

1,1,1,2,2,2,2,3,3,3,3-Undecacarbonyl(trimethyl phosphite)-triangulo-triosmium

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Abstract. $\text{Os}_3(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$, monoclinic, $P2_1/c$, $a = 16.552$ (5), $b = 7.945$ (5), $c = 18.030$ (6) Å, $\beta = 113.32$ (8)°, $U = 2177.4$ Å³, $Z = 4$, $D_x = 2.92$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 175.86$ cm⁻¹. The structure was refined to an R of 0.029 for 2781 unique diffractometer data. The carbonyl groups are all terminal, and the ligands define a 'twinned cuboctahedron' around the Os triangle. The trimethyl phosphite group coordinates in an equatorial position.

Introduction. In the structure of $\text{Os}_3(\text{CO})_{12}$ (Churchill & De Boer, 1977), the polyhedron whose vertices are defined by the carbonyl ligands is a 'twinned cuboctahedron' (Wells, 1962). The introduction of a bulky group into this molecule might distort the ligand polyhedron into an icosahedron, as found in $\text{Fe}_3(\text{CO})_{12}$ (Cotton & Troup, 1974). The single-crystal X-ray determination was undertaken to study the nature and extent of any such distortion.

Pale-yellow crystals were grown by slow evaporation from a hexane/dichloromethane mixture. 3306 intensities were measured on an automated Stoe STADI-2 two-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation, and a crystal in the form of an elongated rectangular block $0.17 \times 0.10 \times 0.14$ mm (layers $0-h, 10, l$). L_p and empirical absorption corrections were applied (based on an azimuthal scan of the 040 reflection). Unit-cell dimensions were obtained by a least-squares fit to diffractometer zero-layer ω -angle measurements. Equivalent reflections were then merged to yield 2781 unique observed data [$I > 1.5\sigma(I)$].

The Os atom positions were located by multi-resolution Σ_2 sign expansion, and the C, O and P atoms by difference syntheses; no attempt was made to locate the H atoms. The structure was refined by full-matrix least squares with complex neutral-atom scattering factors and the weighting scheme $w = 1/[\sigma^2(F) + 0.0008|F_o|^2]$. The parameters included anisotropic temperature factors for the Os, P, and the phosphite C and O atoms, interlayer scale factors, and an empirical extinction parameter x which refined to 0.00035 (2); F_c is multiplied by $(1 - 0.0001xF_c^2/\sin \theta)$. The constraint $U_{22} = (U_{11} + U_{33})/2$ was applied to reduce correlation involving interlayer scale factors. The refinement converged to $R' = \Sigma w^{1/2} \Delta / \Sigma w^{1/2} |F_o| = 0.031$. The

final atomic coordinates and isotropic thermal parameters are given in Table 1, while the resulting bond lengths and angles are listed in Tables 2 and 3 respectively.*

Discussion. Each of the Os atoms has a distorted octahedral coordination geometry. All the carbonyl groups

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33095 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors (Å² $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Os(1)	1585 (1)	2406 (1)	-101 (1)	*
Os(2)	3046 (1)	263 (1)	-5 (1)	*
Os(3)	1411 (1)	155 (1)	-1416 (1)	*
P(1)	4115 (2)	956 (4)	1220 (2)	*
O(1)	5047 (5)	383 (10)	1264 (5)	*
O(2)	4098 (6)	70 (10)	1994 (5)	*
O(3)	4226 (6)	2860 (10)	1526 (5)	*
C(1)	5844 (9)	601 (18)	2008 (9)	*
C(2)	3450 (10)	479 (18)	2332 (9)	*
C(3)	4328 (10)	4248 (17)	1059 (8)	*
C(11)	2097 (7)	4074 (15)	-549 (7)	31 (2)
O(11)	2361 (6)	5173 (11)	-809 (6)	46 (2)
C(12)	1179 (7)	715 (14)	411 (7)	30 (2)
O(12)	911 (6)	-190 (12)	773 (6)	54 (3)
C(13)	1995 (8)	3609 (15)	899 (8)	36 (3)
O(13)	2238 (7)	4282 (13)	1499 (6)	54 (2)
C(14)	422 (8)	3304 (15)	-666 (7)	32 (3)
O(14)	-253 (7)	3865 (13)	-979 (6)	60 (3)
C(21)	3457 (8)	1867 (14)	-568 (7)	32 (3)
O(21)	3793 (7)	2779 (12)	-876 (6)	50 (2)
C(22)	2598 (8)	-1414 (16)	510 (8)	39 (3)
O(22)	2432 (7)	-2432 (13)	871 (7)	60 (3)
C(23)	3694 (8)	-1465 (14)	-228 (7)	32 (3)
O(23)	4101 (7)	-2547 (12)	-325 (6)	55 (3)
C(31)	1779 (8)	1974 (15)	-1902 (8)	35 (3)
O(31)	1932 (7)	3047 (13)	-2263 (7)	55 (3)
C(32)	1015 (8)	-1552 (14)	-881 (7)	31 (2)
O(32)	724 (7)	-2600 (13)	-622 (7)	58 (3)
C(33)	1841 (8)	-1461 (15)	-1953 (8)	35 (3)
O(33)	2089 (7)	-2388 (13)	-2280 (7)	58 (3)
C(34)	240 (8)	430 (15)	-2182 (8)	34 (3)
O(34)	-454 (7)	629 (14)	-2659 (7)	61 (3)

* Anisotropic thermal parameters for these atoms have been deposited.

are terminal, and the trimethyl phosphite ligand coordinates in an equatorial position on Os(2). The three metal atoms define an equilateral triangle with an average Os—Os distance of 2.897 (10) Å. This value is 0.02 Å longer than the mean metal—metal distance [2.877 (3) Å] recently reported for Os₃(CO)₁₂ (Churchill & De Boer, 1977), and may be due to the presence of the bulky phosphite ligand causing an expansion of the ligand packing; the Os₃ triangle also expands to maintain the optimum overall molecular geometry. There should then be a compensating

Table 2. Bond lengths (Å)

Os(2)—Os(1)	2.908 (4)	O(2)—P(1)	1.573 (11)
Os(3)—Os(1)	2.892 (4)	O(3)—P(1)	1.596 (10)
Os(3)—Os(2)	2.890 (4)	C(1)—O(1)	1.472 (17)
C(11)—Os(1)	1.917 (14)	C(2)—O(2)	1.465 (16)
C(12)—Os(1)	1.896 (14)	C(3)—O(3)	1.437 (16)
C(13)—Os(1)	1.911 (15)	O(11)—C(11)	1.155 (15)
C(14)—Os(1)	1.922 (14)	O(12)—C(12)	1.170 (15)
C(21)—Os(2)	1.914 (14)	O(13)—C(13)	1.129 (15)
C(22)—Os(2)	1.931 (15)	O(14)—C(14)	1.126 (15)
C(23)—Os(2)	1.881 (14)	O(21)—C(21)	1.178 (15)
C(31)—Os(3)	1.910 (15)	O(22)—C(22)	1.139 (16)
C(32)—Os(3)	1.923 (14)	O(23)—C(23)	1.147 (15)
C(33)—Os(3)	1.908 (15)	O(31)—C(31)	1.161 (16)
C(34)—Os(3)	1.895 (14)	O(32)—C(32)	1.149 (15)
P(1)—Os(2)	2.285 (5)	O(33)—C(33)	1.118 (16)
O(1)—P(1)	1.580 (10)	O(34)—C(34)	1.142 (15)

Table 3. Bond angles (°)

Os(3)—Os(1)—Os(2)	59.8 (1)	C(32)—Os(3)—Os(1)	88.2 (4)
Os(3)—Os(2)—Os(1)	59.8 (1)	C(32)—Os(3)—Os(2)	88.1 (4)
Os(2)—Os(3)—Os(1)	60.4 (1)	C(32)—Os(3)—C(31)	175.7 (5)
P(1)—Os(2)—Os(1)	102.9 (2)	C(33)—Os(3)—Os(1)	153.7 (4)
P(1)—Os(2)—Os(3)	162.8 (1)	C(33)—Os(3)—Os(2)	93.4 (5)
C(11)—Os(1)—Os(2)	86.1 (4)	C(33)—Os(3)—C(31)	91.5 (6)
C(11)—Os(1)—Os(3)	89.9 (5)	C(33)—Os(3)—C(32)	92.8 (6)
C(12)—Os(1)—Os(2)	90.2 (4)	C(34)—Os(3)—Os(1)	105.5 (5)
C(12)—Os(1)—Os(3)	91.2 (4)	C(34)—Os(3)—Os(2)	165.8 (4)
C(12)—Os(1)—C(11)	174.9 (5)	C(34)—Os(3)—C(31)	89.9 (6)
C(13)—Os(1)—Os(2)	105.1 (5)	C(34)—Os(3)—C(32)	89.6 (6)
C(13)—Os(1)—Os(3)	164.8 (4)	C(34)—Os(3)—C(33)	100.7 (6)
C(13)—Os(1)—C(11)	90.0 (6)	O(1)—P(1)—Os(2)	110.2 (5)
C(13)—Os(1)—C(12)	87.6 (6)	O(2)—P(1)—Os(2)	118.1 (5)
C(14)—Os(1)—Os(2)	152.0 (4)	O(2)—P(1)—O(1)	100.8 (6)
C(14)—Os(1)—Os(3)	92.3 (5)	O(3)—P(1)—Os(2)	120.1 (4)
C(14)—Os(1)—C(11)	92.1 (6)	O(3)—P(1)—O(1)	106.2 (6)
C(14)—Os(1)—C(12)	92.8 (6)	O(3)—P(1)—O(2)	99.1 (6)
C(14)—Os(1)—C(13)	102.8 (6)	C(1)—O(1)—P(1)	121.1 (9)
C(21)—Os(2)—Os(1)	92.3 (4)	C(2)—O(2)—P(1)	122.9 (9)
C(21)—Os(2)—Os(3)	87.6 (4)	C(3)—O(3)—P(1)	123.3 (9)
C(21)—Os(2)—P(1)	92.9 (5)	O(11)—C(11)—Os(1)	174.4 (10)
C(22)—Os(2)—Os(1)	87.9 (5)	O(12)—C(12)—Os(1)	172.8 (10)
C(22)—Os(2)—Os(3)	89.9 (5)	O(13)—C(13)—Os(1)	178.3 (11)
C(22)—Os(2)—P(1)	90.0 (5)	O(14)—C(14)—Os(1)	177.9 (11)
C(22)—Os(2)—C(21)	177.0 (5)	O(21)—C(21)—Os(2)	173.1 (10)
C(23)—Os(2)—Os(1)	161.1 (4)	O(22)—C(22)—Os(2)	172.2 (12)
C(23)—Os(2)—Os(3)	101.8 (5)	O(23)—C(23)—Os(2)	176.5 (11)
C(23)—Os(2)—P(1)	95.4 (5)	O(31)—C(31)—Os(3)	173.5 (11)
C(23)—Os(2)—C(21)	91.2 (6)	O(32)—C(32)—Os(3)	174.4 (11)
C(23)—Os(2)—C(22)	87.6 (6)	O(33)—C(33)—Os(3)	178.7 (12)
C(31)—Os(3)—Os(1)	87.8 (5)	O(34)—C(34)—Os(3)	177.6 (12)
C(31)—Os(3)—Os(2)	91.4 (5)		

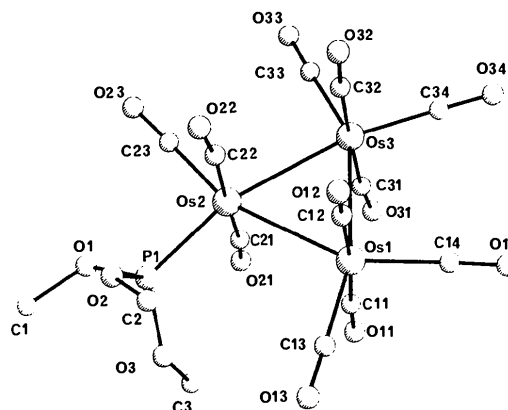


Fig. 1. Molecular structure and numbering scheme.

shortening of the Os—P and Os—C bonds. The Os—P distance is significantly shorter than the single-bond values of 2.33 and 2.35 Å in [Os₃H(CO)₉(PPh₃)(PPh₂C₆H₄)] (Bradford, Nyholm, Gainsford, Guss, Ireland & Mason, 1972). None of the Os—C or C—O bond lengths deviate from their respective means of 1.910 (14) and 1.147 (20) Å by more than 2.6σ, and may be considered as essentially equal. This Os—C distance is 0.019 Å shorter than the mean value [1.929 (6) Å] in the dodecacarbonyl. The bond parameters in the phosphite ligand are close to their idealized values.

In the molecular structure (Fig. 1) the ligand polyhedron approximates to a 'twinned cuboctahedron', and there is no significant distortion towards icosahedral geometry, where two of the ligands would be bridging. The cone angle for P(OCH₃)₃ is 107° (Tolman, 1977), so it seems that a bulky ligand with a wider cone angle, or replacement of several carbonyls by these ligands, would be required to expand the ligand polyhedron sufficiently to permit an icosahedral arrangement.

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