

Reactions of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ with Fluoride Ion Sources: Formation of Fluorine-Terminated Siloxanes

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Received 2 October 1992

ABSTRACT

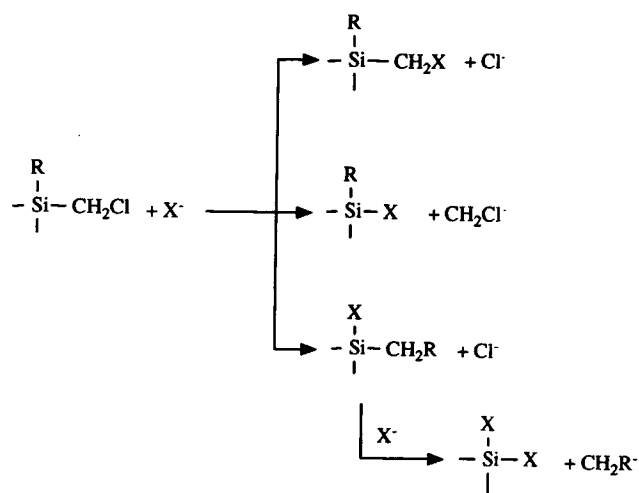
The fluoride ion-induced rearrangement of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ was expected to provide either PhMeSiHF (migration of hydride) or $(\text{PhCH}_2)\text{SiH}_2\text{F}$ (migration of phenyl). However, when $\text{Bu}_4\text{N}^+\text{F}^-$ (commercial TBAF) is added to $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$, a mixture of fluorine-terminated siloxanes, $\text{FPhMeSiO}(\text{PhMeSiO})_x\text{SiMePhF}$, is obtained. The presence of the Me group suggests a rapid anion-induced migration of hydride to produce PhMeSiHF which reacts further with water present in TBAF samples. When the reaction mixture is cooled to 0°C or is monitored at the early stage of the reaction, the major products are PhMeSiF_2 , $\text{PhMeSi}(\text{OH})\text{F}$, $\text{PhMeSi}(\text{OH})_2$, and FPhMeSiOSiMePhF which are proposed as the building blocks for the siloxanes. When dried CsF in CH_3CN is used, the major products are PhMeSiF_2 and PhMeSiH_2 which are assumed to form from the fluoride ion-induced disproportionation of PhMeSiHF . The reaction chemistry is rationalized in terms of hypervalent intermediates. The fluoride ion-induced reactions of PhMeSiH_2 and PhMeSiCl_2 are also described and compared to those of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$.

INTRODUCTION

The reaction of chloromethylsilanes with anions can result in substitution at carbon or attack at silicon

Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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SCHEME 1

that results in either a 1,2-rearrangement or loss of the chloromethyl substituent, as illustrated for a general case in Scheme 1 [1]. With alkoxide anions, protic solvents favor substitution at carbon and aprotic solvents facilitate the 1,2-rearrangement [1c]. A 1,2-rearrangement is usually favored with fluoride ion, and reactions conducted in aromatic solvents provide fewer by-products than those conducted in any other solvent system [1b,1c]. Both the elimination of CH_2Cl^- and rearrangement reactions are believed to involve pentacoordinate intermediates [1].

Most investigations of reactions of nucleophiles with chloromethylsilanes involve $\text{RR}'\text{R}''\text{SiCH}_2\text{Cl}$, where all substituents are organic groups. The general migratory aptitude from silicon to carbon appears to be vinyl > phenyl > alkyl

[1c–1e]. A preliminary study of the reaction of KOH with $\text{Me}_2\text{Si}(\text{H})\text{CH}_2\text{Cl}$ in EtOH showed that about 70% rearrangement to Me_3SiOH and 30% solvolysis to $\text{Me}_2\text{Si}(\text{OH})\text{CH}_2\text{Cl}$ occurs [2]. In this case, hydrogen migrates in preference to alkyl.

As part of a program to develop hydrosilanes as starting materials to produce new organosilicon compounds, we studied the reaction of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ with two fluoride sources. It was anticipated that the products obtained would depend on the relative migratory aptitude of Ph^- to give $\text{PhCH}_2\text{SiH}_2\text{F}$ or of H^- to give PhMeSiHF . In either case, a useful "bifunctional" silicon compound would result. Reactions were conducted with commercial tetrabutylammonium fluoride in THF or with CsF in acetonitrile. In actual practice, the products were not quite as simple as anticipated, in part due to the presence of water in the fluoride sources. This study describes the preferential migration of hydride in the reaction of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ and subsequent facile fluoride-induced processes of the initially formed products.

RESULTS

Reaction $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ with TBAF

The reactions of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ were conducted at various temperatures with commercial tetrabutylammonium fluoride (TBAF; 1 M in THF) at varying Si:F ratios in dried THF. The products and product distributions were determined by a combination of GC and GCMS techniques, and the results are summarized in Table 1.

When reactions were conducted at room temperature for approximately 1/2 hour, no products based on a monosilane were observed. Instead, fluorine-terminated siloxanes containing PhMeSi units were obtained. Heating the reaction mixture resulted in slow conversion to longer siloxanes. The limit of condensation that could be observed by GC was the heptasiloxane (tentative assignment), and that which could be demonstrated by GCMS was the hexasiloxane. The results clearly show that rearrangement of hydride from silicon to the carbon of the chloromethyl group is a rapid process, but subsequent reactions with water present in commercial TBAF solutions must occur. The direct product from a hydride rearrangement would be PhMeSiHF which was not observed under the conditions employed. The monosilane products that precede the formation of siloxane products should be observed at an earlier stage of the reaction or at lower temperatures. When the reaction mixture is analyzed after 5 minutes at either 0°C or room temperature, the major product is the monosilane $\text{MePhSi}(\text{OH})\text{F}$ which would arise from the solvolysis of PhMeSiHF . Even at this stage of the reaction, however, siloxane products are evident, and

these are the only conditions where a hydroxide terminated siloxane was observed.

When the reaction is run at room temperature with a ratio of Si to F of 2, the rearrangement is rapid, but after 3 hours, about half of the products are still monosilanes. With a deficiency of fluoride ions, the siloxanes that are formed are both fluoride and hydride terminated. To determine whether the reaction is catalytic in fluoride ion, the reaction was run with a ratio of Si to F of about 15. Under these conditions, little reaction of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ occurs, although two siloxanes are present that contain a chloromethyl substituent in about 7% total yield.

Samples of TBAF are difficult to dry, but a recent report described the ammonolysis of hydrosilanes in the presence of commercial TBAF that had been "carefully" dried over molecular sieves [3]. Although the same method was employed to dry samples of TBAF, the only monosilane observed from the reaction of the "dried" TBAF and $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ was MePhSiF_2 , and the other products were siloxanes. In this particular experiment, a high concentration of Bu_3N was observed. In reactions conducted with commercial TBAF, this amine was rarely observed even as a minor component in reaction mixtures.

Reaction of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ with CsF

When the reaction of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ was conducted with CsF in acetonitrile, the major products were the monosilanes PhMeSiH_2 and PhMeSiF_2 in a nearly 1:1 ratio. Although the samples of CsF were dried, a small amount of water was still present, as evidenced by the observed monosilanes with OH groups (about 4%) and siloxanes (about 6%). These were the only conditions where significant quantities of PhMeSiH_2 were observed.

Reaction of PhMeSiH_2 and PhMeSiCl_2 with Fluoride Sources

For comparison purposes, the reaction of PhMeSiH_2 and of PhMeSiCl_2 with TBAF and CsF under the conditions utilized for the study of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ was examined, and the results are summarized in Table 2. When PhMeSiH_2 is treated with commercial TBAF, gas evolution occurs, with the major identified products being the siloxanes HOPhMeSiOSiMePhOH and $(\text{PhMeSiO})_x$ ($x = 3, 4$), and the only fluorine containing products are MePhSiFX ($X = \text{F}, \text{OH}$) and FPhMeSiOSiMePhOH . The GC ratio between the monosilanes and the disiloxane is about 3.5:1. In contrast, the reaction of PhMeSiH_2 with CsF is slow, and 96% remains after 2 hours. Even after 6 days, more than half the starting silane is present in the reaction mixture. Reaction of PhMeSiCl_2 does provide the two mon-

TABLE 1 Products Produced from the Reaction of Fluoride Sources with Ph(ClCH₂)SiH₂

Product ^a	TBAF ^b						TBAF ^c Si/F = 1 5 Minutes RT	CsF ^d Si/F = 3/4 20 Minutes RT
	Si/F = 1			Si/F = 2		Si/F ~ 15		
	5 Minutes 0°C	5 Minutes RT	30 Minutes ^e RT	16 Hours Heat	5 Minutes RT	1 Hour ^f RT		
Monosilanes								
MePhSiH ₂	—	11	—	—	21	—	—	38
MePhSiF ₂	8.7	4.3	—	—	—	0.5	27	47
MePhSi(OH)F	48	47	—	—	22	—	—	1.0
MePhSi(OH) ₂	2.7	2.6	—	—	—	2.3	—	1.9
Siloxanes								
F(MePhSiO) _x SiMePhF								
x = 1	15	18	62	33	26 ^g	—	14	3.1
2	4.9	1.2	25	25	5 ^h	—	3.3	—
3	1.8	1.5	11	17	—	—	—	—
4–6	—	—	—	15 ⁱ	—	—	—	—
FMePhSiOSiMePhOH	10	5.2	—	—	—	—	—	—
(MePhSiO) ₃	1.8	—	—	—	10	—	2.3	2.8
Additional components	6.8 ^j	10 ^k	—	8.2 ^l	16 ^m	11 ⁿ	53 ^o	6.2 ^p

^aProducts determined by GC and GCMS. Numbers in columns are percentages from uncorrected GC integration data. ^bCommercial TBAF (1 M in THF; < 5% H₂O). ^cDried commercial TBAF (see the Experimental section). ^dDried (see the Experimental section). ^eData obtained after workup. ^fUnreacted starting material (86%). ^gIncludes HPhMeOSiMePhX (X = F, H). ^hIncludes F(PhMeSiO)₂SiPhMeH. ⁱx = 4 (7.7); 5 (5.1); 6 (1.7). ^jThree unidentified components. ^kFour unidentified components. ^lMinor unidentified components, each < 2%. ^mFour unidentified components. ⁿHPh(ClCH₂)Si-OSiRPhH [R = Me (2.5); CH₂Cl (4.7)] and an unidentified component (4.0%). ^oBrC₆H₅ (impurity in starting material) (11%); Bu₃N (39%); (PhMeSiO)₄ (2.3%); three unidentified components (4.3%). ^pUnreacted starting material (3.1%); unidentified component (3.1%).

TABLE 2 Products from the Reaction of PhMeSiH₂ and PhMeSiCl₂ with Fluoride Sources^a

Products ^a	PhMeSiH ₂		PhMeSiCl ₂	
	TBAF/1.5 Hours	CsF ^b /6 Days	TBAF/15 Minutes	CsF/4 Days
Monosilanes				
PhMeSiF ₂	2.1	—	32	16
MePhSi(OH)F	5.5	5.7	18	42
Siloxanes				
FPhMeSiOSiMePhF	—	—	41	35
FPhMeSiOSiMePhOH	11	—	6.2	3.9
HOPhMeSiOSiMePhOH	22	—	—	—
(PhMeSiO) _x				
x = 3	14	1.5	—	—
x = 4	29	12	—	—
X(PhMeSiO) ₂ SiMePhX	3.6 ^c	—	1.2 ^d	2.9 ^d
Additional Components	13 ^e	81 ^f	1.8 ^g	—

^aProducts determined by GC and GCMS. Numbers in columns are percentages from uncorrected GC integration data. ^bDried CsF (see the Experimental section). ^cX = OH, tentative identification. ^dX = F. ^eFive unidentified components. ^fUnreacted starting material (66%) and eight unidentified components (15%). ^gTwo unidentified components.

osilanes, PhMeSiF₂ and PhMeSi(OH)F, as well as the disiloxane, FPhMeSiOSiMePhF, the sum of which constitutes about 90% of the products.

DISCUSSION

The reaction of Ph(ClCH₂)SiH₂ with commercial TBAF and with CsF provided products that con-

tained [PhMeSi] units which result from anion-induced rearrangement of hydride from silicon to carbon. No products incorporating [PhCH₂SiH] units that would result from rearrangement of a phenyl group from silicon to carbon could be identified. With the fluoride sources utilized in this study, commercial TBAF (<5% water) and CsF, which is difficult to dry, no PhMeSiFH was ob-

served under various reaction conditions (see Table 1).

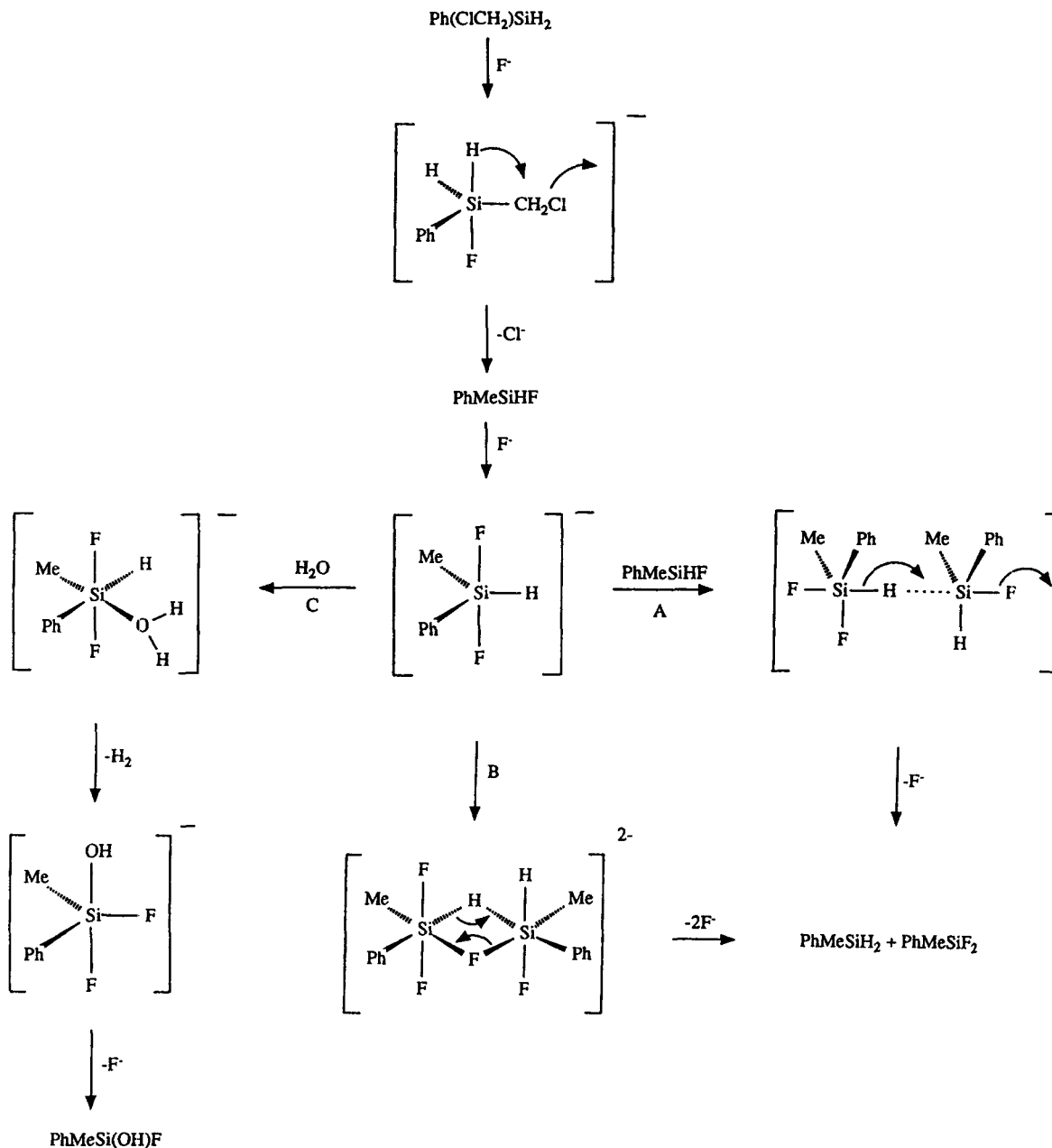
The mixed hydrofluoride, PhMeSiHF, has been reported from the reaction of PhMe(TfO)SiH (formed from Ph₂MeSiH and HOTf) with 1.2 equivalent of KF in DMF (18-crown-6 as catalyst), but Me₂SiHF was identified only as an intermediate in the conversion of (Me₂SiH)₂O to Me₂SiF₂ with NaHF₂ [5]. With dried CsF, the monosilanes PhMeSiH₂ and PhMeSiF₂ are the major products in a 5:4 ratio. With commercial TBAF solutions, the major monosilane produced is PhMeSi(OH)F. Mixed hydroxyfluorosilanes are normally isolated only when a sufficiently bulky substituent is present at silicon [6].

The results suggest that, if PhMeSiHF is formed, subsequent disproportionation occurs, and when water is present, hydrolysis of the SiH bond occurs faster than disproportionation. It is likely that both disproportionation and hydrolysis are initiated by fluoride ion, and possible intermediates in the reaction pathway are outlined in Scheme 2. In the case of disproportionation, fluoride ion could induce hydride transfer to a second silicon center. However, evidence is accumulating that six-coordinate intermediates are also important in nucleophilic processes that occur at silicon [7a]. *Ab initio* MO calculations of simple systems have demonstrated that a pentacoordinate silicon center can accept an incoming nucleophile without the bond to the leaving group breaking [7b]. The disproportionation of [MePhSiF₂H]⁻ through a six-coordinate intermediate (route B, Scheme 2) is similar to that recently suggested for the redistribution of groups in [H₂Si(OR)₃]⁻ [8a]. Alternatively, the hydride transfer shown in route A may occur through a bridged intermediate involving mixed six-coordinate and five-coordinate silicon centers, as shown in Fig. 1. The latter was preferred over the former in a recently reported study of hydride transfer between penta- and tetra-coordinate silicon derivatives [8b]. The hydrolysis of [PhMeSiF₂H]⁻ through the six-coordinate intermediate (route C, Scheme 2) is analogous to that suggested for alcoholysis of [H₂Si(OR)₃]⁻ conducted in THF [9]. Loss of OH⁻ from an intermediate, such as [PhMeSiF₂(OH)]⁻, would generate the MePhSiF₂ also observed under a variety of conditions in the reaction of Ph(ClCH₂)SiH₂ with TBAF. Similarly, loss of hydride from [PhMeSiF₂H]⁻ would generate PhMeSiF₂, and the H⁻ would be solvolyzed by water to give OH⁻ and H₂.

When PhMeSi(OH)F is formed, it is likely that condensation of this monomer gives rise to the disiloxane, FPhMeSiOSiMePhF. The presence of hydroxide-terminated disiloxane in the early stage of the reaction suggests that the condensation of PhMeSi(OH)F and PhMeSi(OH)₂ also takes place. Undoubtedly, FPhMeSiOSiPhMe(OH) reacts with

PhMeSi(OH)F to provide some of the trisiloxane F(PhMeSiO)₂SiPhMeF that is observed. Since all monomers are converted to fluoride-terminated siloxanes within 30 minutes at room temperature and the siloxanes continue to increase in chain length, some redistribution or disproportionation process of all the siloxanes must occur. This process may also be fluoride ion-induced, since, as siloxanes are produced, the fluoride ion concentration must actually increase. In a related reaction, the cleavage of SiO bonds by F⁻ has been utilized for deprotecting alcohols [10]. Scheme 3 shows a possible F⁻ induced process for reaction of two disiloxanes to produce a trisiloxane. The transfer of a "siloxide" group through a noncharged intermediate, as shown in Figure 2, cannot be precluded. In all bridged intermediates leading to disproportionation, a bulky siloxy group must bridge the two silicon centers, thus these processes should occur more slowly. Whether redistribution of siloxanes is anion-induced or not, it is likely that reaction involves the less sterically hindered terminal silicon center, in which case either PhMeSiF₂ (from an intermediate such as that shown in Fig. 2) or [PhMeSiF₃]⁻ (Scheme 2) is formed. Although [K(18-crown-6)] [PhMeSiF₃] is described as stable to air and moisture [11] and [Et₄N] [PhMeSiF₃] is prepared from MePhSiF₂ and Et₄NF · H₂O [12], Corriu and co-workers have shown that PhMeSiF₃⁻ {[K(18-crown-6)]⁺ counter ion} is more reactive toward strong nucleophiles (RM, RO⁻, complex hydrides) than the neutral MePhSiF₂ [13]. Since it is probable that OH⁻ is generated during the reaction of the monosilanes produced from the starting chloromethylsilane, conversion of either PhMeSiF₂ or PhMeSiF₃⁻ by hydroxide to PhMeSi(OH)F could occur. Subsequent conversion of PhMeSi(OH)F to the disiloxane would recycle the monosilane into the redistribution reactions. That the reactions of siloxanes with fluoride sources can be even more complicated is indicated by the observation that Me₃SiOSi(CH₂Cl)Me₂ exhibits no reaction with KF, and many products were formed which were not identified with CsF [1b]. Recently, Voronkov and co-workers have reported that fluorosilanes react (neat) with Me₃SiOSiMe₃ to give mixed siloxanes, RR'SiFOSiMe₃ (R = alkyl or F), and it appears that no reaction occurs in solvents. The mixed siloxanes, R'F₂SiOSiMe₃, disproportionate at 20°C, but Me₃SiOSiPhMeF is stable at 200°C. Silyl fluorides also react with HMe₂SiOSiMe₂H, but PhMeSiF₂ was the slowest reacting fluoride of those studied [11]. These results suggest that the disproportionation of F(PhMeSiO)_xSiPhMeF observed in the current study could be accelerated by fluoride ion.

The reaction sequence just outlined for Ph(ClCH₂)SiH₂ was rationalized through nucleophilic activation of the hydrolysis of SiH bonds. A related activation in the alcoholysis of hydrosi-



SCHEME 2

lanes has been known for some time [15] and, more recently, was reported in the ammonolysis of hydrosilanes [16]. To obtain a comparison between the reactivity of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ and PhMeSiH_2 , the latter was treated with commercial TBAF (Table 2). The SiF-containing products are found to be minor, and the major products are the result of conversion of PhMeSiH_2 to HOPhMeSiOSiMePhOH and cyclotrisiloxanes which can be rationalized through the hydrolysis product $\text{PhMeSi}(\text{OH})_2$. The usual fate of hydroxyl-terminated sil-

oxanes is the formation of cyclics, as observed in this case. In an analogous manner, reaction of ammonia with PhMeSiH_2 promoted by fluoride ion (dried TBAF in THF) was reported to produce oligocyclosilazanes, $(\text{PhMeSiNH})_n$ [16]. With $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$, the most rapid reaction appears to be the rearrangement process which involves incorporation of a fluoride substituent at the silicon center. Subsequent reactions lead to linear siloxanes that are fluorine-terminated and do not cyclize under the conditions employed in these ex-

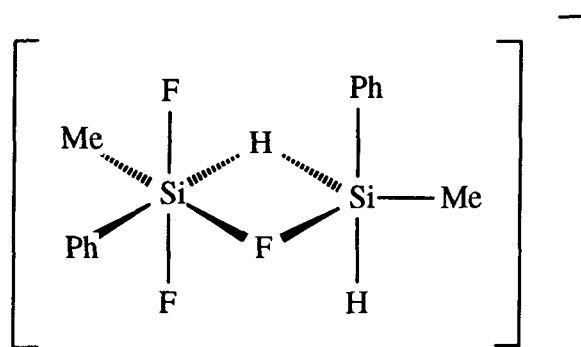
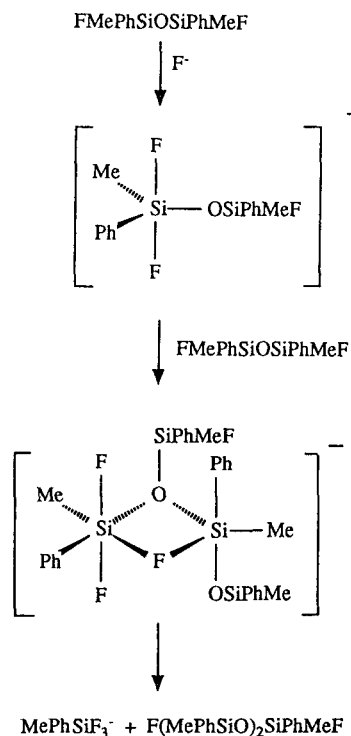


FIGURE 1 Bridged intermediate for disproportionation of PhMeSiHF with mixed five- and six-coordinate silicon centers.

periments. Thus, the two precursors, PhMeSiH_2 and $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$, provide siloxanes with the same repeat unit but a different distribution of linear to cyclic siloxane products and different chain-terminating substituents for the linear siloxanes.

When PhMeSiCl_2 was reacted with TBAF and CsF that contained an unknown quantity of water, the products incorporated fluoride (Table 2). The usual cyclosiloxanes that result from the hydrolysis of dichlorosilanes were not observed. Transition metal fluorides have been used to convert chlorosilanes to fluorosilanes, but the water usually present in alkali metal halides causes the for-



SCHEME 3

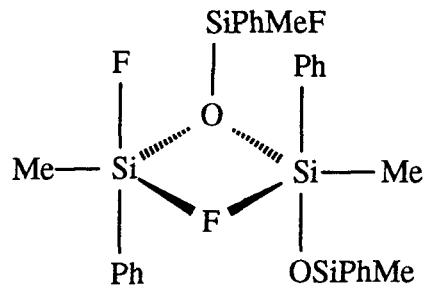


FIGURE 2 Bridged intermediate for disproportionation of siloxanes derived from two tetrahedral silicon centers.

mation of siloxane by-products. If the desired fluorosilane is sufficiently volatile, it can be separated from the by-products, as was the case when Me_3SiCl was converted to Me_3SiF with dry KF in chlorobenzene in the presence of 18-crown-6 and added water [17]. The maximum yield was 40%, and the fluorosilane was not obtained in the absence of water. In most studies, siloxane products have not been identified but are probably related to those that are observed from PhMeSiCl_2 .

A few preliminary experiments have been performed with PhSiH_3 and commercial TBAF and also with dried CsF . In the TBAF reactions, solid, THF insoluble product was isolated, which contained SiOSi and SiPh absorptions in the IR spectrum. The solid obtained from the reaction with CsF contained SiOSi , SiPh , and SiH IR bands, and the oil contained SiOSi , SiPh , SiH , and SiOH bands. A GC trace of the oil contained no observable products. Reactions of a trifunctional silane can lead to cross-linking and, thus, to high molecular weight products that would not be observable under GC conditions. These experiments suggest that, if a Ph group migrates in the reaction of $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ to give trifunctional $\text{PhCH}_2\text{SiH}_2\text{F}$, subsequent reactions would give products that would not be observed under the conditions of the measurements that were used. However, the ^1H NMR spectral data of reaction products from $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$ do not show signals due to the presence of benzyl groups, and, thus, products resulting from phenyl migration should be <5%.

In summary, the reactions of commercial TBAF (<5% water), a homogenous fluoride source, and CsF , a heterogeneous fluoride source, provide different product distributions upon reaction with $\text{Ph}(\text{ClCH}_2)\text{SiH}_2$. Both fluorides initiate a rapid 1,2-rearrangement of the hydride on silicon to the carbon of the chloromethyl group to provide monosilane products based on a PhMeSi unit, but the direct rearrangement reaction product PhMeSiHF is not observed. With TBAF, hydrolysis provides $\text{PhMeSi}(\text{OH})\text{F}$, and subsequent reactions provide a series of fluorine-terminated siloxanes, $\text{F}(\text{PhMeSiO})_x\text{SiMePhF}$. Under heterogeneous conditions with dried CsF , a mixture of PhMeSiF_2 and

PhMeSiH₂, consistent with the disproportionation of PhMeSiHF, was obtained. Under the homogeneous conditions provided by TBAF, the fluoride ion promotes additional processes leading to siloxanes. That the process requires stoichiometric fluoride was demonstrated by reactions run with a deficiency of TBAF, where the products produced were PhMeSiH₂ and H-terminated siloxanes. The reaction of PhMeSiH₂ with TBAF demonstrates that fluoride ion promotes hydrolysis to provide hydroxy-terminated siloxanes and cyclosiloxanes with product distributions not observed from Ph(ClCH₂)SiH₂. Thus, the reaction of Ph(ClCH₂)SiH₂ provides a unique series of F-terminated siloxanes of which only the disiloxane has been previously reported [18a] and which also exhibit a different reactivity from the known chlorine-terminated series, Cl(PhMeSiO)_xSiPhMeCl ($x = 1-4$) [18].

EXPERIMENTAL

General

All reactions, unless otherwise noted, were carried out under an atmosphere of dry N₂ or Ar using standard Schlenk techniques. Solvents were dried using standard methods, and all glassware was dried in an oven at 110–120°C prior to use. Commercial compounds MePhSiCl₂, PhSiCl₃, (ClCH₂)SiCl₃, LiAlH₄, Bu₄N⁺F⁻/THF (1 M, <5% H₂O), and CsF were used as supplied unless otherwise noted.

The ¹H NMR spectra were recorded on an EM-360 NMR spectrometer. All ¹H NMR data were collected using CDCl₃ as a solvent and TMS as an internal standard, and centers of multiplets are given except for the aromatic region. Mass spectral data were collected on a Hewlett-Packard Model 5988A GC/MS instrument equipped with an RTE-A data system, and gas chromatographic separations were performed in a split injection mode using a 12.5 m (HP-1) capillary column. Data are included when >5% of the base peak. Gas chromatographic separations were performed on a Shimadzu GC-14A gas chromatograph, using a J&W Scientific 15 m × 0.53 i.d., 1.5 μm film DB-5 column with temperature programming from 60–320°C, isothermal at 60°C/2 min, then a ramp of 20°C/min. The injector temperature was 275°C, and the detector temperature was 350°C. Integrations were recorded on a Shimadzu CR601 Chromatopac and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer model 1600 FT-IR Spectrophotometer as thin films or as KBr pellets.

Chloromethylphenylsilane

Distilled ether (100 mL) and chloromethyltrichlorosilane (8.10 mL, 65.0 mmol) were placed in a three-necked flask equipped with a reflux con-

denser, a pressure addition funnel, and a stir bar. Phenylmagnesium bromide (21.7 mL, 3.0 M), either used as commercially available or prepared from bromobenzene and magnesium turnings, was injected into the addition funnel. The Grignard reagent was added dropwise with stirring to the diluted silane. After addition was complete, the reaction mixture was refluxed for 1.5 hours. Lithium aluminum hydride (1.70 g, 44.8 mmol) was added to the reaction flask in portions, and then the reaction mixture was stirred for 17 hours at room temperature and chilled in an ice bath and the excess LiAlH₄ hydrolyzed with chilled 5% hydrochloric acid. The ether layer was separated and washed three times with deionized water, and the aqueous layers were extracted 3 times with ether. The combined ether layers were dried over sodium sulfate. After removal of the volatile material, the residual phenylchloromethylsilane was distilled at 5 mm Hg to give 4.33 g of clear oil, bp 71–73°C (98% by GC analysis) in a 43% overall yield. IR: SiPh 1430 cm⁻¹, SiH 2160 cm⁻¹; ¹H NMR (CDCl₃): δ 3.0 (t, 2.0, CH₂Cl), 4.4 (t, 2.0, SiH), 7.2–7.7 (m, 5.0, SiPh); *m/e* 156 (M⁺, 14%), 107 (M⁺-CH₂Cl), 105, 91, 78.

General Reaction of Chloromethylphenylsilane with Commercial TBAF

Distilled THF and either Ph(ClCH₂)SiH₂ or TBAF solutions are placed in a three-necked flask equipped with a condenser, septum, and stir bar. Either TBAF or Ph(ClCH₂)SiH₂ was then added dropwise, whereupon gas evolution and an exothermic reaction were observed. After suitable periods, aliquots were removed and added to a vial that contained ether and deionized water. When reactions were terminated, bulk ether (5 mL) and deionized water (5 mL) were added to the reaction flask and the ether layer was separated, washed with deionized water, and dried over sodium sulfate. Removal of the volatiles provided an oil. Aliquots were analyzed (GC) immediately after removal from the reaction mixture, and the products were verified by GCMS.

Si/F = 1. a. 0°C. Distilled THF (5.0 mL) and Ph(ClCH₂)SiH₂ (0.44 g, 2.8 mmol) were reacted at 0°C for 20 minutes with Bu₄N⁺F⁻ (TBAF) (2.8 mL, 1.0 M). After workup, 0.30 g of a yellow-orange oil was obtained.

The GC analysis of an aliquot taken after 5 minutes showed MePhSiF₂ (8.7%), MePhSi(OH)F (48%), MePhSi(OH)₂ (2.7%), FMePhSiOSiPhMeF (15%), FMePhSiOSiPhMeOH (10%), FMePhSiO(PhMeSiO)SiPhMeF (4.9%), (MePhSiO)₃ (1.8%), FMePhSiO(SiPhMeO)₂SiPhMeF (1.8%), and three unidentified components (6.8%). FPhMeSiF *m/e* 158 (M⁺ 44%), 143 (M⁺-Me), 91, 77, 65, 51; F(PhMeSi)OH *m/e* 156 (M⁺ 25%), 141 (M⁺-Me), 91,

77, 51; HO(PhMeSi)OH *m/e* 154 (M^+ 100%), 139 (M^+ -Me), 128, 115, 102, 89, 76, 63, 51; [FPhMeSi]₂O *m/e* 294 (M^+ 90%), 279 (M^+ -Me), 259 (M^+ -Me-HF), 217 (M^+ -Ph), 201 (M^+ -Me-PhH), 165, 143 (PhSiF₂⁺), 125 (PhSiHF⁺), 91, 47; FPhMeSiOSiMePhOH *m/e* 292 (M^+ 43%), 277 (M^+ -Me), 259 (M^+ -Me-H₂O), 215 (M^+ -Ph), 199 (M^+ -Me-PhH), 165, 137, 123, 91, 51; F(PhMeSiO)₂SiMePhF *m/e* 430 (M^+ 9.5%), 415 (M^+ -Me), 352 (M^+ -PhH), 337 (M^+ -Ph-Me), 276 (M^+ -PhMe₂SiF), 259, 197 (Ph₂MeSi⁺), 161, 91, 77; F(PhMeSiO)₃SiMePhF *m/e* 566 (M^+ 2.4%), 551 (M^+ -Me), 489 (M^+ -Ph), 412 (M^+ -PhMe₂SiF), 377, 319, 315, 259, 197, 181, 165, 135, 91; (PhMeSiO)₃ *m/e* 408 (M^+ 9.4%), 393 (M^+ -Me), 330 (M^+ -PhH), 315 (M^+ -PhH-Me), 253, 223, 195, 150, 91, 77; IR: SiOSi 1096 cm⁻¹, 1128 cm⁻¹, SiOH 3304 cm⁻¹.

b. Room temperature. A solution of Ph(ClCH₂)SiH₂ (0.56 g, 3.2 mmol) was injected into a flask containing TBAF (5.2 mL, 1.0M) and distilled THF (10.0 mL), and the mixture was stirred at room temperature for 1/2 hour. After workup, removal of the volatiles provided 0.54 g of yellow oil.

An aliquot taken after 5 minutes showed the following composition (GC %): MePhSiH₂ (11%), MePhSiF₂ (4.3%), MePhSi(OH)F (47%), MePhSi(OH)₂ (2.6%), [FMePhSi]₂O (18%), FMePhSiOSiPhMeOH (5.3%), F(MePhSiO)_xSiPhMeF (*x* = 2, 1.2%; 3, 1.5%), and four unidentified components (10%). The residual oil showed the following composition (GC %): FMePhSiOSiPhMeF (62%), F(PhMeSiO)₂SiPhMeF (25%), F(MePhSiO)₃SiPhMeF (11%), and seven unidentified components ranging from 1–2% each.

c. Refluxing THF. To THF (10.0 mL) and TBAF (3.10 mL, 1.0 M) was slowly added Ph(ClCH₂)SiH₂ (0.490 g, 3.13 mmol). The reaction mixture bubbled violently and generated heat for approximately 10 seconds after the silane had been added. The reaction mixture was heated at reflux for 16 hours before workup, which provided 0.432 g of pale orange oil. Analysis of the oil showed the following composition (GC %): F(PhMeSiO)_xSiPhMeF, *x* = 1 (34%), 2 (26%), 3 (17%), 4 (7.9%), 5 (5.2%), 6 (1.8%), and unidentified minor products (8.2%). F(PhMeSiO)₄SiPhMeF *m/e* 702 (M^+ absent), 688 (M^+ -Me), 471, 393, 333, 275, 259, 197, 135, 91. F(PhMeSiO)₅SiPhMeF *m/e* 838 (M^+ absent), 607 (M^+ -Ph-PhMe₂SiH), 410, 259, 197, 135. IR (product mixture): SiOSi 1096 cm⁻¹, 1127 cm⁻¹.

Si/F = 2. TBAF (1.5 mL, 1.0 M) was added to a flask containing chloromethylphenylsilane (0.50 g, 3.2 mmol) and THF (10.0 mL), and the reaction mixture was stirred at room temperature for 3 hours. Workup provided 0.42 g of yellow oil. Analysis of an aliquot removed after 5 minutes showed the following composition (GC %): PhMeSiH₂ (21%), PhMeSi(OH)F (22%), XPhMeSiOSiMePhX' (*X* = *X'* = H, F; *X* = H, *X'* = F; combined, 26%),

F(PhMeSiO)₂SiPhMeX (*X* = H, F; combined, 5%), (PhMeSiO)₃ (10%), and four unidentified components (16%). HPhMeSiOSiMePhH *m/e* 258 (M^+ 9.2%), 243 (M^+ -Me), 195, 179, 165, 135, 121, 105, 89, 59, 43; HPhMeSiOSiMePhF *m/e* 276 (7.9%), 275 (M^+ -H), 261 (M^+ -Me), 198 (M^+ -H-Ph), 197, 183 (Ph₂SiH⁺), 139, 91, 77; H(PhMeSiO)₂SiMePhF *m/e* 412 (2.6%), 397 (M^+ -Me), 335 (M^+ -Ph), 334, 333, 319 (M^+ -Me-PhH), 259, 257, 256, 241, 197, 135, 91.

Si/F ~ 15. TBAF (0.25 mL, 1.0 M) was injected into a flask containing Ph(ClCH₂)SiH₂ (0.574 g, 3.67 mmol) and THF (6.0 mL). Analysis of an aliquot taken 5 minutes after addition indicated the following composition (GC %): Ph(ClCH₂)SiH₂ (92%), PhMeSiF₂ (1.2%), PhMeSi(OH)₂ (2.1%), and five unidentified components ranging from 0.5 to 1.3%. After 1 hour, the following composition was observed: Ph(ClCH₂)SiH₂ (86%), PhMeSiF₂ (0.5%), PhMeSi(OH)₂ (2.3%), HPh(ClCH₂)SiOSiRPhH (*R* = Me, 2.5%; ClCH₂, 4.7%), and unidentified components (4.0%). After 2 days at room temperature, water (5 mL) and hexanes (5 mL) were added to the reaction flask. The hexane layer was separated, washed with water, and dried over sodium sulfate. Removal of the volatiles provided 0.47 g of colorless oil. Analysis (GC) of this oil showed the following composition: Ph(ClCH₂)SiH₂ (79%), PhMeSi(OH)₂ (2.5%), HPh(ClCH₂)SiOSiRPhH (*R* = Me, 1.8%; ClCH₂, 14.1%), and an unidentified component (2.8%). Kugelrohr distillation of this oil at 0.1 mm Hg, 35°C, provided 0.10 g colorless residual oil: Ph(ClCH₂)SiH₂ (12%), PhMeSi(OH)₂ (7.4%), HPh(ClCH₂)SiOSiRPhH (*R* = Me, 9.7%; ClCH₂, 71%). ¹H NMR (CDCl₃): δ 0.4 (d, 0.40, CH₃), 2.9 (d, 3.9, CH₂Cl), 4.35 (t, 0.40, SiH), 5.0 (t, 1.7, SiH), 7.0–7.8 (m, 14, SiPh); HPh(Cl³⁵CH₂)SiOSiMePhH, *m/e* 292 (M^+ , absent), 277 (M^+ -Me), 243 (M^+ -CH₂Cl), 213, 165, 121 (PhMeSiH⁺), 91, 79; HPh(Cl³⁵CH₂)SiOSi(CH₂Cl³⁵)PhH, *m/e* 326 (M^+ , absent), 277 (M^+ -CH₂³⁵Cl), 241 (M^+ -CH₂Cl-HCl), 227, 199, 185, 157, 141, 119, 105, 91, 65, 51.

Reaction of Chloromethylphenylsilane with Dried TBAF

A sample of commercial TBAF solution (8.8 g) was dried over molecular sieves (3.5 g) which had been activated by heating under vacuum in an oil bath at 150°C in a Schlenk tube for 36 hours [19].

Chloromethylphenylsilane (0.30 mL, 86%; remaining component, C₆H₅Br) was added to a Schlenk tube containing freshly dried THF (5.0 mL) which had been degassed with argon. Slow addition of dried TBAF (1.50 mL, 1.0 M) resulted in heat and gas evolution. After 5 minutes at room temperature, analysis of an aliquot showed the following components: PhMeSiF₂ (27%), C₆H₅Br (11%), Bu₃N (39%), FPhMeSiOSiMePhF (14%), F(PhMeSiO)₂SiMePhF (3.3%), (PhMeSiO)₃ (2.3%),

(PhMeSiO)₄ (2.2%), and three unidentified components (4.3%).

Other attempts with separately dried samples of commercial TBAF produced similar results.

Reaction of Chloromethylphenylsilane with Dry CsF

Chloromethylphenylsilane (0.92 g, 5.9 mmol) was injected into a Schlenk tube containing distilled acetonitrile (2.5 mL) and CsF (1.21 g, 7.97 mmol) which had been dried by heating under vacuum at 190°C for 16 hours. The mixture fumed, heat was evolved, and a white, fluffy solid formed. Analysis of an aliquot taken 20 minutes after the addition of the silane showed the following composition: PhMeSiF₂ (38%), PhMeSiH₂ (47%), PhMeSi(OH)F (1.0%), PhMeSi(OH)₂ (1.9%), Ph(ClCH₂)SiH₂ (3.1%), FPhMeSiOSiMePhF (3.1%), (PhMeSiO)₃ (2.8%), and an unidentified component (3.1%). Analysis of an aliquot taken 2 days after addition of the silane gave the following composition: PhMeSiF₂ (45%), PhMeSiH₂ (42%), PhMeSi(OH)F (1.5%), PhMeSi(OH)₂ (2.7%), FPhMeSiOSiMePhF (8.0%), F(PhMeSiO)₂SiMePhF (1.3%), and two unidentified components (3.1%).

After having been stirred for 3 days at room temperature, distilled ether (5 mL) was added to the reaction mixture and the white solid (0.98 g) was removed by filtration. Removal of the volatiles provided 0.76 g of clear oil. Analysis of this oil showed the presence of PhMeSiF₂ (40%), PhMeSiH₂ (44%), PhMeSi(OH)₂ (2.8%), FPhMeSiOSiMePhF (6.4%), and four unidentified components ranging from 0.9 to 1.6%.

Reaction of Phenylmethylsilane with TBAF

When TBAF (3.1 mL, 1.0 M) was added to a flask containing THF (10.0 mL) and PhMeSiH₂ (0.38 g, 3.1 mmol), gas evolution was observed. Analysis of an aliquot taken 1.5 hours after the addition of TBAF showed the following composition (GC %): PhMeSiF₂ (2.1%), PhMeSi(OH)F (5.5%), FPhMeSiOSiMePhOH (11%), HO(PhMeSiO)_xSiMePhOH {*x* = 1, 22%; 2 (tentative identification), 3.6%}, (PhMeSiO)_x (*x* = 3, 14%; 4, 29%), and five unidentified components (13%). The usual workup after 3.5 hours provided 0.50 g yellow oil. The GC/GCMS analysis of the oil showed the presence of PhMeSiF₂ (2.7%), PhMeSi(OH)F (9.2%), XPhMeSiOSiMePhOH (*X* = F, 13%; OH, 22%), (PhMeSiO)_x (*x* = 3, 16%; 4, 23%), and four unidentified components (14.2%). HOPhMeSiOSiMePhOH *m/e* 290 (M⁺ 8.6%), 275 (M⁺-Me), 257 (M⁺-Me-H₂O), 213 (M⁺-Ph), 197 (Ph₂MeSi⁺), 181, 135 (PhMe₂Si⁺), 121 (PhMeSiH⁺), 91, 77, 51; (PhMeSiO)₄ *m/e* 544 (M⁺ 4.1%), 529 (M⁺-Me), 451 (M⁺-Me-PhH), 373, 315, 253, 218, 179, 156, 91, 77.

Reaction of Phenylmethylsilane with Dry CsF

Methylphenylsilane (0.72 g, 5.9 mmol) was added to a Schlenk tube containing freshly distilled dried acetonitrile (5.0 mL) and dried CsF (0.89 g, 5.8 mmol). A small amount of gas evolution was observed. Aliquots were prepared for analysis by adding a small amount of the sample to a vial containing distilled ether and removing the solid by filtration through celite. Analysis (GC) of an aliquot taken 2 hours after the addition of the PhMeSiH₂ showed 96% unreacted starting material and (PhMeSiO)₃ (1.5%). After having been stirred for 6 days at room temperature, distilled ether (5 mL) was added to the contents of the Schlenk tube and the dark brown solid (0.55 g) which had formed was removed by filtration. Removal of the volatiles from the filtrate provided 0.25 g of dark orange oil. Analysis (GC) showed the presence of PhMeSiH₂ (66%), PhMeSi(OH)F (5.7%), (PhMeSiO)_x (*x* = 3, 1.5%; 4, 12%), and eight unidentified components (15%).

Reaction of Dichloromethylphenylsilane with TBAF

When TBAF (5.2 mL, 1.0 M) was injected into a flask containing PhMeSiCl₂ (0.50 g, 2.6 mmol) in distilled THF (5.0 mL), an exothermic reaction resulted. Analysis (GC) taken of an aliquot 15 minutes after the addition of TBAF showed the following composition: PhMeSiF₂ (32%), PhMeSi(OH)F (18%), XPhMeSiOSiMePhF (*X* = F, 41%; OH, 6.2%), and three unidentified components. After 1 day, the reaction mixture contained PhMeSiF₂ (50%), PhMeSi(OH)F (25%), XPhMeSiOSiMePhF (*X* = F, 17%; OH, 4.0%), F(PhMeSiO)₂SiMePhF (1.2%), and an unidentified component (1.8%). The usual workup after 2 days at room temperature provided 0.28 g of an orange oil. Analysis (GC) of the oil indicated only the presence of siloxanes, F(PhMeSiO)_xSiMePhF (*x* = 1, 7%; 2, 22%; 3, 33%) as well as peaks assigned to pentasiloxane (*x* = 4) and hexasiloxane (*x* = 5).

Reaction of Dichloromethylphenylsilane with CsF

To the flask containing a slurry of distilled acetonitrile (5.0 mL) and CsF (0.425 g, 2.78 mmol) was added MePhSiCl₂ (0.34 g, 1.40 mmol). After 4 days at room temperature, water (5 mL) and ether (5 mL) were added to the reaction flask. The ether layer was dried over sodium sulfate, and removal of the volatiles provided 0.15 g of a clear oil. A GC analysis of this oil showed the following composition: MePhSiF₂ (16%), MePhSi(OH)F (42%), FMePhSiOSiPhMeF (35%), FMePhSiOSiPhMeOH (3.9%), and F(MePhSiO)₂SiPhMeF (2.9%).

Reaction of Phenylsilane with TBAF

A very exothermic reaction occurred when TBAF (8.0 mL, 1.0 M) was added dropwise to a flask that contained PhSiH₃ (0.96 g, 8.10 mmol) in distilled THF (5.0 mL). An aliquot was prepared 1 hour after the addition of TBAF by adding a sample to bulk ether and deionized water and filtering through celite. No silicon-containing products were present in this aliquot. After 1 day, water (5 mL) and ether (5 mL) were added to the orange solution and the white solid (0.39 g) was removed by filtration. FTIR (KBr pellet): 1095 cm⁻¹ (SiOSi); 1430 cm⁻¹ (PhSi).

Reaction of Phenylsilane with dry CsF

Phenylsilane (0.90 g, 8.40 mmol) was added to a Schlenk tube containing dried acetonitrile (5 mL) and CsF (1.28 g, 8.43 mmol). Moderate gas evolution was observed for 1 minute after the addition of the silane. An aliquot was prepared after 15 minutes by adding a sample of the reaction mixture to distilled ether and removing the white solid by filtration through celite. Analysis (GC) showed no peaks up to 320°C. After 2 days stirring at room temperature, distilled ether was added to the orange-brown solution and the pale-yellow solid was removed by filtration. IR (KBr): 1104 cm⁻¹ (SiOSi); 1428 cm⁻¹ (PhSi); 2190 cm⁻¹ (HSi). Removal of the volatiles from the filtrate provided 0.72 g of viscous orange-yellow oil. IR (thin film): 1117 cm⁻¹ (SiOSi); 1428 cm⁻¹ (PhSi); 2190 cm⁻¹ (HSi); 3358 cm⁻¹ (HOSi).

ACKNOWLEDGMENT

The authors gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Additional support was provided by an Improved Research Quality Grant from the University of Missouri—St. Louis and a Brunngraber Fellowship (JLH).

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