**Gas Phase Formation of Methylgermylene (**HGeCH3)

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**ABSTRACT**

The methylgermylene species (HGeCH3; X1A’) has been synthesized via the bimolecular gas phase reaction of ground state methylidyne radicals (CH) with germane (GeH4) under single collision conditions in crossed molecular beams experiments. Augmented by electronic structure calcu­la­tions, this elementary reaction was found to proceed thro­ugh barrierless insertion of the methylidyne radical in one of the four ger­ma­nium – hydrogen bonds on the doublet potential energy surface yielding the germylmethyl (CH2GeH3; X2A’) collision complex. This insertion is followed by a hydrogen shift from germanium to carbon and uni­mole­cular decomposition of the methylgermyl (GeH2CH3; X2A’)intermediate by atomic hydrogen elimi­nation leading to singlet methylgermylene (HGeCH3; X1A’). Our inves­ti­gation provides a glimpse at the largely unknown reaction dynamics and isomerization processes of the carbon-germa­ni­um system, which are quite distinct from those of the isovalent carbon system thus providing insights in­to the intriguing chemical bonding of organo germanium species on the most funda­mental, microscopic level.

Since the discovery of the main group element germanium (Ge) by Clemens Winkler in 1886,[[1](#_ENREF_1)] the chemistry of germanium has prompted extensive interest from the organometallic,[[2](#_ENREF_2)] physical chemistry,[[3](#_ENREF_4)] and theoretical chemistry[[4](#_ENREF_5)] communities predominantly due to the often exo­tic chemical bonding and molecular structures of organo germanium species compared to their iso­va­lent hydrocarbon counterparts.[[5](#_ENREF_9)] Particular attention has been devoted to reactive interme­diates connected to germyl free radicals (GeH3),[[6](#_ENREF_16)] germylenes (GeH2),[[7](#_ENREF_18)] and germynes (GeH).[[8](#_ENREF_20)] Although Langmuir’s concept of isoelectronicity in which ‘two molecular entities with



**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 germanium (green) with hydrogen atoms color coded in white.

the same number of valance electrons have similar chemistries’[[9](#_ENREF_23)] predicts that the chemical bonding and molecular structures of ethylene (C2H4), disilene (Si2H4) and digermene (Ge2H4) should be alike, the geometries of these isovalent species differ strongly. The D2h symmetric ethylene (C2H4; **1**; X1A1g) is planar and represents the global minimum on the C2H4 potential energy surface (PES) with both carbon atoms sp2 hybridized. For the heavier analogue of C2H4, a non-planar structure was first reported by Márquez et al..[[10](#_ENREF_25)]. The thermodynamically most stable Si2H4 species – the trans-bent disilene (Si2H4; 3; X1Ag) molecule – has a C2h point group and carries two pyramidal silene moieties with each silicon atom being sp3 hybridized (Scheme 1).[[11](#_ENREF_26)] For the chemistries of digermene,the most stable Ge2H4 species – the trans-bent digermene (Ge2H4; **3**; X1Ag) molecule – also belongs to the C2h point group and holds two germene moieties, in which each germanium atom is sp3 hybridized (Scheme 1).[[11](#_ENREF_26)] This finding initially proposed that germanium can hardly form germanium-germanium double bonds as a result of the covalent ra­dius of the germanium atom which inhibits neighboring atomic 4pz orbitals from approaching sufficiently close to form π molecular orbitals.[[12](#_ENREF_28)] The diverse electronic structures of these systems are exem­pli­fied when contemplating the Cs symmetric triplet methylcarbene (CH3CH; **2**; X3A”), sing­let silylsilylene (SiH3SiH) and sing­let germylgermylene (GeH3GeH; **4**; X1A’) depicting triplet-singlet and singlet-triplet splittings of 16–25, 54–56 and 77–95 kJmol-1, respectively.[[7b](#_ENREF_19), [13](#_ENREF_29)] The peculiar molecular structures of ger­ma­­­nium-based species are best reflected in terms of the non-classical mono-bridged H2Ge(μ-H)GeH (**5**; X1A), square di-bridged-trans-HGe(μ-H2)GeH (**6**; X1Ag), and square di-bridged-cis- HGe(μ-H2)GeH (**7**; X1A1) species, whose isovalent carbon counter­parts do not exist.[[14](#_ENREF_31)] This mir­rors the stability of hydrogen-bridged dinuclear germanium-based species in the absence of carbon. Therefore, a replacement of isovalent carbon by germanium can lead to species, who­se carbon-analogue structures do not exist.

Although substantial research has been devoted to an understanding of the chemical structures and bonding of the homonuclear systems (C2H4; Si2H4; Ge2H4), new attention need to be paid to the meticulous experimental characterization of the formation of free heteronuclear GeCH4 species, which has been tentatively detected. Gas-phase kinetics of the reactions of germylenes have been studied[[15](#_ENREF_32)] and methylgermylene (HGeCH3; 8; X1A’) was first tentatively characterized via laser flash photolysis of 1,3,4-trimethylgermacyclopent-3-ene; the UV spectrum and rate constants of its reactions with 10 different substrates were measured.[[16](#_ENREF_33)] In 2010, HGeCH3 was inferred from matrix isolation studies[[17](#_ENREF_35)] via the ν3 and ν5 modes at 1803 and 1230 cm-1 . Electronic structure calculations predicted the existence of three structural isomers. Singlet methylgermylene (HGeCH3; **8;** X1A’) repre­sents the thermodynamically most stable structure with singlet germene (H2GeCH2; **9**; X1A1) and triplet germylmethylene (HCGeH3; **10**; X3A’’) being less stable by 45 and 266 kJmol-1, respectively. The shortage of experimental data classifies the GeCH4 system as a proto­type target to provide fundamental perspectives on the chemical reactivity and synthe­sis of carbon- and germanium-bearing species together with information on their chemical bonding and electronic structure.

     Here, we report on the experimental observation of the methylgermylene species (HGeCH3; X1A’) under single collision conditions in the gas phase via the reaction of ground state methylidyne radicals (CH; X2Π) with germane (GeH4; X1A1) exploiting the crossed molecular beam me­thod and combining the experimental data with electronic structure calculations. This system explores the outcome of the elementary reaction of the simplest organic radical (methylidyne) with the prototype of a closed shell germanium bearing species (germane) to initiate a carbon-germanium bond coupling eventually forming the simplest representative of an organometallic alkylgermylene: methylgermylene. The chemical reaction dynamics are initiated on the doublet surface by a barrier-less insertion of the methylidyne radical with its carbon atom into a germanium – hydrogen bond followed by a hydrogen shift within the collision complex and uni­mole­cular decomposition through atomic hydrogen loss leading to singlet methyl­ger­my­lene (HGeCH3; X1A’). These findings reveal an exotic germa­ni­um chemistry yielding methyl­germy­l­ene, which strongly diverge from those of the iso­valent methylidyne – methane system.[[18](#_ENREF_36)] By probing the formation of methylgermylene under single collision conditions in the gas phase, the nascent reaction products are ‘isolated’ and fly away undisturbed after the reactive collision between the methylidyne radical and germane. This prevents secondary collisions of the initial reaction products such as dimerization of methyl­germylene thus providing a new synthetic route under controlled experimental conditions to the prototype of the organogermylenes class. This enables us to synthesize a highly reactive molecule and to unravel its molecular structure and chemical reactivity at the most fundamental, microscopic level.

     The reactive scattering experiments were carried out utilizing a crossed molecular beam apparatus at a collision energy of 20.6 ± 0.3 kJmol-1 (Supporting Information; Table S1). The neutral reaction products were ionized at 80 eV by electron impact within a triply differentially pumped quadrupole mass spectrometric detector held at 6×10-12 Torr. The ions were then mass-and velocity-analyzed to record angular resolved time-of-flight (TOF) spectra. Considering the natural isotope abundances of carbon [12C (98.9 %), 13C (1.1 %)] and of germanium [70Ge (20.4 %), 72Ge (27.3 %), 73Ge (7.7 %), 74Ge (36.7 %), 76Ge (7.8 %)], the reactive scattering signal was probed from mass-to-charge (m/z) of m/z = 93 (76Ge13CH4+) to m/z = 82 (70Ge12C+) with signal at m/z = 88 (76Ge12C+/74Ge12CH2+/73Ge13CH2+/73Ge12CH3+/72Ge13CH3+/72Ge12CH4+) depic­ting the best signal-to-noise ratio; the signals at m/z = 90 (76Ge12CH2+/76Ge13CH+/ 74Ge12CH4+/74Ge13CH3+/73Ge13CH4+) and m/z = 89(76Ge12CH+/76Ge13C+/74Ge12CH3+/ 74Ge13CH2+/73Ge 12CH4+/73Ge13CH3+/72Ge13CH4+) were collected at levels of 22 ± 2% and 38 ± 3%, res­pec­tively, com­­pared to m/z = 88. The TOF spectra recorded at distinct mass-to-charge

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**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 = 88 recorded in the reaction of the methylidyne radical with germane (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, germanium, and hydrogen are color coded in gray, green, and white, respectively.

ratios exhibit in­dis­tin­guishable patterns and are superimposable after scaling proposing the existence of one reac­tion channel, i.e. the likely formation of 74Ge12CH4 isomer(s) along with atomic hydrogen. The angular resolved TOF spectra were collected at m/z = 88 (74Ge12CH2+) revealing a laboratory angular distri­bution spread over at least 40o within the scattering plane spanned by the methy­li­dyne and germane molecular beams (Figure 1). Ions at higher (93-89) and lower (87-82) mass-to-charge ratios are connected to isotopologues and/or isotopomers of 74Ge12CH2+ (m/z = 88) along with their frag­ment ions originating upon electron impact ionization of the neutral pro­duct(s) in the elec­tron impact ionizer.

    Considering the natural abundances of carbon and germanium along with complex frag­men­tation patterns of neutral organo germanium species, it is crucial to transform the experimental data from the laboratory to the center-of-mass (CM) reference frame in an attempt to untangle the molecular formulae and the structural isomer(s) of the reaction product(s) along with the underlying chemical dynamics accompanying their formation.[[19](#_ENREF_38)] The laboratory data can be fit with a single channel defined by the mass combination of the products of 90 amu (74Ge12CH4; hereafter: GeCH4) and 1 amu (H) with ion counts at m/z = 89 and 88 predominantly arising from dissociative electron impact ionization of the parent molecule in the ionizer. It should be stressed that no sensible fit could be achieved with a mass combination of 89 amu (74Ge12CH3) plus 2 amu (H2) with the simulated TOF spectra being too fast and laboratory angular distribution too broad. The best fit center-of-mass translational energy (P(ET)) and angular distributions (T(θ)) for the atomic hydro­gen loss channel are depicted in Figure 2. A close inspection of the center-of-mass translational energy flux distribution, *P(E*T*)*, assists in the identification of the GeCH4 isomer formed. For molecules born without rovibrational excitation, the maximum trans­la­tio­nal energy, *E*max, represents the sum of the reaction exoergicity plus the collision energy. Conse­quently, a subtract­i­on of the collision energy (20.6 ± 0.3 kJ mol−1) from the maximum trans­la­tio­nal energy (284 ± 15 kJ mol−1) reveals that the formation of GeCH4 along with atomic hydrogen is exoergic by 263 ± 15 kJ mol−1. A comparison of this data with the energetics obtained from electronic structure computations for distinct GeCH4 iso­mers **p1** to **p3**, i.e. methyl­germylene (HGeCH3; **p1;** X1A’; ΔrG = -255 ± 4 kJmol-1), germene (H2GeCH2; **p2;** X1A1; ΔrG = -210 ± 4 kJmol-1), and germyl­me­thylene (HCGeH3; **p3**; X3A’’; ΔrG = +10 ± 4 kJmol-1) (Figure 3), suggests at least the forma­tion of methylgermylene (HGeCH3; **p1**) in its 1A’ electronic ground state. Contributions from the thermodynamically less stable germene (H2GeCH2; **p2**) and methylgermylene (HGeCH3; **p3**) isomers cannot be excluded at the present stage since they might be masked in the low energy section of the center-of-mass transla­tional energy distribution. Further, the distribution maximum of the *P(E*T*)* is relatively broad (2 – 80 kJmol-1). This flat

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**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 the flux contour map (c) leading to the formation of methylgermylene plus atomic hydrogen in the reaction of methylidyne with germane. 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. The flux contour map represents the flux intensity of the reactive scattering products as a function of the CM scattering angle (θ) and product velocity (u). The color bar indicates the flux gradient from high (H) intensity to low (L) intensity. Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

plateau suggests more than one exit transition state of which at least one is tight and a second one is loose.[[20](#_ENREF_39)] A single, loose exit transition state would be reflected in a *P(E*T*)* peaking very close to zero translational energy, which is clearly not observed. Finally, the cen­ter-of-mass angular distri­butions (T(θ)) depicts intensity over the complete angular range from 0° to 180° (Figure 2) suggesting indirect scattering dyna­mics thro­ugh the formation of GeCH5 com­plex(es) having lifetimes lon­ger than the(ir) rotational periods.[[21](#_ENREF_40)] The weak polari­za­tion, i.e. the flat T(θ) distribution, is the result of the inability of the light hydrogen atom to carry away significant angular momentum.[[19](#_ENREF_38)] In conclusion, our study reveals that at least the thermo­dy­namically most stable methylgermylene isomer (HGeCH3; **p1**) is formed via the reac­tion of the simplest organic radical (methylidyne) with the prototype of a closed shell germanium hy­dride (germane) under single collision con­di­tions.

    We are now merging the aforementioned experimental data with the computed potential ener­gy surfa­ce (PES) to propose the underlying reaction mechanism(s) (Figure 3; Figure S1; Suppor­ting Information). Supported by the calculated minimal potential energy profile for the entrance channel (Figure S4), the reac­ti­on of the methylidyne radical with germane is initiated on the doublet PES via a barrierless in­sertion of the methylidyne radical into one of the chemically equivalent germanium-hydrogen bonds leading to the germylmethyl (CH2GeH3; X2A’) collision complex **i1**. Interestingly, the potential energy does not change smoothly along the profile shown in Figure S4 because the reaction coordinate is more complex than the R(Ge-C) distance. Initially, at R > 3.8 Å, methylidyne simply approaches germane. Next, the germane molecule rotates to point one of its hydrogen atoms toward the carbon atom and this hydrogen atom transfers from germanium to carbon. The hydrogen shift completes between R = 3.2 and 3.1 Å resulting in a sharp potential energy decrease. Finally, the newly formed CH2 group approaches the GeH3 species thus finalizing the formation of the Ge-C bond. Intermediate **i1** can iso­me­rize via a hydrogen shift from the germanium to the carbon atom yielding the methyl­ger­myl (GeH2CH3; X2A’)intermediate **i2** through a barrier of 151 kJmol-1. The methyl­germyl radi­cal represents the global minimum of the GeCH5 PES. The energy difference be­twe­en **i1** and **i2** of 72 kJmol-1 along with the barrier to isomerization of 151 kJmol-1 correlate nicely with earlier computational studies by Osamura et al. (60-69 kJmol-1)[[17](#_ENREF_35)] and Kudo and Nagase (151-160 kJmol-1).[[22](#_ENREF_41)]The methyl­ger­myl radical (GeH2CH3; X2A’; **i2**) was found to undergo unimolecular decomposition via atomic hydrogen loss from the GeH2 moiety via a lose exit transition state le­ad­ing to the experimentally observed singlet methylgermylene (HGeCH3; X1A’; **p1**) product. The computations also identified two pathways leading to the thermodynamically less favora­ble ger­mene isomer (H2GeCH2; **p2**) involving a unimolecular decomposition of **i1** and **i2** with exit tran­sition states of the hydrogen atom loss located 2 and 5 kJmol-1, respectively, above the energy of the separated pro­duct. The energy difference between **p1** and **p2** of 45 kJmol-1 agrees well with Schaefer et al.’s results of 48 kJmol-1.[[23](#_ENREF_42)] Further, chemically activated germylmethyl radicals (CH2GeH3; X2A’; **i1**) can decompose without an exit barrier to the least stable isomer: triplet germyl­me­thylene (HCGeH3; **p3**).

     To shed further light on the nature of the product isomers formed (**p1**-**p3**; Scheme 1; Figure 3) and on the elusive molecular hydrogen loss pathway (**p4**-**p7**; Figure S1), statistical rate constants and branching ratios were computed via the Rice-Ramsperger-Kassel-Mar­cus (RRKM) theory (Sup­por­­ting Information). These data suggest that within the limit of a com­ple­te intramolecular energy rando­mi­za­tion under single collision conditions, the atomic hydro­gen loss represents the nearly exclusive channel (99.981 %) with only a minor contribution from mo­le­cular hydrogen elimination (0.019 %). This is in full agreement with our experimental results and the failed detection of the molecular hydrogen loss. With respect to the atomic hydrogen channel, RRKM the­ory predicts a formation of methylgermylene (HGeCH3; **p1**) and germene (H2GeCH2; **p2**) with nearly equal branching ratios of 48 % and 52 %; 36 % and 16 % of germene are formed via uni­mo­le­cu­lar decomposition of **i1** and **i2**, respectively. The thermo­dynamically least stable isomer germyl­me­­­thylene (HCGeH3; **p3**) was predicted not to be formed.



**Figure 3.** Potential energy surface for the reaction of the methylidyne radical with germane involving atomic hydrogen loss pathways. Optimized Cartesian coordinates of the atoms and vibrational frequencies are compiled in Table S2; a complete potential energy surface including the molecular hydrogen loss pathways is presented in Figure S1. Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

     To summarize, experiments and theory converge on the formation of the thermodynamically most stable methylgermylene isomer (HGeCH3; **p1;** X1A’) via the elementary reaction of methylidyne with germane. Under single collision conditions, the reaction is initiated by the barrierless insertion of the methylidyne radical into the germanium-hydrogen bond forming the germylmethyl (CH2GeH3; X2A’) collision complex **i1**, which then isomerizes via hydrogen



**Scheme 2.** Molecular structures, point groups, relative energies (kJ mol-1), bond distances (pm), and selected bond angles (degrees) for triplet (T) and singlet (S) methylcarbene (CH3CH) and methyl­germylene (HGeCH3). Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

migration to the methyl­ger­myl (GeH2CH3; X2A’)intermediate **i2**. The latter ejects atomic hydrogen via loose exit transition state yielding methylgermylene (HGeCH3; **p1**) in overall strongly exoergic reaction. RRKM cal­culations predict further that if the system undergoes a complete energy redistribution, ger­me­ne (H2GeCH2; **p2**) may be also formed with a nearly equal fraction compared to methyl­ger­my­lene (HGeCH3; **p1**). Note that methylgermylene and ger­me­ne can be interconverted through a barrier of 187 kJmol-1 with respect to methylgermylene (Figure S2). Hence, the transition state is located below the energy of the separated reactants. Therefore, in multi­collision environments, methylgermylene formed with sufficient internal ener­gy might not only overcome the barrier to iso­me­ri­zation to ger­me­ne, but ger­me­ne may also transfer part of the internal energy to a third body collider (batch molecule) thus stabilizing ger­me­ne and making it available for spectroscopic detection.

     The preference of the singlet multiplicity for methyl­germylene (HGeCH3; **p1**; X1A’), but energetically favored triplet methylcarbene (CH3CH; **2**; X3A’’) can be rationalized exploiting valence bond theory (Scheme 2). Here, carbon has valence 2s and 2p orbitals, which are close in energy. Therefore, promotion of an electron from 2s to 2p and hybridization of 2s and 2p orbitals is rather favorable. Therefore, in carbenes, electrons of the carbon atom are sp2-hybri­di­zed; when one considers electrons available for bonding, there are 4 valence unpaired electrons, three of them on sp2 hybrid orbitals and the last one on the pz orbital of the carbon atom. Thus, for methylcarbene, two sp2 electrons form bonds with hydrogen and the methyl group and the remaining two are still unpaired and according to Hund’s rule should have parallel spins, hence the triplet ground state X3A’’. This is corroborated quantitatively by the natural bond population analysis (NBO) showing that in triplet CHCH3 the carbon atom of the methylidyne contributes to the C-C and C-H bonds its sp2 hybrid orbitals (30% s and 70% p), whereas two unpaired electrons are localized one on the sp2 hybrid (34% s and 66% p) and the other on the pure p orbital of the C atom. The sp2 hybridization is also consistent with the HCC angle (133°, Scheme 2) in triplet CHCH3.On the other hand, germanium is much less sus­ceptible to promo­tion and hybridization due to the much larger energy gap between the 4s and 4p orbitals. Without pro­motion and hybridization, germanium has only two 4p electrons avail­able for bonding, whereas two 4s electrons remain paired and hence are maintained as a lone pair. The p electrons form bonds with hydrogen and the methyl group with the bond angle close to 900, i.e. 93.40 in singlet methyl­germylene since the 4p orbitals are mutually per­pen­di­cu­lar to each other. Hence, all electrons are paired leading to the singlet ground state X1A’. Again, the NBO analysis supports this picture showing that in singlet GeHCH3 the Ge atom contributes predominantly its p orbitals into the Ge-C and Ge-H bonds (respectively, 86% and 89%), while the lone pair on Ge mostly includes the contribution from its s orbital (78%) and only little mixing between Ge’s s and p orbitals takes place. Energetically spoken, the orbital picture described above results in singlet – triplet gaps of 12 kJmol-1 for methyl­carbene in favor of triplet and of 45 kJmol-1 for methyl­germylene in favor of singlet.

In conclusion, our combined experimental and computational investigation of the elementary gas phase reaction of ground state methylidyne radicals with germane expose a barrierless and over­all exoergic route to eventually synthesize the singlet methylgermylene (HGeCH3; X1A’; **p1**) under single collision conditions. The chemical dynamics are initiated by insertion of methylidyne into a germanium-hydrogen bond followed by isomerization of the germyl­methyl collision complex (CH2GeH3; X2A’; **i1**) via hydrogen shift to the methyl­ger­myl intermediate (GeH2CH3; X2A’; **i2**) and subsequent ejection of a hydrogen atom to form methyl­ger­mylene (HGeCH3; X1A’; **p1**). These dynamics are distinctive from the isovalent methylidyne – methane reaction (Figure S3).[[18](#_ENREF_36)] The initial barrierless insertion of methylidyne into a carbon-hydrogen bond of methane leads to an ethyl collision complex which then emits atomic hydrogen to yield the ethylene molecule (C2H4; **1**; X1A1g) via a tight exit transition state rather than the thermodynamically less stable triplet methylcarbene (CH3CH; **2**; X3A’’). The energy difference of 291 kJmol-1 for ethylene versus triplet methylcarbene and 45 kJmol-1 for singlet methyl­germylene (HGeCH3; **p1;** X1A’) versus germene (H2GeCH2; **p2**; X1A1) along with the dissimilar dynamics can be understood in terms of the double bond rule stating that elements of the third period should not form multiple bonds with themselves or with other elements. For singlet methyl­germylene (HGeCH3; **p1;** X1A’), the charge distributions calculated exploiting natural bond population analysis conclude that the germanium atom is positively (+0.76 e) and carbon nega­tively (-1.09 e) charged thus revealing the ylide character of singlet methyl­germylene (Sup­ple­mentary Information; Table S3). All together, the isovalency of germanium and carbon supplies a deceptive prediction of reactivity in this system. This effects how we rationalize chemical bonding, molecular structure, and the underlying reaction mechanisms of isovalent sys­tems. The results of the methylidyne – germane system lead to a better under­standing and planning of a directed synthesis of small organo germanium speciescom­pared to recent preparations via, e.g., thermal decomposition of bicyclic molecules and pho­to­lysis or air sensitive precursors.[[5a](#_ENREF_9)] Considering that the hydrogen atom(s) in germane can be replaced by side groups, the elementary reaction of methylidyne with germane reflects the prototype reaction leading to alkylgermylenes which may be difficult to make by other means. Thus, this system can serve as a test bed toward an intimate understanding of the formation of organo germanium species on the molecular level.

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**Conflict of interest**

The authors declare no conflict of interest.

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Singlet methylgermylene (HGeCH3) is synthesized in the gas phase through carbon-germanium bond coupling via the barrierless elementary reaction of the methylidyne radical (CH) with germane (GeH4) under single collision conditions thus revealing an unexpected chemistry that is distinct from analogous reactions comprising carbon bearing species.