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Silicon−Carbon Unsaturated Compounds. 63. The Formation of Silacyclopropenes from Thermal Reactions of Acylpolysilanes with Bis(silyl)acetylenes

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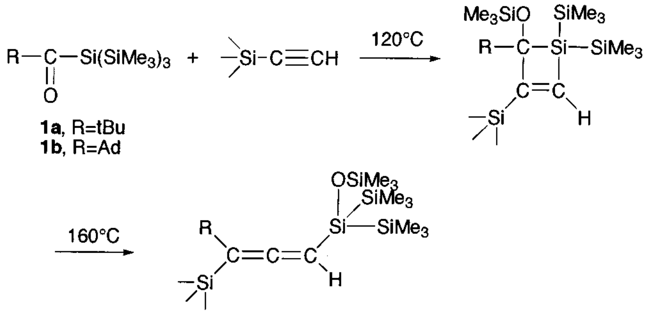
Summary: The cothermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane with bis(trimethylsilyl)acetylene, bis(dimethylphenylsilyl)acetylene, and bis(methyldiphenylsilyl)acetylene afforded the respective adducts, silacyclopropenes, probably via isomerization of [2 + 2] cycloadducts arising from the reactions of silenes formed thermally from acylpolysilanes with bis(silyl)acetylenes. Thermolysis of the silacyclopropene formed from pivaloyltris(trimethylsilyl)silane and bis(trimethylsilyl)acetylene with 2,3-dimethyl-1,3-butadiene gave a 3,4-dimethyl-1-silacyclopent-3-ene derivative.

Introduction

Highly strained silicon compounds, silacyclopropenes, show unique chemical behavior and undergo a wide variety of reactions, depending on the substituents on the silicon atom and also on the ring carbon atoms.[1−5] However, at present, no convenient methods for the synthesis of the silacyclopropenes have been published so far. To our knowledge, two methods have been reported for the synthesis of these compounds. One involves the photolysis of phenylethynyldisilanes and -trisilanes,[3i,6] while the other comprises addition of various silylenes to alkynes.[1,2,6,7] Therefore, it is of great adavantage to find a convenient synthetic method to develop the chemistry of the silacyclopropenes.

Recently, we have reported that the cothermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane (**1a** and **1b**) with monosilyl-substituted acetylenes at 120 °C produces 2-*tert*-butyl- and 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-3-silyl-1-silacyclobutenes, which undergo isomerization at 160 °C to give the ring-opened allene derivatives.[8] During the course of our investigation concerning the thermal reactions of acylpolysilanes with alkynes, we found that the thermolysis of **1a** and **1b** with bis(trimethylsilyl)acetylene gives silacyclopropenes derived from a 1:1 adduct. In this paper we report that the cothermolysis of **1a** and **1b** with bis(silyl)acetylenes affords silacyclopropenes in high yields.



Results and Discussion

When the cothermolysis of pivaloyltris(trimethylsilyl)silane **1a** with bis(trimethylsilyl)acetylene was carried out in a sealed glass tube at 160 °C for 12 h, 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene (**2a**) was obtained in 87% yield. In marked contrast to the cothermolysis with monosilyl-substituted acetylenes, in which the allene derivatives were produced, no allene derivative and also other products were detected in the reaction mixture by either GLC analysis or spectrometric analysis. The ^{1}H NMR spectrum of **2a** shows the presence of three kinds of trimethylsilyl protons at δ −0.01, 0.23, and 0.24 ppm, in addition to a single resonance at 1.30 ppm due to *tert*-butyl protons. The ^{13}C NMR spectrum of **2a** reveals resonances due to three kinds of trimethylsilyl carbons, one quaternary sp^{3} carbon, and a single resonance of olefinic carbons, as well as two resonances of *tert*-butyl carbons. Its ^{29}Si

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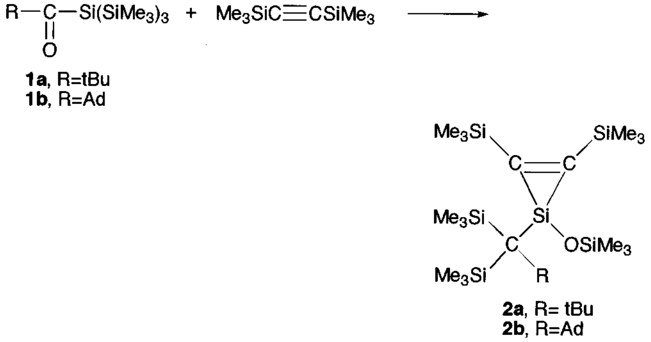
Scheme 1



NMR spectrum indicates the presence of four nonequivalent silicon atoms at −94.8, −14.1, −1.0, and 8.4 ppm. These results are wholly consistent with the structure proposed for **2a**. A similar reaction of adamantoyltris(trimethylsilyl)silane (**1b**) with bis(trimethylsilyl)acetylene proceeded cleanly to give a product similar to **2a**, 1-[(adamantyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene (**2b**), in 82% isolated yield (Scheme 1). Again, no other volatile products were detected in the reaction mixture. The DEPT NMR spectrum of **2b** shows the presence of three kinds of TMS methyl carbons at 0.70, 2.27, and 6.72 ppm, one methine carbon at 29.86 ppm, and two methylene carbons at 36.63 and 44.63 ppm. Its QUAT NMR spectrum reveals three resonances at 29.43, 40.54, and 205.85 ppm. These results are consistent with the proposed structure for **2b**.

The formation of products **2a** and **2b** can best be understood in terms of [2 + 2] cycloaddition of the silenes produced thermally from acylpolysilanes **1a** and **1b** with bis(trimethylsilyl)acetylene, followed by isomerization involving trimethylsilyl−trimethylsiloxy exchange to give an intermediate **A**, and then ring contraction to the three-membered cyclic system. The ring contraction from a silicon-containing four-membered cyclic compond to a silacyclopropane system has been reported previously.[9] The present results differ from those found for the analogous cothermolysis with monosilyl acetylenes, in which the allene derivatives are produced. The formation of the silacyclopropene, but not the allene derivatives, in the present reaction may be understood on steric grounds. Examination of molecular models of the expected allene derivatives arising from **1a** and **1b** with bis(trimethylsilyl)acetylene show that steric interactions of the trimethylsiloxybis(trimethylsilyl)silyl group and also the *tert*-butyl group on allenic carbons with the respective trimethylsilyl groups on the same carbon atoms are very severe. The steric interactions are less severe in **2a** and **2b**, so these are probably formed in the reactions of **1a** and **1b** with bis(trimethylsilyl)acetylene. The cothermolysis of **1a** with bis(dimethylphenylsilyl)acetylene at 160 °C again gave 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,3-bis(dimethylphenylsilyl)-1-silacycloprop-2-ene (**3a**) analogous to **2a** in 81% isolated yield. Similar cothermolysis of **1b** with bis(dimethylphenylsilyl)acetylene at 160 °C in a sealed tube produced 1-[(adamantyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,3-bis(dimethylphenylsilyl)silacycloprop-2-ene (**3b**) in 78% yield (Scheme 3). With bis(methyldiphenylsilyl)acetylene **1a** and **1b** also reacted under the same conditions to give 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,3-bis(methyldiphenylsilyl)-1-silacycloprop-2-ene (**4a**) and 1-[(adamantyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,3-bis(methyldiphenylsilyl)-1-silacycloprop-2-ene (**4b**) in 80% and 74% yields, respectively. The structures of **3a**, **3b**, **4a**, and **4b** were verified by spectrometric analysis, as well as by elemental analysis (see Experimental Section).

The present silacyclopropenes **2**−**4** are stable toward oxygen and moisture in air. They can be readily isolated by column chromatography without decomposition. Mass spectra of these compounds show parent ions corresponding to the respective calculated molecular weights and ions corresponding to the molecular weights of silylenes.

To date, four types of reactions have been reported for the thermolysis of the silacyclopropenes: polymerization without forming volatile products,[1,3c] extrusion of silylenes,[2a,3c] head-to-tail dimerization,[3f,10] and isomerization to alkynes or cyclic compounds.[3c,h,i,5b] To learn more about the thermal behavior of the silacyclopropenes, we carried out the thermolysis of **2a**.

When **2a** was heated in the presence of dimethylphenylsilane in a sealed tube at 200 °C, bis(trimethylsilyl)acetylene was obtained in 60% yield, but no silylene insertion products such as 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-2,2-dimethyl-2-phenyl-1-trimethylsiloxydisilane were detected in the reaction mixture. Perhaps, the silylene bearing bulky substituents on the silicon atom cannot insert into a silicon−hydrogen bond. In contrast with the hydrosilane, 2,3-dimethyl-1,3-butadiene reacted with the present silylene to give an adduct. Thus, the cothermolysis of **2a** with 2,3-dimethyl-1,3-butadiene under the same conditions afforded 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-2,3-dimethyl-1-trimethylsiloxysilacyclopent-3-ene (**5**) in 52% yield, along with a 73% yield of bis(trimethylsilyl)acetylene (Scheme 4). No other volatile products were detected by either GLC or spectrometric analysis of the mixture.

In conclusion, the cothermolysis of acylpolysilanes **1a** and **1b** with bis(silyl)acetylenes at 160 °C afforded the respective silacyclopropenes **2**−**4** in high yields. Treatment of **2a** with 2,3-dimethyl-1,3-butadiene produced 1-silacyclopent-3-ene **5**, arising from formal 1,4-addition of silylene to the 1,3-butadiene.

Experimental Section

General Procedure. All reactions of acylpolysilanes **1a** and **1b** with bis(silyl)acetylenes were carried out in a degassed sealed tube (1.0 cm × 15 cm). Yields for **2a** and **5** were determined by analytical GLC with the use of pentadecane as an internal standard, on the basis of the acylpolysilanes used. Yields of the products **2b**, **3a**, **3b**, **4a**, and **4b** were calculated on the basis of the isolated products. NMR spectra were recorded on a JNM-LA300 spectrometer and a JNM-LA500 spectrometer. 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. Gel permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd.).

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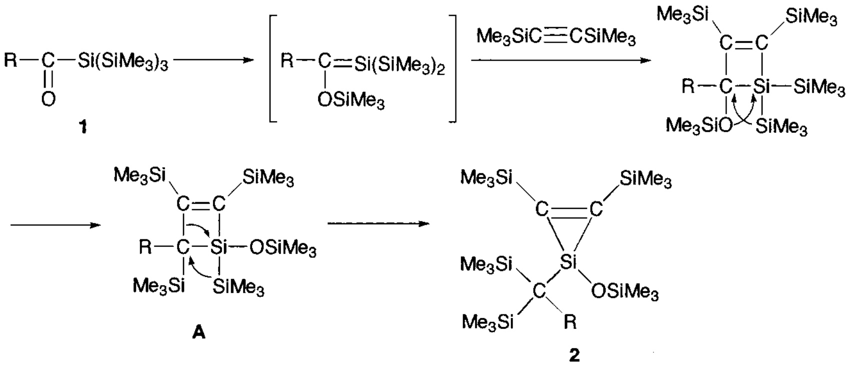
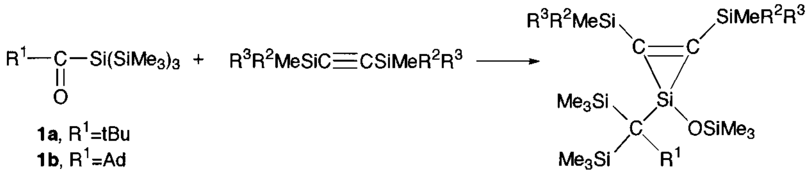
Scheme 2



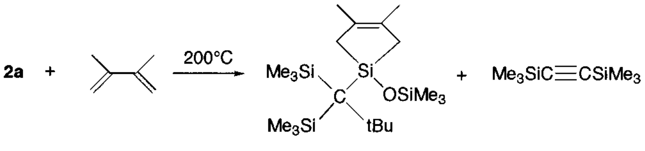
Scheme 3



1a, R^1=tBu
1b, R^1=Ad

3a, R^1= tBu, R^2=Ph, R^3=Me
3b, R^1=Ad, R^2=Ph, R^3=Me
4a, R^1= tBu, R^2=R^3=Ph
4b, R^1=Ad, R^2= R^3=Ph

Scheme 4



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Materials. Acylpolysilanes **1a** and **1b** were prepared according to the method reported by Brook et al.[11,12]

Preparation of Bis(dimethylphenylsilyl)acetylene. To a suspension of di-Grignard regent prepared from 0.10 mol of ethylmagnesium bromide and acetylene in 150 mL of ether was added 17.05 g (0.10 mol) of chlorodimethylphenylsilane through a dropping funnel over a period of 30 min. About 120 mL of ether was removed by distillation, and 150 mL of THF was added to the mixture. The mixture was heated to reflux for 2 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over magnesium sulfate. After the solvent was evaporated, bis(dimethylphenylsilyl)acetylene (11.02 g, 75%) was isolated by column chromatography: MS *m/z* 294 (M^+); IR 3070, 3021, 2962, 2898, 1625, 1429, 1249, 1114, 817, 781, 759, 730, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.46 (s, 12H, Me_2Si), 7.37−7.43 (m, 6H, phenyl ring protons), 7.66−7.68 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −0.86 (MeSi), 113.65 (sp carbon), 127.85, 129.41, 133.73, 136.74 (phenyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) −22.6. Anal. Calcd for $C_{18}H_{22}Si_2$: C, 73.40; H, 7.53. Found: C, 73.37; H, 7.49.

Preparation of Bis(methyldiphenylsilyl)acetylene. To a suspension of di-Grignard regent prepared from 0.10 mol of ethylmagnesium bromide and acetylene in 150 mL of ether was added 23.57 g (0.10 mol) of chloromethyldiphenylsilane through a dropping funnel over a period of 30 min. Ether (120 mL) was removed by distillation, and 150 mL of THF was added to the mixture. The mixture was heated to reflux for 2 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over magnesium sulfate. After the solvent was evaporated, bis(methyldiphenylsilyl)acetylene (14.83 g, 71%) was isolated by column chromatography: MS *m/z* 418 (M^+); IR 3068, 3048, 3021, 2960, 1429, 1251, 1114, 794, 763, 734, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.78 (s, 6H, MeSi), 7.38−7.45 (m, 12H, phenyl ring protons), 7.71−7.73 (m, 8H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −2.10 (MeSi), 113.73 (sp carbon), 127.95, 129.73, 134.55, 134.91 (phenyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) −26.2. Anal. Calcd for $C_{28}H_{26}Si_2$: C, 80.32; H, 6.26. Found: C, 80.24; H, 6.31.

Thermolysis of 1a with Bis(trimethylsilyl)acetylene. A mixture of 0.1917 g (0.577 mmol) of **1a** and 0.1189 g (0.699 mmol) of bis(trimethylsilyl)acetylene was heated in a sealed glass tube at 160 °C for 12 h. The mixture was analyzed by GLC as being **2a** (87% yield). Product **2a** was isolated by column chromatography: MS *m/z* 502 (M^+); IR 2954, 2898, 1456, 1365, 1251, 1029, 838, 752, 680, 623 cm^{-1}; ^1H NMR δ ($CDCl_3$) −0.01 (s, 9H, Me_3Si), 0.23 (s, 18H, Me_3Si), 0.24 (s, 18H, Me_3Si), 1.30 (s, 9H, tBu); ^{13}C NMR δ ($CDCl_3$) 0.62, 2.31, 6.16 (Me_3Si), 24.05 ($C(SiMe_3)_2$), 34.35 (Me_3C), 37.62 (CMe_3), 206.26 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −94.8, −14.1, −1.0, 8.4. Anal. Calcd for $C_{22}H_{54}OSi_6$: C, 52.51; H, 10.82. Found: C, 52.52; H, 10.76.

Thermolysis of 1b with Bis(trimethylsilyl)acetylene. A mixture of 0.1980 g (0.483 mmol) of **1b** and 0.1115 g (0.656 mmol) of bis(trimethylsilyl)acetylene was heated at 160 °C for 12 h. Product **2b** (0.2297 g, 82% isolated yield) was isolated by column chromatography: MS *m/z* 580 (M^+); IR 2956, 2904, 2849, 1449, 1247, 1026, 840, 770 cm^{-1}; ^1H NMR δ ($CDCl_3$) −0.01 (s, 9H, Me_3Si), 0.24 (s, 36H, Me_3Si), 1.65−2.08 (m, 15H, Ad); ^{13}C NMR δ ($CDCl_3$) 0.70, 2.27, 6.72 (Me_3Si), 29.43 ($C(SiMe_3)_2$), 29.86, 36.63, 40.54, 44.63 (Ad), 205.85 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −96.5, −14.1, −1.9, 7.7. Anal. Calcd for $C_{28}H_{60}OSi_6$: C, 57.85; H, 10.40. Found: C, 57.55; H, 10.58.

Thermolysis of 1a with Bis(dimethylphenylsilyl)acetylene. A mixture of 0.1768 g (0.533 mmol) of **1a** and

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0.2128 g (0.724 mmol) of bis(dimethylphenylsilyl)acetylene was heated at 160 °C for 12 h. Product **3a** (0.2703 g, 81% isolated yield) was isolated by column chromatography: MS *m*/*z* 626 (M^+); IR 3070, 2956, 2900, 1427, 1251, 1110, 1031, 840, 769, 734, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.02 (s, 9H, Me_3Si), 0.14 (s, 18H, Me_3Si), 0.39 (s, 6H, Me_2Si), 0.40 (s, 6H, Me_2Si),[13] 1.13 (s, 9H, tBu), 7.29−7.36 (m, 6H, phenyl ring protons), 7.50−7.53 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −1.15, −0.87 (Me_2Si),[13] 2.48, 6.10 (Me_3SiO and Me_3Si), 24.23 ($C(SiMe_3)_2$), 34.21 (Me_3C), 37.35 (CMe_3), 127.60, 128.87, 134.48, 138.81 (phenyl ring carbons), 205.74 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −94.9, −19.1, −1.0, 8.1. Anal. Calcd for $C_{32}H_{58}OSi_6$: C, 61.27; H, 9.32. Found: C, 61.06; H, 9.62.

Thermolysis of 1b with Bis(dimethylphenylsilyl)acetylene. A mixture of 0.2301 g (0.561 mmol) of **1b** and 0.1699 g (0.578 mmol) of bis(dimethylphenylsilyl)acetylene was heated at 160 °C for 12 h. Product **3b** (0.3082 g, 78% isolated yield) was isolated by column chromatography: MS *m*/*z* 704 (M^+); IR 2954, 2902, 2846, 1427, 1251, 1110, 1033, 840, 769, 730, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.03 (s, 9H, Me_3Si), 0.13 (s, 18H, Me_3Si), 0.42 (s, 12H, Me_2Si), 1.59 (br s, 6H, Ad), 1.91−1.97 (m, 9H, Ad), 7.27−7.39 (m, 6H, phenyl ring protons), 7.50−7.52 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −0.88, −0.73 (Me_2Si),[13] 2.43, 6.66 (Me_3SiO and Me_3Si), 28.17 ($C(SiMe_3)_2$), 29.71, 36.46, 40.40, 44.49 (Ad), 127.58, 128.85, 134.48, 138.82 (phenyl ring carbons), 205.11 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −96.6, −19.1, −2.0, 7.4. Anal. Calcd for $C_{38}H_{64}OSi_6$: C, 64.70; H, 9.14. Found: C, 64.83; H, 9.16.

Thermolysis of 1a with Bis(methyldiphenylsilyl)acetylene. A mixture of 0.1670 g (0.503 mmol) of **1a** and 0.2451 g (0.586 mmol) of bis(methyldiphenylsilyl)acetylene was heated at 160 °C for 12 h. Product **4a** (0.2998 g, 80% isolated yield) was isolated by column chromatography: MS *m*/*z* 750 (M^+); IR 3070, 2956, 1429, 1251, 1110, 1031, 840, 786, 736, 721, 698, 673 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.08 (s, 9H, Me_3Si), 0.12 (s, 18H, Me_3Si), 0.54 (s, 6H, MeSi), 1.02 (s, 9H, tBu), 7.25−7.39 (m, 12H, phenyl ring protons), 7.46−7.51 (m, 8H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −2.27 (MeSi), 2.71, 6.25 (Me_3SiO and Me_3Si), 24.38 ($C(SiMe_3)_2$), 34.24 (Me_3C), 37.23 (CMe_3), 127.57, 127.58, 129.00, 129.08, 135.48, 135.56, 136.55, 136.79 (phenyl ring carbons),[13] 205.86 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −94.2, −23.8, −0.7, 8.1. Anal. Calcd for $C_{42}H_{62}OSi_6$: C, 67.13; H, 8.32. Found: C, 67.47; H, 8.60.

Thermolysis of 1b with Bis(methyldiphenylsilyl)acetylene. A mixture of 0.1590 g (0.388 mmol) of **1b** and 0.1862 g (0.445 mmol) of bis(methyldiphenylsilyl)acetylene was heated at 160 °C for 12 h. Product **4b** (0.2376 g, 74% isolated yield) was isolated by column chromatography: MS *m*/*z* 828 (M^+); IR 2948, 2904, 2848, 1429, 1251, 1108, 1041, 838, 788, 736, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.05 (s, 18H, Me_3Si), 0.08 (s, 9H, Me_3Si), 0.53 (s, 6H, MeSi), 1.28−2.05 (m, 15H, Ad), 7.17−7.52 (m, 20H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −1.98 (MeSi), 2.69, 6.75 (Me_3SiO and Me_3Si), 28.03 ($C(SiMe_3)_2$), 29.62, 36.22, 40.45, 44.35 (Ad), 127.57, 127.59, 128.90, 129.03, 135.47, 135.49, 136.79, 136.83 (phenyl ring carbons),[13] 205.23 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −96.2, −23.5, −2.0, 7.0. Anal. Calcd for $C_{48}H_{68}OSi_6$: C, 69.50; H, 8.26. Found: C, 69.38; H, 8.49.

Thermolysis of 2a in the Presence of Dimethylphenylsilane. A mixture of 0.1390 g (0.277 mmol) of **2a** and 0.2537 g (1.87 mmol) of dimethylphenylsilane was heated in a sealed glass tube at 200 °C for 12 h. The mixture was analyzed by GLC as being bis(trimethylsilyl)acetylene (60% yield). A silylene insertion product could not be detected by spectrometric analysis. All spectral data for bis(trimethylsilyl)acetylene were identical with those of the authentic sample.

Thermolysis of 2a in the Presence of 2,3-Dimethyl-1,3-butadiene. A mixture of 0.2240 g (0.446 mmol) of **2a** and 0.1426 g (1.74 mmol) of 2,3-dimethyl-1,3-butadiene was heated in a sealed glass tube at 200 °C for 12 h. The mixture was analyzed by GLC as being **5** (52% yield) and bis(trimethylsilyl)acetylene (73%). Product **5** and bis(trimethylsilyl)acetylene were isolated by recycling HPLC: MS *m*/*z* 414 (M^+); IR 2956, 2927, 1253, 1172, 1029, 840, 755 cm^{-1}; ^1H NMR δ (C_6D_6) 0.16 (s, 9H, Me_3Si), 0.41 (s, 18H, Me_3Si), 1.37 (s, 9H, tBu), 1.44 (br d, 2H, CH_2, $J = 17$ Hz), 1.78 (s, 6H, Me), 1.89 (br d, 2H, CH_2, $J = 17$ Hz); ^{13}C NMR δ ($CDCl_3$) 1.91, 6.20 (Me_3Si), 19.41 (CH_3), 30.90 ($C(SiMe_3)_2$), 32.16 (CH_2), 33.81 (Me_3C), 37.67 (CMe_3), 130.35 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −2.0, 7.3, 13.4. Anal. Calcd for $C_{20}H_{46}OSi_4$: C, 57.89; H, 11.17. Found: C, 57.69; H, 11.43. All spectral data for bis(trimethylsilyl)acetylene were identical with those of the authentic sample.

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(13) The presence of two resonances due to methyl protons and methyl carbons for the Me_2PhSi groups in **3a** and **3b** and eight resonances due to phenyl carbons for the Ph_2MeSi groups in **4a** and **4b** is probably due to hindered rotation.