B(C₆F₅)₃-Catalyzed Selective Chlorination of Hydrosilanes

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Abstract: *The chlorination of Si−H bonds often requires stoichiometric amounts of metal salts in conjunction with hazardous reagents, such as tin chlorides, Cl₂, and CCl₄. The catalytic chlorination of silanes often involves the use of expensive transition-metal catalysts. By a new simple, selective, and highly efficient catalytic metal-free method for the chlorination of Si−H bonds, mono-, di-, and trihydrosilanes were selectively chlorinated in the presence of a catalytic amount of B(C₆F₅)₃ or Et₂O·B(C₆F₅)₃ and HCl with the release of H₂ as a by-product. The hydrides in di- and trihydrosilanes could be selectively chlorinated by HCl in a stepwise manner when Et₂O·B(C₆F₅)₃ was used as the catalyst. A mechanism is proposed for these catalytic chlorination reactions on the basis of competition experiments and density functional theory (DFT) calculations.*

$\mathbf{T}$he development of frustrated Lewis pairs (FLPs) and their use in catalysis over the last decade[1] has triggered a renewed interest in the chemistry of B(C₆F₅)₃ (**1**). In 2013, Stephan and co-workers reported FLP-type reactivity of the adduct Et₂O·B(C₆F₅)₃ (**2**) in its ability to activate dihydrogen; this reactivity was used for the hydrogenation of Ph₂C=CH₂.[2] Later, **2** was used as a catalyst for the hydrogenation of ketones and aldehydes.[3] The ability of **1** to activate Si−H bonds through η¹ coordination lead to several unique catalytic reduction processes. The first evidence of Si−H bond activation by **1** was reported by Piers and co-workers in the catalytic hydrosilylation of ketones and aldehydes.[4] Later, by using a hydrosilane with a stereogenic silicon center as a stereochemical probe, Rendler and Oestreich verified the nature of the Si−H bond activation step in the hydrosilylation of the carbonyl compounds.[5b] Rosenberg and co-workers reported the catalytic hydrosilylation of thiobenzophenone by a similar approach.[6] Gevorgyan and co-workers showed that **1** can also catalyze the hydrosilylation of polar C=C double bonds through the same Si−H bond activation process.[7] This activation was also successfully applied in catalytic dehydrocoupling reactions between silanes and alcohols,[4b] thiols,[8] and amines.[9] We decided to use this activation in the chlorination of hydrosilanes through a dehydrocoupling reaction with HCl.

Chlorosilanes play an important role in a number of partially interrelated fields, such as organic synthesis, medicinal chemistry, and polymer science.[10] In organic synthetic

chemistry, chlorosilanes are widely used for the installation of silyl protecting groups on alcohol, phenol, amine, alkyne CH, and carboxy functionalities.[10c–g] They are extensively used as the precursors in "carbon-to-silicon-switch" methodology in medicinal research, in which the effect of the replacement of a carbon atom with a silicon atom in biologically active molecules is investigated with the purpose of designing new drugs.[11] Sterically bulky chlorosilanes are often used for the preparation of sterically encumbered amino-functionalized organocatalysts.[12] Halogenated silanes and their derivatives have also been employed as Lewis acids for various organic transformations.[13] The synthesis of widely used silicon-based polymers and materials, both in industry and the laboratory,[14] usually involves the use of chlorosilanes as major precursors.

The chlorination of Si−H bonds was first reported during the 1940s and 1950s by the research groups of Sommer and Gilman.[15] In 1964, Sommer et al. reported the chlorination of silanes (Si−H) by treatment with chlorine gas in carbon tetrachloride.[16] Later, the chlorination of Si−H bonds was performed with Pd on an alumina or carbon support (5–10% catalyst loading) and gaseous hydrochloric acid, which was bubbled into the reaction mixture.[17] Chlorosilanes have also been prepared catalytically by using Ni^II and Pd^II chlorides in tetrachloromethane.[18] The chlorination of Si−H bonds under the catalysis of palladium dichloride in a mixture of THF and hexachloroethane has also been reported.[19] In 2012, FeCl₃ catalyzed chlorination of Si−H bonds with acyl chlorides as chloride source was achieved.[20] However, the methods described above show poor selectivity for the monochlorination of di- and trihydrosilanes (R₂SiH₂ and RSiH₃). The efficient synthesis of dichlorohydrosilanes (RSi(H)Cl₂) is of high importance in the production of functional polysiloxanes.[21] However, the selective monochlorination of R₂SiH₂ and mono- and dichlorination of RSiH₃ is challenging, and only a few viable methods have been described so far. The monochlorination of dihydrosilanes was achieved by the use of stoichiometric amounts of SnCl₄, thus producing tin dichloride as a by-product, which precipitated from the reaction medium.[22] In 1992, Ishikawa and co-workers reported a less toxic method for the selective chlorination of R₂SiH₂ and RSiH₃ based on the use of stoichiometric copper chloride in combination with a catalytic amount of copper iodide.[23] Most methods for the chlorination of hydrosilanes lack selectivity, and many suffer from the extensive use of toxic, corrosive, and carcinogenic reagents and solvents. Furthermore, in many of these processes, the formation of by-products requires additional purification of the obtained chlorosilanes.

Herein we show that a catalytic amount of **1** or **2** can be used for the activation of various hydrosilanes, which in the presence of HCl can be selectively chlorinated to give the

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Supporting information for this article can be found under:
http://dx.doi.org/10.1002/anie.201700324.

corresponding chlorosilanes. Importantly, di- and trihydrosilanes can be selectively chlorinated in a stepwise manner when **2** is used as the catalyst. A mechanism for these chlorination reactions is proposed on the basis of both competition experiments and DFT calculations.

We first attempted the stoichiometric reaction of Me₂Si-(Cl)H with **1** and excess LiCl as the chloride source in toluene. However, this reaction did not lead to the chlorination of the Si−H bond, and Me₂Si(Cl)H remained intact. We assumed that the low solubility of LiCl was the reason for the lack of reactivity in this system. Therefore, to increase its solubility, Et₂O was added to the reaction mixture. Immediately afterwards, an NMR spectrum of the mixture showed the partial conversion of Me₂Si(Cl)H into Me₂SiCl₂ and the formation of the salt [Li][HB(C₆F₅)₃] (Scheme 1). The addition of HCl to this reaction mixture resulted in the evolution of H₂ gas and the regeneration of **1** (Scheme 1). We therefore decided to attempt the catalytic chlorination of hydrosilanes with HCl and a catalytic amount of **2**.

$$Me_2Si(Cl)H + LiCl + B(C_6F_5)_3 \xrightarrow{\text{Et}_2\text{O/toluene}} Me_2SiCl_2 + [Li][HB(C_6F_5)_3]$$
(1)
HCl
H₂
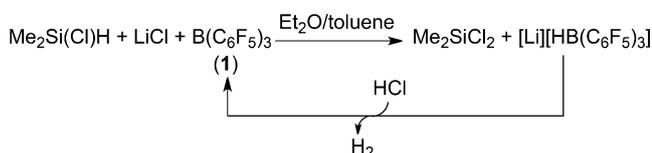
Scheme 1. Stoichiometric chlorination of Me₂Si(Cl)H with **1** and LiCl as the chloride source.

First, we treated Et₃SiH with **2** (1 mol%) in toluene and HCl.[24] After 15 min, the chlorination product, Et₃SiCl, was observed by ¹H–²⁹Si HMBC NMR spectroscopy as the only silicon-containing product (Table 1, entry 1). A control experiment in which Et₃SiH was treated with HCl without a catalyst did not give any conversion into Et₃SiCl. In the

presence of **2** (10 mol%) and HCl, Me₂Si(Cl)H was chlorinated to give Me₂SiCl₂ at room temperature in 16 h (Table 1, entry 2). The chlorination of Ph₂Si(Cl)H was significantly slower, and after 6 days in presence of **2** (10 mol%) had reached only 61% conversion into Ph₂SiCl₂ (Table 1, entry 3). The silyl-substituted hydrosilane tBuMe₂Si(Me)₂SiH underwent chlorination to give tBuMe₂Si(Me)₂SiCl cleanly in 18 h (Table 1, entry 4). This method is also compatible with silanes bearing a siloxy group; thus, Ph₂(Et₃SiO)SiH was converted into the corresponding silyl chloride in 16 h (Table 1, entry 5).

Interestingly, in many of these catalytic reactions, donor-free **1** was observed by ¹⁹F NMR spectroscopy after the reaction. To check whether Et₂O had any effect on these reactions, we performed the chlorination of Et₃SiH with **1**. We found that, in contrast to the reaction with LiCl, in which Et₂O was necessary, this reaction yielded Et₃SiCl quantitatively in 15 min (Table 1, entry 6). The reaction of Ph₂SiH₂ with HCl and **2** (1 mol%) gave the product of monochlorination, Ph₂Si(H)Cl, with complete conversion after 16 h (Table 1, entry 7). The chlorination of PhMeSiH₂ with **2** (1 mol%) yielded the monochlorination product, PhMeSi-(Cl)H, after 12 min (Table 1, entry 8). The product of dichlorination was obtained quantitatively from PhMeSiH₂ upon stirring for 16 h with **2** (10 mol%; Table 1, entry 9).

Even though Et₂O in **2** did not have an effect on the chlorination reactions of Et₃SiH and Me₂Si(Cl)H, it had a very substantial effect on the selectivity of the chlorination of PhSiH₃. Hence, PhSiH₃ in the presence of **2** (10 mol%) and HCl gave PhSi(Cl)H₂ and PhSi(H)Cl₂ in an 84:16 ratio after 10 min (Table 1, entry 10). However, when **1** (10 mol%) was used as the catalyst for the same reaction, an 87:13 mixture of PhSi(H)Cl₂ and PhSi(Cl)H₂ was obtained after 10 min. (Table 1, entry 13). The reaction of PhSiH₃ with **2** (10 mol%) gave a mixture of mono- and dichlorinated products, PhSi(H)Cl₂ (88%) and PhSi(Cl)H₂ (12%), after 16 h (Table 1, entry 12). In contrast, only the dichlorinated product PhSi(H)Cl₂ was obtained upon stirring with **1** (10 mol%) at room temperature for 16 h (Table 1, entry 15). When a smaller amount of **2** (1 mol%) was used for the chlorination of PhSiH₃, the reaction led to the selective formation of the monochlorinated product, PhSi-(Cl)H₂ (Table 1, entry 11). The same amount of **1** led to the formation of PhSi(Cl)H₂ in 94% yield (Table 1, entry 14). Notably, no alkyl−Si, Ar−Si, Si−Si, or SiO−Si bond cleavage, which often occurs when previously reported halogenation methods are used,[6,25] was observed in these catalytic reactions.

We believe that, similarly to hydrosilylation catalyzed by **1**,[4–7,26] the activation of Si−H bonds by **1** is the key step in the chlorination of hydrosilanes with HCl. Thus, the

Table 1: Chlorination of Si−H bonds under the catalysis of **1** (or **2**).

$$R_{4-n}SiH_n \xrightarrow[\text{toluene}]{\substack{\text{catalyst} \\ \text{HCl}}} R_{4-n}SiCl_n$$

catalyst:
B(C₆F₅)₃ (**1**)
or
Et₂O•B(C₆F₅)₃ (**2**)

Entry	R₄₋ₙSiHₙ	Catalyst (mol%)	t [h]	Product (yield[a])
1	Et₃SiH	**2** (1)	0.25	Et₃SiCl (99)
2	Me₂Si(Cl)H	**2** (10)	16	Me₂SiCl₂ (90)
3[b]	Ph₂Si(Cl)H	**2** (10)	150	Ph₂SiCl₂ (61)
4	tBuMe₂Si(Me)₂SiH	**2** (10)	18	tBuMe₂Si(Me)₂SiCl (99)
5	Ph₂(Et₃SiO)SiH	**2** (1)	16	Ph₂(Et₃SiO)SiCl (ca. 90)
6	Et₃SiH	**1** (1)	0.25	Et₃SiCl (99)
7	Ph₂SiH₂	**2** (1)	16	Ph₂Si(Cl)H (99)
8[b]	PhMeSiH₂	**2** (1)	0.20	PhMeSi(Cl)H (99)
9	PhMeSiH₂	**2** (10)	16	PhMeSiCl₂ (99)
10	PhSiH₃	**2** (10)	0.17	PhSi(Cl)H₂ (84), PhSi(Cl)₂H (16)
11	PhSiH₃	**2** (1)	0.17	PhSi(Cl)H₂ (>99.5), PhSi(Cl)₂H (<0.5)
12[c]	PhSiH₃	**2** (10)	16	PhSi(Cl)H₂ (12), PhSi(Cl)₂H (88)
13	PhSiH₃	**1** (10)	0.17	PhSi(Cl)H₂ (13), PhSi(Cl)₂H (87)
14	PhSiH₃	**1** (1)	0.17	PhSi(Cl)H₂ (94), PhSi(Cl)₂H (6)
15[b]	PhSiH₃	**1** (10)	16	PhSi(Cl)₂H (99)

[a] Yields were calculated by ¹H NMR spectroscopy. [b] PhMeSiCl₂, Ph₂SiCl₂, and PhSi(Cl)₂H were also obtained selectively in a stepwise chlorination reaction. [c] Full conversion into PhSi(Cl)₂H was observed after the addition of another portion of HCl and stirring for another 10 h.

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Angew. Chem. Int. Ed. **2017**, *56*, 1–6

[Si]−H−B(C$_6$F$_5$)$_3$ intermediate reacts with HCl to form the corresponding chlorosilane ([Si]−Cl) and H$_2$ as a by-product (Figure 1 c).
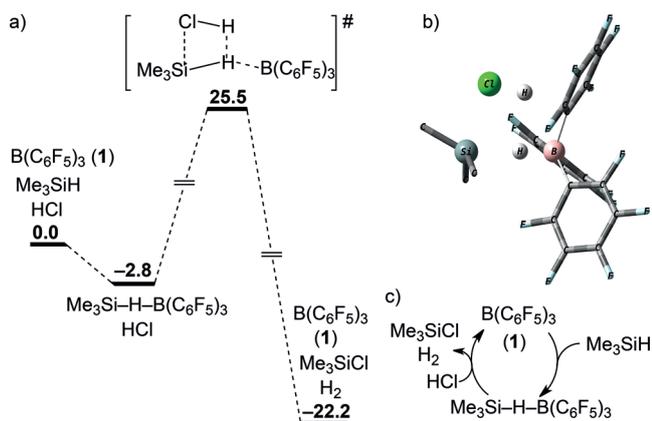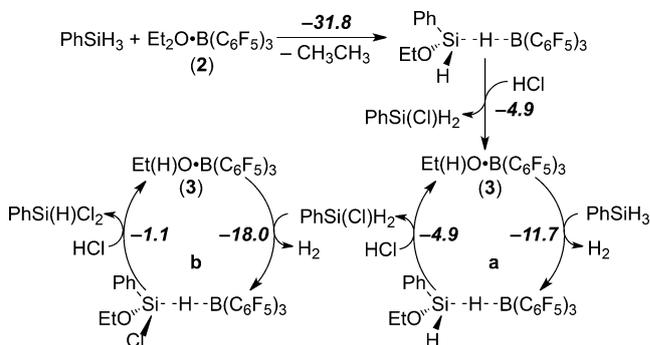

Figure 1. a) DFT calculation at the BP86(D3)/def2-SVP level of theory of the catalytic reaction profile. Gibbs free energies are given in kcal mol^{-1} relative to the starting materials. b) Computed transition-state geometry (nonrelevant hydrogen atoms are omitted for clarity). c) Proposed catalytic cycle.

To get a better understanding of the mechanism, we performed DFT calculations at the BP86(D3)/def2-SVP[27] level of theory on the reaction of **1**, Me$_3$SiH, and HCl. B(C$_6$F$_5$)$_3$ (**1**) interacts with both Me$_3$SiH and HCl, thus resulting in Me$_3$SiH···B and HCl···B distances of 1.49 and 3.26 Å, respectively. The Me$_3$SiH···B interaction is exergonic ($\Delta G = -2.81$ kcal mol^{-1}) and exothermic ($\Delta H = -16.28$ kcal mol^{-1}), whereas the HCl···B interaction is endergonic ($\Delta G = 1.93$ kcal mol^{-1}) and exothermic ($\Delta H = -7.28$ kcal mol^{-1}). Furthermore, unlike in the calculated Me$_3$Si−H−B(C$_6$F$_5$)$_3$ intermediate, in which the Si−H bond is elongated as a result of activation (from 1.51 to 1.58 Å), the H−Cl bond in free HCl and in HCl···B(C$_6$F$_5$)$_3$ remains the same length (1.30 Å). These calculations support our suggestion that the key intermediate in this reaction is Me$_3$Si−H−B(C$_6$F$_5$)$_3$, which is similar to that proposed previously.[4–7,26] However, we believe that the next step is different from the previously proposed formation of a borohydride/silylcarboxonium ion pair[4,5] because the calculated Gibbs free energy for the formation of the salt [Me$_3$Si−ClH][H−B(C$_6$F$_5$)$_3$] is strongly endergonic ($\Delta G = 77.04$ kcal mol^{-1}). In contrast, the calculated energy for the reaction of HCl with the activated Si−H bond in a concerted fashion leading to H$_2$, Me$_3$SiCl, and **1** has a reasonable activation barrier ($\Delta G^{\pm}$) of 28.30 kcal mol^{-1}; furthermore, the liberation of H$_2$ drives this reaction towards the chlorination products (Figure 1 a).

We believe that the mechanism is different in cases in which **2** is used as the catalyst (instead of **1**) in the chlorination reactions. When **2** was added to hydrosilanes, we immediately observed the cleavage of Et$_2$O and the formation of ethane and ethoxysilane in the reaction mixture before the addition of HCl. Similar reactivity was previously reported by Gevorgyan et al.[28] In the next step, we believe that the formed ethoxysilane is chlorinated in the presence of HCl to

form the corresponding silyl chloride and EtOH. The chlorination of alkoxysilanes by HCl was previously reported by Ishikawa and co-workers.[29] We therefore believe that the active catalyst in this reaction is Et(H)O·B(C$_6$F$_5$)$_3$ (**3**; Scheme 2). Namely, the reaction of **3** with [Si]−H leads to

Scheme 2. Catalytic a) mono- and b) dichlorination of PhSiH$_3$ with **2**. Gibbs free energies determined by DFT calculations at the BP86(D3)/def2-SVP level of theory are given next to the arrows in kcal mol^{-1}.

dehydrocoupling products [Si]−OEt; similar reactivity was previously shown by Piers and co-workers.[4b] The formed alkoxysilane reacts with HCl to form the corresponding chlorosilane and EtOH (Scheme 2). To support this suggestion, we performed this reaction in a stepwise manner; that is, we first treated Et$_3$SiH with Et$_2$O in the presence of **1** to obtain Et$_3$SiOEt, and then added HCl, which led to the formation of Et$_3$SiCl.

We believe that this reactivity is the main reason for the successful stepwise chlorination of PhSiH$_3$ and tested this hypothesis by performing two competition experiments. In the first experiment, the rate of etherification versus the rate of chlorination of Ph$_2$Si(Cl)H was compared (Ph$_2$Si(Cl)H was chosen because it gives the slowest reaction times, and thus is the easiest substrate to follow). We observed that the etherification, through Et$_2$O cleavage, was much faster than the chlorination reaction; that is, Ph$_2$Si(Cl)H reached full conversion into Ph$_2$Si(OEt)Cl after 10 min, whereas the chlorination reaction reached only 61% conversion after 6 days (Table 1, entry 3). This result supports our hypothesis that the first step in our catalytic cycle is the formation of the alkoxysilane species. In the second experiment, a 1:1 mixture of Ph$_2$SiH$_2$ and Ph$_2$Si(Cl)H was treated with EtOH (0.2 equiv) and **1** (1 mol%). It was found that only the Ph$_2$SiH$_2$ reacted, whereas the Ph$_2$Si(Cl)H remained intact, thus indicating that hydrosilanes (R$_n$SiH$_{4-n}$) react faster than hydrochlorosilanes (R$_n$Si(Cl)H$_{3-n}$) with EtOH, possibly owing to the more hydridic nature of the former. This reactivity may explain the observation that the dichlorinated silane is obtained only after all of the starting hydrosilane has been converted into the monochlorinated product, that is, that stepwise chlorination occurs (for example, in the chlorination of PhSiH$_3$).

To gain further support for our hypothesis, we performed DFT calculations at the BP86(D3)/def2-SVP[27] level of theory on the proposed catalytic cycles of the mono- and dichlorination processes of PhSiH$_3$ (Scheme 2). According to

these calculations, the cleavage of Et_2O by $PhSiH_3$ to form ethane (ethane was observed experimentally by ^1H NMR spectroscopy) and $Ph(EtO)HSi-H-B(C_6F_5)_3$ is strongly exergonic with $\Delta G = -31.8$ kcal mol^{-1}. Substitution of the ethoxy group by chlorination to give $Ph(Cl)SiH_2$ and **3** is also exergonic ($\Delta G = -4.9$ kcal mol^{-1}). The dehydrocoupling of Et–OH and $PhSiH_3$ leading to $Ph(EtO)HSi-H-B(C_6F_5)_3$ and H_2 has a ΔG value of -11.7 kcal mol^{-1}, and the reaction is driven towards the products owing to the evolution of hydrogen gas (H_2 was also observed by ^1H NMR spectroscopy). Catalytic cycle **a** (Scheme 2) is completed when the EtO–[Si] bond is chlorinated by HCl. The first step in catalytic cycle **b**, which is the dehydrocoupling reaction of EtOH with $Ph(Cl)SiH_2$, is strongly exergonic ($\Delta G = -18.0$ kcal mol^{-1}; Scheme 2). The second step in catalytic cycle **b** is the chlorination of the EtO–[Si] bond ($\Delta G = -1.1$ kcal mol^{-1}). The steps in the proposed catalytic cycle have a negative ΔG value overall, with an overall Gibbs free energy for the $PhSiH_3$ dichlorination process of -43 kcal mol^{-1}. On the basis of the competition experiments described above, we think that catalytic cycle **b** starts only after all of the $PhSiH_3$ has been converted into $Ph(Cl)SiH_2$ (catalytic cycle **a**).

In conclusion, we have demonstrated that hydrosilanes can be chlorinated in the presence of catalytic amounts of **1** (or **2**). Furthermore, the selective chlorination of di- and trihydrosilanes in a stepwise manner was possible when **2** was used as the catalyst. We suggest that the difference in the reactivity between the two catalytic reactions lies in the existence of two distinct mechanisms. In the reaction catalyzed by **1**, the proposed mechanism is the direct chlorination of the activated $[Si]-H-B(C_6F_5)_3$ intermediate. In contrast, when **2** is used, the proposed catalyst is **3**, and the chlorination proceeds via a $[Si]-OEt$ species. We are continuing to study the mechanism and scope of the approach presented herein for the synthesis of other halogenated silanes.

Conflict of interest

The authors declare no conflict of interest.

Keywords: borane catalysis · chlorination · frustrated Lewis pairs · Lewis acids · silanes

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Communications

Halogenation

K. Chulsky,
R. Dobrovetsky* ———   ▪▪▪▪–▪▪▪▪

B(C$_6$F$_5$)$_3$-Catalyzed Selective Chlorination
of Hydrosilanes
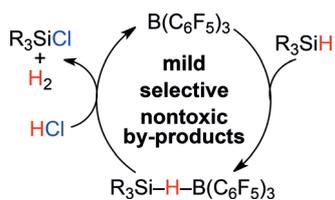
Cl-early a winning combination: Hydrosilanes underwent selective chlorination upon treatment with HCl in the presence of a catalytic amount of B(C$_6$F$_5$)$_3$ with the liberation of H$_2$ (see scheme). For the chlorination of di- and trihydrosilanes, the adduct Et$_2$O·B(C$_6$F$_5$)$_3$ was found to be the more selective catalyst.