Angewandte
Highlights

PN Chemistry

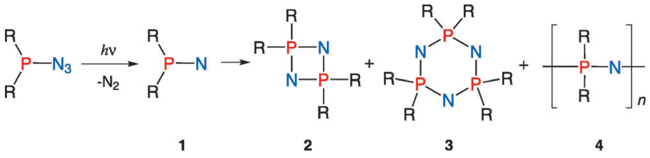
DOI: 10.1002/anie.201208533

Stabilized Transient R_2PN Species**

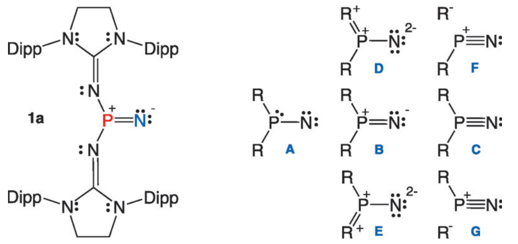
Axel Schulz and Alexander Villinger*

bond theory · nitrenes · phosphazenes · reactive intermediates · stabilization

Transient species play a central role in chemical reactions. Studying such compounds is thus of vital importance when considering how to influence chemical reactions, for example, with regard to the selectivity, yield, or reaction conditions. Investigating the electronic situation, together with tailoring the reactivity of such intermediates by (partial) stabilization, enables selective control of chemical reactions in which transient species occur as key intermediates. The stabilization can be achieved by suitable substitution that, for example, leads to a delocalization of charges or also to kinetic stabilization if very large, bulky residues are used. In the area of phosphorus–nitrogen chemistry, the isolation of a range of highly reactive PN species by specific stabilization has been in the focus for more than 20 years.[1] In this Highlight, we discuss the stabilization of transient R_2PN und R_2NP species on the basis of a study by the Bertrand research group[2a] where they reported the isolation of a long sought after nitridophosphane(V) (denoted by Bertrand and coworkers as stabilized phosphinonitrene (**1**)) of the monomer of oligo/polyphosph(V)-azene (Scheme 1).



Scheme 1. Synthesis of oligo-/polyphosph(V)-azenes by azide decomposition.



Scheme 2. Left: The first isolated nitridophosphane(V) (Dipp = 2,6-diisopropylphenyl). Right: Lewis diagrams of **1**: 1) with a P^{III} atom: **A** (singlet) phosphinonitrene; 2) with a P^{V} atom: **B** isophosph(V)-azene; **C**, **F**, **G**: nitridophosphane(V).

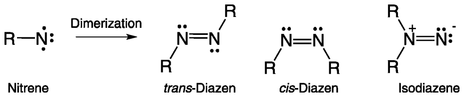
The research groups of Bertrand and Marjoral have been working since the beginning of the 1980s on the breakdown of azidophosphanes ($R_2P\text{-}N_3$) under UV radiation,[2b,c] and postulated the transient occurrence of a highly reactive phosphinonitrene (species **1** in Scheme 1, Lewis representation **A** in Scheme 2) on the basis of specifically deployed trapping reactions (e.g. with MeOH, Me_2NH, Me_3SiCl) or isolated dimers (species **2** in Scheme 1). This assumed intermediate has now been successfully isolated and completely characterized by using a sterically challenging bis(imidazolidine-2-iminato) residue (Scheme 2, left), since species **1a** was found to be stable in solution and in the solid state at room temperature. In an elegant reaction cycle the authors were able to show that **1a** (a special example of family **1**) still possesses enough reactivity to act as a nitrogen atom transfer reagent. Thus, **1a** reacts with isopropylisonitrile to give carbodiimide $R_2P\text{-}NCN\textit{i}Pr$, which in turn can be degraded to $\textit{i}Pr_2NCN$ with isopropyl trifluoromethanesulfonate. The most interesting structural characteristic of **1a** is, apart from the planar P atom, the extremely small P–N distance of 1.457(8) Å, which lies in the range of a P–N triple bond and is even smaller than that in Mes*-N≡P$^+$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) with 1.475(8) Å[1a] (cf. Σr_{cov}: P–N 1.82, P=N 1.62, P≡N 1.44 Å).[1b,c] Calculations show very strongly polarized P–N bonds ($q(P) = 1.92$, $q(N_{terminal}) = -1.22e$) with in-plane and out-of-plane delocalization of the free electron pairs on the N atoms (Scheme 2, right).[1a] The complicated bond situation in the π-bond area of the NP(N)N unit can also be described to a good approximation as Y aromatic, which corresponds to a resonance between the Lewis formulas **B**↔**D**↔**E** (Scheme 2).(3) The energetically best Lewis formula according to a natural bond orbital (NBO) analysis is shown in Scheme 2 (left). This is consistent with the oxidation of the phosphorus atom ($P^{III}\rightarrow P^{V}$), which occurs immediately when the molecular nitrogen splits off under UV radiation. The phosphorus atom transfers its free electron pair almost completely onto the terminal nitrogen atom. This means that the Lewis formula **A** with a P^{III} atom (electron sextet on the N atom) should have the least importance of all the Lewis formulas considered.

---

[*] Prof. Dr. A. Schulz, Dr. A. Villinger
Institut für Chemie Universität Rostock und
Leibniz Institut für Katalyse Rostock
A.-Einstein-Straße 3a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de
Homepage: http://www.schulz.chemie.uni-rostock.de/

[**] This work was supported by the University of Rostock and the Leibniz Institute for Catalysis.

We consider the naming of species **1a** as phosphinonitrene definitely worth discussing, as in our opinion this describes neither the bond situation nor the following chemical stages. We want to lead the discussion entirely in the spirit of Shakespeare's: "*What's in a name? that which we call a rose— By any other name would smell as sweet.*" The following names can be found in the literature for **1**: nitrido-λ^5-phosphane(V), σ^3,λ^5-nitridophosphorane, nitrilo-λ^5-phosphane, isophosph(V)-azene, and phosph(V)-azine. The designation phosphinonitrene is given to a formula analogous to the stabilized carbenes.[4] Nitrenes are described as neutral, electron-poor molecular species with a monovalent nitrogen atom which is surrounded by an electron sextet (Scheme 3).

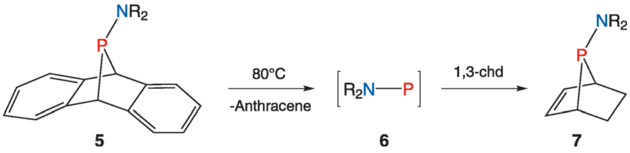


Scheme 3. Dimerization of nitrene to diazene (also diimine).

(In contrast, carbenes have a divalent C atom and no local $C_{\infty v}$ symmetry, as on the N atom.) In the absence of trapping reagents, the naked nitrene R–N dimerizes to form the diazene (Scheme 3). In contrast to the nitrene R–N (and also to the stabilized carbenes), the species **1a** does not dimerize to form a diazene, and the singly coordinated N atom in species **1a** with a charge of $-1.22\,e$ is not electron poor in the σ- or π-bond regions, as the NBO and molecular orbital (MO) analyses also prove. Thus, it is much more the high polarity and less the nitrene character of the P–N bond which produces the high reactivity and which is ultimately responsible for the fast oligomerization (Scheme 1)—unless large sterically challenging residues protect the strongly polarized P–N bond, in particular the strongly negatively charged, otherwise unprotected N atom, as in species **1a**.[5] Both the structural (planar P atom, P–N triple bond length) and theoretical aspects of the bond (strong negative N atom, positive P^V atom) and the experimental results (no NN dimerization, but [2+2] cycloaddition or oligo-/polymerization, no addition to monoolefins or conjugated dienes) show that the λ^3-phosphinonitrene is better understood in terms of the monomer σ^3,λ^5-nitridophosphane(V) or isophosph(V)-azene.[1d]

This situation is in accordance with earlier investigations of transient N*i*Pr$_2$-substituted λ^5-nitridophosphane(V) $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PN}$, which undergoes a [2+2] cycloaddition to give the corresponding cyclodiphosph(V)-azene, which was isolated and structurally characterized as the first phosphazene dimer.[2d] The fact that no trimer **3** or oligomer species **4** could be observed implies kinetic stabilization by the sterically challenging N*i*Pr$_2$ residues. As Wehmschulte et al. showed, small changes in the steric demand are enough to destabilize the dimer with respect to the trimer.[6] Thus, either the dimer bis(azido)cyclodiphosph(V)-azene $[\mathrm{NP(N_3)(2,6\text{-}Mes_2C_6H_3)}]_2$ (**2**) or the trimer *trans*-tris(azido)cyclotriphosph(V)-azene $[\mathrm{NP(N_3)(C_6H_3\text{-}2,6(4\text{-}}t\mathrm{BuC_6H_4)_2)}]_3$ (**3**) was formed from the corresponding terphenyl-substituted diazidophosphanes terP$(\mathrm{N_3})_2$ (terphenyl = ter = 2,6-Mes$_2$C$_6$H$_3$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) or 2,6(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$) by oxidative elimination of nitrogen through an intramolecular Staudinger reaction. The occurrence of a nitridophosphane(V) in the reaction of R^1R^2PCl ($R^1 = R^2 =$ Ph or $R^1 =$ Ph, $R^2 =$ Cl) with Me$_3$Si-NSN-SiMe$_3$ was also discussed; in the presence of a Lewis acid such as GaCl$_3$ this likewise resulted in a cyclodiphosph(V)-azene **2**, stabilized as a GaCl$_3$ adduct.[7] Given the low steric demand of the residue R, the kinetik stabilization from the formation of adducts with GaCl$_3$ or AlCl$_3$ can be regarded as the reason for the occurrence of a dimer instead of the oligomer species. Likewise, the polymerization of phosphoranimine salts $[\mathrm{R_2P{=}NSiMe_3}][\mathrm{X}]$ (R = aryl, alkyl, halogen, OCH$_2$CF$_3$; X = Br, OTf), which are regarded as key intermediates in the thermal cationic condensation polymerization of phosphoranimine monomers, can be prevented by forming adducts with bases such as *N*,*N*-dimethylaminopyridine (dmap), as was shown by Manners and co-workers with a range of N-silylated derivatives.[8] If the base is removed, the formation of trimers **3** or polymeric polyphosph(V)-azenes **4** can be thermally initiated again.

Analogous to the phosphinonitrenes, the constitutional isomers aminophosphinidenes (also aminophosphanylidenes) R$_2$NP can be formally considered as carbene analogues (Scheme 4, species **6**). Just recently, Velian and Cummins succeeded in the production of a dibenzo-7λ^3-phosphanorbornadiene, R$_2$NP**A** (R = SiMe$_3$, *i*Pr; **A** = anthracene, species **5**), by reduction of the corresponding amino(dichloro)phosphane, R$_2$NPCl$_2$, with magnesium anthracene.[9] The phosphanorbornadiene **5** can be considered here as the source of transient aminophosphinidenes **6**. While the thermolysis leads to oligomeric cyclophosphanes $(\mathrm{R_2NP})_n$ (R = SiMe$_3$, $n = 3$; R = *i*Pr, $n = 4$) with release of anthracene, it was shown that the *i*Pr$_2$NP unit can also be trapped in the presence of 1,3-cyclohexadiene (1,3-chd), whereby *i*Pr$_2$NP-(1,3-chd) (**7**) is formed. This carbene-like reactivity had already been observed by Power and co-workers; these species were trapped and structurally characterized from the reaction of (Me$_3$Si)$_2$NPCl$_2$ with Na$_2$[Cr(CO)$_5$] as the reducing agent—both the aminophosphinidene, stabilized as a [Cr(CO)$_5$] complex with the formula $[(\mathrm{Me_3Si})_2\mathrm{NP(Cr(CO)_5)_2}]$, and similarly the dimer diphosphene, $(\mathrm{Me_3Si})_2\mathrm{N\text{-}P{=}P\text{-}N(SiMe_3)_2}$, coordinated to [Cr(CO)$_5$].[10] In addition, Niecke et al. succeeded in the formal release and subsequent transfer/addition, reaction with diisopropylaminophosphinidenes, which were generated in situ by elimination of Me$_3$Si-Cl from *i*Pr$_2$NP(Cl)SiMe$_3$.[11] Thus, the aminophosphinidenes clearly show the expected



Scheme 4. Synthesis of *i*Pr$_2$NP(1,3-chd) via the in situ generation of an aminophosphinidene.

reactivity (PP-dimerization/oligomerization, addition to dienes etc.) corresponding to the analogous Lewis diagram **A** (Scheme 2), in contrast to the formal phosphinonitrene reported by Bertrand and co-workers.

The synthesis of a nitridophosphane(V), R_2PN, the monomer of the (oligo-)polyphosphazenes, which is stable at room temperature, is a milestone in molecular chemistry. Up to now, in situ produced aminophosphinidenes, R_2NP, could only be proven when stabilized on metal fragments or by trapping reactions.

Received: October 23, 2012

---

[1] a) E. Niecke, M. Nieger, F. Reichert, *Angew. Chem.* **1988**, *100*, 1781–1782; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1715–1716; b) P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770–12779; c) E. Niecke, D. Gudat, *Angew. Chem.* **1991**, *103*, 251–270; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 217–237; d) X. Zeng, H. Beckers, H. Willner, *Angew. Chem.* **2009**, *121*, 4922–4925; *Angew. Chem. Int. Ed.* **2009**, *48*, 4828–4831.

[2] a) F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* **2012**, *337*, 1526–1528; b) G. Sicard, A. Baceiredo, G. Bertrand, J.-P. Majoral, *Angew. Chem.* **1984**, *96*, 450–451; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 459–460; c) A. Baceiredo, G. Bertrand, J.-P. Majoral, F. El Anba, G. Manuelt, *J. Am. Chem. Soc.* **1985**, *107*, 3945–3949; d) A. Baceiredo, G. Bertrand, J.-P. Majoral, G. Sicard, J. Jaud, J. Galy, *J. Am. Chem. Soc.* **1984**, *106*, 6088–6089.

[3] a) P. Gund, *J. Chem. Educ.* **1972**, *49*, 100–104; b) A. Gobbi, P. I. MacDougall, G. Frenking, *Angew. Chem.* **1991**, *103*, 1038–1040; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1001–1003.

[4] a) R. H. Crabtree, *Coord. Chem. Rev.* **2007**, *251*, 595–896; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[5] R. Ahlrichs, H. Schiffer, *J. Am. Chem. Soc.* **1985**, *107*, 6494–6498.

[6] R. Wehmschulte, M. A. Khan, S. I. Hossain, *Inorg. Chem.* **2001**, *40*, 2756–2762.

[7] C. Hubrich, D. Michalik, A. Schulz, A. Villinger, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1403–1408.

[8] K. Huynh, E. Rivard, A. J. Lough, I. Manners, *Inorg. Chem.* **2007**, *46*, 9979–9987.

[9] A. Velian, C. C. Cummins, *J. Am. Chem. Soc.* **2012**, *134*, 13978–13981.

[10] R. A. Bartlett, H. V. R. Dias, K. M. Flynn, H. Hope, B. D. Murray, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1987**, *109*, 5693–5698.

[11] a) E. Niecke, R. Streubel, M. Nieger, D. Stalke, *Angew. Chem.* **1989**, *101*, 1708–1710; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1673–1674; b) R. Streubel, E. Niecke, *Chem. Ber.* **1990**, *123*, 1245—1251.