

## Synthesis of Tris(silyl)methanes by Modified Direct Process

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Direct reaction of elemental silicon with a mixture of (dichloromethyl)silanes **1** [ $\text{Cl}_{3-n}\text{Me}_n\text{SiCHCl}_2$ ;  $n = 0$  (**a**),  $n = 1$  (**b**),  $n = 2$  (**c**),  $n = 3$  (**d**)] and hydrogen chloride has been studied in the presence of copper catalyst using a stirred bed reactor equipped with a spiral band agitator at various temperatures from 240 °C to 340 °C. Tris(silyl)methanes with Si-H bonds, **3a-d** [ $\text{Cl}_{3-n}\text{Me}_n\text{SiCH}(\text{SiHCl}_2)_2$ ], and **4a-d** [ $\text{Cl}_{3-n}\text{Me}_n\text{SiCH}(\text{SiHCl}_2)(\text{SiCl}_3)$ ], were obtained as the major products and tris(silyl)methanes having no Si-H bond, **5a-d** [ $\text{Cl}_{3-n}\text{Me}_n\text{SiCH}(\text{SiCl}_3)_2$ ], as the minor product along with byproducts of bis(chlorosilyl)methanes, derived from the reaction of silicon with chloromethylsilane formed by the decomposition of **1**. In addition to those products, trichlorosilane and tetrachlorosilane were produced by the reaction of elemental silicon with hydrogen chloride. The decomposition of **1** was suppressed and the production of polymeric carbosilanes reduced by adding hydrogen chloride to **1**. Cadmium was a good promoter for the reaction, and the optimum temperature for this direct synthesis was 280 °C.

### Introduction

The silicon-carbon bond forming reactions such as direct synthesis,<sup>1</sup> hydrosilylations,<sup>2</sup> and organometallic reactions<sup>3</sup> are fundamental methods for the preparation of organosilicon compounds. Among direct Si-C bond forming reactions, the direct synthesis of methylchlorosilanes<sup>4</sup> from elemental silicon and methyl chloride reported by Rochow in the early 1940's is the basic technique most widely used in the silicone industry and organosilicon chemistry as well. Although a vast number of reports on the direct reactions of elemental silicon with organic chlorides are available in the literature,<sup>1,3,4</sup> the reports on the direct reaction of polychlorinated alkanes such as methylene chloride and chloroform are scarce.<sup>5,6</sup> In 1958, the direct reaction of chloroform with elemental silicon in the presence of copper catalyst was first reported in the literature by Muller and Seitz.<sup>5</sup> Later, Fritz and Matern reported the same reaction using a fluidized-bed reactor at 320 °C.<sup>7</sup> The products obtained from the reaction of elemental silicon with chloroform were branched or cyclic carbosilanes containing from one up to twelve silicon atoms, but tris(silyl)methanes were not produced. The deactivation of elemental silicon and copper catalyst was the major problem partly due to the decomposition of the starting compound and partly due to the high boiling polycarbosilanes produced.

We have previously reported the direct reaction of elemental silicon with a mixture of hydrogen chloride and chlorinated organic compounds such as ( $\alpha$ -chloromethyl)silanes,<sup>8</sup> allyl chloride,<sup>9</sup> dichloromethane,<sup>10</sup> and chloroform<sup>11</sup> to give Si-H containing bis(silyl)methanes, allylchlorosilanes, bis(chlorosilyl)methanes, and tris(chlorosilyl)methanes, respectively. The decomposition of the starting materials was suppressed and the production of high boilers reduced by adding hydrogen chloride to the reactants.<sup>8-12</sup> This success in the modified direct synthesis of new Si-H containing orga-

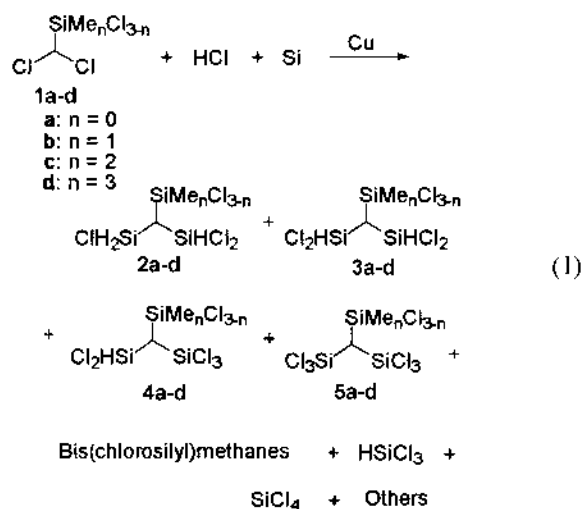
nochlorosilanes prompted us to apply this hydrogen chloride incorporating method to the direct reaction of elemental silicon with dichloromethyl group containing organosilanes. Since methyl or chlorine groups are substituted on the silicon atom of the starting (dichloromethyl)silanes, the Si-H containing tris(chlorosilyl)methane products were expected to be different from the tris(silyl)methanes derived from the reaction of chloroform.<sup>12</sup>

We wish to report the results obtained from the direct reaction of elemental silicon with a mixture of (dichloromethyl)silanes and hydrogen chloride in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at a carefully controlled temperature between 240 °C and 340 °C.

### Results and Discussion

A 1 : 4 mixture of (dichloromethyl)silanes **1** [ $\text{Cl}_{3-n}\text{Me}_n\text{SiCHCl}_2$ ;  $n = 0$  (**a**),  $n = 1$  (**b**),  $n = 2$  (**c**),  $n = 3$  (**d**)] and hydrogen chloride was reacted with the contact mixture<sup>11</sup> prepared from elemental silicon and copper catalyst using a stirred reactor equipped with a spiral band agitator at a flow rate of 6.93 g/h of **1** at the reaction temperature of 280 °C for 3 h. Product mixtures were collected and distilled into three fractions, low boiling products of trichlorosilane and tetrachlorosilane, bis(chlorosilyl)methanes, and tris(chlorosilyl)methanes. The composition of each fraction was determined by GLC. The products were purified by preparative GLC and subsequent spectral analysis led to the assignments of the structures for the products (eq. 1). The products of bis(chlorosilyl)methanes are the same as those obtained in the direct reaction of silicon with a mixture of ( $\alpha$ -chloromethyl)silanes and hydrogen chloride,<sup>8</sup> indicating that some of the starting (dichloromethyl)silanes decomposed to ( $\alpha$ -chloromethyl)silanes during the reaction. Most of tris(chlorosilyl)methane products are different from the tris(chlorosilyl)methanes

obtained from the reaction of elemental silicon with a mixture of chloroform and hydrogen chloride,<sup>12</sup> because the starting (dichloromethyl)silanes have substituents such as methyl or chlorine on the silicon atom. Trichlorosilane and tetrachlorosilane are the products from the reaction of silicon with hydrogen chloride.<sup>7</sup> The optimum reaction conditions such as reaction temperature, the mixing ratio of the reactants, and catalyst/promoter effects for the synthesis of tris(silyl)methanes were studied in details.



**Effect of Reaction Temperature.** (Dichloromethyl)dichloromethylsilane (**1b**) was used as representative among (dichloromethyl)silanes **1a-d** for the direct synthesis of tris(silyl)methanes. A 1 : 4 mixture of **1b** and hydrogen chloride reacted with the contact mixture using the stirred reactor described above at a flow rate of 6.93 g/h of **1b** at the different reaction temperatures from 240 °C up to 340 °C for 3 h. Product mixtures were collected and distilled into three fractions, low boiling products of trichlorosilane and tetrachlorosilane, bis(chlorosilyl)methanes, and tris(chlorosilyl)methanes. The products were purified by preparative GLC and subsequent spectral analysis led to the assignments of the structures for four tris(chlorosilyl)methanes as 2-(dichlorosilyl)-1,1,3-trichloro-1,3-disilabutane (**2b**), 2-(dichlorosilyl)-1,1,3,3-tetrachloro-1,3-disilabutane (**3b**), 2-(dichlorosilyl)-1,1,1,3,3-pentachloro-1,3-disilabutane (**4b**), and 2-(trichlorosilyl)-1,1,1,3,3-pentachloro-1,3-disilabutane (**5b**). The productions of Si-H containing compounds **2b-4b** as major products suggest that both of **1b** and hydrogen chloride reacted with the same silicon atom, and the reactivities of two reactants are comparable. The minor products of bis(chlorosilyl)methanes are derived from the direct reaction of silicon with a mixture of ( $\alpha$ -chloromethyl)dichloromethylsilane formed by the decomposition of **1b** during the reaction and hydrogen chloride.<sup>8</sup> It has been reported that tris(chlorosilyl)methanes do not decompose to bis(chlorosilyl)methanes under the reaction conditions.<sup>11</sup> The amounts and compositions of products collected from the direct reaction of **1b** at various reaction temperatures are summarized in Table 1.

**Table 1.** Reaction Temperature Effect on the Direct Reaction of **1b**

entry no.	reacn temp °C	g <sup>b</sup>	products						
			tris(chlorosilyl)methanes				bis. <sup>d</sup>	high boilers	
			wt %	distribution (%) <sup>c</sup>					wt %
			<b>2b</b>	<b>3b</b>	<b>4b</b>	<b>5b</b>			
1	240	19.4	63	trace	38	42	20	27	10
2	260	22.1	72	2	50	36	12	25	3
3	280	27.0	75	4	73	21	2	14	11
4	300	25.1	73	3	58	33	6	18	9
5	320	24.6	67	3	51	38	7	22	11
6	340	22.7	71	3	43	43	11	26	3

<sup>a</sup>20.8 g of **1b** was used during 3 h. Catalyst cocatalyst - Cu (10%)Cd (0.5%). Mole ratio of **1b** HCl = 1/4. <sup>b</sup>Low boilers, HSiCl<sub>3</sub> and SiCl<sub>4</sub>, are excluded for simplicity. <sup>c</sup>GLC area percentages. <sup>d</sup>Bis(chlorosilyl)methanes

As shown in Table 1, trichlorosilane and tetrachlorosilane distilled from the product mixture were excluded for simplicity. The formations of **3b** and **5b** can be explained by the reaction of one mol of **1b** with two silicon atoms and 2 mol of hydrogen chloride or two silicon atoms and 2 mol of chlorine,<sup>3</sup> respectively. Similarly, the formation of product **4b** can be explained by the reaction of **1b** with two silicon atoms, 1 mol of hydrogen chloride, and 1 mol of chlorine.

The total amount of products and the percentage of **3b** were the highest at 280 °C and decreased at temperatures below or above 280 °C, while the percentages of **4b** and **5b** increased. The results indicate that the reactivity and selectivity were the best at 280 °C. Comparing the modified reaction of methylene chloride,<sup>12</sup> the 73 percent yield of **3b** is more than double of the corresponding bis(dichlorosilyl)methane production. The optimum reaction temperature of 280 °C is same as the temperature for the direct synthesis of bis(silyl)methanes from methylene chloride.<sup>12</sup> The results indicate that the silyl substitution of the starting compounds improves greatly the selectivity, but does not enhance the reactivity of C-Cl bonds toward the direct reaction. However, the reaction temperature is about 40 degree lower than that for the direct reaction of monochlorinated methanes such as methyl chloride,<sup>2,16</sup> and ( $\alpha$ -chloromethyl)silanes<sup>7,17</sup> without using hydrogen chloride. This result is consistent with the higher reactivity of **1b** than those of monochlorinated organic compounds.<sup>10</sup> The reaction even proceeded at the temperature as low as 240 °C, but the total weight of product mixture and the selectivity for **3b** decreased as the temperature decreased below 240 °C probably due to inefficient removal of the high boiling products from the reactor. It is interesting to note that the production of bis(chlorosilyl)methanes was the lowest at the temperatures below 280 °C and increased at the temperatures above, probably due to higher decomposition of **1**. The percentage of polymeric carbosilanes was 11% and comparable with the literature value for the reaction with chloroform.<sup>12</sup>

**Promoters.** Useful copper catalysts for the reaction of alkyl chloride with silicon include copper metal, copper

**Table 2.** Effect of the Catalyst and Cocatalyst on the Direct Reaction of **1b**<sup>a</sup>

entry no.	cat/cocat	g <sup>b</sup>	products						bis. <sup>d</sup> wt %	high boilers wt %
			tris(chlorosilyl)methanes				wt %	wt %		
			wt %	distribution (%) <sup>f</sup>						
			<b>2b</b>	<b>3b</b>	<b>4b</b>	<b>5b</b>				
7	Cu	24.0	71	26	51	39	8	26	3	
8	Cu/Cd	27.0	75	4	73	21	2	14	11	
9	Cu/Zn	16.7	76	4	62	29	6	21	3	

<sup>a</sup>20.8 g of **1b** was used during 3 h; reaction Temperature = 280 °C; mole ratio of **1b**:HCl = 1:4. <sup>b</sup>Low boilers, HSiCl<sub>3</sub> and SiCl<sub>4</sub>, are excluded for simplicity. <sup>c</sup>GLC area percentages. <sup>d</sup>Bis(chlorosilyl)methanes.

salts, and partially oxidized copper.<sup>2</sup> In addition to copper catalyst, a number of metals such as zinc, aluminum, tin, magnesium, etc. are known to be promoters for direct reactions.<sup>13,14</sup> The promoters are normally incorporated in a smaller quantity less than 1%. Zinc is known as one of the most effective promoters for the direct synthesis of methylchlorosilanes.<sup>17</sup> Cadmium is known as one of the most effective promoters for the direct synthesis of bis(chlorosilyl)methanes,<sup>8,9</sup> tris(sila)alkanes<sup>16</sup> and tris(chlorosilyl)methane.<sup>12</sup> The product distributions from the direct reaction of **1b** in the presence of different promoters are given in Table 2.

As shown in the Table 2, the amounts (percentages) of products **2b-5b** in the product mixtures varied, 24.0 g (71%), 27.0 g (75%), and 16.7 g (76%) with no promoter, cadmium, and zinc, respectively. The yields of products and the selectivity for Si-H bond containing tris(chlorosilyl)methanes in the direct reaction with cadmium as a promoter were slightly improved, while the reaction with zinc promoter gave the lowest yield. This indicates that zinc is not a promoter but an inhibitor and cadmium is a good promoter for this reaction. These are consistent with the results observed for the direct reactions of silicon with ( $\alpha$ -chloromethyl)silanes, allyl chloride, methylene chloride, and chloroform.<sup>8-12</sup>

**Mixing Ratio of the Reactants.** The amounts and distributions of products obtained from the direct reaction using various mixing ratios of hydrogen chloride/**1b** ranging from 2 to 8 in the presence of copper catalyst/cadmium cocatalyst at 280 °C for 3 h are given in Table 3.

In order to produce the compound **3b**, 2 mol of hydrogen chloride should be available for each 1 mol of **1b**. Considering that trichlorosilane is produced from the reaction of hydrogen chloride with silicon, the required mixing ratio of **1b** to hydrogen chloride for this reaction was 1:2 at minimum to prevent the polycarbosilanes production. As shown in Table 3, the total amount of products and the selectivity of **3b** increased with an increase from 1:2 to 1:4 of **1b** to hydrogen chloride ratio, indicating that the decomposition of **1b** to hydrogen chloride and chlorine were suppressed under these reaction conditions as shown in other systems.<sup>7-9</sup> However, the worse results were obtained by changing from 1:6 to 1:8, suggesting that the optimum mixing ratio of **1b** to hydrogen chloride in the direct synthesis of **1b** was 1:4.

**Reactivity and Selectivity of (Dichloromethyl)silanes.**

**Table 3.** Effect of Mixing Ratio of the Reactants<sup>a</sup>

entry no.	mole ratio <b>1b</b> :HCl	g <sup>b</sup>	products							bis. <sup>d</sup> wt %	high boilers wt %
			tris(chlorosilyl)methanes				wt %	wt %			
			wt %	distribution (%) <sup>f</sup>							
			<b>2b</b>	<b>3b</b>	<b>4b</b>	<b>5b</b>					
10	1:2	22.4	62	trace	39	46	15	31	8		
11	1:4	27.0	75	4	73	21	2	14	11		
12	1:6	22.2	80	1	57	34	8	19	1		
13	1:8	26.2	71	trace	34	45	21	26	3		

<sup>a</sup>20.8 g of **1b** was used during 3 h; catalyst/cocatalyst = Cu (10%)Cd (0.5%); reaction temperature = 280 °C. <sup>b</sup>Low boilers, HSiCl<sub>3</sub> and SiCl<sub>4</sub>, are excluded for simplicity. <sup>c</sup>GLC area percentages. <sup>d</sup>Bis(chlorosilyl)methanes.

**Table 4.** Results of the Direct Reactions of (Dichloromethyl)silanes

entry no.	reactant 1	#	g <sup>a</sup>	products							bis. <sup>d</sup> wt %	high boiler wt %
				tris(chlorosilyl)methanes				wt %	wt %			
				wt %	distribution (%) <sup>f</sup>							
				<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>					
14	<b>1a</b>	22.9	28.5	75	<b>2a</b> , 7	<b>3a</b> , 72	<b>4a</b> , 18	<b>5a</b> , 3	19	6		
15	<b>1b</b>	20.8	27.0	75	<b>2b</b> , 4	<b>3b</b> , 73	<b>4b</b> , 21	<b>5b</b> , 2	14	11		
16	<b>1c</b>	18.6	27.5	86	<b>2c</b> , 6	<b>3c</b> , 71	<b>4c</b> , 21	<b>5c</b> , 2	13	1		
17	<b>1d</b>	16.5	25.9	85	<b>2d</b> , 4	<b>3d</b> , 72	<b>4d</b> , 12	<b>5d</b> , 11	14	6		

<sup>a</sup>(Dichloromethyl)silanes, 0.035 mol, was used during 1 h; catalyst cocatalyst = Cu (10%)Cd (0.5%); mole ratio of reactant **1**:HCl = 1:4; reaction temperature = 280 °C. <sup>b</sup>Low boilers, HSiCl<sub>3</sub> and SiCl<sub>4</sub>, are excluded for simplicity. <sup>c</sup>GLC area percentages. <sup>d</sup>Bis(chlorosilyl)methanes.

The direct reaction was extended to other (dichloromethyl)silanes **1a, c, d** under the optimized reaction conditions and the results are shown in Table 4.

As shown in Table 4, the selectivity for two Si-H bonds containing products **3a-d** was higher than 71% for all four cases and was the highest for **1b** and the lowest for **1d**, although the differences are not great. Similar results have been observed for the direct reaction of (chloromethyl)silanes.<sup>8</sup> These results suggest that the reactivity and selectivity of (dichloromethyl)silanes do not vary greatly depending upon the electronic nature of the substituents on the silicon atom.

## Experimental Section

**Reagents and Physical Measurements.** (Dichloromethyl)silanes **1a-d** were prepared according to the literature methods.<sup>21</sup> Anhydrous hydrogen chloride (99.999%) was purchased from a Solkatic Chemicals and used without further purification. Copper powder was purchased from Alcan Metal Powders (NJ, USA) and cadmium, zinc from Aldrich Chemical Co. Elemental silicon (Si, 98%; Fe, 0.50%; Ca, 0.25%; Al, 0.24%; C, 0.08%; S, 0.05%; P, 0.05%) was purchased from Samchuck Mining Co. (Kangwondo, Korea) or OSL-5-4855 (Si, 99.1%; Al, 0.29%; Ca, 0.037%;

Fe, 0.30%; Ti, 0.035%) from Elkem Silicon (Oslo, Norway). The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80-100 mesh chromosorb W/AW,  $\frac{1}{8}$  in.  $\times$  1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. Product yields were determined chromatographically with *n*-dodecane as an internal standard, if not described in details. Samples for characterization were purified by preparative GLC using a Donam system series DS 6200 gas chromatograph, thermal conductivity detector and a 4 m  $\times$  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 Unity Plus 600 (FT, 600 MHz,  $^1\text{H}$ ), Bruker AMX 500 (FT, 500 MHz,  $^1\text{H}$ ; 125 MHz,  $^{13}\text{C}$ ), or a Varian Gem 300 (FT, 300 MHz,  $^1\text{H}$ ; 75 MHz,  $^{13}\text{C}$ ) spectrometer in  $\text{CDCl}_3$  solvent. Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS. High-resolution mass spectra (HRMS) were obtained at the Korea Basic Science Institute on a JMS-700 Mstation Mass Spectrometer (JEOL, Japan) at electron energy of 70 eV.

**Reactor.** The same Pyrex glass tube reactor for the direct synthesis of tris(chlorosilyl)methanes was used as described elsewhere.<sup>7</sup>

**General Procedure for the Direct Reaction of 1b.** A mixture of metallic silicon (90.0 g, 100-325 mesh) and 10.0 g of copper catalyst was placed in the reactor made of Pyrex glass tube (25 mm inner diameter  $\times$  350 mm length).<sup>7</sup> The mixture was dried at the 300 °C for 5 h with stirring with dry nitrogen flush. Then the temperature was raised to 350 °C and methyl chloride was introduced at a rate of 240 mL/min to activate the contact mixture for 4 h. After removing products such as dichlorodimethylsilane and methyltrichlorosilane formed during activation process, 0.5 g of cadmium was added to the reactor as a promoter at room temperature. After the temperature was raised to 280 °C, 1b was introduced using a syringe pump into the evaporator attached at the bottom of the reactor at a rate of 6.93 g/h. At the same time gaseous hydrogen chloride was introduced at a rate of 101 mL/min (mol ratio of 1b: hydrogen chloride is 1 : 4). About 2 min after starting the reaction, it was observed that the reaction temperature was raised slightly due to the exothermic nature of the reaction and then the liquid product was collected at the receiver. After 3 h of reaction, 32.5 g of the product mixture was collected in receiver cooled to 15 °C. The mixture (5.5 g) of low boilers  $\text{HSiCl}_3$  and  $\text{SiCl}_4$  were distilled off under an atmosphere from the reaction mixture. The remaining reaction mixture was vacuum-distilled to give bis(chlorosilyl)methanes (3.9 g), tris(chlorosilyl)methanes (20.2 g), and several unidentified high boilers (2.0 g). 0.9 g of residue was remained. The mixture of tris(chlorosilyl)methanes was 2b (4%), 3b (73%), 4b (21%), and 5b (2%).

Data for 2b:  $^1\text{H}$  NMR  $\delta$  1.06 (s, 3H,  $\text{CH}_3$ ), 1.28 (s, 1H, CH), 5.06 (d,  $J = 2.2$  Hz, 2H,  $\text{SiH}_2$ ), 5.82 (s, 1H, SiH).  $^{13}\text{C}$  NMR  $\delta$  8.20 ( $\text{CH}_3$ ), 16.44 (CH). HRMS calcd for  $\text{C}_2\text{H}_6\text{Cl}_3\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 288.8220, found m/e 288.8209.

Data for 3b:  $^1\text{H}$  NMR  $\delta$  1.10 (s, 3H,  $\text{CH}_3$ ), 1.56 (s, 1H, CH), 5.85 (s, 2H,  $\text{SiH}_2$ ),  $^{13}\text{C}$  NMR  $\delta$  8.55 ( $\text{CH}_3$ ), 22.97 (CH).

HRMS calcd for  $\text{C}_2\text{H}_5\text{Cl}_6\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 322.7830, found m/e 322.7827. Data for 4b:  $^1\text{H}$  NMR  $\delta$  1.15 (s, 3H,  $\text{CH}_3$ ), 1.84 (s, 1H, CH), 5.89 (s, 1H, SiH).  $^{13}\text{C}$  NMR  $\delta$  8.64 ( $\text{CH}_3$ ), 26.99 (CH). HRMS calcd for  $\text{C}_2\text{H}_4\text{Cl}_7\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 356.7441, found m/e 356.7454. Data for 5b:  $^1\text{H}$  NMR  $\delta$  1.18 (s, 3H,  $\text{CH}_3$ ), 2.12 (s, 1H, CH).  $^{13}\text{C}$  NMR  $\delta$  9.12 ( $\text{CH}_3$ ), 30.83 (CH). HRMS calcd for  $\text{CHCl}_3\text{Si}_3$  ((M- $\text{CH}_3$ )<sup>+</sup>) m/e 376.6894, found m/e 376.6902.

**Direct Reaction of (Dichloromethyl)trichlorosilane (1a).** Using the procedure described in the direct reaction of 1b, a gaseous 1 : 4 mixture of 1a (7.64 g/h) and hydrogen chloride (101 mL/min) was introduced to the reactor for 3 h. 31.3 g of the product mixture was collected in receiver. The mixture (2.8 g) of low boilers  $\text{HSiCl}_3$  and  $\text{SiCl}_4$  were distilled off under an atmosphere from the reaction mixture. The remaining reaction mixture was vacuum-distilled to give bis(chlorosilyl)methanes (5.3 g), tris(chlorosilyl)methanes (21.3 g), and several unidentified high boilers (1.6 g). 0.3 g of residue was remained. The mixture of tris(chlorosilyl)methanes was 2-(chlorosilyl)-1,1,1,3,3-pentachloro-1,3-disilapropane (2a, 7%), 2-(dichlorosilyl)-1,1,1,3,3-pentachloro-1,3-disilapropane (3a, 72.0%), 2-(dichlorosilyl)-1,1,1,3,3,3-hexachloro-1,3-disilapropane (4a, 18%), and 2-(trichlorosilyl)-1,1,1,3,3,3-hexachloro-1,3-disilapropane (5a, 3%).<sup>19</sup>

Data for 2a:  $^1\text{H}$  NMR  $\delta$  1.57 (s, 1H, CH), 5.10 (d,  $J = 2.5$  Hz, 2H,  $\text{SiH}_2$ ), 5.85 (s, 1H, SiH).  $^{13}\text{C}$  NMR  $\delta$  19.31 (CH). HRMS calcd for  $\text{C}_3\text{H}_9\text{Cl}_4\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 308.7674, found m/e 308.7650.

**Direct Reaction of (Dichloromethyl)dimethylchlorosilane (1c).** Using the procedure described in the direct reaction of 1b, a gaseous 1 : 4 mixture of 1c (6.21 g/h) and hydrogen chloride (101 mL/min) was introduced to the reactor for 3 h. 29.9 g of the product mixture was collected in receiver. The mixture (2.4 g) of low boilers  $\text{HSiCl}_3$  and  $\text{SiCl}_4$  were distilled off under an atmosphere from the reaction mixture. The remaining reaction mixture was vacuum-distilled to give bis(chlorosilyl)methanes (3.6 g), tris(chlorosilyl)methanes (23.6 g), and several high boilers (0.2 g). 0.1 g of residue was remained. The mixture of tris(chlorosilyl)methanes was 1,1,3-trichloro-3-methyl-2-(chlorosilyl)-1,3-disilabutane (2c, 6%), 1,1,3-trichloro-3-methyl-2-(dichlorosilyl)-1,3-disilabutane (3c, 71%), 1,1,3-trichloro-3-methyl-2-(trichlorosilyl)-1,3-disilabutane (4c, 21%), and 1,1,1,3-tetrachloro-3-methyl-2-(trichlorosilyl)-1,3-disilabutane (5c, 2%). Data for 2c:  $^1\text{H}$  NMR  $\delta$  0.31 (s, 6H,  $\text{CH}_3$ ), 0.49 (s, 1H, CH), 4.96 (d,  $J = 2.4$  Hz, 2H,  $\text{SiH}_2$ ), 5.72 (s, 1H, SiH).  $^{13}\text{C}$  NMR  $\delta$  4.20, 4.31 ( $\text{CH}_3$ ), 12.86 (CH). HRMS calcd for  $\text{C}_3\text{H}_9\text{Cl}_4\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 268.8766, found m/e 268.8746.

Data for 3c:  $^1\text{H}$  NMR  $\delta$  0.78 (s, 6H,  $\text{CH}_3$ ), 1.25 (s, 1H, CH), 5.83 (s, 2H,  $\text{SiH}_2$ ),  $^{13}\text{C}$  NMR  $\delta$  4.91 ( $\text{CH}_3$ ), 19.87 (CH). HRMS calcd for  $\text{C}_3\text{H}_8\text{Cl}_5\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 302.8376, found m/e 302.8361. Data for 4c:  $^1\text{H}$  NMR  $\delta$  0.80 (s, 6H,  $\text{CH}_3$ ), 1.54 (s, 1H, CH), 5.86 (s, 1H, SiH).  $^{13}\text{C}$  NMR  $\delta$  4.67, 5.20 ( $\text{CH}_3$ ), 24.04 (CH). HRMS calcd for  $\text{C}_3\text{H}_7\text{Cl}_6\text{Si}_3$  ((M-H)<sup>+</sup>) m/e 336.7987, found m/e 336.7953. Data of 5c:  $^1\text{H}$  NMR  $\delta$  0.84 (s, 6H,  $\text{CH}_3$ ), 1.82 (s, 1H, CH).  $^{13}\text{C}$  NMR  $\delta$  5.33, 5.41 ( $\text{CH}_3$ ), 28.05 (CH). HRMS calcd for  $\text{C}_2\text{H}_4\text{Cl}_7\text{Si}_3$  ((M- $\text{CH}_3$ )<sup>+</sup>)

m/e 356.7441, found m/e 356.7456.

**Synthesis of 1,1-Dichloro-3,3-dimethyl-2-(dichlorosilyl)-1,3-disilabutane (3d).** Using the procedure described in the direct reaction of **1b**, a gaseous 1:4 mixture of (dichloromethyl)trimethylsilane (**1d**, 5.50 g/h) and hydrogen chloride (101 mL/min) was introduced to the reactor for 3 h. 27.3 g of the product mixture was collected in receiver. The mixture (1.4 g) of low boilers HSiCl<sub>3</sub> and SiCl<sub>4</sub> were distilled off under an atmosphere from the reaction mixture. The remaining reaction mixture was vacuum-distilled to give bis(chlorosilyl)methanes (3.5 g), tris(chlorosilyl)methanes (20.7 g), and several high boilers (1.4 g). 0.2 g of residue was remained. The mixture of tris(chlorosilyl)methanes was 1,1-dichloro-3,3-dimethyl-2-(chlorosilyl)-1,3-disilabutane (**2d**, 4%), 1,1-dichloro-3,3-dimethyl-2-(dichlorosilyl)-1,3-disilabutane (**3d**, 72%), 1,1-dichloro-3,3-dimethyl-2-(trichlorosilyl)-1,3-disilabutane (**4d**, 12%), and 1,1,1-trichloro-3,3-dimethyl-2-(trichlorosilyl)-1,3-disilabutane (**5d**, 11%).

Data for **2d**: <sup>1</sup>H NMR δ 0.33 (s, 9H, CH<sub>3</sub>), 0.54 (s, 1H, CH), 4.98 (d, *J* = 2.28 Hz, 2H, SiH<sub>2</sub>), 5.73 (s, 1H, SiH). <sup>13</sup>C NMR δ 1.07 (CH<sub>3</sub>), 12.95 (CH). HRMS calcd for C<sub>4</sub>H<sub>12</sub>Cl<sub>3</sub>Si<sub>3</sub> ((M-H)<sup>+</sup>) m/e 248.9312, found m/e 248.9309.

Data for **3d**: <sup>1</sup>H NMR δ 0.35 (s, 9H, CH<sub>3</sub>), 0.82 (s, 1H, CH), 5.75 (d, *J* = 0.9 Hz, 2H, SiH). <sup>13</sup>C NMR δ 1.15, 1.18 (CH<sub>3</sub>), 16.56 (CH). HRMS calcd for C<sub>4</sub>H<sub>11</sub>Cl<sub>4</sub>Si<sub>3</sub> ((M-H)<sup>+</sup>) m/e 282.8923, found m/e 282.8913. Data for **4d**: <sup>1</sup>H NMR δ 0.40 (s, 9H, CH<sub>3</sub>), 1.12 (s, 1H, CH), 5.78 (s, 1H, SiH). <sup>13</sup>C NMR δ 1.41 (CH<sub>3</sub>), 20.91 (CH). HRMS calcd for C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>Si<sub>3</sub> ((M-CH<sub>3</sub>)<sup>+</sup>) m/e 302.8376, found m/e 302.8352. Data for **5d**: <sup>1</sup>H NMR δ 0.45 (s, 9H, CH<sub>3</sub>), 1.43 (s, 1H, CH). <sup>13</sup>C NMR δ 1.86 (CH<sub>3</sub>), 25.04 (CH); HRMS calcd for C<sub>3</sub>H<sub>7</sub>Cl<sub>6</sub>Si<sub>3</sub> ((M-CH<sub>3</sub>)<sup>+</sup>) m/e 336.7987, found m/e 336.7953.

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