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Two Phosphaalkene Radical Cations with Inverse Spin Density Distributions†

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Two phosphaalkene radical cations 1•+ and 2•+ have been reported. 1•+ is stable in the solid state and has been structurally characterized. 2•+ only keeps persistent in solution. 1•+ is described as a phosphorus-centered radical, while 2•+ as a delocalized radical with little contribution from phosphorus.

Phosphorus-centered radicals are of long-standing interest since they are involved in many chemical reactions, biological processes and organic syntheses.1–7 Constant effort has resulted in the isolation and structural characterization of a number of stable neutral radicals,8,16 radical anions17–19 and radical cations20–26 of phosphorus. In 2010, Bertrand et al. reported a crystalline phosphinyl radical featuring a cationic substituent, in which bulky protecting carbene ligands were used.26 Phosphaalkenes, RP=CR₂, as one class of low-coordinate organophosphorus compounds, have been extensively studied27–31 and their redox behaviors in solution suggest the formation of radical cations upon one-electron oxidation.32–39 We recently have succeeded in stabilization of a phosphaalkene radical anion upon one electron reduction with potassium or lithium.17 Herein we report two phosphaalkene radical cations with inverse spin density distributions.

In 2003, Geoffroy et al. reported the radical cation of phosphaalkene, 1•+PF₆⁻, as a powder but without structural justification.40 In order to isolate and structurally characterize this cation, we decide to use oxidants of weakly coordinating anions. Neutral phosphaalkene (I) was synthesized by following literature methods.40–41 Upon one-electron oxidation with Ag[Al(OR₄)₄] (OR₄ = OC(CF₃)₃)42 in CH₂Cl₂ at room temperature, I was converted to purple radical cation I•+ in a moderate yield of 56.6 % (Fig. 1a). The UV-vis absorption spectrum (Fig. 1b) of I•+-[Al(OR₄)₄] in CH₂Cl₂ shows two characteristic absorptions at 550 and 768 nm, which can be assigned to HOMO→LUMO (β) and HOMO→LUMO (β) electronic transitions, respectively (Fig. S1 in the SI), according to TD-DFT calculations at the UPBE0/6-31G(d) level. Subsequently, the product was studied by single-crystal X-ray diffraction and EPR spectroscopy, in conjunction with DFT calculations.

Fig. 1 (a) Oxidation reaction of I with Ag[Al(OR₄)₄] (OR₄ = OC(CF₃)₃) and (b) Absorption spectra of 1×10⁻⁶ M I and 1•+-[Al(OR₄)₄] in CH₂Cl₂ at 25 °C.

Crystals suitable for X-ray crystallographic studies were obtained in CH₂Cl₂ solvent at −20 °C. The structure of I•+ is shown in Fig. 2a. Some important structural parameters, along with those of the partially oxidized molecule of I (i.e. in the coordination complex [Cu{Mes*PC(NMe₂)₂}₂]BF₄,43 denoted as Ico), are given in Table S2 in the SI. The radical cation I•+ adopts a V-shaped geometry with the C33–P1–C39 angle of 103.8(2)°. Compared to “neutral” Ico, the P1–C39 bond...
(1.865(5) Å) significantly lengthens, while the P1–C33 bond (1.818(5) Å) greatly shortens, and both of them are very close to normal P–C single bond lengths (1.84–1.87 Å).14 In addition, the N1–C39 (1.331(7) Å) and N2–C39 (1.326(7) Å) bond lengths in 1+ are shorter than those in I (1.362 and 1.372 Å) (Table S2). These structural data suggest a phosphinyl radical bearing a cationic substituent.26

The crystal structure of 1+ was well reproduced by DFT calculations at the UBPE0/6-31G(d) level.25 Consistent with the experimental data, the P1–C39 bond length becomes longer, whereas the P1–C33 and N1–C39 (N2–C39) bond lengths become shorter, while other structural parameters show no significant changes from I to 1+ (Table S2 and Fig. S2). The alteration of P1–C39 bond length can be rationalized by the nature of the P1–C39 bonding. As shown in Fig. S3 in the SI, the HOMO of 1+ is mainly π (P1=C39), an in-phase combination of p orbitals of phosphorus and carbon atoms. The decrease in the occupation of the π (P1=C39) orbital leads to the lengthening of the P1–C39 bond. This result is further supported by the Wiberg bond index (WBI) of the P1–C39 bond (WBI = 1.08).

The experimental EPR spectra are similar to the radical cations of 1+ in solution reported by Geoffroy31 and agree well with the results of DFT calculations. The solution EPR spectrum of 1+ at 273 K shows a doublet signal (g = 2.0074) due to the coupling with 31P nucleus (Fig. 3a). The hyperfine coupling constant (hfc), a(31P) = 101.6 G, is within the range of stable phosphorus radical cations (42-263 G) (Table S3). The EPR signals of 1+,[Al(OR)3]2– show high-resolution anisotropic hyper-couplings in frozen CHCl3 solution at 77 K (Fig. 3b). The g-factors and hfc tensors were determined as follows: g± = 2.0062, a±(31P) = 295.3 G, gz = 2.0182, a±(31P) = 27.4 G. The ratios of isotropic and anisotropic hyperfine constants between the radicals and phosphorus atoms suggest that 68.2 % and 2.46 % spins are localized on the 3p (P) and 3s (P) orbitals in 1+, respectively. Consistent with these experimental data, DFT calculations at the UBPE0/6-31G(d) level confirm that the spin density of 1+ is mainly localized at phosphorus (80.9%) with small contributions from the nitrogen atoms (5.7% for N2 and 5.9% for N1, Fig. 2b). The degree of spin density localization is higher compared to Bertrand et al.’s work (67% at phosphorus).26

In order to investigate the effect of the polarity (Fig. S4) of P–C bond on radical stability, compound 2, which has inverse electron density (P–C) in comparison with compound 1 (P–C), was synthesized according to the literature.26 The reaction of Ag[Al(OR)3] with 2 led to a Ag-phosphaalkene coordination complex, but the one-electron oxidation of 2 occurred with one equiv NO,[Al(OR)3]2– in CHCl3 at −50 °C, which afforded a green solution of 2+. The green solution gradually turned yellow and an intramolecular cyclization product 2a was obtained in a yield of 46.9 % upon work-up, which was identified by 1H NMR and a preliminary crystal structure (Fig. S5). The EPR spectrum of 2+ was measured in CHCl3 at 273 K (g = 1.9008, a(31P) = 23.9 G, a(3H) = 4.2 G) (Fig. 5a). The data show the 31P hyperfine coupling is dramatically smaller than those in traditional localized phosphorus radicals (Table S3) and 1+, indicating a significant degree of delocalization of spin density. This is supported by DFT calculation on 2+, which predicts that the spin density is delocalized over phosphorus (9.7 %) and the fluorene group (Fig. 5b). The calculated a(31P) for 2+ (13.5 G) was also considerably smaller than that for 1+ (102.7 G), agreeing well with the experimental results.
In conclusion, we herein have described the synthesis and characterization of two phosphaalkene radical cations $1^+$ and $2^+$. Experimental and computational results show that $1^+$ is a phosphorus-centered radical, while $2^+$ is a delocalized radical over the fluorene group with little contribution from the phosphorus atom. In addition, the stability of $1^+$ is higher than $2^+$ due to the effect of the polarity of $P=C$ bond. Further studies of oxidized phosphaalkene with various ligands and their chemical reactivities are underway.

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Notes and references

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