Evidence of the Lewis-Amphoteric Character of Tris(pentafluoroeethyl)silanide, [Si(C₂F₅)₃]⁻

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Abstract: According to a first view on the geometrical and electronic structure of the tris(pentafluoroeethyl)silanide, this anion appears as a Lewis base. Quantum chemical calculations on perfluoroalkylated silanides show significantly lower HOMO and LUMO energy levels in comparison to their non-fluorinated counterparts, which implies reduced Lewis basicity and increased Lewis acidity of the [Si(C₂F₅)₃]⁻ ion. With these findings and a HOMO–LUMO gap of 4.80 eV similar to N-heterocyclic silylenes (NHSis), perfluoroalkyl silanides are predestined to exhibit Lewis-amphoteric behavior similar to silylenes. Deprotonation of Si(C₂F₅)₃H with sterically demanding phosphazene bases afforded thermally stable phosphazencium salts of the [Si(C₂F₅)₃]⁻ anion, which add to benzaldehyde, benzophenone, CS₂, and CO₂ in various manners. This behavior also mirrors the reactivity of silylenes towards ketones as well as heterocumulenes and is rationalized by Lewis amphotericity being inherent in these silanides.

Introduction

In keeping with the Lewis definition, amphoteric species possess electron-deficient (Lewis acidic) and electron-rich (Lewis basic) centers. These reactive positions may be located on two different well separated atoms within one molecule. In a special class of Lewis-amphoteric systems, the so-called frustrated Lewis pairs (FLPs), an adduct formation is effectively prevented by sterically demanding substituents, which leads to their inherent capability to activate or incorporate a large variety of small molecules such as H₂, CO₂, CS₂, SO₂, NO₂, NO, CO, or unsaturated hydrocarbons.

Yet another class of Lewis-amphoteric species derives from main group IV elements (C, Si, Ge, Sn, and Pb) in the oxidation state +II. Here, the Lewis acidic as well as the Lewis basic position are located at the same center, namely the divalent tetravalent atom. The HOMO of these species displays a significant s-orbital character, whereas the LUMO is usually represented by an empty p-orbital. It is noteworthy that stable germynes, stannylenes, and plumbylenes were long known before reports on stable divalent silicon compounds as Si(q₄-C₂H₅)₂ (Jutzi, 1986) or the first stable N-heterocyclic silylene [HC-NMe₂]⁺ (Denk & West, 1994). The latter species are the higher homologues of N-heterocyclic carbene (NHCs), the first of which has been presented by Arduengo III in 1991. Denk’s seminal discovery stimulated further intense research on silylene chemistry. Due to their unique Lewis amphoteric properties, silylenes proved to be versatile and valuable building blocks in organosilicon chemistry, reacting readily with multiple bonds as present in alkenes, alkynes, ketones, imines, azides, as well as heteroallenes X≡C≡Y (X, Y = O, S, NR with R = alkyl). Many of these transformations are initiated by side-on additions. It is considered that silylenes with larger bite angles and small HOMO–LUMO gaps are more reactive than those with contrary properties. Thus, for example, acyclic silylenes (HOMO–LUMO gap ca. 2 eV) can even activate H₂ affording silanes, whereas NHSis cannot (HOMO–LUMO gap ca. 5 eV).

Quantum chemical calculations on the tris(trifluoromethyl)silanylidene anion, [Si(CF₃)₃]⁻, disclose a HOMO–LUMO gap of 4.80 eV as well as lower HOMO and LUMO energy levels (−7.06 eV; −2.26 eV) in comparison to the non-fluorinated analogue, [Si(CH₃)₃]⁻ (−6.88 eV; −2.10 eV) (Figure 1). This is clearly due to the strong electron withdrawing effect of the perfluoroalkyl groups. These computations point to a reduced Lewis basicity and in turn an increased Lewis acidity of the perfluorinated species.

Thus, we were interested in whether or not perfluoroalkyl silanides display Lewis amphoteric character similar to silylenes. To cast some light on this issue we investigated syntheses, structures, and reactivities of salts featuring the
[Si(C₅F₅)₃]⁻ ion and support our experimental findings by computational studies.

**Results and Discussion**

While the precursor for the [Si(C₅F₅)₃]⁻ ion, the tris(pentafluoroethyl)siliane, Si(C₅F₅)₃H, has been originally synthesized over four steps, an improved and more efficient synthesis is based upon the treatment of SiCl₃H with three equivalents of in situ generated pentafluoroethylolithium, LiC₅F₅-dibutyl ether and subsequent isothermal distillation (Scheme 1).

![Scheme 1. Improved synthesis of Si(C₅F₅)₃H.](image)

The most straightforward approach to obtain Li[Si(C₅F₅)₃]⁻, the low-temperature deprotonation of Si(C₅F₅)₃H by LiDA, had to be discarded due to the notorious thermolability of the product at temperatures above −80°C. As demonstrated recently, phosphazenium cations, [R₆P=N(H)Bu⁺ with R being Me₃N⁺ ([Me₃P,H⁺]), (Me₅Nₓ)₃N⁺ ([(Me₅P,H⁺)³⁺, and (Et₃N)₂P=N⁺ ([Et₃P,H⁺⁺), are weakly coordinating and thus predisposed to stabilize reactive anions like hydroxide trihydrate [OH(OH₂)₃]⁻,[22] silanol silanolates,[23] or the weakly coordinating aluminate [Al(C₅F₅)₃]⁻.[24] Consistently, deprotonation of Si(C₅F₅)₃H with sterically demanding phosphazen bases R₆P=NBu affords [Si(C₅F₅)₃]⁻ salts in high yields (Scheme 2). The colorless products are sufficiently robust to be handled at room temperature. Elemental analyses confirm their purity (see Supporting Information).

Single crystals of [Et₃P,H⁺][Si(C₅F₅)₃] were grown from a chilled solution in diethyl ether. The salt crystallizes in the triclinic space group P1 with Z = 4 (Figure 2). One of the two symmetrically independent anions shows some disorder. Due to the particularly weak interaction with the phosphazenium cation, the [Si(C₅F₅)₃]⁻ ion is observed under so-called pseudo-gas phase conditions.[25] The C-Si-C angles of the [Si(C₅F₅)₃]⁻ ion are significantly smaller (94.0(2)–95.8(2)°) than in the silane Si(C₅F₅)₃H (107.7(3)–108.7(3)°)[18] which indicates a higher p-orbital character in the Si–C bond and a higher s-orbital character in the lone pair of the silicon atom.

![Figure 2. Molecular structure of the non-disordered anion in [Et₃P,H⁺][Si(C₅F₅)₃] in the solid state.](image)

Analogously to Lewis amphoteric silylenes,[26–28] the [Si(C₅F₅)₃]⁻ ion undergoes a side-on addition with carbonyl compounds like benzaldehyde and benzophenone to afford a phosphazenium salt of the corresponding oxasiliranide anion 1a and 1b (Scheme 3).

![Scheme 3. Reaction of [R₆P=N(H)Bu⁺][Si(C₅F₅)₃] salts with benzaldehyde and benzophenone.](image)

**Si NMR chemical shifts of pentafluoroethyl-substituted silicon compounds nicely correlate with the coordination number of the silicon atom and are thus useful in deducing the coordination number of the silicon atom.** Thus, tetracoordinated silanes exhibit chemical shifts in the range of +10 to −90 ppm. Penta- and hexacoordinated pentafluoroethyl silicon compounds show chemical shifts of −95 to −150 ppm ([SiR₆]⁻) and −150 to −200 ppm ([SiR₆]⁻), respectively.[19,20,29] In keeping with this, 1a and 1b feature a ²³Si NMR chemical shift of −127.5 ppm and −122.8 ppm, respectively. The ¹³C NMR chemical shift of the RPhC moiety shifts from 194.0 ppm in benzaldehyd[e][30] to 75.5 ppm in 1a and from 196.3 ppm in benzophe-
non[30] to 78.9 ppm in 1b. Negative ESI mass spectra reveal the molecular ion peaks of 1a and 1b at m/z values of 491 for [Si(CF₃)₃(η²-CPhH)O]⁺ (1a) and 567 for [Si(CF₃)₃(η²-CPhH)O]⁻ (1b).

Single crystals of [tmgP]⁺[1b] were grown by slow evaporation of a diethyl ether solution. The phosphazenium salt of thiasiliranide (1b) crystallizes in the triclinic space group P1 with Z = 4; one of the anions is disordered. 1b displays the geometry of a highly distorted square pyramid (τ = 0.18 in the non-disordered anion and τ = 0.12 in the disordered one)[31] with a C₆F₅ substituent at the apex (Figure 3). The structural motif of a three-membered Si–O–C heterocycle is quite familiar from the side-on addition of silylenes to carbonyl compounds.[20–28] The Si1–O1 and the C26–O1 bond in the three-membered ring of 1b are comparable to those of reported penta- and tetracoordinated oxasiliranes. The Si1–C26 bond of 1b (192.6(3) pm) is only about 4 pm shorter than the C26–Si bond (266.0(1) pm) as counterion.

Thermal ellipsoids are represented with a probability of 50%. The cation and hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–O1 165.5(2), C26–O1 152.0(4), Si1–C26 192.6(3); O1–Si1–C26 49.5(1), C26-O1-Si1 74.6(2), O1–C26–Si1 55.9(1).

Figure 3. Molecular structure of the non-disordered anion [Si(CF₃)₃(η²-CPhH)O]⁻ (1b) in the crystal with [tmgP]⁺ as counterion.[32] Thermal ellipsoids are represented with a probability of 50%. The cation and hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Si–O1 165.5(2), C26–O1 152.0(4), Si–C26 192.6(3); O1–Si–C26 49.5(1), C26–O1–Si1 74.6(2), O1–C26–Si1 55.9(1).

Figure 4. Molecular structure of [Si(CF₃)₃(η²-CS₂)]⁻ (2) in the solid state with [tmgP]⁺ as counterion.[33] Thermal ellipsoids are represented with a probability of 50%. The cation and minor occupied disordered C₆F₅ groups have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–S1 266.0(1), Si1–C26 184.3(2), C26–Si1 169.6(2), C26–S1 165.3(2), C26–Si1–C26 39.2(1), Si1–S1–C26 43.4(1), Si1–C26–S1 97.4(1), Si1–C26–S2 131.1(1), S1–C26–S2 131.5(1).

Figure 5. Thiasiliranide I, thiasiliranide ion II, and η²-CS₂ complex III.

Significantly longer than in tetracoordinated thiasiliranide I (209.3 pm)[30] and 10 pm longer than in pentacoordinated thiasiliranide ion II (256.9 pm). However, the Si1–S1 bond is much shorter than the sum of the van der Waals radii (390 pm)[33] which implies some degree of silicon–sulfur bonding. Surprisingly, the C26–S2 bond (165.3(2) pm) is only about 4 pm shorter than the C26–S1 bond (169.6(2) pm) and both are in the range of typical C–S double bonds (ca. 167 pm).[34] This bond situation is also observed in η²-CS₂ transition metal complexes (e.g. 163.3 and 169.3 pm in III).[35] In comparison, C–S bonds in crystallized CS₂ are about 154 pm.[36]
Since CO$_2$ is one of the main greenhouse gases known, enormous efforts have been made to capture, store, and activate CO$_2$ for the synthesis of value-added products. Apart from transition metal complexes,$^{[39]}$ some silylenes are known to successfully activate CO$_2$. $^{[40]}$ Most silylenes form dimeric species like, for example, IV$^{[41]}$ whereas only a few of them lead to compounds like V–VIII with chelating carbonate ligands (Figure 6).$^{[42]}$

![Figure 6. Examples of known silicon carbonates.](image)

When a [Si(CF$_3$)$_3$]$^-$ salt is treated with an excess of CO$_2$, the corresponding salt of silicon carbonate 3 is formed (Scheme 5). The formation of CO was monitored by IR spectroscopy of the gas phase.

![Scheme 5. Reaction of [R$_2$PN(H)Bu][Si(CF$_3$)$_3$] with CO$_2$.](image)

The $^{39}$F NMR spectrum of 3 reveals signals at $-79.6$ ppm and $-121.0$ ppm resulting from the CF$_3$ and CF$_2$ groups. In accordance with a pentacoordinated silicon center, 3 features a resonance at $-119.0$ ppm in the $^{29}$Si NMR spectrum. The carbonyl carbon atom resonates in the $^{13}$C NMR spectrum at $148.6$ ppm. In the IR spectrum, the ν(C=O) mode is detected at $1703$ cm$^{-1}$.

Upon evaporation of the solvent, decomposition of 3 to [(F$_3$C)$_2$CO] and other unidentified species occurs. Nevertheless, single crystals of [EtP$_2$H][Si(CF$_3$)$_3$](η$^2$-CO$_2$)] were obtained by diffusion of n-heptane in a Et$_3$O/THF solution of the silicon carbonate salt at $-40^\circ$C. [EtP$_2$H][Si(CF$_3$)$_3$](η$^2$-CO$_2$)] crystallizes in the monoclinic space group P2$_1$/c (Figure 7). Silicon carbonate 3 exhibits a highly distorted geometry with a slight tendency to a trigonal bipyramid ($\tau = 0.53$). The SiI–O2 bond (181.5(2) pm) is about 11 pm longer than the SiI–O1 bond (170.1(2) pm). Both Si–O bond lengths are in the range of known silicon carbonates ($171.5–180.4$ pm).$^{[40,41]}$ The C4I–O3 bond length is comparable to the ones in other silicon carbonates, underlining its double-bond character. The sum of the angles about C4I of 359.9° confirms a planar coordination sphere. Though some silicon carbonates are known, to the best of our knowledge 3 represents the first structurally characterized negatively charged silicon carbonate of the type [SiR$_3$(η$^2$-CO$_2$)]$^-$ with exclusively organic substituents R = aryl, alkyl.

### Computational Studies

In order to support our experimental findings, we performed computational studies at B3LYP/6-31 + G(3d,p) level of theory$^{[40]}$ concerning the mechanism of the side-on addition of the tris(trifluoromethyl)silanide ion, [Si(CF$_3$)$_3$]$^-$, to formaldehyde, benzaldehyde, benzophenone, and CS$_2$ as well as of the reaction with CO$_2$. To reduce computational cost, electronically similar trifluoromethyl groups instead of pentafluoroethyl groups were used. For the same reason we only investigated the addition of formaldehyde in more detail. For each depicted transition state an intrinsic reaction coordinate calculation was performed to ensure that they indeed connect the correct minima. Further details are given in the Supporting Information.

The addition of formaldehyde to [Si(CF$_3$)$_3$] is a concerted process leading to the product [Si(CF$_3$)$_3$(η$^2$-CH$_2$O)]$^-$. Figure 8 shows a distortion/interaction diagram$^{[40]}$ for the reaction path in relation to the Si–Cformaldehyde distance. Unsurprisingly, the energy required for distortion of the reactants increases with decreasing distance. For values above $265$ pm the interaction energy between the fragments outweighs the energy required for distortion due to long-range interactions of the negatively charged silanide and the dipole of formaldehyde. We located a weakly bound complex as a minimum with a Si–C distance of 367 pm and a change in electronic energy ($\Delta E$, zero-point corrected) of $-21.3$ kJ mol$^{-1}$ relative to the starting com-
Change in energy (zero-point corrected) and Gibbs free energy along the reaction pathway of \([\text{Si}-(\text{CF}_3)_3]^+ + \text{CH}_2\text{O}\) in relation to the Si–C$_\text{formaldehyde}$ distance. The change in energy is given relative to the starting compounds. The transition state is marked with an arrow.

Figures 8 and 9 show the change in Gibbs free energy along the reaction pathway of \([\text{Si}-(\text{CF}_3)_3]^+ + \text{CH}_2\text{O}\). The value is given for room temperature. However, the change in Gibbs free energy (\(\Delta G\)) is +6.0 kJ mol$^{-1}$, indicating that this complex has very little influence on the outcome of the reaction.

Furthermore, we performed an NBO analysis\(^{[44]}\) of the silanide as well as of the transition state. In \([\text{Si}-(\text{CF}_3)_3]^+\) the highest Lewis-NBO is the lone pair at the silicon atom (occupancy: 1.92) and the lowest non-Lewis-NBOs are antibonding and located at the Si–C bonds (occupancy: 0.05 each). The transition state is best described as an alcoholate with a Si–C$_\text{formaldehyde}$ bond. However, the occupancy of the three lone pairs at the oxygen atom is relatively low (1.62, 1.88, and 1.98), whereas the antibonding Si–C$_\text{formaldehyde}$ (occupancy: 0.33) is relatively highly occupied due to an extremely large stabilization value from delocalization of one lone pair into this antibonding Si–C NBO (256.6 kJ mol$^{-1}$). The antibonding Si–C$_\text{trifluoromethyl}$ NBOs have higher OCC values than the corresponding ones in \([\text{Si}-(\text{CF}_3)_3]^+\) (anti-periplanar to O: 0.15, synclinal to O: 0.08 each). Delocalization of the lone pairs at the oxygen atom into the Si–C antibond in trans position has stabilization values of 7.1 kJ mol$^{-1}$ and 3.1 kJ mol$^{-1}$.

In contrast to the perfluorinated silanide, the non-fluorinated \([\text{Si}-(\text{CH}_3)_3]^+\) ion attacks only the carbon atom of formaldehyde, forming \([\text{Si}-(\text{CH}_3)_3](\eta^1-\text{CH}_2\text{O})]^+\) (Figure 10). \([\text{Si}-(\text{CH}_3)_3](\eta^1-\text{CH}_2\text{O})]^+\) is 82.1 kJ mol$^{-1}$ higher in energy and therefore immaterial to the reaction. Since no transition state between the starting compounds and \([\text{Si}-(\text{CH}_3)_3](\eta^1-\text{CH}_2\text{O})]^+\) was found, we performed a relaxed potential energy scan along the Si–C$_\text{formaldehyde}$ bond to gain some insight into the reaction path (Figure 11). Apparently, it is a highly exothermic reaction with no activation barrier.

![Figure 8](image8.png)  
**Figure 8.** Distortion/interaction diagram of the reaction path of \([\text{Si}-(\text{CF}_3)_3]^+ + \text{CH}_2\text{O}\) in relation to the Si–C$_\text{formaldehyde}$ distance. The change in energy is given relative to the starting compounds. The transition state is marked with an arrow.

![Figure 9](image9.png)  
**Figure 9.** Change in Gibbs free energy along the reaction pathway of \([\text{Si}-(\text{CF}_3)_3]^+ + \text{CH}_2\text{O}\).

![Figure 10](image10.png)  
**Figure 10.** Change in Gibbs free energy along the reaction pathway of \([\text{Si}-(\text{CF}_3)_3]^+ + \text{CH}_2\text{O}\).

![Figure 11](image11.png)  
**Figure 11.** Plot of the electronic energy in relation to the Si–C$_\text{formaldehyde}$ distance obtained by a relaxed potential energy scan.

The addition of \([\text{Si}-(\text{CF}_3)_3]^+\) to benzaldehyde, benzophenone, and CS$_2$ proceeds analogously to the reaction with formaldehyde. The reaction parameters are given in Table 1. The activation barrier of the addition to the bulkier benzaldehyde is higher than of the addition to formaldehyde. The addition to benzophenone has the highest activation barrier. Since the reaction time was by far the longest, this is consistent with the experimental results. The \(\Delta G\) value is positive, which contradicts the experiment, but those values are known to be error-prone.

Contrary to the other reactions, CO$_2$ does not add side-on in a concerted mechanism to \([\text{Si}-(\text{CF}_3)_3]^+\). Stationary points are shown in Figure 12. Although we located two local energy minima along the reaction pathway, \([\text{Si}-(\text{CF}_3)_3](\eta^1-\text{CO}_2)^+]\) and \([\text{Si}-(\text{CF}_3)_3](\eta^1-\text{CO}_2)^+]\) were found, we performed a relaxed potential energy scan.

### Table 1: Change in energy (zero-point corrected) and Gibbs free energy (298.15 K, 1.0 atm) for the transition state (\(\Delta E^*\) and \(\Delta G^*\)) and the product (\(\Delta E\) and \(\Delta G\)) of the concerted side-on addition of \([\text{Si}-(\text{CF}_3)_3]^+\) to formaldehyde, benzaldehyde, benzophenone, and CS$_2$.

| Substrate | \(\Delta E^*\) (TS) [kJ mol$^{-1}$] | \(\Delta E\) (Product) [kJ mol$^{-1}$] | \(\Delta G^*\) (TS) [kJ mol$^{-1}$] | \(\Delta G\) (Product) [kJ mol$^{-1}$] |
|-----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| CH$_2$O   | 17.9                        | −71.1                       | 63.8                        | −23.1                       |
| PhCHO     | 38.2                        | −59.7                       | 90.7                        | −4.4                        |
| Ph$_2$O   | 58.4                        | −45.5                       | 115.3                       | 9.9                         |
| CS$_2$    | 37.2                        | −52.3                       | 70.0                        | −7.9                        |

[a] Note that the reaction was carried out at temperatures below −20°C due to decomposition of the product, but \(\Delta G\) is given for room temperature.
Coordinating cations stabilize the reactive anion. This allows the structural characterization of the anion under so-called pseudo-gas phase conditions. Most importantly, while exploring the reactivity of the [Si(CF₅)₂]⁻ ion, we disclosed its formal Lewis amphoteric behavior. Just like silylenes, the anion displays Lewis basic and Lewis acidic character. This is evident by the side-on additions to benzaldehyde, benzophenone, and CS₂, as well as by the activation of CO₂. We isolated and structurally characterized novel negatively charged species like oxasiliranide 1b, thiasiliranide 2, and silicon carbonate 3. To the best of our knowledge, 1b and 3 represent the first examples of structurally characterized negatively charged hypervalent three- and four-membered heterocycles [R₂Si(η²-CR'-O)]⁻ and [R₂Si(η²-CO₂)]⁻ (R, R' = alkyl, aryl, H) with organic substituents. Preliminary investigations show that the tris(pentafluoroethyl)silanide catalyzes hydroboration of carbonyl compounds like benzaldehyde with triethylsilane via the herein isolated oxasiliranide 1a (Scheme 6). Detailed studies concerning this hydroboration and the activation of other small molecules by [Si(C₃F₈)₂]⁻ are in progress.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** activation of small molecules · Lewis amphoteric · perfluoroalkyl · silanides · weakly coordinating cations

In this Research Article we reported on high yielding (up to 94%) syntheses of room-temperature stable [Si(C₃F₈)₂]⁻ salts utilizing phosphazenium cations, which as weakly coordinating cations stabilize the reactive anion. This allows the structural characterization of the anion under so-called pseudo-gas phase conditions. Most importantly, while exploring the reactivity of the [Si(CF₅)₂]⁻ ion, we disclosed its formal Lewis amphoteric behavior. Just like silylenes, the anion displays Lewis basic and Lewis acidic character. This is evident by the side-on additions to benzaldehyde, benzophenone, and CS₂, as well as by the activation of CO₂. We isolated and structurally characterized novel negatively charged species like oxasiliranide 1b, thiasiliranide 2, and silicon carbonate 3. To the best of our knowledge, 1b and 3 represent the first examples of structurally characterized negatively charged hypervalent three- and four-membered heterocycles [R₂Si(η²-CR'-O)]⁻ and [R₂Si(η²-CO₂)]⁻ (R, R' = alkyl, aryl, H) with organic substituents. Preliminary investigations show that the tris(pentafluoroethyl)silanide catalyzes hydroboration of carbonyl compounds like benzaldehyde with triethylsilane via the herein isolated oxasiliranide 1a (Scheme 6). Detailed studies concerning this hydroboration and the activation of other small molecules by [Si(C₃F₈)₂]⁻ are in progress.

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