

Chiral phosphorus(III) triflates†

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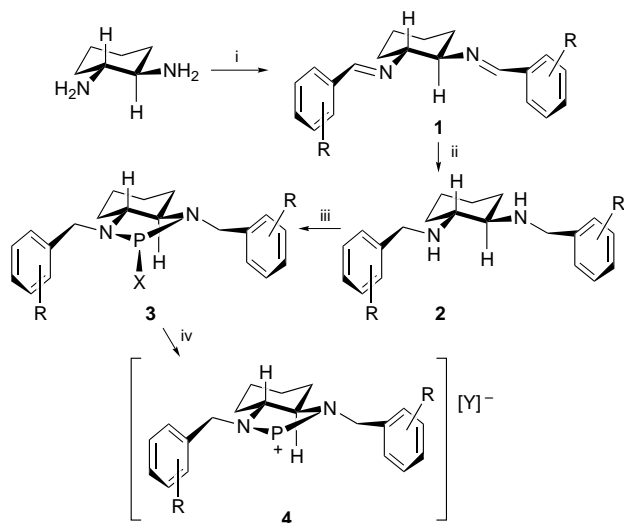
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A C_2 -symmetric bicyclic diazaphospholidine framework supports a phosphorus centre within an inherently chiral environment which displays both solution- and solid-phase behaviour consistent with ambiphilic phosphonium character.

In recent years, chemists have become increasingly interested in main-group analogues of carbenes,¹ principally those of Si,² Ge,³ Sn,⁴ As⁵ and P.⁶ Indeed of these heterocarbenes, the phosphorus analogues, $\sigma^{2\lambda^3}$ phosphonium cations, have received significant attention over the past 20 years and much is known of their organic and coordination chemistry.⁷ However, we report here a class of phosphonium compound which possesses the significant ‘added value’ of chirality; an effective $\sigma^{2\lambda^3}$ phosphorus atom possessing both electrophilic and nucleophilic properties contained within a chiral, C_2 -symmetric, coordination sphere; an environment which, for the first time, opens up significant possibilities in asymmetric synthesis, analysis and catalysis.⁸

The appropriate synthetic procedures are outlined in Scheme 1.⁹

Various experiments shed light upon the nature of the interaction between phosphorus and trifluoromethylsulfonate (triflate) in **4a**[OTf]. A single ³¹P NMR resonance is observed at $\delta +271.1$ (0.54 mol dm⁻³, 300 K, CH₂Cl₂), well within the range expected for two-coordinate phosphonium cations (δ 110–515)⁷ along with intriguing, non-linear concentration-dependent ³¹P NMR behaviour at room temp.; a 24-fold increase in concentration from 0.025–0.6 M results in a $\Delta\delta$ of +5.98 ppm. We interpret such behaviour as evidence of a dynamic interaction between phosphorus and triflate oxygen(s) at room temperature leading to a more ‘naked’ phosphonium cation with slightly lower frequency δ_P at higher dilution. Consistently, ³¹P NMR chemical shifts of **4a**[OTf] (0.3



Scheme 1 Reagents and conditions: i, ArCHO; Ar = functionalised phenyl (Ph **a**, 4-NMe₂C₆H₄ **b**, 1-C₁₀H₇ **c**, 2-C₁₀H₇ **d**, 4-MeOC₆H₄ **e**); ii, LiAlH₄, thf; iii, PX₃ (X = Cl, Br, I), NEt₃ (2 equiv.); iv, AlCl₃ or Me₃SiOSO₂CF₃ (TMSOTf). [Y] = [AlCl₄]⁻, [OTf]⁻

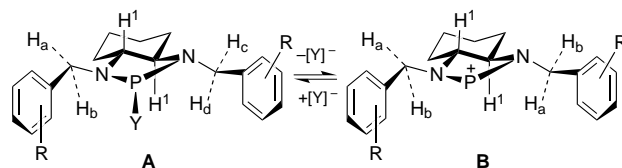
mol dm⁻³, CH₂Cl₂), reveal a linear dependence upon temperature between 295 K (δ_P 269.2) and 203 K (δ_P 274.2) with a slope of -5.4×10^{-2} ppm K⁻¹; higher temperatures presumably favouring uncoordinated phosphonium cation as suggested by the low-frequency perturbation of δ_P . This behaviour contrasts with the configurationally stable $\sigma^{3\lambda^3}$ phosphorus derivative **3a**-Ph which shows linear behaviour but in the opposite direction with $\Delta\delta$ of +4.2 ppm between 203 and 298 K and slope $+4.6 \times 10^{-2}$ ppm K⁻¹.

Further evidence for a dynamic interaction between phosphorus and triflate in **4a**[OTf] is revealed upon examination of the ¹H NMR spectrum. Should **4a**[OTf] possess a static covalent or slowly exchanging configuration at phosphorus, then the methylene hydrogens on each benzyl substituent (H_a, H_b) should express themselves as two distinct [ABX] patterns (Scheme 2; **A**, X = P Y = triflate). Indeed, in the configurationally fixed derivative **3a**-Ph (Y = Ph; Scheme 2; **A**, Y = Ph), two [ABX] patterns are indeed observed centred at δ 4.31 (²J_{HH} 14.7, ³J_{PH} 14.6 Hz) and 3.67 (²J_{HH} 14.9, ³J_{PH} 12.7 Hz). However, between 300 and 200 K only a single [ABX] pattern is observable for the methylene hydrogens of **4a**[OTf] centred at δ 4.55 (²J_{HH} 14.5, ³J_{PH} 11.3 Hz), behaviour consistent with local C_2 symmetry at the phosphorus atom of **4a**[OTf] caused presumably by rapid exchange of coordinated (Scheme 2, **A**) and uncoordinated triflate (Scheme 2, **B**). It is possible to perturb the interaction between phosphorus and triflate in solution *via* ³¹P NMR titration experiments. Thus, addition of 10 equiv. of NBuⁿ₄[OTf] to a CH₂Cl₂ solution of **4a**[OTf] (0.02 mol dm⁻³, 300 K) results in a small perturbation to δ_P $\Delta\delta$ of +4.4 ppm.

Presumably, this perturbation reflects a dynamic process such that higher concentrations of triflate favour increased interactions with phosphorus and consequently, a shift in δ_P to high frequency.

¹⁹F NMR and solution conductivity studies are also supportive of this conclusion. Variable-temperature ¹⁹F NMR studies on **4a**[OTf] (CD₂Cl₂, 203–293 K, referenced to C₆F₆ at δ -162.9) reveal behaviour which parallels that of ionic NBuⁿ₄[OTf] more closely than covalent Me₃SiOTf (Fig. 1). Me₃SiOTf and NBuⁿ₄[OTf] possess solution molar conductivities Λ (thf, 296 K, 0.11 mol dm⁻³) of 0.03 and 3.14 Ω^{-1} cm² mol⁻¹, respectively, whilst the corresponding measurements under the same conditions for **4a**[OTf] reveal a molar conductivity Λ of 0.43 Ω^{-1} cm² mol⁻¹. It is clear that **4a**[OTf], although formally a weak electrolyte and less conducting than the ionic triflate NBuⁿ₄[OTf], is a stronger electrolyte than Me₃SiOTf by a factor of 14; consistent with significant yet dynamic solution interaction between phosphorus and triflate in **4a**[OTf].¹⁰

A single-crystal X-ray study of racemic **4a**[OTf] reveals a formally two-coordinate trivalent phosphorus centre in which



Scheme 2 Relationship between coordinated (**A**) and uncoordinated (**B**) in **4**[Y]; Y = *e.g.* [AlCl₄]⁻, [O₃SCF₃]⁻, [C₅H₅N]

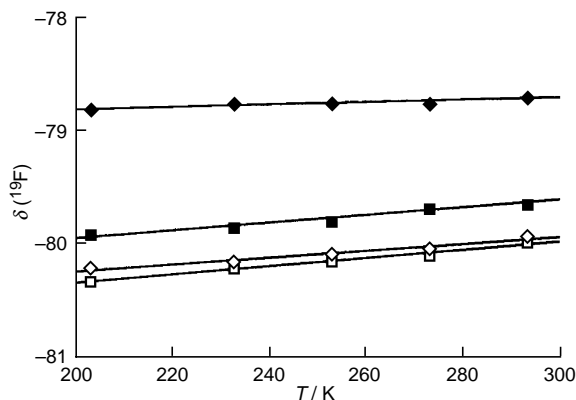


Fig. 1 Plot of ^{19}F NMR chemical shifts of **4a**[OTf] (■), **4a**-Py[OTf] (◇), $\text{NBu}_4^+\text{[OTf]}^-$ (□) and $\text{Me}_3\text{SiO}_3\text{SCF}_3$ (◆) vs. temperature (CH_2Cl_2 , 0.1 mol dm^{-3})

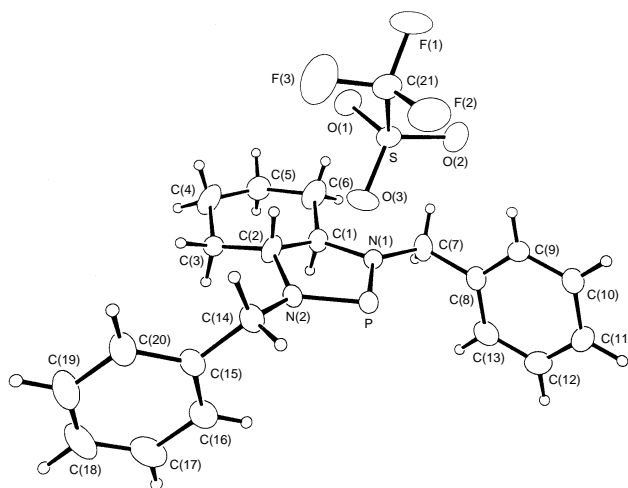


Fig. 2 Molecular structure of **4a**[OTf] with atom numbering scheme. Selected bond lengths (Å) and angles ($^\circ$): P–N(1) 1.616(3), P–N(2) 1.625(3), N(1)–C(1) 1.465(5), N(1)–C(7) 1.468(5), N(2)–C(2) 1.470(5), N(2)–C(14) 1.469(5), P–O(1) 2.841(5), P–O(3') 2.755(5), N(1)–P–N(2) 94.9(2), C(1)–N(1)–C(7) 119.6(3), C(1)–N(1)–P 113.5(3), C(7)–N(1)–P 126.5(3), C(2)–N(2)–C(14) 121.0(3), C(2)–N(2)–P 112.8(3), C(14)–N(2)–P 121.4(3).

both nitrogen atoms possess significant sp^2 character as evidenced by their trigonal-planar environment, the deviations of N(1) and N(2) from the best-fit planes connecting atoms P(1)C(1)C(7) and P(1)C(2)C(14) are -0.05 and $+0.19$ Å, respectively [sum of angles around N(1) and N(2), 359.6 and 355.2° , respectively (Fig. 2)]. Such trigonal planarity is expected to facilitate effective delocalisation of formal positive charge on phosphorus through P–N π -bonding. Arguably the most interesting features are connected with the phosphorus–triflate interaction. P(1) has close contacts to one oxygen atom of each of two triflate groups in the crystal at distances of 2.841 and 2.755 Å; these interactions are well within the van der Waals distance for a phosphorus–oxygen interaction (*ca.* 3.35 Å) but are nevertheless >1 Å longer than expected for a single P–O covalent bond (*ca.* 1.63 Å).¹¹ Furthermore, the two O–P bond vectors are directed along the axes expected for interaction with opposite lobes of a vacant phosphorus 3p orbital of a formally $\sigma^2\lambda^3$ phosphonium cation [the angles between the P–O vectors and normals to the plane N(1)P(1)N(2) are 11.5 and 10.2°]. The conclusion from the solid state is that phosphorus–triflate interactions are present although likely to be significantly weaker than for a formal P–O single covalent bond,¹² in agreement with solution data.

Ambiphilic behaviour may be demonstrated for **4a**[OTf] by its interaction with (i) $\text{BH}_3\cdot\text{thf}$ to afford a species with a direct

P–B linkage, presumably $\{N,N'\text{-[trans-1,2-C}_6\text{H}_{10}(\text{NCH}_2\text{Ph})_2\text{]-PBH}_3(\text{thf})\}\text{[OTf]}$ (δ_{P} 96.2, peak separation 85 Hz resulting from $^1J_{\text{PB}}$, thf, 0.34 mol dm^{-3}) and (ii) pyridine to afford the adduct $\{N,N'\text{-[trans-1,2-C}_6\text{H}_{10}(\text{NCH}_2\text{Ph})_2\text{]P-NC}_5\text{H}_5\}\text{[OTf]}$ (δ_{P} 168.3, CH_2Cl_2 , 0.075 mol dm^{-3}).¹² Variable-temperature ^{19}F NMR experiments on the latter reveal behaviour commensurate with ionic triflate character (Fig. 1) whilst ^1H NMR spectroscopy reveals that pyridine exchange is rapid on the NMR timescale at 300 K; a single [ABX] pattern being observed for the benzyl methylene hydrogens. We are currently building upon these preliminary observations to examine the potential of chiral phosphonium salts such as **4a**[OTf] in asymmetric synthesis, analysis, coordination chemistry and catalysis.

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Footnotes

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: <http://chemistry.rsc.org/rsc/cceha.htm>. Supplementary material (including synthetic, analytical and spectroscopic details for compounds 1–4) is available electronically upon e-mail request to T.P.Kee@chem.leeds.ac.uk

‡ All new compounds returned satisfactory microanalyses.

§ *Crystal structure data for 4a*[OTf]: $\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_2\text{PS}$, $M = 472.45$, monoclinic, space group $P2_1/a$, $a = 13.961(2)$, $b = 11.292(2)$, $c = 15.742(2)$ Å, $\beta = 114.846(12)^\circ$, $U = 2251.9(6)$ Å³, $Z = 4$, $D_c = 1.39$ Mg m^{-3} , $F(000) = 984$, $\mu = 2.399$ mm⁻¹, $T = 160$ K; crystal size $0.70 \times 0.34 \times 0.08$ mm. 3472 reflections were measured at 190 K on a Stoe STAD14 4-circle diffractometer operating in the ω - θ scan mode using graphite monochromated Cu-K α radiation ($\lambda = 1.54184$ Å). Data were corrected for absorption empirically using azimuthal ψ -scans (max., min. transmission factors 0.215, 0.559, respectively). The structure was solved by direct methods¹³ and was refined by full-matrix least-squares analysis on F^2 using all the unique data.¹⁴ $wR = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2} = 0.1598$ for all data, conventional R [on F values of 3280 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0713, goodness of fit $S = 1.183$ on all F^2 for 275 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to idealised positions using a riding model. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for his material should quote the full literature citation and the reference number 182/483.

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