

# Versatile method for introduction of bulky substituents to alkoxychlorosilanes

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## Abstract

The reactions of various alkoxytrichlorosilanes prepared in situ from tetrachlorosilane and alcohols, with Grignard reagents bearing a bulky substituent such as the isopropyl, *sec*-butyl, and cyclohexyl group afforded triisopropyl-, tri(*sec*-butyl)-, and tricyclohexylalkoxysilane in high yields. The reactions of *n*-butoxytrichlorosilane with these Grignard reagents produced triisopropyl-, tri(*sec*-butyl)-, and tricyclohexyl(*n*-butoxy)silane in 94%, 96%, and 92% yields, respectively. Methoxymethyldichlorosilane reacted with the same Grignard reagents to give diisopropyl-, di(*sec*-butyl)-, and dicyclohexylmethoxymethylsilane in 84%, 83%, and 83% yields. Treatment of methoxydimethylchlorosilane with the Grignard reagents readily afforded isopropyl-, *sec*-butyl-, and cyclohexylmethoxydimethylsilane in excellent yields. Similar treatment of methoxydimethylchlorosilane with *tert*-butylmagnesium chloride gave *tert*-butylmethoxydimethylsilane in 62% yield.

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## 1. Introduction

The reactions of Grignard reagents with chlorosilanes and alkoxychlorosilanes offer a convenient route to the synthesis of various industrial useful organosilicon compounds. However, some limitations are encountered for the synthesis of organosilicon compounds bearing bulky substituents on the silicon atom. For examples, the reactions of 4 equiv. of isopropylmagnesium chloride with tetrachlorosilane and tetramethoxysilane in THF afford diisopropyldichlorosilane and diisopropyldimethoxysilane, respectively, as the major products. In these reactions, no triisopropylchlorosilane and triisopropylmethoxysilane are produced. Indeed, it is difficult to prepare tri(alkyl)chlorosilanes with sterically bulky substituents on the silicon atom by the Grignard

method. It has been reported that the tri(alkyl)chlorosilanes with the bulky substituents at the silicon center can only be prepared by the reaction of the Grignard reagent with tetrachlorosilane in the presence of a catalyst such as copper cyanide. The reaction of *tert*-butyl-Grignard reagent with dimethyldichlorosilane affords no *tert*-butyldimethylchlorosilane, although the reaction in the presence of a catalytic amount of copper cyanide gives *tert*-butyldimethylchlorosilane in moderate yield [1]. The use of more reactive organolithium reagents than Grignard reagents, however, affords the tri(alkyl)chlorosilanes with bulky substituents [2]. The reactions of the organolithium reagents having the *sec*- and *tert*-alkyl group with di(alkyl)dichlorosilanes readily produce the respective tri(alkyl)chlorosilanes. On the other hand, hydrochlorosilanes react with the Grignard reagents involving a bulky substituent to give the tri-substituted hydrosilanes [3]. For examples, the reaction of trichlorosilane with 3 molar equiv. of isopropylmagnesium chloride produces triisopropylsilane in high yield. Similarly, the

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reaction of *tert*-butylmagnesium chloride with dimethylchlorosilane affords *tert*-butyldimethylsilane in high yield.

In an effort to introduce the bulky groups onto the silicon atom of tetrachlorosilane, we have found that the reaction of isopropylmagnesium chloride with alkoxytrichlorosilanes prepared by a one-pot procedure from tetrachlorosilane and alcohols readily affords triisopropylalkoxysilanes. In this paper, we report the syntheses of tri(alkyl)alkoxysilanes with bulky substituents on the silicon atom, which are commercially important materials. We also report the reactions of methoxymethyldichlorosilane and methoxydimethylchlorosilane with the bulky Grignard reagents.

## 2. Results and discussion

### 2.1. Reaction of *iso*-PrMgCl with alcohol and then with tetrachlorosilane

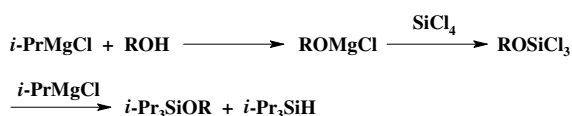
First we investigated the reactions of alkoxytrichlorosilanes with isopropylmagnesium chloride to prepare triisopropylalkoxysilanes. The alkoxytrichlorosilanes used in this reaction were prepared by the reaction of tetrachlorosilane with alkoxy magnesium chlorides, which were synthesized in situ by the reaction of isopropylmagnesium chloride with alcohols. The reaction was carried out according to the following method, that is, 1 equiv. of alcohols was added to a THF solution involving 5 equiv. of isopropylmagnesium chloride, followed by addition of 1 equiv. of tetrachlorosilane to the resulting mixture, and the mixture was heated to reflux after addition of toluene. In these reactions, triisopropylalkoxysilanes were obtained in moderate yields, together with significant amounts of triisopropylsilane (Scheme 1). As can be seen in Table 1, the reaction of meth-

oxytrichlorosilane with isopropyl-Grignard reagent gave triisopropylmethoxysilane in 59% yield, along with a 19% yield of triisopropylsilane (run 1).

The reactions with alkoxytrichlorosilanes having an *n*-BuO and *n*-HexO group as the alkoxy substituent with isopropyl-Grignard reagent gave the respective triisopropylalkoxysilanes in moderate yields (run 2 and 3). The similar reactions with *sec*- and *tert*-alkoxytrichlorosilane, however, afforded triisopropylalkoxysilanes in low yields (run 4 and 5). Especially, the reaction with *tert*-butoxytrichlorosilane gave the product only in 7% yield (run 5). In the absence of alcohol, however, the reaction of tetrachlorosilane with isopropylmagnesium chloride in THF afforded triisopropylchlorosilane only in ca. 1% yield, along with triisopropylsilane and diisopropylchlorosilane in 26% and 68% yields, even in the presence of a copper cyanide catalyst. These results clearly indicate that triisopropyl substituted silicon compounds can readily be prepared by introducing an alkoxy group onto the silicon atom of tetrachlorosilane, and the steric bulkiness of the alkoxy group highly influences the product yields in the reaction with the Grignard reagents.

Magnesium methoxide and sodium methoxide can also be used as the source of the methoxy group for the preparation of methoxytrichlorosilane. Thus, the reaction of 3.4 equiv. of isopropylmagnesium chloride with 1 equiv. of tetrachlorosilane in the presence of 0.5 equiv. of Mg(OMe)<sub>2</sub> in a THF–toluene solution produced triisopropylmethoxysilane in 51% yield, in addition to a 28% yield of triisopropylsilane (run 6). Similar reaction of isopropyl-Grignard reagent with tetrachlorosilane in the presence of NaOMe gave the product in 44% yield, together with a 29% yield of triisopropylsilane (run 7). The low yield of triisopropylmethoxysilane in this reaction, compared with that obtained from run 1, may be ascribed to the poor solubility of sodium methoxide in the THF–toluene solution.

It is well-known that ethylene oxide reacts with the Grignard reagent to give the ring-opened magnesium alkoxide. We have found that the magnesium alkoxide formed from the reaction of ethylene oxide with isopropylmagnesium chloride can also be used as the source of alkoxy compound for the synthesis of triisopropylalkoxysilanes. Thus,



Scheme 1.

Table 1  
Reaction of SiCl<sub>4</sub> with *i*-PrMgCl in the presence of metal alkoxide

Run	SiCl <sub>4</sub> (mmol)	ROH (mmol)	<i>i</i> -PrMgCl (mmol)	<i>i</i> -Pr <sub>3</sub> SiOR	<i>i</i> -Pr <sub>3</sub> SiOR		<i>i</i> -Pr <sub>3</sub> SiH	
					Yield <sup>a</sup> (%)	Yield <sup>b</sup> (%)	Yield <sup>a</sup> (%)	
1	42	MeOH	42	208	<i>i</i> -Pr <sub>3</sub> SiOMe	59	53	19
2	42	<i>n</i> -BuOH	42	208	<i>i</i> -Pr <sub>3</sub> SiOBu- <i>n</i>	51	45	17
3	42	<i>n</i> -HexOH	42	208	<i>i</i> -Pr <sub>3</sub> SiOHex- <i>n</i>	41	35	18
4	42	<i>i</i> -PrOH	42	208	<i>i</i> -Pr <sub>3</sub> SiOPr- <i>i</i>	39	33	18
5	42	<i>t</i> -BuOH	42	208	<i>i</i> -Pr <sub>3</sub> SiOBu- <i>t</i>	7		12
6	42	(MeO) <sub>2</sub> Mg	42	208	<i>i</i> -Pr <sub>3</sub> SiOMe	51		28
7	42	MeONa	42	208	<i>i</i> -Pr <sub>3</sub> SiOMe	44		29
8	42	Ethyleneoxide	42	208	<i>i</i> -Pr <sub>3</sub> SiOCH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	47	40	15

<sup>a</sup> Yield was determined by analytical GLC.

<sup>b</sup> Yield of isolated compounds.

the reaction of 1 equiv. of ethylene oxide with 5 equiv. of isopropyl-Grignard reagent, and then 1 equiv. of tetrachlorosilane in THF–toluene, afforded isopentoxytriisopropylsilane in 47% yield, along with a 15% yield of triisopropylsilane (run 8).

## 2.2. Reaction of tetrachlorosilane with alcohol and then with Grignard reagents

Next we carried out the reaction of tetrachlorosilane with 1 equiv. of alcohol, followed by treatment with Grignard reagents to suppress the formation of the reductive product, Si–H compound. Thus, the reaction of tetrachlorosilane with 1 equiv. of methanol in THF at room temperature, and then treatment of the resulting mixture with 5 equiv. of isopropylmagnesium chloride in THF–toluene gave triisopropylmethoxysilane and triisopropylsilane, in 53% and 4% yields, respectively (run 9), as shown in Table 2. The reaction of tetrachlorosilane with *n*-butyl alcohol and then with isopropylmagnesium chloride under the same conditions produced triisopropyl(*n*-butoxy)silane in 51% yield, along with a 1% yield of triisopropylsilane (run 10). These results indicate that the formation of the reductive product, triisopropylsilane is appreciably suppressed owing to the formation of alkoxytrichlorosilane in the initial step in the reaction.

The suppression for the formation of the hydrosilane has also been observed in the reactions of tetrachlorosilane with *sec*-butyl- and cyclohexylmagnesium chloride. The reaction of tetrachlorosilane with 1 equiv. of *n*-butyl alcohol in THF, followed by treatment of the resulting mixture with *sec*-butylmagnesium chloride in THF–toluene afforded tri(*sec*-butyl)(*n*-butoxy)silane and tri(*sec*-butyl)silane in 67% and 2% yields (run 11). Similar reaction of tetrachlorosilane with methanol, and then with cyclohexylmagnesium chloride gave tri(cyclohexyl)methoxysilane and tri(cyclohexyl)silane in 51% and 1% yields, respectively (run 12). The fact that the initial formation of alkoxytrichlorosilanes in the Grignard coupling leads to the suppression of the production of trialkylsilane indicates that trichlorohydrosilane is formed by the reaction of the Grignard reagents with tetrachlorosilane, but not with alkoxytrichlorosilanes. Once the alkoxytrichlorosilanes were formed in the reactions, coordination of the alkoxy group in the alkoxytrichlorosilanes to the magnesium atom in Grignard reagents would take place. Consequently, the for-

mation of the reductive product, alkoxydichlorosilane, would be suppressed.

## 2.3. Reaction of alkoxychlorosilanes with Grignard reagents

Since the reaction of tetrachlorosilane with isopropylmagnesium chloride produces no triisopropylchlorosilane, triisopropylalkoxysilanes formed in the above reactions should be produced by the reaction of alkoxytrichlorosilanes with isopropylmagnesium chloride. Therefore, we carried out the GC–mass spectrometric analysis of the mixture obtained by the reaction of tetrachlorosilane with *n*-butyl alcohol in the absence of isopropyl-Grignard reagent. The results indicated that *n*-butoxytrichlorosilane was produced in 59% yield, along with di(*n*-butoxy)dichlorosilane (18%), tri(*n*-butoxy)chlorosilane (8%), tetra(*n*-butoxy)silane (4%), and 11% of the unreacted starting tetrachlorosilane. For the purpose of the preparation of triisopropylalkoxysilanes in much higher yields, it is essential to prepare the alkoxytrichlorosilanes in high yields. In fact, the reaction of pure *n*-butoxytrichlorosilane with the bulky Grignard reagents afforded the corresponding *n*-butoxytri(alkyl)silanes in excellent yields. Thus, the reaction of *n*-butoxytrichlorosilane with 4 equiv. of isopropylmagnesium chloride in a THF–toluene solution at 90 °C gave *n*-butoxytriisopropylsilane in 94% yield (run 13), as shown in Table 3. Treatment of *n*-butoxytrichlorosilane with *sec*-butyl- and cyclohexyl-Grignard reagent under the same conditions afforded *n*-butoxytri(*sec*-butyl)silane and *n*-butoxytri(cyclohexyl)silane in 96% and 92% yields, respectively (run 14 and 15). These results clearly indicate that the reactivity of a Cl–Si bond toward the Grignard reagents can be greatly enhanced by introducing the alkoxy group onto the silicon atom. In these reactions, coordination of the alkoxy group on the silicon atom to the Grignard reagent presumably plays an important role for the formation of trialkyl-substituted alkoxy-silanes.

The Grignard reagents involving a *sec*-alkyl group readily react with alkoxytrichlorosilanes to give tri(*sec*-alkyl)alkoxysilanes, however, similar reaction of *tert*-butylmagnesium chloride with *n*-butoxytrichlorosilane produced no tri- and di(*tert*-butyl)-substituted silicon compounds (run 16), although the reaction of alkoxydimethylchlorosilane with *tert*-butyl-Grignard reagent gave alkoxy(*tert*-butyl)dimethylsilane in high yield.

Table 2  
Reaction of SiCl<sub>4</sub> with alcohol and then with Grignard reagents

Run	SiCl <sub>4</sub> (mmol)	R'OH (mmol)	RMgCl (mmol)	R <sub>3</sub> SiOR'		R <sub>3</sub> SiH			
					Yield <sup>a</sup> (%)	Yield <sup>b</sup> (%)	Yield <sup>a</sup> (%)		
9	42	MeOH	42	<i>i</i> -PrMgCl	208	<i>i</i> -Pr <sub>3</sub> SiOMe	53	<i>i</i> -Pr <sub>3</sub> SiH	4
10	42	<i>n</i> -BuOH	42	<i>i</i> -PrMgCl	208	<i>i</i> -Pr <sub>3</sub> SiOBu- <i>n</i>	51	<i>i</i> -Pr <sub>3</sub> SiH	1
11	93	<i>n</i> -BuOH	93	<i>s</i> -BuMgCl	465	<i>s</i> -Bu <sub>3</sub> SiOBu- <i>n</i>	67	<i>s</i> -Bu <sub>3</sub> SiH	2
12	94	MeOH	94	<i>c</i> -HexMgCl	470	<i>c</i> -Hex <sub>3</sub> SiOMe	51	<i>c</i> -Hex <sub>3</sub> SiH	1

<sup>a</sup> Yield was determined by analytical GLC.

<sup>b</sup> Yield of isolated compounds.

Table 3  
Reaction of alkoxychlorosilanes with Grignard reagents

Run	Cl <sub>x</sub> Si(OR') <sub>4-x</sub>	(mol)	RMgCl	(mol)	R <sub>x</sub> Si(OR') <sub>4-x</sub>	Yield <sup>a</sup> (%)	Yield <sup>b</sup> (%)
13	Cl <sub>3</sub> SiOBu- <i>n</i>	0.029	<i>i</i> -PrMgCl	0.12	<i>i</i> -Pr <sub>3</sub> SiOBu- <i>n</i>	94	90
14	Cl <sub>3</sub> SiOBu- <i>n</i>	0.34	<i>s</i> -BuMgCl	1.75	<i>s</i> -Bu <sub>3</sub> SiOBu- <i>n</i>	96	84
15	Cl <sub>3</sub> SiOBu- <i>n</i>	0.029	<i>c</i> -HexMgCl	0.12	<i>c</i> -Hex <sub>3</sub> SiOBu- <i>n</i>	92	85
16	Cl <sub>3</sub> SiOBu- <i>n</i>	0.17	<i>t</i> -BuMgCl	0.85	<i>t</i> -BuCl <sub>2</sub> SiOBu- <i>n</i>		22
17	Cl <sub>2</sub> Si(OBu- <i>n</i> ) <sub>2</sub>	0.11	<i>i</i> -PrMgCl	0.42	<i>i</i> -Pr <sub>2</sub> Si(OBu- <i>n</i> ) <sub>2</sub>	94	86
18	ClSi(OBu- <i>n</i> ) <sub>3</sub>	0.11	<i>i</i> -PrMgCl	0.42	<i>i</i> -PrSi(OBu- <i>n</i> ) <sub>3</sub>	93	85
19	Si(OBu- <i>n</i> ) <sub>4</sub>	0.082	<i>i</i> -PrMgCl	0.33	<i>i</i> -PrSi(OBu- <i>n</i> ) <sub>3</sub>	95	85
20	Si(OMe) <sub>4</sub>	0.20	<i>i</i> -PrMgCl	0.44	<i>i</i> -Pr <sub>2</sub> Si(OMe) <sub>2</sub>	93	91

<sup>a</sup> Yield was determined by analytical GLC.

<sup>b</sup> Yield of isolated compounds.

We also investigated the reaction of di(*n*-butoxy)dichlorosilane and tri(*n*-butoxy)chlorosilane with isopropylmagnesium chloride, to learn whether or not the *n*-butoxy group can be replaced by the isopropyl group. Thus, the reaction of di(*n*-butoxy)dichlorosilane with 4 equiv. of isopropylmagnesium chloride at 90 °C in a mixed solvent of THF and toluene in a ratio of 1:1.5 gave di(*n*-butoxy)diisopropylsilane in 94% yield (run 17). Similar reaction of tri(*n*-butoxy)chlorosilane with 4 equiv. of isopropyl-Grignard reagent afforded tri(*n*-butoxy)isopropylsilane in 93% yield (run 18). The results show that in both cases, only the chlorine atom can be replaced by the isopropyl group, but the *n*-butoxy group on the silicon atom is stable toward the Grignard reagent [4]. Again, the results indicate that introduction of the alkoxy group onto the silicon atom can greatly enhance the reactivity of the chlorine atoms on this silicon toward the Grignard reagent with a bulky substituent. In the reaction of tetra(*n*-butoxy)silane with isopropylmagnesium chloride, however, one of the *n*-butoxy groups can be replaced by an isopropyl group. Thus, the reaction of tetra(*n*-butoxy)silane with 4 equiv. of isopropylmagnesium chloride at 90 °C in a THF–toluene solution afforded tri(*n*-butoxy)isopropylsilane in 95% yield (run 19). Even in the prolonged reaction, no di- or triisopropylsilicon derivative was produced at all. However, the reaction of tetramethoxysilane with isopropyl-Grignard reagent under the same conditions produced diisopropylmethoxysilane in 93% yield (run 20). In this reaction, no triisopropylmethoxysilane was detected by GC–mass spectrometric analysis of the reaction mixture.

#### 2.4. Reaction of tetrachlorosilane with isopropylmagnesium chloride and then with methanol

When 4.8 equiv. of a THF solution of isopropylmagnesium chloride was added to 1 equiv. of tetrachlorosilane in THF, followed by addition of 1 equiv. of methanol to the resulting mixture, triisopropylmethoxysilane and triisopropylsilane were obtained in 59% and 26% yields, respectively (run 21), as shown in Table 4. Inverse addition of tetrachlorosilane in THF to isopropylmagnesium chloride (4.8 equiv.) in THF, and then addition of methanol (1 equiv.) gave the similar results. Two products, triisopropylmethoxysilane and triisopropylsilane were obtained in 61% and 27% yields (run 22). In both cases, significant amount of triisopropylsilane was obtained. When a toluene solution of tetrachlorosilane was added to isopropylmagnesium chloride (4.8 equiv.) in THF, followed by addition of methanol (1 equiv.), again triisopropylsilane was obtained in 28% yield, along with a 57% yield of triisopropylmethoxysilane (run 23). We followed the progress of reaction by GLC, and found that the formation of triisopropylsilane was observed only in the early stage of the reaction. Presumably, trichlorosilane is formed by the reaction of tetrachlorosilane with isopropylmagnesium chloride, and trichlorosilane thus formed reacts with isopropylmagnesium chloride to give triisopropylsilane (Scheme 2) [5].

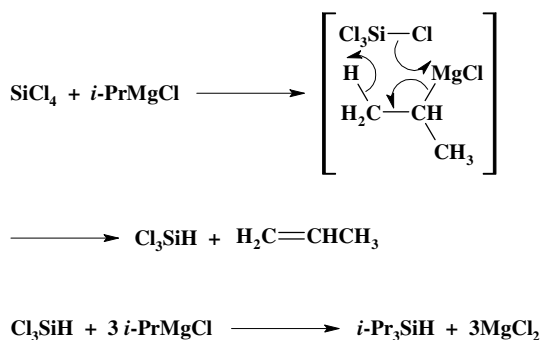
Interestingly, when isopropylmagnesium chloride in THF was added to a toluene solution of tetrachlorosilane, the yield of triisopropylsilane decreased significantly. Thus,

Table 4  
Reaction of *i*-PrMgCl with SiCl<sub>4</sub> dissolved in hydrocarbon, followed by treatment with MeOH

Run	SiCl <sub>4</sub> (mol)	<i>i</i> -PrMgCl (mol)	Diluent of SiCl <sub>4</sub>	Solvent of <i>i</i> -PrMgCl	MeOH (mol)	Addition	<i>i</i> -Pr <sub>3</sub> SiOMe		<i>i</i> -Pr <sub>3</sub> SiH
							Yield <sup>a</sup> (%)	Yield <sup>b</sup> (%)	Yield <sup>a</sup> (%)
21	0.12	0.58	THF	THF	0.12	<i>i</i> -PrMgCl	59	55	26
22	0.40	1.90	THF	THF	0.40	SiCl <sub>4</sub>		61	27
23	0.12	0.58	Toluene	THF	0.12	SiCl <sub>4</sub>	57	53	28
24	0.12	0.70	Toluene	THF	0.12	<i>i</i> -PrMgCl	78	75	7
25	0.07	0.42	Toluene	Toluene–THF	0.07	SiCl <sub>4</sub>	80	76	7
26	0.07	0.42	Isooctane	Isooctane–THF	0.07	SiCl <sub>4</sub>	78	74	6

<sup>a</sup> Yield was determined by analytical GLC.

<sup>b</sup> Yield of isolated compounds.



Scheme 2.

treatment of isopropylmagnesium chloride (5.8 equiv.) in THF with a toluene solution of tetrachlorosilane, followed by addition of methanol (1 equiv.), produced triisopropylsilane in only 7% yield. In this reaction, the desired triisopropylmethoxysilane was increased up to 78% yield (run 24). When a toluene solution of tetrachlorosilane was added to isopropyl-Grignard reagent (5.8 equiv.) in a mixed solvent of toluene–THF, followed by treatment with methanol (1 equiv.) gave triisopropylmethoxysilane and triisopropylsilane in 80% and 7% yields, respectively (run 25). Similarly, the reaction of isopropyl-Grignard reagent in an isooctane–THF solution with tetrachlorosilane in isooctane, and then addition of methanol afforded triisopropylmethoxysilane in 78% yield, in addition to a 6% yield of triisopropylsilane (run 26). These results clearly indicate that the use of hydrocarbon rich media in the reaction of isopropylmagnesium chloride with tetrachlorosilane can suppress the production of triisopropylsilane.

### 2.5. Reaction of methoxymethyldichloro- and methoxydimethylchlorosilane with Grignard reagents having a bulky substituent

The reactions of methyltrichlorosilane with Grignard reagents having a bulky alkyl group afford dialkylmethyl-

chlorosilanes in moderate yields. For examples, treatment of methyltrichlorosilane with isopropylmagnesium chloride in a mixed solvent of THF–toluene produced diisopropylmethylchlorosilane in 73% yield (run 27), as shown in Table 5. Similar treatment of methyltrichlorosilane with *sec*-butyl- and cyclohexylmagnesium chloride, however, gave di(*sec*-butyl)- and di(cyclohexyl)methylchlorosilane only in 17% and 25% yields, in addition to small amounts of the respective dialkylmethylsilanes (run 29 and 31).

We have found that the present method involving transformation of tetrachlorosilane to alkoxytrichlorosilane, followed by treatment with Grignard reagents can also be used for the synthesis of dialkylmethyl- and alkyl dimethylalkoxysilanes in excellent yields. Thus, the reaction of 4 equiv. of isopropylmagnesium chloride with 1 equiv. of methanol, followed by treatment of the resulting mixture with methyltrichlorosilane afforded diisopropylmethylmethoxysilane in 84% yield (run 28). Treatment of *sec*-butylmagnesium chloride with methanol and then with methyltrichlorosilane produced di(*sec*-butyl)methylmethoxysilane in 83% yield. Similarly, the reaction of cyclohexyl-Grignard reagent with methanol and methyltrichlorosilane gave dicyclohexylmethylmethoxysilane in 83% yield (run 30 and 32). These results clearly indicate that introduction of the methoxy group onto the silicon atom in methyltrichlorosilane can greatly enhance the reactivity of the remaining Cl–Si bond for Grignard coupling.

Similar improvements of the reactivity of the Cl–Si bond in the chlorosilanes for Grignard coupling have been observed in the reaction of dimethyldichlorosilane with Grignard reagents. Thus, introduction of the methoxy group onto the silicon atom in dimethyldichlorosilane always affords the products in Grignard coupling in excellent yields (run 33–38). In particular, the reaction of *tert*-butylmagnesium chloride with dimethyldichlorosilane gave no coupling product, *tert*-butyldimethylchlorosilane, while introduction of the methoxy group onto the silicon atom

Table 5  
Reaction of MeSiCl<sub>3</sub> and Me<sub>2</sub>SiCl<sub>2</sub> with Grignard reagents in the presence or absence of MeOH

Run	Chlorosilane (mol)		Grignard reagents (mol)		MeOH (mol)	Methoxy- or Chlorosilane		Hydrosilane		
						Yield <sup>a</sup> (%)	Yield <sup>b</sup> (%)		Yield <sup>a</sup> (%)	
27	MeSiCl <sub>3</sub>	0.12	<i>i</i> -PrMgCl	0.48	None	<i>i</i> -Pr <sub>2</sub> MeSiCl	73		<i>i</i> -Pr <sub>2</sub> MeSiH	0
28	MeSiCl <sub>3</sub>	1.0	<i>i</i> -PrMgCl	4.0	1.0	<i>i</i> -Pr <sub>2</sub> MeSiOMe	84	64	<i>i</i> -Pr <sub>2</sub> MeSiH	0
29	MeSiCl <sub>3</sub>	0.12	<i>s</i> -BuMgCl	0.48	None	<i>s</i> -Bu <sub>2</sub> MeSiCl	17		<i>s</i> -Bu <sub>2</sub> MeSiH	29
30	MeSiCl <sub>3</sub>	1.0	<i>s</i> -BuMgCl	4.0	1.0	<i>s</i> -Bu <sub>2</sub> MeSiOMe	83	70	<i>s</i> -Bu <sub>2</sub> MeSiH	1
31	MeSiCl <sub>3</sub>	0.12	<i>c</i> -HexMgCl	0.48	None	<i>c</i> -Hex <sub>2</sub> MeSiCl	25		<i>c</i> -Hex <sub>2</sub> MeSiH	4
32	MeSiCl <sub>3</sub>	0.25	<i>c</i> -HexMgCl	1.0	0.25	<i>c</i> -Hex <sub>2</sub> MeSiOMe	83	74	<i>c</i> -Hex <sub>2</sub> MeSiH	1
33	Me <sub>2</sub> SiCl <sub>2</sub>	0.048	<i>i</i> -PrMgCl	0.072	None	<i>i</i> -PrMe <sub>2</sub> SiCl	80		<i>i</i> -PrMe <sub>2</sub> SiH	0
34	Me <sub>2</sub> SiCl <sub>2</sub>	0.24	<i>i</i> -PrMgCl	0.6	0.24	<i>i</i> -PrMe <sub>2</sub> SiOMe	90	77	<i>i</i> -PrMe <sub>2</sub> SiH	0
35	Me <sub>2</sub> SiCl <sub>2</sub>	0.043	<i>s</i> -BuMgCl	0.12	None	<i>s</i> -BuMe <sub>2</sub> SiCl	79		<i>s</i> -BuMe <sub>2</sub> SiH	0
36	Me <sub>2</sub> SiCl <sub>2</sub>	0.45	<i>s</i> -BuMgCl	1.35	0.45	<i>s</i> -BuMe <sub>2</sub> SiOMe	90	71	<i>s</i> -BuMe <sub>2</sub> SiH	0
37	Me <sub>2</sub> SiCl <sub>2</sub>	0.041	<i>c</i> -HexMgCl	0.12	None	<i>c</i> -HexMe <sub>2</sub> SiCl	74		<i>c</i> -HexMe <sub>2</sub> SiH	3
38	Me <sub>2</sub> SiCl <sub>2</sub>	0.24	<i>c</i> -HexMgCl	0.71	0.24	<i>c</i> -HexMe <sub>2</sub> SiOMe	90	72	<i>c</i> -HexMe <sub>2</sub> SiH	0
39	Me <sub>2</sub> SiCl <sub>2</sub>	0.072	<i>t</i> -BuMgCl	0.18	None	<i>t</i> -BuMe <sub>2</sub> SiCl	0		<i>t</i> -BuMe <sub>2</sub> SiH	0
40	Me <sub>2</sub> SiCl <sub>2</sub>	0.072	<i>t</i> -BuMgCl	0.18	0.072	<i>t</i> -BuMe <sub>2</sub> SiOMe	62	54	<i>t</i> -BuMe <sub>2</sub> SiH	0

<sup>a</sup> Yield was determined by analytical GLC.

<sup>b</sup> Yield of isolated compounds.



in dimethyldichlorosilane afforded *tert*-butyldimethylmethoxysilane in 62% yield (run 40).

In conclusion, the reaction of alkoxy magnesium chlorides with tetrachlorosilane, followed by treatment of the resulting mixture with isopropylmagnesium chloride gave triisopropylalkoxysilanes in good yields. Treatment of tetrachlorosilane with isopropylmagnesium chloride in THF-hydrocarbon, followed by addition of methanol afforded triisopropylmethoxysilane in high yield. The reactions of *n*-butoxytrichlorosilane with isopropyl-, *sec*-butyl-, and cyclohexylmagnesium chloride produced the respective trialkyl(*n*-butoxy)silanes in excellent yields. Similar reactions of methoxymethyldichlorosilane and methoxydimethylchlorosilane with isopropyl-, *sec*-butyl- and cyclohexyl-Grignard reagent produced the corresponding dialkylmethylmethoxysilanes and alkyl dimethylmethoxysilanes in high yields. Treatment of methoxydimethylchlorosilane with *tert*-butylmagnesium chloride afforded *tert*-butyldi-methylmethoxysilane in good yield.

### 3. Experimental

#### 3.1. General procedure

All reactions were carried out under an atmosphere of dry nitrogen. NMR spectra were recorded on a JEOL JNM-LA 300 spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. Mass spectra were measured on a JEOL JMS-Automass SUN 200 instrument. Yields of the products were determined by analytical GLC with the use of hydrocarbon such as tridecane and octadecane as an internal standard. Tetrahydrofuran and toluene used as a solvent were dried over sodium under a nitrogen atmosphere and distilled just before use.

##### 3.1.1. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 1)

In a 300-ml flask was placed 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution. To this was added 1.33 g (0.042 mol) of methanol over a period of 30 min. The mixture was stirred at room temperature for 1 h, and to this was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. After evaporation of ca. 45 ml of the solvents at 70–95 °C over a period of 3 h, the residue was hydrolyzed with saturated aqueous solution of ammonium chloride. The organic layer was separated and washed with water, and analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (59% yield) and *i*-Pr<sub>3</sub>SiH (19% yield). The mixture was fractionally distilled to give 4.2 g (53% yield) of *i*-Pr<sub>3</sub>SiOMe.

##### 3.1.2. One-pot synthesis of *i*-Pr<sub>3</sub>SiOBu-*n* from SiCl<sub>4</sub> (run 2)

To a solution prepared from 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution and 3.1 g (0.042 mol) of *n*-BuOH was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOBu-*n* (51%

yield) and *i*-Pr<sub>3</sub>SiH (17% yield). The mixture was fractionally distilled to give 4.3 g (45% yield) of *i*-Pr<sub>3</sub>SiOBu-*n*. All spectral data obtained for *i*-Pr<sub>3</sub>SiOBu-*n* are identical with those of the authentic sample reported previously [6,7].

##### 3.1.3. One-pot synthesis of *i*-Pr<sub>3</sub>SiOHex-*n* from SiCl<sub>4</sub> (run 3)

To a solution prepared from 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution and 4.3 g (0.042 mol) of *n*-HexOH was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOHex-*n* (41% yield) and *i*-Pr<sub>3</sub>SiH (18% yield). The mixture was fractionally distilled to give 3.8 g (35% yield) of *i*-Pr<sub>3</sub>SiOHex-*n*. All spectral data obtained for *i*-Pr<sub>3</sub>SiOHex-*n* are identical with those of the authentic sample reported previously [8].

##### 3.1.4. One-pot synthesis of *i*-Pr<sub>3</sub>SiOPr-*i* from SiCl<sub>4</sub> (run 4)

To a solution prepared from 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution and 2.5 g (0.042 mol) of *i*-PrOH was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOPr-*i* (39% yield) and *i*-Pr<sub>3</sub>SiH (18% yield). The mixture was fractionally distilled to give 3.0 g (33% yield) of *i*-Pr<sub>3</sub>SiOPr-*i*. All spectral data obtained for *i*-Pr<sub>3</sub>SiOPr-*i* are identical with those of the authentic sample reported previously [9].

##### 3.1.5. One-pot synthesis of *i*-Pr<sub>3</sub>SiOBu-*t* from SiCl<sub>4</sub> (run 5)

To a solution prepared from 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution and 3.1 g (0.042 mol) of *t*-BuOH was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOBu-*t* (7% yield) and *i*-Pr<sub>3</sub>SiH (12% yield).

##### 3.1.6. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 6)

To a solution prepared from 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution and 1.8 g (0.021 mol) of Mg(OMe)<sub>2</sub> was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (51% yield) and *i*-Pr<sub>3</sub>SiH (28% yield).

##### 3.1.7. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 7)

To a mixture prepared from 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl-THF solution and 2.3 g (0.042 mol) of NaOMe was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 1 h at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (44% yield) and *i*-Pr<sub>3</sub>SiH (29% yield).

### 3.1.8. One-pot synthesis of *i*-Pr<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>CHMe<sub>2</sub> from SiCl<sub>4</sub> (run 8)

To a solution prepared from 100 ml (0.21 mol) of a 2.08M-*i*-PrMgCl–THF solution and 2.1 g (0.042 mol) of ethylene oxide was added 7.1 g (0.042 mol) of SiCl<sub>4</sub> over a period of 30 min at 30–40 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>CHMe<sub>2</sub> (47% yield) and *i*-Pr<sub>3</sub>SiH (15% yield). The mixture was fractionally distilled to give 4.1 g (40% yield) of *i*-Pr<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>CHMe<sub>2</sub>: b.p. 105 °C/9 Torr; MS *m/z* 245 (M + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.88 (d, 6H, H<sub>3</sub>CCCCO, *J* = 6.8 Hz), 1.00–1.10 (m, 3H, HC–Si), 1.04 (d, 18H, H<sub>3</sub>CCSi, *J* = 6.8 Hz), 1.42 (dt, 2H, –H<sub>2</sub>C–CO, *J* = 6.8 Hz, 6.8 Hz), 1.64–1.77 (m, 1H, –HC–CCO), 3.68 (t, 2H, –H<sub>2</sub>CO, *J* = 6.8 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) 12.2 (HC–Si), 18.1 (MeCSi), 22.8 (MeCCCCO), 24.8 (–CH–CCO), 42.3 (–CH<sub>2</sub>–CO), 61.8 (–CH<sub>2</sub>–O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) 11.3. Anal. Calc. for C<sub>14</sub>H<sub>32</sub>OSi: C, 68.78; H, 13.19. Found: C, 68.68; H, 13.10%.

### 3.1.9. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 9)

To 7.1 g (0.042 mol) of SiCl<sub>4</sub> in 50 ml of THF was added 1.33 g (0.042 mol) of methanol over a 30-min period, and stirred at the room temperature for 30 min. To this mixture was added 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl–THF solution over a period of 30 min at 30–65 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (53% yield) and *i*-Pr<sub>3</sub>SiH (4% yield).

### 3.1.10. One-pot synthesis of *i*-Pr<sub>3</sub>SiOBu-*n* from SiCl<sub>4</sub> (run 10)

To a solution prepared from 7.1 g (0.042 mol) of SiCl<sub>4</sub> in 50 ml of THF and 3.1 g (0.042 mol) of *n*-BuOH was added 100 ml (0.21 mol) of a 2.08 M-*i*-PrMgCl–THF solution over a period of 30 min at 30–65 °C, and then 25 ml of dry toluene. The mixture was concentrated and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOBu-*n* (51% yield) and *i*-Pr<sub>3</sub>SiH (1% yield).

### 3.1.11. One-pot synthesis of *s*-Bu<sub>3</sub>SiOBu-*n* from SiCl<sub>4</sub> (run 11)

To a solution prepared from 15.7 g (0.093 mol) of SiCl<sub>4</sub> in 50 ml of THF and 6.86 g (0.093 mol) of *n*-BuOH was added 250 ml (0.47 mol) of *s*-BuMgCl in a mixed solvent of THF–toluene (1:1.5) at –10–0 °C over a period of 2.5 h. The mixture was heated to reflux for 8 h and hydrolyzed in the usual way, and then analyzed by GLC, as being *s*-Bu<sub>3</sub>SiOBu-*n* (67% yield) and *s*-Bu<sub>3</sub>SiH (2% yield). The mixture was fractionally distilled to give 15.1 g (60% yield) of *s*-Bu<sub>3</sub>SiOBu-*n*. All spectral data obtained for *s*-Bu<sub>3</sub>SiOBu-*n* are identical with the authentic sample prepared below.

### 3.1.12. One-pot synthesis of *c*-Hex<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 12)

A mixture consisting of 15.9 g (0.094 mol) of SiCl<sub>4</sub> in 50 ml of THF, 3.00 g (0.094 mol) of methanol, and 250 ml (0.47 mol) of a *c*-HexMgCl–THF solution was heated to reflux for 5 h and then hydrolyzed in the usual way. The mixture was analyzed by GLC, as being *c*-Hex<sub>3</sub>SiOMe (51% yield) and *c*-Hex<sub>3</sub>SiH (1% yield). After evaporation of the solvents, white crystals were obtained. Recrystallization from hexane gave 11.6 g (40% yield) of *c*-Hex<sub>3</sub>SiOMe: m.p. 31.5–32.0 °C. All spectral data obtained for *c*-Hex<sub>3</sub>SiOMe are identical with those of the authentic sample reported previously [10].

### 3.1.13. Synthesis of *n*-BuOSiCl<sub>3</sub>

To 101.9 g (0.60 mol) of SiCl<sub>4</sub> was added 44.5 g (0.60 mol) of *n*-BuOH at room temperature. The mixture was heated to reflux for 1 h and distilled under reduced pressure to give 50 g (40% yield) of *n*-BuOSiCl<sub>3</sub>: b.p. 66–74 °C/62 Torr. All spectral data obtained for *n*-BuOSiCl<sub>3</sub> are identical with those of an authentic sample [11].

### 3.1.14. Reaction of *n*-BuOSiCl<sub>3</sub> with *i*-PrMgCl (run 13)

To 50 g of a mixed solvent (THF/toluene = 1/1.5) containing 0.12 mol of *i*-PrMgCl was added 6.2 g (0.029 mol) of *n*-BuOSiCl<sub>3</sub> at 90–100 °C for 10 min. The mixture was heated at 90 °C for 5 h, and then hydrolyzed as the usual manner. The organic layer was analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOBu-*n* (94% yield). The organic layer was distilled under reduced pressure to give 6.1 g (90% yield) of *i*-Pr<sub>3</sub>SiOBu-*n*: b.p. 100–102 °C/12 Torr.

### 3.1.15. Reaction of *n*-BuOSiCl<sub>3</sub> with *s*-BuMgCl (run 14)

To 875 g of a mixed solvent (THF/toluene = 1/1) containing 1.75 mol of *s*-BuMgCl was added 72.7 g (0.34 mol) of *n*-BuOSiCl<sub>3</sub> at 60–90 °C for 5 min. The mixture was heated at 90–100 °C for 27 h, and then hydrolyzed as the usual manner. The organic layer was analyzed by GLC, as being *s*-Bu<sub>3</sub>SiOBu-*n* (96% yield), and then distilled under reduced pressure to give 78.7 g (84% yield) of *s*-Bu<sub>3</sub>SiOBu-*n*: b.p. 120–122 °C/7 Torr; MS *m/z* 273 (M + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.81–0.94 (m, 3H, HC–Si), 0.89–1.03 (m, 21H, CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)– and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO), 1.11–1.24 (m, 3H, CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)– and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO), 1.27–1.40 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)– and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO), 1.42–1.56 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)– and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO), 1.61–1.74 (m, 3H, CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)– and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO), 3.64 (t, 2H, –H<sub>2</sub>C–O, *J* = 6.5 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) 13.60, 13.63, 13.65, 13.69, 13.72, 13.73 (CH<sub>3</sub>–C–C(CH<sub>3</sub>)–), 13.9 (CH<sub>3</sub>–C–C–), 19.0 (–CH<sub>2</sub>– in a *n*-BuO group), 19.7, 19.76, 19.80 (CH–Si), 24.5, 24.56, 24.58 (C–CH<sub>2</sub>–C(C)–), 35.1 (–CH<sub>2</sub>– in a *n*-BuO group), 63.1 (CH<sub>2</sub>O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) 10.5. Anal. Calc. for C<sub>16</sub>H<sub>36</sub>OSi: C, 70.51; H, 13.31. Found: C, 70.47; H, 5.89%.

### 3.1.16. Reaction of *n*-BuOSiCl<sub>3</sub> with *c*-HexMgCl (run 15)

To 50 ml of a mixed solvent (THF/toluene = 1/1.5) containing 0.12 mol of *c*-HexMgCl was added 6.2 g (0.029 mol) of *n*-BuOSiCl<sub>3</sub> at 5–25 °C for 10 min. The mixture was heated at 90–100 °C for 17 h, and then hydrolyzed as the usual manner. GLC analysis of the organic layer showed the presence of *c*-Hex<sub>3</sub>SiOBu-*n* in 92% yield. The solvent was evaporated and the crystalline residue was recrystallized with hexane to give 8.8 g (85% yield) of *c*-Hex<sub>3</sub>SiOBu-*n*: m.p. 131.0–131.5 °C. All spectral data obtained for *c*-Hex<sub>3</sub>SiOBu-*n* were identical with those reported in the literature [12].

### 3.1.17. Reaction of *n*-BuOSiCl<sub>3</sub> with *t*-BuMgCl (run 16)

In a 1-l four-necked flask was placed 700 g of a mixed solvent (THF/toluene = 1/1) containing 0.85 mol of *t*-BuMgCl. To this was added 35.1 g (0.17 mol) of *n*-BuOSiCl<sub>3</sub> at 25 °C for 2 h. The mixture was heated at 90–100 °C for 12 h. To the mixture was added 200 ml of tetraethylene glycol dimethyl ether, and then distilled under reduced pressure to give 8.7 g (22% yield) of *t*-BuCl<sub>2</sub>SiOBu-*n*: b.p. 95–96 °C/69 Torr; MS *m/z* 233, 231, 229 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.93 (t, 3H, H<sub>3</sub>C–CC, *J* = 7.4 Hz), 1.08 (s, 9H, H<sub>3</sub>C–CSi), 1.35–1.45 (m, 2H, –H<sub>2</sub>C–), 1.55–1.64 (m, 2H, –H<sub>2</sub>C–), 3.88 (t, 2H, –H<sub>2</sub>C–O, *J* = 6.4 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) 13.7 (CH<sub>3</sub>), 18.8 (–CH<sub>2</sub>–), 22.8 (C–Si), 24.8 (CH<sub>3</sub>), 33.7 (–CH<sub>2</sub>–), 64.4 (CH<sub>2</sub>O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) –8.7. Anal. Calc. for C<sub>8</sub>H<sub>18</sub>Cl<sub>2</sub>OSi: C, 41.92; H, 7.92. Found: C, 42.03; H, 7.97%.

### 3.1.18. Synthesis of (*n*-BuO)<sub>2</sub>SiCl<sub>2</sub>, (*n*-BuO)<sub>3</sub>SiCl, and (*n*-BuO)<sub>4</sub>Si

To 322.8 g (1.9 mol) of SiCl<sub>4</sub> was added 281.7 g (3.8 mol) of *n*-BuOH at room temperature. The mixture was heated to reflux for 1 h, and distilled under reduced pressure to give 53 g (11% yield) of (*n*-BuO)<sub>2</sub>SiCl<sub>2</sub>: b.p. 89–91 °C/7.5 Torr, 130 g (24% yield) of (*n*-BuO)<sub>3</sub>SiCl: b.p. 105–108 °C/4.5 Torr, and 26 g (4% yield) of (*n*-BuO)<sub>4</sub>Si: b.p. 121–123 °C/4.5 Torr. All spectral data obtained for (*n*-BuO)<sub>2</sub>SiCl<sub>2</sub>, (*n*-BuO)<sub>3</sub>SiCl, and (*n*-BuO)<sub>4</sub>Si are identical with those of the authentic samples [13–15].

### 3.1.19. Reaction of (*n*-BuO)<sub>2</sub>SiCl<sub>2</sub> with *i*-PrMgCl (run 17)

To 200 g of a mixed solvent (THF/toluene = 1/1.5) containing 0.42 mol of *i*-PrMgCl was added 26.0 g (0.11 mol) of (*n*-BuO)<sub>2</sub>SiCl<sub>2</sub> at 90–100 °C for 10 min. The mixture was heated at 90 °C for 12 h, and then hydrolyzed as the usual manner. The organic layer was analyzed by GLC, as being *i*-Pr<sub>2</sub>Si(OBu-*n*)<sub>2</sub> (94% yield). The organic layer was distilled under reduced pressure to give 23.8 g (86% yield) of *i*-Pr<sub>2</sub>Si(OBu-*n*)<sub>2</sub>: b.p. 107–108 °C/7.5 Torr; MS *m/z* 261 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.90 (t, 6H, H<sub>3</sub>C–CC, *J* = 7.3 Hz), 0.96–1.03 (m, 2H, HC–Si), 1.01 (d, 12H, H<sub>3</sub>C–CSi, *J* = 6.6 Hz), 1.36 (tq, 4H, –H<sub>2</sub>C–, *J* = 7.3, 7.3 Hz), 1.47–1.57 (tt, 4H, –H<sub>2</sub>C–, *J* = 6.5, 7.3 Hz), 3.71 (t, 4H, –H<sub>2</sub>C–O, *J* = 6.5 Hz); <sup>13</sup>C NMR δ

(CDCl<sub>3</sub>) 13.2 (C–Si), 13.9 (CH<sub>3</sub>–CC), 17.4 (CH<sub>3</sub>–CSi), 19.0 (–CH<sub>2</sub>–), 35.0 (–CH<sub>2</sub>–), 62.6 (CH<sub>2</sub>O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) –10.0. Anal. Calc. for C<sub>14</sub>H<sub>32</sub>O<sub>2</sub>Si: C, 64.55; H, 12.38. Found: C, 64.40; H, 12.28%.

### 3.1.20. Reaction of (*n*-BuO)<sub>3</sub>SiCl with *i*-PrMgCl (run 18)

To 200 g of a mixed solvent (THF/toluene = 1/1.5) containing 0.42 mol of *i*-PrMgCl was added 30.0 g (0.11 mol) of (*n*-BuO)<sub>3</sub>SiCl at 90–100 °C for 10 min. The mixture was heated at 90 °C for 12 h, and then hydrolyzed as the usual manner. The organic layer was analyzed by GLC, as being *i*-PrSi(OBu-*n*)<sub>3</sub> (93% yield). The organic layer was distilled under reduced pressure to give 26.2 g (85% yield) of *i*-PrSi(OBu-*n*)<sub>3</sub>: b.p. 113–114 °C/6 Torr; MS *m/z* 291 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.89 (t, 9H, H<sub>3</sub>C–CC, *J* = 7.1 Hz), 0.94–1.02 (m, 1H, HC–Si), 0.99 (d, 6H, H<sub>3</sub>C–CSi, *J* = 7.3 Hz), 1.34 (tq, 6H, –H<sub>2</sub>C–, *J* = 7.1, 7.7 Hz), 1.52 (tt, 6H, –H<sub>2</sub>C–, *J* = 6.5, 7.7 Hz), 3.72 (t, 6H, –H<sub>2</sub>C–O, *J* = 6.5 Hz); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) 11.0 (C–Si), 13.8 (CH<sub>3</sub>–CSi), 17.4 (CH<sub>3</sub>–CC), 18.9 (–CH<sub>2</sub>–), 34.7 (–CH<sub>2</sub>–), 62.6 (CH<sub>2</sub>O). All spectral data obtained for *i*-PrSi(OBu-*n*)<sub>3</sub> are identical with those of an authentic sample [16].

### 3.1.21. Reaction of (*n*-BuO)<sub>4</sub>Si with *i*-PrMgCl (run 19)

To 150 g of a mixed solvent (THF/toluene = 1/1.5) containing 0.33 mol of *i*-PrMgCl was added 26.3 g (0.082 mol) of (*n*-BuO)<sub>4</sub>Si at 90–100 °C for 10 min. The mixture was heated at 90 °C for 12 h, and then hydrolyzed as the usual manner. The organic layer was analyzed by GLC, as being *i*-PrSi(OBu-*n*)<sub>3</sub> (95% yield). The organic layer was distilled under reduced pressure to give 23.0 g (85% yield) of *i*-PrSi(OBu-*n*)<sub>3</sub>: b.p. 113–114 °C/6 Torr.

### 3.1.22. Reaction of *i*-PrMgCl with (MeO)<sub>4</sub>Si (run 20)

To 229 g (0.44 mol) of an *i*-PrMgCl–THF–Toluene solution (THF/Toluene = 1/1) was added 30.4 g (0.20 mol) of (MeO)<sub>4</sub>Si over a 30 min period at 60–70 °C. The mixture was heated to reflux for 12 h, and then hydrolyzed as the usual manner. The organic layer was analyzed by GLC, as being *i*-Pr<sub>2</sub>Si(OMe)<sub>2</sub> (93% yield). No *i*-Pr<sub>3</sub>SiOMe was detected in the reaction mixture. The organic layer was fractionally distilled to give 32.2 g (91% yield) of *i*-Pr<sub>2</sub>Si(OMe)<sub>2</sub>: b.p. 93–95 °C/80 Torr. All spectral data obtained for *i*-Pr<sub>2</sub>Si(OMe)<sub>2</sub> are identical with those of an authentic sample [17].

### 3.1.23. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 21)

To 21.2 g (0.12 mol) of SiCl<sub>4</sub> in 100 ml of THF was added 228 g (0.58 mol) of a THF solution of *i*-PrMgCl over a period of 30 min at 40–50 °C. To this was added 3.84 g (0.12 mol) of methanol without cooling. The mixture was heated to reflux for 4 h, and hydrolyzed in the usual way, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (59% yield) and *i*-Pr<sub>3</sub>SiH (26% yield). The mixture was fractionally distilled to give 12.9 g (55% yield) of *i*-Pr<sub>3</sub>SiOMe.



### 3.1.24. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 22)

To 873 ml (1.9 mol) of an *i*-PrMgCl–THF solution was added 68.0 g (0.40 mol) of SiCl<sub>4</sub> over a period of 1.5 h at 40–50 °C, and then 12.8 g (0.40 mol) of methanol without cooling. The mixture was heated to reflux for 4 h, and hydrolyzed in the usual way. The mixture was fractionally distilled with the use of a packed column to give 46.0 g (61% yield) of *i*-Pr<sub>3</sub>SiOMe (b.p. 108–110 °C/45–49 Torr) and 17.2 g (27% yield) of *i*-Pr<sub>3</sub>SiH (b.p. 101–106 °C/90–115 Torr). All spectral data obtained for *i*-Pr<sub>3</sub>SiOMe and *i*-Pr<sub>3</sub>SiH are identical with those of the authentic samples reported previously [6,10].

### 3.1.25. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 23)

To 228 g (0.58 mol) of a THF solution of *i*-PrMgCl was added 21.2 g (0.12 mol) of SiCl<sub>4</sub> in 100 ml of toluene and 3.84 g (0.12 mol) of methanol. The mixture was concentrated and hydrolyzed as the usual manner, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (57% yield) and *i*-Pr<sub>3</sub>SiH (28% yield). The mixture was fractionally distilled to give 12.5 g (53% yield) of *i*-Pr<sub>3</sub>SiOMe.

### 3.1.26. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 24)

To 21.2 g (0.12 mol) of SiCl<sub>4</sub> in 100 ml of toluene was added 275 g (0.70 mol) of a THF solution of *i*-PrMgCl and 3.84 g (0.12 mol) of methanol. The mixture was concentrated and hydrolyzed as the usual manner, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe (78% yield) and *i*-Pr<sub>3</sub>SiH (7% yield). The mixture was fractionally distilled to give 17.6 g (75% yield) of *i*-Pr<sub>3</sub>SiOMe.

### 3.1.27. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 25)

To 200 ml (0.42 mol) of an *i*-PrMgCl–THF solution was added 400 ml of toluene, and then 400 ml of the solvents was distilled off from the reaction mixture. To this was added 12.4 g (0.073 mol) of SiCl<sub>4</sub> in 100 ml of toluene and 2.33 g (0.073 mol) of methanol. The mixture was heated to reflux for 8 h, and hydrolyzed as the usual manner. GLC analysis of the mixture showed the presence of *i*-Pr<sub>3</sub>SiOMe and *i*-Pr<sub>3</sub>SiH in 80% and 7% yields. The mixture was fractionally distilled to give 10.4 g (76% yield) of *i*-Pr<sub>3</sub>SiOMe.

### 3.1.28. One-pot synthesis of *i*-Pr<sub>3</sub>SiOMe from SiCl<sub>4</sub> (run 26)

To 200 ml (0.42 mol) of an *i*-PrMgCl–THF solution was added 400 ml of isooctane, and then 400 ml of the solvents was distilled off from the reaction mixture. To this was added 12.4 g (0.073 mol) of SiCl<sub>4</sub> in 100 ml of isooctane and 2.33 g (0.073 mol) of methanol. The mixture was heated to reflux for 8 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOMe

(78% yield) and *i*-Pr<sub>3</sub>SiH (6% yield). The mixture was fractionally distilled to give 10.2 g (74% yield) of *i*-Pr<sub>3</sub>SiOMe.

### 3.1.29. Preparation of *i*-Pr<sub>3</sub>SiOBu-*t*

To 34.0 g (0.20 mol) of SiCl<sub>4</sub> was added 11.9 g (0.16 mol) of *t*-BuOH at room temperature. The mixture was heated to reflux for 1 h, and then distilled under reduced pressure to give 26.6 g (64% yield) of *t*-BuOSiCl<sub>3</sub>: 65 °C/148 Torr. To 4.2 g (0.020 mol) of *t*-BuOSiCl<sub>3</sub> in 50 ml of THF was added 86 ml (0.060 mol) of an *i*-PrLi–pentane solution over a period of 2 h at –10–0 °C, and the mixture was stirred at 0 °C for 1 h. The mixture was hydrolyzed with water and analyzed by GLC, as being *i*-Pr<sub>3</sub>SiOBu-*t* (85% yield). The mixture was fractionally distilled to give 2.7 g (59% yield) of *i*-Pr<sub>3</sub>SiOBu-*t*: b.p. 77 °C/9 Torr; MS *m/z* 231 (M + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.99–1.04 (m, 21H, H<sub>3</sub>C–CSi and HC–Si), 1.26 (s, 9H, H<sub>3</sub>C–CO); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>), 13.3 (CH–Si), 18.3 (CH<sub>3</sub>–CSi), 32.2 (CH<sub>3</sub>–CO), 71.3 (CO); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>), 5.7. Anal. Calc. for C<sub>13</sub>H<sub>30</sub>OSi: C, 67.75; H, 13.12. Found: C, 67.70; H, 13.08%.

### 3.1.30. Reaction of *i*-PrMgCl with SiCl<sub>4</sub> in the presence of a CuCN catalyst

To a mixture of 100 g (0.25 mol) of an *i*-PrMgCl–THF solution and 0.0445 g (49.7 × 10<sup>–2</sup> mmol) of CuCN was added 8.5 g (0.050 mol) of SiCl<sub>4</sub>. The mixture was heated to reflux for 4 h, and analyzed by GLC, as being *i*-Pr<sub>2</sub>SiCl<sub>2</sub> (68% yield), *i*-Pr<sub>3</sub>SiH (26% yield), and *i*-Pr<sub>3</sub>SiCl (less than 1% yield). All spectral data obtained for *i*-Pr<sub>2</sub>SiCl<sub>2</sub> are identical with those of the authentic sample reported previously [18].

### 3.1.31. One-pot synthesis of *i*-Pr<sub>2</sub>MeSiOMe from MeSiCl<sub>3</sub> (run 28)

To 1.33 l (4.0 mol) of an *i*-PrMgCl–THF solution was added 32.0 g (1.0 mol) of methanol, and then 149.5 g (1.0 mol) of MeSiCl<sub>3</sub>. The mixture was heated to reflux for 5 h, and hydrolyzed as the usual manner. The mixture was analyzed by GLC, as being *i*-Pr<sub>2</sub>MeSiOMe (84% yield). The mixture was fractionally distilled to give 96.7 g (64% yield) of *i*-Pr<sub>2</sub>MeSiOMe: b.p. 58 °C/38 Torr; MS *m/z* 161 (M + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.02 (s, 3H, Me–Si), 0.86–0.95 (m, 2H, HC–Si), 0.98 (d, 6H, Me–C, *J* = 8.1 Hz), 1.00 (d, 6H, Me–C, *J* = 6.8 Hz), 3.48 (s, 3H, Me–O); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –6.7 (Me–Si), 13.2 (HC–Si), 17.0 (Me–C), 17.1 (Me–C), 51.3 (Me–O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) 19.5. Anal. Calc. for C<sub>8</sub>H<sub>20</sub>OSi: C, 59.93; H, 12.57. Found: C, 59.90; H, 12.57%.

### 3.1.32. One-pot synthesis of *s*-Bu<sub>2</sub>MeSiOMe from MeSiCl<sub>3</sub> (run 30)

To 1.6 kg (4.0 mol) of a *s*-BuMgCl–THF–Toluene (1.6/1) solution was added 32.0 g (1 mol) of methanol, and then 149.5 g (1.0 mol) of MeSiCl<sub>3</sub>. The mixture was heated to reflux for 6 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *s*-Bu<sub>2</sub>MeSiOMe (83% yield)

and *s*-Bu<sub>2</sub>MeSiH (1% yield). The mixture was fractionally distilled to give 124.7 g (70% yield) of *s*-Bu<sub>2</sub>MeSiOMe: b.p. 78–81 °C/16–18 Torr; MS *m/z* 189 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.02 (s, 3H, Me–Si), 0.67–0.80 (m, 2H, HC–Si), 0.91–1.00 (m, 12H, H<sub>3</sub>CCC(CH<sub>3</sub>)–), 1.09–1.26 (m, 2H, CCH<sub>2</sub>C(C)–Si), 1.51–1.69 (m, 2H, CCH<sub>2</sub>C(C)–Si), 3.45 (s, 3H, Me–O); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –8.2, –8.0, –7.8 (Me–Si), 13.1, 13.16, 13.23 (Me–C), 13.27, 13.34, 13.4 (Me–C), 20.4, 20.5, 20.6 (HC–Si), 24.21, 24.23, 24.3 (CH<sub>2</sub>–C(C)–Si), 51.1 (Me–O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) 18.2. Anal. Calc. for C<sub>10</sub>H<sub>24</sub>OSi: C, 63.76; H, 12.84. Found: C, 63.70; H, 12.80%.

### 3.1.33. One-pot synthesis of *c*-Hex<sub>2</sub>MeSiOMe from Me<sub>2</sub>SiCl<sub>3</sub> (run 32)

To 417 g (1.0 mol) of a *c*-HexMgCl–THF solution was added 8.01 g (0.25 mol) of methanol, and then 37.4 g (0.25 mol) of Me<sub>2</sub>SiCl<sub>3</sub>. The mixture was heated to reflux for 4 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *c*-Hex<sub>2</sub>MeSiOMe (83% yield) and *c*-Hex<sub>2</sub>MeSiH (0.6% yield). The mixture was fractionally distilled to give 35.6 g (74% yield) of *c*-Hex<sub>2</sub>MeSiOMe: b.p. 129 °C/7 Torr; MS *m/z* 241 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) –0.01 (s, 3H, Me–Si), 0.78 (broad s, 2H, HC–Si), 1.20 (broad s, 10H, ring protons), 1.71 (broad s, 10H, ring protons), 3.46 (s, 3H, Me–O); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –8.4 (Me–Si), 24.9 (HC–Si), 27.0, 27.1, 27.3, 27.9, 28.0 (CH<sub>2</sub>), 51.3 (Me–O); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) 15.2. Anal. Calc. for C<sub>14</sub>H<sub>28</sub>OSi: C, 69.93; H, 11.74. Found: C, 69.87; H, 11.75%.

### 3.1.34. One-pot synthesis of *i*-PrMe<sub>2</sub>SiOMe from Me<sub>2</sub>SiCl<sub>2</sub> (run 34)

To 250 ml (0.6 mol) of an *i*-PrMgCl–THF solution was added 7.69 g (0.24 mol) of methanol, and then 31.0 g (0.24 mol) of Me<sub>2</sub>SiCl<sub>2</sub>. The mixture was heated to reflux for 4 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *i*-PrMe<sub>2</sub>SiOMe (90% yield). The mixture was fractionally distilled to give 24.6 g (77% yield) of *i*-PrMe<sub>2</sub>SiOMe: b.p. 104–105 °C/760 Torr; MS *m/z* 133 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.05 (s, 6H, Me–Si), 0.80–0.97 (m, 1H, HC–Si), 0.96 (d, 6H, Me–C, *J* = 6.2 Hz), 3.43 (s, 3H, Me–O); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –5.0 (Me–Si), 14.2 (HC–Si), 16.8 (Me–C), 50.5 (Me–O). All spectral data obtained for *i*-PrMe<sub>2</sub>SiOMe are identical with those reported in the literature [19].

### 3.1.35. One-pot synthesis of *s*-BuMe<sub>2</sub>SiOMe from Me<sub>2</sub>SiCl<sub>2</sub> (run 36)

To 500 g (1.35 mol) of a *s*-BuMgCl–THF solution was added 14.3 g (0.45 mol) of methanol, and then 57.4 g (0.45 mol) of Me<sub>2</sub>SiCl<sub>2</sub>. The mixture was heated to reflux for 6 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *s*-BuMe<sub>2</sub>SiOMe (90% yield). The mixture was fractionally distilled to give 46.2 g (71% yield) of *s*-BuMe<sub>2</sub>SiOMe: b.p. 128 °C/760 Torr; MS *m/z* 147 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.07 (s, 6H, Me–Si), 0.65–

0.71 (m, 1H, HC–Si), 0.94 (t, 3H, Me–CC, *J* = 7.2 Hz), 0.95 (d, 3H, Me–CSi, *J* = 7.5 Hz), 1.12–1.22 (m, 1H, –H<sub>2</sub>C–), 1.52–1.61 (m, 1H, –H<sub>2</sub>C–), 2.92 (s, 3H, Me–O); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –4.4 (Me–Si), 13.0 (Me–CSi), 13.3 (HC–Si), 21.8 (Me–CC), 24.1 (–CH<sub>2</sub>–), 50.4 (Me–O). All spectral data obtained for *s*-BuMe<sub>2</sub>SiOMe are identical with those reported in the literature [20,21].

### 3.1.36. One-pot synthesis of *c*-HexMe<sub>2</sub>SiOMe from Me<sub>2</sub>SiCl<sub>2</sub> (run 38)

To 300 ml (0.71 mol) of a *c*-HexMgCl–THF solution was added 7.59 g (0.24 mol) of methanol, and then 30.6 g (0.24 mol) of Me<sub>2</sub>SiCl<sub>2</sub>. The mixture was heated to reflux for 5 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *c*-HexMe<sub>2</sub>SiOMe (90% yield). The mixture was fractionally distilled to give 34.8 g (72% yield) of *c*-HexMe<sub>2</sub>SiOMe: b.p. 92–93 °C/41 Torr; MS *m/z* 173 (*M* + 1)<sup>+</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 0.04 (s, 6H, Me–Si), 0.67–0.75 (m, 1H, HC–Si), 1.06–1.21 (m, 5H, –H<sub>2</sub>C–), 1.72 (brs, 5H, –H<sub>2</sub>C–), 3.43 (s, 3H, Me–O); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) –4.7 (Me–Si), 26.4 (HC–Si), 26.8, 26.9, 27.9 (–CH<sub>2</sub>–), 50.5 (Me–O). All spectral data obtained for *c*-HexMe<sub>2</sub>SiOMe are identical with those reported in the literature [4,21,22].

### 3.1.37. One-pot synthesis of *t*-BuMe<sub>2</sub>SiOMe from Me<sub>2</sub>SiCl<sub>2</sub> (run 40)

To a solution prepared from 9.3 g (0.072 mol) of Me<sub>2</sub>SiCl<sub>2</sub> and 2.31 g (0.072 mol) of methanol was added 100 ml (0.18 mol) of a *t*-BuMgCl–THF solution at 20–25 °C for 30 min. The mixture was heated to reflux for 6 h and hydrolyzed as the usual manner, and then analyzed by GLC, as being *t*-BuMe<sub>2</sub>SiOMe (62% yield). The mixture was fractionally distilled to give 5.6 g (54% yield) of *t*-BuMe<sub>2</sub>SiOMe: b.p. 117–118 °C/760 Torr. All spectral data obtained for *t*-BuMe<sub>2</sub>SiOMe are identical with those reported in the literature [23].

## References

- [1] (a) A. Shirahata, Jpn. Tokkyo, JP 2069791; (b) N. Sakamoto, H. Taniguchi, A. Inada, M. Fujikawa, Jpn. Tokkyo, JP 2854832.
- [2] H. Gilman, R.N. Clark, J. Am. Chem. Soc. 69 (1947) 1499–1500.
- [3] A. Funatsu, T. Kubota, M. Endo, Jpn. Kokai Tokkyo Koho, JP 2001-039990.
- [4] I.I. Lapkin, R.G. Mukhina, N.F. Kirillov, Zh. Obshch. Khim. 57 (1987) 146–151.
- [5] (a) A.F. Reid, C.J. Wilkins, J. Chem. Soc. (1955) 4029–4034; (b) R. Corriu, G. Royo, J. Organomet. Chem. 40 (1972) 229–249; (c) N.W. Cusa, F.S. Kipping, J. Chem. Soc. (1933) 1040–1043; (d) M.C. Harvey, W.H. Nebergall, J.S. Peake, J. Am. Chem. Soc. 79 (1957) 2762–2764; (e) N.S. Marans, L.H. Sommer, F.C. Whitmore, J. Am. Chem. Soc. 73 (1951) 5127–5130; (f) L.H. Sommer, C.L. Frye, G.A. Parker, J. Am. Chem. Soc. 86 (1964) 3276–3279; (g) L.H. Sommer, G.A. Parker, C.L. Frye, J. Am. Chem. Soc. 86 (1964) 3280–3282.
- [6] L. Horner, J. Mathias, J. Organomet. Chem. 282 (1985) 155–174.
- [7] R.F. Cunico, L. Bedell, J. Org. Chem. 45 (1980) 4797–4798.

- [8] M. Weidebruch, W.J. Schiffer, *Organomet. Chem.* 90 (1975) 145–157.
- [9] J.S. Davies, C.L. Higginbotham, E.J. Tremeer, C. Brown, R.C. Treadgold, *J. Chem. Soc., Perkin Trans. 1* (1992) 3043–3048.
- [10] M.B. Lacout-Loustalet, J.P. Dupin, F. Metras, J. Valade, *J. Organomet. Chem.* 31 (1971) 337–368.
- [11] (a) H.A. Brune, *Chemische Berichte* 97 (1964) 2829–2847;  
(b) N.S. Kozlov, L.F. Akhmetshina, *Sb. Nauch. Tr., Perm. Politekh. Inst.* 18 (1966) 135–138.
- [12] M. Takakusa, *Bull. Chem. Soc. Jpn.* 36 (1963) 287–289.
- [13] D. Mochizuki, A. Shimojima, K. Kuroda, *J. Am. Chem. Soc.* 124 (2002) 12082–12083.
- [14] (a) A. Radecki, R.P. Staszewski, L. Kentzer, *Roczniki Chem.* 39 (1965) 819–826;  
(b) N.S. Kozlov, L.F. Akhmetshina, *Sb. Nauch. Tr., Perm. Politekh. Inst.* 18 (1966) 135–138.
- [15] (a) M.H.P.V. Genderen, H.M. Buck, *Recl. Trav. Chim. Pays-Bas, CODEN: RTCPA3* 106 (1987) 449–452;  
(b) H.A. Brune, *Chem. Ber., CODEN: CHBEAM* 98 (1965) 1998–2008.
- [16] R.C. Hartlein, C.R. Olson, *Ger. Offen.* 2,059,112.
- [17] Z. Lasocki, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 12 (1964) 281–287.
- [18] (a) D.C. Hurd, W.A. Yarnall, *J. Am. Chem. Soc.* 71 (1949) 755–756;  
(b) A.D. Petrov, N.P. Smetankina, G.I. Nikishin, *Zh. Obshch. Khim.* 25 (1955) 2332–2335.
- [19] R. Bakhtiar, C.M. Holznagel, D.B. Jacobson, *J. Am. Chem. Soc.* 114 (1992) 3227–3235.
- [20] V.J. Tortorelli, M. Jones Jr., *J. Am. Chem. Soc.* 102 (1980) 1425–1426.
- [21] V.J. Tortorelli, M. Jones Jr., S. Wu, Z. Li, *Organometallics* 2 (1983) 759–764.
- [22] (a) M. Ishikawa, M. Kumada, *J. Organomet. Chem.* 81 (1974) C3–C5;  
(b) C.G. Pitt, A.E. Friedman, D.H. Rector, M.C. Wani, *J. Organomet. Chem.* 121 (1976) 37–43.
- [23] (a) J. Schraml, M. Kviclova, V. Blechta, J. Cermak, *Magn. Reson. Chem.* 35 (1997) 659–662;  
(b) S.L. Ioffe, L.M. Makarenkova, V.A. Tartakovskii, *Izv. Akad. Nauk. SSSR. Ser. Khim.* 23 (1974) 463–465;  
(c) W.J. Leigh, R. Boukherroub, C. Kerst, *J. Am. Chem. Soc.* 120 (1998) 9504–9512;  
(d) G.S. Kim, D. Huffman, C.W. Dekock, *Inorg. Chem.* 28 (1989) 1279–1283.