Crystal and Molecular Structure of Tricarbonyliodotris(dimethylphenylphosphino)tungsten(II) Tetraphenylborate

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Crystals of the title compound are triclinic, space group $P1$, $Z = 1$, with $a = 12·216(9)$, $b = 10·100(8)$, $c = 10·287(11)$ Å, $\alpha = 100·55(9)$, $\beta = 104·87(12)$, $\gamma = 89·31(8)$°. The structure was solved by heavy-atom methods from 3866 independent reflections, collected by counter methods and refined to R 0·052. The cation is a seven-co-ordinate monomer; the co-ordination sphere has a (1 : 2 : 2 : 2) C_s geometry which is intermediate between the capped trigonal prism and the capped octahedron though more similar to the former. The iodine atom occupies the unique position [W–I(1) 2·840(1) Å]. This ligand has four nearest neighbours, two carbonyl groups [W–C 1·994(18), 2·000(16) Å] and two phosphorus atoms [W–P 2·576(4), 2·614(5) Å]. The third carbonyl group [W–C 1·933(20) Å] and third phosphorus atom [W–P 2·528(5) Å] are in the remaining edge. The twisting of the phenyl rings in the anion is as expected.

THE geometry of most seven-co-ordinate complexes as determined by X-ray crystallography can be related to one of three ideal types [pentagonal bipyramid, (1 : 5 : 1), D_{5h}, PB; capped trigonal prism, (1 : 4 : 2), C_{2v}, CTP; capped octahedron, (1 : 3 : 3), C_{3v}, CO]. Many attempts have been made [1-4] to predict the geometry of a complex of particular stoicheiometry assuming that one of these polyhedra would be found. Two of the factors thought important are (*a*) a correspondence of stoicheiometry with the symmetry of the polyhedron [1] and (*b*) a requirement that the least-crowded sites in a particular polyhedron are occupied first by multiply-bonded atoms and second by halogen atoms in preference to other ligands.[2,3] We have determined, and report here, the crystal structure of a complex $[W(CO)_3(PMe_2Ph)_3I]^+BPh_4^-$, where (*a*) and (*b*) conflict. The cation (I) has the stoicheiometry 1 : 3 : 3 and thus one might expect its geometry to be CO with iodine in the capping position. This is sterically feasible as a large halogen atom can

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[1] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.

[2] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 1830.

[3] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 2664.

[4] R. B. VanDreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, 1971, **93**, 2887.

occupy this unique position [*cf.* bromine in $MoBr_4(PMe_2Ph)_3$ [5]] and PMe_2Ph ligands can occupy the capped face (also in ref. 5). According to (*b*), however, in a CO a halogen atom would occupy the least sterically crowded site, in the uncapped face, as in *e.g.* $MoBr_2(CO)_2(dam)_2$ [dam = bis(diphenylarsino)methane [6]] and $MoBr_2(CO)_3(dpe)$ [dpe = 1,2-bis(diphenylphosphino)ethane [7]]. These examples contain two halogens; of those structures containing one halogen, most are CTP with one halogen in the unique (and least-crowded) capping position.[3]

EXPERIMENTAL

The complex was prepared by a procedure based on the method of ref. 8. Iodine (0·23 g) in carbon tetrachloride (45 ml) was slowly added (*ca.* 30 min) to a solution of $W(CO)_3(PMe_2Ph)_3$ in carbon tetrachloride (40 ml). The sticky brown solid product was dissolved in methanol (20 ml) and a solution of sodium tetraphenylborate (0·4 g) in methanol (20 ml) was added. The complex $[W(CO)_3(PMe_2Ph)_3I]^+BPh_4^-$ was filtered off, air dried, and recrystallised from toluene–dichloromethane.

Crystal Data.—$C_{51}H_{53}BIO_3P_3W$, $M = 1127{\cdot}8$, Triclinic, $a = 12{\cdot}216(9)$, $b = 10{\cdot}100(8)$, $c = 10{\cdot}287(11)$ Å, $\alpha = 100{\cdot}55(9)$, $\beta = 104{\cdot}87(12)$, $\gamma = 89{\cdot}31(8)°$, $U = 1204{\cdot}6$ Å^3, $D_m = 1{\cdot}57(3)$, $Z = 1$, $D_c = 1{\cdot}55$, $F(000) = 560$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 34·98 cm^{-1}. Space group $P1$.

A crystal with dimensions *ca.* 0·8 × 0·6 × 1·5 mm was mounted with the (111) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. For the latter, 15 high-angle reflections were used in a least-squares procedure. The apparatus was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with the stationary-crystal–stationary-counter method, and a counting time of 10 s. Individual backgrounds were taken for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were monitored during the course of the experiment but no significant change in intensity was detected. 4268 Independent reflections were measured with $2\theta < 50°$. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03I^2)]^{\frac{1}{2}}$, where E is the estimated background of the reflection. 3866 Reflections with $I > 3\sigma(I)$ were used in subsequent calculations. No extinction correction was applied. An absorption correction was applied, minimum and maximum values of the transmission coefficient ranging between 0·24 and 0·36, by use of program ABSORB.[9]

Structure Determination.—The tungsten atom was placed at the origin, and successive Fourier syntheses used to locate the positions of the remaining atoms. The structure was refined with tungsten and iodine anisotropic and the remaining 58 atoms isotropic by block-matrix least-squares using just four blocks. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_0 and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_0 < 50$ and $\sqrt{w} = F_0/50$ for $F_0 > 50$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre with programs described in ref. 9, and on a 1904S computer at Reading University. Atomic scattering factors for tungsten, iodine, phosphorus, carbon, oxygen, and boron were taken from ref. 10, as were the corrections for the real and imaginary part of the anomalous dispersion for tungsten, iodine, and phosphorus. The anisotropic temperature factor is defined as $\exp -0{\cdot}25 \sum_i\sum_j h_ih_jU_{ij}b_ib_j$ $(i,j = 1,2,3)$ where b_i is the $i^{\rm th}$ reciprocal lattice dimension. The isotropic thermal parameter is $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The final R was 0·052. The equivalent refinement with all co-ordinates reversed gave R 0·072 and the present enantiomorph was considered correct. In the final cycle of refinement all shifts were $< 0{\cdot}080\sigma$. Final co-ordinates and thermal parameters, together with their standard deviations are listed in Table 1. Bond distances and angles are given in Table 2. Final observed and calculated structure factors are listed in a Supplementary Publication (No. SUP 21014, 12 pp., 1 microfiche).*

DISCUSSION

The cation (I) is a discrete monomer in which the tungsten atom is bonded to an iodine atom, three carbonyl groups, and three phosphorus atoms. The (1 : 3 : 3) CO structure which corresponds to the 1 : 3 : 3 stoicheiometry of the cation is not found. Instead, the iodine has four nearest neighbours in the co-ordination sphere (see Figure 1), P(1), P(2), C(1), and C(2). The co-ordination sphere has approximate C_s symmetry with none of the equivalent angles differing by more than 1·5°. The geometry of (I) is close to two ideal geometries, either a CTP with I(1) in the capping position (L_{cp}),† C(1), C(2), P(1), P(2) in the capped quadrilateral face (L_{qf}) and P(3), C(3) in the remaining edge (L_e), or as a CO with P(3) in the capping position

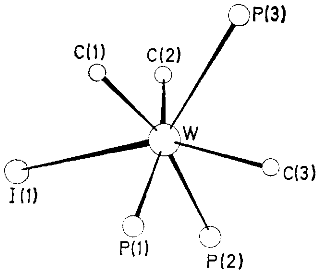

FIGURE 1 The co-ordination sphere of (I), showing that the geometry can be viewed either as a CTP with I(1) in the capping position or as a CO with P(3) in the capping position

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* For details, see notice to authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

† The symbols in parentheses following the description of each site represent a ligand occupying such a site.

[5] M. G. B. Drew, J. D. Wilkins, and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 1278.

[6] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626.

[7] M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329.

[8] J. R. Moss and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 595.

[9] 'X-Ray '67,' system of programs, J. M. Stewart, University of Maryland Technical Report TR 67 58, 1967, revised July 1970.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

(L_{cp}), C(1)—(3) in the capped face (L_c), and P(1), P(2), I(1) in the uncapped face (L_u).

Only the angles involving I(1) differ from the mean values in a CTP by more than 2°; I(1)–W–L_{qf} [L_{qf} = C(1), C(2), P(1), P(2)] are 78·8, 78·3, 86·2, and 85·2° (mean 81·9°). The I(1)–W–L_e angles [L_e = P(3), C(3)] are 136·1, 152·6 (mean 144·4°). As these deviations from a CTP are towards values which would be found in the CO,* it is clear that the (1 : 2 : 2 : 2) geometry

Table 1

Final positional parameters (×10⁴) and thermal parameters (×10³), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*
W	0000[a]	0000[a]	0000[a]	*b*
I(1)	2151(1)	0569(1)	−0393(1)	*b*
P(1)	−0134(4)	−2061(5)	−1932(5)	50(1)
P(2)	1148(4)	−1067(5)	2045(5)	53(1)
P(3)	−1753(4)	1305(4)	0164(4)	46(1)
C(1)	−0420(14)	0818(17)	−1676(17)	47(4)
O(1)	−0623(11)	1258(14)	−2652(14)	79(3)
C(2)	0521(14)	1659(17)	1422(17)	47(4)
O(2)	0802(12)	2643(14)	2231(15)	83(4)
C(3)	−1107(15)	−1189(18)	0290(18)	51(4)
O(3)	−1751(13)	−1887(15)	0513(15)	88(4)
C(11)	0761(16)	−3469(19)	−1548(19)	56(4)
C(12)	0347(18)	−4494(22)	−1047(22)	67(5)
C(13)	1118(19)	−5574(22)	−0751(23)	71(5)
C(14)	2190(18)	−5553(22)	−0900(22)	68(5)
C(15)	2571(20)	−4545(24)	−1416(22)	68(5)
C(16)	1861(18)	−3466(22)	−1712(22)	68(5)
C(18)	0194(17)	−1758(21)	−3471(21)	64(5)
C(19)	−1578(20)	−2824(23)	−2636(24)	74(6)
C(21)	1749(16)	0162(19)	3568(20)	57(4)
C(22)	2786(21)	0801(25)	3741(26)	80(6)
C(23)	3241(24)	1833(30)	4867(30)	96(7)
C(24)	2624(23)	2184(27)	5863(28)	87(7)
C(25)	1661(20)	1613(24)	5757(24)	77(6)
C(26)	1153(20)	0592(23)	4567(23)	73(6)
C(28)	2340(20)	−2031(23)	1763(23)	72(5)
C(29)	0346(22)	−2280(27)	2650(27)	86(7)
C(31)	−3086(14)	0518(16)	−0980(17)	45(4)
C(32)	−3330(17)	0586(20)	−2350(21)	64(5)
C(33)	−4367(21)	−0050(25)	−3239(25)	79(6)
C(34)	−5089(23)	−0658(27)	−2662(23)	87(7)
C(35)	−4829(21)	−0728(26)	−1319(25)	81(6)
C(36)	−3816(19)	−0145(21)	−0450(22)	67(5)
C(38)	−1996(18)	1608(21)	1876(22)	67(5)
C(39)	−1748(16)	2995(19)	−0156(19)	57(4)
B	6011(19)	5896(23)	2801(23)	56(5)
C(51)	6209(15)	7487(18)	3042(18)	52(4)
C(52)	5359(17)	8279(21)	2388(21)	64(5)
C(53)	5375(18)	9642(21)	2617(22)	66(5)
C(54)	6350(21)	10340(24)	3556(23)	76(6)
C(55)	7204(20)	9679(24)	4227(24)	75(6)
C(56)	7125(17)	8314(21)	3969(21)	62(5)
C(61)	7183(16)	5204(20)	3576(20)	59(5)
C(62)	7188(21)	4342(25)	4591(26)	71(6)
C(63)	8261(25)	3760(28)	5161(30)	93(7)
C(64)	9189(25)	4049(31)	4937(30)	99(8)
C(65)	9256(23)	4913(27)	3978(28)	88(7)
C(66)	8222(18)	5419(21)	3289(22)	66(5)
C(71)	4976(15)	5656(18)	3425(19)	54(4)
C(72)	5068(26)	6113(30)	4838(29)	89(8)
C(73)	4094(24)	5989(28)	5392(29)	92(7)
C(74)	3108(23)	5442(28)	4581(28)	87(7)
C(75)	3001(24)	4997(29)	3154(29)	94(7)
C(76)	3881(18)	5060(22)	2645(22)	68(5)
C(81)	5818(16)	5182(19)	1162(19)	55(4)
C(82)	6060(17)	5891(21)	0226(21)	63(5)
C(83)	5901(20)	5364(24)	−1112(24)	75(6)
C(84)	5429(21)	4071(25)	−1606(25)	80(6)
C(85)	5205(21)	3285(25)	−0758(23)	79(6)
C(86)	5400(18)	3839(21)	0674(22)	65(5)

[a] Parameters fixed. [b] Anisotropic thermal parameters (×10⁴):

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	407(3)	407(3)	382(3)	62(2)	97(2)	66(2)
I(1)	497(7)	643(8)	727(9)	42(6)	203(6)	182(6)

Table 2

Molecular dimensions, distances (Å) and angles (°)

(*a*) The cation

W–I(1)	2·840(1)	W–C(1)	1·994(18)
W–P(1)	2·576(4)	W–C(2)	2·000(16)
W–P(2)	2·614(5)	W–C(3)	1·933(20)
W–P(3)	2·528(5)		

L · · · L distances and L–W–L angles in the co-ordination sphere

	I(1)	P(1)	P(2)	P(3)	C(1)	C(2)	C(3)
I(1)		86·2(1)	85·2(1)	136·1(1)	77·8(5)	78·3(6)	152·6(5)
P(1)	3·71		98·4(1)	119·6(1)	77·5(5)	164·4(6)	76·5(5)
P(2)	3·70	3·93		121·0(2)	162·7(5)	79·5(5)	76·7(5)
P(3)	4·98	4·41	3·93		74·7(5)	73·6(5)	71·4(5)
C(1)	3·10	2·90	4·56	2·78		99·9(7)	117·9(7)
C(2)	3·12	4·54	2·99	2·75	3·06		117·5(8)
C(3)	4·64	2·84	2·87	2·65	3·36	3·36	

C(1)–O(1)	1·14(2)	W–C(1)–O(1)	177·1(16)
C(2)–O(2)	1·16(2)	W–C(2)–O(2)	178·2(14)
C(3)–O(3)	1·16(3)	W–C(3)–O(3)	177·6(15)

	n = 1	*n* = 2	*n* = 3
P(*n*)–C(*n*1)	1·82(2)	1·80(2)	1·84(2)
P(*n*)–C(*n*8)	1·81(2)	1·80(2)	1·83(2)
P(*n*)–C(*n*9)	1·84(2)	1·86(2)	1·80(2)
C(*n*1)–C(*n*2)	1·39(3)	1·38(3)	1·38(3)
C(*n*2)–C(*n*3)	1·46(3)	1·41(3)	1·44(3)
C(*n*3)–C(*n*4)	1·36(3)	1·41(4)	1·39(4)
C(*n*4)–C(*n*5)	1·37(4)	1·29(4)	1·35(4)
C(*n*5)–C(*n*6)	1·41(3)	1·45(3)	1·39(3)
C(*n*6)–C(*n*1)	1·40(3)	1·41(3)	1·39(3)
W–P(*n*)–C(*n*1)	117·6(6)	113·4(7)	115·1(5)
W–P(*n*)–C(*n*8)	116·5(7)	116·3(8)	113·8(7)
W–P(*n*)–C(*n*9)	113·4(8)	116·2(8)	115·8(8)
C(*n*1)–P(*n*)–C(*n*8)	101·5(10)	103·7(9)	104·9(9)
C(*n*1)–P(*n*)–C(*n*9)	104·6(10)	103·8(10)	104·6(9)
C(*n*8)–P(*n*)–C(*n*9)	100·9(10)	101·8(12)	101·0(10)
P(*n*)–C(*n*1)–C(*n*2)	119·1(15)	120·4(17)	118·9(15)
P(*n*)–C(*n*1)–C(*n*6)	119·2(16)	122·0(15)	119·5(13)
C(*n*2)–C(*n*1)–C(*n*6)	121·5(19)	117·3(18)	121·7(16)
C(*n*1)–C(*n*2)–C(*n*3)	115·8(21)	121·9(26)	118·4(21)
C(*n*2)–C(*n*3)–C(*n*4)	122·0(23)	118·2(26)	118·1(22)
C(*n*3)–C(*n*4)–C(*n*5)	121·0(22)	122·4(23)	122·6(23)
C(*n*4)–C(*n*5)–C(*n*6)	119·3(23)	120·2(25)	120·0(26)
C(*n*5)–C(*n*6)–C(*n*1)	120·2(22)	119·9(22)	119·2(21)

(*b*) The anion

	n = 5	*n* = 6	*n* = 7	*n* = 8
B–C(*n*1)	1·59(3)	1·66(3)	1·60(3)	1·67(3)
C(*n*1)–C(*n*2)	1·41(3)	1·48(4)	1·42(3)	1·39(3)
C(*n*2)–C(*n*3)	1·35(3)	1·46(4)	1·46(5)	1·35(3)
C(*n*3)–C(*n*4)	1·42(3)	1·26(5)	1·34(4)	1·39(3)
C(*n*4)–C(*n*5)	1·34(3)	1·45(5)	1·43(4)	1·36(4)
C(*n*5)–C(*n*6)	1·36(3)	1·42(3)	1·32(4)	1·44(3)
C(*n*6)–C(*n*1)	1·43(2)	1·40(3)	1·44(3)	1·41(3)

C(51)–B–C(61)	109·8(15)	C(61)–B–C(71)	111·7(18)
C(51)–B–C(71)	106·0(16)	C(61)–B–C(81)	103·2(16)
C(51)–B–C(81)	112·0(18)	C(71)–B–C(81)	114·3(15)

	n = 5	*n* = 6	*n* = 7	*n* = 8
B–C(*n*1)–C(*n*2)	119·9(15)	122·3(20)	120·0(18)	121·1(17)
B–C(*n*1)–C(*n*6)	128·8(17)	121·0(19)	125·3(17)	121·3(19)
C(*n*2)–C(*n*1)–C(*n*6)	111·0(17)	116·6(19)	114·5(21)	117·6(18)
C(*n*1)–C(*n*2)–C(*n*3)	125·5(17)	116·9(25)	120·2(22)	123·2(20)
C(*n*2)–C(*n*3)–C(*n*4)	117·3(19)	124·0(30)	120·7(27)	119·1(25)
C(*n*3)–C(*n*4)–C(*n*5)	121·9(21)	122·0(28)	119·6(29)	121·7(23)
C(*n*4)–C(*n*5)–C(*n*6)	117·8(20)	116·9(26)	120·5(23)	119·0(21)
C(*n*5)–C(*n*6)–C(*n*1)	126·5(19)	123·1(23)	124·3(21)	119·2(22)

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* The L_{qf} = C(1), C(2) angles would be L_c–W–L_u angles (mean 77·7°) and L_{qf} = P(1), P(2) angles would be L_c–W–L_c angles (mean 89·9°). Similarly L_e = P(3) is a L_{cp}–W–L_u angle (mean 125·6°) and L_e is a L_u–W–L_c angle (mean 159·9°).

with C_s symmetry is intermediate between the two ideal geometries.

Probable seven-co-ordinate geometries have been calculated[11] for molecules of the type AB_7 based solely upon mutual repulsion of ligands or electron pairs on the surface of a sphere, by use of the formula $E = \sum_{i \neq j} r_{ij}^{-n}$, where r_{ij} is the distance between pairs of ligands and n is a constant. For certain values of n, C_s and C_2 geometries * are found to have lower energies than the three ideal types CO, CTP, and PB. It is therefore possible that in (I) the arrangement of the seven ligands has the minimum energy considering only repulsions between pairs of ligands. An alternative explanation that the distortions from the CTP are due to some inter- or intra-molecular effect involving atoms not directly bonded to the metal is possible and will now be discussed.

The orientations of the methyl and phenyl groups around the W-P bonds are illustrated in Figure 2 and the relevant dihedral angles and intramolecular distances are listed in Tables 3 and 4. P(3) Has three near neighbours, C(1)—(3), and the three carbon atoms bonded to P(3) are staggered with respect to these three carbonyl groups such that all nine dihedral angles of the type C(n)-W-P(3)-C(3m) (n = 1,2,3, m = 1,8,9) are greater than 47°. The other two phosphorus atoms have four nearest neighbours and dihedral angles involving I(1) are large (>40°). The smallest dihedral angles for P(1) are P(2)-W-P(1)-C(11) −12·4, C(1)-W-P(1)-C(18) 29·6, and C(3)-W-P(1)-C(19) 36·1° giving close contacts C(1),O(1) ··· C(18) 3·10, 3·23 and C(3),O(3) ··· C(19) 3·07, 3·27 Å. The orientation of the P(1)-C(11) bond almost in the plane of the W,P(1),P(2) atoms ensures that the orientation of groups around P(2) is different, as the equivalent orientation would lead to a close C(11) ··· C(2m) contact.† Even so, the actual orientation around P(2) is surprising and may therefore be due to intramolecular forces. The three P(2)-C(2m) bonds are staggered with respect to P(1) and I(1) but two of them are eclipsed with respect to C(3) and C(2), thus the C(3)-W-P(2)-C(29) and C(2)-W-P(2)-C(21) dihedral angles are −0·8 and 0·8°, giving remarkably close contacts of C(3),O(3) ··· C(29) 3·00, 2·99, and C(2),O(2) ··· C(21) 2·98, 3·15 Å. All three phenyl rings are planar and their orientations [Table 3(b)] are approximately perpendicular to the respective W-P bond. Intramolecular distances involving ring atoms, other than C(n1), are >3·38 Å.

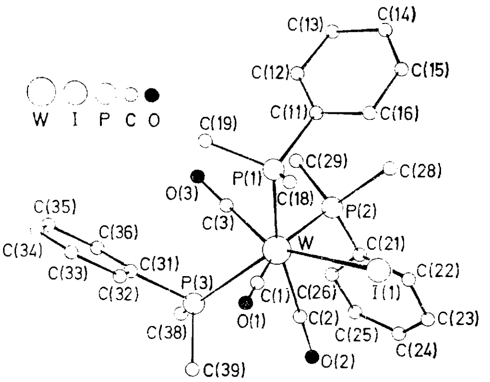

FIGURE 2 The cation

TABLE 3

(a) Dihedral angles (°) for atoms i–W–j–k, where the i–W–j angle is <100°

	m = 1	m = 8	m = 9
C(1)–W–P(1)–C(1m)	150·5	29·6	−87·0
C(3)–W–P(1)–C(1m)	−86·4	152·7	36·1
I(1)–W–P(1)–C(1m)	72·2	−48·7	−165·3
P(2)–W–P(1)–C(1m)	−12·4	−133·3	110·1
I(1)–W–P(2)–C(2m)	79·8	−40·2	160·0
P(1)–W–P(2)–C(2m)	165·2	45·2	−74·6
C(2)–W–P(2)–C(2m)	0·8	−119·2	121·0
C(3)–W–P(2)–C(2m)	−121·0	119·0	−0·8
C(1)–W–P(3)–C(3m)	74·8	−164·0	−47·6
C(2)–W–P(3)–C(3m)	−179·7	−58·5	57·9
C(3)–W–P(3)–C(3m)	−52·3	68·9	−174·7

(b) Other dihedral angles *

	n = 1	n = 2	n = 3
C(n2)–C(n1)–P(n)–C(n8)	−141·6	41·8	157·8
C(n2)–C(n1)–P(n)–C(n9)	−36·9	147·9	51·9
C(n2)–C(n1)–P(n)–W	90·0	−85·2	−76·3

* The equivalent angles, with C(n6) replacing C(n2) differ by ca. 180° from these values.

(c) Angles between planes in the anion are: (5)–(6) 62·0, (5)–(7) 84·5, (5)–(8) 64·1, (6)–(7) 59·5, (6)–(8) 82·3, and (7)–(8) 53·0°.

TABLE 4

Intramolecular distances <3·50 Å (excluding those between atoms bonded to the same atom)

P(3) ··· O(2)	3·43	C(3) ··· C(38)	3·31
P(3) ··· O(3)	3·31	O(3) ··· C(19)	3·27
C(1) ··· C(18)	3·10	O(3) ··· C(29)	2·99
C(1) ··· C(32)	3·44	O(3) ··· C(31)	3·30
C(1) ··· C(39)	3·14	O(3) ··· C(36)	3·11
O(1) ··· C(18)	3·23	C(51) ··· C(82)	3·01
O(1) ··· C(32)	3·49	C(51) ··· C(66)	3·20
O(1) ··· C(39)	3·41	C(51) ··· C(72)	3·10
C(2) ··· C(21)	2·98	C(81) ··· C(52)	3·25
C(2) ··· C(22)	3·38	C(81) ··· C(66)	3·16
C(2) ··· C(26)	3·49	C(81) ··· C(76)	3·14
C(2) ··· C(38)	3·23	C(61) ··· C(56)	3·10
C(2) ··· C(39)	3·24	C(61) ··· C(86)	3·29
O(2) ··· C(21)	3·15	C(61) ··· C(72)	3·23
O(2) ··· C(22)	3·28	C(71) ··· C(52)	3·11
O(2) ··· C(26)	3·40	C(71) ··· C(86)	3·24
O(2) ··· C(38)	3·50	C(71) ··· C(62)	3·06
C(3) ··· C(19)	3·07	C(52) ··· C(82)	3·23
C(3) ··· C(29)	3·00	C(56) ··· C(66)	3·24
C(3) ··· C(31)	3·10	C(62) ··· C(72)	3·17
C(3) ··· C(36)	3·40		

None of these close contacts can be directly related to the preference for C_s rather than C_{2v} symmetry for (I). There is no evidence that intermolecular forces are

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* Just as the present C_s structure is derived from the CTP by moving two adjacent L_{qf} (phosphorus) atoms from the capping atom, so a C_2 geometry is derived from the CTP by moving mutually *trans*-L_{qf} atoms away from the capping atom.

† This is only true because the PMe_2Ph ligands are unidentate. When a bidentate ligand occupies adjacent sites, such repulsions are more easily minimised. An example would be diars [*o*-phenylenebis(dimethylarsine)] in refs. 3 and 13.

[11] H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, 1968, **7**, 488.

responsible and so we conclude that mutual repulsions between the seven atoms bonded to the metal are responsible for the (1 : 2 : 2 : 2) geometry. In $[W(CO)_4(diars)I]^+$,[12] (II), a CTP with iodine in the capping position, and two arsenic atoms and two carbonyl groups in the capped quadrilateral face, the I–W–L_{qf} angles are 81·3(1) for L_{qf} = As and 79·8(7) for L_{qf} = C, values which compare well with those found in more symmetrical cations.[1,3] This difference in geometry between (I) and (II) could be due to three factors: the difference in ligand–ligand repulsions; the carbon atoms in (I) being *ca.* 0·2 Å closer to the metal because of the smaller radius of phosphorus compared with arsenic; and in the bidentate diars in (II) the methyl groups can be kept well away from the iodine.[3,12] Whatever the reason both (I) and (II) have similar minimum I · · · C contacts of 3·70 Å despite the differences in I–W–L_{qf} angles.

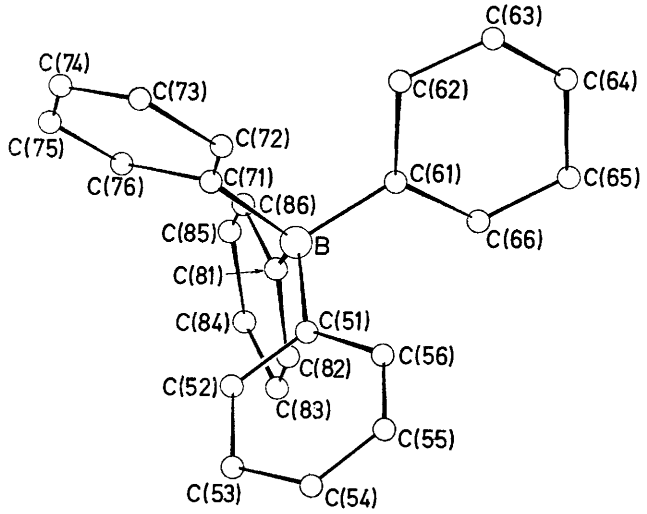

FIGURE 3 The anion

The W–P(1) bond [2·576(4) Å] is significantly shorter than W–P(2) [2·614(5) Å] and this must reflect the greater steric crowding for P(2). Both are much longer than W–P(3) [2·528(5) Å] because they are both *trans* to W–CO bonds. Similar variations are discussed in ref. 7. The three carbonyl bond lengths in (I) are also different, W–C(1) and W–C(2) [1·994(18) and 2·000(16) Å] being longer than W–C(3) [1·933(20) Å]. A similar difference of *ca.* 0·06 Å is also quoted in refs. 1 and 12. The W–I(1) bond length [2·840(1) Å] is equivalent to that found for Mo–I in $[Mo(CNR)_6I]^+$ (R = t-butyl) which is equal to the sum of atomic radii.[1]

The angles in the capped quadrilateral face of (I) are remarkably symmetric in that while P(1)–W–P(2) is 98·4°, reasonable enough given the bulkiness of the two ligands, the C(1)–W–C(2) angle on the opposite edge of the face is 99·9°. In (II) the same symmetric arrangement in the face is found with C–W–C 80·8° opposite to a bidentate diars ligand with As–W–As 77·8°. In both structures (and in those in refs. 1 and 3) the smallest bites in the capped quadrilateral face are parallel to the $L_e \cdots L_e$ edge.

In the cation, the mean P–C bond length is 1·82 Å. The phenyl ring dimensions are as expected. In the anion the mean B–C bond length is 1·63 Å. The relative orientations of the rings, which are all planar are shown in Figure 3. Angles between pairs of ring planes in this anion [13] are usually very similar, independent of cation and packing. For the present anion, the mean angle between planes is 67·6° with mean deviations of 10·6°, values which fit in well with both calculated and observed values.[13]

TABLE 5

Intermolecular contacts <3·75 Å

O(2) · · · C(75)	3·43	C(85) · · · C(32^{IV})	3·61
C(74) · · · C(23)	3·71	C(85) · · · C(36^{IV})	3·69
C(55) · · · O(1^{I})	3·71	C(63) · · · C(38^{IV})	3·61
C(62) · · · C(19^{I})	3·67	C(64) · · · C(38^{IV})	3·61
C(63) · · · C(19^{I})	3·74	C(84) · · · C(39^{IV})	3·63
C(55) · · · C(32^{I})	3·69	C(85) · · · C(39^{IV})	3·63
C(54) · · · C(33^{I})	3·71	C(76) · · · C(14^{V})	3·64
C(55) · · · C(33^{I})	3·58	C(53) · · · C(22^{V})	3·74
C(73) · · · C(34^{I})	3·61	C(52) · · · C(28^{V})	3·58
C(82) · · · O(3^{II})	3·43	C(75) · · · C(28^{V})	3·55
C(53) · · · C(36^{II})	3·58	C(76) · · · C(28^{V})	3·60
C(54) · · · C(38^{II})	3·37	C(25) · · · O(1^{VI})	3·63
C(55) · · · C(38^{II})	3·68		
C(63) · · · O(1^{III})	3·71		
C(65) · · · O(2^{IV})	3·49		
C(85) · · · C(31^{IV})	3·48		

Roman numeral superscripts refer to atoms in the following equivalent positions, relative to the reference molecule (Table 1) at x, y, z:

I	$1 + x, 1 + y, 1 + z$	IV	$1 + x, y, z$
II	$1 + x, 1 + y, z$	V	$x, 1 + y, z$
III	$1 + x, y, 1 + z$	VI	$x, y, 1 + z$

Intermolecular contacts are shown in Table 5 and the large number <3·75 Å suggests that the molecules are packing particularly effectively in space group $P\bar{1}$.

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