Triphenylmethyl tris(*p*-methoxyphenyl)phosphonium cation: a structurally characterized phosphonium analog of hexaphenylethane

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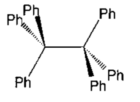
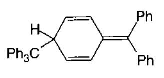
Reaction of tris(*p*-methoxyphenyl)phosphine with $[Ph_3C][B(Ar_F)_4]$ $[Ar_F = 3,5\text{-}(CF_3)_2C_6H_3]$ afforded $[Ph_3CP(4\text{-}OMeC_6H_4)_3][B(Ar_F)_4]$, a structural analog of hexaphenylethane, which shows a very long P–C distance [1.931(3) Å] in the solid state, indicating a strong steric repulsive interaction between the two parts of the phosphonium cation.

Since Gomberg's first attempted synthesis of hexaphenylethane (**A**) exactly a century ago[1] this relatively simple molecule has remained an elusive synthetic target. Attempts to prepare this species *via* dimerization of triphenylmethyl radicals have invariably led to rearrangements, and subsequent isolation of the "Gomberg dimer" (**B**).[2] However, the preparation of a sterically encumbered derivative of hexaphenylethane, namely Ar_3CCAr_3 (Ar = 3,5-*tert*-Bu_2-C_6H_3), has been reported and a central C–C distance of 1.67(3) Å was determined by X-ray diffraction[3] in close agreement with the theoretically predicted distance of 1.64 Å.[4] The principal reason for our current inability to isolate unsubstituted hexaphenylethane is thought to be the steric repulsive interaction between the two trityl fragments.[1,5]

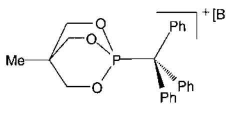


A

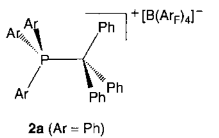


B

During recent investigations of highly electrophilic metal complexes containing tied-back phosphite ligands,[6] we synthesized and structurally characterized the phosphite cation **1**. As a logical extension of this work, we then prepared and characterized the phosphonium salts **2**, which are isoelectronic analogs of hexaphenylethane. A search of the literature revealed few reports of similar phosphonium analogs of **A**, and no structural characterization of this class of compounds appears to have been documented to date.[7,8] Here we report the preparation and structural characterization of **1** and **2b**.



1



2a (Ar = Ph)
2b (Ar = 4-OMeC₆H₄)

Results and discussion

Compound **1** was readily prepared as colorless crystals in 86% yield by reaction of the tied-back phosphite $P(OCH_2)_3CMe$[9] with $[Ph_3C][B(Ar_F)_4]$ $[Ar_F = 3,5\text{-}(CF_3)_2C_6H_3]$[10] in methylene chloride at room temperature, followed by crystallization from CH_2Cl_2–hexane. **1** is air- and light-stable and was characterized by ^1H, ^{13}C, ^{31}P NMR and elemental analysis. The ^{31}P NMR chemical shift (54.2 ppm) is significantly upfield shifted from the 90.4 ppm of the free phosphite. The solid-state structure of **1** was determined by an X-ray diffraction study, and the molecular geometry is shown in Fig. 1. The structure displays a typical tetrahedral geometry about the central carbon atom C(6), with the three phenyl groups adopting a propeller arrangement. The central P(1)–C(6) bond [1.818(4) Å], average P–O distance [1.552(3) Å] and average C(6)–C_{phenyl} distance [1.547(5) Å] are not unusual. Looking down the P(1)–C(6) axis, it can be seen that the substituents on the phosphorus atom and C(6) are not perfectly staggered, with the O(3)–P(1)–C(6)–C(13) torsion angle being 158.2° rather than 180° for a staggered structure.

The triphenylphosponium complex $[Ph_3CPPh_3][B(Ar_F)_4]$ (**2a**) was similarly prepared as colorless crystals. The single ^{31}P NMR resonance observed in **2a** (26.7 ppm) is downfield shifted compared to the -3.1 ppm of free triphenylphosphine. However, attempts to obtain single-crystal X-ray diffraction data for this complex were unsuccessful. In order to prepare a substituted derivative of **2a**, tris(*p*-methoxyphenyl)phosphine was treated with one equivalent of $[Ph_3C][B(Ar_F)_4]$ to afford $[Ph_3CP(4\text{-}OMeC_6H_4)_3][B(Ar_F)_4]$ (**2b**) as an air-stable white

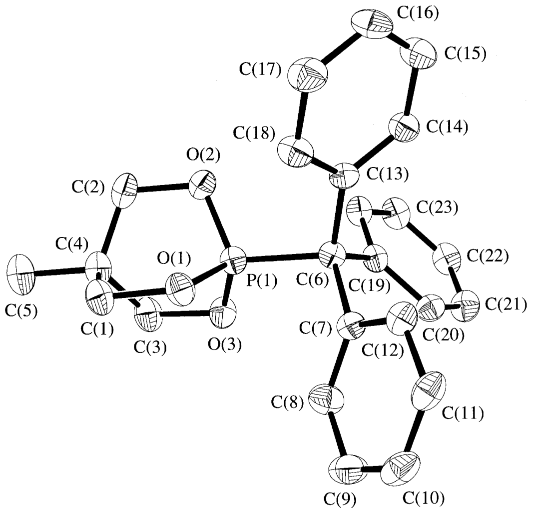


Fig. 1 Thermal ellipsoid plot of the molecular structure of the cationic portion of $[Ph_3CP(OCH_2)_3CMe][B(Ar_F)_4]$ (**1**). Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.553(3), P(1)–O(2) 1.555(3), P(1)–O(3) 1.549(3), P(1)–C(6) 1.818(4), C(6)–C(7) 1.546(5), C(6)–C(13) 1.546(5), C(6)–C(19) 1.549(5); O(1)–P(1)–O(2) 106.76(15), O(1)–P(1)–O(3) 107.06(15), O(2)–P(1)–O(3) 106.74(15), O(1)–P(1)–C(6) 111.17(15), O(2)–P(1)–C(6) 112.53(15), O(3)–P(1)–C(6) 112.21(16).

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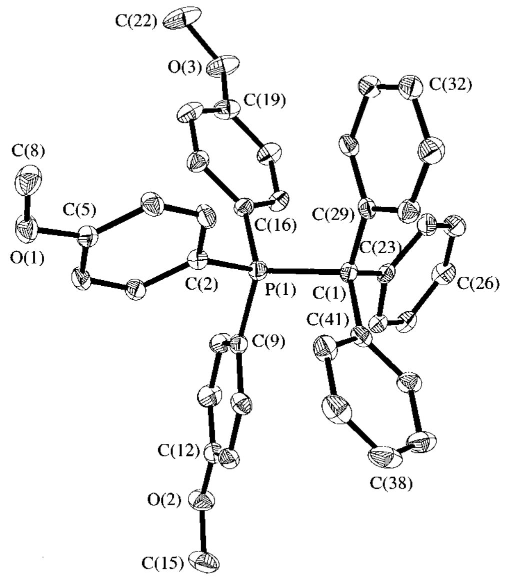

Fig. 2 Thermal ellipsoid plot of the molecular structure of the cationic portion of $[Ph_3CP(4\text{-}OMeC_6H_4)_3][B(Ar_F)_4]$ (**2b**). Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.931(3), P(1)–C(2) 1.804(4), P(1)–C(9) 1.798(4), P(1)–C(16) 1.798(4); C(2)–P(1)–C(9) 107.03(17), C(9)–P(1)–C(16) 108.05(16), C(16)–P(1)–C(2) 106.19(17), C(9)–P(1)–C(1) 109.63(16), C(2)–P(1)–C(1) 114.29(16), C(16)–P(1)–C(1) 111.37(16).

solid. As observed in compound **2a**, the ^{31}P NMR chemical shift of **2b** (23.5 ppm) is significantly downfield from the −7.9 ppm observed for the free phosphine. Single crystals suitable for X-ray diffraction analysis were grown from mixed THF–hexane solvent, and the molecular structure of **2b** is shown in Fig. 2. The cationic $[Ph_3CP(4\text{-}OMeC_6H_4)_3]^+$ moiety in **2b** adopts a conformation that is very close to staggered, with the C(23)–C(1)–P(1)–C(2) torsion angle being 173.6°. The central P(1)–C(1) bond distance of 1.931(3) Å is much longer than the average P(1)–C_{phenyl} distance of 1.800(3) Å, and appears to be one of the longest P–C bonds reported in the literature. Among the few directly comparable P–C distances is that of 1.924(4) Å observed in the sterically congested phosphonium salt $[P(tert\text{-}Bu)_4][BF_4]$.[11] Other examples of P–C distances between a triphenylphosphonium moiety and a tertiary carbon atom include 1.880(3) Å in $[Ph_3P\text{–}C(Me)_2CS_2]$,[12] 1.867(7) Å in $[(4\text{-}MeC_6H_4)_3P\text{–}C(Me)_2CH_2C(O)Me]$[13] and 1.857(8) Å in $[Ph_3P\text{–}(cyclo\text{-}C_5H_9)C(O)OEt]$.[14] In contrast to the long P(1)–C(1) distance, the average P(1)–C_{phenyl} distance of 1.800(3) Å is actually shorter than the 1.828(4) Å found in tris(*p*-methoxyphenyl)phosphine itself.[15] Consideration of the angles about P(1) also gives some insight into the steric interaction between the two sets of phenyl groups. While the C_{phenyl}–P(1)–C_{phenyl} angles are very close to tetrahedral values [averaging 107.07(17)°], the C(1)–P(1)–C_{phenyl} angles are somewhat larger, averaging 111.76(16)°. Thus the phenyl rings bound to the phosphorus atom are effectively pushed back away from the rings of the trityl moiety.

Both the exceptionally long P(1)–C(1) distance and the deviation around the tetrahedral phosphorous atom in **2b** clearly show a significant steric repulsive interaction between the sets of methoxyphenyl and phenyl groups. As a further indication of this steric interaction, we note that tris(*o*-tolyl)phosphine does not react with $[Ph_3C][B(Ar_F)_4]$ under the conditions used to prepare **2a** and **2b**.

Experimental

General procedures and techniques

All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques, or under oxygen-free helium in a Vacuum Atmospheres drybox. Hexane and toluene were dried by passage through columns of activated alumina and activated Cu-0226 S copper catalyst (Engelhard). THF was dried by passage through a column of activated alumina. Methylene chloride was distilled from P_2O_5 under argon. CD_2Cl_2 was degassed, dried over P_2O_5, and then trap-to-trap distilled before use. NMR spectra were recorded at 22 °C on a Varian Unity 300 spectrometer. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in dichloromethane-d_2, set at δ 5.32. Elemental analyses were performed on a Perkin–Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Syntheses

$[Ph_3CP(OCH_2)_3CMe][B(Ar_F)_4]$ (1). To a mixture of $P(OCH_2)_3CMe$ (18.3 mg, 0.121 mmol) and $[Ph_3C][B(Ar_F)_4]$ (137 mg, 0.124 mmol) was added CH_2Cl_2 (5 mL) at room temperature. The mixture was stirred for 30 min; hexane was then layered on top of the CH_2Cl_2 to give **1** (125 mg, 86%) as colorless crystals. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.05 (s, 3H), 4.83 (d, 6H, $J = 5.6$ Hz), 7.12 (m, 6H), 7.47 (m, 9H), 7.56 (s, 4H), 7.73 (s, 8H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 13.6, 36.9 (d, $J = 34.2$ Hz), 89.1 (d, $J = 7.7$ Hz), 117.9, 130.1, 130.5, 130.6, 130.7, 133.8, 135.3. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 54.2. Anal. calc. for $C_{56}H_{36}BF_{24}O_3P$: C, 53.59; H, 2.87. Found: C, 53.53; H, 2.96%.

$[Ph_3CPPh_3][B(Ar_F)_4]$ (2a). This compound was prepared in a manner directly analogous to that of **1**, using PPh_3 and $[Ph_3C][B(Ar_F)_4]$ (91% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ 6.82 (dd, 6H, $J = 11.5$, 7.4 Hz), 6.99 (d, 6H, $J = 8.3$ Hz), 7.32 (t, 6H, $J = 8.0$ Hz), 7.45 (dt, 6H, $J = 7.9$, 3.6 Hz), 7.53 (dt, 3H, $J = 7.3$, 1.2 Hz), 7.55 (s, 4H), 7.72 (s, 8H), 7.78 (t, 3H, $J = 8.3$ Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 117.9, 129.6, 130.7, 130.9, 132.4, 132.5, 135.2, 135.5, 135.6, 135.8. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 26.7. Anal. calc. for $C_{69}H_{42}BF_{24}P$: C, 60.53; H, 3.07. Found: C, 60.17; H, 3.04%.

$[Ph_3CP(4\text{-}OMeC_6H_4)_3][B(Ar_F)_4]$ (2b). This compound was prepared as for **1**, using $P(4\text{-}OMeC_6H_4)_3$ and $[Ph_3C][B(Ar_F)_4]$ (85% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 9H), 6.70 (t, 6H, $J = 9.9$ Hz), 6.90 (dd, 6H, $J = 9.2$, 2.6 Hz), 7.00 (d, 6H, $J = 7.8$ Hz), 7.34 (t, 6H, $J = 7.8$ Hz), 7.49 (t, 3H, $J = 7.4$ Hz), 7.54 (s, 4H), 7.74 (s, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 110.4, 115.5, 116.1, 116.2, 117.7, 123.0, 126.6, 128.9, 129.3, 130.2, 132.1, 132.2, 135.0, 136.8, 137.0, 137.1, 162.3 (q, $J = 50.0$ Hz), 165.1 (d, $J = 3.2$ Hz, $PCPh_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.5.

X-Ray crystallography

Data were collected on a Bruker P4/CCD/PC diffractometer, cooled to 203 K with a Bruker LT-2 temperature device, using a sealed, graphite-monochromated Mo-Kα X-ray source ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a combination of φ and ω scans, with 20 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement was handled using SMART[16] software. Frame integration and final cell parameter calculations were carried out using SAINT[17] software. The final cell parameters were determined using a least-squares fit to 4402 reflections. The data were corrected for absorption using the SADABS[18] program. Decay of reflection intensity was not observed.

Table 1 Crystallographic data for $[Ph_3CP(OCH_2)_3CMe][B(Ar_F)_4]$ (**1**) and $[Ph_3CP(4\text{-}OMeC_6H_4)_3][B(Ar_F)_4]$ (**2b**)

	1	**2b**
Empirical formula	$C_{58}H_{40}BCl_4F_{24}O_3P$	$C_{72}H_{48}BF_{24}O_3P$
Formula weight	1424.48	1458.88
T/K	203(2)	203(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	14.1573(7)	14.2714(8)
b/Å	25.7899(15)	15.7335(9)
c/Å	17.8733(10)	17.2879(9)
α/°		113.553(1)
β/°	108.646(1)	104.959(1)
γ/°		97.734(1)
U/Å^3	6183.3(6)	3311.7(3)
Z	4	2
μ/mm^{-1}	0.333	0.158
Reflections collected	22 661	12 747
Independent reflections	8419 [R(int) = 0.0280]	8914 [R(int) = 0.0214]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0685$, $wR_2 = 0.2022$	$R_1 = 0.0640$, $wR_2 = 0.1693$
R indices (all data)	$R_1 = 0.0854$, $wR_2 = 0.2149$	$R_1 = 0.0835$, $wR_2 = 0.1793$

The structures were solved using direct methods and difference Fourier techniques. The initial solution revealed the majority of all non-hydrogen atom positions. The remaining atomic positions were determined from subsequent Fourier synthesis. Structure solution, refinement, graphics and creation of publication tables were performed using SHELXTL NT.[19] Additional details of data collection and structure refinement are listed in Table 1.

CCDC reference number 440/198. See http://www.rsc.org/suppdata/nj/b0/b003233f/ for crystallographic files in .cif format.

$[Ph_3CP(OCH_2)_3CMe][B(Ar_F)_4]$ (1). Two dichloromethane molecules were found in the lattice. The chlorine atoms of one solvent dichloromethane, and several fluorine atoms of the $[B(Ar_F)_4]$ anion were refined as two, one-half occupancy positions due to disorder. Hydrogen atom positions were idealized, and refined using the riding model, with isotropic temperature factors fixed to 1.2 (1.5 for methyl) times the equivalent isotropic U of the carbon atom to which they were bound. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Hydrogen atoms were not placed on the disordered dichloromethane molecule.

$[Ph_3CP(4\text{-}OMeC_6H_4)_3][B(Ar_F)_4]$ (2b). Hydrogen atom positions were fixed (C–H = 0.93 Å for aromatic 0.96 Å for methyl). The hydrogen atoms were refined using the riding model, with isotropic temperature factors fixed to 1.5 (methyl) or 1.2 (all others) times the equivalent isotropic U of the carbon atom to which they were bound. The final refinement included anisotropic temperature factors on all non-hydrogen atoms.

Acknowledgements

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