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

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# Abstract

Selective synthesis of halosilanes has been examined. Various types of halosilanes and halohydrosilanes, such as  $R_3SiX$ ,  $R_2SiHX$ ,  $R_2SiX_2$ ,  $RSiH_2X$ ,  $RSiH_2X$ ,  $RSiH_2$  (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.

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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 chlorohydrosilane with chlorovinylsilane, followed by electroreductive coupling of the product [4]. There may be also needed in some cases the use of more

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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.

$$\begin{array}{cccc} & M^{\text{Me}} & M^{\text{Me}} & M^{\text{Me}} & M^{\text{Me}} & M^{\text{Me}} \\ & H+S+CI + H_2C=CH+S+CI & \longrightarrow & C+S+CH_2CH_2+S+CI & \longrightarrow & \left( \begin{array}{c} & M^{\text{Me}} M^{\text{Me}} \\ & S+S+CH_2CH_2 \\ & Ph & Ph & Ph \end{array} \right)_n \\ & & Ph & Ph & Ph \end{array}$$

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 CuCl<sub>2</sub> or CuBr<sub>2</sub>. 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 fluorohydrosi-

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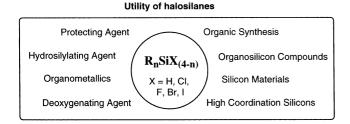
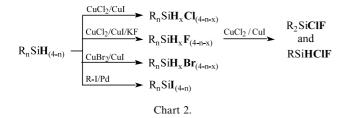


Chart 1.



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 iodosilanes 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 bromosilanes 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 CCl<sub>4</sub> in the presence of a catalytic amount of PdCl<sub>2</sub> affords chlorosilanes in high yields [9,10]. Radical-induced hydrogen-halogen exchange between hydrosilanes and CCl<sub>4</sub> 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 MePhSiH<sub>2</sub> with CuCl<sub>2</sub> in the electrolytic cell without a charge overnight afforded an appreciable amount of MePhSiCl<sub>2</sub>.

$$2R_2SiHCl + 2e^- \xrightarrow{Pt-Cu} R_2HSi-SiHR_2(+R_2SiCl_2)$$
(2)

We examined about the chlorination ability of CuCl<sub>2</sub> towards triorganosilanes in diethyl ether [15], but the reaction did not proceed with CuCl<sub>2</sub> alone unless a catalyst like Pt surface is present. When a catalytic amount of CuI was added to CuCl<sub>2</sub>, however, the reaction in ether proceeded very smoothly to give chlorosilanes [16]. Thus, treatment of Me<sub>2</sub>PhSiH (1) with 2 equiv molar of CuCl<sub>2</sub> in the presence of a catalytic amount of CuI at room temperature for 13 h produced Me<sub>2</sub>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 CuCl<sub>2</sub> and a catalytic amount of CuI is hereafter named as the 'CuCl2-CuI' reagent. Treatment of other triorganohydrosilanes like MePh<sub>2</sub>SiH (2) and Bu<sub>2</sub>MeSiH (3) with 2 equiv of the CuCl<sub>2</sub>-CuI reagent also afforded the respective chlorosilanes 2a and 3a in high yields. In a case of bulky hydrosilane, t-BuMe<sub>2</sub>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-BuMe<sub>2</sub>SiCl (4a) after 60 h of the reaction.

$$R_{2}R'Si-H \xrightarrow[1-4]{2CuCl_{2}, CuI} R_{2}R'Si-Cl$$
(3)  
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  $CuCl_2$  is necessary for replacing one Si–H by Si–Cl suggests that a certain reactive species such as CuICl or CuI<sub>2</sub> 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  $R_2SiHCl$ ,  $RSiH_2Cl$ , and  $RSiHCl_2$ , from the corresponding hydrosilanes. For example, the reaction of  $Et_2SiH_2$  (5) with 2 equiv of  $CuCl_2-CuI$  in diethyl ether at room temperature for 43 h yielded  $Et_2SiHCl$ 

(5a) in 68% yield as the sole product, while similar reaction of MePhSiH<sub>2</sub> (6) for 36 h afforded MePhSiHCl (6a) in 77% yield (Eq. (4)). In both cases, the monochloro derivatives were formed selectively. Neither the dichlorosilanes nor other products were observed.

$$\begin{array}{c} \mathbf{RR'SiH}_2 \xrightarrow[ether]{2CuCl_2, CuI} \mathbf{RR'SiHCl} \\ \mathbf{5, 6} \end{array} \tag{4}$$

**5a**, R = R' = Et, 68% **6a**, R = Me, R' = Ph, 77%

Selective chlorination of trihydrosilane is also possible. Thus, treatment of PhSiH<sub>3</sub> (7) with 2 equiv of CuCl<sub>2</sub>-CuI in ether at room temperature for 72 h afforded PhSiH<sub>2</sub>Cl (7a) in 70% yield (Eq. (5)), in addition to a trace amount (< 2%) of PhSiHCl<sub>2</sub> (7b). Similar treatment of 7 with 4 equiv of CuCl<sub>2</sub>-CuI for 94 h gave only 7b in 66% yield (Eq. (6)).

$$\frac{\text{PhSiH}_{3}}{7} \xrightarrow[\text{ether}]{\text{ether}} \text{PhSiH}_{2}\text{Cl} \quad 7a, 70\%$$
(5)

$$\stackrel{\text{4CuCl}_2, \text{ CuI}}{\stackrel{\text{ether}}{\longrightarrow}} \text{PhSiHCl}_2 \quad 7b, \quad 66\% \tag{6}$$

1,2-Dihydrodisilanes also react with 2 equiv of CuCl<sub>2</sub>-CuI under the same conditions to give monochlorinated disilanes as the main product (Eq. (7)). Thus, treatment of HMePhSiSiPhMeH (8) with 2 equiv of the reagent afforded ClMePhSiSiPhMeH (8a) in 59% yield, together with a 4% yield of dichlorodisilane 8b, while the reaction of HEt<sub>2</sub>SiSiEt<sub>2</sub>H (9) produced ClEt<sub>2</sub>SiSiEt<sub>2</sub>H (9a, 57%), along with 1,2-dichlorodisilane (9b) (16%) and 9 (11%). Although the selectivity decreased a little for dihydrodisilanes, the desired products 8a and 9a could be readily isolated from byproducts by fractional distillation. On the other hand, treatment of 8 and 9 with 4 equiv of CuCl<sub>2</sub>-CuI gave 8b (79%) and 9b (90%), respectively, as the sole product (Eq. (8)).

$$\operatorname{HRR'Si-SiRR'H}_{\mathbf{8},\mathbf{9}} \xrightarrow{\operatorname{2CuCl_2, CuI}}_{\operatorname{ether}} \operatorname{CIRR'Si-SiRR'H}$$
(7)

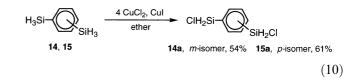
8a, R = Me, R' = Ph, 59% 9a, R = R' = Et, 57%

$$\stackrel{\text{4CuCl}_2, \text{ CuI}}{\xrightarrow{\text{ether}}} \text{CIRR'Si-SiRR'Cl}$$
(8)

**8b**, R = Me, R' = Ph, 79% **9b**, R = R' = Et, 90%

The other examples are demonstrated for the chlorination of dihydro- and trihydrosilanes 10-13 bearing a fluoroalkyl group (Eq. (9)) [17]. All these reactions proceeded selectively with 2 equiv of CuCl<sub>2</sub>-CuI, and the corresponding monochlorinated silanes 10a-13awere obtained as the sole volatile products. Moreover, the reactions of *m*- and *p*-bissilylbenzenes (14, 15) with 4 equiv of the reagent produced bis(chlorosilyl)benzenes, in which each silyl group was monochlorinated (Eq. (10)).

$$R_{f}CH_{2}CH_{2}SiRH_{2} \xrightarrow[ether]{ether} R_{f}CH_{2}CH_{2}SiRHCl \qquad (9)$$
10a,  $R_{f} = CF_{3}$ ,  $R = Me$ , 57%  
11a,  $R_{f} = C_{4}F_{9}$ ,  $R = Me$ , 49%  
12a,  $R_{f} = C_{8}F_{17}$ ,  $R = Me$ , 61%  
13a,  $R_{f} = C_{8}F_{17}$ ,  $R = H$ , 65%



# 2.1.2. Chlorination of hydrogermanes

Halogermanes are useful reagents in the synthesis of a variety of organogermanium compounds [18]. Of these, halohydrogermanes are of high importance, as exemplified by dehydrohalogenative coupling of chlorohydrogermanes forming a Ge–Ge bond [19]. A few methods for the synthesis of halohydrogermanes, including redistribution reactions of organohydrogermanes with tetrachlorogermane [20] and selective monohalogenation of dihydrogermanes with HgCl<sub>2</sub>, ClCH<sub>2</sub>OCH<sub>3</sub> in the presence of AlCl<sub>3</sub> as the catalyst, or *N*-bromosuccinimide, have been published to date [21]. However, these monohalogenation reactions involve the use of toxic or costly reagents. Although partial hydrogenation of dihalogermanes has been also reported, it may be applied to only some special cases [22].

As the extension of selective chlorination of hydrosilanes with the CuCl<sub>2</sub>-CuI reagent, we found that this reagent system works also well in the case of hydrogermanes [23]. Thus, when Et<sub>2</sub>GeH<sub>2</sub> was treated with 2 equiv of CuCl<sub>2</sub>-CuI in ether at room temperature for 1 h, Et<sub>2</sub>GeHCl was obtained in 73% yield (Eq. (11) and Table 1), while the reaction with 4 equiv of the reagent for 8 h gave Et<sub>2</sub>GeCl<sub>2</sub> in 85% yield (Eq. (12)). Hex<sub>2</sub>GeH<sub>2</sub> also reacted with 2 equiv of the reagent within 3 h to give Hex<sub>2</sub>GeHCl in 65% yield. In this case, however, a trace of Hex<sub>2</sub>Ge(OEt)Cl was formed. The ethoxy group would come from the solvent, ether. The reaction of Hex<sub>2</sub>GeH<sub>2</sub> in toluene was found to be much slow, but under reflux for 5 h, Hex2GeHCl was obtained in 91% yield as the sole product. Monochlorination of Hex2-GeH<sub>2</sub>, Ph<sub>2</sub>GeH<sub>2</sub>, and PhGeH<sub>3</sub> took place in the absence of CuI, although a longer reaction time was required to complete the chlorination. This is in marked contrast to the chlorination of hydrosilanes, which occurs only in the presence of the CuI catalyst. These hydrogermanes were also converted to dichlorogermanes in high yields by heating with 4 equiv of CuCl<sub>2</sub> in the presence of CuI in toluene under reflux for several days (Eq. (12)).

 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> GeIICl (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.

$$\mathbf{R}_{4-n}\mathbf{G}\mathbf{e}\mathbf{H}_n \xrightarrow[\text{ether or toulene}]{2\operatorname{CuCl}_2, \operatorname{CuI}} \mathbf{R}_{4-n}\mathbf{G}\mathbf{e}\mathbf{H}_{n-1}\mathbf{C}\mathbf{l}$$
(11)

$$\stackrel{4\mathrm{CuCl_2, Cul}}{\underset{\text{ether or toulene}}{\overset{\mathrm{den}}{\longrightarrow}}} \mathbf{R}_{4-n} \mathbf{GeH}_{n-2} \mathbf{Cl}_2$$
(12)

The present reaction is oxidative in nature and  $CuCl_2$  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 phenyl-germanes 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>, NaBF<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  $CuCl_2-CuI$  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  $CuCl_2-CuI-KF$  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.

$$R_{2}R'SiH \xrightarrow{2CuCl_{2}-CuI, KF}_{THF} R_{2}R'SiF$$
(13)  
1c, R = Me, R' = Ph, 82%  
2c, R = Ph, R' = Me, 78%

For these reactions, the use of 2 equiv of  $CuCl_2$  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  $CuCl_2$  in THF, the reaction did not proceed, which suggests that the starting hydrosilane is first converted to a chlorosilane with the  $CuCl_2$ –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].

$$\underset{\mathbf{2}}{\text{MePh}_{2}\text{SiH}} \xrightarrow{\text{2CuCl}_{2}-\text{CuI}} \underset{\mathbf{THF}}{\text{MePh}_{2}\text{SiCl}} \xrightarrow{\text{KF}} \underset{\mathbf{2a}}{\text{MePh}_{2}\text{SiF}} (14)$$

We applied these reactions to the synthesis of fluorodiorganosilanes ( $R_2SiHF$ ) from the corresponding diorganosilanes ( $R_2SiH_2$ ). 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  $R_2SiHF$  from  $R_2SiF_2$  as well as  $R_2SiH_2$  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  $Ph_2SiH_2$  (17) for 1 h afforded  $Ph_2SiHF$  (17c) in 81% isolated yield, while the reaction of MeMesSiH<sub>2</sub> (18) for 24 h produced MeMesSiHF (18c) in 75% isolated yield. Rather slow reaction rate of MeMesSiH<sub>2</sub> may be caused by steric hindrance due to the mesityl substituent. In all cases, the mono-fluoro derivatives were obtained as the sole product. Neither difluorosilanes nor other products were detected in the distillates.

$$RR'SiH_{2} \xrightarrow{2CuCl_{2}-CuI, KF} RR'SiHF$$
(15)  
**16c**, R = R' = Hex, 81%  
**17c**, R = R' = Ph, 81%  
**18c**, R = Me, R' = Mes, 75%

Similar treatment of MePhSiH<sub>2</sub> (6) with 2 equiv of the CuCl<sub>2</sub>-CuI-KF reagent in THF at room temperature for 1 h produced MePhSiHF (6c) in 72% yield after distillation, together with an 8% yield of MePhSiF<sub>2</sub>, while the reaction with 4 equiv of the reagent for 48 h gave MePhSiF<sub>2</sub> 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 CuF<sub>2</sub> as the fluoride salt in THF formed mainly MePhSiF<sub>2</sub> [41], together with a disiloxane which was presumably resulted by water in the highly hygroscopic CuF<sub>2</sub> salt.

$$\underset{\mathbf{6}}{\text{MePhSiH}_2} \xrightarrow{2\text{CuCl}_2 - \text{CuI}, \text{ CsF}} \text{MePhSiH} \quad \mathbf{6c}, 68\%$$
(16)

The present method is not restricted to the dihydrosilanes, but can be applied to the partial fluorination of trihydrosilanes, RSiH<sub>3</sub> (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 RSiH<sub>2</sub>F and a small amount of RSiHF<sub>2</sub>. Thus, treatment of PhSiH<sub>3</sub> (7) for 77 h and *n*-HexSiH<sub>3</sub> (19) for 42 h with 2 equiv of the CuCl<sub>2</sub>-CuI reagent in this manner afforded PhSiH<sub>2</sub>F (7c) and *n*-HexSiH<sub>2</sub>F (19c) in 64 and 58% yield, respectively, as the sole volatile product, while PhSiHF<sub>2</sub> (7d) and *n*-HexSiHF<sub>2</sub> (19d) could be obtained when 4 equiv of the reagent was used (Eq. (18)). PhSiF<sub>3</sub> (7e) was obtained also by the reaction with 6 equiv of the reagent for 1 week (Eq. (19)).

$$\underset{7, 19}{\text{RSiH}_{3}} \xrightarrow{\text{2CuCl_2-CuI, KF}} \text{RSiH}_{2}\text{F}$$
(17)

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

$$\frac{4\text{CuCl}_2 - \text{CuI}, 2\text{KF}}{\text{ether}} \text{RSiHF}_2$$
(18)

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

$$\stackrel{6CuCl_2-CuI, 3KF}{\longrightarrow} RSiF_3$$
(19)

7e, R = Ph, 53%

We extended the present method to the synthesis of mixed halosilanes. When MePhSiHF (**6c**) prepared from MePhSiH<sub>2</sub> in the manner described above was treated with 2 equiv of the CuCl<sub>2</sub>–CuI reagent in THF at room temperature for 10 h, MePhSiClF (**6f**) was obtained in 74% yield after distillation of the resulting mixture (Eq. (20)). Similar treatment of Ph<sub>2</sub>SiHF (**17c**) with 2 equiv of the CuCl<sub>2</sub>–CuI reagent in THF at 40 °C for 24 h afforded Ph<sub>2</sub>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%).

$$\begin{array}{l} RR'SiHF \xrightarrow{2CuCl_2-CuI} RR'SiClF \\ \hline 6c, 17c \\ \end{array} R = Me, R' = Ph, 74\% (83\%) \\ 17f, R = R' = Ph, 67\% (70\%) \end{array}$$
(20)

Chlorofluorohydrosilanes can be also synthesized from trihydrosilanes. Thus, when  $PhSiH_2F$  (7c) prepared from  $PhSiH_3$  was treated with 2 equiv of the CuCl<sub>2</sub>-CuI reagent in ether at room temperature for 58 h, PhSiHClF (7f) was obtained in 61% yield, while similar treatment of *n*-HexSiH<sub>2</sub>F (19c) with 2 equiv of this reagent for 48 h afforded *n*-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.

$$\begin{array}{ccc} \text{RSiH}_2\text{F} & \xrightarrow{2\text{CuCl}_2 - \text{CuI}} & \text{RSiHClF} \\ \hline \textbf{7c}, & \textbf{19c} & & \\ \end{array} \tag{21}$$

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

Interestingly, PhSiCl<sub>2</sub>F and *n*-HexSiCl<sub>2</sub>F were not produced, even when 7c, 7f, 19c, and 19f were treated with the excess of the CuCl<sub>2</sub>–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 CuCl<sub>2</sub>–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)).

$$Et_{3}SiH \xrightarrow{2CuBr_{2}-CuI}_{ether} Et_{3}SiBr 20g, 82\%$$
(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.

 $\begin{array}{ll} RR'SiH_{2} & \xrightarrow{2CuBr_{2}-CuI} & R_{2}SiHBr \\ \textbf{6, 16, 17} & \text{ether } (\textbf{6, 16) or toluene } (\textbf{17}) \\ \textbf{6g, } R = Me, R' = Ph, 68\% \\ \textbf{16g, } R = R' = n\text{-Hex, } 73\% \\ \textbf{17g, } R = R' = Ph, 64\% \end{array}$  (23)

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  $CuBr_2-CuI$  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.

$$\begin{array}{ccc} \text{RSiH}_{3} & \xrightarrow{2\text{CuBr}_{2}-\text{CuI}} & \text{RSiH}_{2}\text{Br} \\ \text{7, 19} & \text{ether (19) or benzene (7)} \end{array}$$

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

$$\frac{4\text{CuBr}_2 - \text{CuI}}{\text{benzene}} \text{RSiHBr}_2$$
(25)

**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  $CuBr_2$ -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 1,2dihydrodisilanes. Thus, when  $HEt_2SiSiEt_2H$  (9) was treated with 2 equiv of the reagent in benzene at room temperature for 4 h,  $HEt_2SiSiEt_2Br$  (9g) was obtained in 58% isolated yield, together with a 10% yield of  $Et_2SiHBr$  (Eq. (26)).

$$\begin{array}{ccc} \text{HEt}_2\text{SiSiEt}_2\text{H} & \xrightarrow{2\text{CuBr}_2 - \text{CuI}} & \text{HEt}_2\text{SiSiEt}_2\text{Br} \\ \textbf{9} & \xrightarrow{\text{benzene}} & \text{HEt}_2\text{SiSiEt}_2\text{Br} \\ \textbf{9g}, & 58\% \end{array}$$
(26)

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  $I_2$  and HI [59], an Se-Si bond by  $I_2$  [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  $Et_3SiH$  (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.

 $\begin{array}{ll} R_{2}R'Si-H+CH_{3}-I & \xrightarrow[room temp.]{cat. PdCl_{2}} \\ R_{2}R'Si-I+CH_{3}-H & (27) \end{array}$   $\begin{array}{ll} Ii, \ R = Me, \ R' = Ph, \ 83\% \\ 2i, \ R = Ph, \ R' = Me, \ 91\% \end{array}$ 

**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  $Ph_3SiH$  (21) with MeI is somewhat different from the others. In this case, the product  $Ph_3SiI$  (21i) was produced as solids, and therefore the reaction was carried out in benzene under reflux. When  $PdCl_2$  was added to the solution, the reaction began smoothly, but the activity of  $PdCl_2$  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  $Et_2SiI_2$  (5i) from  $Et_2SiH_2$  (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 MePh- $SiI_2$  (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 produced 6i in 87% yield [64b].

$$Et_{2}SiH_{2} + 2RI \xrightarrow{\text{cat. PdCl}_{2}}_{60-70 \text{ °C}} Et_{2}SiI_{2} + Et_{2}RSiI + RH$$
(28)  

$$R = \text{Me:}5i, 37\% + 20i, 20\%$$
  

$$R = Et:5i, 31\% + 20i, 36\%$$
  

$$R = i \text{-Pr:}5i, 74\%$$
  

$$MePhSiH_{2} + 2i \text{-}C_{3}H_{7}I \xrightarrow{\text{cat. PdCl}_{2} \text{ or NiCl}_{2}}_{100 \text{ °C}}$$
  

$$6$$
  

$$MePhSiI_{2} + 2C_{3}H_{8}$$
(29)  

$$6i, 87\%$$

Trihydrosilanes such as PhSiH<sub>3</sub> (7) and *n*-HexSiH<sub>3</sub> (19) were also iodinated nicely with the use of *i*-PrI at 90 °C to give the corresponding triiodosilanes 7i and 19i in high yields (Eq. (30)).

$$\begin{array}{l} \text{RSiH}_{3} + 3i - \text{C}_{3}\text{H}_{7}\text{I} \quad \frac{\text{cat. PdCl}_{2}}{90 \text{ }^{\circ}\text{C}} \quad \text{RSiI}_{3} + 3\text{C}_{3}\text{H}_{8} \\ \textbf{7, 19} \\ \textbf{7i, R} = \text{Ph, 80\% 19i, R} = n - \text{Hex, 86\%} \end{array}$$
(30)

#### 2.4.2. Bromination of hydrosilanes

The H–Br exchange reactions of hydrosilanes with alkyl or allyl bromides in the presence of a catalytic amount of PdCl<sub>2</sub> or NiCl<sub>2</sub> also proceeded with the liberation of alkanes to give brominated products in good to high yields (Table 2) [64b]. The reactions proceeded more rapidly when allyl bromide, rather than ethyl and propyl bromide, was used as the halide. Typically, PdCl<sub>2</sub>-catalyzed bromination of Me<sub>2</sub>PhSiH (1) with EtBr or *n*-PrBr completed by refluxing the mixture without solvent for 12 h, while with allyl bromide, 1 was wholly consumed within 1 h to give

Table 2

Metal-catalyzed bromination of hydrosilanes

Silane	Bromide <sup>a</sup>	Catalyst <sup>b</sup> , conditions	Product (isolated yield)
Me <sub>2</sub> PhSiH (1)	EtBr <i>n</i> -PrBr allylBr allylBr	PdCl <sub>2</sub> , 50 °C, 12 h PdCl <sub>2</sub> , 80 °C, 12 h PdCl <sub>2</sub> , 80 °C, 12 h PdCl <sub>2</sub> , 80 °C, 1 h NiCl <sub>2</sub> , 80 °C, 16 h	<b>1g</b> (88%)
$MePh_2SiH$ (2)	EtBr allylBr allylBr	PdCl <sub>2</sub> , 50 °C, 36 h PdCl <sub>2</sub> , 80 °C, 1 h NiCl <sub>2</sub> , 80 °C, 24 h	<b>2g</b> (91%)
$Et_2SiH_2$ (5)	EtBr allylBr	PdCl <sub>2</sub> , 50 °C, 72 h NiCl <sub>2</sub> , 80 °C, 24 h	2 2 8 7
MePhSiH (6)	allylBr allylBr	PdCl <sub>2</sub> , 80 °C, 36 h NiCl <sub>2</sub> , 80 °C, 50 h	MePhSiBr <sub>2</sub> ( <b>6g</b> , 79%) <b>6g</b> (80%)
PhSiH <sub>3</sub> (21)	allylBr allylBr	PdCl <sub>2</sub> , 80 °C, 60 h NiCl <sub>2</sub> , 80 °C, 90 h	PhSiBr <sub>3</sub> ( <b>21g</b> 88%) <b>21g</b> (65%) <sup>c</sup>

<sup>a</sup> Bromide 1.4–4 equiv.

<sup>b</sup> PdCl<sub>2</sub> 1 mol% or NiCl<sub>2</sub> 2-6 mol%.

<sup>c</sup> NiCl<sub>2</sub> (11 mol%) was added in eight portions in every 10-12 h.

Me<sub>2</sub>PhSiBr (1g) in 88% yield. Similar NiCl<sub>2</sub>-catalyzed bromination of 1 with allyl bromide required a larger amount of the catalyst and a longer reaction period to complete the conversion, compared to the reaction with PdCl<sub>2</sub>. Lower activity of NiCl<sub>2</sub> relative to PdCl<sub>2</sub> is evident for tribromination of PhSiH<sub>3</sub> (21), in which the Ni catalyst was deactivated during the reaction progress and continuous addition of the catalyst was necessary to promote further the reaction. In contrast to this, PhSiBr<sub>3</sub> (21g) was obtained in 88% yield from 21 with only 1 mol% of the PdCl<sub>2</sub>-catalyst.

Although partially brominated products were found to be formed by GC–MS analyses of the reaction mixtures in low yields in the bromination of di- and trihydrosilanes, they were readily separated from the perbrominated products by fractional distillation.

# 2.4.3. Halogenation of hydrogermanes

It has been reported that heating hydrogermanes with alkyl halides at 80-90 °C for several hours leads to the formation of halogermanes in high yield [65]. In contrast to this, PdCl<sub>2</sub>-catalyzed halogenaton of hydrogermanes with allyl halides proceeded even at room temperature (Table 3) [64b]. In these reactions, allyl halide must be used as the halogen source. Indeed, no reactions occurred when Hex<sub>3</sub>GeH (22) was treated with EtBr at 50 °C in the presence of the PdCl<sub>2</sub> catalyst, while Hex<sub>3</sub>GeBr (22j) was obtained in 80% yield by the reaction with allyl bromide at room temperature. Similarly, the reactions of Et<sub>3</sub>GeH (23), Ph<sub>3</sub>GeH (24), Hex<sub>2</sub>GeH<sub>2</sub> (25), and Ph<sub>2</sub>GeH<sub>2</sub> (26) proceeded readily with allyl bromide to give high yields of bromogermanes 23j-26j, respectively. On the other hand, a longer reaction period was required to complete the tribromination of HexGeH<sub>3</sub> (27) and the product HexGeBr<sub>3</sub> (27j) was isolated in rather low yield (58%).

Table 3 PdCl<sub>2</sub>-catalyzed halogenation at room temperature <sup>a</sup>

Silane	Halide <sup>b</sup>	Time (h)	Product (isolated yield)
Et <sub>3</sub> GeH (23)	allylBr	3	Et <sub>3</sub> GeBr (23j, 84%)
Hex <sub>3</sub> GeH (22)	allylBr	3	Hex <sub>3</sub> GeBr (22j, 80%)
Ph <sub>3</sub> GeH (24)	allylBr	3	Ph <sub>3</sub> GeBr (24j, 72%)
Hex <sub>2</sub> GeH <sub>2</sub> (25)	allylBr	6	Hex <sub>2</sub> GeBr <sub>2</sub> (25j, 92%)
Ph <sub>2</sub> GeH <sub>2</sub> (26)	allylBr	4	Ph2GeBr2 (26j, 81%)
$HexGeH_3$ (27)	allylBr	53	HexGeBr <sub>3</sub> (27j, 58%)
Et <sub>3</sub> GeH (23)	allylI	6	Et <sub>3</sub> GeI (23k, 83%)
Hex <sub>3</sub> GeH (22)	allylI	12	Hex <sub>3</sub> GeI (22k, 84%)
Ph <sub>3</sub> GeH (24)	allylI	12	Ph <sub>3</sub> GeI (24k, 98%) <sup>c</sup>
$Hex_2GeH_2$ (25)	allylI	3	Hex <sub>2</sub> GeI <sub>2</sub> (25k, 80%)
Ph <sub>2</sub> GeH <sub>2</sub> (26)	allylI	5	Ph2GeI2 (26k, 75%)
$HexGeH_3$ (27)	allylI	12	HexGeI <sub>3</sub> (27k, 87%)

<sup>a</sup> PdCl<sub>2</sub> 1–3 mol%.

<sup>b</sup> Halide 1.5–4 equiv.

<sup>c</sup> Benzene was added after 6 h to dissolve the product Ph<sub>3</sub>GeI.

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  $PdCl_2$  at 60 °C for 70 h,  $Hex_3GeI$  (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 bromosilation products in good yields [25c]. Iodo- and bromosilanes, however, exhibit high tendency to undergo hydrolytic cleavage of the Sihalogen 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  $Me_3SiNEt_2$ -MeI reagent [68].

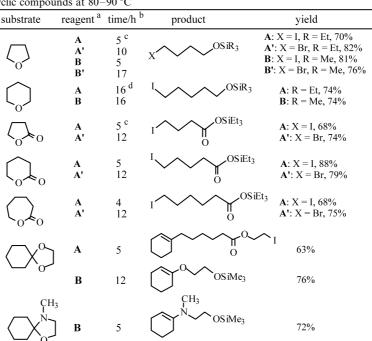
More recently, we found in cooperation with Yamamoto that treatment of 1:1 mixtures of hydrosilanes and alkyl iodides with a catalytic amount of PdCl<sub>2</sub> (R<sub>3</sub>SiH– R'I–PdCl<sub>2</sub>) produces high yields of iodosilanes by hydride/iodide exchange [64]. In order to explore further the 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  $\omega$ halo- $\alpha$ -siloxyalkanes (Eq. (31)). They may be potentially useful in organic synthesis as silyl-protected hydroxyalkyl [72] or carboxyalkyl halides.

$$\bigcap_{O} \xrightarrow{\text{reagent A or B}} X \xrightarrow{OSiR_3} (31)$$
A: Et<sub>3</sub>SiH/Mel/PdCl<sub>2</sub>, A': Et<sub>3</sub>SiH/Ally/Br/PdCl<sub>2</sub>
B: Me<sub>3</sub>SiNEt<sub>2</sub>/Mel, B': Me<sub>3</sub>SiNEt<sub>2</sub>/Ally/Br

Some representative results are picked up in Table 4, where four kinds of the reagent systems, Et<sub>3</sub>SiH-MeI- $PdCl_2$  (A),  $Et_3SiH$ -AllylBr- $PdCl_2$  (A'),  $Me_3SiNEt_2$ -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 ringopened products (not shown in the table).

The reactions of cyclohexanone ethylene acetal with 1 equiv of reagent B proceeded smoothly to afford a ringopened siloxyethyl enol ether as the sole volatile product in 76% yield, while N-methy-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  $\alpha$ 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 halosilyation of cyclic compounds at 80–90 °C



<sup>a</sup> **A**: Et<sub>3</sub>SiH/Mel/PdCl<sub>2</sub>, **A**': Et<sub>3</sub>SiH/AllylBr/PdCb, **B**: Me<sub>3</sub>SiNEt<sub>2</sub>/Mel, **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  $\varepsilon$ -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)).

$$Me_{3}SiNEt_{2} + MeI \rightleftharpoons Me_{3}Si(NEt_{2}Me)^{+}I^{-}$$
(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 diethylor dibutylamine at 60 °C for 5 h produced the corresponding O-silyl-protected amino acids in good yields.

$$Br (n_{1}) OSiEt_{3} \xrightarrow{2R_{2}NH} R_{2}N (n_{1}) OSiEt_{3}$$

$$n = 3 \ G 5 \qquad n = 3, R = Et, 78\% \qquad n = 3, R = Bu, 72\%$$

$$n = 4, R = Et, 71\% \qquad n = 4, R = Bu, 84\%$$

$$n = 5, R = Et, 73\% \qquad n = 5, R = Bu, 74\%$$
(33)

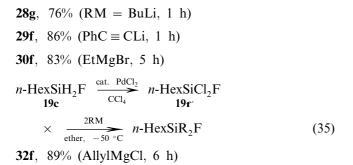
#### 2.5.2. Chlorofluorosilanes

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  $(R = Bu \text{ or } PhC \equiv C)$  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(fluorosilylethynyl)arenes selectively, which then reacted with another dilithio- $\pi$  reagent to give the desired alternating polymers in moderate to good yields.

*n*-HexSiClF 
$$\xrightarrow{\text{RM}}_{\text{ether, }-50 \circ \text{C}}$$
 *n*-Hex<sub>2</sub>SiRF (34)  
**28f**, 82% (BuLi, 1 h) **31f**, 89% (ViMgBr, 2.5 h)



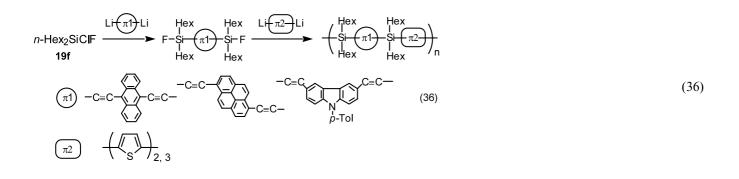
32g, 78% (RM = AllylMgCl, 6 h)

some examples for their application have been demonstrated using iodosilanes and chlorofluorosilanes. Further studies on utilization of halosilanes are under progress.

#### 4. Experimental conditions

### 4.1. General remarks

Representative procedures are shown below. All reactions were carried out under an inert atmosphere.



#### 3. Summary

We have discussed novel strategies for the synthesis of various halosilanes from hydrosilanes. With the use of Cu(II)-based reagents, selective chlorination, bromination, and fluorination of hydrosilanes could be achieved to give various types of halosilanes, such as R<sub>3</sub>SiX,  $R_2SiHX$ ,  $R_2SiX_2$ ,  $RSiH_2X$ ,  $RSiHX_2$  (X = Cl, Br, F), selectively in high yields. Mixed halosilanes like chlorofluorosilanes could be also obtained by applying this method. The present method is also applicable to selective chlorination of hydrogermanes. On the other hand, iodo- and bromosilanes and germanes could be obtained in good yields by Pd- or Ni-catalyzed hydridehalogen exchange reactions between hydrosilanes and alkyl or allyl halides. Halosilanes and halogermanes thus obtained may be utilized as useful starting materials or reagents in fields of organometallic chemistry and synthetic organic chemistry, for examples, as the building units for constructing silicon- or germane-containing functionality materials and high coordination silicon derivatives, and as the reagents for protecting labile functional groups, hydrosilylating unsaturated bonds, cleaving C-O bonds, introducing a silvl unit as the synthetic auxiliary, and so on. In this point of view,

Other reactions were also performed in similar manners. For the purpose of bromination and fluorination with copper reagents,  $CuBr_2$  or a 2:1 mixture of  $CuCl_2$  and KF were used, respectively, in place of  $CuCl_2$  used in chlorination.

#### 4.2. Chlorination of $MePhSiH_2$ with copper reagent

To a pre-dried mixture of CuCl<sub>2</sub> (252 mmol) and CuI (6 mmol) in a 500-mL flask were added MePhSiH<sub>2</sub> (6, 125 mmol) and dry ether (300 mL), and the mixture was stirred at room temperature for 36 h. The resulting mixture was filtered to remove copper salts, concentrated, and distilled to give MePhSiHCl (6a, 77% yield), boiling point (b.p.) 76-78 °C/21 mmHg.

# 4.3. Chlorination of MePhSiHF with copper reagent

A mixture of CuCl<sub>2</sub> (72 mmol), CuI (0.26 mmol), MePhSiHF (**6c**, 37 mmol), and 100 mL of THF in a 200mL flask was stirred at room temperature for 10 h. The mixture was filtered, concentrated, and distilled to give MePhSiClF (**6f**, 74% yield), b.p.  $75-77 \degree$ C/30 mmHg.

### 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 iodosilylation 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 iodosilylation 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 $Hex_2SiClF$ with $PhC \equiv CLi$

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 9,10di(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)(diethynylanthracene)(silanylene)(bithiophene)] was obtained in 72% yield, Mw = 7300 (Mw/Mn = 1.6).

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