Computational Study of the Reaction between Singlet Silylene and Propene and of Rearrangement Reactions of Methylsilacyclopropane

Per N. Skancke[†]

Department of Chemistry, The University of Tromsø, N-9037 Tromsø, Norway

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The reaction between singlet silylene and propene has been studied by CASPT2N/6-31G*//CASSCF/6-31G* and MP2/6-31G*//RHF/6-31G* calculations where also ring-closing and ring-opening reactions of the resulting methylsilacyclopropane have been included. The predicted reaction energy for the addition is 49.1 kcal/mol, modified to 44.7 kcal/mol when the ΔZPE correction is included. ΔZPE-corrected barriers obtained are 11.3 and 13.2 kcal/mol for the concerted ring closing and hydrogen migration in methylsilacyclopropane starting from the silylenes **4** and **5**, respectively. These values are in good agreement with experimental estimates of 10.4 kcal/mol for the corresponding reaction of alkylsilylenes. The diradicals **6** and **7** resulting from bond ruptures in methylsilacyclopropane have energies that are around 30 kcal/mol above the TS's for the reactions leading to the silylenes. Carbenes, which are also conceivable as reaction products, have energies that are about 40 kcal/mol above the same TS's. Calculations using QCISD(T)/cc-pVDZ//MP2/cc-pVDZ gave a reaction energy of 36.0 kcal/mol, and ring-closing barriers of 12.9 and 14.3 kcal/mol, respectively. The energies of the diradicals **6** and **7** are around 20 kcal/mol above the TS's for the concerted ring opening and hydrogen migration using this method.

Introduction

The kinetics and thermochemistry of decompositions and isomerizations of some alkylsilylenes have been studied in two experimental papers.[1,2] The alkylsilylenes were generated by pyrolysis of silane/olefin mixtures. The mechanism suggested for these reactions was of the so-called Barton-type,[3] in which formation, ring opening, and decomposition of silacyclopropane intermediates play a crucial role. In the first of the experimental papers[1] the kinetics of *sec*-butylsilylene isomerization to 2,3-dimethylsilacyclopropane and the decomposition and isomerization kinetics of the latter were studied. The second paper[2] discussing the decomposition kinetics and thermochemistry of butyl- and pentylsilylenes also gave a revision of some of the conclusions reached on the first one.

The initial step in the pyrolysis of a silane/olefin mixture is a decomposition of silane yielding silylene, which is assumed to be the active species attacking the double bond in the olefin.

Silylene in its closed-shell singlet ground state ($^1A_1$) is known to undergo insertion reactions, and its insertion into a variety of chemical bonds has been studied theoretically.[4] Insertion reactions are also implicitly assumed in experimentally deduced reaction mechanisms such as the ones referred to above,[1,2] where the ring-closure and ring-opening reactions of the silacyclopropane intermediates formed represent intramolecular β-insertions and their reverse.

To our knowledge the reaction between silylene and propene and the ring-opening and ring-closure reactions of the resulting methylsilacyclopropane have not been studied previously by theoretical calculations. A theoretical study of the addition of singlet silylene to ethene has been published.[5] The least motion path for this system having C_{2v} symmetry is forbidden according to the orbital symmetry rules, and the addition was followed under C_s symmetry. The calculations led to the important conclusion that an insertion barrier is predicted at the SCF level but that the barrier vanishes at the MP2 level, *i.e.* when electron correlation is taken into account. The same conclusion was obtained in a very recent MCSCF study also including the interconversion between silacyclopropane and ethylsilylene.[6]

The purpose of the present paper is to perform *ab initio* calculations on the mechanism for and the energetics of the reaction between silylene and propene, including the interconversion between methylsilacyclopropane (**3**) and the two silylenes **4** and **5**. We believe that the results obtained give a realistic account of the experimentally studied reactions involving the larger olefins referred to above. By choosing the smaller olefin we are able to perform high-level calculations at a reasonable cost and at the same time preserve a realistic model for the reactions involving the larger olefins.

The system composed of silylene and propene represents a part of the potential surface for compounds having the general formula C_3H_8Si for which a completely different region has been investigated very recently and where focus was placed on symmetry aspects of the surface.[7]

In order to place the reaction model discussed in the experimental papers into a broader context, we have also included diradicals (**6** and **7**), silenes (**8** and **9**), carbenes (**10** and **12**), and silylpropenes (**11** and **13**) in our study. These are all *a priori* possible reaction products starting from **3**. The species included in our study are shown in Scheme 1. The transition states **TS1**−**TS4** have also been located and characterized, and their energies determined.

Computations

The geometries of species **2**, **3**, **8**, **9**, **11**, and **13** were optimized using RHF calculations, and single-point energies were obtained by MP2 computations.[8] The geometries of **1**, **4**−**7**, **10**, and **12** were optimized using CASSCF(2,2) calculations, and single-point energies were obtained using CASPT2N[9] calculations. Transition states **TS1**−**TS4** were optimized by CASSCF(4,4) calculations, and CASPT2N energies were computed at these geometries. The 6-31G* basis set[10] was used in all these calculations. Analytical vibrational frequencies (unscaled) were computed at all stationary points using the same

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[†] E-mail: pskancke@chem.uit.no.

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SCHEME 1

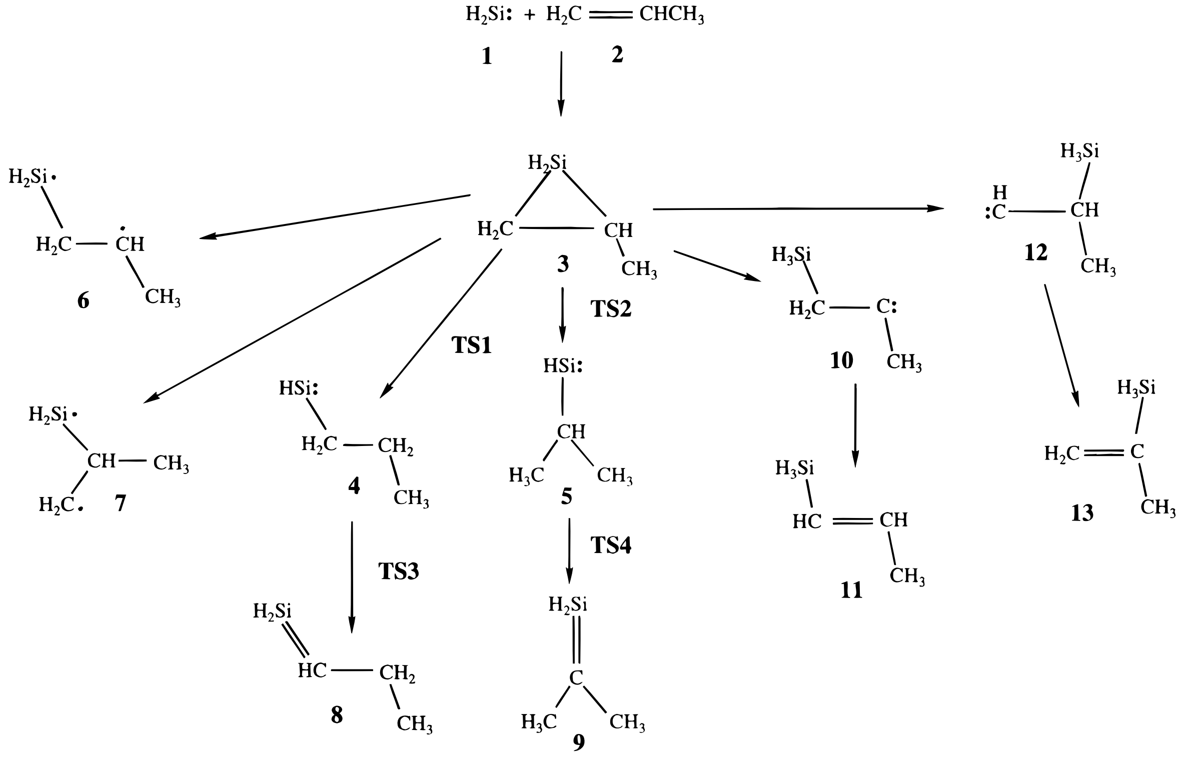

TABLE 1: Absolute Energies (hartrees), Zero-Point Energies (ZPE, kcal/mol), Imaginary Frequencies (cm^{-1}), and Relative Energies (ΔE, kcal/mol) for the Silylene + Propene System[a]

species	$E_{CAS(2,2)}$	$E_{CAS(4,4)}$	$E_{CASPT2N}$	$E_{MP2/RHF}$	ZPE	imag. freq.	Δ*E*
1 + **2**				−407.546 05[b]	61.5		49.1
3				−407.624 31	65.9		0.0
4	−407.131 13		−407.607 05		66.7		10.8
5	−407.127 22		−407.605 25		66.7	172	12.0
6	−407.064 54		−407.543 96		61.8	1133, 333, 226	50.4
7	−407.055 71		−407.535 14		61.2	1054, 346, 193	56.0
8				−407.608 53	65.8		9.9
9				−407.611 66	65.5		7.9
10	−407.062 83		−407.515 78		60.8	281, 174	68.1
11				−407.639 24	64.1		−9.4
12	−407.058 87		−407.519 10		62.2		66.0
13				−407.637 28	64.1		−8.1
TS1		−407.106 96	−407.586 07		64.8	1081	24.0
TS2		−407.102 77	−407.580 84		64.6	1178	27.3
TS3		−407.088 55	−407.552 89		64.0	1557	44.8
TS4		−407.093 59	−407.558 64		63.6	1485	41.2

[a] Basis set 6-31G*. Labeling of species in Scheme 1. [b] Species **1** calculated by CASPT2N/CAS(2,2)

calculational level as in the geometry optimizations. For the species **1**−**7** and **TS1** and **TS2**, geometry optimizations using MP2 calculations and single-point energies obtained by QCISD-(T)[11] computations were also obtained. In these calculations Dunnings correlation consistent double-ζ basis,[12,13] cc-pVDZ, was used. The calculations were performed using the programs Gaussian 94[14] and MOLCAS.[15]

TABLE 2: Absolute Energies (hartrees), Imaginary Frequencies (cm^{-1}), and Relative Energies (Δ*E*, kcal/mol) for the Silylene + Propene System[a]

species	E_{MP2}	$E_{QCISD(T)/MP2}$	imag. freq.	Δ*E*
1 + **2**	−407.607 17	−407.695 63		36.0
3	−407.677 21	−407.753 01		0.0
4	−407.657 38	−407.740 21		8.0
5	−407.655 20	−407.737 55		9.7
6	−407.607 25	−407.684 72		42.9
7	−407.602 41	−407.680 82		45.3
TS1	−407.641 16	−407.719 76	759	20.9
TS2	−407.636 59	−407.714 83	871	24.0

[a] Basis Dunnings correlation consistent set cc-pVDZ. Labeling of species in Scheme 1.

Results and Discussion

The energies obtained by our calculations are given in Tables 1 and 2, and the geometries of the optimized species are presented in Figures 1 and 2. The results of our calculations show that the silylenes **4** and **5** are significantly more stable than the diradicals **6** and **7** and the carbenes **10** and **12**. Furthermore the TS's for the ring-opening reactions leading directly to the silylenes, **TS1** and **TS2**, also have significantly lower energies than the diradicals and the carbenes. This conclusion will not be influenced by the fact that the diradicals have been optimized by constraints leading to imaginary frequencies in the final stationary points. The two small imaginary frequencies found in the stationary point for carbene **10** are associated with rotations of the methyl and silyl groups. As the rotational isomers have roughly the same energy, this

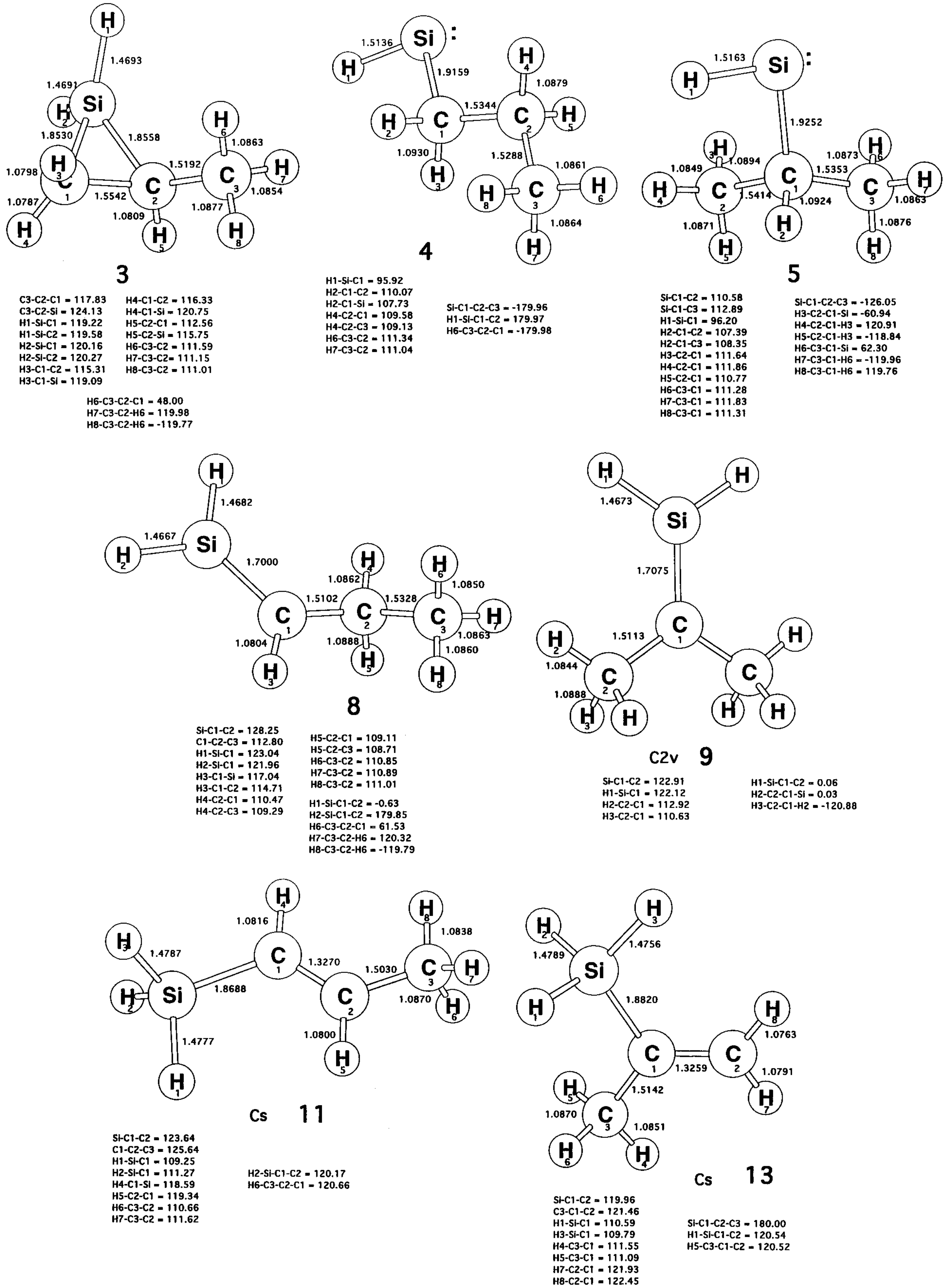

Figure 1. Structural parameters for fully optimized geometries of low-energy species. For calculational levels, see text. Basis 6-31G*.

will not influence the total molecular energy to any significant extent. Because of the relative energies obtained, we arrive at the important conclusion that diradicals are not likely to be of any importance in the reactions involving silylene and propene. Therefore we have not pursued the ring-opening reactions of **3** leading to **6** and **7**. Our conclusion is in accordance with thermochemical arguments in the experimental paper[2] leading to an exclusion of diradicals.

Because of the high relative energies predicted for the carbenes, we have not included a study of the ring openings of **3** leading directly to **10** or **12** via hydrogen shifts from carbon to silicon.

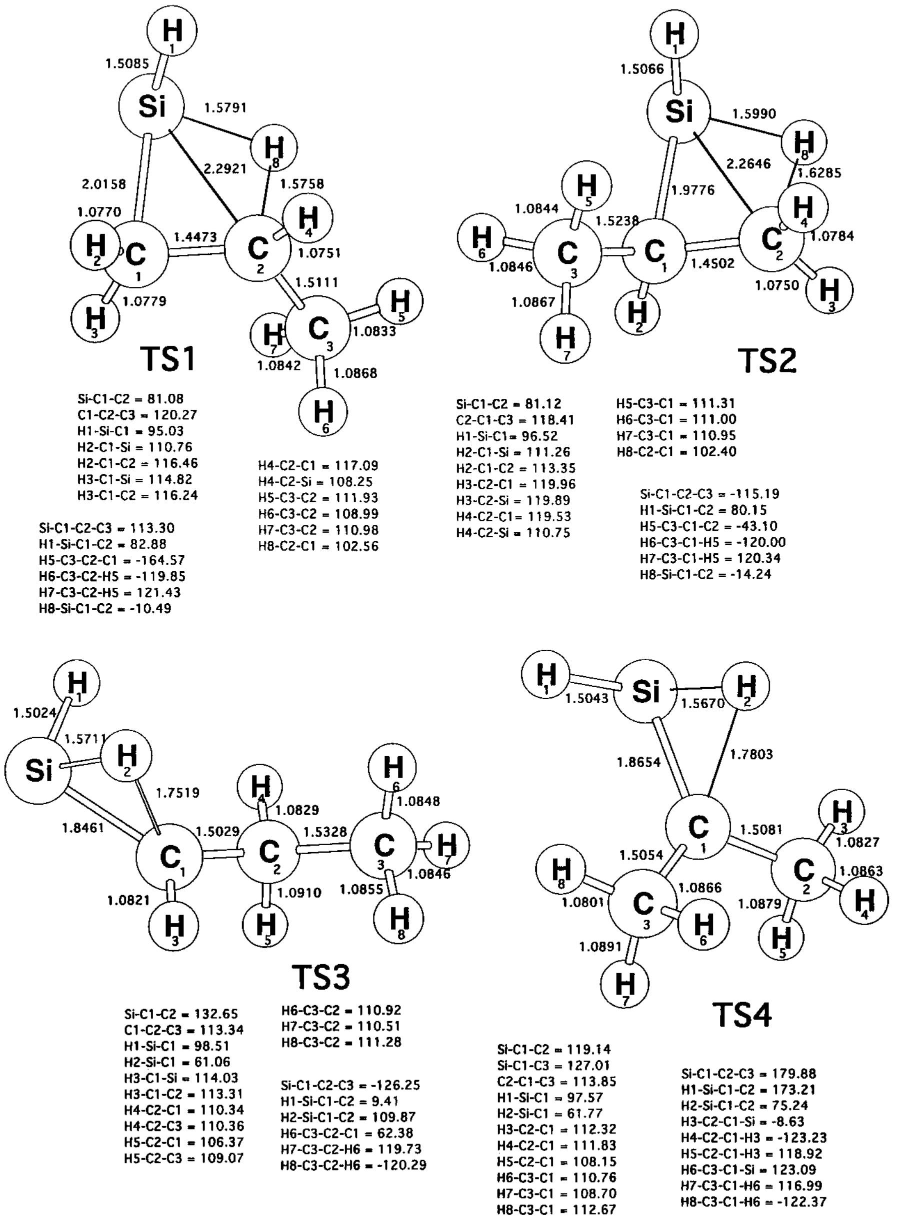

Figure 2. Structural parameters for fully optimized geometries of transition states obtained by CASSCF(4,4)/6-31G* calculations.

The silylpropenes **11** and **13** are found to have the lowest energies of all the species included in our study. Conceivably these species may be obtained either from **3** by consecutive H-shifts going through the corresponding carbenes or by H-shifts directly from the silenes **9** and **11**. The route through the carbenes is very unlikely due to their high energies. We were not able to locate any TS's for the reactions between the silenes and the silylpropenes.

As shown in our previous study[6] of the ethylene case, the preference for ring opening to silylene rather than to a diradical may be traced back to the relative bond dissociation energies of primary silyl and alkyl radicals. These were calculated to differ by around 50 kcal/mol by CASPT2N calculations. The relative energies given in Table 1 furthermore confirm that the silenes **8** and **9** are around 20 kcal/mol less stable than the corresponding silylpropenes **11** and **13**. This difference may be easily explained in terms of the relative strengths of the carbon−carbon and the carbon−silicon π-bonds. The former is found to be 64 kcal/mol,[16] whereas the latter is only 41 kcal/mol.[17] Our prediction that the silylpropenes are the most stable species is also consistent with conclusions reached in an earlier experimental study.[18]

With reference to previous theoretical studies of the addition of singlet silylene to ethene,[5,6] we have assumed that the addition reaction leading to **3** occurs without an energy barrier. The exothermicity of this reaction found here, of 49.1 kcal/mol, is very close to the value of 47.2 kcal/mol obtained in the ethene case using the same calculational method.

The absence of an energy barrier to the addition reaction is in accordance with conclusions reached from the reaction model adopted in the experimental study involving the larger olefins.[2] Alkylsilylene decomposition RRKM falloff calculations for 2-butylsilylene and 2- and 3-pentylsilylenes assuming zero activation energies led to very high Arrhenius constants indicating a very loose TS for the alkylsilylene decomposition reactions. The RRKM high-pressure activation energies for the butyl- and pentylsilylene decompositions were found to be, within uncertainty limits, equal to the decomposition energies. This is consistent with the assigned value of zero for the activation energy of silylene addition to the olefins.

The reaction heat for the decomposition of 2-butylsilylene to 2-butene (*cis*, *trans*) and silylene estimated on the basis of ΔH_f values for the involved species is 26.6 ± 3.4 kcal/mol.[2] Our predicted reaction energies for the decomposition of the silylenes **4** and **5**, corrected for unscaled ΔZPE, are 33.1 and 31.9 kcal/mol, respectively (see Table 1).

Our previous study of the ring opening of silacyclopropane to ethylsilylene and its reverse gave ΔZPE-corrected energy barriers of 22.4 and 11.3 kcal/mol, respectively.[6] In the present investigation we find the values 22.9 and 11.3 kcal/mol for the reaction between **3** and **4** and its reverse, and 26.0 and 13.2 kcal/mol for the corresponding reactions between **3** and **5**.

The generic high-pressure Arrhenius parameters for the ring closing of the alkylsilacyclopropanes give an activation energy for this reaction of 10.4 kcal/mol,[2] *i.e* very close to our predicted values. The corresponding parameters for ring opening and decomposition are influenced by assumed values of ring strain in silacyclopropanes. This is due to the circumstance that modeling of the reaction did not provide any information on the relative stability of alkylsilylenes and their silacyclopropane isomers.[2] For ring opening and decomposition the activation energy expressions $E_o = 14.7 + \Delta E$ kcal/mol and $E_d = 26.1 + \Delta E$ kcal/mol, respectively, were suggested. Here $\Delta E = 49.6 - E$(strain silacyclopropanes), where the value 49.6 kcal/mol is an empirically estimated[2] ring strain value adopted in the modeling of the reactions. Estimates of ring strain in silacyclopropanes have been made by the use of different homodesmic ractions and at different levels of *ab initio* calculations. Values obtained from two different studies, employing calculations including electron correlation, are 35.9[19] and 41.4 kcal/mol,[20] respectively. These strain energies give values for the "experimental" barriers to ring opening and decomposition of alkylsilacyclopropanes of 28.4 and 39.8 kcal/mol, and 22.9 and 34.3 kcal/mol, respectively. The predicted decomposition barriers are lower than the heat of reaction for the same process, thus supporting the assumption of zero barrier for this reaction. The corrected barrier to ring opening thus obtained, 23−28 kcal/mol, is in good agreement with our predictions for methylsilacyclopropane of 22.9 and 26.0 kcal/mol, for reaction **3** to **4** and **3** to **5**, respectively.

The fully optimized geometries of the transition states **TS1** and **TS2** for the concerted ring opening and hydrogen migration leading from **3** to the silylenes **4** and **5**, respectively are shown in Figure 2. The gross features of these TS's are the same as for the corresponding TS in the ethylene case.[6] The geometries lend support to the assumption of a loose structure without internal strain. Noticeable is the long silicon−carbon bond of 2.02 Å in **TS1** and 1.98 Å in **TS2**. The migrating hydrogen is rather close to a normal Si−H equilibrium distance in the stationary point in both cases. A thermochemical study of the shock-induced decomposition of methylsilane[21] gives some information on the activation energy for its reverse reaction, which is a silylene C−H insertion. The barrier for this insertion at 670 K is estimated[2] to be around 10 kcal/mol, *i.e.* very similar to our predicted values of 11.3 and 13.2 kcal/mol for the ring closing of **3**. This consistency lends additional support to the assumption of a loose, complex-like structure for the ring-closing TS in alkylsilacyclopropanes. The low activation energy also explains why larger silacyclic rings are not commonly observed in pyrolysis of silane/olefin mixtures. Detection of silacyclopentane in high yields (30%) by decomposition of *n*-butylsilylene[22] at 1200 K, and the absence of the same product at lower temperatures (640−690 K), could be interpreted in terms of a higher activation for the silacyclopentane ring formation.

Some of the relative energies given in Table 1 are based on absolute energies obtained by different computational methods. In order to gauge the possible effects of the lack of calculational consistency, the species **1**−**7** and **TS1** and **TS2** were optimized also by MP2/cc-pVDZ calculations, and single-point energies were obtained by QCISD(T)/cc-pVDZ computations. The results, given in Table 2, reproduce the general trends in relative energies given in Table 1. Thus the barriers to ring closure, 12.9 and 14.3 kcal/mol, starting from **4** and **5**, respectively, are very close to the corresponding values of 13.2 and 15.3 kcal/mol obtained using the combination of CASPT2N and MP2 calculations. Furthermore, the diradicals **6** and **7** are predicted to have relative energies significantly above **TS1** and **TS2** also using this method.

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