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Theoretical Study of Thermal Isomerization of Silacyclobutene to Cyclopropene

Yoshihito Shiota,[†] Makoto Yasunaga,[†] Akinobu Naka,[‡] Mitsuo Ishikawa,*[,‡] and Kazunari Yoshizawa*[,†]

Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 812-8581, Japan, and Department of Chemistry and Bioscience, Kurashiki University of Science and the Arts, Kurashiki, Okayama 712-8505, Japan

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The reaction pathway and energetics for the conversion of silacyclobutene to cyclopropene, which plays a role as an intermediate in complicated thermal reactions of silacyclobutene, are discussed using B3LYP/6-31+G(d,p) level calculations. There are two reaction pathways in its thermal isomerization: (1) cyclopropene is formed via silabutadiene that is formed by the ring opening of silacyclobutene in a conrotatory process; (2) cyclopropene is directly formed by a 1,2-siloxyl shift in silacyclobutene. The first mechanism involves two-step processes. Two kinds of ring-opening reactions based on the Woodward−Hoffmann rule result in the formation of *cis*- and *trans*-silabutadienes that involve an Si=C double bond. Calculated activation barriers for the formation of *cis*- and *trans*-silabutadienes are 36.5 and 21.8 kcal/mol, respectively. Thus, the trans form is energetically more favorable than the cis form in this ring-opening step. This result is in good agreement with experimental observations that the methanol adduct derived from the trans form is detected in the presence of methanol. However, the next transition state with respect to a 1,4-siloxyl shift takes place only in the cis form, due to the orientation of the siloxyl group. A calculated activation barrier for the 1,4-siloxyl shift in *cis*-silabutadiene is 17.2 kcal/mol. Thus, the first step is the rate-determining step in this two-step mechanism. The second mechanism involves a 1,2-siloxyl shift that leads to the direct formation of cyclopropene. The activation barrier of this reaction is calculated to be 40.0 kcal/mol. IRC calculations are performed to trace this 1,2-siloxyl shift in the second mechanism. Since the activation barrier of the direct formation of cyclopropene is energetically comparable to that of the ring-opening reaction toward the *cis*-silabutadiene, the B3LYP DFT calculations suggest that both reaction pathways are likely to occur under thermal conditions.

Introduction

We have now numerous examples of unsaturated silicon compounds that involve Si=Si, Si=C, and Si=N double bonds. Such unsaturated silicon compounds are highly reactive and used as reagents and reaction intermediates in the synthesis of various organosilicon compounds,[1] but our understanding of mechanistic aspects on various reactivities of unsaturated silicon compounds is still lacking. Gusel'nikov and Flowers demonstrated that silaethylenes or silenes ($R_2Si=CR_2$) are formed as unstable reaction species by the heat treatment of silacyclobutanes.[2,3] The reactive silicon compounds undergo a variety of chemical reactions with substrates and silenes themselves. Silenes are also prepared from acylpolysilanes by photolysis[4−7] or by a Peterson-type reaction.[8−12] Measured and calculated NMR chemical shielding tensors of silenes indicated the presence of a genuine Si=C π bond.[13]

Silacyclobutene undergoes interesting thermal isomerizations that include a 1,2-siloxyl shift with the reconstruction of the carbon framework, resulting in many kinds of final products,[14−16] as shown in Scheme 1. Instead of the 1,2-siloxyl shift, a ring-opening reaction

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* To whom correspondence should be addressed. E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp.

[†] Kyushu University.

[‡] Kurashiki University of Science and the Arts.

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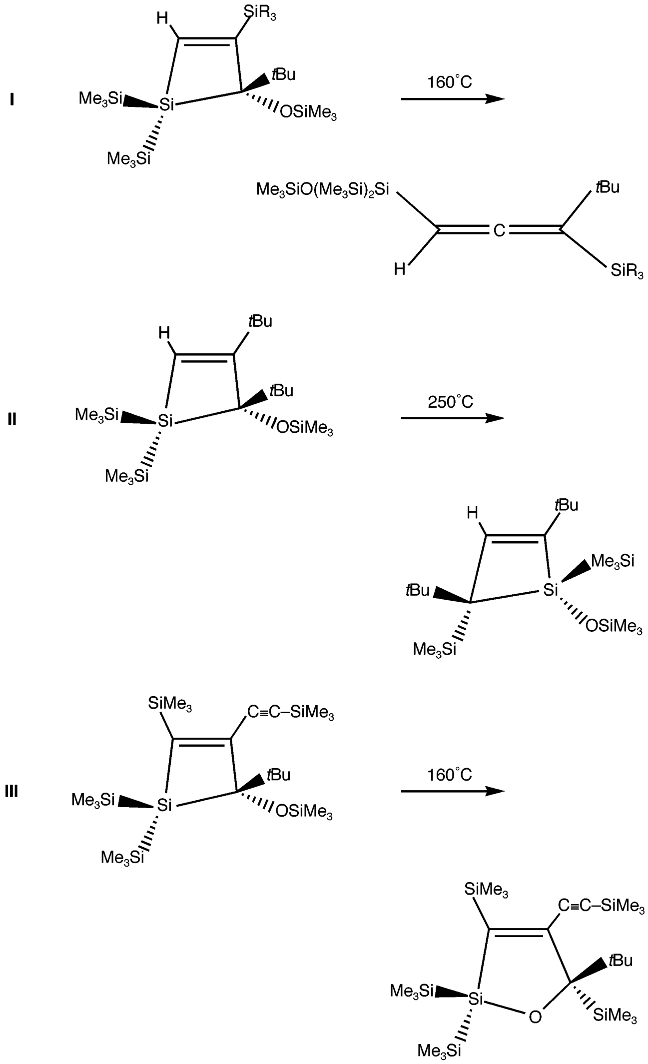
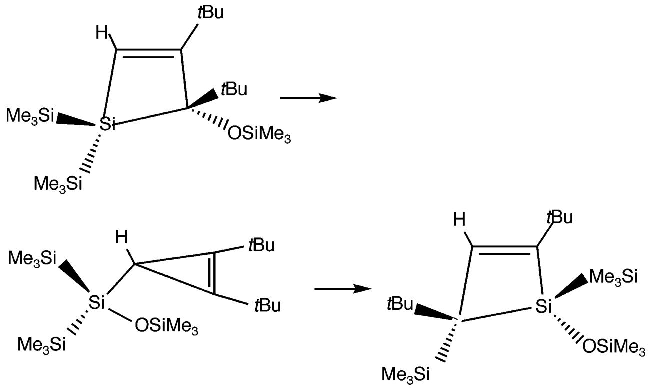
Scheme 1



in silacyclobutene also occurs as a thermal reaction, leading to silabutadiene that involves an Si═C double bond. Although silabutadiene has been considered to exist as a short-lived intermediate, its methanol adduct that is derived from the trans form was detected by using a trapping agent.[15] The ring-opening reaction in the conrotatory motion is a symmetry-allowed process,[17] while the 1,2-siloxyl shift, a symmetry-forbidden process, does not thermally proceed in the carbon system. Once silenes are formed by the ring-opening reaction, the Si═C double bond induces various transformations and migrations to change back to an Si−C single bond. In particular, such reactive species in the silicon system can give rise to a symmetry-forbidden process under thermal conditions. Theoretical consideration of the ring-opening mechanism to silabutadiene promotes a better understanding of the thermal isomerizations that lead to various products.

The products indicated in Scheme 1 are significantly stabilized in energy compared to silacyclobutene, due to the transformation of the C−O bond in the starting compounds to the Si−O bond in the final products as well as the transformation of the Si−Si bond to the C−Si bond. Since the standard bond dissociation energies for Si−O, C−O, C−Si, and Si−Si are 108, 86, 76, and 53 kcal/mol, respectively,[18] the main driving force for the chemical processes from the silacyclobutenes to the final products would arise from the transformations of the weak bonds to the strong bonds.

Scheme 2



Interesting thermal reactions are involved in the chemistry outlined in Scheme 1. The thermal isomerization of silacyclobutene (reaction II) occurs via a cyclopropene derivative as a stable intermediate,[14] as shown in Scheme 2. Cyclopropene was obtained experimentally by the thermal isomerization of silacyclobutene and by the subsequent trapping of cyclopropane using *tert*-butyl alcohol.[15] In the present study we considered the first half of the thermal process in Scheme 2. The purpose of this paper is to address from density functional theory (DFT)[19] computations how the ring opening and the siloxyl shift take place under thermal conditions.

Methods of Calculation

We optimized minima and saddle points on potential energy surfaces using the hybrid density functional B3LYP method[20,21] combined with the 6-31+G(d,p) basis set[22] and performed systematic vibrational analyses for all reaction species to characterize obtained stationary-point structures. After that we carried out additional single-point calculations using the 6-311+G(d,p) basis set.[23] The B3LYP method has been reported to provide excellent descriptions of various reaction profiles, particularly in geometries, heats of reaction, barrier heights, and vibrational analyses.[24] It is pointed out that calculated energies and optimized geometries using the B3LYP method depend on the basis set.[25] Since the comparison of different functionals is useful for quantitative evaluation, we also performed geometry optimization using the MPWPW91 and MPW1PW91 methods.[26] An IRC[27] (intrinsic reaction

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Scheme 3

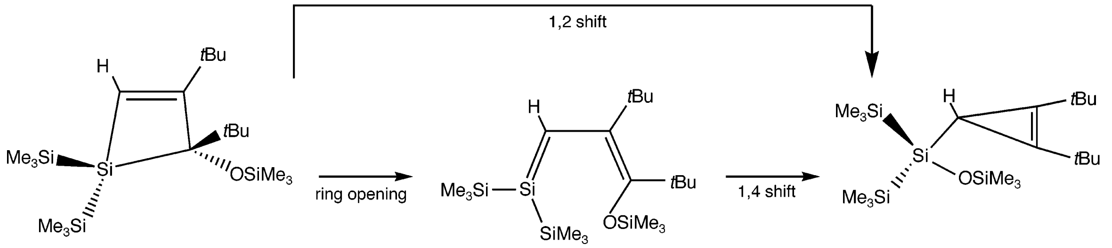

Table 1. Computed Energies (kcal/mol) from Various DFT Methods with the 6-31+G(d,p) Basis Set for the Thermal Isomerization of Silacylobutene[a]

	B3LYP	MPWPW91	MPW1PW91
1	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
TS1a	21.8 (21.7)	18.8 (18.8)	24.8 (24.8)
TS1b	36.5 (36.5)	32.5 (32.6)	40.6 (40.7)
2a	12.4 (12.0)	12.7 (12.5)	16.6 (16.6)
2b	14.5 (14.2)	14.9 (14.7)	18.7 (18.7)
TS2	31.7 (31.2)	31.7 (31.8)	34.8 (34.6)
3	−27.9 (−29.1)	−23.1 (−23.8)	−23.2 (−23.7)
TS3	40.0 (39.7)	38.2 (37.8)	43.8 (43.4)

[a] The values in parentheses are from single-point calculations with the 6-311+G(d,p) basis set.

coordinate) analysis was carried out in the mass-weighted internal coordinate system at the B3LYP/6-31G(d,p) level of theory with the algorithm developed by Gonzalez and Schlegel.[28] We used the Gaussian 98 program package (revision A.11.04) for the calculations.[29]

Results and Discussion

In this section we consider two reaction pathways (Scheme 3), including (i) a 1,4-siloxyl shift via a silabutadiene intermediate that is generated by the ring-opening process and (ii) a direct 1,2-siloxyl shift. The two reaction pathways were found on closed-shell singlet energy surfaces at the B3LYP/6-31+G(d,p) level of theory and were checked by IRC calculations and stability analyses of the wave functions. To evaluate the quality of the B3LYP calculations, we performed geometry optimizations with the pure DFT MPWPW91 and hybrid DFT MPW1PW91 methods and summarized the energies in Table 1. These results suggest that the B3LYP energies are located between the MPWPW91 and MPW1PW91 energies. Thus, we adopted the B3LYP method throughout this study.

Ring-Opening Pathway. We first show how the ring-opening reaction occurs under thermal conditions. There are four possible reaction pathways for the ring opening that lead to silabutadiene **2**. Taking the Woodward−Hoffmann rule into consideration,[18] we can confine the ring-opening processes to the reactions in the conrotatory motion, in which the bonds rotate in the same direction. We determined two concerted processes that lead to **2a** and **2b** via **TS1a** and **TS1b**, respectively, as shown in Figure 1. **TS1a** (**TS1b**) is a transition state in which the Si(1)−C(4) bond is cleaved, the Si(1)−C(4) distance in **TS1a** (**TS1b**) being 2.882 (2.990) Å. As a result of the Si−C bond dissociation, the Si(1)−C(2) and C(3)−C(4) bond distances decrease to 1.801 (1.832) and 1.437 Å (1.465 Å) in **TS1a** (**TS1b**) from 1.868 and 1.560 Å in **1** and are finally changed to 1.751 (1.750) and 1.364 Å (1.372 Å) in **2a** (**2b**). These changes in the bond distances are reasonable and consistent with the reconstruction of the silacyclobutene framework. Calculated energies of **2a** and **2b** are respectively 12.4 and 14.5 kcal/mol relative to **1**. Considering that the energies of unsubstituted butadiene and 1,4-disilabutadiene (Si=C−C=Si) are −9.6 and 38.9 kcal/mol relative to the corresponding cyclobutenes at the B3LYP/6-31G* level, it is interesting to note that the Si=C double bond is correlated with the instability of silabutadiene and 1,4-disilabutadiene. Thus, the instability of the Si=C double bond can be roughly estimated to be 24 kcal/mol. Calculated activation barriers for the ring-opening processes are 21.8 kcal/mol in **TS1a** and 36.5 kcal/mol in **TS1b**. The energy difference of the two transition states is 14.7 kcal/mol, whereas the energy difference between **2a** and **2b** is only 2.1 kcal/mol. Comparison of the two activation barriers tells us that the formation of **2a** is a dominant process in the ring-opening reaction. This result reasonably explains the experimental fact that the trans form (**2a**) was detected by methanol addition, while there was no observation of the cis form (**2b**).

There is an orbital selection rule for the ring-opening reaction, known as torquoselectivity.[30−32] This rule concerns the preference of one of two orbital symmetry-allowed modes to lead to an outward or inward product with respect to a particular substituent, as shown in Scheme 4. Houk and co-workers[30] reported from a theoretical viewpoint that the orbital interaction controls the torquoselectivity in the ring-opening reactions of substituted cyclobutenes. A filled orbital of a donor substituent promotes electrostatic repulsionn, and therefore a donor substituent prefers an outward rotation, while a vacant orbital of an acceptor substituent promotes an inward rotation to maximize the orbital

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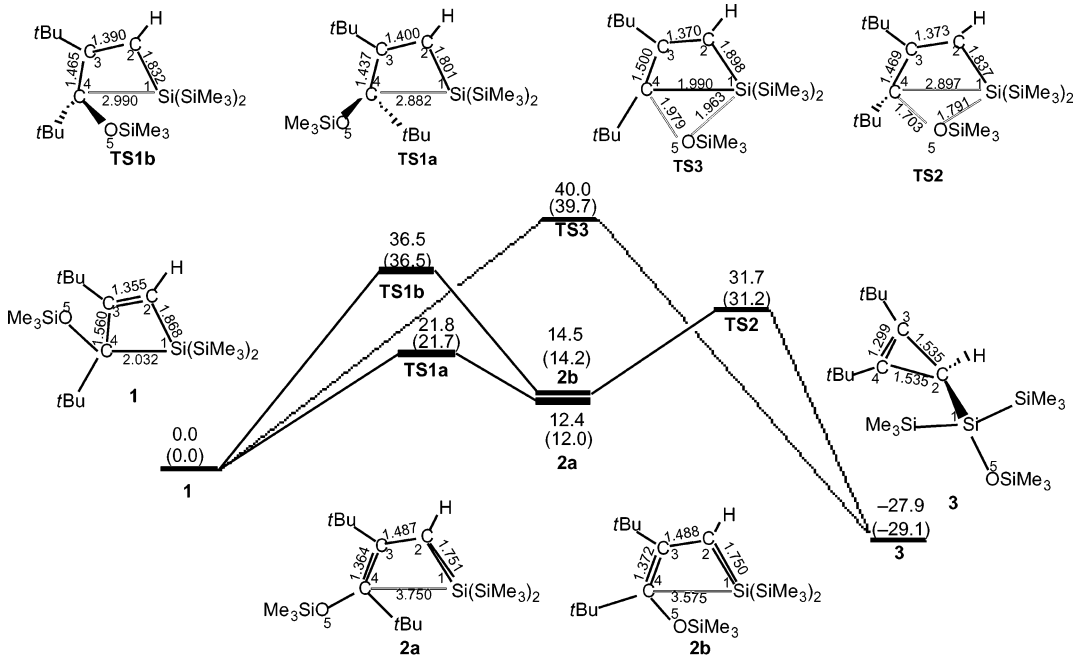


Figure 1. Optimized geometries and energy diagrams for the ring-opening reaction, the 1,2-siloxyl shift, and the 1,4-siloxyl shift at the B3LYP/6-31+G** level of theory. The values in parentheses are relative energies from single-point calculations at the B3LYP/6-311+G** level. Bond distances and energies are in Å and kcal/mol, respectively.

Scheme 4

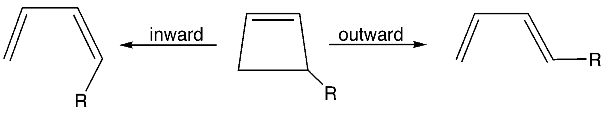
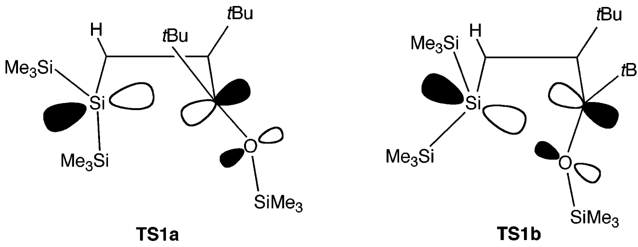


Chart 1



interaction between the filled orbital of the bond being broken and the vacant orbital of an acceptor substituent.

The HOMOs of **TS1a** and **TS1b** are indicated in Chart 1. Since the siloxyl group of **1** works as a donor substituent and has a nonbonding orbital at the oxygen atom, the electrostatic repulsion between the nonbonding orbital and the σ HOMO greatly destabilizes the inward transition state (**TS1b**) relative to the outward one (**TS1a**). Thus, the outward rotation of the siloxyl group is explained by the torquoselectivity rule. Considering the activation energy in each pathway, we can predict from an energetic viewpoint that the reaction pathway through **TS1a** is more favorable in the ring opening of **1** under thermal conditions.

Having described the ring-opening reaction of silacyclobutene on the basis of the torquoselectivity rule, let us next look at the formation of cyclopropene **3**, which is initiated by the 1,4-siloxyl shift. This migration reaction occurs via **TS2**, which connects **2b** and **3**, but there is no transition state that connects **2a** and **3**, due to the unfavorable orientation of the siloxyl group in **2a**. There are two possibilities for the pathway from **2a** to **3**, one-step and two-step processes (cis–trans isomerization of the silabutadiene and 1,4-shift). Despite our best efforts, we could not find the one-step pathway from **2a** to **3**. Although the two-step pathway is possible, its first process, i.e., the cis–trans isomerization, lies more than 60 kcal/mol above the starting material **1**. This two-step pathway is not an important reaction, because it is about 20 kcal/mol higher than **TS1b** and **TS3**. Thus, one of the reaction pathways is the dead end. Figure 1 shows optimized geometries and energy diagrams in the 1,4-siloxyl shift of silabutadiene. **TS2** is a transition state with only one imaginary frequency of 56*i* cm^{-1} corresponding to the cleavage of the C(4)–O(5) bond and the formation of the Si(1)–O(5) bond. These bond lengths are remarkably changed from **2b**: the Si(1)–O(5) bond and the C(4)–O(5) bond distances are 1.791 and 1.703 Å, respectively. Thus, the analysis of the transition state indicates that the C(2)–C(4) bond formation results in a three-membered ring after the 1,4-siloxyl shift. In the three-membered ring of **3** the lengths of the two C–C single bonds and one C–C double bond are 1.535, 1.535, and 1.299 Å, respectively. Since there is no Si=C double bond in this structure, the relative energy is decreased to −27.9 kcal/mol. The relative energy of **TS2** is 31.7 kcal/mol, whereas the formation of **2b** requires 36.5 kcal/mol as an activation barrier. Thus, the first step with respect to the ring opening is the rate-determining step in the two-step mechanism.

The ring-opening reaction can occur in a concerted manner, leading to *cis*- or *trans*-silabutadiene. Although the formation of *trans*-silabutadiene is energetically preferred, according to experiment only *cis*-silabutadiene is transformed into **3** through the 1,4-siloxyl shift. We performed theoretical calculations to examine the reaction of the silabutadiene intermediate with methanol. B3LYP calculations show that the insertions of methanol into **2a** and **2b** are downhill processes with

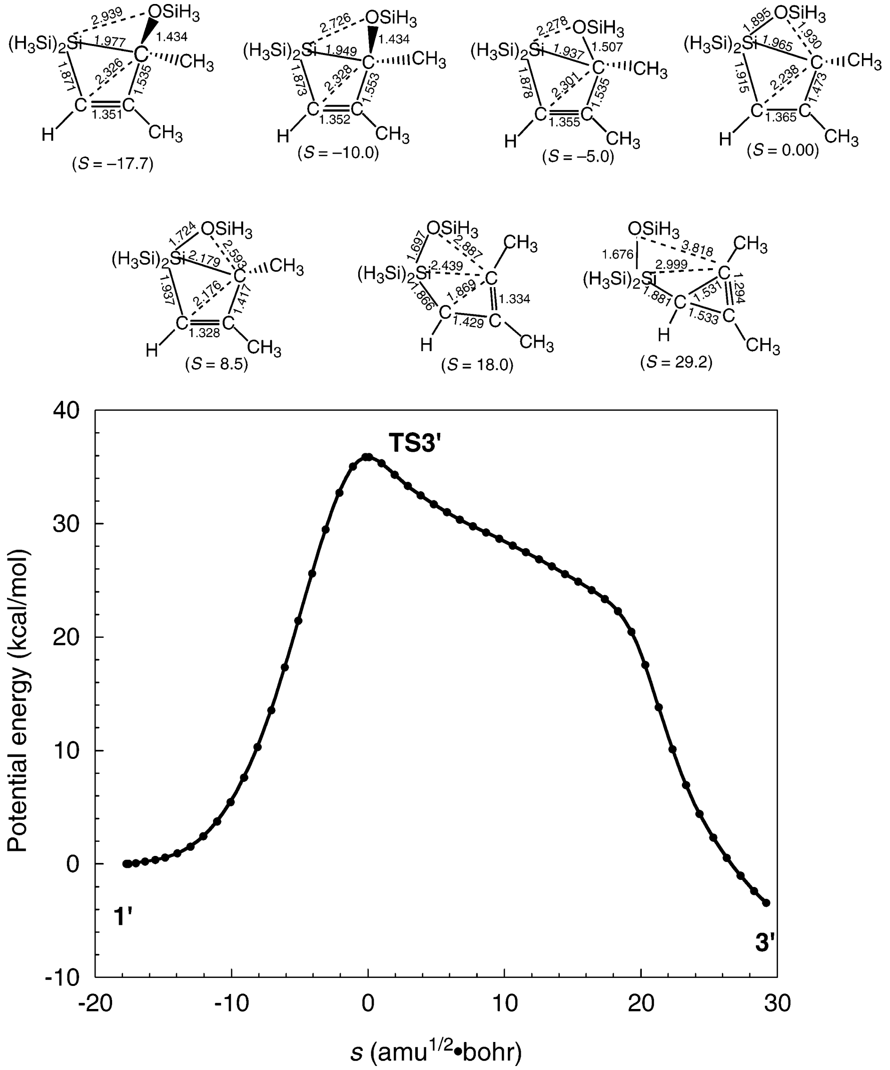


Figure 2. Computed energy profile and snapshots along the IRC of the 1,2-siloxyl shift at the B3LYP/6-31G** level of theory.

exothermic energies of 53.7 and 44.4 kcal/mol, respectively, and that the activation barriers for the methanol insertions into **2a** and **2b** are 5.4 and 6.0 kcal/mol, respectively. These results are in good agreement with the recent theoretical work by Apeloig and co-workers.[33] Once the ring-opening reaction occurs in **1**, the methanol insertion occurs rapidly, due to the small activation barriers. B3LYP calculations for the methanol insertions lead us to conclude that the proportion of the methanol adducts experimentally isolated from the products is determined by the rates of the ring-opening processes. Thus, the fact that the methanol adduct of **2a** is the major product is consistent with the computed energies of **TS1a** and **TS1b**.

Direct Formation Pathway. We tried to search for another reaction intermediate that involves a five-coordinate silicon in the reaction, but we could not find such a species as a local minimum. However, we found a new transition state (**TS3**) that directly connects **1** and **3**. A calculated activation barrier from **1** to **TS3** is 40.0 kcal/mol, which is close to the activation energy from **1** to **TS1b** (36.5 kcal/mol). The difference between **TS3** and **TS1b** is only 3.5 kcal/mol; this one-step process is comparable in energy to the two-step process via *trans*-silabutadiene. This one-step process is associated with a 1,2-siloxyl shift and the formation of a cyclopropene framework; the four-membered ring of silacyclobutene is transformed into the three-membered ring after the siloxyl shift. Figure 1 shows an optimized structure of **TS3**, the imaginary vibrational mode of which (197i cm^{-1}) corresponds to the cleavage of a C−O bond and the formation of an Si−O bond. This transition state involves a five-coordinate silicon because of the presence of the Si(1)−C(4) bond. The C(4)−O(5) and Si(1)−O(5) bonds of **TS3** are 1.979 and 1.963 Å, respectively. The Si(1)−C(2) and Si(1)−C(4) bonds of **TS3** are 1.898 and 1.990 Å, respectively. The C(2)−C(3) bond increases from 1.355 Å in **1** to 1.535 Å in **3**; the C(3)−C(4) bond decreases from 1.560 Å in **1** to 1.299 Å in **3**.

To confirm the reaction pathway and characterize the changes in the geometry, we traced IRC[28] in the direct pathway via **TS3′** using a simple model, as shown in Chart 2. The IRC was constructed from a total of 500 steps to an accuracy of 0.1 amu$^{1/2}$ bohr of s, in which s is the reaction coordinate. **TS3′** was confirmed from the IRC analysis to connect **1′** and **3′**. We display in Figure 3 changes in the geometry and the energy along the reaction pathway, placing $s = 0$ at **TS3′**. Since we found

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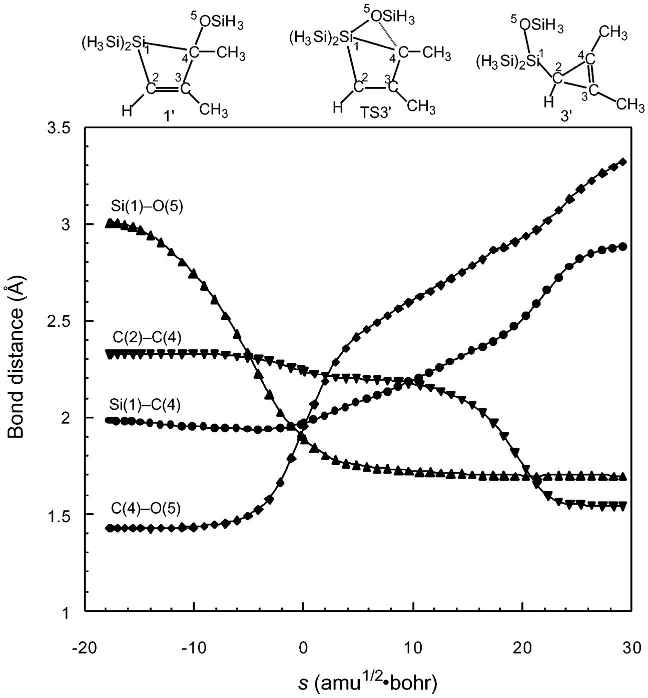
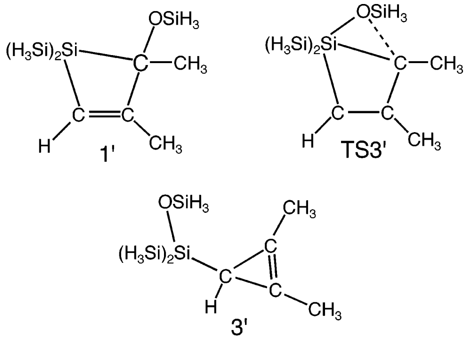


Figure 3. Changes in the geometrical parameters along the IRC of the 1,2-siloxyl shift at the B3LYP/6-31G** level of theory.

Chart 2



little geometrical change between the original model and this simple model, the IRC analysis can describe the direct formation pathway indicated in Chart 2.

Figure 2 shows a plot of the energy profile and snapshots along the IRC. In the 1,2-siloxyl shift, starting from **1′** ($s = -17.7$), silacyclobutene changes to **3′** ($s = 29.2$). The 1,2-siloxyl shift and the formation of the cyclopropene ring occur as a concerted reaction in **TS3**. The IRC calculation tells us that the direct isomerization can be divided into two processes: the 1,2-siloxyl shift occurring in the vicinity of **TS3′** ($s = 0.0$) in the first step and the formation of the cyclopropene framework in the region of $10.0 < s < 20.0$ in the second step. Since the energy profile along the IRC consists of the two peaks corresponding to the first and second steps, this unique profile is consistent with the geometrical change. Computed snapshots at $s = -5.0$, 0.0, and 8.5 show that the Si(1) atom is in an interesting five-coordinate environment, in which the substitution reaction is initiated by the nucleophilic oxygen attack. In the region of $-5.0 < s < 8.5$ the fact that the Si(1)−C(2) bond is slightly increased can be explained by the five-coordination around the Si(1) atom. A detailed description of the reaction profile is given in Figure 2 with respect to the changes in the geometrical parameters. Since the most remarkable change taking place in the path from **1′** to **TS3′** ($s = 0$) is a decrease in the Si(1)−O(5) distance and an increase in the C(4)−O(5) distance, the siloxyl shift occurs in the transition state at $s = 0.0$, while the Si(1)−C(2), C(2)−C(3), C(2)−C(4), and C(3)−C(4) distances have a slight change (≥ 0.1 Å) prior to **TS3′**. The Si(1)−C(4) bond distance initially decreases to 1.937 Å at $s = -5.0$, but after passing **TS3′**, the Si(1)−C(4) bond breaking and the C(2)−C(4) bond forming occur in the region of $0.0 < s < 20.0$. Around $s = 10.0$, the Si(1)−C(4) and C(2)−C(4) distances are 2.18 Å. The Si(1)−C(4) bond breaking and the C(2)−C(4) bond forming occur in the vicinity of $s = 15.0$.

Conclusions

We have demonstrated using B3LYP/6-31+G(d,p) level calculations that the thermal isomerization of silacyclobutene to cyclopropene occurs via two reaction pathways. The first mechanism consists of two-step processes. Two kinds of ring opening based on the Woodward−Hoffmann rule can result in the formation of *cis*- and *trans*-silabutadienes. Since calculated activation barriers for the formation of *cis*- and *trans*-silabutadienes are 36.5 and 21.8 kcal/mol, respectively, the formation of the trans form is energetically more favorable than that of the cis form in this ring-opening step. This result is in good agreement with the experimental observation that only the methanol adduct corresponding to the trans form is detected in the presence of methanol. However, the next transition state with respect to the 1,4-siloxyl shift occurs only in the cis form, due to the orientation of the siloxyl group. A calculated activation barrier for the 1,4-siloxyl shift is 17.2 kcal/mol. Thus, the first step is the rate-determining step in the two-step mechanism. The second mechanism leads to the direct formation of cyclopropene via the 1,2-siloxyl shift, in which the activation barrier is calculated to be 40.7 kcal/mol. The activation barrier of the direct formation of cyclopropene is energetically comparable to that of the ring-opening reaction to *cis*-silabutadiene; the B3LYP DFT calculations suggest that both reaction pathways are likely under thermal conditions. We finally analyzed using an IRC analysis the 1,2-siloxyl shift along the direct formation pathway. The IRC calculations indicate that the 1,2-siloxyl shift can be divided into two processes: the 1,2-siloxyl shift and the formation of the cyclopropene ring.

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