Silicon Complexes

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Pentacoordination of Silicon by Five Different Ligand Atoms: Neutral Silicon(IV) Complexes with SiClSONC and SiISONC Skeletons

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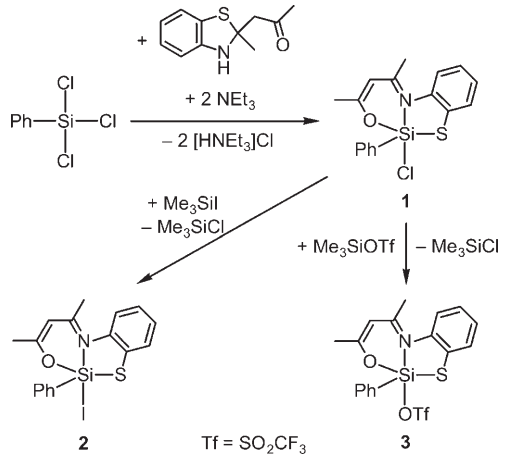
Most of the pentacoordinate silicon(IV) complexes reported in the literature contain carbon, nitrogen, oxygen, and/or fluorine ligand atoms.[1,2] Recently, we have demonstrated that sulfur can also act as a ligand atom for pentacoordination of silicon.[3] Pentacoordinate silicon compounds with five different ligand atoms that are stable in the solid state and in solution have not yet been described[4] and therefore represent a challenging goal for synthetic silicon chemistry. We report herein the first examples of such compounds, the neutral pentacoordinate silicon(IV) complexes **1** (SiClSONC skeleton) and **2** (SiISONC skeleton). Compound **2** is the first higher coordinate silicon(IV) complex with an Si–I bond that has been structurally characterized by single-crystal X-ray diffraction,[5,6] and **3**, with its trifluoromethanesulfonato ligand, contains the novel $SiSO_2NC$ skeleton.

The silicon(IV) complexes **1**–**3** were synthesized according to Scheme 1. Compound **1** was obtained by treatment of trichloro(phenyl)silane with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one[7] and triethylamine to yield a yellow crystalline solid (82% yield). Compounds **2** and **3** were synthesized by reaction of **1** with iodotrimethylsilane and trimethyl(trifluoromethanesulfonato)silane, respectively (**2**, 66% yield; **3**, 78% yield). The identities of **1**–**3** were established by elemental analyses, crystal structure analyses, and solid-state and solution NMR studies.[8,9]



Scheme 1. Synthesis of the neutral pentacoordinate silicon(IV) complexes **1**–**3**.

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The Si coordination polyhedra of **1**–**3** are somewhat distorted trigonal bipyramids, with the carbon, oxygen, and sulfur atoms in the equatorial positions, whereas the nitrogen atom and the fifth ligand atom (**1**, Cl; **2**, I; **3**, O) occupy the axial positions (Figures 1–3). The sum of the bond angles in

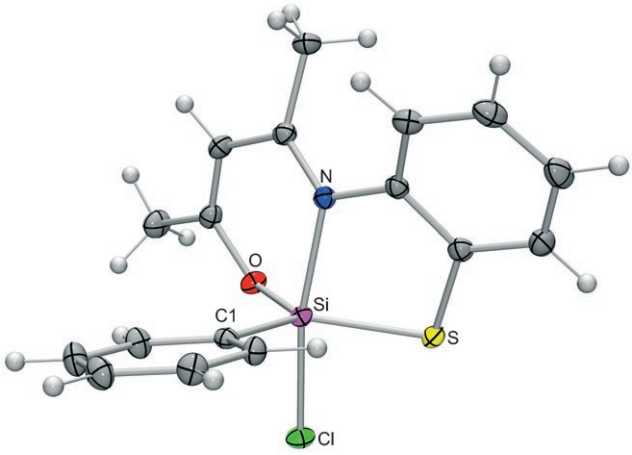

Figure 1. Molecular structure of **1** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Cl 2.1954(4), Si–S 2.1571(4), Si–O 1.6850(8), Si–N 2.0069(10), Si–C1 1.8593(11); Cl-Si-S 85.410(15), Cl-Si-O 87.92(3), Cl-Si-N 167.66(3), Cl-Si-C1 98.26(4), S-Si-O 127.65(3), S-Si-N 85.57(3), S-Si-C1 120.12(4), O-Si-N 90.94(4), O-Si-C1 112.23(5), N-Si-C1 93.54(4).

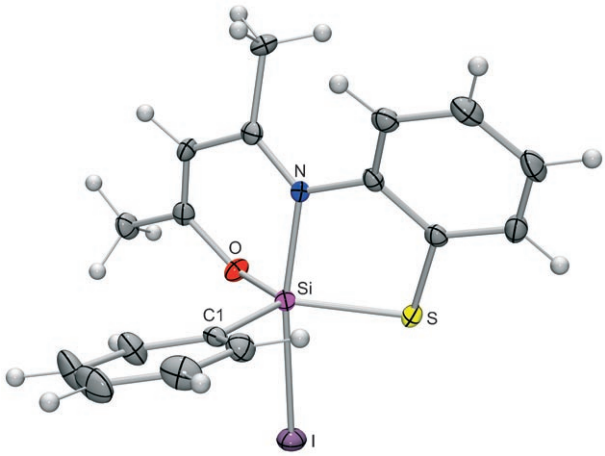

Figure 2. Molecular structure of **2** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–I 2.7396(8), Si–S 2.1262(10), Si–O 1.6655(19), Si–N 1.936(2), Si–C1 1.851(3); I-Si-S 82.48(3), I-Si-O 85.44(7), I-Si-N 167.96(7), I-Si-C1 95.16(8), S-Si-O 124.37(8), S-Si-N 88.53(7), S-Si-C1 122.88(9), O-Si-N 93.12(10), O-Si-C1 112.16(11), N-Si-C1 96.45(10).

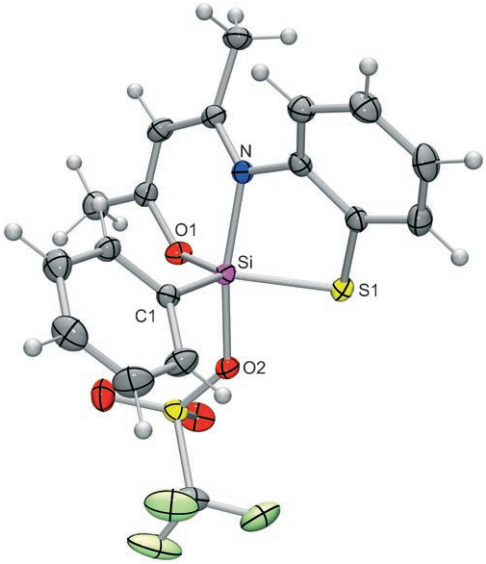

Figure 3. Molecular structure of **3** in the crystal (probability level of displacement ellipsoids 50%; light-green F). Selected bond lengths [Å] and angles [°]: Si–S1 2.1435(8), Si–O1 1.6682(14), Si–O2 1.8744(14), Si–N 1.9238(16), Si–C1 1.8476(19); S1-Si-O1 127.06(6), S1-Si-O2 83.15(5), S1-Si-N 87.10(5), S1-Si-C1 117.42(6), O1-Si-O2 86.29(7), O1-Si-N 92.80(7), O1-Si-C1 115.23(8), O2-Si-N 167.01(7), O2-Si-C1 96.18(7), N-Si-C1 95.91(7).

the equatorial plane of **1** (360.0°), **2** (359.4°), and **3** (359.7°) fits almost perfectly with the ideal value of 360°, whereas the axial N-Si-X (X = Cl, I, O) angles (**1**, 167.66(3)°; **2**, 167.96(7)°; **3**, 167.01(7)°) deviate significantly from the ideal value of 180°.

The angles spanned by the silicon center and its respective ligand atoms in the Si coordination polyhedra of **1**–**3** are very similar, that is, the tridentate S,N,O ligand leads to a certain rigidity and thereby controls the structure. The Si–N distances of **2** and **3** are significantly shorter than that of **1** (Table 1). This shortening (increased bond strength) of the axial Si–N distance in **2** and **3** can be correlated with a decreased strength of the axial Si–I (**2**) and Si–O (**3**) bonds and is in accordance with the same trend observed for the strength of intramolecular Si···O[6c] and Si···S[10] interactions in other pentacoordinate (4+1 coordination) silicon compounds. Interestingly, the decrease in the axial Si–N bond length in **2** and **3** is also accompanied by a slight shortening of the equatorial Si–S, Si–O, and Si–C distances (Table 1). All equatorial bonds of **1**–**3** are somewhat shorter than the sum of the covalent radii, whereas the axial bonds are somewhat longer than the sum of the covalent radii.[11] The Si–I distance of **2** (the first experimentally determined Si–I bond length of a pentacoordinate silicon compound) of 2.7396(8) Å is significantly longer than Si–I bonds observed for tetracoordinate silicon compounds (e.g., Si–I 2.4339(19)–2.5720(13) Å[12]).

Table 1: Comparison of the Si–X (X = S, O, N, C) distances [Å] of **1**–**3**.

Si–X	**1**	**2**	**3**
Si–S	2.1571(4)	2.1262(10)	2.1435(8)
Si–O (**3**: O1)	1.6850(8)	1.6655(19)	1.6682(14)
Si–N	2.0069(10)	1.936(2)	1.9238(16)
Si–C1	1.8593(11)	1.851(3)	1.8476(19)

The isotropic ^{29}Si chemical shifts of **1** ($\delta = -83$ ppm),[13] **2** ($\delta = -91$ ppm),[13] and **3** ($\delta = -81.7$ ppm) in the solid state are very similar to those in CD_2Cl_2 solution (**1**, $\delta = -82.1$ ppm; **2**, $\delta = -92.5$ ppm; **3**, $\delta = -83.7$ ppm), that is, **1**–**3** exist in solution as well.[14] For all three compounds, only one set of signals was observed in the solution ^{1}H, ^{13}C, and ^{29}Si NMR spectra (no diastereomers detected), which is in accordance with the aforementioned rigidity induced by the tridentate ligand. The isotropic ^{15}N chemical shifts of **1** ($\delta = -149.4$ ppm), **2** ($\delta = -163.8$ ppm), and **3** ($\delta = -156.4$ ppm) in the solid state are strongly affected by the monodentate axial ligands (Cl, I, OSO_2CF_3) and correlate with the trend observed for the isotropic ^{29}Si chemical shifts. This can be interpreted in terms of a significant bonding interaction between the silicon and nitrogen atoms of **1**–**3**, which is also reflected in the Si–N distances (1.9238(16)–2.0069(10) Å).

To obtain information about a potential dissociation of the Si–I (**2**) and Si–OTf (**3**) bond in solution (formation of a cationic silicon species and the I^- and OTf^- anion, respectively), ^{29}Si NMR studies in solvents with different polarity were performed. However, because of the poor solubility and/or limited stability of **2** and **3** in most of these solvents, only additional ^{29}Si NMR spectra of **2** in $CDCl_3$ ($\delta = -92.8$ ppm) and CD_3CN ($\delta = -85.2$ ppm)[15] could be recorded. These spectra (and the ^{1}H and ^{13}C NMR spectra as well) are very similar to those obtained in CD_2Cl_2 and indicate that **2** also exists in the more polar solvents $CDCl_3$ and CD_3CN.

In conclusion, with the preparation of **1** and **2**, we have succeeded in synthesizing the first pentacoordinate silicon(IV) complexes with five different ligand atoms (SiClSONC and SiISONC skeletons). These chiral compounds exist in the solid state and in solution, probably with very similar structures. As demonstrated by the synthesis of **2** and **3** from **1**, the chloro ligand of **1** can be easily replaced by other ligands to give further pentacoordinate silicon compounds with novel Si coordination polyhedra (SiISONC and $SiSO_2NC$ skeletons); compound **2** with its iodo ligand is especially remarkable. Thus, compound **1** (and probably **2** and **3** as well) is a promising precursor for the synthesis of further neutral pentacoordinate silicon(IV) complexes with novel Si coordination polyhedra, including further chiral compounds with five different ligand atoms attached to the silicon center. Systematic studies on compounds of this type could further our understanding of the influence of different types of ligand atoms on the bonding situation at pentacoordinate silicon centers, and they offer other new perspectives for the chemistry of higher coordinate silicon. For example, replacement of the monodentate monoanionic ligands of **1**–**3** by bidentate monoanionic ligands could lead to novel neutral hexacoordinate silicon(IV) complexes.

Experimental Section

1: Triethylamine (1.95 g, 19.3 mmol) and trichloro(phenyl)silane (2.04 g, 9.65 mmol) were added at 0 °C one after another to a stirred solution of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one[7]

(2.00 g, 9.64 mmol) in tetrahydrofuran (30 mL). The resulting mixture was allowed to warm to 20 °C and was then stirred for 30 min. The solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate was removed in vacuo, acetonitrile (30 mL) was added to the solid residue, and the resulting suspension was heated until a clear solution was obtained. The solution was allowed to cool to 20 °C (formation of crystals) and was kept at this temperature for 1 h and then at −20 °C for a further 3 h. The yellow crystalline product was filtered off, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h). Yield: 2.72 g (7.86 mmol, 82 %); m.p. > 116 °C (decomp); ^{1}H NMR (500.1 MHz): $\delta = 2.27$ (d, ^4J(H,H) = 0.5 Hz, 3 H; CCH_3), 2.32 (s, 3 H; CCH_3), 5.77 (q, ^4J(H,H) = 0.5 Hz, 1 H; CCHC), 6.97–7.02, 7.14–7.28, 7.42–7.47 ppm (m, 9 H; C_6H_4, C_6H_5); ^{13}C NMR (125.8 MHz): $\delta = 24.1$ (CCH_3), 24.3 (CCH_3), 105.0 (CCHC), 123.6, 124.4, 127.3, 127.8 (2 C), 128.5, 129.8, 132.4 (2 C), 133.9, 137.4, 139.8 (C_6H_4, C_6H_5), 171.1 (CN or CO), 171.5 ppm (CN or CO); ^{29}Si NMR (99.4 MHz): $\delta = -82.1$; ^{13}C VACP/MAS NMR: $\delta = 25.2$ (CCH_3), 27.2 (CCH_3), 106.6 (CCHC), 124.3, 124.7, 127.4, 128.9, 133.4, 138.5 (C_6H_4, C_6H_5), 170.4 (CN or CO), 171.1 ppm (CN or CO); ^{15}N VACP/MAS NMR: $\delta = -149.4$ ppm; ^{29}Si VACP/MAS NMR: $\delta = -83$ ppm (br);[13] elemental analysis (%) calcd for $C_{17}H_{16}ClNOSSi$ ($M_r = 345.92$): C 59.03, H 4.66, N 4.05, S 9.27; found: C 59.2, H 4.8, N 4.1, S 9.2.

2: Iodotrimethylsilane (255 mg, 1.27 mmol) was added at 20 °C to a stirred solution of **1** (400 mg, 1.16 mmol) in dichloromethane (4 mL), and the solution was kept undisturbed at 20 °C for 3 d. The yellow crystalline product was filtered off, washed with diethyl ether (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h). Yield: 333 mg (761 μmol, 66 %); m.p. > 108 °C (decomp); ^{1}H NMR (400.1 MHz): $\delta = 2.35$ (d, ^4J(H,H) = 0.5 Hz, 3 H; CCH_3), 2.37 (s, 3 H; CCH_3), 5.87 (q, ^4J(H,H) = 0.5 Hz, 1 H; CCHC), 7.01–7.08, 7.18–7.30, 7.38–7.44 ppm (m, 9 H; C_6H_4, C_6H_5); ^{13}C NMR (100.6 MHz): $\delta = 24.3$ (CCH_3), 24.5 (CCH_3), 106.0 (CCHC), 123.6, 124.9, 126.6, 128.0 (2 C), 129.1, 130.1, 131.4 (2 C), 135.6, 136.6, 138.9 (C_6H_4, C_6H_5), 171.6 (CN or CO), 172.2 ppm (CN or CO); ^{29}Si NMR (79.5 MHz): $\delta = -92.5$ ppm; ^{13}C VACP/MAS NMR: $\delta = 24.0$ (CCH_3), 27.4 (CCH_3), 109.1 (CCHC), 124.8, 126.4, 127.7, 128.5, 130.1, 134.5, 138.0 (C_6H_4, C_6H_5), 170.2 (CN or CO), 173.0 ppm (CN or CO); ^{15}N VACP/MAS NMR: $\delta = -163.8$ ppm; ^{29}Si VACP/MAS NMR: $\delta = -91$ ppm (br);[13] elemental analysis (%) calcd for $C_{17}H_{16}INOSSi$ ($M_r = 437.37$): C 46.68, H 3.69, N 3.20, S 7.33; found: C 46.3, H 3.8, N 3.2, S 7.3.

3: Trimethyl(trifluoromethanesulfonato)silane (283 mg, 1.27 mmol) was added at 20 °C to a stirred solution of **1** (400 mg, 1.16 mmol) in dichloromethane (18 mL), and the resulting solution was kept undisturbed at 20 °C for 20 h and then at −20 °C for a further 24 h. The yellow crystalline product was filtered off, washed with diethyl ether (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h). Yield: 415 mg (903 μmol, 78 %); m.p. > 103 °C (decomp); ^{1}H NMR (400.1 MHz): $\delta = 2.30$ (d, ^4J(H,H) = 0.6 Hz, 3 H; CCH_3), 2.43 (s, 3 H; CCH_3), 5.86 (q, ^4J(H,H) = 0.6 Hz, 1 H; CCHC), 6.98–7.00, 7.09–7.18, 7.33–7.35, 7.39–7.42 ppm (m, 9 H; C_6H_4, C_6H_5); ^{13}C NMR (100.6 MHz): $\delta = 23.7$ (CCH_3), 24.3 (CCH_3), 105.5 (CCHC), 123.7, 125.1, 128.1 (2 C), 128.5, 129.2, 130.8, 131.4, 133.1 (2 C), 135.0, 136.9 (C_6H_4, C_6H_5), 172.4 (CN or CO), 172.7 ppm (CN or CO);[16] ^{19}F NMR (376.5 MHz): $\delta = -78.1$ ppm; ^{29}Si NMR (99.4 MHz): $\delta = -83.7$ ppm; ^{13}C VACP/MAS NMR: $\delta = 23.6$ (2 C, CCH_3), 106.4 (CCHC), 125.4, 129.1, 131.5, 134.1, 134.9, 136.4 (C_6H_4, C_6H_5), 170.9 (CN or CO), 175.2 ppm (CN or CO); ^{15}N VACP/MAS NMR: $\delta = -156.4$ ppm; ^{29}Si VACP/MAS NMR: $\delta = -81.7$ ppm; elemental analysis (%) calcd for $C_{18}H_{16}F_3NO_4S_2Si$ ($M_r = 459.54$): C 47.05, H 3.51, N 3.05, S 13.96; found: C 46.9, H 3.6, N 3.3, S 14.2.

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[1] Selected reviews dealing with higher coordinate silicon compounds: a) R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927–950; b) V. Pestunovich, S. Kirpichenko, M. Voronkov in *The Chemistry of Organic Silicon Compounds*, *Vol. 2*, *Part 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 1447–1537; c) R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221–273; d) M. A. Brook, *Silicon in Organic*, *Organometallic*, *and Polymer Chemistry*, Wiley, New York, **2000**, pp. 97–114; e) D. Kost, I. Kalikhman, *Adv. Organomet. Chem.* **2004**, *50*, 1–106.

[2] Selected recent publications dealing with higher coordinate silicon compounds: a) J. Wagler, D. Gerlach, U. Böhme, G. Roewer, *Organometallics* **2006**, *25*, 2929–2933; b) I. Kalikhman, B. Gostevskii, M. Botoshansky, M. Kaftory, C. A. Tessier, M. J. Panzner, W. J. Youngs, D. Kost, *Organometallics* **2006**, *25*, 1252–1258; c) E. P. A. Couzijn, A. W. Ehlers, M. Schakel, K. Lammertsma, *J. Am. Chem. Soc.* **2006**, *128*, 13634–13639; d) D. Gerlach, E. Brendler, T. Heine, J. Wagler, *Organometallics* **2007**, *26*, 234–240; e) U. Böhme, B. Günther, *Inorg. Chem. Commun.* **2007**, *10*, 482–484; f) Y. Liu, S. A. Steiner III, C. W. Spahn, I. A. Guzei, I. S. Toulokhonova, R. West, *Organometallics* **2007**, *26*, 1306–1307; g) O. Seiler, C. Burschka, T. Fenske, D. Troegel, R. Tacke, *Inorg. Chem.* **2007**, *46*, 5419–5424; h) D. Troegel, C. Burschka, S. Riedel, M. Kaupp, R. Tacke, *Angew. Chem.* **2007**, *119*, 7131–7135; *Angew. Chem. Int. Ed.* **2007**, *46*, 7001–7005.

[3] O. Seiler, M. Büttner, M. Penka, R. Tacke, *Organometallics* **2005**, *24*, 6059–6062, and references therein.

[4] A pentacoordinate compound with an SiClONCH skeleton has been reported; however, the relatively long N→Si bond (2.1182(17) Å) undergoes rapid dissociation/recombination in solution: I. Kalikhman, B. Gostevskii, V. Kingston, S. Krivonos, D. Stalke, B. Walfort, T. Kottke, N. Kocher, D. Kost, *Organometallics* **2004**, *23*, 4828–4835.

[5] Based on solution NMR studies, the existence of 1-iodosilatrane has been claimed; however, the crystal structure and solid-state NMR data have not been reported: M. G. Voronkov, L. P. Petukhov, V. I. Rakhlin, V. P. Baryshok, B. Z. Shterenberg, R. G. Mirskov, V. A. Pestunovich, *Izv. Akad. Nauk SSSR Ser. Khim.* **1981**, 2412; *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1981**, *30*, 1991.

[6] In general, formally higher coordinate silicon(IV) complexes with Si–I bonds are characterized by only weak Si···I interactions in solution and in the solid state, and are therefore best described as compounds consisting of cationic silicon species and iodide anions: a) I. D. Kalikhman, O. B. Bannikova, L. I. Belousova, G. A. Gostevskii, E. Liepins, O. A. Vyazankina, N. S. Vyazankin, V. A. Pestunovich, *Organomet. Chem. USSR* **1988**, *1*, 379–382; b) M. Chauhan, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Organometallics* **1996**, *15*, 4326–4333; c) V. V. Negrebetsky, P. G. Taylor, E. P. Kramarova, S. Y. Bylikin, I. Y. Belavin, A. G. Shipov, A. R. Bassindale, Y. I. Baukov, *J. Organomet. Chem.* **2006**, *691*, 3976–3988.

[7] R. V. Singh, J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 109–131.

[8] Crystal structure analyses of **1**–**3**: Suitable single crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Bruker Nonius KAPPA APEX II (**1**; Goebel-mirror, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) and Stoe IPDS (**2** and **3**; graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). All structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97). For the CH hydrogen atoms, a riding

model was employed. CCDC 645425 (**1**), 645426 (**2**), and 645427 (**3**) 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/data_request/cif. Selected data for **1**: single crystal of dimensions $0.2\times0.2\times0.1$ mm obtained by slow cooling of a solution in acetonitrile from 80 to 20 °C, $C_{17}H_{16}ClNOSSi$, $M_r=345.91$, analysis at 100(2) K, monoclinic, space group $P2_1/c$ (no. 14), $a=10.9156(3)$, $b=8.5881(3)$, $c=17.0088(5)$ Å, $\beta=94.983(2)°$, $V=1588.45(8)$ Å^3, $Z=4$, $\rho_{calcd}=1.446$ g cm^{-3}, $\mu=0.448$ mm^{-1}, $F(000)=720$, $2\theta_{max}=56.58°$, 33421 collected reflections, 3951 unique reflections ($R_{int}=0.0393$), 201 parameters, $S=1.039$, $R_1=0.0244$ ($I>2\sigma(I)$), wR_2(all data) $=0.0672$, max./min. residual electron density $+0.382/-0.288$ e Å^{-3}. Selected data for **2**: single crystal of dimensions $0.5\times0.2\times0.1$ mm obtained directly from the reaction mixture, $C_{17}H_{16}INOSSi$, $M_r=437.36$, analysis at 173(2) K, orthorhombic, space group *Pbca* (no. 61), $a=8.7076(17)$, $b=17.959(4)$, $c=21.697(4)$ Å, $V=3393.1(12)$ Å^3, $Z=8$, $\rho_{calcd}=1.712$ g cm^{-3}, $\mu=2.082$ mm^{-1}, $F(000)=1728$, $2\theta_{max}=56.24°$, 21542 collected reflections, 4089 unique reflections ($R_{int}=0.0473$), 201 parameters, $S=1.026$, $R_1=0.0301$ ($I>2\sigma(I)$), wR_2 (all data) $=0.0691$, max./min. residual electron density $+0.770/-0.544$ e Å^{-3}. Selected data for **3**: single crystal of dimensions $0.5\times0.4\times0.2$ mm obtained by slow cooling of a solution in dichloromethane from 20 to 4 °C, $C_{18}H_{16}F_3NO_4S_2Si$, $M_r=459.53$, analysis at 173(2) K, monoclinic, space group $P2_1/n$ (no. 14), $a=11.669(2)$, $b=12.247(2)$, $c=13.865(3)$ Å, $\beta=102.47(3)°$, $V=1934.7(7)$ Å^3, $Z=4$, $\rho_{calcd}=1.578$ g cm^{-3}, $\mu=0.392$ mm^{-1}, $F(000)=944$, $2\theta_{max}=56.44°$, 14216 collected reflections, 4699 unique reflections ($R_{int}=0.0494$), 264 parameters, $S=1.037$, $R_1=0.0412$ ($I>2\sigma(I)$), wR_2 (all data) $=0.0988$, max./min. residual electron density $+0.539/-0.326$ e Å^{-3}.

[9] NMR studies on **1**–**3**: The solution ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded at 23 °C on a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz) or a Bruker Avance 400 NMR spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{19}F, 376.5 MHz; ^{29}Si, 79.5 MHz). CD_2Cl_2 was used as the solvent. Chemical shifts were determined relative to internal $CDHCl_2$ (^{1}H, $\delta=5.32$ ppm), internal CD_2Cl_2 (^{13}C, $\delta=53.8$ ppm), external $CFCl_3$ (^{19}F, $\delta=0$ ppm), or external TMS (^{29}Si, $\delta=0$ ppm). Assignment of the ^{13}C NMR data was supported by DEPT135 experiments. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter, 7 mm) containing about 300 mg of sample (^{13}C, 100.6 MHz; ^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz; external standard, TMS (^{13}C, ^{29}Si; $\delta=0$ ppm) or glycine (^{15}N, $\delta=-342.0$ ppm); contact time, 1 ms (^{13}C), 3 ms (^{15}N), or 5 ms (^{29}Si); 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s).

[10] U. H. Berlekamp, A. Mix, B. Neumann, H.-G. Stammler, P. Jutzi, *J. Organomet. Chem.* **2003**, *667*, 167–175.

[11] Covalent radii [Å]: C, 0.73; N, 0.70 (0.75); O, 0.66 (0.73); Si, 1.17; S, 1.04; Cl, 0.99; I, 1.33. Data taken from: *Holleman-Wiberg, Lehrbuch der Anorganischen Chemie*, 101st ed., Walter de Gruyter, Berlin, **1995**, p. 136.

[12] a) J. Yang, I. Guzei, J. G. Verkade, *J. Organomet. Chem.* **2002**, *649*, 276–288; b) D. F. Moser, A. Naka, I. A. Guzei, T. Müller, R. West, *J. Am. Chem. Soc.* **2005**, *127*, 14730–14738; c) G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem.* **2005**, *117*, 8096–8099; *Angew. Chem. Int. Ed.* **2005**, *44*, 7884–7887.

[13] Owing to ^{29}Si,X (X = ^{35}Cl, ^{37}Cl) coupling, the resonance signal in the ^{29}Si VACP/MAS NMR spectrum of **1** is broad, with three maxima ($\delta=-82.2$, -83.0, -83.7 ppm) of different intensities. Due to ^{29}Si,^{127}I coupling, the resonance signal in the ^{29}Si VACP/MAS NMR spectrum of **2** is very broad (FWHH ≈ 380 Hz).

[14] Compound **3** was barely soluble or unstable in most common organic solvents. In CD_2Cl_2 the solubility was sufficient for NMR measurements, but many scans were necessary. Because of the sensitivity of **3** in solution, a freshly prepared sample was used for each measurement (^{1}H, ^{13}C, ^{19}F, ^{29}Si).

[15] Due to the poor solubility of **2** in CD_3CN at 23 °C, the NMR experiments were performed at 60 °C.

[16] The signal for the CF_3 moiety could not be detected in the ^{13}C NMR spectrum.

