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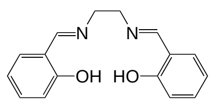
Silicon–Enamine Complexes: Pentacoordinate Silicon Compounds[**]

Jörg Wagler, Uwe Böhme, and Gerhard Roewer*

Organosilicon compounds with hypercoordinate Si atoms are interesting both because of their structural features as well as their use in syntheses and as catalytically active intermediates.[1] Their chemical reactivity is controllable by ligand variation. In addition polysilanes which contain hypercoordinate Si atoms in their skeleton display unique electronic and optical properties.[2] Although there are a large number of compounds with penta- or hexacoordinate Si atoms, to date, the principles for a deliberate "switch" between the penta- and hexacoordination are not known. Nevertheless, recently some examples have been described in which the coordination number of a silicon atom can be controlled by the variation of temperature, solvent, and stoichiometry, or by UV irradiation.[3]

The dianions of the compounds **1** and **2** of the type (sal^{2-}) are well established in transition-metal-complex chemistry. We have shown that their tetradentate donor-atom system $^{-}O\frown N\frown N\frown O^{-}$ enables the synthesis of highly coordinated Si complexes, such as **4**, **5**, and **7**.[4] The remaining Si-bound chlorine atoms in **5** can be exchanged for fluorine atoms, for example, by reaction with ZnF_2, (→**6**; Scheme 1). The hexacoordination in **6** is demonstrated by X-ray crystal-structure analysis.[4]



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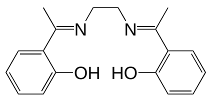

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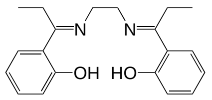

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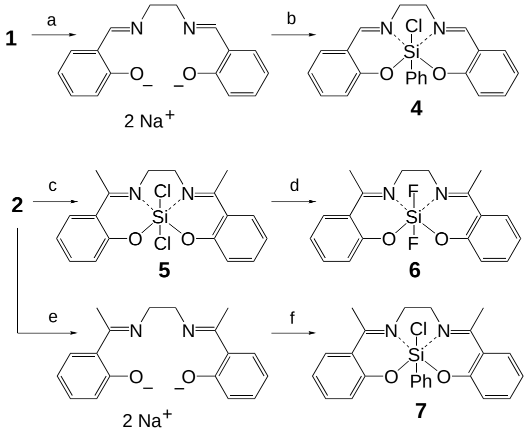

Scheme 1. Syntheses of hexacoordinate silicon–salene complexes. a) NaO*i*Pr/*i*PrOH; b) $PhSiCl_3$/*i*PrOH/88 °C; c) $SiCl_4$/THF/65 °C/2 h; d) ZnF_2/THF/65 °C/1 h; e) 1) NaOMe/THF/MeOH 2) hexane; f) $PhSiCl_3$/THF/30 min.

In contrast to H_2salene (**1**; ethylene-*N*,*N*-bissalicylidenimine), in the methyl- and ethyl-substituted compounds **2** and **3** there is the possibility of imine–enamine tautomerism. However, in complexes with transition-metal ions the enamine structures of **2** and **3** have not yet been observed. To our surprise we found this type of arrangement in the pentacoordinate silicon complexes **8**–**10** (Scheme 2). The synthesis of this new class of enamine complexes can be easily performed by the addition of diethylamine as a base in the reaction of the chlorosilanes $PhSiCl_3$, $MeSiCl_3$, or vinyl$SiCl_3$ with the ligands **2** and **3**. The driving force for this unusual HCl elimination, which is clearly promoted by the hypercoordinate silicon atom, arises from both the high basicity of amine used as well

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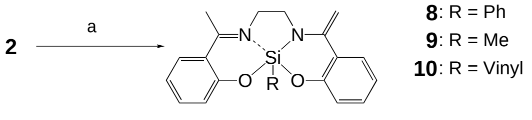
[**] This work has been supported by the Fonds der Chemischen Industrie.



Scheme 2. Synthesis of pentacoordinate silicon complexes with enamine-functionalized salene ligands. a) $RSiCl_3/HNEt_2/THF/65\,^{\circ}C/2.5$ h.

as from the very low solubility of the precipitated ammonium salt $[NH_2Et_2]Cl$.

The X-ray structure analyses of the complexes **8** and **9**[5] reveal the presence of the enamine structure. The structures of both compounds are similar, despite the differences in the conformation of the molecules, which are caused by different substituents at the silicon atom. Therefore, only the structure of the compound **9** will be described (Figure 1). In **9** there is a pentacoordinate silicon atom surrounded by the threefold deprotonated salene ligand **2**. The silicon atom is in a distorted trigonal-bipyramidal coordination environment. The atoms O(1) and N(2) form the axis of the bipyramid with an O(1)-Si(1)-N(2) angle of 176.64(9)°. The atoms N(1), O(2), and C(19) are in the equatorial plane of the bipyramid. The sum of the bonding angles at both the nitrogen atoms is 360°. Thus the atoms N(1) and N(2) are sp^2-hybridized. The C(7)–C(8) bond (1.343(4) Å) is remarkably shortened in comparison with that between C(16)–C(17) (1.509(4) Å) and falls unambiguously within the range of a C–C double bond. Besides both the O atoms of the ligand also the carbon atom C(8) is deprotonated leading to the formation of a silicon-stabilized enamine. This situation has consequences for the shape of the whole molecule: The C(7)–N(1) bond (1.394(3) Å) of the enamine is longer than that of the imine group C(16)–N(2) (1.284(4) Å). The Si(1)–N(2) bond is elongated by 0.26 Å in comparison with the Si(1)–N(1) bond. The chiral molecule crystallizes in the noncentrosymmetric space group $P2_1$. During crystallization conglomerate formation occurs, that is, the crystal investigated consists of only one enantiomer of the compound. The absolute configuration of this molecule has been determined.[6]

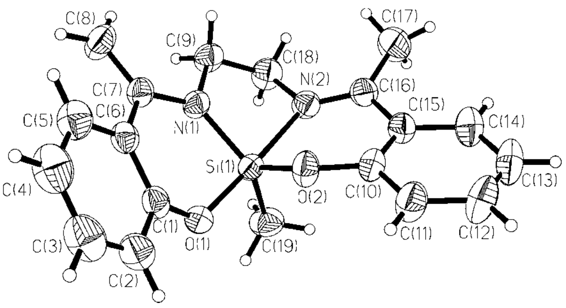


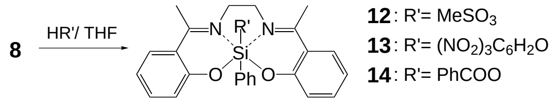
Figure 1. Molecular structure of compound **9** (thermal ellipsoids set at the 50% level); selected bond lengths [Å] and angles [°]: Si(1)-O(2) 1.683(2), Si(1)-O(1) 1.713(2), Si(1)-N(1) 1.756(2), Si(1)-C(19) 1.858(3), Si(1)-N(2) 2.017(2), O(1)-C(1) 1.341(3), O(2)-C(10) 1.349(3), N(1)-C(7) 1.394(3), N(1)-C(9) 1.466(3), N(2)-C(16) 1.284(4), N(2)-C(18) 1.459(3),C(7)-C(8) 1.343(4), C(16)-C(17) 1.509(4); O(2)-Si(1)-O(1) 91.59(9), O(2)-Si(1)-N(1) 120.1(1), O(1)-Si(1)-N(1) 95.2(1), O(2)-Si(1)-C(19) 114.7(1), O(1)-Si(1)-C(19) 94.2(1), N(1)-Si(1)-C(19) 124.0(1), O(2)-Si(1)-N(2) 88.2(1), O(1)-Si(1)-N(2) 176.64(9), N(1)-Si(1)-N(2) 82.0(1), C(19)-Si(1)-N(2) 88.9(1).

The chemical shifts from the solution ^{29}Si NMR spectra of complexes **8**–**10** are given in Table 1 and clearly indicate the pentacoordination of the Si atoms. In the complexes with the ligand **3**, the C atom, in the α position to the imine group, has different substituents. The resulting complexes, which are analogous to the compounds **8**–**10**, form *E*/*Z*-diastereomeres, as we have demonstrated by ^1H NMR and ^{13}C NMR spectroscopy. Formally, the pentacoordinate silicon complexes with enamine structure could originate by 1,4-elimination of hydrogen chloride from initially formed compounds with a hexacoordinate Si atom. The compound **8** could also be prepared by HCl elimination from **7** with Et_2NH or Et_3N. The reverse of this process should be possible: to convert penta- into new hexacoordinate silicon complexes by adding H-acidic molecules, that is, pentacoordinate Si compounds can be used synthetically as precursors for hexacoordinate ones. The driving force for these Brønsted acid addition reactions should be determined by the acidity of the HR′ component (R′=$MeSO_3$, $(NO_2)_3C_6H_2O$, PhCOO). The use of OH acidic molecules leads to a significant energy effect by the formation of additional energetically favorable Si–O bonds. Indeed, the pentacoordinate silicon complexes react with the picric acid, methane sulphonic acid, and benzoic acid by 1,4-addition. With **8** as educt the complexes **12**–**14** were formed, which are almost insoluble in THF (Scheme 3).

Table 1. Yields, melting points, and ^{29}Si NMR spectroscopic data of pentacoordinate Si complexes.

	Yield [%]	M.p. [°C][a]	^{29}Si NMR[b]
8	71	250	– 115.8
9	73	189	– 103.2
10	85	140	– 117.0

[a] The melting points of the hydrolysis-sensitive compounds **8**–**10** were determined under Ar atmosphere in a closed glass capillary. [b] $CDCl_3$ was used as solvent; tetramethylsilane (TMS) as internal standard.



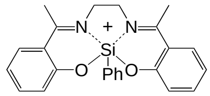
Scheme 3. Synthesis of hexacoordinate silicon–salene complexes.

The resulting hexacoordination of the Si atoms in the solid state is clearly demonstrated by the upfield shift of the signals in the ^{29}Si cross-polarization magic-angle spinning (CPMAS) NMR spectrum, (see Table 2). The assumption, that the

Table 2. Yields, THF content, and ^{29}Si CPMAS NMR spectroscopic data of hexacoordinate Si complexes.

Compound	THF content[a] [equivalents]	Yield [%]	^{29}Si CPMAS NMR $\delta(^{29}Si)$ [ppm]
12	0.5	89	– 174.3
13	2	72	– 173.5
14	1	65	– 186.5

[a] The THF content of isolated products was determined by ^1H NMR spectroscopy and is compatible with the elemental analyses of these compounds.



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addition of an acid initially causes a protonization of the ligands, is supported by the result of the analysis with ESI-MS (compound **8** in THF, formic acid, cation mode), this indicates the formation of the cation **11** (*m*/*z* 398). In principle, acid addition is fast and with high yields. Therefore, this general route seems to be a more favorable synthetic pathway to these hexacoordinate Si compounds than the alternative introduction of the respective acid anions to obtain the complexes **12**–**14** by nucleophilic substitution.

Experimental Section

The syntheses of **2** and **3** were by literature methods.[7]

8: $PhSiCl_3$ (7.5 g, 35.5 mmol) was rapidly added dropwise to a stirred solution of **2** (10.0 g, 33.8 mmol) and diethylamine (13.0 g, 178.1 mmol) in dry THF (400 mL) at room temperature. $NHEt_2 \cdot HCl$ started to precipitate immediately. After 2.5 hours stirring under reflux the mixture was cooled to room temperature and stored overnight in the refrigerator (about 8 °C). Afterwards $NHEt_2 \cdot HCl$ was removed by filtration and the clear yellow solution concentrated. Compound **8** precipitated at room temperature as bright yellow crystals; crystallization took several days. The product was collected by filtration over a G3 frit, washed with a small amount of THF, and dried in vacuo; yield: 9.5 g (23.9 mmol, 71 %); m.p. 250 °C; ^{29}Si NMR (80 mHz): $\delta = -115.8$ ppm ($CDCl_3$); $\delta = -117.1$ ppm ($[D_6]$DMSO); ^{29}Si CPMAS NMR (60 mHz): $\delta = -116.1$ ppm; ^1H NMR (400 mHz, $CDCl_3$): $\delta = 2.42$ (s, 3H, CH_3), 3.38–4.03 (3m, 2H, 1H, 1H, CH_2CH_2), 4.16 (s, 1H, (*Z*)-C=CH_2), 4.63 (s, 1H, (*E*)-C=CH_2), 6.75–7.60 ppm (m, 13H, aromatic protons); ^{13}C NMR (101 mHz, $CDCl_3$): $\delta = 17.1$ (CH_3), 45.8, 46.4 (CH_2CH_2), 85.5 (=CH_2), 119.1, 119.7, 119.8, 120.5, 122.7, 125.7, 126.0, 128.4, 128.9, 135.2, 151.7, 154.4 (salene aromatic carbon atoms), 158.4 (=C−N), 168.8 (C=N), 127.3, 128.2, 131.9, 141.5 (C_6H_5); IR (KBr): $\tilde{\nu} = 1620\ cm^{-1}$ (C=N).

9 and **10** were synthesized analogously to **8**. The products were obtained as solids by crystallization induced by the addition of *n*-hexane to the concentrated filtrate (**9**) or precipitation with *n*-hexane (**10**). **9**: ^{29}Si NMR ($CDCl_3$): $\delta = -103.2$ ppm; ^1H NMR ($CDCl_3$): $\delta = 0.03$ (s, 3H, $SiCH_3$), 2.46 (s, 3H, CCH_3), 3.35–4.05 (3m, 2H, 1H, 1H, CH_2CH_2), 4.10 (s, 1H, (*Z*)-C=CH_2), 4.56 (s, 1H, (*E*)-C=CH_2), 6.75–7.60 ppm (m, 8H, aromatic protons); ^{13}C NMR ($CDCl_3$): $\delta = 1.6$ ($SiCH_3$), 17.0 (CCH_3), 46.2 (CH_2CH_2), 85.8 (=CH_2), 119.1, 119.6, 119.8, 120.4, 122.8, 125.8, 126.9, 128.3, 128.8, 134.9, 151.8, 154.2 (salene aromatic carbon atoms), 158.1 (=C−N), 167.6 (C=N); elemental analysis calcd (%) for $C_{19}H_{20}N_2O_2Si$: C 67.83, H 5.99, N 8.33; found: C 67.69, H 6.30, N 8.07; **10**: ^{29}Si NMR ($CDCl_3$): $\delta = -117.0$; ^1H NMR ($CDCl_3$): $\delta = 2.51$ (s, 3H, CH_3), 3.35–4.03 (3m, 2H, 1H, 1H, CH_2CH_2), 4.13 (s, 1H, (*Z*)-C=CH_2), 4.60 (s, 1H, (*E*)-C=CH_2), 6.75–7.60 (m, 8H, aromatic protons), 5.60–5.75 (m, 3H, CH=CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 17.1$(CH_3), 46.3, 46.7 (CH_2CH_2), 86.1 (=CH_2), 119.1, 119.7, 120.3, 120.4, 122.6, 125.8, 126.4, 128.3, 128.8, 135.0, 151.7, 154.4, (salene aromatic carbon atoms), 158.1 (=C−N), 168.7 (C=N), 132.7, 138.4 (CH=CH_2); elemental analysis calcd (%) for $C_{20}H_{20}N_2O_2Si$: C 68.93, H 5.78, N 8.04; found: C 67.85, H 6.41, N 6.99.

12–**14**: The stoichiometric amount of the acid (CH_3SO_3H, $(NO_2)_3C_6H_2OH$, C_6H_5COOH) dissolved in a small amount of THF was added dropwise to a stirred solution of **8** (about 1 g) in THF (about 40 mL) at about 30 °C. The compounds **12**–**14** precipitated as solids and could be collected by filtration over a G3 frit, washed with a small amount of THF, and dried in vacuo.

Compounds **12** and **14** melt above 200 °C with partial decomposition (turn brown) or decompose without melting. Compound **13** melts at 106 °C; **12**: elemental analysis calcd (%) for $C_{27}H_{30}N_2O_{5,5}SiS$: C 61.11, H 5.70, N 5.28; found: C 59.80, H 5.76, N 5.66; ^{13}C NMR ($[D_6]$DMSO): $\delta = 19.0$ (CH_3), 46.0 (CH_2CH_2), 174.7, 159.2, 150.3, 136.0, 133.0, 130.4, 126.4, 126.2, 120.9, 119.5, 119.2 ppm; **13**: elemental analysis calcd (%) for $C_{38}H_{41}N_5O_{11}Si$: C 59.13, H 5.35, N 9.07; found: C 59.12, H 5.24, N 9.03; ^{13}C NMR ($[D_6]$DMSO): $\delta = 19.1$ (CH_3), 46.0 (CH_2CH_2), 174.7, 160.7, 159.2, 150.4, 141.8, 136.1, 133.0, 130.4, 126.4, 126.2, 125.1, 124.1, 120.9, 119.6, 119.2 ppm; **14**: elemental analysis calcd (%) for $C_{35}H_{36}N_2O_5Si$: C 70.92, H 6.12, N 4.73; found: C 71.52, H 5.65, N 5.38; ^{13}C NMR ($[D_6]$DMSO): $\delta = 18.3$ (CH_3), 45.6 (CH_2CH_2) 172.0, 161.1, 158.2, 134.7, 133.4, 129.7, 127.1, 126.4, 125.2, 120.6, 120.1, 117.5 ppm.

Received: November 7, 2001 [Z18181]

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[5] X-ray structure analyses: The measurements were carried out with an ENRAF-NONIUS-CAD4 diffractometer. The structures were solved by direct methods, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions and were refined by the riding model. The structures were solved and refined on F^2 by full-matrix least-square methods with the programs SHELXS-86 (G. M. Sheldrick, Universität Göttingen, **1986**) and SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**). Compound **9**: $C_{19}H_{20}N_2O_2Si$, $M_r = 336.46$, yellow prism, $0.4 \times 0.3 \times 0.3$ mm, monoclinic, space group $P2_1$, $a = 6.734(1)$, $b = 11.540(6)$, $c = 11.051(5)$ Å, $\beta = 98.77(1)^\circ$, $V = 848.7(6)$ Å^3, $\rho_{calcd} = 1.317\ g\,cm^{-3}$, $F(000) = 356$, $\mu = 1.330\ mm^{-1}$, no absorption correction, $Z = 2$, $\lambda = 1.54178$ Å, $T = 293$ K, $\omega/2\theta$-scans, 6769 measured reflections ($-8 \le h \le 7$, $-14 \le k \le 14$, $-13 \le l \le 13$), 3508 independent and 3182 observed reflections with $I > 2\sigma(I)$, 219 parameters, $R = 0.0596$, $wR_2 = 0.1280$ (all reflections), residual electron density 0.529 and $-0.303\ e\,Å^{-3}$, Flack parameter 0.00(3). Compound **8**: $C_{24}H_{22}N_2O_2Si$, $M_r = 398.53$, pale-yellow crystal, $0.6 \times 0.4 \times 0.4$ mm, monoclinic, space group $P2_1$; $a = 8.795(1)$, $b = 11.491(1)$, $c = 10.739(1)$ Å, $\beta = 112.90(2)^\circ$, $V = 999.8(2)$ Å^3, $\rho_{calcd} = 1.324\ g\,cm^{-3}$, $F(000) = 420$, $\mu = 1.219\ mm^{-1}$, no absorption correction, $Z = 2$, $\lambda = 1.54178$ Å, $T = 293$ K, $\omega/2\theta$-scans, 5022 measured reflections ($-11 \le h \le 11$, $-6 \le k \le 14$, $-13 \le l \le 13$), 2517 independent and 2108 observed reflections with $I > 4\sigma(I)$, 271 parameters, $R = 0.0533$, $wR_2 = 0.1013$ (all reflections), residual electron density 0.348 and $-0.231\ e\,Å^{-3}$, Flack parameter $-0.04(4)$. CCDC-171307 (**9**) and CCDC-165814 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[6] The measurement has been performed with $Cu_{K\alpha}$ radiation, 1661 Friedel pairs were measured (89.9 %), Flack parameter 0.00(3).

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