

A Crystalline Phosphaalkene Radical Anion

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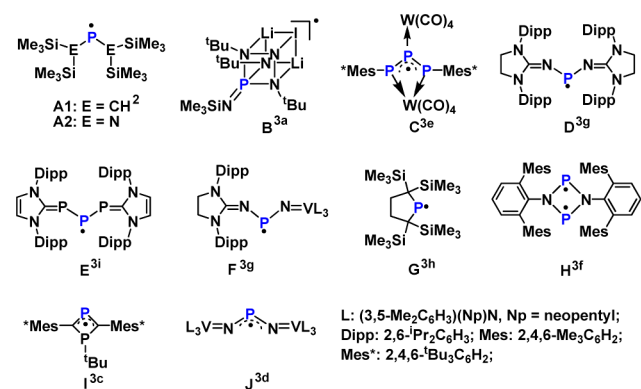
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S Supporting Information

ABSTRACT: Salts containing phosphaalkene radical anions have been isolated and characterized by electron paramagnetic resonance (EPR) spectroscopy, UV–vis absorption spectroscopy, and single-crystal X-ray diffraction. The radical anions feature elongated P–C bonds and an aromatization of fulvene compared to the neutral phosphaalkene. Their EPR spectra and theoretical calculations indicate the spin density of the radicals mainly resides on phosphorus atoms. This work provides the first example of a crystalline phosphaalkene radical anion.

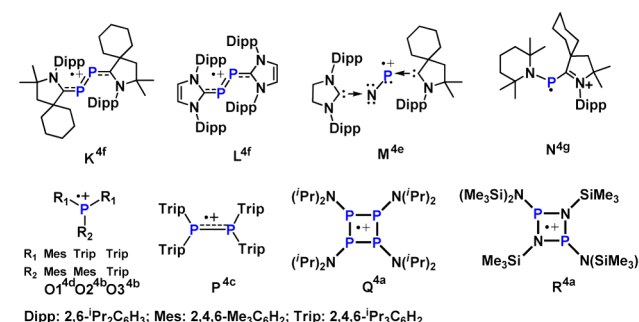
Isolation of stable phosphorus-based radicals is an area of high current interest, because such radicals not only are important for understanding chemical bonding but also play essential roles in biological processes, organic synthesis, and functional materials.¹ Continuous efforts have led to the emergence of a number of stable neutral radicals (Scheme 1)^{2,3}

Scheme 1. Structurally Characterized Neutral Phosphorus Radicals



and radical cations (Scheme 2) of phosphorus,⁴ which were isolated and structurally characterized. In contrast, stable phosphorus radical anions are rare, and most of them have been observed in solution by electron paramagnetic resonance (EPR) spectroscopy.⁵ Only two crystalline phosphorus radical anions, dipotassium 1,2,4-diazaphospholide η^5, η^5 -3,5-Ph₂dp²⁻ (dp = diazaphosphole) and 1,1-bisphosphinosulfide [Ph₂C=C(P(SPh₂)₂)^{•-}, have been reported;^{6a,b} however, EPR spectra and density functional theory (DFT) calculations indicate that the electron spin density mainly resides on carbon atoms rather than phosphorus in these species.^{6c}

Scheme 2. Structurally Characterized Phosphorus Radical Cations



Phosphaalkenes, R'P=CR₂, are one class of low-coordinate organophosphorus compounds that have been extensively studied in syntheses, coordination chemistry, polymer materials, and applications.⁷ Investigation of the redox behavior of phosphaalkenes in solution suggests that radical cations and anions could form upon one-electron oxidation and reduction, respectively.^{5,8} In 2010, Bertrand and co-workers reported a crystalline phosphinyl radical (N in Scheme 2) featuring a cationic substituent by one-electron oxidation of a phosphaalkene.^{4g} In this paper we present the isolation, characterization, and structure of a phosphaalkene radical anion, in which the electron spin density largely resides on the phosphorus atom.

Phosphaalkene **1** was synthesized by the literature method⁹ and exhibits one quasi-reversible one-electron reduction at $E_{1/2} = -1.00$ V versus Hg/Hg₂Cl₂ in the cyclic voltammogram (Figure S1 in the Supporting Information (SI)). Upon one-electron reduction with potassium or lithium in THF or DME, **1** was converted to the purple radical anion salts [K(THF)₃]⁺·**1**^{•-} and [Li(DME)₃]⁺·**1**^{•-} in moderate yields (Scheme 3). The products were subsequently studied by single-crystal X-ray diffraction, EPR spectroscopy, and UV–vis absorption spectroscopy, in conjunction with DFT calculations.

Crystals suitable for X-ray crystallographic studies¹⁰ were obtained in THF and DME solvents. The structures of [K(THF)₃]⁺·**1**^{•-} and [Li(DME)₃]⁺·**1**^{•-} are shown in Figure 1 with structural parameters, some of which along with those of parent molecule **1**⁹ are given in Table S2 in the SI. [Li(DME)₃]⁺·**1**^{•-} consists of discrete cation [Li(DME)₃]⁺ and radical anion **1**^{•-}, while in [K(THF)₃]⁺·**1**^{•-} the solvated K⁺ additionally interacts with fulvene.^{11b} Both radical anions of **1**^{•-} adopt a V-shaped geometry. The P1–C1 bond length in

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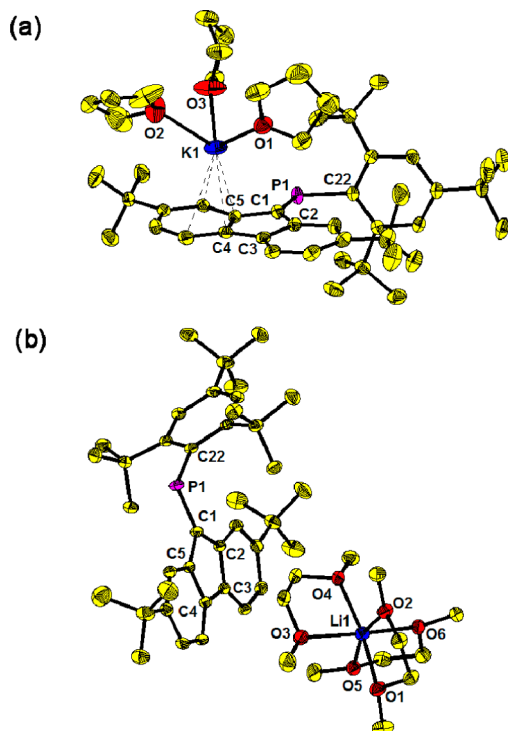
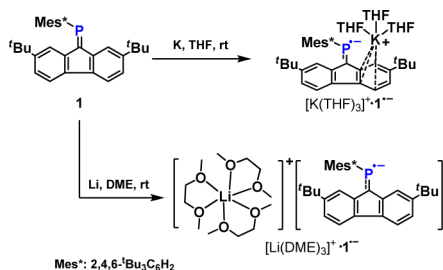
Scheme 3. Reduction Reactions of **1** with K or Li

Figure 1. Thermal ellipsoid (50%) drawings of (a) $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ and (b) $[\text{Li}(\text{DME})_3]^+\cdot\mathbf{1}^{\bullet-}$. Free THF molecules and H atoms are omitted for clarity. Yellow C, purple P, red O, and blue K/Li. Selected bond lengths (Å) and angles (deg): in $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$, P1–C1 1.757(3), P1–C22 1.854(3), C1–C2 1.452(5), C1–C5 1.420(4), C2–C3 1.432(5), C3–C4 1.427(5), C4–C5 1.435(5), K–C5 2.999(3), C1–P1–C22 105.91(14), C5–C1–P1 119.9(2), C2–C1–P1 134.5(2), C5–C1–C2 105.6(3); in $[\text{Li}(\text{DME})_3]^+\cdot\mathbf{1}^{\bullet-}$, P1–C1 1.754(2), P1–C22 1.871(2), C1–C2 1.448(3), C1–C5 1.452(3), C2–C3 1.430(3), C3–C4 1.445(3), C4–C5 1.430(3), C1–P1–C22 106.90(10), C5–C1–P1 120.16(16), C2–C1–P1 134.58(16), C5–C1–C2 105.16(18).

$[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ (1.757(3) Å) is comparable to that in $[\text{Li}(\text{DME})_3]^+\cdot\mathbf{1}^{\bullet-}$ (1.754(2) Å), and both are longer than that of neutral **1** (1.681(5) Å).⁹ In the fulvene, the C2–C3 and C4–C5 bonds become shorter while others (C1–C2, C1–C5, and C3–C4) lengthen upon reduction, showing an aromatization of fulvene. There are no significant changes for other structural parameters from neutral **1** to radical anion $\mathbf{1}^{\bullet-}$.

The crystal structures of $\mathbf{1}^{\bullet-}$ are well reproduced by DFT calculations at the UPBE0/6-31G(d) level.¹¹ Consistent with the experimental data, the P1–C1 bond length becomes longer and the fulvene is aromatized, while other structural parameters show no significant changes from **1** to anion $\mathbf{1}^{\bullet-}$ (Table S2 in the SI). The alteration of P1–C1 bond length can be explained by the nature of the P1–C1 bonding. As shown in Figure S2 in

the SI, the LUMO of **1** mainly is $\pi^*(\text{P1}=\text{C1})$, an out-of-phase combination of p orbitals of phosphorus and carbon atoms. The $\pi^*(\text{P1}=\text{C1})$ orbital (LUMO) in **1** is empty but singly occupied in $\mathbf{1}^{\bullet-}$ (SOMO, Figure 2a). The increase in the

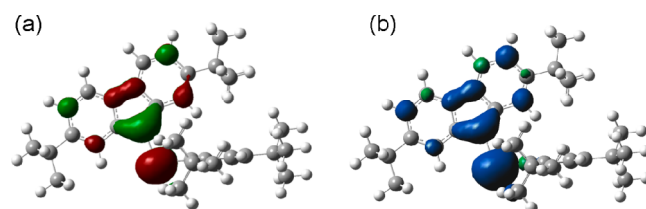
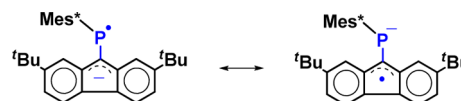


Figure 2. (a) Singly occupied molecular orbital (SOMO) and (b) spin density map of $\mathbf{1}^{\bullet-\text{opt}}$ calculated at the UPBE0/6-31G(d) level.

occupation of the $\pi^*(\text{P1}=\text{C1})$ orbital leads to a lengthening of the P1–C1 bond. In terms of valence bond theory, the lengthening of P1–C1 bond and the aromatization of fulvene can be ascribed to resonance structures as shown in Scheme 4,

Scheme 4. Resonance Structures of $\mathbf{1}^{\bullet-}$ 

with appreciable contribution from the one on the left, i.e., a phosphinyl radical bearing an anionic fulvene. This is supported by the Mulliken spin density distribution (Figure 2b, Table S3 in the SI) as largely resides on phosphorus (0.594) with a small contribution from the adjacent carbon atom of fulvene (0.108).

The experimental EPR spectra are similar to those of the phosphalkene radical anions reported by Geoffroy and co-workers (Table S4 in SI)^{5c,gi} and agree well with the DFT calculations on spin density. The solution EPR spectrum of $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ at 273 K shows a doublet signal ($g = 2.0062$) due to the coupling with ^{31}P nucleus (Figure 3a). The hyperfine coupling constant (hfc), $a(^{31}\text{P}) = 80.4$ G, is within the range of persistent phosphorus radical anions (21.0–118.7 G).⁵ The EPR signals of $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ show high-resolution anisotropic hyper-couplings in the frozen solution at 110 K (Figure 3b). The g -factors and hfc tensors were determined as follows: $g_{\parallel} = 2.0045$, $a_{\parallel}(^{31}\text{P}) = 211$ G, $g_{\perp} = 2.0087$, and $a_{\perp}(^{31}\text{P}) = 10.2$

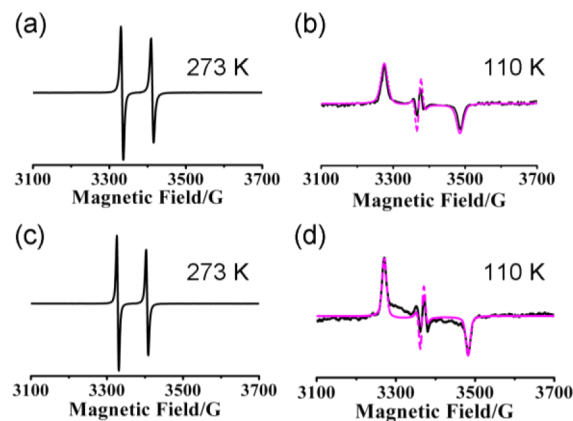


Figure 3. Experimental (black) and simulated (pink) EPR spectra of 1×10^{-3} M solutions of $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ (a,b) and $[\text{Li}(\text{DME})_3]^+\cdot\mathbf{1}^{\bullet-}$ (c,d) in THF at 273 and 110 K.

G. On the basis of the comparison with hfc's of atomic phosphorus, 51.09% and 1.62% spins are localized on the 3p (P) and 3s (P) orbitals in $[\text{K}(\text{THF})_3]^+\cdot\text{I}^{\bullet-}$, respectively. The g -factors and hfc tensors of $[\text{Li}(\text{DME})_3]^+\cdot\text{I}^{\bullet-}$ [$g = 2.0062$, $a = 79.3$ G in solution (Figure 3c); $g_{\parallel} = 2.0038$, $a_{\parallel}(^{31}\text{P}) = 211.5$ G, $g_{\perp} = 2.0091$, $a_{\perp}(^{31}\text{P}) = 8.9$ G in frozen solution (Figure 3d)] are similar to those of $[\text{K}(\text{THF})_3]^+\cdot\text{I}^{\bullet-}$. The above EPR results show that the unpaired electron is considerably localized on the phosphorus atoms in both salts.

The UV-vis absorption spectra (Figure 4) of the radical anions $\text{I}^{\bullet-}$ in THF show two characteristic absorptions in the

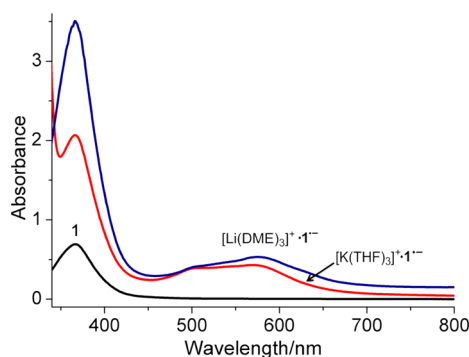


Figure 4. Absorption spectra of 1×10^{-4} M **1** (black), $[\text{K}(\text{THF})_3]^+\cdot\text{I}^{\bullet-}$ in THF (red), and $[\text{Li}(\text{DME})_3]^+\cdot\text{I}^{\bullet-}$ in DME (blue) at 25 °C.

region of 500–600 nm. Judging from the time-dependent DFT (TD-DFT) calculations of $\text{I}^{\bullet-}_{\text{opt}}$ these absorptions are assigned to HOMO (β) \rightarrow LUMO (β) and HOMO (α) \rightarrow LUMO (α) electron transitions (Figure S3 in the SI).

We herein have described the stabilization and structural characterization of the phosphalkene anion salts $[\text{K}(\text{THF})_3]^+\cdot\text{I}^{\bullet-}$ and $[\text{Li}(\text{DME})_3]^+\cdot\text{I}^{\bullet-}$. Their crystals are thermally stable under anaerobic conditions at room temperature. The stability and crystallization are aided by the flanking ^tBu groups of the fulvenes in comparison to previous studies of phosphafulvene radical anions in solution.^{5c,g} Even so, the color of the solution of $\text{I}^{\bullet-}$ in THF or Et₂O gradually fades from purple to yellow.¹² More suitable groups with enhanced steric crowding and electronic property are needed to increase the stability of the radical anions for the future efforts. Our work provides the first example of a crystalline phosphalkene radical anion and suggests that a variety of novel stable radical anions might form upon the reduction of compounds $\text{R}'\text{M}=\text{CR}_2$ (M = heavier group 15 elements).

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, crystallographic data in CIF format, cyclic voltammogram of **1**, structural parameters, thermal ellipsoid drawing of $[\text{K}(\text{THF})_4]^+\cdot[\text{I}^{\bullet-}]^-$, EPR parameters, theoretical calculations, and complete ref 11a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(10) X-ray data for $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ and $[\text{Li}(\text{DME})_3]^+\cdot\mathbf{1}^{\bullet-}$ are listed in Table S1 in the SI. CCDC 1006489 and 1007154, respectively, contain the crystallographic data for these compounds. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(11) (a) All calculations were performed using the Gaussian 09 program suite: Frisch, M. J.; et al. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2010. See SI for geometries, coordinates, and full citation.. (b) In order to check whether or not the K^+ -fulvene interaction affects the geometry of the radical anion, calculation on the whole molecule $[\text{K}(\text{THF})_3]^+\cdot\mathbf{1}^{\bullet-}$ was carried out at the same level. No significant changes in the structural parameters were found in comparison to those of calculated free $\mathbf{1}^{\bullet-}$ (Table S2 in the SI).

(12) A colorless hydrogenation salt of $[\text{K}(\text{THF})_4]^+\cdot[\mathbf{1H}]^-$ was obtained after workup, which further confirms the radical nature of $\mathbf{1}^{\bullet-}$. The structure of $[\text{K}(\text{THF})_4]^+\cdot[\mathbf{1H}]^-$ cannot be completely solved due to disorder of the cation (Figure S4 in the SI). However, the preliminary geometry of the anion $[\mathbf{1H}]^-$ is well reproduced by DFT calculations (Table S5 in the SI).