**Phosphinidene Reactivity of a Transient Vanadium PN Complex**

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Phosphinidene Reactivity of a Transient Vanadium P≡N Complex

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Supporting Information

ABSTRACT: Toward the preparation of a coordination complex of the heterodiatomic molecule PN, P≡N-V[N[′Bu]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[′Bu]Ar)3] (Na[4]) to yield trimeric cyclo-triphosphane [PNV(N-[′Bu]Ar)3] (3) with a core composed exclusively of phosphorus and nitrogen. In the presence of NapS2 (peri-1,8-naphthalene disulfide), NapS2-P-NV(N-[′Bu]Ar)3 (6) is instead generated in 80% yield, suggesting trapping of transient 1. Upon mild heating, 3 readily fragments into dimeric [PNV(N-[′Bu]Ar)3]2 (2), while in the presence of bis(trimethylsilyl)acetylene or cis-4-octene, the respective phosphirenne (Ar[′Bu]N)3VN-PC3(SiMe3)2 (7) or phosphirane (Ar[′Bu]N)3VN-P(C6H5) (8) compounds are generated. Kinetic data were found to be consistent with unimolecular decay of 3, and [2+1]-cycloaddition with radical clocks ruled out a triplet intermediate, consistent with intermediate 1 reacting as a singlet phosphinidene. In addition, both 7 and 8 were shown to reversibly exchange cis-4-octene and bis(trimethylsilyl)acetylene, serving as formal sources of 1, a reactivity manifold traditionally reserved for transition metals.

The state of P≡N solution chemistry contrasts sharply with that of homodiatomic molecules N2 and P2. Indeed, dinitrogen reactivity has been extensively investigated, and new synthetic routes have recently enabled the exploration of the rich chemistry of diphosphorus.3,4 Despite longstanding spectroscopic interest and recent efforts in the development of molecular precursors to PN3,6 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 iminophosphines and related species, 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, 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-[′Bu]Ar)3 (Ar = 3,5-Me2C6H3)11 could provide a protective pocket to accommodate PN within its sterically congested anilide ligand environment. Herein, in pursuit of a terminal complex of PN (1), we report dimeric diphosphene 2 and trimeric cyclo-triphosphane 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-[′Bu]Ar)3] (Na[4]) with CIPA (A = C14H10, anthracene), generating 5 en route to 1 (Scheme 1). Subsequent anthracene elimination from 5 would then produce 1 when provided with sufficient thermal energy. Interestingly, when the reaction was carried out in thawing THF, the dark red solids isolated from the reaction mixture did not show a characteristic signal for the bridgehead protons of a 7-phosphorbornadiene framework by 1H NMR spectroscopy, indicating 5 was not the isolated product. This was confirmed by...
The formation of oligomers such as 2 and 3 is highly reminiscent of phosphinidene reactivity, leading us to consider the possibility of a cyclo-phosphane moiety with monomeric units. An alternative mechanism involving reaction of NapS2 with the steric bulk of its substituents, the metrical parameters of the cyclo-triphosphane structure were not perturbed compared to previously reported P3 cycles. Presumably, formation of 3 occurs first through 5, which loses anthracene to generate 1 that then rapidlyimerizes. 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 CPIA and NapS2 (peri-1,8-naphthalene disulfide, 1.0 equiv), 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 P 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=Π=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 transitioning to 2 for steric reasons.

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Singlet reactivity of putative 1 was unexpected, as CASSCF-NEVPT2 quantum chemical calculations on the model complex PN(V(NH2)3) predicted a triplet ground state with a singlet–triplet gap of 12 kcal/mol (see SI). Stepwise addition of a triplet phosphinidene could not be achieved such that only the major part is depicted, and non-phosphiranyl H-atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: V1–N1 1.679(2), V1–N2 1.657(2), N1–P1 1.716(2), P1–C4 1.878(2), P1–C5 1.879(3); V1–N1–P1 105.30(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-phosphiranyl H-atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: V1–N1 1.675(2), V1–N2 1.894(2), N1–P1 1.894(2), N1–P1 160.09(2), P1–C2 1.878(2), P1–C5 1.7164(2), P1–C11 1.842(4), P1–C12 1.882(3), C2–C3 1.497(5); V1–N1–P1 103.82(2), N1–P1–C11 103.52(2), C1–P1–C12 47.35(2), C2–C1–P1 67.7(2), C3–C2–P1 116.4(3).

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). 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

3 → 1 + [1]

[1] + Me3SiC≡CSiMe3 → 9

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 either 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 \( \frac{d[3]}{dt} = k_{obs}[3] \), assuming that the forward direction of eq 1 is the rate-limiting step. The decay of 3 was thus monitored by \(^{31}\)V NMR spectroscopy at 66 °C in the presence of excess alkyne, revealing the anticipated first-order behavior in 3 in accordance with unimolecular decay \( k_{obs} = (1.34 \pm 0.14) \times 10^{-3} \) 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 isolability 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-

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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 \( 1.3 \times 10^9 \) 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. With a radical ring-opening rate constant of \( 3.4 \times 10^8 \) s\(^{-1}\), the 2,2-difluorocyclopropylcarbiny radical is one the shortest lived calibrated radical clocks. 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. Such behavior is well known for carbenes.

3 = 2 + [1]

[1] + Me3SiC≡CSiMe3 → 9

[1] + [1] → 2

(3)
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 
\[ K_{eq} = \frac{[8]}{[7]} = 1.32 \pm 0.04. \] 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 Mathey\(^{22}\) and Lammertsma\(^{32}\) 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 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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