Synthesis and X-Ray Crystal Structure of (Triphenylmethyl)trimethylphosphonium Tetrafluoroborate †

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The synthesis and X-ray crystal structure of the title compound $[Ph_3CPMe_3]BF_4$ is reported. Crystals are triclinic with a = 7.8400(9), b = 10.6765(7), c = 12.5116(9) Å, α = 87.165(9), β = 80.994(9), γ = 86.768(9)°, U = 1 032.2 Å^3, space group $P\bar{1}$. The structure was solved by direct methods and refined by full-matrix least-squares to R 0.078 for 2 374 diffractometer data. In the cation the P–C(CPh_3) distance [1.895(4) Å] is significantly longer than the P–C(Me) distances [1.787(6)—1.792(6) Å].

TRIPHENYLMETHYL (TRITYL) TETRAFLUROBORATE,[1] $Ph_3C^+BF_4^-$ is a useful reagent [2a] for various reactions such as hydride abstractions and oxidative cleavage and polymerisation of ethers.[2b] In transition-metal organometallic chemistry, $Ph_3C^+BF_4^-$ has usually been used to abstract hydride ions as in the formation of $C_7H_7Mo(CO)_3^+$ from $C_7H_8Mo(CO)_3$, but we have recently described [3] a case of proton addition to a metal complex.

The co-ordination of solvent molecules to the Ph_3C^+ cation has been suggested as a reason for the loss of yellow colouration when $Ph_3C^+BF_4^-$ is dissolved in ethers such as diethyl ether or tetrahydrofuran,[4] but no stable ether complexes have been reported. The addition of light petroleum to a clear concentrated solution of $Ph_3C^+BF_4^-$ in tetrahydrofuran with cooling to −78 °C does give a white crystalline solid in high yield but on warming to room temperature the material decomposes to a sticky brown tar. The pyridinium salt, $[Ph_3CNC_5H_5]BF_4$, used for the preparation of trityl ethers for the temporary protection of the primary alcohol function in a polyfunctional organic molecules,[5] has been reported although no structural details are known. During the course of other work,[3] we isolated and characterised a compound in which the trityl cation is co-ordinated to trimethylphosphine. Triphenylphosphine and several other tertiary phosphine and phosphite complexes, *e.g.* $Ph_3CPR_3^+PF_6^-$, have been described.[6]

The addition of trimethylphosphine to a solution of $Ph_3C^+BF_4^-$ in nitromethane at room temperature gives the phosphonium salt $[Ph_3CPMe_3]BF_4$ in high yield. This is white, crystalline, air-stable, a 1 : 1 electrolyte in nitromethane and is readily recrystallised from methanol. Spectroscopic and analytical data are in accord with the results of a single-crystal X-ray examination. The structure of the $[Ph_3CPMe_3]^+$ cation is shown in Figure 1, which also indicates the crystallographic atom numbering system. Important interatomic distances and angles are given in Table 1.

There are several features of the cation geometry worthy of comment. The three P–C(Me) distances are the same within experimental error [1.787(6)—1.792(6)Å] and are slightly shorter than those in $Me_3P{\cdot}BX_3$ (X = Cl, Br, and I) (1.807—1.849 Å) [7] and $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ [1.804(8)—1.827(4) Å].[8] In contrast, the P–C(CPh_3)

TABLE 1

(a) Bond lengths (Å) and angles (°) in the Me_3PCPh_3 cation

(i) Lengths

P–C(1)	1.895(4)	C(21)–C(22)	1.382(6)
P–C(2)	1.787(6)	C(21)–C(26)	1.386(5)
P–C(3)	1.790(5)	C(22)–C(23)	1.375(7)
P–C(4)	1.792(6)	C(23)–C(24)	1.380(6)
C(1)–C(11)	1.558(5)	C(24)–C(25)	1.369(8)
C(1)–C(21)	1.543(5)	C(25)–C(26)	1.378(6)
C(1)–C(31)	1.544(5)	C(31)–C(32)	1.395(6)
C(11)–C(12)	1.390(5)	C(31)–C(36)	1.388(6)
C(11)–C(16)	1.370(5)	C(32)–C(33)	1.382(6)
C(12)–C(13)	1.380(6)	C(33)–C(34)	1.369(8)
C(13)–C(14)	1.373(7)	C(34)–C(35)	1.378(7)
C(14)–C(15)	1.358(7)	C(35)–C(36)	1.380(6)
C(15)–C(16)	1.390(6)		

(ii) Angles

C(1)–P–C(2)	110.2(2)	P–C(1)–C(11)	107.0(2)
C(1)–P–C(3)	111.3(2)	P–C(1)–C(21)	110.7(2)
C(1)–P–C(4)	113.7(2)	P–C(1)–C(31)	107.0(3)
C(2)–P–C(3)	107.8(3)	C(11)–C(1)–C(21)	109.2(3)
C(2)–P–C(4)	107.1(3)	C(11)–C(1)–C(31)	111.9(3)
C(3)–P–C(4)	106.5(3)	C(21)–C(1)–C(31)	110.9(3)
C(1)–C(11)–C(12)	119.5(3)	C(1)–C(21)–C(22)	120.1(3)
C(1)–C(11)–C(16)	122.6(3)	C(1)–C(21)–C(26)	122.2(4)
C(12)–C(11)–C(16)	117.8(3)	C(22)–C(21)–C(26)	117.5(4)
C(11)–C(12)–C(13)	120.9(4)	C(21)–C(22)–C(23)	121.4(4)
C(12)–C(13)–C(14)	120.2(4)	C(22)–C(23)–C(24)	120.1(5)
C(13)–C(14)–C(15)	119.6(4)	C(23)–C(24)–C(25)	119.3(5)
C(14)–C(15)–C(16)	120.3(4)	C(24)–C(25)–C(26)	120.3(4)
C(11)–C(16)–C(15)	121.2(4)	C(21)–C(26)–C(25)	121.2(4)
C(1)–C(31)–C(32)	120.9(3)	C(32)–C(33)–C(34)	120.8(5)
C(1)–C(31)–C(36)	121.7(3)	C(33)–C(34)–C(35)	119.3(4)
C(32)–C(31)–C(36)	117.3(3)	C(34)–C(35)–C(36)	120.1(5)
C(31)–C(32)–C(33)	120.8(4)	C(31)–C(36)–C(35)	121.6(4)

(b) Geometry of the BF_4^- anion

(i) B–F distances (Å)

B–F(1)	1.347(8)	B–F(4)	1.296(12)
B–F(2)	1.295(9)	B–F(5)	1.451(12)
B–F(3)	1.301(11)	B–F(6)	1.509(15)

(ii) F–B–F angles (°)

F(1)–B–F(2)	113.2(5)	F(2)–B–F(6)	89.1(8)
F(1)–B–F(3)	126.9(8)	F(3)–B–F(4)	67.7(7)
F(1)–B–F(4)	100.5(7)	F(3)–B–F(5)	118.0(8)
F(1)–B–F(5)	102.5(7)	F(3)–B–F(6)	62.9(9)
F(1)–B–F(6)	85.7(7)	F(4)–B–F(5)	68.8(8)
F(2)–B–F(3)	108.3(7)	F(4)–B–F(6)	121.2(10)
F(2)–B–F(4)	136.6(8)	F(5)–B–F(6)	166.1(9)
F(2)–B–F(5)	77.4(7)		

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† No reprints available.

distance is significantly longer [1.895(9) Å], and this lengthening may be attributed to several very short interligand H · · · H contacts (Table 2) or 2.22—2.30 Å. Interestingly, there are no really significant angle distortions around the trityl carbon [107.0(3)—111.9(3)°] and those around the phosphorus atom are rather small [106.5(3)—113.7(2)°]. The fact that most of the steric strain in the cation has been taken up by the P–C bond to the trityl ligand suggests a significant difference in the bond strengths between this bond and those to the methyl groups. It is also noteworthy that the C–Ph bond lengths [1.543(5)—1.558(5) Å] are *ca.* 0.10 Å longer than in the trityl cation for the perchlorate [1.454(18) Å] [9] in which the trityl carbon is three-co-ordinate and has a planar configuration.

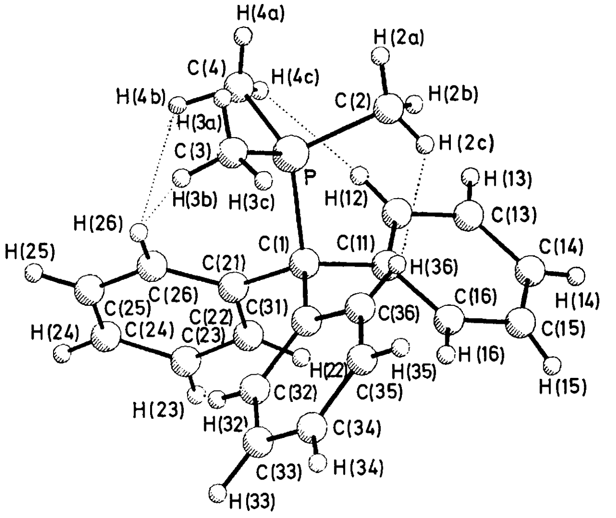

FIGURE 1 Structure of the Me_3PCPh_3 cation showing the atom numbering scheme and significant H · · · H contacts

TABLE 2

Selected non-bonded short contacts (Å)

(*a*) Intramolecular H · · · H contacts (<2.40Å) in the Me_3PCPh_3 cation

H(2c) · · · H(36)	2.30	H(4b) · · · H(26)	2.22
H(3b) · · · H(26)	2.23	H(4c) · · · H(12)	2.26

(*b*) F · · · C contacts (<3.6 Å)

F(1) · · · $C(3^{I})$	3.49	F(4) · · · $C(26^{III})$	3.39
F(1) · · · $C(4^{II})$	3.26	F(4) · · · $C(33^{VI})$	3.31
F(1) · · · $C(4^{III})$	3.43	F(5) · · · $C(2^{I})$	3.43
F(1) · · · $C(26^{III})$	3.45	F(5) · · · $C(3^{I})$	3.56
F(2) · · · $C(2^{I})$	3.16	F(5) · · · $C(4^{I})$	3.43
F(2) · · · $C(2^{IV})$	3.41	F(5) · · · $C(14^{V})$	3.37
F(2) · · · $C(3^{I})$	3.49	F(6) · · · $C(2^{IV})$	3.27
F(2) · · · $C(13^{II})$	3.51	F(6) · · · $C(4^{II})$	3.34
F(2) · · · $C(13^{V})$	3.51	F(6) · · · $C(25^{III})$	3.46
F(3) · · · $C(25^{III})$	3.43		
F(3) · · · $C(33^{VI})$	3.50		
F(3) · · · $C(34^{VI})$	3.31		

Roman numerals denote the following equivalent positions relative to the reference molecule at x,y,z:

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

All the phenyl rings are planar (Table 3) and have dimensions as expected.

TABLE 3

Least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Deviations (Å × 10^3) of relevant atoms are given in square brackets

Plane (1): C(11)—(16)
$5.1441x + 5.7883y + 8.4589z = 11.0450$
[C(1) −65, C(11) 5, C(12) −8, C(13) 5, C(13) 5, C(14) 1, C(15) −4, C(16) 1]

Plane (2): C(21)—(26)
$-3.3117x + 1.0776y + 10.3224z = 5.6069$
[C(1) −0.043, C(21) 17, C(22) 1, C(23) −18, C(24) 18, C(25) 0, C(26) −18]

Plane (3): C(31)—(36)
$4.7293x - 6.2615y + 7.0401z = 6.7213$
[C(1) −30, C(31) −1, C(32) 7, C(33) −2, C(34) −8, C(35) 14, C(36) −10]

Angles (°) between normals to planes:

(1)–(2)	73.2	(2)–(3)	83.3
(1)–(3)	68.8		

The BF_4^- anion is disordered (see Experimental section) with B–F distances ranging from 1.295(9) to 1.509(15) Å. Cation–anion short contacts are listed in Table 2. A view of the unit-cell contents is shown in Figure 2.

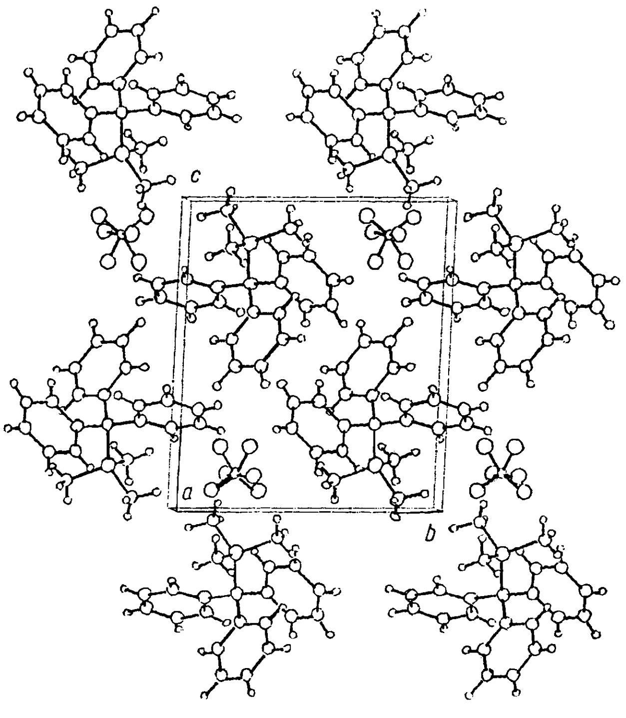

FIGURE 2 The unit-cell contents projected along *a*

EXPERIMENTAL

Microanalyses were by the Imperial College Laboratory. All operations were performed under nitrogen or in vacuum. Nitromethane was dried over 4A molecular sieves and methanol over magnesium methoxide and the latter was distilled under nitrogen before use.

Instruments.—I.r.: Perkin-Elmer 597; N.m.r.: ^1H, Perkin-Elmer R32, ^{31}P and ^{13}C, Varian XL100 (F.T.).

Conductivity data were obtained on a Mullard conductivity bridge type E7566/3 with a matching conductivity cell.

(Triphenylmethyl)trimethylphosphonium Tetrafluoroborate.—Trimethylphosphine (0.14 ml, 1.4 mmol) was added to a solution of trityl tetrafluoroborate (0.45 g, 1.36 mmol) in nitromethane (10 ml) at room temperature. The suspension was stirred (0.5 h) then volatile materials were removed under vacuum and the white residue dissolved in hot (50 °C) methanol (60 ml). The solution was filtered and cooled (−20 °C) to yield white crystals, which were collected and dried under vacuum. A further batch was obtained from the supernatant liquid after evaporation to *ca.* 20 ml and cooling. Yield, 0.52 g, 95%; m.p. (sealed tube under N_2), 250—251 °C. A pale orange liquid is formed on melting which slowly turns pale yellow, then colourless, after *ca.* 0.5 h at 251 °C (Found: C, 64.9; H, 5.9; P, 7.5%; $C_{22}H_{24}BF_4P$ requires C, 65.0; H, 5.9; P, 7.6%).

N.m.r., ^1H in CD_3NO_2 at 35 °C and 90 MHz, referenced to internal $SiMe_4$ (δ 0.0): δ 7.27—7.57 (m), 7.47—7.27 (15 H, m, Ph_3C), δ 2.21 (9 H, d, $^2J_{P-H}$ 13.5 Hz, PMe_3); $^{31}P\{^1H\}$ in CD_3NO_2 at 28 °C and 40.5 MHz, referenced to external 85% H_3PO_4(aq.): (δ 0.0), δ 42.51 (s); $^{13}C\{^1H\}$: δ 134.03 (s, Ph_3C), 129.30, 128.56, 123.00, 122.05 [s, $(C_6H_5)_3C$], 7.42 (d, $^1J_{C-P}$ 49.8 Hz). In the ^{13}C, ^1H coupled spectrum the PMe_3 doublet is split into a quartet of doublets; $^1J_{C-H}$ 80.3 Hz. In CD_3NO_2 (δ 57.3) at 28 °C and 25.2 MHz referenced to $SiMe_4$ (δ 0.0).

I.r. (Nujol mull, KBr plates) cm^{-1}: 3 110w, 3 090w, 3 075w, 3 055w, 3 035m, 3 020m, 3 000m, 1 594w, 1 580w, 1 488m, 1 448s, 1 417w, 1 365m, 1 329m, 1 306m, 1 288w, 1 187w, 1 163w, 1 050s(br), 999m, 963s, 930w, 905w, 852w, 767m, 760m, 755m, 744s, 701s, 656w, 625w, 615w, 521w, 509w, and 496w. Conductivity $\Lambda = 93\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3}M in CH_3NO_2 at 25 °C.

X-ray Crystallography.—Crystals suitable for *X*-ray work were sealed under vacuum in Lindemann capillaries. The crystal system and preliminary unit-cell parameters were determined from oscillation and Weissenberg photographs. Accurate cell-parameters were obtained from least-squares refinement of the setting angles for twenty-five reflections automatically centered on a Nonius CAD 4 diffractometer at the beginning of data collection.

Crystal Data.—$C_{22}H_{24}P{\cdot}BF_4$, $M = 406.2$, Triclinic, $a = 7.844\,0(9)$, $b = 10.676\,5(7)$, $c = 12.511\,6(9)$ Å, $\alpha = 87.165(9)$, $\beta = 80.994(9)$, $\gamma = 86.768(9)°$, $U = 1\,032.2$ Å^3, $D_m = 1.30$ g cm^{-3}, $Z = 2$, $D_c = 1.31$ g cm^{-3}, $F(000) = 424$, Cu-K_α radiation, $\lambda = 1.541\,8$ Å; λ (Cu-K_α) = 14.3 cm^{-1}. Space group $P\bar{1}$.

Three-dimensional *X*-ray diffraction data ($3 < \sigma < 70°$) were collected from a single crystal (0.190 × 0.120 × 0.062 mm) by use of a CAD 4 diffractometer, Cu-K_α radiation (Ni filter) and an ω—2θ scan technique (scan width $0.8 + 0.15 \tan\theta$). All data in one half of reciprocal space (h, $\pm k$, $\pm l$) were measured. Two standard reflections monitored after each hour showed only minor fluctuations in the diffracted beam.

All intensities were corrected for Lorentz and polarisation effects and variable measuring time, but not for absorption or extinction. The total 4 017 data reduced to 3 919 independent intensities (merging *R* 0.013 4) of which 2 374 were defined as observed [$F_o > 3\sigma(F_o)$] and used in the final refinement.

The structure was solved assuming the space group as $P\bar{1}$, a choice finally confirmed by successful refinement. The phosphorus and eighteen carbon atoms in the structure were located from the ' best ' *E* map computed with the automatic direct methods routine in the SHELX 76 program.[10] Four cycles of isotropic least-squares refinement [10] of these atoms was followed by a difference electron-density synthesis which gave the positions of other non-hydrogen atoms in the structure. The BF_4^- anion was found to be disordered with six positions of significant electron density (>1 e Å^{-3}) appropriate for the fluorine

TABLE 4

Final non-hydrogen atomic fractional co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
P	7 490(1)	2 351(1)	8 592(1)
C(1)	6 625(5)	2 477(3)	7 257(3)
C(2)	7 643(9)	3 880(5)	9 081(5)
C(3)	9 601(7)	1 589(6)	8 447(4)
C(4)	6 171(9)	1 481(6)	9 638(4)
C(11)	5 372(5)	3 664(3)	7 289(3)
C(12)	3 937(5)	3 741(4)	8 094(3)
C(13)	2 770(6)	4 760(4)	8 122(4)
C(14)	2 993(7)	5 705(4)	7 335(4)
C(15)	4 377(7)	5 636(4)	6 534(5)
C(16)	5 566(6)	4 618(4)	6 513(3)
C(21)	5 620(5)	1 311(3)	7 114(3)
C(22)	4 162(5)	1 435(4)	6 618(3)
C(23)	3 291(6)	406(4)	6 427(4)
C(24)	3 838(7)	−781(4)	6 762(4)
C(25)	5 305(7)	−926(4)	7 231(4)
C(26)	6 200(6)	106(4)	7 392(3)
C(31)	8 195(5)	2 599(3)	6 352(3)
C(32)	8 454(5)	1 804(4)	5 483(3)
C(33)	9 836(7)	1 938(5)	4 660(4)
C(34)	10 994(7)	2 846(5)	4 682(4)
C(35)	10 785(6)	3 623(5)	5 545(4)
C(36)	9 384(6)	3 514(4)	6 355(4)
B *	1 130(10)	2 447(7)	1 124(5)
F(1)	2 041(5)	1 524(4)	557(3)
F(2)	614(9)	3 362(4)	515(4)
F(3)	1 470(13)	2 911(9)	2 005(6)
F(4)	479(15)	1 812(10)	1 987(8)
F(5)	−643(10)	2 157(11)	1 087(8)
F(6)	2 837(17)	3 055(11)	1 057(15)

* Occupation factors for the atoms in BF_4^- ion: B 1.00, F(1) 1.00, F(2) 0.87, F(3) 0.71, F(4) 0.56, F(5) 0.53, F(6) 0.33.

TABLE 5

Hydrogen-atom fractional co-ordinates (× 10^3), and their bonded distances (Å × 10^2)

Atom	*x*	*y*	*z*	*d*(C–H)
H(2a) *	806(6)	379(4)	973(4)	92(5)
H(2b)	642(8)	419(5)	924(4)	100(6)
H(2c)	772(9)	444(6)	857(5)	85(7)
H(3a)	997(6)	147(4)	912(4)	94(5)
H(3b)	952(7)	80(6)	817(4)	94(6)
H(3c)	1 035(6)	211(4)	798(4)	95(5)
H(4a)	668(9)	159(7)	1 026(4)	92(8)
H(4b)	634(7)	54(6)	943(4)	105(6)
H(4c)	503(10)	172(7)	969(6)	91(8)
H(12)	376(5)	315(4)	863(3)	90(4)
H(13)	181(6)	473(4)	872(4)	97(4)
H(14)	220(6)	636(4)	731(3)	91(4)
H(15)	454(6)	612(4)	593(5)	89(4)
H(16)	648(4)	463(3)	597(3)	91(3)
H(22)	380(5)	222(4)	633(3)	94(4)
H(23)	227(7)	49(5)	608(4)	96(6)
H(24)	319(5)	−150(4)	664(3)	98(4)
H(25)	572(6)	−176(4)	746(3)	97(5)
H(26)	718(5)	−3(4)	774(3)	94(4)
H(32)	771(5)	117(4)	546(3)	92(4)
H(33)	984(7)	130(5)	404(4)	106(6)
H(34)	1 192(6)	298(4)	413(4)	93(4)
H(35)	1 153(5)	427(4)	559(3)	94(4)
H(36)	930(6)	409(4)	689(4)	93(5)

* Hydrogen atoms are numbered according to their parent carbon atoms and distinguished by a, b, or c, if more than one is present.

atoms. These positions were assigned fractional occupancies relative to their peak heights and included in the refinement. All hydrogen-atom positions in the structure were obtained from difference maps and refined isotropically. With anisotropic temperature factors for all non-hydrogen atoms, the refinement finally converged at R 0.078 and R' $[=(\Sigma w\Delta F^2/\Sigma w|F_0|^2)^{\frac{1}{2}}] = 0.073$. The weighting scheme $w = 1/([\sigma^2(F_0) + 0.000\,6|F_0|^2]$ was applied and gave flat analyses of variance with sin θ, $(F_0/F_{\mathrm{max.}})^{\frac{1}{2}}$, parity groups, and reflection indices. Final atomic parameters are given in Tables 4 and 5. Anisotropic thermal parameters for the non-hydrogen atoms, and lists of observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22640 (13 pp.).* Neutral atom scattering factors were taken from ref. 11 for non-hydrogen atoms and from ref. 12 for hydrogen. All computations were performed on the Queen Mary College ICL 1904S and University of London CDC 7600 computers. The diagrams were drawn by use of the program PLUTO [13] and the least-squares plane calculations were done with XANADU.[14]

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