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Chiral phosphorus(III) triflates†

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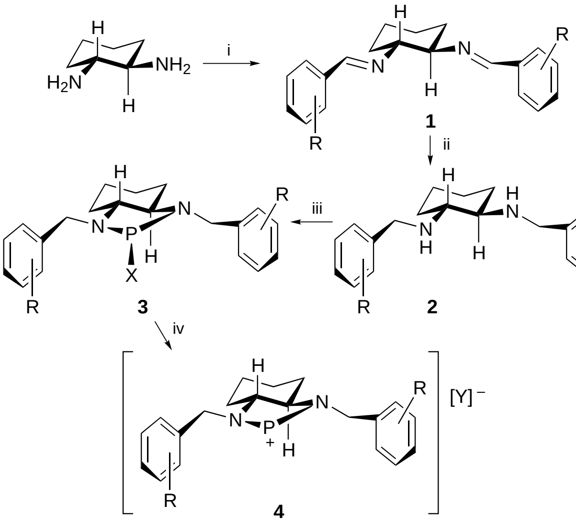
A C_2-symmetric bicyclic diazaphospholidine framework supports a phosphorus centre within an inherently chiral environment which displays both solution- and solid-phase behaviour consistent with ambiphilic phosphenium character.

In recent years, chemists have become increasingly interested in main-group analogues of carbenes,[1] principally those of Si,[2] Ge,[3] Sn,[4] As[5] and P.[6] Indeed of these heterocarbenes, the phosphorus analogues, $\sigma^2\lambda^3$ phosphenium 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 phosphenium 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 ^{31}P NMR resonance is observed at δ +271.1 (0.54 mol dm^{-3}, 300 K, CH_2Cl_2), well within the range expected for two-coordinate phosphenium cations (δ 110–515)[7] along with intriguing, non-linear concentration-dependent ^{31}P 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' phosphenium cation with slightly lower frequency δ_P at higher dilution. Consistently, ^{31}P NMR chemical shifts of **4a**[OTf] (0.3 mol dm^{-3}, CH_2Cl_2), 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 phosphenium 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}.



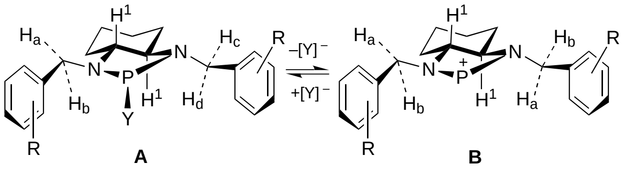
Scheme 1 *Reagents and conditions*: i, ArCHO; Ar = functionalised phenyl (Ph **a**, 4-$NMe_2C_6H_4$ **b**, 1-$C_{10}H_7$ **c**, 2-$C_{10}H_7$ **d**, 4-$MeOC_6H_4$ **e**); ii, $LiAlH_4$, thf; iii, PX_3 (X = Cl, Br, I), NEt_3 (2 equiv.); iv, $AlCl_3$ or $Me_3SiOSO_2CF_3$ (TMSOTf). [Y] = $[AlCl_4]^-$, $[OTf]^-$

Further evidence for a dynamic interaction between phosphorus and triflate in **4a**[OTf] is revealed upon examination of the ^{1}H 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* ^{31}P NMR titration experiments. Thus, addition of 10 equiv. of NBu^n_4[OTf] to a CH_2Cl_2 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.

^{19}F NMR and solution conductivity studies are also supportive of this conclusion. Variable-temperature ^{19}F NMR studies on **4a**[OTf] (CD_2Cl_2, 203–293 K, referenced to C_6F_6 at δ −162.9) reveal behaviour which parallels that of ionic NBu^n_4[OTf] more closely than covalent Me_3SiOTf (Fig. 1). Me_3SiOTf and NBu^n_4[OTf] possess solution molar conductivities Λ (thf, 296 K, 0.11 mol dm^{-3}) of 0.03 and 3.14 Ω^{-1} cm^2 mol^{-1}, respectively, whilst the corresponding measurements under the same conditions for **4a**[OTf] reveal a molar conductivity Λ of 0.43 Ω^{-1} cm^2 mol^{-1}. It is clear that **4a**[OTf], although formally a weak electrolyte and less conducting than the ionic triflate NBu^n_4[OTf], is a stronger electrolyte than Me_3SiOTf by a factor of 14; consistent with significant yet dynamic solution interaction between phosphorus and trfilate 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.* $[AlCl_4]^-$, $[O_3SCF_3]^-$, $[C_5H_5N]$

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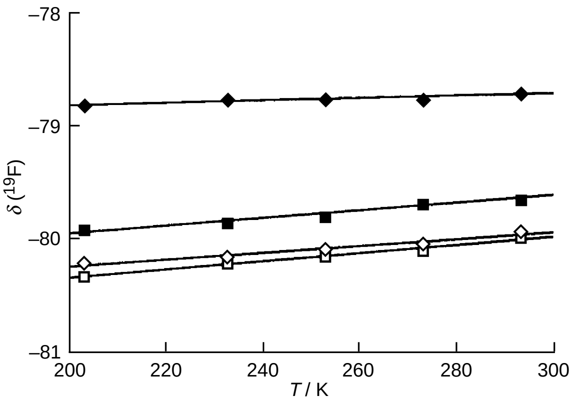

Fig. 1 Plot of ^{19}F NMR chemical shifts of **4a**[OTf] (■), **4a**-Py[OTf] (◇), NBu$^n_4$[OTf] (□) and Me$_3$SiO$_3$SCF$_3$ (◆) *vs.* temperature (CH$_2$Cl$_2$, 0.1 mol dm^{-3})

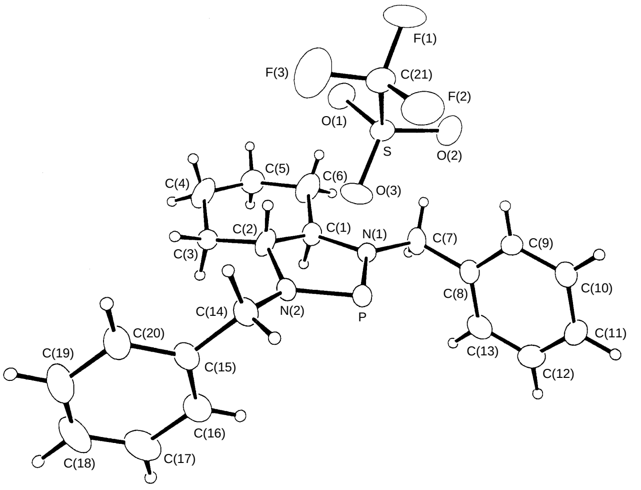

Fig. 2 Molecular structure of **4a**[OTf] with atom numbering scheme. Selected bond lengths (Å) and angles (°): P–N(1) 1.616(3), P–N(2) 1.625(3), N(1)–C(1) 1.465(5), N(1)–C(7) 1.468(5), N(2)–C(2) 1.470(5), N(2)–C(14) 1.469(5), P–O(1) 2.841(5), P–O(3′) 2.755(5). N(1)–P–N(2) 94.9(2), C(1)–N(1)–C(7) 119.6(3), 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 $\sigma^2\lambda^3$ phosphenium 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*) BH$_3$·thf to afford a species with a direct P–B linkage, presumably {*N*,*N*′-[*trans*-1,2-C$_6$H$_{10}$(NCH$_2$Ph)$_2$]-PBH$_3$(thf)}[OTf] (δ_P 96.2, peak separationn 85 Hz resulting from $^1J_{PB}$, thf, 0.34 mol dm^{-3}) and (*ii*) pyridine to afford the adduct {*N*,*N*′-[*trans*-1,2-C$_6$H$_{10}$(NCH$_2$Ph)$_2$]P-NC$_5$H$_5$}[OTf] (δ_P 168.3, CH$_2$Cl$_2$, 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 ^{1}H 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 phosphenium 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/cccenha.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]: C$_{21}$H$_{24}$F$_3$N$_2$PS, M = 472.45, monoclinic, space group $P2_1/a$, a = 13.961(2), b = 11.292(2), c = 15.742(2) Å, β = 114.846(12)°, U = 2251.9(6) Å^3, Z = 4, D_c = 1.39 Mg m^{-3}, F(000) = 984, μ = 2.399 mm^{-1}, T = 160 K; crystal size 0.70 × 0.34 × 0.08 mm. 3472 reflections were measured at 190 K on a Stoe STADI4 4-circle diffractometer operating in the ω–θ scan mode using graphite monochromated Cu-Kα radiation (λ = 1.541 84 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 methods[13] and was refined by full-matrix least-squares analysis on F^2 using all the unique data.[14] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ = 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.

References

1 W. A. Herrmann, L. J. Goossen, C. Kocher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1997, **35**, 2805.
2 P. Blakeman, B. Gehrhus, J. C. Green, J. Heinicke, M. F. Lappert, M. Kindermann and T. Veszpremi, *J. Chem. Soc., Dalton Trans.*, 1996, 1475.
3 H. Suzuki, K. Okabe, S. Uchida, H. Watanabe and M. Goto, *J. Organomet. Chem.*, 1996, **509**, 177.
4 H. Nakazawa, Y. Yamaguchi and K. Miyoshi, *Organometallics*, 1996, **15**, 1337.
5 N. Burford, J. A. C. Clyburne, P. Losier, T. M. Parks and T. S. Cameron, *Phosphorus, Sulfur, Silicon*, 1994, **93**, 301.
6 P. Dyer, A. Baceiredo and G. Bertrand, *Inorg. Chem.*, 1996, **35**, 46.
7 See for example: A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367 and references therein.
8 *UK Pat. Appl.* 9624997.4.
9 V. A. Jones, A. Cawley, H. G. Butler, M. J. Cain, D. S. Brown, M. Thornton-Pett and T. P. Kee, manuscript in preparation.
10 O. Dahl, *Tetrahedron Lett.*, 1982, **23**, 1493.
11 J. E. Huheey, *Inorganic Chemistry. Principles of Structure and Reactivity*, Harper, New York, 3rd edn., 1983, p. A38.
12 For related structural studies see: N. Burford, P. Losier, C. MacDonald, V. Kyrimis, P. K. Bakshi and T. S. Cameron, *Inorg. Chem.*, 1994, **33**, 1434 and references therein.
13 G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467.
14 G. M. Sheldrick, SHELXL-93, program for refinement of crystal structures, University of Gottingen, 1993.

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