Catalytic Hydrosilane Synthesis via Reduction of Alkoxysilanes with Boranes

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Chapter 1

General Introduction

1. Silicone

Silicon is an element that is included as an earth's crustal major component at 25.8%. This is the second most abundant next to oxygen (48%), and much more than carbon (0.08%), which is the same Group 14 element as silicon. Silicon exists in nature as inorganic compounds such as silicon dioxide and silicate. For this reason, silicon has long been used as an inorganic material such as glass, ceramics and bricks. On the other hand, organosilicon materials represented by “silicone” appear in the 19th century, and are nowadays widely used in various fields. Figure 1-1 exhibits a structure of a silicone main chain, which has siloxane bonds with organic substituents on the silicon atoms.

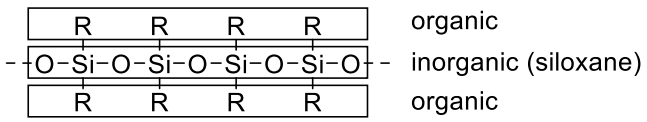


Figure 1-1. Structure of silicone

Silicones can vary their forms (oil, rubber, and resin) depending on their high-dimensional structure. Silicone has various features such as light resistance, flame retardancy, gas permeability. In addition, by introducing various

functional groups, it is possible to produce various high-performance materials with enhanced functions. For example, the introduction of fluoroalkyl groups and polyether groups enhance the chemical resistance and water-solubility, respectively. As a result, silicones are utilized in a wide range of fields such as food, cosmetics, electronic materials, automobiles, pharmaceutical materials, etc.

2. Organosilicon compound

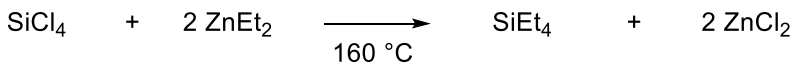
Herein, synthesis of organosilicon compounds as important precursors of silicones, which don't exist in nature, is summarize form the historical point of view.

In 1823, Berzelius reported the synthesis of $SiCl_4$ by the reaction of silicon metal with Cl_2.[1] It is to be noted that he demonstrated the first isolation of silicon metal by reducing SiF_4 with potassium. [1] As a result, synthesis of organosilicon compounds was performed using $SiCl_4$ as a raw material in the early days of organosilicon chemistry.

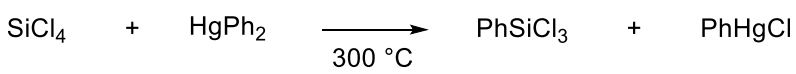
2-1. Synthetic method using organometallic reagents

In 1863, the first organosilicon compound $SiEt_4$ was synthesized by Friedel and Crafts.[2] They found that organosilicon compounds could be prepared by heating $SiCl_4$ with $ZnEt_2$ in sealed tubes at 160 °C (Scheme 1-1(a)). In 1872, Ladenberg reported the synthesis of $PhSiCl_3$ by heating $HgPh_2$ and $SiCl_4$ at 300 °C in a sealed tube (Scheme 1-1(b)).[3] These methods using organozinc- and organomercury reagents are rarely used in recent years because of their low reaction efficiency and toxicity of the reagents. In 1885, Polis reported the synthesis of organosilicon compounds by Wurtz-Fitting reaction using sodium (Scheme 1-1(c)).[4] In 1904, Kipping and coworkers established the synthetic methods of organosilicon compounds using the Grignard reagent (Scheme 1-1(d)).[5] Since then, reactions using organolithium[6] or organoaluminum[7] have also been reported. Since Grignard reagents can be easily prepared and applied to the synthesis of organosilicon compounds with various substituents, the method is now recognized as one of the most important synthetic methods in the organosilicon chemistry.

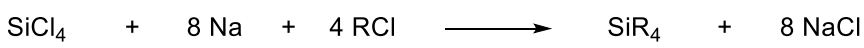
(a) Friedel, Crafts (1863)



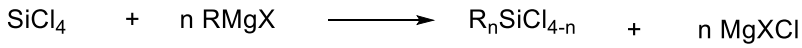
(b) Ladenburg (1872)



(c) Polis (1885)



(d) Kipping (1904-)

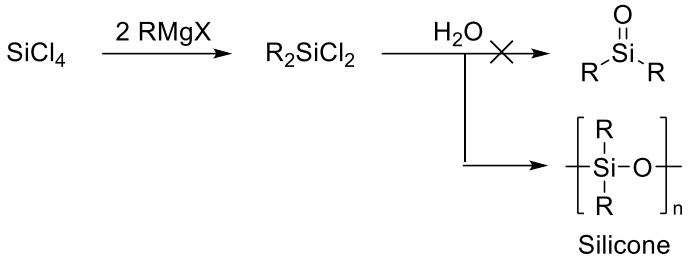


Scheme 1-1. Synthetic method of organosilicon compound using organometallic reagents

2-2. Direct process[8]

As a mass-production method of organosilicon compounds, “direct process” is conducted in the silicon industry. In this section, historical background of the direct method is outlined.

Silicones were first synthesized by Kipping in the 1900's by hydrolysis of dialkyldichlorosilanes synthesized using Grignard reagents. The gummy compound was recognized as the silicon analogue of the ketone because the concept of polymers had not been established at that time, and named “silicone”. Later, it was revealed that “silicone” exhibits a polymer structure whose main chain is composed of siloxane bonds (Scheme 1-2).

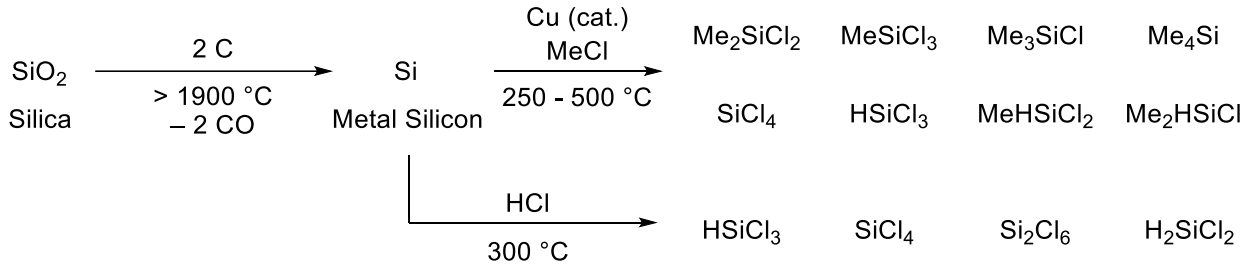


Scheme 1-2. Synthesis of silicone by hydrolysis of chlorosilane

In 1930s, there was an increasing demand for the development of a polymer material with high heat resistance in the electrical industry. In this context, the American glass company, Corning Glass Works, attempted to produce flexible heat-resistant materials which exhibit the properties of both plastics and glasses. Then, Hyde and Delong focused on silicon as one of the constituent elements of glass, and succeeded in developing a silicone resin with high thermal stability by synthesizing various organosilicon compounds using Grignard reagent.[9] Based on this research, Corning Glass Works and Dow Chemical set up Dow Corning Corporation to manufacture silicones, and began industrial production of silicones in 1944.

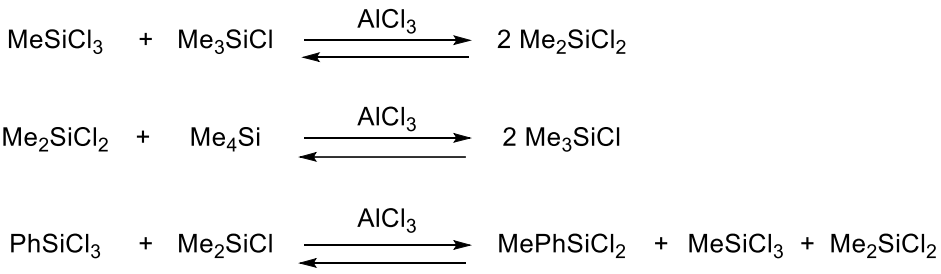
In the same period, General Electric Co. also focused on silicones. Until that time, organosilicon compounds were mainly produced by the reaction of chlorosilanes with Grignard reagents. However, in the synthesis of organosilicon compounds using the Grignard reagent, there are some drawbacks: 1) low yield of dialkyldichlorosilanes, an important raw material of silicones, 2) multi-step-reaction including preparation of Grignard reagents, and adding the reagent to chlorosilane, 3) Formation of magnesium salts as by-products. Based on these backgrounds, a new process for producing organosilicon compounds was developed by Rochow and Gilliam in 1941, and commercial production have been started in 1947. The method is so-called “direct process”, which are utilized in the silicon industry until now. In the direct process, metal silicon obtained by carbon reduction of silicon dioxide in an electric arc furnace is used as a raw material.[10] The metal silicon react with methyl chloride in the presence of a copper catalyst at 250 - 500 °C to obtain a complex mixture including Me_2SiCl_2 (Scheme 1-3).[11] The chlorosilanes having

phenyl group are synthesized in the similar method.[12] Trichlorosilane is similarly produced by treating metal silicon with blowing hydrogen chloride at 300 °C (Scheme 1-3).[13]



Scheme 1-3. Direct process

The resulting mixture is separated by fractional distillation, and less demanding fractions are reconverted to useful chlorosilanes through a process of redistribution reaction (Scheme 1-4).[14] Such exchange reactions were developed by Sauer[14a-c, 14f] and Barry[14d] in the 1940s and 1950s, and it was reported that the reactions proceed efficiently by using $AlCl_3$ and $NaAlCl_4$ as catalysts. As a result of the finding of this Al-catalyzed disproportionation reaction, the utility of the direct method become extremely enhanced as a mass-production of methyl- or phenyl substituted chlorosilanes, which are required in large quantities in silicone production.



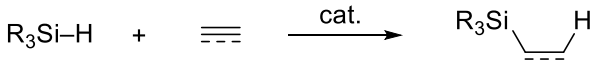
Scheme 1-4. Redistribution of chlorosilane

3. Hydrosilane

As described above, organosilicon compounds are extremely useful compounds. Besides the two organosilicon synthetic methods shown in sections 2-1 and 2-2, other synthetic procedures of organosilicon compounds using hydrosilanes are known. For the production of organosilicon compounds, hydrosilanes, in addition to chlorosilane, are also extremely important raw materials. This section describes the usefulness of hydrosilanes.

3-1. Hydrosilylation[15]

Hydrosilylation is an important reaction widely used in the silicon industry.[16] Hydrosilylation reactions undergo addition of hydrosilanes to olefins and alkynes (Scheme 1-5). Many studies have been conducted since the reaction was initially reported by Sommer's group[17] and Barry[18] in the 1940s.



Scheme 1-5. Hydrosilylation

Various catalysts compounds such as peroxides, amines and phosphines are known as catalysts of hydrosilylation, but metal catalysts, in particular platinum catalysts including Speier's catalyst[19] and Karstedt's catalyst[20] are normally used since they exhibit high activity and high reaction selectivity (Figure 1-2). In recent years, instead of platinum catalysts, various metal catalysts, which are composed of abundant and non-precious metals, have also been reported to date.[21]

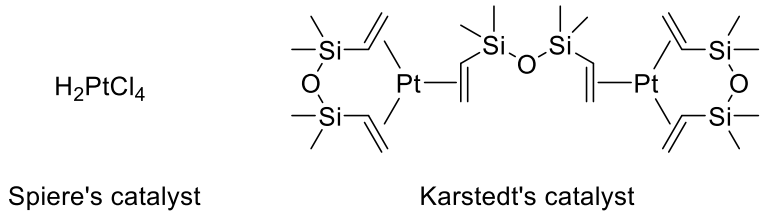
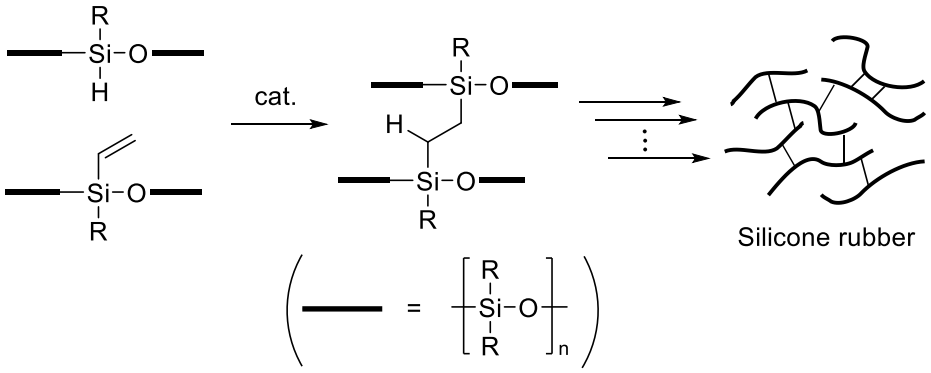


Figure 1-2. Typical platinum catalyst

An advantage of the hydrosilylation is that it is possible to synthesize an organosilicon compound having a functional group on an organic group, which is difficult to be introduced by an approach using an organometallic reagent. For this reason, it is an indispensable reaction in producing raw materials of silicone having various functions and silane coupling agents. Also, since hydrosilylation is an addition reaction, the atomic efficiency of the reaction is high, and by-products of the same amount as the substrate are not formed, and the reaction proceeds even with a small amount of catalyst, so it is also used for the curing reaction of silicones. In this reaction, silicone oil can be converted to rubber or resin by reactions between silicones having vinyl groups and silicones having Si–H bonds (Scheme 1-6).



Scheme 1-6. Curing reaction of silicone by hydrosilylation

3-2. Application of hydrosilane to organic synthesis

3-2-1. Reduction of organic compounds using hydrosilane

Hydrosilanes are widely used in organic synthesis besides hydrosilylation. Among them, hydrosilanes are normally safer and easier-handling reducing agent than metal hydrides such as $LiAlH_4$, with the exception of some hydrosilanes such as silane gas. Hydrosilanes are used in various reduction reactions such as reduction of carbonyl compound, dehalogenation reaction, and deoxygenation reaction of phosphine,[22] because silicon forms a strong bond with electronegative elements such as nitrogen, oxygen and halogen (Figure 1-3).[23]

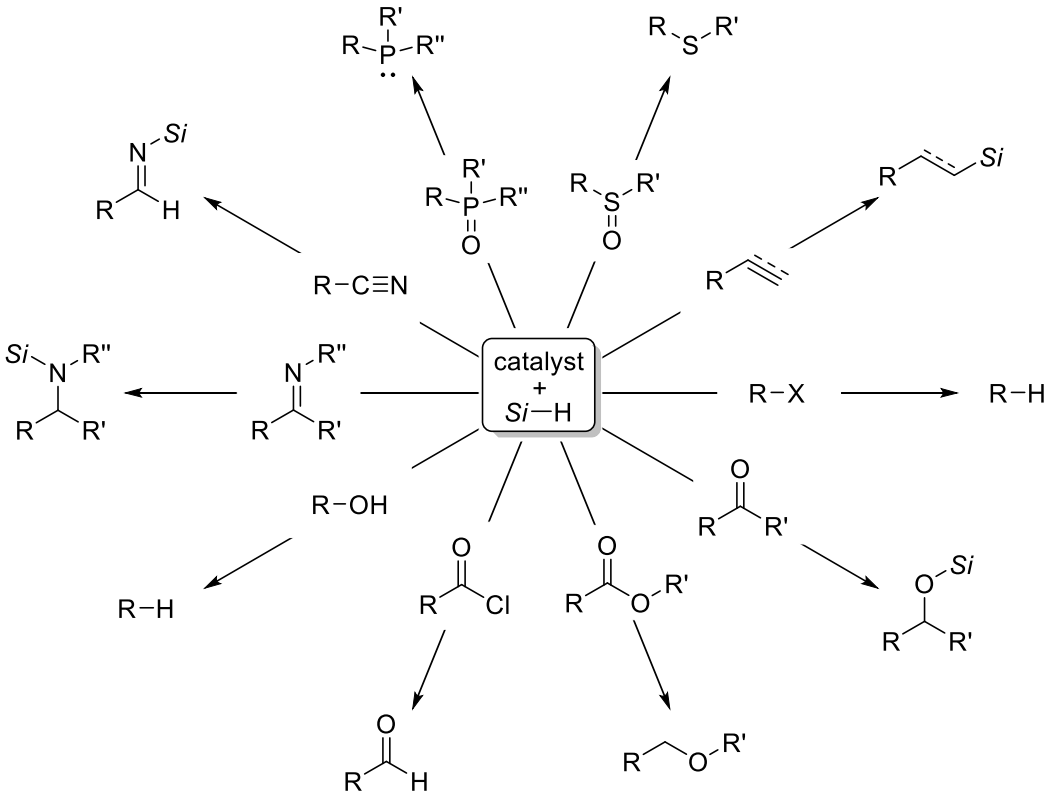
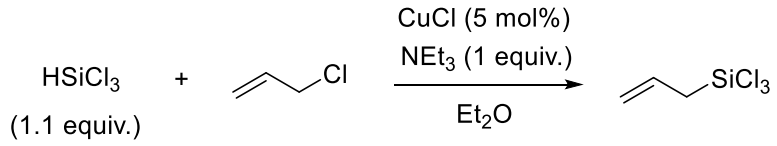


Figure 1-3. Reduction of organic compounds using hydrosilane

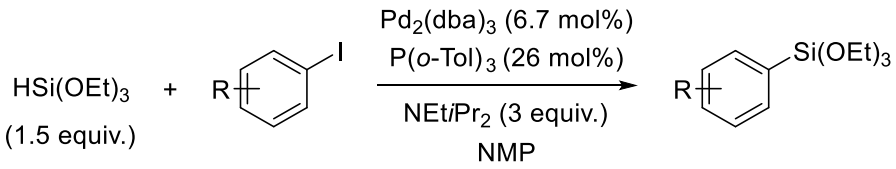
3-2-2. Silylation of organic halides with hydrosilanes

In recent years, new Si–C bond formation reactions using hydrosilanes have been reported. One of them is a silylation of an organic halide using a hydrosilane. Among these reactions, the silylation of allyl chloride with $HSiCl_3$ is well known as a synthetic method of allylsilanes (Scheme 1-7).[24] On the other hand, in the reactions of organic halide with hydrosilane, hydrosilanes mainly act as reducing agents to form a C–H bond, and only a small amount of arylsilane is generated as a by-product.[25]



Scheme 1-6. Synthesis of allylsilane using hydrosilane.

The selective synthesis of arylsilanes was first reported by the reaction of aryl iodide with $HSi(OEt)_3$ in the presence of a palladium catalyst by Masuda's group (Scheme 1-8).[26]



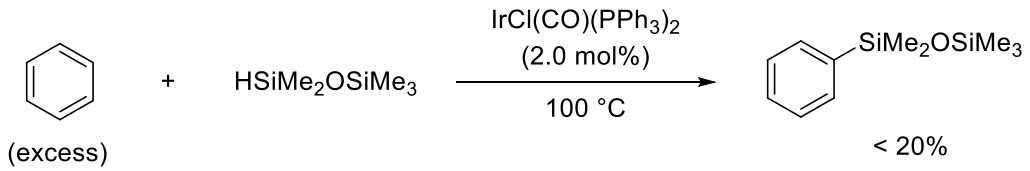
Scheme 1-8. Silylation of aryl iodides with hydrosilanes

Subsequently, various reactions have been reported, such as reactions using a rhodium catalyst having higher functional group tolerance[27] and reactions using aryl bromide as a substrate[28]. The silylation of aryl halide can easily

synthesize arylsilanes having a functional group. For this reason, it is utilized also for the synthesis of arylating agents in Hiyama coupling[29] and for the synthesis of precursors of functional mesoporous silica[30].

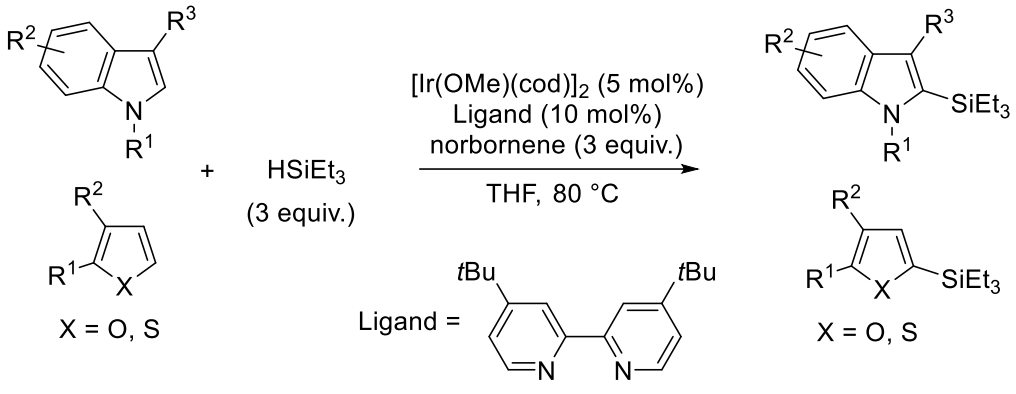
3-2-3. Direct silylation of C–H bonds[31]

Direct silylation of the C–H bond differs from silylation of organic halide, which enables us to reduce reaction steps since it is not necessary to introduce a halogen. Also, ideally, since the by-product is only hydrogen gas, it is an excellent reaction process with high atomic efficiency, and research has been actively conducted in recent years. The direct silylation of benzene reported by Curtls's group in 1982 is an important reaction as the first example of direct silylation of C–H bond, although its yield is very low and impractical. (Scheme 1 -8).[32]



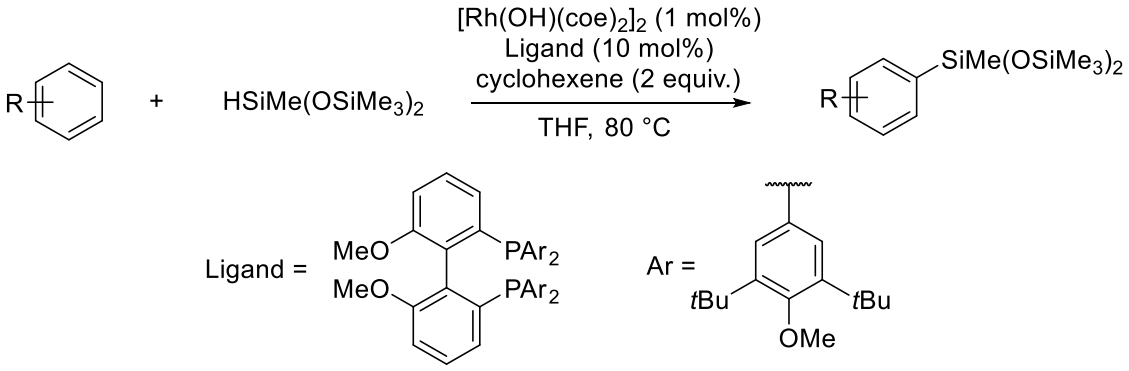
Scheme 1-8. First example of direct silylation of C–H bond.

After that, many reactions have been reported from various groups. However, since activation of inert C–H bonds is generally difficult, there are some problems such as severe reaction conditions, low regioselectivity and narrow substrate scope. Among them, heteroaromatic C–H bond silylation was reported by Falck's group in 2008.[33] In this reaction, 2-position selective silylation reaction of electron-rich heterocycles such as indole, furan and thiophene has been reported using Ir catalyst and norbornene as hydrogen acceptor (Scheme 1-9).



Scheme 1-9. Direct silylation of C–H bonds in heteroaromatic compounds.

Regarding the silylation of the aryl group, Hartwig *et al*. succeeded in constructing a practical reaction using a Rh catalyst and cyclohexene as a hydrogen acceptor in 2014.[34] The reaction proceeds only 1 mol% catalyst loading to achieve good yield and high regioselectivity (Scheme 1-10). In addition, Hartwig's group has also succeeded in developing highly functional group-tolerant reactions using Ir catalysts, and has succeeded in significantly expanding the substrate scope coverage.[35] Furthermore, in this reaction, silylation of pyridine and quinolines, which are relatively electron-deficient heterocycles and cannot be adopted in the previously reported Flack's reactions, is possible.

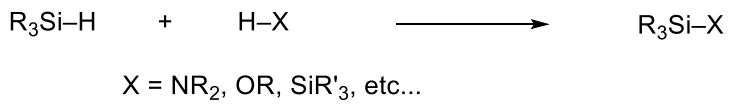


Scheme 1-10. Silylation of aryl C–H bonds

In recent years, Friedel-Crafts C–H silylation of electron rich aromatic compound using Ru complex[36], $B(C_6F_5)_3$[37] and $[H(OEt_2)_2]$ $[BAr^F{}_4]$[38], and C–H silylation via a radical mechanism of heteroaromatic compound using K*t*OBu[39] have also been reported. Thus, the direct silylation of C–H bonds has achieved rapid growth in recent years, and it is a reaction that can be expected for future developments.

3-2-4. Other applications

In addition to above reactions, hydrosilanes are widely used in the synthesis of silicon compounds other than organosilicon compounds.[40] As mentioned above, in the reduction of carbonyl compounds and imines, a Si–N bond and a Si–O bond are formed. It is also known that the Si–N[41] bond and Si–O[42] bond can be also formed by dehydrogenation coupling reactions. Besides, it is also possible to form Si–Si bond[43], Si–P bond[44], and Si–S bond[45].

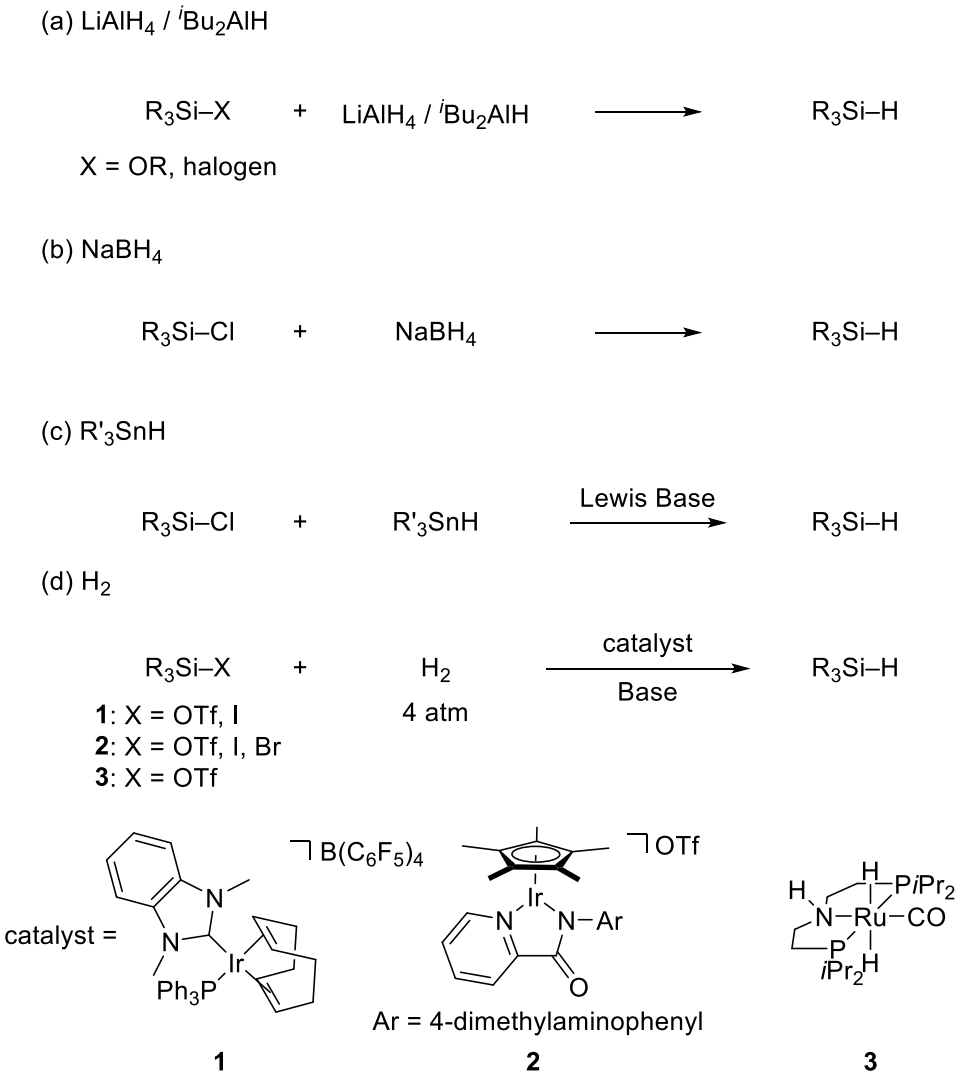


Scheme 1-11. Dehydrogenative coupling

4. Synthesis of hydrosilane

As mentioned above, hydrosilanes are useful compounds which can be used as precursors of various organosilicon compounds and as reducing agents in organic synthesis. Some hydrosilanes, such as $HSiCl_3$ and $MeSiHCl_2$, are synthesized in large quantities as products of the direct process. Many other hydrosilanes are synthesized by reducing chlorosilanes and alkoxysilanes with $LiAlH_4$[46] or $^iBu_2AlH$[47], but these reducing agents are self-igniting and involve dangers in handling and storage. In addition, these reagents have low functional group tolerance. In the reduction of chlorosilane, a reaction using relatively mild reducing agents such as $NaBH_4$[48] or $HSn(nBu)_3$[49] is also

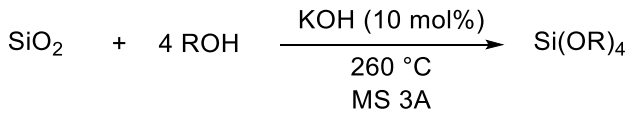
known. Furthermore, in the reduction of the more reactive halosilane, a reaction using hydrogen gas as a reducing agent has also been reported (Scheme 1-12). [50]



Scheme 1-12. Synthetic method of hydrosilane

On the other hand, the reaction using a mild reducing agent of alkoxysilane is very limited. This is because the Si–O bond is very strong (Si–O: 110 kcal / mol)[51] and the alkoxy group is poor leaving group. In recent years, a method of directly synthesizing tetraalkoxysilane by the reaction of silicon dioxide with alcohol has been developed

(Scheme 1-13).[52] Since this reaction can be performed under mild reaction conditions to efficiently produce alkoxysilanes, alkoxysilanes are attracting attention as the next generation of raw materials for synthesizing hydrosilanes and organosilicon compounds at lower cost and lower energy.



Scheme 1-13. Alkoxysilane synthesis via a reaction of silica with alcohol

5. Overview

In this study, we developed two new synthetic methods aiming at development of alkoxysilane reduction reaction under mild conditions. In Chapter 2, the reduction of alkoxysilane with HBpin was carried out using a metallocene-type yttrium complex. In Chapter 3, the borane reduction of alkoxysilane was carried out using Lewis base catalyst. By applying this reaction, a reduction of alkoxysilane was also performed by generating BH_3 from $NaBH_4$ which is inexpensive and easy to handle reductant

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Chapter 2

Reduction of Alkoxysilanes with Borane catalyzed by Metallocene-Type Yttrium Catalysts

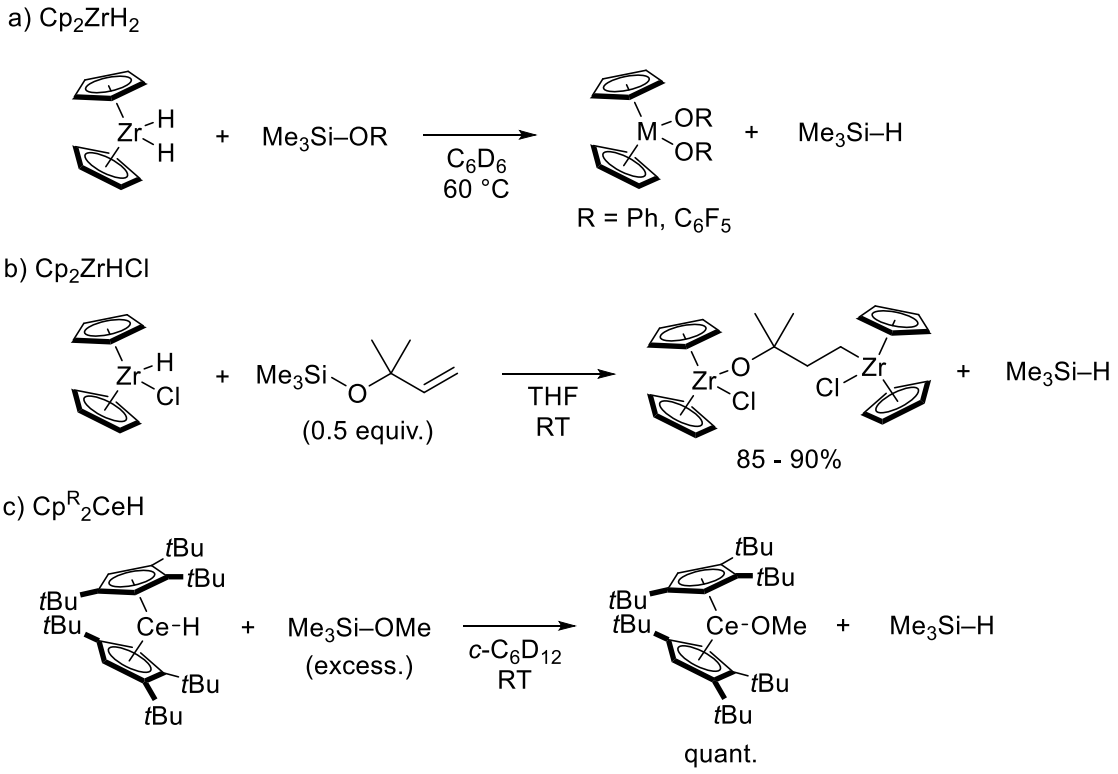
Abstract

The catalytic reduction of alkoxysilanes with the borane HBpin (pin = pinacolato) was achieved using a metallocene-type yttrium complex as a catalyst precursor. Mechanistic study supported the pivotal role of the rigid metallocene structure of the catalyst, which bears two bulky η^5-$C_5Me_4SiMe_3$ ligands, in suppressing the coordination of the side product MeOBpin that is generated during the reaction.

Introduction

This chapter describes the reduction of alkoxysilanes with borane using yttrium catalyst. As mentioned in Chapter 1, it is important to develop efficient synthetic route to achieve reduction of alkoxysilanes. However, the study is challenging because the achievement of this reaction requires the stable Si–O bond (110 kcal / mol)[1] cleavage of alkoxysilanes.

It is widely known that alkoxysilanes can be reduced using $LiAlH_4$.[2] In addition to this, reactions using an early transition metal- or a rare earth metal hydrides are reported so far (Scheme 2-1).[3,4]

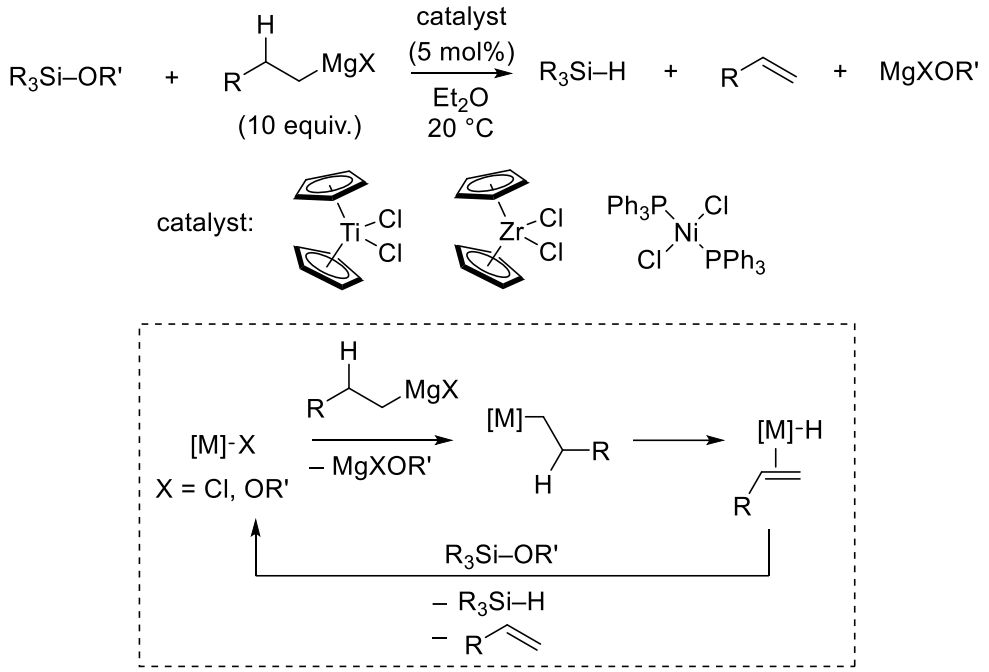


Scheme 2-1. Stoichiometric reduction of alkoxysilanes

For example, a stoichiometric reduction of alkoxysilane using Cp_2ZrH_2, Cp_2ZrHCl, $Cp^R{}_2CeH$ (Cp^R = 1,2,4-tris-*tert*-butylcyclopentadienyl) has been reported.[3] In the reaction using Cp_2ZrH_2, the complex reacted with Me_3SiOR

(R = Ph, C_6F_5) at 60 ° C in benzene-d_6 to form Me_3SiH, $Cp_2Zr(OR)_2$ and insoluble unidentified product (Scheme 2-1(a)).[3a] In the reaction using Cp_2ZrHCl, the complex reacted with $Me_3SiOC(Me)_2CH{=}CH_2$ at room temperature in THF to give $Cp_2Zr(Cl)OC(Me)_2CH_2CH_2Zr(Cl)Cp_2$ in 85-90% yield (Scheme 2-1(b)).[3b] It is considered that Me_3SiH is produced in similar yield in this reaction. $Cp^R{}_2CeH$ (Cp^R = 1,2,4-tris-*tert*-butylcyclopentadienyl) react with excess Me_3SiOMe in C_6D_{12} at room temperature to give $Cp^R{}_2CeH$, $Cp^R{}_2CeOMe$, quantitatively.[3c] The reaction strongly support the concomitant formation of Me_3SiH (Scheme 2-1(c)).

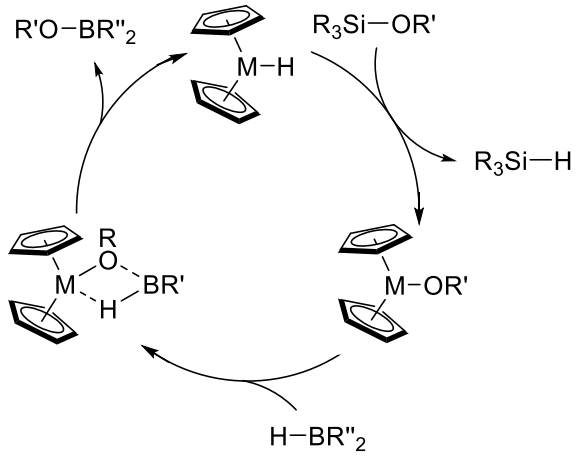
Catalytic reduction of alkoxysilane can be achieved by transition complexes, such as Cp_2TiCl_2, Cp_2ZrCl_2, and $(Ph_3P)_2NiCl_2$.[4] In the presence of 5 mol% of these catalysis, the reaction of EtPh(1-Np)SiOMe (1-Np: 1-naphthyl) with excess amount of EtMgBr in Et_2O at 20 °C give EtPh(1-Np)SiH in 100% (Cp_2TiCl_2), 60% (Cp_2ZrCl_2) and 85% ($(Ph_3P)_2NiCl_2$) yield, respectively. In the reaction, Grignard reagents are used as reductants, which forms reactive hydride species via transmetallation and *β*-hydrogen elimination of the in-situ prepared alkyl complex (Scheme 2-2).[4] The reaction of alkoxysilanes with this hydride species give the corresponding alkoxy complex and hydrosilanes. The resulting alkoxy complex further reacts with Grignard reagent to reproduce the alkyl complex. Although these reactions can convert alkoxysilanes to hydrosilanes with good efficiency, the limited substrate scope and formation of stoichiometric metal wastes are troublesome issues.



Scheme 2-2. Catalytic reduction of alkoxysilanes

Motivated by these drawbacks, in this research, we aimed at development of new synthetic method, which accomplish the reduction of alkoxysilane with a mild reducing agent. As catalysts, a metallocene-type early transition metal- or rare earth hydride complexes were selected. The early transition metal or rare earth hydride complex can reduce the alkoxysilane because their corresponding hydride species exhibit high nucleophilicity and thus are highly reactive for nucleophilic substitution reactions of alkoxysilanes. However, there is another problem in this system, a high oxophilicity of the metals. Thus, it is difficult to regenerate reactive hydride species from the stable alkoxy intermediates. In this context, we focused on borane as a reductant. Boranes exhibit high oxophilicity, and thus can form stable alkoxides (the bond energy B–O: 125 kcal/mol is higher than of Si–O: 110 kcal / mol).[1] Therefore, it is expected that borane as a mild reductant efficiently react with metal alkoxides to reproduce the active hydride complex, so that the reduction of the alkoxysilane proceeds catalytically (Scheme 2-3). Indeed, such the reactions have been already reported in the reduction of carbonyl compounds catalyzed by rare earth metal

complexes.[5]



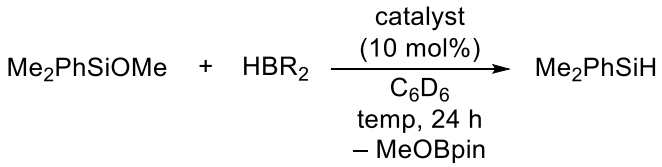
Scheme 2-3. Working hypothesis

Results and discussion

First, we evaluated alkoxysilane reduction with various borane reductant using $Me_2PhSiOMe$ as a model substrate. In the presence of 10 mol% of $Cp^*_2Y(CH_2SiMe_3)(thf)$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[6], $Me_2PhSiOMe$ reacted with HBpin at 80 °C to produce Me_2PhSiH in 29% yield (Table 2-1, entry 1). On the other hand, when using less bulky borane reductant 4,4,6-trimethyl-1,3,2-dioxaborinane (HBtmd) or catechol borane (HBcat), Me_2PhSiH was obtained in a lower yield (Table 2-1, entries 2, 3). When using BH_3·thf or BH_3·SMe_2 as Lewis base adducts, hydrosilane was not formed either (Table 2-1, entries 4, 5). The reaction was then performed using HBpin as a reductant. In the reaction using HBpin in which hydrosilane was obtained in the highest yield, the yield was improved to 48% by raising the reaction temperature to 100 °C (Table 2-1, entry 6). Subsequently, the catalyst screening was conducted based on this reaction condition. $Cp'_2YH(thf)$ (**1**) ($Cp' = \eta^5\text{-}C_5Me_4SiMe_3$)[7] also catalyzed the reaction under identical conditions, albeit that Me_2PhSiH was obtained in a slightly higher yield (57%) (Table 2-1, entry 7). The reaction catalyzed by $Cp_2Y(CH_2SiMe_3)(thf)$ ($Cp = \eta^5\text{-}C_5H_5$)[8], which contains less bulky Cp ligands, resulted in the formation of minor amounts of Me_2PhSiH (4%) (Table 2-1, entry 8). Similar observations were made for the reaction using

less bulky half-metallocene-type yttrium complex Cp'Y(CH_2SiMe_3)$_2$(thf)[9], which afforded Me_2PhSiH in 7% yield (Table 2-1, entry 9). Y(CH_2SiMe_3)$_3$(thf)$_2$[10], which do not contain Cp ligands, did not catalyze the reaction, not even in the presence of $B(C_6F_5)_3$ as a cocatalyst[11] (Table 2-1, entries 10, 11). On the other hand, the catalytic reduction of alkoxysilane did not proceed even when a metallocene type titanium and zirconium complex was used as a catalyst (Table 2-1, entries 12, 13).

Table 2-1. Reduction of $Me_2PhSiOMe$ with various borane reductant catalyzed by group 3 and 4 metal complexes.[a]

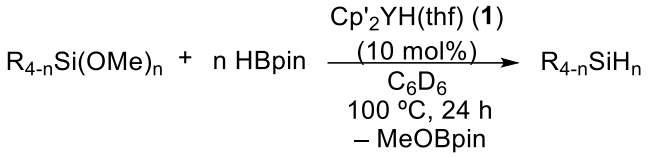


entry	catalyst	HBR_2	temp. (°C)	Me_2PhSiH yield (%)[b]
1	Cp*$_2$Y(CH_2SiMe_3)(thf)	HBpin	80	29
2	Cp*$_2$Y(CH_2SiMe_3)(thf)	HBtmd	80	15%
3	Cp*$_2$Y(CH_2SiMe_3)(thf)	HBcat	80	5%
4	Cp*$_2$Y(CH_2SiMe_3)(thf)	BH_3·thf	80	N.D.[c]
5	Cp*$_2$Y(CH_2SiMe_3)(thf)	BH_3·SMe_2	80	N.D.[c]
6	Cp*$_2$Y(CH_2SiMe_3)(thf)	HBpin	100	48
7	Cp'$_2$YH(thf) (**1**)	HBpin	100	57
8	Cp$_2$Y(CH_2SiMe_3)(thf)	HBpin	100	4
9	Cp'$_2$Y(CH_2SiMe_3)$_2$(thf)	HBpin	100	7
10	Y(CH_2SiMe_3)$_3$(thf)$_2$	HBpin	100	N.D.[c]
11	Y(CH_2SiMe_3)$_3$(thf)$_2$ / $B(C_6F_5)_3$	HBpin	100	N.D.[c]
12	Cp*$_2$TiMe	HBpin	100	N.D.[c]
13	Cp*$_2$ZrMe_2	HBpin	100	2%

[a]Reaction conditions: alkoxysilane (50 μmol), HBR_2 (50 μmol), and catalyst (5 μmol) in C_6D_6 (0.5 mL) for 24 h. [b]Determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c]Not detected.

Using the best catalyst **1**, we subsequently examined the reduction of various alkoxysilanes. Me_2(*n*Oct)SiOMe reacted with HBpin in the presence of 10 mol % of **1** to give Me_2(*n*Oct)SiH in 49% yield (Table 2-2, entry 1). Bulkier Et_3SiOMe also underwent the reduction under identical reaction conditions to give Et_3SiH, albeit in a lower yield (22%) (Table 2-2, entry 2). The yield further decreased to 11% in the reaction of Me_2PhSiOEt with the bulkier ethoxy group (Table 2-2, entry 3). Likewise, the reaction of Me_2PhSiO*i*Pr did not proceed (Table 2-2, entry 4). The reductions of dialkoxysilanes, MePhSi$(OMe)_2$ and Ph_2Si$(OMe)_2$, were similarly carried out to furnish the fully hydrogenated products in moderate yields, accompanied by the slight formation of partial hydrogenated products (Table 2-2, entries 5, 6). The reduction of PhSi$(OMe)_3$ resulted in the formation of the mixture of the hydrogenated product, i.e., $PhSiH_3$ (12%), $PhSiH_2$(OMe) (2%), PhSiH$(OMe)_2$ (6%) (Table 2-2, entry 7).

Table 2-2. Reduction of various alkoxy silanes with HBpin Catalyzed by **1**.[a]



entry	alkoxy silane	conv. (%)[b]	Hydrosilane yield (%)[b]
1	Me_2(*n*Oct)SiOMe	49	Me_2(*n*Oct)SiH (49)
2	Et_3SiOMe	28	Et_3SiH (22)
3	Me_2PhSiOEt	12	Me_2PhSiH (11%)
4	Me_2PhSiO*i*Pr	N.R.[c]	–
5	MePhSi(OMe)$_2$	77	MePhSiH$_2$ (59) MePhSiH(OMe) (8)
6	Ph_2Si(OMe)$_2$	62	Ph_2SiH$_2$ (40) Ph_2SiH(OMe) (4)
7	PhSi(OMe)$_3$	53	PhSiH$_3$ (12) PhSiH$_2$(OMe) (2) PhSiH(OMe)$_2$ (6)

[a]Reaction conditions: alkoxysilane (50 μmol), HBpin (entries 1-4: 50 μmol; entries 5,6: 100 μmol, entry 7: 150 μmol) and **1** (5 μmol, 10 mol%) in C_6D_6 (0.5 mL) at 100 ºC for 24 h. [b]Determined by 1H NMR spectroscopy using mesitylene as an internal standard. [c]No Reaction.

In order to shed light on the underlying reaction mechanism, the following experiments were carried out. Initially, we monitored the reduction of Me_2PhSiOMe catalyzed by **1** at 100 °C using a ^{1}H NMR spectroscopy. After 24 h, the yield of Me_2PhSiH had gradually increased to 56%. After 72 h, the yield reached 63%, and this value did not increase any further upon prolonging the reaction time. During the reaction, the formation of Cp'$_2$Y(μ-OMe)$_2$Bpin (**2**) (24%) and Cp'H (15%) was detected (Figure 2-1).

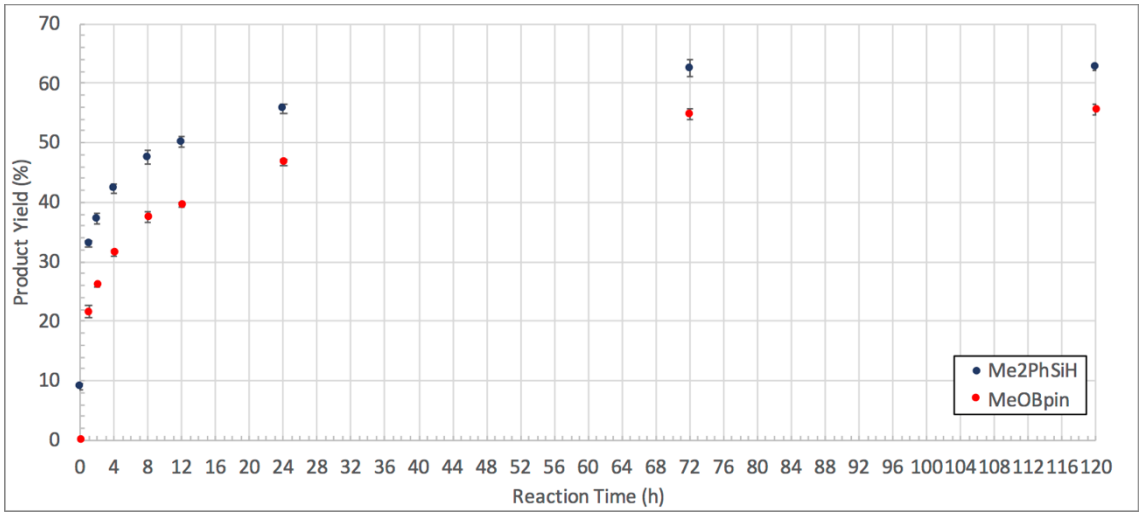
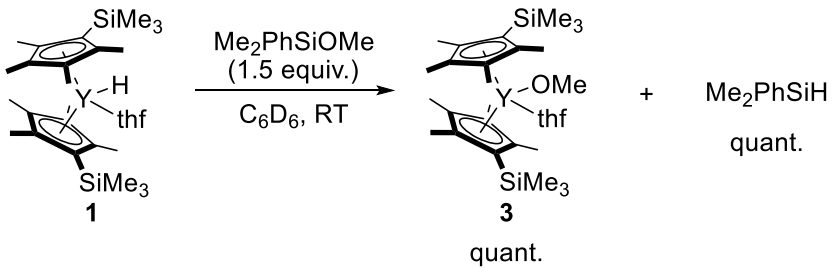
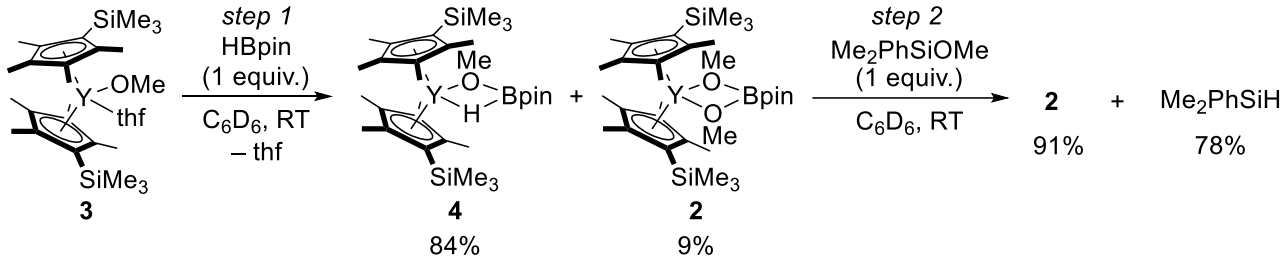


Figure 2-1. Monitoring of the catalytic reaction progress by ^{1}H NMR spectroscopy.

Complex **2** was synthesized independently by the following reaction scheme. The reaction of **1** with $Me_2PhSiOMe$ resulted in the quantitative formation of methoxy complex $Cp'_2Y(OMe)(thf)$ (**3**), accompanied by the formation of Me_2PhSiH (Scheme 2-4). Reaction of **3** with 1 equiv. of HBpin afforded a mixture that contained HBpin adduct **4** (84%) and **2** (9%) (Scheme. 2-5, step 1). This mixture was fully converted into **2** upon treatment with one more equivalent of $Me_2PhSiOMe$, and the formation of Me_2PhSiH (78%) was also detected (Scheme 2-5, step 2). Complexes **2**–**4** exhibit one $SiMe_3$ and two CpMe signals in the ^{1}H and/or ^{13}C NMR spectra. In their ^{11}B NMR spectra, **2** and **4** exhibit one signal at 6.1 ppm and −1.0 ppm, respectively.



Scheme 2-4. Reaction of complex **1** with $Me_2PhSiOMe$.



Scheme 2-5. Reaction of complex **3** with HBpin and $Me_2PhSiOMe$

The solid-state structures of **2**–**4** were determined by single crystal X-ray diffraction analysis (Figure 2-2, Table 2-3). Their core structures around the Y center are comparable to those of previously reported analogous yttrium complexes.[12] The Y–OMe bond in **3** (2.073(2) Å) is somewhat shorter than those in **2** (2.266(3)/2.284(3) Å) and **4** (2.264(2) Å), which is probably due to the bridging coordination mode. Reflective of these values, the Cp'-bite-angle [CEN-Y-CEN (CEN = Cp'-ring centroid)] of **2** (139.36(7)) and **4** (139.57(5)) is slightly larger than that of **3** (136.35(4)). Complexes **2** and **4** are also revealed to exhibit similar bond angles and bond lengths around the Y atom to catalytically active **1**.

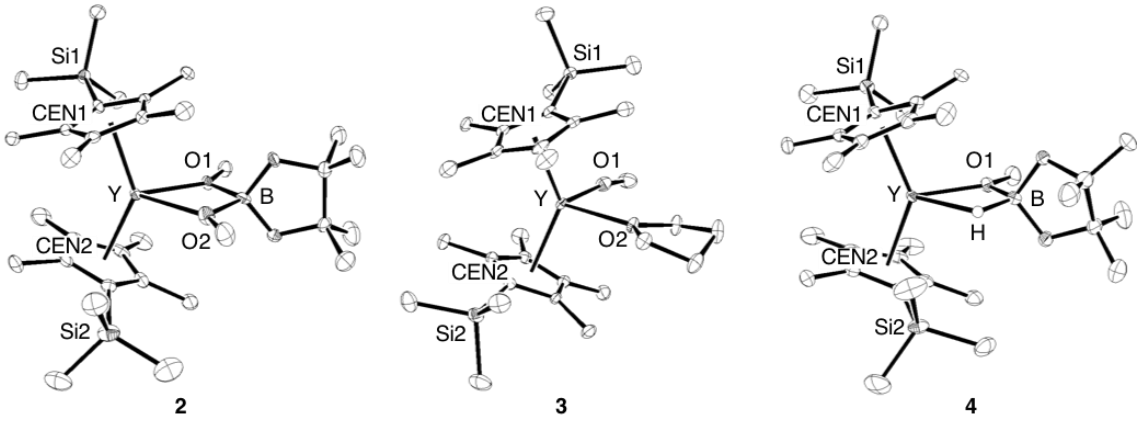


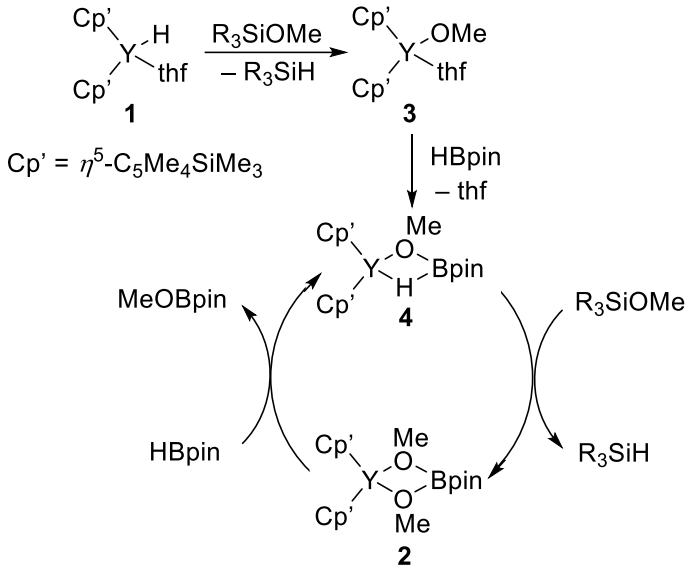
Figure 2-2. Molecular structures of **2**-**4** with probability ellipsoids. Hydrogen atoms are omitted for clarity. (CEN = ring centroid)

Table 2-3. Selected bond distances (Å) and angles (deg) for **2**–**4**

	2	**3**	**4**
Y–CEN1	2.375(2)	2.427(1)	2.354(2)
Y–CEN2	2.382(2)	2.412(1)	2.367(2)
Y–O1	2.266(3)	2.073(2)	2.264(2)
Y–O2	2.284(3)	2.3821(17)	–
B–O1	1.512(6)	–	1.509(4)
B–O2	1.518(6)	–	–
CEN1–Y–CEN2	139.36(7)	136.35(4)	139.57(5)
CEN1–Y–O1	108.31(11)	108.61(7)	109.77(7)
CEN1–Y–O2	106.51(10)	105.00(5)	–
CEN2–Y–O1	106.67(10)	104.43(6)	108.33(7)
CEN2–Y–O2	108.72(11)	104.90(5)	–
O1–Y–O2	59.50(12)	86.16(7)	–
Y–O1–B	102.4(2)	–	97.36(17)
Y–O2–B	101.4(3)	–	–
O1–B–O2	96.4(3)	–	–

We also confirmed that **2** exhibits similar catalytic activity as **1**, i.e., the reduction of $Me_2PhSiOMe$ proceeded in the presence of **2** (10 mol %) at 100 °C to form Me_2PhSiH in 42% yield. This result suggests the inclusion of **2** as the intermediate in the catalytic cycle. Based on these experimental results, we would like to propose a possible reaction pathway (Scheme 2-6). Complex **1** could successively react with alkoxysilane and HBpin to form **4** via **3**. Complex **4** could then engage in a nucleophilic reaction with alkoxysilane to give **2** as well as the corresponding hydrosilane. A subsequent reaction of **2** with HBpin would lead to the regeneration of **4**. The observed formation of free Cp'H detected during the catalytic reaction is likely due to the reactions of **1**–**4** with HBpin, which could be one potential deactivation process for the catalyst. The formation of MeOBpin could also lead to the deactivation

of the highly oxophilic active species. Indeed, the catalytic activity of **1** decreased extremely in the presence of MeOBpin (1 equiv).[13] Considering the suppressed catalytic activity of $[Cp_2Y(CH_2SiMe_3)(thf)]$, $[Cp'Y(CH_2SiMe_3)_2(thf)]$, and $[Y(CH_2SiMe_3)_3(thf)_2]$, which contain less sterically hindered reaction space, this effect is likely mitigated in the case of **1** on account of the rigid metallocene structure that is a result of the bulky Cp' ligands.



Scheme 2-6. Possible reaction pathway.

Conclusion

In summary, we have developed the first example of a catalytic reduction of alkoxysilanes using the mild reductant HBpin. The utility of yttrium-based catalyst **1** has been demonstrated experimentally, and we have shown that the coordination of alkoxyboranes suppresses the catalytic activity of **1**.

Experimental section

General considerations

All manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Benzene was purified by a solvent purification system (MBraun SPS-800). C_6D_6 was dried over sodium benzophenone ketyl and distilled. $Cp^*_2Y(CH_2SiMe_3)(thf)$[6], $Cp'_2YH(thf)$ (**1**)[7], $Cp_2Y(CH_2SiMe_3)(thf)$[8], $Cp'Y(CH_2SiMe_3)_2(thf)_4$[9], $Y(CH_2SiMe_3)_3(thf)_2$[10], Cp^*_2TiMe[14] and $Cp^*_2ZrMe_2$[15] were prepared according to the literature procedures. All other reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. ^1H, ^{11}B, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra (^1H, 600 MHz; ^{11}B, 193 MHz; 13C, 151 MHz; ^{29}Si, 119 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to the residual solvent signals for ^1H and ^{13}C, and to boron trifluoride diethyl ether complex (0.0 ppm) for ^{11}B and to trimethyl(phenyl)silane (–4.7 ppm) for ^{29}Si. Elemental analyses were carried out on a Yanaco CHN CORDER MT-6.

Catalytic reduction of alkoxysilane with hydroborane

A typical procedure (entry 1 in Table 2-1) is as follows. A J-Young NMR tube was charged with a C_6D_6 solution (0.5 mL) of $Cp^*_2Y(CH_2SiMe_3)(thf)$ (2.6 mg, 5.0 μmol), $Me_2PhSiOMe$ (8.4 mg, 50 μmol) and mesitylene (6.0 mg, 50 μmol) as an internal standard. HBpin (6.4 mg, 50 μmol) was added at room temperature, and then the solution was heated at 80 ºC for 24 hours. ^1H NMR was measured to determine NMR yield of Me_2PhSiH (15 μmol, 29%).

Compound characterization data

The products in Table 2-1-2-3, Me_2PhSiH[16], Et_3SiH[16], $MePhSiH_2$[17], MePhSiH(OMe)[18], Ph_2SiH_2[19], $PhSiH_2(OMe)$[20] and $Cp'H$[21] were identified by comparing their ^1H NMR data with those previously reported. $Me_2(n\text{Oct})SiH$[22], $Ph_2SiH(OMe)$[23] and $PhSiH(OMe)_2$[24] were identified by comparing their ^1H NMR data with those synthesized by reported procedure. $PhSiH_3$ and MeOBpin were identified by comparing their ^1H NMR data with it purchased from commercial suppliers.

$Me_2(nOct)SiH$

^{1}H NMR (C_6D_6, RT, ppm): δ 0.06 (d, 6H, $^3J_{HH}$ = 3.6 Hz, Si*Me_2*), 0.57 (m 2H, SiC*H_2*$(CH_2)_6CH_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.0 Hz, $SiCH_2(CH_2)_6C$*H_3*), 1.22-1.42 (m, 12H, $SiCH_2(C$*H_2*$)_6CH_3$)), 4.15 (sep, 1H, $^3J_{HH}$ = 3.6 Hz, SiH).

Et_3SiH

^{1}H NMR (C_6D_6, RT, ppm): δ 0.53 (dq, 6H, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 7.9 Hz, SiC*H_2*CH_3), 0.96 (t, 9H, $^3J_{HH}$ = 7.9 Hz, $SiCH_2C$*H_3*), 3.88 (sep, 1H, $^3J_{HH}$ = 3.2 Hz, SiH).

$MePhSiH_2$

^{1}H NMR (C_6D_6, RT, ppm): δ 0.18 (t, 3H, $^3J_{HH}$ = 4.3 Hz, Si*Me*), 4.49 (q, 2H, $^3J_{HH}$ = 4.3 Hz, Si*H_2*), 7.11-7.19 (m, 3H, m, *p*-C*H*), 7.45 (m, 2H, *o*-C*H*).

MePhSiH(OMe)

^{1}H NMR (C_6D_6, RT, ppm): δ 0.32 (t, 3H, $^3J_{HH}$ = 2.9 Hz, Si*Me*), 3.30 (s, 3H, O*Me*), 5.18 (q, 1H, $^3J_{HH}$ = 2.9 Hz, Si*H*), 7.20 (m, 3H, *m*, *p*-C*H*), 7.56 (m, 2H, *o*-C*H*).

Ph_2SiH_2

^{1}H NMR (C_6D_6, RT, ppm): δ 5.08 (s, 2H, Si*H*), 7.09-7.19 (m, 6H, *m*, *p*-C*H*), 7.51 (m, 4H, *o*-C*H*).

$Ph_2SiH(OMe)$

^{1}H NMR (C_6D_6, RT, ppm): δ 3.40 (s, 3H, O*Me*), 5.61 (s, 1H, Si*H*), 7.09-7.19 (m, 6H, *m*, *p*-C*H*), 7.65 (m, 4H, *o*-C*H*).

$PhSiH_3$

^{1}H NMR (C_6D_6, RT, ppm): δ 4.23 (s, H, Si*H*), 7.07 (m, 2H, *m*, *p*-C*H*), 7.11 (m, 1H, *p*-C*H*), 7.39 (m, 2H, *o*-C*H*).

$PhSiH_2(OMe)$

^{1}H NMR (C_6D_6, RT, ppm): δ 3.27 (s, 3H, O*Me*), 5.14 (s, 1H, Si*H*), 7.55 (m, 2H, *o*-C*H*).

$PhSiH(OMe)_2$

^{1}H NMR (C_6D_6, RT, ppm): δ 3.41 (s, 6H, O*Me*), 5.12 (s, 1H, Si*H*), 7.17-7.20 (m, 3H, *m*, *p*-C*H*), 7.70 (m, 2H, *o*-C*H*).

MeOBpin

^{1}H NMR (C_6D_6, RT, ppm): δ 1.04 (s, 12H, B*pin*), 3.51 (s, 3H, O*Me*).

Cp'H

^{1}H NMR (C_6D_6, RT, ppm): δ –0.02 (s, 9H, Si*Me_3*), 1.82 (s, 6H, Cp*Me*), 1.92 (s, 6H, Cp*Me*), 2.68 (s, 1H, Cp'*H*).

Monitoring of the catalytic reaction progress

A J-Young NMR tube was charged with a C_6D_6 solution (0.5 mL) of **1** (2.7 mg, 5.0 μmol), $Me_2PhSiOMe$ (8.4 mg, 50 μmol) and mesitylene (6.0 mg, 50 μmol) as an internal standard. HBpin (6.4 mg, 50 μmol) was added at room temperature, and then the solution was heated. The reaction was followed by ^{1}H NMR. ^{1}H NMR was measured to determine NMR yield of Me_2PhSiH, MeOBpin, complex **4** (120 h: 1.2 μmol, 24% / **1**) and Cp'H (120 h: 0.75 μmol, 15% / **1**).

Synthesis of Cp'$_2$Y{μ-(OMe)$_2$}Bpin (**2**)

To a benzene (1 mL) solution of **1** (50 mg, 91 μmol) was added $Me_2PhSiOMe$ (30 mg, 182 μmol) and HBpin (12 mg, 91 μmol). The solution was stirred for 24 hours at room temperature. After removal of the solvent under vacuum, the residue was extracted with pentane (5 mL) and filtered through a syringe filter. The filtrate was concentrated under vacuum to ca. 0.5 mL, and stored at –35 ºC to give **2** as a colourless crystal (37 mg, 56 μmol, 62%).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.36 (s, 18H, Si*Me*$_3$), 1.34 (s, 12H, B*pin*), 1.94 (s, 12H, Cp*Me*), 2.36 (s, 12H, Cp*Me*), 3.31 (s, 6H, O*Me*)

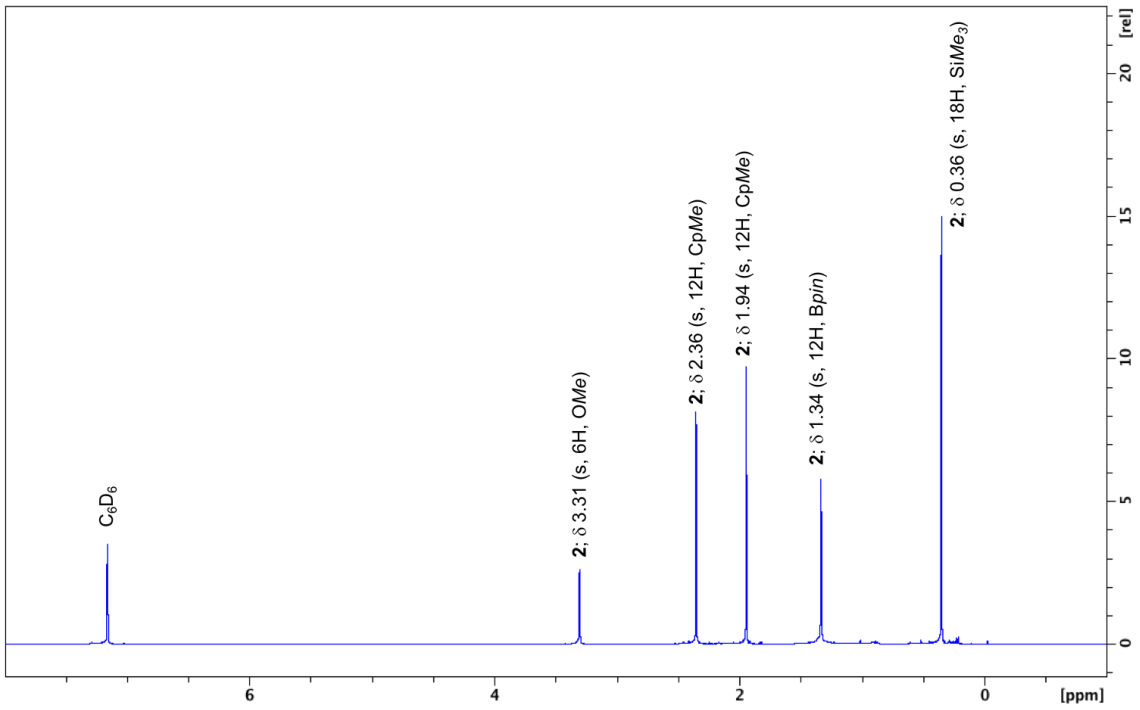
^{13}C NMR (C_6D_6, RT, ppm): δ 2.82 (s, Si*Me*$_3$), 11.5 (s, Cp*Me*), 14.7 (s, Cp*Me*), 28.1 (s, C*Me*$_2$), 50.6 (s, O*Me*) 78.8 (s, *C*Me$_2$), 115.3 (d, $^1J_{C\text{-}Y}$ = 3.0 Hz, *C*$_5$Me$_4$SiMe$_3$), 124.4 (s, *C*$_5$Me$_4$SiMe$_3$), 130.2 (s, *C*$_5$Me$_4$SiMe$_3$)

^{29}Si NMR (C_6D_6, RT, ppm): –10.7 (s, *Si*Me$_3$)

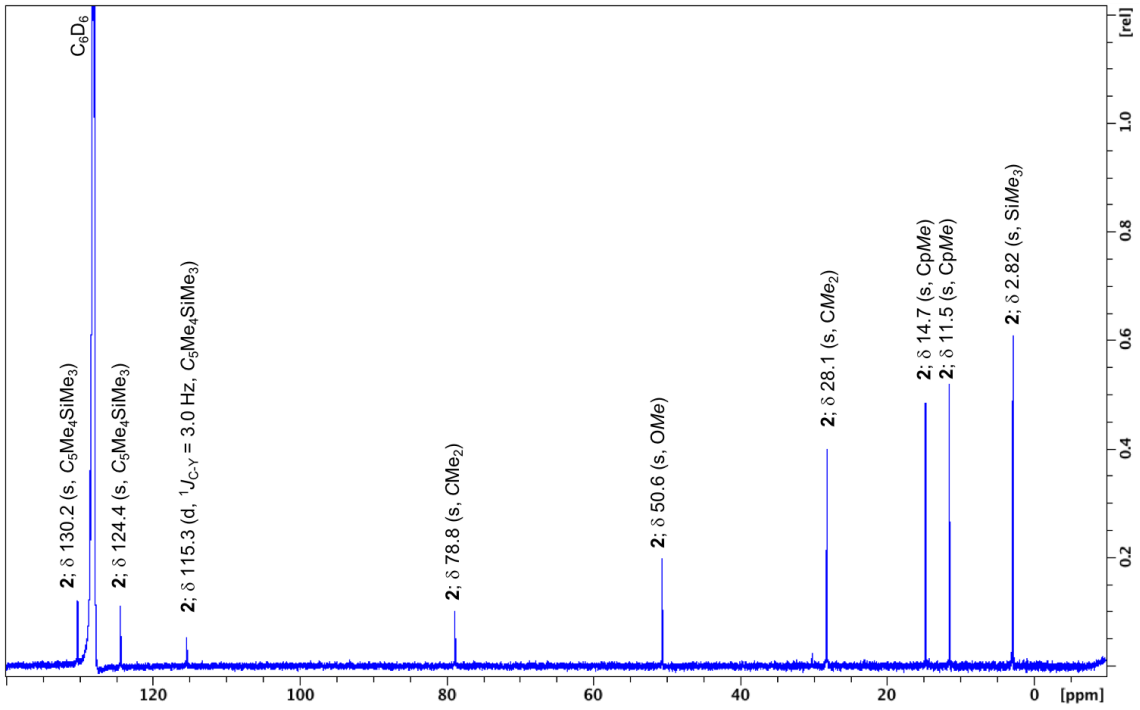
^{11}B NMR (C_6D_6, RT, ppm): 6.1 (s, *B*pin)

Anal. Calcd for $C_{32}H_{60}BO_4Si_2Y$: C, 57.73; H, 9.24. Found: C, 57.95; H, 9.51.

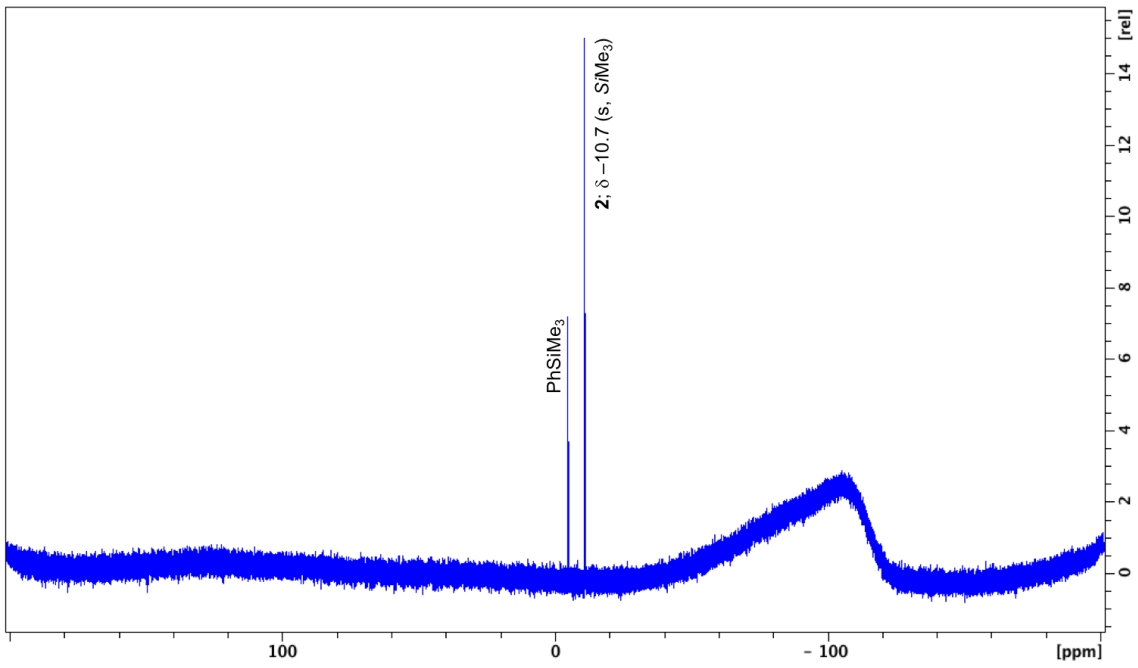
^{1}H NMR:



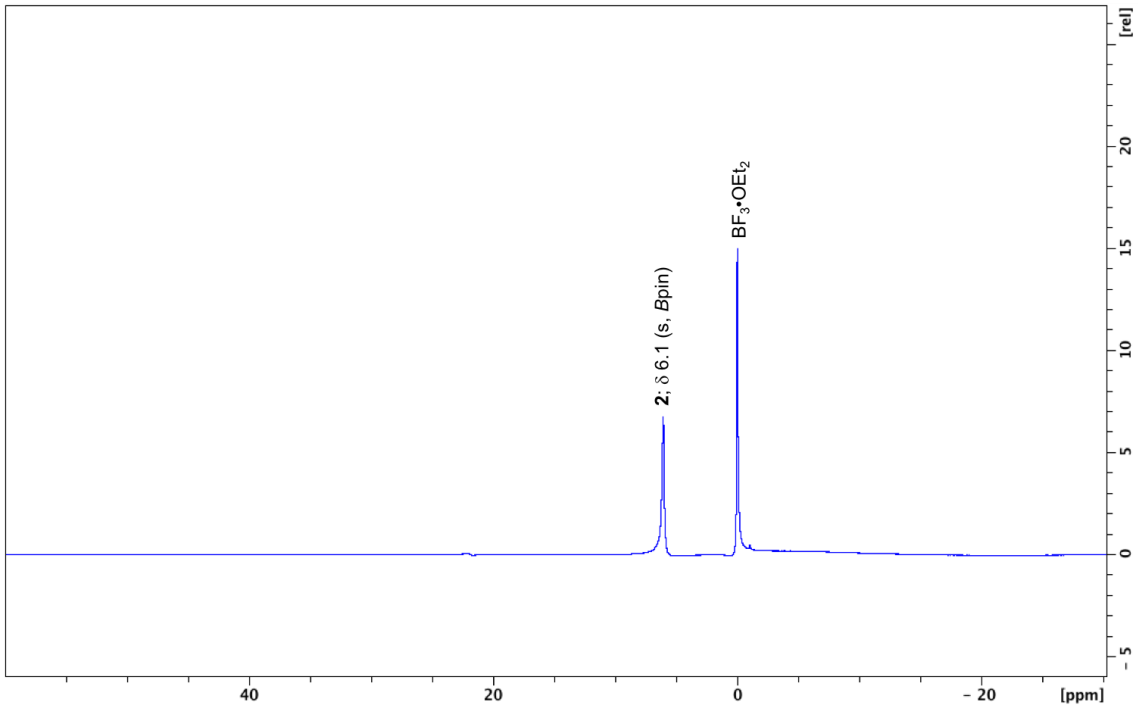
^{13}C NMR:



^{29}Si NMR:



^{11}B NMR:



Synthesis of Cp'$_2$Y(OMe)(thf) (**3**)

To a benzene (1 mL) solution of **1** (50 mg, 91 μmol) was added $Me_2PhSiOMe$ (30 mg, 182 μmol). The solution was stirred for 24 hours at room temperature. After removal of the solvent under vacuum, the residue was extracted with pentane (5 mL) and filtered with a syringe filter. The filtrate was concentrated under vacuum to ca. 0.5 mL, and stored at –35 ºC to give **3** as a colourless crystal (48 mg, 83 μmol, 76%).

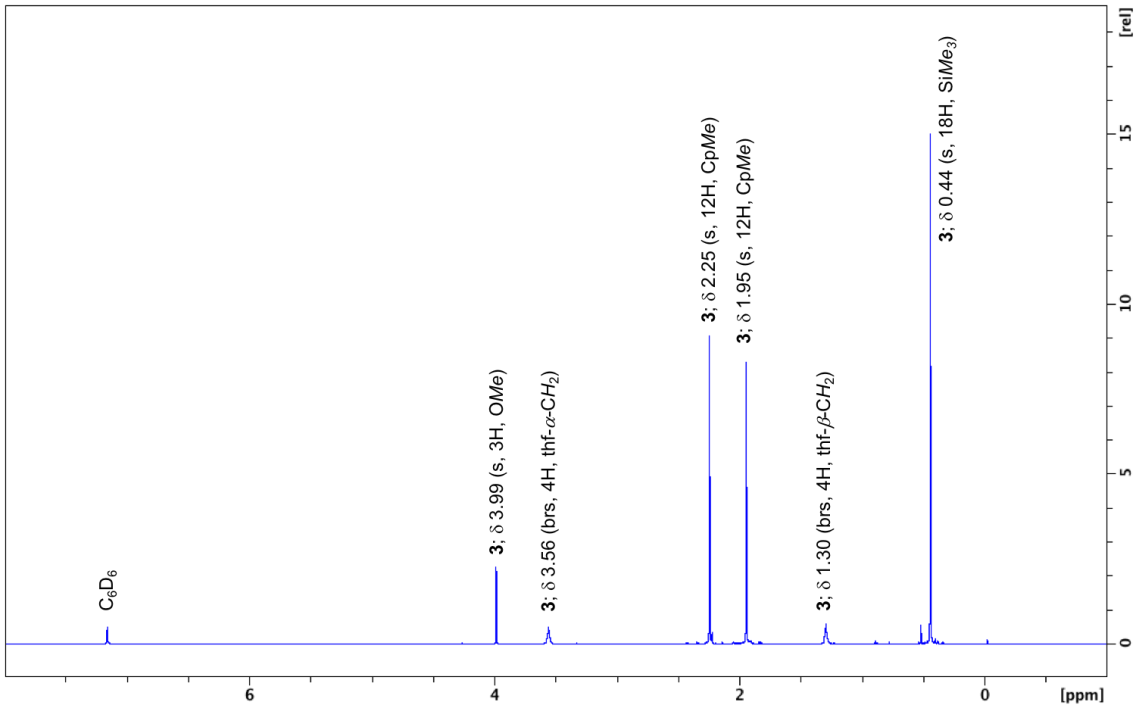
^{1}H NMR (C_6D_6, RT, ppm): δ 0.44 (s, 18H, Si*Me*$_3$), 1.30 (s, 4H, thf-*β-H*), 1.95 (s, 12H, Cp*Me*), 2.25 (s, 12H, Cp*Me*), 3.56 (brs, 4H, thf-*α-H*), 3.99 (s, 3H, O*Me*).

^{13}C NMR (C_6D_6, RT, ppm): δ 2.78 (s, Si*Me*$_3$), 11.7 (s, Cp*Me*), 14.7 (s, Cp*Me*), 25.6 (brs, THF-*β*-C*H*$_2$), 55.5 (d, $^1J_{C\text{-}Y}$ = 4.5 Hz, O*Me*), 71.2 (s, thf-*α*-*C*H$_2$), 113.2 (d, $^1J_{C\text{-}Y}$ = 2.4 Hz, *C*$_5$Me$_4$SiMe$_3$), 121.3 (d, $^1J_{C\text{-}Y}$ = 0.7 Hz, *C*$_5$Me$_4$SiMe$_3$), 126.4 (s, *C*$_5$Me$_4$SiMe$_3$).

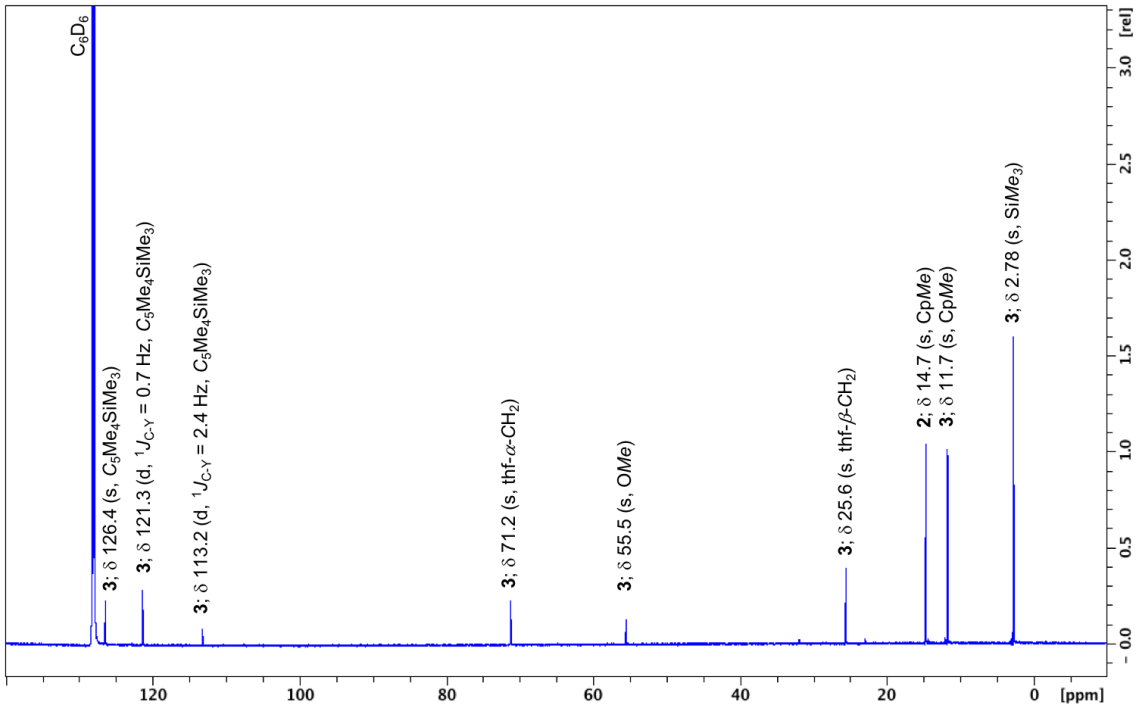
^{29}Si NMR (C_6D_6, RT, ppm): δ –11.0 (s, Si*Me*$_3$).

Anal. Calcd for $C_{29}H_{53}BO_2Si_2Y$: C, 60.18; H, 9.23. Found: C, 60.48; H, 9.38.

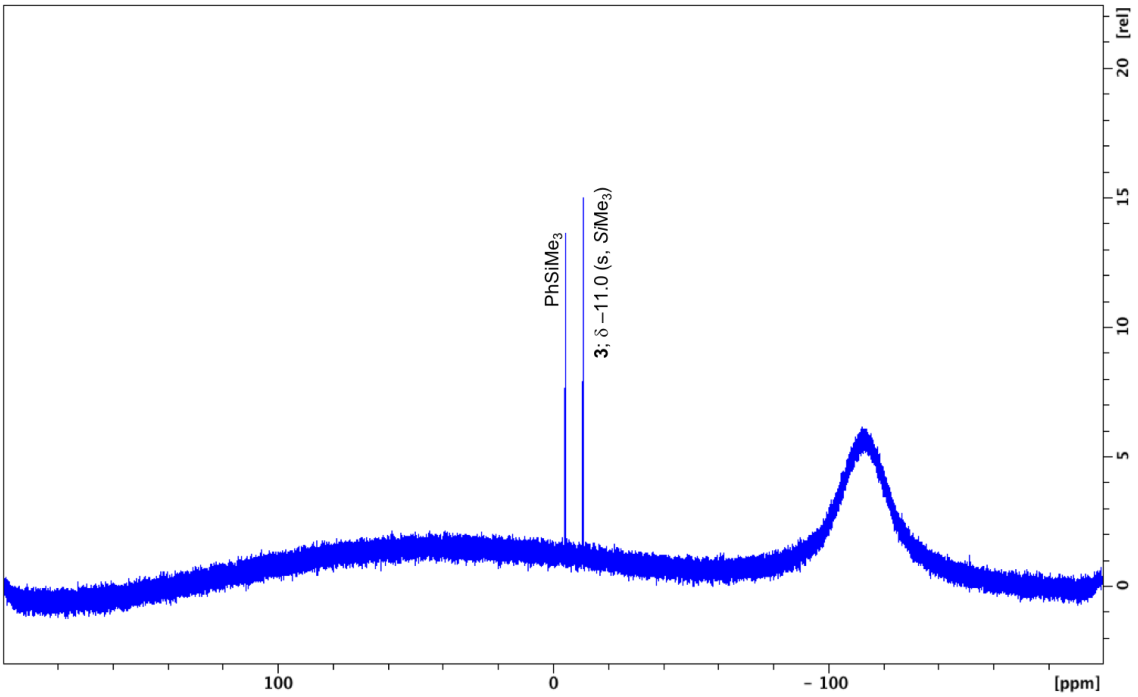
^{1}H NMR:



^{13}C NMR:



^{29}Si NMR:



Synthesis of Cp'$_2$Y(μ-H)(μ-OMe)Bpin (**4**)

To a benzene (1 mL) solution of **3** (40 mg, 69 µmol) was added HBpin (8.8 mg, 69 µmol). The solution was stirred for 24 hours at room temperature. After removal of the solvent under vacuum, the residue was extracted with pentane (5 mL) and filtered through a syringe filter. The filtrate was concentrated under vacuum to ca. 0.5 mL. Complex **4** was contaminated with **2** and isolation of **4** was not successful, but slight amount of single crystals were obtained by recrystallization from cold pentane solution (–35 °C).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.33 (s, 18H, Si*Me*$_3$), 1.25 (brs, 12H, B*pin*), 1.92 (brs, 12H, Cp*Me*), 2.31 (brs, 12H, Cp*Me*), 3.52 (s, 3H, O*Me*). The BH signal is obscured.

^{29}Si NMR (C_6D_6, RT, ppm): δ –10.9 (s, *Si*Me$_3$).

^{11}B NMR (C_6D_6, RT, ppm): δ –1.0 (s, *B*pin).

Reaction of Cp'$_2$YH(thf) (**1**) with $Me_2PhSiOMe$

A J-Young NMR tube was charged with a C_6D_6 solution (0.5 mL) of **1** (2.7 mg, 5.0 μmol), $Me_2PhSiOMe$ (1.2 mg, 7.5 μmol) and mesitylene (2.4 mg, 20 μmol) as an internal standard at room temperature. After 1 hour, ^{1}H NMR was measured to determine NMR yields of **3** (5.0 μmol, 99%) and Me_2PhSiH (5.0 μmol, 99%). Unreacted $Me_2PhSiOMe$ was fully recovered (2.5 μmol, 50%).

Reaction of Cp'$_2$Y(OMe)(thf) (**3**) with HBpin and $Me_2PhSiOMe$

A J-Young NMR tube was charged with a C_6D_6 solution (0.5 mL) of **3** (10.0 mg, 17 μmol) and HBpin (2.1 mg, 17 μmol) and mesitylene (2.1 mg, 17 μmol) as an internal standard at room temperature. After 1 hour, ^{1}H NMR was measured to determine NMR yield of **4** (14 μmol, 84%) and **2** (1.5 μmol, 9%). Then, $Me_2PhSiOMe$ (3.5 mg, 21 μmol) was added to the reaction mixture. After 24 hours, ^{1}H NMR was measured to determine NMR yields of complex **2** (16 μmol, 91%) and Me_2PhSiH (13 μmol, 78%). Unreacted $Me_2PhSiOMe$ was fully recovered (7.4 μmol, 43%).

Catalytic reduction of $Me_2PhSiOMe$ by **2**

A J-Young NMR tube was charged with a C_6D_6 solution (0.5 mL) of **2** (3.3 mg, 5.0 μmol), $Me_2PhSiOMe$ (8.4 mg, 50 μmol) and mesitylene (6.0 mg, 50 μmol) as an internal standard. After the addition of HBpin (6.4 mg, 50 μmol) at room temperature, the solution was kept at 100 ºC for 24 hours. ^{1}H NMR was measured to determine the NMR yield of Me_2PhSiH (21 μmol, 42%). Unreacted $Me_2PhSiOMe$ was fully recovered (29 μmol, 57%).

Catalytic reduction of $Me_2PhSiOMe$ by **1** in the presence of MeOBpin

A J-Young NMR tube was charged with a C_6D_6 solution (0.5 mL) of **1** (2.7 mg, 5.0 μmol), $Me_2PhSiOMe$ (8.4 mg, 50 μmol) and mesitylene (6.0 mg, 50 μmol) as an internal standard. After the addition of HBpin (6.4 mg, 50 μmol) and

MeOBpin (7.9 mg, 50 μmol) at room temperature, the solution was kept at 100 ºC for 24 hours. ^{1}H NMR was measured to determine the NMR yield of Me_2PhSiH (3.0 μmol, 6%). Unreacted $Me_2PhSiOMe$ was fully recovered (47 μmol, 94%).

Single crystal X-ray diffraction studies.

The single crystal X-ray diffraction measurements of complex **2-4** was performed under a cold nitrogen stream on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector using multi-layer mirrore monochromated Mo Kα radiation. The determination of crystal systems and unit cell parameters and data processing were performed with the CrystalClear program package. The data sets were corrected for Lorentz and polarzation effects and absorption. The structure was solved by direct methods using SIR92 program,[25] and refined by full-matrix least squares calculations on F2 for all reflections (SHELXL-97)[26]. The CheckCif examination of **4** exhibits Alert A. this is because of not recongnizing the Cp'-ring-carbon coordination with the Y atom.

Table S2-1. Crystal data and details of the crystal structure determination for complex **2-4**.

complex	**2**	**3**	**4**
formula	$C_{32}H_{60}BO_4Si_2Y$	$C_{29}H_{53}O_2Si_2Y$	$C_{31}H_{58}BO_3Si_2Y$
fw	664.71	578.81	634.68
T (K)	93(2)	93(2)	93(2)
cryst system	triclinic	monoclinic	triclinic
space group	*P*-1 (#2)	$P2_1/c$ (#14)	*P*-1 (#2)
a (Å)	10.286(4)	18.920(4)	10.283(3)
b (Å)	10.637(4)	10.800(2)	10.634(4)
c (Å)	16.711(7)	15.637(5)	16.893(5)
α (deg)	85.83(4)		87.33(2)
β (deg)	81.84(3)	103.687(5)	77.94(2)
γ (deg)	78.75(3)		78.369(19)
V (Å^3)	1773.2(12)	3104.5(11)	1769.4(10)
Z	2	4	2
D_{calcd} (g/cm^3)	1.245	1.238	1.191
μ(Mo K$_\alpha$) (cm^{-1})	17.460	19.803	17.447
$2\theta_{max}$ (deg)	55.0	55.0	55.0
no. of meads reflns	total: 16801	total: 31824	total: 22472
	unique: 7613	unique: 7084	unique: 7950
no. of observation	7613	7084	7950
no. of variables	381	322	362
*R*1[a]	0.0641	0.0421	0.0511
*wR*2 [b]	0.1590	0.0894	0.1277
GOF[c]	1.024	1.096	1.027

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Chapter 3

Synthesis of Hydrosilanes via Lewis Base-Catalyzed Reduction of Alkoxysilane with Borane

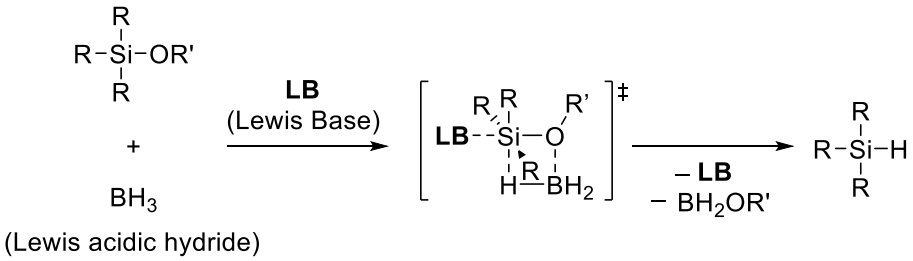
Abstract

Hydrosilanes were synthesized by reduction of alkoxy silanes with BH_3 in the presence of hexamethylphosphoric triamide (HMPA) as a Lewis-base catalyst. The reaction was also achieved using an inexpensive and easily handled hydride source $NaBH_4$, which reacted with EtBr as a sacrificial reagent to form BH_3 in situ.

Introduction

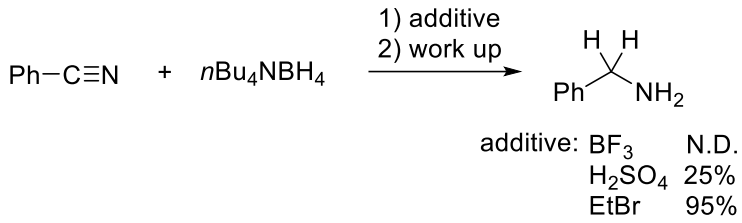
In the reaction using yttrium catalyst in Chapter 2, the catalytic reduction of alkoxysilane with borane was achieved. The reaction cannot utilize simple boranes such as BH_3·thf and BH_3·SMe_2, and require a relatively expensive HBpin. In addition, the reaction is easily suppressed by the in-situ formed byproduct MeOBpin. In this study, we set up to develop a new catalytic system that can efficiently convert alkoxysilanes to hydrosilanes using the more general reducing agent BH_3·thf.

We thus focused on Lewis base catalysts that are not expected to be deactivated by the oxygen atom-coordination. It is known that onece silicon compounds are activated via coordination of Lewis base, they act as efficient nucleophiles.[1] Various organic reactions including Hosomi-Sakurai allylations and Hiyama coupling reactions utilized this intrinsic properties of silicon compounds.[2] Similarly, in the borane reduction of alkoxysilane, it is expected that the Si–O bond(s) in alkoxysilanes is activated via adduct formation with Lewis base (Scheme 3-1).



Scheme 3-1. Working hypothesis

Also, in this research, reduction of alkoxysilane using $NaBH_4$, which is inexpensive and easy-to-handle, was also examined. It is known that BH_3 can be also generated by adding additives to $NaBH_4$. H_2SO_4[3a] and BX_3 (X = F, Cl)[3b], I_2[3c] and haloalkanes[3d] have been reported as additives to generate BH_3 from BH_4^- (Scheme 3-2). In this research, by using EtBr as an additive, formal reduction of alkoxysilane with $NaBH_4$ was achieved.

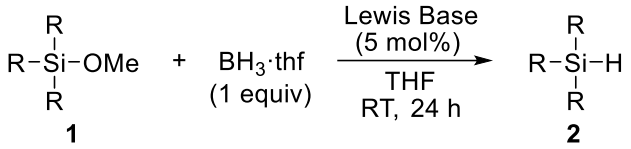


Scheme 3-2. Reduction of nitrile with BH_3 generated from BH_4^-

Results and discussion

First, we evaluated alkoxy silane reduction with BH_3·thf using Me_2(*n*Oct)SiOMe (**1a**) as a model substrate. The reaction of **1a** with 1 equiv. of BH_3·thf was performed at room temperature for 24 h, resulting in the slight formation of the corresponding hydrosilane Me_2(*n*Oct)SiH (**2a**) (Table 3-1, entry 1). The reaction was then performed in the presence of various Lewis bases. We expected that the Lewis base would nucleophilically interact with the Si atom to weaken the strong Si–O bond. Organic amines, pyridine and NEt_3, did not improve the reaction yield (Table 3-1, entries 2 and 3). CsF, dimethylsulfoxide (DMSO), Me_3NO, *N*,*N*'-dimethylpropyleneurea (DMPU), and tetramethylurea, which exhibit higher affinity towards the silicon atom via F- or O-atom coordination, slightly improved the reaction yield (Table 3-1, entries 4–8). Although the use of $(MeO)_3PO$ afforded **2a** only in 6% yield (Table 3-1, entry 9), the reaction catalyzed by Ph_3PO as a stronger Lewis base resulted in the formation of **2a** in 72% yield (Table 3-1, entry 10). Further improvement was achieved by using HMPA to give **2a** in 91% yield (Table 3-1, entry 11). In the reaction, the formation of $B(OMe)_3$ (δ 18.8 ppm) and $HB(OMe)_2$ (δ 28.0 ppm, d, $^1J_{BH}$ = 162 Hz) was confirmed by ^{11}B NMR spectroscopy. Reduction of Et_3SiOMe, $Me_2PhSiOMe$, $MePh_2SiOMe$ similarly proceeded in the presence of HMPA (5 mol%) to furnish the corresponding hydrosilanes in good yields (Table 3-1, entries 12–14).

Table 3-1. Screening of Lewis bases for the reduction of Me_2(*n*Oct)SiOMe (**1a**) with BH_3·thf[a].



Entry	Lewis Base	Alkoxysilane conv. (%)[b]	Hydrosilane yield (%)[b]
1	–	Me_2(*n*Oct)SiOMe (**1a**) (3)	**2a** (2)
2	Pyridine	Me_2(*n*Oct)SiOMe (**1a**) (3)	**2a** (3)
3	NEt_3	Me_2(*n*Oct)SiOMe (**1a**) (3)	**2a** (2)
4	CsF	Me_2(*n*Oct)SiOMe (**1a**) (9)	**2a** (4)
5	DMSO	Me_2(*n*Oct)SiOMe (**1a**) (11)	**2a** (5)
6	Me_3NO	Me_2(*n*Oct)SiOMe (**1a**) (8)	**2a** (8)
7	DMPU	Me_2(*n*Oct)SiOMe (**1a**) (8)	**2a** (8)
8	Tetramethylurea	Me_2(*n*Oct)SiOMe (**1a**) (9)	**2a** (8)
9	$(MeO)_3PO$	Me_2(*n*Oct)SiOMe (**1a**) (7)	**2a** (6)
10	Ph_3PO	Me_2(*n*Oct)SiOMe (**1a**) (73)	**2a** (72)
11	HMPA	Me_2(*n*Oct)SiOMe (**1a**) (91)	**2a** (91)
12	HMPA	Et_3SiOMe (**1b**) (80)	**2a** (75)
13	HMPA	Me_2PhSiOMe (**1c**) (91)	**2a** (88)
14	HMPA	$MePh_2$SiOMe (**1d**) (75)	**2a** (75)

[a]Reaction conditions: alkoxysilane (0.20 mmol), 1M BH_3·thf solution (0.20 mmol) and Lewis base (0.010 mmol) in THF (0.5 mL) at RT for 24 h. [b] Determined by ^{1}H NMR using mesitylene as an internal standard.

Motivated by the discovery of a good catalyst, HMPA, for the reduction of alkoxy silane with BH_3·thf, we next focused on the reaction of alkyl halides with borohydride.[3d, 4] In this reaction, alkyl halides underwent hydride reduction accompanied by the formation of BH_3. By applying this reaction to our borane-reduction of alkoxy silanes, we expected to achieve a formal reduction of alkoxy silanes with $NaBH_4$.

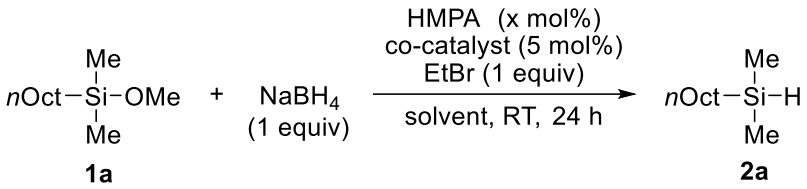
Thus, the HMPA-catalyzed reduction of **1a** (0.20 mmol) with $NaBH_4$ was performed in THF (0.5 mL) in the presence of EtBr (1 equiv.), which has a low boiling point and can be easily removed via evaporation. The reaction

resulted in the slight formation of **2a** (13%) (Table 3-2, entry 1). On the other hand, reducing the amount of the solvent to 0.05 mL increased the yield to 80% (Table 3-2, entry 2). Whereas, complete removal of the solvent slightly decreased the reaction yield (Table 3-2, entry 3).

Then, the effect of the solvent was further analyzed. The reactions were carried out in 1,2-dichloroethane (DCE) or C_6D_6 (0.05 mL), resulting in the formation of **2a** in moderate yields, 50% and 27%, respectively (Table 3-2, entries 5 and 7).

To our surprise, adding nOct$_4$NBr (5 mol%) as a phase transfer catalyst, which could facilitate the reaction of EtBr with $NaBH_4$ as a sparingly soluble substrate, to the reaction in C_6D_6 produced the highest yield (93%) of **2a** (Table 3-2, entry 8) among the examined solvents (Table 3-2, entries 4 and 6). The use of nBu$_4$NBr with shorter alkyl chains decreased the yield of **2a** (34%) (Table 3-2, entry 9). Thus, this reaction is considered to require a phase transfer catalyst having long-chain alkyl with high solubility in nonpolar solvents. It was confirmed that the reaction did not proceed without HMPA or EtBr (Table 3-2, entries 10 and 11). This result indicated that both HMPA and EtBr are necessary for this reaction.

Table 3-2. Optimization of reaction conditions in the reduction of Me_2(*n*Oct)SiOMe (**1a**) with $NaBH_4$[a].



1a **2a**

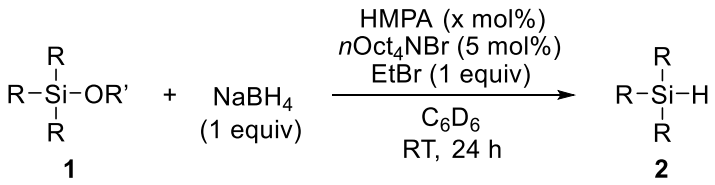
entry	co-catalyst	solvent (mL)	**1a** conv. (%)[b]	**2a** yield (%)[b]
1	–	THF (0.5)	17	16
2	–	THF (0.05)	74	70
3	–	–	67	67
4	*n*Oct_4NBr	THF (0.05)	56	56
5	–	$C_2H_4Cl_2$ (0.05)	51	50
6	*n*Oct_4NBr	$C_2H_4Cl_2$ (0.05)	92	89
7	–	C_6D_6 (0.05)	31	27
8	*n*Oct_4NBr	C_6D_6 (0.05)	93	93 (93)[c]
9	*n*Bu_4NBr	C_6D_6 (0.05)	35	34
10[d]	*n*Oct_4NBr	C_6D_6 (0.05)	N.R.[e]	–
11[f]	*n*Oct_4NBr	C_6D_6 (0.05)	< 1	< 1

[a]Reaction conditions: Me_2(*n*Oct)SiOMe (0.20 mmol), $NaBH_4$ (0.20 mmol), EtBr (0.20 mmol), HMPA (0.010 mmol) and co-catalyst (0.010 mmol) in solvent at RT for 24 h. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. [c]Isolated yield of **2a** in a larger scale reaction. Reaction conditions: Me_2(*n*Oct)SiOMe (2.0 mmol), $NaBH_4$ (2.0 mmol), EtBr (2.0 mmol), HMPA (0.10 mmol) and *n*Oct_4NBr (0.10 mmol) in C_6H_6 (0.5 mL) at RT for 24 h. [d]Without EtBr. [e]No reaction. [f]Without HMPA.

We subsequently examined the reduction of various alkoxy silanes with $NaBH_4$ using the catalyst combination of HMPA and *n*Oct_4NBr (Table 3-3). Reaction of Et_3SiOMe (**1b**) with 1 equiv. of $NaBH_4$ furnished the corresponding hydrosilane Et_3SiH (**2b**) in good yield (96%) in the presence of HMPA (5 mol%), *n*Oct_4NBr (5 mol%) and 1 equiv. EtBr (Table 3-3, entry 1). Likewise, the reduction of $Me_2PhSiOMe$ (**1c**) and $MePh_2SiOMe$ (**1d**) produced the corresponding hydrosilanes, Me_2PhSiH (**2c**) and $MePh_2SiH$ (**2d**) in 90% and 92% yields, respectively

(Table 3-3, entries 2 and 7). It is to be noted that the reactions achieved to furnish the corresponding hydrosilanes with higher yields compared to the BH_3-reduction reactions shown in Table 3-1, entries 12–14. The reduction of Ph_3SiOMe (**1e**) was catalyzed by increased amount of HMPA (20 mol%) to form Ph_3SiH (**2e**) in 94% yield (Table 3-3, entry 8). Reduction of $Me_2(C_6F_5)SiOEt$ (**1f-Et**) resulted in the formation of $Me_2(C_6F_5)SiH$ (**2f**) in moderate yield (69%), even when using 20 mol% of HMPA (Table 3-3, entry 9). Thus, the electron-withdrawing groups on the Si atom likely retard the reaction. Reductions of bulky $Me_2(t\text{Bu})SiOMe$ (**1g**) and $i\text{Pr}_3SiOMe$ (**1h**) proceeded using higher amounts of HMPA (1 equiv.), $NaBH_4$ (2 equiv.) and EtBr (2 equiv.), resulting in the formation of $Me_2(t\text{Bu})SiH$ (**2g**) (64%) and $i\text{Pr}_3SiH$ (**2h**) (32%) (Table 3-3, entries 10 and 11). The reaction yield was also dependent on the size of the alkoxy groups. $Me_2PhSiOEt$ (**1c-Et**) was reduced similarly to $Me_2PhSiOMe$ (**1c**), forming Me_2PhSiH (**2c**) in 86% yield (Table 3-2, entry 3). The use of 20 mol% HMPA promoted the reduction of $Me_2PhSiOi\text{Pr}$ (**1c-*i*Pr**) to furnish the corresponding hydrosilane in 78% yield (Table 3-3, entry 4), whereas reduction of bulkier $Me_2PhSiOt\text{Bu}$ (**1c-*t*Bu**) did not proceed under the same reaction conditions (Table 3-3, entry 5). Reduction of $Me_2PhSiOPh$ (**1c-Ph**) resulted in a 22% yield of Me_2PhSiH (**2c**), even when using 20 mol% of HMPA. The result suggested that a less electron-donating phenoxy group negatively affected the reaction (vide infra).

Table 3-3. Substrate scope in reduction of monoalkoxy silane catalyzed be HMPA. [a]



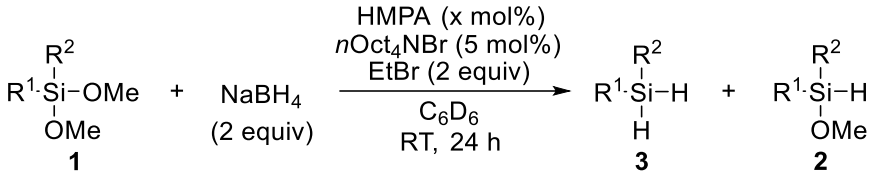
Entry	alkoxy silanes	HMPA (mol%)	Alkoxysilane conv. (%)[b]	Hydrosilane yield (%)[b]
1	Et_3SiOMe (**1b**)	5	96	**2b**: 96
2	$Me_2PhSiOMe$ (**1c**)	5	91	**2c**: 90
3	$Me_2PhSiOEt$ (**1c-Et**)	5	86	**2c**: 86
4	Me_2PhSiO*i*Pr (**1c-*i*Pr**)	20	80	**2c**: 78
5	Me_2PhSiO*t*Bu (**1c-*t*Bu**)	20	N.R.[d]	**2c**: –
6	$Me_2PhSiOPh$ (**1c-Ph**)	20	23	**2c**: 22
7	$MePh_2SiOMe$ (**1d**)	5	92	**2d**: 92
8	Ph_3SiOMe (**1e**)	20	94	**2e**: 94 (91)[f]
9	$Me_2(C_6F_5)SiOEt$ (**1f-Et**)	20	95	**2f**: 69
10[g]	Me_2(*t*Bu)SiOMe (**1g**)	100	85	**2g**: 64
11[g]	*i*Pr_3SiOMe (**1h**)	100	58	**2h**: 32

[a]Reaction conditions: R_3SiOR' (0.20 mmol), $NaBH_4$ (0.20 mmol), EtBr (0.20 mmol), HMPA (entries 1–3: 0.010 mmol; entries 4–9: 0.040 mol; entries 10 and 11: 0.20 mmol) and *n*Oct_4NBr (0.010 mmol) in C_6D_6 (0.05mL) at RT for 24 h. [b]Determined by 1H NMR using mesitylene as an internal standard. [c]Isolated yield in a larger scale reaction. Reaction conditions: R_3SiOR' (2.0mmol), $NaBH_4$ (2.0mmol), EtBr (2.0 mmol), HMPA (0.10 mmol) and *n*Oct_4NBr (0.10 mmol) in C_6H_6 (0.5 mL) at RT for 24 h. [d]No reaction. [e]CH_2Cl_2 (0.05 mL) was used instead of C_6D_6 due to the low solubility of **1e**. f Isolated yield in a larger scale reaction. Reaction conditions: **1e** (2.0 mmol), $NaBH_4$ (2.0 mmol), EtBr (2.0 mmol), HMPA (0.40 mol) and *n*Oct_4NBr (0.10 mmol) in CH_2Cl_2 (0.5 mL) at RT for 24 h. [g]$NaBH_4$ (0.4 mmol) and EtBr (0.4 mmol) were used.

Reduction of dialkoxy silanes was also achieved by treatment with 2 equiv. of $NaBH_4$ and EtBr. The reactions of $MeCySi(OMe)_2$ (**1i**) (Cy = cyclohexyl) or $MePhSi(OMe)_2$ (**1j**) with $NaBH_4$ (2 equiv.) proceeded in the presence HMPA (5 mol%), *n*Oct_4NBr (5 mol%), and EtBr (2 equiv.) to form the corresponding hydrosilanes in good yields,

$MeCySiH_2$ (**3i**) (76%) and $MePhSiH_2$ (**3j**) (71%), respectively (Table 3-4, entries 1 and 2). Bulkier Ph_2SiH_2 (**3k**) and Cyp_2SiH_2 (**3l**) (Cyp = cyclopentyl) were also obtained in good yields using increased amounts of HMPA, 20 mol% and 100 mol%, respectively (Table 3-4, entries 3 and 4). In these reactions, slight amounts of monohydrosilanes were also formed. Reduction of $Cl(CH_2)_3MeSi(OMe)_2$ (**1m**) and $F_3C(CH_2)_2MeSi(OMe)_2$ (**1n**) also proceeded to form the corresponding dihydrosilanes in good yields (Table 3-4, entries 5 and 6).

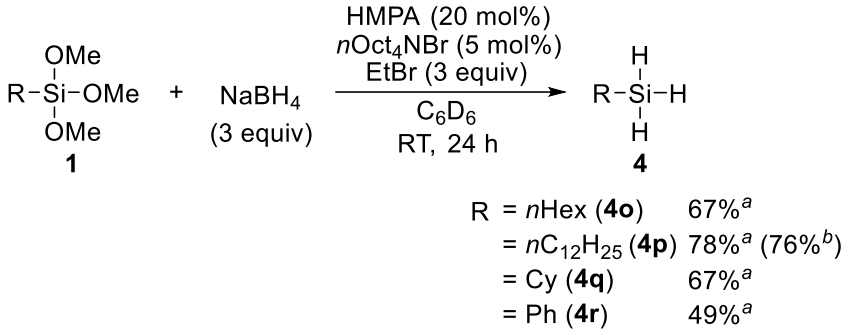
Table 3-4. Substrate scope in reduction of dialkoxy silane catalyzed be HMPA. [a]



Entry	R, R' (**1**)	HMPA (mol%)	Alkoxysilane conv. (%)[b]	Hydrosilane yield (%)[b]
1	Me, Cy (**1i**)	5	81	**3i**: 76 (73)[c] **3i**: 5
2	Me, Ph (**1j**)	5	75	**3j**: 71 (66)[c] **2j**: 5
3	Ph, Ph (**1k**)	20	73	**3k**: 72 (72)[c] **2k**: 3
4	Cyp, Cyp (**1l**)	100	86	**2l**: 77 (72)[c] **2l**: 5
5	Me, $Cl(CH_2)_3$ (**1m**)	5	78	**3m**: 70
6	Me, $F_3C(CH_2)_2$ (**1n**)	20	78	**3n**: 64

[a]Reaction conditions: $R_2Si(OMe)_2$ (0.20 mmol), $NaBH_4$ (0.40 mmol), EtBr (0.40 mmol), HMPA (entries 1, 2 and 5: 0.010 mmol; entries 3 and 6: 0.040 mol; entry 4: 0.20 mmol) and nOct$_4$NBr (0.010 mmol) in C_6D_6 (0.05 mL) at RT for 24 h. [b]Determined by 1H NMR using mesitylene as an internal standard. [c]Isolated yield in a larger scale reaction. Reaction conditions: $R_2Si(OMe)_2$ (2.0 mmol), $NaBH_4$ (4.0 mmol), EtBr (4.0 mmol), HMPA (entries 1 and 2: 0.10 mmol; entry 3: 0.40 mmol, entry 4: 2.0 mmol) and nOct$_4$NBr (0.10 mmol) in C_6H_6 (0.5 mL) at RT for 24 h.

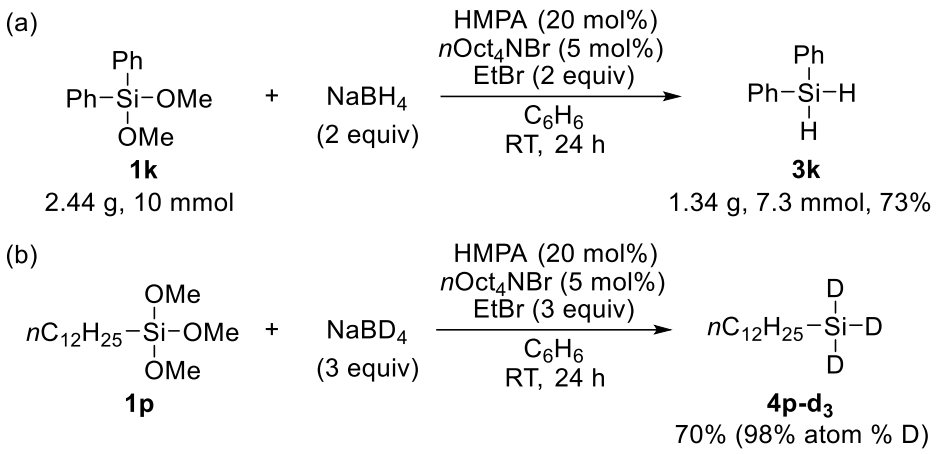
Reduction of trialkoxy silanes was catalyzed by 20 mol% of HMPA to furnish various trihydrosilanes (Scheme 3-3). Trimethoxysilanes with a linear or cyclic alkyl group resulted in the formation of trihydrosilanes in moderate yields. Similarly to the reactions of dialkoxy silanes, the reaction of aryl-substituted $PhSi(OMe)_3$ (**1r**) was somewhat reluctant towards reduction to form $PhSiH_3$ (**4r**) in 49% yield.



Scheme 3-3. Substrate Scope in reduction of trialkoxy silane catalyzed by HMPA. [a]NMR yield. [b]Isolated yield.

To demonstrate the utility of this method, gram-scale synthesis of **3k** from $Ph_2Si(OMe)_2$ (**1k**) (10 mmol) was performed.

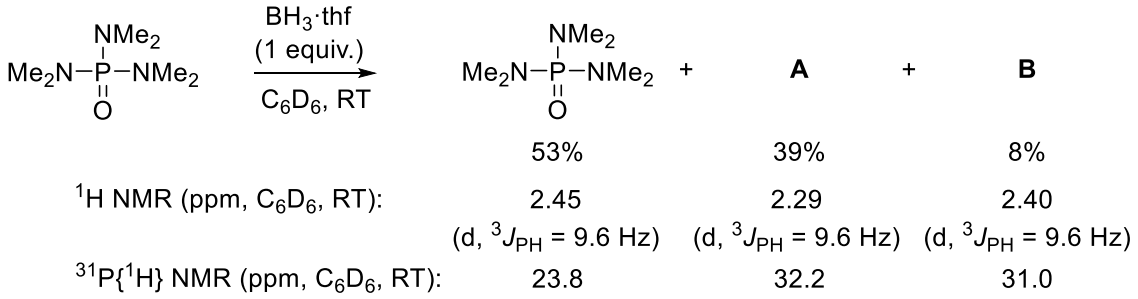
Analytically pure **3k** was obtained via a simple purification procedure comprising successive filtration and evaporation of the resulting reaction mixture (Scheme 3-4(a)). The reaction was also utilized in the synthesis of deuterated hydrosilanes. Thus, the reduction of $nC_{12}H_{25}Si(OMe)_3$ (**1p**) with $NaBD_4$ furnished $nC_{12}H_{25}SiD_3$ (**4p-d$_3$**) in 70% yield (98 atom% D) (Scheme 3-4(b)).



Scheme 3-4. (a) Gram Scale synthesis. (b) Deuterio labelled hydrosilane synthesis.

The mechanism of the reaction is proposed as follows.

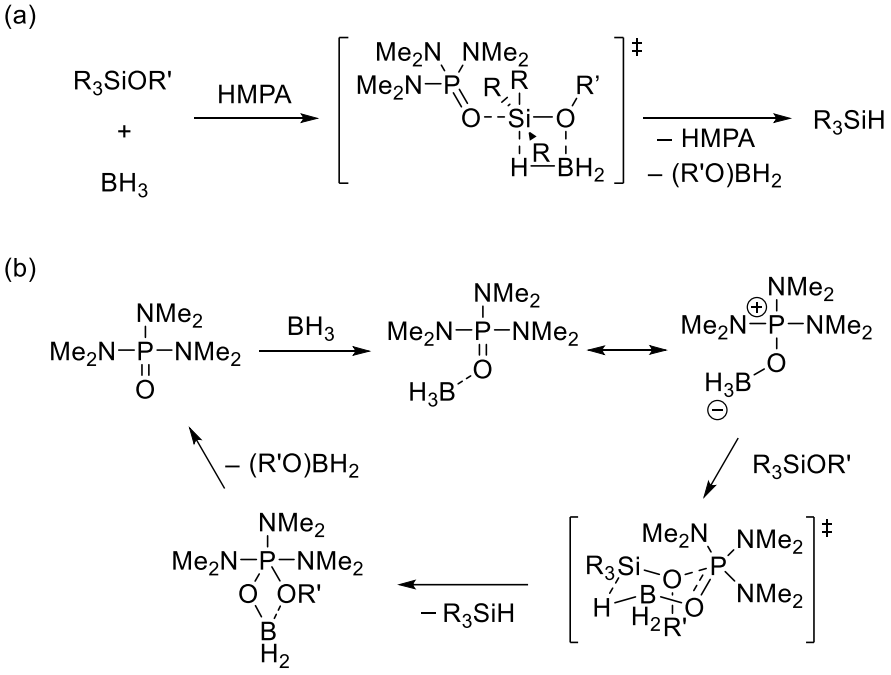
In order to see whether HMPA as the Lewis base interacts with alkoxysilane, the reaction of alkoxysilanes with HMPA was performed and followed by NMR. When HMPA and $Me_2PhSiOMe$ (**1e**) or $Si(OMe)_4$ were mixed in 1:1 or in 1:10 molar ratio, respectively, in C_6D_6, no change in the spectrum was observed in the ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra. Next, the reaction of HMPA with BH_3·thf (1 equiv) was followed. In the ^1H and $^{31}P\{^1H\}$ NMR spectra, new signal sets **A** and **B** appeared in addition to the free HMPA in C_6D_6; i.e., **A** (^1H NMR: 2.29 ppm (d, $^3J_{PH}$ = 9.6 Hz), $^{31}P\{^1H\}$ NMR: 32.2 ppm) and **B** (^1H NMR: 2.40 ppm (d, $^3J_{PH}$ = 9.6 Hz), $^{31}P\{^1H\}$ NMR: 31.0 ppm). The ratio of the integral intensities of the ^1H signal assignable to A, B and HMPA is 53%: 39%: 8%. These results strongly indicated the formation of two new compounds that have interaction of HMPA and BH_3 (Scheme 3-5).



Scheme 3-5. Reaction HMPA with BH_3·thf

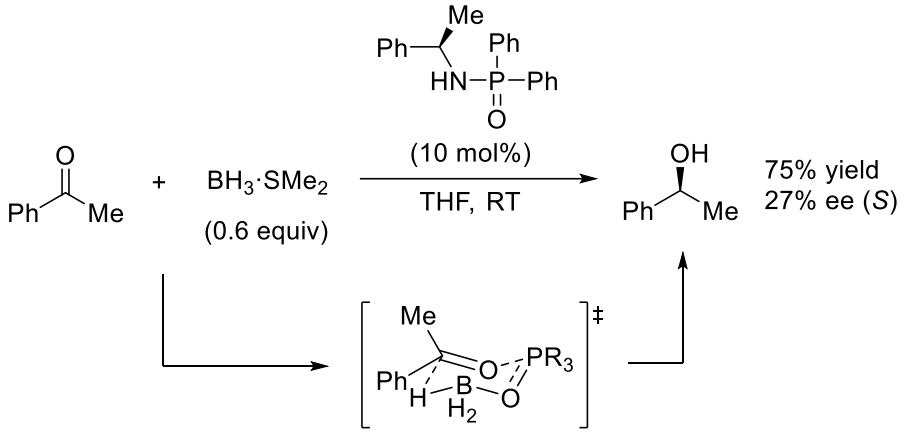
Subsequently, when ^{11}B NMR was measured, one signal was newly observed at δ − 6.5 ppm (q, $^1J_{BH}$ = 105 Hz) in addition to the signals of BH_3·thf (δ 0.3 ppm, q, $^1J_{BH}$ = 106 Hz) and B_2H_6 (δ 18.3 ppm, brs). Since the signal at δ − 6.5 ppm shows a similar coupling pattern to BH_3·thf, one out of **A** and **B** attributed to borane-HMPA complex BH_3·HMPA. Overall, the interaction of borane and HMPA was evidenced.

Based on the above results, the mechanism of this reaction was considered to be the two reaction pathways shown in Scheme 3-6. Although the interaction of HMPA with alkoxysilane was not directly observed, I suggested one mechanism, in which is assisted via the coordination of HMPA to alkoxysilane (Scheme 3-6 (a)).



Scheme 3-6. Possible reaction pathway

The other is the reaction pathway in which borane is activated by the formation of borane complex BH_3·HMPA. It is likely that the nucleophilicity of the H atom become enhanced after the adduct formation, so that the reaction proceeds smoothly via a six-membered ring transition state (Scheme 3-6 (b)). The similar reaction pathway is considered in the borane reduction of carbonyl compounds using a phosphine oxide catalyst (Scheme 3-7).[5]



Scheme 3-7. Borane reduction of carbonyl compounds using phosphine oxide catalyst

In both reactions, coordination of the B or P atom to the alkoxy group on the Si atom plays an important role. This is consistent with the observation that the reaction is retarded when using substrates having a low nucleophilic alkoxy group such as *t*BuO group or PhO groups.

Conclusion

In conclusion, we demonstrated the effective synthesis of hydrosilanes *via* reduction of alkoxy silanes with borane. By using EtBr as a sacrificial reagent, the reactions can also be achieved with easily handled $NaBH_4$ as a hydride source. Mechanistic studies including theoretical studies, are now underway in our group and will be reported in due course.

Experimental section

General considerations

All manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Hexane, C_6H_6, toluene, THF and CH_2Cl_2 were purified by a solvent purification system (MBraun SPS-800 or Glass Contour Ultimate Solvent System). C_6D_6 was dried over sodium benzophenone ketyl and distilled. Me_2PhSiO*i*Pr (**1c-*i*Pr**)[5], $Me_2PhSiOPh$ (**1c-Ph**)[6], $MePh_2SiOMe$ (**1d**)[5], Me_2(*t*Bu)SiOMe (**1g**)[7] and $i Pr_3SiOMe$ (**1h**)[8] were prepared according to the literature procedures. $NaBH_4$ granular (99.99% trace metals basis) was purchased from Sigma-Aldrich Co. LLC. and used without purification. All other reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra (^1H, 600 MHz; ^{11}B, 193 MHz; ^{13}C, 151 MHz; ^{29}Si, 119 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to the residual solvent signals for ^1H and ^{13}C, and to boron trifluoride diethyl ether complex (0.0 ppm) for ^{11}B and to trimethyl(phenyl)silane (–4.7 ppm) for ^{29}Si.

Synthesis of Me_2PhSiO*t*Bu (**1-*t*Bu**)

To a hexane solution (10 mL) of *t*BuOH (0.87 g, 12 mmol), was added $Me_2PhSiCl$ (2.0 g, 12 mmol) and NEt_3 (1.2 g, 12 mmol). The reaction mixture was stirred at room temperature for 24 h. The solution was filtered, and the resulting solid was washed with hexane (20 mL). The filtrate and washings were combined. Fractional distillation was performed to give Me_2PhSiO*t*Bu (**1-*t*Bu**) (0.79 g, 3.8 mmol, 32%).

Catalytic reduction of alkoxysilane with BH_3·thf

A typical procedure (Table 1, entry 11) is as follows. A vial was charged with a THF solution (0.3 mL) of Me_2(*n*Oct)SiOMe (**1a**) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and mesitylene (6.0 mg, 0.050 mmol) as an internal standard. To the solution was added 1 M BH_3·thf THF solution (0.20 mL, 0.20 mmol) at room temperature, and then the solution was stirred for 24 h. The reaction mixture was analyzed by ^{1}H NMR to determine the conversion of **1a** (0.18 mmol, 91%) and the NMR yield of Me_2(*n*Oct)SiH (**2a**) (0.18 mmol, 91%).

Catalytic reduction of alkoxysilane with $NaBH_4$

Determination of NMR yield

Typical procedure 1 (Table 2, entry 8) is as follows. A micro tube (diameter: φ8, length: 50 mm, volume: 1 mL) was charged with a C_6D_6 suspension (0.05 mL) of $NaBH_4$ (7.6 mg, 0.20 mmol), which is pre-grinded in a motar, *n*Oct$_4$NBr (5.6 mg, 0.010 mmol), Me_2(*n*Oct)SiOMe (**1a**) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and mesitylene (6.0 mg, 0.050 mmol) as an internal standard. After EtBr (22 mg, 0.20 mmol) was added, the solution was stirred at room temperature for 24 h (a magnetic stirrer bar: φ1.5 × 8 mm, rotating speed: 1,500 rpm). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1a** (0.19 mmol, 93%) and the NMR yield of Me_2(*n*Oct)SiH (**2a**) (0.19 mmol, 93%).

Determination of isolated yield

Typical procedure 2 (Table 2, entry 8) is as follows. A 3 mL conical vial was charged with a C_6H_6 suspension (0.5 mL) of $NaBH_4$ (76 mg, 2.0 mmol), which is pre-grinded in a motar, (nOct)$_4$NBr (56 mg, 0.10 mmol), Me_2(nOct)SiOMe (**1a**) (410 mg, 2.0 mmol) and HMPA (18 mg, 0.10 mmol). EtBr (220 mg, 2.0 mmol) was added at room temperature, and then the solution was stirred at room temperature for 24 h (a magnetic stirrer bar: φ1.5 × 8 mm, rotating speed: 1,500 rpm). The solution was diluted with hexane (20 mL) and filtered through a silica gel pad (eluent: hexane (100 mL)). The volatiles were removed in vacuo to give Me_2(nOct)SiH (**2a**) as a colourless liquid (319 mg, 1.9 mmol, 93%).

Gram scale synthesis of Ph_2SiH_2 (**2k**)

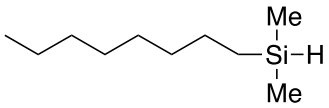
A 10 mL pear shaped flask was charged with a C_6H_6 suspension (2.5 mL) of $NaBH_4$ (0.76 g, 20 mmol), which is pre-grinded in a mortar, nOct$_4$NBr (280 mg, 0.50 mmol), $Ph_2Si(OMe)_2$ (**1k**) (2.4 g, 10 mmol) and HMPA (360 mg, 2.0 mmol) and sealed with a septum equipped with a needle. EtBr (2.2 g, 20 mmol) was added at room temperature, and then the solution was stirred at room temperature for 24 h (a magnetic stirrer bar of φ3 × 10 mm, 1,500 rpm. The solution was diluted with hexane (20 mL) and filtered through a silica gel pad (eluent: hexane (100 mL)). The volatiles were removed in vacuo to give Ph_2SiH_2 (**2k**) as a colorless liquid (1.3 g, 7.3 mmol, 73%).

Compound characterization data

The products in Table 1 and Table 2, Me_2(nOct)SiH (**2a**)[9], Et_3SiH (**2b**)[9], Me_2PhSiH (**2c**)[9], $Me_2(C_6F_5)SiH$ (**2f**)[10], $MeCySiH_2$ (**3i**)[11], MePhSiH(OMe) (**2j**)[9], $MePhSiH_2$ (**3j**)[9], $Ph_2SiH(OMe)$ (**2k**)[9], Ph_2SiH_2 (**3k**)[9], Me{Cl(CH$_2$)$_3$}SiH$_2$ (**3m**)[12], Me{CF$_3$(CH$_2$)$_2$}SiH$_2$ (**3n**)[13], nC$_{12}$H$_{25}$SiH$_3$ (**4p**)[14], $CySiH_3$ (**4q**)[15], and $PhSiH_3$ (**4r**)[9] were identified by comparing their ^{1}H NMR data with those previously reported. MeCySiH(OMe) (**2i**) and $Cyp_2SiH(OMe)$ (**2l**) were identified by comparing their ^{1}H NMR data with those alternatively synthesized by following the reported

procedure.[15] $MePh_2SiH$ (**2d**), Ph_3SiH (**2e**), $Me_2(tBu)SiH$ (**2g**), iPr_3SiH (**2h**) and nHexSiH_3 (**2o**) were identified by comparing their ^{1}H NMR data with commercial sources.

dimethyl(octyl)silane (**2a**)



Reduction with BH_3·thf

The general procedure was followed with Me_2(*n*Oct)SiOMe (**1a**) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH_3·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1a** (0.18 mmol, 91%) and the NMR yield of Me_2(*n*Oct)SiH (**2a**) (0.18 mmol, 91%).

Reduction with $NaBH_4$

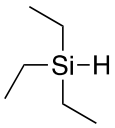
The general procedure 2 was followed with $NaBH_4$ (76 mg, 2.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), Me_2(*n*Oct)SiOMe (**1a**) (410 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: hexane (100 mL)) to provide **2a** as a colorless liquid in 93% (319 mg, 1.9 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.06 (d, 6H, $^3J_{HH}$ = 3.6 Hz, Si*Me*$_2$), 0.57 (m 2H, SiC*H*$_2$(CH$_2$)$_6$CH$_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.0 Hz, SiCH$_2$(CH$_2$)$_6$C*H*$_3$), 1.22-1.42 (m, 12H, SiCH$_2$(C*H*$_2$)$_6$CH$_3$)), 4.15 (sep, 1H, $^3J_{HH}$ = 3.6 Hz, Si*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ –4.3 (s, Si*Me*), 14.3 (s, Si*Oct*), 14.4 (s, Si*Oct*), 23.1 (s, Si*Oct*), 24.8 (s, Si*Oct*), 29.7 (s, Si*Oct*), 29.7 (s, Si*Oct*), 32.3 (s, Si*Oct*), 33.6 (s, Si*Oct*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –12.8 (s).

triethylsilane (**2b**)



Reduction with BH_3·thf

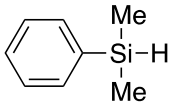
The general procedure was followed with Et_3SiOMe (**1b**) (23 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH_3·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ^1H NMR to determine the conversion of **1b** (0.16 mmol, 80%) and the NMR yield of Et_3SiH (**2b**) (0.15 mmol, 75%).

Reduction with $NaBH_4$

The general procedure 1 was followed with $NaBH_4$ (7.6 mg, 0.20 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), Et_3SiOMe (**1b**) (23 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (22 mg, 0.20 mmol). The resulting solution was analyzed by ^1H NMR to determine the conversion of **1b** (0.20 mmol, 96%) and the NMR yield of Et_3SiH (**2b**) (0.20 mmol, 96%).

^1H NMR (C_6D_6, RT, ppm): δ 0.53 (dq, 6H, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 7.9 Hz, SiCH_2CH$_3$), 0.96 (t, 9H, $^3J_{HH}$ = 7.9 Hz, SiCH$_2$CH_3), 3.88 (sep, 1H, $^3J_{HH}$ = 3.2 Hz, Si*H*).

dimethyl(phenyl)silane (**2c**)



Reduction with BH_3·thf

The general procedure was followed with $Me_2PhSiOMe$ (**1c**) (33 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH_3·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ^1H NMR to determine the conversion of **1c** (0.18 mmol, 91%) and the NMR yield of Me_2PhSiH (**2c**) (0.18 mmol, 88%).

Reduction with $NaBH_4$

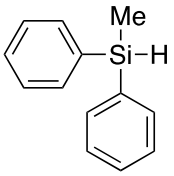
The general procedure 2 was followed with $NaBH_4$ (76 mg, 2.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), $Me_2PhSiOMe$ (**1c**) (330 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: pentane (100 mL)) to provide **2c** as a colorless liquid in 83% (226 mg, 0.17 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.21 (d, 6H, $^3J_{HH}$ = 3.8 Hz, Si*Me*$_2$), 4.63 (sept, 1H, $^3J_{HH}$ = 3.8 Hz, Si*H*), 7.19 (m, 3H, m, *p*-C*H*), 7.47 (m, 2H, *o*-C*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ –3.8 (s, Si*Me*), 128.3 (s, Si*Ph*), 129.5 (s, Si*Ph*), 134.3 (s, Si*Ph*), 137.4 (s, Si*Ph*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –16.7 (s).

methyldiphenylsilane (**2d**)



Reduction with BH_3·thf

The general procedure was followed with $MePh_2SiOMe$ (**1d**) (46 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH_3·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1d** (0.15 mmol, 78%) and the NMR yield of $MePh_2SiH$ (**2d**) (0.15 mmol, 78%).

Reduction with $NaBH_4$

The general procedure 1 was followed with $NaBH_4$ (7.6 mg, 0.2 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), $MePh_2SiOMe$ (**1d**) (46 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (22 mg, 0.2 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1d** (0.18 mmol, 92%) and the NMR yield of

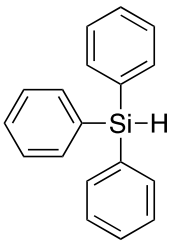
$MePh_2SiH$ (**2d**) (0.18 mmol, 92%).

^1H NMR (C_6D_6, RT, ppm): δ 0.46 (d, 3H, $^3J_{HH}$ = 3.8 Hz, Si*Me*), 5.14 (q, 2H, $^3J_{HH}$ = 3.8 Hz, SiH_2), 7.12-7.20 (m, 3H, *m*, *p*-C*H*), 7.50 (m, 2H, *o*-C*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ –5.0 (s, Si*Me*), 128.3 (s, Si*Ph*), 129.6 (s, Si*Ph*), 135.2 (s, Si*Ph*), 135.5 (s, Si*Ph*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –17.1 (s).

triphenylsilane (**2e**)



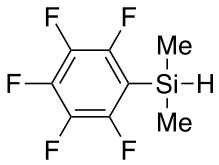
The general procedure 2 was followed with CH_2Cl_2 (0.5 mL), $NaBH_4$ (76 mg, 2.0 mmol), *n*Oct_4NBr (56 mg, 0.10 mmol), Ph_3SiOMe (**1e**) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: toluene (100 mL)) to provide the title compound **2e** as a white solid in 91% (474 mg, 1.8 mmol).

^1H NMR (C_6D_6, RT, ppm): δ 5.71 (s, 1H, Si*H*), 7.09-7.19 (m, 9H, *m*, *p*-C*H*), 7.59 (m, 6H, *o*-C*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ 128.4 (s, Si*Ph*), 130.0 (s, Si*Ph*), 133.7 (s, Si*Ph*), 136.2 (s, Si*Ph*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –17.5 (s).

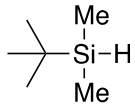
dimethyl(pentafluorophenyl)silane (**2f**)



The general procedure 1 was followed with $NaBH_4$ (7.6 mg, 0.20 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $Me_2(C_6F_5)SiOEt$ (**1f-Et**) (54 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (22 mg, 0.20 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1f-Et** (0.19 mmol, 95%) and the NMR yield of $Me_2(C_6F_5)SiH$ (**2f**) (0.14 mmol, 69%).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.15 (dt, 6H, $^3J_{HH}$ = 3.9 Hz, $^5J_{CF}$ = 0.8 Hz, Si*Me*$_2$), 4.57 (sep, 1H, $^3J_{HH}$ = 3.9 Hz, Si*H*).

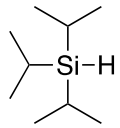
tert-butyldimethylsilane (**2g**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), Me_2(*t*Bu)SiOMe (**1g**) (29 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1g** (0.17 mmol, 85%) and the NMR yield of Me_2(*t*Bu)SiH (**2g**) (0.13 mmol, 64%).

^{1}H NMR (C_6D_6, RT, ppm): δ –0.02 (d, 6H, $^3J_{HH}$ = 3.7 Hz, Si*Me*$_2$), 0.90 (s, 9H, Si*tBu*), 3.87 (sep, 1H, $^3J_{HH}$ = 3.7 Hz, Si*H*).

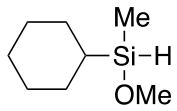
triisopropylsilane (**2h**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), *i*Pr_3SiOMe (**1h**) (38 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^1H NMR to determine the conversion of **1h** (0.12 mmol, 58%) and the NMR yield of *i*Pr_3SiH (**2h**) (0.064 mmol, 32%).

^1H NMR (C_6D_6, RT, ppm): δ 0.95-1.05 (m, 3H, $^3J_{HH}$ = 3.7 Hz, SiC*H*$(CH_3)_2$), 1.07 (d, 18H, $^3J_{HH}$ = 6.5 Hz, SiCH(C*H*$_3)_2$), 3.59 (q, 1H, $^3J_{HH}$ = 2.2 Hz, Si*H*).

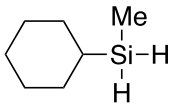
cyclohexyl(methoxy)methylsilane (**2i**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $MeCySi(OMe)_2$ (**1i**) (38 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^1H NMR to determine the conversion of **1i** (0.16 mmol, 81%) and the NMR yield of MeCySiH(OMe) (**2i**) (0.010 mmol, 5%) and $MeCySiH_2$ (**3i**) (0.15 mmol, 76%).

^1H NMR (C_6D_6, RT, ppm): δ 0.10 (d, 3H, $^3J_{HH}$ = 2.9 Hz, Si*Me*), 0.76 (m, 1H, SiC*H*$(CH_2)_5$), 1.14-1.30 (m, 6H, SiCH(C*H*$_2)_5$), 1.62-1.82 (m, 6H, SiCH(C*H*$_2)_5$), 3.33 (s, 3H, O*Me*) 4.61 (qd, 1H, $^3J_{HH}$ = 3.0, 2.9 Hz, Si*H*).

cyclohexyl(methy)lsilane (**3i**)



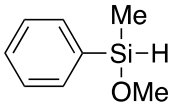
The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*Oct_4NBr (56 mg, 0.10 mmol), $MeCySi(OMe)_2$ (**1i**) (380 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **3i** as a colorless liquid in 73% (187 mg, 1.5 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.00 (t, 3H, $^3J_{HH}$ = 4.2 Hz, Si*Me*), 0.69 (m, 1H, SiC*H*$(CH_2)_5$), 1.07-1.24 (m, 6H, SiCH(C*H*$_2)_5$), 1.57-1.73 (m, 6H, SiCH(C*H*$_2)_5$), 3.82 (qd, 2H, $^3J_{HH}$ = 2.9, 4.2 Hz, Si*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ 14.2 (s, Si*Me*), 22.0 (s, Si*Cy*), 27.0 (s, Si*Cy*), 27.9 (s, Si*Cy*), 29.1 (s, Si*Cy*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –27.1 (s).

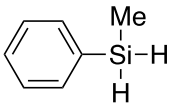
methoxy(methyl)phenylsilane (**2j**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $MePhSi(OMe)_2$ (**1j**) (36 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1j** (0.15 mmol, 75%) and the NMR yield of MePhSiH(OMe) (**2j**) (0.010 mmol, 5%) and $MePhSiH_2$ (**3j**) (0.14 mmol, 71%).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.32 (t, 3H, $^3J_{HH}$ = 2.9 Hz, Si*Me*)), 3.30 (s, 3H, O*Me*), 5.18 (q, 1H, $^3J_{HH}$ = 2.9 Hz, Si*H*), 7.20 (m, 3H, *m*, *p*-C*H*), 7.56 (m, 2H, *o*-C*H*).

methyl(phenyl)silane (**3j**)



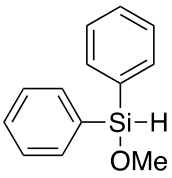
The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*Oct_4NBr (56 mg, 0.10 mmol), $MePhSi(OMe)_2$ (**1j**) (360 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **3j** as a colorless liquid in 66% (161 mg, 1.3 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.18 (t, 3H, $^3J_{HH}$ = 4.3 Hz, Si*Me*), 4.49 (q, 2H, $^3J_{HH}$ = 4.3 Hz, SiH_2), 7.11-7.19 (m, 3H, *m*, *p*-C*H*), 7.45 (m, 2H, *o*-C*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ –7.7 (s, Si*Me*), 128.3 (s, Si*Ph*), 129.8 (s, Si*Ph*), 133.4 (s, Si*Ph*), 135.1 (s, Si*Ph*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –35.5 (s).

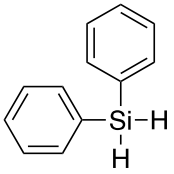
methoxydiphenylsilane (**2k**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $Ph_2Si(OMe)_2$ (**1k**) (49 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1k** (0.15 mmol, 73%) and the NMR yield of $Ph_2SiH(OMe)$ (**2k**) (0.0060 mmol, 3%) and Ph_2SiH_2 (**3k**) (0.14 mmol, 72%).

^{1}H NMR (C_6D_6, RT, ppm): δ 3.40 (s, 3H, O*Me*), 5.61 (s, 1H, Si*H*), 7.09-7.19 (m, 6H, *m*, *p*-C*H*), 7.65 (m, 4H, *o*-C*H*).

diphenylsilane (**3k**)



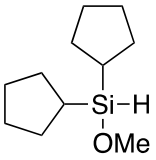
The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), $Ph_2Si(OMe)_2$ (**1k**) (490 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to **3k** as a colorless liquid in 72% (265 mg, 1.4 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 5.08 (s, 2H, Si*H*), 7.09-7.19 (m, 6H, *m*, *p*-C*H*), 7.51 (m, 4H, *o*-C*H*).

^{13}C NMR (C_6D_6, RT, ppm): δ 128.4 (s, Si*Ph*), 130.1 (s, Si*Ph*), 131.7 (s, Si*Ph*), 136.0 (s, Si*Ph*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –33.2 (s).

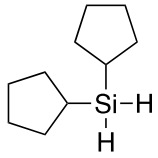
dicyclopentyl(methoxy)silane (**2l**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), $Cyp_2Si(OMe)_2$ (**1l**) (38 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1l** (0.17 mmol, 86%) and the NMR yield of $Cyp_2SiH(OMe)$ (**2l**) (0.010 mmol, 5%) and Cyp_2SiH_2 (**3l**) (0.15 mmol, 77%).

^{1}H NMR (C_6D_6, RT, ppm): δ 1.04 (m, 1H, SiC*H*$(CH_2)_4$), 1.36 (m, 2H, SiCH(C*H*$_2)_4$), 1.46 (m, 2H, SiCH(C*H*$_2)_4$), 1.58 (m, 2H, SiCH(C*H*$_2)_4$), 1.80 (m, 2H, SiCH(C*H*$_2)_4$), 3.43 (s, 3H, O*Me*), 4.57 (t, 2H, $^3J_{HH}$ = 2.3 Hz, Si*H*).

dicyclopentylsilane (**3l**)



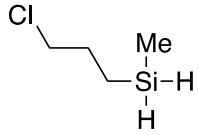
The general procedure 2 was followed with $NaBH_4$ (152 mg, 4.0 mmol), *n*Oct_4NBr (56 mg, 0.10 mmol), $Cyp_2Si(OMe)_2$ (**1l**) (460 mg, 2.0 mmol), HMPA (360 mg, 2.0 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **3l** as a colorless liquid in 72% (242 mg, 1.4 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.99 (m, 1H, SiC*H*$(CH_2)_4$), 1.36 (m, 2H, SiCH(C*H*$_2)_4$), 1.46 (m, 2H, SiCH(C*H*$_2)_4$), 1.58 (m, 2H, SiCH(C*H*$_2)_4$), 1.80 (m, 2H, SiCH(C*H*$_2)_4$), 3.92 (t, 2H, $^3J_{HH}$ = 3.2 Hz, Si*H*$_2$).

^{13}C NMR (C_6D_6, RT, ppm): δ 20.8 (s, Si*Cyp*), 27.2 (s, Si*Cyp*), 30.4 (s, Si*Cyp*).

^{29}Si NMR (C_6D_6, RT, ppm): δ –16.7 (s).

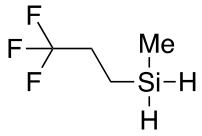
3-chloropropylmethylsilane (**3m**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $Me\{Cl(CH_2)_3\}Si(OMe)_2$ (**1m**) (37 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the conversion of **1m** (0.16 mmol, 78%) and the NMR yield of $Me\{Cl(CH_2)_3\}SiH_2$ (**3m**) (0.14 mmol, 70%).

^{1}H NMR (C_6D_6, RT, ppm): δ –0.11 (t, 3H, $^3J_{HH}$ = 4.2 Hz, Si*Me*), 0.40 (m, 2H, SiC*H*$_2$CH$_2$CH$_2$Cl), 1.46 (m, 2H, SiCH$_2$C*H*$_2$CH$_2$Cl), 3.05 (t, 2H, $^3J_{HH}$ = 6.8 Hz, SiCH$_2$CH$_2$C*H*$_2$Cl), 3.77 (sept, 2H, $^3J_{HH}$ = 4.2 Hz, Si*H*$_2$).

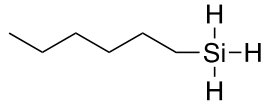
3,3,3-trifluoropropylmethylsilane (**3n**)



The general procedure 1 was followed with $NaBH_4$ (15.2 mg, 0.40 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $Me\{F_3C(CH_2)_2\}Si(OMe)_2$ (**1n**) (37 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ^1H NMR to determine the conversion of **1n** (0.16 mmol, 78%) and the NMR yield of $Me\{F_3C(CH_2)_2\}SiH_2$ (**3n**) (0.13 mmol, 64%).

^1H NMR (C_6D_6, RT, ppm): δ –0.21 (t, 3H, $^3J_{HH}$ = 4.1 Hz, Si*Me*), 0.52 (m, 2H, $SiCH_2CH_2CF_3$), 1.66 (m, 2H, $SiCH_2CH_2CF_3$), 3.63 (sept, 2H, $^3J_{HH}$ = 4.1 Hz, SiH_2).

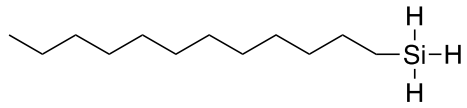
hexylsilane (**4o**)



The general procedure 1 was followed with $NaBH_4$ (22.8 mg, 0.60 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), *n*$HexSi(OMe)_3$ (**1o**) (23 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by ^1H NMR to determine the NMR yield of *n*$HexSiH_3$ (**4o**) (0.13 mmol, 67%).

^1H NMR (C_6D_6, RT, ppm): δ 0.51-0.56 (m, 2H, $SiCH_2(CH_2)_4CH_3$), 0.86 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $SiCH_2(CH_2)_4CH_3$), 1.12-1.35 (m, 8H, $SiCH_2(CH_2)_4CH_3$), 3.61 (t, 3H, $^3J_{HH}$ = 3.9 Hz, SiH_3).

dodecylsilane (**4p**)



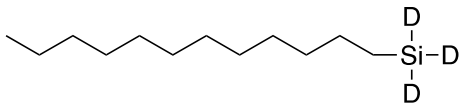
The general procedure 2 was followed with $NaBH_4$ (228 mg, 6.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), nC$_{12}$H$_{25}$Si(OMe)$_3$ (**1p**) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (650 mg, 6.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **4p** as a colorless liquid in 76% (305 mg, 1.5 mmol).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.55 (m, 2H, SiCH_2(CH$_2$)$_{10}$CH$_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.1 Hz, SiCH$_2$(CH$_2$)$_{10}$CH_3), 1.18-1.38 (m, 20H, SiCH$_2$(CH_2)$_{10}$CH$_3$).

^{13}C NMR (C_6D_6, RT, ppm): δ 6.1 (s, Si$C_{12}H_{25}$), 14.3 (s, Si$C_{12}H_{25}$), 23.1 (s, Si$C_{12}H_{25}$), 26.7 (s, Si$C_{12}H_{25}$), 29.6 (s, Si$C_{12}H_{25}$), 29.8 (s, Si$C_{12}H_{25}$), 29.9 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 32.3(s, Si$C_{12}H_{25}$), 32.9 (s, Si$C_{12}H_{25}$).

^{29}Si NMR (C_6D_6, RT, ppm): δ –59.4 (s).

dodecylsilane-d$_3$ (**4p-d$_3$**)



The general procedure 2 was followed with $NaBD_4$ (99 atom% D, 250 mg, 6.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), nC$_{12}$H$_{25}$Si(OMe)$_3$ (**1p**) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (650 mg, 6.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide **4p-d$_3$** as a colorless liquid in 70% (286 mg, 1.4 mmol, 98 atom% D).

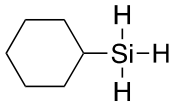
^{1}H NMR (C_6D_6, RT, ppm): δ 0.54 (t, 2H, $^3J_{HH}$ = 7.9 Hz, SiCH_2(CH$_2$)$_{10}$CH$_3$), 0.92 (t, 3H, $^3J_{HH}$ = 7.5 Hz, SiCH$_2$(CH$_2$)$_{10}$CH_3), 1.18-1.38 (m, 20H, SiCH$_2$(CH_2)$_{10}$CH$_3$).

^{13}C NMR (C_6D_6, RT, ppm): δ 5.9 (s, Si$C_{12}H_{25}$), 14.3 (s, Si$C_{12}H_{25}$), 23.1 (s, Si$C_{12}H_{25}$), 26.6 (s, Si$C_{12}H_{25}$), 29.6 (s, Si$C_{12}H_{25}$), 29.8 (s, Si$C_{12}H_{25}$), 30.0 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 30.1 (s, Si$C_{12}H_{25}$), 32.3(s,

Si$C_{12}H_{25}$), 32.8 (s, Si$C_{12}H_{25}$).

^{29}Si NMR (C_6D_6, RT, ppm): δ –60.2 (sept, $^1J_{SiD}$ = 29.3 Hz).

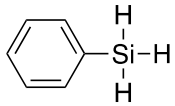
cyclohexylsilane (**4q**)



The general procedure 1 was followed with $NaBH_4$ (22.8 mg, 0.60 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $CySi(OMe)_3$ (**1q**) (23 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the NMR yield of $CySiH_3$ (**4q**) (0.13 mmol, 67%).

^{1}H NMR (C_6D_6, RT, ppm): δ 0.75 (m, 1H, SiC*H*$(CH_2)_5$), 1.05-1.18 (m, 5H, ax-C*H*), 1.50-1.66 (m, 5H, eq-C*H*), 3.58 (d, 3H, $^3J_{HH}$ = 3.1 Hz, SiH_3).

phenylsilane (**4r**)



The general procedure 1 was followed with $NaBH_4$ (22.8 mg, 0.60 mmol), *n*Oct_4NBr (5.6 mg, 0.010 mmol), $PhSi(OMe)_3$ (**1r**) (22 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by ^{1}H NMR to determine the NMR yield of $PhSiH_3$ (**4r**) (0.10 mmol, 49%).

^{1}H NMR (C_6D_6, RT, ppm): δ 4.23 (s, 3H, Si*H*), 7.07 (m, 2H, *m*, *p*-C*H*), 7.11 (m, 1H, *p*-C*H*), 7.39 (m, 2H, *o*-C*H*).

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List of publications

Chapter 2

1) 「Catalytic Reduction of Alkoxysilanes with Borane using a Metallocene-Type Yttrium Complex」

Keiya Aoyagi, Kazuhiro Matsumoto, Shigeru Shimada, Kazuhiko Sato and Yumiko Nakajima, *Organometallics*, **2019**, *38*, 210.

Chapter 3

2) 「Synthesis of Hydrosilanes via Lewis-Base-Catalysed Reduction of Alkoxysilane with $NaBH_4$」

Keiya Aoyagi, Yu Ohmori, Koya Inomata, Kazuhiro Matsumoto, Shigeru Shimada, Kazuhiko Sato and Yumiko Nakajima, *Chem. Commun*., **2019**, *55*, 5859.

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July 2019

Keiya Aoyagi