Crystal Structure of Methyltriphenylphosphonium (η^4-Decaborato)-dimethylthallate(III)

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The title compound crystallizes in the orthorhombic space group *Pbca*, with a = 15.254(1), b = 20.576(2), c = 17.840(2) Å, and Z = 8. The structure was solved from diffractometer data by the heavy-atom method and refined by least squares to R 0.074 for 2 378 observed reflections. The structure is built up from methyltriphenylphosphonium cations with a normal configuration about the phosphorus atom, and $[Tl(\eta^4\text{-}B_{10}H_{12})Me_2]^-$ anions in which the thallium atom is bonded to two methyl groups at 2.22(3) Å and to four boron atoms [B(5) 2.51(2), B(10) 2.61(2), B(6) 2.76(2), and B(9) 2.77(2) Å]. The anion has an approximate mirror-plane containing C_2Tl,B(1), B(3) and there is no indication of preferential η^2-bonding to B(5)–B(6) as implied by the complex ^{11}B n.m.r. spectra of the compound in donor solvents.

THE *nido*-anion $[B_{10}H_{12}]^{2-}$ can co-ordinate in a variety of ways to metals, and examples of η^2-, bis-η^2-, and η^4-bonding are known.[1] A recent study of compounds containing the ions $[Hg(B_{10}H_{12})Me]^-$, $[In(B_{10}H_{12})Me_2]^-$, and $[Tl(B_{10}H_{12})Me_2]^-$ showed that, whereas the first two complexes involved η^4-bonding of the $[B_{10}H_{12}]^{2-}$ anion, the ^{11}B n.m.r. spectrum of the thallium complex was more complicated, implying a lower symmetry and the possibility of η^2-bonding, at least in acetone or tetrahydrofuran solutions.[2] To see whether this structure persists in the solid state, single crystals of $[PMePh_3]^+$-$[Tl(B_{10}H_{12})Me_2]^-$ were prepared and examined by X-ray diffraction techniques.

EXPERIMENTAL

Crystal Data.—$C_{21}H_{36}B_{10}PTl$, M = 631.96, Orthorhombic, a = 15.254(1), b = 20.576(2), c = 17.840(2) Å, U = 5 599.2 Å^3, Z = 8, D_c = 1.499 g cm^{-3}, $F(000)$ 2 464. Space group *Pbca* (D_{2h}^{15}, No. 61). Cu-$K_{\alpha 1}$ radiation, λ = 1.540 51 Å, μ(Cu-$K_{\alpha 1}$) = 117.2 cm^{-1}.

Collection and Processing of Data.—A crystal of dimensions *ca.* 0.1 × 0.2 × 0.4 mm^3 was cut from a larger matrix and mounted approximately about the b axis. Cell dimensions and estimated standard deviations were determined by a least-squares fit on 29 reflections centred by use of the programme SETANG. X-Ray intensity data were collected on an Enraf–Nonius CAD 4 automatic four-circle diffractometer with on-line control through a PDP 8 dedicated computer. Reflections to θ 60° were measured by use of Cu-$K_{\alpha 1}$ radiation, a graphite crystal monochromator, and a scintillation counter. Data were collected in three shells (3—30, 30—44, and 44—60°) as a precaution against crystal decomposition in the X-ray beam. The intensity measurement was carried out by use of the ω—2θ scan technique, each peak being scanned twice, together with an extension of the peak width of 25% on either side to give a measure of the background. Of 4 001 reflections measured, 1 623 were judged unobserved, having $I < 2.58\sigma(I)$, *i.e.* < 99% confidence limit. The nett count of the 606 reflection, measured as a reference every 50 reflections, fell during the period of data collection to 88% of its original value.

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[1] N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev.*, 1974, **3**, 231.

[2] N. N. Greenwood, B. S. Thomas, and D. W. Waite, *J.C.S. Dalton*, 1975, 299.

Data were scaled accordingly using this reflection, and Lorentz and polarisation corrections were applied. Only one quadrant ($+h+k+l$) of the orthorhombic cell was collected.

Solution and Refinement of Structure.—The crystal structure calculations system '*X*-Ray '70'[3] was used for the refinement of this structure, which was solved by Patterson and electron-density syntheses. Isotropic refinement including all the non-hydrogen atoms gave an *R* factor (based on *F*) of 0.116. *R* was further reduced by allowing thallium and phosphorus to refine anisotropically incorporating a dispersion correction for thallium and applying a weighting scheme of the type suggested by Hughes[4] with $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F > F^*$, with F^* 69 found to be the optimum; *R* was thus reduced to 0.077. Phenyl hydrogens were then included in calculated positions, (assuming C–H 1 Å), and a weighted difference Fourier map was calculated in an attempt to locate the remaining hydrogens. All 10 (B–H) terminal hydrogens could be readily identified, and likewise the three methyl hydrogens of the cation. However, the remaining two hydrogens on the borane moiety and the six hydrogens of the $TlMe_2$ group were too close to the heavy thallium atom for their peaks to be distinguishable from the diffraction pattern surrounding the thallium. Rotation of the methyl groups about the Tl–C bonds might also have prevented precise location of these hydrogen atoms. With all but these hydrogens included as a fixed contribution a final *R* of 0.074 was obtained for the 2 378 observed reflections. The weighted factor, *R′*, was 0.101.

Full-matrix least-squares refinement was used, and atomic scattering factors were from ref. 5 except those for hydrogen which were taken from ref. 6. The real and the imaginary parts of the anomalous dispersion correction for thallium were from ref. 7.

TABLE 1

Atomic co-ordinates and thermal parameters, with standard deviations in parentheses

(*a*) Positional and isotropic thermal parameters

Atom	*x*	*y*	*z*	(U/Å^2) × 10^2
Tl	0.031 17(4)	0.225 08(4)	0.232 95(4)	
P	0.258 2(3)	0.070 6(2)	0.499 2(2)	
C(1)	0.236 7(9)	0.005 5(7)	0.436 3(8)	3.2(3)
C(2)	0.231 9(11)	0.019 0(8)	0.354 84(10)	5.0(4)
C(3)	0.217 7(13)	−0.037 9(10)	0.311 6(11)	6.5(5)
C(4)	0.209 2(13)	−0.097 9(10)	0.339 0(11)	6.2(5)
C(5)	0.216 3(12)	−0.109 4(9)	0.414 8(10)	5.5(5)
C(6)	0.229 4(12)	−0.056 9(10)	0.462 5(11)	5.9(5)
C(7)	0.172 7(9)	0.074 7(7)	0.566 6(8)	3.3(4)
C(8)	0.086 1(13)	0.056 3(9)	0.546 9(10)	5.7(5)
C(9)	0.019 3(14)	0.060 9(11)	0.600 8(13)	7.2(6)
C(10)	0.037 4(12)	0.086 1(9)	0.670 4(11)	5.7(4)
C(11)	0.119 5(12)	0.106 4(9)	0.688 7(11)	5.5(5)
C(12)	0.187 6(12)	0.100 9(9)	0.637 4(10)	5.0(4)
C(13)	0.359 5(10)	0.057 7(8)	0.546 8(9)	4.1(4)
C(14)	0.366 1(12)	0.010 0(9)	0.601 4(10)	5.5(5)
C(15)	0.446 6(14)	0.000 4(10)	0.636 6(13)	7.3(6)
C(16)	0.517 3(14)	0.035 0(10)	0.616 5(12)	6.9(5)
C(17)	0.513 4(13)	0.076 1(10)	0.562 2(12)	6.5(5)
C(18)	0.435 7(13)	0.029 0(9)	0.526 2(11)	5.8(5)
C(19)	0.262 0(13)	0.145 5(10)	0.448 5(11)	6.1(5)
C(20)	0.050 0(16)	0.224 9(11)	0.110 2(16)	8.7(7)
C(21)	0.113 5(12)	0.256 5(10)	0.330 0(11)	6.0(5)
B(1)	−0.198 4(13)	0.162 0(9)	0.269 2(11)	4.3(4)
B(2)	−0.204 2(12)	0.236 5(9)	0.316 3(10)	4.3(5)
B(3)	−0.192 6(14)	0.164 5(10)	0.367 9(12)	5.1(5)
B(4)	−0.136 8(14)	0.100 5(10)	0.318 2(12)	5.1(5)
B(5)	−0.133 2(15)	0.229 6(10)	0 236 4(12)	5.2(5)
B(6)	−0.107 9(12)	0.279 5(10)	0.309 2(11)	4.4(4)
B(7)	−0.131 5(13)	0.235 7(9)	0.392 2(11)	4.7(5)
B(8)	−0.087 0(14)	0.141 2(10)	0.395 2(12)	5.0(5)
B(9)	−0.027 5(16)	0.118 1(12)	0.313 0(14)	6.4(6)
B(10)	−0.093 6(15)	0.138 5(10)	0.236 7(13)	5.6(5)

TABLE 1 (*Continued*)

Atom	*x*	*y*	*z*	(U/Å^2) × 10^2
(*b*) Hydrogen atoms included in the refinement but not themselves refined *				
H(2)	0.2375	0.0667	0.3340	5.0
H(3)	0.2100	−0.0317	0.2580	6.5
H(4)	0.2000	−0.1400	0.3000	6.2
H(5)	0.2120	−0.1615	0.4340	5.5
H(6)	0.2350	−0.0584	0.5220	5.9
H(8)	0.0800	0.0333	0.4940	5.7
H(9)	−0.0425	0.0450	0.5860	7.2
H(10)	−0.0125	0.0916	0.7060	5.7
H(11)	0.1300	0.1282	0.7380	5.5
H(12)	0.2480	0.1167	0.6520	5.0
H(14)	0.3080	−0.0150	0.6160	5.5
H(15)	0.4450	−0.0250	0.6820	7.3
H(16)	0.5780	0.0167	0.6460	6.9
H(17)	0.5700	0.0150	0.5400	6.5
H(18)	0.4300	0.1320	0.4840	5.8
H(19,1)	0.2636	0.1882	0.4860	6.1
H(19,2)	0.3214	0.1466	0.4164	6.1
H(19,3)	0.2091	0.1491	0.4127	6.1
(*c*) Terminal hydrogen atoms bonded to boron				
H(t1)	−0.2625	0.1417	0.2400	4.3
H(t2)	−0.2500	0.2833	0.3000	4.3
H(t3)	−0.2425	0.1417	0.4100	5.1
H(t4)	−0.1575	0.0417	0.3200	5.1
H(t5)	−0.1375	0.2500	0.1720	5.2
H(t6)	−0.1000	0.3367	0.3000	4.4
H(t7)	−0.1250	0.2667	0.4400	4.7
H(t8)	−0.0875	0.1330	0.4600	5.0
H(t9)	0.0250	0.0800	0.3260	6.4
H(t10)	−0.1000	0.1233	0.1680	5.6

(*d*) Anisotropic thermal parameters † (Å^2) × 10^4

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl	383(5)	719(5)	476(5)	−16(4)	14(3)	−48(4)
P	306(2)	423(20)	252(17)	−10(16)	−33(17)	−3(19)

* The phenyl hydrogens [H(1)—(18)] are in calculated positions assuming C–H 1.0 Å. All hydrogen temperature factors (including those for hydrogen atoms attached to boron) were given the same value as their parent atoms. † In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}ha^*kb^* + 2U_{13}ha^*lc^* + 2U_{23}kb^*lc^*)]$.

Final positional and thermal parameters are listed in Table 1.*

RESULTS AND DISCUSSION

The compound crystallizes in space group *Pbca* and no crystallographic symmetry conditions are imposed on the molecular structure. The unit cell contains eight $[PMePh_3]^+$ cations and eight $[Tl(B_{10}H_{12})Me_2]^-$ anions packed as indicated in Figure 1. The numbering system for the methyltriphenylphosphonium cation is shown in Figure 2, and interatomic distances and angles are listed

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* Observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 21565 (18 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[3] '*X*-Ray' System, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report TR 6758, version of July 1970.

[4] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

in Table 2. The phenyl rings adopt a propeller-like conformation and there is no significant deviation from the geometry observed in other compounds.[8]

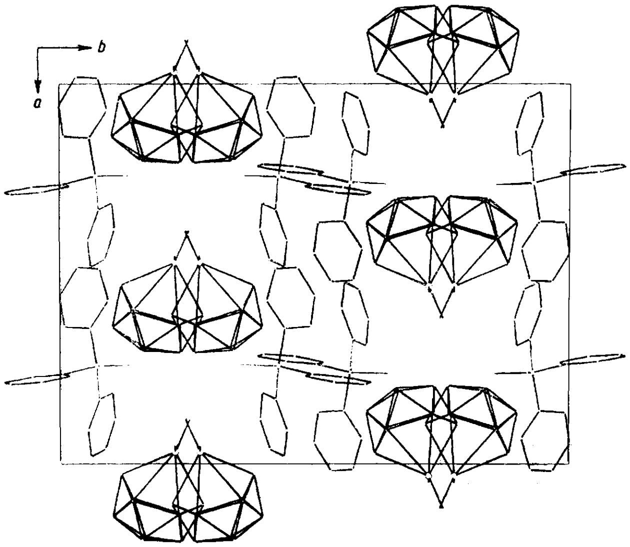

FIGURE 1 Unit cell of $[PMePh_3]^+[Tl(B_{10}H_{12})Me_2]^-$ viewed down the orthorhombic *c* axis

TABLE 2

Interatomic distances (Å) and angles (°) for the cation $[PMePh_3]^+$

(*a*) Distances

P–C(1)	1.78(1)	P–C(13)	1.78(2)
P–C(7)	1.78(1)	P–C(19)	1.79(2)
Mean C–C	1.39(1)	Mean C(19)–H	1.07

(*b*) Angles

C(1)–P–C(7)	109.1(7)	C(7)–P–C(13)	108.7(7)
C(1)–P–C(13)	110.4(7)	C(7)–P–C(19)	108.9(8)
C(1)–P–C(19)	109.6(8)	C(13)–P–C(19)	110.8(8)

Phenyl hydrogen atoms were placed in calculated positions assuming C–H 1.0 Å.

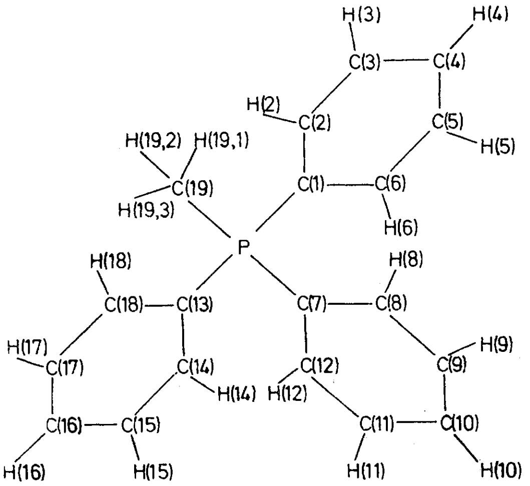

FIGURE 2 Numbering system for atoms in the $[PMePh_3]^+$ cation

The anion comprises a central thallium atom co-ordinated by two methyl groups and a η^4-decaborato-ligand. The geometry and numbering scheme are shown in Figure 3 and detailed interatomic distances and angles are listed in Table 3. Co-ordination can be considered to occur *via* two three-centre two-electron bonds from the formally bidentate *nido*-$[B_{10}H_{12}]^{2-}$ ligand. Thus two electrons are donated from the B(5)–B(6) bond to thallium and two further electrons from the B(9)–B(10) bond. The dihedral angle between the resulting B(5)–Tl–B(6) and B(9)–Tl–B(10) bonds is 66.2°; *cf.* 77.2 and 77.4° for the corresponding angles in the anion $[Zn(\eta^4\text{-}B_{10}H_{12})_2]^{2-}$.[9] Other angles arising from 'tetrahedral' co-ordination at thallium are much closer to 109°,

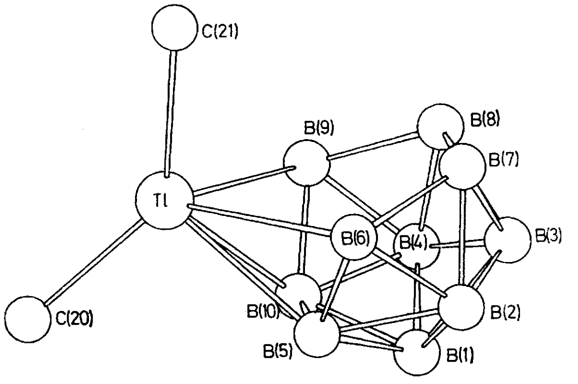

FIGURE 3 Structure and numbering scheme of the anion $[Tl(\eta^4\text{-}B_{10}H_{12})Me_2]^-$; hydrogen atoms are omitted for clarity

TABLE 3

Interatomic distances (Å) and angles (°) for the anion $[Tl(\eta^4\text{-}B_{10}H_{12})Me_2]^-$, with estimated standard deviations in parentheses. Values for decaborane * are in square brackets

(*a*) Distances

B(1)–B(2)	1.75(3) [1.78]	B(2)–B(6)	1.72(3) [1.72]
B(1)–B(4)	1.80(3) [1.77]	B(4)–B(9)	1.71(3) [1.72]
B(2)–B(3)	1.75(3) [1.77]	B(2)–B(5)	1.80(3) [1.79]
B(3)–B(4)	1.80(3) [1.78]	B(4)–B(10)	1.78(3) [1.79]
B(5)–B(10)	1.97(3) [1.97]	B(2)–B(7)	1.75(3) [1.79]
B(7)–B(8)	2.06(3) [1.97]	B(4)–B(8)	1.78(3) [1.79]
B(1)–B(5)	1.81(3) [1.76]	B(5)–B(6)	1.70(3) [1.79]
B(1)–B(10)	1.77(3) [1.75]	B(9)–B(10)	1.74(3) [1.76]
B(3)–B(7)	1.79(3) [1.75]	B(6)–B(7)	1.77(3) [1.76]
B(3)–B(8)	1.75(3) [1.76]	B(8)–B(9)	1.79(3) [1.79]
B(1)–B(3)	1.76(3) [1.77]		
Bonds to thallium			
Tl–B(5)	2.51(2)	Tl–B(10)	2.61(2)
Tl–B(6)	2.76(2)	Tl–C(20)	2.21(3)
Tl–B(9)	2.77(2)	Tl–C(21)	2.23(2)

(*b*) Angles

B(5)–Tl–B(6)	37.3(6)	B(6)–Tl–B(9)	79.6(7)
B(5)–Tl–B(9)	72.2(7)	B(6)–Tl–B(10)	72.7(6)
B(5)–Tl–B(10)	45.2(7)	B(9)–Tl–B(10)	37.7(7)
C(20)–Tl–B(5)	98.9(8)	C(21)–Tl–B(5)	122.1(7)
C(20)–Tl–B(6)	126.2(8)	C(21)–Tl–B(6)	86.1(6)
C(20)–Tl–B(9)	123.5(8)	C(21)–Tl–B(9)	90.7(7)
C(20)–Tl–B(10)	96.9(8)	C(21)–Tl–B(10)	126.0(7)
'Tetrahedral' bond angles			
B(5),B(6)–Tl–C(20)	113.8	B(9),B(10)–Tl–C(21)	107.9
B(5),B(6)–Tl–C(21)	103.3	C(20)–Tl–C(21)	134.1(8)
B(9),B(10)–Tl–C(20)	111.2		
Mean B–H(term)	1.19		

* Taken, with appropriate renumbering of the boron atoms, from A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 1969, **8**, 464.

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[8] R. M. Wing, *J. Amer. Chem. Soc.*, 1968, **90**, 4828.

[9] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc.* (*A*), 1971, 809.

except for the compensating expansion of the dimethylthallium bond angle to 134.1°.

Boron–boron distances within the cluster are as expected. The only notable deviation from values in decaborane(14) itself is the lengthening of B(7)–B(8) from 1.97(1) to 2.06(3) Å, a value which is close to that in $[Zn(\eta^4\text{-}B_{10}H_{12})_2]^{2-}$, *viz.* 2.08(2) Å.[9] Boron–terminal-hydrogen distances are normal. Unfortunately, the two presumed-bridging hydrogen atoms could not be located, though the most likely positions are between B(6)–B(7) and B(8)–B(9) respectively.

The results show that, in the crystalline state, the decaboratodimethylthallate(III) anion features an η^4-$[B_{10}H_{12}]^{2-}$ ligand and that the less symmetrical presumed η^2-structure implied by the ^{11}B n.m.r. spectrum in donor solvents does not persist in the solid. Likewise the positions of the ten terminal hydrogen atoms on the $[B_{10}H_{12}]^{2-}$ ligand give no indication of the presence of a BH_2 group in the complex and the geometry of the TlB_{10} cluster is essentially the same as that found in other complexes containing the η^4-dodecahydro-*nido*-decaborato ligand.[1]

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