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**TRINUCLEAR OSMIUM CLUSTERS CONTAINING AMINOPHOSPHINE  
AND PHOSPHINOAMIDO LIGANDS, SYNTHESIS  
AND MOLECULAR STRUCTURE OF  $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{NHPh})$   
AND  $\text{HOs}_3(\text{CO})_8(\text{PPh}_2\text{NHPh})(\text{PPh}_2\text{NPh})$**

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### Summary

The pyrolysis of the heterocycle  $\text{B}_2\text{H}_4\text{N}_4\text{P}_2\text{Ph}_8$  in the presence of  $\text{Os}_3(\text{CO})_{12}$  yields the osmium clusters  $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{NHPh})$  (**1**),  $\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{NHPh})_2$  (**2**) and  $\text{HOs}_3(\text{CO})_8(\text{PPh}_2\text{NHPh})(\text{PPh}_2\text{NPh})$  (**3**) which contain aminophosphine and phosphinoamido fragments as ligands. The molecular structures of **1** and **3** have been determined by single-crystal X-ray diffraction studies. Crystals of **1** are monoclinic, space group  $P2_1/c$  with  $Z = 4$  in a unit cell of dimensions  $a$  21.881(12),  $b$  8.887(6),  $c$  16.348(9) Å,  $\beta$  98.91(2)°. Crystals of **3** are rhombohedral, space group  $R\bar{3}$  with  $Z = 6$  in a unit cell of dimensions  $a$  21.143(9) Å,  $\alpha$  106.89(3)°. Both structures were solved by direct and Fourier methods and refined by full-matrix least-squares to  $R = 0.0456$  for 2288 observed reflections in **1** and to  $R = 0.0490$  for 4063 observed reflections in **3**. The structure of **1** can be regarded as derived from that of  $\text{Os}_3(\text{CO})_{12}$  by replacing one carbonyl by an aminophosphine ligand (bound through the P atom). In the structure of **3**, one hydride bridges one Os–Os edge of the triangular metal cluster and a phosphinoamido ligand interacts with all three Os atoms (with two through the N atom and with the third through the P atom); a terminal aminophosphine ligand is also present, as in **1**.

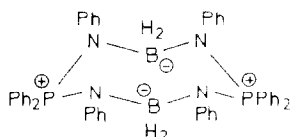
### Introduction

The trinuclear osmium cluster-framework has proved to be a very stable and versatile system for the coordination of reactive molecular fragments [1,2]. The commonest feature in the reactions of  $\text{Os}_3$  clusters with organic molecules is the

metal-promoted cleavage of covalent bonds followed by the incorporation of the fragments into the  $\text{Os}_3$  cluster [3]. In this paper we report the thermal fragmentation of a  $\text{B}_2\text{N}_4\text{P}_2$  octacycle in the presence of  $\text{Os}_3(\text{CO})_{12}$  to give PN fragments that are bound to the  $\text{Os}_3$  framework.

### Results and discussion

1,5-Bis(diphenylphospha)-2,4,6,8-tetrakis(phenylaza)-3,7-bis(dihydrobora)-cyclo-octane, accessible from the reaction of  $\text{PhN}=\text{PPh}_2\text{NHPH}$  and  $\text{Me}_2\text{SBH}_3$  [4], provides electron pairs at the four nitrogen atoms for the coordination to transition-metal systems, and it should be possible to replace several carbonyl groups in dodecacarbonyl-triosmium by this ligand.



However, in the presence of  $\text{Os}_3(\text{CO})_{12}$  the heterocycle disintegrates at elevated temperatures, and only complexes containing PN fragments are isolated, namely the trinuclear clusters  $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{NHPH})$  (**1**),  $\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{NHPH})_2$  (**2**) and  $\text{HOs}_3(\text{CO})_8(\text{PPh}_2\text{NHPH})(\text{PPh}_2\text{NPh})$  (**3**). The three compounds are obtained as air-stable, crystalline solids.

In the mass spectra, the three compounds are characterised by their molecular ions and the complete series of fragment ions arising from the stepwise loss of CO

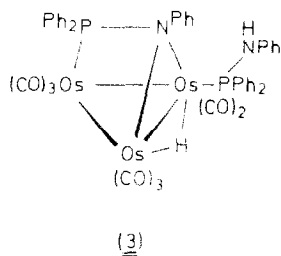
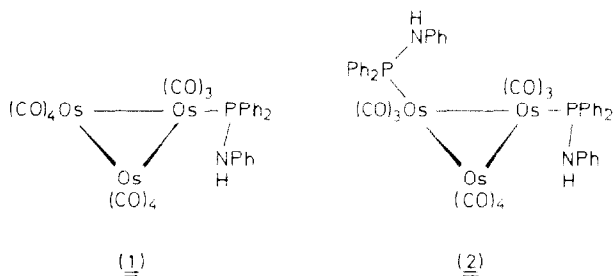


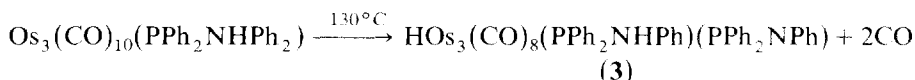
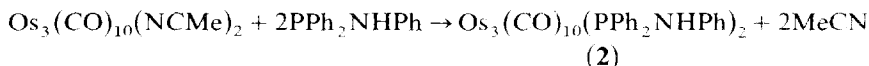
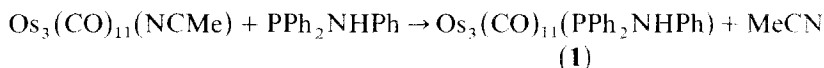
TABLE 1  
SPECTROSCOPIC CHARACTERISATION OF THE CLUSTERS 1-3

	Os <sub>3</sub> (CO) <sub>11</sub> (PPh <sub>2</sub> NHPh) (1)	Os <sub>3</sub> (CO) <sub>10</sub> (PPh <sub>2</sub> NHPh) <sub>2</sub> (2)	HOs <sub>3</sub> (CO) <sub>8</sub> (PPh <sub>2</sub> NHPh)(PPh <sub>2</sub> NPh) (3)
IR (cm <sup>-1</sup> )	$\nu(\text{CO})^a$ 2108w, 2052s, 2038s 2021vs, 1996w, 1984m $\nu(\text{NH})^c$ 3418	$\nu(\text{CO})^b$ 2087w, 2030s, 2006sh, 1996vs, 1958m, 1948sh $\nu(\text{NH})^c$ 3400	$\nu(\text{CO})^b$ 2074s, 2030vs, 1993vs, 1967sh, 1957m, 1935w $\nu(\text{NH})^c$ 3380
<sup>1</sup> H NMR <sup>d</sup> (ppm)	$\delta(\text{C}_6\text{H}_5)$ 6.40-7.80 (m,15) $\delta(\text{NH})$ 4.88 (d,1) J(P,H) 14 Hz	$\delta(\text{C}_6\text{H}_5)$ 6.29-8.00 (m,30) $\delta(\text{NH})$ 4.95 (d,2) J(P,H) 17Hz	$\delta(\text{C}_6\text{H}_5)$ 5.84-7.70 (m,30) $\delta(\text{NH})$ 3.18 (d,1) J(P,H) 19Hz $\delta(\text{Os}_2\text{H})$ -13.50 (t,1) J(P,H) 12Hz
<sup>31</sup> P NMR <sup>d</sup> (ppm)	$\delta$ 20.1	$\delta$ 18.8 (br)	$\delta$ 14.2 (d) J(P,P) 22Hz $\delta$ 25.4 (d) J(P,P) 22Hz
MS <sup>e</sup>	$m/e$ 1161 (molecular ion)	$m/e$ 1410 (molecular ion)	$m/e$ 1354 (molecular ion)

<sup>a</sup> In cyclohexane. <sup>b</sup> In dichloromethane. <sup>c</sup> KBr pellet. <sup>d</sup> In CDCl<sub>3</sub>. <sup>e</sup> Related to <sup>192</sup>Os.

ligands; all the ions display the characteristic isotope pattern of the Os<sub>3</sub> unit. The IR and NMR data, given in Table 1, are in accordance with the molecular structures of **1** and **3**. The structure of **2** is based on the spectroscopic characterisation: The <sup>1</sup>H NMR spectrum shows in addition to the aromatic multiplet only one NH doublet signal indicating the equivalence of the two NH protons. Accordingly, the infrared spectrum exhibits only a single ν(NH) absorption; the typical ν(CO) absorption pattern is consistent with that of Os<sub>3</sub>(CO)<sub>10</sub>(PEt<sub>3</sub>)<sub>2</sub> [5]. In the <sup>31</sup>P NMR spectrum only one broad resonance is observed for the two phosphorus atoms at room temperature, as observed for Os<sub>3</sub>(CO)<sub>10</sub>(PEt<sub>3</sub>)<sub>2</sub> [5]. For **3**, the localisation of the hydride ligand as a bridge between the two nitrogen-bridged osmium atoms is consistent with the <sup>1</sup>H NMR spectrum, in which the resonance at -13.50 ppm falls within the typical region for bridging hydride ligands; the multiplicity of this signal, a doublet of doublets with the inner peaks overlapping to give a triplet-like pattern, is caused by the <sup>31</sup>P-<sup>1</sup>H coupling with the two phosphorus atoms. The fact that the two <sup>31</sup>P-<sup>1</sup>H coupling constants are identical (12 Hz) is due to coincidence, since the non-equivalence of the two phosphorus nuclei is revealed by two individual resonances in the <sup>31</sup>P NMR spectrum.

In an attempt to develop a straightforward synthesis for the three clusters, we obtained **1** and **2** in high yields from the reaction of PPh<sub>2</sub>NHPh with Os<sub>3</sub>(CO)<sub>11</sub>(NCMe) and Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>, respectively; complex **3** was obtained upon heating of **2** under the conditions of the B<sub>2</sub>H<sub>4</sub>N<sub>4</sub>P<sub>2</sub>Ph<sub>8</sub>/Os<sub>3</sub>(CO)<sub>12</sub> pyrolysis. Apparently, **2** is the precursor of **3**, which is formed by loss of CO groups, cleavage of the N-H bond in the aminophosphine ligand, and transfer of the hydride to the metal framework.



The three clusters obey the 18-electron rule. Compound **1** is an analogue of Os<sub>3</sub>(CO)<sub>11</sub>(P<sup>t</sup>Bu<sub>2</sub>NH<sub>2</sub>), which we isolated from the pyrolysis of S(NP<sup>t</sup>Bu<sub>2</sub>) with Os<sub>3</sub>(CO)<sub>12</sub> [6]; the Os<sub>3</sub>NP framework in **3** is related to the Os<sub>3</sub>CP framework in H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>(PEt<sub>2</sub>CMe), accessible from Os<sub>3</sub>(CO)<sub>12</sub> and PEt<sub>3</sub> [7].

*Crystal structures of Os<sub>3</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>NHPh) (**1**) and HOs<sub>3</sub>(CO)<sub>8</sub>(PPh<sub>2</sub>NHPh)(PPh<sub>2</sub>NPh) (**3**)*

The molecular structure of **1** is depicted in Fig. 1 and selected bond distances and angles are given in Table 2.

The structure of **1** can be regarded as derived from that of Os<sub>3</sub>(CO)<sub>12</sub> [8] by replacing one carbonyl group by the PPh<sub>2</sub>NHPh ligand which is bound to the Os(1) atom through the P atom (Os-P bond 2.301(6) Å). This substitution leaves the structure of the Os<sub>3</sub>(CO)<sub>11</sub> portion virtually unaltered, except that some carbonyls (both equatorial and axial) undergo slight displacement because of the steric hindrance of the bulky aminophosphine ligand. The metal triangle is almost

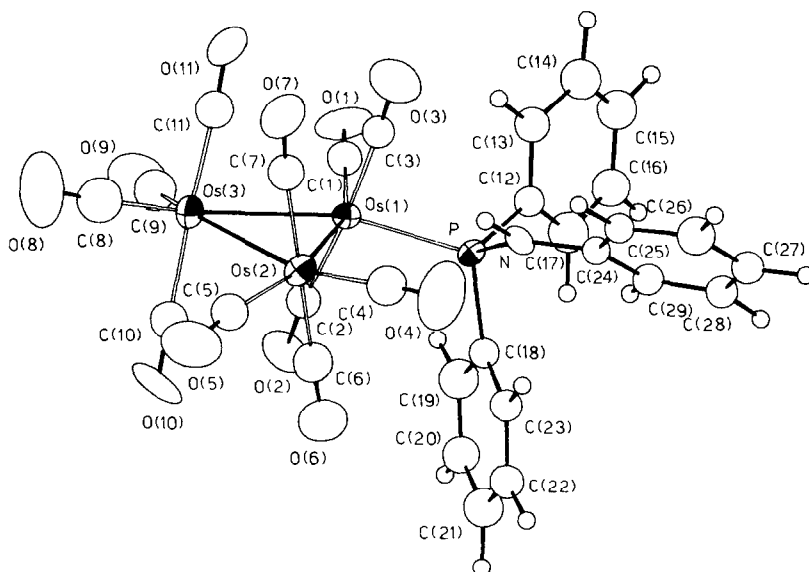


Fig. 1. View of the  $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{NHP})$  molecule with the atomic numbering system (ORTEP diagram, 50% probability ellipsoids).

equilateral, the Os–Os distances being 2.855(3), 2.865(2), 2.879(2) Å. These distances agree well with those reported for  $\text{Os}_3(\text{CO})_{12}$  (average value 2.877(3) Å).

The structure of **1** is similar to that of  $\text{Os}_3(\text{CO})_{11}(\text{P}^i\text{Bu}_2\text{NH}_2)$  [6] where, however, the metal–metal bonds are non-equal (2.881(1), 2.900(1), 2.953(1) Å and 2.889(1), 2.892(1), 2.925(1) Å in the two independent molecules) and the Os–P bond (2.376(4) and 2.399(4) Å in the independent molecules) is much longer than in **1**. In the aminophosphine ligand the P–N and N–C(24) bonds have lengths of 1.72(2) and 1.39(3) Å, and the P–N–C(24) group is almost coplanar with the C(24)–C(29) phenyl ring (the dihedral angle between them is 173.4°) so that  $\pi$  electron delocalization can be postulated in all the systems, with the participation of the lone pair of the amine nitrogen.

The molecular structure of **3** is presented in Fig. 2; selected bond distances and angles are given in Table 3.

The structure of **3** can be regarded as derived from that of **1** by replacement of three carbonyls by the  $\text{PPh}_2\text{NPh}$  and hydride ligands. The metal triangle remains equilateral even through the Os–Os edges (2.798(3), 2.798(3) and 2.801(3) Å) are much shorter than those in **1**. The Os(1)–Os(2) edge is doubly bridged by the hydride, H(1), and by the nitrogen atom, N(2), belonging to the phosphinoamide ligand which interacts with all three osmium atoms and is also bound to the Os(3) atom through the P(2) atom (Os(3)–P(2) 2.326(9) Å). The bridging H(1) and N(2) atoms are on opposite sides of the metal triangle, displaced from it by 0.79 and –1.73 Å, respectively. Both bridges are symmetrical (Os(1)–H(1) 1.76, Os(2)–H(1) 1.80 Å; Os(1)–N(2) 2.24(2), Os(2)–N(2) 2.22(1) Å); the Os(1)–H(1)–Os(2) and the Os(1)–N(2)–Os(2) planes form dihedral angles of 134.3 and 94.2°, respectively, with the metal triangle.

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN THE COMPLEX **1** (with e.s.d.'s in parentheses)

Os(1)–Os(2)	2.879(2)	P–N	1.72(2)
Os(1)–Os(3)	2.855(3)	P–C(12)	1.83(2)
Os(2)–Os(3)	2.865(2)	P–C(18)	1.83(2)
Os(1)–P	2.301(6)	N–C(24)	1.39(3)
Os(1)–C(1)	1.88(3)	C(1)–O(1)	1.14(3)
Os(1)–C(2)	1.91(3)	C(2)–O(2)	1.16(3)
Os(1)–C(3)	1.93(3)	C(3)–O(3)	1.12(3)
Os(2)–C(4)	1.88(3)	C(4)–O(4)	1.13(4)
Os(2)–C(5)	1.84(3)	C(5)–O(5)	1.13(3)
Os(2)–C(6)	1.90(3)	C(6)–O(6)	1.13(4)
Os(2)–C(7)	1.90(3)	C(7)–O(7)	1.18(3)
Os(3)–C(8)	1.87(3)	C(8)–O(8)	1.16(4)
Os(3)–C(9)	1.86(3)	C(9)–O(9)	1.18(4)
Os(3)–C(10)	1.94(3)	C(10)–O(10)	1.14(3)
Os(3)–C(11)	1.89(3)	C(11)–O(11)	1.14(4)
Os(2)–Os(1)–Os(3)	60.0(1)	C(8)–Os(3)–Os(2)	105.5(10)
Os(1)–Os(2)–Os(3)	59.6(1)	C(8)–Os(3)–C(9)	100.9(13)
Os(1)–Os(3)–Os(2)	60.4(1)	C(8)–Os(3)–C(10)	89.6(13)
P–Os(1)–Os(2)	104.0(2)	C(8)–Os(3)–C(11)	90.4(13)
P–Os(1)–Os(3)	161.6(2)	C(9)–Os(3)–Os(1)	94.7(9)
P–Os(1)–C(1)	96.5(8)	C(9)–Os(3)–Os(2)	152.8(9)
P–Os(1)–C(2)	97.1(8)	C(9)–Os(3)–C(10)	93.8(12)
P–Os(1)–C(3)	88.8(7)	C(9)–Os(3)–C(11)	91.3(12)
C(1)–Os(1)–Os(2)	158.4(8)	C(10)–Os(3)–Os(1)	97.8(8)
C(1)–Os(1)–Os(3)	100.8(8)	C(10)–Os(3)–Os(2)	80.0(8)
C(1)–Os(1)–C(2)	90.6(11)	C(10)–Os(3)–C(11)	174.8(11)
C(1)–Os(1)–C(3)	93.4(10)	C(11)–Os(3)–Os(1)	80.8(8)
C(2)–Os(1)–Os(2)	93.7(7)	C(11)–Os(3)–Os(2)	94.9(8)
C(2)–Os(1)–Os(3)	76.3(8)	Os(1)–P–C(12)	116.2(8)
C(2)–Os(1)–C(3)	172.5(10)	Os(1)–P–C(18)	113.8(7)
C(3)–Os(1)–Os(2)	80.3(7)	Os(1)–P–N	112.0(7)
C(3)–Os(1)–Os(3)	96.7(7)	C(12)–P–C(18)	104.3(10)
C(4)–Os(2)–Os(1)	108.6(9)	C(12)–P–N	103.3(10)
C(4)–Os(2)–Os(3)	164.6(9)	C(18)–P–N	106.2(10)
C(4)–Os(2)–C(5)	97.9(12)	P–N–C(24)	128.7(15)
C(4)–Os(2)–C(6)	93.6(12)	Os(1)–C(1)–O(1)	179(2)
C(4)–Os(2)–C(7)	90.8(12)	Os(1)–C(2)–O(2)	172(2)
C(5)–Os(2)–Os(1)	152.4(8)	Os(1)–C(3)–O(3)	177(2)
C(5)–Os(2)–Os(3)	95.5(8)	Os(2)–C(4)–O(4)	176(3)
C(5)–Os(2)–C(6)	93.0(12)	Os(2)–C(5)–O(5)	173(2)
C(5)–Os(2)–C(7)	91.5(12)	Os(2)–C(6)–O(6)	172(2)
C(6)–Os(2)–Os(1)	78.2(9)	Os(2)–C(7)–O(7)	171(2)
C(6)–Os(2)–Os(3)	93.4(8)	Os(3)–C(8)–O(8)	175(3)
C(6)–Os(2)–C(7)	173.2(11)	Os(3)–C(9)–O(9)	174(3)
C(7)–Os(2)–Os(1)	95.5(8)	Os(3)–C(10)–O(10)	179(2)
C(7)–Os(2)–Os(3)	81.2(8)	Os(3)–C(11)–O(11)	177(2)
C(8)–Os(3)–Os(1)	162.3(10)		

The aminophosphine ligand is bound to the Os(1) atom through the P(1) atom as in **1**, but the Os(1)–P(1) distance (2.371(10) Å) is longer than the one found in **1**. The P(1)–N(1) and N(1)–C(21) bond distances are 1.68(3) and 1.39(3) Å, respectively.

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN THE COMPLEX 3 (with e.s.d.'s in parentheses)

Os(1)–Os(2)	2.798(3)	P(1)–C(9)	1.78(2)
Os(1)–Os(3)	2.798(3)	P(1)–C(15)	1.81(3)
Os(2)–Os(3)	2.801(3)	N(1)–C(21)	1.39(4)
Os(1)–P(1)	2.371(10)	P(2)–N(2)	1.73(2)
Os(1)–N(2)	2.24(2)	P(2)–C(27)	1.84(3)
Os(1)–C(1)	1.93(2)	P(2)–C(33)	1.84(2)
Os(1)–C(2)	1.85(4)	N(2)–C(39)	1.43(4)
Os(2)–N(2)	2.22(1)	C(1)–O(1)	1.10(3)
Os(2)–C(3)	1.94(3)	C(2)–O(2)	1.13(5)
Os(2)–C(4)	1.87(3)	C(3)–O(3)	1.10(4)
Os(2)–C(5)	1.96(3)	C(4)–O(4)	1.14(4)
Os(3)–P(2)	2.326(9)	C(5)–O(5)	1.09(3)
Os(3)–C(6)	1.87(4)	C(6)–O(6)	1.12(5)
Os(3)–C(7)	1.87(3)	C(7)–O(7)	1.18(4)
O(3)–C(8)	1.97(4)	C(8)–O(8)	1.11(5)
P(1)–N(1)	1.68(3)		
Os(2)–Os(1)–Os(3)	60.1(1)	C(6)–Os(3)–Os(1)	159.4(11)
Os(1)–Os(2)–Os(3)	60.0(1)	C(6)–Os(3)–Os(2)	100.6(11)
Os(1)–Os(3)–Os(2)	60.0(1)	C(6)–Os(3)–C(7)	99.5(16)
P(1)–Os(1)–Os(2)	106.6(2)	C(6)–Os(3)–C(8)	93.5(16)
P(1)–Os(1)–Os(3)	166.5(2)	C(7)–Os(3)–Os(1)	99.3(12)
P(1)–Os(1)–N(2)	98.6(5)	C(7)–Os(3)–Os(2)	159.1(12)
P(1)–Os(1)–C(1)	97.4(10)	C(7)–Os(3)–C(8)	91.7(16)
P(1)–Os(1)–C(2)	91.5(10)	C(8)–Os(3)–Os(1)	94.1(12)
N(2)–Os(1)–Os(2)	50.8(4)	C(8)–Os(3)–Os(2)	92.8(12)
N(2)–Os(1)–Os(3)	74.6(5)	N(1)–P(1)–Os(1)	113.5(8)
N(2)–Os(1)–C(1)	104.0(12)	N(1)–P(1)–C(9)	106.9(13)
N(2)–Os(1)–C(2)	163.4(10)	N(1)–P(1)–C(15)	104.2(13)
C(1)–Os(1)–Os(2)	146.9(11)	C(9)–P(1)–Os(1)	114.8(10)
C(1)–Os(1)–Os(3)	95.6(11)	C(9)–P(1)–C(15)	104.4(13)
C(1)–Os(1)–C(2)	87.7(13)	C(15)–P(1)–Os(1)	112.1(10)
C(2)–Os(1)–Os(2)	113.6(9)	P(1)–N(1)–C(21)	130.5(19)
C(2)–Os(1)–Os(3)	92.8(10)	P(2)–N(2)–Os(1)	98.1(9)
N(2)–Os(2)–Os(1)	51.5(5)	P(2)–N(2)–Os(2)	97.4(9)
N(2)–Os(2)–Os(3)	74.8(5)	P(2)–N(2)–C(39)	123.0(19)
N(2)–Os(2)–C(3)	98.8(1)	C(39)–N(2)–Os(1)	121.9(16)
N(2)–Os(2)–C(4)	102.4(12)	C(39)–N(2)–Os(2)	127.5(16)
N(2)–Os(2)–C(5)	162.4(9)	Os(1)–N(2)–Os(2)	77.7(6)
C(3)–Os(2)–Os(1)	110.4(10)	N(2)–P(2)–Os(3)	97.8(8)
C(3)–Os(2)–Os(3)	170.3(9)	N(2)–P(2)–C(27)	110.5(11)
C(3)–Os(2)–C(4)	97.2(13)	N(2)–P(2)–C(33)	108.5(13)
C(3)–Os(2)–C(5)	93.2(13)	C(27)–P(2)–Os(3)	117.6(9)
C(4)–Os(2)–Os(1)	143.7(10)	C(27)–P(2)–C(33)	96.9(14)
C(4)–Os(2)–Os(3)	91.4(11)	C(33)–P(2)–Os(3)	125.4(10)
C(4)–Os(2)–C(5)	88.7(13)	Os(1)–C(1)–O(1)	171(3)
C(5)–Os(2)–Os(1)	112.1(8)	Os(1)–C(2)–O(2)	177(3)
C(5)–Os(2)–Os(3)	91.5(9)	Os(2)–C(3)–O(3)	173(3)
P(2)–Os(3)–Os(1)	71.5(2)	Os(2)–C(4)–O(4)	172(3)
P(2)–Os(3)–Os(2)	70.5(2)	Os(2)–C(5)–O(5)	178(3)
P(2)–Os(3)–C(6)	96.7(11)	Os(3)–C(6)–O(6)	178(3)
P(2)–Os(3)–C(7)	101.5(12)	Os(3)–C(7)–O(7)	176(3)
P(2)–Os(3)–C(8)	161.8(12)	Os(3)–C(8)–O(8)	176(4)

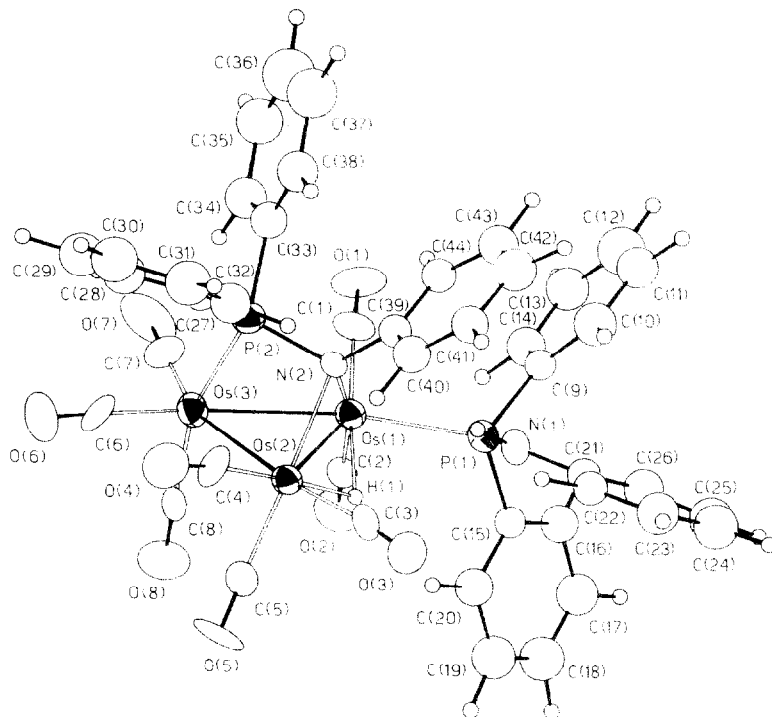


Fig. 2. View of the  $\text{HOs}_3(\text{CO})_8(\text{PPh}_2\text{NHP})(\text{PPh}_2\text{NPh})$  molecule with the atomic numbering system (ORTEP diagram, 40% probability ellipsoids)

and as in **1** the P(1)–N(1)–C(21) group is almost coplanar with the C(21)–C(26) phenyl ring (the dihedral angle being  $170.5^\circ$ ).

The structure of **3** can be compared with that of  $\text{HOs}_3(\text{CO})_9(\text{P}^t\text{Bu}_2\text{NHS})$  [6], in which the  $\text{P}^t\text{Bu}_2\text{NHS}$  interacts with the metals through the P atom to one Os atom and through the S atom to the other two. In this case the hydride does not bridge the same edge as the S atom, and the Os–Os distances in the cluster are very different: 3.048(1) (hydride bridge), 2.753(1) (sulphur bridge), 2.895(1) Å (no bridge).

## Experimental

The reactions were carried out under dry nitrogen and with anhydrous and  $\text{N}_2$ -saturated solvents. For the preparative thin-layer chromatography plates with Merck Kieselgel 60 GF 254 were employed. Spectra were recorded with the following instruments: IR: Perkin–Elmer 297 (solutions) and Beckman 4240 (KBr).  $^1\text{H}$  and  $^{31}\text{P}$  NMR: JEOL FX 90Q. MS: Varian MAT CH7.

### *Pyrolysis of $\text{B}_2\text{H}_4\text{N}_4\text{P}_2\text{Ph}_8$ with $\text{Os}_3(\text{CO})_{12}$*

A solution of 190 mg (0.25 mmol)  $\text{B}_2\text{H}_4\text{N}_4\text{P}_2\text{Ph}_8$  [4] and 160 mg (0.25 mmol)  $\text{Os}_3(\text{CO})_{12}$  in 30 ml acetonitrile was placed into a pressure vessel and heated to  $130^\circ\text{C}$  for 15 h. The solvent was then evaporated and the residue dissolved in 3 ml



$\text{CH}_2\text{Cl}_2$  and separated by TLC (60% cyclohexane, 40% dichloromethane). The two yellow main bands were taken off and extracted with  $\text{CH}_2\text{Cl}_2$ . The extracts were again subjected to thin-layer chromatography: the first fraction (upper band) with a mixture of 95% cyclohexane and 5% dichloromethane as eluant, and the second fraction (lower band) with a mixture of 60% cyclohexane, 20% dichloromethane and 20% diethyl ether as eluant. In the first case the main band gave upon extraction with  $\text{CH}_2\text{Cl}_2$  pure **1**; in the latter case two yellow bands were separated, and after extraction with  $\text{CH}_2\text{Cl}_2$  these gave **2** and **3**. **1** was recrystallised from pentane (orange crystals, yield 40 mg, 14%), **2** from dichloromethane (yellow crystals, yield 40 mg, 11%), and **3** from a dichloromethane/pentane mixture (pale yellow crystals, yield 30 mg, 9%).

#### *Synthesis of 1 and 2 by ligand exchange reactions*

A solution of 0.25 mmol  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  [9] or  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  [9], and 300 mg (1.1 mmol)  $\text{PPh}_2\text{NHPH}$  [10] in 50 ml  $\text{CH}_2\text{Cl}_2$  was stirred at room temperature. After 15 h the solvent is evaporated and the residue dissolved in 5 ml  $\text{CH}_2\text{Cl}_2$  and subjected to TLC (60% cyclohexane, 40% dichloromethane). The main band was extracted with  $\text{CH}_2\text{Cl}_2$ , and the product recrystallised from pentane or dichloromethane, respectively. Yields: **1** 225 mg (78%) and **2** 235 mg (67%).

#### *Synthesis of 3 by pyrolysis of 2*

A solution of 175 mg (0.125 mmol) **2** in 30 ml acetonitrile was heated to 130°C in a pressure vessel. After 15 h the solvent was evaporated, and the residue dissolved in 5 ml  $\text{CH}_2\text{Cl}_2$  then separated by TLC (60% cyclohexane, 40% dichloromethane). The second band was taken off and the product extracted with  $\text{CH}_2\text{Cl}_2$ ; **3** crystallised out after concentration of the solution. Yield: 55 mg (32%).

#### *X-Ray data collections, structure solutions and refinements*

Crystal data and data collection parameters for the two compounds are given in Table 4. Unit cell parameters were obtained by least-squares refinement of the  $\theta$  values of 30 carefully centered reflections. The intensity of one standard reflection was measured after 50 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection for **3**, while a decline of about 34% was observed during the time required to collect the data of **1**. A correction for this decay was applied by scaling the intensities of the standard reflection appropriately. A correction for absorption effects was applied to the data of **1** and **3** [11] (maximum and minimum transmission factor values: 1.192 and 0.8137 for **1**, 1.1564 and 0.8334 for **3**).

Both structures were solved by direct and Fourier methods and refined by full-matrix least-squares using the SHELX system of programs [12] with initially isotropic and then anisotropic thermal parameters for the Os, P, O, N and carbon atoms of the carbonyl groups for **3** and for the Os, P, O and N atoms for **1**. The final Fourier difference map for **3** revealed the presence of solvent molecules (pentane), but disordered and distributed in several positions, so that neither the number nor the occupancy factors could be determined precisely. The hydrogen atoms (except for the hydridic one in **3** clearly localized in the  $\Delta F$  map) were placed at their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The atomic scattering factors, cor-

TABLE 4

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF THE COMPLEXES **1** AND **3**

	<b>1</b>	<b>3</b> <sup>a</sup>
Formula	C <sub>29</sub> H <sub>16</sub> NO <sub>11</sub> Os <sub>3</sub> P	C <sub>44</sub> H <sub>32</sub> N <sub>2</sub> O <sub>8</sub> Os <sub>3</sub> P <sub>2</sub>
Crystal system	monoclinic	rhombohedral
Space group	<i>P</i> 2 <sub>1</sub> / <i>C</i>	<i>R</i> $\bar{3}$
<i>a</i> (Å)	21.881(12)	21.143(9)
<i>b</i> (Å)	8.887(6)	
<i>c</i> (Å)	16.348(9)	
$\alpha$ (°)	90	106.89(3)
$\beta$ (°)	98.91(2)	
$\gamma$ (°)	90	
<i>V</i> (Å <sup>3</sup> )	3141(3)	7895(7)
<i>Z</i>	4	6
<i>F</i> (000)	2112	3792
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.445	1.703
Mol wt	1156.020	1349.293
Cryst.dimens (mm)	0.39 × 0.47 × 0.49	0.29 × 0.38 × 0.57
Linear absorption, (cm <sup>-1</sup> )	122.34	73.39
Diffractometer	Siemens AED	
Scan type	$\theta/2\theta$	
Scan speed	3–12°/min	
Scan width	[ $\theta - 0.55$ ] – [ $\theta + (0.55 + 0.346 \text{tg } \theta)$ ]°	
Radiation	Nb-filtered Mo- <i>K</i> <sub>α</sub> ( $\lambda$ 0.71073 Å)	
2 $\theta$ range (°)	5–44	6–48
Reflections measured	± <i>h, k, l</i>	± <i>h, k, l</i>
Std refln	1 measured after every 50 reflections	
Unique total data	4017	8155
Unique obsd data [ <i>I</i> ≥ 2σ( <i>I</i> )]	2288	4063
No. of variables	261	352
<i>R</i>	4.56	4.90
<i>R</i> <sub>w</sub>	4.95	5.72

<sup>a</sup> All data refer to the complex **3** without solvent molecules, as the number of them is not definite.

rected for anomalous dispersion, were taken from ref. 13. The function minimized in the least-squares calculations was  $\sum w |\Delta F|^2$ ; unit weights were chosen in all the stages of the refinement for **3** and in the first stages in **1**, then weights were applied according to the scheme  $w = K/[\sigma^2(F_0) + gF_0^2]$  with  $K = 0.6235$  and  $g = 0.00144$ .

Final atomic coordinates for the non hydrogen atoms of **1** and **3** are given in Tables 5 and 6, respectively. Calculated coordinates for the hydrogen atoms in **1** and **3**, coordinates for the pentane molecules in **3**, thermal parameters for the non-hydrogen atoms of **1** and **3**, and observed and calculated structure factors for both structures are available from the authors on request.

All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Parma.

TABLE 5

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) (with e.s.d.'s in parentheses) FOR THE NON-HYDROGEN ATOMS OF COMPLEX 1

Atom	x	y	z
Os(1)	2129(1)	2339(1)	2639(1)
Os(2)	1515(1)	-526(1)	2637(1)
Os(3)	1019(1)	1795(1)	1510(1)
P	3060(3)	1963(6)	3483(4)
O(1)	2282(9)	5691(19)	2427(13)
O(2)	2648(8)	1839(20)	1025(10)
O(3)	1509(9)	2760(23)	4170(12)
O(4)	2117(10)	-2218(26)	4145(15)
O(5)	767(10)	-3049(25)	1823(16)
O(6)	2562(9)	-1384(19)	1720(12)
O(7)	493(9)	420(23)	3622(11)
O(8)	-277(11)	846(32)	758(15)
O(9)	1194(11)	4575(26)	497(13)
O(10)	1573(10)	-287(21)	309(11)
O(11)	476(9)	3665(26)	2777(13)
N	2978(8)	908(20)	4342(10)
C(1)	2220(11)	4429(30)	2506(15)
C(2)	2415(11)	1973(27)	1609(16)
C(3)	1743(11)	2570(28)	3619(15)
C(4)	1873(13)	-1614(32)	3576(18)
C(5)	1019(12)	-2033(31)	2126(16)
C(6)	2169(13)	-971(31)	2038(17)
C(7)	872(12)	163(29)	3204(16)
C(8)	224(15)	1144(36)	1058(20)
C(9)	1093(13)	3509(35)	880(18)
C(10)	1366(12)	476(31)	756(17)
C(11)	687(12)	2935(30)	2316(16)
C(12)	3459(10)	3654(26)	3923(14)
C(13)	3116(11)	4517(28)	4393(15)
C(14)	3396(12)	5803(30)	4825(16)
C(15)	3962(12)	6247(21)	4716(16)
C(16)	4297(12)	5397(29)	4204(16)
C(17)	4036(12)	4071(31)	3842(16)
C(18)	3636(10)	989(25)	2974(13)
C(19)	3847(12)	1642(30)	2322(16)
C(20)	4227(11)	853(28)	1887(15)
C(21)	4366(12)	-693(31)	2070(16)
C(22)	4141(11)	-1334(28)	2716(15)
C(23)	3768(10)	-530(26)	3159(14)
C(24)	3422(10)	543(24)	5016(13)
C(25)	3198(10)	-219(25)	5656(13)
C(26)	3612(12)	-624(29)	6371(16)
C(27)	4232(10)	-365(26)	6431(14)
C(28)	4458(10)	410(26)	5753(14)
C(29)	4041(10)	868(25)	5090(13)

TABLE 6

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) (with e.s.d.'s in parentheses) FOR THE NON-HYDROGEN ATOMS OF COMPLEX 3

Atom	x	y	z
Os(1)	8472(1)	1513(1)	4104(1)
Os(2)	7821(1)	618(1)	2622(1)
Os(3)	8911(1)	420(1)	3566(1)
P(1)	7887(4)	2310(4)	4279(3)
P(2)	9434(4)	1388(4)	3305(4)
O(1)	9823(10)	2428(12)	5494(10)
O(2)	7884(13)	815(12)	4967(12)
O(3)	6649(12)	987(12)	1799(13)
O(4)	8068(12)	-162(13)	1346(12)
O(5)	6686(13)	-852(10)	2285(13)
O(6)	9117(14)	-704(12)	2503(14)
O(7)	10102(15)	711(12)	4977(14)
O(8)	7787(16)	-737(16)	3749(19)
N(1)	7536(11)	2457(11)	3540(11)
N(2)	8750(10)	1694(9)	3208(9)
C(1)	9364(16)	2108(15)	4960(16)
C(2)	8123(14)	1086(14)	4654(15)
C(3)	7102(16)	895(14)	2112(16)
C(4)	8008(15)	177(16)	1834(15)
C(5)	7098(15)	-333(15)	2400(13)
C(6)	9052(15)	-274(19)	2902(19)
C(7)	9658(16)	603(17)	4421(20)
C(8)	8208(17)	-312(16)	3707(22)
C(9)	8441(13)	3177(13)	5012(13)
C(10)	8572(18)	3819(18)	4894(18)
C(11)	9023(18)	4488(18)	5497(18)
C(12)	9358(21)	4493(21)	6174(22)
C(13)	9247(18)	3870(19)	6304(18)
C(14)	8781(16)	3204(16)	5695(17)
C(15)	7118(13)	1952(13)	4484(13)
C(16)	7082(15)	2302(15)	5152(15)
C(17)	6459(18)	1981(18)	5256(18)
C(18)	5939(19)	1514(20)	4778(20)
C(19)	5975(19)	970(19)	4125(19)
C(20)	6595(16)	1276(16)	3983(16)
C(21)	7041(14)	2757(14)	3377(14)
C(22)	6760(14)	2706(14)	2670(14)
C(23)	6283(18)	3018(18)	2459(18)
C(24)	6080(19)	3350(19)	2952(20)
C(25)	6293(19)	3376(19)	3613(20)
C(26)	6830(17)	3098(16)	3881(17)
C(27)	9607(13)	1183(13)	2482(13)
C(28)	10032(18)	784(18)	2455(18)
C(29)	10199(19)	590(19)	1845(19)
C(30)	9932(20)	786(20)	1265(20)
C(31)	9501(20)	1153(19)	1305(20)
C(32)	9324(17)	1332(17)	1915(17)
C(33)	10304(15)	2165(15)	3905(15)
C(34)	10702(18)	2157(18)	4566(18)
C(35)	11379(21)	2743(21)	5003(20)
C(36)	11624(25)	3241(25)	4784(25)
C(37)	11260(23)	3274(22)	4128(23)

TABLE 6 (continued)

Atom	x	y	z
C(38)	10568(17)	2672(17)	3684(17)
C(39)	8803(13)	2335(14)	3091(14)
C(40)	8415(16)	2294(16)	2419(16)
C(41)	8445(15)	2890(16)	2295(16)
C(42)	8872(19)	3565(19)	2895(19)
C(43)	9271(17)	3618(17)	3552(17)
C(44)	9241(14)	3005(15)	3691(14)

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