

# Selective synthesis of halosilanes from hydrosilanes and utilization for organic synthesis

Atsutaka Kunai\*, Joji Ohshita

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi, Hiroshima 739-8527, Japan

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## Abstract

Selective synthesis of halosilanes has been examined. Various types of halosilanes and halohydrosilanes, such as  $R_3SiX$ ,  $R_2SiHX$ ,  $R_2SiX_2$ ,  $RSiH_2X$ ,  $RSiHX_2$  ( $X = Cl, Br, F$ ), were obtained by the reactions of the corresponding hydrosilanes with Cu(II)-based reagents selectively in high yields. This method could be also applied to the synthesis of chlorofluorosilanes and chlorohydrogermanes. On the other hand, iodo- and bromosilanes and germanes were obtained by Pd- or Ni-catalyzed hydride–halogen exchange reactions of hydrosilanes with alkyl or allyl halides. Their synthetic applications have been demonstrated by using iodo- and bromosilanes and chlorofluorosilanes.

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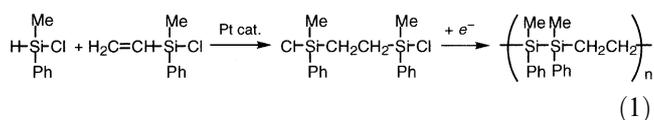
**Keywords:** Hydrosilane; Halosilane; Halohydrosilane; Copper reagent; H-halogen exchange; Synthetic utilization

## 1. Introduction

Organohalosilanes are useful starting materials or reagents in the field of organosilicon chemistry [1] as well as synthetic organic chemistry [2], as illustrated in Chart 1. Among halosilanes, chlorosilanes are supplied by an industrial process, so-called ‘the direct process’ [3], and are widely used for the synthesis of organosilicon compounds or polymers. Thus, enormous examples for the synthetic utility of chlorosilanes have been reported to date.

However, for building up a desired organosilicon molecule, we sometimes require organosilanes having multiple functional groups different in reactivity on the same silicon atom, such as chlorohydro- or chlorofluorosilanes as the starting materials. An example is shown in Eq. (1), where poly[(disilanylene)ethylene] was obtained by Pt-catalyzed hydrosilylation of chlorohydro-silane with chlorovinylsilane, followed by electroreductive coupling of the product [4]. There may be also needed in some cases the use of more

reactive halosilanes such as bromo- or iodosilanes, while upon introduction of an silyl group into highly hindered molecules, striking improvement in yields is often resulted by using fluorosilanes instead of chlorosilanes. Thus, molecular design would be much easier if various halosilanes including halohydrosilanes and mixed halosilanes could be readily obtained in hands.



In this paper, we would like to review our recent work on the selective synthesis of such halosilanes from hydrosilanes, together with some examples for their utilization. As summarized in Chart 2, the chlorination and bromination processes include oxidative halogenation of a hydrosilyl bond with copper(II) chloride or bromide in the presence of a catalytic amounts of CuI to give the chloro- or bromosilyl bond. The characteristic aspect of the reaction is that only one hydrogen on the silicon atom is replaced by a chlorine or bromine atom with the use of 2 equiv of  $\text{CuCl}_2$  or  $\text{CuBr}_2$ . The chlorosilyl bond thus formed can be converted in situ to the fluorosilyl bond with the simultaneous use of KF, which provides also a synthetic route to fluorohydro-

\* Corresponding author. Tel.: +81-824-247727; fax: +81-824-245494.

E-mail address: [akunai@hiroshima-u.ac.jp](mailto:akunai@hiroshima-u.ac.jp) (A. Kunai).

## Utility of halosilanes

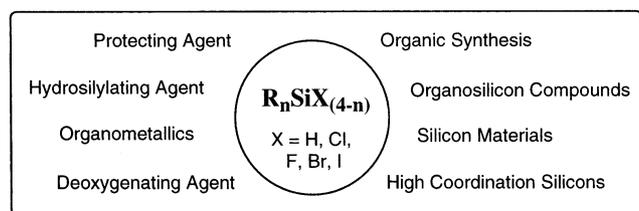


Chart 1.

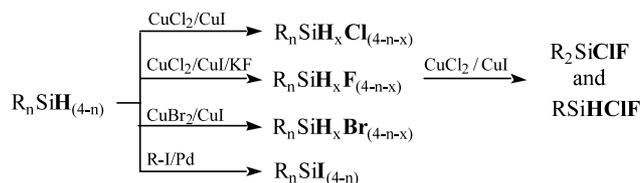


Chart 2.

lanes in one pot. Moreover, chlorofluorosilanes and chlorofluorohydrosilanes could be obtained by subsequent chlorination of the primary product, fluorohydrosilane.

On the other hand, transformation of hydrosilanes to iodosalanes was achieved by Pd-catalyzed hydrogen–iodine exchange reaction between alkyl iodide and the hydrosilyl group, though exhaustive exchange of silyl hydrogens is inevitable. This approach was modified, also for the production of bromosalanes and bromogermanes. The reaction system could be utilized as reagents for ring-opening halosilylation of oxygen-containing ring compounds to give  $\alpha,\omega$ -halosiloxyalkanes.

## 2. Results and discussion

### 2.1. Selective chlorination of hydrosilanes and germanes with copper reagent

#### 2.1.1. Chlorination of hydrosilanes

For the synthesis of chloro-silanes, hydrosilanes are often used as the starting compounds. In fact, several methods are available to date for the synthesis of chlorosilanes from hydrosilanes [5–11]. For example, the reaction of hydrosilanes with  $\text{CCl}_4$  in the presence of a catalytic amount of  $\text{PdCl}_2$  affords chlorosilanes in high yields [9,10]. Radical-induced hydrogen–halogen exchange between hydrosilanes and  $\text{CCl}_4$  also produces chlorosilanes in good yields [12,13]. All methods including these two, however, cannot be applied for the selective synthesis of the silicon compounds that contain both Si–Cl and Si–H bonds. Even if the reaction is performed under controlled conditions, the reaction of polyhydrosilanes always results in a mixture of chlorinated products at each stage.

In early 1990s, when we were examining electroreductive coupling of chlorosilanes on a Pt cathode in dimethoxyethane using Cu as a sacrificial anode [14], we found a curious phenomenon that a small amount of dichlorosilane was formed from chlorohydrosilane along with the expected product, dihydrodisilane (Eq. (2)). We thus assumed that chlorination of the Si–H bond in the starting silane took place with copper salts generated anodically. Actually, stirring  $\text{MePhSiH}_2$  with  $\text{CuCl}_2$  in the electrolytic cell without a charge overnight afforded an appreciable amount of  $\text{MePhSiCl}_2$ .



We examined about the chlorination ability of  $\text{CuCl}_2$  towards triorganosilanes in diethyl ether [15], but the reaction did not proceed with  $\text{CuCl}_2$  alone unless a catalyst like Pt surface is present. When a catalytic amount of CuI was added to  $\text{CuCl}_2$ , however, the reaction in ether proceeded very smoothly to give chlorosilanes [16]. Thus, treatment of  $\text{Me}_2\text{PhSiH}$  (**1**) with 2 equiv molar of  $\text{CuCl}_2$  in the presence of a catalytic amount of CuI at room temperature for 13 h produced  $\text{Me}_2\text{PhSiCl}$  (**1a**) in 82% isolated yield (Eq. (3)). A trace of disiloxane formed from hydrolysis of the product was observed, but no other products were detected by either GLC or spectrometric analysis. The mixture of  $\text{CuCl}_2$  and a catalytic amount of CuI is hereafter named as the ‘ $\text{CuCl}_2$ –CuI’ reagent. Treatment of other triorganohydrosilanes like  $\text{MePh}_2\text{SiH}$  (**2**) and  $\text{Bu}_2\text{MeSiH}$  (**3**) with 2 equiv of the  $\text{CuCl}_2$ –CuI reagent also afforded the respective chlorosilanes **2a** and **3a** in high yields. In a case of bulky hydrosilane, *t*- $\text{BuMe}_2\text{SiH}$  (**4**), the reaction rate was very slow in ether, but the use of tetrahydrofuran (THF) as the co-solvent accelerated markedly the reaction, leading to a 73% yield of *t*- $\text{BuMe}_2\text{SiCl}$  (**4a**) after 60 h of the reaction.



**1a**, R = Me, R' = Ph, 82%

**2a**, R = Ph, R' = Me, 77%

**3a**, R = Bu, R' = Me, 87%

**4a**, R = Me, R' = *t*-Bu, 73%

The facts that a trace amount of CuI catalyzes the present reaction and 2 equiv of  $\text{CuCl}_2$  is necessary for replacing one Si–H by Si–Cl suggests that a certain reactive species such as  $\text{CuICl}$  or  $\text{CuI}_2$  might be formed and plays a role in the present reaction [15], although the detailed mechanism is not clear yet.

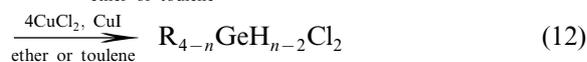
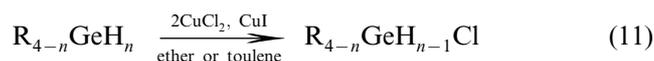
The present method can be applied to the selective chlorination of hydrosilyl bonds to give chlorohydrosilanes, such as  $\text{R}_2\text{SiHCl}$ ,  $\text{RSiH}_2\text{Cl}$ , and  $\text{RSiHCl}_2$ , from the corresponding hydrosilanes. For example, the reaction of  $\text{Et}_2\text{SiH}_2$  (**5**) with 2 equiv of  $\text{CuCl}_2$ –CuI in diethyl ether at room temperature for 43 h yielded  $\text{Et}_2\text{SiHCl}$



Table 1  
Selective chlorination of hydrogermanes with copper reagent

Germane	CuCl <sub>2</sub> (equiv)	CuI (equiv)	Conditions	Product (isolated yield)
Et <sub>3</sub> GeH	2	0.03	Et <sub>2</sub> O, rt, 3 h	Et <sub>3</sub> GeCl (76%)
Hex <sub>3</sub> GeH	2	0.03	Et <sub>2</sub> O, rt, 5 h	Hex <sub>3</sub> GeCl (88%)
Et <sub>2</sub> GeH <sub>2</sub>	2	0.02	Et <sub>2</sub> O, rt, 1 h	Et <sub>2</sub> GeHCl (73%)
	4	0.02	Et <sub>2</sub> O, rt, 8 h	Et <sub>2</sub> GeCl <sub>2</sub> (85%)
Hex <sub>2</sub> GeH <sub>2</sub>	2	0.03	Et <sub>2</sub> O, rt, 3 h	Hex <sub>2</sub> GeHCl (65%) <sup>a</sup>
	2	0.03	toluene, reflux, 5 h	Hex <sub>2</sub> GeHCl (91%)
	2	none	toluene, reflux, 19 h	Hex <sub>2</sub> GeHCl (90%)
	4	0.11	toluene, reflux, 4 days	Hex <sub>2</sub> GeCl <sub>2</sub> (87%)
Ph <sub>2</sub> GeH <sub>2</sub>	2	none	toluene, reflux, 31 h	Ph <sub>2</sub> GeHCl (87%)
	4	0.14	toluene, reflux, 6 days	Ph <sub>2</sub> GeCl <sub>2</sub> (86%)
PhGeH <sub>3</sub>	2	none	toluene, reflux, 19 h	PhGeH <sub>2</sub> Cl (84%)
	4	0.17	toluene, reflux, 9 days	PhGeHCl <sub>2</sub> (88%)

<sup>a</sup> A trace of Hex<sub>2</sub>Ge(OEt)Cl was formed.



The present reaction is oxidative in nature and CuCl<sub>2</sub> acts as the oxidant. Presumably, replacement of the hydrogen atom of hydrogermanes with an electronegative chlorine atom suppresses the further chlorination to provide the high selectivities in the present reactions. The lower reaction rate of the chlorination of phenylgermanes than that of the respective hexylgermanes also seems to reflect the electronegative nature of the phenyl group compared to the hexyl group.

## 2.2. Selective fluorination of hydrosilanes with copper reagent

Fluorosilanes can be used for the synthesis of high coordinated silicon compounds [24] and highly hindered organosilanes [25]. To date, several methods are available for the synthesis of fluorosilanes. The methods involve the reactions of siloxy compounds with NH<sub>4</sub>F in H<sub>2</sub>SO<sub>4</sub> [26], hydrofluoric acid [27], and BF<sub>3</sub> etherate [28], halogen exchange of chlorosilanes with SbF<sub>3</sub> [29], ZnF<sub>2</sub> [30], NH<sub>4</sub>F [31], CuF<sub>2</sub> [32], Na<sub>2</sub>SiF<sub>6</sub> [33], NaPF<sub>6</sub>, NaSbF<sub>6</sub>, NaBF<sub>4</sub> [34], and Me<sub>3</sub>SnF [35], and fluorination of hydrosilanes with AgF [36], PF<sub>5</sub> [37], Ph<sub>3</sub>CBF<sub>4</sub> [38], SbF<sub>3</sub> [39], NOBF<sub>4</sub> or NO<sub>2</sub>BF<sub>4</sub> [40], and CuF<sub>2</sub>-CCl<sub>4</sub> [41]. Although these methods give fluorosilanes in good yields, it is difficult to prepare the fluorosilanes bearing an Si-H bond from hydrosilanes.

In our continuing study on halogenation of hydrosilanes, we found that the hydrosilyl group can be transformed into a fluorosilyl group with the use of the CuCl<sub>2</sub>-CuI reagent in the presence of KF [42]. Thus, when Me<sub>2</sub>PhSiH (**1**) was treated with a mixture of 2 equiv of the CuCl<sub>2</sub>-CuI reagent and 1 equiv of KF (thus CuCl<sub>2</sub>-CuI-KF reagent) in THF at room temperature for 5 h, Me<sub>2</sub>PhSiF (**1c**) was obtained in 82% yield as the

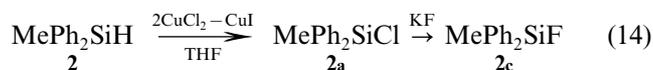
sole product after distillation of the resulting mixture (Eq. (13)). No other products were detected by GLC and spectrometric analysis. Similar reaction of MePh<sub>2</sub>SiH (**2**) with 2 equiv of the CuCl<sub>2</sub>-CuI-KF reagent in THF for 5 h gave MePh<sub>2</sub>SiF (**2c**) selectively in 78% isolated yield.



**1c**, R = Me, R' = Ph, 82%

**2c**, R = Ph, R' = Me, 78%

For these reactions, the use of 2 equiv of CuCl<sub>2</sub> as the oxidant for one H-Si bond is essential. When hydrosilanes were treated with an excess amount of KF and the CuI catalyst in the absence of CuCl<sub>2</sub> in THF, the reaction did not proceed, which suggests that the starting hydrosilane is first converted to a chlorosilane with the CuCl<sub>2</sub>-CuI reagent, and then the resulting Cl atom is replaced by a fluoride ion to form fluorosilanes (Eq. (14)). Such Cl/F exchange on a silicon atom is well known [29–34].



We applied these reactions to the synthesis of fluorodiorganosilanes (R<sub>2</sub>SiHF) from the corresponding diorganosilanes (R<sub>2</sub>SiH<sub>2</sub>). Practically, complete conversion of the starting dihydrosilanes is desirable to get high purity of the products. Moreover, the formation of difluoro compounds must be avoided, because it is hard to separate the desired R<sub>2</sub>SiHF from R<sub>2</sub>SiF<sub>2</sub> as well as R<sub>2</sub>SiH<sub>2</sub> by distillation.

As expected, dialkyl-, alkylaryl-, and diarylsilanes could be readily transformed into the corresponding monofluorosilanes (Eq. (15)). When *n*-Hex<sub>2</sub>SiH<sub>2</sub> (**16**) was treated with 2 equiv of the CuCl<sub>2</sub>-CuI-KF reagent in THF at room temperature, the starting silane disappeared within 1 h, and distillation of the resulting mixture afforded *n*-Hex<sub>2</sub>SiHF (**16c**) in 81% yield as the

sole product. Similar treatment of  $\text{Ph}_2\text{SiH}_2$  (**17**) for 1 h afforded  $\text{Ph}_2\text{SiHF}$  (**17c**) in 81% isolated yield, while the reaction of  $\text{MeMesSiH}_2$  (**18**) for 24 h produced  $\text{MeMesSiHF}$  (**18c**) in 75% isolated yield. Rather slow reaction rate of  $\text{MeMesSiH}_2$  may be caused by steric hindrance due to the mesityl substituent. In all cases, the monofluoro derivatives were obtained as the sole product. Neither difluorosilanes nor other products were detected in the distillates.



**16c**, R = R' = Hex, 81%

**17c**, R = R' = Ph, 81%

**18c**, R = Me, R' = Mes, 75%

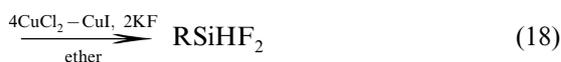
Similar treatment of  $\text{MePhSiH}_2$  (**6**) with 2 equiv of the  $\text{CuCl}_2\text{--CuI--KF}$  reagent in THF at room temperature for 1 h produced  $\text{MePhSiHF}$  (**6c**) in 72% yield after distillation, together with an 8% yield of  $\text{MePhSiF}_2$ , while the reaction with 4 equiv of the reagent for 48 h gave  $\text{MePhSiF}_2$  as the sole product in 61% yield. In order to obtain only the monofluorosilane as the product, we carried out the reaction of **6** under milder conditions. Thus, when the reaction of **6** was carried out using 2 equiv of the reagent including CsF instead of KF in refluxing ether for 1 week, **6c** was obtained as the sole product in 68% yield after distillation (Eq. (16)). On the other hand, the use of  $\text{CuF}_2$  as the fluoride salt in THF formed mainly  $\text{MePhSiF}_2$  [41], together with a disiloxane which was presumably resulted by water in the highly hygroscopic  $\text{CuF}_2$  salt.



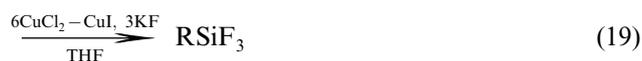
The present method is not restricted to the dihydrosilanes, but can be applied to the partial fluorination of trihydrosilanes,  $\text{RSiH}_3$  (Eq. (17)). In this case, it is desirable to add KF after the end of the chlorination step, since simultaneous addition of these salts produces a mixture of  $\text{RSiH}_2\text{F}$  and a small amount of  $\text{RSiHF}_2$ . Thus, treatment of  $\text{PhSiH}_3$  (**7**) for 77 h and  $n\text{-HexSiH}_3$  (**19**) for 42 h with 2 equiv of the  $\text{CuCl}_2\text{--CuI}$  reagent in this manner afforded  $\text{PhSiH}_2\text{F}$  (**7c**) and  $n\text{-HexSiH}_2\text{F}$  (**19c**) in 64 and 58% yield, respectively, as the sole volatile product, while  $\text{PhSiHF}_2$  (**7d**) and  $n\text{-HexSiHF}_2$  (**19d**) could be obtained when 4 equiv of the reagent was used (Eq. (18)).  $\text{PhSiF}_3$  (**7e**) was obtained also by the reaction with 6 equiv of the reagent for 1 week (Eq. (19)).



**7c**, R = Ph, 64% **19c**, R = Hex, 58%



**7d**, R = Ph, 70% **19d**, R = Hex, 54%



**7e**, R = Ph, 53%

We extended the present method to the synthesis of mixed halosilanes. When  $\text{MePhSiHF}$  (**6c**) prepared from  $\text{MePhSiH}_2$  in the manner described above was treated with 2 equiv of the  $\text{CuCl}_2\text{--CuI}$  reagent in THF at room temperature for 10 h,  $\text{MePhSiClF}$  (**6f**) was obtained in 74% yield after distillation of the resulting mixture (Eq. (20)). Similar treatment of  $\text{Ph}_2\text{SiHF}$  (**17c**) with 2 equiv of the  $\text{CuCl}_2\text{--CuI}$  reagent in THF at 40 °C for 24 h afforded  $\text{Ph}_2\text{SiClF}$  (**17f**) in 67% isolated yield. In both cases, no other products were detected in the reaction mixture. The same reactions in ether proceeded much slower and afforded **6f** and **17f** in a little higher yields (83 and 70%).



**6f**, R = Me, R' = Ph, 74% (83%)

**17f**, R = R' = Ph, 67% (70%)

Chlorofluorohydrosilanes can be also synthesized from trihydrosilanes. Thus, when  $\text{PhSiH}_2\text{F}$  (**7c**) prepared from  $\text{PhSiH}_3$  was treated with 2 equiv of the  $\text{CuCl}_2\text{--CuI}$  reagent in ether at room temperature for 58 h,  $\text{PhSiHClF}$  (**7f**) was obtained in 61% yield, while similar treatment of  $n\text{-HexSiH}_2\text{F}$  (**19c**) with 2 equiv of this reagent for 48 h afforded  $n\text{-HexSiHClF}$  (**19f**) in 59% yield (Eq. (21)). All these mixed halosilanes and halohydrosilanes are thermally stable and could be obtained in pure forms by fractional distillation after filtration of the reaction mixture to remove copper salts. No redistribution reactions of halogens were observed during the distillation.



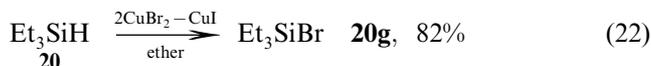
**7f**, R = Ph, 61% **19f**, R = Hex, 59%

Interestingly,  $\text{PhSiCl}_2\text{F}$  and  $n\text{-HexSiCl}_2\text{F}$  were not produced, even when **7c**, **7f**, **19c**, and **19f** were treated with the excess of the  $\text{CuCl}_2\text{--CuI}$  reagent under similar conditions for several days. In all cases, the reaction stopped at the stage of monochlorofluorosilanes, probably because accumulation of electronegative fluorine and chlorine atoms on the silicon center make an increase in oxidation potential of these halosilanes, leading to the decrease in reactivity and the increase in selectivity. Similarly, the reaction of **7d** and **19d** with the  $\text{CuCl}_2\text{--CuI}$  reagent under similar conditions did not afford the corresponding chlorosilanes, and the starting materials were recovered unchanged.

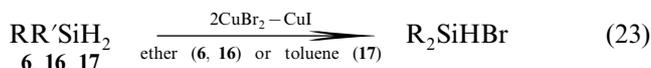
### 2.3. Selective bromination of hydrosilanes with copper reagent

As to bromosilanes, there have been reported several synthetic methods, such as reactions of polybromosilanes with Grignard reagents [43], cleavage of Si–O bonds with PBr<sub>3</sub> [44], cleavage of Si–Ph bonds [26b,45] or Si–Si bonds [46] with Br<sub>2</sub>, Cl/Br exchange of chlorosilanes with AlBr<sub>3</sub> [44a] or MgBr<sub>2</sub> [47], bromination of polyhydrosilanes with Br<sub>2</sub> [44a,48], HBr [49], HgBr<sub>2</sub> [50], or NBS [51], and partial reduction of 1,2-dibromodisilanes with trialkyltin hydrides [52], but it is difficult to obtain selectively a desired type of bromohydrosilane by these methods.

In our continuing study on halogenation of hydrosilanes, we found that hydrosilyl groups can be transformed into bromosilyl groups with the use of CuBr<sub>2</sub>, instead of CuCl<sub>2</sub>, in the presence of a catalytic amount of CuI (thus CuBr<sub>2</sub>–CuI reagent) [53], in a way analogous to chlorination [16]. When Et<sub>3</sub>SiH (**20**) was treated with 2 equiv of the CuBr<sub>2</sub>–CuI reagent in diethyl ether at room temperature for 1.5 h, Et<sub>3</sub>SiBr (**20g**) was obtained in 82% yield after distillation of the reaction mixture (Eq. (22)).



This reagent could be applied for the monobromination of dihydrosilanes (Eq. (23)). Thus, when *n*-Hex<sub>2</sub>-SiH<sub>2</sub> (**16**) was treated in diethyl ether with 2 equiv of the CuBr<sub>2</sub>–CuI reagent at room temperature, the starting silane disappeared within 1 h, and distillation of the resulting mixture afforded *n*-Hex<sub>2</sub>SiHBr (**16g**) in 73% yield as the sole volatile product. Similar treatment of MePhSiH<sub>2</sub> (**6**) for 9 h afforded MePhSiHBr (**6g**) in 68% yield, while the reaction of Ph<sub>2</sub>SiH<sub>2</sub> (**17**) in toluene for 7.5 h produced Ph<sub>2</sub>SiHBr (**17g**) in 64% yield.



**6g**, R = Me, R' = Ph, 68%

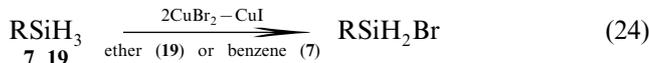
**16g**, R = R' = *n*-Hex, 73%

**17g**, R = R' = Ph, 64%

To obtain further information, we carried out dibromination of dihexylsilane and monitored the progress by GLC. When **16** was treated with 4 equiv of the CuBr<sub>2</sub>–CuI reagent in ether at room temperature, **16** disappeared soon after to generate **16g** as the primary product. This monobromide then diminished slowly and disappeared after 44 h, during which *n*-Hex<sub>2</sub>-Si(OEt)H and *n*-Hex<sub>2</sub>Si(OEt)Br began to increase and became the final products, indicating that the monobromination proceeds quite fast, while dibromination requires much longer time, and the bromide once formed reacts gradually with ether to give ethoxy

derivatives [54]. To suppress undesired reactions, we changed the solvent from ether to benzene. When **16** was treated with 4 equiv of the CuBr<sub>2</sub>–CuI reagent in benzene under reflux for 34 h, *n*-Hex<sub>2</sub>SiBr<sub>2</sub> was obtained in 70% isolated yield.

Mono- and dibrominations of trihydrosilanes are also possible (Eqs. (24) and (25)). When *n*-HexSiH<sub>3</sub> (**19**) was treated with 2 equiv of the CuBr<sub>2</sub>–CuI reagent in ether at room temperature for 12 h, *n*-HexSiH<sub>2</sub>Br (**19g**) was obtained in 64% yield as the sole product after distillation. When **19** was treated with 4 equiv of the CuBr<sub>2</sub>–CuI reagent in benzene at room temperature for 1 week, *n*-HexSiHBr<sub>2</sub> (**19h**) was obtained in 55% isolated yield. Moreover, the reaction of PhSiH<sub>3</sub> (**7**) with 2 equiv of the reagent in benzene at room temperature for 6 h afforded PhSiH<sub>2</sub>Br (**7g**) in 72% yield, while treatment with 4 equiv of the reagent in benzene at room temperature for 40 h produced PhSiHBr<sub>2</sub> (**7h**) in 67% yield.



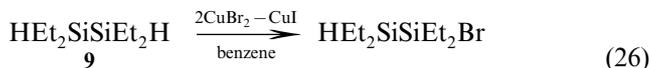
**7g**, R = Ph, 72%    **19g**, R = *n*-Hex, 64%



**7h**, R = Ph, 67%    **19h**, R = *n*-Hex, 55%

On the other hand, attempted tribromination with this reagent did not take place. When **7** was heated under reflux in benzene with 6 equiv of the CuBr<sub>2</sub>–CuI reagent, dibromination completed within 3 h, much faster than the case using 4 equiv of the reagent at room temperature. However, the reaction stopped at this stage, and no tribromide would be formed even after 1 week. Presumably, accumulation of electronegative bromine atoms on the same silicon center decreases the reactivity of the silicon center, as has been observed previously for the chlorination of fluorohydrosilanes [42].

We also performed selective bromination of 1,2-dihydrodisilanes. Thus, when HEt<sub>2</sub>SiSiEt<sub>2</sub>H (**9**) was treated with 2 equiv of the reagent in benzene at room temperature for 4 h, HEt<sub>2</sub>SiSiEt<sub>2</sub>Br (**9g**) was obtained in 58% isolated yield, together with a 10% yield of Et<sub>2</sub>SiHBr (Eq. (26)).



**9g**, 58%

The selectivity of the bromodisilane diminished in this case, but two products could be readily separated by distillation. The monosilane may be produced by the cleavage of an Si–Si bond of disilane with HBr generated during the reaction.

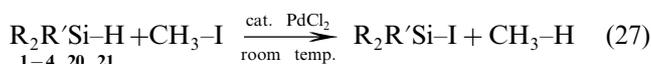
## 2.4. Halogenation by metal-catalyzed hydrogen–halogen exchange reaction

### 2.4.1. Iodination of hydrosilanes

Organic iodosilanes have been shown to be useful reagents in organic synthesis due to their high reactivity. However, the synthesis of the iodosilanes, except for Me<sub>3</sub>SiI has not been extensively studied. The method for the synthesis of Me<sub>3</sub>SiI reported to date involves the reaction of hexamethyldisilane [55], trimethylphenylsilane [26b], allyltrimethylsilane [56], and 1,4-bis(trimethylsilyl)cyclohexa-2,5-diene [57] with I<sub>2</sub>, and the reaction of Me<sub>3</sub>SiCl with NaI in acetonitrile [58]. Organoiodosilanes other than Me<sub>3</sub>SiI have been prepared by the methods involving cleavage of Ph–Si and H–Si bonds by I<sub>2</sub> and HI [59], an Se–Si bond by I<sub>2</sub> [60], and an N–Si bond by HI [61]. It has also been reported that the reaction of triorganosilanes with iodobenzene in the presence of a colloidal Ni catalyst at high temperature produces organoiodosilanes [62].

As an extension of our previous observation for the chlorination of hydrosilanes with the CuCl<sub>2</sub>–CuI reagent, we first examined iodination of Et<sub>3</sub>SiH using a small excess of iodine in the presence of CuI in benzene at room temperature, and obtained Et<sub>3</sub>SiI in high yield. Similar CuI-catalyzed reaction of PhMe<sub>2</sub>SiH with iodine, however, produced PhMe<sub>2</sub>SiI only in low yield, because a Ph–Si bond is readily cleaved by the action of HI generated from the H/I exchange reaction. Moreover, the products were always contaminated with a trace of I<sub>2</sub>. Therefore, we attempted to prepare the iodosilanes by the method that involves no iodine, and found that Si–H/C–I exchange readily takes place in the presence of a palladium chloride catalyst under mild conditions to give a high quality of iodosilanes.

It is known that treatment of organohydrosilanes with chlorocarbons in the presence of a catalytic amount of palladium chloride afforded chlorosilanes in high yields [63]. We modified this method to be used for the synthesis of various types of the iodosilanes [64]. Thus, the reaction of Et<sub>3</sub>SiH (**20**) with 1.8 equiv of methyl iodide in the presence of 0.5 mol% of palladium chloride at room temperature for 1.5 h afforded Et<sub>3</sub>SiI (**20i**) in 85% isolated yield (Eq. (27)). The reaction proceeded cleanly without solvent and **20i** could be readily isolated as a colorless liquid by simple distillation. No other products were detected in the distillate. Similar PdCl<sub>2</sub>-catalyzed reaction of *n*-Bu<sub>2</sub>MeSiH (**3**) at room temperature for 7 h with MeI produced *n*-Bu<sub>2</sub>MeSiI (**3i**) in 77% yield. The formation of methane was verified by mass spectrometric analysis of the gaseous product.



**1i**, R = Me, R' = Ph, 83%

**2i**, R = Ph, R' = Me, 91%

**3i**, R = *n*-Bu, R' = Me, 77%

**4i**, R = Me, R' = *t*-Bu, 97%

**20i**, R = R' = Et, 85%

**21i**, R = R' = Ph, 94%

The reaction rate for the Si–H/C–I exchange is quite slow for the hydrosilanes bearing a bulky substituent on the silicon atom, but increased reaction temperature brings about a considerable reduction in time. For example, the reaction of *t*-BuMe<sub>2</sub>SiH (**4**) with MeI at room temperature requires 24 h for completion of the reaction, while at 60 °C, **4** is completely consumed within 2.5 h to give a 97% yield of *t*-BuMe<sub>2</sub>SiI (**4i**).

It should be stressed that the present reaction can be used for the synthesis of phenyl-substituted iodosilanes. Thus, the reaction of Me<sub>2</sub>PhSiH (**1**) with 2.2 equiv of MeI in the presence of 0.4 mol% of PdCl<sub>2</sub> at room temperature for 4 h gave Me<sub>2</sub>PhSiI (**1i**) in 83% isolated yield. Similarly, the Pd-catalyzed reaction of MePh<sub>2</sub>SiH (**2**) with MeI produced MePh<sub>2</sub>SiI (**2i**) in 91% yield.

The reaction of Ph<sub>3</sub>SiH (**21**) with MeI is somewhat different from the others. In this case, the product Ph<sub>3</sub>SiI (**21i**) was produced as solids, and therefore the reaction was carried out in benzene under reflux. When PdCl<sub>2</sub> was added to the solution, the reaction began smoothly, but the activity of PdCl<sub>2</sub> decreased gradually. By adding the catalyst twice, finally **21i** was obtained in 94% yield.

Diiodomethane, iodoform, or iodobenzene can also be used as the iodide source, though the reactivity of them seems more sensitive to the substituents on Si, compared to MeI. For example, the reaction of **1** with PhI at room temperature for 1 h yielded Me<sub>2</sub>PhSiI in 91% yield. In contrast to this, the reactions of **20** and **4** with PhI were quite slow even at 80 °C and most of the starting hydrosilane was recovered unchanged after 19 h of reaction.

The present method can be applied to the preparation of Et<sub>2</sub>SiI<sub>2</sub> (**5i**) from Et<sub>2</sub>SiH<sub>2</sub> (**5**). When methyl iodide is used as the iodine source, a novel alkyl–hydrogen exchange reaction takes place along with the iodination reaction (Eq. (28)). Thus, when **5** was treated with 3 equiv of MeI in the presence of 4 mol% of PdCl<sub>2</sub> at 60 °C for 24 h, **5i** was obtained in 37% isolated yield, together with a 20% yield of Et<sub>2</sub>MeSiI. The reaction of **5** with 3 equiv of ethyl iodide for 12 h led to a similar result. In order to avoid the formation of trialkyliodosilanes, we tried to use a bulkier alkyl iodide. Thus, when **5** was treated with 2.0 equiv of isopropyl iodide in the presence of 0.5 mol% of PdCl<sub>2</sub> at 70 °C for 24 h, the diiodosilane **5i** was formed as a sole volatile product in 74% yield. Moreover, the reaction of MePhSiH<sub>2</sub> (**6**) with *i*-PrI proceeded cleanly at 100 °C and afforded MePhSiI<sub>2</sub> (**6i**) in 87% yield after 12 h of the reaction (Eq. (29)). NiCl<sub>2</sub> also served as the catalyst, though less active, and the reaction with NiCl<sub>2</sub> under similar conditions for 18 h



The use of allyl iodide is also effective for the iodination of hydrogermanes, compared to MeI. Thus, when **22** was treated with an excess of MeI and a catalytic amount of PdCl<sub>2</sub> at 60 °C for 70 h, Hex<sub>3</sub>GeI (**22k**) was found to be formed only in 25% yield, together with **22** remaining in 70% yield. On the other hand, similar reaction with allyl iodide for 12 h produced **22k** in 84% yield. In contrast to bromination, the reaction of **27** with allyl iodide proceeded smoothly to afford **27k** in 87% yield. The use of NiCl<sub>2</sub> as the catalyst did not obviously accelerate the halogenation of hydrogermanes.

In the present halogenation of hydrosilanes and germanes, the formation of fine black precipitates was observed, immediately after the contact of the reactants with the catalysts. At the same time, the corresponding chlorosilanes were found to be formed by GC–MS analysis of the reaction mixtures. This seems to indicate that the actual active species in these reactions may be metallic Pd and Ni, formed from the reduction of the chlorides with hydrosilanes or germanes. Although we have no clear evidences concerning the reaction mechanism, we tentatively assume that the reaction proceeds via homolytic M–H (M = Si or Ge) bond cleavage on the Pd (or Ni) surface to induce radical chain reactions, or alternatively, via metathesis type reactions on the metal, as estimated by occurrence of H/Me exchange in the reaction of diethylsilane with MeI [16].

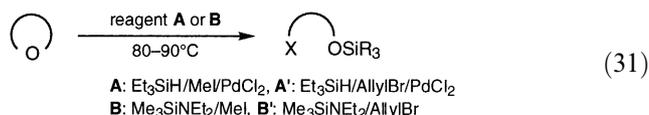
## 2.5. Utility of halosilanes

### 2.5.1. Iodosilanes and bromosilanes

Iodo- and bromosilanes play a unique role in organic synthetic chemistry and their synthetic utilities have been demonstrated [2]. Interaction of cyclic ethers with iodo- or bromotrimethylsilane affords the respective ring opened iodo- or bromosilylation products in good yields [25c]. Iodo- and bromosilanes, however, exhibit high tendency to undergo hydrolytic cleavage of the Si–halogen bond with atmospheric moisture leading to the formation of the respective silanols, unless the silicon atom is substituted by protecting substituent(s) with appropriate steric bulkiness, and therefore, iodo- and bromosilanes are usually difficult to handle as compared with the other halosilanes, chloro- and fluorosilanes. Yamamoto et al. reported that 1:1 mixtures of diethylaminotrimethylsilane with methyl iodide (Me<sub>3</sub>SiNEt<sub>2</sub>–MeI) and allyl bromide (Me<sub>3</sub>SiNEt<sub>2</sub>–AllylBr) behave as synthetic equivalent reagents of Me<sub>3</sub>SiI and Me<sub>3</sub>SiBr, respectively, and the reactions with epoxides afford the corresponding ring-opened 1,2-halosilylation products [66]. The Me<sub>3</sub>SiNEt<sub>2</sub>–MeI reagent reacts also with alkyl esters to give high yields of trimethylsilyl esters with liberation of iodoalkanes [67]. It is also demonstrated that silyl enol ethers are obtained from the reactions of

the respective aliphatic ketones with the Me<sub>3</sub>SiNEt<sub>2</sub>–MeI reagent [68].

More recently, we found in cooperation with Yamamoto that treatment of 1:1 mixtures of hydrosilanes and alkyl iodides with a catalytic amount of PdCl<sub>2</sub> (R<sub>3</sub>SiH–R'I–PdCl<sub>2</sub>) produces high yields of iodosilanes by hydride/iodide exchange [64]. In order to explore further the scope of synthetic utilities of these reaction systems, we studied ring-opening halosilylation of cyclic ethers [69], acetals [70], and lactones [71], which are less strained than epoxides, with Et<sub>3</sub>SiH–RX–PdCl<sub>2</sub> and Me<sub>3</sub>SiNEt<sub>2</sub>–RX (RX = MeI, EtI, EtBr, AllylBr). The reactions led to the one step synthesis of bifunctional ω-halo-α-siloxyalkanes (Eq. (31)). They may be potentially useful in organic synthesis as silyl-protected hydroxyalkyl [72] or carboxyalkyl halides.



Some representative results are picked up in Table 4, where four kinds of the reagent systems, Et<sub>3</sub>SiH–MeI–PdCl<sub>2</sub> (**A**), Et<sub>3</sub>SiH–AllylBr–PdCl<sub>2</sub> (**A'**), Me<sub>3</sub>SiNEt<sub>2</sub>–MeI (**B**), and Me<sub>3</sub>SiNEt<sub>2</sub>–AllylBr (**B'**) are employed. When THF was treated with 1 equiv of reagent **A** at room temperature for 5 h, 1-iodo-4-triethylsiloxybutane was obtained in 70% yield as the sole volatile product, while the reaction with reagent **A'** at 80–90 °C for 10 h afforded the corresponding bromosilylation product in 82% yield. The reaction of THF with reagent **B** (or **B'**) also proceeded cleanly to give the similar products in high yields. Similarly, tetrahydropyran underwent smooth iodosilylation with reagent **A** (or **B**) to afford 1-iodo-5-(triethylsiloxy)pentane in 74% yield. Iodosilylation of 2-MeTHF and 2-tetrahydrofurfuryl alcohol also proceeded smoothly to give the expected ring-opened products (not shown in the table).

The reactions of cyclohexanone ethylene acetal with 1 equiv of reagent **B** proceeded smoothly to afford a ring-opened siloxyethyl enol ether as the sole volatile product in 76% yield, while *N*-methyl-1,3-oxazolidine ring reacted with reagent **B** to give an enamine in 72% yield. The formation of siloxyethyl enol ether is in contrast to the fact that the reactions of ketone acetals with Me<sub>3</sub>SiI give the corresponding deprotected ketones [73]. Similar reactions have been reported for ketone dimethyl acetals, whose reactions with Me<sub>3</sub>SiI in the presence of a slight excess of hexamethyldisilazane give methyl enol ethers by the loss of one methoxy group and an α-hydrogen [74]. On the other hand, the reaction of cyclohexanone ethylene acetal with reagent **A** proceeded in a quite different manner and produced a dimeric product in 63% yield. We tentatively assume that in this case, dimerization of the acetal followed by Pd-assisted C–C bond cleavage might be involved [70].

Table 4  
Ring-opening halosilylation of cyclic compounds at 80–90 °C

substrate	reagent <sup>a</sup>	time/h <sup>b</sup>	product	yield
	<b>A</b>	5 <sup>c</sup>		<b>A</b> : X = I, R = Et, 70%
	<b>A'</b>	10		<b>A'</b> : X = Br, R = Et, 82%
	<b>B</b>	5		<b>B</b> : X = I, R = Me, 81%
	<b>B'</b>	17		<b>B'</b> : X = Br, R = Me, 76%
	<b>A</b>	16 <sup>d</sup>		<b>A</b> : R = Et, 74%
	<b>B</b>	16		<b>B</b> : R = Me, 74%
	<b>A</b>	5 <sup>c</sup>		<b>A</b> : X = I, 68%
	<b>A'</b>	12		<b>A'</b> : X = Br, 74%
	<b>A</b>	5		<b>A</b> : X = I, 88%
	<b>A'</b>	12		<b>A'</b> : X = Br, 79%
	<b>A</b>	4		<b>A</b> : X = I, 68%
	<b>A'</b>	12		<b>A'</b> : X = Br, 75%
	<b>A</b>	5		63%
	<b>B</b>	12		76%
	<b>B</b>	5		72%

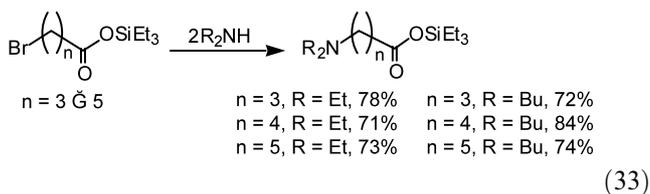
<sup>a</sup> **A**: Et<sub>3</sub>SiH/MeI/PdCl<sub>2</sub>, **A'**: Et<sub>3</sub>SiH/AllylBr/PdCl<sub>2</sub>, **B**: Me<sub>3</sub>SiNEt<sub>2</sub>/MeI, **B'**: Me<sub>3</sub>SiNEt<sub>2</sub>/AllylBr

<sup>b</sup> Reactions with **B** or **B'** were performed in toluene. <sup>c</sup> At room temperature. <sup>d</sup> At 100 °C.

The ring-opening iodo- and bromosilylation of  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -lactones with reagent **A** took place smoothly to give respective *O*-silyl-protected  $\omega$ -haloalkanoic acids in high yields, whereas reagent **B** was inactive towards these lactones and the starting lactones were recovered unchanged, probably because of steric hindrance of reagent **B**. For reagent **B**, a silylammonium salt may act as the active species (Eq. (32)).



To demonstrate synthetic utility of the halosilylation products, we examined conversion of C–halogen bonds to C–N bonds as an example (Eq. (33)). Thus, treatment of the bromosilylated products with 2 equiv of diethyl- or dibutylamine at 60 °C for 5 h produced the corresponding *O*-silyl-protected amino acids in good yields.

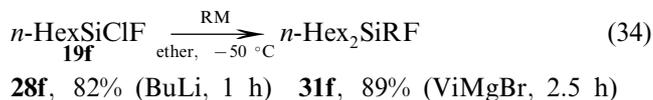


### 2.5.2. Chlorofluorosilanes

As discussed in Section 2.2, chlorofluorosilanes could be obtained from hydrosilanes by using the copper

reagents in two steps (Eq. (20)). The silanes have Si–Cl and Si–F bonds, being different in reactivity, and therefore, selective introduction of a nucleophile may be possible. To demonstrate this, we carried out the reaction of *n*-Hex<sub>2</sub>SiClF (**19f**) with organometallic reagents, RM (Eq. (34)). As expected, when **19f** was treated with organolithium (R = Bu or PhC $\equiv$ C) or organomagnesium reagents (R = Et, Vi, Allyl) at –50 °C, only the Si–Cl bond reacted selectively to afford fluorosilanes **28f**–**32f**. The Si–Cl bonds in *n*-HexSiCl<sub>2</sub>F (**19f'**), which was obtainable from **19c**, also reacted selectively with BuLi or AllylMgBr to give fluorosilanes **28g** and **32g** (Eq. (35)). Fluorosilanes thus obtained still keep a reactive Si–F bond, and thus, introduction of another nucleophile is possible. They may be also utilized as the reagent for building up sterically hindered silicon-containing molecules.

The above findings have enabled us to design silicon polymers with regular alternating arrangement of an Si unit and  $\pi$ -electron system, in which different  $\pi$ -systems could be introduced (Eq. (36)). Thus, the reaction of **19f** with a dilithio- $\pi$  reagent afforded bis(fluorosilyl-ethynyl)arenes selectively, which then reacted with another dilithio- $\pi$  reagent to give the desired alternating polymers in moderate to good yields.





#### 4.4. Pd-catalyzed iodination of Et<sub>3</sub>SiH

In a 50-mL flask was placed a mixture of Et<sub>3</sub>SiH (**20**, 71.5 mmol) and MeI (130 mmol). PdCl<sub>2</sub> (0.33 mmol) was added, and the mixture was stirred at room temperature for 1.5 h. The resulting mixture was distilled to give Et<sub>3</sub>SiI (**20i**, 85% yield), b.p. 76–77 °C/20 mmHg.

#### 4.5. Ring-opening iododisilylation of THF with hydrosilane reagent

A mixture of Et<sub>3</sub>SiH (**20**, 33.4 mmol), THF (32.7 mmol), MeI (47.5 mmol), and PdCl<sub>2</sub> (0.4 mmol) was stirred at room temperature for 5 h. The resulting mixture was distilled to give 1-iodo-4-triethylsiloxybutane (70% yield), b.p. 97–100 °C/2 mmHg.

#### 4.6. Ring-opening iododisilylation of THF with aminosilane reagent

A mixture of Me<sub>3</sub>SiNEt<sub>2</sub> (53.7 mmol), THF (54.0 mmol), MeI (143 mmol), and toluene (20 mL) was stirred at 80–90 °C for 5 h. Ammonium salts were filtered off, and the resulting mixture was distilled to give 1-iodo-4-trimethylsiloxybutane (81% yield), b.p. 53–54 °C/1 mmHg.

#### 4.7. Reaction of Hex<sub>2</sub>SiClF with PhC≡CLi

To a solution of *n*-Hex<sub>2</sub>SiClF (**19f**, 5.5 mmol) in ether (80 mL) was added phenylethynyllithium (5.5 mmol) at –50 °C, and the solution was stirred for 1 h, filtered, and concentrated. The residue was distilled to give *n*-Hex<sub>2</sub>(PhC≡C)SiF (**29f**, 86% yield), b.p. 71 °C/1 mmHg.

#### 4.8. Synthesis of alternating polymer

To a solution of *n*-Hex<sub>2</sub>SiClF (**19f**, 1.6 mmol) in ether (60 mL) was added an ether solution of 9,10-di(lithioethynyl)anthracene (0.8 mmol) at –50 °C, and the solution was stirred at this temperature for 12 h. The resulting solution was added into an ether solution of 5,5'-dilithiobithiophene (0.8 mmol) at –80 °C. The mixture was allowed to warm to room temperature, stirred for 12 h, hydrolyzed with water, and extracted with ether. After usual workup followed by reprecipitation from methanol, poly[(silanylene)(diethynylantracene)(silanylene)(bithiophene)] was obtained in 72% yield, Mw = 7300 (Mw/Mn = 1.6).

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