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Redox Reactions of a Stable Dialkylphosphinyl Radical

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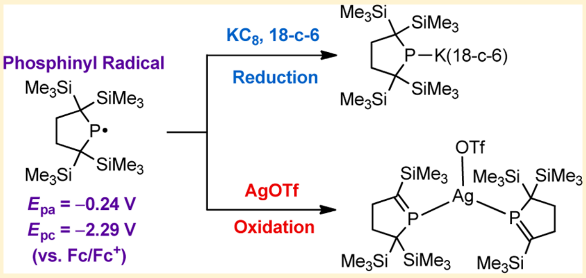
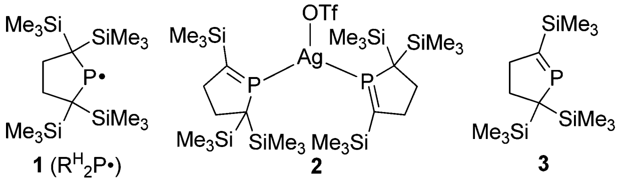
Supporting Information

ABSTRACT: A stable dialkylphosphinyl radical, 2,2,5,5-tetrakis(trimethylsilyl)-1-phosphacyclopentan-1-yl ($R^H{}_2P^\bullet$), showed both irreversible one-electron oxidation and reduction peaks at −0.24 and −2.29 V vs ferrocene/ferrocenium couple. One-electron reduction of $R^H{}_2P^\bullet$ with KC_8 in the presence of 18-crown-6 (18-c-6) or [2.2.2]cryptand (crypt-222) gave the corresponding phosphides $[K(18\text{-c-}6)]^+[R^H{}_2P]^-$ and $[K(\text{crypt-}222)]^+[R^H{}_2P]^-$. Whereas $[K(18\text{-c-}6)]^+[R^H{}_2P]^-$ exists as a contact ion pair, $[K(\text{crypt-}222)]^+[R^H{}_2P]^-$ exists as a solvent-separated ion pair in the solid state. Reaction of $R^H{}_2P^\bullet$ with AgOTf afforded an unexpected product, a silver(I) phosphaalkene complex.



Two-coordinate phosphorus-centered radicals ($R_2P^\bullet$, phosphinyl radicals) are one of the representative reactive intermediates in phosphorus chemistry.[1−3] Since phosphinyl radicals are expected to afford the corresponding phosphides R_2P^- and phospheniums R_2P^+ by redox reactions and these three species still have lone pairs, they can act as redox-active (noninnocent) ligands for transition metals as well as aminyl radicals.[4] Several dicoordinate stable phosphinyl radicals have been studied extensively in recent years; however, the redox behavior of phosphinyl radicals is still unclear. Previously we synthesized the stable and spin-localized dialkylphosphinyl radical **1** ($R^H{}_2P^\bullet$), as shown in Scheme 1.[5] We report herein the redox properties of phosphinyl radical **1**: the electrochemical behavior of **1** using cyclic voltammetry and chemical redox reactions of **1** involving formation of phosphide anions $[K(18\text{-c-}6)]^+\mathbf{1}^-$ and $[K(\text{crypt-}222)]^+\mathbf{1}^-$ (18-c-6 = 18-crown-6, crypt-222 = [2.2.2]cryptand) by reduction with KC_8 and the unexpected formation of the phosphaalkene silver(I) complex **2** by the reaction with AgOTf as an oxidant.

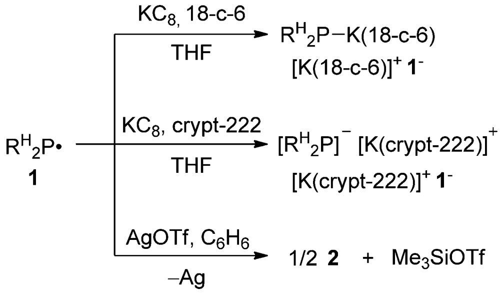
Scheme 1. Phosphinyl Radical and Related Compounds



The cyclic voltammogram of radical **1** in THF showed irreversible oxidation and reduction waves at −0.24 and −2.29 V (vs Fc/Fc^+ couple; Fc = ferrocene) (Figure S14 in the Supporting Information). The reduction potential of **1** (−2.29 V) is more cathodic than that of the structurally similar phosphaalkene **3** (−3.01 V), while the oxidation potential of **1** is considerably lower than that of the dialkylphosphine $R^H{}_2PH$ (E_{pa} = +0.76 V). The low oxidation and reduction potentials of **1** can be explained by the unpaired electron lying on the 3p orbital of the phosphorus atom of **1**.[5a]

Reduction of phosphinyl radical **1** with KC_8 in the presence of 18-c-6 in THF at room temperature for 3 h gave yellow crystals of the potassium phosphide $[K(18\text{-c-}6)]^+\mathbf{1}^-$ in 68% yield (Scheme 2). A similar reaction in the presence of crypt-222 afforded $[K(\text{crypt-}222)]^+\mathbf{1}^-$ as orange crystals in 86% yield. The structures of both $[K(18\text{-c-}6)]^+\mathbf{1}^-$and $[K(\text{crypt-}222)]^+\mathbf{1}^-$ were determined by NMR spectroscopy and X-ray diffraction (XRD) analysis. Both of them are protonated gradually to give $R^H{}_2PH$ in THF.

Scheme 2. Reactions of 1[a]



[a]Abbreviations: 18-c-6, 18-crown-6; crypt-222, [2.2.2]cryptand.

The molecular structure of $[K(18\text{-c-}6)]^+\mathbf{1}^-$ is a contact ion pair structure with monomeric form (Figure 1a), while $[K(\text{crypt-}222)]^+\mathbf{1}^-$ exists as a solvent-separated ion pair in the solid state (Figure S17 in the Supporting Information).[6] The shortest distance between the potassium and phosphorus atoms in $[K(18\text{-c-}6)]^+\mathbf{1}^-$ is 3.3079(11) Å, which is in the range

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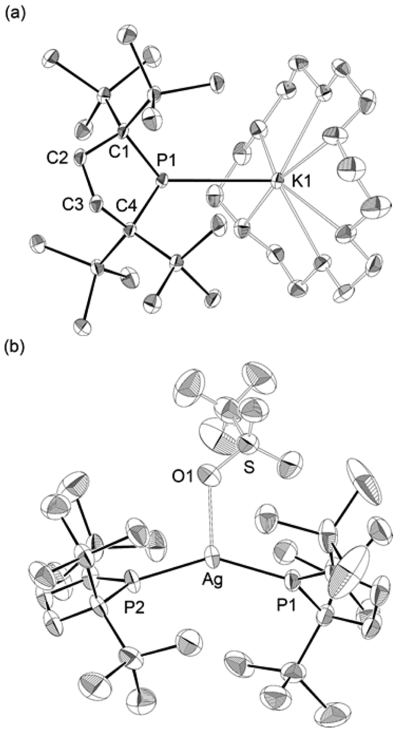

Figure 1. ORTEP drawings of (a) [K(18-c-6)]$^{+}$**1**$^{-}$ and (b) **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

of reported monomeric potassium phosphides (3.2198(10)−3.4822(9) Å).[7] The electropositive potassium atom of the phosphide [K(18-c-6)]$^{+}$**1**$^{-}$ increases the p character of its nonbonding electron pair orbital; the sum of the bond angles around the phosphorus atom is 344.16(9)°, which is larger than those of $\mathrm{R^{H}_{2}PCl}$ (304.76(9)°).[5]

Reaction of **1** with 1.5 equiv of AgOTf in C_6H_6 at room temperature afforded the phosphaalkene silver(I) complex **2** and Me_3SiOTf in 92% and 90% yields with the precipitation of silver, instead of the expected phosphenium cation $\mathrm{R^{H}_{2}P^{+}}$. Reaction of **1** with 1 equiv of AgOTf gave **2** and unreacted **1**. The molecular structure of **2** determined by XRD analysis is shown in Figure 1b. The silver atom adopts a planar three-coordinated geometry with two cyclic phosphaalkenes and one OTf ligand: the sum of the bond angles around the Ag atom is 360.0(1)°.[8]

The formation of the silver complex **2** can be explained by the following mechanism. Initial formation of phosphinosulfonate $\mathrm{R^{H}_{2}POTf}$ (**4**) by the oxidation of phosphinyl radical **1** with AgOTf and the subsequent elimination of trimethylsilyl triflate from **4** provide **3**. Coordination of the resulting phosphaalkene **3** to 1/2 equiv of AgOTf provides **2**.[9,10] Reactions of (1) phosphaalkene **3** with AgOTf, giving **2**, and (2) $\mathrm{R^{H}_{2}PCl}$ with AgOTf, giving **3**, support the aforementioned mechanism.[11]

In conclusion, we disclosed the redox behavior of the isolable phosphinyl radical **1**. Radical **1** shows oxidation and reduction irreversible waves at −0.24 and −2.29 V. Corresponding to the observed electrochemical redox behavior, reduction of **1** with KC_8 gave the phosphides [K(18-c-6)]$^{+}$**1**$^{-}$ and [K(crypt-222)]$^{+}$**1**$^{-}$, and oxidation of **1** with AgOTf afforded an unexpected product, phosphaalkene silver(I) complex **2**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, a table, and CIF and XYZ files giving details of the preparations and spectral and XRD data for new compounds and computational data for computed structures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00323.

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The authors declare no competing financial interest.

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(6) The ^{31}P resonances due to anionic phosphorus of [K(18-c-6)]$^{+}$**1**$^{-}$ and [K(crypt-222)]$^{+}$**1**$^{-}$ in benzene-d_6 appear at −35.8 and −31.4 ppm, respectively.

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(8) For phosphaalkene silver(I) complexes, see: (a) Deschamps, E.; Deschamps, B.; Dormieux, J. L.; Ricard, L.; Mézailles, N.; Le Floch, P. *Dalton Trans.* **2006**, 594−602. (b) Hayashi, A.; Okazaki, M.; Ozawa, F. *Organometallics* **2007**, *26*, 5246−5249.

(9) Theoretical calculations predict that formation of **4** from an ion pair of phosphenium cation $R^{H}_{2}P^{+}$ and TfO^{-} and subsequent elimination of trimethylsilyl triflate from **4** to provide **3** are exothermic. For details, see the Supporting Information.

(10) Reaction of **1** with $[Ag(benzene)_3]^{+}[B(C_6F_5)_4]^{-}$ gave phosphaalkene **3** in 33% yield, unidentified compounds, and a black precipitate that was presumably elemental silver. No ^{31}P resonances assignable to the phosphenium cation $R^{H}_{2}P^{+}$ were observed in low-field region (350−750 ppm).

(11) Details of reactions of **3** with AgOTf and of $R^{H}_{2}PCl$ with AgOTf are described in the Supporting Information.