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Computational Study of Isomerization Reactions of Silacyclopropene

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CASPT2//CASSCF and hybrid DFT calculations have found that the barrier to the concerted ring opening of silacyclopropene (**1**) to vinylsilylene (**2**) is lower than the barrier to forming silylacetylene (**5**). The ΔZPE-corrected barriers, obtained by (12,12)CASPT2 calculations, are 32.2 and 38.7 kcal/mol, respectively, and the corresponding values obtained by B3LYP calculations are 35.8 and 42.2 kcal/mol. Rearrangement of **1** to silylvinylidene (**3**) is predicted to be the rate-determining step in the formation of **5**. The barrier to ring closure of **2** to **1** is computed to be 31.5 kcal/mol by (12,12)CASPT2 and 31.7 kcal/mol by B3LYP. The CASPT2 barrier height is essentially the same as that for rearrangement of **2** to 1-silaallene (**4**), but B3LYP predicts that the formation of **4** from **2** requires ca. 3 kcal/mol less than closure of **2** to **1**. Our results thus support the hypothesis that the observed generation of equal amounts of the two isotopomers of **1** from monodeuterated **2** is the result of a kinetically competitive equilibrium between **2** and **4**. Interconversion between **4** and **5** by two consecutive [1,2]-hydrogen shifts and involving formation of diradical **6** is found to be prevented by high energy barriers (>70 kcal/mol).

Introduction

Walsh et al. have studied the kinetics of the addition of silylene (SiH_2) to ethene[1] and to acetylene.[2] In each system opening of an initially formed three-membered ring to a silylene, generating respectively ethylsilylene (CH_3CH_2SiH) and vinylsilylene ($H_2C{=}CHSiH$), was proposed.

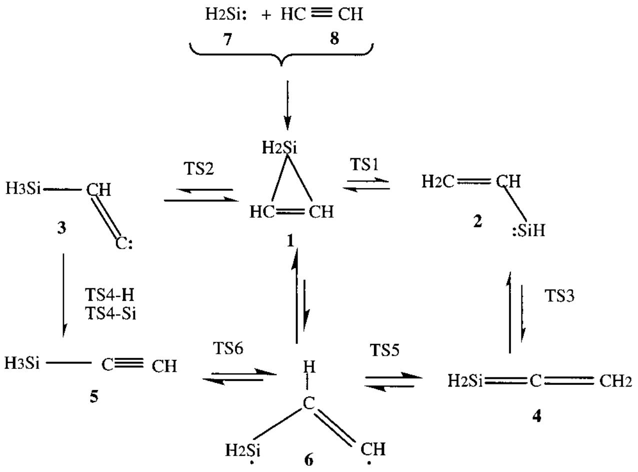
There is experimental evidence for formation of ethylsilylene from silirane,[3] and in a previous computational study we found a retrograde C−H insertion reaction to form ethylsilylene to be, by far, the lowest energy pathway for silirane ring opening.[4] Experimental[5] and computational[6] studies of the ring-opening reactions of substituted siliranes have reached the same conclusion.

Experimental evidence for ring opening of silirene (**1**) to vinylsilylene (**2**) also exists, for both the unsubstituted parent[3a,7] (Scheme 1) and derivatives.[8] It was for the latter that the occurrence of this type of retrograde C−H insertion reaction was first proposed by Barton.[8]

Walsh proposed a second mode of ring opening for **1**, involving retrograde Si−H bond insertion to form silylvinylidene (**3**).[2] The intermediacy of silylvinylidenes provides an attractive mechanism for explaining the formation of silylacetylenes as the major products of silirene rearrangements.[3a,7−9] Analogy for **3** being formed from **1** and being the immediate precursor of silylacetylene (**5**) comes from computational[10] and experimental[11] studies that implicate propenylidene in the ring opening of cyclopropene.

Evidence for the reversible formation of 1-silaallene (**4**) from **2** was reported in a paper by Maier and co-workers that described the matrix isolation of **1**.[12] Flash vacuum pyrolysis of 1,1,1-trimethyl-2-vinyldisilane resulted in elimination of trimethylsilane, and formation of **2** as the primary pyrolysis product was confirmed by chemical trapping of it with butadiene. Although **2** was not among the molecules that were found in the matrix, **1** and **5** were identified. The authors postulated that **1** is formed from **2** by silylene insertion into the cis vinylic C−H bond, and they further speculated that rearrangement of molecules of **1**, formed with excess energy, leads to **5**, presumably via the intermediacy of **3**. Acetylene (**8**), which was also detected in the matrix, could also have been formed by fragmentation of “hot” molecules of **1**.

SCHEME 1



Although **4** was not detected by Maier and co-workers, they obtained evidence for its reversible formation by pyrolyzing a precursor that generated **2** with deuterium, rather than hydrogen, attached to silicon. Silylene insertion into the cis vinylic C−H bond should have led exclusively to **1** with deuterium still attached only to silicon. Instead, **1** was found to contain roughly equal amounts of deuterium attached to silicon and to carbon, and H/D scrambling was also observed in **5**.

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Maier interpreted these findings in terms of reversible formation of **4** from **2**. This interpretation requires that **4** be less thermodynamically stable than both **1** and **5**, because **4** was not detected in the product mixture. In addition, the rate of rearrangement of **2** to **4** by a 1,2-hydrogen shift must be at least competitive with the rate of closure of **2** to **1**.

However, reversible ring opening of **1** to **3** provides another possible mechanism for H/D scrambling in **1**. Minimal requirements for this mechanism to be viable are that **3** be a discrete intermediate and that it recloses to **1** faster than it isomerizes to **5**.

Maier and co-workers reported the results of MP2/6-31G** calculations on some of the possible intermediates on the C_2H_4Si potential surface. These calculations found that **4** is, indeed, considerably higher in energy than **1** and that **5** is lower in energy than **1** by 11.9 kcal/mol. Silylene **2** was computed to be only 9.1 kcal/mol higher in energy than **1** and 5.7 kcal/mol lower in energy than silaallene **4**. Similar results were obtained by Lien and Hopkinson at the RHF level of theory.[13] However, neither Maier nor Lien and Hopkinson reported the energies of the transition states connecting **2** to **1** and **4** or **1** to **5**.

Single-point QCISD calculations with larger basis sets by Vanquickenborne and co-workers[14] found nearly the same relative energies for **1**, **2**, and **5** as the MP2/6-31G** calculations of Maier and co-workers. The geometries of these three intermediates were optimized, and the transition states connecting **1** to **2** and **5** were located at the MP2/6-31G** level of theory. However, the energy of **4** was not reported, and the authors stated that they were unable to find a local minimum corresponding to vinylidene **3**. Since Maier and co-workers also performed MP2/6-31G** geometry optimizations, their failure to report an energy for **3** is also likely to have been due to their failure to find a local minimum for it.

Among the questions that were not addressed by either set of calculations are the following: (a) What is the energy of TS3, which connects **2** to **4**, relative to TS1, which connects **2** to **1**? (b) Does the failure of the MP2/6-31G** calculations to find an intermediate corresponding to **3** mean that 3-silylvinylidene is not an intermediate in this reaction, or is this failure an artifact of calculations performed at this particular level of theory? (c) If **3** does exist as a local energy minimum, is TS2 lower in energy than TS4, as required for **3** to be an intermediate in H/D exchange in **1**? (d) What role, if any, does diradical **6** play in the ring opening of **1** to **4** and **5**, and does **6** provide a low-energy pathway for the direct rearrangement of **4** to **5**?

To answer these questions, we have performed CASSCF, CASPT2, and DFT calculations on the molecules in Scheme 1 and on the transition states connecting them. In this paper we report the results of these calculations and discuss how they affect the interpretation of the experiments that have been performed on **1** and its isomers.

Computational Methodology

The geometries of the closed-shell molecules **1**, **4**, **5**, and **8** were optimized using RHF calculations, and MP2 single-point energies were computed at the optimized geometries.[15] The geometry of **7** was optimized by (2,2)CASSCF calculations, and its single-point energy was evaluated using (2,2)CASPT2 calculations.[16] For the species **2**, **3**, and **6** (4,4)CASSCF calculations, which correlated the pair of nonbonding electrons and the pair of π electrons in each double bond, were used in the optimizations, and single-point energies were evaluated using (4,4)CASPT2 calculations.

Two of the transition states, TS1 and TS2, were located using (6,6)CASSCF calculations, and (6,6)CASPT2 energies were computed for these two transition states and for **1**−**3** as well. TS2 was also reoptimized using (10,10)CASSCF calculations (vide infra). In addition to the two pairs of electrons correlated in the (4,4)CASSCF and (4,4)CASPT2 calculations on **2** and **3**, the pair of electrons in the breaking R−H bond (R = Si in TS1 and R = C in TS2) was correlated in the (6,6)CASSCF and (6,6)CASPT2 calculations.

The other four transition states, TS3−TS6, were located using (4,4)CASSCF. For TS3 and TS4 both (4,4)CASPT2 and (6,6)-CASPT2 single-point energies were calculated. The very high energies computed at the (4,4)CASSCF level for TS5 and TS6 led us to omit performing (6,6)CASPT2 energy calculations for the former and any CASPT2 calculations for the latter. The 6-31G* basis set was used for all the calculations.[17]

Analytical vibrational frequencies were computed at each stationary point, using the same level of theory at which the geometry was optimized. Zero-point energies (ZPE) were evaluated from the unscaled vibrational frequencies obtained. All of the calculations were performed using the programs contained in Gaussian 94[18] or MOLCAS,[19] except for the (10,10)CASSCF calculations on TS2 which were carried out with GAMESS.[20]

To gauge the effect of increasing the sizes of the active spaces on the CASPT2 relative energies of the stationary points in Scheme 1, we also carried out CASPT2 calculations with the largest active space that was computationally feasible. Ideally calculations including all 16 valence electrons in 16 orbitals would have been performed, but such calculations were impossible with the hardware available to us. Therefore, except for **7**, **8**, and TS6, we carried out (12,12)CASSCF and (12,12)-CASPT2 calculations for all of the species in Scheme 1. In these calculations the 12 electrons in the six highest filled MOs were correlated, using the corresponding six virtual orbitals.

The optimized geometries of TS1−TS6 are shown in Figure 1. The CASSCF, MP2, and CASPT2 total and relative energies and the ZPE corrections to them are given in Table 1.

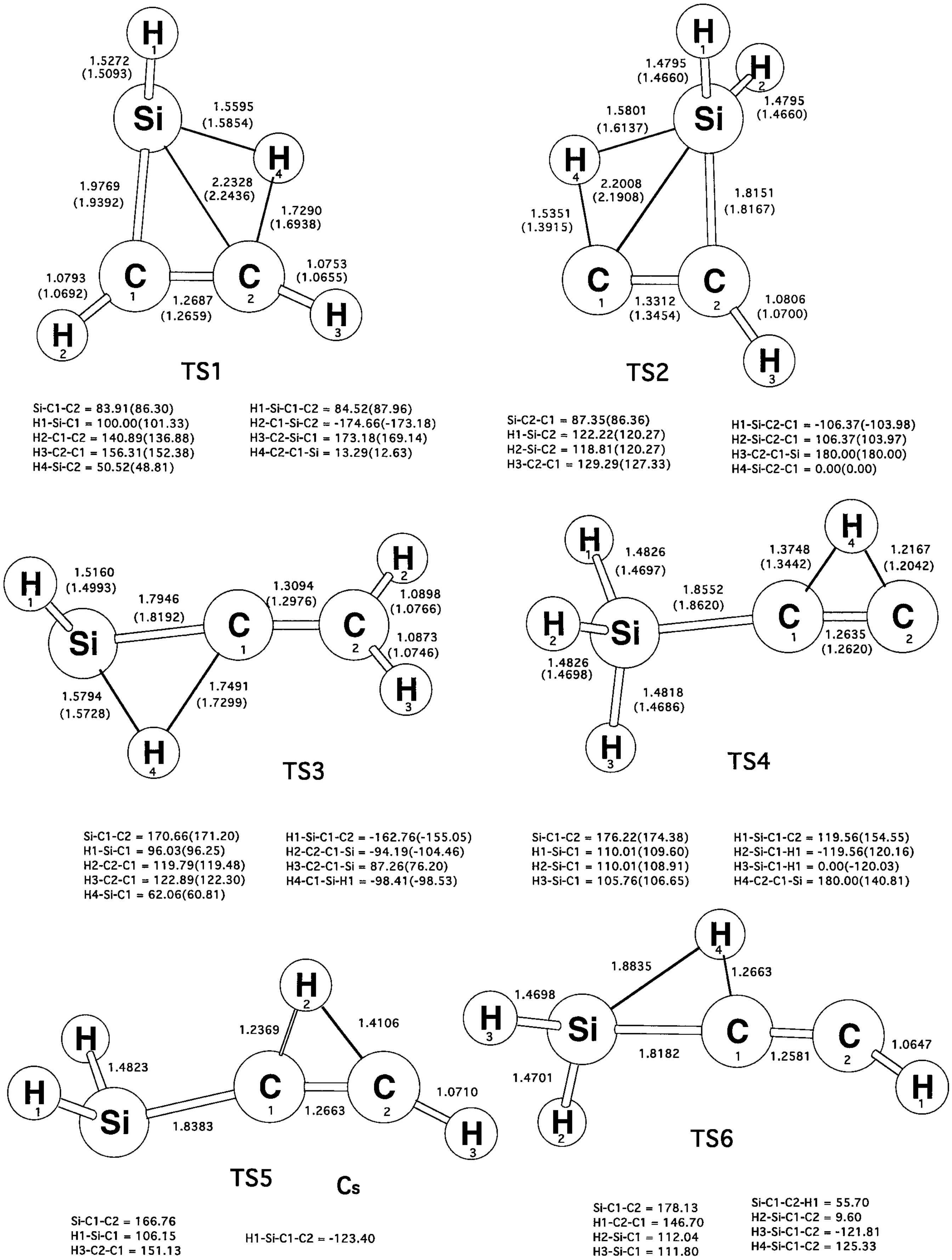
To obtain an additional assessment of the reliability of our theoretical predictions we also carried out density functional theory (DFT) calculations,[21] using Becke's 3-parameter (B3) hybrid-exchange functional[22] and the nonlocal correlation functional of Lee, Yang, and Parr (LYP).[23] Absolute and relative energies obtained by this method are given in Table 2, and the B3LYP-optimized geometries of TS1−TS4 are shown in Figure 1.

Results and Discussion

Absolute and relative energies obtained by CASPT2N//CASSCF calculations and zero-point energies are given in Table 1. Corresponding energies calculated by B3LYP are given in Table 2. Figure 2 shows the ZPE-corrected relative energies, obtained by the CASPT2N//CASSCF and B3LYP calculations.

The relative CASPT2 energies in Table 1 are seen to be fairly independent of the size of the active space chosen for the different species. Recovering more of the correlation energy of **1** variationally at the (12,12)CASPT2 level, rather than by MP2 perturbation theory, gives a systematic lowering of the energies of **2**−**8** and all of the transition states, relative to **1**, without any reordering of their sequence. The largest shifts in relative energies of ca. 7 kcal/mol are found for the silaallene **4** and the TS leading to it (TS3).

It is reassuring to note the rather good agreement between the (12,12)CASPT2 relative energies in Table 1 and the B3LYP



Si-C1-C2 = 83.91(86.30)
H1-Si-C1 = 100.00(101.33)
H2-C1-C2 = 140.89(136.88)
H3-C2-C1 = 156.31(152.38)
H4-Si-C2 = 50.52(48.81)

H1-Si-C1-C2 = 84.52(87.96)
H2-C1-Si-C2 = -174.66(-173.18)
H3-C2-Si-C1 = 173.18(169.14)
H4-C2-C1-Si = 13.29(12.63)

Si-C2-C1 = 87.35(86.36)
H1-Si-C2 = 122.22(120.27)
H2-Si-C2 = 118.81(120.27)
H3-C2-C1 = 129.29(127.33)

H1-Si-C2-C1 = -106.37(-103.98)
H2-Si-C2-C1 = 106.37(103.97)
H3-C2-C1-Si = 180.00(180.00)
H4-Si-C2-C1 = 0.00(0.00)

Si-C1-C2 = 170.66(171.20)
H1-Si-C1 = 96.03(96.25)
H2-C2-C1 = 119.79(119.48)
H3-C2-C1 = 122.89(122.30)
H4-Si-C1 = 62.06(60.81)

H1-Si-C1-C2 = -162.76(-155.05)
H2-C2-C1-Si = -94.19(-104.46)
H3-C2-C1-Si = 87.26(76.20)
H4-C1-Si-H1 = -98.41(-98.53)

Si-C1-C2 = 176.22(174.38)
H1-Si-C1 = 110.01(109.60)
H2-Si-C1 = 110.01(108.91)
H3-Si-C1 = 105.76(106.65)

H1-Si-C1-C2 = 119.56(154.55)
H2-Si-C1-H1 = -119.56(120.16)
H3-Si-C1-H1 = 0.00(-120.03)
H4-C2-C1-Si = 180.00(140.81)

Si-C1-C2 = 166.76
H1-Si-C1 = 106.15
H3-C2-C1 = 151.13

H1-Si-C1-C2 = -123.40

Si-C1-C2 = 178.13
H1-C2-C1 = 146.70
H2-Si-C1 = 112.04
H3-Si-C1 = 111.80

Si-C1-C2-H1 = 55.70
H2-Si-C1-C2 = 9.60
H3-Si-C1-C2 = -121.81
H4-Si-C1-C2 = 125.33

Figure 1. Optimized geometries for TS1−TS4 using B3LYP/6-31G* calculations. Values in parentheses are obtained by (6,6)CASSCF/6-31G* for TS2 and by (4,4)CASSCF/6-31G* calculations for TS1, TS3, and TS4. Optimized geometries for TS5 and TS6 are obtained by (4,4)CASSCF/6-31G* calculations. Bond lengths are in Å and angles in degrees.

TABLE 1: Absolute Energies (hartrees), ZPE (kcal/mol), Relative Energies (Δ*E*, kcal/mol), and ZPE-Corrected Relative Energies (kcal/mol) for C_2H_4Si, Computed with the 6-31G* Basis Set[a]

	$E_{CAS(n,n)}$			E_{CASPT2}					ΔE_{CASPT2}			Δ*E*(12,12)
species	(4,4)	(6,6)	(12,12)	(0,0)	(4,4)	(6,6)	(12,12)	ZPE	(*n*,*n*)[b]	(6,6)	(12,12)	+ ΔZPE
1		366.96118	367.01454	367.24439		367.24830	367.25212	31.7	0	0		0
2	366.93793		367.02108		367.24135		367.25173	32.2	1.9		0.2	0.7
3	366.90445		366.99632		367.18874		367.20185	27.8	34.9		31.5	27.6
4	366.92332		366.99613	367.22155			367.24070	30.9	14.3		7.2	6.4
5	366.98268		367.07268	367.25845			367.27256	29.6	−8.8		−12.8	−14.9
6	366.88982		366.99043		367.19581		367.20522	29.0	30.5		29.4	26.7
7 + **8**				367.15792[c]				26.4	54.3[c]			
TS1		366.88927	366.94940			367.18233	367.19529	28.2	38.9	41.4	35.7	32.2
TS2		366.87813	366.93739			367.16974	367.18353	27.4	46.8	49.3	43.0	38.7
TS3	366.85860	366.88729	366.95223		367.17711	367.18402	367.19593	28.7	42.2	40.3	35.3	32.3
TS4−H	366.88825	366.91462	366.96254		367.17500	367.18010	367.18981	25.2	43.5	42.8	39.1	32.6
TS4−Si	366.90270		366.99515				367.20470	27.4			29.8	25.5
TS5	366.81411		366.92496		367.13378		367.14369	25.1	69.4		68.0	61.4
TS6	366.80856							25.3				

[a] Imaginary frequencies (cm^{-1}): TS1, 1184i; TS2, 1025i; TS3, 1513i; TS4−H, 1265i; TS4−Si, 194i; TS5, 2133i; TS6, 1182i. [b] For **1**, **4**, and **5** $n = 0$ (i.e., energies are MP2//RHF); for **2**, **3**, **6**, TS3, TS4−H, and TS5 $n = 4$; and for TS1 and TS2 $n = 6$. [c] Value based on CASPT2//(2,2)CASSCF for **7** + MP2//RHF for **8**.

TABLE 2: Absolute Energies (hartrees), ZPE (kcal/mol), Relative Energies (Δ*E*, kcal/mol), and ZPE-Corrected Relative Energies for C_2H_4Si Obtained by B3LYP Calculations with the 6-31G* Basis Set

species	*E*	ZPE	Δ*E*	Δ*E* + ΔZPE
1	−368.02825	29.4	0	0
2	−368.02358	30.6	2.9	4.1
3	−367.97496	25.9	33.4	29.9
4	−368.01286	28.6	9.7	8.9
5	−368.03930	27.4	−6.9	−8.9
7 + **8**	−367.93879	24.1	56.1	50.8
TS1	−367.96756	27.1	38.1	35.8
TS2	−367.95581	26.1	45.5	42.2
TS3	−367.97288	27.0	34.7	32.3
TS4−H	−367.96151	23.9	41.9	36.4

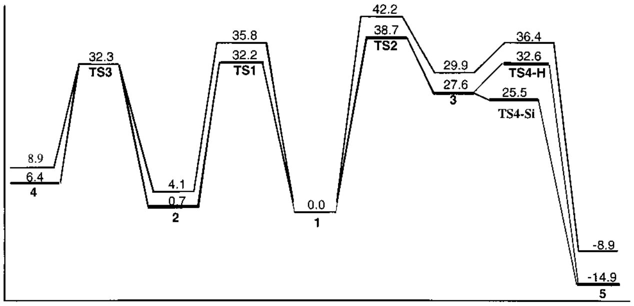


Figure 2. Relative energies (kcal/mol), corrected for differences in ZPE. Bold lines represent (12,12)CASPT2 and thin lines represent B3LYP energies, calculated with the 6-31G* basis set.

relative energies in Table 2. Except for **5**, the (12,12)CASPT2 energies, relative to that of **1**, are all 1−3 kcal/mol lower than those computed by B3LYP.

At both levels of theory **1** and **2** are found to have very similar energies. Therefore, since **3** is computed to be >30 kcal/mol higher in energy than **1**, it is perhaps not surprising that opening of the ring in **1** to form **2** via TS1 is computed to require ca. 7 kcal/mol less energy than ring opening via TS2 to **3**.

The barrier to H-migration in **3** via TS4-H in the very exothermic reaction to form **5** is substantially lower than the corresponding barrier to shift of hydrogen via TS3 in the slightly endothermic rearrangement of **2** to **4**. In fact, after correction for ZPE differences, TS2 is also computed to be ca. 6 kcal/mol higher in energy than TS4-H. Therefore molecules that cross TS2 have more than enough energy to cross TS4-H to form **5**, which our calculations find to be the lowest energy species in Scheme 1.

Since barriers to silyl migrations are frequently quite low,[24] we also investigated the rearrangement of **3** to **5** by a [1,2]-silyl shift. At the (4,4)CASSCF level we located a transition state for this process (TS4-Si), 1.1 kcal/mol above **3** at the (4,4)-CASSCF level and 1.8 kcal/mol higher at (12,12)CASSCF. However, upon including dynamic correlation, TS4-Si was actually found to have a (12,12)CASPT2N energy 1.7 kcal/mol below that of the carbene.

At the B3LYP level **3** was found to have a vibrational frequency of only 20 cm^{-1}, associated with a normal mode that leads to a [1,2]-silyl migration. An attempt actually to locate TS4-Si by B3LYP calculations failed. Our CASPT2 and B3LYP calculations both indicate that, if a potential energy minimum for **3** exists at all, it must be extremely shallow. Therefore, since **3** is at best a very transient intermediate in the rearrangement of **1** to **5**, its reclosure to **1** cannot be the pathway by which hydrogen scrambling occurs in the experiment performed by Maier and co-workers.[12]

As already noted, Vanquickenborne and co-workers were unable to locate an equilibrium structure corresponding to the carbene **3** with the MP2/6-31G** geometry optimizations that they employed.[14] In fact, when we tried to reoptimize the (4,4)-CASSCF equilibrium geometry of **3** at the MP2/6-31G** level of theory, we found that this geometry optimization led to **5**, thus confirming the finding of Vanquickenborne and co-workers that **3** is not an intermediate on the MP2/6-31G** potential energy surface.

The geometry and relative energy of the transition state, found by Vanquickenborne and co-workers to connect **1** and **5**, indicate strongly that it corresponds to our TS2, which connects **1** to **3**. IRC calculations at the (10,10)CASSCF level demonstrated unequivocally that our TS2 does, indeed, connect **1** to **3**. In our calculations the energy of TS2 is computed to be >7 kcal/mol higher than that of both TS1 and TS3. Therefore, equilibration of **1**, **2**, and **4** should be much faster than rearrangement of **1** to **5**.

Although our calculations find **1** and **2** to have similar energies, the energy of **4** is calculated to be higher than that of both **1** and **2**. The latter finding is in agreement with the experimental fact that **4** is not observed when **1** is generated from either the rearrangement of **2** or from the addition of silylene (**7**) to acetylene (**8**).

Our computational results are consistent with the suggestion by Maier and co-workers that reversible rearrangement of **2** to **4** provides a pathway for the H/D scrambling that they observed in the formation of **1** from **2**-d_1.[12] After correction for ZPE differences, the (12,12)CASPT2 energies of TS1 for ring closure of **2** to **1** and TS3 for hydrogen scrambling in **2** via formation of **4** are essentially identical. The differences in entropies and heat capacities between TS1 and TS3 do not alter this conclusion. The $T\Delta S$ and $T\Delta C_v$ corrections at 500 K are found to be 0.4 and 0.2 kcal/mol, respectively. On the other hand, our B3LYP calculations predict that TS1 is >3 kcal/mol higher in energy than TS3, which leads to the expectation that H/D scrambling in **2** should be faster than formation of **1**. The report by Maier and co-workers that "the silacyclopropene isotopomers ... are formed in approximately the ratio 1:1",[12] is, at least superficially, in better agreement with our B3LYP results.

However, since **5** is apparently also formed under the conditions used to generate **2** by flash vacuum pyrolysis, an appreciable fraction of the molecules of **2** must be formed with enough excess energy to rearrange to **1** and then pass over TS2, before being thermally deactivated. Since our CASPT2 and B3LYP calculations both find TS2 to be considerably higher in energy than TS1 and TS3, it seems likely that an even larger fraction of the molecules of **2** are formed with enough excess energy to rearrange to **1** and then recross TS1 back to **2**. If, under the reaction conditions, formation of **1** from **2** is reversible, TS3 need not be lower in energy than TS1 in order for nearly equal amounts of the two possible isotopomers of **1**-d_1 to have been observed.[25]

It is possible that ring opening of **1** to diradical **6**, followed by a hydrogen shift from carbon to silicon, might provide a lower energy pathway from **1** to **5** than passage over TS2. Similarly, a hydrogen shift from C-2 to C-1 in **6** would afford an alternative pathway from **1** to **4**. To investigate these two possibilities, we attempted to optimize a geometry for diradical **6**.

(4,4)CASSCF optimization of an assumed planar geometry of **6** gave a stationary point having an energy of 59.9 kcal/mol above that of **1** but with an imaginary vibrational frequency of 184i cm^{-1}. The corresponding energy and frequency obtained by UDFT calculations were 63.3 kcal/mol and 802i cm^{-1}. In both sets of calculations the vibrational mode associated with the imaginary frequency is a twist around the Si−C bond.

At the (4,4)CASSCF level it was possible to optimize the geometry of a nonplanar intermediate in the ring closure of **6** to **1**, which was separated from **1** by a barrier of 2.3 kcal/mol. IRC calculations at this level confirmed that the transition state at the top of this barrier does connect the intermediate to **1**. However, when the CASSCF active space was expanded to (12,12) or when dynamic electron correlation was included at either the (4,4)- or (12,12)CASPT2 levels, the energy of the (4,4)CASSCF transition state for ring closure dropped well below that of the intermediate.

The (12,12)CASSCF and CASPT2 results strongly suggest that there really is no intermediate in the ring closure of **6** to **1**. The apparent existence of such an intermediate in the (4,4)-CASSCF calculations is an artifact, caused by an overestimation at this level of theory of the barrier to inversion of the pyramidalized silyl radical center in this putative intermediate.[26] Upon inclusion of sufficient electron correlation, the energy required for silyl radical inversion becomes small enough for closure of **6** to **1** to occur without a barrier.

(4,4)CASSCF optimizations of the transition states connecting **6** to **4** and **5** led to TS5 and TS6, respectively. As shown in Table 1, the ZPE-corrected (4,4)CASPT2 relative energy of TS5 is 62.8 kcal/mol, which is 27.4 kcal/mol above that of **6**, and the (4,4)CASSCF energy of TS6 was found to be even higher than that of TS5. The very high energies computed for these two transition states make ring opening of **1** to either **4** or **5** via diradical **6** or an interconversion between **4** and **5** through **6** very unlikely reaction channels.

Previous MP2 calculations[27] have demonstrated that there is no barrier to the addition of **7** to **8**, and we saw no reason to perform similar calculations. For the energy of the addition reaction leading to **1** we find a value of 49.0 kcal/mol using MP2//RHF calculations on **1** and **8** and CASPT2//(2,2)CASSCF calculations on **7**, corrected for ZPE differences. B3LYP calculations predict a reaction energy of 50.8 kcal/mol. Previous calculations[27] at the MP4/6-31G**//RHF/3-21G* level give the almost identical value of 50.4 kcal/mol, when corrected to 298 K. The QCI//MP2 calculations by Vanquickenborne and co-workers[14] give the slightly lower value of 47.6 kcal/mol.

Note Added in Proof: At the suggestion of a Referee, we have located the transition structure that connects **4** directly with **5** via a symmetry-forbidden 1,3-hydrogen shift. As expected the energy of this transition structure is much higher than that of TS2, the highest energy point on the pathway connecting **4** to **5** via **2**, **1** and **3**. After ZPE correction the (12,12)CASPT2N energy of the TS that connects **4** directly with **5** is 51.4 kcal/mol above that of **4**, i.e. nearly 20 kcal/mol above TS2.

Conclusions

The results of our CASPT2 and B3LYP calculations have allowed us to provide answers to the four questions posed in the Introduction. We find (a) TS3, which connects **2** to **4**, has essentially the same relative CASPT2 energy (35.3 kcal/mol above that of **1**) as TS1 which connects **2** to **1**. Our B3LYP calculations place TS3 at 34.7 kcal/mol, which is 3.4 kcal/mol lower than the B3LYP energy of TS1. (b) If vinylidene **3** is, in fact, a local minimum in the ring opening of **1** to **5**, **3** exists in an extremely shallow energy well and is a very transient intermediate. Rearrangement of **3** to **5** occurs by a [1,2]-silyl shift via TS4-Si, rather than by a [1,2]-hydrogen shift via the higher energy TS4-H. (c) The much lower energy of TS4-Si than TS2 rules out **3** as a viable intermediate for H/D scrambling in **1**. (d) Diradical **6** is a high-energy transition state for site exchange of the two hydrogens attached to silicon in **1**. TS5 and TS6, which connect **6** to **4** and **5**, respectively, are too high in energy to be of any importance in the isomerization reactions of **1**.

Our calculations find the lowest energy pathway for ring opening of **1** to involve a retrograde silylene insertion into a vinylic C−H bond, forming **2** by a mechanism first proposed by Barton 15 years ago.[8] **2** is computed to be only slightly higher in energy than **1** and to be separated from reclosure to **1** by a barrier comparable to or slightly higher than that for isomerization of **2** to **4**. Thus, our computational results support the proposal of Maier and co-workers, that reversible formation of **4** provides the lowest energy pathway for the H/D scrambling that they observed in the generation of **1** from **2**, labeled with deuterium.[12]

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(25) In **1** the statistical ratio of the **1**-d_1 and **2**-d_1 isotopomers is 1:1. However, in **5** the statistical ratio of isotopomers with deuterium attached to silicon and to carbon is 3:1. Therefore, the finding that "the former predominates"[12] does not necessarily imply that, unlike the case in **1**, a nonstatistical distribution of deuterium in found in **5**.

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