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Stereochemistry of Disilanylene-Containing Cyclic Compounds. Thermal Reactions of *cis*- and *trans*-3,4-Benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene

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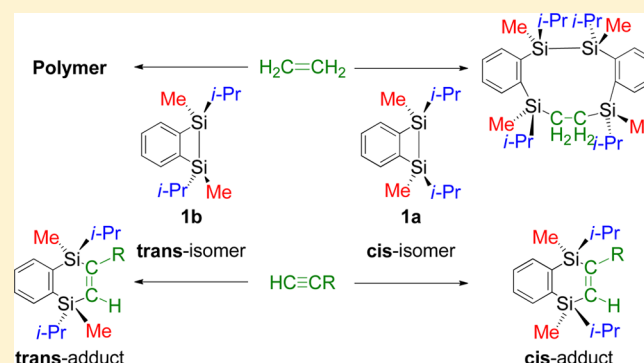
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S Supporting Information

ABSTRACT: The thermal reaction of *cis*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a**) with *tert*-butyl alcohol at 300 °C for 24 h proceeded with high stereospecificity to give *erythro*-1-(*tert*-butoxyisopropylmethylsilyl)-2-(isopropylmethylsilyl)benzene (**2a**) in 71% yield, as a single stereoisomer. A similar reaction of *trans*-benzodisilacyclobutene (**1b**) with *tert*-butyl alcohol produced the *threo* isomer **2b** in 81% yield, as the sole product. The photolysis of **1a,b** in the presence of *tert*-butyl alcohol afforded a mixture of two adducts formed by the reaction of 1-[2-(isopropylmethylsilyl)phenyl]-1-isopropylsilene with *tert*-butyl alcohol, respectively. The reaction of **1a** with ethylene in an autoclave at 300 °C for 24 h gave 3,4,9,10-dibenzo(*r*-1)-*trans*-2,trans-5,5-cis-8-tetraisopropyl-1,2,5,8-tetrasilacyclododeca-3,9-diene (**10a**), as a single stereoisomer in 71% yield. The reaction of **1b** with ethylene under the same conditions, however, produced poly[1,2-bis(isopropylmethylsilylene)phenylene-ethylene], whose molecular weight was determined to be 61000 ($M_w/M_n = 2.32$), relative to polystyrene standards. The reaction of **1a** with 1-hexyne, *tert*-butylacetylene, phenylacetylene, and (trimethylsilyl)acetylene in benzene in a sealed degassed tube at 150 or 200 °C proceeded stereospecifically to give the respective *cis*-5,6-benzo-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene derivatives (**11a–14a**) in high yields as the sole products. The reaction of **1b** with the alkynes under the same conditions afforded the respective *trans*-benzodisilacyclohexadienes (**11b–14b**), as the sole stereoisomers in high yields. Theoretical treatment for the reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) with *tert*-butyl alcohol and acetylene indicated that the substrates react directly with **1c** to give the respective adducts. For the reaction of **1c** with acetylene, it has been shown that the acetylene molecule inserts directly into a silicon–silicon bond in **1c** to give the benzodisilacyclohexadiene system. Such direct reactions of the substrates with **1c** were shown to be energetically more advantageous than the reaction of *o*-quinodisilane, 1,2-bis(dimethylsilylene)cyclohexa-3,5-diene, arising from a conrotatory ring-opening reaction of **1c** with substrates.



INTRODUCTION

The chemistry of benzodisilacyclobutenes is interesting because of their high strain energy, which results in high reactivity. They show unique behavior in photochemical and thermal reactions and also in transition-metal-catalyzed reactions.^{1–9} The thermal reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene proceeds with ring opening to give poly[(*o*-

tetramethyldisilanylene)phenylene] with high molecular weight.⁷ The thermal reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with *tert*-butyl alcohol, aldehydes, and alkynes, however, afford the respective adducts.^{8,11} With *tert*-

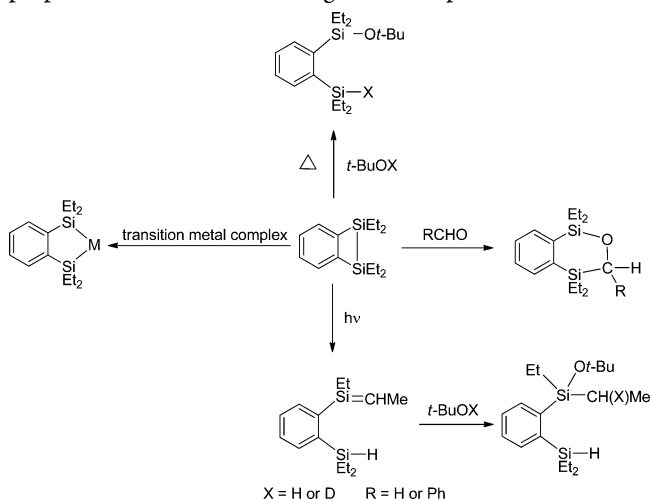
Received: August 15, 2013

Published: October 28, 2013



butyl alcohol, tetraethylbenzodisilacyclobutene produces an alcohol adduct, while with aldehydes and alkynes, the benzodisilacyclobutene gives products arising from insertion of the C–O and C–C bonds into the silicon–silicon bond in the benzodisilacyclobutene. In these reactions, we have proposed the formation of *o*-quinodisilane as a reactive intermediate.¹¹

On the other hand, the photolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene proceeds by a route quite different from that of the thermolysis, to afford a silene intermediate, 1-ethyl-1-[2-(diethylsilyl)phenyl]-1-silaprop-1-ene, derived from radical scission of a silicon–silicon bond in the disilacyclobutenyl ring, followed by intramolecular disproportionation of the resulting biradical species.¹⁰



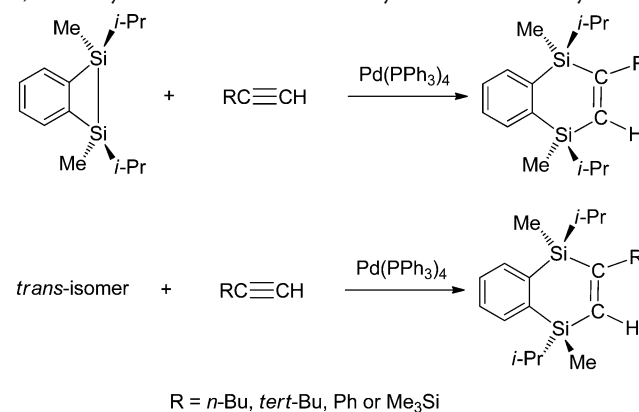
The benzotetraethyldisilacyclobutene readily reacts with arenes, alkenes, and alkynes in the presence of a catalytic amount of the transition-metal complexes, to give the respective adducts in high yields. The types of products thus formed depend highly on the nature of the metals in the transition-metal complexes used as the catalysts. In these reactions, we have proposed the transient formation of *o*-quinodisilane–metal complexes and also 3,4-benzo-1-metalla-2,5-disilacyclopent-3-ene, which play an important role in the production of the adducts.^{11,12}

The synthesis and some reactions of benzobis(disilacyclobut-3-enes) have also been reported. Matsumoto et al.^{13a,b} have reported that the palladium-catalyzed reaction of benzo-[1,2:4,5]bis(tetraethyl-1,2-disilacyclobut-3-ene) proceeds with metathesis of the silicon–silicon bond to give hexadecasilacyclopentane and its open-chain homologues. We have reported the palladium- and platinum-catalyzed reactions of benzo[1,2,4,5]bis(tetraethyl-1,2-disilacyclobut-3-ene) with alkynes, in which 1:2 adducts generated from insertion of alkyne into the two silicon–silicon bonds in the starting compound are produced.^{13c,d}

Recently, we have investigated the stereochemistry of benzodisilacyclobutenes and demonstrated that the palladium-catalyzed reactions of *cis*- and *trans*-3,4-benzo-1,2-di-*tert*-butyl-1,2-dimethyl-1,2-disilacyclobut-3-ene and *cis*- and *trans*-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene with alkynes, such as phenylacetylene, 1-hexyne, and diphenylacetylene, proceed stereospecifically to give the respective 5,6-benzo-1,4-disilacyclohexa-2,5-dienes.^{12f–h}

According to the Woodward–Hoffmann rules¹⁴ in carbon chemistry, cyclobutenes are smoothly transformed into butadienes with a conrotatory fashion by heat treatment. It is

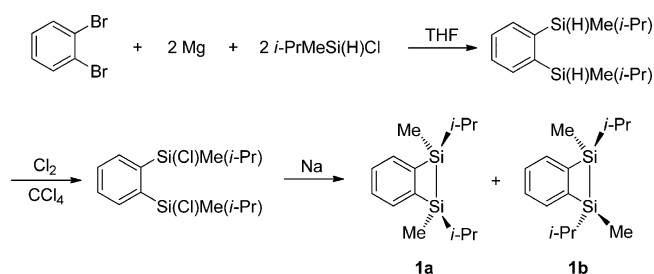
of considerable interest to us to investigate whether or not the stereochemistry in carbon compounds can be applied to the thermal reactions of the benzodisilacyclobutene system. During the course of our investigation concerning the stereochemistry of *cis*- and *trans*-benzodisilacyclobutene with various substrates, we found that the thermal reactions of *cis*- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene with alkynes proceed smoothly at relatively low temperature to give the products, arising from insertion of a triple bond in alkyne into a silicon–silicon bond of the benzodisilacyclobutenyl ring, but these compounds do not react with alkenes, with the one exception of ethylene, even at higher temperature. In this paper we report the stereochemistry and reaction mechanism for the thermal reaction of *cis*- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene with *tert*-butyl alcohol, ethylene, and monosubstituted acetylenes. We also report theoretical calculations for the reactions of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene with *tert*-butyl alcohol and acetylene.



RESULTS AND DISCUSSION

The starting compounds, *cis*- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a**, **1b**) were prepared by the reaction of *o*-dibromobenzene with 2 equiv of magnesium in the presence of 2 equiv of chloroisopropylmethylsilane in THF, followed by treatment of the resulting 1,2-bis(hydrosilyl)benzene with chlorine gas in a carbon tetrachloride solution and a sodium condensation reaction of 1,2-bis(chloroisopropylmethyl)benzene in refluxing toluene, as reported previously (Scheme 1). Both **1a** and **1b** were

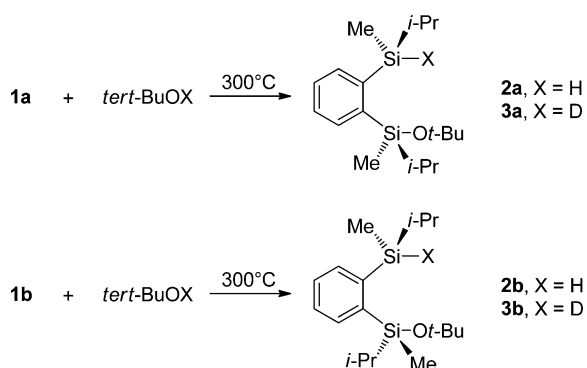
Scheme 1



separated by fractional distillation with the use of a spinning band column with 50 theoretical plates, as isomerically pure forms.^{12h} The *cis* configuration of **1a** was determined by X-ray crystallographic analysis of 5,6-benzo-1,4-diisopropyl-1,4-dimethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene obtained from the palladium-catalyzed reaction of **1a** with diphenylacetylene, which proceeds with retention of the configuration.^{12h}

Thermal Behavior of 1a,b in the Presence of *tert*-Butyl Alcohol. We first examined the thermal reactions of *cis*- and *trans*-benzodisilacyclobutenes **1a,b** with *tert*-butyl alcohol to elucidate an intermediate such as *o*-quinodisilane, which might be involved in the reaction. When **1a,b** were heated with *tert*-butyl alcohol at 250 °C for 24 h, no adducts were formed; the starting compounds **1a,b** were recovered unchanged. The result indicates that no reactive intermediates such as biradicals and *o*-quinodisilane are produced at this temperature. However, at temperatures higher than 250 °C, **1a,b** reacted with *tert*-butyl alcohol to give the respective adducts in high yields. Thus, treatment of **1a** with *tert*-butyl alcohol in a sealed glass tube at 300 °C for 24 h gave an alcohol adduct, 1-(*tert*-butoxyisopropylmethylsilyl)-2-(isopropylmethylsilyl)benzene (**2a**), which was tentatively assigned as an *erythro* isomer, in 71% yield as the sole product (Scheme 2).

Scheme 2



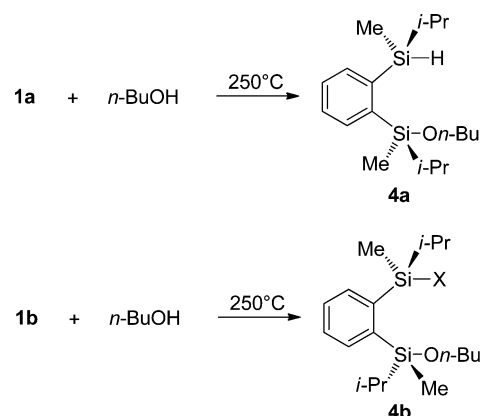
No other isomers were detected by spectrometric analysis in the reaction mixture, indicating that the reaction proceeded with high stereospecificity. The structure for **2a** was verified by mass and ^1H , ^{13}C , and ^{29}Si NMR spectrometric analysis (see the Experimental Section). Similar treatment of **1b** with *tert*-butyl alcohol at 300 °C for 24 h gave a stereoisomer different from **2a**, the *threo* isomer **2b**, in 81% yield. Again, no other isomers were detected in the reaction mixture.

The reaction of **1a** with *tert*-butyl alcohol- d_1 under the same conditions produced *erythro*-1-(*tert*-butoxyisopropylmethylsilyl)-2-(deuterioisopropylmethylsilyl)benzene (**3a**) in 35% yield, together with 48% of the unchanged starting compound **1a**. As expected, no other stereoisomers were detected in the reaction mixture. The ^2H NMR spectrum for **3a** showed a signal at 4.66 ppm, indicating that a D–Si bond was formed in the thermal reaction. A similar reaction of **1b** with *tert*-butyl alcohol- d_1 again proceeded stereospecifically to give a *threo* isomer (**3b**) as a single stereoisomer in 39% yield, along with 52% of the unchanged starting compound **1b**. Benzodisilacyclobutenes **1a,b** have a bulky isopropyl group on each silicon atom and, therefore, are very sensitive to the steric interaction in their reactions. *tert*-Butyl alcohol- d_1 , bearing the larger deuterium atom instead of hydrogen, seems to be much more prone to steric repulsion than *tert*-butyl alcohol, consequently resulting in lower yields of the products **3a,b**.

As expected, the thermal reaction of **1a,b** with the less hindered alcohol *n*-butyl alcohol proceeded readily at low temperature to give alcohol adducts in high yields. When a mixture of **1a** and *n*-butyl alcohol was heated in a sealed tube at 250 °C for 24 h, 1-(*n*-butoxyisopropylmethylsilyl)-2-(isopropylmethylsilyl)benzene (**4a**), tentatively assigned as an

erythro isomer, was obtained in 85% yield as a single stereoisomer (Scheme 3). A similar reaction of **1b** with *n*-

Scheme 3



butyl alcohol afforded *threo*-1-(*n*-butoxyisopropylmethylsilyl)-2-(isopropylmethylsilyl)benzene (**4b**) in 83% yield. Again, no other isomers were detected in the reaction mixture. The structures of **4a,b** were confirmed by spectrometric analysis (see the Experimental Section). These results strongly suggest that *n*-butyl alcohol and also *tert*-butyl alcohol add directly to **1a,b** to give the ring-opened products but not to the *o*-quinodisilane intermediate.

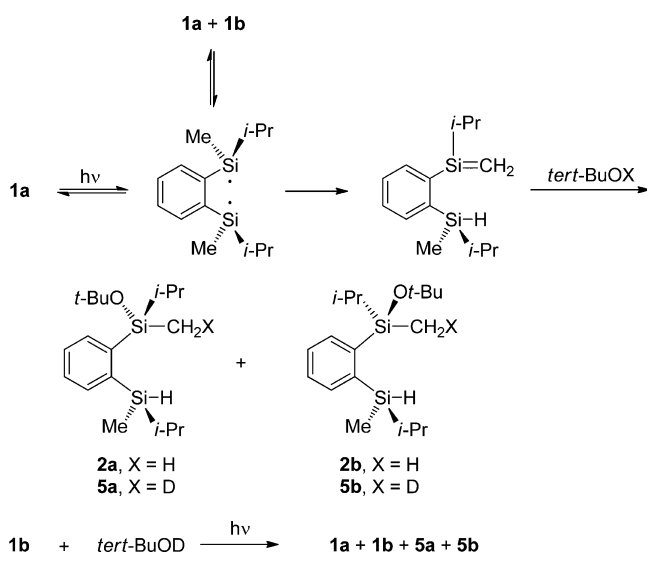
Theoretical treatment for the ring-opening reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) in the thermal reaction, as shown below, indicated that the energy for the ring-opening reaction involving homolytic scission of a silicon–silicon bond, leading to biradical species, is lower than that of the conrotatory ring opening to produce *o*-quinodisilane. Therefore, we thought that the thermolyses of **1a,b** might involve biradical species as the reactive intermediate and carried out their photolyses in the presence of *tert*-butyl alcohol. As reported previously, the photolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene led to the formation of the biradical intermediate, arising from homolytic scission of the silicon–silicon bond, followed by intramolecular disproportionation of the resulting biradical intermediate to produce the corresponding silene.^{8,10}

Irradiation of **1a** in the presence of *tert*-butyl alcohol in hexane with a low-pressure mercury lamp afforded a mixture of *erythro*- and *threo*-1-(*tert*-butoxyisopropylmethylsilyl)-2-(isopropylmethylsilyl)benzene (**2a,b**) in a ratio of 1:1.1, in 37% combined yield, and a mixture consisting of **1a,b** (23% combined yield) in a ratio of 2.8:1, indicating that the photochemical *cis* and *trans* isomerization of **1a** took place. In this photolysis, two stereoisomers of *cis*- and *trans*-3,4-benzo-2,5-diisopropyl-2,5-dimethyl-1-oxa-2,5-disilacyclopent-3-ene (**6a,b**) were also obtained in 12% combined yield.¹⁵ All spectral data for **6a,b** were identical with those obtained by the reaction of **1a,b** with *m*-chloroperoxybenzoic acid, respectively.¹²ⁱ

The photolysis of **1a** in the presence of *tert*-butyl alcohol- d_1 afforded a mixture of two alcohol- d_1 adducts, *erythro*- and *threo*-1-[(*tert*-butoxy)(deuteriomethyl)isopropylsilyl]-2-(isopropylmethylsilyl)benzene (**5a,b**), in 42% combined yield, along with two stereoisomers of *cis* and *trans* cyclic siloxanes, **6a,b** (16% combined yield) and a mixture of benzodisilacyclobutenes **1a,b** (12%). The position of the deuterium atom in the alcohol adducts was confirmed by spectrometric analysis and

verified to be attached on the methyl carbon bonded to the silicon atom, but not on the silicon atom, as shown in Scheme 4. In fact, the ^{13}C NMR spectrum indicated triplet signals at

Scheme 4



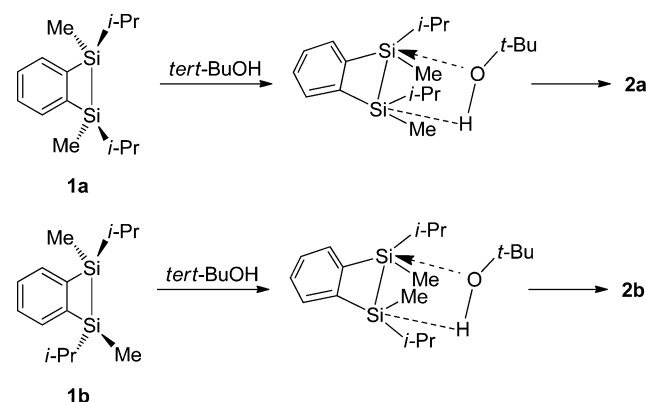
−1.79 and −1.33 ppm due to deuterio-substituted methyl carbons in **5a,b**, respectively. The ^2H NMR spectrum for **5a,b** also showed a signal at 0.57 ppm attributable to the deuteriomethyl group.

Irradiation of **1b** with *tert*-butyl alcohol under the same conditions also afforded a mixture of **2a** and **2b** in 40% combined yield, in a ratio of 0.9:1, together with the *cis* and *trans* cyclic siloxanes **6a,b** in 32% combined yield and 14% of a mixture of **1a** and **1b**. With *tert*-butyl alcohol-*d*₁, **1b** again gave a mixture of **5a** and **5b** in a ratio of 1:1, in 38% combined yield, and a mixture of the *cis* and *trans* cyclic siloxanes **6a,b** in 43% combined yield, along with 18% of a mixture of benzodisilacyclobutenes **1a,b**.

These results clearly show that the photolysis of **1a,b** proceeds with homolytic scission of the silicon–silicon bond to give the biradical with a triplet state, which undergoes intramolecular hydrogen abstraction to afford the 1-[2-(isopropylmethylsilyl)phenyl]-1-isopropylsilene. The silene thus formed reacts with *tert*-butyl alcohol to give the two stereoisomers **2a,b**, respectively.

In contrast with the photolysis, the thermal reaction of **1a,b** with *tert*-butyl alcohol proceeds stereospecifically to give the respective adducts. Therefore, we thought that the thermal reactions might involve *o*-quinodisilane as the reactive intermediate, but not biradical species. The theoretical calculations for the reaction of benzotetramethyldisilacyclobutene **1c** with *tert*-butyl alcohol, however, indicated that the direct addition of *tert*-butyl alcohol to the benzodisilacyclobutene is more advantageous than the reaction involving *o*-quinodisilane. According to the theoretical calculations shown below, addition of *tert*-butyl alcohol to **1a,b** occurs in the plane involving the benzodisilacyclobutenyl ring and the H–O bond in *tert*-butyl alcohol, as shown in Scheme 5. Thus, the oxygen atom of the hydroxyl group in *tert*-butyl alcohol attacks directly one of the two silicon atoms in **1a,b**, and then the hydrogen atom is transferred to another silicon atom, to give **2a,b**, respectively.

Scheme 5



Thermal Behavior of **1a,b** in the Absence of a Trapping Agent.

We have previously reported that the thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene in the absence of a trapping agent at 250 °C produced 4,5-benzo-1,1,2,2,3,3-hexaethyl-1,2,3-trisilacyclopent-4-ene and 2,3,5,6-dibenzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene, derived from dimerization of the *o*-quinodisilane intermediate.¹¹ Since compounds **1a,b** did not undergo thermolysis at 250 °C, we carried out the reaction at 300 °C and found that the reaction proceeded to give the products in low yields. Thus, heating **1a** in a degassed sealed glass tube at 300 °C for 24 h gave two stereoisomers (**7a** and **8a**) of 4,5-benzo-1,2,3-triisopropyl-1,2,3-trimethyl-1,2,3-trisilacyclopent-4-ene in a ratio of 1:1, in 6% combined yield, and *trans*-2,3,5,6-dibenzo-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**9a**) in 1% yield, along with the unchanged starting compound **1a** (Scheme 6).

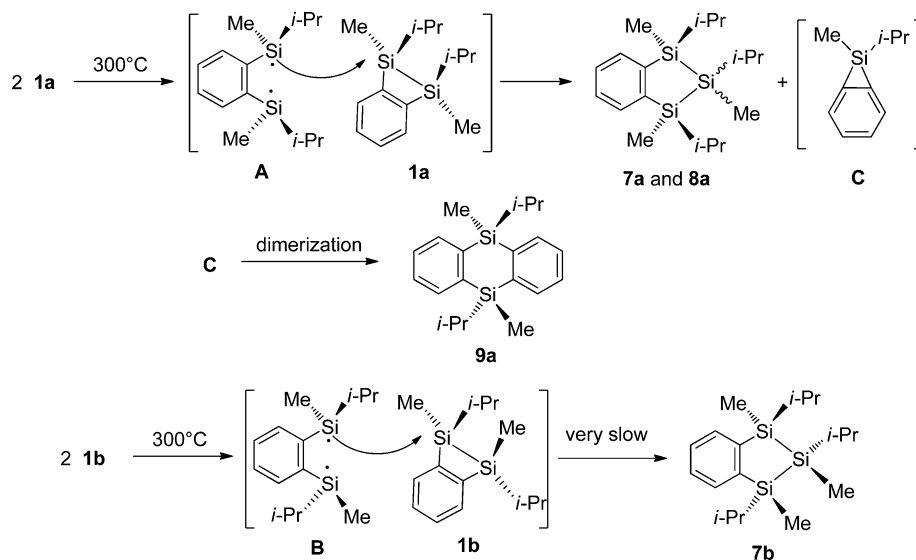
The products **7a–9a** were isolated by the use of recycling preparative HPLC. Unfortunately, all attempts to separate **7a** from **8a** were unsuccessful. Therefore, the structures of **7a** and **8a** were confirmed by spectrometric analysis, using a 1:1 mixture (see Experimental Section), although we could not determine their configurations. The structure of **9a** was also verified by spectrometric analysis and tentatively assigned to have the *trans* configuration.

On the basis of the theoretical treatment shown below (see Figure 2), the energies of the biradical intermediates, singlet and triplet biradicals, arising from scission of the silicon–silicon bond are shown to be lower than that of *o*-quinodisilane by approximately 12 kcal/mol. The energy difference between singlet and triplet states is very small, only 1.44 kcal/mol, but the singlet state is more stable than the triplet. Moreover, the thermal reaction involves no abstraction of a hydrogen atom; therefore, the singlet biradical intermediate seems to play an important role in the formation of the products.

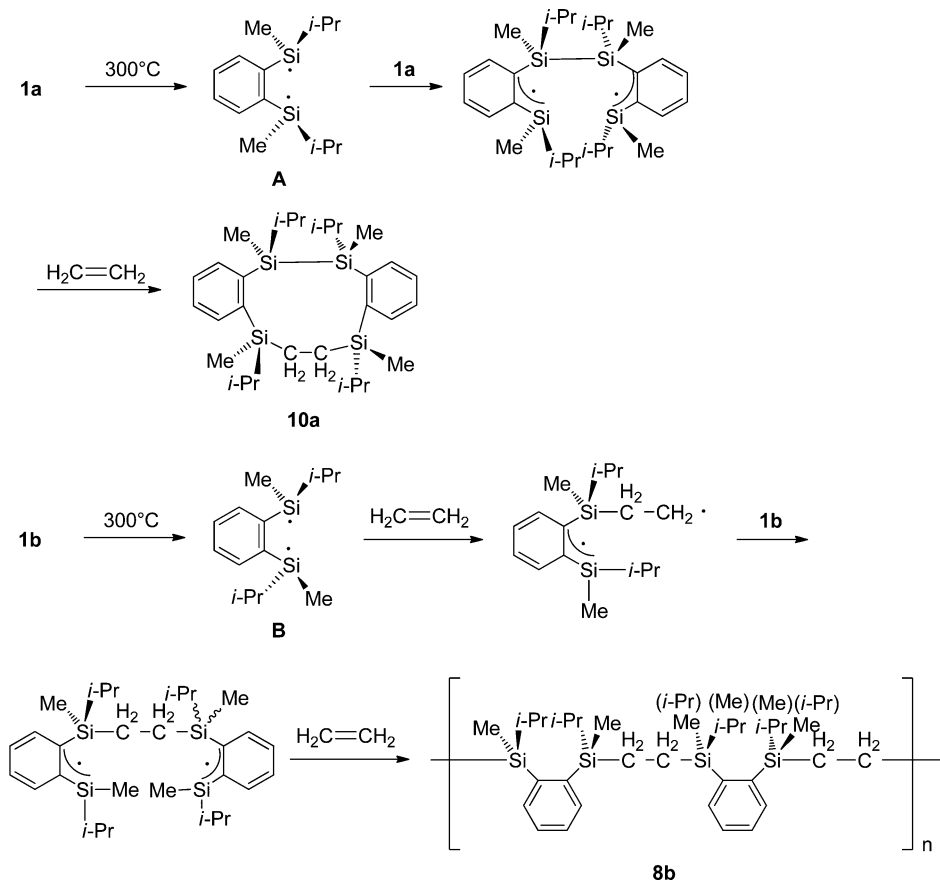
The formation of the products **7a–9a** may be best explained by addition of a singlet biradical (A) formed thermally from **1a** to the starting compound **1a**, followed by splitting to **7a** and **8a** and the benzosilacyclopentene intermediate (C) as reported in the thermolysis of benzotetraethyldisilacyclobutene.¹¹ The intermediate C thus formed would undergo σ dimerization^{4,16} to produce dibenzodisilacyclohexadiene **9a**. The formation of *trans* isomer **9a** by a σ -dimerization reaction^{4,16} of the 1,2-benzo-3-silacyclopentene intermediate C seems to be sterically more favorable than that of the *cis* isomer.

A similar thermolysis of **1b** at 300 °C for 24 h gave a single stereoisomer, whose configuration was different from those of

Scheme 6



Scheme 7



7a and **8a**, in 1% yield, together with the unchanged starting compound **1b**. We tentatively assigned this compound as 4,5-benzo(*r*-1)-*trans*-2,*trans*-3-triisopropyl-1,2,3-trimethyl-1,2,3-trisilacyclopent-4-ene (**7b**). Again, the formation of **7b** may be understood by the reaction of singlet biradical (**B**) with **1b**, analogously to the reaction of **A** with **1a**.

Thermal Reaction of 1a,b with Ethylene. The thermal reaction of **1a,b** with alkenes such as 1-hexene and propylene at 300 °C afforded no adducts at all. However, with ethylene, **1a,b**

reacted to give the respective adducts under the same conditions in high yields. Thus, treatment of **1a** with ethylene in benzene in an autoclave at 300 °C for 24 h proceeded cleanly to give a crystalline product, consisting of two molecules of **1a** and one ethylene molecule, 3,4,9,10-dibenzo(*r*-1)-*trans*-2,*trans*-5,*cis*-8-tetraisopropyl-1,2,5,8-tetramethyl-1,2,5,8-tetrasilacyclododeca-3,9-diene (**10a**), in 71% yield (Scheme 7). In this reaction, a small amount of *cis*-3,4-benzo-2,5-diisopropyl-2,5-dimethyl-1-oxa-2,5-disilacyclopent-3-ene, whose retention time

on GLC was identical with that of the authentic sample,¹²ⁱ was formed, but no 1:1 adduct, *cis*-2,3-benzo-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohex-2-ene was detected in the resulting mixture. All spectral data for the product **10a** were identical with those obtained by the palladium-catalyzed reaction of **1a** with ethylene,¹²ⁱ indicating that the reaction proceeds with high stereospecificity.

A similar reaction of **1b** with ethylene in benzene proceeded to afford a quite different type of product. Treatment of **1b** with ethylene in benzene at 300 °C for 24 h gave white polymeric substances. Neither a 1:1 adduct nor a 1:2 adduct such as **10a** was detected in the resulting mixture. Reprecipitation of the polymeric substances from benzene–methanol afforded poly-[1,2-bis(isopropylmethylsilylene)phenylene–ethylene] (**8b**), whose molecular weight was determined to be 61000 ($M_w/M_n = 2.32$) relative to polystyrene standards, in 75% yield. The ¹H NMR spectrum for the polymer **8b** reveals four broad signals at 0.20, 0.59, 0.78, and 1.08 ppm, due to the methylsilyl protons, ethylene protons, and methyl protons and methine protons of the isopropyl group, respectively, as well as broad signals attributable to the phenylene ring protons at 7.14 and 7.42 ppm. Its ²⁹Si NMR spectrum shows four signals at 3.6, 3.7, 3.8, and 3.9 ppm.

In contrast to the direct reactions of **1a,b** with *tert*-butyl alcohol and monosubstituted acetylene discussed below, in the reactions of **1a,b** with ethylene, a singlet biradical intermediate, as in the thermolyses of **1a,b** in the absence of a trapping agent, seems to play a role in the formation of 1:2 adduct **10a** and alternative copolymer **8b**. Thus, the formation of the 1:2 adduct **10a** may be understood in terms of the reactions shown in Scheme 7: addition of the singlet biradical **A** to **1a**, giving the dimeric biradical, and the reaction of the resulting dimeric biradical with ethylene. That the reaction proceeds with retention of configuration may also be explained as follows. In the benzodisilacyclobutene **1a**, both of the less bulky methyl groups on the disilanylene moiety are located on one side of the plane consisting of the benzodisilacyclobutenyl ring, and therefore, one of two silyl radicals in the intermediate **A** can add stereospecifically to one of the two silicon atoms in **1a** from the less hindered side. On the other hand, for the formation of alternative copolymer **8b**, the sterically bulky isopropyl groups in compound **1b** are located on both sides, above and below the benzodisilacyclobutenyl ring, and would prevent the approach of a silyl radical in **B** to the silicon atom of **1b**. However, ethylene, which is a smaller molecule, can react with **B** to give the alternative copolymer **8b**. The result is consistent with the production of **7b** in extremely low yield in the thermolysis of **1b** in the absence of a trapping agent.

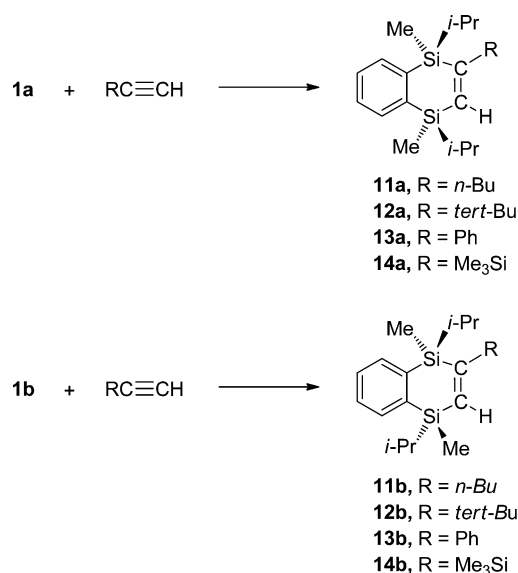
The formation of a silicon–silicon bond in the dimerization of some silenes has been reported.¹⁷ Retention of the configuration of the silyl center in the radical reaction has also been reported.^{12f} For example, the reaction of *cis*- and *trans*-3,4-benzo-1,2-di-*tert*-butyl-1,2-dimethyl-1,2-disilacyclobut-3-ene with oxygen in the presence of azobis(isobutyro)nitrile in refluxing benzene proceeds stereospecifically to produce *cis*- and *trans*-3,4-benzo-2,5-di-*tert*-butyl-2,5-dimethyl-1-oxa-2,5-disilacyclopent-3-ene, respectively.^{12f}

Thermal Reactions of 1a,b with Monosubstituted Alkynes. In marked contrast to the reaction of **1a,b** with *tert*-butyl alcohol and ethylene, **1a,b** readily react with monosubstituted alkynes to give the respective adducts at much lower temperature in high yields. When **1a** was heated with 1-hexyne in a sealed glass tube at 150 °C for 24 h, *cis*-5,6-benzo-2-butyl-

1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**11a**), arising from formal insertion of a triple bond of alkyne into the silicon–silicon bond in **1a**, was obtained in 62% yield, along with 34% of the unchanged starting compound **1a**. At higher temperature, **1a** gave **11a** in higher yield. Thus, the reaction of **1a** with 1-hexyne at 200 °C for 24 h afforded **11a** in 76% yield as the sole product. No other stereoisomers were detected in the reaction mixture by spectrometric analysis.

All spectral data for the product **11a** were identical with those obtained by the palladium-catalyzed reaction of **1a** with 1-hexyne.^{12h} The fact that no stereoisomers were detected in the reaction mixture shows that the reaction proceeded with high stereospecificity. The reaction of *trans* isomer **1b** with 1-hexyne at 200 °C for 24 h again proceeded stereospecifically to produce *trans*-5,6-benzo-2-butyl-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**11b**), whose spectral data were identical with those of the authentic sample,^{12h} in 67% yield as the sole stereoisomer (Scheme 8).

Scheme 8



Surprisingly, the reaction of *cis* isomer **1a** with *tert*-butylacetylene, bearing a bulky substituent on the sp carbon atom, took place readily at 200 °C for 24 h to give the single stereoisomer *cis*-benzodisilacyclohexadiene (**12a**) in 91% yield as the sole product. The reaction of **1b** with *tert*-butylacetylene under the same conditions readily produced *trans*-benzodisilacyclohexadiene (**12b**) in 90% yield. Again, no other stereoisomers were detected in the product. Similar treatment of **1a,b** with phenylacetylene at 150 °C for 24 h gave *cis*- and *trans*-benzodisilacyclohexadiene (**13a,b**) in 77% yields, respectively. Both **1a** and **1b** also reacted with silyl-substituted acetylene to give the addition products. Thus, treatment of **1a** with (trimethylsilyl)acetylene in a sealed glass tube at 200 °C for 24 h again proceeded stereospecifically to produce *cis*-benzodisilacyclohexadiene (**14a**) in 77% yield, while **1b** yielded the *trans* isomer **14b** in 55% yield as the sole product. All spectral data for **12a–14a** and **12b–14b** were identical with those obtained by the palladium-catalyzed reactions of **1a,b** with the corresponding alkynes.^{12h}

With monosubstituted acetylene, **1a,b** readily react to give the corresponding benzodisilacyclohexadienes at 150 or 200 °C; however, **1a,b** do not react with disubstituted acetylenes,

such as 3-hexyne and diphenylacetylene, even at higher temperature. For example, when a mixture of **1a** and diphenylacetylene was heated in a sealed glass tube at 300 °C for 24 h, no adduct was formed. No 1:1 adduct was detected in the reaction mixture by mass spectrometric analysis.

In the thermal reactions of **1a,b** with monosubstituted acetylene at 150 or 200 °C, it seems unlikely that the *o*-quinodisilane intermediate or singlet biradical intermediate plays a role in the formation of the benzodisilacyclohexadienes. In fact, the theoretical calculations shown below indicated that a new type of addition reaction, including direct interaction between a terminal carbon atom in alkynes and a silicon–silicon σ bond in **1a,b**, may be involved in the formation of the benzodisilacyclohexadienes.

Theoretical Calculations. To clarify the mechanism for the reactions of the *cis*- and *trans*-benzodisilacyclobutenes **1a,b** with *tert*-butyl alcohol and monosubstituted acetylenes, we have carried out density functional calculations, using the ω B97X-D method¹⁸ combined with the 6-311G(d,p) basis set.¹⁹ 3,4-Benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) was used as the starting compound for the reactions. The optimized structures were verified by vibrational analysis: i.e., the equilibrium structures have no imaginary frequencies, and the transition state structures have only one imaginary frequency.

We first investigated the reaction mechanism via conrotatory ring-opening reactions involving scission of the silicon–silicon bond of **1c**, leading to a closed-shell ring-opened product, *o*-quinodisilane (**15**). The optimized structures of **15** and the transition state (TS-**15**) from **1c** to **15** are illustrated in Figure 1. The energy profile for this reaction is shown in Figure 2. The structure of TS-**15** is close to that of the ring-opened product *o*-quinodisilane (**15**). Furthermore, the energy difference between the transition state TS-**15** (70.90 kcal/mol) and **15** (70.87 kcal/mol) is quite small (0.03 kcal/mol). This is consistent with the B3LYP/6-31G(d,p) calculations previously reported by Yoshizawa and co-workers.²⁰ It is interesting to note that the silicon atoms in **15** are nonplanar, a trigonal pyramid with a pyramidalization angle of 20.4°, and the wave function of **15** is shown to be unstable. Therefore, the electronic state of **15** should not be the closed-shell singlet but the open-shell biradical at the ground state. The vertical energy of the open-shell singlet biradical state is 5.21 kcal/mol lower than that of the closed-shell singlet state of **15**. Then, we optimized the structures of the open-shell singlet biradical (**¹16**; see Figure 1) and the triplet biradical (**³16**), respectively. The singlet biradical **¹16** is 12.97 kcal/mol more stable than that of **15**, and the triplet biradical **³16** is 1.44 kcal/mol less stable than that of **¹16**. The result indicates that the singlet biradical **¹16** is the ground state for the ring-opened product. In the structure of **¹16**, the silicon atom is highly pyramidalized with a pyramidalization angle of 32.8° and the spin density is strongly localized on the silicon atom (0.817e). The result indicates that the destabilization energy by losing aromaticity of the benzene ring is larger than the stabilization energy gained by extension of the π conjugation. We could not optimize the structure of the transition state TS-**¹16** leading to **¹16**, but the vertical energy of the open-shell singlet biradical state with the optimized structure of TS-**15** could be calculated to be –6.54 kcal/mol. Therefore, the activation energy for the formation of **¹16** would be estimated to be less than 64.36 kcal/mol. Thus, the activation energy for the ring-opening process to the formation of the biradical seems to still be large for the thermally allowed reactions observed experimentally.

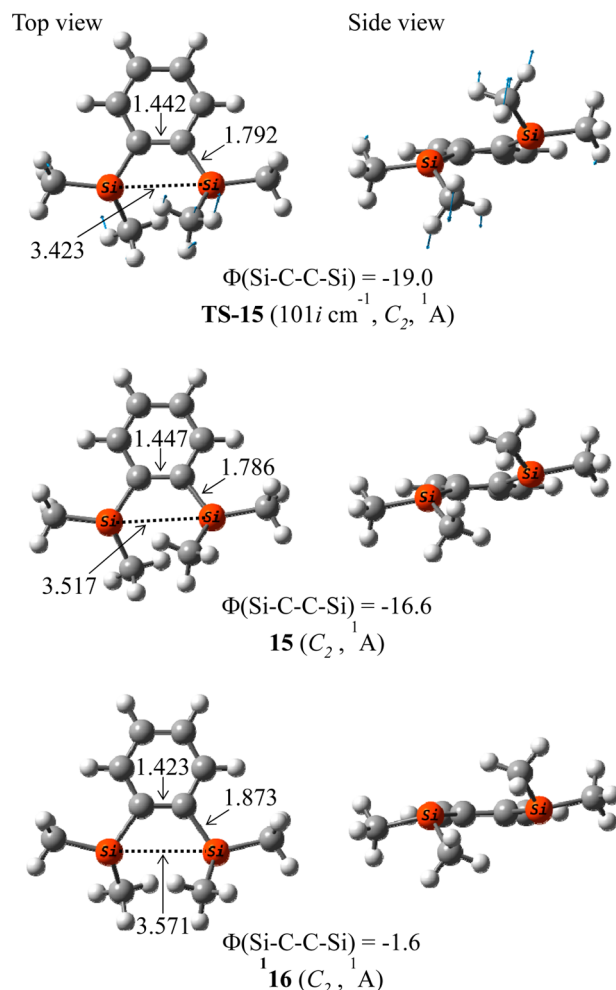


Figure 1. Optimized structures of the closed-shell ring-opening transition state TS-**15**, closed-shell ring-opened state **15** and open-shell singlet biradical ring-opened state **¹16** for 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) at the ω B97X-D/6-311G(d,p) level. Selected bond lengths are given in Å and dihedral angles (Φ) in deg. The blue arrows in TS-**15** indicate the vibrational mode of the reaction coordinate.

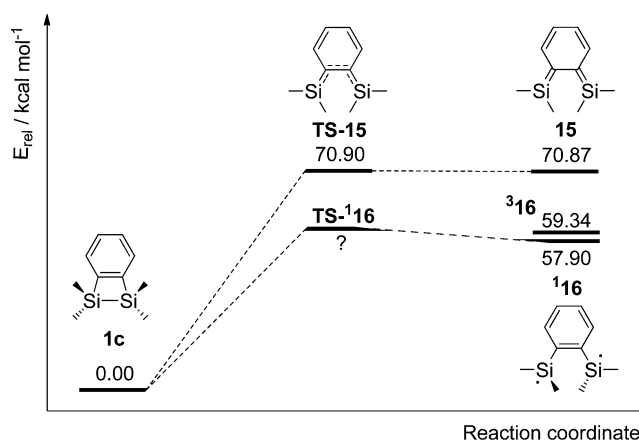


Figure 2. Energy profile for the ring-opening reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) at the ω B97X-D/6-311G(d,p) level.

Therefore, we have extensively investigated the alternative reaction routes leading to the addition products observed

experimentally. As the result, we found novel reaction pathways which involve no ring-opening process: that is, **1c** reacts with the substrates directly to give the adducts. This mechanism involves the attacks of *tert*-butyl alcohol and acetylene onto a silicon atom or a silicon–silicon bond of **1c**, respectively. In the case of *tert*-butyl alcohol, the oxygen atom attacks one of the two silicon atoms of the starting compound **1c**, and then the hydrogen atom in the hydroxyl group is transferred to another silicon atom to finally afford the product **2c**. The optimized structure of the transition state **TS-2c** from **1c** to **2c** is illustrated in Figure 3. The energy profile for this reaction is

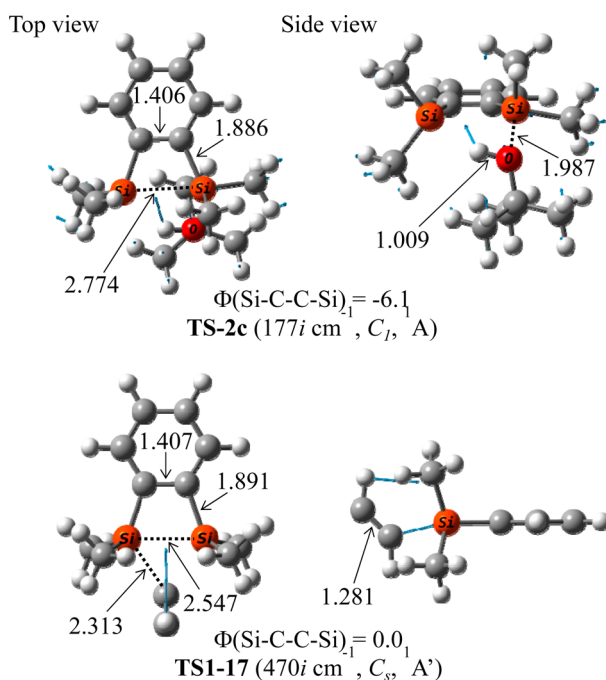


Figure 3. Optimized structures of transition states **TS-2c** and **TS1-17** in a new reaction path without a ring-opened state for the thermal reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) with *tert*-butyl alcohol and acetylene at the ω B97X-D/6-311G(d,p) level. Selected bond lengths are given in Å and dihedral angles (Φ) in deg. The blue arrows in each transition state indicate the vibrational mode of the reaction coordinate.

shown in Figure 4. The activation energy calculated for this reaction is 23.39 kcal/mol, and this value is sufficiently small to allow the thermal reaction. Furthermore, this reaction would proceed with high stereospecificity to produce the alcohol adduct, which is also consistent with the experimental results.

In the reaction of **1c** with acetylene, we found that acetylene inserts directly into the silicon–silicon bond in the starting compound **1c**, to give the six-membered intermediate **IM-17** through the two transition states **TS1-17** and **TS2-17**. Interestingly, the structure of the transition state **TS1-17** indicates the presence of an appreciable interaction between one of the ethynyl carbons in acetylene and the silicon–silicon σ bond of **1c**. As shown in Figure 3, the charge transfer at the transition state **TS1-17** plays an important role in this mechanism. Then, **TS1-17** leads to the five-membered-ring structure of the transition state **TS2-17**. The intermediate **IM-17** thus formed is readily transformed into the final product (**17**), via the biradical transition state **TS3-17**, as displayed in Figure 5. In this mechanism, the activation energy for **1c** with acetylene is calculated to be 32.16 kcal/mol, and this value is

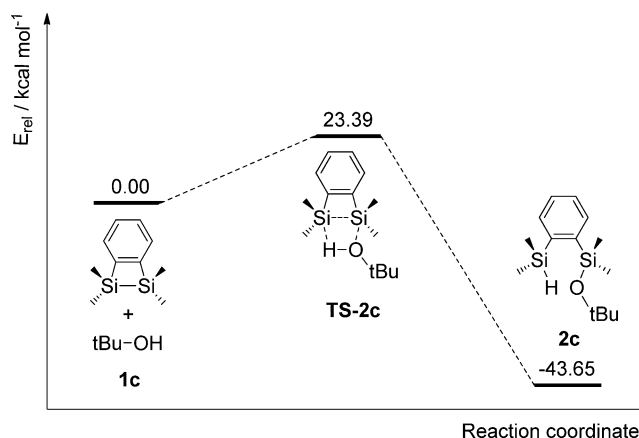


Figure 4. Energy profile for the reaction between **1c** and *tert*-butyl alcohol without a ring-opening process at the ω B97X-D/6-311G(d,p) level.

sufficiently small to produce the acetylene insertion product in the thermal reaction. Moreover, the reaction definitely proceeds with retention of the configuration, as observed experimentally. Further detailed theoretical investigations into the thermal reaction of **1a,b** are now in progress and will be published elsewhere.

In conclusion, all thermal reactions reported here proceeded with high stereospecificity to give the respective adducts. The thermolysis of **1a,b** in the presence of *tert*-butyl alcohol or *tert*-butyl alcohol-*d*₁ at 300 °C proceeded stereospecifically to give the respective adducts, arising from direct addition of the alcohol to **1a,b**. In contrast to the thermal reactions, the photochemical reactions of **1a,b** afforded silene intermediates derived from radical scission of the silicon–silicon bond in the disilacyclobutenyl ring, followed by disproportionation of the resulting triplet biradical, and the silenes thus formed reacted with *tert*-butyl alcohol to give the adducts. The reaction of **1a** with ethylene at 300 °C afforded the product **10a**, consisting of two molecules of **1a** and one molecule of ethylene, as the sole stereoisomer. A similar reaction of **1b** with ethylene, however, gave poly[1,2-bis(isopropylmethylsilylene)phenylene–ethylene] (**8b**) with a 1:1 ratio of **1b** and ethylene, whose molecular weight was determined to be 61000, as the sole product. The reaction of **1a,b** with alkynes, however, proceeded at lower temperature (150 or 200 °C) with high stereospecificity to give the respective *cis*- and *trans*-5,6-benzo-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-dienes. Theoretical investigations for the reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**1c**) with *tert*-butyl alcohol indicated that the alcohol adds directly to **1c** to give the adduct, while with acetylene **1c** reacts to afford 1,4-disilacyclohexa-2,5-diene derived from direct insertion of acetylene into the silicon–silicon σ bond in **1c**.

EXPERIMENTAL SECTION

The thermal reactions of **1a,b** with *tert*-butyl alcohol and alkynes were carried out in a degassed sealed glass tube (1.0 cm × 15 cm). Similar reactions with ethylene were performed in a 10 mL autoclave. NMR spectra were measured on JNM-LA300 and JNM-LA500 spectrometers. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Mass spectra were measured on a JEOL Model JMS-700 instrument. *cis*- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a,b**) were separated by a TSA-SB2 spinning band type distillation column (Taika Kogyo). Melting points were measured with a Yanaco MP S3

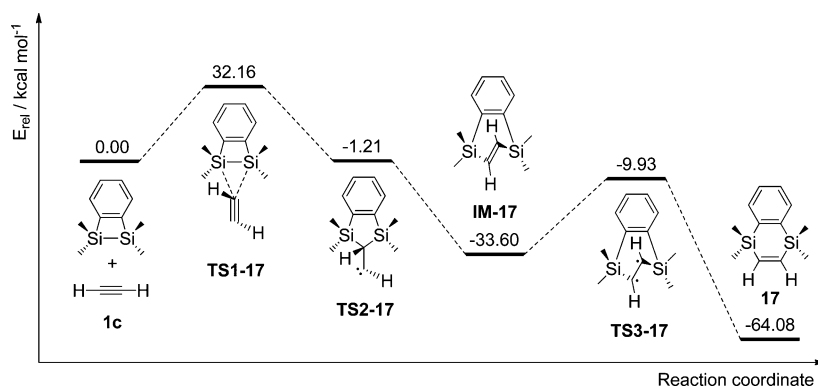


Figure 5. Energy profile for the reaction between 1c and acetylene without a ring-opening process at the ω B97X-D/6-311G(d,p) level.

apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Tetrahydrofuran used as a solvent was dried over sodium/benzophenone under a nitrogen atmosphere and carbon tetrachloride was dried over P_4O_{10} and distilled before use. Benzene and toluene were dried over sodium and distilled before use.

Thermal Reaction of 1a with *tert*-Butyl Alcohol. A mixture of 0.140 g (0.56 mmol) of 1a and 0.231 g (3.12 mmol) of *tert*-butyl alcohol was heated in a sealed glass tube at 300 °C for 24 h. The mixture was analyzed by GLC as being 2a (71% yield). The product 2a (colorless liquid) was isolated by column chromatography: MS m/z 279 ($M^+ - i\text{-Pr}$); IR 3045, 2956, 2941, 2864, 2162, 1464, 1363, 1250, 1196, 1119, 1045, 926, 881, 829, 781, 742, 710 cm^{-1} ; ^1H NMR δ (CDCl_3) 0.28 (d, 3H, MeSi, $J = 3.4$ Hz), 0.48 (s, 3H, MeSi), 0.82 (d, 3H, MeCH, $J = 7.3$ Hz), 0.98 (d, 6H, MeCH, $J = 7.3$ Hz), 1.04 (d, 3H, MeCH, $J = 7.3$ Hz), 1.07–1.20 (m, 2H, HC), 1.24 (s, 9H, *t*-Bu), 4.56 (quint, 1H, HSi, $J = 3.4$ Hz), 7.31–7.34 (m, 2H, phenylene ring protons), 7.52–7.53 (m, 1H, phenylene ring proton), 7.70–7.72 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl_3) –6.10, –1.51 (MeSi), 13.10, 16.12, 17.05, 17.31, 17.99, 18.94 (Me₂CH), 32.15 (Me₃C), 72.62 (CMe₃) 127.60, 127.67, 134.73, 135.12, 142.89, 146.19 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) –10.3, –0.5. Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{OSi}_2$: C, 67.01; H, 10.62. Found: C, 66.82; H, 10.74.

Thermal Reaction of 1b with *tert*-Butyl Alcohol. A mixture of 0.119 g (0.48 mmol) of 1b and 0.201 g (2.71 mmol) of *tert*-butyl alcohol was heated in a sealed tube at 300 °C for 24 h. The resulting mixture was analyzed by GLC as being 2b (81% yield). The product 2b (colorless liquid) was isolated by column chromatography: MS m/z 279 ($M^+ - i\text{-Pr}$); IR 3043, 2956, 2864, 2154, 1464, 1363, 1250, 1196, 1119, 1059, 1045, 924, 881, 833, 781, 742, 719 cm^{-1} ; ^1H NMR δ (CDCl_3) 0.26 (d, 3H, MeSi, $J = 3.7$ Hz), 0.48 (s, 3H, MeSi), 0.88 (d, 3H, MeCH, $J = 7.3$ Hz), 0.96 (d, 3H, MeCH, $J = 7.3$ Hz), 0.99 (d, 3H, MeCH, $J = 7.3$ Hz), 1.06 (d, 3H, MeCH, $J = 7.3$ Hz), 1.11–1.20 (m, 2H, HC), 1.27 (s, 9H, *t*-Bu), 4.52 (quint, 1H, HSi, $J = 3.4$ Hz), 7.31–7.35 (m, 2H, phenylene ring protons), 7.52–7.54 (m, 1H, phenylene ring proton), 7.74–7.76 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl_3) –5.91, –1.07 (MeSi), 12.70, 16.11, 17.17, 17.31, 18.01, 18.99 (Me₂CH), 32.15 (Me₃C), 72.60 (CMe₃) 127.61, 127.69, 134.66, 135.24, 142.75, 146.17 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) –10.0, –0.6. Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{OSi}_2$: C, 67.01; H, 10.62. Found: C, 67.13; H, 10.62.

Thermal Reaction of 1a with *tert*-Butyl Alcohol-*d*₁. A mixture of 0.144 g (0.58 mmol) of 1a and 0.241 g (3.21 mmol) of *tert*-butyl alcohol-*d*₁ was heated in a sealed tube at 300 °C for 24 h. The mixture was analyzed by GLC as being 3a (35% yield) and 48% of the unchanged starting compound 1a. The product 3a (colorless liquid) was isolated by column chromatography. Data for 3a: MS m/z 280 ($M^+ - i\text{-Pr}$); ^1H NMR δ (CDCl_3) 0.27 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 0.82 (d, 3H, MeCH, $J = 7.3$ Hz), 0.97 (d, 6H, MeCH, $J = 7.3$ Hz), 1.04 (d, 3H, MeCH, $J = 7.3$ Hz), 1.07–1.20 (m, 2H, HC), 1.24 (s, 9H, *t*-Bu), 7.31–7.34 (m, 2H, phenylene ring protons), 7.51–7.53 (m, 1H, phenylene ring proton), 7.69–7.71 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl_3) –6.18, –1.54 (MeSi), 13.04, 16.11, 17.06, 17.32, 17.99, 18.94 (Me₂CH), 32.15 (Me₃C), 72.62 (CMe₃)

127.61, 127.69, 134.73, 135.11, 142.85, 146.17 (phenylene ring carbons); ^2H NMR δ (CDCl_3) 4.66.

Thermal Reaction of 1b with *tert*-Butyl Alcohol-*d*₁. A mixture of 0.130 g (0.52 mmol) of 1b and 0.21 g (2.80 mmol) of *tert*-butyl alcohol-*d*₁ was heated in a sealed tube at 300 °C for 24 h. The mixture was analyzed by GLC as being 3b (39% yield) and 52% of the unchanged starting compound 1b. The product 3b (colorless liquid) was isolated by column chromatography. Data for 3b: MS m/z 280 ($M^+ - i\text{-Pr}$); ^1H NMR δ (CDCl_3) 0.26 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 0.89 (d, 3H, MeCH, $J = 7.3$ Hz), 0.97 (d, 3H, MeCH, $J = 7.3$ Hz), 0.99 (d, 3H, MeCH, $J = 7.3$ Hz), 1.06 (d, 3H, MeCH, $J = 7.3$ Hz), 1.16 (sep, 2H, HC, $J = 7.3$ Hz), 1.27 (s, 9H, *t*-Bu), 7.32–7.34 (m, 2H, phenylene ring protons), 7.53–7.55 (m, 1H, phenylene ring proton), 7.75–7.77 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl_3) –6.00, –1.10 (MeSi), 12.63, 16.09, 17.18, 17.32, 18.01, 18.99 (Me₂CH), 32.15 (Me₃C), 72.60 (CMe₃) 127.62, 127.71, 134.67, 135.23, 142.71, 146.14 (phenylene ring carbons); ^2H NMR δ (CDCl_3) 4.61.

Thermal Reaction of 1a with *n*-Butyl Alcohol. A mixture of 0.176 g (0.71 mmol) of 1a and 0.269 g (3.63 mmol) of *n*-butyl alcohol was heated in a sealed glass tube at 250 °C for 24 h. The mixture was analyzed by GLC as being 4a (85% yield). The product 4a (colorless liquid) was isolated by column chromatography: exact mass calcd for $\text{C}_{18}\text{H}_{34}\text{OSi}_2$ [M^+] 322.2149, found 322.2133; MS m/z 332 (M^+); IR 3046, 2956, 2865, 2150, 1463, 1383, 1252, 1119, 1095, 909, 882, 832, 790, 738 cm^{-1} ; ^1H NMR δ (CDCl_3) 0.29 (d, 3H, MeSi, $J = 3.7$ Hz), 0.43 (s, 3H, MeSi), 0.94 (t, 3H, CH₃, $J = 7.3$ Hz), 0.98 (d, 3H, MeCH, $J = 7.3$ Hz), 1.01 (d, 3H, MeCH, $J = 7.3$ Hz), 1.03 (d, 3H, MeCH, $J = 7.3$ Hz), 1.05 (d, 3H, MeCH, $J = 7.3$ Hz), 1.15–1.27 (m, 2H, HC), 1.40 (sex, 2H, CH₂, $J = 7.3$ Hz), 1.54–1.62 (m, 2H, CH₂), 3.68 (dt, 1H, OCH, $J = 16.8$ Hz, 7.3 Hz), 3.70 (dt, 1H, OCH, $J = 16.8$ Hz, 7.3 Hz), 4.46 (quint, 1H, HSi, $J = 3.7$ Hz), 7.34–7.38 (m, 2H, phenylene ring protons), 7.56–7.59 (m, 1H, phenylene ring proton), 7.66–7.69 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl_3) –6.18, –4.32 (MeSi), 12.60, 13.93, 15.45, 17.32, 17.38, 17.87, 18.90, 19.10 (Me₂CH, CH₂CH₃), 34.93 (CH₂), 63.04 (OCH₂), 127.76, 128.05, 134.87, 134.96, 143.10, 144.17 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) –9.2, 7.5.

Thermal Reaction of 1b with *n*-Butyl Alcohol. A mixture of 0.147 g (0.59 mmol) of 1b and 0.225 g (3.04 mmol) of *n*-butyl alcohol was heated in a sealed tube at 250 °C for 24 h. The resulting mixture was analyzed by GLC as being 4b (83% yield). The product 4b (colorless liquid) was isolated by column chromatography: exact mass calcd for $\text{C}_{18}\text{H}_{34}\text{OSi}_2$ [M^+] 322.2149, found 322.2152; MS m/z 332 (M^+); IR 3044, 2956, 2864, 2151, 1462, 1383, 1251, 1096, 882, 830, 788, 738 cm^{-1} ; ^1H NMR δ (CDCl_3) 0.29 (d, 3H, MeSi, $J = 3.7$ Hz), 0.42 (s, 3H, MeSi), 0.93 (t, 3H, CH₃, $J = 7.3$ Hz), 0.95 (d, 3H, MeCH, $J = 7.3$ Hz), 1.00 (d, 3H, MeCH, $J = 7.3$ Hz), 1.02 (d, 3H, MeCH, $J = 7.3$ Hz), 1.05 (d, 3H, MeCH, $J = 7.3$ Hz), 1.13–1.25 (m, 2H, HC), 1.39 (sex, 2H, CH₂, $J = 7.3$ Hz), 1.54–1.61 (m, 2H, CH₂), 3.66 (dt, 1H, OCH, $J = 16.5$ Hz, 7.3 Hz), 3.68 (dt, 1H, OCH, $J = 16.5$ Hz, 7.3 Hz), 4.45 (quint, 1H, HSi, $J = 3.7$ Hz), 7.34–7.37 (m, 2H, phenylene ring protons), 7.55–7.59 (m, 1H, phenylene ring proton), 7.65–7.68

(m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl_3) -6.17 , -4.40 (MeSi), 12.81 , 13.93 , 15.46 , 17.32 (2C), 17.92 , 18.91 , 19.08 (Me_2CH , CH_2CH_3), 34.90 (CH_2), 63.05 (OCH_2), 127.76 , 128.05 , 134.87 , 135.01 , 143.09 , 144.13 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) -9.0 , 7.7 .

Photochemical Reaction of 1a with *tert*-Butyl Alcohol. A solution of 0.312 g (1.26 mmol) of **1a** and 0.9360 g (12.6 mmol) of *tert*-butyl alcohol in 65 mL of hexane was placed in a 70 mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated at ambient temperature for 40 min with a slow stream of argon bubbling through the mixture. After the solvent was evaporated off, the residue was chromatographed on a silica gel column, with hexane as the eluent, to give 0.148 g (0.46 mmol) of a mixture of **2a** and **2b** in a ratio of $1:1.1$ (37% combined yield), 0.040 g (0.15 mmol) of *cis* and *trans* cyclic siloxanes **6a,b** (12% combined yield), and 0.070 g (0.28 mmol) of a mixture of **1a,b** (23%). All spectral data for **2a,b** and **6a,b** are identical with those of the authentic samples.

Photochemical Reaction of 1b with *tert*-Butyl Alcohol. A mixture of 0.312 g (1.25 mmol) of **1b** and 0.948 g (12.8 mmol) of *tert*-butyl alcohol in 65 mL of hexane was irradiated with a low-pressure mercury lamp at ambient temperature for 50 min. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as the eluent, to give 0.160 g (0.50 mmol) of the mixture of **2a,b** in a ratio of $0.9:1$ (40% combined yield), 0.105 g (0.40 mmol) of **6a,b** (32% combined yield), and 0.043 g (0.17 mmol) of the mixture of **1a,b** (14%). All spectral data for **2a,b** and **6a,b** are identical with those of the authentic samples.

Photochemical Reaction of 1a with *tert*-Butyl Alcohol- d_4 . A mixture of 0.316 g (1.27 mmol) of **1a** and 0.958 g (12.8 mmol) of *tert*-butyl alcohol- d_4 in 65 mL of hexane was irradiated with a low-pressure mercury lamp for 50 min at ambient temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as the eluent, to give 0.172 g (0.53 mmol) of the mixture of **5a,b** in a ratio of $1:1$ (42% combined yield), 0.055 g (0.21 mmol) of **6a,b** (16% combined), and 0.038 g (0.15 mmol) of the mixture of **1a,b** (12%). Data for **5a,b**: MS m/z 280 ($\text{M}^+ - i\text{-Pr}$); IR 3043 , 2956 , 2864 , 2160 , 1464 , 1363 , 1250 , 1196 , 1119 , 1059 , 1045 , 881 , 831 , 742 cm^{-1} ; ^1H NMR δ (CDCl_3) 0.25 (d, 3H, MeSi, $J = 3.7$ Hz), 0.28 (d, 3H, MeSi, $J = 3.7$ Hz), 0.46 (br s, 4H, CH_2D), 0.82 (d, 3H, MeCH, $J = 7.3$ Hz), 0.88 (d, 3H, MeCH, $J = 7.3$ Hz), 0.95 (d, 3H, MeCH, $J = 7.3$ Hz), 0.975 (d, 6H, MeCH, $J = 7.3$ Hz), 0.983 (d, 3H, MeCH, $J = 7.3$ Hz), 1.04 (d, 3H, MeCH, $J = 7.3$ Hz), 1.06 (d, 3H, MeCH, $J = 7.3$ Hz), 1.08 – 1.20 (m, 4H, HC), 1.24 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 4.52 (quint, 1H, SiH, $J = 3.7$ Hz), 4.56 (quint, 1H, SiH, $J = 3.7$ Hz), 7.30 – 7.34 (m, 4H, phenyl ring protons), 7.51 – 7.54 (m, 2H, phenyl ring protons), 7.69 – 7.77 (m, 2H, phenyl ring protons); ^{13}C NMR δ (CDCl_3) -6.05 , -5.86 (MeSi), -1.79 (t, CH_2D , $J = 18.1$ Hz), -1.33 (t, CH_2D , $J = 18.1$ Hz), 12.74 , 13.14 , 16.14 (2C), 17.07 , 17.20 , 17.33 (2C), 18.02 , 18.04 , 18.96 , 19.02 (*i*-Pr), 32.12 (Me_3C , 2C), 72.60 , 72.62 (CMe_3), 127.64 , 127.65 , 127.71 , 127.74 , 134.68 , 134.74 , 135.13 , 135.26 , 142.75 , 142.88 , 146.17 , 146.19 (phenyl ring carbons); ^2H NMR δ (CDCl_3) 0.57 .

Photochemical Reaction of 1b with *tert*-Butyl Alcohol- d_4 . A mixture of 0.315 g (1.27 mmol) of **1b** and 0.949 g (12.6 mmol) of *tert*-butyl alcohol- d_4 in 65 mL of hexane was irradiated for 60 min at ambient temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as the eluent, to give 0.154 g (0.48 mmol) of the mixture of **5a,b** in a ratio of $1:1$ (38% combined yield), 0.146 g (0.55 mmol) of **6a,b** (43% combined yield), and 0.057 g (0.23 mmol) of the mixture of **1a,b** (18%). All spectral data for **5a,b** and **6a,b** are identical with those of the authentic samples.

Reaction of 1a,b with *m*-Chloroperoxybenzoic Acid. In a 50 mL two-necked flask fitted with a stirrer and condenser were placed 0.300 g (1.21 mmol) of **1a** and 0.304 g (1.76 mmol) of *m*-chloroperoxybenzoic acid in 25 mL of benzene. The mixture was stirred at room temperature for 4.5 h. At this point, GLC analysis of the mixture showed that **1a** was completely transformed into **6a** (colorless liquid). The solvent was evaporated off, and the residue was chromatographed on a silica gel column, with hexane as the eluent, to

give 0.299 g (94% yield) of **6a**: MS m/z 221 ($\text{M}^+ - i\text{-Pr}$); IR (cm^{-1}) 2942 , 2865 , 1462 , 1252 , 1111 , 997 , 923 , 883 , 795 , 740 ; ^1H NMR δ (CDCl_3) 0.29 (s, 6H, Me), 0.98 – 1.07 (m, 14H, *i*-Pr), 7.38 (dd, 2H, phenylene ring protons, $J = 5.3$ Hz, $J = 3.1$ Hz), 7.57 (dd, 2H, phenylene ring protons, $J = 5.3$ Hz, $J = 3.1$ Hz); ^{13}C NMR δ (CDCl_3) -3.08 (Me), 15.42 (CHMe_2), 16.77 , 16.91 (Me_2C), 128.76 , 131.74 , 147.19 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) 16.1 . Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{OSi}_2$: C, 63.57 ; H, 9.15 . Found: C, 63.18 ; H, 9.15 . Similar treatment of **1b** (0.315 g, 1.268 mmol) and *m*-chloroperoxybenzoic acid (0.304 g, 1.761 mmol) in hexane afforded **6b** (colorless liquid, 0.341 g, 94% yield): MS m/z 264 (M^+); IR (cm^{-1}) 2954 , 2863 , 1463 , 1251 , 1112 , 997 , 925 , 881 , 829 , 792 , 746 , 728 ; ^1H NMR δ (CDCl_3) 0.32 (s, 6H, Me), 0.95 – 1.05 (m, 14H, *i*-Pr), 7.37 (dd, 2H, phenylene ring protons, $J = 5.3$ Hz, $J = 3.1$ Hz), 7.55 (dd, phenylene ring protons, $J = 5.3$ Hz, $J = 3.1$ Hz); ^{13}C NMR δ (CDCl_3) -2.88 (Me), 15.37 (CHMe and MeC), 16.74 (MeC), 128.71 , 131.62 , 146.92 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) 16.6 . Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{OSi}_2$: C, 63.57 ; H, 9.15 . Found: C, 63.50 ; H, 9.03 .

Thermolysis of 1a at 300°C . A 0.1860 g portion (0.748 mmol) of compound **1a** was heated in a degassed sealed tube at 300°C for 24 h. The resulting mixture was analyzed by GLC as being a mixture consisting of **7a** and **8a** (6%) and product **9a** (1%). Unfortunately, compounds **7a** and **8a** could not be isolated, but compound **9a** (colorless liquid) was separated by column chromatography. The ratio of **7a** and **8a** was determined to be $1:1$ by ^1H NMR spectrometric analysis. Data for **7a** and **8a**: MS m/z 334 (M^+); ^1H NMR δ (CDCl_3) 0.10 (s, 3H, MeSi), 0.29 (s, 6H, MeSi), 0.33 (s, 6H, MeSi), 0.35 (s, 3H, MeSi), 0.98 – 1.18 (m, 35H, MeCH, CHSi), 1.21 (d, 6H, MeCH, $J = 7.1$ Hz), 1.36 (sep, 1H, CHSi, $J = 7.1$ Hz), 7.29 – 7.33 (m, 4H, phenylene ring protons), 7.52 – 7.57 (m, 4H, phenylene ring protons); ^{13}C NMR δ (CDCl_3) -12.32 , -10.43 , -6.43 , -4.81 (MeSi), 11.25 , 11.50 , 14.61 , 14.71 (CHSi), 18.48 , 18.99 , 19.03 , 19.18 , 20.67 , 21.19 (MeCH), 127.62 , 127.70 , 133.72 , 134.13 , 149.35 , 150.01 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) -40.3 , -37.7 , -7.0 , -6.5 . Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{Si}_3$: C, 64.59 ; H, 10.24 . Found: C, 64.50 ; H, 10.48 . Data for **9a**: HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{Si}_2$ 324.1722 , found 324.1730 ; MS m/z 324 (M^+); ^1H NMR δ (CDCl_3) 0.51 (s, 3H, MeSi), 0.87 (d, 12H, MeCH, $J = 7.4$ Hz), 1.08 (sep, 2H, CHSi, $J = 7.4$ Hz), 7.39 – 7.41 (m, 4H, phenylene ring protons), 7.63 – 7.65 (m, 4H, phenylene ring protons); ^{13}C NMR δ (CDCl_3) -3.75 (MeSi), 15.81 (CHSi), 17.80 (MeCH), 127.91 , 133.69 , 143.25 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) -14.5 .

Thermolysis of 1b at 300°C . A 0.1352 g portion (0.544 mmol) of compound **1b** was heated in a degassed sealed tube at 300°C for 24 h. The resulting mixture was analyzed by GLC as being product **7b** (1%). Compound **7b** (colorless liquid) was separated by column chromatography: MS m/z 334 (M^+); ^1H NMR δ (CDCl_3) 0.25 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 0.33 (s, 3H, MeSi), 0.98 – 1.20 (m, 3H, CHSi), 0.97 (d, 3H, MeCH, $J = 7.0$ Hz), 1.035 (d, 3H, MeCH, $J = 7.0$ Hz), 1.042 (d, 3H, MeCH, $J = 7.0$ Hz), 1.13 (d, 3H, MeCH, $J = 7.0$ Hz), 1.17 (d, 3H, MeCH, $J = 7.0$ Hz), 1.19 (d, 3H, MeCH, $J = 7.0$ Hz), 7.31 (d, 1H, phenylene ring protons, $J = 3.3$ Hz), 7.33 (d, 1H, phenylene ring protons, $J = 3.3$ Hz), 7.56 (d, 1H, phenylene ring protons, $J = 3.3$ Hz), 7.58 (d, 1H, phenylene ring protons, $J = 3.3$ Hz); ^{13}C NMR δ (CDCl_3) -11.15 , -5.30 , -4.02 (MeSi), 11.18 , 14.73 , 14.93 (CHSi), 18.78 , 19.06 (2C), 19.25 , 21.00 , 21.24 (MeCH), 127.67 , 127.81 , 133.55 , 133.83 , 149.52 , 149.97 (phenylene ring carbons); ^{29}Si NMR δ (CDCl_3) -38.8 , -6.4 , -6.2 . Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{Si}_3$: C, 64.59 ; H, 10.24 . Found: C, 64.19 ; H, 10.49 .

Thermal Reaction of 1a with Ethylene. In a 10 mL autoclave was placed 0.294 g (1.18 mmol) of **1a** in 0.5 mL of dry benzene. To this was introduced ethylene until the pressure reached 50 kg/cm 2 . The contents of the autoclave were heated at 300°C for 24 h. The resulting white crystals were recrystallized from ethanol to give 0.220 g (71% yield) of **10a**: all spectral data for **10a** are identical with those of the authentic sample.¹²¹

Thermal Reaction of 1b with Ethylene. In a 10 mL autoclave was placed 0.515 g (1.07 mmol) of **1b** in 0.5 mL of benzene under a pressure of ethylene at 50 kg/cm 2 . The contents of the autoclave were heated at 300°C for 24 h. The resulting white solids were

reprecipitated from benzene–methanol to give 0.430 g (75% yield) of the polymer **8b**, including an ethylene and disilacyclobutene unit in a ratio of 1:1: mp 104–105 °C; M_w 61000 ($M_w/M_n = 2.32$); ^1H NMR ($\delta(\text{CDCl}_3)$) 0.20 (br s, 6H, MeSi), 0.59 (br s, 4H, CH_2Si), 0.78 (br s, 12H, MeCH), 1.08 (br s, 2H, CHMe), 7.14 (br s, 2H, phenylene ring protons), 7.42 (br s, 2H, phenylene ring protons); ^{13}C NMR ($\delta(\text{CDCl}_3)$) –4.9, –4.8 (MeSi), 6.7 (CH_2Si), 13.8 (CHMe), 17.9, 18.2 (MeCH), 127.1, 136.3, 143.8 (phenylene ring carbons); ^{29}Si NMR ($\delta(\text{CDCl}_3)$) 3.6, 3.7, 3.8, 3.9.

Thermal Reaction of 1a with 1-Hexyne. A mixture of 0.153 g (0.62 mmol) of **1a** and 0.206 g (2.51 mmol) of 1-hexyne was heated in a degassed sealed tube at 200 °C for 24 h. The resulting mixture was chromatographed on a silica gel column with hexane as eluent, to give 0.088 g (76% yield) of **11a**. No other isomers were detected by GLC and spectrometric analyses. All spectral data for **11a** were identical with those of the authentic sample.

Thermal Reaction of 1b with 1-Hexyne. A mixture of 0.154 g (0.62 mmol) of **1b** and 0.216 g (2.63 mmol) of 1-hexyne was heated in a sealed tube at 200 °C for 24 h. The mixture was chromatographed on a silica gel column with hexane as eluent, to give 0.136 g (67% yield) of **11b**. All spectral data for **11b** were identical with those of the authentic sample.

Thermal Reaction of 1a with *tert*-Butylacetylene. A mixture of 0.154 g (0.62 mmol) of **1a** and 0.233 g (2.84 mmol) of *tert*-butylacetylene was heated in a degassed sealed tube at 200 °C for 24 h. The resulting mixture was chromatographed on a silica gel column with hexane as eluent to give 0.186 g (91% yield) of **12a**. No other stereoisomers were detected in the reaction mixture. All spectral data for **12a** are identical with those of the authentic sample.^{12h}

Thermal Reaction of 1b with *tert*-Butylacetylene. Treatment of a mixture consisting of 0.148 g (0.60 mmol) of **1b** and 0.165 g (2.01 mmol) of *tert*-butylacetylene at 200 °C for 24 h gave 0.178 g (90% yield) of **12b**. All spectral data for **12b** were identical with those of the authentic sample.^{12h}

Thermal Reaction of 1a with Phenylacetylene. A mixture of 0.176 g (0.71 mmol) of **1a** and 0.287 g (2.81 mmol) of phenylacetylene was heated in a degassed tube at 150 °C for 24 h. The resulting mixture was chromatographed on a silica gel column with hexane as eluent, to give 0.190 g (77% yield) of **13a**. No other isomers were detected in the mixture. All spectral data for **13a** are identical with those of the authentic sample.^{12h}

Thermal Reaction of 1b with Phenylacetylene. Treatment of a mixture consisting of 0.190 g (0.77 mmol) of **1b** and 0.199 g (2.01 mmol) of phenylacetylene at 150 °C for 24 h gave 0.205 g (77% yield) of **13b**. All spectral data for **13b** are identical with those of the authentic sample.^{12h}

Thermal Reaction of 1a with (Trimethylsilyl)acetylene. A mixture of 0.183 g (0.74 mmol) of **1a** and 0.235 g (2.39 mmol) of (trimethylsilyl)acetylene was heated at 200 °C for 24 h. The resulting mixture was chromatographed on a silica gel column with hexane as eluent to give 0.190 g (77% yield) of **14a**. No other isomers were detected in the mixture. All spectral data for **14a** are identical with those of the authentic sample.^{12h}

Thermal Reaction of 1b with (Trimethylsilyl)acetylene. Treatment of a mixture consisting of 0.144 g (0.56 mmol) of **1b** and 0.273 g (2.78 mmol) of (trimethylsilyl)acetylene at 200 °C for 24 h gave 0.111 g (55% yield) of **14b**. All spectral data for **14b** are identical with those of the authentic sample.^{12h}

Theoretical Calculations. The structures of the reactants, products, and transition states (TSs) for both reactions were optimized by the density functional $\omega\text{B97X-D}$ method¹⁸ combined with the 6-311G(d,p) basis set.¹⁹ Vibrational mode analyses were carried out to confirm that the TS has an only one imaginary frequency mode and an equilibrium structure has no imaginary frequency mode. The relative energies were corrected with zero-point vibrational energies. All calculations were carried out with the Gaussian 09 program.²¹

■ ASSOCIATED CONTENT

■ Supporting Information

Tables giving Cartesian coordinates for all compounds derived from theoretical treatment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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■ ACKNOWLEDGMENTS

We thank Sumitomo Chemical Co., Ltd. and Hokko Chemical Industry Co., Ltd. for financial support. L.A. is indebted to the JSPS for the fellowship provided. Numerical calculations were carried out on the TSUBAME2.0 supercomputer at the Tokyo Institute of Technology, Tokyo, Japan, and on the supercomputer at the Research Center for Computational Science, Okazaki, Japan.

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