Radicals

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A Persistent Dipotassium 1,2,4-Diazaphospholide Radical Complex: Synthesis, X-Ray Structure, and Bonding**

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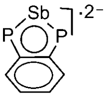
Dedicated to Professor Herbert W. Roesky

What happens when an electron is added to a five-membered heterocyclic ring obeying the $4n+2$ Hückel rule? If a 7-π-electron system results, is the aromaticity destroyed? Early[1] and more recent evidence on persistent radicals containing low-valent Group 15 elements[2] is inconclusive. Phosphorus-based aromatic ring systems (e.g., phosphinine, biphosphinine, planar phospholes, 1,2,4-triphosphole), especially those with ($\sigma^2\lambda^3$) P atoms, have low-lying π* lowest unoccupied molecular orbitals (LUMOs) owing to effective σ*(P−R)–π*(1,3-diene) orbital interactions and might accommodate extra electrons.[3] For example, treatment of solutions of 1-phenyl-2,5-diphenylphosphole or pentaphenylphosphole with metallic potassium at low temperatures led to color changes,[4] and the corresponding EPR spectra[4a] exhibited large doublet splitting.[4b] Prolonged contact of such phospholes with potassium gave signals possibly attributable to anion radicals, but identification was not definite.[4b,5] Recently, Wright and co-workers reported that reduction of a 6πe⁻ aromatic anion $[1,2\text{-}C_6H_4P_2Sb]^-$ afforded a diamagnetic tetraanion $[1,2\text{-}C_6H_4P_2Sb]_2{}^{4-}$,[6] which DFT computations indicated might be a dimer of two 7πe⁻ dianion radicals (**A**). Probably owing to their high reactivity, anion radicals derived by reduction of five-membered heterocyclic aromatic systems have never been characterized structurally[7] before the present work.



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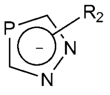
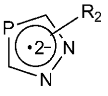


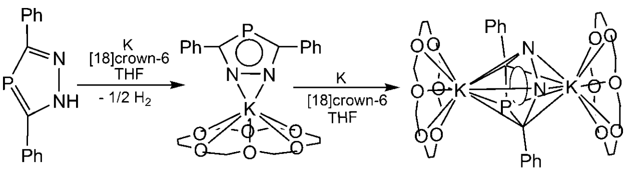
B



C

The deprotonated 1*H*-1,2,4-diazaphosphole group $[3,5\text{-}R_2dp]^-$ (**B**) is a mixed nitrogen–phosphorus ($\sigma^2\lambda^3$) analogue of Cp⁻ and may be viewed as the combination of phospholyl[3,8] and pyrazolato (pz)[9] ions. Theoretical analyses and photoelectron spectra suggested that azaphospholes containing $\sigma^2\lambda^3$ phosphorus atoms are highly aromatic.[10] In preliminary experiments, we applied our strategy for the preparation of metal 1,2,4-diazaphospholide complexes[11] to the deprotonation of 3,5-diphenyl-1,2,4-diazaphosphole (**1**)[12] with metallic potassium. The potassium 3,5-diphenyl-1,2,4-diazaphospholide $[(3,5\text{-}Ph_2dp)K\cdot 0.67\,THF]_n$[11a] product, a colorless complex, reacted further with metallic potassium to afford a fairly THF-soluble black paramagnetic substance, which was stable in the solid state at ambient temperature. But what is the site of the unpaired electron in this unexpected species, represented by structure **C**? Is the π system or the low-valent phosphorus atom ($\sigma^2\lambda^3$) involved? We now describe the synthesis and X-ray analysis of an [18]crown-6 complex of dipotassium 3,5-diphenyl-1,2,4-diazaphospholide as well as its theoretical investigation. We believe that this is the first structurally characterized dianion radical of a five-membered aromatic ring.

The reaction of **1** with one equivalent of metallic potassium in the presence of [18]crown-6 in THF gave a terminally coordinated complex $[(\eta^2\text{-}3,5\text{-}Ph_2dp)K(\eta^6\text{-}[18]crown\text{-}6)]$ (**2**) in 85 % yield as air- and moisture-sensitive colorless crystals (Scheme 1).[13] However, crystals of **2** are persistent in an inert atmosphere (N_2) at room temperature and are readily soluble in THF and DMSO. Further treatment of **2** with potassium in the presence of [18]crown-6 afforded a THF-soluble complex $[K(\eta^6\text{-}[18]crown\text{-}6)]^+[(\eta^5,\eta^5\text{-}3,5\text{-}Ph_2dp)^{\bullet 2-}][K(\eta^6\text{-}[18]crown\text{-}6)]^+$ ($\mathbf{3}^{\bullet 2-}[K([18]c\text{-}6)]_2{}^{2+}$) containing a dianion radical moiety $[(\eta^5,\eta^5\text{-}3,5\text{-}Ph_2dp)^{\bullet 2-}]$ ($\mathbf{3}^{\bullet 2-}$) as highly air- and moisture-sensitive black crystals in 65 % yield. At room temperature, $\mathbf{3}^{\bullet 2-}[K([18]c\text{-}6)]_2{}^{2+}$ is persistent for



1 **2** $\mathbf{3}^{\cdot 2-}[K(\eta^6\text{-}[18]crown\text{-}6)]_2{}^{2+}$

Scheme 1. Preparation of complexes **2** and $\mathbf{3}^{\bullet 2-}[K(\eta^6\text{-}[18]crown\text{-}6)]_2{}^{2+}$.

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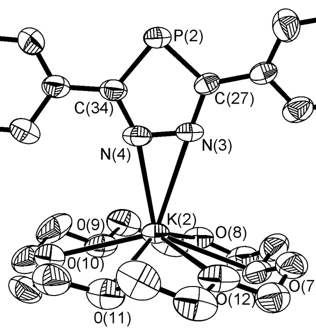


Figure 1. Molecular structure of one form of **2** in the unit cell (thermal ellipsoids set at 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: N(3)–N(4) 1.349(6), N(3)–C(27) 1.333(6), C(27)–P(2) 1.741(5), K(2)–N(3) 2.913(5), K(2)–N(4) 2.726(5), K(2)–O(7–12) 2.808–2.941; N(4)-N(3)-C(27) 112.9(4), C(27)-P(2)-C(34) 86.4(3).

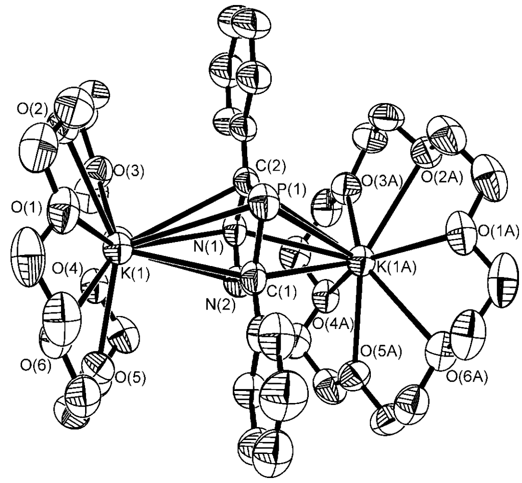


Figure 2. Molecular structure of $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ (thermal ellipsoids set at 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: N(1)–N(2) 1.351(8), N(1)–C(2) 1.382(9), C(1)–P(1) 1.764(9), K(1)–N(1) 3.044(3), K(1)–N(2) 2.944(3), K(1)–C(1) 3.132(5), K(1)–C(2) 3.317(5), K(1)–P(1) 3.549(2), K–O 2.788(4)–2.989(5); N(1)-N(2)-C(1) 111.7(6), N(2)-C(1)-P(1) 114.3(7), P(1)-C(2)-N(1) 112.5(6), N(2)-N(1)-C(2) 114.4(6), C(1)-P(1)-C(2) 87.1(4). Symmetry code: A ≡ $x, -y+1/2, z$.

months in the solid state but decomposes slightly in 1,2-dimethoxyethane (DME) or THF. The mass spectra of both complexes only show $[\mathrm{K}(\eta^6\text{-}[18]\mathrm{crown}\text{-}6)]^+$ ion peaks with the correct isotopic distributions ($m/z = 303$ for **2** and $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$). The only resonances of **2** in the ^{1}H NMR spectrum ([D$_6$]DMSO, 25 °C) are at $\delta = 7.10$–7.87(m, phenyl rings) and 3.52 ppm (s, [18]crown-6 ligands). The single, sharp resonance at $\delta = +64.83$ ppm in the ^{31}P NMR spectrum is like that of $[(3,5\text{-}\mathrm{Ph_2dp})\mathrm{K}]$[11a,b] in THF solution at +67.19 ppm. While no ^{1}H or ^{31}P signals for $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ were detected in [D$_8$]THF at 25 °C, probably owing to paramagnetic broadening,[14] the magic-angle spinning (MAS) ^{31}P NMR spectrum of solid-state $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ exhibited two broad resonances at $\delta = -5.49$ and -10.18 ppm (Supporting Information, Figure 1).[13] These two ^{31}P signals for only one independent isomer may be due to 1,2,4-diazaphospholide disorder in the crystal structure, similar to that observed recently in related cases.[15] The drastic upfield ^{31}P shifts relative to the signals of $[(3,5\text{-}\mathrm{Ph_2dp})\mathrm{K}]$[11a,b] and **2** suggest higher electron density at the phosphorus atom in $\mathbf{3}^{\bullet 2-}$.

Signals in the EPR spectra of $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ are assigned to the 3,5-diphenyl-1,2,4-diazaphospholide dianion radical $\mathbf{3}^{\bullet 2-}$(Supporting Information, Figure 2).[13] Completely symmetrical signals with large doublet splitting detected in THF at ambient temperature at $g = 2.0043 \pm 0.0001$ (indicating the unpaired electron in an organic group) are consistent with hyperfine coupling to phosphorus ($I = 1/2$, $A_{\mathrm{iso}}(^{31}\mathrm{P}) = 11.63$ G) and resemble those observed for the possible anion radicals of substituted phenylphospholes at low temperatures.[4b] The observed significantly lower phosphorus coupling ($A_{\mathrm{iso}}(^{31}\mathrm{P}) = 11.63$ G) than observed in noncyclic phosphinyls ($A_{\mathrm{iso}}(^{31}\mathrm{P}) = 63$–108 G)[7] and in the π system of five-membered heterocyclic phenyl-substituted phospholes ($A_{\mathrm{iso}}(^{31}\mathrm{P}) = 23.5$–31.3 G)[4b] suggests greater delocalization of the unpaired electron on 1,2,4-diazaphospholide (to the coplanar phenyl rings) rather than the electron being restricted to the heterocycle.

The X-ray structure of **2** revealed two slightly different conformations of the η^2-3,5-diphenylphospholide and η^6-[18]crown-6 ligands in the unit cell (only one is shown in Figure 1; see the Supporting Information, Figure 3 for the other).[13] The unequal K–N bond lengths in both are consistent with slipped η^2-bonding[16] and may be compared with those found in $[(\eta^2,\eta^4\text{-}3,5\text{-}\mathrm{Ph_2dp})\mathrm{K}(\mathrm{Et_2O})]_n$ (K–N 2.7504(15), 2.7348(16) Å)[11b] and in a pyrazolato potassium complex.[17] The difference in bond length may be due to interactions with the [18]crown-6 ligands.[18] The angles between the plane of the 1,2,4-diazaphospholide $\mathrm{C_2N_2P}$ core and the approximate plane of the six oxygen atoms of the [18]crown-6 ligand average 86°.

In sharp contrast to the approximate η^2-coordination mode of the 1,2,4-diazaphospholide ligands in **2**, the X-ray structure of the $\mathbf{3}^{\bullet 2-}$ dianion radical complex (Figure 2) reveals a triple-decker "inverse sandwich" stabilized by two $[\mathrm{K}(\eta^6\text{-}[18]\mathrm{crown}\text{-}6)]^+$ counterions (monoclinic, space group $P2_1/m$). Owing to the steric effects of the bulky [18]crown-6 ligand complexation, each potassium ion coordinates further in η^5 fashion (π bonding) to the 1,2,4-diazaphospholide ring symmetrically at opposite faces of the heterocycle. The 19.43° dihedral angles between each best [18]crown-6 oxygen plane and the heterocyclic core may be ascribed to the N and P electronegativity difference and the large phosphorus radius. The two capping [18]crown-6 ligands in $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ are eclipsed, as in the orientations in several triple-decker Group 8 metal species with central cyclopentadienyl ligands.[19] The perfect coplanarity of the phenyl and the heterocyclic rings (C_s symmetry) in **3** differs significantly from the twisted conformations resulting from the intramolecular interactions of the adjacent phenyl rings and nitrogen lone pairs in **2** and in 1,2,4-diazphospholide complexes.[11b–d] The π-bonded K–N bonds in $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ (K(1)–N(1) 3.044(3), K(1)–N(2) 2.944(3) Å) resemble those in π-bonded $[(\eta^2,\eta^4\text{-}3,5\text{-}\mathrm{Ph_2dp})\mathrm{K}(\mathrm{Et_2O})]_n$ (2.9653(16), 3.0220(17) Å).[11b]

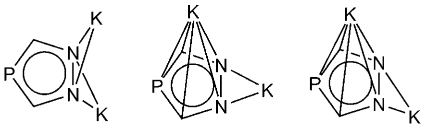
The K–P distance (3.549(2) Å) is 0.285 Å longer than that in a kalocene potassium phospholide (K–P 3.264(1) Å)[20] but is 0.34 Å shorter than that in $[(\eta^2,\eta^4\text{-}3,5\text{-}\mathrm{Ph_2dp})\mathrm{K}(\mathrm{Et_2O})]_n$.[11b] The potassium atoms are displaced toward the 1,2,4-diazaphospholide N–N bond; the dihedral angle is 80.58° between the N(1)N(2)K(1) and the 1,2,4-diazaphospholide planes.[11c]

Why is the $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ dianion radical stable (persistent) at room temperature? Where is its "extra" unpaired electron, that is, what is the spin density distribution and the electronic structure? How aromatic are the heterocyclic rings in these species? We addressed these questions computationally by analyzing increasingly complex models sequentially. These included $(\mathrm{RC})_2\mathrm{N_2P}^{2-}$, $(\mathrm{RC})_2\mathrm{N_2PK}$, $(\mathrm{RC})_2\mathrm{N_2PK}^-$, $(\mathrm{RC})_2\mathrm{N_2PK_2}^+$, $(\mathrm{RC})_2\mathrm{N_2PK_2}$ first with R = H (with and without the crown ethers) and then with $\mathrm{R} = \mathrm{C_6H_5}$ (see the Supporting Information, Table 1 for details of the geometries, atom charges, NICS values,[21] and energies).

The aromatic stabilization of the parent $(\mathrm{CH})_2\mathrm{N_2P}^-$ anion is quite large. Its block-localized wavefunction (BLW)[22] resonance energy (RE), 59.4 kcal mol^{-1}, rivals that of benzene (61.4 kcal mol^{-1})[23] at the B3LYP/6–31G(d) level. Even larger BLW-RE values, 71.2 and 77.8 kcal mol^{-1}, were computed for $(\mathrm{CH})_2\mathrm{N_2PK}$ and $(\mathrm{CH})_2\mathrm{N_2PK_2}^+$, respectively. NICS(0) of $(\mathrm{CH})_2\mathrm{N_2P}^-$ also is large, ($\delta = -13.5$ ppm, benzene $\delta = -7.6$ ppm), as is the more significant NICS(0)$_{\pi zz}$ value ($\delta = -30.0$ ppm; benzene $\delta = -35.7$ ppm).[24] That all the five-membered-ring bond lengths (Supporting Information, Table 1)[13] lie between those of isolated single and double bonds (C–P 1.87, C=P 1.56 Å; C–N 1.47, C=N 1.28 Å; N–N 1.45, N=N 1.10 Å) also confirms the large degree of electronic delocalization. Substantial aromatic stabilization of the $\mathrm{C_2N_2P}^{2-}$ ring in $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ must contribute importantly to the stability of this open-shell complex.

The computed charges and spin densities (SD; Supporting Information, Table 1)[13] show that the "extra" electron in the $(\mathrm{RC})_2\mathrm{N_2P}^{2-}$ dianion radical models resides mainly on the phosphorus atom, with some involvement of the carbon atoms in the sigma singly occupied molecular orbital (SOMO; see the Supporting Information, Figure 4).[13] Unexpectedly, the K atoms in the models with two potassium ions compete successfully with the phosphorus atom for the SD.

However, the simplified $(\mathrm{CH})_2\mathrm{N_2PK_2}$ radical model did not resemble the C_{2v} "inverse sandwich" X-ray structure, as one K atom optimized from a central location above a ring face (Scheme 2, left side) to a NN-bridging position on the ring perimeter (shown in the center in Scheme 2). Moreover, the short K–K separation (3.775 Å), as well as the charges and SDs of approximately 0.5, show that $\mathrm{K_2}^+$ units are present. Indeed, when one electron is removed, the K$^+$ ions in the $(\mathrm{CH})_2\mathrm{N_2PK_2}^+$ cation separate more widely (Scheme 2, right side) and possess near unit (+0.981 and +0.963) natural charges.



Scheme 2. Structures emphasizing the different K placements in the "inverse sandwich" $(\mathrm{CH})_2\mathrm{N_2PK_2}$ (C_{2v}, left), the $(\mathrm{CH})_2\mathrm{N_2PK_2}$ minimum (C_s, middle), and the $(\mathrm{CH})_2\mathrm{N_2PK_2}^+$ minimum (C_s, right).

The analogous set of mono- and dipotassium models with two phenyl substituents (but without the crown ethers) behaved similarly. In particular, $(\mathrm{CPh})_2\mathrm{N_2PK_2}$ did not achieve the SD favored by the full complex. Notably, both the K charges and their SDs were 0.5 each. The three rings had essentially no SD. Even the singlet $(\mathrm{CPh})_2\mathrm{N_2PK_2}^+$ cation optimized to C_s symmetry (Scheme 2, right) rather than to a C_{2v} inverse sandwich structure.

Truncated models retaining the crown ethers (but without the phenyl groups) also failed to mimic experiment. Even when complexed by crown ethers, the K atoms (with +0.424 charges) retain the spin density. The computed SD on the P atom was only 0.025. Thus, the phenyl groups are essential to help stabilize the extra electron of the radical.

Agreement of the computational and experimental findings was only achieved by including both the crown ethers and the phenyl substituents (see the Mulliken spin density plot for the full radical species $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$; Figure 3). The crown ethers complex better to K$^+$ than to K$^{0.5+}$ and thus delocalize the spin density away from the K atoms to the P atom as well as to some carbon atoms of the three aromatic rings of the full system.

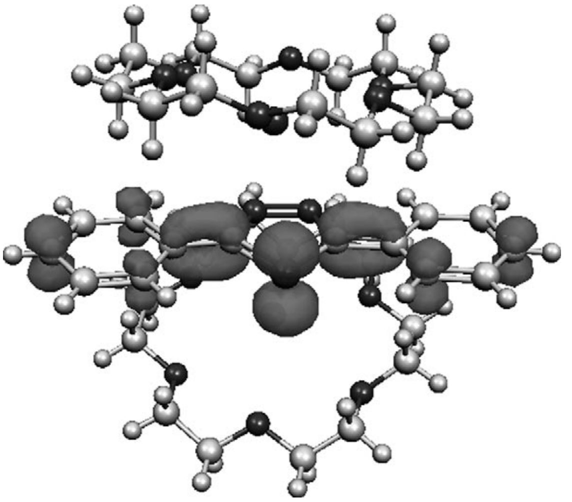


Figure 3. Representation of the spin density (shown in gray) from B3LYP/6-311+G** Mulliken spin population analysis of $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ on the full experimental geometry.

In conclusion, one-electron reduction of the 6πe$^-$-aromatic 1,2,4-diazaphospholide anion salt (**2**) by metallic potassium generates a stable dianion radical ($\mathbf{3}^{\bullet 2-}$) stabilized by $[\mathrm{K}([18]\mathrm{c}\text{-}6)]^+$ counterions. DFT computations indicated that the unpaired electron SD in $\mathbf{3}^{\bullet 2-}[\mathrm{K}([18]\mathrm{c}\text{-}6)]_2^{2+}$ is highly delocalized, not just to the phosphorus atom but also to the heterocyclic and phenyl rings. The crown ether coordinated K$^+$ ions do not share the SD and favor less crowded "inverse sandwich" sites above (and below) the heterocyclic ring. Our results suggest that an extensive family of analogous five-membered aromatic ring dianion radicals might exist.

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