

Communications to the Editor

A Room Temperature Stable 1,3-Diphosphaallyl Radical

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All carbon allyl radicals play a fundamental role in both organic and theoretical chemistry:¹ they are the simplest example of a species exhibiting negative spin density on the central carbon atom and frequently appear as intermediates in heterocyclic chemistry. Many allyl radicals containing one or more heteroatoms have also been intensively studied,² but curiously very little is known concerning those incorporating a phosphorus atom.³ 1 σ^4 -Phosphaallyl radicals **A** have been spectroscopically observed but the presence of the ylidic bond makes their electronic structure barely comparable with those of classical 3 π -electron systems.⁴ Koenig *et al.* reported that the photolysis of 3-chlorodiphosphiranes gave rise to diphosphiranyl radicals **B**, which underwent a ring-opening reaction affording 1,3-diphosphaallyl radicals **C**. However, direct observation of these short lived radicals **B** and **C** was not possible in the temperature range from -90 to 30 °C, and their transient existence was postulated based on the ESR spectra of spin-trapping products.⁵ Recently, we have demonstrated that the diphosphacyclopropenium ion 1⁺^{6a} and the four-membered heterocycle 2⁺ were stabilized forms of the transient 1 $\sigma^1,3\sigma^3$ - and 1 $\sigma^2,3\sigma^2$ -diphosphaallyl cations 3⁺ and 4⁺, respectively.^{6b} These results prompted us to investigate the redox properties of the diphosphirenium salt 1⁺, and here, we report the synthesis of a stable 1,3-diphosphaallyl radical 4^{*}, as well as the results of *ab initio*

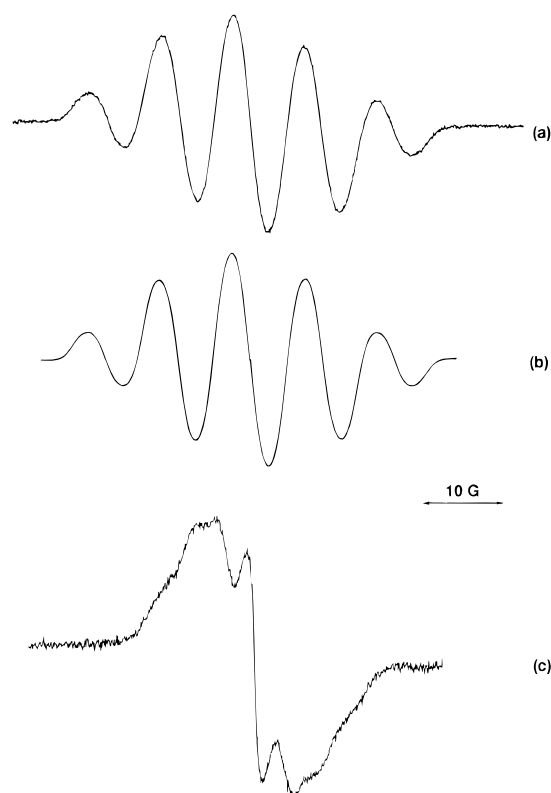
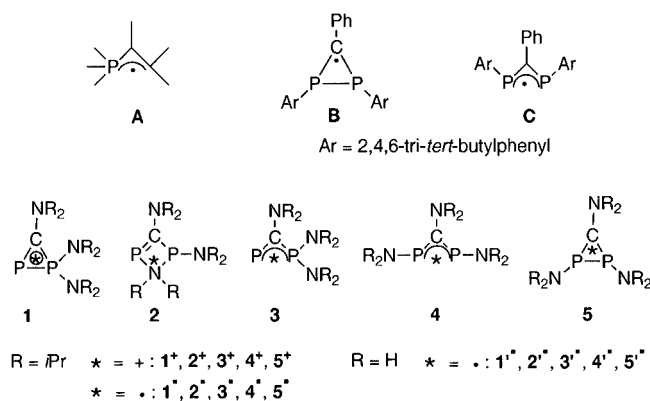


Figure 1. (a) Experimental ESR spectrum attributed to the radical 4^{*} in THF at 293 K. (b) Simulated spectrum [hf coupling constants employed: $a_p = 9.4$ G (2 P), $a_N = 9.9$ G (1 N), and $a_N = 1.5$ G (2 N)]. (c) Experimental ESR spectrum attributed to the radical 4^{*} in the solid state at 293 K.

Scheme 1



calculations on the radical isomers 1^{*}–5^{*} (amino instead of diisopropylamino groups) (Scheme 1).

Cyclic voltammetry of heterocycle 1⁺(BF₄⁻) in dichloromethane (0.1 M *n*-Bu₄N⁺BF₄⁻, 100 mV/s) at room temperature under argon exhibited an irreversible reduction peak at $E_p^{\text{red}} = -1.55$ V vs SCE. This result implies that reduction of 1⁺ provides an unstable radical which rearranges *via* a chemical process. Preparative scale electrolysis of cation 1⁺ was performed at room temperature: reduction at -1.6 V passed 1

(7) Elemental analysis of crystals of 4^{*} [found: C, 56.50; H, 10.32; N, 9.86] is in agreement with C₁₉H₄₂N₃P₂·0.5CH₂Cl₂ [calcd: C, 56.17; H, 10.39; N, 10.08]. The presence of CH₂Cl₂ was confirmed by ¹H and ¹³C NMR spectroscopies, after oxidation of a CDCl₃ solution of 4^{*}. All attempts to remove CH₂Cl₂ from the crystals gave rise to a red oily material.

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(1) For example, see: Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275. Giese, B.; Damm, W.; Batra, R. *Org. Chem.* **1994**, *7*, 355. Olivella, S.; Solé, A.; Bofill J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2160. Pasto, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8164. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513. Walton, J. C. *Rev. Chem. Intermed.* **1984**, *5*, 249.

(2) For example, see: Schoeller, W. W.; Haug, W.; Strutwolf, J.; Busch, T. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1751. Wiberg, K. B.; Cheesman, J. R.; Ochterski, J. W.; Frisch, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6535. Coolidge, M. B.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2354. Reddy, M. V. V. S.; Celalyan-Berthier, A.; Geoffroy, M.; Morgantini, P. Y.; Weber, J.; Bernardinelli, G. *J. Am. Chem. Soc.* **1988**, *110*, 2748. Ahrens, W.; Berndt, A. *Tetrahedron Lett.* **1974**, 3741.

(3) Tordo, P. In *The Chemistry of Organophosphorus Compounds*; Patai, P., Hartley, F., Eds.; J. Wiley: New York, 1990; Vol. 1, p 137.

(4) Geoffroy, M.; Rao, G.; Tancic, Z.; Bernardinelli, G. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2391. Geoffroy, M.; Rao, G.; Tancic, Z.; Bernardinelli, G. *J. Am. Chem. Soc.* **1990**, *112*, 2826. Baban, J. A.; Cooksey, C. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 781.

(5) Gouygou, M.; Tachon, C.; Koenig, M.; Dubourg, A.; Declercq, J.-P.; Jaud, J.; Etemad-Moghadam, G. *J. Org. Chem.* **1990**, *55*, 5750.

(6) (a) Castan, F.; Baceiredo, A.; Fischer, J.; De Cian, A.; Commenges, G.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8160. (b) Soleilhavoup, M.; Canac, Y.; Polozov, A. M.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1994**, *116*, 6149. (c) Treutler, O.; Ahlrichs, R.; Soleilhavoup, M. *J. Am. Chem. Soc.* **1993**, *115*, 8788.

Table 1. Calculated Parameters for Derivatives **2[•]**–**5[•]** at UHF/6–31g* Level of Optimization

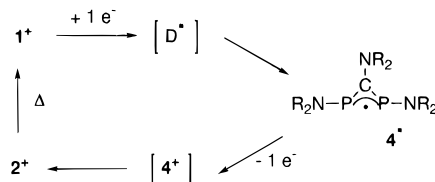
	2[•] 	3[•] 	4[•] 	5[•]
energy ^a	32.4	6.2	0	27.4
P ¹ C ^b	1.781	1.722	1.763	1.805
P ² C ^b	1.785	1.851	1.763	1.812
P ¹ N ^b	1.917		1.728	1.717
P ² N ^b	1.681, 1.861 ^e	1.711, 1.722	1.728	1.714
CN ^b	1.419	1.386	1.384	1.384
P ¹ P ² ^b	2.780	3.079	3.002	2.180
P ¹ CP ² ^c	102.5	119.0	116.7	74.1
P ¹ ^d	0.30 (0.06)	1.74 (0.20)	0.85 (0.20)	-0.06 (0.10)
	<i>0.10</i>	<i>0.06</i>	<i>0.43</i>	<i>0.46</i>
P ² ^d	-0.04 (-0.04)	0.05 (0.09)	0.85 (0.20)	0.01 (-0.01)
	<i>0.87</i>	<i>0.87</i>	<i>0.43</i>	<i>0.46</i>
C ^d	0.76 (0.18)	-0.74 (-0.13)	-0.69 (-0.11)	0.89 (0.24)
	<i>-0.31</i>	<i>-0.25</i>	<i>-0.22</i>	<i>-0.26</i>
N ¹ ^d	-0.01 (0.01)	-0.03 (-0.02)	0.01 (0.03)	0.04 (0.02)
	<i>-1.06</i>	<i>-1.04</i>	<i>-1.03</i>	<i>-1.02</i>
N ² ^d	0.01 (0.05)	0.01 (0.02)	0.01 (0.03)	0.01 (0.07)
	<i>-1.03</i>	<i>-1.05</i>	<i>-1.03</i>	<i>-1.01</i>
N ³ ^d	-0.09 (-0.04)	-0.04 (-0.01)	-0.04 (-0.05)	0.10 (0.05)
	<i>-0.86</i>	<i>-0.84</i>	<i>-0.85</i>	<i>-0.82</i>

^a Relative energy (kcal mol⁻¹) at (p)MP4SDTQ(fc)/6–31g*/UHF/6–31g* level, with zero-point vibrational energy correction. ^b Bond distances (Å). ^c Bond angles (deg). ^d Total atomic spin densities, Fermi contact analysis in parentheses, and total atomic charges in italic. ^e Exo- and endocyclic bond lengths.

equiv of charge and gave a deeply red, highly oxygen-sensitive solution of a paramagnetic species **4[•]**. The radical **4[•]** can also be generated by adding lithium metal to a THF solution of **1⁺**. Despite its high solubility in all classical solvents, the radical **4[•]** prepared in dichloromethane⁷ has been isolated as red crystals, not suitable for an X-ray diffraction study, from a pentane solution at -20 °C [60% yield, mp = 95–96 °C (dec.)]. The molecular weight of **4[•]** obtained from mass spectroscopy [(FAB/MNBA 374 (M⁺))] demonstrated that no fragmentation occurred during the reduction process of **1⁺**. The ESR signal from a THF solution of **4** [*g* = 2.0048] (Figure 1a) did not change in the temperature range from -60 to 25 °C and was retained in the solid state with broadening of the lines (Figure 1c). The splitting pattern (5 lines, 1:3:4:3:1) can be explained by the presence of two equivalent phosphorus nuclei and one nitrogen atom which would exhibit similar hyperfine coupling constants; however, the broadness of the signals suggests additional hyperfine coupling. The optimum simulation of the experimental spectrum gave the following values: *a*_P = 9.4 G (2 P), *a*_N = 9.9 G (1 N), and *a*_N = 1.5 G (2 N).

The results of *ab initio* calculations⁸ performed on radical **1[•]** and four of its possible isomers (**2[•]**–**5[•]**) are summarized in Table 1. From these results, the symmetrical diphosphaallyl radical **4[•]** is the only possible isomer which could give the observed symmetrical ESR spectrum. Indeed, in structures **2[•]** and **3[•]** the phosphorus nuclei are obviously inequivalent, while in isomer **5[•]** the pyramidalization of the ring carbon atom (C–N³ is bent out of the ring plane by $\theta = 34.9^\circ$) destroys the symmetry of the molecule. Note that the unsymmetrical three-membered ring radical **1[•]** is not an energy minimum, which is in good agreement with the experimental results, and that **4[•]** is the most stable radical on the energy surface.

We then studied the oxidation reaction of radical **4[•]**. The

Scheme 2

cyclic voltammetry (100 mV/s) of **4[•]** showed an irreversible oxidation wave at -0.15 V vs SCE. However, at 5 V/s, the oxidation process became quasi-reversible. Preparative oxidation of radical **4[•]** *via* electrolysis in CH₂Cl₂ (0.1 M *n*-Bu₄N⁺BF₄⁻, 100 mV/s) regenerated diphosphirenium salt **1⁺**(BF₄⁻) (60% yield). Interestingly, when the oxidation of **4[•]** was performed in CDCl₃ using trifluoromethanesulfonic acid, we initially observed the formation by ³¹P NMR of the cationic four-membered heterocycle **2⁺**(CF₃SO₃⁻) (AX system at 211 and 181 ppm, *J*_{PP} = 35 Hz) at -50 °C. As previously observed,^{6b} **2⁺** rearranged after a few minutes at room temperature affording the diphosphacyclopropenium salt **1⁺** (90% yield). Since we have already shown that the 1σ²,3σ²-diphosphaallyl cation **4⁺** was the direct precursor of **2⁺**, these results corroborate that the starting paramagnetic species was indeed the diphosphaallyl radical **4[•]**.

Scheme 2 summarizes the overall process. The structure of the initial transient radical **D[•]**, as well as the nature of the chemical process leading to **4[•]**, remains uncertain and might involve other transient radicals such as **3[•]** or **5[•]**.

Before this work, among the 1σ²,3σ²-diphosphaallyl systems, only a few stable anions were known,⁹ and no cations have been isolated.¹⁰ The 1σ²,3σ²-diphosphaallyl radical **4[•]** completes the series and, moreover, is certainly one of first isolated allyl radical.

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(8) All of the quantum chemical calculations were performed with the *Gaussian 94* set of program systems. *Gaussian 94* (Revision A.1); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. W.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995. The eigenvalue for $\langle S^2 \rangle$ of each doublet species was 0.77–0.78, after spin projection. All species were characterized as energy minima by corresponding vibrational analysis. Electron correlation corrections were performed at MP4SDTQ(fc) level with spin projection (Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530).

(9) Thelen, V.; Schmidt, D.; Nieger, M.; Niecke, E.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 313. Gouyguou, M.; Veith, M.; Couret, C.; Escudié, J.; Huch, V.; Koenig, M. *J. Organomet. Chem.* **1996**, *514*, 37. Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 751. Appel, R.; Schuhn, W.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 416. Karsch, H. H. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 419.

(10) Evidence for the transient formation of 1σ²,3σ²-diphosphaallyl cations has been reported: Karsch, H. H.; Reischer, H. U.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 454. Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 740. Fleischer, U.; Grützmacher, H.; Krüger, U. *J. Chem. Soc., Chem. Commun.* **1991**, 302. Schmidpeter, A.; Jochem, G. *Tetrahedron Lett.* **1992**, *33*, 471.