

# Low-Temperature Gas-Phase Formation of Methanimine ( $\text{CH}_2\text{NH}$ ; $X^1A'$ )—the Simplest Imine—under Single-Collision Conditions

Zhenghai Yang, Iakov A. Medvedkov, Shane J. Goettl, and Ralf I. Kaiser\*



Cite This: *J. Phys. Chem. Lett.* 2023, 14, 8500–8506



Read Online

ACCESS |



Metrics & More

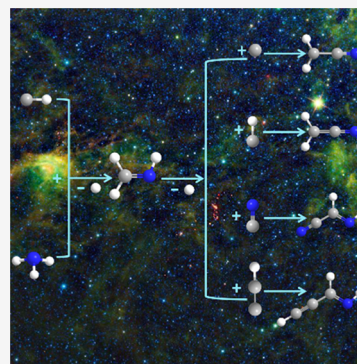


Article Recommendations



Supporting Information

**ABSTRACT:** The D1-methanimine molecule ( $\text{CHDNH}$ ;  $X^1A'$ )—the simplest (deuterated) imine—has been prepared through the elementary reaction of the D1-methylidyne ( $\text{CD}$ ;  $X^2\Pi$ ) with ammonia ( $\text{NH}_3$ ;  $X^1A_1$ ) under single collision conditions. As a highly reactive species with a carbon–nitrogen double bond and a key building block of biomolecules such as amino acids and nucleobases, methanimine is of particular significance in coupling the nitrogen and carbon chemistries in the interstellar medium and in hydrocarbon-rich atmospheres of planets and their moons. However, the underlying formation mechanisms of methanimine in these extreme environments are still elusive. The directed, low-temperature gas-phase formation of D1-methanimine will deepen our fundamental understanding of low-temperature molecular growth processes via carbon–nitrogen bond coupling. Considering the recent detection of the interstellar D1-methylidyne radical, the investigation of the  $\text{CD}-\text{NH}_3$  system also suggests a promising pathway for future astronomical observations of D1-methanimine as a molecular tracer of gas phase deuterium enrichment in deep space.



One of the fundamental questions about the origins of life on early Earth is the untangling of key reaction pathways in the prebiotic chemical evolution from small to complex, often biologically relevant molecules.<sup>1</sup> Methanimine ( $\text{CH}_2\text{NH}$ ,  $X^1A'$ )—the simplest imine—has received particular attention since this molecule represents a fundamental building block of biomolecules like amino acids and nucleobases.<sup>2,3</sup> Extraterrestrial sources of amino acids have been highly debated.<sup>4</sup> The simplest amino acid, glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), has not been detected in the interstellar medium (ISM) to date,<sup>5</sup> but the existence was confirmed in the coma of comet 67P/Churyumov-Gerasimenko.<sup>6</sup> Here, methanimine ( $\text{CH}_2\text{NH}$ ) has been implicated as a vital intermediate in the formation of aminoacetonitrile ( $\text{NCCH}_2\text{NH}_2$ ) and glycine via the Strecker synthesis.<sup>7</sup> Therefore, an experimental study of the *in situ* synthesis of methanimine ( $\text{CH}_2\text{NH}$ ) via carbon–nitrogen bond coupling might unveil the fundamental mechanisms of the formation of amino acids in deep space.

Methanimine is a highly reactive molecule carrying a carbon–nitrogen double bond with a bond length of 128.3 pm;<sup>8</sup> similar to carbon–carbon double bonds,<sup>9,10</sup> the carbon–nitrogen double bond is prone to attack by unsaturated hydrocarbons radicals<sup>2</sup> or polymerize with unsaturated imines forming complex structures such as hexamethylenetetramine ( $(\text{CH}_2)_6\text{N}_4$ ).<sup>7</sup> In the ISM, more complex imines have also been observed astronomically: ethanimine ( $\text{CH}_3\text{CHNH}$ ),<sup>11</sup> ketenimine ( $\text{CH}_2\text{CNH}$ ),<sup>12</sup> 3-imino-1,2-propadienyldiene ( $\text{CCCNH}$ ),<sup>13</sup> cyanomethanimine ( $\text{HNCHCN}$ ),<sup>14,15</sup> Z-propargylimine ( $\text{HCCCHNH}$ ),<sup>16</sup> and allylimine ( $\text{CH}_2\text{CHCHNH}$ ).<sup>17</sup> As the simplest representative, methanimine plays a central role in the formation of more complex

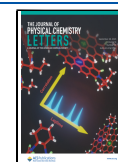
imines through molecular mass growth processes upon reactions with reactive radicals such as methylidyne ( $\text{CH}$ ), cyano ( $\text{CN}$ ), and ethynyl ( $\text{C}_2\text{H}$ ).<sup>2</sup> The reaction between the cyano radical and methanimine may account for the formation of cyanomethanimine,<sup>18</sup> an important intermediate to the adenine ( $\text{C}_5\text{H}_5\text{N}_5$ )—a purine nucleobase in the nucleic acids of deoxyribonucleic acid (DNA).<sup>19</sup>

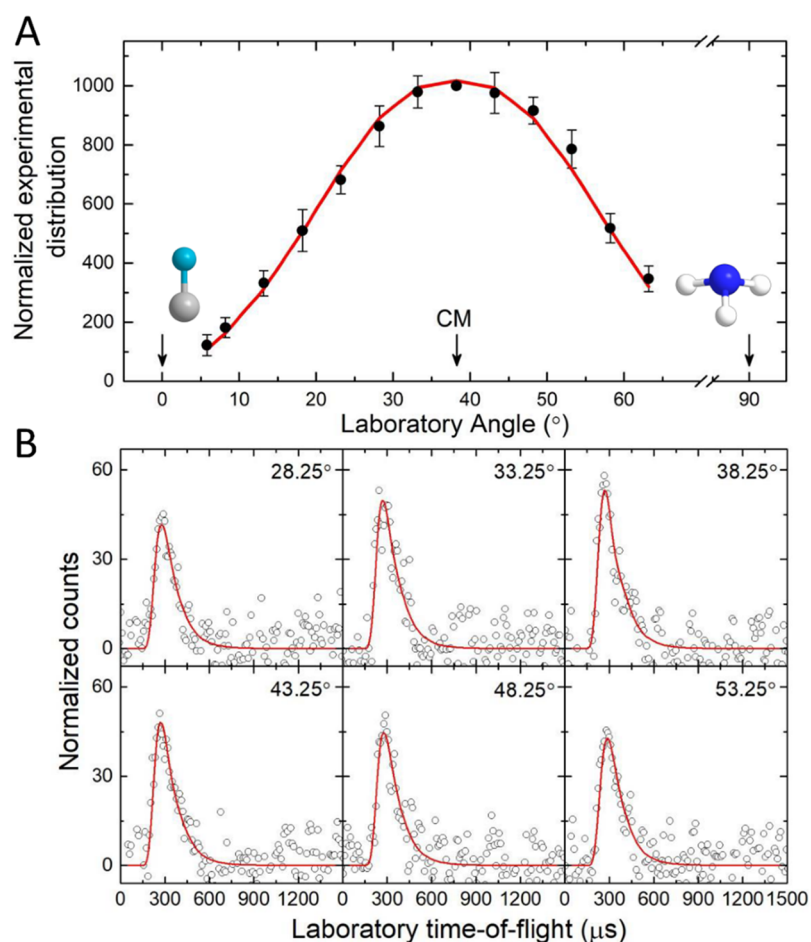
Gas-phase methanimine was first detected in the molecular cloud of Sagittarius B2 (Sgr B2) in 1973.<sup>20</sup> High fractional abundances of  $3.3 \times 10^{-8}$  were also noticed in massive protostellar envelopes of Orion KL<sup>21</sup> and of  $8.1 \times 10^{-10}$  in the cold core of L183.<sup>22</sup> The presence of methanimine was also inferred in Titan's upper atmosphere from Cassini's Ion and Neutral Mass Spectrometer (INMS) data with a mole fraction of  $1 \times 10^{-5}$  at 1100 km.<sup>7,23</sup> Considering the rapid reactions with unsaturated hydrocarbons and nitriles, methanimine represents an excellent candidate and initiator of the complex chain of reactions ultimately leading to the formation of nitrogen-rich aerosol layers of Titan.<sup>7,24</sup> However, despite the importance of methanimine ( $\text{CH}_2\text{NH}$ ) in the ISM and in hydrocarbon-rich atmospheres of planets and their moons, the underlying formation pathways of methanimine ( $\text{CH}_2\text{NH}$ ) are still in their infancy. Previous works observed the methanimine

Received: August 23, 2023

Accepted: September 14, 2023

Published: September 18, 2023





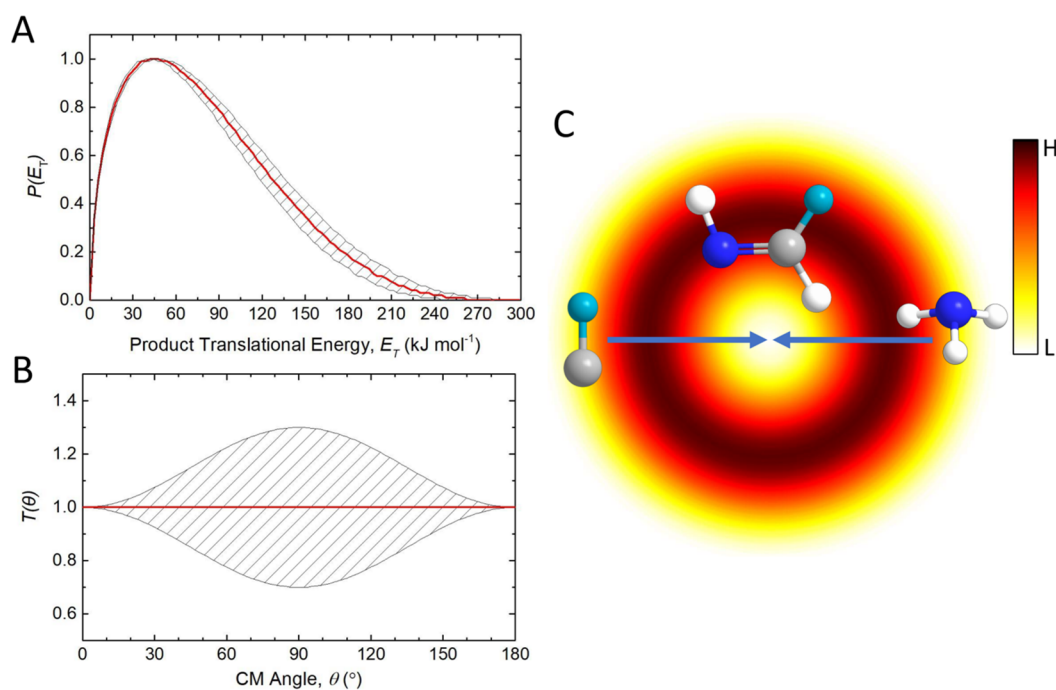
**Figure 1.** Laboratory angular distribution (A) and time-of-flight spectra (B; data collected at  $m/z = 30$  ( $\text{CHDNH}^+$ )) collected in the reaction of the D1-methylidyne radical (CD) with ammonia ( $\text{NH}_3$ ). The circles represent the experimental results; the red lines, the best fits. Colors of the atoms are carbon (gray), deuterium (light blue), nitrogen (blue), and hydrogen (white).

transient in the pyrolysis of methyl azide ( $\text{CH}_3\text{N}_3$ )<sup>25</sup> and methylamine ( $\text{CH}_3\text{NH}_2$ ).<sup>26,27</sup> In the contemporary astrochemical modelings, methanimine is speculated to be produced via the neutral–neutral gas-phase reactions of  $\text{N}(^2\text{D})$  with methane ( $\text{CH}_4$ ) or ethane ( $\text{C}_2\text{H}_6$ )—although excited state nitrogen atoms do not live sufficiently long enough in the ISM to react,<sup>28,29</sup> there are unstudied radical–radical reactions of imidogen (NH) with methyl ( $\text{CH}_3$ ),<sup>21</sup> successive hydrogenation of hydrogen cyanide (HCN),<sup>3</sup> and/or postulated dissociative electron recombination with  $\text{CH}_x\text{N}^+$  ions.<sup>22</sup> However, predicted fractional abundances of methanimine ( $\text{CH}_2\text{NH}$ ) in cold molecular clouds, which are defined through temperatures of about 10 K, fall 1 to 2 orders of magnitude shorter than observed astronomically as in, e.g., the molecular cloud L183.<sup>22,30</sup> Therefore, critical pathway(s) to methanimine ( $\text{CH}_2\text{NH}$ ) are clearly lacking. The methylidyne (CH)—ammonia ( $\text{NH}_3$ ) gas phase reaction represents such a pathway. Only recently, the D1-methylidyne (CD) radical was detected in the ISM.<sup>31</sup> Thus, the D1-methylidyne (CD)—ammonia ( $\text{NH}_3$ ) pathway is also promising for future astronomical observation of D1-methanimine ( $\text{CHDNH}$ ). Kinetic measurements were conducted by Zabarnick et al.<sup>32</sup> and Bocherel et al.<sup>33</sup> exploiting the PLP (pulse laser photolysis)—LIF (laser-induced fluorescence) method; these works revealed fast reaction rates of  $2.21 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 23 K. In 2012, Blitz et al.<sup>34</sup> determined the hydrogen atom yield to be  $0.89 \pm 0.07$

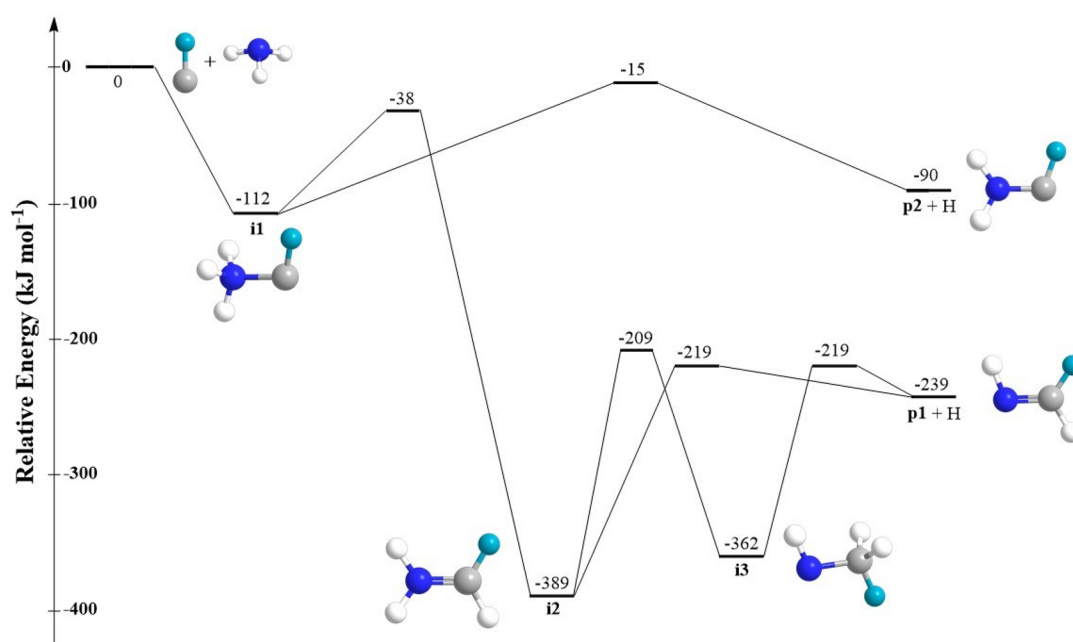
and combined these studies with high-level *ab initio* calculations. More recently, this reaction was investigated under multiple collision conditions at 373 K and 4 Torr in a flow reactor with the predominant formation of methanimine inferred.<sup>35</sup>

To shed light on the role of the methylidyne–ammonia system in the gas phase preparation of methanimine ( $\text{CH}_2\text{NH}$ ), we conducted the gas phase reaction of the D1-methylidyne (CD;  $X^2\Pi$ ) radical with ammonia ( $\text{NH}_3$ ;  $X^1A_1$ ) under single collision conditions in a crossed molecular beam machine. Merged with electronic structure calculations, these studies provide compelling evidence of the facile, barrierless formation of D1-methanimine ( $\text{CHDNH}$ , 30 amu). This work affords a viable route to methanimine ( $\text{CH}_2\text{NH}$ ) in low temperature extraterrestrial environments such as in L183 and Titan’s upper atmosphere, thus deepening our fundamental understanding of the prebiotic chemistry and the low-temperature molecular growth processes through carbon–nitrogen coupling in our galaxy.

To eliminate the background signal at a mass-to-charge ( $m/z$ ) of 29, the reaction was conducted by exploiting the D1-methylidyne radical (CD; 14 amu). The reactive scattering signal was observed at  $m/z = 30$  ( $\text{H}_2\text{DCN}^+/\text{HD}^{13}\text{CN}^+/\text{H}_3^{13}\text{CN}^+$ ); within our signal-to-noise limits, no signal could be detected at  $m/z = 31$  ( $\text{H}_3\text{DCN}^+/\text{H}_2\text{D}^{13}\text{CN}^+/\text{H}_2\text{D}^{13}\text{CN}^+$ ). These findings indicate that no  $\text{H}_3\text{DCN}$  adducts survived the



**Figure 2.** CM translational energy (A), angular (B) flux distributions, and the associated flux contour map (C) for the reaction of a D1-methylidyne radical (CD) with ammonia (NH<sub>3</sub>). The red lines indicate the best fit; shaded areas represent the error limits.

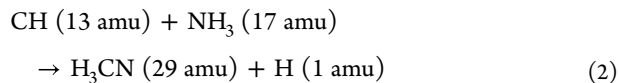
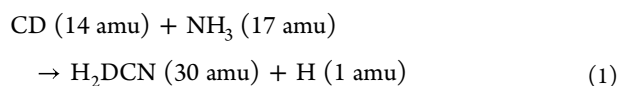


**Figure 3.** Potential energy surface (PES) for the reactions of the D1-methylidyne radical (CD) with ammonia (NH<sub>3</sub>). The energies of the intermediates, transition states, and the products are extracted from Blitz et al.<sup>34</sup>

flight time from the interaction region to the detector and that H<sub>2</sub>D<sup>13</sup>CN isotopologues were not synthesized in sufficiently high number densities to be detected under our experimental conditions. Consequently, angular resolved time-of-flight (TOF) spectra were accumulated at  $m/z = 30$  in 5° intervals from 6° to 64° and integrated and normalized to the TOF at the center-of-mass (CM) angle of 38.2°; this procedure yielded the laboratory angular distribution (LAD) as depicted in Figure 1. The LAD shows a forward–backward symmetry and peaks at a CM angle of 38.2°, suggesting indirect reaction

dynamics and the existence of long-lived H<sub>3</sub>DCN complex(es). It should be noted that the data collected at  $m/z = 30$  could be fit with an atomic hydrogen loss (1 amu) channel forming the heavy H<sub>2</sub>DCN (30 amu) counter fragment; all attempts to replicate the experimental data with molecular-hydrogen (H<sub>2</sub>, 2 amu) or atomic deuterium (D, 2 amu) elimination pathways failed. Therefore, our experimental data alone reveal the formation of H<sub>2</sub>DCN isomers in the CD–NH<sub>3</sub> reaction with the hydrogen atom ejected from the NH<sub>3</sub> reactant.





While the experimental data provide compelling evidence for the formation of products with the molecular formula  $\text{H}_2\text{DCN}$  along with atomic hydrogen emitted from ammonia, a forward convolution approach is required to obtain critical information on the underlying reaction dynamics, mechanism(s), and isomer(s) prepared. This is achieved by transforming the data from the laboratory frame to the CM frame.<sup>36,37</sup> This yields the CM translational energy,  $P(E_T)$ , and angular  $T(\theta)$  flux distributions (Figure 2). Best fits of the experimental data are achieved with a single channel involving the D1-methylidyne (CD) versus atomic hydrogen (H) exchange pathway with a product mass combination of 30 amu ( $\text{H}_2\text{DCN}$ ) plus 1 amu (H; reaction 1). A detailed inspection of  $P(E_T)$  reveals a maximum translational energy release ( $E_{\text{max}}$ ) of  $262 \pm 18 \text{ kJ mol}^{-1}$ , which denotes the sum of the reaction exoergicity plus the collision energy  $E_c$  ( $16.9 \pm 0.3 \text{ kJ mol}^{-1}$ ) for those products formed without rovibrational excitation. Therefore, the reaction energy can be determined to be  $245 \pm 18 \text{ kJ mol}^{-1}$  under our experimental conditions. Furthermore, the average translational energy of the products is calculated to be  $81 \pm 6 \text{ kJ mol}^{-1}$ , revealing that  $31 \pm 5\%$  of the available energy is transformed into the translational degrees of freedom of the products. The  $P(E_T)$  distribution peaks at  $45 \pm 3 \text{ kJ mol}^{-1}$  suggesting that the reaction intermediate decomposes via a tight exit transition state, i.e., a process which involves a significant electron rearrangement. Last, the best fit  $T(\theta)$  distribution is forward–backward symmetric and reflects nonzero and isotropic flux over the complete scattering range from  $0^\circ$  to  $180^\circ$ ; this finding reveals that the reaction proceeds with indirect reaction dynamics through the formation of a  $\text{H}_3\text{DCN}$  complex(es) holding a lifetime longer than the rotational period(s).<sup>38</sup> This information is also visualized in the flux contour map (Figure 2c), which presents a complete image of the reaction.

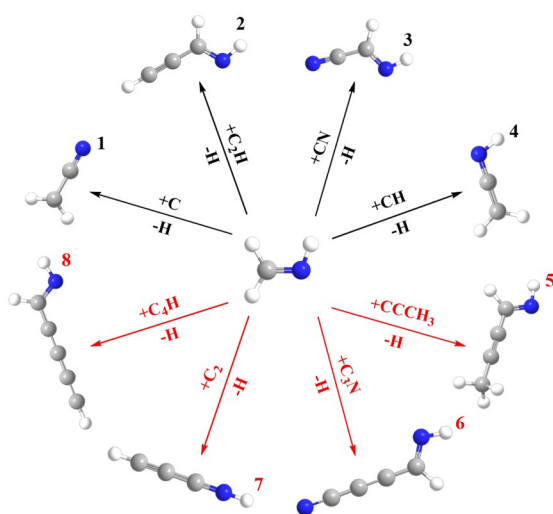
Having elucidated the atomic hydrogen loss pathways forming  $\text{H}_2\text{DCN}$  in the bimolecular gas-phase reaction of D1-methylidyne with ammonia under single collision conditions, we are now merging our experimental data with electronic structure calculations<sup>34,35</sup> (Figure 3) to further unveil the underlying reaction dynamics and the nature of the isomer formed. Note that our experiments utilized the D1-methylidyne radical, but calculations were conducted for the methylidyne radical. However, as proposed in multiple reactions,<sup>8,39,40</sup> due to the difference in zero point energies, the difference in energetics of the intermediates, transition state, and products of reaction systems with (partially) deuterated or nondeuterated reactants should be less than  $5 \text{ kJ mol}^{-1}$ ; this discrepancy lies within the experimental uncertainties of our results. Two products can be formed in exoergic reactions: **p1** ( $\text{CHDNH}$ ; D1-methanimine;  $-239 \text{ kJ mol}^{-1}$ ;  $X^1A'$ ) and **p2** ( $\text{CDNH}_2$ ; D1-aminomethylene;  $-90 \text{ kJ mol}^{-1}$ ;  $X^1A'$ ). A comparison of the experimentally derived reaction energy of  $-245 \pm 18 \text{ kJ mol}^{-1}$  reveals that at least **p1** is formed in the CD– $\text{NH}_3$  reaction. The calculations suggest that the reaction of the D1-methylidyne radical (CD) with ammonia is initiated on the doublet surface through the

barrierless addition of CD to the nonbonding electron pair of the nitrogen atom of ammonia leading to the formation of carbon–nitrogen bond along with a datively bound intermediate  $\text{DCNH}_3$  (**i1**) residing  $112 \text{ kJ mol}^{-1}$  below the separated reactants. Intermediate **i1** can isomerize to D1-methanimine (**i2**;  $\text{CHDNH}_2$ ;  $-389 \text{ kJ mol}^{-1}$ ), which represents the global minimum of the  $\text{CDNH}_3$  PES, via a transition state residing  $74 \text{ kJ mol}^{-1}$  above **i1** via a hydrogen (H) shift from nitrogen to carbon. Alternatively, **i1** can undergo unimolecular decomposition to thermodynamically less stable isomer **p2** through hydrogen emission from the  $\text{NH}_3$  moiety. Intermediate **i1** and **p2** are connected with a transition state lying only  $15 \text{ kJ mol}^{-1}$  below the separated reactants. How can the most stable isomer **p1** be formed? First, intermediate **i2** can eliminate a hydrogen from the amino ( $\text{NH}_2$ ) moiety through a tight exit transition state. Second, **i2** can further isomerize to **i3** ( $\text{CH}_2\text{DNH}$ ; D1-methylamino;  $-362 \text{ kJ mol}^{-1}$ ) passing a barrier of  $180 \text{ kJ mol}^{-1}$  followed by atomic hydrogen loss from the methyl group. Overall, two pathways to **p1** and a single mechanism to **p2**, i.e., **i1**  $\rightarrow$  **i2**  $\rightarrow$  **p1**, **i1**  $\rightarrow$  **i2**  $\rightarrow$  **i3**  $\rightarrow$  **p1**, and **i1**  $\rightarrow$  **p2**, are identified. Recall that our experimental data were collected at  $m/z = 30$ , which could be replicated only with an atomic hydrogen loss channel; this pathway was verified in the electronic structure calculations as well. The atomic deuterium (D) loss pathway from the  $\text{CH}_2\text{D}$  group of **i3** forming **p1** is not included in the PES. Which of these pathways is dominant to form **p1**? The Rice–Ramsperger–Kassel–Marcus (RRKM) calculations by Blitz et al.<sup>34</sup> reveal that methanimine represents the dominant product in the CH– $\text{NH}_3$  reaction contributing 96% throughout the temperature range from 20 to 320 K. Only 4% of the datively bound intermediate **i1** were suggested to lose one hydrogen atom to **p2** considering the unfavorable barrier of H elimination of **i1** to **p2** ( $97 \text{ kJ mol}^{-1}$ ) compared to that of the competing process of **i1** to **i2** ( $74 \text{ kJ mol}^{-1}$ ). Bourgalais et al.<sup>35</sup> also observed the absence of the deuterium loss channel in the flow reactor experiment of D1-methylidyne with ammonia suggesting that the ratio of the second hydrogen transfer from the nitrogen atom to the carbon atom (**i2**  $\rightarrow$  **i3**) is minimal compared to the hydrogen elimination forming **p1** from **i2**. If **i3** carrying a  $\text{CH}_2\text{D}$  group is formed, then the subsequent H/D elimination from the carbon atom should lead to  $\text{CHDNH}$  and  $\text{CH}_2\text{NH}$ .

Overall, the highly reactive closed-shell molecule D1-methanimine ( $\text{CHDNH}$ ) was synthesized from the “bottom up” through the barrierless elementary reaction of D1-methylidyne (CD;  $X^2\Pi$ ) with ammonia ( $\text{NH}_3$ ;  $X^1A_1$ ). Under single collision conditions, the primary reaction products “fly away” unperturbed without consecutive reactions like dimerization.<sup>36</sup> The advantages of the crossed molecular beam experiments in studying the reaction mechanisms are demonstrated in the formation of a molecule (D1-methanimine) with a highly reactive carbon–nitrogen double bond. The reaction dynamics of the CH– $\text{NH}_3$  system are quite distinct from those of the isovalent SiH– $\text{NH}_3$  system. In the SiH– $\text{NH}_3$  reaction, aminosilylene ( $\text{HSiNH}_2$ ;  $^1A'$ ) is formed via hydrogen atom loss from the nitrogen atom of the initial collision complex silyleneammonia ( $\text{HSiNH}_3$ ); any hydrogen shift from nitrogen to carbon is hindered considering a significant barrier of  $110 \text{ kJ mol}^{-1}$ ; further, the prospective silanimine ( $\text{H}_2\text{SiNH}$ ;  $^1A'$ ) product—the isovalent species of methanimine—is  $70 \text{ kJ mol}^{-1}$  higher in energy than aminosilylene ( $\text{HSiNH}_2$ ;  $^1A'$ ). These results reflect a favorable  $\pi$ -type

back-donation into the empty  $p_z$  orbital of the silicon atom from the nonbonding electron pair of nitrogen.<sup>8</sup>

The facile formation of the carbon–nitrogen double bond via the reaction of methylidyne with ammonia—two abundant reactants in cold molecular clouds with fractional abundances of  $3.5 \times 10^{-8}$  and a few  $10^{-5}$  in the dense core of the Orion molecular cloud, respectively, relative to molecular hydrogen<sup>41–44</sup>—holds important implications for extraterrestrial chemistry,<sup>2,45</sup> with the D1-methylidyne (CD) radical only detected recently with a CD/CH ratio of  $0.016 \pm 0.003$ .<sup>31</sup> Thus, the potential role of the CH–NH<sub>3</sub> system in the formation of methanimine (CH<sub>2</sub>NH) in low-temperature interstellar environments is supported by the crucial prerequisites of abundant reactants, the absence of entrance barriers in the exoergic bimolecular reactions, and rapid low-temperature rate coefficients. Methanimine represents an important precursor to build up chemical complexity in deep space. As depicted in Figure 4, cyanomethyl (1, H<sub>2</sub>CCN),<sup>46</sup> Z-



**Figure 4.** Central role of methanimine (CH<sub>2</sub>NH) leading to complex interstellar molecules (1–8) in the gas phase. Barrierless reactions with black arrows lead to molecules already identified in the interstellar medium, while reactions color coded with red arrows produce hitherto unidentified molecules in deep space.

propargylimine (2, HCCCHNH),<sup>16</sup> cyanomethanimine (3, HNCHCN),<sup>14,15</sup> and ketenimine (4, CH<sub>2</sub>CNH),<sup>12</sup> which have been identified in molecular clouds, can be formed via the hydrogen atom elimination pathways in the reactions of methanimine (CH<sub>2</sub>NH) with atomic carbon (C), ethynyl (C<sub>2</sub>H), cyano (CN), and methylidyne (CH), respectively. More complex molecules like methylpropargylimine (5, CH<sub>3</sub>CCCHNH), 3-cyanopropargylimine (6, NCCCCHNH), iminopropynylidene (7, HCCCCHNH), and 2,4-pentadiynylimine (8, HCCCCCHNH) are predicted to be formed via bimolecular reactions of 1-propynyl (CCCH<sub>3</sub>), cyanoethynyl (C<sub>3</sub>N), dicarbon (C<sub>2</sub>), and butadiynyl (C<sub>4</sub>H) and represent promising candidates for astronomical detections utilizing, e.g., the Atacama Large Millimeter/submillimeter Array (ALMA) or the Robert C. Byrd 100 m Green Bank Telescope (GBT).<sup>47,48</sup> Overall, the preparation of the carbon–nitrogen double bond under low-temperature conditions deepens our understanding of the exotic chemistry in extreme environments and sheds light on fundamental molecular mass growth

processes involving methylidyne, ammonia, and methanimine in our universe.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.3c02360>.

Detailed experimental methods, experimental parameters (Table S1) (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Ralf I. Kaiser – Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States; [orcid.org/0000-0002-7233-7206](https://orcid.org/0000-0002-7233-7206); Email: [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu)

### Authors

Zhenghai Yang – Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States

Iakov A. Medvedkov – Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States

Shane J. Goettl – Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States; [orcid.org/0000-0003-1796-5725](https://orcid.org/0000-0003-1796-5725)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jpcllett.3c02360>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Basic Energy Sciences (DE-FG02-03ER15411) to the University of Hawaii.

## ■ REFERENCES

- (1) Miller, S. L. A Production of Amino Acids under Possible Primitive Earth Conditions. *Science* **1953**, *117*, 528–529.
- (2) Lupi, J.; Puzzarini, C.; Barone, V. Methanimine as a Key Precursor of Imines in the Interstellar Medium: The Case of Propargylimine. *Astrophys. J. Lett.* **2020**, *903*, L35.
- (3) Luthra, H.; Wakelam, V.; Sharma, M. K.; Chandra, S. Predictions of Gas-Phase Methanimine (CH<sub>2</sub>NH) Abundance in Cold Cores. *Mon. Not. R. Astron. Soc.* **2023**, *521*, 2181–2186.
- (4) Cobb, A. K.; Pudritz, R. E. Nature's Starships. I. Observed Abundances and Relative Frequencies of Amino Acids in Meteorites. *Astrophys. J.* **2014**, *783*, 140.
- (5) Snyder, L. E.; Lovas, F. J.; Hollis, J. M.; Friedel, D. N.; Jewell, P. R.; Remijan, A.; Ilyushin, V. V.; Alekseev, E. A.; Dyubko, S. F. A Rigorous Attempt to Verify Interstellar Glycine. *Astrophys. J.* **2005**, *619*, 914.
- (6) Altwegg, K.; Balsiger, H.; Bar-Nun, A.; Berthelier, J.-J.; Bieler, A.; Bochler, P.; Briois, C.; Calmonte, U.; Combi, M. R.; Cottin, H.; et al. Prebiotic Chemicals—Amino Acid and Phosphorus—In the Coma of Comet 67P/Churyumov-Gerasimenko. *Sci. Adv.* **2016**, *2*, No. e1600285.
- (7) Skouteris, D.; Balucani, N.; Faginas-Lago, N.; Falcinelli, S.; Rosi, M. Dimerization of Methanimine and Its Charged Species in the Atmosphere of Titan and Interstellar/Cometary Ice Analogs. *Astron. Astrophys.* **2015**, *584*, A76.
- (8) Yang, Z.; He, C.; Goettl, S.; Kaiser, R. I.; Azyazov, V. N.; Mebel, A. M. Directed Gas-Phase Formation of Aminosilylene (HSiNH<sub>2</sub>;

- X<sup>1</sup>A′): The Simplest Silicon Analogue of an Aminocarbene, under Single-Collision Conditions. *J. Am. Chem. Soc.* **2021**, *143*, 14227–14234.
- (9) Gu, X.; Guo, Y.; Zhang, F.; Mebel, A. M.; Kaiser, R. I. Reaction Dynamics of Carbon-Bearing Radicals in Circumstellar Envelopes of Carbon Stars. *Faraday Discuss.* **2006**, *133*, 245–275.
- (10) Parker, D. S. N.; Mebel, A. M.; Kaiser, R. I. The Role of Isovalency in the Reactions of the Cyano (CN), Boron Monoxide (BO), Silicon Nitride (SiN), and Ethynyl (C<sub>2</sub>H) Radicals with Unsaturated Hydrocarbons Acetylene (C<sub>2</sub>H<sub>2</sub>) and Ethylene (C<sub>2</sub>H<sub>4</sub>). *Chem. Soc. Rev.* **2014**, *43*, 2701–2713.
- (11) Loomis, R. A.; Zaleski, D. P.; Steber, A. L.; Neill, J. L.; Muckle, M. T.; Harris, B. J.; Hollis, J. M.; Jewell, P. R.; Lattanzi, V.; Lovas, F. J.; et al. The Detection of Interstellar Ethanamine (CH<sub>3</sub>CHNH) from Observations Taken during the GBT PRIMOS Survey. *Astrophys. J. Lett.* **2013**, *765*, L9.
- (12) Lovas, F. J.; Hollis, J. M.; Remijan, A. J.; Jewell, P. R. Detection of Ketenimine (CH<sub>2</sub>CNH) in Sagittarius B2(N) Hot Cores. *Astrophys. J.* **2006**, *645*, L137.
- (13) Kawaguchi, K.; Takano, S.; Ohishi, M.; Ishikawa, S.-I.; Miyazawa, K.; Kaifu, N.; Yamashita, K.; Yamamoto, S.; Saito, S.; Ohshima, Y.; et al. Detection of HNCCC in TMC-1. *Astrophys. J.* **1992**, *396*, L49–L51.
- (14) Zaleski, D. P.; Seifert, N. A.; Steber, A. L.; Muckle, M. T.; Loomis, R. A.; Corby, J. F.; Martinez, O.; Crabtree, K. N.; Jewell, P. R.; Hollis, J. M.; et al. Detection of E-Cyanomethanimine toward Sagittarius B2(N) in the Green Bank Telescope PRIMOS Survey. *Astrophys. J. Lett.* **2013**, *765*, L10.
- (15) Rivilla, V.; Martín-Pintado, J.; Jiménez-Serra, I.; Zeng, S.; Martín, S.; Armijos-Abendaño, J.; Requena-Torres, M. A.; Aladro, R.; Riquelme, D. Abundant Z-Cyanomethanimine in the Interstellar Medium: Paving the Way to the Synthesis of Adenine. *Mon. Not. R. Astron. Soc.: Lett.* **2019**, *483*, L114–L119.
- (16) Bizzocchi, L.; Prudenzano, D.; Rivilla, V. M.; Pietropolli-Charmet, A.; Giuliano, B. M.; Caselli, P.; Martín-Pintado, J.; Jiménez-Serra, I.; Martín, S.; Requena-Torres, M. A.; et al. Propargylimine in the Laboratory and in Space: Millimetre-Wave Spectroscopy and Its First Detection in the ISM. *Astron. Astrophys.* **2020**, *640*, A98.
- (17) Alberton, D.; Bizzocchi, L.; Jiang, N.; Melosso, M.; Rivilla, V. M.; Charmet, A. P.; Giuliano, B. M.; Caselli, P.; Puzzarini, C.; Alessandrini, S.; et al. Laboratory Spectroscopy of Allylimine and Tentative Detection towards the G+0.693–0.027 Molecular Cloud. *Astron. Astrophys.* **2023**, *669*, A93.
- (18) Vazart, F.; Latouche, C.; Skouteris, D.; Balucani, N.; Barone, V. Cyanomethanimine Isomers in Cold Interstellar Clouds: Insights from Electronic Structure and Kinetic Calculations. *Astrophys. J.* **2015**, *810*, 111.
- (19) Oró, J. Mechanism of Synthesis of Adenine from Hydrogen Cyanide under Possible Primitive Earth Conditions. *Nature* **1961**, *191*, 1193–1194.
- (20) Godfrey, P. D.; Brown, R. D.; Robinson, B. J.; Sinclair, M. W. Discovery of Interstellar Methanimine (Formaldimine). *Astrophys. Lett.* **1973**, *13*, 119.
- (21) Suzuki, T.; Ohishi, M.; Hirota, T.; Saito, M.; Majumdar, L.; Wakelam, V. Survey Observations of a Possible Glycine Precursor, Methanimine (CH<sub>2</sub>NH). *Astrophys. J.* **2016**, *825*, 79.
- (22) Turner, B. E.; Terzieva, R.; Herbst, E. The Physics and Chemistry of Small Translucent Molecular Clouds. XII. More Complex Species Explainable by Gas-Phase Processes. *Astrophys. J.* **1999**, *518*, 699.
- (23) Vuitton, V.; Yelle, R. V.; McEwan, M. J. Ion Chemistry and N-Containing Molecules in Titan's Upper Atmosphere. *Icarus* **2007**, *191*, 722–742.
- (24) Balucani, N. Elementary Reactions of N Atoms with Hydrocarbons: First Steps towards the Formation of Prebiotic N-Containing Molecules in Planetary Atmospheres. *Chem. Soc. Rev.* **2012**, *41*, 5473–5483.
- (25) Bock, H.; Dammel, R. Gas-Phase Reactions. 66. Gas-Phase Pyrolyses of Alkyl Azides: Experimental Evidence for Chemical Activation. *J. Am. Chem. Soc.* **1988**, *110*, 5261–5269.
- (26) Johnson, D. R.; Lovas, F. J. Microwave Detection of the Molecular Transient Methyleneimine (CH<sub>2</sub>=NH). *Chem. Phys. Lett.* **1972**, *15*, 65–68.
- (27) Pearson, R.; Lovas, F. J. Microwave Spectrum and Molecular Structure of Methyleneimine (CH<sub>2</sub>NH). *J. Chem. Phys.* **1977**, *66*, 4149–4156.
- (28) Balucani, N.; Bergeat, A.; Cartechini, L.; Volpi, G. G.; Casavecchia, P.; Skouteris, D.; Rosi, M. Combined Crossed Molecular Beam and Theoretical Studies of the N(<sup>2</sup>D) + CH<sub>4</sub> Reaction and Implications for Atmospheric Models of Titan. *J. Phys. Chem. A* **2009**, *113*, 11138–11152.
- (29) Balucani, N.; Leonori, F.; Petrucci, R.; Stazi, M.; Skouteris, D.; Rosi, M.; Casavecchia, P. Formation of Nitriles and Imines in the Atmosphere of Titan: Combined Crossed-Beam and Theoretical Studies on the Reaction Dynamics of Excited Nitrogen Atoms N(<sup>2</sup>D) with ethane. *Faraday Discuss.* **2010**, *147*, 189–216.
- (30) McGuire, B. A.; Loomis, R. A.; Burkhardt, A. M.; Lee, K. L. K.; Shingledecker, C. N.; Charnley, S. B.; Cooke, I. R.; Cordiner, M. A.; Herbst, E.; Kalenskii, S.; et al. Detection of Two Interstellar Polycyclic Aromatic Hydrocarbons via Spectral Matched Filtering. *Science* **2021**, *371*, 1265–1269.
- (31) Jacob, A. M.; Menten, K. M.; Wyrowski, F.; Sipilä, O. First Detection of Deuterated Methylidyne (CD) in the Interstellar Medium. *Astron. Astrophys.* **2023**, *675*, A69.
- (32) Zabarnick, S.; Fleming, J. W.; Lin, M.-C. Kinetics of Methylidyne (CH X<sup>2</sup>Π) Radical Reactions with Ammonia and Methylamines. *Chem. Phys.* **1989**, *132*, 407–411.
- (33) Bocherel, P.; Herbert, L. B.; Rowe, B. R.; Sims, I. R.; Smith, I. W. M.; Travers, D. Ultralow-Temperature Kinetics of CH (X<sup>2</sup>Π) Reactions: Rate Coefficients for Reactions with O<sub>2</sub> and NO (T = 13–708 K), and with NH<sub>3</sub> (T = 23–295 K). *J. Phys. Chem.* **1996**, *100*, 3063–3069.
- (34) Blitz, M. A.; Talbi, D.; Seakins, P. W.; Smith, I. W. M. Rate Constants and Branching Ratios for the Reaction of CH Radicals with NH<sub>3</sub>: A Combined Experimental and Theoretical Study. *J. Phys. Chem. A* **2012**, *116*, 5877–5885.
- (35) Bourgalais, J.; Caster, K. L.; Durif, O.; Osborn, D. L.; Le Picard, S. D.; Goulay, F. Product Detection of the CH Radical Reactions with Ammonia and Methyl-Substituted Amines. *J. Phys. Chem. A* **2019**, *123*, 2178–2193.
- (36) Yang, Z.; Sun, B.-J.; He, C.; Li, J.-Q.; Chang, A. H. H.; Kaiser, R. I. Gas-Phase Preparation of 1-Germavinylidene (H<sub>2</sub>CGe; X<sup>1</sup>A<sub>1</sub>), the Isovalent Counterpart of Vinylidene (H<sub>2</sub>CC; X<sup>1</sup>A<sub>1</sub>), via Non-Adiabatic Dynamics through the Elementary Reaction of Ground State Atomic Carbon (C; <sup>3</sup>P) with Germane (GeH<sub>4</sub>; X<sup>1</sup>A<sub>1</sub>). *J. Phys. Chem. Lett.* **2023**, *14*, 430–436.
- (37) Vernon, M. F. Molecular Beam Scattering. Ph.D. Thesis, University of California, Berkeley, CA, 1983.
- (38) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, 2005.
- (39) Goettl, S. J.; Doddipatla, S.; Yang, Z.; He, C.; Kaiser, R. I.; Silva, M. X.; Galvaio, B. R. L.; Millar, T. J. Chemical Dynamics Study on the Gas-Phase Reaction of the D1-Silyldiyne Radical (SiD; X<sup>2</sup>Π) with Deuterium Sulfide (D<sub>2</sub>S) and Hydrogen Sulfide (H<sub>2</sub>S). *Phys. Chem. Chem. Phys.* **2021**, *23*, 13647–13661.
- (40) Zhang, F.; Kao, C. H.; Chang, A. H. H.; Gu, X.; Guo, Y.; Kaiser, R. I. A Crossed Molecular Beam Study on the Reaction of Boron Atoms with Methylacetylene and Partially Deuterated Methylacetylene. *ChemPhysChem* **2008**, *9*, 95–105.
- (41) Sheffer, Y.; Rogers, M.; Federman, S. R.; Abel, N. P.; Gredel, R.; Lambert, D. L.; Shaw, G. Ultraviolet Survey of CO and H<sub>2</sub> in Diffuse Molecular Clouds: The Reflection of Two Photochemistry Regimes in Abundance Relationships. *Astrophys. J.* **2008**, *687*, 1075.
- (42) Ho, P. T. P.; Townes, C. H. Interstellar Ammonia. *Annu. Rev. Astron. Astrophys.* **1983**, *21*, 239–270.

(43) Ungerechts, H.; Walmsley, C. M.; Winnewisser, G. Ammonia and Cyanoacetylene Observations of the High Density Core of L 183 (L 134N). *Astron. Astrophys.* **1980**, *88*, 259–266.

(44) Genzel, R.; Ho, P. T. P.; Bieging, J.; Downes, D.  $\text{NH}_3$  in Orion-KL: A New Interpretation. *Astrophys. J.* **1982**, *259*, L103–L107.

(45) Danger, G.; Borget, F.; Chomat, M.; Duvernay, F.; Theule, P.; Guillemin, J.-C.; Le Sergeant d'Hendecourt, L.; Chiavassa, T. Experimental Investigation of Aminoacetonitrile Formation through the Strecker Synthesis in Astrophysical-Like Conditions: Reactivity of Methanimine ( $\text{CH}_2\text{NH}$ ), Ammonia ( $\text{NH}_3$ ), and Hydrogen Cyanide (HCN). *Astron. Astrophys.* **2011**, *535*, A47.

(46) Irvine, W. M.; Friberg, P.; Hjalmarson, A.; Ishikawa, S.; Kaifu, N.; Kawaguchi, K.; Madden, S. C.; Matthews, H. E.; Ohishi, M.; Saito, S.; et al. Identification of the Interstellar Cyanomethyl Radical ( $\text{CH}_2\text{CN}$ ) in the Molecular Clouds TMC-1 and Sagittarius B2. *Astrophys. J.* **1988**, *334*, L107–L111.

(47) Hollis, J. M.; Jewell, P. R.; Lovas, F. J.; Remijan, A.; Møllendal, H. Green Bank Telescope Detection of New Interstellar Aldehydes: Propenal and Propanal. *Astrophys. J.* **2004**, *610*, L21.

(48) McGuire, B. A.; Shingledecker, C. N.; Willis, E. R.; Burkhardt, A. M.; El-Abd, S.; Motiyenko, R. A.; Brogan, C. L.; Hunter, T. R.; Margulès, L.; Guillemin, J.-C.; et al. ALMA Detection of Interstellar Methoxymethanol ( $\text{CH}_3\text{OCH}_2\text{OH}$ ). *Astrophys. J. Lett.* **2017**, *851*, L46.