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## Ring Opening of Silacyclobutane

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## Abstract

Multiconfigurational self-consistent field (MCSCF) wave functions, augmented by second order perturbation theory to partially recover the dynamic correlation, suggest that the most likely route from silacyclobutane to products ethylene + silene is initial cleavage of a ring CC bond to form a trans  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, followed by rupture of the central SiC bond. This prediction is in agreement with the available experimental results. While this trans diradical is predicted to be a minimum on the MCSCF ground state potential energy surface, the transition state separating this species from products disappears when dynamic correlation is added. Therefore, the bottleneck on this part of the potential energy surface is likely to be the transition state for the initial CC bond cleavage. The alternative mechanism that is initiated by cleavage of a ring SiC bond leads to an analogous trans  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical. The transition state leading to this species is the highest point on this minimum energy path and is nearly 6 kcal/mol higher in energy than the transition state that leads to the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical. A transition state for the concerted decomposition has also been found, but this structure is much higher in energy ( $\sim 10$  kcal/mol) than the highest point on the preferred route. Comparison of the multireference perturbation theory and coupled cluster CCSD(T) results suggests that production of propylsilylene should be both thermodynamically and kinetically competitive with the formation of ethylene + silene. This is consistent with the mechanism proposed by one of us in 1984.

## Disciplines

Chemistry

## Comments

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## Ring Opening of Silacyclobutane

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**Abstract:** Multiconfigurational self-consistent field (MCSCF) wave functions, augmented by second order perturbation theory to partially recover the dynamic correlation, suggest that the most likely route from silacyclobutane to products ethylene + silene is initial cleavage of a ring CC bond to form a trans  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, followed by rupture of the central SiC bond. This prediction is in agreement with the available experimental results. While this trans diradical is predicted to be a minimum on the MCSCF ground state potential energy surface, the transition state separating this species from products disappears when dynamic correlation is added. Therefore, the bottleneck on this part of the potential energy surface is likely to be the transition state for the initial CC bond cleavage. The alternative mechanism that is initiated by cleavage of a ring SiC bond leads to an analogous trans  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical. The transition state leading to this species is the highest point on this minimum energy path and is nearly 6 kcal/mol higher in energy than the transition state that leads to the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical. A transition state for the concerted decomposition has also been found, but this structure is much higher in energy ( $\sim 10$  kcal/mol) than the highest point on the preferred route. Comparison of the multireference perturbation theory and coupled cluster CCSD(T) results suggests that production of propylsilylene should be both thermodynamically and kinetically competitive with the formation of ethylene + silene. This is consistent with the mechanism proposed by one of us in 1984.

### Introduction

The gas phase thermal decomposition of silacyclobutane has been of long-standing interest, since it is the simplest silicon analog of cyclobutane, itself the subject of many studies as the product of the dimerization of ethylene.<sup>1</sup> The demonstration by Guselnikov in 1969 that 1,1-methylsilacyclobutane thermally decomposed into ethylene and dimethylsilene [ $\text{Me}_2\text{Si}=\text{CH}_2$ ] was without question the starting point for more than two decades of intensive research on reactive intermediates in organosilicon chemistry.<sup>2</sup> Indeed for some time this was the only method by which one could generate species containing silicon–carbon double bonds, which previously had been thought to be incapable of existence! Despite the importance of this reaction, the central question of whether it occurs via a concerted mechanism or by a diradical process in which one ring bond is broken first to form an intermediate diradical, followed by the breaking of the remaining central bond, has not been answered. This problem is similar to the long-studied question of concerted vs stepwise decomposition of cyclobutane to two ethylenes<sup>1</sup> and

to the analogous competition in the decomposition of 1,3-disilacyclobutane to two silenes,<sup>3</sup> with the important difference that in silacyclobutane there is at most  $C_s$  symmetry. A second important difference between cyclobutane and silacyclobutane is that in the latter compound there are two possible initiating diradical processes: one can imagine either an initial cleavage of a ring SiC bond to form a  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical (SiC diradical) or an initial cleavage of a ring CC bond to form a  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical (CC diradical). Therefore, the second step would be the subsequent cleavage of either the central CC bond (from the SiC diradical) or the central SiC bond (from the CC diradical). Over a decade ago, several groups independently studying the pyrolyses of substituted silacyclobutanes, provided strong evidence that the C–C bond is the site of initial homolysis.<sup>4–6</sup>

There have been several theoretical studies of the reaction of two ethylene molecules to form cyclobutane.<sup>1</sup> On the ground state potential energy surface, multiconfigurational wave functions with modest basis sets suggest that the (symmetry-forbidden) concerted decomposition to two ethylenes can only proceed through a second-order saddle point, whereas the trans tetramethylene diradical is a minimum, separated from products (2  $\text{C}_2\text{H}_4$ ) by a small barrier. Extensive multireference wave functions with large basis sets, however, find a gauche tetramethylene structure sitting in a broad, flat region that leads to either cyclobutane or two ethylenes.<sup>11</sup> The potential energy surface for the dimerization of silene has been studied by

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Ahlich and Heinzmann<sup>7</sup> at the Hartree–Fock (HF) level of theory, by Morokuma et al. using singles and doubles configuration interaction (CISD) at HF geometries,<sup>8</sup> and by Seidel, Grev, and Schaefer using two-configuration self-consistent field (TCSCF), CISD and coupled cluster (CCSD) geometries and energies.<sup>3</sup> The latter study was the most extensive and included analyses of both the preferred head-to-tail and the head-to-head mechanisms. These authors found that the head-to-tail dimerization proceeds by a concerted mechanism, whereas the head-to-head dimerization is a two-step process involving a diradical intermediate.

The decomposition mechanism for mono-silacyclobutane has not been the subject of theoretical investigation. The current work provides a detailed examination of the competing processes for the decomposition of silacyclobutane, with primary emphasis on competing ring opening mechanisms. In addition to the ring opening mechanisms discussed above, two other competing processes are examined in this work. One of these is the concerted SiC ring opening and 1,2-H shift to form propylsilylene. This mechanism was proposed by Barton, Davidson, and co-workers<sup>4</sup> as being competitive with the decomposition to ethylene + silene. An analogous process for silacyclopropane was proposed by the same authors and the transition state for the production of ethylsilylene was recently determined by Skancke and Borden using MCSCF wave functions.<sup>9</sup> The second competing process of interest is the 1,1-H<sub>2</sub> elimination to form silacyclobutylidene.

## II. Theoretical Methods

Because diradicals are expected to play a central role in the mechanisms under investigation, computational methods based on single-configuration (that is, Hartree–Fock) wave functions are not likely to be generally reliable. Therefore, the basic wave functions used in this work are of the multiconfigurational (MC) self-consistent field (SCF) type. In particular, the approach used here is that commonly referred to as FORS<sup>10</sup> (for fully optimized reaction space) or CASSCF<sup>11</sup> (for complete active space SCF). The fundamental idea is to identify those orbitals and electrons that directly participate in the chemical process to be studied, add the corresponding antibonding orbitals, and then consider the resulting set of  $m$  orbitals and  $n$  electrons as comprising an “active space”. One then constructs an MCSCF wave function from this MCSCF( $n,m$ ) active space from a variationally optimized linear combination of all electronic configurations (consistent with the desired space and spin symmetry) that can be obtained by distributing the  $n$  active electrons among the  $m$  active orbitals.

For silacyclobutane, an MCSCF(8,8) active space was used. The eight electrons are those in the two CC and two SiC bonds of the parent ring molecule; the eight orbitals are the corresponding SiC and CC bonding and antibonding orbitals. These are conveniently obtained by determining the localized molecular orbitals (LMOs)<sup>12</sup> and then using these LMOs to construct a corresponding set of antibonding MOs.

All geometries were determined at the MCSCF(8,8) level of theory, using the 6-31G(d) basis set<sup>13</sup> and analytic gradients. Stationary points were then characterized by determining the Hessian (matrix of energy second derivatives, obtained by double differencing analytic gradients) and then diagonalizing the Hessian to assess the number of negative roots (imaginary vibrational frequencies: none for a minimum, one for a transition state, more than one for a higher order saddle point). Starting from each transition state (TS) identified in this manner, the

minimum energy path (MEP) was determined using the second-order Gonzalez–Schlegel algorithm<sup>14</sup> to confirm that each TS does indeed connect the expected minima. The stepsize used in these MEP calculations varied from 0.1 to 0.01 amu<sup>1/2</sup> bohr.<sup>15</sup> Zero-point vibrational energies were also determined at this MCSCF(8,8)/6-31G(d) level of theory. Final energetics for the competing ring opening mechanisms were obtained with second-order multireference perturbation theory (MRMP),<sup>16</sup> at the MCSCF(8,8)/6-31G(d) geometries. These single-point MRMP calculations were performed using both the 6-31G(d) and 6-311G(d,p)<sup>17</sup> basis sets. All of the MCSCF and MRMP calculations were performed using the GAMESS suite of programs.<sup>18</sup>

The two competing processes mentioned in the Introduction, formation of propylsilylene and silacyclobutylidene, are not expected to involve diradicals and were therefore investigated using second-order perturbation theory<sup>19</sup> and the same 6-31G(d) basis set. The MP2/6-31G(d) geometries, vibrational frequencies, and minimum energy paths were determined in a manner analogous to that described above for the MCSCF(8,8) wave functions. Final energetics were obtained at the MP2 geometries by using singles and doubles coupled cluster calculations, with triple excitations included perturbatively.<sup>20</sup> These CCSD(T) calculations were performed with ACESII,<sup>21</sup> using both the 6-31G(d) and 6-311G(d,p) basis sets. All of the MP2 calculations were performed with GAMESS.

## III. Results and Discussion

**A. Decomposition to Ethylene + Silene.** As discussed in the Introduction, there are three apparent routes that may lead to the products ethylene and silene: (1) a two-step process via cleavage of a Si–C bond and a  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical; (2) a two-step process via cleavage of a C–C bond and a  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical; (3) a concerted one-step dissociation. Therefore, in addition to the reactant silacyclobutane and the products, there may be as many as two diradical intermediates and five transition states. Indeed, all of these stationary points are found on the MCSCF(8,8) ground state potential energy surface. A schematic of this part of the potential energy surface is given in Scheme 1 and is discussed in detail in the following paragraphs.

**Potential Energy Minima.** The MCSCF geometries for silacyclobutane and ethylene + silene are shown in Figures 1a and 1b, respectively. Note that, at the MRMP/6-311G(d,p) level of theory, the overall decomposition is predicted to be endothermic by 34.9 kcal/mol.

The geometries for the two diradicals are shown in Figures 2a and 2b, respectively. The heavy atom framework is trans planar in both diradicals, and the arrangement of the hydrogens is staggered. In both diradicals the terminal CH<sub>2</sub> groups are essentially planar, with the sum of the angles about the carbon

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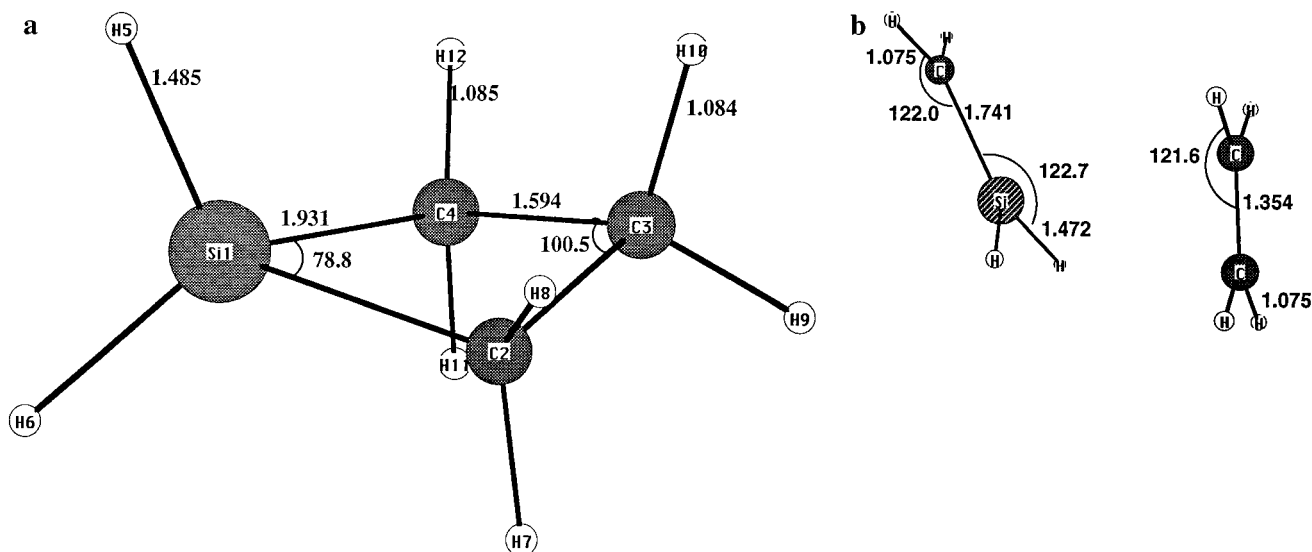
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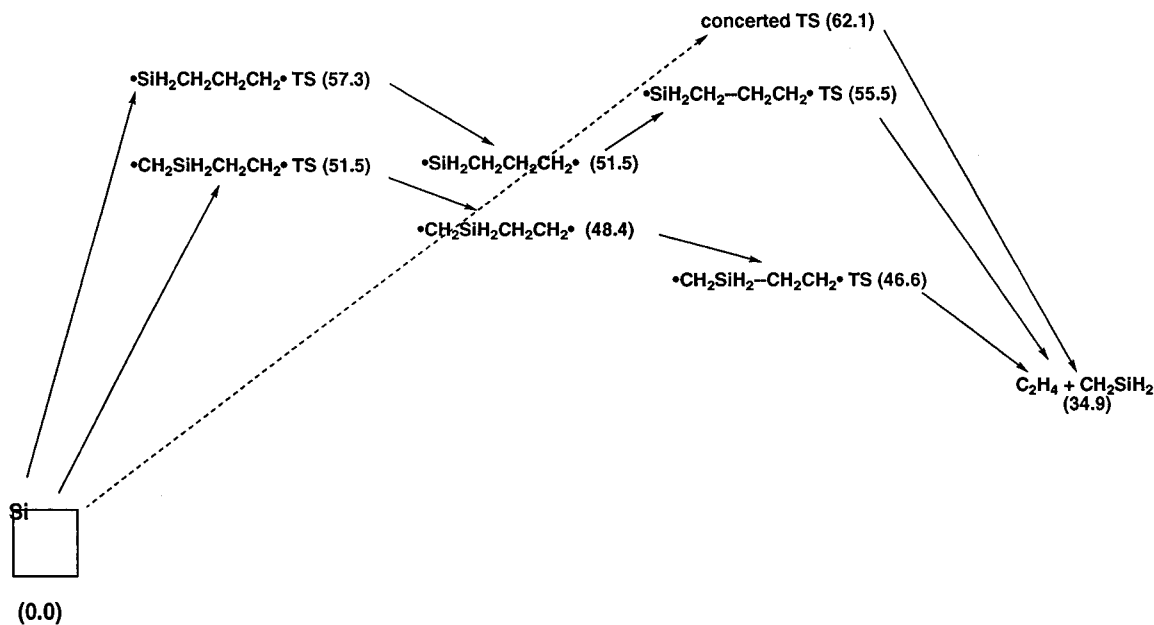
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**Figure 1.** (a) CASSCF silacyclobutane. Ring dihedral 1–2–3–4 =  $-20.2^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silene + ethylene = 34.9 kcal/mol. (b) CASSCF/6-31G(d) geometries of silene and ethylene.

**Scheme 1.** Schematic MRMP/6-311G(d,p)//CASSCF(8,8)/6-31G(d) + ZPE Energy Level Diagram for Silacyclobutane  $\rightarrow$  Ethylene + Silene (kcal/mol)

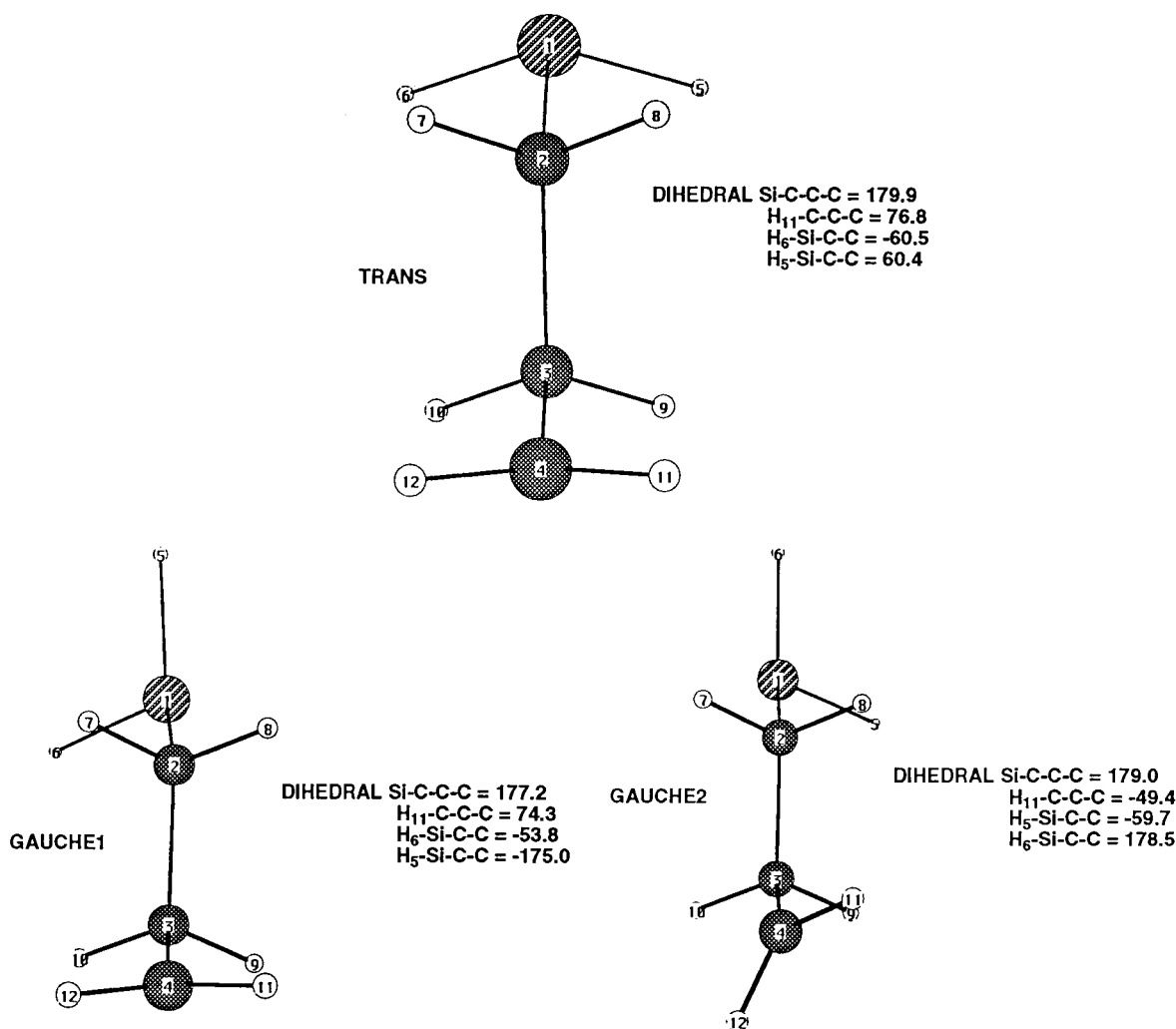


approximately equal to  $360^\circ$ . The terminal  $\text{SiH}_2$  group in the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, on the other hand, is pyramidal. The central CC bond in this latter species is predicted to be  $0.007 \text{ \AA}$  longer than that in the parent ring, while the central SiC bond in the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical is  $0.057 \text{ \AA}$  longer than the corresponding bond in silacyclobutane. On the other hand, the terminal CC and SiC bonds are shorter in the diradicals than in the ring. This is especially true in the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, in which the terminal SiC bond has decreased by  $0.064 \text{ \AA}$  to  $1.867 \text{ \AA}$  and the terminal CC bond has decreased by  $0.096 \text{ \AA}$  to  $1.498 \text{ \AA}$ . The corresponding changes in the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical are  $0.009 \text{ \AA}$  for SiC and  $0.081 \text{ \AA}$  for CC.

The bond length changes upon diradical formation may be probed further by means of the calculated *ab initio* bond orders, as defined by Mayer.<sup>22</sup> These bond orders were determined

for silacyclobutane using the RHF wave functions, since the MCSCF mixing is quite small, and for the diradicals using the triplet unrestricted Hartree–Fock (UHF) wave functions, all at the MCSCF geometries. In the parent ring compound, the SiC and CC bond orders are calculated to be 0.953 and 0.940, respectively, suggesting a somewhat stronger SiC bond. This very likely reflects the greater strain in the CC bond. In the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, the central SiC bond order decreases to 0.903, from 0.953 in the ring, while the terminal SiC and CC bond orders increase from 0.953 to 0.983 and from 0.940 to 0.977, respectively. This suggests that the central bond in this diradical is somewhat weakened, while the terminal bonds are strengthened, in anticipation of the eventual formation of ethylene + silene. Interestingly, the bond order of the central CC bond in the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical is predicted to increase to 0.956, from 0.940 in the ring, despite the very small increase in the bond length. This probably reflects the release of strain in the ring bond. The bond order of the terminal SiC bond in this diradical decreases very slightly, from 0.953 in

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Scheme 2. SiH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> Conformational Isomers

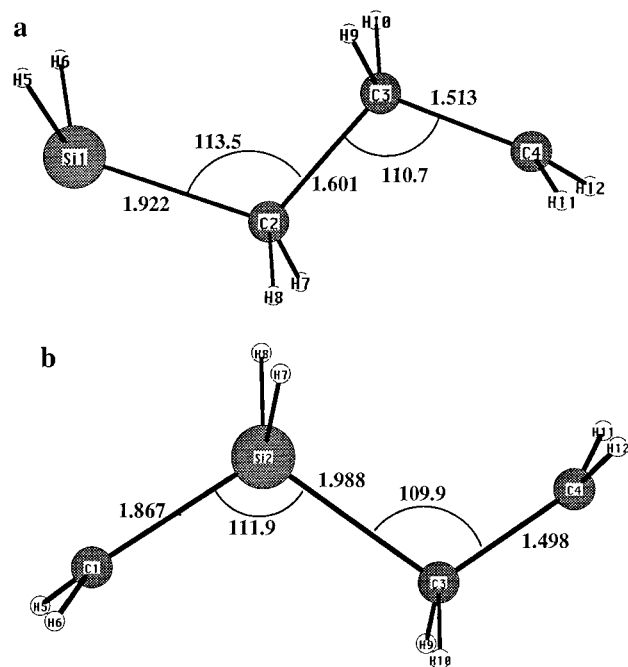
the ring to 0.943 (recall the very small change in the corresponding bond length), while the bond order of the terminal CC bond increases from 0.953 to 0.974. All of the bond order changes are larger in the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical.

At the MRMP/6-311G(d,p) level of theory, including vibrational zero-point energy corrections, the two diradicals are on the order of 50 kcal/mol higher in energy than silacyclobutane. The  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical is predicted to be 3.1 kcal/mol lower in energy than the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical (Scheme 1), so *thermodynamically* breaking the ring CC bond is somewhat more favorable than breaking the ring SiC bond. This is consistent with the calculated bond orders and with the experimental observations.

In addition to the trans staggered structure shown in Figure 2a, two other conformational minima (positive definite CASSCF(8,8) Hessians) have been found on the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, potential energy surface. The three structures correspond to internal rotations about the terminal SiC and CC bonds, and are shown schematically in Scheme 2. The structures referred to as gauche1 and gauche2 are predicted to be 2.5 and 3.1 kcal/mol higher in energy than the trans staggered structure, at the MRMP/6-311G(d,p) level of theory. Paths connecting gauche1 with trans and with gauche2 have been determined by using the appropriate dihedral angle as reaction coordinate and optimizing the remaining geometry at the CASSCF(8,8)/6-31G(d) level of theory. The highest point on the gauche1 to trans path is 0.03 kcal/mol higher in energy than gauche1 at the MRMP/6-311G(d,p) level of theory. The highest point on the

gauche1 to gauche2 path is 0.01 kcal/mol higher in energy than gauche2 at the same level of theory. Therefore, the two gauche structures are barely stable, if they exist at all.

**Transition States.** The transition state structures that connect silacyclobutane with the two diradicals are shown in Figure 3. The heavy atom framework in each transition state is twisted by about 120°. The  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  transition state is about 5 kcal/mol higher in energy than the corresponding diradical, while the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  transition state is about 3 kcal/mol higher in energy than its corresponding diradical. Therefore, the energy order of the transition states is the same as that for the diradicals, and breaking the CC ring bond is again favored relative to breaking the ring SiC bond, in agreement with the experimental observations. The minimum energy path (MEP) starting from the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  transition state leads smoothly to silacyclobutane in one direction and to the gauche2  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical in the other direction. As noted earlier, there is only a very small barrier separating this species from the more stable trans structure. The MEP starting from the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  transition state leads smoothly to the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical in one direction, but finds a very shallow minimum on the way toward the ring structure. This shallow minimum has a CSiCC dihedral angle of  $-72.2^\circ$ , is 0.7 kcal/mol below the transition state at the CASSCF(8,8) level of theory, and has a maximum CASSCF barrier of 2 kcal/mol separating it from the ring. It is likely that this species does not exist at higher levels of theory. Note that both species are already essentially diradicals at the (late) transition states. The



**Figure 2.** (a) CASSCF/6-31G(d) structure of diradical from Si-C cleavage; dihedrals SiCCC =  $-179.9^\circ$ , HSiCC =  $\pm 60.5^\circ$ , HCCC =  $\pm 60.8^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 51.5 kcal/mol. (b) CASSCF/6-31G(d) structure of diradical due to C-C cleavage: dihedrals CSiCC =  $179.9^\circ$ , HCSiC =  $\pm 81.8^\circ$ , HCCSi =  $\pm 78.0^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 48.4 kcal/mol.

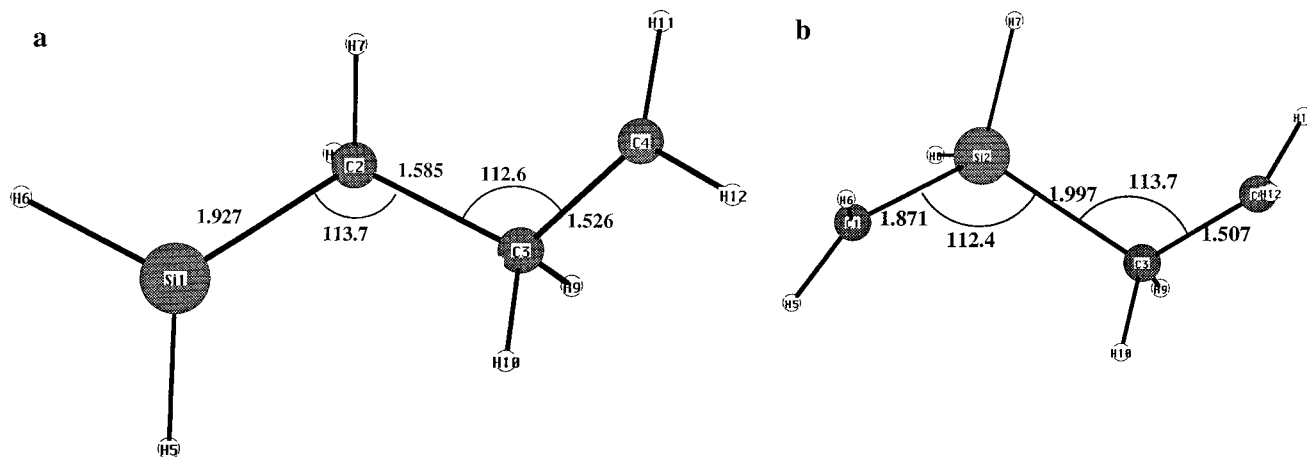
sum of the natural orbital occupation numbers (NOON) for those orbitals that correspond to antibonding MOs in the ring is 0.8 and 1.0 for the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  and  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  transition states, respectively. These are essentially the same as the analogous values for the diradicals themselves.

The transition state structures that correspond to dissociating the two diradicals into ethylene + silene are shown in Figure 4. In each transition state, the central bond is now quite stretched, while the terminal bonds have shortened considerably, illustrating that the double bonds are well on their way to being formed. This notion is supported by the calculated UHF bond orders. The bond order of the central CC bond in the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical has now decreased to 0.731, while the bond orders of the terminal SiC and CC bonds have increased to 0.953 and 1.096, respectively. It is not surprising

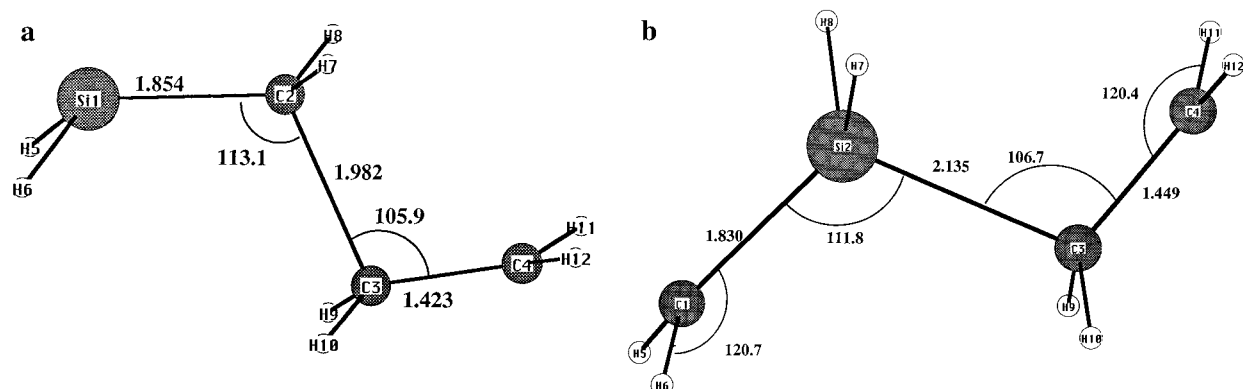
that the CC bond is strengthened more than the SiC bond. Similar trends are found for the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  transition state. The central SiC bond order is 0.877, while the bond orders for the terminal SiC and CC bonds are 0.990 and 1.000, respectively.

There is still considerable diradical character in these two transition states: The net number of electrons in orbitals that correspond to ring antibonding MOs is 0.51 and 0.65 for the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  and  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradicals, respectively. Starting from each CASSCF(8,8) transition state, the minimum energy path leads smoothly to the appropriate diradical in one direction and to separated products in the other direction. The transition state leading from the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical to products is 4.0 kcal/mol higher in energy than the diradical at the MRMP/6-311G(d,p) level of theory when zero-point energies are included. On the other hand, the CASSCF transition state that leads from the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical to products is actually found to be slightly lower in energy than the diradical when dynamic correlation (MRMP) and zero-point energy corrections are added to the CASSCF energies. Therefore, this transition state may not even exist at the higher levels of theory. In any event, the net MRMP/6-311G(d,p) energetic requirement to get from silacyclobutane to products via the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical is about 6 kcal/mol greater than the requirement to proceed via the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical (see Scheme 1). This result is consistent with experimental observations.<sup>4-6</sup> One consistent difference between the two pathways is that the two terminal carbon atoms along the  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical path are essentially planar and therefore "ready" to complete the formation of the incipient double bonds. On the other hand, the terminal Si in the  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical is pyramidal, even in the transition state connecting the diradical with products. For example, in the transition state that connects this diradical to products, the sum of the three angles about the terminal C is  $358.3^\circ$ , whereas the analogous value for the terminal silicon is  $335.9^\circ$ . Therefore, the terminal Si must planarize upon dissociation to ethylene + silene. This planarization process is expected to have a barrier that is similar in magnitude to the 5 kcal/mol barrier in silyl radical.<sup>23</sup>

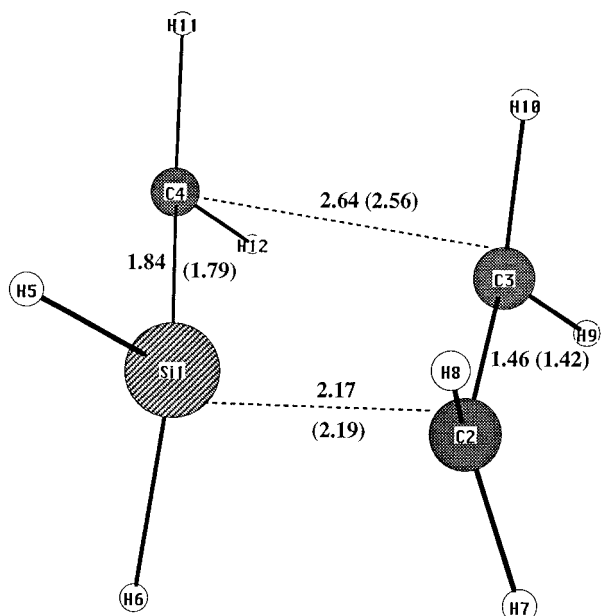
The transition state structure corresponding to the concerted dissociation of the ring to ethylene + silene is shown in Figure 5. At the MRMP/6-311G(d,p) level of theory, with zero-point corrections included, this transition state is 62.1 kcal/mol higher in energy than silacyclobutane. This is considerably higher in



**Figure 3.** (a) CASSCF/6-31G(d) TS for Si-C ring opening: dihedrals SiCCC =  $-121.4^\circ$ , HSiCCC =  $(-55.6^\circ, -177.5^\circ)$ , HCCC =  $(-50.0^\circ, 152.3^\circ)$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 57.3 kcal/mol, energy relative to diradical minimum = 5.8 kcal/mol. (b) CASSCF/6-31G(d) TS for C-C ring opening: dihedrals CSiCC =  $-114.3^\circ$ , HCSiC =  $(-81.8^\circ, 81.3^\circ)$ , HCCSi =  $\pm 78.0^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 51.5 kcal/mol, energy relative to diradical = 3.1 kcal/mol.



**Figure 4.** (a) CASSCF/6-31G(d) TS for  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot \rightarrow \text{CH}_2=\text{CH}_2 + \text{SiH}_2=\text{CH}_2$ : dihedrals  $\text{SiCCC} = 180.0^\circ$ ,  $\text{HSiCC} = \pm 62.5^\circ$ ,  $\text{HCCC} = \pm 82.4^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 55.5 kcal/mol; energy relative to diradical = 4.0 kcal/mol. (b) CASSCF/6-31G(d) TS for  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot \rightarrow \text{CH}_2=\text{CH}_2 + \text{SiH}_2=\text{CH}_2$ : dihedrals  $\text{CSiCC} = 180.0^\circ$ ,  $\text{HCSiC} = \pm 77.4^\circ$ ,  $\text{HCCSi} = 80.8^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 46.6 kcal/mol, energy relative to diradical = -1.8 kcal/mol.



**Figure 5.** CASSCF/6-31G(d) TS concerted dissociation: ring dihedral =  $0.1^\circ$ ; MRMP/6-311G(d,p) + ZPE energy relative to silacyclobutane = 62.1 kcal/mol (MP2/6-31G(d) distances are given in parentheses).

energy than the highest point on both the CC and SiC ring opening paths. Note that the heavy atom framework of this transition state is essentially planar. Animation of the minimum energy path<sup>15</sup> shows that the silacyclobutane rings twists into a planar arrangement, prior to the concerted, but asynchronous, ring opening. The diradical character of the concerted transition state (0.29 electrons outside of the closed-shell bonding orbitals) is much less than that at any of the other stationary points between silacyclobutane and products on the potential energy surface. This may be compared with 0.09 electrons in silacyclobutane and 0.22 electrons in ethylene + silene.

**B. Competing Reactions.** One of us<sup>4</sup> has suggested that a concerted ring opening of silacyclobutane, combined with a 1,2-H shift, to form propylsilylene ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{SiH}$ ), may be competitive with the formation of ethylene + silene. Skancke and Borden have recently studied the ring opening mechanisms in silacyclop propane, using CASSCF(4,4) wave functions.<sup>9</sup> The results of these authors are in concert with the proposed decomposition of propylsilylene via reversible silacyclop propane formation<sup>4</sup> in that they find, in addition to CC and SiC ring

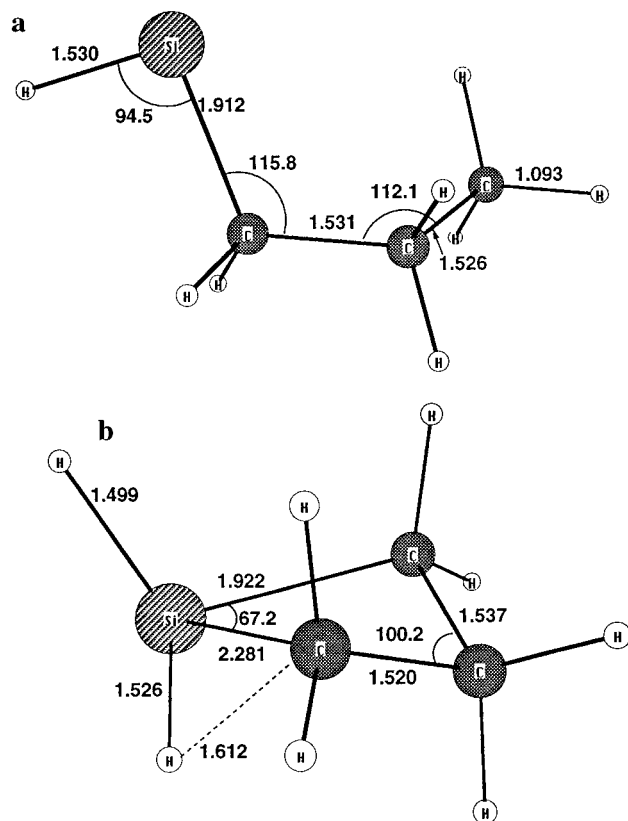
openings, a competitive, low-energy route to ethylsilylene ( $\text{CH}_3\text{CH}_2\text{SiH}$ ) via a concerted 1,2-H shift from Si to C with a concomitant SiC ring opening. Since the transition state for this concerted process is likely to have a minimal amount of diradical character (similar to that in the concerted transition state discussed in the previous paragraph), this process was studied using MP2/6-31G(d) geometries, followed by CCSD(T) single-point energies at the MP2 geometries (denoted CCSD(T)/MP2). In order to compare these results with those discussed in the previous section, the geometries of silacyclobutane, ethylene, and silene were reoptimized using MP2 as well. The CCSD(T)/MP2 energies were then obtained for the reactants and products, and the CCSD(T)/CASSCF(8,8) energy was then determined for the concerted transition state. The MP2 minimum energy path was determined for the reaction, to verify that the transition state smoothly connects silacyclobutane with propylsilylene.<sup>15</sup> The structures of propylsilylene and the transition state connecting silacyclobutane with propylsilylene are shown in Figure 6. It is clear from the structure of the transition state that one SiH hydrogen is migrating to an adjacent carbon, while the Si bond to that carbon is breaking.

Yet another reaction which might compete with decomposition of silacyclobutane to ethylene + silene is the 1,1- $\text{H}_2$  elimination to yield silacyclobutylidene. This reaction was studied in a manner analogous to that described in the previous paragraph, that is, MP2 geometry optimizations and minimum energy path determinations, followed by CCSD(T) energy evaluations at the MP2 stationary points. The resulting structures for silacyclobutylidene and the associated transition state are shown in Figure 7. Note that the leaving hydrogens in the transition state are rather asymmetric, with bond distances that differ by about 0.15 Å, even though the ring itself is quite symmetric.

The energetics for the two alternative reaction paths are compared with the synchronous concerted reaction and with the reactant and products at the CCSD(T) level of theory in Table 1, for both the 6-31G(d) and 6-311G(d,p) basis sets. Note that there is very little basis set affect on the energetics of this system. The concerted transition state geometry has been determined using both the CASSCF wave functions discussed above and MP2, both with the 6-31G(d) basis set. It may be verified in both Figure 5 and Table 1 that the structure and CCSD(T)/6-311G(d,p) energetics are very similar for both structures. Thermodynamically, propylsilylene is clearly a competitive product, since it is predicted to be  $\sim 17$  kcal/mol lower in energy than ethylene + silene. Silacyclobutylidene +  $\text{H}_2$  is predicted to be  $\sim 3$  kcal/mol higher in energy than the

(23) Calculated at the RMP2/6-311G(d,p)/RHF/6-311G(d,p) + ZPE level of theory.





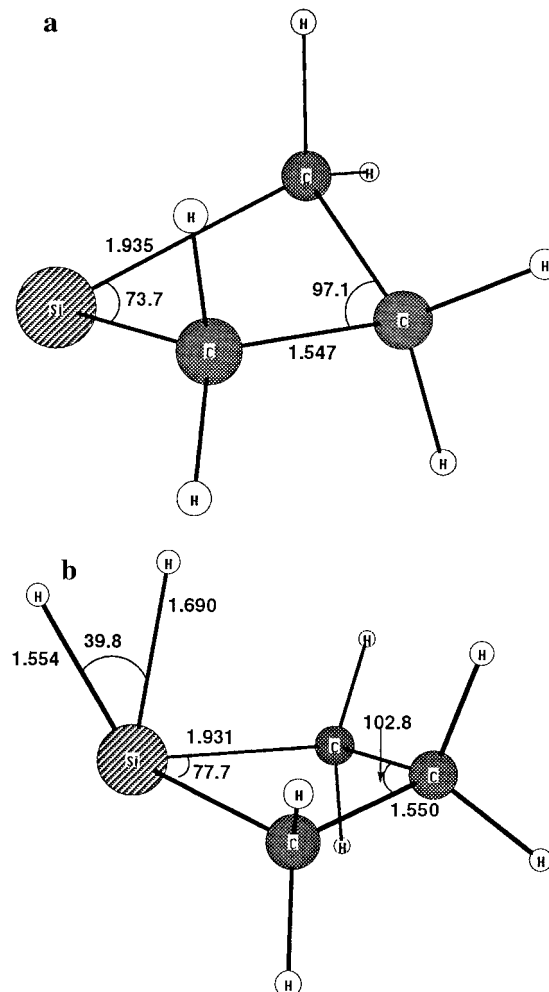
**Figure 6.** (a) MP2/6-31G(d) structure for *n*-propylsilylene: dihedral SiCCC =  $-70.7^\circ$ , HSiCCC =  $173.2^\circ$ , CCCH =  $80.0^\circ$ . (b) MP2/6-31G(d) TS connecting propylsilylene with silacyclobutane: dihedral SiCCC =  $30.6^\circ$ .

observed products, and the associated barrier is only 5 kcal/mol below that of the concerted reaction at this level of theory. On the basis of the results in Scheme 1, one would conclude that this route is not competitive with the lowest energy path: cleavage of a ring CC bond, followed by diradical formation.

The barrier leading to propylsilylene is found to be 57.6 kcal/mol above silacyclobutane. This is 13 kcal/mol lower than the synchronous concerted transition state. On the basis of the MRMP energies discussed earlier (see Scheme 1), this would place the transition state that leads to propylsilylene at roughly 2 kcal/mol lower in energy than the highest point on the route that leads to ethylene + silene via CC bond breaking. Therefore, this process is predicted to be competitive with the decomposition to ethylene + silene. This is consistent with the mechanism proposed in ref 3. In a forthcoming paper, we will present a detailed theoretical picture of the fate of alkylsilylenes with considerable experimental evidence for the ability of silicon to "walk" up and down a hydrocarbon chain via reversible silacyclopropane formations.

#### IV. Summary and Conclusions

The MCSCF wave functions, augmented by second-order perturbation theory to partially recover the dynamic correlation, suggest that the most likely route from silacyclobutane to products ethylene + silene is initial cleavage of a ring CC bond to form a trans  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical, followed by rupture of the central SiC bond. This prediction is in agreement with the available experimental results.<sup>4-6</sup> While this trans diradical is predicted to be a minimum on the CASSCF(8,8) ground state potential energy surface, the transition state separating this species from products disappears when dynamic correlation is



**Figure 7.** (a) MP2/6-31G(d) structure for silacyclobutylidene: dihedral SiCCC =  $30.4^\circ$ . (b) MP2/6-31G(d) transition state connecting silacyclobutane with silacyclobutylidene: dihedral SiCCC =  $-14.7^\circ$ .

**Table 1.** Relative CCSD(T)/MP2 Energies<sup>a</sup>

structure	relative energy (kcal/mol)	
	6-31G(d)	6-311G(d,p)
silacyclobutane	0.0	0.0
ethylene + silene	41.7	42.0
propylsilylene	23.8	25.3
silacyclobutylidene + H <sub>2</sub>	41.6	44.7
concerted transition state	73.1 <sup>b</sup>	70.7 <sup>b</sup> (68.6)
propylsilylene transition state	58.2	57.6
silacyclobutylidene transition state	66.2	65.7

<sup>a</sup> Zero-point vibrational energies are included. <sup>b</sup> The CASSCF(8,8) geometry for the concerted transition state was used. For the 6-311G(d,p) basis set, the CCSD(T) relative energy using the MP2/6-31G(d) geometry is given in parentheses.

added. Therefore, the bottleneck on this part of the potential energy surface is likely to be the transition state for the initial CC bond cleavage; that is, once sufficient energy is provided to break a ring CC bond, the reaction is downhill to products, with no intervening stable intermediates. Therefore, at the highest level of theory considered here, one may view this as a highly asynchronous concerted route to ethylene + silene, a route along which there is considerable diradical character. Using MRMP/6-311G(d,p), with vibrational zero-point energy corrections, the transition state is predicted to be about 51 kcal/mol above silacyclobutane. The reverse barrier, for formation of the four-membered ring from silene + ethylene is predicted to be 16.6 kcal/mol at the same level of theory.

The alternative mechanism that is initiated by cleavage of a ring SiC bond leads to an analogous trans  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical. The transition state leading to this species is the highest point on this minimum energy path and is nearly 6 kcal/mol higher in energy than the energy required to break a ring CC bond and to produce a  $\cdot\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\cdot$  diradical. The greater ring strain in the CC, than in the SiC, bond in the four-membered ring probably plays a role in the smaller CC bond strength in the ring. Whereas the bond energies of simple, unstrained CC and SiC bonds are the same within experimental error,<sup>24</sup> the bond order of the CC bond is smaller than that in the SiC bond in silacyclobutane, and it takes 6 kcal/mol less energy to break the CC bond than to break the SiC bond. The stability of the trans  $\cdot\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  diradical (that is, the existence of the barrier separating it from products) is likely to be related to the pyramidal geometry at the Si, since planarization of this center only comes at an energetic cost, estimated to be about 5 kcal/mol. Therefore, a combination of differential (CC vs SiC) ring strain and the need to planarize the SiH<sub>2</sub> center is responsible for the CC bond cleavage being the preferred route to ethylene + silene.

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(24) Wiberg, K. B. *J. Chem. Educ.* **1996**, *73*, 1089.

A transition state for the largely synchronous concerted decomposition has also been found, but this structure is much higher in energy (~10 kcal/mol) than the highest point on the preferred route.

Comparison of the MRMP and CCSD(T) results suggests that production of propylsilylene should be both thermodynamically and kinetically competitive with the formation of ethylene + silene. This is consistent with the mechanism proposed by Barton et al. in 1984. New experiments in support of that mechanism will be considered in a future paper.

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**Supporting Information Available:** Animations of the minimum energy paths are available through the Internet only. See any current masthead page for ordering and Internet access instructions.

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