**Perfluoroalkyl Silicon Compounds**

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# Synthesis of Five- and Six-Coordinate Tris(pentafluoroethyl)fluorosilicates**

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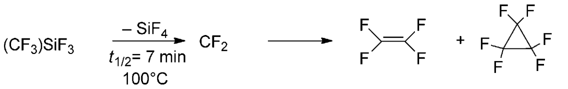
*Dedicated to Professor Werner Uhl on the occasion of his 60th birthday*

**Abstract:** *The research area of perfluoroalkylsilanes is still in its infancy. Although there are already many examples of difluorotriorganylsilicates, the first example of a completely characterized trifluorotriorganylsilicate is presented, the dianion* $[Si(C_2F_5)_3F_3]^{2-}$. *The strongly electron-withdrawing influence of the pentafluoroethyl groups appears to be a fundamental cause of the stability of this compound. This dianion is also the first structurally characterized example of a tris(pentafluoroethyl)silicon compound. The synthesis and complete characterization of* $[PPh_4]_2[Si(C_2F_5)_3F_3]$ *and* $[PPh_4][Si(C_2F_5)_3F_2]$ *along with the precursor* $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ *was achieved from* $SiCl_4$ *and* $LiC_2F_5$.

The chemistry of (perfluoroalkyl)silanes has essentially been restricted to trifluoromethyl derivatives. Owing to the high fluorophilicity of silicon, these compounds decompose by $CF_2$ elimination and the formation of Si–F bonds. Generally the thermolability of $(CF_3)SiX_3$ derivatives increases with increasing electronegativity of the substituent X.[1,2] With regard to the pronounced group electronegativity of the $CF_3$ unit, silanes with more than one $CF_3$ substituent should be highly sensitive. In keeping with this, $(CF_3)_3SiCl$ and $(CF_3)_3SiNEt_2$ have not been isolated to date, and information on their existence is limited to spectroscopic evidence.[2] Despite claims otherwisein the literature,[3] $Si(CF_3)_4$ is still elusive.

According to Sharp and Coyle, the thermal stabilities of $(CF_3)SiF_3$ and $(C_2F_5)SiF_3$ differ considerably, which may be rationalized by the increased tendency to extrude $CF_2$ in comparison to $CF(CF_3)$ [Eqs. (1),(2)].[4]



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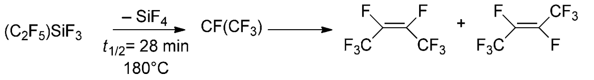

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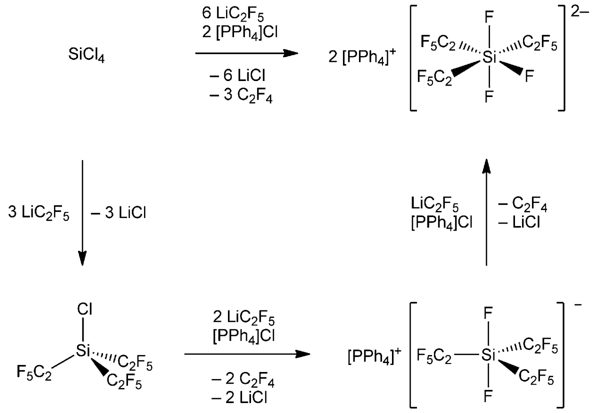
Despite the knowledge of this fact for about 40 years, only a few pentafluoroethyl silanes have been synthesized. Moreover, based on Sharp's and Coyle's observations, the existence of silanes with more than two pentafluoroethyl substituents at ambient temperature is very conceivable.

Herein we report our results on the combination of three pentafluoroethyl substituents at a six-coordinate silicon center. Reaction of $SiCl_4$ with a tenfold excess of $LiC_2F_5$[5] and the subsequent cation exchange with $[PPh_4]Cl$ afforded a mixture of $[PPh_4]_2[Si(C_2F_5)_3F_3]$ and $[PPh_4][Si(C_2F_5)_3F_2]$.[6] The course of this transformation involves the initial formation of $(C_2F_5)_3SiCl$ from $SiCl_4$ and three equivalents of $LiC_2F_5$ (Scheme 1). The next two equivalents of $LiC_2F_5$ serve as fluoride sources, which convert the Lewis acidic $(C_2F_5)_3SiCl$ into the tris(pentafluoroethyl)difluorosilicate ion. Addition of a further fluoride ion by release from the sixth equivalent of $LiC_2F_5$ eventually furnished the six-coordinate tris(pentafluoroethyl)trifluorosilicate dianion.



**Scheme 1.** The multistep reaction of $SiCl_4$ with an excess of $LiC_2F_5$.

The preparation of salts containing exclusively the five-coordinate anion $[Si(C_2F_5)_3F_2]^-$ has been achieved by treating the initially obtained reaction mixture of $SiCl_4$ and $LiC_2F_5$ in diethyl ether with dry HCl gas [Eq. (3)]. The compound $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ was isolated after filtration of the resulting mixture and removal of all volatile components in

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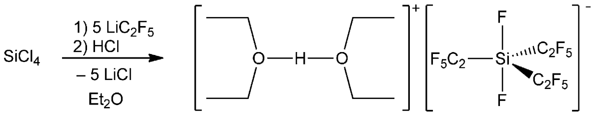

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vacuo. The product is a colorless liquid with a vapor pressure of less than 1 mbar at 20 °C.

The composition of the product $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ can be rationalized from the integration of the $^1H$ NMR spectrum of the neat liquid (Figure 1). The data of the cation, $[H(OEt_2)_2]^+$, are in agreement with literature data.[7] The resonance in the $^{29}Si$ NMR spectrum is observed at −111 ppm which is split into a triplet of septets owing to $^1J(Si,F)$ and $^2J(Si,F)$ couplings of 318 Hz and 37 Hz, respectively.

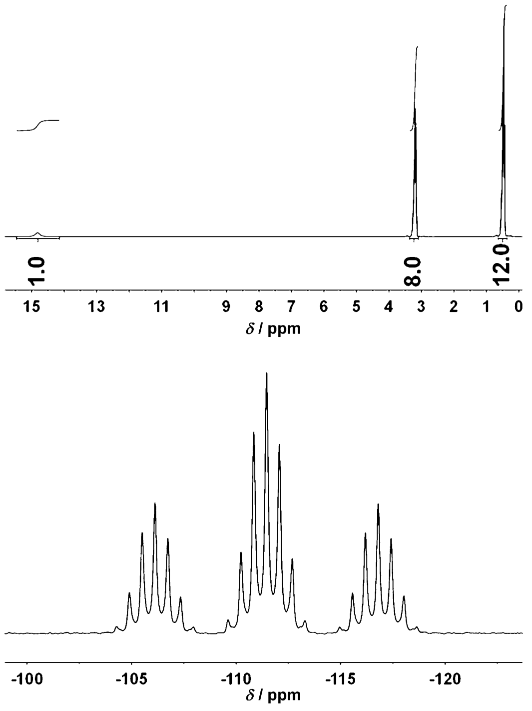
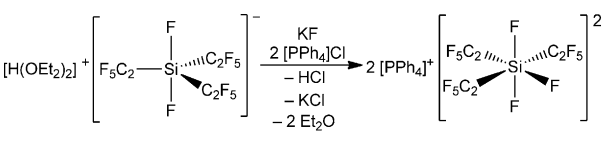


**Figure 1.** $^1H$ NMR spectrum (top) and $^{29}Si$ NMR spectrum (bottom) of neat $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ (RT, [D$_6$]acetone as external lock).

Adding $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ to an aqueous KF solution leads to the selective formation of the six-coordinate silicate, which can be transformed into its tetraphenylphosphonium salt upon addition of $[PPh_4]Cl$. Using this procedure allows the isolation of $[PPh_4]_2[Si(C_2F_5)_3F_3]$ [Eq. (4)]. The



(4)

product crystallizes with one molecule $CH_2Cl_2$ in the triclinic space group $P\bar{1}$.[8] The molecular structure of the dianion $[Si(C_2F_5)_3F_3]^{2-}$ is depicted in Figure 2. The substituents of $[Si(C_2F_5)_3F_3]^{2-}$ show a meridional constitution, as it is found for the isoelectronic phosphate ion, $[P(C_2F_5)_3F_3]^-$.[9,10] The Si–F bond lengths are about 169 pm and do not vary significantly. The Si–C3 bond of the pentafluoroethyl group *trans* to the fluorine atom is slightly elongated (205 pm) with respect to the Si–C distances of the trans oriented pentafluoroethyl groups (Si–C5 202 pm and Si–C1 203 pm). All of the intermolecular contacts exceed the sum of the corresponding van der Waals radii, and therefore do not influence the molecular structure of the anion.

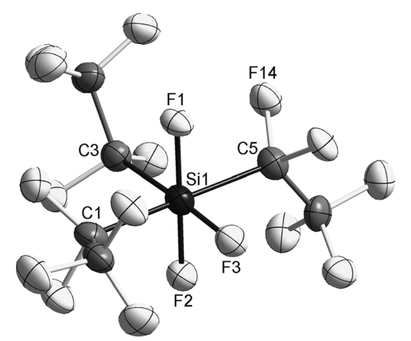


**Figure 2.** Molecular structure of $[Si(C_2F_5)_3F_3]^{2-}$ in $[PPh_4]_2[Si(C_2F_5)_3F_3]\cdot CH_2Cl_2$ (ellipsoids are set at 50% probability). Selected bond lengths [pm] and angles [°]: Si1–F1 169.2(3), Si1–F2 168.6(3), Si1–F3 168.5(3), Si1–C1 202.8(5), Si1–C3 205.0(5), Si1–C5 202.2(5); F1-Si1-F3 92.0(1), F2-Si1-F3 90.0(1), F1-Si1-C3 91.6(2), F1-Si1-C5 87.4(2), C3-Si1-C5 93.7(2).

The first-order $^{29}Si$ NMR resonance of the $[Si(C_2F_5)_3F_3]^{2-}$ ion exhibits the expected doublet of triplet splitting with two different $^1J(Si,F)$ couplings of 315 Hz and 202 Hz. A further septet splitting is caused by a $^2J(Si,F)$ coupling of 32 Hz. A possible coupling to the $CF_3$ groups, the $^3J(Si,F)$ coupling, could not be observed. The chemical shift of −180.8 ppm lies in the expected range for six-coordinate silicon species.

In conclusion, the chemistry of perfluoroalkyl silanes is still at its infancy. Although several examples of triorganyl difluorosilicates are known,[11] the dianion $[Si(C_2F_5)_3F_3]^{2-}$ is the first example of a fully characterized triorganyl trifluorosilicate. The strong electron-withdrawing effect of the pentafluoroethyl groups seems to be essential to stabilize this unusual compound. More generally, this compound is the first structurally characterized example of a tris(perfluoroalkyl)silicon compound.[12]

We succeeded in the preparation and full characterization of $[PPh_4]_2[Si(C_2F_5)_3F_3]$ and $[PPh_4][Si(C_2F_5)_3F_2]$ and their precursor $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ from $SiCl_4$ and $LiC_2F_5$ as starting materials, and a mechanism for the multistep generation of these silicates was presented. Future studies in our laboratory are focused on neutral tris(pentafluoroethyl)silanes and the most challenging silane $Si(C_2F_5)_4$.

## Experimental Section

All of the chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled in a dry $N_2$ atmosphere using Schlenk techniques. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer ($^{29}Si$ 59.6 MHz, $^{19}F$ 282.4 MHz, $^1H$

300.1 MHz) with positive shifts being downfield from the external standards (TMS ($^{29}$Si, $^{1}$H), $CCl_3F$ ($^{19}$F)). ESI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. C, H, and N analyses were carried out with a HEKAtech Euro EA 3000 apparatus.

Synthesis of $[PPh_4][Si(C_2F_5)_3F_2]$: $HC_2F_5$ (24 g, 200 mmol) is condensed at −85 °C onto a degassed solution of 1.6 M *n*-butyllithium in hexane (100 mL, 160 mmol) in diethyl ether (500 mL). After stirring for 20 min a sample of $SiCl_4$ (3.4 g, 20 mmol) was added. The reaction mixture was allowed to slowly warm to room temperature within 150 min. At RT the reaction mixture was stirred under an HCl atmosphere. The precipitate was filtrated off, and the solvent was removed at reduced pressure. The remaining liquid (10.5 g) with an estimated composition $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ was dissolved in $CH_2Cl_2$ and a solution of $[PPh_4]Cl$ (6.6 g, 17.6 mmol) in $CH_2Cl_2$ was added. After evaporating the solvent at reduced pressure, $[PPh_4][Si(C_2F_5)_3F_2]$ (13.4 g, 17.6 mmol, 88 % with respect to $SiCl_4$) was obtained as a colorless solid that decomposes above 90 °C.

Elemental analysis (%) calcd for $C_{30}H_{20}F_{17}PSi$: C 47.2, H 2.6 %; found: C 47.2 %, H 2.7 %. $^{29}$Si NMR ($Et_2O$, RT): $\delta = -109.3$ ppm (t, sept, $^{1}J(\mathrm{Si,F}) = 315$ Hz, $^{2}J(\mathrm{Si,F}) = 37$ Hz); $^{19}$F NMR ($Et_2O$, RT): $\delta = -83.6$ (t, 9 F, $CF_3$, $^{4}J(\mathrm{F,F}) = 7.5$ Hz), −113.0 (m, 2 F, $SiF_2$, $^{1}J(\mathrm{Si,F}) = 315$ Hz), −126.9 ppm (t, 6 F, $CF_2$, $^{3}J(\mathrm{F,F}) = 7.5$ Hz); ESI-MS [*m*/*z*]: negative: 422.7 (32, $[Si(C_2F_5)_3F_2]^-$), 322.7 (100, $[Si(C_2F_5)_2F_3]^-$), 222.7 (9, $[Si(C_2F_5)F_4]^-$), positive: 339.0 (100, $[PPh_4]^+$); IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3091 vw, 3066 vw, 1588 w, 1485 w, 1439 m, 1319 m, 1183 vs, 1131 vs, 1107 vs, 1037 s, 996 s, 970 s, 923 w, 882 w, 840 vw, 815 m, 757 w, 745 w, 721 s, 689 s, 617 w, 592 w, 557 w, 524 vs, 507 vs, 453 w, 426 m, 401 w.

Synthesis of $[PPh_4]_2[Si(C_2F_5)_3F_3]$: $HC_2F_5$ (5.4 g, 45 mmol) was condensed at −85 °C onto a degassed solution of 1.6 M *n*-butyllithium in hexane (25 mL, 40 mmol) in diethyl ether (500 mL). After stirring for 20 min a sample of $SiCl_4$ (0.63 g, 3.8 mmol) was added. The reaction mixture was allowed to warm up to room temperature within 150 min. At RT the reaction mixture was stirred under an HCl atmosphere. The precipitate was filtered off, and the solvent was removed at reduced pressure. The remaining liquid was extracted with an aqueous KF solution (0.54 g in 50 mL $H_2O$). To the aqueous phase, a solution of $[PPh_4]Cl$ (3.1 g (8.3 mmol) in 20 mL $H_2O$) was added. The white precipitate was separated by centrifugation, washed with water, and dried under reduced pressure. $[PPh_4]_2[Si(C_2F_5)_3F_3]$ (2.1 g, 1.9 mmol, 50 % with respect to $SiCl_4$) was obtained as a colorless solid that decomposes above 110 °C.

$^{29}$Si NMR ($CH_3CN$, RT): $\delta = -180.8$ ppm (t, d, sept, $^{1}J(\mathrm{Si,F}) = 315$ Hz, $^{1}J(\mathrm{Si,F}) = 202$ Hz, $^{2}J(\mathrm{Si,F}) = 32$ Hz); $^{19}$F NMR ($CH_3CN$, RT): $\delta = -80.5$ (m, 3 F, $CF_3$), −81.5 (m, 6 F, $CF_3$), −109.4 (m, 1 F, SiF, $^{1}J(\mathrm{Si,F}) = 202$ Hz), −122.3 (m, 2 F, $CF_2$), −123.3 (m, 4 F, $CF_2$), −133.6 ppm (m, 2 F, $SiF_2$, $^{1}J(\mathrm{Si,F}) = 315$ Hz); ESI-MS [*m*/*z*]: negative: 422.7 (1, $[Si(C_2F_5)_3F_2]^-$), 322.7 (100, $[Si(C_2F_5)_2F_3]^-$), 222.7 (19, $[Si(C_2F_5)F_4]^-$) 118.9 (3, $C_2F_5^-$), positive: 339.0 (100, $[PPh_4]^+$); IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3086 vw, 3059 vw, 1586 w, 1484 w, 1439 m, 1315 m, 1302 m, 1188 vs, 1159 vs, 1108 vs, 1097 vs, 995 s, 935 s, 751 w, 722 s, 689 s, 588 w, 562 w, 549 w, 524 vs, 465 w, 424 w, 401 m.

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[8] Data collection for X-ray structure determination of $[PPh_4]_2[Si(C_2F_5)_3F_3]\cdot CH_2Cl_2$ was performed on a Bruker Nonius KappaCCD diffractometer at 100(2) K using graphite-monochromated MoKα radiation ($\lambda = 71.073$ pm). The structure was solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97: G. M. Sheldrick, *Acta. Crystallogr. Sect. A* **2008**, *64*, 112–122). All non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically. Data for $[PPh_4]_2[Si(C_2F_5)_3F_3]\cdot CH_2Cl_2$: colorless crystal, $M_r = 1205.83\ \mathrm{g\,mol^{-1}}$, triclinic space group $P\bar{1}$, $a = 1032.51(3)$, $b = 1303.55(3)$, $c = 2144.09(7)$ pm, $\alpha = 99.30(1)$, $\beta = 102.39(1)$, $\gamma = 107.77(1)°$, $V = 2602.6(1) \times 10^6\ \mathrm{pm^3}$, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.539\ \mathrm{g\,cm^{-3}}$, $F(000) = 1224$; 42294 reflections up to $\theta = 27$ collected, 11585 independent reflections, thereof 8480 with $I > 2\sigma(I)$, 703 parameters. *R* values: $R_1 = 0.0809$ for reflections with $I > 2\sigma(I)$, $wR_2 = 0.24$ for all data. CCDC 941548 contains 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.

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