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An efficient photochemical route towards triplet ethynylphosphinidene, HCCP

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Abstract: While the archetypal free phosphinidene, H-P, has been studied for over a century, reports on uncomplexed, univalent phosphorus compounds are very sparse. Here we demonstrate production of HCCP in solid argon through the UV-induced rearrangement and subsequent dehydrogenation of phosphapropyne, CH₃CP. Migration of H atoms along the CCP backbone of CH₃CP resulted in production of the previously unobserved species 1-phosphapropadiene, CH₂=C=PH, followed by ethynylphosphine, HCCPH₂.

Phosphinidenes, the phosphorus analogues of nitrenes, have long been known as ligands in transition metal complexes,^[1] but only a handful of the free species have been experimentally characterized. The hydride (HP),^[2] cyanophosphinidene (PCN),^[3] and ethynylphosphinidene (HCCP)^[4] were detected as inseparable gaseous components produced through electrical discharge or high energy irradiation. Mesitylphosphinidene was observed in a solvent following the photolysis of mesitylphosphirane.^[5] Phenylphosphinidene was later produced^[6] in a cryogenic argon matrix (just like mesitylphosphinidene)^[7] from the corresponding phosphirane. Reaction of silicon atom with PH₃, also in an argon matrix, showed the presence of H₃SiP (silylphosphinidene).^[8] Recently, a singlet phosphino-phosphinidene, stable at room temperature, was synthesized.^[9] All other known phosphinidenes have triplet electronic ground states.

Given the presence of HCCN^[10] and the CCP radical^[11] in the interstellar medium, HCCP has been theorized as a potentially detectable species of astrochemical interest.^[12] The rotational spectrum^[4] and theoretical studies^[13] of HCCP indicated a linear, allenic structure, H—C≡C=Ė, with a significant contribution from the H—C≡C—Ė electronic configuration (Tab.

S4). For HCCN,^[14] the prevailing arrangement, H—C≡C=Ė, is accompanied by a significant carbenic admixture, H—Ė—C≡N. A theoretical (coupled cluster) study^[13a] did not reveal any potential energy minimum that would correspond to an analogous phosphorus-bearing carbene, H—Ė—C≡P. Although both HCCX species have a triplet ground state, the singlet-triplet energy gap, very small for HCCN (3 kJ/mol),^[15] is 75 kJ/mol for HCCP.^[13a]

HCCN has been formed through photolysis of diazoacetonitrile (N₂CHCN) and tentatively through VUV photolysis of acetonitrile (CH₃CN).^[16] The synthesis of the phosphorus analogue of diazoacetonitrile remains a challenge while that of phosphapropyne^[17] (CH₃CP, **1**) is known. No photodegradation studies have been carried out for any C₂H₃P-stoichiometry compound.

Scheme 1. Isomerisation of phosphapropyne **1** followed by dehydrogenation of ethynylphosphine **2**.

Previous studies of Guillemin et al.^[18] have shown that ethynylphosphine (HC≡CPH₂, **3**) rearranges to **1** in a reaction catalyzed by a strong Lewis base or a weak Bronsted base at high temperature in a vacuum gas-solid reaction. The authors proposed an intermediate species, phosphapropadiene (CH₂=C=PH, **2**), although it has never been observed experimentally. Herein, we report the UV-induced rearrangement

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Table 1. IR spectroscopic identification of phosphapropadiene ($\text{CH}_2=\text{C}=\text{PH}$, **2**) produced upon CH_3CP photolysis

Mode ^a		Theory (B3LYP/aug-cc-pVTZ) ^b				Experiment (Argon matrix)			
		Freq. ^c (cm^{-1})	Intensity (km mol^{-1})	Isotopic shifts (cm^{-1})		Freq. (cm^{-1})	Relative intensity (%)	Isotopic shifts (cm^{-1})	
				$^{13}\text{CH}_2\text{CPH}$	CD_2CPD			$^{13}\text{CH}_2\text{CPH}$	CD_2CPD
ν_3	PH stretching	2222.8	68	0.1	653.0	2264.4	79	0.0	620.6
ν_4	CC stretching	1729.4	79	22.3	34.8	1732.9	100	20.8	26.0
ν_6	CH_2 rocking	933.9	3.3	7.5	172.9	954.8	5.8	7.6	165.6
ν_7	PH bending	865.6	20	0.4	235.5	884.9	57	0.0	230.4
ν_8	CH_2 wagging	850.6	61	7.7	176.2	847.0	79	7.5	154.6

[a] Five bands of the highest DFT-predicted IR intensity (listed here) were experimentally observed. [b] Table S2 collects all fundamental modes and Table S3 shows DFT-predicted geometry of **2**. [c] Scaling factor 0.96.

and dehydrogenation of phosphalkyne **1** isolated in a cryogenic argon matrix, finally leading to HCCP, with species **2** and **3** being formed en route (Scheme 1).

Precursor **1** was isolated in solid argon at a molar ratio of 1:1000 ($T=6\text{ K}$) and exposed to Hg-lamp radiation with peak emission at 254 nm. The progress of photoreactions was monitored using FTIR and UV/visible absorption spectroscopy.

Figure 1. Evolution of concentrations over the course of 254 nm photolysis of CH_3CP (**1**) in solid Ar, scaled with respect to the initial concentration of the precursor. Integrated band intensities measured at 1556 cm^{-1} (**1**), 1733 cm^{-1} (**2**; $\text{CH}_2=\text{C}=\text{PH}$), 3311 cm^{-1} (**3**; $\text{HC}\equiv\text{CPH}_2$), and 3284 cm^{-1} (HCCP) were used in conjunction with the respective B3LYP/aug-cc-pVTZ absolute IR band strengths of 43 km/mol , 79 km/mol , 66 km/mol , and 76 km/mol . Common ordinate scale for the species **1**, **3**, and HCCP; 10-fold vertical expansion for species **2**.

At early stages of irradiation, the strongest product bands are directly attributable to the phosphine **3** based on their perfect match with a reference spectrum of a freshly synthesized sample made from diethyl ethynylphosphonate^[19] (see Fig. S2 and Tab. S1 for the relevant IR-spectroscopic data). Closer analysis reveals the presence of the allenic species **2**, hypothesized in the work of Guillemin et al.^[18] Its identification is based on DFT computations assisted by photochemistry of isotopically labeled precursors, $^{13}\text{CH}_3\text{CP}$ and CD_3CP (Tab. 1, Tab. S2, Fig. S3). The

maximum concentration of **2** is reached prior to that of **3** (Fig. 1), suggesting a stepwise hydrogen migration from methyl group towards the phosphorus atom.

Figure 2. Identification of HCCP. Top: IR spectrum (bands pointing downwards) theoretically derived (B3LYP/aug-cc-pVTZ, harmonic approximation, scaling factor 0.96) for the ground triplet electronic state of HCCP. Bottom: spectrum resulting from prolonged 254 nm irradiation of phosphapropyne (**1**) in solid Ar; $\nu_1 - \nu_4$ refer to the identified bands of HCCP. Bands due to **1** and **3** (ethynylphosphine) are labeled accordingly (see Fig. S4, for the IR spectrum of matrix-isolated **1**). Asterisk indicates an artefact feature (736 cm^{-1}) originating in the CsI substrate window.

The decay of all $\text{C}_2\text{H}_3\text{P}$ species was observed upon prolonged photolysis (Fig. 1), and dehydrogenation turned out to be the main process. The final product, HCCP (ethynyl phosphinidene), was unambiguously identified using isotopic labelling, use of different photolysis wavelengths to identify related bands, and comparison with DFT-predicted IR spectra and their isotopic shifts as illustrated in Figs. 2 and S1. Observed experimental IR absorption data along with theoretical values, including isotopic shifts, are listed in Table 2.

In addition to aiding the identification of photoproducts experiments involving precursor **1** with ^{13}C -substituted methyl group also shed light on the isomerization mechanism. Photolysis

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Table 2. IR-spectroscopic identification of ethynylphosphinidene, HCCP.

Mode		Theory (B3LYP/aug-cc-pVTZ) ^a					Experiment (Argon matrix)				
		Freq. (cm ⁻¹)	Intensity (km mol ⁻¹)	Isotopic shifts (cm ⁻¹)			Freq. (cm ⁻¹)	Intensity (km mol ⁻¹)	Isotopic shifts (cm ⁻¹)		
				H ¹³ CCP	HC ¹³ CP	DCCP			H ¹³ CCP	HC ¹³ CP	DCCP
v ₁	CH stretching	3307.9	76	14.5	0.4	795.8	3287.8	100.0	13.9	1.4	768.1
v ₂	CC stretching	1786.7	4.6	26.2	38.2	83.8	1814.2 and 1807.9	7.3 and 7.0	24.9	35.3	86.5
v ₃	CP stretching	678.3	15	8.1	6.4	9.5	696.1	13	8.3	7.3	14.7
v ₄	CH bending	564.6	36	4.5	0.8	112.1	564.7	73	4.1	0.4	116.8
v ₅	C-P bending	299.6	10	1.3	8.5	20.5	out of detection range				

[a] Scaling factor 0.96.

Scheme 2. Molecular rearrangements over the course of ¹³CH₃CP photolysis. The exact identity of a deduced CCP ring-bearing structure is unknown; see text.

of ¹³CH₃CP gave rise, as anticipated, to the ¹³CH₂=C=PH isotopomer of **2**. However, the formation of both H¹³CCPH₂ and HC¹³CPH₂ (Tab. S1 and Fig. S2), with a ratio of approx. 1:1, was observed. This suggests that the rearrangement from **2** to **3** proceeds through a phosphacyclopene-like species (Scheme 2). Either one of the two CP bonds may break within a ring, leading to the two observed ¹³C-isotopomers of **3**. This scrambling is conserved upon extended photolysis where the final products H¹³CCP and HC¹³CP appear in equal amounts. The cyclic intermediate may correspond either to a saddle point or a local energy minimum of the ground or excited state (singlet or triplet) potential energy surface. Its structure may resemble 1H-phosphirene (Scheme 2). Pertinent quantum chemical computations are under way to identify the nature of this species.

The lack of any preference for H¹³CCP over HC¹³CP among the products of ¹³CH₃CP photolysis implies that ethynylphosphinidene is not produced through direct dehydrogenation of either **1** or **2** but rather by loss of H₂ from **3**. In a separate experiment involving Hg-lamp photolysis of pure **3** in solid argon, HCCP was the final product. However, species **1** and **2** were also generated (Fig. S5), demonstrating the reversibility of photoisomerization reactions **1**→**2** and **2**→**3**.

The course of photolysis of CH₃CP was also monitored using electronic absorption spectroscopy (Fig. S6), providing first insights into the electronic spectra of species **1-3** and HCCP. As

photolysis progresses, the characteristic spectrum of CH₃CP is gradually eclipsed by two absorption maxima at 243 and 237 nm by 40 minutes of photolysis. These features, tentatively assigned to species **2**, disappear upon extensive irradiation while new absorption features appear, including strong bands at 277 and 259 nm as well as weaker features between 350 and 290 nm, at least partially due to HCCP. None of these features can be assigned to **3** whose spectrum is featureless.

In summary, photolysis of phosphapropyne (CH₃CP, **1**) in a cryogenic argon matrix with mid-UV radiation results in formation of triplet HCCP. Dehydrogenation is preceded by the appearance of the C₂H₃P isomers CH₂=C=PH (**2**) and HC≡CPH₂ (**3**). Isotopic labelling experiments suggest passage through a 3-membered ring in the **2**→**3** isomerization. This photochemical route for production of matrix isolated HCCP paves the way for the experimental exploration of its reactivity and electronic structure.

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Keywords: phosphinidene • rearrangement • phosphapropyne • photochemistry • HCCP • matrix isolation • phosphapropadiene

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Triplet HCCP is produced as the final product of the UV induced rearrangement and subsequent dehydrogenation of phosphapropyne, $\text{CH}_3\text{C}\equiv\text{P}$, in solid Ar. Phosphaallene $\text{CH}_2=\text{C}=\text{PH}$, and ethynylphosphine, $\text{HC}\equiv\text{CPH}_2$ are produced as H atoms are transferred along the CCP skeleton prior to dehydrogenation.