J|A|C|S
COMMUNICATIONS

A Crystalline Phosphinyl Radical Cation

Olivier Back,[†] Mehmet Ali Celik,[‡] Gernot Frenking,[‡] Mohand Melaimi,[†] Bruno Donnadieu,[†] and Guy Bertrand[*,†]

UCR−CNRS Joint Research Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California, Riverside, California 92521-0403, and Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35032 Marburg, Germany

Received May 29, 2010; E-mail: guy.bertrand@ucr.edu

Abstract: One-electron oxidation of a readily available phosphaalkene 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 phospheniumyl radical (carbene−$RP^{+\bullet}$).

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 stable[2] 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**).[4e] Here we report the preparation of a phoshinyl 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−$(RO)_2P(O)\bullet$],[6] (carbene−$BR_2\bullet$),[7] and (carbene−$ML_n\bullet$)[6] adducts cannot be isolated, they are significantly more stable than the corresponding free phosphonyl, boryl, and metal radicals. Encouraged by the isolation of radical cations **VI**, each of which can be viewed as a $P_2^{+\bullet}$ fragment capped by two carbenes,[4e] we envisioned that an $RP^{+\bullet}$ unit could also be stabilized by a bulky and strong electron-donating carbene.[8] Obviously, such a carbene−phospheniumyl 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.[4e] Phosphaalkene **2** was prepared in two steps by addition of (2,2,6,6-tetramethylpiperidino)phosphine dichloride[9] 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 ^{31}P NMR signal (136 ppm) and low field ^{13}C 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 $Ph_3C^+B(C_6F_5)_4^-$ to a benzene solution of **2**. After workup, the radical cation $\mathbf{2}^{+\bullet}$ 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]

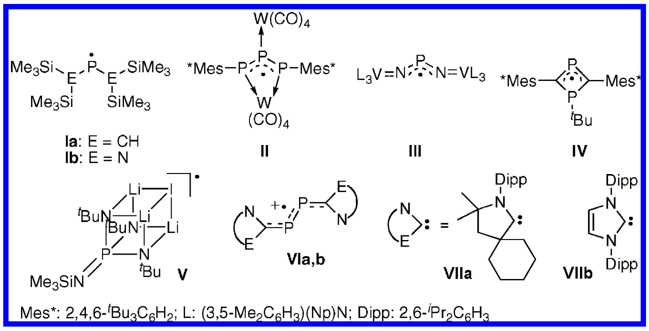
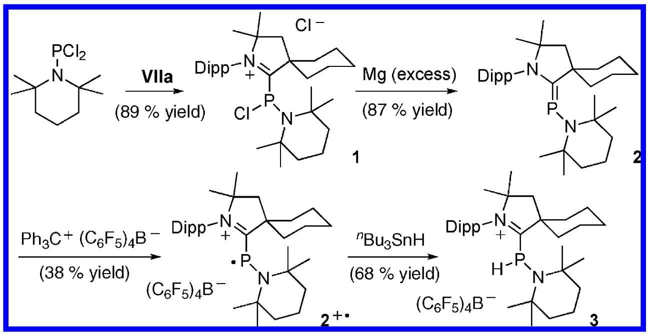


Figure 1. Phosphorus radicals structurally characterized in the gas phase (**I**) and in the solid state (**II**−**VI**)

Scheme 1



In the solid state, radical cation $\mathbf{2}^{+\bullet}$ 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 $\mathbf{2}^{+\bullet}$ 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,

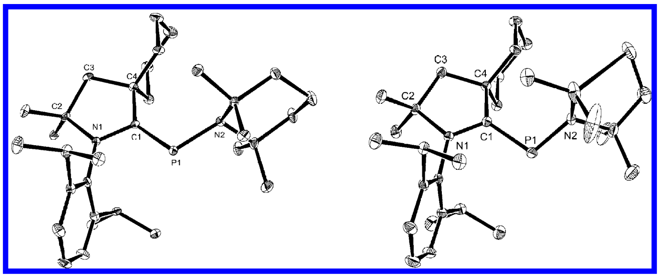


Figure 2. Molecular views (with 50% thermal ellipsoids) of (left) **2** and (right) $\mathbf{2}^{+\bullet}$. For clarity, the counterion [$B(C_6F_5)_4^-$] and hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) in **2**: P1−N2, 1.7655(11); P1−C1, 1.7376(14); N1−C1, 1.3805(16); N2−P1−C1, 108.90(6); N1−C1−C4, 106.90(11). In $\mathbf{2}^{+\bullet}$: 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).

[†] University of California, Riverside.
[‡] Philipps-Universität Marburg.

10.1021/ja1046846 © 2010 American Chemical Society

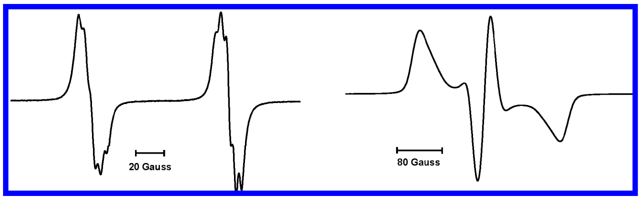


Figure 3. EPR spectra of $\mathbf{2}^{+\bullet}$ in (left) a fluorobenzene solution at 298 K and (right) a frozen solution at 100 K.

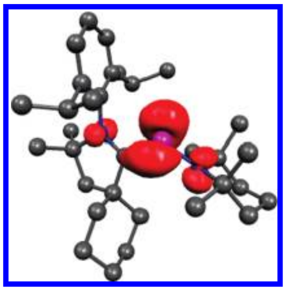


Figure 4. Spin density for $\mathbf{2}^{+\bullet}$ calculated at the (U)M05-2X/def2-SVP level. Red surfaces indicate regions of α density excess.

respectively, and are comparable to those observed in the gas-phase electron diffraction study of **I** (P−C, 1.85 Å; P−N, 1.62 Å).[3] Moreover, the N1−C1 bond distance in $\mathbf{2}^{+\bullet}$ (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 phoshinyl radical bearing a cationic substituent.

The room-temperature EPR spectrum of $\mathbf{2}^{+\bullet}$ in fluorobenzene displays a doublet of multiplets ($g = 2.007$) due to a large hyperfine coupling constant with the phosphorus nucleus [$a(^{31}\mathrm{P}) = 99$ G] and a small constant with one or two nitrogen nuclei [$a(^{14}\mathrm{N}) \approx 4$ G] (Figure 3, left). The hyperfine coupling constant with P is comparable to those observed for phosphinyl radicals $\mathbf{I}^3$ [$a(^{31}\mathrm{P}) =$ 96.3 (**Ia**) and 91.8 (**Ib**) G], for which the odd electron resides predominantly in a 3p(P) valence orbital. The EPR spectrum of $\mathbf{2}^{+\bullet}$ 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 [$a_{xx}(\mathrm{P}) = a_{yy}(\mathrm{P}) = 23$ G and $a_{zz}(\mathrm{P}) = 247$ G, with $g_{xx} = g_{yy} = 2.009$ and $g_{zz} = 2.018$]. These values suggest that ∼57 and ∼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 method[13] confirmed that the spin density in $\mathbf{2}^{+\bullet}$ 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 $\mathbf{2}^{+\bullet}$, excess $^n\mathrm{Bu}_3\mathrm{SnH}$ 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 $\mathbf{2}^{+\bullet}$ (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 $\mathbf{2}^{+\bullet}$ 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 **I**, by electrostatic repulsion. With the same strategy, a variety of novel stable radicals should become accessible.

Acknowledgment. Financial support from the NSF (CHE-0924410) and the DFG are gratefully acknowledged. We thank Dr. D. Borchardt (UCR) for EPR assistance.

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

References

(1) For reviews, see: (a) Armstrong, A.; Chivers, T.; Boere, R. T. *ACS Symp. Ser.* **2006**, *917*, 66. (b) Marque, S.; Tordo, P. *Top. Curr. Chem.* **2005**, *250*, 43. (c) Power, P. P. *Chem. Rev.* **2003**, *103*, 789. (d) Geoffroy, M. *Recent Res. Dev. Phys. Chem.* **1998**, *2*, 311.
(2) For examples, see: (a) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, Y.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582. (b) Ndiaye, B.; Bhat, S.; Jouaiti, A.; Berclaz, T.; Bernardinelli, G.; Geoffroy, M. *J. Phys. Chem. A* **2006**, *110*, 9736. (c) Cataldo, L.; Dutan, C.; Misra, S. K.; Loss, S.; Grützmacher, H.; Geoffroy, M. *Chem.—Eur. J.* **2005**, *11*, 3463. (d) Rosa, P.; Gouverd, C.; Bernardinelli, G.; Berclaz, T.; Geoffroy, M. *J. Phys. Chem. A* **2003**, *107*, 4883. (e) Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Geoffroy, M.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 6241. (f) Loss, S.; Magistrato, A.; Cataldo, L.; Hoffmann, S.; Geoffroy, M.; Röthlisberger, U.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 723. (g) Sasaki, S.; Murakami, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 340.
(3) (a) Hinchley, S. L.; Morrison, C. A.; Rankin, D. W. H.; Macdonald, C. L. B.; Wiacek, R. J.; Cowley, A. H.; Lappert, M. F.; Gundersen, G.; Clyburne, J. A. C.; Power, P. P. *Chem. Commun.* **2000**, 2045. (b) Hinchley, S. L.; Morrison, C. A.; Rankin, D. W. H.; Macdonald, C. L. B.; Wiacek, R. J.; Voigt, A.; Cowley, A. H.; Lappert, M. F.; Gundersen, G.; Clyburne, J. A. C.; Power, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 9045. (c) Bezombes, J. P.; Borisenko, K. B.; Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E.; Rankin, D. W. H.; Robertson, H. E. *Dalton Trans.* **2004**, 1980.
(4) (a) Scheer, M.; Kuntz, C.; Stubenhofer, M.; Linseis, M.; Winter, R. F.; Sierka, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2600. (b) Ito, S.; Kikuchi, M.; Yoshifuji, M.; Arduengo, A. J., III; Konovalova, T. A.; Kispert, L. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 4341. (c) Agarwal, P.; Piro, N. A.; Meyer, K.; Muller, P.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3111. (d) Armstrong, A.; Chivers, T.; Parvez, M.; Boere, R. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 502. (e) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369.
(5) A radical cation featuring a phosphorus center in a remote position has been fully characterized. See: Biaso, F.; Cantat, T.; Mezailles, N.; Ricard, L.; Le Floch, P.; Geoffroy, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7036.
(6) Tumanskii, B.; Sheberla, D.; Molev, G.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 7408.
(7) (a) Matsumoto, T.; Gabbai, F. P. *Organometallics* **2009**, *28*, 4252. (b) Walton, J. C.; Makhlouf Brahmi, M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solovyev, A.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 2350. (c) Ueng, S.-H.; Solovyev, A.; Yuan, X.; Geib, S. J.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Newcomb, M.; Walton, J. C.; Curran, D. P. *J. Am. Chem. Soc.* **2009**, *131*, 11256.
(8) For other examples of highly reactive fragments stabilized by singlet carbenes, see: (a) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008**, *130*, 14970. (b) Back, O.; Kuchenbeiser, G.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5530. (c) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206. (d) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069. (e) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2007**, *129*, 14180. (f) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 7052. (g) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701. (h) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Chem.—Eur. J.* **2010**, *16*, 432.
(9) King, R. B.; Sadani, N. D. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 149.
(10) (a) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705. (b) Jazzar, R.; Dewhurst, R. D.; Bourg, J. B.; Donnadieu, B.; Canac, Y.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2899.
(11) It should be noted that $\mathbf{2}^{+\bullet}$ cocrystallizes with various amounts of the corresponding chlorophosphine, which likely results from the abstraction of Cl• from residual traces of chlorine-containing reagents used in preceding steps of the synthesis. For the structure shown in the right panel of Figure 2, 6% chlorophosphine was present.
(12) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.
(13) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

JA1046846