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Phosphorus Compounds

New Phosphorus Analogues of Nitrogen Classics—No Carbon Copies

*Dietrich Gudat**

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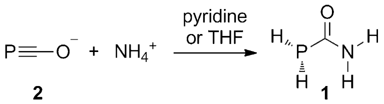
That elements from the same group of the Periodic Table of Elements exhibit similar chemical properties is a basic and widely accepted concept in chemistry, and backed by many cases where compounds of homologous elements with equal stoichiometry exhibit similar structures or reactivity. However, during the last few decades, in particular, chemists have synthesized more and more compounds of heavier main-group elements that had different molecular structures or chemical behavior from their lighter congeners. This development changed the perspective by emphasizing the somewhat neglected aspect that the electronic properties of the heavier elements in a group differ fundamentally from those of the lightest (second row) element.[1] The reasons for this disparity—major factors are the much larger atomic radii of the heavier elements and their reluctance to undergo isovalent hybridization or form multiple bonds—are now well understood,[1] but comparative studies of homologous molecules remain exciting test cases for probing our appreciation of chemistry from new and changing perspectives. Analyzing such examples can help to refine and deepen insight into structure, bonding, and reactivity beyond the particular species involved. From this angle, recent reports[2,3] on two phosphorus-containing analogues of long-known and fundamentally important nitrogen compounds warrant particular consideration.

The recently reported synthesis of parent phosphinecarboxamide (carbamoylphosphine) **1** by Jupp and Goicoechea[2] (Scheme 1) parallels Friedrich Wöhler's epoch-making synthesis of urea from silver cyanate and ammonium chloride, which is often considered the birth of synthetic organic chemistry.[4] Liquid **1** is remarkably air and water stable, and its ability to act as a hydrogen-bond donor through its NH_2 group permitted isolation of a crown ether complex that was characterized by single-crystal X-ray diffraction. The molecule features a planar amide unit with restricted rotation around the C–N bond, and a pyramidal, freely rotating PH_2 moiety. DFT calculations predict a large HOMO–LUMO gap and sizeable HOMO delocalization between the phosphorus and oxygen lone pairs of electrons, which provides a reasonable explanation for the air stability.



Scheme 1. Synthesis of phosphinecarboxamide.

The structural and dynamic properties of **1** reveal nothing unusual, and it is rather its synthesis from the higher congener of cyanate—phosphaethynolate **2**—that deserves a closer look. Anion **2** was first prepared by Becker et al. as early as 1992,[5] but interest was only raised through the recent discovery of alternative synthetic routes.[6] Reaction studies showed that **2** undergoes [2+2] cycloadditions with heterocumulenes and electrophile-induced self-dimerization processes that are uncommon or even unprecedented for cyanate.[6] The studies also showed that both anions also differ in their coordination properties.[7] The reaction of **2** with ammonium salts now establishes a case where the reactivity of phosphaethynolate clearly parallels that of its lighter congener. Although seeming at first glance a paradox, both the analogy and the disparities in the behavior of the two anions can be traced back to the same origins, namely a higher electrophilicity of PCO^- compared to NCO^- and a stronger tendency of the former to forsake π bonds for the formation of σ-bonded frameworks, and may thus be considered to manifest different sides of the typical reactivity of a "heavier" multiple bond system. Interestingly, heating a solution of **1** does not return the starting materials, but produces PH_3 and isocyanic acid.[2] Since there seems to be no evidence that this process is reversible, one may argue that the synthesis of **1** from PH_3 and isocyanic acid is unfeasible, and the synthetic potential of the phosphorus-containing multiple bond in PCO^- is a crucial prerequisite for the formation of **1**.

In a further noteworthy reaction, Robinson and coworkers studied the oxygenation of the diphosphorus species **3** to give **4** (Scheme 2), which features an O_2PPO_2 core enclosed by two imidazole fragments.[3] Similar to starting material **3**, the product was considered[3] a donor–acceptor

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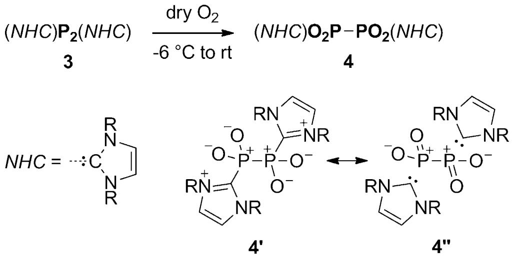
[*] Prof. Dr. D. Gudat
Institut für Anorganische Chemie, University of Stuttgart
Pfaffenwaldring 55, Stuttgart (Germany)
E-mail: gudat@iac.uni-stuttgart.de
Homepage: http://www.iac.uni-stuttgart.de/AKGudat



Scheme 2. Synthesis of **4** and archetypal resonance structures **4′** and **4″** (lone pairs of electrons on atoms other than C are omitted; the "no-bond" notation for the P−C bonds of **4″** was chosen to avoid the need to draw arrows in a resonance structure; R = 2,6-*i*$Pr_2C_6H_3$).

complex consisting of a Lewis-acidic and formally neutral diphosphorus tetroxide unit, which by itself represents a unique topological analogue of N_2O_4, and two neutral carbene ligands which extend the phosphorus coordination sphere to tetrahedral (this tendency is a well-known corollary of the greater atomic radius and lower electronegativity of phosphorus atom compared to nitrogen and is, for example, also visible in the structural divergence of polymeric $(HPO_3)_n$ and monomeric HNO_3). Support for this interpretation was mainly derived from XRD studies on anhydrous **4** and the dihydrate **4**$(H_2O)_2$, as well as from complementary DFT calculations. The structural studies revealed that the P−C and P−P bonds are longer than normal and vary in length upon hydration, and that the P−O bonds exhibit partial double bond character. The calculations predict low covalent P−C and P−P bond orders, but also suggest that the highly polar P_2O_4 core carries a net negative charge of −0.8. While the weakness and flexibility of the P−C bonds may indeed be seen as indicators of dative bonding,[8] the sizable charge transfer between the molecular fragments also implies some betaine character, and putting all the pieces together thus yields an ambiguous picture. Along with the recent criticism on the inflationary use of dative bonds in the discussion of the electronic structure of main-group element compounds,[9] the bonding in **4** is presumably more realistically described in terms of a superposition of both donor–acceptor-type (e.g. **4″**) and zwitterionic (e.g. **4′**) canonical structures. This representation of **4** as a hybrid between a Lewis base complex of P_2O_4 and a zwitterionic hypophosphonate is in line with the similarity of the bond lengths in the P_2O_4 units of **4** and a structurally characterized hypophosphate salt with the anion $[(RO)O_2P\text{-}PO_2(OR)]^{2-}$ ($R = SiMe_3$),[10] as well as with the reported description of pyridine adducts of dithiophosphoryl chloride, $(py)(Cl)PS_2$,[11] and some phosphinates featuring isolated, carbene-substituted RPO_2 fragments.[12] In accord with the generally superior thermal stability of P−P over N−N single bonds, the fragmentation of **4** into two molecules of (*NHC*)PO_2 (*NHC* = N-heterocyclic carbene) that mimics the easily occurring cleavage of N_2O_4 was not observed.

Even if the synthesis of **4** from **3** and O_2 parallels reported reactions of *C*-diaminophosphaalkenes,[12,13] the persistence of the P−P bond through the oxidation process seems remarkable. Notwithstanding that mechanistic details still remain unclear, oxygenation of this bond is presumably prevented by the effective steric shielding of the P_2O_4 core by the extremely bulky substituents. Since hypophosphates or hypophosphites are usually accessed through reductive pathways, the synthesis of **4** in any case outlines a new and complementary strategy to generate partially oxygenated polyphosphorus species by the controlled oxidation of precursors containing phosphorus in a low oxidation state. In connection with the prospect of utilizing ligand-exchange reactions to replace the bulky "carbene donors", this approach may open new avenues for studies of further unusual and, most likely, highly reactive phosphorus–oxygen compounds.

In summary, phosphinecarboxamide **1** and the donor–acceptor adduct/betaine **4** bear some formal resemblance to homologous nitrogen compounds (urea, N_2O_4), but exhibit peculiar deviations in their syntheses, structures, and chemical properties. This once more accentuates the doctrine that the electronic properties of the heavier elements in a group differ from those of the lightest congener. The new compounds offer great potential for the development of innovative applications or new synthetic pathways that may pave a way to further exciting molecules.

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[13] Since the bond-length distribution in the C_2P_2 core of **3** allows this species to also be considered as 1,1,4,4-tetraamino-2,3-diphosphabutadiene, its reactivity complies to the general pattern.