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Gas-Phase Reactions

Directed Gas Phase Formation of Silene (H_2SiCH_2)

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Abstract: The silene molecule (H_2SiCH_2; X^1A_1) has been synthesized under single collision conditions via the bimolecular gas phase reaction of ground state methylidyne radicals (CH) with silane (SiH_4). Exploiting crossed molecular beams experiments augmented by high-level electronic structure calculations, the elementary reaction commenced on the doublet surface through a barrierless insertion of the methylidyne radical into a silicon-hydrogen bond forming the silylmethyl (CH_2SiH_3; X^2A') complex followed by hydrogen migration to the methylsilyl radical (SiH_2CH_3; X^2A'). Both silylmethyl and methylsilyl intermediates undergo unimolecular hydrogen loss to silene (H_2SiCH_2; X^1A_1). The exploration of the elementary reaction of methylidyne with silane delivers a unique view at the widely uncharted reaction dynamics and isomerization processes of the carbon–silicon system in the gas phase, which are noticeably different from those of the isovalent carbon system thus contributing to our knowledge on carbon silicon bond couplings at the molecular level.

Langmuir's perception of isovalency in which "two molecular entities with the same number of valence electrons have similar chemistries"[1] has been fundamental in understanding basic principles of molecular structure and reactivity of isovalent systems and in advancing modern concepts of chemical bonding.[2] Special devotion has been attributed to reactive intermediates containing the main group XIV elements carbon (C) and silicon (Si), which have both four valence electrons and hence are isovalent. Although the Langmuir's concept envisages that the molecular structures and chemical bonding of the isovalent C_2H_4 and Si_2H_4 systems should be identical, the actual geometries of both systems differ remarkably.[3] Here, the D_{2h} symmetric ethylene molecule (C_2H_4; 1; X^1A_{1g}) represents the global minimum of the C_2H_4 potential energy surface (PES) and is planar with both carbon atoms sp^2 hybridized. The thermodynamically most stable Si_2H_4 species—the *trans*-bent disilene (Si_2H_4; 3; X^1A_g) molecule—has a C_{2h} point group and carries two pyramidal silene moieties with each silicon atom being sp^3 hybridized (Scheme 1).[4] This discovery originally recommended that silicon—in strong contrast to carbon—barely develops silicon=silicon double bonds due to the larger covalent radius of the silicon atom which prevents atomic $3p_z$ orbitals from coming necessarily close to establish π molecular orbitals.[5] The distinct chemical bonding can be further recognized when comparing the C_s symmetric triplet methylcarbene (CH_3CH; 2; X^3A') and singlet silylsilylene (SiH_3SiH; 4; X^1A') depicting triplet–singlet and singlet–triplet splittings of 12 and 55 kJ mol^{-1}, respectively.[6] The exotic molecular structures of silicon-bearing molecules are well revealed considering the nonclassical monobridged $H_2Si(\mu\text{-}H)SiH$ (5; X^1A) species. The isovalent carbon analog does not exist as a local minimum, but represents a transition state in the isomerization of ethylene (C_2H_4; 1; X^1A_{1g}) to singlet methylcarbene (CH_3CH; a^1A') (Scheme 2).[7] Therefore, a replacement of isovalent carbon by silicon directs the formation of molecules, whose carbon counterparts do not exist.[3b]

Despite extensive research aimed to understand the molecular structure and chemical bonding of the homonuclear systems (C_2H_4; Si_2H_4), a *directed* gas phase synthesis of heteronuclear $SiCH_4$ species along with the underlying chemical dynamics of their formation has remained elusive to date.[3a, 8] Since Gusel'nikow and co-workers' pioneering preparation of 1,1-dimethylsilene as a transient intermediate from the pyrolysis of 1,1-dimethyl-l-silacyclobutane,[9] silene intermediates have received considerable attention from the preparative synthetic and physical (in)organic chemistry communities.[10] In 1981, Brook et al. synthesized $(Me_3Si)_2Si{=}C(OSiMe_3)$ the first stable silene at room temperature, depicting a planar arrangement of the substituents connected to the silicon=carbon double bond.[11] Wiberg et al. reported the synthesis of the electrophilic $Me_2Si{=}C(SiMe\textit{t}Bu_2)(SiMe_3)$ molecule[12] carrying alkyl substituents at silicon and trialkylsilyl groups at the carbon atom.[13] The silene parent ($H_2C{=}SiH_2$) was isolated at 10 K in an argon matrix in 1981[14] with its structure studied by Bailleux et al.[15] Maier et al. isolated silene (H_2SiCH_2; **6**; X^1A_1) together with its thermodynamically less stable methylsilylene isomer ($HSiCH_3$; **7**; X^1A') (+10 kJ mol^{-1}) in low temperature argon matrices and explored their photochemical conversion at 254 nm (471 kJ mol^{-1}) and 400 nm (299 kJ mol^{-1})—energies sufficiently

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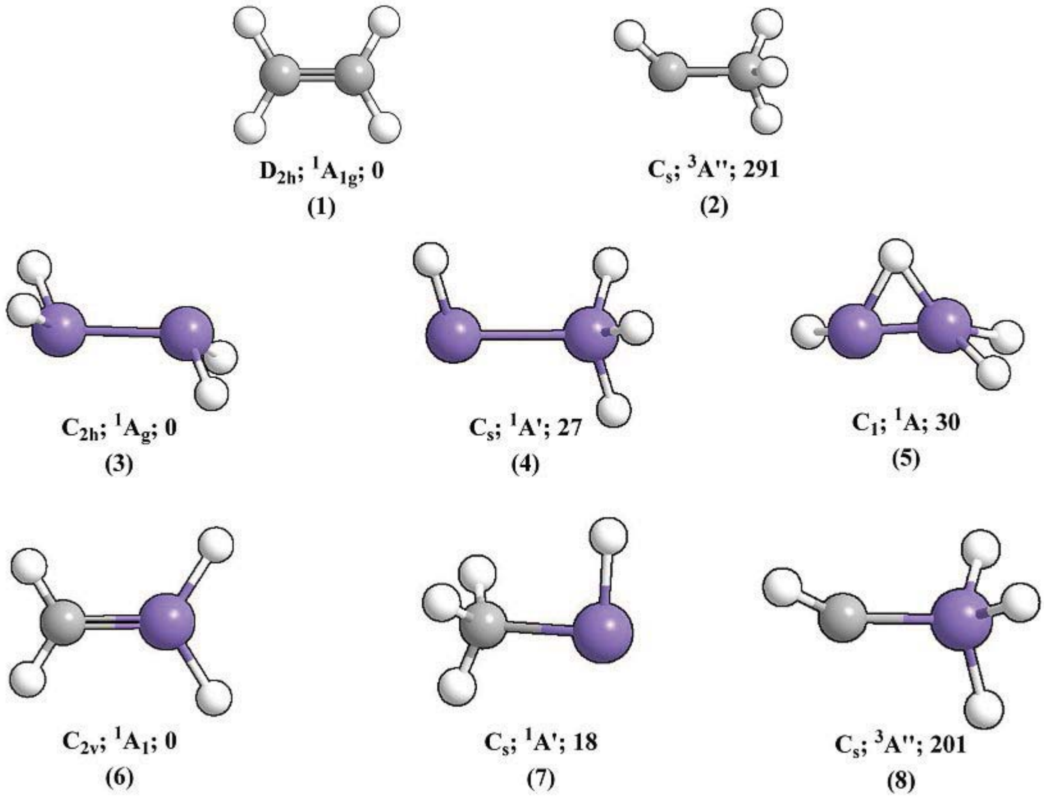
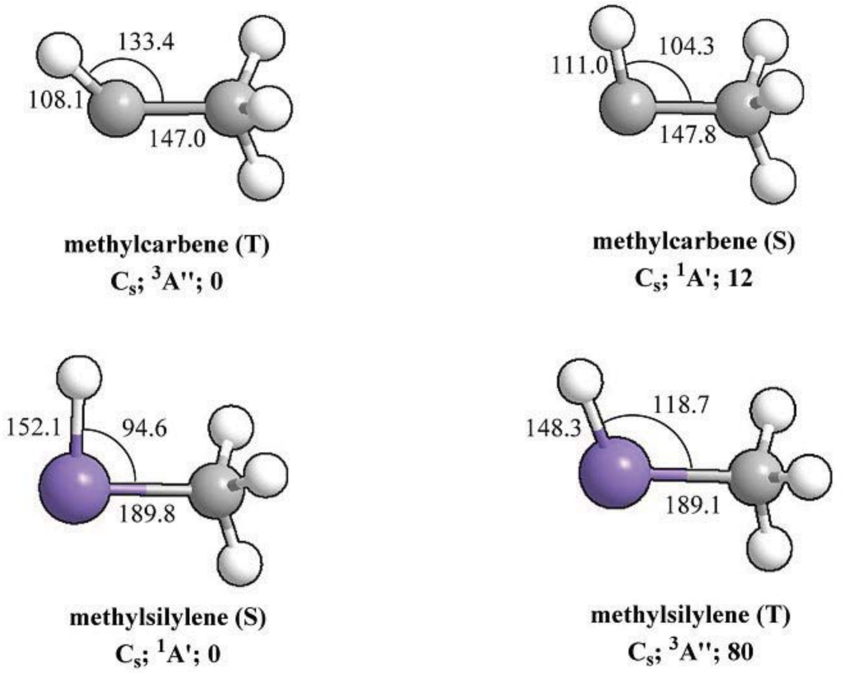


Scheme 1. Structures, point groups, electronic ground state wave functions, and relative energies (kJ mol^{-1}) of homo- and heteronuclear tetrahydrides of main group XIV elements involving carbon (gray) and silicon (purple) with hydrogen atoms color coded in white.



Scheme 2. Molecular structures, point groups, relative energies (kJ mol^{-1}), bond distances (pm), and selected bond angles (degrees) for triplet and singlet methylcarbene (CH_3CH) and methylsilylene ($HSiCH_3$). Carbon, silicon, and hydrogen are color coded in gray, purple, and white, respectively.

high enough to overcome the 152 kJ mol^{-1} barrier for the hydrogen shift from the silicon to the carbon atom.[16] The third isomer silylcarbene ($HCSiH_3$; **8**; X^3A')[8d,17] could not be observed. Bennett et al. observed the formation of both silene (H_2SiCH_2; **6**; X^1A_1) and methylsilylene ($HSiCH_3$; **7**; X^1A') in low temperature silane matrices and explored their decomposition to methylsilylidyne ($SiCH_3$; X^2A'') and silenyl (H_2CSiH; X^2A').[18] Therefore, the absence of fundamental information on the chemical dynamics leading to silene and methylsilylene defines the $SiCH_4$ system as a benchmark to provide critical perspectives on the chemical reactivity and synthesis of carbon- and silicon-bearing species via carbon-silicon bond coupling together with information on their chemical bonding and electronic structure.

Here, we report the gas phase formation of silene (H_2SiCH_2; **6**; X^1A_1) under single collision conditions through the elementary reaction of ground state methylidyne radicals (CH; $X^2\Pi$) with silane (SiH_4; X^1A_1) merging crossed molecular beam experiments and electronic structure calculations. The chemical dynamics commence on the doublet surface via a barrierless insertion of the methylidyne radical with its carbon atom into a silicon—hydrogen bond forming the silylmethyl (CH_2SiH_3; X^2A') intermediate. This intermediate may emit a hydrogen atom to form the silene (H_2SiCH_2; X^1A_1) or undergoes a hydrogen migration from the silicon to the carbon atom yielding the methylsilyl (SiH_2CH_3, X^2A') radical intermediate prior to its decomposition via atomic hydrogen loss from the methyl group to silene (H_2SiCH_2; X^1A_1). This system can be classified as a prototype to elucidate the consequence of the reaction of the simplest organic radical (methylidyne) with the simplest saturated silicon-bearing molecule (silane) to commence a carbon-silicon bond linkage ultimately synthesizing the simplest representatives of a closed shell (silene) organosilicon species. By exploring the formation of silene in the gas phase under single collision conditions, the emerging reaction products fly away uninterrupted after their formation. Consecutive collisions of the initial reaction products such as dimerization[19] and cycloadditions cannot take place hence offering a universal synthetic route under controlled experimental conditions to silenes. By substituting the hydrogen atom(s) of the reactants, the directed synthesis of previously elusive substituted silenes, which are not accessible by traditional synthetic chemistry routes, can be targeted in an attempt to elucidate basic principles of molecular structure and chemical reactivity at the microscopic level.

The crossed molecular beams experiments were conducted at a collision energy of 18.9(±0.1) kJ mol^{-1} by intersecting supersonic beams of the methylidyne radical (CH) with silane (SiH_4) perpendicularly (Supporting Information; Table S1). The neutral reaction products were ionized by electron impact at 80 eV within a triply differentially pumped quadrupole mass spectrometric detector, and then mass- and velocity-analyzed to record angular resolved time-of-flight (TOF) spectra (Figure 1). Accounting for the natural isotope abundances of carbon [^{12}C (98.9 %), ^{13}C (1.1 %)] and of silicon [^{30}Si (3.1 %), ^{29}Si (4.7 %), ^{28}Si (92.2 %)], reactive scattering signal was probed from mass-to-charge (m/z) of $m/z = 47$ ($^{30}Si^{13}CH_4^+$) to $m/z = 40$ ($^{28}Si^{12}C^+$); signals at $m/z = 43$ ($^{30}Si^{13}C^+$ / $^{30}Si^{12}CH^+$ / $^{29}Si^{13}CH^+$ / $^{29}Si^{12}CH_2^+$ / $^{28}Si^{13}CH_2^+$ / $^{28}Si^{12}CH_3^+$) and at $m/z = 42$ ($^{30}Si^{12}C^+$ / $^{29}Si^{13}C^+$ / $^{29}Si^{12}CH^+$ / $^{28}Si^{13}CH^+$ / $^{28}Si^{12}CH_2^+$) represent the best signal-to-noise ratio with signal at $m/z = 43$ collected at a level of 81(±2) % compared to $m/z = 42$.

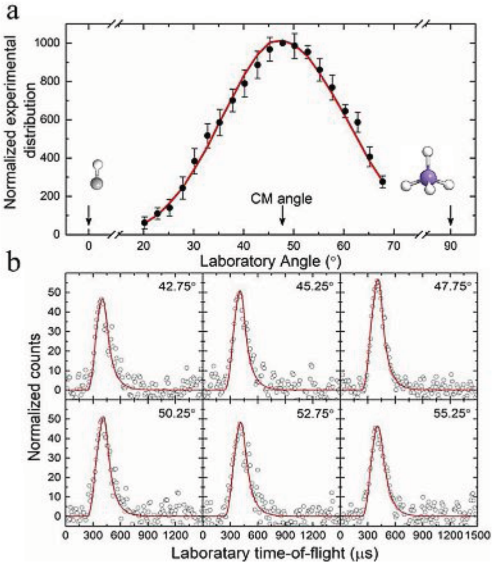


Figure 1. Laboratory angular distribution and the associated time-of-flight spectra. Laboratory angular distribution at mass-to-charge ratio (m/z) of $m/z = 43$ recorded in the reaction of the methylidyne radical with silane (a), and the time-of-flight spectra recorded at distinct laboratory angles overlaid with the best fits (b). The solid circles with their error bars represent the normalized experimental distribution with ±1σ uncertainty; the open circles indicate the experimental data points of the time-of-flight spectra. The red lines represent the best fits obtained from the optimized center-of-mass (CM) functions, as depicted in Figure 2. Carbon, silicon, and hydrogen are color coded in gray, purple, and white, respectively.

Note that TOF spectra at $m/z = 44$ and 45 could not be collected with reasonable signal-to-noise ratios because of the inherent background in the detector originating from CO_2^+ and $^{13}CO_2^+$, respectively. The TOF spectra exhibit indistinguishable patterns and are superimposable after scaling proposing the existence of only one reaction channel. The angular resolved TOF spectra were collected at $m/z = 43$ ($^{28}Si^{12}CH_3^+$) revealing a laboratory angular distribution with a maximum at the center-of-mass (CM) angle of 48.5(±0.2)°; this distribution is spread over at least 47° within the scattering plane spanned by the methylidyne and silane molecular beams and shows a forward-backward symmetry. This finding proposed indirect scattering dynamics through the formation of $SiCH_5$ complex(es). Ions at higher (47–46) and lower (42–40) mass-to-charge ratios are connected to isotopologues and/or isotopomers of $^{28}Si^{12}CH_3^+$ ($m/z = 43$) along with their fragment ions originating upon electron impact ionization of the neutral product(s) in the electron impact ionizer.

Accounting for the natural isotopic abundances of carbon and silicon together with the complex fragmentation patters of neutral organosilicon molecules and the inability to record TOF spectra with a reasonable signal-to-noise ratio at $m/z = 44$, it is critical to transform the TOF data and the laboratory angular distribution from the laboratory to the center-of-mass (CM) reference frame. This assists in elucidating the molecular formulae and the structural isomer(s) of the reaction product(s) together with the chemical dynamics leading to their formation.[20] The laboratory data can be replicated with a single reaction channel of the mass combination of the products of 44 amu ($^{28}Si^{12}CH_4$; hereafter: $SiCH_4$) and 1 amu (H) with ion counts from $m/z = 43$ to 40 arising from dissociative electron impact ionization of the parent molecules in the ionizer. It is

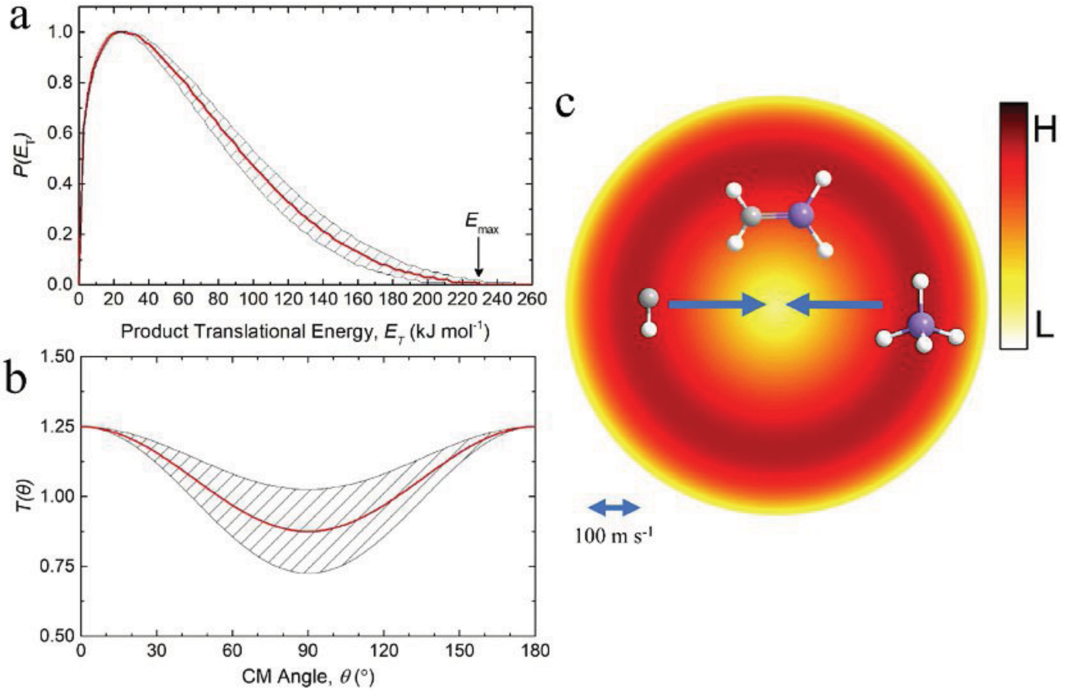


Figure 2. Center-of-Mass (CM) distributions and the associated flux contour map. CM translational energy flux distribution (a), CM angular flux distribution (b), and the top view of their corresponding flux contour map (c) leading to the formation of silene (H_2CSiH_2) plus atomic hydrogen in the reaction of methylidyne with silane. Shaded areas indicate the error limits of the best fits accounting for the uncertainties of the laboratory angular distribution and TOF spectra; the red solid lines define the best-fit functions. Carbon, silicon, and hydrogen are color coded in gray, purple, and white, respectively.

important to highlight that the laboratory data could not be replicated with a mass combination of the products of 43 amu ($^{28}Si^{12}CH_3$) plus 2 amu (H_2); in this scenario, the simulated TOF spectra are too fast and laboratory angular distribution would be too broad. The best fit center-of-mass translational energy distribution ($P(E_T)$) and angular distribution ($T(\theta)$) are displayed in Figure 2. For those molecules formed without internal excitation, the high energy cutoff of the $P(E_T)$ of 229(±20) kJ mol^{-1} represents the sum of the reaction exoergicity plus the collision energy. Therefore, a subtraction of the collision energy reveals that the reaction is exoergic by 210(±20) kJ mol^{-1}. Comparison of these data with the energetics obtained from electronic structure computations for distinct $SiCH_4$ isomers **p1** to **p3**, that is, silene (H_2SiCH_2; **p1**; X^1A_1; $\Delta_rG = -213(\pm 10)$ kJ mol^{-1}), methylsilylene ($HSiCH_3$; **p2**; X^1A'; $\Delta_rG = -195(\pm 10)$ kJ mol^{-1}), and silylmethylene ($HCSiH_3$; **p3**; X^3A''; $\Delta_rG = -12(\pm 10)$ kJ mol^{-1}) (Figure 3), reveals that silene (H_2SiCH_2; **p1**; X^1A_1) and/or methylsilylene ($HSiCH_3$; **p2**; X^1A') represent likely reaction products. Contributions from the thermodynamically less stable silylmethylene isomer ($HCSiH_3$; **p3**; X^3A'') cannot be discounted for since this isomer might be masked in the low energy section of the center-of-mass translational energy distribution. Also, the distribution maximum of the $P(E_T)$ close to 20 kJ mol^{-1} proposed that at least one reaction pathway to **p1** and/or **p2** holds a rather tight exit transition state. Finally, the center-of-mass angular distributions ($T(\theta)$) shows intensity over the complete angular range from 0° to 180° and is forward–backward symmetric (Figure 2); this finding proposed indirect (complex forming) scattering dynamics through the formation of $SiCH_5$ complex(es) with lifetimes longer than the(ir) rotational periods.[21] In summary, our study reveals that silene (H_2SiCH_2; **p1**; X^1A_1) and/or methylsilylene ($HSiCH_3$; **p2**; X^1A') are formed via indirect scattering dynamics through the bimolecular collision of the simplest organic radical (methylidyne) with the prototype of a closed shell silicon hydride (silane).

The experimental data are now merged with the computed potential energy surface (PES) to reveal the underlying reaction mechanism(s) (Figure 3; Figure S1; Supporting Information). Supplemented by the calculated minimal potential energy profile for the entrance channel, the computations reveal a barrierless insertion of the methylidyne radical into one of the chemically equivalent silicon–hydrogen bonds on the doublet surface forming the silylmethyl (CH_2SiH_3; X^2A') intermediate **i1**. This intermediate may emit a hydrogen atom to form the thermodynamically most stable silene molecule (H_2SiCH_2; **p1**; X^1A_1) or undergoes a hydrogen shift from the silicon to the carbon atom yielding the methylsilyl radical intermediate **i2** (SiH_2CH_3; X^2A') prior to its decomposition by atomic hydrogen elimination from the methyl group to silene (H_2SiCH_2; **p1**; X^1A_1). The energy difference between **i1** and **i2** and of **p1** and **p2** of 35 and 18 kJ mol^{-1}agree nicely with an earlier computational study by Osamura et al. (39 and 10 kJ mol^{-1}).[18a,22] The computations also revealed reaction pathways to the thermodynamically less stable isomers methylsilylene ($HSiCH_3$; **p2**; X^1A') and silylmethylene ($HCSiH_3$; **p3**; X^3A'') via exit barrierless decomposition of **i2** and **i1**, respectively. To provide further information on the product isomers formed (**p1**–**p3**; Scheme 1; Figure 3) and on the elusive molecular hydrogen loss pathway (**p4**–**p7**; Figure S1), statistical rates and branching ratios were comput-

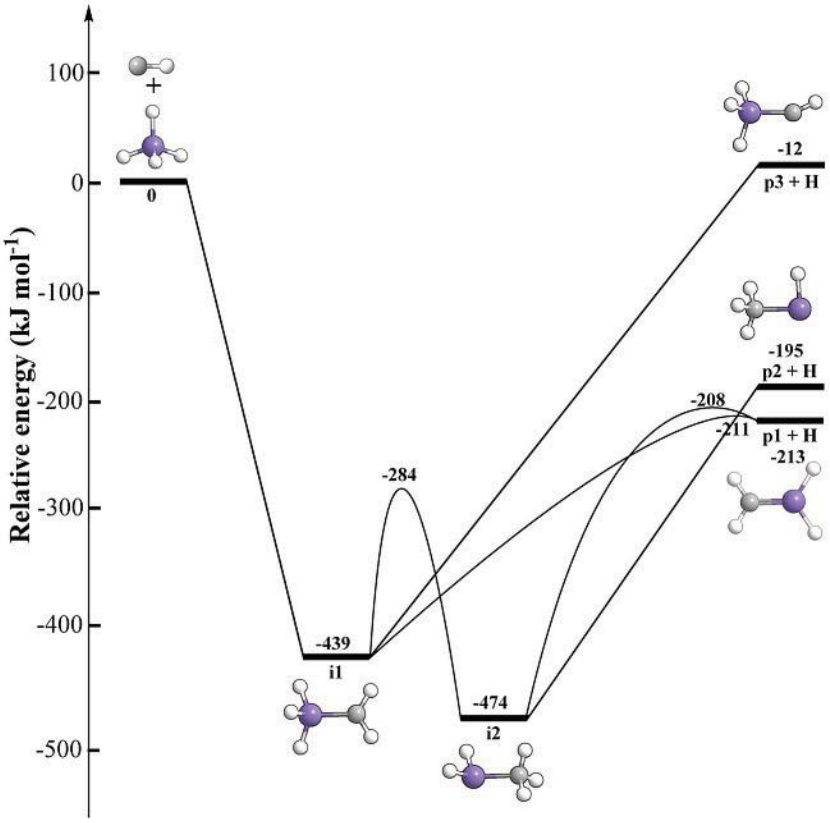


Figure 3. Potential energy surface for the reaction of the methylidyne radical with silane involving atomic hydrogen loss pathways. Cartesian coordinates of the atoms vibrational frequencies are compiled in Table S3; a complete potential energy surface including the molecular hydrogen loss pathways is presented in Figure S1. Carbon, silicon, and hydrogen are color coded in gray, purple, and white, respectively.

ed via the Rice–Ramsperger–Kassel–Marcus (RRKM) theory within the limit of a complete intramolecular energy randomization (Supporting Information). These studies show that under single collision conditions, the atomic hydrogen loss represents the exclusive channel with no contributions from molecular hydrogen elimination. This is in full agreement with our experimental results and the nondetection of the molecular hydrogen loss pathway. Considering the atomic hydrogen loss channel, RRKM theory predicts a predominant formation of silene (H_2SiCH_2; **p1**; X^1A_1) (96(±2)%) with 79(±4)% originating from **i1** and 17(±2)% from **i2**. Branching ratios of methylsilylene ($HSiCH_3$; **p2**; X^1A') were found to be 4(±2)%. As expected, the thermodynamically least stable silylmethylene isomer ($HCSiH_3$; **p3**; X^3A'') was predicted not to be formed.

To conclude, our combined experimental and computational investigation of the elementary reaction of ground state methylidyne radicals with silane reveal a barrierless and overall exoergic route to eventually synthesize silene (H_2SiCH_2; **p1**; X^1A_1) under single collision conditions as provided in crossed molecular beam experiments. The chemical dynamics are triggered by an insertion of methylidyne with its carbon atom into one of the four silicon−hydrogen bond yielding the silylmethyl intermediate (CH_2SiH_3; X^2A') **i1**. This intermediate ejects a hydrogen atom from the silyl moiety to form silene (H_2SiCH_2; **p1**; X^1A_1) or undergoes a hydrogen shift from the silicon to the carbon atom yielding the methylsilyl radical intermediate **i2** (SiH_2CH_3; X^2A') prior to its decomposition via hydrogen atom loss from the methyl group to silene (H_2SiCH_2; **p1**; X^1A_1). The methylidyne–silane system acts as a benchmark to a better understanding and directed synthesis of small organosilicon molecules compared to recent preparations via, for example, photolysis and pyrolysis of precursors. Considering that the hydrogen atom(s) in silane can be substituted by (organic) side groups, the elementary reaction of methylidyne with silane represents the prototype reaction of a hitherto overlooked reaction class in the gas phase forming a previously difficult to synthesize class of silenes thus serving as a test bed toward a detailed understanding of the synthesis of hitherto elusive organosilicon molecules at the molecular level.

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Conflict of interest

The authors declare no conflict of interest.

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