Selective Synthesis of Fluoro-, Fluorohydro-, and Chlorofluorosilanes from Hydrosilanes with the Use of a $CuCl_2$(CuI)/KF Reagent

Atsutaka Kunai,* Tomohiro Sakurai, Eiji Toyoda, and Mitsuo Ishikawa*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739, Japan

Received October 5, 1995[⊗]

A selective synthesis of fluoro-, fluorohydro-, and chlorofluorosilanes from hydrosilanes has been examined. The reaction of Me_2PhSiH and $MePh_2SiH$ with a mixture consisting of 2 equiv of $CuCl_2$, 1 equiv of KF, and a catalytic amount of CuI in THF at room temperature afforded Me_2PhSiF and $MePh_2SiF$ in high yields, respectively. With slight modification of this reaction, *n*-Hex_2SiHF, Ph_2SiHF, MeMesSiHF, MePhSiHF, $PhSiH_2F$, and $PhSiHF_2$ could be readily prepared from the corresponding polyhydrosilanes selectively in high yields. Treatment of MePhSiHF and Ph_2SiHF with 2 equiv of $CuCl_2$ in the presence of a catalytic amount of CuI afforded the respective chlorofluorosilanes, MePhSiClF and Ph_2SiClF.

Introduction

Halosilanes are useful starting materials in synthetic organosilicon chemistry. Of these, fluorosilanes can be used for the synthesis of highly coordinated silicon compounds[1] and highly hindered organosilanes.[2] To date, several methods are available for the synthesis of fluorosilanes. The methods involve the reactions of siloxy compounds with NH_4F in H_2SO_4,[3] hydrofluoric acid,[4] and BF_3 etherate,[5] halogen exchange of chlorosilanes with SbF_3,[6] ZnF_2,[7] NH_4F,[8] CuF_2,[9] Na_2SiF_6,[10] $NaPF_6$, $NaSbF_6$, $NaBF_4$,[11] and Me_3SnF,[12] and fluorination of hydrosilanes with AgF,[13] PF_5,[14] Ph_3CBF_4,[15] SbF_3,[16] $NOBF_4$ or NO_2BF_4,[17] and CuF_2/CCl_4.[18] Although these methods give fluorosilanes in good yields, it is difficult to prepare the fluorosilanes bearing an Si−H bond from hydrosilanes. For the synthesis of the fluorohydrosilanes, Van Dyke and co-workers reported partial fluorination of polyhydrosilanes with PF_5[14] or Ph_3CBF_4.[15] Tang et al. reported monofluorination of dihydrosilanes with SbF_3.[16] However, a toxic[14,16] or costly[15] reagent must be used for these methods; moreover, these reactions are restricted to only the hydrosilanes bearing alkyl substituents.[14−16]

In an effort to find a more convenient and general way for the synthesis of fluorosilanes, we have found that a silyl hydrogen can readily be replaced by a fluorine atom upon treatment with a reagent composed of 2 equiv of $CuCl_2$, 1 equiv of KF, and a catalytic amount of CuI. Since the reaction proceeds with high selectivity under mild conditions, this method provides a convenient route for the synthesis of various types of fluoro-, fluorohydro-, and chlorofluorosilanes from the corresponding hydrosilanes.

Results and Discussion

Previously, we reported that various types of chloro- and chlorohydrosilanes such as R_2SiHCl, R_2SiCl_2, $RSiH_2Cl$, and $RSiHCl_2$ can be obtained selectively by the reaction of the corresponding organohydrosilanes with $CuCl_2$ and a catalytic amount of CuI ($CuCl_2$(CuI) reagent).[19] In this reaction, only one hydrogen on the silicon atom is replaced by a chlorine atom with the use of 2 equiv of this reagent.[19a] For example, the reaction of methylphenylsilane with 2 equiv of the $CuCl_2$(CuI)

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) For recent reviews, see: (a) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rapport, Z., Eds.; John Wiley: New York, 1989; Part 2, Chapter 20. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C.. *Chem. Rev.* **1993**, *93*, 1371. See also: (c) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 2422. (d) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099.

(2) (a) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (b) Nakadaira, Y.; Ohara, K.; Sakurai, H. *J. Organomet. Chem.* **1986**, *309*, 247. (c) Wiberg, N.; Neruda, B. *Chem. Ber.* **1966**, *99*, 740. (d) Weidenbruch, M.; Kramer, K. *J. Organomet. Chem.* **1985**, *291*, 159.

(3) (a) Flood, E. A. *J. Am. Chem. Soc.* **1933**, *55*, 1735. (b) Pray, B. O.; Sommer, L. H.; Goldberg, G. M.; Kerr, G. T.; DiGregio, P. A.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 433. (c) Kumada, M.; Yamaguchi, M.; Yamamoto, Y.; Nakajima, J.; Siina, K. *J. Org. Chem.* **1956**, *21*, 1264.

(4) (a) Marans, N. S.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1951**, *73*, 5127. (b) Eaborn, C. *J. Chem. Soc.* **1952**, 2846. (c) Bluestein, B. A. *J. Am. Chem. Soc.* **1948**, *70*, 3068. (d) Booth, H. S.; Freedman, M. L. *J. Am. Chem. Soc.* **1950**, *72*, 2847.

(5) (a) Sommer, L. H.; Ansul, G. R. *J. Am. Chem. Soc.* **1955**, *77*, 2482. (b) Knoth, W. H.; Lindsay, R. V. *J. Org. Chem.* **1958**, *23*, 1392. (c) Horner, L.; Mathias, J. *J. Organomet. Chem.* **1985**, *282*, 155.

(6) Booth, H. S.; Suttle, J. F. *J. Am. Chem. Soc.* **1946**, *68*, 2658.

(7) (a) Newkirk, A. E. *J. Am. Chem. Soc.* **1946**, *68*, 2736. (b) Hengge, E.; Schrank, F. *J. Organomet. Chem.* **1986**, *299*, 1.

(8) Wilkins, C. J. *J. Chem. Soc.* **1951**, 2726.

(9) Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M; Kumada M. *Organometallics* **1982**, *1*, 355.

(10) Damrauer, R.; Simon, R. A.; Kanner, B. *Organometallics* **1988**, *7*, 1161.

(11) Farooq, O.; Tiers, G. V. D. *J. Org. Chem.* **1994**, *59*, 2122.

(12) Roesky, H. W.; Herzog, A.; Keller, K. *Z. Naturforsch., B* **1994**, *49*, 981.

(13) Anderson, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 5083.

(14) Finch, M. A.; Marcus, L. H.; Smirnoff, C.; Van Dyke, C. H.; Viswanathan, N. *Syn. Inorg. Met.-Org. Chem.* **1971**, 103.

(15) Bulkowsky, J. E.; Stacy, R.; Van Dyke, C. H. *J. Organomet. Chem.* **1975**, *87*, 137.

(16) Hong, C. M.; Witt, S. D.; Tang, Y. N. *J. Fluorine Chem.* **1983**, *23*, 359.

(17) Prakash, G. K. S.; Wang, Q.; Li, X.; Olah, G. A. *New J. Chem.* **1990**, *14*, 791.

(18) Yoshida, J.; Tsujishima, H.; Nakano, K.; Teramoto, T.; Nishiwaki, K.; Isoe, S. *Organometallics* **1995**, *14*, 567.

(19) (a) Kunai, A.; Kawakami, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1992**, *11*, 2708. (b) Ishikawa, M.; Toyoda, E.; Ishii, M.; Kunai, A.; Yamamoto, Y.; Yamamoto, M. *Organometallics* **1994**, *13*, 808.

S0276-7333(95)00787-4 CCC: $12.00

Scheme 1

$$MePhSiH_2 \xrightarrow[Et_2O,\ room\ temp.]{2\ CuCl_2\ (CuI)} MePhSiHCl$$

$$PhSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{2\ CuCl_2\ (CuI)} PhSiH_2Cl$$

$$PhSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{4\ CuCl_2\ (CuI)} PhSiHCl_2$$

reagent in ether at room temperature for 6 h yielded chloromethylphenylsilane in 77% isolated yield. Chloro- and dichlorophenylsilane can also be synthesized selectively from phenylsilane in 70% and 66% yields, respectively (Scheme 1).[19a]

In our continuing study on halogenation of hydrosilanes, we found that the hydrosilyl group can be transformed directly into a fluorosilyl group with the use of the $CuCl_2$(CuI) reagent in the presence of KF (Table 1). Thus, when Me_2PhSiH was treated with a mixture of 2 equiv of the $CuCl_2$(CuI) reagent and 1 equiv of KF ($CuCl_2$(CuI)/KF reagent) in THF at room temperature for 5 h, Me_2PhSiF was obtained in 82% yield as the sole product after distillation of the resulting mixture (Scheme 2). No other products were detected by GLC and spectrometric analysis. Similar reaction of $MePh_2SiH$ with 2 equiv of the $CuCl_2$(CuI)/KF reagent in THF gave $MePh_2SiF$ selectively in 78% isolated yield.

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 at all. This fact clearly suggests that the starting hydrosilane is converted to a chlorosilane by the action of the $CuCl_2$(CuI) reagent at the first step, as in the synthesis of chlorosilanes.[19] Then, the resulting Cl atom is replaced by a fluoride ion to form fluorosilanes (Scheme 3). Such Cl/F exchange on a silyl group is well-known.[6−11]

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 (Scheme 4). For example, when di-*n*-hexylsilane was treated with 2 equiv of the $CuCl_2$(CuI)/KF reagent in THF at room temperature, the starting *n*-Hex_2SiH_2 disappeared completely within 1 h, and distillation of the resulting mixture afforded fluorodi-*n*-hexylsilane in 81% yield as the sole product. Similar treatment of diphenylsilane with this reagent for 1 h afforded fluorodiphenylsilane in 81% isolated yield, while the reaction of methylmesitylsilane for 24 h produced fluoromethylmesitylsilane in 75% isolated yield. Rather slow reaction rate of $MeMesSiH_2$ 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.

Similar treatment of methylphenylsilane with 2 equiv of the $CuCl_2$(CuI)/KF reagent in THF at room temperature for 1 h produced fluoromethylphenylsilane in 72% yield after distillation, together with an 8% yield of difluoromethylphenylsilane, while the reaction with 4 equiv of the reagent for 48 h gave difluoromethylphenylsilane as the sole volatile product in 61% isolated yield. In order to obtain only the monofluorosilane as the product, we carried out the reaction of $MePhSiH_2$ under milder conditions. Thus, when the reaction of $MePhSiH_2$ was carried out using 2 equiv of the reagent including CsF instead of KF in refluxing ether for 1 week, MePhSiHF was obtained as the sole product in 68% yield after distillation (Scheme 5). On the other hand, the use of CuF_2 as the fluoride salt in THF formed mainly $MePhSiF_2$, together with a disiloxane which was presumably resulted by water in the highly hygroscopic CuF_2 salt.

The present method is not restricted to the dihydrosilanes but can be applied to the partial fluorination of trihydrosilanes. For example, fluoro- and difluorophenylsilane can be synthesized from phenylsilane (Scheme 6). In these cases, separate addition of the $CuCl_2$(CuI) reagent and KF is suitable, since simultaneous addition of these salts produces a mixture of $PhSiH_2F$ and a small amount of $PhSiHF_2$. Thus, $PhSiH_3$ was first treated with 2 equiv of the $CuCl_2$(CuI) reagent in ether for 24 h to produce $PhSiH_2Cl$, and then 1 equiv of KF was added to the resulting mixture. After the mixture was stirred for 48 h, $PhSiH_2F$ was obtained in 64% yield as the sole product. When $PhSiH_3$ was treated with 4 equiv of the $CuCl_2$(CuI) reagent in ether for 72 h and then with 2 equiv of KF for 5 h, $PhSiHF_2$ was obtained in 70% yield after distillation. Moreover, treatment of $PhSiH_3$ with 6 equiv of the $CuCl_2$(CuI) reagent and 3 equiv of KF for 1 week gave $PhSiF_3$ in 53% yield.

Mono- and difluorinations of *n*-hexylsilane also proceed selectively. Thus, when *n*-$HexSiH_3$ was treated with 2 equiv of the $CuCl_2$(CuI) reagent for 30 h and then with 1 equiv of KF for 12 h, *n*-$HexSiH_2F$ was obtained in 58% yield, while similar treatments of *n*-$HexSiH_3$ with 4 equiv of the $CuCl_2$(CuI) reagent for 48 h and then with 2 equiv of KF for 14 h produced *n*-$HexSiHF_2$ in 54% yield (Scheme 7).

We extended the present method to the synthesis of mixed halosilanes. When MePhSiHF prepared from $MePhSiH_2$ in the manner described above was treated with 2 equiv of the $CuCl_2$(CuI) reagent in THF at room temperature for 10 h, MePhSiClF was obtained in 74% yield after distillation of the resulting mixture (Scheme 8). Similar treatment of Ph_2SiHF with 2 equiv of the $CuCl_2$(CuI) reagent in THF at 40 °C for 24 h afforded Ph_2SiClF in 67% isolated yield. In both cases, no other products were detected in the reaction mixture. The same reactions in ether proceeded much slower but afforded MePhSiClF and Ph_2SiClF selectively in 83% and 70% yields, respectively.

Chlorofluorohydrosilanes can be also synthesized from trihydrosilanes. Thus, when $PhSiH_2F$ prepared from $PhSiH_3$ was treated with 2 equiv of the $CuCl_2$(CuI) reagent in ether at room temperature for 58 h, PhSiHClF was obtained in 61% yield, while similar treatment of *n*-$HexSiH_2F$ with 2 equiv of this reagent for 48 h afforded *n*-HexSiHClF in 59% yield (Scheme 9).

Interestingly, $PhSiCl_2F$ and *n*-$HexSiCl_2F$ were not produced, even when $PhSiH_2F$, PhSiHClF, *n*-$HexSiH_2F$, and *n*-HexSiHClF were treated with the excess of the

Table 1. Reaction of Hydrosilanes with a $CuCl_2$(CuI)/KF Reagent

hydrosilane (mmol)	$CuCl_2$[a] (mmol)	fluoride (mmol)	solvent (mL)	temp	time (h)	product (isolated yield/%)
Me_2PhSiH (44)	89	KF (48)	THF (100)	r.t.	5	Me_2PhSiF (82)
$MePh_2SiH$ (31)	69	KF (35)	THF (100)	r.t.	5	$MePh_2SiF$ (78)
n-Hex_2SiH_2 (26)	50	KF (26)	THF (100)	r.t.	1	*n*-Hex_2SiHF (81)
Ph_2SiH_2 (26)	56	KF (29)	THF (100)	r.t.	1	Ph_2SiHF (81)
$MeMesSiH_2$ (24)	49	KF (25)	THF (100)	r.t.	24	MeMesSiHF (75)
$MePhSiH_2$ (41)	82	KF (43)	THF (100)	r.t.	1	MePhSiHF (72) $MePhSiF_2$ (8)
$MePhSiH_2$ (41)	165	KF (83)	THF (150)	r.t.	48	$MePhSiF_2$ (61)
$MePhSiH_2$ (17)	34	CsF[b] (105)	Et_2O (100)	reflux	1 week	MePhSiHF (68)
$PhSiH_3$ (99)	199	KF[c] (101)	Et_2O (200)	r.t.	72	$PhSiH_2F$ (64)
$PhSiH_3$ (93)	373	KF[d] (188)	Et_2O (250)	r.t.	77	$PhSiHF_2$ (70)
$PhSiH_3$ (47)	277	KF (140)	THF (150)	r.t.	1 week	$PhSiF_3$ (53)
n-$HexSiH_3$ (137)	276	KF[e] (137)	Et_2O (150)	r.t.	42	*n*-$HexSiH_2F$ (58)
n-$HexSiH_3$ (93)	370	KF[f] (187)	Et_2O (200)	r.t.	62	*n*-$HexSiHF_2$ (54)
MePhSiHF (37)	72	none	THF (100)	r.t.	10	MePhSiClF (74)
Ph_2SiHF (19)	40	none	THF (100)	40 °C	24	Ph_2SiClF (67)
MePhSiHF (28)	65	none	Et_2O (100)	r.t.	44	MePhSiClF (83)
Ph_2SiHF (20)	40	none	Et_2O (100)	reflux	1 week	Ph_2SiClF (70)
$PhSiH_2F$ (80)	163	none	Et_2O (100)	r.t.	58	PhSiHClF (61)
n-$HexSiH_2F$ (53)	105	none	Et_2O (150)	r.t.	48	*n*-HexSiHClF (59)

[a] CuI (1−3%) was included as the catalyst. [b] CsF was added portionwise. [c] KF was added after stirring for 24 h. [d] KF was added after stirring for 72 h. [e] KF was added after stirring for 30 h. [f] KF was added after stirring for 48 h.

Scheme 2

$Me_2PhSiH \xrightarrow[THF,\ room\ temp.]{2\ CuCl_2\ (CuI)\ /\ KF} Me_2PhSiF$

$MePh_2SiH \xrightarrow[THF,\ room\ temp.]{2\ CuCl_2\ (CuI)\ /\ KF} MePh_2SiF$

Scheme 3

$MePh_2SiH \xrightarrow{2\ CuCl_2\ (CuI)} MePh_2SiCl \xrightarrow{KF} MePh_2SiF$

Scheme 4

$RR'SiH_2 \xrightarrow[THF,\ room\ temp.]{2\ CuCl_2\ (CuI)\ /\ KF} RR'SiHF$

R=R'=*n*-Hex, R=R'=Ph, R=Me, R'=Mes → R=R'=*n*-Hex, R=R'=Ph, R=Me, R'=Mes

Scheme 5

$MePhSiH_2 \xrightarrow[Et_2O,\ reflux]{2\ CuCl_2\ (CuI)\ /\ CsF} MePhSiHF$

Scheme 6

$PhSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{2\ CuCl_2\ (CuI)\ /\ KF} PhSiH_2F$

$PhSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{4\ CuCl_2\ (CuI)\ /\ 2\ KF} PhSiHF_2$

$PhSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{6\ CuCl_2\ (CuI)\ /\ 3\ KF} PhSiF_3$

Scheme 7

n-$HexSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{2\ CuCl_2\ (CuI)\ /\ KF}$ *n*-$HexSiH_2F$

n-$HexSiH_3 \xrightarrow[Et_2O,\ room\ temp.]{4\ CuCl_2\ (CuI)\ /\ 2\ KF}$ *n*-$HexSiHF_2$

$CuCl_2$(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 makes an increase in oxidation potential of these halosilanes, leading to the decrease in reactivity and the increase in selectivity. Similarly, the reaction of $PhSiHF_2$ and *n*-$HexSiHF_2$ with the $CuCl_2$(CuI) reagent under similar conditions did not afford the corresponding chlorosilanes, and the starting materials were recovered unchanged.

Scheme 8

$MePhSiHF \xrightarrow[THF,\ room\ temp.]{2\ CuCl_2\ (CuI)} MePhSiClF$

$Ph_2SiHF \xrightarrow[THF,\ 40\ °C]{2\ CuCl_2\ (CuI)} Ph_2SiClF$

Scheme 9

$RSiH_2F \xrightarrow[Et_2O,\ room\ temp.]{2\ CuCl_2\ (CuI)} RSiHClF$

R=Ph, R=*n*-Hex → R=Ph, R=*n*-Hex

Experimental Section

General Procedures. Diethyl ether and tetrahydrofuran used as a solvent were dried over sodium benzophenone ketyl and distilled just before use. KF was "spray dried" grade and was dried in vacuo at 100 °C before use. Di-*n*-hexylsilane, *n*-hexylsilane, and methylmesitylsilane were synthesized. Other hydrosilanes were purchased or prepared by methods cited in previous work.[19] All fluorination reactions of hydrosilanes were carried out under an atmosphere of dry nitrogen. Products were separated from the reaction mixture by filtration followed by distillation of the filtrate through a short distillation column. The results of the fluorination reactions are summarized in Table 1. Representative experimental procedures are described below.

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. ^1H, ^{13}C, and ^{29}Si NMR spectra were determined with JEOL Model EX-270 and Bruker AMX-400 spectrometers using deuteriochloroform as the solvent. Mass spectra were measured on Simadzu Model QP-1000 and Hitachi M80-B instruments. Analytical and spectroscopic data for the fluorination products are summarized in Table 2.

Preparation of Di-*n*-hexylsilane. (a) Di-*n*-hexyldiphenylsilane. To a solution of 185 g (0.731 mol) of dichlorodiphenylsilane in 200 mL of ether was added dropwise *n*-hexylmagnesium bromide prepared from the reaction of 248 g (1.50 mol) of bromohexane and 36.0 g (1.48 mol) of magnesium in 200 mL of ether. The mixture was stirred at room temperature

(20) Ishikawa, N.; Kuroda, K. *Nippon Kagaku Zasshi* **1968**, *89*, 1261; *Chem. Abstr.* **1969**, *70*, 96852y.
(21) Kuroda, K.; Ishikawa, N. *Nippon Kagaku Zasshi* **1969**, *90*, 322; *Chem. Abstr.* **1969**, *70*, 115213j.
(22) (a) Schott, V. G.; Schneider, P.; Kelling, H. *Z. Anorg. Allg. Chem.* **1973**, *398*, 293. (b) Kelling, H.; Schneider, P.; Schott, V. G. *Z. Anorg. Allg. Chem.* **1973**, *398*, 301.
(23) Tamao, K.; Hayashi, T.; Ito, Y. *Organometallics* **1992**, *11*, 182.
(24) Ishikawa, N.; Kuroda, K. *Kogyo Kagaku Zasshi* **1969**, *72*, 2602; *Chem. Abstr.* **1970**, *72*, 100813x.

Table 2. Analytical and Spectroscopic Data for the Products

Me_2PhSiF:[20] bp 59−60 °C/30 mmHg; MS *m*/*z* 154 (M^+), 139 ($M^+ - Me$); ^1H NMR (δ in $CDCl_3$) 0.49 (δ, $J_{H-F} = 7.3$ Hz, 6H, SiMe), 7.40−7.46 (m, 3H, phenyl H) 7.58−7.62 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) −1.18 (d, $J_{C-F} = 15.8$ Hz, SiMe), 128.00, 130.30, 132.99 (phenyl HC), 136.12 (d, $J_{C-F} = 17.1$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) 27.53 (d, $J_{Si-F} = 277.6$ Hz); ^{19}F NMR (δ in $CDCl_3$) −161.7 (sept, $J_{H-F} = 7.3$ Hz); exact mass calcd for $C_8H_{11}FSi$ (M^+) 154.0613, found 154.0648

$MePh_2SiF$:[21] bp 97−98 °C/4 mmHg (lit.[21] bp 92−93 °C/2 mmHg); MS *m*/*z* 216 (M^+), 201 ($M^+ - Me$) 139 ($M^+ - Ph$); ^1H NMR (δ in $CDCl_3$) 0.76 (d, $J_{H-F} = 7.3$ Hz, 3H, SiMe), 7.38−7.47 (m, 6H, phenyl H), 7.60−7.64 (m, 4H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) −2.44 (d, $J_{C-F} = 14.7$ Hz, SiMe), 128.03, 130.55 (phenyl *m*,*p*-C), 133.93 (d, $J_{C-F} = 2.5$ Hz, phenyl *o*-C), 134.27 (d, $J_{C-F} = 17.1$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) 15.05 (d, $J_{Si-F} = 279.9$ Hz)

n-Hex_2SiHF: bp 135−137 °C/40 mmHg; MS *m*/*z* 236 (M^+), 217 ($M^+ - F$); ^1H NMR (δ in $CDCl_3$) 0.70−0.80 (m, 4H, $SiCH_2$), 0.87 (t, 6H, CH_3, $J = 6.1$ Hz) 1.03−1.51 (m, 16H, CH_2), 4.69 (dp, 1H, SiH, $J_{H-F} = 52.6$ Hz, $J_{H-H} = 2.0$ Hz); ^{13}C NMR (δ in $CDCl_3$) 14.05, 22.46, 22.55, 31.53, 32.60 ($SiCH_2C_5H_{11}$), 14.12 (d, $J_{C-F} = 12.4$ Hz, $SiCH_2C_5H_{11}$); ^{29}Si NMR (δ in $CDCl_3$) 21.38 (d, $J_{Si-F} = 288.9$ Hz) ^{19}F NMR (δ in $CDCl_3$) −179.6 (dp, $J_{H-F} = 52.6$ Hz, $J_{H-F} = 7.1$ Hz); exact mass calcd for $C_{12}H_{27}FSi$ (M^+) 218.1865, found 218.1907

Ph_2SiHF:[5c,7b,10,22a] bp 96−98 °C/1 mmHg (lit.[5c] bp 76 °C/0.7 mmHg, lit.[22a] bp 108 °C/2 mmHg); MS *m*/*z* 202 (M^+), 183 ($M^+ - F$); ^1H NMR (δ in $CDCl_3$) 5.63 (d, $J_{H-F} = 54.4$ Hz, 1H, SiH), 7.42−7.54 (m, 3H, phenyl H) 7.60−7.69 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 128.23, 131.20, 134.39 (phenyl HC), 131.99 (d, $J_{C-F} = 15.9$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) −3.04 (d, $J_{Si-F} = 286.9$ Hz)

MeMesSiHF: bp 97−99 °C/20 mmHg; MS *m*/*z* 182 (M^+), 167 ($M^+ - Me$), 63 ($M^+ - Mes$); ^1H NMR (δ in $CDCl_3$) 0.57 (dd, $J_{H-F} = 7.9$ Hz, $J_{H-H} = 3.0$ Hz, 3H, SiMe), 2.43 (s, 3H, mesityl *p*-Me), 2.43 (d, $J_{H-H} = 1.7$ Hz, 6H, mesityl *o*-Me), 5.51 (dq, $J_{H-F} = 53.8$ Hz, $J_{H-H} = 3.0$ Hz, 1H, SiH), 6.84 (s, 2H, mesityl ring H); ^{13}C NMR (δ in $CDCl_3$) −0.66 (d, $J_{C-F} = 14.6$ Hz, SiMe), 21.15 (mesityl *p*-Me), 22.46 (mesityl *o*-Me), 128.73, 140.70, 144.21 (mesityl ring C), 127.84 (d, $J_{C-F} = 13.5$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) 5.34 (d, $J_{Si-F} = 283.2$ Hz); ^{19}F NMR (δ in $CDCl_3$) −170.1 (dq, $J_{H-F} = 53.8$ Hz, $J_{H-F} = 7.9$ Hz); exact mass calcd for $C_{10}H_{15}FSi$ (M^+) 182.0925, found 182.0922

MePhSiHF:[22] bp 55−56 °C/30 mmHg (lit.[22a] bp 74 °C); MS *m*/*z* 140 (M^+), 125 ($M^+ - Me$); ^1H NMR (δ in $CDCl_3$) 0.59 (dd, $J_{H-F} = 7.9$ Hz, $J_{H-H} = 2.6$ Hz, SiMe), 5.22 (dq, $J_{H-F} = 54.4$ Hz, $J_{H-H} = 2.6$ Hz, 1H, SiH), 7.38−7.47 (m, 3H, phenyl H), 7.60−7.64 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) −2.41 (d, $J_{C-F} = 14.6$ Hz, SiMe), 128.16, 130.91, 133.55 (phenyl HC), 133.85 (d, $J_{C-F} = 15.9$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) 15.37 (d, $J_{Si-F} = 282.7$ Hz)

$MePhSiF_2$:[4a,11,23] bp 73−74 °C/73 mmHg (lit.[4a] bp 141 °C, lit.[11] bp 138−142 °C); MS *m*/*z* 158 (M^+), 143 ($M^+ - Me$); ^1H NMR (δ in $CDCl_3$) 0.60 (t, $J_{H-F} = 6.3$ Hz, SiMe), 7.41−7.50 (m, 3H, phenyl H), 7.53−7.66 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) −5.03 (t, $J_{C-F} = 19.5$ Hz, SiMe), 128.14, 131.81, 133.42 (phenyl HC), 129.88 (d, $J_{C-F} = 19.5$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) −11.88 (t, $J_{Si-F} = 290.7$ Hz)

$PhSiH_2F$: bp 112−113 °C; MS *m*/*z* 126 (M^+); ^1H NMR (δ in $CDCl_3$) 5.23 (d, $J_{H-F} = 51.2$ Hz, 2H, SiH), 7.44−7.65 (m, 3H, phenyl H) 7.68−7.89 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 128.3, 131.45 (phenyl *m*,*p*-C), 134.42 (d, $J_{C-F} = 1.7$ Hz, phenyl *o*-C), 130.96 (d, $J_{C-F} = 14.4$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) −6.67 (d, $J_{Si-F} = 286.4$ Hz); ^{19}F NMR (δ in $CDCl_3$) −187.8 (t, $J_{H-F} = 51.2$ Hz); exact mass calcd for C_6H_7FSi (M^+) 126.0300, found 126.0311

$PhSiHF_2$:[22a] bp 106−107 °C (lit.[22a] bp 117 °C); MS *m*/*z* 144 (M^+); ^1H NMR (δ in $CDCl_3$) 5.19 (t, $J_{H-F} = 69.3$ Hz, 1H, SiH), 7.44−7.58 (m, 3H, phenyl H) 7.60−7.70 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 128.96, 132.60 (phenyl *m*,*p*-C), 133.42 (t, $J_{C-F} = 1.8$ Hz, phenyl *o*-C), 128.23 (t, $J_{C-F} = 15.9$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) −22.58 (t, $J_{Si-F} = 297.6$ Hz)

$PhSiF_3$:[10] bp 99−100 °C (lit.[10] bp 96−99 °C); MS *m*/*z* 162 (M^+), 143 ($M^+ - F$); ^1H NMR (δ in $CDCl_3$) 7.45−7.52 (m, 2H, phenyl H), 7.60−7.66 (m, 1H, phenyl H), 7.72−7.75 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 120.51 (q, ipso C, $J_{C-F} = 22.9$ Hz), 128.75, 133.56, 134.71 (phenyl HC); ^{29}Si NMR (δ in $CDCl_3$) −86.0 (q, $J_{Si-F} = 270.3$ Hz); ^{19}F NMR (δ in $CDCl_3$) −140.8

n-$HexSiH_2F$: bp 112−113 °C; MS *m*/*z* 134 (M^+), 133 ($M^+ - H$), 132 ($M^+ - 2H$), 115 ($M^+ - F$); ^1H NMR (δ in $CDCl_3$) 0.83−0.94 (m, 5H, $SiCH_2$ and CH_3), 1.31−1.53 (m, 8H, $-CH_2-$), 4.76 (dt, 2H, SiH, $J_{H-F} = 49.1$ Hz, $J_{H-H} = 2.4$ Hz); ^{13}C NMR (δ in $CDCl_3$) 13.32 (d, $SiCH_2$, $J_{C-F} = 11.8$ Hz), 14.01, 22.45, 22.52, 31.50, 32.24 (CH_3 and CH_2); ^{29}Si NMR (δ in $CDCl_3$) 2.39 (d, $J_{Si-F} = 282.6$ Hz); ^{19}F NMR (δ in $CDCl_3$) −193.4 (tt, $J_{H-F} = 49.1$ Hz, $J_{H-F} = 7.6$ Hz); exact mass calcd for $C_6H_{15}FSi$ (M^+) 134.0926, found 134.0930

n-$HexSiHF_2$: bp 106−107 °C; MS *m*/*z* 152 (M^+), 151 ($M^+ - H$), 133 ($M^+ - F$); ^1H NMR (δ in $CDCl_3$) 0.83−0.90 (m, 5H, $SiCH_2$ and CH_3), 1.25−1.54 (m, 8H, $-CH_2-$), 4.78 (t, 1H, SiH, $J_{H-F} = 67.0$ Hz); ^{13}C NMR (δ in $CDCl_3$) 13.27(t, $SiCH_2$, $J_{C-F} = 12.0$ Hz), 13.97, 20.36, 22.42, 31.35, 32.20 (CH_3 and CH_2); ^{29}Si NMR (δ in $CDCl_3$) −12.54 (t, $J_{Si-F} = 304.2$ Hz); ^{19}F NMR (δ in $CDCl_3$) −141.2 (dt, $J_{H-F} = 67.0$ Hz, $J_{H-F} = 5.5$ Hz); exact mass calcd for $C_6H_{14}F_2Si$ (M^+) 152.0832, found 152.0836

$MePhSiClF$:[24] bp 75−77 °C/30 mmHg (lit.[24] bp 91 °C/54 mmHg); MS *m*/*z* 174 (M^+), 159 ($M^+ - Me$), 159 ($M^+ - F$), 139 ($M^+ - Cl$), 97 ($M^+ - Ph$); ^1H NMR (δ in $CDCl_3$) 0.83 (d, $J_{H-F} = 6.3$ Hz, 3H, SiMe), 7.42−7.55 (m, 3H, phenyl H) 7.62−7.69 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 0.64 (d, $J_{C-F} = 15.8$ Hz, SiMe), 128.34, 131.77, 133.19 (phenyl HC), 133.55 (d, $J_{C-F} = 12.2$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) 8.21 (d, $J_{Si-F} = 312.5$ Hz)

Ph_2SiClF:[24] bp 107−108 °C/1 mmHg (lit.[24] bp 101−102 °C/3 mmHg); MS *m*/*z* 236 (M^+), 201 ($M^+ - Cl$), 159 ($M^+ - Ph$); ^1H NMR (δ in $CDCl_3$) 7.38−7.57 (m, 3H, phenyl H) 7.64−7.74 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 128.34, 131.95, 134.21 (phenyl HC), 130.27 (d, $J_{C-F} = 18.3$ Hz, ipso C); ^{29}Si NMR (δ in $CDCl_3$) −7.11 (d, $J_{Si-F} = 313.7$ Hz)

PhSiHClF: bp 144−146 °C; MS *m*/*z* 160 (M^+), 159 ($M^+ - H$), 125 ($M^+ - Cl$), 83 ($M^+ - Ph$); ^1H NMR (δ in $CDCl_3$) 5.70 (d, 1H, SiH, $J_{H-F} = 63.8$ Hz), 7.43−7.60 (m, 3H, phenyl H), 7.68−7.73 (m, 2H, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 128.5, 132.5, 133.4 (phenyl HC), 129.9 (d, ipso C, $J_{C-F} = 15.3$ Hz); ^{29}Si NMR (δ in $CDCl_3$) −10.28 (d, $J_{Si-F} = 314.7$ Hz); ^{19}F NMR (δ in $CDCl_3$) −143.0 (d, $J_{H-F} = 64.0$ Hz); exact mass calcd for C_6H_6ClFSi (M^+) 159.9911, found: 159.9924

n-HexSiHClF: bp 141−142 °C; MS *m*/*z* 168 (M^+), 133 ($M^+ - Cl$); ^1H NMR (δ in $CDCl_3$) 0.88 (t, 3H, CH_3, $J = 6.8$ Hz), 1.02−1.18 (m, 2H, $SiCH_2$), 1.24−1.54 (m, 10H, $-CH_2-$), 5.27 (dt, 1H, SiH, $J_{H-F} = 61.5$ Hz, $J_{H-H} = 1.1$ Hz); ^{13}C NMR (δ in $CDCl_3$) 13.99, 21.02, 22.42, 31.33, 31.93 (CH_3 and CH_2), 17.11 (d, $SiCH_2$, $J_{C-F} = 11.4$ Hz); ^{29}Si NMR (δ in $CDCl_3$) 3.27 (d, $J_{Si-F} = 259.7$ Hz); ^{19}F NMR (δ in $CDCl_3$) −144.8 (dt, $J_{H-F} = 61.5$ Hz, $J_{H-F} = 4.6$ Hz); exact mass calcd for $C_6H_{14}ClFSi$ (M^+) 168.0535, found 168.0479

for 24 h and then refluxed for 24 h. The resulting mixture was hydrolyzed and extracted with hexane. The extract was dried over magnesium sulfate and concentrated. The residue was distilled under reduced pressure to give 112 g (0.318 mol, 44% yield) of dihexyldiphenylsilane: bp 180−185 °C/1 mmHg; MS *m*/*z* 352 (M^+), 275 ($M^+ - Ph$), 267 ($M^+ - Hex$); ^1H NMR (δ in $CDCl_3$) 0.83−1.53 (m, 26H, Hex), 7.26−7.36 (m, 6H, phenyl *o*,*p*-H), 7.48−7.57 (m, 4H, phenyl *m*-H); ^{13}C NMR (δ in $CDCl_3$) 12.60, 14.07, 22.61, 23.70, 31.45, 33.43 (Hex), 134.81, 128.93, 127.67 (Ph), 136.61 (ipso); ^{29}Si NMR (δ in $CDCl_3$) −6.50.

(b) Dichlorodi-*n*-hexylsilane. Dihexyldiphenylsilane (112

g, 0.318 mol) obtained as above was treated with hydrogen chloride in the presence of a catalytic amount of aluminum chloride in 200 mL of benzene at room temperature for 48 h. Acetone (5 mL) was added to deactivate aluminum chloride, and the resulting mixture was filtered, concentrated, and distilled under reduced pressure to give 69.75 g of dichlorodihexylsilane (0.259 mol, 81% yield): bp 103−104 °C/1 mmHg; MS *m*/*z* 268 (M^+), 183 (M^+ − Hex); ^{1}H NMR (δ in $CDCl_3$) 0.88 (t, 6H, CH_3, J = 6.6 Hz), 1.08 (dd, 4H, $SiCH_2$, J = 9.4 Hz, J = 6.8 Hz), 1.29−1.67 (m, 16H, CH_2); ^{13}C NMR (δ in $CDCl_3$) 14.05, 20.33, 22.32, 22.46, 31.31, 32.11 (Hex); ^{29}Si NMR (δ in $CDCl_3$) 33.36.

(c) Di-*n*-hexylsilane. Dichlorodihexylsilane (69.75 g, 0.259 mol) obtained as above was added dropwise into a solution of 4.94 g (0.130 mol) of lithium aluminum hydride in 100 mL of ether. The solution was stirred at room temperature for 24 h. The resulting mixture was hydrolyzed with aqueous hydrochloric acid and extracted with hexane. The extract was dried over magnesium sulfate and concentrated. The residue was distilled under reduced pressure to give 44.6 g of dihexylsilane (0.223 mol, 86% yield): bp 108−110 °C/15 mmHg; MS *m*/*z* 200 (M^+), 115 (M^+ − Hex); ^{1}H NMR (δ in $CDCl_3$) 0.62−0.70 (m, 4H, $SiCH_2$), 0.88 (t, 6H, CH_3, J = 6.6 Hz), 1.27−1.36 (m, 16H, CH_2), 3.63 (p, 2H, SiH, J = 3.6 Hz); ^{13}C NMR (δ in $CDCl_3$) 9.17, 14.11, 22.57, 25.41, 31.56, 32.58 (Hex); ^{29}Si NMR (δ in $CDCl_3$) −28.63. Anal. Calcd for $C_{12}H_{28}Si$: C, 71.91; H, 14.08. Found: C, 71.90; H, 13.91.

Preparation of Methylmesitylsilane. (a) Dichloromethylmesitylsilane. To an ice-cooled solution of 80.0 g (0.535 mol) of trichloromethylsilane in 200 mL of ether was added dropwise a solution of mesityllithium prepared from the reaction of 100 g (0.503 mol) of mesityl bromide and 20.0 g (2.88 mol) of lithium in 100 mL of ether. The mixture was stirred for 24 h, filtered, and concentrated. The residue was distilled under reduced pressure to give 81.25 g (0.349 mol, 69% yield) of dichloromethylmesitylsilane: bp 140−145 °C/12 mmHg; mp 65−67 °C; MS *m*/*z* 232 (M^+), 217 (M^+ − Me), 119 (Mes^+); ^{1}H NMR (δ in $CDCl_3$) 1.26 (s, 3H, SiMe), 2.33 (s, 6H, mesityl *o*-Me), 2.62 (s, 3H, mesityl *p*-Me), 6.93 (s, 2H, mesityl ring H); ^{13}C NMR (δ in $CDCl_3$) 13.07 (SiMe), 21.04 (mesityl *p*-Me), 24.42 (mesityl *o*-Me), 129.94 (mesityl ring HC), 127.15, 141.64, 144.26 (ipso C); ^{29}Si NMR (δ in $CDCl_3$) 17.54.

(b) Methylmesitylsilane. Dichloromethylmesitylsilane (30.0 g, 129 mmol) thus obtained was added dropwise into an ice-cooled solution of 3.00 g (79.1 mmol) of lithium aluminum hydride in 100 mL of ether. The solution was stirred at room temperature for 24 h. The resulting mixture was hydrolyzed with aqueous hydrochloric acid and extracted with hexane. The extract was dried over magnesium sulfate and concentrated. The residue was distilled under reduced pressure to give 19.1 g of methylmesitylsilane (116 mmol, 90% yield): bp 110−111 °C/25 mmHg; MS *m*/*z* 164 (M^+), 149, (M^+ − Me), 119 (Mes^+); ^{1}H NMR (δ in $CDCl_3$) 0.34 (t, 3H, SiMe, J = 4.3 Hz), 2.27 (s, 3H, mesityl *p*-Me), 2.44 (s, 6H, mesityl *o*-Me), 4.43 (q, 2H, SiH, J = 4.3 Hz), 6.85 (s, 2H, mesityl ring H); ^{13}C NMR (δ in $CDCl_3$) −7.29 (SiMe), 21.10 (mesityl *p*-Me), 23.40 (mesityl *o*-Me), 128.16 (mesityl *m*-CH), 129.15, 139.41, 144.37 (ipso C); ^{29}Si NMR (δ in $CDCl_3$) −49.76. Anal. Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.81. Found: C, 72.76; H, 9.91.

Preparation of *n*-Hexylsilane.[25] To a solution of 9.2 g (0.24 mol) of lithium aluminum hydride in 150 mL of ether was added dropwise 70 g (0.32 mol) of trichlorohexylsilane. The mixture was stirred at room temperature for 12 h. The resulting mixture was hydrolyzed with aqueous hydrochloric acid, and the aqueous layer was extracted with ether. The organic layer and extracts were dried over magnesium sulfate and then concentrated. The residue was distilled under atmospheric pressure to give 34.3 g (0.295 mol, 92% yield) of *n*-hexylsilane: bp 113−114 °C; MS *m*/*z* 116 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.74 (tq, 2H, $SiCH_2$, J = 7.7 Hz, J = 3.9 Hz), 0.88 (t, 3H, CH_3, J = 6.9 Hz), 1.19−1.45 (m, 8H, $-CH_2-$), 3.47 (t, 3H, SiH, J = 3.9 Hz); ^{13}C NMR (δ in $CDCl_3$) 6.02, 14.09, 22.65, 26.45, 31.61, 32.33 (Hex); ^{29}Si NMR (δ in $CDCl_3$) −59.29; exact mass calcd for $C_6H_{16}Si$ (M^+) 116.1021, found 116.1021.

Preparation of Fluorodimethylphenylsilane. In a 200-mL flask fitted with a condenser were placed 12.0 g (89.3 mmol) of $CuCl_2$, 0.10 g (0.53 mmol) of CuI, and 2.78 g (47.9 mmol) of KF. The contents of the flask were dried at 100 °C for 12 h under reduced pressure, cooled, and filled with dry nitrogen. To this were added 5.94 g (43.6 mmol) of Me_2PhSiH and 100 mL of THF, and the mixture was stirred by magnetic stirrer at room temperature for 5 h. The resulting mixture was filtered to remove the salts, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 5.53 g (35.9 mmol, 82% yield) of Me_2PhSiF, bp 59−60 °C/30 mmHg.

Preparation of Fluorodi-*n*-hexylsilane. A mixture of 6.78 g (50.4 mmol) of $CuCl_2$, 0.14 g (0.74 mmol) of CuI, and 1.48 g (25.5 mmol) of KF in a 200-mL flask was predried in a manner as described above. To this were added 5.24 g (26.2 mmol) of *n*-Hex_2SiH_2 and 100 mL of THF, and the mixture was stirred at room temperature for 1 h. The resulting mixture was filtered, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 4.60 g (21.1 mmol, 81% yield) of *n*-Hex_2SiHF, bp 135−137 °C/40 mmHg.

Preparation of Fluoromethylphenylsilane. To a predried mixture of 4.51 g (33.5 mmol) of $CuCl_2$, 0.05 g (0.26 mmol) of CuI, and 2.53 g (16.7 mmol) of CsF in a 200-mL flask were added 2.04 g (16.7 mmol) of $MePhSiH_2$ and 100 mL of ether, and the mixture was stirred under reflux for 1 week, during which additional CsF was supplied portionwise (5 times, totally 105 mmol). The resulting mixture was filtered, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 1.60 g (11.4 mmol, 68% yield) of MePhSiHF, bp 55−56 °C/30 mmHg (lit.[22a] bp 74 °C).

Preparation of Fluorophenylsilane. To a predried mixture of 26.8 g (199 mmol) of $CuCl_2$ and 0.10 g (0.53 mmol) of CuI in a 300-mL flask were added 10.7 g (98.9 mmol) of $PhSiH_3$ and 200 mL of ether, and the mixture was stirred at room temperature for 24 h. Then, anhydrous KF (5.85 g, 101 mmol) was added, and the mixture was stirred for a further 48 h. The resulting mixture was filtered, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 8.02 g (63.6 mmol, 64% yield) of $PhSiH_2F$, bp 112−113 °C.

Preparation of Chlorofluoromethylphenylsilane. To a predried mixture of 9.62 g (71.6 mmol) of $CuCl_2$ and 0.05 g (0.26 mmol) of CuI in a 200-mL flask were added 5.14 g (36.7 mmol) of MePhSiHF and 100 mL of THF, and the mixture was stirred at room temperature for 10 h. The resulting mixture was filtered, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 4.76 g (27.3 mmol, 74% yield) of MePhSiClF, bp 75−77 °C/30 mmHg (lit.[24] bp 91 °C/54 mmHg).

Acknowledgment. We express our appreciation to Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Asia Ltd., Toshiba Silicone Co. Ltd., Sumitomo Electric Industry, Kaneka Corp., and the Japan High Polymer Center for financial support.

OM950787F

(25) *n*-Hexylsilane can also be obtained from Petrarch Systems.