

# Preparation of F(ArSiMe)<sub>2</sub>F and Observation of Crystallization-Induced Asymmetric Transformation in *meso*-/*rac*-F(ArSiMe)<sub>2</sub>F and Anion-Induced Epimerization of *meso*-F(ArSiMe)<sub>2</sub>F

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Fluorination of the hydrogen-terminated disilanes H[(*p*-XC<sub>6</sub>H<sub>4</sub>)SiMe]<sub>2</sub>H (X = H, F, OMe, Me) and H(<sup>n</sup>BuSiMe)<sub>2</sub>H has been achieved with CuF<sub>2</sub>·2H<sub>2</sub>O in refluxing CCl<sub>4</sub> to give fluorine-terminated oligomers initially as a 1:1 mixture of diastereomers. Higher yields of F[(*p*-XC<sub>6</sub>H<sub>4</sub>)SiMe]<sub>2</sub>F with fewer byproducts from silicon–silicon bond cleavage were achieved with CuCl<sub>2</sub>/CuI/KF in THF, and H(PhSiMe)<sub>3</sub>H was also successfully fluorinated with this mixture. Crystallization of the initially formed diastereomeric mixture of F[(*p*-XC<sub>6</sub>H<sub>4</sub>)SiMe]<sub>2</sub>F from solvent resulted in the isolation of the solid *meso* forms, while the mother liquors still contained the two diastereomers in an approximate 1:1 ratio. The enrichment of one of the diastereomers through crystallization meets the criteria for asymmetric transformation (AT). The structures of all four *meso*-F[(*p*-XC<sub>6</sub>H<sub>4</sub>)SiMe]<sub>2</sub>F compounds were determined by X-ray crystallography. Both fluoride and chloride salts cause epimerization of *meso*-F(ArSiMe)<sub>2</sub>F to a statistical mixture of *meso* and *rac* diastereomers.

## Introduction

One of the challenges in silicon chemistry is the development of methods that can be useful for the elaboration of functional groups in easily accessible organosilicon systems. Many of the methods that have been developed utilize monosilane precursors and are not necessarily transferable to disilanes and/or other silicon oligomers. Oligomers of the type H(PhMeSi)<sub>x</sub>H (x = 2–4) are readily available from the dehydrocoupling of the monosilane precursor, PhMeSiH<sub>2</sub>.<sup>1</sup> New oligomers may be formed from H(PhMeSi)<sub>x</sub>H through the controlled removal of the phenyl substituents with triflic acid and subsequent substitution of the silyl triflate<sup>1b</sup> produced. However, new oligomers may also be realized through the replacement of the SiH bonds in H(PhMeSi)<sub>x</sub>H. In the development of the conversion of SiH-terminated oligomers to SiF-terminated oligomers novel isomerization processes were observed in the diastereomers of the disilanes, F(ArMeSi)<sub>2</sub>F.<sup>2</sup> In this full report we describe the synthesis of F(PhMeSi)<sub>2</sub>F from hydrosilane precursors by three reactions adapted from those previously reported for monosilanes as well as the crystallization-induced asymmetric transformation (abbreviated as AT) of the 1,2-difluorodisilanes.

## Results

Fluorosilanes are usually prepared from the reaction of a chlorosilane with a metal or nonmetal fluoride or

with aqueous HF.<sup>3</sup> Formation of silicon oligomers that contain fluorine substituents generally has required a more cumbersome approach that involved removal of an organic group in an oligomer with acids such as sulfuric acid<sup>4</sup> and triflic acid<sup>5</sup> followed by treatment with a fluoride source (such as LiF or NH<sub>4</sub>HF<sub>2</sub>). Recently, the conversion of hydrosilanes to fluorosilanes by reaction with CuF<sub>2</sub>·2H<sub>2</sub>O/CCl<sub>4</sub><sup>6</sup> and CuCl<sub>2</sub>(CuI)/KF/THF (or Et<sub>2</sub>O)<sup>7</sup> has been reported, although only monosilane precursors were investigated. With both copper salt systems it is likely that the SiH is converted to SiCl, which then exchanges with the fluoride source, although the mechanisms are unknown.<sup>6,7</sup> Since 2 equiv of CuCl<sub>2</sub> is required per SiH bond, the use of the CuCl<sub>2</sub>(CuI)/KF system provides some control over the number of SiH bonds that are converted.

Dehydrocoupling of ArMeSiH<sub>2</sub> in the presence of cyclooctene catalyzed by Cp<sub>2</sub>TiCl<sub>2</sub>/2<sup>n</sup>BuLi provided the oligomers H(ArMeSi)<sub>x</sub>H (x = 2–4; Ar = C<sub>6</sub>H<sub>5</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>). The conditions of the condensation were selected to favor the disilane as the major product.<sup>1b</sup> The disilane H(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H was prepared by treating H(PhMeSi)<sub>2</sub>H with 2 equiv of triflic acid followed by addition of 2 equiv of *p*-FC<sub>6</sub>H<sub>4</sub>MgBr.

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These four disilanes, all as 1:1 mixtures of diastereomers, were then used as substrates for fluorination.

**Reaction of  $\alpha,\omega$ -Dihydrodisilanes with Copper Halides.** In the original report, reactions of monosilane substrates with  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  were conducted with an excess of the copper salt ( $\text{Cu/Si} \approx 3/1$ ) in refluxing  $\text{CCl}_4$  overnight.<sup>6</sup> When these conditions were employed for the fluorination of  $\text{H}(\text{PhSiMe})_2\text{H}$ , the major product was  $\text{PhMeSiF}_2$ , resulting from cleavage of the Si–Si bond. In subsequent experiments it was possible to observe a sudden exotherm after a variable initiation period of 1–3 h when the copper salts changed color from blue to blue-green. In most cases an aliquot of the reaction mixture at this point showed that the starting material had been consumed and that the desired product,  $\text{F}(\text{PhSiMe})_2\text{F}$ , had formed in addition to the monosilane,  $\text{PhMeSiF}_2$ . In some runs, chlorinated disilanes were observed after the onset of the exotherm, and in these cases heating was continued briefly until the chlorinated products disappeared. Additional heating was usually accompanied by increased formation of monosilane as well as production of the disiloxane  $\text{FPhMeSiOSiPhMeF}$  and decreased amounts of the desired 1,2-difluorodisilane. Since the reactions of  $\text{H}(\text{PhSiMe})_2\text{H}$  with  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  tended to result in the formation of  $\text{F}(\text{PhSiMe})_2\text{F}$  contaminated with  $\text{FPhMeSiOSiPhMeF}$ , which was difficult to remove, pure samples of  $\text{F}(\text{PhSiMe})_2\text{F}$  were prepared in the initial studies<sup>2</sup> by reaction of the trisilane,  $\text{H}(\text{PhSiMe})_3\text{H}$ , with  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . In this case both  $\text{F}(\text{PhSiMe})_2\text{F}$  and  $\text{F}(\text{PhSiMe})_3\text{F}$  were formed, as well as  $\text{PhMeSiF}_2$ . The trisilane was contaminated with a small percentage of trisiloxane.

The reaction of  $\text{H}(\text{PhSiMe})_x\text{H}$  with the combination  $\text{CuCl}_2(\text{CuI})/\text{KF}$  in THF at room temperature provided  $\text{F}(\text{PhSiMe})_x\text{F}$  ( $x = 2$  (92%), 3 (63%)), and fewer cleavage products were observed. The fluorination of  $\text{H}(p\text{-XC}_6\text{H}_4\text{-SiMe})_2\text{H}$  ( $X = \text{Me, OMe, F}$ ) under these conditions was also successful, producing  $\text{F}(\text{ArSiMe})_2\text{F}$  in yields from 78 to 85%. This milder fluorination method is more efficient and can also be used more effectively for the fluorination of oligomers higher than the disilane.

A more traditional route to fluorosilanes involves the treatment of chlorosilanes with  $\text{HF}/\text{EtOH}$ .<sup>9</sup> The disilane,  $\text{F}(\text{PhSiMe})_2\text{F}$ , was also prepared by this route in order to provide a reaction procedure that did not involve a metal-containing reagent. Chlorination of  $\text{H}(\text{PhSiMe})_2\text{H}$  with *N*-chlorosuccinimide followed by treatment with  $\text{HF}/\text{EtOH}$  provided  $\text{F}(\text{PhSiMe})_2\text{F}$  in 44% yield. No effort was made to maximize the yield.

**Isomerization of  $\text{rac-F}(\text{ArSiMe})_2\text{F}$  to  $\text{meso-F}(\text{ArSiMe})_2\text{F}$ .** The freshly distilled oil of the disilane  $\text{F}(\text{PhSiMe})_2\text{F}$  exhibited a 1:1 ratio of the two diastereomers (*meso* and *rac*). When the oil solidified, the ratio between the two diastereomers became 1:3. If the oil (1:1 ratio) was dissolved in hexanes and allowed to crystallize, a single diastereomer (55% based on the original mass) was obtained but the mother liquor still exhibited a 1:1 ratio of the two diastereomers. Continued crystallization from the mother liquor also provided a single diastereomer, while the solution maintained an approximate 1:1 ratio of the two diastereomers. Samples of  $\text{F}(\text{PhSiMe})_2\text{F}$  prepared from all three methods exhibited this transformation. A similar pattern was observed for the remaining  $\text{F}(\text{ArSiMe})_2\text{F}$  systems, although en-

richment of a single diastereomer in the  $\text{Ar} = p\text{-MeOC}_6\text{H}_4$  case required recrystallization from  $i\text{-PrOH}$ .<sup>10</sup> A single diastereomer when  $\text{Ar} = p\text{-MeOC}_6\text{H}_4$  could only be obtained from the slow evaporation of a hexane solution of a 2:1 (*meso:rac*) mixture. The isolated single diastereomer in each of the four cases corresponded to the isomer with the longer GC retention time and the more upfield of the two SiMe doublets in the  $^1\text{H}$  NMR spectra. The crystal structures of all four derivatives verified that the isolated diastereomer was the *meso* form.

The enrichment of one diastereomer through crystallization is a characteristic of the phenomenon of asymmetric transformation (AT).<sup>11</sup> The main requirement for the observation of AT is that epimerization of diastereomers occurs faster than crystallization. The use of crystallization-induced asymmetric transformation for control of heteroelement configuration has been described recently by Vedejs for oxazaborolidinone complexes in a series of papers.<sup>12</sup>

**Crystal Structures of  $\text{meso-F}(\text{ArSiMe})_2\text{F}$ .** The solid-state structures of all four isolated disilanes,  $\text{F}(p\text{-XC}_6\text{H}_4\text{SiMe})_2\text{F}$  ( $X = \text{H, F, OMe, Me}$ ), have been determined, and in each case the isolated diastereomer was the *meso* form. The ORTEP plots for the four structures are shown in Figure 1, and selected bond distances and angles are given in Table 1. The Si–Si bond distances are within the range of 2.33–2.37 Å found in molecules with little steric strain, and the Si–C distances are on the low end of typical lengths that fall between 1.86 and 1.91 Å. Such shortening is found when Si is bonded to  $\text{sp}^2$  C centers and/or to very electronegative elements.<sup>13</sup> The Si–F distance appears to be longer than is usually observed for four-coordinate silicon systems (1.500 Å) and is closer to values observed for Si–F in five-coordinate silicon derivatives (1.602 Å).<sup>14</sup> The F–Si–C angles are all less than the C–Si–C angles, consistent with Bent's rule.<sup>15</sup>

**Isomerization of  $\text{meso-F}(\text{ArMeSi})_2\text{F}$  to a  $\text{meso/rac}$  Mixture.** Addition of TBAF ( $\leq 10\%$  relative to the disilane) results in an exothermic reaction and immediate isomerization of the *meso* forms to the 1:1 statistical mixture of the *meso* and *rac* diastereomers. Larger concentrations of TBAF (20 mol %) cause cleavage of the Si–Si bond and formation of monosilanes. Attempts to slow the rate of the isomerization at lower temper-

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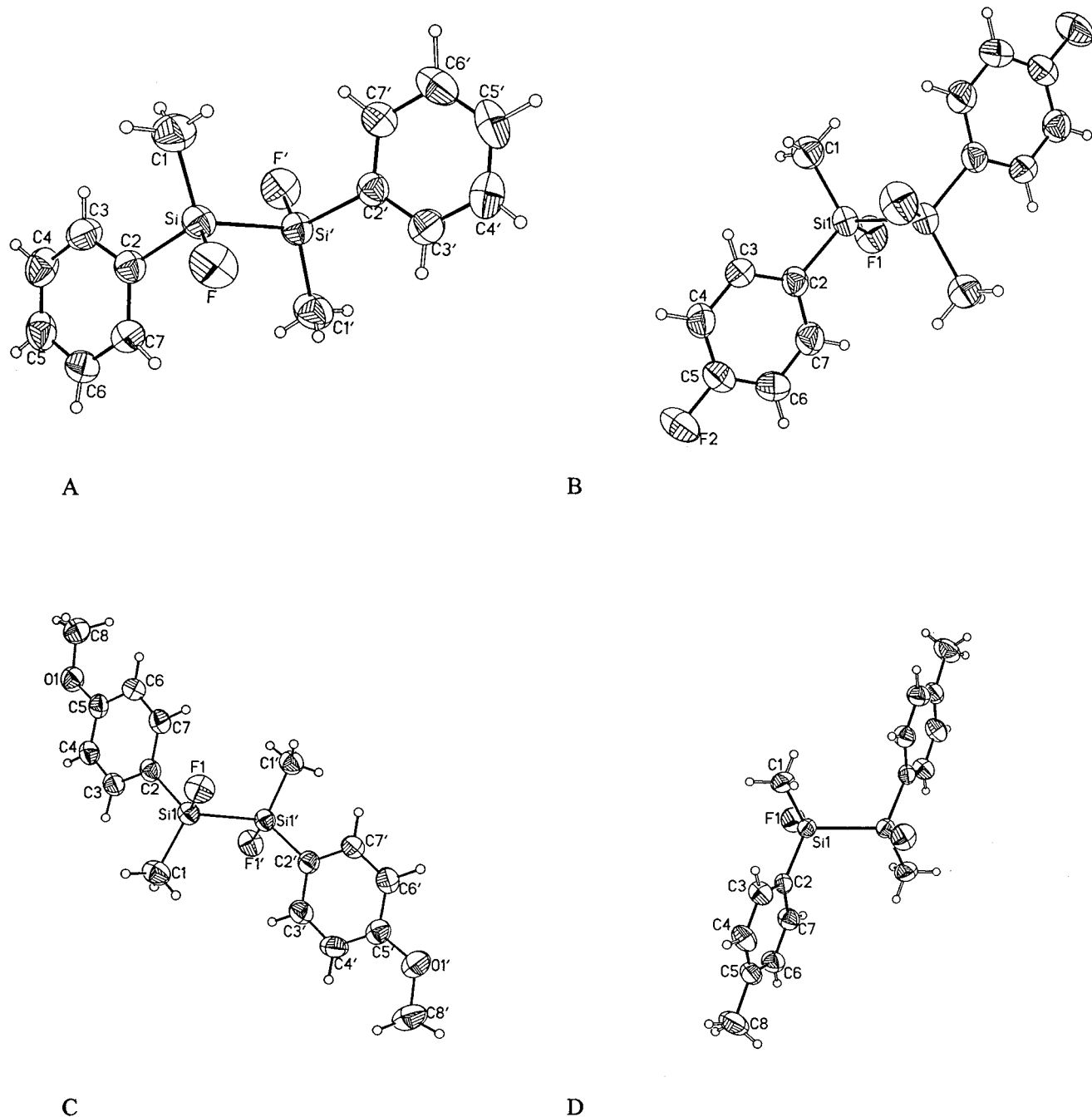
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**Figure 1.** ORTEP plots of  $\text{meso-F}(p\text{-X-C}_6\text{H}_4\text{SiCH}_3)_2\text{F}$  with 50% probability ellipsoids: (A)  $\text{X} = \text{H}$ ; (B)  $\text{X} = \text{F}$ ; (C)  $\text{X} = \text{OCH}_3$ ; (D)  $\text{X} = \text{CH}_3$ .

atures and with less aggressive fluoride sources such as  $[\text{Bu}_4\text{N}][\text{Ph}_3\text{SnF}_2]$  were unsuccessful, and covalent fluoride sources such as  $\text{Ph}_2\text{SiF}_2$  and  $\text{Ph}_3\text{SnF}$  failed to promote the isomerization. The ionic chloride  $\text{Bz}_2\text{Me}_2\text{N}^+\text{Cl}^-$  ( $\text{Bz} = \text{benzyl}$ ) also initiates isomerization of the *meso* diastereomer to the *rac* diastereomer, to form a 1:1 mixture of *meso* and *rac* forms, but more slowly than does fluoride ion. Covalent nucleophiles such as acetonitrile are capable of promoting conversion of the *meso* diastereomer to the statistical mixture of diastereomers, but not at a catalytic level.

### Discussion

**Halogenation.** The fluorination of SiH bonds in the  $\text{H}(\text{PhSiMe})_x\text{H}$  oligomers has been successfully accom-

plished by two routes that utilize  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  ( $x = 2, 3$ ) and  $\text{CuCl}_2/\text{CuI}/\text{KF}$  ( $x = 2, 3$ ) or by a third method that involves chlorination (NCS) followed by treatment with  $\text{HF}/\text{EtOH}$ . The highest yield of fluorine-terminated oligomers is produced from  $\text{CuCl}_2/\text{CuI}/\text{KF}$ , and this may be due, in part, to the fact that the combination of salts can be dried prior to use. The main problem with  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  as a fluorinating agent is that 2–3 equiv of the copper salt may be required for each SiH bond. Since cleavage of Si–Si bonds is observed with  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , an excess of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  and prolonged exposure of the oligomer substrates to the fluorinating conditions should be avoided. A second disadvantage is that the solvent  $\text{CCl}_4$  is required for effective transformations (THF and  $\text{ClCH}_2\text{CH}_2\text{Cl}$  provided either no products or poorer

**Table 1. Selected Bond Distances and Angles in *meso*-F(*p*-XC<sub>6</sub>H<sub>4</sub>SiCH<sub>3</sub>)<sub>2</sub>F**

param	X = H <sup>a</sup>	X = F	X = OMe	X = Me
Distances (Å)				
Si–Si	2.3477(10)	2.3460(19)	2.3421(7)	2.3410(13)
Si–F	1.6094(18)	1.6071(16)	1.6123(12)	1.6145(17)
	1.6103(17)		1.6160(12)	
Si–C(1) (Me)	1.841(4)	1.846(2)	1.847(2)	1.842(3)
	1.850(4)		1.849(2)	
Si–C(2) (Ar)	1.859(3)	1.865(2)	1.859(1)	1.856(2)
	1.858(3)		1.854(2)	
Angles (deg)				
F–Si–C(1)	107.71(16)	108.66(11)	108.12(10)	108.34(14)
	107.65(16)		108.25(9)	
F–Si–C(2)	106.79(11)	107.08(9)	106.11(8)	107.09(10)
	106.68(11)		106.38(8)	
F–Si–Si'	106.04(9)	105.55(7)	106.15(6)	105.03(7)
	105.58(9)		113.54(9)	
C(1)–Si–C(2)	112.53(15)	111.55(11)	112.27(11)	111.90(13)
	111.97(16)		112.58(10)	
C(3)–C(2)–C(7)	117.4(2)	117.08(18)	117.10(19)	116.8(2)
	117.1(3)		116.00(19)	
C(4)–C(5)–C(6)	119.5(3)	122.9(2)	119.8(2)	118.0(2)
	120.3(3)		119.5(2)	

<sup>a</sup> The second number listed for a specific parameter is the value for the primed atoms. <sup>b</sup> C(2) is bound to silicon, and C(5) is bound to the *para* substituent.

yields<sup>6</sup>), and CCl<sub>4</sub> is proposed to be responsible for the formation of intermediate silicon–chlorine bonds.<sup>16</sup> The salt combination that includes CuCl<sub>2</sub> provided milder, room-temperature conditions for fluorination and did not appear to promote significant cleavage of Si–Si bonds. In both routes using copper halide the sequence of reactions leading from SiH to SiF may involve conversion of SiH to SiCl prior to formation of SiF.

The CuCl<sub>2</sub>/CuI combination in ether has been used to chlorinate both monosilanes and disilanes, including H(PhSiMe)<sub>2</sub>H.<sup>8</sup> The procedure utilized >4 equiv of CuCl<sub>2</sub> and required 122 h to produce a 79% yield of Cl(PhSiMe)<sub>2</sub>Cl. The mechanism of the reaction is not known, but the authors proposed that iodosilanes were formed, followed by reaction of the iodosilane with CuCl<sub>2</sub> to give the chlorosilane.<sup>8</sup> The same investigators also developed the combination of CuCl<sub>2</sub>(CuI)/KF as a fluorinating agent for monosilanes. Since CuI/KF was an ineffective fluorinating agent in the absence of CuCl<sub>2</sub>, chlorination of SiH was assumed to precede the formation of the fluorosilane.<sup>7</sup> However, the halogenation of disilanes with CuCl<sub>2</sub>/CuI/KF may be more complicated, as the fluorination of both SiH bonds occurs much more rapidly (4–5 h in THF) than is suggested from the corresponding chlorination with CuCl<sub>2</sub>/CuI (≥120 h in Et<sub>2</sub>O<sup>8</sup> or THF<sup>17</sup>). With CuCl<sub>2</sub>/CuI, the halogenation of H(PhSiMe)<sub>2</sub>Cl clearly occurs much more slowly than the halogenation of H(PhSiMe)<sub>2</sub>H.<sup>8</sup> Thus, it appears that, in chlorination of the disilane, the incorporation of the first SiCl deactivates the second SiH bond to chlorine substitution. It is possible that when KF is present in the CuCl<sub>2</sub>/CuI mixture, the H(PhSiMe)<sub>2</sub>Cl (if formed) is rapidly converted to H(PhSiMe)<sub>2</sub>F and subsequent

deactivation to the second halogen substitution does not occur. This implies that the mixed halide Cl(PhSiMe)<sub>2</sub>F, which is observed in the reaction mixtures, forms from H(PhSiMe)<sub>2</sub>F much more rapidly than does Cl(PhSiMe)<sub>2</sub>Cl from H(PhSiMe)<sub>2</sub>Cl. However, another, and possibly more likely, explanation is that the combination of CuCl<sub>2</sub> and KF forms a more effective halogenating agent (in THF) that then provides F(PhSiMe)<sub>2</sub>F at a more rapid rate.

**Crystallization-Induced Asymmetric Transformation (AT).** The conversion of *rac*-F(PhSiMe)<sub>2</sub>F to the *meso* diastereomer became obvious during the first attempts to recrystallize the 1:1 mixture of diastereomers of F(PhSiMe)<sub>2</sub>F. The formation of a single diastereomer upon recrystallization is not without precedence, but a mother liquor that retained the *meso* and *rac* isomers in approximately a 1:1 ratio was not anticipated. These observations are characteristic of crystallization-induced asymmetric transformation or AT.<sup>11</sup> The requirements for the observation of crystallization induced AT are (1) rapid interconversion between diastereomers and (2) one of the diastereomers forming a crystalline solid. Cases of the AT phenomenon may be traced back to the mid-19th century but were not recognized at the time.<sup>11b,d</sup> An early example of a silicon-containing system that exhibited AT is the 2-siloxazolidone-5-heterocycle formed from the reaction of PhMeSi(MeNac)<sub>2</sub> with  $\alpha$ -amino acids.<sup>18</sup>

The isomerization of the diastereomers of 1,2-difluoro-1,2-diaryl-1,2-dimethyldisilanes meets the criteria established for crystallization-induced AT. To determine if the AT phenomenon persists if the aryl groups in the disilane are replaced with alkyl groups (alkyl  $\neq$  Me), F(BuSiMe)<sub>2</sub>F (two diastereomers in a 1:1 ratio) was prepared as an acyclic model of the previously studied 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane. Both the *cis* and *trans* forms of the cyclic disilane are liquids at room temperature. Slow isomerization of the *trans* form (neat) to the *cis* form occurred over 18 days in a sealed ampule to give a *cis/trans* ratio of approximately 1:3.4. In this case the stereomutation occurred faster in the presence of an excess of EtOH.<sup>19</sup> When a sample of F(BuSiMe)<sub>2</sub>F (1:1 mixture of diastereomers) was dissolved in an equal volume of hexane and stored at 0 °C for 1 week, slow epimerization to a 3:2 mixture of diastereomers was observed. No conditions have yet been found where a solid formed from the oil or from the oil dissolved in solvent. Since no solids are involved in the stereomutation of the disilacyclohexane example or of F(BuSiMe)<sub>2</sub>F, the observed stereomutation does not fit the currently established criteria for an AT process. It is possible that stereomutation may simply be a general feature of 1,2-difluorodisilanes.

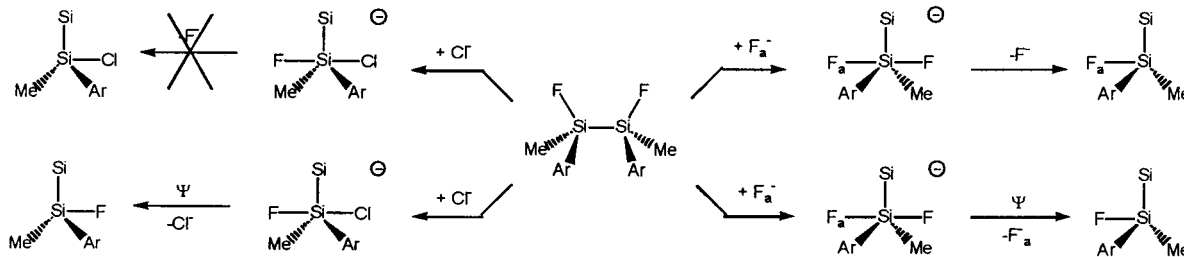
Additional examples of the AT phenomenon probably exist in disilane chemistry, but these are not readily identified unless data are available for both the isolated solid and the resultant mother liquor. Certainly, disilane cases in which substitution reactions are performed on a 1:1 mixture of diastereomers resulting in diastereomeric products in *other than* a 1:1 ratio (in the absence

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(17) The monochlorination of H(PhSiMe)<sub>2</sub>H with SOCl<sub>2</sub>/CCl<sub>4</sub>, NCS/CCl<sub>4</sub>, or CuCl<sub>2</sub>(CuI)/THF occurs within 3 h. Introduction of a second chlorine to give Cl(PhSiMe)<sub>2</sub>Cl requires 72 h (SOCl<sub>2</sub>) to ≥120 h (NCS or CuCl<sub>2</sub>): Trankler, K. A.; Corey, J. Y. Unpublished observations.

(18) However, this case also was not described in terms of the AT phenomenon: Klebe, J. F.; Finbeiner, H. *J. Am. Chem. Soc.* **1968**, *90*, 7255–7261.

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**Figure 2.** Possible epimerization pathways for reaction of  $\text{meso-F}(\text{ArSiMe})_2\text{F}$  with  $\text{F}^-$  (exchange or pseudorotation) or  $\text{Cl}^-$  (pseudorotation). Substituents at the second silicon center are omitted for clarity.

of reagents that could direct chirality) are suspect. There are at least two recent examples that fit this description that involve 1,2-dichlorodisilane derivatives. Tanaka reported that the reaction of  $\text{Me}_3\text{Si}(\text{PhSiOTf})_2\text{SiMe}_3$  (1:1 mixture of diastereomers) with  $\text{CH}_2\text{BrCl}/\text{BuLi}$  gave  $\text{Me}_3\text{Si}(\text{PhSiCH}_2\text{Cl})_2\text{SiMe}_3$  as an oil that solidified to a single diastereomer (80% yield; unknown stereochemistry).<sup>20</sup> A second example in the same study involved the reaction of  $\text{Cl}(\text{RSiCH}_2\text{Cl})_2\text{Cl}$  ( $\text{R} = \text{SiMe}_3$ ; an oil as a 1:1 mixture of diastereomers) with  $\text{MeCON}(\text{Me})\text{SiMe}_3$  to

give  $\text{Cl}[\text{RSiCH}_2\text{N}(\text{Me})\text{C}(\text{O})\text{Me}]_2\text{Cl}$ <sup>21</sup> as a solid that was recrystallized from hexane to give the *rac* isomer in 81% yield with no trace of the *meso* form.<sup>20</sup> Another possible example involving a 1,2-dichlorodisilane is  $\text{Cl}(\text{MeSiNMePh})_2\text{Cl}$  prepared from reaction of  $\text{PhMeNH}$  with 1,2- $\text{Me}_2\text{Si}_2\text{Cl}_4$ . The crude product was recrystallized from pentane/ether to give a solid that contained a 1:6 mixture of *meso* and *rac* diastereomers.<sup>22</sup>

It is not clear whether changing the halide in  $\text{F}(\text{PhSiMe})_2\text{F}$  to  $\text{Cl}(\text{PhSiMe})_2\text{Cl}$  results in the retention of the AT phenomenon. An attempt to obtain a single diastereomer of  $\text{Cl}(\text{PhSiMe})_2\text{Cl}$ , prepared as a 1:1 mixture of diastereomers from reaction of  $\text{PhMgX}$  with 1,2- $\text{Me}_2\text{Si}_2\text{Cl}_4$ , by recrystallization from hexane failed.<sup>19</sup> However, recently, *meso-Cl}(\text{PhSiMe})\_2\text{Cl} was isolated by recrystallization from pentanes and crystallographically characterized, but the method of preparation and isolation of the diastereomers was not provided.<sup>23</sup> It is intriguing that in two of the three 1,2-dichlorodisilane systems that were described in the previous paragraph in this section the *rac* form is enhanced, whereas in the 1,2-difluorodisilanes that are the subject of the current study it is the *meso* form that is enhanced.*

**Isomerization of *meso*-1,2-Difluorodisilanes.** The return of  $\text{meso-F}(\text{ArSiMe})_2\text{F}$  to the statistical mixture of 1:1 *meso* and *rac* disilanes is achieved rapidly by addition of catalytic quantities (<10%) of ionic fluoride sources. The isomerization is rapid even at  $-90^\circ\text{C}$  (toluene- $d_8$ ). A similar isomerization can also be promoted by an ionic chloride source such as  $\text{Bz}_2\text{Me}_2\text{N}^+\text{Cl}^-$  ( $\text{Bz} = \text{benzyl}$ ), but at a slower rate than that produced by  $\text{F}^-$ . Whereas  $\text{meso-F}(\text{PhSiMe})_2\text{F}$  is isomerized by TBAF too rapidly to measure by  $^1\text{H}$  NMR spectroscopy, the epimerization with  $\text{Bz}_2\text{Me}_2\text{N}^+\text{Cl}^-$  (20 mol %) to a 1:1 ratio of *meso* and *rac* isomers occurs over a 5 h period. No chlorosilane products resulting from exchange of  $\text{Cl}^-$  with  $\text{SiF}$  were observed when the statistical mixture of  $\text{F}(\text{PhSiMe})_2\text{F}$  diastereomers had been produced. A GC trace of a sample of  $\text{meso-F}(\text{PhSiMe})_2\text{F}$  dissolved in acetonitrile- $d_3$  showed that epimerization to a statistical mixture of diastereomers had occurred.

The reaction of ammonium halides with monosilanes,  $\text{R}_3\text{Si}^*\text{X}$  ( $\text{R}_3 = \alpha\text{-Naph}(\text{Ph})\text{Me}$ ), results in racemization ( $\text{X} = \text{Cl}$ ; halide = Cl, Br, I) or exchange ( $\text{X} = \text{Cl}$ , halide = F (90% inversion);  $\text{X} = \text{Br}$ , halide =  $\text{Cl}^-$  (predominant inversion)),<sup>24</sup> Racemization of  $\text{R}_3\text{Si}^*\text{F}$  occurs in the presence of  $\text{R}'\text{NH}_3^+\text{F}^-$  (0.01–1% relative to the silane;  $\text{R}' = \text{c-C}_6\text{H}_{11}$ ), and the authors favored an  $\text{S}_{\text{N}}2$ -Si fluoride–fluoride exchange mechanism.<sup>25</sup> The racemization of  $\text{R}_3\text{Si}^*\text{F}$  by  $\text{R}'\text{NH}_3^+\text{Cl}^-$  ( $\text{R} = \text{c-C}_6\text{H}_{11}$ ) also appears to occur<sup>26</sup> but is complicated by autocatalytic kinetics due to formation of  $\text{RNH}_3^+\text{F}^-$ .<sup>25</sup> Racemization of  $\text{R}_3\text{Si}^*\text{F}$  by nucleophiles without  $\text{F}^-$  displacement has been observed (referred to as  $\text{S}_{\text{N}}2^*\text{-Si}$  with EO return<sup>24</sup> and later in terms of pseudorotation of five-coordinate intermediates by Sommer<sup>25</sup>).<sup>27</sup> This type of process could account for the epimerization observed when  $\text{F}(\text{ArSiMe})_2\text{F}$  is dissolved in  $\text{CH}_3\text{CN}$  or, in the current study, when ionic  $\text{F}^-$  is added.

A tentative rationale for the *anion*-induced epimerization of  $\text{meso-F}(\text{ArSiMe})_2\text{F}$  by  $(\text{n-Bu})_4\text{N}^+\text{F}^-$  and by  $\text{Bz}_2\text{Me}_2\text{N}^+\text{Cl}^-$  is proposed in Figure 2. It is probable that the epimerization caused by  $\text{F}^-$  involves a direct  $\text{S}_{\text{N}}2$  displacement of  $\text{SiF}$  by  $\text{F}^-$  (inversion of the silicon center and exchange of fluoride), although a contribution from the pseudorotation mechanism is also possible. The epimerization initiated by  $\text{Cl}^-$  does not lead to an  $\text{S}_{\text{N}}2$  type displacement of  $\text{F}^-$  (i.e., no  $\text{Cl}^-$  is incorporated into the disilane); thus, a pseudorotation mechanism is more probable in this case. Similar proposals have been suggested for the isomerization of *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane<sup>19</sup> and the alcohol-induced racemization of a chiral fluorosilane without displacement of fluoride ion.<sup>11</sup> The observed rate dif-

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(26) The racemization of  $\text{R}_3\text{Si}^*\text{F}$  by  $\text{RNH}_3^+\text{Cl}^-$  ( $\text{R} = \text{c-C}_6\text{H}_{11}$ ) was examined in  $\text{MeOH}/\text{CCl}_4$  mixtures and is complicated by autocatalytic kinetics due to formation of  $\text{RNH}_3^+\text{F}^-$  from  $\text{HF}$  generated during the course of the racemization.<sup>23</sup>

(27) (a) Bassindale, A., Reaction Mechanisms of Nucleophilic Attack at silicon. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Part 1, Chapter 13. (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43–198. (c) Sommer, L. H., *Stereochemistry, Mechanism and Silicon*; McGraw-Hill: New York, 1965. (d) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1981**, *74*, 1–28.

ference between the  $F^-$ -induced epimerization and the  $Cl^-$ -induced epimerization could result from the operation of two different mechanisms, and this possibility is currently being explored.

Tamao and co-workers have shown that difluorosilicates derived from triorganofluorosilanes can be stabilized in the presence of [2.2.2]cryptand and the adducts isolated as stable salts.<sup>28</sup> However, when *meso*- $F(PhSiMe)_2F$  was treated with dried KF and [2.2.2]-cryptand in benzene, no product identifiable as  $[FPhMeSiSiPhMeF_2]^- [K^+ / [2.2.2]cryptand]$  was observed.

### Conclusion

This study has shown that the fluorination of SiH bonds in hydrogen-terminated silicon oligomers by methods originally developed for monosilane substrates can be employed successfully with suitable modification of the published conditions. The combination  $CuCl_2/Cu/KF$  in THF (or  $Et_2O$ ) appears to provide higher yields of fluorine-terminated oligomers, but both this combination and that of  $CuF_2 \cdot 2H_2O/CCl_4$  give products of silicon-silicon bond cleavage on prolonged contact with the metal salts. The fluorination of  $H(ArSiMe)_2H$  (1:1 ratio of diastereomers) provides  $F(ArSiMe)_2F$  initially as a 1:1 mixture of diastereomers. On solidification of the distilled oil or upon crystallization of the oil dissolved in hexane (or  $^1PrOH$ ), the *meso* diastereomer is isolated, while analysis of the filtrate reveals an approximate 1:1 ratio of the diastereomers. This behavior is characteristic of crystallization-induced asymmetric transformation (AT).<sup>11</sup> The role of AT in organosilicon chemistry has certainly not been recognized as such, nor has it been exploited as a tool to control stereochemistry. A recent example of the utility of AT is the  $AgF$ -catalyzed epimerization of  $((R)-PhMeCH)_2NSiPh(\alpha-Naph)F$  (as a mixture of the  $R,R_{Si}$  and  $R,S_{Si}$  diastereomers) in  $CH_3NO_2$ , where the  $R,R_{Si}$  form precipitated in 68% yield with 96% de.<sup>29</sup> Although not described as such, this system is an example that meets the criteria for AT. The observation of AT in this case illustrated a new route to optically active silicon compounds in two steps through reaction of the  $R,R_{Si}$  form with MeLi followed by reaction with  $HBF_4 \cdot OEt_2$  to give  $(R)-(\alpha-Naph)PhMeSiF$ .<sup>29</sup>

The isolation of a single diastereomer of  $F(PhSiMe)_2F$  also allows conversion to other *meso* derivatives through nucleophilic substitution processes that usually exhibit high stereoselectivity. To illustrate this possibility, *meso*- $F(PhSiMe)_2F$  was reduced with  $LiAlH_4$  to give *meso*- $H(PhSiMe)_2H$  as a white crystalline solid in 63% yield after one recrystallization from hexane.

The precipitation of *meso*- $F(ArSiMe)_2F$  from a solution of an initially statistical mixture of the two diastereomers combined with the observation of a *meso:rac* ratio near 1:1 in the mother liquor after removal of the precipitate requires conversion of the *rac* diastereomer to the *meso* diastereomer and an equilibration of the two forms. Currently we speculate that such an epimerization *in the absence* of external nucleophiles may occur by an intermolecular exchange through  $Si \cdots F \cdots Si$

bridges. Thus, when external nucleophiles are absent, the *rac* form converts to the *meso* form when the *meso* form is removed from solution through precipitation. A related bridged complex has been proposed as the intermediate in halide exchange between  $(\alpha-Naph)-PhSiHF$  and  $Me_3SiCl$ , although this particular process is assisted by a nucleophile and the proposed intermediate is six-coordinate.<sup>30</sup> In the presence of an external nucleophile the reverse process, the conversion of the *meso* form to a statistical mixture of diastereomers, occurs, although the rate of the epimerization can be a function of the nature of the external nucleophile. In the present case, epimerization induced by  $Cl^-$  is slower than that caused by  $F^-$ . A plausible (but not exclusive) explanation for the isomerization and rate difference could be an  $S_N2$  type substitution with fluoride ion but formation of an intermediate five-coordinate complex followed by pseudorotation with chloride ion. A pseudorotation process may also occur with fluoride ion, and this possibility cannot be excluded at this time, nor can a process that involves a six-coordinate silicon center. In the 1,2-disilanes that are the subject of the current study, the presence of a nucleophile is required to maintain a statistical mixture of diastereomers. In the absence of such a nucleophile, precipitation of the more stable diastereomer occurs (in a suitable solvent) and the mixture becomes enhanced in one of the forms (in this case the *meso* form) or converted to one form (the more stable crystalline solid) and crystallization-induced AT is observed.

The fact that silicon centers can exhibit an expanded octet in contrast to carbon suggests that AT processes could be observed with greater frequency in silicon chemistry. Our current efforts are focused on attempts to elucidate the structural components necessary to observe isomerization and epimerization phenomena in silicon oligomer chemistry through examination of various substituents, including other 1,2-dihalides (i.e.,  $Cl-(ArSiMe)_2Cl$ ), as well as to examine other nucleophiles that may cause epimerization of *meso*-disilanes.

### Experimental Section

**General Considerations.** All reactions were performed in flame-dried glassware under dry nitrogen on a dual-manifold Schlenk line. Solvents were distilled from Na/benzophenone or Na/9-fluorenone<sup>31</sup> prior to use.  $CCl_4$  was stored over molecular sieves. The following reagents were used as supplied commercially:  $p-FC_6H_4Br$ ,  $LiAlH_4$  (LAH),  $CuF_2 \cdot 2H_2O$ ,  $^tBu_4N^+F^-$  (TBAF; 1.0 M in THF, <5%  $H_2O$ ),  $Bz_2Me_2N^+Cl^-$  (Bz = benzyl),  $CH_3CN$ , HF (48%), *N*-chlorosuccinimide, and [2.2.2]cryptand. Commercial HOTf was distilled before use. The following reagents were prepared by literature methods:  $XC_6H_4MeSiH_2$  (X = H,<sup>32</sup> Me,<sup>32</sup> OMe<sup>33</sup>),  $H(PhSiMe)_2H$ ,<sup>1a</sup>  $H(PhSiMe)_3H$ ,<sup>1a</sup>  $H(BuSiMe)_2H$ ,<sup>1b</sup>  $F(PhSiMe)_2F$ ,<sup>2</sup>  $[^nBu_4N][Ph_3SnF_2]$ ,<sup>34</sup> and  $Ph_2-SiF_2$ .<sup>6</sup>

High-resolution mass spectral data were collected using a JEOL MStation JMS700. Low-resolution mass spectral data (EI, 70 eV) were collected on a Hewlett-Packard Model 5988A

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instrument. Gas chromatographic analyses were performed on a Shimadzu Model GC-14A gas chromatograph utilizing a 24 m DB-5 capillary column. Preparative gas chromatography was performed on a Varian Model 705 (15% SE30; 20 ft × 3/8 in. column). Proton, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} nuclear magnetic resonance spectra were recorded using either a Varian Unity plus 300 equipped with a tunable broadband probe or a Bruker ARX-500 instrument equipped with a broadband or inverse probe. Spectra are referenced internally to residual solvent peaks (CHCl<sub>3</sub> or C<sub>6</sub>H<sub>6</sub>) or to TMS. <sup>19</sup>F NMR data were collected on a Varian XL-300 with a multiple-nucleus probe using CFCl<sub>3</sub> or C<sub>6</sub>F<sub>6</sub> as an external reference or on the Bruker ARX-500. Spectra were recorded at room temperature unless specified otherwise; the chemical shifts of the centers of multiplets are listed, and coupling constants are given in Hz. The DEPT sequence was utilized in collecting <sup>29</sup>Si NMR data.<sup>35</sup>

Unless specified otherwise, Kugelrohr distillations were used to purify liquid samples. Melting points are uncorrected and were obtained on either a Hoover capillary apparatus (oil bath) or an Electrotherm Engineering Ltd. Digital melting point apparatus, Series IA9100. Analyses were performed by Atlantic Microlab, Inc.

**H(*p*-MeC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H.** Titanocene dichloride (1.22 g, 4.90 mmol) was added to toluene (2.5 mL) and cooled to 0 °C with stirring. Cyclooctene (5.0 mL) and *n*-butyllithium (3.9 mL, 2.5 M) were added by syringe, resulting in the formation of a deep blue mixture. *p*-Tolylmethylsilane (10.0 g, 73.5 mmol) was added, and the reaction mixture was stirred at 90 °C and monitored by GC. The reaction was quenched after 5 h by adding 100 mL of hexanes and bubbling air through the mixture. The insoluble material was removed by filtration, and the volatiles were removed. The resultant oil was distilled to give H(*p*-TolSiMe)<sub>2</sub>H (bp 120–135 °C/0.15 mmHg; 2.88 g, 29%) as a colorless oil. Other oligomers, tri- and tetrasilanes, were distilled from the residue (bp 140–240 °C/0.05 mmHg, 2.2 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.40 (overlapping d, SiCH<sub>3</sub>), 2.32 (s, ArCH<sub>3</sub>), 4.37 (overlapping q, SiH), 7.12 (d, ArH), 7.34 (d, ArH). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>): δ -37.32, -37.81. HRMS: *m/e* calcd for <sup>12</sup>C<sub>16</sub><sup>1</sup>H<sub>22</sub><sup>28</sup>Si<sub>2</sub> 270.1260; obsd 270.1261.

**H(*p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H.** Titanocene dichloride (0.178 g, 0.715 mmol) in toluene (2.5 mL) was cooled to 0 °C. Cyclooctene (5.0 mL) and *n*-butyllithium (0.58 mL, 2.5 M) were added, followed by (*p*-methoxyphenyl)methylsilane (5.73 g, 37.7 mmol). The reaction was conducted at 23–28 °C for 96 h. Quenching and distillation provided H(*p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H (bp 130–140 °C/0.1 mmHg; 2.43 g, 43%) as a colorless oil. Other oligomers were also obtained (bp 200–240 °C/0.15 mmHg, 1.45 g). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.41 (overlapping d, SiCH<sub>3</sub>), 3.26 (s, OCH<sub>3</sub>), 4.73 (overlapping q, SiH), 6.80 (m, ArH), 7.43 (m, ArH). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -37.00, -37.43. HRMS: *m/e* calcd for <sup>12</sup>C<sub>16</sub><sup>1</sup>H<sub>22</sub><sup>16</sup>O<sub>2</sub><sup>28</sup>Si<sub>2</sub> 302.1158, obsd 302.1150.

**H(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H.** H(PhMeSi)<sub>2</sub>H (6.00 g, 24.8 mmol) was added to 30 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the solution was cooled to -23 °C (CCl<sub>4</sub>, dry ice bath). HOTf (8.9 mL, 0.10 mol) was then added by syringe with stirring, resulting in a brown viscous mixture. This was stirred at room temperature for 30 min. The Grignard reagent was prepared separately by the slow addition of BrC<sub>6</sub>H<sub>4</sub>F (13.0 mL, 118 mmol) to Mg (3.84 g, 158 mmol) in 150 mL of Et<sub>2</sub>O followed by reflux for 45 min. The Grignard reagent was added to the silyl triflate dropwise at 0 °C, and the mixture was stirred for an additional 1 h at 0 °C and allowed to stand overnight at room temperature. Deionized water (200 mL) was then added along with saturated NH<sub>4</sub>Cl to quench the mixture. The Et<sub>2</sub>O layer was collected, and the aqueous layer was washed with portions of Et<sub>2</sub>O. The combined organic layers were dried over anhydrous sodium sulfate. The volatiles were removed in vacuo, resulting in a pale yellow oil which was distilled to give H(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H

(bp 80–95 °C/0.05 mmHg; 6.24 g, 91%) as a colorless oil. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.24 (2 overlapping d, SiCH<sub>3</sub>), 3.49 (2 overlapping q, SiH), 6.79 (m, ArH), 7.15 (m, ArH). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -35.77, -37.65. <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>): δ -116.27 (m), -111.9 (m). HRMS: *m/e* calcd for <sup>12</sup>C<sub>14</sub><sup>1</sup>H<sub>22</sub><sup>28</sup>Si<sub>2</sub><sup>19</sup>F<sub>2</sub> 278.0759, obsd 278.0758.

**Fluorination of H(ArSiMe)<sub>2</sub>H with CuF<sub>2</sub>·2H<sub>2</sub>O (General).** A mixture of H(ArSiMe)<sub>2</sub>H (*x* = 2, 3; 4–5 mmol), CuF<sub>2</sub>·2H<sub>2</sub>O (12–15 mmol), and CCl<sub>4</sub> (20 mL) was added to a three-necked flask fitted with a condenser, and the slurry was heated to reflux. After a variable induction period (usually 1–3 h) an exotherm occurred and the insoluble blue salts turned to a pale blue-green or brown color. The color change in the salts usually signaled the end of the reaction, as indicated by gas chromatographic analysis of an aliquot. If the substitution of both SiH bonds was incomplete, as indicated by the presence of H(ArSiMe)<sub>2</sub>F by GCMS, heating was continued until the starting material was consumed and the intermediate monofluorinated or the chlorinated disilanes had been converted to the 1,2-difluorodisilane. Prolonged heating in the presence of the copper salts should be avoided for optimum yields of F(ArSiMe)<sub>2</sub>F. Several byproducts were observed and increased in percentage after continued heating in the presence of the copper salts. After it was cooled, the reaction mixture was filtered through Celite and the solvent removed. Kugelrohr distillation of the resultant liquid gave a colorless oil containing both *meso* and *rac* diastereomers of F(ArSiMe)<sub>2</sub>F by GC, GCMS, and <sup>1</sup>H NMR. The most abundant byproducts observed in the fluorination with CuF<sub>2</sub>·2H<sub>2</sub>O were associated with SiSi bond cleavage that resulted in the formation of ArMeSiF<sub>2</sub> and ArMeSiHF, which were identified by GCMS. Ar = Ph: GCMS for PhMeSiF<sub>2</sub> (*m/e* assignment, % of base peak) 158 (M<sup>+</sup>, 48%), 143 [(M - Me)<sup>+</sup>, 100%], 81 [(M - Ph)<sup>+</sup>, 12%]; GCMS for PhMeSiHF (*m/e* assignment, % of base peak) 140 (M<sup>+</sup>, 13%), 139 [(P - H)<sup>+</sup>, 100%], 125 [(P - Me)<sup>+</sup>, 21%]. The monosilanes were observed as approximately 10% of the products when half of the starting material had been consumed (Ar = Ph).

Varying amounts of both diastereomers of the disiloxane (FArSiMe)<sub>2</sub>O were also observed. Ar = Ph: GCMS for (FPhSiMe)<sub>2</sub>O (*m/e* assignment, % of base peak) 294 (M<sup>+</sup>, 75%), 279 [(M - Me)<sup>+</sup>, 86%], 201 [(M - Me - C<sub>6</sub>H<sub>5</sub>)<sup>+</sup>, 100%].

**F(*p*-MeC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (2b).** Reaction of H(*p*-MeC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H (3.2 g, 7.9 mmol) with CuF<sub>2</sub>·2H<sub>2</sub>O (8.0 g, 58 mmol) in CCl<sub>4</sub> (20 mL) gave colorless F(*p*-MeC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (bp 118–130 °C/0.2 mmHg, 1.23 g, 51%) containing [F(*p*-MeC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>O] (1.6% by GC). The distillate solidifies, and recrystallization from hexanes provided white, crystalline *meso*-**2b** (0.31 g, containing 4% *rac*-**2b**), mp 71.8–73.1 °C. Data for *meso*-**2b** are as follows. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.51 (A<sub>3</sub>B<sub>3</sub>XY, SiCH<sub>3</sub>), 2.0 (s, ArCH<sub>3</sub>), 6.99 (d, CH), 7.52 (d, CH). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.59 (J<sub>SiF</sub> = 309 Hz, J<sub>SiF</sub> = 36 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (127 MHz, C<sub>6</sub>D<sub>6</sub>): δ -0.83 (dd, J<sub>CF</sub> = 7.2 Hz, J<sub>CF</sub> = 4.8 Hz, SiCH<sub>3</sub>), 21.9 (s, CCH<sub>3</sub>), 131.2 (s), 132.2 (m), 133.6 (s), 139.6 (s). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>): δ -179.9 (m). Mass spectrum (*m/e* relative intensities): 306 (M<sup>+</sup>, 2.3), 225 (Me(*p*-Tol)<sub>2</sub>Si<sup>+</sup>, 100), 134 (Me(*p*-Tol)Si<sup>+</sup>, 44), 119 ((*p*-Tol)Si<sup>+</sup>, 32). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>Si<sub>2</sub>F<sub>2</sub>: C, 62.70; H, 6.58. Found: C, 62.72; H, 6.58. The sample utilized for the structure determination was further recrystallized from <sup>1</sup>PrOH.

Cooling of the filtrate from the initial recrystallization to -52 °C provided a second crop, 0.22 g (*meso/rac* = 88/12). The hexanes in the filtrate were removed and the residue recrystallized from EtOH at -52 °C to give a third crop, 0.21 g (*meso/rac* = 94/6; containing 3.5% {F(*p*-Tol)MeSi}<sub>2</sub>O). The filtrate from the third crop showed a 1:1 ratio of *meso* and *rac* isomers of **2b**.

**F(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (2c).** Reaction of H(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H (0.754 g, 2.71 mmol) with CuF<sub>2</sub>·2H<sub>2</sub>O (2.6 g, 19 mmol) in CCl<sub>4</sub> (18 mL) gave colorless F(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (bp 105–135 °C/0.1 mmHg, 0.46 g, 54%). The distillate solidifies, and recryst-

(35) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193–218.

tallization from hexanes provided white, crystalline *meso-2c*, mp 61.6–62.1 °C. Data for *meso-2c* are as follows. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.37 (A<sub>3</sub>B<sub>3</sub>XY, SiCH<sub>3</sub>), 6.79 (m, arom CH), 7.29 (m, arom CH). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.08 (dd, <sup>1</sup>J<sub>SiF</sub> = 310 Hz, <sup>2</sup>J<sub>SiF</sub> = 36 Hz). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>): δ -109.1 (m), -179.8 (m). Mass spectrum (*m/e* (relative intensities)): 278 (P<sup>+</sup>, 4.6), 233 (Me(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si<sup>+</sup>, 100), 139 (Me(*p*-FC<sub>6</sub>H<sub>4</sub>)SiH<sup>+</sup>, 86), 123 ((*p*-FC<sub>6</sub>H<sub>4</sub>)Si<sup>+</sup>, 42), 120 (23). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>Si<sub>2</sub>F<sub>4</sub>: C, 53.48; H, 4.49. Found: C, 53.77; H, 4.53.

After removal of two additional crops of *meso-2c*, the filtrate showed a 1:1 ratio for the two diastereomers of **2c**.

**F[(*p*-MeOC<sub>6</sub>H<sub>4</sub>)SiMe]<sub>2</sub>F (2d).** Reaction of H(*p*-MeOC<sub>6</sub>H<sub>4</sub>-SiMe)<sub>2</sub>H (1.22 g, 4.04 mmol) with CuF<sub>2</sub>·2H<sub>2</sub>O (5.2 g, 38 mmol) in CCl<sub>4</sub> (10 mL) gave colorless F(*p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (bp 140–150 °C/0.05 mmHg, 1.21 g, 88%), which solidified, mp 65–70 °C. Recrystallization of the solid (91 mg) from <sup>1</sup>PrOH provided white **2d** (61 mg; *meso/rac* = 66/33) with mp 75.6–81.2 °C. The filtrate from the recrystallization showed *meso/rac-2d* ≈ 50/50. Slow evaporation of a hexane solution of the *meso/rac* = 66/33 solid provided crystals of the pure *meso* isomer (mp 84 °C) that were suitable for X-ray analysis. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.55 (A<sub>3</sub>B<sub>3</sub>XY, J<sub>HSiCH</sub> = 8.7, 6H, SiCH<sub>3</sub>), 3.24 (s, 6H, OCH<sub>3</sub>), 6.77 (t, 4H, CH<sub>arom</sub>), 7.54 (t, 4H, CH<sub>arom</sub>). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.64 (dd, <sup>1</sup>J = 309 Hz, <sup>2</sup>J = 37 Hz). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>): δ -178 (m). Mass spectrum (*m/e* (relative intensities)): 323 ((P - Me)<sup>+</sup>, 29), 257 (Me(*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si<sup>+</sup>, 51), 181 (23), 169 (FMe(*p*-MeOC<sub>6</sub>H<sub>4</sub>)Si<sup>+</sup>, 69), 150 (Me(*p*-MeOC<sub>6</sub>H<sub>4</sub>)Si<sup>+</sup>, 80), 135 ((*p*-MeOC<sub>6</sub>H<sub>4</sub>)Si<sup>+</sup>, 100), 126 (19). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>Si<sub>2</sub>O<sub>2</sub>F<sub>2</sub>: C, 56.77; H, 5.91. Found: C, 56.56; H, 6.03.

**F(BuMeSi)<sub>2</sub>F.** Reaction of H(BuMeSi)<sub>2</sub>H (0.90 g, 4.5 mmol) with CuF<sub>2</sub>·2H<sub>2</sub>O (4.1 g, 30.0 mmol) in CCl<sub>4</sub> (20 mL) gave F(BuMeSi)<sub>2</sub>F as a colorless oil (bp 135–150 °C/0.10 mmHg, 0.40 g, 37%) which did not solidify, even after extended storage at -55 °C. The diastereomers, therefore, could not be isolated from one another. The <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopic data were obtained from a mixture enriched in the longer retention time diastereomer obtained from preparative gas chromatography. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ratio of diastereomers 14): δ 0.28 (m, 6H, SiCH<sub>3</sub>), 0.76 (m, 4H, CH<sub>2</sub>), 0.84 (t, 6H, CH<sub>3</sub>), 1.27 (m, 4H, CH<sub>2</sub>), 1.39 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>; ratio of diastereomers 1.4): -0.78 (m, SiCH<sub>3</sub>), 14.2 (s), 17.6 (m), 25.3 (s), 26.8 (s) (Si-Bu). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>; ratio of diastereomers 1): δ 30.15 (d,d), 27.2 (d,d). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>, ratio of diastereomers 14): δ -180.63 (m). Mass spectrum (*m/e* (relative intensities)): 238 (P<sup>+</sup>, 0.29), 181 ((P - Bu)<sup>+</sup>, 4.1), 139 (2.2), 125 (3.7), 117 (2.3), 100 (BuMeSi<sup>+</sup>, 14.6). A sample suitable for analysis was obtained by preparative gas chromatography. Anal. Calcd for C<sub>10</sub>H<sub>24</sub>Si<sub>2</sub>F<sub>2</sub>: C, 50.37; H, 10.14. Found: C, 50.44; H, 9.98.

In an effort to obtain crystals of F(BuMeSi)<sub>2</sub>F, a sample of a 1:1 mixture of the diastereomers was dissolved in an equal volume of hexane and stored at 0 °C. After 1 week, the ratio of the diastereomers in the solution was 1:3.4.

**Reaction of H(PhMeSi)<sub>3</sub>H with CuF<sub>2</sub>·2H<sub>2</sub>O.** A stirred mixture of CCl<sub>4</sub> (22 mL), H(PhMeSi)<sub>3</sub>H (3.0 g, 8.3 mmol), and CuF<sub>2</sub>·2H<sub>2</sub>O (6.9 g, 50 mmol) was heated to reflux. After 1.5 h the solid turned a light green and the GC trace of an aliquot showed that F(PhMeSi)<sub>3</sub>F (31%) and F(PhMeSi)<sub>2</sub>F (58%) were present. After 2.5 h, F(PhMeSi)<sub>2</sub>F (69%) and F(PhMeSi)<sub>3</sub>F (29%) were present. After the usual workup, a fraction, bp 110–120 °C/0.1 mmHg, 1.5 g, was obtained that contained F(PhMeSi)<sub>2</sub>F (97% by GC). The oil solidified to give a solid with a mp 62–68 °C. Continued distillation provided a second fraction, 0.83 g (25%), bp 135–145 °C/0.1 mmHg, that contained F(PhMeSi)<sub>3</sub>F (93%) and F(PhMeSiO)<sub>2</sub>SiPhMeF (6.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, in part): δ 0.84, 0.79, 0.78, 0.77 (4 d, <sup>3</sup>J<sub>HCSiF</sub> = 8.6 Hz, SiMe<sub>term</sub>); 0.76, 0.71, 0.68 (3 s, SiMe<sub>int</sub>), 7.4 (complex m, arom). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): δ -175.5 (q), -175.7 (q), -176.2 (q), -176.4 (q). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 23.68, 23.66, 23.39, 23.36 (4 d, <sup>1</sup>J<sub>SiF</sub> = 313 Hz, SiMe<sub>term</sub>); -51.79, -51.86,

-51.92 (3 t, SiMe<sub>int</sub>). Mass spectrum (*m/e* (relative intensities)): 398 (P<sup>+</sup>, 0.25), 240 (Ph<sub>2</sub>Me<sub>2</sub>Si<sub>2</sub><sup>+</sup>, 49.3), 225 (Ph<sub>2</sub>MeSi<sub>2</sub><sup>+</sup>, 20.7), 197 (Ph<sub>2</sub>MeSi<sup>+</sup>, 100), 135 (PhMe<sub>2</sub>Si<sup>+</sup>, 62.9). Anal. Calcd for C<sub>21</sub>H<sub>24</sub>Si<sub>3</sub>F<sub>2</sub>: C, 63.27; H, 6.07. Found: C, 62.44; H, 6.12.

**Fluorination of H(ArSiMe)<sub>2</sub>H with CuCl<sub>2</sub>/CuI/KF (General).** A mixture of CuCl<sub>2</sub> (18–20 mmol), CuI (5% relative to disilane), and KF (2.5 equiv) was added to a round-bottom flask that contained a stir bar. The solid mixture was heated to 100 °C in an oil bath under vacuum (0.1 mmHg) for 12–16 h. Freshly distilled THF was added after the apparatus had been cooled to room temperature. A rust-orange slurry was formed, which was stirred for 10 min. Next, H(ArMeSi)<sub>2</sub>H was added by syringe with stirring, and the mixture was allowed to react at room temperature. Approximately 1 h later the mixture had turned to a gray-brown slurry in a yellow-green solution. Aliquots were taken throughout the reaction to monitor the progress of formation of F(ArSiMe)<sub>2</sub>F. In the reaction of H(ArSiMe)<sub>2</sub>H, intermediate fluorination products were observed, including Cl(ArSiMe)<sub>2</sub>F (for example, Ar = C<sub>6</sub>H<sub>5</sub>: *m/e* 294, Cl(PhMeSi)<sub>2</sub>F<sup>+</sup>; *m/e* 155, PhMeSiCl<sup>+</sup>; *m/e* 139, PhMeSiF<sup>+</sup>). After 4–5 h the starting material and the chlorinated intermediates were consumed. The mixture was added to 50 mL of hexanes and then filtered through Celite to remove solid material from the clear yellow liquid. The volatiles were then removed by rotavaporation, leaving a viscous brown oil which was purified by distillation. The spectral properties for each of the 1,2-difluorodisilanes were identical with those prepared by the CuF<sub>2</sub> method. In each case, no observable cleavage byproducts were observed and only minor siloxanes were present (<2–3% by GC).

**F(PhMeSi)<sub>2</sub>F.** Reaction of H(PhMeSi)<sub>2</sub>H (1.00 g, 4.13 mmol) with CuCl<sub>2</sub> (2.45 g, 18.2 mmol), CuI (38.8 mg, 0.203 mmol), and KF (603 mg, 10.4 mmol) in THF (50 mL) gave F(PhMeSi)<sub>2</sub>F (1.05 g, 92% yield).

**F(*p*-TolSiMe)<sub>2</sub>F.** Reaction of H(*p*-TolSiMe)<sub>2</sub>H (46.3 mg, 1.71 mmol) with CuCl<sub>2</sub> (1.03 g, 7.66 mmol), CuI (16 mg, 0.084 mmol), and KF (25.8 mg, 4.44 mmol) in THF (50 mL) gave F(*p*-TolSiMe)<sub>2</sub>F (40.6 mg, 77.5% yield) containing very little siloxane byproduct and no observable cleavage products.

**F(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F.** Reaction of H(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H (1.00 g, 3.60 mmol) with CuCl<sub>2</sub> (2.45 g, 18.2 mmol), CuI (40 mg, 0.21 mmol), and KF (603 mg, 3.17 mmol) in THF (50 mL) gave F(*p*-FC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (0.97 g, 85% yield).

**F(*p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F.** Reaction of H(*p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>H (1.00 g, 3.31 mmol) with CuCl<sub>2</sub> (1.96 g, 14.6 mmol), CuI (31.5 mg, 0.165 mmol), and KF (0.481 g, 8.27 mmol) in THF (50 mL) gave F(*p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (0.80 g, 71% yield).

**Fluorination of H(PhSiMe)<sub>3</sub>H with CuCl<sub>2</sub>/CuI/KF.** A flame-dried flask was charged with CuCl<sub>2</sub> (1.63 g, 12.2 mmol), CuI (0.026 g, 0.14 mmol), and KF (0.40 g, 6.9 mmol). The solid reagents were dried by slowly heating to 90 °C under vacuum (0.01 mmHg) for 10 h and cooled to room temperature before 50 mL of freshly distilled THF was added, producing an orange slurry. H(PhSiMe)<sub>3</sub>H (1.00 g, 2.76 mmol) was added, and after approximately 45 min the mixture became a white slurry. The mixture was allowed to react at room temperature with stirring, and the reaction progress was monitored by GC. After 5 h, no starting material was observed and the slurry was filtered through Celite to remove the solids. The solvent was removed from the yellow filtrate to give a viscous pale yellow oil. Kugelrohr distillation provided a yellow oil, bp 140–150 °C/0.1 mmHg (0.70 g, 63%). The oil had the same spectroscopic characteristics as F(PhSiMe)<sub>3</sub>F produced from CuF<sub>2</sub>·2H<sub>2</sub>O.

**Fluorination of H(PhMeSi)<sub>2</sub>H with *N*-Chlorosuccinimide and Then HF/EtOH.** A mixture of *N*-chlorosuccinimide (NCS; 1.1 g, 8.3 mmol) and H(PhMeSi)<sub>2</sub>H (1.0 g, 4.1 mmol) was added to 20 mL of CCl<sub>4</sub>. A sunlamp was used to initiate the reaction, and the slurry was allowed to react at room temperature with stirring overnight and then heated to reflux for 30 min. GC analysis revealed the presence of both



Table 2. Crystallographic Data for *meso*-F(*p*-X-C<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F

	X = H	X = F	X = OMe	X = Me
formula	C <sub>14</sub> H <sub>16</sub> F <sub>2</sub> Si <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> F <sub>4</sub> Si <sub>2</sub>	C <sub>16</sub> H <sub>20</sub> F <sub>2</sub> O <sub>2</sub> Si <sub>2</sub>	C <sub>16</sub> H <sub>20</sub> F <sub>2</sub> Si <sub>2</sub>
<i>M<sub>r</sub></i>	278.45	314.43	338.50	306.50
space group	<i>Pca</i> 2 <sub>1</sub>	<i>P2<sub>1</sub>/n</i>	<i>Pca</i> 2 <sub>1</sub>	<i>P2<sub>1</sub>/c</i>
<i>a</i> , Å	17.213(2)	6.269(4)	21.3050(2)	10.1008(3)
<i>b</i> , Å	5.8205(5)	5.850(5)	5.7137(1)	14.1190(4)
<i>c</i> , Å	14.696(2)	21.154(18)	14.2518(1)	6.0213(2)
α, deg	90	90	90	90
β, deg	90	98.46	90	103.40
γ, deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	1472.3(2)	767.4(10)	1734.88	835.35(4)
<i>Z</i>	4	2	4	2
<i>D</i> (calcd), Mg/m <sup>3</sup>	1.256	1.361	1.296	1.219
temp, K	295(2)	298(2)	223(2)	218(2)
θ range, deg	2.37–30.00	1.95–26.33	1.91–27.49	2.07–27.49
no. of obsd rflns	9697	4274	29167	16324
no. of indep rflns	3146	1461	3996	1906
<i>R</i> 1 <sup>a</sup>	0.0352	0.0363	0.0337	0.0648
w <i>R</i> 2 <sup>b</sup>	0.0862	0.1064	0.0769	0.1265
GOF	1.060	1.054	1.016	1.406
Flack <i>x</i>	0.1(1)	-	-0.01(9)	-

<sup>a</sup> Final *R* indices (*I* > 2σ(*I*)). <sup>b</sup> From all data.

Cl(PhMeSi)<sub>2</sub>Cl and the starting material; therefore, heating was continued for an additional 1 h. Insoluble material was filtered and the solvent removed from the filtrate in vacuo. The residue was then dissolved in 20 mL of absolute ethanol and transferred to a 150 mL Teflon Erlenmeyer flask containing a stir bar. A glass condenser was fitted to the Teflon flask, and HF (49%, 1.5 mL) was then added to the solution via a pipet. The reaction mixture was slowly heated to 75 °C in a temperature-controlled oil bath. After 2 h the solution was poured into water (100 mL) and extracted with 4 × 20 mL portions of Et<sub>2</sub>O. The combined Et<sub>2</sub>O extracts were then washed with brine solution (15 mL, 2×) and dried over MgSO<sub>4</sub>. Removal of the Et<sub>2</sub>O provided a pale yellow liquid. GC analysis and the <sup>1</sup>H NMR spectrum confirmed the presence of the two diastereomers of F(PhMeSi)<sub>2</sub>F in a 1:1 ratio. Cooling of the oil to -52 °C produced a white solid (0.48 g, 42%). Recrystallization from hexanes gave a white solid, mp 70–71.5 °C, whose spectroscopic data were identical with those of the *meso* isomer prepared from the metal halide route. A GC analysis of the filtrate showed that both diastereomers were present in approximately a 1:1 ratio.

**Catalyzed Epimerization of *meso*-F(PhMeSi)<sub>2</sub>F. a. <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> (TBAF).** To a sample of *meso*-F(PhSiMe)<sub>2</sub>F (0.12 g, 0.43 mmol, containing <1% FPhMeSiOSiPhMeF) in hexane was added TBAF (1 M, 0.04 mL, 10% relative to the disilane). The solution bubbled and became warm. A GC analysis of an aliquot of the resulting reaction mixture showed the presence of the two diastereomers of F(PhSiMe)<sub>2</sub>F in a 1:1 ratio in addition to siloxane (7%).

A sample of *meso*-F(PhSiMe)<sub>2</sub>F (20 mg, 7.2 × 10<sup>-2</sup> mmol) was dissolved in CDCl<sub>3</sub> and a <sup>1</sup>H NMR spectrum obtained. A solution of TBAF (1 M, 3.6 μL; 5 mol % relative to the disilane) was injected and the <sup>1</sup>H NMR spectrum taken immediately after mixing. A statistical distribution of diastereomers of F(PhSiMe)<sub>2</sub>F was observed. The experiments were repeated at -90 °C in tol-*d*<sub>6</sub>, and chilled TBAF was added. Again, a statistical distribution of the diastereomers was present by the time the measurement was completed.

**b. Bz<sub>2</sub>Me<sub>2</sub>N<sup>+</sup>Cl<sup>-</sup>.** A sample of *meso*-F(PhSiMe)<sub>2</sub>F (25 mg, 8.9 × 10<sup>-2</sup> mmol) was dissolved in CDCl<sub>3</sub>, and a CDCl<sub>3</sub> solution of Bz<sub>2</sub>Me<sub>2</sub>N<sup>+</sup>Cl<sup>-</sup> (4.7 mg, 20 mol % relative to the disilane) was added. Epimerization to a statistical mixture of diastereomers occurred over a 5 h period at ambient probe temperatures (298 K).

**c. CH<sub>3</sub>CN.** A sample of *meso*-F(PhSiMe)<sub>2</sub>F (13.2 mg) was dissolved in CD<sub>3</sub>CN (0.5 mL). The GC of an aliquot taken immediately after mixing showed that both diastereomers were present in a 1:1 ratio.

A sample of *meso*-F(PhSiMe)<sub>2</sub>F (10 mg) was dissolved in CDCl<sub>3</sub>, and CH<sub>3</sub>CN (20 mol % relative to the disilane) was added. After 1 week no epimerization was observed to take place. The experiment was repeated with a 10× concentration of CH<sub>3</sub>CN, and no epimerization was observed after 3 days.

**Noncatalyzed Epimerization.** A sample of *meso*-F(PhMeSi)<sub>2</sub>F (100% by GC) was dissolved in dry toluene under a nitrogen atmosphere. The solution was heated to reflux, and the diastereomer ratio was monitored over time. After 13 h the diastereomer ratio was 3:1 *meso:rac*. After this point, siloxanes began to form and heating was discontinued.

**Reduction of *meso*-F(PhMeSi)<sub>2</sub>F.** To LAH (0.15 g, 4.0 mmol) dissolved in freshly distilled Et<sub>2</sub>O (30 mL) was added dropwise by syringe *meso*-F(PhMeSi)<sub>2</sub>F (1.06 g, 3.81 mmol) dissolved in dry Et<sub>2</sub>O (10 mL). The mixture was stirred at room temperature overnight and then added to saturated aqueous NH<sub>4</sub>Cl (30 mL) and diluted with water (100 mL). The separated ether layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The volatiles were removed in vacuo, resulting in a colorless, viscous liquid, which proved to be highly enriched in a single diastereomer by GC analysis (less than 10% of the other diastereomer). The liquid was mixed with a small amount of hexanes and placed in a freezer at -52 °C. A white crystalline solid (63% yield) was produced as a single diastereomer, mp 34.8–36.1 °C. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, in part): δ 0.345 (d, *J* = 4.52, SiCH<sub>3</sub>); 4.8 (q, <sup>3</sup>*J*<sub>HCSiH</sub> = 4.60, <sup>3</sup>*J*<sub>HSiSiH</sub> = 2.65, SiH). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -7.45 (CH<sub>3</sub>), 128.3, 129.3, 134.9, 135.2 (C<sub>6</sub>H<sub>5</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -32.0.

**Reaction of H(PhMeSi)<sub>2</sub>H with KF/[2.2.2] Cryptand.** In an NMR tube fitted with a PTFE valve and containing *meso*-F(PhMeSi)<sub>2</sub>F (35 mg, 1.3 × 10<sup>-4</sup> mol) was placed KF (6.0 mg, 1.0 × 10<sup>-4</sup> mol) previously dried under vacuum at 100 °C for 12 h and [2.2.2]cryptand (47 mg). Approximately 1 mL of C<sub>6</sub>D<sub>6</sub> was added, resulting in a colorless solution containing a small amount of insoluble white material, presumably KF. A <sup>1</sup>H NMR spectrum was obtained, revealing no change in the characteristic SiMe signals of F(PhMeSi)<sub>2</sub>F. The mixture was allowed to react for 3 days while spinning in the spectrometer. After this period of time the mixture appeared as two layers: a colorless upper layer and a viscous brown lower layer. The solvent was removed in vacuo on a Schlenk line. This left a colorless solid material that was washed with freshly distilled Et<sub>2</sub>O, resulting in the formation of a white precipitate. The white precipitate was washed three times with Et<sub>2</sub>O and then dissolved in DMSO-*d*<sub>6</sub>, and a <sup>1</sup>H NMR spectrum was obtained. The spectrum revealed the signals corresponding to [2.2.2]-cryptand, but no signals other than a minor resonance corre-

sponding to the original disilane were observed in any significant amounts.

**X-ray Structure Determination.** Crystals with appropriate dimensions were mounted on glass fibers in a random orientation. Preliminary examinations and data collections were performed using a Bruker SMART charge coupled device (CCD) Detector system or a Siemens P4RA single-crystal X-ray diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Preliminary unit cell constants were determined with a set of 45 narrow frames ( $0.3^\circ$  in  $\omega$ ) scans in case of CCD data sets or by using random search/rotation photograph in case of P4RA diffractometer.

In the case of the area detector the data set collected consists of 4028 frames of intensity data collected with a frame width of  $0.3^\circ$  in  $\omega$  and a counting time of 15–30 s/frame at a crystal to detector distance of 4.930 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. SMART and SAINT software packages (Bruker Analytical X-ray, Madison, WI, 1999) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of  $xyz$  centroids. Collected data were corrected for systematic errors using SADABS<sup>36</sup> based on the Laue symmetry using equivalent reflections.

In the case of the P4RA instrument, data were collected by a  $\omega$ - $2\theta$  scan ( $2.4 < 2\theta < 60.0^\circ$ ). Data collection and reduction was accomplished by XSCANS (Siemens Analytical Instruments, 1995). No absorption correction was applied to the data.

Crystal data and intensity data collection parameters are listed in Table 2. Structure solution and refinement were carried out using the SHELXTL software package.<sup>37</sup> The structures were solved by direct methods and refined success-

fully in the listed space groups. Full-matrix least-squares refinement was carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$ . The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using an appropriate riding model (AFIX m3). Structure refinement parameters are listed in Table 2. Selected geometrical parameters are listed in Table 1. Projection plots of the molecules with non-hydrogen atoms represented by 50% probability ellipsoids and showing the atom labeling are presented in Figure 1.

Complete listings of positional and isotropic displacement coefficients, geometrical parameters, and anisotropic displacement coefficients for the non-hydrogen atoms are submitted as Supporting Information (Tables 1–20). Tables of calculated and observed structure factors are available in electronic format.

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**Supporting Information Available:** Tables of crystal structure data and refinement details, atomic coordinates and equivalent isotropic parameters, and hydrogen coordinates and isotropic displacement parameters for F[(*p*-XC<sub>6</sub>H<sub>4</sub>SiMe)<sub>2</sub>F (X = H, F, OMe, Me). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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