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An Unexpected Ring Contraction: Phenylsilane to Silacyclopentane

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In the reaction of dimethoxymethylphenylsilane with Li in an excess of chlorotrimethylsilane, the phenyl group was readily reduced to give dimethoxymethyl(Ttc)silane (**1**; Ttc = 3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl) in 45% yield. In addition, the diastereomeric isomers of 2-[2,2-bis(trimethylsilyl)ethylidene]-1-methoxy-1-methyl-3,4,5-tris(trimethylsilyl)silolane (**2a**,**b**) were also produced via an unexpected ring contraction in 20% and 8% yields, respectively. The structures of **2a**,**b** were revealed by X-ray single-crystal crystallography.

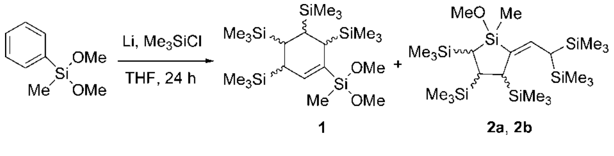
Introduction

The chemistry of five- and six-membered heterocycles with one silicon atom in the ring has attracted much interest due to the synthetic usefulness of these species.[1–3] These heterocycles have generally been synthesized by (a) cycloadditions of reactive intermediates (silenes and silylenes),[2,3] (b) ring expansion reactions via rearrangement,[3] (c) transformations of unsaturated compounds using metal-catalyzed reactions,[3,4] or (d) intramolecular cyclizations.[3,5]

Interestingly, when [3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl]dimethoxymethylsilane is synthesized by a Birch-type reductive polysilylation reaction[6] of dimethoxymethylphenylsilane with Li in an excess of chlorotrimethylsilane, unexpected five-membered silicon-carbon heterocycles are obtained. In this paper we report the synthesis and structural characterization of the unexpected ring-contracted products 2-[2,2-bis(trimethylsilyl)ethylidene]-1-methoxy-1-methyl-3,4,5-tris(trimethylsilyl)silolanes. This is the first example of a five-membered silicon–carbon heterocyclic compound synthesized through an intramolecular ring contraction.

Results and Discussion

The reaction of dimethoxymethylphenylsilane with Li metal in an excess of chlorotrimethylsilane was carried out in THF solvent at room temperature and monitored by using gas chromatography. After the solution was stirred for 24 h at room temperature, it turned from colorless to dark brown, and all the starting material was consumed, indicating that the reaction was completed. The phenyl group was readily reduced to give the expected product **1** in 45% yields.[6,7] Surprisingly, the unexpected five-membered heterocycles **2a**,**b** were also produced in 20% and 8% yield.



After flash column chromatography, **2a**,**b** were isolated as colorless crystals by recrystallization in *n*-pentane. Isomers **2a**,**b** were characterized by NMR, GC/MS, EA, HRMS, and X-ray single-crystal crystallography. Compound **1** consisted of four conformational isomers due to the different positions of trimethylsilyl substituents in the Ttc group.[8]

Diastereomers **2a** (*RSSR*) and **2b** (*SRRR*) were characterized by X-ray crystallography (Figures 1 and 2). The Si(1)−C(1) (1.851(3) Å) and Si(1′)−C(1′) (1.844(4) Å) bonds are shorter than the typical Si−C(sp^2) single bond (<1.86 Å).[9] Double-bond lengths of C(1)−C(6) (1.352(4) Å) and C(1′)−C(6′) (1.345(5) Å) are longer than those obtained from ab initio calculations, which show values between 1.269 and 1.323 Å.[10] The sum of the three angles around C(1) (359.8°) and C(1′) (359.4°) clearly show almost planar structures around C(1) and C(1′). The sums of the interior angles of **2a**,**b** were 534.2 and 533.76°, respectively (Table 1), indicating nearly planar structures of the five-membered silicon−carbon heterocycles. This differs from those of previous reports, in which silacyclopentanes have twisted-ring structures.[11] The reason for this planarity may be the steric hindrance of trimethylsilyl substituents in the five-membered ring.

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[8] The four isomers appeared in the GC/MS. These isomers differ in the position of the Ttc substituent.[7b] Among the various isomers, one isomer was separated by flash column chromatography as a colorless oil and identified with NMR, GC/MS, and HRMS.

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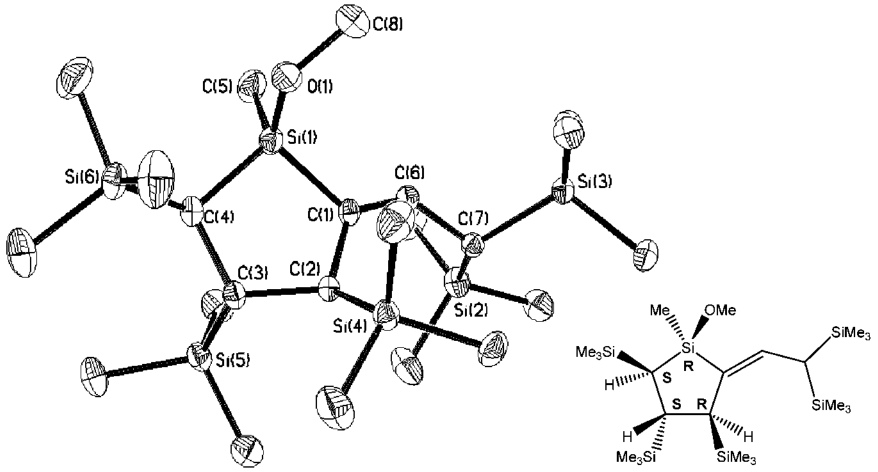

Figure 1. ORTEP drawing of **2a**, shown with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−C(1) = 1.851(3), C(1)−C(2) = 1.517(4), C(2)−C(3) = 1.605(4), C(3)−C(4) = 1.590(4), C(4)−Si(1) = 1.861(3), C(1)−C(6) = 1.352(4); Si(1)−C(1)−C(2) = 109.1(2), Si(1)−C(1)−C(6) = 122.8(2), C(2)−C(1)−C(6) = 127.9(3).

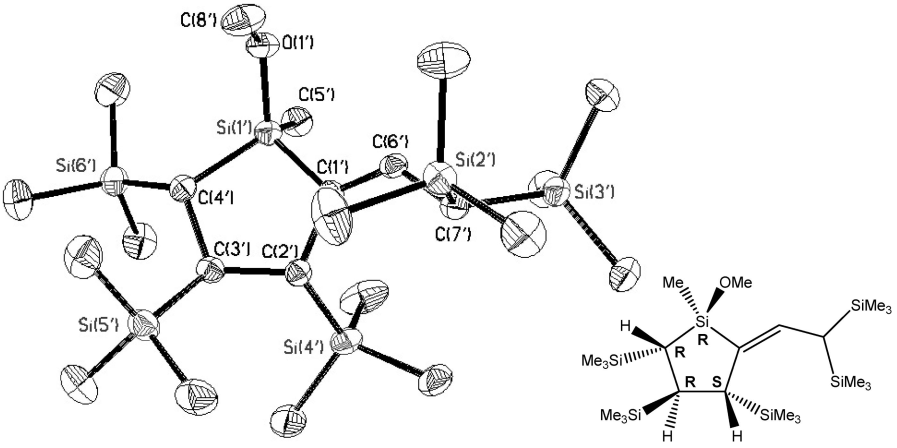

Figure 2. ORTEP drawing of **2b** shown with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si(1′)−C(1′) = 1.844(4), C(1′)−C(2′) = 1.520(5), C(2′)−C(3′) = 1.608(5), C(3′)−C(4′) = 1.586(5), C(4′)−Si(1′) = 1.867(4), C(1′)−C(6′) = 1.345(5); Si(1′)−C(1′)−C(2′) = 110.5(2), Si(1′)−C(1′)−C(6′) = 121.9(3), C(2′)−C(1′)−C(6′) = 127.0(3).

Table 1. Selected Bond Angles (deg) for the Crystal Structures of 2a,b

2a		2b	
C(1)−Si(1)−C(4)	97.12(13)	C(1′)−Si(1′)−C(4′)	95.26(16)
Si(1)−C(1)−C(2)	109.11(19)	Si(1′)−C(1′)−C(2′)	110.5(2)
C(1)−C(2)−C(3)	109.1(2)	C(1′)−C(2′)−C(3′)	109.4(3)
C(2)−C(3)−C(4)	113.2(2)	C(2′)−C(3′)−C(4′)	113.3(3)
C(3)−C(4)−Si(1)	105.67(4)	C(3′)−C(4′)−Si(1′)	105.3(2)
sum	534.2	sum	533.76

Plausible mechanisms for the formations of **1** and **2a**,**b** are shown in Scheme 1. **1** was synthesized via the well-known Birch-type reductive polysilylation pathway involving radical anion species.[6,7] For the formation of **2a**,**b**, the possibility that **1** may act as a precursor for **2a**,**b** prompted us to carry out conditional experiments for clarification. When 2 equiv of Li and 1 equiv of Me_3SiCl were added to the reaction mixture in order to reduce **1** further, no reaction took place, which indicates that **1** is stable in an excess of Li and Me_3SiCl. From this we conclude that **1** could not be the precursor for **2a**,**b**.

The most plausible mechanism may begin with the reactive intermediate species **a**, which has an allylic moiety formed from the consecutive reductive silylation processes. Intermediate **a** reacts intermolecularly with chlorotrimethylsilane to give **1** via Wurtz-type coupling and is rearranged intramolecularly to generate intermediate **b**, giving the product **3** through a ring-closing reaction. One can expect a silylation product of **b** with trimethylchlorosilane. However, we did not observe it, which suggests that intermediate **a** reacts readily with chlorotrimethylsilane to give **1**, while intermediate **b** rapidly undergoes a concerted rearrangement to give the five-membered-ring product. Finally, two consecutive reductive silylations involving a radical rearrangement of **3** produce the five-membered heterocyclic compounds **2a**,**b**.

To verify this mechanism, the reductive silylation reaction was carried out under incomplete reduction to get product **3**. For example, the reaction of dimethoxymethylphenylsilane was carried out using 4 equiv (instead of 8 equiv) of Li in an excess of Me_3SiCl. When the reaction mixture of incomplete reduction products was treated with H_2O, the expected **3** was obtained in 20% yield as well as **1** and **2** in 15% and 48% GC yields, respectively. **3** consisted of the two diastereomeric isomers **3a**,**b** due to the different conformations of trimethylsilyl groups on the ring. After column chromatography, **3a**,**b** were isolated as

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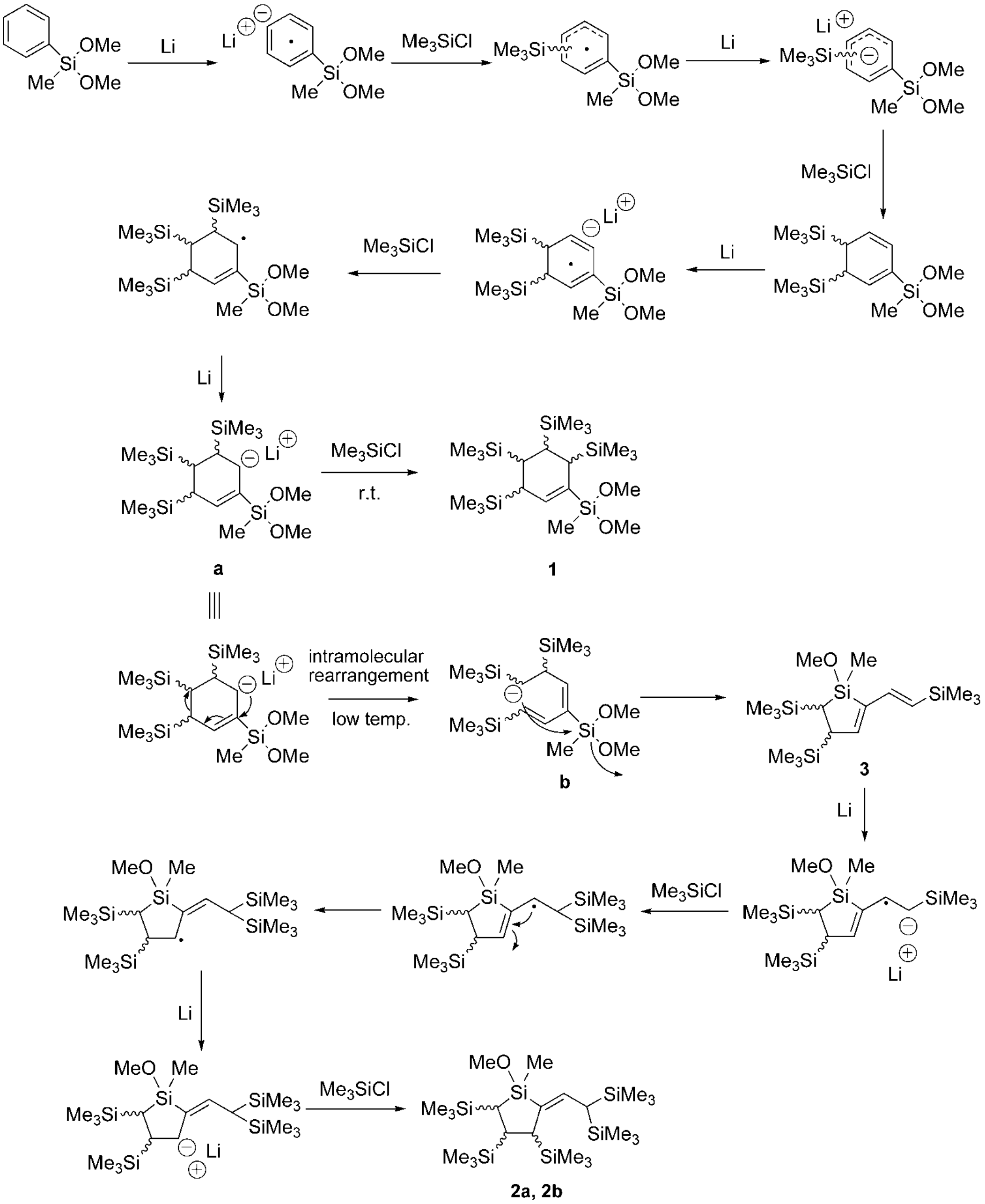
Scheme 1. Plausible Mechanisms for the Formations of 2a,b



a colorless oil. The reaction of **3a**,**b** with 2 equiv of lithium in an excess of Me_3SiCl gave only the five-membered silicon−carbon heterocycles **2a**,**b**, quantitatively and stereospecifically, as shown in Scheme 2, which strongly supports the mechanism shown in Scheme 1.

The intramolecular rearrangement of species **a** is competitive with a Wurtz-type coupling reaction to produce **1**. To clarify this, temperature-dependent experiments were carried out at both −78 °C and room temperature. When the reaction described previously was carried out at −78 °C for 24 h, yields of **2a**,**b** increased over the yields at room temperature (given in parentheses); **1**, 39% (45%); **2a**, 27% (20%); **2b**, 15% (8%). This result suggests that the intramolecular reaction of **a** may be a more favored and faster reaction than the intermolecular reaction at low temperature.

Conclusions

In this work, the reaction of dimethoxymethylphenylsilane with Li metal in excess Me_3SiCl in THF is observed to produce the products **2a**,**b**, contracted from six- to five-membered rings, as well as the expected products **1** synthesized via a Birch-type reductive silylation. This result is the first example of the synthesis of five-membered silicon−carbon heterocycles via an intramolecular ring contraction pathway.

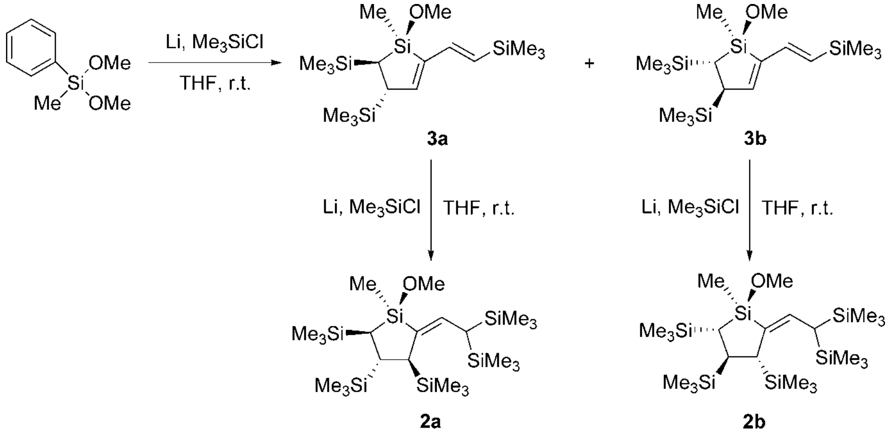
Experimental Section

General Comments. In all reactions in which air-sensitive chemicals were used, the reagents and solvents were dried prior to use. THF was distilled from Na/Ph_2CO. Other starting materials were purchased as reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. All manipulations were performed using standard Schlenk techniques under a nitrogen or argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer and referenced to residual protons of the solvent with chemical shifts of the atom of tetramethylsilane (external standard) being reported in δ (ppm). Analyses of product mixtures were accomplished using an HP 5890 II Plus instrument with FID (HP-

Table 2. Crystallographic Data and Structural Refinement Details for 2a,b

	2a	**2b**
empirical formula	$C_{23}H_{56}OSi_6$	$C_{23}H_{56}OSi_6$
fw	517.22	517.22
temp (K)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens		
a (Å)	9.5333(15)	9.330(5)
b (Å)	13.396(2)	13.422(7)
c (Å)	14.371(2)	14.544(8)
α (deg)	82.678(3)	82.699(10)
β (deg)	81.324(3)	82.082(10)
γ (deg)	70.564(2)	71.186(9)
V (Å^3)	1704.9(5)	1700.8(16)
Z	3	3
calcd density (Mg/m^3)	1.499	1.515
abs coeff (mm^{-1})	0.385	0.387
F(000)	846	858
cryst size (mm^3)	0.86 × 0.34 × 0.04	0.73 × 0.58 × 0.41
θ range for data collecn (deg)	1.44−25.57	1.61−25.56
index ranges	$-11 \le h \le 11$ $-16 \le k \le 16$ $-17 \le l \le 17$	$-10 \le h \le 11$ $-14 \le k \le 16$ $-14 \le l \le 17$
no. of rflns collected	13 091	9059
no. of indep rflns	6342 (R(int) = 0.0459)	6243 (R(int) = 0.0457)
completeness to θ = 25.56 (%)	98.9	97.8
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	6342/0/271	6243/0/271
goodness of fit on F^2	1.803	0.971
final R indices ($I > 2\sigma(I)$)	R1 = 0.0863, wR2 = 0.2250	R1 = 0.0659, wR2 = 0.1581
R indices (all data)	R1 = 0.1423, wR2 = 0.2361	R1 = 0.1206, wR2 = 0.1756

Scheme 2. Syntheses of 2a,b from 3a,b



5, 30 m column) with dried decane as an internal standard. Mass spectra were recorded on a low-resolution (Agilent Technologies GC/MS: 6890N, 5973N mass selective detector) EI mass spectrometer and a high-resolution Autospec M363 series instrument. Preparative gel permeation chromatography (GPLC) was performed on an LC-10 instrument with JAI Gel AJ1H+2H columns with chloroform as solvent.

Crystallographic Data Collection. The crystal evaluation and data collection were performed on a Bruker CCD diffractometer with Mo Kα (λ = 0.710 73) radiation employing a 2 kW sealed-tube X-ray source operating at 1.6 kW and a diffractometer to crystal distance of 4.9701 cm. The highly redundant data sets were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The systematic absences in the diffraction data were consistent for the space group that yielded chemically reasonable and computationally stable results of refinement. A successful solution was obtained by the direct methods from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms bonded to carbon atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Crystal data and structural refinement details are given in Table 2.

Synthesis of 1 and 2 at –78 °C (or Room Temperature). A solution of dimethoxymethylphenylsilane (5.0 g, 0.027 mol) in THF (25 mL) was added to a mixture of chlorotrimethylsilane (17.0 mL, 0.135 mol) and lithium (1.50 g, 0.216 mol) at −78 °C in THF (125 mL). The reaction mixture was stirred for about 24 h at –78 °C (or room temperature). The color of the solution turned from colorless to dark brown. In this reaction, **1** and **2a**,**b** were produced in 39% (45%), 27% (20%), and 15% (8%) yields, respectively (yield at room temperature). The solution was warmed to room temperature and treated with saturated aqueous ammonium chloride. The organic layer was separated and dried over sodium bicarbonate. After organic solvent was removed using a rotary evaporator, the residue was distilled under vacuum. The crude material was purified by silica gel chromatography (*n*-hexane). After removal of the solvent, a white powder was obtained and recrystallized from pentane to give colorless crystals of **2a**. After the separation of the residue mixture by recycle preparative HPLC (chloroform, 5 mL/min, 25 cycles), **2b** was obtained as colorless crystals. Four isomeric [3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl]dimethoxymethylsilanes which appeared in the GC/MS were obtained. Among the four isomers, compound **1** was separated by silica gel chromatography (1/100 ether/hexane) as a colorless oil.

Spectral data for **1** are as follows. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.03 (s, 9H, Si(C*H*$_3$)$_3$), 0.05 (s, 9H, Si(C*H*$_3$)$_3$), 0.07 (s, 9H, Si(C*H*$_3$)$_3$), 0.08 (s, 9H, Si(C*H*$_3$)$_3$), 0.26 (s, 3H, SiC*H*$_3$), 1.02 (dd, *J* = 8.5, 5.5 Hz, 1H, C*H*), 1.37 (d, *J* = 5.5 Hz, 1H, C*H*), 1.39 (d, *J* = 8.8 Hz, 1H, C*H*), 1.75 (d, *J* = 6.5 Hz, 1H, C*H*), 3.49 (s, 6H, OC*H*$_3$), 6.29 (d, *J* = 1.9 Hz, 1H, vinyl *H*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ –0.56, 0.41, 0.46, 0.68 (Si(*C*H$_3$)$_3$), 10.85 (Si−*C*H$_3$), 22.17, 22.90, 24.36, 29.59 (*C*H), 49.91 (O*C*H$_3$), 133.16, 138.35 (vinyl *C*). ^{29}Si NMR (CDCl$_3$, 79 MHz): δ –16.9 (*Si*OMe), 4.4 (*Si*Me$_3$), 4.8 (*Si*Me$_3$), 5.0 (*Si*Me$_3$), 8.1 (*Si*Me$_3$). MS: *m*/*z* (relative intensity) 474 (m$^+$, 3.5), 459 (17.0), 401 (25.6), 297 (89.6), 223 (63.2), 207 (79.9), 73 (100.0). HRMS: 474.2657 (M$^+$ calcd), 474.2658 (found). Anal. Calcd for $C_{21}H_{50}O_2Si_5$: C, 53.09; H, 10.61. Found;: C, 52.97; H, 10.59.

Spectral data for **2a** are as follows. Mp: 84–86 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ –0.01 (s, 9H, Si(C*H*$_3$)$_3$), 0.04 (s, 9H, Si(C*H*$_3$)$_3$), 0.07 (s, 18H, Si(C*H*$_3$)$_3$), 0.1 (s, 9H, Si(C*H*$_3$)$_3$), 0.22 (s, 3H, SiC*H*$_3$), 1.26 (m, 1H, C*H*), 1.41 (dd, *J* = 9.8 and 6.0 Hz, 1H, C*H*), 1.51 (d, *J* = 12.7, 1H, C*H*), 2.21 (dd, *J* = 6.0 and 2.3 Hz, 1H, C*H*), 3.45 (s, 3H, OC*H*$_3$), 5.64 (dd, *J* = 12.5 and 2.3 Hz, 1H, vinyl *H*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ –3.52 (Si−*C*H$_3$), –0.67, 0.68, 0.80, 1.17, 1.21 (Si(*C*H$_3$)$_3$), 15.02, 24.31, 24.55, 32.42 (*C*H), 50.27 (O*C*H$_3$), 134.29, 141.18 (vinyl *C*). ^{29}Si NMR (CDCl$_3$, 79 MHz): δ 0.5 (*Si*Me$_3$ × 2), 3.7 (*Si*Me$_3$), 7.0 (*Si*Me$_3$), 10.0 (*Si*Me$_3$), 21.6 (*Si*OMe). MS: *m*/*z* (relative intensity) 516 (m$^+$, 1.4), 501 (3.4), 443 (16.9), 412 (10.2), 339 (30.5), 251 (100.0), 73 (100.0). HRMS: 516.2947 (M$^+$ calcd), 516.2943 (found). Anal. Calcd for $C_{23}H_{56}$: C, 53.41; H, 10.91. Found: C, 53.52; H, 10.94.

Spectral data for **2b** are as follows. Mp: 70–71 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.05 (s, 9H, Si(C*H*$_3$)$_3$), 0.06 (s, 9H, Si(C*H*$_3$)$_3$), 0.07 (s, 9H, Si(C*H*$_3$)$_3$), 0.08 (s, 9H, Si(C*H*$_3$)$_3$), 0.09 (s, 9H, Si(C*H*$_3$)$_3$), 0.23 (s, 3H, SiC*H*$_3$), 1.27 (m, 1H, C*H*), 1.56 (d, *J* = 12.7 Hz, 1H, C*H*), 1.59 (dd, *J* = 8.1 and 4.7 Hz, 1H, C*H*), 2.26 (dd, *J* = 4.6 and 2.0 Hz, 1H, C*H*), 3.37 (s, 3H, OC*H*$_3$), 5.59 (dd, *J* = 12.6 and 2.0 Hz, 1H, vinyl *H*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ –0.82 (Si−*C*H$_3$), –0.79, 0.19, 0.38, 0.46, 0.60 (Si(*C*H$_3$)$_3$), 10.85, 22.18, 24.38, 29.60 (*C*H), 50.69 (O*C*H$_3$), 133.18, 138.36 (vinyl *C*). ^{29}Si NMR (CDCl$_3$, 79 MHz): δ 0.2 (*Si*Me$_3$), 0.3 (*Si*Me$_3$), 1.1 (*Si*Me$_3$), 3.7 (*Si*Me$_3$), 5.9 (*Si*Me$_3$), 25.6 (*Si*OMe). MS: *m*/*z* (relative intensity) 516 (m$^+$, 0.3), 501 (0.8), 443 (8.5), 339 (26.3), 251 (40.7), 73 (100.0). Anal. Calcd for $C_{23}H_{56}$: C, 53.41; H, 10.91. Found: C, 53.55; H, 10.89.

Synthesis of 3. To a mixture of chlorotrimethylsilane (27.9 mL, 0.220 mol) and lithium (1.53 g, 0.220 mol) at 0 °C in THF (100 mL) was added a solution of dimethoxymethylphenylsilane (10 g, 0.055 mol) in THF (25 mL). The solution was then stirred for 2 h at 0 °C, forming **3**. Next the reaction mixture was treated with saturated aqueous ammonium chloride at room temperature. After addition of *n*-hexane, precipitated compounds were removed by filtration and volatiles were distilled under vacuum. The crude material was purified by silica gel chromatography (1/100 ether/hexane) to afford **3a**,**b** as colorless oils in 15% (3.1 g) and 7% (1.4 g) yields, respectively.

Spectral data for **3a** are as follows. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.00 (s, 9H, Si(C*H*$_3$)$_3$), 0.05 (s, 9H, Si(C*H*$_3$)$_3$), 0.06 (s, 9H, Si(C*H*$_3$)$_3$), 0.41 (s, 3H, SiC*H*$_3$), 0.74–1.41 (m, 2H, C*H*), 3.33 (s, 3H, OC*H*$_3$), 5.41 (d, *J* = 18.8 Hz, 1H, C*H*), 5.80–5.87 (m, 1H, vinyl *H*), 6.24 (d, *J* = 18.8 Hz, 1H, vinyl *H*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ –2.73, –0.89, −0.72 (Si(*C*H$_3$)$_3$), –1.29 (Si−*C*H$_3$), 23.58, 43.19 (*C*H), 52.18 (O*C*H$_3$), 123.9, 128.1, 133.8, 146.2 (vinyl *C*). ^{29}Si NMR (CDCl$_3$, 79 MHz): δ −7.9 (*Si*Me$_3$), −0.2 (*Si*Me$_3$), −0.2 (*Si*Me$_3$), 26.5 (*Si*OMe). MS: *m*/*z* (relative intensity) 370 (m$^+$, 19.5), 355 (16.1), 266 (90.2), 251 (61.1), 178 (100.0), 73 (90.9). HRMS: 370.2000 (M$^+$ calcd), 370.0665 (found). Anal. Calcd for $C_{17}H_{38}OSi_4$: C, 55.06; H, 10.33. Found; C, 55.11; H, 10.31.

Spectral data for **3b** are as follows. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.00 (s, 18H, Si(C*H*$_3$)$_3$), 0.05 (s, 9H, Si(C*H*$_3$)$_3$), 1.10–1.11 (m, 1H, C*H*), 1.67 (d, *J* = 12.6, 1H, C*H*), 3.30 (s, 3H, OC*H*$_3$), 5.66 (d, *J* = 12.6 Hz, 1H, vinyl *H*), 5.98–6.00 (m, 1H, vinyl *H*), 6.59 (d, *J* = 7.28 Hz, 1H, vinyl *H*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ –3.418 (Si−*C*H$_3$), –1.201, –0.367 (Si(*C*H$_3$)$_3$), 21.11, 25.88 (*C*H), 50.38 (O*C*H$_3$), 131.8, 133.8, 135.2, 135.6 (vinyl *C*). ^{29}Si NMR (CDCl$_3$, 79 MHz): δ 0.4 (*Si*Me$_3$), 0.5 (*Si*Me$_3$), 1.0 (*Si*Me$_3$), 16.2 (*Si*OMe). MS: *m*/*z* (relative intensity) 370 (m$^+$, 3.20), 355 (0.01), 266 (8.48), 251 (8.26), 178 (13.8), 73 (100).

Reaction of 3 with Li and Chlorotrimethylsilane. A solution of **3a** (0.45 g, 1.2 mmol) in THF (10 mL) was added to a mixture of chlorotrimethylsilane (0.46 mL, 3.6 mmol) and lithium (17 mg, 2.4 mmol) at room temperature in THF (40 mL). The solution was stirred for 2 h at that temperature; **2a** was formed quantitatively. **2b** was also synthesized quantitatively from the reaction of **3b** (0.16 g, 0.43 mmol) with Li (6 mg, 0.86 mmol) and chlorotrimethylsilane (0.16 mL, 1.3 mmol).

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Supporting Information Available: CIF files giving crystallographic data for compounds **2a**,**b**. This materials is available free of charge via the Internet at http://pubs.acs.org.

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