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Nonacarbonyl-di-μ-hydrido-(triphenylphosphine)-*triangulo*-triosmium

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Abstract. $C_{27}H_{17}O_9Os_3P$, $Os_3(C_{18}H_{15}P)(CO)_9H_2$, monoclinic, $P2_1/n$, $a = 8.756$ (3), $b = 16.899$ (7), $c = 20.142$ (9) Å, $\beta = 98.31$ (2)°, $U = 2949.1$ Å³, $Z = 4$, $D_c = 2.45$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 12.98$ mm⁻¹. The structure was refined to an R of 0.035 for 4078 unique diffractometer data. The three Os atoms define an isosceles triangle. The triphenylphosphine group bonds in an equatorial site on one of the Os atoms associated with the short Os–Os bond. The carbonyl ligands are all terminal, and their distribution suggests that both hydride ligands bridge the short Os–Os edge.

Introduction. $H_2Os_3(CO)_{10}$ is of interest because it is a particularly reactive molecule and has been used as a starting material in many reactions leading to the formation of complex cluster species (Bryan, Johnson & Lewis, 1977). Its reactivity is thought to be due to the unsaturation of one Os–Os bond. The nature of the bonding in this system is not well understood. Recent X-ray (Churchill, Hollander & Hutchinson, 1977) and combined X-ray/neutron (Orpen, Rivera, Bryan, Pippard, Sheldrick & Rouse, 1978) studies have shown that both hydrides bridge the short unsaturated Os–Os edge. An X-ray analysis of the title compound was undertaken to investigate the influence of the presence of a phosphine ligand on the Os–Os bonding and on the cluster geometry as a whole.

The title compound was prepared by reacting triphenylphosphine with $H_2Os_3(CO)_{10}$ in hexane, and refluxing the product, $H_2Os_3(CO)_{10}P(C_6H_5)_3$, to remove a carbonyl group (Zuccaro, 1979). Recrystallization from hexane yielded dark-purple, rectangular blocks. 4240 intensities were recorded ($1.5 < \theta < 25.0°$) on a Philips PW 1100 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, a θ–2θ scan, and a crystal $0.288 \times 0.272 \times 0.224$ mm. Lp corrections, and semi-empirical absorption corrections based on a pseudo-ellipsoid model and 372 azimuthal scan data from 14 independent reflections were applied; transmission factors ranged from 0.539 to 0.678 for the full data set. Equivalent reflections were averaged to give 4078 unique observed intensities [$F > 4\sigma(F)$]. Cell dimensions were derived from the angular measurements of 25 strong reflections ($10.0 < \theta < 15.0°$).

The Os atoms were located by multisolution Σ_2 sign expansion; positions of all the other non-hydrogen atoms were found from a subsequent difference synthesis. The structure was refined by full-matrix least squares with complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and weights $w = 0.4991/[\sigma^2(F) + 0.0002|F_o|^2]$. The refined parameters included anisotropic thermal parameters for Os, P, and the carbonyl C and O atoms, a common isotropic temperature factor for the phenyl H atoms, and an empirical extinction parameter x, which refined to 0.00071 (2); F_c is multiplied by $(1 - 0.0001xF_c^2/\sin \theta)$. The phenyl rings were refined as rigid groups with the constraints: C–C 1.395 Å,

Table 1. Atom coordinates (×10⁴)

Table 1. *Atom coordinates* $(\times 10^4)$

	x	y	z
Os(1)	614 (1)	1733 (1)	2768 (1)
Os(2)	2689 (1)	558 (1)	2824 (1)
Os(3)	2796 (1)	1589 (1)	3932 (1)
P(1)	−860 (3)	1652 (1)	1691 (1)
C(11)	−1014 (13)	1915 (7)	3255 (6)
C(12)	812 (12)	2823 (7)	2698 (5)
C(21)	2271 (12)	17 (6)	1973 (6)
C(22)	4887 (15)	590 (7)	2881 (6)
C(23)	2876 (12)	−376 (7)	3373 (5)
C(31)	4001 (12)	2298 (7)	3461 (6)
C(32)	4584 (16)	1176 (8)	4504 (6)
C(33)	1346 (18)	858 (8)	4241 (6)
C(34)	2025 (14)	2426 (7)	4421 (5)
O(11)	−1969 (10)	2033 (7)	3584 (5)
O(12)	907 (11)	3497 (5)	2658 (5)
O(21)	2064 (10)	−315 (5)	1479 (4)
O(22)	6187 (10)	628 (6)	2920 (5)
O(23)	2937 (11)	−913 (5)	3710 (5)
O(31)	4672 (10)	2729 (6)	3180 (5)
O(32)	5626 (14)	919 (8)	4818 (6)
O(33)	459 (16)	454 (7)	4421 (5)
O(34)	1569 (12)	2936 (6)	4699 (5)
C(101)	296 (8)	1633 (4)	1003 (3)
C(102)	1594 (8)	2118 (4)	1043 (3)
C(103)	2455 (8)	2144 (4)	512 (3)
C(104)	2018 (8)	1683 (4)	−58 (3)
C(105)	720 (8)	1197 (4)	−98 (3)
C(106)	−141 (8)	1172 (4)	432 (3)
C(201)	−2231 (8)	846 (3)	1507 (4)
C(202)	−3601 (8)	957 (3)	1069 (4)
C(203)	−4601 (8)	321 (3)	904 (4)
C(204)	−4230 (8)	−425 (3)	1177 (4)
C(205)	−2860 (8)	−536 (3)	1615 (4)
C(206)	−1861 (8)	100 (3)	1780 (4)
C(301)	−2047 (8)	2539 (4)	1525 (4)
C(302)	−1625 (8)	3154 (4)	1126 (4)
C(303)	−2464 (8)	3859 (4)	1073 (4)
C(304)	−3725 (8)	3949 (4)	1418 (4)
C(305)	−4147 (8)	3334 (4)	1816 (4)
C(306)	−3308 (8)	2629 (4)	1870 (4)

Table 2. Bond lengths (Å) and angles (°)

Table 2. *Bond lengths* (Å) *and angles* (°)

Os(2)—Os(1)	2·683 (2)		C(11)—Os(1)	1·869 (12)
Os(3)—Os(1)	2·813 (2)		C(12)—Os(1)	1·858 (12)
Os(3)—Os(2)	2·822 (2)		C(21)—Os(2)	1·930 (12)
P(1)—Os(1)	2·361 (2)		C(22)—Os(2)	1·912 (13)
C(101)—P(1)	1·831 (7)		C(23)—Os(2)	1·921 (11)
C(201)—P(1)	1·818 (7)		C(31)—Os(3)	1·933 (13)
C(301)—P(1)	1·828 (7)		C(32)—Os(3)	1·935 (13)
O(11)—C(11)	1·156 (13)		C(33)—Os(3)	1·938 (14)
O(12)—C(12)	1·145 (13)		C(34)—Os(3)	1·904 (11)
O(21)—C(21)	1·133 (13)		O(31)—C(31)	1·137 (13)
O(22)—C(22)	1·132 (14)		O(32)—C(32)	1·120 (15)
O(23)—C(23)	1·130 (12)		O(33)—C(33)	1·132 (14)
O(34)—C(34)	1·131 (13)			
Os(3)—Os(1)—Os(2)	61·7 (1)		P(1)—Os(1)—Os(2)	105·8 (1)
Os(3)—Os(2)—Os(1)	61·4 (1)		P(1)—Os(1)—Os(3)	167·3 (1)
Os(2)—Os(3)—Os(1)	56·9 (1)		C(11)—Os(1)—P(1)	97·7 (3)
C(11)—Os(1)—Os(2)	131·5 (4)		C(12)—Os(1)—P(1)	91·9 (3)
C(11)—Os(1)—Os(3)	93·1 (3)		C(12)—Os(1)—C(11)	87·9 (5)
C(12)—Os(1)—Os(2)	131·9 (3)		C(22)—Os(2)—C(21)	97·3 (5)
C(12)—Os(1)—Os(3)	95·1 (3)		C(23)—Os(2)—C(21)	96·5 (4)
C(21)—Os(2)—Os(1)	105·8 (3)		C(23)—Os(2)—C(22)	89·3 (5)
C(21)—Os(2)—Os(3)	167·1 (3)		C(32)—Os(3)—C(31)	93·7 (5)
C(22)—Os(2)—Os(1)	130·6 (3)		C(33)—Os(3)—C(31)	169·2 (5)
C(22)—Os(2)—Os(3)	90·9 (3)		C(33)—Os(3)—C(32)	95·1 (6)
C(23)—Os(2)—Os(1)	129·3 (3)		C(34)—Os(3)—C(31)	93·0 (5)
C(23)—Os(2)—Os(3)	93·5 (3)		C(34)—Os(3)—C(32)	106·0 (5)
C(31)—Os(3)—Os(1)	83·7 (3)		C(34)—Os(3)—C(33)	90·5 (5)
C(31)—Os(3)—Os(2)	87·3 (3)		C(101)—P(1)—Os(1)	114·1 (2)
C(32)—Os(3)—Os(1)	157·1 (4)		C(201)—P(1)—Os(1)	119·3 (2)
C(32)—Os(3)—Os(2)	100·4 (4)		C(301)—P(1)—Os(1)	110·0 (3)
C(33)—Os(3)—Os(1)	85·7 (4)		C(201)—P(1)—C(101)	104·6 (3)
C(33)—Os(3)—Os(2)	85·0 (3)		C(301)—P(1)—C(101)	103·7 (3)
C(34)—Os(3)—Os(1)	96·8 (3)		C(301)—P(1)—C(201)	103·6 (3)
C(34)—Os(3)—Os(2)	153·5 (3)		C(102)—C(101)—P(1)	118·7 (2)
O(11)—C(11)—Os(1)	176·7 (10)		C(106)—C(101)—P(1)	121·2 (2)
O(12)—C(12)—Os(1)	178·8 (10)		C(202)—C(201)—P(1)	120·8 (2)
O(21)—C(21)—Os(2)	177·9 (9)		C(206)—C(201)—P(1)	119·1 (2)
O(22)—C(22)—Os(2)	178·3 (10)		C(302)—C(301)—P(1)	121·7 (2)
O(23)—C(23)—Os(2)	177·1 (10)		C(306)—C(301)—P(1)	117·9 (2)
O(31)—C(31)—Os(3)	178·0 (10)		O(34)—C(34)—Os(3)	178·3 (11)
O(32)—C(32)—Os(3)	177·6 (13)		O(33)—C(33)—Os(3)	177·4 (14)

C—C—C 120·0°, C—H 1·08 Å, C—C—H 120·0°. The hydridic H atoms were not located. The refinement converged to $R = 0·035$ and $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0·037$. The final atomic coordinates for the non-hydrogen atoms are listed in Table 1, bond lengths and angles in Table 2.*

Discussion. The three Os atoms lie at the vertices of an isosceles triangle. The triphenylphosphine ligand bonds in an equatorial site on Os(1) with the P atom lying in the plane of the Os₃ triangle. Os(1) is also bound to two terminal carbonyl ligands. Os(2) is bound to three carbonyls and Os(3) has two equatorial and two axial ligands coordinated to it (Fig. 1).

* Lists of structure factors, hydrogen-atom coordinates, and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34484 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. The molecular structure of $H_2Os_3(CO)_9P(C_6H_5)_3$. H atoms have been omitted for clarity.

The short Os—Os bond appears to be unaffected by the presence of the phosphine group and its length is not significantly different from the 2·680 (2) Å in $H_2Os_3(CO)_{10}$ (Orpen *et al.*, 1978). Os(1)—Os(3) *trans* to the P atom is similar in length to the two unbridged bonds (mean 2·815 Å) in the parent dihydride but

Os(2)—Os(3) is slightly longer. The Os—P length is longer than the 2·285 (5) Å in $Os_3(CO)_{11}P(OCH_3)_3$ (Benfield, Johnson, Raithby & Sheldrick, 1978). In the latter complex the introduction of the phosphite ligand also has little effect on individual Os—Os distances but causes an expansion of the twinned cuboctahedral ligand polyhedron and consequently the Os_3 triangle. In $H_2Os_3(CO)_9P(C_6H_5)_3$ little expansion of the icosahedral ligand polyhedron is observed. In this case a small increase in size of the ligand polyhedron might cause the molecule to adopt the twinned-cuboctahedral geometry which would require energetically unfavourable ligand rearrangement.

The distribution of ligands is similar to that in $H_2Os_3(CO)_{10}$ (Orpen et al., 1978) where both hydrides bridge the short Os—Os edge. The phosphine ligand appears to have little increase in steric influence over the carbonyl in this case, the Os(1)—Os(2)—C(21) and Os(2)—Os(1)—P(1) angles being equal. The fact that hydride ligands exert a steric influence has been illustrated by Orpen (1978). The Os—Os—C(carbonyl) angles (mean 130·8°) involving Os(1), Os(2), C(11), C(12), C(22) and C(23) show that the carbonyls bend away from the short Os(1)—Os(2) edge. This indicates that in this molecule both hydrides also bridge the short edge and lie above and below the Os_3 plane.

Although the light atoms were not located as accurately as in the neutron study (Orpen et al., 1978) the trends in Os—C distances are the same. The Os—C trans to the proposed hydride positions (mean 1·890 Å) are shorter than the equatorial Os—C bonds (mean 1·923 Å) which are in turn shorter than the axial bonds associated with Os(3) (mean 1·934 Å). This may be explained in terms of competition for back donation of electron density from the Os atoms. The hydrides have no empty orbitals of suitable energy to compete for back donation with the carbonyls trans to them so the Os—C bonds are short. When two carbonyls are trans to each other there is considerable competition so the Os—C bonds are individually longer. The two Os(1)—C distances (mean 1·864 Å) are shorter than the two equivalent Os(2)—C distances (mean 1·917 Å). This may be caused by the phosphine pushing electron density on to Os(1) which is taken up by stronger back-bonding to the carbonyls. The phosphine is a better σ donor but a poorer π acceptor than the carbonyl ligand.

The carbonyls are all approximately linear with a mean Os—C—O angle of 177·8°; the average C—O distance is 1·135 Å.

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Manganese(II) Malonate Dihydrate: a Reinvestigation

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Abstract. $C_3H_2O_4^{2-} \cdot Mn^{2+} \cdot 2H_2O$, $Mn(C_3H_2O_4) \cdot 2H_2O$, orthorhombic, $Pca2_1$, $a = 9·62$ (1), $b = 7·36$ (1), $c = 8·33$ (1) Å, $M_r = 193·0$, $V = 589·8$ Å^3, $Z = 4$, $D_x = 2·17$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0·71069$ Å) $= 2·32$ mm^{-1}. Each Mn^{2+} ion is octahedrally coordinated by four carboxylate O atoms and two *trans* water O atoms. Mn—O distances lie between 2·127 (3) and 2·232 (5) Å. Four O atoms in the malonate ligand are involved in coordination to three different Mn^{2+} ions forming an extensive polymeric network parallel to (001). Each H atom from water molecules is involved in a hydrogen bond linking the layers along c. The structure was refined to an R of 0·032 for 760 diffractometer data.