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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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**ABSTRACT:** Herein we report the synthesis of the acyclic carbene-stabilized diphospha(aminyl) radical CAAC<sup>Me</sup>PNPCAAC<sup>Me</sup> **4** (CAAC<sup>Me</sup>=1-[2,6-bis(isopropyl)phenyl]-3,3,5,5-tetramethyl-2-pyrrolidinylidene) by a facile one-pot, 7-electron reduction of hexachlorophosphazene chloride [Cl<sub>3</sub>PNPCl<sub>3</sub>][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 [**5**]<sup>+</sup> and [**6**]<sup>-</sup>, respectively. The cation [**5**]<sup>+</sup> exhibits conformational flexibility in the solution state between the expected W-shaped geometry [**5**<sub>b</sub>]<sup>+</sup> and a previously unobserved linear heteroallene type structure [**5**<sub>a</sub>]<sup>+</sup>, which was characterized in the solid state. The equilibrium was explored both computationally and experimentally, showing that [**5**<sub>a</sub>]<sup>+</sup> is favored over [**5**<sub>b</sub>]<sup>+</sup> both enthalpically ( $\Delta H = -2.9 \times 10^3 \pm 80$  J mol<sup>-1</sup>) and entropically ( $\Delta S = 4.2 \pm 0.25$  J mol<sup>-1</sup> K<sup>-1</sup>). The formal amide [**6**]<sup>-</sup> 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 **K26**<sub>2</sub>, which exhibits both  $\mu,\kappa$ -P, $\kappa$ -P and  $\eta^3$ -PNP coordination modes. Protonation of [**6**]<sup>-</sup> leads to the formation of an amine **7**, which features a trigonal planar geometry around nitrogen.

# Introduction

The design of stable nitrogen radicals is a longstanding challenge in synthetic chemistry.<sup>1-3</sup> Acyclic aminyl radicals of the type 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.



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 (Cl<sub>3</sub>P=NTMS) and hexachlorophosphazene chloride ([Cl<sub>3</sub>PNPCl<sub>3</sub>][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 Cl<sub>3</sub>P=NTMS and [Cl<sub>3</sub>PNPCl<sub>3</sub>][Cl] with cyclic alkylamino carbene 1-[2,6-bis(isopropyl)phenyl]-3,3,5,5-tetramethyl-2-pyrrolidinylidene (CAAC<sup>Me</sup>).

#### **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 CAAC<sup>Me</sup>, 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 [CAAC<sup>Me</sup>-Cl][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 PCl<sub>3</sub> completed the PNP core, leading to a single product as observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectrometry with two resonances integrating 1:1 at 176.2 and 109.5 ppm (Figure S22). These data were assigned to the CAAC<sup>Me</sup>stabilized *P*-chloro-*N*-dichlorophosphino-iminophosphine **2** based on its solid-state structure (Figure 1) and mass spectrum (M<sup>+</sup> = 466.10 amu, {M-Cl}<sup>+</sup> = 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-Cl 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-Cl 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][C1] (Figure 1) in which the cation  $[3]^+$  is present as a racemate. This suggests that the minor species observed in the solution is the *meso* diastereomer of  $[3]^+$  (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  $[3]^+$  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  $[3]^+$  are similar to N-heterocyclic carbene adducts of stable iminophosphines reported by Burford and coworkers,67-68 and include unusually small Ccarbene-P-Cl angles (ca. 90°) along with long Ccarbene-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 [ClPNPC1][Cl]. The cation can be described with resonance structures  $[Cl-P^+N=P-Cl] \leftrightarrow [Cl-P=N-P^+Cl]$  in which the empty porbital 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 [ClPNPC1]<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**][C1], the reaction of [Cl<sub>3</sub>PNPCl<sub>3</sub>][C1] with 4 eq. (or more) of CAAC<sup>Me</sup> in THF solution was found to lead to rapid formation of a colorless solution over a yellow precipitate. Dissolution of the precipitate in CD<sub>2</sub>Cl<sub>2</sub> and subsequent NMR analysis revealed the presence of two <sup>31</sup>P{<sup>1</sup>H} resonances ( $\delta_P = 141.6, 108.1$ ) in a *ca*. 1:2 ratio (Figure S2), corresponding to [**3**]<sup>+</sup>, while the <sup>1</sup>H NMR spectrum is consistent with the formation of three CAAC<sup>Me</sup> containing compounds in an approximately 6:2:1 ratio (Figure S3). The latter two resonances match the spectrum for [**3**]<sup>+</sup>, while the most intense one is consistent with the formation of 2 eq. of the 2-chloropyrrolium salt [CAAC<sup>Me</sup>-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<sup>Me</sup> effected the 4e<sup>-</sup> reduction of [Cl<sub>3</sub>PNPCl<sub>3</sub>][Cl]. Unfortunately, the similar solubilities of [CAAC<sup>Me</sup>-Cl][Cl] and [**3**]<sup>+</sup> 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<sup>Me</sup>-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<sub>3</sub>PNPCl<sub>3</sub>][Cl] with CAAC<sup>Me</sup> with commonly used strong reducing agents, such as magnesium or potassium, resulted in mixtures of diamagnetic species by <sup>31</sup>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  $C_6D_6$  solution; however, heating  $C_6D_6$  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 ( $\varepsilon = 1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) as well as two less intense absorptions at *ca*. 700 nm ( $\varepsilon = 1.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 340 nm ( $\varepsilon = 2.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) (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  $g_{iso} = 2.004$  and hyperfine coupling to the central nitrogen atom ( $a_N = 5.99$  G) as well as to both phosphorus ( $2 \times a_P = 6.20$  G) and carbene nitrogen atoms ( $2 \times a_N = 3.05$  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 × 2.42 G, in good agreement with the values from spectral simulation. However, at 2 × -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 ( $E_{1/2}^{\text{ox}} = -1.09 \text{ vs. Fc/Fc}^+$ ), which occurs at a significantly more positive potential than that reported for the triazyl radicals **I** and **II** (*cf.*  $E_{1/2}^{\text{ox}} = -1.17/-1.38$  V vs. Ag/AgCl in THF,<sup>17</sup> *ca.*  $-1.76/-1.97 \text{ vs. Fc/Fc}^+$ )<sup>84-86</sup> and a partially reversible reduction event ( $E_{1/2}^{\text{red}} = -2.08 \text{ vs. Fc/Fc}^+$ ), 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 $[5]^+$

Treatment of **4** with one equivalent of the mild oxidant [CPh<sub>3</sub>][SbF<sub>6</sub>] in DCM resulted in an immediate color change from pink to blue-purple, from which a dark blue microcrystalline solid [**5**][SbF<sub>6</sub>] could be isolated in excellent yield (Scheme 3). Analysis of the material by <sup>31</sup>P{<sup>1</sup>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 <sup>1</sup>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 <sup>1</sup>H NMR spectrum (Figure S10). Variable temperature <sup>1</sup>H NMR spectrometry shows a sharpening of both sets of resonances at lower temperatures (Figure S9).



Scheme 3. Oxidation of 4 to  $[5]^+$  and equilibrium between  $[5_a]^+$  and  $[5_b]^+$ 

Analysis of the solid-state structure of  $[5]^+$  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)°) 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 ([**5**<sub>a</sub>]<sup>+</sup>) and W-shaped ([**5**<sub>b</sub>]<sup>+</sup>) geometries are stable minima on the potential energy surface in the gas phase, with [**5**<sub>a</sub>]<sup>+</sup> favored by -11 and -18 kJ mol<sup>-1</sup> in enthalpy and Gibbs energy at 298 K. The calculated chemical shifts of [**5**<sub>a</sub>]<sup>+</sup>and [**5**<sub>b</sub>]<sup>+</sup> are 163.9 and 261.2 ppm, respectively, and in reasonable agreement with the NMR data of [**5**]<sup>+</sup> in solution (*vide supra*). Van't Hoff analysis of the equilibrium in CD<sub>2</sub>Cl<sub>2</sub> (Figure S11) showed that [**5**<sub>a</sub>]<sup>+</sup> is slightly favored over [**5**<sub>b</sub>]<sup>+</sup> 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  $[5_a]^+$ . Ellipsoids are drawn at 50% probability. Hydrogen atoms and counterion are omitted for clarity. Select bond lengths (Å) and angles (°) for  $[5a]^+$  [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  $[5]^+$  is reminiscent of that known for the bis(triphenylphosphine)iminium cation,<sup>66</sup> [Ph<sub>3</sub>PNPPh<sub>3</sub>]<sup>+</sup>, 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  $[5_a]^+$  and  $[5_b]^+$  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,  $C_{carbene}$ -P and  $C_{carbene}$ -N distances. Formally,  $[5]^+$  can be viewed as the biscarbene adduct of the linear [PNP]<sup>+</sup> cation, with electron donation primarily from CAAC<sup>Me</sup> to [PNP]<sup>+</sup>. Natural population and bond orbital analyses conducted for  $[5_a]^+$  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). Secondorder 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 4 and  $[6]^-$ , vide infra). The charge distribution (partial charges of +0.77 and -1.15 e on N and P, respectively) and NBO description of  $[5_b]^+$  is similar to  $[5_a]^+$  but the N atom is  $sp^2$ -hybridized, consistent with the bent PNP angle. Electron localization function (ELF) analyses performed for  $[5]^+$  show a similar picture (Figure S40). In  $[5_a]^+$ , the central N atom is surrounded by two monosynaptic V(N) and two disynaptic V(N,P) basins with average populations of  $2 \times 1.93$  and  $2 \times 1.70$  e<sup>-</sup>, respectively, whereas  $[5_b]^+$  shows one monosynaptic V(N) and two disynaptic V(N,P) basins with populations of 2.59 and  $2 \times 2.28 \text{ e}^-$ , 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 $[6]^{-1}$

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 monometric potassium amide monosolvate (calculated value 778 Da), although the exact solution structure is unclear.



Scheme 4. Reduction of 4 to K6sol 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 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 130.4 ppm (Tol- $d_8$ ), which splits into a doublet (J = 4 Hz) in the <sup>31</sup>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 <sup>31</sup>P NMR spectrum of the isolated material reveals 7 to be the major component (*ca.* 96 %, Figures S13 and S14) while the <sup>1</sup>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 <sup>31</sup>P NMR spectrum and correlation was observed in the <sup>1</sup>H–<sup>31</sup>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 ( $\Sigma_{LN}$ = 359°) 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  $[5]^+$  to  $[6]^-$  through 4, followed by protonation at nitrogen. The reduction introduces two electrons to the  $\pi$ -type LUMO of  $[5]^+$ , *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  $[6]^-$  (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 is 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  $\rightarrow$  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>501</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 **K**<sub>2</sub>6<sub>2</sub> was obtained (Scheme 4, Figure 8) in which neither fragment binds to potassium in  $\kappa^1$ -N or  $\mu^2$ -N fashion expected of bulky potassium amides. In **K**<sub>2</sub>6<sub>2</sub>, one fragment bridges two inequivalent potassium ions through the PNP core, binding to each in  $\kappa^1$ -P fashion, while the diisopropylphenyl fragments of both CAAC<sup>Me</sup> ligands associate to both potassium ions through cation- $\pi$  interactions. The other fragment associates with one potassium ion through the  $\pi$ -face of the PNP moiety in  $\eta^3$ fashion, while the diisopropylphenyl group of one of the CAAC<sup>Me</sup> ligands interacts with the other potassium ion through cation- $\pi$  interactions. Dissolution of crystals of **K**<sub>2</sub>6<sub>2</sub> 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 **K**<sub>6s01</sub>, indicating that the dimeric structure is disassembled by interactions with the solvent.



**Figure 8.** Molecular structure of **K**<sub>2</sub>**6**<sub>2</sub>. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) for **K**<sub>2</sub>**6**<sub>2</sub>: 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<sub>crypt</sub>][6] could be isolated as red-orange crystalline needles after work-up (Scheme 4, Figure 9). [K<sub>crypt</sub>][6] crystalizes 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)° vs. 114.5(3)°). The geometry optimized structure of [6]<sup>-</sup> has a PNP bond angle of 116.7° (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**]<sup>-</sup>. Ellipsoids are shown at 50% probability. Only one crystallographically independent molecule of [**6**]<sup>-</sup> 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 <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[K_{crypt}][6]$  contain only resonances attributable to the potassium-cryptate cation (Figure S16), while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a broad signal at 205.9 ppm ( $v_{\frac{1}{2}} = 450$  Hz, Figure S17), suggestive of paramagnetic character. In the solid state, [Kcrypt][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  $[Cl_3PNPCl_3][Cl]$  by formal 7 e<sup>-</sup> 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  $[5]^+$  and  $[6]^-$ , respectively.  $[5]^+$  exists in a dynamic equilibrium between the expected bent nitrenium structure  $[5_b]^+$  and a linear heteroallene like species  $[5_a]^+$ , 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  $[6]^-$  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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