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Were Reactions of Triplet Silylenes Observed?

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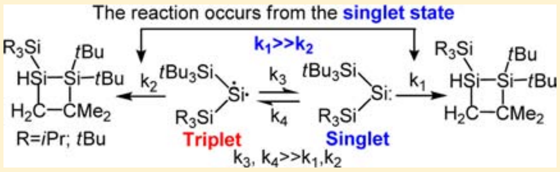
Supporting Information

ABSTRACT: The observation that (iPr$_3$Si)(tBu$_3$Si)Si: (**1**) yields an intramolecular C−H bond insertion product at room temperature, together with earlier computational predictions that triplet **1** is slightly more stable (or isoenergetic) than singlet **1** and additional considerations, led previous investigators to conclude that **1** is the first silylene to exhibit triplet electronic state reactivity. In this paper we test, using DFT and *ab initio* methods, whether the occurrence of intramolecular C−H bond insertion indeed indicates the presence of a triplet-state silylene. DFT calculations at the B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level show that singlet (iPr$_3$Si)(tBuMe$_2$Si)Si: (**9**), a close model of singlet **1**, inserts intramolecularly into a C−H bond of the tBu group with a barrier of 22.7 kcal/mol (22.2 kcal/mol at SCS-MP2/cc-PVTZ). However, for *triplet* **9** the barrier of this insertion reaction is significantly higher, 34.6 kcal/mol (41.9 kcal/mol at SCS-MP2/cc-PVTZ). *This implies that at room temperature the intramolecular insertion reaction of the singlet is 10^9−10^{12} faster than that of the triplet.* We conclude, in contrast to previous conclusions, that the observed intramolecular C−H bond insertion reactions of **1** as well as of (tBu$_3$Si)$_2$Si: (**2**) occur from the singlet state. *Furthermore, the occurrence of an intramolecular C−H bond insertion cannot serve as evidence for the presence of a triplet silylene,* either in cases where the singlet and triplet states are nearly isoenergetic (e.g., **1** and **9**) or even for silylenes where the triplet state is the ground state (e.g., **2**), because the corresponding singlet silylenes insert intramolecularly much faster. The search for a genuine reaction of a triplet silylene has to continue.



INTRODUCTION

Silylenes (R$_2$Si:),[1] the silicon analogues of carbenes (R$_2$C:),[2] are among the most important reactive intermediates in organosilicon chemistry and as such attract considerable interest.[1] A fundamental difference between silylenes and carbenes is the multiplicity of their ground state. Methylene (CH$_2$) is a ground-state ^{3}B$_1$ *triplet*, with the ^{1}A$_1$ singlet state lying ca. 9 kcal/mol higher in energy.[2] In contrast, SiH$_2$ is a ^{1}A$_1$ ground-state *singlet*, with the ^{3}B$_1$ triplet state lying 18−21 kcal/mol higher in energy.[1,3] The reversal of the ground-state multiplicity on going from methylene to silylene has stimulated numerous experimental and theoretical studies,[1−3] and it has a marked effect on the chemistry of silylenes in comparison with that of carbenes.[1,2]

The reactions of singlet and triplet carbenes were studied extensively both experimentally and theoretically.[2] Special attention was devoted to their prototypic insertion and addition reactions. Insertion reactions of silylenes are at the center of this paper, and we therefore review shortly the available computational studies for both carbenes and silylenes.

It is generally accepted that a singlet carbene undergoes C−H bond insertion in a concerted single-step process through a triangular transition state in which the empty p-orbital of the carbene interacts with the filled σ(C−H) orbital[4a,b] (Figure 1a). In contrast, insertion of a triplet carbene occurs in two steps, via a linear hydrogen abstraction transition state occurring in the first step[4c,5] (Figure 1b).

Computational studies on the insertion of singlet CH$_2$ (^{1}A$_1$) into CH$_4$ at both the MP2/6-31G(d) and the B3LYP/6-31G(d,p) levels of theory found that it is a barrierless reaction.[4a,b] Calculations at QCISD(T)/6-31G(d)//QCISD(T)/6-31G(d) found a negative activation barrier of −2.4 kcal/mol [−4.2 kcal/mol at QCISD(T)/6-31+G(2df,p)//QCISD(T)/6-31G(d)].[4b] The insertion of singlet methylene into a C−H bond of ethane occurs in a single step, and the calculated barrier is −6.4 kcal/mol at MP2/6-31G(d) [−11.0 kcal/mol at MP4SDTQ/6-31G(d)],[4b] while for the insertion into CH$_3$Cl the activation barrier is 5.4 kcal/mol at MCSCF(MP2)(4,4)/6-31G(d)//MCSCF(4,4)/6-31G(d) [13.2 kcal/mol at MCSCF(4,4)/6-31G(d)//MCSCF(4,4)/6-31G(d)].[6]

In contrast, a relatively high activation barrier of 17.9 kcal/mol (UMP3/6-31G(d,p)//UHF/3-21G) was calculated for the insertion of triplet CH$_2$ (^{3}B$_1$) into a C−H bond of methane. The reaction proceeds in two steps: a rate-determining hydrogen abstraction step to form two methyl radicals (Figure 1b) which in a second barrierless step recombine to produce ethane.[5] The activation barrier calculated for abstraction of hydrogen from CH$_3$Cl by ^{3}B$_1$ CH$_2$ is even higher than that from CH$_4$, 22.4 kcal/mol at MCSCF(MP2)(4,4)/6-31G(d)//MCSCF(4,4)/6-31G(d) [24.1 kcal/mol at MCSCF(4,4)/6-31G(d)//MCSCF(4,4)/6-31G(d)].[6] A barrier of 24.4 kcal/mol (MP3/6-31G(d)) was calculated for hydrogen abstraction by triplet methylene from ethylene.[7]

In contrast to the barrierless insertion reaction of singlet methylene into CH$_4$,[4a,b] the calculated barrier for the insertion

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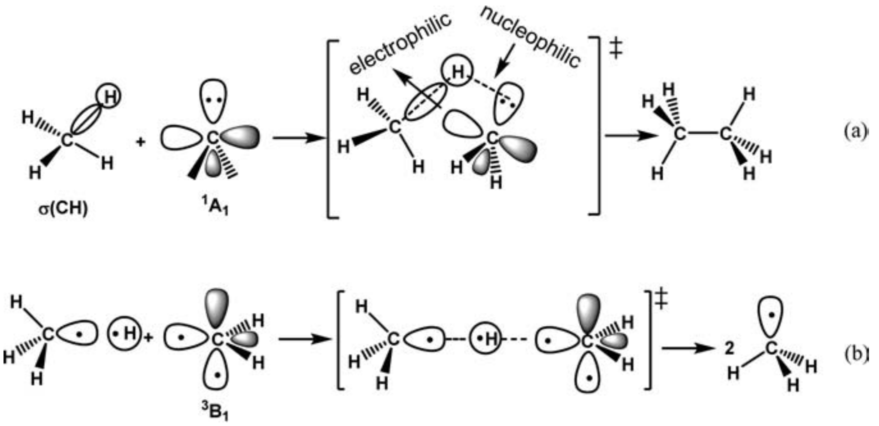


Figure 1. Schematic representation of the mechanistic insertion of CH_2 into methane: (a) singlet CH_2 ($^1A_1$) and (b) triplet CH_2 ($^3B_1$).

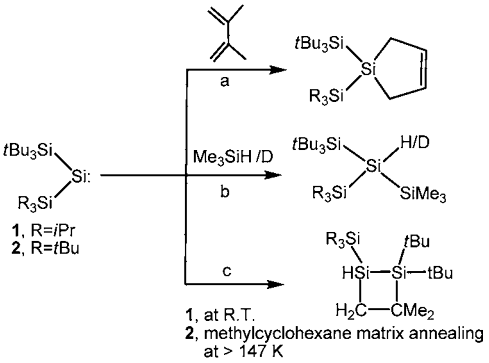
of singlet SiH_2 into a C−H bond of CH_4 is high, 22 kcal/mol at MP4SDTQ/6-311G(d,p)//MP2/6-31G(d).[8] The best estimated experimental gas-phase value is 14 ± 3 kcal/mol (at 610 K).[9a] The authors state that, due to the very small rate constant measured for this bimolecular insertion reaction, this process is unlikely to be observed.[9a] However, intramolecular unimolecular insertion of singlet silylene into C−H bonds has been observed.[9b,10] These insertion reactions occur despite their high barriers; e.g., the activation barrier for the intramolecular C−H insertion of Me_2HSiCH_2SiH to form 1,3-disilacyclobutane was estimated from kinetic data to be 29 kcal/mol[10a] (of which ca. 13 kcal/mol are attributed to ring strain in the transition state[10b]). A barrier of ca. 20 kcal/mol was estimated experimentally for other intramolecular insertion reactions of singlet silylenes.[10b] Recently Boo and co-workers[11,12] studied computationally, using a variety of DFT functionals and basis sets as well as *ab initio* MP2 level calculations, the insertion pathways of several silylenes which were studied earlier experimentally.[10a] According to these calculations, the Gibbs free energy barriers at 800 K for the intramolecular C−H insertion of singlet Me_3SiSiH, $Me_2HSiSiMe$, and $Me_3SiSiMe$ to form the corresponding disilacyclopropanes via a four-membered ring (4-MR) transition state are 19.8, 23.0, and 21.5 kcal/mol, respectively, while the Gibbs free energy barriers for the insertion of the related alkyl-substituted silylenes, Me_2HSiCH_2SiH and MeH_2SiCH_2SiMe, to form 1,3-disilacyclobutane via a five-membered ring (5-MR) transition state are 31.7 and 34.9 kcal/mol (at MP2/aug-cc-PVTZ//B3LYP/aug-cc-pvDZ), respectively.[11] These computational results are consistent with the experimental data.[10a] The above studies show that the intramolecular insertion barriers are significantly lower for *silyl*-substituted silylenes than for *alkyl*-substituted silylenes, and this Si vs C substituent effect is even more pronounced when taking into account the higher ring strain in the 4-MR vs the 5-MR insertion reaction transition state of the studied silylenes. The lower activation energies found for silyl- vs alkyl-substituted silylenes correlate with the smaller singlet−triplet energy gap ($\Delta E_{S\text{-}T}$) of silyl-substituted silylenes (e.g., −8.4 kcal/mol for $(H_3Si)_2Si$:) vs alkyl-substituted silylenes (−25.6 kcal/mol for Me_2Si:). A similar correlation between $\Delta E_{S\text{-}T}$ and the activation energy for intermolecular C−H bond insertion of germylenes was found computationally.[13]

Insertion reactions of triplet silylenes have been hardly studied computationally. Hydrogen abstraction from CH_4 by a triplet SiH_2 forming a silyl radical and a methyl radical, the first step in the insertion of triplet silylenes into C−H bonds (similarly to (b) in Figure 1), was calculated to have a barrier of 32.6 kcal/mol (UMP3/6-31G(d,p)//UHF/3-21G),[5] significantly higher than the calculated activation barrier of 22 kcal/mol for the insertion of singlet SiH_2 into CH_4.[8] Recently, Boo and co-workers calculated that the Gibbs free energy (800 K) barrier for the intramolecular insertion reaction of triplet $Me_3SiSiMe$ into its γ(C−H) bond is 47.8 kcal/mol (MP2/aug-cc-PVTZ), significantly higher than that for the singlet ground state (21.5 kcal/mol).[12]

Until recently, only ground-state singlet silylenes were known.[1] Generation of triplet ground-state silylenes turned out to be very difficult, encountering many failures.[1b,14] In the early unsuccessful efforts to generate triplet silylenes, bulky alkyl substituents, e.g., 1-adamantyl, were used.[14] This approach was stimulated by the theoretical prediction by Gordon[15] that by forcing the RSiR bond angle to be wider than ca. 125° a reversal of the ground state multiplicity occurs and the triplet state is lower in energy than the singlet state. Disappointingly, R_2Si: (R = 1-adamantyl) was determined to be a ground-state singlet on the basis of the high degree of stereospecificity of the diadamantylsilirane decomposition and the $(1\text{-adamantyl})_2Si$:− olefin addition reaction.[14] Later computational studies showed that electropositive substituents, such as bulky silyl substituents, should be used to obtain a triplet ground-state silylene.[16a,b] For example, $(1\text{-adamantyl})_2Si$: is calculated to have a singlet ground state with $\Delta E_{S\text{-}T}$ = −15.9 kcal/mol,[16b] while for $(1\text{-silaadamantyl})_2Si$: $\Delta E_{S\text{-}T}$ = +0.9 kcal/mol, and $((t\mathrm{Bu})_3Si)_2Si$: is calculated to be a ground-state triplet with $\Delta E_{S\text{-}T}$ = +7.1 kcal/mol[16b] (BLYP/DZVP-ECP//BLYP/DZVP-ECP; 4.5 kcal/mol at BLYP/TZVP[16c]). The theoretical prediction that $((t\mathrm{Bu})_3Si)_2Si$: has a triplet ground state was supported by its recent synthesis and characterization by electron paramagnetic resonance (EPR) spectroscopy.[17]

To date, only three experimental studies claimed the generation of triplet silylenes.[17−21] In 2001, Gaspar et al. generated photolytically $(i\mathrm{Pr}_3Si)(t\mathrm{Bu}_3Si)Si$: (**1**).[18] This silylene is predicted by theory to have nearly isoenergetic singlet and triplet states ($\Delta E_{S\text{-}T}$ = 0.1 kcal/mol (B3LYP/6-31+G(d,p), triplet more stable, current study; −1.0 kcal/mol, singlet more stable, ref 16c). Silylene **1** reacts with 2,3-dimethylbutadiene to give the 1,4-addition product (Scheme 1, path a) and with Me_3SiH/Me_3SiD to give Si−H/D bond insertion (Scheme 1, path b), two typical reactions of singlet silylenes.[1g] However, in the absence of trapping reagents, intramolecular insertion into a δ(C−H/D) bond occurs, yielding the corresponding disilacy-

Scheme 1



clobutane product (Scheme 1, path c). On the basis of the observation of the unusual intramolecular insertion reaction, the authors concluded that while an equilibrium may exist between the nearly isoenergetic (as predicted by theory) singlet and triplet states of silylene **1**, *only the triplet silylene is reacting* in the intramolecular δ(C−H) insertion reaction, thus shifting the singlet−triplet equilibrium toward the triplet state.[18a,b] On the basis of literature data, the authors assumed that an intramolecular δ(C−H) bond insertion reaction which occurs from the singlet state should have an activation barrier higher than 20 kcal/mol (see above).[9,10] This assumption, in combination with the assumption that for the triplet silylene the two-step abstraction−recombination mechanism for C−H bond insertion (Figure 1b) has a lower barrier than the single step C−H bond insertion of a singlet silylene, led to the conclusion that the intramolecular δ(C−H) insertion reaction observed under mild conditions occurs from the triplet state.[16c,22] Additional support for this conclusion was provided later by a study of the thermal decomposition of a silirane ring to produce silylene **1**,[19] which in the absence of trapping reagents, also yielded the corresponding 1,2-disilacyclobutane (Scheme 1, path c). The activation barrier for this insertion reaction was estimated indirectly from competition reactions to be smaller than 10 kcal/mol,[19] significantly lower than previous estimates (experimental and theoretical) of the barriers for intramolecular C−H bond insertion reactions of singlet silylenes,[10] thus leading Gaspar et al. to conclude that silylene **1** reacts from its triplet state.[19,22]

In 2003, Sekiguchi et al. generated $(tBu_3Si)_2Si$: (**2**) and presented EPR spectroscopic evidence that **2** has a triplet ground state.[17] **2** has larger silyl substituents than **1**, and is predicted by theory to be a ground state triplet with a larger singlet-triplet energy gap ($\Delta E_{S\text{-}T}$ = 4.5−7.1 kcal/mol) (Table 1)[16b,c,17] than that of **1**. They also showed that **2**, like **1**, undergoes intramolecular δ(C−H) bond insertion, yielding 1,2-disilacyclobutane (Scheme 1, path c). The spectroscopic EPR evidence for the presence of a triplet silylene led also these authors to conclude that the 1,2-disilacyclobutane product is derived from the reaction of triplet **2**,[17] as concluded earlier for **1**.[18a,b,19,22] In a recent study, Sekiguchi et al. reported the synthesis of metallasilylenes, $(t\text{-}Bu_3Si)SiM$ (M = Li, K), which were characterized as triplets by their EPR spectra.[20,23] However, reactions of these silylenes were not yet reported.

Is the conclusion that silylenes **1** and **2** insert intramolecularly from their triplet state[17,18a,b,19,22] correct? According to the calculations, **1** has nearly isoenergetic singlet and triplet states (Table 1)[16c], and **2** is a ground-state triplet ($\Delta E_{S\text{-}T}$ = 4.5−7.1 kcal/mol, Table 1). The relatively small singlet−triplet energy gaps suggest that the two states may exist in equilibrium[18] and therefore both states can react, and the intramolecular insertion product (Scheme 1, path c) can in principle result from reaction of either the singlet state or the triplet state of silylenes **1** and **2**. Previous gas-phase studies showed that at elevated temperatures, singlet ground-state silylenes can undergo intramolecular C−H bond insertion to form disilacyclobutanes and siliranes (see above).[10] The barrier for the reaction from the singlet state is indeed high, but what is the barrier height for the δ(C−H) insertion reaction from the triplet state? Is the barrier from the triplet state indeed significantly lower than that from the singlet state as previously assumed,[16c,19,22] or is it higher than that from the singlet state as indicated by the calculated high barrier for H abstraction from CH_4 by triplet H_2Si:[5] and by the calculated barrier for the intramolecular δ(C−H) bond insertion of $Me_3SiSiMe$?[12]

In this paper we study computationally this important mechanistic question, using both *ab initio* and DFT methods, aiming to determine which electronic state of silylenes **1** and **2** is responsible for the experimentally observed intramolecular C−H bond insertion reaction, the singlet state or the triplet state? The answer to this question will indicate if the observed δ(C−H) bond insertion can serve as a mechanistic tool for determining the presence of a triplet silylene.

■ COMPUTATIONAL METHODS

Calculations were performed using both *ab initio*[24] and density functional theory (DFT)[25] methods, as implemented in the Gaussian 03 and Gaussian 09 series of programs.[26] The geometries of all molecules were fully optimized, and vibrational frequencies computed at the same level of theory were used to characterize the stationary points as minima (no imaginary eigenvalues) or transition states (one imaginary eigenvalue) and to calculate the zero-point vibrational energy (ZPE) corrections. For the DFT calculations we have used the hybrid B3LYP[27] density functional with the 6-31+G(d,p)[28] basis set. To evaluate the reliability of the calculated B3LYP/6-31+G(d,p) geometries and energies of the stationary points on the reaction path, we performed, for $H_3Si(CH_3CH_2SiH_2)Si$:, *ab initio* MP2,[29] SCS-MP2,[30] and CCSD(T)[31] calculations with the 6-31+G(d,p) and cc-PVTZ[32] basis sets. Dispersion effects were calculated using B3LYPD[30a,33] and wB97XD.[34] The detailed results are presented in the Supporting Information (SI, Tables 2S and 3S). Singlet biradical species were calculated using broken-symmetry DFT with the guess=mix keyword.[26]

The discussion below is based (unless stated otherwise) on relative energies calculated at B3LYP/6-31+G(d,p)+ZPE for the singlet states and at UB3LYP/6-31+G(d,p)+ZPE for the triplet states and singlet biradical species. ΔG and ΔH values are calculated at 298 K. These methods allow us to study relatively large systems that model closely the experimentally studied silylenes **1** and **2**. Corrections based on higher level *ab initio* calculations of the smaller model $H_3Si(CH_3CH_2SiH_2)Si$: are discussed.

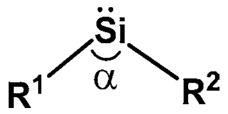
■ RESULTS AND DISCUSSION

Silylenes **1**−**10** (Scheme 2), which include the experimentally studied silylenes **1** and **2** and several model silylenes **3**−**10**, were studied computationally.

Singlet−Triplet Energy Gap. The calculated singlet−triplet energy gaps, $\Delta E_{S\text{-}T}$, and the optimized bond angle α at the silylenic center (Scheme 2) of H_2Si:, Me_2Si:, and **1**−**10** are given in Table 1.

The calculated singlet−triplet energy gap for the simplest disilylsilylene, $(H_3Si)_2Si$, is −8.4 kcal/mol (singlet more stable), significantly smaller than $\Delta E_{S\text{-}T}$ of H_2Si: (−20.7 kcal/mol) or Me_2Si: (−25.5 kcal/mol), as also pointed out in earlier

Scheme 2



1, R^1 = *i*Pr_3Si, R^2 = *t*Bu_3Si; **2**, $R^1 = R^2$ = *t*Bu_3Si; **3**, $R^1 = R^2 = H_3Si$; **4**, R^1 = H, $R^2 = CH_3CH_2SiH_2$; **5**, $R^1 = H_3Si$, $R^2 = CH_3CH_2SiH_2$; **6**, $R^1 = Me_3Si$, $R^2 = CH_3CH_2SiH_2$; **7**, $R^1 = R^2 = Me_3Si$; **8**, R^1 = *i*Pr_3Si, $R^2 = CH_3CH_2SiH_2$; **9**, R^1 = *i*Pr_3Si, R^2 = *t*$BuMe_2Si$; **10**, $R^1 = R^2$ = *i*Pr_3Si

Table 1. Calculated[a] Singlet−Triplet Energy Differences ($\Delta E_{S\text{-}T}$, kcal/mol) and the Optimized Bond Angle at the Silylenic Center (α, deg)[b] of Several Silylenes

silylene[b]	$\Delta E_{S\text{-}T}$[c]	α, singlet	α, triplet
H_2Si	−20.0	91.5	118.5
Me_2Si	−25.6	98.0	118.6
$(H_3Si)_2Si$: (**3**)	−8.4	92.7	126.4
$H(CH_3CH_2SiH_2)Si$: (**4**)	−12.6[d]	90.1	121.3
$H_3Si(CH_3CH_2SiH_2)Si$: (**5**)	−7.1[e]	95.9	126.4
$Me_3Si(CH_3CH_2SiH_2)Si$: (**6**)	−3.7	99.0	127.2
$(Me_3Si)_2Si$: (**7**)	−2.8	101.8	129.8
i$Pr_3Si(CH_3CH_2SiH_2)Si$: (**8**)	−2.1	107.1	128.3
iPr_3Si(*t*$BuMe_2Si)Si$: (**9**)	−1.1[f]	108.7	133.4
(*i*$Pr_3Si)_2Si$: (**10**)	−1.3[g]; 1.7[h]	106.2[g]	143.3[g]
iPr_3Si(*t*$Bu_3Si)Si$: (**1**)	0.1; −1.0[g]	119.3	143.3
(*t*$Bu_3Si)_2Si$: (**2**)	4.7[i]	131.8	151.1

[a]At UB3LYP/6-31+G(d,p)//UB3LYP/6-31+G(d,p)+ZPE. [b]See Scheme 2. [c]$\Delta E_{S\text{-}T} = E_{singlet} - E_{triplet}$. A positive value indicates a triplet ground state. [d]−6.8 kcal/mol at MP2/6-31+G(d,p) and −9.9 kcal/mol at CCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p). [e]−7.5 kcal/mol (B3LYP/cc-PVTZ), −1.9 kcal/mol (MP2/6-31+G(d,p)), −5.2 kcal/mol (MP2/cc-PVTZ), −4.8 kcal/mol (CCSD(T)/6-31+G-(d,p)), −7.7 kcal/mol (CCSD(T)/cc-PVTZ), and −8.7 kcal/mol (SCS-MP2/cc-PVTZ). [f]−5.0 kcal/mol at SCS-MP2/cc-PVTZ. [g]At BLYP/TZVP.[16c] [h]At BLYP/DZVP-ECP.[16b] [i]7.1 kcal/mol at BLYP/DZVP-ECP[16b] and 4.5 kcal/mol at BLYP/TZVP.[16c]

studies.[16a,b,d] As the size of the silyl substituents increases, the SiSiSi bond angle α is widened (Table 1), and consequently $\Delta E_{S\text{-}T}$ decreases.[35] The singlet and triplet states of silylenes **1** (R^1 = *i*Pr_3Si, R^2 = *t*Bu_3Si) and its close model **9** (R^1 = *i*Pr_3Si, R^2 = *t*$BuMe_2Si$) are nearly isoenergetic at B3LYP/6-31+G(d,p) (Table 1), and thus for both **1** and **9** a multiplicity reversal may occur with other computational methods (Table 1). Only for the highly congested (*t*$Bu_3Si)_2Si$:, the calculated $\Delta E_{S\text{-}T}$ = 4.5−7.1 kcal/mol (Table 1) is large enough to secure that **2** has a triplet ground state also at higher levels of theory and thus also in reality.

Intramolecular δ(C−H) Bond Insertion. In the following discussion we use the term "C−H bond insertion" to imply silicon intramolecular insertion into a δ(C−H) bond, leading to a 1,2-disilacyclobutane product as shown in Scheme 1, path c. Stationary points on the singlet and triplet potential energy surfaces (PESs) are denoted by adding the letters "s" and "t", respectively, to the compound number (e.g., **9s**). A schematic drawing of the reaction paths for the intramolecular δ(C−H) bond insertion of singlet and triplet silylenes (e.g., **9**) is shown in Figure 2. Due to the large size of the experimentally studied silylenes **1** and **2**, we could carry out calculations of the reactions paths only for smaller model silylenes, the largest being **9**. The relative energies and the geometrical parameters of important points along the PESs for δ(C−H) bond insertion for singlet and triplet $H_3Si(CH_3CH_2SiH_2)Si$: (**5**), $Me_3Si(CH_3CH_2SiH_2)Si$: (**6**), *i*$Pr_3Si(CH_3CH_2SiH_2)Si$: (**8**), and *i*Pr_3Si(*t*$BuMe_2Si)Si$: (**9**)[36] are given in Tables 2 and 3, respectively. The structures of the transition states for the insertion of **9s** and **9t**, **b** and **e**, respectively, are shown in Figure 3. In the discussion below we will use mainly Gibbs free energies, ΔG, and Gibbs free energies of activation, $\Delta G_s^\#$ and $\Delta G_t^\#$ (the subscripts s and t denote singlet and triplet state energies, respectively) at 298 K, calculated at B3LYP/6-31+G(d,p) for the singlets and at UB3LYP/6-31+G(d,p) for the triplets and for the singlet biradicals. The relative free energies differ from the relative energies, ΔE+ZPE, by only ca.

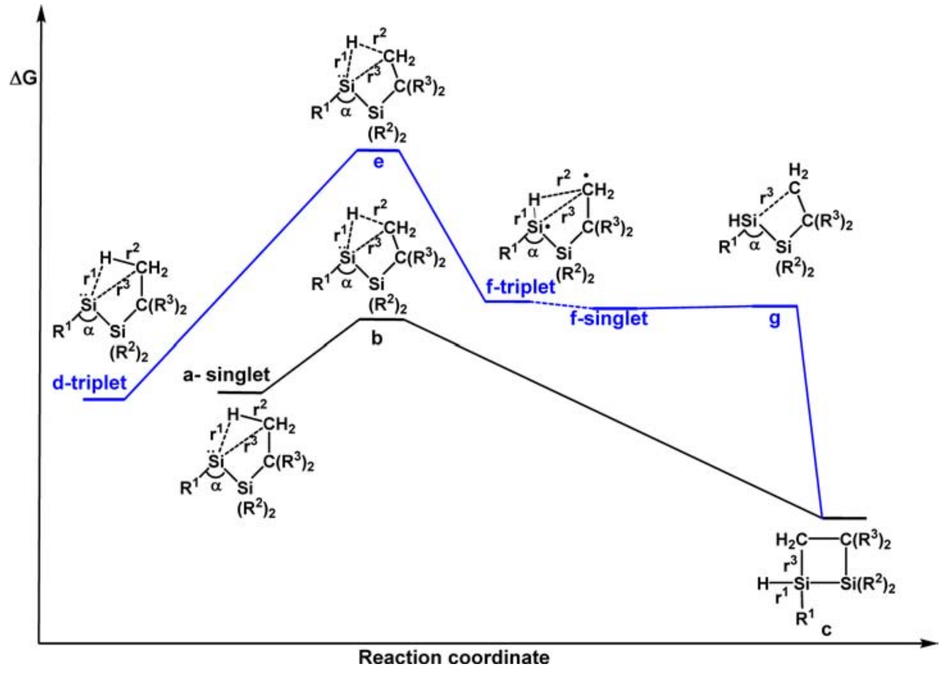


Figure 2. Schematic drawing of the reaction paths for intramolecular δ(C−H) bond insertion in singlet-state (**a**) and triplet-state (**d**) silylenes.

Table 2. Calculated Relative Energies (kcal/mol),[a] Selected Bond Lengths (r, Å),[b] and SiSiSi Bond Angle (α, deg)[b] of Stationary Points a, b, and c along the Intramolecular δ(C−H) Bond Insertion Reaction Path of Singlet Silylenes 5, 6, 8, and 9

		energy				geometry			
silylene	stationary point	ΔE or $\Delta E^{\#}$	ΔE+ZPE or (ΔE+ZPE)$^{\#}$	ΔH^{c} or $\Delta H^{\#}$	ΔG^{c} or $\Delta G^{\#}$	α	r^1	r^2	r^3
5s	**a**	0.0	0.0	0.0	0.0	95.9	3.914	1.096	4.324
6s		0.0	0.0	0.0	0.0	99.0	3.968	1.096	4.375
8s		0.0	0.0	0.0	0.0	107.1	4.171	1.096	4.525
9s		0.0	0.0	0.0	0.0	108.7	3.687	1.095	3.424
5s[d]	**b** (TS)	30.1	27.9	27.1	29.1	108.6	1.522	1.663	2.420
6s		24.8	22.5	21.6	24.1	116.9	1.532	1.598	2.389
8s		24.6	22.0	21.3	23.1	120.9	1.534	1.579	2.397
9s		22.7	20.1	19.5	21.5	126.7	1.537	1.573	2.389
5s	**c**	−24.5	−24.5	−26.3	−23.6	–	1.493	–	1.938
6s		−26.6	−27.9	−28.7	−26.5	–	1.498	–	1.942
8s		−27.5	−29.2	−29.8	−28.4	–	1.498	–	1.944
9s		−29.3	−31.0	−31.5	−29.7	–	1.500	–	1.945

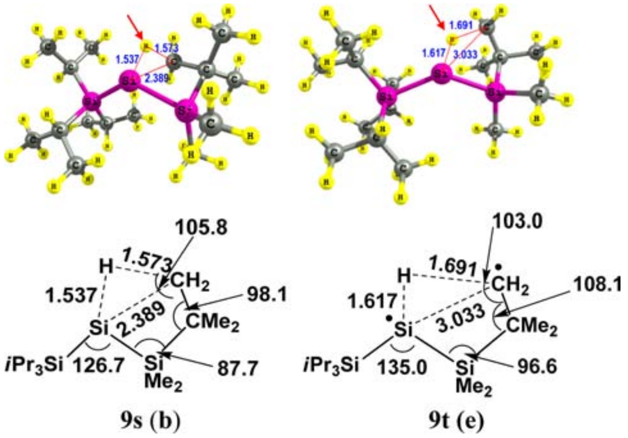
[a] At B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p). [b] See definitions in Figure 2. [c] At 298 K. [d] At MP2/6-31+G(d,p), $\Delta E^{\#}$, (ΔE+ZPE)$^{\#}$, $\Delta H^{\#}$, and $\Delta G^{\#}$ are 27.4, 24.9, 24.1, and 26.3 kcal/mol, respectively. At CCSD(T)/cc-PVTZ, $\Delta E^{\#}$ = 27.9 kcal/mol. For reaction barriers calculated at additional computational levels, see Table 3S.

1.5 kcal/mol for the stationary points on the singlet PESs and by ca. 3.2 kcal/mol for the triplet PESs, indicating a small entropy effect for both surfaces.

Intramolecular δ(C−H) Bond Insertion of Singlet Silylenes. The intramolecular insertion of singlet silylenes, **a**, into a δ(C−H) bond is a concerted single step reaction proceeding via a relatively late transition structure **b** to form the final 1,2-disilacyclobutane product **c** (Figure 2). Product **c** is more stable than the corresponding singlet silylene **a** by 26.5, 28.4, and 29.7 kcal/mol for $Me_3Si(CH_3CH_2SiH_2)Si$: (**6s**), $i$$Pr_3Si(CH_3CH_2SiH_2)Si$: (**8s**), and $i$$Pr_3Si$($t$$BuMe_2Si$)Si: (**9s**), respectively (Table 2). These intramolecular insertion reactions are considerably less exothermic than the intermolecular insertion of SiH_2 into the C−H bond of C_2H_6, −46 kcal/mol (−48 kcal/mol at MP4(SDTQ)/6-31G(d)//HF/3-21G(d)[37]), reflecting the strain in the 1,2-disilacyclobutane ring.[38] The analogous insertion reaction of CH_2 into a C−H bond in C_2H_6 is much more exothermic, −105 kcal/mol (−118 kcal/mol at MP4-(SDTQ)/6-31G(d)//HF/6-31G(d)[37]).

In the transition state for δ(C−H) intramolecular insertion, the silylenic silicon atom forms relatively short partial bonds to the δ-hydrogen (r^1) and to the δ-carbon (r^3), and the breaking δ(C−H) bond (r^2) is considerably elongated (for notations of r^n see Figure 2). For example, in the transition state of **9s** (**b**), r^1, r^2, and r^3 are 1.537, 1.573, and 2.389 Å, respectively (Figure 3), compared to 3.687, 1.095, and 3.424 Å in **9s**. In the insertion product of **9s** (**c**), r^1 and r^3 are 1.500 and 1.945 Å, respectively. On the basis of these geometrical parameters, we define the transition state as being relatively "late".

For singlet $i$$Pr_3Si$($t$$BuMe_2Si$)Si: (**9s**), a close model of **1s**, the free energy activation barrier, $\Delta G_s^{\#}$ (at 298 K), for the intramolecular δ(C−H) bond insertion reaction is 21.5 kcal/mol. $\Delta G_s^{\#}$ increases somewhat upon decreasing the substituent's size, being 23.1, 24.1 and 29.1, kcal/mol for $i$$Pr_3Si(CH_3CH_2SiH_2)Si$: (**8s**), $Me_3Si(CH_3CH_2SiH_2)Si$: (**6s**), and $H_3Si(CH_3CH_2SiH_2)Si$ (**5s**), respectively. These barriers are similar to those calculated for the intramolecular C−H bond insertion in $Me_2HSiSiMe$, Me_3SiSiH, and $Me_3SiSiMe$ to form the corresponding disilacyclopropanes,[11,12,39] but they are significantly higher than the indirect experimental estimate for **1** of only 10 kcal/mol.[19] To test the reliability of the B3LYP calculations, the intramolecular insertion barrier ($\Delta E_s^{\#}$) for **5s** was calculated using a variety of DFT and *ab initio* methods (see Table 3S). We find a very good agreement between $\Delta E_s^{\#}$ calculated at B3LYP/6-31+G(d,p) (30.1 kcal/mol) and those calculated at CCSD(T)/cc-PVTZ (28.0 kcal/mol) and SCS-MP2/cc-PVTZ (28 kcal/mol). Close agreement was also found for $\Delta E_s^{\#}$ of the intramolecular insertion of **9s** calculated at B3LYP/6-31+G(d,p) (22.7 kcal/mol) and that calculated at SCS-MP2/cc-PVTZ (22.2 kcal/mol). The above calculations support the reliability of the DFT-calculated activation barriers for the singlet-state insertion reaction.



9s (b) **9t (e)**

Figure 3. Calculated (B3LYP/6-31+G(d,p)) transition state structures **b** and **e** (bond lengths in Å, bond angles in degrees) for the intramolecular δ(C−H) bond insertion in singlet silylene **9s** and triplet silylene **9t**.

Intramolecular δ(C−H) Bond Insertion of Triplet Silylenes. The mechanism for intramolecular δ(C−H) bond insertion of triplet-state silylenes **d**, leading to product **c**, consists of two steps (Figure 2). In the first step, which is the rate-determining step, a δ-hydrogen is abstracted by the silylenic silicon atom via transition state **e**, forming a triplet 1,4-biradical, **f-triplet**. For **6t**, **8t**, and **9t**, TS **e** is calculated to be relatively "late", with the δ(C−H) bond r^2 in TS **e** significantly elongated to ca. 1.69 Å

Table 3. Calculated Relative Energies (kcal/mol),[a] Selected Bond Lengths (r, Å),[b] and SiSiSi Bond Angle (α, deg) of Stationary Points c–f along the Intramolecular δ(C–H) Bond Insertion Path of Triplet Silylenes 5t, 6t, 8t, and 9t

		energy				geometry[b]			
silylene	stationary point[b]	ΔE or $\Delta E^{\#}$	ΔE or $(\Delta E + \text{ZPE})^{\#}$	ΔH or $\Delta H^{\#c}$	ΔG or $\Delta G^{\#c}$	α	r^1	r^2	r^3
5t	**d**	0.0	0.0	0.0	0.0	126.4	3.520	1.096	4.009
6t		0.0	0.0	0.0	0.0	127.2	3.526	1.096	4.018
8t		0.0	0.0	0.0	0.0	128.3	3.523	1.096	4.015
9t		0.0	0.0	0.0	0.0	133.4	3.647	1.095	3.506
5t[d]	e (TS)	33.1	28.4	28.0	29.7	126.8	1.621	1.674	3.039
6t		33.5	28.6	32.3	29.4	127.5	1.626	1.678	3.058
8t		33.6	28.5	28.3	29.0	129.7	1.624	1.681	3.058
9t		34.7	30.3	29.8	32.3	135.0	1.617	1.691	3.033
6t	**f-triplet**	19.4	14.8	19.4	14.3	121.9	1.496	3.906	3.967
8t		19.9	15.2	15.7	14.9	123.6	1.496	3.852	3.970
9t		21.7	17.8	18.1	18.8	132.5	1.498	3.776	3.803
6t	**f-singlet**[e]	18.8	14.2	18.7	14.8	120.9	1.497	4.007	4.170
5t	c (singlet)	−31.5	−33.1	−33.8	−29.9	–	1.493	–	1.938
6t		−30.3	−32.1	−28.7	−29.5	–	1.498	–	1.942
8t		−29.6	−31.7	−32.2	−29.1	–	1.498	–	1.944
9t		−30.7	−32.1	−32.7	−28.9	–	1.500	–	1.945

[a] At UB3LYP/6-31+G(d,p)//UB3LYP/6-31+G(d,p). [b] See definitions in Figure 2. [c] At 298 K. [d] At MP2/6-31+G(d,p), $\Delta E^{\#}$, $(\Delta E + \text{ZPE})^{\#}$, $\Delta H^{\#}$, and $\Delta G^{\#}$ are 41.9, 37.0, 36.6, and 38.4 kcal/mol, respectively. At CCSD(T)/cc-PVTZ, $\Delta E^{\#}$ = 36.5 kcal/mol. For reaction barriers calculated at additional computational levels, see Table 3S. [e] Located only for silylene **6**.

from that in triplet silylene **d** (1.096 Å), while the forming Si–H bond (r^1) is significantly shortened from 3.5 Å in **d** to 1.62 Å in TS **e**. The SiSiSi angle is hardly changed between **d** and **e** (Table 3, Figure 3). In the second step, the **f-triplet** crosses to the singlet biradical, **f-singlet**. For silylenes **4** and **6**, the energy difference between singlet and triplet intermediates **f** is only ca. 0.7 kcal/mol (in favor of the singlet state).[40] In the second step a Si–C bond is formed via transition state **g**, leading to the 1,2-disilacyclobutane product **c**.[41] For triplet H($CH_3CH_2SiH_2$)Si: (**4t**), TS **g** lies only 0.6 kcal/mol $(\Delta E + \text{ZPE})^{\#}$ above **f-singlet**. Unfortunately, TS **g** could not be located for **6t**, **8t**, and **9t**, but it is reasonable to assume based on the calculations for **4t** that it lies close in energy to the corresponding **f-singlet**, or that once **f-singlet** is formed it collapses without a barrier to product **c**.

The main conclusion from Table 3 is that for all four triplet silylenes the rate-determining activation barriers for intramolecular insertion are high, with $\Delta G^{\#}$ = 29.7 [38.4 at MP2/6-31+G(d,p)], 29.4, 29.0, and 32.3 kcal/mol for **5t**, **6t**, **8t**, and **9t**, respectively.[42] All attempts to locate a lower energy barrier for **9t** failed. Thus, $\Delta G^{\#}$ for the triplet state of iPr$_3$Si-(tBuMe$_2$Si)Si: (**9t**) is by 10.8 kcal/mol (B3LYP/6-31+G(d,p)) higher than for the insertion reaction of the corresponding singlet-state silylene **9s** (Tables 2 and 3).

While a good agreement was found between the reaction barriers ($\Delta E_s^{\#}$) calculated for **5s** at B3LYP and a variety of *ab initio* methods (Tables 2 and 3S), calculations for the intramolecular C–H insertion reaction of **5t** reveal that $\Delta E_t^{\#}$ values calculated using *ab initio* methods are higher, by 3–9 kcal/mol, than those calculated at B3LYP/6-31+G(d,p) (Table 3S). For example, $\Delta E_t^{\#}$ (**5t**) = 41.9 at MP2/6-31+G(d,p), 40.1 kcal/mol at SCS-MP2/cc-PVTZ//B3LYP/6-31+G(d,p), and 36.5 kcal/mol at CCSD(T)/cc-PVTZ//B3LYP/6-31+G(d,p), compared to 33.1 kcal/mol at B3LYP/6-31+G(d,p). Thus, for **5**, $\Delta\Delta E^{\#} = \Delta E_t^{\#} - \Delta E_s^{\#}$, the energy difference between the activation barriers for the two states, is actually larger with *ab initio* methods than that calculated at B3LYP/6-31+G(d,p); i.e., $\Delta\Delta E^{\#}$ for **5** changes from 3 kcal/mol at B3LYP/6-31+G(d,p) to 9 kcal/mol at CCSD(T)/cc-PVTZ, to 12 kcal/mol at SCS-MP2/cc-PVTZ, and to 14.5 kcal/mol at MP2/6-31+G(d,p) (Table 3S). For **9**, $\Delta\Delta E^{\#}$ = 20.1 kcal/mol at SCS-MP2/cc-PVTZ, compared to 11.9 kcal/mol at B3LYP/6-31+G-(d,p).[42,43] The *ab initio* calculations indicate that B3LYP/6-31+G(d,p) underestimates the barriers for the triplets and thus $\Delta\Delta E^{\#}$ by ca. 6–8 kcal/mol.

Taking this correction into account, we estimate that the Gibbs free energy of activation, $\Delta G_t^{\#}$, for the intramolecular insertion reaction of triplet silylene **9t** and thus of the closely related experimentally studied silylene **1** and **2** is by as much as ca. 17 kcal/mol higher in energy than that of singlet silylene **9s**. Thus, the calculations predict that at room temperature the insertion reactions of **1** and **2** proceed some *10^{12} times faster from the singlet state than from the triplet state.*

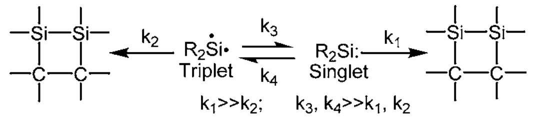
Mechanistic Implications. The formation of a 1,2-disilacyclobutane product by an intramolecular δ(C–H) bond insertion reaction of silylenes (iPr$_3$Si)(tBu$_3$Si)Si: (**1**) and (tBu$_3$Si)$_2$Si: (**2**) in the absence of trapping reagents led previous researchers to conclude that these silylenes react from their triplet electronic state.[17−19,22] For **1** this conclusion was largely based on two considerations: (1) the computational prediction that the triplet and singlet states are nearly isoenergetic[16b,c] and thus may be in fast equilibrium even if the triplet is slightly higher in energy, and (2) the assumption that triplet silylenes insert much faster intramolecularly into C–H bonds than singlet silylenes.[16c,18,19,22] Silylene **2** was concluded to have a triplet ground state on the basis of its EPR spectrum[17] and on theoretical calculations,[16b] and it was thus assumed that the 1,2-disilacyclobutane insertion product is obtained from the triplet state,[17] similarly to **1**.[16c,18,19]

The calculations presented in this paper clearly show that the barrier for the intramolecular δ(C−H) bond insertion of $(i\mathrm{Pr_3Si})(t\mathrm{BuMe_2Si})\mathrm{Si}$: (**9**), a close model to the experimentally studied silylenes **1** and **2**, is significantly higher for insertion from the triplet state than from the singlet state. For triplet **9**, $\Delta G_t^{\#}$ = 32.3 kcal/mol ($\Delta E_t^{\#}$ = 34.6 kcal/mol at B3LYP/6-31+G(d,p) and 41.3 kcal/mol at SCS-MP2/cc-PVTZ), compared to $\Delta G_s^{\#}$ = 21.5 kcal/mol ($\Delta E_s^{\#}$ = 22.7 kcal/mol at B3LYP/6-31+G(d,p) and 22.2 kcal/mol at SCS-MP2/cc-PVTZ) for the singlet state **9s**. Thus, the difference between the activation energies of the triplet and singlet states, $\Delta\Delta E^{\#}$, is very large, 11.9 kcal/mol at B3LYP/6-31+G(d,p) and 20.1 kcal/mol at SCS-MP2/cc-PVTZ. Corrections based on higher level calculations for smaller silylenes (see discussion above and Table 3S) leads us to estimate that, *for* **9**, *$\Delta G_t^{\#}$ is ca. 17 kcal/mol larger than $\Delta G_s^{\#}$*. These activation energies imply that *singlet* disilylsilylenes insert intramolecularly into a δ(C−H) bond at room temperature by a factor of ca. *10^9−10^{12} faster* (depending on the level of calculations) than the corresponding *triplet* silylenes, contrary to the earlier assumptions.[17−19,22] Furthermore, tunneling is expected to further favor the singlet reaction vs the triplet reaction because of its significantly lower reaction barrier.[44] It is also safe to conclude that, although the calculations explicitly describe reactions in the gas phase, they are valid also in solution, especially as the studied reaction is intramolecular, involves neutral species, and occurs in a nonpolar solvent, methylcyclohexane. Furthermore, the calculated difference in the reactivities of the singlet and triplet states, $\Delta\Delta E^{\#}$, is much larger than a possible computational error or a solvent effect.

On the basis of the calculations, we conclude that although **1** has nearly degenerate singlet and triplet states and **2** has a triplet ground state, as predicted theoretically[16] (Table 1) and verified experimentally,[2,17] *the intramolecular δ(C−H) bond insertion reactions observed for these silylenes*[17−19] *occur predominantly from the singlet state whether a ground state or not, in contrast to previous conclusions.*[17−19] *Therefore, the occurrence of an intramolecular δ(C−H) bond insertion does not indicate the presence of a triplet silylene, and it cannot be used to indicate that a particular silylene has a triplet ground state or reacts via the triplet state.*

Our proposed mechanism for the intramolecular insertion of **1** and **2** and related silylenes is shown in Scheme 3. According to this mechanism, the singlet and triplet states are in fast equilibrium relative to the reactions leading to products (k_3, $k_4 \gg k_1$, k_2).[45] The calculations show that at room temperature $k_1/k_2 \approx 10^9$−10^{12}, and therefore the reacting species is the singlet, while the much less reactive triplet is being "siphoned off", even if the triplet is the ground state (e.g., for **2**[46]).[47] Scheme 3 is a typical Curtin−Hammet principle situation,[48] where when a fast equilibrium between intermediates exists (k_3, $k_4 \gg k_1$, k_2), the products are determined by the intermediate that reacts faster, in this case the singlet state ($k_1 \gg k_2$). Even for $(t\mathrm{Bu_3Si})_2\mathrm{Si}$:, which no doubt is a triplet ground state[17] (calculated $\Delta E_{\text{S-T}}$ = 5.2 kcal/mol[16b]), intramolecular δ(C−H) bond insertion occurs from the singlet state "siphoning off" the much higher concentration of the triplet ground state, which however reacts at rt 10^9−10^{12} slower. For **2**, for which $\Delta E_{\text{S-T}}$ is significantly larger than for **1**, this can be also interpreted in terms of a two-state reactivity case, in which the triplet crosses to the singlet surface en route to the lower energy singlet TS **b**.[49]

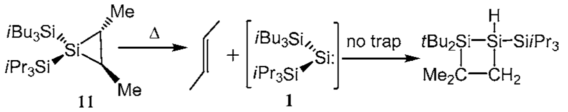
Scheme 3



If reaction products are to be used as a mechanistic tool for indicating the presence of a triplet-state silylene, then a different trapping reagent, which reacts faster with the triplet state than with the singlet state, has to be developed. However, the exploration of reactions of triplet silylenes is extremely difficult, as it might be difficult to compete with the much faster reactions of the singlet state, even in cases when the triplet state is significantly more stable than the singlet state.

A common chemical test to determine whether a singlet-state or a triplet-state species reacts is the stereochemistry observed upon addition to *cis*- or *trans*-2-butene. Generally singlet addition yields retention of stereochemistry while triplet addition yields *cis*−*trans* product mixtures (Skell's rule).[50] Confirmed singlet silylenes, such as 1-$\mathrm{Ad_2Si}$:, indeed yield retention of stereochemistry when added to *cis*- or *trans*-2-butene.[14] Kinetic studies of the thermal decomposition of silirane **11** (Scheme 4) have shown that the extrusion of **1** is concerted and stereospecific.[19] Microscopic reversibility[48] dictates that the addition of silylene **1** to *trans*-2-butene must also be stereospecific.[19] The addition of $(i\mathrm{Pr_3Si})_2\mathrm{Si}$: (**10**), for which the singlet and triplet states are also calculated to be nearly isoenergetic,[16b,c] to *cis*- and *trans*-2-butene forming silirane is also stereospecific.[18b,c,19] However, the authors stated that the observed streospecificity is not necessarily an indication that the reacting species is the singlet silylene, as stereospecificity may be observed also if the triplet state is the reacting species but rotation about the C−C bond in the intermediate biradical is slow relative to triplet−singlet intersystem crossing and ring closure to yield the silirane.[18b,c,19]

Scheme 4



Based on the results of our study, a more straightforward explanation of the stereospecificity in these fragmentation−addition reactions is that the reacting (or forming) species is the singlet state, "siphoning away" the triplet state if formed. Unfortunately **2**, a triplet ground state, does not add to *trans*-2-butene, probably due to steric reasons.[17] It would be very interesting to study the stereochemistry of the addition of $t\mathrm{Bu_3SiSiLi}$, clearly a ground-state triplet,[20] to *cis*- and *trans*-2-butene. This may reveal for the first time the chemistry of a triplet silylene.[51]

■ CONCLUSIONS

The calculations reported in this paper clearly show that the observed intramolecular δ(C−H) bond insertion product from silylenes **1** and **2** results from reactions of the singlet-state silylenes, in contrast to previous conclusions[17−19] that these reactions occur from the triplet state. The reacting species are the singlet states, although **2** is a triplet ground state and for **1** the singlet and triplet states are nearly isoenergetic. The calculations predict that the intramolecular C−H bond insertion reaction of the singlet state is 10^9−10^{12} faster at rt than that from the triplet state, and therefore the intramolecular insertion reaction *does not* indicate the presence of a *triplet* silylene, even in cases where the triplet state is significantly more stable than the singlet state. If products are to be used as probes for the presence of triplet ground-state silylenes, then other reactions, in which the triplet reacts at a similar rate or preferably faster than the singlet, need to be found.[51]

In conclusion, reactions of triplet silylenes have not yet been observed, and it remains a challenge to explore their chemistry and reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculated Cartesian coordinates and total energies of the species discussed in the paper (Table 1S); $\Delta E_{\text{S-T}}$ of silylenes calculated with the inclusion of dispersion effects (Table 2S); Calculated reaction barriers for silylenes **5** and **9** at several DFT and *ab initio* levels of calculations (Table 3S); $\Delta E_{\text{S-T}}$ of singlet and triplet $(H_3Si)_2Si$ as a function of their SiSiSi bond angle (Figure 1S). This material is available free of charge via Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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(35) Curves of $\Delta E_{S\text{-}T}$ for singlet and triplet $(H_3Si)_2Si$ as a function of α are shown in Figure 1S.

(36) For singlet **9s**, a conformational analysis was performed using the Universal Force-field with the "Conformers" module of the Accelrys Materials Studio 6.0 package. This analysis resulted in 22 465 structures. Those were further divided into 10 clusters on the basis of geometrical parameters. Ten structures (one from each cluster) with the largest RMS geometry deviation from each other and from all the rest were subject to B3LYP/6-31+G(d,p) optimizations. The largest energy difference among these conformers is only 3.5 kcal/mol, showing that the orientation of the substituents has a relatively small effect on the energies. For **9t**, and for the TSs for the insertion reaction from both the singlet and triplet silylenes, we carried out several full geometry optimizations starting from different rotational conformers, but the resulting structures for each of them differed by no more than 1 kcal/mol. The discussion in the paper is based on the most stable singlet and triplet conformers of **9** and their corresponding lowest energy transition structures.

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(38) The calculated Gibbs free energy exothermicity of the intramolecular C−H bond insertion reaction of $Me_3SiSiMe$ to form the corresponding disilacyclopropane is even smaller, 13.9 kcal/mol (aug-cc-PVTZ).[12]

(39) (a) The intermolecular C−H insertion barriers of SiH_2 into the C−H bond of C_2H_6 and of Me_2Si: and $(H_3Si)_2Si$: into the C−H bond of CH_4 are 29.1 (MP4/6-31G(d)//HF/3-21G),[37] 23.6, and 15.3 kcal/mol (B3LYP/6-31+G(d,p)), respectively. The lower barrier for the insertion of $(H_3Si)_2Si$: relative to those of H_2Si and Me_2Si is in agreement with the predicted correlation between $\Delta E_{S\text{-}T}$ and the insertion barrier.[13]

(40) The **f-singlets** of **8** and **9** could not be located, as they collapse to the products.

(41) Dissociation of the **f-singlet** to ethylene and disilene was also considered, but the high barrier for this reaction (ca. 28 kcal/mol for **6** and **8**) suggests that this reaction route does not compete with ring closure to form the disilacyclobutane product (also when entropy is included).

(42) We note that the size of the substituents has a very small effect on the energy barrier of the rate-determining step for the intramolecular C−H bond insertion reactions of the triplet state, while in the singlet state the energy barrier decreases for silylenes with larger substituents (Tables 2, 3, and 3S).

(43) For $Me_3SiSiMe$, $\Delta\Delta G^{\#} = \Delta G_t^{\#} - \Delta G_s^{\#} = 26.3$ kcal/mol at MP2/aug-cc-PVTZ.[12]

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(45) (a) Fast equilibrium between the singlet and triplet states of **1** was previously suggested by Gaspar et al., who, however, attributed the intramolecular δ(C−H) bond insertion observed for **1** and its intermolecular Si−H insertion into trimethylsilane to the triplet state.[18,19] This mechanism, involving fast singlet−triplet equilibrium and an assumption that the triplet reacts faster than the singlet, was later reiterated in a computational study by Yoshida et al.[16c]

(46) The Supporting Information of ref 17 states that the photolysis of the silirane which forms disilacyclobutane (at ca. 147 K), via silylene **2** as an intermediate, was repeated 45 times in order to accumulate enough disilacyclobutane for an NMR study. This low productivity is consistent with the calculations and is due to the low population of singlet **2** at 147 K ($[S]/[T] \approx 10^{-11}$). However, despite this low singlet population, because the reaction of singlet silylene at 147 K (we also note that the actual temperature at which the insertion reaction occurs is probably higher than 147 K: A. Sekiguchi, private correspondence) is 10^{16}−10^{25} times faster than that of the triplet, also at this low temperature **2** reacts from its singlet state, "siphoning off" the triplet silylene.

(47) (a) Even if the triplet-to-singlet intersystem crossing rate is relatively slow,[47b] the calculated 10^9−10^{12} faster reaction rate of the singlet-state silylene dictates that the insertion product formation occurs from the singlet state. (b) For SiH_2 the Landau−Zener calculated transition probability is 3% for the singlet-to-triplet crossing. See: Matsunaga, N.; Koseki, S.; Gordon, M. S. *J. Chem. Phys.* **1996**, *104*, 7988−7995.

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