The Crystal and Molecular Structures of the Trimethylphosphine–Boron Trihalide Complexes: (CH₃)₃PBCl₃, (CH₃)₃PBBr₃ and (CH₃)₃PBI₃

By Donald L. Black and Robert C. Taylor

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104, *U.S.A.*

An X-ray diffraction study of single crystals of the trimethylphosphine complexes of BCl_3, BBr_3 and BI_3 has shown the chloro and bromo complexes to have $P2_1/m$ monoclinic unit cells with $Z=2$, and the iodo complex to have a *Pnma* orthorhombic unit cell with $Z=4$. Unit-cell parameters are as follows: $TMP.BCl_3$, $a=6·957$ (1), $b=10·630$ (1), $c=6·476$ (1) Å, $\beta=112·76$ (1)°; $TMP.BBr_3$, $a=7·091$ (2), $b=10·996$ (2), $c=6·672$ (1) Å, $\beta=112·38$ (1)°; $TMP.BI_3$, $a=13·033$ (1), $b=11·636$ (1), $c=7·282$ (1) Å. The structures were solved with the help of three-dimensional sharpened Patterson functions and show the chloro and bromo compounds to be isomorphous. Refinement of 761, 855 and 567 observed reflections for the chloro, bromo and iodo compounds, respectively, using anisotropic thermal factors yielded conventional R values of 0·044, 0·047 and 0·033. The molecules are shown to possess a P–B dative bond, a staggered conformation and effective $3m$ (C_{3v}) symmetry. Average P–C bond lengths for the chloro and bromo complexes are 1·81 (1) Å while the P–C distance in the iodo complex is 1·845 (12) Å. The three P–B distances are 1·957 (5), 1·924 (12) and 1·918 (15) Å, respectively, while the boron–halogen bond distances average 1·855 (5), 2·022 (7) and 2·249 (12) Å. The C–P–C bond angles are very nearly tetrahedral, with no trend noticeable. The X–B–X angles are somewhat larger and close to 111° and also show no trend.

Introduction

Although there has been considerable recent interest in the correlation of molecular properties of Lewis type complexes, particularly the dative bond distances, with chemical properties such as stability, acid strength and base strength, the data available are still too limited for complete understanding. This is particularly so for compounds containing P–B bonds where there are some unexpected features in the relatively few compounds that have been studied. The present work was undertaken to provide results which could be compared with those from the trimethylamine–boron halide series (Clippard, Hanson & Taylor, 1971) and also to provide the necessary basis for a satisfactory spectroscopic study. No previous structural studies of any trimethylphosphine–boron halide complexes were found in the literature although a microwave study of the trimethylphosphine–borane complex has been reported (Bryan & Kuczkowski, 1972) in which the P–B distance was found to be 1·901 Å. In other Lewis complexes involving phosphorus and boron, P–B distances have varied from about 1·83 to 1·96 Å (Kuczkowski & Lide, 1967; Pasinski & Kuczkowski, 1971).

Experimental

Preparation of compounds

All three complexes are stable white solids which can be handled in air with no difficulty. The chloro and bromo complexes were prepared by direct reaction between trimethylphosphine and the boron trihalide at low temperatures. The iodo complex was prepared in benzene solution. All complexes were purified by sublimation *in vacuo*. Single crystals were grown by slow evaporation of chloroform solutions. Attempts to grow a single crystal of the BF_3 complex failed owing to the dissociation of the complex.

Unit-cell parameters and space group

Precession photographs with Cu $K\alpha$ radiation showed the crystal system of the chloro and bromo adducts to be monoclinic and that of the iodo to be orthorhombic. Systematic absences of $0k0$ were noted for odd k in the patterns of the chloro and bromo compounds, indicating the centrosymmetric space group $P2_1/m$ or the non-centrosymmetric group $P2_1$. Photographs of the ($h0l$), ($0kl$), ($h1l$) and ($1kl$) layers of the iodo complex exhibited systematic absences $0kl$ for $k+l$ odd and $hk0$ for h odd, characteristic of the centrosymmetric space group *Pnma* or the non-centrosymmetric group $Pn2_1a$. In both cases, the centrosymmetric group was verified by the structure determination.

Accurate lattice parameters for each complex were determined by least-squares refinement of the Bragg angle for 29 high scattering angle reflections which had been carefully measured on a Syntex four-circle automatic diffractometer. Approximate densities of the crystals determined by flotation led to values of $Z=2$ for the Cl and Br compounds and $Z=4$ for the iodo. Densities, unit-cell parameters and other associated data are shown in Table 1.

Collection and treatment of intensity data

The Supper–Pace diffractometer used and the method of data collection were essentially the same as for the trimethylamine complexes described previously (Clippard, Hanson & Taylor, 1971). Mo radiation was employed for all three compounds. Selected crystals of the chloro and bromo complexes were mounted with the a axis parallel to the goniometer spindle and nets of $(0kl)$, $(1kl)$ ... $(6kl)$ collected. For the iodo complex, the direct c axis was parallel to the spindle and the nets were $(hk0)$, $(hk1)$ ... $(hk6)$. The numbers of observed reflections, respectively, were 761, 855, and 567 for the chloro, bromo and iodo compounds.

A balanced filter technique with Zr and Y foils was used to filter the radiation. Integrated intensities were corrected for Lorentz, polarization and absorption effects. Crystal dimensions were $0.5 \times 0.30 \times 0.15$ mm, $0.50 \times 0.34 \times 0.10$ mm, and $0.55 \times 0.26 \times 0.07$ mm, respectively, for the three compounds. Transmission factors for each reflection of the chloro and bromo compounds were calculated (Burnham, 1966) from these measurements and the integrated intensities corrected accordingly. The absorption corrections for the iodo complex were made using the empirical method of Arndt & Willis (1966).
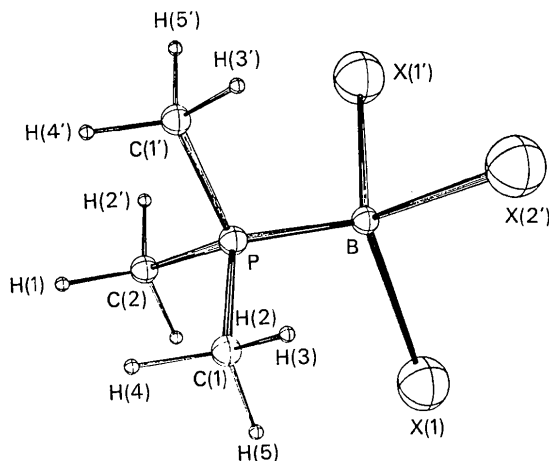

Fig. 1. The numbering of the atoms in an asymmetric unit of a $(CH_3)_3PBX_3$ molecule.

Structure determination and refinement

The atomic scattering factors used in the structure determination and refinement were generated from the theoretical functions of Cox & Bonham (1967). The structure determinations was carried out by the X-RAY 67 package of computer programs (Stewart, 1967). Preliminary determination across nets had shown that the scale factors relating the intensities in various nets were close to unity. This factor was assumed in scaling the raw data. Patterson coefficients were calculated and three-dimensional Patterson functions with the origin removed were computed. From these, the halogen atom peaks were located after which the remaining non-hydrogen atoms were found by means of difference Fourier plots. Fractional coordinates and isotropic temperature factors for all non-hydrogen atoms were then refined with a full-matrix least-squares program (Schilling, 1968) using half a molecule as the asymmetric unit. When improvement ceased, anisotropic temperature factors were introduced. Since secondary extinction appeared to be significant in these compounds, reflections were corrected for this factor and the isotropic extinction coefficient was included among the parameters being refined. The weighting scheme employed for the structure factors was that of Hughes (1941) which had been found satisfactory for the trimethylamine–boron halide complexes.

After some refinement with anisotropic temperature factors, a discrepancy was noted for some 15 reflections involving both the bromo and iodo compounds. Inspection of the original data showed these discrepancies could all be accounted for by a high noise level in the observed reflection, small errors in the crystal dimensions which could affect the absorption corrections, or attenuation of the diffracted beam by the beam stop. Reflections affected by the first or last factors were deleted from the refinement and the latter continued for a few more cycles.

The difference Fourier synthesis for the chloro compound showed very weak peaks which could be attributed to the hydrogen atoms. Near the end of the refinement, the hydrogen atoms were introduced and the positions of all atoms refined for a few cycles
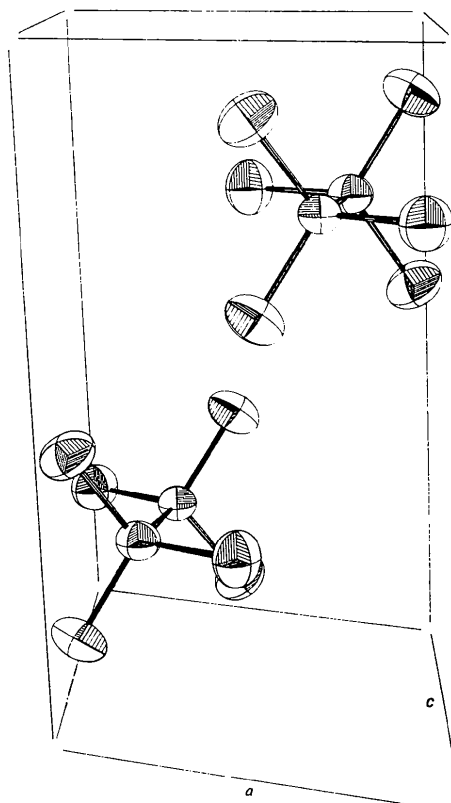
Table 1. *Unit-cell parameters for* $(CH_3)_3PBX_3$

	$(CH_3)_3PBCl_3$	$(CH_3)_3PBBr_3$	$(CH_3)_3PI_3$
a (Å)	6.957 ± 0.001	7.091 ± 0.002	13.033 ± 0.001
b	10.630 ± 0.001	10.996 ± 0.002	11.636 ± 0.001
c	6.476 ± 0.0005	6.672 ± 0.001	7.282 ± 0.001
β (°)	112.76 ± 0.01	112.38 ± 0.01	
Cell volume (Å³)	441·6	481·1	1104·3
Molecules/cell	2	2	4
Measured density (g cm⁻³)	1·4	2·2	2·8
Calculated density (g cm⁻³)	1·45	2·25	2·81
Linear absorption coefficients for Mo $K\alpha$ (cm⁻¹)	11	138	92
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/m$	$P2_1/m$	$Pnma$

Table 2. *Fractional atomic coordinates* ($\times 10^4$)
for $(CH_3)_3PBX_3$ *crystals*

E.s.d.'s are in parentheses.

Atom in asymmetric unit	x	y	z
$(CH_3)_3PBCl_3$			
B	3413 (8)	2500*	2104 (8)
C(1)	7629 (7)	1131 (4)	4571 (7)
C(2)	7033 (10)	2500*	484 (9)
P	6440 (2)	2500*	2939 (2)
Cl(1)	2536 (2)	1075 (1)	476 (2)
Cl(2)	2962 (2)	2500*	4738 (2)
H(1)	861 (14)	2500*	109 (11)
H(2)	674 (9)	179 (5)	1 (8)
H(3)	733 (8)	114 (5)	593 (9)
H(4)	927 (9)	119 (5)	512 (8)
H(5)	730 (9)	50 (6)	384 (8)
$(CH_3)_3PBBr_3$			
B	3613 (17)	2500*	2288 (17)
C(1)	7690 (13)	1198 (8)	4625 (15)
C(2)	7163 (17)	2500*	691 (19)
P	6522 (4)	2500*	3068 (4)
Br(1)	2433 (1)	1004 (1)	531 (1)
Br(2)	3086 (2)	2500*	5031 (2)
$(CH_3)_3PBI_3$			
B	6184 (12)	2500*	4950 (21)
C(1)	5164 (10)	1235 (10)	8201 (15)
C(2)	7075 (12)	2500*	8842 (23)
P	5893 (3)	2500*	7533 (5)
I(1)	7070 (1)	929 (1)	4258 (1)
I(2)	4658 (1)	2500*	3495 (1)

* These coordinates are defined from the space-group requirements.

Fig. 2. A unit cell of $(CH_3)_3PBCl_3$ with methyl H's omitted. The unique monoclinic b axis points up the page and the thermal ellipsoids have been scaled to include 50% probability.

Table 3. *Thermal parameters for* $(CH_3)_3PBX_3$ ($\times 10^4$)

E.s.d.'s are in parentheses.

The β_{ij} are defined in the anisotropic temperature-factor expression $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+kl\beta_{23}+hl\beta_{13})\right]$.

Atom in asymmetric unit	β_{11}	β_{22}	β_{33}	$\beta_{12}^{\dagger}$	β_{13}	β_{23}^{*}
$(CH_3)_3PBCl_3$						
B	224 (16)	68 (5)	283 (16)	0	91 (13)	0
C(1)	304 (14)	108 (4)	419 (15)	52 (5)	117 (12)	61 (6)
C(2)	336 (20)	112 (6)	348 (17)	0	173 (15)	0
P	212 (4)	60 (1)	233 (4)	0	83 (3)	0
Cl(1)	329 (4)	999 (4)	435 (4)	−48 (1)	108 (3)	−67 (1)
Cl(2)	296 (5)	146 (2)	320 (5)	0	164 (3)	0
$(CH_3)_3BBr_3$						
B	221 (29)	70 (9)	227 (26)	0	95 (20)	0
C(1)	268 (24)	77 (7)	464 (32)	43 (10)	45 (21)	79 (11)
C(2)	208 (29)	124 (13)	332 (33)	0	131 (23)	0
P	178 (6)	55 (2)	211 (6)	0	51 (4)	0
Br(1)	289 (3)	81 (1)	380 (4)	−43 (1)	78 (2)	−49 (1)
Br(2)	262 (4)	146 (2)	274 (4)	0	124 (3)	0
$(CH_3)_3PBI_3$						
B	56 (10)	63 (12)	155 (32)	0	9 (14)	0
C(1)	127 (10)	100 (10)	208 (25)	−44 (9)	43 (13)	34 (13)
C(2)	91 (13)	118 (17)	235 (37)	0	−65 (17)	0
P	57 (2)	62 (3)	131 (7)	0	−2 (3)	0
I(1)	91 (1)	79 (1)	287 (2)	17 (1)	29 (1)	−24 (1)
I(2)	61 (1)	164 (1)	172 (2)	0	−18 (1)	0

* From symmetry requirements, β_{12} and β_{23} were 0 for atoms lying on the mirror plane.

assigning a constant isotropic temperature factor of 6·0 to the hydrogens. Refinement of hydrogen positions was not attempted for the bromo and iodo compounds. The final R values obtained were 0·044, 0·047 and 0·033 for the respective compounds. Final fractional coordinates are given in Table 2 with the corresponding temperature factors in Table 3.

The final fractional coordinates, thermal parameters and variance-covariance matrices of associated errors were provided as input to the computer program *ORFFE* (Busing, Martin & Levy, 1964) which calculated interatomic distances, angles, principal axes of thermal motion and the corresponding uncertainties. Rigid-body 'riding' corrections for the effect of thermal motion on the molecular parameters (Busing & Levy, 1964) were also computed. These corrections were not appreciable for the P–B distances but proved significant for the P–C and B–X distances. The final corrected parameters are listed in Table 4.* A sketch of a complete molecule, $(CH_3)_3PBX_3$, is shown in Fig. 1 and gives the atom numbering. The hydrogen atoms have been shown at positions based on the evidence from the chloro compound. However, the uncertainties there are large and no evidence was obtained about hydrogen positions for the bromo and iodo com-

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30786 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
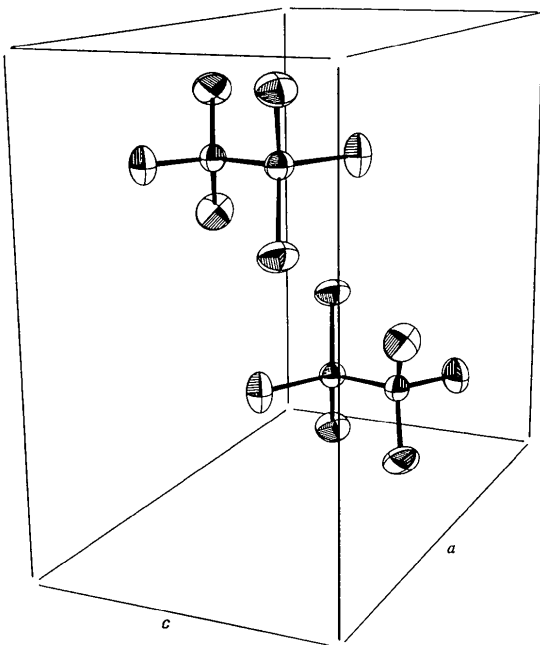

Fig. 3. One-half of a unit cell of $(CH_3)_3PBI_3$ with methyl H's omitted. The crystallographic *b* axis points up to the page and the thermal ellipsoids have been scaled to include 50 % probability.

pounds. Their placement must therefore be considered tentative. A unit cell of the chloro compound is shown in Fig. 2 and a half unit cell of the iodo complex is portrayed in Fig. 3. The unit cell of the bromo compound has been omitted since it is isomorphous with the chloro.

Table 4. *Corrected molecular parameters of crystalline* $(CH_3)_3PBX_3$ *complexes*

E.s.d.'s are in parentheses.

	$(CH_3)_3PBCl_3$	$(CH_3)_3PBBr_3$	$(CH_3)_3PBI_3$
Bond distances (Å)			
B——P	1·957 (5)	1·924 (12)	1·918 (15)
C(1)–P	1·822 (4)	1·806 (8)	1·849 (10)
C(2)–P	1·807 (6)	1·825 (12)	1·838 (15)
B——X(1)	1·850 (3)	2·025 (6)	2·237 (9)
B——X(2)	1·866 (5)	2·016 (10)	2·272 (16)
C(2)–H(1)	1·02 (9)		
C(2)–H(2)	0·81 (5)		
C(1)–H(3)	0·98 (5)		
C(1)–H(4)	1·06 (5)		
C(1)–H(5)	0·80 (6)		
Bond angles (°)			
X(1)–B——X(2)	110·9 (2)	110·6 (4)	110·6 (5)
X(1)–B——X(3)	111·8 (2)	110·0 (5)	110·9 (6)
C(1)–P——C(2)	108·0 (2)	107·2 (4)	107·6 (5)
C(1)–P——C(3)	107·8 (3)	107·3 (7)	108·1 (8)
X(1)–B——P	108·0 (2)	108·9 (4)	108·9 (5)
X(2)–B——P	107·0 (2)	107·8 (5)	106·6 (7)
C(1)–P——B	111·3 (2)	111·8 (3)	111·4 (4)
C(2)–P——B	110·3 (2)	111·3 (5)	110·3 (8)
H(1)–C(2)–H(2)	103 (4)		
H(3)–C(1)–H(4)	106 (4)		
H(3)–C(1)–H(5)	116 (5)		
H(4)–C(1)–H(5)	106 (5)		

Discussion

The structures for the three compounds confirm the presence of a P–B dative bond as adduced from the chemical evidence, and show that the skeletal atoms of each molecule have effective $3m$ (C_{3v}) symmetry with a staggered conformation. Although all the P–C and B–X distances in a given molecule did not refine to exactly the same values as demanded by true $3m$ symmetry, it is felt that the small differences found represent statistical fluctuations rather than any intrinsic differences in the bonds. The evidence for the hydrogen atom positions in the chloro complex is consistent with an overall $3m$ (C_{3v}) symmetry although, as was mentioned, the uncertainties are such that a firm conclusion cannot be made.

As might be expected, there is a close similarity between the trimethylphosphine and trimethylamine complexes of the boron halides, the chloro and bromo complexes in fact being isomorphous. In both series, the iodo compounds are dissimilar, presumably because of steric factors. However, the packing of molecules related by a 2_1 axis along the **b** direction is similar in the monoclinic and orthorhombic cells.

The dative bond distances in the trimethylamine complexes exhibit a slight shortening in the sequence

from the chloro to the iodo adduct which agrees with the order of acid strengths established from chemical data. However, the differences found are within the uncertainty range and consequently do not provide significant corroboration of the chemical evidence. A similar trend is present in the trimethylphosphine complexes and is somewhat more marked than in the trimethylamine case, although still modest. Steric crowding in these molecules may be partially responsible for the small variation in the dative bond distances compared, for example, with the $CH_3CN.BX_3$ complexes where the change in the dative bond distance with acid is much more dramatic (Swanson, Shriver & Ibers, 1969).

The P–B distance in $(CH_3)_3PBH_3$, the only other trimethylphosphine complex for which structural data have been reported (Bryan & Kuczkowski, 1972), is 1·901 Å which is shorter by 0·02 to 0·06 Å than any of the P–B distances in the compounds studied here. In the trimethylamine series, the B–N distance in the BH_3 complex has been reported at 1·609 Å (Durig, Li & Odom, 1973) which is very nearly identical with the same distance in the BCl_3 complex (1·611 Å) and longer than the B–N distances in the bromo and iodo complexes. The relative position of the BH_3 complexes with respect to the BX_3 complexes is thus in accord with chemical results, which indicate that trimethylphosphine is a better donor towards BH_3 than is trimethylamine, whereas the reverse is true for the boron halide acids where trimethylamine gives more stable complexes.

The relationships in the case of phosphine and fluorophosphine complexes is less clear. The complex PF_3BH_3, for example, has a P–B distance of 1·836 Å (Kuczkowski & Lide, 1967), much shorter than any of the P–B distances in the trimethylphosphine series, and yet it is a very unstable compound almost completely dissociated at 0 °C. Phosphine–borane on the other hand is also unstable and dissociates readily, but has a P–B distance of 1·937 Å (Durig, Li, Carreira & Odom, 1973). Phosphine–boron halide complexes are known, but to date no structural data have been reported. Further structural work on compounds containing the phosphorus–boron dative bond is much to be desired.

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