Synthesis and characterisation of phosphido-bridged hexaosmium "raft" clusters; crystal structure of $Os_6H_2(CO)_{18}(\mu_3\text{-PPh})$

Caroline M. Hay, John G. Jeffrey, Brian F.G. Johnson, Jack Lewis and Paul R. Raithby

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received May 16th, 1988)

Abstract

Treatment of the activated "raft" cluster $Os_6(CO)_{20}(NCMe)$ with PR^1R^2H ($R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = H$) at room temperature affords the phosphine-substituted cluster $Os_6(CO)_{20}(PR^1R^2H)$ ($R^1 = R^2 = Ph$ (1); $R^1 = Ph$, $R^2 = H$ (2)) in quantitative yield. Thermolysis of **1** in toluene gives a single orange-brown product characterised as $Os_6H(CO)_{16}(\mu\text{-PPh}_2)$ (3). This complex is also obtained from the thermolysis of $Os_6(CO)_{17}(PPh_2H)$, which has the bicapped tetrahedral metal framework. Thermolysis of **2** gives two products, characterised as $Os_6H_2(CO)_{18}(\mu_3\text{-PPh})$ (4) and the known complex $Os_5(CO)_{15}(\mu_4\text{-PPh})$ (5). The structure of **4** has been established by a single-crystal X-ray diffraction study. The metal framework consists of a central Os_3 triangle each side of which is bridged by another Os atom to give an arrangement of four triangles sharing three common edges. Three of these triangles are approximately coplanar, but the fourth, which is asymmetrically capped by the phosphorus atom of the $\mu_3\text{-PPh}$ group, is tilted by 72.4° from the Os_5 plane. Complex **4** crystallises in space group $P\bar{1}$ with a 9.733(2), b 10.555(1), c 17.585(2) Å, α 95.87(1), β 94.47(2), γ 105.60(1)°, $Z = 2$; 4591 observed data with $F > 4\sigma(F)$ were refined by blocked full-matrix least squares to $R = 0.080$, $R_w = 0.079$.

Introduction

The recent discovery of a high yield route to derivatives of the planar "raft" cluster, $Os_6(CO)_{21}$ [1] has led to increased interest in the chemistry of these species. The planarity of the metal framework in these clusters permits an analogy to be drawn between the structural chemistry of these molecules and that on the surfaces of metals in heterogeneous systems. Much of the research so far reported on the chemistry of the cluster carbonyl "rafts" has been aimed at exploiting this analogy.

Theoretical calculations [2] indicate that there is low-lying unfilled molecular orbital in these "raft" clusters, and this has been confirmed by their ease of the electro-chemical reduction to the dianion [1], by the formation of the capped oxygen cluster, $Os_6(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_{18}$ [3], and by the formation of the alkyne derivative $Os_6(CO)_{20}\{C\!=\!C(H)Ph\}$ via the reaction of $Os_6(CO)_{20}(NCMe)$ with a terminal alkyne [4]. An aromatic ring has also been shown to coordinate over a "raft" framework in a related ruthenium cluster complex [5]. In this paper we report the reactions of some phosphines with the activated cluster $Os_6(CO)_{20}(NCMe)$ to give substitution products. Subsequent thermolysis of these products gives complexes which contain doubly- or triply-bridging phosphorus donor ligands. Chemical evidence suggests that these clusters are stabilised by the presence of the bridging phosphorus ligands, as previously observed for other cluster systems [6].

Results and discussion

The mono-substituted derivatives $Os_6(CO)_{20}(PR^1R^2H)$ ($R^1 = R^2 = Ph$ (1); $R^1 =$ Ph, $R^2 = H$ (2)) are prepared by from the reaction of the appropriate primary or secondary phosphine with the activated cluster $Os_6(CO)_{20}(NCMe)$. The complexes were characterised by IR and ^1H NMR spectroscopy (Table 1). The solution IR spectra in the carbonyl region for the two complexes are essentially identical, showing signals only assignable to terminal ligands. The band pattern is similar to that observed for the equatorially mono-substituted tertiary phosphine and phos-phite complexes $Os_6(CO)_{20}(PR_3)$ (R = Ph, OMe) [1]. In the ^1H NMR spectra of 1 and 2 the resonances assigned to the phenyl groups is normal and the signals for the protons attached to the phosphorus atoms appear as doublets, with $^1J(P\text{–}H)$ ranging from 326 to 399 Hz. Because of the presence of the phosphine ligands molecular weights could not be established by mass spectrometry. However, the available data are consistent with the retention of the "raft" metal framework observed in $Os_6(CO)_{17}\{P(OMe)_3\}_4$ [7] in 1 and 2, and with the fact that the phosphine ligands occupy equatorial sites in both cases.

Thermolysis of $Os_6(CO)_{20}(PPh_2H)$ (1) in toluene for 12 h affords the bridged phosphine cluster, $Os_6H(CO)_{16}(PPh_2)$ (3), in 90% yield. In this case a molecular ion consistent with this formulation is observed in the mass spectrum, and additional peaks indicating the successive loss of sixteen carbonyls are also observed. The presence of a metal hydride, presumably formed by transfer from the phosphine ligand, is confirmed by the ^1H NMR spectrum (Table 1), which shows a broad signal in the bridging hydride region. A variable temperature study indicates that this hydride is fluxional, and at $-80°C$ the limiting spectrum is obtained; a doublet is obtained with $^2J(P\text{–}H)$ coupling of 6 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a resonance assignable to a μ_2-bridging PPh_2 group. The data are consistent with with a metal framework geometry for 3 based on the bicapped tetrahedral arrange-ment observed for $Os_6(CO)_{18}$ [8] and its phosphine derivatives $Os_6(CO)_{17}(PR_3)$ [9]. By way of conformation, 3 may also be prepared by thermolysis of $Os_6(CO)_{17}$-(PPh_2H), prepared by the reaction of PPh_2H with $Os_6(CO)_{17}(NCMe)$. The coordi-nation sites of the hydride and bridging PPh_2 ligand cannot be established from the spectroscopic data, but a possible structure based on that of the related cluster, $Os_6H(CO)_{16}(C_5H_4N)$ [10], is shown in Fig. 1, which also indicates possible sites for the fluxional hydride ligand.

Table 1

IR and NMR spectroscopic data

Compound	^{1}H NMR (δ, ppm)	^{31}P NMR (δ, ppm)	IR (ν(CO) cm^{-1})
$Os_6(CO)_{20}(PPh_2H)$ (1)	7.54, m, 10H (C_6H_5) 6.40, d, 399 Hz, 1H (PH)	–	2126s, 2091s, 2071m 2041s, 2022m, 2000w 1959w
$Os_6(CO)_{20}(PPhH_2)$ (2)	7.57, m, 5H (C_6H_5) 6.00, d, 326 Hz, 2H (PH_2)	–	2126w, 2092s, 2072m 2041s, 2022m, 2001w 1958w
$Os_6H(CO)_{16}(PPh_2)$ (3)	7.51, m, 10H (C_6H_5) −12.94, d, 6 Hz, 1H (OsHOs)	33.0, s, br	2096m, 2065w, 2050m 2032s, 2009m, 1993w 1952vw
$Os_6H_2(CO)_{18}(PPh)$ (4)	7.57, m, 5H (C_6H_5) −18.00, d, 10 Hz, 2H (OsHOs)	89.1, s, br	2120w, 2094vs, 2070m 2047s, 2038s, 2015s 2010s, 1950w
$Os_5(CO)_{15}(PPh)$ (5)	7.54, s, 5H (C_6H_5)	–	2100w, 2062vs, 2031s 1932w

By contrast, the thermolysis of $Os_6(CO)_{20}(PPhH_2)$ (2) in toluene for 7 h yields two products. The major purple product has been characterised as the hexaosmium cluster $Os_6H_2(CO)_{18}(\mu_3\text{-}PPh)$ (4) and the minor red product as the known pentaosmium cluster $Os_5(CO)_{15}(\mu_4\text{-}PPh)$ (5) [11]. The spectroscopic data for 5 are given in Table 1, and are consistent with the previous assignments [11]; the proposed structure with the PPh ligand capping the square face of the square-based pyramid is illustrated in Fig. 2. A related cluster, $Os_5(CO)_{15}\{P(OMe)_3\}$, has been characterised by crystallographic techniques [12].

The mass spectrum of $Os_6H_2(CO)_{18}(\mu_3\text{-}PPh)$ (4) displays a peak corresponding to the molecular ion, while the ^{1}H NMR spectrum for the complex shows the presence of two equivalent bridging hydrides which couple to the capping phosphorus atom, $^2J(P-H) = 10$ Hz. The hydrides are presumably formed by transfer from the phosphine ligand. In the ^{31}P NMR spectrum there is a low field signal consistent with the presence of the capping PPh group.

In order to establish the molecular structure of $Os_6H_2(CO)_{18}(\mu_3\text{-}PPh)$ (4) a single-crystal X-ray analysis was undertaken. The crystal consists of discrete hexaosmium cluster units separated by normal Van der Waals distances. The molecular structure is shown in Fig. 3 and lists of bond lengths and bond angles are presented in Tables 2 and 3, respectively. The metal arrangement in 4 consists of a central Os_3 triangle [Os(2)Os(3)Os(5)] each side of which is bridged by another Os atom, so that the whole framework may be described as four triangles sharing three

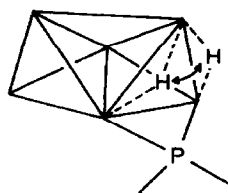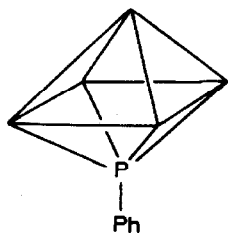Fig. 1. Possible structure for $Os_6H(CO)_{16}(\mu\text{-}PPh_2)$ (3) showing possible hydride positions.

Fig. 2. Proposed structure for $Os_5(CO)_{15}(\mu_4\text{-PPh})$ (5).

common edges. This arrangement is similar to that found in the structure of $Os_6(CO)_{17}\{P(OMe)_3\}_4$ [7], except that whereas the six Os atoms in the tetraphosphite are approximately coplanar, the triangle Os(3)Os(5)Os(6) in **4** is tilted by 72.4° with respect to the Os(1)Os(2)Os(3)Os(4)Os(5) plane. The Os(3)Os(5)Os(6) triangle is asymmetrically capped by a μ_3-PPh group, and it is noteworthy that the P(1) atom in this ligand is close to being coplanar with the Os(1)–Os(5) plane, lying 0.47 Å from it; the dihedral angle between the Os_5 and Os_2P planes 14.7°. The small dihedral angle of 6.7° between the Os(1)Os(2)Os(3) and Os(2)Os(3)Os(5) triangles, and of 7.0° between the Os(2)Os(3)Os(5) and Os(2)Os(4)Os(5) triangles, reflects the near planarity of the Os_5 unit.

The eighteen carbonyl ligands are terminally bound to the metals; four each to Os(1) and Os(4), three each to Os(2) and Os(6), and two each to Os(3) and Os(5). All are essentially linear. The two hydride ligands were not located directly in the
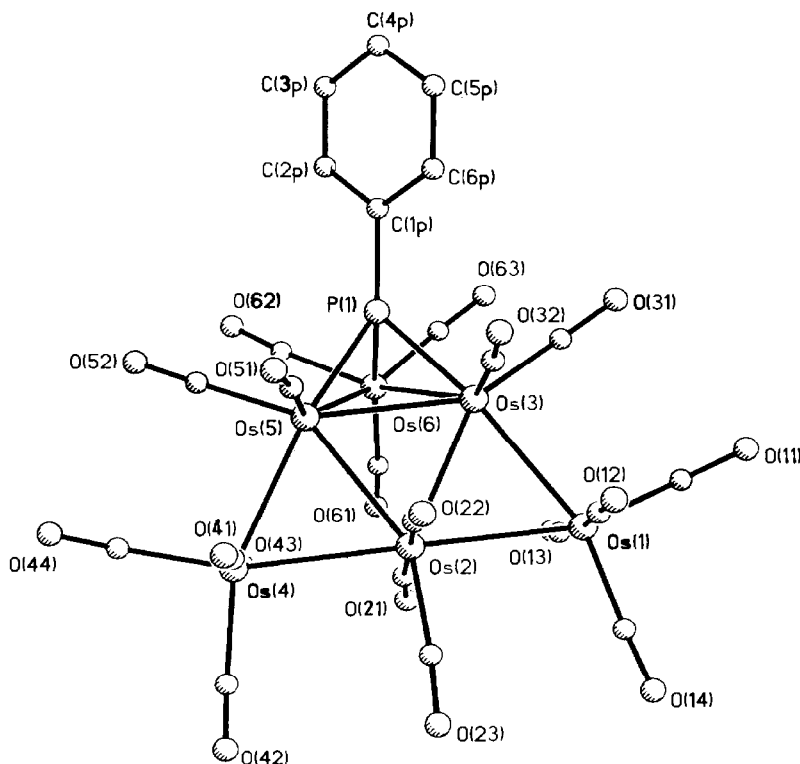

Fig. 3. The molecular structure of $Os_6(\mu\text{-H})_2(CO)_{18}(\mu_3\text{-PPh})$ (4) showing the atom numbering scheme.

Table 2

Bond lengths (Å)

Os(1)–Os(2)	2.877(2)	Os(1)–Os(3)	2.834(2)
Os(1)–C(11)	1.815(35)	Os(1)–C(12)	1.891(32)
Os(1)–C(13)	1.956(54)	Os(1)–C(14)	1.899(34)
Os(2)–Os(3)	2.800(1)	Os(2)–Os(4)	2.862(2)
Os(2)–Os(5)	2.823(2)	Os(2)–C(21)	1.950(36)
Os(2)–C(22)	1.965(35)	Os(2)–C(23)	1.905(33)
Os(3)–Os(5)	2.765(2)	Os(3)–Os(6)	3.060(2)
Os(3)–P(1)	2.287(8)	Os(3)–C(31)	1.925(33)
Os(3)–C(32)	1.836(33)	Os(4)–Os(5)	2.846(1)
Os(4)–C(41)	1.980(31)	Os(4)–C(42)	1.963(36)
Os(4)–C(43)	1.894(31)	Os(4)–C(44)	2.019(39)
Os(5)–Os(6)	3.036(1)	Os(5)–P(1)	2.310(7)
Os(5)–C(51)	1.947(36)	Os(5)–C(52)	1.941(39)
Os(6)–P(1)	2.329(8)	Os(6)–C(61)	1.982(34)
Os(6)–C(62)	1.909(45)	Os(6)–C(63)	1.896(31)
P(1)–C(1P)	1.794(21)	C(11)–O(11)	1.215(47)
C(12)–O(12)	1.261(43)	C(13)–O(13)	1.140(63)
C(14)–O(14)	1.157(48)	C(21)–O(21)	1.083(47)
C(22)–O(22)	1.103(45)	C(23)–O(23)	1.175(42)
C(31)–O(31)	1.150(45)	C(32)–O(32)	1.181(44)
C(41)–O(41)	1.138(39)	C(42)–O(42)	1.095(46)
C(43)–O(43)	1.122(39)	C(44)–O(44)	1.128(49)
C(51)–O(51)	1.048(43)	C(52)–O(52)	1.143(56)
C(61)–O(61)	1.140(50)	C(62)–O(62)	1.132(62)
C(63)–O(63)	1.173(41)		

analysis, but potential energy calculations [13] indicate that they bridge the two long edges Os(3)–Os(6) (3.060(2) Å) and Os(5)–Os(6) (3.036(1) Å) of the μ_3-P capped Os_3 triangle. These two edges are ca. 0.25 Å longer than the average value of 2.84(5) Å for the other Os–Os distances in the cluster. There is, however, considerable variation in distances for the remaining Os–Os contacts. The Os–Os edges radial to the inner triangle are significantly longer (average 2.86(1) Å) than those in the central triangle (average 2.80(2) Å). A similar trend is observed in $Os_6(CO)_{17}\{P-(OMe)_3\}_4$ [7], however the effect is accentuated here by the presence in the central triangle of the short edge, Os(3)–Os(5), at 2.765(2) Å, which is common to the μ_3-P capped triangle. This capping phosphinidine ligand presumably exerts a shortening effect on this edge, as has been noted for other cluster systems [14]. In this context it is of interest to compare the bond parameters within the "$Os_2H_2(CO)_7P$" unit in 4 with those in the related trinuclear clusters $Os_3(\mu_2$-H$)_2(CO)_9(\mu_3$-PPh) [15] and $Ru_3(\mu_2$-H$)_2(CO)_8(PPh_3)(\mu_3$-PPh) [16], where the "$Os_3(CO)_{11}$" fragment in 4 may be viewed as having been replaced by two terminal carbonyls. In all three cases the trend in the lengths of the metal–metal edges is the same, with two long hydride bridged edges and a short unbridged edge. The trends in M–P distances are also similar, showing asymmetry in the coordination of the capping phosphorus atom. The longest distance, Os(6)–P(1) (2.329(8) Å), in 4 is associated with the Os atom which is coordinated to both hydrides, while the comparative distance in $Os_3H_2(CO)_9(\mu_3$-PPh) [15] is 2.358(10) Å.

In terms of electron counting, if the μ_3-PPh group acts as a four electron donor, the cluster 4 is a 90 electron system, and this count is consistent with the observed

Table 3

Bond angles (°)

Os(3)–Os(1)–Os(2)	58.7(1)	C(11)–Os(1)–Os(2)	160.3(12)
C(11)–Os(1)–Os(3)	102.2(12)	C(12)–Os(1)–Os(2)	83.7(9)
C(12)–Os(1)–Os(3)	87.1(9)	C(12)–Os(1)–C(11)	90.9(15)
C(13)–Os(1)–Os(2)	92.3(13)	C(13)–Os(1)–Os(3)	85.3(15)
C(13)–Os(1)–C(11)	90.6(18)	C(13)–Os(1)–C(12)	172.4(18)
C(14)–Os(1)–Os(2)	103.1(9)	C(14)–Os(1)–Os(3)	161.5(9)
C(14)–Os(1)–C(11)	96.2(15)	C(14)–Os(1)–C(12)	94.7(14)
C(14)–Os(1)–C(13)	92.6(18)	Os(3)–Os(2)–Os(1)	59.9(1)
Os(4)–Os(2)–Os(1)	168.1(1)	Os(4)–Os(2)–Os(3)	118.7(1)
Os(5)–Os(2)–Os(1)	118.5(1)	Os(5)–Os(2)–Os(3)	58.9(1)
Os(5)–Os(2)–Os(4)	60.1(1)	C(21)–Os(2)–Os(1)	85.4(9)
C(21)–Os(2)–Os(3)	95.0(9)	C(21)–Os(2)–Os(4)	82.9(9)
C(21)–Os(2)–Os(5)	93.8(11)	C(22)–Os(2)–Os(1)	96.9(9)
C(22)–Os(2)–Os(3)	88.8(9)	C(22)–Os(2)–Os(4)	94.9(9)
C(22)–Os(2)–Os(5)	87.7(10)	C(22)–Os(2)–C(21)	176.2(12)
C(23)–Os(2)–Os(1)	88.9(9)	C(23)–Os(2)–Os(3)	148.1(9)
C(23)–Os(2)–Os(4)	93.3(9)	C(23)–Os(2)–Os(5)	152.7(9)
C(23)–Os(2)–C(21)	88.4(14)	C(23)–Os(2)–C(22)	88.7(14)
Os(2)–Os(3)–Os(1)	61.4(1)	Os(5)–Os(3)–Os(1)	122.0(1)
Os(5)–Os(3)–Os(2)	60.9(1)	Os(6)–Os(3)–Os(1)	116.2(1)
Os(6)–Os(3)–Os(2)	94.0(1)	Os(6)–Os(3)–Os(5)	62.6(1)
P(1)–Os(3)–Os(1)	165.2(2)	P(1)–Os(3)–Os(2)	113.7(2)
P(1)–Os(3)–Os(5)	53.4(2)	P(1)–Os(3)–Os(6)	49.1(2)
C(31)–Os(3)–Os(1)	88.3(12)	C(31)–Os(3)–Os(2)	149.1(12)
C(31)–Os(3)–Os(5)	147.3(13)	C(31)–Os(3)–Os(6)	94.5(14)
C(31)–Os(3)–P(1)	94.1(13)	C(32)–Os(3)–Os(1)	97.7(10)
C(32)–Os(3)–Os(2)	97.3(8)	C(32)–Os(3)–Os(5)	95.2(9)
C(32)–Os(3)–Os(6)	145.5(10)	C(32)–Os(3)–P(1)	96.8(10)
C(32)–Os(3)–C(31)	92.3(15)	Os(5)–Os(4)–Os(2)	59.3(1)
C(41)–Os(4)–Os(2)	83.9(8)	C(41)–Os(4)–Os(5)	86.5(8)
C(42)–Os(4)–Os(2)	100.5(11)	C(42)–Os(4)–Os(5)	159.1(10)
C(42)–Os(4)–C(41)	94.8(14)	C(43)–Os(4)–Os(2)	161.9(9)
C(43)}Os(4)–Os(5)	103.5(9)	C(43)–Os(4)–C(41)	90.6(13)
C(43)–Os(4)–C(42)	97.1(14)	C(44)–Os(4)–Os(2)	93.9(10)
C(44)–Os(4)–Os(5)	85.9(9)	C(44)–Os(4)–C(41)	174.3(12)
C(44)–Os(4)–C(42)	90.7(15)	C(44)–Os(4)–C(43)	89.9(14)
Os(3)–Os(5)–Os(2)	60.1(1)	Os(4)–Os(5)–Os(2)	60.6(1)
Os(4)–Os(5)–Os(3)	120.4(1)	Os(6)–Os(5)–Os(2)	94.1(1)
Os(6)–Os(5)–Os(3)	63.5(1)	Os(6)–Os(5)–Os(4)	115.3(1)
P(1)–Os(5)–Os(2)	112.1(2)	P(1)–Os(5)–Os(3)	52.7(2)
P(1)–Os(5)–Os(4)	164.2(2)	P(1)–Os(5)–Os(6)	49.4(2)
C(51)–Os(5)–Os(2)	94.7(11)	C(51)–Os(5)–Os(3)	97.0(10)
C(51)–Os(5)–Os(4)	93.6(9)	C(51)–Os(5)–Os(6)	150.3(9)
C(51)–Os(5)–P(1)	101.2(9)	C(52)–Os(5)–Os(2)	147.1(10)
C(52)–Os(5)–Os(3)	150.8(10)	C(52)–Os(5)–Os(4)	86.7(10)
C(52)–Os(5)–Os(6)	96.5(11)	C(52)–Os(5)–P(1)	98.3(10)
C(52)–Os(5)–C(51)	91.3(16)	Os(5)–Os(6)–Os(3)	54.0(1)
P(1)–Os(6)–Os(3)	47.9(2)	P(1)–Os(6)–Os(5)	48.8(2)
C(61)–Os(6)–Os(3)	118.7(11)	C(61)–Os(6)–Os(5)	118.7(8)
C(61)–Os(6)–P(1)	164.4(10)	C(62)–Os(6)–Os(3)	143.1(12)
C(62)–Os(6)–Os(5)	95.1(11)	C(62)–Os(6)–P(1)	97.8(13)
C(62)–Os(6)–C(61)	92.4(16)	C(63)–Os(6)–Os(3)	101.0(12)
C(63)–Os(6)–Os(5)	147.0(12)	C(63)–Os(6)–P(1)	99.0(11)
C(63)–Os(6)–C(61)	91.3(14)	C(63)–Os(6)–C(62)	97.2(16)
Os(5)–P(1)–Os(3)	74.0(2)	Os(6)–P(1)–Os(3)	83.0(3)

Table 3 (continued)

Os(6)–P(1)–Os(5)	81.7(3)	C(1P)–P(1)–Os(3)	128.0(8)
C(1P)–P(1)–Os(5)	137.5(7)	C(1P)–P(1)–Os(6)	131.1(8)
C(2P)–C(1P)–P(1)	119.3(16)	C(6P)–C(1P)–P(1)	120.7(17)
O(11)–C(11)–Os(1)	172.3(36)	O(12)–C(12)–Os(1)	177.0(22)
O(13)–C(13)–Os(1)	174.8(40)	O(14)–C(14)–Os(1)	177.1(27)
O(21)–C(21)–Os(2)	168.7(34)	O(22)–C(22)–Os(2)	172.5(31)
O(23)–C(23)–Os(2)	175.1(27)	O(31)–C(31)–Os(3)	166.8(39)
O(32)–C(32)–Os(3)	175.1(28)	O(41)–C(41)–Os(4)	172.8(24)
O(42)–C(42)–Os(4)	169.3(38)	O(43)–C(43)–Os(4)	176.4(25)
O(44)–C(44)–Os(4)	175.8(32)	O(51)–C(51)–Os(5)	172.1(33)
O(52)–C(52)–Os(5)	173.5(36)	O(61)–C(61)–Os(6)	173.3(34)
O(62)–C(62)–Os(6)	174.0(33)	O(63)–C(63)–Os(6)	169.2(38)

metal framework geometry which is similar to that in the other 90 electron "raft" molecules [1,7].

Experimental

Reaction of Os$_6$(CO)$_{20}$(NCMe) with PPh$_2$H

Os$_6$(CO)$_{20}$(NCMe) (10 mg) was dissolved in freshly distilled dichloromethane (20 cm^3) and a dilute solution of PPh$_2$H was added under a N$_2$ at room temperature. After 5 min vigorous stirring the solvent was removed under vacuum and the blue-green solid was purified by TLC (35% CH$_2$Cl$_2$/hexane as eluent) to quantitative yields of Os$_6$(CO)$_{20}$(PPh$_2$H) (1).

Reaction of Os$_6$(CO)$_{20}$(NCMe) with PPhH$_2$

The reaction was carried out as above but starting from Os$_6$(CO)$_{20}$(NCMe) and a dilute solution of PPhH$_2$. The solvent was removed under vacuum, and then the residue kept under vacuum for a further hour to ensure removal of the excess of phosphine. The blue product was characterised as Os$_6$(CO)$_{20}$(PPhH$_2$) (yield 90%) but no further purification was attempted.

Thermal reaction of Os$_6$(CO)$_{20}$PPh$_2$H (1)

Os$_6$(CO)$_{20}$PPh$_2$H (10 mg) was dissolved in toluene (30 cm^3). The solution was stirred and heated slowly under N$_2$, and the reaction monitored by TLC and IR spectroscopy. After 12 h at a temperature of 70°C there had been a significant colour change from blue to orange-brown, and the solvent removed under vacuum. The products were separated by TLC (35% CH$_2$Cl$_2$/hexane as eluent). An orange-red product was isolated and characterised as Os$_6$H(CO)$_{16}$PPh$_2$ (3) (yield 90%). Mass spectrum m/z 1784. Anal. Found: C, 19.97; H, 1.08; P, 1.52. C$_{28}$H$_{11}$O$_{16}$Os$_6$P calcd.: C, 18.82; H, 0.616; P, 1.74%.

Thermal reaction of Os$_6$(CO)$_{20}$PPhH$_2$ (2)

A solution of Os$_6$(CO)$_{20}$PPhH$_2$ (20 mg) in toluene (30 cm^3) was kept at a temperature of 70°C for 7 h, during which the colour of the solution changed from blue to purple. The solvent was removed under vacuum and two products (one purple, one red) were separated by TLC (50% CH$_2$Cl$_2$/hexane as eluent). The

Table 4

Atomic coordinates ($\times 10^4$)

	x	y	z
Os(1)	1323(1)	3254(1)	941(1)
Os(2)	3771(1)	4175(1)	2085(1)
Os(3)	1598(1)	1880(1)	2222(1)
Os(4)	6443(1)	4719(1)	3032(1)
Os(5)	4066(1)	2573(1)	3244(1)
Os(6)	3583(1)	74(1)	2118(1)
P(1)	2251(6)	608(7)	3084(4)
C(1P)	1135(21)	−413(19)	3680(11)
C(2P)	1636	−1355	4031
C(3P)	779	−2161	4492
C(4P)	−581	−2026	4604
C(5P)	−1082	−1083	4254
C(6P)	−224	−277	3792
C(11)	−452(42)	2348(36)	480(21)
O(11)	−1700(35)	1838(29)	231(18)
C(12)	536(32)	4362(29)	1584(16)
O(12)	−52(28)	5055(24)	2004(16)
C(13)	2158(51)	1984(48)	395(27)
O(13)	2557(36)	1221(31)	36(15)
C(14)	1764(35)	4456(32)	204(18)
O(14)	1977(31)	5161(30)	−263(18)
C(21)	4744(36)	3287(32)	1364(19)
O(21)	5277(33)	2951(31)	898(14)
C(22)	2899(34)	5176(32)	2815(18)
O(22)	2418(26)	5831(24)	3169(16)
C(23)	4385(34)	5728(31)	1596(18)
O(23)	4839(32)	6723(23)	1338(17)
C(31)	−92(42)	514(38)	1769(21)
O(31)	−1236(33)	−156(30)	1579(23)
C(32)	564(32)	2669(29)	2853(17)
O(32)	−30(27)	3174(28)	3303(15)
C(41)	5630(30)	5916(28)	3684(16)
O(41)	5303(26)	6654(22)	4099(13)
C(42)	7638(40)	6140(36)	2535(20)
O(42)	8177(28)	7041(27)	2299(17)
C(43)	7831(33)	4751(28)	3856(17)
O(43)	8618(26)	4703(22)	4346(13)
C(44)	7122(39)	3348(34)	2397(20)
O(44)	7441(22)	2585(30)	2006(17)
C(51)	3394(36)	3625(33)	4030(19)
O(51)	3154(29)	4185(20)	4503(14)
C(52)	5348(4)	2126(35)	4008(21)
O(52)	6149(39)	1805(33)	4401(19)
C(61)	4767(35)	126(31)	1248(18)
O(61)	5500(40)	67(28)	778(18)
C(62)	4801(43)	−676(39)	2722(22)
O(62)	5431(43)	−1221(35)	3068(20)
C(63)	2279(38)	−1546(35)	1649(19)
O(63)	1305(41)	−2451(27)	1389(18)

major, purple, product was characterised as $Os_6H_2(CO)_{18}(PPh)$ (4) (yield 80%) while the minor, red, product was characterised as $Os_5(CO)_{15}(PPh)$ 5. 4 Mass spectrum m/z 1738. Anal. Found: C, 17.24; H, 0.95; P, 1.46. $C_{24}H_7O_{18}Os_6P$ calcd.: C, 16.3; H, 0.50; P, 1.74%. 5 Mass spectrum m/z 1486.

Crystal structure determination of $Os_6H_2(CO)_{18}(\mu_3\text{-}PPh)$ (4)

Suitable single crystals were obtained as blue-black hexagonal plates from CH_2Cl_2/hexane solution. A crystal with dimensions (distance from face to centre): 0.167(100, $\overline{1}$00) × 0.086(001, 00$\overline{1}$) × 0.095(011, 0$\overline{1}\overline{1}$) × 0.089(01$\overline{1}$, 0$\overline{1}$1) × 0.158 (10$\overline{1}$, $\overline{1}$01) × 0.143 ($\overline{1}$10, 1$\overline{1}$0) mm was mounted on a glass fibre with epoxy resin.

Crystal data. $C_{24}H_7O_{18}Os_6P$, $M = 1755.47$ Triclinic, a 9.733(2), b 10.555(1), c 17.585(2) Å, α 95.87(1), β 94.47(2), γ 105.60(1)°, V 1720 Å³ (by least-squares refinement for 50 automatically centred reflections in the range $18 < 2\theta < 25°$), space group $P\overline{1}$ (No. 2), $Z = 2$, D_c 3.388 g cm^{-3}, $F(000)$ 1532, graphite monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 221.80 cm^{-1}.

Data collection and processing. Stoe-Siemens AED four-circle diffractometer, 24 step ω-θ scan with ω scan width = 0.05°, scan time 0.75–3.0 s per step; 6503 reflections measured ($5.0 \le 2\theta \le 50.0°$, $+h$, $\pm k$, $\pm l$), (6060 unique, merging $R = 0.043$ after numerical absorption correction (maximum and minimum transmission factors 0.079, 0.043)), giving 4591 with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Computer assisted Patterson interpretation (Os atoms) followed by Fourier difference techniques for the remaining non-hydrogen atoms. Blocked full-matrix least-squares with Os, P and O atoms anisotropic. The phenyl group was treated as a rigid body with C–C distances fixed at 1.395 Å and C–C–C angles at 120°C. The weighting scheme $w = 1.608/[\sigma^2(F) + 0.001|F|^2]$ gave satisfactory agreement analyses. The final converged R and R_w values are 0.080 and 0.079. A final difference map showed ripples of ca. 5 eÅ^{-3} close to the Os atom positions. Complex neutral atom scattering factors were employed [17], and all computations were performed on the University of Cambridge IBM 3084Q using SHELX76 and SHELX86 [18]. The final atomic fractional coordinates are presented in Table 4 *.

References

1 R.J. Goudsmit, J.G. Jeffrey, B.F.G. Johnson, J. Lewis, R.S.C. McQueen, A.J. Sanders and J.-C. Liu, J. Chem. Soc., Chem. Commun., (1986) 24.
2 D.M.P. Mingos and D.G. Evans, Organometallics, 2 (1983) 35.
3 R.J. Goudsmit, B.F.G. Johnson, J. Lewis, P.R. Raithby and K.H. Whitmire, J. Chem. Soc., Chem. Commun., (1983) 246.

---

* Details of thermal parameters, complete lists of bond parameters, and structure factor tables may be obtained from the authors.

4 J.G. Jeffrey, B.F.G. Johnson, J. Lewis, P.R. Raithby and D.A. Welch, J. Chem. Soc., Chem. Commun., (1986) 318.

5 S. Bhaduri, K. Sharma and P.G. Jones, J. Chem. Soc., Chem. Commun., (1987) 1769.

6 S.A. MacLaughlin, N.J. Taylor and A.J. Carty, Organometallics, 3 (1984) 392; M. Muller and H. Vahrenkamp, Chem. Ber., 116 (1983) 2311; 116 (1983) 2322; F. Iwasaki, M.J. Mays, P.R. Raithby, P.L. Taylor and P.J. Wheatley, J. Organomet. Chem., 213 (1981) 185.

7 R.J. Goudsmit, B.F.G. Johnson, J. Lewis, P.R. Raithby and K.H. Whitmire, J. Chem. Soc., Chem. Commun., (1982) 640.

8 R. Mason, K.M. Thomas and D.M.P. Mingos, J. Am. Chem. Soc., 95 (1973) 3802.

9 C. Couture, D.H. Farrar, M.P. Gomez-Sal, B.F.G. Johnson, R.A. Kamarudin, J. Lewis and P.R. Raithby, Acta Crystallogr., C 42 (1986) 163.

10 B.F.G. Johnson, J. Lewis, M. McPartlin and M.A. Pearsall, unpublished results.

11 S.B. Colbran, B.F.G. Johnson, F.J. Lahoz, J. Lewis and P.R. Raithby, J. Chem. Soc., Dalton Trans., in press.

12 J.M. Fernandez, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1978) 1015.

13 A.G. Orpen, J. Chem. Soc., Dalton Trans., (1980) 2509.

14 H. Vahrenkamp, Phil. Trans., Roy. Soc., London, A, 308 (1982) 17.

15 K. Natarajan, L. Zsolnai and G. Huttner, J. Organomet. Chem., 220 (1981) 365.

16 M.J. Mays, P.L. Taylor and K. Henrick, Acta Crystallogr., B, 38 (1982) 365.

17 International tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4.

18 SHELX76, Crystal Structure Solving Package, G.M. Sheldrick, Cambridge, 1976; SHELX86, Direct Methods Package, G.M. Sheldrick, Göttingen, 1986.