Organometallics **1997,** *16,* 93−96

Direct Synthesis of Tris(chlorosilyl)methanes Containing Si−H Bonds

Joon Soo Han, Seung Ho Yeon, Bok Ryul Yoo, and Il Nam Jung*

Organometallic Chemistry Laboratory, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Received July 2, 1996[⊗]

Direct reaction of elemental silicon with a mixture of chloroform and hydrogen chloride has been studied in the presence of a copper catalyst using a stirred reactor equipped with a spiral band agitator at various temperatures from 280 to 340 °C. Tris(chlorosilyl)methanes **1a**−**e** with Si−H bonds were obtained as the major products along with byproducts of bis(chlorosilyl)methanes, derived from the reaction of silicon with methylene chloride formed by the decomposition of chloroform, and trichlorosilane and tetrachlorosilane produced from the reaction of elemental silicon with hydrogen chloride. The decomposition of chloroform was suppressed and the production of polymeric carbosilanes reduced by adding hydrogen chloride to chloroform. The deactivation problem of elemental silicon due to the decomposition of chloroform and polycarbosilanes was eliminated. Cadmium was a good promoter for the reaction, while zinc was found to be an inhibitor for this particular reaction.

Introduction

The direct reaction of elemental silicon with alkyl chlorides is an important synthetic method, being used on a large scale in the silicone industry.[1,2] Since Rochow and Patnode reported the direct synthesis of methylchlorosilane in 1945,[3] a vast number of reports on the direct reactions of elemental silicon with organic chlorides are available in the literature.[2] But reports on the direct reaction of polychlorinated alkanes such as methylene chloride and chloroform are scarce.[4,5] In 1958, the direct reaction of chloroform with elemental silicon in the presence of a copper catalyst was first reported by Müller and Seitz.[4] Later, Fritz and Matern studied the same reaction using a fluidized-bed reactor at about 320 °C.[6] The products obtained from the reaction with chloroform were branched compounds of formulas $(Cl_2XSi)_3CH$ ($X = H$ or Cl) and $Cl_3Si[(XCl_2Si)CH]_nSiCl_2Y$ ($Y = CH_2SiCl_2X$, $n = 1-2$) as well as cyclic carbosilanes of formula $[SiCl_2CH(SiCl_2Z)]_x$ ($Z = X$ or Y, $x = 3$) consisting of compounds containing from one silicon atom up to seven silicon atoms. The deactivation of elemental silicon and copper catalyst was the major problem due in part to the decomposition of the starting chloroform and in part to the high boiling polycarbosilanes produced. This is why this direct reaction has never been used on a large scale in industry.

$$CHCl_3 \xrightarrow{Si/Cu}$$

$$(Cl_2XSi)_3CH + Cl_3Si[(XCl_2Si)CH]_nSiCl_3Y +$$
$$X = H \text{ or } Cl \qquad Y = CH_2SiCl_2X,\ n = 1-3$$
$$[SiCl_2CH(SiCl_2Z)]_x + \text{others}$$
$$Z = X \text{ or } Y,\ x = 3$$

We have previously reported the direct synthesis of Si−H-containing bis(silyl)methanes,[7] allylchlorosilanes,[8] and bis(chlorosilyl)methane[9] by reacting elemental silicon with a mixture of hydrogen chloride and chlorinated organic compounds such as (α-chloromethyl)silanes, allyl chloride, and dichloromethane, respectively. In the reaction with methylene chloride Si−H-containing bis(chlorosilyl)methanes were obtained as the major products. The decomposition of methylene chloride was suppressed and the production of high boiling byproducts reduced by adding hydrogen chloride to the methylene chloride.

This success in the direct synthesis of bis(chlorosilyl)methanes prompted us to apply this hydrogen-chloride-incorporating method to the direct reaction of chloroform with elemental silicon. We studied the direct reaction of elemental silicon with a mixture of chloroform 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 280 and 340 °C. The decomposition of chloroform to hydrogen chloride was expected to be suppressed and the production of oligomeric and polymeric carbosilanes to be reduced by adding hydrogen chloride to the chloroform. The Si−H-containing tris(chlorosilyl)methanes obtained may be valuable new starting materials for industrial applications such as a silicon carbide precursor, ceramic binder, cross-linker, etc., because they easily undergo hydrosilylation with al-

---

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1996.

(1) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York and London, 1968.

(2) (a) Petrov, A. D.; Mironov, V. F.; Ponomarenko, V. A.; Chernyshev, 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., Eds.; *Catalyzed Direct Reactions of Silicon*; Elsevier: Amsterdam, 1993.

(3) (a) Rochow, E. G. U.S. 2,380,995; *Chem. Abstr.* **1945**, *39*, 4889. (b) Rochow, E. G.; Patnode, W. I. U.S. 2,380,996; *Chem. Abstr.* **1945**, *39*, 4889.

(4) Müller, R.; Seitz, G. *Chem. Ber.* **1958**, *91*, 22.

(5) Patnode, W. I; Schiessler, R. W. U.S. 2,381,000 and 2,381,002; *Chem. Abstr.* **1945**, *39*, 4888−9.

(6) Fritz, G.; Matern, E. *Carbosilanes*: *Synthesis and Reactions*; Springer-Verlag: New York, 1986.

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

(8) Yeon, S. H.; Lee, B. W.; Kim, S.-I.; Jung, I. N. *Organometallics* **1993**, *12*, 4887.

(9) Yeon, S. H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem.* **1996**, *516*, 91−95.

S0276-7333(96)00534-1 CCC: $14.00

Table 1. Amount and Distribution of Products from the Direct Reaction of Chloroform[a]

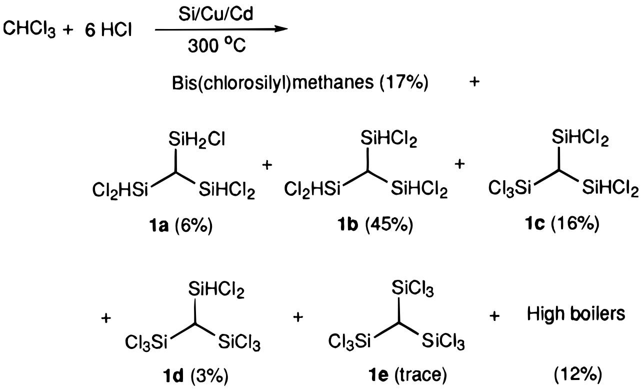
			tris(chlorosilyl)methanes						others	
				distribution,[d] %						
collcn[b] no.	unreacted $CHCl_3$, g	products,[c] g	wt %	**1a**	**1b**	**1c**	**1d**	**1e**	**2**,[e] wt %	high boilers, wt %
1–5		379	71	9	64	23	4	a trace	17	12
6–8	a trace	211	66	5	52	35	7	1	22	12
9–10	7	118	64	4	47	36	10	3	23	13

[a] Feeding rate of $CHCl_3$ = 11.4 g/h. Reaction temperature = 300 °C. Catalyst/cocatalyst = Cu (10%)/Cd (0.5%). Mole ration of $CHCl_3$/HCl = 1/6. [b] Product mixtures reveived at every 4 h were weighed and analyzed by GLC. [c] 98 g, 66 g, and 40 g of $HSiCl_3$ and $SiCl_4$, distilled from nos. 1–5, 6–8, and 9–10, respectively, are excluded for simplicity. [d] GLC area percentage. [e] 2 = bis(chlorosilyl)methanes.

kenes and alkynes and react with organometallic reagents, alcohols and amines to afford new useful organosilicon compounds in which Si–C, Si–O, and Si–N bonds are formed. We report here the results obtained in our study of the direct reaction of elemental silicon with a mixture of chloroform and hydrogen chloride.

Results and Discussion

(a) Effect of Hydrogen Chloride Addition to Chloroform. A 1:6 mixture of chloroform and hydrogen chloride was reacted with a contact mixture of elemental silicon and copper catalyst using a stirred reactor equipped with a spiral band agitator at flow rate of 11.4 g/h of chloroform at 300 °C for 40 h. Product mixtures were collected and analyzed by GLC at every 4 h. The reaction was stopped after 40 h, as the starting chloroform was recovered in about 9% yield. Product mixtures were distilled into three fractions, low boiling products of (trichlorosilane and tetrachlorosilane), bis(chlorosilyl)methanes **2**, and tris(chlorosilyl)methanes **1**. The composition of each fraction was determined by GLC. The products were purified by preparative GLC, and subsequent spectral analysis led to the assignment of the structure for five tris(chlorosilyl)methanes as 2-(chlorosilyl)-1,1,3,3-tetrachloro-1,3-disilapropane (**1a**), 2-(dichlorosilyl)-1,1,3,3-tetrachloro-1,3-disilapropane (**1b**), 2-(dichlorosilyl)-1,1,1,3,3-pentachloro-1,3-disilapropane (**1c**), 2-(dichlorosilyl)-1,1,1,3,3,3-hexachloro-1,3-disilapropane (**1d**), and all chlorinated 2-(trichlorosilyl)-1,1,1,3,3,3-hexachloro-1,3-disilapropane (**1e**). That the major products are Si–H-containing tris(chlorosilyl)methanes suggests that the reactivities of chloroform and hydrogen chloride are comparable. The minor products of **2** are the same as those obtained in the direct reaction of silicon with a mixture of methylene chloride and hydrogen chloride,[9] indicating that some of the starting chloroform decomposed to methylene chloride during the reaction. Trichlorosilane and tetrachlorosilane are known to be the products of the reaction of silicon with hydrogen chloride.[7]



The amount and compositions of products collected from the direct reaction of chloroform carried out under various reaction conditions are summarized in Table 1.

In Table 1, trichlorosilane and tetrachlorosilane distilled from the product mixture were excluded for simplicity. The formation of **1b**,**e** can be explained by the reaction of 1 chloroform molecule with 3 silicon atoms and 3 of hydrogen chlorides or 3 silicon atoms and 3 of chlorines, respectively.[3] Similarly, **1c**,**d** can be formed by the reaction of 1 chloroform molecule with 3 silicon atoms, 2 of hydrogen chlorides and 1 chlorine, or 3 silicon atoms, 1 hydrogen chloride, and 2 chlorines, respectively.

The production of **1a**–**e** decreased from 71% in the collection nos. 1–5 to 64% in the collection nos. 9 and 10, while that of **2** slightly increased from 17% to 23%. Among **1a**–**e** the composition of the products with higher chlorine content increased as the reaction proceeded. These results are consistent with the results reported in the literature[3,10] that the selectivity for dichlorosilyl group containing compounds decreases slightly and that of higher chlorinated compounds increases as silicon is consumed and the content of copper catalyst becomes higher. Although 9% of the starting chloroform was recovered in the last collection, the selectivity for **1** was still retained at a high level in the product mixture suggesting that the reactivity remained about the same but that the contact time of the chloroform with silicon was not long enough. In contrast to the direct reaction of chloroform without the addition of hydrogen chloride,[4] the production of polymeric carbosilanes was negligible. The formation of **1d**,**e** also was reported in the reaction of elemental silicon with chloroform without hydrogen chloride addition, indicating the conversion of chloroform to hydrogen chloride and chlorine at the reaction temperature.[4] In the direct reaction, Lewis acids such as aluminum chloride and zinc chloride can be formed by the reaction of hydrogen chloride with metal impurities such as aluminum, zinc, titanium, etc. inevitably present in the elemental silicon metal.[11,14] It is well-known that the hydrogen–chlorine exchange reaction between Si–H

---

(10) (a) Kolster, B. H.; Vlutger, J. C.; Voorhoeve, R. J. H. *Rec. Trav. Chim.* **1964**, *83*, 737. (b) Frank, T. C.; Kester, K. B.; Falconer, J. L. *J. Catal.* **1985**, *91*, 44.

(11) Doyle, M. P.; Mcosker, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.

(12) Emeleus, H. J.; Maddock, A. G. *J. Chem. Soc.* **1944,** 293.

(13) (a) Jenkins, J. W.; Post, W. *J. Org. Chem.* **1950**, *15*, 556. (b) Gilman, H.; Miles, D. H.; Moore, L. O.; Gerow, C. W. *J. Org. Chem.* **1959**, *24*, 219.

(14) (a) Moedritzer, K. *J. Organomet. Chem.* **1968**, *12*, 69. (b) Weyenberg, D.; Bey, A. P. *J. Organomet. Chem.* **1965**, *3*, 489.

Table 2. Reaction Temperature Effect on the Direct Reaction of Chloroform[a]

			tris(chlorosilyl)methanes						others	
				distribution,[c] %						
expt entry no.	reacn temp, °C	products,[b] g	wt %	**1a**	**1b**	**1c**	**1d**	**1e**	**2**,[d] wt %	high boilers, wt %
2	280	47	65	12	59	24	5	1	22	13
3	300	45	70	11	63	21	5	1	18	12
4	320	43	68	11	56	26	6	2	20	12
5	340	38	66	9	54	28	7	2	21	13

[a] Chloroform, 22.8 g was used during 2 h. Catalyst/cocatalyst = Cu (10%)/Cd (0.5%). Mole ratio of $CHCl_3/HCl$ = 1/6. [b] Byproducts, $HSiCl_3$ and $SiCl_4$, are excluded for simplicity. [c] GLC area percentage. [d] **2** = bis(chlorosilyl)methanes.

Table 3. Effect of the Catalyst and Cocatalyst on the Direct Reaction of Chloroform[a]

				tris(chlorosilyl)methanes						others	
					distribution,c %						
expt entry no.	catal/cocatal	unreacted $CHCl_3$, g	products,[b] g	wt %	**1a**	**1b**	**1c**	**1d**	**1e**	**2**,[d] wt %	high boilers, wt %
6	Cu		42	66	7	51	31	9	2	21	13
3	Cu/Cd		45	70	11	63	21	5	1	18	12
7	Cu/Zn	5	17	33	2	18	36	30	14	52	15

[a] Chloroform, 22.8 g, was used during 2 h. Reaction temperature = 300 °C. Mole ratio of $CHCl_3/HCl$ = 1/6. [b] Byproducts, $HSiCl_3$ and $SiCl_4$, are excluded for simplicity. [c] GLC area percentage. [d] **2** = bis(chlorosilyl)methanes.

of silane and C−Cl of alkyl chloride occurs easily in the presence of a Lewis acid.[11,14] This exchange reaction might be responsible for the formation of methylene chloride which then reacted with elemental silicon to give **2**.

To test if **1** decomposes to **2** under the direct reaction conditions, the same reaction was carried out by using tris(dichlorosilyl)methanes, **1a** (1.5%), **1b** (98.3%), and **1c** (0.2%), instead of chloroform. The composition of recovered tris(dichlorosilyl)methanes included **1a** (1.1%), **1b** (96.2%), **1c** (2.0%), and **1d** (0.7%), and no other products were detected in appreciable amounts. This result indicates that **2** was not derived from the decomposition of **1** during the reaction but that it was formed in the reaction with methylene chloride derived from the chloroform. The Si−H content of **1** slightly decreased to about 2%, indicating that the conversion of Si−H to Si−Cl by the attack of hydrogen chloride[12] or chlorine[13] during the reaction was not significant.

(b) Effect of Reaction Temperature. The same reaction was carried out with a 1:6 mixture of chloroform and hydrogen chloride at the reaction temperatures from 280 up to 340 °C for 2 h. The total amount and the composition of products are summarized in Table 2. As shown in Table 2, the amount of the products decreased slightly as the reaction temperature increased from 280 to 340 °C. The selectivity for **1b** was the highest at 300 °C and decreased slightly at temperatures below or above 300 °C. The production of **2** increased as the temperature increased from 300 to 340 °C, probably due to the higher decomposition rate of chloroform to methylene chloride at higher temperature.[10b] The reaction temperature of 300 °C is considerably lower than that used for monochlorinated methanes such as methyl chloride[2,16] and (α-chloromethyl)silanes,[7,17] indicating the higher reactivity of chloroform compared with those of monochlorinated organic compounds. The reaction even proceeded at a temperature as low as 240 °C, but the production percentage of **1** and the selectivity for **1b** decreased as the temperature decreased below 280 °C. This lower selectivity may be attributed to the inefficient removal of the high boiling products.

(c) Promoters. Useful copper catalysts for the reaction of alkyl chloride with silicon include copper metal, copper salts, and partially oxidized copper.[2] In addition to copper catalyst, a number of metals such as zinc, aluminum, tin, magnesium, etc. are known to be promoters.[10b,18] These normally are incorporated in quantities smaller than 1%. Zinc is known as one of the most effective promoters for the direct synthesis of methylchlorosilanes.[18d] Cadmium is known as one of the most effective promoters for the direct synthesis of bis(chlorosilyl)methanes[8,9] and trisilaalkanes.[17] The product distributions from the direct reaction of chloroform in the presence of different promoters are given in Table 3.

As shown in Table 3, the amount of product (the percentage of **1** inthe product mixtures) varied, 42 g (66%), 45 g (70%), and 17 g (33%), with no promoter, cadmium, and zinc, respectively. The yield of product and the selectivity for **1** in the direct reaction with cadmium as cocatalyst were drastically improved, while a greater amount of chloroform was recovered in the reaction with zinc promoter. This indicates that zinc is not a promoter but an inhibitor and that cadmium is a good promoter for this reaction. This is consistent with the results observed in the direct reactions of silicon with (α-chloromethyl)silanes, allyl chloride, and methylene chloride.[7−9]

(d) Mixing Ratio of the Reactants. The amounts and distributions of products obtained from the direct reaction using various mixing ratios of hydrogen chloride/chloroform ranging from 4.5 to 9 in the presence of copper catalyst/cadmium cocatalyst at 300 °C for 2 h are given in Table 4.

In order to produce compound **1b**, 3 mol of hydrogen chloride should be available for each 1 mol of chloroform. Considering that trichlorosilane is produced from the

---

(15) (a) Dolgov, B. N.; Borisov, S. N.; Voronkov, M. G. *Russ. J. Gen. Chem.* **1957**, *27*, 789. (b) Kanner, B.; Lewis, K. M. U.S. 4,599,441; *Chem. Abstr.* **1986**, *105*, 115201v. (c) Whitmore, F. C.; Pietrusza, E. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1947**, *69*, 2108.

(16) (a) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963. (b) Rochow, E. G. U.S. 2,380,995; *Chem. Abstr.* **1945**, *39*, 4889.

(17) (a) Jung, I. N.; Lee, G.-H.; Yeon, S. H.; Suk, M.-Y. *Bull. Kor. Chem. Soc.* **1991**, *12*, 445. (b) Jung, I. N.; Lee, G.-H.; Yeon, S. H.; Suk, M.-Y. U.S. 5,075,477; *Chem. Abstr.* **1992**, *116*, 174424v.

(18) (a) Banholzer, W. F.; Burrell, M. C. *J. Catal.* **1988**, *114*, 259. (b) Banholzer, W. F.; Lewis, N.; Ward, W. J. *J. Catal.* **1986**, *101*, 405. (c) Ward, W. J.; Ritzer, A. L.; Carrol, K. M.; Flock, J. W. *J. Catal.* **1986**, *100*, 240. (d) Bluestein, B. A. *J. Am. Chem. Soc.* **1948**, *70*, 3068.

Table 4. Effect of Mixing Ratio of the Reactants[a]

			tris(chlorosilyl)methanes						others	
				distribution,[c] %						
expt entry no.	mole ratio $CHCl_3$:HCl	products,[b] g	wt %	**1a**	**1b**	**1c**	**1d**	**1e**	**2**,[d] wt %	high boilers, wt %
8	1:4.5	40	68	7	57	27	7	2	19	13
3	1:6	45	70	11	63	21	5	1	18	12
9	1:9	47	70	9	65	20	5	1	18	12

[a] Chloroform, 22.8 g, was used during 2 h. Catalyst/cocatalyst = Cu (10%)/Cd (0.5%). Reaction temperature = 30 °C. [b] Byproducts, $HSiCl_3$ and $SiCl_4$, are excluded for simplicity. [c] GLC area percentage. [d] 2 = bis(chlorosilyl)methanes.

reaction of hydrogen chloride with silicon, the required mixing ratio of chloroform to hydrogen chloride for this reaction was 1:3 at the minimum to prevent the polycarbosilanes production. As shown in Table 4, the total amount of products increased with an increase from 1:4.5 to 1:9 of the chloroform to hydrogen chloride ratio. When the mixing ratio of hydrogen chloride to chloroform was increased from 4.5:1 up to 6:1, the yield of **1a**−**e** and selectivity for **1b** increased, indicating that the decomposition of chloroform to hydrogen chloride and chlorine was suppressed under these reaction conditions as shown in other systems.[7−9] However, similar results were obtained by changing from a 6:1 to a 9:1 ratio, suggesting that the optimum mixing ratio of hydrogen chloride to chloroform in the direct synthesis of chloroform from an industrial point of view is 6:1.

Experimental Section

Reagents and Physical Measurements. Chloroform was purchased from J. T. Baker Inc. and washed twice with a sufficient amount of water to remove ethyl alcohol added as a stabilizer and then dried over calcium chloride with reflux for 2 h under dry nitrogen and distilled before use. Anhydrous hydrogen chloride was purchased from Matheson Co. and used without further purification. Copper powder was purchased from Alcan Metal Powders (Elizabeth, NJ), and cadmium and zinc were 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). Reaction products were analyzed by analytical GLC over a 1.5 m by $^1/_8$ in. o.d. stainless steel column packed with packing material (10% OV-101 on Chromosorb W) using a Varian 3300 gas chromatograph, equipped with a thermal conductivity detector. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer or a Varian Unity plus 600 spectrometer using $CDCl_3$ (taken as δ 7.27) as the internal lock. Mass spectra were obtained from Hewlett Packard 5890 Series II gas chromatograph equipped with Model 5972 mass selective detector. High-resolution mass spectra (HRMS) of **1a**,**b** were obtained at the Korea Basic Science Institute on a VG70-VSEQ mass spectrometer at an ionizing voltage of 70 eV.

Reactor. The reactor for the direct synthesis of tris(chlorosilyl)methanes was same as described elsewhere.[7]

General Procedure for the Direct Reaction of Chloroform. A mixture of 360 g of metallic silicon (100−325 mesh) and 40.0 g of copper catalyst was placed in a Pyrex glass tub reactor, 50 mm inner diameter and 400 mm length, with an electrical heating wire coiled outside and equipped with a spiral band agitator. The mixture was dried at 300 °C for 5 h with stirring while a dry nitrogen flush was maintained. Then the temperature was raised to 350 °C and methyl chloride was introduced at the rate of 240 mL/min to activate the contact mixture for 4 h. After removal of products formed (such as dichlorodimethylsilane and methyltrichlorosilane) during the activation process, 2.00 g of cadmium was added to the reactor as a promoter at room temperature. After the temperature was raised to 300 °C, chloroform was introduced, using a syringe pump, into the evaporator attached at the bottom of the reactor at the rate of 11.4 g/h. At the same time gaseous hydrogen chloride was introduced at the rate of 302 mL/min (mol ratio of chloroform/hydrogen chloride is 1:6). About 2 min after the reaction was started, it was observed that the reaction temperature was raised slightly due to the exothermic nature of the reaction, and then liquid product was collected in the receiver.

After 40 h of reaction, 919 g of the products, collected in the receiver cooled to −20 °C, was distilled at atmospheric pressure to give 185 g of trichlorosilane, 19 g of tetrachlorosilane, and 7 g of chloroform. The distillation was continued under vacuum to give bis(chlorosilyl)methanes, 148 g, and tris(chlorosilyl)methanes, 475 g. The residue was bulb to bulb distilled to give 85 g of a mixture of high boiling products. The amount of nondistillable polymeric materials was negligible. GC/mass spectroscopic analysis of the high boiling products showed that they contained linear and cyclic carbosilanes with silicon−hydrogen bonds as reported previously.[4,6]

Data for bis(dichlorosilyl)(chlorosilyl)methane (**1a**): ^{1}H NMR ($CDCl_3$) δ 1.38 (tt, $J = 1.3$, 2.6 Hz, 1H, CH), 5.07 (d, $J = 2.6$ Hz, 2H, SiH_2), 5.84 (d, $J = 1.3$ Hz, 2H, SiH); ^{13}C NMR ($CDCl_3$) δ 15.0 (CH); HRMS (EI) calcd for $CH_4Cl_5Si_3$ (M − H) *m/e* 274.8064, found *m/e* 274.8062. Data for tris(dichlorosilyl)methane (**1b**): ^{1}H NMR ($CDCl_3$) δ 1.52 (q, $J = 1.4$ Hz, 1H, CH), 5.77 (d, $J = 1.4$ Hz, 3H, SiH); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH); HRMS caclcd for $CH_3Cl_6Si_3$ (M − H) *m/e* 308.7674, found *m/e* 308.7669. Data for bis(dichlorosilyl)(trichlorosilyl)methane[4] (**1c**): ^{1}H NMR ($CDCl_3$) δ 1.77 (t, $J = 0.7$ Hz, 1H, CH), 5.79 (d, $J = 0.7$ Hz, 2H, SiH); ^{13}C NMR ($CDCl_3$) δ 25.4 (CH). Data for bis(trichlorosilyl)(dichlorosilyl)methane[4] (**1d**): ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 1H, CH), 5.83 (s, 1H, SiH); ^{13}C NMR ($CDCl_3$) δ 29.4 (CH). Data for tris(trichlorosilyl)methane[4] (**1e**): ^{1}H NMR ($CDCl_3$) δ 2.83 (s, CH); ^{13}C NMR ($CDCl_3$) δ 33.0 (CH).

Using the same procedure as above, reactions were carried out with different promoters such as cadmium or zinc, varying the mixing ratio of hydrogen chloride to chloroform ranging from 4.5 to 9 and varying reaction temperatures from 280 °C to 340 °C to optimize the reaction conditions for the direct synthesis of Si−H-containing tris(chlorosilyl)methanes.

Acknowledgment. We are grateful for the financial support of this work by the Ministry of Science and Technology.

OM9605342