**Gas Phase Synthesis of the Elusive Trisilacyclopropyl Radical (Si3H5) via Unimolecular Decomposition of Che­mi­cally Activated Doublet Trisilapropyl Radicals (Si3H7)**

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ABSTRACT: The gas phase reaction of the simplest silicon-bearing radical silylidyne (SiH; X2Π) with disilane (Si2H6; X1A1g) was investigated in a crossed molecular beams machine. Combined with electronic structure calculations, our data reveal the synthesis of the previously elusive trisilacyclopropyl radical (Si3H5) – the isovalent counterpart of the cyclopropyl radical (C3H5) - along with molecular hydrogen via indirect scattering dynamics through long-lived, acyclic trisilapropyl (i-Si3H7) colli­sion complex(es). Possibly hydrogen-atom roaming on the doublet surface proceeds to molecular hydrogen loss accompanied by ring closure. The chemi­cal dy­na­mics are quite distinct from the isovalent methylidyne (CH) – etha­ne (C2H6) re­ac­tion, which leads to propylene (C3H6) plus atomic hydrogen, but not to cyclopropyl (C3H5) radical plus molecular hydrogen. The identification of the trisilacyclopropyl radical (Si3H5) opens up preparative pathways for an unusual gas phase chemistry of previously inaccessible ring-strained (inorgano)silicon mo­le­cules as a result of single collision events.

**TOC GRAPHICS**



**KEYWORDS:**  Reaction Dynamics; Molecular Beams; Mass Spectrometry; Silanes; Single Collision Conditions; Isoelectronicity; Reactive Intermediates.

For more than a century, Langmuir’s conception of isoelectronicity has be­en influential in as­cer­taining modern perceptions of chemical bonding and molecular structure with particular at­ten­tion dedicated to elucidating the similarities and disparities of the chemistries of carbon and sili­­con along with the methylidyne (CH) and silylidyne (SiH) radicals [1](#_ENREF_1), [2](#_ENREF_2). Main group 14, elements carbon and silicon are in isovalency with four valance electrons each. How­ever, the distinct chemical bonding features of carbon and silicon are evi­dent when com­­paring the SiC2H2 and C3H2 potential energy surfaces and the cyclo­propy­ne (c-C2CH2) and sila­cyclo­propyne (c-C2SiH2) isomers in particular (Scheme 1) [3-5](#_ENREF_3). Singlet cyclo­pro­pyne **I** re­pre­­se­nts a transition state[5](#_ENREF_5), while sila­cyclo­pro­pyne **II** has been found to be a true local mini­mum[3](#_ENREF_3). Con­se­quently, the re­pla­cement of a single carbon by an isovalent silicon atom may lead to novel mo­le­cules, whose car­bon-ana­log counterparts do not exist. Thus (organo)silicon molecules are ex­ploi­ted as be­nch­marks to understand the resemblances, but also distinctions in the chemical bon­ding and molecular structures compared to their iso­va­lent hy­dro­­­carbon counter­parts[6](#_ENREF_6), [7](#_ENREF_7).

**Scheme 1.** Lewis structures of cyclopropyne (c-C2CH2) and silacyclopropyne (c-C2SiH2). I represents a transition state.



   Whereas the chemistries and molecular structures of organosilicon molecules carrying a single silicon atom such as the SiC2Hn (n = 2-8) families has been explored extensively[3](#_ENREF_3), [8-12](#_ENREF_8), higher homologues in this series, in which *all* carbon atoms are substituted by silicon, are scarce[6](#_ENREF_6), [7](#_ENREF_7), [13-16](#_ENREF_13). This is in particular true for the isovalent C3H5 and Si3H5 systems. The resonantly stabi­li­zed, C2v symmetric allyl radical (**III**) represents the global minimum on the C3H5 surface with the 1-propenyl (**IV**), 2-propenyl (**V**), and cyclo­propyl radicals (**VI**) being higher in energy by 50 to 135 kJmol-1 (Scheme 2) [17](#_ENREF_17). The lack of success in isolating *any* free Si3H5 radical exposes the complication of silicon to form silicon-silicon double bonds due to the size of the silicon atom that limits an atomic p orbital from appro­aching suf­fi­ciently close to a second silicon atom to form a π bond. However, electronic structure calcu­lations suggest that the Si3H5 isomer trisilacyclo­propyl (**VII**) and trisilaallyl (**VIII**) should be kinetically stable with **VII** predicted to be energetically favorable by 45 to 70 kJmol-1 (Sche­me 3) [18](#_ENREF_18), [19](#_ENREF_19). Trisilacyclo­propyl (**VII**) belongs to the Cs point group and has a 2A′ electronic ground state. Whereas the allyl radical (**III**) holds a C2v symmetric structure with all atoms within the plane of symmetry, the C2v symmetric trisilaallyl (**IX**) was predicted to have two imaginary frequencies. Instead, trisila­allyl (**VIII**) favors a Cs symmetric energy minimum and a 2A′′ electronic ground state with both terminal SiH2 groups being out-of-plane and highly pyramidal. Frenking et al. re-analyzed the chemical bonding and proposed the cyclic form (**VII**) to be lower in energy than **VIII** since a stronger σ-bonding in **VII** overcompensates the higher Pauli repulsion[20](#_ENREF_20). These considerations highlight the striking differences in the molecular structure and bon­ding of carbon versus silicon (Schemes 2 and 3) thus highlight the necessary to prepare high­er silicon hy­drides to gain insights into resemblances and distinctions in che­mi­cal bon­ding of carbon versus silicon. This comparison is fundamental to our un­der­standing of chemistry and will affect how we think about the chemi­cal structure of (inorgano)silicon molecules in the future, whose chemical bonding is anticipated to be quite dis­tinct from those of the iso­va­le­nt carbon counterparts.

**Scheme 2.** Structures of C3H5 isomers (III - VI). Point groups and relative energies (kJ mol-1) with respect to the individual most stable isomer are also given.



**Scheme 3.** Structures of Si3H5 isomers (VII - IX). Point groups and relative energies (kJ mol-1) with respect to the individual most stable isomer are also given.



    Here, we reveal the results of reaction of ground state silylidyne radicals (SiH; X2Π) with disilane (Si2H6; X1A1g) under single collision conditions to prepare for the very first time the previously elusive trisilacyclopropyl radical (Si3H5) in the gas phase. Contemplated by electronic structure calculations, these findings untangle - through the unimolecular decomposition of chemically activated trisilapropyl radical intermediates (Si3H7) - an exotic silicon chemistry and uncon­ven­ti­o­nal chemical dynamics of silylidyne radicals with disilane, which are fundamentally distinct compared to the iso­valent carbon-based C3H5 system.

     Reactive scattering signal was collected at mass-to-charge ratios (*m/z*) of 91 to 89, very weak ion counts at a level of 10 ± 6 % was detected at m/z = 91 and 90 compared to a strong scattering signal at m/z = 89. Considering the natural abun­dan­ces of silicon (30Si (3.10 %), 29Si (4.67 %), 28Si (92.23 %)), this finding suggests the formation of 28Si3H5 (89 amu) along with molecular hydro­gen (H2, 2 amu); signals at m/z = 91 and 90 originate from 30Si28Si2H5+ and 29Si28Si2H5+ (Figure 1). Therefore, the laboratory data alone provide compelling evidence on the formation of a reaction products with chemical formula Si3H5 plus molecular hydrogen in the reaction of ground state silyli­dyne radicals with disilane, whereas the atomic hydrogen loss and inherent synthesis of Si3H6 isomer(s) is likely closed under our experimental conditions. The laboratory angular distribution obtained at *m/z* = 89 (28Si3H5+) is nearly forward-backward symmetric around the center-of-mass (CM) angle of 42.4° ± 0.6° and spread over 30°(Figure 1). These results propose indirect scattering dynamics involving Si3H7 intermediate(s).



**Figure 1.** Laboratory angular distribution (A) and time-of-flight spectra (B) recorded at a mass-to-charge ratio 89 (Si3H5+) in the reaction of the ground state silylidyne radical with disilane. The circles define the experi­men­tal data and the red lines represent the fitting based on the best-fit center-of-mass functions as depicted in Figure 2. Here CM arrow indicates the center-of-mass angle.

     The ultimate goal of our study is not only to determine the chemical formula of the reaction product (Si3H5), but also to expose the product isomer(s) and the underlying reaction mechanism(s). To gain insight into the reaction dynamics the laboratory data (TOF spectra, laboratory angular distribu­tion) transformed into the CM reference frame by employing forward-convolution routine[21-24](#_ENREF_21) with the product mass combination 89 amu (28Si3H5) plus 2 amu (H2) which yields the transla­tional energy flux distribution *P(ET)* and the angular flux distribution *T(θ)* (Figure 2). The translational energy flux distribution, *P(ET)*, discloses a maximum trans­lational energy (*Emax*) of 104 ± 18 kJ mol-1 which is sum ofcollision energy and the reaction energy. Consequently, by sub­tracting the collision energy from *Emax*, the reaction energy to form Si3H5 along with molecular hydrogen is - 68 ± 18 kJ mol-1. Additionally, the *P(ET)* reveals a distribution maximum away from zero translational energy sug­gesting a tight exit transition state to decom­po­sition via molecular hydrogen elimi­nation[25](#_ENREF_25). Further, the CM angular flux distribution *T(θ)* has forward-backward symmetric distribution and non-zero intensity from 0° to 180° suggests that reaction proceeds through long lived decomposing complex(es).[26](#_ENREF_26), [27](#_ENREF_27)



**Figure 2.** Center-of-mass translational energy flux distribution (A) and angular distribution (B) lead­ing to the formation of the Si3H5 molecules plus molecular hydrogen in the reac­ti­on of ground state silylidyne radical with disilane. Shaded areas indicate the ac­cept­able upper and lower error limits of the fits. The red solid lines define the best-fit functions.

     Conceivable Si3H5 isomer(s) accessed via the elementary gas phase reaction of ground state silylidy­ne radicals with disilane can be discovered by comparing the experi­men­tally determined reaction energy (-68 ± 18 kJ mol-1) with the reaction energies obtained from our electronic structure calculations for distinct Si3H5 isomers (Figure 3; Theoretical Methods; Supporting In­for­­mation). Among the 27 Si3H5 isomers, the reaction energy to prepare the thermodynamically most stable isomer – the trisilacyclopropyl radical (Si3H5) (**2p1**) – along with molecular hydrogen of -60 ± 4 kJ mol-1 agrees well with the experimentally derived reaction energy. Therefore, we can conclude that at least the trisilacyclopropyl radical (Si3H5) represents a product of bimolecular reactions of the silylidy­ne radical with disilane. Considering our collision energy of 36.0 ± 0.5 kJ mol-1, the Si3H5 isomers **2p2** to **2p19** might also contribute to the reactive scattering signal, and their presence could be masked by the low energy section of the center-of-mass translational energy distribution (Figure 2). Note that for completeness, we also explored the energetics of the atomic hydrogen loss leading to 20 Si3H6 isomers (Figure 4). Even the formation of the thermodynamically most stable trisilacyclopropane isomer (**1p1**) is endoergic by 30 kJ mol-1. We attempted to fit the laboratory data also with a hydrogen loss channel leading to trisilacyclopropane (**1p1**), but the resulting TOFs are too slow and the simulated laboratory angular distribution is too narrow. Therefore - if formed at all - trisilacyclopropane (**1p1**) would represent only a minor fraction of the products. Consequently, in the bimolecular reaction of silylidyne radicals with disilane, at least the trisilacyclopropyl radical (Si3H5) (**2p1**) is formed via molecular hydrogen loss on the doublet surface.



**Figure 3.** B3LYP/cc-pVTZ computed structures of doublet Si3H5 isomers along with their point groups and symmetries of the electronic wave functions. The CCSD(T)/CBS[28](#_ENREF_28)//B3LYP/cc-pVTZ relative energies of products are given in kJ mol−1 with respect to the energies of the separated reactants. The CCSD(T)-F12/CBS//B3LYP/cc-pVTZ energies of p1 and p7 are in parentheses.



**Figure 4.** B3LYP/cc-pVTZ computed structures of singlet Si3H6 isomers along with their point groups and symmetries of the electronic wave functions. The CCSD(T)/CBS[28](#_ENREF_28)//B3LYP/cc-pVTZ relative energies of the products are given in kJ mol−1 with respect to the energies of the separated reactants.

     What are the underlying reaction mechanisms leading to trisilacyclopropyl radical (Si3H5) (**2p1**)? Our computations suggest that the reaction commences with a barrierless approach of silylidyne (SiH) to a silicon-hydrogen bond of disilane (Si2H6) to form intermediate **i0** residing 57 kJ mol-1 below the energy of the separated reactants (Figure 5). This intermediate features one hydrogen atom of the attacked disilane molecule moving to a bridging position between two silicon atoms with the Si-H distances in the bridge being 166 and 167 pm; these distances are longer than a regular Si-H bonds of 148 - 149 pm. The Si-Si bond distance in the Si-H-Si bridge is 261 pm is also longer than that in a regular single Si-Si bond of typically 236 pm. **i0** isomerizes to the *n*-trisilapropyl radical intermediate (SiH3SiH2SiH2) **i1** via a barrier of 26 kJ mol-1. During this isomerization, the bridging hydrogen atom shifts to the silicon atom of the former silylidyne reactant, and the formation of the single Si-Si bond is completed. The transition state for this process is very peculiar as it features two symmetric hydrogen atoms bridging the forming Si-Si bond. Intrinsic reaction coordinate (IRC) calculations in the reverse direction bring the system to an inflection point representing another symmetric transition state with two bridging hydrogen atoms reflected by the symmetry plane but with a sharpened HSiH angle in the bridge. IRC calculations from this new transition state/inflection point lead to two different enantiomers of **i0** with one of the two distinct hydrogens staying in the bridging position. Inter­mediate **i1** resides in a deep potential energy well of 183 kJ mol-1 relative to the separated reactants and may rearrange to the *i*-trisilapropyl radical (SiH3SiHSiH3) **i2** via a 1,2-H migration overcoming a 141 kJ mol-1 barrier. The molecular hydrogen elimination process from **i1** to the trisilacyclopropyl radical (Si3H5) (**2p1**) can proceed via two different mechanisms. In the conventional mechanism, the molecular hydrogen emission takes place from the SiH3 moiety. At the first step, two Si-H bonds elongate, and a new H-H bond forms in intermediate **i3**, which represents a complex of SiHSiH2SiH2 with the molecular hydrogen having a stretched H-H bond coordinated to the SiH group. Complex **i3** then decomposes with the hydrogen molecule leaving and a new Si-Si bond formed leading to the trisilacyclopropyl radical (Si3H5) (**2p1**). The relative energies of the transition state connecting **i1** and **i3** as well as **i3** and **2p1** calculated at the CCSD(T)-F12/CBS/B3LYP/cc-pVTZ level of theory are 32 and 34 kJ mol-1, respectively. In addition to this conventional H2 elimination pathway, an alternative hydrogen atom roaming pathway was also found. As illustrated in Figure S1 in the SI, in the roaming pathway, a hydrogen atom is nearly eliminated from **i1** to form a trisilacyclocyclopropane (Si3H6) product (**1p1**), but then comes back to abstract another hydrogen atom from a SiH2 group to produce the trisilacyclopropyl radical (Si3H5) (**2p1**). The roaming transition state between **i1** and **2p1** is located at 34 kJ mol-1 above the energy of the separated reactants at the CCSD(T)-F12/CBS/B3LYP/cc-pVTZ level and hence is competitive with the conventional molecular hydrogen loss via intermediate **i3**. For completeness, it shall be mentioned that the dissociation channel of the intermediate **i2** include a hydrogen atom loss from one of the SiH3 groups forming trisilapropene (**1p2**) without an exit barrier. Molecular hydrogen loss from intermediate **i2** via a roaming transition state 82 kJ mol-1 above the reactants leads to trisilaallyl (**2p7**). Considering our collision energy of 36 kJ mol-1, neither **1p2** nor **2p7** is energe­tica­lly accessible. According to these computations, the pathways from **i1** to the trisilacyclo­propyl radical (Si3H5) (**2p1**) are preferred. Noteworthy, our preliminary calculations indicate that there exist other reaction pathways to **2p7** that are lower in energy than the roaming channel shown in Figure 5. Since these pathways are not directly relevant to the formation of **2p1** observed experimentally, they will be reviewed in a future more detailed publication.



**Figure 5.** Potential energy diagram of the silylidyne – disilane system leading to the trisilacyclopropyl radical (Si3H5) calculated at the CCSD(T)-F12/CBS//B3LYP/cc-pVTZ level of theory. Relative energies are given in kJ mol-1 with respect to the reactants. For the critical transition states ts: i1→2p1, ts: i1→i3, and ts: i3→2p1, bold numbers show refined relative energies evaluated taking into account core electronic correlation, anharmonicity, and B2PLYPD3 geometry (ts: i1→i3 and ts: i3→2p1) corrections (top**).** Geometries of the critical transition states ts: i1→2p1, ts: i1→i3, and ts: i3→2p1 optimized at the B3LYP/cc-pVTZ, B2PLYPD3/cc-pVTZ (italic numbers), and CCSD/cc-pVTZ (bold numbers) levels of theory. Relative energies of the transition states with respect to the reactants are given in kJ mol-1 as calculated at the CCSD(T)-F12/CBS//B3LYP/cc-pVTZ + ZPE(B3LYP/cc-pVTZ), CCSD(T)-F12/CBS//B2PLYPD3/cc-pVTZ + ZPE(B2PLYPD3/cc-pVTZ) (italic), CCSD(T)-F12/CBS//CCSD/cc-pVTZ + ZPE(B3LYP/cc-pVTZ) (ts: i1→2p1) or CCSD(T)-F12/CBS//CCSD/cc-pVTZ + ZPE(B2PLYPD3/cc-pVTZ) (ts: i1→i3 and ts: i3→2p1) (bold) levels of theory, not including core electronic correlation and anharmonicity corrections (bottom).

     The transition states for the molecular hydrogen loss channel connecting **i1** and **i3**, **i3** and **2p1**, and **i1** and **2p1** at the CCSD(T)-F12/CBS//B3LYP/cc-pVTZ level have energies slightly below the collision energy of 36 kJ mol-1 of the experiment. We then explored the influence of the level of theory on the energies of the critical transition states. Let us first consider the effect of the theoretical method for geometry optimization (Figure 5). The use of the B2PLYPD3 and CCSD levels for **i1** → **2p1** results in a significant shortening of the forming H-H bond from 167 pm to 140 pm and 128 pm and slight elongation of the breaking Si-H bond from 150 to 153 and 155 pm, whereas the remaining geometric parameters remain essentially the same. These changes result in the increase of the single-point relative energy of the for **i1** → **2p1** transition state computed at the CCSD(T)-F12 level from 34 to 37 and 40 kJ mol-1. The geometric changes are also significant in **i1** → **i3** where, in going from B3LYP to B2PLYPD3 the breaking Si-H bonds noticeably shorten, while the forming H-H bond strongly elongates. Here, the B2PLYPD3 and CCSD optimized geometries are very similar. In the meantime, the CCSD(T)-F12/CBS single-point energy changes very slightly, from 32 kJ mol-1 with the B3LYP optimized geometry to 31 and 31 kJ mol-1 with the B2PLYPD3 and CCSD geometries, respectively. For **i3** → **2p1**, the B3LYP and B2PLYPD3 geometries are similar, whereas the CCSD structure features somewhat longer Si-H distances toward the leaving hydrogen molecule. The relative CCSD(T)-F12/CBS single-point energies with the three different geometries are very close, within 0.5 kJ mol-1 from one another. Taking the geometries which give the lowest CCSD(T)-F12/CBS energies of the transition states, we considered further corrections to the CCSD(T)-F12/CBS//B3LYP/cc-pVTZ energy of the roaming **i1** → **2p1** and to the CCSD(T)-F12/CBS//B2PLYPD3/cc-pVTZ energies of **i1** → **i3** and **i3** → **2p1**. The core correlation correction is insignificant for **i1** → **2p1** (+0.03 kJ mol-1), but decreases the relative energies of **i1** → **i3** and **i3** → **2p1** by 1.4 and 0.8 kJ mol-1, respectively. The anharmonic ZPE corrections are calculated to be -1.8, -1.0, -2.4, and -3.6 kJ mol-1 for silylidyne plus disilane, **i1** → **2p1**, **i1** → **i3**, and **i3** → **2p1**, respectively leading to the increase of the relative energy of **i1** → **2p1** by 0.8 kJ mol-1 and the reduction of the relative energies of **i1** → **i3** and **i3** → **2p1** by 0.6 and 1.8 kJ mol-1. Incorporating all the corrections, for core electronic correlation, anharmonicity, and B2PLYPD3 geometry, we obtain the relative energies of **i1** → **2p1**, **i1** → **i3**, and **i3** → **2p1** as 35, 29, and 31 kJ mol-1, respectively. These results indicate that the conventional molecular hydrogen loss pathway via the intermediate **i3** is certainly feasible under the current experimental conditions, whereas the roaming pathway has a slightly higher required energy but still below the experimental collision energy and hence may contribute, especially considering the possibility of hydrogen atom tunneling. Considering the complexity of this system, a presentation of a complete surface along with the search for transition states is beyond the scope of this *Letter*, but will be conducted in the future. A more detailed analysis of various dissociation pathways leading to a variety of Si3H5 isomers would allow evaluating their relative yields if the reaction follows statistical behavior.

To conclude, the bimolecular gas phase reaction of ground state silylidyne radicals (SiH; X2Π) with disilane (Si2H6; X1A1g) depicted indirect scattering dynamics via Si3H7 colli­sion complex(es) along with the formation the previously elusive trisilacyclopropyl radical (Si3H5; X2A′) in an overall exoergic reaction (experimental: -68 ± 18 kJ mol-1; computational: -60 ± 4 kJ mol-1). The (roaming mediated) reaction dynamics involve the formation of two key intermediates **i0** and **i1** (n-trisilapropyl) – on the doublet surface; the endoergic atomic hydrogen loss chan­nels are not open. In strong contrast, the isovalent methylidyne (CH) – ethane (C2H6) system so­lely leads to propylene (C3H6; X1A′) plus *atomic* hydrogen, whereas the *molecular* hydrogen loss to the allyl radical (C3H5; X2A2) and/or the cyclopropyl radical (C3H5; X2A′) are closed. On the Si3H5 potential energy surface, the Cs symmetric trisilacyclopropyl radical is the most stable isomer which is in contrast with its carbon analog where the C2v symmetric allyl radical **(III)** is the global energy minimum. The stability between the cyclic and allyl radical of Si3H5 and C3H5 dictated by σ-bonding and Pauli repulsion. The trisilacyclopropyl radical has bond length of 232 pm for two equivalent H2Si-SiH bonds, 242 pm for the H2Si-SiH2 bond, these are about 87-90 pm longer than Cs symmetric cyclopropyl radical. The dominating σ-bonding prevailing over Pauli repulsion stabilizes the trisilacyclopropyl radical, whereas in its carbon analog a stronger Pauli repulsion due to shorter bonds decreases its stability [20](#_ENREF_20). Therefore, the classical isovalency of the silicon atom and carbon envisages an improper reactivity in this system. This discovery ultimately effects our perception on the chemical reactivity of silicon-based systems and on the thermochemistry, chemical bonding, and reaction mechanism classifying the silylidyne – disilane system as a significant benchmark to a better understanding of the formation of small (inorgano)silicon molecules in the gas phase under single collision conditions. This contrast of the distinct chemistries of carbon and silicon is fundamental to our understanding of reactivities of silicon and will influence how we explain chemical bonding involving silicon and how we anticipate chemical structure and reactivity in the future.

**Experimental Methods**

The elementary reaction of ground state silylidyne radicals (SiH, X2Π) with disilane (Si2H6; X1A1g) was explored in a universal crossed molecular beams machine [29](#_ENREF_29). A pulsed beam of helium seeded silylidyne radicals was produced *in situ* by pho­to­dissociation of disilane at 193 nm at 60 Hz in the primary source chamber. The pulsed beam of the silylidyne radicals passed through a skimmer and a four-slit chopper wheel rotating at 120 Hz; the chopper wheel chose a pulse of the silylidyne radical beam with a well-defined peak velocity (vp) and speed ratio (S) of 1756 ± 14 ms-1 and 14.4 ± 1.3, respectively. A pulsed beam of disilane (99.998%, Voltaix) was generated by a second piezoelectric valve operating at 120 Hz, a pulse width of 80 μs, and a peak voltage of -400 V with a backing pressure of 550 Torr; this resulted in a peak velocity and speed ratio of 750 ± 15 ms-1 and 7.2 ± 0.4 for the disilane pulse, and a collision energy in the intersection region of the scattering chamber of 36.0 ± 0.5 kJmol-1; the center-of-mass (CM) angle was calculated to be 42.4º ± 0.6°. The 120 Hz repetition rate of both pulsed valves and 60 Hz frequency of the photodissociation laser allows a “laser-on” minus “laser-off” subtraction to eliminate potential background contributions. Any reactively scattered products were then mass filtered after ionization exploiting a quadrupole mass filter and detected by a Daly-type TOF detector located in a rotatable, triply-differentially pumped ultrahigh vacuum chamber (6 10-12 Torr) after electron-impact ioni­za­tion of the neutral products at an electron energy of 80 eV and an emission current of 2 mA. This detector is rotatable within the plane defined by both supersonic beams allowing the collection of angular-resolved TOF spectra. At each angle, up to 1 106 TOF spectra were recorded. The TOF spectra were then integrated and normalized to the intensity of the TOF at the CM angle to obtain the product angular distribution in the laboratory frame.

**Theoretical Methods**

Geometries of the reactants, products, intermediates and transition states involved in the silylidyne plus disilane reaction were optimized using the hybrid B3LYP[30](#_ENREF_30), [31](#_ENREF_31) density functional theory (DFT) method with Dunning’s correlation consistent cc-pVTZ basis set. [32](#_ENREF_32) Vibrational frequencies of all species were computed at the same B3LYP/cc-pVTZ level of theory. For the reactants and critical transition states involved in the pathways for molecular hydrogen loss from Si3H7 intermediates, geometry optimization was also carried out at the doubly hybrid DFT B2PLYPD3/cc-pVTZ level of theory[33](#_ENREF_33), [34](#_ENREF_34) including Grimme’s dispersion correction[35](#_ENREF_35) and using the coupled clusters CCSD/cc-pVTZ approach. [36-39](#_ENREF_36) For the B2PLYPD3/cc-pVTZ optimized structures, vibrational frequencies were recalculated using the same method. Single-point energies were then refined at the explicitly correlated coupled clusters CCSD(T)-F12 level[40](#_ENREF_40), [41](#_ENREF_41) with single and double excitations and perturbative treatment of triple excitations. The CCSD(T)-F12 calculations were carried out with the cc-pVTZ-f12 and cc-pVQZ-f12 basis sets[32](#_ENREF_32), [42](#_ENREF_42) and the energies were then extrapolated to the complete basis set (CBS) limit using the following expression: [43](#_ENREF_43) ECBS = Ecc-pVQZ-f12 + (Ecc-pVQZ-f12 – Ecc-pVTZ-f12)×0.69377. For the reactants and critical transition states, the CCSD(T)-F12/CBS energies were calculated not only for B3LYP but also for B2PLYPD3 and CCSD optimized geometries. For these species, the energies were further refined by taking into account the core electron correlation effects via CCSD(T)-F12 calculations with the cc-pCVTZ-f12 and cc-pCVQZ-f12 basis sets[44](#_ENREF_44) extrapolated to CBS limit, which included all core electrons except 1s of Si atoms in the correlation treatment. Finally, anharmonicity corrections to zero-point vibrational energies were evaluated through calculations of anharmonic frequencies at the B3LYP/cc-pVTZ level of theory using vibrational perturbation theory to the second order (VPT2). [45](#_ENREF_45) The B3LYP, B2PLYPD3 calculations, CCSD geometry optimizations, and VPT2 computations of anharmonic frequencies were performed using the GAUSSIAN 09 package [46](#_ENREF_46) whereas the CCSD(T)-F12 calculations were carried out employing MOLPRO 2010. [42](#_ENREF_42)

ASSOCIATED CONTENT

**Supporting Information**.

The following files are available free of charge. Profile of the potential energy surface for the roaming pathway connecting intermediate **i1** with the **p1** product of the molecular hydrogen loss obtained via intrinsic reaction coordinate (IRC) calculations for the corresponding transition state at the B3LYP/6-311G\*\* level of theory followed by geometry optimization of the final IRC structures, optimized Cartesian coordinates (Å), and vibrational frequencies(cm-1) of reactants, H and H2 dissociation products, intermediates, transition states involved in the formation of 2p1 and 2p7 products from silylidyne radical (SiH) + disilane (Si2H6) reaction (file type, i.e., PDF).

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

**ACKNOWLEDGMENT**

The Hawaii group thanks the National Science Foundation (NSF) for support under award CHE-1360658. Computer resources at the National Center for High-Performance Computing of Taiwan were utilized in the calculations.

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