



Selective catalytic monoreduction of dichlorooligosilanes with Grignard reagents



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ABSTRACT

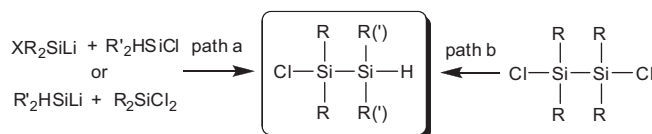
Transition metal-catalyzed monoreduction of dichlorooligosilanes with Grignard reagents is reported. Among the examined catalysts, group 4 metal chlorides such as TiCl_4 and Cp_2TiCl_2 gave the highest reactivity and good selectivity. The reducing power is effectively controlled by changing the catalysts and Grignard reagents to achieve sufficient selectivity depending on the oligosilane substrates.

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Studies on oligosilanes with unique properties and structures are one of the most rapidly developing research areas in organosilicon chemistry. For example, linear oligosilanes with fixed conformations,¹ push–pull oligosilanes,² polysilane dendrimers,³ and organosilicon clusters^{4–15} have recently been reported. To construct these oligosilanes, the design of appropriate organosilicon building blocks is very important.

1-Chloro-2-hydrodisilanes are simple but versatile organosilicon building blocks because two different groups can be introduced to the chlorosilane and hydrosilane moieties. In some special cases, 1-chloro-2-hydrodisilanes have been reported to be formed by silylene insertion to chlorohydrosilanes¹⁶ and by addition of hydrogen chloride to disilenes.^{17,18} More commonly, 1-chloro-2-hydrodisilanes can be synthesized by the reaction of (diethylamino)silyllithium with chlorohydrosilane followed by deaminochlorination¹⁹ and the reaction of hydrosilyllithium with dichlorosilane^{16a,20} (Scheme 1, path a). This method has usefully been used in the synthesis of 1-chloro-2-hydrodisilanes with different R and R' groups at the 1,1- and 2,2-positions, respectively.^{19,20}

For the synthesis of more simple 1-chloro-2-hydrodisilanes such as 1-chloro-2-hydro-1,1,2,2-tetramethyldisilane, selective monoreduction of readily available 1,2-dichlorodisilanes is a more desirable way (Scheme 1, path b). However, the desymmetrization of symmetrically substituted disilanes is not easy. For example, the reduction of 1,2-dichloro-1,1,2,2-tetramethyldisilane (**1**) with lithium aluminum hydride does not give 1-chloro-2-hydro-1,1,2,2-tetra-



Scheme 1. Methodologies for the synthesis of 1-chloro-2-hydrodisilanes.

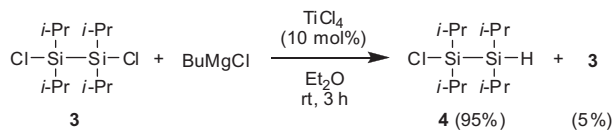
methyldisilane (**2**) selectively.²¹ Important progress in solving this problem was made by Roewer and co-workers.²² They reduced 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane with tributyltin hydride in the presence of a catalytic amount of tetrabutylphosphonium iodide and obtained 1-chloro-3-hydro-1,1,2,2,3,3-hexamethyltrisilane in 67% yield together with the starting compound and 1,3-dihydro-1,1,2,2,3,3-hexamethyltrisilane.²² Improvement of this method would lead to a practical synthetic way to 1-chloro-2-hydrodisilanes and their homologs. Another desymmetrization is the monochlorination of 1,2-dihydrodisilanes. Ishikawa, Kunai, Ohshita, and co-workers have reported selective monochlorination of 1,2-dihydrodisilanes with copper salts to give the corresponding 1-chloro-2-hydrodisilanes.²³

We report herein the transition metal-catalyzed reduction of 1,2-dichlorodisilanes with Grignard reagents. Although this reduction method has been reported for several decades,²⁴ the application was limited only to monosilanes. We found that the monoreduction of dichlorodisilanes by this method gives 1-chloro-2-hydrodisilanes selectively without Si–Si bond breaking. We also applied this method to longer dichlorooligosilanes.

A typical experimental procedure is as follows (Scheme 2). A solution of BuMgCl (3.2 equiv to disilane **3**) in diethyl ether was added dropwise to a solution of 1,2-dichloro-1,1,2,2-tetra-

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Scheme 2. Monoreduction of **3** with 3.2 equiv of BuMgCl and a catalytic amount of TiCl₄.

Table 1

Monoreduction of 1,2-dichlorodisilane **3** with 3.2 equiv of BuMgCl in the presence of various transition metal catalysts

Entry	Catalyst	Reaction time (h)	3 ^a (%)	4 ^a (%)
1	Cp ₂ TiCl ₂	1	1	97
2	TiCl ₄	3	5	95
3	ZrCl ₄	6	11	89
4	NbCl ₅	24	0	98
5	CrCl ₃	24	35	65
6	CoCl ₂	24	93	7
7	NiCl ₂	24	90	10

^a Yields were determined by GC.

Table 2

Monoreduction of 1,2-dichlorodisilane **3** with various Grignard reagents in the presence of TiCl₄

Entry	RMgCl (equiv)	Reaction time (h)	3 ^a (%)	4 ^a (%)
1	BuMgCl (3.2)	3	5	95
2	BuMgCl (1.6)	21	0	100
3	<i>i</i> -PrMgCl (3.2)	4.5	0	98
4	<i>i</i> -BuMgCl (3.2)	4	1	97
5	<i>t</i> -BuMgCl (3.2)	24	14	86

^a Yields were determined by GC.

disilane (**3**) in diethyl ether containing 10 mol % of TiCl₄ at 0 °C. The mixture was stirred at room temperature for 3 h. The GC analysis showed the formation of 1-chloro-2-hydro-1,1,2,2-tetraisopropyl-disilane (**4**) in 95% yield together with 5% of the remaining **3**.

The results of the monoreduction of **3** with BuMgCl in the presence of various transition metal catalysts are summarized in Table 1. Among the examined transition metal catalysts, Cp₂TiCl₂ showed the highest reactivity. The reaction was completed within 1 h (entry 1), and **4** was selectively formed in 97% yield. The reactivity of TiCl₄ and ZrCl₄ is lower, but the reactions were completed in 3 and 6 h, respectively to give **4** in good yields (entries 2 and 3). The reactivity of group 5 (NbCl₅, entry 4) and 6 (CrCl₃, entry 5) catalysts are much milder than the group 4 catalysts. The reduction with CoCl₂ (entry 6) or NiCl₂ (entry 7) did not proceed well, and most of the starting material **3** remained unchanged. These results show that early transition metal catalysts are more effective in this monoreduction. No reaction took place when the reaction was carried out without any catalysts.

We also examined the effect of Grignard reagents in the presence of TiCl₄ (Table 2). Although the reactivity changes depending on the employed Grignard reagents, high selectivity was preserved, and only a trace or small amount of the corresponding dihydrodisilane was detected. As shown in entry 2, the amount of BuMgCl can be reduced to 1.6 equiv without loss of the yield and selectivity although the prolonged reaction time was needed. The reducing ability of BuMgCl, *i*-PrMgCl and *i*-BuMgCl is almost the same (entries 1, 3 and 4). The reducing ability of *t*-BuMgCl, however, is significantly lower than those of others (entry 5). Probably, this is due to strong steric hindrance of the *tert*-butyl group.

Selective monoreduction of various dichlorodisilanes was examined by optimizing the reaction conditions such as the alkyl group of the Grignard reagent, its amount, and the reaction time (Table 3). Although Cp₂TiCl₂ is the best catalyst for the monoreduction of the isopropyl-substituted dichlorodisilane as shown in Table 1, its reactivity is too high in the case of the methyl-substituted dichlorodisilanes. As a result, dihydrooligosilanes were formed as by-products, and the selectivity of the monoreduction decreases. As TiCl₄ was found to have suitable reactivity to control the selectivity, we used TiCl₄ in the reduction of the methyl-substituted dichlorodisilanes. When 1,3-dichlorotrisi-

Table 3

Monoreduction of various dichlorooligosilanes with Grignard reagents in the presence of TiCl₄

Entry	Oligosilane	RMgCl (equiv)	Reaction time (h)	Product, yield ^a (%)
1	$ \begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \\ \quad \quad \\ \text{Cl}-\text{Si}-\text{Si}-\text{Si}-\text{Cl} \\ \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \\ \mathbf{5} \end{array} $	BuMgCl (4.0)	24	$ \begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \\ \quad \quad \\ \text{H}-\text{Si}-\text{Si}-\text{Si}-\text{H} \\ \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \\ \mathbf{6}, 65 \end{array} $
2	5	<i>i</i> -PrMgCl (4.0)	24	6 , 90
3	5	<i>i</i> -PrMgCl (2.0)	3	$ \begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \\ \quad \quad \\ \text{Cl}-\text{Si}-\text{Si}-\text{Si}-\text{H} \\ \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \\ \mathbf{7}, 87 \text{ (67)} \end{array} $
4	$ \begin{array}{c} \text{Me} \quad \text{Me} \\ \quad \\ \text{Cl}-\text{Si}-\text{Si}-\text{Cl} \\ \quad \\ \text{Me} \quad \text{Me} \\ \mathbf{1} \end{array} $	<i>t</i> -BuMgCl (2.1)	6.5	$ \begin{array}{c} \text{Me} \quad \text{Me} \\ \quad \\ \text{Cl}-\text{Si}-\text{Si}-\text{H} \\ \quad \\ \text{Me} \quad \text{Me} \\ \mathbf{2}, 100 \end{array} $
5	$ \begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \quad \quad \quad \\ \text{Cl}-\text{Si}-\text{Si}-\text{Si}-\text{Si}-\text{Cl} \\ \quad \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \mathbf{8} \end{array} $	<i>i</i> -PrMgCl (2.0)	2.5	$ \begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \quad \quad \quad \\ \text{X}-\text{Si}-\text{Si}-\text{Si}-\text{Si}-\text{H} \\ \quad \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \mathbf{9}: \text{X} = \text{Cl}, 80 \text{ (58)} \\ \mathbf{10}: \text{X} = \text{H}, 17 \end{array} $
6	$ \begin{array}{c} \text{Me}_2 \\ \\ \text{Cl}-\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}-\text{Cl} \\ \quad \\ \text{Me}_2 \quad \text{Me}_2 \\ \mathbf{11} \end{array} $	<i>i</i> -PrMgCl (2.0)	20	$ \begin{array}{c} \text{Me}_2 \\ \\ \text{X}-\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}-\text{H} \\ \quad \\ \text{Me}_2 \quad \text{Me}_2 \\ \mathbf{12}: \text{X} = \text{Cl}, 47^{\text{b}} \\ \mathbf{13}: \text{X} = \text{H}, 46^{\text{b}} \end{array} $

^a Yields were determined by GC. Isolated yields were given in parentheses.

^b NMR yields.

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