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Communication

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$B(C_6F_5)_3$-Catalyzed C–Si/Si–H Cross-Metathesis of Hydrosilanes

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Supporting Information Placeholder

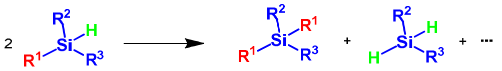
ABSTRACT: The substituent redistribution of hydrosilanes on silicon through C–Si and Si–H bond cleavage and reformation is of great interest and importance, but this transformation is usually difficult to achieve in a selective fashion. By using electron-rich aromatic hydrosilanes, we have achieved for the first time the selective C–Si/Si–H bond homo- and cross-metathesis of a series of hydrosilanes in the presence of a boron catalyst $B(C_6F_5)_3$. This protocol features simple reaction conditions, high chemoselectivity, wide substrate scope, and high functionality tolerance, offering a new pathway for the synthesis of multi-substituted functional silanes.

Organosilicon compounds play a vital role in synthetic organic chemistry and materials science.[1] Therefore, the investigation of C–Si bond formation and cleavage has constantly attracted interest in the chemical community.[2,3] One particularly interesting reaction is the substituent redistribution or disproportionation of hydrosilanes on silicon, which converts one hydrosilane to two or more organosilicon compounds through C–Si and Si–H bond cleavage and reformation (Scheme 1a).[4-9] However, in spite of being conceptually curious and potentially useful as a synthetic route, this transformation has not been well examined to date. The redistribution of hydrosilanes was often observed as a side-reaction of transition-metal-catalyzed dehydrocoupling of hydrosilanes[5a,d,f] or in stoichiometric transformations mediated by some organometallic complexes,[5b,c,e] while sporadic examples of some catalytic versions were also reported.[4,6-8] The stoichiometric substituent exchange of tertiary hydrosilanes promoted by $[Ph_3C][B(C_6F_5)_4]$ was reported as a useful route for the generation of triarylsilylium ions.[9] The reactions (either stoichiometric or catalytic) reported to date often suffered from poor selectivity or limited substrate scope. In particular, the selective C–Si/Si–H cross-metathesis of two different hydrosilanes has remained unknown to date.

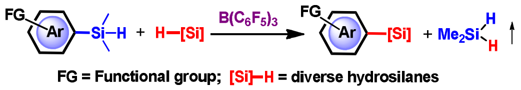
Boron Lewis acids, such as $B(C_6F_5)_3$, have recently received much attention as efficient catalysts for Si–H bond activation and related transformations.[10,11] In the course of our recent studies on the $B(C_6F_5)_3$-catalyzed aromatic C–H silylation with hydrosilanes,[11i] we noticed that some hydrosilanes could undergo redistribution in the presence of $B(C_6F_5)_3$. Herein we report our studies on the $B(C_6F_5)_3$-catalyzed redistribution reactions of various hydrosilanes. By appropriately tuning the electronic properties of the hydrosilane substrates, we have successfully achieved for the first time both homo- and cross-metathesis of a wide range of hydrosilanes in a selective fashion (Scheme 1b). This protocol offers an easy access to diverse silylated aromatic compounds from hydrosilanes.

Scheme 1. Substituent Redistribution of Hydrosilanes on Silicon

(a) Previous work: Disproportionation of a hydrosilane to two or more organosilicon compounds



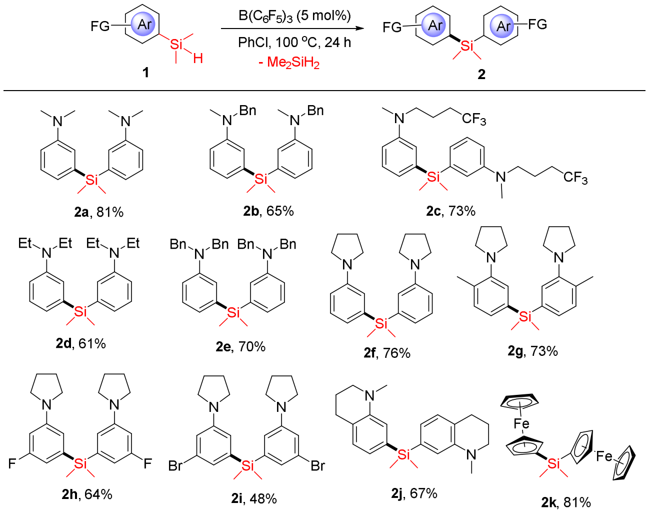
(b) **This work**: Selective cross-metathesis of two different hydrosilanes



On the basis of our previous studies of the $B(C_6F_5)_3$-catalyzed C–H silylation of electron-rich arenes with hydrosilanes,[11i] we envisioned that the introduction of an electron-donating group to the aromatic ring of an aryl substituent in hydrosilanes might promote the aryl group transfer and thus enable selective substituent redistribution at the Si atom. By examining a set of aryl hydrosilanes (See Table S1 in Supporting Information), we found that tertiary hydrosilanes with an aryl group having the *N*,*N*-dimethylamino substituent at the meta position selectively underwent aryl/hydride exchange in the presence of 5 mol % $B(C_6F_5)_3$ at 100 °C in chlorobenzene.[12] Besides the *N*,*N*-dimethylamino group, other amino groups such as ethyl-, benzyl-, and trifluoroalkyl-substituted amino groups as well as cyclic amino units all worked effectively for the aryl (Ar) redistribution of a series of hydrosilanes having a general formula of $ArMe_2SiH$, which exclusively afforded the corresponding diaryl dimethyl silane products such as **2a–2j** in high yields with release of Me_2SiH_2 (Table 1).[13] The C–F and C–Br bonds (cf. **2c, 2h** and **2i**), which are useful in organic synthesis, were compatible with the catalytic reaction conditions. In addition to the aminoaryl-substituted hydrosilanes, ferrocenyl dimethyl hydrosilane also selectively underwent the redistribution reaction to give the di(ferrocenyl) dimethyl silane product **2k** in 81% yield.

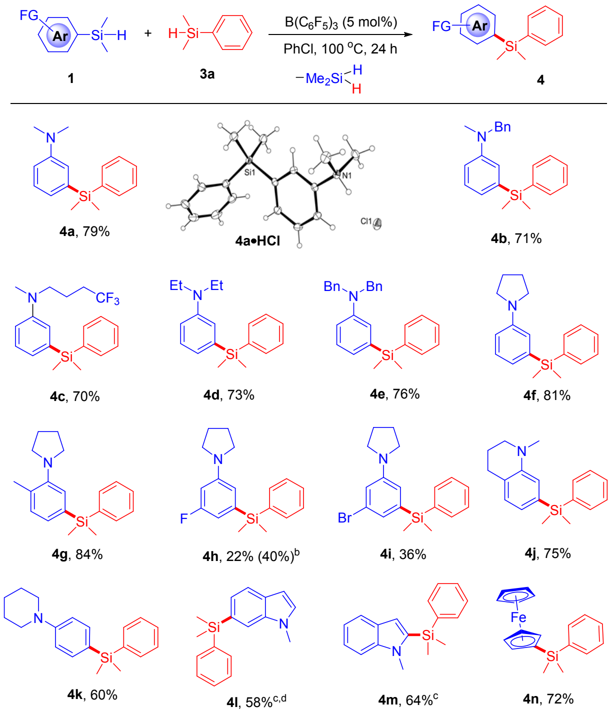
With the success of the selective redistribution (homo-metathesis) of the electron-rich aryl hydrosilanes, we then examined their cross-metathesis with other hydrosilanes. At first, the reaction of $(m\text{-}Me_2NC_6H_4)Me_2SiH$ (**1a**) with 2 equiv. of $PhMe_2SiH$ (**3a**) was carried out in the presence of 5 mol % of $B(C_6F_5)_3$, which afforded the cross-metathesis product $(m\text{-}Me_2NC_6H_4)PhMe_2Si$ (**4a**) in 79% isolated yield with release of Me_2SiH_2 (Table 2).[13] The solid structure of the HCl adduct of **4a** was confirmed by single-crystal X-ray analysis (Table 2). The homo-metathesis product of **1a** was formed in less than 5% yield (**2a**), while Ph_2Me_2Si (a homo-metathesis product of **3a**) was negligible (see Table S2 in Supporting Information). In a similar fashion, the cross-metathesis reaction between **3a** and a series of acyclic and cyclic amino aryl dimethyl hydrosilanes also selectively took place, affording the corresponding mixed aryl phenyl dimethyl silane products such as **4b**−**4g** and **4j**,**k** in 60−84% yields. The electron-withdrawing fluorine- and bromine-substituted aryl silanes showed relatively lower activity for the present cross-metathesis reaction, which gave the expected products (such as **4h** and **4i)** in 22−40% yields under the similar conditions. Indolyl dimethyl hydrosilanes were suitable partners for the cross-metathesis with **3a**, giving the corresponding mixed indolyl phenyl dimethyl silane products such as **4l** and **4m** in 58−64% yields albeit with 10 mol % $B(C_6F_5)_3$. Moreover, ferrocenyl dimethyl silane also showed high reactivity with **3a**, affording the mixed ferrocenyl phenyl dimethyl silane product **4n** in 72% yield.

Table 1. $B(C_6F_5)_3$-Catalyzed Selective Substituent Redistribution of Hydrosilanes[a]



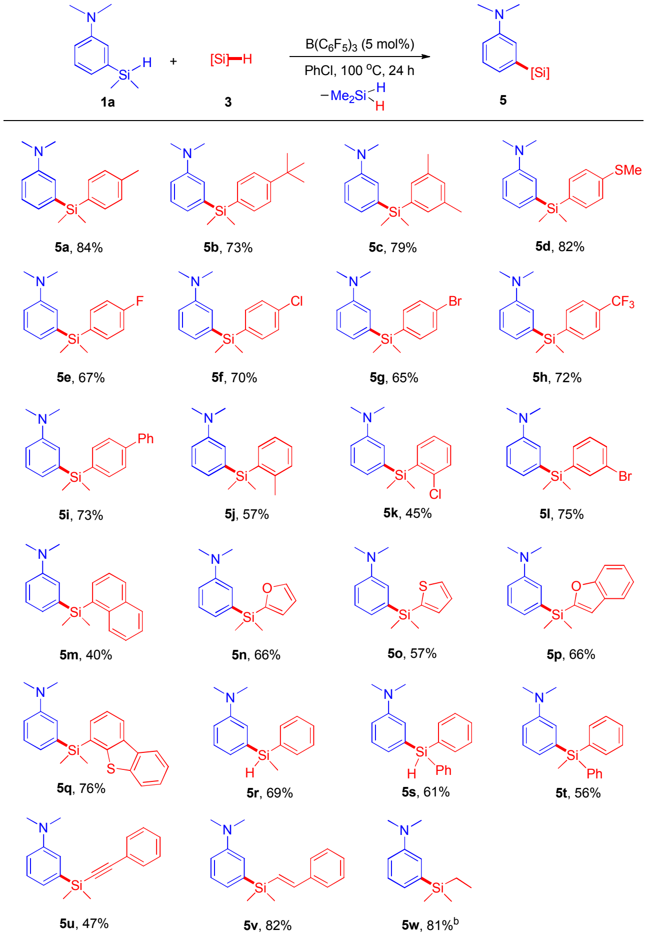
[a]Reaction conditions: hydrosilane **1** (0.25 mmol), $B(C_6F_5)_3$ (5.0 mol %) and chlorobenzene (0.5 mL) under N_2 at 100 °C for 24 h. Isolated yield.

Table 2. $B(C_6F_5)_3$-Catalyzed Cross-Metathesis of $PhMe_2SiH$ with Various Electron-rich Hydrosilanes[a]



[a]Reaction conditions: hydrosilane **1** (0.25 mmol), **3a** (0.50 mmol), $B(C_6F_5)_3$ (5.0 mol %) and chlorobenzene (0.5 mL) under N_2 at 100 °C for 24 h, unless otherwise noted. Isolated yield. [b]120 °C, 48 h, 0.75 mmol of $PhMe_2SiH$. [c]$B(C_6F_5)_3$ (10.0 mol %). [d]120 °C, 36 h, 0.75 mmol of $PhMe_2SiH$.

Table 3. $B(C_6F_5)_3$-Catalyzed Cross-Metathesis of (*m*-$Me_2NC_6H_4$)Me_2SiH with Various Hydrosilanes[a]

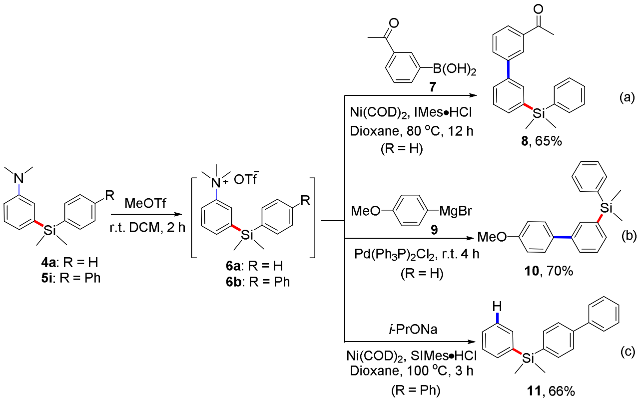


[a]Reaction conditions: **1a** (0.25 mmol), hydrosilane **3** (0.50 mmol), $B(C_6F_5)_3$ (5.0 mol %) and chlorobenzene (0.5 mL) under N_2 at 100 °C for 24 h. Isolated yield. [b]1.25 mmol of $EtMe_2SiH$ was used.

We then chose **1a** as an electron-rich partner for the cross-metathesis with various hydrosilanes. Some representative results are summarized in Table 3. A wide range of aryl dimethyl hydrosilanes bearing alkyl, phenyl, trifluoromethyl, methylsulfide, and halogen (F, Cl, Br) substituents at the aromatic ring smoothly reacted with **1a**, selectively affording the desired cross-metathesis products such as **5a**−**l** in moderate to high yields. A substituent at the *ortho* position of the aromatic ring (see **5j** and **5k**) slightly lowered the reactivity, possibly because of the steric hindrance. Many kinds of heteroaromatic groups such as thienyl, furyl, benzofuryl and dibenzothienyl were compatible with this catalyst system, giving the corresponding cross-metathesis products such as **5n**−**5q** in 57−76% yields. Secondary hydrosilanes such as $PhMeSiH_2$ and Ph_2SiH_2 were also suitable for the cross-metathesis with **1a**, affording the desired products **5r** and **5s** in 69% and 61% yields, respectively. The reaction of diphenyl methyl silane Ph_2MeSiH with **1a** gave the desired cross-metathesis product **5t** in 56% yield, despite relatively high steric bulkiness. Moreover, dimethyl hydrosilanes bearing an alkynyl, alkenyl, or ethyl group were also suitable substrates for the reaction with **1a**, affording the desired cross-metathesis reaction products **5u**−**5w** in moderate to good yields.

Amino group-containing organosilicon compounds are known to be important components in many functional materials and pharmaceuticals.[14] Furthermore, amino groups can also undergo synthetically useful transformations.[15] To demonstrate the usefulness of the reaction products obtained in this work, the *N*,*N*-dimethylaminophenyl-containing products **4a** and **5i** were examined. Treatment of **4a** and **5i** with methyl trifluoromethanesulfonate (MeOTf) in CH_2Cl_2 easily generated the quaternary ammonium salts **6a** (R = H) and **6b** (R = Ph), respectively in almost quantitative yields (Scheme 2). The reaction of **6a** with the arylboronic acid **7** in the presence of a nickel catalyst[16] afforded the corresponding cross-coupling product **8** in 65% isolated yield (Scheme 2a). Similarly, the reaction of **6a** with the Grignard reagent **9** in the presence of a palladium catalyst[17] gave the cross-coupling product **10** in 70% yield (Scheme 2b). Treatment of **6b** with ^{i}PrONa in the presence of a nickel catalyst[18] easily yielded the deamination product **11** (Scheme 2c).

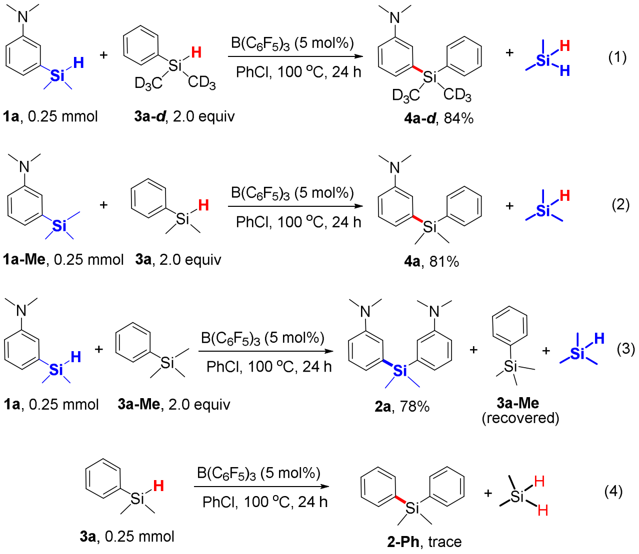
Scheme 2. Examples of transformation of *N*,*N*-dimethylaminophenyl silane products 4a and 5i



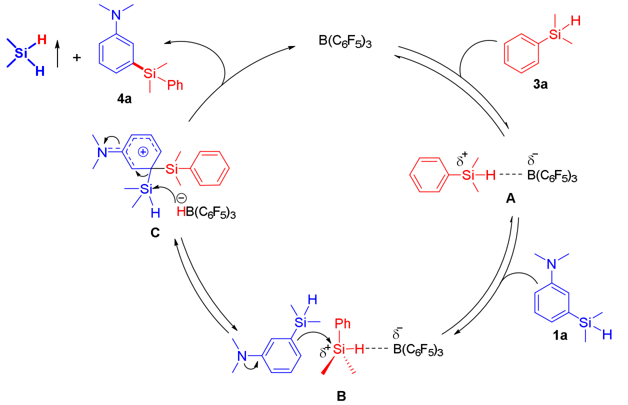
To gain information on the reaction mechanism, we carried out several control experiments as shown in Scheme 3. The reaction of (m-$Me_2NC_6H_4$)Me_2SiH (**1a**) with $Ph(CD_3)_2SiH$ (**3a-*d***) exclusively yielded the CD_3-containing cross-metathesis product (m-$Me_2NC_6H_4$)$Ph(CD_3)_2Si$ (**4a-*d***) with release of Me_2SiH_2 (Scheme 3, eq. 1), suggesting that the electron-rich $Me_2NC_6H_4$ group in **1a** was transferred to the silicon atom of $Ph(CD_3)_2SiH$. In consistence, the reaction of the quaternary silane (m-$Me_2NC_6H_4$)Me_3Si (**1a-Me**) with $PhMe_2SiH$ (**3a**) selectively gave (m-$Me_2NC_6H_4$)$PhMe_2Si$ (**4a**), as a result of migration of the $Me_2NC_6H_4$ group and release of Me_3SiH (Scheme 3, eq. 2). In contrast, in the coexistence of (m-$Me_2NC_6H_4$)Me_2SiH (**1a**) and $PhMe_3Si$ (**3a-Me**), the homo-metathesis product of **1a**, namely **2a**, was selectively formed with release of Me_2SiH_2, while $PhMe_3Si$ remained unchanged (Scheme 3, eq. 3). No cross-metathesis product was observed. Under the same conditions, the redistribution of $PhMe_2SiH$ (**3a**) was very slow, giving only a trace amount of the redistribution product Ph_2Me_2Si (**2-Ph**) (Scheme 3, eq. 4; see also Table S1 in Supporting Information). These results clearly demonstrate that transfer of the relatively electron-rich $Me_2NC_6H_4$ group is much easier than that of Ph and a Si–H unit is essential to receive the transfer of the $Me_2NC_6H_4$ group in the present redistribution reactions.

On the basis of the above experimental observations, a possible reaction mechanism for the $B(C_6F_5)_3$-catalyzed cross-metathesis reaction between **1a** and **3a** is proposed in Scheme 4. An interaction between $B(C_6F_5)_3$ and the hydride in **3a** could give a weak adduct like **A**, in which the Si−H bond could be polarized to generate a cationic Si center.[9,10a,e,11a-d] The approach of **1a** to **A** from the back side may promote the migration of the electron-rich $Me_2NC_6H_4$ group from the Si atom in **1a** to that in **3a** via **B** to give **C**.[11a-c,12] Release of the volatile Me_2SiH_2 from **C** would finally give the cross-metathesis product **4a** and regenerate $B(C_6F_5)_3$.

Scheme 3. Substituent Redistribution Involving Different Tertiary and Quaternary Silanes



Scheme 4. A Possible Mechanism of C−Si/Si−H Bond Cross-Metathesis of 1a and 3a.



In summary, we have achieved for the first time the selective C–Si/Si–H bond cross-metathesis of two different hydrosilanes as well as the metal-free catalytic redistribution of a series of electron-rich aromatic hydrosilanes by using the commercially available $B(C_6F_5)_3$ as a catalyst. The reaction takes place selectively through migration of a relatively electron-rich aryl group such as $Me_2NC_6H_4$ to the Si atom of a hydrosilane unit which is activated by the H---$B(C_6F_5)_3$ interaction. A wide range of hydrosilanes are applicable for this selective transformation. Aromatic and aliphatic C–X (X = F, Cl, Br) bonds as well as alkenyl, alkynyl, and various heteroaromatic groups are compatible. This protocol offers a concise access to diverse silylated aromatic compounds and may open a new window to the chemistry of boron and silicon.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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(12) In the case of ortho- and para-*N*,*N*-dimethylaminophenyl silanes, desilylation was observed. For examples of electrophilic desilylation, see: *Angew. Chem., Int. Ed.* **2017**, *56*, 52 and references cited therein.

(13) The ^{1}H NMR signals of Me$_2$SiH$_2$ (500 MHz, C$_6$D$_5$Cl) were observed at δ 0.04 (t, J = 4.0 Hz, 6 H) and 3.83−3.87 (m, 2 H). **Caution**: Me$_2$SiH$_2$ is a flammable gas (bp = –20 °C), so safety precautions should be made when opening the reaction vessel at the end of the reaction. Especially, precautions are required to run these reactions in large scales. No accident was encountered in our studies. Also see: Buslov, I.; Keller, S. C.; Hu, X. *Org. Lett.* **2016**, *18*, 1928 and references cited therein.

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