

# Role of Diagonal Silicon–Carbon Interaction in the [2 + 2] Cycloaddition of Silene and Acetylene

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Mechanistic aspects of a series of thermal reactions that start from acylpolysilane are discussed from B3LYP density functional theory calculations. The chemistry includes the 1,3-silyl migration on acylpolysilane that leads to the formation of silene and the [2 + 2] cycloaddition between silene and acetylene that gives rise to silacyclobutene, an organosilicon four-membered ring compound. Calculated energies for these reactions are reasonable as chemical processes that proceed under thermolysis conditions. There are two kinds of reaction pathways in the 1,3-silyl migration on acylpolysilane with respect to the stereochemistry of the migrating silyl group; one is a retention pathway and the other is an inversion pathway. The retention pathway is energetically preferred to the inversion pathway, being fully consistent with previous results about similar reactions. Silene thus formed undergoes [2 + 2] cycloaddition with acetylene in a two-step manner, resulting in the formation of silacyclobutene. The reason that this “symmetry-forbidden” reaction occurs under thermolysis conditions is considered from intrinsic reaction coordinate calculations as well as orbital interaction analyses. Because the orbital amplitude is significant on the Si atom of silene, the interaction in the region between the silene Si atom and the diagonal acetylene C atom is dominant in the initial stages of the ring-closure process. Consequently, the formation of the diagonal Si–C bond has a preference over that of the proper Si–C bond finally formed in the four-membered ring. This initial process is important in the avoidance of the symmetry restriction arising from the unfavorable HOMO–LUMO overlap in the [2 + 2] cycloaddition.

## Introduction

There are many 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 syntheses of various organosilicon compounds;<sup>1</sup> however, our understanding of mechanistic aspects of the diverse chemical reactivities of unsaturated silicon compounds is still lacking. Our interest in this study is the reaction of silaethylene or silene (R<sub>2</sub>-Si=CR<sub>2</sub>)<sup>2</sup> with acetylene. Gusef'nikov and Flowers<sup>3,4</sup> demonstrated that silenes are formed as unstable reaction species by the heat treatment of silacyclobutanes

and that the resultant reactive silicon compounds undergo a variety of chemical reactions with substrates and silenes themselves. Silenes are also prepared by the photolysis,<sup>1c,5–7</sup> Peterson-type reaction,<sup>8–12</sup> and thermolysis<sup>13–18</sup> of acylpolysilanes. We are able to capture

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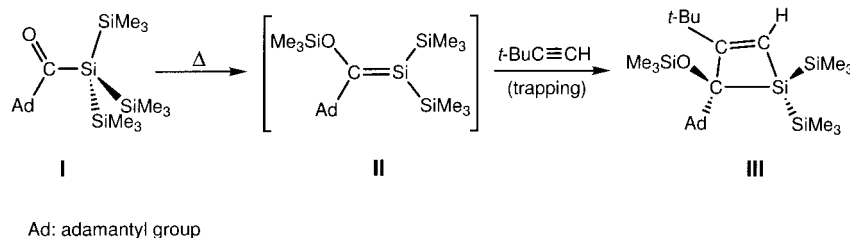
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## Scheme 1



silenes thus formed as a reactive intermediate by using acetylene as a trapping agent through [2 + 2] cycloaddition that leads to the formation of silacyclobutenes.<sup>5,7,13,19,20</sup> Measured and calculated NMR chemical shielding tensors of silenes demonstrated that they have a genuine Si=C double bond.<sup>21</sup>

As indicated in Scheme 1, Ishikawa and collaborators prepared silacyclobutene **III** from the thermolysis of acylpolysilane **I** and performed the trapping of silene **II** using *tert*-butylacetylene as shown in Scheme 1.<sup>22</sup> An X-ray measurement demonstrated that this reaction occurs with high regioselectivity. Interesting thermal reactions are involved in the chemistry outlined in Scheme 1, that is, the thermal 1,3-silyl migration on acylpolysilane and the [2 + 2] cycloaddition between silene and acetylene. According to the Woodward–Hoffmann rules,<sup>23</sup> such [2 + 2] cycloaddition reactions are symmetry-forbidden in carbon systems and do not thermally proceed; however, in this organosilicon process various [2 + 2] cycloaddition reactions were confirmed to occur with various trapping agents under thermolysis conditions.<sup>22</sup> We approach the mechanism and energetics of these interesting chemical processes by means of computational quantum chemistry. The purpose of this paper is to address from density functional theory (DFT)<sup>24</sup> computations how these elementary reactions take place under thermolysis conditions.

### Method of Calculation

We carried out detailed computational analyses for the reactants, products, and transition states (TSs) of a series of thermal reactions starting from acylpolysilane using a hybrid Hartree–Fock/DFT method, the so-called B3LYP method.<sup>25–27</sup> This hybrid method consists of the nonlocal exchange functional of Becke's three-parameter set<sup>25,26</sup> and the nonlocal correlation functional of Lee, Yang, and Parr.<sup>27</sup> It has been successfully applied to many organic and organometallic reactions, giving structures and energetics reasonably well. We used the 6-31G\* basis set, a reliable double- $\zeta$  basis set with polarization functions for carbon, oxygen, and silicon.<sup>28–30</sup> This level of theory is sufficient for a reasonable description of the general profiles of the thermal processes with respect to the unsaturated silicon compounds. We traced Fukui's intrinsic

**Table 1. Computed Total Energies and Zero-Point Vibrational Energies of All Reaction Species at the B3LYP/6-31G\* Level of Theory<sup>a</sup>**

reaction species	energy (au)	ZPVE (kcal/mol)
<b>1</b>	−1316.62232	77.2
<b>2</b>	−1316.60596	78.6
methylacetylene	−116.65327	35.0
<b>3</b>	−1433.34489	116.9
<b>TS</b> <sub>1-2ret</sub>	−1316.57147	77.5
<b>TS</b> <sub>1-2inv</sub>	−1316.53814	77.2
<b>TS</b> <sub>2-3</sub>	−1433.21423	112.9

<sup>a</sup> ZPVE is the zero-point vibrational energy; 1 au = 27.21 eV = 627.5 kcal/mol.

reaction coordinate (IRC)<sup>31</sup> from a transition state toward both reactant and product directions along the imaginary mode of vibration of the transition state with the algorithm developed by Gonzalez and Schlegel.<sup>32</sup> Each IRC was obtained from a total of about 200 steps in an accuracy of 0.1 amu<sup>1/2</sup>bohr of *s*, in which *s* is the length of the IRC. We performed systematic vibrational mode analyses in order to characterize a local minimum that has no imaginary frequency mode and a saddle point that has only one imaginary frequency mode and took corrections of zero-point vibrational energies into account in all stationary structures discussed in this study. We used the Gaussian 98 ab initio program for the DFT computations.<sup>33</sup> Computed total energies and zero-point vibrational energies of all reaction species are listed in Table 1.

### Results and Discussion

Using a reasonable model indicated in Scheme 2, we computed and analyzed the thermolysis of acylpolysilane **1** that finally leads to silacyclobutene **3** via silene **2** as a reactive intermediate. Figure 1 shows a computed energy diagram for the overall reaction pathway. The relative energies in units of kcal/mol are measured from the total energy of **1** + methylacetylene as a standard. Optimized geometries of the reaction species are shown in Figure 2. In the following sections we discuss how the 1,3-silyl migration and the [2 + 2] cycloaddition proceed under thermolysis conditions.

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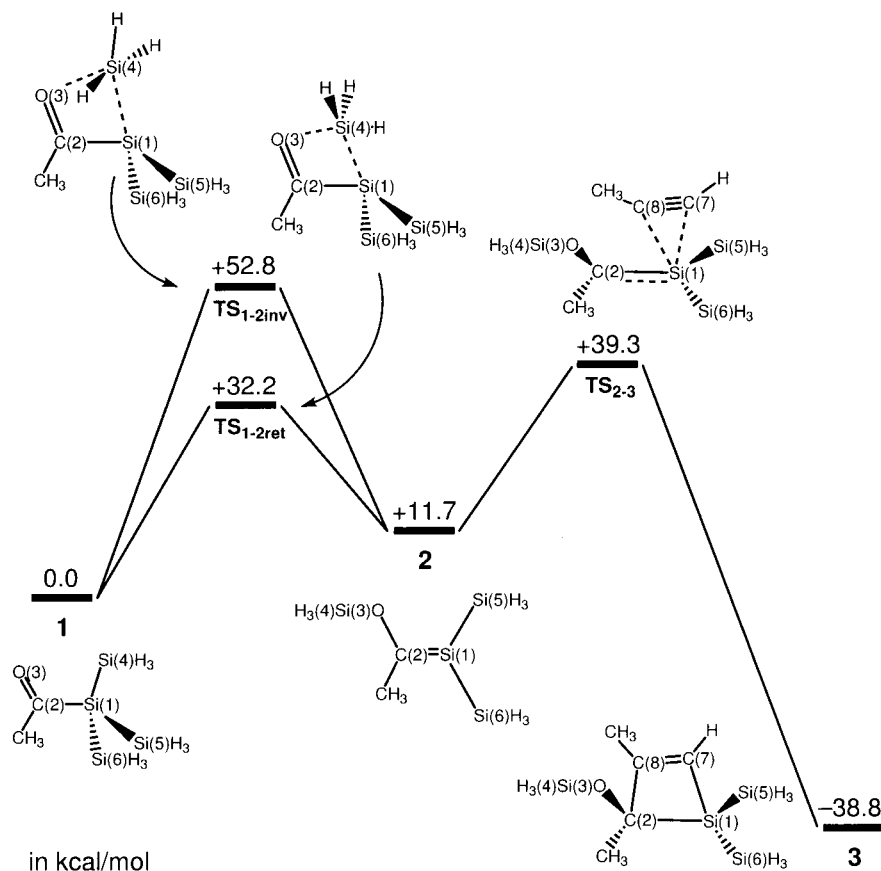
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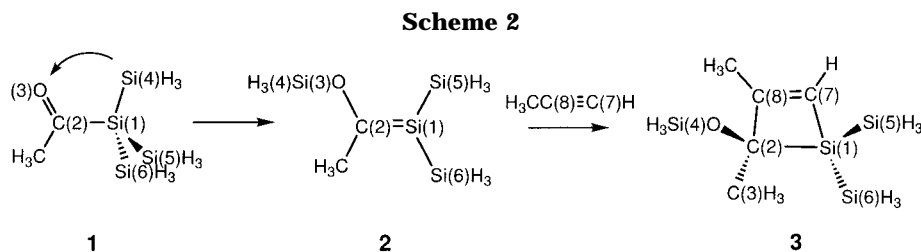
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**Figure 1.** Energy diagram for the 1,3-silyl migration on acylpolysilane **1** that generates silene **2** and for the [2 + 2] cycloaddition of silene and acetylene at the B3LYP/6-31G\* level of theory.



**1,3-Silyl Migration on Acylpolysilane.** Theoretical analyses for related 1,3-silyl migrations on allylsilane and formylmethylsilane were reported by our group<sup>34</sup> and by Takahashi and Kira.<sup>35,36</sup> Although in these processes two concerted reaction pathways that lead to retention and inversion of stereochemistry at the migrating silicon atom are possible, the activation energies for the retention pathway are lower in general than those of the inversion pathway at various levels of quantum chemical calculation. We compared the two reaction pathways for the silyl migration on **1**. The 1,3-silyl migration on **1** produces **2** via the retention pathway involving **TS**<sub>1-2ret</sub>; the activation energy for this chemical process was computed to be 32.2 kcal/mol. In contrast, the inversion pathway via **TS**<sub>1-2inv</sub> was computed to require 52.8 kcal/mol as the activation energy for the 1,3-silyl migration. Thus, the retention pathway is 20.6 kcal/mol lower than the inversion pathway at the B3LYP/6-31G\* level of theory, this

result being in good agreement with previous results on similar reactions.<sup>34–36</sup> According to Takahashi and Kira,<sup>36</sup> the activation energy for the 1,3-silyl shift on formylmethylsilane in the retention pathway is about 32 kcal/mol and the inversion pathway lies about 30 kcal/mol above the retention pathway at the second-order Møller–Plesset (MP2) perturbation level of theory<sup>37</sup> employing various basis sets. Thus, the energetics of our DFT computations is fully consistent with that from the earlier MP2 computations on the relevant chemical reaction.

Let us next turn our attention to Figure 2, which depicts optimized geometries of the transition states **TS**<sub>1-2ret</sub> and **TS**<sub>1-2inv</sub>, in which retention and inversion of stereochemistry take place at the migrating silyl group, respectively. The imaginary frequency of **TS**<sub>1-2ret</sub> is 252.8i cm<sup>-1</sup> and that of **TS**<sub>1-2inv</sub> is 496.0i cm<sup>-1</sup>. The migrating silyl group is trigonal pyramidal in **TS**<sub>1-2ret</sub> on the retention pathway, whereas it is planar in **TS**<sub>1-2inv</sub> on the inversion pathway. However, the four-centered structures in both transition states are very

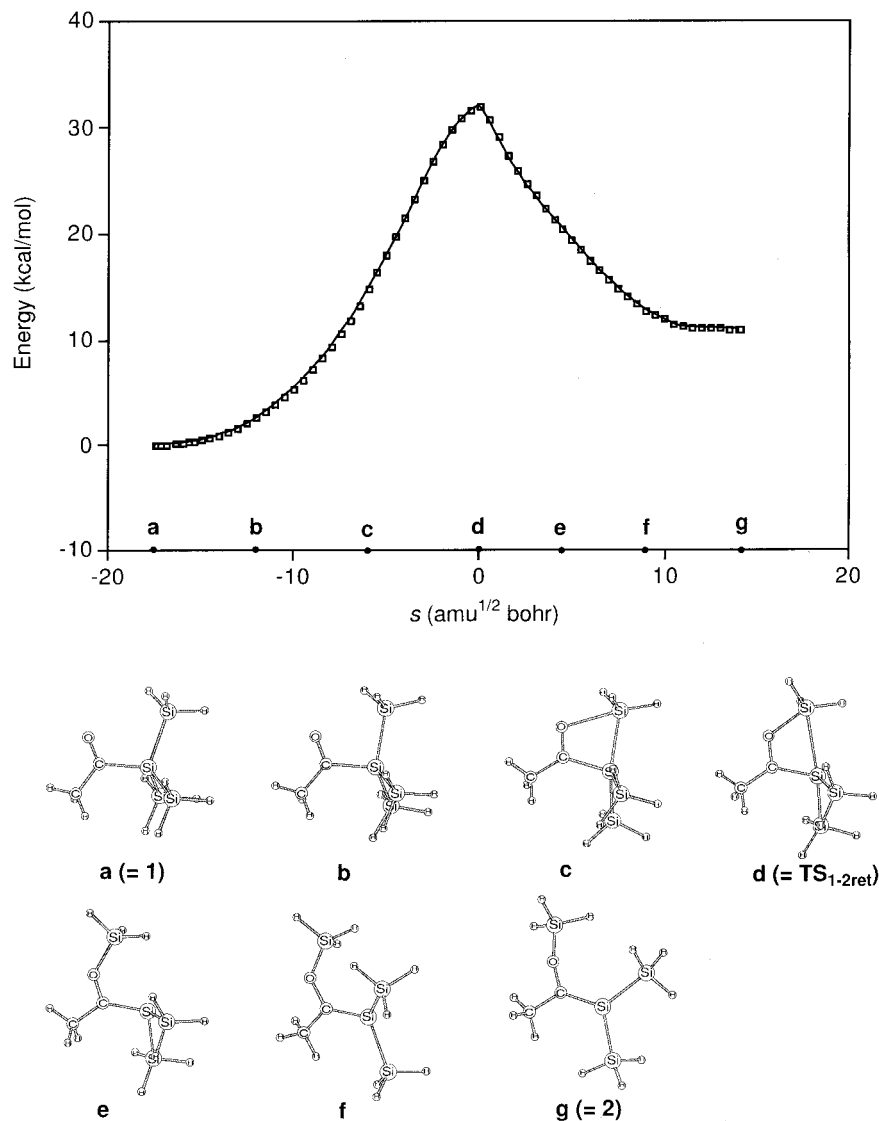
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**Figure 3.** Energy profile and IRC snapshots for the 1,3-silyl migration via the retention pathway.

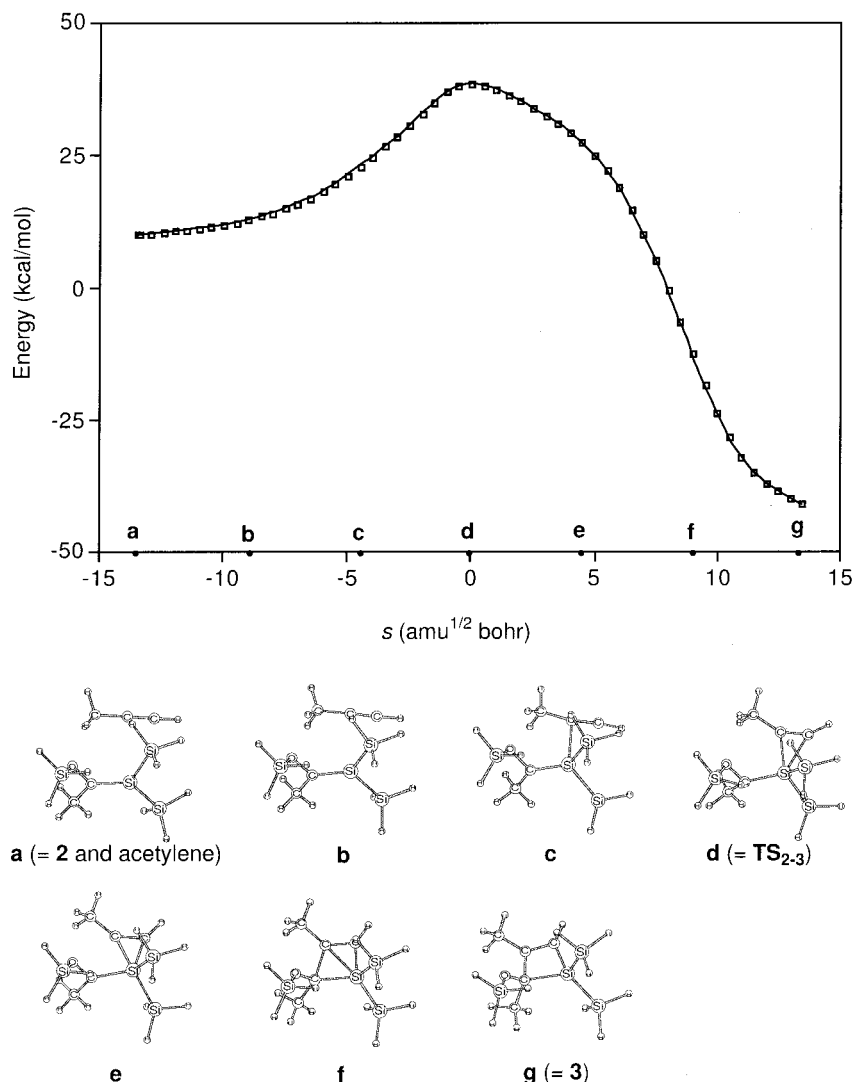
B3LYP/6-31G\*\* level).<sup>39</sup> Thus, our DFT computational result strongly suggests that the [2 + 2] cycloaddition reactions can thermally proceed between silenes and acetylenes. The transition state  $\text{TS}_{2-3}$  is of course not symmetrical; it has a very striking geometrical feature. In this transition state structure, the Si(1)–C(7) bond being formed is 2.268 Å, while the C(2)–C(8) bond being formed is 2.929 Å. Surprisingly, the Si(1)–C(7) distance is shorter than the C(2)–C(8) distance, so the silicon–carbon bond is formed in the earlier stages of the reaction, followed by the formation of the carbon–carbon bond.

To aid the understanding of this reaction, we performed IRC calculations along the [2 + 2] cycloaddition pathway. The IRC was traced from  $\text{TS}_{2-3}$  ( $s = 0$ ) along the imaginary mode of vibration toward both reverse ( $s < 0$ ) and forward ( $s > 0$ ) directions. Figure 4 illustrates a change in energy and snapshots of the reacting system along the IRC, in which **d** is the starting point of an IRC run that corresponds to  $\text{TS}_{2-3}$ , **a** is the terminal point of an IRC run in the reverse reaction, and **g** is the terminal point in the forward reaction. The geom-

etries of **a** and **g** show that our IRC calculation successfully leads to the true local minima for both directions, that is, the reactant and the product.

Figure 5a shows computed bond distances between silene **2** and methylacetylene along the IRC of the [2 + 2] cycloaddition. At the reactant point **a**, there is of course little interaction between **2** and acetylene. In the initial stages of this cycloaddition, C(8) of methylacetylene approaches Si(1) of **2**, and consequently the Si(1)–C(8) distance is slightly shorter than the Si(1)–C(7) distance. This is a very interesting finding from this IRC analysis. The reacting system reaches the transition state **d**, but no bond is yet formed between C(2) and C(8) at this point. As mentioned above, the Si(1)–C(7) distance is much shorter than the C(2)–C(8) distance, so the formation of the silicon–carbon bond has a preference over the formation of the carbon–carbon bond in the ring-closure process. In the second half of the reaction, C(8) approaches C(2), and finally the Si(1)–C(8) distance is increased before the reacting system reaches the product point **g**. These geometrical features are totally different from those expected for relevant cycloaddition reactions in carbon systems.<sup>23</sup> Figure 5b shows computed bond distances of the Si(1)=

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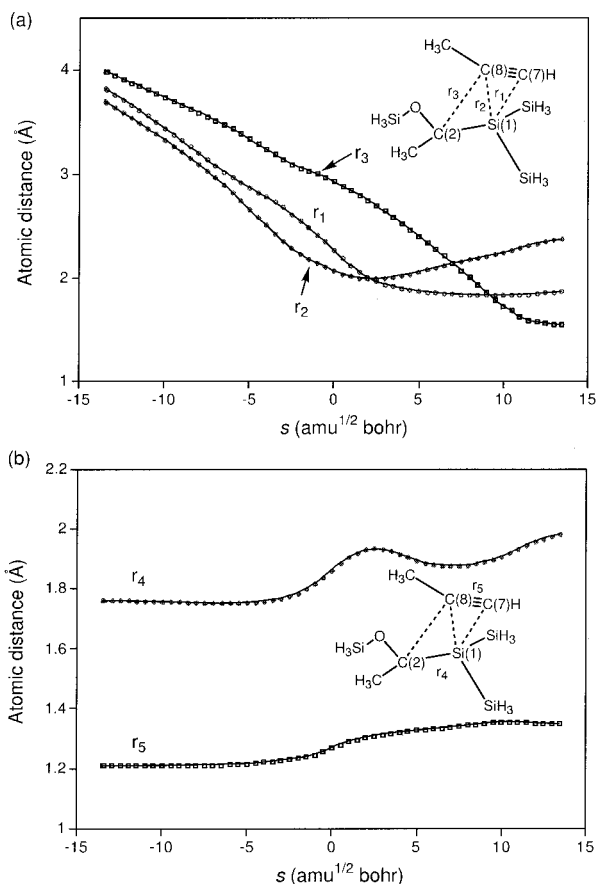
**Figure 4.** Energy profile and IRC snapshots for the [2 + 2] cycloaddition of silene and methylacetylene.

C(2) double bond of silene **2** and the triple bond of acetylene. This result visualizes that the Si(1)=C(2) double bond is partially cleaved into a single bond and that the C(7)≡C(8) triple bond is also partially cleaved into a double bond.

Although this [2 + 2] cycloaddition can be viewed as a concerted but nonsynchronous process, this is more likely to be viewed as a stepwise reaction with a diradical character. Gordon et al.<sup>40</sup> studied a relevant ring opening of silacyclobutane that leads to ethylene and silene from multiconfigurational self-consistent-field calculations and demonstrated that a diradical species is involved as an intermediate in the course of the reaction. According to their calculations, the concerted pathway lies ~10 kcal/mol above the stepwise pathway. Further ab initio calculations at a multiconfigurational level of theory are necessary to better describe this reaction, but we did not pursue that at this time. Rather than doing higher-level ab initio calculations, we chose a way to understand the interesting reaction that is symmetry-forbidden but occurs under thermolysis conditions in terms of Mulliken charge and orbital interaction analyses.

Computed Mulliken charges of **2**, **TS<sub>2-3</sub>**, and **3** are listed in Table 2. We see in this table that Si(1) is positively charged and C(8) is negatively charged as the [2 + 2] cycloaddition proceeds. Thus, a significant charge transfer occurs from silene to acetylene through a significant interaction between Si(1) and C(8). This charge transfer is a main driving force for this “symmetry-forbidden” [2 + 2] cycloaddition actually occurring under thermolysis conditions. To look at the charge transfer and the governing orbital interaction, we show in Figure 6 the HOMO of **TS<sub>2-3</sub>** drawn by contour and iconic representations. One of the nearly degenerate  $\pi^*$  LUMOs of methylacetylene has a good interaction with the HOMO of **2**, and the HOMO of the united system **TS<sub>2-3</sub>** has both characters in it. Because the orbital amplitude is significant on Si(1), the interaction in the region between Si(1) and C(8) is dominant in the orbital interaction. Consequently, the formation of the Si(1)–C(8) bond has a preference over that of the Si(1)–C(7) bond in the initial stages of the ring-closure process. This initial process plays an important role in the avoidance of the symmetry restriction that arises from the unfavorable overlap between the HOMO of silene and the LUMO of acetylene. As the charge transfer occurs from Si(1) to C(8), the  $\pi^*$  orbital of methylacety-

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**Figure 5.** Changes in some important bond distances along the IRC for the [2 + 2] cycloaddition of silene and methylacetylene.

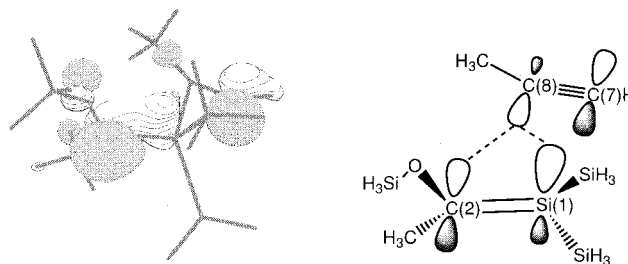
**Table 2. Atomic (Mulliken) Charges for 2, Methylacetylene, TS<sub>2-3</sub>, and 3**

	2 + methylacetylene	TS <sub>2-3</sub>	3
Si(1)	-0.021	+0.338 (+0.359)	+0.307 (+0.328)
C(2)	+0.255	+0.084 (-0.141)	+0.167 (-0.058)
C(7)	-0.461	-0.360 (+0.101)	-0.272 (+0.189)
C(8)	+0.304	+0.066 (-0.238)	+0.085 (-0.219)

<sup>a</sup> The values in parentheses are relative values from **2** + methylacetylene.

lene is partially occupied and the C≡C triple bond is reductively cleaved to lead to the formation of a double bond. This is a main reason that this interesting [2 + 2] cycloaddition thermally occurs, but of course this does not lead to an example of breakdown of the Woodward–Hoffmann rules. This reaction is also reasonably controlled by the orbital interactions especially by the in-phase diagonal interaction between Si(1) and C(8).

Regioselectivity of this [2 + 2] cycloaddition is an interesting issue in this thermal process. There are two isomers as products of this cycloaddition reaction depending on the orientation of methylacetylene, 3-methylsilacyclobutene (**3**), and 2-methylsilacyclobutene. We calculated which isomer is preferred in energy. DFT



**Figure 6.** HOMO of TS<sub>2-3</sub> in the [2 + 2] cycloaddition of silene and methylacetylene.

calculations tell us that **3** lies 0.07 kcal/mol below the 2-methyl isomer and the corresponding transition states are similar in energy. Therefore the two reaction pathways are comparable in energy when we use methylacetylene as a trapping agent.

## Conclusions

We have studied the mechanism and energetics for a series of thermal reactions starting from acylpolysilane, the 1,3-silyl migration on acylpolysilane that generates silene and the [2 + 2] cycloaddition of silene and acetylene, at the B3LYP/6-31G\* level of density functional theory. There are two kinds of reaction pathways in the 1,3-silyl migration with respect to the stereochemistry of the migrating silyl group. The retention pathway is energetically preferred to the inversion pathway, and silene thus formed should retain the stereochemistry of the silyl group. The [2 + 2] cycloaddition of silene and acetylene, the computed activation energy of which is 27.6 kcal/mol, is expected from an IRC analysis to occur in a two-step manner, resulting in the formation of silacyclobutene. We considered the reason that this “symmetry-forbidden” reaction occurs under thermolysis conditions in terms of orbital interaction analyses. Because the orbital amplitude is larger on the Si atom of silene, the interaction in the region between the silene Si atom and the diagonal acetylene C atom plays an important role in the initial stages of the ring-closure process. Consequently, the formation of the “diagonal Si–C bond” has a preference over that of the proper Si–C bond that is finally formed in the four-membered ring. This initial process effectively decreases the symmetry restriction arising from the unfavorable HOMO–LUMO interaction in the [2 + 2] cycloaddition.

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