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The crystal and molecular structure of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$

Brian F. G. Johnson, Jack Lewis, Ebbe Nordlander*† and Paul R. Raithby*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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Abstract—The crystal structure of the phosphide-bridged cluster $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **4** has been determined. The cluster consists of two Os_3 triangles which are linked by a PH_2 moiety which is terminally bound to each triangle. The acetonitrile ligand is axially coordinated and the hydride bridges the Os—Os edge to which the phosphide moiety and the acetonitrile are coordinated. The molecular structure of **4** resembles those of the related clusters $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **1** and $[Os_6(\mu\text{-}H)(CO)_{21}(CNBu^t)(\mu\text{-}PH_2)]$ **2** although the dihedral angles between the two osmium triangles vary for **1**, **2** and **4**. The relative orientation of the two linked metal triangles in **4** (as well as **1** and **2**) differs from that of the phosphite-substituted analogue $[Os_6(\mu\text{-}H)(CO)_{20}\{P(OMe)_3\}_2(\mu\text{-}PH_2)]_3$; this difference is attributed to steric factors. © 1997 Elsevier Science Ltd

Keywords: osmium; phosphide bridge; crystal structure.

Linking of mononuclear complexes through phosphide-bridges is a common and well documented phenomenon. There are also numerous examples of transition metal complexes in which the metals are linked by $\mu\text{-}PH_2$ bridges without any supporting metal–metal bonds, Schäfer *et al.* [1–8] have synthesized several such complexes. Ang *et al.* [9] have published an example of a $\mu\text{-}PH(CF_3)$-unit linking two clusters and we have shown that the terminal phosphine ligand of $[Os_3(CO)_{11}(PH_3)]$ may be used to form $\mu\text{-}PH_2$ bridges by oxidative addition to a suitably labilised (cluster) metal centre [10–12]. Several hexanuclear phosphido-bridged osmium carbonyl clusters have been synthesised by this method. The phosphido-bridged cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ has similarly been used to form hexanuclear phosphinidene-bridged clusters [13,14].

The crystal structures of a number of these phosphido- and phosphinidene-linked clusters have been determined [10–14]. The phosphinidene bridges in the clusters $[Os_6(\mu\text{-}H)_2(CO)_{21-n}(L)_n(\mu\text{-}PH)]$ ($n = 1$, L = NCMe, $P(OMe)_3$; $n = 2$, L = $P(OMe)_3$) [12–14] bring two trinuclear osmium clusters into close proximity and it appears that steric requirements of the ligands dictate the relative orientation (in the solid state) of the two metal triangles in these compounds (*vide infra*). The crystal structures of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **1** [11], $[Os_6(\mu\text{-}H)(CO)_{21}(CNBu^t)(\mu\text{-}PH_2)]$ **2** [12] and $[Os_6(\mu\text{-}H)(CO)_{20}\{P(OMe)_3\}_2(\mu\text{-}PH_2)]$ **3** [12] indicate that there are similar steric constraints on the orientations of the clusters in phosphido-bridged clusters. Here we wish to report the crystal and molecular structure of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **4** and compare its molecular parameters to those of **1**, **2** and **3**.

EXPERIMENTAL

The cluster $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **4** was synthesised as previously described [11]; gentle heating of a toluene solution of $[Os_3(CO)_{11}(PH_3)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ results in the formation of **4**. Crystals of **4** grew as orange platelets from a chloroform/hexane solution and a suitable crystal was mounted on a glass fibre. Data were collected using a Nicolet R3mV three-circle diffractometer (293 K, graphite monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å). The unit cell was determined by least-squares refinement of diffractometer angles from 30 automatically centered reflections in the range $15 < 2\theta < 20°$. The crystal used had a relatively large

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* Authors to whom correspondence should be addressed.

† Present address: Inorganic Chemistry 1, Chemical Center, Lund University, Box 124, S-221 00 Lund, Sweden. E-mail: Ebbe.Nordlander@inorg.lu.se

Table 1. Crystal data and data-collection parameters for the structure of $[Os_6(\mu\text{-H})(CO)_{21}(NCMe)(\mu\text{-PH}_2)]$ **4**

Formula	$C_{23}H_6NO_{21}Os_6P$
M	1804.46
Crystal colour, habit	Orange block
Crystal size (mm)	0.25 × 0.32 × 0.33
Crystal System	Monoclinic
Space Group	$P2_1/n$ (no. 14)
a (Å)	11.161(7)
b (Å)	12.532(4)
c (Å)	26.603(14)
α (°)	90
β (°)	90.03(5)
γ (°)	90
Z	4
U (Å^3)	3721
D_c (g cm^{-3})	3.32
F(000)	3160
2θ Range (°)	5.0 to 45.0
Scan mode	96 step ω/2θ
Scan speed (° min^{-1})	3.00 to 29.30
Scan range (ω) (°)	1.40 + K_α separation
μ (mm^{-1})	21.59
Absorption Correction	semi-emprirical
Max./Min. transmission	0.252/0.040
Reflections measured	5326 ($\pm h$, $+k$, $-l$)
Unique reflections	4501
R(int)	0.018
Observed reflections (criterion)	3224 ($F > 6\sigma(F)$)
Weighting scheme	$[\sigma^2(F)+0.0014F^2]^{-1}$
R	0.100
R'	0.106
Largest feature in final difference map (eÅ^{-3})	2.7

Background measurement: stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time, 3 standard reflections measured every 97 reflections. Three check reflections showed no significant variations during data collection.

Table 2. Selected bond lengths (Å) and bond angles (°) for $[Os_6(\mu\text{-H})(CO)_{21}(NCMe)(\mu\text{-PH}_2)]$ **4**

Os(1)—Os(2)	3.039(4)
Os(1)—Os(3)	2.896(4)
Os(1)—P(1)	2.363(18)
Os(2)—Os(3)	2.879(4)
Os(2)—N(1)	2.093(50)
Os(4)—Os(5)	2.849(4)
Os(4)—Os(6)	2.890(4)
Os(4)—P(1)	2.418(18)
Os(5)—Os(6)	2.893(4)
N(1)—C(1)	1.140(88)
C(1)—C(2)	1.367(87)
Os(2)—Os(1)—Os(3)	58.0(1)
Os(2)—Os(1)—P(1)	114.5(4)
Os(3)—Os(1)—P(1)	172.4(4)
P(1)—Os(1)—C(11)	86.3(18)
P(1)—Os(1)—C(12)	87.6(21)
P(1)—Os(1)—C(13)	87.9(25)
Os(1)—Os(2)—Os(3)	58.5(1)
Os(1)—Os(2)—N(1)	89.9(12)
Os(3)—Os(2)—N(1)	91.3(12)
Os(1)—Os(3)—Os(2)	63.5(1)
Os(5)—Os(4)—Os(6)	60.5(1)
Os(5)—Os(4)—P(1)	158.6(4)
Os(6)—Os(4)—P(1)	101.1(5)
P(1)—Os(4)—C(41)	86.6(22)
P(1)—Os(4)—C(42)	87.8(17)
P(1)—Os(4)—C(43)	100.1(15)
Os(4)—Os(5)—Os(6)	60.4(1)
Os(4)—Os(6)—Os(5)	59.0(1)
Os(1)—P(1)—Os(4)	123.7(7)
Os(2)—N(1)—C(1)	175.5(46)
N(1)—C(1)—C(2)	175.1(44)

mosaic spread. Crystals of better quality could not be obtained despite repeated efforts. Details of the crystal data and intensity collection are summarized in Table 1. The structure was solved by centrosymmetric direct methods (Os atom positions) followed by Fourier difference techniques. Full-matrix least-squares refinements on *F* with Os, P, N and Os atoms anisotropic were carried out using SHELXTL-PLUS [15] installed on a Micro-Vax II computer. Additional constraints were placed on some of the carbonyl ligands; Os—C 1.900(1) Å, C—O 1.160(1) Å. No attempt was made to locate hydrogen atoms in the structure. Selected bond lengths and bond angles for **4** are presented in Table 2.

RESULTS AND DISCUSSION

The molecular structure of **4** is shown in Fig. 1; it resembles that of $[Os_6(\mu\text{-H})(CO)_{22}(\mu\text{-PH}_2)]$ **1**. As has been observed for **1** [11], the Os—Os bond distances of **4** are very similar to those in $[Os_3(CO)_{12}]$ [16], except for one: the length of the Os(1)—Os(2) edge is 3.039(4) Å. In addition, the C(21)—O(21) carbonyl ligand is bent away from this edge [C(21)—Os(2)—Os(1) = 121.1(18)°]; these facts suggest that the hydride is bridging the Os(1)—Os(2) edge. The two Os—P distances are different, albeit not at the 3σ level; Os(1)—P is 2.363(18) Å and Os(4)—P is 2.418(18) Å. The σ-donor bond to the 47-electron fragment (Os(1)—P) is thus shorter than the σ-donor/π-acceptor bond to the 46-electron fragment which is expected if a localised bonding scheme is invoked for μ-PH_2 bridges [7]. However, the situation is the reverse in **1**, **2** and **3**. There are probably several factors, including steric effects, which influence the Os—P bond lengths in the clusters discussed here and it does not appear possible to draw definite conclusions from bond distances alone. The Os(1)—P—Os(4) angle in **4** is 123.7(7)°, which—as pointed out by Schäfer *et al.* [7]—is surprisingly large for a four-coordinate phosphorus. Table 3 lists some structural parameters for the phosphide moieties of μ-PH_2-linked metal complexes; there does not appear

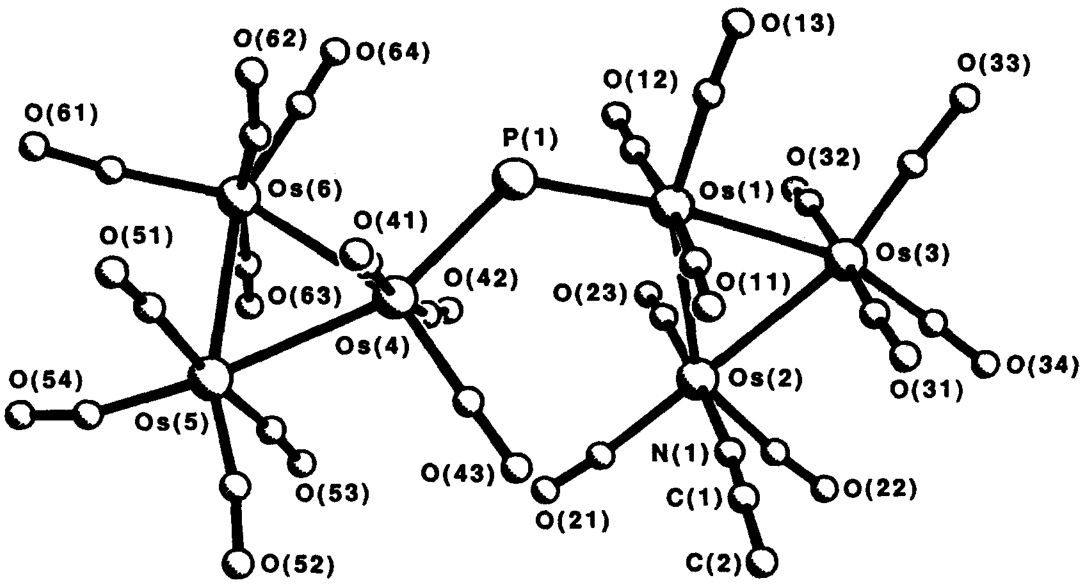


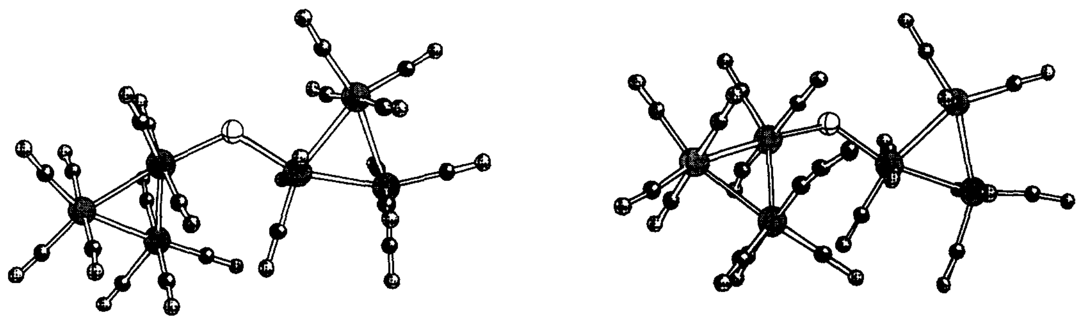
Fig. 1. The molecular structure of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **4** showing the atom numbering scheme.

to be a significant variation in the bond angles around the phosphorus atom in these compounds.

The dihedral angles between the osmium triangles in **4** (55.2°) is larger than those observed for $[Os_6(\mu\text{-}H)(CO)_{21}(CNBu^t)(\mu\text{-}PH_2)]$ **2** (49.3°), $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **1** (35.0°) and $[Os_6(\mu\text{-}H)(CO)_{20}\{P(OMe)_3\}_2(\mu\text{-}PH_2)]$ **3** (25.5°). Whether this difference is due to steric effects or possibly a crystal packing phenomenon is not entirely clear. However, examination of the crystal packing of **1**, **2**, **3** and **4** reveals that there are no unusually short intermolecular distances in these crystal structures. The variations are probably attributable to subtle steric interactions between the ligands of the two metal triangles. Figure 2 shows the structures of **1**, **2**, **3** and **4** in similar projections. It is evident that the parent carbonyl cluster **1** and the axially substituted clusters **2** and **4** have similar relative orientations of the osmium cluster triangles although the dihedral angles vary. While the crystal structure of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH(CF_3)]$ is not directly comparable to the above-mentioned phosphido-bridged clusters, it is nevertheless interesting to note that a similar orientation of the two cluster triangles is found in the molecular structure of this compound. The dihedral angle between the metal triangles in this $PH(CF_3)$ bridged cluster is 88.8°, i.e. considerably larger than those observed for **1**, **2** and **4**. On the other hand, the orientation of the two Os_3 clusters in the phosphite-substituted cluster $[Os_6(\mu\text{-}H)(CO)_{20}\{P(OMe)_3\}_2(\mu\text{-}PH_2)]$ **3** is considerably different from the above-mentioned compounds. In this cluster, the two triangles have a similar orientation. This means that the substituted "$Os_3(\mu\text{-}H)(CO)_9\{P(OMe)_3\}_2$" cluster fragment is rotated by approximately 120 degrees when compared to the orientation of the corresponding "$Os_3(\mu\text{-}H)(CO)_{11}$" fragment in the parent carbonyl cluster **1**. We have noticed a similar reorientation of substituted cluster triangles in phosphinidene-bridged hexanuclear osmium clusters; the two "$Os_3(\mu\text{-}H)(CO)_9(L)$" (L=NCMe, $P(OMe)_3$) fragments in the clusters $[Os_6(\mu\text{-}H)(CO)_{20}(NCMe)(\mu_3\text{-}PH)]$ **5** and $[Os_6(\mu\text{-}H)(CO)_{20}\{P(OMe)_3\}(\mu\text{-}PH_2)]$ **6** differ in relative orientation by approximately 180 degrees [12]. It appears that this difference in orienta-

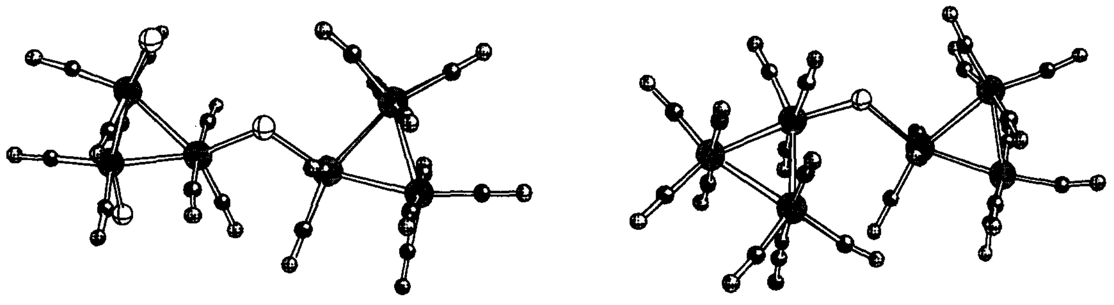
Table 3. Some structural parameters of unsupported phosphide (μ-PH_2) bridges

Formula	M—P(σ) (Å)	M—P(σ/π) (Å)	M—P—M (°)	Reference
$[Cp(CO)_2Fe(\mu\text{-}PH_2)Fe(CO)_4]$	2.290(1)	2.265(1)	124.8	7
$[Cp(CO)_2Fe(\mu\text{-}PH_2)Mn(CO)_2Cp']$				
Molecule 1	2.300(1)	2.243(2)	126.8(1)	7
Molecule 2	2.291(2)	2.248(2)	126.0(1)	
$[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$	2.373(5)	2.407(4)	124.3(2)	11
$[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$	2.418(18)	2.363(18)	123.7(7)	This work
$[Os_6(\mu\text{-}H)(CO)_{21}(CNBu^t)(\mu\text{-}PH_2)]$	2.356(6)	2.405(7)	125.4(3)	12
$[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}_2(\mu_3\text{-}PH)]$	2.362(8)	2.390(7)	124.0(4)	12



$[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ (1)

$[Os_6(\mu\text{-}H)(CO)_{21}(CNBu^t)(\mu\text{-}PH_2)]$ (2)



$[Os_6(\mu\text{-}H)(CO)_{20}(P(OMe)_3)_2(\mu\text{-}PH_2)]$ (3)

$[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ (4)

Fig. 2. The molecular structures of $[Os_6(\mu\text{-}H)(CO)_{22}(\mu\text{-}PH_2)]$ **1**, $[Os_6(\mu\text{-}H)(CO)_2(CNBu^t)(\mu\text{-}PH_2)]$ **2**, $[Os_6(\mu\text{-}H)(CO)_{20}\{P(OMe)_3\}_2(\mu\text{-}PH_2)]$ **3** and $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\mu\text{-}PH_2)]$ **4**. The structures are displayed so that the right-hand "$Os_3(CO)_{11}$" fragments are shown in similar projections. The methyl and methoxy-substituents of the isonitrile and phosphite ligands in **2** and **3** have been omitted for the sake of clarity.

tion is due to steric reasons; cluster **6** cannot adopt the framework structure of **5** without significant steric interaction between the equatorial phosphite ligand of one osmium triangle and carbonyl ligands of the second cluster triangle. It may be that if **4** were to adopt a structure more similar to that of **1**, **2** and **3**, the possibility of a similar steric interaction between phosphite and carbonyl ligands would arise and that this is the reason for the fact that **4** adopts a structure which is significantly different from those of the other phosphido-bridged clusters discussed here.

One further point of interest in the structures of these phosphido-bridged clusters is the slight twist of the ligand arrangement of the osmium atoms comprising the metal triangles which do not possess a hydride. The "$Os_3(\mu\text{-}H)(CO)_{11-n}(L)_n(\mu\text{-}PH_2)$"-fragments may be viewed as very bulky ligands attached to these osmium triangles. According to the Ligand Polyhedral Model [17,18] the structures adopted by clusters (in the solid state) are in part dependent on the overall ligand arrangement around the metal deltahedron. Steric interactions between ligands may force a rearrangement of the ligand polyhedron and thus effect a different cluster structure.

Considering the ligands as hard spheres, there are some common polyhedral arrangements which twelve ligands may adopt. The one which results in least steric interactions between the ligands is the icosahedron. There are two suitable orientations of a metal triangle within an icosahedron of ligands; one generates a structure of D_3 symmetry, in which all ligands are terminally coordinated but "twisted" with respect to the plane of the metal triangle, the other generates a structure of C_2v symmetry, in which two ligands bridge a metal–metal edge. The latter is the structure adopted by $[Fe_3(CO)_{12}]$ in the solid state [19]. The two orientations within this polyhedron are related by a 30° rotation of the metal triangle. Another arrangement of twelve ligands is the anti-cuboctahedron. The only suitable orientation of the metal triangle within such a polyhedron is one that generates a structure of D_3h symmetry with all terminal ligands. This is the arrangement which has been found for the solid state structures of $[M_3(CO)_{12}]$ (M=Ru [20], OS [16]). The reason that these clusters adopt this sterically less favourable structure is attributed to electronic factors; interactions between the frontier orbitals of three $M(CO)_4$-fragments of C_2v symmetry are optimised in this structure. Thus, there is an interplay between steric and electronic factors which determine the structure of triangular M_3L_{12}-complexes-complexes. It has been argued that the introduction of bulky ligands into the ligand sphere may cause the steric factor to dominate and enforce a "twist" of the ligands so that a structure akin to the D_3 structure is adopted. This has been observed for phosphine/phosphite-substituted derivatives of $[M_3(CO)_{12}]$ (M = Ru, Os) [21] and appears to be the case for the phosphido-bridged clusters discussed here. This (re)orientation of the ligands is most pronounced for **1** and **4**. The Os(5)—Os(4)—Os(6)—C(62) torsion angle for **4** is approximately 104.3° while the corresponding angle for **1** is 106.2°, indicating a "twist" of approximately 15° for these two compounds.

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