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Accessing an Aromatic Diphosphatriazolate Anion by Formal Inorganic “Click” Chemistry

Christian Hering-Junghans and Eric Rivard**

Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

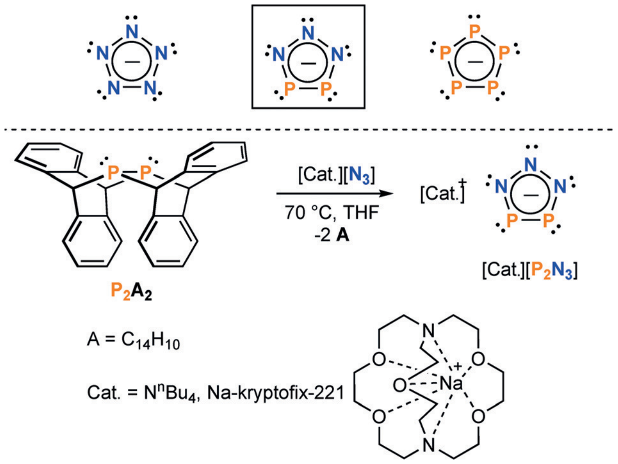
anions · aromaticity · diphosphatriazolate · isoelectronic analogues · N,P ligands

Aromaticity is a fundamental chemical concept that continues to drive experimental and theoretical pursuits. The initially recognized members of the aromatic family were planar cyclic species with delocalized $4n+2$ π electrons ($n=1, 2, 3,\ldots$) that exhibited high stability. The iconic 6π aromatic molecule benzene, C_6H_6, was first isolated by Faraday in 1828, and named as “bicarburet of hydrogen” since the C/H ratio in benzene was originally incorrectly determined to be 2:1.[1] Another 6π aromatic hydrocarbon, the cyclopentadienyl anion $[C_5H_5]^-$, spurred the rapid growth of organometallic chemistry, with a Nobel prize awarded in 1973 to Fischer and Wilkinson for their contributions to metallocene chemistry.[2] In addition to these impressive examples, it should be stated that the realm of what constitutes aromaticity is continually evolving as bonding models become more sophisticated.[3]

Phosphorus is often referred to as a carbon copy and this relationship allows one to rationalize the aromatic characteristics and coordination properties of *cyclo*-$[P_5]^-$ (which is isolobal to $[C_5H_5]^-$).[4] $[P_5]^-$ was first prepared in low yields by Baudler et al., and now can be conveniently prepared directly from P_4 and sodium metal in diglyme.[5] In contrast, the valence isoelectronic $[N_5]^-$ homocycle has only been generated as a transient species (from neutral pentazoles *para*-R-C_6H_4-*cyclo*-N_5) and identified by tandem mass spectrometry experiments.[6]

However, anions of the type $[P_nN_{5-n}]^-$ ($n=1$–4) have eluded synthesis so far. In this context, the recent report by Velian and Cummins on the preparation of the stable 6π aromatic anion $[P_2N_3]^-$ provides an important missing link in inorganic chemistry and represents another convincing case where P–P multiple bonding can be supported without the aid of hindered coligands (Scheme 1).[7]

A salt containing the $[P_2N_3]^-$ ion was obtained by combining the masked source of diphosphorus, $P_2\mathbf{A}_2$ ($\mathbf{A}=C_{14}H_{10}$),[8] with a stoichiometric excess of $[n\text{Bu}_4\text{N}][N_3]$ in THF at 70 °C for 3 h. The quantitative formation of the diphosphatriazolate salt $[n\text{Bu}_4\text{N}][P_2N_3]$ was noted by ^{31}P NMR spectroscopy ($\delta=334$ ppm) and mass spectrometry (electrospray ionization, $m/z=104.9$ for $[P_2N_3]^-$). The authors reported the ineffective separation of the $[n\text{Bu}_4\text{N}][P_2N_3]$ product from excess $[n\text{Bu}_4\text{N}][N_3]$. Consequently, [Na-kryptofix-221]$[N_3]$ was employed as an alternative N_3^- source in the reaction with $P_2\mathbf{A}_2$ (Scheme 1). This afforded air- and moisture-sensitive crystals of [Na-kryptofix-221]$[P_2N_3]$ (**1**) that were suitable for X-ray diffraction studies. Despite the presence of twofold positional disorder involving the $[P_2N_3]^-$ ion in **1**, structural refinement was possible and revealed an approximately C_{2v}-symmetric planar five-membered P_2N_3 ring. Short intraring P–P (2.069(1) Å) and N–N (1.310(2), 1.326(2) Å) distances suggest the presence of π-electron delocalization and multiple bonding (Figure 1). For reference, the P=P double bond in Mes*P=PMes* (Mes* = 2,4,6-$t\text{Bu}_3C_6H_2$) is 2.034(2) Å.[9]



Scheme 1. Top: *Cyclo*-$[N_5]^-$ (left), $[P_2N_3]^-$ (middle), and *cyclo*-$[P_5]^-$ (right).[5–7] Bottom: Reaction of $P_2\mathbf{A}_2$ with $[\text{Cat.}][N_3]$ to yield $[\text{Cat.}][P_2N_3]$.

Computations were carried out to determine the degree of aromaticity in *cyclo*-$[P_2N_3]^-$. NRT (Natural Resonance Theory) calculations support an overall bonding mode with effective delocalization of π electrons. The nucleus-independent chemical shift (NICS) is of particular interest for computational chemists to probe aromaticity. Negative values are indicative of aromaticity, whereas positive values suggest antiaromaticity. It is also important to scan NICS values along the z-axis (the z-axis pierces the ring-plane perpendicularly at a ring critical point) at different distances from the ring plane

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[*] Dr. C. Hering-Junghans, Prof. Dr. E. Rivard
Department of Chemistry, University of Alberta
11227 Saskatchewan Dr., T62 2G2 Edmonton, Alberta (Canada)
E-mail: heringju@ualberta.ca
erivard@ualberta.ca
Homepage: http://www.chem.ualberta.ca/~erivard/

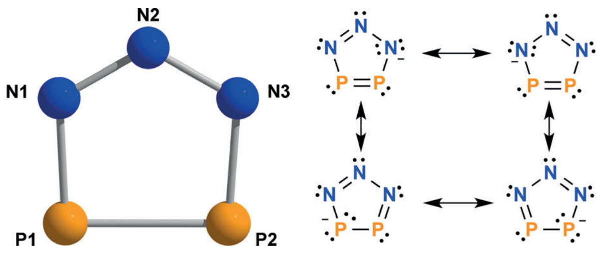
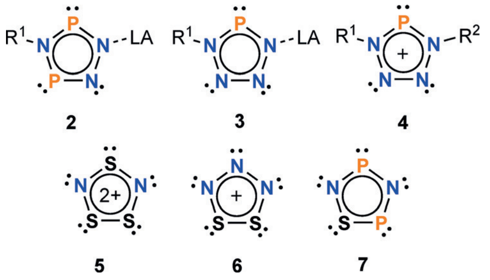


Figure 1. Left: POV-ray depiction of the molecular structure of the anion in [Na-kryptofix-221][P_2N_3] (**1**). Right: The four most important resonance structures obtained by NRT analysis.

to obtain a NICS profile, which should show a minimum for an aromatic system.[10] For $[P_2N_3]^-$, this minimum was determined to be 0.6 Å above the plane, thus deeming the anion to be aromatic.

The ^{15}N-labeled salt [Na-kryptofix-221][$P_2NN^{15}N$] (**1^{15}N**) was synthesized and the 1,2-atom connectivity of the phosphorus atoms was confirmed by ^{31}P and ^{15}N NMR as well as vibrational spectroscopy. The Raman spectra of **1** and **1^{15}N** showed a ν(PP) band at 519 cm^{-1}, consistent with the presence of a P=P multiple bond. Starting from P_2**A**$_2$ and free N_3^-, two possible reaction pathways were discussed by the authors: 1) a dissociative mechanism involving the initial formation of molecular P_2 and subsequent cyclization with free N_3^-, and 2) an associative route via transient P_2**A** that reacts with N_3^-. These individual pathways are similar energetically and thus, both likely contribute to the overall reaction.[7,8] Formally, the reaction can be described as a "click" reaction.[6b] The utilization of P_2**A**$_2$ as a source of molecular P_2 under mild conditions represents a powerful tool in preparative inorganic chemistry; alternatively, P_2 can be generated in equilibrium with white phosphorus (P_4) at high temperatures (above 800 °C) or by photolysis ($\lambda = 254$ nm) of a P_4 solution in hexanes at 65 °C.[11]

The formation of binary five-membered PN rings of any form remains rare. Schulz and co-workers demonstrated that $(Me_3Si)_2NN(SiMe_3)PCl_2$ functions as a source of $Me_3Si{-}NNP$, which readily oligomerizes in the presence of $GaCl_3$ to yield the PN heterocycle $[P_2N_3\{N(SiMe_3)_2\}]\cdot(GaCl_3)_x$ (**2**, Scheme 2; $x = 1$ and 2).[12] The neutral tetrazaphosphole $[PN_4(Mes^*)]\cdot GaCl_3$ (**3**) also shows a strongly delocalized 6π-electron system and is readily obtained in the reaction of the phosphaimine Mes*NPCl with Me_3SiN_3 and $GaCl_3$. Cationic tetrazaphospholium salts $[PN_4R(Mes^*)][AlCl_4]$ (**4**) are formed by [3+2] cyclization between $[Mes^*NP][AlCl_4]$ and organic azides RN_3 (R = *t*Bu, Et_3C).[13] In contrast to $[P_2N_3]^-$, these species are stabilized by bulky substituents and donor–acceptor interactions with Lewis acids.



Scheme 2. Known binary five-membered heterocycles: 1,3-diphosphatriazoles (**2**), tetrazapnictoles (**3**), and tetrazaphospholium cations (**4**) (R^1 = Mes*; LA = $GaCl_3$; R^2 = *t*Bu, Et_3C), 1,2,4,3,5-trithiadiazolium dication (**5**), 1,2-dithiatriazolium cation (**6**), and the neutral 2,4-dithia-3,5-diphosphathiole (**7**).

Notable five-membered inorganic, aromatic, and substituent-free heterocyclic species include: $[N_2S_3]^{2+}$ (**5**), $[N_3S_2]^+$ (**6**), and the neutral species SN_2P_2 (**7**, Scheme 2). Salts of *cyclo*-$[N_2S_3]^{2+}$ were first prepared by Passmore and co-workers in 1994 by the efficient [3+2] cyclization between [SN]X and [SNS]X (X = AsF_6^- and SbF_6^-) in liquid SO_2.[14] This trithiadiazolium dication is not stable in solution and its formation in the solid state is driven by the high lattice energy of the 1:2 salts. $[S_2N_3]^+$ was synthesized by combining $[NSCl]_3$ and $HgCl_2$ in CH_2Cl_2, which resulted in complex redox processes, where both $[S_2N_3]_4[Hg_3Cl_{10}]$ and $[S_2N_3]_2[Hg_2Cl_6]$ were formed in low but reproducible yields, along with various $[S_3N_4]^+$ salts.[15] Just recently, Zeng, Beckers, and co-workers prepared the neutral SN_2P_2 heterocycle (**7**, Scheme 2) by flash pyrolysis of $SP(N_3)_3$ at 1000 K and trapped the product in an argon matrix at 16 K. This product was characterized by IR spectroscopy with structural assignments facilitated by computational investigations, which also suggest that **7** is formed by the head-to-tail dimerization of gaseous SNP to cyclic $[SNP]_2$, followed by loss of sulfur.[16]

The isolobal analogue of $[P_2N_3]^-$, *cyclo*-$[P_5]^-$, has been explored as a ligand in transition-metal chemistry as it offers additional coordination sites in relation to the ubiquitous $[C_5H_5]^-$ ion. For example, Scheer and co-workers demonstrated that the hybrid sandwich complex $[(\eta^5\text{-}Cp^*)Fe(\eta^5\text{-}P_5)]$ ($Cp^* = C_5Me_5$) could further coordinate with copper(I) halides. The resulting species adopt large (nanoscale) fullerene-like topologies and represent nice examples of self-assembly.[17] In this context it will be interesting to investigate the coordination properties of $[P_2N_3]^-$ towards metals and determine if $[P_2N_3]^-$ can be used as a building block to obtain next generation solid-state architectures by salt-elimination chemistry (e.g. by reacting $[P_2N_3]^-$ with various main group element halides).[18]

The isolation of the first salt containing the binary 6π-electron aromatic 1,2-diphoshatriazolate $[P_2N_3]^-$ ion marks a breakthrough in synthetic inorganic chemistry. Remarkably, its synthesis was achieved using a synthon for molecular P_2. The concept of using "container molecules" such as P_2**A**$_2$ in synthesis might enable future access to exotic species such as molecular PN or PO^+ under mild conditions.

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