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Silicon−Carbon Unsaturated Compounds. 60. Reactions of Lithium Silenolates with Dienes

Joji Ohshita,* Shin Masaoka, Yasuyo Morimoto, and Makoto Sano

*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 739, Japan*

Mitsuo Ishikawa*

*Department of Chemical Technology, Kurashiki University of Science and the Arts, 2640
Nishinoura, Tsurashima, Kurashiki, Okayama 712, Japan*

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The chemical properties of lithium silenolates toward dienes were studied. The reaction of lithium 2-*tert*-butyl-1,1-bis(trimethylsilyl)silen-2-olate (**1a**) with butadiene at −40 °C, followed by hydrolysis, afforded 2-*tert*-butyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol, derived from [2 + 4] cycloaddition of **1a** with butadiene, in 94% yield. Similar treatment of lithium 2-adamantyl-1,1-bis(trimethylsilyl)silen-2-olate (**1b**) gave the respective adduct in 87% yield. The reactions of lithium silenolates **1a**,**b** with 2,3-dimethylbutadiene, isoprene, and 1,3-pentadiene proceeded in a fashion similar to those with butadiene to give the [2 + 4] cycloadducts in high yields. The reactions of **1a**,**b** with 2,3-dimethylbutadiene and butadiene at room temperature gave the products originated from 1,1-bis(trimethylsilyl)-silacyclohexa-1,4-diene intermediates. The crystal structure of 10-adamantyl-2,3,6,7-tetramethyl-9-(trimethylsilyl)-9-silabicyclo[4.4.0]deca-2,6-diene (**6b**), which was obtained from the reaction of **1b** with 2,3-dimethylbutadiene at room temperature, was determined by a single-crystal X-ray diffraction study.

Introduction

The chemistry of lithium enolates has been extensively investigated and widely used for the synthesis of various organic compounds.[1] On the other hand, no reports on the chemistry of lithium silenolates, silicon analogs of lithium enolates, had been published until recently, when we reported the first example for the synthesis of lithium silenolates.[2] We have demonstrated that treatment of acyltris(trimethylsilyl)silane with (tris(trimethylsilyl)silyl)lithium affords lithium silenolates in almost quantitative yields, if the starting acyltris(trimethylsilyl)silanes have no enolizable protons and involve a bulky substituent, such as a *tert*-butyl, adamantyl, and mesityl group, at the carbonyl carbon atom.[3] The NMR spectra for lithium 2-mesityl-1,1-bis-(trimethylsilyl)silen-2-olate show that the central silicon atom has sufficient sp^2 character, while, in the lithium 2-*tert*-butyl- and 2-adamantyl-1,1-bis(trimethylsilyl)-silen-2-olates, the spectra indicate that the anionic charge localizes moderately on the central silicon atoms. Both types of lithium silenolates react readily with electrophiles, such as water, alkyl halides, and chlorosilanes, to produce coupling products. We have also reported that oxidative coupling reactions of lithium silenolates with palladium dichloride afford the first examples of bis(acyl)-substituted polysilanes in high yields.[4]

In an effort to develop the chemistry of the lithium silenolates, we investigated the chemical behavior of these compounds toward unsaturated carbon compounds. In this paper, we report the reactions of lithium silenolates with dienes, which produce the corresponding 1:1 adducts in high yields. We also describe the formation of cyclic silenes arising from Peterson-type olefination of the adducts.

Results and Discussion

Reactions of Lithium Silenolates with Dienes at Low Temperature. When lithium 2-*tert*-butyl-1,1-bis-(trimethylsilyl)silen-2-olate (**1a**) was treated with butadiene in THF at −40 °C and the resulting mixture was hydrolyzed with water, 2-*tert*-butyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol (**2a**) was obtained in 94% yield, as shown in Scheme 1. Similar treatment of lithium 2-adamantyl-1,1-bis(trimethylsilyl)silen-2-olate (**1b**) with butadiene at −62 °C afforded 2-adamantyl-1,1-bis-(trimethylsilyl)silacyclohex-4-en-2-ol (**2b**) in 87% yield. The reactions of **1a**,**b** with 2,3-dimethylbutadiene also proceeded smoothly at the temperature from −40 to −30 °C to give the corresponding adducts, 2-*tert*-butyl- and 2-adamantyl-4,5-dimethyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol (**3a**,**b**) in 82% and 98% yields, respectively. The structures of products **2a**,**b** and **3a**,**b** were verified by spectrometric analysis (see Experimental Section). IR spectra of **2a**,**b** and **3a**,**b** reveal broad

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

(1) For a review, see: Caine, D. In Comprehensive Organic Synthesis; Pergamon Press: Oxford, U.K., 1991; Vol. 3, Chapter 1.1.

(2) Ohshita, J.; Masaoka, Y.; Masaoka, S.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. *J. Organomet. Chem.* **1994**, *473*, 15.

(3) Ohshita, J.; Masaoka, Y.; Masaoka, S.; Hasebe, H.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. *Organometallics* **1996**, *15*, 3136.

(4) Ohshita, J.; Masaoka, S.; Ishikawa, M. *Organometallics* **1996**, *15*, 2198.

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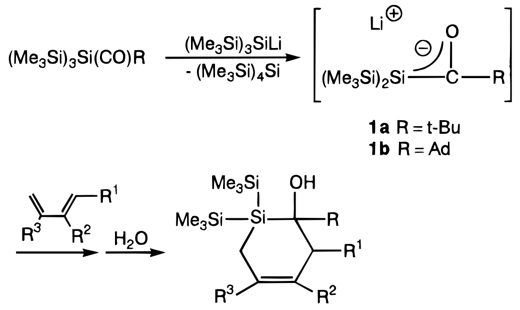
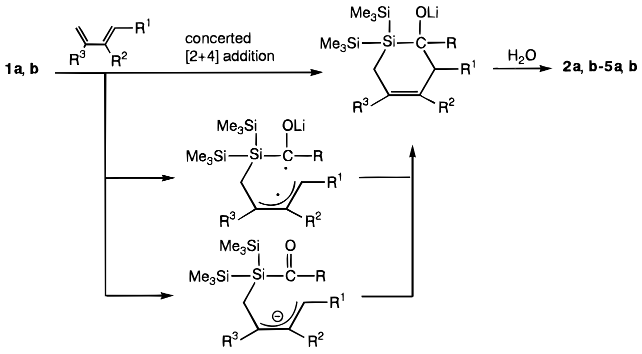
Scheme 1



2a R = t-Bu, R^1 = R^2 = R^3 = H
2b R = Ad, R^1 = R^2 = R^3 = H
3a R = t-Bu, R^1 = H, R^2 = R^3 = Me
3b R = Ad, R^1 = H, R^2 = R^3 = Me
4a R = t-Bu, R^1 = R^3 = H, R^2 = Me
4b R = Ad, R^1 = R^3 = H, R^2 = Me
5a R = t-Bu, R^1 = Me, R^2 = R^3 = H
5b R = Ad, R^1 = Me, R^2 = R^3 = H

Scheme 2



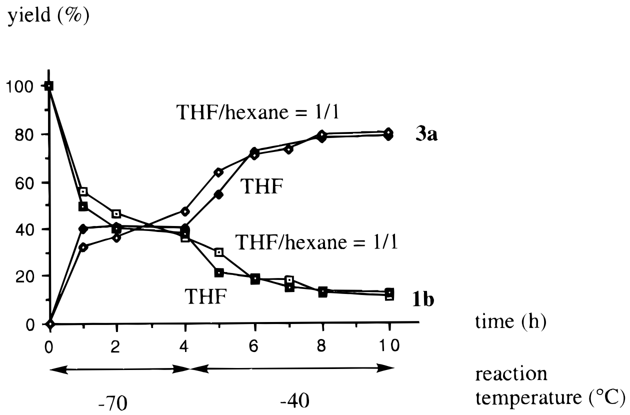


Figure 1. Plots of the yields of **1b** and **3b** versus reaction time in the reactions of **1b** and 2,3-dimethylbutadiene in THF and 1/1 THF/hexane.

absorption bands at about 3500 cm^{-1}, due to the stretching frequencies of an O−H bond. Their ^{1}H NMR spectra show signals at 1.33−1.75 ppm and 2.10−2.42 ppm, characteristic of the allylic methylene protons of 1-silacyclohex-4-ene ring systems.[5]

The formation of **2a**,**b** and **3a**,**b** may be explained by concerted [2 + 4] cycloaddition of lithium silenolates with dienes or by stepwise addition of lithium silenolates to the dienes via radical or anionic intermediates, as shown in Scheme 2. In order to learn more about the reaction mechanism, we examined the solvent effects on the reaction of **1b** with 2,3-dimethylbutadiene. As can be seen in Figure 1, changing the solvent from THF to 1/1 THF/hexane did not exert an unambiguous influence on the reaction, indicating that an anionic intermediate plays little role in this reaction.

In order to learn the regioselectivities in the cycloaddition of lithium silenolates with dienes, we carried out the reactions of **1a**,**b** with isoprene and 1,3-pentadiene. Thus, when **1a** was treated with isoprene at −40 °C and the resulting mixture was hydrolyzed with water, 2-*tert*-butyl-4-methyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol (**4a**) was obtained in 90% yield. No other regioisomers were detected in the reaction mixture. The structure of **4a** was verified by spectrometric analysis. The location of the methyl group on the silacyclohexene ring was confirmed by ^{1}H−^{13}C long range COSY spectroscopy. In this spectrum, couplings of the methyl protons at 1.62 ppm with the C3 carbon and olefinic carbons are observed, in addition to those of a proton on the C3 carbon at 2.04 ppm with the *tert*-butyl quarter carbon and the C2 carbon. These results are wholly consistent with the structure proposed for **4a**. Similar treatment of **1b** with isoprene, followed by hydrolysis, gave 2-adamantyl-4-methyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol (**4b**) in 83% yield, as the sole volatile product.

The reaction of **1a** with 1,3-pentadiene also proceeded with regiospecificity to give 2-*tert*-butyl-3-methyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol (**5a**) in 91% yield. Compound **5a** was found to be a mixture consisting of *cis*- and *trans*-isomers in a ratio of 2:1 by its NMR spectrometry. All spectral data obtained for **5a** are also consistent with the proposed structure. The geometry of isomers of **5a** with respect to the C2−C3 bond was confirmed by NOE-FID difference experiments at 270 MHz. Thus, saturation of a proton on C3 of the *cis*-isomer caused the enhancement of methyl protons on the C3 and *tert*-butyl protons, while irradiation of the *tert*-butyl protons resulted in the enhancement of the proton on C3. For the *trans*-isomer, saturation of methyl protons on C3 led to the enhancement of *tert*-butyl protons. Lithium silenolates **1b** reacted with 1,3-pentadiene again regiospecifically to give 2-*tert*-butyl-3-methyl-1,1-bis(trimethylsilyl)silacyclohex-4-en-2-ol (**5b**) in 66% yield. This reaction proceeded quite slowly, and the use of a large excess of pentadiene is necessary to obtain **5b** in high yield. In fact, when **1b** was treated with 1 equiv of pentadiene, **5b** was obtained only in 21% yield, together with 51% of the starting **1b**. Compound **5b** consists of *cis*- and *trans*-isomers in a ratio of 5:1.

Silacyclohexenols obtained from the reactions of **1a**,**b** and dienes are rather unstable and treating them with silica gel column chromatography led to a decrease in the yields. Especially, less substituted compounds **2a**,**b** decomposed slowly upon letting them stand in air at room temperature to give complex mixtures whose ^{1}H NMR spectra show only unsolved multiplets.

In contrast to lithium silenolates **1a**,**b**, lithium 2-mesityl-1,1-bis(trimethylsilyl)silen-2-olates (**1c**) did not react with 2,3-dimethylbutadiene at −40 °C. Upon warming of the reaction mixture to room temperature, a complex mixture consisting of many products in low yields was obtained. All attempts to isolate the products analogous to **3a**,**b** by changing the reaction conditions and stoi-

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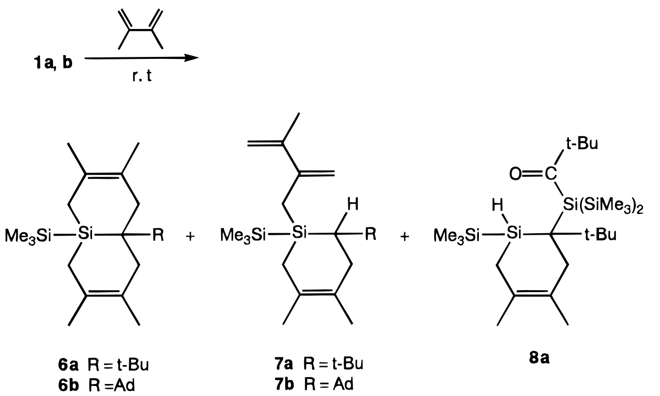
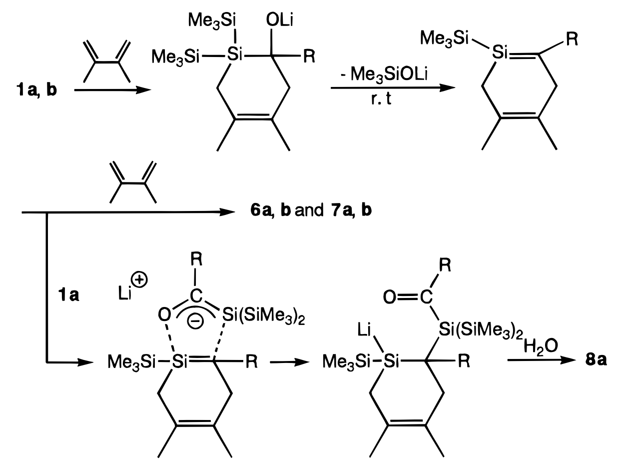
[5] (a) Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128. (b) Ohshita, J.; Masaoka, Y.; Ishikawa, M.; Takeuchi, T. *Organometallics* **1993**, *12*, 876.

Scheme 3



Scheme 4

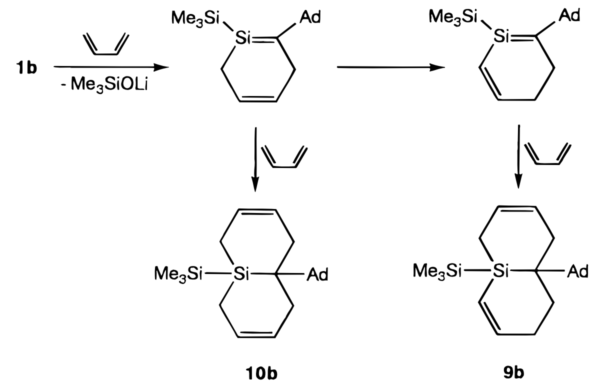


chiometry of the starting materials were unsuccessful. In all cases, many volatile products in low yields were produced, together with large amounts of nonvolatile products.

Formation of Silenes from the Reactions of 1a,b with Dienes. When **1a** was treated with excess 2,3-dimethylbutadiene at room temperature, three products, 10-*tert*-butyl-2,3,6,7-tetramethyl-9-(trimethylsilyl)-9-silabicyclo[4.4.0]deca-2,6-diene (**6a**), 2-*tert*-butyl-4,5-dimethyl-1-(3-methyl-2-methylenebut-3-enyl)-1-(trimethylsilyl)-1-silacyclohex-4-ene (**7a**), and 2-*tert*-butyl-4,5-dimethyl-2-[pivaloylbis(trimethylsilyl)silyl]-1-(trimethylsilyl)-1-silacyclohex-4-ene (**8a**) were obtained in 21%, 38%, and 5% yields, respectively, as shown in Scheme 3. The structures of the products **6a**, **7a**, and **8a** were verified by spectrometric analysis (see Experimental Section). The IR spectrum of **8a** reveals an absorption band at 2135 cm^{-1} due to the stretching frequencies of an Si−H bond, indicating that the (pivaloyl)bis(trimethylsilyl)silyl group is attached to the C2 carbon but not to the silicon atom.

The formation of products **6a** and **7a** can be best understood in terms of Peterson-type olefination of the lithium silacyclohexenolate arising from [2 + 4] cycloaddition of **1a** and 2,3-dimethylbutadiene, producing a cyclic silene intermediate (Scheme 4). The silene thus formed would react with 2,3-dimethylbutadiene to give **6a** and **7a**. For **8a**, addition of lithium silenolate **1a** to the silene arising from Peterson-type olefination would be involved. Usually, addition of the anion in organolithium reagents and Grignard reagents to silenes occurs at the silicon atom but not at the carbon atom,[5b,6] reflecting the smaller electron negativity of silicon compared to that of carbon. Interaction of carbonyl oxygen of **1a** with the silene silicon atom to form the five-membered-ring transition state seems to be the reason for addition of **1a** to the silene carbon atom but not to the silicon atom. Interactions of electron-donating molecules with silenes have been reported previously.[7]

Scheme 5



The reaction of **1b** with 2,3-dimethylbutadiene proceeded in a fashion similar to that for **1a** to give 10-adamantyl-2,3,6,7-tetramethyl-9-(trimethylsilyl)-9-silabicyclo[4.4.0]deca-2,6-diene (**6b**) and 2-adamantyl-4,5-dimethyl-1-(3-methyl-2-methylenebut-3-enyl)-1-(trimethylsilyl)-1-silacyclohex-4-ene (**7b**) in 29% and 21% yields, respectively. In this reaction, no product analogous to **8a** was detected.

The reaction of **1b** with butadiene under the same conditions gave the products 10-adamantyl-9-(trimethylsilyl)-9-silabicyclo[4.4.0]deca-1,6-diene (**9b**) and 10-adamantyl-9-(trimethylsilyl)-9-silabicyclo[4.4.0]deca-2,6-diene (**10b**) in 23% and 13% yields, respectively. Again, intermediacy of a cyclic silene would be involved in this system (Scheme 5). Unfortunately, all attempts to separate **9b** from **10b** were unsuccessful. Therefore, the structures of **9b** and **10b** were verified by spectrometric analysis of the mixture (see Experimental Section). Compound **10b** is probably produced from [2 + 4] cycloaddition of the silene with butadiene, analogous to **6a**,**b**, while migration of a carbon−carbon double bond in the silacyclohexa-1,4-diene ring to the 1,3-diene system would be involved for the formation of **9b**. In this reaction, many products in less than 5% yields and a large amount of nonvolatile products were also formed. This may be due to the decomposition of products **9b** and **10b** in the reaction system. In fact, standing the mixture of **9b** and **10b** in air at room temperature resulted in the formation of large amounts of nonvolatile substances.

Similar treatment of **1a**,**b** with an excess of 1,3-pentadiene at room temperature afforded no volatile products but gave nonvolatile products.

X-ray Structure Analysis of 6b. The structure of **6b** was determined by a single-crystal X-ray diffraction

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(6) (a) Brook, A. G.; Chiu, P.; McClenaghnan, J.; Lough, A. J. *Organometallics* **1991**, *10*, 3292. (b) Luderer, F.; Reinke, H.; Oehme, H. *J. Organomet. Chem*. **1996**, *510*, 181.

(7) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 17.

(8) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, Chapter 3.

Table 1. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 6b

mol formula	$C_{26}H_{44}Si_2$
mol wt	412.81
space group	$P2_1/a$
cell dimens	
a, Å	10.788(1)
b, Å	15.990(2)
c, Å	14.549(1)
α, deg	90.0
β, deg	96.137(8)
γ, deg	90.0
V, Å^3	2495.2(4)
D_{calcd}, Mg/m^3	1.099
Z	4
cryst size, mm^3	0.4 × 0.4 × 0.3
cryst color	colorless
μ, mm^{-1}	1.23
diffractometer	Rigaku AFC-6C
temp, K	298
wavelength, Å	1.5418 (Cu Kα)
monochrometer	graphite crystal
scan type	$\omega-2\theta$
scan speed, deg/min	4
scan width, deg	$0 < 2\theta < 126$
diffraction geometry	symmetrical A
range of h,k,l	
h	$-12 \le h \le 12$
k	$0 \le k \le 18$
l	$0 \le l \le 17$
no. of unique reflns	4033
no. of obsd reflns ($\lvert F_o\rvert \ge 3\sigma(F_o)$)	3013
R	0.060
R_w[a]	0.057

[a] Weighting scheme: $(\sigma(F_o)^2 + 0.0004\lvert F_o\rvert^2)^{-1}$.

Table 2. Bond Lengths (Å) and Angles (deg) for 6b with Their Esd's in Parentheses

Bond Lengths

Si1−Si2	2.358(1)	Si1−C3	1.927(3)	Si1−C7	1.892(4)
Si1−C11	1.888(4)	Si2−C16	1.862(7)	Si2−C17	1.860(6)
Si2−C18	1.868(6)	C3−C4	1.569(5)	C3−C8	1.571(5)
C3−C19	1.574(4)	C4−C5	1.512(5)	C5−C6	1.319(6)
C5−C12	1.525(8)	C6−C7	1.504(6)	C6−C13	1.520(6)
C8−C9	1.517(5)	C9−C10	1.324(5)	C9−C14	1.500(6)
C10−C11	1.507(5)	C10−C15	1.507(6)	C19−C20	1.539(5)
C19−C21	1.534(5)	C19−C22	1.554(5)	C20−C23	1.534(5)
C21−C25	1.535(5)	C22−C27	1.539(5)	C23−C24	1.527(5)
C23−C28	1.530(6)	C24−C25	1.525(5)	C25−C26	1.535(6)
C26−C27	1.525(6)	C27−C28	1.514(6)		

Bond Angles

Si2−Si1−C3	129.0(1)	Si2−Si1−C7	107.0(1)
Si2−Si1−C11	104.9(1)	C3−Si1−C7	103.3(2)
C3−Si1−C11	103.4(2)	C7−Si1−C11	108.0(2)
Si1−Si2−C16	117.9(2)	Si1−Si2−C17	113.1(2)
Si1−Si2−C18	103.8(3)	C16−Si2−C17	107.8(3)
C16−Si2−C18	107.3(4)	C17−Si2−C18	106.1(3)
Si1−C3−C4	105.6(2)	Si1−C3−C8	106.3(2)
Si1−C3−C19	116.4(2)	C4−C3−C8	105.9(3)
C4−C3−C19	112.2(3)	C8−C3−C19	109.9(2)
C3−C4−C5	118.0(3)	C4−C5−C6	119.7(4)
C4−C5−C12	115.2(4)	C6−C5−C12	125.0(4)
C5−C6−C7	119.3(3)	C5−C6−C13	124.9(4)
C7−C6−C13	115.8(4)	Si1−C7−C6	110.4(3)
C3−C8−C9	115.7(3)	C8−C9−C10	120.1(3)
C8−C9−C14	115.3(3)	C10−C9−C14	124.6(4)
C9−C10−C11	119.4(3)	C9−C10−C15	124.2(4)
C11−C10−C15	116.3(3)	Si1−C11−C10	108.3(3)
C3−C19−C20	110.6(3)	C3−C19−C21	111.2(2)
C3−C19−C22	113.1(3)	C20−C19−C21	107.8(3)
C20−C19−C22	106.9(3)	C21−C19−C22	106.9(3)
C19−C20−C23	111.7(3)	C19−C21−C25	112.3(3)
C19−C22−C27	111.0(3)	C20−C23−C24	110.4(3)
C20−C23−C28	108.7(3)	C24−C23−C28	109.9(3)
C23−C24−C25	108.7(3)	C21−C25−C24	109.9(3)
C21−C25−C26	108.7(3)	C24−C25−C26	109.7(3)
C25−C26−C27	109.0(3)	C22−C27−C26	109.4(3)
C22−C27−C28	109.8(3)	C26−C27−C28	110.2(4)
C23−C28−C27	109.2(3)		

study. Cell dimensions, data collection and refinement parameters, and selected bond lengths and angles for **6b** are summarized in Tables 1 and 2. ORTEP views of **6b** are presented in Figure 2, along with the atom-numbering scheme. As shown in Figure 2, the crystal structure of **6b** involves a 9-siladecalin-2,6-diene system, composed of two boat-shaped silacyclohexene rings. The trimethylsilyl and adamantyl groups are located in a cis fashion with respect to the central Si−C bond. Although all bond distances and angles for compound **6b** shown in Table 2 are accepted values, the central Si−C bond (1.927 Å) is slightly longer than the standard values (1.87 Å),[8] presumably due to the steric repulsion between the trimethylsilyl and adamantyl groups.

Experimental Section

General Methods. All reactions were carried out in the dark under an atmosphere of purified argon. NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer. Mass spectra were measured on a Shimadzu QP-1000 spectrometer. Exact mass spectra were measured on a Hitachi M-80B spectrometer. Yields were calculated on the basis of acyltris(trimethylsilyl)silanes used.

Materials. THF was dried over sodium−potassium alloy and distilled just before use. Lithium silenolates **1a**−**c** were prepared from the reactions of (tris(trimethylsilyl)silyl)lithium with the corresponding acyltris(trimethylsilyl)silanes as reported previously.[3]

Reaction of 1a with Butadiene. To a mixture of **1a** prepared from 0.5257 g (1.5737 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 3.6 mL of THF was added 1.1 g (20.3 mmol) of butadiene at −93 °C. The resulting mixture was stirred for 16 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC, using 38.9 mg (0.2734 mmol) of decane as an internal standard, as being **2a** (94% yield). Product **2a** was isolated by preparative GLC: Mp 75.5−76.0 °C; MS m/z 314 (M^+); ^1H NMR (δ in C_6D_6) 0.19 (s, 9H, Me_3Si), 0.26 (s, 9H, Me_3Si), 1.03 (s, 10H, *t*-Bu and OH), 1.34 (dd, 1H, H on C6, $^2J_{gem} = 17.8$, $^3J_{H-HC5} = 6.7$ Hz), 1.67 (br d, 1H, H on C6, $^2J_{gem} = 17.8$ Hz), 2.11 (ddd, 1H, H on C3, $^2J_{gem} = 18.2$, $^3J_{H-HC4} = 5.6$ Hz, $^4J_{H-HC5} = 1.2$ Hz), 2.33 (br d, 1H, H on C3, $^2J_{gem} = 18.2$ Hz), 5.47 (ddd, 1H, H on C4, $^3J_{H-HC5} = 10.3$ Hz, $^3J_{H-HC3} = 5.6$, 2.6 Hz), 5.93 (dddd, 1H, H on C5, $^3J_{H-HC4} = 10.3$ Hz, $^3J_{H-HC6} = 6.7$ Hz, $^3J_{H-HC6} = 3.9$, $^4J_{H-HC3} = 1.2$ Hz); ^{13}C NMR (δ in C_6D_6) 0.4, 0.9 (Me_3Si), 8.8 (C6), 27.1 (*t*-Bu), 37.2, (C3), 37.5 (*t*-Bu), 77.2 (C2), 127.5, 127.9 (C4 and C5); ^{29}Si NMR (δ in C_6D_6) −48.2 (Si−$SiMe_3$), −16.3 ($SiMe_3$), −14.2 ($SiMe_3$); IR ν_{O-H} 3587 cm^{-1}; exact MS calculated for $C_{15}H_{34}OSi_3$ (M^+) m/z 314.1910, found m/z 314.1827.

Reaction of 1b with Butadiene. To a mixture of **1b** prepared from 0.6133 g (1.4926 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 5.6 mL of THF was added 1.2 g (22.2 mmol) of butadiene at −92 °C. The resulting mixture was stirred for 18 h at −62 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC, using 22.6 mg (0.1588 mmol) of decane as an internal standard, as being **2b** (87% yield). Product **2b** was isolated

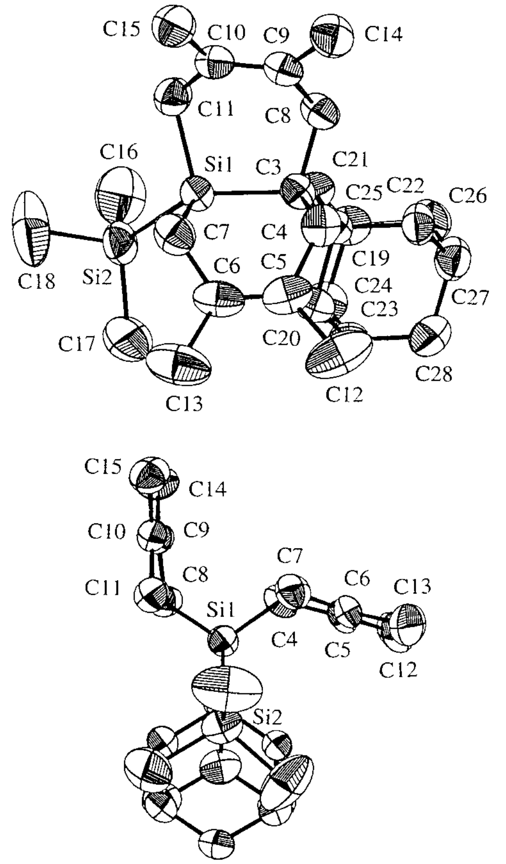

Figure 2. ORTEP drawing of compound **6b** with a top (top) and side view (bottom).

by preparative GLC: Mp 89.0−89.5 °C; MS *m/z* 392 (M^+); ^{1}H NMR (δ in C_6D_6) 0.20 (s, 9H, Me_3Si), 0.27 (s, 9H, Me_3Si), 1.33 (dd, 1H, H on C6, $^2J_{gem} = 17.8$, $^3J_{H-HC5} = 6.7$ Hz), 1.71 (br s, 10H, Ad and H on C6), 1.78 (br d, 4H, Ad, $J = 12.1$ Hz, overlapping with OH proton), 2.02 (br s, 3H, Ad), 2.16 (br dd, 1H, H on C3, $^2J_{gem} = 18.2$, $^3J_{H-HC4} = 5.3$ Hz), 2.35 (br d, 1H, H on C3, $^2J_{gem} = 18.2$ Hz), 5.43−5.45 (m, 1H, H on C4), 5.91−5.95 (m, 1H, H on C5); ^{13}C NMR (δ in C_6D_6) 0.5, 1.0 (Me_3Si), 8.7 (C6), 29.2 (Ad), 35.8, (C3), 37.8, 38.9, 39.1 (Ad), 78.2 (C2), 127.5, 127.8 (C4 and C5); ^{29}Si NMR (δ in C_6D_6) −50.1 (Si−SiMe$_3$), −16.3 ($SiMe_3$), −14.0 ($SiMe_3$); IR ν_{O-H} 3480 cm^{-1}; exact MS calculated for $C_{21}H_{39}OSi_3$ ($M^+ - 1$) *m/z* 391.2306, found *m/z* 391.2278.

Reaction of 1a with 2,3-Dimethylbutadiene. To a mixture of **1a** prepared from 0.744 g (2.24 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 5.0 mL of THF was added 0.24 mL (2.12 mmol) of 2,3-dimethylbutadiene at −80 °C. The resulting mixture was stirred for 7 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC as being **3a** (82% yield). Product **3a** was isolated by preparative GLC: MS *m/z* 342 (M^+); ^{1}H NMR (δ in C_6D_6) 0.21 (s, 9H, Me_3Si), 0.32 (s, 9H, Me_3Si), 1.12 (s, 9H, *t*-Bu), 1.37 (d, 1H, H on C6, $^2J_{gem} = 15.2$ Hz), 1.40 (s, 1H, OH), 1.59 (s, 3H, Me), 1.75 (d, 1H, H on C6, $^2J_{gem} = 15.2$ Hz), 1.77 (s, 3H, Me), 2.10 (d, 1H, H on C3, $^2J_{gem} = 17.2$ Hz), 2.39 (d, 1H, H on C3, $^2J_{gem} = 17.2$ Hz); ^{13}C NMR (δ in C_6D_6) 0.6, 0.8 (Me_3Si), 16.1 (C6), 21.7 (Me), 23.4 (Me), 27.1 (*t*-Bu), 37.3 (C3), 44.3 (*t*-Bu), 78.6 (C2), 126.9, 125.7 (C4 and C5); IR ν_{O-H} 3440 cm^{-1}; exact MS calculated for $C_{17}H_{38}OSi_3$ (M^+) *m/z* 342.2228, found *m/z* 342.2197.

Reaction of 1b with 2,3-Dimethylbutadiene. To a mixture of **1b** prepared from 0.5403 g (1.3149 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 5.4 mL of THF was added 0.149 mL (1.3181 mmol) of 2,3-dimethylbutadiene at −80 °C. The resulting mixture was stirred for 12 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC, using 13.0 mg (0.0655 mmol) of tetradecane as an internal standard, as being **3b** (98% yield). Product **3b** was isolated by preparative GLC: Mp 89.0−89.5 °C; MS *m/z* 420 (M^+); ^{1}H NMR (δ in C_6D_6) 0.25 (s, 9H, Me_3Si), 0.36 (s, 9H, Me_3Si), 1.33 (br d, 1H, H on C6, $^2J_{gem} = 17.3$ Hz), 1.38 (br d, 1H, H on C6, $^2J_{gem} = 17.3$ Hz), 1.62 (s, 3H, Me), 1.76 (br s, 6H, Ad), 1.79 (br s, 4H, Me and OH) 1.82 (br s, 3H, Ad), 1.91 (br d, 3H, Ad, $J = 11.8$ Hz), 2.07 (br t, 3H, Ad, $J = 2.6$ Hz), 2.17 (d, 1H, H on C3, $^2J_{gem} = 17.3$ Hz), 2.42 (d, 1H, H on C3, $^2J_{gem} = 17.3$ Hz); ^{13}C NMR (δ in C_6D_6) 0.6, 1.0 (Me_3Si), 15.9 (C6), 21.8 (Me), 23.7 (Me), 29.3, 37.8, 39.0, 39.1 (Ad), 43.0, (C3), 79.2 (C2), 126.7, 128.5 (C4 and C5); ^{29}Si NMR (δ in C_6D_6) −47.1 (Si−SiMe$_3$), −16.0 ($SiMe_3$), −14.6 ($SiMe_3$); IR ν_{O-H} 3468 cm^{-1}; exact MS calculated for $C_{23}H_{44}OSi_3$ (M^+) *m/z* 420.2842, found *m/z* 420.2770. Anal. Calcd for $C_{23}H_{44}OSi_3$: C, 65.64; H, 10.54. Found: C, 65.72; H, 10.72.

Reaction of 1a with Isoprene. To a mixture of **1a** prepared from 0.588 g (1.770 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 4 mL of THF was added 0.20 mL (2.01 mmol) of isoprene at −89 °C. The resulting mixture was stirred for 16 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC as being **4a** (90% yield). Product **4a** was isolated by preparative GLC: Mp 32.5−33.0 °C; MS *m/z* 328 (M^+); ^{1}H NMR (δ in C_6D_6) 0.18 (s, 9H, Me_3Si), 0.28 (s, 9H, Me_3Si), 1.07 (s, 9H, *t*-Bu), 1.33 (dd, 1H, H on C6, $^2J_{gem} = 17.5$ Hz, $^2J_{H-HC5} = 7.0$ Hz), 1.54 (s, 1H, OH), 1.62 (s, 3H, Me), 1.66 (br d, 1H, H on C6, $^2J_{gem} = 17.5$ Hz), 2.04 (d, 1H, H on C3, $^2J_{gem} = 18.0$ Hz), 2.34 (d, 1H, H on C3, $^3J_{gem} = 18.0$ Hz), 5.70 (br d, 1H, H on C5, $^3J_{H-HC6} = 7.0$ Hz); ^{13}C NMR (δ in C_6D_6) 0.4, 0.8 (Me_3Si), 8.5 (C6), 26.2 (Me), 27.2, 37.4 (*t*-Bu), 42.3 (C3), 77.5 (C2), 121.6 (C5), 134.1 (C4); ^{29}Si NMR (δ in C_6D_6) −49.0 ($SiSiMe_3$), −16.3, −14.4 ($SiMe_3$); IR ν_{O-H} 3588 cm^{-1}; exact MS calculated for $C_{16}H_{35}Si_3$ (M^+ − OH) *m/z* 311.2044, found *m/z* 311.2035.

Reaction of 1b with Isoprene. To a mixture of **1b** prepared from 0.514 g (1.251 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 2 mL of THF was added 0.13 mL (1.25 mmol) of isoprene at −90 °C. The resulting mixture was stirred for 18 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC as being **4b** (83% yield). Product **4b** was isolated by preparative GLC: MS *m/z* 406 (M^+); ^{1}H NMR (δ in C_6D_6) 0.24 (s, 9H, Me_3Si), 0.34 (s, 9H, Me_3Si), 1.37 (dd, 1H, H on C6, $^2J_{gem} = 17.5$ Hz, $^2J_{H-HC5} = 7.0$ Hz), 1.40 (s, 1H, OH), 1.66 (s, 3H, Me), 1.71 (br d, 1H, H on C6, $^2J_{gem} = 17.5$ Hz), 1.75 (s, 6H, Ad), 1.80 (br d, 3H, Ad, $J = 12.1$ Hz), 1.89 (br d, 3H, Ad, $J = 11.9$ Hz), 2.06 (br s, 3H, Ad), 2.12 (d, 1H, H on C3, $^2J_{gem} = 18.1$ Hz), 2.40 (d, 1H, H on C3, $^3J_{gem} = 18.1$ Hz), 5.74 (br d, 1H, H on C5, $^3J_{H-HC6} = 7.0$ Hz); ^{13}C NMR (δ in C_6D_6) 0.5, 0.8 (Me_3Si), 8.3 (C6), 26.2 (Me), 29.2, 37.7, 39.0, 39.1 (Ad), 40.9 (C3), 78.6 (C2), 121.6 (C5), 133.9 (C4); ^{29}Si NMR (δ in C_6D_6) −50.6 ($SiSiMe_3$), −16.2, −14.1 ($SiMe_3$); IR ν_{O-H} 3488 cm^{-1}; exact MS calculated for $C_{22}H_{42}OSi_3$ (M^+) *m/z* 406.2541, found *m/z* 406.2481.

Reaction of 1a with 1,3-Pentadiene. To a mixture of **1a** prepared from 0.568 g (1.710 mmol) of pivaloyltris(trimethylsilyl)silane and an equimoler amount of (tris(trimethylsilyl)-

silyl)lithium in 2 mL of THF was added 0.20 mL (2.01 mmol) of 1,3-pentadiene at −90 °C. The resulting mixture was stirred for 16 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC as being **5a** (91% yield). Attempts to separate *cis*- and *trans*-isomers of **5a** from the mixture were unsuccessful and were analyzed as the mixture. Data for *cis*-**5a**: MS *m/z* 328 (M^+); ^{1}H NMR (δ in C_6D_6) 0.25 (s, 9H, Me_3Si), 0.32 (s, 9H, Me_3Si), 1.06 (d, 3H, Me on C3, $^3J_{H-HC3} = 7.1$ Hz), 1.18 (s, 9H, *t*-Bu), 1.32 (s, 1H, OH), 1.49 (dd, 2H, H on C6, $^3J_{H-HC5} = 5.2$ Hz, $^4J_{H-HC4} = 1.7$ Hz), 2.50 (dq, 1H, H on C3, $^3J_{H-Me} = {}^3J_{H-HC4} = 7.1$ Hz), 5.53 (ddt, 1H, H on C4, $^3J_{H-HC5} = 10.1$ Hz, $^3J_{H-HC3} = 7.1$ Hz, $^4J_{H-HC6} = 1.7$ Hz), 5.90 (dt, 1H, H on C5, $^3J_{H-HC4} = 10.1$ Hz, $^3J_{H-HC6} = 5.2$ Hz); ^{13}C NMR (δ in C_6D_6) 1.2, 1.4 (Me_3Si), 8.7 (C6), 18.9 (Me), 28.7, 38.2 (*t*-Bu), 42.6 (C3), 84.3 (C2), 128.2, 135.0 (C4 and C5); ^{29}Si NMR (δ in C_6D_6) −43.7 ($SiSiMe_3$), −15.4, −12.8 ($SiMe_3$); IR ν_{O-H} 3558 cm^{-1}; exact MS calculated for $C_{16}H_{36}OSi_3$ (M^+) *m/z* 328.2072, found *m/z* 328.2050. Data for *trans*-**5a**: ^{1}H NMR (δ in C_6D_6) 0.26 (s, 9H, Me_3Si), 0.30 (s, 9H, Me_3Si), 1.06 (d, 3H, Me on C3, $^3J_{H-HC3} = 7.0$ Hz), 1.11 (s, 9H, *t*-Bu), 1.32 (s, 1H, OH), 1.36 (ddt, 1H, H on C6, $^2J_{H-HC6} = 16.6$ Hz, $^3J_{H-HC5} = 7.4$ Hz, $^4J_{H-HC4} = {}^5J_{H-HC3} = 0.8$ Hz), 1.66 (ddt, 1H, H on C6, $^2J_{H-HC6} = 16.6$ Hz, $^3J_{H-HC5} = 3.9$ Hz, $^4J_{H-HC4} = {}^5J_{H-HC3} = 2.4$ Hz), 5.30 (dddd, 1H, H on C4, $^3J_{H-HC5} = 11.1$ Hz, $^3J_{H-HC3} = 4.0$ Hz, $^4J_{H-HC6} = 2.4$ and 0.8 Hz), 5.93 (1H, H on C5, overlapping with signals of *cis*-**5a**); ^{13}C NMR (δ in C_6D_6) 0.9, 1.1 (Me_3Si), 8.6 (C6), 18.9 (Me), 28.9, 38.8 (*t*-Bu), 39.5 (C3), 81.2 (C2), 126.8, 136.8 (C4 and C5); ^{29}Si NMR (δ in C_6D_6) −39.4 ($SiSiMe_3$), −15.8, −13.6 ($SiMe_3$).

Reaction of 1b with 1,3-Pentadiene. To a mixture of **1b** prepared from 0.505 g (1.2292 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 2 mL of THF was added 2.00 mL (20.10 mmol) of 1,3-pentadiene at −90 °C. The resulting mixture was stirred for 29 h at −40 °C 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC as being **5b** (66% yield). Product **5b** was isolated by preparative GLC. Attempts to separate *cis*- and *trans*-isomers of **5b** from the mixture were unsuccessful and were analyzed as the mixture. Data for *cis*-**5b**: MS *m/z* 406 (M^+); ^{1}H NMR (δ in C_6D_6) 0.28 (s, 9H, Me_3Si), 0.33 (s, 9H, Me_3Si), 1.12 (d, 3H, Me on C3, $^3J_{H-HC3} = 7.1$ Hz), 1.50 (d, 2H, H on C6, $^3J_{H-HC5} = 5.6$ Hz), 1.76 (s, 6H, Ad), 1.80 (s, 1H, OH), 1.89 (br d, 3H, Ad, $J = 12.7$ Hz), 1.95 (br d, 3H, Ad, $J = 11.7$ Hz), 2.06 (br s, 3H, Ad), 2.60 (dq, 1H, H on C3, $^3J_{H-Me} = {}^3J_{H-HC4} = 7.1$ Hz), 5.53 (ddd, 1H, H on C4, $^3J_{H-HC5} = 10.0$ Hz, $^3J_{H-HC3} = 7.1$ Hz, $^4J_{H-HC6} = 1.2$ Hz), 5.90 (dt, 1H, H on C5, $^3J_{H-HC4} = 10.0$ Hz, $^3J_{H-HC6} = 5.6$ Hz); ^{13}C NMR (δ in C_6D_6) 1.3, 1.7 (Me_3Si), 8.7 (C6), 19.5 (Me), 29.4, 37.7, 39.8, 40.2 (Ad), 41.6 (C3), 84.8 (C2), 128.0 (C5), 135.1 (C4); ^{29}Si NMR (δ in C_6D_6) −46.6 ($SiSiMe_3$), −15.2, −12.7 ($SiMe_3$); IR ν_{O-H} 3542 cm^{-1}; exact MS calculated for $C_{22}H_{42}OSi_3$ (M^+) *m/z* 406.2541, found *m/z* 406.2519 (as a mixture with *trans*-**5b**). Data for *trans*-**5b**: MS *m/z* 406 (M^+); ^{1}H NMR (δ in C_6D_6) 0.28 (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 1.07 (d, 3H, Me on C3, $^3J_{H-HC3} = 7.0$ Hz), 1.30 (dd, 1H, H on C6, $^3J_{gem} = 16.3$ Hz, $^3J_{H-HC5} = 8.2$ Hz), 1.70 (br s, 7H, Ad and H on C6), 1.80 (s, 7H, OH and Ad), 2.02 (s, 3H, Ad), 2.60 (m, 1H, H on C3, overlapping with the signals of *cis*-**5b**), 5.35 (ddd, 1H, H on C4, $^3J_{H-HC5} = 10.4$ Hz, $^3J_{H-HC3} = 4.2$ Hz, $^4J_{H-HC6} = 3.0$ Hz), 5.90 (1H, H on C5, overlapping with the signals of *cis*-**5b**); ^{13}C NMR (δ in C_6D_6) 1.1, 1.5 (Me_3Si), 8.0 (C6), 18.2 (Me), 29.3, 37.4 (Ad), 38.1 (C3), 40.0, 40.9 (Ad), 82.3 (C2), 127.7 (C5), 137.2 (C4); ^{29}Si NMR (δ in C_6D_6) −41.7 ($SiSiMe_3$), −16.0, −13.4 ($SiMe_3$).

Reaction of 1a with 2,3-Dimethylbutadiene at Room Temperature. To a mixture of **1a** prepared from 0.697 g (2.09 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 7.0 mL of THF was added 0.52 mL (4.60 mmol) of 2,3-dimethylbutadiene at −80 °C. The resulting mixture was stirred for 5 h at room temperature and then hydrolyzed with water. After usual workup as above, the products were analyzed by GLC as being **6a** (21% yield), **7a** (38% yield), and **8a** (5% yield). Products **6a**−**8a** were isolated by preparative TLC. Data for **6a**: MS *m/z* 334 (M^+); ^{1}H NMR (δ in C_6D_6) 0.24 (s, 9H, Me_3Si), 1.04 (s, 9H, *t*-Bu), 1.35 (d, 2H, H on C1 and C8, $^2J_{gem} = 15.3$ Hz), 1.42 (d, 2H, H on C1 and C8, $^2J_{gem} = 15.3$ Hz), 1.76 (br s, 12H, Me), 1.91 (d, 2H, H on C4 and C5, $^2J_{gem} = 14.8$ Hz), 2.20 (d, 2H, C4 and C5, $^2J_{gem} = 14.8$ Hz); ^{13}C NMR (δ in C_6D_6) −0.1 (Me_3Si), 18.8 (C1 and C8), 21.7 (Me), 22.1 (Me), 28.7 (C10), 36.2 (*t*-Bu), 40.8 (C4 and C5), 41.8 (C4 and C5), 125.8, 127.7 (C═C). Anal. Calcd for $C_{20}H_{38}Si_2$: C, 71.77; H, 11.44. Found: C, 71.60; H, 11.28. Data for **7a**: MS *m/z* 334 (M^+); ^{1}H NMR (δ in C_6D_6) 0.26 (s, 9H, Me_3Si), 1.03 (s, 1H, H on C2), 1.06 (s, 9H, *t*-Bu), 1.42 (d, 1H, H on C6, $J = 16.3$ Hz), 1.50 (d, 1H, H on C6, $J = 16.3$ Hz), 1.76 (s, 3H, Me), 1.82 (s, 3H, Me), 1.90 (s, 3H, Me), 1.96 (d, 1H, H on C3, $J = 14.2$ Hz), 1.97−2.16 (m, 2H, butenyl HCSi), 2.07 (d, 1H, H on C3, $J = 14.2$ Hz), 4.93 (s, 1H, H_2C═), 5.00 (s, 1H, H_2C═), 5.08 (s, 1H, H_2C═), 5.18 (s, 1H, H_2C═); ^{13}C NMR (δ in C_6D_6) 0.1 (Me_3Si), 19.2 (C6), 20.5 (Me), 21.3 (Me), 22.4 (Me), 22.5 (butenyl CH_2Si), 30.7 (*t*-Bu), 32.9 (C2), 34.4 (C3), 40.3 (*t*-Bu), 111.3, 114.0 (CH_2═), 125.5, 129.0 (C4 and C5), 143.7, 146.1 (C═CH_2); exact MS calculated for $C_{20}H_{38}Si_2$ (M^+) *m/z* 334.2509, found *m/z* 334.2452. Data for **8a**: MS *m/z* 512 (M^+); ^{1}H NMR (δ in C_6D_6) 0.27 (s, 9H, Me_3Si), 0.49 (s, 9H, Me_3Si), 0.58 (s, 9H, Me_3Si), 1.08 (s, 9H, *t*-Bu), 1.17 (s, 9H, *t*-Bu), 1.38 (d, 1H, H on C6, $^2J_{gem} = 17.2$ Hz), 1.64 (s, 3H, Me), 1.72 (s, 3H, Me), 1.75 (d, 1H, H on C6, $J = 17.2$ Hz), 2.45 (d, 1H, H on C3, $^2J_{gem} = 19.5$ Hz), 2.94 (s, 1H, HSi), 2.98 (d, 1H, H on C3 $^2J_{gem} = 19.5$ Hz); ^{13}C NMR (δ in $CDCl_3$) 0.7, 2.9, 3.0 (Me_3Si), 21.4, 21.8, 24.0, 29.4 (*t*-Bu), 30.7, 35.6, 37.5, 47.3, 64.3 (Me and ring CH_2), 128.8, 129.0 (C═C), 221.4 (C═O); IR ν_{Si-H} 2135 cm^{-1}; exact MS calculated for $C_{25}H_{56}Si_5O$ (M^+) *m/z* 512.3174, found *m/z* 512.3131.

Reaction of 1b with 2,3-Dimethylbutadiene at Room Temperature. To a mixture of **1b** prepared from 0.596 g (1.45 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 2.0 mL of THF was added 0.50 mL (4.42 mmol) of 2,3-dimethylbutadiene at −90 °C. The resulting mixture was stirred for 13 h at room temperature 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC, using 0.0108 g (0.0544 mmol) of tetradecane as an internal standard, as being **6b** (29% yield) and **7b** (21% yield). Products **6b** and **7b** were isolated by preparative GPC eluting with benzene. Data for **6b**: Mp 132.0−133.5 °C; MS *m/z* 412 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.15 (s, 9H, Me_3Si), 1.20 (d, 2H, H on C1 and C8, $^2J_{gem} = 14.8$ Hz), 1.28 (d, 2H, H on C1 and C8, $^2J_{gem} = 14.8$ Hz), 1.63−1.66 (m, 12H, Ad), 1.64 (s, 6H, Me), 1.66 (s, 6H, Me), 1.73 (d, 2H, H on C4 and C5, $^2J_{gem} = 15.2$ Hz), 1.96 (br s, 3H, Ad), 2.19 (d, 2H, H on C4 and C5, $^2J_{gem} = 14.5$ Hz); ^{13}C NMR (δ in $CDCl_3$) 0.0 (Me_3Si), 18.6 (C1 and C8), 21.8, 22.2 (Me), 29.0, 37.4, 38.1 (Ad), 39.1 (C4 and C5), 39.6 (Ad), 42.5 (C10), 125.7, 127.5 (C═C); ^{29}Si NMR (δ in $CDCl_3$) −17.6, −15.8. Anal. Calcd for $C_{26}H_{44}Si_2$: C, 75.65; H, 10.74. Found: C, 75.37; H, 10.87. Data for **7b**: Mp 78.5−80.0 °C; MS *m/z* 412 (M^+); ^{1}H NMR (δ in C_6D_6) 0.30 (s, 9H, Me_3Si), 0.88 (dd, 1H, H on C2, $^3J_{H-HC3} = 11.7$ and 4.1 Hz), 1.48 (s, 1H, H on C6), 1.49 (s, 1H, H on C6), 1.55−1.74 (m, 12H, Ad), 1.78 (s, 3H, Me on C4), 1.83 (s, 3H, Me on C5), 1.92 (s, 3H, MeC═), 1.95 (d, 1H, butenyl HCSi, $^2J_{gem} = 13.9$ Hz), 2.01 (br s, 4H, Ad and H on C3), 2.10 (d, 1H, butenyl HCSi, $^2J_{gem} = 13.9$ Hz), 2.13 (dd, 1H, H on C3, $^2J_{gem} = 14.0$ Hz, $^3J_{H-HC2} = 4.1$ Hz), 4.94 (s, 1H, $\mathit{CH}{=}CH_2Si$), 5.02 (s, 1H, $\mathit{CH}{=}CMe$), 5.09 (s, 1H, $\mathit{CH}{=}CH_2Si$), 5.20 (s, 1H, $\mathit{CH}{=}CMe$); ^{13}C NMR (δ in C_6D_6) 0.3 (Me_3Si), 19.0 (C6), 20.5 (Me on C4), 21.3 (butenyl MeC═), 22.4 (Me on C5), 22.8 (butenyl CH_2Si), 29.4 (Ad), 32.0 (C3), 35.1, 37.5 (Ad), 42.1 (C2), 43.3 (Ad), 111.3 ($\mathit{CH_2}{=}CCH_2Si$), 114.1 ($\mathit{CH_2}{=}CMe$), 125.6 (C5), 129.3 (C4), 143.7 (${=}\mathit{C}CH_2Si$), 146.2 (${=}\mathit{C}Me$); ^{29}Si NMR (δ in C_6D_6) −20.4, −16.9. Anal. Calcd for $C_{26}H_{44}Si_2$: C, 75.65; H, 10.74. Found: C, 75.47; H, 10.82.

Reaction of 1b with Butadiene. To a mixture of **1b** prepared from 0.5288 g (1.2869 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 4.9 mL of THF was added 0.3 g (5.55 mmol) of butadiene at −89 °C. The resulting mixture was stirred for 18 h at room temperature 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 and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC using 21.5 mg (0.1511 mmol) decane as an internal standard, as being **9b** (23% yield) and **10b** (13% yield). A mixture of **9b** and **10b** was separated from the residue by preparative GPC eluting with benzene. Attempts to isolate **9b** and **10b** were unsuccessful, and therefore they were analyzed as the mixture. Data for **9b**: MS m/z 356 (M^+); ^{1}H NMR (δ in C_6D_6) 0.31 (s, 9H, Me_3Si), 1.34 −1.41 (br d, 1H, H on C8, overlapping with the signals of **10b**), 1.42 −1.49 (br d, 1H, H on C8, overlapping with the signals of **10b**), 1.54 (dt, 1H, H on C4, $^2J_{gem} = 13.8$ Hz, $^3J_{H-HC3} = 4.1$ Hz),1.63−1.74 (m, 10H, Ad, and H on C4, overlapping with the signals of **10b**), 1.86 (br d, 3H, Ad $J = 12.2$ Hz), 2.01 (s, 3H, Ad), 2.17 (br s, 2H, H on C3), 2.21 (br s, 2H, H on C5), 5.82 (dt, 1H, H on C1, $^3J_{H-HC2} = 13.4$ Hz, $^4J_{H-HC3} = 1.8$ Hz), 5.84−5.86 (m, 2H, H on C6 and C7), 6.70 (dt, 1H, H on C2, $^3J_{H-HC1} = 13.4$ Hz, $^3J_{H-HC3} = 3.5$ Hz); ^{13}C NMR (δ in C_6D_6) −0.5 (Me_3Si), 12.4 (C9), 28.6 (C4), 28.7 (C5), 29.3 (C3), 29.5 (Ad), 33.2 (C10), 37.7 (Ad), 38.6 (Ad), 39.1 (Ad), 126.3 (C6), 127.0 (C1), 130.9 (C7), 146.9 (C2); ^{29}Si NMR (δ in C_6D_6) −17.3, −34.7; exact MS calculated for $C_{22}H_{36}Si_2$ m/z 356.2510, found m/z 356.2432 (as a mixture with **10b**). Data for **10b**: MS m/z 356 (M^+); ^{1}H NMR (δ in C_6D_6) 0.26 (s, 9H, Me_3Si), 1.39−1.44 (m, 4H, H on C1 and C8, overlapping with the signals of **9b**), 1.63−1.74 (m, 9H, Ad, overlapping with the signals of **9b**), 2.01 (br s, 3H, Ad, overlapping with the signals of **9b**), 2.02 (br d, 2H, H on C4 and C5, $^2J_{gem} = 17.5$ Hz), 2.30 (br d, 2H, H on C4 and C5, $^2J_{gem} = 17.5$ Hz), 5.65−5.70 (m, 2H, olefinic protons), 5.84−5.86 (m, 2H, olefinic protons overlapping with the signals of **9b**); ^{13}C NMR (δ in C_6D_6) −0.4 (Me_3Si), 11.9 (C1), 29.4 (Ad), 32.8 (C4), 35.2 (C10), 37.6 (Ad), 38.7 (Ad), 39.6 (Ad), 125.1, 130.6 (C═C); ^{29}Si NMR (δ in C_6D_6) −27.0, −16.5.

X-ray Crystallographic Analysis of 6b. All unique diffraction maxima with $0 < 2\theta < 126.0°$ were recorded on a Rigaku AFC-6C automated four-circle diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). A total of 3013 observed reflections for **6b** ($I > 3\sigma(I)$) were used in the least-squares refinement. The structures were solved by Monte-Carlo direct methods[9] using the MULTAN 78 program system[10] and refined by the full-matrix least-squares program.[11] Atomic scattering factors were taken ref 12. All computations were performed on the HITAC M-680/180E system at the Information Processing Center of Hiroshima University using the CRYSTAN program system.[13] Anisotropic temperature factors were used for refinement of non-hydrogen atoms. Finally, R and R_w factors of 0.060 and 0.057 were obtained.

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Supporting Information Available: Tables of atomic coordinates and B values and anisotropic thermal parameters **6b** and ^{1}H and ^{13}C NMR spectra of compounds **2a**,**b**, **3a**, **4a**,**b**, **5a**,**b**, **7a**, **8a**, **9b**, and **10b** (13 pages). Ordering information is given on any current masthead page.

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