

Formation of the 2,3-Dimethyl-1-silacycloprop-2-enylidene Molecule via the Crossed Beam Reaction of the Silyldiyne Radical (SiH; $X^2\Pi$) with Dimethylacetylene (CH_3CCCH_3 ; X^1A_{1g})

Tao Yang, Aaron M. Thomas, Beni B. Dangi, and Ralf I. Kaiser*

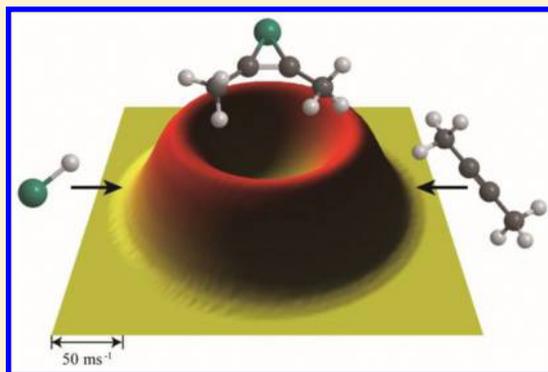
Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States

Mei-Hung Wu, Bing-Jian Sun, and Agnes H. H. Chang*

Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan

Supporting Information

ABSTRACT: We carried out crossed molecular beam experiments and electronic structure calculations to unravel the chemical dynamics of the reaction of the silyldiyne ($-d_1$) radical (SiH/SiD; $X^2\Pi$) with dimethylacetylene (CH_3CCCH_3 ; X^1A_{1g}). The chemical dynamics were indirect and initiated by the barrierless addition of the silyldiyne radical to both carbon atoms of dimethylacetylene forming a cyclic collision complex 2,3-dimethyl-1-silacyclopropenyl. This complex underwent unimolecular decomposition by atomic hydrogen loss from the silicon atom via a loose exit transition state to form the novel 2,3-dimethyl-1-silacycloprop-2-enylidene isomer in an overall exoergic reaction (experimentally: $-29 \pm 21 \text{ kJ mol}^{-1}$; computationally: $-10 \pm 8 \text{ kJ mol}^{-1}$). An evaluation of the scattering dynamics of silyldiyne with alkynes indicates that in each system, the silyldiyne radical adds barrierlessly to one or to both carbon atoms of the acetylene moiety, yielding an acyclic or a cyclic collision complex, which can also be accessed via cyclization of the acyclic structures. The cyclic intermediate portrays the central decomposing complex, which fragments via hydrogen loss almost perpendicularly to the rotational plane of the decomposing complex exclusively from the silyldiyne moiety via a loose exit transition state in overall weakly exoergic reaction leading to ((di)methyl-substituted) 1-silacycloprop-2-enylidenes (-1 to -13 kJ mol^{-1} computationally; -12 ± 11 to $-29 \pm 21 \text{ kJ mol}^{-1}$ experimentally). Most strikingly, the reaction dynamics of the silyldiyne radical with alkynes are very different from those of C1–C4 alkanes and C2–C4 alkenes, which do not react with the silyldiyne radical at the collision energies under our crossed molecular beam apparatus, due to either excessive entrance barriers to reaction (alkanes) or overall highly endoergic reaction processes (alkenes). Nevertheless, molecules carrying carbon–carbon double bonds could react, if the carbon–carbon double bond is either consecutive like in allene (H_2CCCH_2) or in conjugation with another carbon–carbon double bond (conjugated dienes) as found, for instance, in 1,3-butadiene ($\text{H}_2\text{CCHCHCH}_2$).



1. INTRODUCTION

During the past few years, the dimethylacetylene molecule (2-butyne; CH_3CCCH_3) has received considerable attention by the reaction dynamics community to investigate sterical effects of replacing one or both hydrogen atoms by bulky methyl group(s) (CH_3) in the acetylene (C_2H_2) molecule, under bimolecular reactions with the cyano radical (CN ; $X^2\Sigma^+$),^{1,2} boronyl radical (BO ; $X^2\Sigma^+$),³ atomic carbon (C ; ^3P),^{4–6} singlet and triplet dicarbon (C_2 ; $X^1\Sigma_g^+$, $a^3\Pi_u$),⁷ and atomic boron (B ; ^2P) (Scheme 1).^{8,9} Considering the reactions with the diatomic cyano and boronyl radicals, the reaction dynamics were dictated by adding doublet radicals with their respective radical center located at the carbon and boron atom, to one of the carbons in the carbon–carbon triple bond followed by loss of atomic hydrogen and/or the methyl group. The reaction dynamics with atomic carbon and dicarbon molecule are more complex.

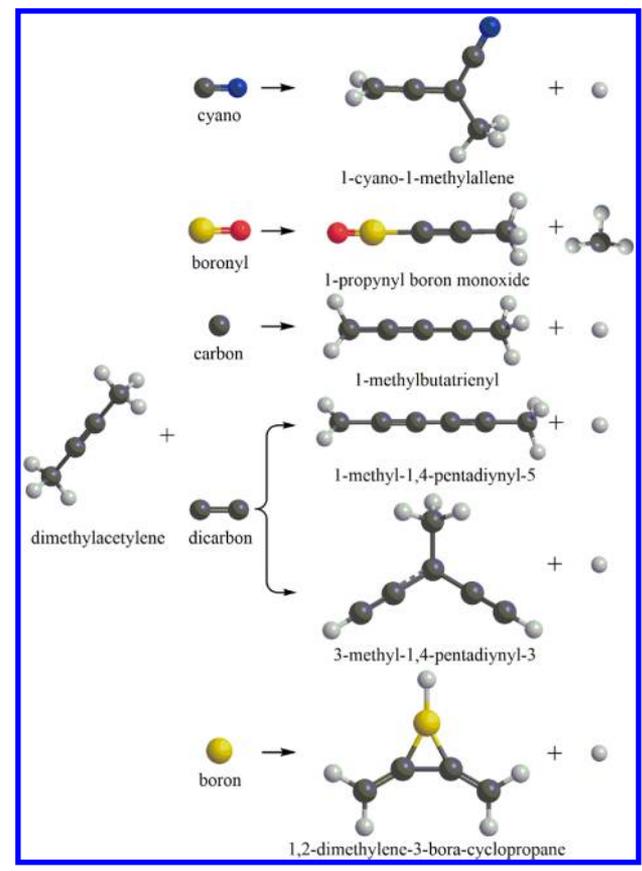
In the case of ground state atomic carbon, the carbon atom adds to either one or both carbon atoms, yielding triplet collision complexes, which eventually isomerize via ring closure/ring opening to yield the acyclic triplet dimethylpropargylene intermediate ($\text{CH}_3\text{CCCCH}_3$) before ejecting atomic hydrogen from the methyl group forming the 1-methylbutatrienyl radical ($\text{CH}_3\text{CCCCH}_2$). On the singlet surface, dicarbon follows an indirect reaction mechanism governed by adding dicarbon to the central acetylene carbons of dimethylacetylene followed by multiple isomerizations (ring closure/ring opening) to form eventually the 2,4-hexadiyne intermediate ($\text{CH}_3\text{CCCCCH}_3$), which then ejects atomic hydrogen leading

Received: July 13, 2016

Revised: August 26, 2016

Published: August 29, 2016

Scheme 1. Reaction Products of Cyano (CN), Boronyl (BO), Carbon (C), Dicarbon (C₂), and Boron (B) with Dimethylacetylene (CH₃CCCH₃) Studied under Single Collision Conditions in a Crossed Molecular Beam Machine



to the 1-methyl-1,4-pentadiynyl-5 radical (CH₃CCCCCH₂). On the triplet surface, dicarbon molecule adds barrierlessly to both carbons concurrently or to one central carbon of dimethylacetylene leading to an intermediate CH₃C(CC)-CCH₃, which further isomerizes prior to atomic hydrogen loss, yielding the 3-methyl-1,4-pentadiynyl-3 radical (HCCC(CH₃)-CCH). Atomic boron also exhibits rather unique reaction dynamics. The reaction is initiated by the interaction of the boron atom with the π electron density of the dimethylacetylene molecule, which forms a 2,3-dimethyl-1-boracyclopropenylidene radical intermediate (*c*-BC₂(CH₃)₂). However, rather than undergoing ring opening, this intermediate isomerizes via a hydrogen shift from carbon to boron, followed by atomic hydrogen decomposition from the remaining methyl group. This process forms the cyclic 1,2-dimethylene-3-boracyclopropane product. These considerations suggest that the reaction dynamics involving dimethylacetylene with the doublet radicals of cyano and boronyl (addition–elimination) differ strongly from those with carbon/dicarbon (addition–ring closure/opening–atomic hydrogen loss) and in particular from atomic boron (addition–cyclization–hydrogen migration–atomic hydrogen loss).

To date, these reactions with dimethylacetylene studied under single collision conditions only involve atoms/radicals of the elements in the second row of the periodic table: boron, carbon, nitrogen, and oxygen. To expand these investigations to radicals carrying third row elements, we present data here on the crossed molecular beam reaction of the silylydine radical

(SiH; X²Π) with dimethylacetylene (CH₃CCCH₃; X¹A_{1g}) and combine these investigations with electronic structure calculations. These studies will then be compared to the related silylydine–acetylene (SiH–HCCCH)¹⁰ and silylydine–methylacetylene (SiH–CH₃CCH)¹¹ systems studied previously in our group. Finally, we contemplate the reaction dynamics of silylydine with the corresponding C1–C4 alkanes and C2–C4 alkenes, as well as two special cases: allene (H₂CCCH₂)¹² and 1,3-butadiene (H₂CCHCHCH₂).¹³

2. EXPERIMENT

The gas phase reactions of the silylydine (SiH; X²Π) and silylydine-*d*₁ (SiD; X²Π) radical with dimethylacetylene (CH₃CCCH₃; X¹A_{1g}) were investigated respectively in a universal crossed molecular beam machine at the University of Hawaii at Manoa.^{14–21} A pulsed beam of silylydine radicals was prepared by photolysis of disilane (Si₂H₆; 99.998%; Voltaix) seeded in helium (He; 99.9999%; Gaspro) in a fraction of 0.5% as well as backing pressure of 2 atm.¹² This gas mixture was fed into a piezoelectric valve operating at 120 Hz, –400 V amplitude and a pulse width of 80 μ s, and the released pulsed beam was intercepted by a 1 mm \times 4 mm laser spot from an ArF excimer laser (Compex 110, Coherent, Inc.) of 60 Hz and 30 mJ per pulse, which is located 1 mm downstream from the nozzle. The silylydine-*d*₁ radical beam was produced *in situ* by ablating a rotating silicon rod with the output of a Nd:YAG laser (Quanta-Ray Pro 270, Spectra-Physics) operating at 30 Hz and 266 nm with pulse energies of 10–15 mJ and seeding the ablated species in deuterium gas (D₂, 99.7% D; Icon Isotopes) released at 4 atm backing pressure by a piezoelectric valve operating at 60 Hz, –400 V amplitude, and pulse width of 80 μ s.¹⁰ Prior to arriving at the center of interaction region, the silylydine(-*d*₁) radicals passed through a stainless steel skimmer and a four-slit chopper wheel operating at 120 Hz, and the latter was able to select the pulsed beam with a well-defined peak velocity (v_p) and speed ratio (*S*) of 1715 \pm 13 m s⁻¹ and 13.1 \pm 1.9 for silylydine, and of 1981 \pm 38 m s⁻¹ and 5.2 \pm 1.0 for silylydine-*d*₁, respectively. The primary radical beam crossed perpendicularly the most intense part of a pulsed dimethylacetylene beam (C₄H₆, Sigma-Aldrich) released by a second pulsed valve operating at –400 V amplitude, 120 Hz (for silylydine plus dimethylacetylene)/60 Hz (for silylydine-*d*₁ plus dimethylacetylene), pulse width of 80 μ s at a backing pressure of 550 Torr. Peak velocity and speed ratio for the dimethylacetylene beam were determined to be 780 \pm 10 m s⁻¹ and 8.2 \pm 0.4, resulting in nominal collision energies (E_c) of 33 \pm 1 kJ mol⁻¹ (SiH + C₄H₆) and 41 \pm 2 kJ mol⁻¹ (SiD + C₄H₆), as well as center-of-mass (CM) angles of 40.0 \pm 0.7° and 35.8 \pm 1.1°, respectively. The rotational temperature of the silylydine radical beam (SiH; X²Π) was determined via laser-induced fluorescence (LIF) technique to be mainly 40 \pm 10 K.¹²

In the triply differentially pumped detection system, the neutral products were first ionized by an 80 eV electron impact ionizer before filtering with a quadrupole mass spectrometer (QMS; Extrel QC 150). Selected ions at a specific mass-to-charge ratio (*m/z*) traveled toward a doorknob shape stainless steel target of –22.5 kV, whose surface is coated with a thin layer of aluminum, thus enabling a subsequent electron cascade upon the impact of the ions. Thereafter, the electrons flew toward an organic scintillator and generated a photon pulse that was further amplified by a photomultiplier tube (PMT, Burle, Model 8850) of –1.35 kV. The PMT signal was filtered by a

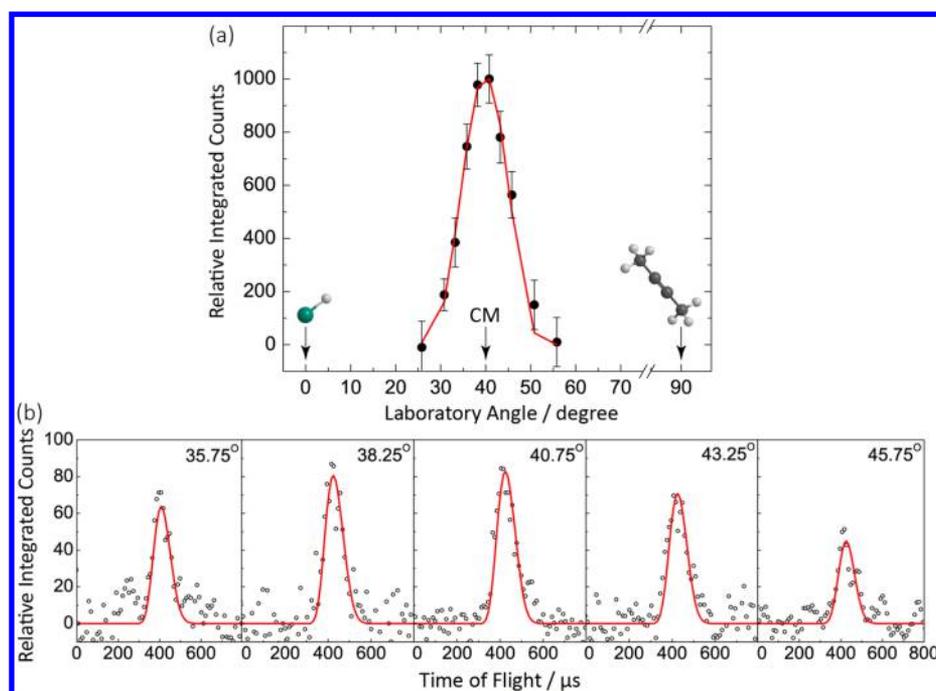


Figure 1. Laboratory angular distribution (a) and the selected time-of-flight (TOF) spectra (b) recorded at a mass-to-charge ratio (m/z) of 82 (SiC_4H_6^+) for the reaction of the silylydne radical (SiH ; $X^2\Pi$) with dimethylacetylene (H_3CCCCH_3 ; X^1A_{1g}). The solid circles represent the integrated counts at discrete angles with 1σ error bars, and the open circles represent the data points of the TOF spectra. The solid lines represent the fits obtained from the forward-convolution routine.

discriminator (Advanced Research Instruments, Model F-100TD) and fed into a multichannel scaler. The time-of-flight (TOF) spectra were then integrated and normalized before generating the product laboratory angular distribution. The laboratory data will also be converted into the CM functions by a forward-convolution routine.^{22,23} This method exploits a parametrized set or point-form translational energy flux distribution ($P(E_T)$) and angular flux distribution ($T(\theta)$) in the CM frame, to iteratively fit the laboratory angular distribution and the TOF spectra until best fits are obtained. The reactive cross section is based on an $E_c^{-1/3}$ energy dependence, which is used for barrierless reactions governed by long-range attractive forces within the line-of-center model.²⁴

3. THEORY

The SiH ($X^2\Pi$) plus CH_3CCCH_3 (X^1A_{1g}) reaction was explored computationally on the adiabatic doublet SiC_4H_7 potential energy surface (PES). We identified possible collision complexes and characterized the relevant isomerization and dissociation channels. Here, the optimized geometries of the collision complexes, intermediates, transition states, and dissociation products were obtained along with the harmonic frequencies by density functional B3LYP^{25–28}/cc-pVTZ and MP2/cc-pVTZ calculations. The CCSD^{29–32}(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies were then computed and extrapolated to complete basis set limits,³³ CCSD(T)/CBS, with B3LYP/cc-pVTZ zero-point energy corrections. The energies were expected to have an accuracy of 8 kJ mol^{-1} .³⁴ GAUSSIAN09 programs³⁵ were facilitated in the electronic structure calculations.

4. RESULTS

The scattering products for the silylydne radical (SiH ; $X^2\Pi$) reaction with dimethylacetylene (CH_3CCCH_3 ; X^1A_{1g}) were

monitored at $m/z = 83$ (SiC_4H_7^+), 82 (SiC_4H_6^+), 81 (SiC_4H_5^+), and 68 (SiC_3H_4^+). The TOF signal at $m/z = 82$ depicts the best signal-to-noise ratio with data recorded at $m/z = 83$ too weak to observe any signal. This suggests that no SiC_4H_7 is observable under our experimental conditions. The TOF spectra at $m/z = 82$, 81 , and 68 depict identical patterns after scaling; this proposes that the molecular hydrogen loss (SiC_4H_5) and the methyl group loss (SiC_3H_4) channels are both closed under current experimental conditions. Therefore, the TOFs and the laboratory angular distribution were obtained at $m/z = 82$ from 25.75° to 55.75° at an interval of 2.50° (Figure 1); the forward-backward symmetry of the laboratory angular distribution suggests indirect scattering dynamics via a SiC_4H_7 complex.³⁶ Because the atomic hydrogen loss can originate from either the dimethylacetylene or the silylydne reactant, we also conducted the reaction of the silylydne- d_1 radical (SiD ; $X^2\Pi$) with dimethylacetylene and collected TOF spectra at $m/z = 82$ and 83 probing the deuterium loss (SiC_4H_6^+) and/or the hydrogen loss ($\text{SiC}_4\text{H}_5\text{D}^+$) (Figure 2). An inspection of the TOF data reveals no intensity at $m/z = 83$, suggesting that atomic hydrogen loss is absent, and that only the atomic deuterium loss channel is open. In conclusion, the reaction of silylydne with dimethylacetylene involves the formation a SiC_4H_7 complex, which eventually decomposes via an atomic hydrogen loss from the silylydne moiety leading to SiC_4H_6 product isomer(s).

We are also able to reveal the underlying reaction dynamics by converting the laboratory data into the CM reference frame; this yields the CM translational energy flux distribution ($P(E_T)$) along with the CM angular flux distribution ($T(\theta)$) (Figure 3). First of all, the TOF data and laboratory angular distribution could be fit with a single channel of the product mass combination of 82 amu (SiC_4H_6) and 1 amu (H). In addition, the $P(E_T)$ extends up to a maximum energy of $62 \pm$

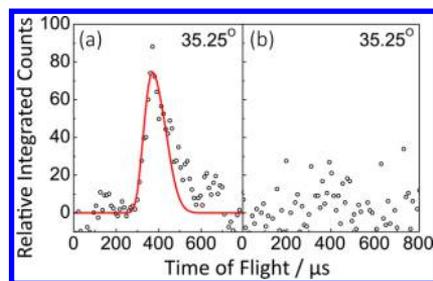


Figure 2. Center-of-mass TOF data for the reaction of the silyldyne- d_1 radical (SiD ; $X^2\Pi$) with dimethylacetylene at m/z of 82 (SiC_4H_6^+ (a)) and 83 ($\text{SiC}_4\text{H}_5\text{D}^+$ (b)), respectively. The open circles represent the experimental data, and the red line represents the fit obtained from the forward-convolution routine.

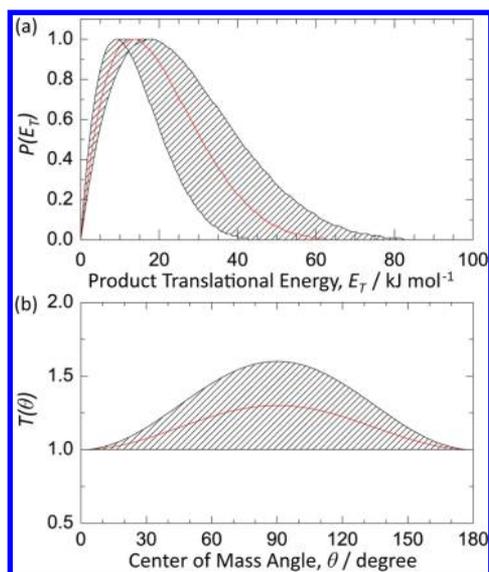


Figure 3. Center-of-mass translational energy flux distribution $P(E_T)$ (a) and angular flux distribution $T(\theta)$ (b) for the reaction of the silyldyne radical with dimethylacetylene forming SiC_4H_6 product isomer(s) via an atomic hydrogen emission. The hatched areas define the error limits.

20 kJ mol^{-1} ; this high-energy cutoff represents the sum of the collision energy and the absolute value of the reaction exoergicity for those reactants born without internal excitation. We therefore obtain a reaction exoergicity of $-29 \pm 21 \text{ kJ mol}^{-1}$ to form the SiC_4H_6 isomer(s) plus atomic hydrogen. Further, the $P(E_T)$ shows a distribution maximum of about 8–18 kJ mol^{-1} , indicating the existence of a rather loose exit transition state upon decomposition of the SiC_4H_7 complex. Considering the concept of the microscopic reversibility, we expect a rather low (or no) entrance barrier for the reversed reaction of hydrogen addition to the SiC_4H_6 product.³⁶ A closer look at the CM angular flux distribution $T(\theta)$ reveals intensity spanning from 0° to 180° , implying the formation of a SiC_4H_7 complex and hence indirect reaction dynamics.³⁶ We also noticed a forward–backward scattering pattern, indicating that the lifetime of the decomposing complex is longer than its rotational period.³⁷ At last, the $T(\theta)$ depicts a pronounced intensity maximum at 90° . This feature reflects that the decomposition of the SiC_4H_7 complex involves geometric constraints, in which the hydrogen atom leaves almost parallel to the total angular momentum vector J and perpendicularly to the molecular plane of the decomposing complex.³⁸

5. DISCUSSION

We combine our experimental findings with the computational results of the reaction for the silyldyne radical (SiH ; $X^2\Pi$) with dimethylacetylene (CH_3CCCH_3 ; X^1A_{1g}) (Figure 4; Supporting Information). The electronic structure calculations suggest that the silyldyne radical adds barrierlessly to both carbon atoms of the acetylene moiety of dimethylacetylene (CH_3CCCH_3), forming intermediate **i1** (2,3-dimethyl-1-silacyclopropenyl, -165 kJ mol^{-1}). Please note that the efforts to form the intermediates **i2** and **i3** in one step from the reactants were not successful, but both intermediates can be connected to **i1**. The acyclic structures **i2** and **i3** can undergo trans–cis isomerization via a barrier of only 21 kJ mol^{-1} above **i2**; the latter then follows ring closure to **i1** by passing a transition state located only 31 kJ mol^{-1} above **i2**, but still below the energy of the separated reactants. Note that **i2** could in principle also isomerize via methyl group migration from the carbon to the silicon atom forming **i5**, but the barrier is 40 and 50 kJ mol^{-1} higher than the competing isomerization from **i2** to **i1** and from **i2** to **i3**, respectively. Therefore, **i2** is expected to rearrange to the cyclic intermediate **i1** or isomerize to **i3** via a barrier of 21 kJ mol^{-1} . The intermediate **i1** can either undergo a hydrogen atom shift from the methyl group to the silicon and break the silicon–carbon bond to form **i4**, after overcoming a barrier of 181 kJ mol^{-1} , or proceed through a hydrogen migration from silicon to the neighboring carbon as well as the silicon–carbon bond rupture via a barrier of 99 kJ mol^{-1} , leading to **i7**, which later forms **i8** via a tricyclic ring formation and a methyl group migration to the silicon atom. The intermediate **i4** can subsequently isomerize to **i6** by recyclization via a barrier of 57 kJ mol^{-1} . What is the ultimate fate of the intermediates **i1**–**i8**? Our computations identified multiple decomposition pathways including atomic hydrogen loss and methyl group loss. The unimolecular decompositions of **i1** via atomic hydrogen loss to the cyclic 2,3-dimethyl-1-silacycloprop-2-enylidene isomer **p1**, and of **i8** via methyl group loss to the cyclic 2-methyl-1-silacycloprop-2-enylidene isomer **p10**, represent the thermodynamically most favorable pathways following an overall exoergicity of -10 and -43 kJ mol^{-1} without any exit barrier, respectively. All remaining decomposition pathways via atomic hydrogen or methyl group loss leading to **p2**–**p9** are endoergic by between 28 and 219 kJ mol^{-1} . Even though **i5** can form **p2** via a methyl group loss, **i5** has to be formed from **i1** or **i2** via a barrier of 93 or 37 kJ mol^{-1} above the separated reactants; hence, this pathway is not competitive compared to the hydrogen loss pathway from **i1** as well as methyl loss from **i8**, which originates from **i1** and **i7**. Considering that all the pathways to products **p2**–**p9** are energetically closed under our collision energy of 33 kJ mol^{-1} , the calculations predict that the formations of the cyclic 2,3-dimethyl-1-silacycloprop-2-enylidene isomer **p1** plus atomic hydrogen and the cyclic 2-methyl-1-silacycloprop-2-enylidene isomer **p10** plus methyl group represent the possible open channels.

We further combine our experimental results with the theoretical calculations to gain more insights into the reaction dynamics. First of all, our experimental findings only confirmed the detection of the product isomer(s) from atomic hydrogen loss channel; neither molecular hydrogen loss nor methyl group loss products were able to be revealed. Further, the indirect scattering dynamics involving SiC_4H_7 complex(es) was predicted from the laboratory angular and the CM angular distributions. In addition, the theoretically predicted formation

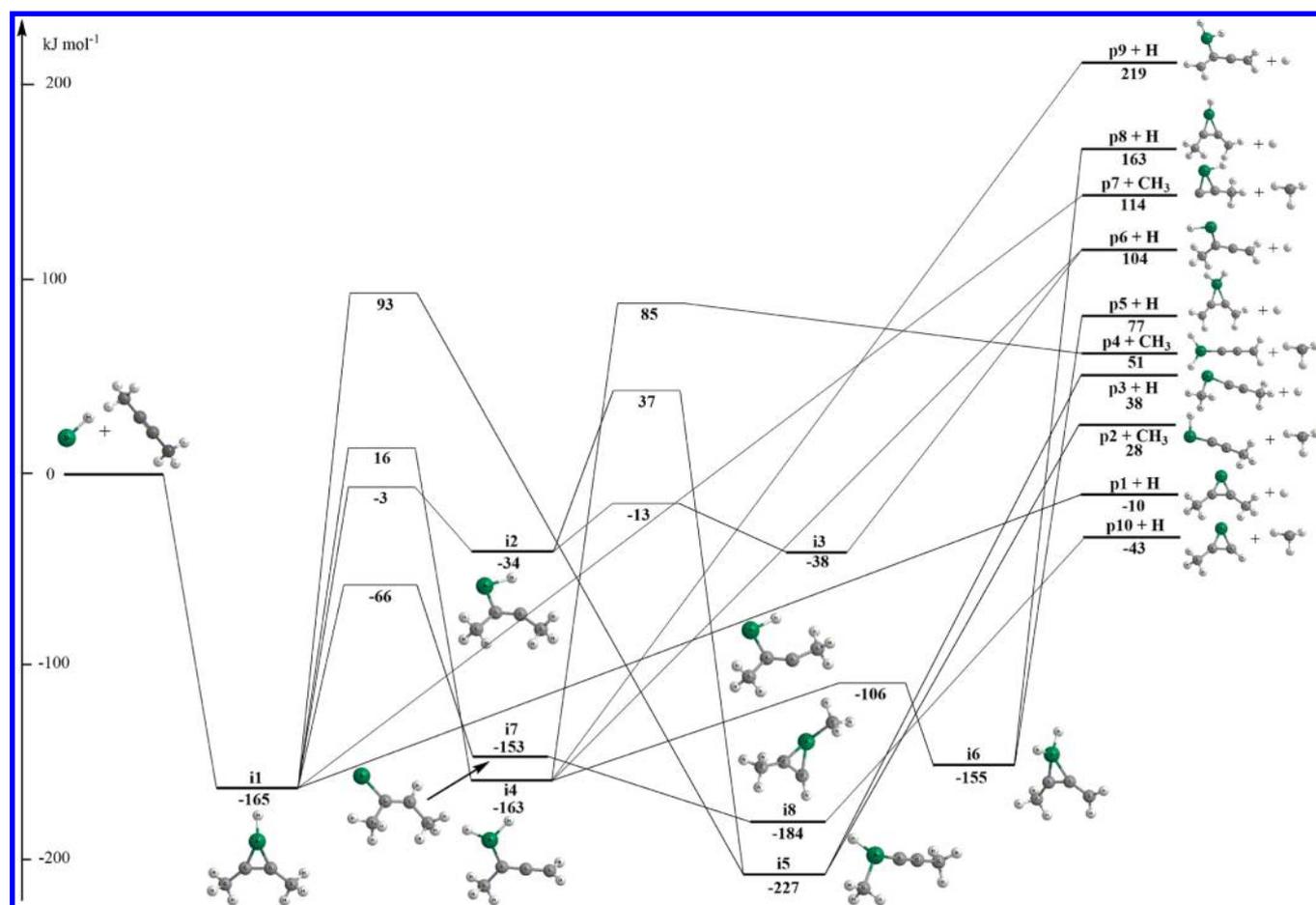


Figure 4. Potential energy surface for the reaction of the silylydine radical with dimethylacetylene.

of **p1** and the reaction exoergicity of $-10 \pm 8 \text{ kJ mol}^{-1}$ connect well with the experimentally derived reaction exoergicity of $-29 \pm 21 \text{ kJ mol}^{-1}$. Also, the loose exit transition state was predicted on the basis of the CM translational energy distribution. More importantly, experiments with silylydine- d_1 reveal that *only* a deuterium atom is lost from the silylydine moiety. This mechanism gains full support from the computations, which predict that the emitted hydrogen atom from the decomposing complex **i1** originates solely from the Si–H group, but not from any methyl group. In summary, the reaction of the silylydine radical with dimethylacetylene is dictated by indirect (complex forming) scattering dynamics and initiated by the barrierless addition of the silylydine radical (SiH) to both carbon atoms of the carbon–carbon triple bond of the dimethylacetylene molecule yielding **i1**. The intermediate **i1** was found to live longer than its rotational period and fragments via a loose exit transition state through atomic hydrogen elimination to form the 2,3-dimethyl-1-silacycloprop-2-enylidene isomer **p1** in an overall exoergic reaction (experimentally, $-29 \pm 21 \text{ kJ mol}^{-1}$; computationally, $-10 \pm 8 \text{ kJ mol}^{-1}$). This yields an enthalpy of formation of the previously elusive 2,3-dimethyl-1-silacycloprop-2-enylidene isomer to be $275 \pm 21 \text{ kJ mol}^{-1}$ (experimentally) and $294 \pm 8 \text{ kJ mol}^{-1}$ (computationally).

The reaction dynamics of the silylydine–dimethylacetylene system mirror the chemical dynamics elucidated for the silylydine–acetylene^{10,39} and silylydine–methylacetylene¹¹ reactions studied earlier. In all reactions, the silylydine radical adds without entrance barrier to the carbon–carbon triple bond either to one or simultaneously to both carbon atoms, yielding

acyclic and cyclic intermediates, which are bound between 34–74 and 152–174 kJ mol^{-1} . The cyclization from the acyclic intermediates to the cyclic intermediates involves low-lying transition states of only 0–31 kJ mol^{-1} . Finally, all cyclic intermediates were found to decompose via loose exit transition states in overall weakly exoergic reactions (-1 to -13 kJ mol^{-1} computationally; -12 ± 11 to $-29 \pm 21 \text{ kJ mol}^{-1}$ experimentally) solely via hydrogen atom emission from the silylydine moiety yielding the 1-silacycloprop-2-enylidene (silylydine–acetylene system), 2-methyl-1-silacycloprop-2-enylidene (silylydine–methylacetylene system), and 2,3-dimethyl-1-silacycloprop-2-enylidene (silylydine–dimethylacetylene system) products.

It is interesting to compare the reaction dynamics of the silylydine–alkyne systems with the corresponding silylydine–alkane and silylydine–alkene reactions. As a matter of fact, crossed molecular beam reactions of the silylydine radical with C1 to C4 alkanes (methane, CH_4 ; ethane, C_2H_6 ; propane, C_3H_8 ; *n*-butane and isobutane, C_4H_{10}) and C2 to C4 alkenes (ethylene, C_2H_4 ; propene, C_3H_6 ; butenes, C_4H_8) conducted in our laboratory at collision energies of up to 40 kJ mol^{-1} *did not reveal any reactive scattering signal*. Our electronic structure calculations at the B3LYP/cc-pVTZ//CCSD(T)/CBS level of theory predict that the insertion of the silylydine radical in any carbon–hydrogen bond of the alkane is associated with high entrance barriers of 94 kJ mol^{-1} (methane), 77 kJ mol^{-1} (ethane), 74–77 kJ mol^{-1} (propane), and 70–76 kJ mol^{-1} (*n*-butane and isobutane) (Supporting Information). These barriers to insertion are essentially higher than the collision

energy of up to 40 kJ mol⁻¹ and hence cannot be overcome. Therefore, on the basis of our crossed beam studies and electronic structure calculations, we can conclude that silyldiyne radicals do not react with alkanes under our experimental conditions. Considering the alkenes, our computations at the B3LYP/cc-pVTZ//CCSD(T)/CBS level of theory revealed that the overall reactions via atomic hydrogen loss and/or methyl loss are highly endoergic by 92 kJ mol⁻¹ for ethylene, 51–103 kJ mol⁻¹ for propene, and 50–115 kJ mol⁻¹ for butenes (Supporting Information). Consequently, on the basis of these considerations and the lack of any reactive scattering product in the silyldiyne–alkene systems, we can conclude that silyldiyne radicals do not react with alkenes under single collision conditions.

6. CONCLUSIONS

Crossed molecular beam experiments and electronic structure calculations were exploited to investigate the chemical dynamics for the reaction of the silyldiyne radical (SiH; X²Π) with dimethylacetylene (CH₃CCCH₃; X¹A_{1g}). The reaction was found to involve indirect dynamics and is initiated by the barrierless addition of silyldiyne to both carbon atoms of dimethylacetylene leading to a cyclic collision complex 2,3-dimethyl-1-silacyclopropenyl, which later proceeds through atomic hydrogen loss from the silicon atom via a loose exit transition state forming the 2,3-dimethyl-1-silacycloprop-2-enylidene molecule in an overall exoergic reaction (experimentally, -29 ± 21 kJ mol⁻¹; computationally, -10 ± 8 kJ mol⁻¹). A comparison of these dynamics with those of the silyldiyne–acetylene and silyldiyne–methylacetylene systems proposes that for these alkynes, the silyldiyne radical adds without entrance barrier to one or to both carbon atoms of the acetylene moiety of the alkyne forming an acyclic doublet radical intermediate or a cyclic collision complex, which can also be accessed via cyclization of the acyclic intermediates. The cyclic intermediate represents the key decomposing complex, which is predicted to fragment through hydrogen loss almost perpendicularly to the rotational plane of the decomposing complex from the silyldiyne moiety via a loose exit transition state in overall weakly exoergic reactions to ((di)methyl-substituted) 1-silacycloprop-2-enylidenes. The reaction dynamics of the silyldiyne radicals with C2 to C4 alkynes are quite distinct from the reactions with the corresponding alkanes and alkenes, which do not react with the silyldiyne radical under our experimental conditions. Here, the processes for alkanes have significant entrance barriers to insertion into carbon–hydrogen bonds ranging from 94 kJ mol⁻¹ (methane) to 70 kJ mol⁻¹ (butanes). In the case of alkenes, despite the barrierless additions to the carbon–carbon double bond of alkenes, the overall reactions are highly endoergic (50–115 kJ mol⁻¹ for C2 to C4 alkenes). However, molecules carrying carbon–carbon double bonds could “open up” their reactivity, if the carbon–carbon double bond is either consecutive such as in allene (H₂CCCH₂) or in conjugation with a second carbon–carbon double bond (conjugated dienes) as found in 1,3-butadiene (H₂CCHCHCH₂). As a matter of fact, crossed beam reactions of the silyldiyne radical with allene and 1,3-butadiene revealed the formation of two cyclic molecules via indirect scattering dynamics and atomic hydrogen loss in overall exoergic reactions: 2-methyl-1-silacycloprop-2-enylidene (c-SiC₃H₄)¹² and 1-silacyclopenta-2,4-diene (silole; c-SiC₄H₆)¹³ respectively. Therefore, the present study concludes the combined experimental and computational investigations on the reactions

of the silyldiyne radical with C1 to C4 hydrocarbons (alkanes, alkenes, alkynes) along with allene and conjugated dienes such as 1,3-butadiene.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b06995.

Table S1, optimized Cartesian coordinates (Å), rotational constants (GHz), and vibrational frequencies (cm⁻¹) of intermediates, transition states, and dissociation products for the silyldiyne with dimethylacetylene reaction on the adiabatic doublet ground state potential energy surface of SiC₄H₇; Table S2, calculated energies of intermediates, transition states, and dissociation products; Table S3, formation energies and entrance barriers of silyldiyne with C1–C4 alkanes; Table S4, reaction energies of silyldiyne with C2–C4 alkenes; Figure S1, potential energy surface for the reaction of silyldiyne with dimethylacetylene (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*Ralf I. Kaiser. E-mail: ralfk@hawaii.edu. Phone: +1-808-956-5731.

*Agnes H. H. Chang. E-mail: hhchang@mail.ndhu.edu.tw. Phone: +886-03-863-3596.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation (NSF) for support under award CHE-1360658. Computer resources at the National Center for High-performance Computer of Taiwan were utilized in the calculations.

■ REFERENCES

- Balucani, N.; Asvany, O.; Chang, A.; Lin, S.; Lee, Y.; Kaiser, R.; Bettinger, H.; Schleyer, P. v. R.; Schaefer, H., III Crossed Beam Reaction of Cyano Radicals with Hydrocarbon Molecules. II. Chemical Dynamics of 1-Cyano-1-methylallene (CNCH₃CCCH₃; X¹A₁) Formation from Reaction of CN (X²Σ⁺) with Dimethylacetylene CH₃CCCH₃ (X¹A₁). *J. Chem. Phys.* **1999**, *111*, 7472–7479.
- Kaiser, R. I.; Balucani, N. The Formation of Nitriles in Hydrocarbon-rich Atmospheres of Planets and Their Satellites: Laboratory Investigations by the Crossed Molecular Beam Technique. *Acc. Chem. Res.* **2001**, *34*, 699–706.
- Kaiser, R. I.; Maity, S.; Dangi, B. B.; Su, Y.-S.; Sun, B.-J.; Chang, A. H. H. A Crossed Molecular Beam and ab initio Investigation of the Exclusive Methyl Loss Pathway in the Gas Phase Reaction of Boron Monoxide (BO; X²Σ⁺) with Dimethylacetylene (CH₃CCCH₃; X¹A_{1g}). *Phys. Chem. Chem. Phys.* **2014**, *16*, 989–997.
- Huang, L.; Lee, H.; Mebel, A.; Lin, S.; Lee, Y.; Kaiser, R. A Combined Crossed Beam and ab initio Investigation on the Reaction of Carbon Species with C₄H₆ Isomers. II. The Dimethylacetylene Molecule, H₃CCCCH₃ (X¹A_{1g}). *J. Chem. Phys.* **2000**, *113*, 9637–9648.
- Kaiser, R. I.; Mebel, A. M. The Reactivity of Ground-State Carbon Atoms with Unsaturated Hydrocarbons in Combustion Flames and in the Interstellar Medium. *Int. Rev. Phys. Chem.* **2002**, *21*, 307–356.
- Kaiser, R. I. Experimental Investigation on the Formation of Carbon-bearing Molecules in the Interstellar Medium via Neutral-neutral Reactions. *Chem. Rev.* **2002**, *102*, 1309–1358.

- (7) Parker, D. S.; Maity, S.; Dangi, B. B.; Kaiser, R. I.; Landera, A.; Mebel, A. M. Understanding the Chemical Dynamics of the Reactions of Dicarbon with 1-Butyne, 2-Butyne, and 1, 2-Butadiene – Toward the Formation of Resonantly Stabilized Free Radicals. *Phys. Chem. Chem. Phys.* **2014**, *16*, 12150–12163.
- (8) Sillars, D.; Kaiser, R.; Galland, N.; Hannachi, Y. Crossed-Beam Reaction of Boron Atoms, B (2P_j), with Dimethylacetylene, CH_3CCCH_3 (X^1A_1): Untangling the Reaction Dynamics to Form the 1,2-Dimethylene-3-bora-cyclopropane Molecule. *J. Phys. Chem. A* **2003**, *107*, 5149–5156.
- (9) Balucani, N.; Zhang, F.; Kaiser, R. I. Elementary Reactions of Boron Atoms with Hydrocarbons - Toward the Formation of Organo-Boron Compounds. *Chem. Rev.* **2010**, *110*, 5107–5127.
- (10) Parker, D. S.; Wilson, A. V.; Kaiser, R. I.; Mayhall, N. J.; Head-Gordon, M.; Tielens, A. G. On the Formation of Silacyclopropenylidene ($c\text{-SiC}_2\text{H}_2$) and its Role in the Organosilicon Chemistry in the Interstellar Medium. *Astrophys. J.* **2013**, *770*, 33.
- (11) Yang, T.; Dangi, B. B.; Kaiser, R. I.; Bertels, L. W.; Head-Gordon, M. A Combined Experimental and Theoretical Study on the Formation of the 2-Methyl-1-silacycloprop-2-enylidene Molecule via the Crossed Beam Reactions of the Silyliidyne Radical (SiH ; $X^2\Pi$) with Methylacetylene (CH_3CCH ; X^1A_1) and D4-Methylacetylene (CD_3CCD ; X^1A_1). *J. Phys. Chem. A* **2016**, *120*, 4872–4883.
- (12) Yang, T.; Dangi, B. B.; Maksyutenko, P.; Kaiser, R. I.; Bertels, L. W.; Head-Gordon, M. Combined Experimental and Theoretical Study on the Formation of the Elusive 2-Methyl-1-silacycloprop-2-enylidene Molecule under Single Collision Conditions via Reactions of the Silyliidyne Radical (SiH ; $X^2\Pi$) with Allene (H_2CCCH_2 ; X^1A_1) and D4-Allene (D_2CCCD ; X^1A_1). *J. Phys. Chem. A* **2015**, *119*, 12562–12578.
- (13) Yang, T.; Dangi, B. B.; Thomas, A. M.; Sun, B. J.; Chou, T. J.; Chang, A. H.; Kaiser, R. I. Gas-Phase Synthesis of 1-Silacyclopenta-2,4-diene. *Angew. Chem., Int. Ed.* **2016**, *55*, 7983–7987.
- (14) Gu, X.; Kaiser, R. I. Reaction Dynamics of Phenyl Radicals in Extreme Environments: A Crossed Molecular Beam Study. *Acc. Chem. Res.* **2009**, *42*, 290–302.
- (15) Guo, Y.; Gu, X.; Kawamura, E.; Kaiser, R. I. Design of a Modular and Versatile Interlock System for Ultrahigh Vacuum Machines: A Crossed Molecular Beam Setup as a Case Study. *Rev. Sci. Instrum.* **2006**, *77*, 034701.
- (16) 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.
- (17) Kaiser, R. I.; Maksyutenko, P.; Ennis, C.; Zhang, F.; Gu, X.; Krishtal, S. P.; Mebel, A. M.; Kostko, O.; Ahmed, M. Untangling the Chemical Evolution of Titan's Atmosphere and Surface – From Homogeneous to Heterogeneous Chemistry. *Faraday Discuss.* **2010**, *147*, 429–478.
- (18) Balucani, N.; Asvany, O.; Kaiser, R.-I.; Osamura, Y. Formation of Three $\text{C}_4\text{H}_3\text{N}$ Isomers from the Reaction of CN ($X^2\Sigma^+$) with Allene, H_2CCCH_2 (X^1A_1), and Methylacetylene, CH_3CCH (X^1A_1): A Combined Crossed Beam and Ab Initio Study. *J. Phys. Chem. A* **2002**, *106*, 4301–4311.
- (19) Balucani, N.; Mebel, A. M.; Lee, Y. T.; Kaiser, R. I. A Combined Crossed Molecular Beam and Ab Initio Study of the Reactions $\text{C}_2(X^1\Sigma_g^+, a^3\Pi_u) + \text{C}_2\text{H}_4 \rightarrow n\text{-C}_4\text{H}_3(X^2A') + \text{H}(^2S_{1/2})$. *J. Phys. Chem. A* **2001**, *105*, 9813–9818.
- (20) Kaiser, R.; Chiong, C.; Asvany, O.; Lee, Y.; Stahl, F.; Schleyer, P. v. R.; Schaefer, H., III. Chemical Dynamics of D1-methyldiacetylene (CH_3CCCCD ; X^1A_1) and D1-ethynylallene (H_2CCCH (C_2D); X^1A') Formation from Reaction of C_2D ($X^2\Sigma^+$) with Methylacetylene, CH_3CCH (X^1A_1). *J. Chem. Phys.* **2001**, *114*, 3488–3496.
- (21) Kaiser, R. I.; Ting, J. W.; Huang, L. C. L.; Balucani, N.; Asvany, O.; Lee, Y. T.; Chan, H.; Stranges, D.; Gee, D. A Versatile Source to Produce High-Intensity, Pulsed Supersonic Radical Beams for Crossed-Beam Experiments: The Cyanogen Radical CN ($X^2\Sigma^+$) as a Case Study. *Rev. Sci. Instrum.* **1999**, *70*, 4185–4191.
- (22) Vernon, M. F. *Molecular Beam Scattering*; University of California at Berkeley: Berkeley, CA, 1983.
- (23) Weiss, P. S. *The Reaction Dynamics of Electronically Excited Alkali Atoms with Simple Molecules*; University of California at Berkeley: Berkeley, CA, 1986.
- (24) Levine, R. D.; Bernstein, R. B.; Lee, Y. T. Molecular Reaction Dynamics and Chemical Reactivity. *Phys. Today* **1988**, *41*, 90.
- (25) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (26) Becke, A. D. Density-functional Thermochemistry. I. The Effect of the Exchange-Only Gradient Correction. *J. Chem. Phys.* **1992**, *96*, 2155–2160.
- (27) Becke, A. D. Density-functional Thermochemistry. II. The Effect of the Perdew-Wang Generalized-Gradient Correlation Correction. *J. Chem. Phys.* **1992**, *97*, 9173–9177.
- (28) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.
- (29) Purvis, G. D., III; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.
- (30) Hampel, C.; Peterson, K. A.; Werner, H.-J. A Comparison of the Efficiency and Accuracy of the Quadratic Configuration Interaction (QCISD), Coupled Cluster (CCSD), and Brueckner Coupled Cluster (BCCD) Methods. *Chem. Phys. Lett.* **1992**, *190*, 1–12.
- (31) Knowles, P. J.; Hampel, C.; Werner, H.-J. Coupled Cluster Theory for High Spin, Open Shell Reference Wave Functions. *J. Chem. Phys.* **1993**, *99*, 5219–5227.
- (32) Deegan, M. J.; Knowles, P. J. Perturbative Corrections to Account for Triple Excitations in Closed and Open Shell Coupled Cluster Theories. *Chem. Phys. Lett.* **1994**, *227*, 321–326.
- (33) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr Benchmark Calculations with Correlated Molecular Wave Functions. IV. The Classical Barrier Height of the $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ Reaction. *J. Chem. Phys.* **1994**, *100*, 7410–7415.
- (34) Peterson, K. A.; Dunning, T. H., Jr Intrinsic Errors in Several *ab initio* Methods: The Dissociation Energy of N_2 . *J. Phys. Chem.* **1995**, *99*, 3898–3901.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. *Gaussian 09*, Revision D.01; Gaussian: Wallingford, CT, U.S.A., 2009.
- (36) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, U.K., 2005.
- (37) Herschbach, D. R. Reactive Collisions in Crossed Molecular Beams. *Discuss. Faraday Soc.* **1962**, *33*, 149–161.
- (38) Kaiser, R.; Parker, D.; Zhang, F.; Landera, A.; Kislov, V.; Mebel, A. PAH Formation under Single Collision Conditions: Reaction of Phenyl Radical and 1, 3-Butadiene to Form 1, 4-Dihydronaphthalene. *J. Phys. Chem. A* **2012**, *116*, 4248–4258.
- (39) Yang, T.; Dangi, B. B.; Thomas, A. M.; Kaiser, R. I. Untangling the Reaction Dynamics of the Silyliidyne Radical (SiH ; $X^2\Pi$) with Acetylene (C_2H_2 ; $X^1\Sigma_g^+$). *Chem. Phys. Lett.* **2016**, *654*, 58–62.