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A Cyclic Divalent N(I) Species Isoelectronic to Carbodiphosphoranes

Jiaxin Tian,^a Marie Cordier,^b Christophe Bour,^a Audrey Auffrant^{*b} and Vincent Gandon^{*ab}

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The formation of a rare type of diphosphazenium 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.¹ In 2006, Frenking et al. reported theoretical evidence suggesting that carbodiphosphoranes (R₃P)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).^{2,3} This rendition with two lone pairs of electrons at the central carbon accounts for the bent structure of such molecules⁴ 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.5,6 and eventually synthesized by Bertrand and coworkers.⁷ This new paradigm has continuously stimulated developments in carbon(0) chemistry directed towards catalysis, coordination chemistry, optoelectronics, material applications, etc.⁸ 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).9

In 2009, Patel and Bharatam provided computational evidence that guanidine derivatives such as IV are actually best described L→N⊕←L as species that are isoelectronic to carbodicarbenes.¹⁰ Tamm pointed out that salts containing such cations were reported as early as 1968.¹¹ A few more carbenestabilized N(I) compounds were synthesized,¹² as well as bis(silylene)-stabilized monovalent nitrogen complexes (V).13 They were computationally studied¹⁴ and linked to cations such as $N^{\scriptscriptstyle +}(N_2)_2{}^{15}$ and $N^{\scriptscriptstyle +}(CO)_2,{}^{16}$ as well as previously reported drugs.¹⁷ Revisiting the bonding model of all these carbenestabilized 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

Ecole Polytechnique, Institut Polytechnique de Paris, route de Saclay, 91120 Palaiseau France. Email: audrey.auffrant@polytechnique.edu electrons at the central nitrogen atoms (VI).^{10,14} The corresponding salts such as $[X][N(PPh_3)_2]^{18}$, $[X][N(P(NMe_2)_3)_2]^{19}$ and others were indeed characterized in the solid state.²⁰



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.^{12b} Their low nucleophilicity and base resistance explain the applicability of such cations, not in coordination chemistry in contrast to C(0) species,²¹ but in medicinal chemistry¹⁶ and as phase transfer organocatalysts for the carbodicarbenes analogues,^{12c,22,23} or as spectator cations for the carbodiphosphorane analogues.^{12b}

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.²⁴ 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 cycloguanyl cation and related compounds have been recognized so far as a cyclic divalent N(I) species (Figure 2).¹⁷ *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?

a. Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, Université Paris-Saclay, Bâtiment 420, 91405 Orsay cedex (France). Email: vincent.gandon@universite-paris-saclay.fr

^{b.} Laboratoire de Chimie Moléculaire (LCM), CNRS UMR 9168

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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,²⁵ compound **1** (Scheme 1) was prepared by ortho-lithiation of [PPh₃-NH^tBu⁺][Br⁻] with BuLi,²⁶ followed by addition of 1-cyanophosphole-2,5-diphenylphosphole.²⁷ 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 AgPF₆ 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_2Cl_2 (${}^{3}J_{P,P}$ = 8.0 Hz). These signals are more deshielded than those reported for phosphole silver complexes²⁸ but in the range of those described for a cyclic iminosphophorane silver complex.²⁹



 $\mbox{Scheme 1}.$ Synthesis of the cyclic divalent N(I) species $\mbox{\bf 3}$ starting from the aminophosphonium $\mbox{\bf 1}$

The *tert*-butyl free diphosphazenium structure of **3** was evidenced by X-ray diffraction analysis (Figure 3).[§] 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.³⁰ 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 Ph₃P=NtBu.³¹



Figure 3. Molecular structure of the cyclic divalent N(I) cation **3**.[§] Thermal ellipsoids are drawn at the 50% probability level. H atoms, counterion (PF₆⁻) 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⁺) has been computed, as well as its unknown C(0) analogue AC. We also used the following parent compounds: $(Ph_3P)_2N^+$, $(Me_3P)_2N^+$, $(Ph_3P)_2C$ and $(Me_3P)_2C$, which were already computed,^{10,14} 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 $(Me_3P)_2N^+$, $(Ph_3P)_2C$ 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^+ and $(Ph_3P)_2N^+$, 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⁺ species (cationic part of 3)

The two lone pairs can give rise to donor-acceptor adducts with electrophiles such as H⁺ or AuCl (Table 1). The first and second proton affinities (PA)³¹ are much higher for **A**N⁺ and (Ph₃P)₂N⁺ than for (Me₃P)₂N⁺. They are yet much lower than those computed for carbodiphosphoranes, especially the second PA.^{14b} Although the level of the π - and σ -orbitals is not the only factor which determines the donor strength,^{14b} this correlation is basically respected. It is noticeable that PPh₃ and **A** strongly strengthen the N-H bonds compared to PMe₃ (~ 167 vs 137 kcal/mol for the 1st PA and 54/64 vs 1.5 kcal/mol for the 2nd PA).

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



1 st

2nd

2nd

AN⁺	113.6	-12.01 (x=9) -12.73 (x=12)	167.2	54.1	39.5	26.7
(Ph ₃ P) ₂ N ⁺	135.2	-12.11 (x=12)	167.3ª	64.6	28.1 ^c	27.6
(Me₃P)₂N⁺ A C	147.3 105.3	-12.24 (x=13) -12.54 (x=0)	137 Ab	1 5	28.4	21.9
		-12.65 (x=1)	137.4*	1.5	28.4	21.0
		-6.78 (x=1)	288.2	178.8	76.0	55.4
(Ph ₃ P) ₂ C	124.9	-6.01 (x=0) -6.41 (x=1)	283.5	187.3	70.0 ^d	60.8
(Me ₃ P) ₂ C	134.0	-5.73 (x=0)	281.9	157.5	75.4	62.9
		-5.97 (x=1)				

^{*a*} 167.4 kcal/mol in ref 14b. ^{*b*} 139.5 kcal/mol in ref 10. ^{*c*} 25.9 kcal/mol in ref 14b. ^{*d*} 63.1 kcal/mol in ref 14b.

This effect is not obvious on the 1st PA of the carbodiphosphoranes, which remains in a narrow range (288-282 kcal/mol), and a bit more significant on the 2nd PA (179/187 vs 158 kcal/mol). N(I) compounds also form weaker donor-acceptor adducts with one or two AuCl units compared to carbodiphosporanes.³³ Nevertheless, the BDE of the monogold complexes is significantly higher with the cyclic **A**N⁺ species than with (Ph₃P)₂N⁺ or (Me₃P)₂N⁺ (~ 40 vs ~ 28 kcal/mol). On the other hand, the second BDE is similar between **A**N⁺ and (Ph₃P)₂N⁺

(~ 27 kcal/mol), but higher than that of (Me₃P)₂N⁺ (~ 22 kcal/mol). Going back to the ε (HOMO-x) eigenvalues, one can infer that the cyclic nature of **A**N⁺ renders the central nitrogen a better π -donor, which in first approximation makes it better suited to react with transition metals. At the same time, the π and the σ orbitals are low-lying compared to carbodiphosphoranes, which might considerably reduce their nucleophilicity. In that respect, attempts to react **3** with AuCl(THT), GaCl₃, BF₃·OEt₂ and HBF₄·OEt₂ 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.

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