**Directed Gas Phase Preparation of Singlet Ethyl­silanediyl Carbene (HCCSiH; X1A') - The Dramatically Different Silacarbene Counterpart of Triplet Propargylene (HCCCH; X3B)**

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**ABSTRACT**

Ethyl­silanediyl carbene (HCCSiH; X1A') has been prepared in the gas phase through the elementary reaction of singlet dicarbon (C2) with silane (SiH4) under single collision conditions. Merged with electronic structure calcu­lations, our study reveals an exotic barrierless reaction pathway involving 1,1-insertion of dicarbon into one of the silicon-hydrogen bonds followed by hydrogen migration to form the 3-sila-methylacetylene (HCCSiH3) intermediate. The intermediate undergoes unimolecular decomposition through molecular hydrogen loss to ethyl­silanediyl carbene (HCCSiH; Cs; X1A'). The dicarbon-silane system defines a benchmark to explore the consequence of a single collision between the simplest ‘only-carbon’ molecule (dicarbon) with the prototype of a closed-shell silicon hydride (silane) yielding a non-classical silacarbene, whose molecular geometry and electronic structure are quite distinct from the isovalent triplet propargylene (HCCCH; C2; 3B) carbon-counterpart. These organosilicon transients cannot be prepared through traditional organic, synthetic methods, thus opening up a versatile path to access the previously largely elusive class of silacarbenes.

     Since the groundbreaking detection of cyclopropenylidene (c-C3H2, X1A1, **1**), vinylidene­carbene (H2CCC, X1A1, **2**), and propargylene (HCCCH, X3B, **3**) in the laboratory and in inter­stellar along with circumstellar environments,1 isomers of C3H2 (**1-3**) and their isovalent SiC2H2 species (**4-9**) have attracted substantial interest of the physical (organic) and computational chemistry communities from the fundamental points of view of chemical bonding and electronic structure theory (Scheme 1). Singlet cyclopropenylidene (c-C3H2; **1**;C2v;1A1) represents the global minimum of the C3H2 surface; this isomer can be best described as a highly unsaturated (parti­ally) 2π-Hückel aromatic, C2v symmetric three membered ring molecule with an apical carbene carbon. Cyclo­pro­penylidene was first detected by Reisenauer et al. in low temperature argon matrices at 10 K1 prior to its identification in a helium – acetylene gas discharge2 and toward the Taurus Molecular Clods (TMC-1). Photon exposure at 313 nm converts cyclopropenylidene (c-C3H2; **1**;C2v;1A1) to triplet propargylene (HCCCH; **3**; C2; 3B), which itself isomerizes to singlet vinylidenecarbene (H2CCC; **2**; C2v; 1A1)3. The latter was identified in a helium – acetylene discharge prior to its observation toward TMC-14. The *C*2 symmetric triplet propar­gylene (HCCCH; **3**; C2; 3B) holds an exotic electronic structure with each unpaired formally localized at each terminal carbon atom. This results in a 1,3-diradical, which is at least 53 kJ mol-1 more stable than its a1A' singlet state5. Crossed molecular beam studies revealed that cyclo­propenyl­i­dene (**1**) together with vinylidenecarbene (**2**) and/or propargylene (**3**) can be prepared through elementary gas phase reactions of methylidyne (CH(X2Π) with acetylene (C2H2(X1g+))6 and of ground state carbon atoms (C(3P)) with the vinyl radical (C2H3 (X2A’))7.

     The substitution of a single carbon atom by an isovalent silicon atom leads to SiC2H2 isomers (**4-9**). In analogy to the isovalent cyclopropenylidene (c-C3H2, X1A1, **1**), singlet 1-sila­cyclo­pro­penylidene (c-SiC2H2; **4**; C2v; 1A1) represents the global minimum on the SiC2H2 surface.8 Maier et al. generated **4** by pulsed flash pyrolysis 2-ethynyl-1,1,1-trimethyldisilane and trapping in argon matrix at 10 K.9 These authors also revealed that co-condensation of atomic silicon and acetylene in an argon matrix leads to addition of silicon to the carbon-carbon triple bond and -after inter system crossing (ISC) - to 1-silacyclopropenylidene (c-SiC2H2; **4**; C2v; 1A1).10 Izuha et al. recorded the rotational spectrum of **4** after discharging a mixture of silane (SiH4), acetylene (C2H2), and helium.11 Photolysis of **4** in an argon matrix leads to the higher energy isomers ethylsilanediyl (HCCSiH; **6**; Cs; 1A'), vinylidenesilanediyl (SiCCH2; **5**; C2v; 1A1), and sila­cyclo­propyne (c-CCSiH2; **8**; C2v; 1A1).9 Among these higher energy isomers, only singlet vinylidene­silanediyl (SiCCH2; **5**; C2v; 1A1) was characterized via Fourier transform microwave spectros­copy.12 It is important to note that the carbon analog of **8** - the singlet cyclopropyne molecule c-CCCH2 (X1A1) - is a saddle point; triplet cyclo­propyne (a3B2), however, was found to be a local minimum.13 This reveals that a replacement of a single carbon by an isovalent silicon atom leads to molecules such as silacyclopropyne (c-CCSiH2; **8**; C2v; 1A1), whose carbon analog does not exist.9 Considering the complexity of a *directed* gas phase synthesis under single collision conditions, which so far has led only to the preparation of silacyclopropenylidene (c-SiC2H2; **4**; C2v; 1A1),14 and the short life times of these transient species under ‘bulk’ conditions, free silacarbenes 1-silacyclo­propenylidene (**4**), vinylidenesilanediyl (**5**), ethylsilane­diyl (**6**), ethynyl­i­sily­lene (**7**), sila­cyclopropyne (**8**), and silavinylidenecarbene (**9**) exemplify one of the most ob­scu­red classes of orga­nic transient molecules.

     Here, we present a peek into the unknown gas phase chemistry of ethyl­silanediyl carbene (HCCSiH; **6**; Cs; 1A') - the isovalent counterpart of triplet propargylene (HCCCH; **3**; C2; 3B). This is achieved by preparing ethyl­silanediyl carbene under single-collision conditions via the bimole­cu­lar reaction of singlet dicarbon (C2) with silane (SiH4) employing the crossed mole­cular beams method and merging the experiments with electronic structure calculations and dynamics simulations. An investigation at the most funda­mental, microscopic level reveals new insights into the reaction mecha­ni­sms and inherent chemical dynamics through which highly reactive organo­silicon molecules such as ethyl­silanediyl (HCCSiH; **6**) are synthesized by excluding successive reac­tions in the gas phase. Besides the physical organic chemistry viewpoint of understanding structure, reactivity and bond breaking processes, the dicarbon – silane system is also attractive from the astro­phy­sical viewpoint to elucidate fundamental reaction pathways to silacarbenes, which so far have eluded detection in interstellar and carbon-rich circumstellar environments although the dicarbon and silane reactants are omnipresent in carbon-rich envelopes such as of the carbon-star IRC+10216. Our approach reveals previously obscure gas phase chemis­try that directly accesses a fascina­ting class of highly unsaturated silacarbenes under controlled conditions: ethyl­silanediyl carbene (HCCSiH; **6**).

The crossed molecular beams studies were carried out at a collision energy of 22.0 ± 0.3 kJ mol-1.15 Dicarbon was produced by photodissociation of tetrachloroethylene (C2Cl4, Sigma Aldrich, 99.9 %) at 248 nm seeded in helium (99.9999%; AirGas) at levels of 1.4 % at 300 K.16 The supersonic beam of dicarbon (C2; X1Ʃ+g/a3Πu; 24 amu) crossed a beam of silane (SiH4; X1A1; 32 amu) perpendicularly in the interaction region of the scattering chamber (Methods; Table S1). Time-of-flight spectra (TOF) and the product angular distribution of the reactively scattered products were recorded in the scattering plane at mass to charge ratios (*m*/*z*) from *m*/*z* = 56 (C2H4Si+) to 52 (C2Si+) exploiting a triply differentially pumped quadrupole mass spectrometer (QMS) operated at 10-11 Torr in conjunction with an electron impact ionizer (80 eV; 2 mA).

     Reactive scattering signal was detected from m/z = 54 to 52. Accounting for the natural isotope abundances of silicon of 30Si(3.1 %), 29Si(4.67 %), and 28Si(92.23 %) and bearing in mind that after scaling, the TOF spectra recorded from *m*/*z* = 54 to 52 are superimposable, these data propose the existence of a single reaction channel leading to C2H228Si isomer(s) (54 amu) (hereafter: C2H2Si ) along with molecular hydro­gen (2 amu). Neither adducts (C2H428Si; 56 amu) nor the atomic hydrogen loss pathway forming C2H3Si isomer(s) (53 amu) were observable. Reactive scattering signal was then collected at *m*/*z* = 54 (C2H2Si+) depicting the best signal-to-noise ratio for the TOF spectra and the resulting laboratory angular distribution (Figure 1). The laboratory angular distribution is very broad and spread over at least 55° in the scattering plane indicating a substantial energy release into the translational degrees of freedom of the products. Furthermore, the nearly forward-backward symmetry of the laboratory angular distribution implies indirect scattering dynamics involving metastable C2H4Si collision complex(es).

     To obtain fundamental information on the underlying reaction mechanisms leading to C2H2Si isomer(s), the laboratory data were fit with a forward-convolution routine eventually providing an angular flux distribution, *T*(*θ*), and a translational-energy flux distribution, *P*(*ET*), in the center-of-mass reference frame (Figure 2). The laboratory data could be replicated with a single channel fit leading to the formation of C2H2Si (54 amu) isomers plus molecular hydrogen (2 amu). The center-of-mass trans­la­ti­onal energy distri­bu­ti­on, P(ET), displays a high energy cutoff of 270 ± 20 kJ mol-1. Under favorable circumstances, for mole­cules formed without internal excitation, the high energy cutoff is the sum of the reaction exoer­gi­city plus the collision energy. In this limit, a subtraction of the collision energy would suggest that that the reaction is exoergic by 248 ± 20 kJ mol-1. Further, the P(ET) peaks away from zero translational energy revealing a broad plateau from 30 to 70 kJ mol-1; this finding would be consistent with a tight exit transition state and hence significant electron reorganization upon decomposition of the C2H4Si intermediate(s) upon molecular hydrogen loss. In addition, the center-of-mass angular distribution, *T*(*θ*), exhibits flux over the complete angular range from 0° to 180°. This finding is indicative of indirect (complex forming) dynamics involving C2H4Si intermediate(s), whose life time(s) is/are longer than the(ir) rotational period(s).

     For complex poly-atomic systems, it is beneficial to combine crossed molecular beam studies with electronic structure calculations (Figure 3). These calculations pre­dict the overall reaction energies and barriers to reaction to an accu­racy of about 5 kJ mol-1. Our computations (Methods) revealed the existence of six C2H2Si isomers (**p1-p6**) formed in reactions that are overall exoergic by between 487 ± 5 and 264 ± 5 kJ mol-1. The relative stabilities of these isomers correlate well with previous computational studies by Mebel et al., Ghambarian et al., Talbi, Schaefer et al., and Thor­wirth et al.17–22 Our computations suggest that for singlet dicarbon, the reaction is initiated by a de-facto barrierless insertion of the singlet and dicarbon molecules into one of the four silicon-hydrogen bonds of silane leading to singlet 3-sila-methyl­ace­tylene (HCCSiH3; [**i1**]) (Figure 4). This C3v symmetric intermediate is the global mini­mum on the singlet C2H4Si potential energy surface. The pathway from the reactants to 3-sila-methylacetylene (HCCSiH3; [**i1**]) is downhill by more than 600 kJ mol-1 and overall barrierless. Two mechanisms to reach this intermediate, potentially depending on the starting configuration, seem possible. Firstly, as observed in both ab initio dynamics trajectories, and geometry optimizations, 1,1-dicarbon insertion occurs into one of the four chemically equivalent Si-H bonds in conjunction with rapid hydrogen migration (Figure 4a). Second, some trajectories also show initial hydrogen abstraction, yielding an ethynyl radical (CCH) and a silyl radical (SiH3) immediately followed by recombination of the radical fragments to (HCCSiH3; [**i1**]) (Figure 4b); this pathway suggests the possibility of a roaming mechanism. Starting from [**i1**], multiple isomerization pathways access sila-cyclopropene (c-C2SiH4; [**i2**]), 1-sila-2-methylvinylidene (SiCH(CH3); [**i3**]), 3-sila-vinylcarbene (C2H3SiH; [**i4**]), and 1-sila-allene (H2CCSiH2; [**i5**]) involving hydrogen shifts along with ring closure/opening through transition states located well below the energy of the separated reactants. The computations also reveal eight unimolecular decomposition path­ways to the reaction products (**p1-p6**) with overall tight exit transition states located between 37 and 93 kJmol-1 above the initially formed products. While no pathway to **p4** was found from the intermediates, **p4** can be accessed in principle via isomeri­zation of **p3** and/or **p5** (Figure S2). On the triplet surface, our computations show that the C2H4Si intermediates are much higher in energy than their singlet counterparts; the reactions will therefore cross over to the singlet surface if possible. The singlet-triplet gap during a typical ab initio trajectory of the silane – triplet dicarbon reaction becomes negligible as the dicarbon molecule nears silane, providing an avenue for the triplet reactants to cross over to the singlet surface via spin-orbit coupling. Only singlet intermediates are therefore predicted.

     Under normal circumstances, a comparison of the experimentally derived reaction energy of 240 ± 20 kJ mol-1 with the computed reaction energies leading to the products **p1-p6** would reveal the nature of the (dominant) reaction channel. In the present situation, however, the present reaction is more complex. Based on the experimental findings, this procedure would suggest the formation of silacyclopropyne (c-CCSiH2; **p6**; X1A1). This product can be accessed via unimolecular decomposition of 1-sila-allene (H2CCSiH2; [**i5**]), which in turn is accessible from singlet 3-sila-methyl­ace­tylene (HCCSiH3; [**i1]**) via hydrogen migration (pathway 1) and also through the isomerization sequence [**i1**] → [**i2**] → [**i4**] → [**i5**] (pathway 2). However, considering the energies of the transition states for pathways 1 and 2 of 173 kJ mol-1 and up to 236 kJ mol-1, respectively, the unimolecular decomposition of 3-sila-methyl­ace­tylene (HCCSiH3; [**i1]**) to ethylsilanediyl (HCCSiH; **p3**) via an exit transition state located only 37 kJ mol-1 above the final products should be preferred. Since all four hydrogen atoms in silane are chemically equivalent, it is not feasible to conduct crossed beam experiments with partially deu­te­rated reactants to trace the lost hydrogen(s) and/or deuterium(s).23 One possible explanation to converge the aforementioned finding is that ethylsilanediyl (HCCSiH; **p3**) does form in the crossed beam reaction, but the products are highly internally (rovibrationally) excited so that less than the experimentally derived reaction energy is released into the translational degrees of freedom of the final products. This in turn would result in a P(ET) with a lower maximum translational energy than expected based on the computational predictions. The products can further isomerize, due to an abundance of rovibrational energy and relatively low barriers between products; this of course will not affect the product translational energy however.

     To test this hypothesis, we conducted Rice–Ramsperger–Kassel–Marcus (RRKM) calcu­lations and also carried out quasiclassical trajectory calculations (QCT) (Me­thods). RRKM theory assumes complete randomization of the avail­able energy. Starting from the initial collision complex 3-sila-methyl­ace­tylene (HCCSiH3; [**i1]**), the RRKM treatment at a collision energy of 22 kJmol-1 predicts a predominant formation of ethylsilanediyl (HCCSiH; **p3**; 90 %) and vinylidenesilanediyl (SiCCH2; **p2**; 8 %) with only minor contributions of the remaining isomers of 2 % (Supplementary Information). These initially formed products can further isomerize, however RRKM theory predicts that substantial fractions of **p3** exceeding 55 %will remain after 1 ns even with the maximum possible product internal energy (Supplementary Information). Hereafter, quasiclassical trajectory (QCT) calculations were carried out (Methods; Supplementary Information). The­se calculations bridge the dynamics experiments with the the­o­re­­tical understanding of the reaction and also provide theoretically predicted center-of-mass trans­lational energy distri­bu­tions (P(ET)) (Figure 2); these predicted distributions can be exploi­ted then to fit the experimental data (Figure 1). The QCT calculations were launched from the transition states, as the hot intermediates are too long-lived to study on a reasonable QCT timescale; trajectories run for 2.5 ps from the hot intermediates showed no reaction. The dynamics studies leading to ethylsilanediyl (HCCSiH; **p3**) predict a center-of-mass translational energy distribution with a high energy cutoff of 250 ± 20 kJ mol-1. Within the error limits, this data correlates nicely with the best fit center-of-mass functions based on our experimental data of 250 ± 20 kJ mol-1 (Figure 2). Therefore, we can conclude that the QCT treatment of the trajectories to ethylsilanediyl (HCCSiH; **p3**) suggests that ethylsilanediyl (HCCSiH; **p3**) is formed highly rovibrationally excited. This internal energy in turn results in a P(ET) with a maximum translational energy well below the computed reaction energy of 406 ± 5 kJ mol-1. Nevertheless, the distribution maximum of the predicted P(ET) is shifted by about 25 kJ mol-1 to higher energies. This might be caused by leakage of zero point energy (explicitly considered in quasi-classical dynamics) into other modes, leading to greater peak translational energies of the products than expected. Essentially, this shift results in simulated TOF spectra which are slightly faster than recorded experimentally; likewise, this excess energy is reflected in a much broader laboratory angular distribution than determined experi­mentally (Figure 1). Nevertheless, despite this open issue, RRKM studies, QCT calculations, and the experiments can be reconciled with the formation of highly rovibrationally excited ethyl­silane­diyl carbene (HCCSiH; **p3**) along with molecular hydrogen in an overall exoergic and entrance barrierless bimolecular reaction.

     From the viewpoint of electronic structure and chemical bonding, it is educational to compare singlet ethyl­silane­diyl carbene (HCCSiH; X1A1) with triplet propargylene (HCCCH; X3B) (Sche­me 2). The replacement of a carbon atom by an isovalent silicon atom first changes the geometry from *C*2 to Cs and the multiplicity from a triplet to a singlet. This dramatic switch can be best rationalized by defining triplet propargylene as a 1,3-diradical with parallel spin, but singlet ethyl­silane­diyl as a sila­carbene with both electrons paired and localized at the silicon atom. This agrees with previous theoretical studies showing silicon tends to avoid multiple bonds, instead preferring to localize nonbonding electrons onto the silicon atom24. This is clearly seen through the geometries of propargylene and ethylsilanediyl. Propargylene has two C-C bonds with length 1.27Å – somewhere between the length of a typical double and triple bond; the substitution of one carbon for a silicon in ethylsilanediyl leads to a Si-C bond length of 1.84Å, more consistent with a single bond. The H-Si-C bond angle of 93.2º in ethylsilanediyl compared to 162.0º in propargylene shows that the lone pair on the silicon resides in an atomic orbital with a large amount of s character while the unpaired electrons in propargylene reside in p orbitals; this is consistent with previous studies of silicon containing compounds, where the behavior is attributed to the inert pair effect24–26.

     To conclude, our crossed molecular beam, statistical, and quasi classical trajectory study of the gas phase reaction of singlet and triplet dicarbon with silane affords persuasive evidence for the very first directed gas phase preparation of the Cs symmetric singlet ethylsilanediyl carbene (HCCSiH; **p3**; 1A’). The reaction of singlet dicarbon is initiated by a barrier­less insertion of dicarbon into the silicon-hydrogen bond of silane leading effectively via 1,2-insertion to the singlet 3-sila-methyl­ace­tylene (HCCSiH3; [**i1**]) collision complex. Alternatively, dicarbon may abstract a hydrogen yielding an ethynyl radical (CCH) and a silyl radical (SiH3) followed by either rapid recombination or possibly, a delayed roaming mediated reaction of the radical fragments to 3-sila-methyl­acetylene. Triplet dicarbon ends up at the same intermediate through spin orbit coupling between the triplet and singlet surfaces. This intermediate then undergoes pre­do­mi­nantly unimo­le­cu­lar decomposition via molecular hydrogen loss to highly rovibra­tio­nally excited singlet ethylsilanediyl carbene (HCCSiH; **p3**; 1A’). The initial insertion of dicarbon to form a bound 3-sila-methyl­ace­tylene (HCCSiH3; [**i1**]) inter­mediate essentially bypasses the traditionally ‘expected’ route via singlet silylcarbene (CCH(SiH3)) through 1,1-insertion, which was revealed not to be a local mini­mum. This insertion process is in strong contrast to the isovalent dicarbon – methane system, in which dicarbon inserts through 1,1-insertion with only one carbon atom yielding a bound singlet methyl­carbene (CCH(CH3)) intermediate, which isomerizes via hydrogen migration to singlet methyl­acetylene (HCCSiH; 1A’)27. This defines the dicarbon – silane system as a prototype of a novel, exotic insertion mechanism throu­gh carbon-silicon bond formation eventually leading to highly un­saturated singlet ethylsilanediyl carbene (HCCSiH; **p3**; 1A’) thus clarifying our under­standing of molecular structure, reactivity, and the dynamics of reaction mechanisms invol­ving silicon. The facile preparation and identification of gas phase singlet ethylsilanediyl carbene (HCCSiH; **p3**; 1A’) also has significant implications to the chemistry in circumstellar environments of carbon-rich Asymptotic Giant Branch (AGB) stars such as IRC+10216. The astronomical detection of silicon carbides (SiC, c-SiC2, c-SiC3, SiC4)28 along with silane (SiH4) 29 and methylsilane (CH3SiH3)30 toward IRC+10216 documents a striking gas phase chemistry, whose initial silicon-carbon bond formation mechanisms are only beginning to emerge.31 The prospective identification of hydrogenated silicon-carbon clusters such as singlet ethylsilanediyl carbene via rotational spectroscopy exploiting the Atacama Large Millimeter/submillimeter Array would exploit circumstellar envelopes as natural laboratories for an exotic silicon-carbon chemistry under extreme conditions thus exploring unusual reaction mechanisms such as dicarbon insertion processes through astronomical observations guided by laboratory experiments under single collision conditions combined with a theoretical investi­gation of fundamental elementary reactions leading to silicon-carbon bond formation in deep space.

**Methods**

*Experimental Methods.*The elementary reaction of dicarbon (C2; X1Ʃ+g/a3Πu) with silane (SiH4; X1A1) was explored in the gas phase under single collision conditions in a crossed molecular beams machine.15 A pulsed molecular beam of dicarbon was prepared via photodissociation of tetrachloroethylene (C2Cl4, Sigma Aldrich, 99.9 %) at 248 nm seeded in helium (99.9999%; AirGas) at levels of 1.4 % at 300 K. The dicarbon beam passes through a stainless steel skimmer, and a four-slot chopper wheel selects a well-defined peak velocity (*υ*p) and speed ratio (S) (Table S1). This part of the radical beam is crossed perpendicularly with a pulsed silane beam (99.9997 %; Linde) in the interaction region of the scattering chamber resulting in a collision energy (*E*col) of 22.0 ± 0.3 kJ mol-1 and a center-of-mass (CM) angle of 35.5 ± 0.4○, respectively. The reactively scattered products were monitored exploiting a triply differentially pumped quadrupole mass spectrometer (QMS) operating in the time-of-flight (TOF) mode after electron-impact ionization of the neutral species. Ions selected with a specific mass-to-charge ratio (*m*/*z*) were accelerated toward a stainless steel target coated with a thin layer of aluminum, and the ions trigger an electron cascade. The electrons traveled toward an organic scintillator to generate a photon pulse amplified by a photomultiplier tube (PMT). The time-of-flight spectra (TOF) were integrated and normalized to obtain the product angular distribution in the laboratory frame (LAB) and the laboratory data was converted to the CM frame using a forward-convolution routine. This method initially chooses the product translational energy distribution (*P*(*E*T­)) and angular distribution (*T*(*θ*)) in the CM frame to reproduce the TOF spectra and laboratory angular distribution.

*Theoretical Methods.* The reactant, intermediate, and product structures were obtained via geometry optimization using the ωB97M-V32 density functional along with the def2-tzvpd basis set33,34. Frequency calculations confirmed no imaginary frequencies for all structures. Transition state structures were obtained using the freezing string method followed by a transition state search, again using the ωB97M-V functional along with the def2-tzvpd basis set. Frequency calculations confirmed a single imaginary frequency for each transition state structure. Third order Møller-Plesset theory using DFT orbitals (sMP3:ωB97M-V)35 and coupled cluster theory with single, double, and perturbative triple excitations (CCSD(T))36 were then performed on all structures using the aug-cc-pVXZ family of basis sets37–39 to obtain high accuracy results in the complete basis set limit, using the formula:

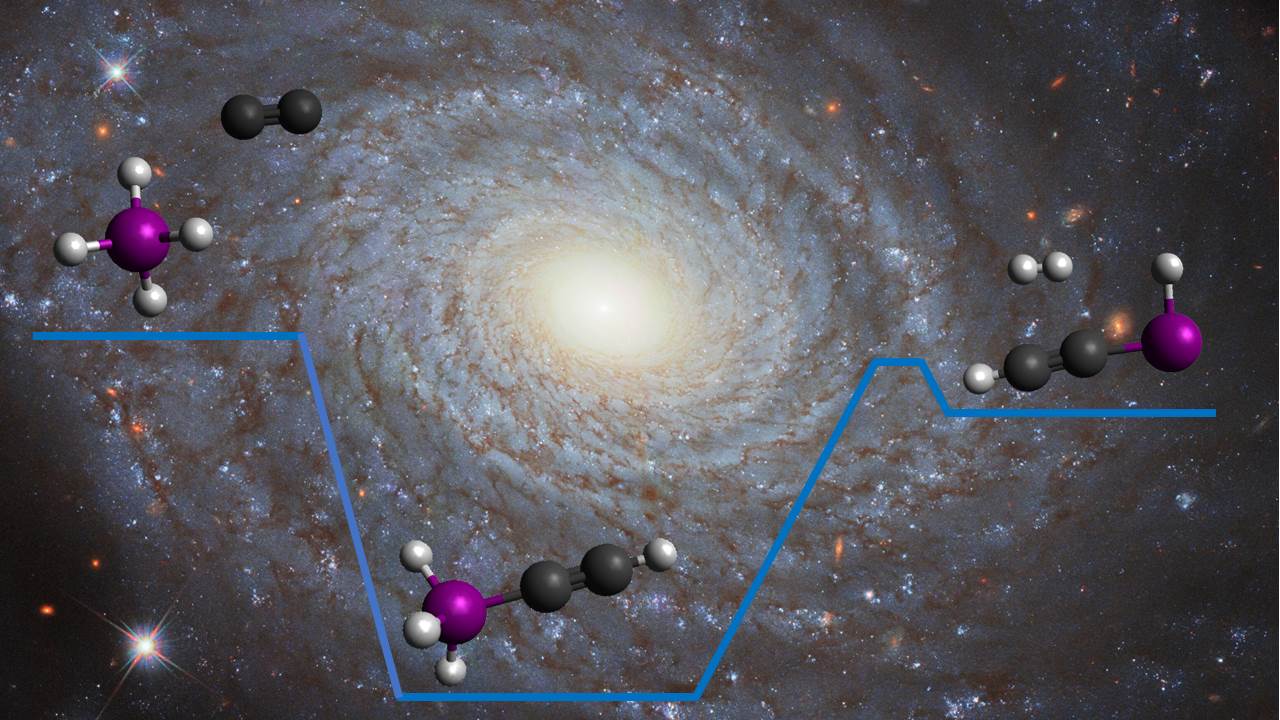
Where the complete basis set extrapolation for MP3: ωB97M-V is given by:

The energy of the C2 molecule was computed by calculating the computationally simpler triplet state, then correcting with an experimental singlet-triplet gap.

QCT trajectories were run starting from the transition state geometries, as the intermediate structures are too long-lived to study via AIMD. Only the i1→p3, i4→p1, and i4→p2 transition states were considered, as these accounted for the vast majority of products according to RRKM theory. Excess energy at each geometry was distributed randomly among the real modes of the transition states. 200 trajectories for each transition state were run for 240 fs, in which time all trajectories fell to either intermediates or products. All trajectories were run with the ωB97X-D3 functional40 and the def2-sv(p) basis set. All computations were run with the Q-Chem suite of electronic structure programs41.

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