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# Interaction of Carbene and Olefin Donors with $[Cl_2PN]_3$: Exploration of a Reductive Pathway toward $(PN)_3$

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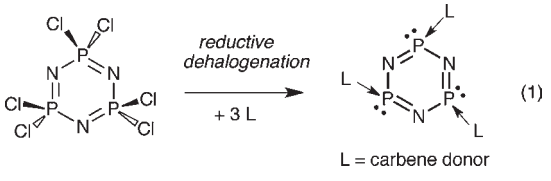
Supporting Information

**ABSTRACT:** The iminophosphine−phosphazene [$P^{III}$−$P^{V}$] heterocyclic adduct [IPr·$PN(PCl_2N)_2$] was prepared via reduction of the cyclic phosphazene $[Cl_2PN]_3$ in the presence of the carbene donor IPr {IPr = $[(HCNDipp)_2C:]$, where Dipp = 2,6-$^{i}Pr_2C_6H_3$}. By contrast, the treatment of $[Cl_2PN]_3$ with the N-heterocyclic olefin IPr=$CH_2$ yielded the olefin-grafted phosphazene ring $[(IPr{=}CH)P(Cl)N(PCl_2N)_2]$.

The use of N-heterocyclic carbenes (NHCs) as supporting ligands to isolate/stabilize inorganic species that were either unknown or inaccessible using conventional methods is a rapidly developing avenue of research.[1] In this regard, the synthesis of NHC adducts featuring reactive entities, such as :BH, $:SiX_2$ (X = Cl and Br), :Si=Si:, $P_2$, and PH, represent particularly noteworthy achievements.[2] These breakthroughs have substantially expanded our general knowledge of bonding in inorganic chemistry and have facilitated the discovery of a number of useful chemical transformations involving once elusive inorganic species as reagents.[3]

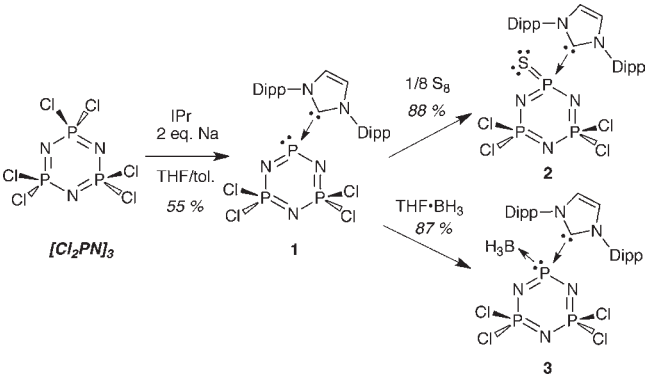
Our recent syntheses of stable inorganic methylene and ethylene adducts ($:EH_2$ and $H_2EE'H_2$, where E and E′ = Si, Ge, and/or Sn),[4,5] have provided an impetus to explore the preparation of NHC-supported complexes of phosphorus mononitride (PN) and/or its oligomers $(PN)_x$. Molecular PN was originally generated and studied via matrix-isolation techniques[6] and was later identified as a component of interstellar space.[7] In addition, PN represents a heavier analogue of $N_2$ and is thus an attractive species from a fundamental standpoint. In this Communication, we report a potential route toward isolating an adduct of $(PN)_3$ under ambient conditions. Our strategy relies upon reduction of the readily available cyclic precursor $[Cl_2PN]_3$ in the presence of carbon-based donors to yield a stable complex of $(PN)_3$ (eq 1).[8,9] The present study is conceptually linked with the elegant synthesis of a formal bis(carbene) adduct of PN by Bertrand and co-workers in 2010.[10]




(1)

The interaction of the hindered carbene IPr {IPr = $[(HCNDipp)_2C:]$, where Dipp = 2,6-$^{i}Pr_2C_6H_3$} with $[Cl_2PN]_3$ in the presence of sodium metal as a reductant yielded a new crystalline product, which exhibited an $AX_2$ splitting pattern in the $^{31}P$ NMR spectrum [$\delta_A$ 101.4 (t, $J$ = 86.9 Hz); $\delta_X$ 6.1 (d, $J$ = 86.9 Hz)]. The disparate nature of the observed chemical shifts suggested the presence of a single product with two phosphorus environments in different oxidation states. Single-crystal X-ray crystallography[11] later identified this species as the novel iminophosphine−phosphazene [$P^{III}$−$P^{V}$] adduct [IPr·$PN(PCl_2N)_2$] (**1**; Scheme 1 and Figure 1).

**Scheme 1. Synthesis of the Iminophosphine−Phosphazene Adduct 1 and Representative Chemistry**




Attempts to further reduce the remaining $P^{V}$ centers in **1** with additional equivalents of IPr and sodium yielded no discernible reaction. Compound **1** could also be obtained in low isolated yield (13%) when $[Cl_2PN]_3$ was directly combined with 2 equiv of IPr in the absence of sodium; the low yield of **1** stems from the formation of a number of unidentified side products during the reaction. Importantly, this latter transformation reveals that IPr can also serve as a dehalogenation/reducing agent.[8]

As shown in Figure 1, **1** contains a carbene-ligated P center with a $C_{IPr}$−P distance [C(1)−P(1)] of 1.8791(13) Å. This value is elongated compared to the C−P distances in the cationic phosphorus bisadduct $[(ImMe_2{}^{i}Pr_2)\cdot P\cdot(ImMe_2{}^{i}Pr_2)]Cl$ (where $ImMe_2{}^{i}Pr_2$ = $[(MeCN{}^{i}Pr)_2]C:$) [1.824(3) Å ave][8b] and is much longer than the $C_{IPr}$−P linkages within IPr·$P_2$·IPr [1.7504(17) Å], wherein significant P−$C_{IPr}$ $\pi$ bonding is present.[2e] The $P_3N_3$ heterocycle in **1** adopts an envelope conformation with pyramidal geometry about the apical P(1) atom in the ring [angle sum = 307.3(1)°]. Compound **1** also features considerable intraring P−N bond-length variation, with long P−N bonds of 1.6770(12) and 1.6845(13) Å involving the three-coordinate P(1) center, while the remaining P−N distances vary from 1.5423(12) to 1.5923(13) Å;

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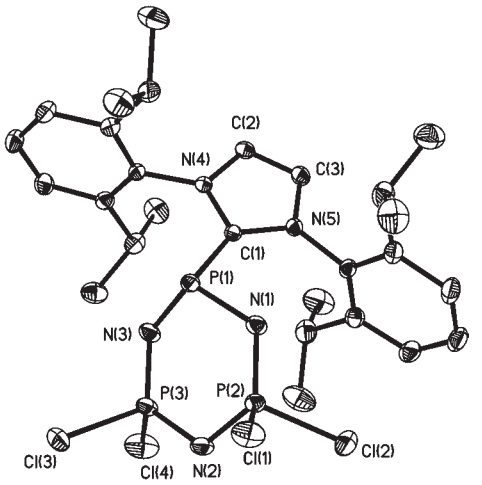



**Figure 1.** Thermal ellipsoid plot (30% probability level) for **1** with hydrogen atoms and toluene solvate omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−P(1) 1.8791(13), P(1)−N(1) 1.6770(12), P(1)−N(3) 1.6845(13), P(2)−N(1) 1.5423(12), P(2)−N(2) 1.5900(13), P(3)−N(2) 1.5923(13), P(3)−N(3) 1.5543(13); C(1)−P(1)−N(1) 99.05(6), C(1)−P(1)−N(3) 100.14(6), N(1)−P(1)−N(3) 108.12(6).

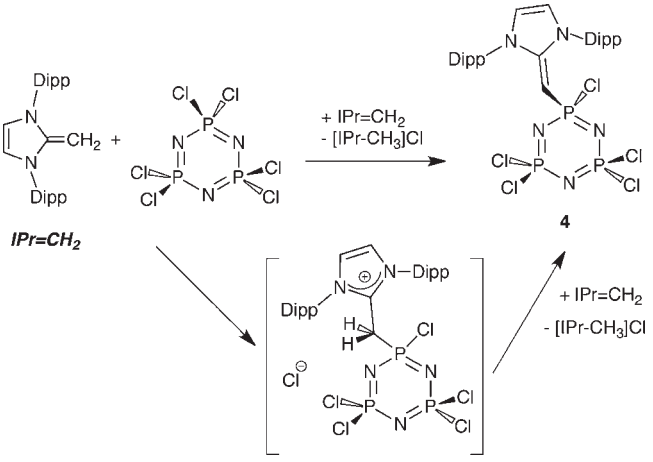
the latter bond lengths are in the range usually observed in phosphazene heterocycles.[12]

The above-mentioned data support the presence of a stereochemically active phosphorus lone pair in **1**. Congruently, **1** reacted rapidly with sulfur to afford the novel phosphine sulfide [IPr·(S)PN(PCl$_2$N)$_2$] (**2**) as a colorless solid (Scheme 1 and Figure S1).[11] The NMR spectra for **2** were consistent with the presence of phosphazene environments, and correspondingly short P−N distances of 1.5595(17)−1.6256(16) Å were observed by X-ray crystallography.[11] Despite the presence of a terminal sulfido group in **2**, the dative $C_{IPr}$−P(1) interaction [1.8582(18) Å] was similar in length to the carbene−phosphorus interaction within the reduced precursor **1** [1.8791(13) Å]. For comparison, the P═S bond distance in **2** [1.9361(7) Å] lies within the typical bond length values determined for phosphine sulfides, R$_3$P═S [e.g., 1.950(3) Å within Ph$_3$P═S].[13] Oxidation of the carbene-bound phosphorus center in **1** with a chalcogen is reminiscent of prior work by Kuhn and co-workers, who prepared the phosphonium selenide complex [Ph$_2$P(Se)·ImMe$_2$$^i$Pr$_2$]AlCl$_4$ via the direct oxidation of an NHC phosphenium (Ph$_2$P$^+$) adduct with selenium.[9c] Of note, we were also able to coordinate BH$_3$ to the phosphorus donor site in **1** to yield the stable adduct [IPr·P(BH$_3$)N(PCl$_2$N)$_2$] (**3**); however, attempts to obtain crystals suitable for X-ray crystallographic analysis were unsuccessful.[11]

Inspired by the recent use of the N-heterocyclic olefin IPr═CH$_2$ as a donor ligand in low-oxidation-state main-group chemistry,[4c,14] we subsequently investigated the reaction of IPr═CH$_2$ with [Cl$_2$PN]$_3$. As illustrated in Scheme 2, the sole phosphorus-containing product in the reaction was the alkene-substituted heterocycle [(IPr═CH)P(Cl)N(PCl$_2$N)$_2$] (**4**). Interestingly, the same product is obtained when the reaction is conducted in the presence of sodium metal as a potential reductant.

The formation of **4** likely involves the initial nucleophilic displacement of a phosphorus-bound chloride in [Cl$_2$PN]$_3$ by IPr═CH$_2$, followed by deprotonation (HCl elimination) in the presence of excess basic IPr═CH$_2$ to generate an alkenyl

**Scheme 2. Synthesis of the Alkene-Substituted Phosphazene 4**



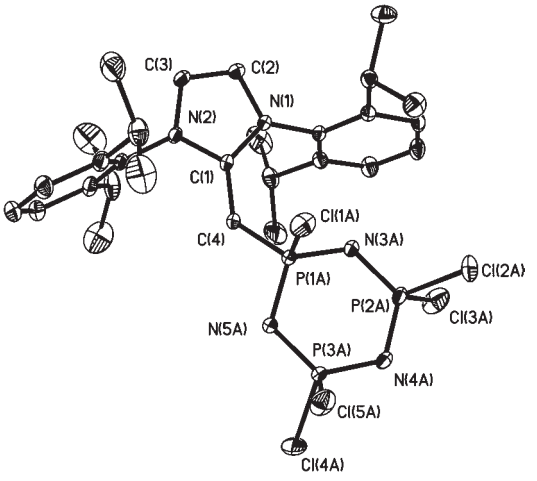
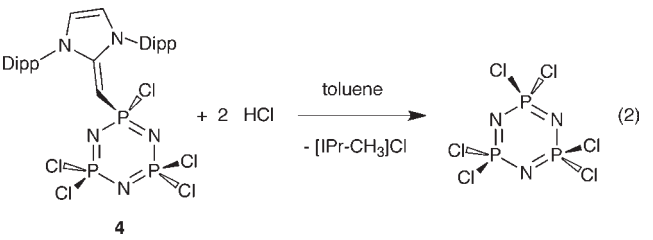




**Figure 2.** Thermal ellipsoid plot (30% probability level) for **4** with hydrogen atoms and solvate omitted. The N$_3$P$_3$Cl$_5$ group was disordered over two positions (70:30), and only the major orientation is shown for clarity. Selected bond lengths (Å) and angles (deg) with values due to the minor orientation of the N$_3$P$_3$Cl$_5$ group in brackets: C(1)−C(4) 1.398(2), C(4)−P(1A) 1.687(2) [1.708(3)], P(1A)−N(3A) 1.6089(17), P(1A)−N(5A) 1.610(2), P(2A)−N(3A) 1.5617-(16), P(2A)−N(4A) 1.583(2), P(3A)−N(4A) 1.583(2), P(3A)−N(5A) 1.567(2); C(1)−C(4)−P(1A) 129.07(14) [132.52(17)].

IPr═CH group at phosphorus. The latter process yields the insoluble imidazolium salt [IPrCH$_3$]Cl, which was isolated in pure form by filtration.[11,15] Attempts to functionalize the remaining P−Cl bonds in **4** with excess IPr═CH$_2$ failed; however, the IPr═CH residue was readily cleavable from the phosphazene ring by treatment with anhydrous HCl, regenerating [Cl$_2$PN]$_3$ in the process (eq 2).





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Compound **4** was also characterized by single-crystal X-ray crystallography (Figure 2). The phosphazene heterocycle **4** contains P−N bond lengths in the narrow range of 1.5617(6)−1.610(2) Å, while the exocyclic P−C interaction is significantly shorter [P(1A)−C(4) = 1.692(4) Å ave] than the dative P−$C_{IPr}$ linkages within the heterocyclic adducts **1** and **2**. Furthermore, the short P−C distance in **4** is accompanied by the substantial lengthening of the proximal P(1)−Cl(1) bond length [2.088(2) Å ave] relative to the P−Cl distance observed in phenyl-substituted phosphazene [PhP(Cl)N($PCl_2N$)$_2$] [2.021(2) Å].[16] These metrical parameters suggest that the IPr═CH substituent is strongly electron-releasing, thereby leading to a weakening of the adjacent P−Cl interaction. Unfortunately, our attempts to remove a chloride ion from **4** using the known halide abstractors Ag[A] (A = $O_3SCF_3^-$ and $SbF_6^-$) led to inseparable product mixtures in place of the desired cyclophosphazene cation [(IPr═CH)PN($PCl_2N$)$_2$]$^+$ ([**4**]$^+$).[17]

In summary, partial reductive dehalogenation of [$Cl_2PN$]$_3$ in the presence of the carbene donor IPr affords the novel mixed $P^{III}$−$P^V$ heterocyclic adduct **1**; this species was also reacted with sulfur to give the sulfido adduct **2**. A divergent reaction pathway was observed between IPr═$CH_2$ and [$Cl_2PN$]$_3$, leading to the olefin-bound cyclophosphazene **4**. Future work will focus on the reduction of [$Cl_2PN$]$_3$ in the presence of less hindered NHC coligands in order drive the system toward a fully dehalogenated (PN)$_3$ heterocycle. The ability to prepare metastable complexes of (PN)$_3$ should lead to the discovery of new binary P−N materials upon controlled removal of the stabilizing ligands,[3b,e] with potential applications in materials science envisioned.[18]

## ■ ASSOCIATED CONTENT

**Supporting Information.** Full synthetic procedures and X-ray crystallographic information files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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