2360 *Organometallics* **1993,** *12,* 2360–2362

Direct Synthesis of Bis(silyl)methanes Containing Si–H Bonds

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

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

Received December 1, 1992

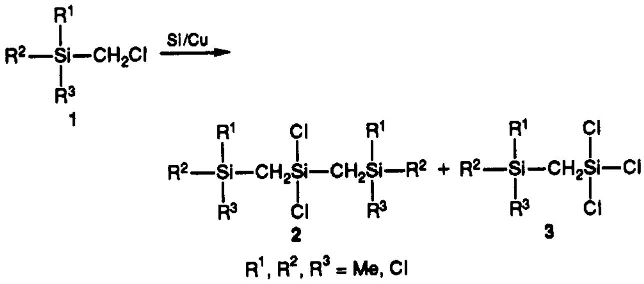
Summary: A series of Si–H-containing bis(silyl)methanes has been prepared by reacting directly elemental silicon simultaneously with (chloromethyl)silanes and hydrogen chloride in the presence of a copper catalyst using a stirred reactor equipped with a spiral band agitator at carefully controlled temperatures between 280 and 340 °C. Bis(silyl)methanes containing dichlorosilyl groups were obtained as the major products and trichlorosilyl-group-containing bis(silyl)methanes as minor products. Cadmium was a good promoter for the reaction, while zinc was found to be an inhibitor.

Organochlorosilanes with Si–H bonds are very useful starting materials for silicones, because they undergo hydrosilylation[1] and Si–H/C–Cl exchange reactions[2] with unsaturated organic compounds to give organosilicon compounds with various functional groups such as vinyl or phenyl. Methyldichlorosilane is obtained in about 3–5% yield as a byproduct in the direct reaction of elemental silicon with methyl chloride.[3] The yield was increased up to 9.5% by adding 15% of hydrogen chloride to methyl chloride in the direct synthesis of methylchlorosilanes.[4] Although the presence of hydrogen chloride in the synthesis of methylchlorosilanes with methyl chloride appears to increase the content of methyldichlorosilane, larger amounts of hydrogen chloride favor the formation of methyltrichlorosilane and trichlorosilane.[3] To our knowledge, no other direct reaction of the mixed gases incorporating hydrogen chloride with silicon has been successful in the preparation of Si–H-containing organochlorosilanes.

$$\mathrm{Si} + \mathrm{CH_3Cl} \rightarrow (\mathrm{CH_3})_2\mathrm{SiCl_2} + \mathrm{CH_3HSiCl_2}\ (3\text{–}5\%) + \text{others}$$

We have been studying the direct synthesis of trisilaalkanes by reaction of (chloromethyl)silanes **1** with elemental silicon.[5] Trisilaalkanes **2** were obtained as the major products and bis(silyl)methanes **3** were minor products.

We report herein the preparation of Si–H-containing bis(silyl)methanes by directly reacting elemental silicon simultaneously with **1** and hydrogen chloride.



Results and Discussion

Reactor. The direct synthesis is the most widely used industrial method for the preparation of methylchlorosilanes.[2] The direct process can be carried out either in fixed-bed,[6] stirred-bed,[7] or fluidized-bed[8] reactors. The process with the stirred-bed reactors has advantages over the fixed-bed operation in that the heat of reaction can be removed more easily and the movement of the powders causes fresh surface to be continuously exposed.[9] The metal powder was agitated in an up-and-down motion in a vertical reactor by means of a spiral band rotated by a central shaft while a stream of methyl chloride was passed upward through it.[10]

As the reaction rate and the composition of the products in the direct process are known to be highly temperature-dependent,[11] it is very important to maintain the reaction temperature at an accurately specified temperature and to prevent any hot spots from developing in the agglomerates of the solid phase. It is reported that at higher temperatures the deposition of carbon on the surface of the metal mixture occurs, which decreases the reactivity and the selectivity as well.[11] This is why the reactor for the direct synthesis of organochlorosilane must have a high thermal stability and an efficient heat transfer. The diagram of the stirred-bed reactor, equipped with a spiral band agitator used for the direct synthesis of bis(silyl)methanes containing Si–H bonds, is shown in Figure 1.

Reaction Temperature. A 1:3 mixture of (chloromethyl)dimethylchlorosilane (**1b**) and hydrogen chloride was reacted with the contact mixture[12] of elemental silicon and copper catalyst, and the product distributions at various reaction temperatures are shown in Table I. As

---

[1] Lukevits, E. Y.; Voronkov, M. G. *Organic Insertion Reactions of Group IV Elements*; Consultants Bureau: New York, 1966.

[2] Petrov, A. D.; Mironov, B. E.; Ponomarenko, V. A.; Chernyshev, E. A. *Synthesis of Organosilicon Monomers*; Consultants Bureau: New York, 1964.

[3] Voorhoeve, R. J. H. *Organohalosilanes: Precursors to Silicones*; Elsevier: New York, 1967.

[4] Halm, R. L.; Zapp, R. H. U.S. Patent 4,966,986; *Chem. Abstr.* **1991,** *114,* 102385u.

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

[6] Voorhoeve, R. J.; Vulugter, J. C. *Recl. Trav. Chim. Pays-Bas* **1963,** *82,* 605.

[7] Koklik, J.; Bažant, V. *Collect. Czech. Chem. Commun.* **1961,** *26,* 417.

[8] Reed, C. E.; Coe, J. T. U.S. Patent 2,389,931; *Chem. Abstr.* **1946,** *40,* 1536.

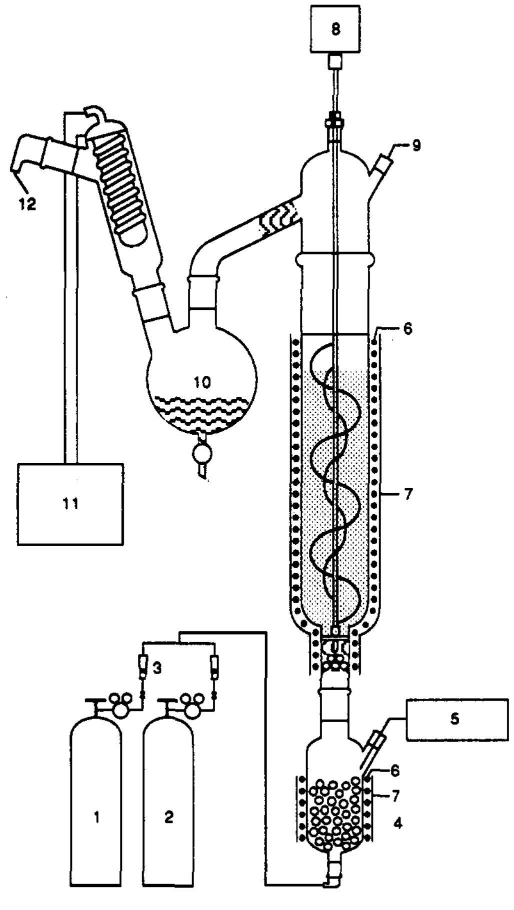
[9] Grohm, H.; Paudert, R. *Chem. Tech.* (*Leipzig*) **1951,** *10,* 307.

[10] Sheller, J. E.; Davis, J. L. U.S. Patent 2,449,821; *Chem. Abstr.* **1949,** *43,* 10516.

[11] Klebamskii, A. L.; Fikhtengolts, V. S. *J. Gen. Chem. U.S.S.R. USSR* (*Engl. Transl.*) **1957,** *27,* 2693.

[12] Voorhoeve, R. J.; Vulugter, J. C. *J. Catal.* **1965,** *4,* 123.

0276-7333/93/2312-2360$04.00/0



1. Hydrogen Chloride
2. Nitrogen
3. Flowmeter
4. Preheater
5. Syringe Pump
6. Heating Wire
7. Insulation Jacket
8. Stirring Motor
9. Metal Inlet
10. Receiver
11. Cooler
12. Vent

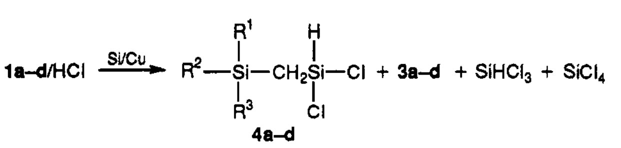
Figure 1. Reactor for the direct synthesis of bis(silyl)methanes.

Table I. Effects of Reaction Temperature on the Direct Synthesis[a]

expt no.	reacn temp (°C)	amt of products (g)	composition of products (%)			
			1b	**3b**	**4b**	others
1	280	308.0	19.0	12.5	46.9	21.6
2	300	314.6	6.3	14.5	55.3	23.9
3	320	333.9	8.8	14.4	58.5	18.3
4	340	315.9	4.8	20.5	48.8	25.9

[a] 234.8 g of the starting silane was used for 6-h reaction.

Scheme I


$$\mathbf{1a\text{–}d}/\mathrm{HCl} \xrightarrow{\mathrm{Si/Cu}} \mathrm{R^2{-}\overset{R^1}{\underset{R^3}{Si}}{-}CH_2\overset{H}{\underset{Cl}{Si}}{-}Cl} + \mathbf{3a\text{–}d} + \mathrm{SiHCl_3} + \mathrm{SiCl_4}$$

4a–d

$R^1 = R^2 = R^3 = CH_3$: **1a**,**4a** (44.3%), **3a** (15.8%)
$R^1 = R^2 = CH_3$, $R^3 = Cl$: **1b**,**4b** (58.5%), **3b** (14.4%)
$R^1 = CH_3$, $R^2 = R^3 = Cl$: **1c**,**4c** (41.4%), **3c** (19.2%)
$R^1 = R^2 = R^3 = Cl$: **1d**,**4d** (45.4%), **3d** (19.0)

shown in Table I, 19% of the starting compound was recovered when the reaction temperature was 280 °C, while the recovery was significantly lower at temperatures above 300 °C. 1,1,3-Trichloro-3-methyl-1,3-disilabutane (**4b**) was obtained as the major product, and the yield was around 50% for all four cases. 1,1,1,3-Tetrachloro-1,3-disilabutane (**3b**) was obtained as a minor product. The yield of **3b** was around 14% at reaction temperatures below 320 °C but increased to 20.5% at 340 °C, indicating higher decomposition of the starting compound. The major product was presumably derived from the reaction in which 1 mol of each of the reacting gases reacted simultaneously with the same silicon atom. Considering that **3b** was the minor product from the reaction of elemental silicon with **1b**,[5] its formation might well be explained by the reaction of a silicon atom with 1 mol of **1b** followed by chlorine abstraction reactions. In order to test this mechanism, the same reaction was carried out using 1,2-dichloroethane instead of hydrogen chloride, a higher yield of **3b** being expected because of the ease of dechlorination of 1,2-dichloroethane.[13] The mechanism was confirmed by the fact that **3b** was obtained as the major product from the reaction.

Besides the products **3b** and **4b**, several other minor byproducts were also obtained. The byproducts were identified as trichlorosilane (8.7%), tetrachlorosilane (3.0%), 2,4,4,6-tetrachloro-2,4,6-trisilaheptane (3.1%; **2b**), and 2,4,4,5,5,7-hexachloro-2,7-dimethyl-2,4,5,7-tetrasilaoctane (0.3%). The first two compounds are known to be products of the reaction of hydrogen chloride and silicon,[17] and the last two byproducts are also reported to be products derived from the reaction of **1b** with silicon.[5] The production ratio of trichlorosilane and tetrachlorosilane was about 3:1, which would be normally obtained from the direct reaction of silicon with hydrogen chloride.[14] A lower yield of trichlorosilane would be expected if trichlorosilane coupled with **1b** to give **3b**. This result suggests that **3b** was not derived from the coupling reaction.

The reaction was extended to other (chloromethyl)silanes (**1a**,**c**,**d**), and the results are shown in Scheme I. As shown in Scheme I, the selectivity for **4** was higher than 40% for all four cases and was the highest for **1b** and the lowest for **1c**. The selectivities for **4** are much higher than the ~10% for the methyldichlorosilane produced in the similar reaction of silicon with a mixture of methyl chloride and hydrogen chloride.[4] This indicates that the reactivity of **1** with silicon is greater than that of methyl chloride and close to that of hydrogen chloride.

Catalyst and Cocatalyst. Useful copper catalysts for the reaction of alkyl chlorides with silicon include copper metal, copper salts, and partially oxidized copper.[3] In addition to the copper catalyst, a number of metals such as zinc, aluminum, and magnesium are known promoters. Zinc is known as one of the most effective cocatalysts for the direct synthesis of methylchlorosilanes.[15] Cadmium is also known as one of the best promoters for the direct synthesis of trisilaalkanes.[5] For these reasons zinc and cadmium were selected and tested as cocatalysts. The promoters are normally incorporated in smaller quantities of less than 1%. The product distributions from the reaction of **1b** with elemental silicon in the presence of different cocatalysts are shown in Table II.

As shown in Table II, the yields of compound **4b** were 33.0%, 15.5%, and 58.5% with no promoter, zinc, and cadmium, respectively. It is also interesting to note that the recoveries of **1b** and contents of trichlorosilane and

---

(13) Patnode, W. I.; Scheisler, R. W. U.S. Patent 2,381,000; *Chem. Abstr.* **1945**, *39*, 4889.

(14) (a) Friedel, C.; Ladenburg, A. *Justus Liebigs Ann. Chem.* **1867**, *143*, 118. (b) Combes, C. *C.R. Hebd. Seances Acad. Sci.* **1896**, *122*, 531. (c) Stock, A.; Zeidler, L. *Ber. Dtsch. Chem. Ges.* **1923**, *56B*, 986.

(15) Bluestein, B. A. *J. Am. Chem. Soc.* **1948**, *70*, 3068.

Table II. Effect of the Catalyst and Cocatalyst on the Direct Synthesis[a]

expt no.	cat./cocat.	amt of products (g)	composition of products (%)			
			1b	**3b**	**4b**	others
5	Cu	308.4	14.8	26.9	33.0	25.3
6	Cu/Zn	358.7	31.6	8.9	15.5	44.0
3	Cu/Cd	333.9	8.8	14.4	58.5	18.3

[a] 234.8 g of the starting silane was used for 6-h reaction at 320 °C.

tetrachlorosilane are much higher when zinc is used. This indicates that zinc is not a promoter but an inhibitor for this reaction. This is consistent with the results observed for the direct reaction of 1 with silicon in the absence of hydrogen chloride.[5] It was also found that the amount of total products and 4 increased as the hydrogen chloride content increased, while the amount of the other products decreased. On the other hand, the yield of 3 decreased as the hydrogen chloride content increased. This result rules out the secondary reaction of 4 with hydrogen chloride to give 3 and hydrogen.

Experimental Section

Organosilicon reagents were purchased from Hüls America Inc. and used without further purification. Hydrogen chloride was purchased from Matheson Co. Copper powder was purchased from Alcan Metal Powders (NJ). Cadmium powder was purchased from Aldrich Chemical Co. Silicon metal (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). Analytical GLC was performed on a Varian 3300 gas chromatograph equipped with a TCD and a $^1/_8$ in. × 0.5 m packed column (5% OV-101 on Chromosorb W). NMR spectra were recorded on a Varian Gemini 300 spectrometer using $CDCl_3$ as the internal lock. High-resolution mass spectra were obtained on a VG 70-SEQ spectrometer.

Reactor and Preparations of Contact Mixtures. The reactor was made of Pyrex glass, 50 mm inner diameter and 400 mm length, with an electrical heating wire coiled outside the reactor. A spiral band agitator was made of $^1/_4$ in. stainless steel tube which was doubly coiled with a 4-mm stainless steel tube. Reaction temperatures were measured with a thermocouple (type K) which was placed inside the stirrer rod through the hole in the stirrer motor. Gas flow rates were controlled by a Matheson 603 flow meter. To collect the products, coolant (−23 °C) was circulated to the condenser. A mixture 360 g of elemental silicon (100–325 mesh) and 40.0 g of copper was placed in the reactor, and the mixture was dried at 300 °C for 5 h with a dry nitrogen flush. At this point, 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 2.00 g of cadmium powder was added at 30 °C, the inside temperature of the contact mixture was controlled to 320 °C.

General Procedure for the Direct Reaction of 1a–d. The reacting chloromethylsilane was introduced to the evaporator attached at the bottom of the reactor at the rate of 36 mL/h by a syringe pump. The nitrogen flow rate was controlled to 240 mL/min, and the hydrogen chloride flow rate was controlled to 290 (for **1a**), 296 (for **1b**), 315 (for **1c**), and 319 mL/min (for **1d**). About 5 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 the liquid product was collected in the receiver. The product was drained at 1- or 2-h periods and analyzed for the composition by the gas chromatographic method. After the reaction was finished, all the collected products were combined and fractionally distilled into the individual components using a 10 mm × 400 mm (active column length) stainless steel helix-packed vacuum-jacketed fractionating column; these components were analyzed for the structures. All the compounds were distilled as colorless liquids.

Compound 4a: bp 145–146 °C, lit.[16] bp 145–146 °C; yield 44%; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H, $SiCH_3$), 0.59 (d, J = 2.4 Hz, 2 H, $SiCH_2Si$), 5.60 (t, J = 2.4 Hz, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ 9.8 ($SiCH_2Si$), 0.6 ($SiCH_3$).

Compound 4b:[17] bp 155–157 °C; yield 58%; ^1H NMR ($CDCl_3$) δ 0.58 (s, 6 H, $SiCH_3$), 1.00 (d, J = 2.3 Hz, 2 H, $SiCH_2Si$), 5.65 (t, J = 2.3 Hz, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ 13.0 ($SiCH_2Si$), 4.1 ($SiCH_3$).

Compound 4c: bp 166–167 °C; yield 41%; ^1H NMR ($CDCl_3$) δ 0.94 (s, 3 H, $SiCH_3$), 1.34 (d, J = 2.3 Hz, 2 H, $SiCH_2Si$), 5.69 (t, J = 2.3 Hz, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ 16.0 ($SiCH_2Si$), 7.6 ($SiCH_3$); HRMS calcd for $C_2H_5Cl_4Si_2$ (M − H) m/e 224.8684, found m/e 224.8685.

Compound 4d: bp 165–166 °C, lit.[18] bp 166–167 °C; yield 45%; ^1H NMR ($CDCl_3$) δ 1.64 (d, J = 2.2 Hz, 2 H, $SiCH_2Si$), 5.72 (t, J = 2.2 Hz, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ 18.6 ($SiCH_2Si$).

Acknowledgment. This research was supported financially by the Ministry of Science and Technology (Project 2N0841).

OM920758U

---

[16] Dannels, B. F.; Post, H. W. *J. Org. Chem.* **1957**, *22*, 748.

[17] Bush, R. D.; Golino, C. M.; Sommer, L. H. *J. Am. Chem. Soc.* **1974**, *96*, 7105.

[18] (a) Miller, R.; Seitz, G. *Chem. Ber.* **1958**, *91*, 22. (b) Egorochkin, A. N.; Khidekel, M. L.; Razuvaev, G. A.; Mironov, V. F.; Kravchenko, A. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1964**, 1312.