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# Synthesis of a Carbene-Stabilized (Diphospha)aminyl Radical and its One Electron Oxidation and Reduction to Nonclassical Nitrenium and Amide Species

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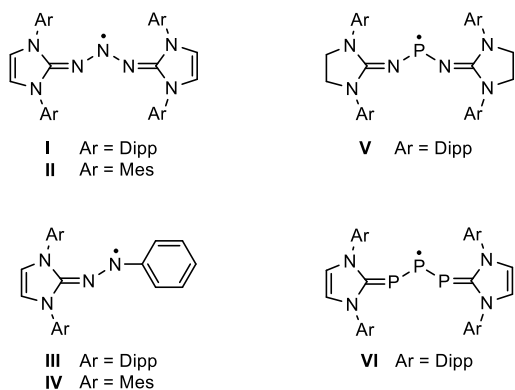
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**ABSTRACT:** Herein we report the synthesis of the acyclic carbene-stabilized diphospha(aminyl) radical  $\text{CAAC}^{\text{Me}}\text{PNPCAAC}^{\text{Me}}$  **4** ( $\text{CAAC}^{\text{Me}}=1\text{-[2,6-bis(isopropyl)phenyl]-3,3,5,5-tetramethyl-2-pyrrolidinylidene}$ ) by a facile one-pot, 7-electron reduction of hexachlorophosphazene chloride  $[\text{Cl}_3\text{PNPCl}_3][\text{Cl}]$ . The PNP radical **4** features a conjugated framework with spin density primarily localized on the central nitrogen atom as well as the flanking carbenes. Unlike other tripnictogen radicals, **4** undergoes facile one-electron oxidation and reduction to yield non-classical nitrenium and amide species  $[\mathbf{5}]^+$  and  $[\mathbf{6}]^-$ , respectively. The cation  $[\mathbf{5}]^+$  exhibits conformational flexibility in the solution state between the expected W-shaped geometry  $[\mathbf{5}_b]^+$  and a previously unobserved linear heteroallene type structure  $[\mathbf{5}_a]^+$ , which was characterized in the solid state. The equilibrium was explored both computationally and experimentally, showing that  $[\mathbf{5}_a]^+$  is favored over  $[\mathbf{5}_b]^+$  both enthalpically ( $\Delta H = -2.9 \times 10^3 \pm 80 \text{ J mol}^{-1}$ ) and entropically ( $\Delta S = 4.2 \pm 0.25 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The formal amide  $[\mathbf{6}]^-$  displays remarkable flexibility in its coordination chemistry, due to the presence of multiple Lewis basic centers, as evidenced by the structure of its potassium complex **K262**, which exhibits both  $\mu, \kappa\text{-P}, \kappa\text{-P}$  and  $\eta^3\text{-PNP}$  coordination modes. Protonation of  $[\mathbf{6}]^-$  leads to the formation of an amine **7**, which features a trigonal planar geometry around nitrogen.

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## Introduction

The design of stable nitrogen radicals is a longstanding challenge in synthetic chemistry.<sup>1-3</sup> Acyclic aminyl radicals of the type  $\text{NRR}'$  remain particularly elusive, despite being implicated as critical intermediates in a variety of chemical transformations of synthetic organic or biological importance,<sup>3-7</sup> as well as their potential utility in polymer synthesis and materials applications.<sup>8-9</sup> Accordingly, few structurally characterized examples of these compounds have been realized.<sup>10-19</sup> One major hurdle in the development of this chemistry is the lack of well-defined synthetic methodologies. An increasingly popular strategy for the generation of isolable  $p$ -block radical species is the reduction of main-group halides or pseudo-halides in the presence of, or ligated by, stable carbenes, *e.g.*  $N$ -heterocyclic (NHCs) or cyclic alkylamino carbenes (CAACs), leading to the formation of the carbene-stabilized radical species.<sup>20-23</sup> Unfortunately, the instability of binary nitrogen halides precludes their use in synthesis,<sup>24</sup> rendering the use of strategies employed for other  $p$ -block elements impractical. While other nitrogen sources, such as azides and arylimidazolium dyes,<sup>16-17, 25-28</sup> have been successfully used in the generation of carbene-stabilized nitrogen radicals (Chart 1), this field remains under-developed compared to that of related  $p$ -block elements, such as phosphorus,<sup>29-32</sup> and the development of additional nitrogen synthons is highly desirable.



Dipp = 2,6-diisopropylphenyl,  
Mes = 1,3,5-trimethylbenzene = mesityl

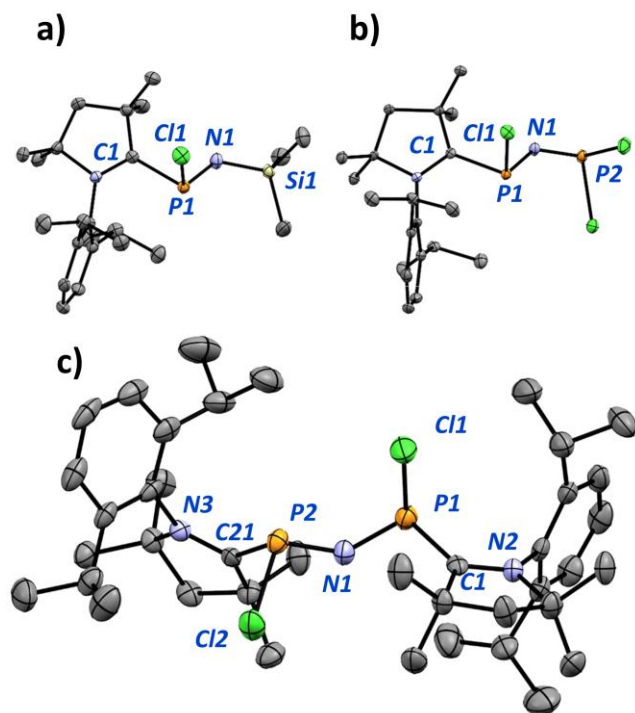
**Chart 1.** Select carbene-stabilized nitrogen and phosphorus radicals.

Potential candidates for the generation of nitrogen radicals using reductive approaches are halophosphazenes *P*-trichloro-*N*-trimethylsilyl-phosphoranimine ( $\text{Cl}_3\text{P}=\text{NTMS}$ ) and hexachlorophosphazene chloride ( $[\text{Cl}_3\text{PNP}\text{Cl}_3][\text{Cl}]$ ). These long-known compounds are readily accessible on gram scale<sup>33-36</sup> and have been extensively used in the synthesis of chlorophosphazene rings and polymers,<sup>33, 37-41</sup> although little is known about their reduction chemistry.<sup>42</sup> Exhaustive reduction of these materials should provide a convenient route to binary PN molecules, an elusive class of compounds of longstanding interest as inorganic analogues of archetypal hydrocarbons,<sup>43-44</sup> energetic materials,<sup>45-49</sup> and components of interstellar media.<sup>50-53</sup> Further, the presence of terminal chlorophosphorane moieties should allow for facile extension of well-explored carbene-phosphorus chemistry<sup>23, 29, 54-62</sup> to a formally nitrogen-based system. With these considerations in mind, we have explored the reactivity of  $\text{Cl}_3\text{P}=\text{NTMS}$  and  $[\text{Cl}_3\text{PNP}\text{Cl}_3][\text{Cl}]$  with cyclic alkylamino carbene 1-[2,6-bis(isopropyl)phenyl]-3,3,5,5-tetramethyl-2-pyrrolidinylidene ( $\text{CAAC}^{\text{Me}}$ ).

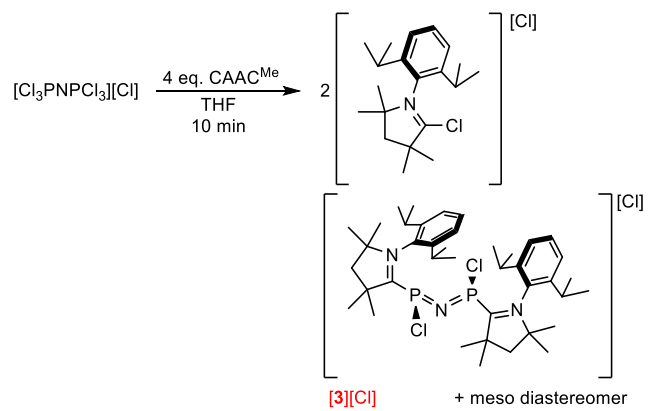
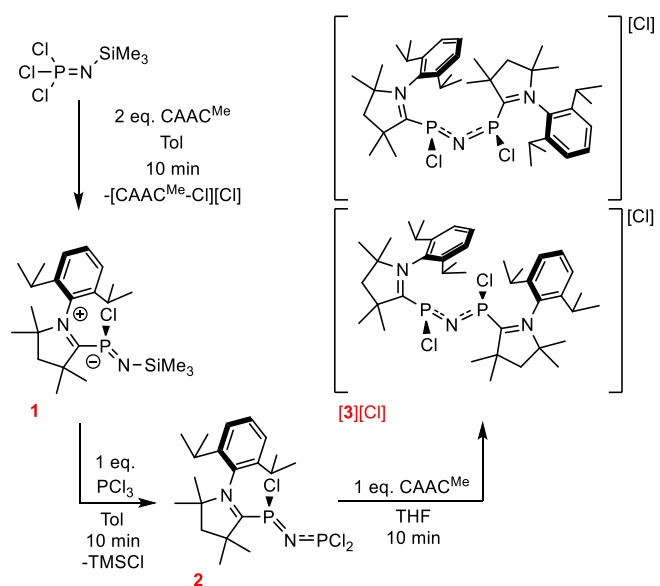
## Results and Discussion

### 1. Synthesis and Characterization of **1**, **2**, and **[3]**<sup>+</sup>

We first attempted the construction of the PNP core in a stepwise fashion by treating *P*-trichloro-*N*-trimethylsilyl-phosphoranimine<sup>36, 63</sup> with 2 eq. of  $\text{CAAC}^{\text{Me}}$ , which effected both reduction and simultaneous ligation of the generated highly reactive *P*-chloro-*N*-trimethylsilyl-iminophosphine, a proposed, but never observed, intermediate in the phosphine-mediated dehalogenation of this phosphoranimine.<sup>64-65</sup> The resulting thermally-sensitive adduct **1** can be readily isolated from the by-product  $[\text{CAAC}^{\text{Me}}\text{-Cl}][\text{Cl}]$  (*vide infra*) by filtration and isolated as pure, red crystalline solid in 74% yield. Compound **1** was characterized by multinuclear NMR spectrometry (Figures S18-S20) and single crystal X-ray diffraction (Figure 1). Treatment of **1** with excess  $\text{PCl}_3$  completed the PNP core, leading to a single product as observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrometry with two resonances integrating 1:1 at 176.2 and 109.5 ppm (Figure S22). These data were assigned to the  $\text{CAAC}^{\text{Me}}$ -stabilized *P*-chloro-*N*-dichlorophosphino-iminophosphine **2** based on its solid-state structure (Figure 1) and mass spectrum ( $\text{M}^+ = 466.10$  amu,  $\{\text{M}-\text{Cl}\}^+ = 431.13$  amu, Figure S1).



**Figure 1.** Molecular structure of **1** (a), **2** (b) and **[3]<sup>+</sup>** (c). Ellipsoids are drawn at 50% probability. Only one crystallographically independent molecule of **1** is shown. Hydrogen atoms and the counter anion in the structure of **[3][Cl]** are omitted for clarity. Select bond lengths (Å) and angles (°) for **1**: C1-P1 1.906(1); N1-P1 1.569(1); N1-Si1 1.700(1); P1-Cl1 2.2924(5); N2-C1 1.299(2) C1-P1-Cl1 86.59(4); P1-N1-Si1 128.99(8). Select bond lengths (Å) and angles (°) for **2**: C1-P1 1.891(1); N1-P1 1.625(2); N1-P2 1.584(1); P1-Cl1 2.1296(7); C1-N2 1.296(2) C1-P1-Cl1 90.74(1); P1-N1-P2 132.5(1). Select bond lengths (Å) and angles (°) for **3** [calculated values in square brackets]: C1-P1 1.905(2) [1.897]; C21-P2 1.898(3) [1.878]; N1-P1 1.591(3) [1.604]; N1-P2 1.599(3) [1.604]; P1-Cl1 2.149(2) [2.136]; P2-Cl2 2.130(1) [2.158]; C1-N2 1.289(4) [1.291]; N2-C21 1.294(3) [1.291]; P1-N1-P2 137.1(2) [133.3].



**Scheme 1.** Synthesis of compounds **1**, **2**, and **[3][Cl]**.

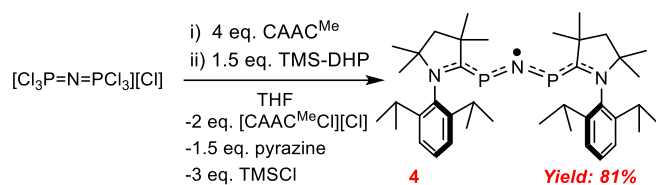
Addition of 1 eq. of CAAC<sup>Me</sup> to a THF solution of **2** led to rapid precipitation of brown-yellow crystals. Dissolution of the precipitate in CD<sub>2</sub>Cl<sub>2</sub> and subsequent NMR spectrometric analysis revealed the presence of two <sup>31</sup>P{<sup>1</sup>H} resonances at 141.6 and 108.1 ppm in a ca. 1:2 ratio (Figure S24), while the <sup>1</sup>H NMR spectrum is indicative of two CAAC<sup>Me</sup>-containing complexes (Figure S23). Both species show a loss of mirror symmetry in the CAAC<sup>Me</sup> moiety on the NMR timescale as evidenced by the doubling of all resonances, except those corresponding to the aryl *para*-H, and the splitting of the resonances of ring methylene protons into characteristic AB doublet of doublets, suggestive of low symmetry. Single crystal X-ray diffraction studies revealed the formation of [3][Cl] (Figure 1) in which the cation [3]<sup>+</sup> is present as a racemate. This suggests that the minor species observed in the solution is the *meso* diastereomer of [3]<sup>+</sup> (Scheme 1). The single phosphorus and carbene environments observed by NMR for both species can be explained by rapid inversion at nitrogen in solution that is distinctive to phosphazene cations.<sup>66</sup> Accordingly, DFT (see SI for full computational details) calculations performed on [3]<sup>+</sup> showed the barrier ( $\Delta G^\ddagger$ ) for nitrogen inversion to be only 19 kJ mol<sup>-1</sup>. The metrical parameters of **1**, **2**, and [3]<sup>+</sup> are similar to *N*-heterocyclic carbene adducts of stable iminophosphines reported by Burford and coworkers,<sup>67-68</sup> and include unusually small C<sub>carbene</sub>-P-Cl angles (*ca.* 90°) along with long C<sub>carbene</sub>-P (*ca.* 1.90 Å) and short C<sub>carbene</sub>-N (*ca.* 1.29 Å) and N-P (*ca.* 1.59 Å) bond lengths indicative of single and multiple bond character, respectively, as drawn in Scheme 1.<sup>69</sup> Formally, [3][Cl] can be viewed as the biscarbene adduct of the heteroallene salt [ClPNPCl][Cl]. The cation can be described with resonance structures [Cl-P<sup>+</sup>-N=P-Cl] ↔ [Cl-P=N-P<sup>+</sup>-Cl] in which the empty *p*-orbital on the phosphorous atom (one on each structure) is perfectly poised to accept an electron pair from CAAC<sup>Me</sup>. This is also borne out by DFT calculations on [ClPNPCl]<sup>+</sup> that show the LUMO and LUMO+1 to be linear combinations of *p*-orbitals with the greatest contributions from the two phosphorus atoms.

In an attempt to develop a more expedient route to  $[3][Cl]$ , the reaction of  $[Cl_3PNPCl_3][Cl]$  with 4 eq. (or more) of  $CAAC^{Me}$  in THF solution was found to lead to rapid formation of a colorless solution over a yellow precipitate. Dissolution of the precipitate in  $CD_2Cl_2$  and subsequent NMR analysis revealed the presence of two  $^{31}P\{^1H\}$  resonances ( $\delta_P = 141.6, 108.1$ ) in a *ca.* 1:2 ratio (Figure S2), corresponding to  $[3]^+$ , while the  $^1H$  NMR spectrum is consistent with the formation of three  $CAAC^{Me}$  containing compounds in an approximately 6:2:1 ratio (Figure S3). The latter two resonances match the spectrum for  $[3]^+$ , while the most intense one is consistent with the formation of 2 eq. of the 2-chloropyrrolium salt  $[CAAC^{Me}-Cl][Cl]$ ,<sup>59, 70</sup> which was confirmed by independent synthesis (Figure S4; see SI for full synthetic details). This suggests that 2 eq. of  $CAAC^{Me}$  effected the  $4e^-$  reduction of  $[Cl_3PNPCl_3][Cl]$ . Unfortunately, the similar solubilities of  $[CAAC^{Me}-Cl][Cl]$  and  $[3]^+$  prevented their isolation or separation from the mixture. Nevertheless, the expedient one-step synthesis of this mixture proved to be advantageous for further synthetic work as  $[CAAC^{Me}-Cl][Cl]$  could be removed after additional reactions.

## 2. Reduction of $[3]^+$ to Radical 4

Attempts to reduce either isolated  $[3][Cl]$  or  $[3][Cl]$  generated *in situ* from the reaction of  $[Cl_3PNPCl_3][Cl]$  with  $CAAC^{Me}$  with commonly used strong reducing agents, such as magnesium or potassium, resulted in mixtures of diamagnetic species by  $^{31}P$  NMR spectrometry. However, the use of 1.5 eq. of mild, salt-free, reducing agent 1,4-bis(trimethylsilyl)dihydropyrazine (TMS-DHP)<sup>71-73</sup> with isolated or freshly generated suspensions of  $[3][Cl]$  in THF resulted in the immediate formation of a dark pink solution over a white precipitate (Scheme 2). Filtration and removal of volatiles afforded the radical 4 as a dark pink solid in 81% yield, the identity of which was confirmed by mass spectrometry ( $M+H = 647.45$  amu, Figure S6), solution magnetic moment (Evans method,  $\mu_{eff} = 1.78 \mu_B$ ),<sup>74</sup> single crystal X-ray diffraction (Figure 2), and EPR spectrometry (Figure 3).

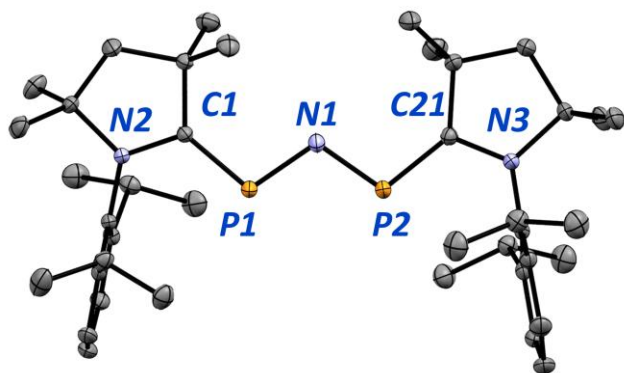




TMS-DHP = 1,4-bis(trimethylsilyl)dihydropyrazine

## Scheme 2. Synthesis of carbene-stabilized PNP radical **4**.

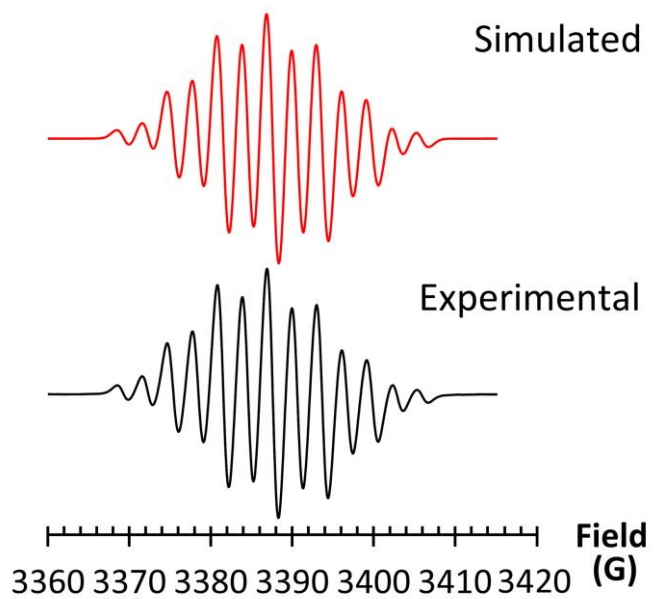
Radical **4** is stable at ambient temperature for months as a solid in tightly sealed vials under an inert atmosphere and at least one week in C<sub>6</sub>D<sub>6</sub> solution; however, heating C<sub>6</sub>D<sub>6</sub> solutions to 80 °C for 48 h leads to the formation multiple unidentified diamagnetic phosphorus species by <sup>31</sup>P{<sup>1</sup>H} NMR spectrometry, while exposure to oxygen results in immediate loss of the characteristic pink color and degradation. Furthermore, **4** does not react with H-atom transfer reagents 9,10-dihydroanthracene or xanthene, unlike related NHC-stabilized triazenyl radicals **I** and **II** (Chart 1),<sup>17</sup> suggesting an N-H bond strength for the corresponding amine (*vide infra*) of less than 315 kJ mol<sup>-1</sup>.<sup>75-76</sup>



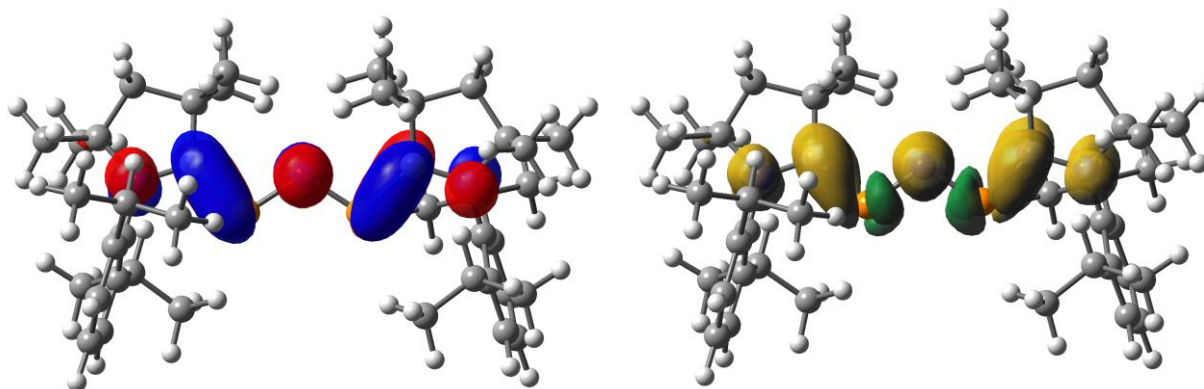
**Figure 2.** Molecular structure of **4**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) for **4** [calculated values in square brackets]: N1-P1 1.667(1) [1.651]; N1-P2 1.660(1) [1.651]; C1-P1 1.738(1) [1.736]; C21-P2 1.743(1) [1.736]; C1-N2 1.367(1) [1.358]; C21-N3 1.366(1) [1.358]; P1-N1-P2 110.75(6) [114.4].

The UV-VIS absorption spectrum of **4** in THF consists of a strong, broad peak with  $\lambda_{\max} = 550$  nm ( $\epsilon = 1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) as well as two less intense absorptions at *ca.* 700 nm ( $\epsilon = 1.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 340 nm ( $\epsilon = 2.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) (Figure S7). The solid-state structure of **4** is characterized by a nearly planar orientation of the central PNP fragment and CAAC<sup>Me</sup> ligands, with metrical parameters indicative of multiple bond character and extensive delocalization throughout the PNP-carbene framework (Figure 2).<sup>69</sup> The EPR spectrum of **4** in toluene solution at 298 K reveals a 13-line multiplet (Figure 3) that could be successfully simulated with  $g_{\text{iso}} = 2.004$  and hyperfine coupling to the central nitrogen atom ( $a_{\text{N}} = 5.99$  G) as well as to both phosphorus ( $2 \times a_{\text{P}} = 6.20$  G) and carbene nitrogen atoms ( $2 \times a_{\text{N}} = 3.05$  G).

DFT calculations well reproduce the W-shape geometry of **4** with a nearly planar CPNPC unit (Figure 2). The singly occupied molecular orbital (SOMO) of **4** is of  $\pi$ -type and C<sub>carbene</sub>-P bonding and N-C<sub>carbene</sub> and N-P anti-bonding (Figure 4), resembling the SOMOs of NHC-stabilized triazenyl radicals **I** and **II** (Chart 1). The calculated spin density of **4** mirrors the shape of the SOMO (Figure 4), with additional  $\beta$ -spin contributions on phosphorus atoms that arise from spin polarization effects. As is evident from the shape of the SOMO and the associated population analyses, only around 35% of  $\alpha$ -spin density resides on the central nitrogen atom in **4**, with the remainder spread over the C<sub>carbene</sub> and N atoms on the two CAAC<sup>Me</sup> ligands. Thus, **4** is only formally a nitrogen-centered radical and its lack of reactivity with common H-atom transfer reagents is consistent with the calculated N-H bond enthalpy of 274 kJ mol<sup>-1</sup> at 298 K for the corresponding amine in the gas phase. The calculated hyperfine coupling constants for **4** show coupling to all three nitrogen atoms, 4.70 and  $2 \times 2.42$  G, in good agreement with the values from spectral simulation. However, at  $2 \times -15.1$  G, the calculations significantly overestimate the spin-polarization induced phosphorus couplings.

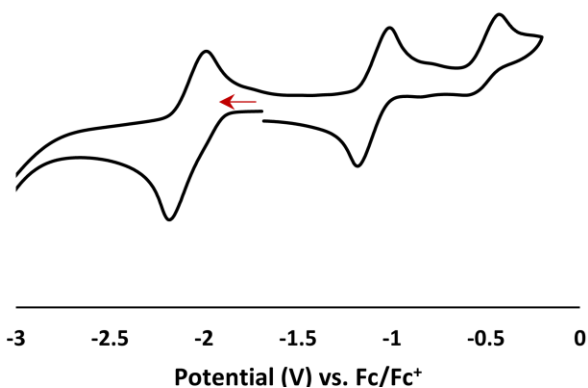


**Figure 3.** Simulated and experimental (in toluene at 298 K) EPR spectrum of **4**.



**Figure 4.** Calculated SOMO (left, isosurface value 0.04) and spin density (right, isosurface value 0.002) of **4**.

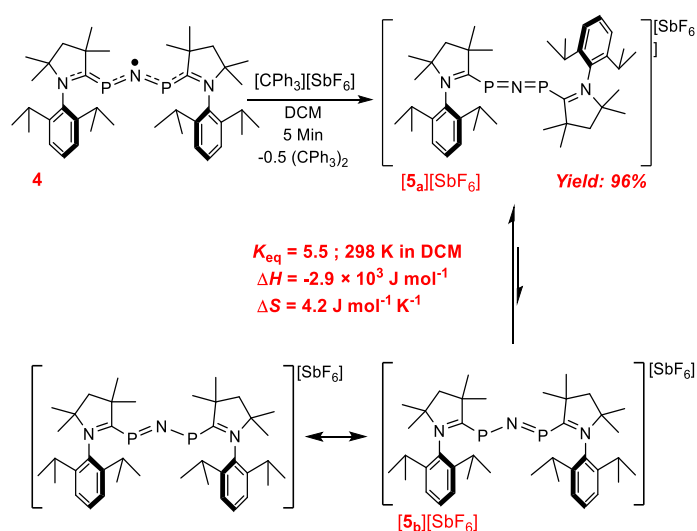
Because the synthesis of related carbene stabilized triazenyl and triphosphorus radicals was accomplished by one-electron reduction of the corresponding azido and phosphonium cations,<sup>17, 25, 31</sup> and owing to the growing importance of cationic nitrenium species as potential organocatalysts and ligands,<sup>19, 77-83</sup> the ability of **4** to act as a precursor to a phosphorus-stabilized nitrenium cation was explored. The cyclic voltammogram of **4** in THF (Figure 5) revealed both the anticipated reversible oxidation wave ( $E_{1/2}^{\text{ox}} = -1.09$  vs. Fc/Fc<sup>+</sup>), which occurs at a significantly more positive potential than that reported for the triazolyl radicals **I** and **II** (cf.  $E_{1/2}^{\text{ox}} = -1.17/-1.38$  V vs. Ag/AgCl in THF,<sup>17</sup> ca.  $-1.76/-1.97$  vs. Fc/Fc<sup>+</sup>)<sup>84-86</sup> and a partially reversible reduction event ( $E_{1/2}^{\text{red}} = -2.08$  vs. Fc/Fc<sup>+</sup>), which has not been previously observed for related compounds (Chart 1). Accordingly, both the chemical one-electron oxidation and reduction of **4** were investigated.



**Figure 5.** Cyclic voltammogram of **4** (in THF, 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>], ~1 mM analyte, 100 mV s<sup>-1</sup> scan rate, Pt working electrode).

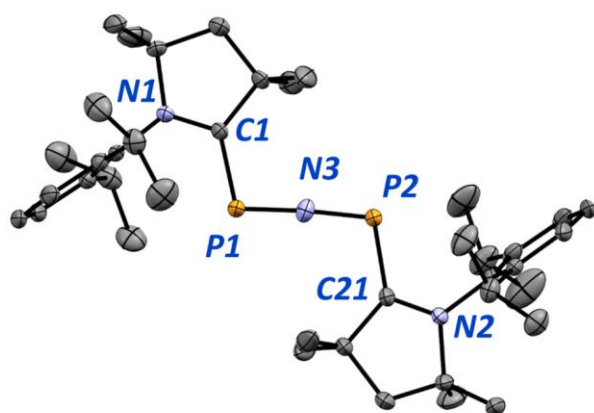
### 3. Chemical Oxidation of **4** to **[5]**<sup>+</sup>

Treatment of **4** with one equivalent of the mild oxidant  $[\text{CPh}_3][\text{SbF}_6]$  in DCM resulted in an immediate color change from pink to blue-purple, from which a dark blue microcrystalline solid  $[\mathbf{5}][\text{SbF}_6]$  could be isolated in excellent yield (Scheme 3). Analysis of the material by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrometry revealed the presence of two resonances at 269.6 ppm and 185.1 ppm in a *ca.* 1:5.5 ratio (Figure S8), while the  $^1\text{H}$  NMR spectrum at 298 K shows two sets of broadened peaks indicative of dynamic exchange (Figure S9), which was further supported by the presence of negatively phased off-diagonal peaks in the 2D-EXSY  $^1\text{H}$  NMR spectrum (Figure S10). Variable temperature  $^1\text{H}$  NMR spectrometry shows a sharpening of both sets of resonances at lower temperatures (Figure S9).



**Scheme 3.** Oxidation of **4** to  $[\mathbf{5}]^+$  and equilibrium between  $[\mathbf{5}_a]^+$  and  $[\mathbf{5}_b]^+$

Analysis of the solid-state structure of  $[\mathbf{5}]^+$  by single crystal X-ray diffraction studies revealed not the expected bent W-shaped cation previously reported for related azido and phosphonium salts,<sup>17, 25, 31, 87</sup> but a heteroallene type structure (Figure 6) featuring a nearly linear central PNP unit ( $175.8(2)^\circ$ ) and C-P (1.826(2) and 1.842(2) Å) and N-P bond lengths (1.581(2) and 1.589(2) Å) suggestive of single and multiple bonding.<sup>69</sup> DFT calculations (PBE1PBE-D3/def2TZVP) indicated that both linear ( $[\mathbf{5}_a]^+$ ) and W-shaped ( $[\mathbf{5}_b]^+$ ) geometries are stable minima on the potential energy surface in the gas phase, with  $[\mathbf{5}_a]^+$  favored by  $-11$  and  $-18$  kJ mol<sup>-1</sup> in enthalpy and Gibbs energy at 298 K. The calculated chemical shifts of  $[\mathbf{5}_a]^+$  and  $[\mathbf{5}_b]^+$  are 163.9 and 261.2 ppm, respectively, and in reasonable agreement with the NMR data of  $[\mathbf{5}]^+$  in solution (*vide supra*). Van't Hoff analysis of the equilibrium in CD<sub>2</sub>Cl<sub>2</sub> (Figure S11) showed that  $[\mathbf{5}_a]^+$  is slightly favored over  $[\mathbf{5}_b]^+$  both in enthalpy ( $\Delta H = -2.9 \times 10^3 \pm 80$  J mol<sup>-1</sup>) and in entropy ( $\Delta S = 4.2 \pm 0.25$  J mol<sup>-1</sup> K<sup>-1</sup>), giving  $\Delta G = -4.2$  kJ mol<sup>-1</sup> at 298 K.



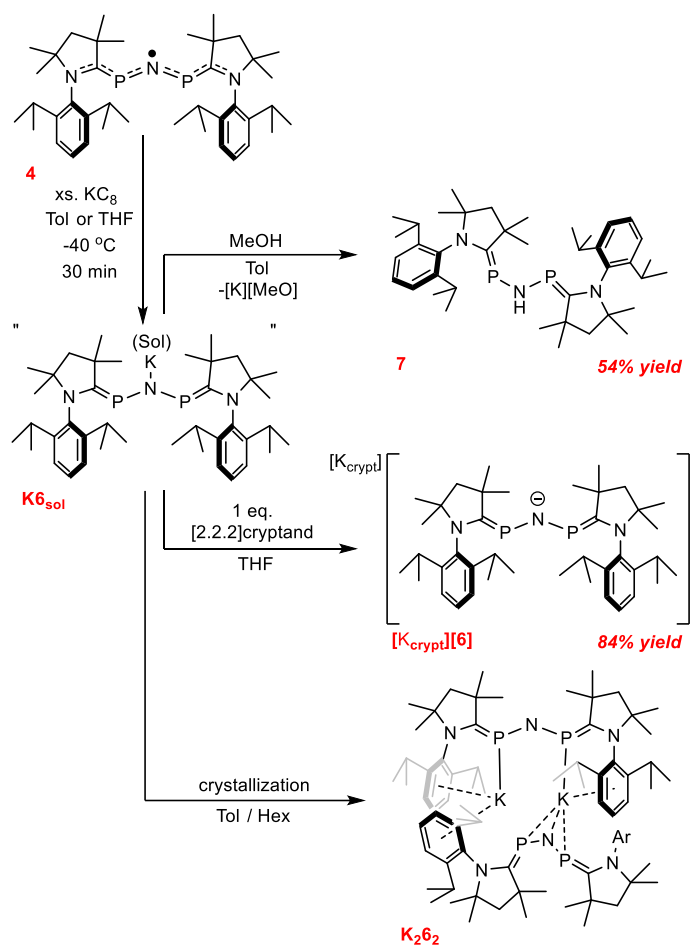
**Figure 6.** Molecular structure of  $[\mathbf{5}_a]^+$ . Ellipsoids are drawn at 50% probability. Hydrogen atoms and counterion are omitted for clarity. Select bond lengths (Å) and angles ( $^\circ$ ) for  $[\mathbf{5}_a]^+$  [calculated values in square brackets]: N3-P1 1.589(2) [1.585]; N3-P2 1.581(2) [1.585]; C1-P1 1.826(2) [1.825]; C21-P1 1.842(2) [1.825]; C1-N1 1.308(3) [1.306]; C21-N2 1.306(3) [1.306]; P1-N1-P2 175.8(2) [180.0]; C1-P1-N3 103.9(1) [103.5].

The structural dichotomy observed for  $[\mathbf{5}]^+$  is reminiscent of that known for the bis(triphenylphosphine)iminium cation,<sup>66</sup>  $[\text{Ph}_3\text{PNPPh}_3]^+$ , whose PNP moiety has a very shallow bending potential and can adopt either bent or linear geometry in the solid state, though only the bent form is a stable minimum on the potential energy surface. Examination of the calculated structures for  $[\mathbf{5}_a]^+$  and  $[\mathbf{5}_b]^+$  shows that the key bond parameters are not significantly affected by the PNP angle, with only very minor differences (less than 0.05 Å) observed in the key N-P,  $C_{\text{carbene}}\text{-P}$  and  $C_{\text{carbene}}\text{-N}$  distances. Formally,  $[\mathbf{5}]^+$  can be viewed as the biscarbene adduct of the linear  $[\text{PNP}]^+$  cation, with electron donation primarily from  $\text{CAAC}^{\text{Me}}$  to  $[\text{PNP}]^+$ . Natural population and bond orbital analyses conducted for  $[\mathbf{5}_a]^+$  indicate a slightly positively charged PNP fragment (partial charges of +0.77 and  $-1.25$  e on N and P, respectively) in which the N atom is  $sp$ -hybridized with one  $p$ -orbital engaging in  $\pi$ -type bonding interactions with the P atoms (a 3c-4e hyperbonded PNP triad) and the other one holding a lone pair of electrons (Figure S39). Second-order perturbative estimates of donor-acceptor interactions show that the electrons in the PNP unit are highly delocalized, indicating that an idealized single Lewis structure description of bonding is inadequate (also applies to  $\mathbf{4}$  and  $[\mathbf{6}]^-$ , *vide infra*). The charge distribution (partial charges of +0.77 and  $-1.15$  e on N and P, respectively) and NBO description of  $[\mathbf{5}_b]^+$  is similar to  $[\mathbf{5}_a]^+$  but the N atom is  $sp^2$ -hybridized, consistent with the bent PNP angle. Electron localization function (ELF) analyses performed for  $[\mathbf{5}]^+$  show a similar picture (Figure S40). In  $[\mathbf{5}_a]^+$ , the central N atom is surrounded by two monosynaptic  $V(\text{N})$  and two disynaptic  $V(\text{N},\text{P})$  basins with average populations of  $2 \times 1.93$  and  $2 \times 1.70$   $e^-$ , respectively, whereas  $[\mathbf{5}_b]^+$  shows one monosynaptic  $V(\text{N})$  and two disynaptic  $V(\text{N},\text{P})$  basins with populations of 2.59 and  $2 \times 2.28$   $e^-$ , respectively. The standard deviations and relative fluctuations associated with these basins are all rather high, indicating correlation between basin populations and, thereby, high degree of delocalization.

#### 4. Chemical Reduction of **4** to [**6**]<sup>-</sup>

Given the unanticipated results observed in the oxidation chemistry of **4** and the presence of a partially reversible reduction wave in its cyclic voltammogram, the chemical reduction of **4** was also pursued. Treatment of either THF or aromatic hydrocarbon solutions of **4** with one or more equivalents of KC<sub>8</sub> led to the formation of a deep red-orange solution, which contains resonances for one major product **K6<sub>sol</sub>** (> 92–98 %) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (Figure S28) with a highly solvent dependent chemical shift ( $\delta_P = 185.9$  (THF-*d*<sub>8</sub>), 177.4 (Tol-*d*<sub>8</sub>) and 172.0 (C<sub>6</sub>D<sub>6</sub>)), as well as an additional peak at 130.4 ppm (Tol-*d*<sub>8</sub>) corresponding to byproduct **7** (*vide infra*) and representing the balance of the phosphorus content. The <sup>1</sup>H NMR spectra in all solvents examined are consistent with one major CAAC<sup>Me</sup> containing product of apparent C<sub>2v</sub> symmetry (Figure S29), though the resonances in THF are significantly broadened. Further, the molecular weight of **K6<sub>sol</sub>** in toluene solution was determined by <sup>1</sup>H-DOSY NMR spectrometry (Figure S12) using the external calibration curve method<sup>88</sup> to be 783 Da, which is in excellent agreement with the formulation of **K6<sub>sol</sub>** in toluene as a monomeric potassium amide monosolvate (calculated value 778 Da), although the exact solution structure is unclear.

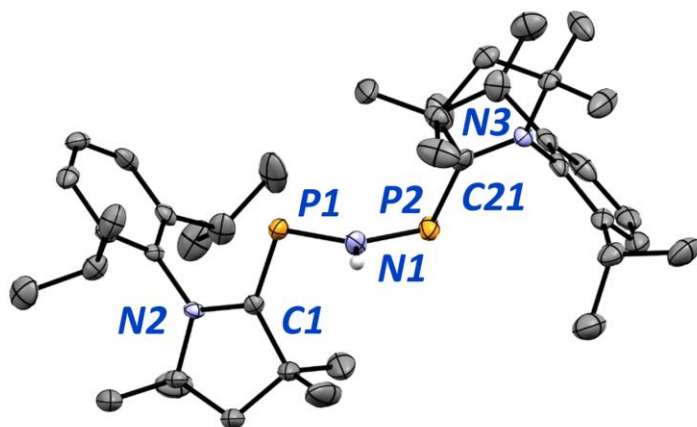




**Scheme 4.** Reduction of **4** to **K6<sub>sol</sub>** and subsequent reactivity.

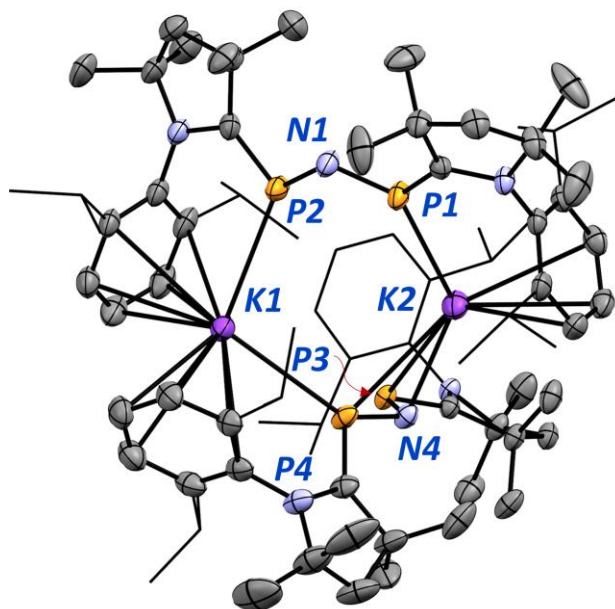
All attempts to isolate the species by solvent removal led to an increase in the amount of a diamagnetic phosphorus byproduct **7** characterized by a peak in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 130.4 ppm (Tol- $d_8$ ), which splits into a doublet ( $J = 4$  Hz) in the  $^{31}\text{P}$  NMR spectrum, suggestive of nitrogen-centered protonation, despite rigorously anhydrous conditions. Correspondingly, treatment of a freshly prepared toluene solution of **K6<sub>sol</sub>** with excess dry, degassed methanol leads to immediate formation of a bright yellow solution, from which a bright yellow solid can be isolated in 54 % overall yield from **4**. The  $^{31}\text{P}$  NMR spectrum of the isolated material reveals **7** to be the major component (*ca.* 96 %, Figures S13 and S14) while the  $^1\text{H}$  NMR spectrum shows a broad triplet peak at 1.67 ppm integrating to one proton relative to peaks for the CAAC<sup>Me</sup> moieties (Figure S15). Further, the observed coupling constant matches that of **7** in the  $^{31}\text{P}$  NMR spectrum and correlation was observed in the  $^1\text{H}$ - $^{31}\text{P}$  NMR HMBC NMR spectrum, consistent with formulation of **7** as an amine. Nitrogen-centered protonation was further supported by determination of the solid-state structure of **7** by single crystal X-ray diffraction (Figure 7).

The structure of **7** (Figure 7) shows a trigonal planar geometry ( $\Sigma\angle N = 359^\circ$ ) around nitrogen, suggesting  $sp^2$  hybridization. However, at 1.732(4) and 1.719(3) Å, the two N-P bonds are indicative of single bond character, while the two C-P bonds, 1.735(3) and 1.742(5) Å, are clearly of multiple bond character.<sup>69</sup> The bonding in **7** can be understood by considering its formation *via* reduction of **[5]**<sup>+</sup> to **[6]**<sup>-</sup> through **4**, followed by protonation at nitrogen. The reduction introduces two electrons to the  $\pi$ -type LUMO of **[5]**<sup>+</sup>, *i.e.*, the SOMO of **4** (Figure 4), that is C<sub>carbene</sub>-P bonding and N-P anti-bonding; the  $\pi$ -type P-N-P bonding orbital is significantly lower in energy and doubly occupied in **[5]**<sup>+</sup>, **4**, and **[6]**<sup>-</sup>. Thus, the C-P and N-P bonds in **[6]**<sup>-</sup> are short and long, respectively, and the central nitrogen atom is highly electron rich and, thereby, susceptible to protonation. The structure of **[6]**<sup>-</sup> (*vide infra*) is in good agreement with this description and further shows that the carbon atoms of the two CAAC<sup>Me</sup> ligands are twisted by *ca.* 20° from the plane defined by the central PNP fragment. This is significantly less than in **7** in which the ligands are almost perpendicular to the PNP plane, presumably to alleviate repulsion between the N-H proton and the substituents on the carbene moiety. As the PNP fragment is better at delocalizing electron density than an NNN unit in **I**, the geometry around the central nitrogen atom in **7** is planar, not pyramidal, complemented with increased phosphinidene character at the P atoms. Calculations probing the possible reactivity of **7** as a hydrogen atom donor (*vide supra*) showed that the transformation **7** → **4** + ½ H<sub>2</sub> has a positive reaction enthalpy of 68 kJ mol<sup>-1</sup> at 298 K in the gas phase, in agreement with experimental observations of the stability of **7**.



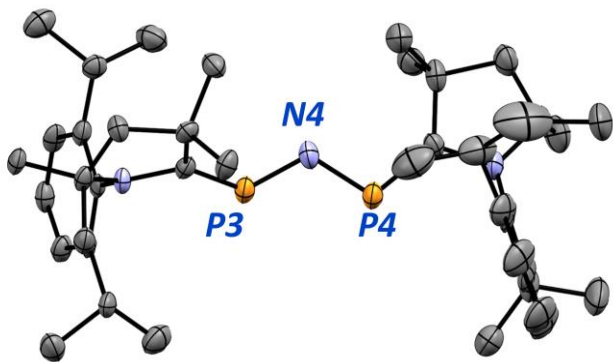
**Figure 7.** Molecular structure of **7**. Ellipsoids are drawn at 50% probability. Hydrogen atoms attached to carbon are omitted. Select bond lengths (Å) and angles (°) [calculated values in square brackets]: N1-P1 1.732(4) [1.718]; N1-P2 1.719(3) [1.718]; N1-H1 0.78(5) [1.007]; C1-P1 1.735(3) [1.723]; C21-P2 1.742(5) [1.723]; C1-N2 1.364(5) [1.360]; C21-N3 1.369(5) [1.360]; P1-N1-P2 123.6(2) [121.3]; P1-N1-H1 118(3) [119.4], P2-N1-H1 118(3) [119.4].

While both the apparent solution structure and protonation of **K6<sub>sol</sub>** is consistent with the alkali metal amide formulation, its solid-state structure reveals this descriptor to belie the rich coordination available to anion [**6**]<sup>−</sup>. Deep red crystals suitable for X-ray diffraction experiments could be grown from a toluene/n-hexane mixture, the analysis of which shows the solid-state structure to be neither a dimer with a bridging K<sub>2</sub>N<sub>2</sub> core, nor a toluene solvate typical of bulky potassium amide species.<sup>89-92</sup> Instead, an asymmetric dimeric solvent free structure **K262** was obtained (Scheme 4, Figure 8) in which neither fragment binds to potassium in κ<sup>1</sup>-N or μ<sup>2</sup>-N fashion expected of bulky potassium amides. In **K262**, one fragment bridges two inequivalent potassium ions through the PNP core, binding to each in κ<sup>1</sup>-P fashion, while the diisopropylphenyl fragments of both CAAC<sup>Me</sup> ligands associate to both potassium ions through cation-π interactions. The other fragment associates with one potassium ion through the π-face of the PNP moiety in η<sup>3</sup>-fashion, while the diisopropylphenyl group of one of the CAAC<sup>Me</sup> ligands interacts with the other potassium ion through cation-π interactions. Dissolution of crystals of **K262** in C<sub>6</sub>D<sub>6</sub> and analysis by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed resonances matching the spectrum of the symmetric species **K6<sub>sol</sub>**, indicating that the dimeric structure is disassembled by interactions with the solvent.



**Figure 8.** Molecular structure of **K262**. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) for **K262**: N1-P1 1.647(2); N1-P2 1.646(2); P1-K2 3.2395(9); P2-K1 3.215(1); C1-P1 1.702(3); C21-P2 1.705(3); N4-P3 1.677(2); N4-P4 1.670(2); N4-K2 2.760(2); P3-K2 3.5548(9); P4-K2 3.338(1); C41-P3 1.701(1); C61-P4 1.700(3); P1-N1-P2 115.2(1); P3-N4-P4 112.3(1).

To better examine the structure and bonding of free anion  $[6]^-$  in the absence of potentially confounding influence from potassium ions, a freshly prepared THF solution of **K6<sub>sol</sub>** was treated with [2.2.2]-cryptand that resulted in subtle darkening of the solution, from which charge-separated salt  $[K_{\text{crypt}}][6]$  could be isolated as red-orange crystalline needles after work-up (Scheme 4, Figure 9).  $[K_{\text{crypt}}][6]$  crystallizes with two sets of independent molecules per asymmetric unit, with the anionic fragments featuring similar bond lengths, differing mostly in the central PNP bond angle ( $119.1(3)^\circ$  vs.  $114.5(3)^\circ$ ). The geometry optimized structure of  $[6]^-$  has a PNP bond angle of  $116.7^\circ$  (Figure 9), exactly in the middle of the two experimental angles, which suggests that the variance observed in the solid-state data can be attributed to packing effects.



**Figure 9.** Molecular structure of  $[6]^-$ . Ellipsoids are shown at 50% probability. Only one crystallographically independent molecule of  $[6]^-$  is shown. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) [calculated values in square brackets]: N4-P3 1.674(4) [1.650]; N4-P4 1.641(5) [1.650]; P3-C41 1.699(4) [1.698]; P4-C61 1.707(5) [1.698]; P3-N4-P4 119.1(3) [116.7].

Curiously, despite the diamagnetic nature of **6**, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $[\text{K}_{\text{crypt}}][\mathbf{6}]$  contain only resonances attributable to the potassium-cryptate cation (Figure S16), while the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a broad signal at 205.9 ppm ( $\nu_{1/2} = 450$  Hz, Figure S17), suggestive of paramagnetic character. In the solid state,  $[\text{K}_{\text{crypt}}][\mathbf{6}]$  is EPR silent, while in solution only the signal for **4** was detected, indicating facile reoxidation despite the use of rigorously purified solvents.

## Conclusions

In summary, this work presents the first synthesis of a carbene-stabilized PNP radical, **4**, in a convenient one-pot procedure from free carbene and phosphazene salt  $[\text{Cl}_3\text{PNPCl}_3][\text{Cl}]$  by formal  $7 e^-$  reduction. The radical exhibits a delocalized electronic structure, with spin density distributed almost equally between the central nitrogen atom and the carbene ligands. Radical **4** was amenable to both one electron oxidation and reduction to formal nitrenium and amide species  $[\mathbf{5}]^+$  and  $[\mathbf{6}]^-$ , respectively.  $[\mathbf{5}]^+$  exists in a dynamic equilibrium between the expected bent nitrenium structure  $[\mathbf{5}_b]^+$  and a linear heteroallene like species  $[\mathbf{5}_a]^+$ , which has not been previously observed, and may have important implications for the growing field of cationic nitrogen chemistry. While displaying some chemistry typical of amides, such as nitrogen-centered protonation, the anion  $[\mathbf{6}]^-$  also exhibits exceptional flexibility in its coordination mode, suggestive of a potentially diverse

coordination chemistry, and may serve as convenient synthon for nucleophilic installation of a redox active fragment to inorganic and organic compounds. The sum of these findings shows that the bonding and structure of low-valent PNP species differ substantially from the previously reported all-nitrogen and all-phosphorus congeners, across multiple species and oxidation states, and suggests that other binary PN fragments may display unexpected properties and accordingly warrant further investigation.

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