1-Methyl-1-phenylphosphiranium Triflate: Synthesis, Structure and Reactivity

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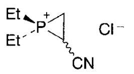
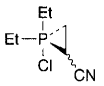
1-Phenylphosphirane reacts with methyl triflate to give 1-methyl-1-phenylphosphiranium triflate, which reacts with acetylenes to give the corresponding phosphirenium salts.

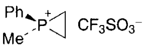
The chemistry of three-membered phosphorus heterocycles is a burgeoning field of considerable interest.[1] Although saturated phosphiranes are accessible by a variety of routes, and tertiary phosphines are readily alkylated to give stable phosphonium ions, the synthesis and characterisation of a phosphiranium salt has yet to be reported. In 1969 the structures **1a** (phosphiranium) or **1b** (λ^5-phosphirane) were assigned to the product of the reaction between chlorodiethylphosphine and acrylonitrile on the basis of analytical, IR and ^1H NMR data.[2] In other work, phosphiranium salts were proposed as products of the reaction between certain 9-phosphabicyclo[6.1.0]phosphines and trialkyloxonium salts, although only melting points were given.[3] Phosphiranium cations have also been postulated as reactive intermediates in the solvolysis of (2-chloroethyl)diphenylphosphine,[4] in the reaction of the bis[α-bromobenzyl]diphenylphosphonium cation with triethylamine,[5] in Ramberg–Bäcklund type reactions of phosphonium salts,[6] and in eliminations of 1,2-phosphinoylalcohols.[7] Theoretical calculations indicate that the phosphiranium ion $[H_2PCH_2CH_2]^+$ is of lower energy than the primary phosphine $H_2PCH_2CH_2$.[8] Here, we report that 1-methyl-1-phenylphosphiranium trifluoromethanesulfonate **2** is readily prepared from 1-phenylphosphirane and methyl trifluoromethanesulfonate (methyl triflate), and that the salt is a convenient precursor of substituted phosphirenium salts by reaction with acetylenes.



1a



1b



2

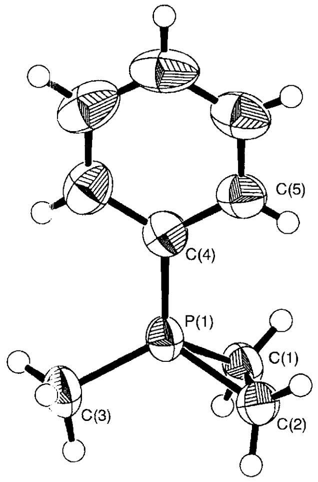
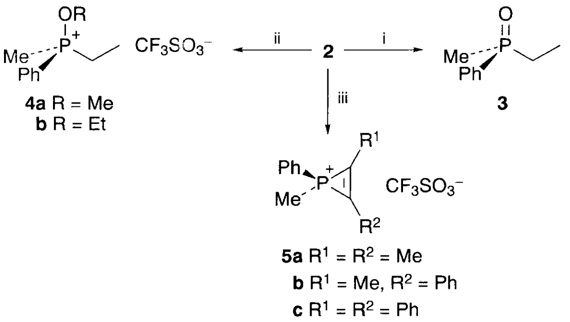


Fig. 1 An ORTEP plot of the cation of **2** with key atoms numbered. Selected interatomic distances (Å) and angles (°), and torsion angle (°), are as follows: P–C(1) 1.761(4), P–C(2) 1.756(5), P–C(3) 1.779(5), P–C(4) 1.763(4), C(1)–C(2) 1.533(6), P–C(1)–C(2) 64.0(3), C(1)–C(2)–P 64.3(3), C(1)–P–C(2) 51.7(2), C(1)–P–C(3) 118.8(3), C(2)–P–C(3) 117.6(3), C(1)–P–C(4) 119.1(2), C(2)–P–C(4) 119.1(2), C(1)–P–C(4)–C(5) −48.0(4).



Scheme 1 *Reagents and conditions*: i, H_2O, 5 min; ii, MeOH or EtOH, 5 min; iii, RC≡CR in CH_2Cl_2, 1 week

Treatment of 1-phenylphosphirane[9] (8.37 mmol) in benzene (30 ml) with methyl triflate (16.80 mmol) at 20 °C affords, after 3 h, colourless crystals of pure **2** in 73% yield, having mp 75–78 °C (decomp.).† The salt can be stored for several weeks under argon without decomposition. Spectroscopic data for **2**,‡ in particular the high-field shift of the phosphorus resonance (δ_P −96.79), support the proposed structure. The crystal and molecular structures of the salt have been determined and the structure of the cation of **2** is shown in Fig. 1.§ The phosphorus–carbon bonds in the phosphiranium ion are shorter by *ca.* 0.06 Å and the carbon–carbon bond are *ca.* 0.02 Å longer than the corresponding bonds in the neutral complexes *fac*-$[Mo(CO)_3(PhPCH_2CH_2)_3]$[9] and $[W(CO)_5(PhPCH_2CH_2)]$.[10] The phosphorus–carbon distances in **2** are also shorter than those in the related four-membered 1,1-di-*tert*-butylphosphetanium ion, *viz.* 1.81 Å (av.).[11] The C(1)–P–C(2) angle in **2** of 51.7(2)° compares with the angles of 48.88(16)° and 48.6(7)° in the molybdenum and tungsten complexes, respectively.

The salt **2** is moderately stable to the atmosphere but reacts with water to give (±)-ethylmethylphenylphosphine oxide **3**[12] and with primary alcohols to form the (±)-alkoxyphosphonium salts **4a,b** (Scheme 1). In neat triflic acid, however, **2** appears to be stable indefinitely. Treatment of **2** with dimethyl- or methylphenyl-acetylene in dichloromethane affords over 1 week the corresponding substituted phosphirenium salts **5a** and (±)-**5b** in high yield, thereby effecting the formal transfer of the methylphenylphosphenium ion from ethylene to the alkynes. The reaction with diphenylacetylene is less efficient giving *ca.* 50% of the known phosphirenium salt **5c**, having δ_P −109.2 in $[^2H_2]$dichloromethane [lit.[13] δ_P −109.9].

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Footnotes

† Satisfactory elemental analyses were obtained.

‡ *Selected spectroscopic data* for **2**: ^1H NMR (299.9 MHz, CD_2Cl_2; all *J* in Hz) δ 2.45 (d, $^2J_{HP}$ 18.3, 3 H, CH_3), 2.36–2.57 (m, 4 H, CH_2CH_2), 7.61–7.90 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2) δ 3.10 (d, $^1J_{CP}$ 51.6, CH_3), 7.82 (d, $^1J_{CP}$ 6.6, CH_2CH_2); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, ref. H_3PO_4) δ −96.79; FAB MS *m/z* 151 ($C_9H_{12}P$, [M − OTf]$^{+\cdot}$). For **4a**: ^1H NMR (299.9 MHz, CD_2Cl_2) δ 1.26 (dt, $^3J_{HP}$ 20.4, $^3J_{HH}$ 7.8, 3 H, PCH_2CH_3), 2.44 (d, $^2J_{HP}$ 12.6, 3 H, PCH_3), 2.60–2.82 (m, 2 H, PCH_2CH_3), 3.93 (d, $^3J_{HP}$ 12.3, 3 H, $POCH_3$), 7.60–7.95 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2) δ 5.12 (d, $^2J_{CP}$ 4.4, CH_2CH_3), 8.09 (d, $^1J_{CP}$ 63.6, PCH_3), 19.18 (d, $^1J_{CP}$ 67.0, PCH_2CH_3), 57.06 (d, $^2J_{CP}$ 7.7, $POCH_3$); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, ref. H_3PO_4) δ 89.63; FAB MS *m/z* 183 ($C_{10}H_{16}OP$, [M −

OTf]$^{+\cdot}$). For **4b**: ^{1}H NMR (200.0 MHz, $\mathrm{CD_2Cl_2}$) δ 1.24 (dt, $^3J_{\mathrm{HP}}$ 20.6, $^3J_{\mathrm{HH}}$ 7.7, 3 H, $\mathrm{PCH_2C}\mathit{H}_3$), 1.43 (tm, $^3J_{\mathrm{HH}}$ 6.5, 3 H, $\mathrm{OCH_2C}\mathit{H}_3$), 2.42 (d, $^2J_{\mathrm{HP}}$ 12.8, 3 H, $\mathrm{PCH_3}$), 2.53–2.83 (m, 2 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 4.09–4.35 (m, 2 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 7.60–7.95 (m, 5 H, Ph); ^{13}C{^{1}H} NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$) δ 5.14 (d, $^2J_{\mathrm{CP}}$ 5.2, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$), 8.52 (d, $^1J_{\mathrm{CP}}$ 63.5, $\mathrm{PCH_3}$), 16.22 (d, $^3J_{\mathrm{CP}}$ 7.1, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 19.49 (d, $^1J_{\mathrm{CP}}$ 66.8, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 67.86 (d, $^2J_{\mathrm{CP}}$ 7.9, $\mathrm{POCH_3}$); ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$, ref. $\mathrm{H_3PO_4}$) δ 86.12. For **5a**: ^{1}H NMR (300.1 MHz, $\mathrm{CD_2Cl_2}$) δ 2.30 (d, $^2J_{\mathrm{HP}}$ 17.2, 3 H, $\mathrm{PCH_3}$), 2.34 (d, $^3J_{\mathrm{HP}}$ 16.2, 6 H, $\mathrm{CCH_3}$), 7.45–7.90 (m, 5 H, Ph); ^{13}C{^{1}H} NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$) δ 7.48 (d, $^1J_{\mathrm{CP}}$ 55.1, $\mathrm{PCH_3}$), 10.42 (d, $^2J_{\mathrm{CP}}$ 1.7, $\mathrm{C}\mathit{C}\mathrm{H_3}$); ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$, ref. $\mathrm{H_3PO_4}$) δ −103.58; FAB MS *m/z* 177 ($\mathrm{C_{11}H_{14}P}$, [M − OTf]$^{+\cdot}$). For (±)-**5b**: ^{1}H NMR (200.0 MHz, $\mathrm{CD_2Cl_2}$) δ 2.59 (d, $^2J_{\mathrm{HP}}$ 17.0, 3 H, $\mathrm{PCH_3}$), 2.74 (d, $^3J_{\mathrm{HP}}$ 17.2, 3 H, $\mathrm{CCH_3}$), 7.20–8.05 (m, 10 H, Ph); ^{13}C{^{1}H} NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$) δ 7.86 (d, $^1J_{\mathrm{CP}}$ 55.0, $\mathrm{PCH_3}$), 11.64 (s, $\mathrm{C}\mathit{C}\mathrm{H_3}$); ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$, ref. $\mathrm{H_3PO_4}$) δ −104.80; FAB MS *m/z* 239 ($\mathrm{C_{16}H_{16}P}$, [M −OTf]$^{+\cdot}$).

§ *Crystal data* for **2**: $\mathrm{C_{10}H_{12}F_3O_3P_3S}$, M_r = 300.23, colourless plates from dichloromethane, space group $P2_1/c$, a = 6.675(3), b = 27.585(9), c = 7.271 Å, β = 104.88(4)°, U = 1294.0(9) Å^3, Z = 4; D_c = 1.541 g cm^{-3}, μ(Cu-Kα) = 37.62 cm^{-1}. Rigaku AFC6R diffractometer; T = 213 K, ω–2θ scan method. A total of 1995 unique data were collected in the range of $3 \leqslant 2\theta \leqslant 120.1°$ of which 1412 [$I > 3\sigma(I)$] were used for the refinement. The structure was solved by direct methods and expanded by Fourier techniques and refined anisotropically by a full-matrix procedure, R = 0.043. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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