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Journal of Organometallic Chemistry 664 (2002) 85–93

Journal of Organo metallic Chemistry

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Osmacycles containing the $\{(Ph_2PE)_2N\}^-$ ligand (E = S or Se): synthesis and crystal structures

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Received 22 August 2002; received in revised form 20 September 2002; accepted 20 September 2002

Abstract

The reaction of $(Ph_2P)_2NH$ (dppa) or $Ph_2PN(H)P(O)Ph_2$ (HL) with $[Os(\eta^6\text{-cym})Cl_2]_2$ [cym = p-$CH_3C_6H_4CH(CH_3)_2$] in THF affords the orange, neutral mononuclear complexes $[OsCl_2(\eta^6\text{-cym})P\text{-dppa}]$ (**1a**) or $[OsCl_2(\eta^6\text{-cym})P\text{-HL}]$ (**2**), respectively, bearing a pendant $-PPh_2$ or $-P(O)Ph_2$ group. Complex **1a** isomerises smoothly in $CDCl_3$ solution to give the cationic P,P'-chelate complex $[OsCl(\eta^6\text{-cym})P,P'\text{-dppa}]Cl$ (**1b**). Compound **2** can further be converted into the yellow P,O-chelate complexes $[OsCl(\eta^6\text{-cym})P,O\text{-HL}][BF_4]$ (**3**) and $[OsCl(\eta^6\text{-cym})P,O\text{-L}]$ (**4**) [L = $Ph_2PNP(O)Ph_2$] upon treatment with either $Ag[BF_4]$ or ^{t}BuOK, respectively. Chloro bridge cleavage of $[Os(\eta^6\text{-cym})Cl_2]_2$ with the potassium salt of either $\{Ph_2P(S)\}_2N^-$ or $\{Ph_2P(Se)\}_2N^-$ yields the orange neutral complexes $[OsCl(\eta^6\text{-cym})\{E,E'\text{-}Ph_2P(E)\}_2N]$ (E = S **5**, E = Se **6**). All new compounds were characterised by a combination of NMR spectroscopy (^1H and $^{31}P\{^1H\}$), IR spectroscopy, microanalysis and X-ray crystallography. The five- (Os–P–N–P–O) and six-membered (Os–E–P–N–P–E) osmacycles represent the first examples of crystallographically characterised osmium(II) metallocycles.

Keywords: Arene complexes; Crystal structure; Inorganic heterocycle; Osmacycle; NMR spectroscopy; Phosphorus ligands

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1. Introduction

The coordination and organometallic chemistry of phosphorus based ligands bearing a P–N–P skeleton continues to attract much interest [1–6]. We, and others, have reported on studies with $HN(PPh_2)_2$ [7] which serves as a useful precursor to the phosphine oxide $Ph_2PN(H)P(O)Ph_2$ (HL) [8,9] and the chalcogenides $HN\{P(E)Ph_2\}_2$ (E = O, S, Se) [10,11]. The latter compounds can readily be deprotonated affording $N\{P(E)Ph_2\}_2^-$ ligands [10,11] in which various ligating modes have been observed, the most common of which is the E,E'-chelation mode. Recent interest in these anionic ligands has resulted in several publications addressing coordination studies with V [12], Cr [12], Mn [13], Ru [14–16], Rh [16], Ir [16,17], Pd [18,19], Pt [19] and Zn [19], rare-earth metals [20,21] and Group 16 heavy elements [22]. To the best of our knowledge these ligands have not been investigated in detail with osmium although Leung et al. recently reported some osmium(VI) complexes of $\{Ph_2P(E)\}_2N$ (E = S or Se) [23,24]. The same group [14,15], and ourselves [25], have also described some complexes with ruthenium. We wish to describe here our studies using ligands bearing a P–N–P skeletal backbone in the preparation of a series of new "half sandwich" osmium(II) complexes and include the X-ray structures of six examples.

2. Experimental

2.1. Materials

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. All solvents were distilled prior to use. The compounds $(Ph_2P)_2NH$ [7], $Ph_2PN(H)P(O)Ph_2$ [8], $K\{Ph_2P(E)\}_2N$ (E = S [10], E =

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PII: S0022-328X(02)01967-8

Se [11]) and $[Os(\eta^6\text{-cym})Cl_2]_2$ [26] were prepared according to published procedures.

2.2. Instrumentation

IR spectra were recorded as KBr pellets over the range 4000–200 cm^{-1} using a Perkin–Elmer system 2000 FT spectrometer. The ^1H-NMR spectra were recorded on a Bruker AC250 FT spectrometer (250 MHz) with chemical shifts (δ) reported relative to external Me_4Si (see Table 1). The $^{31}P\{^1H\}$-NMR spectra were recorded on a JEOL FX90Q spectrometer (36.2 MHz) with chemical shifts (δ) reported relative to external 85% H_3PO_4; all ^1H-NMR spectra (250 or 400 MHz) were recorded in $CDCl_3$ solutions unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

2.3. X-ray crystallography

All measurements were made on a Bruker AXS SMART 1000 CCD area-detector diffractometer, at 150 K, using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) and narrow frame exposures (0.3°) in ω. Cell parameters were refined from the observed (ω) angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for **1a**, **3** and **5**) and refined on F^2 values for all unique data by full-matrix least-squares. Table 2 gives further details. All non-hydrogen atoms were refined anisotropically. H-atoms, located in difference maps, were constrained with a riding model except H(1), H(2) and H(3) in **3** where the coordinates were freely refined; U(H) was set to 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Complex **2** contains two similar molecules in the asymmetric unit. The asymmetric unit of **3** contains two cations, two anions and one MeOH of crystallisation. In **4** the two phenyl rings on P(2) have all six carbon atoms disordered over two sets of positions, roughly equally occupied. This disorder was modelled with restraints on geometry and displacement parameters. In **5** C(43) was disordered over two sets of positions with ca. 75:25 occupancy ratio and was modelled as described above. There are two molecules with minor conformational differences in the asymmetric unit. Compound **6** has one phenyl ring [C(11) > C(16)] disordered over two sets of positions with C(11) common to both and ca. 65:35 occupancy ratio. There is also a $CHCl_3$ molecule disordered over two sets of positions with ca. 60:40 occupancy ratio. These two disordered groups were modelled as described above. Programs used were Bruker AXS SMART and SAINT for diffractometer control and frame integration [27], Bruker SHELXTL for structure solution, refinement and molecular graphics [28], and local programs.

2.4. Preparation of complexes

2.4.1. $OsCl_2(\eta^6\text{-cym})P\text{-}Ph_2PN(H)PPh_2$ (*1a*)

To a solution of $[Os(\eta^6\text{-cym})Cl_2]_2$ (0.025 g, 0.031 mmol) in THF (10 ml) was added $HN(PPh_2)_2$ (0.026 g, 0.068 mmol) as a solid and the reaction stirred at room temperature for 6 h. The solvent was removed under vacuum and the yellow residue extracted into $CHCl_3$ (2 ml). The extract was filtered through Celite to remove insoluble material before addition of 60:80 petroleum (10 ml) to give **1a** as a yellow microcrystalline solid. Yield: 0.042 g, 82%. IR: 3318, 3286 ν(NH); 920, 906 ν(PN) cm^{-1}. The isomer $[OsCl(\eta^6\text{-cym})P,P'\text{-}Ph_2PN(H)PPh_2]Cl$ (**1b**) was observed immediately, as the only phosphorus containing species, upon addition of NEt_3 to a $CDCl_3$ solution of **1a**.

2.4.2. $OsCl_2(\eta^6\text{-cym})P\text{-}Ph_2PN(H)P(O)Ph_2$ (*2*)

To a solution of $[Os(\eta^6\text{-cym})Cl_2]_2$ (0.086 g, 0.109 mmol) in THF (10 ml) was added $Ph_2PN(H)P(O)Ph_2$ (0.088 g, 0.219 mmol) as a solid. The solution was stirred for ca. 5–10 min whereupon an orange solid deposits. After stirring the mixture for ca. 2 h, the volume of the solvent was reduced by half and 60:80 petroleum (10 ml) added. Solid **2** was collected by suction filtration and dried in vacuo. Yield: 0.152 g, 88%. IR: 3253 ν(NH); 1214 ν(PO); 931 ν(PN) cm^{-1}.

2.4.3. $[OsCl(\eta^6\text{-cym})P,O\text{-}Ph_2PN(H)P(O)Ph_2][BF_4]$ (*3*)

To a suspension of $Ag[BF_4]$ (0.030 g, 0.154 mmol) in CH_2Cl_2 (20 ml) was added **2** (0.103 g, 0.129 mmol) as a solid. After stirring the mixture for 2 h in the dark, AgCl was removed over a Celite plug. The volume was reduced in vacuo to ca. 1–2 ml and Et_2O (20 ml) added. The solid was collected by suction filtration and dried in vacuo. Yield: 0.085 g, 76%. IR: 3226 ν(NH); 1130 ν(PO); 923 ν(PN) cm^{-1}.

Compound **3** could also be prepared by protonation of **4** with $HBF_4 \cdot OEt_2$ ($^{31}P\{^1H\}$-NMR evidence).

2.4.4. $[OsCl(\eta^6\text{-cym})P,O\text{-}Ph_2PNP(O)Ph_2]$ (*4*)

To a suspension of **2** (0.045 g, 0.565 mmol) in CH_3OH (HPLC grade, 0.5 ml) was added ^tBuOK (0.008 g, 0.0713 mmol). After stirring for 5 min the crude solid was filtered and dried briefly. The solid was dissolved in CH_2Cl_2 (4 ml) and 60:80 petroleum (10 ml) added. Solid **4** was collected by suction filtration and dried in vacuo. Yield: 0.025 g, 56%. IR: 1127 ν(PO); 1009, 996 ν(PN) cm^{-1}.

Table 1
Selected analytical and spectroscopic data for **1a**–**6**

Compound	^{31}P (ppm)	^{1}H(arom) (ppm)	^{1}H(cym) (ppm)	$^{1}H\{CH(CH_3)_2\}$ (ppm)	$^{1}H(CH_3)$ (ppm)	$^{1}H\{CH(CH_3)_2\}$ (ppm)	C (calc)	H (calc)	N (calc)	*m*/*z*
1a	25.6, 23.9 [a]	7.91–7.23 [b]	5.49 d, 5.36 d (4.0)	2.41 sep (6.8)	2.09 s	0.89 d (6.8)	46.45 (46.70) [h]	3.89 (4.05)	2.86 (1.56)	781 [M]
2	20.6, 20.3 [c]	7.82–7.14 [d]	5.39 d, 5.23 d (4.0)	2.26 sep (8.0)	1.98 s	0.79 d (8.0)	50.90 (51.25)	4.40 (4.45)	1.50 (1.75)	797 [M]
3	70.2, 51.3 [e]	7.94–7.21	5.76 d, 5.52 d, 5.40 d, 5.26 d	2.35 sep (6.8)	2.05 s	0.98 d (6.8)	47.50 (48.15)	4.15 (4.15)	1.65 (1.65)	762 [M – BF_4]
4	79.0, 46.5 [f]	8.01–7.11	5.69 d, 5.33 dd, 4.74 d	2.27 sep	2.04 s	1.06 d (6.8), 0.66 d (7.2)	53.60 (53.70)	4.35 (4.50)	1.65 (1.85)	760 [M]
5	37.1	8.12–6.99	5.34 d, 5.20 d (2.5)	2.52 sep (5.0)	1.79 s	1.04 d (5.0)	50.65 (50.50)	4.20 (4.25)	1.80 (1.75)	774 [M – Cl]
6	26.5 [g]	8.13–6.96	5.29 d, 5.16 d (2.5)	2.56 sep (5.0)	1.83 s	1.02 d (5.0)	45.15 (45.25)	3.70 (3.80)	1.50 (1.55)	867 [M – Cl]

[a] ^{2}J(PP) 22 Hz.
[b] 5.01 [^{2}J(PH) 8.0 Hz], N*H*.
[c] ^{2}J(PP) not observed.
[d] 6.26 [^{2}J(PH) 8.0, 4.0 Hz], N*H*.
[e] ^{2}J(PP) 26 Hz.
[f] ^{2}J(PP) 33 Hz.
[g] *J*(PSe) 558 Hz.
[h] Contains 1 mol. $CHCl_3$. d = doublet, sep = septet, s = singlet.

Table 2
Crystal data for **1a**–**6**

	1a	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{34}H_{35}Cl_2NOsP_2\cdot CHCl_3$	$C_{34}H_{35}Cl_2NOOsP_2$	$C_{34}H_{35}BClF_4NOOsP_2\cdot 0.5CH_3OH$	$C_{34}H_{34}ClNOOsP_2$	$C_{34}H_{34}ClNOsP_2S_2$	$C_{34}H_{34}ClNOsP_2Se_2\cdot CHCl_3$
Formula weight	900.04	796.67	864.05	760.21	808.33	1021.50
Colour	Orange	Orange	Yellow	Yellow	Orange	Orange
Crystal size (mm)	0.05 × 0.19 × 0.21	0.03 × 0.10 × 0.15	0.10 × 0.22 × 0.32	0.03 × 0.18 × 0.35	0.10 × 0.28 × 0.42	0.11 × 0.22 × 0.26
a (Å)	9.6697(6)	12.0507(12)	19.1828(7)	12.0713(3)	18.9525(12)	10.8566(7)
b (Å)	10.5947(6)	12.5536(12)	19.4869(7)	19.6922(5)	20.7398(16)	12.0657(8)
c (Å)	18.2349(11)	23.919(2)	20.4310(7)	25.2746(2)	18.0663(10)	16.3466(11)
α (°)	95.930(2)	95.758(2)				109.467(2)
β (°)	90.070(2)	100.706(2)	115.486(2)		116.034(5)	96.154(2)
γ (°)	105.058(2)	112.778(2)				108.176(2)
V (Å^3)	1793.56(19)	3218.4(5)	6894.2(4)	6008.0(3)	6380.8(7)	1864.1(2)
System	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/c$	$P\bar{1}$
Z	2	4	8	8	8	2
Total data	16 134	27 960	49 981	44 465	55 713	13 558
Unique data	8364	14 360	12 140	5912	15 362	6537
R_{int}	0.0223	0.0553	0.0310	0.0336	0.0482	0.0149
R ($F^2 > 2\sigma(F^2)$)	0.0261	0.0474	0.0386	0.0471	0.0348	0.0455
R_w (all data)	0.0532	0.1084	0.0942	0.0985	0.0783	0.1196

2.4.5. [OsCl(η^6-cym)S,S′-$Ph_2P(S)NP(S)Ph_2$] (5)

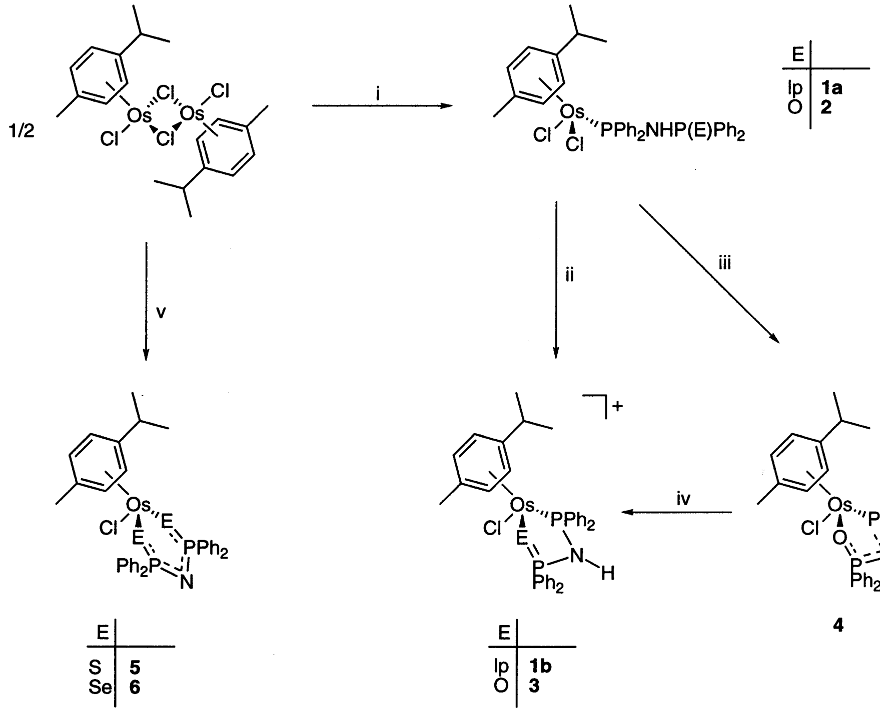
To a solution of [Os(η^6-cym)Cl_2]$_2$ (0.025 g, 0.031 mmol) in THF (10 ml) was added K{$Ph_2P(S)$}$_2$N (0.033 g, 0.068 mmol) as a solid and the reaction stirred at room temperature for 2 h. The solvent was removed under vacuum and the yellow residue extracted into $CHCl_3$ (2 ml). The extract was filtered through Celite to remove insoluble material before addition of 60:80 petroleum (10 ml) ether gave **5** as an orange microcrystalline solid. Yield: 0.042 g, 76%. IR: 1198, 1173 ν(PN); 572 ν(PS) cm^{-1}.

Compound **6** could also be prepared in a similar manner. Yield: 0.050 g, 89%. IR: 1203, 1172 ν(PN); 542 ν(PSe) cm^{-1}.

3. Results and discussion

The dimeric complex [Os(η^6-cym)Cl_2]$_2$ reacts with two equivalents of HN(PPh_2)$_2$ (dppa) or $Ph_2PN(H)P(O)Ph_2$ (HL) in THF solution to form the monomeric complexes, **1a** and **2**, respectively (Scheme 1) as orange, air stable solids. For **2**, this general bridge cleavage procedure has successfully been used in our laboratories for the preparation of various metal complexes containing HL [8,29]. Compound **2** can also be used for the preparation of *P*,*O*-chelate complexes. Hence either chloride abstraction with Ag[BF_4] or, treatment with ^{t}BuOK, affords the cationic and neutral complexes, **3** and **4**, respectively (Scheme 1). In the latter case, deprotonation yields an anionic chelating *P*,*O*-[$Ph_2PNP(O)Ph_2$]$^-$ ligand. Independently **3** can be prepared by protonation of **4** with $HBF_4\cdot OEt_2$. By contrast **1a** undergoes smooth isomerisation to afford the cationic complex **1b** containing an Os–P–N–P chelate ring. Reaction of [Os(η^6-cym)Cl_2]$_2$ with K{$Ph_2P(E)$}$_2$N (E = S; E = Se) at room temperature, in THF solution, affords the monomeric osmium(II) complexes **5** and **6**. Analytical and selected spectroscopic data for **1a**–**6** are presented in Table 1.

The ^{31}P{^{1}H}-NMR data for **1a**–**6** are especially diagnostic. Hence for compounds **1a** and **2**, the ^{31}P resonances are shifted downfield upon complexation with respect to the free ligands [dppa δ (P) 43.1 ppm; HL δ (P) 27.8, 25.2 ppm, ^2J(PP) 59 Hz (in $CDCl_3$)] [8]. For **1a**, two doublets at 25.6 and 23.9 ppm [^2J(PP) 22 Hz] imply two dissimilar phosphorus environments (one *P*-coordinated and the other noncoordinated) and this is further supported by single crystal X-ray studies (see below). Monodentate behaviour of this type has also been observed with $Ph_2PN(H)C_6H_4PPh_2$ [30] where exclusively only the $Ph_2PN(H)$– centre participates in metal complexation. In contrast **2** shows two closely spaced resonances at δ(P) 20.6 and 20.3 ppm which, upon *P*,*O*-chelation as seen for both **3** and **4**, significantly move downfield as a consequence of five-membered chelate ring formation. The ^{31}P{^{1}H}-NMR data for **5** and **6** are consistent with *E*,*E*′-coordination, and in the latter case, a *J*(PSe) coupling of 558 Hz was observed and is similar to previously reported examples [17]. The ^{1}H-NMR data for **1a**–**6** are broadly as expected and show marginal variation in the position of the η^6-cym resonances as a consequence of varying the ligands/different ligating modes adopted. Two sets of doublets are clearly observed for the C_6H_4 protons of the arene ring for **1a**, **2**, **5** and **6** whereas for **3** (and **4**) all



Scheme 1. Preparation of compounds **1a**–**6**. (i) dppa or HL, THF, (ii) NEt_3 (for **1b**) or $Ag[BF_4]$, CH_2Cl_2, (iii) ^tBuOK, CH_3OH, (iv) $HBF_4{\cdot}OEt_2$, (v) $K\{Ph_2P(S)\}_2N$ or $K\{Ph_2P(Se)\}_2N$, THF.

four aromatic Hs are unique. This presumably arises from the three different ligands about the Os(II) centre accounting for the four unique C_6H_4 environments. Other characterising data are given in Table 1 and Section 2.

Crystallographic studies (Tables 2 and 3) reveal structures for **1a**–**6** that are very much in keeping with simple predictions, with overall pseudo tetrahedral ‘piano-stool’ geometries. A comparison of **1a** and **2** is noteworthy here. Both compounds comprise an η^6-cymene, two chlorides and an η^1-*P*-bound phosphino(amine) ligand (Figs. 1 and 2). The Os–Cl, Os–P and Os–C_{arene} bond lengths are similar for both compounds. The P(1)–N(1) distances [1.674(2) in **1a**; 1.689(6) (molecule I) and 1.692(6) Å (molecule II) in **2**] are comparable whilst the N(1)–P(2) bond length in **1a** [1.711(2) Å] is longer than in **2** [1.665(6) (molecule I) and 1.663(6) Å (molecule II)]. Furthermore the P–N–P angle in **1a** [124.71(14)°] is contracted with respect to that found in **2** [132.0(4) (molecule I) and 127.1(4)° (molecule II)]. The short P=O distance compares well with that of HL [8] and known metal complexes in which the phosphoryl group is non-coordinating [8,29]. Within the *p*-cymene ring, C(7) and C(8) are 0.003 and 0.022 Å out of the arene C_6 mean plane and bent away from Os (for **1a**). For **2**, C(7) [and C(41)] are out of the C(1) > C(6) [C(35) > C(40)] mean planes by 0.020 Å (0.068 Å) towards Os. C(8) is bent 0.038 Å away from Os in molecule I (0.011 Å away from Os in molecule II). There is also one molecule of $CHCl_3$ per osmium complex (in **1a**). The solvent forms short $C{-}H\cdots Cl_{coord}$ contacts to Cl(1) and Cl(2) [H(35)···Cl(1) 2.683 Å, H(35)···Cl(2) 2.785 Å] in contrast to $N{-}H\cdots Cl_{coord}$ contacts [H(1)···Cl(1) 2.931 Å, H(1)···Cl(2) 2.790 Å, H(1)···Cl(3′) 2.793 Å] which are best described as very weak H-bonds. In **2** there is also an $N{-}H\cdots Cl_{coord}$ intramolecular H-bond [H(1)···Cl(2) 2.479 Å (molecule I), H(2A)···Cl(3) 2.675 Å (molecule II)].

The X-ray structure of **3** (Fig. 3, Table 3) shows that the osmium(II) centre is bound by a chelating *P*,*O*-$Ph_2PNHP(O)Ph_2$, an η^6-cymene and a chloride ligand. In molecule I the OsP_2O substituents are essentially planar to within 0.019 Å with N(1) 0.190 Å out of this plane. An envelope conformation is observed as indicated by a hinge angle of 12.8° between the OsP_2O/P_2N planes. In molecule II the OsP_2O substituents are essentially planar to within 0.022 Å with P(3) lying furthest out of this plane. Within the *p*-cymene ring the Me and ^{i}Pr groups both show distortions. Hence C(7) is bent 0.049 Å towards, and C(8) 0.258 Å away, from Os (molecule I) and C(41) 0.185 Å/C(42) 0.076 Å away from Os (molecule II). There is also a series of intermolecular hydrogen bonds between molecules I and II, a methanol solvate molecule and one of the two BF_4^- counterions [N(1)···F(8) 2.917, H(1)···F(8) 2.10(2) Å, N(1)–H(1)···F(8) 168(6)°; N(2)···O(3) 2.821(8), H(2)···O(3) 1.98(2) Å, N(2)–H(2)···O(3) 173(6)°; O(3)···F(6) 2.840(12), H(3)···F(6) 2.03(5) Å, O(3)–H(3)···F(6) 159(12)°].

Table 3
Selected bond lengths (Å) and angles (°) for **1a**–**6**

	1a	**2** [a] (E = O)	**3** [a] (E = O)	**4** (E = O)	**5** [a] (E = S)	**6** (E = Se)
Bond lengths						
Os(1)–Cl(1)	2.4199(7)	2.414(2) [2.423(2)]	2.3814(16) [2.3901(18)]	2.4136(16)	2.4232(12) [2.4172(13)]	2.4168(16)
Os(1)–Cl(2)	2.4213(7)	2.428(2) [2.426(2)]				
Os(1)–P(1)	2.3432(8)	2.350(2) [2.334(2)]	2.3309(15) [2.3041(16)]	2.3432(17)		
Os(1)–E(1)			2.136(4) [2.141(4)]	2.153(4)	2.4321(14) [2.4463(13)]	2.5345(7)
Os(1)–E(2)					2.4398(12) [2.4407(12)]	2.5582(6)
E(1)–P		1.473(5) [1.485(6)]	1.519(4) [1.508(4)]	1.524(5)	2.0305(17) [2.0283(17)]	2.1843(19)
E(2)–P(2)					2.0191(17) [2.0229(17)]	2.1831(17)
P(1)–N(1)	1.674(2)	1.689(6) [1.692(6)]	1.715(4) [1.697(5)]	1.637(6)	1.597(4) [1.599(4)]	1.601(5)
N(1)–P(2)	1.711(2)	1.665(6) [1.663(6)]	1.648(5) [1.646(5)]	1.586(5)	1.600(4) [1.600(4)]	1.596(5)
Os(1)–C$_{centroid}$	1.700	1.692 [1.692]	1.707 [1.709]	1.690	1.677 [1.680]	1.674
Bond angles						
Cl(1)–Os(1)–Cl(2)	85.02(3)	85.60(7) [84.59(7)]				
Cl(1)–Os(1)–P(1)	87.05(3)	86.71(7) [84.50(7)]	85.34(6) [86.15(6)]	89.45(6)		
Cl(2)–Os(1)–P(1)	85.38(3)	84.53(7) [86.90(7)]				
O(1)–Os(1)–P(1)			83.71(11) [83.26(12)]	81.21(12)		
O(1)–Os(1)–Cl(1)			82.44(12) [81.55(14)]	84.00(12)		
Os(1)–P(1)–N(1)	113.59(9)	110.9(2) [110.3(2)]	103.76(17) [105.45(19)]	109.01(19)		
N(1)–P(2)–O(1)		115.8(3) [111.9(3)]	107.8(2) [108.0(3)]	114.8(3)		
P(2)–O(1)–Os(1)			123.4(2) [123.4(2)]	118.4(2)		
Cl(1)–Os(1)–E(1)					85.39(5) [81.19(4)]	83.10(5)
Cl(1)–Os(1)–E(2)					79.79(4) [83.06(4)]	80.56(4)
E(1)–Os(1)–E(2)					91.54(4) [87.71(4)]	85.73(2)
Os(1)–E(1)–P(1)					110.56(6) [108.03(6)]	101.16(5)
Os(1)–E(2)–P(2)					105.43(6) [103.25(6)]	100.99(5)
E(1)–P(1)–N(1)					117.98(16) [118.54(15)]	117.7(2)
E(2)–P(2)–N(1)					117.27(15) [116.43(15)]	116.5(2)
P(1)–N(1)–P(2)	124.71(14)	132.0(4) [127.1(4)]	120.0(3) [119.8(3)]	114.1(3)	126.5(3) [127.7(3)]	131.6(3)

[a] Two molecules in the asymmetric unit.

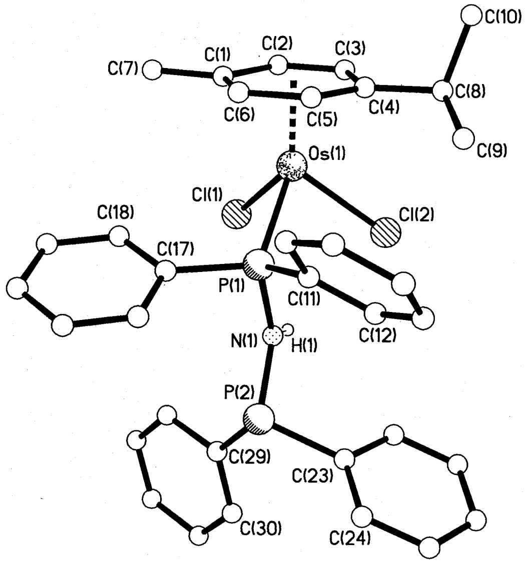


Fig. 1. The molecular structure of **1a** (all C–H atoms omitted for clarity, $CHCl_3$ solvent molecule not shown).

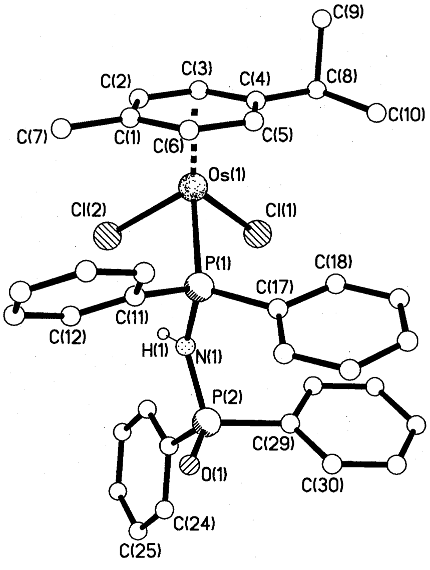


Fig. 2. The molecular structure of **2** (all C–H atoms omitted for clarity; two similar molecules in the asymmetric unit).

The X-ray structure of **4** (Fig. 4, Table 3) reveals the osmium(II) centre is bound by a chelating, anionic $[Ph_2PNP(O)Ph_2]^-$, a chloride and an η^6-cymene ligand.

The Os–P–N–P–O ring conformation in **4** is planar to within 0.028 Å with N lying 0.219 Å out of this plane. The OsP_2O versus P_2N hinge angle is 14.9° and the ring

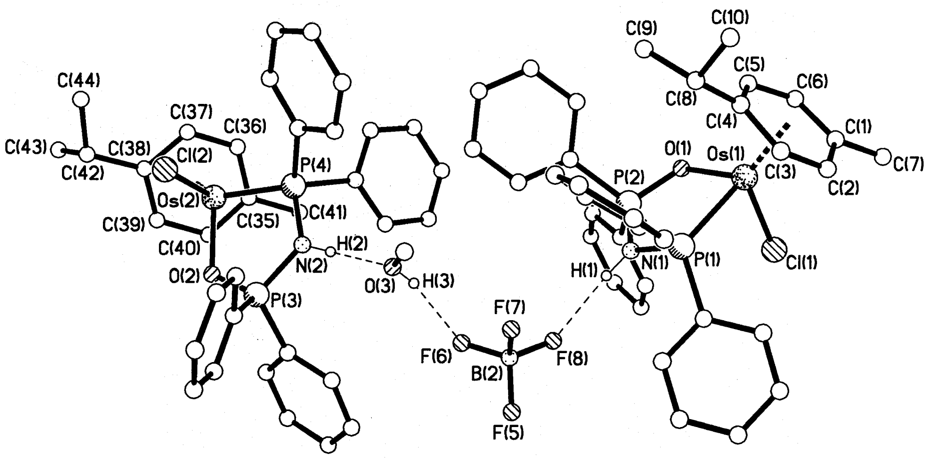


Fig. 3. The structure of **3** (all C–H atoms and the non H-bonded BF_4^- anion omitted for clarity).

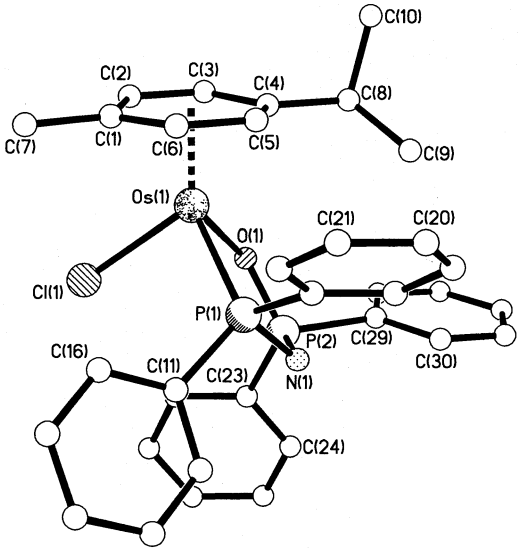


Fig. 4. The molecular structure of **4** (all C–H atoms omitted for clarity).

adopts an envelope conformation. The C(7) group is 0.072 Å out of the p-cymene C_6 mean plane towards Os and C(8) is 0.050 Å in the same direction. There are no significant inter/intramolecular interactions.

A brief comparison of the OsP_2NO metallacycles is especially noteworthy. In **3**, the P–N, N–P and P–O distances are 1.715(4), 1.648(5) and 1.519(4) Å for molecule I [1.697(7), 1.648(5) and 1.508(4) Å for molecule II], respectively and similar to those in the free ligand $Ph_2PNHP(O)Ph_2$ [8]. Within the P–N–P–O backbone of $[Ph_2PNP(O)Ph_2]^-$ in **4** there is a significant shortening of the P–N bonds [1.637(6) and 1.586(5) Å] and a small lengthening of the P–O bond [1.524(5) Å] as a consequence of deprotonation. Compounds **3** and **4** represent rare examples of crystallographically characterised osmium(II) arene complexes containing O/P/Cl donor atoms [31–33].

Both $\{Ph_2P(S)\}_2N^-$ and $\{Ph_2P(Se)\}_2N^-$ act as chelating ligands through their respective chalcogens. The Os–S [2.4321(14) and 2.4398(12) Å for molecule I; 2.4463(13) and 2.4407(12) Å for molecule II] and Os–Se [2.5345(7) and 2.5582(6) Å] distances in **5** and **6** are comparable to those recently described by Leung et al. for a series of six-coordinate Os(VI) complexes [23,24]. For **5** and **6** (Figs. 5 and 6, Table 3) the conformation of the Os–E–P–N–P–E rings are best described as "boat-like". The P_2S_2 portion is non-planar and the S–P–P–S torsion angle is 25° (molecule I) and 18° (molecule II). In **6**, the Se_2P_2 fragment is planar to within 0.017 Å with N lying 0.356 Å out of this plane. The $OsSe_2$ versus Se_2P_2 hinge angle is 67.6° and Se_2P_2 versus P_2N is 33°. Within the metallacyles the E–P/N–P distances are longer/shorter than in free $HN\{P(E)Ph_2\}_2$ (E = S or Se) and

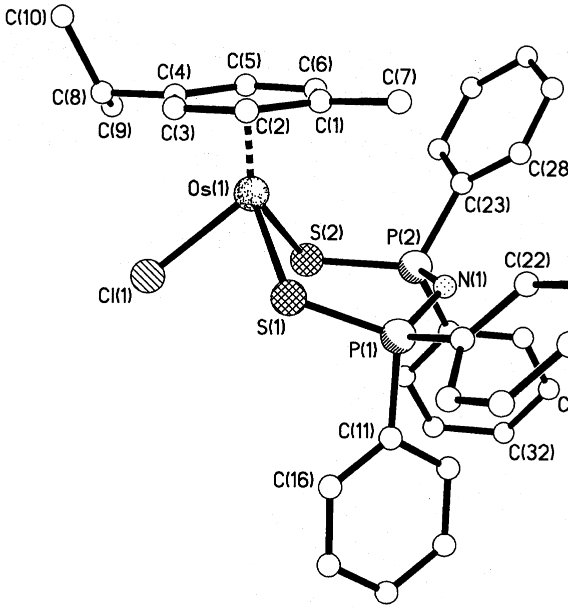


Fig. 5. The molecular structure of **5** (all C–H atoms omitted for clarity; two similar molecules in the asymmetric unit).

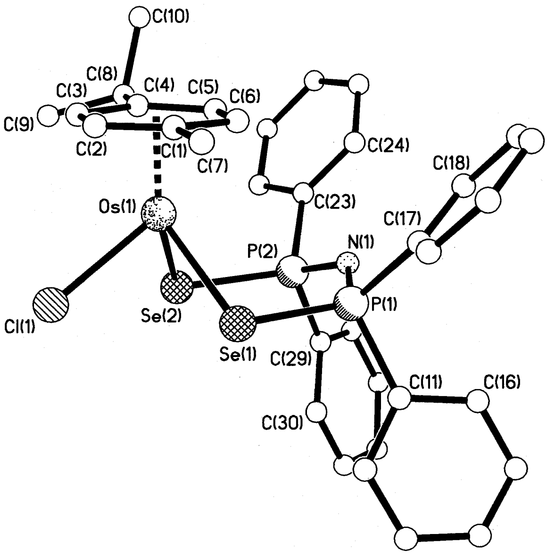


Fig. 6. The molecular structure of **6** (all C–H atoms omitted for clarity, $CHCl_3$ solvent molecule not shown).

indicative of appreciable charge delocalisation within the osmacycle formed. In **5**, C(7) is bent 0.050 Å from the *p*-cymene mean plane (away from Os) and C(8) is planar to within 0.008 Å (for molecule I); C(41) is 0.011 Å towards Os with C(42) bent 0.100 Å away from Os (for molecule II).

4. Conclusions

The facile syntheses of a range of new osmium(II) complexes containing P–N–P derived ligands have been demonstrated for the first time. These ligand systems afford complexes which are air stable and readily characterised by multinuclear NMR and X-ray techniques. Furthermore metallacycles **5** and **6** represent the first crystallographically characterised examples of osmium(II) arene complexes bearing either Cl/S/S or Cl/Se/Se donor sets.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 190893–98 (compounds **1a**–**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank Loughborough University for support and the EPSRC National Mass Spectrometry Service Centre at Swansea.

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