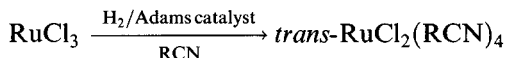
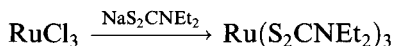


Figure 1.52 Isomeric forms of $\text{Ru}_2(\text{S}_2\text{CNET}_2)_5$.

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]



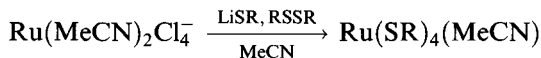
This compound has an octahedral coordination sphere slightly distorted towards a trigonal prism. Oxidation by air leads to $\text{Ru}_2(\text{S}_2\text{CNET}_2)_5$ which exists in two isomeric forms (Figure 1.52) [138].

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 t_{bp} 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).

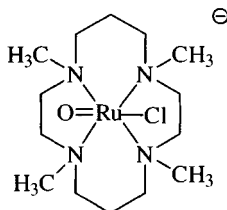
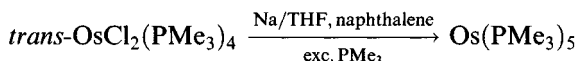


Figure 1.53 A ruthenium(IV) macrocyclic complex.

The presence of a Ru=O bond can be diagnosed from the presence of an IR band *c.* 825 cm^{-1} ; the bond length, at 1.76 \AA , is slightly longer than in dioxoruthenium(VI) complexes [140].

1.10 Complexes of osmium(0)

Osmium is notable for the range of binary carbonyls it forms [141]: $\text{Os}(\text{CO})_5$, $\text{Os}_2(\text{CO})_9$, $\text{Os}_3(\text{CO})_{12}$, $\text{Os}_4(\text{CO})_x$ ($x = 14, 15, 16$), $\text{Os}_5(\text{CO})_y$ ($y = 16, 18, 19$), $\text{Os}_6(\text{CO})_z$ ($z = 18, 21$), $\text{Os}_7(\text{CO})_{21}$, $\text{Os}_8(\text{CO})_{23}$ and $\text{Os}_{10}(\text{CO})_{26}$. From the perspective of this book, the relevant compounds are $\text{Os}(\text{PF}_3)_5$, $\text{Os}[\text{P}(\text{OMe})_3]_5$ and $\text{Os}(\text{PMe}_3)_5$, all with *tbp* structures [142]. The last, prepared by reduction of an osmium(II) complex:



It is a very reactive substance, picking up traces of H^+ to form $\text{Os}(\text{PMe}_3)_5\text{H}^+$ and undergoing facile metallation (Figure 1.54).

1.11 Osmium complexes in oxidation states (II–IV)

Within the osmium complexes in oxidation states (II–IV) [11, 12] the stability of the +4 oxidation state becomes more important. Ammine and tertiary phosphine complexes have been selected for detailed examination.

1.11.1 Ammine complexes

Many of the ammine complexes are osmium(III) compounds; the +2 state is less stable than with ruthenium, as expected, and osmium(II) compounds

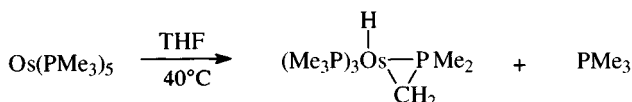


Figure 1.54 Metallation of $\text{Os}(\text{PMe}_3)_5$.

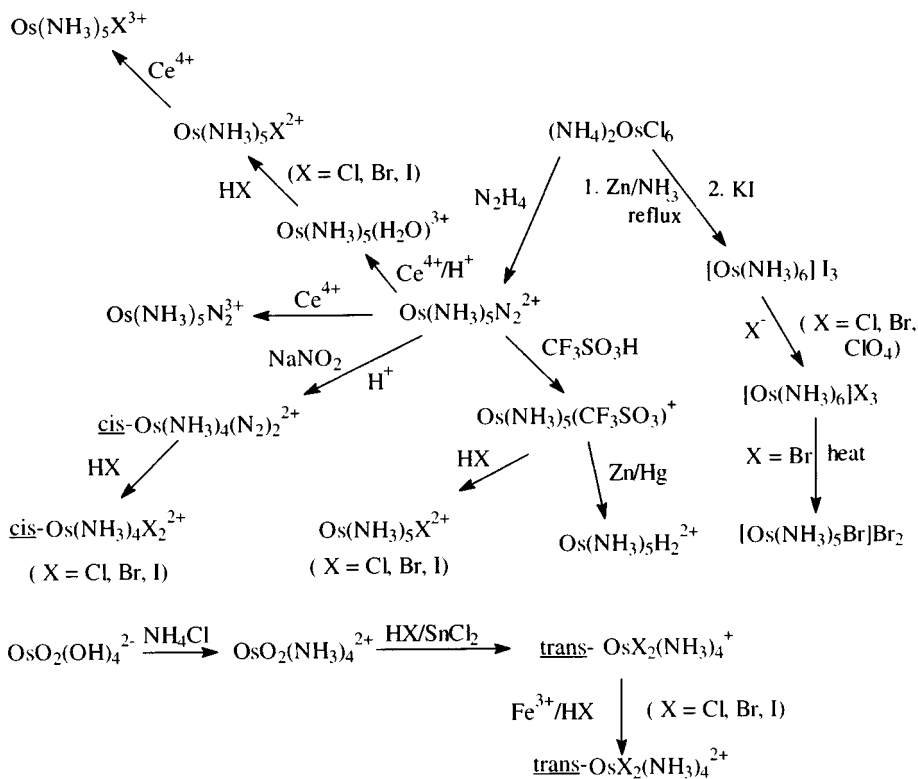


Figure 1.55 Syntheses of osmium ammine complexes.

are only really stable in the presence of good π -acceptors (N_2 , CO) [143]. Osmium(IV) ammines can often be made by oxidation of the corresponding Os(III) compounds. Figure 1.55 summarizes many syntheses.

The most remarkable complex is the osmium(VI) nitrido species $\text{OsN}(\text{NH}_3)_4^{3+}$ (IR $\nu(\text{Os}\equiv\text{N})$ 1090 cm^{-1}) [144].

The dinitrogen complex $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ is a useful synthetic intermediate, while the presence of the weakly nucleophilic triflate group enables it to be easily removed in the synthesis of the dihydrogen complex.

The dinitrogen complex (Figure 1.56) has a rather short Os– N_2 bond (1.842 Å) indicating some multiple bond character while the *trans*-Os–N bond is slightly longer than the others, but not significantly different. The N_2 ligand shows $\nu(\text{N}–\text{N})$ at 2022 cm^{-1} in the IR spectrum [145].

Some bis(dinitrogen) complexes exist, generally as *cis*-isomers (presumably this minimizes competition for the metal t_{2g} electron density in π -bonding). Unlike ruthenium, osmium(III) dinitrogen complexes do exist, showing osmium(III) to be a better π -donor; not surprisingly, they are more labile than the osmium(II) species.

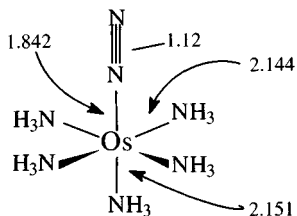
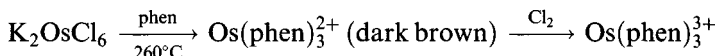
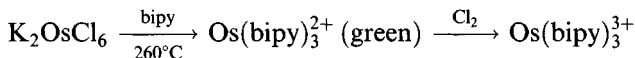


Figure 1.56 Bond lengths in $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$.

Reaction of the osmium(III) pentammines with zinc amalgam gives an osmium species that is stable in solution for some hours (and may be $[\text{Os}^{\text{IV}}(\text{NH}_3)_5(\text{OH})(\text{H})]^{2+}$). It is capable of forming $\text{Os}(\text{NH}_3)_5\text{L}^{2+}$ adducts with π -acids like MeCN [146].

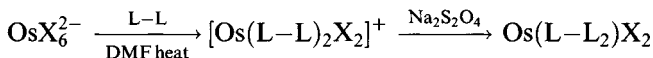
Osmium complexes of bi- and polydentate amines

The simplest systems are the tris(chelates) of phen and bipy

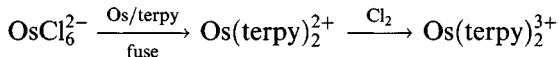


Os–N bond lengths in $\text{Os}(\text{bipy})_3(\text{PF}_6)_2$ (isostructural with the ruthenium analogue) and $\text{Os}(\text{phen})_3(\text{ClO}_4)_2\text{H}_2\text{O}$ are 2.062 Å and 2.066–2.082 Å, respectively [147].

Other complexes include



(X = Cl, Br, I; L–L = phen, bipy)



With ethylenediamine, high oxidation states become a possibility (Figure 1.57), sometimes involving a deprotonated ligand (see also section 1.12.1) [148].

The structure of the deprotonated ethylenediamine complex $[\text{Os}(\text{en-H})_2\text{en}]\text{Br}_2$ has been confirmed (Figure 1.58); the Os=NH bonds (2.11–2.19 Å) indicating clear multiple bond character. It can be used as a source of ‘conventional’ ethylenediamine complexes.

$\text{Os}\text{en}_2\text{H}_2^{2+}$ is in fact a dihydrogen complex (Figure 1.59).

In aqueous solution, the water molecule (L) can be replaced by other ligands including a range of biomolecules. The nature of the molecule bound affects the position and relaxation time of the dihydrogen resonance (and also J_{HD} when D_2O is present). Both the dihydrogen and the water can

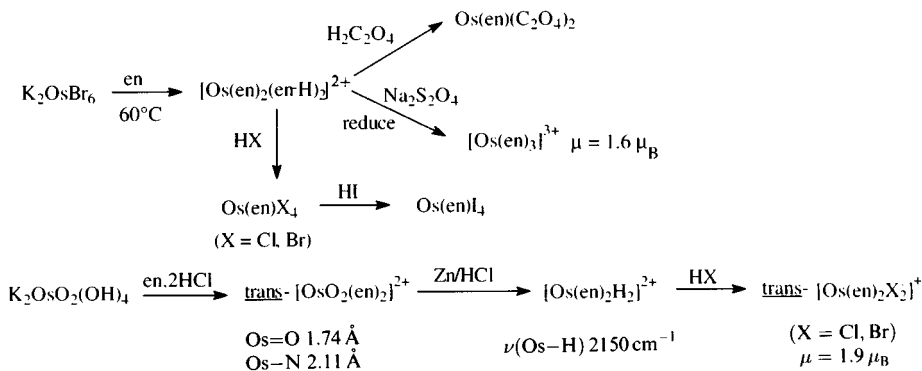


Figure 1.57 Ethylenediamine complexes of osmium.

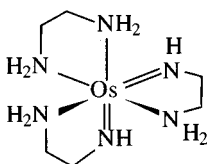


Figure 1.58 The cation in the deprotonated ethylenediamine complex $[\text{Os}(\text{en-H})_2\text{en}]\text{Br}_2$.

be replaced by unsaturated molecules (ethene and ethyne) [149]. On reaction with sodium acetate, $[\text{Os}(\text{en})_2\text{H}_2]^{2+}$ forms $[\text{Os}(\eta^2\text{-H}_2)\text{en}_2(\text{OAc})]^+$, which has $\text{Os}-\text{H}$ of 1.59–1.60 Å (neutron-diffraction, $\text{H}-\text{H}$ 1.34 Å), which is shorter than in classical hydrides like $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ (1.66 Å) indicating the strength of the $\text{Os}-\text{H}$ bond [150].

1.11.2 Tertiary phosphine complexes

Syntheses of some of these important tertiary phosphine complexes are summarized in Figure 1.60, which represent reactions typical of a tertiary phosphine (e.g. PMe_2Ph), showing complexes in the oxidation states +6, +4, +3 and +2 [78a].

The osmium(VI) complexes $\text{OsO}_2\text{X}_2(\text{PR}_3)_2$ are not generally obtainable with the smaller alkyl and alkyl(aryl)phosphines, which tend to be good

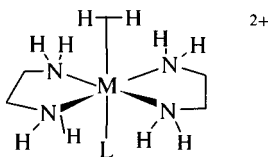


Figure 1.59 The dihydrogen complex cation $[\text{Os}(\text{en})_2\text{H}_2(\text{L})]^{2+}$ (L, e.g. H_2O).

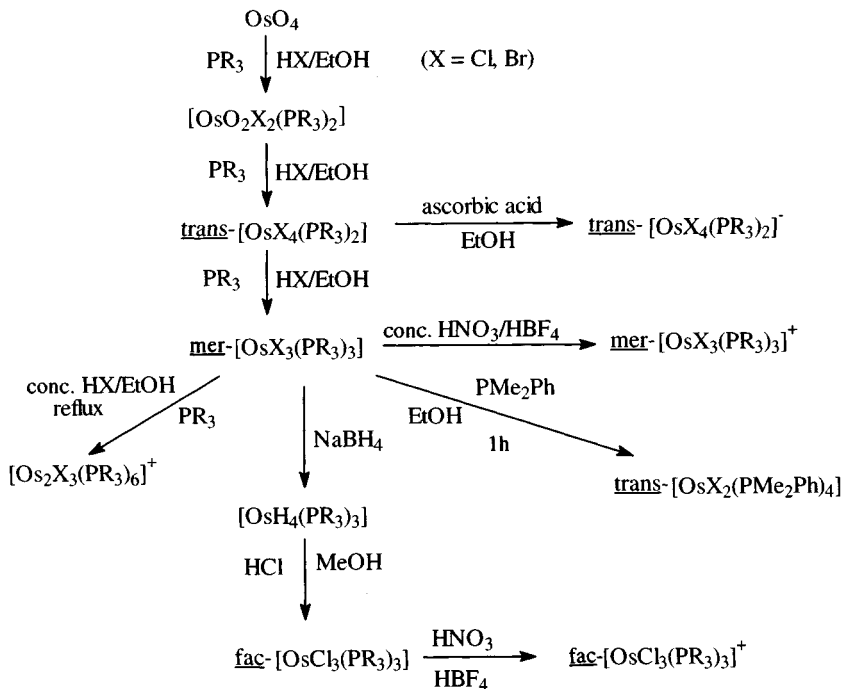
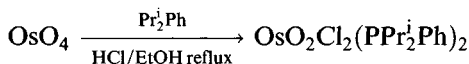


Figure 1.60 Syntheses of some osmium complexes of tertiary phosphines.

reducing agents; with the bulky PPR_2^iPh , $\text{OsO}_2\text{Cl}_2(\text{PPR}_2^i\text{Ph})_2$ is obtained after 3 h reflux



These compounds give characteristic 'osmyl' IR bands (840 cm^{-1} in $\text{OsO}_2\text{Cl}_2(\text{PPh}_3)_2$) [151].

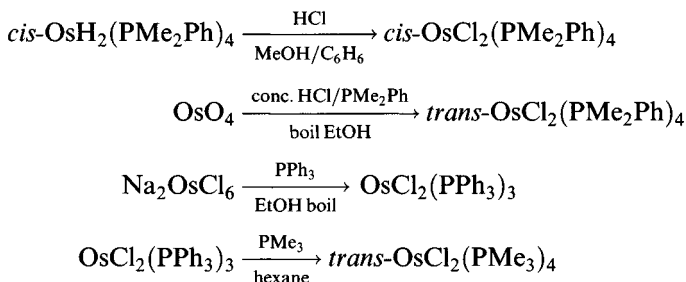
The osmium(IV) complexes are only obtained by this route with fairly unreactive phosphines and arsines (e.g. PBu_2Ph) but they are conveniently made by oxidation of $\text{mer-OsX}_3(\text{QR}_3)_3$ ($\text{Q} = \text{P, As}$) with the halogen in CHCl_3 , or CCl_4 and refluxing.

The general product of $\text{OsO}_4/\text{acid}/\text{phosphine}$ reflux is $\text{mer-OsX}_3(\text{PR}_3)_3$, important starting materials for other syntheses. The *fac*-isomer cannot be made directly, instead the *mer*-isomer is treated with borohydride, making $\text{OsH}_4(\text{PR}_3)_3$, which on reaction with HX in methanol gives $\text{fac-OsX}_3(\text{PR}_3)_3$, though this is not a general method. (Neither can a photochemical route, as used for $\text{IrX}_3(\text{PR}_3)_3$ (section 2.13.3), be used.)

Distinguishing between the *fac*- and *mer*-isomers is theoretically possible with far-IR spectra, as the *mer*-isomer (C_{2v} symmetry in the coordination sphere) should give rise to three $\nu(\text{Os-X})$ stretching bands, while the C_{3v}

cis-isomer should give rise to just two; in practice, both isomers tend to give just two bands (possibly owing to overlapping bands or accidental degeneracies) [78a, 152]. There are significant differences in the visible/UV spectra, but ESR spectra of these low spin d^5 complexes show clear differences: the *fac*-isomer of $\text{OsCl}_3(\text{PBU}_2\text{Ph})_3$ has an axially symmetric g -tensor ($g_{\perp} = 1.83$, $g_{\parallel} = 1.28$) while the *mer*-isomer gives rise to a 'rhombic' spectrum ($g_1 = 3.33$, $g_2 = 1.66$, $g_3 = 0.36$) [153].

The magnetic moments for these osmium(III) complexes are, as expected, in the range 1.9–2.2 μ_B . Reduction of *mer*- $\text{OsX}_3(\text{PR}_3)_3$ has been studied in various ways. The usual product of extended reflux with the phosphine/HCl mixture or from using amalgamated zinc in thf under argon is the dimeric species $[\text{Os}_2\text{Cl}_3(\text{PR}_3)_6]^+$, analogous to ruthenium complexes (section 1.8.2). However, some monomeric osmium(II) complexes can be made



The last route is used analogously for ruthenium(II) complexes.

Electrochemical reduction of *mer*- $\text{OsCl}_3(\text{PMe}_2\text{Ph})_3$ affords $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]^-$ [154]. At room temperature in donor solvents, a species $\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{solvent})$ is formed; the initial product is the *trans,mer*-isomer which on standing reverts to the thermodynamically more stable product (Figure 1.61). *trans,mer*- $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{MeCN})]$ has $\text{Os}-\text{Cl} = 2.432\text{--}2.447 \text{ \AA}$, $\text{Os}-\text{N} 2.06 \text{ \AA}$ and $\text{Os}-\text{P} 2.350\text{--}2.362 \text{ \AA}$ (*trans* to P) and 2.298 \AA (*trans* to N) [154].

A compound *trans*- $\text{OsCl}_2(\text{PMe}_2\text{Ph})_4$ has been isolated from the solution and is believed to contain one very loosely bound phosphine, possibly attached through a metal-ring π -bond or $\text{Os}-\text{H}-\text{C}$ agostic interaction.

By comparison, oxidation of *mer*- $\text{Os}(\text{PR}_3)_3\text{Cl}_3$ systems affords paramagnetic osmium(IV) species *mer*- $\text{Os}(\text{PR}_3)_3\text{Cl}_3^+$ (the corresponding *fac*-species can only be oxidized electrochemically) [152]. Other osmium(IV)

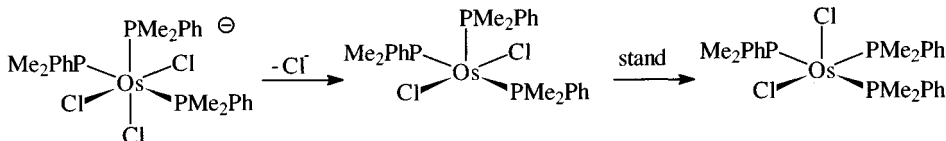


Figure 1.61 Electroreduction of $\text{OsCl}_3(\text{PMe}_2\text{Ph})_3$.

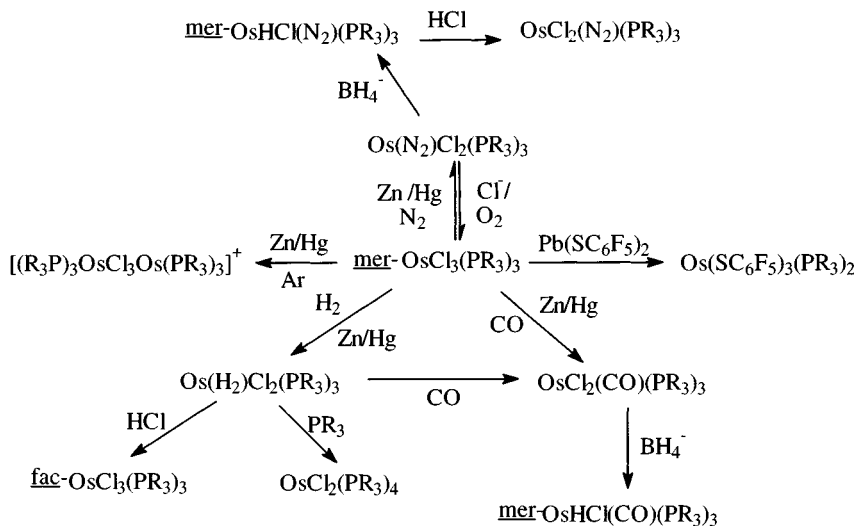
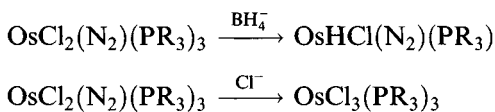


Figure 1.62 Reactions of $\text{OsCl}_3(\text{PR}_3)_3$.

complexes, $\text{trans-OsX}_4(\text{PR}_3)_2$, were mentioned earlier: they are paramagnetic with magnetic moments rather below the spin only value for two unpaired electrons ($\mu = 1.6 \mu_B$ for $\text{trans-OsCl}_4(\text{PEt}_3)_2$). These complexes are reduced (ascorbic acid/ethanol) to $\text{trans}[\text{OsCl}_4(\text{PR}_3)_2]^-$, low spin osmium(III) complexes ($\mu = 2.0 \mu_B$ for $\text{Ph}_4\text{P}^+[\text{OsCl}_4(\text{PEt}_2\text{Ph})_2]^-$).

The solutions of $\text{mer-OsCl}_3(\text{PR}_3)_3$ undergo an interesting reduction with zinc amalgam [155] to form $\text{OsCl}_2(\text{PR}_3)_2\text{L}$ (Figure 1.62), where L is a molecule abstracted from the atmosphere in the reaction flask; if a noble gas, incapable of coordination, is employed, coordinative saturation is obtained by dimerization to $[(\text{PR}_3)_3\text{OsCl}_3\text{Os}(\text{PR}_3)_3]^+$.

The dinitrogen complex is stable to borohydride reduction but the nitrogen is displaced by chloride



The halides in $\text{mer-OsCl}_3(\text{PR}_3)_3$ can be replaced by a thiolate ligand to give paramagnetic $\text{Os(SC}_6\text{F}_5)_3(\text{PR}_3)_2$; an agostic Os–F–C interaction is believed to complete the coordination sphere of osmium [156].

Considerable structural information is available on osmium complexes of tertiary phosphines, arsines and stibines (Table 1.13) [152, 157].

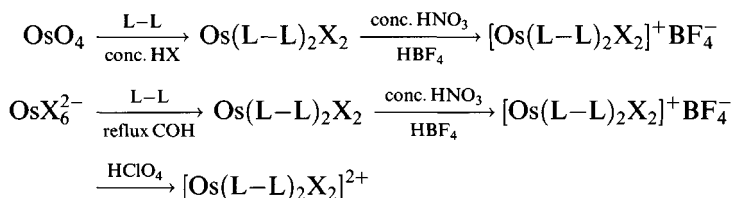
Comparison with data (mainly obtained from EXAFS measurements) on osmium diarsine complexes (Table 1.14) shows that as the oxidation state increases, osmium–halogen bonds shorten whereas Os–P and Os–As bonds lengthen. Bond shortening is predicted for bonds with ionic character,

Table 1.13 Bond lengths in $\text{OsY}_a(\text{QR}_3)_b$ (Å)

	Oxidation state	Os–Q		Os–Y	
		<i>trans</i> -Q	<i>trans</i> -Y	<i>trans</i> -Y	<i>trans</i> -Q
<i>trans</i> - $\text{OsCl}_4(\text{PMe}_2\text{Ph})_2$	4	2.448		2.319	
<i>trans</i> - $\text{OsBr}_4(\text{AsPh}_3)_2$	4	2.569		2.451–2.472	
<i>mer</i> - $\text{OsCl}_3(\text{PMe}_2\text{Ph})_3$	3	2.408	2.350	2.347	2.439
<i>trans</i> - $\text{OsCl}_4(\text{PEt}_3)_2$	3	2.371–2.386		2.375–2.386	
<i>fac</i> - $\text{OsCl}_3(\text{PEt}_2\text{Ph})_3$	3		2.375–2.380		2.442–2.449
<i>trans</i> - $\text{OsCl}_2(\text{PMe}_3)_4^+$	3	2.398–2.419		2.352	
<i>mer</i> - $\text{OsBr}_3(\text{SbPh}_3)_3$	3	2.640–2.654	2.644	2.507–2.508	2.522

as the size of the metal ion decreases with increasing oxidation state and electrostatic attraction. The opposite tendency in Os–P and Os–As bonds has been rationalized in terms of a weaker attraction for the ‘soft’ donor atom as the metal becomes a harder acid (with increasing oxidation state); steric repulsion effects may also play a part [158].

Complexes of diphosphines and diarsines can be prepared by various routes; the following are typical



(L–L, e.g. *o*-C₆H₄(QMe₂)₂ (Q = P, As), Ph₂PC₂H₄PPh₂, etc.).

As noted above, structural information is available from EXAFS data (Table 1.14).

In *trans*-Os(dppe)₂Cl₂CH₂Cl₂, Os–P is 2.348–2.372 Å, Os–Cl is 2.434 Å (compare Ru–P 2.369–2.389 Å, Ru–Cl 2.436 Å in Ru(dppe)₂Cl₂) [159]. In *trans*-Os(dppe)₂Br₂ Os–P is 2.365–2.378 Å and Os–Br is 2.674 Å.

Table 1.14 Bond lengths in *trans*-[Os(*o*-C₆H₄(AsMe₂)₂)₂X₂]ⁿ⁺ (Å)

X	<i>n</i>	Oxidation state	Os–As	Os–X
Cl	0	2	2.404	2.41
Cl	1	3	2.460 (2.459 (X))	2.349 (2.337 (X))
Cl	2	4	2.512	2.278
Br	0	2	2.407	2.558, ^a 2.548 ^b
Br	1	3	2.443	2.515, ^a 2.485 ^b
Br	2	4	2.517	2.400, ^a 2.384 ^b

Data obtained from EXAFS measurements except X (X-ray).

^a From Os L-edge; ^b From Br K-edge.

Hydride complexes

Osmium forms a large number of hydridophosphine complexes, principally mononuclear. The three main families are $\text{OsH}_6(\text{PR}_3)_2$, $\text{OsH}_4(\text{PR}_3)_3$ and $\text{OsH}_2(\text{PR}_3)_4$.

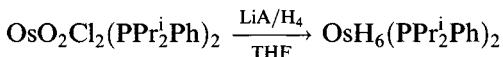
Hexahydrides

$\text{OsH}_6(\text{PMe}_2\text{Ph})_2$ is synthesized by reduction of $\text{Ph}_4\text{As}^+\text{OsCl}_4(\text{PMe}_2\text{Ph})_2^-$



It is a pale yellow oil characterized by ^1H NMR (1 : 2 : 1 triplet showing two phosphines with $\delta = -8.6$ ppm) and IR spectroscopy ($\delta(\text{Os}-\text{H})$ 2028, 1980, 1869 cm^{-1}) [160].

Crystalline $\text{OsH}_6(\text{PPr}_2^i\text{Ph})_2$ was also made by reduction:



Its ^1H NMR spectrum supports the formulation (triplet at $\delta = -9.21$ ppm, $J(\text{P}-\text{H})$ 9 Hz, $J(\text{Os}-\text{H})$ 40 Hz) and the structure was established by X-ray and neutron diffraction (Figure 1.63); unlike $\text{IrH}_5(\text{PR}_3)_2$ (section 2.15) the two phosphorus atoms are not colinear with the metal ($\text{P}-\text{Os}-\text{P}$ 155°) [161]: the geometry round the osmium is an irregular dodecahedron.

The $\text{Os}-\text{H}$ bonds are $1.637-1.668\text{ \AA}$; since the shortest $\text{H}-\text{H}$ contacts are 1.65 \AA , it is clearly a 'classical' hydride rather than a $\eta^2\text{-H}_2$ complex. Other hexahydrides OsH_6L_2 ($\text{L} = \text{PPr}_3$, PBU_2Me) have lately been reported. On protonation with HBF_4 , $[\text{OsH}_7(\text{PPr}_3)_2]^+$ is formed, believed to be $[\text{OsH}_3(\text{H}_2)_2(\text{PPr}_3)_2]^+$; this reacts with MeCN forming hydrides such as $[\text{OsH}_3(\text{MeCN})_2(\text{PPr}_3)_2]^+$ [162].

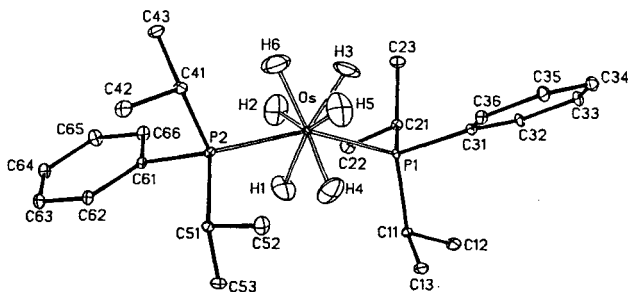
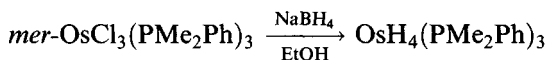


Figure 1.63 The structure of $\text{OsH}_6(\text{PPr}_2^i\text{Ph})_2$. (Reprinted with permission from *Inorg. Chem.*, 1987., **26**, 2930. Copyright (1987) American Chemical Society.)

Tetrahydrides

Several of these complexes have been made:



with others (L = PBu_3 , PPh_3 , PEt_2Ph , AsEtPh_2) synthesized by the same general route [160, 163].

The low-frequency NMR spectrum of $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ shows a 1:3:3:1 quartet owing to coupling with three equivalent phosphines ($\delta = 8.81$ ppm, $J(\text{P-H})$ 6.2 Hz) and IR bands to O-H stretching at 2033, 1970, 1861 and 1806 cm^{-1} (in C_6H_6). The equivalence of the phosphines could be the result of strong P-P coupling or (more likely) of the molecule being fluxional in solution; in the solid state the structure (Figure 1.64) is a distorted pentagonal bipyramid.

The axial P-Os-P angle is 166° , so the three atoms are not quite colinear (Os-P 2.311 Å); the unique Os-P bond is slightly longer at 2.347 Å, showing a *trans*-effect of hydride. Os-H bonds average 1.663 Å [164].

In the similar $\text{OsH}_4(\text{PEt}_2\text{Ph})_3$, the Os-P bonds are 2.296 Å (axial) and 2.339 Å (equatorial).

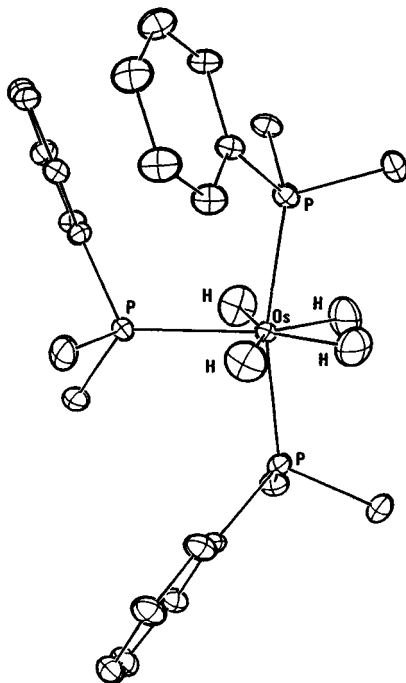
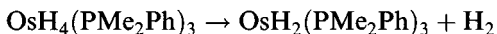


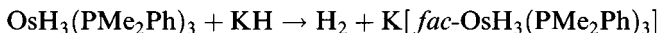
Figure 1.64 The structure of $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$. (Reprinted with permission from *J. Am. Chem. Soc.*, 1977, **99**, 7557. Copyright (1977) American Chemical Society.)

preference of neutral phosphine ligands for axial sites [165]: $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ undergoes photodissociation



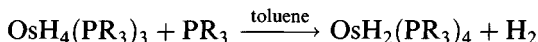
Under high hydrogen pressure, $\text{OsH}_6(\text{PMe}_2\text{Ph})_2$ is formed, with excess phosphine *cis*- $\text{OsH}_2(\text{PMe}_2\text{Ph})_4$. However, photolysis *in vacuo* gives dimers $\text{Os}_2\text{H}_4(\text{PMe}_2\text{Ph})_6$ and $\text{Os}_2\text{H}_4(\text{PMe}_2\text{Ph})_5$, the former decomposing further to afford a very unusual paramagnetic osmium(III) species, $[\text{OsH}_4(\text{PMe}_2\text{Ph})_2]^-$.

Deprotonation of $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ with excess KH in thf at 70°C leads to lipophilic $\text{K}^+[\text{fac-OsH}_3(\text{PMe}_2\text{Ph})_3]^-$. In the solid state, this has a dimeric structure with phenyl rings helping it present a hydrocarbon-like exterior to solvents (Os–H 1.66–1.69 Å, Os–P 2.271–2.28 Å) [166].



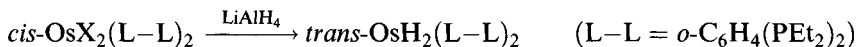
Dihydrides

Reaction of $\text{OsH}_4(\text{PR}_3)_3$ with tertiary phosphines gives dihydrides $\text{OsH}_2(\text{PR}_3)_4$ ($\text{PR}_3 = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PEt}_2\text{Ph}$, etc.) [163]:



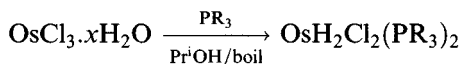
The IR spectra show two $\nu(\text{Os-H})$ bands (1950 and 1920 cm^{-1} for $\text{PR}_3 = \text{PMe}_2\text{Ph}$); this supports a *cis*-structure (a *trans*-structure would only give one band), a conclusion supported by the NMR data. These compounds, therefore, have rigid structures.

Some diphosphines give *trans*-dihydrides



These have simple IR spectra with only one $\nu(\text{Os-H})$ band.

With some bulky phosphines, $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_2$ have been obtained (PR_3 , e.g. $\text{PPr}_3^1, \text{PMeBu}_2^1$) [167]



These are diamagnetic 16 electron species (reaction in methanol or 2-methoxyethanol gives $\text{OsH}(\text{CO})\text{Cl}(\text{PR}_3)_2$, presumably because the alcohol is oxidized to an aldehyde that can be a source of CO) (Figure 1.65). These

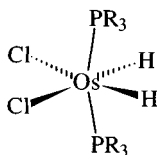
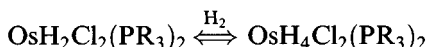
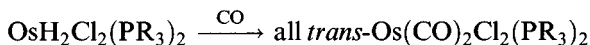
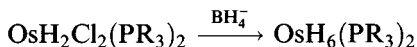
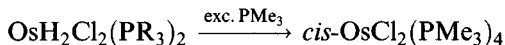


Figure 1.65 Structure of the hydride $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_2$.

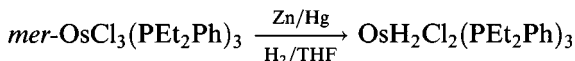
complexes have *cis*-arrangements of the hydride and chloride ligands with *trans*-phosphines with very distorted octahedral coordination, with R–Os–P 112° and Cl–Os–Cl 83°; they are fluxional in solution.

The PMeBu_2^i and PPR_3^i complexes react to attain an 18 electron system in various ways

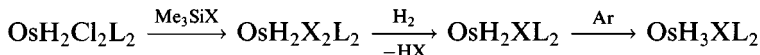


The structure of $\text{OsH}_4\text{Cl}_2(\text{PPR}_3^i)_2$ shows *cis*-chlorides and *trans*-phosphines occupying four vertices of an octahedron, but the hydrogens were not located [168].

With less bulky phosphines, 18 electron $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_3$ are known



$\text{OsH}_2\text{Cl}_2(\text{PPR}_3^i)_2$ can be converted into trihydrides $\text{OsH}_3\text{X}(\text{PPR}_3^i)_2$

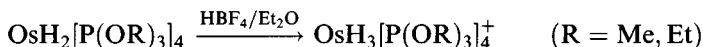


(L = PPR_3^i ; X = Cl, Br, I)

NMR and other evidence suggests [169] that these are 'classical' octahedral hydrides (with, as usual, *trans*-phosphines).

Cationic hydrides

Several cationic hydrides have been studied in detail [170] to assess whether they are classical hydrides or dihydrogen complexes. $\text{OsH}_3(\text{PPh}_3)_4^+$ appears to be a classical hydride but $\text{OsH}_5(\text{PPh}_3)_3^+$ is thought to be $\text{OsH}_3(\eta^2\text{-H}_2)(\text{PPh}_3)_3^+$ and $\text{OsH}_3[\text{P}(\text{OR})_3]_4^+$ is $\text{OsH}(\eta^2\text{-H}_2)[\text{P}(\text{OR})_3]^+$. These are typically made by protonation:



NMR evidence has been used to support similar structures *trans*- $[\text{OsH}(\eta^2\text{-H}_2)(\text{R}_2(\text{CH}_2)_2\text{PR}_2)_2]^+$ (R = Ph, Et); an X-ray diffraction study (R = Ph) has shown the planar OsP_4 arrangement but without locating the hydrogens [171]. MO calculations for $[\text{OsH}_5(\text{PR}_3)_3]^+$ predict the (observed) dodecahedral structure [172]; the crystal structure of $[\text{OsH}_5(\text{PMe}_2\text{Ph})_3]\text{BF}_4$ shows that it is a classical hydride (Os–H 1.62–1.65 Å) but with rather short H–H distances.

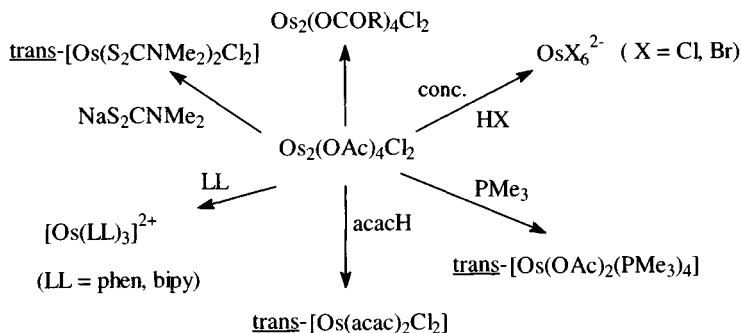
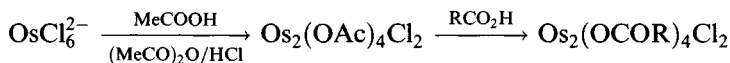


Figure 1.66 Reactions of the dimeric $\text{Os}_2(\text{OAc})_4\text{Cl}_2$.

1.11.3 Carboxylate complexes

The carboxylate complexes of osmium have been studied less than the ruthenium analogues [173].

Reaction of OsCl_6^{2-} with acetic acid/acetic anhydride mixtures containing concentrated HCl gives the diosmium compound $\text{Os}_2(\text{OAc})_4\text{Cl}_2$ (rather than mixed-valence species, see section 1.8.3); other carboxylates can be made by carboxylate exchange:



(R = C_3H_7 , CH_2Cl , $o\text{-PhC}_6\text{H}_4$, etc.).

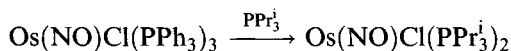
They have binuclear tetracarboxylate-bridged 'lantern' structures: in the butyrate Os-Os is 2.301 Å and Os-Cl 2.417 Å. Most reactions involve cleavage of the Os-Os bond (Figure 1.66).

1.11.4 Nitrosyl complexes [12, 115]

The pattern of behaviour in osmium nitrosyls seems to be similar to that seen with ruthenium, though fewer data are available. The most common type of complex has octahedrally coordinated osmium(II) with linear Os-N-O linkage. Some syntheses are shown in Figure 1.67.

The $\{\text{Os}(\text{NO})\}^6$ compound $\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$ doubtless has linear nitrosyls, like the ruthenium analogues (section 1.8.5) and $\text{Os}(\text{NO})\text{Cl}_5^{2-}$.

A recent report concerns the $\{\text{Os}(\text{NO})\}^8$ compound $\text{trans-Os}(\text{NO})\text{Cl}(\text{PPr}_3)_2$, which has a linear Os-N-O linkage [174]



Introducing the bulky tri(isopropyl)phosphine causes a decrease in coordination number. This 16 electron compound undergoes a range of

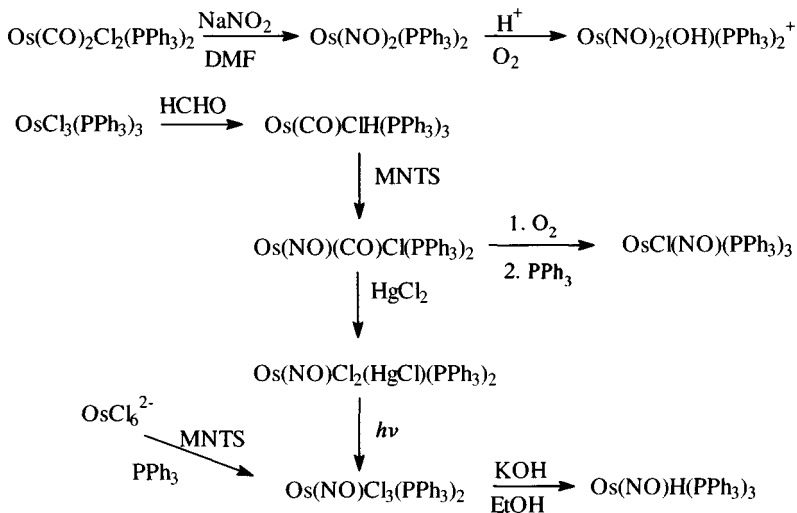
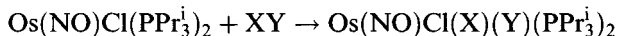
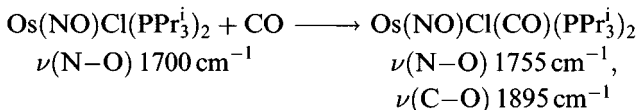


Figure 1.67 Syntheses of some osmium nitrosyl complexes.

oxidative-addition reactions to afford 18 electron species.



(XY = H₂, I₂, HCl, MeI, MeOH)



Os(NO)₂(PPh₃)₂, an {Os(NO)₂}₅¹⁰ system, is tetrahedral like the ruthenium analogue (Os–N 1.771–1.776 Å, Os–N–O 174.1–178.7°; ν(N–O) 1616, 1665 cm⁻¹) and is converted on oxidation in acid solution to the dinitrosyl [Os(NO)₂(OH)(PPh₃)₂]⁺, which has two widely separated IR bands (1842, 1632 cm⁻¹ in the BF₄ salt); the two modes of nitrosyl coordination are confirmed by the crystal structure (Figure 1.68) [175].

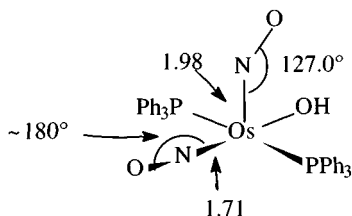
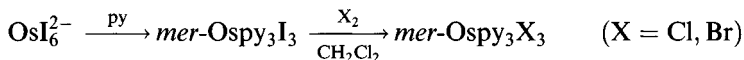


Figure 1.68 The structure of [Os(NO)₂(OH)(PPh₃)₂]⁺.

1.11.5 Other osmium complexes

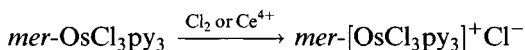
Osmium forms a 6-coordinate acetylacetonate, $\text{Os}(\text{acac})_3$, isomorphous with the ruthenium analogue; unlike ruthenium, however, the osmium(IV) complexes $\text{Os}(\text{acac})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) can be made (*cis*- and *trans*-isomers exist) from OsX_6^{2-} and Hacac , as can $\text{Os}(\text{acac})\text{X}_4^-$ [176].

The pyridine complexes of osmium(III) result from reductive substitution



while under different conditions the osmium(II) complexes Ospy_4X_2 can be made.

The osmium(IV) complexes can be made by oxidation of the osmium(III) systems [152]:



$\text{mer-OsCl}_3\text{py}_3$ has also been made by electroreduction of OsCl_6^{2-} in pyridine. The Os—Cl distances are 2.376 Å (*trans* to py) and 2.357–2.359 Å (*trans* to Cl) with corresponding Os—N distances of 2.086 (*trans* to Cl) and 2.090–2.097 Å (*trans* to N) [177].

The sulphur-containing analogue of the acetylacetonate $\text{Os}(\text{MeCSCHCSMe})_3$ results from the reaction of OsO_4 with acetylacetone and H_2S . The most thoroughly studied complexes, as with ruthenium, are the dithiocarbamates, both $\text{Os}(\text{S}_2\text{CNET}_2)_n$ ($n = 3, 4$) resulting from the reaction of OsCl_6^{2-} with $\text{NaS}_2\text{CNET}_2$. Oxidation of $\text{Os}(\text{S}_2\text{CNET}_2)_3$ gives $\text{Os}(\text{S}_2\text{CNET}_2)_3\text{X}$; where X is a halide, the product is probably a 7-coordinate monomer. When $\text{X} = \text{PF}_6$, dimeric ions $[\text{Os}_2(\text{S}_2\text{CNET}_2)_6]^{2+}$ have been isolated in the solid state: bridging dithiocarbamate enables the osmium to have pentagonal bipyramidal 7-coordination [178]. Thiolates have also been reported in the (+4) state [179].

Dissolving OsCl_5 in MeCN at room temperature leads to reduction and the formation of *cis*- $\text{OsCl}_4(\text{MeCN})_2$. Most nitrile complexes, however, feature phosphines and arsines as co-ligands. Reaction of $\text{OsCl}_3(\text{AsPh}_3)_3$ with *p*-tolylisocyanide gives the three isomers of $\text{OsCl}_3(\text{RNC})_2(\text{AsPh}_3)$ ($\text{R} = p\text{-MeC}_6\text{H}_4$) [180].

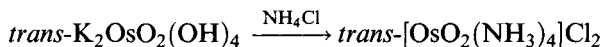
1.12 Compounds in high oxidation states

There is a vigorously expanding chemistry of compounds of ruthenium and osmium in high oxidation states [3, 4, 11, 12], particularly of dioxo and nitrido compounds, though recently some striking developments have taken place in imide chemistry.

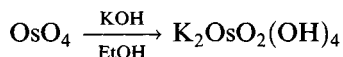
1.12.1 Compounds of the MO_2^{2+} group

The osmium MO_2^{2+} compounds are much more numerous and have greater stability.

The first component to be identified was the yellow ammine (Frémy, 1844):



though the most important is probably $OsO_2(OH)_4^{2-}$



OsO_2^{2+} , sometimes called the 'osmyl' group, is usually linear (a few *cis*-dioxo linkages are known) with short Os–O bonds (around 1.8 Å) indicative of π -bonding. The osmium uses two orbitals (one is shown in Figure 1.69) to form two π -bonds with the two oxygen atoms, giving rise to two bonding, two non-bonding and two anti-bonding π -orbitals.

The bonding and non-bonding orbitals, together with the two Os–O σ -bonding orbitals are occupied by the 12 electrons from the two oxide ions. The two electrons from Os^{6+} occupy the low-lying d_{xy} orbital, giving rise to the observed characteristic absorptions in the IR spectrum *c.* 830–850 cm^{-1} (e.g. in $OsO_2(NH_3)_4Cl_2$ at 828 cm^{-1} , with the corresponding symmetric stretching frequency at 865 cm^{-1}) [181].

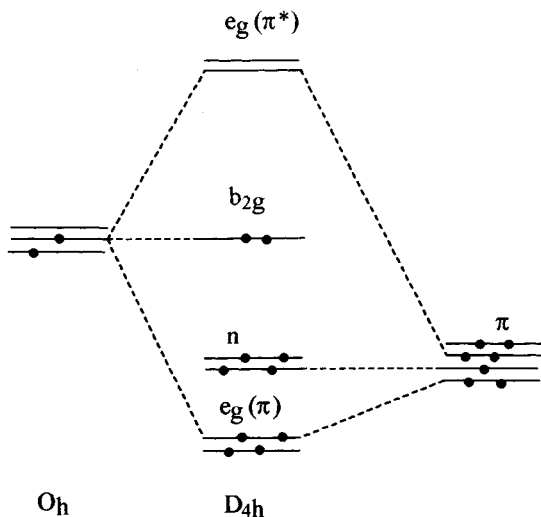


Figure 1.69 The π -bonding in the osmyl ion OsO_2^{2+} .

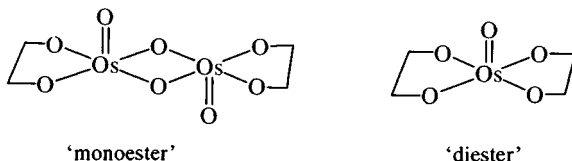
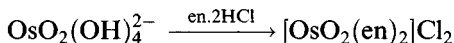
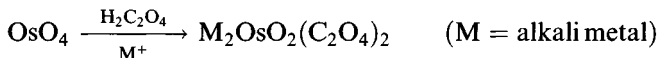
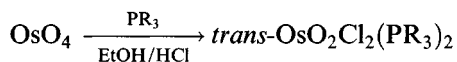


Figure 1.70 Products of the reaction of OsO_4 with alkenes.

Compounds that are O- and N-donors like oxalate and ethylenediamine are able to support the +6 oxidation state



(the latter having $\text{Os}=\text{O}$ 1.74 Å, $\text{Os}-\text{N}$ 2.11 Å, $\text{O}-\text{Os}-\text{O}$ 180°), but it is perhaps more surprising that tertiary phosphine complexes exist in this state (section 1.11.2)

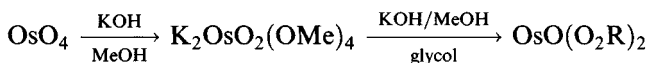


(PR_3 , e.g. PPh_3 , PMe_2Ph , PPr_2^iPh), though short reaction times are necessary to prevent further reduction and the trialkyl phosphines are too strongly reducing to allow the isolation of their complexes [140].

Osmate esters are important intermediates in the reactions of OsO_4 in the stereospecific *cis*-hydroxylation of alkenes and other unsaturated molecules [182].

Alkenes (R) react with OsO_4 to give two kinds of esters: the so-called monoesters $\text{OsO}_2(\text{O}_2\text{R})$, which are actually dimers, $(\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2)$ and diesters $\text{OsO}(\text{O}_2\text{R})_2$ (Figure 1.70) [183].

The reaction of OsO_4 with alkenes is accelerated by nitrogenous bases (e.g. pyridine) forming an intermediate $\text{OsO}_2(\text{O}_2\text{R})\text{L}_2$ that on hydrolysis gives the *cis*-diol $\text{R}(\text{OH})_2$. Some salts are known of the type $\text{K}_2[\text{OsO}_2(\text{O}_2\text{R})_2]$ (R, e.g. Me), which can be converted into esters



The product has a square pyramidal structure (IR $\nu(\text{Os}-\text{O})$ 992 cm^{-1}) (Figure 1.71).

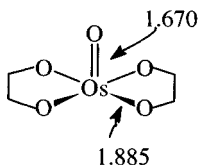


Figure 1.71 Bond lengths in the ester $\text{OsO}(\text{OCH}_2\text{CH}_2\text{O})_2$.

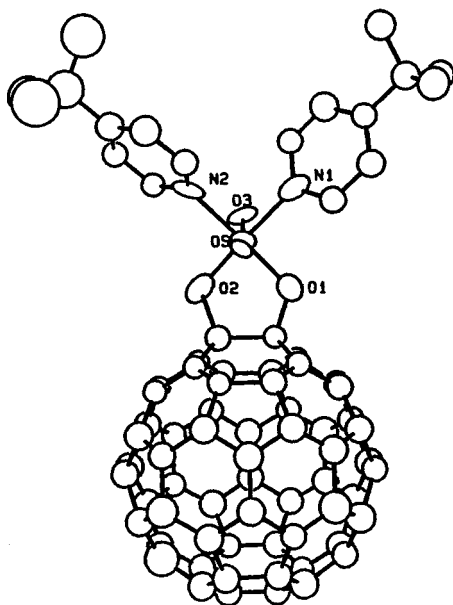
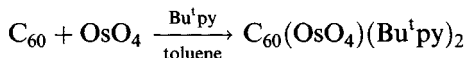


Figure 1.72 The structure of $(C_{60})OsO_4(Bu^1py)_2$. (Reprinted with permission from *Science*, 1991, 252, 312.) Copyright (1991) American Association for the Advancement of Science.)

A striking example of the ability of OsO_4 to add to unsaturated C–C linkages is provided by its reaction with C_{60} , buckminsterfullerene (Figure 1.72) [184]

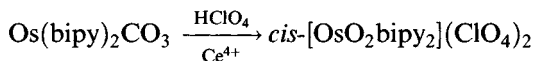


The olive-green osmium(VI) octaethylporphyrin complex $OsO_2(OEP)$ (IR $\nu(Os-O)$ 825 cm^{-1}) is representative of a number of ‘osmyl’ porphyrins [185]; they can readily be transformed into a number of osmium porphyrins in lower oxidation states (Figure 1.73).

$OsO_2(OEP)$ has $Os=O$ 1.745 \AA and $Os-N$ 2.052 \AA . $OsO_2(TMP)$ has $Os=O$ 1.743 \AA , $Os-N$ 2.066 \AA (TMP = tetramesitylporphyrin).

The osmium(VI) arylimide $Os(TTP)(NAr)_2$ (TTP = tetra(*p*-tolyl)porphyrin; $Ar = p\text{-NO}_2C_6H_4$) also has short $Os=NAr$ distances ($1.820\text{--}1.822\text{ \AA}$) [186].

One of the rare examples of a compound with a *cis*- OsO_2 group is made:



The green *cis*-compound isomerizes to the beige *trans*-isomer on heating in MeCN [187]. Another *cis*-compound is *cis*- $[OsO_2(OAc)_3]$, with O–Os–O 125° ; two acetates are monodentate and one is bidentate.

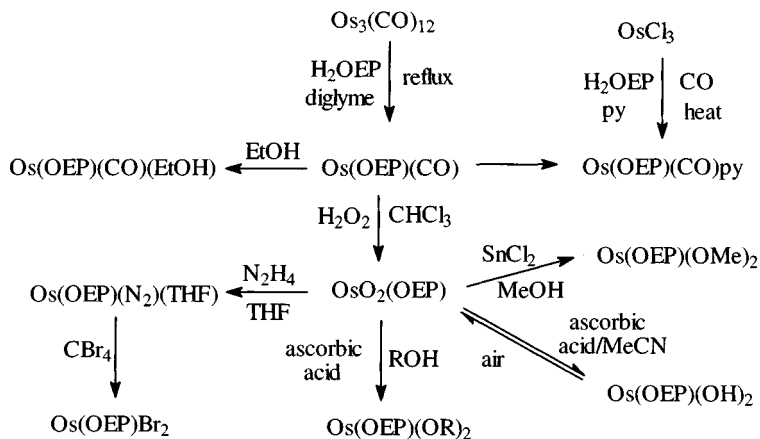
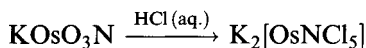


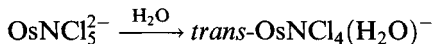
Figure 1.73 Osmium porphyrin complexes.

1.12.2 Nitride complexes

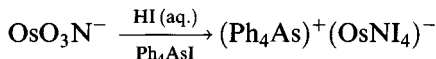
Another type of osmium(VI) compound involving multiple bonds can be viewed as a derivative of OsN^{3+} . The nitrides have attracted interest as they are often photoluminescent



The $\text{Os}\equiv\text{N}$ group has a strong *trans*-influence, reflected in both the labilization of the *trans*-chloride (a similar reaction occurs with OsNBr_5^{2-}) and in the pronounced lengthening of the *trans*-Os–Cl bond (2.605 Å versus 2.362 Å).



With large organic cluster ions (e.g. Ph_4As^+) pink 5-coordinate OsNX_4^- ($\text{X} = \text{Cl}, \text{Br}$) is obtained. Red OsNI_4^- is made:



All the OsNX_4^- complexes are distorted square pyramids (with N–Os–X angles of 103.7 to 104.5°) [188]. The stability of an osmium(VI) to iodine bond is unusual and is presumably owing to the extensive $\text{Os}\equiv\text{N}$ π -bonding reducing the positive charge on the metal and stabilizing it to reduction.

IR and structural data for these species are given in Table 1.15 [189].

A definite nitrido coordination chemistry has grown up including abstraction of sulphur from thiocyanate (Figure 1.74).

$[\text{OsN}(\text{S}_2\text{Cl}_2(\text{CN})_2)_2]^-$ is square pyramidal (Os $\equiv\text{N}$ 1.639 Å, $\nu(\text{Os}-\text{N})$ 1074 cm^{-1}).

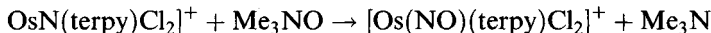
Pyrazine (1,4-diazine) will bridge two OsNCl_4 fragments in $[\text{Cl}_4\text{NOs}(\text{pyrazine})\text{OsNCl}_4]^{2-}$ where the chlorines are bent slightly away from the terminal N (IR $\nu(\text{Os}-\text{N})$ 1105 cm^{-1} , Os–N 1.63 Å) [190].

Table 1.15 IR and structural data for OsNX₄Y species

	$\nu(\text{Os-N})$ (cm ⁻¹)	Os-N (Å)	Os-X (Å)	Os-Y (Å)
OsNCl ₅ ²⁻	1084	1.614	2.361	2.605
OsNBr ₅ ²⁻	1085	—	—	—
OsNCl ₄ (H ₂ O) ⁻	—	1.74	2.34	2.50
OsNBr ₄ (H ₂ O) ⁻	1109	1.67	2.486	2.42
OsNCl ₄ ⁻	1123	1.604	2.320	—
OsNBr ₄ ⁻	1119	1.583	2.457	—
OsNI ₄ ⁻	1107	1.616	2.662	—

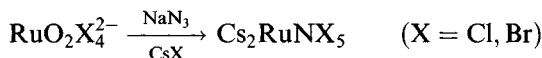
Phosphine complexes like OsN(PMe₃)₂(R₂)Cl (R = CH₂SiMe₃) with chloride *trans* to nitride, and *trans*-phosphines and *trans*-alkyls, have been made [191].

Me₃NO (but not Ph₃PO or C₅H₅NO) oxidizes a nitride group into a nitrosyl



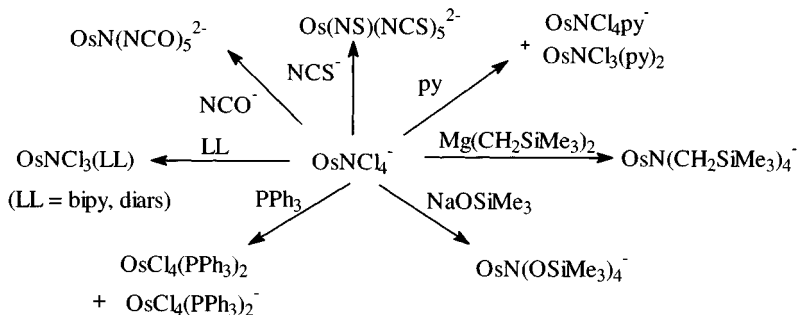
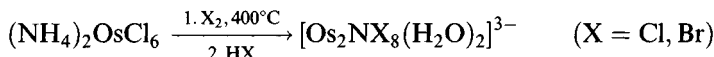
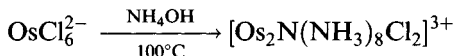
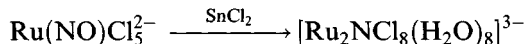
The change in formal oxidation state from osmium(VI) to osmium(II) is noteworthy [192].

A similar chemistry has been found for ruthenium nitrides. They can be made, starting from ice-cold RuO₂X₄²⁻ solutions:



Again, with big 'organic' cations (Ph₄As, Bu₄N) 5-coordinate RuNX₄⁻ are formed. Ph₄AsRuNCl₄ is isomorphous with the osmium analogue (Ru-N 1.570 Å; $\nu(\text{Ru-N})$ 1092 cm⁻¹).

A number of dimeric nitride-bridged complexes have been synthesized [193]

**Figure 1.74** Osmium nitrido complexes.

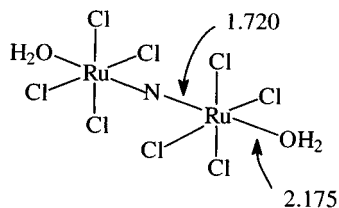


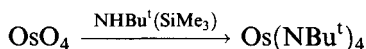
Figure 1.75 The structure of the dimeric nitrido complex $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$.

They resemble the oxygen-bridged $[\text{M}_2\text{OCl}_{10}]^{4-}$ (section 1.3.6) (Figure 1.75) with M–N stretching frequencies similar to those in the mononuclear complexes (1108 cm^{-1} in $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2]\text{Cl}_3$).

$\text{Os}_2\text{N}(\text{S}_2\text{CNR}_2)_5$ has a dithiocarbamate bridge as well as the nitride bridge.

1.12.3 Imides

Organic imide ligands have also been used to stabilize high oxidation states. The best example of this is the osmium(VIII) compound $\text{Os}(\text{NBu}^t)_4$, which has a distorted tetrahedral OsN_4 core (N–Os–N 104.6 – 111.9° ; Os–N 1.750 \AA) [194].



It is a volatile orange–red crystalline solid (m.p. 30°C), stable to over 100°C . On reduction with tertiary phosphines or sodium amalgam, $\text{Os}(\text{NBu}^t)_3$ is formed, which is dimeric $(\text{Bu}^t\text{N})_2\text{Os}(\mu\text{-NBu}^t)_2\text{Os}(\text{NBu}^t)_2$. This can be oxidized to the osmium(VII) dication with concomitant shortening in the Os–Os distance from 3.1 to 2.68 \AA .

The planar 3-coordinate $\text{Os}(\text{NAr})_3$ (Figure 1.76) ($\text{Ar} = 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$) doubtless owes its monomeric character to the greater bulk of the aryl substituent.

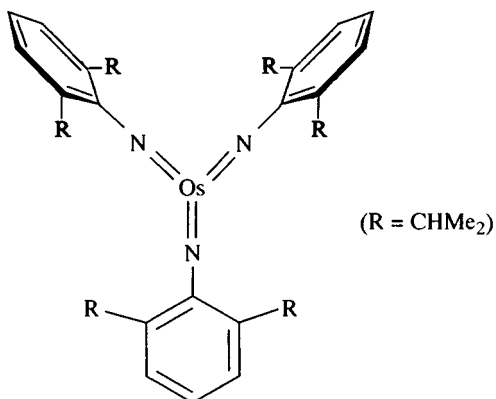
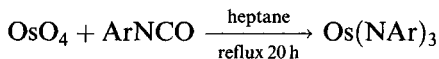


Figure 1.76 The 3-coordinate osmium(VI) imide $\text{Os}(\text{NAr})_3$ ($\text{Ar} = 2,6\text{Pr}_2^i\text{C}_6\text{H}_3$).

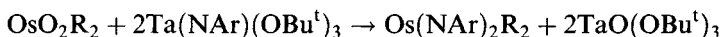
In the solid state, the orientations of the rings differ markedly, but in solution only one NMR signal is seen even at -90°C . The short Os–N bonds (1.736–1.738 Å) show multiple-bond character.

When $\text{Os}(\text{NAr})_3$ is prepared by



it does not form Lewis base adducts but tends to be reduced to *trans*- $\text{Os}(\text{NAr})_2(\text{PR}_3)_2$ (with pyHCl) and *trans*- $\text{Os}(\text{NAr})_2(\text{PR}_3)_2$ (with phosphines). Oxidation of $\text{Os}(\text{NAr})_2(\text{PMe}_2\text{Ph})_2$ with Me_3NO gives $\text{Os}(\text{NAr})_2\text{O}_2$ (IR $\nu(\text{Os}-\text{O})$ 883, 877 cm^{-1}). OsO_4 reacts with $\text{Mo}(\text{NAr})_2(\text{OBu}^t)_2$ to give $\text{Os}(\text{NAr})_2\text{O}_2$ and $\text{Os}(\text{NAr})_3\text{O}$ [195].

Imidoaryls can be made [196]:

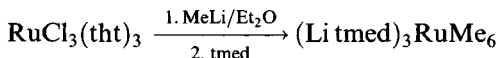


($\text{R} = \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{Bu}^t, \text{CH}_2\text{CMe}_2\text{Ph}$; $\text{NAr} = \text{NC}_6\text{H}_3(2,6\text{-Pr}^i)_2$).

1.13 Simple alkyls and aryls

Ruthenium and osmium form some remarkably stable alkyls and aryls compounds, often in unusually high oxidation states.

Like rhodium and iridium, ruthenium forms a (thermally unstable above 0°C) hexamethylate anion



($\text{tht} = \text{C}_4\text{H}_8\text{S}$; $\text{tmed} = \text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$).

Alkyls Ru_2R_6 ($\text{R} = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3$) have been made using $\text{Ru}_2(\text{OAc})_4\text{Cl}$ as starting materials; they have staggered ethane-like structures with, formally, Ru–Ru triple bonds. Though pyrophoric and light sensitive, they are thermally stable (melting above 100°C); ruthenium inserts oxygen at low temperatures to form asymmetrically dioxygen bridged alkyls (Figure 1.77).

The short Ru–O bond has multiple-bond character (IR $\nu(\text{Ru}-\text{O})$ 908 cm^{-1}).

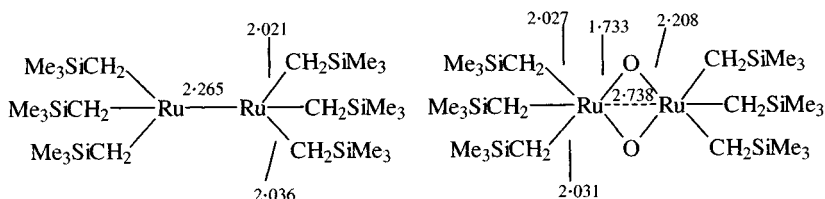


Figure 1.77 The structure of two ruthenium alkyls.

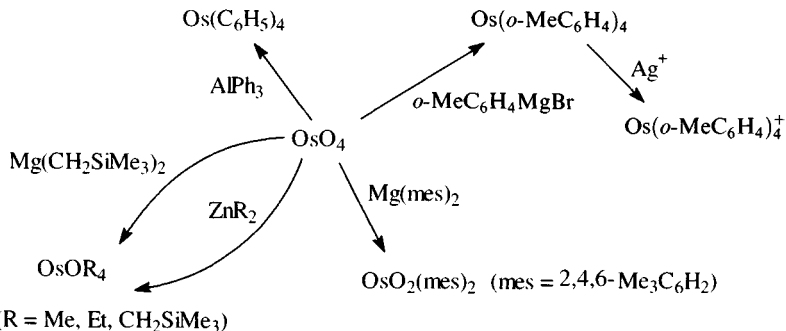
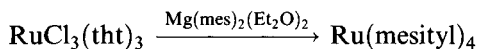
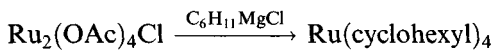


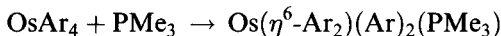
Figure 1.78 Syntheses of osmium alkyls and aryls.

Ruthenium(IV) compounds are prepared by:



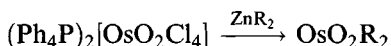
(tht, tetrahydrothiophen). The latter can be oxidized with NOPF_6 to form paramagnetic $\text{Ru}(\text{mesityl})_4^+\text{PF}_6^-$. Both the ruthenium(IV) compounds have essentially tetrahedral geometries (Ru–C 2.01–2.02 Å; C–Ru–C 98.9–127.4° in the mesityl) [197].

Osmium forms a number of compounds in the +4, +5 and +6 states. OsAr_4 (Ar = Ph, *o*-tolyl, cyclohexyl) has tetrahedral coordination of osmium (e.g. Os–C 1.994 Å in $\text{Os}(\text{C}_6\text{H}_5)_4$). The tetraphenyl and tetra(cyclohexyl) compounds are air sensitive, but the *o*-tolyl is very inert (stable to O₂, CO, NO) presumably owing to the *ortho*-methyls shielding the osmium; the latter can be oxidized to paramagnetic $\text{Os}(\text{o-tolyl})_4^+$ (with little change in the Os–C bond length). Osmium(IV) tetraaryls undergo a reductive elimination in the presence of PR_3 (R, e.g. Me, OMe, OEt) by an associative mechanism [198].



(Ar = 2-MeC₆H₄).

The volatile (50°C, 0.1 mmHg) air-stable osmium(VI) mesityl $\text{OsO}_2(\text{mes})_2$ is also diamagnetic (5d²); it has IR bands at 918–950 cm⁻¹ owing to Os–O stretching. There is some distortion from tetrahedral geometry (O–Os–O 136°, C–Os–C 96°) possibly owing to the steric influence of the non-bonding electron pair. The corresponding xylyl also exists [199]. Zinc dialkyls can be used to make OsO_2R_2 systems:



(R = CH₂CMe₃, CH₂SiMe₃, CH₂CMe₂Ph, mesityl).

Alkydene and alkylidyne compounds have also been made [200].

The diamagnetic OsOR_4 (again osmium(VI)) has square pyramidal structures ($\text{Os}=\text{O}$ 1.681 Å, $\text{Os}-\text{Me}$ 2.086 Å in OsOMe_4) and is volatile *in vacuo* at room temperature (IR $\nu(\text{Os}=\text{O})$ 1013 cm^{-1}); the related $\text{OsO}(\text{CH}_2\text{SiMe}_3)_4$ melts at 15°C (IR $\nu(\text{Os}=\text{O})$ 1040 cm^{-1}). In $\text{OsO}(\text{CH}_2\text{CHMe}_2)_4$, $\text{Os}=\text{O}$ is 1.642 Å and $\text{Os}-\text{C}$ 2.120 Å ($\nu(\text{Os}=\text{O})$ 990 cm^{-1}) [201].