Synthesis of Chlorosilanes from (Fluoroalkyl)silanes, Bis(silyl)benzenes, and α,ω-Dihydropolysiloxanes

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The reaction of (fluoroalkyl)silanes $CF_3CH_2CH_2SiMeH_2$, $C_4F_9CH_2CH_2SiMeH_2$ (**2a**), $C_8F_{17}CH_2CH_2SiMe_2H$, $C_8F_{17}CH_2CH_2SiMeH_2$ (**3a**), and $C_8F_{17}CH_2CH_2SiH_3$ with 2 equiv of $CuCl_2$ in the presence of a catalytic amount of CuI in ether gave the respective monochloro(fluoroalkyl)silanes selectively. The reaction of **2a** and **3a** with 4 equiv of $CuCl_2$ (CuI) yielded no dichloro derivatives, while treatment of these compounds with CCl_4 in the presence of a $PdCl_2$ catalyst gave the respective dichloro compounds. Similar reaction of 1,3- and 1,4-bis(silyl)benzene with 4 equiv of $CuCl_2$ (CuI) afforded 1,3- and 1,4-bis(chlorosilyl)benzene in high yields. The reaction of $HMe_2Si(OSiMe_2)_nOSiMe_2H$ ($n = 0, 2,$ and 3) (**8a–10a**) with 4 equiv of $CuCl_2$ (CuI) underwent redistribution to give a series of α,ω-dichloropolysiloxanes, $ClMe_2Si(OSiMe_2)_nOSiMe_2Cl$. Treatment of α,ω-dihydropolysiloxanes **8a–10a** with a catalytic amount of $PdCl_2$ in refluxing carbon tetrachloride produced the respective α,ω-dichloropolysiloxanes in high yields.

Introduction

Chlorosilanes are useful starting materials for the synthesis of organosilicon compounds including silicon containing polymers. For the synthesis of chlorosilanes, hydrosilanes are often used as the starting compounds. In fact, several methods are available for the synthesis of chlorosilanes from hydrosilanes.[2–8] For example, the reaction of hydrosilanes with carbon tetrachloride in the presence of a catalytic amount of palladium chloride affords chlorosilanes in high yields.[6,7] Radical induced hydrogen–chlorine exchange between hydrosilanes and carbon tetrachloride also produces chlorosilanes in good yields.[9,10] All methods including these two, however, cannot be applied for the selective synthesis of $RSiH_2Cl$ and $RSiHCl_2$ from $RSiH_3$, and R_2SiHCl from R_2SiH_2.

Recently, we have found that the reaction of $RSiH_3$ and R_2SiH_2 with 2 equiv of $CuCl_2$ in the presence of a catalytic amount of CuI in ether affords selectively $RSiH_2Cl$ and R_2SiHCl in high yields, while the reaction of $RSiH_3$ with 4 equiv of $CuCl_2$ (CuI) produces $RSiHCl_2$ in high yield.[11]

Cunico and Dexheimer have reported that the reaction of hydrosilanes and $CuCl_2$ in acetonitrile produces chlorosilanes in high yields.[8] In ether solution, however, treatment of hydrosilanes with $CuCl_2$ in the absence of a CuI catalyst gives no chlorosilanes, but the starting materials are recovered unchanged. In this paper we report the synthesis of chlorosilanes which can be used as the starting compounds for the useful industrial materials, using the $CuCl_2$–CuI method.

Results and Discussion

(Fluoroalkyl)silanes.[12] When a mixture of (fluoroalkyl)methylsilane $R_fCH_2CH_2Si(R)H_2$ (**1a**, $R_f = CF_3$, R = Me) and 2 equiv of $CuCl_2$ in the presence of a catalytic amount of CuI in diethyl ether was stirred at room temperature for 33 h, the reaction proceeded cleanly to give chloro(fluoroalkyl)methylsilane (**1b**). Distillation of the resulting mixture after filtration of inorganic solids under a dry nitrogen atmosphere gave **1b** in 57% isolated yield (Scheme 1).

Scheme 1

$$R_fCH_2CH_2Si(R)H_2 + 2CuCl_2 \xrightarrow{CuI}$$

1a, $R_f = CF_3$, R = Me
2a, $R_f = C_4F_9$, R = Me
3a, $R_f = C_8F_{17}$, R = Me
4a, $R_f = C_8F_{17}$, R = H

$$R_fCH_2CH_2Si(R)HCl$$

1b, $R_f = CF_3$, R = Me
2b, $R_f = C_4F_9$, R = Me
3b, $R_f = C_8F_{17}$, R = Me
4b, $R_f = C_8F_{17}$, R = H

Although compound **1a** was completely converted to **1b** after a 33-h reaction at room temperature, it was found that the longer reaction time was necessary for complete transformation of **2a–4a** into products **2b–4b**. Thus, when

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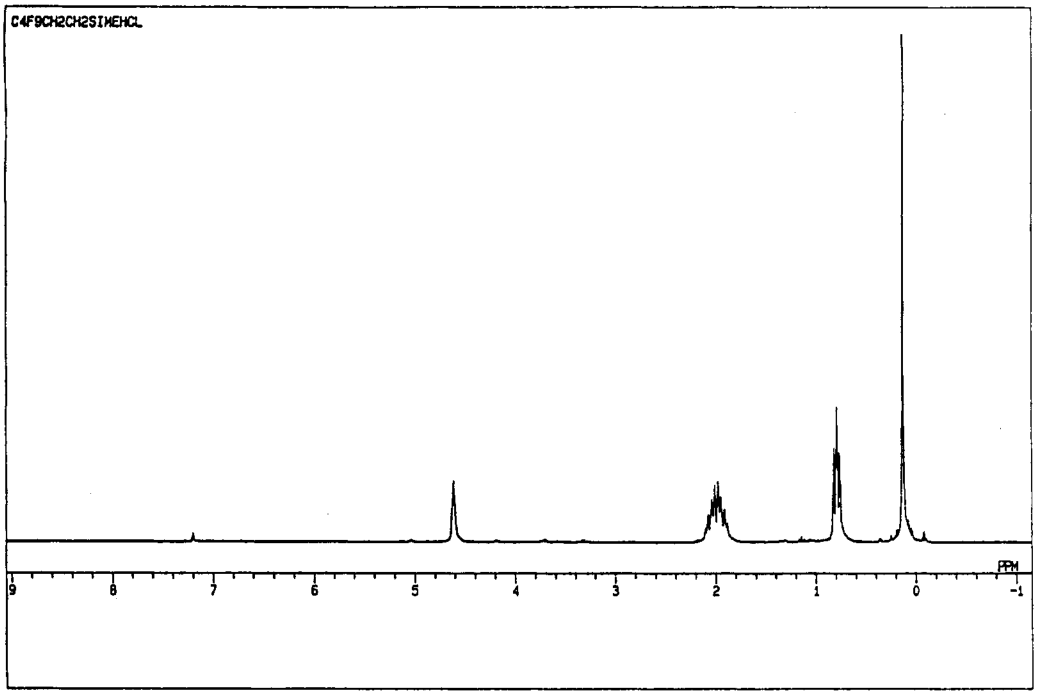

Figure 1. ^1H NMR spectrum of **2b** in C_6D_6.

2a ($R_f = C_4F_9$, R = Me) was treated with 2 equiv of $CuCl_2$ (CuI) under the same conditions for 11 h, only 29% of **2a** was consumed to give the chlorosilane **2b**. However, the reaction of **2a** with $CuCl_2$ (CuI) for 71 h led to approximately 100% conversion of **2a**, giving **2b** in 87% yield (GLC yield).[13] Fractional distillation of the mixture after filtration of the resulting inorganic salts afforded **2b** in 49% isolated yield. Similar treatment of **3a** ($R_f = C_8F_{17}$, R = Me) with $CuCl_2$ (CuI) for 69 h produced **3b** in 91% yield (GLC yield). Distillation of the mixture gave **3b** in 60% isolated yield. (Fluoroalkyl)silane **4a** ($R_f = C_8F_{17}$, R = H) also reacted with $CuCl_2$ (CuI) for 69 h to give **4b** in 65% isolated yield. In all reactions, no other products were detected in the reaction mixture by ^1H and ^{13}C NMR spectrometric analysis.

A change in reaction temperature brought about a considerable reduction in time. Thus, the reaction of **2a** with 2 equiv of $CuCl_2$ (CuI) at refluxing temperature for 9 h produced **2b** in 76% GLC yield, while **4a** for 10 h gave **4b** in 94% GLC yield.

Products **1b**–**4b** are very sensitive to moisture and are readily hydrolyzed in air to produce siloxanes. Consequently, when the reaction mixture is analyzed by GLC, small amounts of siloxanes are always detected. However, the products isolated by distillation involve no siloxanes, as indicated by ^1H and ^{13}C NMR spectrometric analysis. The ^1H NMR spectrum of **2b** obtained from distillation is shown in Figure 1, as a typical example.

Previously, we reported that the reaction of $PhSiH_3$ with 4 equiv of $CuCl_2$ (CuI) gave dichlorophenylsilane in high yield. A similar reaction of **4a** with 4 equiv of $CuCl_2$ (CuI), however, afforded no dichlorosilyl derivative. Again, monochloro compound **4b** was obtained as the sole product.

As expected, (fluoroalkyl)dimethylsilane could be readily converted to the corresponding chlorosilane. Thus, treatment of $C_8F_{17}CH_2CH_2SiMe_2H$ (**5a**) with 2 equiv of $CuCl_2$ (CuI) in ether at room temperature for 57 h gave $C_8F_{17}CH_2CH_2SiMe_2Cl$ (**5b**)[14] in 67% isolated yield. The $CuCl_2$ (CuI) method affords no dichlorosilyl derivatives from fluoroalkylsilanes described here. However, we found that the palladium-catalyzed Si–H/C–Cl exchange reaction can be used for the preparation of dichloro(fluoroalkyl)silanes.[15] Thus, treatment of **2a** with a catalytic amount of $PdCl_2$ in refluxing carbon tetrachloride for 67 h gave $C_4F_9CH_2CH_2SiMeCl_2$ (**2c**) in 61% yield, while a similar reaction of **3a** with carbon tetrachloride produced $C_8F_{17}CH_2CH_2SiMeCl_2$ (**3c**) in 84% yield.

Mass Spectrometric Analysis for Chloro(fluoroalkyl)silanes. The combustion elemental analysis for chloro(fluoroalkyl)silanes reported here is not in accord with their theoretical values. Carbon contents for all chloro(fluoroalkyl)silanes are always determined as the value higher than their calculated ones. Therefore, we carried out mass spectrometric analysis for these compounds. The mass spectrum for **1b** clearly shows its molecular ion, while all compounds having a $C_4F_9CH_2CH_2$ and $C_8F_{17}CH_2CH_2$ group reveal no molecular ions. Mass spectra for **2b**, **2c**, **3b**, **3c**, and **5b**, which have both a methyl group and chlorine on the silicon atom revealed the presence of the ions corresponding to $[M - CH_3]^+$ as the highest mass fragment. Compound **4b** that has no methyl group on the silicon atom, however, showed neither a molecular ion nor the ion corresponding to $[M - CH_3]^+$, but an ion at *m/z* 409 ($C_{10}F_{15}H_4^+$) was detected as the highest mass fragment.

Interestingly, mass spectra for **2b** and **2c** revealed an ion at *m/z* 209 ($C_6F_7H_4^+$), in addition to $[M - CH_3]^+$ ions, and the respective silyl cations, $Cl(Me)HSi^+$ for **2b** and $Cl_2(Me)Si^+$ for **2c**, as important fragments. Similarly, the ion at *m/z* 409 ($C_{10}F_{15}H_4^+$) and the respective silyl cations were observed in their fragments for **3b**, **3c**, and **5b**. The fragment ions at *m/z* 209 and 409 were also detected as the largest fragments, in the mass spectra for the starting compounds **2a**–**5a**. Again, neither molecular ions nor $[M - CH_3]^+$ ions were detected for **2a**–**5a**. Moreover, both of

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[13] In the GLC analysis of the reaction mixtures, siloxanes were always produced in 6–10% yields in handling the mixture; and therefore we calculated the yields of chlorosilanes using the sum of the peaks for siloxanes and chlorosilanes.

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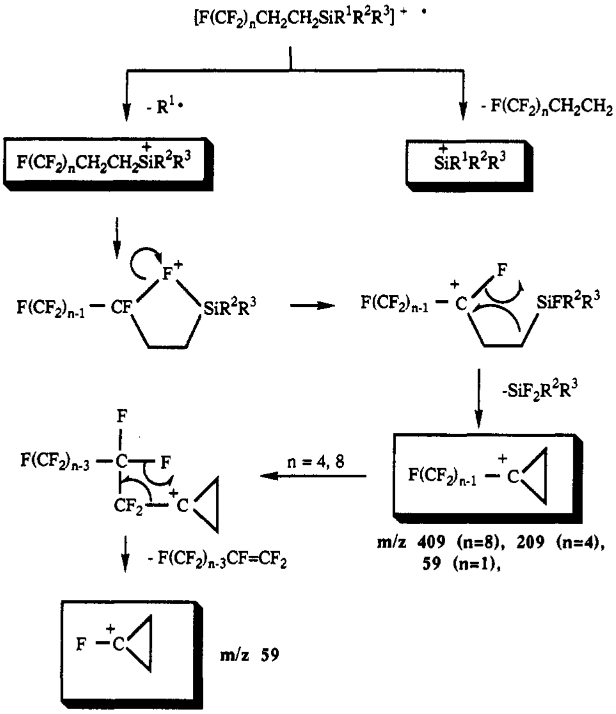
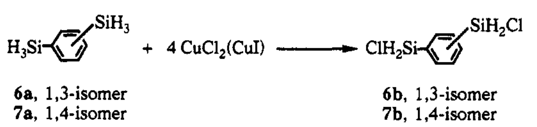
Scheme 2



Scheme 3



the starting compounds and products revealed the presence of a fragment ion at m/z 59 ($C_3H_4F^+$). The compositions of ions m/z 409, 209, and 59 were confirmed by high resolution mass spectrometry (see Experimental Section). We suggest the fragmentation pattern leading to important ions from the initially formed radical cation as shown in Scheme 2.

Bis(silyl)benzene. This method can also be used for selective synthesis of bis(chlorosilyl)benzenes from bis(silyl)benzenes. Thus, the reaction of 1,3-bis(silyl)benzene (**6a**)[16] with 4 equiv of $CuCl_2$ (CuI) in ether at room temperature afforded 1,3-bis(chlorosilyl)benzene (**6b**) in 54% isolated yield (Scheme 3).

A similar reaction of 1,4-bis(silyl)benzene (**7a**)[17] under the same conditions produced 1,4-bis(chlorosilyl)benzene (**7b**) in 61% yield. The reactions proceeded cleanly to give bis(chlorosilyl)benzenes **6b** and **7b**, and no other products were detected by GLC analysis. Products **6b** and **7b** are highly sensitive to moisture, but they can be readily isolated by distillation from the reaction mixture.

α,ω-Dihydropolysiloxanes. We attempted to prepare α,ω-dichloropolysiloxane oligomers from the corresponding α,ω-dihydropolysiloxanes. In all cases, not only the transformation of Si–H bonds to Si–Cl bonds but also redistribution reaction to give a series of α,ω-dichloropolysiloxane oligomers was observed. Thus, the reaction of 1,1,3,3-tetramethyldisiloxane (**8a**)[18] with 4 equiv of $CuCl_2$ (CuI) in ether at room temperature for 43 h afforded a mixture consisting of a series of $ClMe_2Si(OSiMe_2)_nOSiMe_2Cl$[19] with $n = 0$ (15% yield), $n = 1$ (23%), $n = 2$ (24%), $n = 3$ (10%), $n = 4$ (6%), and $n = 5$–11 (less than 5%). In early stages of the reaction, α-chloro-ω-hydropolysiloxanes were observed in the reaction mixture. After 43 h of reaction, however, all of α-chloro-ω-hydropolysiloxanes were transformed into α,ω-dichloropolysiloxanes. Lower homologs of $ClMe_2Si(OSiMe_2)_nOSiMe_2Cl$ with $n = 0$ and $n = 1$ were isolated by fractional distillation of the resulting mixture, and their structures were verified by spectrometric analysis. The structures of α,ω-dichloropolysiloxanes with $n = 2$ and 3 were confirmed by comparison of their GLC retention times with those of authentic samples, as well as by GC–mass spectrometric analysis. Higher homologs with $n = 4$–11 were identified by GC–mass spectrometric analysis of the mixture (Scheme 4).

Scheme 4

$$\begin{array}{l} HMe_2Si(OSiMe_2)_nOSiMe_2H \xrightarrow{4CuCl_2(CuI)} \\ \quad \mathbf{8a}, n = 0 \\ \quad \mathbf{9a}, n = 2 \\ \quad \mathbf{10a}, n = 3 \\ \qquad\qquad\qquad\qquad ClMe_2Si(OSiMe_2)_nOSiMe_2Cl \end{array}$$

The reaction of 1,7-dihydrooctamethyltetrasiloxane (**9a**)[20] with 4 equiv of $CuCl_2$ (CuI) in refluxing ether for 32 h resulted in the redistribution giving a homologous series of $ClMe_2Si(OSiMe_2)_nOSiMe_2Cl$ with $n = 0$ (5% yield), $n = 1$ (32%), $n = 2$ (23%), $n = 3$ (7%), $n = 4$ (5%), and $n = 5$–11 (less than 5%). Treatment of 1,9-dihydrodecamethylpentasiloxane (**10a**) with 4 equiv of $CuCl_2$ (CuI) in ether at room temperature for 125 h gave a result similar to that of **9a**. A series of α,ω-dichloropolysiloxanes $ClMe_2Si(OSiMe_2)_nOSiMe_2Cl$ with $n = 1$ (1% yield), $n = 2$ (5%), $n = 3$ (19%), $n = 4$ (12%), $n = 5$ (5%), and $n = 6$–12 (less than 3%), arising from the redistribution, and the hydrogen–chlorine exchange reaction was obtained. In this reaction, α,ω-dihydropolysiloxanes with $n = 1$ (2%), $n = 2$ (20%), $n = 3$ (starting compound, 18%), and $n = 4$ (3%) were also detected.

Interestingly, the reaction of **8a** with 4 equiv of $CuCl_2$ (CuI) in the presence of a 10-fold excess of hexamethyldisiloxane in refluxing ether for 20 h afforded a series of permethylated polysiloxanes, $Me_3Si(OSiMe_2)_nOSiMe_3$ with $n = 1$[19] (41% yield), $n = 2$[19] (24%), $n = 3$[19] (23%), $n = 4$[19] (6%), and $n = 5$–8[21] (less than 3%) (Scheme 5). In this reaction, chloropentamethyldisiloxane was detected by GC–mass spectrometric analysis, but no α,ω-dichloropolysiloxanes were detected in the reaction mixture. Careful analysis of the reaction mixture by GC–mass spectrometric analysis indicated that chlorotrimethylsilane was also produced. The same results were obtained when α,ω-dihydropolysiloxane **9a** was treated with 4 equiv of $CuCl_2$ (CuI) in the presence of a 10-fold excess of hexamethyldisiloxane in refluxing ether for 95 h. In this reaction, a series of $Me_3Si(OSiMe_2)_nOSiMe_3$ with $n = 1$ (45% yield), $n = 2$ (25%), $n = 3$ (21%), $n = 4$ (6%), and $n = 5$–7 (less than 1%) was formed.

The present redistribution reaction is observed only for compounds which have an Si–H bond. In fact, treatment of decamethyltetrasiloxane with 4 equiv of $CuCl_2$ (CuI) in refluxing ether for 40 h afforded no products derived from the redistribution reaction, but the starting permethylated polysiloxane was recovered unchanged. The reaction of 1,3-dichlorotetramethyldisiloxane with 4 equiv of $CuCl_2$

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(CuI) under the same conditions yielded no products, again the starting dichlorotetramethyldisiloxane was recovered quantitatively.

Scheme 5

$$\mathbf{8a}\text{ or }\mathbf{9a} + 10Me_3SiOSiMe_3 \xrightarrow{4CuCl_2\ (CuI)} Me_3Si(OSiMe_2)_nOSiMe_3 + Me_3SiCl$$

Interestingly, when a mixture of triethylsilane and a large excess of hexamethyldisiloxane was heated to reflux in the presence of 2 equiv of $CuCl_2$ (CuI) in ether for 60 h, 1,1,1-triethyltrimethyldisiloxane[22] was obtained in 71% yield, in addition to an 8% yield of chlorotriethylsilane.[23] Chlorotrimethylsilane was also detected in the resulting mixture by GC–mass spectrometric analysis. These results clearly indicate that the hydrogen–trimethylsiloxy exchange between triethylsilane and hexamethyldisiloxane occurs (Scheme 6). A detailed mechanism for redistribution of α,ω-dihydropolysiloxanes is still unknown, but presumably the reaction proceeds with exchange of hydrogen with a siloxy group, as observed in the reaction of triethylsilane and hexamethyldisiloxane.

By using the palladium dichloride-catalyzed Si–H/C–Cl exchange reaction, α,ω-dihydropolysiloxanes can be readily transformed into α,ω-dichloropolysiloxanes. When tetramethyldisiloxane **8a** was heated to reflux in carbon tetrachloride in the presence of a palladium dichloride catalyst, the reaction proceeded cleanly to produce 1,3-dichlorotetramethyldisiloxane (**8b**)[19] in 82% yield. No other products were observed in the reaction mixture. Similar treatment of **9a** and **10a** with carbon tetrachloride in the presence of the palladium catalyst afforded 1,7-dichlorooctamethyltetrasiloxane (**9b**)[19] and 1,9-dichlorodecamethylpentasiloxane (**10b**)[19] in 77% and 72% yields, respectively.

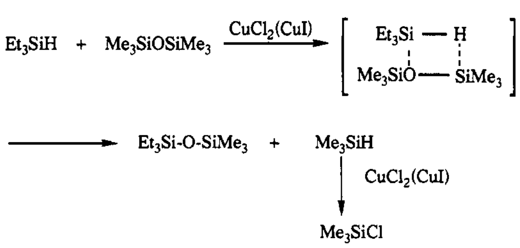
In conclusion, the reaction of fluoroalkyl-substituted silanes with $CuCl_2$ (CuI) gave selectively monochloro(fluoroalkyl)silanes. Similar reaction of 1,3- and 1,4-bis(silyl)benzene affords the respective bis(chlorosilyl)benzene as the sole product, while α,ω-dihydropolysiloxanes undergo redistribution and also the hydrogen–chlorine exchange reaction to give a homologous series of α,ω-dichloropolysiloxanes.

Experimental Section

General Procedure. Diethyl ether used as a solvent was dried over sodium benzophenone–ketyl and distilled just before use. Copper salts, $CuCl_2$ and CuI, used for all reactions were dried at 100 °C under reduced pressure for 8 h just before use. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on JEOL Model JNM-EX 270 and Bruker AM-X 400 spectrometers. IR spectra were measured on a Perkin-Elmer 1600-FT infrared spectrometer. Low-resolution mass spectra were measured on a Simadzu Model QP-1000 instrument. High-resolution mass spectra were measured on a Hitachi M-80B mass spectrometer.

All reactions of fluoroalkylsilanes with $CuCl_2$(CuI) were carried out at room temperature under an atmosphere of dry nitrogen, and the products were separated from the reaction mixture by distillation after filtration of the mixture to remove inorganic salts. The redistribution reaction of α,ω-dihydropolysiloxanes was monitored by GLC, and the yields of the products were determined by GLC using tridecane as an internal standard.

Scheme 6



Preparation of Chloro(3,3,3-trifluoropropyl)methylsilane (1b). A mixture of 10.1 g (71.0 mmol) of $CF_3CH_2CH_2SiMeH_2$, 19.1 g (142.1 mmol) of anhydrous $CuCl_2$, and 0.725 g (3.81 mmol) of anhydrous CuI in 250 mL of ether was stirred at room temperature for 33 h. The resulting mixture was filtered to remove copper salts. Fractional distillation of the filtrate afforded 7.1 g (57% yield) of $CF_3CH_2CH_2SiMeHCl$: bp 98–100 °C; ^1H NMR (δ, in $CDCl_3$) 0.54 (δ, 3H, MeSi, J = 3.1 Hz), 1.10–1.15 (m, 2H, $CF_3CH_2\mathit{CH_2}Si$), 2.16–2.21 (m, 2H, $CF_3\mathit{CH_2}CH_2Si$), 4.84 (br m, 1H, HSi); ^{13}C NMR (δ, in $CDCl_3$) –0.76 (MeSi), 9.15 ($CF_3CH_2\mathit{CH_2}Si$), 28.03 (q, $CF_3\mathit{CH_2}CH_2Si$, J_{CF} = 30.6 Hz), 127.21 (q, C_8F_{17}, J_{CF} = 276.3 Hz); MS m/z 176 ($M^{\bullet+}$), 161 ($[M - CH_3]^+$), 79 ($HClMeSi^+$), 59 ($C_3H_4F^+$); IR 2967, 2136 cm^{-1}; exact mass calcd for $C_4H_8ClF_3Si$ 176.0035, found 176.0018.

Preparation of Chloro(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsilane (2b). A mixture of 9.96 g (34.1 mmol) of $C_4F_9CH_2CH_2SiMeH_2$, 9.28 g (69.0 mmol) of $CuCl_2$, and 0.347 g (1.82 mmol) of CuI in 200 mL of ether was stirred at room temperature for 71 h. The resulting mixture was filtered to remove copper salts and distilled fractionally to give 5.50 g (49% yield) of $C_4F_9CH_2CH_2SiMeHCl$: bp 146–148 °C; ^1H NMR (δ, in $CDCl_3$) 0.56 (d, 3H, MeSi, J = 3.0 Hz), 1.11–1.19 (m, 2H, $C_4F_9CH_2\mathit{CH_2}Si$), 2.11–2.27 (m, 2H, $C_4F_9\mathit{CH_2}CH_2Si$), 4.82–4.90 (br m, 1H, HSi); ^{13}C NMR (δ, in $CDCl_3$) –0.73 (MeSi), 7.03 ($C_4F_9CH_2\mathit{CH_2}Si$), 25.15 (t, $C_4F_9\mathit{CH_2}CH_2Si$, J_{CF} = 23.8 Hz), 104.51–123.76 (m, C_4F_9); ^1H NMR (δ, in C_6D_6) 0.13 (d, 3H, MeSi, J = 3.3 Hz), 0.75–0.82 (m, 2H, $C_4F_9CH_2\mathit{CH_2}Si$), 1.91–2.04 (m, 2H, $C_4F_9\mathit{CH_2}CH_2Si$), 4.55–4.62 (br m, 1H, HSi); ^{13}C NMR (δ, in C_6D_6) –1.34 (MeSi), 7.05 ($C_4F_9CH_2\mathit{CH_2}Si$), 25.34 (t, $C_4F_9\mathit{CH_2}CH_2Si$, J_{CF} = 23.8 Hz), 105.5–125.0 (m, C_4F_9); MS m/z 311 ($[M - CH_3]^+$), 209 ($C_6H_4F_7^+$), 79 ($HClMeSi^+$), 59 ($C_3H_4F^+$); IR 2966, 2172 (Si–H), 1220, 885 cm^{-1}; exact mass calcd for $C_6H_5ClF_9Si$ ($[M - Me]^+$) 310.9704, found 310.9664.

Preparation of Chloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)methylsilane (3b). A mixture of 9.99 g (20.3 mmol) of $C_8F_{17}CH_2CH_2SiMeH_2$, 5.53 g (41.1 mmol) of $CuCl_2$, and 0.200 g (1.05 mmol) of CuI in 200 mL of ether was stirred at room temperature for 69 h. The resulting mixture was filtered, and the filtrate was concentrated. The residue was then distilled under reduced pressure to give 6.42 g (61% yield) of $C_8F_{17}CH_2CH_2SiMeHCl$: bp 104–107 °C (20 mmHg); ^1H NMR (δ, in $CDCl_3$) 0.56 (d, 3H, MeSi, J = 3.0 Hz), 1.11–1.20 (m, 2H, $C_8F_{17}CH_2\mathit{CH_2}Si$), 2.10–2.30 (m, 2H, $C_8F_{17}\mathit{CH_2}CH_2Si$), 4.80–4.90 (br m, 1H, HSi); ^{13}C NMR (δ, in $CDCl_3$) –0.73 (MeSi), 7.08 ($C_8F_{17}CH_2\mathit{CH_2}Si$), 25.26 (t, $C_8F_{17}\mathit{CH_2}CH_2Si$, J_{CF} = 23.8 Hz), 106.29–121.89 (m, C_8F_{17}); MS m/z 511 ($[M - CH_3]^+$), 409 ($C_{10}H_4F_{15}^+$), 79 ($HClMeSi^+$), 59 ($C_3H_4F^+$); IR 2967, 2172 (HSi), 1205, 887, 842 cm^{-1}; exact mass calcd for $C_{10}H_5ClF_{17}Si$ ($[M - Me]^+$) 510.9576, found 510.9669.

Preparation of Chloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane (4b). A mixture of 10.04 g (21.0 mmol) of $C_8F_{17}CH_2CH_2SiH_3$, 5.73 g (42.63 mmol) of $CuCl_2$, and 0.208 g (1.09 mmol) of CuI in 160 mL of ether was stirred at room temperature for 69 h. The resulting mixture was filtered, and the filtrate was distilled under reduced pressure to give 6.99 g (65% yield) of $C_8F_{17}CH_2CH_2SiH_2Cl$: bp 94–96 °C (21 mmHg); ^1H NMR (δ, in $CDCl_3$) 1.24–1.32 (m, 2H, $C_8F_{17}CH_2\mathit{CH_2}Si$), 2.12–2.35 (m, 2H, $C_8F_{17}\mathit{CH_2}CH_2Si$), 4.76–4.80 (br m, 2H, HSi); ^{13}C NMR (δ, in $CDCl_3$) 4.53 ($C_8F_{17}CH_2\mathit{CH_2}Si$), 25.41 (t, $C_8F_{17}\mathit{CH_2}CH_2Si$, J_{CF} = 23.2 Hz), 104.19–123.56 (m, C_8F_{17}); m/z 409 ($C_{10}H_4F_{15}^+$), 65 (H_2ClSi^+), 59 ($C_3H_4F^+$); IR 2949, 2166 (HSi), 1204, 869, 658 cm^{-1}; exact mass calcd for $C_{10}H_4F_{15}$ 409.0073, found 409.0084.

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Reaction of 2a with 2 equiv of $CuCl_2$ at Refluxing Temperature. A mixture of 0.950 g (3.25 mmol) of **2a**, 0.920 g (6.84 mmol) of $CuCl_2$, and 25 mg (0.13 mmol) of CuI in 15 mL of ether was heated to reflux, and the reaction was monitored by GLC. After 9 h of reaction, chlorosilane **2b** was formed in 76% GLC yield.

Reaction of 4a with 2 equiv of $CuCl_2$ at Refluxing Temperature. A mixture of 1.050 g (2.20 mmol) of **4a**, 0.679 g (5.05 mmol) of $CuCl_2$, and 20 mg (0.11 mmol) of CuI in 15 mL of ether was heated to reflux for 10 h. The mixture was analyzed by GLC as being chlorosilane **4b** 94% GLC yield.

Reaction of 4a with 4 equiv of $CuCl_2$ in the Presence of a Catalytic Amount of CuI. A mixture of 9.99 g (20.9 mmol) of **4a**, 11.40 g (84.8 mmol) of $CuCl_2$, and 0.209 g (1.10 mmol) of CuI in 300 mL of ether was stirred at room temperature for 189 h. The resulting mixture was filtered, and the filtrate was distilled under reduced pressure to give 4.71 g (32% yield) of $C_8F_{17}CH_2CH_2SiH_2Cl$: bp 87–90 °C (15 mmHg). All spectral data of the product were identical with those of an authentic sample.

Preparation of Chloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilane (5b). Into a 300-mL flask fitted with a condenser was placed a mixture of 8.85 g (17.5 mmol) of $C_8F_{17}CH_2CH_2SiMe_2H$, 4.97 g (37.0 mmol) of $CuCl_2$, and 64 mg (0.34 mmol) of CuI in 150 mL of ether. The mixture was stirred by a magnetic stirrer at room temperature for 57 h. The resulting mixture was filtered and the filtrate was fractionally distilled under reduced pressure to give 6.35 g (67% yield) of $C_8F_{17}CH_2CH_2SiMe_2Cl$: bp 103–104 °C (12 mmHg); ^1H NMR (δ, in $CDCl_3$) 0.47 (s, 6H, Me_2Si), 1.00–1.12 (m, 2H, $CH_2\mathit{CH_2}Si$), 2.05–2.27 (m, 2H, $\mathit{CH_2}CH_2Si$); ^{13}C NMR (δ, in $CDCl_3$) 1.26 (Me_2Si), 8.63 ($CH_2\mathit{CH_2}Si$), 25.23 (t, $\mathit{CH_2}CH_2Si$, J_{CF} = 23.8 Hz), 106.25–122.41 (m, C_8F_{17}); MS m/z 525 ($[M - CH_3]^+$), 409 ($C_{10}H_4F_{15}^+$), 93 (Me_2ClSi^+), 59 ($C_3H_4F^+$); IR 2969, 2908, 1205, 1070, 900, 851 cm^{-1}; exact mass calcd for $C_{11}H_7ClF_{17}Si$ ($[M - Me]^+$) 524.9733, found 524.9630; calcd for $C_{10}H_4F_{17}$ 409.0072, found 409.0058; calcd for C_3H_4F 59.0297, found 59.0314.

Preparation of Dichloro(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsilane (2c). A solution of 4.78 g (16.1 mmol) of $C_4F_9CH_2CH_2SiMeH_2$ and ca. 10 mg (0.056 mmol) of palladium dichloride in 50 mL of carbon tetrachloride was refluxed for 60 h. The solvent was evaporated, and the residue was distilled to give 3.54 g (61% yield) of $C_4F_9CH_2CH_2SiMeCl_2$: bp 163–164 °C; ^1H NMR (δ, in $CDCl_3$) 0.85 (s, 3H, MeSi), 1.32–1.38 (m, 2H, $C_4F_9CH_2\mathit{CH_2}Si$), 2.16–2.35 (m, 2H, $C_4F_9\mathit{CH_2}CH_2Si$); ^{13}C NMR (δ, in $CDCl_3$) 4.73 (MeSi), 11.57 ($C_4F_9CH_2\mathit{CH_2}Si$), 24.64 (t, $C_4F_9\mathit{CH_2}CH_2Si$, J_{CF} = 23.2 Hz), 107.99–121.72 (m, C_4F_9); MS m/z 345 ($[M - Me]^+$), 209 ($C_6H_4F_7^+$), 113 (Cl_2MeSi^+), 59 ($C_3H_4F^+$); IR 2910, 1221, 880 cm^{-1}; exact mass calcd for $C_6H_4Cl_2F_9Si$ ($[M - CH_3]^+$) 344.9314, found 344.9309.

Preparation of Dichloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)methylsilane (3c). A solution of 5.327 g (10.822 mmol) of $C_8F_{17}CH_2CH_2SiMeH_2$ and ca. 10 mg (0.056 mmol) of palladium dichloride in 50 mL of carbon tetrachloride was refluxed for 61 h. The solvent was evaporated, and the residue was distilled under reduced pressure to give 5.05 g (84% yield) of $C_8F_{17}CH_2CH_2SiMeCl_2$: bp 113–114 °C (16 mmHg); ^1H NMR (δ, in $CDCl_3$) 0.85 (s, 3H, MeSi), 1.32–1.38 (m, 2H, $C_8F_{17}CH_2\mathit{CH_2}Si$), 2.16–2.29 (m, 2H, $C_8F_{17}\mathit{CH_2}CH_2Si$); ^{13}C NMR (δ, in $CDCl_3$) 4.89 (MeSi), 11.70 ($C_8F_{17}CH_2\mathit{CH_2}Si$), 24.80 (t, $C_8F_{17}\mathit{CH_2}CH_2Si$, J_{CF} = 23.2 Hz) 105.55–120.45 (m, C_8F_{17}); MS m/z 545 ($[M - CH_3]^+$), 409 ($C_{10}H_4F_{15}^+$), 113 (Cl_2MeSi^+), 59 ($C_3H_4F^+$); IR 2954, 2912, 1204, 897, 741 cm^{-1}; exact mass calcd for $C_{11}H_7ClF_{17}Si$ ($[M - Cl]^+$) 524.9732, found 524.9604; calcd for C_3H_4F 59.0297, found 59.0319.

Preparation of 1,3-Bis(chlorosilyl)benzene (6b). Into a 300-mL flask fitted with a condenser was placed a mixture of 6.5 g (47 mmol) of 1,3-bis(silyl)benzene (**6a**), 25.3 g (190 mmol) of $CuCl_2$, and 0.455 g (2.4 mmol) of CuI in 105 mL of ether. The mixture was stirred with a magnetic stirrer at room temperature for 39 h. The resulting mixture was filtered, and the filtrate was distilled under reduced pressure to give 5.3 g (54% yield) of **6b**: bp 135–136 °C (62 mmHg); ^1H NMR (δ, in C_6D_6) 4.96 (s, 4H, H–Si), 6.92 (t, 1H, ring proton (C5), J = 7.26 Hz), 7.33 (dd, 2H, ring protons (C4, 6), J = 1.32, J = 7.26 Hz), 7.64 (br t, 1H, ring proton (C2); ^{13}C NMR (δ, in C_6D_6) 128.4, 130.7, 137.3, 140.0; MS m/z 206 ($M^{\bullet+}$); IR 3072, 2183, 1578, 1373, 936, 852 cm^{-1}; exact mass calcd for $C_6H_8Cl_2Si_2$ 205.9542, found 205.9527.

Preparation of 1,4-Bis(chlorosilyl)benzene (7b). Into a 200-mL flask fitted with a condenser was placed a mixture of 6.0 g (43 mmol) of 1,4-bis(silyl)benzene (**7a**), 23.6 g (180 mmol) of $CuCl_2$, and 0.403 g (2.1 mmol) of CuI in 90 mL of ether. The mixture was stirred at room temperature for 18 h. The resulting mixture was filtered and the filtrate was distilled under reduced pressure to give 5.4 g (61% yield) of **7b**: bp 140 °C (71 mmHg); ^1H NMR (δ, in C_6D_6) 4.97 (s, 4H, H–Si), 7.25 (s, 4H, ring protons); ^{13}C NMR (δ, in $CDCl_3$) 133.7, 134.1; MS m/z 206 ($M^{\bullet+}$); IR 3055, 2183, 1136, 935, 846 cm^{-1}. Anal. Calcd for $C_6H_8Cl_2Si_2$: C, 34.78; H, 3.89. Found: C, 34.58; H, 3.88.

Preparation of 1,3-Dichlorotetramethyldisiloxane (8b). A solution of 10.5 g (78.1 mmol) of **8a** and ca. 10 mg (0.056 mmol) of palladium dichloride in 100 mL of carbon tetrachloride was stirred at room temperature for 44 h. Fractional distillation of the reaction mixture afforded 12.957 g (82% yield) of **8b**:[19] bp 135–137 °C; ^1H NMR (δ, in $CDCl_3$) 0.49 (s, 12H, MeSi); ^{13}C NMR (δ, in $CDCl_3$) 3.92 (MeSi); MS m/z 187 ($[M - CH_3]^+$), 167 ($[M - Cl]^+$); IR 2969, 1403, 1262, 1078 (Si–O–Si) 808, 676 cm^{-1}.

Preparation of 1,7-Dichlorooctamethyltetrasiloxane (9b). A solution of 10.1 g (35.7 mmol) of **9a** and ca. 10 mg (0.056 mmol) of palladium dichloride in 50 mL of carbon tetrachloride was stirred at room temperature for 21 h. The solvent was evaporated, and the residue was distilled under reduced pressure to give 9.7 g (77% yield) of **9b**:[19] bp 112–114 °C (20 mmHg); ^1H NMR (δ, in $CDCl_3$) 0.14 (s, 12H, MeSi), 0.45 (s, 12H, MeSi); ^{13}C NMR (δ, in $CDCl_3$) 0.78, 4.05 (MeSi); MS m/z 335 ($[M - CH_3]^+$), 315 ($[M - Cl]^+$); IR 2965, 1411, 1263, 1044 (Si–O–Si) 804 cm^{-1}.

Preparation of 1,9-Dichlorodecamethylpentasiloxane (10b). A solution of 8.34 g (23.4 mmol) of **10a** and ca. 10 mg (0.056 mmol) of palladium dichloride in 100 mL of carbon tetrachloride was stirred at room temperature for 70 h. The solvent was evaporated, and the residue was distilled under reduced pressure to give 7.19 g (72% yield) of **10b**:[19] bp 70–72 °C (1 mmHg); ^1H NMR (δ, in $CDCl_3$) 0.09 (s, 6H, MeSi), 0.13 (s, 12H, MeSi), 0.44 (s, 12H, MeSi); ^{13}C NMR (δ, in $CDCl_3$) 0.83, 0.94, 4.03 (MeSi); MS m/z 409 ($[M - CH_3]^+$), 389 ($[M - Cl]^+$); IR 2964, 1412, 1261, 1033 (Si–O–Si), 793 cm^{-1}.

Reaction of 1,1,3,3-Tetramethyldisiloxane (8a) with 4 equiv of $CuCl_2$ (CuI). A mixture of 14.76 g (110 mmol) of **8a**, 61.51 g (457 mmol) of $CuCl_2$, and 1.096 g (5.75 mmol) of CuI in 300 mL of ether was stirred at room temperature. The redistribution reaction was monitored by GLC. After 124 h, the resulting mixture was filtered and the filtrate was fractionally distilled to give 2.64 g (12% yield) of 1,3-dichlorotetramethyldisiloxane (**8b**) and 4.78 g (16% yield) of 1,5-dichlorohexamethyltrisiloxane. For **8b**: bp 138–139 °C; All spectral data of **8b** were identical with those of an authentic sample. For 1,5-dichlorohexamethyltrisiloxane: bp 183–189 °C; ^1H NMR (δ, in $CDCl_3$) 0.16 (s, 6H, MeSi), 0.45 (s, 12H, MeSi); ^{13}C NMR (δ, in $CDCl_3$) 0.76, 4.01 (MeSi); MS m/z 261 ($[M - CH_3]^+$); IR 2963, 1411, 1261, 1090 (Si–O–Si), 801 cm^{-1}.

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Supplementary Material Available: Figures of ^1H NMR spectra of **1b**, **3b**, **4b**, **5b**, **2c**, **3c**, and **6c**, which were isolated by distillation (7 pages). Ordering information is given on any current masthead page.

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