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Structure of Dibromodicarbonylbis(triphenylphosphine)osmium(II)

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Abstract. $[OsBr_2(CO)_2[P(C_6H_5)_3]_2]$, $M_r = 930{\cdot}61$, monoclinic, $C2/c$, $a = 24{\cdot}332\ (2)$, $b = 9{\cdot}568\ (2)$, $c = 16{\cdot}207\ (1)$ Å, $\beta = 115{\cdot}882\ (6)^\circ$, $V = 3394{\cdot}7\ (7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}82$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 62{\cdot}14$ cm^{-1}, $F(000) = 1800$, $T = 295$ K, $R = 0{\cdot}035$, 2994 unique reflections measured, 2186 observed ($I > 3\sigma I$). Preparation by reaction of bis(tetra-*n*-butylammonium) hexabromoosmate(IV) with triphenylphosphine in refluxing acetic acid/acetic anhydride. The molecule contains an Os atom in octahedral coordination with three disordered Br/CO atoms/molecules, a single ordered CO molecule and two *trans* triphenylphosphine groups bonded to Os through their P atoms.

Experimental. Schlenk apparatus used for preparation. Mixed solvent prepared by combining acetic acid (20 ml) and acetic anhydride (3 ml) and refluxing under N_2 for 2 h. Bis(tetra-*n*-butylammonium) hexabromoosmate(IV) (0·8898 g, 0·772 mmol) and triphenylphosphine (1·7875 g, 6·82 mmol) combined as solids in second flask and evacuated for 30 min. Solvent and solids combined and refluxed under N_2 for 18 h. White–yellow crystals washed with CH_2Cl_2 to obtain white solid and yellow solution. Volume of yellow solution reduced by half to dark-brown solution, hexane layered over solution, brown crystals obtained after 3–4 d. Data collected from a nearly orthogonal, 0·30 × 0·19 × 0·16 mm crystal fragment cut from a brown, platy, parent crystal. Rigaku AFC-5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speed 10° min^{-1}, maximum of three scan repetitions to obtain $\sigma F/F < 0{\cdot}10$, $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}60$ Å^{-1}. Lattice parameters from least-squares fit of 25 strong ($F_o > 50{\cdot}0$) reflections in 2θ range 35–44°. 3273 reflections measured (h 0 to 28, k 0 to 11, l −19 to 19), 279 redundant and/or systematically extinct reflections deleted, data set comprised 2994 unique reflections. 2186 reflections considered observed ($I > 3\sigma I$), $R_{\text{int}} = 0{\cdot}2\%$ for 83 equivalent reflections. Three standard reflections ($\bar{2}00$, $\bar{6}02$ and $\bar{1}\bar{1}1$), measured at 100 reflection intervals, varied by 0·1, −0·8 and −0·4% respectively; no decay correction applied. Data corrected for Lorentz, polarization and absorption (empirical ψ-scan method, five reflections, transmission range 0·86–1·0). Os-atom position from Patterson map; Br, P, CO and phenyl C sites from Fourier and difference Fourier syntheses. Full-matrix least-squares refinement of F magnitudes, atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974), extinction corrections not applied. Unusually large thermal parameters of Br atoms indicated disorder, site-occupancy refinement of Br positions led to occupancy values given in Table 1. Subsequent difference Fourier synthesis revealed peaks along the Os–Br vectors, on either side of the Br sites, whose bond lengths corresponded to those of CO. Two CO molecules added to the model with fixed (1·0−occupancy of corresponding Br atom) occupancy factors, refinement continued. Partially occupied C and O sites refined to unreasonable positions, due to apparent limitations of the least-squares method in handling disordered atomic sites which are in close proximity (Br—O and Br—C distances less than 0·5 Å in the disordered sites), problem aggravated by large disparity in electron density between Br and CO. Positions of C and O in disordered sites calculated and fixed assuming locations along the Os–Br vectors, Os—C and Os—O distances fixed at values obtained for the ordered CO site, B's fixed at 4·0 Å^2. Structure again refined to convergence, H-atom positions plus disordered C and O sites regenerated, refinement repeated. H and CO generation/refinement continued until parameter shifts became insignificant. Final refinement was performed with 201 variables including a scale factor, positional parameters, and anisotropic thermal parameters for all non-H atoms (with the exception of the disordered CO atoms whose positions and B's were fixed). Phenyl-ring H atoms were placed in geometrically correct positions (C—H = 0·95 Å) and fixed, B's of H atoms were set at $1{\cdot}2 \times B_{\text{eq}}$ of associated C atom. Convergence yielded $R = 0{\cdot}035$, $wR = 0{\cdot}046$ $[w = 1/\sigma^2(|F_o|)]$, $S = 1{\cdot}12$

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Table 1. *Positional and equivalent isotropic thermal parameters for the non*-H *atoms and their e.s.d.'s*

$B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha)$.

	x	y	z	Occupancy	B_{eq}(Å^2)
Os	0	0·17295 (4)	$\frac{1}{4}$	0·50	2·16 (2)
Br(1)	0	0·4379 (2)	$\frac{1}{4}$	0·37	3·78 (7)
Br(2)	−0·05651 (7)	0·1513 (2)	0·0780 (1)	0·63	4·52 (7)
P(1)	−0·09425 (9)	0·1711 (2)	0·2666 (1)	1·00	2·39 (7)
O(1)	0	−0·143 (2)	$\frac{1}{4}$	0·50	7·9 (7)
C(1)	−0·0907 (4)	0·2342 (8)	0·3753 (6)	1·00	2·6 (3)
C(2)	−0·0716 (6)	0·369 (1)	0·4029 (8)	1·00	4·9 (5)
C(3)	−0·0708 (7)	0·424 (1)	0·4820 (9)	1·00	6·2 (6)
C(4)	−0·0889 (5)	0·346 (1)	0·5351 (7)	1·00	5·0 (5)
C(5)	−0·1045 (7)	0·212 (1)	0·5129 (8)	1·00	6·2 (6)
C(6)	−0·1082 (5)	0·155 (1)	0·4315 (7)	1·00	4·6 (4)
C(7)	−0·1218 (4)	−0·0079 (9)	0·2575 (6)	1·00	2·8 (3)
C(8)	−0·1717 (5)	−0·054 (1)	0·1821 (7)	1·00	4·1 (4)
C(9)	−0·1870 (6)	−0·197 (1)	0·1726 (8)	1·00	6·1 (6)
C(10)	−0·1530 (8)	−0·288 (1)	0·238 (1)	1·00	6·2 (6)
C(11)	−0·1038 (6)	−0·245 (1)	0·315 (1)	1·00	5·3 (5)
C(12)	−0·0873 (5)	−0·106 (1)	0·3246 (7)	1·00	4·0 (4)
C(13)	−0·1595 (4)	0·2712 (9)	0·1856 (6)	1·00	2·6 (3)
C(14)	−0·1568 (4)	0·352 (1)	0·1168 (6)	1·00	3·3 (3)
C(15)	−0·2075 (5)	0·428 (1)	0·0573 (7)	1·00	4·1 (4)
C(16)	−0·2612 (4)	0·421 (1)	0·0669 (7)	1·00	4·7 (4)
C(17)	−0·2640 (5)	0·342 (1)	0·1357 (8)	1·00	5·9 (5)
C(18)	−0·2128 (5)	0·270 (1)	0·1953 (8)	1·00	5·1 (5)
C(19)	0	−0·029 (1)	$\frac{1}{4}$	0·50	3·1 (5)
C(20)*	−0·0433	0·1564	0·1181	0·37	4·0
C(21)*	0	0·3751	$\frac{1}{4}$	0·13	4·0
O(2)*	−0·0677	0·1471	0·0440	0·37	4·0
O(3)*	0	0·4885	$\frac{1}{4}$	0·13	4·0

* Calculated atomic coordinates; fixed isotropic temperature factor.

and $(\Delta/\sigma)_{max} = 0{\cdot}04$. Final difference Fourier syntheses showed $\Delta\rho_{max} = 0{\cdot}90$ e Å^{-3}, located near the Os site, and $\Delta\rho_{min} = -1{\cdot}07$ e Å^{-3}, located 0·3 Å from O(2). Atomic coordinates and isotropic temperature factors are given in Table 1, while Table 2 presents selected interatomic distances and angles.* The drawing of the molecule (Fig. 1) shows the disordered Br/CO sites as if the Br atoms and CO molecules are present simultaneously, an obviously impossible configuration; the drawing was prepared in this manner so that all of the atomic positions could be shown. All computer programs are from the *TEXSAN* crystal-structure-analysis package (Molecular Structure Corporation, 1985).

Table 2. *Selected bond distances* (Å), *bond angles* (°), *and their e.s.d.'s*

Os	P(1)		2·423 (2)	O(1)	C(19)		1·09 (2)
Os	Br(1)		2·535 (2)	P(1)	C(1)		1·828 (8)
Os	Br(2)		2·522 (2)	P(1)	C(7)		1·821 (9)
Os	C(19)		1·93 (1)	P(1)	C(13)		1·828 (8)
C(19)	Os	P(1)	89·58 (5)	Br(2)	Os	Br(1)	94·70 (4)
C(19)	Os	Br(2)	85·30 (4)	C(7)	P(1)	C(1)	104·5 (4)
C(19)	Os	Br(1)	180·00	C(7)	P(1)	C(13)	105·1 (4)
P(1)	Os	P(1)′	179·17 (9)	C(7)	P(1)	Os	109·3 (3)
P(1)	Os	Br(2)	92·09 (6)	C(1)	P(1)	C(13)	100·4 (4)
P(1)	Os	Br(2)′	87·84 (6)	C(1)	P(1)	Os	117·1 (3)
P(1)	Os	Br(1)	90·42 (5)	C(13)	P(1)	Os	119·0 (3)
Br(2)	Os	Br(2)′	170·60 (9)	O(1)	C(19)	Os	180·00

Primed atoms are related to unprimed by axis of twofold symmetry.

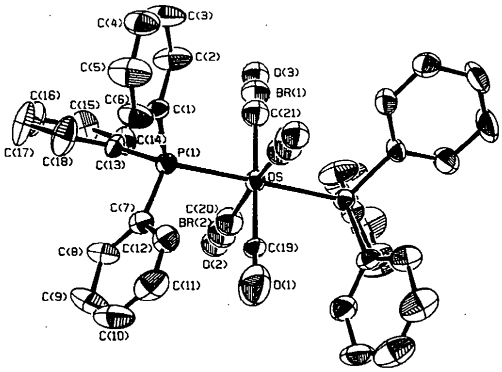

Fig. 1. Molecular structure and numbering scheme; thermal ellipsoids at the 50% probability level. Atoms O(3), Br(1), C(21), Os, C(19) and O(1) lie on a twofold axis of symmetry.

Related literature. This compound is one of a group derived from reaction of the hexabromoosmate(IV) ion with triphenylphosphine (Hinckley, Matusz, Kibala & Robinson, 1987).

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* Lists of structure factors, anisotropic thermal parameters, distances and angles involving the phenyl rings, H-atom coordinates, intermolecular distances, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44887 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.