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# Dioxo- and nitrido-osmium complexes with imidodiphosphinochalcogenido ligands $[N(QPR_2)_2]^-$ (Q = S or Se; R = Ph or $Pr^i$)

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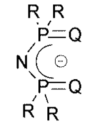
Reactions of *trans*-$K_2[Os^{VI}O_2(OH)_4]$ with 2 equivalents of $HN(QPR_2)_2$ yielded the dioxoosmium(VI) complexes *trans*-$[OsO_2\{N(QPR_2)_2\}_2]$ (Q = S, R = Ph **1** or $Pr^i$ **2**; Q = Se, R = Ph **3**). Complexes **1**–**3** have been characterised by X-ray crystallography. The Os–O distances in **1**–**3** are 1.739, 1.734 and 1.748 Å, respectively. *trans*-$[OsN\{N(QPR_2)_2\}_2Cl]$ (R = $Pr^i$, Q = S; R = Ph, Q = Se) were obtained by reactions of $[NBu_4^n][OsNCl_4]$ with $K[N(QPR_2)_2]$. Treatment of $[OsN\{N(SPPh_2)_2\}_2][BF_4]$ with $[NBu_4^n][OsO_3N]$ resulted in formation of a $\mu$-nitrido $Os^{VIII}$–$Os^{VI}$ complex $[OsN\{N(SPPh_2)_2\}_2(NOsO_3)]$, in which the $[NOsO_3]^-$ is *trans* to the terminal nitride ligand. The $Os^{VI}$–N, $Os^{VI}$–N(Os) and $Os^{VIII}$–N distances are 1.617(12), 2.318(11), and 1.719(11) Å, respectively; the Os(1)–N(4)–Os(2) angle being 159.2(7)°. Treatment of $[OsN\{N(SPPh_2)_2\}_2][BF_4]$ with $[NBu_4^n][ReO_4]$ or $[NBu_4^n]_2[M_6O_{19}]$ gave heterometallic $\mu$-oxo complexes *trans*-$[OsN\{N(SPPh_2)_2\}_2(OReO_3)]$ or *trans*-$[\{OsN[N(SPPh_2)_2]_2\}_2(M_6O_{19})]$ (M = Mo or W), respectively. Reaction of $[NH_4]_2[OsCl_6]$ with $K[N(SPPh_2)_2]$ in the presence of $PPh_3$ or treatment of **3** with $C_6F_5SH$ led to isolation of the osmium(III) homoleptic complexes $[Os\{N(SPR_2)_2\}_3]$ (R = $Pr^i$ or Ph). The geometry around Os in the latter is pseudo octahedral, and the average S–Os–S angle and average Os–S distance are 96.06(5)° and 2.450 Å, respectively. Osmium(III) phosphoraniminate complexes $[Os(NPMePh_2)(PMePh_2)\{N(SPPh_2)_2\}_2]$ and *trans*-$[Os(NPPh_3)(PPh_3)\{N(SePPh_2)_2\}_2]$ were prepared by the respective nitridoosmium(VI) complex with $PMePh_2$ or $PPh_3$. Reaction of complex **1** or **2** with hydrazine hydrate afforded air-sensitive osmium(II) dinitrogen species, presumably $[Os\{N(SPR_2)_2\}_2(N_2)]$ (R = Ph or $Pr^i$), which exhibit IR $\nu(N_2)$ at 2060 and 2040 $cm^{-1}$, respectively.

## Introduction

The monoanions imidodiphosphinochalcogenides $[N(QPR_2)_2]^-$ (Q = chalcogen, R = alkyl or alkoxy) are known to bind to p-, d-, and f-block metal ions exhibiting rich structural diversity.[1–4] These ligands are of interest due to their uses as lanthanide NMR shift reagents[5] and catalysts.[6]



$[N(Ph_2PQ)_2]^-$

Owing to the convenient synthetic routes to $HN(QPR_2)_2$ and related compounds developed by Woollins and co-workers,[7] the co-ordination chemistry of imidodiphosphinochalcogenides has become an active area of investigation as exemplified by the plethora of publications reported in the last few years.[1–4] There are, however, relatively few studies on their complexes with Group 8 transition metals, particularly osmium.[3,8,9] The only isolated osmium complexes with $[N(QPR_2)_2]^-$ ligands are the sulfide complexes $[Os_3(CO)_{10}\{Ph_2P(SH)NP(S)Ph_2\text{-}S,S'\}]$ and $[Os_3H(CO)_9\{Ph_2P(S)NP(S)Ph_2\text{-}S,S'\}]$, which were synthesized from $[Os_3(CO)_{11}(MeCN)]$ and $HN(SPPh_2)_2$,[10] and the nitrido-osmium(VI) complex $[OsN\{N(SPPh_2)_2\}_2X]$ (X = Cl or $CF_3CO_2$).[11] High-valent osmium complexes with related 1,1- or 1,2-dithiolate ligands including *trans*-$[OsO_2(S_2CNEt_2)_2]$,[12] $[OsN(mnt)_2]^-$ (mnt = maleonitriledithiolate)[13] and $[OsN(C_6H_4S_2)_2]^-$ ($[C_6H_4S_2]^{2-}$ = benzene-1,2-dithiolate)[14] have also been reported. To our knowledge, there are no reports on nitrido- or oxo-osmium complexes with chelating selenide ligands. As part of our programme to develop homogeneous catalysts based on molecular metal–sulfur and selenium complexes, we have recently synthesized some ruthenium(II) complexes with $[N(QPR_2)_2]^-$, which were found to activate $H_2$, $SO_2$[15] and hydrazine,[16] and catalyse norbornene polymerisation.[17] Herein we describe the synthesis and crystal structures of oxo- and nitrido-osmium(VI) complexes with $[N(QPR_2)_2]^-$ (Q = S or Se; R = Ph or $Pr^i$), and their reactions with phosphines and hydrazine.

## Results and discussion

### Dioxoosmium(VI) complexes

The synthetic methodology based on the reaction of *trans*-$K_2[Os^{VI}O_2(OH)_4]$ with Brønsted acids[18] was employed to prepare dioxoosmium(VI) complexes with $[N(QPR_2)_2]^-$ (Q = S or Se, R = Ph or $Pr^i$). Thus, interactions of *trans*-$K_2[Os^{VI}O_2(OH)_4]$ with 2 equivalents of $HN(QPR_2)_2$ in MeOH led to precipitation of *trans*-$[OsO_2\{N(QPR_2)_2\}_2]$ (Q = S, R = Ph **1** or $Pr^i$ **2**; Q = Se, R = Ph **3**) in good yields [eqn. (1)].

Recrystallisation from $CH_2Cl_2$–$Et_2O$ afforded air-stable orange crystals that are suitable for X-ray diffraction. The solid structures of complexes **1**–**3** are shown in Figs. 1–3, respectively; the corresponding selected bond lengths and angles are

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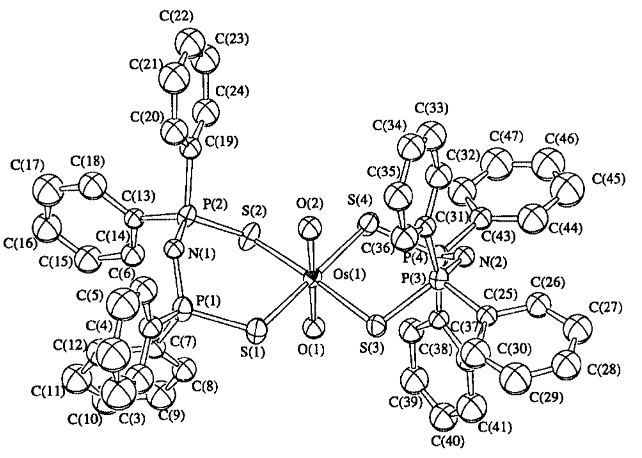


**Fig. 1** Molecular structure of *trans*-[$OsO_2\{N(SPPh_2)_2\}_2$] **1**.

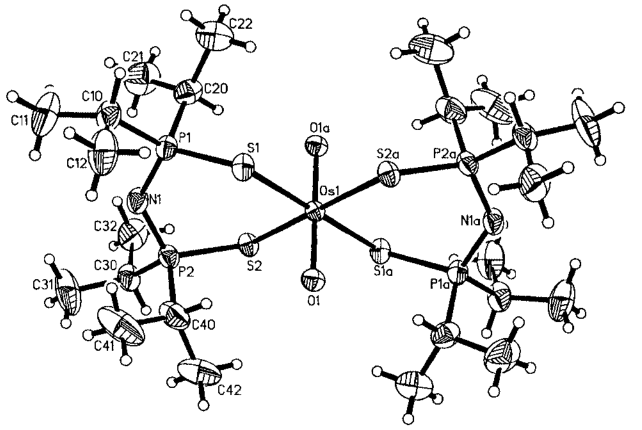


**Fig. 2** An ORTEP[19] diagram of *trans*-[$OsO_2\{N(SPPr^i_2)_2\}_2$] **2** at the 50% probability level.

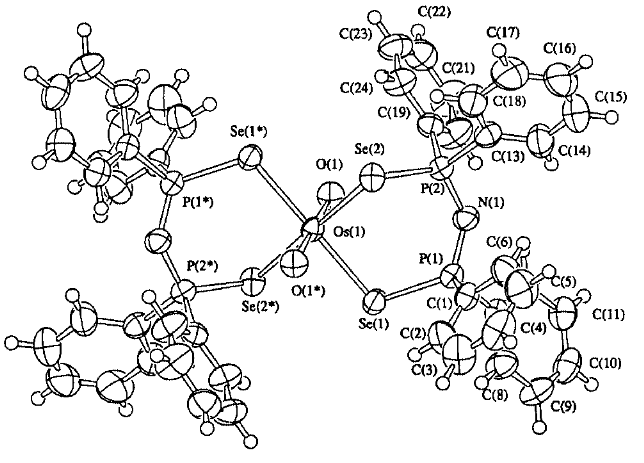
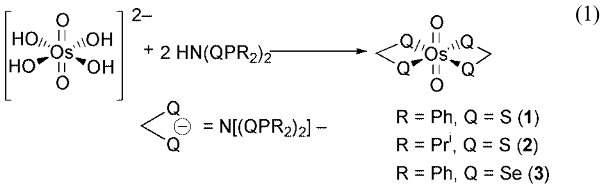


**Fig. 3** A view of molecular structure of *trans*-[$OsO_2\{N(SePPh_2)_2\}_2$] **3**.



(1)

**Table 1** Selected bond lengths (Å) and angles (°) for *trans*-[$OsO_2$-$\{N(SPPh_2)_2\}_2$]·$CH_2Cl_2$(**1**·$CH_2Cl_2$)

| | | | |
|---|---|---|---|
| Os(1)–S(1) | 2.448(2) | Os(1)–S(2) | 2.458(2) |
| Os(1)–S(3) | 2.477(2) | Os(1)–S(4) | 2.465(2) |
| Os(1)–O(1) | 1.745(5) | Os(1)–O(2) | 1.732(5) |
| S(1)–P(1) | 2.040(3) | S(2)–P(2) | 2.031(3) |
| S(3)–P(3) | 2.034(3) | S(4)–P(4) | 2.029(3) |
| S(1)–Os(1)–S(2) | 100.75(7) | S(1)–Os(1)–S(3) | 79.46(7) |
| S(1)–Os(1)–S(4) | 179.54(7) | S(2)–Os(1)–S(3) | 174.32(7) |
| S(2)–Os(1)–S(4) | 78.82(7) | S(3)–Os(1)–S(4) | 100.95(7) |
| S(1)–Os(1)–O(1) | 89.5(2) | S(1)–Os(1)–O(2) | 89.8(2) |
| S(2)–Os(1)–O(1) | 86.0(2) | S(2)–Os(1)–O(2) | 93.3(2) |
| S(3)–Os(1)–O(1) | 88.3(2) | S(3)–Os(1)–O(2) | 92.4(2) |
| S(4)–Os(1)–O(1) | 90.3(2) | S(4)–Os(1)–O(2) | 90.4(2) |
| O(1)–Os(1)–O(2) | 178.9(2) | Os(1)–S(1)–P(1) | 108.9(1) |
| Os(1)–S(2)–P(2) | 110.2(1) | Os(1)–S(3)–P(3) | 106.71(10) |
| Os(1)–S(4)–P(4) | 105.2(1) | | |

**Table 2** Selected bond lengths (Å) and angles (°) for *trans*-[$OsO_2$-$\{N(SPPr^i_2)_2\}_2$] **2**

| | | | |
|---|---|---|---|
| Os(1)–S(1) | 2.463(1) | Os(1)–S(2) | 2.457(1) |
| Os(1)–O(1) | 1.748(3) | S(1)–P(1) | 2.046(1) |
| S(2)–P(2) | 2.043(1) | | |
| S(1)–Os(1)–S(1a) | 180.00(1) | S(1)–Os(1)–S(2) | 99.8(1) |
| S(1)–Os(1)–S(2a) | 80.2(1) | S(1)–Os(1)–O(1) | 91.4(1) |
| S(1)–Os(1)–O(1a) | 90.2(1) | S(2)–Os(1)–O(1) | 88.6(1) |
| S(2a)–Os(1)–O(1a) | 91.4(1) | O(1)–Os(1)–O(1a) | 180.0(1) |
| Os(1)–S(1)–P(1) | 107.9(1) | Os(1)–Se(2)–P(2) | 107.8(1) |

Symmetry code: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

**Table 3** Selected bond lengths (Å) and angles (°) for *trans*-[$OsO_2$-$\{N(SePPh_2)_2\}_2$] **3**

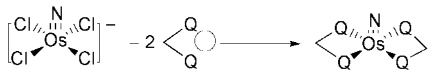
| | | | |
|---|---|---|---|
| Os(1)–Se(1) | 2.5843(4) | Os(1)–Se(2) | 2.5895(4) |
| Os(1)–O(1) | 1.734(3) | Se(1)–P(1) | 2.204(1) |
| Se(2)–P(2) | 2.194(1) | | |
| Se(1)–Os(1)–Se(1a) | 180.0 | Se(1)–Os(1)–Se(2) | 99.41(1) |
| Se(1)–Os(1)–Se(2a) | 80.59(1) | Se(1)–Os(1)–O(1) | 89.84(10) |
| Se(1)–Os(1)–O(1a) | 90.16(10) | Se(2)–Os(1)–O(1) | 87.25(9) |
| Se(2)–Os(1)–O(1a) | 92.75(9) | O(1)–Os(1)–O(1a) | 180.0 |
| Os(1)–Se(1)–P(1) | 106.46(3) | Os(1)–Se(2)–P(2) | 101.88(3) |

Symmetry code: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

given in Tables 1–3. To our knowledge, **3** is the first example of an oxoosmium complex in a Se-only ligand environment. For **1**–**3** the geometry around Os is pseudo octahedral with the Os lying within 0.05 Å from the $Q_4$ plane. The average Os=O distances of 1.739, 1.734 and 1.748 Å for **1**, **2** and **3**, respectively, are typical for *trans*-dioxoosmium(VI) compounds (*e.g.* 1.747 Å for *trans*-[$OsO_2(S_2CNEt_2)_2$]).[12] The average Os–Se distance of 2.5869(4) Å for **3** is obviously longer than the average Os–S distances for **1** [2.462(2) Å] and **2** [2.460(1) Å]. The $\nu_{asym}$-$(O=Os=O)_{as}$ stretching modes for complexes **1**–**3** are located at 848, 842 and 844 cm$^{-1}$, respectively, which are comparable to that for *trans*-[$OsO_2(S_2CNEt_2)_2$] (839 cm$^{-1}$).[12] The $^{31}P$-$\{^1H\}$ NMR spectra display single resonances due to magnetically equivalent phosphorus atoms in the respective imidodiphosphinochalcogenido ligands. The $^{31}P$ resonances for $HN(QPPh_2)_2$ [Q = S (δ 56.87) and Se (δ 52.26)] were found to shift to a higher frequencies (δ 37.45 and 27.74) upon coordination to osmium. A similar finding has been observed for [$Y(\eta^5$-$C_5H_5)_2\{N(QPPh_2)_2\}_2$].[4]

## Nitridoosmium(VI) complexes

Following the synthetic route to *trans*-[$OsN\{N(SPPh_2)_2\}_2Cl$] **4**,[11] the nitridoosmium complexes *trans*-[$OsN\{N(QPR_2)_2\}_2Cl$] (Q = Se, R = Ph **5**; Q = S, R = Pr$^i$ **6**) were prepared from [$NBu_4^n$][$OsNCl_4$] and K[$N(QPR_2)_2$], isolated as air-stable orange crystals [eqn. (2)]. Single crystals of **5** were obtained by recrystallisation from $CH_2Cl_2$–$Et_2O$. A preliminary diffraction study[20] [cell parameters: $a = 10.825(1)$, $b = 26.338(2)$, $c = 10.155(1)$ Å, $\alpha = 91.38(2)$, $\beta = 111.89(2)$, $\gamma = 90.11(2)°$, $U = 2685.7(1)$ Å$^3$; space group $P\bar{1}$ (no. 2)] revealed that it is isostructural with the sulfide analogue **4**.[9] Unfortunately, due to poor



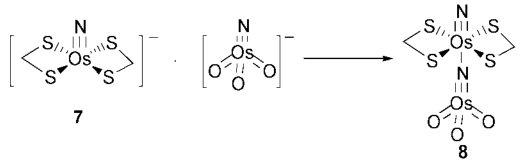
(2)

R = Ph, Q = S (**4**)
R = Ph, Q = Se (**5**)
R = Pr$^i$, Q = S (**6**)

quality of the crystal, low *R* values were obtained. The IR spectra of **5** and **6** show medium-intensity bands at *ca.* 1070 cm$^{-1}$, which are assigned as $\nu$(Os≡N). The $^{31}$P NMR spectrum of **5** displays a signal at $\delta$ 29.87 with satellites arising from coupling to the $^{77}$Se nuclei ($I = \frac{1}{2}$, 7.8% abundant). The observed $^{77}$Se–$^{31}$P coupling constant of 511 Hz is comparable to that for [La($\eta^5$-C$_5$H$_5$){N(SePPh$_2$)$_2$}$_2$] (611 Hz).[4] The $^{31}$P chemical shifts for the nitrido complexes **4** ($\delta$ 60.70) and **6** ($\delta$ 60.43) are more downfield than those for the dioxo analogues **1** and **2**.

## Dimetallic osmium nitrido complexes

Previously, we found that the chloride in complex **4** is labile and can be displaced easily. Thus, reaction of **4** with AgBF$_4$ afforded five-co-ordinate [OsN{N(SPPh$_2$)$_2$}$_2$][BF$_4$] **7**.[11] Owing to co-ordinative unsaturation, cationic **7** may serve as a building block for heterobimetallic complexes. In this connection, its reactions with anionic oxo and nitrido complexes and polyoxometalates were attempted. Treatment with an equimolar amount of [NBu$^n_4$][OsO$_3$N] gave the Os$^{VIII}$–Os$^{VI}$ complex *trans*-[OsN{N(SPPh$_2$)$_2$}$_2$(NOsO$_3$)] **8**, which was isolated as air-stable orange crystals [eqn. (3)].



(3)

The IR $\nu$(Os=O) for complex **8** at 886 and 900 cm$^{-1}$ are higher than those of free [OsO$_3$N]$^-$ (871 and 891 cm$^{-1}$), indicating that [OsO$_3$N]$^-$ is co-ordinated to Os$^{VI}$ instead of a counter anion, and that the Os–O bonds in [OsO$_3$N]$^-$ are strengthened upon co-ordination. Similar findings have been found for other dinuclear nitrido(trioxo)osmate(VIII) complexes.[21] The IR bands at 1058 and 1062 cm$^{-1}$ are tentatively assigned to the Os$^{VI}$≡N and Os$^{VIII}$≡N–Os$^{VI}$ stretching modes. The structure of **8** has been established by X-ray crystallography. Fig. 4 shows a perspective view; selected bond lengths and angles are given in Table 4. To our knowledge, **8** is the first osmium complex containing two nitride ligands although oligomeric $\mu$-nitrido complexes of earlier transition metals are well documented.[22] The ligand [NOsO$_3$]$^-$ binds to Os$^{VI}$ *via* the nitride, and the resulting Os–N–Os linkage is slightly bent with an angle of 159.2(7)°. A similar bent nitride bridge has been observed for [Ru(oep)(NO)(NOsO$_3$)] (oep = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion).[23] The geometry around Os$^{VI}$ is pseudo octahedral with a N(3)–Os(1)–N(4) angle of 177.7(5)°, while that around Os$^{VIII}$ is distorted tetrahedral with average N–Os(2)–O and O–Os(2)–O angles of 112.7(9) and 105.3(10)°, respectively. The Os(1) · · · Os(2) distance across the nitride bridge is 4.037(11) Å. The observed Os$^{VI}$–N, Os$^{VI}$–N(Os$^{VIII}$), and Os$^{VIII}$–N distances of 1.617(12), 2.318(11), and 1.719(11) Å are consistent with the formulation of a Os$^{VI}$-N (nitride) triple bond, Os–N(Os) dative bond, and Os$^{VIII}$-N (nitride) triple bond, and the unsymmetric nitride bridge N≡Os–N≡Os. The Os$^{VIII}$–O distances are comparable to those of [Au(PPh$_3$)(NOsO$_3$)].[21]

**Table 4** Selected bond lengths (Å) and angles (°) for *trans*-[OsN{N(SPPh$_2$)$_2$}$_2$(NOsO$_3$)]·MeOH (**8**·MeOH)

| | | | |
|---|---|---|---|
| Os(1)–S(1) | 2.404(4) | Os(1)–S(2) | 2.408(4) |
| Os(1)–S(3) | 2.433(4) | Os(1)–S(4) | 2.412(4) |
| Os(1)–N(3) | 1.617(12) | Os(1)–N(4) | 2.318(11) |
| Os(2)–N(4) | 1.719(11) | Os(2)–O(1) | 1.630(21) |
| Os(2)–O(2) | 1.599(16) | Os(2)–O(3) | 1.764(13) |
| S(1)–P(1) | 2.048(5) | S(2)–P(2) | 2.056(6) |
| S(3)–P(3) | 2.052(4) | S(4)–P(4) | 2.064(5) |
| S(1)–Os(1)–S(2) | 100.9(1) | S(1)–Os(1)–S(3) | 77.5(1) |
| S(1)–Os(1)–S(4) | 162.5(1) | S(2)–Os(1)–S(3) | 155.8(1) |
| S(2)–Os(1)–S(4) | 79.9(1) | S(3)–Os(1)–S(4) | 94.6(1) |
| S(1)–Os(1)–N(3) | 99.9(5) | S(2)–Os(1)–N(3) | 101.3(4) |
| S(3)–Os(1)–N(3) | 102.8(4) | S(4)–Os(1)–N(3) | 97.0(5) |
| S(1)–Os(1)–N(4) | 82.2(3) | S(2)–Os(1)–N(4) | 79.1(3) |
| S(3)–Os(1)–N(4) | 177.7(5) | N(4)–Os(1)–N(4) | 80.8(3) |
| N(3)–Os(1)–N(4) | 177.7(5) | N(4)–Os(2)–O(1) | 114.5(7) |
| N(4)–Os(2)–O(2) | 115.1(6) | N(4)–Os(2)–O(3) | 108.5(9) |
| O(1)–Os(2)–O(2) | 112.7(9) | O(1)–Os(2)–O(3) | 89.0(9) |
| O(2)–Os(2)–O(3) | 114.3(9) | Os(1)–S(1)–P(1) | 111.0(2) |
| Os(1)–S(2)–P(2) | 109.7(2) | Os(1)–S(3)–P(3) | 102.6(2) |
| Os(1)–S(4)–P(4) | 109.9(2) | | |

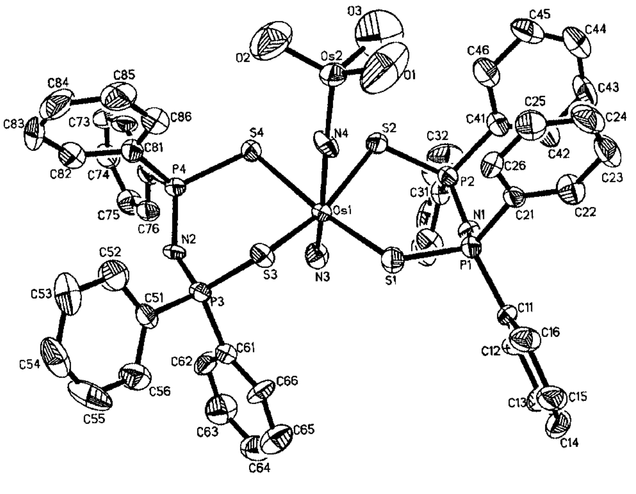
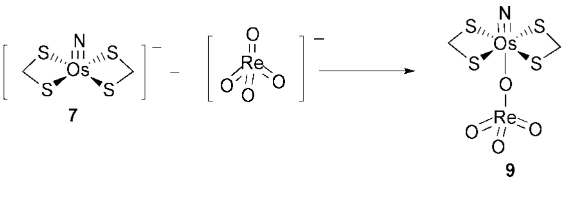


**Fig. 4** An ORTEP diagram of *trans*-[OsN{N(SPPh$_2$)$_2$}$_2$(NOsO$_3$)] **8** at the 50% probability level.

## Heterobimetallic $\mu$-oxo complexes

The success in isolation of an Os$^{VIII}$NOs$^{VI}$ complex prompted us to prepare analogous heterometallic $\mu$-oxo-osmium complexes. Thus, treatment of **7** with [NBu$^n_4$][ReO$_4$] in CH$_2$Cl$_2$ led to formation of the Os$^{VI}$–Re$^{VII}$ complex [OsN{N(SPPh$_2$)$_2$}$_2$(OReO$_3$)] **9** in good yield [eqn. (4)]. The $\nu$(Re=O) for **9** (942 cm$^{-1}$) is lower than that for free [ReO$_4$]$^-$ (970 cm$^{-1}$), indicating that [ReO$_4$]$^-$ is co-ordinating to Os$^{VI}$. Treatment of **7** with [NPr$^n_4$][RuO$_4$] resulted in immediate formation of a dark insoluble precipitate apparently due to decomposition of the complex. It seems likely that upon co-ordination to the Lewis acidic Os$^{VI}$ the activated perruthenate(VII) is a powerful oxidant[24] that is capable of oxidising the electron-rich imidodiphosphinosulfide ligand.



(4)

Reactions of complex **7** with [NBu$^n_4$]$_2$[M$_6$O$_{19}$] (M = Mo or W) in CH$_2$Cl$_2$–acetone resulted in precipitation of the polyoxometalate complexes *trans*-[{OsN[N(SPPh$_2$)$_2$]$_2$}$_2$(M$_6$O$_{19}$)] (M = Mo **10** or W **11**) [eqn. (5)]. Recrystallisation from *N*,*N*-dimethylformamide (dmf)–CH$_2$Cl$_2$–Et$_2$O afforded analytically pure orange crystals of **10** and **11**. The FAB mass spectra of the complexes show molecular ions corresponding to [OsN{N(SPPh$_2$)$_2$]$_2$}$_2$(M$_6$O$_{19}$)]$^+$, indicating that the trinuclear structure remains intact in the gas phase. To our knowledge, **10** and

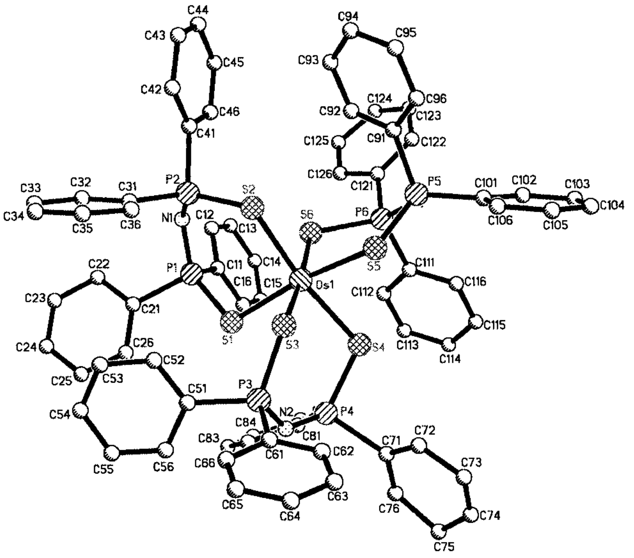
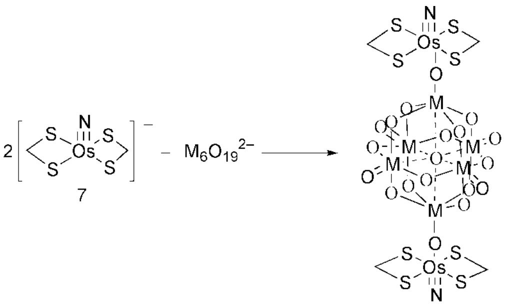


Fig. 5 Perspective view of $[Os\{N(SPPh_2)_2\}_3]$ **13**.

(5)



**11** are the first examples of $Os^{VI}$-containing polyoxometalates.[25] They are only sparingly soluble in $CH_2Cl_2$ and acetone, but readily dissolved in dmf and dimethyl sulfoxide (dmso), in which they behave as 1 : 2 electrolytes due to ligand dissociation. Accordingly, the $^{31}P$ resonances for **10** and **11** in dmso-$d_6$ are virtually identical with that for **7**. The IR $\nu(M{=}O)$ for **10** (746, 814 and 998 $cm^{-1}$) and **11** (572, 816 and 980 $cm^{-1}$) are similar to those for $[M_6O_{19}]^{2-}$ (742, 810 and 990 $cm^{-1}$ for M = Mo; and 586, 816 and 980 $cm^{-1}$ for M = W).

### Homoleptic osmium(III) complexes $[Os^{III}\{N(SPR_2)_2\}_3]$

Treatment of complex **2** with $C_6F_5SH$ led to isolation of the osmium(III) homoleptic complex $[Os\{N(SPPr^i_2)_2\}_3]$ **12**, which was presumably formed *via* reduction of **2** by $C_6F_5SH$ and subsequent co-ordination of the osmium(III) intermediate with a dissociated $[N(SPPr^i_2)_2]^-$. It may be noted that the ruthenium congener $[Ru\{N(SPPh_2)_2\}_3]$ was also obtained by the reaction of $[RuNCl_4]^-$ with $K[N(SPPh_2)_2]$.[15] Complex **12** could be synthesized directly from $[NH_4]_2[OsCl_6]$ and $K[N(SPPr^i_2)_2]$ in the presence of $PPh_3$. Similarly treatment of $[NH_4]_2[OsCl_6]$ with $K[N(SPPh_2)_2]$ in the presence of $PPh_3$ afforded $[Os\{N(SPPh_2)_2\}_3]$ **13**. Complexes **12** and **13** are highly soluble in non-polar solvents such as hexane and diethyl ether. The measured magnetic moment of *ca.* 1.7 $\mu_B$ for **12** is consistent with the formulation of osmium(III). The solid-state structure of **13** has been confirmed by X-ray crystallography. Fig. 5 shows a perspective view; selected bond lengths and angles are listed in Table 5. The geometry around osmium is pseudo octahedral with the average S–Os–S angle of 96.06(5)°. The average Os–S distance [2.450(12) Å] is slightly shorter than those in **1** [2.462(2) Å] and **2** [2.460(1) Å], indicative of the steric congestion around Os in this tris chelate complex.

### Reduction of osmium(VI) complexes with tertiary phosphines

It is well known that nitridoosmium(VI) complexes react with tertiary phosphines to give osmium(IV) phosphoraniminate species.[26] Treatment of **4** with an excess of $PMePh_2$ at room temperature gave an air-stable red solid analysed as $[Os(NPMePh_2)(PMePh_2)\{N(SPPh_2)_2\}_2]$ **14** [eqn. (6)]. The FAB mass spectrum of **14** shows the molecular ion at *m*/*z* 1500, consistent with the proposed formula. The measured magnetic moment of *ca.* 1.8 $\mu_B$ is consistent with the osmium(III) formulation. The IR spectrum of **14** shows $\nu(P{=}N)$ at 1146 $cm^{-1}$, which is higher than that for *trans*-$[Os(tpy)Cl_2(NPPh_3)][PF_6]_2$ (tpy = 2,2′ : 6′,2″-terpyridine; 1112 $cm^{-1}$).[27] It seems possible that the reaction between **4** and $PMePh_2$ initially gave an osmium(IV) phosphoraniminate intermediate, presumably $[Os(NPMePh_2)Cl\{N(SPPh_2)_2\}_2]$, which was further reduced by $PMePh_2$ to give the osmium(III) product. Similarly, reaction of **5** with $PPh_3$ under reflux resulted in isolation of $[Os(NPPh_3)\{(PPh_3)N(SePPh_2)_2\}_2]$ **15**, which was characterised by mass spectrometry and elemental analyses.

(6)

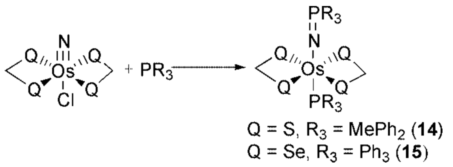


Table 5 Selected bond lengths (Å) and angles (°) for $[Os\{N(SPPh_2)_2\}_3]$ **13**

| | | | |
|---|---|---|---|
| Os(1)–S(1) | 2.4013(12) | Os(1)–S(2) | 2.4034(13) |
| Os(1)–S(3) | 2.4369(13) | Os(1)–S(4) | 2.3991(13) |
| Os(1)–S(5) | 2.4305(12) | Os(1)–S(6) | 2.3884(13) |
| S(1)–P(1) | 2.0217(19) | S(2)–P(2) | 2.0339(19) |
| S(3)–P(3) | 2.0251(18) | S(4)–P(4) | 2.0225(19) |
| S(5)–P(5) | 2.0329(18) | S(4)–P(4) | 2.0196(18) |
| S(1)–Os(1)–S(2) | 96.95(5) | S(3)–Os(1)–S(4) | 90.63(5) |
| S(5)–Os(1)–S(6) | 100.59(4) | S(1)–Os(1)–S(3) | 90.92(4) |
| S(1)–Os(1)–S(4) | 92.72(5) | S(1)–Os(1)–S(5) | 169.87(4) |
| S(1)–Os(1)–S(6) | 88.99(5) | S(2)–Os(1)–S(3) | 86.54(5) |
| S(2)–Os(1)–S(4) | 169.96(4) | S(2)–Os(1)–S(5) | 86.72(5) |
| S(2)–Os(1)–S(6) | 88.19(5) | S(3)–Os(1)–O(5) | 79.84(4) |
| S(3)–Os(1)–S(6) | 174.68(5) | S(4)–Os(1)–S(5) | 83.30(5) |
| S(4)–Os(1)–S(6) | 94.69(5) | Os(1)–S(1)–P(1) | 111.06(7) |
| Os(1)–S(2)–P(2) | 113.55(7) | Os(1)–S(3)–P(3) | 110.09(6) |
| Os(1)–S(4)–P(4) | 110.54(7) | Os(1)–S(5)–P(5) | 113.81(6) |
| Os(1)–S(6)–P(6) | 112.16(6) | | |

### Reduction of dioxoosmium(VI) complexes

No reactions were found between $PPh_3$ and complex **1** or **2**. Treatment of **1** with $PMe_3$ gave a cream coloured oily material, presumably a low valent osmium phosphine species, which did not show any $\nu(OsO_2)$ band in the IR spectrum. We have not been able to crystallise this oily material for microanalysis. Reaction of **1** with hydrazine hydrate in thf gave an exceedingly air-sensitive brown solid [eqn. (7)]. The IR spectrum shows a new band at 2060 $cm^{-1}$ assignable to $\nu(N_2)$. This air-sensitive complex is therefore tentatively formulated as an osmium dinitrogen species $[Os\{N(SPPh_2)_2\}_2(\eta^1\text{-}N_2)]$ **16**. Similarly treatment of **2** with hydrazine afforded $[Os\{N(SPPr^i_2)_2\}_2(\eta^1\text{-}N_2)]$ **17**, which exhibits $\nu(N_2)$ at 2040 $cm^{-1}$. It may be noted that reaction of $[Os(oep)O_2]$ with dinitrazine hydrate in thf yielded a well defined osmium(II) dinitrogen complex $[Os(oep)(\eta^1\text{-}N_2)(thf)]$, which displays IR $\nu(N_2)$ at 2030 $cm^{-1}$.[28] Complexes **16** and **17** are air sensitive both in the solid state and solutions, in

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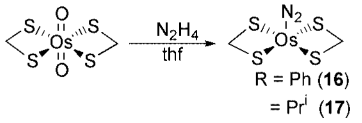

which they decomposed to give unknown paramagnetic species. We have not been able to obtain pure samples for elemental analysis and X-ray diffraction study. Recrystallisation of **16** from $CH_2Cl_2$–MeOH in air led to isolation of an orange crystalline solid analysed as $[Os_2N\{N(SPPh_2)_2\}_4]$ **18**. The proposed formula for **18** was further supported by the observation of a parent ion at *m/z* 2188 in the FAB mass spectrum. Unfortunately we were not able to obtain single crystals of **18** for X-ray diffraction study despite several attempts. On the other hand, recrystallisation of **17** from $Et_2O$–hexane in air led to isolation of the dioxo complex **2** identified by IR and NMR spectroscopy. It appears that upon dissociation of the dinitrogen ligand the resulting unsaturated $[Os\{N(SPPr^i)_2\}_2]$ species is a strong reducing agent and is capable of activating dioxygen. It may be noted that air oxidation of $[Os(por)(N_2)(thf)]$ (por = porphyrin dianion) in alcohols afforded dialkoxoosmium(IV)[29] species whereas $[Os(por)(dmso)_2]$ underwent aerobic oxidation to give dioxoosmium(VI) porphyrins.[30]

### Electrochemistry

Formal potentials of $Os[N(QPR_2)_2]$ complexes have been determined by cyclic voltammetry in $CH_2Cl_2$. The cyclic voltammograms of dioxoosmium(VI) complexes **1** and **2** show irreversible reduction waves at −1.54 and −1.41 V *vs.* $Cp_2Fe^{+/0}$, respectively, which are attributed to the respective $Os^{VI}$–$Os^{V}$ reductions. The $Os^{VI}$–$Os^{V}$ reduction for the selenide analogue **3** was found at a similar potential (−1.41 V), indicating that the donor strength for $[N(SePPh_2)_2]^-$ should be comparable to that for $[N(SPPh_2)_2]^-$. The $Os^{VI}$-$Os^{V}$ potentials for the nitrido complexes **5** and **6** (−1.21 and −1.34 V, respectively) are slightly less negative than those for the oxo congeners. For the $Os^{VIII}$–$Os^{VI}$ dimetallic complex **8** an irreversible reduction wave at −1.69 V, tentatively assigned to the $Os^{VIII}$–$Os^{VII}$ reduction for $[OsNO_3]^-$, was observed. No reduction at the $Os^{VI}$ in **8** was found. The $Os^{VIII}$–$Os^{VII}$ potential for **8** is more negative than that for free $[OsNO_3]^-$ (−1.45 V), indicative of electron delocalisation between the $Os^{VIII}$and $Os^{VI}$. The cyclic voltammograms of complexes **12** and **13** display reversible couples at −0.57 and −0.54 V, respectively, which are assigned to the respective $Os^{IV}$–$Os^{III}$ couple. For comparison, the $Ru^{IV}$–$Ru^{III}$ couple for the ruthenium analogue $[Ru\{N(SPPh_2)_2\}_3]$ occurs at 0.21 V.[15] For complex **13** an irreversible oxidative wave at +0.89 V attributable to the ligand-centred oxidation was also found. Complex **16** exhibits a reversible couple at −0.51 V that was assigned to the $Os^{IV}$–$Os^{III}$ couple. For comparison, the $Os^{IV}$–$Os^{III}$ potentials for *trans*-$[Os(NPPh_3)(salophen)Cl]$ (salophen = *N*,*N′*-bis(salicylidene)-*o*-phenylenediamine dianion)[26] and $[OsL_{OEt}(NPPh_3)Cl_2]$ ($L_{OEt} = [Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3]^-$)[31] are −0.21 and −0.72 V, respectively.

## Conclusion

Dioxo- and nitrido-osmium(VI) complexes with imidodisphosphinochalcogenido ligands have been synthesized and structurally characterised. The dioxoosmium(VI) complexes were reduced by benzenethiol and hydrazine to afford the homoleptic osmium(III) complexes or osmium(II)–dinitrogen complexes, respectively. Five-coordinate $[OsN\{N(SPPh_2)_2\}_2][BF_4]$ reacts with nitrido- and oxo-metal complexes to give the corresponding heterometallic $\mu$-nitrido and $\mu$-oxo complexes. Reaction of $[OsN\{N(SPPh_2)_2\}_2Cl]$ with tertiary phosphines led to formation of osmium(III) phosphoraniminate complexes.

## Experimental

### General considerations

All synthetic manipulations, unless otherwise stated, were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, mass spectra on a Finnigan TSQ 7000 spectrometer and NMR spectra on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for $^1H$ and $^{31}P$, respectively. Chemical shifts ($\delta$ in ppm) were reported with reference to $SiMe_4$ ($^1H$) and 85% $H_3PO_3$ ($^{31}P$). Magnetic moments for solid samples were measured by a Sherwood magnetic susceptibility balance at room temperature. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag–$AgNO_3$ (0.1 M in acetonitrile), respectively, and the scan rate was 100 mV $s^{-1}$. Formal potentials ($E°$) were measured in $CH_2Cl_2$ solutions with 0.1 mol $dm^{-3}$ $[NBu^n_4][PF_6]$ as supporting electrolyte and reported with reference to the ferrocenium–ferrocene couple. Elemental analyses were performed by Medac Ltd., Surrey, UK.

### Materials

$HN(QPR_2)_2$ were synthesized from $HN(PR_2)_2$ and the corresponding elemental chalcogen $Q_8$ (Q = S or Se) in a manner similar to published procedures.[32,33] $K[N(QPR_2)_2]$ were made from $HN(QPR_2)_2$ and $KOBu^t$ in MeOH. The complexes $[NBu^n_4][OsNCl_4]$,[34] $K_2[OsO_2(OH)_4]$,[35] $[NH_4]_2[OsCl_6]$,[36] $[OsN\{N(SPPh_2)_2\}_2Cl]$ **4** and $[OsN\{N(SPPh_2)_2\}_2][BF_4]$ **7**,[11] $[NBu^n_4][OsO_3N]$[37] and $[NBu^n_4]_2[M_6O_{19}]$ (M = Mo or W)[38] were prepared according to the literature methods. Other reagents were purchased from Aldrich and used as received.

### Preparations

***trans*-$[OsO_2\{N(SPPh_2)_2\}_2]$ 1.** To a solution of *trans*-$K_2[OsO_2(OH)_4]$ (0.15 g, 0.41 mmol) in MeOH (10 $cm^3$) were added 2 equivalents of $HN(SPPh_2)_2$ (0.37 g, 0.82 mmol). The reaction mixture was stirred in air for 1 h. The orange precipitate was collected, washed with MeOH and $Et_2O$, and recrystallised from $CH_2Cl_2$–hexane. Yield: 0.34 g (74%). NMR ($CDCl_3$): $^1H$, $\delta$ 7.29–7.87 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 37.45 (s). IR (Nujol, $cm^{-1}$): 848s [$\nu$(Os=O)]. MS (FAB): *m/z* 1121 ($M^+$ + 1). $E°$ = −1.54 V ($Os^{VI}$–$Os^{V}$, irreversible) (Found: C, 51.1; H, 3.5; N, 2.3. Calc. for $C_{48}H_{40}N_2O_2OsP_4S_4$: C, 51.5; H, 3.6; N, 2.5%).

***trans*-$[OsO_2\{N(SPPr^i_2)_2\}_2]$ 2.** This was prepared similarly to complex **1** from *trans*-$K_2[OsO_2(OH)_4]$ (0.10 g, 0.27 mmol) and $HN(SPPr^i_2)_2$ (0.17 g, 0.54 mmol). Slow evaporation of a $CH_2Cl_2$-$Et_2O$ solution afforded orange crystals. Yield: 0.14 g (61%). NMR ($CDCl_3$): $^1H$, $\delta$ 1.25 (dt, 48H, $(CH_3)_2CH$) and 2.51 (sept, 8H, $(CH_3)_2CH$); $^{31}P$-$\{^1H\}$, $\delta$ 60.70 (s). IR (Nujol, $cm^{-1}$): 842s [$\nu$(Os=O)]. $E°$ −1.41 V ($Os^{VI}$–$Os^{V}$, irreversible) (Found: C, 33.7; H, 6.5; N, 3.3. Calc. for $C_{24}H_{56}N_2O_2OsP_4S_4$: C, 34.0; H, 6.7; N, 3.3%).

***trans*-$[OsO_2\{N(SePPh_2)_2\}_2]$ 3.** This complex was prepared similarly to **1** using $HN(SePPh_2)_2$ (0.44 g, 0.82 mmol) instead of $HN(SPPh_2)_2$. Orange red crystals of **3** were obtained in 78% yield. NMR ($CDCl_3$): $^1H$, $\delta$ 7.29–7.86 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 27.74 (s). IR (Nujol, $cm^{-1}$): 844s [$\nu$(Os=O)]. MS (FAB): *m/z* 1308 ($M^+$ + 1). $E°$ = −1.41 V ($Os^{VI}$–$Os^{V}$, irreversible) (Found: C, 43.6; H, 3.0; N, 2.1. Calc. for $C_{48}H_{40}N_2O_2OsP_4Se_4$: C, 44.1; H, 3.1; N, 2.1%).

***trans*-$[OsN\{N(SePPh_2)_2\}_2Cl]$ 5.** To a solution of $[NBu^n_4]$-$[OsNCl_4]$ (0.05 g, 0.09 mmol) in MeOH (20 $cm^3$) was added $K[N(SePPh_2)_2]$ (0.12 g, 0.21 mmol), and the mixture stirred at room temperature for 2 h. The orange solid was collected, washed with MeOH, and recrystallised from $CH_2Cl_2$–$Et_2O$. Yield: 0.08 g (55%). NMR ($CDCl_3$): $^1H$, $\delta$ 7.23–7.79 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 29.87 (s). IR (Nujol, $cm^{-1}$): 1069s [$\nu$(Os≡N)]. MS (FAB): *m/z* 1290 ($M^+$ − Cl). $E°$ = −1.21 V ($Os^{VI}$–$Os^{V}$, irreversible) (Found: C, 43.7; H, 3.2; N, 3.1. Calc. for $C_{48}H_{40}ClN_3OsP_4Se_4$: C, 43.5; H, 3.0; N, 3.2%).

**Table 6** Selected crystallographic data for *trans*-$[OsO_2\{N(SPPh_2)_2\}_2]\cdot CH_2Cl_2$ (**1**·$CH_2Cl_2$), *trans*-$[OsO_2\{N(SPPr^i_2)_2\}_2]$ **2**, *trans*-$[OsO_2\{N(SePPh_2)_2\}_2]$ **3**, *trans*-$[OsN\{N(SPPh_2)_2\}_2(NOsO_3)]\cdot MeOH$ (**8**·MeOH) and $[Os\{N(SPPh_2)_2\}_2]$ **13**

| | **1**·$CH_2Cl_2$ | **2** | **3** | **8**·MeOH | **13** |
|---|---|---|---|---|---|
| Empirical formula | $C_{49}H_{42}Cl_2N_2O_2OsP_4S_4$ | $C_{24}H_{56}N_2O_2OsP_4S_4$ | $C_{48}H_{40}N_2O_2OsP_4Se_4$ | $C_{49}H_{44}N_4O_4Os_2P_4S_4$ | $C_{72}H_{60}N_3OsP_6S_6$ |
| $M_r$ | 1204.12 | 847.06 | 1306.79 | 1385.4 | 1535.61 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/a$ (no. 14) | $P2_1/n$ (no. 14) | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $a$/Å | 13.298(1) | 13.783(1) | 10.756(1) | 12.881(2) | 10.953(2) |
| $b$/Å | 21.226(2) | 9.710(1) | 15.378(2) | 13.688(2) | 14.611(2) |
| $c$/Å | 18.002(2) | 15.481(2) | 14.369(1) | 15.615(2) | 22.038(2) |
| $\alpha$/° | | | | 92.00(2) | 82.64(1) |
| $\beta$/° | 101.50(2) | 115.38(3) | 99.64(2) | 100.22(2) | 86.66(1) |
| $\gamma$/° | | | | 94.86(2) | 78.73(1) |
| $U$/Å$^3$ | 4975.9(9) | 1871.9(7) | 2343.2(4) | 2696.1(7) | 3428.3(8) |
| $Z$ | 4 | 2 | 2 | 2 | 2 |
| $T$/K | 298 | 298 | 298 | 298 | 298 |
| $\mu$/mm$^{-1}$ | 3.006 | 3.823 | 6.005 | 5.029 | 2.227 |
| Measured reflections | 31452 | 4565 | 4250 | 8668 | 12301 |
| Independent reflections | 9527 | 4368 | 3962 | 7889 | 12044 |
| $R_{int}$ | 0.0470 | 0.0321 | 0.0490 | 0.0393 | 0.0272 |
| $R1$ | 0.029 | 0.0282 | 0.030 | 0.0578 | 0.0378 |
| $Rw(F)$ or $wR2(F^2)$ | 0.036[a] | 0.0362[b] | 0.036[a] | 0.0609[b] | 0.0838[b] |

[a] $Rw$. [b] $wR2$.

***trans*-$[OsN\{N(SPPr^i_2)_2\}_2Cl]$ 6.** This was prepared similarly to complex **5** using $K[N(SPPr^i_2)_2]$ instead of $K[N(SePPh_2)_2]$. Yield: 0.05 g (34%). NMR ($CDCl_3$): $^1H$, $\delta$ 1.31 (m, 48H, $(CH_3)_2CH$) and 2.59 (m, 8H, $(CH_3)_2CH$)); $^{31}P$-$\{^1H\}$, $\delta$ 60.43 (s). IR (Nujol, cm$^{-1}$): 1070s [$\nu$(Os≡N)]. MS (FAB): *m*/*z* 828 ($M^+ - Cl$). $E° = -1.34$ V ($Os^{VI}$-$Os^V$, irreversible) (Found: C, 33.2; H, 6.4; N, 4.7. Calc. for $C_{24}H_{56}ClN_3OsP_4S_4$: C, 33.4; H, 6.5; N, 4.9%).

***trans*-$[OsN\{N(SPPh_2)_2\}_2(NOsO_3)]$ 8.** To a solution of $[OsN\{N(SPPh_2)_2\}_2][BF_4]$ **7** (0.10 g, 0.084 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added 1 equivalent of $[NBu^n_4][OsO_3N]$ (0.05 g, 0.08 mmol) and the reaction mixture stirred at room temperature for 1 h, during which time there was a change from yellow to orange. The solvent was pumped off and the orange residue recrystallised from $CH_2Cl_2$–hexane to give orange crystals. Yield: 0.06 g (52%). NMR ($CDCl_3$): $^1H$, $\delta$ 7.30–7.83 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 40.21 (s). IR (Nujol, cm$^{-1}$): 886s and 900s [$\nu$(Os=O)], 1058s and 1062s [$\nu$(Os≡N)]. MS (FAB): *m*/*z* 1354 ($M^+$). $E° = -1.69$ V ($Os^{VIII}$–$Os^{VII}$, irreversible) (Found: C, 41.8; H, 3.1; N, 3.9. Calc. for $C_{48}H_{40}N_4O_3Os_2P_4S_4$: C, 42.6; H, 3.0; N, 4.1%).

***trans*-$[OsN\{N(SPPh_2)_2\}_2(OReO_3)]$ 9.** To a solution of complex **7** (0.10 g, 0.084 mmol) in $CH_2Cl_2$ (25 cm$^3$) was added 1 equivalent of $[NBu^n_4][ReO_4]$ (0.04 g, 0.083 mmol) and the mixture stirred at room temperature for 2.5 h, during which it changed from brown-yellow to brown-orange. The solvent was pumped off and the residue recrystallised from $CH_2Cl_2$–hexane to give bright yellow crystals. Yield: 0.071 g (62%). NMR ($CDCl_3$): $^1H$, $\delta$ 7.31–7.87 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 39.96 (s). IR (Nujol, cm$^{-1}$): 942s [$\nu$(Re=O)], 1056s and 1061s [$\nu$(Os≡N)]. MS (FAB): *m*/*z* 1352 ($M^+$) (Found: C, 42.8; H, 3.1; N, 3.2. Calc. for $C_{48}H_{40}N_3O_4OsReP_4S_4$: C, 42.7; H, 3.0; N, 3.1%).

***trans*-$[\{OsN[N(SPPh_2)_2]_2\}_2(M_6O_{19})]$ (M = Mo 10 or W 11).** Complexes **10** and **11** were prepared by the same procedure as for **9** using $[NBu^n_4]_2[Mo_6O_{19}]$ (0.06 g, 0.042 mmol) and $[NBu^n_4]_2[W_6O_{19}]$ (0.08 g, 0.042 mmol), respectively, instead of $[NBu^n_4][ReO_4]$. Characterisation data for **10**: yield 0.057 g (44%); NMR (dmso-$d_6$) $^1H$, $\delta$ 7.55–7.95 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 38.03 (s); IR (Nujol, cm$^{-1}$) 998s, 814s and 746s [$\nu$(Mo=O)], 1057s and 1065s [$\nu$(Os≡N)]; MS (FAB) *m*/*z* 3083 ($M^+ + 1$) (Found: C, 38.1; H, 2.8; N, 2.5. Calc. for $C_{96}H_{80}Mo_6N_6O_{19}Os_2P_8S_8$: C, 37.4; H, 2.6; N, 2.7%) Characterisation data for **11**: yield 0.11 g (72%); NMR (dmso-$d_6$) $^1H$, $\delta$ 7.54–7.96 (m, phenyl H); $^{31}P$-$\{^1H\}$, $\delta$ 38.00 (s); IR (Nujol, cm$^{-1}$) 980s, 816s and 572s [$\nu$(W=O)], 1054s and 1066s [$\nu$(Os≡N)]. MS (FAB) *m*/*z* 3608 ($M^+ + 1$) (Found: C, 32.7; H, 2.6; N, 2.5. Calc. for $C_{96}H_{80}N_6O_{19}Os_2P_8S_8W_6$: C, 31.9; H, 2.2; N, 2.3%).

**$[Os\{N(SPPr^i_2)_2\}_3]$ 12.** To a solution of complex **2** (0.10 g, 0.12 mmol) was added excess of $C_6F_5SH$ (*ca.* 0.1 cm$^3$). The reaction mixture was stirred at room temperature overnight, during which it changed from orange to violet. The solvent was evaporated by a Rotavapor and the residue purified by column chromatography (neutral alumina). The product was eluted with toluene as a violet band. Recrystallisation from hexane afforded an air stable violet solid. Yield: 0.054 g (40%). MS (FAB): *m*/*z* 1126 ($M^+$). $E° = -0.57$ V ($Os^{IV}$–$Os^{III}$) (Found: C, 39.1; H, 7.5; N, 3.3. Calc. for $C_{36}H_{84}N_3OsP_6S_6$: C, 38.4; H, 7.5; N, 3.7%).

**$[Os\{N(SPPh_2)_2\}_3]$ 13.** To a solution of $[NH_4]_2[OsCl_6]$ (0.10 g, 0.23 mmol) in MeOH (25 cm$^3$) was added $K[N(SPPh_2)_2]$ (0.23 g, 0.46 mmol) and $PPh_3$ (0.12 g, 0.46 mmol), and the reaction mixture heated at reflux overnight. The solvent was pumped off and the brown residue recrystallised from $CH_2Cl_2$–hexane to afford reddish brown crystals. Yield: 0.22 g (63%). MS (FAB): *m*/*z* 1536 ($M^+$). $\mu_{eff} = 1.7\ \mu_B$. $E° = -0.54$ V ($Os^{IV}$–$Os^{III}$) (Found: C, 56.1; H, 3.6; N, 2.8. Calc. for $C_{72}H_{60}N_3OsP_6S_6$: C, 56.3; H, 3.9; N, 2.7%).

**$[Os(NPMePh_2)(PMePh_2)\{N(SPPh_2)_2\}_2]$ 14.** To a solution of complex **4** (0.10 g, 0.09 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added an excess of $MePPh_2$ (*ca.* 0.05 cm$^3$). The resulting red mixture was stirred at room temperature overnight and evaporated to dryness. The residue was washed with hexane and $Et_2O$. Recrystallisation from $CH_2Cl_2$–hexane afforded a paramagnetic red crystalline solid. Yield: 0.07 g (53%). MS (FAB): *m*/*z* 1500 ($M^+$). $\mu_{eff} = 1.8\ \mu_B$. $E° = -0.51$ V ($Os^{IV}$–$Os^{III}$) (Found: C, 57.8; H, 4.6; N, 2.7. Calc. for $C_{74}H_{66}N_3OsP_6S_4\cdot CH_2Cl_2$: C, 59.1; H, 4.5; N, 2.8%).

**$[Os(NPPh_3)(PPh_3)\{N(SePPh_2)_2\}_2]$ 15.** A mixture of complex **5** (0.07 g, 0.05 mmol) and $PPh_3$ (0.035 g, 0.13 mmol) in $CH_2Cl_2$ (20 cm$^3$) was heated at reflux for 1 h during which it changed from orange to red. The solvent was removed *in vacuo* and the residue washed with $Et_2O$. Recrystallisation from $CH_2Cl_2$–$Et_2O$ afforded a paramagnetic red crystalline solid. Yield: 0.03 g (34%). MS (FAB): *m*/*z* 1814 ($M^+$) (Found: C, 56.8; H, 4.2; N, 2.5. Calc. for $C_{84}H_{70}N_3OsP_6Se_4$: C, 55.6; H, 3.9; N, 2.3%).

**Reaction of complex 1 or 2 with hydrazine hydrate.** To a suspension of complex **1** or **2** (50 mg) in thf (20 $cm^3$) was added hydrazine hydrate (*ca.* 0.1 $cm^3$ of a 30% solution in water). The reaction mixture was stirred at room temperature for 2 h. Solvent was then pumped off and the residue washed with MeOH and $Et_2O$ to give an air sensitive brown solid, presumably the osmium(II) dinitrogen species $[Os\{N(QPPh_2)_2\}_2(N_2)]$. Yield: *ca.* 40%. IR (Nujol, $cm^{-1}$): 2060 (Q = S) or 2056 (Q = Se) [$\nu(N_2)$]. We have not been able to obtain analytically pure samples for these air-sensitive compounds because they were found to decompose in halogenated solvents.

### X-Ray crystallography

Pertinent crystallographic data and other experimental details for complexes **1**–**3**, **8** and **13** are summarised in Table 6. Data were collected on a Rigaku AFC7R (for **1**), Siemens P4 diffractometer (for **2**, **8** and **13**) and a MAR Research Image-plate diffractometer (for **3**) using Mo-Kα radiation ($\lambda = 0.71073$ Å). All the structures were solved by direct methods and refined by full-matrix least squares. Structure **8** was refined with the disordered oxygen atom O(3) in the $[NOsO_3]^-$ moiety split into two sites with occupancy of 0.5 each. Calculations were carried out using the TEXSAN (for **1** and **3**)[39] and SHELXL (for **2**, **8** and **13**)[40] crystallographic software packages.

CCDC reference number 186/2073.

See http://www.rsc.org/suppdata/dt/b0/b003798m/ for crystallographic files in .cif format.

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## References

1 A. Davison and E. S. Switkes, *Inorg. Chem.*, 1971, **10**, 837; A. Davison and D. Reger, *Inorg. Chem.*, 1971, **10**, 1967.

2 I. Haiduc and I. Silaghi-Dumitrescu, *Coord. Chem. Rev.*, 1986, **74**, 127; C. Silvestru, R. Rösler, I. Haiduc, R. Cea-Olivares and G. Espinosa-Pérez, *Inorg. Chem.*, 1995, **34**, 3352.

3 J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2893; T. Q. Ly and J. D. Woollins, *Coord. Chem. Rev.*, 1998, **176**, 451, and references cited therein.

4 C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 1999, **38**, 5478; C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 2000, **39**, 1216; C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 2000, **39**, 1222.

5 C. Alvarez, N. Goasdoue, N. Platzer, I. Rodriguez and H. Rudler, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 1002; C. Alvarez, L. Barkaoui, N. Goasdoue, J. C. Daran, N. Platzer, H. Rudler and J. Vaissermann, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1507.

6 H. Rudler, B. Denise, J. R. Gregorio and J. Vaissermann, *Chem. Commun.*, 1997, 2299.

7 P. Bhattacharyya and J. D. Woollins, *Polyhedron*, 1995, **14**, 3367; P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2489; R. Cea-Olivares, J. Novosad, J. D. Woollins, A. M. Z. Slawin, V. García-Montalvo, G. Espinosa-Pérez and P. García y García, *Chem. Commun.*, 1996, 519; P. Bhattacharyya, A. M. Z. Slawin and M. B. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2467.

8 T. S. Lobana, *Prog. Inorg. Chem.*, 1989, **37**, 495.

9 A. M. Z. Slawin, M. D. Smith and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1877.

10 E. N. M. Ho and W.-T. Wong, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 915.

11 W.-H. Leung, J. L. C. Chim, I. D. Williams and W.-T. Wong, *Inorg. Chem.*, 1999, **38**, 3000.

12 W. P. Griffith and J. M. Jolliffe, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 3483.

13 W.-H. Leung, M.-C. Wu, C.-M. Che, W.-T. Wong and K.-F. Chin, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2519.

14 D. Sellmann, M. W. Wemple, W. Donaubauer and F. W. Heinemann, *Inorg. Chem.*, 1997, 36, 1397.

15 W.-H. Leung, H. Zheng, J. L. C. Chim, J. Chan, W.-T. Wong and I. D. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 423.

16 Q.-F. Zhang, H. Zheng, W.-Y. Wong, W.-T. Wong and W.-H. Leung, submitted for publication.

17 W.-H. Leung, K.-K. Lau, Q.-F. Zhang, W.-T. Wong and B. Tang, *Organometallics*, 2000, **19**, 2084.

18 F. C. Anson, J. A. Christie, T. J. Collins, R. J. Coots, T. T. Furutani, S. L. Gipson, J. T. Keech, T. E. Krafft, B. D. Santarsiero and G. H. Spies, *J. Am. Chem. Soc.*, 1984, **106**, 4460; W.-K. Cheng, K.-Y. Wong, W.-F. Tong, T.-F. Lai and C.-M. Che, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 91.

19 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

20 Q.-F. Zhang, W.-H. Leung and W.-T. Wong, unpublished work.

21 W.-H. Leung, J. L. C. Chim and W.-T. Wong, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3153; W.-H. Leung, J. L. C. Chim and W.-T. Wong, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3277; W.-H. Leung, J. L. C. Chim and W.-T. Wong, *Inorg. Chem.*, 1998, **37**, 6382.

22 K. Dehnicke and J. Strähle, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 955.

23 W.-H. Leung, J. L. C. Chim, W. Lai, L. Lam, W.-T. Wong, W. H. Chan and C. H. Yeung, *Inorg. Chim. Acta*, 1999, **290**, 28.

24 T.-C. Lau and C.-K. Mak, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 943.

25 M. T. Pope and A. Müller, *Polyoxometalates*, Kluwer Academic Publishers, Dordrecht, 1994, p. 237; P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77.

26 D. Pawson and W. P. Griffith, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 417; K. Dehnicke and J. Strähle, *Polyhedron*, 1989, **8**, 707; M. Bakirm, P. S. White, A. Dovletoglou and T. J. Meyer, *Inorg. Chem.*, 1991, **30**, 2835; T.-W. Wong, T.-C. Lau and W.-T. Wong, *Inorg. Chem.*, 1999, **38**, 6181.

27 K. D. Demadis, M. Bakir, B. G. Klesczewski, D. S. Williams, P. S. White and T. J. Meyer, *Inorg. Chim. Acta*, 1998, **270**, 511.

28 J. W. Buchler and P. D. Smith, *Angew. Chem.*, *Int. Ed. Engl.*, 1974, **13**, 745; Z.-Y. Li, J.-S. Huang, M. C.-W. Chan, K.-K. Cheung and C.-M. Che, *Inorg. Chem.*, 1997, **36**, 3064.

29 C.-M. Che, J.-S. Huang, Z.-Y. Li, C.-K. Poon, W.-F. Tong, T.-F. Lai, M. C. Cheng, C. C. Wang and Y. Wang, *Inorg. Chem.*, 1992, **31**, 5220.

30 W.-C. Chung, PhD Thesis, The University of Hong Kong, 1986.

31 W.-H. Leung, E. Y. Y. Chan, T. C. Y. Lai and W.-T. Wong, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 51.

32 F. T. Wang, J. Najdzionek, K. L. Leneker, H. Wasserman and D. M. Braitsch, *Synth. Inorg. Metal-Org. Chem.*, 1978, **8**, 120.

33 P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1607.

34 W. P. Griffith and D. Pawson, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 1315.

35 K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.*, 1960, 973.

36 F. P. Dwyer and J. W. Hogarth, *Inorg. Synth.*, 1957, **5**, 206.

37 A. F. Clifford and C. S. Kobayashi, *Inorg. Synth.*, 1960, **6**, 204.

38 N. H. Hur, W. G. Klemperer and R.-C. Wang, *Inorg. Synth.*, 1989, **27**, 77.

39 TEXSAN, Crystal Structure Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

40 G. M. Sheldrick, *SHELXL V5.1 Software Reference Manual*, Bruker AXS Inc., Madison, WI, 1997.