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Borohydride catalyzed redistribution reaction of hydrosilane and chlorosilane: a potential system for facile preparation of hydrochlorosilanes†

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Various borohydrides were found to catalyze the redistribution reaction of hydrosilane and chlorosilane in different solvents to produce hydrochlorosilanes efficiently and facilely. The redistribution reaction was affected by solvent and catalyst. The substrate scope was investigated in HMPA with $LiBH_4$ as catalyst. A possible mechanism was proposed to explain the redistribution process.

Hydrochlorosilanes, with both Si–H and Si–Cl bonds on the silicon center, have attracted much attention in past decades for their importance in the production of functional polysiloxanes, polysilanes, polysilazanes, and other silicon-containing materials.[1] However, the facile and highly selective preparation of this type of compound has remained a great challenge, especially for bulk production. The important commercially available hydrochlorosilanes, $MeSiHCl_2$ and $MeSiH_2Cl$, are obtained as by-products from the Müller–Rochow Direct Process.[2]

Regarding the preparation of hydrochlorosilanes, much research work has been focused on the redistribution reaction between hydrosilane and chlorosilane, selective chlorination of hydrosilane, and partial reduction of chlorosilane.[3] In 1947, Sommer *et al.* first reported the redistribution reaction between hydrosilane and chlorosilane catalyzed by $AlCl_3$.[3a] Then the quaternary ammonium salt and tertiary amine were found also can catalyze the redistribution.[3b–d] However, both of them require relatively high temperature and strict operation conditions, which cause extra cost and limitation of available substrates. Preparation of hydrochlorosilane by partial reduction of chlorosilane has been an attractive subject. $NaBH_4$ was reported to partially reduce dialkyldichlorosilane to dialkylchlorosilane in hexamethyl phosphoric triamide (HMPA), but the mechanism of the selectivity in this reduction system was not well understood.[4d] Attempts to produce hydrochlorosilane by reduction of chlorosilane with $LiAlH_4$, the commonly used reductants, have not been realized facilely and efficiently because of the intractable over reduction.[4]

The research on the preparation of hydrochlorosilanes by selective chlorination of hydrosilanes has made great progress in past decades. In 1992, Kunai reported a simple method for selective chlorination of hydrosilane using stoichiometric $CuCl_2$ in the presence of CuI.[5a,b] The catalytic efficiency was further improved by adding ceramic spheres into the system.[5c] Chulsky and Dobrovetsky studied the selective chlorination of Si–H bond with HCl gas in the presence of $B(C_6F_5)_3$ or $B(C_6F_5)_3/Et_2O$ catalyst, and proposed the corresponding mechanisms in 2017.[6a] Recently, Sturm reported that the Si–H can be activated by Lewis base, such as ethers, amines, and chloride ions. The activated Si–H was then selectively chlorinated by the HCl/ether solution.[6b] Though various catalytic systems for selective chlorination of hydrosilane have been developed, most of them have been limited in laboratory synthesis, due to disadvantages of high cost or strict operation conditions. It is still an important issue to achieve simple and economic preparation of hydrochlorosilanes.

Herein we demonstrate a borohydride catalyzed redistribution reaction system, which leads to a facile and flexible preparation of hydrochlorosilane. During the preparation of $Cl_2CHSiMeH_2$ (**1**) by reduction of $Cl_2CHSiMeCl_2$ (**2**) using borohydrides in THF, hydrochlorosilane $Cl_2CHSiMeHCl$ (**3**) was unexpectedly detected when chlorosilane **2** was accidentally mixed with an ether solution of hydrosilane **1** that contained some $LiBH_4$ residue. We guessed that the formation of **3** may be from the redistribution reaction of **1** and **2**, while $LiBH_4$ served as a catalyst. To verify the conjecture and to comprehend the possible solvent effect, we examined the reaction of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in different solvents in the presence of $LiBH_4$ (Table 1). As expected, the redistribution reaction proceeded in various solvents, particularly those with relatively high polarity, *e.g.*, tetrahydrofuran (THF), CH_3CN, diethylene glycol dimethyl ether (diglyme), 1,3-dimethyl-2-imidazolidinone (DMI), and HMPA (Table 1, entries 2–6). The relatively high conversion and selectivity encouraged us to further investigate the redistribution reaction, which may be a useful way to synthesize hydrochlorosilane. Although CH_3SiHCl_2 was unexpectedly formed in

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Table 1 Solvent optimization of redistribution reaction of $ClCH_2SiH_3/ClCH_2SiCl_3$[a]

$ClCH_2SiH_3 + ClCH_2SiCl_3 \xrightarrow[RT,\ 16\ h]{LiBH_4(cat.)} ClCH_2SiH_2Cl + ClCH_2SiHCl_2$

Entry	Solvent	Product (yield)[b]
1	None	No reaction
2	Diglyme	CH_3SiHCl_2: 6%, $ClCH_2SiHCl_2$: 63%, $ClCH_2SiH_2Cl$: 12%
3	THF	$ClCH_2SiHCl_2$: 63%, $ClCH_2SiH_2Cl$: 16%
4	CH_3CN	$ClCH_2SiHCl_2$: 71%, $ClCH_2SiH_2Cl$: 11%
5	DMI	$ClCH_2SiHCl_2$: 71%, $ClCH_2SiH_2Cl$: 14%
6	HMPA	$ClCH_2SiHCl_2$: 72%, $ClCH_2SiH_2Cl$: 9%
7	Bu_2O	No reaction
8	Et_2O	No reaction
9	Toluene	No reaction

[a] Reaction conditions: $ClCH_2SiH_3$ (0.01 mol), $ClCH_2SiCl_3$ (0.02 mol), $LiBH_4$ (3.0 mol/%), THF (5 mL), room temperature. [b] Yields were determined by ^1H NMR.

a yield of 6% in diglyme, suggesting the C–Cl bond also participated in the redistribution reaction with Si–H bond (Table 1, entry 2), there were few detected CH_3SiHCl_2 in THF, DMI, or HMPA. It may be attributed to the different solvation effects of $LiBH_4$, which resulted in their different reductive activity toward the chloromethyl group.

We further optimized the catalyst with the substrate system of $ClCH_2SiCl_3/ClCH_2SiH_3$ as a model (Table 2). It is found that in THF, all examined lithium salt, $LiBH_4$, $LiBEt_3H$, and $LiAlH_4$, can catalyze the redistribution reaction (Table 2, entries 1–5), but $NaBH_4$ and KBH_4 which have poor solubility cannot (Table 2, entries 6 and 7). Changed the solvent from THF to diglyme, a better solvent for $NaBH_4$ and KBH_4, the redistribution reaction proceeded, though the yield of product is low (see ESI, Fig. 35 and 36†). This result indicated that the solubility of catalyst in solvent is important for the reaction. With the increase of catalyst dosage, the yield of hydrochlorosilane increased (Table 2, entries 1–4). Besides, the metal counterion of BH_4^- also affects the redistribution reaction. With 4 mol% of $LiBH_4$ or $NaBH_4$ as catalyst, the conversion efficiencies for the redistribution reaction of $Cl_2CHSiMeCl_2/Cl_2CHSiMeH_2$ are 67% and 15%, respectively, though both of them can be dissolved in diglyme completely (see ESI, Fig. 36 and 37†). The possible reason may be (a) the different solvation effects of $LiBH_4$ and $NaBH_4$ in diglyme, which is related to the character of metal ion, and (b) the different solubility of the formed metal chloride, LiCl and NaCl.[7]

Then under the optimized condition, we investigated the substrate scope of the redistribution reaction in the $LiBH_4$/HMPA system (Table 3). The redistribution reaction of Si–H and Si–Cl proceeded efficiently for various substituted hydrosilane and chlorosilane substrates. The substituents include chloroalkyl, alkyl, and phenyl groups. Especially, for α-chloromethyl silane substrates, *e.g.*, $ClCH_2SiCl_3/ClCH_2SiH_3$, $ClCH_2SiMeCl_2/ClCH_2SiMeH_2$, $Cl_2CHSiMeCl_2/Cl_2CHSiMeH_2$, the redistribution was completed in half an hour (Table 3, entries 1–4). The stronger electron-withdrawing effect of the substituents on silicon center may be the reason. For the reaction system of $RSiCl_3/RSiH_3$, namely, the substrate has more available redistribution groups, different predominated product was achieved through adjustment of the proportion of hydrosilane and chlorosilane in reactants (Table 3, entries 1, 2, 6 and 7). The $LiBH_4$ catalyzed redistribution reaction in HMPA has yields ranging from 56% to 85%. Further work is still needed to realize a thorough and selective redistribution, however, the advantages of its very simple and mild reaction condition, easily acquired catalysts, relatively fast reaction rate, and high conversion efficiency suggest a great potential of the

Table 2 Catalyst optimization of redistribution reaction of $ClCH_2SiH_3/ClCH_2SiCl_3$[a]

$ClCH_2SiH_3 + ClCH_2SiCl_3 \xrightarrow[THF,\ RT,\ 20\ h]{catalyst} ClCH_2SiH_2Cl + ClCH_2SiHCl_2$

Entry	Cat.	Cat. (mol%)	Product (yield)[b]
1	$LiBH_4$	0.4	$ClCH_2SiHCl_2$: 10%, $ClCH_2SiH_2Cl$: 20%
2	$LiBH_4$	0.8	$ClCH_2SiHCl_2$: 32%, $ClCH_2SiH_2Cl$: 27%
3	$LiBH_4$	1.5	$ClCH_2SiHCl_2$: 55%, $ClCH_2SiH_2Cl$: 18%
4	$LiBH_4$	3.0	$ClCH_2SiHCl_2$: 63%, $ClCH_2SiH_2Cl$: 16%
5	$LiBEt_3H$	3.0	$ClCH_2SiHCl_2$: 68%, $ClCH_2SiH_2Cl$: 12%
6	$NaBH_4$	3.0	No reaction
7	KBH_4	3.0	No reaction
8	$LiAlH_4$	3.0	$ClCH_2SiHCl_2$: 18%, $ClCH_2SiH_2Cl$: 21%

[a] Reaction conditions: $ClCH_2SiH_3$ (0.01 mol), $ClCH_2SiCl_3$ (0.02 mol), THF (5 mL), room temperature. [b] Yields were determined by ^1H NMR.

Table 3 Redistribution reaction between hydrosilane and chlorosilane in HMPA catalyzed by $LiBH_4$[a]

$$R_{4-x}SiH_x + R_{4-x}SiCl_x \xrightarrow[HMPA]{LiBH_4(cat.)} R_{4-x}SiH_{x-y}Cl_y$$

Entry	$R_{4-x}SiH_x/R_{4-x}SiCl_x$	Ratio	Cat. (mol%)	t (h)	Product (yield)[b]
1	$ClCH_2SiH_3/ClCH_2SiCl_3$	1 : 2	3	0.5	$ClCH_2SiHCl_2$: 75%, $ClCH_2SiH_2Cl$: 9%
2	$ClCH_2SiH_3/ClCH_2SiCl_3$	2 : 1	3	0.5	$ClCH_2SiHCl_2$: 23%, $ClCH_2SiH_2Cl$: 56%
3	$ClCH_2SiMeH_2/ClCH_2SiMeCl_2$	1 : 1	2	0.5	$ClCH_2SiMeHCl$: 74% (62%[c])
4	$Cl_2CHSiMeH_2/Cl_2CHSiMeCl_2$	1 : 1	4	0.5	$Cl_2CHSiMeHCl$: 85% (72%[c])
5	Et_2SiH_2/Et_2SiCl_2	1 : 1	4	8	Et_2SiHCl:72%
6	$PhSiH_3/PhSiCl_3$	1 : 2	3	2	$PhSiHCl_2$: 61%$PhSiH_2Cl$: 10%
7	$PhSiH_3/PhSiCl_3$	2 : 1	3	2	$PhSiHCl_2$:12%$PhSiH_2Cl$: 61%
8	$PhMeSiH_2/PhMeSiCl_2$	1 : 1	4	2	$PhMeSiHCl$: 66%
9	Ph_2SiH_2/Ph_2SiCl_2	1 : 1	4	8	Ph_2SiHCl: 63%

[a] Reaction conditions: [entry 3–5, 8 and 9] hydrosilane (0.01 mol), chlorosilane (0.01 mol); [entry 1 and 6] hydrosilane (0.01 mol), chlorosilane (0.02 mol); [entry 2 and 7] hydrosilane (0.02 mol), chlorosilane (0.01 mol); HMPA (5 mL), room temperature. [b] Yields determined by ^1H NMR. [c] Isolated yield in a larger scale reaction. Reaction conditions: hydrosilane (0.2 mol), chlorosilane (0.2 mol), HMPA (10 mL), $LiBH_4$ (2 mol%), room temperature.

redistribution method in achieving more economic and efficient preparation of hydrochlorosilanes.

To demonstrate the utility of the redistribution strategy, larger scale syntheses of hydrochlorosilane $ClCH_2SiMeHCl$ and $ClCH_2SiMeHCl$ were carried out. After finishing the reaction, all the volatiles were first removed by vacuum distillation to give a silane mixture, which was then submitted to a packed column fractional distillation to produce pure hydrochlorosilane product, such as $ClCH_2SiMeHCl$ or $Cl_2CHSiMeHCl$. The simple manipulation and good yield indicated its high potential for industrial application.

On the other hand, the redistribution system also provides a possible reference for the partial reduction of chlorosilane to prepare hydrochlorosilane with $NaBH_4$, $LiAlH_4$, and other common reductants. For the $NaBH_4$/HMPA partial reduction system reported by Hiiro,[4d] the reduction selectivity of chlorosilane can be easily understood from the perspective of the redistribution system herein, *i.e.*, in the presence of deficient amount of borohydrides, hydrochlorosilanes can be produced from the redistribution reaction between the *in situ* formed hydrosilane products and the chlorosilane substrates. It is also easy to comprehend that partial reduction of chlorosilane can be easily achieved with $LiAlH_4$ as reductant, if the solvents which are effective for the redistribution system are used.

To make clear the mechanism, we further investigated the redistribution reaction. The Si–Cl bond of chlorosilane substrates can be reduced to Si–H bond by borohydrides, with BH_3 and chloride salt as the by-products (see ESI, Fig. 51†). Thus, our initial consideration is that BH_3, which is formed *in situ* during the reduction reaction, may play the role of catalyst. However, the experiment proved that BH_3 alone cannot catalyze the redistribution reaction (Table 4, entry 1). The Si–Cl reduction process of chlorosilane substrate with borohydrides is easily understood by referring to the well-studied substitution reaction at silicon center using nucleophiles,[8] *i.e.*, the negative BH_4^- attacks to the partial positive silicon center to form a pentacoordinate intermediate of chlorosilane in the first step, then looses BH_3 and Cl^- to form corresponding silane product. We assumed that the chlorination process of Si–H may also undergo a similar process, *i.e.*, Si–H was first activated through the formation of pentacoordinate intermediate with Cl^- that formed in the Si–Cl reduction process. Then the *in situ* formed Lewis acid BH_3 during the Si–Cl reduction process interacted with the activated Si–H bond, which further promoted the Si–H bond dissociation. The early reported research on the ability of $B(C_6F_5)_3$ and Cl^- to activate Si–H bond[6b,9] provides a good proof for reasonability of the envisaged chlorination process.

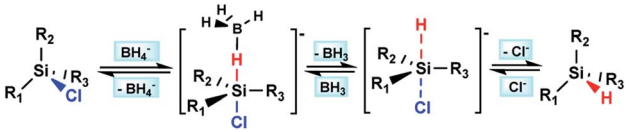
According to the above hypothesis, we proposed a possible Si–H/Si–Cl redistribution mechanism demonstrated as Scheme 1, in which the process of Si–H chlorination and Si–Cl reduction occur simultaneously. To verify it, the redistribution reaction of $ClCH_2SiCl_3/ClCH_2SiH_3$ catalyzed by BH_3/LiCl or LiCl

Table 4 Control experiments of redistribution reaction of $ClCH_2SiH_3$/$ClCH_2SiCl_3$[a]

$$ClCH_2SiH_3 + ClCH_2SiCl_3 \xrightarrow[RT,\ THF]{catalyst} ClCH_2SiH_2Cl + ClCH_2SiHCl_2$$

Entry	Catalyst	t (h)	Product (yield)[b]
1	BH_3	20	No reaction
2	LiCl	5	$ClCH_2SiHCl_2$: 40%, $ClCH_2SiH_2Cl$: 23%
3	BH_3, LiCl	5	$ClCH_2SiHCl_2$: 62%, $ClCH_2SiH_2Cl$: 18%
4	$LiBH_4$	5	$ClCH_2SiHCl_2$: 62%, $ClCH_2SiH_2Cl$: 18%

[a] Reaction conditions: $ClCH_2SiH_3$ (0.01 mol), $ClCH_2SiCl_3$ (0.02 mol), catalyst (3.0 mol/%), THF (5 mL), room temperature. [b] Yields were determined by ^1H NMR.



Scheme 1 The possible mechanism of borohydrides catalyzed Si–H/Si–Cl redistribution reaction.

alone was performed. As expected, LiCl can catalyze the redistribution of $ClCH_2SiCl_3$/$ClCH_2SiH_3$, and introduction of BH_3 can further accelerate the reaction obviously (Table 4, entry 2 and 3). Besides, almost identical results were achieved when the same amount of $LiBH_4$ or BH_3/LiCl was used (Table 4, entry 3 and 4). The results indicate the similar catalytic effect of BH_4^- and BH_3/LiCl, which can be well explained by the mechanism proposed in Scheme 1.

To get a better understanding of the possible mechanism in Scheme 1, a DFT calculation at the B3LYP/6-311G (d, p)[10] level of theory was performed on the pentacoordinate intermediates $[ClCH_2SiCl_3–H–BH_3]^-$ (**I**) and $[ClCH_2SiCl_3–H]^-$ (**II**), which was formed in the redistribution of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ according to the mechanism we proposed. The solvation effect of THF was also considered with SMD model. The calculation result shows that the apical Si–H bond in intermediate **II** lengthens from l.47 Å to 1.49 Å, while it is elongated from 1.49 Å to 1.65 Å in intermediate **I**. Calculation results on the other possible pentacoordinate intermediates in the redistribution of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ were similar. It may reflect the role BH_3 or Cl^- plays in the activation of Si–H bond in the chlorination process as the mechanism we proposed.

In conclusion, we have demonstrated that borohydrides catalyzed redistribution reaction between hydrosilane and chlorosilane in different solvents efficiently. The new catalytic redistribution system works for a broad scope of substituted hydrosilane and chlorosilane substrates. The very simple and mild reaction condition, the easily acquired catalysts, the relatively fast reaction rate, and high conversion efficiency are all advantages of the redistribution system. Further improvement of the redistribution system is currently under investigation in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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