# Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 2148

PAPER

# Synthesis and structural characterisation of neutral pentacoordinate silicon(IV) complexes with a tridentate dianionic N,N,S chelate ligand<sup>†</sup>

Claudia Kobelt,<sup>*a*</sup> Christian Burschka,<sup>*a*</sup> Rüdiger Bertermann,<sup>*a*</sup> C. Fonseca Guerra,<sup>*b*</sup> F. Matthias Bickelhaupt<sup>*b*</sup> and Reinhold Tacke<sup>\**a*</sup>

Received 8th July 2011, Accepted 5th October 2011 DOI: 10.1039/c1dt11306b

A series of novel neutral pentacoordinate silicon(IV) complexes with  $SiClSN_2C$ ,  $SiBrSN_2C$ ,  $SiSN_3C$ ,  $SiSON_2C$ ,  $SiS_2N_2C$ ,  $SiSeSN_2C$  and  $SiTeSN_2C$  skeletons (compounds 1–12) was synthesised, starting from PhSiCl<sub>3</sub>, PhSiBr<sub>3</sub>, PhSi(NCO)<sub>3</sub>, MeSiCl<sub>3</sub> or C<sub>6</sub>F<sub>5</sub>SiCl<sub>3</sub>. Compounds 1–12 contain (i) a tridentate dianionic N, N, S chelate ligand (derived from 2-{[(pyridin-2-yl)methyl]amino}benzenethiol), (ii) a phenyl, methyl or pentafluorophenyl group and (iii) a monodentate monoanionic ligand (Cl, Br, NCO, NCS, N<sub>3</sub>, OS(O)<sub>2</sub>CF<sub>3</sub>, OPh, SPh, SePh, TePh). The pentacoordinate silicon(IV) complexes 1–12 were characterised by elemental analyses, NMR spectroscopic studies in the solid state and in solution and crystal structure analyses. These experimental investigations were complemented by computational studies.

# Introduction

Most of the higher-coordinate silicon(IV) complexes reported in the literature contain small, strongly electronegative (hard) ligand atoms, such as fluorine, chlorine, oxygen, nitrogen and/or carbon atoms.<sup>1,2</sup> In a series of more recent studies, however, we have demonstrated that soft chalcogen ligand atoms (sulfur, selenium, tellurium) can also be introduced into the coordination sphere of the hard silicon(IV) coordination centre.<sup>3</sup> In continuation of these studies, we have now succeeded in synthesising the novel neutral pentacoordinate silicon(IV) complexes 1-12 (Scheme 1). These compounds contain (i) a tridentate dianionic N, N, S chelate ligand (derived from 2-{[(pyridin-2-yl)methyl]amino}benzenethiol),4 (ii) a phenyl, methyl or pentafluorophenyl group and (iii) a monodentate monoanionic ligand (Cl, Br, NCO, NCS, N<sub>3</sub>, OS(O)<sub>2</sub>CF<sub>3</sub>, OPh, SPh, SePh, TePh). The silicon(IV) complexes synthesised contain an SiClSN<sub>2</sub>C (1, 7, 12), SiBrSN<sub>2</sub>C (2), SiSN<sub>3</sub>C (3-5),  $SiSON_2C$  (6, 8),  $SiS_2N_2C$  (9),  $SiSeSN_2C$  (10) or  $SiTeSN_2C$  (11) skeleton. To the best of our knowledge, all these coordination skeletons have not yet been described in the literature. We report herein on the synthesis of compounds 1-12 (1-3, 5 and 6 were isolated as hemitoluene solvates) and their characterisation by

R Х Ph CI 1 2 Ph Br 3 Ph NCO NCS 4 Ph 5 Ph  $N_3$ 6 Ph OS(O)<sub>2</sub>CF<sub>3</sub> 7 Me CI 8 Me OPh 9 Me SPh 1–12 10 SePh Me 11 Me TePh 12 C<sub>6</sub>F<sub>5</sub> Cl

Scheme 1 Structural formulas of the neutral pentacoordinate silicon(IV) complexes 1–12 investigated in this study.

elemental analyses, NMR spectroscopic studies in the solid state and in solution and crystal structure analyses. In order to get more information about the structure of these compounds in solution, the experimental investigations were complemented by computational studies. The investigations reported herein were performed as part of our ongoing systematic studies on highercoordinate silicon(IV) compounds, with a special emphasis on the characterisation of the novel silicon coordination polyhedra synthesised.

# Experimental

# **General procedures**

All syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were

<sup>&</sup>lt;sup>a</sup>Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, D-97074, Würzburg, Germany. E-mail: r.tacke@uni-wuerzburg.de; Fax: (+49)931-31-84609; Tel: (+49)931-31-85250

<sup>&</sup>lt;sup>b</sup>Department of Theoretical Chemistry, Amsterdam Center for Multiscale Modeling, VU University, De Boelelaan 1083, NL-1081 HV, Amsterdam, The Netherlands

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Cartesian coordinates and ADF total energies of 7, 7a and 7b in  $CH_2Cl_2$ . CCDC reference numbers 832632–832642 and 845196 for 1–12. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11306b

determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The solution <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>77</sup>Se and <sup>125</sup>Te NMR spectra were recorded at 23 °C on a Bruker DRX-300 (1H, 300.1 MHz; 13C, 75.5 MHz; 29Si, 59.6 MHz) or a Bruker Avance 500 NMR spectrometer (<sup>13</sup>C, 125.8 MHz; <sup>29</sup>Si, 99.4 MHz; <sup>77</sup>Se, 95.4 MHz; <sup>125</sup>Te, 157.8 MHz) using CD<sub>2</sub>Cl<sub>2</sub> or [D<sub>6</sub>]DMSO as the solvent. Chemical shifts (ppm) were determined relative to internal CHDCl<sub>2</sub> (<sup>1</sup>H,  $\delta$  5.32; CD<sub>2</sub>Cl<sub>2</sub>), internal CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C,  $\delta$  53.8; CD<sub>2</sub>Cl<sub>2</sub>), internal [D<sub>5</sub>]DMSO (<sup>1</sup>H,  $\delta$  2.49; [D<sub>6</sub>]DMSO), internal [D<sub>6</sub>]DMSO (<sup>13</sup>C,  $\delta$  39.5; [D<sub>6</sub>]DMSO), internal C<sub>2</sub>HDCl<sub>4</sub> (<sup>1</sup>H,  $\delta$  5.97; C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>), internal C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (<sup>13</sup>C,  $\delta$  74.2; C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>), external tetramethylsilane (TMS) (<sup>29</sup>Si,  $\delta$  0; CD<sub>2</sub>Cl<sub>2</sub>, [D<sub>6</sub>]DMSO), external Me<sub>2</sub>Se with 5% w/w C<sub>6</sub>D<sub>6</sub> (<sup>77</sup>Se,  $\delta$  0; CD<sub>2</sub>Cl<sub>2</sub>) or external Ph<sub>2</sub>Te<sub>2</sub> (0.1 M in CDCl<sub>3</sub>) (<sup>125</sup>Te,  $\delta$  422.0; CD<sub>2</sub>Cl<sub>2</sub>). Assignment of the <sup>13</sup>C NMR data was supported by DEPT 135 and <sup>1</sup>H,<sup>1</sup>H and <sup>1</sup>H, <sup>13</sup>C correlation experiments. The thermocouple used with the probe for the VT NMR studies was calibrated for higher and lower temperatures according to ref. 5 using an 80% solution of ethane-1,2-diol in [D<sub>6</sub>]DMSO and a 4% solution of MeOH in [D<sub>4</sub>]MeOH containing a trace of HCl, respectively. Solid-state <sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si and <sup>77</sup>Se VACP/MAS NMR spectra and <sup>125</sup>Te{<sup>1</sup>H} HPDec/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom-layer rotors of ZrO<sub>2</sub> (diameter, 7 mm) containing 200-300 mg of sample (13C, 100.6 MHz; 15N, 40.6 MHz; <sup>29</sup>Si, 79.5 MHz; <sup>77</sup>Se, 76.3 MHz; <sup>125</sup>Te, 126.2 MHz; external standard, TMS (<sup>13</sup>C, <sup>29</sup>Si;  $\delta$  0), glycine (<sup>15</sup>N;  $\delta$  –342.0), Me<sub>2</sub>Se (<sup>77</sup>Se;  $\delta$  0) or Te(OH)<sub>6</sub> (<sup>125</sup>Te;  $\delta$  685.5 and 692.2); spinning rate, 6–7 kHz; contact time, 1 ms  $({}^{13}C)$ , 3 ms  $({}^{15}N)$  or 5 ms  $({}^{29}Si$ ,  $^{77}$ Se); 90° <sup>1</sup>H transmitter pulse length, 3.6 µs; repetition time, 4–5 s).

#### Syntheses

Pentacoordinate silicon(IV) complex 1.0.5C7H8. Trichlorophenylsilane (4.87 g, 23.0 mmol) was added dropwise at 20 °C within 2 min to a stirred solution of 14 (5.00 g, 23.1 mmol) and triethylamine (4.87 g, 48.1 mmol) in tetrahydrofuran (200 ml), and the reaction mixture was stirred at 20 °C for 2.5 h. The resulting precipitate was filtered off, washed with tetrahydrofuran (10 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, followed by the addition of toluene (160 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with diethyl ether  $(2 \times 5 \text{ ml})$  and dried *in vacuo*  $(40 \degree \text{C}, 6 \text{ h}, 0.01 \text{ mbar})$ . Yield: 4.97 g (12.4 mmol, 54%). Mp: 211 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.35 (s, 1.5 H, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 4.84 and 4.89 (AB system,  ${}^{2}J({}^{1}H, {}^{1}H) = 18.1 \text{ Hz}, 2 \text{ H}, \text{ NC}H_{2}C), 6.64-6.70, 6.74-6.86, 6.97-$ 7.10, 7.12-7.31, 7.34-7.46, 7.60-7.66, 7.96-8.03 and 8.38-8.42 (m, 15.5 H,  $C_6H_4$ ,  $C_6H_5$ ,  $NC_5H_4$ ,  $C_6H_5CH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>; the resonance signals marked with an asterisk refer to the toluene molecule):  $\delta 21.5^*$  (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.7 (NCH<sub>2</sub>C), 111.4, 120.1, 122.4, 123.6, 124.4, 125.6\*, 125.9, 126.1, 128.3 (2 C), 128.5\* (2 C), 128.6, 129.3\* (2 C), 130.8 (2 C), 131.1, 138.3\*, 141.5, 142.5, 144.8 and 153.4 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5CH_3$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –70.9. <sup>13</sup>C VACP/MAS NMR:  $\delta$ 22.0 (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.1–51.0 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 112.8, 116.5, 119.0, 120.6-124.0 (m, 5 C), 122.8, 125.3, 127.0, 129.1 (2 C), 131.4 (2 C), 134.3, 134.7, 141.3, 143.2 (2 C), 145.5, 151.4 and

152.4 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5CH_3$ ). <sup>15</sup>N VACP/MAS NMR: δ –297.5 (NCH<sub>2</sub>C), –125.9 (NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR: δ –76 (br.). Anal. Calcd for C<sub>21.5</sub>H<sub>19</sub>ClN<sub>2</sub>SSi (401.01): C, 64.40; H, 4.78; N, 6.99; S, 8.00. Found: C, 64.1; H, 4.8; N, 7.0; S, 8.0.

Pentacoordinate silicon(IV) complex 2.0.5C<sub>7</sub>H<sub>8</sub>. Tribromophenylsilane (1.45 g, 4.20 mmol) was added dropwise at 20 °C within 1 min to a stirred solution of 14 (900 mg, 4.16 mmol) and triethylamine (850 mg, 8.40 mmol) in toluene (60 ml), and the reaction mixture was stirred at 20 °C for 1.5 h. The resulting precipitate was filtered off, washed with toluene  $(2 \times 10 \text{ ml})$ and discarded. The solvent of the filtrate (including the wash solutions) was removed in vacuo, followed by the addition of toluene (15 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20  $^{\circ}\mathrm{C}$ and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with diethyl ether  $(2 \times 5 \text{ ml})$  and dried *in vacuo*  $(40 \text{ }^{\circ}\text{C}, 5 \text{ h}, 0.01 \text{ mbar})$ . Yield: 1.18 g (2.65 mmol, 64%). Mp: 188 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.35 (s, 1.5 H, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 4.88 and 4.92  $(AB \text{ system}, {}^{2}J({}^{1}H, {}^{1}H) = 18.2 \text{ Hz}, 2 \text{ H}, \text{NC}H_{2}C), 6.71-6.88, 6.97-$ 7.07, 7.11-7.21, 7.22-7.31, 7.36-7.49, 7.61-7.69, 7.95-8.04 and 8.39–8.47 (m, 15.5 H,  $C_6H_4$ ,  $C_6H_5$ ,  $NC_5H_4$ ,  $C_6H_5CH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>; the resonance signals marked with an asterisk refer to the toluene molecule):  $\delta$  21.5\* (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.5 (NCH<sub>2</sub>C), 111.6, 120.2, 122.4, 123.7, 124.3, 125.6\*, 125.9, 128.2 (2 C), 128.5\* (2 C), 128.7, 129.3\* (2 C), 131.0 (2 C), 131.5, 138.3\*, 141.6, 142.5, 144.9, 145.6 and 153.1 (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub>H<sub>4</sub>,  $C_6H_5CH_3$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -79.1. <sup>13</sup>C VACP/MAS NMR:  $\delta$  23.4 (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.7–51.6 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 113.4, 117.3, 119.3, 121.2–124.6 (m, 4 C), 125.5 (2 C), 127.1, 129.5 (3 C), 130.5, 132.3 (3 C), 135.2, 142.2, 143.5 (2 C), 145.5 and 152.6 (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>). <sup>15</sup>N VACP/MAS NMR: δ-296.8 (NCH<sub>2</sub>C), -125.0 (NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  –84 (br.). Anal. Calcd for C<sub>21.5</sub>H<sub>19</sub>BrN<sub>2</sub>SSi (445.46): C, 57.97; H, 4.30; N, 6.29; S, 7.20. Found: C, 58.1; H, 4.5; N, 6.3; S, 7.3.

Pentacoordinate silicon(IV) complex 3.0.5C<sub>7</sub>H<sub>8</sub>. Tri(cyanato-N)phenylsilane (1.10 g, 4.76 mmol) was added dropwise at 20 °C within 2 min to a stirred solution of 14 (1.03 g, 4.76 mmol) and triethylamine (963 mg, 9.52 mmol) in toluene (60 ml), and the reaction mixture was stirred at 20 °C for 3 h. The resulting precipitate was filtered off, washed with toluene  $(2 \times 10 \text{ ml})$ and discarded. The solvent of the filtrate (including the wash solutions) was removed in vacuo, followed by the addition of toluene (20 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with diethyl ether (2 × 5 ml) and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 1.12 g (2.75 mmol, 58%). Mp: 183 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.36 (s, 1.5 H, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 4.81 and 4.86 (AB system,  ${}^{2}J({}^{1}H, {}^{1}H) = 18.0$  Hz, 2 H, NCH<sub>2</sub>C), 6.73–6.84, 7.00– 7.06, 7.12-7.22, 7.22-7.30, 7.31-7.45, 7.62-7.68, 7.97-8.04 and 8.29–8.34 (m, 15.5 H,  $C_6H_4$ ,  $C_6H_5$ ,  $NC_5H_4$ ,  $C_6H_5CH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>; the resonance signals marked with an asterisk refer to the toluene molecule):  $\delta$  21.5\* (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.8 (NCH<sub>2</sub>C), 111.2, 120.0, 122.5, 123.5, 124.6, 125.6\*, 126.0, 126.5, 128.3 (2 C), 128.5, 128.6\* (2 C), 129.3\* (2 C), 130.5 (2 C), 138.2\*, 141.4, 143.1, 144.0, 144.4 and 153.7 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5$ CH<sub>3</sub>, NCO). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –87.9. <sup>13</sup>C VACP/MAS NMR:  $\delta$  21.9 ( $C_6H_5CH_3$ ), 45.3–48.8 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 110.3, 111.5, 118.7, 119.2, 120.2, 121.2, 121.4, 123.0 (3 C), 124.2, 124.5, 125.2, 127.9, 128.9, 129.7 (2 C), 136.0, 139.0, 141.2, 142.3 (2 C), 143.9 and 152.8 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5CH_3$ , NCO). <sup>15</sup>N VACP/MAS NMR:  $\delta$  –300.4 (NCH<sub>2</sub>C), -178.4 (NCO), -126.1 (N $C_5H_4$ ). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  –89 (br.). Anal. Calcd for C<sub>22.5</sub>H<sub>19</sub>N<sub>3</sub>OSSi (407.57): C, 66.31; H, 4.70; N, 10.31; S, 7.87. Found: C, 66.1; H, 4.7; N, 10.3; S, 7.6.

Pentacoordinate silicon(IV) complex 4. Trimethyl(thiocyanato-N)silane (262 mg, 2.00 mmol) was added at 20 °C in a single portion to a stirred solution of 1.0.5C<sub>7</sub>H<sub>8</sub> (800 mg, 1.99 mmol) in acetonitrile (20 ml), and the reaction mixture was stirred at 20 °C for 2 h. The volatile components were removed in vacuo, and acetonitrile (20 ml) was added to the residue. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with *n*-pentane (5 ml) and dried in vacuo (20 °C, 4 h, 0.01 mbar). Yield: 670 mg (1.77 mmol, 89%). Mp: 236 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ4.79 and 4.87 (AB system,  ${}^{2}J({}^{1}H, {}^{1}H) = 18.1 \text{ Hz}, 2 \text{ H}, \text{ NC}H_{2}C), 6.58-6.85, 6.92-7.08,$ 7.18-7.29, 7.29-7.37, 7.42-7.55, 7.66-7.73, 7.98-8.09 and 8.29-8.35 (m, 13 H,  $C_6H_4$ ,  $C_6H_5$ ,  $NC_5H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 48.8 (NCH<sub>2</sub>C), 111.4, 120.3, 122.8, 123.8, 125.0, 126.5, 128.4 (2 C), 128.9, 129.7, 130.3, 130.8 (2 C), 141.8, 142.5, 143.3, 143.8 and 153.8 ( $C_6H_4$ ,  $C_6H_5$ ,  $NC_5H_4$ , NCS). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ-89.3. <sup>13</sup>C VACP/MAS NMR: δ43.8-46.5 (m (<sup>13</sup>C,<sup>14</sup>N coupling), NCH<sub>2</sub>C), 47.1–49.4 (m (<sup>13</sup>C,<sup>14</sup>N coupling), NCH<sub>2</sub>C), 110.9, 112.3, 120.9 (2 C), 121.6, 122.1, 123.0, 124.8 (3 C), 125.5 (2 C), 127.4, 128.2 (3 C), 128.7–130.3 (m, 6 C), 130.8 (2 C), 133.9, 138.8, 139.6, 140.3, 140.7–142.4 (4 C), 143.1, 143.9, 150.4 and 152.3 (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub>H<sub>4</sub>, NCS). <sup>15</sup>N VACP/MAS NMR: δ -304.0 (NCH<sub>2</sub>C), -302.8 (NCH<sub>2</sub>C), -135.0 (NC<sub>5</sub>H<sub>4</sub>), -123.1 ( $NC_5H_4$ ), NCS not detected. <sup>29</sup>Si VACP/MAS NMR:<sup>6</sup>  $\delta$ -90 (br.). Anal. Calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub>Si (377.57): C, 60.44; H, 4.00; N, 11.13; S, 16.99. Found: C, 60.3; H, 4.1; N, 11.1; S, 17.0.

Pentacoordinate silicon(IV) complex 5.0.5C7H8. Azidotrimethylsilane (227 mg, 1.97 mmol) was added at 20 °C in a single portion to a stirred solution of 1.0.5C<sub>7</sub>H<sub>8</sub> (700 mg, 1.75 mmol) in toluene (50 ml), and the reaction mixture was stirred at 20 °C for 2.5 h. The volatile components were removed in vacuo, and toluene (30 ml) was added to the residue. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20  $^{\circ}$ C and kept undisturbed at –20  $^{\circ}$ C for 16 h. The resulting yellow crystalline solid was isolated by filtration, washed with n-pentane (5 ml) and dried in vacuo (20 °C, 5 h, 0.01 mbar). Yield: 354 mg (867 µmol, 50%). Mp: 192 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.35 (s, 1.5 H,  $C_6H_5CH_3$ , 4.79 and 4.87 (AB system,  ${}^2J({}^1H, {}^1H) = 17.9$  Hz, 2 H, NCH<sub>2</sub>C), 6.74–6.85, 7.01–7.08, 7.12–7.29, 7.30–7.42, 7.60–7.66, 7.83-7.95, 8.27-8.33 and 8.39-8.47 (m, 15.5 H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>,  $NC_5H_4$ ,  $C_6H_5CH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz,  $CD_2Cl_2$ ; the resonance signals marked with an asterisk refer to the toluene molecule):  $\delta$  21.5\* (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.8 (NCH<sub>2</sub>C), 111.2, 119.9, 122.4, 123.7, 124.4, 125.6\*, 126.9, 128.3 (2 C), 128.48, 128.51\* (2 C), 129.3\* (2 C), 130.0, 130.1 (2 C), 138.3\*, 141.4, 143.4, 144.5,

145.1 and 153.6 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5$ CH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -81.7. <sup>13</sup>C VACP/MAS NMR: δ 23.7 ( $C_6H_5CH_3$ ), 46.0–49.3 (m (<sup>13</sup>C,<sup>14</sup>N coupling), NCH<sub>2</sub>C), 110.4, 112.0, 119.7, 120.8–124.1 (m, 4 C), 125.7, 126.7, 128.1 (2 C), 129.6 (2 C), 130.8 (2 C), 132.0–135.6 (m, 2 C), 138.8, 139.7, 142.2 (2 C), 147.3 and 152.8 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5$ CH<sub>3</sub>). <sup>15</sup>N VACP/MAS NMR: δ -300.0 (NCH<sub>2</sub>C), -294.2 (SiNNN), -194.8 (SiNNN), -137.8 (SiNNN), -131.5 (N $C_5H_4$ ). <sup>29</sup>Si VACP/MAS NMR: δ -85 (br.). Anal. Calcd for C<sub>21.5</sub>H<sub>19</sub>N<sub>5</sub>SSi (407.57): C, 63.36; H, 4.70; N, 17.18; S, 7.87. Found: C, 63.4; H, 4.7; N, 16.9; S, 8.1.

Pentacoordinate silicon(IV) complex 6.0.5C7H8. Trifluoromethanesulfonatotrimethylsilane (442 mg, 1.99 mmol) was added at 20 °C in a single portion to a stirred solution of 1.0.5C7H8 (800 mg, 1.99 mmol) in acetonitrile (20 ml), and the reaction mixture was stirred at 20 °C for 2 h. The volatile components were removed in vacuo, and toluene (20 ml) was added to the residue. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with n-pentane (5 ml) and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 560 mg (1.09 mmol, 55%). Mp: 137 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.35 (s, 1.5 H, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 4.88 and 4.96 (AB system,  ${}^{2}J({}^{1}H, {}^{1}H) = 20.0 \text{ Hz}, 2 \text{ H}, \text{ NC}H_{2}C), 6.80-6.93, 7.03-7.39, 7.42-$ 7.52, 7.72-7.83 and 8.08-8.21 (m, 15.5 H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub>H<sub>4</sub>,  $C_6H_5CH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz,  $CD_2Cl_2$ ; the resonance signals marked with an asterisk refer to the toluene molecule):  $\delta$ 21.5\* (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 48.5 (NCH<sub>2</sub>C), 111.8, 120.7, 122.9, 124.1, 124.9, 125.6\*, 126.6, 128.5 (2 C), 128.6\* (2 C), 129.3, 129.4\* (2 C), 129.6, 131.0 (2 C), 138.3\*, 141.9, 142.0, 142.5, 144.4 and 154.3 (C<sub>6</sub>H<sub>4</sub>,  $C_6H_5$ , N $C_5H_4$ ,  $C_6H_5CH_3$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -74.2. <sup>13</sup>C VACP/MAS NMR:  $\delta$  21.5 (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 47.5–49.2 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 110.5, 111.8, 120.0, 121.2–124.5 (4 C), 125.4, 126.0, 126.8, 127.3, 128.2, 129.5 (3 C), 130.9, 132.3, 141.5, 142.1, 143.3 (2 C), 144.0 and 152.0 (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub>H<sub>4</sub>,  $C_6H_5CH_3$ ), CF<sub>3</sub> not detected. <sup>15</sup>N VACP/MAS NMR:  $\delta$  -300.2 (NCH<sub>2</sub>C), -134.3 (NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -82 (br.). Anal. Calcd for C<sub>22.5</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>Si (514.62): C, 52.51; H, 3.72; N, 5.44; S, 12.46. Found: C, 52.1; H, 3.8; N, 5.5; S, 12.2.

Pentacoordinate silicon(IV) complex 7. Trichloromethylsilane (2.63 g, 17.6 mmol) was added dropwise at 20 °C within 1 min to a stirred solution of 14 (3.80 g, 17.6 mmol) and triethylamine (3.55 g, 35.1 mmol) in tetrahydrofuran (75 ml), and the reaction mixture was stirred at 20 °C for 2 h. The resulting precipitate was filtered off, washed with tetrahydrofuran (10 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, followed by the addition of acetonitrile (14 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with *n*-pentane  $(2 \times 5 \text{ ml})$  and dried in vacuo (40 °C, 6 h, 0.01 mbar). Yield: 2.60 g (8.88 mmol, 50%). Mp: 208 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.04 (s, 3 H, CH<sub>3</sub>), 4.69 and 4.72 (AB system,  ${}^{2}J({}^{1}H,{}^{1}H) = 17.8$  Hz, 2 H, NCH<sub>2</sub>C), 6.34–6.44, 6.61–6.78, 6.93–7.09, 7.19–7.26, 7.38– 8.09, 8.25–8.40, 8.62–8.69 and 8.77–8.81 (m, 8 H, C<sub>6</sub>H<sub>4</sub>, NC<sub>5</sub>H<sub>4</sub>).  $^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): \delta 16.1 (CH_3), 48.6 (NCH_2C),$ 

111.1, 119.8, 122.6, 123.4, 124.5, 126.0, 135.6, 141.3, 143.0, 144.0 and 153.5 ( $C_6H_4$ , N $C_3H_4$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –64.0. <sup>13</sup>C VACP/MAS NMR: δ18.6 (CH<sub>3</sub>), 46.7–50.5 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 111.5, 118.7, 119.0, 122.1, 123.8, 124.7, 125.6, 130.4, 139.8, 142.3 and 154.4 ( $C_6H_4$ , N $C_5H_4$ ). <sup>15</sup>N VACP/MAS NMR: δ –297.3 (NCH<sub>2</sub>C), –128.0 (N $C_3H_4$ ). <sup>29</sup>Si VACP/MAS NMR: δ –70 (br.). Anal. Calcd for C<sub>13</sub>H<sub>13</sub>CIN<sub>2</sub>SSi (292.86): C, 53.32; H, 4.47; N, 9.57; S, 10.95. Found: C, 53.3; H, 4.6; N, 9.5; S, 11.2.

Pentacoordinate silicon(IV) complex 8. Compound 13 (1.21 g, 5.84 mmol) was added dropwise at 20 °C within 1 min to a stirred solution of 14 (1.26 g, 5.83 mmol) and triethylamine (1.18 g, 11.7 mmol) in tetrahydrofuran (25 ml), and the reaction mixture was stirred at 20 °C for 20 min. The resulting precipitate was filtered off, washed with tetrahydrofuran (10 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, followed by the addition of acetonitrile (5 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 2 d. The resulting yellow crystalline solid was isolated by filtration, washed with n-pentane (5 ml) and dried in vacuo (20 °C, 5 h, 0.01 mbar). Yield: 1.02 g (2.91 mmol, 50%). Mp: 155 °C (dec.). <sup>1</sup>H NMR (300.1 MHz,  $CD_2Cl_2$ ):  $\delta$  0.86 (s, 3 H,  $CH_3$ ), 4.73 and 4.75 (AB system,  ${}^{2}J({}^{1}H,{}^{1}H) = 18.0 \text{ Hz}, 2 \text{ H}, \text{ NC}H_{2}\text{C}), 6.59-6.80, 6.83-6.91, 6.93-$ 7.35, 7.49-7.65, 7.97-8.05 and 8.70-8.75 (m, 13 H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub> $H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  12.5 (CH<sub>3</sub>), 49.2 (NCH<sub>2</sub>C), 110.6, 120.6 (2 C), 121.2, 122.4, 123.0, 124.4, 126.5, 129.5 (2 C), 130.8, 140.9, 144.1 (2 C), 144.2, 154.0 and 155.6  $(C_6H_4, C_6H_5, NC_5H_4)$ . <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ -70.0. <sup>13</sup>C VACP/MAS NMR: δ13.6 (CH<sub>3</sub>), 46.7–49.9 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 110.4, 118.5, 120.6, 121.9, 123.3, 125.0 (2 C), 127.2, 128.6, 130.0, 131.0, 141.1 (2 C), 142.4, 143.4, 153.1 and 155.8 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ). <sup>15</sup>N VACP/MAS NMR:  $\delta$  –295.7 (NCH<sub>2</sub>C), -129.4 (NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR: δ -73 (br.). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>OSSi (350.52): C, 65.11; H, 5.18; N, 7.99; S, 9.15. Found: C, 65.0; H, 5.3; N, 8.0; S, 9.2.

Pentacoordinate silicon(IV) complex 9. Benzenethiol (172 mg, 1.56 mmol) was added dropwise at 20 °C within 1 min to a stirred solution of 7 (456 mg, 1.56 mmol) and triethylamine (158 mg, 1.56 mmol) in tetrahydrofuran (20 ml), and the reaction mixture was stirred at 20 °C for 30 min. The resulting precipitate was filtered off, washed with tetrahydrofuran (10 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, followed by the addition of acetonitrile (3 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 2 d. The resulting yellow crystalline solid was isolated by filtration, washed with n-pentane  $(2 \times 5 \text{ ml})$  and dried in vacuo (40 °C, 4 h, 0.01 mbar). Yield: 284 mg (775 µmol, 50%). Mp: 171 °C (dec.). <sup>1</sup>H NMR (300.1 MHz,  $CD_2Cl_2$ ):  $\delta$  1.13 (s, 3 H,  $CH_3$ ), 4.66 and 4.68 (AB system,  ${}^{2}J({}^{1}H,{}^{1}H) = 18.5 \text{ Hz}, 2 \text{ H}, \text{ NCH}_{2}C), 6.53-6.79, 6.80-7.02, 7.06-$ 7.31, 7.51–7.56, 7.89–7.96 and 8.46–8.51 (m, 13 H,  $C_6H_4$ ,  $C_6H_5$ , NC<sub>5</sub> $H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  16.1 (CH<sub>3</sub>), 48.9 (NCH<sub>2</sub>C), 110.7, 119.2, 122.4, 123.3, 123.5, 126.3, 127.0, 128.8 (2 C), 131.0, 135.4 (2 C), 135.9, 141.0, 143.8, 144.2 and 154.2  $(C_6H_4, C_6H_5, NC_5H_4)$ . <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -59.8. <sup>13</sup>C VACP/MAS NMR: δ 15.6 (*C*H<sub>3</sub>), 47.9–50.7 (m (<sup>13</sup>C, <sup>14</sup>N coupling), N*C*H<sub>2</sub>C), 110.3, 119.7, 121.4, 122.4, 125.4 (2 C), 128.7, 130.0, 130.7, 134.6, 135.2 (2 C), 135.7, 139.1, 140.9, 143.5 and 152.8 ( $C_6$ H<sub>4</sub>,  $C_6$ H<sub>5</sub>, N*C*<sub>5</sub>H<sub>4</sub>). <sup>15</sup>N VACP/MAS NMR: δ –300.5 (*N*CH<sub>2</sub>C), –127.8 (*N*C<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR: δ –61 (br.). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>Si (366.58): C, 62.25; H, 4.95; N, 7.64; S, 17.49. Found: C, 62.2; H, 5.1; N, 7.9; S, 17.1.

Pentacoordinate silicon(IV) complex 10. Benzeneselenol (762 mg, 4.85 mmol) was added dropwise at -18 °C within 1 min to a stirred solution of 7 (1.42 g, 4.85 mmol) and triethylamine (491 mg, 4.85 mmol) in tetrahydrofuran (25 ml), and the stirred reaction mixture was allowed to warm up to 20 °C within 20 min. The resulting precipitate was filtered off, washed with tetrahydrofuran (10 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, followed by the addition of acetonitrile (5 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with n-pentane (5 ml) and dried in vacuo (20 °C, 3 h, 0.01 mbar). Yield: 1.06 g (2.56 mmol, 53%). Mp: 175 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.23 (s, 3 H,  $CH_3$ , 4.70 and 4.71 (AB system,  ${}^{2}J({}^{1}H, {}^{1}H) = 18.8$  Hz, 2 H, NCH<sub>2</sub>C), 6.52-6.82, 6.83-7.04, 7.07-7.30, 7.46-7.54, 7.76-7.84 and 7.97–8.03 (m, 13 H,  $C_6H_4$ ,  $C_6H_5$ ,  $NC_5H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 17.3 (CH<sub>3</sub>), 48.8 (NCH<sub>2</sub>C), 111.0, 119.3, 122.4, 122.9, 123.5, 126.6, 126.9, 128.9 (2 C), 131.1, 133.4, 136.2 (2 C), 140.8, 142.8, 144.2 and 153.6 (C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -70.2 (<sup>77</sup>Se satellites,  ${}^{1}J({}^{29}\text{Si}, {}^{77}\text{Se}) = 136 \text{ Hz}$ ).  ${}^{77}\text{Se} \text{ NMR} (95.4 \text{ MHz}, \text{CD}_2\text{Cl}_2)$ :  $\delta$  194.5. <sup>13</sup>C VACP/MAS NMR:  $\delta$  14.5 (CH<sub>3</sub>), 44.3–49.0 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 109.1, 117.5, 119.4, 119.8, 121.5, 123.0 (2 C), 125.8, 127.9, 128.1, 129.4, 134.6 (2 C), 137.8, 139.9, 141.2 and 150.9 ( $C_6H_4$ ,  $C_6H_5$ , N $C_5H_4$ ). <sup>15</sup>N VACP/MAS NMR:  $\delta$  -301.7 (NCH<sub>2</sub>C), -125.3 (NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -70 (br.) (<sup>77</sup>Se satellites not detected). <sup>77</sup>Se VACP/MAS NMR:  $\delta$  236.8. Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>SSeSi (413.48): C, 55.19; H, 4.39; N, 6.78, S, 7.76. Found: C, 55.2; H, 4.5; N, 7.1; S, 7.9.

**Pentacoordinate silicon(IV) complex 11.** Phenyl trimethylsilyl telluride (1.23 g, 4.44 mmol) was added at -18 °C in a single portion to a stirred solution of 7 (1.30 g, 4.44 mmol) in acetonitrile (40 ml), and the stirred reaction mixture was allowed to warm up to 20 °C within 20 min. The volatile components were removed in vacuo, and acetonitrile (5 ml) was added to the residue. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting orange crystalline solid was isolated by filtration, washed with *n*-pentane (5 ml) and dried in vacuo (20 °C, 3 h, 0.01 mbar). Yield: 1.20 g (2.59 mmol, 58%). Mp: 163 °C (dec.). <sup>1</sup>H NMR (300.1 MHz,  $CD_2Cl_2$ :  $\delta$  1.35 (s, 3 H,  $CH_3$ ), 4.71 and 4.75 (AB system,  ${}^{2}J({}^{1}H,{}^{1}H) = 18.2 \text{ Hz}, 2 \text{ H}, \text{ NCH}_{2}C), 6.52-6.82, 6.83-7.04, 7.07-$ 7.30, 7.46–7.54, 7.76–7.84 and 7.97–8.03 (m, 13 H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, NC<sub>5</sub> $H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  18.1 (CH<sub>3</sub>), 47.7 (NCH<sub>2</sub>C), 110.2, 118.4, 121.4, 121.8, 122.8, 125.9, 126.2, 128.1 (2 C), 130.5, 138.2, 139.2 (2 C), 139.7, 141.1, 143.3 and 151.9 (C<sub>6</sub>H<sub>4</sub>,  $C_6H_5$ , N $C_5H_4$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -90.6  $(^{125}\text{Te satellites}, {}^{1}J(^{29}\text{Si}, ^{125}\text{Te}) = 367 \text{ Hz}). {}^{125}\text{Te NMR} (157.8 \text{ MHz},$ 

CD<sub>2</sub>Cl<sub>2</sub>): δ 135.3. <sup>13</sup>C VACP/MAS NMR: δ 21.7 (CH<sub>3</sub>), 46.7–51.0 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 111.3, 119.0, 121.3, 123.2, 125.0, 126.1 (2 C), 128.0, 129.3, 130.2, 133.4, 138.3, 140.2 (2 C), 142.6, 145.3 and 152.7 ( $C_6H_4$ ,  $C_6H_5$ , NC<sub>5</sub>H<sub>4</sub>). <sup>15</sup>N VACP/MAS NMR: δ –303.7 (NCH<sub>2</sub>C), –133.0 (NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si VACP/MAS NMR: δ –92 (br.) (<sup>125</sup>Te satellites not detected). <sup>125</sup>Te{<sup>1</sup>H} HPDec/MAS NMR: δ 104.5. Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>SSiTe (462.12): C, 49.38; H, 3.93; N, 6.06, S, 6.94. Found: C, 49.4; H, 3.9; N, 6.2; S, 6.6.

Pentacoordinate silicon(IV) complex 12. Trichloropentafluorophenylsilane<sup>7</sup> (4.88 g, 16.2 mmol) was added dropwise at 20 °C within 2 min to a stirred solution of 14 (3.50 g, 16.2 mmol) and triethylamine (3.28 g, 32.4 mmol) in tetrahydrofuran (80 ml), and the reaction mixture was stirred at 20 °C for 3 h. The resulting precipitate was filtered off, washed with tetrahydrofuran (20 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, followed by the addition of acetonitrile (100 ml). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 1 d. The resulting yellow crystalline solid was isolated by filtration, washed with *n*-pentane  $(2 \times 10 \text{ ml})$  and dried in vacuo (40 °C, 4 h, 0.01 mbar). Yield: 4.66 g (10.5 mmol, 65%). Mp: 227 °C (dec.). <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 4.81 and 4.88 (AB system,  ${}^{2}J({}^{1}H,{}^{1}H) = 18.0 \text{ Hz}, 2 \text{ H}, \text{ NC}H_{2}\text{C}), 6.43-6.48, 6.75-6.86, 7.00-$ 7.09, 7.18-7.23, 7.49-7.57, 7.68-7.74, 8.08-8.16 and 8.44-8.50 (m, 8 H, C<sub>6</sub> $H_4$ , NC<sub>5</sub> $H_4$ ).). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 47.8 (NCH<sub>2</sub>C), 111.6, 116.6–117.3 (m, C-1, C<sub>6</sub>F<sub>5</sub>), 120.5, 122.6, 124.0, 124.9, 126.0, 129.4, 137.6 (dm,  ${}^{1}J({}^{13}C, {}^{19}F) = 252$  Hz, C-2/C-6,  $C_6F_5$ ), 141.4, 141.9 (dm,  ${}^{1}J({}^{13}C, {}^{19}F) = 253$  Hz, C-4,  $C_6F_5$ ), 142.2, 143.4, 146.8 (dm,  ${}^{1}J({}^{13}C, {}^{19}F) = 241$  Hz, C-3/C-5, C<sub>6</sub>F<sub>5</sub>) and 153.8 (C<sub>6</sub>H<sub>4</sub>, NC<sub>5</sub>H<sub>4</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -84.8 to -84.4 (m). <sup>13</sup>C VACP/MAS NMR:  $\delta$  45.2–49.8 (m (<sup>13</sup>C, <sup>14</sup>N coupling), NCH<sub>2</sub>C), 113.9, 119.6, 120.3, 122.5, 123.3, 124.3, 125.1, 131.3, 140.0, 146.2 and 154.0 (C<sub>6</sub>H<sub>4</sub>, NC<sub>5</sub>H<sub>4</sub>), C<sub>6</sub>F<sub>5</sub> not well resolved/detectable. <sup>15</sup>N VACP/MAS NMR:  $\delta$  –297.8  $(NCH_2C)$ , -95.0  $(NC_5H_4)$ . <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -88 (br.). Anal. Calcd for C<sub>18</sub>H<sub>10</sub>ClF<sub>5</sub>N<sub>2</sub>SSi (444.89): C, 48.60; H, 2.27; N, 6.30; S, 7.21. Found: C, 48.6; H, 2.3; N, 6.3; S, 7.0.

Dichloromethylphenoxysilane (13). A solution of triethylamine (4.06 g, 40.1 mmol) and phenol (3.78 g, 40.2 mmol) in tetrahydrofuran (180 ml) was added dropwise at -40 °C to a stirred solution of trichloromethylsilane (6.00 g, 40.1 mmol) in tetrahydrofuran (40 ml). Subsequently, the reaction mixture was allowed to warm up to 20 °C and then stirred for 18 h at this temperature. The resulting precipitate was filtered off, washed with tetrahydrofuran (20 ml) and discarded. The solvent of the filtrate (including the wash solution) was removed by distillation at ambient pressure, followed by distillation of the residue in vacuo (58 °C, 5 mbar) to give a colorless liquid. Yield: 2.72 mg (13.1 mmol, 33%). Bp: 58 °C (5 mbar). <sup>1</sup>H NMR (300.1 MHz,  $CD_2Cl_2$ ):  $\delta 1.00$  (s, 3 H,  $CH_3$ ), 7.06–7.13 (m, 2 H, H-2/H-6,  $C_6H_5$ ), 7.14-7.18 (m, 1 H, H-4, C<sub>6</sub>H<sub>5</sub>) and 7.31-7.39 (m, 2 H, H-3/H-5,  $C_6H_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.80 (CH<sub>3</sub>), 120.3 (2 C) (C-2/C-6, C<sub>6</sub>H<sub>5</sub>), 124.1 (C-4, C<sub>6</sub>H<sub>5</sub>), 130.2 (2 C) (C-3/C-5,  $C_6H_5$ ), 152.3 (C-1,  $C_6H_5$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz,  $CD_2Cl_2$ ): δ-11.7. Anal. Calcd for C<sub>7</sub>H<sub>8</sub>Cl<sub>2</sub>OSi (207.13): C, 40.59; H, 3.89. Found: C, 40.6; H, 3.9.

2-{[(Pyridin-2-yl)methyl]amino}benzenethiol (14)<sup>8</sup>. This synthesis was performed analogously to the preparation of 4-methyl-2-[(pyridin-2-yl)amino)phenol:9 A solution of 2aminobenzenethiol (5.00 g, 39.9 mmol) and pyridin-2carboxaldehvde (4.47 g, 41.7 mmol) in methanol (150 ml) was stirred at 65 °C for 3 h and then cooled to 20 °C. After the solvent was removed in vacuo, ethanol (40 ml) was added to the residue. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20 °C. The resulting yellow crystalline solid was isolated by filtration and redissolved in methanol (200 ml), and the resulting solution was cooled to 0 °C. Subsequently, sodium borohydride (15.1 g, 399 mmol) was added in small portions over a period of 3 h (caution: brisk gas evolution!). The resulting mixture was allowed to warm up to 20 °C and was then stirred at 65 °C for 4 h. After the solvent was removed in vacuo, water (200 ml) was added to the residue, and the resulting suspension was neutralised with glacial acetic acid (20 ml). The aqueous phase was extracted with dichloromethane  $(3 \times 50 \text{ ml})$ , and the combined organic phases were washed with water (50 ml) and dried over anhydrous sodium sulphate. After the solvent was removed in vacuo, the remaining green oil was redissolved in methanol (200 ml) and the resulting solution cooled to 0 °C. Subsequently, sodium borohydride (15.1 g, 399 mmol) was again added in small portions over a period of 3 h. The resulting mixture was allowed to warm up to 20 °C and was then stirred at 65 °C for 4 h. After the solvent was removed in vacuo, water (200 ml) was added to the residue, and the resulting suspension was neutralised with glacial acetic acid (20 ml). The aqueous phase was extracted with dichloromethane  $(3 \times 50 \text{ ml})$ , and the combined organic phases were washed with water (50 ml) and dried over anhydrous sodium sulphate. The solvent was removed in vacuo to give a dark green oily liquid. Yield: 7.94 g (36.7 mmol, 92%). <sup>1</sup>H NMR (300.1 MHz, [D<sub>6</sub>]DMSO): δ 3.34 (br. s, 1 H, SH), 4.46 (s, 2 H, NCH<sub>2</sub>C), 5.33 (br. s, NH), 7.45–7.60 (m, 3 H, H-4/H-5/H-6, C<sub>6</sub>H<sub>4</sub>), 8.07–8.17 (m, 3 H, H-3/H-5, NC<sub>5</sub>H<sub>4</sub>, H-3, C<sub>6</sub>H<sub>4</sub>), 8.23–8.34 (m, 1 H, H-4, NC<sub>5</sub>H<sub>4</sub>) and 8.68–8.74 (m, 1 H, *H*-6, NC<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, [D<sub>6</sub>]DMSO):  $\delta$ 48.3 (NCH<sub>2</sub>C), 122.5 (C-6, C<sub>6</sub>H<sub>4</sub>), 123.3 (C-2, C<sub>6</sub>H<sub>4</sub>), 125.9 (C-4, C<sub>6</sub>H<sub>4</sub>), 126.1 (C-3, NC<sub>6</sub>H<sub>4</sub>), 126.6 (C-5, NC<sub>6</sub>H<sub>4</sub>), 135.4 (C-5, C<sub>6</sub>H<sub>4</sub>), 137.8 (C-3, C<sub>6</sub>H<sub>4</sub>), 149.1 (C-4, NC<sub>5</sub>H<sub>4</sub>), 150.3 (C-1, C<sub>6</sub>H<sub>4</sub>), 153.7 (C-6, NC<sub>5</sub>H<sub>4</sub>) and 169.0 (C-2, NC<sub>5</sub>H<sub>4</sub>). Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>S (216.31): C, 66.63; H, 5.59; N, 12.95; S, 14.82. Found: C, 66.7; H, 5.5; N, 12.9; S, 14.8.

#### Crystal structure analyses

Suitable single crystals of  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ ,  $3.0.5C_7H_8$ , 4,  $5.0.5C_7H_8$ ,  $6.0.5C_7H_8$  and 7-12 were obtained as described in the experimental section dealing with the syntheses. The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (7: Bruker Nonius KAPPA APEX II diffractometer, Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, Montel mirror;  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ ,  $3.0.5C_7H_8$ , 4,  $5.0.5C_7H_8$ ,  $6.0.5C_7H_8$  and 8-12: Stoe IPDS diffractometer, graphite-monochromated Mo-K $\alpha$ radiation,  $\lambda = 0.71073$  Å). All structures were solved by direct methods.<sup>10</sup> The non-hydrogen atoms were refined anisotropically.<sup>10</sup> A riding model was employed in the refinement of the *CH* hydrogen atoms. The crystallographic data for the structures



Scheme 2 Syntheses of compounds 1-3, 7, 8 and 12.

reported in this paper have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication nos. 832632–832642 and 845196.†

#### **Results and discussion**

#### Syntheses

The pentacoordinate silicon(IV) complexes 1–3, 7, 8 and 12 were synthesised according to Scheme 2 by treatment of trichlorophenylsilane, tribromophenylsilane, tri(cyanato-*N*)phenylsilane, trichloromethylsilane, trichloropentafluorophenylsilane and dichloromethylphenoxysilane (13), respectively, with 1 molar equivalent of 2-{[(pyridin-2-yl)methyl]amino}benzenethiol (14) and 2 molar equivalents of triethylamine (yields:  $1.0.5C_7H_8$ , 54%;  $2.0.5C_7H_8$ , 64%;  $3.0.5C_7H_8$ , 58%; 7, 50%; 8, 50%; 12, 65%). Tetrahydrofuran (1, 7, 8, 12) or toluene (2, 3) served as the solvent. Compounds 1–3 were isolated as hemitoluene solvates.

The pentacoordinate silicon(IV) complexes **4–6** were obtained according to Scheme 3 by treatment of the corresponding chlorosilicon(IV) complex **1** with 1 molar equivalent (or an excess) of trimethyl(thiocyanato-*N*)silane, azidotrimethylsilane and trifluoromethanesulfonatotrimethylsilane, respectively (yields: **4**, 89%; **5**·0.5C<sub>7</sub>H<sub>8</sub>, 50%; **6**·0.5C<sub>7</sub>H<sub>8</sub>, 55%). Toluene (**5**) or acetonitrile (**4**, **6**) served as the solvent. Compounds **5** and **6** were isolated as hemitoluene solvates. The pentacoordinate silicon(IV) complex **11** was synthesised analogously by reaction of the corresponding chlorosilicon(IV) complex **7** with phenyl trimethylsilyl telluride in acetonitrile (yield: 58%).

The pentacoordinate silicon(IV) complexes **9** and **10** were synthesised according to Scheme 4 by treatment of the corresponding chlorosilicon(IV) complex **7** with 1 molar equivalent of benzenethiol and benzeneselenol, respectively, and 1 molar equivalent of triethylamine (yields: **9**, 50%; **10**, 53%). Tetrahydrofuran served as the solvent.

The racemic compounds  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ ,  $3.0.5C_7H_8$ , 4,  $5.0.5C_7H_8$ ,  $6.0.5C_7H_8$  and 7-12 were isolated as yellow crystalline solids, which showed a remarkable thermal stability (see Experimental section). Their identities were established by elemental analyses (C, H, N, S), NMR spectroscopic studies in the solid state (<sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si, <sup>77</sup>Se, <sup>125</sup>Te) and in solution (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>77</sup>Se, <sup>125</sup>Te) and by crystal structure analyses.

#### Crystal structure analyses

Compounds  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ ,  $3.0.5C_7H_8$ , 4,  $5.0.5C_7H_8$ ,  $6.0.5C_7H_8$  and 7–12 were structurally characterised by single-



Scheme 3 Syntheses of compounds 4–6 and 11.



Scheme 4 Syntheses of compounds 9 and 10.

crystal X-ray diffraction. The hemitoluene solvates  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ ,  $3.0.5C_7H_8$ ,  $5.0.5C_7H_8$  and  $6.0.5C_7H_8$  crystallise with an embedded toluene molecule, which lies about a twofold axis  $(1.0.5C_7H_8-3.0.5C_7H_8)$  or a centre of symmetry  $(5.0.5C_7H_8$  and  $6.0.5C_7H_8$ ). Compounds  $1.0.5C_7H_8-3.0.5C_7H_8$  and compounds

Compound	$1{\cdot}0.5C_7H_8$	$2 \cdot 0.5 C_7 H_8$	$3 \cdot 0.5 C_7 H_8$	4	$5 \cdot 0.5 C_7 H_8$	$6 \cdot \mathbf{0.5C}_7 \mathbf{H}_8$
Empirical formula Formula mass [g mol <sup>-1</sup> ]	C <sub>21.5</sub> H <sub>19</sub> ClN <sub>2</sub> SSi 400 99	$C_{21.5}H_{19}BrN_2SSi$ 445.45	C <sub>22.5</sub> H <sub>19</sub> N <sub>3</sub> OSSi 407 56	C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> S <sub>2</sub> Si 377 55	C <sub>21.5</sub> H <sub>19</sub> N <sub>5</sub> SSi 407 57	$C_{22.5}H_{19}F_3N_2O_3S_2Si$ 514 61
	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
$\lambda(M_0 - K_0)$ [Å]	0 71073	0 71073	0 71073	0 71073	0 71073	0 71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group (no.)	C2/c (15)	$C_{2/c}(15)$	$C_{2/c}(15)$	<i>Phca</i> (61)	$P2_{1}/n$ (14)	$P\overline{1}(2)$
a[Å]	21.132(3)	21.133(4)	21.439(4)	11.1469(13)	12.0354(17)	9.972(2)
b [Å]	12.5246(17)	12.662(3)	12.6603(18)	22.193(3)	13.1538(18)	11.273(2)
c [Å]	17.107(2)	17.279(4)	16.963(2)	29.661(5)	12.9714(18)	11.806(2)
$\alpha$ [°]	90	90	90	90	90	65.48(3)
B[°]	120.487(13)	121.25(3)	118.544(15)	90	95.259(17)	73.49(3)
ν[°]	90	90	90	90	90	74 68(3)
V [Å <sup>3</sup> ]	3901.6(9)	3952.5(14)	4044.5(10)	7337.6(17)	2044.9(5)	1141.3(4)
Z	8	8	8	16	4	2
$\rho_{\text{calcd}} [\text{g cm}^{-1}]$	1.365	1.497	1.339	1.367	1.324	1.497
$\mu [\mathrm{mm}^{-1}]$	0.373	2.255	0.238	0.362	0.235	0.339
F(000)	1672	1816	1704	3136	852	530
Crystal dimensions [mm]	$0.5 \times 0.5 \times 0.4$	$0.5 \times 0.2 \times 0.2$	$0.5 \times 0.25 \times 0.25$	$0.5 \times 0.4 \times 0.3$	$0.5 \times 0.4 \times 0.3$	$0.48 \times 0.32 \times 0.15$
$2\theta$ range [°]	5.04-58.22	5.00-58.22	5.10-58.28	4.58-55.98	4.84-58.30	6.34-58.30
Index ranges	$-28 \le h \le 28$ ,	$-28 \le h \le 28$ ,	$-29 \le h \le 29$ ,	$-13 \le h \le 14$ ,	$-16 \le h \le 16$ ,	$-13 \le h \le 13$ ,
C	$-17 \le k \le 17$ ,	$-17 \le k \le 17$ ,	$-17 \le k \le 17$ ,	$-28 \le k \le 29$ ,	$-17 \le k \le 17$ ,	$-15 \le k \le 15$ ,
	$-23 \le l \le 23^{\circ}$	$-23 \le l \le 23$	$-23 \le l \le 23^{\circ}$	$-39 \le l \le 39^{\circ}$	$-17 \le l \le 17^{\prime}$	$-16 \le l \le 16$
Number of collected	24326	26240	31456	60861	23950	16511
reflections						
Number of independent	5193	4998	5407	8810	5456	5598
reflections						
$R_{\rm int}$	0.0333	0.0527	0.0582	0.0484	0.0390	0.0418
Number of parameters	242	257	260	451	278	323
Number of restraints	0	0	0	0	57	48
Sa	1.080	0.960	1.062	1.058	1.075	1.031
Weight parameters $a/b^b$	0.0495/2.8691	0.0494/0.0000	0.0632/2.4713	0.0956/2.3500	0.0698/0.4612	0.0628/0.2554
$R_1^c [I > 2\sigma(I)]$	0.0366	0.0317	0.0452	0.0571	0.0476	0.0383
$WR_2^d$ (all data)	0.0975	0.0795	0.1262	0.1711	0.1345	0.1110
Max./min. residual electron density [e $Å^{-3}$ ]	+0.417/-0.306	+0.462/-0.570	+0.373/-0.541	+1.343/-0.844	+0.556/-0.356	+0.403/-0.325

**Table 1** Crystallographic data for compounds  $1 \cdot 0.5C_7H_8$ ,  $2 \cdot 0.5C_7H_8$ ,  $3 \cdot 0.5C_7H_8$ , 4,  $5 \cdot 0.5C_7H_8$  and  $6 \cdot 0.5C_7H_8$ 

 ${}^{a}S = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)\}^{o.5}; n = \text{number of reflections}; p = \text{number of parameters.} {}^{b}w^{-1} = \sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ with } P = [\max(F_{o}^{2}, 0) + 2F_{c}^{2}]/3.$   ${}^{c}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma ||F_{o}| \cdot {}^{d}wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}]\}^{o.5}.$ 

**9** and **10** are isomorphous. The crystal data and experimental parameters used for the crystal structure analyses are given in Tables 1 and 2. The molecular structures of **1–12** are shown in Fig. 1–12; selected bond lengths and angles are given in the respective captions.

The Si-coordination polyhedra of **1–12** are (strongly) distorted trigonal bipyramids. The maximum deviations from the ideal 90°, 120° and 180° angles range from 7.22(14)° to 12.74(9)°, from 2.2(2)° to 17.79(7)° and from 8.72(12)° to 17.52(8)°, respectively (Table 3). The Berry distortions are in the range 9.4–55.0% (Table 3).<sup>11</sup> With Berry distortions of 54.6% and 55.0%, the Si-coordination polyhedra of **3** and **4** are even better described as strongly distorted square pyramids. In all cases, the sulphur and the pyridine-nitrogen atom of the *N*,*N*,*S* ligand of **1–12** occupy the two axial positions, whereas the amino-nitrogen atom occupies an equatorial site.

The axial Si–S bond lengths of **1–12** amount to 222.98(9)–227.92(7) pm (Table 4), with a maximum deviation of 4.94 pm. These distances are similar but somewhat shorter than those axial Si–S distances of pentacoordinate silicon(IV) compounds reported in the literature [228.42(6)–238.53(6)].<sup>36,3c,3e,3i</sup> The Si–N(pyridine) bond lengths are in the range 197.00(14)–202.94(16) pm (maximum deviation, 5.94 pm), and the Si–N(amino) bond lengths

range from 174.38(13) pm to 177.09(16) pm (maximum deviation, 2.71 pm) (Table 4). These data demonstrate that the Si–S and Si–N bond lengths in question are only slightly affected by the two monodentate ligands of **1–12** (Ph, Me,  $C_6F_5$ ; Cl, Br, NCO, NCS, N<sub>3</sub>, OS(O)<sub>2</sub>CF<sub>3</sub>, OPh, SPh, SePh, TePh).

The equatorial Si–E (E = S, Se, Te) bond lengths of the trigonal-bipyramidal Si-coordination polyhedra of **9–11** deserve a special discussion as the number of reference data in the literature is very limited, especially in the case of Si–Se (five reference compounds)<sup>3i</sup> and Si–Te bonds (one reference compound).<sup>3i</sup> According to tendency, the equatorial Si–E bond lengths of **9** [Si–S, 220.87(8) pm], **10** [Si–Se, 234.49(7) pm] and **11** [Si–Te, 256.08(12) pm (occupation factor, 94.4%) and 255.4(8) pm (occupation factor, 5.6%)] are slightly longer compared to the respective reference data reported in the literature [Si–S, <sup>3a–3f,3j</sup> 212.51(7)–218.81(6) pm; Si–Se,<sup>3i</sup> 228.46(4)–234.39(8) pm; Si–Te,<sup>3i</sup> 251.84(4) pm].

# NMR studies

Compounds  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ ,  $3.0.5C_7H_8$ , 4,  $5.0.5C_7H_8$ , 6.0.5C<sub>7</sub>H<sub>8</sub> and 7–12 were studied by NMR spectroscopy in the solid state (<sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si, <sup>77</sup>Se, <sup>125</sup>Te) and in solution (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si,

#### Table 2 Crystallographic data for compounds 7–12

Compound	7	8	9	10	11	12
	·					
Empirical formula	$C_{13}H_{13}ClN_2SSi$	$C_{19}H_{18}N_2OSSi$	$C_{19}H_{18}N_2S_2S_1$	$C_{19}H_{18}N_2SSeSi$	$C_{19}H_{18}N_2SSiTe$	$C_{18}H_{10}ClF_5N_2SSi$
Formula mass [g mol <sup>-1</sup> ]	292.85	350.50	366.56	413.46	462.10	444.88
	100(2)	173(2)	173(2)	173(2)	173(2)	173(2)
$\lambda$ (Mo-K $\alpha$ ) [A]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Trigonal	Monoclinic
Space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)	R3 (148)	$P2_1/c$ (14)
a [Å]	7.1864(15)	10.258(2)	7.5524(15)	7.5484(12)	18.327(2)	7.7449(10)
<i>b</i> [Å]	9.7269(19)	7.6485(12)	16.297(3)	16.447(4)	18.327(2)	15.308(2)
c [Å]	18.971(4)	22.037(5)	14.284(3)	14.428(2)	18.327(2)	15.082(2)
α [°]	90	90	90	90	116.627(17)	90
$\beta$ [°]	96.328(5)	94.92(3)	97.34(3)	97.973(19)	116.627(17)	98.831(15)
γ[°]	90	90	90	90	116.627(17)	90
$V[Å^3]$	1318.0(5)	1722.7(6)	1743.6(6)	1773.8(6)	2869.9(6)	1767.0(4)
Z	4	4	4	4	6	4
$\rho_{\text{calcd}} [\text{g cm}^{-1}]$	1.476	1.351	1.396	1.548	1.604	1.672
$\mu [\mathrm{mm}^{-1}]$	0.521	0.266	0.377	2.305	1.729	0.460
F(000)	608	736	768	840	1368	896
Crystal dimensions [mm]	$0.40 \times 0.22 \times 0.17$	$0.5 \times 0.5 \times 0.2$	$0.5 \times 0.2 \times 0.2$	$0.5 \times 0.3 \times 0.2$	$0.5 \times 0.3 \times 0.2$	$0.6 \times 0.4 \times 0.3$
$2\theta$ range [°]	4.32-64.72	5.68-58.24	5.76-58.42	5.70-58.36	5.22-58.42	5.32-58.14
Index ranges	$-9 \le h \le 10$ ,	$-14 \le h \le 14$ ,	$-10 \le h \le 10$ ,	$-10 \le h \le 10$ ,	$-25 \le h \le 25$ ,	$-10 \le h \le 10$ ,
0	$-14 \le k \le 14$ ,	$-10 \le k \le 10$ ,	$-22 \le k \le 22$ ,	$-22 \le k \le 22$ ,	$-24 \le k \le 25$ ,	$-20 \le k \le 20$ ,
	$-27 \le l \le 28^{\circ}$	$-30 \le l \le 30^{\circ}$	$-19 \le l \le 19^{\circ}$	$-19 \le l \le 19^{\circ}$	$-25 \le l \le 25$	$-20 \le l \le 20^{\circ}$
Number of collected	35821	26739	22364	24275	45772	23304
reflections						
Number of independent	4669	4556	4684	4716	5129	4706
reflections						
$R_{\rm int}$	0.0360	0.0375	0.0476	0.0622	0.0542	0.0371
Number of parameters	171	218	218	218	232	253
Number of restraints	4	0	0	0	0	0
Sa	1.132	1.082	1.057	1.049	1.068	1.078
Weight parameters $a/b^b$	0.0270/0.9168	0.0502/0.5564	0.0624/0.5214	0.0521/0.0445	0.0095/9.5443	0.0522/0.4979
$R_1^c [I > 2\sigma(I)]$	0.0337	0.0382	0.0404	0.0294	0.0471	0.0348
$wR_2^d$ (all data)	0.0853	0.1045	0.1134	0.0797	0.0987	0.0957
Max./min. residual electron	+0.523/-0.288	+0.291/-0.271	+0.338/-0.351	+0.566/-0.327	+0.698/-1.064	+0.420/-0.370
density [e Å <sup>-3</sup> ]						

 ${}^{a} S = \{ \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p) \}^{0.5}; n = \text{number of reflections}; p = \text{number of parameters.} {}^{b} w^{-1} = \sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ with } P = [\max(F_{o}^{2}, 0) + 2F_{c}^{2}]/3.$   ${}^{c} R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma ||F_{o}| . {}^{d} wR_{2} = \{ \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}] \}^{0.5}.$ 

Table 3 Maximum deviations [°] from the ideal  $90^{\circ}$ ,  $120^{\circ}$  and  $180^{\circ}$  angles and Berry distortions [%] of  $1-12^{\circ}$ 

Compound	$\Delta 90^{\circ}$	$\Delta 120^{\circ}$	$\Delta 180^{\circ}$	Berry distortion <sup>b</sup>	Skeleton
1	10.71(5)	15.87(5)	14.66(4)	46.8	SiClSN <sub>2</sub> C
2	10.56(7)	15.64(6)	14.55(4)	46.3	SiBrSN <sub>2</sub> C
3	11.55(5)	17.79(7)	16.41(5)	54.6	SiSN <sub>3</sub> C
4	12.74(9)/9.73(9)	17.39(14)/6.79(12)	17.52(8)/10.90(7)	55.0/27.1	SiSN <sub>3</sub> C
5	7.28(7)	12.84(8)	9.03(5)	24.8	SiSN <sub>3</sub> C
6	7.42(7)	13.41(7)	8.89(5)	22.5	SiSON <sub>2</sub> C
7	8.2(2)	12.19(13)	11.56(4)	32.7	SiClSN <sub>2</sub> C
8	7.75(6)	7.22(7)	11.38(4)	21.3	SiSON <sub>2</sub> C
9	8.34(7)	6.14(6)	11.81(5)	22.2	$SiS_2N_2C$
10	8.40(7)	6.74(7)	11.66(5)	21.7	SiSeSN <sub>2</sub> C
11	7.22(14)	2.2(2)	8.72(1)	9.4	$SiTeSN_2C$
12	6.58(5)	9.16(5)	7.64(4)	23.6	SiClSN <sub>2</sub> C

<sup>77</sup>Se, <sup>125</sup>Te; solvent  $CD_2Cl_2$ ). The data obtained (see Experimental) confirm the identities of the compounds studied.

As can be seen from Table 5, the respective isotropic  $^{29}$ Si chemical shifts in the solid state and in solution are (very) similar, indicating that the pentacoordinate silicon(iv) complexes 1–12 exist both in the solid state and in solution. This assumption is further supported by all the other NMR spectroscopic data

obtained. The isotropic <sup>29</sup>Si chemical shifts of 1-12 range from -61/-59.8 ppm (9, solid state/solution) to -92/-90.6 ppm (11, solid state/solution), indicating a strong influence of the different silicon-bound ligands on the <sup>29</sup>Si chemical shifts.

As shown exemplarily for  $1.0.5C_7H_8$ ,  $2.0.5C_7H_8$ , 10 and 11 in Fig. 13, the resonance signals in the solid-state <sup>29</sup>Si NMR spectra of all the compounds studied are broadened and (in some cases)

Table 4 Si-S, Si-N1 and Si-N2 bond lengths [pm] of 1-12<sup>a</sup>

Compound	Si–S	Si–N1	Si–N2	Skeleton
1	224.87(6)	199.58(12)	176.37(12)	<i>Si</i> ClSN <sub>2</sub> C
2	224.77(8)	199.58(18)	176.16(19)	SiBrSN <sub>2</sub> C
3	224.69(7)	199.72(15)	176.64(15)	SiSN <sub>3</sub> C
4	224.04(11)/224.48(10)	198.1(3)/201.2(2)	175.2(2)/175.3(2)	SiSN <sub>3</sub> C
5	227.10(8)	197.74(17)	175.98(15)	SiSN <sub>3</sub> C
6	222.98(9)	197.00(14)	174.92(16)	SiSON <sub>2</sub> C
7	225.20(6) <sup>b</sup>	198.03(12) <sup>b</sup>	174.92(11) <sup>b</sup>	SiClSN <sub>2</sub> C
8	227.92(7)	198.44(13)	176.78(13)	SiSON <sub>2</sub> C
9	226.34(7)	202.84(15)	176.90(14)	SiS <sub>2</sub> N <sub>2</sub> C
10	226.16(8)	202.94(16)	177.09(16)	SiSeSN <sub>2</sub> C
11	$227.9(6)^{c}$	$199.2(6)^{c}$	$176.0(3)^{c}$	SiTeSN <sub>2</sub> C
12	223.62(6)	197.81(13)	174.38(13)	SiClSN <sub>2</sub> C

<sup>*a*</sup> Compounds 1–3, 5 and 6 were studied as hemitoluene solvates. <sup>*b*</sup> Molecule with the occupation factor of 71.1%. <sup>*c*</sup> Molecule with the occupation factor of 94.4%.





Fig. 1 Molecular structure of 1 in the crystal of  $1.0.5C_7H_8$  (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–Cl 214.30(7), Si–S 224.87(6), Si–N1 199.58(12), Si–N2 176.37(12), Si–Cl 187.61(14); Cl–Si–S 89.85(2), Cl–Si–N1 88.32(4), Cl–Si–N2 135.87(5), Cl–Si–Cl 107.34(5), S–Si–N1 165.34(4), S–Si–N2 88.67(4), S–Si–Cl 100.71(5), N1–Si–N2 82.57(5), N1–Si–Cl 93.72(6), N2–Si–Cl 116.25(6).

slightly structured. This can be explained by  ${}^{1}J({}^{29}Si,X)$  couplings  $(X = {}^{14}N (I = 1); {}^{35}Cl (I = 3/2), {}^{37}Cl (I = 3/2); {}^{79}Br (I = 3/2), {}^{81}Br (I = 3/2))$  and interactions of the  ${}^{29}Si$  nucleus with the neighboring quadrupole nuclei.

Comparison of the <sup>29</sup>Si chemical shifts of **1–12** in the solid state and in solution (Table 5) clearly demonstrates that these pentacoordinate silicon(IV) complexes also exist in solution. However, in some cases a significant low-field shift in solution is observed, with the largest differences observed for **1**, **2**, **6** and **7** ( $\Delta \delta^{29}$ Si = 5–8 ppm). It may be speculated that these differences result from the presence of a dynamic equilibrium between the pentacoordinate silicon(IV)

Fig. 2 Molecular structure of 2 in the crystal of  $2.0.5C_7H_8$  (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si-Br 232.80(13), Si-S 224.77(8), Si-N1 199.58(18), Si-N2 176.16(19), Si-C1 188.0(2); Br-Si-S 89.39(3), Br-Si-N1 88.70(6), Br-Si-N2 135.64(6), Br-Si-C1 107.16(7), S-Si-N1 165.45(6), S-Si-N2 88.76(6), S-Si-C1 100.56(7), N1-Si-N2 82.56(8), N1-Si-C1 93.78(8), N2-Si-C1 116.73(9).

complexes A (= 1–12) and the related tetracoordinate species B (generated by cleavage of the Si–N(pyridine) bond) and/or B' (generated by cleavage of the Si–X bond) (Scheme 5).

To get more information about this hypothetic equilibrium, VT <sup>29</sup>Si NMR studies of **1**, **7**, **10** and **12** in CD<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (7 only) were performed. As shown for the chlorosilicon(IV) complex **7** in Fig. 14, a high-field shift of the <sup>29</sup>Si resonance signal was observed upon cooling from 23 °C to -90 °C, with a chemical shift of  $\delta^{29}$ Si = -67.0 ppm at -90 °C.

An analogous behavior was observed for the two chlorosilicon(IV) complexes 1 ( $\delta^{29}$ Si = -73.6 ppm, -90 °C) and 12



**Fig. 3** Molecular structure of **3** in the crystal of  $3 \cdot 0.5C_7H_8$  (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–S 224.69(7), Si–N1 199.72(15), Si–N2 176.64(15), Si–N3 176.81(17), Si–C1 187.40(16), O–C19 116.9(2), N3–C19 116.0(2); S–Si–N1 163.59(5), S–Si–N2 88.89(5), S–Si–N3 90.21(6), S–Si–C1 101.55(5), N1–Si–N2 82.23(7), N1–Si–N3 87.20(7), N1–Si–C1 94.74(7), N2–Si–N3 137.79(7), N2–Si–C1 115.61(7), N3–Si–C1 105.89(8), Si–N3–C19 158.55(16), N3–C19–O 177.8(2).

**Table 5** Comparison of the isotropic  ${}^{29}$ Si chemical shifts [ppm] of 1–12in the solid state (T = 22 °C) and in solution (solvent, CD<sub>2</sub>Cl<sub>2</sub>; T = 23 °C)<sup>a</sup>

Compound	$\delta^{29} \mathrm{Si}^{b}$ (solid state)	$\delta^{\scriptscriptstyle 29}{ m Si}$ (solution)
1	-76	$-70.9(-73.6)^{\circ}$
2	-84	-79.1
3	-89	-87.9
4	-90	-89.3
5	-85	-81.7
6	-82	-74.2
7	-70	$-64.0(-67.0)^{\circ}$
8	-73	-70.0
9	-61	-59.8
10	-70	$-70.2^{d} (-73.9)^{c}$
11	-92	-90.6 <sup>e</sup>
12	-88	-84.5 (-87.0)°

<sup>*a*</sup> Compounds 1–3, 5 and 6 were studied as hemitoluene solvates. <sup>*b*</sup> Centre of a broadened (slightly structured) resonance signal. <sup>*c*</sup> The <sup>29</sup>Si chemical shift in parentheses refer to T = -90 °C. <sup>*d*</sup> <sup>77</sup>Se satellites, <sup>1</sup>J(<sup>29</sup>Si,<sup>77</sup>Se) = 136 Hz. <sup>*e*</sup> <sup>125</sup>Te satellites, <sup>1</sup>J(<sup>29</sup>Si,<sup>125</sup>Te) = 367 Hz.

 $(\delta^{29}\text{Si} = -87.0 \text{ ppm}, -90 \text{ °C})$ , which could be interpreted in terms of an increase in population of the corresponding pentacoordinate species **A** (see Scheme 5). On the other hand, heating of a solution of **7** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> from 23 °C to 90 °C leads to a low-field shift ( $\delta^{29}\text{Si} = -61.9 \text{ ppm}, 90 \text{ °C}$ ) (Fig. 15), which would be in accordance with a decrease in population of **A**.

In the case of the silicon(IV) complex 10, there is almost no difference in the <sup>29</sup>Si chemical shifts in the solid state and in



Fig. 4 Molecular structure of 4 (molecule 1) in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si1–S1 224.04(11), Si1–N1 198.1(3), Si1–N2 175.2(2), Si1–N3 177.6(3), Si1–C1 186.5(3), S2–C19 157.3(3), N3–C19 118.0(4); S1–Si1–N1 162.48(8), S1–Si1–N2 89.76(9), S1–Si1–N3 88.62(11), S1–Si1–C1 102.74(9), N1–Si1–N2 82.54(11), N1–Si1–N3 86.50(12), N1–Si1–C1 94.76(11), N2–Si1–N3 137.39(14), N2–Si1–C1 113.11(12), N3–Si1–C1 108.75(15), Si1–N3–C19 159.3(3), N3–C19–S2 177.5(4) [molecule 2: Si1–S1 224.48(10), Si1–N1 201.2(2), Si1–N2 175.3(2), Si1–N3 178.0(2), Si1–C1 187.9(3), S2–C19 159.5(3), N3–C19 117.2(4); S1–Si1–N1 169.10(7), S1–Si1–N2 89.50(8), S1–Si1–N3 93.70(8), S1–Si1–C1 99.73(9), N1–Si1–N2 81.93(10), N1–Si1–N3 86.14(10), N1–Si1–C1 90.75(11), N2–Si1–N3 126.79(12), N2–Si1–C1 125.41(12), N3–Si1–C1 106.31(12), Si1–N3–C19 174.2(3), N3–C19–S2 178.9(3)].



Scheme 5 Hypothetic dynamic equilibrium between the pentacoordinate silicon(IV) complexes A and the related tetracoordinate species B (neutral) and/or B' (cationic).

solution (Table 5), suggesting that the existence of the two potential tetracoordinate species **B** and **B'** in solution can be neglected. Nevertheless, a high-field shift of the <sup>29</sup>Si resonance signal of **10** was observed upon cooling from 23 °C to -90 °C, with a chemical shift of  $\delta^{29}$ Si = -73.9 ppm at -90 °C. In conclusion, the results of the VT <sup>29</sup>Si NMR studies of **1**, **7**, **10** and **12** reflect a significant temperature dependence of the <sup>29</sup>Si chemical shifts and do not support the existence of the hypothetic equilibria  $\mathbf{A} \rightleftharpoons \mathbf{B}$  and/or  $\mathbf{A} \leftrightharpoons \mathbf{B'} + \mathbf{X}^-$ . This finding is further confirmed by the results of computational studies with **7** (see below).

#### **Computational studies**

We have conducted a computational study to elucidate the nature of the hypothetic product mixture shown in Scheme 5 by





**Fig. 5** Molecular structure of **5** in the crystal of  $5 \cdot 0.5C_7H_8$  (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–S 227.10(8), Si–N1 197.74(17), Si–N2 175.98(15), Si–N3 180.51(17), Si–C1 188.42(19), N3–N4 117.8(2), N4–N5 115.1(3); S–Si–N1 170.97(5), S–Si–N2 88.91(6), S–Si–N3 95.92(6), S–Si–C1 96.03(6), N1–Si–N2 82.72(7), N1–Si–N3 86.44(7), N1–Si–C1 91.57(7), N2–Si–N3 126.67(8), N2–Si–C1 125.13(8), N3–Si–C1 107.16(8), Si–N3–N4 125.27(15), N3–N4–N5 175.5(3).



Scheme 6 Hypothetic dynamic equilibrium between the pentacoordinate silicon(IV) complex 7 and the related tetracoordinate species 7a (neutral) and/or 7b (cationic).

computing the structures and relative energies of the pentacoordinate silicon(IV) complex 7 and the potentially formed tetracoordinate species 7a and 7b (Scheme 6), using density functional theory (DFT). The study was furthermore reinforced by computing the <sup>29</sup>Si chemical shifts of 7, 7a and 7b relative to tetramethylsilane (SiMe<sub>4</sub>).

All calculations were performed using the Amsterdam Density Functional (ADF) program,<sup>12</sup> using density functional theory at BP86/TZ2P for geometry optimisation and energies,<sup>13</sup> and at SAOP/ET-pVQZ//BP86/TZ2P<sup>14</sup> for <sup>29</sup>Si NMR chemical shifts relative to SiMe<sub>4</sub>.<sup>15</sup> In all cases, solvation in dichloromethane was simulated using the conductor-like screening model (COSMO).<sup>16</sup> All stationary points were verified to be minima through vibrational analysis. Gibbs free energies were computed using electronic energies augmented with the COSMO free energies of solvation plus the gas-phase entropy correction of the solute.

**Fig. 6** Molecular structure of **6** in the crystal of **6** $\cdot$ 0.5C<sub>7</sub>H<sub>8</sub> (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–S 222.98(9), Si–O1 177.37(13), Si–N1 197.00(14), Si–N2 174.39(16), Si–C1 187.89(17); S–Si–O1 96.30(5), S–Si–N1 171.11(5), S–Si–N2 89.78(6), S–Si–C1 97.08(6), O1–Si–N1 84.07(6), O1–Si–N2 122.26(6), O1–Si–C1 106.59(7), N1–Si–N2 82.58(7), N1–Si–C1 91.30(7), N2–Si–C1 129.57(8).



Fig. 7 Molecular structure of 7 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–Cl 212.50(6), Si–S 225.20(6), Si–N1 198.03(12), Si–N2 174.92(11), Si–Cl 186.9(4); Cl–Si–S 91.30(3), Cl–Si–N1 89.03(4), Cl–Si–N2 130.77(5), Cl–Si–C1 107.81(13), S–Si–N1 168.44(4), S–Si–N2 88.56(4), S–Si–C1 98.2(2), N1–Si–N2 82.50(5), N1–Si–Cl 92.7(2), N2–Si–Cl 120.91(16). The data given refer to the molecule with the occupation factor of 71.1%.

The results of the COSMO-BP86/TZ2P calculations are summarised in Table 6. The most stable species in the hypothetic equilibrium depicted in Scheme 6 is the pentacoordinate silicon(IV) complex 7. The second most favorable species, 7a (neutral), is



Fig. 8 Molecular structure of 8 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–S 227.92(7), Si–O 168.54(12), Si–N1 198.44(13), Si–N2 176.78(13), Si–C1 187.89(15); S–Si–O 95.84(4), S–Si–N1 168.62(4), S–Si–N2 88.44(5), S–Si–C1 96.67(6), O–Si–N1 84.11(5), O–Si–N2 124.03(6), O–Si–C1 112.78(7), N1–Si–N2 82.25(6), N1–Si–C1 93.81(7), N2–Si–C1 122.08(7).

**Table 6** Computed relative Gibbs free energies  $G_{rel}$  [kcal mol<sup>-1</sup>] and <sup>29</sup>Si chemical shifts [ppm] of **7**, **7a** and **7b** in dichloromethane<sup>*a*</sup>

$G_{ m rel}$	$\delta^{_{29}}{ m Si}$ (theor.)	$\delta^{_{29}}{ m Si}$ (exp.)
0.0	-63.7	-70 (solid state)/-64.0 (solution in CD <sub>2</sub> Cl <sub>2</sub> )
6.4 20.0	16.6 32.0	(001441011 11 02 2012)
	<i>G</i> <sub>rel</sub> 0.0 6.4 20.0	$G_{\rm rel}$ $\delta^{29} {\rm Si}$ (theor.)           0.0         -63.7           6.4         16.6           20.0         32.0

<sup>a</sup> Computed at COSMO-BP86/TZ2P (structures and energies) and COSMO-SAOP/ET-pVQZ//COSMO-BP86/TZ2P (chemical shifts).

6.4 kcal mol<sup>-1</sup> higher in Gibbs free energy and may thus be present as trace. The ionic species **7b**(+ Cl<sup>-</sup>) has a 20.0 kcal mol<sup>-1</sup> higher Gibbs free energy and can therefore be ruled out in the equilibrium. The dominant presence of **7** in the product mixture, indicated by the computed relative energies, is further confirmed by the perfect agreement between the computed ( $\delta^{29}$ Si = -63.7 ppm) and experimentally established <sup>29</sup>Si chemical shift of **7** in solution ( $\delta^{29}$ Si = -64.0 ppm). Finally, all attempts to optimise square pyramidal variants of **7** yielded spontaneous geometric relaxation towards the trigonal bipyramidal structure of **7**. Therefore, we conclude that the computational data are strongly in support of the predominance of the pentacoordinate silicon(IV) complex **7** in solution.

As shown by additional computations, the experimentally observed difference between the <sup>29</sup>Si chemical shift of 7 in the solid state ( $\delta^{29}$ Si = -70 ppm) and solution ( $\delta^{29}$ Si = -64.0 ppm) can be largely ascribed to structural changes upon dissolution of 7 (Tables 7 and 8, Fig. 16). The <sup>29</sup>Si chemical shift of 7 computed



Fig. 9 Molecular structure of 9 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–S1 226.34(7), Si–S2 220.87(8), Si–N1 202.84(15), Si–N2 176.90(14), Si–C1 187.78(18); S1–Si–S2 97.66(3), S1–Si–N1 168.19(5), S1–Si–N2 88.65(5), S1–Si–C1 98.34(7), S2–Si–N1 81.83(5), S2–Si–N2 124.17(5), S2–Si–C1 113.86(6), N1–Si–N2 82.01(6), N1–Si–C1 92.60(8), N2–Si–C1 119.94(8).

Table 7 Computed and experimental  $^{29}$ Si chemical shifts [ppm] for different structures of  $7^{a,b}$ 

Structure	NMR medium	$\delta^{_{29}}{ m Si}$ (theor.)	$\delta^{29}$ Si (exp.)
in CH <sub>2</sub> Cl <sub>2</sub>	$\begin{array}{c} CH_2Cl_2\\ CH_2Cl_2\\ vacuum \end{array}$	-63.7	-64.0
in the crystal		-71.6	-70
in the crystal		-69.0	-70

<sup>*a*</sup> Solution-phase structures computed at COSMO-BP86/TZ2P.<sup>*b*</sup> Chemical shifts in the gas phase or in dichloromethane (COSMO) computed at SAOP/ET-pVQZ.

for the solution phase and for the crystal structure amounts to  $\delta^{29}$ Si = -63.7 ppm and  $\delta^{29}$ Si = -71.6 ppm, respectively, if solvent effects (CH<sub>2</sub>Cl<sub>2</sub>) are taken into account in the NMR calculations of both structures. Using the same experimental crystal structure of 7 but omitting medium effects in the NMR computation (*i.e.*, gas-phase NMR) yields a <sup>29</sup>Si chemical shift of  $\delta^{29}$ Si = -69.0 ppm. Both computed  $\delta^{29}$ Si chemical shifts (-71.6 and -69.0 ppm) agree within *ca.* 1 ppm with the experimental value (-70 ppm).

# Conclusion

With the synthesis of compounds 1-12, a new class of neutral pentacoordinate silicon(IV) complexes has been made available. These compounds contain (i) a tridentate dianionic N,N,S chelate ligand derived from  $2-\{[(pyridin-2-yl)methyl]amino\}$  benzenethiol, (ii) a phenyl, methyl or pentafluorophenyl group and (iii) a



Fig. 10 Molecular structure of 10 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–Se 234.49(7), Si–S 226.16(8), Si–N1 202.94(16), Si–N2 177.09(16), Si–C1 187.8(2); Se–Si–S 97.18(3), Se–Si–N1 82.23(5), Se–Si–N2 124.16(6), Se–Si–C1 113.26(7), S–Si–N1 168.34(5), S–Si–N2 89.23(6), S–Si–C1 98.06(7), N1–Si–N2 81.60(7), N1–Si–C1 92.83(8), N2–Si–C1 120.60(9).



Fig. 11 Molecular structure of 11 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–Te 256.08(12), Si–S 227.9(6), Si–N1 199.2(6), Si–N2 176.0(3), Si–C1 187.2(5); Te–Si–S 86.97(7), Te–Si–N1 94.22(11), Te–Si–N2 119.23(12), Te–Si–C1 118.56(17), S–Si–N1 171.28(12), S–Si–N2 89.10(12), S–Si–C1 96.1(2), N1–Si–N2 82.78(14), N1–Si–C1 90.9(2), N2–Si–C1 122.2(2). The data given refer to the molecule with the occupation factor of 94.4%.

Table 8 Bond angles  $[^\circ]$  of the crystal structure and the computed structure of 7 in dichloromethane

Angle	Crystal structure	Computed structure <sup>a</sup>		
S-Si-N <sub>ax</sub>	168	170		
Cl-Si-Neg	131	123		
Cl-Si-C	108	109		
N <sub>eq</sub> -Si-C	121	127		
S-Si-Cl	91	95		
S-Si-Neg	89	88		
S-Si-C	98	96		
Nax-Si-Cl	89	88		
Nax-Si-Neg	83	82		
N <sub>ax</sub> -Si-C	93	92		
<sup><i>a</i></sup> Computed structure in dichloromethane at COSMO-BP86/TZ2P.				

monodentate monoanionic ligand (Cl, Br, NCO, NCS, N<sub>3</sub>,  $OS(O)_2CF_3$ , OPh, SPh, SePh, TePh). The silicon(IV) complexes synthesised contain quite novel Si-coordination skeletons:  $SiCISN_2C$ ,  $SiBrSN_2C$ ,  $SiSN_3C$ ,  $SiSON_2C$ ,  $SiS_2N_2C$ ,  $SiSeSN_2C$  and  $SiTeSN_2C$ . Compounds 1–12 represent further examples of pentacoordinate silicon(IV) complexes that contain soft chalcogen ligand atoms. In this context, compounds 9 ( $SiS_2N_2C$  skeleton), 10 ( $SiSeSN_2C$ ) and 11 ( $SiTeSN_2C$ ) are especially remarkable as they contain two chalcogen ligand atoms (S/S, S/Se, S/Te).

Compounds 1–12 exist both in the solid state and in solution. The Si-coordination polyhedra in the crystal are best described as (strongly) distorted trigonal bipyramids, with the sulphur and pyridine-nitrogen atom of the N,N,S ligand in the two axial sites.



Fig. 12 Molecular structure of 12 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Si–Cl 211.78(6), Si–S 223.62(6), Si–N1 197.81(13), Si–N2 174.38(13), Si–Cl 192.42(14); Cl–Si–S 93.39(3), Cl–Si–N1 88.07(4), Cl–Si–N2 128.63(5), Cl–Si–Cl 110.84(5), S–Si–N1 172.36(4), S–Si–N2 89.83(4), S–Si–Cl 96.26(5), N1–Si–N2 83.42(5), N1–Si–Cl 90.22(6), N2–Si–Cl 119.72(7).

The transformation of the neutral pentacoordinate chlorosilicon(IV) complexes 1 and 7 into the corresponding derivatives 4– 6 and 9–11 demonstrates 1 and 7 to be versatile precursors for the preparation of further pentacoordinate silicon(IV) complexes by replacement of the chloro ligand with other monodentate



Fig. 13 <sup>29</sup>Si VACP/MAS NMR spectra ( $v_{rot} = 7 \text{ kHz}$ , T = 22 °C) of 1.0.5C<sub>7</sub>H<sub>8</sub> (A), 2.0.5C<sub>7</sub>H<sub>8</sub> (B), 10 (C) and 11 (D).



Fig. 14 Temperature dependence of the  ${}^{29}$ Si NMR spectrum of 7 (solvent, CD<sub>2</sub>Cl<sub>2</sub>; 99.4 MHz).

monoanionic ligands. In this context, the synthetic potential of compounds **2–6** with their (pseudo)halogeno (**2–5**) and trifluoromethanesulfonato (**6**) groups is also of interest. Studies on this subject are in progress.

# Acknowledgements

R. T. thanks the State of Bavaria for financial support. C. F. G. and F. M. B. thank the National Research School Combination–Catalysis for an NRSC-C fellowship for C. F. G. and the Netherlands Organization for Scientific Research (NWO-CW and NWO-NCF) for further financial support.



Fig. 15 Temperature dependence of the  $^{29}\text{Si}$  NMR spectrum of 7 (solvent, C\_2D\_2Cl\_4; 99.4 MHz).



**Fig. 16** Structure of **7** in the crystal determined by single-crystal X-ray diffraction (left) and structure of **7** in dichloromethane computed at COSMO-BP86/TZ2P (right) (bond lengths given in Å).

# References

- 1 Selected reviews dealing with higher-coordinate silicon(IV) 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 (ed.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, 1998, 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 and 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 (ed.: P. Jutzi, U. Schubert), Wiley-VCH, Weinheim, 2003, pp. 324-337; (g) D. Kost and I. Kalikhman, Adv. Organomet. Chem., 2004, 50, 1-106; (h) D. Kost and I. Kalikhman, Acc. Chem. Res., 2009, 42, 303-314; (i) E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers and K. Lammertsma, Z. Anorg. Allg. Chem., 2009, 635, 1273-1278.
- 2 Selected recent publications dealing with higher-coordinate silicon(IV) compounds: (a) S. Yakubovich, I. Kalikhman and D. Kost, Dalton Trans., 2010, 39, 9241-9244; (b) P. Bombicz, I. Kovács, L. Nyulászi, D. Szieberth and P. Terleczky, Organometallics, 2010, 29, 1100-1106; (c) E. Kertsnus-Banchik, B. Gostevskii, M. Botoshansky, I. Kalikhman and D. Kost, Organometallics, 2010, 29, 5435-5445; (d) S. Cota, M. Beyer, R. Bertermann, C. Burschka, K. Götz, M. Kaupp and R. Tacke, Chem.-Eur. J., 2010, 16, 6582-6589; (e) R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, D. Kratzert, S. Merkel and D. Stalke, Angew. Chem., Int. Ed., 2010, 49, 3952-3955; (f) D. Schöne, D. Gerlach, C. Wiltzsch, E. Brendler, T. Heine, E. Kroke and J. Wagler, Eur. J. Inorg. Chem., 2010, 461-467; (g) A. R. Bassindale, M. Sohail, P. G. Taylor, A. A. Korlyukov and D. E. Arkhipov, Chem. Commun., 2010, 46, 3274-3276; (h) R. S. Ghadwal, K. Pröpper, B. Dittrich, P. G. Jones and H. W. Roesky, Inorg. Chem., 2011, 50, 358-364; (i) S. Yakubovich, B. Gostevskii, I. Kalikhman, M. Botoshansky, L. E. Gusel'nikov, V. A.

Published on 21 December 2011. Downloaded by Heinrich Heine University of Duesseldorf on 11/09/2013 05:42:16.

Pestunovich and D. Kost, *Organometallics*, 2011, **30**, 405–413; (*j*) K. Junold, C. Burschka, R. Bertermann and R. Tacke, *Dalton Trans.*, 2011, **40**, 9844–9857.

- 3 (a) R. Willeke and R. Tacke, Z. Anorg. Allg. Chem., 2001, 627, 1537-1541; (b) R. Tacke, M. Mallak and R. Willeke, Angew. Chem., Int. Ed., 2001, 40, 2339–2341; (c) R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler and R. Tacke, Organometallics, 2003, 22, 4104-4110; (d) O. Seiler, M. Büttner, M. Penka and R. Tacke, Organometallics, 2005, 24, 6059-6062; (e) D. Troegel, C. Burschka, S. Riedel, M. Kaupp and R. Tacke, Angew. Chem., Int. Ed., 2007, 46, 7001-7005; (f) S. Metz, C. Burschka, D. Platte and R. Tacke, Angew. Chem., Int. Ed., 2007, 46, 7006-7009; (g) S. Metz, C. Burschka and R. Tacke, Eur. J. Inorg. Chem., 2008, 4433-4439; (h) S. Metz, C. Burschka and R. Tacke, Organometallics, 2009, 28, 2311-2317; (i) B. Theis, S. Metz, C. Burschka, R. Bertermann, S. Maisch and R. Tacke, Chem.-Eur. 2009, 15, 7329-7338; (j) S. Metz, B. Theis, C. Burschka and R. Tacke, Chem.-Eur. J., 2010, 16, 6844-6856; (k) K. Junold, C. Burschka, R. Bertermann and R. Tacke, Dalton Trans., 2010, 39, 9401-9413
- 4 Selected publications dealing with higher-coordinate silicon(IV) complexes with pyridine ligands: (a) T. R. van den Ancker, C. L. Raston, B. W. Skelton and A. H. White, Organometallics, 2000, 19, 4437–4444; (b) C. Jones, P. C. Junk, S. G. Leary, N. A. Smithies and J. W. Steed, Inorg. Chem. Commun., 2002, 5, 533–536; (c) M. Nakash, D. Gut and M. Goldvaser, Inorg. Chem., 2005, 44, 1023–1030; (d) E. Brendler, E. Wächtler and J. Wagler, Organometallics, 2009, 28, 5459–5465; (e) G. W. Fester, J. Wagler, E. Brendler, U. Böhme, D. Gerlach and E. Kroke, J. Am. Chem. Soc., 2009, 131, 6855–6864.
- 5 S. Braun and S. Berger, 200 and More Basic NMR Experiments, VCH, Weinheim, 2004, pp. 141–148.

- 6 In contrast to the <sup>13</sup>C and <sup>15</sup>N VACP/MAS NMR spectra, the <sup>29</sup>Si VACP/MAS NMR spectrum of **4** shows only one broadened signal due to quadrupole <sup>14</sup>N coupling and did not show two separated chemical shifts for the two crystallographically independent molecules in the crystal.
- 7 Synthesis of C<sub>6</sub>F<sub>5</sub>SiCl<sub>3</sub>: H. J. Frohn, M. Giesen, A. Klose, A. Lewin and V. V. Bardin, *J. Organomet. Chem.*, 1996, **506**, 155–164.
- 8 U. Brand and H. Vahrenkamp, Chem. Ber., 1996, 129, 435-440.
- 9 L. Durán Pachón, A. Golobič, B. Kozlevčar, P. Gamez, H. Kooijman, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta*, 2004, 357, 3697–3702.
- 10 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.
- 11 The Berry distortions were analysed by using the PLATON program system; A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148–155.
- 12 (a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, J. Comput. Chem., 2001, 22, 931–967; (b) http://www.scm.com.
- 13 (a) S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys., 1980, 58, 1200–1211; (b) A. D. Becke, Phys. Rev. A: At., Mol., Opt. Phys., 1988, 38, 3098–3100; (c) J. P. Perdew, Phys. Rev. B: Condens. Matter, 1986, 33, 8822–8824 (Erratum: Ibid. 1986, 34, 7406).
- 14 P. R. T. Schipper, O. V. Gritsenko, S. J. V. van Gisbergen and E. J. Baerends, J. Chem. Phys., 2000, 112, 1344–1352.
- 15 G. Schreckenbach and T. Ziegler, J. Phys. Chem., 1995, 99, 606-611.
- 16 (a) A. Klamt and G. Schüürmann, J. Chem. Soc., Perkin Trans. 2, 1993, 799–805; (b) A. Klamt, J. Phys. Chem., 1995, 99, 2224–2235; (c) C. C. Pye and T. Ziegler, Theor. Chem. Acc., 1999, 101, 396–408; (d) M. Swart, E. Rösler and F. M. Bickelhaupt, Eur. J. Inorg. Chem., 2007, 3646–3654.