

# Preparation, first X-ray structure analysis and reactivity of hexacoordinate silicon compounds with a tetradentate azomethine ligand

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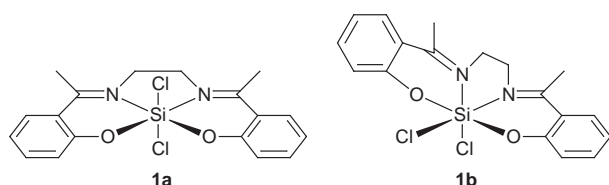
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Hexacoordinate silicon compounds and polymers with the tetradentate azomethine ligand *N,N'*-ethylenebis(2-hydroxyacetophenoneimine) ( $H_2salen^*$ ) have been prepared and characterized; the X-ray structure analysis of  $(salen^*)SiF_2$  clearly demonstrates the octahedral coordination of the silicon atom.

Hypervalent silicon compounds attract interest from both the structural and reactivity point of view.<sup>1</sup> The isolation of such compounds allows detailed insight into mechanistic pathways of nucleophilic substitution at silicon.<sup>1e</sup> On the other hand compounds based on such synthons should exhibit interesting properties as electronic materials. Different types of hypercoordinate silicon compounds have so far been reported: (a) the initial compounds were octahedral fluorosilicate  $[SiF_6]^{2-}$  and derivatives thereof,<sup>2</sup> (b) derivatives of 2,2'-bipyridyl, (c) complexes with different bidentate ligands such as 1,3-diketones, 2-dimethylaminomethylphenyl or 1,2-diolates, (d) phthalocyaninato derivatives.<sup>1</sup>

We set out to synthesize hexacoordinate silicon complexes containing the  $salen^*$  ligand. This ligand is able to chelate to silicon atom through four donor atoms. There are some rare examples of  $salen$  silicon compounds known from the literature,<sup>3</sup> but characterization of these compounds seems doubtful.<sup>4</sup> Structural aspects are uncertain owing to the lack of crystal structure data.

Transition metal  $salen$  complexes have been investigated extensively.<sup>5</sup> Different types of  $salen$  ligands have been applied recently, mainly in transition metal complex catalysts, for the transformation of organic substrates.<sup>6</sup> We used a slightly modified  $salen$  ligand [*N,N'*-ethylenebis(2-oxyacetophenoneimine) =  $salen^*$ ] with methyl groups at the azomethine carbon instead of hydrogen. This prevents unwanted side reactions caused by the azomethine protons. The key compound  $(salen^*)SiCl_2$  **1** can be prepared by two different routes (i and ii, Scheme 1).<sup>‡</sup> Elemental analysis indicates the formation of a complex of the composition  $(salen^*)SiCl_2$ . Preparation of **1** via reaction of  $H_2salen^*$  with  $SiCl_4$  (route i) yields a product with two  $^{29}Si$  NMR signals and 18 signals in the  $^{13}C$  NMR spectrum. This points to the formation of two different isomers **1a** and **1b** in a ratio of 1 : 1, according to the intensity of the signals. The same type of isomerism has been observed in tin  $salen$  compounds and confirmed by Mössbauer spectroscopy.<sup>7</sup>

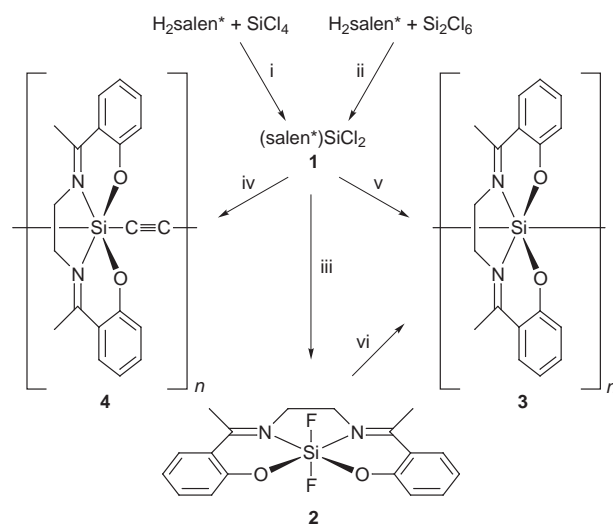


The extremely high field shift of the  $^{29}Si$  NMR signals for the isomers of **1** ( $\delta -186.1$ ,  $-188.0$ ) indicates the presence of hexacoordinate silicon atoms. Reaction of  $Si_2Cl_6$  with  $H_2salen^*$  (ii in Scheme 1) gives only one isomer with nine signals in the

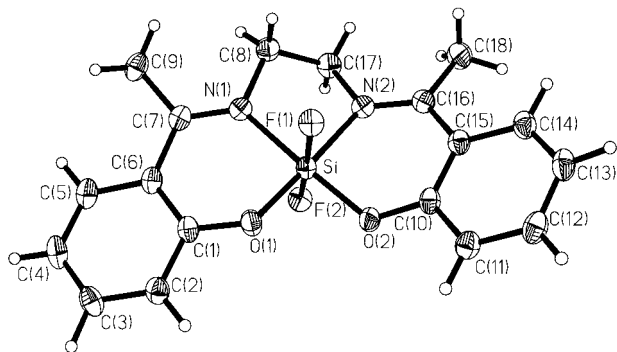
$^{13}C$  NMR spectrum and one  $^{29}Si$  NMR signal at  $\delta -188$ . Hydrogen chloride and hydrogen are evolved in this reaction.

The chlorine atoms in **1** can be substituted for fluorine by treating **1** with  $ZnF_2$  in THF. For the preparation of the fluoro derivative **2** the mixture of isomers **1a** and **1b** was used. The resulting product **2** represents only one isomer as concluded from NMR data. This information hints to a rearrangement of the coordination sites of the  $salen^*$  ligand during nucleophilic substitution of the chlorine by fluorine. The mechanism of this reaction as well as the energy differences between the isomers **1a** and **1b** seem to be quite interesting and will be subject of further investigation. Complex **2** is more soluble in organic solvents than the chloro derivative and we were able to obtain single crystals of **2** by recrystallization from acetonitrile. The X-ray crystal structure analysis of **2** provides the molecular structure shown in Fig. 1.§ It was solved and refined in space group  $P2_1/a$  with four molecules of **2** and four molecules of acetonitrile per unit cell. There is a distorted octahedral coordination geometry around silicon. The fluorine atoms are situated at axial positions (*trans* isomer), whereas the  $salen^*$  ligand occupies the four equatorial positions.

There are a number of crystal structures of bis(chelate) compounds with hexacoordinate silicon. Most of these have essentially a tetrahedral arrangement around silicon with the coordinated nitrogen donor atoms 'capping' the tetrahedra at relatively large distances (N–Si between 2.5 and 3.0 Å).<sup>8</sup> The Si–F distance in **2** corresponds well with bond length found in other hypervalent silicon compounds (1.60–1.73 Å).<sup>1d,9</sup> The Si–O and Si–N distances are remarkably short compared to other hexacoordinate silicon compounds.<sup>8</sup> The distortion of the octahedral coordination environment around silicon probably originates from the conformation of the chelating  $salen^*$  ligand.



**Scheme 1** Reagents and conditions: i and ii, THF, 2 h, reflux, 90%; iii,  $ZnF_2$ , THF, 1 h reflux, 20%, extraction with THF; iv,  $LiCCl$  or  $BrMgCCMgBr$ , THF-*n*-hexane, 6 h reflux; v,  $(salen^*)SiCl_2$  and K in ratio 1 : 2, toluene, 6 h reflux; vi,  $(salen^*)SiF_2$  and Li, THF, 2 h room temp.

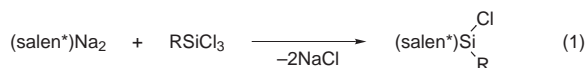


**Fig. 1** Crystal structure of **2**. Selected bond distances (Å) and angles (°): Si–F(1) 1.677(1), Si–F(2) 1.670(1), Si–O(1) 1.721(1), Si–O(2) 1.724(1), Si–N(1) 1.931(2), Si–N(2) 1.937(2); F(1)–Si–F(2) 172.40(5), O(1)–Si–N(2) 178.00(6), O(2)–Si–N(1) 1.76.75(6), F(1)–Si–O(1) 91.68(6), F(1)–Si–O(2) 93.85, F(1)–Si–N(1) 86.93(5), F(1)–Si–N(2) 87.36(6), F(2)–Si–O(1) 93.17(6), F(2)–Si–O(2) 92.00(6), F(2)–Si–N(1) 86.96(5), F(2)–Si–N(2) 87.60(6).

There is a considerable torsion along the atoms N(1)–C(8)–C(17)–N(2) of *ca.* 46°. The result of this is that one azomethine unit is bended under and the other above the plane N(1)SiN(2).

Experiments to obtain stacked polymers **3** by reaction of **1** or **2** with alkaline metals or magnesium are very promising. These polymers are poorly soluble in organic solvents and more stable towards moisture than the monomers. They have been characterized by elemental analysis, IR and NMR spectroscopy. Furthermore it is possible to react **1** with dilithium acetylide or the corresponding Grignard reagent to obtain polymers of type **4** which are linked by Si–C≡C–Si units (Scheme 1). Polymers with similar backbone but different chelating ligands have been described recently.<sup>10</sup>

Complexes of the type (salen\*)Si(Cl)R **5** and **6** are available by reaction of Na<sub>2</sub>(salen\*) with RSiCl<sub>3</sub> [R = Me, Ph; eqn. (1)]. Only one isomer is formed in both cases as revealed by NMR data. At present it is not possible to decide whether these are the *cis*- or *trans*-isomers. These organosilicon compounds are more soluble in organic solvents than **1**.



R = Me **5** or Ph **6**

Investigations relating to electric conductivity and optical properties of the new class of silicon polymers **3** and **4** will be carried out in the future. Further studies to explore the chemistry of these truly hexacoordinate silicon compounds are under way.

## Notes and References

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‡ Selected spectroscopic data: All new compounds gave satisfactory analytical data.

(salen\*)SiCl<sub>2</sub> **1a/1b**: [NMR, (CD<sub>3</sub>)<sub>2</sub>SO δ] mixture of isomers <sup>13</sup>C, C<sup>1</sup> 157.3/158.1, C<sup>2</sup> 118.8/119.4, C<sup>3</sup> 135.1/136.9, C<sup>4</sup> 120.6/120.7, C<sup>5</sup> 129.9/131.2, C<sup>6</sup> 120.2/120.5, C<sup>7</sup> 176.4/171.6, C<sup>8</sup> 46.1/46.7, C<sup>9</sup> 18.6/20.7; <sup>29</sup>Si, –186.1/–188.0; IR ν(C=N) 1630 cm<sup>-1</sup>, ν(Si–Cl) 521 cm<sup>-1</sup>, δ(Si–O–C) 1104 cm<sup>-1</sup>.

(salen\*)SiCl<sub>2</sub> **1a** from Si<sub>2</sub>Cl<sub>6</sub>: [NMR, (CD<sub>3</sub>)<sub>2</sub>SO δ] <sup>13</sup>C, C<sup>1</sup> 157.3, C<sup>2</sup> 119.4, C<sup>3</sup> 136.9, C<sup>4</sup> 120.7, C<sup>5</sup> 131.2, C<sup>6</sup> 120.5, C<sup>7</sup> 176.4, C<sup>8</sup> 46.7, C<sup>9</sup> 20.7; <sup>1</sup>H, δ C<sup>2</sup>–C<sup>5</sup> 6.8–8.1, C<sup>8</sup> 4.2, C<sup>9</sup> 1.5; <sup>29</sup>Si –188.0.

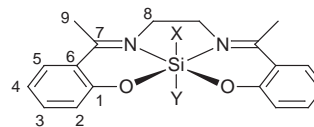
(salen\*)SiF<sub>2</sub> **2**: (NMR, CDCl<sub>3</sub> δ) <sup>13</sup>C, C<sup>1</sup> 160.3, C<sup>6</sup> 121.9, C<sup>7</sup> 170.7, C<sup>8</sup> 46.4, C<sup>9</sup> 18.2; <sup>29</sup>Si, 187.9 [t<sup>2</sup>J(SiF) 179.2 Hz]; IR ν(C=N) 1610 cm<sup>-1</sup>, ν(Si–F) 954 cm<sup>-1</sup>.

[(salen\*)Si]<sub>n</sub>, **3**: (NMR, solid state, δ) <sup>29</sup>Si, –130 (br); IR ν(C=N) 1613 cm<sup>-1</sup>, δ(Si–O–C) 1100 cm<sup>-1</sup>.

[(salen\*)SiCC]<sub>n</sub>, **4**: [NMR, (CD<sub>3</sub>)<sub>2</sub>SO δ] <sup>13</sup>C, C<sup>1</sup> 168.4, C<sup>6</sup> 120.0, C<sup>7</sup> 169.1, C<sup>8</sup> 51.4, C<sup>9</sup> 22.2; <sup>29</sup>Si –88 (br); IR ν(C=N) 1607 cm<sup>-1</sup>, ν(Si–C) 840 cm<sup>-1</sup>, Raman: ν(C≡C) 2260 cm<sup>-1</sup>.

(salen\*)MeSiCl **5**: [NMR, (CD<sub>3</sub>)<sub>2</sub>SO δ] <sup>13</sup>C, C<sup>1</sup> 158.4, C<sup>6</sup> 120.9, C<sup>7</sup> 175.9, C<sup>8</sup> 45.3, C<sup>9</sup> 19.2, C<sup>19</sup> (Si–Me) 5.9; <sup>29</sup>Si, –150.7; IR ν(C=N) 1629 cm<sup>-1</sup>, ν(Si–Cl) 509 cm<sup>-1</sup>, ν(Si–C) 798 cm<sup>-1</sup>.

(salen\*)PhSiCl **6**: [NMR, (CD<sub>3</sub>)<sub>2</sub>SO, δ] <sup>13</sup>C, C<sup>1</sup> 159.7, C<sup>6</sup> 121.1, C<sup>7</sup> 179.8, C<sup>8</sup> 46.9, C<sup>9</sup> 18.2; <sup>29</sup>Si, –173.1; IR ν(C=N) 1612 cm<sup>-1</sup>, ν(Si–Cl) 488 cm<sup>-1</sup>, ν(Si–C) 840 cm<sup>-1</sup>.



§ Crystal data for (salen\*)SiF<sub>2</sub> **2** (white crystals from MeCN): C<sub>20</sub>H<sub>21</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Si·CH<sub>3</sub>CN, monoclinic space group P2<sub>1</sub>/a, a = 12.3826(5), b = 10.8405(5), c = 13.8507(5) Å, β = 98.800(5); U = 1837.3(1) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.451 g cm<sup>-3</sup>, μ = 1.503 mm<sup>-1</sup>, F(000) = 840. A single crystal of approximate dimensions 0.2 × 0.5 × 0.6 mm was mounted on a glass fibre under paraffin oil and transferred to the diffractometer. Data were collected at –10 °C on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu–Kα radiation (λ = 1.5418 Å) with ω–2θ scans. The structure was solved by direct methods and refined by full matrix least squares on F<sup>2</sup> with anisotropic thermal parameters. Hydrogen atom positions were located and isotropically refined. R = 0.0431 for 3358 reflections (F<sub>o</sub> > 2σF<sub>o</sub>) and 0.0482 for all 3784 reflections, GOF = S = 1.033. CCDC 182/854.

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- Compare for instance the wrong data of elemental analysis in ref. 3(b). The calculated sum formula was given with C<sub>14</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>Si and the found data fitted this formula well. The correct formula should be C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Si!
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