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# A Cyclic Divalent N(I) Species Isoelectronic to Carbodiphosphoranes

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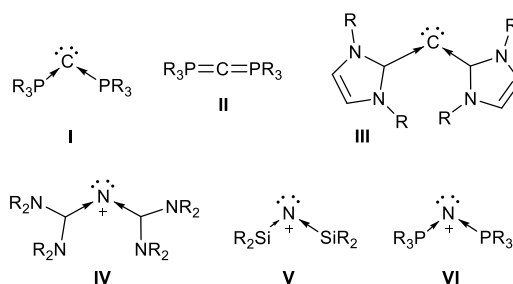
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**The formation of a rare type of diphosphazanium cation is described. Its synthesis features a unique oxidative dealkylation of an iminophosphorane-phosphole by a silver(I) salt. DFT study of this compound reveals the low valent character of the N(I) center.**

Rethinking organic compounds with donor-acceptor bonds instead of electron-sharing ones has allowed the identification of hitherto unrecognized low oxidation states of main group elements and the development of molecules with new properties.<sup>1</sup> In 2006, Frenking et al. reported theoretical evidence suggesting that carbodiphosphoranes ( $R_3P)_2C$  are better described as divalent carbon(0) compounds of type  $R_3P \rightarrow C(0) \leftarrow PR_3$  (Figure 1, I) rather than C(IV)  $R_3P=C=PR_3$  allene species (II).<sup>2,3</sup> This rendition with two lone pairs of electrons at the central carbon accounts for the bent structure of such molecules<sup>4</sup> and explains their ability to undergo double protonation or metalation. Shortly after, carbodicarbenes (NHC) $\rightarrow C(0) \leftarrow$ (NHC) (III) were computationally predicted by Frenking et al.<sup>5,6</sup> and eventually synthesized by Bertrand and coworkers.<sup>7</sup> This new paradigm has continuously stimulated developments in carbon(0) chemistry directed towards catalysis, coordination chemistry, optoelectronics, material applications, etc.<sup>8</sup> The  $L \rightarrow E \leftarrow L$  donor-acceptor way of thinking molecules proved also relevant with low oxidation main group elements such as Si(0), Ge(0), Sn(0), B(I), P(I) and N(I).<sup>9</sup>

In 2009, Patel and Bharatam provided computational evidence that guanidine derivatives such as IV are actually best described as  $L \rightarrow N^{\oplus} \leftarrow L$  species that are isoelectronic to carbodicarbenes.<sup>10</sup> Tamm pointed out that salts containing such cations were reported as early as 1968.<sup>11</sup> A few more carbene-stabilized N(I) compounds were synthesized,<sup>12</sup> as well as bis(silylene)-stabilized monovalent nitrogen complexes (V).<sup>13</sup> They were computationally studied<sup>14</sup> and linked to cations such as  $N^+(N_2)_2$ <sup>15</sup> and  $N^+(CO)_2$ ,<sup>16</sup> as well as previously reported drugs.<sup>17</sup> Revisiting the bonding model of all these carbene-stabilized divalent N(I) species raised the question of the existence of phosphane-stabilized  $NL_2^+$  compounds. Computations showed that  $R_3P \rightarrow N(I)^+ \leftarrow PR_3$  cations (R = Me, Ph) display bent geometries and have two lone pairs of

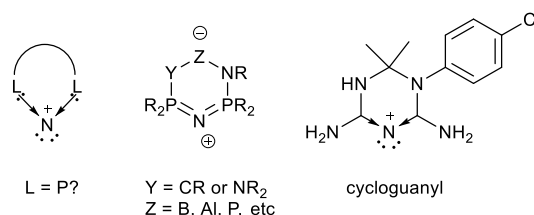
electrons at the central nitrogen atoms (VI).<sup>10,14</sup> The corresponding salts such as  $[X][N(PPh_3)_2]$ <sup>18</sup>,  $[X][N(P(NMe_2)_3)_2]$ <sup>19</sup> and others were indeed characterized in the solid state.<sup>20</sup>



**Figure 1.** Representative structures of carbodiphosphoranes (I, II), carbodicarbenes (III) and divalent N(I) cations (IV, V and VI).

The main difference between isoelectronic  $L \rightarrow C \leftarrow L$  and  $L \rightarrow N^{\oplus} \leftarrow L$  species is the much lower nucleophilicity of the latter due to the formal positive charge.<sup>12b</sup> Their low nucleophilicity and base resistance explain the applicability of such cations, not in coordination chemistry in contrast to C(0) species,<sup>21</sup> but in medicinal chemistry<sup>16</sup> and as phase transfer organocatalysts for the carbodicarbenes analogues,<sup>12c,22,23</sup> or as spectator cations for the carbodiphosphorane analogues.<sup>12b</sup>

A few cyclic  $[R_3P=N^+=PR_3]$  systems have also been described as P(V)-N(III) species. Most of them belong to the 6-membered cyclophosphazene type (Figure 2) and thus cannot be related to bis-phosphane chelated N(I) species.<sup>24</sup> Expanding the family of phosphane-stabilized divalent N(I) compounds appears useful for several reasons: *i*) phosphane ligands are readily available. *ii*) Bis-phosphanes are much more common than bis-carbenes. In fact, to the best of our knowledge, only the cycloquanyl cation and related compounds have been recognized so far as a cyclic divalent N(I) species (Figure 2).<sup>17</sup> *iii*) Chelating ligands could lead to more acute bending angles and possibly affect the electronic properties of the N(I) center.

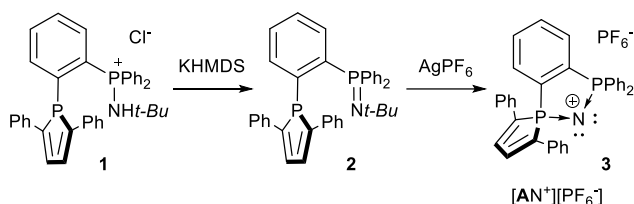


**Figure 2.** Cyclic divalent N(I) species?

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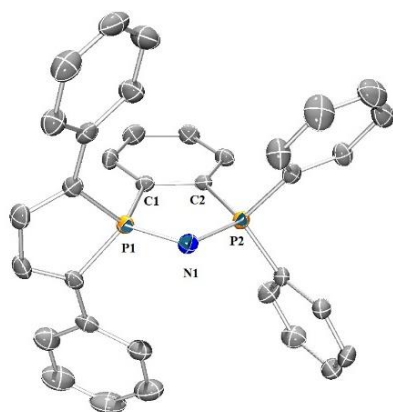
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We describe herein the serendipitous isolation of a cyclic divalent bis-phosphane stabilized nitrenium ion and its theoretical analysis. With the aim to synthesize some new chelating ligands derived from phospholes and iminophosphoranes,<sup>25</sup> compound **1** (Scheme 1) was prepared by *ortho*-lithiation of [PPh<sub>3</sub>-NH<sup>t</sup>Bu]<sup>+</sup>[Br<sup>-</sup>] with BuLi,<sup>26</sup> followed by addition of 1-cyanophosphole-2,5-diphenylphosphole.<sup>27</sup> After aqueous workup, **1** was isolated in 70% as a yellow solid. The deprotonation of **1** with potassium hexamethyldisilazane gave the desired phosphole-iminophosphorane derivative **2**. The potassium salt was removed by centrifugation and AgPF<sub>6</sub> was added in an attempt to make the corresponding silver complex. However, after overnight stirring at room temperature, compound **3** precipitated from the reaction mixture (65% yield over the two steps). The two phosphorus nuclei of this compound resonate at 55.9 and 58.7 ppm in CD<sub>2</sub>Cl<sub>2</sub> (<sup>3</sup>J<sub>P,P</sub> = 8.0 Hz). These signals are more deshielded than those reported for phosphole silver complexes<sup>28</sup> but in the range of those described for a cyclic iminophosphorane silver complex.<sup>29</sup>



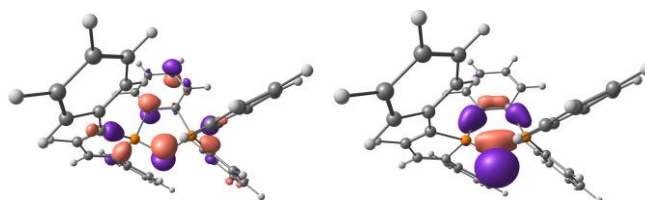
**Scheme 1.** Synthesis of the cyclic divalent N(I) species **3** starting from the aminophosphonium **1**

The *tert*-butyl free diphosphaenium structure of **3** was evidenced by X-ray diffraction analysis (Figure 3).<sup>5</sup> It displays a planar bicyclic structure. The P-N bonds have similar lengths (1.600(2) and 1.614(2) Å). These values are typical of those measured in iminophosphoranes and are quite shorter than those expected for single P-N bonds.<sup>30</sup> The P1-N1-P2 angle in **3** is 112.8(1)°. The phosphole plane is almost orthogonal to the bicycle plane (dihedral angle 86.12°), while the phenyl substituents are tilted relative to the phosphole plane by 9.3 and 37.0°. It seems clear that the iminophosphorane **2** has undergone a Ag(I)-promoted oxidative amine dealkylation, followed by P-N bond formation. We are not aware of any similar reactivity pattern described in the literature apart from the photochemical N-C bond cleavage of Ph<sub>3</sub>P=N<sup>t</sup>Bu.<sup>31</sup>



**Figure 3.** Molecular structure of the cyclic divalent N(I) cation **3**.<sup>5</sup> Thermal ellipsoids are drawn at the 50% probability level. H atoms, counterion (PF<sub>6</sub><sup>-</sup>) are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1-N1 1.600(2), P2-N1 1.614(2), P2-C2 1.811(3), C1-C2 1.398(4), P1-C1 1.807(3); P1-N1-P2 112.8(1), N1-P1-C1 103.1(1), N1-P2-C2 102.6(1), C2-C1-P1 110.7(2), C1-C2-P2 110.7(2).

To gain insight into the electronic properties of the title compound, DFT calculations were performed at the M062X/6-311G(d,p) level of theory (see the ESI for details). The cationic part of **3** (noted AN<sup>+</sup>) has been computed, as well as its unknown C(0) analogue AC. We also used the following parent compounds: (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>, (Me<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>, (Ph<sub>3</sub>P)<sub>2</sub>C and (Me<sub>3</sub>P)<sub>2</sub>C, which were already computed,<sup>10,14</sup> but not at the same level of theory. Analysis of the frontier orbitals revealed the presence of two lone pairs of electrons at the central atoms. The HOMOs of (Me<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>, (Ph<sub>3</sub>P)<sub>2</sub>C and AC have π-type symmetry, with the largest coefficients at the central nitrogen and carbon atom respectively. The HOMO-1 orbitals have σ-type symmetry, mainly localized at the central atoms. For AN<sup>+</sup> and (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>, the HOMOs are concentrated on the aromatic rings. Similar π- and σ-orbitals located at the central atom can yet be found in HOMO-9/HOMO-12 and HOMO-12/HOMO-13 respectively (Figure 4; see the ESI for the other compounds).



**Figure 4.** HOMO-9 (left) and HOMO-12 (right) of the AN<sup>+</sup> species (cationic part of **3**)

The two lone pairs can give rise to donor-acceptor adducts with electrophiles such as H<sup>+</sup> or AuCl (Table 1). The first and second proton affinities (PA)<sup>31</sup> are much higher for AN<sup>+</sup> and (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> than for (Me<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>. They are yet much lower than those computed for carbodiphosphoranes, especially the second PA.<sup>14b</sup> Although the level of the π- and σ-orbitals is not the only factor which determines the donor strength,<sup>14b</sup> this correlation is basically respected. It is noticeable that PPh<sub>3</sub> and **A** strongly strengthen the N-H bonds compared to PMe<sub>3</sub> (~ 167 vs 137 kcal/mol for the 1<sup>st</sup> PA and 54/64 vs 1.5 kcal/mol for the 2<sup>nd</sup> PA).

**Table 1.** Calculated PNP angles, eigenvalues ε of selected orbitals, proton affinities (PA) and bond dissociation energies.

$$\begin{aligned} & \text{1}^{\text{st}} \text{ PA } (-\Delta H_{298}) & \text{2}^{\text{nd}} \text{ PA } (-\Delta H_{298}) \\ \text{L}_2\ddot{\text{E}}: + \text{H}^+ & \longrightarrow \text{L}_2\ddot{\text{E}}\text{H}^+ & + \text{H}^+ & \longrightarrow \text{L}_2\text{EH}_2^{2+} \\ \\ & \text{1}^{\text{st}} D_e (-\Delta E_{298}) & \text{2}^{\text{nd}} D_e (-\Delta E_{298}) \\ \text{L}_2\ddot{\text{E}}: + \text{AuCl} & \longrightarrow \text{L}_2\ddot{\text{E}}\text{AuCl} & + \text{AuCl} & \longrightarrow \text{L}_2\text{E}(\text{AuCl})_2 \end{aligned}$$

(E = N<sup>+</sup> or C)

AE

L <sub>2</sub> E	PNP (°)	ε(HOMO-x) (eV)	PA (kcal/mol)		D <sub>e</sub> (AuCl) (kcal/mol)	
			1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>

AN <sup>+</sup>	113.6	-12.01 (x=9) -12.73 (x=12)	167.2	54.1	39.5	26.7
(Ph <sub>3</sub> P) <sub>2</sub> N <sup>+</sup>	135.2	-12.11 (x=12) -12.24 (x=13)	167.3 <sup>a</sup>	64.6	28.1 <sup>c</sup>	27.6
(Me <sub>3</sub> P) <sub>2</sub> N <sup>+</sup>	147.3	-12.54 (x=0) -12.65 (x=1)	137.4 <sup>b</sup>	1.5	28.4	21.8
AC	105.3	-6.15 (x=0) -6.78 (x=1)	288.2	178.8	76.0	55.4
(Ph <sub>3</sub> P) <sub>2</sub> C	124.9	-6.01 (x=0) -6.41 (x=1)	283.5	187.3	70.0 <sup>d</sup>	60.8
(Me <sub>3</sub> P) <sub>2</sub> C	134.0	-5.73 (x=0) -5.97 (x=1)	281.9	157.5	75.4	62.9

<sup>a</sup> 167.4 kcal/mol in ref 14b. <sup>b</sup> 139.5 kcal/mol in ref 10. <sup>c</sup> 25.9 kcal/mol in ref 14b. <sup>d</sup> 63.1 kcal/mol in ref 14b.

This effect is not obvious on the 1<sup>st</sup> PA of the carbodiphosphoranes, which remains in a narrow range (288–282 kcal/mol), and a bit more significant on the 2<sup>nd</sup> PA (179/187 vs 158 kcal/mol). N(I) compounds also form weaker donor-acceptor adducts with one or two AuCl units compared to carbodiphosphoranes.<sup>33</sup> Nevertheless, the BDE of the monogold complexes is significantly higher with the cyclic AN<sup>+</sup> species than with (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> or (Me<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> (~ 40 vs ~ 28 kcal/mol). On the other hand, the second BDE is similar between AN<sup>+</sup> and (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> (~ 27 kcal/mol), but higher than that of (Me<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> (~ 22 kcal/mol). Going back to the  $\epsilon$  (HOMO-x) eigenvalues, one can infer that the cyclic nature of AN<sup>+</sup> renders the central nitrogen a better  $\pi$ -donor, which in first approximation makes it better suited to react with transition metals. At the same time, the  $\pi$  and the  $\sigma$  orbitals are low-lying compared to carbodiphosphoranes, which might considerably reduce their nucleophilicity. In that respect, attempts to react **3** with AuCl(THT), GaCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> and HBF<sub>4</sub>·OEt<sub>2</sub> were unsuccessful.

In conclusion, an unprecedented silver(I)-promoted oxidative amine dealkylation of an iminophosphorane-phosphole allowed the synthesis of a new type of bis-phosphane chelated nitrenium compound. According to its theoretical analysis, this species is best described as a divalent low oxidation N(I) species holding two lone pairs at the nitrogen atom. It is isoelectronic to carbodiphosphoranes but much less nucleophilic.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

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