Crystal Structure of Tetrabromotris(dimethylphenylphosphine)molybdenum(IV)

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Summary In tetrabromotris(dimethylphenylphosphine)-molybdenum(IV), the metal atom has a capped octahedral (C_{3v}) environment with a bromine atom occupying the unique capping position.

From our study of seven-co-ordinate complexes by *X*-ray analysis, we had observed that molecules, such as $Mo(CO)_2(dpe)Br_2$,[1] $Mo(CO)_2(dam)_2Br_2$,[2] $[W(CO)_4Br_3]^-$,[3] and $W(CO)_3(dam)I_2$,[4]† which contained two or three, bromine or iodine atoms had capped octahedral symmetry with the large halogen atoms occupying positions in the uncapped face to minimise ligand ··· ligand repulsions. (In that face, Br–M–Br, I–M–I angles are *ca.* 90°.) We were, however, uncertain as to the configuration of a molecule which contained four bromine atoms in the co-ordination sphere and accordingly we have determined the structure of $Mo(PPhMe_2)_3Br_4$, (I).

Brown-orange crystals were prepared by the published method.[5] Crystals were trigonal, spacegroup $P\bar{3}$, with $a = 15{\cdot}624(9)$, $c = 7{\cdot}578(6)$ Å, $U = 1602{\cdot}0$ Å^3, $M = 829{\cdot}6$ for $C_{24}H_{33}P_3Br_4Mo$, $Z = 2$.

The intensities of 793 independent reflections above background ($2\theta < 45°$) were measured on a G.E. XRD 5 manual diffractometer by the stationary-crystal–stationary-counter method. The structure has been solved by

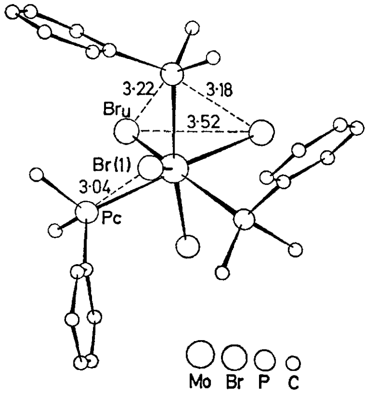

Figure. *Compound* (I). *Ligand ··· ligand contacts* <4·0 Å *are shown.*

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† Abbreviations: dpe is 1,2-bis(diphenylphosphino)ethane, dam is bis(diphenylarsino)methane.

Patterson and Fourier methods and refined (Mo, Br, P anisotropic; C isotropic) to R 0·08. The molecule has crystallographic C_3 symmetry but the co-ordination sphere of molybdenum can be considered as capped octahedral C_{3v} (see Figure). The angles for the molecule are Br(1)–Mo–P_c 74·5(2), Br(1)–Mo–Br_u 127·4(1), P_c–Mo–P_c 113·2(2), Br_u–Mo–Br_u 86·9(2), $(P_c\text{–Mo–}Br_u)_{trans}$ 158·0(2), $(P_c\text{–Mo–}Br_u)_{cis}$ 76·5(1), 78·0(1)°.

The structure falls into the pattern established[1–4] for such polyhedra, in that three bromine atoms occupy the uncapped face [Mo–Br_u 2·560(5) Å] where steric effects are lowest and three phosphorus atoms the capped face [Mo–P_c 2·580(7) Å]. The fourth bromine atom occupies the unique capping position [Mo–Br(1) 2·425(7) Å], which is farthest from the uncapped face. This position is more sterically crowded than one in the uncapped face (closest contacts are 3 Br(1) $\cdots$ P_c 3·04 Å and Br_u $\cdots$ P_c 3·18, 3·22 Å respectively) and it can be predicted that a bromine atom would only occupy it when a position in the uncapped face is unavailable, as in (I). Thus, in a seven-co-ordinate complex containing one large ligand, bromine or iodine, it is likely that this atom would occupy a position in the uncapped face. However, this geometry would be akin to a capped trigonal prism[1] with the large atom in the unique capping position. Such a polyhedron has been observed in $Mo(CNR)_6I$.[6]

The bond-lengths in (I) can be compared to those found in the octahedral dichlorotris(diethylphenylphosphine)oxomolybdenum(IV),[7] which are Mo–Cl(*trans* to P) 2·424 Å, Mo–P(*trans* to Cl) 2·522 Å and Mo–P(*trans* to P) 2·567 Å. The Mo–Br_u bond lengths in (I) are equivalent to this Mo–Cl distance (octahedral radii Cl 0·99, Br 1·14 Å), while the Mo–P_c distances are slightly greater than in this compound, possibly due to steric crowding of the capped face. The Mo–Br(1) bond is considerably shorter than the Mo–Br_u bonds by 0·13 Å, a difference for which there is no obvious explanation.

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[1] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626.
[2] M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329.
[3] M. G. B. Drew and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 457.
[4] M. G. B. Drew and A. P. Wolters, to be published.
[5] J. R. Moss and B. L. Shaw, *J. Chem. Soc. (A)*, 1970, 595.
[6] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.
[7] L. M. Muir and K. W. Muir, *J.C.S. Dalton*, 1972, 621