VIP Direct fluorination Very Important Paper

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Synthesis of Tris- and Tetrakis(pentafluoroethyl)silanes**

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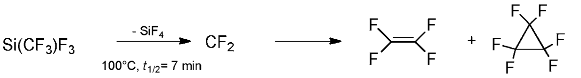
Dedicated to Professor G.-V. Röschenthaler on the occasion of his 70th birthday

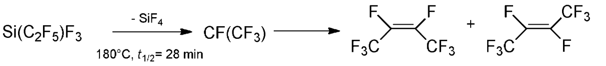
Abstract: *The synthesis and complete characterization of functional, highly Lewis acidic tris(pentafluoroethyl)silanes as well as tetrakis(perfluoroalkyl)silanes $Si(C_2F_5)_4$ and $Si(C_2F_5)_3CF_3$ by direct fluorination is described. The reaction of $SiCl_4$ with LiC_2F_5 invariably affords (pentafluoroethyl)fluorosilicates. To avoid silicate formation by fluoride transfer from LiC_2F_5 the Lewis acidity of the silane has to be decreased by electron-donating substituents, such as dialkylamino groups. The easily accessible $Si(C_2F_5)_3NEt_2$ is a valuable precursor for a series of tris(pentafluoroethyl)silanes.*

The thermal stability of trifluoromethylsilanes strongly depends on the nature of the ancillary substituents. Their decomposition is a result of the high fluorophilicity of silicon and occurs through CF_2 elimination with formation of Si–F bonds. The Ruppert–Prakash reagent, $Si(CF_3)Me_3$, is a fairly stable and versatile reagent for the introduction of trifluoromethyl groups in organic and inorganic compounds.[1] The decomposition temperatures of trifluoromethylsilanes decrease with an increasing electron withdrawal by the additional substituents. Owing to the pronounced group electronegativity of the CF_3 unit silanes with more than one CF_3 substituent are highly sensitive. $Si(CF_3)_3NEt_2$, for example, was generated and characterized at low temperatures, but could not be isolated because of its thermolability.[2] Recently the generation of $Si(CF_3)_4$ was reported by the reaction of CF_3H, $KN(SiMe_3)_2$(KHMDS), and $SiCl_4$ at low temperatures.[3] The complexity of the reaction mixture and the instability of this compound prevented its unambiguous characterization and isolation.

Sharp and Coyle reported on the different thermal stability of $Si(C_2F_5)F_3$ and $Si(CF_3)F_3$ [Eq. (1), (2)].[4] The pentafluoroethyl derivative seems to be considerably more stable. Based on this result the question is intriguing as to whether the thermal stability of tris- and tetrakis(pentafluoroethyl)silanes will allow their straightforward synthesis and isolation.

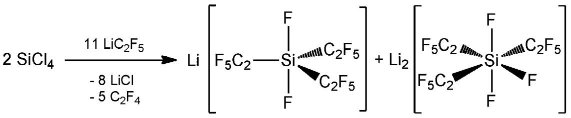


(1)



(2)

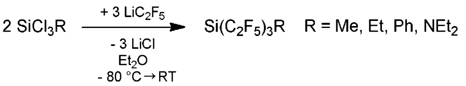
Recently we succeeded in the preparation of the (perfluoroalkyl)fluorosilicates $[Si(C_2F_5)_3F_2]^-$ and $[Si(C_2F_5)_3F_3]^{2-}$ from $SiCl_4$ and LiC_2F_5 [Eq. (3)].[5]



(3)

During the formation of these silicates, the transfer of C_2F_5 groups as well as of fluoride ions occurs. The reaction is initiated by the formation of $Si(C_2F_5)_3Cl$ from $SiCl_4$ and three equivalents of LiC_2F_5. Subsequently the strong Lewis acid $Si(C_2F_5)_3Cl$ reacts with LiC_2F_5 to afford the silicates $[Si(C_2F_5)_3F_2]^-$ and $[Si(C_2F_5)_3F_3]^{2-}$ instead of the anticipated $Si(C_2F_5)_4$. The neutral pentafluoroethylsilanes are only intermediates in this process and are not preparatively accessible by the reaction of $SiCl_4$ with various amounts of LiC_2F_5. Clearly for the synthesis of neutral tris(pentafluoroethyl)silanes from chlorosilanes and LiC_2F_5 it is crucial to prevent any silicate formation. This can be achieved by reducing the Lewis acidity of the silane by an electron donating alkyl-, aryl-, or amino substituent.

Treatment of alkyl-, aryl-, and aminotrichlorosilanes with three equivalents of LiC_2F_5 furnishes the corresponding tris(pentafluoroethyl)silanes as colorless liquids which are stable at room temperature [Eq. (4)].[6] While $Si(CF_3)_3NEt_2$ is described as thermally highly sensitive compound, $Si(C_2F_5)_3NEt_2$ does not decompose when heated to 180 °C for 2 h.



$$2\ SiCl_3R \xrightarrow[\substack{-\ 3\ LiCl \\ Et_2O \\ -\ 80\ ^\circ C \rightarrow RT}]{+\ 3\ LiC_2F_5} Si(C_2F_5)_3R \quad R = Me, Et, Ph, NEt_2 \qquad (4)$$

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Reaction of $Si(C_2F_5)_3NEt_2$ with gaseous HCl or HBr leads to the corresponding chloro- and bromosilane in high a yield [Eq. (5)].[4] Owing to the pronounced Lewis acidity of $Si(C_2F_5)_3F$, the combination of $Si(C_2F_5)_3NEt_2$ with anhydrous HF gave rise to the formation of the salt $[NEt_2H_2][Si(C_2F_5)_3F_2]$ [Eq. (6)]. In contrast to this reaction, treatment of neat $Si(C_2F_5)_3Cl$ or $Si(C_2F_5)_3Br$ with SbF_3 yields $Si(C_2F_5)_3F$ [Eq. (7)] as a colorless liquid which solidifies at −110 °C. A twinned crystal was obtained by in situ crystallization of the liquid sealed in a glass capillary by manually generating a suitable seed crystal slightly below the melting point first, followed by slowly cooling to −173 °C. The fluorosilane, $Si(C_2F_5)_3F$, crystallizes in the monoclinic space group $P2_1/n$ (Figure 1).

$$Si(C_2F_5)_3NEt_2 \xrightarrow[-\,[NEt_2H_2]X]{+\,2\,HX} Si(C_2F_5)_3X \quad X = Cl, Br \tag{5}$$

$$Si(C_2F_5)_3NEt_2 \xrightarrow{+\,2\,HF} [NEt_2H_2][Si(C_2F_5)_3F_2] \tag{6}$$

$$Si(C_2F_5)_3X \xrightarrow[-\,SbXF_2]{+\,SbF_3} Si(C_2F_5)_3F \quad X = Cl, Br \tag{7}$$

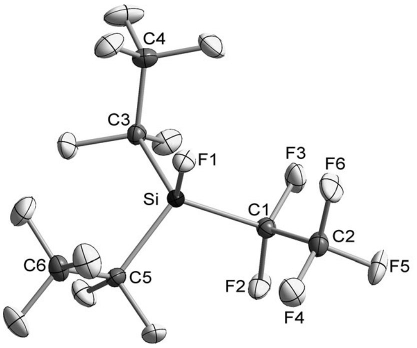


Figure 1. Molecular structure of $Si(C_2F_5)_3F$ (thermal ellipsoids are set at 50% probability). Selected bond lengths [pm] and angles [°]: Si–F1 156.7(1), Si–C1 192.9(1), Si–C3 193.0(2), Si–C5 192.4(2), C1–F2 135.9(2), C1–F3 136.0(2), C2–F4 132.7(2), C2–F5 132.5(2), C2–F6 132.3(2); F1–Si–C1 108.4(1), F1–Si–C3 108.8(1), F1–Si–C5 108.5(1), C1–Si–C3 109.9(1), C1–Si–C5 110.2(1), C5–Si–C3 111.0(1); F1–Si–C3–C4 19.9(3), F1–Si–C1–C2 29.1(3), F1–Si–C5–C6 32.8(3).

The Si–F distance of 156.7(1) pm is in the expected range (d(Si–F) 158.5(1) pm in $Si(C_6F_5)_3F$,[7] d(Si–F) 156(1) pm in SiF_4[8]). The F-Si-C angles are slightly more acute than the C-Si-C angles. The C–F bond lengths for the CF_2 groups exceed those of the CF_3 group (CF_2: $d_ø$(C-F) 135.9(2) pm, CF_3: $d_ø$(C-F) 132.5(6) pm). The different dihedral angles F1-Si-C-C reflect a distortion from local C_3 symmetry (19.9(1)°, 29.1(1)°, and 32.8(1)°).

To demonstrate the high Lewis acidity of $Si(C_2F_5)_3F$ it was treated with $[P(C_2F_5)_3F_3]^-$ salts, whereby the phosphorane, $P(C_2F_5)_3F_2$, and ionic liquids with the $[Si(C_2F_5)_3F_2]^-$ ion [Eq. (8)] are cleanly generated.[4] In Table 1 some calculated fluoride ion affinities (FIA)[9] are given for comparison.

$$[EMIM][P(C_2F_5)_3F_3] + Si(C_2F_5)_3F \longrightarrow [EMIM][Si(C_2F_5)_3F_2] + P(C_2F_5)_3F_2 \tag{8}$$

[EMIM] = 1-Ethyl-3-methylimidazolium

Table 1: Fluoride ion affinity (FIA) of some Lewis acids (B3LYP/6-311++G(2d)).[10]

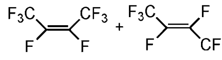
Lewis acid	FIA [kJ mol^{-1}][a]
$Si(C_2F_5)_3F$	420.0
AsF_5	416.5
$P(C_2F_5)_3F_2$	389.3
PF_5	357.1
SiF_4	299.3

[a] FIA = $-\Delta_r G^\ominus$.

According to these calculations, the Lewis acidity of $Si(C_2F_5)_3F$ is comparable with that of AsF_5.

In keeping with the investigations of Sharp and Coyle heating of gaseous $Si(C_2F_5)_3F$ for 1 h at 180 °C led to the disintegration of most C_2F_5 groups by elimination of $CF(CF_3)$. The resulting reaction mixture contains $Si(C_2F_5)F_3$, SiF_4, *cis*- and *trans*-perfluorobut-2-ene, as well as some other fluorocarbons [Eq. (9)].

$$Si(C_2F_5)_3F \xrightarrow{180\ °C,\ 1\ h,\ 100\ mbar} \underset{80\ :\ 20}{Si(C_2F_5)F_3 + SiF_4} + \tag{9}$$



+ fluorocarbons

Thermolysis of $Si(C_2F_5)_3F$ at 50 °C for 60 h proceeds differently. *cis*- and *trans*-perfluorobut-2-ene can only be detected as traces in the reaction mixture. Instead $Si(C_2F_5)_2F_2$ and $Si(C_2F_5)_4$ are formed by ligand exchange [Eq. (10)]. This surprising result is in accord with a high thermal stability of $Si(C_2F_5)_4$. Because $Si(C_2F_5)_4$ is not accessible by the reaction of $Si(C_2F_5)_3Cl$ and LiC_2F_5, a different synthetic strategy to access this compound was designed. The reaction of $SiMe_4$ and Si_2Me_6 with elemental fluorine has been investigated by Lagow and co-workers.[11] The direct fluorination of methylsilanes gives SiF_4, fluorocarbons, and only partially fluorinated methylsilanes as pyrophoric and explosive compounds. This result is not necessarily due to the instability of Si–C bonds towards elemental fluorine as the expected products $Si(CF_3)_4$ and $Si(CF_3)_3F$ themselves are thermally sensitive compounds which could spontaneously decompose. Therefore we investigated the direct fluorination of $Si(C_2F_5)_3C_2H_5$ [Eq. (11)].

$$Si(C_2F_5)_3F \xrightarrow{50\ °C,\ 60\ h,\ 100\ mbar} \underset{5\ :\ 90\ :\ 5}{Si(C_2F_5)_4 + Si(C_2F_5)F_3 + Si(C_2F_5)_2F_2} \tag{10}$$

$$Si(C_2F_5)_3C_2H_5 \xrightarrow[-\,5\,HF]{+\,5\,F_2} Si(C_2F_5)_4 \tag{11}$$

The gas phase reaction of $Si(C_2F_5)_3C_2H_5$ with five equivalents of elemental fluorine produces a mixture of $Si(C_2F_5)_4$, $Si(C_2F_5)_3F$, $Si(C_2F_5)_2F_2$, SiF_4, HF, and C_2F_6. By isothermal distillation $Si(C_2F_5)_4$ can be isolated in a 30% yield.

The ^{29}Si NMR spectrum of $Si(C_2F_5)_4$ shows a nonet at $\delta = -35.2$ with the expected ^2J(Si,F) coupling of 39 Hz (Figure 2).

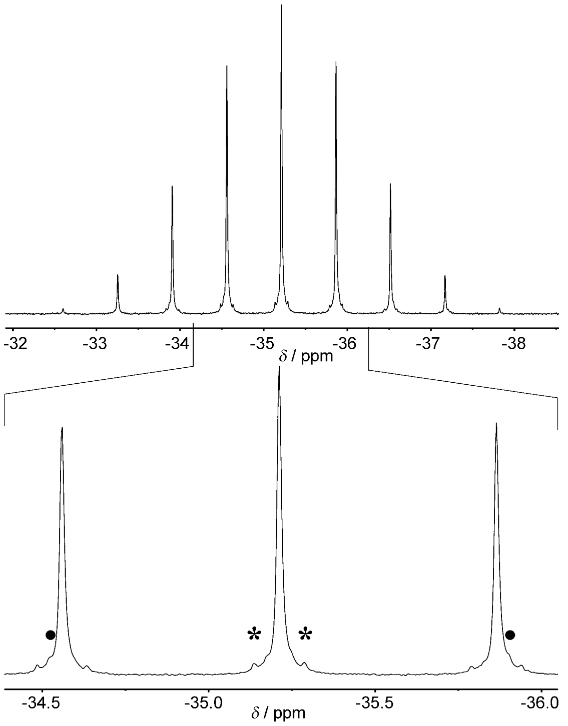


Figure 2. Top: ^{29}Si NMR spectrum of neat $Si(C_2F_5)_4$ with [D$_6$]acetone as external lock. Bottom: ^{13}C satellites of the central part of the nonet (^1J(Si,C) = 82 Hz (●)), ^2J(Si,C) = 8 Hz (*)).

Single crystals were obtained by in situ crystallization slightly below the melting point of −82 °C. $Si(C_2F_5)_4$ crystallizes in the monoclinic space group $P2_1/c$ (Figure 3)[12] with two nearly congruent molecules per asymmetric unit, so only one will be discussed in the following. The coordination of the silicon atom strongly deviates from tetrahedral symmetry with two smaller C-Si-C angles of about 102° (C3-Si-C5 and C7-Si-C1) and of about 113° for the remaining ones. As for $Si(C_2F_5)_3F$ the C–F distances of the CF_2 groups are slightly elongated in comparison with those of the CF_3 groups (CF_2, $d_{\varnothing}$(C–F) 136.4(3) pm; CF_3, $d_{\varnothing}$(C–F) 133.0(3) pm).

To our knowledge this is the first synthesis of a tetrakis(perfluoroalkyl)silane by direct fluorination. Larger quantities of $Si(C_2F_5)_4$ could also be obtained by thermolysis of liquid $Si(C_2F_5)_3F$ at 70 °C for 2 weeks and subsequent isothermal distillation of the crude product.

The remarkable difference in the thermal stability of trifluoromethyl- and (pentafluoroethyl)silanes can be rationalized by the different tendency to eliminate the corresponding carbene, CF_2 or $CF(CF_3)$, respectively. To further study this different behavior we also investigated the reaction of $Si(C_2F_5)_3CH_3$ with elemental fluorine [Eq. (12)].

$$Si(C_2F_5)_3CH_3 \xrightarrow[-3\,HF]{+3\,F_2} Si(C_2F_5)_3CF_3 \qquad (12)$$

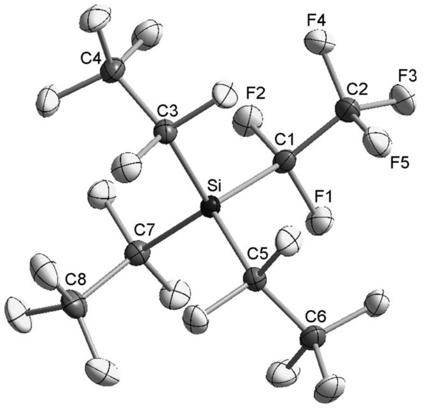


Figure 3. Molecular structure of $Si(C_2F_5)_4$ in the crystal (thermal ellipsoids are set at 50% probability). Selected bond lengths [pm] and angles [°]: Si–C1 194.2(1), Si–C3 194.5(1), Si–C5 194.7(1), Si–C7 194.4(1), C1–F1 136.8(2), C1–F2 136.3(1), C2–F3 132.7(2), C2–F4 133.1(2), C2–F5 133.6(2); C1–Si–C3 112.1(1), C1–Si–C5 113.4(1), C1–Si–C7 103.0(1), C3–Si–C5 102.4(1), C7–Si–C3 113.5(1), C7–Si–C5 112.8(1).

Isothermal distillation of the reaction mixture yields a colorless liquid containing $Si(C_2F_5)_3CF_3$ (40%), $Si(C_2F_5)_3F$ (54%), and $Si(C_2F_5)_2F_2$ (6%). After 14 h at room temperature 90% of the initial amount of $Si(C_2F_5)_3CF_3$ had decomposed to $Si(C_2F_5)_3F$ and C_2F_4 [Eq. (13)].

$$2\,Si(C_2F_5)_3CF_3 \xrightarrow{RT} 2\,Si(C_2F_5)_3F + C_2F_4 \qquad (13)$$

In conclusion, silicon carbon bonds of alkylsilanes are clearly inert to a direct fluorination in the gas phase. Thus, $Si(C_2F_5)_4$ and $Si(C_2F_5)_3CF_3$ are accessible by direct fluorination of $Si(C_2F_5)_3C_2H_5$ and $Si(C_2F_5)CH_3$, respectively. Both compounds represent first examples of tetrakis(perfluoroalkyl)silanes. Whereas $Si(C_2F_5)_4$ decomposes only at elevated temperatures, $Si(C_2F_5)_3CF_3$ already liberates difluorocarbene at room temperature. Pentafluoroethylsilicon compounds are thermally significantly more stable than their corresponding trifluoromethyl counterparts. Owing to its thermal sensitivity, $Si(CF_3)_3NEt_2$ could not be isolated to date. The pentafluoroethyl derivative, $Si(C_2F_5)_3NEt_2$, does not decompose on heating to 180 °C and is accessible on a large scale by the reaction of $SiCl_3NEt_2$ and LiC_2F_5. Based on the versatile reactivity of the silicon–nitrogen bond, this compound is a potential starting material for the synthesis of a series of tris(pentafluoroethyl)silanes.

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[12] Data for X-ray structure determination of $Si(C_2F_5)_3F$ were collected on a Bruker Nonius KappaCCD diffractometer, for $Si(C_2F_5)_4$ on an Agilent SuperNova diffractometer with EOS detector, at 100(2) K using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm). The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97: G. M. Sheldrick, *Acta. Cryst. Sect. A* **2008**, *64*, 112–122). All atoms were refined anisotropically. Data for $Si(C_2F_5)_3F$: colorless crystal, $M_r = 404.15\ \mathrm{g\,mol^{-1,}}$ monoclinic space group $P2_1/n$, $a = 858.3(1)$, $b = 1382.7(1)$, $c = 1061.7(1)$ pm, $\beta = 112.64(1)°$, $V = 1162.9(2) \times 10^6\ \mathrm{pm^3}$, $Z = 4$, $\rho_{calcd} = 2.308\ \mathrm{g\,cm^{-3}}$, $F(000) = 776$; 11821 reflections up to $\theta = 25$ collected, thereof 9621 with $I > 2\sigma(I)$, 2048 independent reflections, 209 parameters. R-values: $R_1 = 0.0462$ for refl. with $I > 2\sigma(I)$, $wR_2 = 0.124$ for all data. Data for $Si(C_2F_5)_4$: colorless crystal, $M_r = 504.17\ \mathrm{g\,mol^{-1}}$, monoclinic space group $P2_1/c$, $a = 1220.99(3)$, $b = 1232.30(3)$, $c = 2004.00(5)$ pm, $\beta = 91.144(2)°$, $V = 3014.7(1) \times 10^6\ \mathrm{pm^3}$, $Z = 8$, $\rho_{calcd} = 2.222\ \mathrm{g\,cm^{-3}}$, $F(000) = 1936$; 50510 reflections up to $\theta = 30$ collected, 8822 independent reflections, thereof 6722with $I > 2\sigma(I)$, 523 parameters. R-values: $R_1 = 0.0316$ for refl. with $I > 2\sigma(I)$, $wR_2 = 0.076$ for all data. CCDC 973139 ($Si(C_2F_5)_3F$) and 973140 ($Si(C_2F_5)_4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..