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Preparation of $F(ArMeSi)_2F$ and Isomerization of the Diastereomers

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Summary: Reaction of $H(ArMeSi)_2H$ (Ar = C_6H_5, ***1a****; p-$CH_3C_6H_4$,* ***1b****; p-FC_6H_4,* ***1c****; p-$MeOC_6H_4$,* ***1d****) with $CuF_2{\cdot}2H_2O$ provides $F(ArMeSi)_2F$,* ***2a−d****, as a 1:1 mixture of diastereomers. meso-**2a**, **2b**, and **2c** crystallize from a hexane solution of the diastereomeric mixture, leaving a mother liquor that still contains a rac/meso ratio near 1:1. Partial conversion of the rac/meso mixture of **2d** to meso-**2d** occurred during recrystallization from ${}^iPrOH$. Reaction of meso-**2** with catalytic quantities of ionic fluoride sources results in formation of a statistical mixture of meso/rac-**2**.*

Silicon oligomers $H(PhMeSi)_xH$ are readily available through dehydrocoupling of $PhMeSiH_2$.[1] Such oligomers contain two types of functional groups: SiPh and SiH. As part of a program to explore the range of substitution reactions of these oligomers, the removal of the phenyl groups with triflic acid was developed. The SiOTf group could be replaced with organic groups by reaction with active organometallics or converted to additional SiH bonds with lithium aluminum hydride.[1] The terminal SiH bonds in $H(PhMeSi)_2H$ provide additional potential for substitution chemistry in the oligomers. Recently, convenient methods to convert hydrosilanes to fluorosilanes with $CuF_2{\cdot}2H_2O/CCl_4$ [2] and $CuCl_2(CuI)/KF/THF$ (or Et_2O)[3] were published, although only monosilanes were investigated in both studies. Organofluorosilanes are of interest in organosilicon chemistry for unique electron-transfer reactions[4] and for the synthesis of highly coordinated silicon compounds.[5] Fluorosilanes are traditionally prepared from the reaction of a chlorosilane precursor with a fluoride salt.[6]

Through careful modification of the fluorination conditions reported by Yoshida, Isoe, and co-workers it was possible to convert $H(PhMeSi)_2H$ (**1a**) with $CuF_2{\cdot}2H_2O$ to $F(PhMeSi)_2F$ (**2a**), which was isolated by Kugelrohr distillation (reduced pressure) as a 1:1 mixture of diastereomers.[7a] The major byproduct was $PhMeSiF_2$, which would result from the cleavage of the SiSi bond during the fluorination or through subsequent reaction of the product disilane.[7b] The concentration of the monosilane byproduct increased if the product mixture was left for prolonged periods in contact with the copper(II) fluoride salt. A similar reaction of **1b−d** with $CuF_2{\cdot}2H_2O$ produced $F(ArMeSi)_2F$ [Ar = *p*-MeC_6H_4 (**2b**), *p*-FC_6H_4 (**2c**),[8] and *p*-$MeOC_6H_4$ (**2d**)] (Scheme 1). The byproducts, $ArMeSiF_2$, ArMeSiHF, and $(FArMeSi)_2O$ were identified in the reaction mixtures by GCMS before isolation of the disilane diastereomers. Although the Me doublets of the two diastereomers of **2** overlapped in the ${}^1H$ NMR spectrum, the signals for *meso*- and *rac*-

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(1) Corey, J. Y.; Kraichely, D. M.; Huhmann, J. L.; Braddock-Wilking, J.; Lindeberg, A. *Organometallics* **1995**, *14*, 2704.

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

(3) Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1996**, *15*, 2478.

(4) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962.

(5) For example reviews of higher coordinate organosilicon compounds see: a. Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1989, Part 2, Chapter 20. B. Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Revs.* **1993**, *93*, 1371.

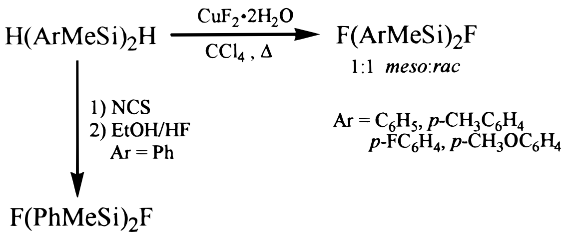
(6) Selected examples: (a) SbF_3: Booth, H. S.; Suggle, J. F. *J. Am. Chem. Soc.* **1946**, *68*, 2658. (b) ZnF_2: Hengge, E.; Schrank, F. *J. Organomet. Chem.* **1986**, *299*, 1. (c) Na_2SiF_6: Damrauer, R.; Simon, R. A.; Kanner, B. *Organometallics* **1988**, *7*, 1161. (d) Me_3SnF: Roesky, H. W.; Herzog, A.; Keller, K. *Z. Naturforsch. B* **1994**, *49*, 981. (e) $CuF_2{\cdot}2H_2O$: Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983.

(7) (a) A mixture of $H(PhMeSi)_2H$ (1.04 g, 4.30 mmol), $CuF_2{\cdot}2H_2O$ (2.0 g, 12.9 mmol), and CCl_4 (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. The color change in the salts usually signaled the end of the reaction, as indicated by gas chromatographic analysis of an aliquot. If incomplete, heating was continued until the starting material was consumed and the intermediate chlorinated disilanes (identified by GCMS) had been converted to $F(PhMeSi)_2F$. Prolonged heating in the presence of the copper salts increased the concentration of the $PhMeSiF_2$ byproduct.[7b] After cooling, the reaction mixture was filtered through Celite and the solvent removed. The resulting oil was purified by Kugelrohr distillation, giving a colorless liquid, bp 100−120 °C/0.05 mmHg, containing both *meso*- and *rac*-diastereomers by GC (52:48) as well as by GCMS and ${}^1H$ NMR. The distilled oil was dissolved in hexanes and cooled to −52 °C to give a white solid, which was recrystallized from hexanes to give $F(PhMeSi)_2F$,[7c] mp 71.8−72.2 [0.66 g, 55% yield based on $H(PhMeSi)_2H$], as a single diastereomer. A GC trace of the mother liquor remaining after removal of the solid revealed the presence of both diastereomers in approximately equal proportions. A crystal structure showed that the isolated diastereomer was *meso*-$F(PhMeSi)_2F$. *meso*- + *rac*-$F(PhMeSi)_2F$: ${}^1H$ NMR (500 MHz, C_6D_6, in part): δ 0.45 (center of pseudotriplet; CH_3). *meso*-$F(PhMeSi)_2F$: ${}^1H$ NMR (500 MHz, C_6D_6, in part): δ 0.447 (A_3B_3XY, ${}^3J_{HSiCH} = 8.9$, 6H, CH_3). ${}^{13}C\{{}^1H\}$ NMR (125 MHz, C_6D_6): δ −0.7 (CH_3), 128.6, 130.8, 133.4 and 133.5 (C_6H_5). ${}^{29}Si\{{}^1H\}$ NMR (99 MHz, C_6D_6): δ 15.29 (dd, ${}^1J_{SiF} = 308$ Hz, ${}^2J_{SiF} = 36$ Hz). ${}^{19}F$ NMR (470 Hz, C_6D_6): δ −180.69 (m). Mass spectrum [*m*/*e* (relative intensities)]: 278 (P^+, 2.6), 197 (Ph_2MeSi^+, 100), 139 ($PhMeSiF^+$, 33), 120 ($PhMeSi^+$, 82), 105 ($PhSi^+$, 60). Anal. calcd for $C_{14}H_{16}Si_2F_2$: C, 60.39; H, 5.79. Found: C, 59.86; H, 6.04. The *rac*-isomer was enriched by preparative gas chromatography (OV 17 column, 10 ft by 1/4 in.) of a sample of the freshly distilled oil product (*rac*/*meso* = 1:1) to provide a sample of *rac*/*meso* = 88:12. *rac*-$F(PhMeSi)_2F$. ${}^1H$ NMR (500 MHz, C_6D_6, in part): δ 0.462 (m, ${}^3J_{HSiCH} = 8.8$). ${}^{13}C\{{}^1H\}$ NMR (125 MHz, C_6D_6): δ 0.40 (m, CH_3), 128.7, 128.9, 131.1, 133.9 (C_6H_5). ${}^{29}Si\{{}^1H\}$ NMR (99 MHz, C_6D_6): δ 15.15 (dd, ${}^1J_{SiF} = 310$, ${}^2J_{SiF} = 35$). ${}^{19}F$ NMR (470 MHz, C_6D_6): δ, −180.56 (m). (b) Cleavage of SiSi bonds in $Me_3SiSiMe_3$ by anhydrous TBAF in HMPA has been reported: Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 914. (c) The diastereomeric mixture of $F(PhMeSi)_2F$ with a mp 59.0−62.0 °C has been previously reported from the reaction of $Cl(PhMeSi)_2Cl$ with $ZnF_2{\cdot}4H_2O$. Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87.

(8) The disilane precursor, $H(ArMeSi)_2H$ (Ar = *p*-FC_6H_4) was prepared by removal of the phenyl groups of $H(PhMeSi)_2H$ with triflic acid followed by reaction with *p*-FC_6H_4MgBr. This alternative procedure is required since (*p*-FC_6H_4)$MeSiH_2$ does not undergo dehydrocoupling with Cp_2TiCl_2/n-BuLi.

10.1021/om000113r CCC: $19.00

Scheme 1



diastereomers in the ^{29}Si{^{1}H} and ^{19}F NMR spectra were resolved.

When the diastereomeric mixture of F(PhMeSi)$_2$F was dissolved in hexanes and cooled to −50 °C, a white precipitate was produced, which was recrystallized to give a single diastereomer with a mp 71.8−72.2 °C [55% based on the starting H(PhMeSi)$_2$H]. A crystal structure verified the presence of the center of symmetry characteristic of the *meso*-isomer. In a similar manner, white solids were isolated for both **2b** and **2c**, and both were shown to be the *meso*-isomer by crystal structure determinations.[9] All *meso*-forms were characterized by elemental analyses, spectroscopic methods (see Figure 1a for a partial ^{1}H spectrum of *meso*-**2a**), and X-ray analysis. Both diastereomers of **2d** coprecipitated from hexanes, and no enrichment of *meso*-**2d** was observed in this solvent. However, a single recrystallization from ^{i}PrOH resulted in a solid with *meso/rac* **2d** ≈ 3/1 (75% recovery of original 1:1 mixture employed).[10] Slow evaporation of a hexane solution of the *meso*-enriched sample of **2d** provided crystals of *meso*-**2d** suitable for a crystal structure.[9]

Although the filtrate obtained after removal of crystalline *meso*-**2a** was expected to contain mainly the *rac*-isomer, it in fact consisted of nearly a 1:1 ratio of the two diastereomers. Similar results were observed after removal of successive crops in the recrystallization of *meso*-**2b** and *meso*-**2c**. Partial conversion of *rac*-**2d** to *meso*-**2d** occurred during recrystallization from ^{i}PrOH, leaving a filtrate that was 1:1 in the two diastereomers. Thus, isomerization of the *rac*-isomer to the *meso*-isomer takes place in all four cases. To determine whether this isomerization occurred as a result of metal residue left from the synthetic method, an alternative route to **2a** was developed that did not involve metal salts. After conversion of **1a** to Cl(PhMeSi)$_2$Cl with *N*-chlorosuccinimide, ethanolic HF was added to convert the chloride to F(PhMeSi)$_2$F (Scheme 1).[11] Distillation provided the 1:1 diastereomeric mixture as a clear, colorless oil with the same spectroscopic properties as that produced from **1a** and CuF$_2$•2H$_2$O. This sample also became enriched in the *meso*-form, as observed in samples of **1a** produced from metal salts.

Isomerization of *meso*-**2** to a statistical mixture of diastereomers was observed in the presence of fluoride sources. Addition of tetrabutylammonium fluoride, TBAF (5 to 10 mol %), to solutions of *meso*-**2a**,**b**,**c** or *meso*-enriched **2d** (CDCl$_3$ or C$_6$D$_6$) and immediate monitoring by ^{1}H NMR showed isomerization to a mixture of diastereomers. The overlapping, complex Me doublets of the diastereomeric mixture produced from *meso*-**2a** are illustrated in Figure 1b. The 1:1 ratio of diastereomers was confirmed by GC analysis. Repeating the experiment at lower temperature (−50 °C) did not slow the isomerization sufficiently to be monitored on the NMR time scale.

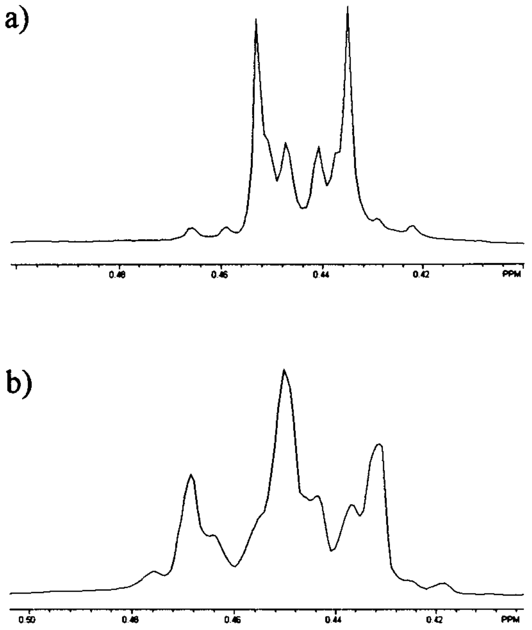


Figure 1. (a) Methyl region ^{1}H NMR spectrum of *meso*-F(PhMeSi)$_2$F. (b) Methyl region ^{1}H NMR spectrum of 1:1 *meso:rac* mixture.

Initiation of the isomerization of *meso*-**2a** by potentially less nucleophilic fluoride sources was then examined in an effort to slow conversion rates. A possible candidate was the tin complex [n-Bu$_4$N][Ph$_3$SnF$_2$], which was found to be less aggressive than TBAF by Gingras.[12] When the ^{1}H NMR study was conducted with the tin complex, the isomerzation of *meso*-**2a** was still too rapid to be monitored. An attempt was made to utilize a covalent fluoride such as Ph$_2$SiF$_2$ to initiate the isomerization of the *meso*-isomer, but no change of the *meso*-form was observed after 1 week in the presence of 10 mol % of Ph$_2$SiF$_2$. Other nucleophiles, in principle, could also promote isomerization of the *meso*-disilane. For instance, when *meso*-**2a** was dissolved in CH$_3$CN, the statistical mixture of diastereomers formed. However, no conversion was observed at a catalytic level of CH$_3$CN.

A possible mechanism that would account for a nucleophilic conversion of the *meso*-isomer to a statistical mixture of diastereomers is summarized in Scheme 2. Inversion at silicon could take place by a simple substitution of fluoride by fluoride through axial entry of F$^-$ and axial departure of F$^-$ (inversion at silicon). Alternatively, pseudorotations of the five-coordinate intermediate that forms could ultimately lead to the statistical mixture of diastereomers. However, in this latter possibility the two electronegative fluoride ligands must enter the higher energy equatorial sites. A related scheme involving pseudorotation has been proposed for

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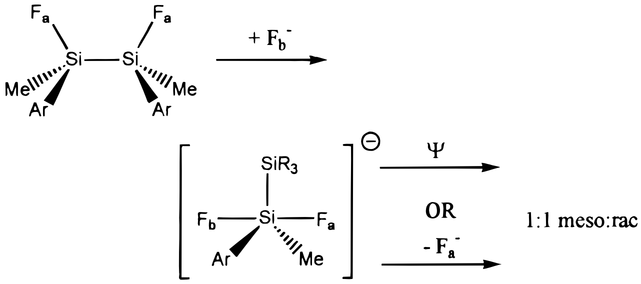
[9] Details of the structures of **2** will be published with the full paper.

[10] Chiral α-naphthylphenylmethylfluorosilane dissolved in pentane or ^{t}BuOH is racemized by addition of MeOH without displacement of F$^-$. Sommer, L. H.; Rodewald, P. G. *J. Am. Chem. Soc.* **1963**, *85*, 3898.

[11] Modification of a published procedure: Eaborn, C. *J. Chem. Soc.* **1952**, 2846.

[12] Gingras, M. *Tetrahedron Lett.* **1991**, *32*, 7381.

Scheme 2



epimerization of the 1:1 diastereomeric mixture of {bis[(*R*)-1-phenylethyl]amino}(1-naphthyl)phenylfluorosilane, **3**, to (*R*)(*R*)$_{Si}$-**3**,[13] although in the disilane case fluoride ion was used to produce a statistical mixture of diastereomers from a single diastereomer. Disilanes with different *p*-substituted aryl groups could possibly alter the electronic character at silicon sufficiently to perturb the rate of conversion of the diastereomers. However this was not realized in the derivatives studied thus far. It may be necessary to examine other nucleophiles in order to determine if higher valent silicon centers can be observed in these disilane systems. With the ionic fluoride sources utilized in this study, it was necessary to keep the concentration of fluoride ion $\leq$ 10% to avoid products resulting from the cleavage of the silicon−silicon bond of the disilane.[7b] The necessity of low concentrations of fluoride may preclude the isolation of a fluoride complex, as was described recently in the case of potassium organofluorosilicates stabilized by [2.2.2] cryptand.[14]

The isolation of a single F(ArMeSi)$_2$F diastereomer provided the opportunity to explore the stereochemistry of substitution reactions of the SiF bond. Reduction of *meso*-**2a** with LiAlH$_4$ provided H(PhMeSi)$_2$H, which was purified by Kugelrohr distillation to give a clear liquid. Crystallization from hexanes at −52 °C provided a white solid, mp 34.5−34.8 °C, as a single diastereomer. The diastereomer was determined to be the *meso*-form from a preliminary crystal structure determination.[15] Since reduction of a silyl fluoride with LiAlH$_4$ occurs with inversion,[5a] the *meso*-isomer should be the major product.

The mixture of F(ArMeSi)$_2$F diastereomers may be equilibrated by some process, most likely an intermolecular process, in a nonpolar solvent such as hexane. As the more insoluble *meso*-form precipitates, the *rac*-form converts to *meso* to reestablish the statistical mixture. If excess fluoride ion is present, the statistical mixture can be maintained since *meso*-**2** is converted to a *meso*/*rac* mixture. Indeed, it is possible that isomerization of silicon centers in 1,2-difluorodisilanes could be a general phenomenon. For example, stereomutation has been reported for *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane.[16]

Whether other nucleophiles promote isomerization of F(ArMeSi)$_2$F or other substituted diastereomeric disilanes X(RR′Si)$_2$X (X = electronegative substituent such as OR) undergo this isomerization is currently under investigation, as is the possible extension to related tri- and tetrasilanes.

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Supporting Information Available: Experimental details and characterization data for **2b**−**d** and the crystal data and structure refinement summary. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Kawachi, A.; Maeda, H.; Mitsudo, K; Tamao, K. *Organometallics* **1999**, *18*, 4530.

[14] Yamaguchi, S.; Akiyama, S.; Tamao, K. *Organometallics* **1999**, *18*, 2851.

[15] The crystal structure was sufficiently adequate to provide connectivity and the conformation but not of sufficient quality to provide bond distances and angles. Corey, J. Y.; Rath, N. P.; Wymann, D. S., unpublished work.

[16] When *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (**3**) was stored in a sealed ampule for 18 days, isomerization to a mixture of *cis*:*trans*-**3** $\approx$ 1:3.4 occurred. The isomerization was also promoted by the addition of ethanol to benzene solutions of *cis*- or *trans*-**3**. (a) Tamao, K.; Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1969**, 73. (b) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organometal. Chem.* **1971**, *31*, 17.