

# Equilibrium between Tetra-, Penta-, and Hexacoordinate Imine and Enamine Chelates of Silicon: Crystal Structure and Variable-Temperature NMR

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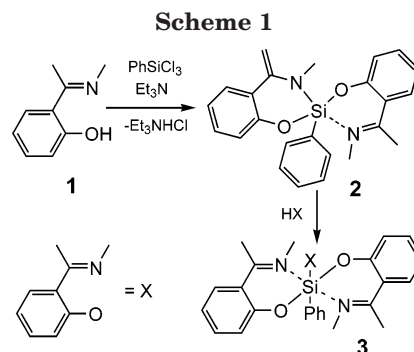
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**Summary:** The Si-coordination sphere in the novel pentacoordinate silicon bischelate  $\eta^2(N,O)$ -*N*-methyl-*o*-oxyacetophenoneiminato-*N'*-methyl-*N'*-1-(2-oxyphenyl)vinyllaminatophenylsilicon, **2**, which was analyzed by variable-temperature  $^{29}\text{Si}$  NMR spectroscopy and X-ray crystallography, was found to be temperature dependent. The addition of a third equivalent of the chelating ligand yields the hexacoordinate silicon complex bis- $[\eta^2(N,O)$ -*N*-methyl-*o*-oxyacetophenoneiminato]- $\eta^1(O)$ -*N*-methyl-*o*-oxyacetophenoneiminato)phenylsilicon, **3**, which undergoes Si–O bond cleavage as well as Si–N bond formation in solution.

In recent years interest in hypercoordinate silicon compounds has grown considerably.<sup>1</sup> Research is becoming more and more focused on complexes with flexible coordination spheres with the aim of observing their temperature- and solvent-dependent fluxional behavior. Phenomena such as temperature-dependent ionic<sup>2a–d</sup> and nonionic<sup>2e</sup> dissociation, flip-flop mechanism,<sup>3</sup> solvent- and temperature-dependent diastereomeric rearrangement of the coordination sphere,<sup>4</sup> and equilibration between tetra- and pentacoordinate silicon compounds,<sup>5</sup> or even photochemically induced switching of the coordination number<sup>6</sup> have been reported.

Recently we have found an innovative way of switching between coordination numbers five and six by



eliminating acids from imine-functionalized or adding acids to enamine-functionalized silicon complexes containing salen-type ligands.<sup>7</sup> In this article we focus on transferring this principle to silicon complexes of the bidentate  $\langle O, N \rangle$ -chelating ligand **1** (Scheme 1).

Unlike the situation in analogous complexes containing tetradentate salen-type ligands, **1** is not forced to coordinate at the silicon atom via its imine nitrogen atom. Nevertheless, the imine nitrogen atom does bond to the silicon atom in the solid state. The resulting pentacoordination was confirmed by crystal structure analysis (Figure 1).

The coordination sphere of the Si atom is nearly trigonal bipyramidal (91% TBP).<sup>2a</sup> Both Si–N bonds are in axial position. In comparison with other molecular structures of pentacoordinate silicon bis-chelates<sup>2,9</sup> which involve two axial Si–N bonds, this result does not seem surprising. But there are two dative Si–N bonds in those complexes. Kost et al. isolated pentacoordinate silicon bis-chelates with two covalent Si–N bonds<sup>10a</sup> in equatorial position, as well as a silicon bis-chelate with a dative and a covalent Si–N bond<sup>10b</sup>—also in equatorial position! In contrast to these results, the axial arrange-

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(8) Crystal structure of **2**: formula  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2\text{Si}$ ; monoclinic space group  $P2_1/m$ ; unit cell  $a = 8.8530(10)$  Å,  $b = 17.0160(10)$  Å,  $c = 14.010(2)$  Å,  $\beta = 100.385(10)^\circ$ ; determined at 198(2) K;  $R(wR_2) = 0.0663$  (0.1033 for all data). Selected bond distances [Å] and angles [deg]: Si1–N1 1.804(1), Si1–N2 2.081(2), Si1–O1 1.655(2), Si1–O2 1.664(2), Si1–C31 1.878(3), C7–N1 1.378(3), C17–N2 1.293(3), N1–Si1–N2 175.07(10), O1–Si1–O2 120.51(10), O1–Si1–C31 120.10(10), O2–Si1–C31 117.11(10).

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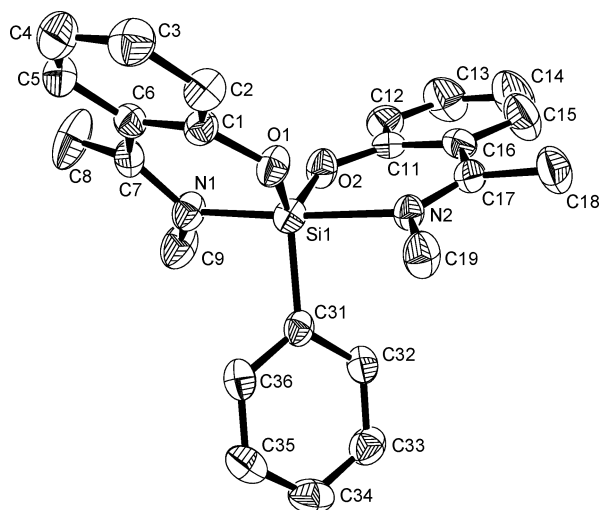
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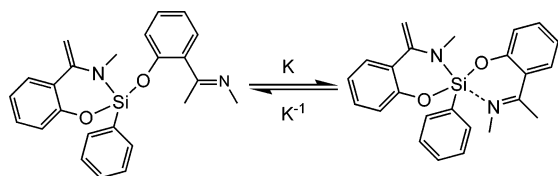
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**Figure 1.** Molecular structure of **2** in the crystal<sup>8</sup> (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted).

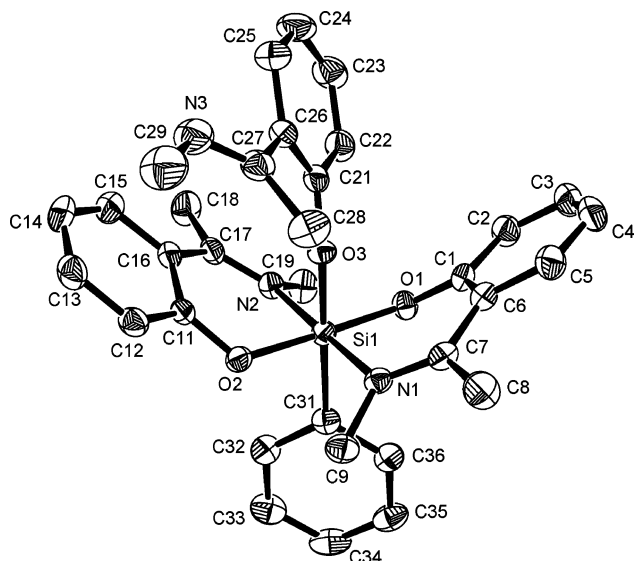
### Scheme 2



ment of a dative as well as a covalent Si–N bond in a trigonal bipyramidal coordination sphere in **2** represents a new ligand pattern.

Pentacoordination of the Si atom in **2** is confirmed by solid state <sup>29</sup>Si NMR spectroscopy ( $\delta$  –109.4 ppm) and X-ray crystal structure analysis. In contrast, its coordination behavior in solution is quite different. The <sup>29</sup>Si NMR spectra of **2** recorded at room temperature in various solvents give a chemical shift value that is still typical for tetracoordinate silicon atoms connected to four  $\pi$ -donor atoms. But regarding the solvents used, there are significant differences that may originate from a ligand exchange equilibrium between tetra- and pentacoordinate species in solution (Scheme 2) (CDCl<sub>3</sub>:  $\delta$  = –62.5 ppm at 20 °C; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  = –70.5 ppm at 22 °C; toluene-*d*<sub>8</sub>  $\delta$  = –70.1 ppm at 22 °C).

It is obvious that the tendency of the complex to become pentacoordinate is less favorable in chloroform. The relatively high acceptor number of chloroform is assumed to be the main reason. Thus, a dipolar interaction between the lone pair of the imine nitrogen atom and the acidic chloroform proton may prevent the imine-N atom from coordinating to the Si atom. The variable-temperature <sup>29</sup>Si NMR spectra of **2** recorded in methylene chloride show only one signal, which is shifted from –111.5 ppm at –50 °C to –70.5 ppm at 22 °C. Thus, we can conclude that there is a rapid exchange between tetra- and pentacoordinate Si species. The measured chemical shift value was  $\delta$  = –113.3 ppm in the temperature region between –50 and –55 °C, before the solution suddenly solidified. This indicates a much better shielding of the Si nucleus in cold solution than in the solid state at room temperature. In the crystal the relatively long dative Si–N bond (2.08 Å) (which possibly is due to steric reasons for better crystalliza-



**Figure 2.** Molecular structure of **3** in the crystal<sup>11</sup> (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and solvent molecule [0.5 *p*-xylene] omitted).

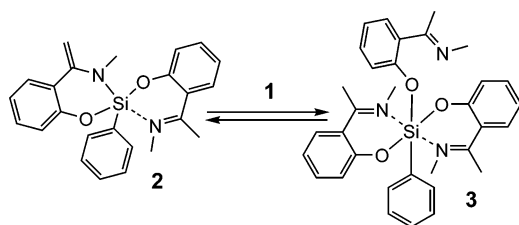
tion) should be responsible for the lower shielding. It is not possible to estimate the chemical shift value for the tetracoordinate species in methylene chloride due to the low boiling point of this solvent. In contrast, very useful data were found in CDCl<sub>3</sub> ( $\delta$  = –58.4 ppm at 45 °C, –58.2 ppm at 50 °C). Based on these values, the equilibrium concentrations of the tetra- and the pentacoordinate species as well as the equilibrium constant *K* were determined at each temperature level. A linearized plot of ln *K* versus 1/*T* gives the thermodynamic data  $\Delta H$  = –31.5 kJ mol<sup>–1</sup> and  $\Delta S$  = –116.7 J mol<sup>–1</sup> K<sup>–1</sup> for the observed chelation reaction.

The formation of the pentacoordinate species **2** is an exothermic process. This result was confirmed by quantum chemical calculations, [MP2/6-311+G(2d,p)]. The formation of the dative Si–N bond was estimated to result in a reaction enthalpy of about –25 kJ mol<sup>–1</sup> (see Supporting Information). However, at room temperature the formation of the tetracoordinate species is favored due to a positive value of the reaction entropy. This gain in entropy on release of the imine nitrogen atom from its dative bond is believed to originate from an extended number of rotational degrees of freedom in the tetra-coordinate species **2**.

In analogy with pentacoordinate silicon complexes with an enamine-functionalized salen-type ligand, **2** also can react with acids to yield adducts. An interesting case is the addition of a third equivalent of the chelating ligand **1** to complex **2** to yield **3** (Scheme 1). This novel compound was characterized by solid state <sup>29</sup>Si NMR spectroscopy ( $\delta$  –182.6 ppm) as well as by crystal structure analysis (Figure 2) to confirm hexacoordination of the silicon atom.

The coordination sphere of the silicon atom in **3** is octahedral with two trans-configured monodentate ligands. Almost all known molecular structures of neutral hexacoordinate silicon bis-chelates have *cis* orientation of the two monodentate ligands. Only a few structures of neutral octahedral silicon bis-chelates with trans-situated monodentate donors are known.<sup>2c,d,12</sup> Unlike these molecules with five-membered chelate

Scheme 3



rings, **3** has two six-membered chelate rings as well as trans configuration of the monodentate ligands.

Compound **3** is easily soluble in chloroform and slightly soluble in toluene, but characterization of the pure compound **3** in solution was not possible (see NMR spectra, Supporting Information)! Nearly complete dissociation of **3** into **2** and **1** was found to occur in  $\text{CDCl}_3$  as well as in toluene- $d_8$  (Scheme 3).  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra revealed the coexistence of both **1** and **2** in solution.

Surprisingly, the dissociation of a Si–O bond occurs and a dative Si←N bond is transformed into a covalent Si–N bond. This unusual behavior arises from the higher coordination number of the silicon atom. We expected this dissociation to occur for three reasons: The ligand **1** is stabilized by a hydrogen bridge O–H–N, which originates from the interaction between the imine and hydroxo groups.<sup>13</sup> The chelating effect of a  $\eta^2$ -coordinating ⟨O,N⟩-chelating ligand enables an easier formation of the covalent Si–N bond. Finally, the leaving group (**1**) is only slightly bonded to the silicon atom. There is a long Si–O bond distance (Si1–O3: 1.77 Å), but there is no chelate effect to stabilize this connection.

Altogether, these results clearly demonstrate that there is an interesting dynamic in the silicon coordination sphere of such imine and amino chelates. Different bonding situations regarding the exchange of ligands can be controlled by variation of solvent and temperature, respectively. The herein presented novel hypercoordinate organosilicon complexes represent ideal model compounds to study these interactions in detail.

### Experimental Section

Syntheses were carried out under an inert atmosphere of dry argon using standard Schlenk techniques.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$

(11) Crystal structure of **3**: formula  $\text{C}_{37}\text{H}_{40}\text{N}_3\text{O}_3\text{Si}$ ; monoclinic space group  $P2_1/n$ ; unit cell  $a = 11.889(2)$  Å,  $b = 21.871(4)$  Å,  $c = 12.464(3)$  Å,  $\beta = 101.94(3)^\circ$ ; determined at 198(2) K;  $R(wR_2) = 0.0729$  (0.1110 for all data). Selected bond distances [Å] and angles [deg]: Si1–N1 1.959(2), Si1–N2 1.948(2), Si1–O1 1.759(2), Si1–O2 1.759(2), Si1–O3 1.772(2), Si1–C31 1.939(2), C7–N1 1.300(3), C17–N2 1.301(3), C27–N3 1.274(3), N1–Si1–N2 177.12(8), O1–Si1–O2 178.40(8), O3–Si1–C31 176.22(9), O1–Si1–N1 90.42(8), O2–Si1–N2 88.89(8), O1–Si1–N2 90.56(8), O2–Si1–N1 90.06(8).

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NMR spectra (solution) were recorded on a Bruker DPX 400 spectrometer using TMS as an internal standard.  $^{29}\text{Si}$  solid state NMR spectra were recorded on a Bruker MSL 300 spectrometer. Melting points were determined in sealed capillaries and have not been corrected. Single-crystal X-ray analyses were carried out on a Bruker NONIUS KappaCCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Detailed data for the crystal structures of **2** and **3** can be found in the Supporting Information.

**Complex 2.** Ligand **1** (5.46 g, 36.6 mmol)<sup>14</sup> was dissolved in THF (70 mL), and triethylamine (7.0 g, 69.3 mmol) was added. To this stirred mixture was added dropwise phenyltrichlorosilane (3.90 g, 18.4 mmol). The resulting mixture was stored at 8 °C overnight. Then the triethylamine-hydrochloride was removed by filtration and washed with THF (20 mL) to give a yellow filtrate. The solvent was removed under reduced pressure, and an oily yellow product was obtained. This was mixed with chloroform (0.8 mL) and *n*-hexane (8 mL) to give a yellow crystalline product after 2 days. The crystals were filtered off, washed with 5 mL of chloroform/hexane (1:4), and dried under vacuum. Yield: 4.70 g (11.7 mmol, 64%). Mp: 101 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.25 (s, 3H, N=C–CH<sub>3</sub>), 2.67 (s, 3H, C–N–CH<sub>3</sub>), 3.24 (s, 3H, C=N–CH<sub>3</sub>), 4.09 (s, 1H, C=CH<sub>2</sub>), 4.71 (s, 1H, C=CH<sub>2</sub>), 6.9–7.7 (m, 13H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  18.6 (N=C–CH<sub>3</sub>), 32.1 (C–N–CH<sub>3</sub>), 39.3 (C=N–CH<sub>3</sub>), 83.1 (C=CH<sub>2</sub>), 119.2, 120.0, 121.9, 122.5, 123.7, 126.7, 128.1, 129.0, 129.5, 130.3 (2 $\times$ ), 131.1, 133.1, 134.7, 148.1, 150.8, 151.0 (Ar, C=CH<sub>2</sub>), 168.8 (C=N).  $^{29}\text{Si}$  NMR: ( $\text{CDCl}_3$ , 20 °C)  $\delta$  –62.5; ( $\text{CD}_2\text{Cl}_2$ , 22 °C)  $\delta$  –70.5; (toluene- $d_8$ , 22 °C)  $\delta$  –70.1; (solid state, CP/MAS)  $\delta$  –109.4. Anal. Calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2\text{Si}$ : C, 71.97; H, 6.04; N, 6.99. Found:<sup>15</sup> C, 70.89; H, 6.71; N, 6.88.

**Complex 3.** **2** (1.32 g, 3.3 mmol) was dissolved in hot *p*-xylene (40 mL), and a solution of **1** (0.49 g, 3.3 mmol, in 10 mL of *p*-xylene) was added. The hot mixture was filtered and then stored at room temperature over 3 days. The colorless crystalline product was filtered off, washed with *p*-xylene (2 mL), and dried under vacuum. Yield: 0.65 g (1.08 mmol, 33%). Mp: 108 °C.  $^{29}\text{Si}$  NMR: (solid state, CP/MAS)  $\delta$  –182.6; ( $\text{CDCl}_3$ )  $\delta$  –184.0. Anal. Calcd for  $\text{C}_{37}\text{H}_{40}\text{N}_3\text{O}_3\text{Si}$ : C, 73.72; H, 6.69; N, 6.97. Found:<sup>15</sup> C, 70.93; H, 6.83; N, 7.16.

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**Supporting Information Available:** Crystallographic data for **2** and **3**, variable-temperature NMR data of **2**, solution NMR spectra of **1** ( $^1\text{H}$ ,  $^{13}\text{C}$ ), **2** ( $^1\text{H}$ ,  $^{13}\text{C}$ ), and **3** ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ) as well as results of quantum chemical calculations are available free of charge via the Internet at <http://pubs.acs.org>.

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(15) The elemental analyses were repeatedly (3 times) carried out with and without addition of  $\text{V}_2\text{O}_5$ . The nitrogen and hydrogen contents were found to agree with their proposed values. Unfortunately, the found carbon content deviates from the calculated value. In NMR spectra, however, there was no indication for a significant presence of byproducts or solvents.