**Gas-Phase Preparation of 1-Germavinylidene (H2CGe; X1A1) – the Isovalent Counterpart of Vinylidene (H2CC; X1A1) - via Non-Adiabatic Dynamics through the Elementary Reaction of Ground State Atomic Carbon (C; 3P) with Germane (GeH4; X1A1)**

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**ABSTRACT**

1-Germavinylidene (H2CGe; X1A1) - the germanium analogue of vinylidene (H2CC; X1A1) - was prepared via a directed gas-phase synthesis through the bimolecular reaction of ground state atomic carbon (C; 3P) with germane (GeH4; X1A1) under single collision conditions. The reaction commences with the barrierless insertion of carbon into the Ge-H bond followed by intersystem crossing (ISC) from the triplet to singlet surface and atomic hydrogen migration to germylene (H2GeCH2) which predominantly decomposes via molecular hydrogen loss to 1-germavinylidene (H2CGe; X1A1). Therefore, the replacement of a single carbon atom in the acetylene−vinylidene system by germanium critically impacts the chemical bonding, molecular structure, and thermo­dy­namical stability of the carbene-type structures favoring 1-germavinylidene (H2CGe) com­pa­red to germyne (HGeCH) by 160 kJ mol-1. Hence, the carbon-germane system represents a ben­ch­­mark in the exploration of the chemistries of main group 14 elements with germanium-bearing systems showing little similarities with the isovalent carbon system.

**TOC Graphic**

**图表, 气泡图

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     The very first isolation of disilenes (Si=Si) in 1981 by West et al. challenged the conven­tional wisdom of the “Double Bond Rule”,[1](#_ENREF_1) i.e. a postulate that main group 14 elements heavier than carbon cannot form homo- and heteronuclear multiple bonds.[2](#_ENREF_2),[3](#_ENREF_3) As of today, stable compounds carrying homonuclear double bonds (E=E, E = Si, Ge, Sn, Pb)[4-6](#_ENREF_4) such as disilene, digermene, distannene, and diplumbene have been synthesized and - although more challenging - triply bonded compounds including disilyne (Si≡Si),[7](#_ENREF_7) digermyne (Ge≡Ge),[8](#_ENREF_8) distannyne (Sn≡Sn),[9](#_ENREF_9) diplumbyne (Pb≡Pb)[10](#_ENREF_10) were isolated as well. These heavier analogues of alkynes (E≡E) display *trans*-bent geometries with decreased R-E-E angles from 137.44° (disilyne) to 94.26° (diplum­byne) and decreased bond orders from silicon to lead culminating nearly 90° bending angles and a formal single bond in diplumbynes (RPbPbR)[10](#_ENREF_10) marking a strong contrast to acetylene and its linear geometry.

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**Scheme 1**. Molecular geometries of H2CC, H2SiSi, and H2CGe isomers including selected bond angles (degrees), bong distances (Å), relative energies (kJ mol-1), electronic states, and point groups.

As for the heteronuclear multiple bonds, an understanding of the chemical bonding of the chemistry of heteronuclear alkene analogues (C=E, E = Si, Ge, Pb)[2](#_ENREF_2),[11-14](#_ENREF_11) along with heteronuclear alkyne analogues involving the C≡Si bond[15-18](#_ENREF_15) is beginning to emerge. For the H2CGe isomers, singlet 1-germavinylidene (H2C=Ge) represents the global minimum; the simplest germyne (HC≡GeH) - the *trans*-bent isomer - is less stable by about 160 kJ mol-1.[19](#_ENREF_19) This strongly contrasts the carbon analogue acetylene (HC≡CH) – vinylidene (H2C=C) system with acetylene being more stable than vinylidene by 186 kJ mol-1.[19-21](#_ENREF_19) Previous electronic structure calculations revealed that the 1-germavinylidene (H2CGe; X1A1), germyne(HCGeH; X1A') and 2-germavinylidene (CGeH2; X1A1) isomers are planar; nonclassical monobridged or dibridged isomers such as Ge(*µ*-H)SiH and Ge(*µ*-H2)Si in the SiGeH2 system do not represent local minima.[20](#_ENREF_20) 1-Germavinylidene (H2CGe) was first explored via electric discharge of tetramethylgermane in argon. Therein, the LIF (laser induced fluorescence) spectra of 1-germavinylidene was obtained.[22](#_ENREF_22) After that, a series of studies were conducted focusing on 1-germavinylidene investigating the B1B2−X1A1 and A1A2−X1A1 transitions along with the corres­ponding vibrational frequencies of the ground and A states.[23](#_ENREF_23),[24](#_ENREF_24) However, compared to silynes (R-Si≡Si-R), the preparative synthesis of germynes (R-Ge≡C-R) has been still poorly explored consi­de­ring their high reactivity through dimerization leading to four-member ring sructures.[25](#_ENREF_25),[26](#_ENREF_26) Even germynes with small substituents (RC≡GeR, R = F, H, OH, CH3, SiH3) are extremely difficult to prepare.[26](#_ENREF_26) In 2001, Bibal et al. reported the first synthesis of the germyne Ar-Ge≡C-SiMe3 [Ar = 2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)phenyl] as a highly reactive intermediate.[27](#_ENREF_27) In 2011, the isolation and characterization of the first persistent phosphine-stabilized germyne was accomplished (*C*-phosphino-*Ge*-aminogermyne).[28](#_ENREF_28) However, the Ge−C bond length was deter­mi­ned to be 1.887 Å, which is longer compared to the 1.712 Å bond length for the germyne stem compound (HC≡GeH) ranging between that of a Ge−C single (1.95-2.00 Å) and a double bond Ge=C bond (1.77-1.83 Å). This has been interpreted through the effects of the electron-withdrawing and π-donating substituents.[26](#_ENREF_26),[28](#_ENREF_28) The electronic and steric effects of bulky substituents are best reflected in the reversed order of stability of substituted molecules with RC≡GeR (R = Tbt, SiMe(Si*t*Bu3)2) representing the global minimum.[26](#_ENREF_26)

The crossed molecular beam approach provides ideal experimental conditions to prepare exotic species including 1-germavinylidene (H2CGe) and germyne (HCGeH) through the reac­tion of ground state carbon (C; 3P) with germane (GeH4; X1A1) in the gas phase.[29](#_ENREF_29),[30](#_ENREF_30) Consi­de­ring the single collision conditions of the experiments, the bimolecular reaction products fly away undisturbed thus excluding consecutive collisions such as dimerization and cyclo­addition; these experimental conditions provide a universal, directed synthetic route to highly reactive germylenes and germynes under controlled conditions considering that the hydrogen atom of the germane reactants can be substituted by any (in)organic functional group.[5](#_ENREF_5),[26](#_ENREF_26) Our experiments along with computational and statistical calculations suggest that singlet 1-germavinylidene (H2CGe; X1A1) represents the main product (50.97%) succeeded by germyne (HCGeH; X1A'; 18.88%) and 2-germavinylidene (CGeH2; X1A1; 30.15% Table S1). Our study reveals that the reaction commences with a barrierless insertion of atomic carbon into the Ge-H bond of germane followed by intersystem crossing (ISC) of the triplet intermediate germyl­methylene (HCGeH3; a3A'') to singlet germylmethylene (HCGeH3; X1A). The latter undergoes facile hydrogen migration to germylene (H2CGeH2; X1A1), which either decom­poses via molecular hydrogen loss to 1-germavinylidene or undergoes another hydrogen shift to methylgermylene (CH3GeH; X1A') prior to unimolecular decomposition to 1-germavinylidene. These nonadiabatic reaction dynamics may serve as a universal template initiating advanced studies in the gas phase preparation of highly reactive, dinuclear main group hydrides of various degrees of hydrogenation involving germanium for a better understanding of their chemical bonding and molecular structures at the molecular level.

     The time-of-flight (TOF) spectra collected in the carbon – germane system was searched for from m/z = 92 (76GeCH4+) to 84 (70GeCH2+) accounting for the natural isotope abundance of carbon [12C (98.9%), 13C (1.1%)] and germanium [70Ge (20.5%), 72Ge (27.4%), 73Ge (7.8%), 74Ge (36.7%), 76Ge (7.8%)]. Best signal was observed at 88 (C74GeH2+/C73GeH3+/13C74GeH+/ 13C73GeH2+/C76Ge) with ion counts at m/z = 89 (C74GeH3+/13C74GeH2+/13C73GeH3+/C76GeH/ 13C76Ge) accumulated at a level of only 16 ± 3%. No definite signal could be detected at 91 and 92 indicating that no CGeH4 adducts survive the flight time from the interaction region to the electron impact ionizer within our detector. Signal at m/z = 88 can be best fit with a single channel via molecular hydrogen elimination and the preparation of CGeH2 (88 amu) (Figure 1). Signal at lower mass-to-charge ratios originate predominantly from dissociative ionization of the neutral product. It should be noted that the dicarbon (C2) and tricarbon (C3) were also produced in the experiment; under our experimental conditions, their contribution could be minimized to less than 5%. However, no signal at higher masses was detectable suggesting that neither dicarbon nor tricarbon accounts for reactive scattering signal at m/z = 88. The LAD (laboratory angular distribution) is spread at least over 50° from 17° to 65° with a maximum around the CM angle of 53.3 ± 0.6° (Figure 1). These findings propose indirect scattering dynamics and the formation of the long-lived CGeH4 complex(es), which can fragment to CGeH2 isomer(s) through molecular hydrogen loss.

图表, 折线图, 直方图

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**Figure 1**. LAD (A) and TOFs (B) recorded in the C−GeH4 reaction at m/z = 88. The solid circles with their error bars represent the normalized experimental distribution; the open circles indicate the experimental data. The red lines represent the best fits obtained with reaction channel of C + 74GeH4 → C74GeH2 + H2 and the blue line represent reaction channel of C + 76GeH4 → C76GeH2 + H2. Colors of the atoms: carbon, gray; germanium, green; and hydrogen, white.

     To elucidate the underlying reaction mechanisms, the experimental data (TOFs, LAD) were transformed from the laboratory to the CM reference frame. The experimental data were replicated with a single molecular loss channel of a mass combination of m/z = 88 (H2CGe) and 2 (H2). It should be noted that all attempts to fit the laboratory data with an atomic hydrogen loss channel failed. Figure 2 depicts the resulting center of mass translational and angular flux distributions, *P(E*T*)* and *T(θ), o*f the best fits. Inspecting the CM functions, the *P(E*T*)* reveals a maximum translation energy *E*max of 302 ± 22 kJ mol-1, which corresponds to the sum of the collision energy (35.5 ± 1.2 kJ mol-1) and the reaction exoergicity for those products formed without internal excitation. Hence, a reaction energy of -266 ± 23 kJ mol-1 is derived. Further, the *P(E*T*)* displays a most probable energy of 32 ± 2 kJ mol-1 suggesting a tight exit transition state of the unimolecular decomposition of the CGeH4 intermediate(s) to the final products. Also, the *T(θ)* is forward-backward symmetric with respect to the distribution minimum at 90o (Figure 2). These findings propose indirect reaction dynamics with the long-lived CGeH4 intermediates (lifetime longer than or comparative with the rotational period) and geometrical constraints of the decomposing complex(es) with molecular hydrogen emitted nearly within the rotational plane of the decomposing intermediate nearly perpendicularly to the total angular momentum vector.[31](#_ENREF_31)

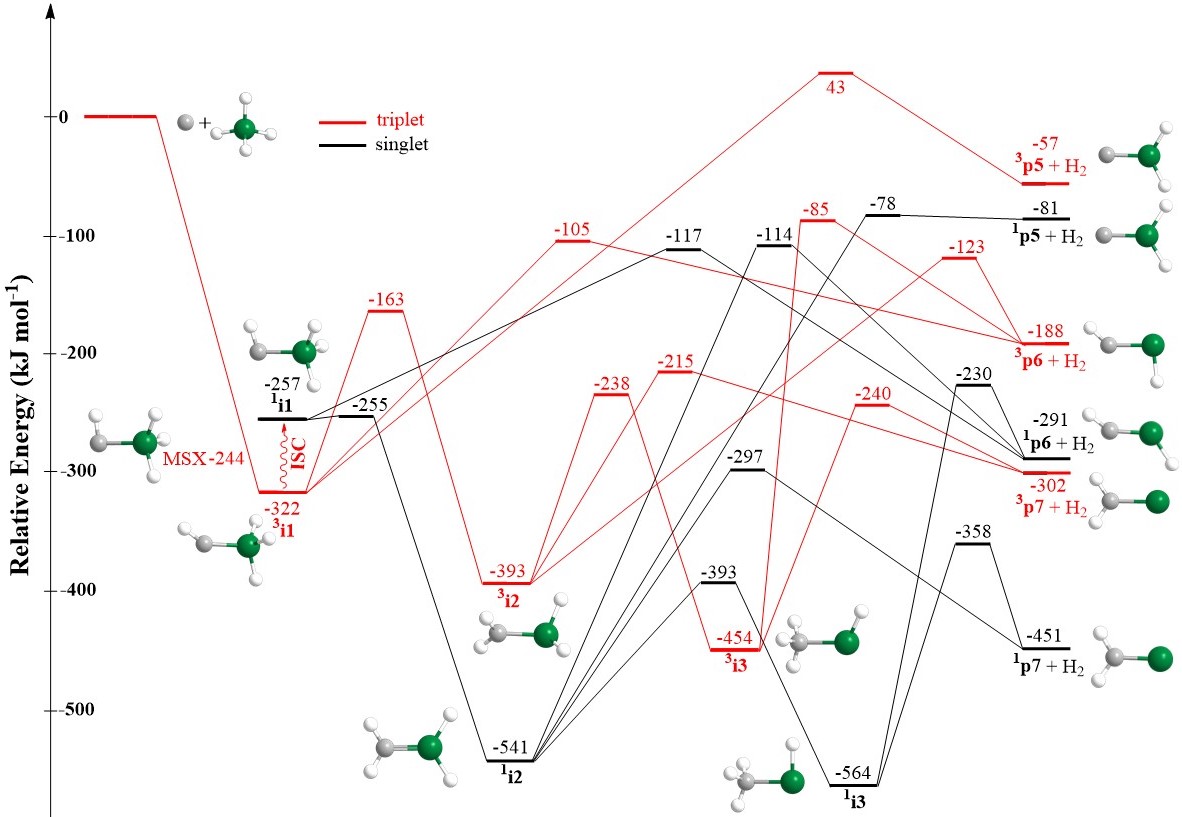


**Figure 2**. CM translational energy (A), angular flux distributions (B) and the corresponding flux contour map (C) for the C−GeH4 system. The red lines represent the best-fit; shaded areas depictthe error limits of the best fits.

     Our experimental data unravel an exoergic molecular hydrogen loss channel with a reaction energy of -266 ± 23 kJ mol-1 through indirect reaction dynamics. We combine these experimental results now with electronic structure calculation results to explore the underlying mechanisms and to determine structural isomer(s) formed (Figure 3, Figure S1). Our calculation revealed three singlet (**1p5**-**1p7**) and three triplet CGeH2 isomers (**3p5**-**3p7**). 1-Germavinylidene (H2CGe; X1A1; **1p7**) with a germanium-carbon π bond represents the most stable isomer on the singlet surface followed by *trans*-bent germyne(HCGeH; X1A'; **1p6**) and 2-germavinylidene (CGeH2; X1A1; **1p5**). The H2CGe – HCGeH - CGeH2 order of stability of the singlet species mirrors the triplet isomers with the latter less stable by 20 to 150 kJ mol-1. This sequence of stability agrees well with previous calculations.[19](#_ENREF_19),[32](#_ENREF_32) How can these products be formed? The calculations reveal that the reaction of ground state atomic carbon (3P) with germane (X1A1) is initiated on the triplet surface via barrierless insertion of carbon into one of the four germanium-hydrogen bonds forming triplet germylmethylene (HCGeH3; a3A''; **3i1**) residing 322 kJ mol-1 below the separated reactants. **3i1** can undergo unimolecular decomposition to the triplet *trans*-bent isomer **3p6** (HCGeH; triplet germyne; a3A'') via molecular hydrogen elimination from the germyl group through a barrier of 217 kJ mol-1 or isomerizes to **3i2** (H2CGeH2; a3A; triplet germylene) via hydrogen migration. The transition state connecting **3i1** and **3p5** (CGeH2; triplet 2-germavinylidene) is located 43 kJ mol-1 above the separated reactants; considering our collision energy, this transition state cannot be overcome under our experimental conditions. Once formed on the triplet surface, **3i2** can dissociate to **3p6-3p7** through molecular hydrogen loss channels orundergoes a hydrogen atom shift from germanium to carbon yielding the most stable intermediate on the triplet surface **3i3** (H3CGeH; methylgermylene; a3A'') followed by molecular hydrogen ejection; this results in the formation of **3p7** (H2CGe; triplet 1-germavinylidene; a3A2) or **3p6**.

     How might the singlet isomers **1p5-1p7** be formed? **3i1** is predicted toundergo intersystem crossing (ISC) to singlet **1i1** (germylmethylene; X1A; HCGeH3) with the seam of crossing (MSX) reflecting a similar geometry to that of **1i1**; this MSX ranges 78 kJ mol-1 above **3i1**, but only 13 kJ mol-1 above **1i1**. Two reaction channels can be accessed from **1i1,** namely the unimolecular decomposition to **1p6** or isomerization to **1i2** (H2CGeH2; X1A1; germylene) via hydrogen migration. Besides isomerization to **1i3** (methylgermylene; X1A'; H3CGeH),the loss of molecular hydrogen from germanium of **1i2** leads to **1p7**,whereas molecular hydrogen eliminationfrom carbon results in **1p5**; cleavage of both the C-H and Ge-H bonds forms **1p6**. Finally, **1p7** and **1p6** can also be accessed from **1i3**,the most stable structure on the PES. Therefore, two reaction routes commencing with **1i1** to the thermodynamically most stable product, 1-germavinylidene (**1p7**), are identified on the singlet surface including **1i1→1i2→1i3→1p7** and **1i1→1i2→1p7**. Three routes are revealed computationally to **1p6**, namely **1i1→1p6**, **1i1→1i2→1p6**, and **1i1→1i2→1i3→1p6**; one pathway is assigned to **1p5**, i.e., **1i1→1i2→1p5**.

Which are the dominating reaction products? A comparison of the experimentally derived reaction exoergicity of 266 ± 23 kJ mol-1 with the computational reaction energies (Figure 3) suggests that the formation of three isomers (**3p6, 1p5, 3p5**) can be excluded since the reactions are exoergic by only 188 ± 8, 81 ± 8, and 57 ± 8 kJ mol-1, respectively. However, synthesis of the remaining three structures (**1p7, 3p7, 1p6**) should be reflected in reaction energies of 451 ± 8, 302 ± 8, or 291 ± 8 kJ mol-1, respectively, which are clearly higher than the experimentally derived data of 266 ± 23 kJ mol-1. Therefore, **1p7, 3p7,** and/or **1p6** must be formed highly rovibrationally excited. As observed recently in the dicarbon – silane[33](#_ENREF_33) and methylidyne – dimethylacetylene systems,[34](#_ENREF_34) this would shift the maximum translational energy release to lower values thus providing a rationale for the discrepancy between the computed reaction energies and the experimentally derived data. We can utilize the theoretically predicted structures of the exit transition states of the molecular hydrogen losses to **3p7** and **1p5 − 1p7** to narrow down potential products even further. Recall that the center-of-mass angular distribution reveals that the molecular hydrogen loss commences nearly within the rotational plane of the decomposing complex. A detailed inspection of the geometries of these exit transition states reveals that among the possible products, only the singlet species **1p5 − 1p7** fulfill this requirement for transition states **1i2**→**1p5** (0.9°), **1i3**→**1p6** (0.8°), **1i1**→**1p6** (0.7°), **1i2**→**1p7** (5.2°), and **1i3**→**1p7** (10.1°) (Figure 4). This finding also proposes that ISC from the triplet to the singlet manifold is rapid with non-adiabatic dynamics dictating the **3i1**→**1i1** pathway followed by rapid hydrogen shift through a barrier of only 2 kJ mol-1 to **1i2**. The favorable ISC can also be understood in terms of the heavy atom effect (germanium) and that the competing **3i1**→**3i2** pathway is unfavorable considering the barrier of 159 kJ mol-1 for the atomic hydrogen shift.



**Figure 3.** Triplet (red) and singlet (black) molecular hydrogen loss pathways of the C (3P) - GeH4 (X1A1) system.

Considering the remaining five pathways (**1i2**→**1p5**, **1i2**→**1p6**, **1i2**→**1p7**, **1i2**→**1i3**→**1p6**, **1i2**→**1i3**→**1p7**), a close inspection of the energies of the transition states reveals that the formation of 1-germavinylidene (**1p7**) is favorable. This conclusion also gains full support from Rice−Ramsperger−Kassel−Marcus (RRKM) calculations and a dominating formation of 1-germavinylidene (**1p7**; 50.97%; Table S1) compared to *trans*-bent germyne (**1p6**; 18.88%) and 2-germavinylidene (**1p5**; 30.15%) (Supporting Information) thus providing an elegant route to the gas phase preparation of 1-germavinylidene (**1p7**) under single collision conditions via non-adiabatic reaction dynamics. This pathway is also favorable compared to a potential atomic hydrogen loss to form methylgermylidene (CH3Ge; 2A'') via **1i2**→**1i3**→**2p4** (Figure S1) as evidenced through the non-experimental detection of the atomic hydrogen loss pathway.

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**Figure 4**. Calculated geometries of the exit transition states resulting in **1p5** − **1p7**.

     Overall, utilizing the crossed molecular beam machine combined with electronic structure and statistical calculations, our study marks the first directed gas phase formation of 1-germavinylidene (H2CGe; X1A1) via the elementary reaction of the ground state carbon (C; 3P) with germane (GeH4; X1A1) – the simplest closed-shell germanium-carrying molecule – via non-adiabatic reaction dynamics. The reaction commences on the triplet surface with the barrierless insertion of atomic carbon into one of the four germanium – hydrogen bonds leading to triplet germylmethylene (HCGeH3; a3A''). The latter undergoes rapid intersystem crossing to the singlet manifold and singlet germylmethylene (HCGeH3; X1A), which then isomerizes nearly instantaneously through hydrogen shift to germylene (H2CGeH2; X1A1) followed by either decomposition via molecular hydrogen loss to 1-germavinylidene (H2CGe; X1A1) or another hydrogen shift to methylgermylene (CH3GeH; X1A') prior to unimolecular decomposition to 1-germavinylidene (H2CGe; X1A1). The preparation of the unstable molecules with multiple bonds has been studied utilizing various methods including laser flash photolysis,[35](#_ENREF_35) matrix isolation,[32](#_ENREF_32) electric discharge,[22](#_ENREF_22) and vacuum gas solid reactions.[36](#_ENREF_36) However, directed gas-phase preparation of extremely unstable molecules and determination of the corresponding angular distribution and translational energy information without consecutive collisions and wall effects are still needed. Here, our findings demonstrate the unique potential of crossed molecular beam experiments to prepare unstable, even highly unsaturated organometallic molecules in the gas phase, which are not accessible through classical preparative synthetic methods.[25](#_ENREF_25),[26](#_ENREF_26)

**METHODS**

***Experimental Section*.** C-GeH4 reaction was performed at the University of Hawaii.[37](#_ENREF_37) The helium-seeded supersonic beam of ground state atomic carbon was prepared via ablation of a graphite rod.[38](#_ENREF_38) The pulsed carbon beam was characterized by the peak velocity *v*p of 2560 ± 52 m s-1. The primary carbon beam crossed perpendicularly with a germane beam (*v*p = 531 ± 5 m s-1) leading to a center-of-mass (CM) angle of 53.3 ± 0.6° and a collision energy of 35.5 ± 1.2 kJ mol-1 (Table S2). The reactively scattered products were monitored via a rotatable detector at ultrahigh-vacuum conditions (8×10-12 Torr). The TOF spectra were collected at different angles between 17° and 65° with respect to the primary beam. These laboratory data were converted via forward-convolution to the CM frame yielding the CM translational energy (*P(E*T*)*) and angular (*T(θ)*) flux distributions, along with information of the reaction dynamics.[31](#_ENREF_31),[39](#_ENREF_39)

***Computational Studies*.** The geometries of species along H and H2 loss channels on adiabatic ground-state singlet and triplet potential surfaces are optimized via the coupled cluster[40](#_ENREF_40),[41](#_ENREF_41) CCSD/cc-pVTZ calculations, (some with MP2/cc-pVTZ) (Table S3; Table S4). Their energies are refined to complete basis set limits[42](#_ENREF_42) (CCSD(T)/CBS) with CCSD/cc-pVTZ (some with MP2/cc-pVTZ ) zero-point energy corrections, which are derived by extrapolating the CCSD(T)/cc-pVTZ, CCSD(T)/cc-pVDZ, and CCSD(T)/cc-pVQZ energies. The **3i1** and **1i1** minimum-energy crossing point is located by employing CPMCSCF/TZVPP calculation, and the corresponding CCSD(T)/CBS energy is also obtained. MOLPRO[43](#_ENREF_43) and GAUSSIAN16[44](#_ENREF_44) programs were utilized in the surface-crossing and coupled cluster calculations, respectively. Moreover, the energy dependent RRKM (Rice−Ramsperger−Kassel−Marcus) rate constants[45](#_ENREF_45) are then calculated based on CCSD/cc-pVTZ harmonic frequencies and zero-point corrected CCSD(T)/CBS energies. The saddle-point approach[45](#_ENREF_45),[46](#_ENREF_46) is used to compute number of states for transition states, and density of states for intermediates. Note that all the species are considered as a collection of harmonic oscillators. Eventually, the product branching ratios are estimated by solving the *ab initio* reaction path-based rate equations with the numerical Runge-Kutta method.

**SUPPORTING INFORMATION**

Detailed experimental and computational methods, atomic hydrogen loss pathways of the C-GeH4 reaction (Figure S1), the computed RRKM results (Table S1), experimental parameters (Table S2), vibrational frequencies and infrared intensities (Table S3), optimized coordinates structures involved in the C-GeH4 reaction (Table S4).

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**Conflicts of Interest**

There are no conflicts to declare.

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