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Carbidotridecacarbonylhydrido(trimethyl diphosphito)pentaosmium, $HOs_5C(CO)_{13}[OP(OCH_3)OP(OCH_3)_2]$

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Abstract. $C_{17}H_{10}O_{18}P_2Os_5$, triclinic, $P\bar{1}$, $a = 9.743$ (5), $b = 16.541$ (10), $c = 18.877$ (9) Å, $\alpha = 91.19$ (4), $\beta = 103.55$ (4), $\gamma = 90.25$ (5)°, $U = 2956.7$ Å^3, $Z = 4$, $D_x = 3.40$ g cm^{-3}, μ(Mo $K\alpha$) = 208.0 cm^{-1}. The structure was refined to an R of 0.045 for 6137 unique diffractometer data. The asymmetric unit consists of two similar molecules. The Os_5C unit forms a distorted trigonal bipyramid with the C atom at the centre; the unusual diphosphite ligand is attached to three Os atoms (through P, P and O).

Introduction. The title compound is one of a number of products isolated by Fernandez, Johnson & Lewis (1977) by thin-layer chromatography from the pyrolysis of $Os_3(CO)_{11}[P(OCH_3)_3]$. Structural elucidation required a crystal structure determination.

Yellow crystals were grown from ethyl acetate/hexane. Intensities were determined with a Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and a crystal ground to a sphere of diameter 0.19 mm. Semi-empirical absorption corrections based on a pseudo-ellipsoid model and 756 azimuthal scan data from 26 independent reflexions gave transmission coefficients ranging from 0.137 to 0.098 for the full data set; the merging R for the azimuthal data dropped from 0.0275 to 0.0236 on applying these corrections. 7586 intensities were measured for $2.5 < 2\theta < 60.0°$ and averaged to give 7118 unique data of which 6137 with $F > 5\sigma(F)$ based on counting statistics were employed for structure refinement. Cell dimensions were determined from the diffractometer settings for 15 strong reflexions. The structure was solved by multisolution $\sum_2$ sign expansion; the 10 independent Os atoms were found to be the highest peaks in the best E map. The remaining non-hydrogen atoms were located from difference syntheses. The structure was refined by blocked-matrix least squares with anisotropic temperature factors for Os and P, and the C and O atoms isotropic. In view of the relatively large uncertainties in the light-atom positions, a weak constraint was applied in the form of extra observational equations to make the C—O lengths equal. The mean C—O distance refined to 1.151 (4) Å; the constraint did not significantly increase R. Complex

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times 10^3$)

	x	y	z	U
Os(11)	894 (1)	2202 (1)	1095 (1)	*
Os(12)	3187 (1)	3292 (1)	1579 (1)	*
Os(13)	5074 (1)	1961 (1)	1645 (1)	*
Os(14)	2943 (1)	1463 (1)	352 (1)	*
Os(15)	2936 (1)	1886 (1)	2458 (1)	*
P(16)	2947 (7)	3392 (4)	358 (3)	*
P(17)	66 (6)	2994 (4)	119 (3)	*
C(100)	2964 (23)	2041 (13)	1380 (11)	22 (5)
C(111)	−206 (26)	2781 (15)	1617 (13)	40 (6)
O(111)	−940 (20)	3127 (11)	1918 (10)	52 (5)
C(112)	−378 (27)	1305 (14)	857 (14)	41 (6)
O(112)	−1144 (22)	761 (12)	728 (11)	64 (6)
C(121)	1913 (25)	4110 (14)	1643 (13)	37 (6)
O(121)	1153 (23)	4628 (13)	1708 (12)	69 (6)
C(122)	4771 (27)	3980 (16)	1859 (15)	47 (7)
O(122)	5751 (23)	4402 (13)	1972 (12)	66 (6)
C(131)	5880 (33)	908 (16)	1779 (17)	58 (8)
O(131)	6333 (26)	264 (14)	1774 (13)	82 (7)
C(132)	6073 (24)	2341 (14)	993 (12)	30 (5)
O(132)	6643 (22)	2614 (12)	583 (11)	62 (6)
C(133)	6376 (29)	2414 (17)	2449 (14)	49 (7)
O(133)	7123 (24)	2700 (13)	2956 (12)	72 (7)
C(141)	2536 (27)	466 (13)	694 (13)	36 (6)
O(141)	2315 (21)	−145 (11)	926 (10)	55 (5)
C(142)	4439 (23)	1072 (14)	−34 (13)	31 (5)
O(142)	5371 (21)	827 (12)	−255 (11)	63 (6)
C(143)	1596 (26)	1248 (15)	−524 (12)	40 (6)
O(143)	787 (23)	1101 (13)	−1056 (11)	65 (6)
C(151)	2909 (28)	764 (13)	2491 (14)	40 (6)
O(151)	2940 (25)	72 (13)	2542 (12)	76 (7)
C(152)	1373 (22)	1902 (13)	2891 (12)	26 (5)
O(152)	416 (20)	1871 (12)	3142 (10)	58 (5)
C(153)	4314 (25)	1925 (15)	3364 (12)	41 (6)
O(153)	5205 (19)	1989 (11)	3881 (10)	46 (5)
O(160)	3326 (15)	2621 (8)	−16 (8)	24 (3)
O(161)	3689 (17)	4127 (10)	86 (9)	35 (4)
C(161)	3627 (34)	4271 (19)	−679 (17)	59 (8)
O(170)	1288 (15)	3545 (8)	−78 (8)	23 (3)
O(171)	−589 (18)	2643 (10)	−672 (9)	35 (4)
C(171)	−1882 (34)	2152 (18)	−867 (16)	57 (8)
C(172)	−1641 (36)	4211 (19)	−330 (17)	63 (9)
O(172)	−1032 (18)	3618 (10)	258 (9)	35 (4)
Os(24)	4839 (1)	2243 (1)	6094 (1)	*
Os(22)	1062 (1)	2850 (1)	5637 (1)	*
Os(21)	3310 (1)	3485 (1)	6755 (1)	*
Os(23)	2274 (1)	1283 (1)	5889 (1)	*
Os(25)	1569 (1)	2181 (1)	7083 (1)	*
P(26)	2575 (7)	3223 (3)	4945 (3)	*
P(27)	3819 (7)	4417 (4)	5994 (3)	*

Table 1 (*cont.*)

	x	*y*	*z*	*U*
C(200)	2832 (23)	2376 (13)	6335 (11)	21 (4)
C(241)	5566 (28)	1818 (15)	7008 (13)	41 (6)
O(241)	6129 (26)	1589 (14)	7567 (12)	78 (7)
C(242)	5639 (29)	1390 (15)	5619 (14)	46 (7)
O(242)	6046 (25)	878 (13)	5306 (12)	74 (7)
C(243)	6488 (30)	2871 (18)	6174 (17)	59 (8)
O(243)	7496 (28)	3267 (15)	6253 (14)	93 (8)
O(221)	−416 (29)	2351 (17)	4944 (14)	51 (8)
C(221)	−1243 (22)	2047 (12)	4474 (11)	59 (6)
C(222)	179 (27)	3869 (14)	5582 (14)	41 (6)
O(222)	−385 (23)	4476 (13)	5601 (12)	67 (6)
C(211)	4882 (25)	3653 (15)	7535 (13)	37 (6)
O(211)	5834 (24)	3709 (14)	8035 (12)	75 (7)
C(212)	2231 (22)	4255 (12)	7090 (12)	24 (5)
O(212)	1492 (21)	4718 (11)	7276 (11)	58 (5)
C(231)	2525 (28)	1043 (15)	4942 (11)	39 (6)
O(231)	2645 (21)	916 (11)	4362 (10)	52 (5)
C(232)	445 (26)	773 (17)	5704 (15)	48 (7)
O(232)	−687 (23)	516 (13)	5541 (12)	71 (6)
C(233)	3280 (29)	353 (15)	6306 (14)	44 (7)
O(233)	3835 (25)	−223 (13)	6551 (12)	76 (7)
C(251)	244 (33)	1349 (18)	7159 (17)	58 (8)
O(251)	−281 (38)	751 (19)	7278 (19)	139 (12)
C(252)	2962 (31)	1852 (19)	7883 (15)	58 (8)
O(252)	3823 (27)	1698 (15)	8389 (14)	88 (8)
C(253)	785 (31)	2895 (17)	7670 (16)	53 (8)
O(253)	204 (28)	3351 (16)	7955 (14)	92 (8)
O(260)	3916 (17)	2710 (9)	5051 (8)	31 (4)
O(261)	2071 (18)	3306 (10)	4101 (9)	35 (4)
C(261)	771 (28)	3697 (16)	3766 (14)	41 (6)
O(270)	3183 (16)	4164 (9)	5142 (8)	29 (4)
O(271)	5382 (20)	4591 (11)	5923 (10)	48 (5)
C(271)	6392 (31)	5031 (17)	6557 (15)	50 (7)
O(272)	3164 (18)	5271 (10)	6090 (9)	36 (4)
C(272)	3411 (33)	5956 (18)	5646 (16)	54 (8)

* Anisotropic thermal parameters have been deposited.

Table 2. *Selected bond lengths* (Å)

Molecule 1		Molecule 2	
Os(11)–Os(12)	2·831 (3)	Os(21)–Os(22)	2·843 (3)
Os(11)–Os(14)	2·951 (3)	Os(21)–Os(24)	2·963 (3)
Os(11)-Os(15)	2·920 (3)	Os(21)–Os(25)	2·903 (4)
Os(12)–Os(13)	2·861 (3)	Os(22)–Os(23)	2·857 (3)
Os(12)–Os(15)	2·927 (3)	Os(22)–Os(25)	2·902 (3)
Os(13)–Os(14)	2·911 (3)	Os(23)–Os(24)	2·899 (3)
Os(13)–Os(15)	2·866 (4)	Os(23)–Os(25)	2·890 (4)
C(100)–Os(11)	1·983 (24)	C(200)–Os(21)	1·992 (22)
C(100)–Os(12)	2·096 (23)	C(200)–Os(22)	2·078 (22)
C(100)–Os(13)	2·004 (24)	C(200)–Os(23)	1·998 (22)
C(100)–Os(14)	2·141 (24)	C(200)–Os(24)	2·120 (26)
C(100)–Os(15)	2·064 (24)	C(200)–Os(25)	2·107 (26)
P(16)–Os(12)	2·272 (8)	P(26)–Os(22)	2·277 (9)
P(17)–Os(11)	2·274 (8)	P(27)–Os(21)	2·261 (8)
O(160)–Os(14)	2·113 (16)	O(260)–Os(24)	2·127 (17)
P(16)–P(160)	1·532 (17)	P(26)–P(260)	1·537 (18)
P(16)–O(170)	1·656 (16)	P(26)–O(270)	1·667 (17)
P(17)–O(170)	1·613 (18)	P(27)–O(270)	1·627 (16)

Mean bond lengths (averaged over both molecules) (Å)

C–O	1·151	P–O(methyl)	1·570
Os–C	1·884	O–C(methyl)	1·479

Table 3. *Selected mean bond angles* (°), *averaged over both molecules*

Os–C–O	175·5	(O)C–Os–C(O)	93·0
P–O–Os	120·6	P–O–P	118·4
O–P–O	102·5	P–O–C	121·3
Os(1)–C–Os(3)	176·6	Os(2)–C–Os(4)	124·6
Os(2)–C–Os(5)	88·6	Os(4)–C–Os(5)	146·7

The other Os–C–Os angles (*i.e.* the axial to equatorial angles in a trigonal bipyramid) all fall within the range 88·2 to 91·2°.

neutral-atom scattering factors and the weighting scheme $w = [\sigma^2(F) + 0{\cdot}000355F^2]^{-1}$ were employed. The refinement converged to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}F_o = 0{\cdot}043$ and $R = 0{\cdot}045$. Positional and isotropic thermal parameters are presented in Table 1, selected bond lengths and angles in Tables 2 and 3.*

Discussion. The Os_5C cluster geometry is related to the tetragonal pyramid predicted by Wade's (1975) theory for a 74-electron system, and probably present in $Os_5C(CO)_{15}$ (Eady, Johnson & Lewis, 1975). The two P atoms replace carbonyls, but the presence of the extra bond to O and the H atom makes $HOs_5C(CO)_{13}$-$[OP(OCH_3)OP(OCH_3)_2]$ a 76-electron cluster, consistent with the breaking of one Os–Os bond. Thus one edge of the square pyramid [Os(12)···Os(14) 3·74; Os(22)···Os(24) 3·72 Å] becomes much longer than a normal Os–Os bond; these two Os atoms are bridged by a P–O unit, making an Os–C–Os–P–O– five-membered ring. An analogous four-membered Ru–P–O–Ru– ring has been reported (Bruce, Howard, Nowell, Shaw & Woodward, 1972). Within the rela-

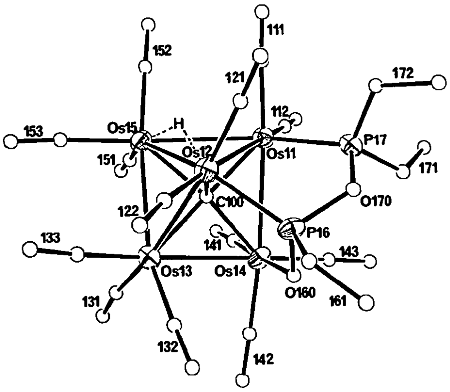

Fig. 1. Molecule 1, showing 50% probability ellipsoids for the anisotropic atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33386 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

tively large experimental uncertainties, the carbide lies on the line joining Os(1) and Os(3), and in the plane of the other three Os atoms. The cluster may thus be described as a trigonal bipyramid, distorted considerably from equilateral geometry in the equatorial plane (as shown by the angles given in Table 3).

Potential-energy calculations based on the ligand configuration indicate that the hydride bridges the edge Os(12)–Os(15) [Os(22)–Os(25) in the second molecule]; suitable holes in the close-packed carbonyl arrangement can be seen in Figs. 1 and 2. This assignment is consistent with the relatively large P–H coupling (36 Hz) observed in the NMR spectrum; the H and P atoms are both bonded to the same Os. Unusually, the hydride does not bridge the longest Os–Os bond. Except for the orientation of one of the OCH_3 groups, the overall molecular geometry is very similar for the two independent molecules. However, the bond lengths involving Os(25) are in some cases significantly different from those involving Os(15) [*e.g.* Os(25)–Os(22) 2·902 (3), Os(15)–Os(12) 2·927 (3), Os(25)–Os(23) 2·890 (4), Os(15)–Os(13) 2·866 (4) Å]. Os(25) is relatively anisotropic, and the orientation of C(251)–O(251) is significantly different from that of C(151)–O(151). These observations are all consistent with some disorder of the bridging hydride in the second molecule, *i.e.* with the hydride bridging Os(25)–Os(23) rather than Os(25)–Os(22) in some molecules. This type of disorder might well be fluxional on an NMR time scale in solution, *i.e.* only an average hydride chemical shift and P–H coupling would be seen.

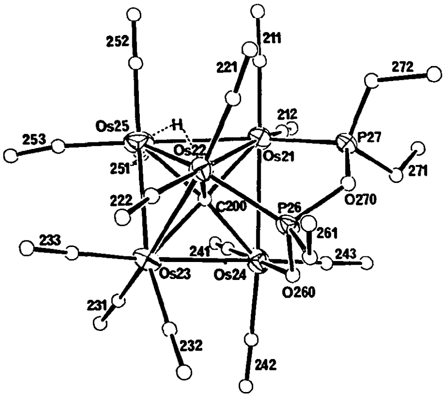

Fig. 2. Molecule 2, showing 50% probability ellipsoids for the anisotropic atoms.

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Carbidotetradecacarbonylhydrido(dimethyl phosphonato)pentaosmium, $HOs_5C(CO)_{14}[OP(OCH_3)_2]$

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Abstract. $C_{17}H_7O_{17}POs_5$, monoclinic, $P2_1/n$, a = 9·200 (4), b = 31·809 (13), c = 9·486 (4) Å, β = 103·13 (3)°, U = 2703·4 Å^3, Z = 4, D_x = 3·60 g cm^{-3}, μ(Mo $K\alpha$) = 235·4 cm^{-1}. The structure was refined to an R of 0·039 for 4781 unique diffractometer data. The Os atoms define a distorted trigonal bipyramid, with a carbide lying in the equatorial plane. The phosphonate ligand coordinates to two Os atoms to form an Os–P–O–Os linkage.

Introduction. The pyrolysis of $Os_3(CO)_{11}[P(OCH_3)_3]$ yields a number of pentanuclear clusters containing