(250 MHz, [D$_6$]acetone): δ = 13.68 (s, br, 1 H; NH **6a**), 9.57 (s, 3 H; OH **6a**, **6b**), 7.25 (d, 2 H; Ar-H **6b**), 7.10 (t, 1 H; Ar-H **6a**), 6.89 (t, 1 H; Ar-H **6b**), 6.56 (d, 2 H; Ar-H **6a**); ^{13}C{^{1}H} NMR (62.90 MHz, [D$_3$COD]: δ = 230.0 (carbene-C), 222.7 (*trans*-CO **6b**), 218.8 (*trans*-CO **6a**), 218.2 (*cis*-CO **6b**), 216.0 (*cis*-CO **6a**), 175.6 (NC **6a**), 155.9, 130.7, 107.4, 106.9 (Ar-C **6a**), 156.0, 126.1, 114.4, 121.1, 111.6, 102.3 (Ar-C **6b**); MS (70 eV): *m/z* 327 (M^+ **6a**, **6b**, 17.0%), 187 (M^+ −5CO, 100).

[10] a) K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH, Weinheim, **1983**; b) B. Crociani in *Reactions of Coordinated Ligands, Vol. 1* (Ed.: P. S. Braterman), Plenum Press, New York, **1985**.

[11] Correct elemental analysis for **7**–**10**. **7**: ^{1}H NMR (250 MHz, [D$_6$]acetone, 1:2-triethylamine adduct): δ = 7.02 (m, 3 H; Ar-H), 2.88 (quart, 12 H; NCH$_2$), 1.15 (t, 18 H: CH$_2$-CH_3), O-H-Resonance signal was not observed; IR (KBr, of the crystalline solid **7**): $\tilde{\nu}$[cm^{-1}] = 3418 (m, O-H ··· N), 2154 (m, NC), 2062 (s, CO), 1988 (sh, CO), 1914 (vs br, CO). – **8**: ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 7.08 (m, 3 H; Ar-H), 2.89 (s, 12 H; NCH$_2$); IR (KBr): $\tilde{\nu}$[cm^{-1}] = 3421 (m, O-H ··· N), 2149 (m, NC), 2061 (s, CO), 1990 (sh, CO), 1922 (vs br, CO). – **10**: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.18 (t, 1 H; Ar-H), 6.80 (d, 2 H; Ar-H), 4.26 (s, 3 H; NCH$_3$), 3.97 (s, 3 H; OCH$_3$); ^{13}C{^{1}H} NMR (62.90 MHz, CD$_2$Cl$_2$): δ = 231.1 (carbene-C), 222.3 (*trans*-CO), 217.7 (*cis*-CO), 155.3, 147.2, 126.7, 122.6, 107.6, 104.2 (Ar-C), 57.0 (OCH$_3$), 37.4 (NCH$_3$); MS (70 eV): *m/z* 355 (M^+, 13.0%).

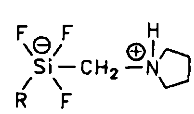
[12] The size and the scattering power of crystals of **7** were very small. For this reason, only a limited data set with $F_o^2 \geq 3\sigma(F_o^2)$ was available for the calculations. In order to keep the number of refinement parameters small, the six atoms of the aromatic ring were refined with isotropic thermal parameters. Crystals of **8** contained two almost identical molecules of **8** and one acetone molecule (the methyl groups of which were disordered) in the asymmetric unit. Structure parameters: **7** [**8** · 0.5(CH$_3$)$_2$CO] {**10**}: C$_{18}$H$_{20}$CrN$_2$O$_7$ [C$_{19.5}$H$_{20}$CrN$_3$O$_{7.5}$] {C$_{14}$H$_9$CrNO$_7$}, monoclinic [orthorhombic] {monoclinic}, space group $P2_1/c$ [$Pbca$] {$P2_1/n$}, a = 12.713(8) [18.200(5)] {6.885(3)}, b = 15.328(8) [21.691(6)] {13.969(4)}, c = 11.950(6) [23.700(4)] {15.772(3)} Å, β = 117.92(4) [90.0] {97.83(2)}°, V = 2058(4) [9356(7)] {1502.8(14)} Å^3, Z = 4 [16] {4}, $\rho_{exp.}$ = 1.37 [1.32] {1.58}, $\rho_{calcd.}$ = 1.383 [1.330] {1.570} g cm^{-3}, Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), μ(Mo$_{K\alpha}$) = 5.8 [5.2] {7.8} cm^{-1}, 2688 [5821] {2641} symmetry-independent data measured at −100(5) [20(5)] {20(5)} °C in the 2θ range 2–45 [2–45] {2–50}°. Structure solution with Patterson methods, refinement of the position parameters of all non-hydrogen atoms with anisotropicic thermal parameters (ring atoms in **7** isotropic). C–H atomic positions calculated [d(C–H) = 0.95 Å] with $B_{eq(H)} = 1.3\,B_{eq(C)}$; no hydrogen atoms were calculated for acetone in **8**·0.5(CH$_3$)$_2$CO; H 1 in **7** and all O–H in **8**·0.5(CH$_3$)$_2$CO were found and refined with constant B_{eq} = 4.0 Å^2. R = 4.90 [6.95] {3.76}, R_w = 6.14 [9.06] {4.85} for 901 [3551] {1764} structure factors $F_o^2 \geq 3\sigma(F_o^2)$ [absorption correction for **7** and **8**·0.5(CH$_3$)$_2$CO] and 226 [559] {208} variables.

[13] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository numcalcd CSD-58127 and the journal citation.

Hexacoordinate Silicon in a Compound with an F$_5$SiC Unit**

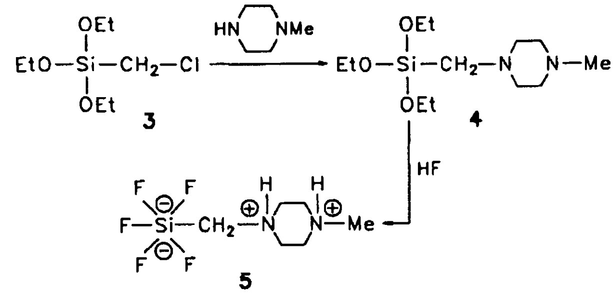
Reinhold Tacke* and Mathias Mühleisen

Anions with penta- and hexacoordinate silicon such as [RSiF$_4$]$^-$, [RSiF$_5$]$^{2-}$, and [R$_2$SiF$_4$]$^{2-}$ (R = organic substituent) have been known for about thirty years.[1] More recently salts containing the anions [R$_2$SiF$_3$]$^-$[2] and [R$_3$SiF$_2$]$^-$[2c, 3] have also been reported. Whereas the aforementioned λ^6Si-organofluorosilicates have not been structurally characterized, the structural chemistry of λ^5Si-organofluorosilicates has been investigated in great detail in the past few years.[4] We have recently extended these studies with investigations on zwitterionic (molecular) λ^5Si-organofluorosilicates[5] (examples: zwitterions **1**[5a] and **2**[5d]). We report here on the synthesis and structural characterization of **5**·H$_2$O, the first zwitterionic λ^6Si-organofluorosilicate. The zwitterion **5** is the first molecular compound of hexacoordinate silicon with an F$_5$SiC unit and contains a hexacoordinate (formally twofold negatively charged) Si atom and two tetracoordinate (formally single positively charged) N atoms. The crystal structure analysis of **5**·H$_2$O is the first solid-state structural characterization of an λ^6Si species with an F$_5$SiC unit.



1: R = F
2: R = Me

The λ^6Si-silicate **5** was prepared by the reaction of (chloromethyl)triethoxysilane (**3**)[6] with 1-methylpiperazine to yield silane **4**, which was treated with hydrofluoric acid; the product was isolated as monohydrate **5**·H$_2$O.



Compound **5**·H$_2$O crystallizes in the space group $P\bar{1}$ with one pair each of crystallographically independent zwitterions and water molecules in the asymmetric unit.[7] The crystal structure is dominated by intermolecular N–H ··· F and O–H ··· F hydrogen bonds. All of the donor functions are involved in the three-dimensional hydrogen-bonding network, which has a marked surplus of acceptor functions (donor/acceptor ratio 8:34). The structures of the two independent zwitterions (Fig. 1) are very similar. The Si–C distances [194.6(1) and 194.3(2) pm] are distinctly greater than those in the zwitterionic λ^5Si-organofluoro-

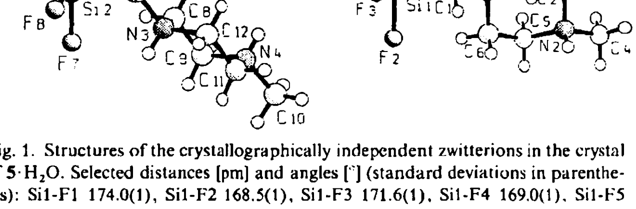


Fig. 1. Structures of the crystallographically independent zwitterions in the crystal of **5**·H$_2$O. Selected distances [pm] and angles [°] (standard deviations in parentheses): Si1-F1 174.0(1), Si1-F2 168.5(1), Si1-F3 171.6(1), Si1-F4 169.0(1), Si1-F5 170.8(1), Si1-C1 194.6(1); F1-Si1-F2 177.59(5), F1-Si1-F3 89.27(5), F1-Si1-F4 87.73(5), F1-Si1-F5 87.47(5), F1-Si1-C1 89.54(5), F2-Si1-F3 91.40(5), F2-Si1-F4 89.97(5), F2-Si1-F5 91.81(5), F2-Si1-C1 92.79(5), F3-Si1-F4 88.31(5), F3-Si1-F5 176.56(5), F3-Si1-C1 89.02(5), F4-Si1-F5 90.45(5), F4-Si1-C1 176.21(5), F5-Si1-C1 92.06(5). – Si2-F6 171.7(1), Si2-F7 168.8(1), Si2-F8 172.9(1), Si2-F9 169.2(1), Si2-F10 170.5(1), Si2-C7 194.3(2); F6-Si2-F7 177.87(5), F6-Si2-F8 89.24(5), F6-Si2-F9 88.13(5), F6-Si2-F10 89.69(5), F6-Si2-C7 89.33(5), F7-Si2-F8 89.59(5), F7-Si2-F9 90.04(5), F7-Si2-F10 91.38(5), F7-Si2-C7 92.47(5), F8-Si2-F9 87.82(5), F8-Si2-F10 176.57(5), F8-Si2-C7 91.03(5), F9-Si2-F10 88.89(5), F9-Si2-C7 177.23(6), F10-Si2-C7 92.21(5).

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silicates investigated previously.[5] In contrast, the Si–F distances [168.5(1)–174.0(1) pm] are comparable in length to the axial Si–F bonds in the latter compounds.[5] Similar distances were also determined for the $[SiF_6]^{2-}$ ion (typically in the region of 168–170 pm).[4a] The bond angles in $5 \cdot H_2O$ deviate only slightly from the ideal values of 180° [maximum deviation 3.8 and 3.4°] and 90° [maximum deviation 2.8 and 2.5°], and thus the coordination polyhedra around the two Si atoms may be described as only slightly distorted octahedra. The relevant structural parameters are listed in the legend to Figure 1.

NMR spectroscopic investigations[8] have shown that **5** is also present as a zwitterion in solution (D_2O, $[D_6]$DMSO). The presence of the quaternary ammonium centers can be inferred indirectly from the chemical shifts of the ring protons in D_2O and $[D_6]$DMSO and from the detection of the NH protons in $[D_6]$DMSO. The hexacoordination at silicon is demonstrated indirectly by the ^{19}F NMR spectrum of **5** in D_2O (two signals with an intensity ratio of 4:1); in contrast, the spectrum of **5** in $[D_6]$DMSO shows only a relatively broad ^{19}F resonance signal, which could indicate dynamic molecular processes. ^{29}Si NMR spectra of **5** in D_2O and $[D_6]$DMSO could not be obtained (^{29}Si CP/MAS NMR: $\delta = -177.2$).

Experimental Procedure

4: A solution of **3** [6] (16.9 g, 79.4 mmol), 1-methylpiperazine (7.95 g, 79.4 mmol), and triethylamine (12.1 g, 120 mmol) in toluene (200 mL) was stirred under reflux for 24 h and then at room temperature for 48 h. Solvent and unreacted triethylamine were removed under reduced pressure, and the residue was treated with *n*-pentane (300 mL). The precipitate was filtered off, and the filtrate was concentrated under reduced pressure and then fractionally distilled using a Vigreux column to provide a colorless, clear liquid; yield 17.9 g (82%), b.p. 90 °C/0.2 Torr: correct C,H,N analysis; ^{1}H NMR ($[D_6]$DMSO): $\delta = 1.13$ (t, $^3J(H,H) = 7.0$ Hz, 9H; CCH_3), 1.87 (s, 2H; $SiCH_2$), 2.10 (s, 3H; NCH_3), 2.10–2.40 (m, 8H; ring H), 3.76 (q, $^3J(H,H) = 7.0$ Hz, 6H; CH_2O); ^{13}C NMR ($[D_6]$DMSO): $\delta = 18.5$ (CCH_3), 44.0 ($SiCH_2$), 46.1 (NCH_3), 55.4, 56.2, 58.2 (CH_2O, ring C); EI-MS: *m/z* (%): 276 (21) $[M^+]$, 261 (5) $[M^+ - CH_3]$, 247 (14) $[M^+ - C_2H_5O]$, 206 (100).

$5 \cdot H_2O$: Hydrofluoric acid (1.5 M, 12.1 mL, 18.2 mmol HF) was added dropwise at 0 °C over 1 h to a stirred solution of **4** (1.00 g, 3.62 mmol) in water (20 mL). The resulting clear solution was stirred for 2 h at 0 °C and then treated with ethanol (100 mL), which caused a solid to precipitate. After the solid was removed by filtration, the filtrate was concentrated to ca. 10 mL under reduced pressure. Ethanol (100 mL) was added and the precipitated solid filtered off. The combined precipitates were washed with ethanol (3 × 10 mL) and then recrystallized from water at room temperature (crystallization by slow evaporation of the solvent). The crystals obtained were dried in a stream of nitrogen (room temperature): yield 685 mg (74%) colorless crystals. M.p. 202–204° (decomp); correct C,H,N,F analysis; ^{29}Si CP/MAS NMR (59.6 MHz, $\nu_{rot} = 3740$ Hz, contact time 4 ms, time between pulses 3 s, 1958 accumulated spectra): $\delta = -177.2$ ($\nu_{1/2} = 675$ Hz); ^{1}H NMR (D_2O): $\delta = 2.25$ (s, 2H; $SiCH_2$), 3.00 (s, 3H; CH_3), 3.25–4.05 (m, 8H; ring H); ^{1}H NMR ($[D_6]$DMSO): $\delta = 2.15$–2.30 (m, 5H; CH_3, $SiCH_2$), 2.75–3.00 (m, 4H; ring H), 3.25–3.35 (m, 6H; ring H, H_2O), 8.4 (br.s, 2H; NH); ^{13}C NMR (D_2O): $\delta = 46.0$ (CH_3), 53.9, 54.9 (ring C), 60.5 (m, unresolved C,F couplings; $SiCH_2$); ^{13}C NMR ($[D_6]$DMSO): $\delta = 45.2$ (CH_3), 51.7, 54.4 (ring C), $SiCH_2$ not detected; ^{19}F NMR (D_2O): $\delta = -113.7$ (s, 4F), -123.5 (s, 1F); ^{19}F NMR ($[D_6]$DMSO): $\delta = -112.1$ (br.s, $\nu_{1/2} = 63$ Hz); FD-MS (DMSO, 11 kV): *m/z* (%): 236 (9) $[(M - 2H)^+]$, 198 (100) $[(M - 2HF)^+]$.

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[1] Review: R. Müller, *Organomet. Chem. Rev.* **1966**, *1*, 359–377.

[2] a) D. Schomburg, R. Krebs, *Inorg. Chem.* **1984**, *23*, 1378–1381; b) R. Damrauer, S. E. Danahey, *Organometallics* **1986**, *5*, 1490–1494; c) J. J. Harland, J. S. Payne, R. O. Day, R. R. Holmes, *Inorg. Chem.* **1987**, *26*, 760–765; d) S. E. Johnson, J. S. Payne, R. O. Day, J. M. Holmes, R. R. Holmes, *ibid.* **1989**, *28*, 3190–3198; e) S. E. Johnson, J. A. Deiters, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **1989**, *111*, 3250–3258; f) R. O. Day, C. Sreelatha, J. A. Deiters, S. E. Johnson, J. M. Holmes, L. Howe, R. R. Holmes, *Organometallics* **1991**, *10*, 1758–1766; g) K. Tamao, T. Hayashi, Y. Ito, *ibid.* **1992**, *11*, 182–191.

[3] D. A. Dixon, W. B. Farnham, W. Heilemann, R. Mews, M. Noltemeyer, *Heteroatom Chem.* **1993**, *4*, 287–295.

[4] Reviews: a) S. N. Tandura, M. G. Voronkov, N. V. Alekseev, *Top. Curr. Chem.* **1986**, *131*, 99–189; b) W. S. Sheldrick in *The Chemistry of Organic Silicon Compounds, Part 1* (Eds.: S. Patai, Z. Rappoport), John Wiley, Chichester, **1989**, pp. 227–303; c) R. R. Holmes, *Chem. Rev.* **1990**, *90*, 17–31; d) C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *ibid.* **1993**, *93*, 1371–1448.

[5] a) R. Tacke, J. Becht, G. Mattern, W. F. Kuhs, *Chem. Ber.* **1992**, *125*, 2015–2018; b) R. Tacke, A. Lopez-Mras, J. Becht, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1012–1016; c) R. Tacke, J. Becht, A. Lopez-Mras, J. Sperlich, *J. Organomet. Chem.* **1993**, *446*, 1–8; d) R. Tacke, J. Becht, A. Lopez-Mras, W. S. Sheldrick, A. Sebald, *Inorg. Chem.* **1993**, *32*, 2761–2766; e) for analogous zwitterionic Si–O compounds see R. Tacke, M. Mühleisen, P. G. Jones, *Angew. Chem.* **1994**, *106*, 1250–1252; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1186–1188, and references therein.

[6] Synthesis of **3**: J. E. Noll, J. L. Speier, B. F. Daubert, *J. Am. Chem. Soc.* **1951**, *73*, 3867–3871.

[7] Crystal data for $5 \cdot H_2O$: $C_6H_{17}F_5N_2OSi$, triclinic, $P\bar{1}$, $a = 743.8(1)$, $b = 1207.1(2)$, $c = 1240.7(2)$ pm, $\alpha = 74.25(1)$, $\beta = 82.28(1)$, $\gamma = 74.61°$, $V = 1.0313(3)$ nm^3, $Z = 4$, $T = -70$ °C. A colorless prism (0.80 × 0.55 × 0.21 mm) was mounted in paraffin oil (type DAB 8, USP XX, Merck). A STADI-4 Stoe diffractometer ($Mo_{K\alpha}$ irradiation, $2\theta_{max} = 56°$) was used to measure 5346 intensities, of which 4965 were independent ($R_{int} = 0.022$). After an empirical absorption correction, the structure was solved by direct methods and refined on F^2 (program SHELXL-93, G. M. Sheldrick, Universität Göttingen). The final $R_w(F^2)$ value was 0.101, the conventional $R(F)$ value was 0.036 (for 407 parameters). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-58125.

[8] Measurement conditions: 250.1 (^{1}H), 62.9 (^{13}C), and 235.4 MHz (^{19}F); ca. 22 °C; $[D_5]$DMSO ($\delta = 2.49$) and $(CH_3)_3Si(CH_2)_3SO_3Na$ ($\delta = 0$) as internal ^{1}H NMR standards in $[D_6]$DMSO and D_2O, respectively; $[D_6]$DMSO ($\delta = 39.90$) and $(CH_3)_3Si(CH_2)_3SO_3Na$ ($\delta = 0$) as internal ^{13}C NMR standards in $[D_6]$DMSO and D_2O, respectively; $CFCl_3$ ($\delta = 0$) as internal ^{19}F NMR standard in $[D_6]$DMSO and as external ^{19}F NMR standard in D_2O.

Iterative Divergent/Convergent Approach to Linear Conjugated Oligomers by Successive Doubling of the Molecular Length: A Rapid Route to a 128Å-Long Potential Molecular Wire[**]

Jeffry S. Schumm, Darren L. Pearson, and
James M. Tour*

The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized.[1] Even though state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime,[2] the possibility of electronic conduction based upon single or small packets of molecules has not been addressed, and the feasibility of molecular electronics remains theoretically controversial.[1–3] In an attempt to assess the possibility of molecular wire[4] conduction by spanning the 100 Å probe gaps with small packets of molecules, we describe here the synthesis of phenylalkyne oligomers that remain in a near-linear conformation owing to the 1,4-substitution of the phenylene units and the linearity of the alkyne moiety. This arrangement should minimize undesired conformational changes during adhesion and testing in the nanofabricated probes. Our approach to such a molecular framework involves a rapid iterative method that doubles molecular length with each iteration.[5] We obtained an air- and light-stable, linear conjugated oligomer that is 128 Å long which could also serve as a useful model for understanding

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