



# Tris(pentafluoroethyl)silanol Derivatives and the Lewis Amphoteric Tris(pentafluoroethyl)silanolate Anion, $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]^-$

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Dedicated to Professor Reint Eujen on the occasion of his 75th birthday

**Abstract:** While alkyl-substituted siloxanes are widely known, virtually nothing is known about perfluoroalkyl siloxanes and their congener species, the silanols and silanolates. We recently reported on the tris(pentafluoroethyl)silanide ion,  $[\text{Si}(\text{C}_2\text{F}_5)_3]^-$ , which features Lewis amphoteric character deriving from the pentafluoroethyl substituents and their strong electron-withdrawing properties. Transferring this knowledge, we investigated the Lewis amphoteric behavior of the tris(pentafluoroethyl)silanolate,  $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]^-$ . In order to examine such Lewis amphoteric behavior, we first developed a strategy for the synthesis of the corresponding silanol  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$ , which readily condenses at room temperature to the hexakis(pentafluoroethyl)disiloxane,  $(\text{C}_2\text{F}_5)_3\text{SiOSi}(\text{C}_2\text{F}_5)_3$ . Deprotonation of  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$  employing a sterically demanding phosphazene base allows the characterization of the first example of a dimeric triorganosilanolate: the dianionic hexakis(pentafluoroethyl)disilanolate,  $[\{\text{Si}(\text{C}_2\text{F}_5)_3\text{O}\}_2]^{2-}$ , implies Lewis amphoteric character of the monomeric  $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]^-$  anion.

disiloxanes by organolithium compounds and alkali metal hydroxides, yielding the corresponding silanolates in addition to several other products.<sup>[2]</sup> This achievement was fundamental for the convenient synthesis of several lithium silanolates,<sup>[3]</sup> as well as germanolates and stannolates.<sup>[4]</sup> Another well-established synthesis for silanolates is based upon deprotonation of the corresponding silanols. Despite the preparation of a number of silanolates,<sup>[5]</sup> only a few of them were structurally characterized.<sup>[6]</sup> Whereas alkalimetal silanolates usually are coordination polymers in the solid state,<sup>[7]</sup> dimers are rare and monomers are virtually unknown.<sup>[6,8]</sup>

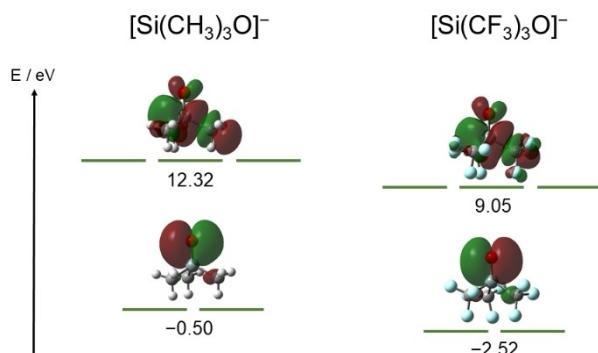
In contrast to vast activities in the field of alkylsubstituted silanolates and their coordination compounds, virtually nothing is reported about their counterparts with exclusively perfluoroalkyl substituents.<sup>[9]</sup> However, the strong electron-withdrawing character of the perfluoroalkyl groups is likely to influence the reactivity of silanolates and their coordination compounds to an intriguing extent. The tris(pentafluoroethyl)silanide ion,  $[\text{Si}(\text{C}_2\text{F}_5)_3]^-$ , as we recently presented, resembles silylenes with respect to its Lewis amphoteric character: it reacts as a Lewis base as well as a Lewis acid.<sup>[10]</sup> This unique behavior is due to the electron-withdrawing character of the perfluoroalkyl substituents, which results in energetically low-lying HOMO and LUMO compared to those in its non-fluorinated counterpart.<sup>[10]</sup> Calculations of the Kohn-Sham and natural bond orbitals (NBOs) of trimethylsilanolate,  $[\text{Si}(\text{CH}_3)_3\text{O}]^-$ , and tris(trifluoromethyl)silanolate,  $[\text{Si}(\text{CF}_3)_3\text{O}]^-$ , anions provide ambiguous results (cf. Supporting Information). For the Kohn-Sham orbitals<sup>[11]</sup> only the HOMO is energetically lowered upon the transition from the non-fluorinated  $[\text{Si}(\text{CH}_3)_3\text{O}]^-$  to the fluorinated  $[\text{Si}(\text{CF}_3)_3\text{O}]^-$  anion implying a lower Lewis basicity at the oxygen atom of the tris(trifluoromethyl)silanolate. Contrary to our expectations the LUMO energy of  $[\text{Si}(\text{CF}_3)_3\text{O}]^-$  is slightly increased indicating a lower Lewis acidity at the silicon atom of the tris(trifluoromethyl)silanolate. However, the corresponding NBO analysis<sup>[12]</sup> shows the expected tendency: The lowest non-Lewis NBOs and the highest Lewis NBOs of  $[\text{Si}(\text{CF}_3)_3\text{O}]^-$  are both energetically lowered implying a reduced Lewis basicity at the oxygen atom in addition to an increased Lewis acidity at the silicon atom of the tris(pentafluoroethyl)silanolate anion (Figure 1). According to this NBO analysis, the tris(trifluoromethyl)silanolate,  $[\text{Si}(\text{CF}_3)_3\text{O}]^-$ , and the experimentally more easily accessible tris(pentafluoroethyl)silanolate,  $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]^-$ , should show Lewis amphoteric behavior.

The discovery of the *Müller-Rochow Direct Process* in the early 1950s was not only a milestone for the 'silicone' industry,<sup>[1]</sup> but it also aroused great interest in siloxane chemistry in general. Thus, not only siloxanes,  $\text{R}_3\text{SiOSiR}_3$  (R = alkyl, aryl), and silanols,  $\text{R}_3\text{SiOH}$ , but also silanolate salts,  $\text{M}[\text{R}_3\text{SiO}]$ , attracted considerable attention by researchers in the following years. In 1954 Hartzfeld et al. reported on syntheses and cleavage of some

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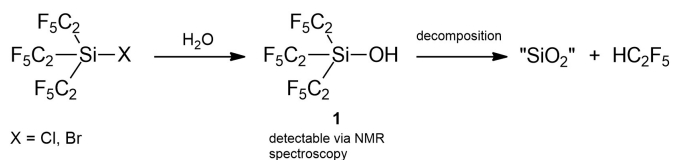
**Figure 1.** Lewis and non-Lewis NBOs of  $[\text{Si}(\text{CH}_3)_3\text{O}]^-$  and  $[\text{Si}(\text{CF}_3)_3\text{O}]^-$  (B3LYP/6-311++G(3df,2p)); isosurface value =  $0.05 \text{ e}^-/\text{au}^3$ ).<sup>[12]</sup>

Motivated by these findings, we established a protocol for the synthesis of tris(pentafluoroethyl)silanol as a precursor for the corresponding silanolate ion  $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]^-$ .

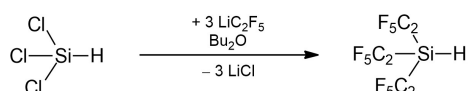
Generally, silanols are synthesized by hydrolysis of organosilicon halides and silyl ethers or by oxidation of the corresponding silanes.<sup>[13]</sup> When brought into contact with water, tris(pentafluoroethyl)silicon halides<sup>[14]</sup> are hydrolyzed to transient  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$ , which can be observed by NMR spectroscopy but unfortunately eluded isolation by decomposition (Scheme 1).

Apparently, the Si–C bonds in pentafluoroethyl substituted silicon species are very sensitive to hydrolytic cleavage. Thus, the preparation of pentafluoroethylsilanols has to be performed by oxidation under anhydrous conditions. For this purpose,  $\text{NO}_2$  seems to be a suitable reagent. The required silane  $\text{Si}(\text{C}_2\text{F}_5)_3\text{H}$  is easily accessible through reaction of  $\text{SiCl}_3\text{H}$  with three equivalents of pentafluoroethyl lithium,  $\text{LiC}_2\text{F}_5$ , in *n*-dibutyl ether and subsequent isothermic distillation (Scheme 2).<sup>[10]</sup>

Since silanols tend to condense, neat  $\text{Si}(\text{C}_2\text{F}_5)_3\text{H}$  was treated with  $\text{NO}_2$  at  $-20^\circ\text{C}$  in the presence of molecular sieves to intercept liberated water. Initially, the tris(pentafluoroethyl)silanol, **1**, is formed, which can be isolated at  $-40^\circ\text{C}$  by condensation from the reaction mixture in 36% yield. When the reaction mixture is warmed up to ambient temperature, slow



**Scheme 1.** Hydrolyzation of  $\text{Si}(\text{C}_2\text{F}_5)_3\text{X}$  (X = Cl, Br) to transient  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$  (1) decomposing to "SiO<sub>2</sub>" and  $\text{HC}_2\text{F}_5$ .

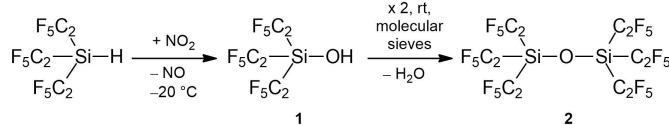


**Scheme 2.** Synthesis of  $\text{Si}(\text{C}_2\text{F}_5)_3\text{H}$ .

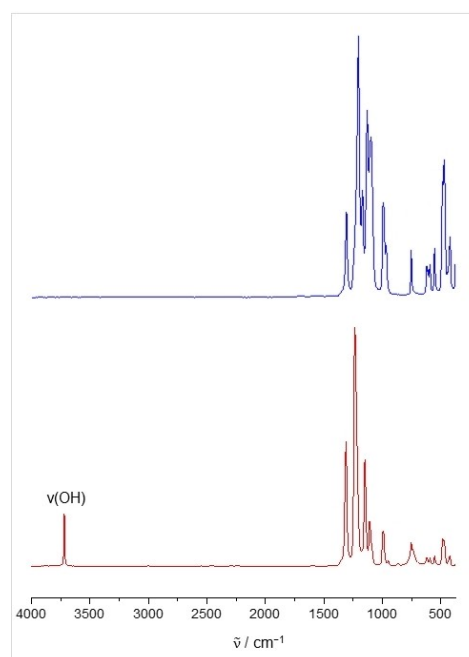
condensation of the silanol takes place, affording hexakis(pentafluoroethyl)disiloxane, **2** (Scheme 3).

In the  $^{29}\text{Si}$  NMR spectrum of tris(pentafluoroethyl)silanol,  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$ , the  $^{29}\text{Si}$  nucleus gives rise to a septet with a  $^2J_{\text{Si,F}}$  coupling constant of 41 Hz at  $-38.7$  ppm. This signal is shifted by 5.3 ppm in comparison to the resonance of  $\text{Si}(\text{C}_2\text{F}_5)_3\text{H}$ .<sup>[15]</sup> In the  $^1\text{H}$  NMR spectrum of **1** the proton of the hydroxyl unit is observed as a broad multiplet at 4.6 ppm. In the gas phase IR spectrum, a sharp band at  $3719 \text{ cm}^{-1}$  is observed due to the OH-stretching vibration of  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$ . This band disappears entirely in the IR spectrum of hexakis(pentafluoroethyl)disiloxane, **2** (Figure 2).

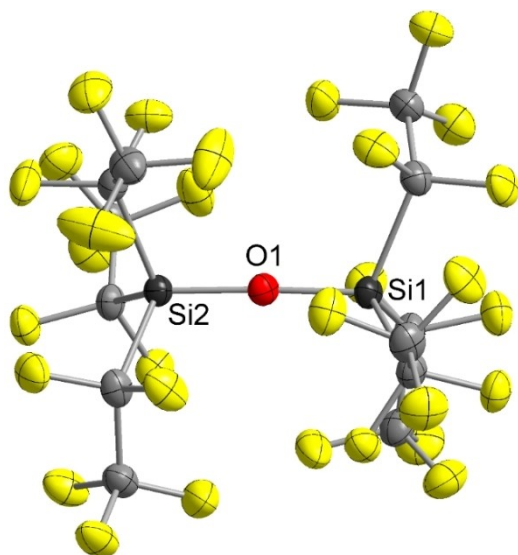
In the  $^{29}\text{Si}$  NMR spectrum of **2**, the magnetically equivalent  $^{29}\text{Si}$  nuclei resonate at  $-44.5$  ppm giving rise to a septet with a  $^2J_{\text{Si,F}}$  coupling constant of 44 Hz. A positive EI mass spectrum reveals a fragment ion peak of  $[(\text{C}_2\text{F}_5)_3\text{SiOSi}(\text{C}_2\text{F}_5)_2\text{F}]^{+\bullet}$  at  $m/z = 685$  beside several other fragments. Disiloxane **2** sublimates at  $5^\circ\text{C}$ , allowing to grow single crystals suitable for X-ray diffraction.  $(\text{C}_2\text{F}_5)_3\text{SiOSi}(\text{C}_2\text{F}_5)_3$ , **2**, crystallizes in the space group  $P\bar{1}$  with two almost identical discrete molecules per asymmetric unit (Figure 3). Both molecules display an almost linear Si–O–Si backbone with angles of  $177.6(2)^\circ$  and  $179.2(2)^\circ$ , respectively, which are comparable to the Si–O–Si angle in the sterically crowded molecule  $(^t\text{Bu}_3\text{Si})_2\text{O}$  ( $179.1^\circ$ ).<sup>[16]</sup> All Si–C bond lengths



**Scheme 3.** Synthesis of silanol  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$  (**1**), and disiloxane  $(\text{C}_2\text{F}_5)_3\text{SiOSi}(\text{C}_2\text{F}_5)_3$  (**2**).



**Figure 2.** IR spectra of silanol **1** (bottom) and disiloxane **2** (top).

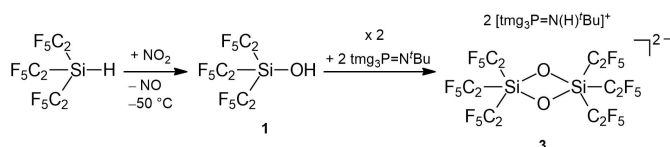


**Figure 3.** Molecular structure of one molecule of  $(\text{C}_2\text{F}_5)_3\text{SiOSi}(\text{C}_2\text{F}_5)_3$ , **2**.<sup>[18]</sup> Thermal ellipsoids are depicted with a probability of 50%. Selected bond lengths [pm] and angles [°]: Si1–O1 160.4(2), Si2–O1 160.5(2), Si1–C1 192.4(3), Si1–C3 192.5(4), Si1–C5 193.0(3); Si1–O1–Si2 177.6(2).

(160.4(2)–160.5(2) pm) are comparable to those of other disiloxanes with electron-withdrawing substituents like  $(\text{Cl}_3\text{Si})_2\text{O}$  (159.2 pm).<sup>[17]</sup>

Since sterically demanding phosphazanium cations are exceptional in stabilizing reactive anions,<sup>[19]</sup> we combined in situ generated silanol **1** with the phosphazene base  $\text{tmg}_3\text{P}=\text{N}^+\text{Bu}$  ( $\text{tmg}$  = tetramethylguanidyl) at  $-50^\circ\text{C}$  targeting salt  $[\text{tmg}_3\text{P}=\text{N}(\text{H})^+\text{Bu}][\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]$ . However, after warm up of the reaction mixture to ambient temperature, the dimeric species  $[\text{tmg}_3\text{P}=\text{N}(\text{H})^+\text{Bu}]_2[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]_2$  was isolated in a 94% yield, underlining the formally Lewis amphoteric character of the tris(pentafluoroethyl)silanolate anion,  $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]^-$  (Scheme 4).  $[\text{tmg}_3\text{P}=\text{N}(\text{H})^+\text{Bu}]_2[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]_2$  represents a colorless solid and is not air- and moisture-sensitive.

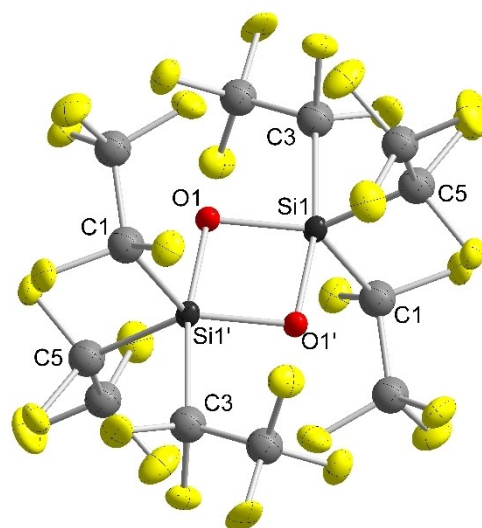
Whereas tetracoordinated pentafluoroethyl substituted silanes exhibit  $^{29}\text{Si}$  chemical shifts ranging from +10 to –90 ppm, penta- and hexa-coordinated silicon compounds are characterized by chemical shifts from –95 to –150 ppm and –150 to –200 ppm, respectively.<sup>[14,20]</sup> In keeping with this, the  $^{29}\text{Si}$  NMR spectrum of hexakis(pentafluoroethyl)disilanolate, **3**, displays a septet at –117.6 ppm with a  $^2J_{\text{Si,F}}$  coupling constant of 30 Hz. ESI mass spectra show the molecular ion peak of the cation at an  $m/z$  value of 445 ( $[\text{tmg}_3\text{P}=\text{N}(\text{H})^+\text{Bu}]^+$ ) and the peak for the



**Scheme 4.** Synthesis of the disilanolate salt  $[\text{tmg}_3\text{P}=\text{N}(\text{H})^+\text{Bu}]_2[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]_2$ .

protonated dianion at  $m/z = 803$  ( $[\text{Si}(\text{C}_2\text{F}_5)_3\text{OSi}(\text{C}_2\text{F}_5)_3\text{OH}]^-$ ). Single crystals of  $[\text{tmg}_3\text{P}=\text{N}(\text{H})^+\text{Bu}]_2[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]_2$  were obtained by diffusion of *n*-hexane into a chloroform solution. The oxygen-bridged disilanolate salt crystallizes in the triclinic space group  $P\bar{1}$  with one molecule per unit cell (Figure 4). The anion is disordered on an inversion center (part 1 and part 2). The  $(\text{C}_2\text{F}_5)_3\text{SiO}$  units are each arranged in a distorted trigonal bipyramid with one oxygen atom (O1 or O1') and a  $\text{C}_2\text{F}_5$  group (C3) in axial position. The axial O–Si–C angles amount to  $170.0(8)^\circ$  in part 1 resp.  $173.3(8)^\circ$  in part 2. The axial Si1–O1' bonds (175(3) pm resp. 178(3) pm) are only slightly longer compared to the equatorial Si1–O1 bond (166(1) pm for both parts). An elongation of the Si1–C3 bond (205(1) pm resp. 204(1) pm) compared to the other Si–C bonds ranging between 196(1) pm and 198(1) pm can also be observed. The O–Si–C and C1–Si–C5 angles in the equatorial plane differ from the ideal angles of  $120^\circ$ , but together they form a total angle of  $359.9^\circ$ . The  $\text{Si}_2\text{O}_2$  four-membered ring is planar. Bond lengths and angles of the  $\text{Si}_2\text{O}_2$  ring in **3** are comparable to already known  $\text{Si}_2\text{O}_2$  four membered ring systems.<sup>[21]</sup> The structural motif of a  $\text{Si}_2\text{O}_2$  four-membered ring with a hypervalent silicon atom is also quite familiar and can be obtained, for example, by oxidation of the so-called heteroleptic silylenes with  $\text{O}_2$  or  $\text{N}_2\text{O}$ .<sup>[21]</sup> To the best of our knowledge, all structurally characterized compounds of this type represent neutral species. Thus, the hexakis(pentafluoroethyl)disilanolate, **3**, represents the first example of a structurally characterized, negatively charged dimeric triorganosilanolate  $[\text{R}_3\text{SiO}]_2^{2-}$  with R being exclusively organic substituents.

In this contribution, we devised a convenient synthesis of the tris(pentafluoroethyl)silanolate, **1**,  $\text{Si}(\text{C}_2\text{F}_5)_3\text{OH}$ , which readily



**Figure 4.** Molecular structure of  $[\text{Si}(\text{C}_2\text{F}_5)_3\text{O}]_2^{2-}$ , **3**, (part 1) in the solid state with two  $[\text{tmg}_3\text{PN}(\text{H})^+\text{Bu}]^+$  units as counterions. Thermal ellipsoids are depicted with a probability of 50%.<sup>[18]</sup> Both cations and part 2 of the disordered dianion were omitted for the sake of clarity. Selected bond lengths [pm] and angles [°] of part 1: Si1–O1 166(1), Si1–O1' 178(3), Si1–C1 198(1), Si1–C3 205(1), Si1–C5 198.9(8); O1–Si1–O1' 83.0(4), Si1–O1–Si1' 93(1), O1'–Si1–C3 170.0(8), O1–Si1–C3 87(1), C3–Si1–C1 93.1(6), C3–Si1–C5 91.0(4), O1–Si1–C1 124(1), O1–Si1–C5 136.0(9), C1–Si1–C5 99.9(7).

condenses to the corresponding disiloxane **2**,  $(C_2F_5)_3SiOSi(C_2F_5)_3$ . Disiloxane **2** was isolated utilizing molecular sieves as a water absorber and reveals an almost linear Si—O—Si backbone.

Deprotonation of  $Si(C_2F_5)_3OH$  at low temperatures results in the formation of the dimeric species  $[[Si(C_2F_5)_3O]_2]^{2-}$  underlining the Lewis amphoteric character of the tris(pentafluoroethyl) silanolate anion  $[Si(C_2F_5)_3O]^-$ . The  $[[Si(C_2F_5)_3O]_2]^{2-}$  dianion represents the first example of a structurally characterized dimeric triorganyl silanolate  $[[R_3SiO]_2]^{2-}$  (R = alkyl, aryl). Investigations concerning the reactivity of the hexakis-(pentafluoroethyl)disilanolate,  $[[Si(C_2F_5)_3O]_2]^{2-}$ , are in progress.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Lewis amphoteric · perfluoroalkyls · silicon · silanolates · silanol · siloxanes

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