

# Reactions of Lithium Silenolates with Carbonyl Compounds

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The chemical behavior of lithium silenolates,  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OLi})\text{R}$  (**1a**, R = Mes; **1b**, R = *t*-Bu), toward carbonyl compounds was studied. Treatment of lithium silenolates **1a** and **1b** with benzaldehyde and then with chlorotriethylsilane afforded products derived from the reactions of the lithium silenolates with 2 equiv of benzaldehyde, followed by coupling of the resulting anions with chlorotriethylsilane, in good yields. Treatment of **1a** and **1b** with mesityl aldehyde under the same conditions proceeded similarly to give the respective adducts in high yields, while the reaction of **1a** with acetophenone gave the adduct only in low yield. Similar reactions of **1a** and **1b** with mesityl methyl ketone, however, afforded no adducts but produced lithium 1-mesitylethenolate and the respective acylbis(trimethylsilyl)silanes.

## Introduction

Metal enolates have been extensively investigated and frequently used as synthetic tools in organic chemistry.<sup>1</sup> In the course of our studies concerning the reactions of acylpolysilanes with organolithium reagents,<sup>2</sup> we have found that the reactions of acyltris(trimethylsilyl)silanes with silyllithium reagents proceed with replacement of a trimethylsilyl group by lithium to give the corresponding lithium 1-silen-2-olates, including the first stable silicon analogs of lithium enolates.<sup>4</sup> These reactions afforded the respective lithium silenolates in almost quantitative yields, if the starting acyltris(trimethylsilyl)silanes have a sterically bulky substituent on the carbonyl carbon atom and involve no enolizable protons. The lithium silenolates, thus, formed react readily with water and alkyl halides at the silicon center to give Si-substituted products in high yields. Interestingly, the reactions of lithium silenolates with chlorotriethylsilane proceed in two ways, depending on the substituent at the carbonyl carbon atom. Lithium silenolates having an alkyl group at the carbonyl carbon react with the chlorosilane at the silicon center to give the corresponding acylpolysilanes by Si-silylation, while lithium silenolates with an aryl substituent undergo O-silylation to give the respective silenenes. These findings are wholly consistent with those of their NMR spectrometry, which shows that the anionic charge is sufficiently delocalized over the Si–C–O unit in the aryl-substituted silenolates, while the anionic charge in the alkyl-substituted silenolates localizes moderately on the central silicon atoms. Quite recently, we have also demonstrated that treatment of lithium silenolates with palladium dichloride gives the oxidative coupling products bis(acyl)-substituted polysilanes.<sup>5</sup>

In an effort to develop the chemistry of the lithium silenolates as new synthetic tools, we studied the reactions of lithium silenolates  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OLi})\text{R}$  (**1a**, R = Mes; **1b**, R = *t*-Bu) with carbonyl compounds.

## Results and Discussion

**Reactions of Lithium Silenolates with Aldehydes.** When lithium 2-mesityl-1,1-bis(trimethylsilyl)-1-silen-2-olate (**1a**) was treated with a mixture consisting of 2.5 equiv of benzaldehyde and 1.5 equiv of chlorotriethylsilane in THF at  $-100^\circ\text{C}$ , (*E*)- and (*Z*)-1-mesityl-2-phenyl-1- $\{[\text{phenyl}(\text{trimethylsiloxy})\text{methyl}]\text{-(triethylsiloxy)}(\text{trimethylsilyl})\text{siloxy}\}$ ethene (**2a/2a'** and **3a/3a'**) were obtained in 44% and 29% yields, respectively (Scheme 1). The diastereomeric mixtures of **2a/2a'** and **3a/3a'** could be separated from the reaction mixture by chromatography on a silica gel column. However, all attempts to separate a diastereomer from the mixtures **2a/2a'** and **3a/3a'** were unsuccessful. Therefore, products **2a/2a'** and **3a/3a'** were characterized by spectrometric and elemental analysis of the mixtures. The diastereomeric ratios of **2a/2a'** and **3a/3a'** obtained from the reaction at  $-100^\circ\text{C}$  were calculated to be 1.1/1 for **2a/2a'** and 14/1 for **3a/3a'**, on the

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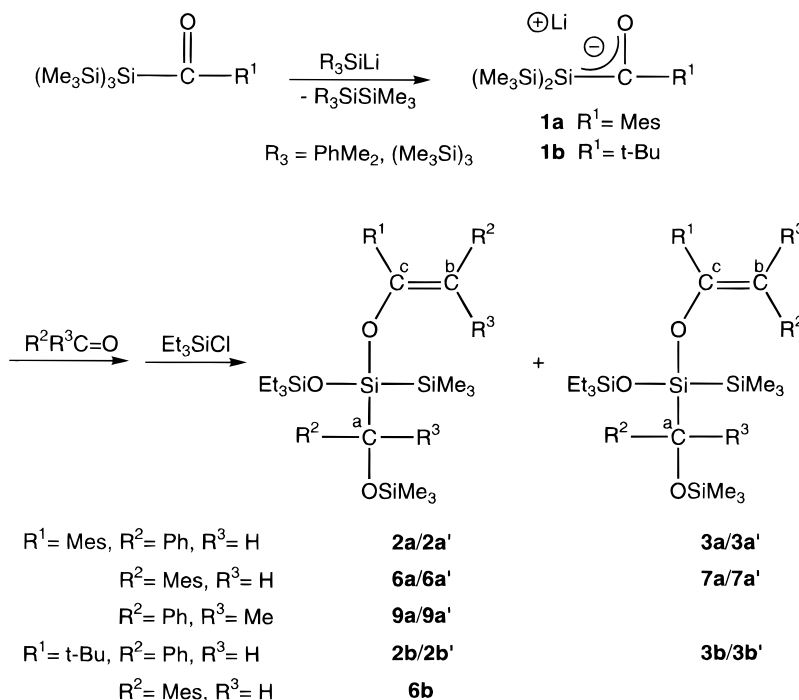
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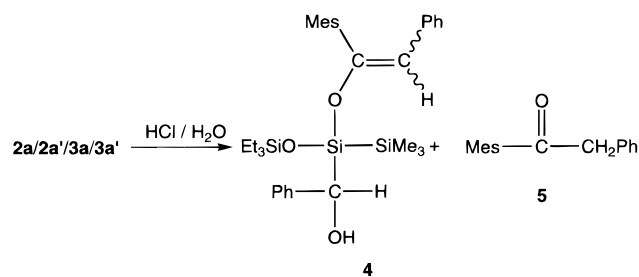
## Scheme 1



basis of the integral ratios in their  $^1\text{H}$  NMR spectra. The diastereomeric ratio for **3a/3a'** decreased with increasing the reaction temperature, and the reaction at  $12^\circ\text{C}$  gave product **3a/3a'** in 24% yield, whose diastereomeric ratio was determined to be 5.0/1, together with a 26% yield of **2a/2a'**, with the ratio of 1.1/1.

The structures of the products were confirmed by spectrometric and elemental analysis. For **3a**, the  $^1\text{H}$ - $^{13}\text{C}$  COSY spectrum shows the coupling of a signal due to an alkoxy methyne proton ( $\text{H}^a$ ) at 4.68 ppm and a carbon signal ( $\text{C}^a$ ) at 73.5 ppm, as well as that of an olefinic proton ( $\text{H}^b$ ) at 5.42 ppm and a carbon signal at 113.3 ppm characteristic of the  $\beta$ -carbon of an enol unit ( $\text{C}^b$ ). The  $^1\text{H}$ - $^{13}\text{C}$  long range COSY spectrum reveals that  $\text{H}^a$  couples with  $\text{C}^a$  and ortho carbon atoms on a phenyl ring ( $\text{Ph}^a$ ), indicating the presence of a  $\text{Ph}^a\text{H}^a\text{C}^a\text{O}$ - unit. In this spectrum, couplings of  $\text{H}^b$  with ortho carbon atoms of the other phenyl group ( $\text{Ph}^b$ ) and those of the mesityl ring protons with  $\text{C}^c$  are also observed, indicating the presence of a  $\text{Ph}^b(\text{H}^b)\text{C}^b=\text{C}^c(\text{Mes})\text{O}$ - fragment.  $^{29}\text{Si}$  NMR spectrometric analyses, including  $^1\text{H}$ - $^{29}\text{Si}$  COSY experiments for **3a**, indicate the presence of a  $\text{Me}_3\text{SiSi}$ -,  $\text{Me}_3\text{SiO}$ -, and  $\text{Et}_3\text{SiO}$ - unit. These results are wholly consistent with the structure proposed for **3a**. Although two-dimensional NMR spectrometry could not be carried out for **3a'**, due to its low yield, all of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals of **3a'** are observed in the same region as those of **3a**, indicating that **3a'** must have the same skeletal structure as that of **3a**. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra for **2a/2a'** are quite similar to those of **3a/3a'**, except for the signals due to an olefinic proton ( $\text{H}^b$ ) of **2a** and **2a'** which appear at lower field by approximately 1 ppm than those of **3a** and **3a'**, indicating that **2a/2a'** and **3a/3a'** have the same skeletal structure with a different geometry on the olefin moiety. The presence of a  $\text{Ph}^a\text{H}^a\text{C}^a\text{O}$ - and  $\text{Ph}^b(\text{H}^b)\text{C}^b=\text{C}^c\text{O}$ - unit in **2a** and **2a'** was also confirmed by two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  NMR experiments, although unlike **3a**, the location of the mesityl group can not be confirmed. The geometries

## Scheme 2

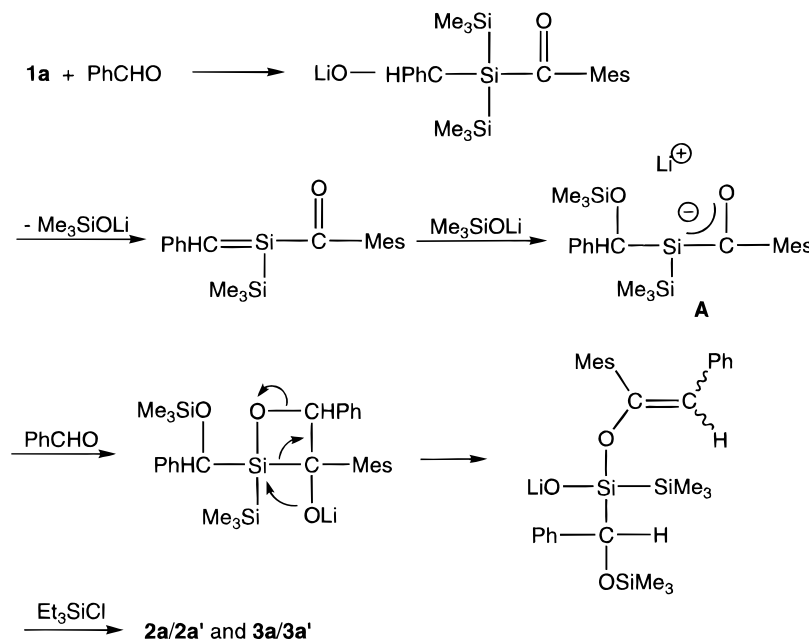


of the enol unit in **2a/2a'** and **3a/3a'** were confirmed by their  $^1\text{H}$ - $^1\text{H}$  NOESY spectra. Thus, for **2a/2a'**,  $\text{H}^a$  couples with trimethylsilyl protons while  $\text{H}^b$  couples with trimethylsilyloxy protons. For **3a/3a'**, couplings of  $\text{H}^a$  with trimethylsilyl and trimethylsiloxy protons and those of  $\text{H}^b$  with mesityl methyl protons are observed.

We carried out the hydrolysis of **2a/2a'** and **3a/3a'** to confirm their structures. Thus, when an ether solution of the mixture of **2a/2a'/3a/3a'** in a ratio of 9/8/14/1 was treated with a 3 N HCl aqueous solution at room temperature, 1-mesityl-2-phenyl-1-[(hydroxyphenylmethyl)-(triethylsiloxy)(trimethylsilyl)siloxy]ethane (**4**) and benzyl mesityl ketone (**5**) were obtained in 28% and 33% yields, respectively (Scheme 2). Although compound **4** was obtained as a single isomer, evidence for the geometry of this olefin has not been obtained at present. The formation of **5** clearly indicates the presence of a 1-mesityl-2-phenylethenoxy unit in **2a/2a'** and **3a/3a'**.

All attempts to prepare a 1:1 adduct of **1a** and benzaldehyde by changing the stoichiometry of the starting materials and the reaction conditions were unsuccessful. For example, when **1a** was treated with a mixture consisting of 1.5 equiv of benzaldehyde and 1 equiv of chlorotriethylsilane at  $-80^\circ\text{C}$ , a 1:1 mixture of **2a/2a'** and **3a/3a'** in the diastereomeric ratios of 1.7/1 and 3.5/1 was obtained in 32% yield. In this reaction, no other volatile products were observed by either gas-liquid chromatography (GLC) or gel permeation chroma-

Scheme 3



tography (GPC) analysis of the reaction mixture, but large amounts of nonvolatile products were produced.

The formation of **2a/2a'** and **3a/3a'** can be explained by a series of reactions, including addition of lithium silenolate **1a** across the C–O double bond of benzaldehyde to produce a lithium alkoxide as the initial step, as shown in Scheme 3. Peterson-type elimination of trimethylsilyloxy lithium producing a silenone intermediate, followed by addition of trimethylsilyloxy lithium to the resulting silenone, gives a lithium silenolate intermediate (**A**). Silenolate **A** reacts with another molecule of benzaldehyde in a [2 + 2] cycloaddition fashion to give the four-membered ring. The different chemical behavior of silenolate **A** toward benzaldehyde from that of **1a**, which is proposed to react with benzaldehyde as a nucleophile in the first step, may be explained in terms of substitution of the central silicon atom with a bulky substituent. Replacement of a trimethylsilyl group in lithium silenolate **1a** with the bulkier ( $\alpha$ -trimethylsilyloxy)benzyl group in **A** might increase the  $sp^2$  character of the central Si–C bond of **A**. Consequently, intermediate **A** is expected to react with benzaldehyde as a silene, rather than silyllithium, to give the cycloaddition product. Ring opening of the resulting four-membered compound produces a siloxylithium, which reacts with chlorotriethylsilane to give **2a/2a'** and **3a/3a'**. Peterson-type olefination leading to the formation of silenes<sup>2,3</sup> and cycloaddition of lithium silenolates have been reported previously.<sup>6</sup>

Recently, we have demonstrated that treatment of **1a** with chlorotriethylsilane affords 2-(triethylsilyloxy)-2-mesityl-1,1-bis(trimethylsilyl)silene by O-silylation.<sup>4</sup> Therefore, one might consider the possibility that the formation of a silene arising from **1a** and chlorotriethylsilane is involved in the initial step, and the silene, thus, formed reacts with benzaldehyde to give **2a/2a'** and **3a/3a'**. However, when we carried out the reaction of **1a** with benzaldehyde at  $-81^\circ\text{C}$  in the absence of

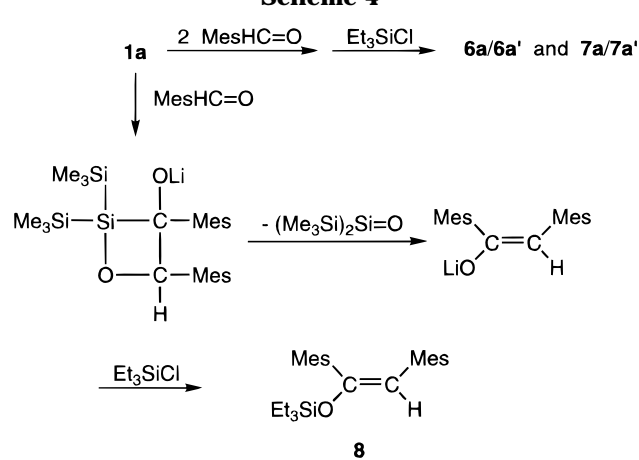
chlorotriethylsilane and analyzed the resulting mixture by GLC, almost all of the starting **1a** was found to be consumed at this stage. Addition of chlorotriethylsilane to the mixture led to the formation of **2a/2a'** and **3a/3a'** in 40% and 32% yields, respectively, in good agreement with the mechanism proposed.

Similarly, treatment of lithium 2-*tert*-butyl-1,1-bis(trimethylsilyl)-1-silen-2-olate (**1b**) with benzaldehyde and then chlorotriethylsilane under the same conditions gave (*E*)- and (*Z*)-1-*tert*-butyl-2-phenyl-1-[[phenyl-(trimethylsilyloxy)methyl](triethylsilyloxy)(trimethylsilyloxy)ethene (**2b/2b'** and **3b/3b'**) in 29% and 30% yields, respectively (see Scheme 1). The structures of **2b/2b'** and **3b/3b'** were verified by spectrometry (see Experimental Section). The diastereomeric ratios for **2b/2b'** and **3b/3b'** were determined to be 3.5/1 and 1.2/1, on the basis of the integral ratios in their  $^1\text{H}$  NMR spectra. The formation of products **2b/2b'** and **3b/3b'** can be understood in terms of a similar mechanism to that of **2a/2a'** and **3a/3a'**. The production of these compounds indicates that the reaction course with benzaldehyde is not affected by the substituent at the carbonyl carbon atom in the lithium silenolates, in contrast to the reactions of lithium silenolates with chlorotriethylsilane.<sup>4b</sup>

Next, we carried out the reactions of **1a** and **1b** with mesityl aldehyde in the hope of obtaining 1:1 addition products. However, when **1a** was treated with 2.2 equiv of mesityl aldehyde and then 1.2 equiv of chlorotriethylsilane at  $-92^\circ\text{C}$ , (*E*)- and (*Z*)-1,2-dimesityl-1-[[mesityl-(trimethylsilyloxy)methyl](triethylsilyloxy)(trimethylsilyloxy)ethene (**6a/6a'** and **7a/7a'**) were obtained in 24% and 37% yields, respectively, with diastereomeric ratios of 3.1/1 for **6a/6a'** and 6.6/1 for **7a/7a'** (Schemes 1 and 4). In this reaction, (*E*)-1,2-dimesityl(triethylsilyloxy)ethene (**8**) was also obtained in 14% yield. The (*E*)-geometry of **8** was confirmed by nuclear Overhauser effect-free induction decay (NOE-FID) difference experiments at 270 MHz. The formation of **8** clearly indicates that [2 + 2] cycloaddition of **1a** and mesityl aldehyde leading to a four-membered ring intermediate

(6) (a) Bravo-Zhivotovskii, D.; Apeloig, Y.; Ovchinnikov, Y.; Igonin, V.; Struchkov, Y. T. *J. Organomet. Chem.* **1993**, *446*, 123. (b) Ohshita, J.; Masaoka, S.; Sano, M. H.; Ishikawa, M. *Organometallics*, in press.

Scheme 4

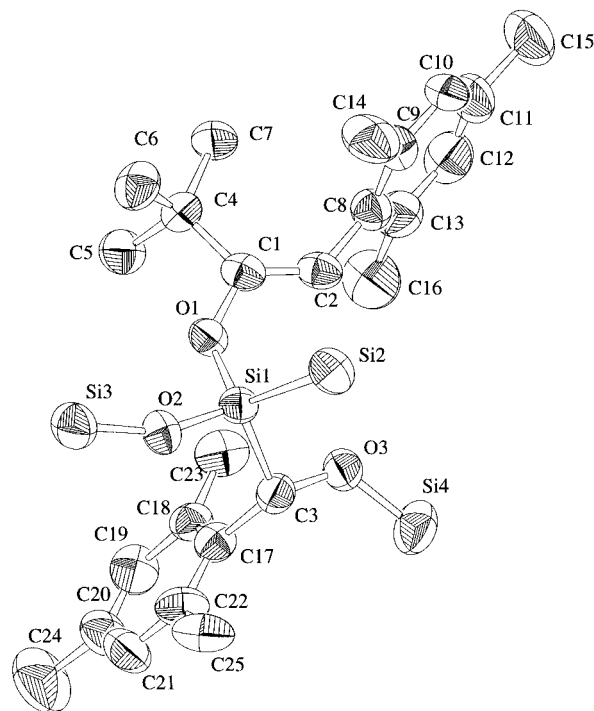


is involved in this reaction, as shown in Scheme 4. The four-membered ring system would split into two fragments, giving lithium 1,2-dimesitylenolate, which reacts with chlorotriethylsilane to afford compound **8** and bis(trimethylsilyl)silane. Similar [2 + 2] cyclodimerization of lithium silenolates has been reported previously.<sup>4b,6a</sup>

The reaction of **1b** with mesityl aldehyde, followed by quenching with chlorotriethylsilane, gave (*E*)-1-*tert*-butyl-2-mesityl-1-[mesityl(trimethylsilyloxy)methyl]-(triethylsilyloxy)(trimethylsilyl)siloxy}ethene (**6b**) in 51% yield as a single isomer. In this reaction, no products analogous to **7a/7a'** and **8** were detected by GLC analysis of the reaction mixture. The crystal structure of compound **6b** was determined by an X-ray diffraction study. The asymmetric unit contains two crystallographically independent and essentially identical molecules. An ORTEP drawing of one of them is depicted in Figure 1. Cell dimensions, data collection and refinement parameters, and selected bond distances and angles are given in Tables 1 and 2.

**Reactions with Acetophenone and Mesityl Methyl Ketone.** In contrast to the reactions of lithium silenolates with benzaldehyde and mesityl aldehyde, which gave the respective adducts in high yields, the reaction of **1a** with acetophenone gave adduct **9a/9a'** with a diastereomeric ratio of 2.7/1 in only 13% yield. In this reaction, many volatile products in less than 5% yields and large amounts of nonvolatile products were formed, indicating that reactions other than the addition of **1a** to the ketone are involved. The reaction of **1a** with a mixture of acetone and chlorotriethylsilane at -80 °C in THF also gave a complex mixture. Although many products were produced in less than 5% yields, no products arising from addition of **1a** to acetone were detected by GLC and high-pressure liquid chromatography (HPLC) analysis of the reaction mixture.

In order to learn more about the reactions of lithium silenolates with enolizable ketones, we carried out the reaction of **1a** with mesityl methyl ketone. Interestingly, it was found that the reaction proceeded in a quite different fashion from those with aldehydes to give mesitylbis(trimethylsilyl)silane (**10a**) and mesityl-1-(triethylsilyloxy)ethene (**11**) in 41% and 93% yields, respectively (Scheme 5). The result clearly shows that the H-Li exchange reaction between **1a** and the enolizable ketone occurs. The lower yield of **10a** than that of **11** may be ascribed to some decomposition of **10a**



**Figure 1.** ORTEP drawing of a molecular fragment of compound **6b**. Alkyl groups on the silicon atoms are omitted for clarity.

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

|  |   |
|--|---|
| mol formula  | C <sub>37</sub> H <sub>64</sub> Si <sub>4</sub> |
| mol wt   | 669.25  |
| space group  | P2 <sub>1</sub> /n                              |
| cell dimens  |   |
| <i>a</i> , Å   | 21.768 (6)                                      |
| <i>b</i> , Å   | 11.275 (5)                                      |
| <i>c</i> , Å   | 35.260 (6)                                      |
| α, deg   | 90.0  |
| β, deg   | 97.97 (2)                                       |
| γ, deg   | 90.0  |
| <i>V</i> , Å <sup>3</sup>  | 8570 (4)  |
| <i>Z</i>   | 8   |
| <i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>                            | 1.297   |
| <i>F</i> (000)   | 3660  |
| cryst size, mm <sup>3</sup>  | 0.8 × 0.4 × 0.1                                 |
| cryst color  | colorless                                       |
| μ, mm <sup>-1</sup>  | 1.886   |
| diffractometer   | Rigaku AFC-6C                                   |
| temp, K  | 298   |
| wavelength, Å  | 1.5418 (Cu Kα)                                  |
| monochromator  | graphite crystal                                |
| scan type  | ω-2θ  |
| scan speed, deg/min  | 4   |
| scan width, deg  | 0 < 2θ < 125.9                                  |
| diffractometer geometry  | symmetrical A                                   |
| range of <i>h</i> , <i>k</i> , <i>l</i>                                  |   |
| <i>h</i>   | 0 ≤ <i>h</i> ≤ 25                               |
| <i>k</i>   | 0 ≤ <i>k</i> ≤ 13                               |
| <i>l</i>   | -41 ≤ <i>l</i> ≤ 41                             |
| no. of unique reflns   | 13 407  |
| no. of obsd reflns ( <i> F<sub>o</sub></i> ≥ 3σ( <i>F<sub>o</sub></i> )) | 4893  |
| <i>R</i>   | 0.073   |
| <i>R</i> <sub>w</sub> <sup>a</sup>                                       | 0.074   |

<sup>a</sup> Weighting scheme is (σ(*F<sub>o</sub>*)<sup>2</sup> + 0.0004|*F<sub>o</sub>*|<sup>2</sup>)<sup>-1</sup>.

under the conditions used. The reaction of **1b** with mesityl methyl ketone proceeded in a similar fashion to that of **1a** to give bis(trimethylsilyl)pivaloylsilane (**10b**) and **11** in 75% and 68% yields, respectively.

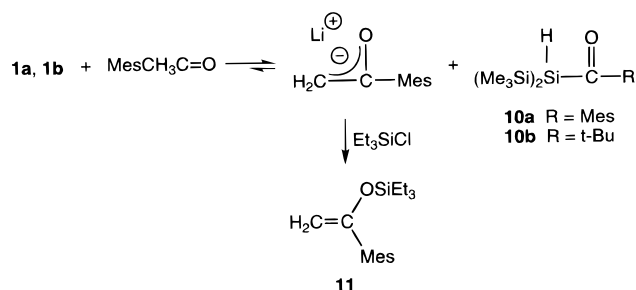
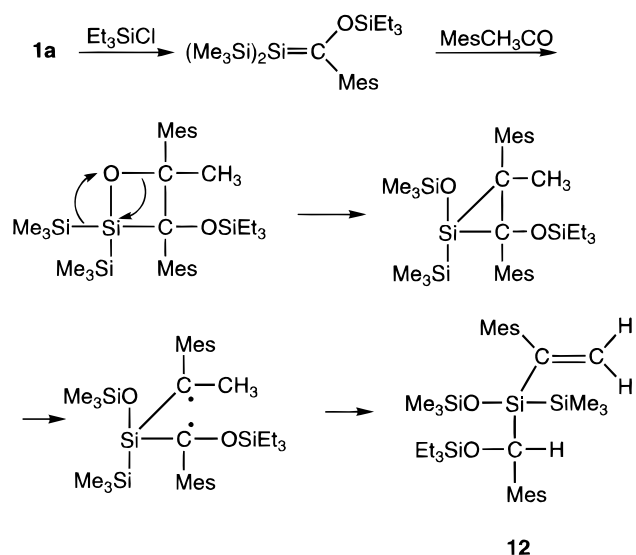
When **1a** was treated with a mixture of mesityl methyl ketone and chlorotriethylsilane, 1-mesityl-1-[mesityl(trimethylsilyloxy)methyl]-1-(trimethylsilyloxy)-

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

| Bond Lengths |          |        |          |        |          |
|--------------|----------|--------|----------|--------|----------|
| Si1-Si2      | 2.352(4) | Si1-O1 | 1.640(7) | Si1-O2 | 1.626(7) |
| Si1-C3       | 1.91(1)  | Si3-O2 | 1.633(8) | Si4-O3 | 1.650(7) |
| O1-C1        | 1.39(1)  | O3-C3  | 1.44(1)  | C1-C2  | 1.33(1)  |
| C1-C4        | 1.54(1)  | C2-C8  | 1.48(1)  | C3-C17 | 1.53(1)  |

| Bond Angles |          |            |           |
|-------------|----------|------------|-----------|
| Si2-Si1-O1  | 118.0(3) | Si2-Si1-O2 | 106.5(3)  |
| Si2-Si1-C3  | 108.2(3) | O1-Si1-O2  | 105.0(4)  |
| O1-Si1-C3   | 112.2(4) | O2-Si1-C3  | 106.2(4)  |
| Si1-O1-C1   | 133.4(7) | Si1-O2-Si3 | 157.0(5)  |
| Si4-O3-C3   | 124.7(6) | O1-C1-C2   | 119.7(10) |
| O1-C1-C4    | 110.6(9) | C2-C1-C4   | 129(1)    |
| C1-C2-C8    | 130(1)   | Si1-C3-O3  | 107.1(7)  |
| Si1-C3-C17  | 117.1(7) | O3-C3-C17  | 115.9(8)  |

**Scheme 5****Scheme 6**

trimethyldisilanyl}ethene (**12**) was obtained in 90% yield (Scheme 6). The same product was obtained in 95% yield by a two-step addition, first chlorotriethylsilane and then mesityl methyl ketone, to a THF solution of **1a**. The structure of **12** was verified by spectrometric and elemental analysis. The  $^1\text{H}$ - $^{13}\text{C}$  NMR COSY experiments for compound **12** show the presence of a HC-OR and  $\text{H}_2\text{C}=\text{C}$  unit. The  $^1\text{H}$ - $^{13}\text{C}$  long range COSY NMR spectrum reveals couplings of the alkoxy methyne proton with ring carbons of a mesityl group and those of the olefinic protons with the other mesityl ring carbons.  $^{29}\text{Si}$  NMR spectrometric analysis, including  $^1\text{H}$ - $^{29}\text{Si}$  COSY experiments, indicates the presence of  $\text{SiSiMe}_3$ ,  $\text{Me}_3\text{SiO}$ , and  $\text{Et}_3\text{SiO}$  units. These results are wholly consistent with the structure proposed for compound **12**. The formation of **12** can be explained by [2 + 2] cycloaddition of the silene formed from the reaction of **1a** with chlorotriethylsilane

with mesityl methyl ketone, followed by ring contraction of the resulting four-membered cyclic intermediate, leading to the silacyclopropane derivative, and then homolytic scission of a carbon-carbon bond in the three-membered ring.

**Experimental Section**

**General.** 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.

**Materials.** THF was dried over sodium-potassium alloy and distilled just before use. Lithium silenolates **1a** and **1b** were prepared as reported in the literature.<sup>4b</sup> Yields were calculated on the basis of the acyltris(trimethylsilyl)silane used.

**Reaction of 1a with Benzaldehyde.** To a solution of **1a** prepared from 0.388 g (0.981 mmol) of mesityltris(trimethylsilyl)silane and an equimolar amount of dimethylphenylsilyllithium in 2 mL of THF was added a mixture of 0.260 g (2.454 mmol) of benzaldehyde and 0.222 g (1.470 mmol) of chlorotriethylsilane at  $-100^\circ\text{C}$ . The resulting mixture was allowed to warm to room temperature over a period of 3.5 h and was 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 washed with water. After evaporation of the solvent, the residue was analyzed by GLC, using 87.1 mg (0.385 mmol) of hexadecane as an internal standard, as being **2a/2a'** (29% yield) and **3a/3a'** (44% yield). Products **2a/2a'** and **3a/3a'** were separated as colorless viscous oils from the mixture by preparative GPC, eluting with benzene. The diastereomeric ratios for the products were calculated to be 1.1/1 for **2a/2a'** and 14/1 for **3a/3a'** on the basis of the integral ratios in the  $^1\text{H}$  NMR spectra. Data for **2a** (as a mixture with **2a'**): MS  $m/z$  648 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ) 0.07 (s, 9H,  $\text{Me}_3\text{Si}$ ), 0.35 (s, 9H,  $\text{Me}_3\text{SiO}$ ), 0.62 (q, 6H,  $J = 7.9$  Hz,  $\text{CH}_3\text{CH}_2\text{Si}$ ), 0.96 (t, 9H,  $J = 7.9$  Hz,  $\text{CH}_3\text{CH}_2\text{Si}$ ), 2.12 (s, 3H,  $p$ -Me), 2.27 (s, 3H,  $o$ -Me), 2.30 (s, 3H,  $o$ -Me), 4.69 (s, 1H, HCPH), 6.46 (s, 1H, HC=C), 6.78 (s, 1H, Mes ring proton), 6.82 (s, 1H, Mes ring proton), 6.95–7.35 (m, 10H, Ph);  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )  $-0.4$  ( $\text{Me}_3\text{SiO}$ ), 0.6 ( $\text{Me}_3\text{Si}$ ), 6.69 ( $\text{CH}_3\text{CH}_2\text{Si}$ ), 6.74 ( $\text{CH}_3\text{CH}_2\text{Si}$ ), 20.0 ( $o$ -Me), 20.1 ( $o$ -Me), 21.2 ( $p$ -Me), 72.7 (CHPh), 112.3 (=CHPh), 125.8, 126.3, 126.5, 127.1, 127.4, 128.11, 128.14, 128.3, 128.6, 128.9, 128.95, 128.99, 129.0, 128.5 (Ph overlapping with signals of **2a'**), 134.8 ( $ipso$ -Mes), 136.1, 136.05 ( $o$ -Mes), 136.9 (=CMes), 137.8 ( $p$ -Mes), 142.3 ( $ipso$ -Ph), 150.7 ( $ipso$ -Ph);  $^{29}\text{Si}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )  $-30.5$  ( $\text{SiSiMe}_3$ ),  $-22.5$  ( $\text{Me}_3\text{SiSi}$ ), 11.4 ( $\text{OSiEt}_3$ ), 19.9 ( $\text{OSiMe}_3$ ); IR  $\nu_{\text{Si-O}}$  1065  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{56}\text{O}_3\text{Si}_4$ : C, 66.61; H, 8.69. Found: C, 66.56; H, 8.50. Data for **2a'**:  $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ) 0.03 (s, 9H,  $\text{Me}_3\text{Si}$ ), 0.38 (s, 9H,  $\text{Me}_3\text{SiO}$ ), 0.62 (q, 6H,  $J = 7.9$  Hz,  $\text{CH}_3\text{CH}_2\text{Si}$ ), 0.99 (t, 9H,  $J = 7.9$  Hz,  $\text{CH}_3\text{CH}_2\text{Si}$ ), 2.13 (s, 3H,  $p$ -Me), 2.34 (s, 3H,  $o$ -Me), 2.40 (s, 3H,  $o$ -Me), 4.76 (s, 1H, HCPH), 6.40 (s, 1H, HC=C), 6.84 (s, 1H, Mes ring proton), 6.87 (s, 1H, Mes ring proton), 6.95–7.35 (m, 10H, Ph);  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )  $-0.4$  ( $\text{Me}_3\text{SiO}$ ), 0.4 ( $\text{Me}_3\text{Si}$ ), 6.69 ( $\text{CH}_3\text{CH}_2\text{Si}$ ), 6.74 ( $\text{CH}_3\text{CH}_2\text{Si}$ ), 20.0 ( $o$ -Me), 20.1 ( $o$ -Me), 21.2 ( $p$ -Me), 72.2 (CHPh), 112.1 (=CHPh), 135.0 ( $ipso$ -Mes), 136.12, 136.3 ( $o$ -Mes), 136.8 (=CMes), 137.9 ( $p$ -Mes), 142.9 ( $ipso$ -Ph), 151.0 ( $ipso$ -Ph), other phenyl ring carbons are overlapping with those of **2a**.  $^{29}\text{Si}$  NMR signals are overlapping with those of **2a**. Data for **3a** (as a mixture with **3a'**): MS  $m/z$  648 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ) 0.06 (s, 9H,  $\text{Me}_3\text{Si}$ ), 0.08 (s, 9H,  $\text{Me}_3\text{SiO}$ ), 0.52 (q, 6H,  $J = 7.9$  Hz,  $\text{CH}_3\text{CH}_2\text{Si}$ ), 0.94 (t, 9H,  $J = 7.9$  Hz,  $\text{CH}_3\text{CH}_2\text{Si}$ ), 2.15 (s, 3H,  $p$ -Me), 2.34 (s, 3H,  $o$ -Me), 2.35 (s, 3H,  $o$ -Me), 4.68 (s, 1H, HCPH), 5.42 (s, 1H, HC=C), 6.76 (s, 2H, Mes ring protons), 6.99–7.28 (m, 6H, Ph), 7.39 (d, 2H,  $J = 7.3$  Hz, Ph), 7.63 (d, 2H,  $J = 7.3$  Hz, Ph);  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ )  $-0.7$  ( $\text{Me}_3\text{Si}$ ), 0.8

(Me<sub>3</sub>SiO), 6.7 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.3 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.7 (*o*-Me), 21.0 (*p*-Me), 73.5 (CHPh), 113.3 (=CHPh), 126.0, 126.6, 128.0 (*m*- and *p*-Ph), 128.3 (*o*-Ph), 128.4 (*m*- or *p*-Ph), 128.7, 128.8 (*m*-Mes), 129.0 (*o*-Ph), 136.8 (=CMes), 136.9, 137.0 (*o*-Mes), 137.3, 137.4 (*ipso*- and *p*-Mes), 142.4 (*ipso*-Ph), 148.4 (*ipso*-Ph); <sup>29</sup>Si NMR (δ, C<sub>6</sub>D<sub>6</sub>) -30.5 (SiSiMe<sub>3</sub>), -22.7 (Me<sub>3</sub>SiSi), 11.3 (OSiEt<sub>3</sub>), 19.8 (OSiMe<sub>3</sub>); IR ν<sub>Si-O</sub> 1058 cm<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>56</sub>O<sub>3</sub>-Si<sub>4</sub>: C, 66.61; H, 8.69. Found: C, 66.53; H, 8.68. Data for **3a'**: <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>) 0.05 (s, 9H, Me<sub>3</sub>Si), 0.23 (s, 9H, Me<sub>3</sub>SiO), 0.38 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 0.89 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.38–2.44 (3H, Me overlapping with signals of **3a**), 2.46 (s, 3H, Me), 2.55 (s, 3H, Me), 4.47 (s, 1H, HCPh), 5.62 (s, 1H, HC=C), 6.98 (s, 1H, Mes ring proton), 7.05 (s, 1H, Mes ring proton), 7.25–7.49 (m, 8H, Ph), 7.88 (d, 2H, *J* = 7.9); <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>) -0.9 (Me<sub>3</sub>SiO), 0.5 (Me<sub>3</sub>Si), 6.0 (CH<sub>3</sub>CH<sub>2</sub>Si), 6.8 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.7 (Me), 72.1 (CHPh), 112.6 (=CHPh), 125.6, 125.9, 127.4, two Mes methyl carbons and 12 phenyl ring carbons are overlapping with those of **3a**.

**Hydrolysis of a Mixture of 2a/2a'/3a/3a'**. A mixture of 0.435 g (0.670 mmol) of **2a/2a'/3a/3a'** in a ratio of 9/8/14/1 in 10 mL of ether was treated with 20 mL of 3 N HCl at room temperature for 137 h. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After evaporation of the solvent, the residue was analyzed by GLC, using 0.044 g (0.240 mmol) of tridecane as an internal standard, as being **4** (33% yield) and **5** (28% yield). Products **4** and **5** were isolated by preparative GPC, eluting with benzene. All spectral data obtained for compound **5** are identical with those of the authentic sample. Data for **4**: colorless viscous oil; MS *m/z* 576 (M<sup>+</sup>); <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.04 (s, 9H, Me<sub>3</sub>Si), 0.59 (q, 6H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.01 (t, 9H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.14 (br s, 1H, HO), 2.18 (s, 3H, *o*- or *p*-Me), 2.40 (s, 3H, *o*- or *p*-Me), 2.49 (s, 3H, *o*-Me), 4.47 (s, 1H, HCPh), 5.53 (s, 1H, HC=C), 6.80 (s, 1H, Mes ring proton), 6.84 (s, 1H, Mes ring proton), 7.05–7.32 (m, 6H, Ph), 7.70 (d, 2H, *J* = 7.6 Hz, Ph), 7.70 (d, 2H, Ph, *J* = 7.6 Hz); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) -1.1 (Me<sub>3</sub>Si), 6.6 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.2 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.7 (*o*-Me), 20.9, 21.0 (*o*- and *p*-Mes), 71.5 (CHPh), 113.5 (=CHPh), 125.8, 125.9, 126.1, 128.1, 128.2, 128.3, 128.4 (Ph CH carbons), 136.6 (*o*-Mes), 136.9 (*ipso*-Mes), 137.1, 137.6 (*o*- and *p*-Mes), 143.2, 148.4 (*ipso*-Ph), two sp<sup>2</sup> carbons are overlapping; <sup>29</sup>Si NMR (δ, C<sub>6</sub>D<sub>6</sub>) -28.2 (SiSiMe<sub>3</sub>), -22.3 (Me<sub>3</sub>SiSi), 12.6 (OSiEt<sub>3</sub>); IR ν<sub>Si-O</sub> 1056 cm<sup>-1</sup>, ν<sub>O-H</sub> 3542 cm<sup>-1</sup>. Exact MS calcd for C<sub>33</sub>H<sub>48</sub>O<sub>3</sub>Si<sub>3</sub> (M<sup>+</sup>), 576.2909; found, 576.2952.

**Preparation of Compound 5.** To a suspension of 3.74 g (28.05 mmol) of aluminum trichloride was added slowly 4.25 g (24.19 mmol) of phenylacetyl chloride at 0 °C. The mixture was stirred at 0 °C for 3 h, and then 3.87 g (32.3 mmol) of mesitylene was added to the mixture at 0 °C. The resulting mixture was allowed to stir for 12 h at room temperature and was 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 washed with water. After evaporation of the solvent, the residue was chromatographed on a silica gel, eluting with hexane/ethyl acetate = 5/1, to give 5.01 g (87% yield) of compound **5**. Data for **5**: pale yellow solid; mp 108.0–109.0 °C; MS *m/z* 238 (M<sup>+</sup>); <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 2.01 (s, 6H, *o*-Me), 2.08 (s, 3H, *p*-Me), 3.77 (s, 2H, H<sub>2</sub>CPh), 6.61 (s, 2H, Mes ring proton), 7.08–7.16 (m, 5H, Ph); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) 19.2 (*o*-Me), 20.9 (*p*-Me), 51.9 (CHPh), 127.1, 128.6, 130.2, 133.0, 134.1, 138.2, 139.9 (ring and olefinic carbons), 205.8 (C=O); IR ν<sub>C=O</sub> 1697 cm<sup>-1</sup>. Exact MS calcd for C<sub>16</sub>H<sub>15</sub>O (M<sup>+</sup> - Me), 223.1122; found, 223.1094. Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O: C, 85.67; H, 7.61. Found: C, 85.59; H, 7.60.

**Reaction of 1b with Benzaldehyde.** To a solution of **1b**, prepared from 0.664 g (2.00 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of tris(trimethylsilyl)silyllithium in 2 mL of THF was added 0.452 g (4.25 mmol) of benzaldehyde. After the mixture was stirred for 18 h at -80 °C, 0.386 g (2.56 mmol) of chlorotriethylsilane was added at this temperature. The resulting mixture was allowed to warm

to room temperature over a period of 8 h and was 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 washed with water. After evaporation of the solvent, the residue was chromatographed on a silica gel column, eluting with hexane, to give 340 mg (29% yield) of **2b/2b'** and 352 mg (30% yield) of **3b/3b'** as colorless viscous oils. Data for **2b** (as a mixture with **2b'**): MS *m/z* 586 (M<sup>+</sup>); <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.16 (s, 9H, Me<sub>3</sub>Si), 0.41 (s, 9H, Me<sub>3</sub>SiO), 0.62 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.00 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.23 (s, 9H, *t*-Bu), 4.95 (s, 1H, HCPh), 6.35 (s, 1H, HC=C), 7.08 (br t, 1H, *J* = 7.3 Hz, Ph), 7.11 (br t, 2H, *J* = 7.3 Hz, Ph), 7.16–7.26 (m, 4H, Ph), 7.38 (d, 2H, *J* = 7.9 Hz, Ph), 7.44 (d, 2H, *J* = 7.6 Hz, Ph); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) -0.3 (Me<sub>3</sub>SiO), 0.5 (Me<sub>3</sub>Si), 6.6 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.0 (CH<sub>3</sub>CH<sub>2</sub>Si), 30.1, 37.2 (*t*-Bu), 71.7 (CHPh), 107.7 (=CHPh), 126.2, 126.4, 126.7, 128.0, 128.2, 128.4, 130.5, 134.1 (phenyl CH overlapping with those of **2b'**), 138.6, 143.2 (*ipso*-Ph), 159.7 (=C-*t*-Bu); <sup>29</sup>Si NMR (δ, C<sub>6</sub>D<sub>6</sub>) -36.0 (SiSiMe<sub>3</sub>), -23.9 (Me<sub>3</sub>SiSi), 8.6 (OSiEt<sub>3</sub>), 17.9 (OSiMe<sub>3</sub>); IR ν<sub>Si-O</sub> 1071 cm<sup>-1</sup>. Exact MS calcd for C<sub>31</sub>H<sub>54</sub>O<sub>3</sub>-Si<sub>4</sub> (M<sup>+</sup>), 586.3146; found, 586.3083. Data for **2b'**: <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.12 (s, 9H, Me<sub>3</sub>Si), 0.41 (s, 9H, Me<sub>3</sub>SiO), 0.71 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.07 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.14 (s, 9H, *t*-Bu), 4.75 (s, 1H, HCPh), 6.24 (s, 1H, HC=C), 7.04–7.40 (m, 6H, Ph), 7.32 (d, 2H, *J* = 8.3 Hz, Ph), 7.50 (d, 2H, *J* = 7.3 Hz, Ph); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) -0.3 (Me<sub>3</sub>SiO), 0.6 (Me<sub>3</sub>Si), 6.7 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.1 (CH<sub>3</sub>CH<sub>2</sub>Si), 72.5 (CHPh), 107.5 (=CHPh), other signals are overlapping with those of **2b**. <sup>29</sup>Si NMR signals are overlapping with those of **2b**. Data for **3b** (as a mixture with **3b'**): MS *m/z* 586 (M<sup>+</sup>); <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.05 (s, 9H, Me<sub>3</sub>Si), 0.16 (s, 9H, Me<sub>3</sub>SiO), 0.83 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.12 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.25 (s, 9H, *t*-Bu), 4.75 (s, 1H, HCPh), 5.73 (s, 1H, HC=C), 7.04–7.40 (m, 8H, Ph), 7.70 (d, 2H, *J* = 7.6 Hz, Ph); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) -0.6 (Me<sub>3</sub>SiO), 0.7 (Me<sub>3</sub>Si), 7.2 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.4 (CH<sub>3</sub>CH<sub>2</sub>Si), 29.1, 37.2 (*t*-Bu), 72.2 (CHPh), 105.0 (=CHPh), 126.0, 126.06, 126.11, 126.5, 126.7, 127.2, 127.6, 128.6, 129.4 (phenyl CH overlapping with signals of **3b'**), 137.6, 143.0 (*ipso*-Ph), 160.2 (C=C); IR ν<sub>Si-O</sub> 1059 cm<sup>-1</sup>. Exact MS calcd for C<sub>31</sub>H<sub>54</sub>O<sub>3</sub>Si<sub>4</sub> (M<sup>+</sup>), 586.3146; found, 586.3062. Data for **3b'**: <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.10 (s, 9H, Me<sub>3</sub>Si), 0.21 (s, 9H, Me<sub>3</sub>SiO), 0.72 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.09 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.12 (*t*-Bu), 4.87 (s, 1H, HCPh), 5.73 (s, 1H, HC=C), 7.04–7.40 (m, 8H, Ph), 7.48 (d, 2H, *J* = 7.3 Hz, Ph); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) -0.4 (Me<sub>3</sub>SiO), 0.7 (Me<sub>3</sub>Si), 7.1 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.3 (CH<sub>3</sub>CH<sub>2</sub>Si), 28.8, 37.2 (*t*-Bu), 71.5 (CHPh), 105.0 (=CHPh), 137.7, 142.6, 160.3 (Ph), 160.3 (=C-*t*-Bu), phenyl ring CH signals are overlapping with those of **3b**.

**Reactions of 1a and 1b with Mesityl Aldehyde, Acetophenone, and Mesityl Methyl Ketone.** All reactions of **1a** and **1b** with mesityl aldehyde, acetophenone, and mesityl methyl ketone were carried out the same as those with benzaldehyde. Yields of the products were determined by GLC analysis, using a hydrocarbon as an internal standard. Products **6a/6a'**, **7a/7a'**, **8**, **9a/9a'**, **6b**, **10a**, **10b**, **11**, and **12** were isolated by GPC, eluting with benzene, or MPLC on a silica gel column, eluting with hexane. All spectral data obtained for **10a** and **10b** were identical with those reported previously.<sup>4b</sup>

Data for **6a** (as a mixture with **6a'**): colorless solid; mp 65.0–66 °C; MS *m/z* 732 (M<sup>+</sup>); <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.08 (s, 9H, Me<sub>3</sub>Si), 0.48 (s, 9H, Me<sub>3</sub>SiO), 0.56 (q, 6H, *J* = 8.0 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 0.94 (t, 9H, *J* = 8.0 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.05 (s, 3H, Mes), 2.09 (s, 3H, Me), 2.167 (s, 3H, Me), 2.28 (s, 3H, Me), 2.31 (s, 3H, Me), 2.385 (s, 3H, Me), 2.393 (s, 3H, Me), 2.40 (s, 3H, Me), 2.67 (s, 2H, Me), 5.52 (s, 1H, HCMes), 6.41 (s, 1H, HC=C), 6.68 (s, 2H, Mes ring proton), 6.73 (s, 3H, Mes ring proton), 6.84 (s, 1H, Mes ring protons); <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.0 (Me<sub>3</sub>Si), 0.42 (Me<sub>3</sub>SiO), 6.5 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.0 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.83, 20.86, 20.93, 21.3 (2C), 21.4, 21.5 (2C), 23.3 (Mes), 69.1 (CHMes), 110.8 (=CHMes), 127.9, 128.53, 129.13, 129.19, 129.22, 130.7, 132.0, 134.54, 134.69, 135.6, 135.7, 136.60, 136.63 (2C), 136.71, 136.81, 137.3, 138.2, 150.6 (Mes ring and olefinic carbons); <sup>29</sup>Si

NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –22.4 (SiSiMe<sub>3</sub>), –21.2 (Me<sub>3</sub>Si), 12.4 (OSiEt<sub>3</sub>), 18.4 (OSiMe<sub>3</sub>); IR  $\nu_{\text{Si-O}}$  1064, 1019 cm<sup>-1</sup>. Anal. Calcd for C<sub>42</sub>H<sub>68</sub>O<sub>3</sub>Si<sub>4</sub>: C, 68.79; H, 9.35. Found: C, 68.62; H, 9.28.

Data for **6a'**: <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.08 (s, 9H, Me<sub>3</sub>Si), 0.31 (s, 9H, Me<sub>3</sub>SiO), 0.77 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.08 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.05 (s, 3H, Mes), 2.09 (s, 3H, Me), 2.155 (s, 3H, Me), 2.31 (s, 6H, Me), 2.32 (s, 3H, Me), 2.385 (s, 3H, Me), 2.41 (s, 3H, Me), 2.68 (s, 3H, Me), 5.34 (s, 1H, HCMes), 6.45 (s, 1H, HC=C), 6.65 (s, 1H, Mes ring proton), 6.68 (s, 2H, Mes ring protons), 6.73 (s, 2H, Mes ring protons), 6.80 (s, 1H, Mes ring proton); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –0.5 (Me<sub>3</sub>SiO), 0.39 (Me<sub>3</sub>Si), 6.9 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.2 (CH<sub>3</sub>CH<sub>2</sub>Si), 21.0, 21.7, 22.5 (Mes, 6 Mes methyl carbons are overlapping with those of **6a**), 68.5 (CHPh), 111.4 (=CHMes), 128.47, 129.03, 129.07, 129.09, 129.13, 131.0, 132.1, 134.50, 134.65, 135.5, 136.9, 136.2, 136.78, 136.9, 137.2, 138.9, 150.2 (Mes ring and olefinic carbons, 2 signals of ring and olefinic carbons are overlapping with those of **6a**); <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –25.4 (SiSiMe<sub>3</sub>), –22.0 (Me<sub>3</sub>Si), 12.2 (OSiEt<sub>3</sub>), 18.3 (OSiMe<sub>3</sub>).

Data for **7a** (as a mixture with **7a'**): colorless viscous oil; MS *m/z* 732 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.03 (s, 9H, Me<sub>3</sub>Si), 0.15 (s, 9H, Me<sub>3</sub>SiO), 0.40 (q, 6H, *J* = 8.8 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 0.89 (t, 9H, *J* = 8.8 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.05 (s, 3H, Mes), 2.16 (s, 3H, Me), 2.24 (s, 3H, Me), 2.31 (s, 3H, Me), 2.44 (s, 3H, Me), 2.49 (s, 6H, Me), 2.58 (s, 3H, Me), 2.63 (s, 3H, Me), 5.02 (s, 1H, HCMes), 5.39 (s, 1H, HC=C), 6.70 (s, 1H, Mes ring proton), 6.76 (s, 1H, Mes ring proton), 6.85 (s, 2H, Mes ring protons), 6.93 (s, 2H, Mes ring protons); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –0.3 (Me<sub>3</sub>SiO), 0.5 (Me<sub>3</sub>Si), 6.5 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.4 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.8, 21.0, 21.1, 21.4, 21.8, 21.99, 22.1 (2C), 23.4 (*o*- and *p*-Mes), 69.6 (CHMes), 111.7 (=CHMes), 128.5, 128.6, 128.8, 129.0, 129.1, 130.46 (*o*-Mes), 132.0, 135.2, 135.69, 135.74, 136.56, 136.62, 137.2, 137.3 (2C), 137.4, 137.7, 138.2, 147.7 (Mes ring and olefinic carbons); <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –26.0 (SiSiMe<sub>3</sub>), –21.7 (Me<sub>3</sub>Si), 11.3 (OSiEt<sub>3</sub>), 17.9 (OSiMe<sub>3</sub>); IR  $\nu_{\text{Si-O}}$  1055, 1018 cm<sup>-1</sup>. Exact MS calcd for C<sub>42</sub>H<sub>68</sub>O<sub>3</sub>Si<sub>4</sub> (M<sup>+</sup>), 732.4241; found, 732.4240.

Data for **7a'**: <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.02 (s, 9H, Me<sub>3</sub>Si), 0.04 (s, 9H, Me<sub>3</sub>SiO), 0.40 (q, 6H, *J* = 8.8 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.03 (t, 9H, *J* = 8.8 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.98 (s, 3H, Mes), 2.16 (s, 3H, Me), 2.24 (s, 3H, Me), 2.31 (s, 3H, Me), 2.41 (s, 3H, Me), 2.42 (s, 6H, Me), 2.53 (s, 3H, Me), 2.61 (s, 3H, Me), 4.95 (s, 1H, HCPh), 5.36 (s, 1H, HC=C), 6.70 (s, 1H, Mes ring proton), 6.76 (s, 1H, Mes ring proton), 6.85 (s, 2H, Mes ring protons), 6.90 (s, 2H, Mes ring protons); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –0.4 (Me<sub>3</sub>SiO), 0.7 (Me<sub>3</sub>Si), 6.7 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.5 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.9, 21.2, 21.6, 21.91 (3C), 21.97, 22.9 (Mes, one Mes methyl carbon is overlapping with those of **7a**), 69.4 (CHMes), 111.9 (=CHMes), 128.8, 129.2, 130.50 (3C, *o*-Mes), 135.4, 135.9, 136.4, 137.0, 137.1, 137.6, 138.6, 147.8 (Mes ring and olefinic carbons, 5 signals of ring and olefinic carbons are overlapping with those of **7a**).

Data for **8**: colorless solid; mp 73.5–74.5 °C; MS *m/z* 394 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.40 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 0.73 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.19 (s, 3H, *p*-Me), 2.24 (s, 3H, *p*-Me), 2.54 (s, 6H, *o*-Me), 2.60 (s, 6H, *o*-Me), 5.62 (s, 1H, HC=C), 6.85 (s, 2H, Mes ring proton), 6.94 (s, 2H, Mes ring proton); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 5.4 (CH<sub>3</sub>CH<sub>2</sub>Si), 6.5 (CH<sub>3</sub>CH<sub>2</sub>Si), 21.0 (*p*-Me), 21.1 (*p*-Me), 21.3 (*o*-Me), 21.6 (*o*-Me), 112.4 (=CHMes), 128.9 (2C), 132.3, 135.7, 136.6, 137.0, 137.1, 137.2 (Mes), 148.2 (=C(Mes)-O); <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 19.0; IR  $\nu_{\text{Si-O}}$  1059 cm<sup>-1</sup>. Exact MS calcd for C<sub>26</sub>H<sub>38</sub>O<sub>2</sub>Si (M<sup>+</sup>), 394.2689; found, 394.2657.

Data for **9a** (as a mixture with **9a'**): colorless viscous oil; MS *m/z* 676 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.16 (s, 18H, Me<sub>3</sub>Si), 0.59 (q, 6H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 0.98 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.90 (s, 3H, Me-CPh), 2.05 (s, 3H, *p*-Me), 2.15 (s, 3H, *o*-Me), 2.22 (s, 3H, MeC=), 2.28 (s, 3H, *o*-Me), 6.58 (s, 1H, Mes ring proton), 6.64 (s, 1H, Mes ring proton), 6.84–7.28 (m, 8H, Ph), 7.50 (d, 2H, *J* = 7.3 Hz, Ph); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.2 (Me<sub>3</sub>SiO), 3.2 (Me<sub>3</sub>Si), 6.9 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.4 (CH<sub>3</sub>CH<sub>2</sub>Si), 18.6 (Me-CPh), 20.9, 21.0, 21.1 (Me-Mes), 25.0 (MeC=), 76.4 (CMePh), 118.8 (=CMePh), 125.9, 127.0, 127.77, 127.84, 128.3,

128.4 (phenyl CH), 128.6, 128.7 (*m*-Mes), 135.3 (*ipso*-Mes), 137.0, 137.1 (*o*-Mes), 137.3 (*p*-Mes), 142.5 (=CMe), 144.4 (*ipso*-Ph(-CMe)), 147.1 (*ipso*-Ph(-C=C)); <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –35.4 (SiSiMe<sub>3</sub>), –23.0 (Me<sub>3</sub>Si), 11.1 (OSiEt<sub>3</sub>), 14.2 (OSiMe<sub>3</sub>); IR  $\nu_{\text{Si-O}}$  1067 cm<sup>-1</sup>. Anal. Calcd for C<sub>38</sub>H<sub>60</sub>O<sub>4</sub>Si<sub>4</sub>: C, 67.41; H, 8.93. Found: C, 67.36; H, 8.73.

Data for **9a'**: <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.10 (s, 9H, Me<sub>3</sub>Si), 0.16 (s, 9H, Me<sub>3</sub>SiO), 0.74 (q, 6H, *J* = 7.4 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.08 (t, 9H, *J* = 7.8 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.90 (s, 3H, Me-CPh), 2.02 (s, 3H, *p*-Me), 2.10 (s, 3H, *o*-Me), 2.13 (s, 3H, *o*-Me), 2.19 (s, 3H, MeC=), 6.55 (s, 1H, Mes ring proton), 6.58 (s, 1H, Mes ring proton), 6.84–7.51 (m, 8H, Ph), 7.50 (d, 2H, *J* = 7.3 Hz, Ph); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.1 (Me<sub>3</sub>Si), 3.2 (Me<sub>3</sub>SiO), 7.2 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.4 (CH<sub>3</sub>CH<sub>2</sub>Si), 18.5 (Me-CPh), 20.9, 21.0, 21.1 (Me-Mes), 25.0 (MeC=), 76.7 (CMePh), 118.9 (=CMePh), 125.9, 127.0, 127.77, 127.84, 128.3, 128.4, 128.6, 128.7, 135.1 (overlapping with a signal of **9a**), 137.0, 137.1, 137.3 (phenyl and Mes ring carbons), 142.5 (=CMe), 144.4, 147.2 (overlapping with a signal of **9a ipso**-Ph).

Data for **6b**: colorless solid; mp 107.3–108.5 °C; MS *m/z* 655 (M<sup>+</sup> – Me); <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.03 (s, 9H, Me<sub>3</sub>Si), 0.32 (s, 9H, Me<sub>3</sub>SiO), 0.78 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.083 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.084 (s, 9H, *t*-Bu), 2.17 (s, 3H, *p*-Me), 2.19 (s, 3H, *p*-Me), 2.41 (s, 3H, *o*-Me (MesCHO)), 2.47 (s, 6H, *o*-Me), 2.71 (s, 3H, *o*-Me (MesCH=)), 5.31 (s, 1H, HCMes), 5.98 (s, 1H, HC=C), 6.76 (s, 1H, Mes ring proton), 6.85 (s, 3H, Mes ring protons); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –0.4 (Me<sub>3</sub>Si), 0.4 (Me<sub>3</sub>SiO), 6.9 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.2 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.9 (*p*-Me), 21.1 (*p*-Me), 21.6 (*o*-Me (MesCH-O)), 21.9 (*o*-Me (MesCH-O)), 22.0 (*o*-Me (MesCH=)), 22.6 (*o*-Me (MesCH=)), 28.8, 38.1 (*t*-Bu), 68.5 (CHMes), 104.8 (=CMeH), 128.2, 128.5, 129.1, 130.9 (*m*-Mes), 134.4, 134.5, 135.6, 135.8, 136.4, 136.6, 136.9, 138.4, 157.2 (Mes ring and olefinic carbons); <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –25.5 (SiSiMe<sub>3</sub>), –22.2 (Me<sub>3</sub>Si), 11.7 (OSiEt<sub>3</sub>), 18.3 (OSiMe<sub>3</sub>); IR  $\nu_{\text{Si-O}}$  1066 cm<sup>-1</sup>. Anal. Calcd for C<sub>37</sub>H<sub>66</sub>O<sub>3</sub>Si<sub>4</sub>: C, 66.20; H, 9.91. Found: C, 65.93; H, 9.97.

Data for **11**: colorless viscous oil; MS *m/z* 276 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.71 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 1.01 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.17 (s, 3H, *p*-Me), 2.48 (s, 3H, *o*-Me), 4.24 (s, 1H, olefinic proton), 4.71 (s, 1H, olefinic proton), 6.81 (s, 2H, Mes ring protons); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 5.3 (CH<sub>3</sub>CH<sub>2</sub>Si), 6.9 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.3 (*o*-Me), 20.9 (*p*-Me), 94.4 (=CH<sub>2</sub>), 128.5, 135.8, 136.86, 136.95, 156.0 (Mes ring and olefinic carbons); IR  $\nu_{\text{Si-O}}$  1008 cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>28</sub>O<sub>2</sub>Si: C, 73.85; H, 10.21. Found: C, 73.47; H, 10.20.

Data for **12**: colorless viscous oil; MS *m/z* 583 (M<sup>+</sup> – Me); <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.11 (s, 9H, Me<sub>3</sub>Si), 0.54 (s, 9H, Me<sub>3</sub>SiO), 0.66 (q, 6H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 0.99 (t, 9H, *J* = 7.9 Hz, CH<sub>3</sub>CH<sub>2</sub>Si), 2.18 (s, 3H, *p*-Me), 2.22 (s, 3H, *p*-Me), 2.47 (s, 3H, *o*-Me), 2.57 (s, 6H, *o*-Me), 2.58 (s, 3H, *o*-Me), 4.39 (s, 1H, HC=), 4.95 (s, 1H, HC=), 5.80 (s, 1H, HCO), 6.76 (s, 1H, Mes ring proton), 6.80 (s, 1H, Mes ring proton), 6.87 (s, 2H, Mes); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –0.3 (Me<sub>3</sub>Si), 1.3 (Me<sub>3</sub>SiO), 5.5 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.3 (CH<sub>3</sub>CH<sub>2</sub>Si), 20.8 (*o*-Me), 20.9 (*p*-Me), 21.1 (*p*-Me), 21.5 (*o*-Me), 23.2 (*o*-Me), 70.1 (HCMes), 93.5 (=CH<sub>2</sub>), 128.5, 129.4, 130.5 (*m*-Mes), 133.4 (*o*-Mes), 135.8 (*o*-Mes), 135.9 (*p*-Me), 136.6 (*ipso*-Mes), 136.9 (*p*-Mes), 137.8 (*ipso*-Mes), 138.5 (*o*-Mes), 157.9 (=CMeO); <sup>29</sup>Si NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –18.2 (SiSiMe<sub>3</sub>), –17.3 (Me<sub>3</sub>Si), 14.9 (OSiEt<sub>3</sub>), 19.3 (OSiMe<sub>3</sub>); IR  $\nu_{\text{Si-O}}$  1003 cm<sup>-1</sup>. Anal. Calcd for C<sub>33</sub>H<sub>58</sub>O<sub>2</sub>Si<sub>4</sub>: C, 66.15; H, 9.76. Found: C, 66.10; H, 9.74.

**X-ray Crystallographic Analysis of 6b.** All unique diffraction maxima with  $0 < 2\theta < 125.9^\circ$  were recorded on a Rigaku AFC-6C automated four-circle diffractometer using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A total of 4893 observed reflections for **6b** ( $I > 3\sigma(I)$ ) were used in the least-squares refinement. The structure was solved by SIR92 direct methods<sup>7</sup> and expanded using DIRDIF94 Fourier

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techniques.<sup>8</sup> The non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors were taken from Cromer and Waber.<sup>9</sup> Anomalous dispersion effects were included in  $F_{\text{calc}}$ ;<sup>10</sup> the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley.<sup>11</sup> The values for the mass attenuation coefficients are those of Creagh and Hubbel.<sup>12</sup> All calculations were performed using the teXsan<sup>13</sup> crystallographic software package of Molecular Structure Corporation.

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**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **2b/2b'**, **3b/3b'**, and **7a/7a'** and an ORTEP drawing with a full atomic numbering scheme and tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters for **6b** (16 pages). Ordering information is given on any current masthead page.

OM960693L

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(13) Crystal Structure Analysis Package, Molecular Structure Corporation, 1985, 1992.