

Phosphinidene Reactivity of a Transient Vanadium $P\equiv N$ Complex

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S Supporting Information

ABSTRACT: Toward the preparation of a coordination complex of the heterodiatomic molecule PN, $P\equiv N-V(N[{}^t\text{Bu}]\text{Ar})_3$ (**1**, Ar = 3,5-Me₂C₆H₃), we report the use of CIPA (A = C₁₄H₁₀, anthracene) as a formal source of phosphorus(I) in its reaction with Na[NV(N[{}^t

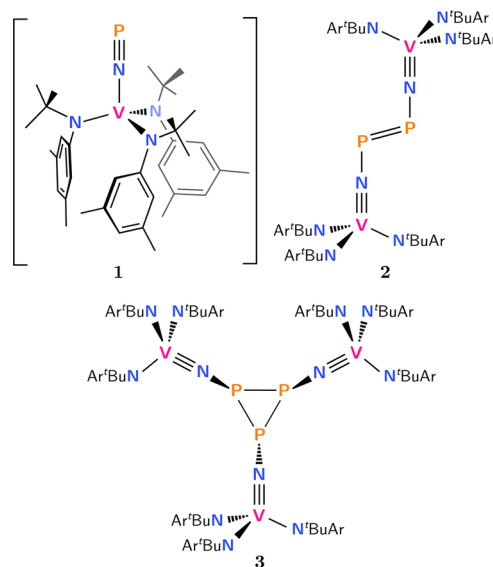


Figure 1. Molecular depiction of monomeric (**1**), dimeric (**2**), and trimeric (**3**) complexes of PN.

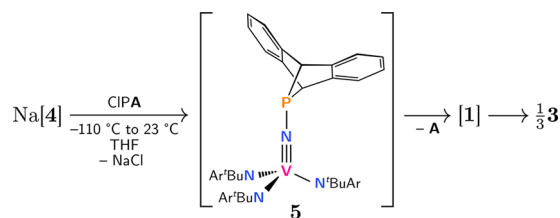
terminal complex of PN (**1**), we report dimeric diphosphene **2** and trimeric cyclotriphosphane **3**, the latter serving as a synthetic equivalent of **1** under mild conditions (Figure 1).

The key P–N bond was envisioned to form through treatment of the previously reported Na[NV(N[{}^t

The state of $P\equiv N$ solution chemistry contrasts sharply with that of homodiatomic molecules N₂ and P₂. Indeed, dinitrogen reactivity has been extensively investigated,¹ and new synthetic routes have recently enabled the exploration of the rich chemistry of diphosphorus.^{2,3} Despite longstanding spectroscopic interest⁴ and recent efforts in the development of molecular precursors to PN^{5,6} the chemistry of this interstellar species remains virtually unexplored. While there are rare examples of main-group molecules containing low-coordinate phosphorus–nitrogen units such as iminophosphines⁷ and related species,⁸ PN lacks even coordination complexes.⁹

Presumably, the lack of reports on PN chemistry is tied to the difficulty of accessing an appropriate synthetic precursor. Just so, our group has had longstanding interest in anthracene-based molecular precursors as a platform for the delivery of reactive small fragments upon mild heating. In this vein, precursors to phosphinidenes,⁵ P₂,³ and HCP¹⁰ have allowed their access under conditions amenable to organic and organometallic synthesis. We aimed to leverage this anthracene delivery platform to generate a PN complex, bridging the chemistry of small molecules and low-valent early transition metals. We hypothesized that V(N[{}^t

Scheme 1. Synthesis of 3, Depicting Putative Intermediates 5 and 1



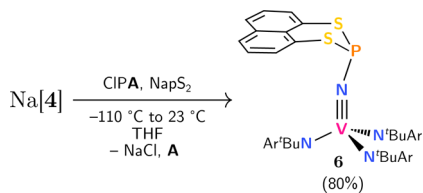
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^{51}V NMR spectroscopy, which showed broad resonances centered at 212 ($\Delta\nu_{1/2}$ 2100 Hz) and 77 ppm ($\Delta\nu_{1/2}$ 810 Hz), integrating to a 2:1 ratio. An identical pattern was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product, which exhibited two broad resonances with a 2:1 integration at 201 ($\Delta\nu_{1/2}$ 1040 Hz) and 112 ppm ($\Delta\nu_{1/2}$ 760 Hz). Conclusive identification of this product as trimeric **3** was facilitated by X-ray crystallography, revealing a cyclo-triphosphane moiety with monomeric units oriented in a two-up, one-down conformation. The V–N distance of 1.698(2) Å was similar to those found in other related species,^{13,14} while the average P–N distance of 1.754 Å was consistent with a short single bond.^{12,15} Despite the conspicuous steric bulk of its substituents, the metrical parameters of the cyclotriphosphane substructure were not perturbed compared to previously reported P_3 cycles.¹⁶ Presumably, formation of **3** occurs first through **5**, which loses anthracene to generate **1** that then rapidly trimerizes. Low-temperature NMR experiments between -60 and 23 °C did not lead to the observation of **5** or **1**.

To corroborate the intermediacy of **1**, a thawing solution of Na[**4**] was mixed with a thawing solution of ClPA and NapS₂ (*peri*-1,8-naphthalene disulfide, 1.0 equiv),¹⁷ the latter serving as a trap for putative **1**. Upon workup, the vanadium iminophosphine **6** was isolated in 80% yield. The crystal structure of **6** displayed a V≡N triple bond with a length of 1.6947(2) Å and a N–P single bond of 1.74993(2) Å (Scheme 2). Importantly,

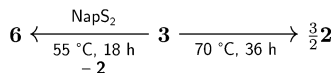
Scheme 2. Synthesis of **6** in the Presence of NapS₂



formation of **6** was unlikely to involve **3**, as no reactivity was observed between **3** and NapS₂ after 2 h at 23 °C. An alternative associative mechanism involving reaction of NapS₂ with **5** was similarly judged improbable upon finding that Me₂NPA reacted very slowly with NapS₂, forming <40% of NapS₂PNMe₂ in 24 h at 23 °C.

This same product **6** was observed upon heating a benzene-*d*₆ solution of **3** in the presence of 3 equiv of NapS₂ to 55 °C for 18 h, consistent with thermal transfer of **1** from **3**. Integrations by ^1H NMR spectroscopy showed consumption of only 1 equiv of NapS₂ to generate **6** (Scheme 3). Accompanying the formation

Scheme 3. Thermal Decomposition of **3** to **2** and Generation of **6** in the Presence of NapS₂



of **6**, a new resonance centered at 191 ppm ($\Delta\nu_{1/2}$ 450 Hz) was identified in the ^{51}V NMR spectrum, along with a $^{31}\text{P}\{^1\text{H}\}$ NMR signal characteristic of diphosphenes at 643 ppm ($\Delta\nu_{1/2}$ 170 Hz). In the absence of the NapS₂ trap, heating **3** at 70 °C for 36 h resulted in complete conversion of **3** to diphosphene **2**, isolated in 90% yield. The compound was unambiguously identified by X-ray crystallography after crystallization from benzene. Once again, the short V–N length of 1.6933(1) Å was consistent with a triple bond, while the P–N length of 1.6530(1) Å suggested a

single bond. However, the P–P length of 2.0787(7) Å appeared significantly shorter than the P–P single bonds of **3**, being in the expected range for a diphosphene P=P double bond. Together, these data suggest that **3** undergoes thermal [2+1]-retrocycloaddition to generate monomeric **1**, which is prone to rapid dimerization. It is conceivable that generation of **6** from **3** and NapS₂ at high temperatures occurs through an associative mechanism rather than through **1** in solution. However, such a mechanism is unlikely in the case of **3** transforming to **2** for steric reasons.

The formation of oligomers such as **2** and **3** is highly reminiscent of phosphinidene reactivity,^{5,18,19} leading us to consider $:\ddot{\text{P}}-\text{N}\equiv\text{V}(\text{N}[\text{tBu}]\text{Ar})_3$ as a possible resonance structure of putative **1** (see Figure 2 and SI). While the formation of

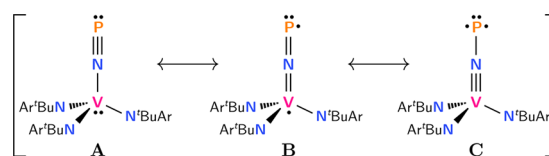
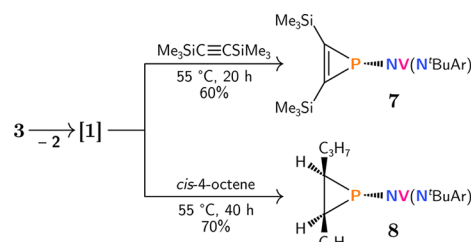


Figure 2. Resonance structures of monomer **1**.

diphosphenes or cyclic oligomers is a common reactivity pathway for phosphinidenes,^{19,20} the transfer of a phosphinidene unit from a bare cyclo-triphosphane under such mild conditions is unprecedented.^{21,22} In analogy to the predicted increased stability of ketimide-substituted phosphinidenes,²³ the vanadium nitride substituent appears especially well-suited to stabilize low-valent phosphorus via electronic delocalization across the V–N–P π system.¹³ Our computational studies corroborate this assertion, revealing a remarkably low P=P bond dissociation enthalpy of 41.2 kcal/mol for the model diphosphene [PNV(NMe₂)₃]₂, sharply contrasting with the value for [PN(SiMe₃)₂]₂ of 80.3 kcal/mol (see SI).

In an effort to transfer a monomeric unit from **3** to a substrate less likely to react through an associative mechanism, **3** was stirred in the presence of excess bis(trimethylsilyl)acetylene at 23 °C in toluene (Scheme 4). After 48 h, a new product was

Scheme 4. Preparation of Phosphirene **7** and Phosphirane **8** from Thermolysis of **3**



observed at -104 ppm ($\Delta\nu_{1/2}$ 320 Hz) by ^{51}V NMR spectroscopy. Warming the solution to 55 °C drove the reaction to completion within 20 h; the target phosphirene **7** was isolated from the reaction mixture in 60% yield.

Similar thermolysis of a benzene solution of **3** at 55 °C in the presence of excess *cis*-4-octene led to the formation of **8**, isolated in 70% yield. ^1H NMR spectroscopy and a single-crystal X-ray diffraction study (Figure 3a) confirmed formation of a single stereoisomer. Such stereospecific cycloaddition often implicates a singlet intermediate according to the Skell hypothesis²⁴ and is reminiscent of previously reported phosphinidene reactivity.^{5,25}

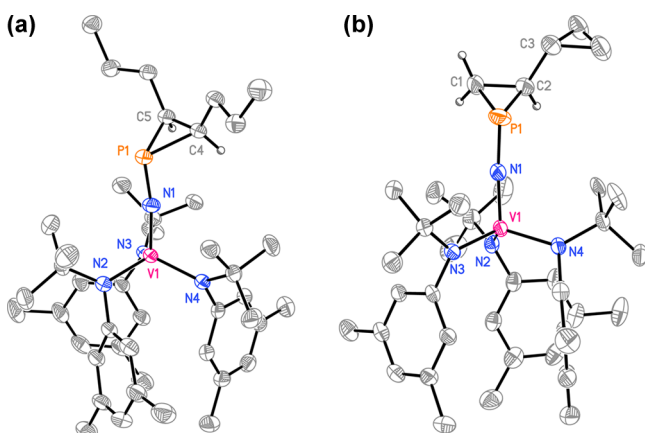
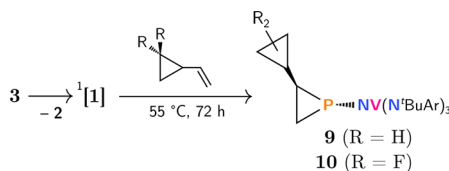


Figure 3. (a) Molecular structure of **8** from a single-crystal X-ray diffraction study at 100 K, shown with 50% probability ellipsoids. Non-phosphinidene H-atoms and positional disorder are omitted for clarity. Selected interatomic distances [Å] and angles [°]: V1–N1 1.6799(2), V1–N2 1.894(2), N1–P1 1.7164(2), P1–C4 1.878(2), P1–C5 1.879(3); V1–N1–P1 165.83(1), N1–P1–C4 103.52(1), N1–P1–C5 105.30(1), C4–P1–C5 47.44(1). (b) Molecular structure of **9** from a single-crystal X-ray diffraction study at 100 K, shown with 50% probability ellipsoids. Only the major part is depicted, and non-phosphinidene H-atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: V1–N1 1.675(2), V1–N2 1.894(2), N1–P1 1.732(2), P1–C1 1.842(4), P1–C2 1.882(3), C2–C3 1.497(5); V1–N1–P1 160.09(2), N1–P1–C1 103.82(2), C1–P1–C2 47.35(2), C2–C1–P1 67.7(2), C3–C2–P1 116.4(3).

Singlet reactivity of putative **1** was unexpected, as CASSCF-NEVPT2 quantum chemical calculations on the model complex PNV(NH₂)₃ predicted a triplet ground state with a singlet–triplet gap of 12 kcal/mol (see SI). Stepwise addition of a triplet phosphinidene would have been expected to result in scrambling to form some amount of the *trans* isomer.²⁶

To further investigate the spin state of presumed monomer transfer, a benzene solution of **3** was heated at 55 °C for 72 h in the presence of 10 equiv of vinylcyclopropane as a radical clock (Scheme 5).²⁷ Upon workup, **9** was isolated as the major species.

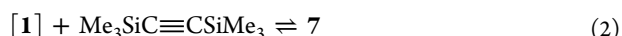
Scheme 5. Transfer of **1** to Vinylcyclopropane and 1,1-Difluoro-2-vinylcyclopropane, Illustrating the Expected Singlet Phosphinidene Addition Products



As evidenced by multinuclear and 2D NMR spectroscopy as well as X-ray crystallography, **9** was formed stereoselectively, most likely due to the bulky anilide ligand environment. More importantly, these data confirmed that **9** contained an intact cyclopropane ring, consistent with concerted singlet phosphinidene transfer (Figure 3b). Vinylcyclopropane's high ring-opening rate constant of $1.3 \times 10^8 \text{ s}^{-1}$ makes a triplet intermediate unlikely, though a stepwise addition mechanism in which the rate of P–C bond formation is much faster than the rate of cyclopropane ring opening would also generate **9**.²⁶ With a radical ring-opening rate constant of $3.4 \times 10^{11} \text{ s}^{-1}$, the 2,2-difluorocyclopropylcarbonyl radical is one of the shortest lived

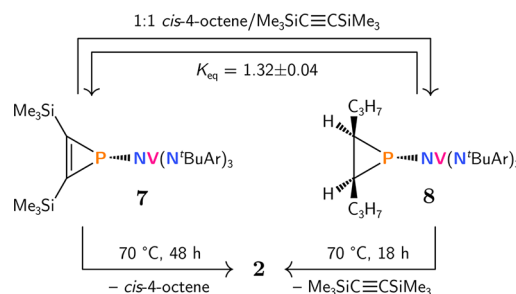
calibrated radical clocks.²⁸ Repeating the transfer experiment with 1,1-difluoro-2-vinylcyclopropane yielded two diastereoisomers of **10**, as evidenced by multinuclear and 2D NMR spectroscopy, allowing reasonable exclusion of a triplet reactive intermediate. These data are consistent with fragmentation of **3** to singlet **1**, which is rapidly intercepted before intersystem crossing to the more stable triplet state.²⁶ Such behavior is well known for carbenes.²⁹

The low solubility of **2** prevented a kinetic analysis on the transformation of **3** into **2**, but the reaction between **3** and bis(trimethylsilyl)acetylene could be monitored by NMR spectroscopy to investigate dissociative production of putative **1**. The time evolution of the various implicated species can be rationalized according to eqs 1–3.



In a reversible process, **3** presumably fragments via [2+1]-retrocycloaddition, giving rise to the reactive intermediate **1**, which can then engage in [2+1]-cycloaddition with bis(trimethylsilyl)acetylene or dimerize to generate **2**. Using a large excess of bis(trimethylsilyl)acetylene, pseudo-first-order conditions can be achieved such that $d[\mathbf{7}]/dt = k_{\text{obs}}[\mathbf{3}]$, assuming that the forward direction of eq 1 is the rate-limiting step. The decay of **3** was thus monitored by ⁵¹V NMR spectroscopy at 66 °C in the presence of excess alkyne, revealing the anticipated first-order behavior in **3** in accordance with unimolecular decay ($k_{\text{obs}} = (1.34 \pm 0.14) \times 10^{-3} \text{ s}^{-1}$). Halving the concentration of alkyne did not produce a corresponding change in k_{obs} , suggesting zeroth-order dependence. Together, these data indicate that an associative mechanism involving direct reaction of the alkyne with **3** is unlikely. Supporting the equilibrium depicted in eq 1, decay of **3** to **2** in the absence of a trap required 13 h at 66 °C in THF, standing in sharp contrast with the 30 min required for complete decay of **3** in the presence of bis(trimethylsilyl)acetylene.

Scheme 6. Thermolysis of **7** and **8** To Generate **2**, and Substrate “Hopping” between **7** and **8**



The isolobality of alkenes and diphosphenes draws a clear analogy between **3** and **8**, leading one to question if **8** (or even **7**) can serve as a source of **1**. Heating a solution of **7** or **8** in benzene-*d*₆ at 70 °C for 18 h resulted in the formation of **2**, releasing bis(trimethylsilyl)acetylene or *cis*-4-octene respectively, suggesting that both **7** and **8** can indeed serve as formal sources of **1** (Scheme 6). To test this hypothesis, a solution of **8** and excess bis(trimethylsilyl)acetylene in benzene-*d*₆ was heated at 70 °C for 18 h, resulting in 82% conversion to **7**. In the same way,

heating a solution of **7** in the presence of excess *cis*-4-octene resulted in 84% conversion to **8**.

In the presence of equimolar amounts of *cis*-4-octene and bis(trimethylsilyl)acetylene, we found that $K_{\text{eq}} = [\mathbf{8}]/[\mathbf{7}] = 1.32 \pm 0.04$. Notably, no *trans*-4-octene was detected throughout all the transfer experiments, consistent with singlet phosphinidene transfer. While phosphorus(III/V) redox cycles are well established,³⁰ reversible binding of unsaturated hydrocarbons through a phosphorus(I/III) cycle is highly reminiscent of transition-metal behavior.³¹ Facile transfer of **1** to unactivated olefins complements the recent report of an isolable phosphinidene by Bertrand, for which binding to the strongly activated maleic anhydride was described.²⁵ Phosphinidene “hopping” between olefins is more evocative of recent reports from Mathey²² and Lammertsma³² on metal-bound phosphinidene generation from phosphirane transition-metal complexes.

A molecular precursor has been used to prepare unique organometallic complexes featuring an unconventional PN linkage, providing an exciting first glimpse into the chemistry of complexed PN as a reactive intermediate. The facile transfer of a phosphinidenoid unit from **3**, **7**, and **8** suggests that the $V(N^t\text{Bu}Ar)_3$ platform could be further exploited in the quest for stabilizing reactive main-group species. Current work is focused on expanding upon the reactivity of the interstellar molecule PN³³ as well as modifying the supporting anilide ligand framework with the goal of obtaining an isolable monomeric PN complex.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10545.

Experimental details, characterization data, computational details, and tables of Cartesian coordinates (PDF)

X-ray crystallographic data for **2**, **3**, **6**, **8**, and **9** (CIF)

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Notes

The authors declare no competing financial interest.

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