

A Crystalline Phosphinyl Radical Cation

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Abstract: One-electron oxidation of a readily available phosphoalkene derived from a cyclic (alkyl)(amino)carbene affords a phosphorus-centered radical cation that is indefinitely stable both in solution and in the solid state, allowing a single X-ray diffraction study to be performed. This species can be regarded as a phosphinyl radical bearing a cationic substituent or, alternatively, as a carbene-stabilized phosphoniumyl radical (carbene–RP^{•+}).

The involvement of a variety of phosphorus-centered radicals in chemical reactions has been recognized for many decades.¹ Some of these paramagnetic species are persistent or even stable² in solution at room temperature. The gas-phase electron diffraction structures of phosphinyl radicals **Ia** and **Ib** (Figure 1) have been reported.³ However in the solid state, despite bulky substituents, compounds **I** dimerize, which readily explains why only a few phosphorus radicals (**II–VI**)^{4,5} have been structurally characterized by single-crystal X-ray diffraction studies. All these compounds are resonance-stabilized radicals, and consequently, the calculated spin density at a single phosphorus center is rather small (maximum 0.44e for **VIb**).^{4c} Here we report the preparation of a phosphinyl radical featuring a cationic substituent, for which the spin density is mainly localized at a single phosphorus atom (0.67e). It is stable at room temperature both in solution and in the solid state, allowing a crystallographic study to be performed.

Recent reports have shown that although [carbene–(RO)₂P(O)•],⁶ (carbene–BR₂•),⁷ and (carbene–ML_n•)⁸ adducts cannot be isolated, they are significantly more stable than the corresponding free phosphinyl, boryl, and metal radicals. Encouraged by the isolation of radical cations **VI**, each of which can be viewed as a P₂^{•+} fragment capped by two carbenes,^{4c} we envisioned that an RP^{•+} unit could also be stabilized by a bulky and strong electron-donating carbene.⁸ Obviously, such a carbene–phosphoniumyl adduct can also be regarded as a phosphinyl radical featuring a cationic substituent. To obtain the desired radical cation, a synthetic strategy similar to that used for the preparation of **VI** was chosen.^{4c} Phosphaalkene **2** was prepared in two steps by addition of (2,2,6,6-tetramethylpiperidino)phosphine dichloride⁹ to cyclic (alkyl)(amino)carbene **VIIa**¹⁰ followed by reduction with excess magnesium (Scheme 1). The strong polarization of the PC bond was indicated by the relatively high field ³¹P NMR signal (136 ppm) and low field ¹³C NMR chemical shift (207 ppm). Not surprisingly, because of the electron-rich P nucleus, a one-electron oxidation readily occurred at 25 °C upon addition of Ph₃C⁺B(C₆F₅)₄[–] to a benzene solution of **2**. After workup, the radical cation **2^{•+}** was isolated as a dark-brown powder in 38% yield (mp 94–96 °C), and single crystals were grown by layering hexane on top of a fluorobenzene solution at 5 °C.¹¹

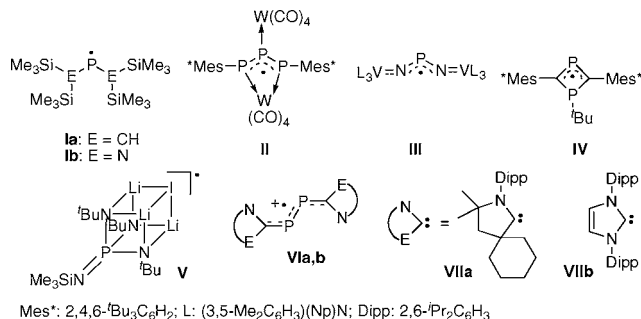
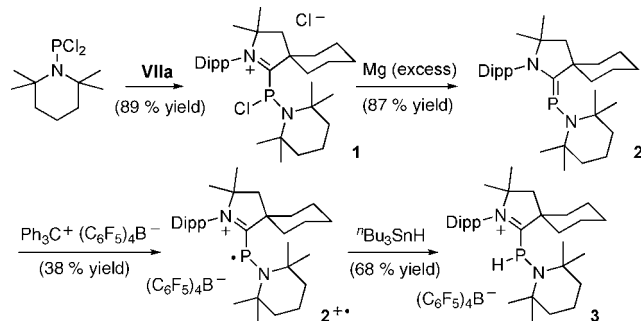


Figure 1. Phosphorus radicals structurally characterized in the gas phase (**I**) and in the solid state (**II–VI**)

Scheme 1



In the solid state, radical cation **2^{•+}** adopts a V-shaped geometry with a N2–P1–C1 angle of 107.3° (Figure 2, right). The P1–C1 (1.81 Å) and P1–N2 (1.68 Å) bond lengths in **2^{•+}** are significantly longer and shorter, respectively, than the corresponding ones in **2** (1.74 and 1.77 Å) (Figure 2, left). These two bond distances are at the lower ends of the ranges for P–C and P–N single bonds,

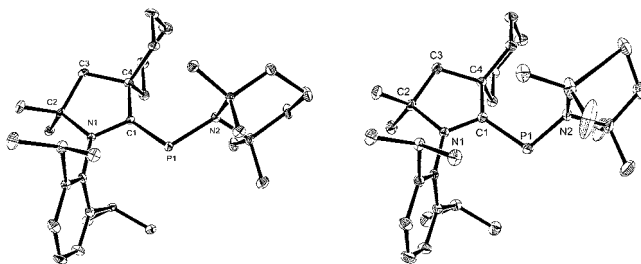


Figure 2. Molecular views (with 50% thermal ellipsoids) of (left) **2** and (right) **2^{•+}**. For clarity, the counterion [B(C₆F₅)₄[–]] and hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) in **2**: P1–N2, 1.7655(11); P1–C1, 1.7376(14); N1–C1, 1.3805(16); N2–P1–C1, 108.90(6); N1–C1–C4, 106.90(11). In **2^{•+}**: P1–N2, 1.6805(14); P1–C1, 1.8137(17); N1–C1, 1.318(2); N2–P1–C1, 107.26(8); N1–C1–C4, 110.18(13).

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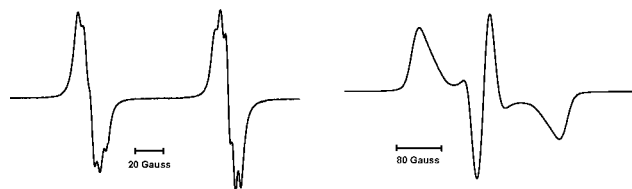


Figure 3. EPR spectra of $2^{+\bullet}$ in (left) a fluorobenzene solution at 298 K and (right) a frozen solution at 100 K.

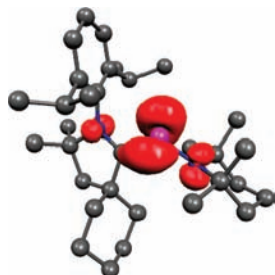


Figure 4. Spin density for $2^{+\bullet}$ calculated at the (U)M05-2X/def2-SVP level. Red surfaces indicate regions of α density excess.

respectively, and are comparable to those observed in the gas-phase electron diffraction study of **1** (P–C, 1.85 Å; P–N, 1.62 Å).³ Moreover, the N1–C1 bond distance in $2^{+\bullet}$ (1.32 Å) is shorter than that in **2** (1.38 Å), indicating a double bond. Collectively, these data are in agreement with those expected for a phosphinyl radical bearing a cationic substituent.

The room-temperature EPR spectrum of $2^{+\bullet}$ in fluorobenzene displays a doublet of multiplets ($g = 2.007$) due to a large hyperfine coupling constant with the phosphorus nucleus [$a(^{31}\text{P}) = 99$ G] and a small constant with one or two nitrogen nuclei [$a(^{14}\text{N}) \approx 4$ G] (Figure 3, left). The hyperfine coupling constant with P is comparable to those observed for phosphinyl radicals **1**³ [$a(^{31}\text{P}) = 96.3$ (**1a**) and 91.8 (**1b**) G], for which the odd electron resides predominantly in a 3p(P) valence orbital. The EPR spectrum of $2^{+\bullet}$ in a frozen fluorobenzene solution at 100 K was also measured (Figure 3, right) and simulated, allowing the determination of the principal values of the phosphorus hyperfine coupling tensor [$a_{xx}(\text{P}) = a_{yy}(\text{P}) = 23$ G and $a_{zz}(\text{P}) = 247$ G, with $g_{xx} = g_{yy} = 2.009$ and $g_{zz} = 2.018$]. These values suggest that ~ 57 and $\sim 2\%$ of the unpaired electron are localized on the 3p and 3s orbitals of phosphorus, respectively.¹² Consistent with these experimental data, calculations at the (U)M05-2X/def2-SVP level using the NBO method¹³ confirmed that the spin density in $2^{+\bullet}$ is localized mainly at phosphorus (67%) with small contributions from the nitrogen atoms (16% for N2 and 10% for N1) (Figure 4).

To probe chemically the radical behavior of $2^{+\bullet}$, excess $n\text{Bu}_3\text{SnH}$ in benzene was added at 25 °C. The color changed immediately from dark-brown to light-orange. After workup, phosphine **3** was obtained as a pale-yellow powder (Scheme 1). Notably, the geometric parameters observed for **3** are very similar to those of $2^{+\bullet}$ (P–C, 1.84 Å; P–N, 1.68 Å; C–N, 1.31 Å), confirming again the phosphinyl nature of the latter.

The stability of phosphinyl radical $2^{+\bullet}$ is due partly to steric factors but more importantly to the presence of the cationic substituent. It prevents the dimerization observed for other phosphinyl radicals, such as **1**, by electrostatic repulsion. With the same strategy, a variety of novel stable radicals should become accessible.

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Supporting Information Available: Full experimental details, including the electrochemical study, absolute energies, and optimized geometries of $2^{+\bullet}$, and X-ray crystallographic data for **2**, $2^{+\bullet}$, and **3** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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