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Cite this: DOI: 10.1039/c5dt00656b

Received 13th February 2015,
Accepted 24th March 2015

DOI: 10.1039/c5dt00656b

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Two phosphalkene radical cations with inverse spin density distributions†

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Two phosphalkene radical cations $1^{+\bullet}$ and $2^{+\bullet}$ have been reported. $1^{+\bullet}$ is stable in the solid state and has been structurally characterized. $2^{+\bullet}$ only remains persistent in solution. $1^{+\bullet}$ is described as a phosphorus-centered radical, while $2^{+\bullet}$ 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 anions^{17–19} and radical cations^{20–26} 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 Phosphalkenes, $R^2P=CR_2$, as a class of low-coordinate organophosphorus compounds, have been extensively studied^{27–31} and their redox behaviors in solution suggest the formation of radical cations upon one-electron oxidation.^{32–41} We recently have succeeded in the stabilization of a phosphalkene radical anion upon one electron reduction with potassium or lithium.¹⁷ Herein we report two phosphalkene radical cations with inverse spin density distributions.

In 2003, Geoffroy *et al.* reported the radical cation of phosphalkene, $1^{+\bullet}PF_6^-$, as a powder but without structural justification.⁴² In order to isolate and structurally characterize this cation, we decided to use oxidants of weakly coordinating anions. Neutral phosphalkene (**1**) was synthesized by following literature methods.^{42,43} Upon one-electron oxidation with

$Ag[Al(OR_F)_4]$ ($OR_F = OC(CF_3)_3$)⁴⁴ in CH_2Cl_2 at room temperature, **1** was converted to purple radical cation $1^{+\bullet}$ in a moderate yield of 56.6% (Fig. 1a). The UV-vis absorption spectrum (Fig. 1b) of $1^{+\bullet}[Al(OR_F)_4]^-$ in CH_2Cl_2 shows two characteristic absorptions at 550 and 768 nm, which can be assigned to HOMO–1(β) \rightarrow LUMO(β) and HOMO(β) \rightarrow LUMO(β) electronic transitions, respectively (Fig. S1 in the ESI†), 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.

Crystals suitable for X-ray crystallographic studies were obtained in CH_2Cl_2 solvent at $-20^\circ C$. The structure of $1^{+\bullet}$ is shown in Fig. 2a. Some important structural parameters, along with those of the partially oxidized molecule of **1** (*i.e.* in the coordination complex $[Cu\{Mes^*PC(NMe_2)_2\}_2]BF_4$,⁴⁵ denoted

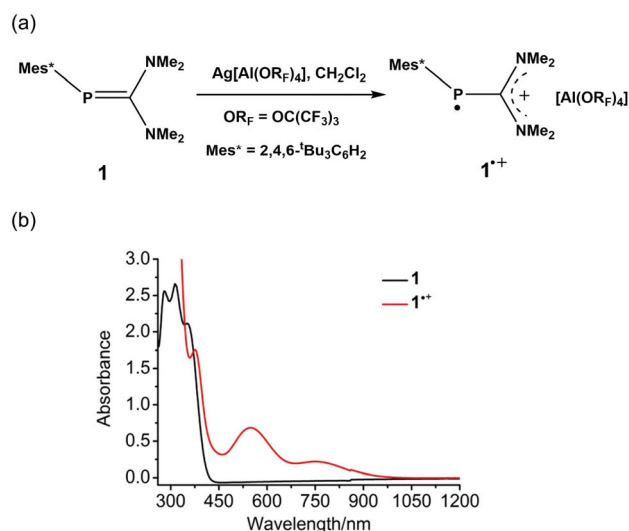


Fig. 1 (a) Oxidation reaction of **1** with $Ag[Al(OR_F)_4]$ ($OR_F = OC(CF_3)_3$) and (b) absorption spectra of 1×10^{-4} M **1** and $1^{+\bullet}[Al(OR_F)_4]^-$ in CH_2Cl_2 at $25^\circ C$.

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†Electronic supplementary information (ESI) available: Full experimental procedures, crystallographic and computational data. CCDC 1049267. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00656b

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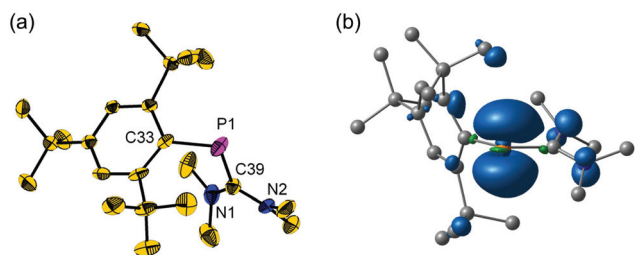


Fig. 2 (a) Thermal ellipsoid (50%) drawing of $1^{+\cdot}[\text{Al}(\text{OR}_\text{F})_4]^-$. The counterion $[\text{Al}(\text{OR}_\text{F})_4]^-$ and hydrogen atoms are omitted for clarity. Selected average bond lengths (Å) and angles (°): P1–C33 1.818(5), P1–C39 1.865(5), N1–C39 1.331(7), N2–C39 1.326(7), C33–P1–C39 103.8(2), N2–C39–N1 119.5(5), N2–C39–P1 115.8(4), N1–C39–P1 124.6(4). (b) Spin density distribution of $1^{+\cdot}$.

as 1_{co}), are given in Table S2 in the ESI.† The radical cation $1^{+\cdot}$ adopts a V-shaped geometry with the C33–P1–C39 angle of 103.8(2)°. Compared to “neutral” 1_{co} , 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).⁴⁶ In addition, the N1–C39 (1.331(7) Å) and N2–C39 (1.326(7) Å) bond lengths in $1^{+\cdot}$ are shorter than those in 1_{co} (1.362 and 1.372 Å) (Table S2†). These structural data suggest a phosphinyl radical bearing a cationic substituent.²⁶

The crystal structure of $1^{+\cdot}$ was well reproduced by DFT calculations at the UPBE0/6-31G(d) level.⁴⁷ 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 1 to $1^{+\cdot}$ (Table S2 and Fig. S2†). The alteration of the P1–C39 bonding can be rationalized by the nature of the P1–C39 bonding. As shown in Fig. S3 in the ESI,† 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 $1^{+\cdot}$ in solution reported by Geoffroy⁴² and agree well with the results of DFT calculations. The solution EPR spectrum of $1^{+\cdot}$ at 273 K shows a doublet signal ($g = 2.0074$) due to the coupling with ^{31}P nucleus (Fig. 3a). The hyperfine coupling constant (hfc), $a(^{31}\text{P}) = 101.6$ G, is within the range of stable phosphorus radical cations (42–263 G) (Table S3†). The EPR signals of $1^{+\cdot}[\text{Al}(\text{OR}_\text{F})_4]^-$ show high-resolution anisotropic hyper-couplings in frozen CH_3CN solution at 77 K (Fig. 3b). The g -factors and hfc tensors were determined as follows: $g_{\parallel} = 2.0062$, $a_{\parallel}(^{31}\text{P}) = 295.3$ G, $g_{\perp} = 2.0182$, $a_{\perp}(^{31}\text{P}) = 27.4$ 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 $1^{+\cdot}$, respectively. Consistent with these experimental

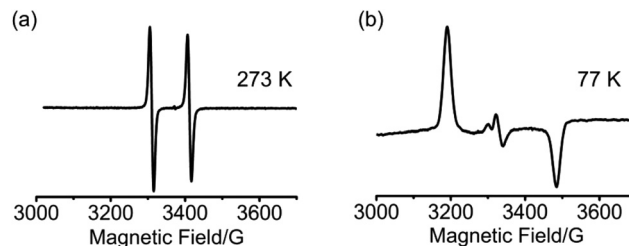


Fig. 3 Experimental EPR spectra of 1×10^{-3} M solutions of $1^{+\cdot}[\text{Al}(\text{OR}_\text{F})_4]^-$ in (a) CH_2Cl_2 at 273 K and (b) frozen CH_3CN at 77 K.

data, DFT calculations at the UPBE0/6-31G(d) level confirm that the spin density of $1^{+\cdot}$ 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 the 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.⁴⁸ The reaction of $\text{Ag}[\text{Al}(\text{OR}_\text{F})_4]$ with **2** led to a Ag-phosphaalkene coordination complex, but the one-electron oxidation of **2** occurred with one equiv. $\text{NO}[\text{Al}(\text{OR}_\text{F})_4]$ ⁴⁹ in CH_2Cl_2 at -50°C , which afforded a green solution of $2^{+\cdot}$ (Fig. 4). 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 $2^{+\cdot}$ was measured in CH_2Cl_2 at 273 K ($g = 1.9008$, $a(^{31}\text{P}) = 23.9$ G, $a(^1\text{H}) = 4.2$ G) (Fig. 5a). The data show that the ^{31}P hyperfine coupling is dramatically smaller than those in traditional localized phosphorus radicals (Table S3†) and $1^{+\cdot}$, indicating a significant degree of delocalization of spin density. This is supported by the DFT calculation on $2^{+\cdot}$, which predicts that the spin density is delocalized over phosphorus (9.7%) and the fluorene

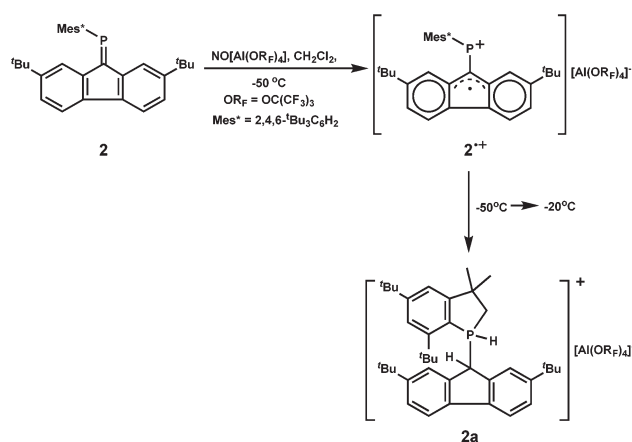


Fig. 4 Oxidation reaction of **2** with $\text{NO}[\text{Al}(\text{OR}_\text{F})_4]$.

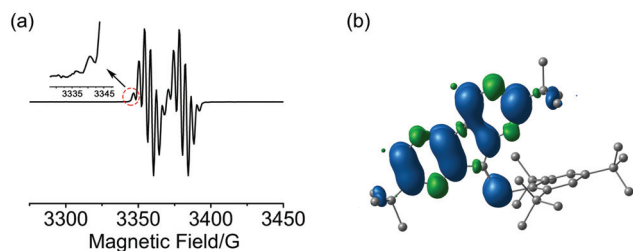


Fig. 5 (a) Experimental EPR spectrum of $2^{+\cdot}[\text{Al}(\text{OR}_\text{F})_4]^-$ in CH_2Cl_2 at 273 K. (b) Spin density distribution of $2^{+\cdot}$.

group (Fig. 5b). The calculated $a(^{31}\text{P})$ for $2^{+\cdot}$ (13.5 G) was also considerably smaller than that for $1^{+\cdot}$ (102.7 G), agreeing well with the experimental results.

In conclusion, we herein have described the synthesis and characterization of two phosphalkene radical cations $1^{+\cdot}$ and $2^{+\cdot}$. Experimental and computational results show that $1^{+\cdot}$ is a phosphorus-centered radical, while $2^{+\cdot}$ is a delocalized radical over the fluorene group with little contribution from the phosphorus atom. In addition, the stability of $1^{+\cdot}$ is higher than $2^{+\cdot}$ due to the effect of the polarity of the $\text{P}=\text{C}$ bond. Further studies of oxidized phosphalkene with various ligands and their chemical reactivities are underway.

We thank the National Natural Science Foundation of China (grant 21171087) and the Natural Science Foundation of Jiangsu Province (grant BK20140014) for financial support. We are grateful to the High Performance Computing Center of Nanjing University for doing the numerical calculations in this paper on its IBM Blade cluster system.

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