

# Neutral Pentacoordinate Halogeno- and Pseudohalogenosilicon(IV) Complexes with an SiSONCX Skeleton (X = F, Cl, Br, I, N, C): Synthesis and Structural Characterization in the Solid State and in Solution

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday*

**Abstract:** A series of neutral pentacoordinate silicon(IV) complexes with an SiSONCX skeleton (X = F, Cl, Br, I, N, or C) was synthesized and structurally characterized by multinuclear solution-state and solid-state NMR spectroscopy and single-crystal X-ray diffraction. These compounds contain an identical tridentate dianionic *S,N,O* ligand, a monodentate (pseudo)halogeno ligand (F, Cl, Br, I, NCS, N<sub>3</sub>, or

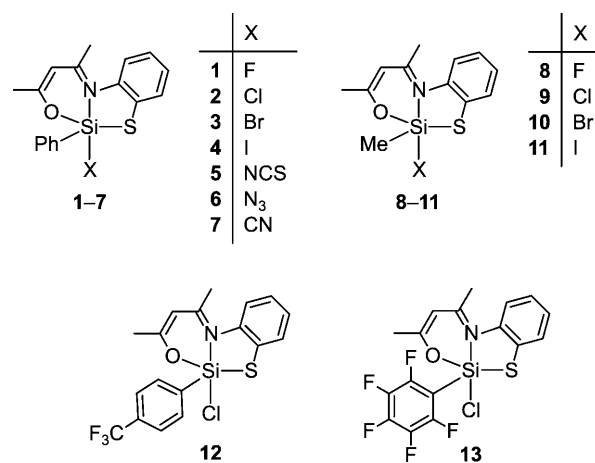
CN), and a monodentate organyl ligand (methyl, phenyl, 4-(trifluoromethyl)phenyl, or pentafluorophenyl). For most of these compounds, a dynamic equilibrium between the pentacoordinate silicon(IV) complex and

two isomeric tetracoordinate silicon species in solution was observed. Most surprisingly, comparison of two series of analogous compounds containing fluoro, chloro, bromo, or iodo ligands demonstrated that pentacoordination in these series of silicon(IV) complexes is favored in the rank order I ≈ Br > Cl > F; i.e., increasing the softness of the halogeno ligand favors pentacoordination.

**Keywords:** halogens • pentacoordination • pseudohalogens • silicon • tridentate ligands

## Introduction

Most of the penta- and hexacoordinate silicon(IV) complexes reported in the literature contain hard ligand atoms, such as fluorine, chlorine, oxygen, nitrogen, and/or carbon.<sup>[1,2]</sup> In recent years, new perspectives for the chemistry of higher-coordinate silicon have been generated by introducing soft chalcogen ligand atoms (sulfur, selenium, tellurium) into the silicon(IV) coordination sphere.<sup>[2r,s,3]</sup> In this context, the neutral pentacoordinate silicon(IV) complex **2** (SiSONCCl skeleton) has been synthesized and structurally characterized both in the solid state and in solution.<sup>[3e]</sup> Compound **2** is a versatile starting material for the synthesis of other neutral pentacoordinate silicon(IV) complexes with novel SiSONCX skeletons (X = O,<sup>[2r,3e]</sup> S,<sup>[2s]</sup> Se,<sup>[2s]</sup> Te,<sup>[2s]</sup> I<sup>[3e]</sup>). For example, treatment of the chlorosilicon(IV) complex **2** with iodotrimethylsilane yields the corresponding iodosi-



con(IV) complex **4** (SiSONCI skeleton).<sup>[3e]</sup> In continuation of these studies, we have now succeeded in synthesizing the related halogeno- and pseudohalogenosilicon(IV) complexes **1** (SiSONCF skeleton), **3** (SiSONCBr), **5** (SiSON<sub>2</sub>C), **6** (SiSON<sub>2</sub>C), and **7** (SiSONC<sub>2</sub>). In addition, we have synthesized compounds **8** (SiSONCF skeleton), **9** (SiSONCCl), **10** (SiSONCBr), and **11** (SiSONCI), which represent derivatives of **1-4** (formal Ph/Me exchange). Furthermore, we have succeeded in synthesizing compounds **12** and **13** (Si-

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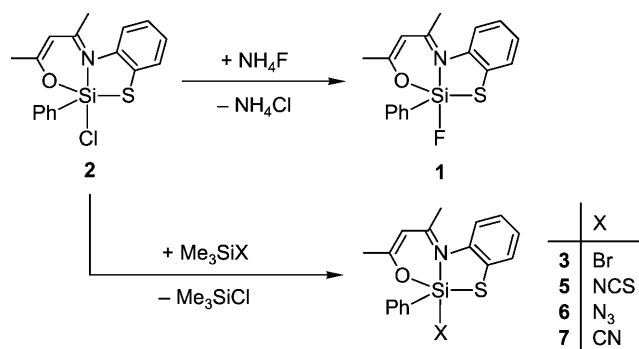
SONCCI skeletons), which are derivatives of **2** and **9** that contain a 4-(trifluoromethyl)phenyl or pentafluorophenyl moiety instead of the silicon-bound phenyl and methyl group, respectively.

The aim of this study was to get information about the impact of the halogeno/pseudohalogeno ligands of **1–7** and **8–11** on the structure of these compounds in the solid state and in solution. In context with the structures in solution, the potential equilibrium between these pentacoordinate silicon(IV) complexes and their corresponding isomeric tetra-coordinate species (see also reference [2s]) was of particular interest. Furthermore, we made comparison of compounds **1–4** (SiPh group, electron-withdrawing) with their corresponding analogues **8–11** (SiMe group, electron-donating) to get information about the importance of the silicon-bound organyl substituent of these compounds on the above-mentioned parameters. In this context, a comparison of the related compounds **2** (phenyl substituent), **12** (4-(trifluoromethyl)phenyl), and **13** (pentafluorophenyl) was also of great interest.

We report here on the synthesis of compounds **1**, **3**, and **5–13** and their structural characterization in the solid state (crystal structure analysis, solid-state NMR spectroscopy) and in solution (NMR spectroscopy). For reasons of comparison, compounds **2**<sup>[3e]</sup> and **4**<sup>[3e]</sup> were included in these studies.

## Results and Discussion

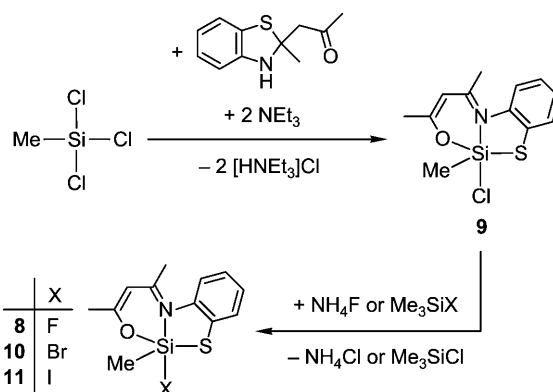
**Syntheses:** The fluorosilicon(IV) complex **1** was synthesized by treatment of **2** with ammonium fluoride in tetrahydrofuran (Scheme 1). The related (pseudo)halogenosilicon(IV)



Scheme 1. Synthesis of compounds **1**, **3**, and **5–7**.

complexes **3** and **5–7** were obtained by reaction of **2** with the corresponding (pseudo)halogenotrimethylsilane Me<sub>3</sub>SiX (**3**, X = Br; **5**, X = NCS; **6**, X = N<sub>3</sub>; **7**, X = CN) in acetonitrile.

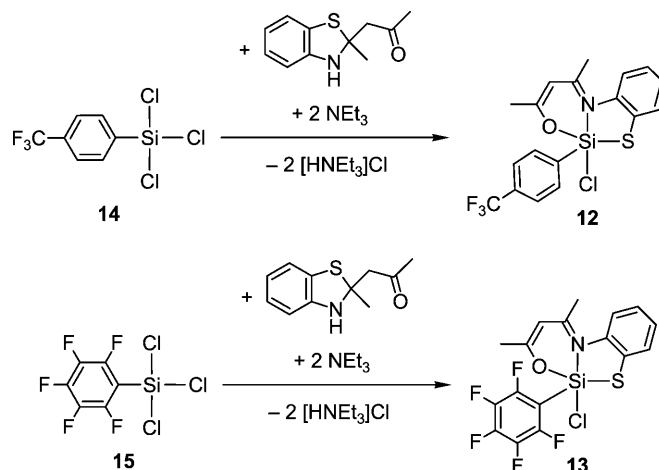
The chlorosilicon(IV) complex **9** was obtained by treatment of trichloro(methyl)silane with one molar equivalent of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one and two molar equivalents of triethylamine in tetrahydrofuran (Scheme 2). The derivatives **8**, **10**, and **11** were pre-



Scheme 2. Synthesis of compounds **8–11**.

pared analogously to **1**, **3**, and **4**, respectively, starting from **9**.

Compounds **12** and **13** were obtained analogously to the synthesis of **9** by treatment of trichloro[4-(trifluoromethyl)phenyl]silane (**14**) and trichloro(pentafluorophenyl)silane (**15**), respectively, with one molar equivalent of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one and two molar equivalents of triethylamine in tetrahydrofuran (Scheme 3).



Scheme 3. Synthesis of compounds **12** and **13**.

Compounds **1**, **3**, and **5–13** were isolated as yellow to orange-colored crystalline solids (yields: **1**, 57%; **3**, 71%; **5**, 86%; **6**, 71%; **7**, 61%; **8**, 13% **9**, 65%; **10**, 68%; **11**, 55%; **12**, 65%; **13**, 59%). Their identities were established by using elemental analyses (C, H, N, S), multinuclear solution-state and solid-state NMR spectroscopy, and single-crystal X-ray diffraction.

**Crystal structure analyses:** Compounds **1**, **3**, and **5–13** were structurally characterized 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 **1**, **3**, and **5–13** in the crystal are

Table 1. Crystallographic data for compounds **1**, **3**, and **5–8**.

	<b>1</b>	<b>3</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
empirical formula	C <sub>17</sub> H <sub>16</sub> FNOSSi	C <sub>17</sub> H <sub>16</sub> BrNOSSi	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Si	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> OSSi	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> OSSi	C <sub>12</sub> H <sub>14</sub> FNOSSi
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	329.46	390.37	368.54	352.49	336.48	267.39
<i>T</i> [K]	101(2)	100(2)	193(2)	193(2)	193(2)	173(2)
$\lambda$ (MoK $\alpha$ ) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group (no.)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (19)
<i>a</i> [Å]	7.7154(3)	10.8252(3)	11.4651(17)	10.9851(9)	12.321(3)	8.5019(15)
<i>b</i> [Å]	15.0871(6)	8.6426(2)	12.7092(13)	9.8585(8)	10.077(2)	9.9818(13)
<i>c</i> [Å]	13.6716(5)	17.4284(4)	12.4947(17)	15.2287(13)	14.083(3)	15.248(2)
$\beta$ [°]	97.699(2)	96.076(2)	90.558(17)	91.742(10)	105.27(3)	90
<i>V</i> [Å <sup>3</sup> ]	1577.07(10)	1621.40(7)	1820.5(4)	1648.5(2)	1686.7(6)	1294.1(3)
<i>Z</i>	4	4	4	4	4	4
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.388	1.599	1.345	1.420	1.325	1.372
$\mu$ [mm <sup>-1</sup> ]	0.292	2.738	0.365	0.281	0.268	0.338
<i>F</i> (000)	688	792	768	736	704	560
crystal dimensions [mm]	0.34 × 0.29 × 0.21	0.22 × 0.13 × 0.11	0.4 × 0.4 × 0.4	0.5 × 0.5 × 0.5	0.4 × 0.3 × 0.2	0.5 × 0.5 × 0.4
2 $\theta$ range [°]	4.04–72.48	3.78–56.64	5.78–56.08	4.92–56.22	5.30–58.10	4.88–58.14
index ranges	–11 ≤ <i>h</i> ≤ 12, –25 ≤ <i>k</i> ≤ 24, –22 ≤ <i>l</i> ≤ 21	–14 ≤ <i>h</i> ≤ 14, –11 ≤ <i>k</i> ≤ 11, –23 ≤ <i>l</i> ≤ 23	–15 ≤ <i>h</i> ≤ 15, –16 ≤ <i>k</i> ≤ 16, –16 ≤ <i>l</i> ≤ 16	–14 ≤ <i>h</i> ≤ 14, –13 ≤ <i>k</i> ≤ 13, –20 ≤ <i>l</i> ≤ 20	–16 ≤ <i>h</i> ≤ 16, –13 ≤ <i>k</i> ≤ 13, –19 ≤ <i>l</i> ≤ 19	–11 ≤ <i>h</i> ≤ 11, –13 ≤ <i>k</i> ≤ 13, –20 ≤ <i>l</i> ≤ 20
reflns collected	78402	49475	20657	18696	20593	18671
independent reflns	7571	4043	4374	3951	4431	3444
<i>R</i> <sub>int</sub>	0.0581	0.0502	0.0494	0.0268	0.0407	0.0359
parameters	201	201	219	219	210	157
<i>S</i> <sup>[a]</sup>	1.091	1.052	1.047	1.039	1.061	1.074
weight parameters <i>a/b</i> <sup>[b]</sup>	0.0444/0.3882	0.0302/0.7958	0.0674/0.2605	0.0504/0.6042	0.0632/0.1056	0.0384/0.4512
<i>R</i> <sub>1</sub> <sup>[c]</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0302	0.0206	0.0407	0.0339	0.0343	0.0302
<i>wR</i> <sub>2</sub> <sup>[d]</sup> (all data)	0.0900	0.0575	0.1119	0.0915	0.0984	0.0770
Flack parameter						–0.01(7)
max./min. residual electron density [e Å <sup>-3</sup> ]	+0.587/–0.290	+0.503/–0.304	+0.331/–0.508	+0.387/–0.402	+0.331/–0.199	+0.284/–0.227

[a]  $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$ ; *n* = number of reflections; *p* = number of parameters. [b]  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , with  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ . [c]  $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ . [d]  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$ .

Table 2. Crystallographic data for compounds **9–13**.

	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>
empirical formula	C <sub>12</sub> H <sub>14</sub> CINOSSi	C <sub>12</sub> H <sub>14</sub> BrNOSSi	C <sub>12</sub> H <sub>14</sub> INOSSi	C <sub>18</sub> H <sub>15</sub> ClF <sub>3</sub> NOSSi	C <sub>17</sub> H <sub>11</sub> ClF <sub>3</sub> NOSSi
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	283.84	328.30	375.29	413.91	435.87
<i>T</i> [K]	100(2)	100(2)	193(2)	193(2)	173(2)
$\lambda$ (MoK $\alpha$ ) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group (no.)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (19)
<i>a</i> [Å]	17.9248(8)	18.1454(13)	11.067(2)	8.1896(10)	11.1904(10)
<i>b</i> [Å]	8.5692(3)	8.6297(6)	8.9631(18)	14.650(3)	12.4881(17)
<i>c</i> [Å]	18.1280(8)	18.1794(12)	14.945(3)	14.984(2)	12.7298(12)
$\beta$ [°]	107.924(2)	108.843(4)	99.94(3)	93.838(16)	90
<i>V</i> [Å <sup>3</sup> ]	2649.34(19)	2694.1(3)	1460.2(5)	1793.7(5)	1778.9(3)
<i>Z</i>	8	8	4	4	4
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.423	1.619	1.707	1.533	1.627
$\mu$ [mm <sup>-1</sup> ]	0.519	3.278	2.403	0.433	0.457
<i>F</i> (000)	1184	1328	736	848	880
crystal dimensions [mm]	0.13 × 0.07 × 0.03	0.3 × 0.3 × 0.1	0.5 × 0.4 × 0.2	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.3
2 $\theta$ range [°]	2.80–62.64	3.86–56.98	5.32–58.16	5.56–58.18	4.56–58.12
index ranges	–25 ≤ <i>h</i> ≤ 25, –12 ≤ <i>k</i> ≤ 12, –26 ≤ <i>l</i> ≤ 26	–24 ≤ <i>h</i> ≤ 23, –11 ≤ <i>k</i> ≤ 11, –23 ≤ <i>l</i> ≤ 24	–15 ≤ <i>h</i> ≤ 15, –11 ≤ <i>k</i> ≤ 11, –20 ≤ <i>l</i> ≤ 20	–10 ≤ <i>h</i> ≤ 10, –20 ≤ <i>k</i> ≤ 20, –20 ≤ <i>l</i> ≤ 20	–15 ≤ <i>h</i> ≤ 12, –17 ≤ <i>k</i> ≤ 17, –16 ≤ <i>l</i> ≤ 17
reflns collected	112870	49700	20260	25507	13702
independent reflns	8564	6555	3744	4576	4704
<i>R</i> <sub>int</sub>	0.0559	0.0477	0.0342	0.0322	0.0508
parameters	313	314	157	237	246
<i>S</i> <sup>[a]</sup>	1.033	1.071	1.096	1.110	1.067
weight parameters <i>a/b</i> <sup>[b]</sup>	0.0294/1.5730	0.0284/3.7850	0.0376/0.9388	0.0524/0.5376	0.0571/0.2612
<i>R</i> <sub>1</sub> <sup>[c]</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0323	0.0306	0.0258	0.0327	0.0351
<i>wR</i> <sub>2</sub> <sup>[d]</sup> (all data)	0.0781	0.0758	0.0681	0.0927	0.0949
Flack parameter					0.00(6)
max./min. residual electron density [e Å <sup>-3</sup> ]	+0.442/–0.302	+0.644/–0.860	+0.452/–0.891	+0.406/–0.353	+0.350/–0.465

[a]  $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$ ; *n* = number of reflections; *p* = number of parameters. [b]  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , with  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ . [c]  $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ . [d]  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$ .

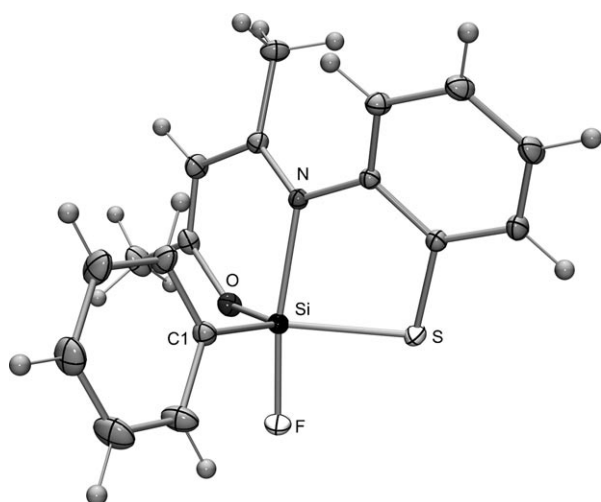


Figure 1. Molecular structure of **1** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S 2.1712(3), Si–F 1.6687(5), Si–O 1.6967(6), Si–N 2.0096(6), Si–C1 1.8745(7); S–Si–F 86.725(19), S–Si–O 123.28(2), S–Si–N 85.126(18), S–Si–C1 121.82(2), F–Si–O 87.59(3), F–Si–N 168.46(3), F–Si–C1 97.11(3), O–Si–N 90.06(3), O–Si–C1 114.89(3), N–Si–C1 94.13(3).

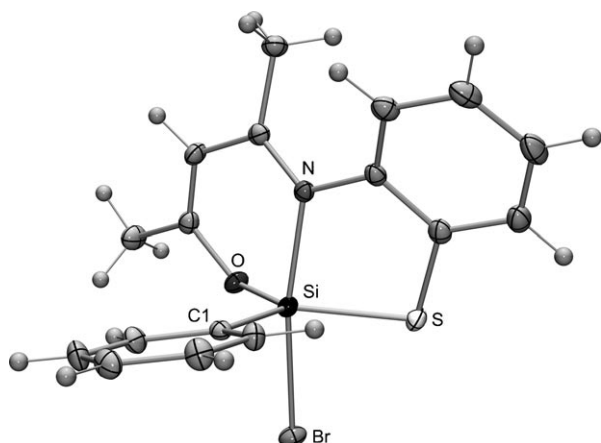


Figure 2. Molecular structure of **3** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Br 2.4051(4), Si–S 2.1501(5), Si–O 1.6802(10), Si–N 1.9851(12), Si–C1 1.8579(13); Br–Si–S 84.544(15), Br–Si–O 86.78(4), Br–Si–N 167.41(3), Br–Si–C1 97.63(4), S–Si–O 127.61(4), S–Si–N 86.51(4), S–Si–C1 119.83(4), O–Si–N 91.71(5), O–Si–C1 112.51(5), N–Si–C1 94.50(5).

shown in Figures 1–11; selected bond lengths and angles are given in the respective figure legends.

The Si-coordination polyhedra of the neutral pentacoordinate silicon(IV) complexes **1**, **3**, and **5–13** are similar to those of **2** and **4** and are best described as distorted trigonal bipyramids. The sulfur and oxygen atoms of the tridentate *S,N,O* ligand and the carbon atom of the respective organyl substituent occupy the equatorial positions, whereas the nitrogen atom of the tridentate *S,N,O* ligand and the (pseudo)halogeno ligand occupy the two axial positions. The axial N–Si–X angles (X = F, Cl, Br, I, NCS, N<sub>3</sub>, CN) of **1–13** are in

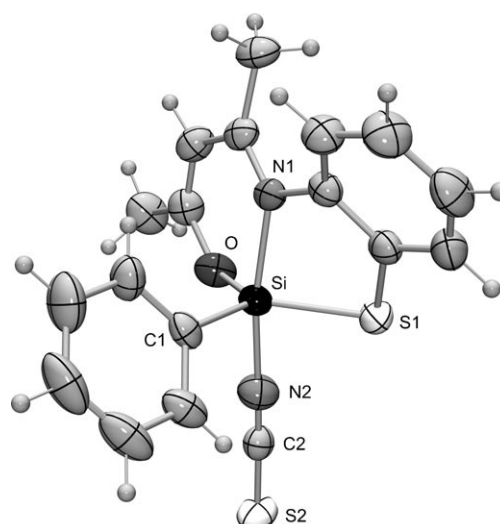


Figure 3. Molecular structure of **5** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S1 2.1548(7), Si–O 1.6788(13), Si–N1 1.9684(13), Si–N2 1.8729(17), Si–C1 1.8697(16), N2–C2 1.138(2), C2–S2 1.6082(18); S1–Si–O 128.49(5), S1–Si–N1 86.48(4), S1–Si–N2 86.62(6), S1–Si–C1 116.66(6), O–Si–N1 91.90(6), O–Si–N2 85.03(7), O–Si–C1 114.76(7), N1–Si–N2 168.30(7), N1–Si–C1 95.24(7), N2–Si–C1 96.31(8), Si–N2–C2 175.23(16), N2–C2–S2 178.33(17).

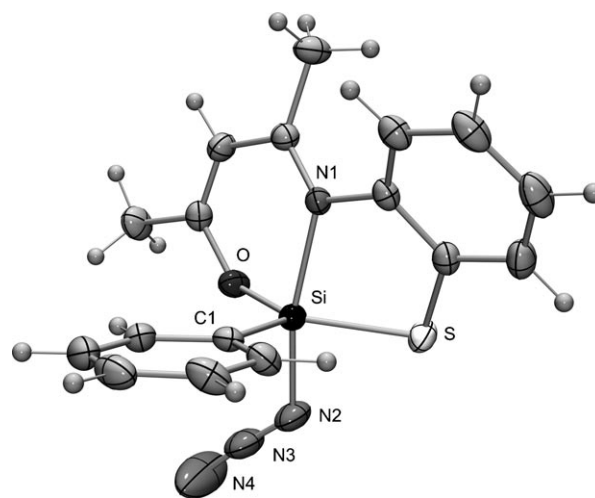


Figure 4. Molecular structure of **6** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S 2.1537(5), Si–O 1.6768(10), Si–N1 2.0071(12), Si–N2 1.8573(14), Si–C1 1.8507(14), N2–N3 1.134(2), N3–N4 1.137(3); S–Si–O 133.52(4), S–Si–N1 84.88(4), S–Si–N2 84.35(5), S–Si–C1 116.73(5), O–Si–N1 90.38(5), O–Si–N2 88.90(6), O–Si–C1 109.71(6), N1–Si–N2 164.41(6), N1–Si–C1 93.65(5), N2–Si–C1 101.24(7), Si–N2–N3 128.66(12), N2–N3–N4 174.6(2).

Table 3. Comparison of the Si–X (X = F, Cl, Br, I) bond lengths [Å] of **1–4** and **8–11**.

Compounds	Si–F	Si–Cl	Si–Br	Si–I
<b>1–4</b>	1.6687(5)	2.1954(4) <sup>[a]</sup>	2.4051(4)	2.7396(8) <sup>[a]</sup>
<b>8–11</b>	1.6673(12)	2.2158(5), 2.2273(5) <sup>[b]</sup>	2.4291(8), 2.4469(8) <sup>[b]</sup>	2.8225(7)

[a] Ref. [3e]. [b] *Molecules I and II*.



Figure 5. Molecular structure of **7** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S 2.1834(6), Si–O 1.6979(9), Si–N1 1.9451(13), Si–C1 1.8681(12), Si–C2 1.9563(16), C2–N2 1.150(2); S–Si–O 138.61(4), S–Si–N1 84.96(3), S–Si–C1 114.48(4), S–Si–C2 84.24(4), O–Si–N1 91.43(5), O–Si–C1 106.87(5), O–Si–C2 87.01(5), N1–Si–C1 97.78(5), N1–Si–C2 161.73(5), C1–Si–C2 100.09(6), Si–C2–N2 175.22(13).

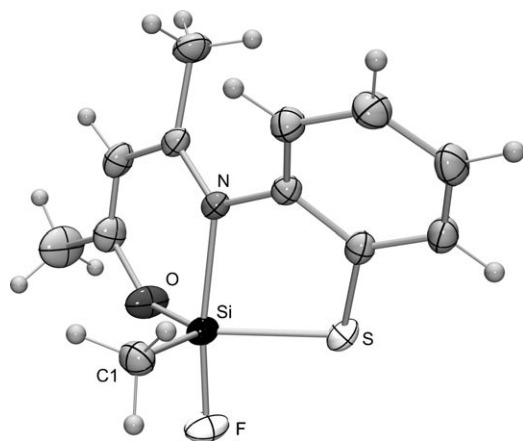


Figure 6. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S 2.1816(6), Si–F 1.6673(12), Si–O 1.6987(13), Si–N 2.0069(13), Si–C1 1.8620(18); S–Si–F 87.64(5), S–Si–O 125.73(6), S–Si–N 84.89(4), S–Si–C1 117.76(6), F–Si–O 87.35(6), F–Si–N 168.97(6), F–Si–C1 98.69(8), O–Si–N 90.43(6), O–Si–C1 116.42(8), N–Si–C1 91.98(7).

the range 161.73(5)–171.56(6)°, and the sum of the equatorial bond angles is between 359.1 and 360.0°.

The Si–X (X = F, Cl, Br, I) bond lengths of the halogenosilicon(IV) complexes **1–4** and **8–11** are given in Table 3. As can be seen from these data, replacement of the SiPh group of **1–4** by an SiMe moiety ( $\rightarrow$  **8–11**) leads to a small elongation of the respective Si–X bonds, except for the SiPh/SiMe pair **1/8** for which almost identical Si–F distances were observed. There are only a few reports on pentacoordinate silicon species with Si–Br bonds, and the Si–Br distances of **3** and **10** are in the range of the reported axial Si–Br bond lengths.<sup>[20,4]</sup> Compounds **4**<sup>[3e]</sup> and **11** represent the first penta-

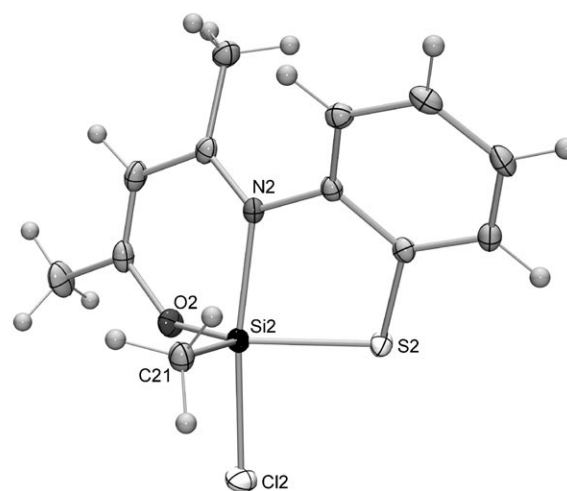
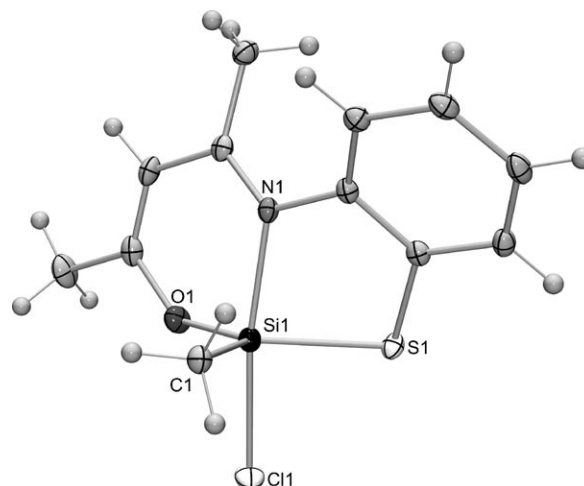


Figure 7. Molecular structures of the two crystallographically independent molecules (*Molecule I*, above; *Molecule II*, below) in the crystal of **9** (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°] of *Molecule I*: Si1–Cl1 2.2158(5), Si1–S1 2.1756(5), Si1–O1 1.6807(10), Si1–N1 1.9832(11), Si1–C1 1.8563(14); Cl1–Si1–S1 86.297(18), Cl1–Si1–O1 87.15(4), Cl1–Si1–N1 167.39(4), Cl1–Si1–C1 98.13(5), S1–Si1–O1 128.76(4), S1–Si1–N1 85.18(3), S1–Si1–C1 116.41(5), O1–Si1–N1 90.96(5), O1–Si1–C1 114.83(6), N1–Si1–C1 93.99(5). Selected bond lengths [Å] and angles [°] of *Molecule II*: Si2–Cl2 2.2273(5), Si2–S2 2.1680(5), Si2–O2 1.6736(10), Si2–N2 1.9798(12), Si2–C21 1.8533(14); Cl2–Si2–S2 86.499(18), Cl2–Si2–O2 87.06(4), Cl2–Si2–N2 168.54(4), Cl2–Si2–C21 98.37(5), S2–Si2–O2 126.08(4), S2–Si2–N2 85.22(4), S2–Si2–C21 119.02(5), O2–Si2–N2 91.43(5), O2–Si2–C21 114.89(6), N2–Si2–C21 92.57(6).

coordinate iodosilicon(IV) complexes that have been structurally characterized by single-crystal X-ray diffraction. The Si–I distances of **4**<sup>[3e]</sup> and **11** are significantly longer than the Si–I bond lengths of tetracoordinate silicon compounds (e.g., Si–I 2.4339(19)–2.5720(13) Å).<sup>[5]</sup>

The Si–E (E = S, O, N, C) bond lengths of the homologous series of the halogenosilicon(IV) complexes **1–4** and **8–11** are listed in Table 4. As can be seen from these data, the Si–E distances in both series of compounds are affected by the nature of the halogeno ligand: The longer the Si–X bond (X = F, Cl, Br, I), the shorter are the analogous Si–E

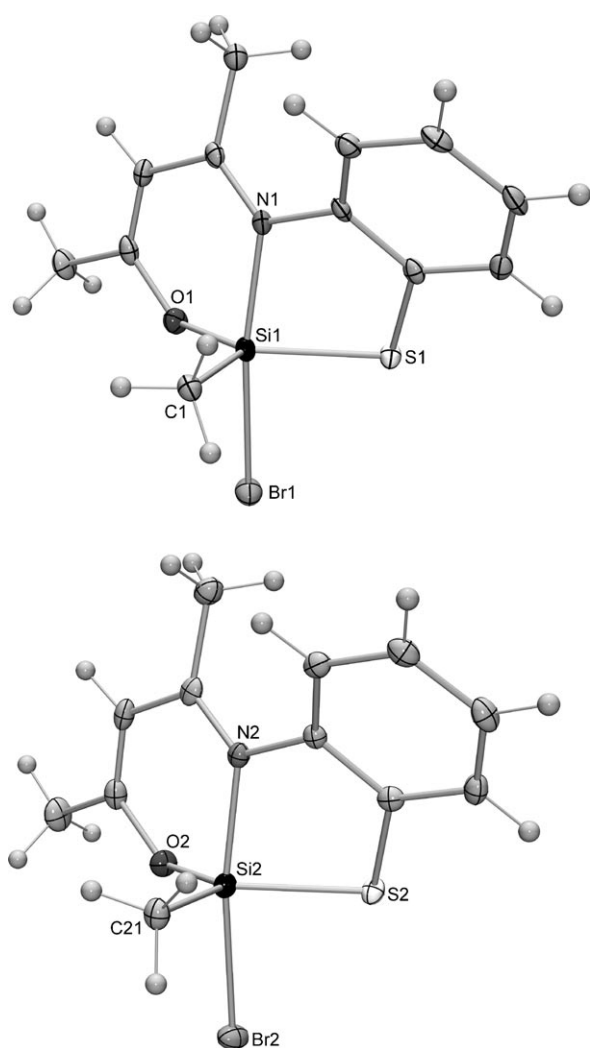


Figure 8. Molecular structures of the two crystallographically independent molecules (*Molecule I*, above; *Molecule II*, below) in the crystal of **10** (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°] of *Molecule I*: Si1–Br1 2.4291(8), Si1–S1 2.1657(10), Si1–O1 1.679(2), Si1–N1 1.958(3), Si1–C1 1.857(3); Br1–Si1–S1 85.37(3), Br1–Si1–O1 85.98(8), Br1–Si1–N1 167.31(8), Br1–Si1–C1 96.85(10), S1–Si1–O1 128.20(9), S1–Si1–N1 86.15(8), S1–Si1–C1 116.86(10), O1–Si1–N1 91.89(10), O1–Si1–C1 114.85(12), N1–Si1–C1 95.40(12). Selected bond lengths [Å] and angles [°] of *Molecule II*: Si2–Br2 2.4469(8), Si2–S2 2.1623(11), Si2–O2 1.672(2), Si2–N2 1.953(3), Si2–C21 1.850(3); Br2–Si2–S2 85.70(3), Br2–Si2–O2 85.55(8), Br2–Si2–N2 168.34(8), Br2–Si2–C21 97.15(10), S2–Si2–O2 125.96(9), S2–Si2–N2 86.12(8), S2–Si2–C21 119.07(10), O2–Si2–N2 92.56(10), O2–Si2–C21 114.91(13), N2–Si2–C21 94.08(12).

bonds, with maximum bond length differences of 0.045/0.048 Å (Si–S bonds), 0.031/0.025 Å (Si–O), 0.074/0.076 Å (Si–N), and 0.024/0.009 Å (Si–C), respectively.

The respective Si–E (E = S, O, N, C) bond lengths of the pseudohalogenosilicon(IV) complexes **5** (X = NCS) and **6** (X = N<sub>3</sub>) are very similar and fit best with those of the related halogenosilicon(IV) complexes **2** (X = Cl) and **3** (X = Br). In contrast, compound **7** (X = CN) with its longer Si–S (2.1834(6) Å) and shorter Si–N bond (1.9451(13) Å) differs from its derivatives **2**, **3**, **5**, and **6**.

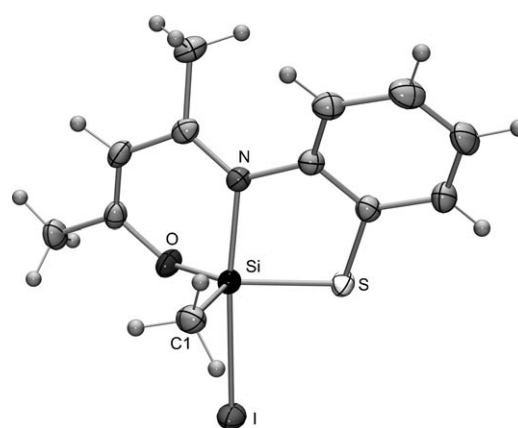


Figure 9. Molecular structure of **11** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–I 2.8225(7), Si–S 2.1338(8), Si–O 1.6733(16), Si–N 1.9312(17), Si–C1 1.858(2); I–Si–S 83.28(3), I–Si–O 83.70(6), I–Si–N 169.19(5), I–Si–C1 93.77(7), S–Si–O 121.95(6), S–Si–N 89.39(6), S–Si–C1 121.18(8), O–Si–N 93.54(8), O–Si–C1 115.96(10), N–Si–C1 96.83(9).

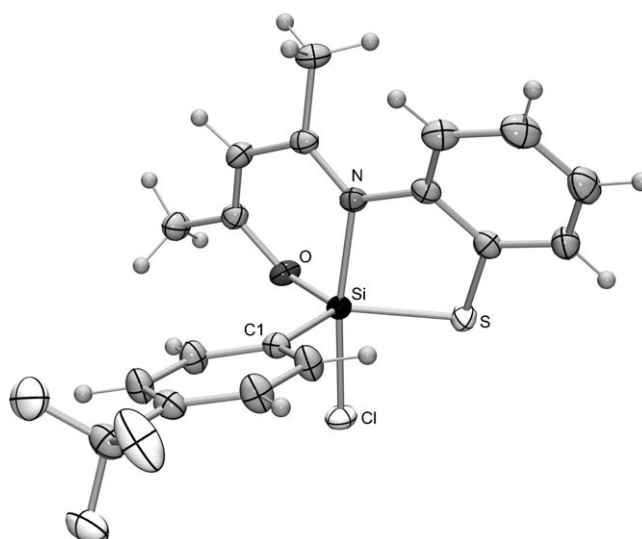


Figure 10. Molecular structure of **12** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Cl 2.2413(6), Si–S 2.1359(6), Si–O 1.6728(11), Si–N 2.0022(12), Si–C1 1.8780(14); Cl–Si–S 85.33(2), Cl–Si–O 87.28(4), Cl–Si–N 170.10(4), Cl–Si–C1 95.86(4), S–Si–O 126.96(4), S–Si–N 87.11(4), S–Si–C1 121.11(5), O–Si–N 92.17(5), O–Si–C1 111.88(6), N–Si–C1 93.52(5).

The Si–N2 distance (1.8729(17) Å) of the Si–NCS moiety of **5** and the almost linear Si–N2–C2 (175.23(16)°) and N2–C2–S2 angles (178.33(17)°) are similar to the respective structural data of other neutral pentacoordinate silicon(IV) complexes with axial thiocyanato-*N* ligands, but to some extent also differs from previously reported data.<sup>[6]</sup> To the best of our knowledge, compound **6** is the first neutral pentacoordinate silicon(IV) complex with an azido ligand that could be structurally characterized by using single-crystal X-ray diffraction. Therefore, the structural features of the Si–N<sub>3</sub> moiety of **6** can only be compared with those of the hexacoordinate dianionic silicon(IV) complex

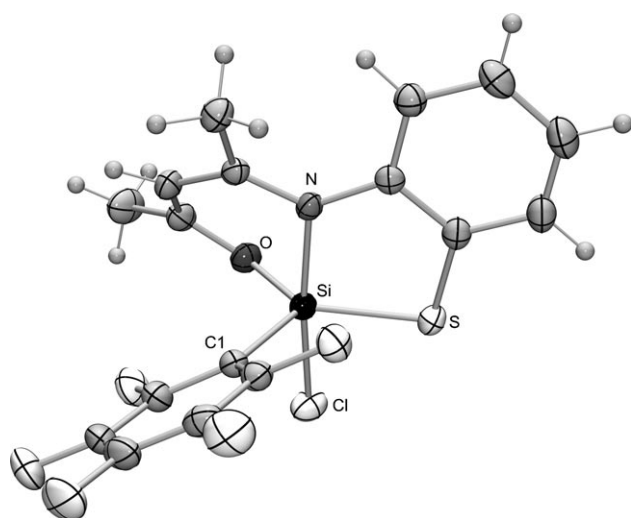


Figure 11. Molecular structure of **13** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Cl 2.2288(7), Si–S 2.1251(7), Si–O 1.7056(14), Si–N 1.9374(17), Si–C1 1.912(2); Cl–Si–S 86.22(3), Cl–Si–O 88.13(6), Cl–Si–N 171.56(6), Cl–Si–C1 94.88(6), S–Si–O 132.39(6), S–Si–N 89.16(5), S–Si–C1 117.35(6), O–Si–N 89.77(7), O–Si–C1 110.23(8), N–Si–C1 93.52(8).

Table 4. Comparison of the Si–E (E = S, O, N, C) bond lengths [Å] of **1–4** and **8–11** and maximum bond length differences  $\Delta_{\max}$  [Å].

Compound and $\Delta_{\max}$	Si–S	Si–O	Si–N	Si–C
<b>1</b> (X = F)	2.1712(3)	1.6967(6)	2.0096(6)	1.8745(7)
<b>2</b> (X = Cl) <sup>[a]</sup>	2.1571(4)	1.6850(8)	2.0069(10)	1.8593(11)
<b>3</b> (X = Br)	2.1501(5)	1.6802(10)	1.9851(12)	1.8579(13)
<b>4</b> (X = I) <sup>[a]</sup>	2.1262(10)	1.6655(19)	1.936(2)	1.851(3)
$\Delta_{\max}$	0.045	0.031	0.074	0.024
<b>8</b> (X = F)	2.1816(6)	1.6987(13)	2.0069(13)	1.8620(18)
<b>9</b> (X = Cl) <sup>[b]</sup>	2.1756(5), 2.1680(5)	1.6807(10), 1.6736(10)	1.9832(11), 1.9798(12)	1.8563(14), 1.8533(14)
<b>10</b> (X = Br) <sup>[b]</sup>	2.1657(10), 2.1623(11)	1.679(2), 1.672(2)	1.958(3), 1.953(3)	1.857(3), 1.850(3)
<b>11</b> (X = I)	2.1338(8)	1.6733(16)	1.9312(17)	1.858(2)
$\Delta_{\max}$	0.048	0.025	0.076	0.009

[a] Reference [3e]. [b] *Molecules I and II*.

[(Ph<sub>3</sub>P)<sub>2</sub>N]<sub>2</sub>[Si(N<sub>3</sub>)<sub>6</sub>].<sup>[7]</sup> The Si–N bond lengths of the [Si(N<sub>3</sub>)<sub>6</sub>]<sup>2–</sup> dianion (1.866(1)–1.881(1) Å) are somewhat longer than the Si–N<sub>2</sub> bond lengths of **6** (1.8573(14) Å). However, the major difference of the Si–N<sub>3</sub> moieties of **6** and the [Si(N<sub>3</sub>)<sub>6</sub>]<sup>2–</sup> dianion concerns the N–N bond lengths of the azido ligand. In principle, two mesomeric structures of the Si–N<sub>3</sub> group are possible, Si–N<sub>α</sub>=N<sub>β</sub>=N<sub>γ</sub> (**A**) and Si–N<sub>α</sub>–N<sub>β</sub>≡N<sub>γ</sub> (**B**). In the case of **6**, the very similar N<sub>2</sub>–N<sub>3</sub> (1.134(2) Å) and N<sub>3</sub>–N<sub>4</sub> distance (1.137(3) Å) indicate the dominance of the mesomeric structure **A**. In contrast, the strong differentiation between the N<sub>α</sub>–N<sub>β</sub> (1.198(2)–1.207(2) Å) and N<sub>β</sub>–N<sub>γ</sub> distance (1.144(2)–1.146(2) Å) of the [Si(N<sub>3</sub>)<sub>6</sub>]<sup>2–</sup> dianion reflect an increased dominance of the mesomeric structure **B**. The structural features of the Si–CN moiety of **7** can only be compared with one neutral penta-coordinate (cyano-*N*)silicon(IV) complex that has been studied by crystal structure analysis.<sup>[8]</sup> The Si–CN bond length (2.050(6) Å) of this trigonal-bipyramidal compound is

Table 5. Comparison of the Si–E (E = Cl, S, O, N, C) bond lengths [Å] of **2**, **12**, and **13**.

Compound	Si–Cl	Si–S	Si–O	Si–N	Si–C
<b>2</b> <sup>[a]</sup>	2.1954(4)	2.1571(4)	1.6850(8)	2.0069(10)	1.8593(11)
<b>12</b>	2.2413(6)	2.1359(6)	1.6728(11)	2.0022(12)	1.8780(14)
<b>13</b>	2.2288(7)	2.1251(7)	1.7056(14)	1.9374(17)	1.912(2)

[a] Reference [3e].

significantly longer than the Si–C<sub>2</sub> bond length of **7** (1.9563(16) Å), whereas the C<sub>2</sub>–N<sub>2</sub> bond length (1.150(2) Å) and the Si–C<sub>2</sub>–N<sub>2</sub> angle (175.22(13)°) of **7** are very similar to the respective data of the reference compound (1.144(8) Å, 175.1(4)°).

As can be seen in Table 5, replacement of the phenyl group of **2** by the more electron-withdrawing 4-(trifluoromethyl)phenyl (→ **12**) or pentafluorophenyl group (→ **13**) leads to different effects: In the case of the Si–Cl and Si–C bonds, an increase in bond lengths was observed, whereas the Si–S and Si–N bond lengths are shortened. In the case of the Si–O bond lengths, a decrease (**12**) and an increase (**13**), respectively, was observed. These effects are not fully understood so far.

**NMR studies:** Compounds **1**, **3**, and **5–13** were characterized by using multinuclear solution-state and solid-state NMR spectroscopy. The NMR-spectroscopic data obtained (see the Experimental Section) are in accordance with the experimentally established crystal structures of these compounds.

Analysis of Table 6 reveals that the isotropic <sup>15</sup>N and <sup>29</sup>Si chemical shifts of **1–13** in the solid state strongly depend on the nature of both the (pseudo)halogeno ligand (compounds

Table 6. Isotropic <sup>15</sup>N and <sup>29</sup>Si chemical shifts of compounds **1–13** in the solid state.

Compound	$\delta^{15}\text{N}$ <sup>[a]</sup> [ppm]	$\delta^{29}\text{Si}$ [ppm]
<b>1</b> (X = F)	–151.5	–89.1
<b>2</b> (X = Cl) <sup>[b]</sup>	–149.4	–83 <sup>[c]</sup>
<b>3</b> (X = Br)	–153.6	–89 <sup>[c]</sup>
<b>4</b> (X = I) <sup>[b]</sup>	–163.8	–91 <sup>[c]</sup>
<b>5</b> (X = NCS)	–157.6	–98.8
<b>6</b> (X = N <sub>3</sub> )	–145.4 or –140.4 <sup>[d]</sup>	–87.1
<b>7</b> (X = CN)	–158.8	–100.8
<b>8</b> (X = F)	–147.9	–77.7
<b>9</b> (X = Cl)	–152.4	–75 <sup>[c]</sup>
<b>10</b> (X = Br)	–160.2	–80 <sup>[c]</sup>
<b>11</b> (X = I)	–169.0	–72 <sup>[c]</sup>
<b>12</b> (X = Cl)	–152.1	–84 <sup>[c]</sup>
<b>13</b> (X = Cl)	–171.1	–93 <sup>[c]</sup>

[a] Nitrogen atom of the tridentate *S,N,O* ligand. [b] Reference [3e]. [c] Broad resonance signal. [d] For details, see the Experimental Section.

**1–7**; F, Cl, Br, I, NCS, N<sub>3</sub>, CN) and the organyl ligand (comparison of **1–4** with **8–11**, Ph/Me exchange; comparison of **2** with **12** and **13**, phenyl/4-(trifluoromethyl)phenyl/pentafluorophenyl exchange). The <sup>15</sup>N chemical shifts are in the range  $\delta = -147.9$  to  $-171.1$  ppm, and the <sup>29</sup>Si chemical shifts range from  $\delta = -72$  to  $-100.8$  ppm. As shown exem-

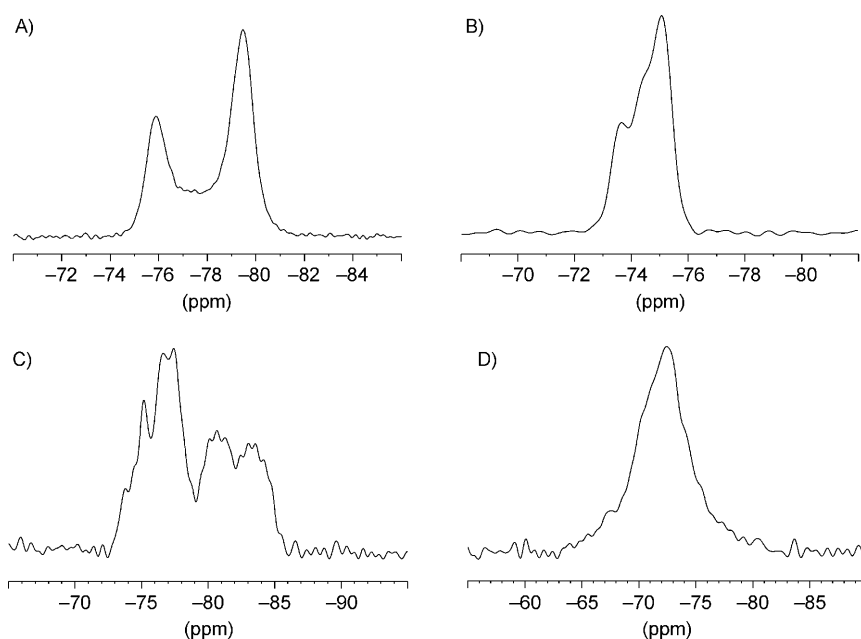


Figure 12. Partial  $^{29}\text{Si}$  VACP/MAS spectra of A) **8** (X=F), B) **9** (X=Cl), C) **10** (X=Br), and D) **11** (X=I). MAS frequencies: A) 7000 Hz, B) 6000 Hz, C) 6500 Hz, and D) 6500 Hz. Spinning side bands have been omitted for clarity.

plarily for **9** (X=Cl), **10** (X=Br), and **11** (X=I) in Figure 12, the  $^{29}\text{Si}$  VACP/MAS NMR spectra of all compounds that contain chloro, bromo, or iodo ligand atoms show broad and structured resonance signals. This phenomenon can be explained by  $^{29}\text{Si}$ ,X couplings (X =  $^{35}\text{Cl}$  ( $I=3/2$ ),  $^{37}\text{Cl}$  ( $I=3/2$ );  $^{79}\text{Br}$  ( $I=3/2$ ),  $^{81}\text{Br}$  ( $I=3/2$ );  $^{127}\text{I}$  ( $I=5/2$ )) and the well-known effect that MAS fails to completely eliminate the effect of dipolar coupling for spin 1/2 when coupled to quadrupole nuclei with a quadrupole frequency comparable to the Zeeman frequency of the nuclei.<sup>[9]</sup> As also shown exemplarily for **8** in Figure 12, a  $^{29}\text{Si}$ , $^{19}\text{F}$  coupling was observed for the two fluorosilicon(IV) complexes **1** and **8**.

The  $^{29}\text{Si}$  chemical shifts of **1–13** determined by solution-state NMR experiments (solvent,  $\text{CD}_2\text{Cl}_2$ ; Table 7) are very similar to those obtained in the solid state and indicate that the pentacoordinate silicon(IV) complexes **1–13** also exist in solution. According to the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the tridentate *O,N,S* ligand it is likely to assume that the configurations

of **1–13** in the solid state and in solution are identical; that is, the oxygen and sulfur atom of this ligand occupy equatorial positions of a distorted trigonal bipyramid, whereas the nitrogen atom occupies an axial position. This assumption is based on a comparison of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **1–13** with those of compounds **16–18**,<sup>[25]</sup> for which a totally different coordination mode is observed: In the case of **16–18**, the oxygen and sulfur atom of the tridentate ligand occupy the two axial positions. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the tridentate ligand allow for differentiation between these two different coordination modes.

Additional solution-state  $^{29}\text{Si}$  NMR experiments with **1–13**,

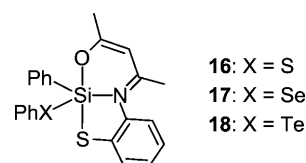
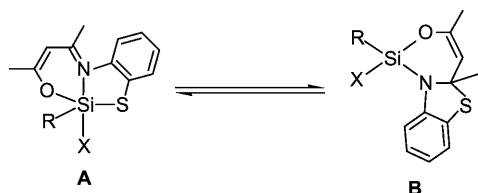


Table 7. Solution-state  $^{29}\text{Si}$  NMR data of compounds **1–13**.

Compound	$\delta$ $^{29}\text{Si}$ (A) [ppm]	$\delta$ $^{29}\text{Si}$ (B) <sup>[a]</sup> [ppm]	Molar ratio A:B <sup>[b]</sup>	Solvent
<b>1</b> (X=F)	-88.1 <sup>[c]</sup>	-53.69 <sup>[c]</sup> -53.68 <sup>[c]</sup>	70:30	$\text{CD}_2\text{Cl}_2$
	-88.1 <sup>[c]</sup>	-53.6 <sup>[c]</sup> -53.4 <sup>[c]</sup>	80:20	$\text{CD}_2\text{CN}$
<b>2</b> (X=Cl)	-81.2	-33.2, -32.8	88:12	$\text{CD}_2\text{Cl}_2$
	-82.3	- <sup>[d]</sup>	95:5	$\text{CD}_2\text{CN}$
<b>3</b> (X=Br)	-86.7	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>4</b> (X=I)	-92.5	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>5</b> (X=NCS)	-98.3	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>6</b> (X=N <sub>3</sub> )	-87.8	-47.3, -47.1	90:10	$\text{CD}_2\text{Cl}_2$
	-86.5	-47.0, -46.4	70:30	$\text{C}_6\text{D}_6$
<b>7</b> (X=CN)	-99.9	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>8</b> (X=F)	-74.1 <sup>[c]</sup>	-37.32 <sup>[c]</sup> -37.26 <sup>[c]</sup>	30:70	$\text{CD}_2\text{Cl}_2$
	-74.8 <sup>[c]</sup>	-36.8 <sup>[c]</sup> -36.7 <sup>[c]</sup>	45:55	$\text{CD}_2\text{CN}$
	-73.3 <sup>[c]</sup>	-37.6 <sup>[c]</sup> -37.2 <sup>[c]</sup>	8:92	$\text{C}_6\text{D}_6$
<b>9</b> (X=Cl)	-71.4	-19.2	80:20	$\text{CD}_2\text{Cl}_2$
	-72.5	-19.3, -19.0	90:10	$\text{CD}_2\text{CN}$
	-70.4	-19.7, -19.1	50:50	$\text{C}_6\text{D}_6$
<b>10</b> (X=Br)	-75.8	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>11</b> (X=I)	-75.6	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>12</b> (X=Cl)	-83.4	- <sup>[d]</sup>	93:7	$\text{CD}_2\text{Cl}_2$
	-84.3	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{CN}$
	-82.4	-34.1, -33.4	83:17	$\text{C}_6\text{D}_6$
	-92 <sup>[f]</sup>	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{Cl}_2$
<b>13</b> (X=Cl)	-93 <sup>[f]</sup>	-	100:0 <sup>[e]</sup>	$\text{CD}_2\text{CN}$
	-91 <sup>[f]</sup>	-	100:0 <sup>[e]</sup>	$\text{C}_6\text{D}_6$

[a] Data for two diastereomers. [b] Ratio determined by  $^1\text{H}$  NMR spectroscopy. [c] The  $^{29}\text{Si}$  NMR resonance signal is a doublet owing to  $^1J(\text{Si},\text{F})$  coupling. [d] The concentration of **B** was too low to determine the  $^{29}\text{Si}$  NMR shift. [e] The existence of traces (<1%) of **B** can not be totally ruled out. [f] The  $^{29}\text{Si}$  NMR resonance signal is a multiplet owing to  $J(^{29}\text{Si},^{19}\text{F})$  couplings.





Scheme 4. Dynamic equilibrium of **1–13** between penta- (**A**) and tetra-coordination (**B**) in solution.

using  $\text{CD}_2\text{Cl}_2$ ,  $\text{CD}_3\text{CN}$ , and  $\text{C}_6\text{D}_6$  as the solvent, revealed, in most cases, the existence of a dynamic equilibrium between the pentacoordinate species **A** and the tetra-coordinate species **B** (existing as two diastereomers), as shown in Scheme 4. The results of these studies are summarized in Table 7. The identities of the tetra-coordinate species of the formula type **B** were established by using  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR studies (data not given); the NMR data of these species are very similar to those reported for the two diastereomers of **B** with  $\text{X}=\text{OPh}$  (one of these diastereomers has been additionally characterized by single-crystal X-ray diffraction).<sup>[25]</sup>

The existence of a dynamic equilibrium could be demonstrated qualitatively by 2D EXSY NMR studies (exchange spectroscopy). This method indicates multisite chemical exchange by cross signals for all exchanging species. As can be seen exemplarily for compound **9** from Figure 13, the  $\text{SiCH}_3$

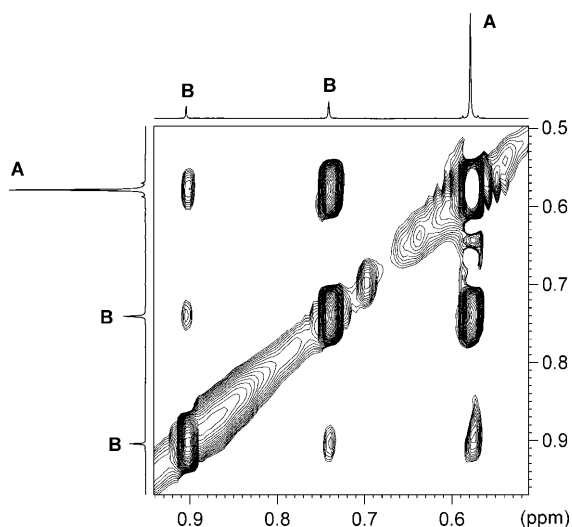


Figure 13. Partial  $^1\text{H},^1\text{H}$  EXSY NMR spectrum of **9** in  $\text{CD}_2\text{Cl}_2$  (**A**,  $\text{SiCH}_3$  resonance signal of the pentacoordinate species; **B**,  $\text{SiCH}_3$  resonance signals of the two diastereomeric tetra-coordinate species).

group of the pentacoordinate species **A** is in direct exchange with the  $\text{SiCH}_3$  groups of the two diastereomeric tetra-coordinate species **B**; furthermore, an exchange between the two isomeric species **B** can be observed.

According to these studies, the molar ratio **A/B** is affected by the (pseudo)halogeno ligand, the organyl ligand, and the solvent. For example, in the case of **13**, within the experi-

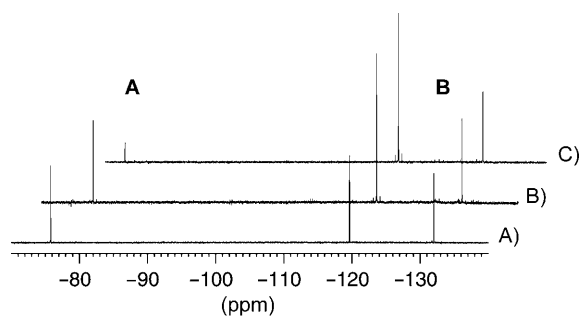


Figure 14.  $^{19}\text{F}$  NMR spectra of **8** in A)  $\text{CD}_3\text{CN}$ , B)  $\text{CD}_2\text{Cl}_2$ , and C)  $\text{C}_6\text{D}_6$  (left: resonance signal of the pentacoordinate species **A**; right: resonance signals of the two diastereomeric tetra-coordinate species **B**).

mental detection limits, exclusively pentacoordination was observed (solvent:  $\text{CD}_3\text{CN}$ ,  $\text{CD}_2\text{Cl}_2$ ,  $\text{C}_6\text{D}_6$ ), whereas tetra-coordination is favored in the case of **8** (ratio **A/B**: 45:55 ( $\text{CD}_3\text{CN}$ ), 30:70 ( $\text{CD}_2\text{Cl}_2$ ), 8:92 ( $\text{C}_6\text{D}_6$ ); Figure 14).

Unfortunately, the poor solubility of some of these silicon(IV) complexes in  $\text{CD}_3\text{CN}$  and  $\text{C}_6\text{D}_6$  did not allow a systematic study of the solvent dependent **A/B** ratio for all compounds, but it appears that pentacoordination is favored in the rank order  $\text{CD}_3\text{CN} > \text{CD}_2\text{Cl}_2 > \text{C}_6\text{D}_6$ ; i.e., the more polar the solvent, the more stable is the pentacoordinate silicon(IV) **A** complex compared to the corresponding tetra-coordinate species **B**.

As can be seen from Table 7, the nature of the halogeno ligand of the silicon(IV) complexes **1–4** and **8–11** significantly affects the **A/B** ratio. In both series of compounds, the halogeno ligands favor pentacoordination in the following order:  $\text{I} \approx \text{Br} > \text{Cl} > \text{F}$ ; i.e., the more electronegative (hard) the halogeno ligand, the lower is the stability of the pentacoordinate silicon(IV) complex **A** compared to the corresponding tetra-coordinate species **B**. Replacement of the electron-withdrawing phenyl group of **1–4** by an electron-donating methyl moiety ( $\rightarrow$  **8–11**) leads to a destabilization of pentacoordination, and exchange of the phenyl group of **2** by the more electron-withdrawing 4-(trifluoromethyl)phenyl ( $\rightarrow$  **12**) and pentafluorophenyl group ( $\rightarrow$  **13**), respectively, leads to a stabilization of pentacoordination. These effects of the organyl ligands are expected, whereas the effect of the halogeno ligands is not understood, if it is assumed that hard ligand atoms should favor pentacoordination of the hard silicon(IV) coordination center ( $\text{F} > \text{Cl} > \text{Br} > \text{I}$ ). To fully understand the effect of the different monodentate ligands on the **A/B** ratio, information on their effect on the stability of the tetra-coordinate species **B** is also necessary.

## Conclusion

In this study, we have demonstrated that the pentacoordinate chlorosilicon(IV) complex **2** and its derivative **9** (Ph/Me exchange) are versatile precursors for the synthesis of related pentacoordinate silicon compounds that contain

other halogeno (F, Br, I) or pseudohalogeno ligands (NCS, N<sub>3</sub>, CN) instead of the chloro ligand. With the synthesis of **9**, **12**, and **13**, we have also demonstrated that derivatives of **2** with other organyl ligands instead of the phenyl group can be prepared. These compounds are expected to be versatile precursors for the synthesis of related pentacoordinate silicon(IV) complexes with other halogeno and pseudohalogeno ligands. In this context, compound **13** with its strongly electron-withdrawing pentafluorophenyl group is particularly promising.

Notably, the pentacoordinate halogenosilicon(IV) complexes **1–4** and **8–13** each contain five different ligand atoms in the silicon coordination sphere; all these compounds contain an SiSONCX skeleton (X = F, Cl, Br, I). The existence of **3**, **4**, **10**, and **11** with their bromo and iodo ligand, respectively, is particularly remarkable.

Compounds **1–13** exist both in the solid state and in solution. They all contain a distorted trigonal-bipyramidal Si-coordination polyhedron, with the oxygen and sulfur atom of the tridentate *S,N,O* ligand in equatorial positions, whereas the nitrogen atom occupies an axial site.

Solution-state NMR studies of **1–13** revealed, in most cases, the existence of a dynamic equilibrium between these pentacoordinate silicon(IV) complexes (**A**) and two isomeric tetracoordinate species (**B**). The **A/B** ratio depends on the nature of the (pseudo)halogeno and organyl ligands and on the solvent. These effects are not yet fully understood. Most surprisingly, in the two series of the halogenosilicon(IV) complexes **1–4** and **8–11**, the halogeno ligands favor pentacoordination in the following rank order:  $I \approx \text{Br} > \text{Cl} > \text{F}$ . This is not what one would expect if it is assumed that hard ligand atoms should favor pentacoordination of the hard silicon(IV) coordination center ( $\text{F} > \text{Cl} > \text{Br} > \text{I}$ ). Clearly, this concept is too simple to explain the trend found for this particular class of compounds. Further studies are necessary to understand this phenomenon.

## Experimental Section

**General procedures:** All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined by using a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The solution-state <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si NMR spectra were recorded at 23 °C by using a Bruker DRX-300 (<sup>1</sup>H, 300.1 MHz; <sup>13</sup>C, 75.5 MHz; <sup>29</sup>Si, 59.6 MHz), a Bruker Avance 400 (<sup>19</sup>F, 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). CD<sub>2</sub>Cl<sub>2</sub>, CD<sub>3</sub>CN, or C<sub>6</sub>D<sub>6</sub> served as the solvent. Chemical shifts (ppm) were determined relative to internal CHDCl<sub>2</sub> (<sup>1</sup>H,  $\delta = 5.32$  ppm; CD<sub>2</sub>Cl<sub>2</sub>), CHD<sub>2</sub>CN (<sup>1</sup>H,  $\delta = 1.93$  ppm; CD<sub>3</sub>CN), C<sub>6</sub>HD<sub>5</sub> (<sup>1</sup>H,  $\delta = 7.28$  ppm; C<sub>6</sub>D<sub>6</sub>), CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C,  $\delta = 53.8$  ppm; CD<sub>2</sub>Cl<sub>2</sub>), CD<sub>3</sub>CN (<sup>13</sup>C,  $\delta = 1.3$  ppm; CD<sub>3</sub>CN), C<sub>6</sub>D<sub>6</sub> (<sup>13</sup>C,  $\delta = 128.0$  ppm; C<sub>6</sub>D<sub>6</sub>), or external TMS (<sup>29</sup>Si,  $\delta = 0$  ppm; CD<sub>2</sub>Cl<sub>2</sub>, CD<sub>3</sub>CN, C<sub>6</sub>D<sub>6</sub>). Assignment of the <sup>13</sup>C NMR data was supported by DEPT 135 experiments and <sup>13</sup>C, <sup>1</sup>H correlation experiments. The mixing time for the <sup>1</sup>H, <sup>1</sup>H EXSY experiment was 800 ms. Solid-state <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si VACP/MAS NMR spectra were recorded at 22 °C by using a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO<sub>2</sub> (diameter, 7 mm) containing approximately 300 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 stan-

dard, TMS (<sup>13</sup>C, <sup>29</sup>Si;  $\delta = 0$  ppm) or glycine (<sup>15</sup>N,  $\delta = -342.0$  ppm); spinning rate, 5–7 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  $\mu$ s; repetition time, 4 s).

**Syntheses of 2 and 4:** Compounds **2** and **4** were synthesized according to reference [3e].

**Synthesis of 1:** Ammonium fluoride (107 mg, 2.89 mmol) was added in a single portion at 20 °C to a stirred solution of **2** (1.00 g, 2.89 mmol) in tetrahydrofuran (15 mL), and the reaction mixture was then stirred at 20 °C for 24 h. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, and the residue was dissolved in toluene (3 mL). The resulting solution was slowly concentrated in vacuo, until the formation of a solid started. Toluene (1 mL) was added, and the mixture was heated until a clear solution was obtained, which was kept undisturbed at 20 °C for 20 h and then at –20 °C for a further 24 h. The resulting precipitate was filtered off, washed with *n*-pentane (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **1** in 57% yield (548 mg, 1.66 mmol) as a yellow crystalline solid. M.p. > 110 °C (decomp); <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.1 MHz):  $\delta = 2.12$  (d, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.5 Hz, 3H; CCH<sub>3</sub>), 2.36 (s, 3H; CCH<sub>3</sub>), 5.83–5.85 (m, 1H; CCHC), 6.97–7.03, 7.04–7.10, 7.18–7.28, 7.33–7.37, 7.48–7.51 ppm (m, 9H; SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 75.5 MHz):  $\delta = 24.0$  (CCH<sub>3</sub>), 24.3 (CCH<sub>3</sub>), 105.0 (CCHC), 124.7, 124.9, 128.5 (d, <sup>4</sup>*J*(<sup>13</sup>C, <sup>19</sup>F) = 4.4 Hz), 128.6 (2 C), 128.8, 130.9, 133.5 (d, <sup>4</sup>*J*(<sup>13</sup>C, <sup>19</sup>F) = 3.6 Hz, 2 C), 133.7 (d, <sup>4</sup>*J*(<sup>13</sup>C, <sup>19</sup>F) = 8.7 Hz), 138.0 (d, <sup>4</sup>*J*(<sup>13</sup>C, <sup>19</sup>F) = 26 Hz), 138.9 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 171.8 (*J*(<sup>13</sup>C, <sup>19</sup>F) = 8.0 Hz, CN or CO), 173.0 ppm (CN or CO); <sup>19</sup>F NMR (CD<sub>3</sub>CN, 376.5 MHz):  $\delta = -83.2$  ppm; <sup>29</sup>Si NMR (CD<sub>3</sub>CN, 59.6 MHz):  $\delta = -88.1$  ppm (d, <sup>1</sup>*J*(<sup>29</sup>Si, <sup>19</sup>F) = 261 Hz); <sup>13</sup>C VACP/MAS NMR:  $\delta = 22.3$  (CCH<sub>3</sub>), 24.8 (CCH<sub>3</sub>), 105.1 (CCHC), 124.7, 125.6 (2 C), 128.0 (2 C), 130.0 (3 C), 131.5, 133.0, 135.7, 137.9 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 170.3 (CN or CO), 171.9 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR:  $\delta = -151.5$  ppm; <sup>29</sup>Si VACP/MAS NMR:  $\delta = -89.1$  ppm (d, <sup>1</sup>*J*(<sup>29</sup>Si, <sup>19</sup>F) = 266 Hz); elemental analysis calcd (%) for C<sub>17</sub>H<sub>16</sub>FNOSSi (329.47): C 61.97, H 4.89, N 4.25, S 9.73; found: C 62.0, H 4.7, N 4.4, S 9.7.

**Synthesis of 3:** Bromotrimethylsilane (266 mg, 1.74 mmol) was added in a single portion at 20 °C to a stirred suspension of **2** (400 mg, 1.16 mmol) in acetonitrile (8 mL). The reaction mixture was heated to 95 °C, and 2 mL of this mixture were removed by distillation at ambient pressure. The remaining solution was slowly cooled to 20 °C (formation of crystals) and then kept undisturbed at –20 °C for 3 days. The resulting precipitate was isolated by filtration, washed with diethyl ether (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **3** in 71% yield (320 mg, 820  $\mu$ mol) as a yellow crystalline solid. M.p. > 130 °C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz):  $\delta = 2.31$  (d, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.34 (s, 3H; CCH<sub>3</sub>), 5.80 (q, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 6.96–7.05, 7.16–7.26, 7.39–7.45 ppm (m, 9H; SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz):  $\delta = 24.2$  (CCH<sub>3</sub>), 24.4 (CCH<sub>3</sub>), 105.4 (CCHC), 123.6, 124.6, 127.0, 127.9 (2 C), 128.8, 129.9, 131.9 (2 C), 134.5, 137.0, 139.6 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 171.5 (CN or CO), 171.6 ppm (CN or CO); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 59.6 MHz):  $\delta = -86.7$  ppm; <sup>13</sup>C VACP/MAS NMR:  $\delta = 24.7$  (CCH<sub>3</sub>), 27.1 (CCH<sub>3</sub>), 106.7 (CCHC), 124.5 (3 C), 126.9 (2 C), 128.6 (2 C), 134.0 (3 C), 137.9 (2 C) (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 170.4 (CN or CO), 171.6 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR:  $\delta = -153.6$  ppm; <sup>29</sup>Si VACP/MAS NMR:  $\delta = -89$  ppm (br.); elemental analysis calcd (%) for C<sub>17</sub>H<sub>16</sub>BrNOSSi (390.38): C 52.31, H 4.13, N 3.59, S 8.21; found: C 52.3, H 4.1, N 3.6, S 8.2.

**Synthesis of 5:** (Isothiocyanato)trimethylsilane (209 mg, 1.59 mmol) was added in a single portion at 20 °C to a stirred suspension of **2** (500 mg, 1.45 mmol) in acetonitrile (11 mL). The reaction mixture was stirred at 20 °C for 10 min, heated to 70 °C, and filtered hot. The filtrate was slowly cooled to 20 °C (formation of crystals) and then kept undisturbed at 20 °C for 4 h and then at –20 °C for a further 20 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **5** in 86% yield (459 mg, 1.25 mmol) as a yellow crystalline solid. M.p. > 100 °C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.1 MHz):  $\delta = 2.23$  (d, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.35 (s, 3H; CCH<sub>3</sub>), 5.77 (q, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 7.00–7.02, 7.12–7.16, 7.22–7.25, 7.27–7.31, 7.41–7.44 ppm (m, 9H;

SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz): δ = 24.1 (CCH<sub>3</sub>), 24.3 (CCH<sub>3</sub>), 105.1 (CCHC), 123.7, 124.6, 127.9, 128.1 (2 C), 128.6, 130.3, 132.4, 133.1 (2 C), 137.27, 137.34 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 135.5 (t, <sup>1</sup>J(<sup>13</sup>C,<sup>15</sup>N) = 24 Hz, NCS), 171.6 (CN or CO), 171.7 ppm (CN or CO); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.4 MHz): δ = -98.3 ppm (t, <sup>1</sup>J(<sup>29</sup>Si,<sup>15</sup>N) = 4.8 Hz); <sup>13</sup>C VACP/MAS NMR: δ = 24.1 (CCH<sub>3</sub>), 26.7 (CCH<sub>3</sub>), 108.0 (CCHC), 124.4, 125.5, 127.2, 128.9 (3 C), 131.5, 132.5, 135.1, 136.0 (2 C), 137.4 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 171.2 (CN or CO), 173.5 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR: δ = -223.0 (SiNCS), -157.6 ppm (SiNC<sub>2</sub>); <sup>29</sup>Si VACP/MAS NMR: δ = -98.8 ppm; elemental analysis calcd (%) for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Si (368.56): C 58.66, H 4.38, N 7.60, S 17.40; found: C 58.6, H 4.4, N 7.6, S 17.8.

**Synthesis of 6:** Azidotrimethylsilane (250 mg, 2.17 mmol) was added in a single portion at 20 °C to a stirred suspension of **2** (600 mg, 1.73 mmol) in acetonitrile (10 mL). The reaction mixture was heated to 95 °C, and 2 mL of this mixture were removed by distillation at ambient pressure. The remaining solution was cooled to 20 °C, and the solid was filtered off and discarded. The filtrate was slowly concentrated in vacuo to a volume of approximately 6 mL (formation of crystals) and was then kept undisturbed at 20 °C for 4 h and then at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **6** in 78 % yield (476 mg, 1.35 mmol) as a yellow crystalline solid. M.p. >115 °C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.1 MHz): δ = 2.25 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.34 (s, 3H; CCH<sub>3</sub>), 5.78 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 6.97-7.00, 7.09-7.13, 7.21-7.24, 7.26-7.29, 7.39-7.41, 7.43-7.45 ppm (m, 9H; SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz): δ = 23.4 (CCH<sub>3</sub>), 24.1 (CCH<sub>3</sub>), 104.6 (CCHC), 123.6, 124.3, 127.9 (2 C), 128.1, 128.3, 129.9, 133.2 (2 C), 133.6, 137.0, 137.2 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 171.3 (CN or CO), 172.2 ppm (CN or CO); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.4 MHz): δ = -87.8 ppm; <sup>13</sup>C VACP/MAS NMR: δ = 20.5 (CCH<sub>3</sub>), 24.8 (CCH<sub>3</sub>), 106.7 (CCHC), 124.1, 126.4, 127.6 (2 C), 128.5, 130.5 (3 C), 131.5, 134.5, 138.0 (2 C) (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>), 170.3 (CN or CO), 170.9 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR: δ = -295.1 (SiN<sub>2</sub>), -210.7 (SiN<sub>2</sub>), -145.4 (CN or SiN<sub>2</sub>), -140.4 ppm (CN or SiN<sub>2</sub>); <sup>29</sup>Si VACP/MAS NMR: δ = -87.1 ppm; elemental analysis calcd (%) for C<sub>17</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>Si (352.49): C 57.93, H 4.58, N 15.89, S 9.10; found: C 58.0, H 4.6, N 15.8, S 9.3.

**Synthesis of 7:** Cyanotrimethylsilane (321 mg, 3.24 mmol) was added in a single portion at 20 °C to a stirred suspension of **2** (935 mg, 2.70 mmol) in acetonitrile (10 mL). The reaction mixture was heated to 95 °C, 5 mL of this mixture were removed by distillation at ambient pressure, and the remaining solid was filtered off and discarded. The solvent of the filtrate was removed in vacuo, acetonitrile (5 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C (formation of crystals) and was then kept undisturbed at this temperature for 2 h and then at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **7** in 61 % yield (558 mg, 1.66 mmol) as an orange-colored crystalline solid. M.p. >170 °C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.1 MHz): δ = 2.25 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.35 (s, 3H; CCH<sub>3</sub>), 5.78 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 6.99-7.03, 7.11-7.32, 7.39-7.52 ppm (m, 9H; SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz): δ = 24.1 (CCH<sub>3</sub>), 24.4 (CCH<sub>3</sub>), 105.4 (CCHC), 123.7, 124.7, 127.9, 128.1 (2 C), 128.7, 130.4, 132.5, 133.5 (2 C), 134.3, 136.8, 137.3 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>, SiCN), 172.1 (SiN or CO), 172.8 ppm (SiN or CO); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.4 MHz): δ = -99.9 ppm; <sup>13</sup>C VACP/MAS NMR: δ = 23.6 (CCH<sub>3</sub>), 23.9 (CCH<sub>3</sub>), 104.2 (CCHC), 124.4, 126.1 (2 C), 127.8, 129.0, 130.2, 131.3, 132.9 (2 C), 136.7, 137.5, 137.8 (2 C) (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>5</sub>, SiCN), 172.0 (SiN or CO), 175.8 ppm (SiN or CO); <sup>15</sup>N VACP/MAS NMR: δ = -158.8 (SiN), -96.6 (SiCN) ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -100.8 ppm; elemental analysis calcd (%) for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Si (336.49): C 64.25, H 4.79, N 8.33, S 9.53; found: C 63.8, H 4.8, N 7.9, S 9.6.

**Synthesis of 8:** Ammonium fluoride (421 mg, 11.4 mmol) was added in a single portion at 20 °C to a stirred solution of **9** (3.07 g, 10.8 mmol) in tetrahydrofuran (40 mL), and the reaction mixture was then stirred at 20 °C for 48 h. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, the residue was dissolved in dichlorome-

thane (6 mL), and the resulting solution was kept undisturbed at -20 °C for 3 weeks. The resulting precipitate was isolated by filtration, washed with *n*-pentane (15 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **8** in 13 % yield (378 mg, 1.41 mmol) as a pale yellow crystalline solid. M.p. >100 °C (decomp); <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.1 MHz): δ = 0.11 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>19</sup>F) = 6.5 Hz, 3H; SiCH<sub>3</sub>), 2.10 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.28 (s, 3H; CCH<sub>3</sub>), 5.84 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 6.55-7.47 ppm (m, 4H; SC<sub>6</sub>H<sub>4</sub>N); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 75.5 MHz): δ = 1.7 (d, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 26 Hz, SiCH<sub>3</sub>), 23.9 (CCH<sub>3</sub>), 24.0 (CCH<sub>3</sub>), 104.8 (CCHC), 124.5, 126.3, 127.8, 128.9 (d, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 3.7 Hz), 134.0 (d, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 8.0 Hz), 138.9 (SC<sub>6</sub>H<sub>4</sub>N), 170.4 (CN or CO), 170.5 ppm (<sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 7.5 Hz, CN or CO); <sup>19</sup>F NMR (CD<sub>3</sub>CN, 376.5 MHz): δ = -75.9 ppm; <sup>29</sup>Si NMR (CD<sub>3</sub>CN, 59.6 MHz): δ = -74.8 ppm (d, <sup>1</sup>J(<sup>29</sup>Si,<sup>19</sup>F) = 265 Hz); <sup>13</sup>C VACP/MAS NMR: δ = 2.3 (SiCH<sub>3</sub>), 24.0 (CCH<sub>3</sub>), 24.5 (CCH<sub>3</sub>), 105.4 (CCHC), 123.3, 125.3, 128.6, 129.0, 133.4, 138.1 (SC<sub>6</sub>H<sub>4</sub>N), 168.7 (CN or CO), 171.6 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR: δ = -147.9 ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -77.7 ppm (d, <sup>1</sup>J(Si,F) = 283 Hz); elemental analysis calcd (%) for C<sub>12</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>2</sub>Si (267.40): C 53.90, H 5.28, N 5.24, S 11.99; found: C 53.7, H 5.4, N 5.4, S 12.0.

**Synthesis of 9:** Trichloro(methyl)silane (3.61 g, 24.2 mmol) was added dropwise within 5 min at 20 °C (water bath) to a stirred mixture of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one (5.00 g, 24.1 mmol), triethylamine (4.88 g, 48.2 mmol), and tetrahydrofuran (80 mL), and the resulting mixture was then stirred at 20 °C for 1 h. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, acetonitrile (25 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained, which was kept undisturbed at 20 °C for 4 h and then at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (15 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **9** in 65 % yield (4.45 g, 15.7 mmol) as a yellow crystalline solid. M.p. >120 °C (decomp); <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.1 MHz): δ = 0.52 (s, 3H; SiCH<sub>3</sub>), 2.12 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.32 (s, 3H; CCH<sub>3</sub>), 5.79 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 7.13-7.25 and 7.36-7.43 ppm (m, 4H; SC<sub>6</sub>H<sub>4</sub>N); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 75.5 MHz): δ = 8.8 (SiCH<sub>3</sub>), 24.0 (CCH<sub>3</sub>), 24.2 (CCH<sub>3</sub>), 105.9 (CCHC), 124.7, 125.3, 127.8, 129.2, 133.9, 138.0 (SC<sub>6</sub>H<sub>4</sub>N), 170.1 (CN or CO), 171.6 ppm (CN or CO); <sup>29</sup>Si NMR (CD<sub>3</sub>CN, 59.6 MHz): δ = -72.2 ppm; <sup>13</sup>C VACP/MAS NMR: δ = 9.4 (SiCH<sub>3</sub>), 24.1 (CCH<sub>3</sub>), 25.4 (CCH<sub>3</sub>), 106.1 (CCHC), 125.5, 126.1, 127.5, 131.2, 133.5, 137.4 (SC<sub>6</sub>H<sub>4</sub>N), 171.1 (CN or CO), 171.7 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR: δ = -152.4 ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -75 ppm (br.); elemental analysis calcd (%) for C<sub>12</sub>H<sub>14</sub>Cl<sub>3</sub>NO<sub>2</sub>Si (283.85): C 50.78, H 4.97, N 4.93, S 11.30; found: C 50.4, H 5.0, N 5.1, S 11.1.

**Synthesis of 10:** Bromotrimethylsilane (674 mg, 4.40 mmol) was added in a single portion at 20 °C to a stirred suspension of **9** (1.00 g, 3.52 mmol) in acetonitrile (10 mL), the reaction mixture was heated to 60 °C, and the undissolved solid was filtered off and discarded. The filtrate was cooled to 20 °C and kept undisturbed at this temperature for 16 h and then at -20 °C for a further 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **10** in 68 % yield (790 mg, 2.41 mmol) as a yellow crystalline solid. M.p. >130 °C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz): δ = 0.76 (s, 3H; SiCH<sub>3</sub>), 2.19 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.5 Hz, 3H; CCH<sub>3</sub>), 2.38 (s, 3H; CCH<sub>3</sub>), 5.73 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.5 Hz, 1H; CCHC), 7.12-7.29 and 7.39-7.42 ppm (m, 4H; SC<sub>6</sub>H<sub>4</sub>N); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz): δ = 10.8 (SiCH<sub>3</sub>), 24.1 (CCH<sub>3</sub>), 24.2 (CCH<sub>3</sub>), 105.4 (CCHC), 123.5, 124.7, 127.4, 128.8, 134.2, 136.9 (SC<sub>6</sub>H<sub>4</sub>N), 170.3 (CN or CO), 170.4 ppm (CN or CO); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 59.6 MHz): δ = -75.8 ppm; <sup>13</sup>C VACP/MAS NMR: δ = 12.0 (SiCH<sub>3</sub>), 24.3 (CCH<sub>3</sub>), 25.7 (CCH<sub>3</sub>), 106.6 (CCHC), 125.5, 126.6 (2 C), 132.0, 133.7, 136.8 (SC<sub>6</sub>H<sub>4</sub>N), 171.6 ppm (2 C, CN and CO); <sup>15</sup>N VACP/MAS NMR: δ = -160.2 ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -80 ppm (br.); elemental analysis calcd (%) for C<sub>12</sub>H<sub>14</sub>BrNO<sub>2</sub>Si (328.30): C 43.90, H 4.30, N 4.27, S 9.77; found: C 43.7, H 4.3, N 4.3, S 9.5.

**Synthesis of 11:** Iodotrimethylsilane (441 mg, 2.20 mmol) was added in a single portion at 20 °C to a stirred suspension of **9** (500 mg, 1.76 mmol) in acetonitrile (4 mL), and the resulting mixture was stirred for 2 min and

then kept undisturbed at 20°C for 16 h and then at -20°C for a further 24 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (5 mL), and dried in vacuo (0.01 mbar, 20°C, 2 h) to give **11** in 55% yield (365 mg, 973 μmol) as a yellow crystalline solid. M.p. >120°C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz): δ = 0.99 (s, 3H; SiCH<sub>3</sub>), 2.22 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.4 Hz, 3H; CCH<sub>3</sub>), 2.45 (s, 3H; CCH<sub>3</sub>), 5.84 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.4 Hz, 1H; CCHC), 7.16–7.29 and 7.33–7.40 ppm (m, 4H; SC<sub>6</sub>H<sub>4</sub>N); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz): δ = 13.2 (SiCH<sub>3</sub>), 24.3 (CCH<sub>3</sub>), 24.4 (CCH<sub>3</sub>), 106.3 (CCHC), 123.6, 125.0, 126.9, 129.1, 134.6, 136.3 (SC<sub>6</sub>H<sub>4</sub>N), 170.4 (CN or CO), 171.6 ppm (CN or CO); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 59.6 MHz): δ = -75.6 ppm; <sup>13</sup>C VACP/MAS NMR: δ = 12.5 (SiCH<sub>3</sub>), 23.5 (CCH<sub>3</sub>), 25.3 (CCH<sub>3</sub>), 109.7 (CCHC), 124.9, 127.5 (2 C), 132.1, 134.5, 136.5 (SC<sub>6</sub>H<sub>4</sub>N), 169.3 (CN or CO), 172.8 ppm (CN or CO); <sup>15</sup>N VACP/MAS NMR: δ = -169.0 ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -72 ppm (br.); elemental analysis calcd (%) for C<sub>12</sub>H<sub>14</sub>INOSSi (375.31): C 38.40, H 3.76, N 3.73, S 8.54; found: C 37.8, H 3.7, N 3.8, S 8.5.

**Synthesis of 12:** Compound **14** (1.45 g, 5.19 mmol) was added dropwise within 5 min at 20°C (water bath) to a stirred solution of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one (1.07 g, 5.16 mmol) and triethylamine (1.05 g, 10.4 mmol) in tetrahydrofuran (20 mL), and the resulting mixture was then stirred at 20°C for 3 h. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, acetonitrile (6 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained, which was then kept undisturbed at 20°C for 16 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20°C, 2 h) to give **13** in 65% yield (1.38 g, 3.33 mmol) as a yellow-orange crystalline solid. M.p. >122°C (decomp); <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500.1 MHz): δ = 2.23 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 3H; CCH<sub>3</sub>), 2.32 (s, 3H; CCH<sub>3</sub>), 5.94 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.6 Hz, 1H; CCHC), 6.99–7.20 and 7.38–7.66 ppm (m, 8H; SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.8 MHz): δ = 24.1 (CCH<sub>3</sub>), 24.5 (CCH<sub>3</sub>), 106.0 (CCHC), 124.8 (SC<sub>6</sub>H<sub>4</sub>N), 125.0 (q, <sup>3</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 3.8 Hz, C-3/C-5, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 125.2 (q, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 271 Hz, CF<sub>3</sub>), 125.4 (SC<sub>6</sub>H<sub>4</sub>N), 127.6 (SC<sub>6</sub>H<sub>4</sub>N), 129.4 (SC<sub>6</sub>H<sub>4</sub>N), 131.4 (q, <sup>2</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 32 Hz, C-4, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 133.58 (SC<sub>6</sub>H<sub>4</sub>N), 133.64 (br. s, C-2/C-6, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 137.8 (SC<sub>6</sub>H<sub>4</sub>N), 145.9 (q, <sup>5</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 1.3 Hz, C-1, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 171.8 (CN or CO), 173.9 ppm (CN or CO); <sup>19</sup>F NMR (CD<sub>3</sub>CN, 376.5 MHz): δ = -63.5 ppm; <sup>29</sup>Si NMR (CD<sub>3</sub>CN, 99.4 MHz): δ = -84.3 ppm; <sup>13</sup>C VACP/MAS NMR: δ = 24.0 (CCH<sub>3</sub>), 27.0 (CCH<sub>3</sub>), 108.6 (CCHC), 126.2 (7 C), 127.5, 130.6, 132.1, 138.9, 144.9 (SC<sub>6</sub>H<sub>4</sub>N, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 168.8 (CN or CO), 172.6 ppm (CN or CO), CF<sub>3</sub> not detected; <sup>15</sup>N VACP/MAS NMR: δ = -152.1 ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -84 ppm (br.); elemental analysis calcd (%) for C<sub>18</sub>H<sub>15</sub>ClF<sub>3</sub>NOSSi (413.92): C 52.23, H 3.65, N 3.38, S 7.75; found: C 52.0, H 3.6, N 3.6, S 7.8.

**Synthesis of 13:** Compound **15** (1.58 g, 5.24 mmol) was added dropwise within 5 min at 20°C (water bath) to a stirred solution of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one (1.09 g, 5.26 mmol) and triethylamine (1.06 g, 10.5 mmol) in tetrahydrofuran (20 mL), and the resulting mixture was stirred at 20°C for 2 h. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, acetonitrile (7 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained, which was then kept undisturbed at 20°C for 14 h and then at -20°C for a further 3 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20°C, 3 h) to give **13** in 59% yield (1.34 g, 3.07 mmol) as a yellow-brown crystalline solid. M.p. >165°C (decomp); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.1 MHz): δ = 2.27 (d, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.5 Hz, 3H; CCH<sub>3</sub>), 2.34 (s, 3H; CCH<sub>3</sub>), 5.85 (q, <sup>4</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 0.5 Hz, 1H; CCHC), 7.01–7.09, 7.20–7.25, 7.46–7.50 ppm (m, 4H; SC<sub>6</sub>H<sub>4</sub>N); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz): δ = 24.2 (CCH<sub>3</sub>), 24.4 (CCH<sub>3</sub>), 105.6 (CCHC), 123.3, 124.9, 127.5, 129.0, 133.1, 136.6 (SC<sub>6</sub>H<sub>4</sub>N), 113.4 (m, C-1, SiC<sub>6</sub>F<sub>5</sub>), 137.4 (dm, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 245 Hz, C-2/C-6, SiC<sub>6</sub>F<sub>5</sub>), 142.0 (dm, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 254 Hz, C-4, SiC<sub>6</sub>F<sub>5</sub>), 147.7 (dm, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 240 Hz, C-3/C-5, SiC<sub>6</sub>F<sub>5</sub>), 171.5 (CN or CO), 171.9 ppm (CN or CO); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376.5 MHz): δ = -162.4 to -162.0, -153.5 to -153.2, -130.2 to -130.0 ppm (m, 5 F, SiC<sub>6</sub>F<sub>5</sub>); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.4 MHz): δ = -92.3 to -92.0 (m) ppm; <sup>13</sup>C VACP/MAS

NMR: δ = 23.1 (CCH<sub>3</sub>), 26.0 (CCH<sub>3</sub>), 110.6 (CCHC), 120.3, 126.3 (2 C), 128.1, 131.5, 138.8 (SC<sub>6</sub>H<sub>4</sub>N), 175.7 (2 C) ppm (CN and CO), SiC<sub>6</sub>F<sub>5</sub> not well resolved/detectable; <sup>15</sup>N VACP/MAS NMR: δ = -171.0 ppm; <sup>29</sup>Si VACP/MAS NMR: δ = -93 ppm (br.); elemental analysis calcd (%) for C<sub>17</sub>H<sub>11</sub>ClF<sub>3</sub>NOSSi (435.88): C 46.85, H 2.54, N 3.21, S 7.36; found: C 46.9, H 2.7, N 3.4, S 7.5.

**Synthesis of 14:** Compound **14** was synthesized according to reference [11]; however, it was not obtained as an intermediate, instead it was isolated and characterized: A solution of 1-bromo-4-(trifluoromethyl)benzene (8.34 g, 37.1 mmol) in diethyl ether (10 mL) was added dropwise within 30 min to a stirred suspension of magnesium turnings (901 mg, 37.0 mmol) in diethyl ether (20 mL), causing the reaction mixture to boil under reflux. The mixture was heated under reflux for a further 2 h, cooled to 20°C, and then added dropwise at 20°C within 20 min to a stirred solution of tetrachlorosilane (25.2 g, 148 mmol) in diethyl ether (60 mL). The mixture was then heated under reflux for 2 h, allowed to cool to 20°C, and stirred at 20°C for 48 h. The resulting solid was filtered off, washed with diethyl ether (10 mL), and discarded. The solvent of the filtrate (including the wash solution) and the excess tetrachlorosilane were removed under reduced pressure, and the residue was purified by distillation in vacuo to yield **14** in 36% as a colorless liquid (3.77 g, 13.5 mmol). B.p. 70–72°C/8 mbar; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500.1 MHz): δ = 7.23–7.27 and 7.39–7.44 ppm (m, 4H; SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125.8 MHz): δ = 124.0 (q, <sup>1</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 273 Hz, CF<sub>3</sub>), 125.3 (q, <sup>3</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 3.8 Hz, C-3/C-5, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 133.7 (br., C-2/C-6, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 134.1 (q, <sup>2</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 33 Hz, C-4, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), 135.3 ppm (q, <sup>3</sup>J(<sup>13</sup>C,<sup>19</sup>F) = 1.2 Hz, C-1, SiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 376.5 MHz): δ = -63.2 ppm; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz): δ = -1.6 ppm.

**Synthesis of 15:** Compound **15** was synthesized according to reference [12].

**Crystal structure analyses:** Suitable single crystals of compounds **1**, **3**, **5–8**, and **10–13** were isolated directly from the respective reaction mixtures. Compound **9** was crystallized by cooling of a saturated solution in dichloromethane to 4°C. 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 (**1**, **3**, **9**, and **10**: Bruker Nonius KAPPA APEX II, Montel mirror, MoK<sub>α</sub> radiation, λ = 0.71073 Å; **5–8** and **11–13**: Stoe IPDS, graphite-monochromated MoK<sub>α</sub> radiation, λ = 0.71073 Å). All structures were solved by direct methods.<sup>[13]</sup> The non-hydrogen atoms were refined anisotropically.<sup>[13]</sup> A riding model was employed in the refinement of the CH hydrogen atoms. CCDC-765906 (**1**), CCDC-765907 (**3**), CCDC-765908 (**5**), CCDC-765909 (**6**), CCDC-765910 (**7**), CCDC-765911 (**8**), CCDC-765912 (**9**), CCDC-765913 (**10**), CCDC-765914 (**11**), CCDC-765915 (**12**), and CCDC-765916 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

- [1] For selected reviews dealing with higher-coordinate silicon(IV) compounds, see: a) R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927–950; b) V. Pestunovich, S. Kirpichenko, M. Voronkov in *The Chemistry of Organic Silicon Compounds*, Vol. 2, Part 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 1447–1537; c) C. Chuit, R. J. P. Corriu, C. Reye in *Chemistry of Hypervalent Compounds* (Ed.: K.-y. Akiba), Wiley-VCH, New York, **1999**, pp. 81–146; d) R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221–273; e) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, **2000**, pp. 97–114; f) R. Tacke, O. Seiler in *Silicon Chemistry: From the Atom to Extended Systems* (Eds.: P. Jutz, U. Schubert), Wiley-VCH, Weinheim, **2003**, pp. 324–337; g) D. Kost, I. Kalikhman, *Adv. Organomet. Chem.* **2004**, *50*, 1–106; h) D. Kost, I. Kalikhman, *Acc. Chem. Res.* **2009**, *42*, 303–314.
- [2] For selected recent publications dealing with higher-coordinate silicon(IV) compounds, see: a) S. Y. Bylikin, A. G. Shipov, E. P. Kramarova, V. V. Negrebetsky, A. A. Korlyukov, Y. I. Baukov, M. B. Hursthouse, L. Male, A. R. Bassindale, P. G. Taylor, *J. Organomet. Chem.* **2009**, *694*, 244–248; b) A. R. Bassindale, D. J. Parker, P. G.

- Taylor, R. Turtle, *Z. Anorg. Allg. Chem.* **2009**, 635, 1288–1294; c) I. Kalikhman, E. Kertsnus-Banchik, B. Gostevskii, N. Kocher, D. Stalke, D. Kost, *Organometallics* **2009**, 28, 512–516; d) S. Yakubovich, B. Gostevskii, I. Kalikhman, D. Kost, *Organometallics* **2009**, 28, 4126–4132; e) E. Kertsnus-Banchik, E. Sela, J. Wagler, I. Kalikhman, D. Kost, *Z. Anorg. Allg. Chem.* **2009**, 635, 1321–1325; f) K. Lippe, D. Gerlach, E. Kroke, J. Wagler, *Organometallics* **2009**, 28, 621–629; g) A. Kämpfe, E. Kroke, J. Wagler, *Eur. J. Inorg. Chem.* **2009**, 1027–1035; h) E. Brendler, T. Heine, A. F. Hill, J. Wagler, *Z. Anorg. Allg. Chem.* **2009**, 635, 1300–1305; i) G. W. Fester, J. Wagler, E. Brendler, U. Böhme, D. Gerlach, E. Kroke, *J. Am. Chem. Soc.* **2009**, 131, 6855–6864; j) R. Gericke, D. Gerlach, J. Wagler, *Organometallics* **2009**, 28, 6831–6834; k) E. P. A. Couzijn, D. W. F. van den Engel, J. C. Slootweg, F. J. J. de Kanter, A. W. Ehlers, M. Schakel, K. Lammertsma, *J. Am. Chem. Soc.* **2009**, 131, 3741–3751; l) E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, K. Lammertsma, *Z. Anorg. Allg. Chem.* **2009**, 635, 1273–1278; m) G. González-García, E. Álvarez, Á. Marcos-Fernández, J. A. Gutiérrez, *Inorg. Chem.* **2009**, 48, 4231–4238; n) M. Yamamura, N. Kano, T. Kawashima, *Z. Anorg. Allg. Chem.* **2009**, 635, 1295–1299; o) R. S. Ghadwal, S. S. Sen, H. W. Roesky, G. Tavcar, S. Merkel, D. Stalke, *Organometallics* **2009**, 28, 6374–6377; p) B. Theis, S. Metz, F. Back, C. Burschka, R. Tacke, *Z. Anorg. Allg. Chem.* **2009**, 635, 1306–1312; q) S. Metz, C. Burschka, R. Tacke, *Chem. Asian J.* **2009**, 4, 581–586; r) S. Metz, C. Burschka, R. Tacke, *Organometallics* **2009**, 28, 2311–2317; s) B. Theis, S. Metz, C. Burschka, R. Bertermann, S. Maisch, R. Tacke, *Chem. Eur. J.* **2009**, 15, 7329–7338.
- [3] For publications dealing with higher-coordinate silicon(IV) compounds containing sulfur, selenium, and/or tellurium ligand atoms, see: a) R. Tacke, M. Mallak, R. Willeke, *Angew. Chem.* **2001**, 113, 2401–2403; *Angew. Chem. Int. Ed.* **2001**, 40, 2339–2341; b) R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, R. Tacke, *Organometallics* **2003**, 22, 4104–4110; c) O. Seiler, M. Büttner, M. Penka, R. Tacke, *Organometallics* **2005**, 24, 6059–6062; d) D. Troegel, C. Burschka, S. Riedel, M. Kaupp, R. Tacke, *Angew. Chem.* **2007**, 119, 7131–7135; *Angew. Chem. Int. Ed.* **2007**, 46, 7001–7005; e) S. Metz, C. Burschka, D. Platte, R. Tacke, *Angew. Chem.* **2007**, 119, 7136–7139; *Angew. Chem. Int. Ed.* **2007**, 46, 7006–7009; f) S. Metz, C. Burschka, R. Tacke, *Organometallics* **2008**, 27, 6032–6034; g) S. Metz, C. Burschka, R. Tacke, *Eur. J. Inorg. Chem.* **2008**, 4433–4439.
- [4] a) A. R. Bassindale, D. J. Parker, P. G. Taylor, N. Auner, B. Herrschaft, *J. Organomet. Chem.* **2003**, 667, 66–72; b) M. Driess, N. Muresan, K. Merz, *Angew. Chem.* **2005**, 117, 6896–6899; *Angew. Chem. Int. Ed.* **2005**, 44, 6738–6741.
- [5] a) J. Yang, I. Guzei, J. G. Verkade, *J. Organomet. Chem.* **2002**, 649, 276–288; b) D. F. Moser, A. Naka, I. A. Guzei, T. Müller, R. West, *J. Am. Chem. Soc.* **2005**, 127, 14730–14738; c) G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem.* **2005**, 117, 8096–8099; *Angew. Chem. Int. Ed.* **2005**, 44, 7884–7887.
- [6] For publications dealing with neutral pentacoordinate silicon(IV) compounds that contain axial thiocyanato-*N* ligands, see: a) O. Seiler, C. Burschka, S. Metz, M. Penka, R. Tacke, *Chem. Eur. J.* **2005**, 11, 7379–7386; b) G. González-García, J. A. Gutiérrez, S. Cota, S. Metz, R. Bertermann, C. Burschka, R. Tacke, *Z. Anorg. Allg. Chem.* **2008**, 634, 1281–1286.
- [7] A. C. Filippou, P. Portius, G. Schnakenburg, *J. Am. Chem. Soc.* **2002**, 124, 12396–12397.
- [8] D. A. Dixon, W. R. Hertler, D. B. Chase, W. B. Farnham, F. Davidson, *Inorg. Chem.* **1988**, 27, 4012–4018.
- [9] J. Böhm, D. Fenzke, H. Pfeifer, *J. Magn. Reson.* **1983**, 55, 197–204.
- [10] The reported chemical shifts are those of the pentacoordinate species.
- [11] J. P. Banovetz, H. Suzuki, R. M. Waymouth, *Organometallics* **1993**, 12, 4700–4703.
- [12] H. J. Frohn, M. Giesen, A. Klose, A. Lewin, V. V. Bardin, *J. Organomet. Chem.* **1996**, 506, 155–164.
- [13] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, 64, 112–122.

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