Articles

Silicon−Carbon Unsaturated Compounds. 75. Thermal Isomerization of 2-Alkyl- and 2-Aryl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclohex-4-enes

Akinobu Naka,*,[†] Shinsuke Ueda,[†] Joji Ohshita,[‡] Atsutaka Kunai,[‡] Toshiko Miura,[#] Hisayoshi Kobayashi,*,[#] and Mitsuo Ishikawa*,[†]

Department of Life Science, Kurashiki University of Science and the Arts, Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan, Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan, and Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

Received March 9, 2008

The thermolysis of 2-*tert*-butyl-, 2-adamantyl-, and 2-phenyl-4,5-dimethyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**1**−**3**), synthesized by the reactions of acylpolysilanes with 2,3-dimethylbutadiene, in a sealed glass tube at 250 °C for 24 h gave the products, arising from dyotropic rearrangement, *cis*-2-*tert*-butyl-, *cis*-2-adamantyl-, and *cis*-2-phenyl-4,5-dimethyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene (**5**−**7**), respectively, in high yields. The theoretical calculations using of 2-methyl-2-siloxy-1,1-bis(silyl)-1-silacyclohex-4-ene as a starting compound and *cis*-2-methyl-1-siloxy-1,2-bis(silyl)-1-silacyclohex-4-ene as a product indicated that a pentacoordinate silicon species plays an important role for the present dyotropic rearrangement. The thermolysis of the 4,5-diphenyl-1-silacyclohex-4-ene derivative **8**, prepared by the reaction of pivaloyltris(trimethylsilyl)silane with 2,3-diphenylbutadiene, also afforded *cis*-2-*tert*-butyl-4,5-diphenyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene (**9**), whose structure was confirmed by X-ray crystallographic analysis. The thermolysis of 4,5-dimethyl-2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**4**) at 250 °C for 24 h, however, produced a ring-contracted compound, 3,4-dimethyl-1-mesityl-1-[trimethylsiloxybis(trimethylsilyl)silyl]cyclopent-3-ene (**10**).

Introduction

It is well-known that acylpolysilanes are useful precursors for the synthesis of a wide variety of silenes, including rather stable silenes.[1] The reactions of the silenes produced by photolysis,[1] thermolysis,[2,3] and Peterson-type reaction[4] with various substrates have been extensively investigated, and many papers concerning these studies have been reported to date. Recently, considerable attention has been focused on the synthesis and reactions of 1-silacyclobutenes and 1-silacyclohexenes, arising from the reaction of the silenes with alkynes[5] and butadienes,[6] and some of their reactions have been used as a novel route to the synthesis of organic compounds.

---

* Corresponding authors. E-mail: ishikawa-m@kcat.zaq.ne.jp (M.I.); kobayashi@chem.kit.ac.jp (H.K.).

[†] Kurashiki University of Science and the Arts.

[‡] Hiroshima University.

[#] Kyoto Institute of Technology.

(1) (a) Brook, A. G. *J. Organomet. Chem.* **1986**, *300*, 21. (b) Brook, A. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 15. (c) Brook, A. G.; Brook, M. A. *Organomet.Chem.* **1996**, *39*, 71. (d) Brook, A. G. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Chapter 21.

(2) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, R.; Kallury, M. R.; Poon, Y. C.; Chan, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

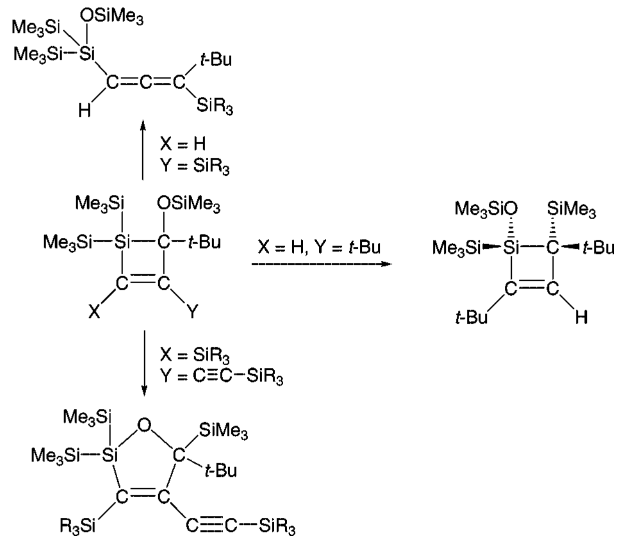
(3) (a) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Organometallics* **1996**, *15*, 3836. (b) Naka, A.; Ishikawa, M.; Matsui, S.; Ohshita, J.; Kunai, A. *Organometallics* **1996**, *15*, 5759. (c) Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **2000**, *611*, 248. (d) Naka, A.; Ikadai; Motoike, S.; Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Ishikawa, M. *Organometallics* **2002**, *21*, 2033. (e) Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Naka, A.; Ishikawa, M. *Organometallics* **2002**, *21*, 3271.

(4) (a) Brook, A. G.; Chiu, P.; McClenaghnan, J.; Lough, A. J. *Organometallics* **1991**, *10*, 3292. (b) Ohshita, J.; Masaoka, Y.; Ishikawa, M. *Organometallics* **1991**, *10*, 3775; **1993**, *12*, 876. (c) Bravo-Zhivotovskii, D.; Brande, V.; Stanger, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326. (d) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228. (e) Krempner, C.; Oehme, H. *J. Organomet. Chem.* **1994**, *464*, C7. (f) Krempner, C.; Renke, H.; Oehme, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1615.

(5) (a) Naka, A.; Ikadai, J.; Motoike, S.; Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Ishikawa, M. *Organometallics* **2002**, *21*, 2033. (b) Shiota, Y.; Yasunaga, M.; Naka, A.; Ishikawa, M.; Yoshizawa, K. *Organometallics* **2004**, *23*, 4744. (c) Milnes, K. K.; Jennings, M. C.; Baines, K. M. *J. Am. Chem. Soc.* **2006**, *128*, 2491. (d) Auner, N.; Mohseni-Ala, J. *Inorg. Chim. Acta* **2006**, *359*, 4677. (e) Tong, H.; Eklof, A. M.; Steel, P. G.; Ottosson, H. *J. Mol. Struct. (THEOCHEM)* **2007**, *811*, 153.

(6) (a) Ottosson, H.; Steel, P. G. *Chem.*−*Eur. J.* **2006**, *12*, 1576. (b) Berry, M. B.; Griffiths, R. J.; Sanganee, M. J.; Steel, P. G.; Whelligan, D. K. *Org. Biomol. Chem* **2004**, *2*, 2381. (c) Sanganee, M. J.; Steel, P. G.; Whelligan, D. K. *Org. Biomol. Chem* **2004**, *2*, 2393. (d) Sellars, J. D.; Steel, P. G. *Org. Biomol. Chem* **2006**, *4*, 3223. (e) Hughes, N. J.; Pullin, R. D. C.; Sanganee, M. J.; Sellars, J. D.; Steel, P. G.; Turner, M. J. *Org. Biomol. Chem.* **2007**, *5*, 2841. (f) Pullin, R. D. C.; Sellars, J. D.; Steel, P. G. *Org. Biomol. Chem* **2007**, *5*, 3201.

10.1021/om800219n CCC: $40.75



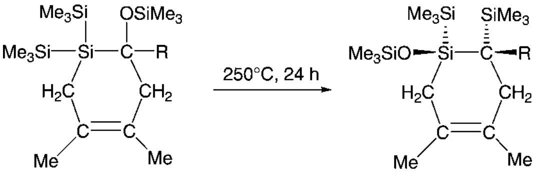
We have found that the silenes generated thermally from the acylpolysilanes readily react with alkynes to give the 1-silacyclobut-3-ene derivatives.[3c,d,7] The thermal properties of the 1-silacyclobut-3-enes thus formed depend highly on the substituents on the sp^2-hybridized carbon atoms in the silacyclobutenyl ring. For example, the thermolysis of 2-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene prepared by the reaction of pivaloyltris(trimethylsilyl)silane with *tert*-butylacetylene proceeds cleanly to give *trans*-2,4-di(*tert*-butyl)-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene in quantitative yields.[3d] No *cis*-isomer was detected in the reaction product by spectrometric analysis. On the other hand, the thermolysis of 2-adamantyl- and 2-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-3-(trimethylsilyl)ethynyl-1-silacyclobut-3-ene formed by the reaction of adamantoyl- and pivaloyltris(trimethylsilyl)silane with bis(trimethylsilyl)-butadiynes proceeds to give 5-adamantyl- and 5-*tert*-butyl-2,5-dihydro-2,2,3,5-tetrakis(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]-1,2-oxasilole in high yields.[7b] Again, no other isomers were detected in the reaction mixtures. Similar thermolysis of 2-*tert*-butyl-2-(trimethylsiloxy)-3-(silyl)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-enes, however, gives the ring-opened products 3-*tert*-butyl-3-(silyl)-1-[trimethylsiloxybis(trimethylsilyl)silyl]-propadienes.

It is of interest to us to investigate the thermal behavior of the silacycloalkenes other than the silacyclobutene system. In this paper we report the thermal isomerization of 2-alkyl- and 2-aryl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-enes, obtained by the reaction of acylpolysilanes with 1,3-butadienes.

Results and Discussion

The starting compounds, 2-*tert*-butyl-, 2-adamantyl-, 2-phenyl-, and 2-mesityl-4,5-dimethyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**1**−**4**), used in the present thermolysis were prepared according to the method reported previously.[8]

Scheme 1



1. R = *t*-Bu
2. R = Ad
3. R = Ph

5. R = *t*-Bu
6. R = Ad
7. R = Ph

When compound **1** was heated in a degassed sealed tube at 250 °C for 24 h, a clean reaction took place to give *cis*-2-*tert*-butyl-3,4-dimethyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene (**5**) in 94% yield (Scheme 1). No *trans*-isomer was detected in the reaction mixture by spectrometric analysis. Since the present isomerization involves migration of two σ-bonds, a Me_3Si-Si bond and a Me_3SiO-C bond, it can be regarded as a sort of dyotropic rearrangement.[9]

The structure of **5** was confirmed by spectrometric and elemental analysis (see Experimental Section). The $^1H-^{29}Si$ COSY NMR spectrum for **5** reveals that the trimethylsiloxy protons at 0.06 ppm couple with the silicon atom at 6.1 ppm, while the trimethylsilyl protons at 0.07 ppm couple with the silicon atom at 0.1 ppm. Similarly, the trimethylsilyl protons at 0.15 ppm couple with the signals at −21.0 and 1.8 ppm. The location of the substituents on the silacyclohexenyl ring for **5** was confirmed by NOE-FID difference experiments at 500 MHz. Thus, irradiation of the *tert*-butyl protons on the sp^3-hybridized carbon atom in the six-membered ring at 1.11 ppm resulted in a strong enhancement of the signals at 0.06 and 0.07 ppm, due to the trimethylsiloxy protons on the ring silicon and the trimethylsilyl protons on the ring carbon attached to the irradiating *tert*-butyl group, as well as the ring methylene protons at 2.10 and 2.60 ppm. Furthermore, saturation of the trimethylsilyl protons on the ring silicon atom at 0.15 ppm led to enhancement of the signals at 0.06 and 0.07 ppm, attributed to the trimethylsiloxy protons and trimethylsilyl protons, respectively, as well as the ring methylene protons at 1.38 ppm. These results clearly indicate that the two trimethylsilyl groups, one on the ring silicon and the other on the ring carbon, are located in a *cis* fashion.

The thermolysis of 2-adamantyl-1-silacyclohex-4-ene (**2**) under the same conditions proceeded stereospecifically to give the rearranged product *cis*-2-adamantyl-4,5-dimethyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene (**6**) in 96% yield. No other volatile products were detected in the reaction mixture. The structure of **6** was confirmed by spectrometric analysis, as well as by elemental analysis (see Experimental Section). Again, the *cis* configuration for **6** was verified by NOE-FID difference experiments at 500 MHz.

Similarly, the thermolysis of 4,5-dimethyl-2-phenyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**3**) at 250 °C for 24 h proceeded with high stereospecificity to give *cis*-4,5-dimethyl-2-phenyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene (**7**) in 90% yield. Again, no other isomers were detected in the reaction mixture. Compound **3** possesses an aryl group on the carbon atom at the 2-position in

---

(7) (a) Naka, A.; Ohnishi, H.; Miyahara, I.; Hirotsu, K.; Shiota, Y.; Yoshizawa, K.; Ishikawa, M. *Organometallics* **2000**, *23*, 4277. (b) Naka, A.; Ohnishi, H.; Miyahara, I.; Hirotsu, K.; Shiota, Y.; Yoshizawa, K.; Ishikawa, M. *Organometallics* **2004**, *23*, 4277. (c) Naka, A.; Ohnishi, H.; Ohshita, J.; Ikadai, J.; Kunai, A.; Ishikawa, M. *Organometallics* **2005**, *24*, 5356.

(8) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Main Group Chem.* **1996**, *1*, 219.

(9) (a) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129. (b) Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189; *Adv.Organomet. Chem.* **1977**, *16*, 33. (c) Fassler, J.; Bienz, S. *Organometallics* **1994**, *13*, 4704. (d) Kira, M.; Iwamoto, T. In *The Chemistry of Organic Silicon Compounds*, Vol. 3; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 2001; Chapter 16. (e) El-Sayed, I.; Guliashvili, T.; Hazell, R.; Gogoll, A.; Ottosson, H. *Org. Lett.* **2002**, *4*, 1915. (f) Cho, S. G. *J. Organomet. Chem.* **1996**, *510*, 25. (g) Yu, Y. M.; Feng, S. Y. *J. Phys. Chem.* **2006**, *110*, 12463.

the 1-silacyclohexenyl ring, but not an alkyl group such as compounds **1** and **2**. As reported previously, the thermal behavior of the 1-silacyclobut-3-ene derivatives depends highly on the substituents on the ring carbon atoms.[7] Therefore, one might consider that the thermal behavior of **3** with a phenyl group on the silacyclohexenyl ring differs from that of **1** and **2**, and the structure of the isomerization product **7** is also different from that of **5** and **6**.

To confirm this, we carried out the NOE-FID difference experiments at 500 MHz for **7**. Thus, irradiation of the trimethylsiloxy protons on the ring silicon atom at −0.02 ppm led to enhancement of the signals at 0.17 and 7.11 ppm, attributable to the trimethylsilyl protons and the phenyl protons, as well as a signal at 0.94 ppm, due to the ring methylene protons. Similar irradiation of the signal at 0.04 ppm, attributed to the trimethylsilyl protons on the sp^3-hybridized ring carbon atom, showed enhancement of the signals at 0.17, 2.57, and 7.11 ppm, due to the trimethylsilyl protons, methylene protons, and phenyl protons, respectively. Saturation of the signal at 0.17 ppm due to the trimethylsilyl protons on the ring silicon atom resulted in enhancement of the signals at −0.02 and 0.04 ppm, attributed to the trimethylsiloxy protons and trimethylsilyl protons, as well as the methylene protons at 0.94 ppm. Furthermore, irradiation of the phenyl protons at 7.11 ppm showed enhancement of the signals at −0.02, 0.04, 2.57, and 7.20 ppm, attributable to the trimethylsiloxy protons, trimethylsilyl protons, methylene protons, and phenyl protons, respectively. These results clearly indicate that compound **7** must have the structure with *cis* configuration, analogous to that of **5** and **6**.

Ottosson and co-workers[9c] have reported that the co-thermolysis of tris(trimethylsilyl)silylamides with 2,3-dimethyl-1,3-butadiene affords *cis*-2-(amino)-4,5-dimethyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-enes, as the sole product. For the formation of these products, they have proposed two reaction pathways leading to the products, one involves [2 + 4] cycloaddition of the silenes, which were produced by exchange of the Me$_3$SiO and Me$_3$Si group in the silenes, generated initially from tris(trimethylsilyl)silylamides, with butadiene, and the other implies [2 + 4] cycloaddition of the initially formed silenes with butadiene, followed by exchange of the Me$_3$SiO and Me$_3$Si group in the resulting [2 + 4] cycloadducts. On the basis of our results (see below), the latter pathway involving exchange of the Me$_3$SiO and Me$_3$Si groups in the cycloadducts seems to be attractive for the isomerization.

In order to get more information about the present dyotropic rearrangement, we investigated the thermolysis of compounds bearing an aryl group on the sp^2-hybridized carbon atoms in the six-membered ring, 2-*tert*-butyl-4,5-diphenyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**8**). When compound **8** was heated in a sealed glass tube at 250 °C for 24 h, *cis*-2-*tert*-butyl-4,5-diphenyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene (**9**) was obtained in 66% yield, as shown in Scheme 2. Again, no *trans*-isomer was detected in the reaction mixture. The fact that **9** has a *cis* configuration was verified by X-ray crystallographic analysis. An ORTEP representation of the molecular structure for **9** is shown in Figure 1.

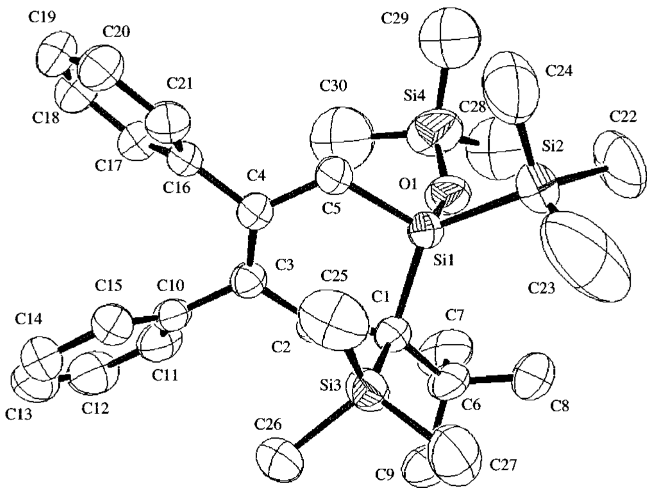
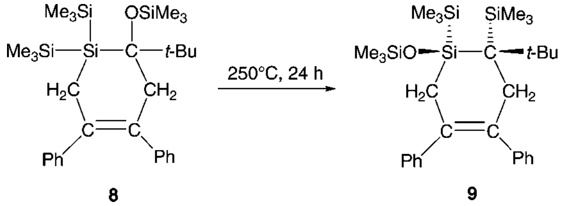
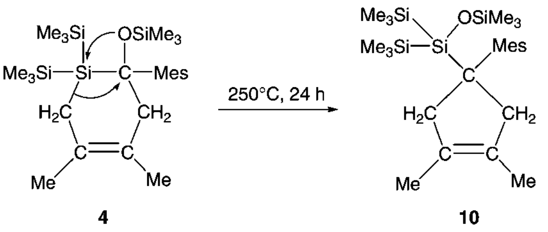


Figure 1. ORTEP diagram for compound **9** showing thermal ellipsoids at the 50% level; hydrogen atoms are omitted for clarity.

Scheme 2



Scheme 3



We thought that if the reactive intermediates were produced during isomerization, they might be quenched by the use of a trapping agent, and we carried out the co-thermolysis of **1**−**3** with methanol. Thus, when compounds **1**−**3** were heated in the presence of methanol as the trapping agent, in a sealed glass tube at 250 °C for 24 h, again, compounds **5**−**7** were obtained in high yields. No other products were detected in the reaction mixture by GLC analysis and also by spectrometric analysis. Furthermore, the thermolysis of **8** in the presence of 2,3-dimethylbutadiene produced **9** as the sole product, indicating that no retro-Diels−Alder reaction took place during the isomerization.

On the basis of the theoretical calculations shown below, the dyotropic rearrangement in the present 1-silacyclohexene derivatives seems to occur via the transition state involving a pentacoordinate silicon atom. For the theoretical study on the dyotropic rearrangements, the results of ab initio calculations for the isomerization reactions of α-silylcarbenium ions[9f] and aminomethylsilane[9g] have been reported to date.

In marked contrast to the thermolysis of **1**−**3**, in which a trimethylsilyl group on the ring silicon and a trimethylsiloxy group on the carbon atom at the 2-position in the 1-silacyclohexenyl ring mutually interchange their positions, the reaction of mesitoyltris(trimethylsilyl)silane with 2,3-dimethylbutadiene proceeded with ring contraction to give a silyl-substituted cyclopentene derivative. Thus, the thermolysis of 2-mesityl-3,4-dimethyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**4**) in a sealed glass tube at 250 °C for 24 h gave 1-mesityl-1-(trimethylsiloxy)bis(trimethylsilyl)silylcyclopent-3-ene (**10**) in 53% yield (Scheme 3). GLC analysis of the reaction mixture indicated that small amounts of the unidentified products were detected. However, no six-membered-ring compound, such as *cis*-2-mesityl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene, was found in the reaction mixture.

The product **10** was readily isolated by column chromatography. The ^{1}H NMR spectrum of **10** shows two signals at −0.03 and 0.12 ppm due to the two trimethylsilyl protons and trimethylsiloxy protons, three signals at 1.59, 2.19, and 2.32 ppm attributed to methyl protons, and two signals at 2.77 and 3.20 ppm, due to the ring methylene protons, as well as mesityl ring protons at 6.72 ppm. The ^{13}C NMR spectrum of **10** reveals two resonances at 0.43 and 2.64 ppm, attributed to the trimethylsilyl carbons, three resonances at 13.63, 20.17, and 26.07 ppm, due to the methyl carbons, and a single resonance at 44.26 ppm attributable to the quarternary sp^{3}-ring carbon, respectively, as well as the resonances due to the methylene carbons, mesityl ring carbons, and olefinic carbons. The ^{29}Si NMR spectrum shows three resonances at −18.6, 6.3, and 11.9 ppm, as expected. These results are wholly consistent with the structure proposed for **10**.

Since the thermal properties of compound **4** are very different from those of **1**−**3**, we thought that **4** might undergo retro [2 + 4] cycloaddition to give the silene and butadiene, and the silene thus formed isomerizes to give mesityl[siloxybis(silyl)silyl]carbene. Addition of the resulting carbene to the butadiene affords compound **10**. To confirm this hypothesis, we investigated the thermolysis of **4** in the presence of isoprene. However, when **4** was heated with isoprene under the same conditions, neither adduct, derived from addition of 2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene to isoprene, nor product arising from addition of the mesityl[trimethylsiloxybis(trimethylsilyl)silyl]carbene to isoprene was obtained. The results clearly indicate that isomerization of **4** leading to the silylcyclopentene **10** involves a 1,2-trimethylsiloxy shift from the mesityl-substituted carbon to the adjacent silicon in the 1-silacyclohexenyl ring and simultaneous migration of the silicon-bound methylene carbon to the mesityl-substituted carbon, but not addition of carbene species to 2,3-dimethylbutadiene. The transformation of **4** to **10** may also be understood in terms of the pentacoordinate silicon species.

Theoretical Calculations. In the thermal isomerization of **1**−**3** and **8**, we thought that a pentacoordinate silicon species plays an important role for the formation of **5**−**7** and **9**. To confirm this idea, we carried out theoretical calculations along the reaction represented by Scheme 1. The substituents on the silacyclohexenyl ring in compounds **1**−**3** and **5**−**7** are rather too large to perform the calculations; all the methyl groups are replaced by hydrogen atoms, and the alkyl and phenyl group designated by R in Scheme 1 are replaced by a methyl group (simplified models). The transition state (TS) is searched first. Then the intrinsic reaction coordinate (IRC) analysis is carried out at the TS for both directions, i.e., reactant and product sides. Since the IRC analysis for the whole reaction path is very time-consuming, it is limited in the neighborhood of TS, and full optimizations are carried out at the end points of IRC analysis. Finally, we confirmed that the full optimizations lead to two local minima (LMs), corresponding to the reactant and product.

The Becke three-parameter Lee−Yang−Parr hybrid-type density functional method is used in this work.[10,11] This method is implemented in the Gaussian 03 program.[12] Parametrization is the one suggested by Pople et al.,[11] i.e., 0.2, 0.8, and 0.72 for the HF, Slater,[13] and Becke[14] exchange functionals and 0.19 and 0.81 for the Vosko−Wilk−Nusair[15] and Lee−Yang−Parr[16] correlation functionals. The Los Alamos effective core potentials are used for the Si atoms along with the corresponding valence basis sets,[17] and only the 3s and 3p electrons are treated explicitly. For the H, C, and O atoms, the Dunning−Huzinaga full double-ζ basis set is employed.[18]

Figure 2 shows the optimized structures with some important internal coordinates for the reactant (LM-1), TS (TS-1), and product (LM-2) in the reactions shown in Scheme 1. For the TS, the numbers in parentheses represent contributions to the reaction coordinate from individual internal coordinates. At TS-1, the Si atom in the six-membered ring is a pentacoordinate structure. For a structural change to the product (LM-2), an OSiH$_3$ group migrates from the C atom at the 2-position in the 1-silacyclohexenyl ring to the adjacent Si atom. Shortening of the Si−OSiH$_3$ bond and stretching of the C−-OSiH$_3$ bond are represented by negative −0.22 and positive 0.56 numbers, respectively. (The positive and negative numbers in parentheses represent increase and decrease of the internal coordinates. This set of numbers corresponds to the effective structural change toward the product, while the set of numbers with opposite signs indicates the direction to the reactant.) Furthermore, a positive number 0.25 for the C−Si−O angle shows an increase of the bond angle, which is an effective deformation to the product. At the same time, one of the two SiH$_3$ groups migrates from the ring Si atom to the adjacent ring C atom. This structural change is also consistent with stretching of the Si−SiH$_3$ bond by 0.24 and with shortening of the C−SiH$_3$ bond by −0.21. Taking the energy of LM-1 as the reference, TS-1 is higher than LM-1 by 181 kJ/mol, and LM-2 is lower by 136 kJ/mol. The IRC analyses and successive full optimizations indicated that LM-1 and LM-2 are smoothly connected through TS-1 involving a pentacoordinate silicon atom.

Next, we examined the reaction profile shown in Scheme 3. The structure of the reactant is the same as the simplified model used in Scheme 1. A new TS labeled as TS-2 and silylcyclopentene (LM-3) are shown in Figure 3. At TS-2, migration of an OSiH$_3$ group from the C atom to the adjacent Si atom in the ring is indicated by a stretching of the C−O bond (0.48) and a shortening of the Si−O bond (−0.17), which is similar to the migration mentioned for the reaction in Scheme 1. Another bond

---

[10] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372; **1993**, *98*, 5648.

[11] Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 319.

[12] Frisch, M. J.; Schlegel, G. E.; Scuseria, M. A.; Robb, J. R. ; Cheeseman, J. A. ; Montgomery, T., Jr.; Vreven, K. N.; Kudin, J. C.; Burant, J. M.; Millam, S. S. ; Iyengar, J. ; Tomasi, V. ; Barone, B. ; Mennucci, M.; Cossi, G.; Scalmani, N.;. Rega, G. A.; Petersson, H. ; Nakatsuji, M. ; Hada, M. ; Ehara, K.; Toyota, R. ; Fukuda, J. ; Hasegawa, M. ; Ishida, T. ; Nakajima, Y. ; Honda, O. ; Kitao, H. ; Nakai, M.;. Klene, X.; Li, J. E. ; Knox, H. P. ; Hratchian, J. B. ; Cross, C. ; Adamo, J. ; Jaramillo, R. ; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, J. W.; Ochterski, P. Y.; Ayala, K.;. Morokuma, G. A.; Voth, P.; Salvador, J. J.; Dannenberg, V. G.; Zakrzewski, S.; Dapprich, A. D.; Daniels, M. C.; Strain, O.; Farkas, D. K.; Malick, A. D.; Rabuck, K.; Raghavachari, J. B.; Foresman, J. V.; Ortiz, Q.; Cui, A. G.; Baboul, S.; Clifford, J.; Cioslowski, B. B.; Stefanov, G.; Liu, A.; Liashenko, P.; Piskorz, I.; Komaromi, R. L.; Martin, D. J.;. Fox, T.; Keith, M. A.;. Al-Laham, C. Y.; Peng, A.; Nanayakkara, M.; Challacombe, P. M. W.; Gill, B.; Johnson, W.; Chen, M. W.; Wong, C.; Gonzalez, J. A.; Pople, C. J. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.

[13] Slater, J. C. *Phys. Rev.* **1951**, *81*, 385.

[14] Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

[15] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200 LWilk, L.; Vosko, S. H. *J. Phys. C: Solid State Phys.* **1982**, *15*, 2139.

[16] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

[17] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

[18] Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976; p 1.

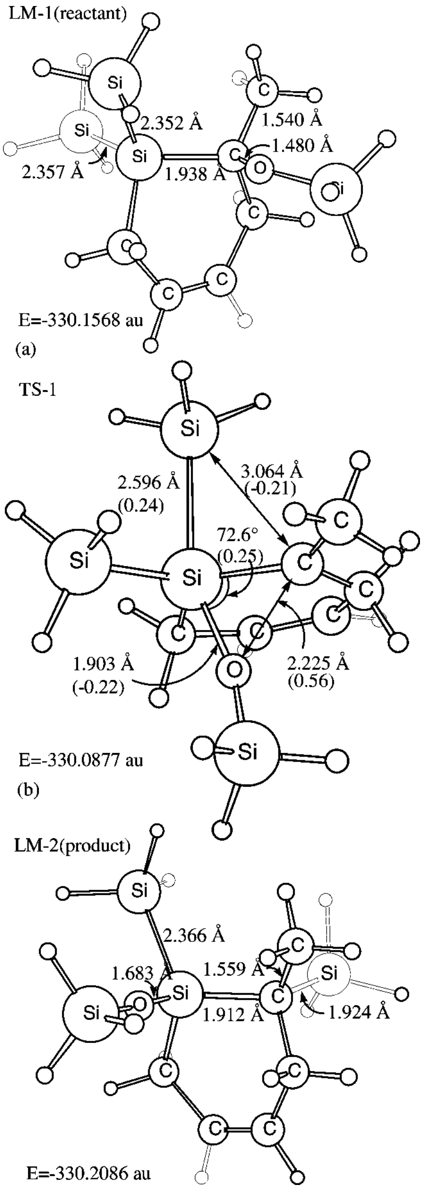


Figure 2. Optimized structures of reactant (LM-1) (a), TS (TS-1) (b), and product (LM-2) (c) for the reaction shown in Scheme 1. Some typical bond lengths are specified. The numbers in parentheses are coefficients of the leading internal coordinates describing the structural change along the reaction coordinate at the TS. The signs of the numbers correspond to the direction from reactant to product.

exchange involves scission of the Si−C bond (0.24) and the formation of the C−C bond (−0.29). These four coefficients clearly indicate the structural change from the reactant (LM-1) to the silylcyclopentene (LM-3). The energy of TS-2 is higher than that of LM-1 by 206 kJ/mol and is higher than that of TS-1 only by 25 kJ/mol. LM-3 is more stable than LM-1 by 108 kJ/mol, but more unstable than LM-2 by 28 kJ/mol.

To examine the influence of simplification in modeling, the structures of reactant (LM-1) and two TSs (TS-1 and TS-2) are optimized again with the models bearing a bulky group, where a methyl group is restored to a *tert*-butyl group and a mesityl group. The energy profiles for the two reactions, which start from LM-1, leading to LM-2 and LM-3, are shown in Figure 4. The energy of TS-2 is higher than that of TS-1 with the simplified models by 25 kJ/mol. Although the activation energies for TSs (measured from LM-1) are reduced by 14−16 kJ/mol with the *tert*-butyl-substituted models and by 52−54 kJ/mol with the mesityl-substituted models, compared to the simplified models, the energy differences between TS-1 and TS-2 are slightly reduced to 23 kJ/mol (only 2 kJ/mol) in both substituents. As a result, the present calculations indicate that the reaction shown in Scheme 1 is more favorable than that involving the ring contraction shown in Scheme 3, regardless of the substituents. Unfortunately, at present, we could not elucidate the differences observed experimentally between the reaction of **1**−**3** and **4**.

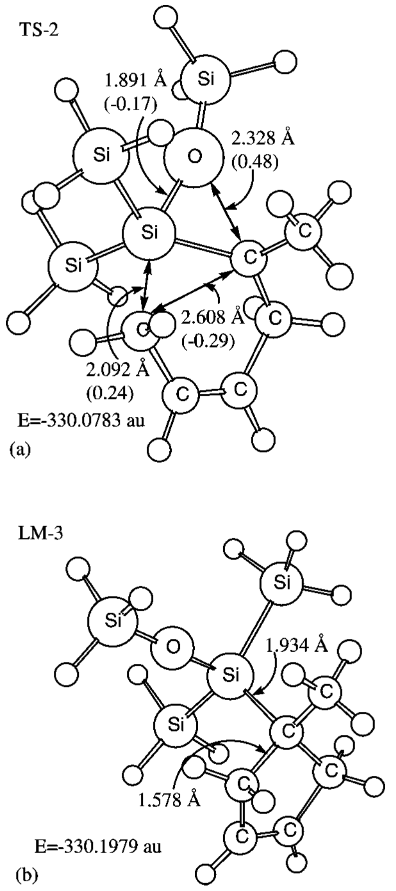


Figure 3. Optimized structures of TS (TS-2) (a) and product (LM-3) (b) for the reaction shown in Scheme 3. For the numbers cited in the figure, see the caption of Figure 2.

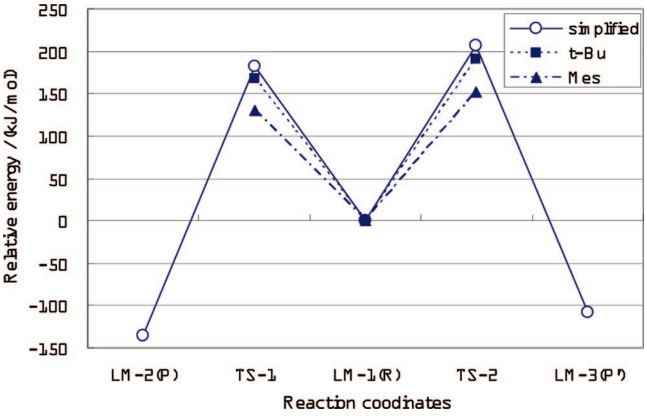


Figure 4. Energy profiles for the two reactions shown in Schemes 1 and 3. The energy of LM-1, which is the third plot, is taken as the reference. The relative energies for TS-1 and TS-2 are compared among the simplified models and models with *tert*-butyl and mesityl groups.

In conclusion, the thermolysis of 2-*tert*-butyl-, 2-adamantyl-, and 2-phenyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-enes in a sealed glass tube at 250 °C for 24 h proceeded to give the respective *cis*-isomers, arising from exchange of the Me_3SiO and Me_3Si group in the starting 1-silacyclohex-4-enes, as the sole product. Similar thermolysis of 2-*tert*-butyl-4,5-diphenyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene at 250 °C for 24 h also produced the *cis*-isomer derived from exchange of the Me_3SiO and Me_3Si groups. The thermolysis of 2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**4**) under the same conditions, however, proceeded with contraction of the 1-silacyclohexenyl ring, to give the silylcyclopentene **10**. Theoretical calculations showed that the pentacoordinate silicon species plays an important role in the exchange of the Me_3SiO and Me_3Si groups on the silacyclohexenyl ring. Although subtle influences by individual substituents could not be explained, the reaction profiles are elucidated clearly. For the formation of **10**, the theoretical calculations suggested that this compound may also be produced via the transition state involving a pentacoordinate silicon atom.

Experimental Section

General Procedure. All reactions of silacyclohexenes were carried out in a degassed sealed glass tube (1.0 cm × 15 cm). Yields of the products **5**−**7**, **9**, and **10** were calculated on the basis of the isolated products. NMR spectra were recorded on JNM-LA300 and JNM-LA500 spectrometers. Infrared spectra were recorded on a JEOL model JIR-DIAMOND 20 infrared spectrophotometer. Low-resolution mass spectra were measured on a JEOL model JMS-700 instrument. Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO).

Materials. Silacyclohexenes **1**−**4**[2a,8,19] were prepared according to the method reported previously.

Thermolysis of 1. Compound **1** (0.0564 g, 0.136 mmol) was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by GLC as being **5**. The product **5** (0.0530 g, 94% isolated yield) was isolated by column chromatography. Anal. Calcd for $C_{20}H_{46}OSi_4$: C, 57.89; H, 11.17. Found: C, 57.77; H, 11.30. MS *m/z* 399 ($M^+ - Me$). IR 2952, 2898, 1440, 1392, 1363, 1251, 1197, 1031, 863, 750, 682 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.06 (s, 9H, Me_3Si), 0.07 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 1.11 (s, 9H, *t*-Bu), 1.17 (d, 1H, ring proton, $J = 18$ Hz), 1.38 (d, 1H, ring proton, $J = 18$ Hz), 1.65 (s, 3H, Me), 1.71 (s, 3H, Me), 2.10 (d, 1H, ring proton, $J = 16$ Hz), 2.60 (d, 1H, ring proton, $J = 16$ Hz); ^{13}C NMR δ ($CDCl_3$) −0.24, 2.30, 3.90 (Me_3Si), 21.86, 23.27 (Me), 26.69 (CH_2Si), 30.56 (quarternary ring carbon), 30.70 (Me_3C), 35.92 (CH_2Si), 36.42 (CMe_3), 126.12, 127.36 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −21.0 ($Me_3\underline{Si}Si$), 0.1 (Me_3SiC), 1.8 ($\underline{Si}SiMe_3$), 6.1 ($OSiMe_3$).

Thermolysis of 2. Compound **2** (0.1025 g, 0.208 mmol) was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by GLC as being **6**. The product **6** (0.0984 g, 96% isolated yield) was isolated by column chromatography. Anal. Calcd for $C_{26}H_{52}OSi_4$: C, 63.34; H, 10.63. Found: C, 63.24; H, 10.30. MS *m/z* 492 (M^+); IR 2957, 2904, 2848, 1450, 1251, 1037, 835, 754, 736, 686, 588 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.06 (s, 9H, Me_3Si), 0.08 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 1.13 (d, 1H, ring proton, $J = 18$ Hz), 1.36 (d, 1H, ring proton, $J = 18$ Hz), 1.63 (s, 3H, Me), 1.70 (s, 3H, Me), 1.58−2.01 (m, 15H, Ad), 2.09 (d, 1H, ring proton, $J = 16$ Hz), 2.68 (d, 1H, ring proton, $J = 16$ Hz); ^{13}C NMR δ ($CDCl_3$) −0.16, 2.24, 4.38 (Me_3Si), 21.93, 23.23 (Me), 26.80 (CH_2Si), 29.56 (Ad), 32.94 (quarternary ring carbon), 33.59 (CH_2Si), 37.21, 38.85, 41.08 (Ad), 126.21, 127.24 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −20.6 ($Me_3\underline{Si}Si$), −0.7 (Me_3SiC), 2.0 ($\underline{Si}SiMe_3$), 5.7 ($OSiMe_3$).

Thermolysis of 3. Compound **3** (0.0635 g, 0.146 mmol) was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by GLC as being **7**. The product **7** (0.0572 g, 90% isolated yield) was isolated by column chromatography. Anal. Calcd for $C_{22}H_{42}OSi_4$: C, 60.76; H, 9.73. Found: C, 60.44; H, 10.00. MS *m/z* 434 (M^+); IR 3054, 2956, 2898, 1596, 1496, 1442, 1251, 1168, 1047, 929, 838, 779, 754 cm^{-1}; ^1H NMR δ ($CDCl_3$) −0.02 (s, 9H, Me_3Si), 0.04 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.94 (br s, 2H, ring protons), 1.59 (s, 3H, Me), 1.70 (s, 3H, Me), 2.51 (d, 1H, ring proton, $J = 18$ Hz), 2.57 (d, 1H, ring proton, $J = 18$ Hz), 7.03−7.24 (m, 5H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −0.98, −0.65, 2.17 (Me_3Si), 20.57 (Me), 20.58 (CH_2Si), 24.20 (Me), 30.33 (quarternary ring carbon), 37.43 (CH_2Si), 123.28, 124.68, 125.07, 127.34, 127.55, 144.94 (phenyl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −21.9 ($Me_3\underline{Si}Si$), −7.3 (Me_3SiC), 3.9 ($\underline{Si}SiMe_3$), 8.5 ($OSiMe_3$).

Synthesis of 8. A mixture of pivaloyltris(trimethylsilyl)silane (0.1075 g, 0.323 mmol) and 2,3-diphenyl-1,3-butadiene (0.2020 g, 0.979 mmol) was heated in a sealed tube at 140 °C for 24 h. The hexane-insoluble materials were filtered off, and the filtrate was evaporated. The residue was chromatographed on silica gel using hexane as the eluent to give product **8** (0.0601 g, 34% isolated yield). Anal. Calcd for $C_{30}H_{50}OSi_4$: C, 66.84; H, 9.35. Found: C, 66.61; H, 9.53. MS *m/z* 538 (M^+); ^1H NMR δ ($CDCl_3$) 0.09 (s, 9H, Me_3Si), 0.11 (s, 9H, Me_3Si), 0.12 (s, 9H, Me_3Si), 0.96 (s, 9H, *t*-Bu), 1.45 (d, 1H, ring proton, $J = 17$ Hz), 2.38 (d, 1H, ring proton, $J = 17$ Hz), 2.59 (d, 1H, ring proton, $J = 19$ Hz), 2.86 (d, 1H, ring proton, $J = 19$ Hz), 6.83−6.99 (m, 10H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) 0.39, 1.11, 2.99 (Me_3Si), 17.15 (CH_2Si), 27.76 (Me_3C), 38.46 (CMe_3), 42.71 (CH_2), 83.64 (CO), 125.26, 125.61, 127.52, 127.56, 128.74, 129.37, 135.06, 135.83 (phenyl ring carbons), 145.20, 147.41 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −46.9 ($\underline{Si}SiMe_3$), −16.1 ($Me_3\underline{Si}Si$), −14.7 ($Me_3\underline{Si}Si$), 5.5 ($OSiMe_3$).

Thermolysis of 8. Compound **8** (0.0393 g, 0.0729 mmol) was heated in a sealed tube at 250 °C for 24 h. The product **9** (0.0261 g, 66% isolated yield) was isolated by column chromatography. Anal. Calcd for $C_{30}H_{50}OSi_4$: C, 66.84; H, 9.35. Found: C, 66.78; H, 9.44. MS *m/z* 538 (M^+); ^1H NMR δ ($CDCl_3$) 0.16 (s, 9H, Me_3Si), 0.21 (s, 18H, Me_3Si), 1.18 (s, 9H, *t*-Bu), 1.65 (d, 1H, ring proton, $J = 19$ Hz), 2.05 (d, 1H, ring proton, $J = 19$ Hz), 2.64 (d, 1H, ring proton, $J = 17$ Hz), 3.28 (d, 1H, ring proton, $J = 17$ Hz), 6.92−7.10 (m, 10H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −0.29, 2.44, 4.30 (Me_3Si), 27.68 (CH_2Si), 30.46 (quarternary ring carbon), 30.76 (Me_3C), 36.32 (CH_2), 36.73 (CMe_3), 125.42 (2C), 127.37, 127.57, 128.66, 129.10, 135.47, 136.62 (phenyl ring carbons), 145.80, 146.60 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −20.4 ($Me_3\underline{Si}Si$), −0.1 (Me_3SiC), 0.8 ($\underline{Si}SiMe_3$), 7.2 ($OSiMe_3$).

Thermolysis of 4. Compound **4** (0.0533 g, 0.112 mmol) was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by GLC as being **10**. The product **10** (0.0293 g, 53% isolated yield) was isolated by column chromatography. Anal. Calcd for $C_{25}H_{48}OSi_4$: C, 62.95; H, 10.14. Found: C, 63.08; H, 10.33. Mp 88−89 °C; MS *m/z* 476 (M^+); IR 2949, 2895, 1479, 1446, 1257, 1034, 837, 752, 688, 629, 557 cm^{-1}; ^1H NMR δ ($CDCl_3$) −0.03 (s, 18H, Me_3Si), 0.12 (s, 9H, Me_3Si), 1.59 (s, 6H, Me), 2.19 (s, 3H, Mes-Me), 2.32 (s, 6H, Mes-Me), 2.77 (d, 2H, ring protons, $J = 14$ Hz), 3.20 (d, 2H, ring protons, $J = 14$ Hz), 6.72 (s, 2H, mesityl ring protons); ^{13}C NMR δ ($CDCl_3$) 0.43, 2.64 (Me_3Si), 13.63 (Me), 20.17, 26.07 (Mes-Me), 44.26 (quarternary ring carbon), 51.63 (CH_2Si), 129.70, 130.74, 132.85, 135.89, 148.67 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −18.6 ($Me_3\underline{Si}Si$), 6.3 ($\underline{Si}SiMe_3$), 11.9 ($OSiMe_3$).

---

(19) Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

Thermolysis of 4 in the Presence of Isoprene. A mixture of compound **4** (0.0735 g, 0.154 mmol) and isoprene (0.0485 g, 0.712 mmol) was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by GLC as being **10**. The product **10** (0.0290 g, 39% isolated yield) was isolated by column chromatography. All spectral data for compound **10** were identical with those of the authentic sample described above.

X-ray Crystallographic Analysis of 9. Data collection was performed on a Rigaku RAXIS-RAPID imaging plate system. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure crystallographic software package.[22,23]

Acknowledgment. We thank Hokko Chemical Industry Co., Ltd. for financial support. We also thank Shin-Etsu Co., Ltd. for the gift of chlorosilanes.

Supporting Information Available: Crystallographic data as a CIF file for **9**. Cartesian coordinates, total energies, and imaginary frequencies for TSs and LMs. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800219N

---

(20) Sheldrick G. M. *SHELX97*; 1997.

(21) DIRDIF99: Beurskens, P. T.; Admiraal, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1999.

(22) *Crystal Structure 3.10*: Crystal Structure Analysis Package; Rigaku and Rigaku/MSC, 2000−2002.

(23) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, UK.