Evidence for Anionic Protection of Phosphenium Centres

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The new phosphenium salt $[P(NPr^i_2)_2][BPh_4]$ has been identified in solution and observed to react with chlorinated solvents, including a facile oxidative addition of CH_2Cl_2 to the cation; in contrast, similar solutions of the $[GaCl_4]^-$ salt are indefinitely stable indicating that the gallate anion suppresses the reactivity of the cation.

Since the first identification of phosphenium cations in the early 1970s numerous derivatives have been characterized in solution, and there are a few reports of isolated salts.[1] Cowley *et al.*[2] confirmed the two-co-ordinate environment for phosphorus in the structure of $[P(NPr^i_2)_2][AlCl_4]$, and we note that most isolated derivatives involve the $[AlCl_4]^-$ anion. Here we illustrate that the kinetic stability (or reactivity) of the phosphenium centre is critically dependent on the nature of the anion, and report for the first time the reaction with CH_2Cl_2, the solvent most commonly used in the study of phosphenium chemistry.[1]

The new phosphenium salts $[P(NPr^i_2)_2][GaCl_4]$[§] and $[P(NPr^i_2)_2][BPh_4]$[¶] were obtained quantitatively in solution from the respective reactions of $PCl(NPr^i_2)_2$ with $GaCl_3$ and $NaBPh_4$ in CH_2Cl_2 or $CHCl_3$–CH_2Cl_2. The gallate salt is indefinitely stable in solution (at least two months), and was readily isolated in high yield and characterized by X-ray crystallography.[‖] However, compound $[P(NPr^i_2)_2][BPh_4]$ (identifiable by the characteristic[1] downfield ^{31}P NMR signal as the only feature in the initial spectrum of the reaction mixture) reacted with the solvent within hours at room temperature to give many phosphorus-containing products including $[PCl(CH_2Cl)(NPr^i_2)_2][BPh_4]$[¶] (isolated in low yield from a reaction in CH_2Cl_2–$CHCl_3$ and identified by X-ray crystallography[**]). The structures of the two cations are shown in Fig. 1. Formation of the $[PCl(CH_2Cl)(NPr^i_2)_2]^+$ cation is the result of oxidative addition of a solvent CH_2Cl_2 molecule to the phosphenium centre. Although this is the first reported insertion of a phosphenium unit into a C–Cl bond, it is consistent with the *carbenic* nature[7] and the susceptibility to oxidation. Indeed, the chemistry of phosphenium cations generally involves phosphonium products.[1,8]

In view of the unique activity of $[P(NPr^i_2)_2][BPh_4]$ towards the solvent, we conclude that intimate ion-pairs[9] or aggregates in solution are responsible for inhibiting related activity for $[P(NPr^i_2)_2][GaCl_4]$ and $[P(NPr^i_2)_2][AlCl_4]$,[2] as well as other phosphenium salts possessing electron-rich anions. Although halogen containing complex anions are weakly basic, their nucleophilicity and basicity is likely to be substantially greater than that of the tetraphenylborate anion. Consequently, we envisage the phosphenium centre of $[P(NPr^i_2)_2][BPh_4]$ as being more susceptible to attack by the weakly nucleophilic solvent.

In the solid state the cation of $[P(NPr^i_2)_2][GaCl_4]$

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[§] In an evacuated vessel, a solution of $GaCl_3$ (0.64 g, 3.6 mmol) in CH_2Cl_2 was added quickly to a solution of $PCl(NPr^i_2)_2$ (1.02 g, 3.75 mmol) in CH_2Cl_2 (total, 30 cm^3) to give a clear yellow solution. A precipitate formed on removal of the solvent, which was recrystallized from CH_2Cl_2 and characterized as $[P(NPr^i_2)_2][GaCl_4]$, yield 1.22 g, 2.75 mmol (76%), m.p. 127.5–128.5 °C (Found: C, 32.70; H, 6.40; N, 6.30. Calc. for $C_{12}H_{28}Cl_4GaN_2P$: C, 32.55; H, 6.35; N, 6.35%). NMR (CD_2Cl_2): ^{31}P-{^1H}, δ 313; ^1H, δ 4.20 (d of septets, $^3J_{PH} = 2.6$, $^3J_{HH} = 6.7$), 1.52 (d, $^3J_{HH} = 6.7$ Hz).

[¶] In an evacuated tube, equimolar mixtures of $PCl(NPr^i_2)_2$ and $NaBPh_4$ in CH_2Cl_2 or CH_2Cl_2–$CHCl_3$ (1:1) (1 cm^3) were examined by ^{31}P NMR spectroscopy at 2 h intervals. A signal at δ 312 {characteristic of $[P(NPr^i_2)_2]^+$} was initially observed as the only feature of the spectrum, but within hours this signal decayed with the appearance of numerous signals in the range δ 100–0. The ^{11}B NMR spectrum of the reaction mixture (δ −7.0) was characteristic of $[BPh_4]^-$. In one experiment, a solution of $PCl(NPr^i_2)_2$ (0.266 g, 1.00 mmol) in CH_2Cl_2 (10 cm^3) was added quickly to a mixture of $NaBPh_4$ (0.344 g, 1.00 mmol) in $CHCl_3$ ($CHCl_3$–CH_2Cl_2, 1:1). After stirring for 10 d, slow removal of the solvent *in vacuo* gave colourless crystals, which were characterized by X-ray crystallography as $[PCl(CH_2Cl)(NPr^i_2)_2][BPh_4]$, yield < 10 mg, m.p. ≈ 180 °C (decomp.) (elemental analyses not obtained). NMR (CD_2Cl_2): ^{31}P, δ 57 (also observed in the reaction mixtures); ^1H (cation), δ 4.45 (d, $^2J_{PH} = 2.6$ Hz), 3.93 (m), 1.41 (m).

[‖] Crystal data for $[P(NPr^i_2)_2][GaCl_4]$: Enraf-Nonius CAD-4 (Mo-Kα = 0.709 26 Å), crystal dimensions 0.20 × 0.45 × 0.25 mm, $M = 442.87$, tetragonal, space group $I4_1cd$, $a = b = 20.014(4)$, $c = 21.466(6)$ Å, $U = 8598$ Å^3, $Z = 16$, $D_c = 1.3684$ g cm^{-3}, $F(000) = 3648$, $\mu = 18.45$ cm^{-1}, observed reflections $[I > 3\sigma(I)] = 617$, variables = 158, structure solved by direct methods using SHELXS 86[3] and refined using SHELX 76,[4] data corrected for Lorentz and polarization effects, absorption corrections applied by DIFABS,[5] hydrogen atoms placed in geometrically calculated positions [d(C–H) 1.08 Å], $R = 0.0540$, $R' = 0.0640$ $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|, R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}; w = 1.3119/[\sigma^2(F) + 0.0092 F^2]\}$, goodness of fit = 0.8434. Selected bond lengths (Å) and angles (°) in the cation P–N(1) 1.587(12), P–N(2) 1.601(13), N(1)–P–N(2) 117.0(7).

[**] Crystal data for $[PCl(CH_2Cl)(NPr^i_2)_2][BPh_4]$: Rigaku AFC5R (Mo-Kα = 0.710 69 Å), crystal dimensions 0.25 × 0.40 × 0.60 mm, $M = 635.51$, monoclinic, space group $P2_1/n$, $a = 10.049(3)$, $b = 21.794(3)$, $c = 16.391(3)$ Å, $\beta = 92.78(2)°$, $U = 3585$ Å^3, $Z = 4$, $D_c = 1.177$ g cm^{-3}, $F(000) = 1360$, $\mu = 2.50$ cm^{-1}, observed reflections $[I > 3\sigma(I)] = 1946$, variables = 387, solution and refinements as for $[P(NPr^i_2)_2][GaCl_4]$, $R = 0.0541$, $R' = 0.0569$ $\{w = 1.000/[\sigma^2(F) + 0.000\,932 F^2]\}$, goodness of fit = 1.859. Selected bond lengths (Å) and angles (°): P–N(1) 1.616(5), P–N(2) 1.622(5), P–C(37) 1.829(6), P–Cl(1) 1.999(3); N(1)–P–N(2) 113.3(3), N(1)–P–C(37) 108.7 (3), N(2)–P–C(37) 111.3(3), N(1)–P–C(1) 110.3(2), N(2)–P–Cl(1) 109.0(2), C(37)–P–Cl(1) 103.9(2).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

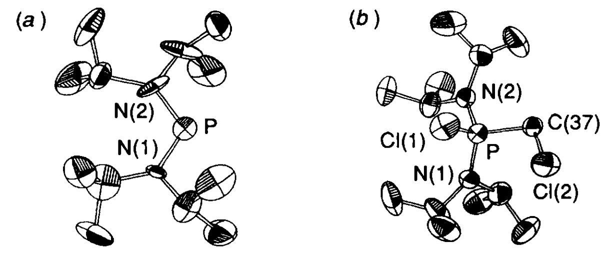

Fig. 1 ORTEP[6] views of cations $[\mathrm{P(NPr^i{}_2)_2}]^+$ (*a*) and $[\mathrm{PCl(CH_2Cl)(NPr^i{}_2)_2}]^+$ (*b*)

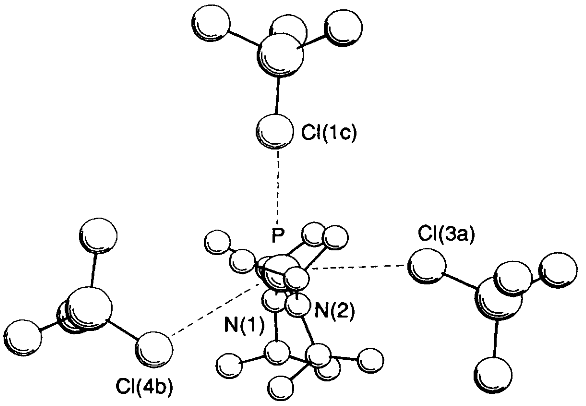

Fig. 2 SNOOPI[10] view of the ionic array in the crystal structure of $[\mathrm{P(NPr^i{}_2)_2}][\mathrm{GaCl_4}]$. Selected inter-ion distances (Å): P–Cl(3) 3.867(6), P–Cl(1) 3.976(6), P–Cl(4) 4.020(6)

{isostructural with $[\mathrm{P(NPr^i{}_2)_2}][\mathrm{AlCl_4}]$[2]} is surrounded by three anions, as illustrated in Fig. 2. Although the closest distances between cations and anions are greater than the sum of the van der Waals radii for the atoms in contact (P···Cl 3.7 Å),[11] they all involve the phosphorus centre. Cation–anion interactions (usually considered as donations from the anion to the cation)[12] are common for other phosphenium salts[13] and non-metal salts in general,[14] but often have little or no effect on the structural features within the cation or the anion.[15] Nevertheless, they represent an important component of the crystal lattice energy, and the relative reactivity of the cation may well be reliant on the magnitude of these electrostatic interactions in solution. We now feel that chemistry of phosphenium cations (in most cases performed in $\mathrm{CH_2Cl_2}$)[1] has been mediated by the presence of electron-rich anions, which '*protect*' the electrophilic centre, and that the cation has a more potent electrophilic reactivity than originally observed. In this context, we are anticipating that the use of essentially non-basic anions such as $[\mathrm{BPh_4}]^-$ will sporn a new phase in the chemistry of the phosphenium centre, and other non-metal cations that are supported by weakly basic anions such as $[\mathrm{AlCl_4}]^-$.

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