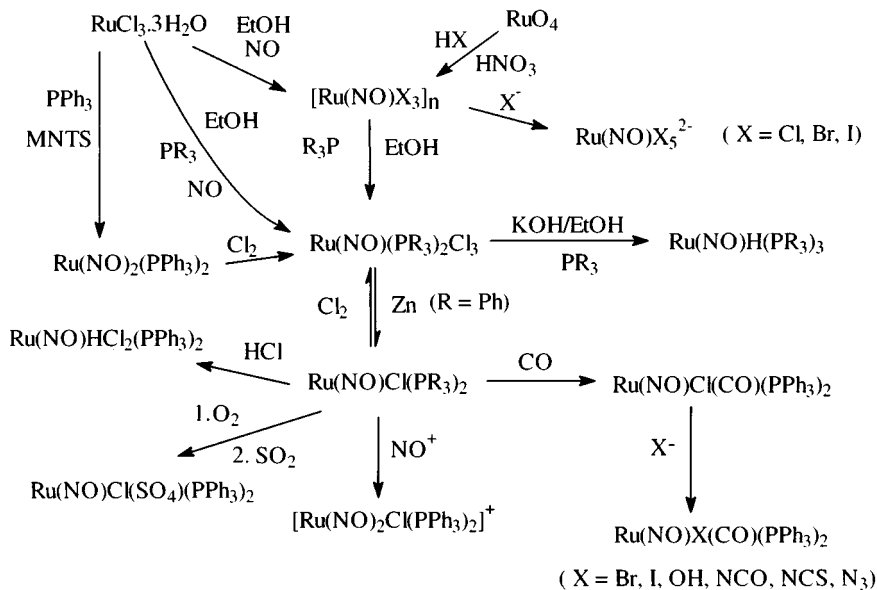


Figure 1.42 Syntheses of ruthenium nitrosyl complexes.

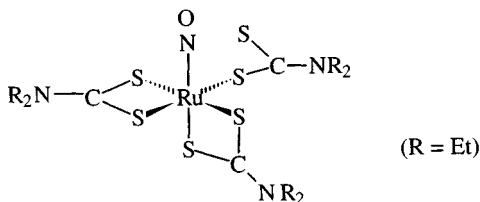
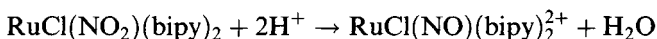
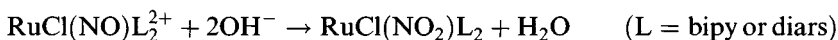


Figure 1.43 The 6-coordinate nitrosyl $\text{Ru}(\text{NO})(\text{S}_2\text{CNEt}_2)_3$.

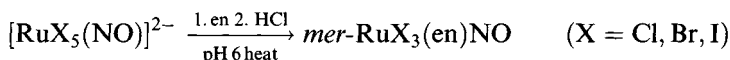
Cases are known where electrophilic attack occurs at nitrite [118]



The NO ligand is usually regarded as a good σ -donor and, therefore, electrophilic, so that the above reaction can be reversed by nucleophilic attack



Complexes of chelating ligands like ethylenediamine (en) and diethylenetriamine (dien) can be made [119]:



Some of the *fac*-isomer was obtained for $\text{X} = \text{Cl}$.

Three isomers of $[\text{Ru}(\text{NO})\text{Cl}(2\text{equ})_2]$ ($2\text{equ} = 2\text{-ethyl-8-quinolinate}$) have been isolated in the solid state; they interconvert in DMSO solution above 100°C (NMR) [120].

Table 1.9 summarizes structural data for a number of ruthenium nitrosyl complexes, along with IR data [121, 122].

Recent study of the $[\text{Ru}(\text{NO})\text{X}_5]^{2-}$ species ($\text{X} = \text{halogen, CN}$) shows that in general the $\text{Ru}-\text{X}$ bond *trans* to nitrosyl is slightly longer than the *cis*- $\text{Ru}-\text{X}$ bond (Table 1.10) [121].

Study of the nitrosyls $\text{Ru}(\text{NO})\text{X}_3(\text{PR}_3)_2$ shows that their photochemical behaviour depends on the tertiary phosphine (Figure 1.44).

Where X is phenyl, the result of irradiation (sunlight, mercury lamp) is the formation of $\text{Ru}(\text{NO})\text{X}_3(\text{PPh}_3)(\text{OPPh}_3)$ ($\text{X} = \text{Cl, Br}$); in the case of the diethylphenylphosphine complex, irradiation causes isomerization to the *cis,mer*-isomer. The *trans,mer*-isomer is the usual synthetic product, but in the case of dimethylphenylphosphine the *fac*-isomer was obtained using short reaction times; it isomerized to the usual *mer,trans*-isomer on heating [123].

$\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}_3$ gives rise to two interesting $\{\text{Ru}(\text{NO})\}^8$ complexes. $\text{Ru}(\text{NO})\text{Cl}(\text{PPh}_3)_2$, similar to Vaska's compound, $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$, undergoes rather similar addition reactions (compare section 2.10.2) [124]. Addition of NO^+ yields $[\text{Ru}(\text{NO})_2\text{Cl}(\text{PPh}_3)_2]^+$, which like the analogous adduct $[\text{Ir}(\text{NO})\text{Cl}(\text{CO})(\text{PPh}_3)_2]^+$ has a bent metal-nitrosyl linkage (Figure 1.45) [125].

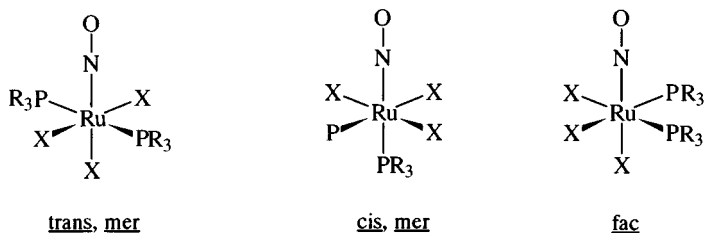
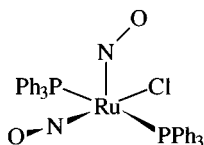
Table 1.9 Ruthenium nitrosyl complexes: structural and IR data

Complex	ν (NO) (cm^{-1})	M–N–O ($^\circ$)	M–N (\AA)
$\text{Na}_2[\text{Ru}(\text{OH})(\text{NO}_2)_4(\text{NO})]^{2-}$	1907	179	1.764
$[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3$	1903	173	1.776
$\text{K}_2[\text{RuCl}_5(\text{NO})]$	1887	175	1.759
$\text{RuCl}(\text{NO})(\text{PPh}_3)_2^+$	1845	180	1.74
$\text{RuH}(\text{NO})(\text{PPh}_3)_3$	1640	176	1.792
<i>trans</i> - $[\text{Ru}(\text{OH})(\text{NO})(\text{bipy})_2](\text{ClO}_4)_2$	1890	175	1.771
$[\text{Ru}(\text{NO})\text{Cl}(\text{bipy})_2]^+$	1912	170	1.751
$\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$	1848	180	1.737
$\text{Ru}(\text{NO})\text{Cl}_3(\text{PMePh}_2)_2$	1855	176	1.744
$\text{Ru}(\text{NO})(\text{S}_2\text{CNEt}_2)_3$	1803	170	1.72
$[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+\text{PF}_6^-$	1845, 1687	178, 138	1.743, 1.853
$\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$	1665, 1615	178, 171	1.762, 1.776
$\text{Ru}(\text{OH})(\text{NO})_2(\text{PPh}_3)_2^+\text{BF}_4^-$	1870, 1665	–	–
$\text{K}_2[\text{RuBr}_5(\text{NO})]$	1880	–	1.739
$\text{K}_2[\text{RuI}_5(\text{NO})]$	1844	–	1.716
$\text{K}_2[\text{RuF}_5(\text{NO})]$	1873	–	1.72
$\text{K}_2[\text{Ru}(\text{CN})_5(\text{NO})]$	1915	–	1.733
<i>mer</i> - $[\text{RuCl}_3(\text{en})\text{NO}]$	1860	174	1.727
$\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2$	1869	180	1.729

(neut diff.)

Table 1.10 Bond lengths in $\text{Ru}(\text{NO})\text{X}_5^{2-}$ (\AA)

X	F	Cl	Br	I	CN
Ru–N	1.72	1.738	1.739	1.716	1.733
Ru–X (<i>cis</i>)	1.958	2.370	2.517	2.719	2.059
Ru–X (<i>trans</i>)	1.91	2.362	2.513	2.726	2.051

**Figure 1.44** The three isomers of $\text{Ru}(\text{NO})(\text{PR}_3)_2\text{X}_3$.**Figure 1.45** The structure of $[\text{Ru}(\text{NO})_2\text{Cl}(\text{PPh}_3)_2]^+$ showing different modes of nitrosyl coordination.

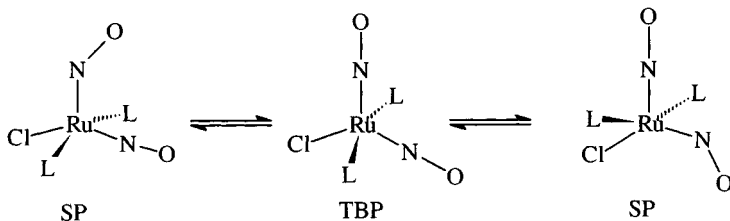
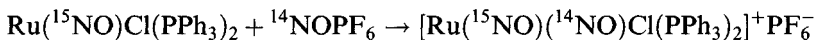


Figure 1.46 A scrambling mechanism envisaged for the interconversion of the metal–nitrosyl linkages in $[\text{Ru}(\text{NO})_2\text{Cl}(\text{PPh}_3)_2]^+$.

Synthesis of this compound from a ^{15}N labelled source revealed that the ^{14}N and ^{15}N were equally distributed between the apical bent nitrosyl (NO^-) and equatorial linear nitrosyl (NO^+):



A scrambling mechanism between them involved a *tbp* intermediate (Figure 1.46).

$\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ has a similar electronic structure to the $[\text{M}(\text{NO})_2(\text{PPh}_3)_2]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) ions and like them has a pseudo tetrahedral structure with linear $\text{Ru}-\text{N}-\text{O}$ [126]. It also resembles them in its oxidative addition reactions (Figure 1.47).

The reaction with CO to afford CO_2 and N_2O is particularly interesting in view of the use of platinum metal compounds in automobile catalytic converters.

The nitrosyls $\text{RuH}(\text{NO})(\text{PR}_3)_3$ are 5-coordinate with trigonal bipyramidal structures and linear $\text{Ru}-\text{N}-\text{O}$ geometries; the hydride and nitrosyl ligands occupy the apical positions (for $\text{RuH}(\text{NO})(\text{PPh}_3)_3$, $\nu(\text{Ru}-\text{H})$ 1970 cm^{-1} , $\nu(\text{N}-\text{O})$ 1640 cm^{-1} ; $^1\text{H NMR}$, $\delta = +6.6\text{ ppm}$ for the hydride resonance). The high-field NMR line is a quartet showing coupling with three equivalent phosphines, which would not be possible in a square pyramidal

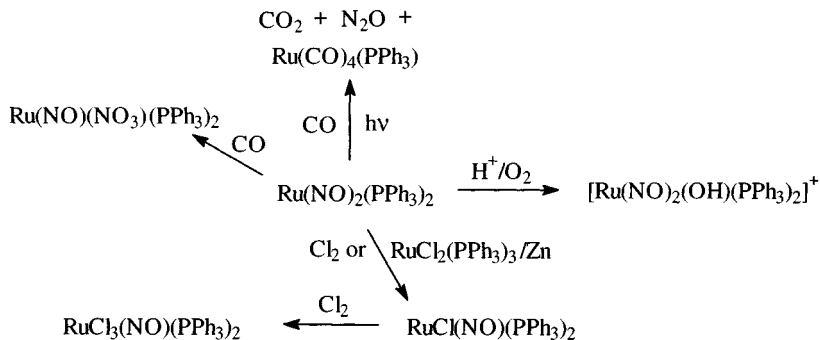


Figure 1.47 Reactions of $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$.

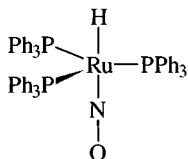
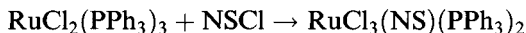


Figure 1.48 The trigonal bipyramidal structure of $\text{RuH}(\text{NO})(\text{PPh}_3)_3$.

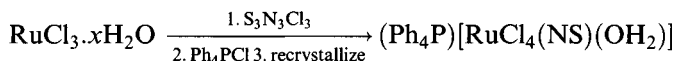
structure; therefore, the structure could be predicted spectroscopically before confirmatory crystallographic evidence was available (Figure 1.48) [127].

Thionitrosyls

A few thionitrosyl complexes have been synthesized. MO calculations suggest that NS is a superior σ -donor and π -acceptor to NO [128]. Syntheses include



(In this compound $\nu(\text{N}-\text{S})$ occurs at $1295\text{--}1310\text{ cm}^{-1}$ compared with $\nu(\text{N}-\text{O})$ at 1875 cm^{-1} in $\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2$)



The structure of this compound shows a roughly linear thionitrosyl linkage ($\text{Ru}-\text{N}-\text{S}$ 171°) with a rather short $\text{Ru}-\text{N}$ bond (1.729 \AA).

1.8.6 Porphyrin complexes

Porphyrin complexes have been the most intensively studied macrocyclic complexes of these metals [129]. They are formed in a wide range of oxidation states (II–VI) and they are, therefore, treated together under this heading, though most of the chemistry for ruthenium lies in the II–IV states. Octaethylporphyrin (OEP) complexes are typical.

Entry into the series involves metallating the porphyrin; this can be done by passing CO through a boiling solution of $\text{Ru}_3(\text{CO})_{12}$ or RuCl_3 with the porphyrin in ethanoic acid. The initial product is the 6-coordinate $\text{Ru}(\text{OEP})(\text{CO})(\text{solvent})$, but the solvent molecule (e.g. EtOH) is easily displaced by other Lewis bases (and by a second molecule of CO if the solution is saturated with CO). Most of the dicarbonyls lose one CO molecule easily on standing but $\text{Ru}(\text{OEP})(\text{CO})_2$ is stable *in vacuo* for some hours; the CO can be displaced, particularly on heating, to afford 6-coordinate $\text{Ru}(\text{OEP})\text{L}_2$ (L, e.g. py, PR_3). $\text{Ru}(\text{OEP})\text{py}_2$ desolvates *in vacuo* at 210°C to a dimer $[\text{RuOEP}]_2$ with a $\text{Ru}-\text{Ru}$ distance of 2.408 \AA , regarded as a double bond; this compound is useful synthetically. While halogen oxidation of $\text{Ru}(\text{OEP})(\text{PR}_3)_2$ proceeds only as far as ruthenium(III) in $\text{Ru}(\text{OEP})(\text{PR}_3)\text{X}$, the unsolvated dimer is oxidized to the ruthenium(IV) state in paramagnetic $\text{Ru}(\text{OEP})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$). These can be used to make the stable diphenyl $\text{Ru}(\text{OEP})\text{Ph}_2$,

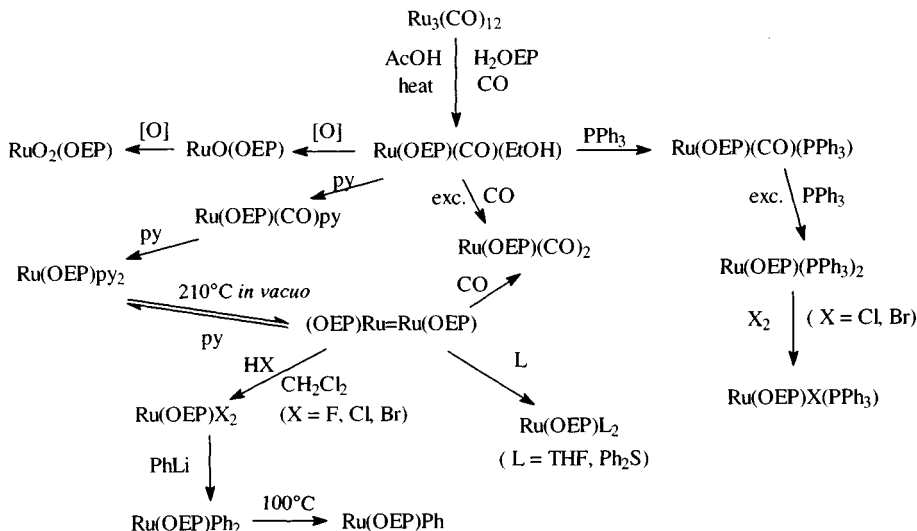
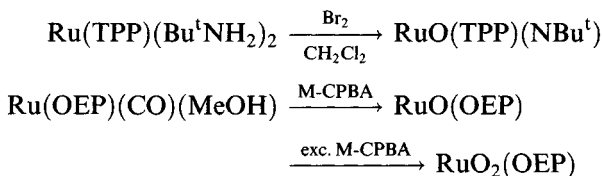


Figure 1.49 Octaethylporphyrin (OEP) complexes of ruthenium.

which on heating in solution undergoes smooth thermolysis to $\text{Ru}(\text{OEP})\text{Ph}$. The Ru–Ru bond in the dimer can also be cleaved (e.g. by py, R_2S) retaining the ruthenium(II) oxidation state (Figure 1.49).

Structural data on ruthenium porphyrins shows that the Ru–N (porphyrin) distance is relatively unaffected by changing the oxidation state, as expected for a metal atom inside a fairly rigid macrocyclic ring (Table 1.11).

High oxidation states are accessible: a *t*-butylimide of ruthenium(VI) can be made by oxidative deprotonation



(M-CPBA = *m*-chloroperoxybenzoic acid).

Table 1.11 Structural data for complexes $\text{Ru}(\text{OEP})(\text{X})(\text{Y})$ (in Å)

Oxidation state	X	Y	Ru–N (porphyrin)	Ru–X	Ru–Y
II	py	py	2.046–2.048	2.100	2.100
II	PPh_3	PPh_3	2.044–2.057	2.438	2.438
II	CO	H_2O	2.051	1.783	2.253
III	PPh_3	Br	2.025–2.047	2.415	2.552
III	Ph	–	2.007–2.048	2.005	–

Water-soluble ruthenium phthalocyanines show promise as photodynamic cancer therapy agents [129b].

1.8.7 EDTA complexes

A considerable number of EDTA complexes of ruthenium have been synthesized [130–132]; there has been interest in their catalytic potential while several compounds have had their structures determined. Synthetic routes relating to these compounds are shown in Figure 1.50.

In all the compounds of known structure, ruthenium is 6-coordinate; therefore, in complexes like $\text{Ru}(\text{EDTA})(\text{H}_2\text{O})$ [131], the acid is penta-dentate, with a free carboxylate group; likewise, in $\text{K}[\text{Ru}(\text{EDTAH}_2)\text{Cl}_2]$ and $[\text{Ru}(\text{EDTAH}_2)(\text{dppm})]$ two of the carboxylates are protonated, so it is tetradentate.

The structure of the aqua complex (Figure 1.51), which is an active intermediate in some catalytic systems, shows the $\text{Ru}-\text{OH}_2$ distance to be some 0.1 Å longer than in the ruthenium(III) hexaqua ion, indicating a possible reason for its lability; the water molecule also lies in a fairly exposed position, away from the bulk of the EDTA group.

The ruthenium(III) complex is oxidized to a paramagnetic ruthenium(V) species, $\text{RuO}(\text{EDTA})$: ($\mu = 1.98 \mu_{\text{B}}$; $\nu(\text{Ru}=\text{O}) 890 \text{ cm}^{-1}$) by NaOCl or

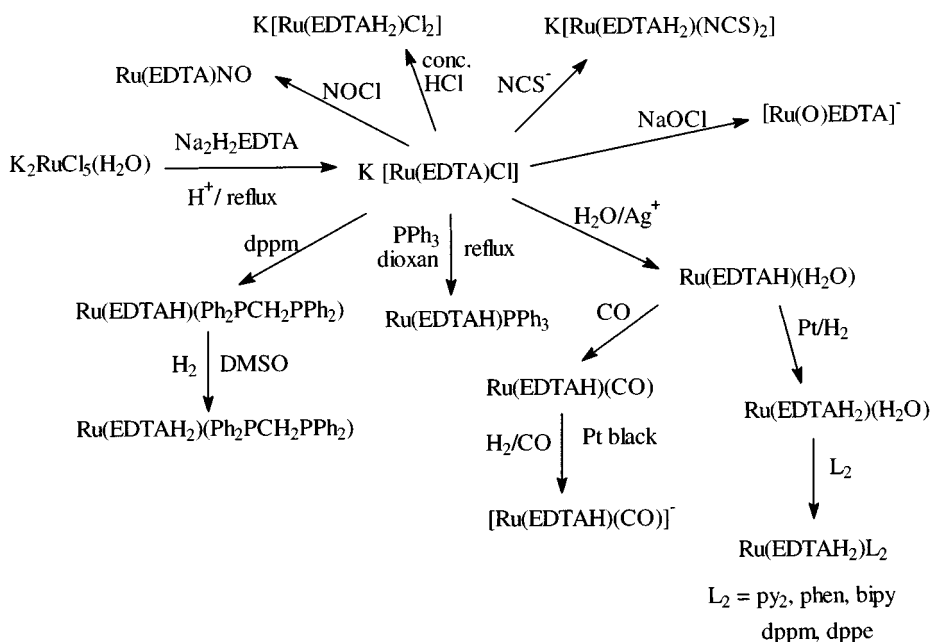


Figure 1.50 Ruthenium complexes of EDTA.

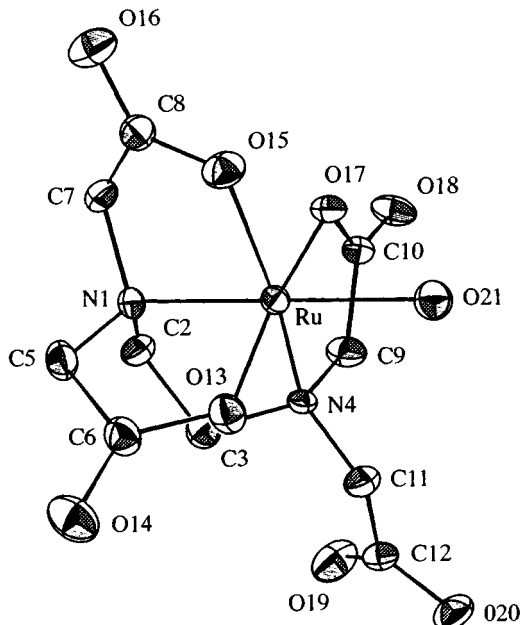


Figure 1.51 The structure of $[\text{Ru}(\text{EDTA-H})(\text{H}_2\text{O})]$. (Reproduced with permission from the *Indian J. Chem., Sect. A*, 1992, 206.)

iodosylbenzene. This compound catalyses epoxidation of alkenes and oxidation of phosphines.

The carbonyl complex $[\text{Ru}(\text{EDTAH})(\text{CO})]^-$ has been reported to be a very good catalyst for reactions like hydroformylation of alkenes, carbonylation of ammonia and amines as well as a very active catalyst for the water gas shift reaction. The nitrosyl $[\text{Ru}(\text{EDTA})(\text{NO})]$ is an oxygen-transfer agent for the oxidation of hex-1-ene to hexan-2-one, and cyclohexane to the corresponding epoxide.

Bond lengths for a number of the ruthenium EDTA complexes are given in Table 1.12.

Table 1.12 Bond lengths in $[\text{Ru}(\text{EDTAH})\text{L}]^{n-}$ systems (Å)

	L				
	H_2O	PPh_3	NO	Cl	CO
<i>n</i>	–	–	–	–	1
Oxidation state of Ru	+3	+3	+3	+3	+2
Ru–N (<i>trans</i> -L)	2.035	2.070	2.095	2.043	2.119
Ru–N (<i>cis</i> -L)	2.49	2.126	2.115	2.114	2.119
Ru–O (<i>trans</i> -O)	1.986, 2.062	1.983, 2.050	2.018, 2.021	2.007	2.063, 2.099
Ru–O (<i>trans</i> -N)	2.004	1.996	2.010	2.067	2.064
Ru–L	2.137	2.363	1.728	2.358	1.843

They demonstrate the sensitivity of the Ru–N bond length to the *trans*-donor atom and also how when a multidentate ligand is involved bond lengths do not necessarily shorten on increasing the oxidation state.

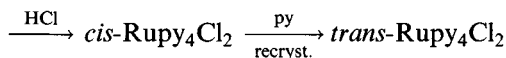
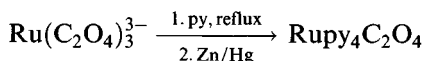
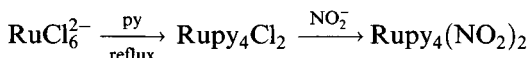
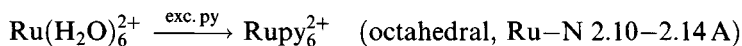
1.8.8 Other complexes of ruthenium

Ruthenium, in its 'normal' oxidation states of II and III, forms a wide range of complexes with most available donor atoms, of which a representative selection are mentioned below.

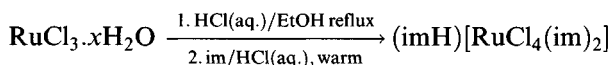
The structures of $[\text{Ru}(\text{HCONMe}_2)_6](\text{CF}_3\text{SO}_3)_x$ ($x = 2, 3$) show a contraction in Ru–O distance from 2.088 Å to 2.02 Å on passing from the +2 to the +3 oxidation state [133a].

There is a wide range of diketonates, such as $\text{Ru}(\text{acac})_3$, with octahedral coordination [133b] (they do not seem, however, to be oxidized to the +4 state; this is possible with osmium); similarly several salts of the tris(oxalato) complex $\text{Ru}(\text{C}_2\text{O}_4)_3^{3-}$ have been isolated.

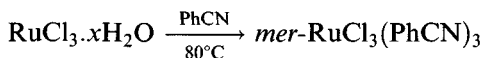
Complexes of pyridine and substituted pyridines, mainly in the +2 state, have been made [134]:



The reaction of the (necessarily) *cis*-oxalato complex with HCl in the last example, ensures the *cis*-configuration for the chloro complex: on recrystallization, the thermodynamically more stable *trans*-isomer forms. *trans*- Rupy_4Cl_2 has Ru–N 2.079 Å and Ru–Cl 2.405 Å. An imidazole complex (imH) *trans*- $[\text{RuCl}_4(\text{im})_2]$ shows promise as a tumour inhibitor and is currently undergoing preclinical trials [135].



Many ruthenium complexes with nitrile ligands also feature tertiary phosphines, but simpler complexes can be synthesized [136]



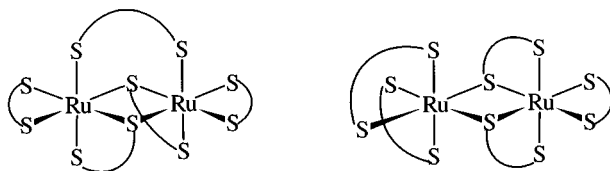
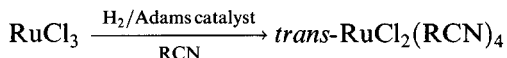
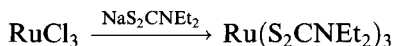


Figure 1.52 Isomeric forms of $\text{Ru}_2(\text{S}_2\text{CNET}_2)_5$.

The structures of both these complexes, typical of ruthenium(III) nitriles, were confirmed by X-ray diffraction; ruthenium(II) nitriles are also possible:



Many ruthenium dithiocarbamates have been synthesized. The ruthenium(III) compounds can be made by standard methods [137]



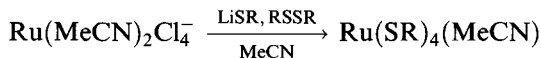
This compound has an octahedral coordination sphere slightly distorted towards a trigonal prism. Oxidation by air leads to $\text{Ru}_2(\text{S}_2\text{CNET}_2)_5$ which exists in two isomeric forms (Figure 1.52) [138].

In contrast, photolytic oxidation of $\text{Ru}(\text{S}_2\text{CNR}_2)_3$ in CHCl_3 or CH_2Cl_2 affords pentagonal bipyramidal $\text{Ru}(\text{S}_2\text{CNR}_2)_3\text{Cl}$ (apical Cl and S) and iodine gives $\text{Ru}(\text{S}_2\text{CNR}_2)_3\text{I}$, again 7-coordinate. Chloroform solutions of $\text{Ru}(\text{S}_2\text{CNR}_2)_3$ react with NO to form $\text{Ru}(\text{NO})(\text{S}_2\text{CNR}_2)_3$ (section 1.8.5), which has 6-coordinate ruthenium with one monodentate dithiocarbamate.

1.9 Complexes of ruthenium(IV)

Compounds containing ruthenium(IV) such as the dithiocarbamates $\text{Ru}(\text{S}_2\text{CNR}_2)_3\text{Cl}$ (section 1.8.6) and the porphyrin complexes (section 1.8.6) were mentioned above. Certain phosphine complexes $\text{RuH}_4(\text{PR}_3)_3$ are best regarded as ruthenium(II) compounds: $\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)(\text{PR}_3)_3$ (section 1.8.2).

Some unusual ruthenium(IV) thiolates have been made [139]



($\text{R} = 2,4,6\text{-Pr}_3\text{C}_6\text{H}_2$, $2,3,5,6\text{-Me}_4\text{C}_6\text{H}$).

They doubtless owe their stability to the bulk of the aryl thiolate ligand; they have tbp structures with equatorial nitrile that can be displaced by CO to give rare carbonyls of a metal in the +4 oxidation state.

Another, and less surprising, example of ruthenium(IV) lies in the oxo complexes with macrocycles like 14-TMC (Figure 1.53).