

Nonequilibrium Formation of Cyanophosphine (H_2PCN)—The Simplest Phosphorus-Containing Nitrile—in Interstellar Ice Analogues

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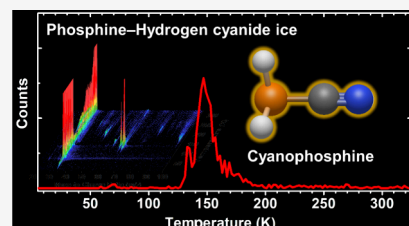


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Supporting Information

ABSTRACT: The detection of phosphorus-bearing molecules along with the high abundance of nitriles in interstellar and circumstellar environments suggests that phosphorus-containing nitriles may form under astrophysical conditions; however, their formation mechanisms have remained elusive. Here, we report the first laboratory formation of cyanophosphine (H_2PCN), the simplest phosphorus-containing nitrile, in low-temperature phosphine–hydrogen cyanide (PH_3 – HCN) interstellar ice analogues exposed to energetic electrons as proxies of galactic cosmic rays (GCRs). Tunable vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) enabled the isomer-selective identification of cyanophosphine in the gas phase during temperature-programmed desorption, establishing it as a promising target for astronomical searches. These results indicate that cyanophosphine forms through GCR-induced bond cleavage in phosphine and hydrogen cyanide to generate phosphino (PH_2) and cyano (CN) radicals, followed by barrierless radical–radical recombination. These findings advance our fundamental understanding of the abiotic synthesis of phosphorus-containing nitriles via nonequilibrium pathways in extraterrestrial environments.



Since its first detection in the circumstellar envelope of the carbon-rich star IRC+10216,^{1–3} phosphine (PH_3) has attracted considerable attention in astrochemistry,^{4,5} physical chemistry,^{6–9} prebiotic chemistry,^{10–12} and theoretical chemistry.¹³ This interest stems from its fundamental role in the abiotic synthesis of biologically relevant phosphorus-containing compounds such as phospholipids, adenosine triphosphate (ATP), and nucleotides.^{5,6,9,14} Laboratory experiments have demonstrated that exposure of phosphine-containing interstellar ice analogues to galactic cosmic ray (GCR) proxies produces a diverse range of biorelevant phosphorus-bearing molecules, including phosphanyloxyphosphane (H_2POPH_2),⁵ phosphine imide (H_3PNH),⁶ phosphinimine (HPNH),⁹ phosphorus oxoacids,¹⁰ alkylphosphonic acids,¹¹ formylphosphine (H_2PCHO),¹⁵ and phosphino formic acid (H_2PCOOH).¹⁶ In addition to phosphine, several other phosphorus-bearing species have been detected in the interstellar medium (ISM) such as phosphorus monoxide (PO) and its cation (PO^+), phosphorus mononitride (PN), silicon phosphide (SiP), phosphinidynemethyl (CP), phosphaethyne (HCP), and phosphinidynethylidyne (CCP);^{17,18} these species can undergo chemical processing by interstellar molecules, thereby expanding interstellar phosphorus chemistry.¹⁹ Notably, approximately 70 nitriles ($\text{R}-\text{C}\equiv\text{N}$) have been detected in interstellar and circumstellar environments, accounting for 20% of some 350 known interstellar molecules;^{20,21} this high fraction of nitriles raises the possibility that phosphorus-containing nitriles may also be present in the

ISM.^{21–24} However, the formation mechanisms of such compounds under astrophysical conditions have remained largely unexplored,^{13,18} particularly for cyanophosphine (H_2PCN , **1**), the simplest phosphorus-containing nitrile.

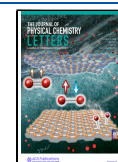
Cyanophosphine (**1**) was first generated through electrical discharge of phosphine and acetonitrile (CH_3CN) seeded in argon; its microwave spectrum was characterized between 10 and 42.5 GHz.²⁵ Subsequent millimeter/submillimeter measurements between 305 and 422 GHz provided more accurate rotational and centrifugal-distortion constants to guide astronomical searches toward Sagittarius B2(N), yielding an abundance upper limit of 7.0×10^{-12} relative to molecular hydrogen (H_2).²⁴ Recent laboratory experiments have demonstrated the formation of the nitrogen analogue of cyanophosphine (**1**), cyanamide (NH_2CN), in electron-irradiated hydrogen cyanide (HCN) ices²¹ and ammonia–methylamine (NH_3 – CH_3NH_2) ice mixtures.²⁶ In analogy, the former study proposed that electron irradiation of phosphine–hydrogen cyanide ices may produce cyanophosphine (**1**) through recombination of phosphino (PH_2) and cyano (CN)

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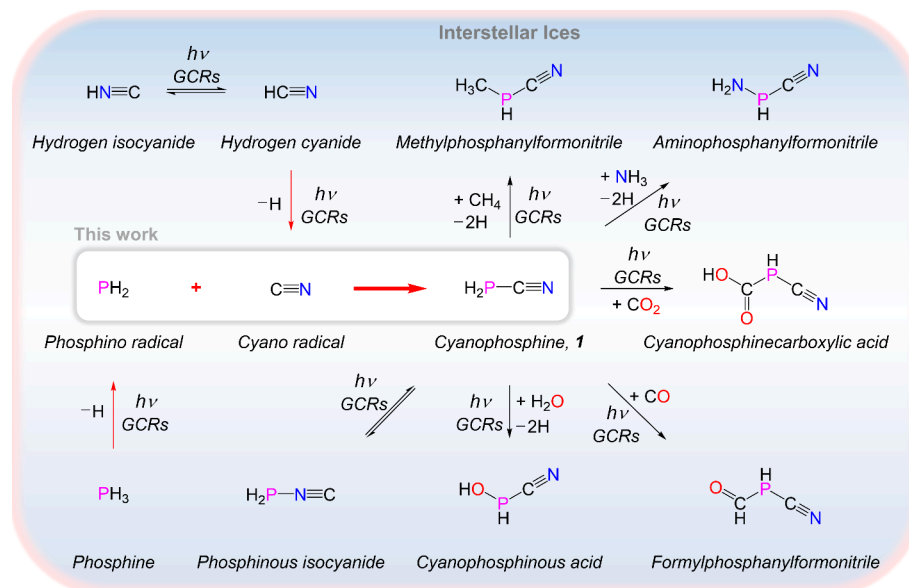


Figure 1. Potential formation of cyanophosphine (1) and its role as a key precursor to complex phosphorus-containing nitriles in interstellar ices.

radicals.²¹ Once formed, cyanophosphine (1) can undergo nonequilibrium chemistry initiated by GCRs and ultraviolet (UV) photons and react with abundant constituents of interstellar ices (Figure 1), including water (H₂O), carbon monoxide (CO), carbon dioxide (CO₂), ammonia (NH₃), and methane (CH₄).^{27,28} The reaction of cyanophosphine (1) with water may yield cyanophosphinous acid (HOPHCN), whereas energetic processing in carbon monoxide and carbon dioxide-containing ices could produce the elusive formylphosphanylformonitrile (HCOPHCN) and cyanophosphinecarboxylic acid (HOOCPHCN), respectively. Likewise, cyanophosphine (1) may react with ammonia and methane to form aminophosphanylformonitrile (NH₂PHCN) and methylphosphanylformonitrile (CH₃PHCN), respectively. Therefore, elucidating the formation mechanism of cyanophosphine (1) itself is essential for understanding the interstellar origins and molecular-growth pathways of complex phosphorus-containing nitriles. However, the formation of cyanophosphine (1) under astrophysical conditions has not yet been demonstrated experimentally.

Here, we report the first laboratory experiments on the formation of cyanophosphine (H₂PCN, 1) in interstellar ice analogues. This is accomplished in low-temperature (5 K) phosphine–hydrogen cyanide (PH₃–HCN) ices irradiated with energetic electrons, which simulate the secondary electrons generated as GCRs interact with interstellar ices within cold molecular clouds.^{29–31} Cyanophosphine (1) was identified isomer-selectively in the gas phase during temperature-programmed desorption (TPD) of the irradiated ices using tunable vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS). Gas-phase phosphine has been detected in the ISM at abundances of up to 4×10^{-7} relative to molecular hydrogen,^{2,3} and is proposed to form efficiently on interstellar grains through sequential hydrogenation of atomic phosphorus.^{32,33} Hydrogen cyanide is ubiquitous in the gas phase across protoplanetary disks,³⁴ star-forming regions,^{35,36} and molecular clouds,³⁷ with abundances as high as 10^{-6} relative to molecular hydrogen.³⁸ Solid hydrogen cyanide has also been tentatively detected on Neptune’s moon Triton³⁹ and is

considered a component of cometary ices.⁴⁰ Therefore, phosphine–hydrogen cyanide ice mixture represents a suitable model interstellar ice system for investigating the formation of cyanophosphine (1). Our results suggest cyanophosphine (1) can form in interstellar ices containing phosphine and hydrogen cyanide and is a suitable candidate for future astronomical searches. Furthermore, these findings provide fundamental insights into GCR-driven nonequilibrium pathways leading to phosphorus-containing nitriles in cold molecular clouds.

All experiments were performed in an ultrahigh vacuum chamber maintained at pressures of a few 10^{-11} Torr.^{31,41} A detailed description of the experimental procedures is provided in the Supporting Information. Phosphine–hydrogen cyanide (PH₃–HCN) ices were prepared at 5 K by independently codepositing PH₃ and helium-seeded HCN onto a polished silver substrate through separate glass capillary arrays yielding a PH₃: HCN ratio of $1.6 \pm 0.4:1$ (Table S1). The total ice thickness was determined by laser interferometry⁴² to be 670 ± 80 nm. The ice mixtures were subsequently irradiated at 5 K with 5 keV electrons for 5 min at a current of 28 nA. The irradiation doses were calculated to be 0.19 ± 0.03 eV per PH₃ molecule and 0.18 ± 0.03 eV per HCN molecule (Table S1). These doses are equivalent to $(7 \pm 2) \times 10^5$ years of processing by GCRs within cold molecular clouds and simulate an early stage of the evolution of a cold molecular cloud.⁴³ Fourier-transform infrared (FTIR) spectra of the PH₃–HCN ices were collected before, during, and after electron irradiation at 5 K (Figure S1 and Table S2). The infrared absorptions of the pristine ices were assigned to the fundamental vibrational modes of PH₃ such as the symmetric/asymmetric P–H stretching modes (ν_1/ν_3) at 2315 and 2335 cm^{−1},⁴² respectively, and those of HCN including the C–H stretching mode (ν_1) at 3132 cm^{−1}, the C≡N stretching mode (ν_3) at 2096 cm^{−1}, and the bending mode (ν_2) at 827 cm^{−1}.⁴⁴ Electron irradiation produced several weak additional absorptions (Figure S1). The band at 2073 cm^{−1} is assigned to the C≡N stretching vibration of cyanide anion (CN[−]),⁴⁰ whereas the absorptions at 2944, 2472, and 1784 cm^{−1} can be attributed to the C–H, P–H, and C=N stretching

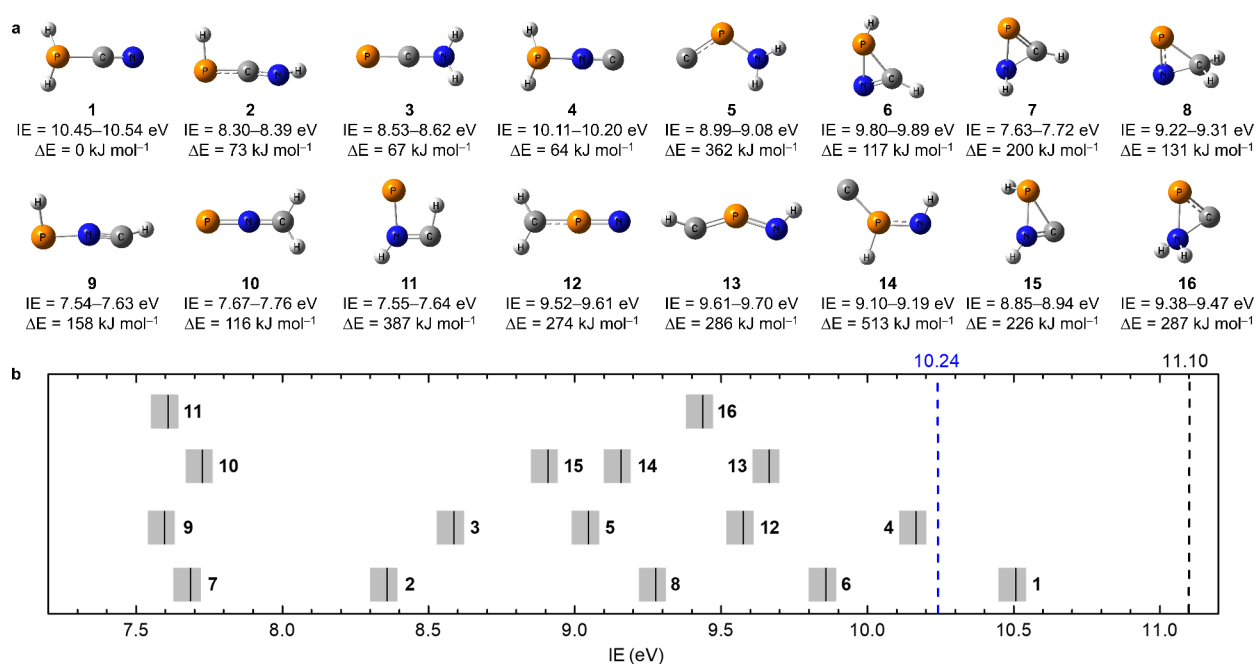


Figure 2. (a) Adiabatic ionization energies (IEs) and relative energies (ΔE) of H_2PCN isomers **1–16** computed in this work at the CCSD(T)/CBS//CCSD/cc-pVTZ level of theory, with zero-point vibrational energy (ZPVE) corrections calculated at the CCSD/cc-pVTZ level. (b) Calculated IEs (black solid lines) and corrected IE ranges (gray areas), incorporating previously established estimates for the combined uncertainty of $-0.03/+0.06$ eV and an additional -0.03 eV correction for thermal and Stark effects (Table S3). VUV photon energies of 11.10 and 10.24 eV were used for PI-ReToF-MS measurements of the irradiated ices during TPD.

vibrations,^{45,46} respectively, of newly formed irradiation products. Notably, the ice mixtures were exposed to a low irradiation dose to suppress sequential reaction pathways and preferentially probe first generation products formed through radical–radical recombination.³¹ Due to the expected low concentration of the formed products in the ices and their strong overlapping functional group absorptions with reactants, H_2PCN species including cyanophosphine (**1**) cannot be identified isomer-specifically by FTIR spectroscopy alone. For instance, the strongest vibrational absorptions of cyanophosphine (**1**) are predicted at 2309, 2303, and 826 cm^{-1} after applying a scaling factor of 0.9412 at the CCSD/cc-pVTZ level of theory,⁴⁷ and overlap closely with the P–H stretching mode (ν_1) of PH_3 at 2315 cm^{-1} and the bending mode (ν_2) of HCN at 827 cm^{-1} . Therefore, a more sensitive analytical method is required for the unambiguous identification of reaction products.^{48,49}

Tunable vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) was utilized to identify H_2PCN isomers based on desorption profiles and their calculated adiabatic ionization energies (IEs). The adiabatic ionization energies (IEs) and relative energies (ΔE) of H_2PCN isomers were computed at the CCSD(T)/CBS//CCSD/cc-pVTZ level of theory, with zero-point vibrational energy (ZPVE) corrections obtained at the CCSD/cc-pVTZ level (Figure 2 and Tables S3–S4). Sixteen H_2PCN isomers were considered computationally, among which cyanophosphine (**1**) was identified as the thermodynamically most stable isomer in the gas phase. The IE ranges incorporate a theoretical uncertainty of $-0.03/+0.06$ eV⁵⁰ and an additional correction of -0.03 eV to account for thermal and Stark effects.⁹ After irradiation, the ices were heated from 5 to 320 K at a rate of 1 K min^{-1} under temperature-programmed desorption (TPD) conditions. During TPD,

molecules desorbing into the gas phase were photoionized with VUV photons, and the resulting ions were separated according to their mass-to-charge (m/z) ratios and detected using a reflectron time-of-flight mass spectrometer. Each mass spectrum was integrated over 3600 acquisition sweeps, corresponding to a collection time of 2 min.

PI-ReToF-MS data were acquired at photon energies of 11.10 and 10.24 eV during TPD of the irradiated PH_3 –HCN ices; the corresponding mass spectra are compiled in Figure 3. Since phosphine (IE = 9.869 ± 0.002 eV)⁵¹ can be photoionized at both 11.10 and 10.24 eV, its broad sublimation events, extending from 48 to 142 K and peaking at 68 K, dominate the recorded ion signals. Focusing on H_2PCN isomers, the TPD profile at $m/z = 59$ recorded at 11.10 eV for the irradiated PH_3 –HCN ice reveals a broad sublimation event extending from 125 to 200 K (Figure 4a), with a minor peak at 134 K and a major peak at 147 K. The former peak at 134 K is attributed to cosublimation of species with diphosphane (P_2H_4),⁴² which exhibits a sublimation event peaking at 132 K (Figure S2). A blank experiment performed under otherwise identical conditions but without irradiation shows a weak peak at 69 K in the TPD profile at $m/z = 59$ (Figure 4a), attributed to the detector saturation during phosphine sublimation, whereas no sublimation events are observed above 80 K. These results demonstrate that the higher-temperature sublimation event at $m/z = 59$ originates from products formed as the result of the electron irradiation. Given the molecular weights of the reactants, the ion signal at $m/z = 59$ can be assigned to close-shell molecules with the molecular formulas H_5CN_3 and/or H_2PCN . The integrated ion signal ratio of $m/z = 60$ to $m/z = 59$ was determined to be $(1.9 \pm 1.0)\%$ (Figure S3), which is close to the expected natural isotopic abundance ratios of formulas H_5CN_3 (2.3%) and H_2PCN (1.5%). Considering the low irradiation doses used to

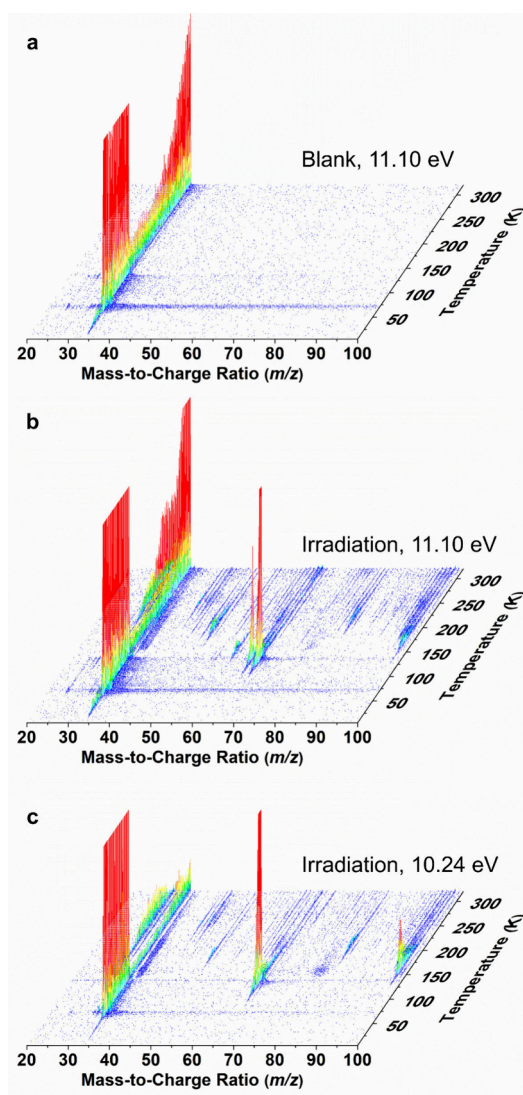


Figure 3. PI-ReToF-MS data recorded during TPD of phosphine–hydrogen cyanide ($\text{PH}_3\text{--HCN}$) ices. Mass spectra for the blank (unirradiated) ice were recorded at 11.10 eV (a), and the irradiated ices recorded at 11.10 eV (b) and 10.24 eV (c).

suppress sequential reactions, the formation of H_5CN_3 isomers would require the incorporation of three HCN molecules through multiple consecutive reaction steps and is therefore unlikely under the present experimental conditions. Consequently, the sublimation events observed at $m/z = 59$ can be assigned to H_2PCN isomers.

At 11.10 eV, all 16 H_2PCN isomers 1–16 can be photoionized (Figure 2). The TPD profile of $m/z = 59$ recorded at this photon energy can be attributed to any of the H_2PCN isomers. Thereafter, the photon energy was reduced to 10.24 eV, at which only cyanophosphine (1; IE = 10.45–10.54 eV) cannot be ionized (Figure 2). The sublimation event disappeared at 10.24 eV (Figure 4a), indicating that this sublimation event can be assigned to cyanophosphine (1). To further confirm the formation of cyanophosphine (1), isomer-selective ultraviolet (UV) photolysis was considered.^{9,52–54} However, the simulated UV spectrum of cyanophosphine (1), calculated at the TD-B3LYP/cc-pVTZ level of theory, partially overlaps with those of isomers 4 and 6 (Figure S4). Consequently, ultraviolet photolysis was not pursued as an

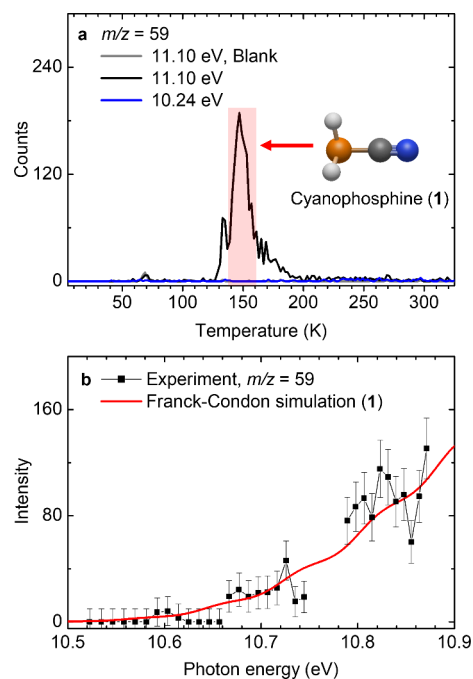


Figure 4. Ion signals recorded during TPD from phosphine–hydrogen cyanide ($\text{PH}_3\text{--HCN}$) ices. (a) TPD profiles of $m/z = 59$ recorded at photoionization energies of 11.10 and 10.24 eV. The red shaded region indicates the peak temperature range (137–161 K) associated with cyanophosphine (1). (b) Photoionization efficiency (PIE) curve of $m/z = 59$ collected over the peak temperature range and corrected for temperature-dependent sublimation rate. The experimental PIE curve is collected from three measurements with different photon-energy ranges and compared with the Franck–Condon simulations for cyanophosphine (1). Atomic colors are white for hydrogen, orange for phosphorus, gray for carbon, and blue for nitrogen.

independent method for the identification of cyanophosphine (1). Alternatively, the photoionization efficiency (PIE) curve at $m/z = 59$ was recorded during TPD and corrected for the corresponding desorption profile. PIE measurements measure the ion signal intensity as a function of photon energy and enable isomer-specific identification among isomers 1, 4 and 6 (Figures S5–S6) through comparison with experimental reference spectra or simulated PIE curves.^{21,55–58} Here, the PIE curve was collected from three measurements between 10.52 and 10.87 eV over the sublimation temperature range of 137–161 K (Figure 4b). The measured PIE curve agrees with the Franck–Condon simulation for cyanophosphine (1), providing further evidence for its formation. The experimental ionization onset was determined to be 10.60 ± 0.05 eV, close to the computed IE of cyanophosphine (1) of 10.45–10.54 eV. Additional ion signals observed at other mass channels and their proposed molecular formulas are provided in Table S5.

Having established compelling evidence for the formation of cyanophosphine (1) in phosphine–hydrogen cyanide ices subjected to energetic-electron irradiation as a proxy for GCR processing within cold molecular clouds, we turn to its potential formation pathways. The initial step involves the unimolecular decomposition of phosphine through P–H bond cleavage to yield the phosphino (PH_2) radical and atomic hydrogen (H) (reaction 1),⁵⁹ an endoergic process requiring 340 ± 4 kJ mol^{−1}.^{60,61} Similarly, GCR-induced processing can lead to C–H bond cleavage in hydrogen cyanide to produce

atomic hydrogen and the cyano (CN) radical via reaction 2, which is endoergic by $523 \pm 1 \text{ kJ mol}^{-1}$.⁶¹ The energy necessary to initiate these reactions can be supplied by the energetic electrons, highlighting the essential role of ionizing sources such as GCRs in generating the radical precursors required for the formation of cyanophosphine (1). Once formed, these radicals can become trapped within the ice matrix at 5 K due to their limited diffusional mobility.³¹ Phosphino and cyano radicals generated at neighboring sites with a favorable geometry can undergo barrierless radical–radical recombination in an exoergic reaction (-428 kJ mol^{-1}),^{60–62} whereas radicals that are initially spatially separated can recombine upon warming during TPD as their molecular mobility increases, yielding cyanophosphine (1) via reaction 3.²¹



In conclusion, we present the first laboratory experiments on the formation of cyanophosphine (H_2PCN , 1)—the simplest phosphorus-containing nitrile—in phosphine–hydrogen cyanide interstellar ice analogues. The low-temperature (5 K) ice mixtures were exposed to energetic electrons, which simulate the secondary electrons generated through the interaction of GCRs with interstellar ices in cold molecular clouds.^{29–31} Irradiation doses of $0.19 \pm 0.03 \text{ eV}$ per PH_3 molecule and $0.18 \pm 0.03 \text{ eV}$ per HCN molecule were deposited, corresponding to $(7 \pm 2) \times 10^5$ years of GCR exposure during the early evolutionary stage of a cold molecular cloud.⁴³ Utilizing tunable vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry, cyanophosphine (H_2PCN , 1) was identified isomer-selectively in the gas phase during TPD, suggesting that it is a promising target for future astronomical searches²⁴ toward sources such as the carbon-rich star IRC +10216, where both phosphine and hydrogen cyanide have been detected.^{3,63} These results reveal a bottom-up, GCR-driven pathway to cyanophosphine (1) in interstellar ices containing phosphine and hydrogen cyanide. Once formed, cyanophosphine (1) may serve as a molecular building block for the synthesis of elusive and complex phosphorus-containing nitriles in interstellar ices (Figure 1), thereby advancing our fundamental understanding of how phosphorus-containing nitriles may emerge through GCR-induced, nonequilibrium chemistry in interstellar environments.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.6c02773>.

Experimental and computational methods, FTIR spectra of phosphine–hydrogen cyanide ices and their assignments, TPD profiles, simulated ultraviolet spectra and PIE curves, experimental parameters, uncertainty analysis of IEs and relative energies, VUV generation parameters, and Cartesian coordinates, vibrational frequencies, and infrared intensities of the calculated H_2PCN structures (DOCX)

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Notes

The authors declare no competing financial interest.

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