

# Si–C coupling reaction of polychloromethanes with $\text{HSiCl}_3$ in the presence of $\text{Bu}_4\text{PCl}$ : Convenient synthetic method for bis(chlorosilyl)methanes

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## Abstract

Coupling reaction of polychloromethanes  $\text{CH}_{4-n}\text{Cl}_n$  ( $n = 2-4$ ) with  $\text{HSiCl}_3$  in the presence of tetrabutylphosphonium chloride ( $\text{Bu}_4\text{PCl}$ ) as a catalyst occurred at temperatures ranging from 30 °C to 150 °C. The reactivity of polychloromethanes increases as the number of chlorine-substituents on the carbon increases. In the reactions of  $\text{CCl}_4$  with  $\text{HSiCl}_3$ , a variety of coupling products such as bis(chlorosilyl)methanes  $\text{CH}_2(\text{SiCl}_3)(\text{SiXCl}_2)$  [ $\text{X} = \text{Cl}$  (**1a**),  $\text{H}$  (**1b**)], (chlorosilyl)trichloromethanes  $\text{Cl}_3\text{CSiXCl}_2$  [ $\text{X} = \text{Cl}$  (**2a**),  $\text{H}$  (**2b**)], and (chlorosilyl)dichloromethanes  $\text{Cl}_2\text{HCSiXCl}_2$  [ $\text{X} = \text{Cl}$  (**3a**),  $\text{H}$  (**3b**)] were obtained along with reductive dechlorination products such as  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  depending on the reaction temperature. In the reaction of  $\text{CCl}_4$ , **2a** is formed at the initial stage of the coupling reaction and converted to give  $\text{CHCl}_3$  at low temperature of 30 °C, to give **1a**, **3a**, and  $\text{CHCl}_3$  at 60 °C, and to afford **1a** as major product and  $\text{CH}_2\text{Cl}_2$  in competition above 100 °C. Si–H bond containing silylmethanes can be formed by the H–Cl exchange reaction with  $\text{HSiCl}_3$ . Reaction of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$  took place at 80 °C to give three compounds **1a**, **3a**, and  $\text{CH}_2\text{Cl}_2$ , and finally **3a** was converted to give **1a** and  $\text{CH}_2\text{Cl}_2$  at longer reaction time. While the condition for the reaction of  $\text{CH}_2\text{Cl}_2$  with  $\text{HSiCl}_3$  required a much higher temperature of 150 °C. Under the optimized conditions for synthesizing bis(chlorosilyl)methanes **1a,b**, a mixture of **1a** and **1b** were obtained as major products in 65% (**1a**:**1b** = 64:1) and 47% (42:5) yields from the reaction of  $\text{CCl}_4$  and  $\text{CHCl}_3$  at 100 °C for 8 h, respectively, and in 41% (34:7) yield from that of  $\text{CH}_2\text{Cl}_2$  at 170 °C for 12 h. In the Si–C coupling reaction of polychloromethanes with  $\text{HSiCl}_3$ , it seems likely that a trichlorosilyl anion generated from the reaction of  $\text{HSiCl}_3$  with  $\text{Bu}_4\text{PCl}$  is an important key intermediate.

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## 1. Introduction

Trichlorosilane ( $\text{HSiCl}_3$ ) undergoes a variety of interesting and useful Si–C bond formation reactions with organometallic reagents [1] and unsaturated organic compounds in the presence of transition metal complexes [2] to give various organosilanes containing Si–Cl bonds as functionalities, which are used as important starting materials in the silicones industry [3]. Another established Si–C bond forming

method is the organic base-catalyzed reaction of activated alkyl chlorides such as benzyl chloride and polychloromethane with  $\text{HSiCl}_3$  [4]. Tertiary amines catalyze the coupling reaction of activated polychloromethanes [4] such as chloroform ( $\text{CHCl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ) [5] with  $\text{HSiCl}_3$  affording bis(chlorosilyl)methanes in moderate yields, respectively. Recently, we have reported successful coupling reactions with organic chlorides affording alkyltrichlorosilanes in high yields in the presence of quaternary phosphonium chloride as a catalyst in place of amine [6,7], the introduction of  $\text{SiCl}_2$  moiety to butadienes to form 1,1-dichlorosilacyclopent-3-enes [8], and the double silylation

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of olefins with  $\text{HSiCl}_3$  to produce  $\alpha,\beta$ -(trichlorosilyl)alkanes as major products [9]. In the coupling reaction of primary alkyl chlorides, their reactivity depends on the substituents at the carbon of C–Cl. The reaction of activated alkyl chlorides such as allyl chlorides and benzyl chlorides occurs at 130 °C, but those of unactivated alkyl chlorides such as 1-hexyl chloride and 1-octyl chloride require the high temperature of 170 °C [7]. The success of these coupling reactions prompted us to extend this reaction to polychloromethanes  $\text{CH}_{4-n}\text{Cl}_n$  ( $n = 2-4$ ), which are expected to react with  $\text{HSiCl}_3$  to yield poly(silyl)methanes as coupling products. The reaction of polychloromethanes with  $\text{HSiCl}_3$  in the presence of  $\text{Bu}_4\text{PCl}$  occurred at the temperatures ranging from 30 °C to 150 °C depending on chlorine-substituents on the carbon to give a variety of Si–C coupling products and reductive dechlorination compounds. Herein, we wish to report the  $\text{Bu}_4\text{PCl}$ -catalyzed reaction of polychloromethanes with  $\text{HSiCl}_3$  and a mechanism for the formation of Si–C coupling compounds in details.

## 2. Results and discussion

### 2.1. Reaction of $\text{CCl}_4$ with $\text{HSiCl}_3$

When the most activated  $\text{CCl}_4$  among the polychloromethanes reacted with  $\text{HSiCl}_3$ , a variety of coupling products such as bis(chlorosilyl)methanes  $\text{CH}_2(\text{SiCl}_3)(\text{SiXCl}_2)$  [ $\text{X} = \text{Cl}$  (**1a**),  $\text{H}$  (**1b**)], (chlorosilyl)trichloromethanes  $\text{Cl}_3\text{CSiXCl}_2$  [ $\text{X} = \text{Cl}$  (**2a**),  $\text{H}$  (**2b**)], and (chlorosilyl)dichloromethanes  $\text{Cl}_2\text{HCSiXCl}_2$  [ $\text{X} = \text{Cl}$  (**3a**),  $\text{H}$  (**3b**)] were obtained along with reductive dechlorination products such as  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  depending on the reaction temperatures (Eq. (1)). Si–H bond containing silylmethanes (**1b–3b**) can be formed by the H–Cl exchange reaction with  $\text{HSiCl}_3$ . The results obtained from the reactions of  $\text{CCl}_4$  with  $\text{HSiCl}_3$  at temperatures ranging from 30 °C to 130 °C are summarized in Table 1.

As shown in Table 1, the reaction of  $\text{CCl}_4$  with  $\text{HSiCl}_3$  occurred at 30 °C and gave a coupling product **2a** (3%) and a reductive dechlorination product  $\text{CHCl}_3$  (42%) as a major product with a 45% consumption of  $\text{CCl}_4$  for 8 h (entry 1). At the higher temperature of 60 °C, a 4 h reaction gave a 76% consumption of  $\text{CCl}_4$  and afforded a 3:2 mixture of **2a** and **2b** and  $\text{CHCl}_3$  in 48% and 27% yields, respectively, (entry 2) and an 8 h reaction with all consumption of  $\text{CCl}_4$  gave a 15:1 mixture of **1a** and **1b**, a 15:1 mixture of **2a** and **2b**, and a 12:1 mixture of **3a** and **3b** in 16%, 16% and 13% yields, respectively, as well as  $\text{CHCl}_3$  in 53% yield (entry 3). When the same reaction was carried out at the temperature of 80 °C, all  $\text{CCl}_4$  was consumed within 2 h to give a 34:3 mixture of **1a** and **1b** and a 14:1 mixture of **3a** and **3b** in 37% and 15% yields along with reductive dechlorination products such as  $\text{CHCl}_3$  (47%) and  $\text{CH}_2\text{Cl}_2$  (1%) (entry 4). In a longer 8 h reaction at 80 °C, the yield of compounds **1** consisted of a 51:3 mixture of **1a** and **1b** increased up to 54% along with  $\text{CH}_2\text{Cl}_2$  (11%), but that of  $\text{CHCl}_3$  decreased to 31%, suggesting that the coupling reaction of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$  takes place at 80 °C (entry 5). The yield of a mixture of **1** was maximized to 69% in an 8 h reaction at 100 °C (entry 6) and then decreased to 53% in a 1 h reaction at a higher temperature of 130 °C (entry 7). When  $\text{HSiMeCl}_2$  was used as a hydrosilane instead of  $\text{HSiCl}_3$ , no Si–C coupling reaction with  $\text{CCl}_4$  even at 80 °C was observed. In the reaction of  $\text{CCl}_4$  with  $\text{HSiCl}_3$ , the coupling product **2a** formed at the beginning stage is an important intermediate leading to silylmethanes **3** and  $\text{CHCl}_3$  (entries 2 and 3), and finally to bis-silylation products **1**.

### 2.2. Reaction of $\text{Cl}_3\text{SiCCl}_3$ (**2a**) with $\text{HSiCl}_3$

In order to look into the reaction pathway to **1** from  $\text{CCl}_4$ , monosilylated compounds **2a**, formed at the early

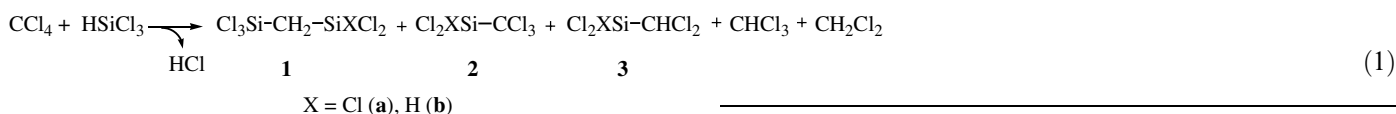


Table 1  
 $\text{Bu}_4\text{PCl}$ -catalyzed reactions of  $\text{CCl}_4$  with  $\text{HSiCl}_3$

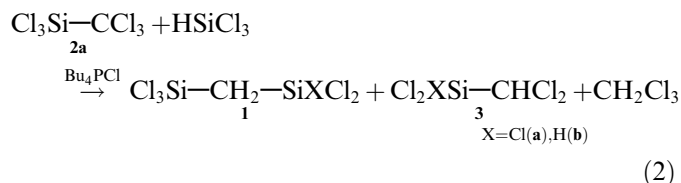
Entry #	$\text{CCl}_4^b$	Reaction conditions		Product yields (%) <sup>c</sup>				
		Temperature (°C)	Time (h)	<b>1</b> ( <b>a:b</b> )	<b>2</b> ( <b>a:b</b> )	<b>3</b> ( <b>a:b</b> )	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$
1	55	30	8	–	3(3:–)	–	42	–
2	24	60	4	–	48 (29:19)	–	27	–
3	–	60	8	16 (15:1)	16 (15:1)	13 (12:1)	53	–
4	–	80	2	37 (34:3)	–	15 (14:1)	47	1
5	–	80	8	54 (51:3)	–	3 (3:–)	31	11
6	–	100	8	69 (67:2)	–	–	–	30
7	–	130	1	53 (52:1)	–	–	–	33

<sup>a</sup> The reaction was carried out using a 10:60:1 mol ratio of  $\text{CCl}_4$ ,  $\text{HSiCl}_3$ , and  $\text{Bu}_4\text{PCl}$ .

<sup>b</sup> Unreacted  $\text{CCl}_4$  (%) remained.

<sup>c</sup> Yields are on the basis of  $\text{CCl}_4$  used and were determined by GLC with use of internal standard.

stage of the reactions with  $\text{CCl}_4$  at low temperatures, were isolated and reacted with  $\text{HSiCl}_3$  in the presence of  $\text{Bu}_4\text{PCl}$  catalyst, respectively. The reaction of **2a** with  $\text{HSiCl}_3$  afforded the bis-silylation compounds **1a**, monosilylated dichloromethanes **3**, and  $\text{CHCl}_3$  (Eq. (2)). The results obtained from the reaction with **2a** are summarized in Table 2



As Table 2 shows, the reaction of **2a** with  $\text{HSiCl}_3$  occurred at 30 °C and afforded the Si–C coupling products **1a** (2%) and **3a** (5%), and  $\text{CHCl}_3$  (8%) with a 16% consumption of **2a** for 1 h (entry 8). In a 4 h reaction, 65% of **2a** was consumed to give **1a**, a 23:3 mixture of **3a** and **3b**, and  $\text{CHCl}_3$  in 7%, 26%, and 32% yields, suggesting that the formation of  $\text{CHCl}_3$  was more favorable than that of **1** at 30 °C (entry 9). When this reaction was carried out at the higher temperature of 60 °C, the yields of **1a** and  $\text{CHCl}_3$  increased from 23% and 38% for a 4 h to 33% and 42% for a 8 h, respectively, but that of the mixture of **3a** and **3b** decreased from 25% to 22% from the 86% and 97% consumptions of **2** for 4 h and 8 h, respectively (entries 10 and 11). The results indicate that compounds **2** are key intermediates converting to form **1** and  $\text{CHCl}_3$ .  $\text{CHCl}_3$  can be formed by the reaction of **2** with HCl in the presence of  $\text{Bu}_4\text{PCl}$ .

### 2.3. Reaction of $\text{CHCl}_3$ with $\text{HSiCl}_3$

In order to look into the reactivity of  $\text{CHCl}_3$ , the reaction of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$  was carried out at the temperatures ranging from 60 to 100 °C. The results obtained from the reaction of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$  are summarized in Table 3.

As shown in Table 3, the reaction of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$  did not occur at 60 °C for 4 h (entry 12), but gave a 3:1 mixture of **1a** and **1b**, and **3a** in 12% and 1% yields, respectively, with a 31% consumption of  $\text{CHCl}_3$  at 80 °C for 8 h (entry 13). Reaction of  $\text{CHCl}_3$  at a higher temperature of 100 °C for 8 h afforded a 9:1 mixture of **1a** and **1b** in 51% yield along with  $\text{CH}_2\text{Cl}_2$  (48%) (entry 14). An 1 h reaction at 130 °C gave a 34:4 mixture of **1a** and **1b** in 38% yield along with  $\text{CH}_2\text{Cl}_2$  (48%), suggesting that **3a** is one of the key intermediates for the formation of **1** and  $\text{CH}_2\text{Cl}_2$  from  $\text{CHCl}_3$  (entry 15).

To test whether tris(chlorosilyl)methanes (**4**) [10] can be readily formed and stable in our reaction conditions, the reaction of **4** with HCl gas was carried out in the presence of  $\text{Bu}_4\text{PCl}$  at room temperature. Compound **4** was immediately decomposed by bubbling of HCl to form **1a** and  $\text{SiCl}_4$  (Eq. (3)). The result suggests that tris(silyl)methanes can be formed from the reactions of  $\text{CCl}_4$  and  $\text{CHCl}_3$  with  $\text{HSiCl}_3$ , but immediately decomposed by HCl to produce **1a** and  $\text{SiCl}_4$ .

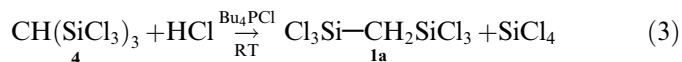


Table 2  
 $\text{Bu}_4\text{PCl}$ -catalyzed reactions of **2a** with  $\text{HSiCl}_3$ <sup>a</sup>

Entry #	<b>2 (a:b)</b> <sup>b</sup>	Reaction conditions		Product yields (%) <sup>c</sup>		
		Temperature (°C)	Time (h)	<b>1a</b>	<b>3 (a:b)</b>	$\text{CHCl}_3$
8	84 (55:29)	30	1	2	5 (5:–)	8
9	35 (31:4)	30	4	7	26 (23:3)	32
10	14 (11:3)	60	4	23	25 (23:2)	38
11	3 (3:–)	60	8	33	22 (21:1)	42

<sup>a</sup> Reaction was carried out using a 10:40:1 mol ratio of **2a**,  $\text{HSiCl}_3$ , and  $\text{Bu}_4\text{PCl}$ .

<sup>b</sup> The number in parenthesis represents **2** (%) remained.

<sup>c</sup> Yields are on the basis of **2** used and were determined by GLC with use of internal standard.

Table 3  
 $\text{Bu}_4\text{PCl}$ -catalyzed reactions of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$

Entry #	$\text{CHCl}_3$ <sup>b</sup>	Reaction conditions		Product yields (%) <sup>c</sup>		
		Temperature (°C)	Time (h)	<b>1 (a:b)</b>	<b>3 (a:b)</b>	$\text{CH}_2\text{Cl}_2$
12	100	60	4			
13	69	80	8	12 (9:3)	1 (1:–)	18
14		100	8	51 (46:5)		48
15		130	1	38 (34:4)		48

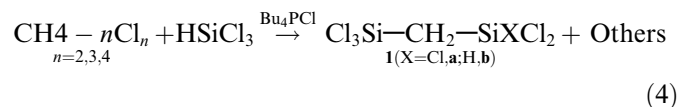
<sup>a</sup> Reaction was carried out using a 10:60:1 mol ratio of  $\text{CHCl}_3$ ,  $\text{HSiCl}_3$ , and  $\text{Bu}_4\text{PCl}$ .

<sup>b</sup> Unreacted  $\text{CHCl}_3$  (%).

<sup>c</sup> Product yields are on the basis of  $\text{CHCl}_3$  used and were determined by GLC with use of internal standard.

#### 2.4. Synthesis of bis(chlorosilyl)methanes

In order to synthesize bis(chlorosilyl)methanes **1**, the reactions were carried out at 5 times scaleup and products **1** were isolated by distillation of the reaction mixtures obtained from the Bu<sub>4</sub>PfCl catalyzed reaction of polychloromethanes such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> with HSiCl<sub>3</sub> under optimum conditions (4). The results are summarized in Table 4



As shown in Table 1, the higher chlorinated methanes, CCl<sub>4</sub> and CHCl<sub>3</sub>, are much more reactive than CH<sub>2</sub>Cl<sub>2</sub> in the coupling reaction with HSiCl<sub>3</sub> at 170 °C. Reactions of CCl<sub>4</sub> and CHCl<sub>3</sub> at 100 °C for 8 h gave the isomeric mixtures of **1a** and **1b** in 65% and 47% isolated yields, respectively. In addition to bis-silylation compounds **1a** and **1b**, CH<sub>2</sub>Cl<sub>2</sub> was obtained as the reductive dechlorination product in 29% and 42% yields, respectively (entries 16 and 17). However, the reaction of CH<sub>2</sub>Cl<sub>2</sub> proceeded slowly at the higher temperature of 170 °C for 24 h gave a 34:7 mixture of bis-silylation products, **1** and methyltrichlorosilane in 41% and 8% yields along with methyltrichlorosilane (12%) and high boilers (entry 18). In the reactions with polychloromethanes, the yields of the mixture of **1a** and **1b** and the ratio of **1a** to **1b** increase as the number of chlorine-substituents on the carbon increases. This Si–C coupling reaction is a useful synthetic process for the preparation of bis(chlorosilyl)methanes starting from polychloromethanes in laboratory scale, even though it were reported that bis(chlorosilyl)methanes were synthesized in 55% and 36% yields from the Si–C coupling reaction of CHCl<sub>3</sub> with HSiCl<sub>3</sub> using excess amount of tertiary amine as a catalyst and HCl scavenger at CH<sub>3</sub>CN solvent [4b] and direction of elemental silicon with a gaseous mixture of CH<sub>2</sub>Cl<sub>2</sub> and HCl at the high temperature of 280 °C [11], respectively.

On the basis of our results, we propose a mechanism for the Bu<sub>4</sub>PfCl-catalyzed coupling reaction of HSiCl<sub>3</sub> with CCl<sub>4</sub> as a representative polychloromethane as shown in Scheme 1. HSiCl<sub>3</sub> undergoes a disproportionation reaction in the presence of Bu<sub>4</sub>PfCl [7] to give dichlorosilane and

tetrachlorosilane as that in the presence of quaternary ammonium chloride as an organic salt catalyst [12]. All chlorosilanes could be involved in coupling reaction. In the first stage of Si–C coupling reaction of CCl<sub>4</sub> with HSiCl<sub>3</sub>, Bu<sub>4</sub>PfCl interacts with HSiCl<sub>3</sub> to form a pentacoordinated intermediate which loses hydrogen chloride to produce a silyl anion intermediate **I** [1,3]. This intermediate **I** reacts with CCl<sub>4</sub> to give Cl<sup>−</sup> and **2a**, which subsequently reacts with the intermediate **I** to afford bis- and tris(silyl)chloromethanes. Compound **2a** and its silylated methane reacts with Cl<sup>−</sup> or the intermediate **I** to give CHCl<sub>3</sub>, **3a**, and bis(trichlorosilyl)chloromethane through reductive desilylation reactions eliminating SiCl<sub>4</sub> or Cl<sub>3</sub>Si–SiCl<sub>3</sub> [13], respectively. Such reductive desilylation compounds undergo repeatedly one more Si–C coupling and reductive desilylation reactions to yield **3a**, bis(trichlorosilyl)chloromethane, and **4** which repeatedly one more to produce CH<sub>2</sub>Cl<sub>2</sub>, Cl<sub>3</sub>SiCH<sub>2</sub>Cl, and **1a**. Finally coupling reactions of CH<sub>2</sub>Cl<sub>2</sub> and Cl<sub>3</sub>SiCH<sub>2</sub>Cl also give bis-silylation products **1**.

In conclusion, we describe the coupling reaction of polychloromethanes with HSiCl<sub>3</sub> in the presence of the quaternary phosphonium chloride catalyst. This research provides useful and important mechanistic information for the Si–C coupling reaction of organic halide with HSiCl<sub>3</sub> in the presence of organic salt catalyst.

### 3. Experimental

#### 3.1. General comments

All reactions were carried out in flame-dried glassware or stainless steel cylinder. All moisture-sensitive liquids were manipulated under anhydrous dinitrogen using cannula techniques. Trichlorosilane, methyldichlorosilane, (trichloromethyl)trichlorosilane, and (dichloromethyl)trichlorosilane were purchased from Gelest, Inc. and used without purification. (*n*-Bu)<sub>4</sub>PfCl was purchased from Aldrich Chem. Co. and used without further purification. Reaction mixtures were analyzed by GLC on a 2.5 m by 1/8 in. stainless steel column packed with packing materials (OV-101 on 80–100 mesh Chromosorb W/AW) or a capillary column (30 m, SE-30) using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a Varian

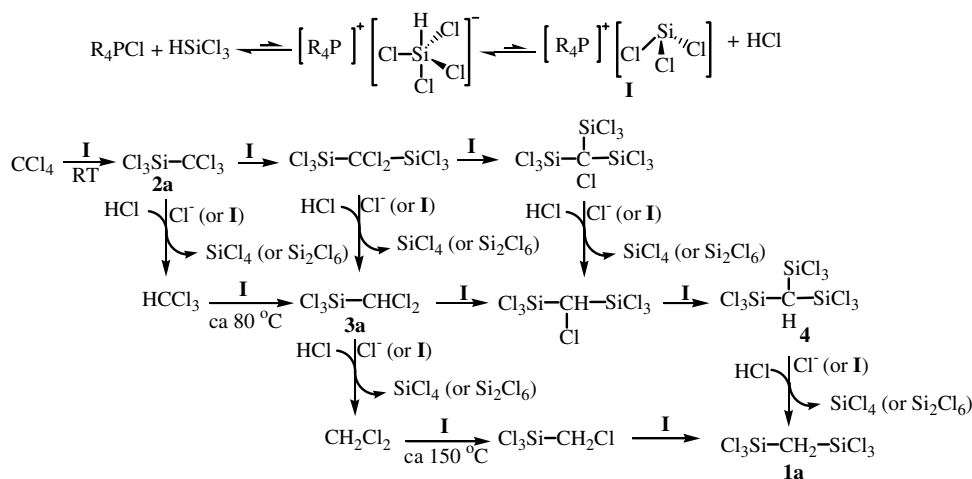
Table 4  
Synthesis of bis(chlorosilyl)methanes from Bu<sub>4</sub>PfCl-catalyzed reaction of polychloromethanes with HSiCl<sub>3</sub><sup>a</sup>

Entry #	CH <sub>4–n</sub> Cl <sub>n</sub> , <i>n</i> <sup>b</sup>	Reaction conditions		Product yields (%) <sup>c</sup>			
		Temperature (°C)	Time (h)	<b>1</b> (a:b)	MeSiCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	Others (g)
16	4 (–)	100	8	65 (64:1)		29	0.28
17	3 (–)	100	8	47 (42:5)		42	0.29
18	2 (12)	170	24	41 (34:7)	8	(12)	2.93

<sup>a</sup> The reaction was carried out using a 20:120:1 mol ratio of CH<sub>4–n</sub>Cl<sub>n</sub>, HSiCl<sub>3</sub>, and Bu<sub>4</sub>PfCl.

<sup>b</sup> The number in parenthesis represents CH<sub>4–n</sub>Cl<sub>n</sub> (%) remained.

<sup>c</sup> Isolated yields on the basis of CH<sub>4–n</sub>Cl<sub>n</sub> used.



Scheme 1.

4290 integrator. The progresses of reaction were also monitored by GLC in the time intervals of 1 h. Product yields were determined by isolation or GLC using *n*-dodecane as the internal standard. GC–MS data were obtained with a HP6890/5973 system (70 eV, EI).

### 3.2. General procedure for the reaction of polychloromethanes

As a representative, the reaction of  $\text{CCl}_4$  with  $\text{HSiCl}_3$  is described as follows: into a 25 mL dried stainless steel bomb with a valve was charged with  $\text{CCl}_4$  (1.00 g, 6.50 mmol),  $\text{HSiCl}_3$  (5.28 g, 39.0 mmol),  $\text{Bu}_4\text{P}\text{Cl}$  (0.19 g, 0.64 mmol), and *n*-dodecane (0.50 mL) under a dry nitrogen atmosphere. The reaction was carried out at 30–130 °C, respectively. Yields are on the basis of  $\text{CCl}_4$  used and were determined by GLC with use of internal standard. The results are summarized in Table 2.

Using the same procedures, the reactions of  $\text{CHCl}_3$  with  $\text{HSiCl}_3$  were carried at 60–100 °C. The results are summarized in Table 3.

In scale up preparation, into a 75 mL dried stainless steel bomb with a valve was charged with  $\text{CCl}_4$  (7.97 g, 51.8 mmol),  $\text{HSiCl}_3$  (42.11 g, 310.9 mmol), and  $\text{Bu}_4\text{P}\text{Cl}$  (0.76 g, 2.6 mmol) under a dry nitrogen atmosphere. The reaction was carried out at 100 °C for 8 h and gave a 98:2 mixture (9.50 g) of **1a** and **1b**,  $\text{CH}_2\text{Cl}_2$  (1.27 g) in 65% and 29% yields, respectively, along with high boilers (0.28 g). Using the same procedures of scaleup preparation above, a reactions of  $\text{CHCl}_3$  (6.19 g, 51.9 mmol) with  $\text{HSiCl}_3$  (42.11 g, 310.9 mmol) at 100 °C for 8 h gave a 90:10 mixture (6.85 g) of **1a** and **1b**, and  $\text{CH}_2\text{Cl}_2$  (1.85 g) in 47% and 42%, respectively, along with high boilers (0.29 g). Using the same procedures of scaleup preparation above, a reaction of  $\text{CH}_2\text{Cl}_2$  (4.40 g, 51.0 mmol) with  $\text{HSiCl}_3$  (42.11 g, 310.9 mmol) at 170 °C for 24 h gave a 83:17 mixture (5.88 g) of **1a** and **1b**, and  $\text{CH}_2\text{Cl}_2$  (0.53 g) in 41% and 12%, respectively, along with high boilers (2.93 g). The results are summarized in Table 1.

### 3.3. Reaction of **2a** with $\text{HSiCl}_3$

Using the general procedure described above, the reactions of **2a** (1.00 g, 3.96 mmol) with  $\text{HSiCl}_3$  (3.22 g, 23.7 mmol),  $\text{Bu}_4\text{P}\text{Cl}$  (0.12 g, 0.41 mmol), and *n*-dodecane (0.50 mL) were carried out at 30 °C and 60 °C, respectively. The results are summarized in Table 4.

### 3.4. Reaction of tris(trichlorosilyl)methane (**4**) with hydrogen chloride

Into a stirred mixture of tris(trichlorosilyl)methane (14.39 g, 34.56 mmol),  $\text{Bu}_4\text{P}\text{Cl}$  (1.02 g, 3.46 mmol), and *n*-dodecane (1.00 mL) was bubbled with anhydrous hydrogen chloride in 10 mL/min at room temperature for 1 h. An exothermic reaction was observed with bubbling of HCl gas. **1a** was obtained in 87% yield along with tetrachlorosilane with 91% consumption of reactant after 1 h.

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