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An ab Initio MO Study of Structure and Reactivity of 4-Silatriafulvene

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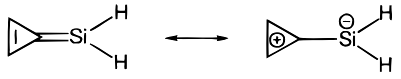
Abstract: The structures and reactions of 4-silatriafulvene were studied in detail by ab initio molecular orbital theory. At the equilibrium structure, 4-silatriafulvene shows severe bending about the Si=C double bond. A planar structure having two conjugated double bonds (an Si=C and a C=C double bond in the cyclopropenyl moiety) is the transition state for flopping between the two degenerate bent structures; the activation energy is within 1 kcal/mol at MP2/6-311++G** + ZPE. It is concluded that 4-silatriafulvene is balanced by two stabilizing factors, aromaticity of the cyclopropenyl moiety and Si=C double-bond formation. The remarkably low reactivity of a 4-silatriafulvene toward water that was found experimentally is reproduced theoretically by comparing the transition structures and activation energies with those of silaethene + water. Intramolecular isomerization from 4-silatriafulvene to silacyclobutadiene via cyclopropenylsilylene is even competitive with the water-addition reaction.

Introduction

Since the first successful observation and synthesis of methylenecyclopropene,[1] the structure and the aromaticity of methylenecyclopropene and 4-heterosubstituted triafulvenes have been extensively discussed.[2−12] On the basis of the different experimental and theoretical arguments, some of these molecules are regarded as aromatic, others as nonaromatic or even antiaromatic species. Cyclopropenone, the most extensively studied 4-heterosubstituted triafulvene, is usually considered as an aromatic molecule,[3,5,7,8,13−15] although some earlier papers[16] questioned this view on the basis of the very small magnetic susceptibility anisotropy or the electron distribution of the molecule. The experimental and theoretical considerations of the aromaticity of these molecules are well summarized in the literature.[8]

Chart 1



1a **1b**

Among the various 4-heterosubstituted triafulvenes having potential aromaticity, 4-silatriafulvene is quite unique with an exo Si=C double bond that is intrinsically polarized as Si^+-C^- in contrast to a typical 4-heterosubstituted triafulvene such as cyclopropenone. The polarity of the Si=C double bond is expected to be reduced by resonance structure **1b** as shown in Chart 1.

Gordon et al.[4] studied the $[C_3SiH_4]$ isomers with the HF/6-31G* ab initio method and indicated a planar equilibrium structure for 4-silatriafulvene (**1**). Later, however, with use of the same level of theory, this geometry was found to be a transition structure[7] and a nonplanar C_s symmetry was

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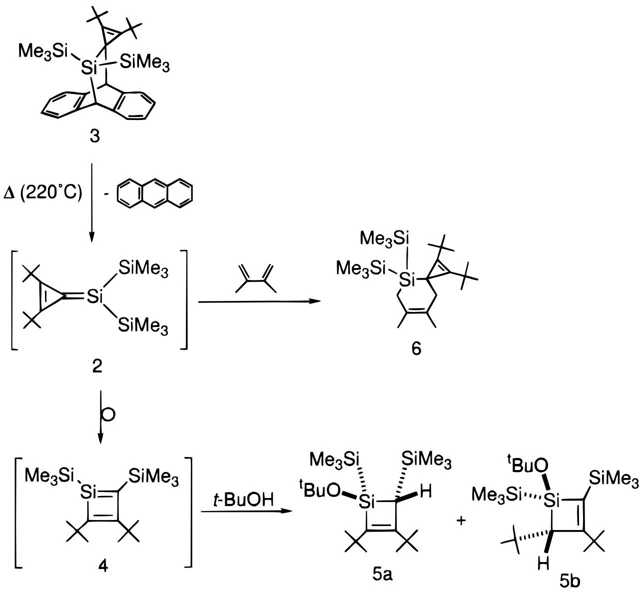
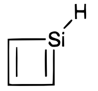
Scheme 1



proved to be an optimum geometry. The lack of planarity was attributed to the antiaromatic character of the ring system. In a recent paper, Burk et al.[8] have confirmed the nonplanar form, but the geometrical data obtained with the MP2/6-31G* level of theory are strongly different from the previous results. The authors insist that the coplanarity of the cyclopropene ring with the substituent is not a prerequisite of aromaticity; **1** is an aromatic molecule, although the degree of aromaticity is not clear. According to the energetic criteria, **1** is the least aromatic of the investigated 4-substituted triafulvenes, while geometric and magnetic criteria predict an intermediate degree of aromaticity.

We have recently reported the generation of a 4-silatriafulvene derivative, 1,2-di-*tert*-butyl-4,4-bis(trimethylsilyl)-4-silamethylenecyclopropene (**2**),[17] via a sila-Peterson reaction[18] of di-*tert*-butylcyclopropenone with tris(trimethylsilyl)silyllithium or thermolysis of an anthracene adduct of **2** (**3**) at 220 °C. As shown in Scheme 1, a reaction of *tert*-butyl alcohol with **2** generated by the thermolysis of **3** does not produce direct alcohol adducts of **2** but four-membered-ring compounds **5a** and **5b**, while **2** reacts with 2,3-dimethylbutadiene to give adduct **6**. Apparently, **5a** and **5b** are produced via isomerization of **2** to a silacyclobutadiene **4** followed by addition of *tert*-butyl alcohol. The results indicate that (1) 4-silatriafulvene **2** reacts much faster with the diene than with the alcohol in contrast to the usual silaethenes and (2) facile isomerization occurs from a silatriafulvene to the corresponding silacyclobutadiene.

Ab initio MO calculations were performed to elucidate characteristics of the structure and reactivity of **1**. Important results of the present study are the following: (1) At the equilibrium structure, **1** shows severe bending about the Si$=$C double bond and a planar structure is found as the transition state for flopping between the two degenerate bent structures with very low activation energy. (2) Addition of water toward **1** proceeds with much higher activation energy than the reaction of silaethene with water, in conformity with our previous experimental results.[17] (3) The most favorable pathway for isomerization of **1** to silacyclobutadiene (**7**) involves rearrangement of **1** to cyclopropenylsilylene (**8**) and then to **7**; the activation energy for the isomerization of **1** to **7** is smaller than that for the addition of water to **1**.



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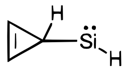

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Calculations

Quantum-chemical calculations were carried out with the GAUSSIAN 94[19] program package. To study the effect of basis and electron correlation, the standard 6-31G* and 6-311++G** basis sets were used with MP2, MP3, MP4SDQ, and QCISD. Second derivatives and harmonic vibrational frequencies were calculated for all the molecules investigated. Zero-point energies (ZPEs) were calculated at the MP2/6-311++G** level. To test the adequacy of the single-reference calculations, the CISD/6-31G* calculations on **1** were carried out as well. The analysis of CI wave functions indicated that the single HF reference provided an appropriate description. (Only the HOMO$-$LUMO doubly excited configuration had a coefficient larger than 0.02 (0.07) apart from the HF reference.) The potential energy curve for the bending motion of silatriafulvene was determined by proceeding along the given reaction coordinate and optimizing all the remaining degrees of freedom.

Transition states for the water-addition reactions and isomerizations were fully optimized by using the eigenvector following method. Each reaction path was confirmed by internal reaction coordinate calculations. Frequency calculations were done for all the obtained transition states and the existence of only one imaginary frequency was checked.

Results and Discussion

Structure. As shown in Figure 1, the optimum structure of **1** at the MP2/6-311++G** level has a C_s symmetry with trans-bent arrangement around the Si$=$C bond; the degree of pyramidalization is larger at Si than at C^3 as found by comparing the angle C$^3-$Si$-$M^1 with M$^2-$C$^3-$Si. The geometry is not sensitive to the basis set used and almost the same geometry is found with the 6-31G* basis set.[20] However, considerable difference between the HF and correlated methods has been found in the deviation from planarity around the Si$=$C double bond, Si$-$C^3 and C$^1-$C^3 bond lengths, and in the C$^1-$C$^3-$C^2 bond angle; the HF calculations give more bent structure (smaller C$^3-$Si$-$M^1 angle) and about 0.1 Å longer Si$-$C bond; the deviation among the results of the correlated calculations is small. Since the extent of the deviation from planarity is related to the singlet$-$triplet separation of the interacting silylene and carbene fragments,[21] the inclusion of electron correlation may be crucial for a reliable description of the molecular geometry of **1**. Therefore, in this paper, our conclusions will be drawn only from the MP2 (and higher level) calculations.

The structures of both planar and nonplanar forms of **1** are compared with those of some related molecules (**9**$-$**19**) in Table 1. While the Si$-$C^3 distance in the planar structure of **1** (1.712 Å) is very close to the ordinary Si$=$C double bond length as

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(20) Detailed geometrical parameters and energies for **1** and their level dependence are given in the Supporting Information.

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Table 1. Selected Bond Lengths, Bond Angles, and Mulliken Charges in **1** and Related Molecules Optimized at the MP2/6-311++G** Level[a]

	bond length (Å)[b]			bond angle (deg)	mulliken charge[b]		
compd	Si−C³	C¹−C³	C¹−C²	C¹C³C²	Si	C³	C¹
1(planar)	1.712	1.468	1.319	53.4	0.324	−0.445	−0.030
					(−0.076)	(−0.087)	(0.136)
1(nonplanar, optimized)	1.743	1.460	1.322	53.9	0.303	−0.390	−0.020
					(−0.067)	(0.004)	(0.158)
9	1.792	1.412	1.346	56.9	0.695	0.200	0.050
10	1.712				0.724	−0.761	
11	1.728	1.511		114.8	0.472	0.137	−0.603
12	1.877				0.883	−0.753	
13		1.449	1.333	54.8		0.435	−0.193
14	1.696	1.488	1.519	61.4	0.558	−0.338	−0.255
15	1.874	1.534	1.302	50.2	0.647	−0.232	−0.241
16		1.515	1.306	51.1		−0.245	−0.146
17	1.860	1.523	1.503	59.1	0.644	−0.227	−0.327
18		1.511	1.511	60.0		−0.229	−0.229
19		1.372	1.372	60.0		0.027	0.027

[a] For numbering scheme, see the structures in the text. [b] Calculated at the HF/6-311++G** level. See ref 26. π-Charges are in parentheses.

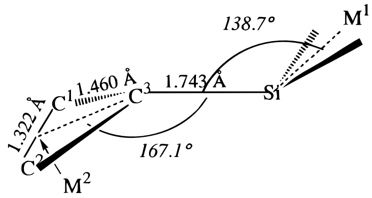
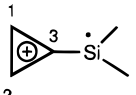


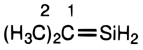
Figure 1. MP2/6-311++G** equilibrium structure of 4-silatriafulvene **1**. M¹ and M² are the points on lines bisecting HSiH and C¹C³C² angles, respectively.



9

$H_2C{=}SiH_2$

10

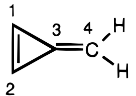


$(H_3C)_2C{=}SiH_2$

11

$H_3C{-}SiH_3$

12



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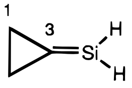

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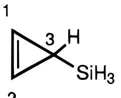

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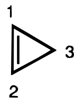

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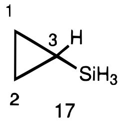

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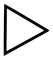


18

19

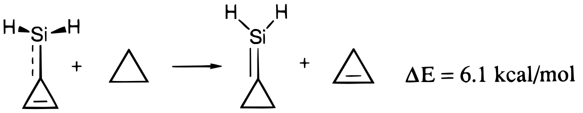
$H_2Si{=}SiH_2$

20

found in **10** and **11**, the distance is significantly longer in the nonplanar form (1.743 Å). The C−C bond lengths in the fully delocalized cyclopropenium cation (**19**) are 1.372 Å, while they are 1.511 Å in the saturated cyclopropane (**18**). It is expected that the difference in the ring CC bond lengths decreases and the C¹−C³−C² angle approaches the ideal 60° as the extent of delocalization in the ring increases; the bond alternation is at the maximum in cyclopropene (**16**) (and in cyclopropenylsilane (**15**)). The three-membered ring in the planar **1** is regarded to consist of a separated C═C bond (1.319 Å) and two short single C−C bonds (1.468 Å), while in the nonplanar **1**, slight equalization can be observed in these CC bond lengths. These facts mean that the contribution of resonance form **1b** in the nonplanar **1** is more important than that in the planar **1**. However, a comparison to the planar methylenecyclopropene **13** leads to the conclusion that the aromatic delocalization of **1** is small even in the nonplanar form. Even in silatriafulvene cation **9**, the Si−C distance is smaller than a regular single bond and the C−C bond lengths differ considerably, indicating that the ring is not fully aromatic.[22]

The charge distribution of **1** also supports the significant contribution of resonance form **1b** (Table 1). The silicon in **1** is far less positive than that in the other Si═C compounds (**10**, **11**, and **14**), while the carbon moiety attached to the silicon is less negative. The charge distribution in **1** depends significantly on the geometry, and the dependence is emphasized in the π-charge distribution of the molecule. Thus, while the molecule moves from the planar to the nonplanar form, the π electrons shift from the ring toward the silicon. An opposite but weaker σ electron stream partly balances the effect and forms the final total charge distribution. As a qualitative description, Figure 2 shows the variation in the shape of HOMO from the planar to the nonplanar form calculated at the HF/6-311++G* geometry. It is clearly demonstrated that the Si−C π-bond found at the planar structure disappears at the nonplanar geometry of **1**, where the silicon atom can be described as a singly bonded trivalent σ^3,λ^3-silicon with a lone electron pair.

An apparent isodesmic reaction as shown in eq 1, which is



(1)

similar to those proposed by Staley[3,5] and others,[6−8,14,15] is used to estimate the stabilization energy of **1**. The reaction energy (ΔE) of eq 1 at the MP2/6-311++G** level is 6.1 kcal/mol, which is comparable with the corresponding ΔE of methylenecyclopropene (**13**, 8.84 kcal/mol) calculated by using a reaction of methylenecyclopropene with cyclopropane to give methylenecyclopropane and cyclopropene.[23] Equation 1 does not take the differences in the ring strain energy, σ-delocalization, hybridization, and the other unknown energetic contributions into account appropriately. In addition, for silatriafulvene there are different geometry species on the two sides of the equation. The existence of an Si═C double bond in **1** is

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(22) Comparison of the CC bond lengths between **15** and **16** and between **17** and **18** shows that a silyl substituent at C³ carbon causes lengthening of the C¹−C³ and C²−C³ bonds together with shortening of the C¹−C² bond. Therefore, the difference among three CC bond lengths in **9** (and also in **1**) may partly be ascribed to the electronic effects of the silyl substituent.

(23) The stabilization of **1** as well as methylenecyclopropene is much smaller than ΔE of benzene (38.9 kcal/mol), which is calculated by using a reaction of benzene with cyclohexane to give cylohexene and 1,3-cyclohexadiene.

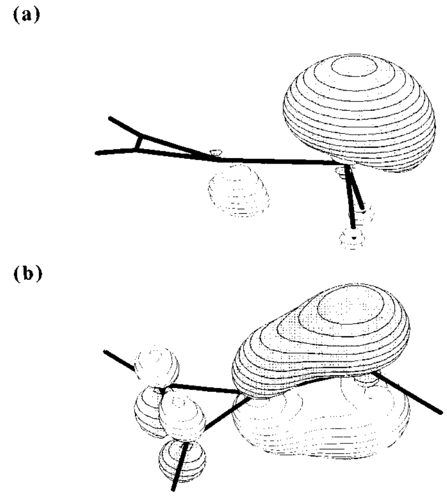

Figure 2. The shape of HOMO in (a) nonplanar and (b) planar 4-silatriafulvene at the HF/6-311++G* level.

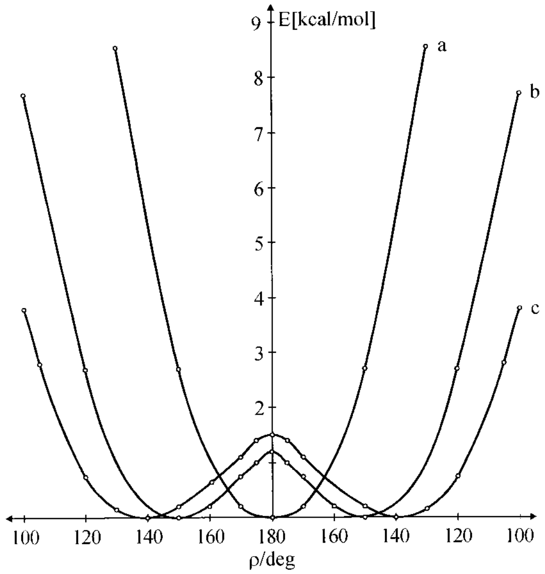

Figure 3. Potential energy curves of (a) silaethene and methylenecyclopropene (two curves are completely overlapped), (b) disilene, and (c) 4-silatriafulvene.

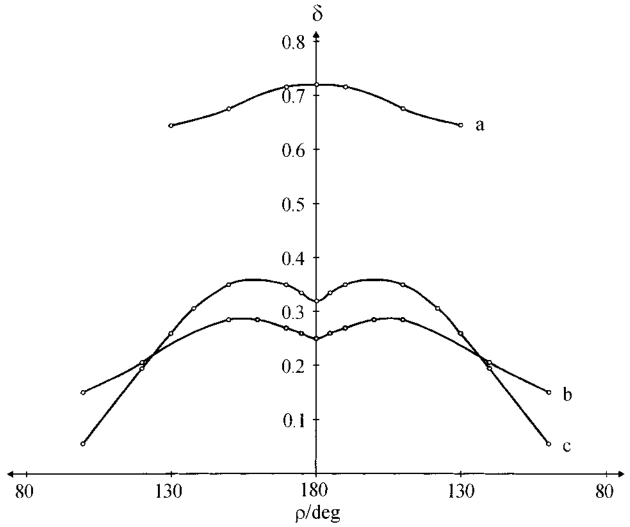

Figure 4. Variation of Mulliken charge on silicon with the bending motion in (a) silaethene, (b) disilene, and (c) 4-silatriafulvene.

questionable as discussed above.[24] The electronic structures of the Si=C and cyclopropenyl ring moieties in **1** are tightly coupled and sensitively balanced; the more aromatic the ring is, the weaker the Si=C π-bond is. Therefore, the reaction of eq 1 cannot be considered as "isodesmic" but gives only information on the *stabilization of the whole molecule* relative to an isolated Si=C bond plus a (localized) C=C bond in the cyclopropene ring.

Because the energy difference between the planar and nonplanar structure of **1** is very small to be between 0.9 and 2.0 kcal/mol depending on the calculation,[20] the C^3-Si-M^1 bending motion is of essential importance in the characterization of the molecule. Bending potential energy surfaces for **1** were calculated by varying the C^3-Si-M^1 angle (ρ). Similar calculations were also carried out for silaethene (**10**), methylenecyclopropene (**13**), and disilene (**20**). As shown in Figure 3, the bending potential of **1** is highly anharmonic and best fitted by the following quadratic potential (energies and angles are given in kcal/mol and deg, respectively):

$$V(\rho) = 60.42048 - 0.81356\rho + (6.35811 \times 10^{-4})\rho^2 + (2.71268 \times 10^{-5})\rho^3 - (8.69928 \times 10^{-8})\rho^4 \tag{2}$$

On the other hand, both the potential functions of **10** and **13** are accidentally superimposable and well approximated with the following harmonic function:

$$V(\rho) = 124.95838 - 1.41848\rho + (4.02547 \times 10^{-3})\rho^2 \tag{3}$$

Disilene **20** is nonplanar with a 0.82 kcal/mol barrier height to planarity at the MP2/6-311++G**+ZPE level, being in good agreement with the previously estimated values of 1−2 kcal/mol.[25] The potential functions of **20** and **1** are very similar and it is likely that at room temperature both molecules perform a large amplitude bending vibration, although the anharmonic bending frequencies are not known.

Figure 4 shows the effect of bending motion on the charge of silicon in molecules **1**, **10**, and **20** at the HF/6-311++G** level.[26] While the trend in the bond lengths of these molecules is the same and the shortest is found at the planar arrangement, two types of charge variations can be observed. Silaethene **10** has the maximum positive charge at the planar structure. The positive charge on the silicon atom of **1** is, however, the greatest at about $\rho = 160°$ and a small minimum can be seen at the planar arrangement. As a similar trend is found in **20**, the origin of the nonplanarity would be the same in both molecules and independent of the aromaticity of the ring.

Reactivity. Two important features of the reactivity of 4-silatriafulvene have been derived experimentally:[17] (1) very low reactivity toward alcohols and (2) facile isomerization to silacyclobutadiene. To elucidate the theoretical bases of the two features, all possible reaction pathways of water-addition to **1** and the isomerization were investigated.[27] Important reaction channels for **1** were revealed by calculations as shown in Figure 5. As a comparison, Figure 6 shows the scheme for the reactions of silaethene **10**. The relative energies of the reactants (R), products (P), and transition states (T) concerning the reactions of **1** and **10** are summarized in Table 2. The

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(24) Following this reasoning, the Si=C double bond in the nonplanar form of **1** and related molecules is here drawn with a broken line.

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(26) Since we discuss only the relative atomic charges, the HF charges were calculated. It was checked that the HF charges gave the same trend as the MP2 charges at several geometrical points.

(27) See Supporting Information for the details including the results of the calculations for the reaction pathways not discussed in the text.

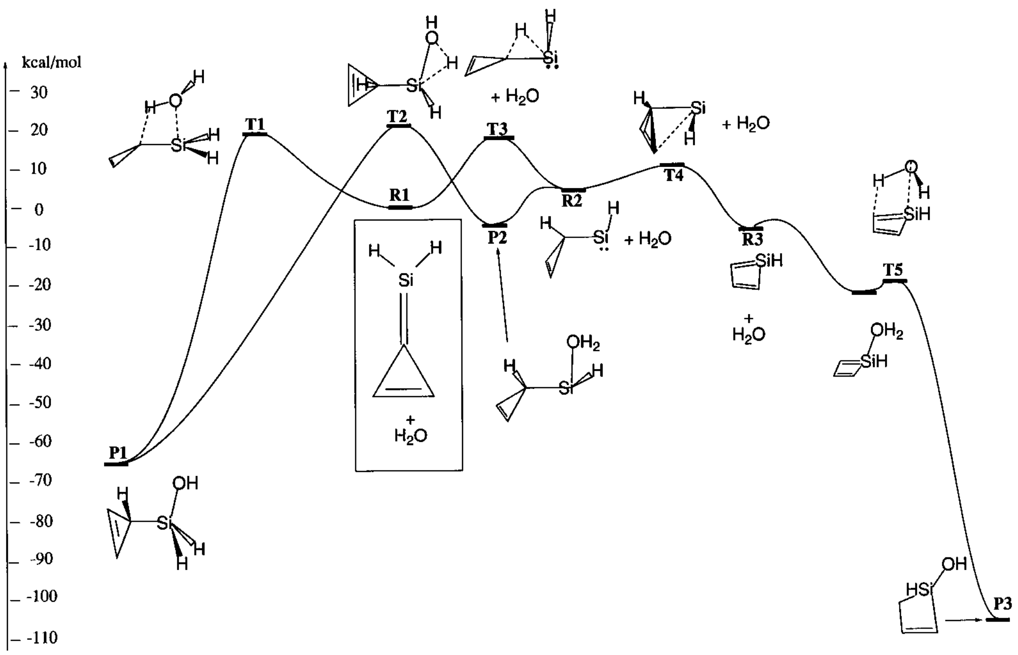

Figure 5. Reaction diagram for isomerization and water-addition of silatriafulvene. Relative energy is the result at the MP2/6-311++G** level.

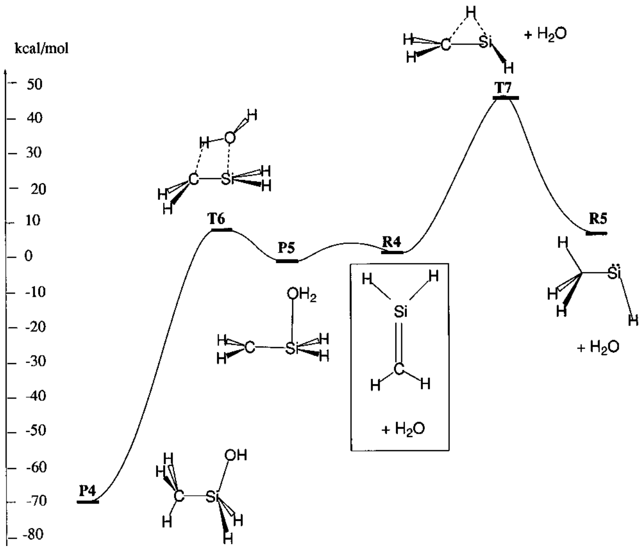

Figure 6. Reaction diagram for isomerization and water-addition of silaethene. Relative energy is the result at the MP2/6-311++G** level.

structural data of the relevant molecules are shown in Figure 7. In the water-addition reactions, the energy is subjected to the basis set superposition error (BSSE). To correct for BSSE, the full counterpoise method[28] has been used at the MP2/6-311++G** level at the geometry of the supermolecules. As shown in Table 2, the BSSE contributions are relatively large (ca. 6 kcal/mol) for the reactions of **1** (and **10**) with water. The reason may be ascribed to the fact that the water molecule has two interacting points with much polarized molecules of **1** (and **10**) at the transition states of the addition reaction.[29]

Prior to discussing the reactivity of **1** toward water, a similar addition reaction of **10** (R4) is described as a reference. The latter reaction was studied earlier by Nagase et al.[30] using the HF/6-31G* level of theory. Since the reported transition state has been found to be a second-order saddle, we have recalculated this reaction using the HF/6-31G*, MP2/6-31G*, and MP2/6-311++G** levels of theory (Table 2 and Figure 6). In the water-addition to **10**, normal (R4-to-P4) and abnormal additions are possible, where the oxygen of water attacks silicon and carbon, respectively. During the normal addition, the formation of a weak complex (P5) is observed in an early stage of the reaction and then the final addition product P4 is produced via the very low energy transition state T6; the activation energy (E_a) is estimated as 9.0 kcal/mol. The abnormal addition to give silylmethanol (E_a = 53.4 kcal/mol by our calculation) cannot compete with the normal addition.

The normal addition pathway for **1** (R1-to-P1) proceeds via transition state T1 without formation of any complexes with E_a of 20.0 kcal/mol. Although the energy difference between normal and abnormal addition pathways in **1** is smaller than that in **10**, the normal addition should still be preferred; E_a for the abnormal addition is 39.2 kcal/mol. Much higher E_a for the normal addition to **1** than the corresponding reaction of **10** explains the low reactivity of **1** toward hydroxylic compounds found experimentally.

Since the interconversion between a silacyclobutadiene and a cyclopropenylsilylene has been observed by Fink et al.,[31] the isomerization of **1** to silacyclobutadiene (**7**) may proceed through the intermediary formation of cyclopropenylsilylene (**8**).

In the isomerization of the parent silaethene to methylsilylene, the energy barrier has been found to be about 40−45 kcal/mol;[32] a similar value is also obtained by our calculations (42.7 kcal/mol). While the activation energy for the isomerization of silaethene to silylcarbene has not been determined, our calculations including electron correlation effects showed that the activation energy is more than 70 kcal/mol, which makes this isomerization very unlikely.

The isomerization of **1** to **8** via path (R1−T3−R2) seems to be an easy process; the reaction energy is only 4.8 kcal/mol

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Table 2. Total Energies (E_T in au) and Relative Energies (E_R in kcal/mol) of Structures Appeared in the Reactions of **1** and **10**[a]

	HF/6-31G*		MP2/6-31G*				MP2/6-311++G**		
	E_T	E_R	E_T	E_R*	E_R	$E_R - E_R$*	E_T	E_R	$E_{R(BSSE)}$
T1	−480.64573	35.0	−481.31202	13.6	14.2	0.6	−481.48960	14.2^b	20.0
T2	−480.64401	36.7	−481.31473	11.9	13.2	1.3	−481.48637	16.9^b	22.4
T3	−404.65370	21.5	−405.10528	19.8	18.8	−1.1	−405.20747	17.0	17.0
T4	−404.67046	13.3	−405.11713	12.4	13.4	1.0	−405.22055	10.7	10.7
T5	−480.71183	−3.6	−481.36930	−22.3	−17.3	5.0	−481.54965	−19.1^b	−14.9
P1	−480.71183	−62.9	−481.44687	−71.0	−67.2	3.7	−481.61614	−62.0^b	
P2	−480.70444	1.9	−481.35051	−10.5	−6.1	4.4	−481.52377	−3.4^b	0.3
P3	−480.87593	−103.5	−481.51433	−113.3	−106.7	6.7	−481.68112	−99.9^b	
R1	−404.68931	0.0	−405.13688	0.0	0.0	0.0	−405.23637	0.0	0.0
R2	−404.67754	9.0	−405.12897	5.0	6.2	1.3	−405.23056	4.8	4.8
R3	−404.67755	9.6	−405.14227	−3.4	−1.9	1.5	−405.24802	−6.3	−6.3
T6	−405.03343	9.1	−405.44607	0.9	1.9	1.1	−405.59993	3.2	9.0
T7	−328.96798	43.5	−329.18010	44.2	43.3	−0.9	−329.25935	42.7	42.7
P4	−405.18107	−83.5	−405.57265	−78.6	−74.2	4.4	−405.71606	−66.6	
P5	−405.05305	−3.2	−405.45521	−4.9	−2.8	2.1	−405.60939	−1.9	−0.1
R4	−329.03726	0.0	−329.25060	0.0	0.0	0.0	−329.32834	0.0	0.0
R5	−329.04654	−5.8	−329.24702	2.3	3.7	1.5	−329.32249	5.1	5.1

[a] Relative energies for T1−T5, P1−P3, and R1−R3 were calculated to R1, while those for T6−T7, P4−P5, and R4−R5 were to R4. E_R, E_R*, and $E_{R(BSSE)}$ indicate the energies with ZPE, without ZPE, and with ZPE + BSSE, respectively. [b] ZPE was calculated with the 6-31G* basis.

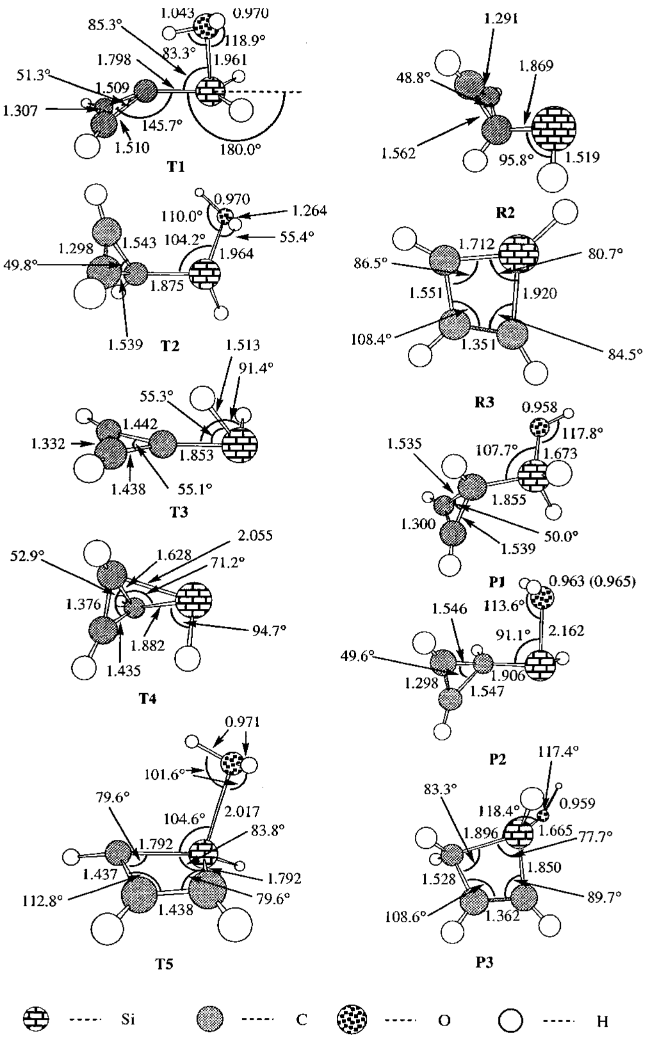

Figure 7. Optimized structures of T1−T5, R2−R3, and P1−P3 at the MP2/6-311++G** level.

and the activation energy is only 17.0 kcal/mol, less than half of the barrier of the corresponding silaethene isomerization. The transition structure T3 can be reached by hydrogen shift from silicon to carbon. Low activation energy of the isomerization of **1** to **8** may be understandable by considering that this reaction path follows the SiH_2 rocking mode of R1 (**1**) whose frequency (214 cm^{-1}) is remarkably lower than those of **10** (471 cm^{-1}) and **14** (652 cm^{-1}).[27] At T3, the silicon is located in the ring plane and the difference among the ring C−C bond lengths is decreased, being suggestive of enhanced aromaticity, the fact of which may be another reason for the low activation energy of the isomerization via T3. Cyclopropenylsilylene **8** (R2) isomerizes to **7** (R3) via a pyramid-like transition state T4 with comparatively low activation energy (E_a = 5.9 kcal/mol). To our knowledge, this is the first theoretical proof about the mechanism of the isomerization of a cyclopropenylsilylene to the corresponding silacyclobutadiene found by Fink et al.[31] Because the overall activation energy for the route R1−T3−R2−T4−R3 (17.0 kcal/mol) is much lower than that for another route from R1 to R3 via a cyclic silylcarbene (E_R = 50.2 kcal/mol), the former is concluded to be the preferred pathway from **1** to **7**.

In contrast to the previous HF calculations,[4] **7** at the MP2 level is more stable by 6.3 kcal/mol than **1**. As shown in Figure 7, the geometry of **7** (R3) clearly indicates the antiaromatic electronic structure. Silacyclobutadiene **7** can easily react with water via the low-energy transition state T5. The existence of the weakly bonded water complex on this path is uncertain, because the complex is found only at the HF level.

The present calculations show that the rate determining step for the reaction sequence from **1** (R1) to **7** (R3) followed by water addition (R1−R2−R3−P3) is the isomerization of R1 to R2 with the activation energy of 17.0 kcal/mol, which is comparable to or even lower than that for the water addition to R1 (20.0 kcal/mol). Experimentally, we have observed facile migration of a trialkylsilyl group from silicon to carbon during isomerization from **2** to **4**, instead of the hydrogen migration investigated theoretically. Since silyl migration from silicon to carbon in 1-silylsilaethene is known to be much easier than the corresponding hydrogen migration in silaethene both experimentally[33] and theoretically,[34] the present theoretical results are compatible with our experimental observation.

A reaction channel of **8** (R2−P2−T2−P1) may lead to P1, the water addition product of **1**, via the formation of a silylene−water complex (P2), which is followed by the migration of a

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hydrogen from oxygen to silicon. The reaction path from R2 to P1 has a rather high activation energy (17.6 kcal/mol), and therefore cannot compete with the isomerization of R2 to R3 ($E_a = 5.9$ kcal/mol).

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Supporting Information Available: Tables of geometrical parameters and total energy of **1**, relative energies in the various reactions of **1**, harmonic vibration frequencies of **1** and related compounds, and figures of a detailed reaction diagram and optimized transition structures (6 pages). See any current masthead page for ordering information and Web access instructions.

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