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Hexacoordinate Silicon-Azomethine Complexes: Synthesis, Characterization, and Properties

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Summary. N,N′-Ethylene-*bis*(2-hydroxyacetophenoneimine) = *salen**H_2 and N,N′-ethylene-*bis*(3,5-di-*tert*-butyl-salicylideneimine) = *salen*‡H_2 react both with $SiCl_4$ under formation of hexacoordinate silicon compounds ((*salen′*)$SiCl_2$, *salen′* = *salen** or *salen*‡). The analogous fluoro derivatives (*salen′*)SiF_2 have been prepared by reaction of (*salen′*)$SiCl_2$ with ZnF_2. X-ray structure analysis of (*salen**)SiF_2 clearly demonstrates the octahedral coordination of silicon. *Salen** acts as a tetradentate chelating ligand, two halogen atoms remaining at the silicon atom. The reduction of (*salen**)$SiCl_2$ by alkaline metal affords polysilanes containing main chain hexacoordinate silicon. Coupling with acetylides results in polycarbosilanes with a Si–C≡C–Si backbone.

Keywords. *Salen* complexes; Hexacoordinate silicon; Silicon complexes.

Hexakoordinierte Silicium-Azomethin-Komplexe: Synthese, Charakterisierung und Eigenschaften

Zusammenfassung. N,N′-Ethylen-*bis*(2-hydroxyacetophenonimin) = *salen**H_2 und N,N′-Ethylen-*bis*(3,5-di-*tert*-butyl-salicylidenimin) = *salen*‡H_2 reagieren mit $SiCl_4$ unter Bildung hexakoordinierter Siliciumverbindungen ((*salen′*)$SiCl_2$, *salen′* = *salen** bzw. *salen*‡). Die analogen Fluorderivate (*salen′*)SiF_2 wurden durch Reaktion von (*salen′*)$SiCl_2$ mit ZnF_2 hergestellt. Die Röntgenstrukturanalyse von (*salen**)SiF_2 zeigt eindeutig eine oktaedrische Koordination des Siliciumatoms. *Salen** wirkt als vierzähniger Chelatligand, zwei Halogenatome verbleiben am Silicium. Die Reduktion von (*salen**)$SiCl_2$ mittels Alkalimetallen führt zu Polysilanen mit hexakoordiniertem Silicium in der Hauptkette des Polymers. Kupplung mit Acetyliden ergibt Polycarbosilane mit einem Si–C≡C–Si-Skelett.

Introduction

Compounds with hypervalent silicon atoms attract interest from both the structural and reactivity point of view [1]. Anions of type **1** are established as tetradentate ligands for transition metal ions [2]. The free acids *salen′*H_2 (*salen′* = different substituents R^1 and R^2) are easily available by condensation of 1,2-diamines with aromatic α-hydroxyaldehydes or benzoylacetone.

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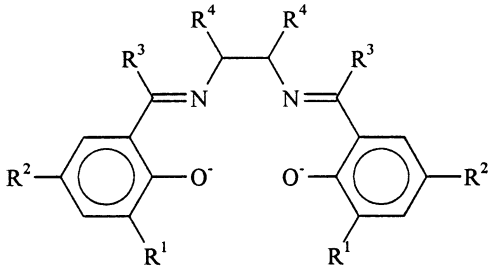
The structures as well as the magnetic and electronic properties of *salen* metal complexes can be tuned by different substituents at the *salen* ligands [3]. Transition metal *salen* complexes have been investigated as model compounds for biologically important porphyrin and corrin complexes, *e.g.* vitamin B_{12} coenzyme [4, 5]. The tetracoordinating *salen* ligand causes similar electronic properties of the resulting metal complexes as the macrocyclic porphyrin or corrin ligands. Thus, similar supernucleophilic properties like in coenzyme B_{12} have been shown for [Co(*salen*)]. It can be reduced to $[Co(salen)]^-$ which reacts with alkyl halides in an oxidative addition to form [R-Co(*salen*)] [6]. Some of these compounds coordinate molecular oxygen [7], and they are efficient catalysts for stereoselective oxygen transfer reactions like the *Jacobsen* epoxidation [8–10].



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Azomethine ligands of type **1** should be able to coordinate also the silicon atom leading to square planar complexes. Further substituents at the silicon atom should create hypercoordinated silicon derivatives. The preparation of hypercoordinated silicon complexes was the target of our investigations. Till now, only some rare examples of *salen* silicon compounds are known from the literature [11], but characterization of these compounds seems to be inconclusive [12]. Structural aspects are uncertain due to the lack of crystal structural data.

Results and Discussion

Owing to expected differences in chemical reactivity and solubility, we used two different *salen* ligands: N,N′-ethylene-*bis*(2-oxyacetophenoneimine) = *salen*$^*H_2$ ($R^1 = R^2 = R^4 = H$, $R^3 = CH_3$) and N,N′-ethylene-*bis*(3,5-di-*tert*-butyl-salicyl-ideneimine) = *salen*$^‡H_2$ ($R^1 = R^2 =$ *tert*-butyl, $R^3 = R^4 = H$). *Salen**H_2 contains methyl groups at the azomethine carbon atom instead of hydrogen. This prevents undesired side reactions caused by the azomethine protons. *Salen*$^‡H_2$ is substituted with two *tert*-butyl groups per phenyl group and should therefore give better soluble compounds. We were able to perform X-ray structure analyses of both ligands as free acids (*salen**H_2(**1a**,) and *salen*$^‡H_2$(**1b**)).

The crystal structure of **1a** is shown in Fig. 1; atomic coordinates, bond lengths, and angles are summarized in Tables 1 and 2, respectively. Crystallographic data and data collection parameters are listed in Table 8.

The crystal structure of **1b** is demonstrated in Fig. 2; atomic coordinates, bond lengths, and angles are listed in Tables 3 and 4, respectively. Crystallographic data and data collection parameters are given in Table 8.

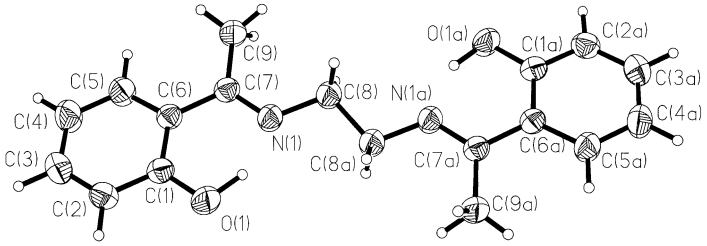


Fig. 1. ORTEP drawing (50% probability ellipsoids) of **1a**

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1a**; $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U*(*eq*)
N(1)	2490(2)	4479(1)	6409(1)	40(1)
O(1)	5443(2)	3932(1)	4792(1)	52(1)
C(1)	6341(2)	3636(1)	6576(2)	39(1)
C(2)	8268(2)	3207(1)	6741(2)	47(1)
C(3)	9190(2)	2875(1)	8511(2)	54(1)
C(4)	8262(3)	2969(1)	10191(2)	57(1)
C(5)	6404(2)	3404(1)	10069(2)	48(1)
C(6)	5397(2)	3750(1)	8278(2)	37(1)
C(7)	3414(2)	4218(1)	8149(2)	37(1)
C(8)	514(2)	4946(1)	6123(2)	43(1)
C(9)	2587(3)	4378(1)	10013(2)	51(1)

Table 2. Bond lengths (Å) and angles (°) for **1a**

Bond	Distance	Structural fragment	Angle
N(1)–C(7)	1.287(1)	C(7)–N(1)–C(8)	121.57(9)
N(1)–C(8)	1.462(2)	O(1)–C(1)–C(2)	118.4(1)
O(1)–C(1)	1.340(1)	O(1)–C(1)–C(6)	121.7(1)
C(1)–C(2)	1.397(2)	C(2)–C(1)–C(6)	119.8(1)
C(1)–C(6)	1.416(2)	C(3)–C(2)–C(1)	120.5(1)
C(2)–C(3)	1.370(2)	C(2)–C(3)–C(4)	120.7(1)
C(3)–C(4)	1.391(2)	C(5)–C(4)–C(3)	119.4(1)
C(4)–C(5)	1.380(2)	C(4)–C(5)–C(6)	121.6(1)
C(5)–C(6)	1.402(2)	C(5)–C(6)–C(1)	117.8(1)
C(6)–C(7)	1.476(2)	C(5)–C(6)–C(7)	121.6(1)
C(7)–C(9)	1.498(2)	C(1)–C(6)–C(7)	120.5(1)
C(8)–C(8)[a]	1.511(2)	N(1)–C(7)–C(6)	117.4(1)
		N(1)–C(7)–C(9)	122.8(1)
		C(6)–C(7)–C(9)	119.7(1)
		N(1)–C(8)–C(8)[a]	109.0(1)

[a] Symmetry transformations used to generate equivalent atoms: −x, −y+1, −z+1

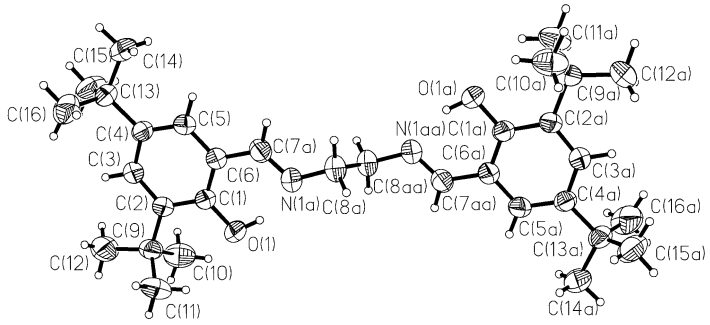


Fig. 2. ORTEP drawing (50% probability ellipsoids) of **1b**

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1b**; $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U*(*eq*)
O(1)	9583(1)	178(2)	3878(1)	62(1)
N(1A)	9642(1)	2404(3)	4690(1)	53(1)
C(7A)	9005(1)	1670(4)	4667(1)	51(1)
C(8A)	9990(1)	3869(3)	5100(1)	56(1)
N(1B)	9453(5)	3235(15)	4490(4)	57(2)
C(7B)	8853(7)	2351(20)	4494(4)	52(3)
C(8B)	9689(7)	5246(19)	4781(4)	70(3)
C(1)	8910(1)	−537(2)	3888(1)	46(1)
C(6)	8598(1)	222(2)	4261(1)	50(1)
C(5)	7908(1)	−534(2)	4277(1)	50(1)
C(4)	7526(1)	−2038(2)	3937(1)	47(1)
C(3)	7857(1)	−2766(2)	3572(1)	49(1)
C(2)	8534(1)	−2067(2)	3530(1)	45(1)
C(9)	8858(1)	−2919(2)	3113(1)	56(1)
C(10)	8969(1)	−1045(3)	2780(1)	79(1)
C(11)	9599(1)	−4022(3)	3351(1)	77(1)
C(12)	8345(1)	−4559(4)	2772(1)	95(1)
C(13)	6774(1)	−2944(2)	3947(1)	55(1)
C(14)	6482(1)	−1824(3)	4348(1)	76(1)
C(15)	6207(1)	−2556(4)	3433(1)	83(1)
C(16)	6847(1)	−5327(3)	4067(1)	97(1)

The bond lengths and angles of the phenyl groups and the ethylene bridges connecting the azomethine units are in the normal range for **1a** and **1b**. Both molecules are located at crystallographic inversion centres. This implies a transoid conformation in the solid state with a torsion angle N(1)–C(8)–C(8a)–N(1a) of 180.0°. The ethylenediamine bridge connecting the aromatic rings in **1b** is disordered. The disorder was resolved with site occupation factors of 0.84 for C(7a)–N(1a)–C(8a) and 0.16 for C(7b)–N(1b)–C(8b). The small site occupation of 16% results in large standard deviations for bonds and angels at C(7b), N(1b), and C(8b).

Table 4. Bond lengths (Å) and angles (°) for **1b**

Bond	Distance	Structural fragment	Angle
O(1)–C(1)	1.355(2)	C(7A)–N(1A)–C(8A)	118.6(2)
N(1A)–C(7A)	1.273(3)	N(1A)–C(7A)–C(6)	122.8(2)
N(1A)–C(8A)	1.451(2)	N(1A)–C(8A)–C(8A)[a]	110.6(2)
C(7A)–C(6)	1.468(3)	C(7B)–N(1B)–C(8B)	119.7(9)
C(8A)–C(8A)[a]	1.512(4)	N(1B)–C(7B)–C(6)	124.4(9)
N(1B)–C(7B)	1.26(1)	C(8B)[a]–C(8B)–N(1B)	109(1)
N(1B)–C(8B)	1.48(1)	O(1)–C(1)–C(6)	120.0(1)
C(7B)–C(6)	1.49(1)	O(1)–C(1)–C(2)	119.8(1)
C(8B)–C(8B)[a]	1.46(2)	C(6)–C(1)–C(2)	120.3(1)
C(1)–C(6)	1.402(2)	C(5)–C(6)–C(1)	120.1(1)
C(1)–C(2)	1.407(2)	C(5)–C(6)–C(7A)	118.3(1)
C(6)–C(5)	1.399(2)	C(1)–C(6)–C(7A)	121.4(1)
C(5)–C(4)	1.372(2)	C(5)–C(6)–C(7B)	118.4(5)
C(4)–C(3)	1.401(2)	C(1)–C(6)–C(7B)	117.3(5)
C(4)–C(13)	1.536(2)	C(4)–C(5)–C(6)	121.5(1)
C(3)–C(2)	1.389(2)	C(5)–C(4)–C(3)	116.8(1)
C(2)–C(9)	1.537(2)	C(5)–C(4)–C(13)	123.3(1)
C(9)–C(11)	1.529(2)	C(3)–C(4)–C(13)	120.0(1)
C(9)–C(12)	1.529(2)	C(2)–C(3)–C(4)	124.8(1)
C(9)–C(10)	1.533(2)	C(3)–C(2)–C(1)	116.6(1)
C(13)–C(16)	1.513(2)	C(3)–C(2)–C(9)	121.8(1)
C(13)–C(15)	1.530(2)	C(1)–C(2)–C(9)	121.6(1)
C(13)–C(14)	1.535(2)	C(11)–C(9)–C(12)	108.0(2)
		C(11)–C(9)–C(10)	109.3(1)
		C(12)–C(9)–C(10)	108.0(1)
		C(11)–C(9)–C(2)	110.4(1)
		C(12)–C(9)–C(2)	111.5(1)
		C(10)–C(9)–C(2)	109.6(1)
		C(16)–C(13)–C(15)	110.5(2)
		C(16)–C(13)–C(14)	108.4(2)
		C(15)–C(13)–C(14)	106.9(1)
		C(16)–C(13)–C(4)	109.6(1)
		C(15)–C(13)–C(4)	109.6(1)
		C(14)–C(13)–C(4)	111.8(1)

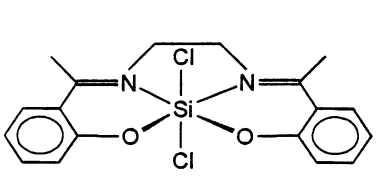
[a] Symmetry transformations used to generate equivalent atoms: −x+2, −y+1, −z+1

The *ortho*-hydroxy-azomethine unit is stabilized in both compounds by intramolecular hydrogen bridges (O–H$\cdots$N) with an H$\cdots$N distance of 1.547 Å in **1a** and 1.766 to 1.796 Å in **1b**. Intermolecular hydrogen bridges are found in the structure of **1a**, with a distance of 2.492 Å for 01$\cdots$H(9c) which is less than the sum of the *van der Waals* radii of oxygen and hydrogen (1.2 Å+1.4 Å = 2.6 Å) [13]. The hydrogen bridges between the molecules are situated in a plane leading to a layered structure. Similar intermolecular hydrogen bridges are prevented in **1b** by the bulky *tert*-butyl groups; therefore, only intramolecular

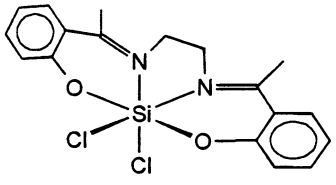
hydrogen bridges are found in the structure of **1b** between O(1) and two hydrogen atoms of the direct neighbouring *tert*-butyl group (O(1)···H(10a) = 2.380 Å, O(1)···H(11a) = 2.332 Å).

The molecules of **1a** are nearly planar in the solid state with only 0.54 Å distance between the planes of the phenyl rings. The planes of the two phenyl rings are 0.769 Å apart from each other in **1b**. The phenyl rings surrounded by bulky *tert*-butyl groups are packed in the crystal lattice of **1b** in a way leaving enough space for the linking *bis*(azomethine)ethylene bridge to be disordered. The transoid conformations for **1a** and **1b** are not retained in solution. Both molecules are able to rotate freely around the bridge N(1)–C(8)–C(8a)–N(1a) in solution, as indicated by the fact that only one set of signals is found in their NMR spectra.

The key compound (*salen**)$SiCl_2$ (**2**) can be prepared *via* three different routes (a, b and c, Scheme 1). Elemental analysis indicates the formation of a complex of the composition (*salen**)$SiCl_2$. Preparation of **2** *via* reaction of *salen**H_2 with $SiCl_4$ (a) yields a product with two ^{29}Si NMR signals and 18 peaks in the ^{13}C NMR spectrum. This points to the formation of two different isomers (**2**-*trans* and **2**-*cis*) in a ratio of 1:1 according to the intensity of the signals. It demonstrates that the $SiCl_2$ unit is not exclusively linear in azomethine complexes as has been pretended in the literature [11]. The same type of isomerism has been observed in tin *salen* compounds and confirmed by *Mössbauer* spectroscopy [14].

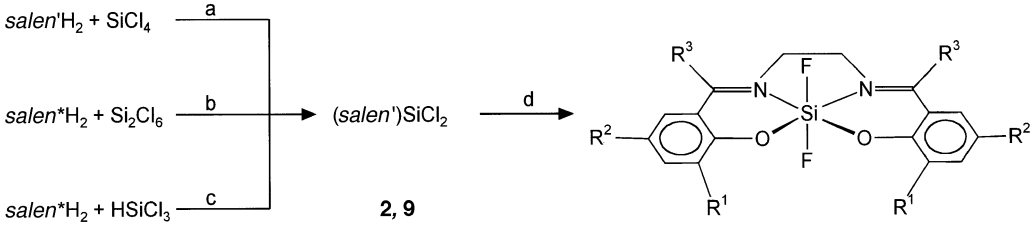


2-*trans*



2-*cis*

The large high field shift of the ^{29}Si NMR signals for the isomers of **2** (−186.1, −188.0 ppm) indicates the presence of hexacoordinate silicon atoms. Reaction of Si_2Cl_6 with *salen**H_2 (b in Scheme 1) gives only one isomer with 9 signals in the ^{13}C NMR spectrum and one ^{29}Si NMR signal at −188 ppm. Both hydrogen chloride and hydrogen are evolved in this reaction.



Scheme 1. *salen′* = *salen**, *salen*‡ a and b: *THF*, 2 h, reflux, 90%; c: *THF*, 6 h, reflux 60%; d: ZnF_2, *THF*, 1 h, reflux, 20%, extraction with *THF*

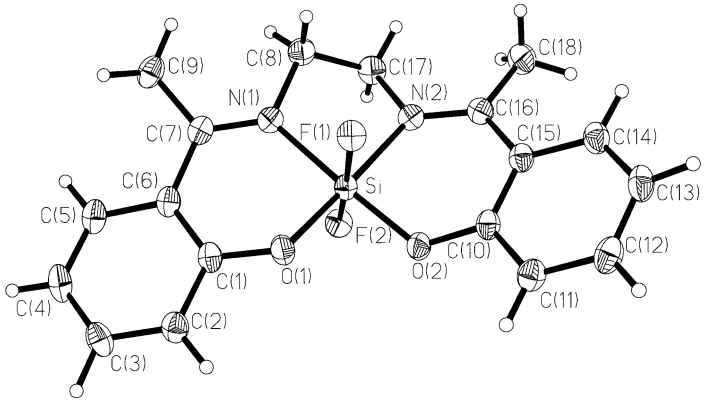


Fig. 3. ORTEP drawing (50% probability ellipsoids) of **3**

The chlorine atoms in **2** and **9** can be substituted by fluorine treating **2** or **9** with ZnF_2 in *THF*. For the preparation of the fluoro derivative **3**, the mixture of isomers **2**-*trans* and **2**-*cis* was used. The resulting product **3** represents only one isomer as concluded from NMR data. This information suggests a rearrangement of the coordination sites of the *salen** ligand during nucleophilic substitution of chlorine by fluorine. The mechanism of this reaction as well as the energy differences between **2**-*trans* and **2**-*cis* seem to be quite interesting and will be the subject of further investigations. Complex **3** is much more soluble in organic solvents than the chloro derivative. Therefore, we were able to obtain single crystals of **3** by recrystallization from acetonitrile. The X-ray crystal structure analysis of **3** provides the structure shown in Fig. 3. Atomic coordinates, bond lengths, and angles are listed in Tables 5, 6, and 7. Crystallographic data and data collection parameters are given in Table 8.

3 represents the first structurally characterized hexacoordinate silicon compound with a tetradentate azomethine ligand. The structure was solved and refined in space group $P2_1/a$ with four molecules **3** and four molecules 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 2.5–3.0 Å). [15] The Si–F distance in **3** corresponds well with bond lengths found in other hypervalent silicon compounds (1.60–1.73 Å) [15, 16]. The distances Si–O and Si–N are remarkably short compared to other hexacoordinate silicon compounds [15]. The distortion of the octahedral coordination environment around silicon probably originates from the conformation of the chelating *salen** ligand. There is a considerable torsion along the atoms N(1)–C(8)–C(17)–N(2) (about 46°). This causes one azomethine unit to fold under and the other one above the plane N(1)–Si–N(2).

Very promising are experiments to obtain stacked polymers **4** by reaction of **2** or **3** with alkaline metals or magnesium (Scheme 2). These polymers are only

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**; $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U(eq)$
Si	3589(1)	1306(1)	2583(1)	19(1)
F(1)	4444(1)	134(1)	2469(1)	24(1)
F(2)	2885(1)	2582(1)	2749(1)	27(1)
N(1)	4581(1)	1773(1)	3745(1)	21(1)
O(1)	2805(1)	398(1)	3224(1)	27(1)
C(1)	2717(1)	407(1)	4164(1)	22(1)
C(2)	1815(2)	−230(2)	4432(1)	26(1)
C(3)	1665(2)	−284(2)	5397(1)	31(1)
C(4)	2395(2)	292(2)	6119(1)	34(1)
C(5)	3291(2)	899(2)	5868(1)	30(1)
C(6)	3481(1)	970(1)	4888(1)	23(1)
C(7)	4473(1)	1568(1)	4647(1)	22(1)
C(8)	5554(2)	2408(2)	3498(1)	27(1)
C(9)	5356(2)	1919(2)	5474(1)	29(1)
N(2)	4511(1)	2315(1)	1899(1)	22(1)
O(2)	2735(1)	958(1)	1514(1)	25(1)
C(10)	3054(1)	744(2)	651(1)	23(1)
C(11)	2452(2)	−107(2)	22(1)	27(1)
C(12)	2750(2)	−382(2)	−875(1)	30(1)
C(13)	3652(2)	192(2)	−1171(1)	30(1)
C(14)	4222(2)	1066(2)	−575(1)	28(1)
C(15)	3942(1)	1369(2)	343(1)	23(1)
C(16)	4572(1)	2284(2)	976(1)	24(1)
C(17)	5199(2)	3149(2)	2573(1)	27(1)
C(18)	5283(2)	3179(2)	529(1)	33(1)
N(3)	5148(3)	3569(3)	7748(2)	72(1)
C(19)	5933(2)	3026(2)	7867(2)	48(1)
C(20)	6935(2)	2319(2)	8012(2)	60(1)

slightly soluble in organic solvents and more stable against moisture than the monomers. They have been characterized by elemental analysis, IR, and NMR . Furthermore, it is possible to react **2** with dilithiumacetylide or the corresponding *Grignard* reagent to obtain polymers of type **5** which are linked by Si–C≡C–Si units (Scheme 1). Polymers with similar backbone but different chelating ligands have been described recently [17].

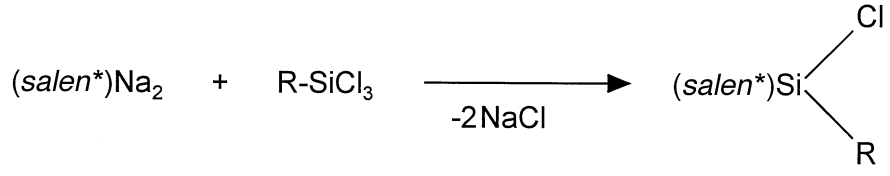
(1)

R = Me (**6**·0.5HCl), Ph (**7**·0.5HCl)

Table 6. Bond lengths (Å) for **3**

Bond	Distance	Bond	Distance
Si–F(2)	1.670(1)	C(7)–C(9)	1.506(2)
Si–F(1)	1.677(1)	C(8)–C(17)	1.519(2)
Si–O(1)	1.721(1)	N(2)–C(16)	1.294(2)
Si–O(2)	1.724(1)	N(2)–C(17)	1.473(2)
Si–N(2)	1.931(2)	O(2)–C(10)	1.336(2)
Si–N(1)	1.937(1)	C(10)–C(11)	1.402(2)
N(1)–C(7)	1.296(2)	C(10)–C(15)	1.412(2)
N(1)–C(8)	1.472(2)	C(11)–C(12)	1.382(2)
O(1)–C(1)	1.324(2)	C(12)–C(13)	1.394(3)
C(1)–C(6)	1.408(2)	C(13)–C(14)	1.378(3)
C(1)–C(2)	1.410(2)	C(14)–C(15)	1.407(2)
C(2)–C(3)	1.380(2)	C(15)–C(16)	1.466(2)
C(3)–C(4)	1.389(3)	C(16)–C(18)	1.506(2)
C(4)–C(5)	1.380(3)	N(3)–C(19)	1.127(4)
C(5)–C(6)	1.415(2)	C(19)–C(20)	1.446(4)
C(6)–C(7)	1.472(2)		

The reaction between *salen**H_2 and organofunctionalized trichlorosilanes gives adducts containing 0.5 equivalents of hydrogen chloride (Eq. (1)). Thermogravimetric analysis shows that the adducts **6** · 0.5HCl and **7** · 0.5HCl lose hydrogen chloride at higher temperatures (**6** · 0.5HCl from 140 to 270°C, **7** · 0.5HCl from 100 to 260°C). The association of hydrogen chloride with complexes **6** and **7** is partially reversed in solution as concluded from the ^{29}Si NMR spectra of these adducts which are identical with those of (*salen**)Si(Cl)*R*.



(2)

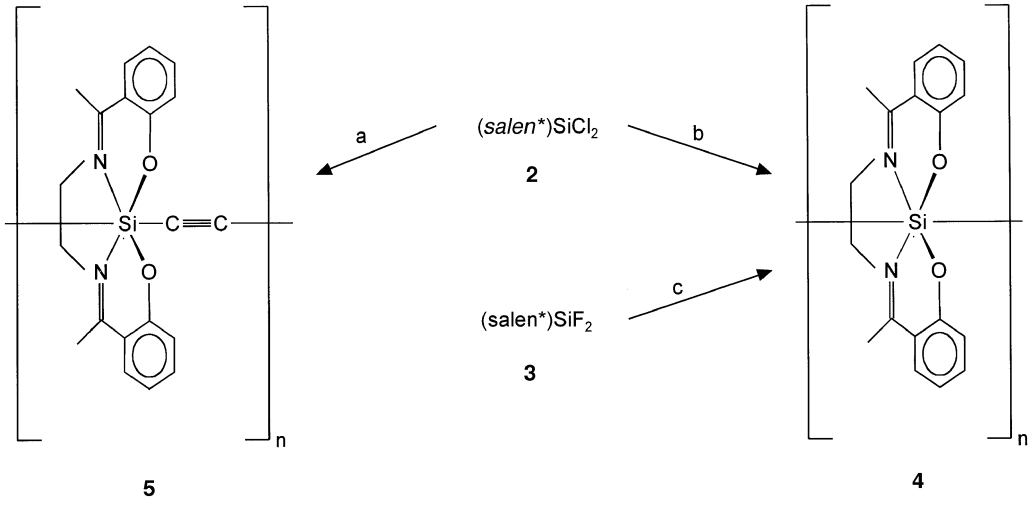
R = Me (**6**), Ph (**7**)

The complexes (*salen**)Si(Cl)*R* are available by reaction of (*salen**)Na_2 with *R*$SiCl_3$ (*R* = Me, Ph; Eq. (2)). Only one isomer is formed in both cases as can be seen from the NMR data. At the moment it is not possible to decide whether these are the *cis*- or *trans*-isomers. *Bis*(organo)silicon-*salen* complexes (*salen**)SiR_2 are accessible by reaction of lithium alkyl compounds Li*R* with (*salen**)$SiCl_2$ (**2**); for instance, (*salen**)Si(*n*-$C_4H_9)_2$ (**8**) results from the interaction between **2** and *n*-C_4H_9Li in *n*-hexane. These organo silicon compounds are better soluble in organic solvents than **2**.

We were successful in preparing (*salen*‡)$SiCl_2$ (**9**), (*salen*‡)SiF_2 (**12**), and (*salen*‡)Si(Cl)*R* (**10** and **11**) by methods analogous to those described for the *salen** derivatives. The nucleophilic substitution of the two chloro substituents in

Table 7. Angles (°) for **3**

Structural fragment	Angle	Structural fragment	Angle
F(2)–Si–F(1)	172.40(5)	C(1)–C(6)–C(5)	117.9(2)
F(2)–Si–O(1)	93.17(6)	C(1)–C(6)–C(7)	121.5(1)
F(1)–Si–O(1)	91.68(6)	C(5)–C(6)–C(7)	120.5(2)
F(2)–Si–O(2)	92.00(6)	N(1)–C(7)–C(6)	120.5(2)
F(1)–Si–O(2)	93.85(6)	N(1)–C(7)–C(9)	121.3(2)
O(1)–Si–O(2)	89.87(6)	C(6)–C(7)–C(9)	118.2(2)
F(2)–Si–N(2)	87.60(6)	N(1)–C(8)–C(17)	107.6(1)
F(1)–Si–N(2)	87.36(6)	C(16)–N(2)–C(17)	121.8(1)
O(1)–Si–N(2)	178.00(6)	C(16)–N(2)–Si	126.8(1)
O(2)–Si–N(2)	91.94(6)	C(17)–N(2)–Si	111.4(1)
F(2)–Si–N(1)	86.9(5)	C(10)–O(2)–Si	125.4(1)
F(1)–Si–N(1)	86.93(5)	O(2)–C(10)–C(11)	117.9(2)
O(1)–Si–N(1)	93.27(6)	O(2)–C(10)–C(15)	122.5(2)
O(2)–Si–N(1)	176.75(6)	C(11)–C(10)–C(15)	119.5(2)
N(2)–Si–N(1)	84.93(6)	C(12)–C(11)–C(10)	120.7(2)
C(7)–N(1)–C(8)	120.9(1)	C(11)–C(12)–C(13)	120.3(2)
C(7)–N(1)–Si	127.6(1)	C(14)–C(13)–C(12)	119.3(2)
C(8)–N(1)–Si	111.5(1)	C(13)–C(14)–C(15)	121.8(2)
C(1)–O(1)–Si	129.9(1)	C(14)–C(15)–C(10)	118.2(2)
O(1)–C(1)–C(6)	123.8(2)	C(14)–C(15)–C(16)	121.0(2)
O(1)–C(1)–C(2)	116.3(2)	C(10)–C(15)–C(16)	120.8(2)
C(6)–C(1)–C(2)	119.8(2)	N(2)–C(16)–C(15)	120.2(2)
C(3)–C(2)–C(1)	120.4(2)	N(2)–C(16)–C(18)	121.1(2)
C(2)–C(3)–C(4)	120.6(2)	C(15)–C(16)–C(18)	118.8(2)
C(5)–C(4)–C(3)	119.5(2)	N(2)–C(17)–C(8)	105.9(1)
C(4)–C(5)–C(6)	121.7(2)	N(3)–C(19)–C(20)	179.4(3)



Scheme 2. a: LiCCLi or BrMgCCMgBr, *THF*/*n*-hexane, 6 h, reflux; b: (*salen**)$SiCl_2$ and K (1:2), toluene, 6 h, reflux; c: (*salen**)SiF_2 and Li, *THF*, 2 h, room temperature

(*salen*‡)$SiCl_2$ (**9**) should be possible under mild conditions. However, all attempts to perform this substitution with *Grignard* reagents, lithium organyls, or silyl lithium compounds failed so far, leading to decomposition of (*salen*‡)$SiCl_2$ in each case. (*Salen*‡)$SiCl_2$ (**9**) for instance reacted with MeMgI under extrusion of **1b**. We assume that the nucleophilic reagents attack the azomethine proton of the ligand. This initializes the decomposition of the *salen*‡ silicon complex.

The UV VIS spectra of the *salen** complexes in acetonitrile are very similar to each other. The long wavelength maxima ($n \rightarrow \pi^*$) are located between 310 and 330 nm. The formation of the (*salen*‡)SiX_2 complexes ($X = Cl$, F) gives rise to significant additional UV absorption in comparison with the free ligand *salen*‡H_2. The band of the ligand at 265 nm is shifted bathochromically in both cases: (*salen*‡)$SiCl_2$ (**9**) to 280 nm, (*salen*‡)SiF_2 (**12**) to 284 nm. A similar effect occurs in the region above 300 nm. The absorption maximum of *salen*‡H_2(332 nm) is moved to longer wavelengths for both complexes (356 nm). These facts lead to the conclusion that the lone pairs at the donor atoms of the ligand are less involved in bonds in the silicon compound than in the free ligand *salen*‡H_2.

The compounds derived from the ligand *salen*‡ are considerably better soluble in common organic solvents than the analogous *salen** complexes due to the four *tert*-butyl groups at the ligand. The inaccessiability of new derivatives by nucleophilic substitution represents a major drawback of this class of compounds. Therefore, we will prepare modified ligand systems with protective alkyl groups at the azomethine carbon atom and additional alkyl groups at the phenyl rings for better solubility.

Experimental

IR spectra were recorded with a Nicolet 510 A spectrometer. Bruker DPX 400 (liquid) and MSL 300 (solid) spectrometers were used for measuring NMR spectra; chemical shifts are referenced to *TMS*. All solvents were distilled from sodium/benzophenone before use. The operations for preparing the silicon complexes were carried out under an atmosphere of Argon. N,N′-Ethylene-*bis*(2-hydroxy-acetophenoneimine) (*salen**H_2, **1a**) [18] and N,N′-ethylene-*bis*(3,5-di-*tert*-butyl-salicylideneimine) (*salen*‡H_2, **1b**) [19] were synthesized as reported previously.

Dichloro-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato))-silane ((salen)*$SiCl_2$, **2**-*trans*/**2**-*cis)*

2.87 g (16.9 mmol) $SiCl_4$ or 2.27 g (8.45 mmol) Si_2Cl_6 were added dropwise to a solution of 5 g (16.9 mmol) (*salen**)H_2 in *THF*. The resulting mixture was refluxed for 2 h and cooled. The precipitated white powder was filtered off with suction, washed with *THF*, and dried under vacuum (5.7 g, 90%).

$C_{18}H_{18}N_2O_2SiCl_2$; calcd.: C 55.0, H 4.6, N 7.1, Si 7.1, Cl 18.1; found: C 54.8, H 5.4, N 7.2, Si 7.1, Cl 19.1; ^{13}C NMR (*DMSO*-d_6, mixture of isomers, δ in ppm): C_1 157.3/158.1, C_2 118.8/119.4, C_3 135.1/136.9, C_4 120.6/120.7, C_5 129.9/131.2, C_6 120.2/120.5, C_7 176.4/171.6, C_8 46.1/46.7, C_9 18.6/20.7; ^{29}Si NMR (DMSO-d_6, mixture of isomers, δ in ppm): −186.1/−188.0; IR: ν(C=N) 1630 cm^{-1}, ν(Si−Cl) 521 cm^{-1}, δ(Si−O−C) 1104 cm^{-1}.

From Si_2Cl_6:^{13}C-NMR (*DMSO*-d_6, δ, ppm): C_1 157.3, C_2 119.4, C_3 136.9, C_4 120.7, C_5 131.2, C_6 120.5, C_7 176.4, C_8 46.7, C_9 20.7; ^1H NMR (DMSO-d_6, δ, ppm): H_2–H_5 6.8–8.1, H_8 4.2, H_9 1.5; ^{29}Si NMR (*DMSO*-d_6, δ, ppm): −188.0.

N,N′-Ethylene-bis(2-hydroxyacetophenoneiminato)-difluorosilane ((*salen**)SiF_2, **3**)

2.6 g (25.4 mmol) ZnF_2 were added to a stirred suspension of 5 g (12.7 mmol) (*salen**)$SiCl_2$ *in THF* during 30 min. The mixture was heated for one hour under reflux and then cooled. The precipitated solid material was extracted with *THF*. After extraction, the filtered white compound was washed with *THF* and dried under vacuum (0.9 g, 20%).

$C_{18}H_{18}N_2O_2SiF_2$; calcd.: C 60.0, H 5.0, N 7.8; found: C 54.5, H 4.9, N 7.6[a]; ^{13}C NMR ($CDCl_3$, δ, ppm): C_1 160.3, C_2–C_5 134.4–116.9, C_6 121.9, C_7 170.7, C_8 46.4, C_9 18.2; ^1H NMR ($CDCl_3$, δ, ppm): H_2–H_5 6.7–8.1, H_8 4.1, H_9 2.3; ^{29}Si NMR ($CDCl_3$, δ, ppm): −187.9, t, $^2J(Si–F) = 179.2$ Hz; IR: ν(C=N) 1610 cm^{-1}, ν(Si–F) 954 cm^{-1}.

Poly-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato))-silane((-salen)*Si-*)n*, **4**)

1 g K was added to a stirred suspension of 5 g (*salen**)$SiCl_2$ in toluene and heated for 6 h under reflux. After cooling the reaction mixture was filtered. From the dark clear filtrate the product was obtained by addition of *n*-hexane (0.4 g, 10%).

($C_{18}H_{18}N_2O_2Si$)*n*; calcd.: C 67.1, H 5.6, N 8.7, Si 8.7; found: C 62.7, H 6.0, N 7.5, Si 8.2[a]; ^{13}C NMR ($CDCl_3$, δ, ppm): $C_{1/7}$ 156 (broad), $C_{2\text{-}6}$ 137–116, C_8 47, C_9 22; ^1H NMR ($CDCl_3$, δ, ppm): $H_{2–5}$ 6.8–7.5, H_8 3.9, H_9 1.5; ^{29}Si NMR (solid state, δ, ppm): −130 (broad); IR: ν (C=N) 1613 cm^{-1}, δ(Si–O–C) 1100 cm^{-1}.

Poly-(μ-ethinyl-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato)))-silane((-salen)*SiCC-*)n*, **5**)

16 mmol LiCCLi or 16 mmol BrMgCCMgBr were slowly added to a stirred suspension of 5 g (12.7 mmol) *salen**$SiCl_2$ in *THF*. The mixture was heated under reflux for 6 h. The light yellow precipitate was filtered off with suction. It can be purified by extraction with *THF* (0.5 g, 10%).

($C_{20}H_{18}N_2O_2Si$)*n*; calcd.: C 69.4, H 5.2, N 8.1, Si 8.1; found: C 62.2, H 5.9, N 7.9, Si 7.4; ^{13}C NMR (*DMSO*-d_6, δ, ppm): C_1 168.4, $C_{2–6}$ 132.6–117, C_7 169.1, C_8 51.4, C_9 22.2; ^1H NMR (*DMSO*-d_6, δ, ppm): $H_{2–5}$ 6.2–7.6, H_8 3.6, H_9 0.86; ^{29}Si NMR (solid state, δ, ppm): −88 (broad); IR: ν(C=N) 1607 cm^{-1}, ν(Si–C) 840 cm^{-1}; *Raman*: ν(C≡C) 2260 cm^{-1}.

Chloro-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato))-methylsilane hemi hydrogen chloride ((salen)*Si(Cl)Me · 0.5HCl, **6** · 0.5HCl)

2.5 g (16.9 mmol) $MeSiCl_3$ were added to a stirred solution of 5 g (16.9 mmol) (*salen**)H_2 in *THF*; the resulting mixture was refluxed for 4 h. After cooling to room temperature, the precipitated white product was filtered off with suction, washed with *THF* and dried under vacuum (5.9 g, 90%).

$C_{19}H_{21}N_2O_2SiCl \cdot 0.5HCl$; Calcd.: C 58.3, H 5.5, N 7.2, Si 7.2, Cl 13.6; found: C 59.1, H 6.0, N 7.3, Si 6.8, Cl 14.8[a]; ^{13}C NMR(*DMSO*-d_6, δ, ppm): C_1 159.1/154.0, $C_{2–6}$ 136.2–116, C_7 185.4/181.4, C_8 46.2, C_9 23.7, C_{14} 6.5; ^1H NMR (*DMSO*-d_6, δ, ppm): $H_{2–5}$ 6.9–7.7, H_8 4.3, H_9 1.75; ^{29}Si NMR (*DMSO*-d_6, δ, ppm): −150.7; ^{29}Si NMR (solid state, δ, ppm): −105.3; IR: ν(C=N) 1629 cm^{-1}, ν(Si–Cl) 509/526 cm^{-1}, ν(Si–C) 799 cm^{-1}, δ(Si–O–C) 1110 cm^{-1}.

Chloro-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato))-phenylsilane hemi hydrogen chloride ((salen)*Si(Cl)Ph · 0.5HCl, **7** · 0.5HCl)

7 · 0.5 HCl was prepared as described for **6** · 0.5HCl (6.9 g, 90%).

$C_{24}H_{23}N_2O_2SiCl \cdot 0.5HCl$; ^{13}C NMR(*DMSO*-d_6, δ, ppm): C_1 158.6/154.0, $C_{2\text{-}6}$/$C_{14a\text{-}d}$ 136.0–116.7, C_7 185.5/182.1, C_8 45.9, C_9 19.4; ^1H NMR (*DMSO*-d_6, δ, ppm): $H_{2\text{-}5}$ 6.7–7.9, H_8 4.0, H_9 2.4;

[a] Determined carbon content too low owing to the formation of silicon carbide during analysis

^{29}Si NMR(*DMSO*-d_6, δ, ppm): −173.1; IR: ν(C=N) 1615 cm^{-1}, ν(Si–Cl)514 cm^{-1}, ν(Si–C)840 cm^{-1}, δ(Si–O–C)1110 cm^{-1}.

Chloro-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato))-methylsilane ((salen)*Si(Cl)Me, **6**)

33.8 mmol NaOMe were added to a stirred mixture of 5 g (16.9 mmol) *salen**H_2 in *THF*/MeOH. After 30 min the disodium salt of the ligand was precipitated by addition of hexane. It was filtered off and dried under vacuum. A mixture of 1.7 g (11.1 mmol) $MeSiCl_3$ and 4 g (11.1 mmol) (*salen**)Na_2 was stirred for 30 min in *THF* at room temperature; then the precipitated product suspension was filtered. Finally, the solid was extracted with *THF*/toluene (0.83 g, 20%).

$C_{19}H_{21}N_2O_2SiCl$; calcd.: C 61.1, H 5.6, N 7.5, Si 7.5, Cl 9.5; found: C 56.6, H 5.2, N 7.4, Si 7.1, Cl 10.6[a]; ^{13}C NMR (*DMSO*-d_6, δ, ppm): C_1 158.4, C_{2-6} 136.2–116.0, C_7 174.8, C_8 46.0, C_9 20.4, C_{14} 6.6; ^{1}H NMR (*DMSO*-d_6, δ, ppm): H_{2-5} 6.7–7.9, H_8 4.2, H_9 1.75, H_{14} 0.2; ^{29}Si NMR (*DMSO*-d_6, δ, ppm): −150.7; ^{29}Si NMR (solid state, δ, ppm): −168.7; IR: ν(C=N) 1629 cm^{-1}, ν(Si–Cl) 509 cm^{-1}, ν(Si–C) 798 cm^{-1}.

Chloro-(N, N′-ethylene-bis(2-hydroxyacetophenoneiminato))-phenylsilane ((salen)*Si(Cl)Ph,**7**)

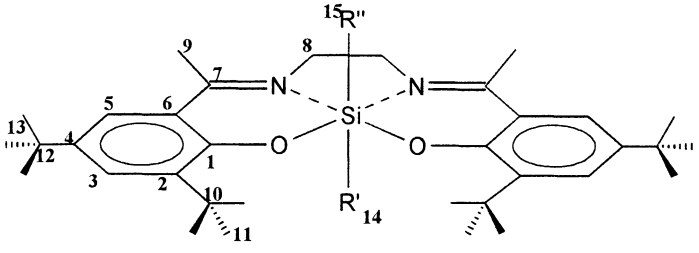
7 was prepared as described for **6** (1.45 g, 30%).

$C_{24}H_{23}N_2O_2SiCl$; calcd.: C 66.3, H 5.3, N 6.4, Si 6.4, Cl 8.2; found: C 64.7, H 4.9, N 6.7, Si 5.8, Cl 9.1[a]; ^{13}C NMR (*DMSO*-d_6, δ, ppm): C_1 159.2, C_{2-6}/C_{14a-d} 136.0–116.0, C_7 174.6, C_8 46.1, C_9 19.1; ^{1}H NMR (*DMSO*-d_6, δ, ppm): H_{2-5}/H_{14b-d} 6.7–7.7, H_8 4.2, H_9 1.75; ^{29}Si NMR (*DMSO*-d_6, δ, ppm): −173.1; IR: ν(C=N) 1612 cm^{-1}, ν(Si–Cl) 488 cm^{-1}, ν(Si–C) 840 cm^{-1}.

Dibutyl-(N,N′-ethylene-bis(2-hydroxyacetophenoneiminato))-salen ((salen)*Si(*n*-$C_4H_9)_2$, **8**)

A solution of 33.8 mmol *n*-BuLi in *n*-hexane was added dropwise to an ice-cooled stirred suspension of 5 g (16.9 mmol) *salen**$SiCl_2$. After stirring for 2 days the mixture was concentrated, and the formed yellow precipitate was extracted with *THF* (1.40 g, 30%).

$C_{26}H_{36}N_2O_2Si$; ^{13}C NMR (*DMSO*-d_6, δ, ppm): C_1 168.7, C_7 169.2, C_8 44.9, C_9 18.0, Si-Bu; ^{29}Si NMR (*DMSO*-d_6, δ, ppm): −215.5; IR: ν(C=N) 1612 cm^{-1}, ν(Si–C) 882 cm^{-1}, δ(Si–O–C) 1050–1110 cm^{-1}.



Numbering scheme for the NMR data of compounds **9–12**

Dichloro-(N,N′-ethylene-bis(3,5-di-tert-butyl-salicylideneiminato))-silane ((salen‡)$SiCl_2$, **9**)

A 100 ml *Schlenk* flask equipped with a magnetic stirring bar was charged with N,N′-ethylene-*bis*(3,5-di-*tert*-butyl-salicylideneimine) (1.6 g, 3 mmol) in 50 ml *THF* and silicon tetrachloride (0.52 g, 0.35 ml, 3 mmol). After 15 min, the mixture was heated under reflux for 3 h; then it was cooled to the room temperature. The mixture volume was diminished to 10 ml by evaporation and 40 ml hexane were added. The yellow product was filtered off and dried under vacuum (yield: 90%).

$C_{32}H_{46}Cl_2N_2O_2Si$ (589.8); calcd.: C 65.16, H 7.86, N 4.75; found: C 64.25, H 7.95, N 6.08; IR (KBr disk): $\nu = 2958$, 2910, 2871 (CH), 1654, 1619 (C=N), 1556, 1475, 1463, 1428 (C=CH) cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm): 8.07 (2H, N–CH), 7.64 and 7.07 (4H, phenyl), 4.25 (4H, CH_2), 1.56 and 1.30 (36H, C–CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): C_7 165.4, C_1 157.8, C_6 116.3, C_8 51.9; ^{29}Si NMR ($CDCl_3$, δ, ppm): −187.6.

The organo(chloro) derivatives (*salen*‡)Si(Cl)*R* (**10** and **11**) were obtained by the same procedure.

Chloro-(N,N′-ethylene-bis(3,5-di-tert-butyl-salicylideneiminato))-methylsilane ((salen‡*)*Si(Cl)Me, **10***)*

Yield: 94%; $C_{33}H_{49}ClN_2O_2Si$; IR (KBr disk): $\nu = 2960$, 2909, 2871 (CH), 1652, 1619 (C=N), 1568, 1476, 1445, 1427 (C=CH) cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm): 9.37 (2H, N=CH), 7.75 and 7.53 (4H, phenyl), 4.50 and 4.64 (4H, CH_2), 1.50 and 1.34 (36H, C–CH_3), 0.45 (3H, Si–CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): C_7 173.2, C_1 156.0, C_6 117.1, C_8 53.9, C_{14} 2.4; ^{29}Si NMR ($CDCl_3$, δ, ppm): −104.5.

Chloro-(N,N′-ethylene-bis(3,5-di-tert-butyl-salicylideneiminato))-phenylsilane (salen‡*)*Si(Cl)Ph, **11***)*

Yield: 83%; $C_{38}H_{51}ClN_2O_2Si$; IR (KBr disk): $\nu = 2964$, 2907, 2871 (CH), 1648, 1617 (C=N), 1571, 1472, 1442, 1431 (C=CH) cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm): 9.66 (2H, N=CH), 7.76 and 7.56 (4H, phenyl), 4.56 and 4.33 (4H, CH_2), 1.38 and 1.35 (36H, C–CH_3), 7.16–7.28 (5H, Si-Ph); ^{13}C NMR ($CDCl_3$, δ, ppm): C_7 174.1, C_1 157.7, C_6 117.3, C_8 52.8, $C_{14a–d}$ 137.1, 130.8, 130.5, 128.2; ^{29}Si NMR ($CDCl_3$, δ, ppm): −118.5.

N,N′-Ethylene-bis(3,5-di-tert-butyl-salicylideneiminato)-difluorosilane ((salen‡*)*SiF_2, **12***)*

A 100 ml *Schlenk* flask equipped with a magnetic stirring bar was charged with dichloro-(N,N′-ethylene-*bis*(3,5-di-*tert*-butyl-salicylideneiminato))-silane (2 g, 3.4 mmol) in 50 ml *THF* and ZnF_2 (1 g, 9.7 mmol). The mixture was heated under reflux for 8 h and then cooled. After filtration, the solution volume was diminished to 10 ml by evaporation of *THF*; then, 40 ml hexane were added. The white product was filtered and dried under vacuum (yield: 94%). The solid is stable on air and moisture. Single crystals for X-ray structure analysis were obtained from acetic ester/cyclohexane.

$C_{32}H_{46}F_2N_2O_2Si$; IR (KBr disk): $\nu = 2964$, 2871 (CH), 1648(C=N), 1565, 1477, 1452, 1426 (C=CH) cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm): 8.16 (2H, N=CH), 7.57 and 7.05 (4H, phenyl), 4.04 (4H, CH_2), 1.57 and 1.29 (36H, C–CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): C_7 164.7, C_1 159.3. C_6 116.8, C_8 53.9; ^{29}Si NMR ($CDCl_3$, δ, ppm): −187.1 ($^1J_{Si\text{-}F} = 172.6$ Hz).

X-ray data collection and structure determination of **1a**, **1b**, *and* **3**

Single crystals were mounted on glass fibres and transferred to the diffractometer. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Cu-K_α radiation ($\lambda = 1.5418$ Å) with ω-2Θ scans. The structures were solved by direct methods and refined by full matrix least squares on F^2 with anisotropic thermal parameters. Idealized positions for the hydrogen atoms were included for **1b** as fixed contributions by using a riding model. In **1a** and **3**, hydrogen atom positions were located and refined isotropically. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

Table 8. Crystal data and structure refinement for compounds **1a**, **1b**, and **3**

	1a	**1b**	**3**
Formula	$C_{18}H_{20}N_2O_2$	$C_{32}H_{48}N_2O_2$	$C_{20}H_{21}F_2N_3O_2Si$
Formula weight	296.36	492,72	401.49
Temperature	293(2) K	293(2) K	172(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54180 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (#14)	C2/c (#15)	$P2_1/a$ (#14)
a	5.762(1) Å	18.921 (2) Å	12.3826(5) Å
b	20.450(1) Å	6.207(1) Å	10.8405(5) Å
c	6.804(1) Å	27.478(2) Å	13.8507(5) Å
β	104.45(1)°	106.55(1)°	98.800(5)°
V	776.4(2) Å^3	3093.4(6) Å^3	1837.34(13) Å^3
Z	2	4	4
Density (calculated)	1.268 g/cm^3	1.058 g/cm^3	1.451 g/cm^3
Absorption coefficient	0.666 mm^{-1}	0.499 mm^{-1}	1.503 mm^{-1}
$F(000)$	316	1080	840
Crystal size	0.2×0.5×0.6 mm	0.15×0.5×1.0 mm	0.2×0.5×0.6 mm
Θ range for data collection	4.32 to 74.89°	3.36 to 74.81°	3.23 to 74.98°
Index ranges	$-7\leq h\leq 6$ $-25\leq k\leq 25$ $0\leq 1\leq 8$	$-23\leq h\leq 23$ $-2\leq k\leq 7$ $-34\leq 1\leq 34$	$0\leq h\leq 15$ $-13\leq k\leq 13$ $-17\leq 1\leq 17$
Reflections collected	3407	8734	7415
Independent reflections	1604 (R(int) = 0.0189)	3185 (R(int) = 0.0414)	3784 (R(int) = 0.0491)
Refinement method		Full-matrix least-squares on F^2	
Absorption correction	none	none	Semi-empirical from psi-scans
Max. and min. transmission	–	–	0.9984 and 0.8824
Data/restraints/parameters	1604/0/140	3185/4/201	3783/0/304
Goodness-of-fit on F^2	1.014	1.024	1.032
Final R indices ($I>2\sigma(I)$)	$R_1 = 0.0407$ $wR_2 = 0.1186$	$R_1 = 0.0557$ $wR_2 = 0.1479$	$R_1 = 0.0431$ $wR_2 = 0.1152$
R indices (all data)	$R_1 = 0.0449$ $wR_2 = 0.1241$	$R_1 = 0.0643$ $wR_2 = 0.1596$	$R_1 = 0.0482$ $wR_2 = 0.1200$
Largest diff. peak and hole	0.253 and −0.244 e · Å^{-3}	0.216 and −0.266 e · Å^{-3}	0.349 and −0.453 e · Å^{-3}

References

[1] (a) Corriu RJP and Young JC (1989) In: Patai S, Rappoport Z (eds) The Chemistry of Organic Silicon Compounds. Wiley, Chichester, 1241; (b) Holmes RR (1990) Chem Rev **90**: 17; (1996) **96**: 927; (c) Corriu RJP (1990) J Organomet Chem **400**: 81; (d) Chuit C, Corriu RJP, Reye C, Young JC (1993) Chem Rev **93**: 1371; (e) Corriu RJP Young JC (1991) In: Patai S, Rappoport Z (eds) The Silicon-Heteroatom Bond. Wiley, Chichester, pp 1 and 49; (f) Auner N, Probst R, Hahn

F, Herdtweck E (1993) J Organomet Chem **459**: 25; (g) Pfrommer B, Tacke R (1998) Europ J Inorg Chem 415; (h) Tacke R, Mühleisen M (1994) Angew Chem **13**: 1431
[2] Hobday MD, Smith TD (1972) Coord Chem Rev **9**: 311 and references cited therein
[3] Nishinaga A, Tajima K, Speiser B, Eichhorn E, Rieker A, Ohya-Nishiguchi H, Ishizu K (1991) Chem Lett 1403
[4] Pratt JM, Craig PJ (1973) Adv Organomet Chem **11**: 331
[5] Schrauzer GN, Sibert JW, Windgassen RJ (1968) J Amer Chem Soc **90**: 6681
[6] Schrauzer GN (1976) Angew Chem **88**: 465
[7] Cameron JH, Morgan PC, Turner SC (1990) J Chem Soc Chem Commun 1617
[8] Horowitz CP, Creager SE, Murray R (1990) Inorg Chem **29**: 1006
[9] Jacobsen EN, Zhang W, Güler ML (1991) J Amer Chem Soc **113**: 6703
[10] Jacobsen EN, Zhang W, Muci AR, Ecker JR, Deng L (1991) J Amer Chem Soc **113**: 7063
[11] (a) Ghose BN (1985) Acta Chimica Hungarica **118**: 191; (b) Siddiqi KS, Aqra FMAM, Shah SA, Zaidi SAA, (1993) Polyhedron **12**: 1967
[12] Compare for instance the wrong data of elemental analysis in [11b]. The calculated sum formula was given with $C_{14}H_{14}N_2Cl_2Si$ and the found data fitted this formula well. The correct formula should be $C_{16}H_{14}N_2O_2Cl_2Si$!
[13] Altmann R, Regen O, Schneider J (1984) Chemisch-technische Stoffwerte – eine Datensammlung. VEB Deutscher Verlag der Grundstoffindustrie, Leipzig
[14] Ruddick JNR, Sams JR (1975) J Inorg Nucl Chem **37**: 564
[15] (a)Breliere C, Carre F, Corriu RJP, Poirier M, Royo G, Zwecker J (1989) Organometallics **8**: 1831; (b) Carre F, Cerveau G, Chuit C, Corriu RJP, Reye C (1992) New J Chem **16**: 63; (c) Carre F, Chuit C, Corriu RJP, Mehdi A, Reye C (1995) Organometallics **14**: 2754
[16] Kalikhman I, Krivonos S, Stalke D, Kottke T, Kost D (1997) Organometallics **16**: 3255
[17] (a) Boyer-Elma K, Carré FH, Corriu RJP, Douglas WE (1995) Chem Commun 725; (b) Shim IW, Risen WM (1984) J Organomet Chem **260**: 171
[18] Pfeiffer P, Breit E, Lübbe E, Tsumaki T (1933) Liebigs Ann Chem **503**: 84, 127
[19] Larrow JF, Jacobsen EN (1994) J Org Chem **59**: 1939

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