

Tris(2-methylphenyl)phosphonium
tetrachloroborate

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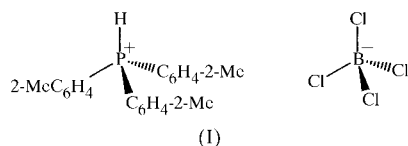
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The title compound, $C_{21}H_{22}P^+ \cdot BCl_4^-$, is the first structurally characterized example of the $[HP(o\text{-tolyl})_3]^+$ cation, presented here with BCl_4^- as the counter-ion. The cation has a near-tetrahedral P atom and the BCl_4^- anion is near-tetrahedral at boron. There are no unusually short cation–anion contacts.

Comment

The title compound, (I), was obtained as a hydrolysis product of the adduct $Cl_3B \cdot P(o\text{-tolyl})_3$ (Batsanov *et al.*, 2000). The structure contains the first crystallographically characterized example of the tris(*o*-tolyl)phosphonium ion.



The average P–C bond length in (I) of 1.7985 (18) Å is *ca* 2% shorter than that in $P(o\text{-tolyl})_3$ (mean P–C 1.836 Å; Cameron & Dahlèn, 1975), and the C–P–C bond angle of 110.69 (14)° is 3% greater than in the parent phosphine [mean C–P–C 102.8 (2)°]. The cation of (I) has a near-tetrahedral P atom [C–P–C 111.09 (9), 109.90 (8) and 111.07 (8)°] and the BCl_4^- anion is near-tetrahedral at boron [Cl–B–Cl range 108.78 (11)–110.40 (11)°]. There are no unusually short cation–anion contacts. The librational corrections to the title structure at 100 K were small and the comparisons of its molecular parameters with published structures remain valid.

A search of the Cambridge Structural Database (Allen *et al.*, 1991) for related $HPPH_3^+$ cations reveals that there are 11 such structures known. The average P–C bond length is 1.788 Å, less than 1% shorter than for the $HP(o\text{-tolyl})_3^+$ cation. This distance would be expected to be shorter because the latter compound has greater steric hindrance about this bond due to the extra methyl groups on the phenyl rings, but the difference is minimal. The overall range of this P–C bond length in the triphenylphosphonium cation is 1.753–1.849 Å,

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presumably displaying a dependence on the counter-ion present. The example with the shortest average P–C bond length contained the $[PrCl_6]^-$ anion (1.769 Å; Hasselgren *et al.*, 1997), and the structure displaying the largest average P–C bond length contained the $[CdBr_4]^{2-}$ dianion (1.809 Å; Majeste *et al.*, 1977). The bond-angle data display few differences, with the average triphenylphosphonium ion C–P–C bond angle of 110.62° being less than 1% different from the value of 110.69 (14)° for the tris(*o*-tolyl)phosphonium ion.

The tetrachloroborate anion shows weak interactions from three of the Cl atoms to three different methyl-group H atoms of the cation, with $D \cdots A$ distances ranging from 3.60 to 3.76 Å and $D-H \cdots A$ angles from 136 to 177°. There is no evidence for the H1 atom of the phosphonium cation being involved in hydrogen bonding.

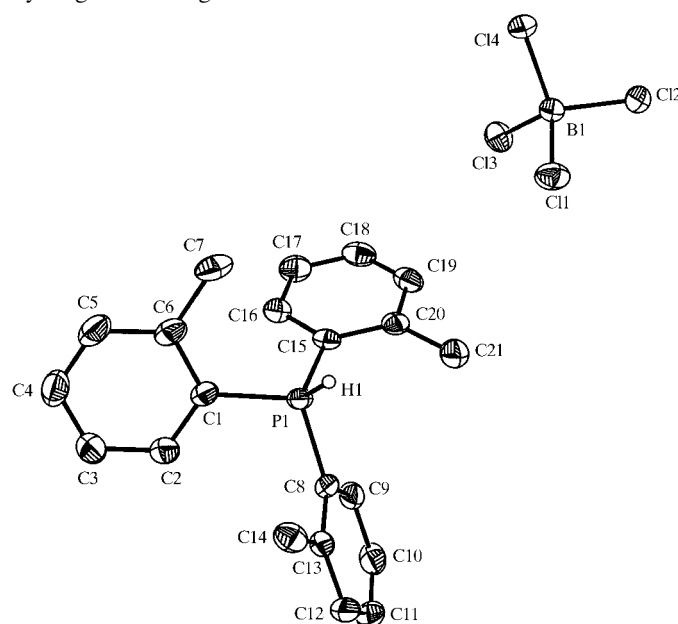


Figure 1

The molecular structure of (I) with displacement ellipsoids at the 70% probability level. The phosphonium proton is shown as a small sphere of arbitrary radius; other H atoms have been omitted for clarity.

Experimental

Addition of BCl_3 to a hexane solution of $P(o\text{-tolyl})_3$ afforded the adduct $Cl_3B \cdot P(o\text{-tolyl})_3$ as a white solid. The solvent was removed and a small amount of the resulting powder was dissolved in dichloromethane. Diffusion of this solution into hexane over several days afforded crystals of (I). The formation of this hydrolysis product is assumed to be due to the presence of adventitious water in the dichloromethane solvent, leading to the formation of HCl on reaction with BCl_3 , with the acid proceeding to form the title compound.

Crystal data

$C_{21}H_{22}P^+ \cdot BCl_4^-$
 $M_r = 457.97$
 Triclinic, $P\bar{1}$
 $a = 9.4160$ (3) Å
 $b = 11.4361$ (3) Å
 $c = 11.5642$ (3) Å
 $\alpha = 118.281$ (1)°
 $\beta = 90.114$ (1)°
 $\gamma = 93.444$ (1)°
 $V = 1093.98$ (5) Å³

$Z = 2$
 $D_x = 1.390$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 869 reflections
 $\theta = 10.19$ – 21.64 °
 $\mu = 0.619$ mm⁻¹
 $T = 100$ (2) K
 Block, colourless
 $0.48 \times 0.18 \times 0.10$ mm

Data collection

Bruker CCD area-detector diffractometer	6059 independent reflections
ω scans	4302 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (<i>XPREP</i> in <i>SHELXTL-NT</i> ; Bruker, 1998)	$R_{\text{int}} = 0.042$
$T_{\text{min}} = 0.814$, $T_{\text{max}} = 0.962$	$\theta_{\text{max}} = 30.47^\circ$
14 295 measured reflections	$h = -12 \rightarrow 13$
	$k = -15 \rightarrow 15$
	$l = -16 \rightarrow 16$
	Intensity decay: none

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.001$	$(\Delta/\sigma)_{\text{max}} = 0.001$
6059 reflections	$\Delta\rho_{\text{max}} = 0.43 \text{ e } \text{\AA}^{-3}$
332 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

P1—C15	1.7968 (18)	P1—C1	1.8009 (18)
P1—C8	1.7977 (18)	P1—H1	1.289 (19)
C15—P1—C8	111.09 (9)	C15—P1—H1	109.1 (8)
C15—P1—C1	109.90 (8)	C8—P1—H1	107.8 (8)
C8—P1—C1	111.07 (8)	C1—P1—H1	107.8 (8)

C—H distances are in the range 0.88 (2)–1.00 (2) \AA .

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1998); software used to prepare material for publication: *SHELXTL-NT*.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C7—H7B \cdots Cl2 ⁱ	0.95 (3)	2.81 (3)	3.758 (2)	177 (2)
C14—H14B \cdots Cl4	0.95 (3)	2.80 (3)	3.599 (2)	141 (2)
C12—H12A \cdots Cl1 ⁱⁱ	0.97 (2)	2.86 (2)	3.616 (2)	135.6 (16)
C21—H21B \cdots Cl1	0.91 (3)	2.85 (3)	3.725 (2)	161 (3)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x-1, y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1003). Services for accessing these data are described at the back of the journal.

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