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Synthesis and Structural Characterization of Novel Neutral Hexacoordinate Silicon(IV) Complexes with $SiS_2O_2N_2$ Skeletons

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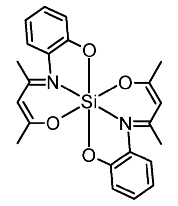
Keywords: Coordination chemistry / Hexacoordination / Silicon / Sulfur / Tridentate ligands

A series of novel hexacoordinate silicon(IV) complexes with two tridentate dianionic S,N,O ligands was synthesized, starting from $Si(NCO)_4$. All the compounds synthesized were structurally characterized by single-crystal X-ray diffraction and/or solid-state NMR spectroscopy. In addition, most of the compounds were characterized by solution NMR spectroscopy.

Introduction

In recent years, a series of novel zwitterionic pentacoordinate silicon compounds with Si–S bonds has been synthesized (compounds with SiS_4C,[1–3] SiS_2O_2C,[3–5] or SiS_2N_2C skeletons[5]) and structurally characterized.[6] These studies have demonstrated that the (soft) sulfur ligand atoms are stably bound to the (hard) silicon coordination center. Compared to the chemistry of pentacoordinate silicon(IV) complexes with Si–S bonds, almost nothing is known about hexacoordinate silicon(IV) complexes with sulfur ligand atoms.[7] As part of our systematic studies on neutral penta- and hexacoordinate silicon compounds (for recent publications, see ref.[8]; in this context, see also refs.[9,10]), we have synthesized the hexacoordinate silicon(IV) complex **1** (SiO_4N_2 skeleton), which contains two tridentate dianionic O,N,O ligands.[8a] A related tridentate dianionic S,N,O ligand has recently been used for the synthesis of the neutral pentacoordinate silicon(IV) complexes **2**–**4**.[8e] In continuation of these studies, we have now succeeded in using this particular tridentate S,N,O ligand (and two structurally related ligands) for the synthesis of the neutral hexacoordinate silicon(IV) complexes **5**, **6**, and **7**·CH_3CN that contain sulfur ligands ($SiS_2O_2N_2$ skeletons). As part of these studies, the tetracoordinate silicon compound **8** was also synthesized.

Compounds **5**, **6**, **7**·CH_3CN, and **8** were structurally characterized in the solid state [single-crystal X-ray diffraction (except for **7**·CH_3CN), VACP/MAS NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si)] and in solution [^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (except for **6**)]. Preliminary results of the studies reported here have already been presented elsewhere.[11]



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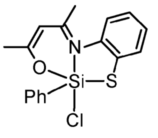

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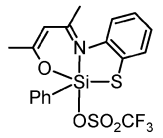

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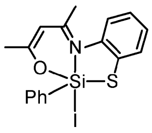

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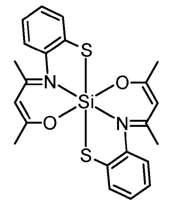

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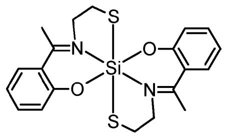

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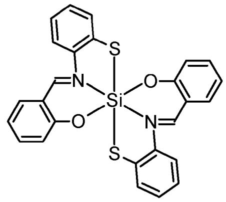

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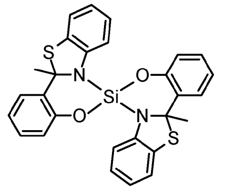

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Results and Discussion

Characterization of the Tridentate S,N,O Ligands

The hexacoordinate silicon(IV) complex **1** was synthesized by treatment of tetra(cyanato-*N*)silane [$Si(NCO)_4$] with two molar equivalents of 4-[(2-hydroxyphenyl)amino]-pent-3-en-2-one.[8a] Literature reports concerning the corresponding sulfur analogue, 4-[(2-mercaptophenyl)amino]-pent-3-en-2-one, and related compounds are rather confusing.[7,12] According to this literature, two isomers (a ring-opened and a ring-closed species) have to be considered for compounds **9**–**12** (the ligands used for the syntheses of **5**–

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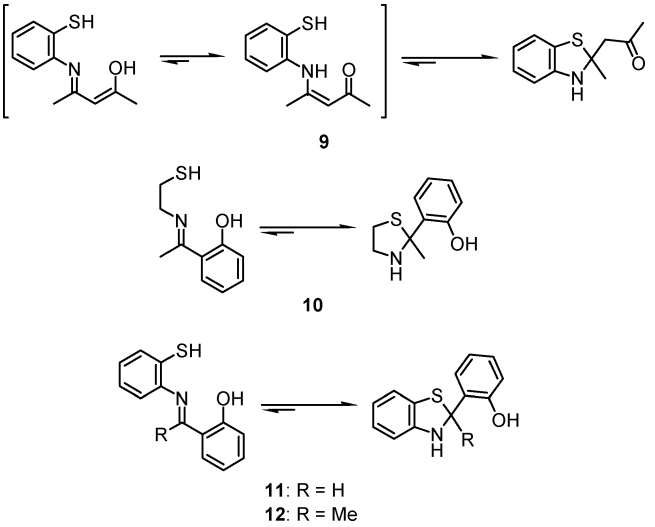
8). To establish the identities of **9**–**12** unequivocally, these compounds were structurally characterized by solid-state (except for **11**)[13] and solution NMR spectroscopy (solvent, CD_3CN). In addition, **9** and **11** were studied by single-crystal X-ray diffraction. According to these studies, compounds **9**, **11**, and **12** exist in the ring-closed form, both in the solid state and in solution. However, the existence of trace amounts of the ring-opened form in solution (i.e., the existence of an equilibrium mixture of the ring-closed and ring-opened form) cannot be totally ruled out (Scheme 1). According to the solid-state NMR spectroscopic studies, compound **10** also exists in the ring-closed form, whereas the solution NMR spectra of **10** show the existence of both the ring-closed and the ring-opened form (ca. 4:1 ratio).[14]

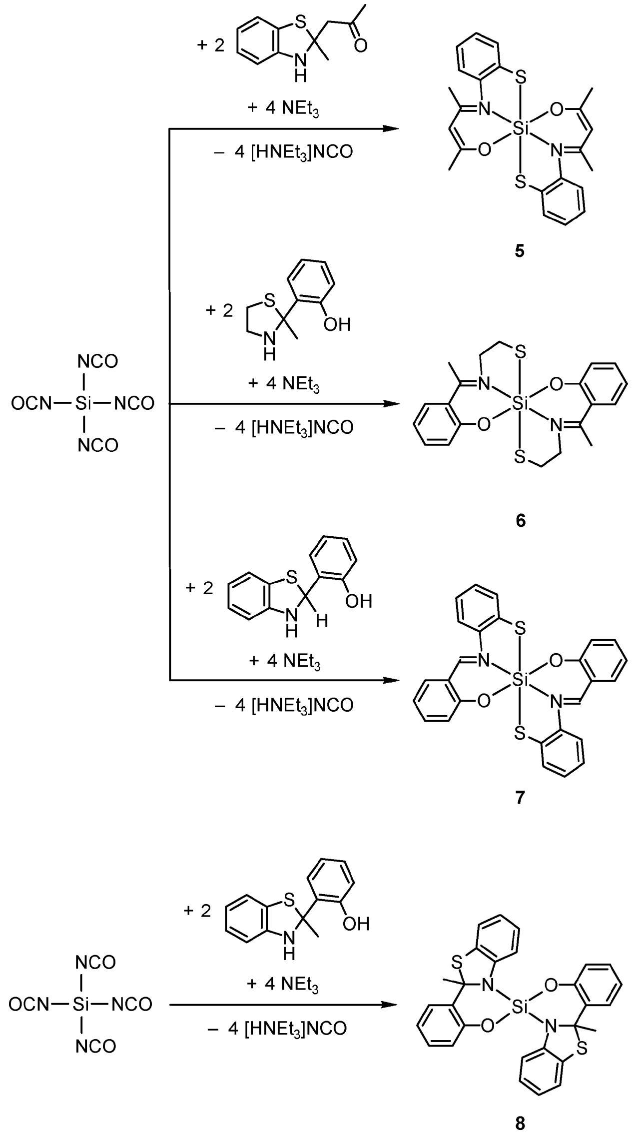


Scheme 1. Ring-opened (left) and ring-closed (right) isomers of **9**–**12**.

Syntheses

Compounds **5**–**8** were synthesized by treatment of $Si(NCO)_4$ with two molar equivalents of the respective tridentate S,N,O ligands, compounds **9**–**12**, and four molar equivalents of triethylamine by using acetonitrile as the solvent (Scheme 2). The crystalline products **5**, **6**, **7**·CH_3CN, and **8** were isolated by filtration, together with the crystalline ammonium salt $[HNEt_3]NCO$, and they were then separated from the latter by dissolving the salt in water.[15] After washing with diethyl ether, compounds **5**, **6**, **7**·CH_3CN, and **8** were obtained as crystalline solids (yields: **5**, 83%; **6**, 82%; **7**·CH_3CN, 82%; **8**, 61%). Compounds **5** (orange), **6** (yellow), and **7**·CH_3CN (dark red, almost black) are intensely colored, whereas **8** is colorless.

The reactions of $Si(NCO)_4$ with **9**–**11** differ totally from the reaction observed for **12**. From a formal point of view, the formation of **5**–**7** can be understood in terms of a reaction of the ring-opened form of **9**–**11**, whereas **8** can be derived from the ring-closed isomer of **12**. However, as is evident from the results described in the section "Characterization of the Tridentate S,N,O Ligands", this would be a superficial interpretation.



Scheme 2. Syntheses of compounds **5**–**8**.

Crystal Structure Analyses

Compounds **5**, **6**, **8**, **9**, and **11** were structurally characterized by single-crystal X-ray diffraction, and their molecular structures in the crystal are shown in Figures 1–5; selected bond lengths and angles are given in the respective figure legends.

The Si-coordination polyhedra of the hexacoordinate silicon(IV) complexes **5** and **6** are best described as distorted octahedra, with a meridional arrangement of the three ligand atoms of each of the two tridentate S,N,O ligands (Figures 1 and 2). The two nitrogen ligand atoms occupy *trans* positions, whereas the two sulfur atoms and the two oxygen atoms are found in *cis* positions to each other. The N–Si–N angles of **5** and **6** are 177.68(10) and 179.72(7)°, respectively, and the S–Si–S and O–Si–O angles are in the range 86.93(6)–89.31(3)°. The maximum deviations of the S–Si–O angles from the ideal 90 and 180° angles amount to 3.36(7) and 5.95(8)°, respectively. The S–Si–N (O–Si–N) angles are in the range 83.67(8)–96.76(7)°

[88.13(9)–90.80(10)°]. The Si–S bond lengths of **5** and **6** are in the range 2.2666(5)–2.2988(9) Å. To the best of our knowledge, these are the first Si–S bond lengths of hexacoordinate silicon compounds determined experimentally. These Si–S distances are longer than the equatorial Si–S bond lengths reported for pentacoordinate silicon compounds with trigonal–bipyramidal coordination polyhedra and similar to the axial ones.[1–5] The Si–O distances [1.7519(10)–1.7650(19) Å] are almost identical with the corresponding Si–O bond lengths observed for compound **1** [1.7593(12) and 1.7763(12) Å].[8a] The Si–N bond lengths of **5** [1.923(2) and 1.904(2) Å] are very similar to those of **1** [1.8966(14) and 1.9024(13) Å][8a] and somewhat shorter than that observed for **6** [1.9525(11) Å].

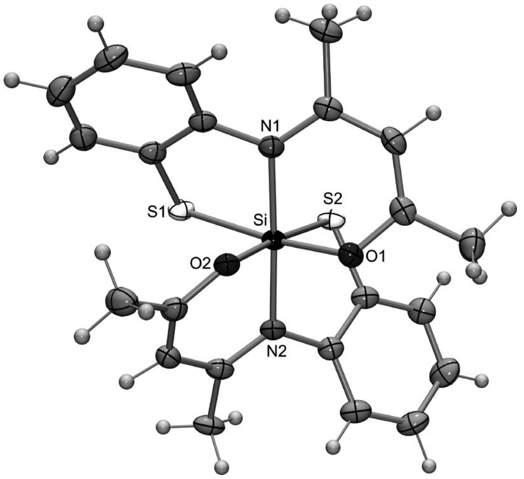


Figure 1. Molecular structure of **5** in the crystal (50% probability level of displacement ellipsoids). Selected bond lengths [Å] and angles [°]: Si–S1 2.2878(10), Si–S2 2.2988(9), Si–O1 1.764(2), Si–O2 1.7650(19), Si–N1 1.923(2), Si–N2 1.904(2); S1–Si–S2 88.07(4), S1–Si–O1 174.05(8), S1–Si–O2 93.36(7), S1–Si–N1 83.67(8), S1–Si–N2 95.00(8), S2–Si–O1 91.16(7), S2–Si–O2 175.03(7), S2–Si–N1 96.76(7), S2–Si–N2 85.08(7), O1–Si–O2 87.91(9), O1–Si–N1 90.57(10), O1–Si–N2 90.80(10), O2–Si–N1 88.13(9), O2–Si–N2 90.05(9), N1–Si–N2 177.68(10).

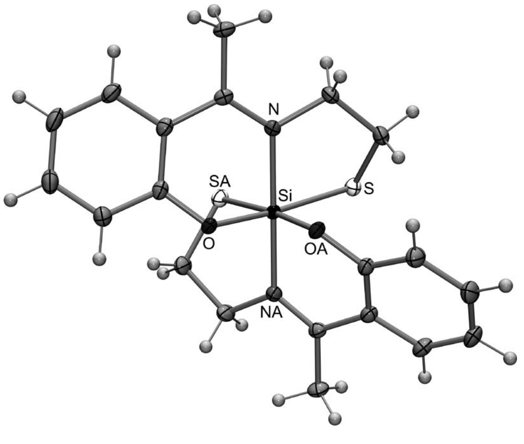


Figure 2. Molecular structure of **6** in the crystal (50% probability level of displacement ellipsoids). Selected bond lengths [Å] and angles [°]: Si–S 2.2666(5), Si–O 1.7519(10), Si–N 1.9525(11); S–Si–SA 89.31(3), S–Si–O 174.84(3), S–Si–OA 92.10(3), S–Si–N 84.83(4), S–Si–NA 95.37(4), O–Si–OA 86.93(6), O–Si–N 90.09(5), O–Si–NA 89.71(5), N–Si–NA 179.72(7).

The Si-coordination polyhedron of the tetracoordinate silicon compound **8** is a distorted tetrahedron with X–Si–X angles (X = O, N) in the range 103.13(5)–117.05(6)° (Figure 3).[16] The Si–O [1.6287(10) and 1.6337(10) Å] and Si–N bond lengths [1.6989(12) and 1.7015(11) Å] are in the typical range observed for tetracoordinate silicon compounds.

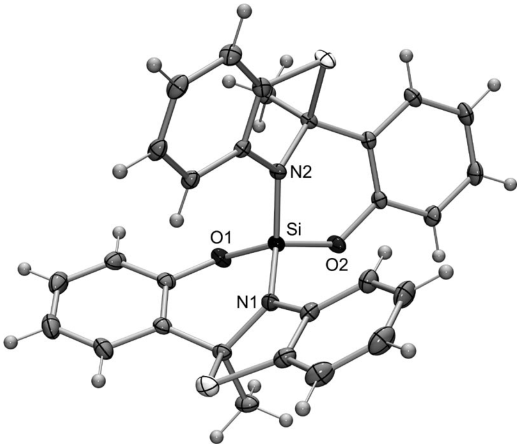


Figure 3. Molecular structure of **8** (site occupancy ca. 90%)[16] in the crystal (50% probability level of displacement ellipsoids). Selected bond lengths [Å] and angles [°]: Si–O1 1.6287(10), Si–O2 1.6337(10), Si–N1 1.7015(11), Si–N2 1.6989(12); O1–Si–O2 104.98(6), O1–Si–N1 103.17(5), O1–Si–N2 116.15(6), O2–Si–N1 117.05(6), O2–Si–N2 103.13(5), N1–Si–N2 112.65(6).

The crystal structures of **9** and **11** clearly demonstrate the existence of the ring-closed isomers (Figures 4 and 5). The molecular structures of these compounds do not need any further discussion.

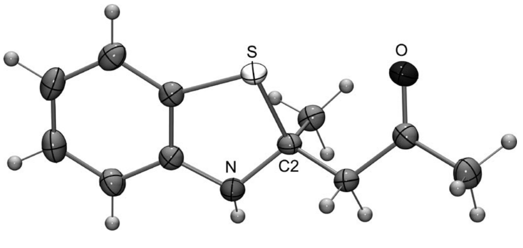


Figure 4. Molecular structure of **9** in the crystal (50% probability level of displacement ellipsoids).

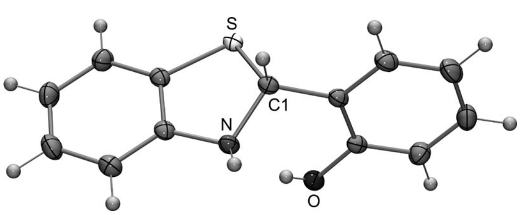


Figure 5. Molecular structure of **11** in the crystal (50% probability level of displacement ellipsoids).

NMR Spectroscopic Studies

Compounds **5**, **6**, **7**·CH_3CN, and **8** were studied by solid-state NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si). The isotropic ^{29}Si

chemical shifts obtained from the VACP/MAS NMR studies of **5**, **6**, and **7**·CH_3CN ($SiS_2O_2N_2$ skeletons) are similar to that of **1**·1/2CH_3CN (SiO_4N_2 skeleton) (**1**·1/2CH_3CN, δ = –165.6 ppm;[8a] **5**, δ = –156.9 ppm; **6**, δ = –172.6 ppm; **7**·CH_3CN, δ = –165 and –169 ppm; Figure 6) and support the existence of hexacoordinate silicon atoms. The ^{29}Si VACP/MAS NMR spectrum of **7**·CH_3CN shows two different resonance signals, which can be explained by a whole-molecule disorder in the crystal. Integration of the two resonance signals gives a ratio of ca. 3:1, which fits with the occupancy ratio observed in the crystal structure analysis of **7**·CH_3CN.[17] The ^{29}Si VACP/MAS NMR spectrum of **8** shows a resonance signal at δ = –71.1 ppm and a second small resonance signal at δ = –73.3 ppm (Figure 6), which is in accordance with the whole-molecule disorder observed in the crystal structure analysis of **8**.[16]

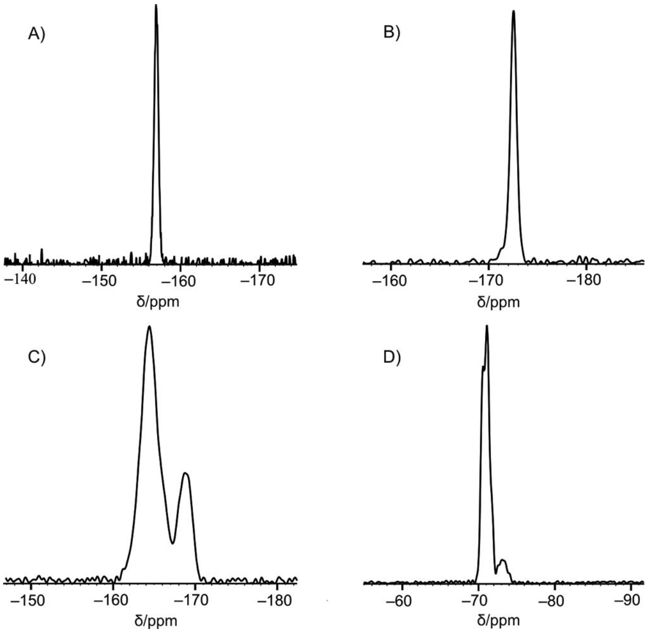


Figure 6. Solid-state ^{29}Si VACP/MAS NMR spectra of **5** (A), **6** (B), **7**·CH_3CN (C), and **8** (D).

Compounds **5**, **7**·CH_3CN, and **8** were also studied by solution NMR spectroscopy (^1H, ^{13}C, ^{29}Si; 296 K), whereas the poor solubility of **6** did not allow such studies. The ^{29}Si chemical shifts of **5** (δ = –157 ppm, $CDCl_3$), **7** (δ = –162.1 ppm, CD_2Cl_2), and **8** (δ = –72.3 ppm, CD_2Cl_2) are very similar to the isotropic ^{29}Si chemical shifts obtained in the solid state, indicating that these hexacoordinate silicon(IV) complexes exist in solution as well. This is further supported by the ^1H and ^{13}C NMR spectroscopic data of these compounds (see Experimental Section).

Whereas the solution ^{29}Si NMR spectrum of **7** shows only one sharp resonance signal at 296 K (δ = –162.1 ppm, CD_2Cl_2), a broad signal was observed for **5** (δ = –157 ppm, $CDCl_3$). High-temperature (353 K) ^{29}Si NMR experiments with solutions of **5** in $C_2D_2Cl_4$ revealed a sharp resonance signal at δ = –156.9 ppm, whereas low-temperature (213 K) experiments resulted in two signals at δ = –155.0 and –158.1 ppm (solvent, CD_2Cl_2). Similar results were obtained in VT ^1H NMR experiments (Figure 7), indicating the presence of two different species at lower temperatures, which undergo a reversible conversion. The nature of these species is unclear, but one could speculate about the presence of two isomers: one with a *mer* coordination of the two tridentate ligands as found in the solid state and one with a *fac* coordination of the two tridentate ligands.[18]

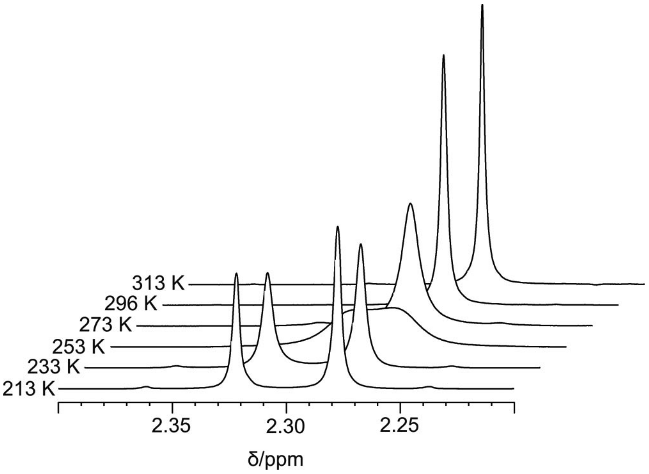


Figure 7. Partial VT ^1H NMR spectra of **5** in CD_2Cl_2 (213, 233, 253, and 273 K) and $C_2D_2Cl_4$ (296 and 313 K), respectively.

Conclusions

Strongly electronegative, small (hard) ligand atoms (e.g., F, O, N, C, Cl) are generally regarded to be ideal candidates to realize higher-coordination of the (hard) silicon coordination center. However, as demonstrated in a series of recent papers, pentacoordinate silicon(IV) complexes with (soft) sulfur ligand atoms can also be synthesized.[1–5] With the synthesis of compounds **5**, **6**, and **7**·CH_3CN ($SiS_2O_2N_2$ skeletons), we now could demonstrate that silicon can also form stable hexacoordinate silicon(IV) complexes with sulfur ligand atoms. These compounds were found to be stable in the solid state and in solution and could be structurally characterized by single-crystal X-ray diffraction and NMR spectroscopy. On the basis of these studies, we are currently attempting to synthesize further hexacoordinate silicon(IV) complexes that contain soft ligand atoms, such as sulfur and selenium. This would offer a significant extension of the chemistry of higher-coordinate silicon, which up to now was mainly based on hard ligand atoms.

Experimental Section

General Procedures: All syntheses were carried out under an atmosphere of dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under an atmosphere of nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus by using samples in sealed capillaries. The ^1H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 23 °C with a Bruker DRX-300 (^1H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz), a Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz), or a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz) by using $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$, or CD_3CN as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ = 7.24 ppm; $CDCl_3$), $CHDCl_2$ (^{1}H, δ = 5.32 ppm; CD_2Cl_2), C_2HDCl_4 (^{1}H, δ = 5.91 ppm; $C_2D_2Cl_4$), CHD_2CN (H, δ = 1.93 ppm; CD_3CN), $CDCl_3$ (^{13}C, δ = 77.0 ppm; $CDCl_3$), CD_2Cl_2 (^{13}C, δ = 53.8 ppm; CD_2Cl_2), $C_2D_2Cl_4$ (^{13}C, δ = 74.2 ppm; $C_2D_2Cl_4$), CD_3CN (^{13}C, δ = 1.3 ppm; CD_3CN), external formamide (^{15}N, δ = –268.0 ppm; CD_3CN), or external TMS (^{29}Si, δ = 0 ppm; $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$). Assignment of the ^{13}C NMR spectroscopic data was supported by DEPT 135 experiments and ^{13}C,^{1}H correlation experiments. The ^{15}N,^{1}H correlation experiments were recorded at 23 °C with a Bruker DRX-300 NMR spectrometer by using CD_3CN as the solvent. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C with a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter, 7 mm) containing ca. 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; δ = 0 ppm) or glycine (^{15}N, δ = –342.0 ppm); spinning rate, 5–6 kHz; 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]. The precursor $Si(NCO)_4$ was synthesized according to ref.[19], and compounds **9**–**12** were synthesized according to ref.[7]

Silicon(IV) Complex 5: Tetra(cyanato-*N*)silane (284 mg, 1.45 mmol) was added in a single portion at 20 °C to a stirred solution of **9** (600 mg, 2.89 mmol) and triethylamine (586 mg, 5.79 mmol) in acetonitrile (40 mL), and the reaction mixture was then kept undisturbed at 20 °C for 3 d. The resulting precipitate was isolated by filtration, washed sequentially with diethyl ether (10 mL), water (15 mL), and again diethyl ether (15 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **5** in 83% yield (525 mg, 1.20 mmol) as an orange crystalline solid. M.p. >185 °C (decomp.). ^{1}H NMR (300.1 MHz, $CDCl_3$, 296 K): δ = 1.5 (br. s, 6 H, CH_3), 2.31 (s, 6 H, CH_3), 5.71 (s, 2 H, CCHC), 6.82–6.97 and 7.18–7.23 (m, 8 H, SC_6H_4N) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 296 K): δ = 24.58 (CH_3), 24.64 (CH_3), 105.4 (C*C*HC), 122.5, 123.0, 127.0, 129.8, 140.7, and 141.5 (SC_6H_4N), 169.7 (CO or CN), 178.7 (CO or CN) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 296 K): δ = –157 (br., poor signal-to-noise ratio, 3072 signal accumulations) ppm. ^{1}H NMR (400.1 MHz, $C_2D_2Cl_4$, 353 K): δ = 1.58 (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3), 5.65 (s, 2 H, CCHC), 6.87–6.95 and 7.16–7.18 (m, 8 H, SC_6H_4N) ppm. ^{13}C NMR (100.6 MHz, $C_2D_2Cl_4$, 353 K): δ = 24.00 (CH_3), 24.04 (CH_3), 104.7 (C*C*HC), 122.2, 122.9, 126.6, 129.5, 140.6, and 141.7 (SC_6H_4N), 169.5 (CO or CN), 178.8 (CO or CN) ppm. ^{29}Si NMR (79.5 MHz, $C_2D_2Cl_4$, 353 K): δ = –156.0 ppm. ^{1}H NMR (500.1 MHz, CD_2Cl_2, 213 K, *Isomer 1*): δ = 1.34 (s, 6 H, CH_3), 2.32 (s, 6 H, CH_3), 5.83 (s, 2 H, CCHC), 6.91–7.02 and 7.18–7.20 (m, 8 H, SC_6H_4N) ppm. ^{1}H NMR (500.1 MHz, CD_2Cl_2, 213 K, *Isomer 2*): δ = 1.97 (s, 6 H, CH_3), 2.28 (s, 6 H, CH_3), 5.61 (s, 2 H, CCHC), 6.91–7.02 (m, 8 H, SC_6H_4N) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 213 K, *Isomer 1*): δ = 23.3 (CH_3), 23.8 (CH_3), 104.4 (C*C*HC), 122.1, 122.3, 126.3, 128.9, 138.1, and 140.8 (SC_6H_4N), 171.4 (CO or CN), 178.3 (CO or CN) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 213 K, *Isomer 2*): δ = 24.1 (CH_3), 24.3 (CH_3), 103.8 (C*C*HC), 122.0, 123.3, 126.5, 128.4, 140.2, and 140.3 (SC_6H_4N), 169.2 (CO or CN), 177.4 (CO or CN) ppm. ^{29}Si NMR (99.4 MHz, CD_2Cl_2, 213 K): δ = –158.1 (*Isomer 2*), –155.0 (*Isomer 1*) ppm. ^{13}C VACP/MAS NMR: δ = 25.4 (3 C, CH_3), 26.7 (CH_3), 104.2 (C*C*HC), 123.2, 125.0, 126.3, 129.7, and 141.3 (SC_6H_4N), 170.0 and 171.0 (CO or CN), 176.9 and 178.8 (CO or CN) ppm. ^{15}N VACP/MAS NMR: δ = –169.2, –161.8 ppm. ^{29}Si VACP/MAS NMR: δ = –156.9 ppm. $C_{22}H_{22}N_2O_2S_2Si$ (438.65): calcd. C 60.24, H 5.06, N 6.39, S 14.62; found C 59.9, H 5.0, N 6.4, S 14.4.

Silicon(IV) Complex 6: Tetra(cyanato-*N*)silane (201 mg, 1.02 mmol) was added in a single portion at 20 °C to a stirred solution of **10** (400 mg, 2.05 mmol) and triethylamine (415 mg, 4.10 mmol) in acetonitrile (40 mL), and the reaction mixture was then kept undisturbed at 20 °C for 3 d. The resulting precipitate was isolated by filtration, washed sequentially with diethyl ether (10 mL), water (15 mL), and again diethyl ether (15 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **6** in 82% yield (345 mg, 832 µmol) as a yellow crystalline solid. M.p. >200 °C (decomp.). ^{13}C VACP/MAS NMR: δ = 24.2 (S*C*H$_2$CH$_2$N or CH$_3$), 26.8 (S*C*H$_2$CH$_2$N or CH$_3$), 53.6 (SCH$_2$*C*H$_2$N), 119.2, 120.8, 122.9, 128.9, and 135.4 (OC_6H_4C), 158.2 (CO), 174.0 (CN) ppm. ^{15}N VACP/MAS NMR: δ = –138.0 ppm. ^{29}Si VACP/MAS NMR: δ = –172.6 ppm. $C_{20}H_{22}N_2O_2S_2Si$ (414.62): calcd. C 57.94, H 5.35, N 6.76, S 15.47; found C 57.6, H 5.4, N 7.4, S 15.3.

Silicon(IV) Complex 7·CH_3CN: Tetra(cyanato-*N*)silane (171 mg, 872 µmol) was added in a single portion at 20 °C to a stirred solution of **11** (400 mg, 1.74 mmol) and triethylamine (353 mg, 3.49 mmol) in acetonitrile (25 mL), and the reaction mixture was then kept undisturbed at 20 °C for 2 d. The resulting precipitate was isolated by filtration, washed sequentially with diethyl ether (10 mL), water (15 mL), and again diethyl ether (15 mL), and then dried in vacuo (0.01 mbar, 20 °C, 30 min)[20] to give **7**·CH_3CN in 82% yield (375 mg, 716 µmol) as a dark-red crystalline solid. M.p. >150 °C (decomp.). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 1.97 (s, 3 H, CH_3CN), 6.26–6.29, 6.88–6.92, 7.07–7.12, 7.15–7.22, 7.23–7.28, 7.39–7.42, and 7.50–7.52 (m, 16 H, SC_6H_4N, OC_6H_4C), 8.685–8.694 (m, 2 H, CCHN) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 2.0 (*C*H$_3$CN), 117.6, 119.7, 120.1, 120.5, 123.8, 129.7, 129.8, 133.7, 138.1, 140.3, 141.7, and 162.8 (SC_6H_4N, OC_6H_4C), 162.5 (CN) ppm. ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ = –162.1 ppm. ^{13}C VACP/MAS NMR: δ = 4.0 (*C*H$_3$CN), 118.7, 128.7, 134.6, 137.9, and 140.0 (SC_6H_4N, OC_6H_4C), 162.0 (CO or CN), 162.5 (CO or CN) ppm. ^{15}N VACP/MAS NMR: δ = –148 (br.) ppm. ^{29}Si VACP/MAS NMR: δ = –169 (br.), –165 (br.) ppm. $C_{28}H_{21}N_3O_2S_2Si$ (523.71): calcd. C 64.22, H 4.04, N 8.02, S 12.25; found C 64.2, H 4.0, N 7.8, S 12.5.

Silicon(IV) Complex 8: Tetra(cyanato-*N*)silane (161 mg, 821 µmol) was added in a single portion at 20 °C to a stirred solution of **12** (400 mg, 1.64 mmol) and triethylamine (333 mg, 3.29 mmol) in acetonitrile (35 mL), and the reaction mixture was then kept undisturbed at 20 °C for 2 d. The resulting precipitate was isolated by filtration, washed sequentially with diethyl ether (10 mL), water (15 mL), and again diethyl ether (15 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **8** in 61% yield (257 mg, 503 µmol) as a colorless crystalline solid. M.p. 215 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 2.04 (s, 6 H, CCH_3), 6.43–6.45, 6.58–6.61, 6.63–6.67, 7.11–7.13, 7.16–7.19, and 7.33–7.37 (m, 16 H, SC_6H_4N, OC_6H_4C) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 36.1 (C*C*H$_3$), 81.3 (*C*CH$_3$), 113.2, 120.0, 122.0, 122.2, 123.6, 125.5, 127.7, 128.1, 130.1, 130.6, 142.3, and 149.0 (SC_6H_4N, OC_6H_4C) ppm. ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ = –72.3 ppm. ^{13}C VACP/MAS NMR:[21] δ = 34.8 (C*C*H$_3$), 36.4 (C*C*H$_3$), 81.1 (*C*CH$_3$), 81.7 (*C*CH$_3$), 111.0, 114.4, 119.8, 121.4, 123.9, 124.9, 125.4, 127.1, 128.7, 130.2, 131.3, 133.3, 141.5, and 149.7 (SC_6H_4N, OC_6H_4C) ppm. ^{15}N VACP/MAS NMR: δ = –287.1, –285.4 ppm. ^{29}Si VACP/MAS NMR: δ = –73.3, –71.1 ppm. $C_{28}H_{22}N_2O_2S_2Si$ (510.71): calcd. C 65.83, H 4.34, N 5.49, S 12.56; found C 65.8, H 4.6, N 5.5, S 12.2.

NMR Spectroscopic Data for Compound 9: ^{1}H NMR (300.1 MHz, CD_3CN): δ = 1.67 (s, 3 H, $SCCH_3$), 2.10 [t, ^{4}J(H,H) = 0.4 Hz, 3

H, C(O)CH$_3$], 3.10–3.23 (m, 2 H, CH$_2$), 5.2 (br. s, 1 H, NH), 6.56–6.59, 6.92–6.94, 6.60–6.65, and 6.83–6.89 (m, 4 H, SC$_6$H$_4$N) ppm. ^{13}C NMR (75.5 MHz, CD$_3$CN): δ = 29.5 (SC*C*H$_3$), 31.2 [C(O)*C*H$_3$], 56.2 (CH$_2$), 75.4 (S*C*CH$_3$), 110.5, 120.2, 122.5, 126.2, 126.4, and 146.9 (SC$_6$H$_4$N), 207.7 (CO) ppm. ^{15}N NMR (30.4 MHz, CD$_3$CN): δ = –286.8 ppm. ^{13}C VACP/MAS NMR: δ = 26.7 (CH$_3$), 30.4 (CH$_3$), 57.9 (CH$_2$), 75.6 (S*C*CH$_3$), 110.1, 121.4, 122.7, 124.8, 126.2, and 146.8 (SC$_6$H$_4$N), 209.2 (CO) ppm. ^{15}N VACP/MAS NMR: δ = –275.7 ppm.

NMR Spectroscopic Data for Compound 10: ^{1}H NMR (500.1 MHz, CD$_3$CN, *ring-closed isomer*): δ = 1.82 (s, 3 H, CCH$_3$), 2.70–2.78 and 3.59–3.64 (m, 2 H, SCH$_2$C*H*$_2$N), 2.98–3.02 and 3.06–3.11 (m, 2 H, SC*H*$_2$CH$_2$N), 3.3 (br. s, 1 H, NH), 6.64–6.66, 6.74–6.79, 7.05–7.08, and 7.44–7.46 (m, 4 H, OC$_6$H$_4$C), 11.9 (s, 1 H, OH) ppm. ^{1}H NMR (500.1 MHz, CD$_3$CN, *ring-opened isomer*): δ = 1.75 [t, ^3J(H,H) = 8.1 Hz, 1 H, SH], 2.34 (s, 3 H, CCH$_3$), 2.85–2.89 (m, 2 H, SC*H*$_2$CH$_2$N), 3.73–3.76 [t, ^3J(H,H) = 6.3 Hz, 2 H, SCH$_2$C*H*$_2$N], 6.79–6.84, 7.26–7.29, and 7.61–7.64 (m, 4 H, OC$_6$H$_4$C), 15.9 (s, 1 H, OH) ppm. ^{13}C NMR (125.8 MHz, CD$_3$CN, *ring-closed isomer*): δ = 31.4 (C*C*H$_3$), 36.1 (S*C*H$_2$CH$_2$N), 51.4 (SCH$_2$*C*H$_2$N), 82.0 (*C*CH$_3$), 117.3, 119.7, 129.61, 130.4, 131.0, and 155.7 (OC$_6$H$_4$C) ppm. ^{13}C NMR (125.8 MHz, CD$_3$CN, *ring-opened isomer*): δ = 15.3 (C*C*H$_3$), 25.9 (S*C*H$_2$CH$_2$N), 53.3 (SCH$_2$*C*H$_2$N), 118.1, 118.9, 120.5, 129.56, 133.2, and 164.1 (OC$_6$H$_4$C), 173.9 (CN) ppm. ^{15}N NMR (30.4 MHz, CD$_3$CN, *ring-closed isomer*): δ = –286.8 ppm. ^{15}N NMR (30.4 MHz, CD$_3$CN, *ring-opened isomer*): δ = –105.1 ppm. ^{13}C VACP/MAS NMR: δ = 30.1 (C*C*H$_3$), 36.4 and 37.4 (S*C*H$_2$CH$_2$N), 50.2 (SCH$_2$*C*H$_2$N), 81.4 and 81.7 (*C*CH$_3$), 116.7, 117.3, 119.8, 121.2, 129.2–131.3, and 154.5 (OC$_6$H$_4$C) ppm. ^{15}N VACP/MAS NMR: δ = –291.9 ppm.

NMR Spectroscopic Data for Compound 11: ^{1}H NMR (300.1 MHz, CD$_3$CN): δ = 5.4 (br. s, 1 H, NH), 6.52–6.53 (m, 1 H, SCH), 6.69–6.78, 6.81–6.87, 6.92–6.97, 7.00–7.03, 7.14–7.20, and 7.32–7.35 (m, 8 H, SC$_6$H$_4$N, OC$_6$H$_4$C) ppm. ^{13}C NMR (75.5 MHz, CD$_3$CN): δ = 66.9 (SCH), 111.3, 116.8, 120.8, 121.4, 122.6, 126.4, 127.60, 127.64, 127.9, 130.4, 147.9, and 155.5 (SC$_6$H$_4$N, OC$_6$H$_4$C) ppm. ^{15}N NMR (30.4 MHz, CD$_3$CN): δ = –304.4 ppm.

NMR Spectroscopic Data for Compound 12: ^{1}H NMR (500.1 MHz, CD$_3$CN): δ = 2.02 (s, 3 H, CCH$_3$), 5.58 (s, 1 H, NH), 6.78–6.86, 6.96–6.99, 7.05–7.07, 7.15–7.19, and 7.43–7.45 (m, 8 H, SC$_6$H$_4$N, OC$_6$H$_4$C) ppm. ^{13}C NMR (125.8 MHz, CD$_3$CN): δ = 29.7 (C*C*H$_3$), 79.7 (*C*CH$_3$), 113.3, 117.9, 120.3, 122.5, 122.6, 126.4, 127.8, 129.4, 129.5, 130.5, 145.7, and 156.3 (SC$_6$H$_4$N, OC$_6$H$_4$C) ppm. ^{15}N NMR (30.4 MHz, CD$_3$CN): δ = –289.7 ppm. ^{13}C VACP/MAS NMR: δ = 26.4 (C*C*H$_3$), 78.7 (*C*CH$_3$), 113.0, 117.9, 121.2, 122.2 (2 C), 125.5 (2 C), 129.3 (2 C), 130.4, 143.5, and 157.1 (SC$_6$H$_4$N, OC$_6$H$_4$C) ppm. ^{15}N VACP/MAS NMR: δ = –285.0 ppm.

Crystal Structure Analyses: Suitable single crystals of **5**, **6**, and **8** were isolated directly from the respective reaction mixtures. Com-

Table 1. Crystal data and the experimental parameters used for the crystal structure analyses of compounds **5**, **6**, **8**, **9**, and **11**.

	5	**6**	**8**	**9**	**11**
Empirical formula	$C_{22}H_{22}N_2O_2S_2Si$	$C_{20}H_{22}N_2O_2S_2Si$	$C_{28}H_{22}N_2O_2S_2Si$	$C_{11}H_{13}NOS$	$C_{13}H_{11}NOS$
Formula mass [g mol^{-1}]	438.65	414.62	510.69	207.28	229.29
T [K]	173(2)	193(2)	98(2)	193(2)	173(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group (no.)	$Pna2_1$ (33)	$C2/c$ (15)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a [Å]	19.9256(16)	19.888(3)	12.4285(3)	8.3759(9)	4.7419(9)
b [Å]	7.9114(8)	8.3983(10)	12.1813(3)	12.8110(12)	10.253(2)
c [Å]	13.1653(9)	12.1408(17)	15.9656(4)	10.4581(12)	11.130(2)
α [°]	90	90	90	90	84.39(2)
β [°]	90	114.237(15)	95.5720(10)	111.537(13)	88.17(2)
γ [°]	90	90	90	90	87.73(2)
V [Å^3]	2075.4(3)	1849.1(4)	2405.70(10)	1043.84(19)	537.92(18)
Z	4	4	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.404	1.489	1.410	1.319	1.416
μ [mm^{-1}]	0.336	0.372	0.302	0.275	0.275
F(000)	920	872	1064	440	240
Crystal dimensions [mm]	$0.3\times0.3\times0.2$	$0.5\times0.4\times0.3$	$0.25\times0.20\times0.17$	$0.5\times0.4\times0.3$	$0.5\times0.3\times0.2$
2θ range [°]	5.12–54.78	5.34–55.84	3.98–61.54	6.24–56.20	5.16–56.06
Index ranges	$-25 \le h \le 25$, $-7 \le k \le 10$, $-12 \le l \le 16$	$-26 \le h \le 25$, $-11 \le k \le 11$, $-15 \le l \le 15$	$-17 \le h \le 17$, $-17 \le k \le 17$, $-22 \le l \le 22$	$-10 \le h \le 10$, $-16 \le k \le 15$, $-13 \le l \le 13$	$-6 \le h \le 5$, $-13 \le k \le 13$, $-14 \le l \le 14$
No. of collected reflections	8509	9157	110383	8512	4880
No. of independent reflections	4190	2190	7449	2368	2394
R_{int}	0.0452	0.0396	0.0506	0.0389	0.0502
No. of reflections used	4190	2190	7449	2368	2394
Restraints	1	0	0	0	0
No. of parameters	266	124	326	132	151
S[a]	1.013	1.052	1.036	1.053	1.031
Weight parameters a/b[b]	0.0494/0.0000	0.0471/1.5727	0.0523/1.9261	0.0448/0.3452	0.0749/0.0516
R_1[c] [$I>2\sigma(I)$]	0.0361	0.0310	0.0390	0.0335	0.0415
wR_2[d] (all data)	0.0861	0.0829	0.1088	0.0901	0.1148
Abs. structure parameters	–0.11(7)				
Max./min. residual electron density [e Å^{-3}]	+0.279/–0.240	+0.371/–0.237	+0.844/–1.106	+0.310/–0.292	+0.380/–0.252

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

pounds **9** and **11** were crystallized by slow cooling of a hot solution in ethanol (ca. 60 °C) to 20 °C. The 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 (**5**, **6**, **9**, and **11**: Stoe IPDS, graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å; **8**: Bruker Nonius KAPPA APEX II, Goebel-mirror, Mo-K_α radiation, λ = 0.71073 Å). All structures were solved by direct methods.[22] The non-hydrogen atoms were refined anisotropically.[23] A riding model was employed in the refinement of the C*H* hydrogen atoms. The crystal data and the experimental parameters used for crystal structure analyses of **5**, **6**, **8**, **9**, and **11** are given in Table 1.

CCDC-692978 (for **5**), -692979 (for **6**), -692980 (for **8**), -692981 (for **9**), and -692982 (for **11**) 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.

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[1] R. Tacke, M. Mallak, R. Willeke, *Angew. Chem.* **2001**, *113*, 2401–2403; *Angew. Chem. Int. Ed.* **2001**, *40*, 2339–2341.

[2] R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, R. Tacke, *Organometallics* **2003**, *22*, 4104–4110.

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

[4] R. Willeke, R. Tacke, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1537–1541.

[5] D. Troegel, C. Burschka, S. Riedel, M. Kaupp, R. Tacke, *Angew. Chem.* **2007**, *119*, 7131–7135; *Angew. Chem. Int. Ed.* **2007**, *46*, 7001–7005.

[6] The existence of two anionic pentacoordinate silicon(IV) complexes with SiS$_5$ skeletons in solution has also been claimed; however, their identities have been established only by solution NMR spectroscopic studies: U. Herzog, *Main Group Met. Chem.* **2001**, *24*, 757–759.

[7] The existence of hexacoordinate silicon(IV) complexes with SiS$_2$O$_2$N$_2$ skeletons has been claimed; however, the analytical evidence for this is rather poor, and some of the data reported are questionable: a) R. V. Singh, J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 109–131; b) S. V. Singh, R. V. Singh, *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 947–960.

[8] Recent publications dealing with neutral penta- and hexacoordinate silicon compounds: a) O. Seiler, C. Burschka, S. Metz, M. Penka, R. Tacke, *Chem. Eur. J.* **2005**, *11*, 7379–7386; b) R. Tacke, R. Bertermann, C. Burschka, S. Dragota, *Angew. Chem.* **2005**, *117*, 5426–5429; *Angew. Chem. Int. Ed.* **2005**, *44*, 5292–5295; c) X. Kästele, P. Klüfers, R. Tacke, *Angew. Chem.* **2006**, *118*, 3286–3288; *Angew. Chem. Int. Ed.* **2006**, *45*, 3212–3214; d) O. Seiler, C. Burschka, T. Fenske, D. Troegel, R. Tacke, *Inorg. Chem.* **2007**, *46*, 5419–5424; e) S. Metz, C. Burschka, D. Platte, R. Tacke, *Angew. Chem.* **2007**, *119*, 7136–7139; *Angew. Chem. Int. Ed.* **2007**, *46*, 7006–7009; f) B. Theis, C. Burschka, R. Tacke, *Chem. Eur. J.* **2008**, *14*, 4618–4630; g) G. González-García, J. A. Gutiérrez, S. Cota, S. Metz, R. Bertermann, C. Burschka, R. Tacke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1281–1286; h) R. Haga, C. Burschka, R. Tacke, *Organometallics*, DOI: 10.1021/om800332.

[9] 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* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, vol. 2, part 2, pp. 1447–1537; c) C. Chuit, R. J. P. Corriu, C. Reye in *Chemistry of Hypervalent Compounds* (Ed.: K.-y. Akiba), Wiley-VCH, New York, **1999**, pp. 81–146; d) R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221–273; e) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, **2000**, pp. 97–114; f) R. Tacke, O. Seiler in *Silicon Chemistry: From the Atom to Extended Systems* (Eds.: P. Jutzi, U. Schubert), Wiley-VCH, Weinheim, **2003**, pp. 324–337; g) D. Kost, I. Kalikhman, *Adv. Organomet. Chem.* **2004**, *5*, 1–106.

[10] Selected recent publications dealing with higher-coordinate silicon compounds: a) D. Gerlach, E. Brendler, T. Heine, J. Wagler, *Organometallics* **2007**, *26*, 234–240; b) U. Böhme, B. Günther, *Inorg. Chem. Commun.* **2007**, *10*, 482–484; c) Y. Liu, S. A. Steiner III, C. W. Spahn, I. A. Guzei, I. S. Toulokhonova, R. West, *Organometallics* **2007**, *26*, 1306–1307; d) J. Wagler, *Organometallics* **2007**, *26*, 155–159; e) J. Wagler, D. Gerlach, G. Roewer, *Inorg. Chim. Acta* **2007**, *360*, 1935–1942; f) J. Wagler, A. F. Hill, *Organometallics* **2007**, *26*, 3630–3632; g) M. Spiniello, J. M. White, *Organometallics* **2008**, *27*, 994–999; h) V. V. Negrebetsky, P. G. Taylor, E. P. Kramarova, A. G. Shipov, S. A. Pogozhikh, Y. E. Ovchinnikov, A. A. Korlyukov, A. Bowden, A. R. Bassindale, Y. I. Baukov, *J. Organomet. Chem.* **2008**, *693*, 1309–1320; i) K. Lippe, D. Gerlach, E. Kroke, J. Wagler, *Inorg. Chem. Commun.* **2008**, *11*, 492–496.

[11] S. Metz, C. Burschka, R. Tacke, *The 14th International Symposium on Organosilicon Chemistry/3rd European Organosilicon Days*, Würzburg, Germany, July 31–August 5, **2005**, Book of Abstracts, Abstract P 159, p. 202.

[12] a) E. C. Alyea, A. Malek, P. H. Merrell, *J. Coord. Chem.* **1974**, *4*, 55–63; b) E. C. Alyea, A. Malek, *Can. J. Chem.* **1975**, *53*, 939–944; c) A. Saxena, J. P. Tandon, A. J. Crowe, *Polyhedron* **1985**, *4*, 1085–1089; d) A. Salifoglou, A. Simopoulos, A. Kostikas, R. W. Dunham, M. G. Kanatzidis, D. Coucouvanis, *Inorg. Chem.* **1988**, *27*, 3394–3406; e) S. Sharma, R. K. Sharma, A. K. Rai, Y. Singh, *J. Chem. Res.* **2005**, 457–460; f) P. K. Panchal, M. N. Patel, *Pharm. Chem. J.* **2006**, *40*, 544–548; g) J. Zhang, Y.-J. Lin, G.-X. Jin, *Organometallics* **2007**, *26*, 4042–4047.

[13] VACP/MAS NMR spectroscopic studies of **11** failed.

[14] NMR spectroscopic studies at different temperatures demonstrated the existence of an equilibrium between the two isomers of **10** (ratio ring-closed/ring-opened form: 4:1, 296 K; 1.5:1, 333 K). The increase in the temperature also resulted in a broadening of the ^{1}H NMR signals of both isomers.

[15] As the crystalline products **5**, **6**, **7**·CH$_3$CN, and **8** are insoluble in water, they do not decompose during this separation step.

[16] In the crystal of **8**, the molecule is disordered (occupancy ratio 90%/10%).

[17] Compound **7**·CH$_3$CN was also studied by single-crystal X-ray diffraction (data not given); however, the poor quality of the crystallographic data set obtained does not allow a detailed structure discussion. Nevertheless, the constitution of **7** could be established unequivocally (the Si-coordination polyhedron of **7** is similar to that of **5** and **6**), and a whole-molecule disorder (occupancy ratio 75%/25%) could be detected. All attempts to recrystallize **7** from other solvents (e.g., CH$_2$Cl$_2$ or THF) failed.

[18] Low-temperature ^{1}H and ^{29}Si NMR spectroscopic experiments of **7** (213 K, CD$_2$Cl$_2$) did not give any evidence for the existence of two different species.

[19] R. G. Neville, J. J. McGee in *Inorganic Syntheses* (Ed.: H. F. Holtzclaw Jr,), McGraw-Hill, New York, **1966**, vol. VIII, pp. 23–31.

[20] Drying in vacuo over a longer period of time led to partial loss of the acetonitrile.

[21] The isotropic ^{13}C NMR shifts given are those of the major species.

[22] a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, *Acta Crystalogr. Sect. A* **1990**, *46*, 467–473.

[23] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.

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