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## COMMUNICATION

# A 1,2,4-Diazaphospholyl Radical and Its Nitrogen-Phosphorus Coupled Dimer: Synthesis, X-Ray Structural Characterization, EPR Analysis, and Computational Studies

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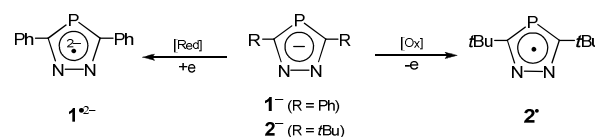
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**The oxidation of 1,2,4-diazaphospholide potassium ( $K^+[2^-]$ ) produces the neutral 1,2,4-diazaphospholyl radical ( $2^\bullet$ ) which can subsequently afford the 2(N)–2(P) dimer involving a N–P linkage.**

Recently, significant progress has been made in the chemistry of metal complexes carrying the 1,2,4-diazaphospholide ligand ( $[3,5-R_2dp]^-$ ).<sup>1</sup> The isolobality of N(P) to CH and the diagonal relationship between P and C<sup>2</sup> suggest that the 1,2,4-diazaphospholides should behave like their corresponding cyclopentadienyl-substituted analogues, especially the phospholyl-<sup>3a</sup> or pyrazolato-ligands.<sup>3b</sup> However, it has shown that 1,2,4-diazaphospholides, a family of mixed low-coordinated phosphorus( $\sigma^2\lambda^3$ )- and nitrogen-containing five-membered heterocyclic species, exhibited subtle differences in both the bonding behaviours and reactivities because of their unique electronic structures.<sup>1,4</sup> As heteroatoms are known to be effective at delocalizing spin density and concomitant stabilizing radicals,<sup>5</sup> the 1,2,4-diazaphospholides, in which each has an aromatic five-membered heterocyclic skeleton,<sup>4</sup> have potential to electronically stabilize the radicals. Indeed, we have demonstrated that 3,5-di-phenyl-1,2,4-diazaphospholide potassium  $K[3,5-Ph_2dp]^-$  ( $K^+[1^-]$ )<sup>1a,b</sup> can be reduced to give a stable dianionic radical species  $[K^+(18-crown-6)]_2(1^{2-})$ ,<sup>1c</sup> as shown in Scheme 1. DFT computations have indicated that the unpaired electron spin

density in  $1^{2-}$  is highly delocalized.<sup>1c</sup> This suggested that further investigations could be rewarding. We have therefore been studying the redox reactivity of 3,5-di-*tert*-butyl-1,2,4-diazaphospholide potassium  $K^+[3,5-tBu_2dp]^-$  ( $K^+[2^-]$ ),<sup>1a,b</sup> and exploring the possibility of utilizing  $2^-$  as a precursor in the preparation of the uncharged radical  $[3,5-tBu_2dp]^\bullet$  ( $2^\bullet$ ), isoelectronic with substituted cyclopentadienyl radicals  $[C_5R_5]^\bullet$ .<sup>6–8</sup> We reasoned that radical  $2^\bullet$  should be generated by oxidizing in appropriate way the  $6\pi$ -aromatic anion  $2^-$ , which is readily formed through the deprotonation of  $H[3,5-tBu_2dp]$ <sup>9</sup> and metallic potassium (or KH).



**Scheme 1.**  $6\pi$ -Aromatic anion ( $1^-$ ,  $2^-$ ), dianionic radical ( $1^{2-}$ ), and possible uncharged radical  $2^\bullet$

The oxidation of  $K^+[2^-]$  by  $FeCl_3$  or  $CuCl_2$  produced a deeply coloured solution that gave no EPR signal (Scheme 2). A group of yellow crystals was obtained from the solution, and EPR measurements showed that the crystals were diamagnetic. Performing the reaction under a similar condition but using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a spin trap gave two strong EPR spectra corresponding to  $DMPO[2^\bullet]$  adduct.<sup>10</sup> As shown in Figure 1, the spectrum of the product of the  $Fe^{3+}$ -oxidized system displays a hyperfine of well-resolved coupling multiplet with 12 observed lines. This clearly indicated that the radical species  $2^\bullet$  was formed in the system.<sup>11</sup> The distinction between a nitrogen coupling constant  $a_N = 14.7$  G, a proton splitting of  $a_H = 14.7$  G and a second nitrogen splitting  $a_{N'} = 3.43$  G suggests a *N*-1,2,4-diazaphospholyl spin adduct structure on the basis of the linewidth of the signals. However, the  $Cu^{2+}$ -

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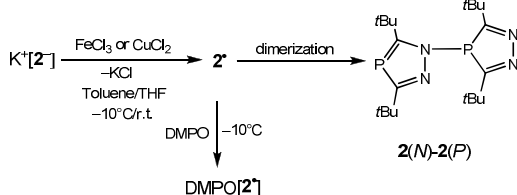
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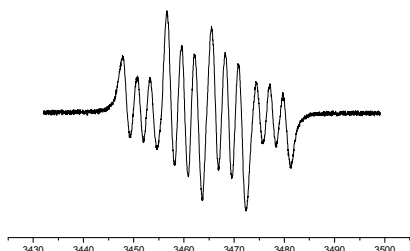
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oxidation systems had broader signals, which were assumed to be caused by the presence of a *P*-1,2,4-diazaphosphoyl connected isomer. Coupling to a *P*-1,2,4-diazaphosphoyl ring would contribute more to line broadening than coupling to the *N*-1,2,4-diazaphosphoyl ring spin adduct.<sup>12</sup> At this point, it is worth noting that a stable nitrogen-containing 1,3-diphosphaaallyl radical  $[R_2NPC(NR_2)PNR_2]^+$  has also present broaden EPR signals that could be attributed to the additional hyperfine coupling.<sup>12c</sup>



**Scheme 2.** Preparation of radical adduct DMPO[2<sup>•</sup>] and the dimer 2(*N*)-2(*P*)

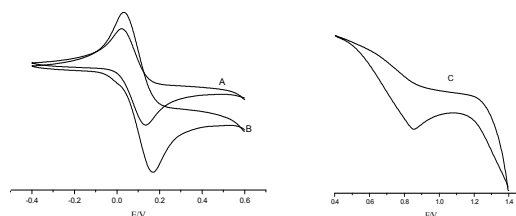
Cyclic voltammetric analysis of  $K^+[2^-]$  was performed in the presence of  $Bu_4N^+PF_6^-$ , and a one-electron irreversible oxidation wave was found for  $2^-/2^{\bullet}$  at  $E^{ox} = +0.86$  V vs.  $AgNO_3/Ag$ .<sup>13</sup> This indicated that  $2^{\bullet}$  was unstable under these conditions and that  $\sigma$ -dimerization could have occurred (Figure 2).<sup>14a</sup> The further reduction of  $2^-$  to form the dianion radical  $2^{2-}$  did not give rise to any additional cyclovoltammogram peaks with potentials between  $-0.4$  to  $0.6$  V. This was consistent with the experimental results that  $2^-$  is quite stable even to the strong reducing agents such as metallic potassium.<sup>1a,b</sup> The oxidation of the neutral radical  $2^{\bullet}$  to form the cation  $2^+$ , which is isolobal to  $[C_5R_5]^+$ , did not result in any additional cyclovoltammogram peaks under these conditions but the  $2^+$  is still highly expected as implied by the recent results that two isoelectronic species with  $[C_5R_5]^+$ , the *nido*-[3,5-*t*Bu<sub>2</sub>-1,2,4-C<sub>2</sub>P<sub>3</sub>]<sup>+</sup> cage<sup>14b,c</sup> and the stable five-membered  $[CSi_3P]^+$  cation,<sup>14d</sup> have been structurally characterized.



**Figure 1.** X-band EPR spectra of the DMPO[2<sup>•</sup>] adduct in anhydrous toluene with  $Fe^{3+}$

The radical  $2^{\bullet}$  could be generated in solution, and the DMPO[2<sup>•</sup>] adduct was persistent under dinitrogen for several hours without any detectable decomposition occurring, but the absence of an EPR signal for  $2^{\bullet}$  suggested that radical  $2^{\bullet}$  was able to self-associate. X-ray crystallographic analysis of the yellow crystals confirmed this inference.<sup>15</sup> The molecular

structure of 3,5-di-*tert*-butyl-1-(3,5-di-*tert*-butyl-1,2,4-diazaphosphol-4-yl)-1,2,4-diazaphosphole dimer (**2(N)-2(P)**), where **2(N)** and **2(P)** represent the rings coupled at a *N*- and a *P*-atom, respectively) formed through *N*-*P* linkage of the two monomers is shown in Figure 3. The *tert*-butyl groups in the dimer have a staggered arrangement to minimize steric repulsions, so that the two halves of the molecule are orthogonal to one another. The **2(N)** ring C-P and N-N bond lengths (1.724(3) Å and 1.377(3) Å, respectively) and C-P-C bond angle (87.9(2)°) are comparable to those found in the previously reported 1,2,4-diazaphospholes.<sup>16a-b,1</sup> The atoms in the **2(N)** ring were found to be perfectly coplanar (N(1)-N(2)-C(1)-P(1), C(2)-P(1)-C(1)-N(2), and C(2)-N(1)-N(2)-C(1) were all 0.0°). However, the five atoms in the **2(P)** ring were not coplanar (N(3A)-N(3)-C(3)-P(2) -10.1(2)° and C(3A)-P(2)-C(3)-N(3) 12.6(2)°).<sup>10</sup> The N(1)-P(2) distance (1.746(3) Å) in **2(N)-2(P)** was found to be 0.049 Å longer than the N-P distance (1.697(1) Å) in a classic aminophosphole.<sup>16c</sup> Natural bond orbital analysis of **2(N)-2(P)** showed that the P(2) atom in the **2(P)** ring had an inequivalent  $sp^3$  hybrid, but that the P(1) atom had an inequivalent  $sp^2$  hybrid and that there was a *p-p*  $\pi$  bond between P(1) and C(2) atoms, consistent with the structure characteristic of **2(N)-2(P)**.<sup>10</sup>



**Figure 2.** The cyclic voltammograms of  $Fc/Fc^+$  (A),  $K^+[2^{\bullet}]$  plus  $Fc/Fc^+$  (B), and  $K^+[2^{\bullet}]$  (C),  $2.5 \times 10^{-3}$  M in toluene containing 0.04 M  $Bu_4N^+PF_6^-$ , were measured at 100  $mVs^{-1}$  at 23°C vs.  $AgNO_3/Ag$ .

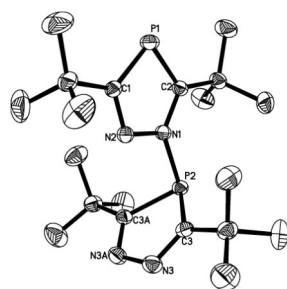
The elemental analysis results completely agreed with the **2(N)-2(P)** formula, and the MALDI-TOF-MS mass spectrum exhibits molecular-ion peaks with the correct isotopic distribution pattern ( $[M+H]^+ = 395$ ).<sup>10</sup> The intense resonances were found at  $\delta = 73.8$  and 97.8 ppm in  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 243 MHz, 23°C) spectrum, and these matched the peaks that were found at  $\delta = 77.0$  and 97.0 ppm, respectively, in the  $^{31}P$  MAS NMR spectrum.<sup>10</sup> These resonances were significantly shifted down-field relative to the corresponding signals of the free heterocyclic ligand  $H[3,5-*t*Bu_2dp]$  ( $^{31}P$   $\delta = +65.4$  ppm)<sup>9</sup> and the potassium salt  $\{(dioxane)K^+[2^-]\}$  ( $^{31}P$   $\delta = +47.6$  ppm).<sup>17a</sup>

The nature of P-N bond dissociation process was assessed by monitoring the  $^{31}P\{^1H\}$  NMR spectrum of a toluene-*d*<sub>8</sub> solution of **2(N)-2(P)** in a sealed NMR tube while heating the solution. The intensities of two resonances assigned to the dimer did not change as the temperature increase to 80°C, so we assumed that the **2(N)-2(P)** does not dissociate back to reform  $2^{\bullet}$  below that temperature. However, radiating the solution with UV-light for 30 minutes cause several resonances at  $\delta = 107.0(s)$ , 80.6(s), 46.4(d), and -33.5(s) ppm, to appear in the  $^{31}P\{^1H\}$  NMR

spectrum. These peaks were not found in the original **2(N)**–**2(P)** spectrum, suggesting that P–N bond dissociation occurs when **2(N)**–**2(P)** is irradiated. The P–N bond dissociation enthalpy was calculated (42.3 kcal·mol<sup>−1</sup>),<sup>10</sup> which is much higher than the bis(pentamethylcyclopentadienyl) C–C bond dissociation enthalpy (measured: 18.8 kcal·mol<sup>−1</sup>,<sup>17b</sup> calculated:<sup>10</sup> 18.1 kcal·mol<sup>−1</sup>).

Coupling of two radical anions or two radical cations is a common outcome in an electrochemical reaction, and such a coupling will cause a doubly charged  $\sigma$ -bonded dimeric species to form.<sup>18</sup> A few of the reports have been made of the dimerization of uncharged cyclic radicals,<sup>19</sup> and the typical examples are the dimers or cages formed by the self-reaction of the neutral pentamethylcyclopentadienyl radical<sup>19c–e</sup> or by the oxidation coupling of tri-, di-, and monophospholides (*vide infra*). The uncharged radical **2**<sup>•</sup> in our study was probably able to dimerize through  $\sigma$ -association, depending on its electronic and steric nature.<sup>20</sup>

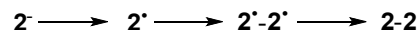
To understand the self-association of the uncharged radical **2**<sup>•</sup>, we performed computational studies of **2**<sup>−</sup>, **2**<sup>•</sup>, the possible product models **2(N1)**–**2(N3)**, **2(N1)**–**2(P2)**, **2(P1)**–**2(P2)**, and the proposed intermediates **2**<sup>•</sup>(N1)–**2**<sup>•</sup>(N3), **2**<sup>•</sup>(N1)–**2**<sup>•</sup>(P2), **2**<sup>•</sup>(P1)–**2**<sup>•</sup>(P2) using the Gaussian 09 program (see Figure SI-8-1 in Electronic Supplementary Information for the optimized geometries).<sup>10,21</sup> The nucleus independent chemical shifts (NICS) for **2**<sup>−</sup> and **2**<sup>•</sup>, −11.3 and −1.3, respectively, and the bond lengths all indicated that **2**<sup>−</sup> is aromatic but that **2**<sup>•</sup> is not aromatic (Table SI-8-2).<sup>22</sup> The spin densities of **2**<sup>•</sup> is 0.892 and 0.127 at P-atom and N-atoms, respectively, indicated that the unpaired electron is largely localized at the P- and N-atoms (Table SI-8-2).



**Figure 3.** X-ray crystal structure of **2(N)**–**2(P)**. The hydrogen atoms were omitted for clarity. Selected bond distances [Å] and angles (deg): N(1)–P(2) 1.746(3), P(2)–C(3) 1.839(2), N(3)–N(3A) 1.449(4), N(1)–N(2) 1.377(3), P(1)–C(2) 1.724(3); C(3A)–P(2)–C(3) 85.32(15), C(1)–P(1)–C(2) 87.93(15), N(2)–N(1)–P(2) 113.85(19), C(2)–N(1)–P(2) 129.7(2).

Assuming that the oxidation of **2**<sup>−</sup> to allow the dimer **2–2** to be formed proceeds through successive multistep pathways (Scheme 3), the key biradical intermediate **2**<sup>•</sup>–**2**<sup>•</sup> with triplet multiplicity should involve the isomers **2**<sup>•</sup>(N1)–**2**<sup>•</sup>(N3), **2**<sup>•</sup>(N1)–**2**<sup>•</sup>(P2), and **2**<sup>•</sup>(P1)–**2**<sup>•</sup>(P2) (Figure SI-8-1).<sup>10</sup> The energy profile of dimerization process shown in Figure SI-8-5 was used to further elucidate the regioselectivity of the oxidation of **2**<sup>−</sup>. The relative energies of the three product models suggested

that the stabilities of the products would decrease in the order of **2(N1)**–**2(N3)** > **2(N1)**–**2(P2)** > **2(P1)**–**2(P2)**. However, the proposed intermediates of **2**<sup>•</sup>(N1)–**2**<sup>•</sup>(P2) were found to have significantly lower energies than the intermediates of the other products. Several P–P linked dimers<sup>23a</sup> and cages (with less substituents<sup>23b</sup>) derived from the oxidation coupling of 1,2,4-triphospholides<sup>23a–b</sup> (or  $-\text{le}^{23c}$ ), phospholide,<sup>23d</sup> and 1,3-diphospholide<sup>23e</sup> by [RuCl<sub>2</sub>(COD)],<sup>23a</sup> [CrCl<sub>3</sub>(thf)<sub>3</sub>],<sup>23b</sup> HgCl<sub>2</sub>,<sup>23b</sup> (or O<sub>2</sub><sup>23c</sup>), TiCl<sub>4</sub>,<sup>23d</sup> FeCl<sub>3</sub>,<sup>23e</sup> and CoBr<sub>2</sub>,<sup>23e</sup> respectively, have been reported



**Scheme 3.** The proposed successive multistep pathways to the the dimer **2–2** by the oxidation of **2**<sup>−</sup>

previously, but the triplet biradical **2**<sup>•</sup>(P1)–**2**<sup>•</sup>(P2) will be in a repulsive state because of the steric effect of bulky tBu groups. The **2**<sup>•</sup>(N1)–**2**<sup>•</sup>(P2) intermediate being more stable than those of other isomers therefore seems to explain why N–P coupling occurs when **2**<sup>•</sup> becomes dimerized. Unlike previously reported  $\pi$ – $\pi$  interaction via a P–P  $\sigma$  bond in 1,1'-diphosphole<sup>24</sup>, the two 1,2,4-diazaphospholyl moieties in **2(N1)**–**2(P2)** are linked via a N–P  $\sigma$  bond with a  $\sigma$ – $\pi$  interaction (Figure SI-8-7).

In conclusion, anion **2**<sup>−</sup>, which incorporates bulky *tert*-butyl groups, was oxidized by FeCl<sub>3</sub> or CuCl<sub>2</sub> to form the neutral radical **2**<sup>•</sup>. The results provided unequivocal evidence for the formation of  $\sigma$ -bonded dimer **2(N)**–**2(P)** through the spontaneous and irreversible association of two uncharged nonaromatic radical **2**<sup>•</sup> at < 80°C and evidenced that the dimer dissociated to form several unidentified species when irradiated with UV-light. We demonstrated that the 1,2,4-diazaphospholides are non-innocent and have unique redox properties allowing them to form dianionic or neutral radicals when the substituents at 3,5-positions are suitably modified.<sup>1c</sup> Importance of five-membered ring radicals in organometallics<sup>25,26</sup> and physical chemistry<sup>27</sup> means that the isolation of other stable neutral 1,2,4-diazaphospholide radicals and exploration of the reactivities of such radicals can be expected to be fruitful paths in the field of 1,2,4-diazaphospholide chemistry.

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## Notes and references

§Syntheses: **[DMPO]2**<sup>•</sup>: To a toluene solution containing K<sup>+</sup>[**2**<sup>−</sup>] (3.0/2.0 mM) were added FeCl<sub>3</sub>/CuCl<sub>2</sub> (1.0 mM) and DMPO (20 mM) in a Schlenk flask. The EPR spectrum for the spin adduct was recorded by an EPR paramagnetic resonance instrument at X-band after the mixture was shaken for about 1 min.

**2(N)**–**2(P)**: To a mixture of K<sup>+</sup>[**2**<sup>−</sup>] (0.71 g, 3.0 mmol)/ (0.47 g, 2.0 mmol) and FeCl<sub>3</sub> (0.16 g, 1.0 mmol)/CuCl<sub>2</sub> (0.15 g, 1.0 mmol) was added toluene (20 mL) via syringe at −10°C. After stirred at −10°C for 24 h the suspension was filtered through a Celite. The filtrate was concentrated under the reduced pressure to afford **2(N)**–**2(P)** as yellow crystals at −20°C (0.24 g, 43%)/(0.15 g, 40%); M.p. 245°C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 1.18 (s, 18 H, CCH<sub>3</sub>), 1.24 (s, 9 H, CCH<sub>3</sub>), 1.71 (s, 9 H, CCH<sub>3</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR



(150 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 197.20, 196.82 (d,  $^1J_{C-P}$  = 57.0 Hz, PC), 190.24, 189.83 (d,  $^1J_{C-P}$  = 61.5 Hz, PC), 186.01, 185.81 (d,  $^1J_{C-P}$  = 30 Hz, PC), 37.78, 37.50 (d,  $^2J_{C-P}$  = 42 Hz, CCH<sub>3</sub>), 36.09, 36.04 (d,  $^2J_{C-P}$  = 7.5 Hz, CCH<sub>3</sub>), 35.98, 35.95 (d,  $^2J_{C-P}$  = 4.5 Hz, CCH<sub>3</sub>), 32.82, 32.77 (d,  $^3J_{C-P}$  = 7.5 Hz, CCH<sub>3</sub>), 32.75, 32.70 (d,  $^3J_{C-P}$  = 7.5 Hz, CCH<sub>3</sub>), 31.34, 31.30 (d,  $^3J_{C-P}$  = 6.0 Hz, CCH<sub>3</sub>) ppm;  $^{31}P\{^1H\}$  NMR (243 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 97.78 (s), 73.81 (s);  $^{31}P$  MAS NMR (202.3 MHz): 77.0 (s), 97.0 (s); IR(KBr, Nujol mull): 1508(m), 1461(s), 1361(s), 1262(s), 1201(s), 1099(s), 1018(s), 800(s), 690(s) cm<sup>-1</sup>; Anal. calcd for C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>P<sub>2</sub> (Mr = 394.47): C, 60.89; H, 9.20; N, 14.20. Found: C, 61.13; H, 9.27; N, 14.14.

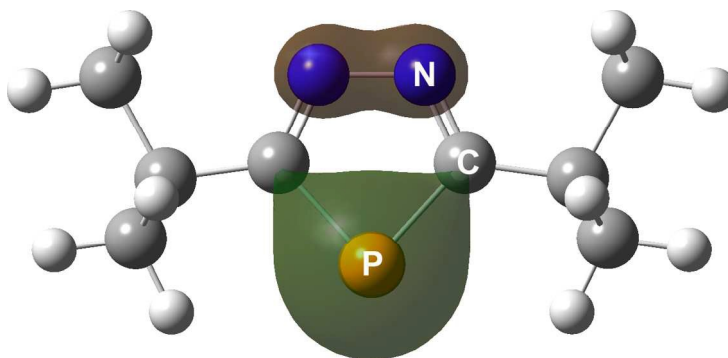
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- 10 The spectroscopic data for **2**<sup>\*</sup>, **2(N)**–**2(P)**, and computation details are contained in the Supporting Materials.
- 11 The main EPR spectral features for the Cu<sup>2+</sup>-oxidation spin-adduct was similar but displayed a hyperfine of fair-resolved coupling multiplet with 11 observed lines. See ref. 10.
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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

The oxidation of 1,2,4-diazaphospholide potassium ( $K^+[2^-]$ ) produced a neutral 1,2,4-diazaphospholyl radical ( $2^\bullet$ ) that was able to self-associate through a N–P coupling to give a 2(N)–2(P) dimer.



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A 1,2,4-Diazaphospholyl Radical and Its Nitrogen-Phosphorus Coupled Dimer: Synthesis, X-Ray Structural Characterization, EPR Analysis, and Bonding