Interstellar Chemistry in a Glovebox: Elusive Diatomic P≡N, Exposed

What does interstellar chemistry have in common with a recent coordination complex of the diatomic molecule P≡N?1 PN is nearing 100 years since its discovery in the lab,2 and it is one of the most common phosphorus-containing molecules detected outside Earth, yet its coordination chemistry remains largely unknown. The study of phosphorus, as a rare biogenic element in outer space, is central to reconstructing a path to its prebiotic chemistry. However, to glimpse into its primordial chemistry, scientists need not only telescopes pointed at gas giants and exoplanets but also the specialized equipment and techniques available to the skilled synthetic chemist.

Chemists have long sought to produce and study the properties of unsaturated di- and triatomics of astrophysical importance such as HCP, PO, P2, or PN. This pursuit is made challenging by the relatively unstable multiple bonds in these molecules, which favor conversion to single-bonded products. Indeed, the relative instability of multiple bonding between main group elements with a principal quantum number ≥3 inspired numerous synthetic and theoretical studies that challenged, and ultimately changed, our understanding of chemical bonding.3 To be isolated, multiple bonds between heavier main group elements are typically protected by sterically encumbering groups designed to prevent their oligomerization.3 However, electronic effects (for example, provided by aromatization) can be remarkably effective on their own in stabilizing multiple bonding at phosphorus.4

But how does one go about assembling these compositionally simple molecules? PN was first produced by electric discharge in vapors of the two elements.2 Outside Earth, the likely precursors to its formation are nitrogen and phosphorus hydrides. Indeed, ammonia—phosphine ices were recently shown to give rise to the PN trimer cyclotriphosphazene under ionizing irradiation.5 However, these synthetic strategies lack scale. Observing vanishing amounts of PN or PN-like molecules in the gas phase under pyrolytic or cryogenic conditions precludes deep exploration of their chemistry.

Assembly of the PN molecule under mild reaction conditions would include first connecting the two pnictogens in a singular fragment. Subsequent multiple bond formation would require at least one of the substituents on the pnictogens to disengage from bonding to the PN unit. For example, this approach has been successfully employed to generate P2 in solution, using the extrusion of a thermodynamically more stable metal complex, or of an aromatized leaving group as driving forces to deprotect the phosphorus atom and form a multiple bond (Figure 1a).6,7 However, when applied to PN, similar strategies have not been as productive (Figure 1b).8,9 Notably, a putative vanadium phosphorus-nitride complex, [V](NP), was transiently generated, ostensibly

Published: September 15, 2020
by extrusion of anthracene, and subsequently trapped either by oligomerization or with a range of unsaturated substrates.8 In the report by Smith and co-workers,1 two terminal metal pnictogen complexes are used as building blocks for a PN fragment. An iron(IV) nitrido complex prone to reductive coupling and a molybdenum(VI) phosphide connect spontaneously to form a bimetallic complex featuring a P−N bridge, [Fe]−N≡P−[Mo]. A key ingredient toward deprotecting the resulting PN unit is the intrinsic lability of the Fe complex. In the presence of isocyanide CNBu, the iron disengages from binding nitrogen and is extruded as the adduct [Fe](CNBu)4, thus revealing the first structurally characterized PN coordination complex, [Mo](PN)− (Figure 2).

As a ligand, PN poses a series of interesting questions: will it coordinate η2 like the diatomic P2, or η1 like its more terrestrially ubiquitous cousin N2? If it coordinates end-on, which will bind to the metal, the nitrogen or phosphorus terminus? The preference for a linear, end-on coordination is immediately apparent in the solid state structure of the anion [Mo](PN)−, which is cocrystallized with small amounts of its positional isomer [Mo](NP)−. Further studies indicate that the coordination primarily via the P terminus could be an artifact of the synthetic path taken to produce this complex. Upon irradiation in the solid state, the PN fragment isomerizes, ostensibly via an η2 binding mode configuration, to the N-bound thermodynamic product [Mo](NP)−. This species is predicted via DFT to be over 25 kcal/mol more stable than the P-bound isomer [Mo](PN)−, thus suggesting that N-bound PN is a better π-acid. However, perhaps unsurprisingly, accumulation of the [Mo](NP)− isomer in solution, which would expose a monocoordinate phosphorus terminus engaged in multiple bonding with nitrogen, could not be accomplished. Is [Mo](NP)− engaging in further reactivity, possibly analogous to the oligomerizations observed for [V](NP)? Would the [V](PN) isomer, if produced, be isolable in its monomeric form?

An important question, when studying reactive small molecules (such as phosphorus mononitride) while bound to a stabilizing group, is how representative of the free, unprotected molecules they truly are. For example, the previously reported PN fragment stabilized by two carbene groups might be better modeled as R2C=N=P=NR2 rather than R2C=N=P=CR2. Indeed, the interpnictogen distance in this biscarbene compound measures 1.709(2) Å, which is significantly longer than that determined for the triple bond in gaseous PN of 1.49086(2) Å. In contrast, the bridging [Fe]−N≡P−[Mo] complex features a very short PN distance of 1.509(6) Å, and a Raman vibrational mode at 1259 cm−1, which is close to that of free PN at 1323 cm−1. Interestingly, the bond metrics for the PN unit of the terminally bound [Mo](PN)− reveal significant multiple bonding character between the two pnictogens: in its P-bound isomeric form, the complex features a P−N interatomic distance of 1.5363(1) Å, which is 0.05 Å shorter than in the N-bound isomer. A topological analysis of these isomers performed by the authors did reveal a set of polar and cylindrically symmetric multiple (triple) PN bonds.

What features of the Mo complex protect the multiple bonding in the exposed PN unit against oligomerization? For comparison, the putative [V](NP)− complex is proposed to have a fleeting existence before undergoing further reactions.8 Inspection of the solid state structures of both isomers of [Mo](PN)− reveals that it is not steric bulk that protects the multiple bonding of the PN ligand. Instead, its stability is attributed based on DFT calculations to π-backbonding interactions between the Mo dxy, dxz non-bonding orbitals with the low-lying π* orbitals of the PN ligand. The overall anionic charge of the complex could be
another stabilizing factor to the [Mo](PN)− molecules although its role is not addressed in this study.

By introducing a synthetic path and coordination platform capable of stabilizing a PN ligand featuring multiple bonding, Smith and coauthors accomplished an important step in elucidating the chemistry of the diatomic PN and demonstrated that kinetically trapped N-terminal isomers of [Mo](PN)− complexes can be isolated in synthetic amounts.1 Developing molecular precursors to unsaturated, and unprotected, di- and triatomics of phosphorus, however, remains key to unlocking their bare reactivity within the controlled environment of a laboratory. Can this discovery spur the next one, of accessing a molecular precursor that can readily release PN under mild conditions and in synthetically relevant amounts?

Developing molecular precursors to unsaturated, and unprotected, di- and triatomics of phosphorus, however, remains key to unlocking their bare reactivity within the controlled environment of a laboratory.

Author Information

Corresponding Author
Alexandra Velian — Department of Chemistry, University of Washington, Seattle, Washington 98195-0005, United States; orcid.org/0000-0002-6782-7139; Email: avelian@uw.edu

Author
Daniel Tofan — Department of Chemistry, University of Washington, Seattle, Washington 98195-0005, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c01148

REFERENCES

(1) Martinez, J. L.; Lutz, S. A.; Beagan, D. M.; Gao, X.; Pink, M.; Chen, C.-H.; Carta, V.; Moënne-Loccoz, P.; Smith, J. M. Stabilization of the Dinitrogen Analogue, Phosphorus Nitride. ACS Cent. Sci. 2020, in press. DOI: 10.1021/acscentsci.0c00944

(2) Curry, J.; Herzberg, L.; Herzberg, G. Spectroscopic Evidence for the Molecule PN. J. Chem. Phys. 1933, 1 (10), 749–749.

(3) Roland, C.; Fischer, R. C.; Power, P. P. π-Bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millennium. Chem. Rev. 2010, 110 (7), 3877–3923.

(4) Velian, A.; Cummins, C. C. Synthesis and Characterization of P2N3−: An Aromatic Ion Composed of Phosphorus and Nitrogen. Science 2015, 348 (6238), 1001–1004.

(5) Zhu, C.; Eckhardt, A. K.; Bergantini, A.; Singh, S. K.; Schreiner, P. R.; Kaiser, R. I. The Elusive Cyclotriphosphazene Molecule and Its Dewar Benzene-Type Valence Isomer (F3N3). Sci. Adv. 2020, 6 (30), No. eaba6934.

(6) Piro, N. A.; Figueroa, J. S.; McKellar, J. T.; Cummins, C. C. Triple-Bond Reactivity of Diposphorus Molecules. Science 2006, 313 (5791), 1276–1279.