

# [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup>-Catalyzed Reactions of Trichlorosilane and Dichloromethylsilane with Vinyltrichlorosilane: New Synthetic Method for 1,1,4,4-Tetrachloro-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane Compounds

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**Summary:** [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup>-catalyzed reactions of trichlorosilane and dichloromethylsilane with vinyltrichlorosilane gave 1,1,4,4-tetrachloro-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane (**1**) and 1,1,4,4-tetrachloro-2,5-bis(methyldichlorosilyl)-1,4-disilacyclohexane (**4**), respectively.

## Introduction

Considerable research has focused on the catalytic transformation of inexpensive chlorosilanes, such as HSiCl<sub>3</sub>, with the aim of developing efficient synthetic methods for industrially applicable carbosilanes.<sup>1</sup> The preparation of organochlorosilanes via the direct reaction of elemental silicon with organic chlorides has been extensively studied, and a large number of reports are available in the literature.<sup>2</sup> Among the few potential synthetic methods for the preparation of carbosilanes, the catalytic dehydrogenative Si–C coupling reaction appears promising. A non-transition metal catalyst system, comprising tetrabutylphosphonium chloride, [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup>, which enables economical transformation of Si–H of HSiCl<sub>3</sub> to Si–C of alkylchlorosilanes, was recently reported.<sup>3,4</sup> This catalytic coupling reaction has provided a

new route to alkylchlorosilanes, some of which could not be prepared by conventional methods, such as direct synthesis.

In this study, an attempt was made to prepare cyclized carbosilanes with silyl substituents by reacting HSiCl<sub>3</sub> or MeHSiCl<sub>3</sub> with vinyltrichlorosilane in the presence of [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup> catalyst. The dimerization process of the HSiCl<sub>3</sub>/vinyltrichlorosilane produced 1,1,4,4-tetrachloro-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane (**1**) as a major product under optimum conditions. On the other hand, in the reaction with MeHSiCl<sub>3</sub>/vinyltrichlorosilane, an unexpected rearrangement was observed during the dimerization process to produce 1,1,4,4-tetrachloro-2,5-bis(methyldichlorosilyl)-1,4-disilacyclohexane (**4**).

## Results and Discussion

A reaction of trichlorosilane with vinyltrichlorosilane was carried out in the presence of 10 mol % of [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup> at 150 °C for 3 h. The reaction produced a mixture of *cis*- and *trans*-1,1,4,4-tetrachloro-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane (**1**) along with 1,2-bis(trichlorosilyl)ethane (**2**) and 1,1,2-tris(trichlorosilyl)ethane (**3**), as shown in Scheme 1.

The yields of compounds **1**, **2**, and **3** were examined as function of trichlorosilane to vinyltrichlorosilane ratios issues. As shown in Table 1, the yield of compound **1** increased from 6% to 44% by increasing the amount of trichlorosilane from 1 to 3 equiv per equiv of vinyltrichlorosilane. However, using 4 equiv of trichlorosilane decreased the yield of **1** to 24% with a concomitant increase in the yields of **2** and **3**.

Repeated recrystallization from hexane allowed the isolation of the *trans* isomer as the first crop. However, tedious trials of fractional recrystallization did not separate the *cis* isomer, which always contained some of the *trans* isomer. Figure 1 shows an ORTEP representation of the *trans*-2,5-disilyl-1,4-disilacyclohexane ring. As shown in Figure 1, the *trans* isomer has C<sub>i</sub> symmetry at the centroid of the six-membered disilacyclohexane ring, with the two silyl groups at the equatorial positions. The ring adopts a chair conformation in which the C1 atom is ca. 1.01 Å above the plane consisting of Si(1), C(2), Si(1<sup>′</sup>), and C(2<sup>′</sup>) atoms, forming a ring-puckering angle α of about 49.9°. All silicon–carbon bond lengths are within the normal range for other silicon–carbon bonds (1.85–1.87 Å).<sup>5</sup> The silicon–chlorine bonds are all within the previously reported silicon–chlorine

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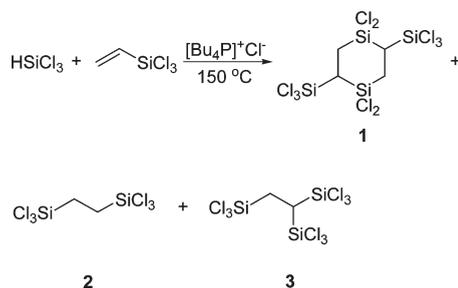
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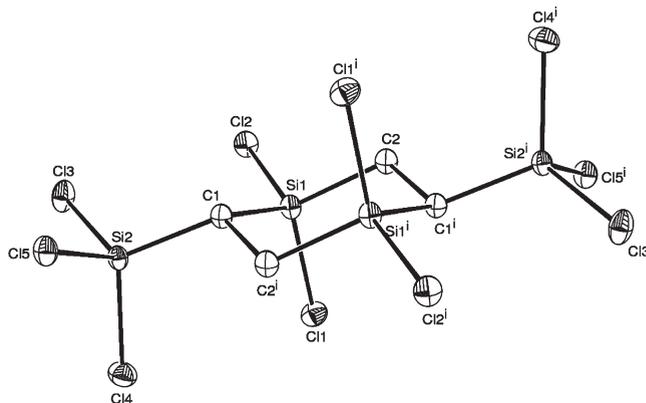
**Scheme 1.  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -Catalyzed Reaction of Vinyltrichlorosilane with Trichlorosilane**

**Table 1. Results of Various Amounts of Trichlorosilane, from 1 to 4 equiv, Referenced to the Amount of Vinyltrichlorosilane**

entry	equiv of $\text{HSiCl}_3$	products in % yields		
		1	2	3
1	1	6	5	56
2	1.6	31	42	27
3	2	36	40	21
4	3	44	28	27
5	4	24	45	30

bond range, around 2.06 Å.<sup>6</sup> Due to silicon atom incorporation into the six-membered ring, there were large variations in the internal bond angles: 108.9(1)° for C(1)–Si(1)–C(2), 109.6(1)° for Si(1)–C(1)–C(2'), and 115.0(1)° for Si(1)–C(1)–C(2'). The observed variations in the internal bond angles are consistent with results from *ab initio* calculation results.<sup>7</sup>

As shown in Scheme 2, based on previous results,<sup>3,4</sup> we suggest a tentative mechanism for the formation of the observed trisilachlorohexane. In the initial step, a quaternary phosphonium chloride reacts with trichlorosilane to form the pentacoordinated hydridotetrachlorosilyl anion in the initial step, which loses hydrogen chloride upon heating to give a tetrabutylphosphonium cation/trichlorosilyl anion pair (I). As suggested by Benkeser,<sup>8</sup> trichlorosilyl anion I may undergo conjugate addition to the vinylsilane to form  $\alpha$ -silyl anion II directly, which could then be cyclized to give the corresponding silacyclopropane III. Generated silacyclopropane is expected to dimerize to give 1 easily owing to its high ring strain.<sup>9</sup> It should be noted that conversion between intermediate II and III could be reversible, since the yields of compounds 1, 2, and 3 varied with trichlorosilane to vinyltrichlorosilane ratio, as shown in Table 1. The formation of 2 and 3 could possibly result from the further reaction of intermediate II with HCl and  $\text{SiCl}_4$ , respectively. The occurrence of  $\text{SiCl}_4$  was supported by facile Si–H/Si–Cl exchange under the  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -catalyzed conditions of  $\text{HSiCl}_3$ . Such a redistribution between Si–H and Si–Cl groups was confirmed by the product analysis of tetrachlorosilane and dichlorosilane from  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -catalyzed reaction of trichlorosilane (see Supporting Information (SI), p 3).

The reaction of dichloromethylsilane with vinyltrichlorosilane was also examined. Since dichloromethylsilane is less


**Figure 1.** X-ray structure of *trans*-1,1,4,4-tetrachloro-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane (1) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

reactive than trichlorosilane, the reaction required higher temperatures and longer reaction times than needed for trichlorosilane: 180 °C for 6 h. As shown in Scheme 3, the  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -catalyzed reaction of dichloromethylsilane with vinyltrichlorosilane gave 1,1,4,4-tetrachloro-2,5-bis(methyl-dichlorosilyl)-1,4-disilacyclohexane (4) as the major product, along with minor amounts of the compound 1,2-bis(dichloro(methyl)silyl)ethane (5) and the bissilylation products (6), as shown in Scheme 3. In this case, facile Si–H/Si–Cl exchange led to more than five bissilylation products, confirmed by GC, and this mixture could not be resolved (see SI, Figure S12).

After repeated recrystallization from hexane, a structural study confirmed the formation of the *trans* isomer similar to the formation of 1. As shown in Figure 2, the six-membered disilacyclohexane ring has a chair conformation with the two methyl-dichlorosilyl groups in the equatorial positions with  $C_i$  symmetry. The ring adopts a chair form in which the apical C atoms are 1.01 Å (ca.) away from the plane consisting of Si(1), C(2), Si(1'), and C(2') atoms, forming a ring-puckering angle  $\alpha$  of about 49.9°.

As shown in Scheme 4, once the primary carbanion intermediate (IV) was generated, the expected dimerization product, 1,4-dichloro-1,4-dimethyl-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane (7), was not the product that was isolated. Instead, compound 4 was obtained as a major product. Primary carbanion, analogous to the secondary  $\alpha$ -silyl carbanion (II) depicted in Scheme 2, could close on the  $\text{SiMeCl}_2$  group to reform the original silacyclopropane V or close on the  $\text{SiCl}_3$  to form silacyclopropane VII. Note that this conversion could be reversible, similar to the mechanism shown in Scheme 2.

In summary,  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -catalyzed reactions of trichlorosilane and dichloromethylsilane with vinyltrichlorosilane produced dimerized disilacyclohexanes, 1 and 4. In particular, for the formation of 4, extensive rearrangements were proposed during the dimerization process. It has been also noted that  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -catalyzed dimerization reactions were regio-specific for both trichlorosilane and dichloromethylsilane.

## Experimental Section

**General Comments.** All reactions were carried out in flame-dried glassware or in a stainless steel bomb. All air-sensitive liquids were transferred using standard syringe or double tipped needle techniques.<sup>10</sup> The reaction mixtures were analyzed by

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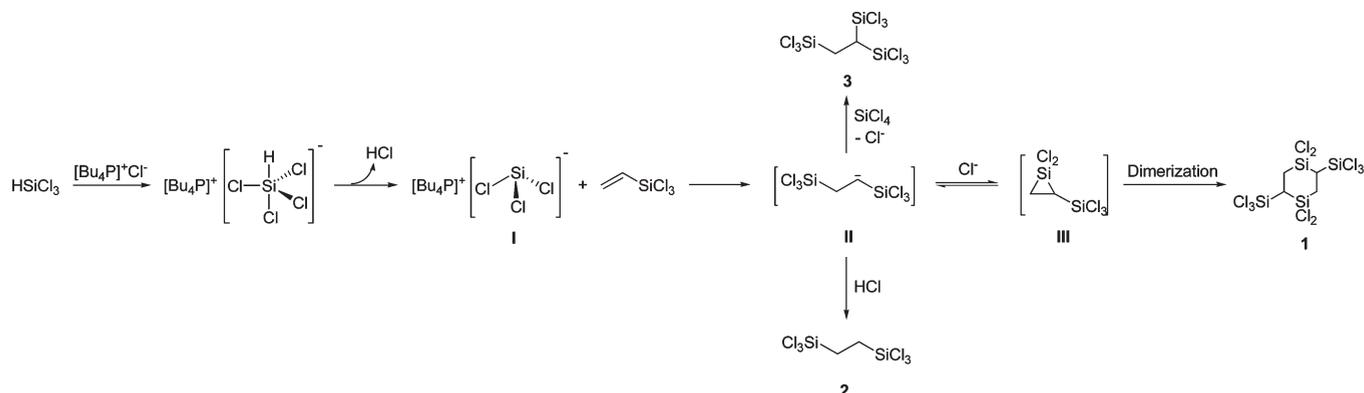
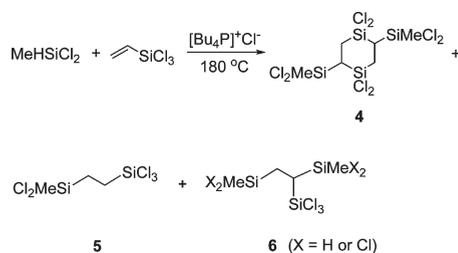
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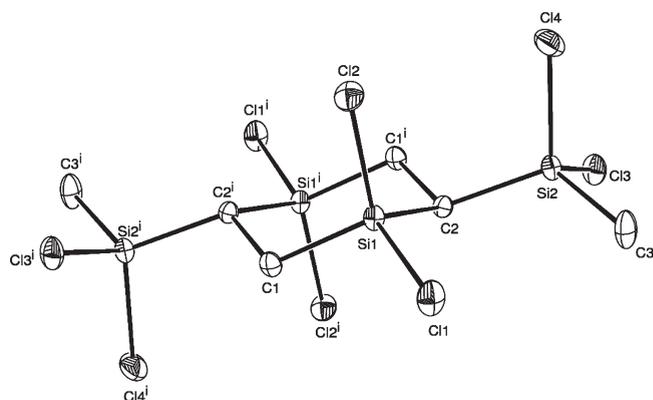
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**Table 2.** Selected Bond Lengths and Angles of Compounds **1** and **4**

Bond Lengths (Å) for <b>1</b>					
Si(1)–C(1)	1.872(3)	Si(1)–C(2)	1.860(3)	Si(1)–Cl(1)	2.049(1)
Si(2)–C(1)	1.854(3)	Si(2)–Cl(3)	2.014(1)	Si(2)–Cl(4)	2.018(1)
Si(2)–Cl(5)	2.036(1)				
Bond Lengths (Å) for <b>4</b>					
C(1)–Si(1)	1.855(2)	C(2)–Si(1)	1.862(2)	Cl(1)–Si(1)	2.0398(8)
Cl(2)–Si(1)	2.0427(8)	Cl(3)–Si(2)	2.0624(8)	Cl(4)–Si(2)	2.0394(9)
Bond Angles (deg) for <b>1</b>					
C(2)–Si(1)–C(1)	109.8(1)	C(2)–Si(1)–Cl(2)	108.3(1)	C(1)–Si(1)–Cl(2)	112.8(1)
C(2)–Si(1)–Cl(1)	107.7(1)	C(1)–Si(1)–Cl(1)	109.0(1)	Cl(2)–Si(1)–Cl(1)	109.1(5)
C(1)–Si(2)–Cl(3)	111.7(1)	C(1)–Si(2)–Cl(4)	111.9(1)	Cl(3)–Si(2)–Cl(4)	109.6(5)
C(1)–Si(2)–Cl(5)	108.2(1)	Cl(3)–Si(2)–Cl(5)	108.08(5)	Cl(4)–Si(2)–Cl(5)	107.18(5)
Bond Angles (deg) for <b>4</b>					
Si(1)–C(2)–Si(2)	119.2(1)	C(1)–Si(1)–C(2)	110.84(9)	C(1)–Si(1)–Cl(1)	108.80(7)
C(2)–Si(1)–Cl(1)	111.40(7)	C(1)–Si(1)–Cl(2)	107.32(8)	C(2)–Si(1)–Cl(2)	109.83(7)
Cl(1)–Si(1)–Cl(2)	108.54(4)	C(3)–Si(2)–C(2)	116.0(1)	C(3)–Si(2)–Cl(4)	111.1(1)
C(2)–Si(2)–Cl(4)	108.79(7)	C(3)–Si(2)–Cl(3)	108.12(9)	C(2)–Si(2)–Cl(3)	106.66(7)
Cl(4)–Si(2)–Cl(3)	105.54(4)				

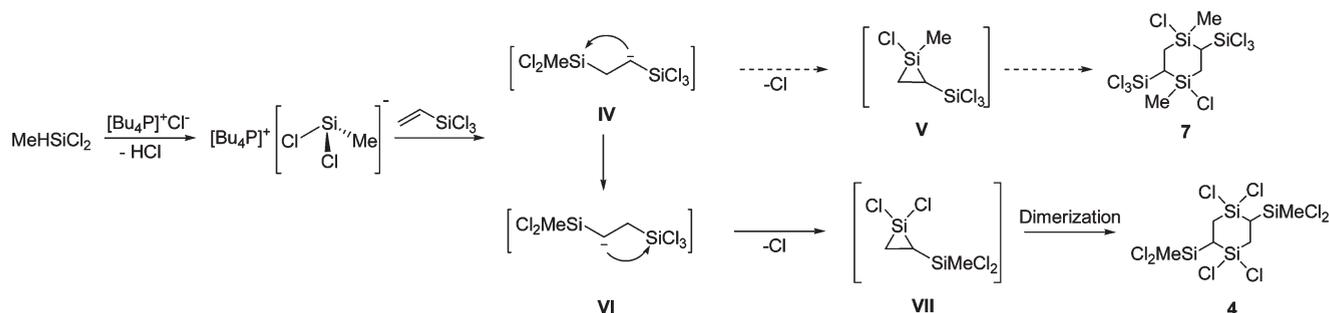
**Scheme 2.** Proposed Reaction Sequence, Involving Trichlorosilyl Anion (**I**), Carbanion (**II**), and Silacyclopropane (**III**) Intermediates for the Formation of Compounds **1**, **2**, and **3****Scheme 3.**  $[\text{Bu}_4\text{P}]^+\text{Cl}^-$ -Catalyzed Reaction of Vinyltrichlorosilane with Dichloromethylsilane

GLC (1.5 m by 1/8 in. stainless steel column packed with packing materials (10% SE-30 or SE-54 on 80–100 mesh Chromosorb P/AW)) using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a Varian 4290 integrator. The progress of the reactions was monitored by GLC at 30 min or 1 h intervals. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 and 75.4 MHz, respectively.  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker DMX 600.13 MHz at the Ochang Branch of the Korean Basic Science Institute. Elemental analyses of solid products **1** and **4** were carried out using a Carlo Erba Instruments CHNS-O EA 1108 analyzer, but measured values were not satisfactory due to the unstable nature of chlorosilanes.

**Figure 2.** X-ray structure of *trans*-1,1,4,4-tetrachloro-2,5-bis(methyl-dichlorosilyl)-1,4-disilacyclohexane (**4**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Therefore, reduced compounds of **1** and **4**, 2,5-bissilyl-1,4-disilacyclohexane (**1'**) and 2,5-bis(methylsilyl)-1,4-disilacyclohexane (**4'**), were used for elemental analysis. Crystal structure data for compound **1**: triclinic, space group  $P\bar{1}$ ,  $a = 6.1896(5)$  Å,  $b = 8.3969(7)$  Å,  $c = 9.0412(9)$  Å,  $\alpha = 89.363(3)^\circ$ ,  $\beta = 80.569(3)^\circ$ ,  $\gamma = 78.809(2)^\circ$ ,  $V = 454.64(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 150(2)$  K, crystal dimension  $0.20 \times 0.15 \times 0.04$  mm<sup>3</sup>, and  $\text{Mo K}\alpha = 1.775$  mm<sup>-1</sup>. Of 4423

Scheme 4. Proposed Mechanism for the Formation of Compound 4



reflections collected in the  $\theta$  range of 3.33° to -27.46°, using  $\omega$  scans on a Rigaku R-axis Rapid S diffractometer, 2047 were unique reflections ( $R_{\text{int}} = 0.026$ , completeness = 98.8%). The structure was solved and refined against  $F_2$  using SHELX97,<sup>11</sup> 94 variables,  $wR_2 = 0.1103$ ,  $R_1 = 0.0394$  ( $F_o^2 > 2\sigma(F_o^2)$ ), GOF = 1.163, and a max./min. residual electron density of 1.321/-0.683 e Å<sup>-3</sup>. Crystal structure data for compound 4: triclinic, space group  $P\bar{1}$ ,  $a = 6.7991(3)$  Å,  $b = 8.6802(4)$  Å,  $c = 9.2531(5)$  Å,  $\alpha = 84.181(2)^\circ$ ,  $\beta = 67.190(2)^\circ$ ,  $\gamma = 71.425(1)^\circ$ ,  $V = 477.01(4)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 150(2)$  K, crystal dimension 0.40 × 0.20 × 0.15 mm<sup>3</sup>, Mo K $\alpha = 1.775$  mm<sup>-1</sup>. Of 4602 reflections collected in the  $\theta$  range of 3.35° to -27.48°, using  $\omega$  scans on a Rigaku R-axis Rapid S diffractometer, 2137 were unique reflections ( $R_{\text{int}} = 0.016$ , completeness = 98.0%). The structure was solved and refined against  $F_2$  using SHELX97,<sup>11</sup> 82 variables,  $wR_2 = 0.0838$ ,  $R_1 = 0.0272$  ( $F_o^2 > 2\sigma(F_o^2)$ ), GOF = 1.220, and a max./min. residual electron density of 0.502/-0.498 e Å<sup>-3</sup>.

**Reaction of Trichlorosilane with Vinyltrichlorosilane in the Presence of [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup>.** Vinyltrichlorosilane (3.0 g, 19 mmol), trichlorosilane (7.5 g, 57 mmol), and [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup> (0.6 g, 2 mmol) were added to a 25 mL stainless steel tube under a dry nitrogen atmosphere. The tube was sealed with a cap, and the reaction mixture was heated at 150 °C for 3 h. After cooling, the reaction mixture was transferred to a 25 mL one-necked flask with a double-tipped needle. The mixture consisted of two layers of an organic phase and a catalyst. The reaction mixture was separated from the catalyst by filtration. The filtrates were separated by bulb-to-bulb vacuum distillation at 82 °C/10 mmHg to give 1,2-bis(trichlorosilyl)ethane (**2**) (1.5 g, 27%), at 98 °C/10 mmHg to give 1,1,2-tris(trichlorosilyl)ethane (**3**) (2.3 g, 28%), and at 175 °C/mmHg to give 1,1,4,4-tetrachloro-2,5-bis(trichlorosilyl)-1,4-disilacyclohexane (**1**) as colorless liquids. Compound **1** was dissolved in hexane and then recrystallized at 0 °C to give **1** (2.2 g, 44%). Repeated recrystallization from hexane allowed the isolation of the pure *trans* isomer as the first crop. Data for **1**: initial *cis-trans* isomer mixture: mp 106–110 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.80–1.85 (t, 2H, Si-CH<sub>2</sub>-Si), 1.57–1.70 (d, 4H, Si-CH<sub>2</sub>-C); <sup>13</sup>C NMR  $\delta$  23.0, 20.8, 17.0, 14.5; <sup>29</sup>Si NMR  $\delta$  21.3, 18.2, 6.2, 5.5; pure *trans* isomer: mp 111–113 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.84–1.88 (t, 2H, Si-CH<sub>2</sub>-Si), 1.64–1.75 (d, 4H, Si-CH<sub>2</sub>-C); <sup>13</sup>C NMR  $\delta$  23.0, 17.0; <sup>29</sup>Si NMR  $\delta$  18.2, 5.5. Data for **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.58 (s, 2H, Si-CH<sub>2</sub>-C); <sup>13</sup>C NMR  $\delta$  16.5. Data for **3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.94–1.98 (t, 1H, Si-CH-Si), 2.05 (d, 2H, Si-CH<sub>2</sub>-C); <sup>13</sup>C NMR  $\delta$  24.5, 18.5.

**Reaction of Dichloromethylsilane with Vinyltrichlorosilane in the Presence of [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup>.** A procedure analogous to that described above was used. Vinyltrichlorosilane (4.0 g, 25 mmol), dichloromethylsilane (8.6 g, 75 mmol), and [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup> (0.7 g, 2.5 mmol) were added to a 25 mL stainless steel tube, and the reaction mixture was heated to 180 °C for 6 h. After cooling, the reaction mixture was transferred to a 25 mL one-necked flask with a double-tipped needle. The reaction mixture was separated from the catalyst by filtration. The filtrates were separated by bulb-to-bulb vacuum distillation at 75 °C/10 mmHg to give

trichloro(2-(dichloro(methyl)silyl)ethyl)silane (**5**) (1.4 g, 20%), at 90 °C/10 mmHg to give bissilylation products (**6**) (3.4 g, 38%), and at 160 °C/10 mmHg to give 1,1,4,4-tetrachloro-2,5-bis(methylchlorosilyl)-1,4-disilacyclohexane (**4**) as colorless liquids. Compound **4** was dissolved in hexane and then recrystallized at 0 °C to give **4** (2.5 g, 42%). Repeated recrystallization from hexane allowed the isolation of the pure *trans* isomer as the first crop. Data for **4**: initial *cis-trans* isomer mixture: mp 86–90 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.82–1.75 (t, 4H, Si-CH<sub>2</sub>-C), 1.56–1.50 (m, 4H, Si-CH<sub>2</sub>-C), 1.41–1.37, 1.29–1.71; <sup>13</sup>C NMR  $\delta$  20.7, 18.2, 16.7, 14.2, 6.5, 6.2, 5.7; <sup>29</sup>Si NMR  $\delta$  27.3, 25.2, 21.1, 18.0; pure *trans* isomer: mp 92–94 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.84, 1.57, 1.43, 0.97 (s, 6H, Si-CH<sub>3</sub>); <sup>13</sup>C NMR  $\delta$  20.7, 16.7, 6.45; <sup>29</sup>Si NMR  $\delta$  25.2, 18.0. Data for **5**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.50 (t, 2H, CH<sub>2</sub>Cl<sub>2</sub>Si-CH<sub>2</sub>-C), 1.27 (t, 2H, Cl<sub>2</sub>Si-CH<sub>2</sub>-C), 0.82 (s, 3H, CH<sub>3</sub>Cl<sub>2</sub>Si-CH<sub>2</sub>); <sup>13</sup>C NMR  $\delta$  16.5, 13.8, 4.8.

**General Procedure for 2,5-Bissilyl-1,4-disilacyclohexane (**1'**) and 2,5-Bis(methylsilyl)-1,4-disilacyclohexane (**4'**).** Lithium aluminum hydride (1.0 g, 26.6 mmol) and dry diethyl ether (20 mL) were added to a 100 mL three-necked flask equipped with a magnetic stir bar, rubber septum, and vacuum adapter. The flask was cooled to 0 °C with constant stirring, and the corresponding chlorosilane (10 mmol) in diethyl ether (10 mL) was added dropwise through a dropping funnel. After the addition, the mixture was warmed to room temperature for 1 h and stirred at room temperature for 3 h. The remaining LiAlH<sub>4</sub> was quenched with a 5% acetic acid aqueous solution at 0 °C, and the organic layer was separated and dried over MgSO<sub>4</sub>. After filtration, the products were distilled at 760 mmHg to give compounds **1'** and **4'**. Data for 2,5-bissilyl-1,4-disilacyclohexane (**1'**): yield 82%; bp 142 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.92–3.83 (m, 4H, CH-SiH<sub>2</sub>-CH<sub>2</sub>), 3.67–3.62 (m, 6H, CH-SiH<sub>3</sub>), 1.26–0.87 (m, 4H, SiH<sub>2</sub>-CH<sub>2</sub>-CH), 0.43–0.49 (m, 2H, SiH<sub>2</sub>-CH-SiH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -3.8 (SiH<sub>2</sub>-CH<sub>2</sub>-CH), -6.4 (CH<sub>2</sub>-CH-SiH<sub>3</sub>). Anal. Calcd for C<sub>4</sub>H<sub>16</sub>Si<sub>4</sub> (176.51): C 27.22, H 9.14. Found: C 27.21, H 9.16. Data for 2,5-bis(methylsilyl)-1,4-disilacyclohexane (**4'**): yield 90%; bp 166 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.77 (q, 4H, CH<sub>2</sub>-SiH<sub>2</sub>-CH), 3.61–3.68 (m, 4H, CH-SiH<sub>2</sub>-CH<sub>3</sub>), 1.20–0.83 (tm, 4H, SiH<sub>2</sub>-CH<sub>2</sub>-CH), 0.34–0.47 (m, 2H, SiH<sub>2</sub>-CH-SiH<sub>2</sub>), 0.18 (t, 6H, CH-SiH<sub>2</sub>-CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  8.0 (Si-CH<sub>2</sub>-CH), 0.3 (Si-CH-Si), -8.9 (Si-CH<sub>3</sub>). Anal. Calcd for C<sub>6</sub>H<sub>20</sub>Si<sub>4</sub> (204.57): C 35.23, H 9.85. Found: C 35.13, H 9.87.

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**Supporting Information Available:** X-ray diffraction data for compounds **1** and **4**. <sup>1</sup>H and <sup>13</sup>C spectra for all compounds and <sup>29</sup>Si NMR for **1** and **4**. GC data for the reaction of dichloromethylsilane with vinyltrichlorosilane in the presence of [Bu<sub>4</sub>P]<sup>+</sup>Cl<sup>-</sup>. This material is available free of charge via the Internet at <http://pubs.acs.org>.