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N,*N*-Difluorotris(*tert*-butyl)silylamine—The First Organosilyl Difluoroamine. Synthesis and Computational Studies

Utpal Majumder, John R. Armantrout, Richard Vaughan Williams,* and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

jshreeve@uidaho.edu

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The synthesis and characterization of the first stable trialkyl(difluoroamino)silane, R_3SiNF_2, as well as of R_3SiNHF and $R_3SiN(CH_3)F$ in moderate yields are reported. The (difluoroamino)silane has promise as a new synthon for the introduction of the $-NF_2$ group into a variety of electrophilic inorganic and organic substrates. Activation barriers and relative energies were calculated for the unimolecular decompositions of Me_3SiCF_3 and t-Bu_3SiNF_2 using density functional theory (B3LYP/6-31G*). The calculated activation energies confirm the long-assumed kinetic stability of Me_3SiCF_3.

Introduction

The thermodynamically favored formation of the extremely strong silicon—fluorine bond has long led designer chemists to believe that the likelihood of formation of a stable R_3Si-NF_2 species was remote. We have now demonstrated that it is indeed possible not only to prepare such a species but that this compound is stable at 25 °C for extended periods. Although prior to Ruppert's seminal work the synthesis of trimethyl(trifluoromethyl)-silane [$(CH_3)_3SiCF_3$] as a stable moiety was deemed unlikely, its extended use as a nucleophilic reagent for introduction of the trifluoromethyl moiety has dramatically contradicted this thinking.[1−3] *N*,*N*-difluoroorgano amines (RNF_2) are well-studied.[4] However, until now *N*-fluoroorganosilylamines ($R_3SiNF_nR'_{2-n}$) have not been reported. Here we describe a new stable (difluoroamino)-silyl compound that is a promising new synthon as a reactive nucleophile for the introduction of the difluoroamino moiety into a large number of inorganic and organic substances with electrophilic centers.

Methodologies developed for preparation of fluoroorgano amines include, for example, interaction of organic substrates with elemental fluorine,[5] tetrafluorohydrazine,[6] difluoroamine,[7−9] CF_3OF, XeF_2, $FClO_3$,[10] $CsSO_4F$,[11] NF_3O,[12] and NF_2SO_3F.[13] In recent years, a number of effective fluorinating N—F reagents whose use is more straightforward for the average bench chemist have emerged. These reagents are ready sources of electrophilic fluorine and are useful for the introduction of fluorine at electron-rich carbon centers, such as aromatic hydrocarbons, olefins, and carbanions.[14] Recently we have reported the effective synthesis of *N*-fluoro and *N*,*N*-difluoroacyclic amines ($RNF_{2-n}H_n$) by employing Selectfluor [1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]-octane bis(tetrafluoroborate), Air Products] with acyclic amines.[15]

Results and Discussion

Organo silylamines have two reactive centers—nitrogen and silicon—which make them attractive for transforma-

* Corresponding author. Tel: (208) 885-6215. Fax: (208) 885-9146.

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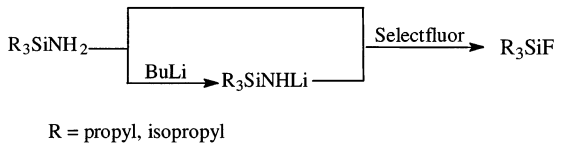
SCHEME 1



tion reactions. The presence of fluorine bonded to nitrogen changes the reactivity of the nitrogen center dramatically, as is indicated by proton chemical shifts in the NMR spectra when NH_2 is compared with NHF (from δ 2−3 to 8−9.5).[15,16] The high affinity of silicon for fluorine is often utilized as a force to drive reactions to completion, e.g., reactions of $(CH_3)_3SiCF_3$ where fluoride ion frequently acts as a catalyst to initiate the transfer of the CF_3 moiety.[1,2,17] Despite this strong thermodynamic driving force, we now describe the syntheses of kinetically stable *N*-fluoroorganosilylamines by using Selectfluor as an electrophilic fluorinating reagent.

In our initial efforts, tripropyl- and tri(isopropyl)-silylamines were reacted with Selectfluor in acetonitrile under a variety of conditions. Trialkylsilyl fluorides (identified from ^1H and ^{19}F NMR spectra and GC/MS) were the sole fluorine-containing products. Similar results were obtained when the amines were metalated prior to reaction with Selectfluor (Scheme 1).

However, quite distinct from other organosilyl compounds, the chemistry of tris(*tert*-butyl)silyl compounds is dictated largely by steric and electronic effects, as is exemplified by the behavior of (*tert*-butyl)$_3$SiX (X = H, Hal, NR_2).[18−20] Tris(*tert*-butyl)silyl compounds are known to be inert toward S_N2−Si displacement reactions.[21,22] No reaction occurs between tris(*tert*-butyl)silane and HF, SbF_3, or $(C_6H_5)CBF_4$,[21] and it is insensitive to either acidic or basic conditions.[22] On the basis of these observations, tris(*tert*-butyl)silylamine seemed a likely starting material for the synthesis of compounds with the Si−N−F linkage.

Tris(*tert*-butyl)silylamine (**1**) was prepared by following the literature procedure[22] using tris(*tert*-butyl)silyl chloride, which is obtained from either SiF_4[23] or $SiHCl_3$.[24] Reaction of **1** with Selectfluor at −5 to 0 °C in acetonitrile gave a mixture of ∼85−90% *t*-Bu_3SiF (**2**)[19−21,23] and ∼15% *t*-Bu_3SiNHF (**3**). Using this methodology, regardless of the ratio of reagents or solvent used, it was not possible to improve the yield of **3**. These results indicated that there were two competing reactions: fluorination at the silicon center and at the nitrogen center. If these reactions proceed in parallel, enhancement of the electron density on the nitrogen atom should favor the formation

SCHEME 2

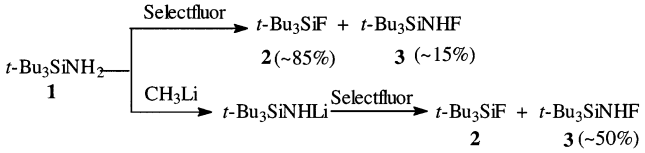
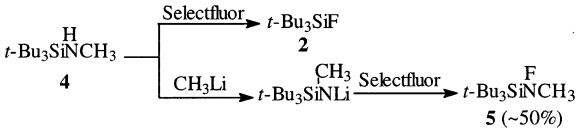


TABLE 1. NMR Data (ppm)

compd	^1H	^{19}F	$^{13}C\{H\}$	$^{29}Si\{H\}$
1	1.16 (s, C−CH_3)		22.1 (s, *t*-Bu)	5.6
	0.20 (s, NH_2)			
3	1.16 (d, C−CH_3)	−190.3 (d)	22.4 (d, *t*-Bu)	10.7 (d)
	9.12 (d, NH)		29.8 (s, C−CH_3)	
4	1.16 (d, C−CH_3)		23.2 (s, *t*-Bu)	2.34 (s)
	2.66 (s, N−CH_3)		31.1 (s, C−CH_3)	
			43.9 (s, N−CH_3)	
5	1.16 (s, C−CH_3)	−105.1 (q)	23.4 (d, *t*-Bu)	10.9 (d)
	3.56 (d, N−CH_3)		30.4 (s, C−CH_3)	
			44.6 (d, N−CH_3)	
6	1.10 (s, C−CH_3)	−8.85 (s)	23.0 (t, *t*-Bu)	24.1 (t)
			30.3 (s, C−CH_3)	

SCHEME 3



of the N−F bond. Although it is expected that electron density can be increased either by introducing an electron-donating substituent on nitrogen or by forming a nitrogen anion, Sommer[22] demonstrated that replacing one hydrogen atom of **1** by an electron-donating CH_3 group to form **4** caused the nucleophilicity of the nitrogen atom to be decreased. Therefore, the nucleophilicity of the nitrogen center of **1** was enhanced via formation of the lithium salt.[22,25] The latter with Selectfluor gave **3** in 50% yield. (Scheme 2). The composition of **3** was confirmed from elemental analysis and mass and NMR (^1H, ^{19}F, ^{29}Si, ^{13}C) spectral analysis. Surprisingly, although molecular ion peaks are not usually observed in the mass spectra for many tris(*tert*-butyl)silyl compounds,[26] a peak assignable to M^+ was present in the MS (EI) spectrum of **3**. The NMR spectral data given in Table 1 confirm the replacement of one N−H bond in **1** by the formation of −NHF in **3**, with the ^{19}F NMR signal being observed at −190.3 ppm, which is consistent with the chemical shift expected for an NHF group.[15,16]

When *N*-methyltris(*tert*-butyl)silylamine[22] (**4**) was reacted with Selectfluor, fluorination occurred only at silicon to form **2**. However, with prior lithiation of **4**, (N-fluoro-*N*-methyl)tris(*tert*-butyl)silylamine (**5**) (50% yield) was obtained. (Scheme 3).

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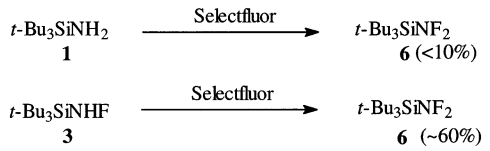
SCHEME 4



For **5**, M^+ is observed with exact mass being determined. The ^{19}F NMR chemical shift for the fluorine bonded to nitrogen appeared as a quartet at −105.1 ppm (Table 1).

Although Selectfluor and other N−F fluorinating reagents have been utilized to selectively fluorinate carbanions in the presence of nitrogen,[12−14] our work is the first example of using nitrogen anions as substrates. The tris(*tert*-butyl)silyl *N*-fluoroamines (**3**, **5**) are thermally stable (40−50 °C for 5 h), colorless solids that are readily soluble in hydrocarbons, CH_2Cl_2, and CH_3CN. They are stable in ambient air, in contrast to most organic fluoroamines. Additionally, they are inert to dilute hydrochloric acid (25%) and to hydrofluoric acid (50%) as well as to Na_2CO_3 (10%). Under GC/MS conditions (column, 30 m; T = 80° → 250 °C), **3** was unchanged, but under similar conditions 20−25% of **5** was converted to the corresponding silyl fluoride.

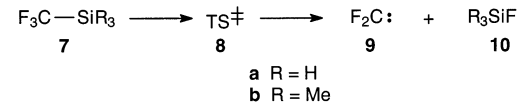
When **3** was allowed to react with a large excess of Selectfluor in dry acetonitrile at 25 °C, a colorless, oily solid (**6**) (~60% yield) was formed. In the ^1H NMR spectrum, (Table l) no N−H resonance was observed. However, a singlet was observed at −8.85 ppm in the ^{19}F NMR spectrum. Triplets observed in the NMR spectra for carbon and silicon support the presence of two fluorine atoms bonded to nitrogen. Under GC/MS conditions, **6** is converted to **2** quantitatively. When **6** was treated with 100% sulfuric acid, the HNF_2 formed was removed as a volatile product and identified via ^{19}F NMR and infrared spectra. This was identical to the product obtained when trityl difluoramine, a known source of HNF_2, was treated in an analogous fashion.[27] In the presence of fluoride ion, perfluoroglutaryl fluoride with **6** gave $[F_2NC(O)CF_2]_2$-CF_2.[28] Both of these reactions demonstrate the ability of **6** to transfer the $-NF_2$ moiety nucleophilicly. Spectral and chemical evidence and elemental analyses support the preparation of N,N-difluorotris(*t*-butyl)silylamine [$(t$-$Bu)_3SiNF_2$].

In early experiments, **1** was reacted with a large excess of Selectfluor to give **6** in very small amounts, but when the intermediate **3** was isolated first, much higher yields of **6** resulted (Scheme 4).

Computational Studies

The long (1.923 Å for **7a**) and weak F_3C−Si bond in trifluoromethylsilanes together with the extreme fluorophilic nature of silicon led to the expectation that trifluoromethylsilanes (e.g., **7**) would be thermally unstable species, fragmenting to give difluorocarbene (**9**) and the corresponding fluorosilane (**10**)[29−31] (Scheme 5).

SCHEME 5



Contrary to this expectation, the trifluoromethylsilanes exhibit surprising thermal stability. Trifluoromethylsilane (**7a**) itself begins to decompose at 180 °C and requires 15 h at 210 °C for complete decomposition.[31] Eujen et al. concluded from the composition of the thermolysis products that difluorocarbene formation is the first step in the thermal fragmentation.[31] They also report in the same study that migration of fluorine from carbon to silicon is important in the mass spectral fragmentations of **7a**.

Considering that the F−N bond is significantly weaker than the F−C bond, our synthesis and isolation of *N*,*N*-difluorotris(*tert*-butyl)silylamine (**6**) demonstrates an even more surprising thermal stability than in the case of the trifluoromethylsilanes. To further investigate the apparent reluctance of **6** to undergo spontaneous decomposition to fluoronitrene (**12**) and the fluorosilane **2**, we examined the energetics of this process and that of the corresponding thermolysis of **7b** (Scheme 5). All calculations were carried out with a 6-31G* basis set, and geometries were optimized using Restricted (RB3LYP) and/or unrestricted (UB3LYP) density functional theory (DFT) as implemented in Jaguar 4.0[32] and Gaussian 98.[33] Analytical energy second derivatives were calculated at each stationary point to confirm their identity as minima or transition structures and to obtain their enthalpies and free energies at 298.15 K.

Initially, optimized structures for **7b**, **9**, **10b,** and the transition structure (TS‡) **8b** were located at the RB3LYP/6-31G* level of theory. We used the intrinsic reaction coordinate (IRC) method in Gaussian 98 (G 98)[33] to "follow the reaction path" from **8b** to starting material and products. The IRC calculation indicated that **7b** is connected to **9** and **10b** through **8b**. Careful examination of TS‡ **8b** revealed that bond cleavage [internuclear distance (r)C−Si = 2.3423 Å in **8b**, cf. 1.9364 Å in **7b**] is considerably more advanced than bond formation [(r)-Si−F = 2.4641 Å in **8b**, cf. 1.6313 Å in **10b**]. This asynchronous reorganization of **7b** suggests a potential for biradical character in **8b**. We therefore carried out a complete UB3LYP/6-31G* investigation of this system. The UB3LYP results are identical with those obtained using RB3LYP, and in each case **7b**, **8b**, **9**, and **10b** are "pure singlets" with $\langle S^2 \rangle = 0$. Similarly, using the

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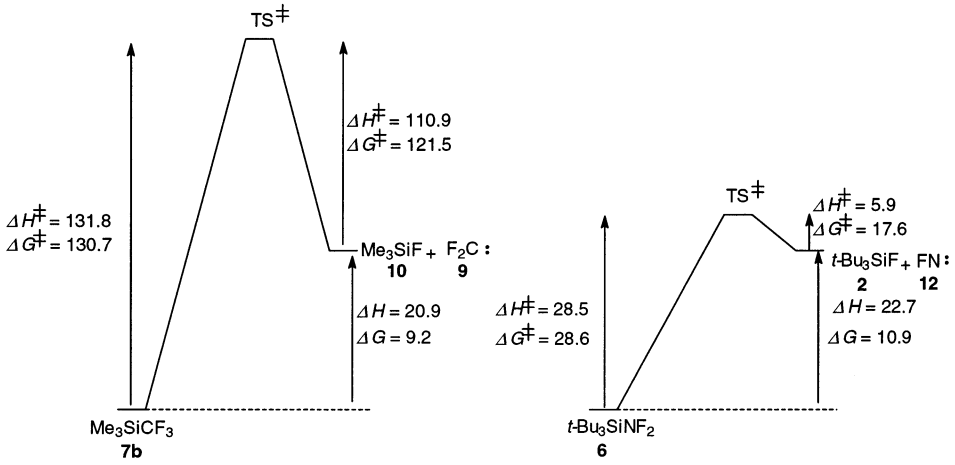
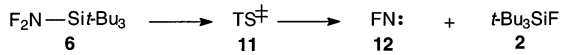


FIGURE 1. Schematic of the energy changes (kcal/mol) upon fragmentation of **7b** and **6**.

SCHEME 6



RB3LYP/6-31G* level of theory, we found the corresponding reaction of **6** to give **12** and **2** followed a more synchronous pathway through TS‡ **11** in which (*r*)N−Si = 2.2791 Å in **11**, cf. 1.8781 Å in **6**, and (*r*)Si−F (shortest) = 1.8075 Å in **11**, cf. 1.6434 Å in **2**. An IRC calculation again assisted in our assignment of **11** as the TS‡ for this fragmentation. In the light of our UB3LYP results for the **7b** fragmentation and the more equal bond formation/cleavage in the TS‡ **11**, we did not use the UB3LYP method with the series **6**−**11**, **12**, and **2**.

In Figure 1 we show the energy changes occurring during thermolysis of **7b** (Scheme 5) and **6** (Scheme 6). It is immediately apparent that there is an enormous activation barrier for the fragmentation of **7b**. The reaction of **7b** to produce **9** and **10b** is also quite strongly endothermic. Doubtless further reaction of difluorocarbene (**9**) would be highly exothermic, leading to an overall thermodynamically favorable decomposition of **7b**. As anticipated, the activation barrier for the thermolysis of **6**, although still appreciable, is significantly lower than that for **7b**. Observation of fragment ions with Si−F bonds in the EI mass spectrum of **6** supports the proposed thermolysis pathway for **6**. The production of **12** and **2** from **6** is also endothermic, and again, further reaction of the nitrene **12** should contribute to a strongly thermodynamically favored decomposition of **6**.

Conclusion

Electrophilic fluorination of organosilylamines substituted with bulky *tert*-butyl groups has resulted in the syntheses of the first three stable *N*-fluorosilylamines. *N*,*N*-Difluorotris(*tert*-butyl)silylamine has much promise as a synthon in nucleophilic reactions. The results from DFT calculations indicate that *t*-Bu_3SiNF_2 should undergo facile thermolysis, while the corresponding activation enthalphy (kcal/mol) for Me_3SiCF_3 is substantial and accounts for the observed experimental kinetic stability.

Experimental Section

All reactions were performed under a dry nitrogen atmosphere. Selectfluor was a gift from Air Products and Chemical, Inc. ^{1}H, ^{19}F, ^{13}C{H}, and ^{29}Si{H} NMR spectra were recorded in $CDCl_3$ on spectrometers operating at 500, 470, 125, and 99 mHz, respectively. Chemical shifts are reported in ppm relative to the appropriate standards: $CFCl_3$ for ^{19}F and TMS for ^{1}H, ^{13}C, and ^{29}Si spectra. GC/MS electron ionization and high-resolution mass (HRMS) spectral data were obtained using suitable mass spectrometers. All starting materials were obtained using standard literature procedures. Elemental analyses were performed either by Desert Analytics, Tucson, AZ or the Chinese Institute of Organic Chemistry, Shanghai. **CAUTION:** Compounds that contain the N−F linkage should be treated as potential explosives. Difluoroamine should not be cooled below its melting point.

Procedure A. A suspension of Selectfluor (1.8 g, 5.5 mmol) in dry acetonitrile (∼60 mL) was added under nitrogen to a solution of tris(*tert*-butyl)silylamine[22] (**1**, 0.55 g, 2.6 mmol) in acetonitrile (∼10 mL) at −5 to 0 °C. After stirring for 2 h, the reaction mixture was warmed to 25 °C and the solvent was removed under vacuum. The residue was extracted with pentane. The product (**3**) was purified by column chromatography (Al_2O_3, pentane) and was obtained in ∼15% yield.

Procedure B. A suspension of Selectfluor (3.5 g, 10.8 mmol) in dry acetonitrile (∼85 mL) was added to a solution of the lithium salt of either **1** or **4** (1.10 g, 5.2 or 4.9 mmol) in dry ether (∼4 mL) at −15 °C under nitrogen. The mixture was warmed to 25 °C. The workup was as in procedure A. The yield was ∼50% of **3** or ∼50−55% of **5.** On the basis of proton and fluorine NMR, the purity of these compounds was ∼94−96%. Analytical purity of the compounds was achieved by recrystallization from acetonitrile at low temperature. Compound **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.16 (d, J_{H-F} = 0.7 Hz, 27H), 9.1 (d, J_{H-F} = 64.5, 1H); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −190.3 (d) (coupling with the CH_3 protons on *tert*-butyl was not resolved at 188 MHz); ^{13}C NMR 50 MHz, $CDCl_3$) δ = 29.8 (s), 22.4 (d, J_{C-F} = 3.5 Hz); ^{29}Si NMR (99.4 MHz, $CDCl_3$) δ = 10.7 (d, J_{Si-F} = 4.7 Hz); HRMS calcd 233.4449, found 233.4464. Anal. (%) Calcd for $C_{12}H_{28}FNSi$: C 61.74, H 12.09, N 6.00, F 8.14. Found: C 61.99, H 12.07, N 5.91, F 8.10.

Compound **5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.16 (s, 27H), 3.56 (d, J_{H-F} = 40.0, 1H); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −105.1 (q); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 23.4 (d, 3C, J_{C-F} = 3.2 Hz), 30.4 (s, 9C), 44.58 (d, 1C, J_{C-F} = 15.6 Hz); ^{29}Si (99.4 MHz, $CDCl_3$) δ = 10.86 (d, J_{Si-F} = 0.7 Hz); HRMS calcd 247.4719, found 247.4734. Anal. (%) Calcd for $C_{13}H_{30}FNSi$: C 63.10, H 12.22, N 5.66, F 7.68. Found: C 61.96, H 12.22, N 5.29, F 6.47.

Procedure C. A suspension of Selectfluor (1.8−2.0 g, 5.6 mmol) in dry acetonitrile (∼60 mL) was added under nitrogen to a solution of **3** (0.45 g, 2 mmol) in acetonitrile (∼10 mL) at 25 °C. After stirring for 10−12 h, the solvent was removed in vacuo. The workup as was in procedure A. After column chromatography, **6** is obtained in 60% yield. Compound **6:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.10 (s); ^{19}F NMR (188 MHz, $CDCl_3$) δ = −8.85 (s); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 30.3 (s), 23.0 (t) (J_{C-F} = 2.5 Hz); ^{29}Si NMR (99.4 MHz, $CDCl_3$) δ = 24.1 (t, J_{Si-F} = 0.65 Hz); MS (EI): *m/e* (species, intensity) 199 ($M^+ - NF_2$, 2.0), 179 ($((CH_3)_2CSi(t\text{-Bu})NF_2)^+$, 99.1), 165 ($((CH_3)C(t\text{-Bu})SiNF_2)^+ + 1$, 16.4), 161 ($(t\text{-Bu})_2SiF^+$, 57.6), 119 ($((t\text{-Bu})SiNHF)^+$, 10.2). Anal. (%) Calcd for $C_{12}H_{27}F_2NSi$: C 57.32, H 10.82, N 5.57. Found: C 56.55, H 9.92, N 5.31.

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Supporting Information Available: Tables of the Cartesian coordinates (Tables S1−S8) and total energies, zero-point corrections, and thermal corrections (Table S9) for compounds **7b**, **8b**, **9**, **10b**, **6**, **11**, **12**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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