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Stable Tetraaryldiphosphine Radical Cation and Dication

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Supporting Information

ABSTRACT: Salts containing tetraaryldiphosphine radical cation $\mathbf{1}^{\bullet+}$ and dication $\mathbf{1}^{2+}$ have been isolated and structurally characterized. Radical $\mathbf{1}^{\bullet+}$ has a relaxed pyramidal geometry, while dication $\mathbf{1}^{2+}$ prefers a planar, olefin-like geometry with a two-electron π bond. The alteration of the geometries of the tetraaryldiphosphine upon oxidation is rationalized by the nature of the bonding. The EPR spectrum showed that the spin density of radical $\mathbf{1}^{\bullet+}$ is mainly localized on phosphorus atoms, which is supported by theoretical calculation.

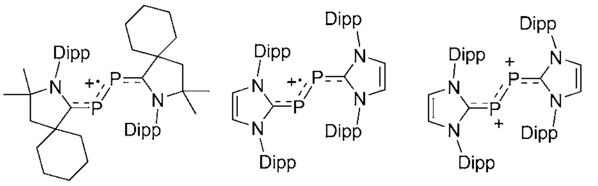
Hydrazine radical cation and dications have been extensively studied and shown to prefer planar, olefin-like geometries with a three- or two-electron π bond (Scheme 1).[1−3] In contrast, their phosphorus analogues are elusive.

Scheme 1

Though diphosphine radical cations $(R_2PPR_2)^{\bullet+}$ have been studied by theoretical calculation and solution electron paramagnetic resonance (EPR) spectroscopy,[4] they have not been isolated, and their crystal structures remain unknown. The dication $(R_2PPR_2)^{2+}$ has not been detected, and its synthesis becomes a challenge, probably because phosphorus is less likely to form multiple bonds than carbon or nitrogen.[1,5] Very recently, however, Bertrand et al. stabilized diphosphene radical cations $(RPPR)^{\bullet+}$ and dications $(RPPR)^{2+}$ using carbenes (Scheme 2),[6] which indicates that oxidized species of diphosphines (R_2PPR_2) may be stabilized and isolated with suitable ligands and counterions.

By using weakly coordinating anions,[7] we recently succeeded in stabilizing aniline, benzidine, anthracene, and triarylphosphine radical cations.[8] These results—especially the isolation of triarylphosphine radical cations[8a]—encouraged us to investigate the oxidation of other phosphine systems. We herein report isolation, characterization, and crystal structures of the radical cation and dication of a tetraaryldiphosphine.

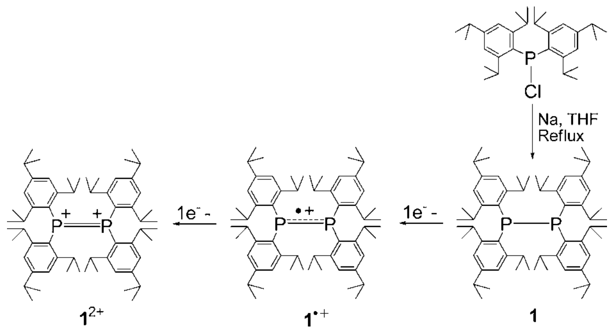
Scheme 2



Dipp: 2,6-$^{i}Pr_2C_6H_3$

Diphosphine **1** was synthesized by the reaction of $Trip_2PCl$ (Trip = 2,4,6-triisopropylphenyl) with sodium (Scheme 3) instead of Mg used in the literature.[9] The cyclic voltammetry of **1** in CH_2Cl_2 at room temperature with $^{n}Bu_4NPF_6$ as a supporting electrolyte showed two well-defined reversible oxidation waves (Figure 1), indicating that radical cation $\mathbf{1}^{\bullet+}$ and dication $\mathbf{1}^{2+}$ are stable under these conditions. Upon one-electron oxidation with $Ag[Al(OR_{Me})_4]$ ($OR_{Me} = OC(CF_3)_2Me$)[10] in CH_2Cl_2, **1** was converted to green radical cation $\mathbf{1}^{\bullet+}$ in a high yield (Scheme 3). The EPR spectra (Figure 2) of $\mathbf{1}^{\bullet+}[Al(OR_{Me})_4]^-$ in CH_2Cl_2 at 273 and 77 K show typical signals of tetraaryldiphosphine radical cations ($g = 2.009$, $a(^{31}P) = 17.6$

Scheme 3



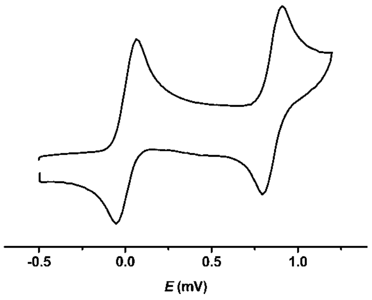


Figure 1. Cyclic voltammogram of **1** (1×10^{-3} M) in CH_2Cl_2, containing 0.1 M $^{n}Bu_4NPF_6$, measured at 100 mV s^{-1} at 20 °C.

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mT in solution, $g_{\parallel} = 2.004$, $a_{\parallel}(^{31}P) = 28.7$ mT, $g_{\perp} = 2.014$, $a_{\perp}(^{31}P) = 14.0$ mT in frozen solution).[4c,d] The ratio of isotropic and anisotropic hyperfine constants between the radical and phosphorus atoms suggests that ~38% and ~4% of the unpaired electron is localized on the 3p (P) and 3s (P) orbitals of each P in $\mathbf{1}^{\bullet+}$, respectively, indicating the phosphorus centers retain a degree of bending.[4c,d] Upon two-electron oxidation with Ag^+ in CH_2Cl_2, **1** was converted to red dication $\mathbf{1}^{2+}$ (Scheme 3).[11] Alternatively, the dication can be obtained by a one-electron oxidation of $\mathbf{1}^{\bullet+}$. The ^{31}P NMR spectrum of $\mathbf{1}^{2+}$ shows one single signal at 168.82 ppm. Both the radical cation and dication are further characterized by elemental analysis and UV absorption spectroscopy ($\lambda_{max} \approx 670$ nm for $\mathbf{1}^{\bullet+}$ and 530 nm for $\mathbf{1}^{2+}$, Figure S1 in the Supporting Information).

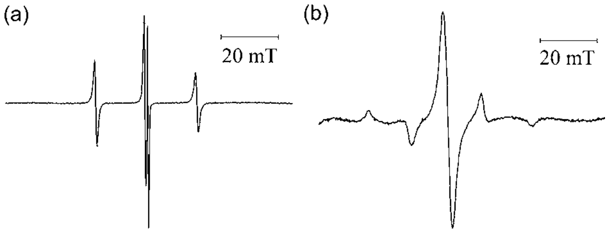

Figure 2. EPR spectra of 1 × 10^{-3} M $\mathbf{1}^{\bullet+}[Al(OR_{Me})_4]^-$ in CH_2Cl_2 solution at (a) 273 and (b) 77 K.

Crystals suitable for X-ray crystallographic studies were obtained by cooling solutions of $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$ in CH_2Cl_2.[12] Although the structure of the precursor **1** was already known[9] and not in doubt, we redetermined its structure at 123 K to enable an isothermal comparison. The structures of $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$ are illustrated as stereoviews in Figure 3. A list of their important structural parameters, as well as those of **1**, is given in Table 1. The data show that removal of electrons from tetraarylphosphine systems has considerable effects on their ground-state structures. The total of three bond angles to phosphorus becomes larger from the precursor **1** to radical cation $\mathbf{1}^{\bullet+}$ to dication $\mathbf{1}^{2+}$. Consequently, **1** becomes less pyramidal upon one-electron removal and completely flattened upon loss of the second electron. Pyramidal $\mathbf{1}^{\bullet+}$ is in contrast with planar hydrazine radical cations $(R_2NNR_2)^{\bullet+}$,[2] while planar, olefin-like $\mathbf{1}^{2+}$ is similar to hydrazine dications $(R_2NNR_2)^{2+}$.[3] The P–C and P–P bond lengths become shorter from **1** to $\mathbf{1}^{\bullet+}$ to $\mathbf{1}^{2+}$. The P–P length of $\mathbf{1}^{\bullet+}$ (2.136(5) Å) is between a P–P double bond (~2.02 Å)[13] and a P–P single bond (~2.20 Å), while dication $\mathbf{1}^{2+}$ clearly shows a P–P double bond (2.021(2) Å).

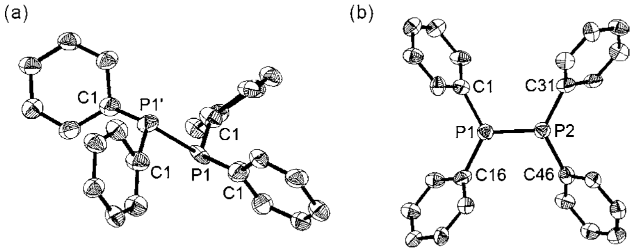

Figure 3. Thermal ellipsoid (50%) drawings of (a) $\mathbf{1}^{\bullet+}$ and (b) $\mathbf{1}^{2+}$ (hydrogen atoms and Pri groups are omitted for clarity). Selected bond length (Å) and angle (deg): in $\mathbf{1}^{\bullet+}$, P1–P1′ 2.136(5), C1–P1 1.832(5), C1–P1 1.844(5), C1–P1′ 1.831(5), C1–P1′ 1.831(5), C1–P1–C1 127.4(2), C1–P1–P1′ 104.3(2), C1–P1–P1′ 103.8(2), C1–P1′–C1 128.4(2), C1–P1′–P1 103.1(2), C1–P1′–P1 103.5(2); in $\mathbf{1}^{2+}$, P1–P2 2.021(2), C1–P1 1.821(5), C16–P1 1.812(5), C31–P2 1.820(5), C46–P2 1.816(5), C1–P1–P2 116.3(1), C1–P1–C16 125.9(2), C16–P1–P2 117.6(1), C31–P2–P1 118.9(1), C31–P2–C46 124.0(2), C46–P2–P1 116.6(1).

Table 1. Experimental and Calculated Structural Parameters (Average) for Tetraaryldiphosphines and Their Cationic Species

	Experimental		
	1	$\mathbf{1}^{\bullet+}$	$\mathbf{1}^{2+}$
P–P(Å)	2.223(1)	2.136(5)	2.021(2)
C–P(Å)	1.888(3)	1.834(5)	1.817(5)
∑ angles to P (deg)	318.3(1)	335.2(2)	359.6(2)
	Calculated		
	2 (C_2)	$\mathbf{2}^{\bullet+}$ (C_2)	$\mathbf{2}^{2+}$ (C_2)
P–P(Å)	2.273	2.172	2.004
C–P(Å)	1.897	1.858	1.818
∑ angles to P (deg)	324.1	340.9	359.9

To explain the experimental results, we carried out some calculations for the model diphosphine $(Dipp)_2PP(Dipp)_2$ (**2**) (Dipp = 2,6-diisopropylphenyl) and its oxdized species $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{2+}$.[14] Full geometry optimizations were performed at the (U)HF/6-31G(d) level, and the obtained stationary points were characterized by frequency calculations. Molecular orbitals and spin density were calculated at the (U)B3LYP/6-31G(d) level. The calculated structural parameters of **2** and its oxidized species are in good agreement with those of X-ray crystal structures of **1**, $\mathbf{1}^{\bullet+}$, and $\mathbf{1}^{2+}$ (Table 1). Consistent with the experimental data, the P–C and P–P distances become shorter, while the total of angles to phosphorus becomes larger from the neutral **2** to radical cation $\mathbf{2}^{\bullet+}$ and dication $\mathbf{2}^{2+}$. The tendency of alteration of the bond lengths and bond angles can be rationalized by the nature of the bonding. As shown in Figure 4, the HOMO of **2** is mainly $\pi^*(P_2)$, i.e., a lone pair localized

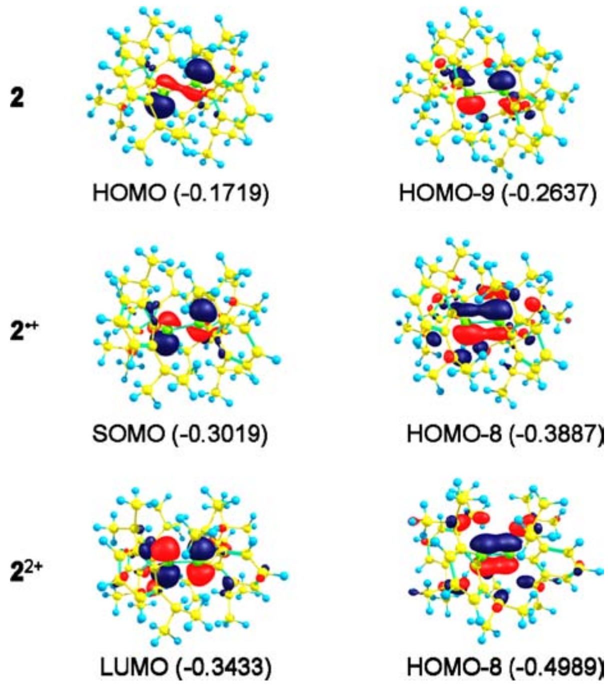

Figure 4. Selected molecular orbitals for **2**, $\mathbf{2}^{\bullet+}$, and $\mathbf{2}^{2+}$. The eigenvalues of the molecular orbitals are given in a.u.

orbital, which is an out-of-phase combination of p orbitals of phosphorus atoms with some s orbital character. In contrast, the $\pi^*(P_2)$ orbital in $\mathbf{2}^{2+}$ is a combination of almost pure 3p orbitals of the phosphorus atoms with a small contribution from carbon atoms. The $\pi^*(P_2)$ orbital in **2** (HOMO) is doubly occupied, but it is singly occupied in $\mathbf{2}^{\bullet+}$ (SOMO) and empty in $\mathbf{2}^{2+}$ (LUMO). The decrease in the occupation of the $\pi^*(P_2)$ orbital leads to a shortening of the P−P bond, and the enhanced p-character causes flattening of geometries.[4c,d] The shortening of the P−C bond length is associated with the change of conjugation, which is n−π conjugation in **2**, but π−π conjugation in $\mathbf{2}^{2+}$, and a mix of n−π and π−π conjugation in $\mathbf{2}^{\bullet+}$. The calculated spin density of $\mathbf{2}^{\bullet+}$ is mainly localized on phosphorus atoms (0.43e ×2), and that for any other atoms is less than 0.02e, which agrees well with the experimental EPR spectrum.

Schoeller and co-workers have reported that one-electron oxidation of diphosphines (R_2P-PR'_2) led to cleavage of the P−P bond, followed by formation of the phosphenium systems (R_2P^+ and R'_2P^+) and re-formation of diphosphines (R_2P-PR_2 and R'_2P-PR'_2). The fact that a similar phenomenon does not occur in the current work probably is due to different electronic properties of the substituents.[15] However, a deep understanding of the difference needs further investigation.

The isolation of stable radicals[16] and 1,2-dications[1b] of heavier main-group elements is of high current interest. A few phosphorus radicals have been structurally characterized in the gas phase[17] or in the solid state.[6,8a,18] We herein have described the stabilization and structural characterization of radical cation $\mathbf{1}^{\bullet+}$ and dication $\mathbf{1}^{2+}$ of a tetraaryldiphosphine. Investigation on the reactivity of these oxidized species is under way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic data (CIF), UV−vis spectra, theoretical calculation, and complete ref 14. 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.

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(11) $\mathbf{1}^{2+}\cdot 2[Al(OR_{Me})_4]^-$ did not afford crystals suitable for X-ray crystallography, and no detailed structure was obtained. Instead, the reaction of **1** with $Ag[Al(OR_F)_4]$[10] (molar ratio = 1:2.1, OR_F = $OC(CF_3)_3$) led to well-crystallized salt $\mathbf{1}^{2+}\cdot 2[Al(OR_F)_4]^-$.

(12) (a) X-ray data for the neutral **1**, $\mathbf{1}^{\bullet+}$, and $\mathbf{1}^{2+}$ are listed in the Table S1 in the Supporting Information. CCDC 92800−928002 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. (b) The P atoms in $\mathbf{1}^{\bullet+}$ are disordered with 25% occupancy; see Figure S2 in the Supporting Information.

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