Short communication

The first synthesis, isolation and X-ray structure of a phosphonium phosphide, $(Ph_3PMe)^+\{[C_6H_2(CF_3)_3\text{-}2,4,6]_2P\}^-$ [1]

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Abstract

The synthesis of a bulky secondary phosphine, Ar_2PH [$Ar = C_6H_2(CF_3)_3$-2,4,6], and its use in the first synthesis and isolation of a phosphonium phosphide, $(Ph_3PMe) + (Ar_2P)^-$, via the deprotonation of Ar_2PH with a nonstabilised phosphorus ylide, $Ph_3P=CH_2$, are reported. An X-ray structure of this salt reveals that cations and anions are weakly associated in the solid state through $C-H\cdots P$ interactions. © 1998 Elsevier Science S.A.
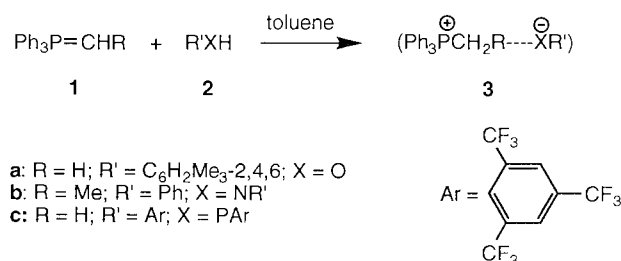
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1. Introduction

The synthesis and characterisation of compounds containing naked organic and organometallic anions has stimulated much interest in terms of their use in organic [1] and polymer [2] synthesis, as well as their structures, focusing not only on the structures of the uncoordinated anions themselves, but also on their propensity to promote weak intermolecular interactions [3,4]. We have used bulky electron-withdrawing groups such as $C_6H_2(CF_3)_3$-2,4,6 (Ar) to stabilise a variety of low-coordinate phosphorus compounds, including diphosphenes [5–7], phosphaalkenes [8] and their transition metal derivatives [5,7,8], suggesting the feasibility of forming a stable phosphide ion, Ar_2P^-. We have also recently shown that the simple acid–base reaction between phosphorus ylides **1** and bulky phenols **2a** [9] or secondary amines **2b** [10] can be utilised to generate hydrogen-bonded, hydrocarbon-soluble organic phos-

phonium aryloxides **3a** and amides **3b** (Scheme 1). Both in solution, and in the crystal, the anions of these salts are naked except for weak $C-H\cdots X$ interactions involving acidic alkyl and aryl C–H groups of the alkyltriphenylphosphonium cation and the negative centre (O or N) of the anion.

We herein report the utilisation of this strategy in the synthesis, isolation and X-ray structural characterisation of the first example of a phosphonium phosphide, $(Ph_3PMc) + (Ar_2P)^-$, **3c** by reaction of $Ph_3P=CH_2$, **1c** with the bulky secondary phosphine Ar_2PH [$Ar = C_6H_2(CF_3)_3$-2,4,6], **2c**.

Ph3P=CHR + R'XH $\xrightarrow{\text{toluene}}$ (Ph3PCH2R----XR')⊕⊖

1   2   3

a: R = H; R' = $C_6H_2Me_3$-2,4,6; X = O
b: R = Me; R' = Ph; X = NR'
c: R = H; R' = Ar; X = PAr

$Ar = C_6H_2(CF_3)_3$

Scheme 1.

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[1] Professor Ken Wade, with our compliments and best wishes, on the occasion of his 65th birthday.

2. Results and discussion

The reaction of equimolar amounts of **1c** and **2c** in toluene solution at room temperature caused the immediate formation of a red precipitate suspended in a deep blue solution. Addition of more toluene and gentle warming completely dissolved the precipitate, and the resulting solution yielded a crop of X-ray quality deep red, plate-like crystals that could be isolated under an inert atmosphere. For the isolated product, the disappearance of the resonance at -65 ppm due to **2c** in the ^{31}P NMR spectra suggested the complete deprotonation of the secondary phosphine in solution to give a phosphonium phosphide **3c** (Scheme 1), and X-ray crystallography confirms the identity of the compound in the solid state as $[(Ph_3PMe)^+(Ar_2P)^-]_2$ (Fig. 1). Selected bond lengths and angles are listed in the figure caption. The geometry of the Ph_3PMe^+ cation is as expected, although that of the anion is more interesting. Such ion-separated R_2P^- anions have been observed before in the crystal, for example in the structures of $[Li(12\text{-}c\text{-}4)_2]^+Ph_2P^-$ [11], $[Na(18\text{-}c\text{-}6)]^+P(CN)_2^- \cdot THF$ [12], $[K(18\text{-}c\text{-}6)]^+P(CN)_2^-]_\infty$ [13] and $(Ph_3\text{-}PNPPh_3)^+[P(CN)Ph]^-$ [14], although only the latter contains a nonmetallic cation as does **3c**. The geometry

of the anion in **3c** is influenced by the steric bulk of the attached Ar groups: the C–P–C angle [109.1(1)°] is greater than found for any of the above examples (95.2 to 105.2°), and the angle between the planes defined by the two aryl groups in **3c** (84.3°) is far greater than found for the equivalent parameter in the Ph_2P^- anion (43.4°) of $[Li(12\text{-}c\text{-}4)_2]^+Ph_2P^-$. Although this twisting may occur primarily to relieve steric interactions between bulky $o\text{-}CF_3$ groups of the two aryl substituents, it also appears to have electronic consequences. The two P–C(*ipso*) bond lengths differ significantly, and while the longer of these two bond vectors essentially lies in the plane of the aryl group [P2–C20–X angle 177° (X = centroid of C20 to C25)], the other deviates in such a way that the P atom lies significantly above the aryl plane [P2–C29–X angle, 166° (X = centroid of C29 to C34)] (Fig. 2a). Both the inequivalent P2–C(*ipso*) bond lengths and the unusual conformation of the anion suggest greater delocalisation of the negative charge into one aryl group. Delocalisation of negative charge into the Ar groups is further evidenced by the irregularity of bond lengths within the two aromatic rings of the anion (see figure caption).

As might be expected on the basis of previous results [9], close contacts between cations and anions are found
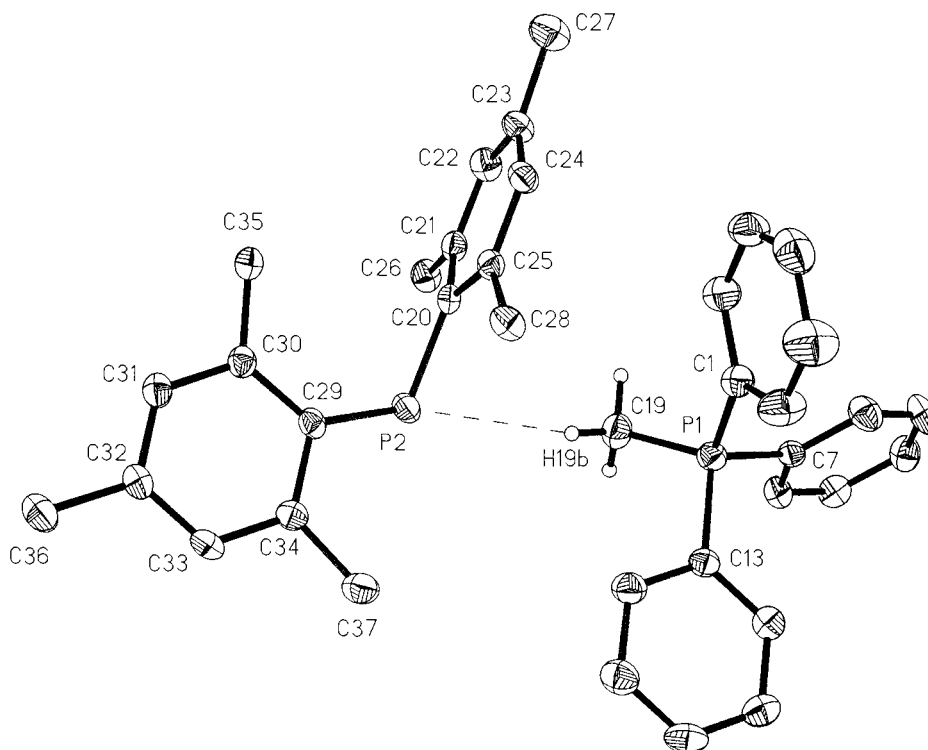

Fig. 1. Molecular structure of **3c** (thermal ellipsoids at the 50% level). All aryl hydrogen and fluorine atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1, 1.723(2); P1–C7, 1.799(2); P1–C13, 1.790(2); P1–C19, 1.785(3); P2–C20, 1.841 (2); P2–C29, 1.803(2); C20–C21, 1.420(3); C20–C25, 1.433(3); C21–C22, 1.394(3); C22–C23, 1.382(3); C23–C24, 1.389(3); C24–C25, 1.391(3); C29–C30, 1.447(3); C29–C34, 1.450(3); C30–C31, 1.390(3); C31–C32, 1.383(3); C32–C33, 1.383(3); C33–C34, 1.391(3); C20–P2–C29, 109.1(1).
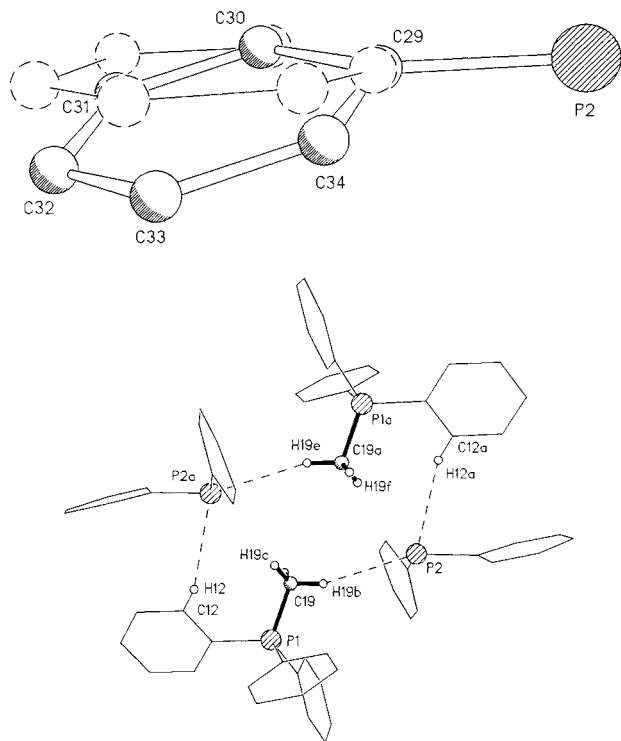
Fig. 2. (a) Superimposition of the two Ar–P groups of **3c** highlighting the distortion from planarity of one of them (C29 to C34, solid lines and atoms). CF$_3$ groups and hydrogen atoms are omitted for clarity. (b) The 'dimeric' structural motif of **3c** highlighting the two shortest C–H$\cdots$P interactions. Aryl groups are shown in outline and all CF$_3$ groups and noninteracting aryl hydrogen atoms are omitted for clarity.

in the crystal, and aggregation in the solid state occurs via C–H$\cdots$P interactions [2] between acidic C–H groups of the cation and the basic phosphorus centre of the anion. One short C–H(alkyl) $\cdots$ P [C19–H19b$\cdots$P2: $D = 3.820(3)$; $d = 2.79$ Å; $\theta = 159°$] and one short C–H(aryl) $\cdots$ P interaction [C12–H12$\cdots$P2a: $D = 3.926(3)$; $d = 2.90$ Å; $\theta = 158°$] define a centrosymmetric 'dimer' (Fig. 2b), while a further slightly longer C–H(alkyl) $\cdots$ P interaction may reinforce the aggregation [C19–H19c $\cdots$ P2a; $D = 4.156(3)$; $d = 3.09$ Å; $\theta = 170°$], although in this case the geometry of the dimer imposed by the other interactions necessitates a close contact in any case.

Further work on this species and other compounds containing the Ar$_2$P$^-$ ion, including temperature- and concentration-dependence studies of colour changes in solution, is in progress.

3. Experimental details

All compounds were treated as air- and moisture-sensitive; accordingly, all reactions and manipulations were carried out in an atmosphere of dry, pure dinitrogen or argon gas, using standard Schlenk procedures or a glove-box. Solvents were distilled over Na/K alloy. PCl$_3$ was purified by distillation prior to use. Bu$_3$SnH and BuLi were used as received from Aldrich.

3.1. Preparation of Ar$_2$PH, **2c**

Bu^{n}Li (2.5 M in hexanes, 31.2 ml, 78 mmol) was added dropwise over 5 min to a stirred solution of ArH [15] (20 g, 71 mmol) in Et$_2$O (100 ml) at $-78°$C. The solution was allowed to warm to room temperature and then stirred for 4 h, yielding a dark brown gelatinous solution. This was then added dropwise over 30 min to a solution of PCl$_3$ (5.3 g, 38.5 mmol) in Et$_2$O (50 ml) at room temperature. The reaction mixture was stirred for 2 h, slowly forming a precipitate of LiCl. The solution was filtered and the solvent removed in vacuo. The resulting crude brown solid was then purified by distillation to give Ar$_2$PCl. Yield, 17.2 g, 71%; b.p. 110–112°C/0.1 mm Hg; m.p. 91–92°C; satisfactory C, H and Cl analyses; ^{31}P NMR (101.256 MHz, CDCl$_3$, 85% H$_3$PO$_4$, 25°C), $\delta = 73.3$ (13-line multiplet, $^4J_{PF} = 42.0$ Hz) ppm; ^{19}F NMR (235.34 MHz, CDCl$_3$, CFCl$_3$, 25°C) $\delta = -54.9$ (d, 12F, $^4J_{PF} = 42.0$ Hz), -64.8 (s, 6F) ppm.

Bu$_3$SnH (4.7 ml, 16.1 mmol) was added dropwise to a solution of Ar$_2$PCl (10 g, 15.9 mmol) in Et$_2$O (50 ml) at room temperature. The solution was stirred for 30 min, then the solvent was removed in vacuo. The crude product was recrystallised from hexane to give **2c**. Yield, 6.23 g, 65%; m.p. 99–100°C; ^{1}H NMR (400 MHz, CDCl$_3$, TMS, 25°C) $\delta = 8.15$ (s, 4H, Ar–H), 6.22 (d, 1H, Ar$_2$P–H, $^1J_{PH} = 250$ Hz); ^{31}P NMR (101.256 MHz, toluene, 85% H$_3$PO$_4$, 25°C), $\delta = -64.6$ (d of m, $^1J_{PH} = 249$ Hz, $^4J_{PF} = 33.0$ Hz) ppm; ^{19}F NMR (235.34 MHz, C$_6$D$_6$, CFCl$_3$, 25°C) $\delta = -63.7$ (s, 6F), -58.6 (d, 12F, $^4J_{PF} = 32$ Hz) ppm.

3.2. Preparation of (Ph$_3$PCH$_3$)$^+$(Ar$_2$P)$^-$, **3c**

Toluene was added to a Schlenk tube containing Ph$_3$P$=$CH$_2$ [16] (0.14 g 0.5 mmol) and Ar$_2$PH (0.30 g, 0.5 mmol). The resulting deep blue solution was stirred at room temperature for 15 min, during which time a red precipitate formed. This was redissolved into a blue solution by further addition of toluene (15 ml) and gentle warming. On standing at room temperature for 2 h, this solution yielded a crop of dark red,

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[2] In all subsequent description of C–H$\cdots$P interactions, D is defined as the C$\cdots$P distance, d as the H$\cdots$P distance and θ as the C–H$\cdots$P angle. All parameters are based on the normalised C–H bond length of 1.08 Å.

X-ray-quality, plate-like crystals of **2c**. Yield 0.24 g 55%, m.p. 129–130°C, ^{1}H NMR (200 MHz, C_6D_6, TMS, 25°C) $\delta = 7.61$ (s, 4H, Ar–H), 7.0–6.6 (m, 15H, Ph–H) 2.27 (d, 3H, CH_3, $^2J_{PH} = 13$ Hz) ppm; ^{31}P NMR (101.256 MHz, C_6D_6, 85% H_3PO_4, 25°C), $\delta = 21.6$ (s, $Ph_3PCH_3^+$), 21.0 (m, Ar_2P^-) ppm; ^{19}F NMR (235.34 MHz, C_6D_6, $CFCl_3$, 25°C) $\delta = -61.2$ (d, 12F, $^4J_{PF} = 33$ Hz), -62.3 (s, 6F) ppm.

3.3. Crystal structure determination of *3c*

$C_{37}H_{22}F_{18}P_2$, $M = 870.49$, dark red plate-like crystal of $0.2 \times 0.2 \times 0.08$ mm size, $T = 150(2)$ K, triclinic, $a = 11.532(1)$, $b = 12.625(1)$, $c = 13.579(1)$ Å, $\alpha = 110.21(1)$, $\beta = 102.85(1)$ $\gamma = 96.96(1)°$, $U = 1765.9(2)$ Å^3 (from 493 reflections $5 < \theta < 30°$), space group $P\bar{1}$, $Z = 2$, $D_c = 1.64$ g cm^{-3}, graphite-monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å, $\mu = 0.25$ mm^{-1}; data collection on a Siemens 3-circle diffractometer with a CCD area detector, ω scan mode, $2\theta \leq 60.2°$, 12 640 total, 9054 unique, 4709 observed ($I > 2\sigma(I)$) data, $R_{int} = 0.0290$. The structure was solved [17] by direct methods and refined [18] by full-matrix least squares against F^2 (non-H atoms anisotropic, all H atoms isotropic, 630 variables/9044 data) to $wR(F^2$, all data) = 0.1178, goodness-of-fit = 0.930, $R(F$, obs. data) = 0.0455; $\Delta\rho_{max} = 0.37$ e Å^{-3}. Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the Cambridge Crystallographic Data Centre.

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