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# Novel neutral hexacoordinate benzamidinatosilicon(IV) complexes with *Si*N<sub>3</sub>OF<sub>2</sub>, *Si*N<sub>3</sub>OCl<sub>2</sub>, *Si*N<sub>3</sub>OBr<sub>2</sub>, *Si*N<sub>5</sub>O and *Si*N<sub>3</sub>O<sub>3</sub> skeletons†‡

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The neutral pentacoordinate monoamidinatosilicon(IV) complex **1** ( $SiN_2Cl_3$  skeleton) and the neutral hexacoordinate monoamidinatosilicon(IV) complexes **2–9** ( $SiN_3OF_2$ ,  $SiN_3OCl_2$ ,  $SiN_3OBr_2$ ,  $SiN_5O$  and  $SiN_3O_3$  skeletons) were synthesised and characterised by elemental analyses, single-crystal X-ray diffraction (except for **1**) and NMR spectroscopy in the solid state and in solution. Compounds **2–9** contain one bidentate monoanionic N,N'-diisopropylbenzamidinato ligand, one bidentate monoanionic N,N'-diisopropylbenzamidinato ligand, one bidentate monoanionic ligand derived from 8-hydroxyquinoline and (i) two identical monoanionic ligands (F, Cl, Br, N<sub>3</sub>, NCO, NCS, OSO<sub>2</sub>CF<sub>3</sub>) or (ii) one bidentate dianionic benzene-1,2-diolato ligand. The dynamic behavior of **2–4** ( $SiN_3OX_2$  skeleton; X = F, Cl, Br) and **9** ( $SiN_3O_3$ ) in solution was studied by multinuclear variable-temperature NMR experiments. Compound **1** was obtained by reaction of SiCl<sub>4</sub> with the corresponding lithium amidinate, and compound **2** was obtained by reaction of **3–9**, in which the two chloro ligands of **2** were substituted by two identical (pseudo)halogeno ligands, two trifluoromethanesulfonato ligands or one benzene-1,2-diolato ligand. Compounds **3** and **4** contain the novel  $SiN_3OBr_2$  and  $SiN_3OF_2$  skeletons, while compounds **5–7** are the first neutral hexacoordinate silicon(IV) complexes with an  $SiN_5O$  skeleton.

# Introduction

In transition metal and main group metal chemistry, coordination compounds with amidinato ligands have been studied extensively. In contrast, the chemistry of silicon complexes containing amidinato ligands is still a largely unexplored field. Only a few higher-coordinate silicon(IV) compounds containing such ligands are known<sup>1,2</sup> (for selected reviews dealing with higher-coordinate silicon compounds, see ref. 3). Very recently, we have reported on a series of neutral hexacoordinate bis(amidinato)silicon(IV) complexes with  $SiN_4F_2$ ,  $SiN_4Cl_2$ ,  $SiN_4Br_2$ ,  $SiN_6$ ,  $SiN_4C_2$ ,  $SiN_4S_2$ , SiN<sub>4</sub>SeS and SiN<sub>4</sub>Se<sub>2</sub> skeletons. In continuation of our systematic studies on higher-coordinate silicon compounds (for recent publications, see ref. 2 and 4), we have now succeeded in synthesising a series of novel neutral hexacoordinate monoamidinatosilicon(IV) complexes, compounds 2-9. These silicon(IV) complexes contain one bidentate monoanionic N,N'-diisopropylbenzamidinato ligand, one bidentate monoanionic ligand derived from 8hydroxyquinoline (in this context, see ref. 5) and (i) two identical monodentate monoanionic ligands (F, Cl, Br, N<sub>3</sub>, NCO, NCS,

 $OSO_2CF_3$ ) or (ii) one bidentate dianionic benzene-1,2-diolato ligand. The novel neutral pentacoordinate monoamidinatosilicon(IV) complex 1 served as the precursor for the synthesis of 2, which was then further converted into 3–9. We report herein on the synthesis of compounds 1–9 (Scheme 1) and their



Scheme 1 Structures of the neutral higher-coordinate silicon(IV) complexes investigated in this study.

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NMR-spectroscopic characterisation in the solid state and in solution. In addition, compounds 2–9 were structurally characterised by single-crystal X-ray diffraction. Furthermore, the dynamic behavior of 2–4 and 9 in solution was studied by multinuclear variable-temperature (VT) NMR experiments.

The main focus of this study was the synthesis and structural characterisation (including the dynamic behavior in solution) of novel neutral hexacoordinate monoamidinatosilicon(IV) complexes. In this context, compounds **3–7** were of particular interest as, to the best of our knowledge, neutral hexacoordinate silicon(IV) complexes with an  $SiN_3OF_2$ ,  $SiN_3OBr_2$  or  $SiN_5O$  skeleton have not yet been described in the literature. The synthesis of compound **9**, with its three different bidentate ligands, was also very challenging (in this context, see also ref. 6).

# 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. Lithium N,N'diisopropylbenzamidinate was synthesised according to ref. 7. Melting points were 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>19</sup>F and <sup>29</sup>Si NMR spectra were recorded at 23 °C on a Bruker Avance 400 (19F, 376.5 MHz) or a Bruker Avance 500 NMR spectrometer (<sup>1</sup>H, 500.1 MHz; <sup>13</sup>C, 125.8 MHz; <sup>29</sup>Si, 99.4 MHz) using CD<sub>2</sub>Cl<sub>2</sub> as the solvent. The <sup>19</sup>F,<sup>19</sup>F EXSY/NOESY (mixing time, 800 ms; recycle delay, 2.0 s) and VT <sup>19</sup>F NMR spectra were recorded on a Bruker DRX 300 NMR spectrometer (<sup>19</sup>F, 282.4 MHz). Chemical shifts (ppm) were determined relative to internal CHDCl<sub>2</sub> (<sup>1</sup>H,  $\delta$  5.32), internal CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C,  $\delta$  53.8), external CFCl<sub>3</sub> (<sup>19</sup>F,  $\delta$  0) or external tetramethylsilane (TMS) (<sup>29</sup>Si,  $\delta$  0). Assignment of the <sup>13</sup>C NMR data was supported by DEPT 135 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. 8 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 and <sup>29</sup>Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom-layer rotors of  $ZrO_2$  (diameter, 7 mm) containing *ca*. 200 mg of sample (<sup>13</sup>C, 100.6 MHz; <sup>15</sup>N, 40.6 MHz; <sup>29</sup>Si, 79.5 MHz; external standard, TMS (<sup>13</sup>C, <sup>29</sup>Si;  $\delta$  0) or glycine (<sup>15</sup>N;  $\delta$  –342.0); spinning rate, 6–7 kHz; contact time, 1 ms (<sup>13</sup>C), 3 ms (<sup>15</sup>N) or 5 ms (<sup>29</sup>Si); 90° <sup>1</sup>H transmitter pulse length, 3.6 µs; repetition time, 4–5 s).

#### Syntheses

**Benzamidinatosilicon(IV)** complex (1). Tetrachlorosilane (15.0 g, 88.3 mmol) was added dropwise at -78 °C within 2 min to a stirred suspension of lithium N,N'-diisopropylbenzamidinate (16.8 g, 79.9 mmol) in diethyl ether (120 ml), and the stirred reaction mixture was then allowed to warm up to 20 °C within 4 h. The solvent was removed *in vacuo*, dichloromethane (80 ml) was added to the residue, and the remaining solid was filtered off and discarded. The solvent of the filtrate was removed *in vacuo*, and acetonitrile (50 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 colorless crystalline solid was isolated by filtration, washed with n-pentane  $(2 \times 20 \text{ ml})$  and dried in vacuo (20 °C, 4 h, 0.01 mbar). Yield: 20.8 g (61.6 mmol, 77%). Mp: >150 °C (dec.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 1.20 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 12 H, CH<sub>3</sub>), 3.65 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 6.8 Hz, 2 H, CH), 7.36–7.39 (m, 2 H, o-C<sub>6</sub>H<sub>5</sub>), 7.56–7.66 (m, 3 H, *p*- and *m*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 22.9 (CH<sub>3</sub>), 47.5 (CH), 127.0 (*i*-C<sub>6</sub>H<sub>5</sub>), 127.4 (2 C) (*o*-C<sub>6</sub>H<sub>5</sub>), 129.6 (2 C)  $(m-C_6H_5)$ , 131.8  $(p-C_6H_5)$ , 173.1 (NCN). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –98.2. <sup>13</sup>C VACP/MAS NMR:  $\delta$ 22.6 (2 C) (CH<sub>3</sub>), 23.9 (2 C) (CH<sub>3</sub>), 46.8 (CH), 48.4 (CH), 125.1  $(C_6H_5)$ , 126.4 (2 C)  $(C_6H_5)$ , 129.4 (2 C)  $(C_6H_5)$ , 133.1  $(C_6H_5)$ , 173.5 (NCN). <sup>15</sup>N VACP/MAS NMR: δ -230.6, -172.6. <sup>29</sup>Si VACP/MAS NMR:  $\delta$  –99.4. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>Cl<sub>3</sub>N<sub>2</sub>Si (337.75): C, 46.23; H, 5.67; N, 8.29. Found: C, 46.2; H, 5.7; N, 8.3.

Benzamidinatosilicon(IV) complex (2). Triethylamine (3.09 g, 30.5 mmol) and 8-hydroxyquinoline (4.43 g, 30.5 mmol) were added at 20 °C in single portions one after another to a stirred solution of 1 (10.3 g, 30.5 mmol) in tetrahydrofuran (150 ml), and the reaction mixture was then stirred at this temperature for 19 h. The resulting precipitate was filtered off, washed with tetrahydrofuran  $(3 \times 20 \text{ ml})$  and discarded. The solvent of the filtrate (including the wash solutions) was removed in vacuo, followed by the addition of acetonitrile (100 ml). The resulting mixture 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  $(2 \times 10 \text{ ml})$  and dried in vacuo (20 °C, 3 h, 0.01 mbar). Yield: 6.40 g (14.3 mmol, 47%). Mp: >210 °C (dec.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -0.15 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8 \text{ Hz}, 3 \text{ H}, CH_{3}), 1.19 \text{ (d, } {}^{3}J({}^{1}H,{}^{1}H) = 6.8 \text{ Hz}, 3 \text{ H},$  $CH_3$ , 1.41 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 3 H,  $CH_3$ , 1.43 (d,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 6.8 Hz, 3 H,  $CH_3$ ), 3.21 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 4.04 (sept,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz, 1 H, CH), 7.24 (br. s, 1 H, o- $C_6H_5$ , 7.29 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.8$  Hz,  ${}^{4}J({}^{1}H, {}^{1}H) = 0.8$  Hz, 1 H, H7,  $C_9H_6NO$ , 7.36 (br. s, 1 H, o- $C_6H_5$ ), 7.41 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.2$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.8 \text{ Hz}, 1 \text{ H}, H5, C_{9}H_{6}\text{NO}), 7.49-7.58 \text{ (m, 3 H, }m\text{- and }$  $p-C_6H_5$ , 7.68 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.2$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.8$  Hz, 1 H, *H*6, C<sub>9</sub>*H*<sub>6</sub>NO), 7.70 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.2$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) = 5.0$  Hz, 1 H, H3, C<sub>9</sub>H<sub>6</sub>NO), 8.52 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.2$  Hz,  ${}^{4}J({}^{1}H, {}^{1}H) = 1.2$ Hz, 1 H, H4,  $C_9H_6NO$ ), 9.06 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 5.0$  Hz,  ${}^{4}J({}^{1}H, {}^{1}H) =$  $1.2 \text{ Hz}, 1 \text{ H}, H2, C_9 H_6 \text{ NO}$ . <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 21.9 (CH<sub>3</sub>), 22.2 (CH<sub>3</sub>), 23.61 (CH<sub>3</sub>), 23.65 (CH<sub>3</sub>), 46.9 (CH), 47.5 (CH), 112.5 (C7, C<sub>9</sub>H<sub>6</sub>NO), 115.6 (C5, C<sub>9</sub>H<sub>6</sub>NO), 122.9 (C3,  $C_9H_6NO$ , 127.4 (br., 2 C) (o- $C_6H_5$ ), 128.95 (i- $C_6H_5$ ), 129.03 (C4a,  $C_9H_6NO$ , 129.3 (br., 2 C) (*m*- $C_6H_5$ ), 130.9 (*p*- $C_6H_5$ ), 131.5 (C6, C<sub>9</sub>H<sub>6</sub>NO), 135.7 (C8a, C<sub>9</sub>H<sub>6</sub>NO) 139.0 (C2, C<sub>9</sub>H<sub>6</sub>NO), 140.6 (C4,  $C_9H_6NO$ ), 152.4 (C8,  $C_9H_6NO$ ), 169.7 (NCN). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –162.4. <sup>13</sup>C VACP/MAS NMR: δ 21.1 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>), 24.6 (2 C) (CH<sub>3</sub>), 46.2 (CH), 48.7 (CH), 113.8, 118.1, 122.6, 124.7, 126.7, 128.7 (4 C), 130.2, 132.5, 135.4, 140.7, 141.1 and 151.4 (C<sub>6</sub>H<sub>5</sub> and C<sub>9</sub>H<sub>6</sub>NO), 168.2 (NCN). <sup>15</sup>N VACP/MAS NMR: δ -209.0 (NCN), -186.8 (NCN), -129.3  $(C_9H_6NO)$ . <sup>29</sup>Si VACP/MAS NMR:  $\delta$  –165.2 (br. s). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>3</sub>OSi (446.45): C, 59.19; H, 5.64; N, 9.41. Found: C, 58.9; H, 5.7; N, 9.5.

Benzamidinatosilicon(IV) complex (3). Bromotrimethylsilane (1.71 g, 11.2 mmol) was added at 20 °C in a single portion to a stirred suspension of 2 (1.66 g, 3.72 mmol) in acetonitrile (30 ml), and the reaction mixture was then stirred at this temperature for 18 h. The volatile constituents were removed in vacuo, and acetonitrile (50 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 4 d. The resulting yellow crystalline solid was isolated by filtration, washed with n-pentane  $(2 \times 5 \text{ ml})$  and dried in vacuo (20 °C, 43 h, 0.01 mbar). Yield: 817 mg (1.53 mmol, 41%). Mp: >180 °C (dec.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ -0.15 (br. s, 3 H, CH<sub>3</sub>), 1.16-1.50 (m, 9 H, CH<sub>3</sub>), 3.3 (m, 1 H, CH), 4.2 (m, 1 H, CH), 7.1–7.8 (m, 9 H, C<sub>6</sub>H<sub>5</sub> and C<sub>9</sub>H<sub>6</sub>NO), 8.6 (m, 1 H, H4,  $C_9H_6NO$ ), 9.1 (m, 1 H, H2,  $C_9H_6NO$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 22.1 (br., 2 C) (CH<sub>3</sub>), 23.4 (br., 2 C) (CH<sub>3</sub>), 47.1 (CH), 47.2 (CH), 112.9 (C7, C<sub>9</sub>H<sub>6</sub>NO), 116.1  $(C5, C_9H_6NO), 123.1 (C3, C_9H_6NO), 127.3 (br., 2 C) (o-C_6H_5),$ 129.1 (*i*-C<sub>6</sub>H<sub>5</sub>), 129.3 (br., 2 C) (*m*-C<sub>6</sub>H<sub>5</sub>), 130.2 (C4a, C<sub>9</sub>H<sub>6</sub>NO), 131.1  $(p-C_6H_5)$ , 131.6 (C6,  $C_9H_6NO$ ), 135.5 (C8a,  $C_9H_6NO$ ), 139.1 (C2, C<sub>9</sub>H<sub>6</sub>NO), 140.2 (C4, C<sub>9</sub>H<sub>6</sub>NO), 151.9 (br.) (C8,  $C_{9}H_{6}NO$ , 170.0 (NCN). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -190 (br. s). <sup>13</sup>C VACP/MAS NMR:  $\delta$  21.2 (CH<sub>3</sub>), 24.3 (CH<sub>3</sub>), 26.1 (CH<sub>3</sub>), 27.6 (CH<sub>3</sub>), 46.8 (CH), 48.9 (CH), 114.5, 115.6, 123.2, 126.6, 127.4 (2 C), 129.6, 130.4 (2 C), 131.4, 132.5, 134.7, 139.1, 140.7 and 150.1 ( $C_6H_5$  and  $C_9H_6NO$ ), 170.3 (NCN). <sup>15</sup>N VACP/MAS NMR: δ -209.1 (NCN), -180.5 (NCN), -129.4 (C<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -200 to -160 (m). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>Br<sub>2</sub>N<sub>3</sub>OSi (535.35): C, 49.36; H, 4.71; N, 7.85. Found: C, 49.7; H, 4.9; N, 7.9.

Benzamidinatosilicon(IV) complex (4). (i) Potassium fluoride (195 mg, 3.36 mmol) was added at 20 °C in a single portion to a stirred mixture of 2 (600 mg, 1.34 mmol), 18-crown-6 (150 mg, 567 µmol) and acetonitrile (20 ml), and the reaction mixture was then stirred at this temperature for 72 h. The solvent was removed in vacuo, and toluene (20 ml) was added to the residue. The remaining solid was filtered off and discarded, and the solvent of the filtrate was removed in vacuo, followed by the addition of acetonitrile (5 ml). The resulting mixture 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 npentane  $(2 \times 5 \text{ ml})$  and dried *in vacuo*  $(20 \text{ }^{\circ}\text{C}, 3 \text{ h}, 0.01 \text{ mbar})$ . Yield: 237 mg (573  $\mu$ mol, 43%). Mp: >210 °C. <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.19 (br. s, 12 H, CH<sub>3</sub>), 3.42 (br. s, 2 H, CH), 7.29 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.7$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H, H7,  $C_9H_6NO$ , 7.30 (br. s, 2 H,  $o-C_6H_5$ ), 7.32 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$ Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H, H5, C<sub>9</sub>H<sub>6</sub>NO), 7.50–7.57 (m, 3 H, *m*- and *p*-C<sub>6</sub>*H*<sub>5</sub>), 7.63 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.3$  Hz,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.7$  Hz, 1 H, H6, C<sub>9</sub>H<sub>6</sub>NO), 7.66 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 5.1 Hz, 1 H, H3,  $C_9H_6NO$ , 8.45 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.3 \text{ Hz}, 1 \text{ H}, H4, C_{9}H_{6}\text{NO}, 9.10 \text{ (dd, } {}^{3}J({}^{1}H,{}^{1}H) =$ 5.1 Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.3$  Hz, 1 H, H2, C<sub>9</sub>H<sub>6</sub>NO).  ${}^{13}C\{{}^{1}H\}$  NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.9 (4 C) (m, CH<sub>3</sub>), 46.5 (2 C) (m, CH), 111.7 (C7, C<sub>9</sub>H<sub>6</sub>NO), 114.6 (C5, C<sub>9</sub>H<sub>6</sub>NO), 122.6 (C3,  $C_{9}H_{6}NO$ , 127.7 (br., 2 C) (*o*- $C_{6}H_{5}$ ), 128.7 (t,  ${}^{4}J({}^{19}F,{}^{13}C) = 2.1$ Hz, i-C<sub>6</sub>H<sub>5</sub>), 129.0 (C4a, C<sub>9</sub>H<sub>6</sub>NO), 130.5 (br., 3 C) (p- and m- $C_6H_5$ ), 131.3 (C6,  $C_9H_6NO$ ), 136.7 (C8a,  $C_9H_6NO$ ), 139.9 (C2,  $C_9H_6NO$ , 140.2 (C4,  $C_9H_6NO$ ) 154.0 (t,  ${}^{3}J({}^{19}F,{}^{13}C) = 2.6$  Hz, C8,

*C*<sub>9</sub>H<sub>6</sub>NO), 170.7 (t, <sup>3</sup>*J*(<sup>19</sup>F,<sup>13</sup>C) = 2.5 Hz, NCN). <sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –140.2 (br. s), –119.1 (br. s). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –161.4 (t, <sup>1</sup>*J*(<sup>29</sup>Si,<sup>19</sup>F) = 192 Hz). <sup>13</sup>C VACP/MAS NMR: δ 21.3 (*C*H<sub>3</sub>), 23.8 (*C*H<sub>3</sub>), 25.3 (2 C) (*C*H<sub>3</sub>), 45.1 (*C*H), 46.7 (*C*H), 112.3, 117.7, 122.7, 125.2, 127.8 (3 C), 129.2 (3 C), 132.7, 135.7, 138.7, 141.5 and 153.1 (*C*<sub>6</sub>H<sub>5</sub> and *C*<sub>9</sub>H<sub>6</sub>NO), 167.8 (*NCN*). <sup>15</sup>N VACP/MAS NMR: δ –217.8 (*NCN*), –190.8 (*NCN*), –125.5 (*C*<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR: δ –170 to –155 (m). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>F<sub>2</sub>N<sub>3</sub>OSi (413.54): C, 63.90; H, 6.09; N, 10.16. Found: C, 63.9; H, 6.0; N, 10.2.

(ii) Silver tetrafluoroborate (631 mg, 3.24 mmol) was added at 20 °C in a single portion to a stirred solution of **2** (724 mg, 1.62 mmol) and triethylamine (328 mg, 3.24 mmol) in tetrahydrofuran (20 ml), and the reaction mixture was then stirred at this temperature for 3 h. The resulting precipitate was filtered off and discarded, and the solvent of the filtrate was removed *in vacuo*, followed by the addition of acetonitrile (15 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 × 5 ml) and dried *in vacuo* (20 °C, 5 h, 0.01 mbar). Yield: 476 mg (1.15 mmol, 71%). The analytical data of the product match with those obtained for the product synthesised according to method (i).

Benzamidinatosilicon(IV) complex (5). Azidotrimethylsilane (1.03 g, 8.94 mmol) was added at 20 °C in a single portion to a stirred suspension of 2 (1.59 mg, 3.56 mmol) in acetonitrile (30 ml), and the reaction mixture was then stirred at this temperature for 17 h. The volatile constituents were removed in vacuo, and acetonitrile (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 °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 (20 °C, 4 h, 0.01 mbar). Yield: 1.53 g (3.33 mmol, 93%). Mp: >190 °C (dec.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -0.19 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8 \text{ Hz}, 3 \text{ H}, CH_{3}, 1.18 \text{ (d}, {}^{3}J({}^{1}H,{}^{1}H) = 6.8 \text{ Hz}, 3 \text{ H},$  $CH_3$ , 1.39 (d,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz, 3 H,  $CH_3$ ), 1.45 (d,  ${}^{3}J({}^{1}H, {}^{1}H) =$ 6.8 Hz, 3 H,  $CH_3$ ), 3.24 (sept,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz, 1 H, CH), 3.74 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 7.2 (br. s, 2 H, o- $C_6H_5$ , 7.29 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.7$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H,  $H7, C_9H_6NO), 7.41 \text{ (dd, } {}^{3}J({}^{1}H, {}^{1}H) = 8.4 \text{ Hz}, {}^{4}J({}^{1}H, {}^{1}H) = 0.9 \text{ Hz},$ 1 H, H5, C<sub>9</sub>H<sub>6</sub>NO), 7.51-7.60 (m, 3 H, p- and m-C<sub>6</sub>H<sub>5</sub>), 7.68 (dd, 1 H,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.4$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.7$  Hz, H6, C<sub>9</sub>H<sub>6</sub>NO), 7.72 (dd, 1 H,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.4$  Hz,  ${}^{3}J({}^{1}H, {}^{1}H) = 5.0$  Hz, H3,  $C_9H_6NO$ , 8.54 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.4$  Hz,  ${}^{4}J({}^{1}H, {}^{1}H) = 1.2$  Hz, 1 H, H4, C<sub>9</sub>H<sub>6</sub>NO), 9.00 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 5.0$  Hz,  ${}^{4}J({}^{1}H, {}^{1}H) = 1.2$ Hz, 1 H, H2, C<sub>9</sub>H<sub>6</sub>NO). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 21.8 (CH<sub>3</sub>), 22.2 (CH<sub>3</sub>), 22.8 (CH<sub>3</sub>), 23.5 (CH<sub>3</sub>), 46.4 (CH), 47.5 (CH), 112.2 (C7, C<sub>9</sub>H<sub>6</sub>NO), 115.5 (C5, C<sub>9</sub>H<sub>6</sub>NO), 122.7 (C3,  $C_9H_6NO$ , 127.0 (br., 2 C) ( $o-C_6H_5$ ), 127.9 ( $i-C_6H_5$ ), 129.0 (C4a, C<sub>9</sub>H<sub>6</sub>NO), 129.6 (br., 2 C) (*m*-C<sub>6</sub>H<sub>5</sub>), 131.0 (*p*-C<sub>6</sub>H<sub>5</sub>), 131.5 (C6, C<sub>9</sub>H<sub>6</sub>NO), 136.5 (C8a, C<sub>9</sub>H<sub>6</sub>NO), 139.8 (C2, C<sub>9</sub>H<sub>6</sub>NO), 140.8  $(C4, C_9H_6NO), 153.0 (C8, C_9H_6NO), 171.2 (NCN).$ <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –167.5. <sup>13</sup>C VACP/MAS NMR: δ 22.2 (3 C) (CH<sub>3</sub>), 24.1 (CH<sub>3</sub>), 45.2 (CH), 47.9 (CH), 111.0, 115.0, 121.7, 125.8, 128.9 (br., 4 C), 131.2 (2 C), 132.3, 135.4, 137.7, 141.2 and 152.3 ( $C_6H_5$  and  $C_9H_6NO$ ), 170.2 (NCN). <sup>15</sup>N VACP/MAS NMR: δ-299.8 (SiNNN), -293.2 (SiNNN), -218.0

(NCN), -208.5 (SiNNN), -204.5 (SiNNN), -187.2 (NCN), -133.0 (br., 2 N) (SiNNN), -130.4 (C<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -169.4. Anal. Calcd for C<sub>22</sub>H<sub>25</sub>N<sub>9</sub>OSi (459.59): C, 57.50; H, 5.48; N, 27.43. Found: C, 57.6; H, 5.6; N, 27.8.

Benzamidinatosilicon(IV) complex (6). Potassium cyanate (461 mg, 5.68 mmol) was added at 20 °C in a single portion to a stirred mixture of 2 (1.26 g, 2.82 mmol), 18-crown-6 (225 mg, 851  $\mu$ mol) and acetonitrile (50 ml), and the reaction mixture was then stirred at this temperature for 19 h. The solvent was removed in vacuo, and toluene (50 ml) was added to the residue. The remaining solid was filtered off and discarded, and the solvent of the filtrate was removed in vacuo, followed by the addition of acetonitrile (10 ml). The resulting mixture 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  $(20 \text{ }^\circ\text{C}, 4 \text{ h}, 0.01 \text{ m})$ mbar). Yield: 714 mg (1.55 mmol, 55%). Mp: >180 °C (dec.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –0.18 (br. d,  ${}^{3}J({}^{1}H,{}^{1}H)$  = 6.8 Hz, 3 H, CH<sub>3</sub>), 1.15 (br. d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 3 H, CH<sub>3</sub>), 1.39 (br. d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 3 H, CH<sub>3</sub>), 1.45 (br. d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 3 H, CH<sub>3</sub>), 3.18 (br. sept,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz, 1 H, CH), 3.77 (br. sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 7.26 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 7.6 Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.8$  Hz, 1 H, H7, C<sub>9</sub>H<sub>6</sub>NO), 7.29 (br. s, 2 H,  $o-C_6H_5$ , 7.40 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.3$  Hz,  ${}^{4}J({}^{1}H, {}^{1}H) = 0.8$  Hz, 1 H, H5, C<sub>9</sub>H<sub>6</sub>NO), 7.50–7.58 (m, 3 H, m- and p-C<sub>6</sub>H<sub>5</sub>), 7.67 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3 \text{ Hz}, {}^{3}J({}^{1}H,{}^{1}H) = 5.0 \text{ Hz}, 1 \text{ H}, H3, C_{9}H_{6}\text{NO}),$ 7.68 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.6$  Hz, 1 H, H6,  $C_9H_6NO$ , 8.51 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.2$  Hz, 1 H, H4, C<sub>9</sub>H<sub>6</sub>NO), 9.00 (br. dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 5.0$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H)$ not resolved, 1 H, H2, C<sub>9</sub>H<sub>6</sub>NO).  ${}^{13}C{}^{1}H{}$  NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.1 (CH<sub>3</sub>), 22.2 (CH<sub>3</sub>), 23.6 (br., 2 C) (CH<sub>3</sub>), 46.6 (CH), 47.4 (CH), 112.3 (C7, C<sub>9</sub>H<sub>6</sub>NO), 115.3 (C5, C<sub>9</sub>H<sub>6</sub>NO), 119.6 (br.) (NCO), 120.9 (br.) (NCO), 122.7 (C3, C<sub>9</sub>H<sub>6</sub>NO), 127.1 (br.) (o-C<sub>6</sub>H<sub>5</sub>), 127.4 (br.) (o-C<sub>6</sub>H<sub>5</sub>), 128.3 (i-C<sub>6</sub>H<sub>5</sub>), 129.1 (C4a, C<sub>9</sub>H<sub>6</sub>NO), 129.4 (br., 2 C) (*m*-C<sub>6</sub>H<sub>5</sub>), 130.9 (*p*-C<sub>6</sub>H<sub>5</sub>), 131.5 (C6,  $C_{9}H_{6}NO$ , 136.2 (C8a,  $C_{9}H_{6}NO$ ), 139.4 (C2,  $C_{9}H_{6}NO$ ), 140.4 (C4,  $C_9H_6NO$ ), 152.9 (C8,  $C_9H_6NO$ ), 170.2 (NCN). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz,  $CD_2Cl_2$ ):  $\delta$  –183.5 (br. s). <sup>13</sup>C VACP/MAS NMR:  $\delta$ 21.2 (CH<sub>3</sub>), 23.2 (2 C) (CH<sub>3</sub>), 26.9 (CH<sub>3</sub>), 45.6 (CH), 48.3 (CH), 112.0, 114.3, 118.5, 122.1, 127.2 (3 C), 128.9, 129.6, 130.9 (2 C), 135.1, 137.7, 140.5 and 152.1 (C<sub>6</sub>H<sub>5</sub> and C<sub>9</sub>H<sub>6</sub>NO), 170.9 (NCN), NCO resonance signals not detected. <sup>15</sup>N VACP/MAS NMR:  $\delta$ -319.9 (NCO), -314.8 (NCO), -218.4 (NCN), -188.0 (NCN), -127.3 (C<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -184.6. Anal. Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>5</sub>O<sub>3</sub>Si (459.58): C, 62.72; H, 5.48; N, 15.24. Found: C, 62.6; H, 5.5; N, 15.4.

**Benzamidinatosilicon(IV) complex (7).** Trimethyl(thiocyanato-N)silane (509 mg, 3.88 mmol) was added at 20 °C in a single portion to a stirred suspension of **2** (787 mg, 1.76 mmol) in acetonitrile (25 ml), and the reaction mixture was then stirred at this temperature for 18 h. The volatile constituents 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 yellow crystalline solid was isolated by filtration, washed with n-pentane  $(2 \times 5 \text{ ml})$  and dried *in vacuo* (20 °C, 4 h, 0.01 mbar). Yield: 682 mg (1.39 mmol, 79%). Mp: >170 °C (dec.).<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –0.15 (d,  ${}^{3}J({}^{1}H,{}^{1}H)$  = 6.8 Hz, 3 H, CH<sub>3</sub>), 1.18  $(d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 3 \text{ H}, CH_{3}), 1.43 (d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz},$ 3 H, CH<sub>3</sub>), 1.49 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 3 H, CH<sub>3</sub>), 3.22 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 3.82 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 7.2 (br. s, 2 H, o-C<sub>6</sub>H<sub>5</sub>), 7.32 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.7$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H, H7, C<sub>9</sub>H<sub>6</sub>NO), 7.47 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$ Hz,  ${}^{4}J({}^{1}H, {}^{1}H) = 0.9$  Hz, 1 H, H5, C<sub>9</sub>H<sub>6</sub>NO), 7.52–7.62 (m, 3 H, pand m-C<sub>6</sub> $H_5$ ), 7.72 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.3$  Hz,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.7$  Hz, 1 H, H6, C<sub>9</sub>H<sub>6</sub>NO), 7.75 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 5.1 Hz, 1 H, H3,  $C_9H_6NO$ , 8.59 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.3$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.2$  Hz, 1 H, H4, C<sub>9</sub>H<sub>6</sub>NO), 8.99 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 5.1 Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.2$  Hz, 1 H, H2, C<sub>9</sub>H<sub>6</sub>NO).  ${}^{13}C{}^{1}H$  NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 21.9 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 23.45 (CH<sub>3</sub>), 23.46 (CH<sub>3</sub>), 46.8 (CH), 47.9 (CH), 112.9 (C7, C<sub>9</sub>H<sub>6</sub>NO), 116.1 (C5, C<sub>9</sub>H<sub>6</sub>NO), 123.0 (C3, C<sub>9</sub>H<sub>6</sub>NO), 127.9 (br., 2 C) (o-C<sub>6</sub>H<sub>5</sub>), 129.0  $(i-C_6H_5)$ , 129.4 (br., 2 C)  $(m-C_6H_5)$  129.6 (C4a,  $C_9H_6NO$ ),  $130.0(p-C_6H_5), 131.3(C6, C_9H_6NO), 136.1(C8a, C_9H_6NO), 139.8$ (C2, C<sub>9</sub>H<sub>6</sub>NO), 141.4 (C4, C<sub>9</sub>H<sub>6</sub>NO), 151.9 (C8, C<sub>9</sub>H<sub>6</sub>NO), 171.9 (NCN), NCS resonance signals not detected. <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –189.3 (quint,  ${}^{1}J({}^{29}Si,{}^{14}N) = 20.5$  Hz). <sup>13</sup>C VACP/MAS NMR: δ 21.9 (CH<sub>3</sub>), 24.5 (CH<sub>3</sub>), 25.6 (CH<sub>3</sub>), 26.4 (CH<sub>3</sub>), 45.4 (CH), 48.5 (CH), 113.9, 117.9, 122.8, 124.4, 126.5, 127.1, 130.1, 132.9, (2 C), 135.1 (3 C), 140.1 (2 C) and 151.1 ( $C_6H_5$ ,  $C_9H_6NO$  and NCS), 172.4 (NCN). <sup>15</sup>N VACP/MAS NMR:  $\delta$  -234.1 (NCS), -231.3 (NCS), -218.6 (NCN), -195.3 (NCN), -130.6 (C<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR:  $\delta$  -190.2. Anal. Calcd for C<sub>24</sub>H<sub>25</sub>N<sub>5</sub>OS<sub>2</sub>Si (491.71): C, 58.62; H, 5.12; N, 14.24; S, 13.04. Found: C, 58.4; H, 5.1; N, 14.1; S, 13.1.

Benzamidinatosilicon(IV) complex (8). Trifluoromethanesulfonatotrimethylsilane (800 mg, 3.60 mmol) was added at 20 °C in a single portion to a stirred suspension of 2 (730 mg, 1.64 mmol) in acetonitrile (30 ml), and the reaction mixture was stirred at this temperature for 17 h. The volatile constituents 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 yellow crystalline solid was isolated by filtration, washed with n-pentane (2  $\times$  5 ml) and dried in vacuo (20 °C, 4 h, 0.01 mbar). Yield: 837 mg (1.24 mmol, 76%). Mp: >160 °C (dec.).<sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –0.16 (d, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz, 3 H, CH<sub>3</sub>), 0.90  $(d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 3 \text{ H}, CH_{3}), 1.35 (d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz},$ 3 H, CH<sub>3</sub>), 1.41 (d,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz, 3 H, CH<sub>3</sub>), 3.36 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 3.82 (sept,  ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$  Hz, 1 H, CH), 7.3 (br. s, 2 H, o-C<sub>6</sub>H<sub>5</sub>), 7.40 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.7$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9 \text{ Hz}, 1 \text{ H}, H7, C_{9}H_{6}\text{NO}), 7.55 \text{ (dd, }{}^{3}J({}^{1}H,{}^{1}H) = 8.4$ Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H, H5, C<sub>9</sub>H<sub>6</sub>NO), 7.56–7.68 (m, 3 H, pand m-C<sub>6</sub> $H_5$ ), 7.79 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.4$  Hz,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.7$  Hz, 1 H, H6, C<sub>9</sub>H<sub>6</sub>NO), 7.87 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.4$  Hz,  ${}^{3}J({}^{1}H,{}^{1}H) =$ 5.1 Hz, 1 H, H3, C<sub>9</sub> $H_6$ NO), 8.72 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.4$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.2 \text{ Hz}, 1 \text{ H}, H4, C_{9}H_{6}\text{NO}, 9.13 \text{ (dd, } {}^{3}J({}^{1}H,{}^{1}H) =$ 5.1 Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.2$  Hz, 1 H, H2, C<sub>9</sub>H<sub>6</sub>NO).  ${}^{13}C{}^{1}H$  NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 21.4 (CH<sub>3</sub>), 22.40 (CH<sub>3</sub>), 22.42 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>), 47.3 (CH), 48.4 (CH), 113.6 (C7, C<sub>9</sub>H<sub>6</sub>NO), 116.8 (C5,  $C_9H_6NO$ , 123.3 (C3,  $C_9H_6NO$ ), 127.4 (C4a,  $C_9H_6NO$ ), 126.8 (br., 2 C) (*o*- $C_6H_5$ ), 128.2 (br., 2 C) (*m*- $C_6H_5$ ), 128.7 (*i*- $C_6H_5$ ), 129.3 (br.) (CF<sub>3</sub>), 130.1 (br.) (CF<sub>3</sub>), 130.3 (*p*-C<sub>6</sub>H<sub>5</sub>), 131.8 (C6, C<sub>9</sub>H<sub>6</sub>NO),

 $136.6(C8a, C_9H_6NO), 140.6(C2, C_9H_6NO), 142.9(C4, C_9H_6NO),$ 151.2 (C8, C<sub>9</sub>H<sub>6</sub>NO), 174.8 (NCN).<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -78.53 (q,  $J({}^{19}F,{}^{19}F) = 1.7$  Hz, CF<sub>3</sub>), -78.31 (q,  $J({}^{19}\text{F}, {}^{19}\text{F}) = 1.7 \text{ Hz}, \text{ CF}_3). {}^{29}\text{Si}\{{}^{1}\text{H}\} \text{ NMR (99.4 MHz, CD}_2\text{Cl}_2): \delta$ -171.2. <sup>13</sup>C VACP/MAS NMR (data for two crystallographically independent molecules):  $\delta 20.6 (2 \text{ C}) (CH_3), 22.3 (4 \text{ C}) (CH_3), 23.2$ (2 C) (CH<sub>3</sub>), 42.6 (br., 4 C) (CH), 112.2 (3 C), 117.9, 119.5, 123.7, 125.0, 126.3 (2 C), 127.1 (3 C), 128.8 (6 C), 129.9 (5 C), 131.7 (3 C), 136.7 (2 C), 142.1, 142.8, 144.5, 145.0, 150.8 and 151.3 (CF<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> and C<sub>9</sub>H<sub>6</sub>NO), 174.2 (NCN), 175.1 (NCN). <sup>15</sup>N VACP/MAS NMR (data for two crystallographically independent molecules): δ-208.8 (2 N) (NCN), -200.9 (NCN), -199.4 (NCN), -140.7 (C<sub>9</sub>H<sub>6</sub>NO), -140.1 (C<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR (data for two crystallographically independent molecules):  $\delta$  –171.0 (2 Si). Anal. Calcd for C<sub>24</sub>H<sub>25</sub>F<sub>6</sub>N<sub>3</sub>O<sub>7</sub>S<sub>2</sub>Si (673.69): C, 42.79; H, 3.74; N, 6.24; S, 9.52. Found: C, 42.5; H, 3.8; N, 6.1; S, 9.6.

Benzamidinatosilicon(IV) complex (9). Triethylamine (592 mg, 5.85 mmol) and benzene-1,2-diol (321 mg, 2.92 mmol) were added at 20 °C in single portions one after another to a stirred solution of 2 (1.30 g, 2.91 mmol) in tetrahydrofuran (35 ml), and the reaction mixture was then stirred at this temperature for 16 h. The resulting precipitate was filtered off and discarded, and the solvent of the filtrate was removed in vacuo, followed by the addition of acetonitrile (35 ml). The resulting mixture was heated until a clear solution was obtained, which was then cooled slowly to 20 °C and kept undisturbed at this temperature for 5 d. The resulting yellow crystalline solid was isolated by filtration, washed with npentane  $(2 \times 5 \text{ ml})$  and dried in vacuo (20 °C, 3 h, 0.01 mbar). Yield: 971 mg (2.01 mmol, 69%). Mp: >180 °C (dec.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –0.2 to 1.4 (m, 12 H, CH<sub>3</sub>), 3.24–3.54 (m, 2 H, CH), 6.54–6.69 (m, 4 H,  $C_6H_4O_2$ ), 7.13 (dd,  ${}^{3}J({}^{1}H, {}^{1}H) =$ 7.7 Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H, H7, C<sub>9</sub>H<sub>6</sub>NO), 7.25 (br. s, 2 H,  $o-C_6H_5$ ), 7.30 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.4$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 0.9$  Hz, 1 H, H5, C<sub>9</sub>H<sub>6</sub>NO) 7.40-7.57 (m, 3 H, p- and m-C<sub>6</sub>H<sub>5</sub>), 7.58-7.65 (m, 2 H, H3 and H6,  $C_9H_6NO$ ), 8.48 (dd,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.4$ Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.2$  Hz, 1 H, H4, C<sub>9</sub>H<sub>6</sub>NO), 9.07 (br. dd, 1 H,  ${}^{3}J({}^{1}H,{}^{1}H)$  and  ${}^{4}J({}^{1}H,{}^{1}H)$  not resolved, H2, C<sub>9</sub>H<sub>6</sub>NO).  ${}^{13}C\{{}^{1}H\}$ NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 22.6 (3 C) (CH<sub>3</sub>), 22.5 (1 C) (CH<sub>3</sub>), 46.4 (2 C) (CH), 111.5 (C7, C<sub>9</sub>H<sub>6</sub>NO), 111.7 (br., 2 C)  $(C_6H_4O_2)$ , 113.8 (br., 2 C)  $(C_6H_4O_2)$ , 118.4 (C5,  $C_9H_6NO$ ), 122.5 (C3, C<sub>9</sub>H<sub>6</sub>NO), 127.6 (br., 2 C) (o-C<sub>6</sub>H<sub>5</sub>), 128.1 (br., 2 C) (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>), 128.9 (i- $C_6H_5$ ), 129.1 (C4a,  $C_9H_6NO$ ), 129.2 (br., 2 C) (m- $C_6H_5$ ), 130.5 (*p*-C<sub>6</sub>H<sub>5</sub>), 131.6 (*C*6, *C*<sub>9</sub>H<sub>6</sub>NO), 136.7 (*C*8a, *C*<sub>9</sub>H<sub>6</sub>NO), 140.8 (C4, C<sub>9</sub>H<sub>6</sub>NO), 142.4 (br.) (C2, C<sub>9</sub>H<sub>6</sub>NO) 150.9 (C8, C<sub>9</sub>H<sub>6</sub>NO), 170.9 (NCN). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –146.6. <sup>13</sup>C VACP/MAS NMR: *δ* 20.0 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 24.2 (CH<sub>3</sub>), 26.5 (CH<sub>3</sub>), 46.0 (br., 2 C) (CH), 109.3, 111.3 (3 C) 112.9, 118.2 (2 C), 122.6, 126.7 (2 C), 128.1, 129.1 (2 C), 130.3, 132.5, 137.1, 138.4, 142.9, 150.5, 152.8 and 154.6 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub> and C<sub>9</sub>H<sub>6</sub>NO), 172.6 (NCN). <sup>15</sup>N VACP/MAS NMR: δ-215.6 (NCN), -198.7 (NCN), -129.3 (C<sub>9</sub>H<sub>6</sub>NO). <sup>29</sup>Si VACP/MAS NMR: δ-145.9. Anal. Calcd for C<sub>28</sub>H<sub>29</sub>N<sub>3</sub>O<sub>3</sub>Si (483.64): C, 69.54; H, 6.04; N, 8.69. Found: C, 69.2; H, 5.9; N, 8.9.

#### Crystal structure analyses

Suitable single crystals of **2–9** were obtained as described in the synthetic procedures in the Experimental section. 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 (Stoe IPDS diffractometer, graphitemonochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å). All structures were solved by direct methods.<sup>9</sup> The non-hydrogen atoms were refined anisotropically.<sup>9</sup> A riding model was employed in the refinement of the *CH* hydrogen atoms. The crystallographic data for the structures are reported in the ESI.<sup>‡</sup>

#### **Results and discussion**

#### Syntheses

The pentacoordinate trichlorosilicon(IV) complex **1** was synthesised according to Scheme 2 by treatment of lithium N,N'-diisopropylbenzamidinate in diethyl ether with a small excess of tetrachlorosilane (yield 77%). Treatment of **1** with one molar equivalent of each 8-hydroxyquinoline and triethylamine in tetrahydrofuran afforded the hexacoordinate dichlorosilicon(IV) complex **2** (Scheme 2; yield 47%).



Scheme 2 Syntheses of compounds 1 and 2.

The hexacoordinate dibromosilicon(IV) complex **3** was prepared according to Scheme 3 by treatment of the corresponding dichlorosilicon(IV) complex **2** with an excess of bromotrimethylsilane in acetonitrile (yield 41%).



The hexacoordinate diffuorosilicon(IV) complex **4** was synthesised according to Scheme 4, starting from the corresponding dichlorosilicon(IV) complex **2**. Compound **4** was obtained by treatment of **2** either with (i) two molar equivalents of potassium fluoride in the presence of 18-crown-6 (yield 43%) or with (ii)



Scheme 4 Syntheses of compound 4.

two molar equivalents each of silver tetrafluoroborate and triethylamine (yield 71%). Acetonitrile and tetrahydrofuran, respectively, served as the solvent. The advantage of the second method is the higher yield (71% vs. 43%) and the much shorter reaction time (3 h vs. 72 h).

The hexacoordinate diazidosilicon(IV) complex **5** and its di(thiocyanato-N) analogue **7** were synthesised according to Scheme 5 by treatment of the corresponding dichlorosilicon(IV) complex **2** with an excess of azidotrimethylsilane and trimethyl(thiocyanato-N)silane, respectively, in acetonitrile (yields: **5**, 93%; **7**, 79%).



Scheme 5 Syntheses of compounds 5 and 7.

Surprisingly, the synthetic method used for the preparation of **3**, **5** and **7** could not be applied to the synthesis of the analogous di(cyanato-N)silicon(IV) complex **6**. After treatment of **2** with an excess of (cyanato-N)trimethylsilane only the starting materials could be reisolated (identification of **2** and Me<sub>3</sub>SiNCO by NMR spectroscopy). However, compound **6** could be synthesised according to Scheme 6 by treatment of **2** with two molar equivalents of potassium cyanate in the presence of 18-crown-6 (yield 55%). Acetonitrile served as the solvent.

The two chloro ligands of 2 could not only be substituted by (pseudo)halogeno ligands. Treatment of the hexacoordinate dichlorosilicon(IV) complex 2 with an excess of trimethyl(trifluoromethanesulfonato)silane in acetonitrile accord-



Scheme 6 Synthesis of compound 6.

ing to Scheme 7 resulted in the formation of the corresponding bis(trifluoromethanesulfonato)silicon(IV) complex **8** (yield 76%).



Scheme 7 Synthesis of compound 8.

Furthermore, it was possible to substitute the two monoanionic chloro ligands of **2** by one dianionic bidentate benzene-1,2-diolato ligand. Thus, treatment of the hexacoordinate dichlorosilicon(IV) complex **2** with one molar equivalent of benzene-1,2-diol and two molar equivalents of triethylamine in tetrahydrofuran according to Scheme 8 afforded the corresponding (benzene-1,2-diolato)silicon(IV) complex **9** (yield 69%).



Scheme 8 Synthesis of compound 9.

Compound 1 was isolated as a colorless crystalline solid, whereas 2–9 were obtained as yellow crystalline solids. All compounds are sensitive against water, and 2–9 are additionally sensitive against light and have to be stored in the dark to prevent slow decomposition.

The identities of **1–9** were established by elemental analyses (C, H, N, S), NMR-spectroscopic studies in the solid state ( ${}^{13}C$ ,  ${}^{15}N$ ,  ${}^{29}Si$ ) and in solution ( ${}^{1}H$ ,  ${}^{13}C$ ,  ${}^{19}F$ ,  ${}^{29}Si$ ) and by crystal structure analyses (except for **1**).

#### Crystal structure analyses

Compounds **2–9** were structurally characterised by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for the crystal structure analyses are given in Tables 1 and 2. The molecular structures of **2–9** are shown in Fig. 1–8; selected bond lengths and angles are given in the respective figure legends.

The Si-coordination polyhedra of the hexacoordinate silicon(IV) complexes **2–9** are distorted octahedra, with maximum deviations

# Table 1 Crystallographic data for compounds 2–5

Compound	2	3	4	5
Empirical formula	C <sub>22</sub> H <sub>25</sub> Cl <sub>2</sub> N <sub>3</sub> OSi	C <sub>22</sub> H <sub>25</sub> Br <sub>2</sub> N <sub>3</sub> OSi	$C_{22}H_{25}F_2N_3OSi$	C <sub>22</sub> H <sub>25</sub> N <sub>9</sub> OSi
Formula mass/g mol <sup>-1</sup>	446.44	535.36	413.54	459.60
T/K	173(2)	173(2)	173(2)	173(2)
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group (no.)	$P2_{1}/c$ (14)	P1 (2)	$P2_{1}/c$ (14)	$P\overline{1}(2)$
a/Å	15.6475(14)	8.1749(16)	14.657(2)	9.3090(19)
b/Å	9.7128(8)	9.919(2)	9.7605(8)	9.898(2)
c/Å	15.3985(16)	14.424(3)	15.470(2)	14.013(3)
$\alpha /^{\circ}$	90	94.61(3)	90	109.12(3)
$\beta/^{\circ}$	107.087(11)	102.42(3)	110.049(16)	94.07(3)
$\gamma/^{\circ}$	90	95.80(3)	90	98.48(3)
V/Å	2237.0(4)	1130.1(4)	2079.0(4)	1196.8(4)
Ζ	4	2	4	2
$ ho_{ m calcd}/ m g~ m cm^{-1}$	1.326	1.573	1.321	1.275
$\mu/\text{mm}^{-1}$	0.362	3.658	0.149	0.132
F(000)	936	540	872	484
Crystal dimensions/mm	$0.5 \times 0.4 \times 0.2$	$0.5 \times 0.2 \times 0.2$	$0.5 \times 0.4 \times 0.3$	$0.5 \times 0.5 \times 0.5$
$2\theta$ range/°	5.02-58.16	4.82-58.22	5.02-55.76	6.20-58.26
Index ranges	$-21 \le h \le 21,$	$-11 \le h \le 11$ ,	$-19 \le h \le 19,$	$-11 \le h \le 12$ ,
-	$-13 \le k \le 13$ ,	$-13 \le k \le 13,$	$-12 \le k \le 12$ ,	$-13 \le k \le 13$ ,
	$-21 \le l \le 21$	$-19 \le l \le 19$	$-19 \le l \le 19$	$-19 \le l \le 19$
Number of collected reflections	31467	16443	15548	13488
Number of independent reflections	5956	5566	4918	5854
R <sub>int</sub>	0.0425	0.0448	0.0369	0.0328
Number of parameters	266	266	266	302
$S^a$	1.066	1.077	1.040	1.102
Weight parameters <i>a/b<sup>b</sup></i>	0.0522/0.7972	0.0722/0.5002	0.0553/0.5034	0.0544/0.4103
$R_1^{c} \left[ I > 2\sigma(I) \right]$	0.0386	0.0381	0.0371	0.0401
$wR_2^d$ (all data)	0.1029	0.1191	0.1025	0.1196
Max./min. residual electron density/e Å <sup>-3</sup>	+0.372/-0.398	+0.644/-0.936	+0.307/-0.301	+0.412/-0.390

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



Fig. 1 Molecular structure of 2 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Cl(1) 2.1738(6), Si–Cl(2) 2.1977(5), Si–O 1.7411(12), Si–N(1) 1.9043(13), Si–N(2) 1.8840(13), Si–N(3) 2.0062(13), N(1)–C(1) 1.3233(19), N(2)–C(1) 1.3384(19); Cl(1)–Si–Cl(2) 93.52(2), Cl(1)–Si–O 95.60(5), Cl(1)–Si–N(1) 164.39(4), Cl(1)–Si–N(2) 95.47(4), Cl(1)–Si–N(3) 90.49(4), Cl(2)–Si–N(3) 49.04(4), Cl(2)–Si–N(1) 90.42(4), Cl(2)–Si–N(2) 94.76(4), Cl(2)–Si–N(3) 173.05(4), O–Si–N(1) 99.57(6), O–Si–N(2) 168.06(6), O–Si–N(3) 84.92(5), N(1)–Si–N(2) 69.14(6), N(1)–Si–N(3) 87.21(5), N(2)–Si–N(3) 90.50(5), Si–N(1)–C(1) 91.29(9), Si–N(2)–C(1) 91.70(9), N(1)–C(1)–N(2) 107.72(13).

from the ideal 90° and 180° angles ranging from 19.70(7)– $21.39(6)^{\circ}$  and 15.22(8)–18.78(7)°, respectively (Table 3). These strong distortions mainly result from the highly strained four-



Fig. 2 Molecular structure of 3 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Br(1) 2.3750(10), Si–Br(2) 2.3703(12), Si–O 1.739(2), Si–N(1) 1.899(3), Si–N(2) 1.861(2), Si–N(3) 1.987(3), N(1)–C(1) 1.327(4), N(2)–C(1) 1.342(4); Br(1)–Si–Br(2) 92.42(5), Br(1)–Si–O 95.18(8), Br(1)–Si–N(1) 164.78(8), Br(1)–Si–N(2) 95.85(8), Br(1)–Si–N(3) 87.44(8), Br(2)–Si–O 90.58(9), Br(2)–Si–N(1) 92.59(10), Br(2)–Si–N(2) 93.85(9), Br(2)–Si–N(3) 175.71(8), O–Si–N(1) 99.13(11), O–Si–N(2) 167.93(12), O–Si–N(3) 85.17(11), N(1)–Si–N(2) 69.48(11), N(1)–Si–N(3) 88.62(12), N(2)–Si–N(3) 90.43(11), Si–N(1)–C(1) 91.25(19), Si–N(2)–C(1) 92.46(18), N(1)–C(1)–N(2) 106.8(2).

membered SiN<sub>2</sub>C ring formed by the amidinato ligand and the silicon coordination centre, with N–Si–N angles ranging from  $68.61(6)^{\circ}$  to  $70.30(7)^{\circ}$ . The two (pseudo)halogeno ligands of

#### Table 2 Crystallographic data for compounds 6–9

Compound	6	7	8	9
Empirical formula	C24H25N5O3Si	C24H25N5OS2Si	$C_{24}H_{25}F_6N_3O_7S_2Si$	C28H29N3O3Si
Formula mass/g mol <sup>-1</sup>	459.58	491.70	673.68	483.63
T/K	173(2)	173(2)	173(2)	173(2)
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group (no.)	$P\overline{1}(2)$	$P2_{1}/c$ (14)	<i>Pbca</i> (61)	$P2_{1}/n$ (14)
a/Å	8.4742(17)	11.5619(18)	23.2733(16)	10.9237(17)
b/Å	10.239(2)	13.4356(18)	16.3163(10)	18.318(2)
c/Å	13.933(3)	16.906(3)	30.800(3)	13.7567(19)
$\alpha/^{\circ}$	94.55(3)	90	90	90
$\beta/^{\circ}$	101.63(3)	109.346(18)	90	111.285(16)
$\gamma/^{\circ}$	95.44(3)	90	90	90
V/Å	1172.8(4)	2478.0(7)	11695.7(16)	2564.9(6)
Z	2	4	16	4
$\rho_{\rm calcd}/{\rm g~cm^{-1}}$	1.301	1.318	1.530	1.252
$\mu/\text{mm}^{-1}$	0.136	0.290	0.309	0.126
F(000)	484	1032	5536	1024
Crystal dimensions/mm	$0.5 \times 0.5 \times 0.4$	$0.5 \times 0.5 \times 0.2$	$0.50 \times 0.25 \times 0.25$	$0.5 \times 0.3 \times 0.1$
$2\theta$ range/°	6.00-58.18	4.84-58.20	4.50-56.20	5.46-55.76
Index ranges	$-11 \le h \le 11$ ,	$-15 \le h \le 15$ ,	$-30 \le h \le 30$ ,	$-14 \le h \le 14$ ,
c	$-14 \le k \le 14$ ,	$-18 \le k \le 18$ ,	$-21 \le h \le 21$ ,	$-24 \le k \le 24,$
	$-19 \le l \le 19^{\circ}$	$-23 \le l \le 23$	$-40 \le h \le 40$	$-16 \le l \le 18$
Number of collected reflections	16905	35139	148865	21567
Number of independent reflections	5726	6609	14160	6122
R <sub>int</sub>	0.0348	0.0457	0.0584	0.0801
Number of parameters	302	302	798	320
Number of restraints	0	0	15	0
Sa	1.087	1.052	1.062	0.945
Weight parameters $a/b^b$	0.0549/0.3588	0.0541/0.8993	0.0610/5.5732	0.0669/0.0000
$R_{l}^{c} [I > 2\sigma(I)]$	0.0429	0.0424	0.0439	0.0438
$wR_2^d$ (all data)	0.1236	0.1159	0.1211	0.1159
Max./min. residual electron density/e Å <sup>-3</sup>	+0.350/-0.400	+0.346/-0.410	+0.666/-0.626	+0.319/-0.281

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



Fig. 3 Molecular structure of 4 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–F(1) 1.5708(9), Si–F(2) 1.6880(9), Si–O 1.7881(11), Si–N(1) 1.8488(11), Si–N(2) 1.9364(12), Si–N(3) 2.0834(12), N(1)–C(1) 1.3536(18), N(2)–C(1) 1.2823(16); F(1)–Si–F(2) 93.90(5), F(1)–Si–O 98.63(5), F(1)–Si–N(1) 161.31(5), F(1)–Si–N(2) 93.70(5), F(1)–Si–N(3) 89.19(5), F(2)–Si–N(3) 174.25(5), O–Si–N(1) 95.72(5), F(2)–Si–N(2) 99.07(5), F(2)–Si–N(3) 87.88(5), N(1)–Si–N(2) 68.97(5), N(1)–Si–N(2) 82.71(5), N(2)–Si–N(3) 85.56(5), Si–N(1)–C(1) 91.72(8), Si–N(2)–C(1) 90.07(9), N(1)–C(1)–N(2) 108.86(11).

2–7, the two trifluoromethanesulfonato ligands of 8 and the two

oxygen ligand atoms of the benzene-1,2-diolato ligand of 9 occupy

*cis* positions, with X–Si–X angles (X = F, Cl, Br, N, O) ranging from 86.48(7)° to 93.90(5)°. The nitrogen atoms of the bidentate N,N ligand and N,O ligand of **2–9** show a *fac* arrangement, and in all cases the nitrogen atom of the N,O ligand and one of the (pseudo)halogeno/trifluoromethanesulfonato ligand atoms of **2– 8** (or one of the oxygen atoms of the benzene-1,2-diolato ligand of **9**) are found in *trans* position. Thus, the structures of the chiral silicon(IV) complexes **2–9** ( $C_1$  symmetry) are characterised by the same configuration. Both enantiomers of **2–9** are found in the crystal.

The Si–O (oxygen atom of the *N*, *O* ligand) bond lengths of **2–9** are in the range 1.7157(14)–1.7881(11) Å (maximum difference *ca.* 0.07 Å) (Table 4). The Si–N(3) (nitrogen atom of the *N*, *O* ligand) are significantly longer and show a higher degree of variation (1.9556(16)–2.0834(12) Å; maximum difference *ca.* 0.13 Å) (Table 4). The Si–N(1) and Si–N(2) (*N*, *N* ligand) bond lengths are in the range 1.8439(16)–1.9364(12) Å (maximum difference *ca.* 0.09 Å) (Table 4). The differences in the bond lengths of the analogous Si–O, Si–N(1), Si–N(2) and Si–N(3) bonds of **2–9** may be the result of both substituent effects and crystal packing effects and are therefore difficult to discuss.

# NMR studies

Compounds **1–9** were characterised by NMR spectroscopy in the solid state (<sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si) and in solution (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>29</sup>Si; solvent,



Fig. 4 Molecular structure of 5 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O 1.7563(11), Si–N(1) 1.9126(12), Si–N(2) 1.8698(13), Si–N(3) 2.0037(15), Si–N(4) 1.8512(13), Si–N(5) 1.8465(15), N(4)–N(6) 1.2109(17), N(5)–N(8) 1.2054(18), N(6)–N(7) 1.140(2), N(8)–N(9) 1.142(2), N(1)–C(1) 1.3206(17), N(2)–C(1) 1.3374(17); O–Si–N(1) 99.23(6), O–Si–N(2) 167.73(5), O–Si–N(3) 84.43(5), O–Si–N(4) 96.30(6), O–Si–N(5) 91.19(6), Si–N(4)–N(6) 119.09(11), Si–N(5)–N(8) 123.28(10), N(1)–Si–N(2) 68.98(5), N(1)–Si–N(3) 87.53(6), N(1)–Si–N(4) 162.95(6), N(1)–Si–N(5) 93.70(7), N(2)–Si–N(3) 91.46(6), N(2)–Si–N(4) 95.02(6), N(2)–Si–N(5) 92.93(6), N(3)–Si–N(4) 87.01(6), N(3)–Si–N(5) 175.59(5), N(4)–Si–N(5) 92.96(6), Si–N(4)–N(6) 119.09(11), N(4)–N(6)–N(7) 176.72(17), Si–N(5)–N(8) 123.28(10), N(5)–N(8)–N(9) 175.28(16), Si–N(1)–C(1) 91.09(8), Si–N(2)–C(1) 92.44(8), N(1)–C(1)–N(2) 107.40(11).



Fig. 5 Molecular structure of 6 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si-O(1) 1.7594(13), Si-N(1) 1.9128(13), Si-N(2) 1.8789(15), Si-N(3) 2.0114(14), Si-N(4) 1.8054(14), Si-N(5) 1.8136(15), O(2)-C(23) 1.1821(19), O(3)-C(24) 1.186(2), N(4)-C(23) 1.1712(19), N(5)-C(24) 1.152(2), N(1)-C(1) 1.319(2), N(2)-C(1) 1.3424(19); O(1)-Si-N1 96.52(6), O(1)-Si-N(2) 164.30(6), O(1)-Si-N(3) 84.40(6), O(1)-Si-N(4) 95.71(7), O(1)-Si-N(5) 91.27(7), Si-N(4)-C(23) 150.63(14), Si-N(5)-C(24) 158.70(15), O(2)-C(23)-N(4) 176.68(19), O(3)-C(24)-N(5) 177.9(2), N(1)-Si-N(2) 68.98(6), N(1)-Si-N(3) 87.99(6), N(1)-Si-N(4) 166.42(7), N(1)-Si-N(5) 92.82(7), N(2)-Si-N(3) 88.95(6), N(2)-Si-N(4) 98.18(7), N(2)-Si-N(5) 95.32(7), N(3)-Si-N(4) 87.34(7), N(3)-Si-N(5) 175.66(7), N(4)-Si-N(5) 92.79(7), Si-N(4)-C(23) 150.63(14), N(4)-C(23)-O(2) 176.68(19), Si-N(5)-C(24) 158.70(15), N(5)-C(24)-O(3) 177.9(2), Si-N(1)-C(1) 91.32(10), Si-N(2)-C(1) 92.06(10), N(1)-C(1)-N(2) 107.61(13).

 $CD_2Cl_2$ ). The NMR data obtained (see Experimental section) confirm the identities of the compounds studied.



Fig. 6 Molecular structure of 7 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O 1.7401(13), Si–N(1) 1.8901(13), Si–N(2) 1.8717(14), Si–N(3) 2.0038(15), Si–N(4) 1.8256(14), Si–N(5) 1.8272(16), S(1)–C(23) 1.5999(17), S(2)–C(24) 1.6051(19), N(4)–C(23) 1.167(2), N(5)–C(24) 1.171(2), N(1)–C(1) 1.3243(19), N(2)–C(1) 1.3409(19); O–Si–N(1) 100.62(6), O–Si–N(2) 169.47(6), O–Si–N(3) 84.76(6), O–Si–N(4) 94.37(6), O–Si–N(5) 88.78(7), N(1)–Si–N(2) 69.47(6), N(1)–Si–N(3) 90.83(6), N(1)–Si–N(4) 164.64(6), N(1)–Si–N(5) 91.12(7), N(2)–Si–N(3) 91.68(6), N(2)–Si–N(4) 95.34(6), N(2)–Si–N(5) 94.81(7), N(3)–Si–N(4) 87.18(6), N(3)–Si–N(5) 173.50(7), N(4)–Si–N(5) 92.55(7), Si–N(4)–C(23) 173.87(14), N(4)–C(23)–S(1) 179.13(17), Si–N(5)–C(24) 162.69(15), N(5)–C(24)–S(2) 179.61(18), Si–N(1)–C(1) 91.44(10), Si–N(2)–C(1) 91.73(9), N(1)–C(1)–N(2) 107.08(13).

As can be seen from Table 5, the respective isotropic <sup>29</sup>Si chemical shifts in the solid state and in solution are very similar, indicating that the penta- and hexacoordinate silicon(IV) complexes **1–9** also exist in solution. This assumption is further supported by all the other NMR data obtained. The isotropic <sup>29</sup>Si chemical shifts of the hexacoordinate silicon(IV) complexes **2–9** vary from -145.9/-146.6 ppm (**9**, solid state/solution) to -190.2/-189.3 ppm (**7**, solid state/solution), indicating a strong dependence of the <sup>29</sup>Si chemical shift on the different silicon-bound ligands.

The <sup>29</sup>Si VACP/MAS NMR spectra of the dihalogenosilicon(IV) complexes **2–4** deserve a special discussion (Fig. 9; in this context, see also ref. 2). Notably, the spectrum of **2** shows a relatively sharp resonance signal although one would expect <sup>29</sup>Si,<sup>35</sup>Cl and <sup>29</sup>Si,<sup>37</sup>Cl couplings (in this context, see ref. 4*e*). In contrast, the spectrum of **3** is characterised by a broad asymmetric "triplet" owing to dipolar <sup>29</sup>Si,<sup>79</sup>Br and <sup>29</sup>Si,<sup>81</sup>Br couplings,<sup>10</sup> and in the case of **4**, <sup>29</sup>Si,<sup>19</sup>F couplings lead to a complex resonance signal (for similar splitting patterns in the <sup>29</sup>Si MAS NMR spectra of other compounds with SiF<sub>2</sub> moieties, see ref. 2 and 11).

Due to the  $C_1$  symmetry of the hexacoordinate silicon(IV) complexes **2–9**, the four methyl groups of their amidinato ligand are diastereotopic. Therefore, four doublets for these methyl groups and two septets for the  $(CH_3)_2CH$  protons are observed in the solution <sup>1</sup>H NMR spectra at 23 °C (**2**, **5–8**) or lower temperatures (**3**, **4**, **9**) (Fig. 10). Quite remarkably, one of the four doublets of **2–9** is found at *ca.* –0.15 ppm and is shifted by *ca.* 1.1–1.5 ppm to higher field compared to the other three doublets. This can be explained by the influence of the diamagnetic ring current of the aromatic ring system of the *N*, *O* ligand on one of the four methyl groups. Indeed, as can be seen from the molecular



Fig. 7 Molecular structures of the two crystallographically independent molecules of 8 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°] of molecule A (top): Si(1)-O(1) 1.7157(14), Si(1)-O(2) 1.7984(14), Si(1)-O(3) 1.8081(14), Si(1)-N(1) 1.8666(17), Si(1)-N(2) 1.8439(16), Si(1)-N(3) 1.9622(17), N(1)-C(1) 1.331(2), N(2)-C(1) 1.334(2); O(1)-Si(1)-O2 96.95(7), O(1)-Si(1)-O(3) 88.24(7), O(2)-Si(1)-O(3) 87.11(7), O(1)-Si(1)-N(1) 101.83(7), O(1)–Si(1)–N(2) 172.11(8), O(1)–Si(1)–N(3) 86.00(7), O(2)-Si(1)-N(1) 161.22(7), O(2)-Si(1)-N(2) 90.92(7), O(2)-Si(1)-N(3) 90.33(7), O(3)-Si(1)-N(1) 93.68(7), O(3)-Si(1)-N(2) 92.77(7), O(3)-Si(1)-N(3) 173.38(7), N(1)-Si(1)-N(2) 70.30(7), N(1)-Si(1)-N(3) 90.71(7), N(2)-Si(1)-N(3) 93.38(7), Si(1)-N(1)-C(1) 91.09(12), Si(1)-N(2)-C(1) 91.99(11), N(1)-C(1)-N(2) 106.61(16). Selected bond lengths [Å] and angles [°] of molecule B (bottom): Si(2)–O(31) 1.7228(14), Si(2)-O(32) 1.7872(14), Si(2)-O(33) 1.7945(14), Si(2)-N(31) 1.8493(16), Si(2)-N(32) 1.8713(17), Si(2)-N(33) 1.9556(16), N(31)-C(31) 1.331(2), N(32)-C(31) 1.329(2), O(31)-Si(2)-O(32) 97.70(7), O(31)-Si(2)-O(33) 88.88(7), O(32)-Si(2)-O(33) 86.48(7), O(31)-Si(2)-N(31) 98.51(7), O(31)-Si(2)-N(32) 168.52(7), O(31)-Si(2)-N(33) 86.31(7), O(32)-Si(2)-N(31) 163.71(7), O(32)–Si(2)–N(32) 93.70(7), O(32)–Si(2)–N(33) 88.45(7), O(33)-Si(2)-N(31) 95.40(7), O(33)-Si(2)-N(32) 93.23(7), O(33)-Si(2)-N(33) 172.49(7), N(31)–Si(2)–N(32) 70.06(7), N(31)–Si(2)–N(33) 91.02(7), N(32)-Si(2)-N(33) 92.62(7), Si(2)-N(31)-C(31) 92.02(11), Si(2)-N(32)-C(31) 91.10(11), N(31)-C(31)-N(32) 106.82(16).



**Table 3** Maximum deviations of the X–Si–X angles (X = ligand atoms) of 2-9 from the ideal 90° and 180° angles

Compound	$\Delta 90^{\circ}$	$\Delta 180^{\circ}$	Skeleton
2	20.86(6)	15.61(4)	SiN <sub>3</sub> OCl <sub>2</sub>
3	20.52(11)	15.22(8)	SiN <sub>3</sub> OBr <sub>2</sub>
4	21.03(5)	18.69(5)	SiN <sub>3</sub> OF <sub>2</sub>
5	21.02(5)	17.05(6)	SiN <sub>5</sub> O
6	21.02(6)	13.58(7)	SiN <sub>5</sub> O
7	20.53(6)	15.36(6)	SiN <sub>5</sub> O
<b>8</b> (A)	19.70(7)	18.78(7)	$SiN_3O_3$
8(B)	19.94(7)	16.29(7)	$SiN_3O_3$
9	21.39(6)	15.79(6)	$SiN_3O_3$

Table 4Selected bond lengths [Å] of 2–9

Compound	Si–O	Si-N(1)	Si-N(2)	Si–N(3)	Skeleton
2	1.7411(12)	1.9043(13)	1.8840(13)	2.0062(13)	SiN <sub>3</sub> OCl <sub>2</sub>
3	1.739(2)	1.899(3)	1.861(2)	1.987(3)	SiN <sub>3</sub> OBr <sub>2</sub>
4	1.7881(11)	1.8488(11)	1.9364(12)	2.0834(12)	SiN <sub>3</sub> OF <sub>2</sub>
5	1.7563(11)	1.9126(12)	1.8698(13)	2.0037(15)	<i>Si</i> N₅O
6	1.7594(13)	1.9128(13)	1.8789(15)	2.0114(14)	SiN5O
7	1.7401(13)	1.8901(13)	1.8717(14)	2.0038(15)	SiN5O
<b>8</b> <sup>a</sup>	1.7157(14) <sup>b</sup>	$1.8666(17)^{c}$	$1.8439(16)^d$	1.9622(17) <sup>e</sup>	$SiN_3O_3$
<b>8</b> <sup>f</sup>	$1.7228(14)^{g}$	$1.8493(16)^{h}$	$1.8713(17)^{i}$	1.9556(16) <sup>j</sup>	$SiN_3O_3$
9	1.7762(12)	1.9026(13)	1.9144(13)	1.9975(14)	$SiN_3O_3$
<sup><i>a</i></sup> Molecule	A. <sup>b</sup> Si(1)-	O(1). <sup>c</sup> Si(1	)–N(1). <sup>d</sup> Si	(1)–N(2). <sup>e</sup>	Si(1)–N(3).
<sup>f</sup> Molecule E	B. g Si(2)–O(3	1). <sup>h</sup> Si(2)–N	(31). <sup><i>i</i></sup> Si(2)–1	N(32). <sup><i>j</i></sup> Si(2)	–N(33).

structures of 2-9 in the crystal (see Crystal structure analyses section), one of the four methyl groups each is in proximity of the aromatic ring system. This finding indicates that the structures of 2-9 in the solid state and in solution are similar.

**Table 5** Comparison of the <sup>29</sup>Si chemical shifts [ppm] of **1–9** in the solid state ( $T = 22 \degree$ C) and in solution ( $T = 23 \degree$ C)

Compound	$\delta^{\scriptscriptstyle 29}{ m Si}$ (solid state)	$\delta^{\scriptscriptstyle 29}{ m Si}({ m solution})^a$	
1	-99.4	-98.2	
2	-165.2	-162.4	
3	-200 to -160 <sup>b</sup>	-190	
4	$-170$ to $-155^{\circ}$	$-161.4^{d}$	
5	-169.4	-167.5	
6	-184.6	-183.5	
7	-190.2	-189.3 <sup>e</sup>	
8	-171.0	-171.2	
9	-145.9	-146.6	

<sup>*a*</sup> Solvent, CD<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup> Complex signal splitting due to dipolar <sup>29</sup>Si,<sup>79</sup>Br and <sup>29</sup>Si,<sup>81</sup>Br couplings.<sup>9</sup> <sup>*c*</sup> Complex signal splitting due to dipolar couplings within the <sup>29</sup>Si<sup>19</sup>F<sub>2</sub> unit.<sup>2,11</sup> <sup>*d*</sup> Triplet, <sup>1</sup>J(<sup>29</sup>Si,<sup>19</sup>F) = 192 Hz. <sup>*e*</sup> Quintet, <sup>1</sup>J(<sup>29</sup>Si,<sup>14</sup>N) = 20.5 Hz.

Coalescence of the four doublets and the two septets to one broad signal each at 23 °C (**4**, **9**) or above (**3**) could be explained by a simultaneous exchange of the two nitrogen sites of the amidinato ligand and the two binding sites of the N,O ligand, which breaks the  $C_1$  symmetry of the complexes (Fig. 10). Upon cooling, sharp resonance signals were observed for the diffuorosilicon(IV) complex **4** (Fig. 10).

The solution <sup>1</sup>H NMR spectra of **2–9** show broadened resonance signals for the *ortho* and *meta* protons of the phenyl group of the amidinato ligand at 23 °C. This can be explained by a not completely hindered rotation of the phenyl group around the *i*-C–CN<sub>2</sub> bond, which is further supported by broadened resonance signals for the *ortho* and *meta* carbon atoms in the <sup>13</sup>C NMR spectra. The temperature dependence of the <sup>1</sup>H NMR resonance signals is shown exemplarily for **4** in Fig. 10.

In addition to the above mentioned findings for compounds 3, 4 and 9, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3 and 9 also show broadened resonance signals for the bidentate N,O ligand, for the resonance signals of the silicon coordination centre, and in the case of 9 for the bidentate O,O ligand. While the broadened resonance signals of compound 3 just become sharp at lower temperature (-60 °C), a complete second set of resonance signals is observed in the respective <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra of 9 at this temperature (ratio, 1:4), indicating the presence of two



Fig. 9 <sup>29</sup>Si VACP/MAS NMR spectra ( $v_{rot} = 7 \text{ kHz}$ ,  $T = 22 \degree \text{C}$ ) of 2 (A), 3 (B) and 4 (C).

diastereomers. These results can be explained by configurational instability of 9 in solution at room temperature resulting in a fast exchange between the two diastereomers; at lower temperatures this exchange becomes slower and both diastereomers can be observed (Fig. 11).

The <sup>29</sup>Si NMR spectrum of the diffuorosilicon(IV) complex **4** in solution at 23 °C shows a triplet (Fig. 12), indicating a dynamic process, which renders the two  ${}^{1}J({}^{29}\text{Si},{}^{19}\text{F})$  coupling constants equal on the NMR time scale. However, at -50 °C a doublet of doublets is found, reflecting the presence of two slightly different  ${}^{1}J({}^{29}\text{Si},{}^{19}\text{F})$  coupling constants (Fig. 12).

Analogously to the <sup>29</sup>Si NMR spectrum, the <sup>19</sup>F NMR spectrum of **4** also shows a temperature dependence (Fig. 13). While at 23 °C two very broad resonance signals are found, at -50 °C an AX system (<sup>2</sup>*J*(<sup>19</sup>F,<sup>19</sup>F) = 22.3 Hz) is observed, again reflecting the non-equivalence of the two fluoro ligands.



Fig. 10 Temperature dependence of the <sup>1</sup>H NMR resonance signals of the  $CH_3CHCH_3$  protons (right), the  $CH_3CHCH_3$  protons (middle) and the protons of the aromatic rings (left, partial spectra) of 4 (solvent,  $CD_2Cl_2$ ; 500.1 MHz). The temperature dependence of the <sup>1</sup>H NMR spectra is completely reversible upon heating/cooling.



**Fig. 11** Temperature dependence of the <sup>29</sup>Si NMR spectrum of **9** (solvent,  $CD_2Cl_2$ ; 99.4 MHz). The temperature dependence of the <sup>29</sup>Si NMR spectrum is completely reversible upon heating/cooling.



**Fig. 12** Temperature dependence of the <sup>29</sup>Si NMR spectrum of **4** (solvent,  $CD_2Cl_2$ ; 99.4 MHz). The temperature dependence of the <sup>29</sup>Si NMR spectrum is completely reversible upon heating/cooling.

The <sup>19</sup>F NMR spectrum of the bis(trifluoromethanesulfonato)silicon(rv) complex **8** shows two quartets at 23 °C  $(J(^{19}F,^{19}F) = 1.7$  Hz, Fig. 14). As <sup>19</sup>F,<sup>19</sup>F NOESY NMR experiments did not indicate interactions between the two trifluoromethyl groups, the <sup>19</sup>F,<sup>19</sup>F coupling observed may result from through-bond interactions (<sup>8</sup>J(<sup>19</sup>F,<sup>19</sup>F) coupling); however, it cannot be excluded that through-space interactions are not monitored by the NOE experiments. The <sup>19</sup>F NMR spectrum shown in Fig. 14 does not suggest an exchange of the two trifluoromethylsulfonato ligands at ambient temperature as observed for the two fluoro ligands of **4** (see above), but <sup>19</sup>F,<sup>19</sup>F EXSY NMR experiments with **8** at 23 °C indicate such kind of exchange process (Fig. 15). Cross peaks between the two trifluoromethyl signals were observed at 23 °C, and at 60 °C the extent of exchange increases, whereas at -60 °C no cross peaks could be observed at all.

While the <sup>29</sup>Si NMR spectrum of the di(cyanato-*N*)silicon(IV) complex **6** in solution shows a relatively sharp singlet at 23 °C, a well resolved quintet ( ${}^{1}J({}^{29}Si, {}^{14}N)$  couplings) is found for the di(thiocyanato-*N*) analogue **7** (Fig. 16). Obviously, only the nitrogen atoms of the two thiocyanato-*N* ligands seem to be responsible for this signal splitting (in this context, see also ref. 12). These differences in the <sup>29</sup>Si NMR spectra of the NCO/NCS analogues **6** (singlet) and **7** (quintet,  ${}^{1}J({}^{29}Si, {}^{14}N)$  coupling) are not yet fully understood but it seems that in complex **6** the quadrupolar relaxation of the  ${}^{14}N$  nuclei is the dominant relaxation process,



**Fig. 13** Temperature dependence of the <sup>19</sup>F NMR spectrum of **4** (solvent,  $CD_2Cl_2$ ; 282.4 MHz). For reasons of visibility, the spectrum at 23 °C has been scaled up by a factor of 60. The temperature dependence of the <sup>19</sup>F NMR spectrum is completely reversible upon heating/cooling.



Fig. 14 <sup>19</sup>F NMR spectrum of 8 at 23 °C (solvent, CD<sub>2</sub>Cl<sub>2</sub>; 376.5 MHz).



Fig. 15  $^{19}$ F, $^{19}$ F EXSY NMR spectrum of 8 at 23  $^{\circ}$ C (solvent, CD<sub>2</sub>Cl<sub>2</sub>; 282.4 MHz).



Fig. 16  $^{29}$ Si NMR spectra of 6 (left) and 7 (right) at 23 °C (solvent, CD<sub>2</sub>Cl<sub>2</sub>; 99.4 MHz).

while in compound 7 the quadrupolar relaxation of the <sup>14</sup>N nuclei is less dominant due to a much smaller electric field gradient, so that the <sup>1</sup> $J({}^{29}\text{Si},{}^{14}\text{N})$  coupling becomes observable.

# Conclusions

With the synthesis of compounds 2–9, a series of novel neutral hexacoordinate monoamidinatosilicon(IV) complexes with  $SiN_3OF_2$ ,  $SiN_3OCl_2$ ,  $SiN_3OBr_2$ ,  $SiN_5O$  and  $SiN_3O_3$  skeletons has been made available. Compounds 3 ( $SiN_3OBr_2$  skeleton), 4 ( $SiN_3OF_2$ ) and 5–7 ( $SiN_5O$ ) are of particular interest as neutral hexacoordinate silicon(IV) complexes with such Si-coordination polyhedra have not yet been reported in the literature. Compound 9 ( $SiN_3O_3$  skeleton) shows also remarkable structural features: this heteroleptic hexacoordinate silicon(IV) complex contains three different bidentate ligands.

To the best of our knowledge, compound 1 (prepared from tetrachlorosilane in a one-step synthesis) is the first neutral pentacoordinate monoamidinatosilicon(IV) complex ( $SiN_2Cl_3$  skeleton) that has been used as a starting material for the synthesis of neutral hexacoordinate silicon(IV) complexes. It has been demonstrated that the dichlorosilicon(IV) complex 2 is a versatile precursor for the synthesis of other neutral hexacoordinate silicon(IV) complexes (compounds 3–9) by substitution of the two chloro ligands by other mono- or bidentate ligands. In the targeted three-step syntheses of 3–9 (SiCl<sub>4</sub>  $\rightarrow$  1  $\rightarrow$  2  $\rightarrow$  3–9), the *N*,*N*'-diisopropylbenzamidinato ligand has been demonstrated to have a high synthetic potential for the chemistry of hexacoordinate silicon(IV) complexes.

Compounds 2-9 show a relatively high thermal stability although they contain a highly strained four-membered SiN<sub>2</sub>C ring, with N-Si-N angles in the range 68.61(6)° to 70.30(7)°. Compounds 2-9 exist both in the solid state and in solution. Their molecular structures ( $C_1$  symmetry) are best described in terms of distorted octahedral Si-coordination polyhedra, with the two (pseudo)halogeno/trifluoromethanesulfonato ligands and the benzene-1,2-diolato ligand atoms, respectively, in cis positions. The nitrogen atoms of the bidentate N,N and N,O ligands of 2–9 adopt a fac arrangement, and the nitrogen atom of the N,O ligand and one of the (pseudo)halogeno/trifluoromethanesulfonato ligands (or one of the oxygen atoms of the benzene-1,2-diolato ligand) are found in *trans* positions; *i.e.*, all compounds studied show the same stereochemical features. According to NMR spectroscopic studies, it is likely that the structures of 2-9 in the solid state and in solution are very similar.

As shown by NMR spectroscopic studies, the free rotation of the phenyl group of 2-9 around the *i*-C-CN<sub>2</sub> bond is

hindered in solution at ambient temperature. In addition, the NMR spectroscopic investigations (including VT and EXSY experiments) revealed the existence of different exchange processes in solution: (i) exchange of the two nitrogen sites of the N,N ligand, (ii) exchange of the nitrogen and oxygen sites of the N,O ligand (leading to diastereomeric species), and (iii) exchange of the two monodentate ligands. The activation barriers of these processes depend on the nature of the two monodentate (pseudo)halogeno/trifluoromethanesulfonato ligand (or the bidentate benzene-1,2-diolato ligand). The mechanism of these exchange processes are coupled with each other.

In conclusion, the amidinato ligand system has been demonstrated to have a high synthetic potential for the chemistry of penta- and hexacoordinate silicon, allowing the synthesis of novel types of element combinations in the silicon coordination sphere (in this context, see also ref. 2) and leading to novel types of static and dynamic stereochemistry.

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