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Phosphine-Catalyzed Si−C Coupling of Bissilylmethanes: Preparation of Cyclic $(Cl_2SiCH_2)_2$ and Linear $Cl_2Si(CH_2SiCl_3)_2$ via Silylene and Silene Intermediates

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Cyclic and linear carbosilanes, $(Cl_2SiCH_2)_2$ (**2**) and $Cl_2Si(CH_2SiCl_3)_2$ (**3**), were produced from phosphine-catalized Si−C coupling reactions of bissilylmethanes, $HCl_2SiCH_2SiX_1X_2Cl$ (X_1, X_2 = Cl (**1**), X_1 = H, X_2 = Cl (**7**), and X_1 = Me, X_2 = Cl (**8**)). The formation of compounds **2** and **3** suggested competing reaction pathways, involving dichlorosilene [$CH_2{=}SiCl_2$] and dichlorosilylene [$:SiCl_2$] intermediates. Each intermediate was either proposed by the product isolation of the trimerized product (**3**) or confirmed by trapping experiments with 2,3-dimethylbutadiene and methylene chloride.

Introduction

Carbosilanes have attracted considerable interest for their potential applications in ceramic,[1] optical,[2] conducting,[3] and electronic materials.[4] The direct reactions of elemental silicon and alkyl chlorides were reported to be the most effective for the preparation of carbosilane compounds, and optimized protocols are now available in the literature.[5] In 1945, Patnode and Schiessler reported the first direct reaction of silicon with CH_2Cl_2 over a copper catalyst.[6] Cyclic and linear organosilanes with the formula $(SiCl_2CH_2)_x$ ($x \geq 3$) and $X_3Si(CH_2)_nSiX_2Y$ (X = Cl, Y = H or Cl, n = 1−4) were produced using this process. However, there was no detailed information regarding the identification of each compound. Later, Fritz, and Matern[7] examined the same reaction using a fluidized-bed reactor at 320 °C and isolated more than 40 carbosilanes ranging from one to 12 silicon atoms, including six- and eight-membered cyclic carbosilanes, $(Cl_2SiCH_2)_3$[8] and $(Cl_2SiCH_2)_4$.[9] Although the reactions were carried out on a large scale using a continuous process, the yields of distillable products were only ~20%, partly due to the decomposition of methylene chloride. Methylene chloride degradation caused carbon deposition on the surfaces of the elemental silicon and copper catalyst, which deactivated the solid reactants. Similar difficulty was encountered in another study, but methylene chloride decomposition was avoided by adding HCl to produce carbosilanes[10] (see eq 1).

$$\mathrm{Si} + CH_2Cl_2/HCl \xrightarrow{\text{Cu-Cd}} (Cl_2HSi)_2CH_2 + Cl_2HSiCH_2SiCl_3 + (Cl_3Si)_2CH_2 + \text{others} \qquad (1)$$

Although the preparation of cyclic and linear carbosilanes has been achieved to some extent by direct synthesis, there is growing demand for the development of a rational synthesis of carbosilanes for the larger scale production of specific

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[1] (a) Seyferth, D. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; ACS: Washington, DC, 1988; Chapter 3. (b) Birot, M; Pilot, J. P.; Dunogues *J. Chem. Rev* **1995**, *95*, 1443. (c) Corriu, R. J. P.; Enders, M.; Huille, S.; Moreau, J. J. E. *Chem. Mater*. **1994**, *6*, 15. (d) Laine, R. M.; Babonneau, F. *Chem. Mater*. **1993**, *5*, 260.

[2] (a) Bobrovsky, A. Y.; Pakhomov, A. A.; Zhu, X.-M.; Boiko, N. I.; Shibaev, V. P.; Stumpe, J. *J. Phys. Chem. B* **2002**, *106*, 540. (b) Li, C. F.; Jin, F.; Dong, X. Z.; Chen, W. Q.; Duan, X. M. *J. Lumin*. **2007**, *127*, 321.

[3] (a) Ohshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R. F.; Ishikawa, M. *Macromolecules* **1992**, *25*, 2134. (b) Brefort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, Th; Garnler, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500.

[4] (a) Son, H. J.; Han, W. S.; Lee, K. H.; Jung, H. J.; Lee, C. M.; Ko, J.; Kang, S. O. *Chem. Mater*. **2006**, *18*, 5811. (b) Ohshita, J.; Takata, A.; Kai, H.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Kunugi, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **2000**, *19*, 4492. (c) Lee, T.; Jung, I.; Song, K. H.; Baik, C.; Kim, S.; Kim, D.; Kang, S. O.; Ko, J. *Organometallics* **2004**, *23*, 4184. (d) Chen, Y.-J.; Luh, T.-Y. *Macromolecules* **2005**, *38*, 4563.

[5] (a) Petrov, A. D.; Mironov, V. F.; Ponomarenko, V. A.; Chemyshev, E. A. *Synthesis of Organosilicon Monomers*; Consultants Bureau: New York, 1964. (b) Voorhoeve, R. J. H. *Organohalosilanes: Precursors to Silicones*; Elsevier: New York, 1967. (c) Lewis, K. M.; Rethwisch, D. G. *Catalyzed Direct Reactions of Silicon*; Elsevier: Amsterdam, 1993.

[6] Petnode, W. I.; Schiessler, R. W. U.S. Patent 2381000, 2381001, 2381002, 1945; *Chem. Abstr*. 1945, 39, 4889.

[7] Fritz, G.; Matern, E. *Carbosilanes: Synthesis and Reactions*; Springer: New York, 1986; pp 46−53.

[8] Fritz, G.; Thielking, H. *Z. Anorg. Allg. Chem*. **1960**, *306*, 39.

[9] Fritz, G.; Haase, R.; Kummer, D. *Z. Anorg. Allg. Chem*. **1984**, *512*, 131.

[10] Yeon, S. H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem*. **1996**, *516*, 91.

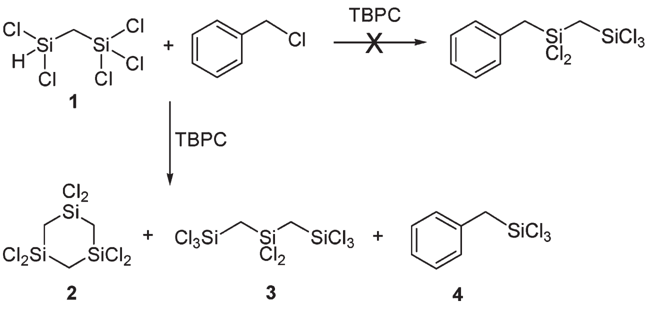
silanes. Among the few potential synthetic methods available, the catalytic Si−C coupling reaction appears to be the most desirable.[11] Indeed, a new type of phosphine-catalyzed Si−C coupling reaction of di- or trichlorosilane with alkyl chlorides was determined for the formation of the corresponding carbosilanes. A wide range of carbosilanes, which would have been unobtainable from the direct method,[12] were prepared using this method. Based on product isolation, phosphine-catalyzed carbosilane generation facilitated dichlorosilylene insertion into the Si−C bond of alkyl chlorides. For example, in the case of $HSiCl_3$, the initial ion pair formation of $[Bu_4P]^+[HSiCl_4]^-$, followed by dehydrochlorination, was proposed to give a dichlorosilylene intermediate, [$:SiCl_2$], which was then inserted into the C−Cl bond of the alkyl chlorides to give the corresponding carbosilanes.[12]

The high yield and facile conversion to carbosilanes by phosphine-catalyzed Si−C coupling prompted us to expand the scope of dehydrochlorination to the reaction of bissilylmethane. A preliminary reaction involving $HCl_2SiCH_2SiCl_3$ (**1**)[10] and benzyl chloride showed that the expected Si−C coupled product was not produced; instead, cyclic and linear carbosilanes, $(Cl_2SiCH_2)_2$ (**2**)[8] and $(CH_2SiCl_3)_2SiCl_2$ (**3**), were isolated.[14] This suggests that there are reaction paths involving different intermediates. Therefore, in light of the formation of cyclic and linear carbosilanes, compounds **2** and **3**, **1** was examined by different trapping experiments to determine the possible intermediates associated with a new reaction mechanism. Indeed, the trapping experiments of compound **1** with 2,3-dimethylbutadiene and methylene chloride revealed a dichlorosilylene intermediate (**A**) from the isolation of 1,1-dichloro-3,4-dimethylsilacyclopent-3-ene (**5**) and bis(trichlorosilyl)methane (**6**), respectively. Furthermore, another intermediate, dichlorosilene (**B**), was proposed on the basis of the product isolation of cyclic carbosilane (**2**). To further confirm the generality of the new mechanism with the proposed dual intermediates, a series of bissilylmethane derivatives, $HCl_2SiCH_2SiX_1X_2Cl$ [$X_1 = H, X_2 = Cl$ (**7**); $X_1 = Me, X_2 = Cl$ (**8**); $X_1, X_2 = Me$ (**9**)], was studied for phosphine-catalyzed reactions to determine if the involvement of the dual intermediates, dichlorosilene (**B**) and dichlorosilylene (**A**), was responsible for the generation of cyclic and linear carbosilanes (**2** and **3**). It was also found that substituents at the silicon atom dictated the formation of carbosilanes. Chlorine substituents at the silicon atom facilitated the phosphine-catalyzed Si−C coupling reaction, as found in compounds **7** and **8**. However, the expected reaction did not proceed when the methyl group replaced chloride, as observed with compound **9**.

Results and Discussion

The expected coupled product, $C_6H_5CH_2SiCl_2CH_2SiCl_3$, was not detected when $HCl_2SiCH_2SiCl_3$ (**1**) was activated thermally in the presence of a catalytic amount (10 mol %) of $[Bu_4P]^+Cl^-$ [(tetrabutyl)phosphonium chloride, TBPC] with $C_6H_5CH_2Cl$ (benzyl chloride) at 180 °C for 2 h. Instead, the reaction gave cyclic (**2**) and linear carbosilanes (**3**) and $C_6H_5CH_2SiCl_3$ in 47%, 16%, and 21% yield, respectively (see Scheme 1).

Scheme 1. TBPC-Catalyzed Reaction of 1 with Benzyl Chloride



Since $C_6H_5CH_2SiCl_3$ was the coupled product between $C_6H_5CH_2Cl$ and dichlorosilylene,[12b] it was assumed that activation of compound **1** involved the generation of dichlorosilylene (**A**) (see Scheme 2). Isolation of cyclic carbosilane (**2**) as a major product strongly suggested other reaction sequences involving different intermediates. As shown in Scheme 2, adequate reasoning for the formation of compound **2** led to the suggestion of a dichlorosilene intermediate (**B**). It was postulated that such a dichlorosilene intermediate (**B**) dimerized in a head-to-tail manner to form [$Cl_2Si(\mu\text{-}CH_2)_2SiCl_2$] (**C**) due to the unstable nature of the Si=C double bond.[15] Further to the high ring strain of disilacyclobutane (**C**), after adding dichlorosilene (**B**), the reaction proceeded to give a cyclic carbosilane (**2**). On the other hand, the insertion of dichlorosilylene (**A**) to disilacyclobutane (**C**) resulted in the formation of a linear carbosilane (**3**). During this insertion, further ring-opening was expected to give a product (**3′**) terminated by a Si−H unit. The isolation of compound **3** confirmed its origin from a facile Si−H/Si−Cl exchange reaction,[16] as shown in Scheme 4.

Figure 1 shows the geometry of compound **2** determined from a X-ray structural study,[17] where each silicon atom is bonded to a methylene unit in an alternating manner to form a six-membered cyclic ring. The trisilacyclohexane ring adopts a stable chair conformation with three dichloro silene units. Table 1 summarizes the selected bond distances and angles. No anomalies were found in both the bond distances and angles in the carbosilane ring.

To corroborate the plausible reaction sequence, the first trapping experiment with 2,3-dimethylbutadiene[18] was carried out under identical reaction conditions. As a result, only the dichlorosilylene (**A**) trapped product, 1,1-dichloro-3,4-dimethylsilacyclopent-3-ene (**5**),[12a] was isolated, as shown in Scheme 5. The isolation of compound **5** provided direct evidence of the involvement of the dichlorosilylene intermediate (**A**). The typical product yields for compounds **2**, **3**,

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(11) Cho, Y. S.; Kang, S. H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Am. Chem. Soc.* **2001**, *123*, 5584.

(12) (a) Kang, S. H.; Han, J. S.; Lee, M. H.; Yoo, B. R.; Jung, I. N. *Organometallics* **2003**, *22*, 2551. (b) Kang, S. H.; Han, J. S.; Yoo, B. R.; Lee, M. S.; Jung, I. N. *Organometallics* **2003**, *22*, 529. (c) Kang, S. H.; Han, J. S.; Lim, W. C.; Jung, I. N.; Lee, M. E.; Yoo, B. R. *Organometallics* **2006**, *25*, 318.

(13) Jung, I. N.; Yeon, S. H.; Han, J. S. *Organometallics* **1993**, *12*, 2360.

(14) Firtz, G. *Angew. Chem., In. Ed. Engl.* **1987**, *26*, 1111.

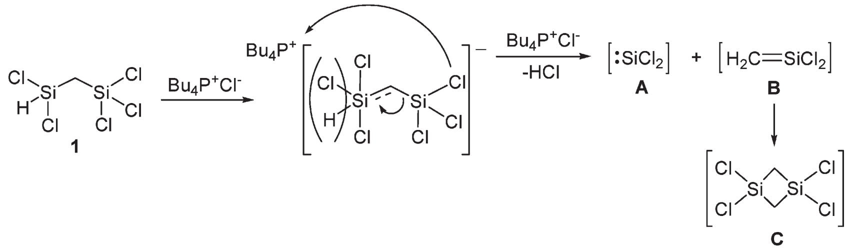
(15) (a) Irwin, R. M.; Cooke, J. M.; Laane, J. *J. Am. Chem. Soc.* **1977**, *99*, 3273. (b) Auner, N.; Grobe, J. *J. Organomet. Chem.* **1981**, *222*, 33. (c) Nametkin, N. S.; Vdovin, V. M.; Zav'yalov, V. I.; Grinberg, P. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, *5*, 929.

(16) Jung, I. N. et al. *Unpublished results for the phosphine-catalyzed Si−H/Si−Cl exchange reactions.*

(17) Fritz, G.; Matern, E. *Carbosilanes: Synthesis and Reactions*; Springer: New York, 1986; p 218.

(18) (a) Dzarnosik, J.; Rickborn, S. F.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1982**, *1*, 1217. (b) Rogers, D. S.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1986**, *5*, 1467.

Scheme 2. Formation of Dichlorosilylene (A) and Dichlorosilene (B) Intermediates



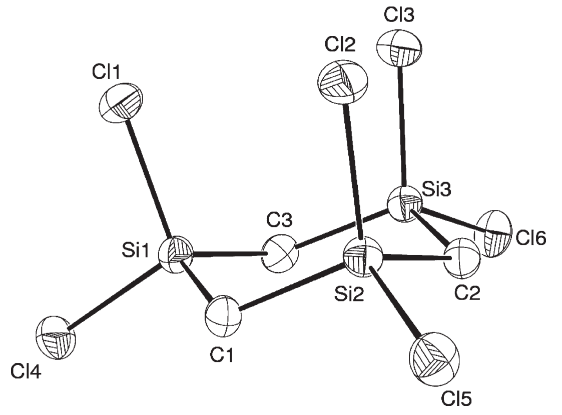
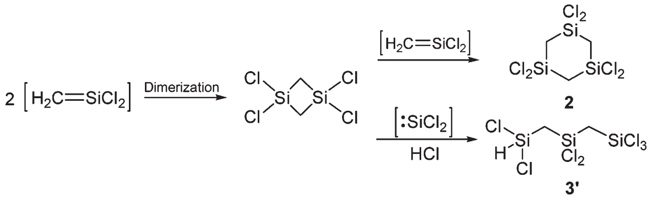


Figure 1. X-ray structure of compound **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Scheme 3. Proposed Mechanism for the Formation of Trisilacyclohexane (2) and Trisilapentane (3′)



Scheme 4. Facile Si−H/Si−Cl Exchange Reaction of 3′ and 3 with $HSiCl_3$

and **5** from the trapping reaction with 2,3-dimethylbutadiene were 42%, 6%, and 17%, respectively. Although 2,3-dimethylbutadiene is a good trapping agent for silenes,[19] the existence of another intermediate, dichlorosilene (**B**), was not confirmed. As a result, a second trapping reaction was carried out using methylene chloride. Similar to the precedent trapping reaction, the dichlorosilylene (**A**) trapped product, $Cl_3SiCH_2SiCl_3$ (**6**), was obtained only in 23% yield along with the cyclic and linear products **2** (54%) and **3** (8%). Although dichlorosilene (**B**) was not trapped and isolated,

Table 1. Selected Bond Lengths and Angles of Compound 2

	Bond Lengths (Å)		
C(1)−Si(2)	1.852(3)	C(1)−Si(1)	1.854(3)
C(2)−Si(3)	1.858(3)	C(2)−Si(2)	1.859(3)
C(3)−Si(3)	1.854(3)	C(3)−Si(1)	1.855(3)
	Bond Angles (deg)		
Si(2)−C(1)−Si(1)	115.7(2)	Si(3)−C(2)−Si(2)	114.5(2)
Si(3)−C(3)−Si(1)	116.4(2)	C(1)−Si(1)−C(3)	110.4(1)

Scheme 5. TBPC-Catalyzed Reaction of 1 with 2,3-Dimethylbuta-1,3-diene

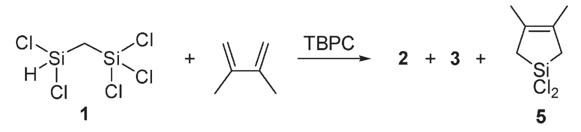


Table 2. Result of Various Dichlorosilylene (A) Trapping Experiments

	products					
					others (%)	
trapping agents	**2** (%)	**3** (%)	trapped product (%)	**1**	low-boiler	polymeric materials
benzyl chloride	47	16	**4** (21)	9	3	3
2,3-dimethylbutadiene	42	6	**5** (17)	20	6	8
methylene chloride	54	8	**6** (23)	8	4	6

Scheme 6. TBPC-Catalyzed Reaction of 1 with Methylene Chloride

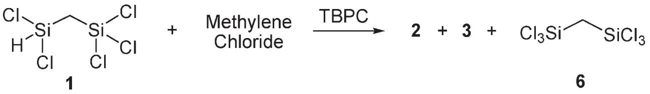


Table 2 lists the results of the trapping experiments involving dichlorosilylene (**A**).

To demonstrate the involvement of the dichlorosilene intermediate (**B**), another trapping experiment was carried out with Me_3SiOMe[20] under identical reaction conditions. However, neither the expected directly trapped product, $Me_3SiCH_2SiCl_2OMe$, nor the indirectly related side product, $MeSiCl_3$, was detected. It was assumed that in the course of the trapping experiment the dichlorosilene intermediate (**B**) reacts readily with gaseous HCl to give $MeSiCl_3$. However, even $MeSiCl_3$ was not detected in the reaction mixture. Despite the lack of both direct and indirect evidence for

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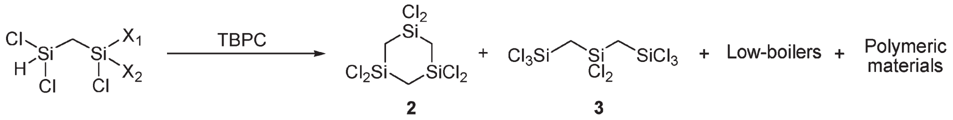
(19) (a) Berry, M. B.; Griffiths, R. J.; Sanganee, M. J.; Steel, P. G.; Whelligan, D. K. *Org. Biomol. Chem.* **2004**, *2*, 2381. (b) Brook, A. G.; Vorsphol, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

(20) Davidson, I. M. T.; Wood, I. T. *Chem. Commun.* **1982**, 550.

Scheme 7. TBPC-Catalyzed Reaction of Various Bissilylmethanes



		Unreacted starting material	**2**	**3**	Low-boilers	Polymeric materials
$X_1 = X_2 = Cl$	**1**	16 %	50 %	14 %	$HSiCl_3$ (7 %)	13 %
$X_1 = H, X_2 = Cl$	**7**	12 %	59 %	9 %	H_2SiCl_2 (9 %)	11 %
$X_1 = Me, X_2 = Cl$	**8**	40 %	37 %	8 %	$MeHSiCl_2$ (5 %)	10 %
$X_1 = X_2 = Me$	**9**	100 %		No Reaction		

the formation of dichlorosilene intermediate (**B**) in this series of trapping experiments, the formation of the cyclic-trimerized product, **2**, suggested the involvement of the dichlorosilene intermediate (**B**).

Finally, $HCl_2SiCH_2SiCl_3$ (**1**) was reacted in the presence of a catalytic amount (10 mol %) of TBPC without a trapping reagent at 180 °C for 3 h, yielding compound **2** as the major product and compound **3**, low-molecular weight silanes, and viscous polymeric materials obtained as minor products. As shown in Scheme 7, a series of bissilylmethane derivarives, $HCl_2SiCH_2SiX_1X_2Cl$ [$X_1 = H$, $X_2 = Cl$ (**7**); $X_1 = Me$, $X_2 = Cl$ (**8**); $X_1, X_2 = Me$ (**9**)] was attempted in place of compound **1** as a variation of the phosphine-catalyzed Si$-$C coupling reactions. A phosphine-catalyzed reaction involving compound **7** yielded compounds **2** and **3**, which was consistent with the result of compound **1**. However, compound **8** produced compounds **2** and **3** in lower yield when one chloride ion at the silicon atom of the bissilylmethane was replaced with one methyl group. Furthermore, compound **9** did not undergo a similar dehydrochlorinative reaction under the same reaction conditions when two methyl groups at the silicon atom were replaced with two chlorides. The differences in reactivity between bissilylmethanes **7**$-$**9** might be related to the electron -donating effect of the methyl groups at the silicon atom due to the difficulty of chloride ion migration to the phosphine cation.

Conclusions

This paper described the unexpected phosphine-catalyzed Si$-$C coupling reaction of compound **1** affording cyclic and linear carbosilanes, compounds **2** and **3**. The formation of compounds **2** and **3** suggested the concurrent generation of two silene intermediates, dichlorosilylene (**A**) and dichlorosilene (**B**). The isolation of cyclic and linear carbosilanes suggested the initial formation of [$Cl_2Si(\mu\text{-}CH_2)_2SiCl_2$] (**C**) from the head-to-tail dimerization of dichlorosilene (**B**). Either cyclic (**2**) or linear (**3**) carbosilane was produced depending on the second addition of the silene intermediates. From a series of Si$-$C coupling reactions with bissilylmethanes (**7**$-$**9**), there appeared to be a general substituent effect, where a chlorine substituent at the silicon atom was found to be most effective.

Experimental Section

General Comments. All reactions were carried out using flame-dried glassware or in a stainless steel bomb. All air-sensitive liquids were transferred using standard syringe or double-tipped needle techniques.[21] The bissilylmethanes were prepared using the same method reported in the literature.[10,13] The reaction mixtures were analyzed by GLC over a 1.5 m × 1/8 in. stainless steel column packed with packing materials (10% SE-30 or SE-54 on 80$-$100 mesh Chromosorb P/AW) using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a Varian 4290 integrator. The progress of the reactions was monitored by GLC at 30 min or 1 h time intervals. The samples for characterization were purified by preparative GLC using a Varian Aerograph series 1400 gas chromatograph with a thermal conductivity detector and a 4 m × 1/8 in. stainless steel column packed with 15% SE-30 or SE-54. The product yields were determined by isolation or GLC using *n*-dodecane as the internal standard. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 and 75.4 MHz, respectively. The chemical shifts are given in ppm relative to the residual proton signal of the solvent ($CDCl_3$ 7.25 ppm (^1H) and $CDCl_3$ 77.0 ppm (^{13}C)) and then referenced to Me_4Si (0.00 ppm). Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. High-resolution tandem mass spectrometry (Jeol LTD JMS-HX 110/110A) was performed at the Seoul Branch of the Korean Basic Science Institute. The GC/MS data were obtained using an Agilent 7000A Triple Quadrupole GC/MS system. The preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (50 kV × 30 mA) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The preliminary unit cell constants were determined using a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude noise. The frames collected were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.[22a] The final cell constants were determined from a global refinement of the *xyz* centroids of the reflections harvested from the entire data set. The structure solution and refinement were performed using the SHELXTL-PLUS software package.[22b]

Preparation of (Dichlorosilyl)(trichlorosilyl)methane (1).[10] A mixture of metallic silicon (360 g, 100$-$325 mesh) and 40 g of copper catalyst was placed in the reactor made from a Pyrex glass tube, 50 mm in internal diameter and 400 mm in length, and electrical heating wire coiled outside and equipped with a spiral band agitator. The mixture was dried at 300 °C for 5 h with stirring with a dry nitrogen flush. The temperature was then increased to 350 °C, and methyl chloride was introduced at 240 mL/min to activate the contact mixture for 4 h. After removing the products formed during the activation process, such as dichlorodimethylsilane and methyltrichlorosilane, 2.0 g of cadmium as a promoter was added to the reactor at room temperature. The temperature was then increased to 280 °C, and methylene chloride was introduced into the evaporator using a syringe pump attached to the bottom of the reactor at a rate of 13.6 g/h. At the same time, gaseous hydrogen chloride was

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(21) Shriver, D. F.; Drezdon, M. A. *Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(22) (a) *SMART and SAINT*; Bruker Analytical X-Ray Division: Madison, WI, 2002. (b) Sheldrick, G. M. *SHELXTL-PLUS Software Package*; Bruker Analytical X-Ray Division: Madison, WI, 2002.

introduced at a rate of 240 mL/min (mole ratio of dichloromethane:hydrogen chloride was 1:4). Approximately 2 min after starting the reaction, the reaction temperature increased slightly due to the exothermic nature of the reaction, and the liquid product was then collected in the receiver. After a 2 h reaction, 45.6 g of the products was collected in the receiver cooled to −20 °C and 46.4 g of low boilers were collected in a dry ice−acetone trap. Gas chromatography showed that the low boilers trapped contained a 20:1 mixture of trichlorosilane and tetrachlorosilane. The product (45.6 g) was distilled at atmospheric pressure to give 15.5 g of trichlorosilane, 1.3 g of tetrachlorosilane, and 0.5 g of methylene chloride. Distillation was continued under vacuum to give 10.1 g of (trichlorosilyl)(dichlorosilyl)methane, 8.7 g of compound **1**, and 2.0 g of bis(trichlorosilylmethane. The residue was distilled bulb to bulk to give 6.9 g of a mixture of high-boiling products but negligible quantities of nondistillable polymeric materials. GC-MS analysis of the high-boiling products showed that they contained linear and cyclic carbosilanes with silicon−hydrogen bonds, as reported previously.[7] Bis(dichlorosilylmethane): bp 146−147 °C; ^{1}H NMR (CDC1$_3$) δ 1.40 (t, 2H, C*H*$_2$); 5.71 (t, 2H, Si-*H*); ^{13}C NMR (CDC1$_3$) δ 14.42. **1**: bp 165−166 °C; ^{1}H NMR (CDCl$_3$) δ 1.64 (d, 2H, C*H*$_2$); 5.72 (t, 1H, Si-*H*); ^{13}C NMR (CDCl$_3$) δ 18.6. (Trichlorosilylmethyl)-trichlorosilane: bp 179−180 °C; ^{1}H NMR (CDCl$_3$) δ 1.88 (s, C*H*$_2$); ^{13}C NMR (CDCl$_3$) δ 22.5.

Reaction of (Dichlorosilyl)(trichlorosilyl)methane (1) with Benzyl Chloride in the Presence of TBPC. Compound **1** (7.5 g, 30 mmol), benzyl chloride (3.8 g, 30 mmol), and TBPC in 50% toluene (0.9 g, 3 mmol) were added to a 25 mL stainless steel tube under a dry nitrogen atmosphere. After sealing the tube with a cap, the reaction mixture was heated to 180 °C for 2 h. After cooling, the reaction mixture was transferred to a 100 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 140−142 °C/10 Torr to give the benzyl chloride (**4**) (21%) and at 170−180 °C/10 Torr to give a mixture of compounds 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (**2**) and 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane (**3**). A mixture of compounds **2** and **3** was dissolved in hexane and then recrystallized at 0 °C to isolate **2** as a white solid (47%) and **3** (16%) as a colorless liquid. Data for compound **2**: ^{1}H NMR (CDCl$_3$) δ 1.46 (s, 6H, Si-C*H*$_2$-Si); ^{13}C NMR δ 17.4. Data for compound **3**: ^{1}H NMR (CDCl$_3$) δ 1.71 (s, 4H, Si-C*H*$_2$-Si); ^{13}C NMR δ 20.3. Data for benzyltrichlorosilane: ^{1}H NMR (CDCl$_3$) δ 2.92 (s, 2H, Si-C*H*$_2$-C), 7.31 (m, 5H, Ar-*H*); ^{13}C NMR (CDCl$_3$) δ 32.9, 126.5, 128.8, 129.3, 132.0.

Reaction of (Dichlorosilyl)(trichlorosilyl)methane (1) with 2,3-Dimethylbutadiene in the Presence of TBPC. Compound **1** (7.5 g, 30 mol), 2,3-dimethylbutadiene (2.5 g, 30 mmol), and TBPC in 50% toluene (0.9 g, 3 mmol) was 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 to 180 °C for 3 h. The filtrates were separated by bulb-to-bulb vacuum distillation to give a mixture of compounds **2** and **3** (170−180 °C/10 Torr) and 1,1-dichloro-3,4-dimethylsilacyclopent-3-ene (**5**) (133 °C/10 Torr, 17%). The mixture of compounds **2** and **3** was dissolved in hexane and recrystallized at 0 °C to give compound **2** as a white solid (42%) and **5** as a colorless liquid (6%). Further vacuum distillation gave compounds **3** (6%) and **5** (17%). Data for compound **5**: ^{1}H NMR (CDCl$_3$) δ 1.75 (s, 6H, C*H*$_3$), 1.88 (d, 4H, C*H*$_2$); ^{13}C NMR (CDCl$_3$) δ 19.2, 29.6, 129.8.

Reaction of (Dichlorosilyl)(trichlorosilyl)methane (1) with Methylene Chloride in the Presence of TBPC. Compound **1** (12.4 g, 50 mol), methylene chloride (2.9 g, 26 mmol), and TBPC in 50% toluene (1.5 g, 5 mmol) was 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 to 180 °C for 3 h. After cooling, the reaction mixture was transferred to a 100 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 to give a mixture of compounds **2**, **3**, and bis(trichlorosilyl)methane (**6**) (170−180 °C/10 Torr). The mixture of compounds **2**, **3**, and bis(trichlorosilyl)methane was dissolved in hexane and recrystallized at 0 °C to give compound **2** as a white solid (54%) and a mixture of compounds **3** and bis(trichlorosilyl)methane as a colorless liquid. Further vacuum distillation gave compound **3** (8%) and bis(trichlorosilyl)methane (23%). Data for bis(trichlorosilyl)methane: ^{1}H NMR (CDCl$_3$) δ 1.86 (s, 2H, Si-C*H*$_2$-Si); ^{13}C NMR (CDCl$_3$) δ 22.4.

Reaction of (Dichlorosilyl)(trichlorosilyl)methane (1) in the Presence of TBPC. Compound **1** (500 g, 2 mol) and TBPC in 50% toluene (82.6 g, 0.2 mol) were added to a 10 L stainless steel autoclave under a dry nitrogen atmosphere. After sealing the tube with a cap, the reaction mixture was heated to 180 °C for 3 h. After cooling, the reaction mixture was transferred to a 2 L one-necked flask with a double-tipped needle. The mixture consisted of two layers of an organic phase and catalyst. The reaction mixture was separated from the catalyst by filtration. The filtrates were separated by bulb-to-bulb vacuum distillation to give a mixture of compounds **2** and **3** (64%, 170−180 °C/10 Torr). The mixture of compounds **2** and **3** was dissolved in hexane and recrystallized at 0 °C to give compounds **2** and **3** as a white solid (50%) and colorless liquid (14%), respectively.

Reaction of Bis(dichlorosilyl)methane (7) in the Presence of TBPC. The procedure was similar to that described for the reaction of (dichlorosilyl)(trichlorosilyl)methane (**1**) in the presence of TBPC. Bis(dichlorosilyl)methane (**7**) (6.8 g, 32 mmol) and TBPC in 50% toluene (0.9 g, 3 mmol) were added to a 25 mL stainless steel tube under a dry nitrogen atmosphere. After sealing the tube with a cap, the reaction mixture was heated to 180 °C for 3 h. The reaction mixture was cooled and separated from the catalyst by filtration. The filtrates were separated by bulb-to-bulb vacuum distillation to give a mixture of **2** and **3** (170−180 °C/10 Torr). The mixture compounds of **2** and **3** was dissolved in hexane and recrystallized at 0 °C to isolate **2** as a white solid (59%) and **3** as a colorless liquid (9%).

Reaction of (Methyldichlorosilyl)(dichlorosilyl)methane (8) in the Presence of TBPC. The procedure was similar to that described for the reaction of (dichlorosilyl)(trichlorosilyl)methane (**1**) in the presence of TBPC. (Methyldichlorosilyl)(dichlorosilyl)-methane (**8**) (7.3 g, 32 mmol) and TBPC in 50% toluene (0.9 g, 3 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 to 180 °C for 3 h. After cooling, the reaction mixture was separated from the catalyst by filtration. The filtrates were separated by bulb-to-bulb vacuum distillation to give a mixture of **2** and **3** (170−180 °C/10 Torr). The mixture compounds of **2** and **3** was dissolved in hexane and recrystallized at 0 °C to isolate **2** as a white solid (37%) and **3** as a colorless liquid (8%).

Reaction of (Dimethylchlorosilyl)(dichlorosilyl)methane (9) in the Presence of TBPC. The reaction procedure was similar to that described for the reaction of (dichlorosilyl)(trichlorosilyl)-methane (**1**) in the presence of TBPC. (Dimethylchlorosilyl)-(dichlorosilyl)methane (**9**) (6.6 g, 32 mmol) and TBPC in 50% toluene (0.9 g, 3 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 to 180 °C for 3 h. After cooling, the reaction mixture was separated from the catalyst by filtration. GC analysis showed that no reaction had occurred.

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Supporting Information Available: Tables and figure showing the X-ray crystallographic details for compound **2** and the spectroscopic data for the materials. This material is available free of charge via the Internet at http://pubs.acs.org.