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

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1 Experimental Procedures

1.1 General Part

All reactions were performed in the absence of water and air utilizing standard Schlenk techniques. Solvents were dried according to usual procedures. Chemicals were obtained from commercial sources and used without further purification.

NMR spectra were either recorded on a Bruker Avance III 300 or Bruker Avance III 500 HD as a pure substance with acetone-[d$_6$] as lock substance in a capillary (also containing CCl$_3$F and trimethyl phosphate) or in the indicated deuterated solvent. Positive shifts are downfield from the external standards (TMS for $^1$H, $^{13}$C and $^{29}$Si, H$_3$PO$_4$ for $^{31}$P, CCl$_3$F for $^{19}$F). IR spectroscopic measurements were performed on a Bruker Alpha-FT-IR spectrometer with a diamond crystal. Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano ESI source. Samples were dissolved in the specified solvent and introduced by static nano ESI utilizing in-house pulled glass emitters. Nitrogen served both as nebulizer gas and dry gas. It was generated by a Bruker nitrogen generator NGM 11. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as calibration standard. The spectra were recorded with the Bruker Daltonik esquireNT 5.2 esquireControl software and DataAnalysisTM software 3.4 was used for processing the spectra. EI mass spectra were recorded on an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Aluminum crucibles were filled with a solution of the sample and the solvent was evaporated. If not otherwise noted, the aluminum crucibles were introduced by push rod. Ions were accelerated by 8 kV in EI mode. The mass axis was externally calibrated with PFK (perfluorokerosine) as calibration standard. The spectra were recorded and processed with the OPUS software (V3.6, Micromass 1998) by accumulation and averaging of several single spectra. The melting points were measured on a Mettler Toledo Mp70 Melting Point System. Elemental analysis was performed by Mikoanalytisches Laboratorium Kolbe (Oberhausen, Germany). SCXRD was performed on a Rigaku Supernova diffractometer.
1.2 Synthesis

Si(C₂F₅)₂OH: NO₂ (300 mg, 6.50 mmol) and Si(C₂F₅)₂H (127 mg, 3.29 mmol) were condensed onto dried and degassed molecular sieves. The reaction mixture was kept at −20 °C for at least half an hour. After removing excess NO₂ and formed NO, the volatile product was condensed into a Young-valve ampoule and stored below −40 °C. Si(C₂F₅)₂OH was obtained in a 36% yield as a colorless liquid with a vapor pressure of 20 mbar at room temperature (480 mg, 1.19 mmol).

¹H NMR (300.1 MHz, neat): δ = 4.6 ppm (m, SiOH);

¹³C (1F) DEPT135 NMR (75.50 MHz, n-pentane): δ = 118.6 (s, -CF₃), 114.1 ppm (s, -CF₂);

¹³C (19F) DEPT135 NMR (75.50 MHz, n-pentane): δ = 159.8 (d, 3JCF = 3 Hz, [CH₃]₂N:C=C-N), 50.3 (s, P=N(H)(CH₂)₃), 40.2 (s, [CH₃]₂N):C=N), 31.3 ppm (d, 3JCF = 4 Hz, P=N(H)(CH₂)₃);

¹⁹F NMR (282.4 MHz, neat): δ = -121.8 ppm (s, -CF₂);

MS (EI, 70 eV, pos.): m/z (80%): [(C₂F₅)₂Si(OSi(C₂F₅)₂F)₂]⁺, 516 (4) [(C₂F₅)₂Si(OSi(C₂F₅)₂F)⁺, 429 (10) [(C₂F₅)₂Si(OSi(C₂F₅)₂F)⁺, 390 (24) [(C₂F₅)₂(C₂F₅)₂SiOSi]⁺, 159 (47) [(C₂F₅)₂SiOSi]⁺, 135 (53) [(C₂F₅)₂CF₂]⁺, 100 (33) [(C₂F₅)₂CF₂]⁺, 81 (100) [(C₂F₅)₂CF₂]⁺, 69 (86) [(C₂F₅)₂CF₂]⁺.

[1mg±P=N(H)Bu][Si(C₂F₅)₂O]₂]: A solution of Si(C₂F₅)₂H (212 mg, 550 µmol) in diethyl ether was cooled to −60 °C before NO₂ (16 mg, 740 µmol) was added by condensation. The chilled reaction mixture was stirred for half an hour before a solution of [mg±P=N(H)Bu][Si(C₂F₅)₂O]₂ (437 mg, 516 mmol, 94%) as a colorless powder. m.p.: >190 °C (decomposition).

¹⁹F NMR (550.2 MHz, CDCl₃): δ = 2.86 (s, 36 H, [(CH₃)₂N]₂C=N-), 1.21 (s, 9 H, P=N(H)(CH₂)₃);

¹³C (1H) NMR (75.5 MHz, CDCl₃): δ = 159.8 (d, 3JCH₂F = 3 Hz, [CH₃]₂N:C=N), 50.3 (s, P=N(H)(CH₂)₃), 40.2 (s, [CH₃]₂N):C=N), 31.3 ppm (d, 3JCH₂F = 4 Hz, P=N(H)(CH₂)₃);
Results and Discussion

2.1 NMR spectra of Si(C$_2$F$_5$)$_3$OH

Figure S1. $^{19}$F NMR spectrum of Si(C$_2$F$_5$)$_3$OH (neat) with acetone-d$_6$ as external standard. * Signals for (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$ and § signals for HC$_2$F$_5$.

Figure S2. $^{29}$Si-$^{19}$F-DEPT30 NMR spectrum of Si(C$_2$F$_5$)$_3$OH (neat) with acetone-d$_6$ as external standard. * Signals for (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$. 

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Figure S3. $^1$H NMR spectrum of Si(C$_2$F$_5$)$_3$OH (neat) with acetone-d$_6$ (*) and trimethyl phosphate (#) as external standard. § Signals for HC$_2$F$_2$.

Figure S4. IR spectrum of Si(C$_2$F$_5$)$_3$OH.
2.2 NMR spectra of (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$

Figure S5. $^{19}$F NMR spectrum of (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$ in pentane with acetone-d$_6$ as external standard.

Figure S6. $^{29}$Si,$^{19}$F-DEPT30 NMR spectrum of (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$ in pentane with acetone-d$_6$ as external standard.
**Figure S7.** $^{19}$F-DEPT135 NMR spectrum of (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$ in pentane with acetone-d$_6$ as external standard.

**Figure S8.** IR spectrum of (C$_2$F$_5$)$_3$SiOSi(C$_2$F$_5$)$_3$. 
2.3 NMR spectra of \([\text{tmg}_3\text{P=N(H)}\text{tBu}_2][\text{Si(C}_2\text{F}_5)_3\text{O}]_2\)]

Figure S9. $^{19}$F NMR spectrum of \([\text{tmg}_3\text{P=N(H)}\text{tBu}_2][\text{Si(C}_2\text{F}_5)_3\text{O}]_2\)] in CDCl$_3$. *Signals for HC$_2$F$_5$.

Figure S10. $^{29}$Si, $^{19}$F-DEPT30 NMR spectrum of \([\text{tmg}_3\text{P=N(H)}\text{tBu}_2][\text{Si(C}_2\text{F}_5)_3\text{O}]_2\)] in CDCl$_3$. 
**Figure S11.** $^{31}$P NMR spectrum of $[\text{Tmg}_3\text{P=N(H)Bu}_2][\text{Si(C_2F_5)_3O}_2]$ in CDCl$_3$.

**Figure S12.** $^{13}$C($^{19}$F)-DEPT135 NMR spectrum of $[\text{Tmg}_3\text{P=N(H)Bu}_2][\text{Si(C_2F_5)_3O}_2]$ in CDCl$_3$. 
Figure S13. $^{13}$C{H} DEPT135 NMR spectrum of $[\text{tmg}_3\text{P=N(H)Bu}_2\{\text{Si(C}_2\text{F}_5\text{)}_3\text{O}_2\}]$ in CDCl$_3$.

Figure S14. $^1$H NMR spectrum of $[\text{tmg}_3\text{P=N(H)Bu}_2\{\text{Si(C}_2\text{F}_5\text{)}_3\text{O}_2\}]$ in CDCl$_3$. 
2.4 DFT-Calculations
Geometry optimization was performed with the B3LYP DFT functional, using the Gaussian 09 program package. The basis set used was 6-311++G(3df,2p) for all atoms. All geometries were fully optimized (Table S1). The NBO calculations were done using the NBO 6 module.

Table S1. Cartesian coordinates of the optimized minimum structures as well as the corresponding electronic energy, the energy with zero point energy correction (ZPE), thermal corrected energy (E\text{therm}), enthalpy (H) and Gibbs free energy (G).

| Molecule | Charge | Cartesian coordinates of optimized structure | Electronic Energy /Hartree | Corrected Energies: ZPE, E\text{therm}, H, G /Hartree |
|----------|--------|---------------------------------------------|---------------------------|-------------------------------------------------|

Table S2. Section of the calculated NBO energy levels for [Si(CF3)O]2- and [Si(CH3)O]2-. The highest Lewis NBOs and the lowest non-Lewis NBOs are highlighted in red and green, respectively.

| Orbital A-B | occupancy | E / Hartree | Orbital A-B | occupancy | E / Hartree |
|-------------|-----------|------------|-------------|-----------|------------|
| BD Si1-C2   | 1.96718   | -0.40093   | BD Si1-C2   | 1.97889   | -0.28846   |
| BD Si1-C3   | 1.96731   | -0.40106   | BD Si1-C6   | 1.97891   | -0.28851   |
| BD Si1-C4   | 1.96727   | -0.40106   | BD Si1-C10  | 1.97888   | -0.28846   |
| BD Si1-O5   | 1.98612   | -0.75126   | BD Si1-O14  | 1.99070   | -0.67569   |
| BD C2-F6    | 1.99553   | -0.88187   | BD C2-H3    | 1.99327   | -0.33738   |
| BD C2-F7    | 1.99595   | -0.88623   | BD C2-H4    | 1.99282   | -0.34070   |
| BD C2-F8    | 1.99580   | -0.88009   | BD C2-H5    | 1.99328   | -0.33738   |
| BD C3-F9    | 1.99575   | -0.88006   | BD C6-H7    | 1.99326   | -0.33735   |
| BD C3-F10   | 1.99553   | -0.88186   | BD C6-H8    | 1.99329   | -0.33738   |
| BD C3-F11   | 1.99598   | -0.88620   | BD C6-H9    | 1.99282   | -0.34070   |
| BD C4-F12   | 1.99554   | -0.88188   | BD C10-H11  | 1.99326   | -0.33735   |
| BD C4-F13   | 1.99593   | -0.88619   | BD C10-H12  | 1.99326   | -0.33736   |
| BD C4-F14   | 1.99577   | -0.88003   | BD C10-H13  | 1.99281   | -0.34069   |
| LP(1) O5    | 1.98126   | -0.51822   | LP(1) O14   | 1.98107   | -0.42221   |
### SUPPORTING INFORMATION

| LP(2) O5 | 1.82613 | -0.09277 | LP(2) O14 | 1.85880 | -0.01851 |
|----------|---------|----------|----------|---------|----------|
| LP(3) O5 | 1.82612 | -0.09277 | LP(3) O14 | 1.85879 | -0.01850 |
| BD* Si1-C2 | 0.14620 | 0.33189 | BD* Si1-C2 | 0.09618 | 0.45283 |
| BD* Si1-C3 | 0.14624 | 0.33248 | BD* Si1-C6 | 0.09620 | 0.45292 |
| BD* Si1-C4 | 0.14623 | 0.33254 | BD* Si1-C10 | 0.09620 | 0.45247 |
| BD* Si1-O5 | 0.01963 | 0.50290 | BD* Si1-O14 | 0.01815 | 0.57360 |
| BD* C2-F6 | 0.08860 | 0.34682 | BD* C2-H3 | 0.00387 | 0.58110 |
| BD* C2-F7 | 0.08320 | 0.35138 | BD* C2-H4 | 0.00593 | 0.57793 |
| BD* C2-F8 | 0.08581 | 0.34391 | BD* C2-H5 | 0.00387 | 0.58050 |
| BD* C3-F9 | 0.08578 | 0.34428 | BD* C6-H7 | 0.00386 | 0.58124 |
| BD* C3-F10 | 0.08859 | 0.34683 | BD* C6-H8 | 0.00387 | 0.58034 |
| BD* C3-F11 | 0.08322 | 0.35093 | BD* C6-H9 | 0.00593 | 0.57802 |
| BD* C4-F12 | 0.08857 | 0.34695 | BD* C10-H11 | 0.00387 | 0.58085 |
| BD* C4-F13 | 0.08319 | 0.35129 | BD* C10-H12 | 0.00386 | 0.58117 |
| BD* C4-F14 | 0.08579 | 0.34381 | BD* C10-H13 | 0.00593 | 0.57811 |

Figure S15. Section of the Kohn-Sham MO energy levels for [Si(CF$_3$)$_3$O]$^-$ (left) and [Si(CH$_3$)$_3$O]$^-$ (right)
2.5 X-ray Data

CCDC 1507501 and 2060880 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/conts/retrieving.html.

Table S3. Structure refinement data of (C₂F₅)₃SiOSi(C₂F₅)₃[a] and [tmg₃P=N(H)ₐBu₂][Si(C₂F₅)₃O]₂[b].

|                          | (C₂F₅)₃SiOSi(C₂F₅)₃[a] | [tmg₃P=N(H)ₐBu₂][Si(C₂F₅)₃O]₂[b] |
|--------------------------|------------------------|----------------------------------|
| Empirical formula        | C₁₆F₇₂O₅Si₂            | C₅₀H₁₄₂F₄₀N₈O₆P₂S₂I₂            |
| Formula weight           | 786.30                 | 1693.55                          |
| Temperature/K            | 100.0(1)               | 100.0(1)                         |
| Crystal system           | triclinic              | triclinic                        |
| Space group              | P.bar                 | P.bar                            |
| a/Å                      | 9.6776(9)              | 10.2965(4)                       |
| b/Å                      | 16.936(2)              | 14.2830(6)                       |
| c/Å                      | 17.0127(19)            | 14.3612(5)                       |
| α/°                      | 117.656(13)            | 67.856(3)                        |
| β/°                      | 105.118(9)             | 86.430(3)                        |
| γ/°                      | 94.654(10)             | 73.428(4)                        |
| Volume/Å³                | 2316.7(5)              | 1872.54(14)                      |
| Z                        | 4                      | 1                                |
| ρ Calc g/cm³             | 2.254                  | 1.502                            |
| μ/mm⁻¹                   | 3.844                  | 1.990                            |
| F(000)                   | 1512.0                 | 876.0                            |
| Crystal size/mm³         | 0.19 x 0.17 x 0.08     | 0.13 x 0.11 x 0.06               |
| 2Θ range for data collection/° | 6.064 to 143.986 | 6.654 to 144.25                  |
| Index ranges             | −11 ≤ h ≤ 11,         | −11 ≤ h ≤ 12,                    |
|                          | −20 ≤ k ≤ 20,         | −17 ≤ k ≤ 16,                    |
|                          | −20 ≤ l ≤ 20          | −17 ≤ l ≤ 13                     |
| Reflections collected    | 65550                  | 15924                            |
| Independent reflections  | 9047                   | 7383                             |
| R(int)                   | 0.0446                 | 0.0221                           |
| R(sigma)                 | 0.0236                 | 0.0299                           |
| Reflections with I > 2σ(I)| 7729                   | 6503                             |
| Data/restraints/parameters | 9047/ 0/ 811         | 7383/ 7/ 725                     |
| Goodness-of-fit on F²    | 1.121                  | 1.028                            |
| Final R indexes [I > 2σ(I)] | R₁ = 0.0490 | R₁ = 0.0309                      |
|                          | wR₂ = 0.1492           | wR₂ = 0.0772                     |
| Final R indexes [all data] | R₁ = 0.0565 | R₁ = 0.0367                      |
|                          | wR₂ = 0.1556           | wR₂ = 0.0817                     |
Supporting Information

\[ (\text{C}_2\text{F}_5)_3\text{SiOSi}(\text{C}_2\text{F}_5)_3 \]

\[ [\text{ImG} = \text{N}(\text{H})\text{Bu}]_2[\{\text{Si}(\text{C}_2\text{F}_5) = \text{O}\}_2] \]

|                     | Largest diff. peak/hole / e Å\(^3\) | CCDC number |
|---------------------|-------------------------------------|-------------|
|                     | 0.82 / -0.40                        | 1507501     |
|                     | 0.30 / -0.27                        | 2060880     |

[a] The crystal data were collected on a SuperNova, Dual, Atlas diffractometer using CuKα (\(\lambda = 1.54184\) Å) radiation. Using Olex2,\(^{[3]}\) the structure was solved with the ShelXS\(^{[4]}\) structure solution program using Direct Methods and refined with the ShelXL\(^{[4]}\) refinement package using Least Squares minimization. [b] The crystal data were collected on a Supernova diffractometer using CuKα (\(\lambda = 1.54184\) Å) radiation. Using Olex2,\(^{[3]}\) the structure was solved with the ShelXT\(^{[5]}\) structure solution program using Intrinsic Phasing and refined with the ShelXL\(^{[6]}\) refinement package using Least Squares minimisation. Disorder of the entire anion on an inversion center with a ratio of 1:1, disordered atoms close to each other were constrained to have equal thermal parameters, the equatorial Si-C bond lengths were restrained to be same as well as the axial Si-O-distances.

References

[1] R. D. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Willingham CT, 2013.

[2] E.D. Glendining, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, NBO 6.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst. 2009, 42, 339.

[4] G. M. Sheldrick, Acta Cryst. 2008, A64, 112.

[5] G. M. Sheldrick, Acta Cryst. 2015, A71, 3.

[6] G. M. Sheldrick, Acta Cryst. 2015, C71, 3.