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Two Stable Phosphorus-Containing Four-Membered Ring Radical Cations with Inverse Spin Density Distributions

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S *Supporting Information*

ABSTRACT: Two phosphorus-containing four-membered ring radical cations $1^{•+}$ and $2^{•+}$ have been isolated and characterized by UV–vis absorption spectroscopy, electron paramagnetic resonance (EPR), and single-crystal X-ray diffraction. Compared with neutral molecules **1** and **2**, radical $1^{•+}$ has elongated P–P bonds and more pyramidalized phosphorus atoms, while shortened P–N_{ring} distances and larger angles around phosphorus centers are observed for $2^{•+}$. EPR studies indicate that for $1^{•+}$ spin density mainly resides on the exocyclic nitrogen atoms with very minor contribution from endocyclic phosphorus atoms, while the situation is opposite for $2^{•+}$. Such an inverse spin density distribution is controlled by the exocyclic substituents, which is supported by DFT calculations.

Isolation of stable radicals of heavier main group elements is an area of high current interest, because they are not only important for understanding of chemical bonding but also play essential roles in biological processes, organic synthesis, and functional materials.[1] Among them phosphorus-based radicals have attracted much attention as chain carriers for radical chain reactions and spin-labels for biomolecules.[1] Phosphorus radicals are generally highly reactive due to their open-shell electron configurations. Although the number of stable phosphorus radical species that were isolated and structurally characterized in the gas phase[2] or in the solid state[3] gradually increases, many phosphorus radicals were only observed in solution by EPR spectroscopy.[4]

Phosphorus is known to form cycles, cages and polymers with itself or nitrogen atom. Cyclotetraphosphines[5] and cyclodiphosphazanes,[6] two phosphorus-containing four-membered rings, have been widely used as scaffolds in the construction of interesting macrocycles and as ligands for metal complexes for applications in homogeneous catalysis. Though crystal structures of neutral phosphorus rings,[5,6] catena-phosphorus cations,[7] and cyclodiphosphadiazenium cations[8] have been documented, no stable and structurally characterized radical cations were reported for phosphorus-containing ring systems. Cyclotetraphosphine radical cations and their lighter analogue tetrazetidine radical cation have been characterized by EPR spectroscopy.[9,10]

Recently crystalline phosphazane and diphosphene radical cations were reported by Bertrand et al. (**I–IV**, Scheme 1).[3f–h] Very recently triarylphosphine and tetraaryldiphosphine radical

Scheme 1. Structurally Characterized Phosphorus Radical Cations

Mes = $2,4,6-Me_3C_6H_2$; Dipp = $2,6-^iPr_2C_6H_3$; Trip = $2,4,6-^iPr_3C_6H_2$
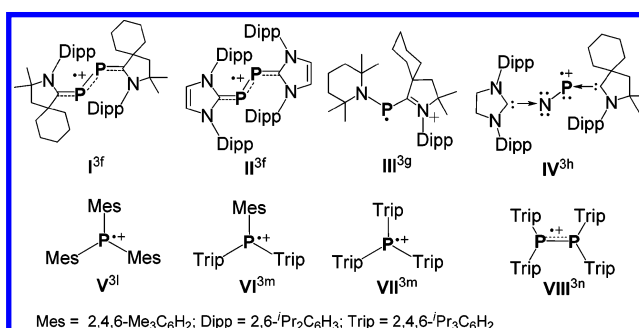
cations have been isolated by Stephan (**V**)[3l] and our group (**VI–VIII**)[3m,n] using weakly coordinating anions.[11] These previous results prompt us to investigate oxidation of phosphorus ring systems. Here we report isolation, characterization, and crystal structures of radical cations of cyclotetraphosphine ($1^{•+}$) and cyclodiphosphazane ($2^{•+}$) (Scheme 2). Two radical cations show inverse electron spin density distributions as on the peripheral atoms (in $1^{•+}$) and ring (in $2^{•+}$), respectively.

Scheme 2. Radical Cations of Cyclotetraphosphine and Cyclodiphosphazane
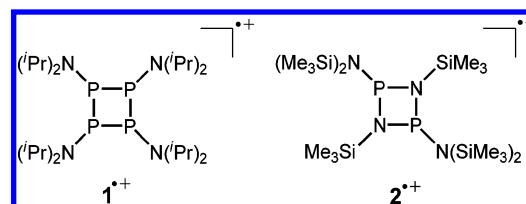
Neutral cyclotetraphosphine **1** was prepared by the dehalogenation of $^iPr_2NPCl_2$ with magnesium,[12] while cyclodiphosphazane **2** was synthesized by the elimination of Me_3SiCl from $[(Me_3Si)_2N]_2PCl$.[13] Treatment of **1** with a mixture of $NOSbF_6$ and $Li[Al(OR_F)_4]$ ($OR_F = OC(CF_3)_3$)[14] in CH_2Cl_2 at $-78\ °C$, followed by a slow warm-up to $-30\ °C$ and stirring for 4h, led to intensely violet radical cation salt $1^{•+}·[Al(OR_F)_4]^-$ in a moderate yield. Red radical cation salt $2^{•+}·SbF_6^-$ was obtained by one-electron oxidation of **2** with $NOSbF_6$ in CH_2Cl_2 at

ambient temperature. Both radical cation salts have been characterized by UV–vis absorption spectroscopy, EPR, and single-crystal X-ray diffraction, in conjunction with DFT calculations.

Crystals suitable for X-ray crystallographic studies were obtained by cooling solutions of salts $1^{\bullet+}\cdot[Al(OR_F)_4]^-$ and $2^{\bullet+}\cdot SbF_6^-$ in CH_2Cl_2.[15] For comparison, we also obtained the colorless crystals of precursors **1** and **2** from hexane and determined their structures (Figures S1 and S2). The structures of the radical cations $1^{\bullet+}$ and $2^{\bullet+}$ are shown as stereoviews in Figure 1. Their important structural parameters, along with
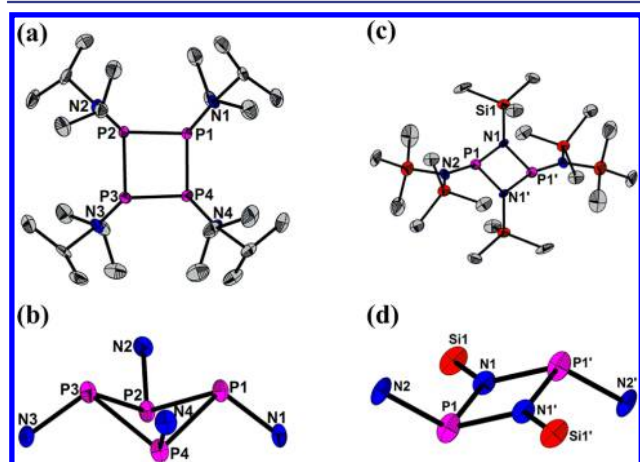

Figure 1. Thermal ellipsoid (50%) drawings of $1^{\bullet+}$ (a, top view; b, side view) and $2^{\bullet+}$ (c, top view; d, side view). Magenta P, blue N, red Si, and gray C. Hydrogen atoms (in a–d), [i]Pr (in b), Me and SiMe$_3$ (in d) are omitted for clarity. Selected bond lengths (Å) and angles (°): in $1^{\bullet+}$, P1–P2 2.2744(15), P2–P3 2.2737(15), P3–P4, 2.2562(16), P1–P4 2.2679(16), N1–P1 1.678(4), N2–P2 1.670(4), N3–P3 1.669(4), N4–P4 1.678(4), N1–P1–P2 104.68(13), N1–P1–P4 106.28(15), P2–P1–P4 81.27(5), N2–P2–P1 103.96(14), N2–P2–P3 104.87(13), P1–P2–P3 80.27(5), N3–P3–P2 106.82(14), N3–P3–P4 106.00(14), P2–P3–P4 81.54(5), N4–P4–P1 105.41(15), N4–P4–P3 105.30(14), P1–P4–P3 80.79(6); in $2^{\bullet+}$, P1–N1 1.696(7), P1–N1' 1.699(7), P1–N2 1.640(7), N1–Si1 1.788(7), N1–P1–N1' 85.2(3), N1–P1–N2 114.3(4), N2–P1–N1' 115.4(4), P1–N1–P1' 94.8(3), Si1–N1–P1 132.7(4), Si1–N1–P1' 132.5(4).

those of the neutral molecules **1** and **2**, are given in Table 1. The structure of $1^{\bullet+}$ (Figure 1a,b) is composed of a puckered P$_4$ ring with four pyramidal phosphorus atoms and all-trans arrangement of exocyclic amino groups relative to each other. The P–P bonds slightly elongate, while both endocyclic P–P–P and exocyclic P–P–N angles become narrower from the

Table 1. Average Bond Lengths (Å) and Angles (°) of 1, $1^{\bullet+}$, 2, and $2^{\bullet+}$

	1	**1**	$1^{\bullet+}$	$1^{\bullet+}$
	(X-ray)	(DFT)	(X-ray)	(DFT)
P–P	2.227	2.239	2.268	2.274
∠P–P–P	82.24	84.96	80.97	84.04
∠P–P–N	107.66	106.88	105.42	104.75
	2	**2**	$2^{\bullet+}$	$2^{\bullet+}$
	(X-ray)	(DFT)	(X-ray)	(DFT)
P–N$_{ring}$	1.732	1.751	1.698	1.725
∠N1–P1–N1'	82.81	82.19	85.2	84.89
∠N1–P1–N2	109.80	108.72	114.3	114.80

precursor **1** to radical cation $1^{\bullet+}$. In contrast, $2^{\bullet+}$ (Figure 1c,d) possesses an essentially square P$_2$N$_2$ core with trigonal planar nitrogen and pyramidalized phosphorus centers. The exocyclic amino substituents adopt a trans configuration relative to the core. The average P–N$_{ring}$ bond lengths in $2^{\bullet+}$ are slightly shorter, while both endocyclic and exocyclic N–P–N bond angles become larger than those of the parent molecule **2**.

The above data show that the removal of one electron has an opposite effect on structural parameter changes of these two rings from neutral to cationic. To rationalize the experimental results and get further insights into their electronic structures, we carried out calculations for species $1^{\bullet+}$ and $2^{\bullet+}$, along with parent molecules **1** and **2**.[16] The calculated structural parameters of $1^{\bullet+}$, $2^{\bullet+}$ and their neutral molecules are in good agreement with those of X-ray crystal structures (Table 1). Consistent with the experimental data, the P–P distances lengthen, and the phosphorus atoms become more pyramidalized from the neutral **1** to radical cation $1^{\bullet+}$, while the P–N$_{ring}$ distances become shorter, and the pyramidalization at phosphorus is relaxed from **2** to $2^{\bullet+}$. An examination of the molecular orbitals of the neutral species **1** and **2** provides important information on such differences. The HOMO of **1** is a combination of lone pair localized orbitals of exocyclic nitrogen atoms with some amounts of P–P σ-bonding orbitals (Figure 2a), while that of **2** is composed of pure lone pair
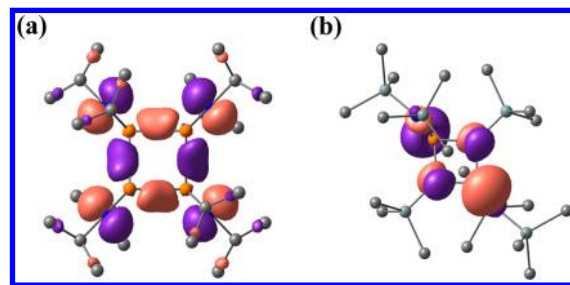

Figure 2. HOMOs of neutral molecules (a) **1** and (b) **2** (isovalue = 0.04).

localized orbitals of phosphorus and nitrogen atoms of the P$_2$N$_2$ ring (Figure 2b). Removal of one electron from HOMO (hence partially from P–P σ-bonding orbitals) of **1** leads to a lengthening of the P–P bond in $1^{\bullet+}$. The shortening of the P–N$_{ring}$ bond lengths in $2^{\bullet+}$ is expected because electron delocalization is much more favored energetically in the radical cation. According to the valence-shell electron-pair repulsion theory, the geometries around phosphorus atoms correspondingly become more pyramidalized in $1^{\bullet+}$, while those in $2^{\bullet+}$ are relaxed.

The absorption spectrum of $1^{\bullet+}$ in CH_2Cl_2 shows three main bands at 528 ($\varepsilon = 10770$), 660 ($\varepsilon = 4678$) and 1048 ($\varepsilon = 7324$) nm, while two (468 nm, shoulder, $\varepsilon = 3800$; 524 nm, $\varepsilon = 8390$) are observed in that of $2^{\bullet+}$ (Figure 3). TD-DFT calculations at the UPBE0/6-31G(d) level[16] indicate peaks at 1048 (for $1^{\bullet+}$) and 524 nm (for $2^{\bullet+}$) are mainly due to HOMO (β) → LUMO (β) transitions (Figures S3 and S4). The higher reactivity of $1^{\bullet+}$ in solution[9] is probably related to its smaller HOMO (β) → LUMO (β) energy gap.

The EPR spectrum of $1^{\bullet+}$ (Figure 4a) in CH_2Cl_2 displays a 13-line signal ($g = 2.0098$) coupling with four phosphorus ($a(^{31}P) = 5.11$ G) and four nitrogen atoms ($a(^{14}N) = 4.94$ G).[17] The ^{31}P hyperfine coupling constant is significantly lower than those observed in phosphinyl (63–108 G),[1e,3g,j,k]
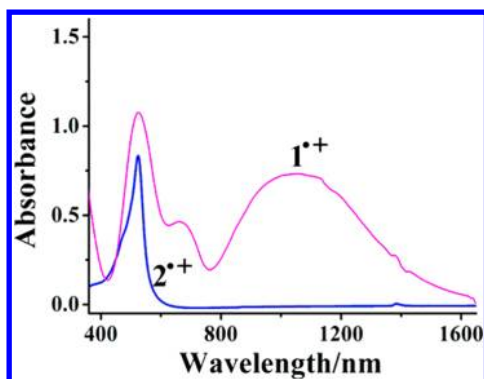
Figure 3. Absorption spectra of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ in CH_2Cl_2 ($\sim 1 \times 10^{-4}$ M, 298 K).

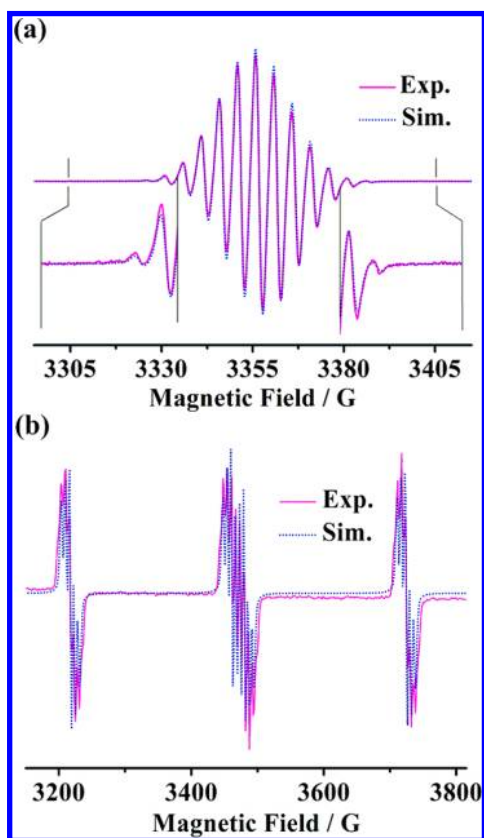**Figure 4.** Experimental (pink solid lines) and simulated (blue dot lines) EPR spectra for 1×10^{-3} M CH_2Cl_2 solutions of (a) $\mathbf{1}^{\bullet+}\cdot$ $[Al(OR_F)_4]^-$ (243 K) and (b) $\mathbf{2}^{\bullet+}\cdot SbF_6^-$ (298 K). Experimental and simulated spectra of $\mathbf{2}^{\bullet+}\cdot SbF_6^-$ are separated in Figure S5.

phosphonyl (300−700 G),[1e] and phosphoniumyl (176−800 G),[1e,3l−n,4a] suggesting a tiny amount of spin density at the phosphorus atoms. The EPR spectrum of $\mathbf{2}^{\bullet+}$ (Figure 4b) in CH_2Cl_2 appears as two almost overlapping doublets (g = 2.0064) arising from coupling with two nonequivalent ^{31}P nuclei ($a(^{31}P) = 263$ and 244 G), which are further split by two nitrogen atoms of the P_2N_2 ring ($a(^{14}N) = 5.90$ G). The large ^{31}P coupling constants indicate substantial amounts of the unpaired electron residing on phosphorus atoms, sharply distinct from $\mathbf{1}^{\bullet+}$.

The analysis of EPR spectra is supported by DFT calculation. The spin density of $\mathbf{1}^{\bullet+}$ (Figure 5a) is mainly delocalized on four exocyclic N atoms (0.211e × 4) and that on each P atom is
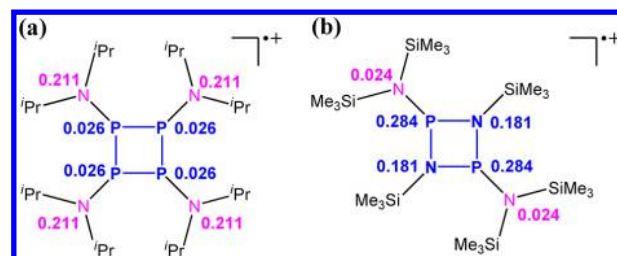

Figure 5. Mulliken atomic spin densities of (a) $\mathbf{1}^{\bullet+}$ and (b) $\mathbf{2}^{\bullet+}$ calculated at the UPBE0/6-31G(d) level.

only about 0.026e, while for $\mathbf{2}^{\bullet+}$ (Figure 5b) most of the spin density is delocalized on P (0.284e × 2) and N (0.181e × 2) atoms of P_2N_2 core. To rationalize the inverse of spin density distribution, a series of molecules with homocyclic P_4, N_4, or heterocyclic P_2N_2 ring substituted either by N^iPr_2 or by $SiMe_3$ were optimized (Figure S6). When exocyclic substituents are confined to N^iPr_2, spin density of all three radical cations mainly resides on the amino groups with very small amount on the rings. By replacement of substituents with $SiMe_3$, however, the spin density is primarily localized on the P_4, P_2N_2, or N_4 ring. Thus, the inverse spin density distribution on $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ is mainly caused by the exocyclic substituents.

We herein described the stabilization and structural characterization of two unprecedented phosphorus-containing four-membered ring radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. Compared with their neutral molecules, the former shows elongated P−P bonds and more pyramidalized phosphorus atoms, while the latter exhibits the shortened P−N_{ring} distances and larger angles around phosphorus centers. EPR studies indicate that for $\mathbf{1}^{\bullet+}$ spin density mainly resides on the exocyclic nitrogen atoms with very minor on endocyclic phosphorus atoms, while for $\mathbf{2}^{\bullet+}$ the situation is opposite. DFT calculations show such an inverse spin density distribution is controlled by the exocyclic substituents. The work suggests that isolation of radical cations of other phosphorus and heavier pnictogen (As, Sb, Bi) ring and cage systems is possible by using weakly coordinating anions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, crystallographic data in CIF formats, crystal structures for neutral molecules **1** and **2**, theoretical calculation, and complete ref 16. 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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(15) X-ray data for $1^{\bullet+}\cdot[Al(OR_F)_4]^-$ and $2^{\bullet+}\cdot SbF_6^-$ are listed in Table S1. CCDC 991499−991502 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(16) 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.

(17) The discrepancy between EPR parameters of $1^{\bullet+}$ and those $(a(^{31}P) = 5\ G, a(^{14}N) = 10\ G)$ reported in the literature[9] is probably caused by the effect of counterions.