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REACTION OF $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ WITH $[Cu(PPh_3)_2BH_4]$. CRYSTAL AND MOLECULAR STRUCTURES OF $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}]$ AND TWO $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_8(PPh_3)_2]$ ISOMERIC CLUSTERS

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Abstract—Reaction of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ with $[Cu(PPh_3)_2BH_4]$ in CH_2Cl_2 at room temperature affords $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}]$ (**1**) and two isomers **2a** and **2b** with a molecular formula $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_8(PPh_3)_2]$. Clusters **1**, **2a** and **2b** are all air- and moisture-stable and have been fully characterized by IR, NMR, MS and X-ray crystallography. The molecular structures of **2a** and **2b** are different in the substitution positions of the PPh_3.

The chemistry of triosmium carbonyl clusters containing phosphine ligands has been extensively studied. However, phosphine-substituted triosmium clusters containing a hydroxyl group are not well established.[1] The structurally characterized examples are $[Os_3H(OH)(CO)_8(Ph_2PCH_2PPh_2)]$,[2] $[Os_3H(OH)(CO)_9(PPh_3)]$,[3] $[Os_3H(OH)(CO)_9(PMe_2Ph)]$[4] and $[Os_3H(OH)(CO)_9(PEt_3)]$.[5]

Herein, we report the reaction of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ with $[Cu(PPh_3)_2BH_4]$, which led to the formation of a range of $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_n(PPh_3)_{10-n}]$ (n = 8,9 or 10) complexes.

EXPERIMENTAL

General

None of the compounds reported here are particularly air-sensitive, however, all reactions were carried out under dry nitrogen using freshly distilled solvents. Products were separated by thin layer chromatography (TLC) on silica gel (type 60 GF_{254} Merck 7730) and using dichloromethane–hexane (4 : 6) as eluent unless otherwise stated. ^1H and ^{31}P NMR data were obtained on a JEOL GSX 270 FT-NMR spectrometer. IR spectra were recorded on a BIO-RAD FTS-7 IR spectrometer between 2200 and 1600 cm^{-1}, mass spectra were recorded on a Finnagan MAT 95 mass spectrometer with the fast atom bombardment (FAB) technique. Spectroscopic data for the clusters **1**, **2a**, **2b** and **3** are given in Table 1.

The complexes $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$[6] and $[Cu(PPh_3)_2BH_4]$[7] were prepared by literature methods.

Reaction of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ *with* $[Cu(PPh_3)_2BH_4]$

A red solution of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ (100 mg, 70.6 mmol) in CH_2Cl_2 (20 cm^3) was stirred with $[Cu(PPh_3)_2BH_4]$ (43 mg, 70.6 mmol) in a 1 : 1 ratio at room temperature. The colour of the solution changed from red to orange–yellow and the solvent was evaporated *in vacuo* after 1.5 h of stirring. The residue was then redissolved in CH_2Cl_2 (2 cm^3) and separated by TLC. Five products were obtained. They were $[H_2Os_3(CO)_{11}]$ (5%, $R_f = 0.90$), $[H(OH)Os_3(PPh_3)(CO)_9]$ (**3**) (5%, $R_f = 0.80$), isomers of **2a** and **2b** (10% yield, $R_f = 0.50$ and 0.55, respectively) and **1** (2%, $R_f = 0.30$). Complexes **2a** and **2b** were recrystallized

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Table 1. Spectroscopic data for the clusters **1**, **2a**, **2b** and **3**

Cluster	IR (cm^{-1}), υ (CO)	^{1}H NMR (δ)	FAB MS (m/z)[a]
1	[b]2111 (w), 2069 (vs)	[d]0.20 (s, 1H, OH)	874 (874)
	2060 (s), 2023 (vs)	−12.75 (s, 1H, OsH)	
	2000 (s), 1989 (s)		
2a	[c]2067 (m), 2022 (s)	[d]7.55 (*m*, 30H, —PPh$_3$)	1342 (1342)
	1986 (s), 1966 (m)	−1.63 [t, J(PH) = 3.66 Hz, 1 H, OH]	
	1950 (m)	−10.90 [t, J(PH) = 6.41 Hz, 1 H, OsH]	
2b	[c]2068 (m), 2004 (s)	[d]7.50 (m, 30H, —PPh$_3$)	1342 (1342)
	1988 (s), 1952 (m)	−1.30 [d, J(PH) = 3.9 Hz, 1 H, OH]	
	1930 (m)	−11.90 [dd, J(PH) = 6.9, 33.5 Hz, 1H, OsH]	
3	[c]2120 (vs), 2092 (m)	[d]7.4 (m, 15H, —PPh$_3$)	1108 (1108)
	2052 (s), 2005 (s)	−1.48 [d, J(PH) = 4.4 Hz, 1H, OH]	
	1972 (s), 1942 (s)	−12.45 [d, J(PH) = 7.33 Hz, 1H, OsH]	

[a] M$^+$ = parent molecular ion based on ^{192}Os and calculated values in parentheses.

[b] Recorded in n-hexane at 298 K.

[c] Recorded in CH$_2$Cl$_2$ at 298 K.

[d] Recorded in CD$_2$Cl$_2$ at 298 K.

vs = very strong, s = strong, m = medium, w = weak, s = singlet, m = multiplet, t = triplet and dd = double doublet.

from a CH$_2$Cl$_2$/n-hexane mixture at −10°C to give orange and yellow crystals, respectively. Complex **1** gave orange crystals upon recrystallization in CH$_2$Cl$_2$/n-hexane over a period of 2 days.

X-ray diffraction studies

Crystal data and collection parameters for **1**, **2a** and **2b** are summarized in Table 2. The intensity data for all compounds were collected at room temperature on a AFC7R four-circle diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Data were corrected for Lorentz, polarization effects and absorption correction by the ψ-scan method[8] was also applied. All structures were solved by direct methods (SIR88)[9] and difference-Fourier techniques and refined by full-matrix least-squares analysis (Os,P anisotropic). Hydrogen atoms were generated in their idealized position (C—H, 0.95 Å), while hydride atoms were estimated from potential energy calculations.[10] All calculations were performed on a Silicon-Graphics computer using the TEXSAN[11] program package. Tables of coordinates, bond lengths, angles and structure factors for all compounds have been deposited with the Editor as supplementary materials.

RESULTS AND DISCUSSION

[N(PPh$_3$)$_2$][Os$_3$(μ-H)(CO)$_{11}$] reacted with [Cu(PPh$_3$)$_2$BH$_4$] in CH$_2$Cl$_2$ at room temperature giving two new compounds (**2a** and **2b**) in moderate yields. [H$_2$Os$_3$(CO)$_{10}$], **1** and **3** were obtained in low yields (less than 5%). However, when the reaction was carried out in a dry ice/acetone bath, only **1** and **3** were obtained in higher yields (approximately 30% each). The formation of **1** is most probably due to the presence of a trace amount of water in [Cu(PPh$_3$)$_2$BH$_4$]. In this reaction, complex **1** was thought to be an intermediate in which the disubstituted phosphine complexes were formed by nucleophilic substitution. A proposed mechanism for the reaction is shown in Scheme 1.

Complex **1** is frequently isolated as a side product from the reaction of triosmium complexes. However, structural characterization of this cluster had not previously been reported. Complex **1** crystallized in the monoclinic system in CH$_2$Cl$_2$/n-hexane mixture over a period of 2 days. The molecular structure of **1** is depicted in Fig. 1 and some selected bond parameters are presented in Table 3.

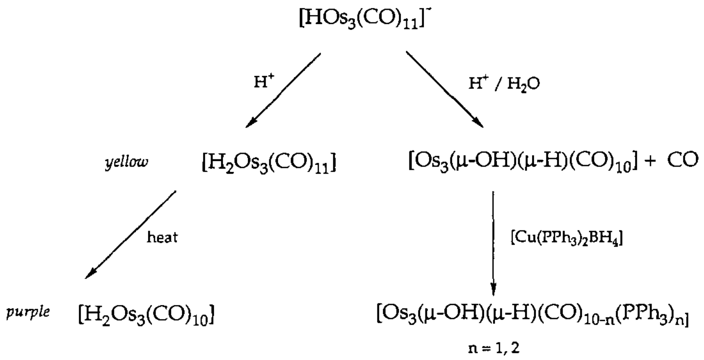
^{1}H NMR of **1** at 298 K shows two high-field singlet signals, which are due to the metal hydride at δ −12.75 and the hydroxyl proton at δ 0.20. The Os(2)—O(11) and Os(3)—O(11) bond lengths are both 2.12(1) Å and the Os(2)—O(11)—Os(3) angle is 83.3(4)°. The dihedral angle between the plane defined by Os(1)—Os(2)—Os(3) and the plane Os(2)—Os(3)—O(11) is 69.7°. The hydride is bridging the Os(2)—Os(3) edge, as evident from the bending of Os(2)—Os(3)—C(10), 121.3(7)°, and Os(3)—Os(2)—C(5), 123.9(6)°, away from the Os(2)—Os(3) edge.

The ^{31}P NMR spectrum of **2a** at 298 K shows

Table 2. Crystal data and data collection parameters for **1**, **2a** and **2b**

	1	**2a**	**2b**
Formula	$C_{10}H_2O_{11}Os_3$	$C_{44}H_{32}O_9P_2Os_3$	$C_{44}H_{32}O_9P_2Os_3$
Formula weight	868.72	1337.31	1337.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	7.357(4)	14.088(3)	15.403(8)
b (Å)	25.012(5)	19.308(2)	16.194(4)
c (Å)	9.052(4)	16.630(4)	17.910(4)
α (°)	90.0	90.0	90.0
β (°)	107.04(3)	112.14(2)	109.32(4)
γ (°)	90.0	90.0	90.0
U (Å^3)	1592(1)	4190(2)	4215(3)
Z	4	4	4
D_{calc} (g cm^{-3})	3.623	2.120	2.107
μ(Mo-K_α) (cm^{-1})	239.14	92.01	91.45
Temperature (°C)	23	23	23
F(000)	1512	2504	2504
Data collection range 2θ (°)	4–45	4–45	4–45
Unique reflections	2144	5680	5745
Observed reflections with $I > 3\sigma(I)$	1763	3627	3465
Transmission factors	0.549–1.000	0.685–1.000	0.676–1.000
R^a	0.036	0.032	0.047
$R_w{}^b$	0.047	0.034	0.041
No. of parameters, P	112	258	258
Weighting scheme^c	$p = 0.005$	$p = 0.006$	$p = 0.002$
Goodness-of-fit, S^d	2.501	1.352	2.202
Largest shift/e.s.d. final cycle	0.03	0.04	0.09
Residual extrema in final difference Fourier (e Å^{-3})	1.20 to −1.31	0.83 to −0.76	2.40 to −1.40

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$.
[c] Weighting scheme: $4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$.
[d] $S = [\Sigma\omega(|F_o| - |F_c|)^2/(N_{obs} - N_{para})]^{1/2}$.



Scheme 1. Proposed mechanism for the reaction of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ with $[Cu(PPh_3)_2BH_4]$.

only a sharp singlet (δ, ppm, reference 85% H_3PO_4), indicating that the the two phosphorus atoms are equivalent. The metal hydride signal of **2a** appears as a broad triplet with equal coupling to the two equivalent phosphorus atoms of the PPh_3 ligands in the ^1H NMR spectrum. The hydroxyl proton resonance is a triplet at δ −1.63, which is coupled [$J_{(PH)} = 3.66$ Hz] to the two equivalent phosphorus

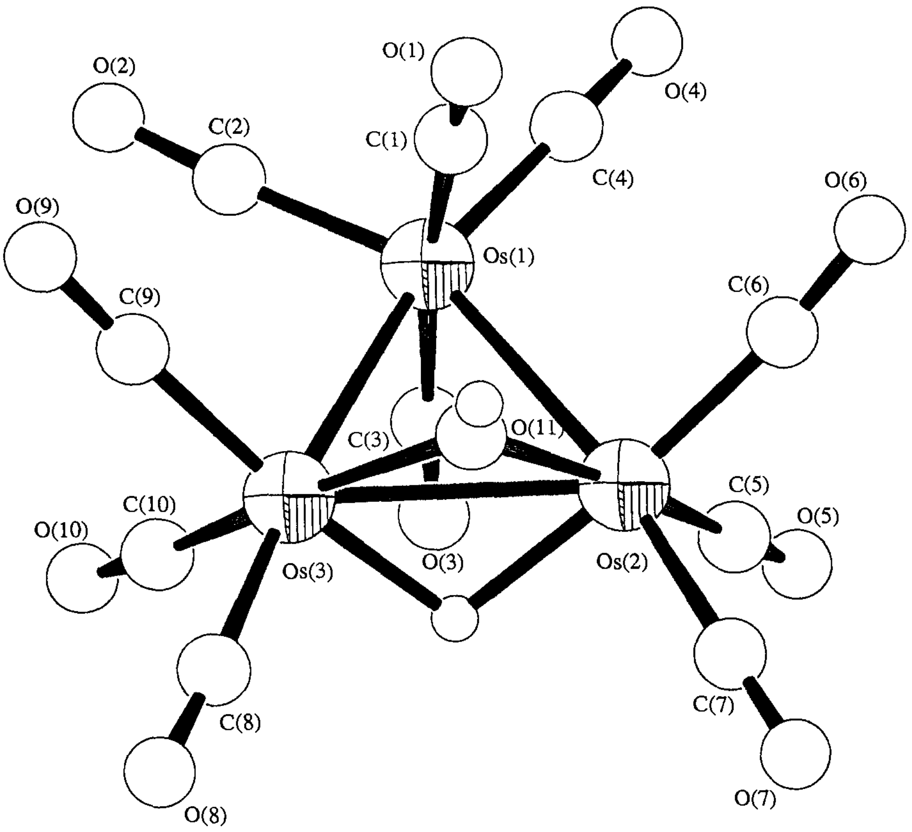


Fig. 1. Perspective view of cluster **1**; the hydride position was obtained from potential energy calculations.

atoms. The NMR data suggested a symmetrical structure for complex **2a** with the PPh_3 ligands at Os(1) and Os(2), the hydride and OH group all bridging the same Os—Os edge of an Os_3 triangle. In order to confirm this and to establish the full molecular structure of **2a**, a single-crystal X-ray study was carried out. The molecular structure is shown in Fig. 2 and some important bond parameters are given in Table 4.

The bridged Os(1)—Os(3) distance of 2.840(1) Å is the longest among the Os—Os bond lengths, which is probably due to the strong steric repulsion of two PPh_3 ligands in equatorial positions. A similar trend has been observed in the structure of $[Os_3H(SPh)(CO)_9(PEt)]$[5] and $[Os_3(CO)_{11}\{P(OMe)_3\}]$.[12] The two phosphorus atoms of PPh_3 lie in the plane of the Os_3 triangle as they deviate from the plane by 0.0379 Å for P(1) and 0.0083 Å for P(2), respectively.

Cluster **2b** shows high-field ^1H NMR signals: a doublet at δ −1.33 and a doublet at δ −11.9, which are due to the OH group and the metal hydride, respectively. The NMR data revealed that the two phosphorus atoms are non-equivalent in this complex. A single-crystal X-ray study was carried out to establish its solid-state structure. The molecular structure of **2b** is shown in Fig. 3 with principal bond parameters being given in Table 5. The two PPh_3 ligands are coordinated at the equatorial positions of Os(1) and Os(2).

In **2b**, the three osmium atoms form a closed triangle with the two phosphorus atoms of the PPh_3

Table 3. Selected bond lengths (Å) and bond angles (°) for **1**

Os(1)—Os(2)	2.831(1)	Os(1)—Os(2)—Os(3)	59.9(1)
Os(1)—Os(3)	2.817(1)	Os(1)—Os(3)—Os(2)	60.3(1)
Os(2)—Os(3)	2.817(1)	Os(1)—Os(2)—O(11)	83.7(3)
Os(2)—O(11)	2.12(1)	Os(1)—Os(3)—O(11)	84.0(3)
Os(3)—O(11)	2.12(1)	Os(2)—Os(1)—Os(3)	59.8(1)
		Os(2)—O(11)—Os(3)	83.3(4)

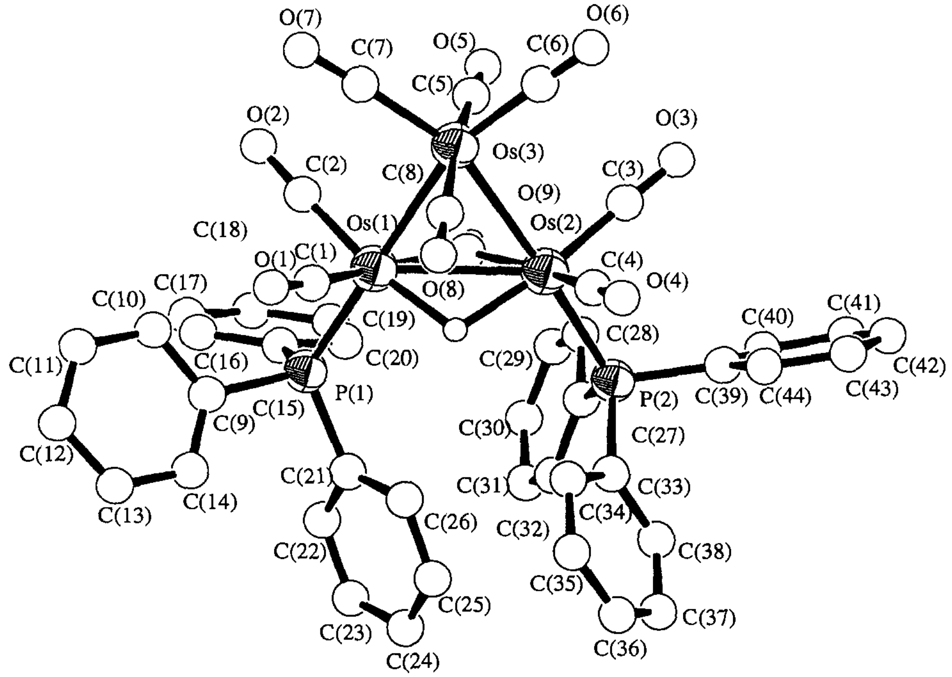


Fig. 2. Perspective view of cluster **2a**; the hydride position was obtained from potential energy calculations.

ligands lying essentially in the plane of the Os$_3$ triangle as they deviate from the plane by 0.065 Å for P(1) and 0.074 Å for P(2), respectively. The Os(1)—P(1) and Os(2)—P(2) bond lengths [2.350(5) and 2.369(4) Å] are similar to the values of 2.361(2) and 2.329(2) Å for the corresponding bonds in [Os$_3$H$_2$(CO)$_9$(PPh$_3$)][13] and [Os$_3$H(OH)(CO)$_9$(PMe$_2$Ph)][4], respectively. The bond parameters within the triphenylphosphine ligand are not significantly different from the free triphenylphosphine.[14] The bridging hydride is not located directly, but its position spanning the Os(1)—Os(3) edge is consistent with bending back of the *cis*-carbonyls [average *cis*-Os—Os—C 126.2(8)°]. The bridge Os(1)—Os(3) distance of 2.798(1) Å is marginally shorter than the other two Os—Os distances found in (3), but the average value of 2.827(8) Å is not significantly different from the average value for the Os—Os bonds [2.877(3) Å] in [Os$_3$(CO)$_{12}$].

Reaction of complex **1** with PPh$_3$ gives complex

Table 4. Selected bond lengths (Å) and bond angles (°) for **2a**

Os(1)—Os(2)	2.844(1)	Os(1)—Os(2)—Os(3)	60.1(2)	Os(1)—O(9)—Os(2)	83.7(3)
Os(1)—Os(3)	2.840(1)	Os(1)—Os(3)—Os(2)	60.2(1)	Os(2)—P(2)—C(27)	112.5(4)
Os(1)—P(1)	2.388(3)	Os(1)—Os(2)—C(3)	133.3(4)	Os(2)—P(2)—C(33)	118.0(4)
Os(1)—O(9)	2.132(8)	Os(1)—Os(2)—C(4)	120.9(4)	Os(2)—P(2)—C(39)	111.8(4)
Os(2)—Os(3)	2.823(1)	Os(1)—Os(2)—P(2)	116.7(1)	C(9)—P(1)—C(15)	105.0(6)
Os(2)—P(2)	2.357(3)	Os(1)—P(1)—C(9)	111.4(4)	C(9)—P(1)—C(21)	100.9(5)
Os(2)—O(9)	2.133(8)	Os(1)—P(1)—C(15)	113.4(4)	C(15)—P(1)—C(21)	101.1(6)
P(1)—C(9)	1.84(1)	Os(1)—P(1)—C(21)	122.9(4)	C(27)—P(2)—C(33)	108.1(6)
P(1)—C(15)	1.84(1)	Os(2)—Os(1)—Os(3)	59.6(1)	C(27)—P(2)—C(39)	105.1(6)
P(1)—C(21)	1.84(1)	Os(2)—Os(1)—C(1)	119.3(4)	C(33)—P(2)—C(39)	100.0(6)
P(2)—C(27)	1.84(1)	Os(2)—Os(1)—C(2)	132.3(4)		
P(2)—C(33)	1.81(1)	Os(2)—Os(1)—P(1)	120.7(1)		
P(2)—C(39)	1.84(1)	Os(3)—Os(1)—O(9)	82.3(2)		
		P(1)—Os(1)—O(9)	97.2(2)		

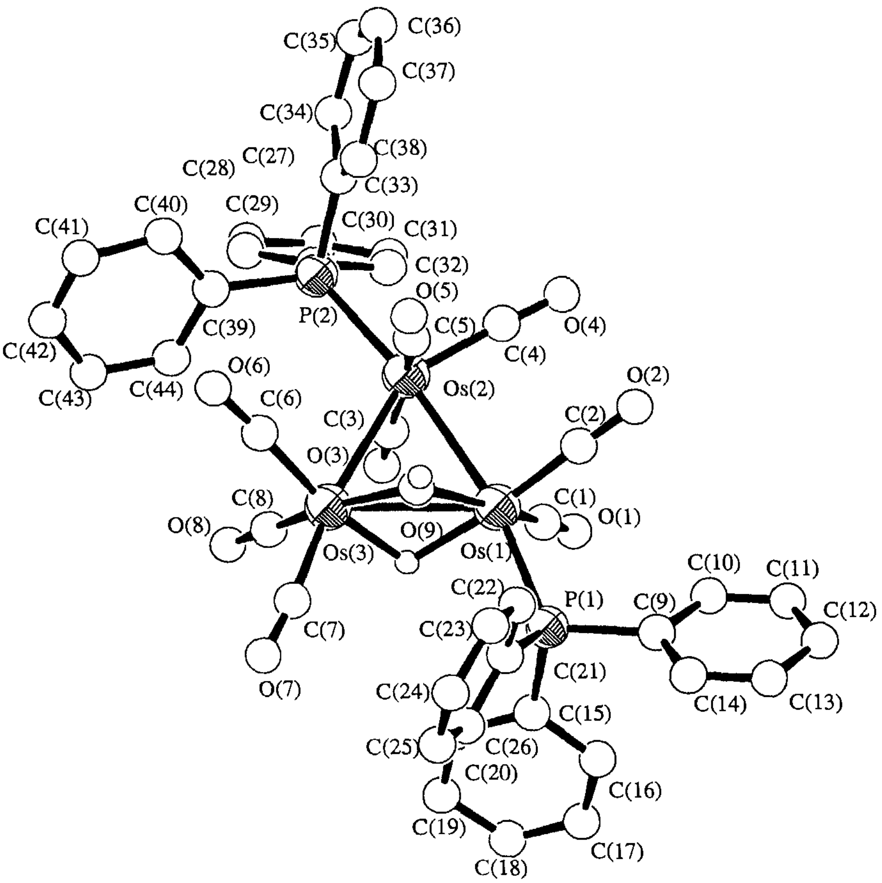


Fig. 3. Perspective view of cluster **2b**; the hydride position was obtained from potential energy calculations.

Table 5. Selected bond lengths (Å) and bond angles (°) for **2b**

Os(1)—Os(2)	2.839(2)	Os(1)—Os(2)—Os(3)	58.9(1)	C(9)—P(1)—C(21)	101.9(8)
Os(1)—Os(3)	2.798(1)	Os(1)—Os(3)—Os(2)	60.3(1)	C(15)—P(1)—C(21)	105.7(8)
Os(1)—P(1)	2.350(5)	Os(1)—Os(3)—C(6)	130.3(6)	C(27)—P(2)—C(33)	101.8(8)
Os(1)—O(9)	2.18(1)	Os(1)—Os(3)—C(8)	118.9(6)	C(27)—P(2)—C(39)	102.1(8)
Os(2)—Os(3)	2.846(1)	Os(1)—Os(2)—P(2)	172.7(1)	C(33)—P(2)—C(39)	105.2(8)
Os(2)—P(2)	2.369(4)	Os(2)—Os(1)—Os(3)	60.6(1)		
Os(3)—O(9)	2.08(1)	Os(2)—Os(1)—P(1)	169.0(1)		
P(1)—C(9)	1.85(2)	Os(2)—P(2)—C(27)	113.9(6)		
P(1)—C(15)	1.83(2)	Os(2)—P(2)—C(33)	115.5(6)		
P(1)—C(21)	1.82(2)	Os(2)—P(2)—C(39)	116.6(6)		
P(2)—C(27)	1.83(2)	Os(3)—Os(1)—C(1)	119.7(5)		
P(2)—C(33)	1.80(2)	Os(3)—Os(1)—C(2)	136.0(6)		
P(2)—C(39)	1.81(2)	Os(3)—Os(2)—P(2)	113.9(1)		
		C(9)—P(1)—C(15)	102.4(8)		

3 as the only product. However, reaction of **1** with PPh_3 in the presence of the tetraethylammonium borohydride leads to the diphosphine-substituted complexes as observed in the $[Cu(PPh_3)_2BH_4]$ reaction. Therefore, the presence of BH_4^- is believed to facilitate the nucleophilic substitution of **1** by phosphine.

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