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Phosphorus Mononitride

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A Different View of Coordination Chemistry: Bis(carbene) Adducts of (P ≡ N) and $(P \equiv N)^+$

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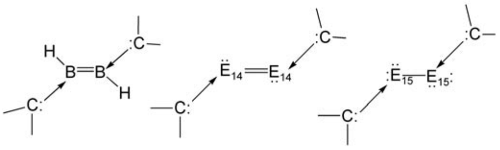
carbene ligands · coordination modes · nitrogen · phosphorus · reactive intermediates

The synthesis and study of small reactive molecules has fascinated generations of chemists. The reactivity of such species and their geometrical and electronic structures has also attracted equal interest. Pragmatic concepts, such as the diagonal relationship in the periodic table or isoelectronic and isolobal compounds, have been fruitful in the correlation of these elusive molecules with existing knowledge and experience. Particularly the chemistry of Group 15 elements provides impressive examples for this idea. In contrast to the inert nature of N_2, which is the only allotrope of the element nitrogen, diphosphorus (P_2) and diarsenic (As_2) are only persistent in the gas phase at high temperatures; under normal conditions, they dimerize to form white phosphorus (P_4) and yellow arsenic (As_4), respectively. To date there is no evidence for the existence of diatomic $P \equiv As$. The only known binary example of a tetrahedral cluster constructed from phosphorus and arsenic atoms is P_3As, which has only recently been prepared and unambiguously characterized.[1] Here the question of small molecules consisting of only P and N atoms arises. The comparison with N_2 and P_2, and with P_4, is obvious. Until now, free monomeric phosphorus mononitride has remained notoriously reluctant towards isolation, despite the fact that numerous compounds with P–N single and double bonds are presented in textbooks and that a P–N triple bond of 1.475 (8) Å has been documented in the stable salt $[2,4,6\text{-}tert\text{-}Bu_3C_6H_2\text{-}N \equiv P]^+[AlCl_4]^-$.[2] Phosphorus mononitride has attracted a lot of interest as a prominent compound in space and in the atmospheres of Jupiter and Saturn. In the laboratory, gaseous PN has been generated by the pyrolysis of solid P_3N_5 at 1050 K[3a] or by halogen abstraction from $(NPCl_2)_3$ with silver metal at 1300 °C in vacuo.[3b] In both cases, PN was trapped in noble gas matrices (Kr, Ar) at $T \leq 20$ K and studied by IR spectroscopy. The PN bond length was experimentally determined to be 1.462 Å, which is close to the calculated value of 1.49 Å.[3c] In contrast to the facile dimerization of P_2 and As_2 in the condensed phase to the familiar tetrahedranes, no such species P_2N_2 could be detected upon warm-up of the matrices to 30 K. Instead, the transient and non-isolable trimeric P_3N_3 was observed. The smallest discrete binary PN molecule to date is the liquid explosive hexaazidocyclotriphosphazene P_3N_{21},[4a] whereas P_3N_5 has a three-dimensional polymeric structure in the solid state.[4b,c] In contrast to the plethora of well-defined transition metal complexes with N_2, P_2, and As_2 ligands, only one single report describes the reaction of PN with metal atoms of the copper group in a matrix at 10 K. The obtained complexes have only been characterized by IR spectroscopy.[5]

Only recently an alternative and most elegant procedure for the stabilization of small reactive molecules, such as B_2H_2 (**A**),[6a] Si_2 (**B**),[6b] Ge_2 (**C**),[6c] P_2 (**D**),[6d] and As_2 (**E**)[6e] involving adduct formation with nucleophilic cyclic singlet carbenes has been presented.



A

B: E_{14}=Si
C: E_{14}=Ge

D: E_{15}=P
E: E_{15}=As

In keeping with this, Bertrand et al. have succeeded in the isolation of phosphorus mononitride by ligation to two carbene donors.[7] The synthesis of this adduct was achieved by the bromination of the N-heterocyclic carbene **1** and the subsequent ammonolysis of the product (Scheme 1). Deprotonmation of the obtained guanidine derivative **2** by *n*Buli and quenching the lithium derivative with PCl_3 afforded compound **3**. Adduct formation of **3** with the stable cyclic aminoalkyl carbene (CAAC) **4** subsequent magnesium reduction eventually yielded the target molecule **5**.

Compound **5** is indefinitely stable in air, and no decomposition occurs by heating a toluene solution under reflux for 24 h. The single-crystal X-ray diffraction study of **5** reveals a planar *trans*-bent geometry (C-N-P-C torsion angle 179.4°) with bond angles of 102.8(1)° and 122.1(1)° at the central P–N unit. The exocyclic bond lengths C–N (1.28(3) Å) and P–C (1.719(2) Å) indicate multiple bonding. In accordance with the molecular structures of L_2P_2 (**D**)[6d] and L_2As_2 (**E**)[6e] (L = cyclic carbene donor), the central P–N distance of 1.709(2) Å has to be attributed to a single bond. Obviously the bond

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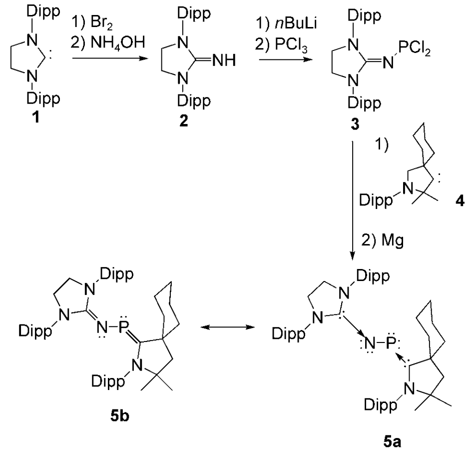

Scheme 1. Synthesis of carbene-stabilized phosphorus mononitride **5**. Dipp = 2,6-diisopropylphenyl.

order $n = 3$ of the free molecules $E \equiv E'$ ($E = E' = P$, As; $E = P$, $E' = N$) decreased from $n = 3$ to $n = 1$ by the formal carbene addition. The electronic ground state of the molecule as that of a P-guanidinyl-functionalized phosphaalkene is better represented by limiting structure **5b** than by **5a**. As was found for P$_2$–dicarbene adduct **D**, compound **5** is also prone to oxidation. The cyclovoltammogram of a THF solution of **5** shows a wave for a reversible one-electron oxidation at $E_{1/2} = -0.51$ V versus Fc$^+$/Fc, and a second irreversible wave at $E_{1/2} = 0.6$ V. Accordingly, derivative **5** is quantitatively oxidized by $[Ph_3C]^+[B(C_6F_5)_4]^-$ on a preparative scale to yield a salt with the radical cation $\mathbf{5}^{+\cdot}$. The complete reversibility of the redox system $\mathbf{5}^{+\cdot}/\mathbf{5}$ is evident from the clean reduction of $\mathbf{5}^{+\cdot}$ with KC$_8$ to the neutral species. According to an X-ray diffraction study, the radical cation maintains a planar *trans*-bent structure, but with a shortened P–N bond (1.645(4) Å) and elongated P–C (1.788(5) Å) and C–N contacts (1.313(5) Å).

What have we learnt?

Bertrand's and Robinson's discoveries impressively confirm the capability of electron-abundant cyclic singlet carbenes to form isolable adducts with small reactive (and otherwise elusive) particles. With respect to the ligation of $P \equiv N$, the potential of this new concept obviously exceeds that of stabilizing instable molecules in transition metal complexes. In view of the great number of unknown small molecules, its limits are not reached at all. In contrast to metal–complex formation between a sterically and electronically unsaturated (Lewis acidic) metal complex fragment and the Lewis basic donor $E \equiv E'$, the new approach is based upon the interaction of $E \equiv E'$ as a Lewis acid with the Lewis basic singlet carbenes. In other words: We now see an "inverse complexation". Moreover, as singlet carbenes such as NHCs are good leaving groups, the use of **5** as a PN transfer reagent is a worthy challenge. Adducts of the type **A**–**E** and **5** would in these cases serve as stable storage compounds for the particular reactive molecule.

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