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 LiBH4 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. 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, MeSiHCl3 and MeSiH2Cl, are obtained as by-products from the Müller–Rochow Direct Process.†

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. In 1947, Sommer et al. first reported the redistribution reaction between hydrosilane and chlorosilane catalyzed by AlCl3. Then the quaternary ammonium salt and tertiary amine were found also can catalyze the redistribution. 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. NaBH4 was reported to partially reduce dialkylchlorosilane to dialkylchlorosilane in hexamethyl phosphoric triamide (HMPA), but the mechanism of the selectivity in this reduction system was not well understood. Attempts to produce hydrochlorosilane by reduction of chlorosilane with LiAlH4, the commonly used reductants, have not been realized facilely and efficiently because of the intractable over reduction.

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 CuCl2 in the presence of CuI. The catalytic efficiency was further improved by adding ceramic spheres into the system. Chulskey and Dobrovetsky studied the selective chlorination of Si–H bond with HCl gas in the presence of B(C6F5)3 or B(C6F5)3/Et2O catalyst, and proposed the corresponding mechanisms in 2017. 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. 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 Cl2CHSiMeH2 (1) by reduction of Cl2CHSiMeCl2 (2) using borohydrides in THF, hydrochlorosilane Cl2CHSiMeHCl (3) was unexpectedly detected when chlorosilane 2 was accidentally mixed with an ether solution of hydrosilane 1 that contained some LiBH4 residue. We guessed that the formation of 3 may be from the redistribution reaction of 1 and 2, while LiBH4 served as a catalyst. To verify the conjecture and to comprehend the possible solvent effect, we examined the reaction of CICH3SiCl3 and CICH2SiH4 in different solvents in the presence of LiBH4 (Table 1). As expected, the redistribution reaction proceeded in various solvents, particularly those with relatively high polarity, e.g., tetrahydrofuran (THF), CH3CN, 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 CH3SiHCl3 was unexpectedly formed in
Table 1  Solvent optimization of redistribution reaction of ClCH2SiH3/ClCH2SiCl3

| Entry | Solvent     | Product (yield) |
|-------|-------------|-----------------|
| 1     | None        | No reaction     |
| 2     | Diglyme     | CH3SiHCl2: 6%, ClSiH2Cl: 63%, ClSiH2Cl: 12% |
| 3     | THF         | ClSiH2Cl: 63%, ClSiH2Cl: 16% |
| 4     | CH3CN       | ClSiH2Cl: 71%, ClSiH2Cl: 11% |
| 5     | DMI         | ClSiH2Cl: 71%, ClSiH2Cl: 14% |
| 6     | HMPA        | ClSiH2Cl: 72%, ClSiH2Cl: 9% |
| 7     | Bu2O        | No reaction     |
| 8     | Eto         | No reaction     |
| 9     | Toluene     | No reaction     |

a Reaction conditions: ClCH2SiH3 (0.01 mol), ClCH2SiCl3 (0.02 mol), LiBH4 (3.0 mol%), THF (5 mL), room temperature. b Yields were determined by 1H NMR.

Table 2  Catalyst optimization of redistribution reaction of ClCH2SiH3/ClCH2SiCl3

| Entry | Cat.   | Cat. (mol%) | Product (yield) |
|-------|--------|-------------|-----------------|
| 1     | LiBH4  | 0.4         | ClSiH2Cl: 10%, ClSiH2Cl: 20% |
| 2     | LiBH4  | 0.8         | ClSiH2Cl: 32%, ClSiH2Cl: 27% |
| 3     | LiBH4  | 1.5         | ClSiH2Cl: 55%, ClSiH2Cl: 18% |
| 4     | LiBH4  | 3.0         | ClSiH2Cl: 63%, ClSiH2Cl: 16% |
| 5     | LiBEt3H | 3.0        | ClSiH2Cl: 68%, ClSiH2Cl: 12% |
| 6     | NaBH4  | 3.0         | No reaction     |
| 7     | KBH4   | 3.0         | No reaction     |
| 8     | LiAlH4 | 3.0         | ClSiH2Cl: 18%, ClSiH2Cl: 21% |

a Reaction conditions: ClCH2SiH3 (0.01 mol), ClCH2SiCl3 (0.02 mol), THF (5 mL), room temperature. b Yields were determined by 1H NMR.
redistribution method in achieving more economic and efficient preparation of hydrochlorosilanes.

To demonstrate the utility of the redistribution strategy, larger scale syntheses of hydrochlorosilane CICH₂SiMeHCl and CICH₂SiMeHCl 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 CICH₂SiMeHCl or Cl₂CHSiMeHCl. 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 NaBH₄, LiAlH₄ and other common reductants. For the NaBH₄/HMPA partial reduction system reported by Hiirō, the reduction selectivity of chlorosilane can be easily understood from the perspective of the redistribution system herein, i.e., 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 LiAlH₄ 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 BH₃ and chloride salt as the by-products (see ESI, Fig. 51†). Thus, our initial consideration is that BH₃, which is formed in situ during the reduction reaction, may play the role of catalyst. However, the experiment proved that BH₃ 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, i.e., the negative BH₃⁻ attacks to the partial positive silicon center to form a pentacoordinate intermediate of chlorosilane in the first step, then looses BH₃ 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 BH₃ 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(C₆F₅)₃ and Cl⁻ to activate Si–H bond 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 CICH₂SiCl₃/CICH₂SiH₃ catalyzed by BH₃/LiCl or LiCl

Table 4 Control experiments of redistribution reaction of CICH₂SiH₃/CICH₂SiCl₃

| Entry | Catalyst | t (h) | Product (yield)b |
|-------|----------|------|-----------------|
| 1     | BH₃      | 20   | No reaction     |
| 2     | LiCl     | 5    | CICH₂SiHCl₂: 40%, CICH₂SiH₂Cl: 23% |
| 3     | BH₃, LiCl| 5    | CICH₂SiHCl₂: 62%, CICH₂SiH₂Cl: 18% |
| 4     | LiBH₄    | 5    | CICH₂SiHCl₂: 62%, CICH₂SiH₂Cl: 18% |

a Reaction conditions: CICH₂SiH₃ (0.01 mol), CICH₂SiCl₃ (0.02 mol), catalyst (3.0 mol%), THF (5 mL), room temperature. b Yields determined by ¹H NMR.
alone was performed. As expected, LiCl can catalyze the redistribution of CICH₂SiCl₃/CICH₂SiH₃, and introduction of BH₃ can further accelerate the reaction obviously (Table 4, entry 2 and 3). Besides, almost identical results were achieved when the same amount of LiBH₄ or BH₃/LiCl was used (Table 4, entry 3 and 4). The results indicate the similar catalytic effect of BH₄⁻ and BH₃/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) level of theory was performed on the pentacoordinate intermediates [CICH₂SiCl₃–H–BH₃]⁻ (I) and [CICH₂SiCl₃–H]⁻ (II), which was formed in the redistribution of CICH₂SiH₃/CICH₂SiCl₃ 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 1.47 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 CICH₂SiH₃/CICH₂SiCl₃ were similar. It may reflect the role BH₃ 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.

**Notes and references**

1 (a) B. Arkles, in Kirk-Ohther Encyclopedia of Chemical Technology, American Cancer Society, 2000; (b) R. M. Laine and A. Selligner, in The Chemistry of Organic Silicon Compounds, John Wiley & Sons, Ltd, 2003, pp. 2245–2316;
(c) W. Xue, M. C. Kung and H. H. Kung, Chem. Commun., 2005, 2164–2166; (d) M. N. Missaghi, C. M. Downing, M. C. Kung and H. H. Kung, Organometallics, 2008, 27, 6364–6366.
2 (a) E. G. Rochow, J. Am. Chem. Soc., 1945, 67, 963–965; (b) D. Seyferth, Organometallics, 2001, 20, 4978–4992.
3 (a) F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, J. Am. Chem. Soc., 1947, 69, 2108–2110; (b) A. Benouargha, D. Boulahia, B. Boutevin, G. Caporiccio, F. Guidapietranta and A. Ratsimihety, Phosphorus, Sulfur, Silicon Relat. Elem., 1996, 113, 79–87; (c) I. N. Jung, B. R. Yoo, J. S. Han and W.-C. Lim, US Pat., US5965762A, 1999; (d) W. Katsuyu and T. Hidenori, European Patent, EP2308884 (A1), 2011.
4 (a) P. A. McCusker and E. L. Reilly, J. Am. Chem. Soc., 1953, 75, 1583–1585; (b) H. E. Opitz, J. S. Peake and W. H. Nebergall, J. Am. Chem. Soc., 1956, 78, 292–294; (c) A. Glüer, J. I. Schweizer, U. S. Karaca, C. Wütele, M. Diefenbach, M. C. Holthausen and S. Schneider, Inorg. Chem., 2018, 57, 13822–13828; (d) H. Takeshi, S. Hideki and K. Fumihiko, US Pat., US4115426A, 1978.
5 (a) A. Kunai, T. Kawakami, E. Toyoda and M. Ishikawa, Organometallics, 1992, 11(7), 2708–2711; (b) A. Kunai and J. Ohshita, J. Organomet. Chem., 2003, 686(1), 3–15; (c) W. Wang, Y. Tan, Z. Xie and Z. Zhang, J. Organomet. Chem., 2014, 769, 29–33.
6 (a) K. Chulsky and R. Dobrovetsky, Angew. Chem., Int. Ed., 2017, 56, 4744–4748; (b) A. G. Sturm, J. I. Schweizer, L. Meyer, T. Santowski, N. Auner and M. C. Holthausen, Chem. - Eur. J., 2018, 24, 17796–17801.
7 (a) H. Hagemann and R. Černý, Dalton Trans., 2010, 39, 6006–6012; (b) H. C. Brown, Boranes in Organic Chemistry, Cornell University Press, 2019, pp. 217–218.
8 (a) R. J. P. Corriu and C. Guerin, in Advances in Organometallic Chemistry, eds. F. G. A. Stone and R. West, Academic Press, 1982, vol. 20, pp. 265–312; (b) R. J. P. Corriu and C. Guerin, J. Organomet. Chem., 1980, 198, 231–320.
9 (a) D. J. Parks and W. E. Piers, J. Am. Chem. Soc., 1996, 118, 9440–9441; (b) J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, J. Org. Chem., 1999, 64, 4887–4892.
10 (a) M. M. Franel, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, J. Chem. Phys., 1982, 77, 3654–3665; (b) A. D. McLean and G. S. Chandler, J. Chem. Phys., 1980, 72, 5639–5648; (c) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, J. Comput. Chem., 1983, 4, 294–301; (d) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., 1980, 72, 650–654; (e) G. W. Spitznagel, T. Clark, P. von Ragüé Schleyer and W. J. Hehre, J. Comput. Chem., 1987, 8, 1109–1116; (f) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 11623–11627.