Silicon−Carbon Unsaturated Compounds. 70. Thermolysis and Photolysis of Acylpolysilanes with Mesitylacetylene

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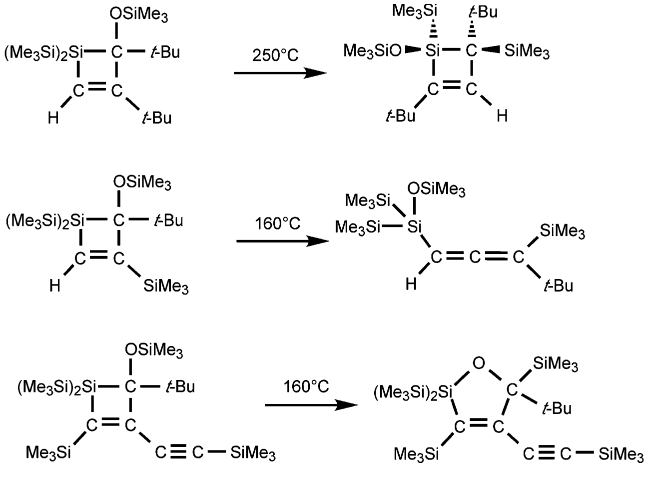
Received March 9, 2005

The thermolyses of adamantoyl-, pivaloyl-, and mesitoyltris(trimethylsilyl)silane (**1a**, **1b**, and **1c**) with mesitylacetylene were investigated. The cothermolysis of **1a** and mesitylacetylene in a sealed glass tube at 160 °C for 24 h afforded the 1:3- and 1:4-adduct, (1*E,*4*Z*)-5-adamantyl-2,4-dimesityl-1-[(mesitylethynyl)bis(trimethylsilyl)silyl]-5-(trimethylsiloxy)penta-1,4-diene (**3a**) and (1*E,*4*Z,*6*Z*)-7-adamantyl-2,4,6-trimesityl-1-[(mesitylethynyl)bis(trimethylsilyl)silyl]-7-(trimethylsiloxy)hepta-1,4,6-triene (**4a**), in 33% and 48% yields. Similarly, the thermolysis of **1b** and **1c** with mesitylacetylene also gave 1:3- and 1:4-adducts (**3b** and **3c**) in 33% and 32% yields and (**4b** and **4c**) in 46% and 19% yields, respectively. The thermolysis of **1a** with a 1:1 mixture of mesitylacetylene and *tert*-butylacetylene at 160 °C for 24 h afforded **3a** and **4a** in 30% and 44% yields, respectively. No products arising from the reaction of **1a** with *tert*-butylacetylene were detected. The reaction of **1a** with mesitylacetylene in the presence of a large excess of dimethylphenylsilane at 160 °C for 24 h gave **3a** and **4a** in 19% and 27% yields, respectively. In the presence of tris(trimethylsilyl)silane, however, the thermolysis of **1a** with mesitylacetylene produced (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]-ethene in high yield, and the starting compound **1a** was recovered. The results of radical addition of tris(trimethylsilyl)silane to mesitylacetylene and *tert*-butylacetylene have also been reported. Irradiation of **1a** in the presence of 1 equiv of mesitylacetylene in hexane with a high-pressure mercury lamp gave a 1:2-adduct, 2-[(*E*)-(2-adamantyl-1-mesityl-2-trimethylsiloxy)ethenyl]-3-mesityl-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**Ca**), **3a**, and **4a** in 6%, 4%, and 2% yields, respectively, in addition to 67% of the unchanged starting compound **1a**. The results of X-ray crystallographic analysis for **3a** and **4a** are described.

Introduction

In the recent past we have investigated the cycloaddition reactions of silenes generated thermally from acylpolysilanes with alkynes, such as *tert*-butylacetylene,[1] silyl-substituted acetylenes,[2] bis(silyl)acetylenes,[3] and bis(silyl)butadiynes,[4] where formal [2+2] cycloadditions were prominent. The thermal behavior of the 1-silacyclobut-3-ene derivatives thus formed depends highly on the substituents on the sp^2-hybridized carbon atoms in the silacyclobutenyl ring. For example, when 2,3-di(*tert*-butyl)-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene formed by the cothermolysis of pivaloyltris(trimethylsilyl)silane with *tert*-butylacetylene was heated in a sealed glass tube at 250 °C, an isomer of the starting compound, *trans*-2,4-di(*tert*-butyl)-1-trimethylsiloxy-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene, was obtained in almost quantitative yield.[1] The thermolysis of 2-*tert*-butyl-2-trimethylsiloxy-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene produced by the reaction of pivaloyltris(trimethylsilyl)silane with trimethylsilylacetylene at 160 °C, however, afforded a ring-



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[†] Kurashiki University of Science and the Arts.

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(1) Naka, A.; Ikadai, J.; Motoike, S.; Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Ishikawa, M. *Organometallics* **2002**, *21*, 2033.

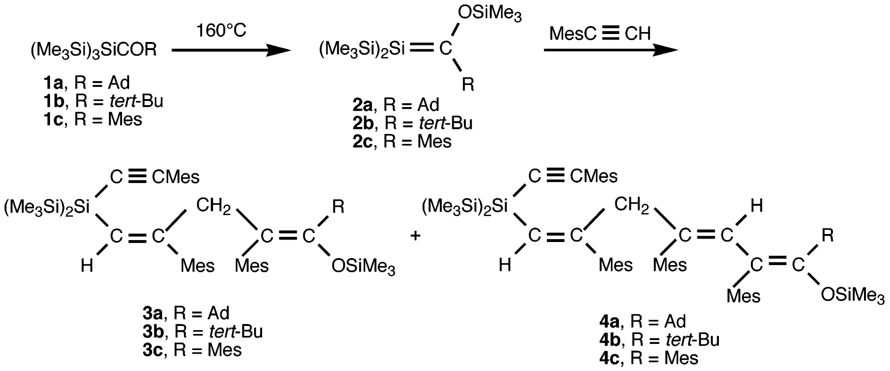
(2) Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **2000**, *611*, 248.

(3) Naka, A.; Ishikawa, M. *Organometallics* **2000**, *19*, 4921.

(4) (a) Naka, A.; Ishikawa, M. *Chem. Lett.* **2002**, 364. (b) Naka, A.; Ohnishi, H.; Miyahara, I.; Hirotsu, K.: Shiota, Y.; Yoshizawa, K.; Ishikawa, M. *Orgaometallics* **2004**, *23*, 4277.

10.1021/om050174v CCC: $30.25

Scheme 1



opened product, a propadiene derivative, in quantitative yield.[2] On the other hand, when 2-*tert*-butyl-3-(trimethylsilylethynyl)-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-1-silacyclobut-3-ene, obtained by the reaction of the pivaloyltris(trimethylsilyl)silane with bis(trimethylsilyl)butadiyne, was heated at 160°C, a dihydrosilole derivative was produced in high yield.[4]

It is of considerable interest to us to investigate the thermal properties of the 1-silacyclobut-3-enes bearing an aryl group on the sp^2-hybridized carbon atom in the 1-silacyclobut-3-ene ring. Therefore, we have examined the reactions of adamantoyl-, pivaloyl-, and mesitoyltris(trimethylsilyl)silane with mesitylacetylene in the hope of obtaining 3-mesityl-1-silacyclobut-3-enes. We have also investigated the photolysis of adamantoyltris(trimethylsilyl)silane with mesitylacetylene to prepare the [2+2] cycloadduct. In marked contrast to the thermolysis of the acylpolysilanes in the presence of various types of acetylenes, in which the 1:1-adducts were produced predominantly, the thermolysis of the acylpolysilanes with mesitylacetylene afforded no 1:1-adducts, but 1:3- and 1:4-adducts were always produced.

Results and Discussion

When a mixture of adamantoyltris(trimethylsilyl)silane (**1a**) and a 4-fold excess of mesitylacetylene in benzene was heated in a sealed glass tube at 160 °C for 24 h, two products, consisting of **1a** and mesitylacetylene in the molar ratio of 1:3 and 1:4, (1*E*,4*Z*)-5-adamantyl-2,4-dimesityl-1-[(mesitylethynyl)bis(trimethylsilyl)silyl]-5-(trimethylsiloxy)penta-1,4-diene (**3a**) and (1*E*,4*Z*,6*Z*)-7-adamantyl-2,4,6-trimesityl-1-[(mesitylethynyl)bis(trimethylsilyl)silyl]-7-(trimethylsiloxy)hepta-1,4,6-triene (**4a**), were obtained in 33% and 48% yields, respectively (Scheme 1). Neither a 1:1-adduct nor 1:2-adduct was detected in the reaction mixture by spectrometric analysis. The thermolysis of pivaloyltris(trimethylsilyl)silane (**1b**) with mesitylacetylene under the same conditions again gave a 1:3-adduct (**3b**) and 1:4-adduct (**4b**) in 33% and 46% yields. Likewise, the cothermolysis of mesitoyltris(trimethylsilyl)silane (**1c**) with mesitylacetylene afforded the 1:3-adduct (**3c**) and 1:4-adduct (**4c**) in 32% and 19% yields, respectively. In both cases, again, no 1:1- and 1:2-adducts were detected by careful spectrometric analyses of the reaction mixtures.

The structures of the products **3a**–**c** and **4a**–**c** were identified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis. The configurations of **3a**–**c** and **4a**–**c** were verified by NOE-FID difference experiments at 300 MHz. The structures of **3a** and **4a** were also confirmed by X-ray crystallographic analysis. The ORTEP drawings for **3a** and **4a** are depicted in Figures 1 and 2.

The formation of the 1:3-adducts, **3a**–**c** and **4a**–**c**, may be explained by a series of reactions involving the

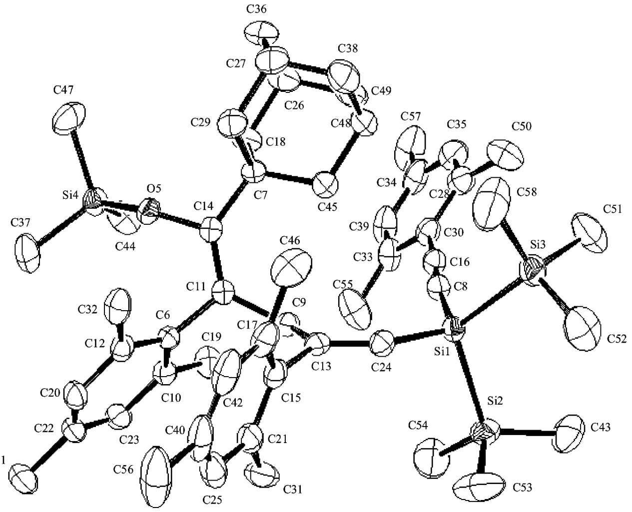


Figure 1. ORTEP drawing of compound **3a**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

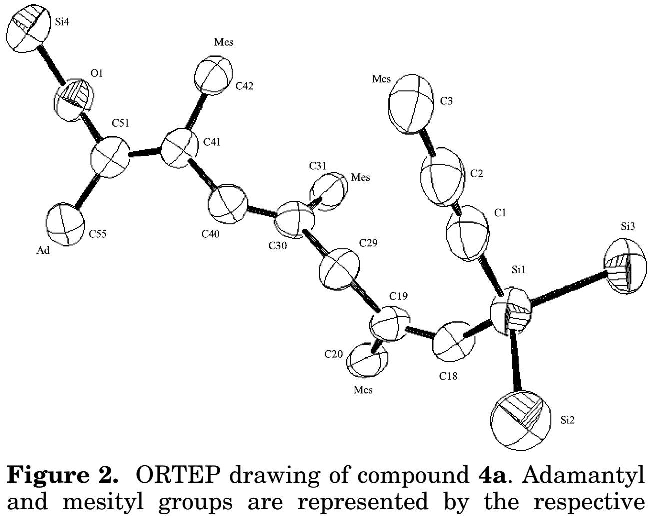
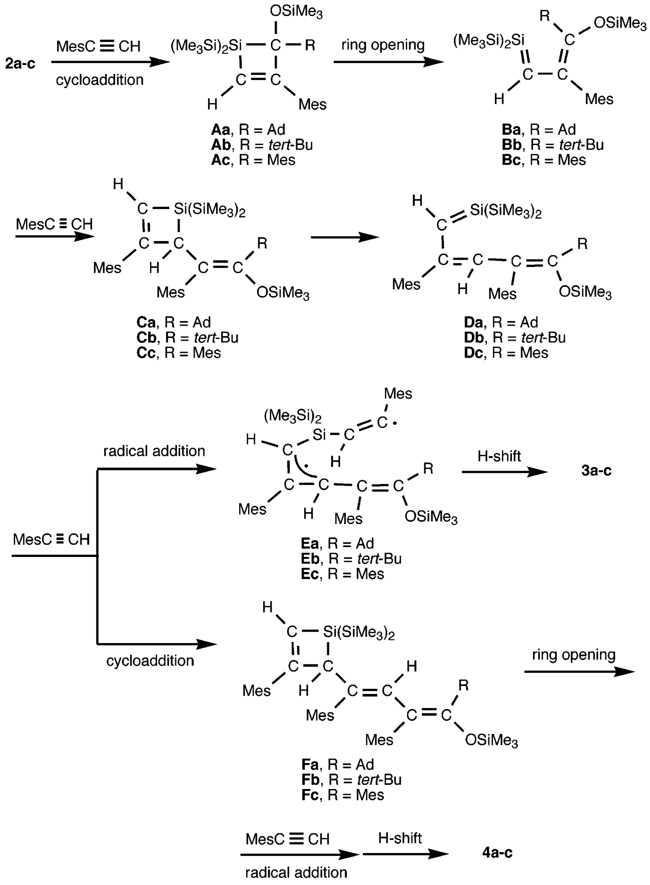


Figure 2. ORTEP drawing of compound **4a**. Adamantyl and mesityl groups are represented by the respective quarter carbons. Methyl groups for trimethylsilyl groups and hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

Scheme 2



radical intermediates,[5] as shown in Scheme 2. In the initial step, formal [2+2] cycloaddition of silenes (**2a**−**c**), generated thermally from **1a**−**c**, with mesitylacetylene takes place to give the 1:1-adducts, silacyclobutenes (**Aa**−**c**). The silacyclobutenes **Aa**−**c** thus formed undergo a ring-opening reaction to produce 1-silabuta-1,3-dienes (**Ba**−**c**), and then the resulting 1-silabuta-1,3-dienes **Ba**−**c** react with mesitylacetylene, yielding the 2-ethenyl-3-mesityl-1-silacyclobut-3-ene derivatives (**Ca**−**c**). In fact, it has been found that the silenes generated thermally from acylpolysilanes undergo formal [2+2] cycloaddition with monosubstituted acetylenes to afford the 1-silacyclobut-3-enes, analogous to **Aa**−**c**.[1] The thermal ring-opening reaction of the 1-silacyclobut-3-ene derivatives, leading to the 1-silabuta-1,3-dienes, has also been demonstrated in the thermolysis of various silacyclobutenes.[4] One might consider that two conrotatory modes of ring-opening of **Aa**−**c** lead to two different stereoisomers of the 1-silabuta-1,3-dienes. However, isomers **Ba**−**c** are sterically more favorable than the others, as reported previously.[4b] The resulting silacyclobutenes **Ca**−**c** undergo ring opening to give the 1-silahexa-1,3,5-trienes (**Da**−**c**) in a manner similar to those of **Aa**−**c**. The stepwise addition of a silicon−carbon double bond in **Da**−**c** to a triple bond of mesitylacetylene proceeds with regio- and stereospecificity to give the diradical intermediates (**Ea**−**c**). The intramolecular disproportionation of the diradical species **Ea**−**c**, involving a hydrogen shift, would afford the products **3a**−**c**.

Likewise, the formation of the 1:4-adducts may be understood in terms of formal [2+2] cycloaddition of the 1-silahexa-1,3,5-triene derivatives **Da**−**c** with mesitylacetylene, leading to the 2-butadienyl-1-silacyclobut-3-ene derivatives (**Fa**−**c**). The ring-opening reaction of **Fa**−**c**, and radical addition of the silene moiety in **Fa**−**c** to mesitylacetylene, produces the radical intermediates, analogous to **Ea**−**c**. Finally, the intramolecular hydrogen shift in the biradical species would afford the products **4a**−**c**.

The absence of 1:1- and 1:2-adducts may be ascribed to the lability of the [2+2] cycloadducts, **Aa**−**c** and **Ca**−**c**. Presumably, these compounds readily undergo ring opening under the conditions used, to give the 1-silabut-1,3-dienes and 1-silahexa-1,3,5-trienes, which react with mesitylacetylene, although the silacyclobutenes formed by the reaction of **1a**,**b** with other acetylenes, such as *tert*-butylacetylene and silyl-substituted acetylene, are rather thermally stable.[1−4]

To get more information about the mechanism for the present reactions, we investigated the reactions of **1a** with mesitylacetylene under various conditions. First, we examined the stoichiometric reaction of **1a** with mesitylacetylene to confirm whether the 1:1- and 1:2-adduct can be produced. Thus, when a mixture of **1a** and 1 equiv of mesitylacetylene in benzene in a sealed tube was heated at 160 °C for 24 h, the products **3a** and **4a** were obtained in 16% and 12% yields, respectively. However, no 1:1- and 1:2-adducts were detected in the reaction mixture by spectrometric analysis.

Interestingly, the reaction of **1a** with a 1:1 mixture of mesitylacetylene and *tert*-butylacetylene at 160 °C for 24 h produced **3a** and **4a** in 30% and 44% yields, respectively. No trace amount of the products originated from the reaction of **1a** with *tert*-butylacetylene was detected in the reaction mixture, indicating that the reaction of **1a** with mesitylacetylene proceeds with greater facility than that with *tert*-butylacetylene.

To trap the radical intermediates, which might be produced in the reaction of **1a** with mesitylacetylene, we carried out the reaction in the presence of hydrosilane as a radical-trapping agent. The thermolysis of **1a** with mesitylacetylene in the presence of a large excess of dimethylphenylsilane in benzene at 160 °C for 24 h again afforded **3a** and **4a** in 19% and 27% yields, respectively. To our surprise, in the presence of ca. 6-fold excess of tris(trimethylsilyl)silane, (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene, arising from addition of tris(trimethylsilyl)silane to mesitylacetylene, was obtained in 80% yield (Scheme 3). No products **3a** and **4a**, arising from the reaction of **1a** with mesitylacetylene, were detected in the reaction mixture. In this reaction, 80% of the starting compound **1a** was recovered. Careful analysis of the recovered starting compound **1a** by GC-mass spectrometry indicated the presence of a trace amount of compound, which shows a parent ion at *m*/*z* 412, corresponding to the calculated molecular weight of [**1a** + 2H]. These results clearly indicate that the silene moiety in **Ba**−**c** or **Da**−**c** adds to a triple bond of mesitylacetylene in a homolytic fashion. In the presence of tris(trimethylsilyl)silane, which has good hydrogen-donating ability, the diradical species generated from

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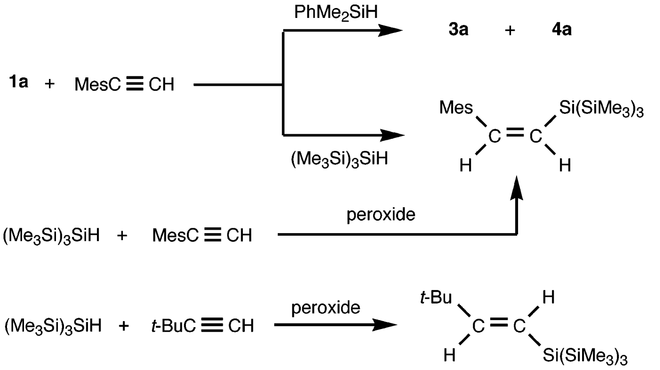
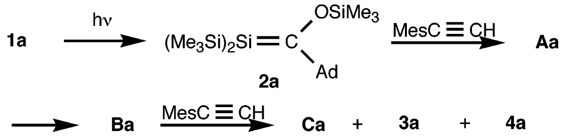
(5) According to the referee's comment, we have investigated some radical reactions to confirm the mechanism for the formation of **3a**−**c** and **4a**−**c** and found that the radical mechanism suggested by the referee is more reasonable than the mechanism involving σ-bond metathesis proposed for the formation of these compounds.

Scheme 3



Scheme 4



the silene moiety abstracts hydrogen from the hydrosilane to give the dihydro product and tris(trimethylsilyl)silyl radical. The tris(trimethylsilyl)silyl radical thus formed adds to mesitylacetylene to give the *Z*-adduct. In fact, the reaction of tris(trimethylsilyl)silane with mesitylacetylene in the presence of a trace amount of **1a** at 160 °C for 24 h afforded (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene in 89% yield, indicating that the silene **2a** generated thermally from **1a** acts as a radical initiator.

Next, we studied the regio- and stereochemistry in the reaction of the silyl radical with mesitylacetylene. The thermolysis of tris(trimethylsilyl)silane with mesitylacetylene in the presence of a catalytic amount of di(*tert*-butyl)peroxide at 160 °C for 24 h proceeded regio- and stereospecifically to give one isomer, (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene in 90% yield. No *E*-isomer was detected in the reaction mixture by spectrometric analysis. The reaction of tris(trimethylsilyl)silane with *tert*-butylacetylene in the presence of a peroxide catalyst under the same conditions, however, afforded exclusively the *E*-isomer, (*E*)-2-*tert*-butyl-1-[tris(trimethylsilyl)silyl]ethene, in 90% yield.[6a,b] In this reaction, no *Z*-isomer was detected at all in the reaction mixture.

When a mixture consisting of tris(trimethylsilyl)silane, mesitylacetylene, and *tert*-butylacetylene in the molar ratio of 1:1:1 in the presence of a di(*tert*-butyl)peroxide catalyst was heated at 160 °C for 24 h, (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene was obtained in 86% yield. No (*E*)-2-(*tert*-butyl)-1-[tris(trimethylsilyl)silyl]ethene was detected in the mixture, indicating that addition of the silyl radical to mesitylacetylene occurs more easily than that to *tert*-butylacetylene. These results are wholly consistent with those obtained from the thermolysis of **1a** with a 1:1 mixture of mesitylacetylene and *tert*-butylacetylene.

The *Z*-configuration of the product arising from radical addition of tris(trimethylsilyl)silane to mesitylacetylene was confirmed by spectrometric analysis. The coupling constant of hydrogen on the sp^2-hybridized carbon atom in the product is $J = 15$ Hz, indicating that this product must have the *Z*-configuration. Furthermore, the *Z*-configuration of the product was also verified by NOE-FID different experiments at 300 MHz. Irradiation of a signal at 0.07 ppm, due to the trimethylsilyl protons on the silicon atom, reveals a strong enhancement of the signal at 6.04 ppm attributed to hydrogen on the ethylene carbon atom and the signal at 2.19 ppm, attributable to methyl protons of the mesityl group, as well as the signal of the mesityl ring protons. Again, these results clearly indicate that the product must have the *Z*-configuration.

In an effort to prepare a 1:1-adduct, we carried out the photochemical reaction of **1a** with mesitylacetylene. Thus, irradiation of **1a** in the presence of 1 equiv of mesitylacetylene with a high-pressure mercury lamp in a hexane solution gave a 1:2-adduct (**Ca**), **3a**, and **4a** in 6%, 4%, and 2% yields, respectively, in addition to 67% of the unchanged starting compound **1a** (Scheme 4). The product **Ca** was identified as 2-[(*E*)-(2-adamantyl-1-mesityl-2-trimethylsiloxy)ethenyl]-3-mesityl-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene by spectrometric analysis. Compound **Ca** thus obtained was found to be rather stable and did not react with mesitylacetylene at room temperature. However, **Ca** reacted readily with mesitylacetylene at high temperature to give the ring-opened adducts. In fact, when a mixture of **Ca** and mesitylacetylene was heated in a sealed tube at 160 °C for 24 h, the adducts **3a** and **4a** were obtained in 16% and 48% yields, respectively.

Since the thermolysis of **1a** with mesitylacetylene gave no 1-silacyclobut-3-ene even in various reaction conditions, we have investigated the thermolysis of 2-adamantyl-3-*tert*-butyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**5**), which can be readily obtained by the reaction of **1a** with *tert*-butylacetylene, with mesitylacetylene. Thus, treatment of **5** with the acetylene in a sealed tube at 160 °C for 24 h gave (*Z*)-2-[adamantyl(trimethylsiloxy)methyl]-2-*tert*-butyl-1-[(mesitylethynyl)bis(trimethylsilyl)silyl]ethene (**6**) and (1*E*,4*Z*,6*Z*)-7-adamantyl-6-*tert*-butyl-2,4-dimesityl-7-trimethylsiloxy-1-[(mesitylethynyl)bis(trimethylsilyl)silyl]-hepta-1,4,6-triene (**7**) in 15% and 30% yields, respectively, as in Scheme 5. Similar thermolysis of **5** with *tert*-butylacetylene, however, afforded no adducts, but the starting silacyclobutene **5** was recovered unchanged. This result shows that the 1-silabuta-1,3-diene generated thermally from **5** readily reacts with mesitylacetylene, but not *tert*-butylacetylene.

The formation of **6** may be explained in terms of radical addition of 1-silabuta-1,3-diene (**Bd**) generated from **5** to mesitylacetylene, followed by a 1,5-hydrogen shift in the resulting biradical intermediate, as shown in Scheme 6. On the other hand, a possible explanation for the production of **7** involves the ring-opening reaction of **5**, leading to the silabutadiene intermediate **Bd**, in the initial step. Formal [2+2] cycloaddition of **Bd** thus formed to mesitylacetylene produces the silacyclobutene derivative (**Cd**), which undergoes further ring opening to give the intermediate (**Dd**). Again, [2+2] cycloaddition of the intermediate **Dd** to mesitylacetylene produces the cycloadduct (**E**). Finally, a stepwise addition of 1-silaocta-1,3,5,7-tetraene generated from **E** to mesi-

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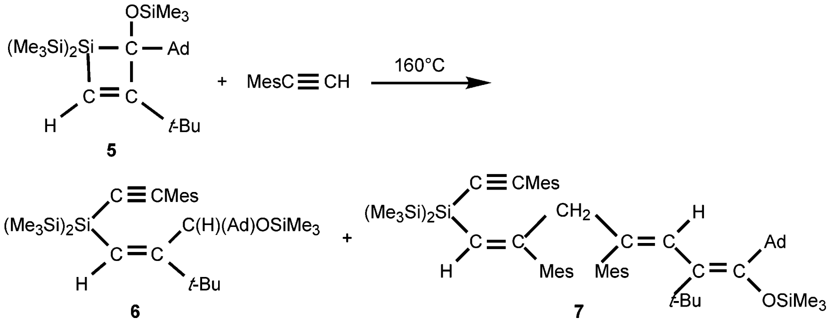
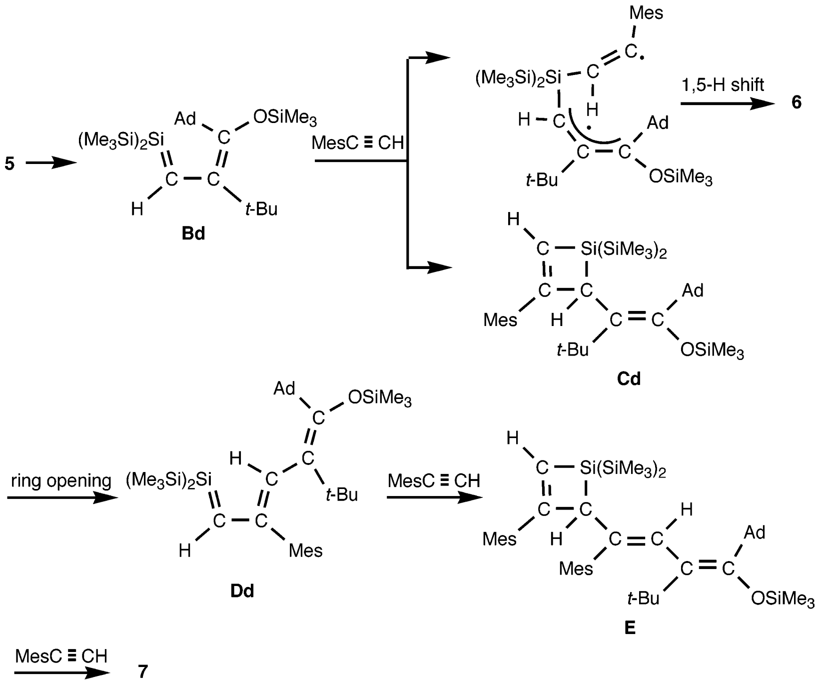
(6) (a) Kopping, B.; Chatgilialoglu, C.; Zahnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994. (b) Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356.

Scheme 5



Scheme 6



tylacetylene, followed by a 1,5-hydrogen shift in the resulting biradical species, affords the product **7**.

In conclusion, the cothermolysis of **1a**−**c** with mesitylacetylene at 160 °C gave 1:3- and 1:4-adducts, arising from radical addition of the 1-silahexa-1,3,5-triene and 1-silaocta-1,3,5,7-tetraene derivatives generated from ring opening of the respective silacyclobutenes to mesitylacetylene, followed by the intramolecular 1,5-hydrogen shift. No 1:1- and 1:2-adducts were detected in the reaction mixtures. The thermolysis of 1-silacyclobut-3-ene **5** with mesitylacetylene afforded compounds **6** and **7**, derived from the reaction of the 1-silabuta-1,3-diene **Bd** and 1-silaocta-1,3,5,7-tetraene derivative, with mesitylacetylene, as the main products. The thermolysis of **1a** with mesitylacetylene in the presence of tris(trimethylsilyl)silane at 160 °C gave the product arising from addition of tris(trimethylsilyl)silane to mesitylacetylene, as the sole product. The photolysis of **1a** with mesitylacetylene yielded 1:2-adduct **Ca**, in addition to the 1:3- and 1:4-adducts, **3a** and **4a**. The reaction of **Ca** with mesitylacetylene at 160 °C readily afforded **3a** and **4a**, respectively. The radical reaction of tris(trimethylsilyl)silane with mesitylacetylene proceeded regio- and stereospecifically to give (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene as the sole product, while the reaction with *tert*-butylacetylene produced exclusively (*E*)-2-*tert*-butyl-1-[tris(trimethylsilyl)silyl]ethene.

Experimental Section

General Procedures. Thermal reactions were carried out in a degassed sealed tube (1.0 cm $\phi \times 15$ cm). Yields of the products were calculated on the basis of the isolated products. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. 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. Acylpolysilanes **1a**−**c** were prepared according to the method reported by Brook et al.[7−9] Benzene and hexane used as a solvent were dried over sodium metal and distilled just before use.

Thermolysis of 1a with Mesitylacetylene. A mixture of 0.2097 g (0.51 mmol) of **1a** and 0.3080 g (2.14 mmol) of mesitylacetylene in 0.5 mL of dry benzene in a sealed glass

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tube was heated at 160 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column using hexane as eluent to give 0.1410 g (33% yield) of **3a** and 0.2441 g (48% yield) of **4a**. Data for **3a**: Anal. Calcd for $C_{53}H_{78}OSi_4$: C, 75.47; H, 9.32. Found: C, 75.39; H, 9.29. Mp 221.5−222.0 °C; MS *m/z* 842 (M^+); IR 2950, 2904, 2850, 2132, 1610, 1450, 1247, 1114, 889, 835 cm^{-1}; ^{1}H NMR δ($CDCl_3$) −0.42 (s, 9H, Me_3Si), 0.20 (s, 18H, Me_3Si), 1.49−1.60 (m, 6H, Ad), 1.70 (s, 6H, Mes-Me), 1.83 (s, 6H, Mes-Me), 1.86 (br s, 3H, Ad), 2.01−2.03 (m, 6H, Ad), 2.19 (s, 3H, Mes-Me), 2.22 (s, 3H, Mes-Me), 2.30 (s, 3H, Mes-Me), 2.51 (s, 6H, Mes-Me), 4.33 (s, 2H, CH_2), 4.83 (s, 1H, HC=C), 6.48 (s, 2H, Mes-H), 6.55 (s, 2H, Mes-H), 6.88 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.77 (Me_3Si), 0.77 (Me_3SiO), 20.13, 20.60, 20.77 (2C), 21.33, 21.39 (Mes-Me), 28.82, 36.76, 37.60, 40.85, 40.89 (Ad, CH_2), 96.89, 108.24 (ethynyl carbons), 114.67, 120.18, 120.95, 127.52, 127.86, 134.62, 135.11 (2C), 135.32, 137.35, 137.63, 139.24, 140.56, 142.58, 154.71, 159.52 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.9, −13.4, 10.2. Data for **4a**: Anal. Calcd for $C_{64}H_{90}OSi_4$: C, 77.82; H, 9.18. Found: C, 77.71; H, 9.15. Mp 198.0−198.5 °C; MS *m/z* 986 (M^+); IR 2950, 2904, 2850, 2134, 1610, 1569, 1249, 1124, 910, 840 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) −0.45 (s, 9H, Me_3Si), 0.18 (s, 18H, Me_3Si), 1.47 (s, 6H, Mes-Me), 1.51 (s, 6H, Mes-Me), 1.63−1.70 (m, 6H, Ad), 1.85−1.87 (br s, 6H, Ad), 1.97 (br s, 3H, Ad), 2.00 (s, 3H, Mes-Me), 2.04 (s, 3H, Mes-Me), 2.15 (s, 6H, Mes-Me), 2.24 (s, 6H, Mes-Me), 2.27 (s, 3H, Mes-Me), 2.29 (s, 3H, Mes-Me), 3.91 (s, 2H, CH_2), 5.08 (s, 1H, HC=C), 6.12 (s, 2H, Mes-H), 6.20 (s, 2H, Mes-H), 6.50 (s, 1H, HC=C), 6.80 (s, 2H, Mes-H), 6.81 (s, 2H, Mes-H); ^{13}C NMR δ($CDCl_3$) −0.81 (Me_3Si), 0.79 (Me_3SiO), 20.26, 20.36, 20.64, 20.71, 20.87, 21.00, 21.18, 21.32 (Mes-Me), 28.74, 36.93, 40.60, 41.11 (Ad), 44.84 (CH_2), 96.41, 108.38 (ethynyl carbons), 116.09, 120.84, 123.41, 127.27 (3C), 128.27, 128.60, 133.71, 134.50, 134.72, 135.34, 136.12, 136.73, 137.00, 137.08, 137.31, 137.62, 140.64, 142.77, 154.12, 157.06 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.2, −14.1, 11.2.

Thermolysis of 1b with Mesitylacetylene. A mixture of 0.2020 g (0.61 mmol) of **1b** and 0.4042 g (2.81 mmol) of mesitylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed using hexane as eluent to give 0.1563 g (33% yield) of **3b** and 0.2578 g (46% yield) of **4b**. Data for **3b**: Anal. Calcd for $C_{47}H_{72}OSi_4$: C, 73.75; H, 9.48. Found: C, 73.68; H, 9.41. Mp 160.0−161.0 °C; MS *m/z* 764 (M^+); IR 2960, 2130, 1608, 1473, 1247, 1147, 1029, 956, 887, 835 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) −0.45 (s, 9H, Me_3Si), 0.20 (s, 18H, Me_3Si), 1.25 (s, 9H, *t*-Bu), 1.71 (s, 6H, Mes-Me), 1.82 (6H, Mes-Me), 2.17 (s, 3H, Mes-Me), 2.21 (s, 3H, Mes-Me), 2.29 (s, 3H, Mes-Me), 2.48 (s, 6H, Mes-Me), 4.24 (s, 2H, CH_2), 4.85 (s, 1H, HC=C), 6.45 (s, 2H, Mes-H), 6.53 (s, 2H, Mes-H), 6.88 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.72 (Me_3Si), 0.62 (Me_3SiO), 20.27, 20.56, 20.76, 20.78, 21.33, 21.35 (Mes-Me), 30.78 (Me_3C), 37.85 (CMe_3), 37.98 (CH_2), 97.08, 108.33 (ethynyl carbons), 114.38, 120.59, 120.97, 127.51, 127.75, 127.88, 134.59, 135.02, 135.14, 137.24, 137.58, 138.63, 140.49, 142.40, 154.56, 158.85 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.4, −13.5, 10.6. Data for **4b**; Anal. Calcd for $C_{58}H_{84}OSi_4$: C, 76.58; H, 9.31. Found: C, 76.57; H, 9.26. Mp. 142.5−143.0 °C; MS *m/z* 908 (M^+); IR 2952, 2130, 1610, 1475, 1247, 1157, 904, 836 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) −0.44 (s, 9H, Me_3Si), 0.19 (s, 18H, Me_3Si), 1.17 (s, 9H, *t*-Bu), 1.47 (s, 6H, Mes-Me), 1.51 (s, 6H, Mes-Me), 2.01 (s, 3H, Mes-Me), 2.02 (s, 3H, Mes-Me), 2.26 (s, 6H, Mes-Me), 2.27 (s, 6H, Mes-Me), 2.28 (s, 3H, Mes-Me), 2.29 (s, 3H, Mes-Me), 3.83 (s, 2H, CH_2), 5.19 (s, 1H, HC=C), 6.14 (s, 2H, Mes-H), 6.19 (s, 2H, Mes-H), 6.49 (s, 1H, HC=C), 6.82 (s, 2H, Mes-H), 6.83 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.77 (Me_3Si), 0.66 (Me_3SiO), 20.01, 20.26, 20.64, 20.70, 20.80, 21.05, 21.32, 21.36 (Mes-Me), 30.42 (Me_3C), 38.16 (CMe_3), 44.66 (CH_2), 96.27, 108.57 (ethynyl carbons), 115.87, 120.86, 124.34, 127.19, 127.25, 127.30, 127.75, 128.79, 133.70, 134.37, 134.67, 135.39, 135.78, 136.63, 136.75, 137.17, 137.40, 137.68, 140.72, 142.66, 154.59, 156.57 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.3, −13.7, 11.1.

Thermolysis of 1c with Mesitylacetylene. A mixture of 0.1918 g (0.49 mmol) of **1c** and 0.2442 g (1.70 mmol) of mesitylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was removed under reduced pressure, and the residue was chromatographed using hexane as eluent to give 0.1296 g (32% yield) of **3c** and 0.0890 g (19% yield) of **4c**. Data for **3c**: Anal. Calcd for $C_{52}H_{74}OSi_4$: C, 75.48; H, 9.01. Found: C, 75.43; H, 9.02. Mp 178.2−179.0 °C; MS *m/z* 826 (M^+); IR 2954, 2132, 1618, 1475, 1243, 1126, 879, 848 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) −0.52 (s, 9H, Me_3Si), 0.12 (s, 18H, Me_3Si), 1.47 (s, 6H, Mes-Me), 1.87 (s, 6H, Mes-Me), 2.12 (6H, Mes-Me), 2.22 (s, 3H, Mes-Me), 2.23 (s, 3H, Mes-Me), 2.28 (s, 3H, Mes-Me), 2.34 (s, 3H, Mes-Me), 2.44 (s, 6H, Mes-Me), 3.95 (s, 2H, CH_2), 4.77 (s, 1H, HC=C), 6.61 (s, 2H, Mes-H), 6.65 (s, 2H, Mes-H), 6.68 (s, 2H, Mes-H), 6.94 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.82 (Me_3Si), 0.10 (Me_3SiO), 19.99, 20.62, 20.84, 20.87, 21.10, 21.23, 21.29, 21.39 (Mes-Me), 37.28 (CH_2), 97.17, 108.10 (ethynyl carbons), 118.96, 120.71, 121.18, 127.56, 127.68, 128.03, 128.06, 134.35, 134.76, 134.80, 135.25, 135.48, 136.89, 137.20, 137.62, 138.18, 140.79, 142.73, 144.89, 157.98 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.8, −13.7, 13.3. Data for **4c**: Anal. Calcd for $C_{63}H_{86}OSi_4$: C, 77.87; H, 8.92. Found: C, 77.73; H, 8.94. Mp 160.5−161.0 °C; MS *m/z* 970 (M^+); IR 2951, 2916, 2132, 1611, 1477, 1246, 1174, 1133, 1041, 872 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) −0.44 (s, 9H, Me_3Si), 0.13 (s, 18H, Me_3Si), 1.67 (s, 6H, Mes-Me), 1.78 (s, 6H, Mes-Me), 1.91 (s, 6H, Mes-Me), 1.94 (s, 3H, Mes-Me), 2.04 (s, 3H, Mes-Me), 2.23 (s, 6H, Mes-Me), 2.25 (s, 6H, Mes-Me), 2.27 (s, 3H, Mes-Me), 2.28 (s, 3H, Mes-Me), 2.36 (s, 3H, Mes-Me), 3.68 (s, 2H, CH_2), 5.07 (s, 1H, HC=C), 5.75 (s, 1H, HC=C), 6.08 (s, 2H, Mes-H), 6.23 (s, 2H, Mes-H), 6.65 (s, 2H, Mes-H), 6.81 (s, 2H, Mes-H), 6.84 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.84 (Me_3Si), 0.46 (Me_3SiO), 20.66, 20.70, 20.73, 20.89, 20.93, 20.95, 21.07, 21.17, 21.31, 21.34 (Mes-Me), 44.93 (CH_2), 96.41, 107.68 (ethynyl carbons), 120.88, 123.17, 126.22, 126.56, 126.75, 127.25, 128.38, 128.52, 133.50, 133.75, 134.19, 134.37 (2C), 134.46 (2C), 134.88, 134.97, 135.30, 135.71, 137.13, 137.24, 139.10, 140.56, 142.35, 147.58, 157.13 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.2, −13.8, 13.1.

Thermolysis of 1a with 1 equiv of Mesitylacetylene. A mixture of 0.2143 g (0.52 mmol) of **1a** and 0.0752 g (0.52 mmol) of mesitylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The low-boiling substances were evaporated in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.0704 g (16% yield) of **3a** and 0.0618 g (12% yield) of **4a**.

Thermolysis of 1a with a 1:1 Mixture of Mesitylacetylene and *tert*-Butylacetylene. A mixture of 0.0559 g (0.14 mmol) of **1a**, 0.0785 g (0.54 mmol) of mesitylacetylene, and 0.0479 g (0.58 mmol) of *tert*-butylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.0344 g (30% yield) of **3a** and 0.0591 g (44% yield) of **4a**.

Thermolysis of 1a with Mesitylacetylene in the Presence of Dimethylphenylsilane. A mixture of 0.0583 g (0.14 mmol) of **1a**, 0.0400 g (0.28 mmol) of mesitylacetylene, and 0.1558 g (1.14 mmol) of dimethylphenylsilane in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.0232 g (19% yield) of **3a** and 0.0378 g (27% yield) of **4a**. No products originated from 1:1- and 1:2-adducts were detected in the reaction mixture.

Thermolysis of 1a with Mesitylacetylene in the Presence of Tris(trimethylsilyl)silane. A mixture of 0.1171 g

(0.29 mmol) of **1a**, 0.0700 g (0.49 mmol) of mesitylacetylene, and 0.4040 g (1.62 mmol) of tris(trimethylsilyl)silane in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column using hexane as eluent to give 0.1525 g (80% yield) of (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene. No products originated from addition of **1a** to mesitylacetylene were detected, but a trace of compound that showed a parent ion at *m/z* 412, corresponding to the calculated molecular weight of [**1a** + 2], was detected by mass spectrometric analysis of the reaction mixture. Data for (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene: Anal. Calcd for $C_{20}H_{40}Si_4$: C, 61.14; H, 10.26. Found: C, 61.04; H, 10.20. MS *m/z* 392 (M^+); ^1H NMR δ ($CDCl_3$) 0.07 (s, 27H, Me_3Si), 2.19 (s, 6H, Mes-Me), 2.27 (s, 3H, Mes-Me), 6.04 (d, 1H, HC=C, *J* = 15 Hz), 6.84 (s, 2H, Mes-H), 7.15 (d, 1H, HC=C, *J* = 15 Hz); ^{13}C NMR δ ($CDCl_3$) 1.20 (Me_3Si), 20.82, 20.94 (Mes-Me), 128.05, 128.55, 135.35, 136.10, 137.68, 144.29 (mesityl and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −89.3, −12.5.

Thermolysis of Tris(trimethylsilyl)silane with Mesitylacetylene in the Presence of 1a. A mixture of 0.1042 g (0.42 mmol) of tris(trimethylsilyl)silane, 0.0725 g (0.50 mmol) of mesitylacetylene, and 0.0140 g (0.034 mmol) of **1a** in 0.5 mL of dry benzene was heated in a sealed glass tube at 160 °C for 24 h. The low-boiling substances were evaporated in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.1465 g (89% yield) of (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene.

Thermolysis of Tris(trimethylsilyl)silane with Mesitylacetylene in the Presence of Di(*tert*-butyl)peroxide. A mixture of 0.0616 g (0.25 mmol) of tris(trimethylsilyl)silane, 0.0413 g (0.29 mmol) of mesitylacetylene, and 0.0018 g (0.012 mmol) of di(*tert*-butyl)peroxide in a sealed glass tube was heated at 160 °C for 24 h. The low-boiling substances were evaporated from the mixture in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.0876 g (90% yield) of (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene.

Thermolysis of Tris(trimethylsilyl)silane with *tert*-Butylacetylene in the Presence of Di(*tert*-butyl)peroxide. A mixture of 0.1294 g (0.52 mmol) of tris(trimethylsilyl)silane, 0.0430 g (0.52 mmol) of *tert*-butylacetylene, and 0.0038 g (0.026 mmol) of di(*tert*-butyl)peroxide in a sealed glass tube was heated at 160 °C for 24 h. The low-boiling substances were evaporated in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.1549 g (90% yield) of (*E*)-2-*tert*-butyl-1-[tris(trimethylsilyl)silyl]ethene: MS *m/z* 330 (M^+); ^1H NMR δ ($CDCl_3$) 0.17 (s, 27H, Me_3Si), 0.99 (s, 9H, *t*-Bu), 5.40 (d, 1H, HC=C, *J* = 19 Hz), 6.04 (d, 1H, HC=C, *J* = 19 Hz); ^{13}C NMR δ ($CDCl_3$) 0.80 (Me_3Si), 22.99 (Me_3C), 35.81 (CMe_3), 113.12, 160.04 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −85.2, −12.9.

Thermolysis of Tris(trimethylsilyl)silane with Mesitylacetylene and *tert*-Butylacetylene in the Presence of Di(*tert*-butyl)peroxide. A mixture of 0.0677 g (0.27 mmol) of tris(trimethylsilyl)silane, 0.0393 g (0.27 mmol) of mesitylacetylene, 0.0232 g (0.28 mmol) of *tert*-butylacetylene, and 0.0020 g (0.014 mmol) of di(*tert*-butyl)peroxide in a sealed glass tube was heated at 160 °C for 24 h. The low-boiling substances were evaporated from the mixture in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.0920 g (86% yield) of (*Z*)-2-mesityl-1-[tris(trimethylsilyl)silyl]ethene. No product, (*E*)-2-*tert*-butyl-1-[tris(trimethylsilyl)silyl]ethene, was detected in the reaction mixture.

Photolysis of 1a with Mesitylacetylene. Into a 100 mL reaction vessel was placed a mixture of 0.3029 g (0.74 mmol) of **1a** and 0.1015 g (0.70 mmol) of mesitylacetylene in 100 mL of dry hexane. The mixture was irradiated with a high-pressure immersion lamp for 10 min. The solvent was evaporated off, and the residue was chromatographed with a silica gel column using hexane as eluent to give 0.0313 g (6% yield) of **Ca**, 0.0270 g (4% yield) of **3a**, and 0.0152 g (2% yield) of **4a**, together with 0.2019 g of **1a**. All spectral data for **3a** and **4a** were identical with those of the authentic samples mentioned above. Data for **Ca**: Anal. Calcd for $C_{42}H_{66}OSi_4$: C, 72.14; H, 9.51. Found: C, 72.01; H, 9.53. MS *m/z* 698 (M^+); IR 2949, 2903, 1612, 1536, 1451, 1242, 1181, 1023, 911, 839 cm^{-1}; ^1H NMR δ ($CDCl_3$) −0.38 (s, 9H, Me_3Si), −0.21 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 1.75 (br s, 9H, Ad), 2.03 (s, 3H, Mes-Me), 2.09 (s, 6H, Mes-Me), 2.10 (s, 3H, Mes-Me), 2.47 (s, 3H, Mes-Me), 2.48 (s, 3H, Mes-Me), 3.43 (s, 1H, CH), 6.06 (s, 1H, Mes-H), 6.14 (s, 1H, Mes-H), 6.49 (s, 2H, Mes-H), 6.89 (s, 1H, HC=C); ^{13}C NMR δ ($CDCl_3$) 0.72, 2.53, 4.87 (Me_3Si), 20.65, 20.68, 20.96, 22.29, 25.09, 26.03 (Mes-Me), 28.59, 36.93, 41.16, 47.43 (Ad), 42.37 (CH), 117.71, 123.85, 127.25, 128.20, 128.34, 128.76, 133.12, 134.19, 134.21, 134.56, 134.76, 137.83, 139.37, 139.55, 141.57, 154.74 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −46.1, −13.2, −11.3, 10.4.

Reaction of Ca with Mesitylacetylene at Room Temperature. A mixture of **1a** (0.2935 g, 0.71 mmol) and mesitylacetylene (0.1030 g, 0.71 mmol) in 100 mL of dry hexane was irradiated with a high-pressure mercury lamp for 10 min. To the resulting photolysis mixture was added 0.1100 g (0.76 mmol) of mesitylacetylene and allowed to stand at room temperature for 5 h. The solvent was evaporated, and the residue was chromatographed with a silica gel column using hexane as eluent to give 0.0299 (6% yield) of **Ca**, 0.0282 g (4% yield) of **3a**, and 0.0120 g (2% yield) of **4a**, together with 0.1950 g of the unchanged starting compound **1a**. All spectral data for **Ca**, **3a**, and **4a** were identical with those of the authentic samples described above.

Thermolysis of Ca with Mesitylacetylene. A mixture of 0.1267 g (0.18 mmol) of **Ca** and 0.0899 g (0.623 mmol) of mesitylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column eluting with hexane to give 0.0245 g (16% yield) of **3a** and 0.0859 g (48% yield) of **4a**.

Synthesis of 5. A mixture of 2.8530 g (6.94 mmol) of **1a** and 1.2011 g (14.6 mmol) of *tert*-butylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 140 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column using hexane as eluent to give 3.2450 g (95% yield) of **5**: Anal. Calcd for $C_{26}H_{52}OSi_4$: C, 63.34; H, 10.63. Found: C, 63.36; H, 10.68. Mp 118.5−120.0 °C; MS *m/z* 492 (M^+); IR 2956, 2902, 1473, 1243, 1089, 1029, 894, 836, 746, 682 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.19 (s, 9H, Me_3Si), 0.23 (s, 18H, Me_3Si), 1.17 (s, 9H, Me_3Si), 1.62−2.05 (m, 15H, Ad), 6.19 (s, 1H, HC=C); ^{13}C NMR δ ($CDCl_3$) 1.27, 1.73, 3.57 (Me_3Si), 29.26, 36.80, 39.80, 39.40, 39.86 (Ad, CH_2), 31.86 (Me_3C), 37.82 (CMe_3), 100.03 (CO), 129.18, 174.05 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −26.1, −18.1, −13.4, 4.6.

Thermolysis of 5 with Mesitylacetylene. A mixture of 0.2040 g (0.41 mmol) of **5** and 0.2293 g (1.59 mmol) of mesitylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. The solvent was evaporated in vacuo, and the residue was treated with a silica gel column using hexane as eluent to give 0.0388 g (15% yield) of **6** and 0.1152 g (30% yield) of **7**. Data for **6**: Anal. Calcd for $C_{37}H_{64}OSi_4$: C, 69.74; H, 10.12. Found: C, 69.56; H, 10.16; MS *m/z* 636 (M^+); IR 2954, 2886, 2134, 1611, 1475, 1451, 1244, 1223, 1086, 891, 835, 796 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.06 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 0.22 (s, 9H, Me_3Si), 1.22 (s, 9H, *t*-Bu), 1.58−1.93 (m, 15H, Ad), 2.27 (s, 3H, Mes-Me), 2.44 (s, 6H, Mes-Me), 4.77 (s, 1H, CH), 5.31 (s, 1H, HC=C), 6.85 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.40, −0.13, 1.03 (Me_3Si), 21.30, 21.43 (Mes-Me), 28.88, 37.15, 38.66, 39.90 (Ad), 33.73 (Me_3C), 38.34 (CMe_3), 85.95 (CO), 96.62, 109.18 (ethynyl carbons), 119.93, 120.70, 127.57, 137.82, 140.79, 166.07 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −70.8, −14.5, −14.2, 14.9. Data for **7**: Anal. Calcd for $C_{59}H_{88}OSi_4$: C, 76.55; H, 9.58. Found:

C, 76.50; H, 9.50. Mp 225.3−226.2 °C; MS *m/z* 924 (M^+); IR 2953, 2135, 1609, 1536, 1243, 1167, 1105, 1074, 947, 836 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.16 (s, 9H, Me_3Si), 0.21 (s, 18H, Me_3Si), 0.64 (s, 9H, *t*-Bu), 1.45 (s, 6H, Mes-Me), 1.54 (s, 6H, Mes-Me), 1.65 (br s, 6H, Ad), 1.78 (br s, 6H, Ad), 1.97 (br s, 3H, Ad), 2.10 (s, 3H, Mes-Me), 2.23 (s, 3H, Mes-Me), 2.28 (s, 3H, Mes-Me), 2.40 (s, 6H, Mes-Me), 3.90 (s, 2H, CH_2), 4.95 (s, 1H, HC═C), 6.35 (s, 1H, HC═C), 6.47 (s, 2H, Mes-H), 6.69 (s, 2H, Mes-H), 6.85 (s, 2H, Mes-H); ^{13}C NMR δ ($CDCl_3$) −0.72 (Me_3Si), 3.16 (Me_3SiO), 20.70, 20.85, 21.25, 21.26 (2C), 21.29 (Mes-Me), 30.62 (Me_3C), 36.43 (CMe_3), 28.85, 36.81, 40.47, 42.28 (Ad), 45.75 (CH_2), 96.72, 108.61 (ethynyl carbons), 120.85, 121.73, 125.07, 127.42 (2C), 128.23 (2C), 132.12, 135.24, 135.45, 135.95, 136.52, 137.47, 140.51 (2C), 142.78, 153.58, 157.80 (mesityl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −73.4, −13.9, 8.6.

Thermolysis of Silacyclobutene 5 with 10 equiv of *tert*-Butylacetylene. A mixture of 0.0538 g (0.11 mmol) of silacyclobutene **5** and 0.0892 g (1.09 mmol) of *tert*-butylacetylene in 0.5 mL of dry benzene in a sealed glass tube was heated at 160 °C for 24 h. GLC and spectrometric analysis of the mixture showed that the starting silacyclobutene **5** was recovered quantitatively.

X-ray Crystallographic Analysis of 3a and 4a. Data collection was performed on a Rigaku RAXIS-RAPID imaging plate system. The structure was solved by direct methods[10] and expanded using Fourier techniques.[11] 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.[12,13]

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

Supporting Information Available: Crystallographic data in CIF format for **3a** and **4a**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

OM050174V

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