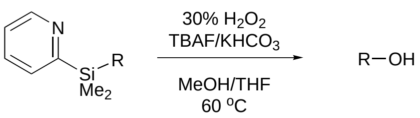
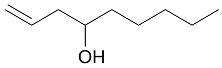
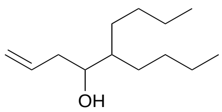
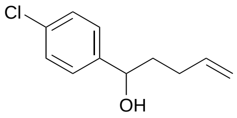
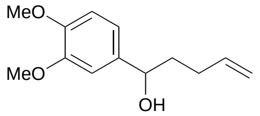
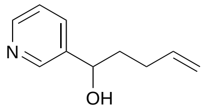
with D_2O; this indicates the reactivity of the resulting α-silyl organomagnesium compound in subsequent reactions.

Having established that intermolecular carbomagnesation across vinylsilane is efficiently directed by a 2-pyridyl group on silicon, we further investigated the three-component coupling reaction of a Grignard reagent, the vinylsilane, and an electrophile (Table 1). Electrophiles such as allyl bromide (entries 1–4) and an iminium salt (entry 5) can be used for the three-component coupling reaction. Interestingly, aryl and heteroaryl halides were also excellent electrophiles when $[Pd(PPh_3)_4]$ was used as catalyst (entries 6–11).[13]

Finally, the three-component coupling adducts were converted into the corresponding alcohols by tetrabutylammonium fluoride (TBAF) mediated H_2O_2 oxidation.[7, 14, 15] Representative results are shown in Table 2. In all cases, oxidation proceeded in good to excellent yields.

Table 2. Oxidation of the coupling products with H_2O_2.[a]



Entry	Coupling adduct	Oxidation product	Yield [%]
1	**2bc**		89
2	**4bc**		89
3	**2dg**		94
4	**2dh**		91
5	**2di**		67

[a] All reactions were performed with 30% H_2O_2 (30 equiv), TBAF (6.0 equiv), and $KHCO_3$ (2.0 equiv) in MeOH/THF (1/1) at 60 °C.

In summary, we have developed a novel strategy for intermolecular carbomagnesation across vinylsilanes by exploiting the $2\text{-PyMe}_2\text{Si}$ group as a removable directing group. By using this protocol, facile addition of primary alkyl Grignard reagents to vinylsilanes was realized for the first time. The extension to other carbometalation processes is currently under investigation.

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[1] For reviews, see a) J. S. Panek in *Comprehensive Organic Synthesis, Vol. 1* (Eds.: B. M. Trost, I. Fleming, S. L. Schreiber), Pergamon, Oxford, **1991**, p. 579; b) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.

[2] a) D. Seyferth, T. Wada, *Inorg. Chem.* **1962**, *1*, 78; b) M. R. Stober, K. W. Michael, J. L. Speier, *J. Org. Chem.* **1967**, *32*, 2740; c) G. R. Buell, R. Corriu, C. Guerin, L. Spialter, *J. Am. Chem. Soc.* **1970**, *92*, 7424; d) K. Tamao, R. Kanatani, M. Kumada, *Tetrahedron Lett.* **1984**, *25*, 1905; e) K. Tamao, T. Iwahara, R. Kanatani, M. Kumada, *Tetrahedron Lett.* **1984**, *25*, 1909; f) K. Tamao, R. Kanatani, M. Kumada, *Tetrahedron Lett.* **1984**, *25*, 1913; g) K. Utimoto, K. Imi, H. Shiragami, S. Fujikura, H. Nozaki, *Tetrahedron Lett.* **1985**, *26*, 2101; h) P. Kocieński, C. Love, D. A. Roberts, *Tetrahedron Lett.* **1989**, *30*, 6753.

[3] Although Buell et al. reported that the addition of primary alkyl Grignard reagents takes place to some extent with ethoxy(vinyl)silanes,[2c] we and others[2d] could not reproduce their results.

[4] Isobe et al. reported that MeMgBr adds to α-silyl-substituted vinylsulfones: A. Herunsalee, M. Isobe, Y. Fukuda, T. Goto, *Synlett* **1990**, 701, and references therein.

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[6] K. Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami, J. Yoshida, *J. Am. Chem. Soc.* **2000**, *122*, 12013.

[7] K. Itami, K. Mitsudo, J. Yoshida, *J. Org. Chem.* **1999**, *64*, 8709.

[8] a) K. Itami, K. Mitsudo, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 5533; b) K. Itami, K. Mitsudo, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 5537; c) K. Itami, T. Nokami, J. Yoshida, *Org. Lett.* **2000**, *2*, 1299.

[9] Because of the ability of $2\text{-PyMe}_2\text{Si}$ group to act as a phase tag,[5] most of the addition products were isolated simply by acid–base extraction.

[10] For a review on CIPE, see: P. Beak, A. I. Meyers, *Acc. Chem. Res.* **1986**, *19*, 356. See also: A. H. Hoveyda, D. A. Evans, G. C. Fu, *Chem. Rev.* **1993**, *93*, 1307.

[11] The same trend was observed for the deprotonation of 2-PySiMe_3 by *t*BuLi.[8a]

[12] Refluxing in Et_2O was required for the addition of PhMgBr.

[13] For metal-catalyzed cross-coupling reactions of α-silyl organomagnesium compounds with aryl and alkenyl halides, see: a) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958; b) K. Tamao, N. Ishida, M. Kumada, *J. Org. Chem.* **1983**, *48*, 2120.

[14] The use of KF instead of TBAF resulted in lower yield of the alcohol.

[15] For reviews on oxidative cleavage of carbon–silicon bonds, see: a) K. Tamao in *Advances in Silicon Chemistry, Vol. 3* (Ed.: G. L. Larson), JAI, Greenwich, **1996**, p. 1; b) I. Fleming, *Chemtracts: Org. Chem.* **1996**, 1; c) G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599.

Pentacoordination of Silicon by Four Covalent Si–S Bonds and One Covalent Si–C Bond**

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Compared to the well-established silicon–oxygen chemistry, significantly less is known about silicon–sulfur chemistry.[1, 2] Except for a preliminary report on two pentacoordinate silicates with SiO_2S_2C skeletons,[3] only tetracoordinate silicon compounds with Si–S bonds have been described. In a series of recent studies, we have realized several hitherto unknown bonding situations of pentacoordinate silicon by

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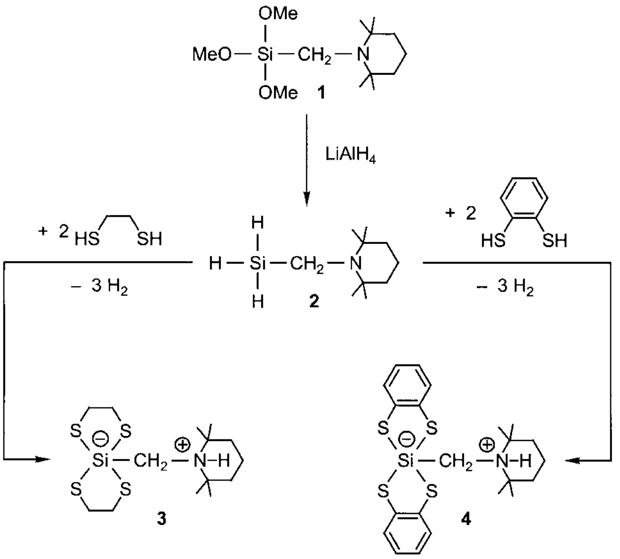
incorporating the pentacoordinate (formally negatively charged) silicon atom in a molecular framework bearing a tetracoordinate (formally positively charged) nitrogen atom, which leads to formation of zwitterionic species.[3] By means of this approach, we have now synthesized the first pentacoordinate silicon compounds with SiS$_4$C frameworks. We report here on the synthesis and structural characterization of the zwitterionic pentacoordinate silicates **3** and **4**.

Compounds **3** and **4** were synthesized from **1**[4] by two-step procedures (Scheme 1). Treatment of the trimethoxysilane **1** with lithium aluminum hydride in diethyl ether gave the trihydridosilane **2** (67% yield), which reacted with 1,2-ethanedithiol or 1,2-benzenedithiol in acetonitrile to give the respective zwitterionic pentacoordinate silicates **3** (83% yield) and **4** (74% yield). Both compounds were isolated as crystalline solids, and their identities were established by elemental analyses (C, H, N), crystal structure analyses, NMR spectroscopic studies in solution (^{1}H, ^{13}C, ^{29}Si; only compound **4**), and solid-state ^{29}Si VACP/MAS NMR experiments.[5, 6]



Scheme 1. Synthesis of the zwitterionic pentacoordinate silicates **3** and **4**.

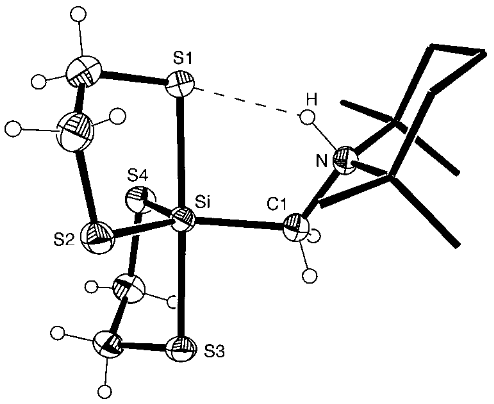


Figure 1. Molecular structure of **3** in the crystal (probability level of displacement ellipsoids 50%; tetramethylpiperidinio moiety represented as stick model for clarity). Selected bond lengths [Å] and angles [°]: Si-S1 2.3366(12), Si-S2 2.1634(14), Si-S3 2.2915(12), Si-S4 2.1675(13), Si-C1 1.939(4); S1-Si-S2 90.99(5), S1-Si-S3 178.47(6), S1-Si-S4 87.43(4), S1-Si-C1 94.45(10), S2-Si-S3 88.03(5), S2-Si-S4 121.50(6), S2-Si-C1 121.81(12), S3-Si-S4 92.08(5), S3-Si-C1 87.07(10), S4-Si-C1 116.60(12); N-H···S1 hydrogen bond: N-H 0.98(4), H···S1 2.29(4), N···S1 3.080(3) Å, N-H···S1 137(3)°.

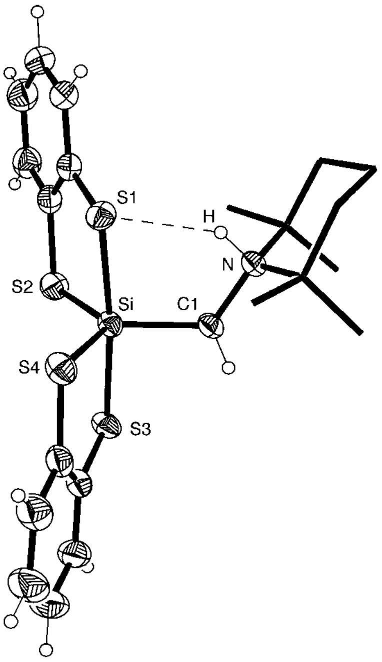


Figure 2. Molecular structure of **4** in the crystal (probability level of displacement ellipsoids 50%; tetramethylpiperidinio moiety represented as stick model for clarity). Selected bond lengths [Å] and angles [°]: Si-S1 2.3280(7), Si-S2 2.1592(9), Si-S3 2.2871(7), Si-S4 2.1588(9), Si-C1 1.929(2); S1-Si-S2 90.84(3), S1-Si-S3 173.89(3), S1-Si-S4 85.36(3), S1-Si-C1 96.54(6), S2-Si-S3 86.19(3), S2-Si-S4 124.92(3), S2-Si-C1 118.48(7), S3-Si-S4 91.96(3), S3-Si-C1 89.58(6), S4-Si-C1 116.54(7); N-H···S1 hydrogen bond: N-H 0.93(3), H···S1 2.30(3), N···S1 3.1017(18) Å, N-H···S1 145(2)°.

The zwitterions crystallize in the space groups $P2_12_12_1$ (**3**) and $P2_1/c$ (**4**) with one molecule each in the asymmetric unit. The Si coordination polyhedra of **3** and **4** in the crystal are slightly distorted trigonal bipyramids with sulfur atoms in the two axial positions (Figures 1 and 2). The equatorial Si–S distances (2.16–2.17 Å) are very similar to those observed for a variety of silicon–sulfur compounds with tetracoordinate silicon atoms and fit with the calculated value for a covalent Si–S single bond (2.17 Å).[1b] The values for the Si–C bonds (1.93–1.94 Å) are in the upper range of the Si–C bond lengths reported so far for zwitterionic pentacoordinate silicates.[3] The axial Si–S distances (2.29–2.34 Å)[7] are 6–8% longer than the equatorial ones, but they are still significantly shorter than the sum of the van der Waals radii of silicon and sulfur (3.90 Å). A similar degree of bond lengthening is observed for other axial and equatorial silicon–element bonds (e.g., Si–O and Si–F) of pentacoordinate silicon compounds with a trigonal-bipyramidal structure.[3] Considering all these structural data, it is concluded that the SiS$_4$C skeletons of **3** and **4** are built up by five covalent bonds and do not involve a bond system in the sense of a [4+1] coordination. This is somewhat surprising in view of the relatively low electronegativity of both carbon and sulfur (Allred–Rochow values: C 2.50, S 2.44). Generally, pentacoordination of silicon is favored by ligand atoms with high electronegativity, such as fluorine, oxygen, and nitrogen atoms.[3, 8] Hence, a theoretical analysis of the bond systems of **3** and **4** is very challenging.

The ^{29}Si chemical shift of **4** ($\delta = -57.2$) in $CDCl_3$ is similar to the isotropic chemical shifts determined by solid-state ^{29}Si VACP/MAS NMR experiments on **3** ($\delta = -53.0$) and **4** ($\delta = -61.0$), and this indicates that **4** also exists in solution.[9] This is further supported by the detection of a signal for the NH group in the ^{1}H NMR spectrum of **4** ($\delta = 7.8$). At room temperature an A_2X spin system was observed for the $SiC(H_A)_2NH_X$ protons of **4**, which indicates that the Λ and Δ enantiomers are not configurationally stable on the NMR time scale. As shown by variable-temperature ^{1}H NMR studies (solvent CD_2Cl_2; temperature range 23 to $-100\,^\circ$C; 300.1 MHz), the Berry-type Λ/Δ enantiomerization becomes slower on cooling, and coalescence was observed at $-95\,^\circ$C. However, the energy barrier for this dynamic process could not be determined, since the expected ABX spin system could not be resolved up to $-100\,^\circ$C.

The surprising stability of the covalent SiS_4C skeletons of **3** and **4** justifies the speculation that further hitherto unknown spirocyclic pentacoordinate silicate frameworks (e.g., SiS_2N_2C and SiN_4C) may also be stable. The hydrogen-elimination route used for the synthesis of **3** and **4** offers a promising approach to the preparation of such compounds.

Experimental Section

2: A solution of **1**[4] (6.00 g, 21.8 mmol) in diethyl ether (20 mL) was added at 0 °C over 1 h to a vigorously stirred suspension of lithium aluminum hydride (1.00 g, 26.3 mmol) in diethyl ether (20 mL). The resulting mixture was stirred at 20 °C for 18 h and then heated under reflux for another 4 h. After filtration, the solvent of the filtrate was removed under reduced pressure, and the crude product distilled in vacuo. Yield: 2.71 g (14.6 mmol, 67 %); b.p. 55 °C/0.1 Torr; ^{1}H NMR (C_6D_6): $\delta = 1.06$ (s, 12 H, CCH_3), 1.42–1.52 (m, 6 H, CCH_2C), 2.12 (q, ^3J(H,H) = 3.4, ^2J(Si,H) = 4.3 Hz, 2 H, $SiCH_2N$), 3.94 (t, ^3J(H,H) = 3.4, ^1J(Si,H) = 191.6 Hz, 3 H, SiH); ^{13}C NMR (C_6D_6): $\delta = 18.1$ (NCC*C*H$_2$C), 25.9 (NC*C*H$_2$C), 27.0 (C*C*H$_3$), 41.4 (Si*C*H$_2$N), 55.2 (N*C*C$_3$); ^{29}Si NMR (C_6D_6): $\delta = -54.2$ (tq, ^1J(Si,H) = 191.6, ^2J(Si,H) = 4.3 Hz); elemental analysis (%) calcd for $C_{10}H_{23}NSi$ ($M_r = 185.4$): C 64.79, H 12.51, N 7.56; found: C 64.4, H 12.4, N 7.7.

3: Compound **2** (504 mg, 2.72 mmol) was added dropwise at 20 °C over 5 min to a stirred solution of 1,2-ethanedithiol (514 mg, 5.46 mmol) in acetonitrile (40 mL). The resulting mixture was stirred at 20 °C for 2 h, the solvent removed in vacuo, and the solid crude product recrystallized from acetonitrile by cooling a saturated solution from 20 to $-20\,^\circ$C to give **3** (834 mg, 83 %) as a colorless crystalline solid. M.p. 116 °C (decomp); ^{29}Si VACP/MAS NMR: $\delta = -53.0$; elemental analysis (%) calcd for $C_{14}H_{29}NS_4Si$ ($M_r = 367.7$): C 45.73, H 7.95, N 3.81; found: C 45.9, H 7.6, N 3.8.

4: The synthesis was carried out analogously to that of **3** (**2**, 935 mg, 5.04 mmol; 1,2-benzenedithiol, 1.44 g, 10.1 mmol; acetonitrile, 20 mL) to give **4** (1.73 g, 74 %) as a colorless crystalline solid. M.p. 173 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 1.21$ (s, 6 H, CCH_3), 1.28 (s, 6 H, CCH_3), 0.91–1.93 (m, 6 H, CCH_2C), 2.92 (d, ^3J(H,H) = 3.6 Hz, 2 H, $SiCH_2N$), 6.76–6.82 and 7.16–7.18 (m, 8 H, $C_6H_4S_2$), 7.8 (br s) NH; ^{13}C NMR ($CDCl_3$): $\delta = 15.9$ (NCC*C*H$_2$C), 21.4 (C*C*H$_3$), 30.0 (C*C*H$_3$), 39.1 (NC*C*H$_2$C), 45.6 (Si*C*H$_2$N), 64.6 (N*C*C$_3$), 124.2 (C4/C5, $C_6H_4S_2$), 126.3 (C3/C6, $C_6H_4S_2$), 139.2 (C1/C2, $C_6H_4S_2$); ^{29}Si NMR ($CDCl_3$): $\delta = -57.2$; ^{29}Si VACP/MAS NMR: $\delta = -61.0$; elemental analysis (%) calcd for $C_{22}H_{29}NS_4Si$ ($M_r = 463.8$): C 56.97, H 6.30, N 3.02; found: C 57.1, H 6.4, N 3.1.

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[1] Reviews on silicon–sulfur chemistry: a) D. A. ('Fred') Armitage in *The Silicon–Heteroatom Bond* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1991**, pp. 213–231; b) H.-G. Horn, *J. Prakt. Chem.* **1992**, *334*, 201–231.

[2] Recent papers on silicon–sulfur chemistry: a) J. Chojnacki, B. Becker, A. Konitz, M. J. Potrzebowski, W. Wojnowski, *J. Chem. Soc. Dalton Trans.* **1999**, 3063–3068; b) U. Herzog, U. Böhme, G. Roewer, G. Rheinwald, H. Lang, *J. Organomet. Chem.* **2000**, *602*, 193–207.

[3] Review on zwitterionic pentacoordinate silicates: R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221–273.

[4] R. Tacke, J. Becht, O. Dannappel, R. Ahlrichs, U. Schneider, W. S. Sheldrick, J. Hahn, F. Kiesgen, *Organometallics* **1996**, *15*, 2060–2077.

[5] Crystal structure analyses of **3** and **4**: 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 (Stoe IPDS; graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The 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. The positions of the NH hydrogen atoms were localized in difference Fourier syntheses and refined freely. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-154812 (**3**) and CCDC-154813 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Selected data for **3**: single crystal of dimensions $0.4 \times 0.4 \times 0.3$ mm obtained by slow cooling of a solution in acetonitrile from 20 to $-20\,^\circ$C, $C_{14}H_{29}NS_4Si$, $M_r = 367.71$, analysis at 173(2) K, orthorhombic, space group $P2_12_12_1$, $a = 9.787(2)$, $b = 11.999(2)$, $c = 15.482(3)$ Å, $V = 1818.1(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.343$ g cm^{-3}, $\mu = 0.580$ mm^{-1}, $F(000) = 792$, $2\theta_{max} = 56.48^\circ$, 10612 collected reflections, 4150 unique reflections ($R_{int} = 0.0342$), 189 parameters, $R_1 = 0.0457$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1238, $S = 1.089$, max./min. residual electron density 0.476/-0.525 e Å^{-3}. Selected data for **4**: single crystal of dimensions $0.3 \times 0.3 \times 0.3$ mm^3 obtained by slow cooling of a solution in acetonitrile from 20 to $-20\,^\circ$C, $C_{22}H_{29}NS_4Si$, $M_r = 463.79$, analysis at 173(2) K, monoclinic, space group $P2_1/c$, $a = 8.8098(18)$, $b = 13.566(3)$, $c = 19.861(4)$ Å, $\beta = 99.60(3)^\circ$, $V = 2340.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.316$ g cm^{-3}, $\mu = 0.466$ mm^{-1}, $F(000) = 984$, $2\theta_{max} = 56.28^\circ$, 14812 collected reflections, 5609 unique reflections ($R_{int} = 0.0400$), 341 parameters, $R_1 = 0.0444$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1250, $S = 1.052$, max./min. residual electron density 0.398/-0.485 e Å^{-3}.

[6] NMR studies on **2**–**4**: The solution ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz). $CDCl_3$ and C_6D_6 were used as solvents. Chemical shifts were determined relative to internal $CHCl_3$ (^{1}H, $\delta = 7.24$, $CDCl_3$), C_6D_5H (^{1}H, $\delta = 7.28$, C_6D_6), $CDCl_3$ (^{13}C, $\delta = 77.0$, $CDCl_3$), C_6D_6 (^{13}C, $\delta = 128.0$, C_6D_6), and external TMS (^{29}Si, $\delta = 0$, $CDCl_3$, C_6D_6). Assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H COSY experiments; assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 7 mm) containing 250 mg (**3**) or 50 mg (**4**) of sample (79.5 MHz; external standard TMS, $\delta = 0$; spinning rate 5 kHz; contact time 5 ms; 90° ^{1}H transmitter pulse length 3.6 µs; repetition time 4 s; number of transients 82 (**3**) or 181 (**4**)).

[7] The axial Si–S1 bonds of **3** and **4** are somewhat longer than the respective axial Si–S3 bonds. This bond lengthening can be explained by the presence of intramolecular N–H ⋯ S1 hydrogen bonds.

[8] Selected reviews on pentacoordinate silicon compounds: 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), Wiley, Chichester, **1989**, pp. 227–303; c) C. Chuit, R. J. P. Corriu, C. Reyé, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448; d) R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927–950; e) D. Kost, I. Kalikhman in *The Chemistry of Organic Silicon Compounds, Vol. 2*, Part 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 1339–1445.

[9] Attempts to characterize **3** by solution NMR spectroscopy (solvents: $CDCl_3$, CD_2Cl_2, C_6D_6, CD_3CN) failed; the NMR data obtained could not be interpreted adequately.