Staudinger Reactivity and Click Chemistry of Anthracene (A) Based Azido Phosphine N_3PA

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Abstract. 11-azido-9,10-dihydro-9,10-phosphanoanthracene (N_3P**A**) has been demonstrated recently as a transfer reagent for molecular PN as it easily dissociates at room temperature into dinitrogen (N_2), phosphorus mononitride (PN) and anthracene (**A**). Here we report further reactivity studies of the N_3P**A** molecule including strain promoted 1,3-dipolar cycloaddition with cyclooctyne and Staudinger type reactivity. Calculations at the DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3(BJ)/cc-pVTZ level of theory indicate that the click reaction is faster than the dissociation of N_3P**A**. The Staudinger type reactivity enabled the transfer of the NP**A** fragment to a base-stabilized silylene. The previously reported intermediate of a vanadium trisanilide with an NP**A** ligand could be isolated in 61% yield and structurally characterized in a single crystal X-ray diffraction experiment. In line with the previously reported phosphinidene reactivity of the transient vanadium phosphorus mononitride complex, thermolysis or irradiation of the complex leads to anthracene elimination and the formation of the corresponding vanadium PN dimer or trimer, respectively.

Inspired by Carpino's hydrazine,[1] the Cummins group developed in the last decade the synthesis of dibenzo-7λ^3-phosphanorbornadiene derivatives that serve as molecular precursors for the release of reactive phosphorous species.[2-10] In an initial study, Velian and Cummins demonstrated the direct reaction of Mg**A**·3THF (**A** = $C_{14}H_{10}$ or anthracene) with phosphorus dichlorides, $RPCl_2$ (R = ${}^tBu$, dbabh (2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene), HMDS ($(Me_3Si)_2N$), ${}^iPr_2N$) to afford 7λ^3-phosphanorbornadiene (RP**A**) derivatives.[2] These RP**A** compounds served as starting materials for the synthesis of further anthracene based molecular precursors for the mild release of small phosphorus bearing species, including P_2 and HCP.[3-5]

Recently, we expanded the scope of RP**A** derivatives with the synthesis and isolation of highly labile N_3P**A** (Figure 1).[11] N_3P**A** was shown to dissociate with a first order kinetics half-life of roughly 30 min at room temperature to anthracene and yellow-brownish polymers. By heating under vacuum N_3P**A** explodes at 42 °C and dinitrogen (N_2), phosphorus mononitride (PN) and **A** were identified as the dissociation products in a molecular beam mass spectrometry (MBMS) study. In solution PN transfer reactivity was demonstrated in the reaction of N_3P**A** with $[(dppe)Fe(Cp^*)(N_2)][BArF_{24}]$ leading to the formation of $[(dppe)Fe(Cp^*)(NP)][BArF_{24}]$ with the PN ligand[12] N-bonded to the iron center due to significant covalent iron pnictogen bond character and associated less unfavorable Pauli repulsion in the metal-ligand interaction. Here we demonstrate further reactivity studies of N_3P**A** with cyclooctyne, a base-stabilized silylene and reinvestigate the proposed reaction mechanism in the synthesis of a transient vanadium PN complex, $PNV(N[^tBu]Ar)_3$ (Ar = 3,5-$Me_2C_6H_3$).

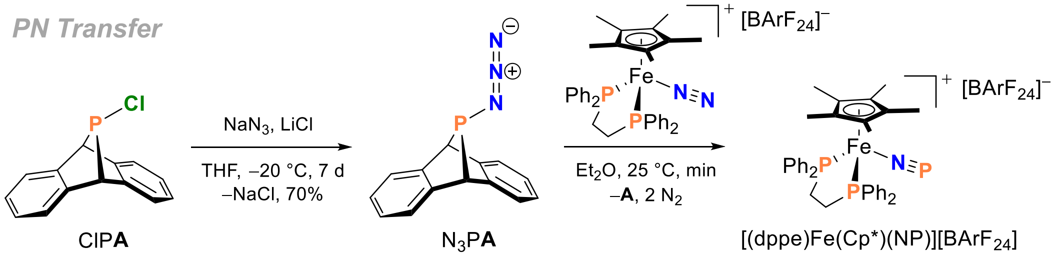

Figure 1: Synthesis of 11-azido-9,10-dihydro-9,10-phosphanoanthracene (N_3P**A**) and PN transfer reactivity with $[(dppe)Fe(Cp^*)(N_2)][BArF_{24}]$.

PN trapping experiments with N_3P**A** were conducted in neat cyclohexadiene and 2,3-dimethyl-1,3-butadiene, respectively. However, stirring the reaction mixture at room temperature or at 60 °C resulted in rapid PN polymerization as indicated by the precipitation of orange-brown polymers and no resonances in the ^{31}P NMR spectrum. The experiment was repeated and the solution irradiated in a quartz NMR tube with $\lambda = 254$ nm light for 10 min at room temperature but the result was the same. Note that rapid polymerization is also reported for gaseous PN, which produces white powder coatings on surfaces and limits high PN concentrations for spectroscopic measurements.[13] The color of the PN polymers is reported to change depending on the nitrogen content.[14-15] In stark contrast to diphosphorus (P_2) PN presumably does not show any triple bond reactivity with dienes under similar mild reaction conditions because of rapid polymerization.[16-17] Further PN trapping experiments with 3,5-diphenyl-2-phosphafuran[18] (DPF), different azide sources or alkynes were also not successful. We calculated the reaction barriers for the [4+2] cycloaddition reactions of 1,3-butadiene with P_2 (Figure 2, left) and PN (Figure 2, right), respectively, at the DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3(BJ)/cc-pVTZ + thermal correction to Gibbs free energy at 298.15 K level of theory. The cycloaddition reaction of 1,3-butadiene with P_2 is highly symmetric and associated with a reaction barrier of 15.3 kcal mol^{-1} at room temperature (Figure 2, left). The low reaction barrier is in good agreement with the previous P_2 trapping experiments.[16-17] Because of the different atomic and orbital sizes of P *vs* N the cycloaddition of 1,3-butadiene and PN is more asymmetric and the computed reaction barrier is increased by 6.6 kcal mol^{-1} to 21.9 kcal mol^{-1}. Note that the energy for *trans-cis* interconversion of 1,3-butadiene is not included here.[19] According to our experimental results, it seems likely that the barrier for PN polymerization is much lower in energy.

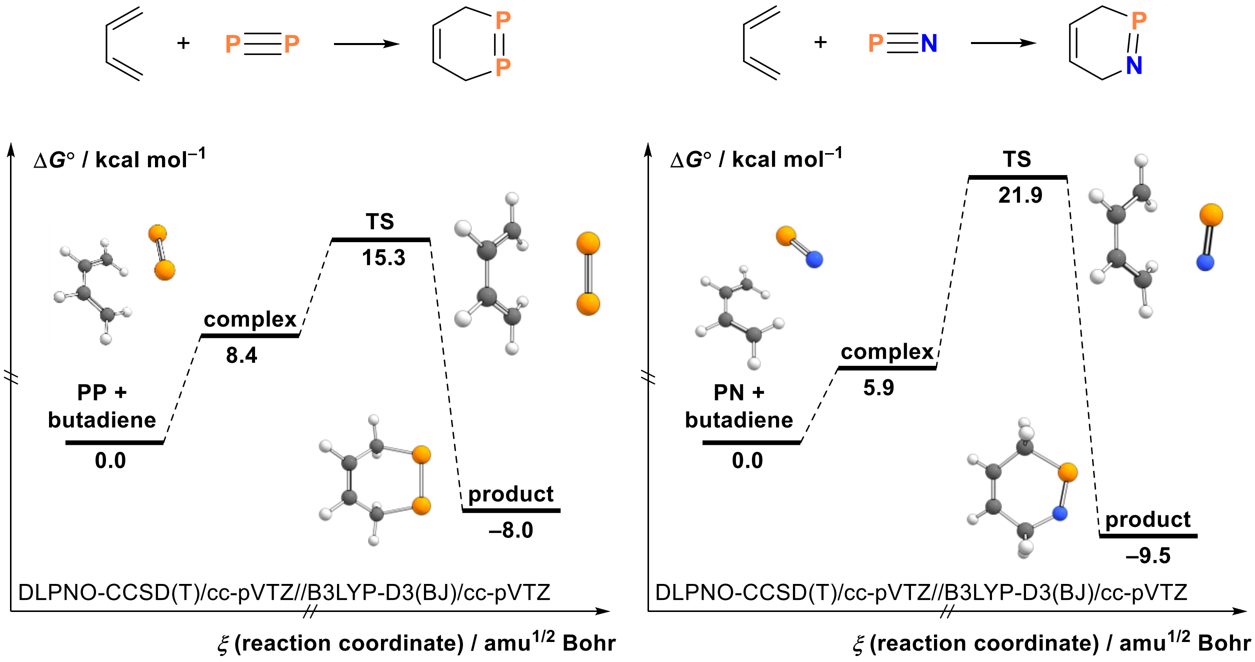

Figure 2: Computed reaction barriers for the [4+2] cycloaddition reactions of 1,3-butadiene with P_2 (left) and PN (right), respectively. Gibbs free energy values are computed for $T = 298.15$ K. Color code: carbon = grey, hydrogen = white, nitrogen = blue, phosphorus = orange.

Addition of cyclooctyne to a stirring solution of N_3P**A** in THF at room temperature did not lead to color changes or the formation of any precipitate. ^{31}P NMR analysis of the reaction mixture revealed a new triplet resonance at δ 154 ppm with a coupling constant of $^3J_{HP} = 13.3$ Hz, indicating that the product formed in this reaction contains a phosphorus center bound to anthracene. A diethyl ether solution of the crude reaction mixture was filtered through a plug of Celite and charcoal to remove free anthracene, and the filtrate was cooled to –20 °C to crystallize out the product. Single crystal X-ray diffraction confirmed triazole **1** as the 1,3-dipolar cycloaddition product (click product) between the azide unit of N_3P**A** and cyclooctyne (Figure 3). The computed low reaction barrier of the strain promoted [3+2]cycloaddition of phenyl azide and cyclooctyne is consistent with our experimental findings.[20] The strain promoted click reaction is faster than the decay of N_3P**A**.[21] After stirring **1** in THF at room temperature for 2 h a small triplet signal at δ 165 ppm appeared in the ^{31}P NMR spectrum. Complete conversion of compound **1** to the species corresponding to the new resonance was achieved by heating the solution for 3 h at 80 °C. Crystals of the product were grown from diethyl ether and characterized by single crystal X-ray crystallography, revealing a [1,2]shift of the P**A** unit to the central nitrogen atom in the triazole ring and the formation of **2** (Figure 3). Surprisingly, we could find no literature precedent for phosphorous substituted triazoles, only related isomeric triazaphospholes are well-studied.[22] Heating of **2** in toluene at 120 °C for 2 h leads to the release of **A** and no resonances in the ^{31}P NMR spectrum. Phosphinidene trapping experiments with an excess of cyclohexene were not successful.

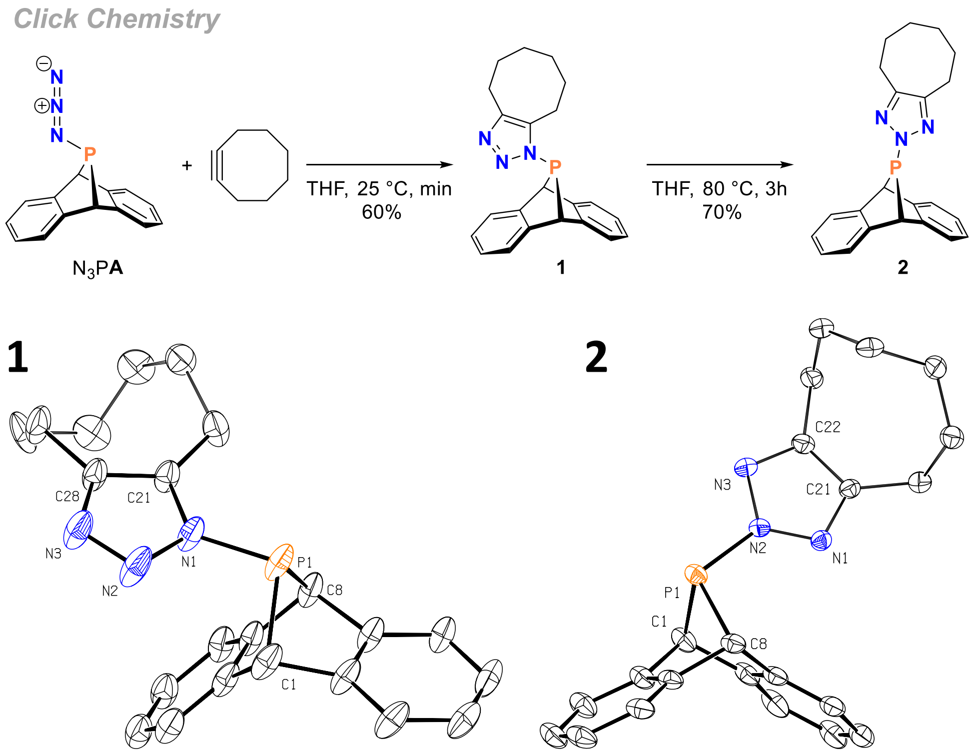

Figure 3: Top: Strain promoted click chemistry of N₃P**A** and cyclooctyne. Bottom: Molecular structures of **1** and **2** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected interatomic distances (Å): **1**: P1−N1 1.7670(14); P1−C1, 1.886(2); P1−C8, 1.8956(18); N1−C21, 1.3549(19); N1−N2, 1.368(2); N2–N3, 1.312(2); and C21–C28, 1.379(2). **2**: P1−N2 1.7564(13); P1−C1, 1.8921(17); P1−C8, 1.9028(17); N1−N2, 1.329(4); N1−C21, 1.324(8); and C21–C22, 1.401(9).

We explored the potential energy surface (PES) around N₃P**A** and cyclooctyne at the DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3(BJ)/cc-pVTZ + thermal correction to Gibbs free energy at 298.15 K level of theory (Figure 4). We located a transition state (**TS1**) that is 20.9 kcal mol^{-1} higher in energy than the two reactants. This barrier is lower in energy (2.4 kcal mol^{-1}) than the previously computed decomposition barrier of N₃P**A** (23.3 kcal mol^{-1}) at the same level of theory. Taking the experimentally determined dissociation barrier for N₃P**A** of $\Delta G^{\ddagger} = 22.1 \pm 1.5$ kcal mol^{-1} at 298 K into account we assume that the computed barriers are in general slightly higher in energy than the experimental ones. Consistent with the high strain energy of cyclooctyne, the reaction is highly exothermic (–58.3 kcal mol^{-1}). A second transition state (**TS2**) that describes the experimentally observed rearrangement is associated with a 26.3 kcal mol^{-1} high reaction barrier. The rearrangement is slightly exothermic by 4.8 kcal mol^{-1}. Note that the computed minima structure for **2** differs from the geometry of the crystalline compound. The triazole ring is rotated by almost 90° around the central P–N bond and is now almost in a parallel position to the anthracene unit.

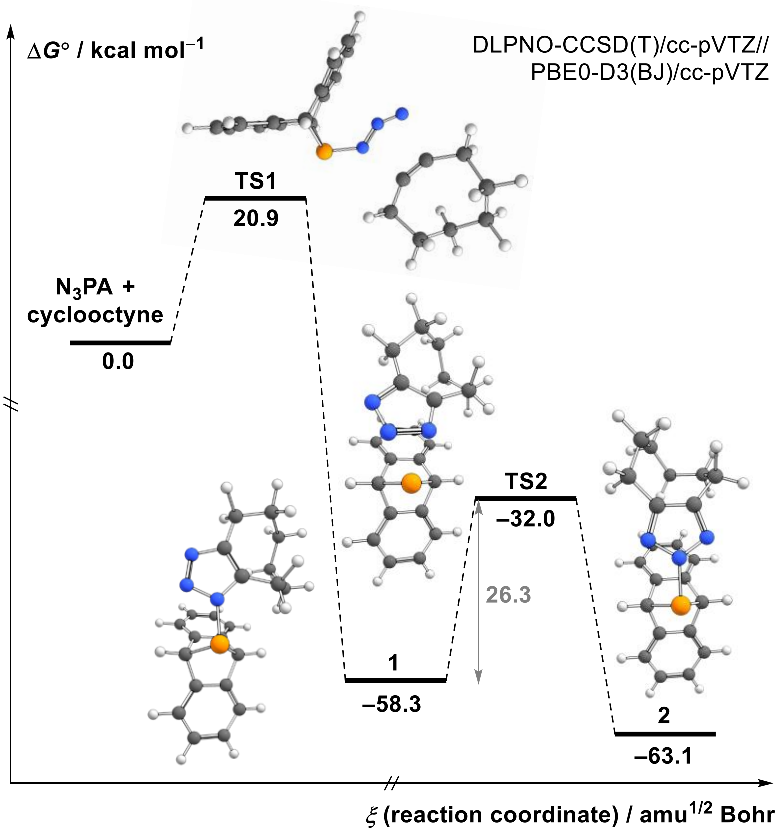

Figure 4: Computed minimum energy pathway for the reaction of $N_3P\mathbf{A}$ with cyclooctyne. Gibbs free energy values are computed for $T = 298.15$ K.

Inspired by the work of Bertrand and co-workers, who demonstrated the stabilization of PN by N-heterocyclic carbenes (NHCs), we investigated the reaction of $N_3P\mathbf{A}$ with an NHC.[23] Addition of $N_3P\mathbf{A}$ to a thawing solution of 2 eq. 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Ipr)[24] resulted in a gas evolution during warming and a color change to orange. After stirring the solution for 1 h we analyzed the crude reaction mixture by $^{31}P\{^{1}H\}$ and ^{31}P NMR spectroscopy and observed a new resonance at 285.5 ppm; note that the NHC-PN adduct by Bertrand and co-workers is reported at 134.0 ppm.[23] However, we were not able to isolate any reaction product. Therefore, we repeated the reaction in a similar fashion with base stabilized silylene (**3**, Figure 5).[25] The thawing yellow solution rapidly became blue, followed by orange and finally slightly yellow after stirring for 30 min during warming. In addition, gas evolution was observed. The ^{31}P NMR spectrum of the crude reaction mixture exhibited a single triplet resonance at δ 154 ppm with a coupling constant of $^{3}J_{HP} = 13.7$ Hz, indicating a clean chemical transformation with the anthracene unit still attached to phosphorus. Single crystal X-ray crystallography on a crystal grown from a pentane solution revealed that a Staudinger type reaction[26] had ensued between $N_3P\mathbf{A}$ and the silylene, leading to the formation of **A**PN-adduct **4**, with concomitant release of dinitrogen (Figure 5). Adduct **4** easily eliminates anthracene when heated, however, no resonances were observed in the ^{31}P NMR spectrum. Additionally, the compound is highly moisture sensitive as accidentally found by X-ray crystallography and AccuTOF-DART MS studies. Upon the addition of water compound **4** almost completely hydrolyzes within seconds and ring opens to compound **5**. Note that there is an intramolecular hydrogen bond between the silanol and the nearby imine function (Figure 5). In contrast to Ipr, **3** is able to stabilize the Staudinger reaction product.

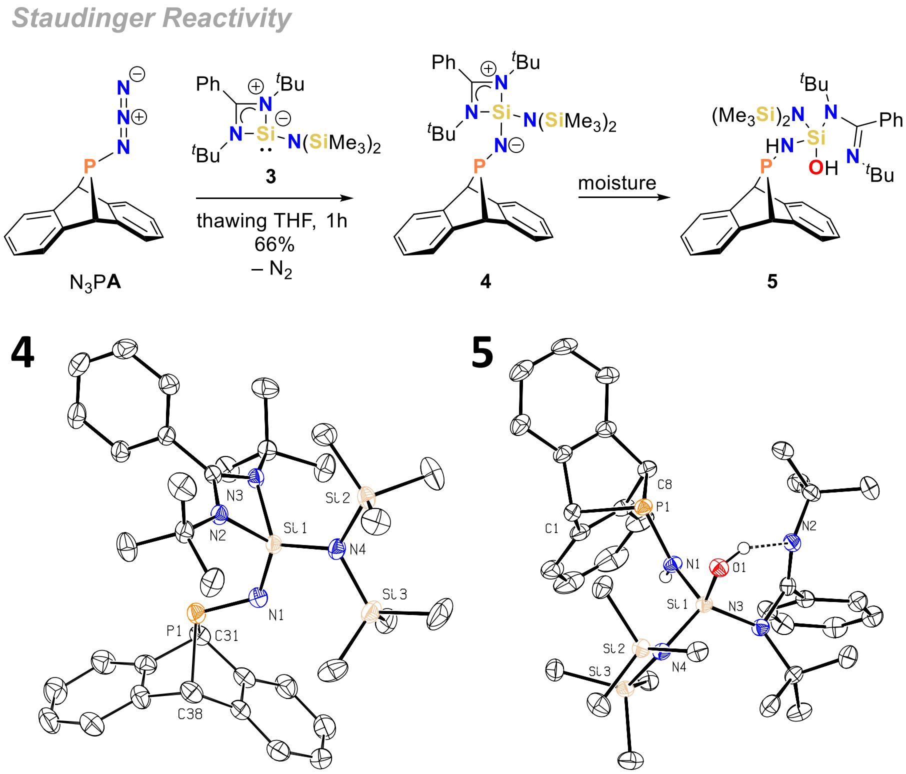

Figure 5: Top: Staudinger type reactivity of N$_3$P**A** and base stabilized silylene **3** followed by hydrolysis. Bottom: Left and right: Molecular structure of **4** and **5** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected interatomic distances (Å): **4**: P1−N1 1.6320(11); P1−C31, 1.937(3); P1−C38, 1.938(3); and N1−Si1, 1.6289(12). **5**: P1−N1 1.6862(18); P1−C1, 1.912(2); P1−C8, 1.926(2); and N1−Si1, 1.7425(18).

The observed Staudinger type reactivity (*vide supra*) motivated us to revisit the proposed reaction mechanism in the formation of the transient vanadium PN complex, (PN)V(N[^{t}Bu]Ar)$_3$.[27] In the reaction of Na[NV(N[^{t}Bu]Ar)$_3$] with ClP**A** only trimeric [(PN)V(N[^{t}Bu]Ar)$_3$]$_3$ (**7**), which forms dimeric [(PN)V(N[^{t}Bu]Ar)$_3$]$_2$ (**8**) upon heating, could be isolated. Anthracene bound (**A**PN)V(N[^{t}Bu]Ar)$_3$ (**6**) and free (PN)V(N[^{t}Bu]Ar)$_3$ were proposed as reactive intermediates in this transformation. However, even in a low temperature NMR experiment between −60 and 23 °C, neither of the intermediates were detected. Hence, the two complexes were assumed to be thermally unstable. The careful addition of solid N$_3$P**A** to a dark green stirring solution of V(N[^{t}Bu]Ar)$_3$ in diethyl ether at room temperature led to an immediate color change to dark red and gas evolution. The crude ^{31}P{^{1}H} and ^{51}V NMR spectra showed broad signals at δ 249 and δ 27 ppm, respectively. In addition a doublet at δ 4.95 ppm was observed in the ^{1}H NMR spectrum, indicative for bridgehead protons of (**A**PN)V(N[^{t}Bu]Ar)$_3$. After workup bright red solids were isolated in 61% yield. A representative sample was crystallized from cold (–20 °C) diethyl ether over 2 days, yielding dark red crystals that were analyzed in a X-ray crystallographic study. This experiment confirmed the formation of (**A**PN)V(N[^{t}Bu]Ar)$_3$ (Figure 6). Heating of the complex in benzene at 80 °C resulted in the formation of dimer **8** via trimeric **7** as followed by ^{51}V NMR spectroscopy (Figure S19). Irradiation of (**A**PN)V(N[^{t}Bu]Ar)$_3$ at room temperature with λ = 254 nm light also releases anthracene, and trimeric [(PN)V(N[^{t}Bu]Ar)$_3$]$_3$ is formed (Figure 6).

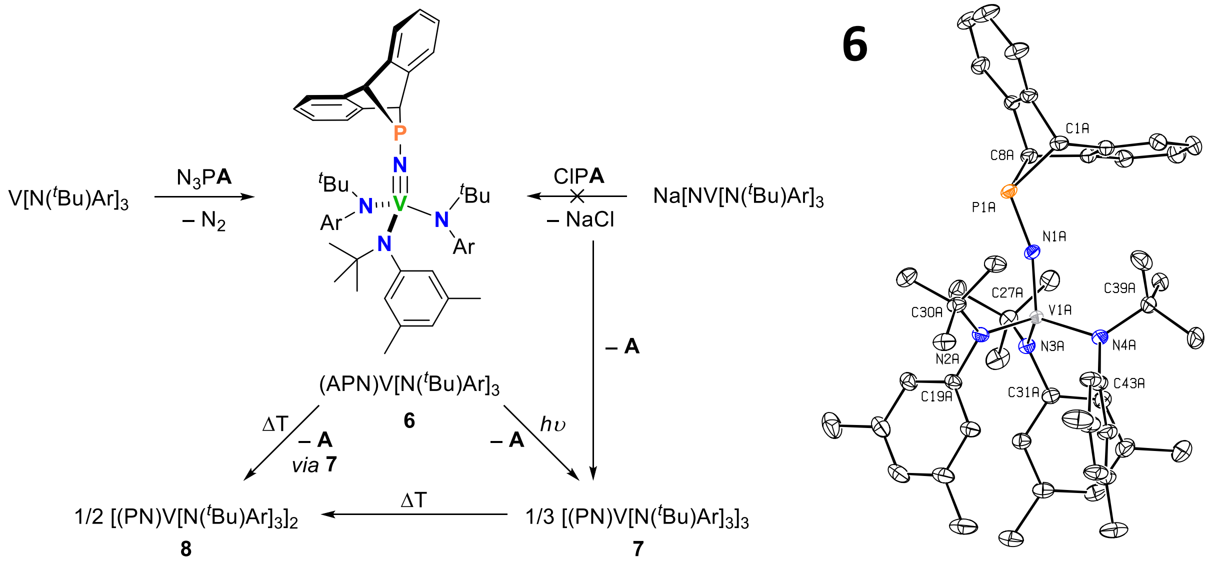

Figure 6: Left: Synthesis of (**A**PN)V(N[^{t}Bu]Ar)$_3$ and subsequent thermally and photochemically induced oligomerization reactions. Right: Molecular structure of (**A**PN)V(N[^{t}Bu]Ar)$_3$ (**6**) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected interatomic distances (Å): P1A–N1A 1.699(1); P1A–C1A, 1.910(1); P1A–C8A, 1.904(1); and N1A–V1A, 1.693(8). Selected interatomic bond angles (°): C1A–P1A–C8A, 79.3(5); P1A–N1A–V1A, 146.8(1).

The niobaziridine–hydride complex Nb(H)(η^2-^{t}Bu(H)CNAr)(N[Np]Ar)$_2$ (Np = neopentyl, Ar = 3,5-$C_6H_3Me_2$) was reported to react with elemental phosphorus (P_4) to yield the bridging diphosphide complex (μ_2:η^2,η^2-P_2)[Nb(N[Np]Ar)$_3$]$_2$.[28] Treatment of the niobaziridine–hydride complex with N$_3$P**A** resulted in a similar reactivity as with the vanadium trisanilide complex (*vide supra*) and the formation of the (**A**PN)Nb(N[^{t}Bu]Ar)$_3$ complex (**9**, Figure S20, see SI for further synthetic details). Heating or treatment of this complex with another equivalent of niobaziridine–hydride complex did not result in the formation of the bridging phosphorus mononitride complex. Besides free anthracene resonances in the ^{1}H NMR spectrum, we only observed a single resonance in the ^{31}P NMR at 115 ppm, which is tentatively assigned to an oligomerized niobium-PN complex based on free anthracene resonances and our findings of the related vanadium system (Figure S17-S18).

Caution

The handling of azide compounds should be done with the necessary safety precautions.[29] No direct explosions of N$_3$P**A** were encountered when it was diluted in organic solvents or carefully dried under vacuum below room temperature. Treatment of transition metal complexes in solution with solid N$_3$P**A** can cause a spontaneous explosive decomposition of N$_3$P**A** and should be avoided or solid N$_3$P**A** only be added in portions of a few milligrams, respectively.

Supporting Information

Full synthetic and computational details, including preparative procedures and spectroscopic data for the characterization of compounds.

CSD Reference Codes

CCDC 2110926–2110930 and 2120073 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Competing financial interests

None.

Materials & Correspondence

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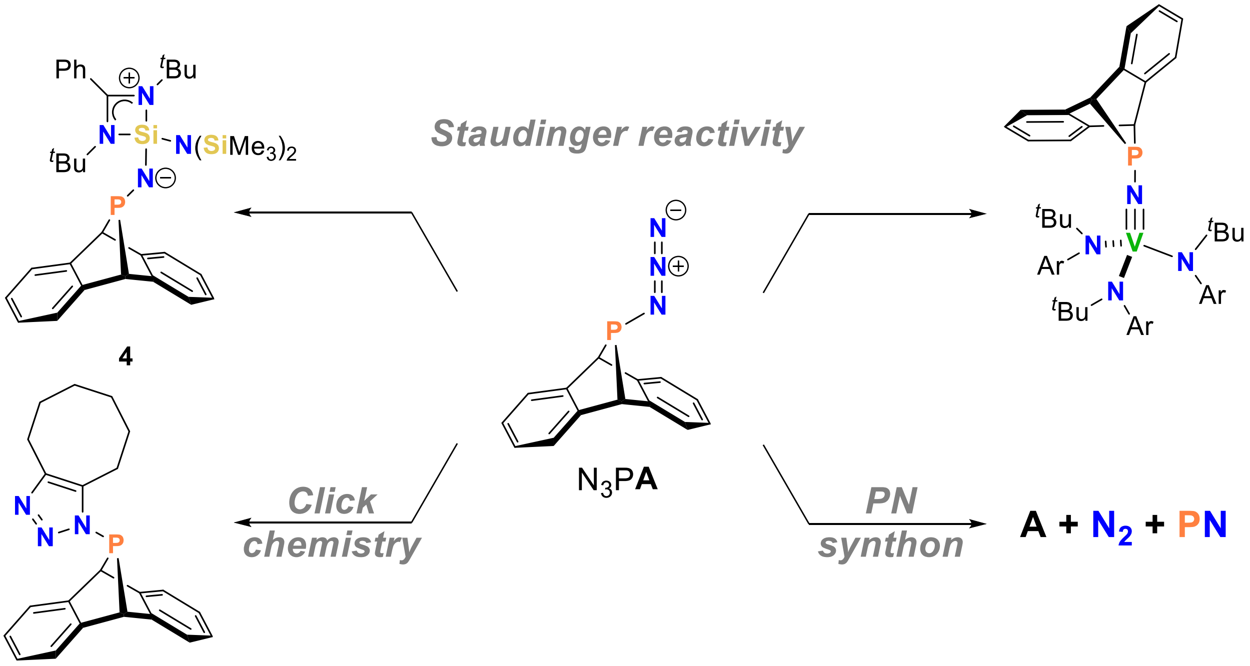
TOC + Synopsis



*Synopsis: Anthracene (**A**) based azido phosphine N_3P**A** is an explosive compound, which may serve as a synthon for PN in reactions with d- and p-block compounds by way of N_2 and anthracene loss. Here we demonstrate new reactivity studies of N_3P**A**, including Staudinger reactivity and [3+2] click chemistry.*