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# Generation and Polymerization of Silacyclopropanes in the Reaction of Bis(chloromethyl)diorganosilanes with Magnesium

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The reaction of bis(chloromethyl)diorganosilanes ($R_2Si(CH_2Cl)_2$: **1a**, R = Me; **1b**, R = allyl; **1c**, R = benzyl; **1d**, R = Ph) with magnesium gives **2a**−**d** (65−90%) of formula $MeR_2SiCH_2(SiR_2CH_2CH_2)_nH$ ($n$ = 1, 2, 3, ...) and dimethyldiorganosilanes **3a**−**d** (17−9%). The trapping reaction of the intermediates generated in the reaction of **1d** with magnesium using $CD_3OD$ gives the corresponding $CD_3OD$-trapped product of the 1,1-diphenylsilacyclopropane intermediate, $Ph_2Si(OCD_3)(CH_2CH_2D)$ (**6′**), along with the deuterated products of $Ph_2Si(CH_2D)(CH_2Cl)$ (**5′**), $Ph_2Si(CH_2D)_2$ (**3d′**), and **2d′**. The results are consistent with a reaction course in which silacyclopropane intermediates are generated in the reaction of **1a**−**d** with magnesium and then polymerized to **2a**−**d**.

## Introduction

The Grignard reaction, well-known as a useful route for carbon−carbon bond formation in organic synthesis, has been widely practiced in the development of organosilicon chemistry,[1] because Grignard reagents easily react with functionalized silicon compounds such as halosilanes, aminosilanes, alkoxysilanes, etc., to give new, useful organosilanes.[2] In such a synthetic Grignard method, bis(α-chloroalkyl)silanes are attractive as a family of potential starting materials for the synthesis of highly ring strained silacyclopropanes[3−7] in the academic field and for the preparation of carbosilanes[8,9] in industry.

Seyferth and co-workers first reported the synthesis of stable silacyclopropane derivatives having bulky substituents, starting from bis(α-bromocyclopropyl)silanes and magnesium.[3] Several other analogues of the silacyclopropanes have been prepared and studied for their reactivities.[4−6] Such isolated silacyclopropanes are significantly stabilized by bulky groups on the ring-carbons.[7] Although bis(α-bromoisopropyl)dimethylsilane served well in the preparation of hexamethylsilacyclopropane,[5] the reaction of bis(α-chloroisopropyl)dimethylsilane with magnesium did not result in ring closure but gave instead a mixture of reduction products such as diisopropyldimethylsilane and dehydrochlorinated products such as dimethylisopropyl(α-methylvinyl)silane and bis(α-methylvinyl)dimethylsilane.[4]

**Table 1. Results on Grignard Reactions of Bis(chloromethyl)diorganosilanes**

| | | products (%) | |
|---|---|---|---|
| reactant **1** | reacn time (h) | **2** (polymer)[a] | **3** |
| **1a** | 3 | **2a**, 80 (46) | **3a**, 10 |
| **1b** | 4 | **2b**, 65 (41) | **3b**, 17 |
| **1c** | 8 | **2c**, 90 (15) | **3c**, 8 |
| **1d** | 2 | **2d**, 80 (44) | **3d**, 9 |

[a] Amount of polymer insoluble in hexane is given in parentheses.

The reactions of bis(chloromethyl)dimethylsilane with lithium or magnesium have been reported to give the corresponding dimetalated compounds which were converted to asymmetric 1,3-disilacyclobutanes or 1-sila-3-germacyclobutanes by coupling with dichlorosilanes or dichlorogermanes, respectively.[10] The yields of 1,3-disilacyclobutanes or 1-sila-3-germacyclobutanes were very low ranging from 21% to 24% due to the production of polymeric byproducts. Although silacyclopropane intermediates, in principle, could be formed in the metalation of bis(chloromethyl)dimethylsilane, the anticipated derivatives of the intermediates were not reported. We report herein evidence for the generation and polymerization of silacyclopropanes in the reactions of bis(chloromethyl)diorganosilanes with magnesium.

## Results and Discussion

**Reaction of Bis(chloromethyl)silanes (1a−d) with Magnesium.** The reaction of bis(chloromethyl)diorga-

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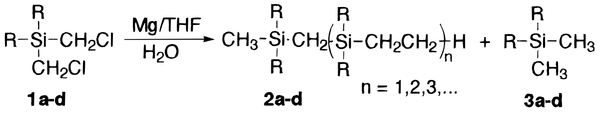
nosilanes (**1a**−**d**) with magnesium in THF at reflux gives high yields of poly(diorganosilapropanes) (**2a**−**d**) along with dimethyldiorganosilanes (**3a**−**d**) as shown in eq 1. The progress of the reactions could be monitored by checking the disappearance of **1a**−**d** by GLC at 30 min time intervals. The results on the Grignard reactions of **1a**−**d** are summarized in Table 1.



$$\mathrm{R{-}\overset{R}{\underset{CH_2Cl}{Si}}{-}CH_2Cl} \xrightarrow[H_2O]{Mg/THF} \mathrm{CH_3{-}\overset{R}{\underset{R}{Si}}{-}CH_2\left(\overset{R}{\underset{R}{Si}}{-}CH_2CH_2\right)_n H} + \mathrm{R{-}\overset{R}{\underset{CH_3}{Si}}{-}CH_3} \quad (1)$$

**1a-d** **2a-d** n = 1,2,3,... **3a-d**

(**a**; R = Me, **b**; R = Allyl, **c**; R = $CH_2Ph$, **d**; R = Ph)

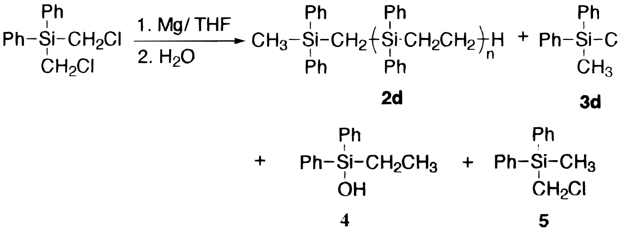
As shown in Table 1, **2a**−**d** of general formula $MeR_2SiCH_2(SiR_2CH_2CH_2)_nH$ (R = Me, allyl, benzyl, phenyl; $n = 1, 2, 3, 4, ...$) with the backbone of alternating ethylene and silicon were obtained as major products in high yield ranging from 65% to 90% depending upon the substituents on the silicon atom. The formation of **2a**−**d** could be explained by the ring-opening polymerization of the silacyclopropane intermediate generated by intramolecular cyclization of the mono-Grignard reagent. The reduction products **3a**−**d** usually were obtained in low yield (9−17%) and apparently formed from the hydrolysis of di-Grignard reagents of **1a**−**d** during the workup.[10b] The reaction of the diphenylsilane compound was faster than those of the corresponding alkylsilanes, and the reaction rate of the less hindered dimethyl compound was faster than that of the bulkier dibenzyl compound. The reaction rate of **1a**−**d** with magnesium depended on the substituents on silicon and decreased in the order: **1d** > **1a** > **1b** > **1c**, indicating that the reactivities of **1** were sensitive to the electronic nature[11] and the steric effect of the substituents on silicon. It is interesting to note that an allyl group-containing polymer (**2c**) was produced, suggesting that this method can be applied to the synthesis of poly(silapropylene) with functionality.

**Characterizations and Properties of Poly(silapropanes) (2a−d).** Volatile compounds of **2a**−**d** were distilled under vacuum and characterized by mass and NMR spectroscopy. The analyses of mass data give useful information on the structures of polymers **2a**−**d**. The GC/MS data of **2a** showed the same base peaks (*m*/*e* 145, $Me_3SiCH_2SiMe_2^+$) in the molecular fragmentation patterns and the increment of dimethylsilapropylene (*m*/*e* 86, $Me_2SiCH_2CH_2$) unit with increasing retention times, suggesting that the polymeric materials (**2a**) have a silapropylene unit in the backbone. Volatiles of **2a** were purified by a preparative GLC, and subsequent analyses by $^1H$ and $^{13}C$ NMR disclosed that they were a mixture of formula $Me_3SiCH_2(SiMe_2CH_2CH_2)_nH$ ($n = 1, 2, 3, ...$) as shown in eq 1. Other polymers **2b**−**d** also were characterized by NMR. $^1H$ and $^{13}C$ NMR data, and average molecular weights for polymers insoluble in hexane solvent are listed in Table 2.

In the $^1H$ NMR spectra, the characteristic peaks due to the ethylene unit in the silapropylene backbone of **2a**−**d** are observed as a singlet between 0.36 and 0.87 ppm. The peaks due to the substituents on silicon appear as a singlet at −0.06 ppm ($CH_3$) in **2a**; doublet (allylic $CH_2$) at 1.54 ppm, multiplet ($CH{=}CH_2$) at 4.81−5.87 ppm in **2b**; broad singlet at 2.23 ppm (benzylic $CH_2$), multiplet (phenyl *H*) at 7.06−7.38 ppm in **2c**; and multiplet (phenyl *H*) at 7.10−7.40 ppm in **2d**. The integration ratio of the protons of the substituents on silicon to the ethylene ($CH_2CH_2$) unit of the polymer backbone provides good information for the structure. As an example, the $^1H$ NMR spectrum of **2a** shows a 3:2 ratio for the methyl and ethylene ($CH_2CH_2$) resonances, indicating that two methylene units are present in the polymer backbone, not one. The assignments of structures based on the data of $^{13}C$ NMR spectra well agree with those of the $^1H$ NMR spectra. Average molecular weights for polymers (**2a**−**d**) insoluble in hexane were relatively low, ranging from $M_w$ 2600 to 5300. Both polymers, **2a**,**d**, are white solids; the others are colorless oily materials. All polymers are soluble in aromatic solvents, diethyl ether, THF, and chloroform.

The thermal stability of polymers **2a**,**d** was measured. In TGA experiments, their thermal stabilities were maintained up to 400 °C and then they rapidly decomposed to give solid residues in 6% and 50% yields for **2a**,**d**, respectively, as the temperature was raised to 500 °C. The significant decomposition of **2d** began slightly later than that of **2a** and gave a higher residue yield, reflecting that the aromatic groups are more thermally stable than the alkyl group.[12]

**1:1 Reaction of 1 and Magnesium.** To observe if the unstable silacyclopropane intermediate is formed by the stoichiometric reaction of **1** and magnesium, a 1:1 reaction of the representative compound **1d** and magnesium was carried out. The reaction for 2 h under the same conditions gave **2d** (72%), **3d** (11%), diphenylethylsilanol ($Ph_2EtSiOH$) (**4**) (2%), and (chloromethyl)-diphenylmethylsilane ($Ph_2(ClCH_2)SiMe$) (**5**) (2%) along with **1d** (12%) recovered (eq 2). The product distribution, except for 12% of **1d** recovered in this reaction, was similar to the results obtained in the reaction using twice as much magnesium. These results strongly suggest that under our reaction conditions the intramolecular ring-closure reaction of mono-Grignard reagents to silacyclopropane intermediates is more favorable than the reaction of such intermediates with magnesium to form di-Grignard reagents. This is consistent with the previous reports for the reaction of bis(α-bromoalkyl)-diorganylsilanes and magnesium.[4−6] Silacyclopropanes were reported to be highly reactive toward air, water, and alcohols[5] and polymerized to higher oligomers having a silapropylene backbone on reaction with methyllithium.[5]



$$\mathrm{Ph{-}\overset{Ph}{\underset{CH_2Cl}{Si}}{-}CH_2Cl} \xrightarrow[2.\ H_2O]{1.\ Mg/THF} \mathrm{CH_3{-}\overset{Ph}{\underset{Ph}{Si}}{-}CH_2\left(\overset{Ph}{\underset{Ph}{Si}}{-}CH_2CH_2\right)_n H} + \mathrm{Ph{-}\overset{Ph}{\underset{CH_3}{Si}}{-}CH_3} + \mathrm{Ph{-}\overset{Ph}{\underset{OH}{Si}}{-}CH_2CH_3} + \mathrm{Ph{-}\overset{Ph}{\underset{CH_2Cl}{Si}}{-}CH_3} \quad (2)$$

**2d** **3d** **4** **5**

**Effects of Reaction Time on Product Distributions.** To observe the distributions of products, **2d**, **3d**,

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**Table 2. Data from $^1H$ and $^{13}C$ NMR and GPC for Polymers (2a−d)[a]**

| 2 | data from NMR[b] | | av molecular weights[c] | | |
|---|---|---|---|---|---|
| | $^1H$ NMR | $^{13}C$ NMR | $M_w$ | $M_n$ | PDI |
| **2a** | $-0.06$ (s, $CH_3$), 0.36 (s, $SiCH_2$) | 4.36 ($CH_3$), 6.62 ($CH_2$) | 3400 | 2400 | 1.4 |
| **2b** | 0.47 (s, $SiCH_2$), 1.50−1.56 (m, allylic*H*), 4.85−4.89 (m, $=CH_2$), 5.76 (m, $=CH$) | 4.74 ($CH_2$), 20.83 (allylic$CH_2$), 112.56 ($=CH_2$), 135.25 ($=CH$) | 2600 | 1200 | 2.2 |
| **2c** | 0.44 (s, $SiCH_2$), 2.23 (s, benzylic$CH_2$), 7.06−7.38 (m, phenyl*H*) | 3.47 ($CH_2$), 21.29 (benzylic$CH_2$), 124.17, 128.26, 139.61 (phenyl*C*) | 5300 | 4500 | 1.2 |
| **2d** | 0.87 (s, $CH_2$), 7.10−7.40 (m, phenyl*H*) | 3.69 ($CH_2$), 127.76, 129.14, 134.98, 135.64 (phenyl*C*) | 4100 | 2600 | 1.6 |

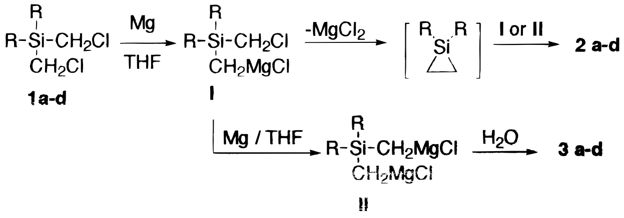
[a] Polymers insoluble in hexane solvent. [b] Chloroform-*d* was used as a solvent. [c] Molecular weights were calibrated by polystyrene standards.

**Table 3. Effect of Reaction Time on Product Distributions (%)**

| reacn time (h) | 1d | 2d (polymer)[a] | 3d | 5 | 6 |
|---|---|---|---|---|---|
| 0 | 100 | | | | |
| 0.5 | trace | 69 (25) | 20 | 2 | 2 |
| 1.0 | trace | 83 (36) | 11 | trace | trace |
| 2.0 | | 84 (41) | 8 | | |
| 4.0 | | 80 (44) | 9 | | |
| 8.0 | | 84 (41) | 8 | | |

[a] Amount of polymer insoluble in hexane solvent.

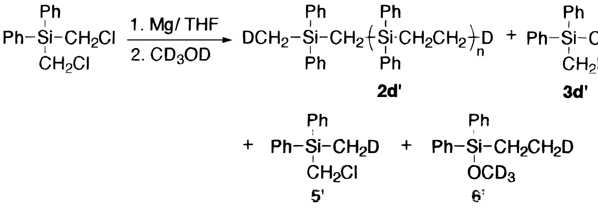
**Scheme 1. Reaction Pathway of 1a−d to 2a−d**



**5** [$Ph_2SiMe(CH_2Cl)$)],[13] and **6** ($Ph_2SiOMeEt$),[14] depending on the reaction time, the reaction mixtures of **1d** with magnesium were quenched with methanol at various reaction times (0.5, 1, 2, 4, and 8 h). These results are summarized in Table 3.

As shown in Table 3, the yield of **3d** decreased from 20% (0.5 h) to 11% (1 h) as the reaction time increased and remained about the same thereafter, suggesting the involvement of the di-Grignard reagent in initiating polymerization. However, the yield of **2d** increased smoothly from 69% (0.5 h) to 83% (1 h) and remained almost constant. The proportion of the polymer insoluble in hexane also increased from 25% (0.5 h) to 41% (2 h), but the average molecular weights of polymers obtained at various reaction times were about the same. Methanol-trapped product **6** of silacyclopropane decreased from 2% (0.5 h) to a trace (1 h) and then finally disappeared. Only 2% of **5** produced from the mono-Grignard reagent was obtained during the first stage of the reaction (0.5 h), reflecting the high reactivity of the mono-Grignard reagent to the intramolecular cyclized silacyclopropane or to the di-Grignard reagent. These results indicate that the silacyclopropane intermediates, generated by an insertion reaction of magnesium to **1d** followed by intramolecular cyclization, undergo a ring open-polymerization to **2d** in the Grignard reaction of **1d**.

**Trapping Reaction of Silacyclopropane Intermediate.** To clarify the generation of the silacyclopropane intermediate, a trapping experiment with $CD_3OD$ was carried out for the reaction mixture of **1d** with magnesium in THF at reflux for 20 min reaction. The trapping product of 1,1-diphenylsilacyclopropane, $Ph_2Si(OCD_3)(CH_2CH_2D)$ (**6′**), was isolated in 3% yield along with the deuterated products of $Ph_2Si(CH_2D)_2$ (**3d′**, 15%), $Ph_2Si(CH_2D)CH_2Cl$ (**5′**, 3%), and **2d′** (62%); 3% of **1d** was recovered (eq 3). The products of **5′** and **3d′** clearly show the formation of the mono- and di-Grignard reagents, respectively. The product **6′** can be explained by the reaction of the 1,1-diphenylsilacyclopropane intermediate with methanol-$d_4$. However, 1,1,4,4,-tetraphenyl-1,4-disilacyclohexane, the dimerization product of the silacyclopropane intermediate,[15] was not detected probably due to the fast polymerization of the unstable silacyclopropanes. It is well-known that silacyclopropane with no bulky substituent can thermally decompose to extrude the silylenes intermediate which can be inserted to silacyclopropane leading to 1,2-disilacyclobutanes[4,16−19] or polymerize to poly(diorganosilylene). However, no silylene-trapped products were detected in the volatile compounds and polymers. The higher yield (62%) of **2d′** than the hydrolyzed product of the di-Grignard reagent **3d′** (15%) indicates that the mono-Grignard reagent is intramolecularly cyclized to silacyclopropane and reacts with a magnesium to give di-Grignard reagent, but the reaction rate for the intramolecular cyclization is faster.



(3)

**Reaction Mechanism.** On the basis of the previous results, we propose a possible reaction pathway for the formation of the polymer as shown in Scheme 1. The reaction of **1a−d** with magnesium affords at first mono-Grignard reagents (**I**), which cyclize intramolecularly to silacyclopropane intermediates or further react with magnesium to give di-Grignard reagents (**II**). The silacyclopropanes which do not have bulky substituents on the ring-carbons do not survive long but undergo a ring-opening polymerization to give **2a−d** by the nu-

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cleophilic attack of the mono- (**I**) and di-Grignard reagents (**II**). The di-Grignard reagents (**II**) which remain would be hydrolyzed to give **3a**−**d** during the workup.

## Experimental Section

**Reagents and Physical Measurements.** All operations were carried out in an inert atmosphere. Solvents, tetrahydrofuran (THF), diethyl ether, and hexane, were dried over sodium benzophenone ketyl and distilled before use. Bis(chloromethyl)dichlorosilane was obtained from Hüls America, Inc., and purified by fractional distillation. Other simple chemicals were purchased from Aldrich Chemical Co. and used without further purification. Products were analyzed by gas−liquid chromatography (GLC) using a capillary column (SE-54, 30 m) and a packed column (10% OV-101 on 80−100 mesh Chromosorb W/AW, 1.5 m × $^1/_8$ in.) on a Varian 3300 gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector, respectively. The samples for characterization were purified by a preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 2 m by $^1/_8$ in. stainless steel column packed with 20% OV-101 on 80−100 mesh Chromosorb P/AW. NMR spectra were recorded on a Varian Gemini 300 spectrometer using chloroform-*d* solvent. Mass spectra were obtained using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a model 5972 mass selective detector. Elemental analyses were performed by the Chemical Analysis Laboratory of the Korea Institute of Science and Technology. Gel permeation chromatography (GPC) was carried out on a Waters Millipore gel permeation chromatograph with Ultrastyragel GPC column series (in sequence, 100, 500, $10^3$, and $10^4$ Å columns) using toluene solvent as an eluent. Molecular weights were calibrated by polystyrene standards.

**Reaction of 1a with Magnesium.** To a mixture of magnesium turnings (3.47 g, 142.8 mmol), a small piece of iodine, and THF (100 mL) was added dropwise bis(chloromethyl)dimethylsilane (**1a**) (9.22 g, 58.68 mmol) with vigorous stirring at reflux. After 3 h of reaction, the reaction mixture cooled to room temperature and was treated with 50 mL of water; 50 mL of hexane was added. The organic layer was separated and 0.57 g (purity; 90%) of tetramethylsilane (10%) was distilled out. The solvent then was evaporated, and the residue was extracted with hexane. The hexane-insoluble white powder was washed with water, and the residual white solid was vacuum-dried to give 2.31 g (46%) consisting of high molecular weight polymers ($M_\mathrm{w}$, 3400; $M_\mathrm{n}$, 2400). The hexane extracts were distilled to give 0.3 g (6%) of volatiles (**2b**), which were of the formula $\mathrm{Me_3SiCH_2(SiMe_2CH_2CH_2)}_n\mathrm{H}$ [$n = 1$ (0.2%), 2 (2%), 3 (1%), 4 (0.2%), ...], under reduced pressure (0.6 mmHg) at oil bath temperatures between room temperature and 250 °C, and 1.71 g (34%) of nonvolatiles (**2b**) ($M_\mathrm{w}$, 620; $M_\mathrm{n}$, 420) remained. The samples for the characterization of volatile products were purified by preparative GLC. Spectroscopic data for volatile products are as follows. Data for 2,2,4,4-tetramethyl-2,4,-disilahexane: $^1$H NMR $\delta$ −0.29 (s, 2H, $\mathrm{SiC}H_2\mathrm{Si}$), −0.00 (s, 6H, $\mathrm{Si(C}H_3)_2$), 0.03 (s, 9H, $\mathrm{Si(C}H_3)_3$), 0.48 (q, 2H, $J = 8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.92 (t, 3H, $J = 8$ Hz, $\mathrm{CH_2C}H_3$); $^{13}$C NMR $\delta$ −1.12 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.36 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 2.17 ($\mathrm{Si(}C\mathrm{H_3)_2}$-Et), 7.39 ($C\mathrm{H_2CH_3}$), 9.55 ($\mathrm{CH_2}C\mathrm{H_3}$); mass spectrum, [*m*/*z* (relative intensity)] 174 (1, M$^+$), 159 (12), 145 (100, $\mathrm{Me_3SiCH_2SiMe_2}^+$), 73 (50, $\mathrm{Me_3Si}^+$), 59 (35). Anal. Calcd for $\mathrm{C_8H_{22}Si_2}$: C, 55.09; H, 12.71. Found: C, 54.63; H, 12.75. Data for 2,2,4,4,7,7-hexamethyl-2,4,7-trisilanonane: $^1$H NMR $\delta$ −0.29 (s, 2H, $\mathrm{SiC}H_2\mathrm{Si}$), −0.06 (s, 6H), −0.01 (s, 6H, $\mathrm{Si(C}H_3)_2$), 0.02 (s, 9H, $\mathrm{Si(C}H_3)_3$), 0.37 (s, 4H, $\mathrm{C}H_2\mathrm{C}H_2$), 0.48 (q, 2H, $J = 8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.92 (t, 3H, $J = 8$ Hz, $\mathrm{CH_2C}H_3$); $^{13}$C NMR $\delta$ −4.43 (central-$\mathrm{Si(}C\mathrm{H_3)_2}$), −1.17 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.39 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 2.02 ($\mathrm{Si(}C\mathrm{H_3)_2}$), 6.42, 6.86 ($C\mathrm{H_2}C\mathrm{H_2}$), 7.37 ($C\mathrm{H_2CH_3}$), 9.97 ($\mathrm{CH_2}C\mathrm{H_3}$); mass spectrum [*m*/*z* (relative intensity)] 260 (3, M$^+$), 146 (15), 145 (100, $\mathrm{Me_3SiCH_2SiMe_2}^+$), 115 (10), 87 (13), 73 (35), 59 (27). Anal. Calcd for $\mathrm{C_{12}H_{32}Si_3}$: C, 55.30; H, 12.37. Found: C, 55.28; H, 12.53. Data for 2,2,4,4,7,7,10,10-octamethyl-2,4,7,10-tetrasiladodecane: $^1$H NMR $\delta$ −0.29 (s, 2H, $\mathrm{SiC}H_2$-Si), −0,06 (s, 12H), −0.01 (s, 6H) $\mathrm{Si(C}H_3)_2$), 0.02 (s, 9H, $\mathrm{Si(C}H_3)_3$), 0.36 (s, 8H, $\mathrm{C}H_2\mathrm{C}H_2$), 0.48 (q, 2H, $J = 8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.92 (t, 3H, $J = 8$ Hz, $\mathrm{CH_2C}H_3$); $^{13}$C NMR $\delta$ −4.45 ($\mathrm{Si(}C\mathrm{H_3)_2}$), −1.15 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.38 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 2.02 ($\mathrm{Si(}C\mathrm{H_3)_2Et}$), 6.39, 6.73 ($C\mathrm{H_2}C\mathrm{H_2}$), 7.39 ($C\mathrm{H_2CH_3}$), 9.99 ($\mathrm{CH_2}C\mathrm{H_3}$); mass spectrum [*m*/*z* (relative intensity)] 346 (2, M$^+$), 1.73 (18), 157 (14), 146 (18), 145 (100, $\mathrm{Me_3SiCH_2SiMe_2}^+$), 143 (57), 129 (10), 99 (11), 87 (23), 73 (81), 59 (40). Anal. Calcd for $\mathrm{C_{16}H_{42}Si_4}$: C, 55.41; H, 12.20. Found: C, 56.03; H, 12.36. Data for 2,2,4,4,7,7,10,10,13,13-decamethyl-2,4,7,10,13-pentasilapentadecane: $^1$H NMR $\delta$ −0.29 (s, 2H, $\mathrm{SiC}H_2\mathrm{Si}$), −0.06 (s, 18H), −0.01 (s, 6H, $\mathrm{Si(C}H_3)_2$), 0.02 (s, 9H, $\mathrm{Si(C}H_3)_3$), 0.36 (s, 12H, $\mathrm{C}H_2\mathrm{C}H_2$), 0.48 (q, 2H, $J = 8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.92 (t, 3H, $J = 8$ Hz, $\mathrm{CH_2C}H_3$); mass spectrum [*m*/*z* (relative intensity)] 432 (2, M$^+$), 173 (10), 159 (18), 157 (38), 146 (17), 145 (100, $\mathrm{Me_3SiCH_2SiMe_2}^+$), 143 (55), 129 (13), 87 (32), 85 (20), 73 (97), 59 (41). Anal. Calcd for $\mathrm{C_{20}H_{52}Si_5}$: C, 55.47; H, 12.10. Found: C, 55.74; H, 12.07. Data for 2,2,4,4,7,7,10,10,13,13,16,16-dodecamethyl-2,4,7,10,13,16-hexasilaoctadecane: $^1$H NMR $\delta$ −0.29 (s, 2H, $\mathrm{SiC}H_2\mathrm{Si}$), −0.06 (s, 24H), −0.01 (s, 6H, $\mathrm{Si(C}H_3)_2$), 0.02 (s, 9H, $\mathrm{Si(C}H_3)_3$), 0.36 (s, 16H, $\mathrm{C}H_2\mathrm{C}H_2$), 0.48 (q, 2H, $J = 8$ Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 0.92 (t, 3H, $J = 8$ Hz, $\mathrm{CH_2C}H_3$); mass spectrum [*m*/*z* (relative intensity)] 518 (1, M$^+$), 173 (16), 159 (20), 157 (40), 146 (13), 145 (83, $\mathrm{Me_3SiCH_2SiMe_2}^+$), 143 (50), 129 (13), 87 (33), 85 (202), 73 (100, $\mathrm{SiMe_3}^+$), 59 (39).

**Reaction of 1b with Magnesium.** Using the procedure previously described, the reaction of **1b** (1.45 g, 6.93 mmol) with magnesium turnings (0.42 g, 17.28 mmol) and a small piece of iodine in THF (10 mL) for 4 h gave **3b** (0.16 g, 17%), **2b** (0.85 g, 24%: $M_\mathrm{w}$, 910; $M_\mathrm{n}$, 710) dissolved in hexane, and polymer **2b** (0.39 g, 41%; $M_\mathrm{w}$, 2600; $M_\mathrm{n}$, 1200) insoluble in hexane.

**Reaction of 1c with Magnesium.** Using the procedure previously described, the reaction of **1c** (1.47 g, 4.75 mmol) with magnesium turnings (0.28 g, 11.52 mmol) and a small piece of iodine in THF (10 mL) for 8 h gave **3c** (0.09 g, 8%), **2c** (0.85 g, 75%: $M_\mathrm{w}$, 1600; $M_\mathrm{n}$, 1200) dissolved in hexane, and **2c** (0.17 g, 15%: $M_\mathrm{w}$, 5300; $M_\mathrm{n}$, 4500) insoluble in hexane.

**Reaction of 1d with Magnesium.** Using the procedure previously described, the reaction of **1d** (1.0 g, 3.56 mmol) with magnesium turnings (0.21 g, 8.64 mmol) and a small piece of iodine in THF (10 mL) for 3 h gave **3d** (0.07 g, 9%), **2d** (0.27 g, 36%: $M_\mathrm{w}$, 1330; $M_\mathrm{n}$, 930) dissolved in hexane, and **2d** (0.33 g, 44%: $M_\mathrm{w}$, 4100; $M_\mathrm{n}$, 2600) insoluble in hexane.

**1:1 Reaction of 1d and Magnesium.** Using the procedure previously described, the reaction of **1d** (1.0 g, 3.6 mmol), magnesium turnings (0.087 g, 3.6 mmol), and a small piece of iodine in THF (10 mL) was carried out for 2 h at reflux. The white precipitate which formed dissolved when the reaction solution was washed with 20 mL of a saturated aqueous ammonium chloride solution. The reaction mixture then was extracted with ethyl ether. The solvent was removed and the residue was distilled to give **3d** (11%), **5** (2%), diphenylethylsilanol (**4**) (2%), and unreacted **1d** (12%). **2d** was obtained in 72% yield.

**Product Distributions and Reaction Time.** To stirred mixtures of magnesium turnings (0.21 g, 8.6 mmol), a small piece of iodine, and THF (10 mL) were added dropwise **1d** (1.0 g, 3.6 mmol) using a syringe pump for 2 min at reflux. At 0.5, 1.0, 2.0, 4.0, and 8.0 h of reaction time, $\mathrm{CH_3OH}$ (1 mL) was added to each of the five flasks, respectively, and worked up as previously described in the reaction of **1a** with magnesium. The distributions of volatile products were determined by analytical GLC.

**Trapping Reaction of Silacyclopropane Intermediate with Methanol-*d*$_4$.** In a reaction procedure similar to the one already described, the reaction of **1d** (1.0 g, 3.6 mmol) with magnesium turnings (0.21 g, 8.5 mmol) and a small piece of iodine in THF (10 mL) was carried out for 20 min at reflux. $CD_3OD$ (1 mL) was added, and the solution was stirred for 20 min without heating. The upper layer was separated and the solvent distilled. The residue mixture was extracted with hexane. The hexane was distilled, and the residual liquid was distilled to give $Ph_2Si(CH_2D)_2$ (**3d′**) (15%), $Ph_2Si(CH_2Cl)CH_2D$ (**5′**) (3%), $Ph_2Si(CH_2CH_2D)(OCD_3)$ (**6′**) (3%), and unreacted **1d** (3%). **2d′** (62%) was also obtained. Data for **3d′**: $^1$H NMR $\delta$ 0.56 (t, $J = 2$ Hz, 4H, $CDH_2$), 7.36−7.57 (m, 10H, phenyl-$H$); $^{13}$C NMR $\delta$ −2.72 (t, $J = 19$ Hz,$CH_2D$), 127.79, 129.07, 134.18, 138.24 (phenyl carbons). Data for **5d′**: $^1$H NMR $\delta$ 0.72 (t, $J = 2$ Hz, 2H, $CDH_2$), 3.27 (s, 2H, $CH_2Cl$), 7.38−7.60 (m, 10H, phenyl $H$); $^{13}$C NMR $\delta$ −5.89 (t, $J = 19$ Hz, $CH_2D$), 28.82 ($CH_2$-Cl), 128.06, 129.93, 134.19, 134.66 (phenyl carbons). Data for **6′**: $^1$H NMR $\delta$ 1.04 (tt, $J = 2$, 8 Hz, 2H, $CDH_2$), 1.16 (t, $J = 8$ Hz, 2H, $CH_2$), 7.37−7.62 (m, 10H, phenyl $H$); $^{13}$C NMR $\delta$ 5.14 ($CH_2CH_2D$), 6.38 (t, $J = 19$ Hz,$CH_2CH_2D$), 50.56 (m, $OCD_3$), 127.84, 129.80, 134.67 (phenyl carbons).

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