Mechanistic Aspects in the Grignard Coupling Reaction of Bis(chloromethyl)dimethylsilane with Trimethylchlorosilane

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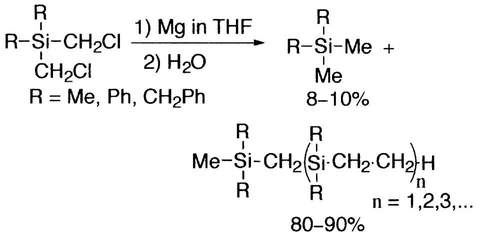
The Grignard reactions of bis(chloromethyl)dimethylsilane (**1**) with trimethylchlorosilane (**2**) in THF give both the intermolecular C–Si coupling and intramolecular C–C coupling products. At beginning stage, **1** reacts with Mg to give the mono-Grignard reagent $ClCH_2Me_2SiCH_2MgCl$ (**I**) which undergoes the C–Si coupling reaction to give $Me_2Si(CH_2SiMe_3)_2$ **3**, or C–C coupling to a mixture of formula $Me_3SiCH_2(SiMe_2CH_2CH_2)_nR^1$ (n = 1, 2, 3, ..; **4a**, R^1 = H: **4b**, R^1 = $SiMe_3$). In the reaction, two reaction pathways are involved: **a**) **I** reacts with **2** to give $Me_3SiCH_2SiMe_2CH_2Cl$ **6** which further reacts with Mg to afford a $Me_2SiCH_2Me_2SiCH_2MgCl$ (**II**) or **b**) **I** cyclizes intramolecularly to a silacyclopropane intermediate **A**, which undergoes a ring-opening polymerization by the nucleophilic attack of the intermediates **I** or **II**, followed by the termination reaction with H_2O and **2**, to give **4a** and **4b**, respectively. As the mole ratio of **2**/**1** increased from 2 to 16 folds, the formation of product **3** increased from 16% to 47% while the formation of polymeric products **4** was reduced from 60% to 40%. The intermolecular C–Si coupling reaction of the pathway **a** becomes more favorable than the intramolecular C–C coupling reaction of the pathways **b** at the higher mole ratio of **2**/**1**.

Introduction

Bis(α-chloroalkyl)silanes have been studied as a family of potential starting materials[1] for the synthesis of highly ring strained silacyclopropanes[2-6] and for the preparation of carbosilanes.[7] Seyferth and his coworkers first reported the synthesis of stable silacyclopropane derivatives having bulky substituents, starting from bis(α-bromocyclopropyl)silanes and magnesium.[2] Several derivatives of the silacyclopropanes, significantly stabilized by bulky groups on the ring-carbons,[6] have been isolated and studied for their reactivities.[3~5] Bis(chloromethyl)dichlorosilane has attracted little attention as a precursor for carbosilane due to the difficulty of separation from other chlorination products,[8a] even though it has been produced as byproduct in large quantity from the photochlorination[8b,c] of dichlorodimethylsilane to afford (chloromethyl)dichloromethylsilane, known as a starting material for flusilazole.[9] The cyclization reaction of bis(chloromethyl)dimethylsilane (**1**) with dichlorosilanes or dichlorogermanes using magnesium or lithium has been reported by Seyferth to give 1,3-disilacyclobutanes or 1-sila-3-germacyclobutanes, respectively, in low yields ranging from 21% to 24% due to the production of unidentified polymeric materials.[10]

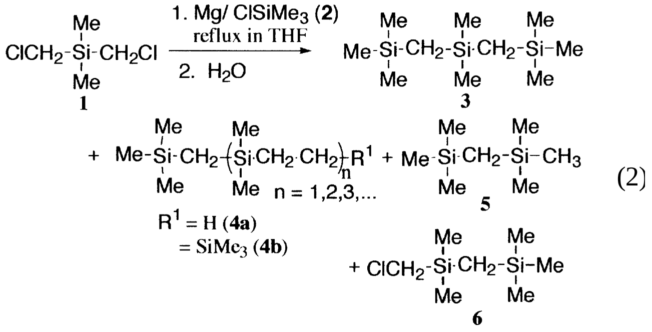
Recently we reported that the reaction of bis(chloromethyl)silanes with Mg at THF reflux temperature gave poly(silapropanes) in 80–90% yields.[11] The formation of poly(silapropanes) was explained by the ring-opening polymerization of the silacyclopropane intermediate generated by intramolecular cyclization of the mono-Grignard reagent (eq 1). This suggests that the polymeric materials obtained by Seyferth[10] from the cyclization reaction of bis(chloromethyl)dimethylsilane with dichlorosilanes were poly(silapropanes) derived from the intramolecular C-C coupling rather than the intermolecular C-Si coupling reaction. The low yields of 1,3-disilacyclobutanes are consistent with that the intermolecular C-Si coupling is less favorable than the intramolecular C-C coupling. In order to look into the details involved in the intramolecular C-C coupling and the intermolecular C-Si coupling reactions, we studied the Grignard coupling reaction of **1** with trimethylchlorosilane (**2**) as a simple chlorosilane. We wish to report the results and propose a probable reaction mechanism for the coupling reactions.



(1)

Results and Discussion

Product Distribution and Reaction Time. To study a reaction pathway to form the C–C and Si–C coupling products, the distributions of products obtained from the Grignard coupling reaction of **1** with **2** in THF at reflux temperature were determined at various reaction time intervals (3, 7, 15, 30, 60, 120, and 240 min). The reaction gave the polymeric products of general formula $Me_3SiCH_2(SiMe_2CH_2CH_2)_nR^1$ (n = 1, 2, 3, ...; **4a**, R^1 = H:[11] **4b**, R^1 = $SiMe_3$) having the backbone of alternating ethylene and silicon along with the intermolecular C–Si coupling products, 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane (**3**),[12] 2,2,4,4-tetramethyl-2,4-disilapentane (**5**),[7c] and 1-chloro-2,2,4,4-tetramethyl-2,4-disilapentane (**6**) as shown in eq 2.



(2)

The distribution of products is plotted against the reaction time in Figure 1. As shown in Figure 1, with 32% consumption of starting material **1**, the C–Si coupling products, **3** (1%), **5** (3%), and **6** (9%), were obtained along with the polymeric product **4** (15%) in a 3 min reaction. Within a 7 min reaction, **4** increased drastically to 49%, while **3**, **5**, **6** smoothly to 5%, 11%, 15%, respectively, with 92% consumption of **1**. These results indicate that the intramolecular C-C coupling is predominant as observed previously in the Grignard reaction of **1** without **2**.[11] However, tetramethylsilane, the hydrolysis product of the di-Grignard reagent, $Me_2Si(CH_2MgCl)_2$, was not detected in the product mixture, suggesting that the formation of di-Grignard reagent in the presence of **2** is not significant. The double C-Si coupling product **3** increased very slowly as compound **5**, the hydrolysis product of the Grignard reagent (**II**) derived from **6**, decreases. After a 4 h reaction, followed by general workup, **5** was obtained in 13% yield, indicating that the coupling reaction of **II** with **2** is slow probably due to the steric hindrance of bulky (trimethylsilyl)methyl substituent on silicon. Until a 7 min reaction, the amount of **6** is higher than those of **3** and **5**, but they turn reversed soon after. These results suggest that **3** is produced by the coupling reaction of **II** with **2** rather the double coupling reaction of the di-Grignard with **2**. To check a possibility for the formation of **4** by the C–C coupling reaction of CH_2–MgCl with CH_2–Cl, the Grignard coupling reaction of compound **6** with **2** under the same reaction condition. Besides the intermolecular C–Si coupling products, **3** (87%) and **5** (13%), such C–C coupling products were not detected.

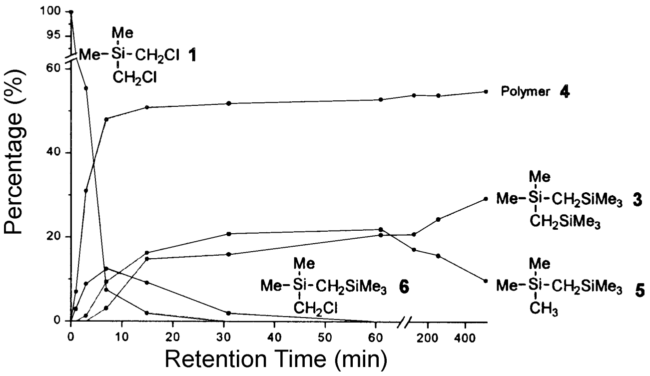


Figure 1. Product distribution *vs* reaction time.

Table 1. Product distribution *vs* mole ratio of $Me_2Si(CH_2Cl)_2$ **1** to Me_3SiCl **2**[a]

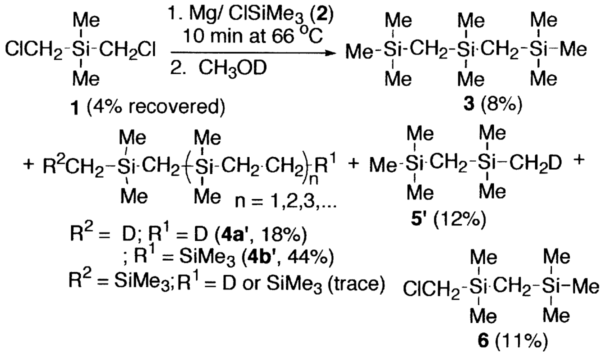
mole ratio of **2**/**1**	reaction time (h)	products 3	4	5	6
2	3	16	60	19	trace
3	3	23	55	18	-
4	3[b]	26		20	-
	24	35	51	7	-
8	3[b]	35		20	-
	24	42	46	8	-
16	3[b]	34		20	-
	12	47	40	9	-

[a] The reaction was carried out at the reflux temperature. [b] The yields of products were determined using dodecane as an internal standard by GLC in 3 h reaction and then isolated in 24 h reaction.

Distribution of Products *vs* Mole Ratio of 2 to 1. To find the optimum condition to obtain **3**, the Grignard coupling reaction of **1** with the simple chlorosilane **2** was carried at various reaction conditions. In this coupling reaction, THF was the best solvent among three aprotic polar solvents, THF, ethyl ether, and dioxane, and the reaction proceeded smoothly at the reflux temperature. The effect of product distribution on the reaction mole ratio of **2** to **1** was studied at reflux temperature in THF. These results obtained by the reaction using various mole ratios are summarized in Table 1.

As shown in the Table 1, as the mole ratio of **2**/**1** increases to 16 from 2 folds, the product **3** increases to 47% from 16% while the mixture of **4** with silapropane unit decrease to 40% from 60%, in particular, from 80% in the reaction without **2** and **5** to 9% from 19%. The sum quantity of both compounds **3** and **5**, coming from the reaction with the Grignard reagent formed from **6**, increases to 56% from 35% as the mole ratio of **2**/**1** increases to 16 from 2 folds. Compound **5**, formed by the hydrolysis of the Grignard reagent derived from **6**, decreases from 20% in a 3 h reaction to 7% in a 24 h reaction. These results indicate that the polymeric product **4** can be reduced by using much excess amount of **2** and the Si-C coupling reaction of the Grignard reagent formed from **6** having bulky trimethylsilyl methyl group with **2** is very slow due to steric hindrance. In these reactions, the higher ratio of **3**/**5** as well as the higher yields of the di-Grignard reagent-trapped products, **3** and **5**, were obtained in higher mole ratio of **2** to **1**. These results suggest strongly that the Si–C coupling reaction of mono-Grignard reagent of **1**, which is generated by the reaction of **1** with magnesium, with **2** is more favorable than the generation of silacyclopropane intermediate, leading to **4**, by the intramolecularly ring closure reaction, when the higher mole ratio of **2**/**1** was used.

Trapping Reaction of Reactive Intermediates by Methanol-*d*$_1$. To trap the reaction intermediates, a mixture of 1:3 Grignard reaction of **1** and **2** in THF at reflux was trapped by CH_3OD in a 10 min reaction. The corresponding deuterated products of 1-deutero-2,2,4,4-tetramethyl-2,4-disilapentane **5'** (12%) and a mixture (62%) of formula $R^2CH_2SiMe_2CH_2(SiMe_2CH_2CH_2)_nR^1$ [n = 1, 2, 3 ..., R^2 = D; R^1 = D (**4a'**, 44%) and R^1 = $SiMe_3$ (**4b'**, 18%): R^2 = $SiMe_3$ (trace)[13]] were obtained along with 1-chloro-2,2,4,4-tetramethyl-2,4-disilapentane (**6**, 11%), **3** (8%), and unreacted **1** (4%) recovered. The methanol-*d*-trapped products of silacyclopropane intermediates, 3-deutero-1,1-dimethyl-1-methoxy-1-silapropane, and a di-deuterated product of di-Grignard reagent derived from **1**, $Me_2Si(CH_2D)_2$, were not observed in detectable amounts (eq 3). In this trapping reaction, the formation of trace amount of **4** ($R^2 = SiMe_3$) reflects that the mono-Grignard reagent formed from **1** but reacts with **2** or CH_3OD to give **6** or involves in the polymerization reaction to **4**. However, 1,1,4,4,-tetramethyl-1,4-disilacyclohexane, the dimerization product of the silacyclopropane intermediate,[14] 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 silylenes intermediate that can be inserted to silacyclopropane leading to 1,2-disilacyclobutanes[3,15-18]or polymerize to poly(diorganosilylene)s. However, silylene-trapped products were not detected in the volatile compounds. This result seems likely that silacyclopropane intermediate generated is rapidly polymerized to give a mixture of **4a'** and **4b'** in the reaction condition. Silacyclopropane intermediates were reported to be highly reactive toward air, water, alcohols[4] and polymerized to higher oligomers having silapropylene backbone on reaction with methyllithium[4] and Grignard reaction condition.[11]

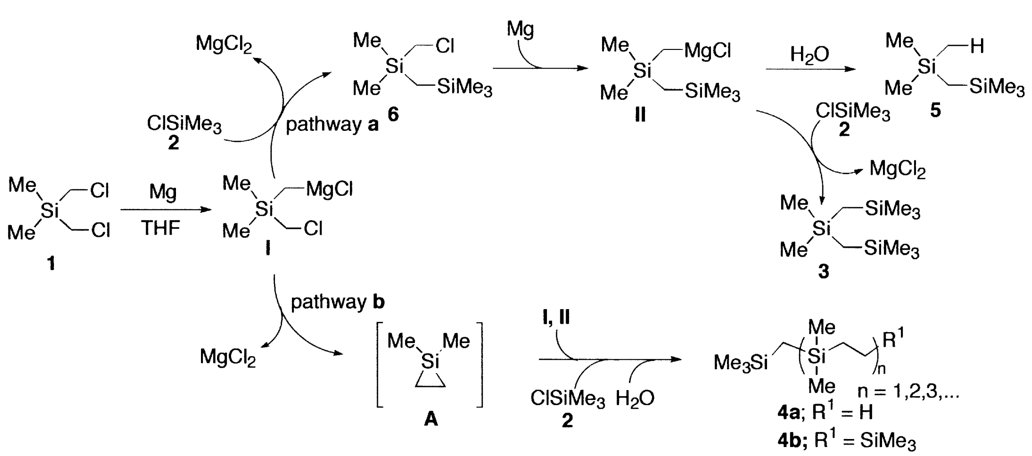


(3)

Reaction Mechanism. On the basis of our results, the reaction pathways to products, **3**, **4**, and **6**, are illustrated in Scheme 1. The reaction of **1** with magnesium affords at first the mono-Grignard reagent **I** that undergoes C–Si or C-C coupling reactions through two pathways to give products; **a**) reacts with **2** to give **6** that reacts with Mg to afford a Grignard reagent **II**, **b**) cyclizes intramolecularly to a silacyclopropane intermediate **A** which undergoes the ring-opening polymerizaition by the nucleophilic attack of Grignard reagents **I** and **II**, followed by the termination reaction with H_2O and **2** to give **4a** and **4b**, respectively. In these polymerization reactions, the ring-opening polymerization initiated by the mono-Grignard reagent **II** might be negligible in the presence of excess amount of **2**. The formation of di-Grignard reagent $Me_2Si(CH_2MgCl)_2$ was not observed in contrast to the previously reported results.[11] As the mole ratio of **2**/**1** increases, the intermolecular C–Si coupling reaction in the pathway **a** becomes more favorable than the intramolecular C-C coupling reaction pathways **b** and the formation of silacyclopropane intermediates **A** is suppressed.

Experimental Section

Reagents and physical measurements. All operations were carried out in an inert gas atmosphere. Solvents, tetrahydrofuran (THF), diethyl ether, and hexane, were dried over sodium benzophenone ketyl and distilled before use. Bis(chloromethyl)dimethylsilane and trimethylchlorosilane were obtained from United Chemical Technologies, 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 Pack-



Scheme 1. Reaction mechanism for the Grignard coupling of **1** with excess **2**.

ard 5890 Series II gas chromatograph equipped with a Model 5972 mass selective detector. Gel permeation chromatography (GPC) was carried out on a Waters Millipore gel permeation chromatograph (GPC) with Ultrastyragel GPC column series (in sequence, 100, 500, 10^3, 10^4 Å columns) using toluene solvent as an eluent. Molecular weights were calibrated by polystyrene standards. HRMS (high resolution mass spectra) were performed by Korea Basic Science Institute, Seoul, Korea.

General Grignard coupling reaction of 1 with 2. Reaction of **1** (2.73 g, 17.4 mmol) with **2** (5.6 g, 51.6 mmol), magnesium turnings (1.0 g, 41.3 mmol), and a small piece of iodine in THF (30 mL) was carried out for 3 h at reflux temperature. The reaction mixture cooled down to room temperature, treated with 10 mL of water, and 50 mL of ethyl ether was added. The organic layer was separated and the solvents were distilled off. The residue was then extracted with hexane (100 mL). Reaction mixture dissolved in hexane layer was distilled to give **5** (0.50 g, 18%), 2,2,4,4-tetramethyl-2,4-disilahexane (trace), **3** (0.93 g, 23%) under an atmospheric pressure and a mixture (0.23 g, *ca* 12% based on Si_5 compound) of volatile, which consisted of Si_3–Si_7 compounds, under reduced pressure (0.6 mmHg) at oil bath temperatures between room temperature and 250 °C. Nonvolatile **4** (0.47 g, *ca* 23%: M_w, 520; M_n, 430), consisting of a 2.5:1 mixture of **4a** and **4b**, was remained. The insoluble white powder in hexane was washed with water and the remained white solid was vacuum–dried to give 0.28 g (*ca* 18%: M_w, 3200; M_n, 2200). Spectroscopic data for volatile products are as follows. For 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane **3**,[12]: ^{1}H NMR δ -0.25 (s, 2H, SiCH_2Si), 0.03 (s, 18H, Si(CH_3)$_3$), 0.05 (s, 6H, Si(CH_3)$_2$); ^{13}C NMR δ 1.45 (Si(CH$_3$)$_3$), 2.36 (SiCH$_2$Si), 5.72 (Si(CH$_3$)$_2$); mass spectrum [m/e (relative intensity)] 218 (13%), 217 (51) ((M-CH$_3$)$^+$), 145 (29), 130 (13), 129 (81), 73 (100, Me$_3$Si$^+$), 59 (18). For 2,2,4,4,7,7-hexamethyl-2,4,7-trisilaoctane: ^{1}H NMR δ -0.29 (s, 2H, SiCH_2Si), -0.03 (s, 9H, Si(CH_3)$_3$), -0.01 (s, 6H, Si(CH_3)$_2$), 0.03 (s, 9H, Si(CH_3)$_3$), 0.37 (s, 4H, CH_2CH_2); ^{13}C NMR δ -2.14 (central-Si(CH$_3$)$_2$), -1.11 (SiCH$_2$Si), 1.43, 2.01 (Si(CH$_3$)$_3$), 8.80, 9.09 (CH$_2$$CH_2$); mass spectrum [m/e (relative intensity)] 246 (2%, M^+), 146 (16), 145 (100, Me$_3$SiCH$_2$SiMe$_2$$^+$), 143 (25), 73 (57), 59 (10). HRMS: 246.1657. Calcd. for $C_{11}H_{30}Si_3$: 246.1655. For 2,2,4,4,7,7,10,10-octamethyl-2,4,7,10-tetrasilaundecane: ^{1}H NMR δ -0.29 (s, 2H, SiCH_2Si), -0.06 (s, 6H), -0.03 (s, 9H), -0.01 (s, 6H), 0.03 (s, 9H, Si(CH_3)$_3$), 0.36 (s, 8H, CH_2CH_2); ^{13}C NMR δ -4.36, -2.15 (central-Si(CH$_3$)$_2$), -1.10 (SiCH$_2$Si), 1.44, 2.03 (Si(CH$_3$)$_3$), 6.71, 8.72, 9.09 (CH$_2$$CH_2$). HRMS: 332.2207. Calcd. for $C_{15}H_{40}Si_4$: 332.2207. A mixture of nonvolatile compounds was characterized by method previously reported.[11] In the data of ^{1}H NMR spectra for nonvolatile compounds, a 2.5 : 1 mixture of **4a** and **4b** was disclosed by the integration ratio of protons of terminal groups (ethyl[11] and SiMe$_3$ (R^1) near to -0.03 ppm) appearing at the chemical shifts different from other peaks of **4a** (R^1 = H) and **4b** (R^1 = SiMe$_3$) of formula Me$_3$SiCH$_2$(SiMe$_2$CH$_2$CH$_2$)$_n$R^1 (n = 1, 2, 3, ...).

Product distribution *vs* various reaction time. By the same reaction procedure, except for reaction times and quenching procedure for reactive intermediates, described above, the reactions were carried out at reaction time intervals of 3, 7, 15, 30, 60, 120, 240, and 360 min, respectively. 10 mL of water was added to each of reaction mixtures obtained from various reaction times, and general worked up. The reaction results are plotted in Figure 1. Data for 1-chloro-2,2,4,4-tetramethyl-2,4-disilapentane **6**: ^{1}H NMR δ -0.14 (s, 2H, SiCH_2Si), 0.05 (s, 9H, SiCH_3), 0.15 (s, 6H, SiCH_3), 2.76 (s, 2H, SiCH_2Cl); ^{13}C NMR δ -1.93 (CH$_2$), 1.17, 1.26 (CH$_3$), 32.41 (CH$_2$Cl); mass spectrum [m/e (relative intensity)] 179 (15%, (M-CH$_3$)$^+$), 153 (20), 151 (55), 146 (18), 145 (100), 73 (39), 59 (15).

Product distributions *vs* the mole ratio of 2/1. By the same reaction procedure, except for using reaction mole ratios, described above, the reactions were carried out using 2, 3, 4, 8, and 16 folds of **2** respect to **1**. After **1** was disappeared, the reactions were worked up. In the cases of 4, 8, 16 folds of mole ratio of **2**/**1**, the samples for the analysis of products were taken in part in 3 h reaction and the reaction mixtures were worked up by a procedure described above. The reaction results are summarized in Table 1.

Trapping reaction of reaction intermediates by CH$_3$OD. By a similar reaction procedure described above, the reaction of **2** (2.68 g, 17.1 mmol) with **1** (5.74 g, 52.8 mmol), magnesium turnings (1.01 g, 41.5 mmol) and a small piece of iodine in THF (30 mL) was carried out for 10 min at reflux temperature. 10 mL of CH$_3$OD and 50 mL of diethyl ether were added and stirred for 20 min at room temperature. The organic layer was separated. The solvents were removed and the reaction mixture was fractional distilled to give 1-deutero-2,2,4,4-tetramethyl-2,4-disilapentane **5'** (0.31 g, 12%), 1-chloro-2,2,4,4-tetramethyl-2,4-disilapentane **6** (0.37 g, 11%), 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane **3** (0.30 g, 8%), and unreacted **1** (0.10 g, 4%). Higher boilers **4'** (0.45 g, 30%: M_w, 590; M_n, 400) soluble in hexane and **4'** (0.31 g, 21%: M_w, 3100; M_n, 2000) insoluble in hexane were obtained. Data for **5'**: ^{1}H NMR δ -0.25 (s, 2H, SiCH_2Si), 0.02 (t, 2H, $J_{\text{H-D}}$ = 2 Hz, CDH_2), 0.03 (s, 15H, SiCH_3); ^{13}C NMR δ 1.02 (CDH$_2$, $J_{\text{C-D}}$ = 18 Hz), 1.32 (CH$_3$), 4.33 (CH$_2$); mass spectrum [m/e (relative intensity)] 161 (1%, M^+), 148 (16), 147 (36), 146 (100, (M-CH$_3$)$^+$), 145 (39), 130 (10), 74 (33), 73 (32), 65 (10), 59 (10). Data of compound **4a'** were characterized by methods described in the previous work.[11]

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13. The GC/MS data showed that the fragmentation peak of 217 (100%, $CH_3SiMe_2CH_2SiMe_2^+$) as a base peak in the trace amounts of volatile compounds were observed, suggesting the production of compound **4** ($R^2 = SiMe_3$) when compared with the GC/Ms data of **4b**.[11] Among the NMR spectra of a mixture of **4**, compound **4** ($R^2 = SiMe_3$) could not be observed due to too smaller amounts compared with **4a** and **4b**.
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