

# Thermal Addition of Disilacyclobutenes and Acetylene: A Theoretical Study on Diels–Alder Type Reactions

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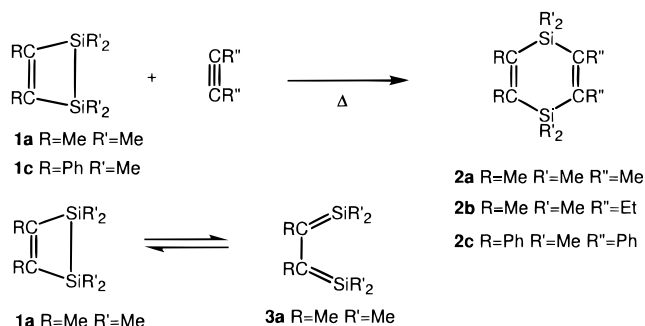
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The reaction pathways for the thermal additions of disilacyclobutenes and acetylene are discussed from B3LYP density-functional-theory computations. Butadiene is more stable in energy than cyclobutene, the corresponding ring compound, whereas disilabutadiene is less stable than disilacyclobutene. From detailed analyses of the potential energy surfaces, disilabutadienes formed by thermal ring opening of disilacyclobutenes are confirmed to play a central role in the addition reactions as intermediates in a manner similar to the Diels–Alder reaction. The activation energies for the symmetry-allowed conrotatory ring opening of 1,2-disilacyclobut-3-ene, 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene, and 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene are 41.5, 46.7, and 61.9 kcal/mol, respectively, and the activation energies for the Diels–Alder coupling reactions with acetylene are 1–4 kcal/mol when measured from the disilabutadiene intermediates at the B3LYP/6-31G\*\* level of theory. Therefore the ring opening should be the rate-determining step in these reactions; once the four-membered ring of disilacyclobutene is opened by heat treatment, the addition reactions should readily take place, leading to six-membered ring products. The transition state for the addition of 1,4-disila-1,3-butadiene and acetylene is symmetrical with respect to the Si–C bonds being formed, whereas those of 1,1,4-tetramethyl-1,4-disila-1,3-butadiene and acetylene and of 1,2-bis(dimethylsilylene)cyclohexa-3,5-diene and acetylene are not symmetrical. There are good reasons that such asymmetrical transition states occur in these Diels–Alder reactions; one is the asymmetrical frontier orbitals in the methyl-substituted disilabutadienes, and the other is just a steric effect of the methyl groups.

## Introduction

Carbon compounds and their silicon analogues show strikingly different features in structure, stability, and reactivity, despite the similar electronic configurations. It is very interesting to investigate whether the stereochemistry in carbon compounds applies to reactions of silicon compounds. The issue that we address in this paper is the reaction pathways for the thermal additions of disilacyclobutenes and acetylene. In 1976 Barton and Kilgour<sup>1</sup> demonstrated that heat treatment of 1,1,2,2,3,4-hexamethyl-1,2-disilacyclobutene (**1a**) in the presence of 2-butyne and 3-hexyne gives 1,1,2,3,4,4,5,6-octamethyl-1,4-disilacyclohexa-2,5-diene (**2a**) and 2,3-diethyl-1,1,4,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (**2b**) in low yields, respectively, as indicated in Scheme 1. They proposed that this thermal reaction should proceed via 1,1,2,3,4,4-hexamethyl-1,4-disilabut-1,3-diene (**3a**) as a possible reaction intermediate in a manner similar to the Diels–Alder reaction, the mechanism of which is well understood in terms of

## Scheme 1



Fukui's frontier orbital theory and the Woodward–Hoffmann rules.<sup>2–4</sup>

Sakurai et al.<sup>5</sup> reported that 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobutene (**1c**) reacts with di-

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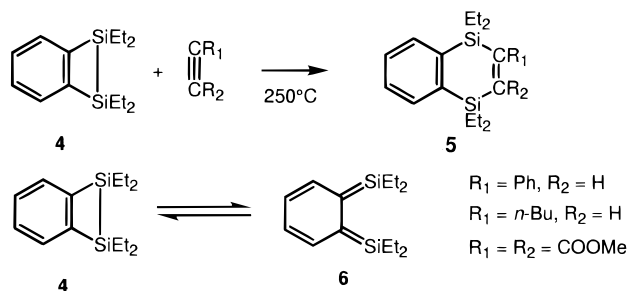
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Scheme 2



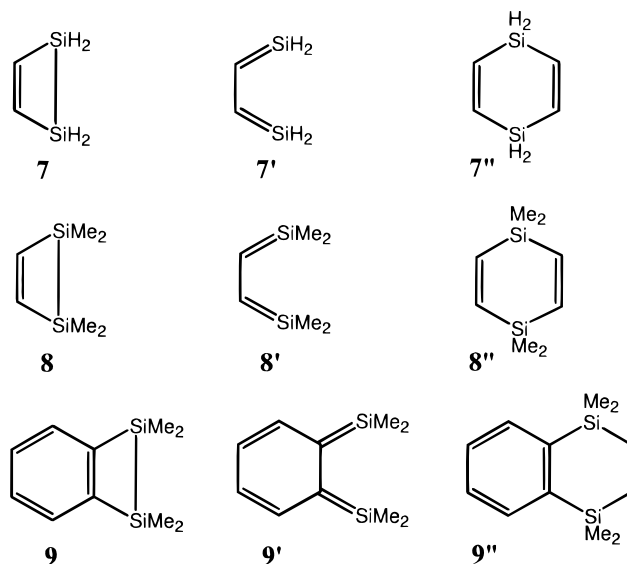
phenylacetylene at 350 °C to lead to 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene (**2c**) in a similar fashion. One can thus agree with Barton and Kilgour<sup>1</sup> that disilabutadienes should be responsible for these Diels–Alder reactions as intermediates. However, these possible intermediates are energetically not stable, in contrast with their carbon analogues, i.e., butadienes, and therefore direct evidence that these reaction intermediates have relevance to these interesting thermal reactions has not yet been found.

Ishikawa et al.<sup>6,7</sup> have studied thermal, photochemical, and transition-metal-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**4**). This silicon compound is thermally rather stable at room temperature, but makes various reactions with substituted acetylenes at 250 °C, leading to 1,4-disilacyclohexa-2,5-dienes (**5**), as shown in Scheme 2.

In such thermal reactions, one can also consider that 1,2-bis(diethylsilylene)cyclohexadiene (*o*-quinodisilane) (**6**) should play a central role as a reaction intermediate. Moreover, Ishikawa et al.<sup>7</sup> have carried out thermal reactions of the benzodisilacyclobutene in the presence of alcohol, aldehyde, or ketone to obtain more detailed information on the reaction intermediate that is considered to be involved in the thermal reactions. All these reactions were confirmed to give final products that suggest the involvement of *o*-quinodisilane as a reaction intermediate.

In considering the mechanism of the [4 + 2] cycloadditions of the silicon compounds mentioned above, we should note that butadiene and its silicon analogue are strikingly different in energetical stability. Butadiene is more stable in energy than the corresponding ring compound, cyclobutene, whereas disilabutadiene is less stable than disilacyclobutene. We expect that this difference in the stability of starting material should significantly affect the energetics of the reaction pathways. In carbon systems we know in detail how dienes and dienophiles behave throughout the reactions in terms of orbital interactions,<sup>2–4</sup> and extensive *ab initio* computational studies<sup>8–24</sup> have been carried out so far concerning many types of Diels–Alder reactions of carbon compounds. Digermacyclobutene and digerma-

Chart 1



butadiene and their interconversion have been also studied from molecular orbital computations.<sup>25</sup> However, our knowledge on the Diels–Alder reactions of the silicon analogues<sup>26,27</sup> is still lacking from the viewpoints of mechanism, stereochemistry, and energetics. We thus decided to perform detailed computational analyses on the thermal reactions of disilacyclobutenes and acetylene using the density functional theory. In the theoretical analyses, we consider the disilacyclobutenes indicated in Chart 1 as starting materials for the Diels–Alder reactions of the corresponding disilabutadienes and acetylene. Disilacyclobutenes studied in this paper are 1,2-disilacyclobut-3-ene (**7**), 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**8**), and 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene (**9**); the corresponding disilabutadienes are 1,4-disila-1,3-butadiene (**7**), 1,1,4,4-tetramethyl-1,3-butadiene (**7'**), and 1,2-bis(dimethylsilylene)cyclohexa-3,5-diene (**9'**); the final acety-

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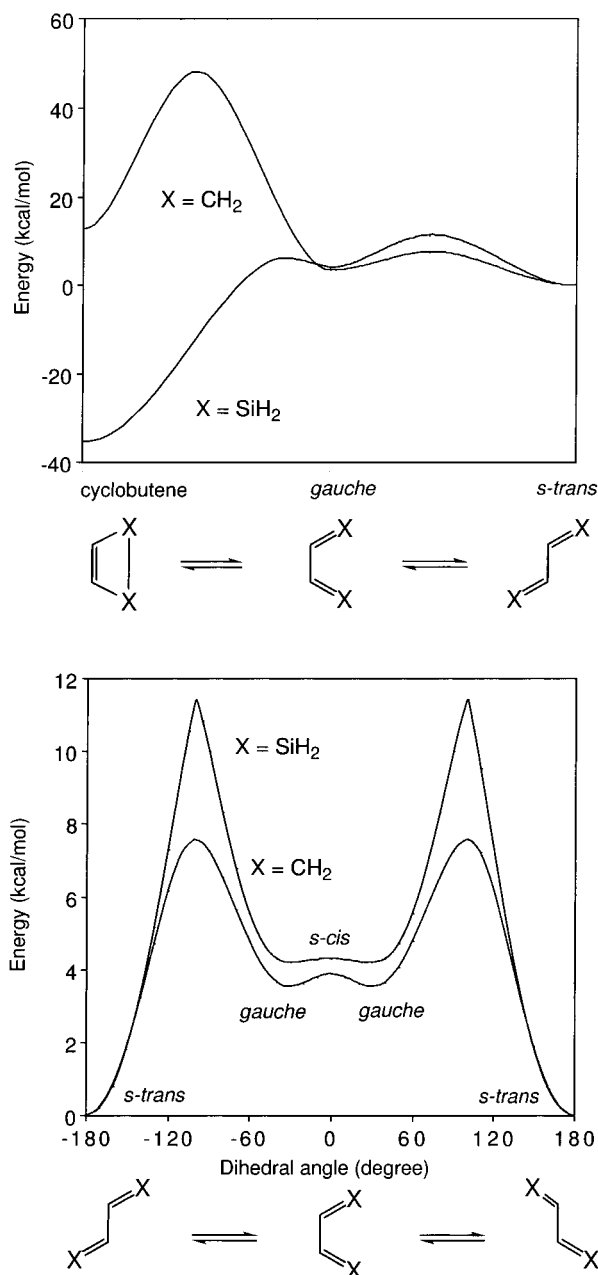
lene adducts are 1,4-disilacyclohexa-2,5-diene (**7''**), 1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**8''**), and 2,3-benzo-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**9''**).<sup>28</sup>

### Method of Calculation

We considered the reaction pathways for the reactions of disilacyclobutenes and acetylene. Detailed analyses for the reactants, products, and transition states (TSs) of the interesting thermal reactions were carried out using a hybrid Hartree–Fock/density-functional-theory (HF/DFT) method (the so-called B3LYP method).<sup>29,30</sup> This method consists of the nonlocal exchange functional of Becke's three-parameter set<sup>29</sup> and the nonlocal correlation functional of Lee, Yang, and Parr.<sup>30</sup> It has been successfully applied to the Diels–Alder reaction of butadiene and ethylene,<sup>8c</sup> providing much better results than the Møller–Plesset perturbation theory method, concerning molecular structures and energetics. We used the 6-31G\*\* basis set, a standard double- $\zeta$  basis set with polarization functions.<sup>31</sup> Vibrational mode analyses were systematically carried out to confirm that on a potential energy surface all optimized geometries correspond to a local minimum that has no imaginary frequency mode or a saddle point that has only one imaginary frequency mode. Corrections of zero-point vibrational energies were taken into account in all stationary structures discussed. The Gaussian 98 ab initio program was used.<sup>32</sup>

### Results and Discussion

**Ring Opening of Disilacyclobutene.** We first show how the relative energies of cyclobutene and 1,2-disilacyclobut-3-ene (**7**) change as a function of the dihedral angles C–C–C and Si–C–C–Si. Figure 1 presents computed relative energies of 1,3-butadiene and 1,4-disila-1,3-butadiene (**7'**) as a function of the dihedral angle at the B3LYP/6-31G\*\* level of theory. As mentioned earlier, butadiene is 9.6 kcal/mol more stable than cyclobutene, whereas **7'** is 38.9 kcal/mol less stable than cyclobutene, which can determine the general features of the Diels–Alder reactions of this carbon system and of its silicon analogue. This is partly because the Si–Si bond (~2.4 Å) is longer than the C–C bond (~1.55 Å), so that the coordination environments at the central carbon atoms of **7** are favorable with respect to the  $sp^2$  bonding characters. Thus, strain energy in the  $Si_2C_2$  four-membered ring is reduced. In both butadienes the *s-trans* form is the most stable structure and the *gauche*



**Figure 1.** Relative energies of cyclobutenes toward butadienes as a function of the dihedral angle X–C–C–X at the B3LYP/6-31G\*\* level.

form is the quasi-stable structure, and the *s-cis* form is the transition state that connects the two equivalent *gauche* forms. The rotational barrier is predicted to be 7.6 and 11.4 kcal/mol in butadiene and **7'**, respectively; therefore interconversion between the *gauche* and the *s-trans* forms is thermally accessible in these compounds.

The Woodward–Hoffmann rules<sup>3,4a</sup> tell us from orbital symmetry relationships that in the carbon system cyclobutene is smoothly transformed into butadiene in a conrotatory process by heat treatment. How this ring-opening reaction proceeds from disilacyclobutenes toward disilabutadienes is a very interesting subject from the viewpoint of orbital symmetry conservation. We thus computed the reaction pathway for the ring opening of **7**. Optimized structures of **7**, **7'**, and the transition state (**TS1**) that connects these silicon compounds are shown

(28) The butadiene form of 3,4-benzo-1,2-disilacyclobutene is very unstable, and an H atom transfer occurs on computations, leading to the formation of SiH and SiH<sub>3</sub> groups despite our best computational efforts. Now we believe that the butadiene form of 3,4-benzo-1,2-disilacyclobutene is less stable in energy than the silylene form of C<sub>6</sub>H<sub>4</sub>–SiHSiH<sub>3</sub>.

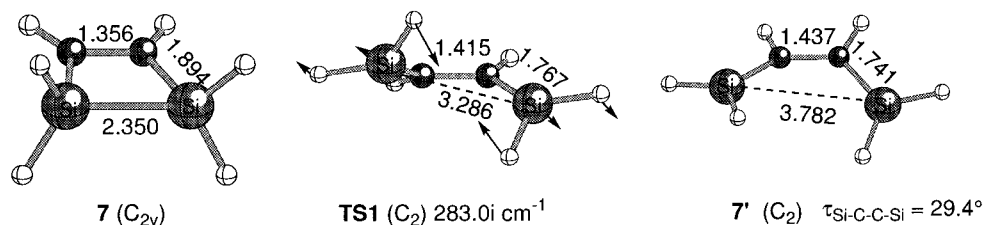
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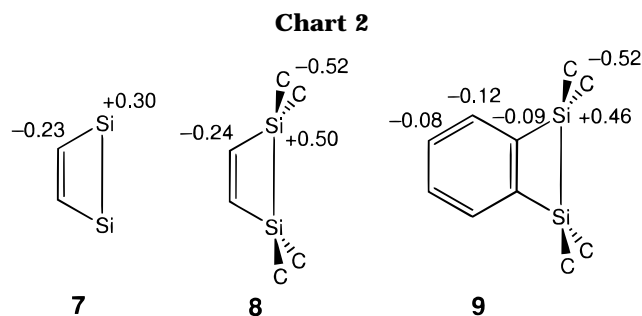
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**Figure 2.** Optimized geometries of 1,2-disilacyclobut-3-ene (**7**), 1,4-disila-1,3-butadiene (**7'**), and their transition state (**TS1**) at the B3LYP/6-31G\*\* level. Bond lengths are in Å.



in Figure 2. The larger balls stand for silicon atoms, and the smaller balls carbon atoms. We confirmed from vibrational analyses that the two stable structures have no imaginary frequency mode and that the transition state has a single imaginary frequency mode. The arrows in the transition state indicate the imaginary vibrational mode of  $283.0\text{ cm}^{-1}$ , which suggests preferred nuclear motions corresponding to a conrotatory process along the reaction coordinate. DFT computations predict that **7** should be transformed into **7'** in the conrotatory process with a large activation energy of  $41.5\text{ kcal/mol}$ ; thus high-temperature treatment should be required for this ring opening to be facile.<sup>1,5</sup> Disilabutadiene thus formed lies  $38.9\text{ kcal/mol}$  above disilacyclobutene at the B3LYP/6-31G\*\* theory.

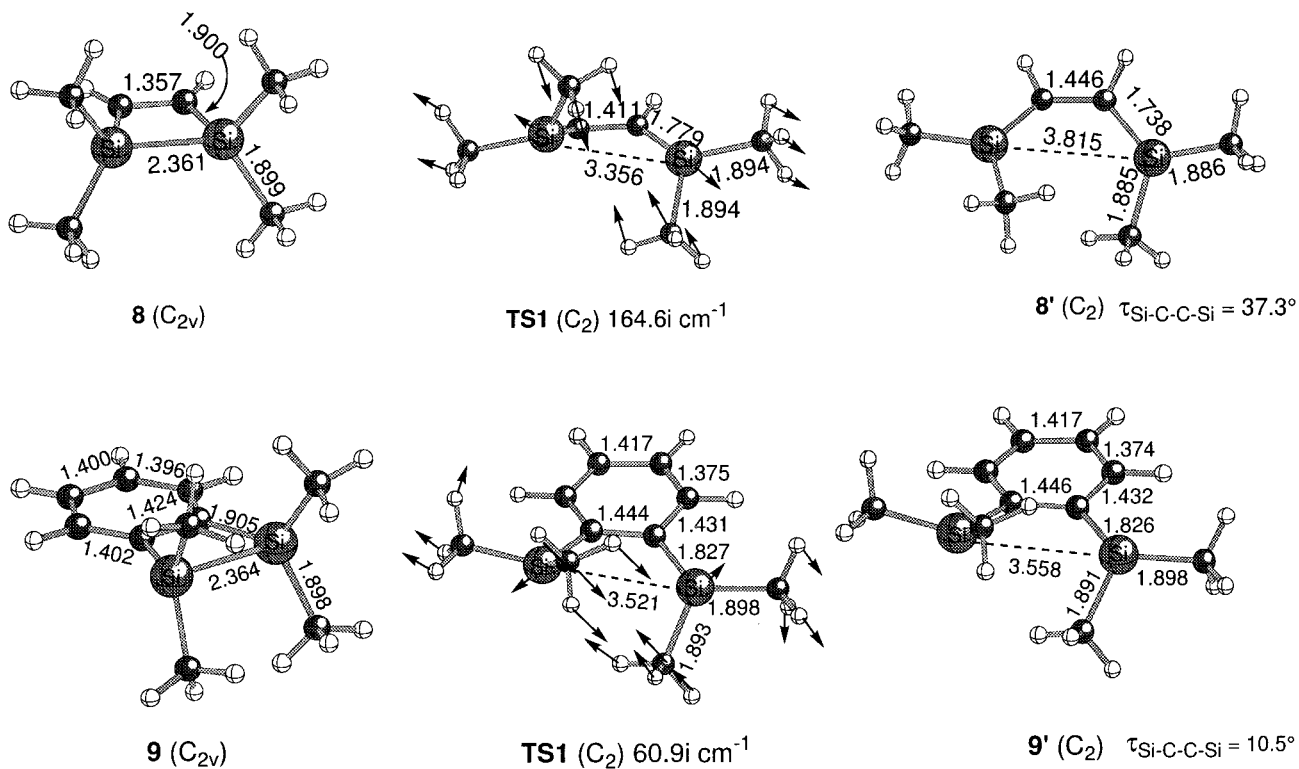
Let us next turn our attention to the ring opening of 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**8**) and 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene (**9**). Computed Mulliken charges of **7**, **8**, and **9** are indicated in Chart 2. The silicon atoms are positively charged, and the carbon atoms are negatively charged. Optimized structures of the disilacyclobutenes, the corresponding disilabutadienes (**8'** and **9'**), and their transition states (**TS1**) are shown in Figure 3. These processes are also predicted from computations to be symmetry-allowed with activation energies of  $46.7$  and  $61.9\text{ kcal/mol}$  for **8** and **9**, respectively, and the disilabutadienes, **8'** and **9'**, thus formed lie  $41.7$  and  $61.7\text{ kcal/mol}$  above **8** and **9**, respectively. We therefore predict that the thermal ring opening of **9** should be difficult compared to that of **7** and **8**. Judging from the sequence of the activation energies for **7** and **8**, the steric repulsion between methyl groups is unlikely to play a role in determining the high activation barrier for the ring opening of **9**. To find a reason that **9** has such a high activation energy, let us compare the optimized structures of **7**, **8**, and **9**. The Si-Si distances of these compounds are nearly equal, approximately  $2.35\text{ Å}$ ; the frequencies of the Si-Si bonds are  $426.8\text{ cm}^{-1}$  for **7**,  $400.6\text{ cm}^{-1}$  for **8**, and  $395.8\text{ cm}^{-1}$  for **9**. From these results we cannot find a good reason that the activation energy for the ring opening of **9** is larger than those of **7** and **8**. A possible reason is the loss of aromatic stabilization energy in the benzene

ring of **9**. Despite the high activation energy, **4** makes various reactions with substituted acetylenes at  $250\text{ }^\circ\text{C}$ , leading to **5** in high yields.<sup>6,7</sup> Later in this paper we will discuss why thermal treatment of benzodisilacyclobutene leads to final acetylene adducts in high yields despite the high activation energy for its ring opening.

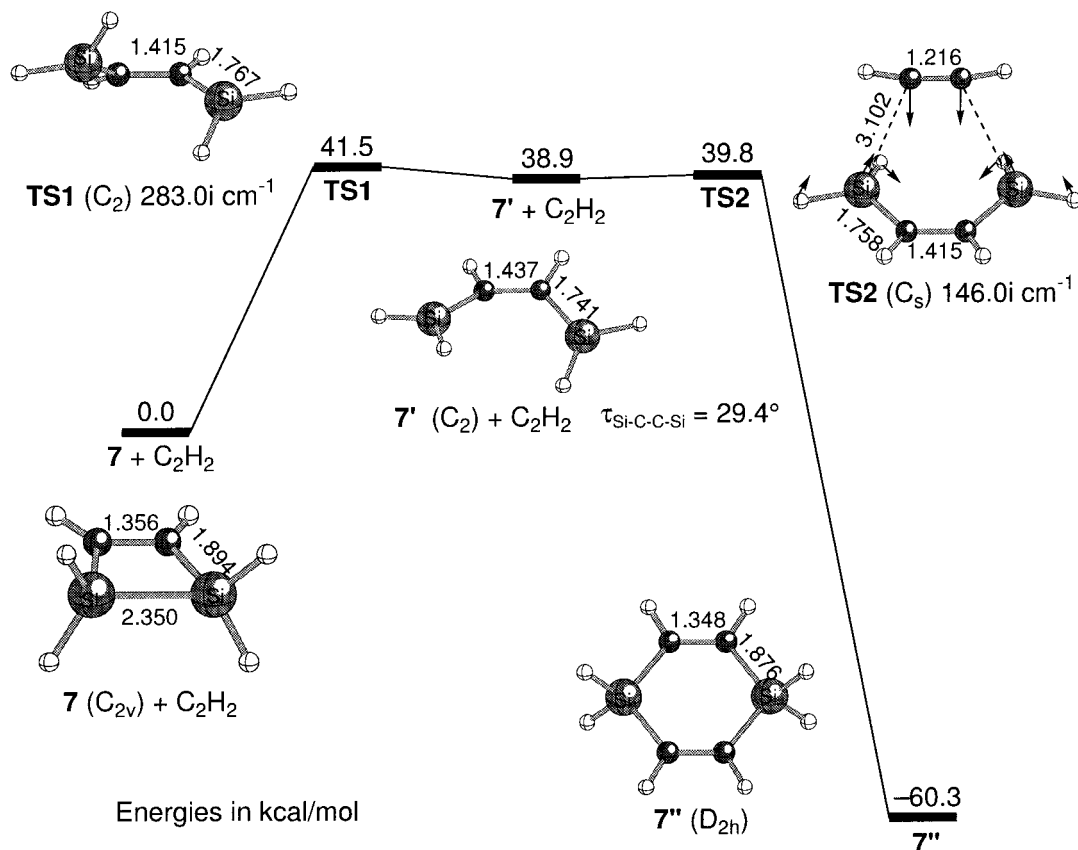
Ishikawa et al.<sup>33</sup> recently performed an X-ray structural analysis of *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene; the Si-Si distance of this disilacyclobutene is  $2.383(9)\text{ Å}$ , and the two Si-C distances are  $1.890(9)$  and  $1.888(9)\text{ Å}$ . Our computational results for **9** indicated in Figure 3 are in excellent agreement with the X-ray structure of this benzodisilacyclobutene.

**Diels-Alder Reaction of Disilabutadiene and Acetylene.** Having described the ring-opening reactions of the three disilacyclobutenes in the previous section, we next address the Diels-Alder reactions of the disilabutadienes thus formed and acetylene. Let us first look at the reaction of **7'** and acetylene. A computed potential energy profile, including zero-point energy corrections, along the two-step concerted reaction pathway for the addition of **7** and acetylene is presented in Figure 4. The relative energies indicated are measured from the dissociation limit, **7** and acetylene. The first transition state (**TS1**) in this illustration is concerned with the ring opening of **7** discussed above, and the second transition state (**TS2**) is concerned with the Diels-Alder reaction of **7'** and acetylene. The activation energy for **TS2** is predicted to be  $0.9\text{ kcal/mol}$  when measured from the intermediate **7'**; we thus expect that this reaction should readily take place if the four-membered ring of **7** is opened by heat treatment. The activation barrier measured from **7** amounts to  $39.8\text{ kcal/mol}$ . Since the product of this Diels-Alder reaction, 1,4-disila-cyclohexa-2,5-diene (**7''**), lies  $60.3\text{ kcal/mol}$  below the reactants, this reaction is considered to be irreversible. We confirmed from vibrational analyses that **7'** is a local minimum point on the potential energy surface, suggesting that this unstable reaction intermediate is responsible for the thermal addition. This reaction intermediate is so high in energy that the activation energy of this Diels-Alder reaction is much smaller than those of the well-known Diels-Alder reactions of butadiene and ethylene ( $24.8\text{ kcal/mol}$  at the B3LYP/6-31G\* level<sup>8c</sup>) and of butadiene and acetylene ( $25.0\text{ kcal/mol}$  at the B3LYP/6-31G\* level<sup>10b</sup>). Disilabutadiene **7'** is unstable in energy, but should exist without doubt as an unstable reaction intermediate, i.e., a local minimum on the potential energy surface. In theoretical chemistry we are able to strictly distinguish between reaction intermediate and transi-

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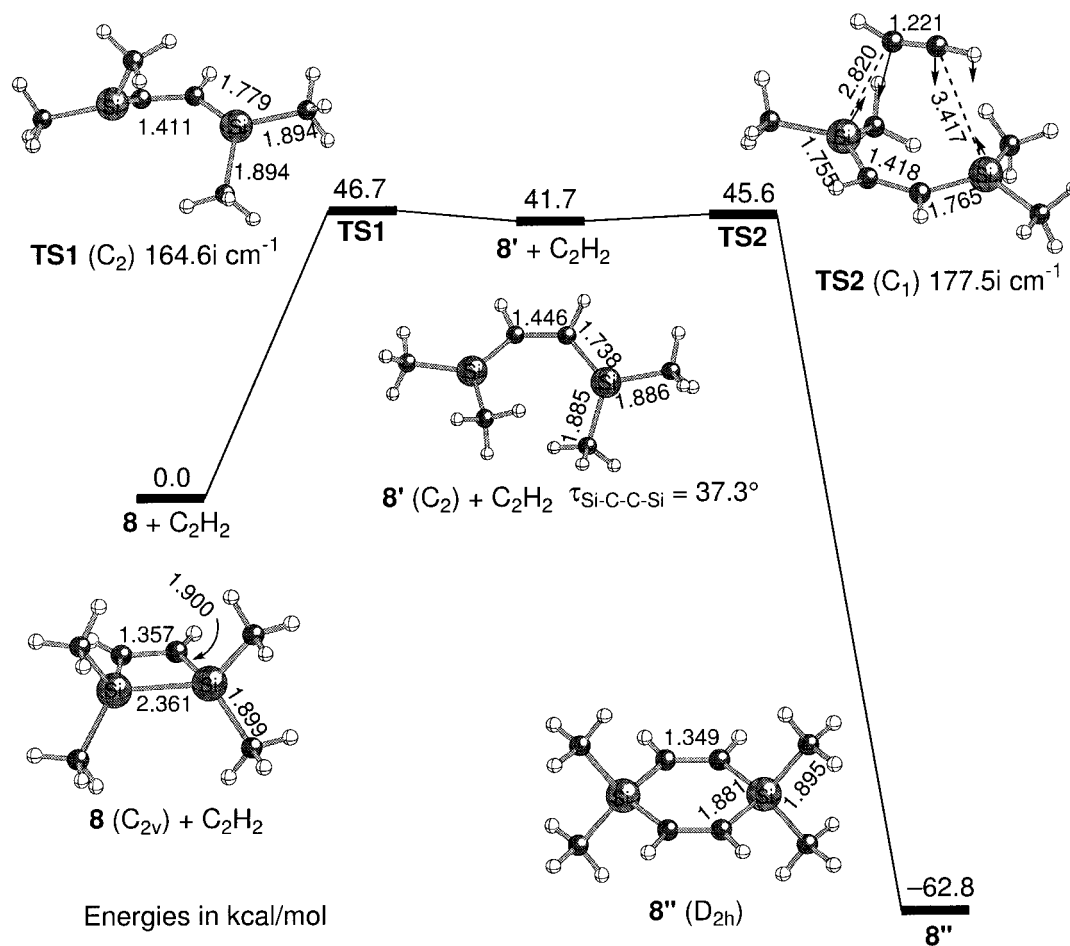
**Figure 3.** Optimized geometries of 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**8**), 1,1,4,4-tetramethyl-1,4-disila-1,3-butadiene (**8'**), 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene (**9**), 1,2-bis(dimethylsilylene)cyclohexa-3,5-diene (**9'**), and the transition states (TS1) for the ring opening at the B3LYP/6-31G\*\* level. Bond lengths are in Å.



**Figure 4.** Computed energy diagram for the addition of **7** and acetylene leading to the final product **7''** via the intermediate **7'**. Bond lengths are in Å.

tion state in terms of vibrational analyses. Since this species has no imaginary frequency mode, it is a stable point on the potential energy surface. However, it may

be impossible to experimentally observe this species judging from the energetics of the reaction pathway presented in Figure 4.



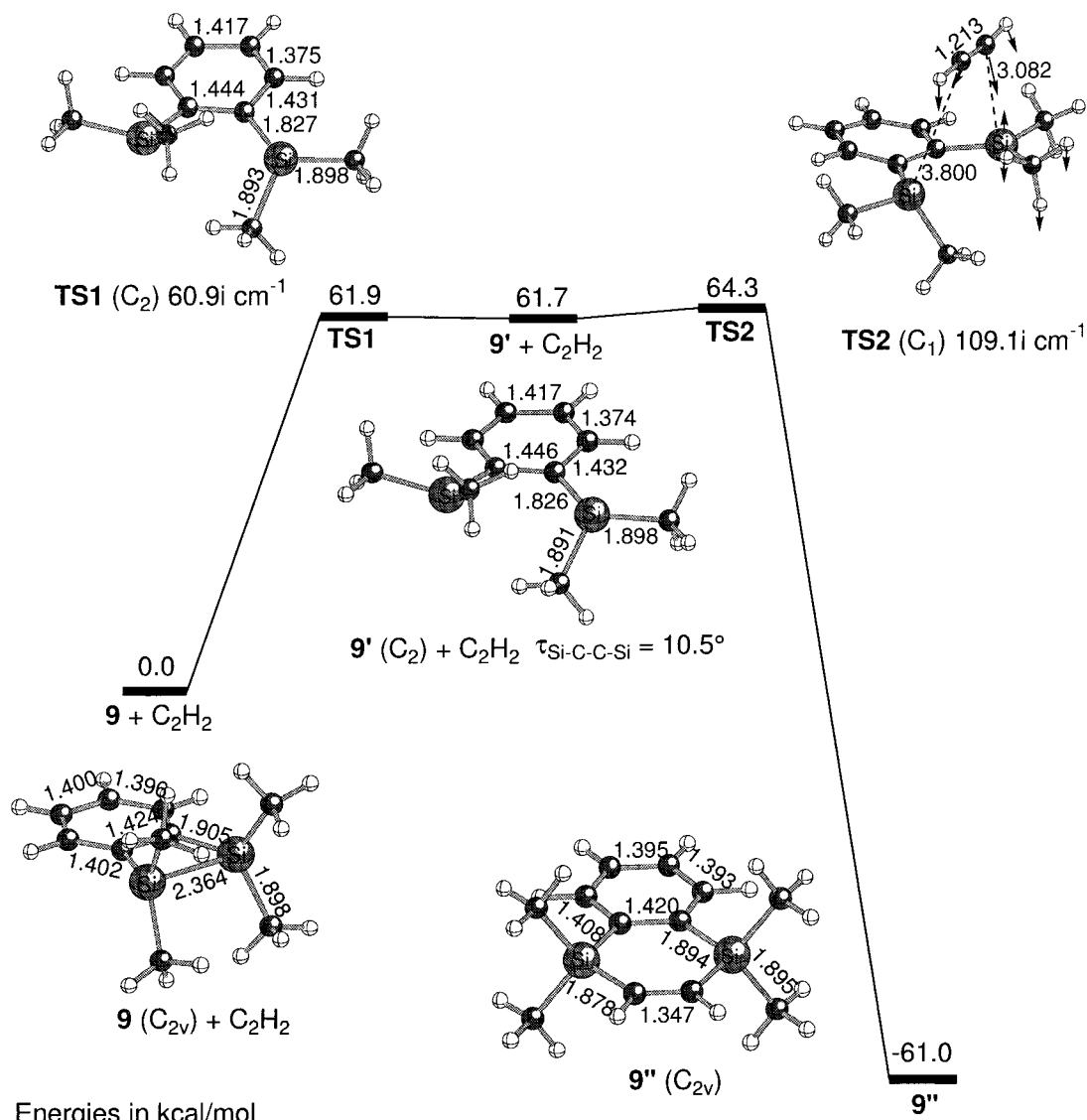
**Figure 5.** Computed energy diagram for the addition of **8** and acetylene leading to the final product **8''** via the intermediate **8'**. Bond lengths are in Å.

Figure 4 also shows optimized geometries of the reaction species along the reaction pathway for the thermal reaction of **7** and acetylene. The transition state for the Diels–Alder reaction **TS2** conserves *C<sub>s</sub>* symmetry, and therefore it is symmetrical with respect to the Si–C bonds being formed. The distance of these Si–C bonds is predicted to be 3.102 Å, which is about 1.6 times as long as the Si–C bond distances of the stable structures. The arrows in the transition state indicate the imaginary vibrational mode of 146.0 cm<sup>-1</sup>; this transition vector is of course symmetrical and conserves *C<sub>s</sub>* symmetry, suggesting preferred nuclear motions along the reaction coordinate. Thus, the transition-state structure is quite appropriate for this synchronous concerted process. We know from the transition vector in **TS2** that the configuration of the H atoms at the silicon atoms is not conserved during this thermal process.

**Diels–Alder Reaction of Substituted Disilabutadienes and Acetylene.** Let us next look at the reactivity of methyl-substituted disilabutadienes, **8'** and **9'**. We present in Figure 5 a computed two-step reaction pathway for the thermal addition of **8** and acetylene. The general profile of this diagram is identical to that of the reaction of **7** and acetylene shown in Figure 4. The activation barrier for the ring opening of **8** is 46.7 kcal/mol, and that for the Diels–Alder addition of **8'** and acetylene is 3.9 kcal/mol. The activation barrier measured from **8** amounts to 45.6 kcal/mol, and therefore higher temperature should be required for this reaction

to be facile. Optimized geometries of **TS2** and the final product 1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**8''**) are also shown in Figure 5. In remarkable contrast to the **TS2** for the thermal addition of **7'** and acetylene in Figure 4, this transition state is not symmetrical with respect to the Si–C bonds being formed. The shorter Si–C bond is 2.820 Å, and the longer one is 3.417 Å. Such an asymmetrical transition-state structure can be ascribed to either a nonsynchronous concerted transition state or a nonconcerted stepwise transition state. We will give some comments on this problem later in this paper.

We finally describe the reaction pathway for the Diels–Alder reaction of **9'** and acetylene. Figure 6 presents a computed energy diagram for the two-step reaction pathway for the thermal addition of **9** and acetylene. The profile of this diagram is essentially identical to that of the reaction of **8** and acetylene shown in Figure 5. The activation barrier for the ring opening of **9** is 61.9 kcal/mol, and that for the Diels–Alder addition of **9'** and acetylene is 2.6 kcal/mol. The activation barrier measured from **9** amounts to 64.3 kcal/mol, and therefore high-temperature treatment is also required for the reaction to be facile. Since the final acetylene adduct, 2,3-benzo-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**9''**), is very stable in energy, the ring opening is also likely to be the rate-determining step in this thermal reaction. The ring opening of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**4**) has been reported to take place at 250 °C,<sup>6,7</sup> as con-

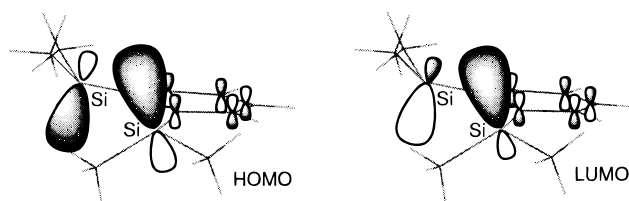


**Figure 6.** Computed energy diagram for the addition of **9** and acetylene leading to the final product **9''** via the intermediate **9'**. Bond lengths are in Å.

firmed from many kinds of reactions that suggest the involvement of *o*-quinodisilane as a reaction intermediate.

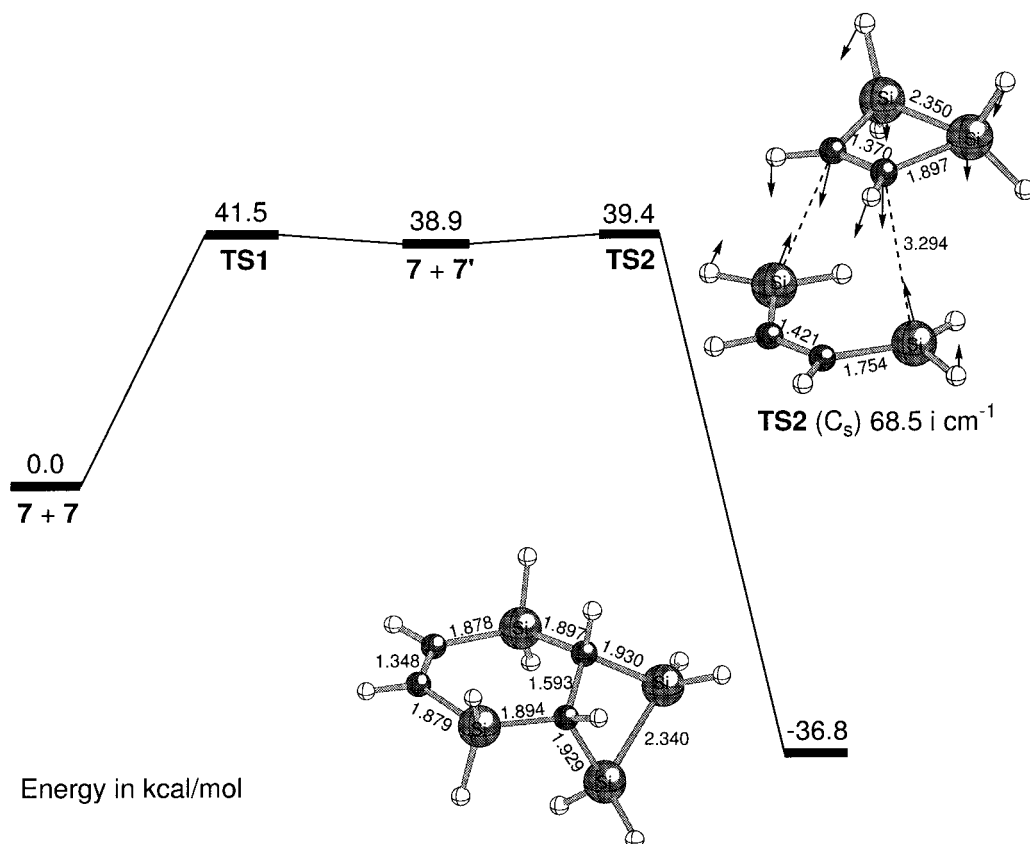
Optimized geometries of **TS2** and the final product are presented in Figure 6. This transition state is also not symmetrical with respect to the Si–C bonds being formed. The shorter Si–C bond is 3.082 Å, and the longer one is 3.800 Å. The shorter bond is in good agreement with the corresponding Si–C bonds of the symmetrical **TS2** in Figure 4, but the longer bond is not. We first recognized that this transition state should be the one for a nonconcerted stepwise Diels–Alder reaction, but this view may be incorrect. This asymmetrical transition-state structure is quite reasonable from the viewpoint of the asymmetrical frontier orbitals of **9'** indicated in Chart 3. The methyl-substituted silylene groups are not planar, and as a consequence *sp* orbital mixing reasonably occurs at the silicon atoms. Therefore the orbital at one silicon is directed upward and that at the other silicon is directed downward with respect to the cyclohexadienyl (benzene) ring. When **9'** interacts with acetylene in the initial stages of this Diels–Alder reaction, one silylene group should play a more domi-

**Chart 3**



nant role and the other one a less dominant role, which can lead to this asymmetrical transition-state structure with shorter and longer Si–C bonds. However, according to the B3LYP computations of Goldstein, Beno, and Houk,<sup>8c</sup> the difference in the free energy of activation for the concerted versus the two-step diradical mechanism for the Diels–Alder reaction of butadiene and ethylene has been predicted to be small (2.3–7.7 kcal/mol). It is therefore difficult to determine whether the asymmetrical transition-state structures in Figures 5 and 6 are those for a nonsynchronous concerted transition state or a nonconcerted stepwise transition state because this could also be a question of lifetimes. The asymmetrical transition-state structures presented in





**Figure 7.** Computed energy diagram for the self-condensation of **7**. Bond lengths are in Å.

Figures 5 and 6 may simply come from a steric effect of the methyl groups.

**Self-Condensation of Disilabutadiene and Disilacyclobutene.** As indicated earlier in this paper, heat treatment of a disilacyclobutene (**1a**) in the presence of 2-butyne and 3-hexyne gives **2a** and **2b**, respectively; however the yields are low. On the other hand, a benzodisilacyclobutene (**4**) reacts with substituted acetylenes leading to **5** in high yields. This experimental contrast is curious considering our prediction that the thermal ring opening of disilacyclobutene should take place more easily than that of benzodisilacyclobutene judging from their energetics. Let us consider why disilacyclobutene and acetylene do not effectively make the thermal addition. A possible reason is the self-Diels–Alder [4 + 2] reaction between disilacyclobutadiene generated by heat treatment and disilacyclobutene. This side reaction is expected to occur because disilacyclobutene has a localized C=C double bond that plays an important role as a dienophile. On the other hand, this type of self-condensation is less possible between  $\alpha$ -quinodisilane and benzodisilacyclobutene because benzodisilacyclobutene involves a stable benzene ring that never plays a role as a dienophile.

The energetics as well as optimized geometries for the self-Diels–Alder reaction of disilacyclobutadiene and disilacyclobutene is presented in Figure 7. We conclude that this self-condensation should reasonably take place once the four-membered ring of disilacyclobutenes is thermally opened as in **TS1**. The transition state for the Diels–Alder reaction **TS2** shows a symmetrical  $C_s$  structure. Since the product has a C=C double bond and a four-membered  $Si_2C_2$  ring, we can expect further reactions to take place leading to complicated oligomeric

**Table 1.** Energetics for the Reaction Species and the Transition States for the Thermal Addition of Disilacyclobutenes and Acetylene at the B3LYP/6-31G\*\* Level of Theory

	energy (au) <sup>a</sup>	ZPE (kcal/mol) <sup>b</sup>
acetylene	-77.32957	16.8
<b>7</b>	-658.76974	41.4
<b>TS1 (7)</b>	-658.70042	39.5
<b>7'</b>	-658.70472	39.6
<b>TS2 (7' + C<sub>2</sub>H<sub>2</sub>)</b>	-736.03391	57.1
<b>7''</b>	-736.20214	62.6
<b>8</b>	-816.09211	113.9
<b>TS1 (8)</b>	-816.01603	112.9
<b>8'</b>	-816.02472	113.3
<b>TS2 (8' + C<sub>2</sub>H<sub>2</sub>)</b>	-893.34869	130.5
<b>8''</b>	-893.52801	134.6
<b>9</b>	-969.75338	144.0
<b>TS1 (9)</b>	-969.65307	143.0
<b>9'</b>	-969.65325	142.9
<b>TS2 (9' + C<sub>2</sub>H<sub>2</sub>)</b>	-1046.97979	160.4
<b>9''</b>	-1047.18628	164.6
<b>TS2 (7' + 7)</b>	-1317.47516	81.8
product (7' + 7)	-1317.60245	85.5

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

silicon–carbon products. Thus, the thermal reaction of disilacyclobutene and acetylene does not proceed quantitatively.

## Conclusions

We have discussed the two-step reaction pathways for the thermal additions of disilacyclobutenes and acetylene from B3LYP/6-31G\*\* DFT computations. Detailed descriptions on the energetics of the reaction species (stable points) and the transition states (saddle points)



investigated in this work are given in Table 1. It has been confirmed that disilabutadienes, which are formed by the ring opening of the corresponding disilacyclobutenes, are involved in the thermal reactions of the silicon compounds as reaction intermediates. The activation energies for the symmetry-allowed conrotatory ring opening of 1,2-disilacyclobut-3-ene (**7**), 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**8**), and 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene (**9**) are 41.5, 46.7, and 61.9 kcal/mol, respectively. The activation energies for the Diels–Alder coupling reactions are 1–4 kcal/mol when measured from the disilabutadiene intermediates and 40–60 kcal/mol when measured from the starting materials. Therefore the ring opening should be the rate-determining step in these reactions in contrast to the Diels–Alder reactions of butadiene. Once the four-membered rings of the disilacyclobutenes are opened by heat treatment, the Diels–Alder additions of disilabutadienes with many kinds of dienophiles should readily take place. The transition state for the addition of 1,4-disila-1,3-butadiene (**7'**) and acetylene is symmetrical with respect to the Si–C bonds being formed, but those of 1,1,4,4-tetramethyl-1,4-disila-1,3-

butadiene (**8'**) and acetylene and of 1,2-bis(dimethylsilylene)cyclohexa-3,5-diene (**9'**) and acetylene are asymmetrical. These asymmetrical transition-state structures can be ascribed to either a nonsynchronous concerted transition state or a nonconcerted stepwise transition state. There are good reasons that such asymmetrical transition states occur in these Diels–Alder reactions. One is asymmetrical frontier orbitals in the methyl-substituted disilabutadienes, and the other is simply a steric effect of the methyl groups.

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