A Molecular Precursor to Phosphaethyne and Its Application in Synthesis of the Aromatic 1,2,3,4-Phosphatriazolate Anion

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S *Supporting Information*

ABSTRACT: Dibenzo-7-phosphanorbornadiene Ph₃PC-(H)P**A** (**1**, **A** = $C_{14}H_{10}$, anthracene) is reported here as a molecular precursor to phosphaethyne (HC≡P), produced together with anthracene and triphenylphosphine. HCP generated by thermolysis of **1** has been observed by molecular beam mass spectrometry, laser-induced fluorescence, microwave spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. In toluene, fragmentation of **1** has been found to proceed with activation parameters of $\Delta H^{\ddagger}$ = 25.5 kcal/mol and $\Delta S^{\ddagger}$ = −2.43 eu and is accompanied by formation of an orange insoluble precipitate. Results from computational studies of the mechanism of HCP generation are in good agreement with experimental data. This high-temperature method of HCP generation has pointed to new reaction chemistry with azide anion to produce the 1,2,3,4-phosphatriazolate anion, $HCPN_3^-$, for which structural data have been obtained in a single-crystal X-ray diffraction study. Negative-ion photoelectron spectroscopy has shown the adiabatic detachment energy for this anion to be 3.555(10) eV. The aromaticity of $HCPN_3^-$ has been assessed using nucleus-independent chemical shift, quantum theory of atoms in molecules, and natural bond orbital methods.

Unsaturated organophosphorus compounds are important to a wide range of chemical disciplines from synthesis[1] to astrochemistry,[2−4] but their study has been limited by reduced stability in comparison with their nitrogen congeners. This is principally caused by the reluctance of phosphorus to participate in π-bonding interactions, rendering such bonds reactive in the absence of kinetically stabilizing bulky substituents.[5] Without steric protection they are seldom isolable, often accessible only at high temperature[6] or through electric discharge.[7] These harsh methodologies are not typically amenable to synthetic chemistry, making necessary the development of alternate routes to such species. To this end, molecular precursors are an exciting avenue of pursuit, allowing for clean generation of small molecules at mild temperatures and enabling reaction chemistry not possible at the temperature extremes.

Our previous work on thermally activated molecular precursors has proven them to be a convenient entryway to reactive small molecule chemistry, such as that of P₂,[8,9] AsP,[10] phosphinidenes,[11] and dimethylgermylene.[12] Interested in expanding our substrate scope, we identified HC≡P, known as phosphaethyne, phosphaacetylene, or methylidynephosphine, as an interesting target species that has recently been discovered in outer space.[4] Early studies of this compound demonstrated moderate stability at low temperature, but fleeting existence under ambient conditions due to rapid polymerization.[13] Several synthetic pathways to phosphaalkynes have been developed,[14,15] but the chemistry of the parent derivative HCP has stagnated; in fact, we are only aware of a single experimental study on the reactivity of HCP.[16] Herein, we report the synthesis of a molecular precursor to phosphaethyne based on fragmentation with concomitant formation of anthracene and triphenylphosphine. Further reactivity of HCP is demonstrated through its [3 + 2] cycloaddition reaction with the azide ion at elevated temperature to yield the aromatic heterocyclic anion $HCPN_3^-$.

Inspired by several reports of ylide fragmentation to yield small molecules,[17] we directed our efforts to substitution of Cl**A** (**A** = $C_{14}H_{10}$, anthracene) with methylenetriphenylphosphorane (eq 1), effectively "sandwiching" phosphaethyne between anthracene

$$\text{Cl}\mathbf{A} \xrightarrow[-\,[\text{Ph}_3\text{PMe}]\text{Cl}]{2\ \text{Ph}_3\text{P}=\text{CH}_2} \qquad (1)$$
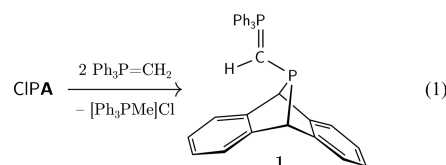
and triphenylphosphine in a manner reminiscent of P₂**A**₂.[9] Accordingly, we found treatment of Cl**A** with 2 equiv Ph₃PCH₂ at −35 °C in THF to yield Ph₃PC(H)P**A** (**1**) along with insoluble [Ph₃PMe]Cl.[18] The desired product could easily be separated from this precipitate by filtration and isolated in 67% yield. The solid-state structure of **1** (Figure 1) shares many characteristics with other RP**A** derivatives with elongated P1−C13 and P1−C14 bonds of 1.935 Å (avg) and an acute C13−P1−C14 angle of 77.92(6)° closely matching metrics reported for amino-substituted species.[11] Furthermore, the ylidic P2−C1
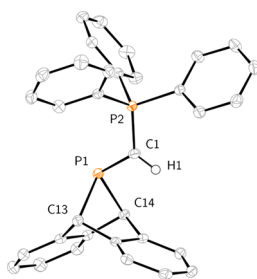
Figure 1. Molecular structure of **1** shown with 50% probability thermal ellipsoids. Solvent molecules and all hydrogen atoms except H1 are omitted for clarity. Selected interatomic distances [Å] and angles [°]: P1−C1 1.7442(15), P1−C13 1.9294(14), P1−C14 1.9412(15), P2−C1 1.6907(15); C1−P1−C13 108.08(7), C1−P1−C14 105.69(7), C13−P1−C14 77.92(6), P1−C1−P2 120.79(9).

distance of 1.6907(15) Å is similar to that of Ph_3PCH_2, reported to be 1.693 Å (avg).[18]

With successful preparation of **1**, we investigated its propensity to fragment thermally into phosphaethyne. Similar RP**A** architectures have allowed facile generation of transient phosphinidenes upon mild heating in benzene-d_6,[11] raising the question: Is **1** capable of transient phosphinidene release, and might this phosphinidene [$Ph_3P=C(H)P$] subsequently break apart into PPh_3 and HCP?

Analysis of solid **1** by thermogravimetric analysis (TGA) revealed a mass-loss event centered about 115 °C suggesting HCP release. Conclusive identification of the evolved gas was obtained by molecular beam mass spectrometry (MBMS) (Figure 2):[9] mass fragments corresponding to HCP (44 m/z)
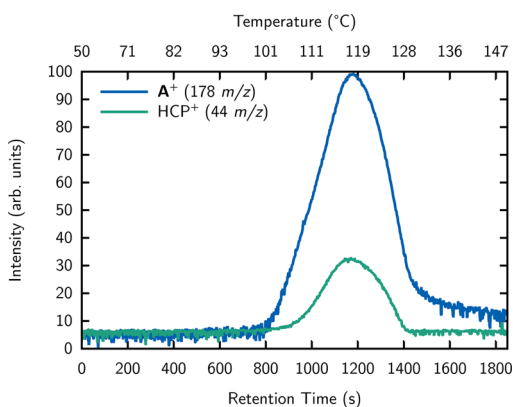

Figure 2. MBMS of **1**.

and anthracene (178 m/z) were simultaneously detected upon heating the solid to ∼120 °C. Incorporation of a ^{13}C label at the ylidic carbon of **1** led to disappearance of the mass fragment at 44 m/z and detection of a mass fragment at 45 m/z, in agreement with $H^{13}CP$ generation. Gas evolved from **1** could be condensed into an NMR tube containing frozen diethyl ether to allow ^{31}P NMR analysis of HCP upon thawing and warming to −60 °C, matching the literature value (−32 ppm).[21] The yield of HCP produced via vacuum transfer was 12% as quantified by ^{31}P NMR spectroscopy using an internal standard.

Molecular precursors to small molecules have been shown to have useful spectroscopic applications, allowing for selective generation of the species of interest in contrast to electric discharge or laser ablation methods.[22] Upon thermolysis of solid **1**, microwave spectroscopy was successfully employed to detect

the $J = 1 \leftarrow 0$ rotational transition of gaseous phosphaethyne at 39951.9 MHz as shown in Figure 3. The measured phosphorus
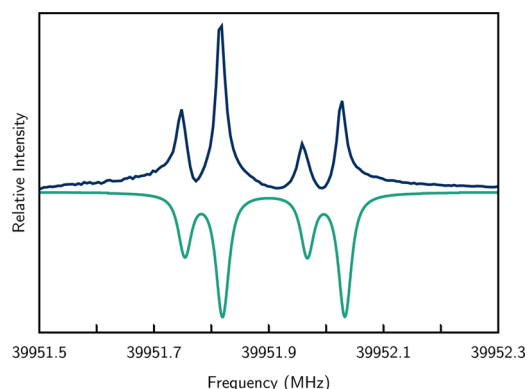

Figure 3. $J = 1 \leftarrow 0$ rotational transition of phosphaethyne evolved by solid **1** at 95 °C. The microwave spectrum displays two hyperfine components from the ^{31}P nucleus ($I = 1/2$) and Doppler doubling. The lower inverted spectrum is a simulation generated with PGOPHER[19] using previously reported rotational and coupling constants.[20]

spin−rotation coupling constant of 46(4) kHz showed excellent agreement with the literature value of 43.64(15) kHz.[20] Laser-induced fluorescence studies were performed using a resistively heated ceramic sample holder to heat **1** in a high-vacuum chamber, revealing rotational transitions within the $\tilde{A}(03^11) \leftarrow \tilde{X}(00^00)$ band of HCP.[23] The estimated temperature of the gas was found to be 300 K, indicating any rotational excitation imparted to the HCP molecules during dissociation was relaxed by collisions with the chamber walls.

Having established the ability of **1** to evolve HCP upon mild thermal activation from the solid into the gas phase, we turned next to solution-phase investigations in order to probe for possible applications of **1** as an HCP source in synthesis. Heating a toluene solution of the precursor to 95 °C for 1.5 h successfully led to complete thermal fragmentation, depositing insoluble orange solids along with anthracene and triphenylphosphine in 51% and 56% yield, respectively, as quantified by ^1H NMR spectroscopy. The orange precipitate was not found to conform to a $(HCP)_x$ empirical formula by combustion analysis, likely indicating partial incorporation of anthracenyl[24] or triphenyl-phosphoranyl moieties. Thus, thermolysis of **1** was not found to cleanly generate the previously reported phosphaethyne polymer,[25] an insoluble black solid[13] formed with traces of P_4.[16]

Monitoring the thermal decomposition of **1** in the absence of a chemical trap at several temperatures by ^1H and ^{31}P NMR spectroscopy allowed a kinetic analysis to be performed. The rate of decay of **1** followed first-order reaction kinetics, giving the rate constants listed in Table S.1. A fit to the Eyring equation gave parameters of $\Delta H^\ddagger = 25.5$ kcal/mol and $\Delta S^\ddagger = -2.43$ eu for thermolysis, consistent with a unimolecular process. No intermediates were observed by NMR spectroscopy during the thermolysis, including HCP, likely due to their fleeting stability at elevated temperatures.

Computational modeling was used to probe the mechanism of **1**'s fragmentation. The thermolysis was predicted to proceed as depicted in Figure 4, involving initial isomerization to a phosphirane, retro-[2 + 1]-cyclization to give a phosphinidene, and final ylide P−C bond scission to yield phosphaethyne. Similar isomerizations to three-membered rings have been postulated for other RP**A** derivatives as well as various silicon-
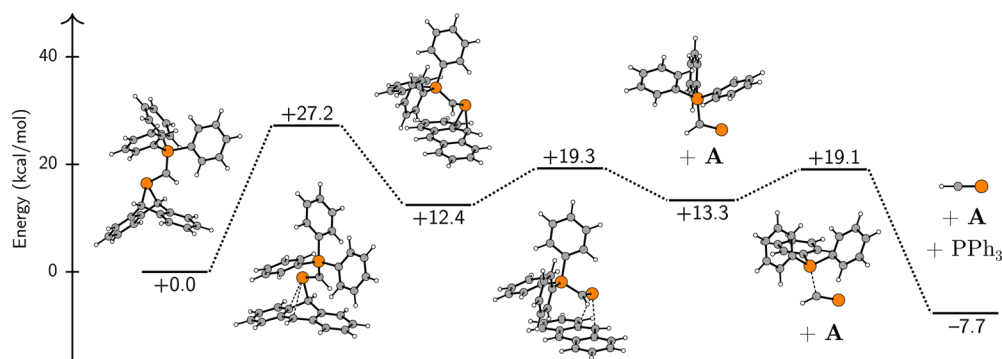
Figure 4. Gibbs free energies (in kcal/mol at 298.15 K) of intermediates and transition states predicted for thermal fragmentation of **1**.

based species.[26] Isomerization to the phosphirane intermediate is predicted to be rate-limiting with a transition state lying energetically uphill with $\Delta H^{\ddagger} = 27.8$ kcal/mol and $\Delta S^{\ddagger} = 1.9$ eu, in agreement with solution-based experimental measurements. Initial PPh$_3$ release was found to be prohibitively endergonic with an activation barrier of $\Delta G^{\ddagger} = 72.7$ kcal/mol at 298.15 K.

With recent success preparing the P$_2$N$_3^-$ anion through "click reaction" of N$_3^-$ and diphosphorus generated from P$_2$A$_2$,[27] we sought to probe reactivity of transient HCP with the azide anion to yield analogous HCPN$_3^-$ as shown in eq 2. Cycloaddition of

$$\mathbf{1} + N_3^- \xrightarrow[-\mathbf{A},\ PPh_3]{\Delta} \left[\begin{array}{c} N \\ (-) \ \| \\ P-N \\ N \end{array}\right] \qquad (2)$$
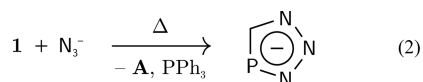
phosphaalkynes with organic azides and other 1,3-dipoles is well precedented,[15,28] but such reactivity with inorganic azide to yield the parent 1,2,3,4-phosphatriazolate[29] anion has not been reported. Heating a THF solution of **1** with 7 equiv tetra-*n*-butylammonium azide (TBAN$_3$) at 80 °C in a high-pressure vessel gave total consumption of **1** and 67% conversion to a new species with a chemical shift of 192 ppm by ^{31}P NMR spectroscopy. Its identity was assigned to be HCPN$_3^-$ by comparison of the ^{1}H, ^{13}C, and ^{31}P NMR signatures of the new species in THF-d_8 with the similar spectroscopic signatures of HCPN$_3$Me[16] as well as those of [K-kryptofix-222][^{1}AdCPN$_3$], which we isolated from a 1:1:1 mixture of ^{1}AdCP, KN$_3$, and Kryptofix-222 in THF in 87% yield. Further, the parent HCPN$_3^-$ ion (86 *m/z*) was detected by negative-ion electrospray ionization mass spectrometry. The [3 + 2] cycloaddition chemistry between HCP and azide was computationally predicted to proceed with a modest activation barrier of $\Delta G^{\ddagger} = 14.4$ kcal/mol at 298.15 K (see SI).

Interestingly, this same cycloaddition chemistry was not successful by vacuum transfer of HCP onto a frozen TBAN$_3$ slurry in THF. Insoluble brown solids rapidly developed upon warming the mixture to −78 °C, even before the THF could thaw fully. This rapid polymerization was not observed in the absence of TBAN$_3$, pointing to nucleophilic azide acting as a polymerization initiator. Cycloaddition of HCP with methyl azide has been reported under these conditions,[16] but the low solubility of TBAN$_3$ at −78 °C in aprotic solvents and the relatively high concentration of HCP provided by vacuum transfer seem to preclude cycloaddition chemistry in favor of polymerization. This points to **1** enabling new transformations of HCP unattainable by traditional vacuum transfer techniques through the gradual release and low concentration of HCP generated by its thermolysis.

Pure HCPN$_3^-$ was obtained by heating **1** with tris-(dimethylamino)sulfonium azide (TASN$_3$) in THF at 85 °C for 3 h, allowing isolation of [TAS][HCPN$_3$] in 14% yield. Diffraction quality crystals were grown by slow vapor diffusion of diethyl ether into a saturated acetonitrile solution at −35 °C (Figure 5). The lack of positional disorder in the anion was likely
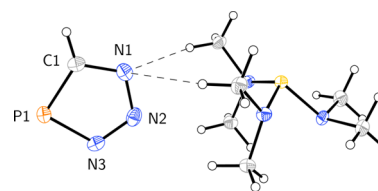

Figure 5. Molecular structure of [TAS][HCPN$_3$] shown with 50% probability thermal ellipsoids. Selected interatomic distances [Å] and angles [°] for HCPN$_3^-$: C1−P1 1.7216(12), P1−N3 1.6838(11), N2−N3 1.3279(15), N1−N2 1.3465(15), C1−N1 1.3400(16); C1−P1−N3 89.54(6), P1−N3−N2 111.97(8), N3−N2−N1 114.90(10), N2−N1−C1 111.56(10), N1−C1−P1 112.03(9).

influenced by two weak cation−anion interactions[30] marked by dashed lines with N⋯H distances of 2.615 Å (avg). The bond metrics of the HCPN$_3^-$ anion match closely to those of ^{1}AdCPN$_3^-$ (see Figure S.20), and all ring interatomic distances demonstrate bond lengths intermediate between single and double bonds,[31] pointing to electron delocalization.

Characterization of the HCPN$_3^-$ heterocycle by negative-ion photoelectron spectroscopy (NIPES) revealed its adiabatic detachment energy (electron affinity of HCPN$_3^{\bullet}$) to be 3.555(10) eV. This value is intermediate between that of 1,2,3-triazolate and P$_2$N$_3^-$, 3.447(4) eV[32] and 3.765(10) eV[33] respectively, but is much different from the values of the aromatic anions C$_5$H$_5^{-[34]}$ and P$_5^{-}$.[35]

A computational evaluation of aromaticity criteria for HCPN$_3^-$ was performed in comparison with six other 6π aromatic five-membered rings: C$_5$H$_5^-$, C$_2$H$_2$N$_3^-$ (1,2,3-triazolate), N$_2$S$_3^{2+}$, N$_5^-$, P$_2$N$_3^-$, and P$_5^-$. The profile of the nucleus-independent chemical shift along the *z* axis (NICS$_{zz}$) shows the largest magnitude at ~0.7 Å above the ring critical point,[36] and analysis of the π orbital contribution to the magnetic susceptibility by quantum theory of atoms in molecules theory reveals 51% contribution.[37] Both criteria are characteristic of an aromatic ring system, and further analysis by natural bond orbital (NBO) methods reveal extensive delocalization (Figure 6). By all measures, the aromaticity of HCPN$_3^-$ seems in line with the other 6π systems of comparison and appears intermediate between that of the 1,2,3-triazolate and P$_2$N$_3^-$ anions.
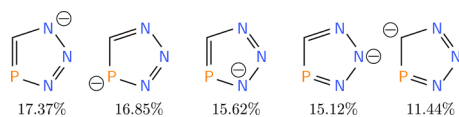
Figure 6. Natural resonance theory (NRT) weights of $HCPN_3^-$ from an NBO analysis.

The confirmation of phosphaethyne release from **1** further demonstrates the utility of well-defined molecular precursors for the clean and mild generation of interesting small molecules. Additional synthetic modifications of **1** and similar precursors are likely to allow for spectroscopic characterization of species currently unknown in the cosmos, giving astrochemists the proper information to search for their presence. Furthermore, the successful reactivity of HCP with azide to yield $HCPN_3^-$ proves the ability of rationally designed molecular precursors to promote reaction chemistry beyond that of traditional means.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03910.

> Experimental details and data (PDF)
> X-ray crystallographic data (CIF)
> X-ray crystallographic data (CIF)
> X-ray crystallographic data (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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