Isolable Diphosphorus-Centered Radical Anion and Diradical Dianion

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Ⓢ *Supporting Information*

ABSTRACT: Two salts containing diphosphorus-centered radical anion $1^{•−}$ and diradical dianion $1^{2−••}$ were obtained by one- and two-electron reductions of an indenofluorene-bridging diphosphaalkene (**1**) with K and KC_8, respectively. The salts have been characterized by electron paramagnetic resonance (EPR) spectroscopy, UV−vis absorption spectroscopy, and single-crystal X-ray diffraction analysis. EPR spectroscopy and theoretical calculations reveal that the spin density of the radicals mainly resides on the phosphorus atoms, and $1^{2−••}$ has an open-shell singlet ground state. $1^{•−}$ and $1^{2−••}$ represent the first isolable and structurally characterized diphosphorus-centered radical anion and dianion.

There has been an ongoing interest in the isolation of radicals of heavier main group elements due to their importance not only in understanding chemical bonding but also in application for their unique physical properties.[1] Synthesis of phosphorus-centered radicals is one of the most attractive radical research topics owing to their vital roles in organic chemistry, biological processes, and materials science.[1a,2] Though a number of stable phosphorus-based monoradicals have been isolated and characterized,[3,4] only a few of them are diphosphorus-centered (Scheme 1). In addition, these diphosphorus-centered mono-radicals are either neutral (**A**)[3h] or cationic (**B−F**).[4b,f,h,i] No diphosphorus radical anion has been isolated.

Scheme 1. Structurally Characterized Diphosphorus-Centered Monoradicals
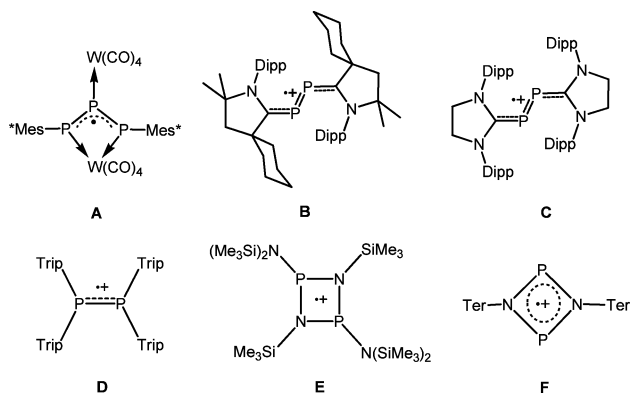
Mes* = 2,4,6-$^tBu_3C_6H_2$; Dipp = 2,6-$^iPr_2C_6H_3$; Trip = 2,4,6-$^iPr_3C_6H_2$; Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$

Diradicals, molecules with two unpaired electrons, are important in understanding the nature of chemical bonds in theoretical chemistry and have fundamental significance in the fields in mechanistic, synthetic, and biological chemistry.[5,6] Continuous efforts have led to the emergence of a number of isolable main group elements-based diradicals,[5d,1b−e] however, stable phosphorus-centered diradicals are extremely rare. Only two examples of phosphorus-centered diradicals, i.e., [TerN(μ-P)]$_2$ (**G**)[4d] and (TerN)$_2$(μ-P)(μ-As) (**H**)[4j] (Scheme 2; Ter =

Scheme 2. Structurally Characterized Phosphorus-Centered Diradicals

Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$
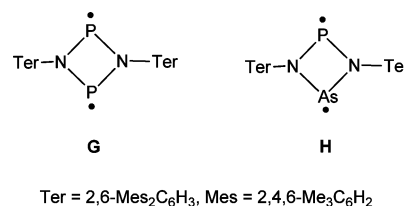
2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$), were isolated. It is noteworthy that, in some four-membered ring diradicals, the phosphorus atoms are only acting as a bridge rather than a radical center.[7] Seemingly it is difficult to find a suitable building block for constructing phosphorus-centered diradical species.

Phosphaalkenes and their oligomers, species bearing one or more unsaturated P=C double bonds, are one class of low-coordinate organophosphorus compounds and have been widely investigated in syntheses, coordination chemistry, as well as polymer materials.[8] They are expected to readily undergo reductions to radical anions owing to the lower-lying π*(P=C) orbitals in comparison to olefins. We previously have prepared a stable phosphaalkene radical anion substituted with ^tBu groups,[4g] which suggests phosphaalkenes may be candidates as building blocks for the synthesis of diphosphorus-centered radical anions and diradical dianions. In fact, the reduction chemistry of diphosphaalkenes has been investigated in solution by EPR spectroscopy, but no radical anions have been isolated.[9] Here we report the synthesis of the novel diphosphaalkene **1** and its one- and two-electron reductions to the first examples of diphosphorus-centered radical anion $1^{•−}$ and diradical dianion $1^{2−••}$.

Diphosphaalkene **1** was synthesized as diastereoisomers (**1a** and **1b**) by the reaction of the dilithium salt of indofluorene,[10] which was *in situ* formed through deprotonation of indofluorene

with ^{n}BuLi and 2 molar equiv of Mes*PCl$_2$ (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) in THF, followed by dehydrochlorination with an excess amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 3). **1a** and **1b** were isolated as orange solids in 17% and

Scheme 3. Synthesis of the Diphosphaalkene 1

Mes* = 2,4,6-tBu$_3$C$_6$H$_2$
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
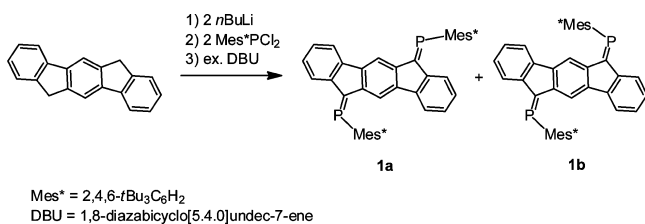
4% yields, respectively. The ^{31}P NMR chemical shifts in CDCl$_3$ (δ 255.3 and 258.5 ppm for **1a**; δ 261.1 ppm for **1b**) are comparable to that of FI* = PMes* (250 ppm, FI* = 2,7-ditetrabutylfluorene).[11] The P−C bond lengths (1.685(5) and 1.693(5) Å for **1a**; 1.688(3) Å for **1b**) determined by single-crystal X-ray diffraction analysis (Figure S1) are in the range (1.60−1.70 Å) for a typical phosphaalkene.[8d]

The cyclic voltammogram of **1a** in THF exhibits one reversible and one quasi-reversible reduction peak at −1.72 and −2.35 V, respectively, versus the Ag/AgNO$_3$ reference electrode (Figure S2). To this end, we performed one- and two-electron reductions of **1a** in order to isolate its radical anion and diradical dianion, respectively. The reaction of **1a** with 1 molar equiv of elemental potassium in the presence of 18-crown-6 afforded the anionic radical salt [(18-c-6)K(THF)$_2$]$^{+}$·**1**$^{•−}$, and the reduction of **1a** with an excess amount of KC$_8$ (4 molar equiv) in THF in the presence of 18-crown-6 produced the dianionic diradical salt [(18-c-6)K(THF)$_2$]$_2^{2+}$·**1**$^{2−••}$, both in moderate yields. Both compounds are also accessible in similar yields with the mixture of **1a** and **1b** as a starting material. The reduced products were subsequently studied by single-crystal X-ray diffraction analysis, EPR spectroscopy, UV−vis absorption spectroscopy and elemental analysis, in conjunction with theoretical calculations.

The singly reduced product [(18-c-6)K(THF)$_2$]$^{+}$·**1**$^{•−}$ was obtained from a concentrated THF solution at −20 °C as deep-green crystals (see Figure 1). It crystallizes in the monoclinic space group P2$_1$/n. The potassium cation is coordinated by one
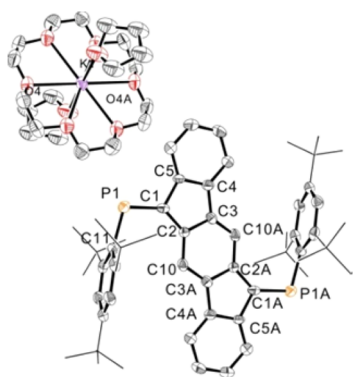
Figure 1. Thermal ellipsoid (at 50% probability) drawing of [(18-c-6)K(THF)$_2$]$^{+}$·**1**$^{•−}$. Hydrogen atoms and disorders are omitted for clarity. Selected bond lengths (Å) and angles (°): P1−C1 1.741(5), C1−C2 1.429(6), C1−C5 1.473(7), C2−C3 1.450(6), C3−C4 1.450(7), C4−C5 1.412(7), C2−C10 1.408(7), C10−C3A 1.380(6); C1−P1−C11 104.4(2), C2−C1−P1 135.6(4).

18-c-6 and two THF molecules. The configuration of the anion is center-symmetric in contrast to that of the starting material **1a**. The mean P−C bond length (1.741(5) Å) is larger than that of the neutral compound **1a** (av. 1.689 Å). The C1−C2, C1−C5, and C3−C4 bonds become shorter, while C2−C3 and C4−C5 bonds lengthen upon reduction, indicating an aromatization of the fulvene moiety.

The crystal structure of **1**$^{•−}$ is well reproduced by DFT calculations at the UWB97XD/6-31G(d) level. The P−C bond lengths (1.732 Å) are fitting well with the experimental data (1.741(5) Å). The elongation of P−C bond lengths in comparison with those of the neutral compound **1** can be explained by the nature of the P−C bonding. As shown in Figure 2a, the singly occupied molecular orbital (SOMO) of **1**$^{•−}$ mainly

(a)   (b)
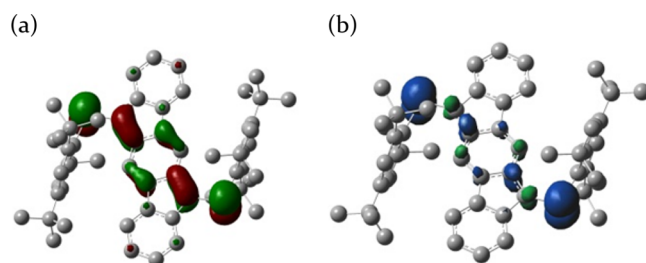
**Figure 2.** (a) SOMO of **1**$^{•−}$ and (b) Mulliken spin density map of **1**$^{•−}$ calculated at the UWB97XD/6-31G(d) level.

consists of the π*(P=C) orbitals with some contribution from the central benzene ring. This is in accordance with the addition of a single electron to the π*(P=C) orbitals. The Mulliken spin density distribution shows that most of the spin density resides on the two phosphorus centers (Figure 2b). The radical anion is stabilized by the resonance structures as shown in Scheme 4.

Scheme 4. Resonance Structures of 1$^{•−}$
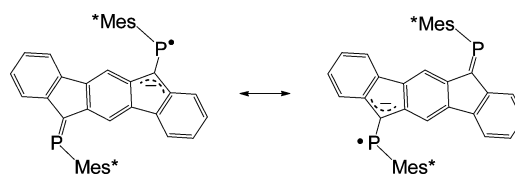
The experimental EPR spectra are comparable to those of other diphosphaalkene anionic radicals reported by Geoffroy et al.[9a,c] The solution EPR spectrum at 298 K shows a triplet signal due to the coupling with two equivalent ^{31}P nuclei (g = 2.0054). The hyperfine coupling constant (hfc), $a(^{31}$P) = 53.3 G, is within the range of persistent phosphorus radical anions (21.0−118.7 G).[9a,c,12] The EPR spectrum of the frozen solution at 110 K shows high-resolution anisotropic hyper-couplings, and the g-factors and hfc tensors were determined as follows: $g_{||}$= 2.0020, $a_{||}(^{31}$P) = 135 G; $g_{\perp}$ = 2.0086, $a_{\perp}(^{31}$P) = 20 G, indicating the spin density mainly resides at the two phosphorus centers, consistent with the calculated result (Figure 3). The UV−vis absorption spectrum of **1**$^{•−}$ in THF at room temperature shows one characteristic absorption at 704 nm (Figure S4), which is assigned to HOMO(β) → LUMO(β) electron transition as judged from the time-dependent DFT (TD-DFT) calculations.

The two-electron reduction of **1** with an excess amount of KC$_8$ in the presence of 18-c-6 afforded the dianionic diradical salt [(18-c-6)K(THF)$_2$]$_2^{2+}$·**1**$^{2−••}$ as dark-brown crystals, which is extremely air-sensitive. It turns to dark-green, then to purple,
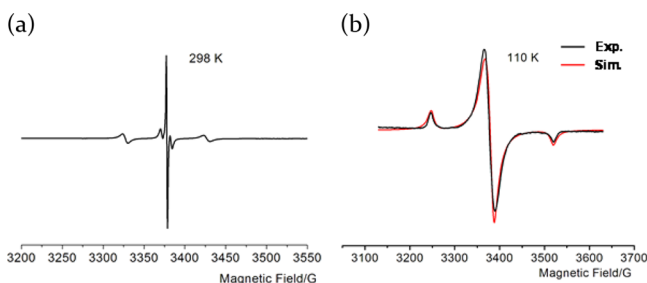
Figure 3. EPR spectra of 1×10^{-3} M solutions of $[(18\text{-c-}6)\text{K(THF)}_2]^+ \cdot \mathbf{1}^{\bullet-}$ in THF at (a) 298 and (b) 110 K. The spectrum at 110 K was simulated and highlighted in red.

once exposed to air. The solid-state structure of $[(18\text{-c-}6)\text{K(THF)}_2]_2^{2+} \cdot \mathbf{1}^{2-\bullet\bullet}$ is shown in Figure 4. It crystallizes in the
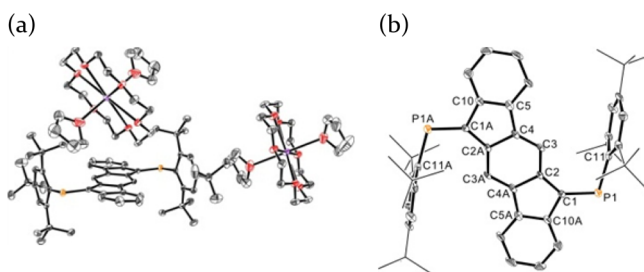

Figure 4. Thermal ellipsoid (at 50% probability) drawings of (a) $[(18\text{-c-}6)\text{K(THF)}_2]_2^{2+} \cdot \mathbf{1}^{2-\bullet\bullet}$ and (b) the anion moiety. Hydrogen atoms and disorders are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.768(2), C1–C2 1.429(3), C2–C3 1.409(3), C3–C4 1.383(3), C2–C4A 1.457(3), C4A–C5A 1.448(3), C5A–C10A 1.422(4); C1–P1–C11 106.13(11), C2–C1–P1 136.66(18), C10A–C1–P1 117.83(18).

triclinic space group $P\text{-}1$. Different from the molecular configuration of $\mathbf{1}^{\bullet-}$, there are two potassium cations each coordinated by two THF and one 18-c-6 in $\mathbf{1}^{2-\bullet\bullet}$, one of which is perpendicular to the dianion. The P–C bonds (1.768(2) Å) are further elongated in comparison with those of $\mathbf{1}^{\bullet-}$, consistent with the increasing occupation of the $\pi^*(\text{P}=\text{C})$ orbitals. Moreover, the P–C bonds are almost in the same plane with the indenofluorene fragment, indicating a π-conjugation of the P–C bonds with the indenofluorene fragment.

Full geometry optimizations of the closed-shell singlet (CS), open-shell singlet (OS), and triplet state (T) were performed at the (U)WB97XD/6-31G(d) level; the selected bond lengths and relative energy are listed in Table S2.[13] The calculated P–C bond lengths decrease from the CS, OS, to T states with those of the OS state fitting the best with the X-ray data. In addition, the OS state has the lowest calculated energy, and the calculated energy differences of $\Delta E_{\text{CS–OS}}$ and $\Delta E_{\text{T–OS}}$ are 10.2 and 6.7 kcal/mol, respectively.[14] Thus, compound $\mathbf{1}^{2-\bullet\bullet}$ has the character of an OS ground state. The Mulliken spin density map shows that the spin density mainly resides at the two phosphorus centers with some contribution from the P–C carbon atoms and central benzene ring (Figure 5).

Two characteristic absorptions at 735 and 677 nm are observed in the UV–vis spectrum (Figure S4), which are assigned to HOMO(α) $\rightarrow$ LUMO(α) and HOMO(β) $\rightarrow$ LUMO(β) electron transitions, respectively, as judged from TD-DFT calculations. The silence of EPR signals except that from the monoradical impurity $\mathbf{1}^{\bullet-}$ is consistent with a singlet ground state of $\mathbf{1}^{2-\bullet\bullet}$.
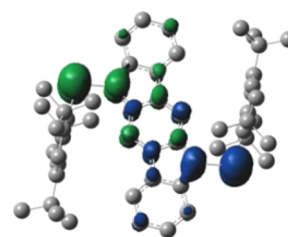
Figure 5. Mulliken spin density map of $\mathbf{1}^{2-\bullet\bullet}$ calculated at the UWB97XD/6-31G(d) level.

In conclusion, we have investigated the chemical reduction reactions of the novel diphosphaalkene **1**. Owing to the rigid and π-conjugated indenofluorene bridge, the singly reduced anion $\mathbf{1}^{\bullet-}$ and the doubly reduced dianion $\mathbf{1}^{2-\bullet\bullet}$ were isolated as stable crystals, which are thermally stable under anaerobic conditions at room temperature. Their EPR spectra and DFT calculations demonstrate that $\mathbf{1}^{\bullet-}$ and $\mathbf{1}^{2-\bullet\bullet}$ are phosphorus-centered radicals. $\mathbf{1}^{\bullet-}$ and $\mathbf{1}^{2-\bullet\bullet}$ represent the first structurally characterized diphosphaalkene radical anions. $\mathbf{1}^{2-\bullet\bullet}$ has an OS ground state as supported by DFT calculations and spectroscopy, which is also the first example of phosphorus-centered diradical dianion. This work provides a new structural motif to construct high-spin molecules. The syntheses of high-spin species based on phosphaalkenes are under investigation in our group.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04081.

Crystallographic data (CIF)
Experimental details and data (PDF)

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Notes
The authors declare no competing financial interest.

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