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Racemization versus retention of chiral information during the formation of silicon and tin complexes with chiral Schiff base ligands

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ABSTRACT

Chiral Schiff base ligands with O,N,O′-coordination ability have been prepared with amino acid esters from the chiral pool. Unfortunately the chiral information is lost during the formation of complexes with these chiral ligands with silicon tetrachloride. This was demonstrated with the help of two X-ray structures which show different reaction products depending on chosen reaction conditions. The reaction of *N*-(salicylidene)-D-phenylglycine methylester (**1a**) with $SiCl_4$ in presence of triethylamine leads to planarization of the amino acid ester and formation of a ketene acetal **2a**. The reaction of *N*-(salicylidene)-L-valinmethylester (**1b**) with $SiCl_4$ without triethylamine leads to racemization of the amino acid ester and formation of the complex **2b**. A mechanism for the formation of both products has been proposed. It is possible to transfer the chiral information present in the ligand system into the complex by using dichlorodimethylstannane for the complex formation. Dimethyltin[*N*-(salicylidene)-D-phenylglycine methylester] (**3a**) crystallizes in the chiral space group $P2_12_12_1$ with one diasteromer in the asymmetric unit. ^{1}H NMR analysis of **3a** with the help of a lanthanide shift reagent proves the presence of only one diasteromer in the bulk material.

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1. Introduction

Silicon and tin complexes with Schiff base ligands have received considerable attention due to their bacteriostatic [1], antimicrobial [2], biocidal [3], bactericidal [4] and fungicidal [5,6] properties or their possible application as antitumor-reagents [6]. Numerous publications about silicon complexes with salen-type ligands [7–10] and with tridentate O,N,O′-ligands [11–14] have been published recently. Now our interest is shifted towards hypercoordinated silicon and tin compounds with chiral ligands. We have recently published the results of penta- and hexacoordinated silicon complexes with chiral Schiff base ligands derived from salicylaldehyde and chiral amino alcohols [15]. Chiral Schiff bases are of certain biological importance as they occur in pyridoxal-depending enzyme-catalyzed biochemical reactions [16,17]. The system salicylaldehyde–amino acid could be considered as a simple model for these complex enzyme systems. Further possible points of interest are the chirality transfer from silicon to carbon [18,19] and the preparation of silanes with silicon centered chirality as reagents or substrates [20,21].

Herein we report the syntheses and structures of silicon and tin complexes of *N*-(salicylidene)-α-amino acids. The X-ray crystal structures surprisingly show the loss of chiral information for the silicon complexes. We will discuss possible reaction mechanisms towards these products. The preservation of chiral information was possible with a tin complex.

2. Experimental

The necessary chemicals were used as commercially available. Reactions with air- or moisture-sensitive reagents were carried out under dry Argon. THF, DME, and triethylamine were distilled from sodium/benzophenone under Argon prior to use. Dichloromethane was distilled under Argon from CaH_2, hexane from $LiAlH_4$. NMR: BRUKER DPX 400, TMS as internal standard – elemental analyses: Foss Heraeus CHN-O-Rapid – Polarimetry: Perkin Elmer Polarimeter 241.

2.1. Preparation of Schiff bases

Ligands **1a** and **1b** were prepared from salicylaldehyde and α-amino acid methylester hydrochlorides in CH_2Cl_2 according to a previously published method [22]. NMR spectroscopic data and elemental analyses for **1a** and **1b** agree well with data which have been published before for these ligands.

2.1.1. Ligand *1a*

D-Phenylglycine methylester hydrochloride (10.0 g, 49.6 mmol) was dissolved in 120 ml of dichloromethane with triethylamine

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(6.9 ml, 49.6 mmol). Salicylaldehyde (4.9 ml, 47.2 mmol) was slowly added, whereby the color of the solution changed slowly to yellow. The reaction mixture was stirred overnight at room temperature before it was extracted twice with approx. 50 ml water. The organic layer was dried with Na_2SO_4, filtered and concentrated in vacuo. The remaining yellow oil crystallized while standing at room temperature, giving 12.33 g **1a** (91% yield), $[\alpha]_D^{20} = +59.3°$ (c = 0.3 g/100 ml $CHCl_3$). m.p. = 64 °C. ^{1}H NMR ($CDCl_3$, TMS, 298 K, ppm) δ = 3.76 (s, 3H, OCH_3); 5.19 (s, 1H, N–CH); 6.86–7.47 (m, 9H, Ar–H); 8.38 (s, 1H, N=CH); 13.12 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, TMS, 298 K, ppm) δ = 52.7 (OCH_3); 74.9 (N–CH); 117.2–137.0 (Ar–C); 161.0 (C–OH); 166.9 (COO); 170.8 (N=CH); Elemental *Anal.* Calc. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.30; H, 5.59; N, 5.06%.

2.1.2. Ligand **1b**

Triethylamine (4.1 ml, 29.6 mmol) was added to as suspension of L-valine methylester hydrochloride (5.0 g, 29.6 mmol) in 90 ml dichloromethane. As salicylaldehyde (2.8 ml, 26.9 mmol) was added slowly the color of the reaction mixture turned yellow. The suspension was stirred at room temperature over night. The solution was washed twice with destilled water and the organic layer was dried with Na_2SO_4. The drying agent was filtered of and the filtrate concentrated in vacuo. The obtained yellow oil was crystallized from ethanol/hexane, giving 2.12 g **1b** (33% yield), $[\alpha]_D^{20} = -38.7°$ (c = 0.3 g/100 ml $CHCl_3$). m.p. = 30 °C. ^{1}H NMR ($CDCl_3$, TMS, 298 K, ppm) δ = 0.96 (m, 6H, CH_3, i-Pr, $^3J_{H-H}$ = 6.7 Hz); 2.37 (m, 1H, CH, i-Pr, $^3J_{H-H}$ = 6.1/6.7 Hz); 3.72 (d, 1H, N–CH, $^3J_{H-H}$ = 6.1 Hz); 3.80 (s, 3H, O–CH_3); 6.86–7.34 (m, 4H, Ar–H); 8.30 (s, 1H, N=CH); 13.15 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, TMS, 298 K, ppm) δ = 18.2/19.4 (CH_3, i-Pr); 31.7 (CH, i-Pr); 52.0 (O–CH_3); 77.8 (N–CH); 117.0–132.7 (Ar–C); 161.0 (C–OH); 166.5 (N=CH); 171.5 (COO); Elemental *Anal.* Calc. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.01; H, 7.27; N, 5.75%.

2.2. Preparation of silicon and tin complexes

The syntheses of the silicon and tin complexes **2a**, **2b** and **3a** were carried out as previously published for titanium complexes with amino acid Schiff bases [23].

2.2.1. Complex **2a**

1a (4.0 g, 14.9 mmol) was dissolved in 150 ml THF and triethylamine (4.3 ml, 30.9 mmol) was added. The mixture was cooled to 0 °C and slowly silicon tetrachloride (1.1 ml, 7.4 mmol) was added. The reaction mixture instantly turned orange and a white precipitate formed. The mixture was stirred magnetically for 2.5 h before filtering. The solvent was removed by reduced pressure from the orange colored filtrate. Single crystals for the X-ray structure analysis where obtained from DME/*n*-hexane (<1% yield). m.p. = 190–192 °C. ^{29}Si NMR ($CDCl_3$, TMS 298 K, ppm): −175.5, −177.1.

2.2.2. Complex **2b**

1b (1.0 g, 4.29 mmol) was dissolved in 40 ml of dichloromethane and silicon tetrachloride (0.5 ml, 4.29 mmol) was added. The color of the reaction mixture immediately turned red and after a while yellow, a white precipitate formed. After 1.5 h of stirring the solvent was removed in vacuo, the residue was stirred at reflux in dichloromethane, and then filtered. Single crystals could be gained from the filtrate stored at 8 °C (0.44 g, 22% yield). m.p. > 350 °C. ^{29}Si NMR (CD_2Cl_2, TMS, 298 K, ppm) δ = −179.2. ^{1}H NMR (CD_2Cl_2, TMS, 298 K, ppm) δ = 1.14–1.27 (m, 12H, CH_3, i-Pr, $^3J_{H-H}$ = 7.0 Hz), 2.43–2.57 (m, 2H, CH, i-Pr, $^3J_{H-H}$ = 6.4/7.0 Hz); 4.03, 4.08 (2d, 2H, N–CH, $^3J_{H-H}$ = 6.4 Hz); 6.67–7.53 (m, 8H, Ar); 8.35, 8.39 (2s, 2H, HC=N). ^{13}C NMR (CD_2Cl_2, TMS, 298 K, ppm)

Table 1
Crystal data and structure refinement for compounds **2a**, **2b**, and **3a**.

Compound	**2a**	**2b**	**3a**
Empirical formula	$C_{32}H_{26}N_2O_6Si$	$C_{24}H_{26}N_2O_6Si$	$C_{17}H_{17}NO_3Sn$
Formula weight	562.64	466.56	402.01
T (K)	100(2)	153(2)	153(2)
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a (Å)	13.7469(3)	10.2958(3)	9.2503(2)
b (Å)	24.2066(5)	11.7003(4)	11.0468(2)
c (Å)	8.1047(1)	19.2626(6)	15.3382(3)
α (°)	90	97.9300(10)	90
β (°)	93.483(1)	91.926(2)	90
γ (°)	90	93.090(2)	90
V (Å^3)	2691.98(9)	2292.94(13)	1567.35(5)
Z	4	4	4
D_{calc} (Mg/m^3)	1.388	1.352	1.704
Absorption coefficient (mm^{-1})	0.138	0.146	1.642
F(000)	1176	984	800
Crystal size (mm)	0.44 × 0.20 × 0.15	0.53 × 0.40 × 0.26	0.39 × 0.35 × 0.20
Theta range for data collection (°)	1.68–28.00	1.76–27.00	2.27–28.00
Limiting indices	$-18 \leqslant h \leqslant 18$, $-31 \leqslant k \leqslant 31$, $-10 \leqslant l \leqslant 10$	$-13 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 14$, $-24 \leqslant l \leqslant 18$	$-12 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 14$, $-20 \leqslant l \leqslant 20$
Reflections collected/unique	44942/6507 [R_{int} = 0.0387]	31145/9956 [R_{int} = 0.0231]	40502/3783 [R_{int} = 0.0225]
Completeness to theta	(28.00°) 100.0%	(27.00°) 99.4%	(28.00°) 100.0%
Absorption correction	Semi-empirical from equivalents		
Maximum and minimum transmissions	0.9796 and 0.9418	0.9630 and 0.9267	0.7348 and 0.5669
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	6507/0/380	9956/129/690	3783/0/209
Goodness-of-fit on F^2	1.023	1.098	1.103
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0358, wR_2 = 0.0833	R_1 = 0.0476, wR_2 = 0.1306	R_1 = 0.0140, wR_2 = 0.0370
R indices (all data)	R_1 = 0.0505, wR_2 = 0.0918	R_1 = 0.0638, wR_2 = 0.1372	R_1 = 0.0146, wR_2 = 0.0373
Absolute structure parameter	–	–	0.034(14)
Largest difference in peak and hole (e A^{-3})	0.336 and −0.321	0.873 and −0.413	0.589 and −0.227

δ = 18.1, 18.9, 20.2, 20.4 (CH_3, i-Pr); 33.3, 33.9, 33.9, 34.1 (CH, i-Pr); 63.7, 69.5 (N–CH), 117.3, 117.4, 119.6, 119.8, 120.6, 120.9, 133.9, 134.1, 138.5, 138.6 (C_{Ar}); 161.2, 161.5, 166.9, 167.7, 173.4 (C_{Ar}, C=N, COO). Elemental *Anal.* Calc. for $C_{24}H_{26}N_2O_6Si$: C, 61.78; H, 5.62; N, 6.00. Found: C, 60.80; H, 4.63; N, 5.33%.

2.2.3. Complex **3a**

1a (3.0 g, 11.1 mmol) was dissolved in 150 ml THF with triethylamine (3.3 ml, 23.9 mmol) and cooled down to 0 °C. When dimethyltindichloride (2.4 g, 11.1 mmol) was added slowly, the color of the mixture turned orange and a white precipitate formed. The reaction mixture was stirred at room temperature over night and its color turned red. The precipitate was filtered and the solvent was removed by reduced pressure. Single crystals for the X-ray structure analysis could be gained from DME/n-hexane, giving 0.45 g (10% yield). m.p. = 203–205 °C, $[\alpha]_D^{20}$ = +144.5° (*c* = 0.2 g/100 ml $CHCl_3$). ^{119}Sn NMR ($CDCl_3$, TMS, 298 K, ppm) δ = −156.0. ^{1}H NMR ($CDCl_3$, TMS, 298 K, ppm) δ = 0.79 (6H, Me–Sn); 5.19 (s, 1H, N–CH); 6.73–7.39 (m, 9H, Ar–H); 8.31 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 298 K, ppm) δ = 8.5 (Sn–Me); 71.1 (N–CH); 117.1–138.2 (Ar–C); 169.0 (C–O–Sn); 171.3 (C=N); 174.0 (C=O). Elemental *Anal.* Calc. for $C_{17}H_{17}NO_3Sn$: C, 50.79; H, 4.26; N, 3.48. Found: C, 50.00; H, 4.62; N, 3.81%.

2.3. X-ray data collection and solution

Single crystal X-ray diffraction data of **2a**, **2b**, and **3b** were collected on a BRUKER NONIUS X8 APEX2 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Structures were solved with direct methods and refined with full-matrix least-squares methods. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in idealized positions and refined isotropically (riding model). Structure solution and refinement of F^2 against all reflections were carried out with the software SHELXS-97 and SHELXL-97, G.M. Sheldrick, Universität Göttingen (1986–1997). Data of structure determination and refinement are summarized in Table 1.

3. Results and discussion

3.1. Syntheses and spectral characterizations

The enantiomerically pure Schiff base ligands **1a** and **1b** could be gained in good yields from the condensation of the amino acid methyl ester hydrochlorides with salicylaldehyde. The complexes **2a**, **2b** and **3a** were prepared in quite low yields through the reaction of the ligands with silicon tetrachoride or dimethyltindichloride, respectively.

The ^{1}H and ^{13}C NMR spectra of the complexes were interpreted by comparing them with the spectra of the free ligands. ^{29}Si, respectively ^{119}Sn NMR spectroscopy gives first information about the presence of higher coordinated central atoms in the complexes under investigation. Complex **2a** shows two signals at ^{29}Si NMR shifts of −175.5 and −177.1 ppm, which imply the existence of two isomers. More detailed NMR spectroscopic analyses could not be realized due to the fact, that the yield of the complex was extraordinary low (<1%).

Complex **2b** has a chemical shift of −179.2 ppm in the ^{29}Si NMR spectrum, which implies hexacoordination. The ^{13}C and ^{1}H NMR spectra show two signals with a slightly different shift for one carbon atom or hydrogen atom respectively, indicating racemization. There are no significant differences between the chemical shifts of the carbon atoms of the free ligand in comparison to that of the complex. In the ^{1}H NMR spectrum the shifts for the hydroxyl hydrogen atom cannot be found because of the complexation of silicon. Furthermore, the absence of the methyl group implies the cleavage of the methyl ester group during the reaction.

Complex **3a** shows a chemical shift of −156.0 ppm in the ^{119}Sn NMR spectrum. This implies a hypercoordinated tin compound. The ^{13}C NMR spectra of the complex and of the free ligand are very similar. The carbonyl carbon, the aromatic carbon with the hydroxyl group and the imin carbon atom show the highest chemical shift due to their neighborhood to the electronegative oxygen or nitrogen atoms (174.0, 171.3, 187.0 ppm). These and the shifts of the aromatic carbon atoms (δ 138.2–117.1 ppm) show no significant differences between the free and the complex bound state. This is to be expected as the aromatic ligand moieties do not take part in the coordination of the central tin ion. The complex has no signal for a methyl ester carbon atom around 52.7 ppm, which is the greatest difference of the two spectra next to the fact, that the two tin bound methyl functions show a shift of 59.0 ppm. After the addition of 10% of europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate], $Eu(tfc)_3$, as shift reagent to the complex diluted in $CDCl_3$, the ^{1}H NMR signal of the proton bound to the asymmetric carbon atom appears shifted towards lower field (now δ = 5.63 ppm instead of 5.20 ppm). Furthermore, it is still a singlet, what shows the enantiomerical purity of the bulk material.

3.2. X-ray structures

Single crystals of complex **2a** could be gained from a mixture of DME/n-hexane. The molecular structure is shown in Fig. 1, selected bond lengths and angles in Tables 2 and 3. The compound crystallizes in the monoclinic crystal system in the space group $P2_1/c$ and has four molecules in the unit cell. Two tridentate O,N,O′-ligands are coordinated at the silicon atom yielding an octahedral coordination geometry. For crystallographic data see experimental section. The bond angles between neighboring atoms at silicon vary

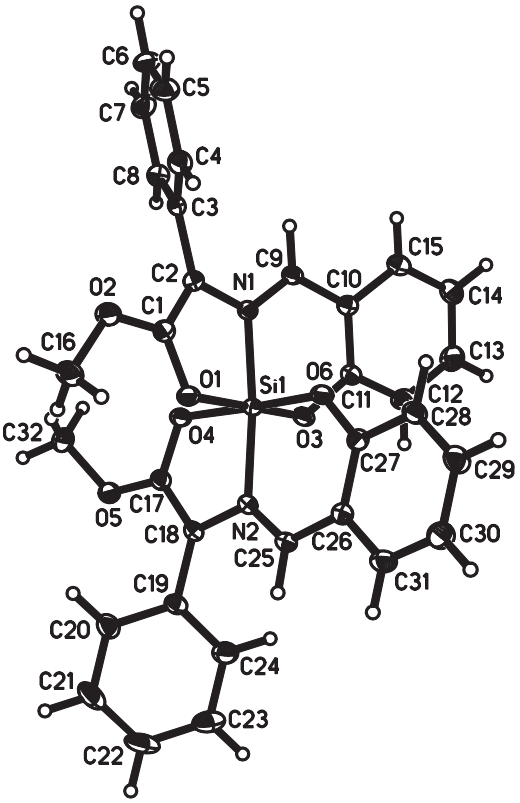


Fig. 1. ORTEP plot of $Si(OC_6H_4CH{=}NC(Ph)COOMe)_2$ (**2a**). The non-hydrogen atoms are drawn with 50% probability ellipsoids.

Table 2
Selected bond lengths of **2a** in Å.

Si1–O1	1.818(1)	N1–C2	1.401(2)
Si1–O3	1.728(1)	N1–C9	1.303(2)
Si1–O4	1.797(1)	C1–C2	1.368(2)
Si1–O6	1.720(1)	N2–C25	1.300(2)
Si1–N1	1.898(1)	N2–C18	1.409(2)
Si1–N2	1.901(1)	C17–C18	1.363(2)

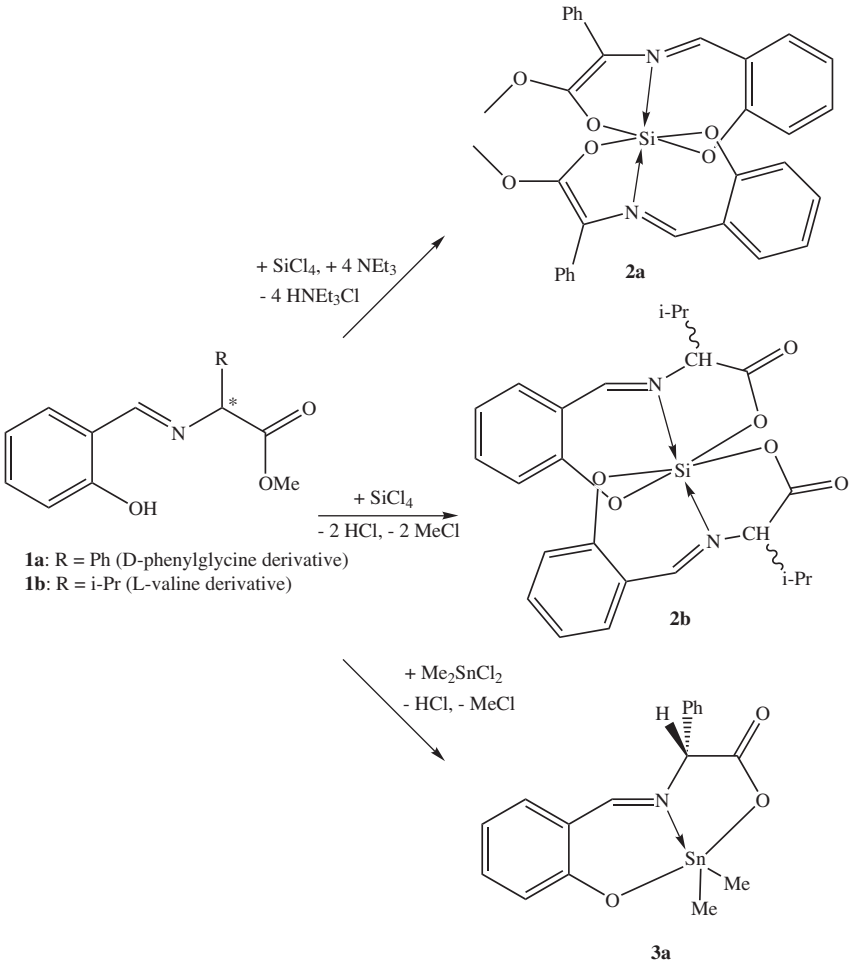
Table 3
Selected bond angles of **2a** in °.

O6–Si1–O3	93.77(5)	O6–Si1–O1	91.54(5)
O3–Si1–O4	88.77(5)	O4–Si1–O1	85.90(5)
O6–Si1–N1	87.44(5)	O3–Si1–N1	93.99(5)
O4–Si1–N1	91.25(5)	O1–Si1–N1	85.23(5)
O6–Si1–N2	95.09(5)	O3–Si1–N2	91.56(5)
O4–Si1–N2	85.97(5)	O1–Si1–N2	88.97(5)
O3–Si1–O1	174.59(5)	O6–Si1–O4	177.22(5)
N1–Si1–N2	173.74(5)		
C1–C2–N1	109.8(1)	C17–C18–N2	109.9(1)
C1–C2–C3	126.8(1)	C17–C18–C19	126.2(1)
N1–C2–C3	123.2(1)	N2–C18–C19	123.8(1)

between 85.23(5)° (O1–Si1–N1) and 95.09(5)° (O6–Si1–N2) indicating the distortion of the coordination polyhedron (see Table 3).

The Si–O distances are comparable to similar octahedral silicon complexes [11,15]. The Si–N distances are longer than the Si-O distances, which can be explained by the coordinative character of these bonds. The angles between 85.23° and 95.09° between neighboring atoms at silicon and nearly 180° between the opposite atoms represent a distorted octahedral coordination geometry. The distortion arises from the shorter bond from silicon to the phenolic oxygen atoms O3 and O6. As a result the silicon atom is not located in the same plane as the atoms O1, O3, N1 and N2 and O4, O6, N1 and N2, respectively. In contrast to this O1, O3, O4 and O6 share one plane with silicon as the angular sum is 360°.

In the coordination sphere of silicon the two ligands (O1, O3, Si1, N1 and O4, O6, Si1, N2) are perpendicular with an angle of 89.74(±0.04)°. If both ligand systems are considered as planar (plane C10 to C15, C9, N1, C2, C1, O1, O2 and second ligand, respectively) their arrangement is also nearly perpendicular with an angle of 78.12° (0.02). Furthermore, the aromatic group (C10–C15) is tilted in comparison to the plane of Si1, O1, O3, and N1 by 26.78(±0.06)°. In the second ligand molecule of the complex the angle between the phenyl group (C26–C31) and the plane Si1, O4, O6, and N2 is only 5.28(±0.05)°. The complex crystallizes in the centrosymmetric space group $P2_1/c$, therefore the compound is not chiral and has no optical activity as it is found in the free enantiomerically pure ligand. The chirality was lost during complex formation. This can be explained by a planarization of the α-carbon atoms C2 and C18 of the amino acid unit. The angular sums around C2 and C18 are 359.8° and 359.9° which confirms planarization of these atoms. This is supported by the bond distances N1-C9, N1–C2, and C1–C2 that imply an enlargement of



Scheme 1.

the conjugated aromatic system of the phenyl group (C10–C15). The same effect is observed between the atoms N2-C25, N2–C18, and C17–C18. Therefore a valence structure with silicon coordinated ketene acetal ligands as shown in Scheme 1 can be assigned to compound **2a**.

Single crystals of complex **2b** were grown from dichloromethane. The compound crystallizes in the triclinic crystal system in the space group *Pbar*1 with two crystallographically independent molecules in the asymmetric unit. The discussion of the structural data will be performed only with one of these molecules. The structural features of the other molecule are very similar. The molecular structure of one molecule is shown in Fig. 2, selected bond lengths and angles in Tables 4 and 5. Two ligand dianions are coordinated around silicon with octahedral coordination geometry. The isopropyl group of one of the two complex ligands is disordered (C15, C16, C17) in this molecule. (One of the amino acid units is disordered in the other crystallographic independent molecule. See CIF-file for details.) The two Si–N-bonds Si1-N1 and Si1–N2 are longer than the Si–O bonds, that implies coordinative bonding. Apparently the methyl ester function of the ligand was transformed into a silyl ester during complex formation. That means the methyl ester group was cleaved off. The octahedral coordination geometry around the silicon atom is distorted with angles between neighboring atoms of 84.62(6)–93.80(7)° and near 180° between axial positioned atoms. The carbon atoms C2 and C14 are tetrahedral (sp^3 hybridization), which can be shown at the sums of the bond angles of the non-hydrogen atoms around these atoms. The sum of the bond angles N1–C2–C1, C1–C2–C3, and N1–C2–C3 is 332.6°. The sum of the bond angles at C14 are 319.2° with C15A and 342.3° with C15B. The compound crystallizes in the centrosymmetric space group $P\bar{1}$, which is an inversion center as symmetry element. Chiral compounds that crystallize in this space group are bound to exist as their racemic form (R and S) in the crystal structure. In the literature several explanations and possibilities for the racemization of amino acids have already been discussed [24–26]. In contrast to **2a**, where the chiral information was lost due to planarization of the amino acid α carbon atom, racemization is the reason for the loss of the optical activity in complex **2b**.

In contrast to the experiments with organosilanes, an enantiomerically pure tin Schiff base complex was isolated from the

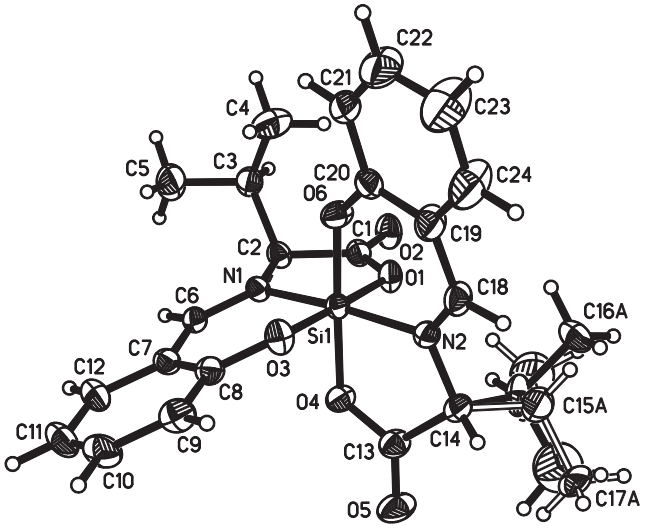


Fig. 2. ORTEP plot of $Si(OC_6H_4CH{=}NCH(i\text{-}Pr)COO)_2$ (**2b**). The non-hydrogen atoms are drawn with 50% probability ellipsoids.

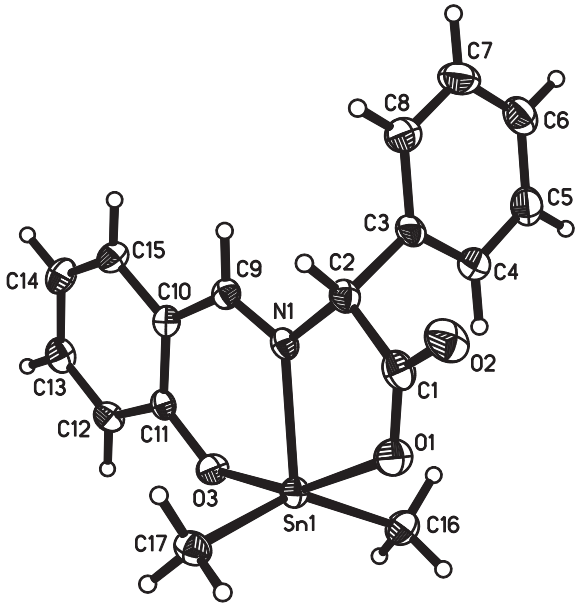


Fig. 3. ORTEP plot of $Me_2Sn(OC_6H_4CH{=}NCH(Ph)COO)$ (**3a**). The non-hydrogen atoms are drawn with 50% probability ellipsoids.

Table 4
Selected bond lengths of **2b** in Å.

Si1–O1	1.786(1)	Si1–O4	1.790(1)
Si1–O3	1.736(1)	Si1–O6	1.724(1)
Si1–N1	1.886(2)	Si1–N2	1.877(2)

Table 5
Selected bond angles of **2b** in °.

O6–Si1–O3	90.37(7)	O6–Si1–O4	178.28(7)
O6–Si1–O1	89.44(7)	O3–Si1–O4	90.32(7)
O3–Si1–O1	178.52(7)	O1–Si1–O4	89.91(7)
O6–Si1–N2	93.79(7)	O6–Si1–N1	93.33(7)
O3–Si1–N2	91.22(7)	O3–Si1–N1	93.80(7)
O1–Si1–N2	90.26(7)	O1–Si1–N1	84.74(4)
O4–Si1–N2	84.62(6)	O4–Si1–N1	88.20(6)
N1–Si1–N2	171.26(7)	N2–C14–C13	105.3(1))
N1–C2–C1	105.5(2)	N2–C14–C15A	111.3(3)
C1–C2–C3	110.5(1)	N2–C14–C15B	115.3(3)
N1–C2–C3	116.4(2)	C13–C14–C15A	102.6(2)
		C13–C14–C15B	121.7(3)

Table 6
Selected bond lengths of **3a** in Å.

Sn1–O1	2.203(1)	Sn1–C16	2.095(2)
Sn1–O3	2.090(1)	Sn1–C17	2.099(2)
Sn1–N1	2.190(1)		

Table 7
Selected bond angles of **3a** in °.

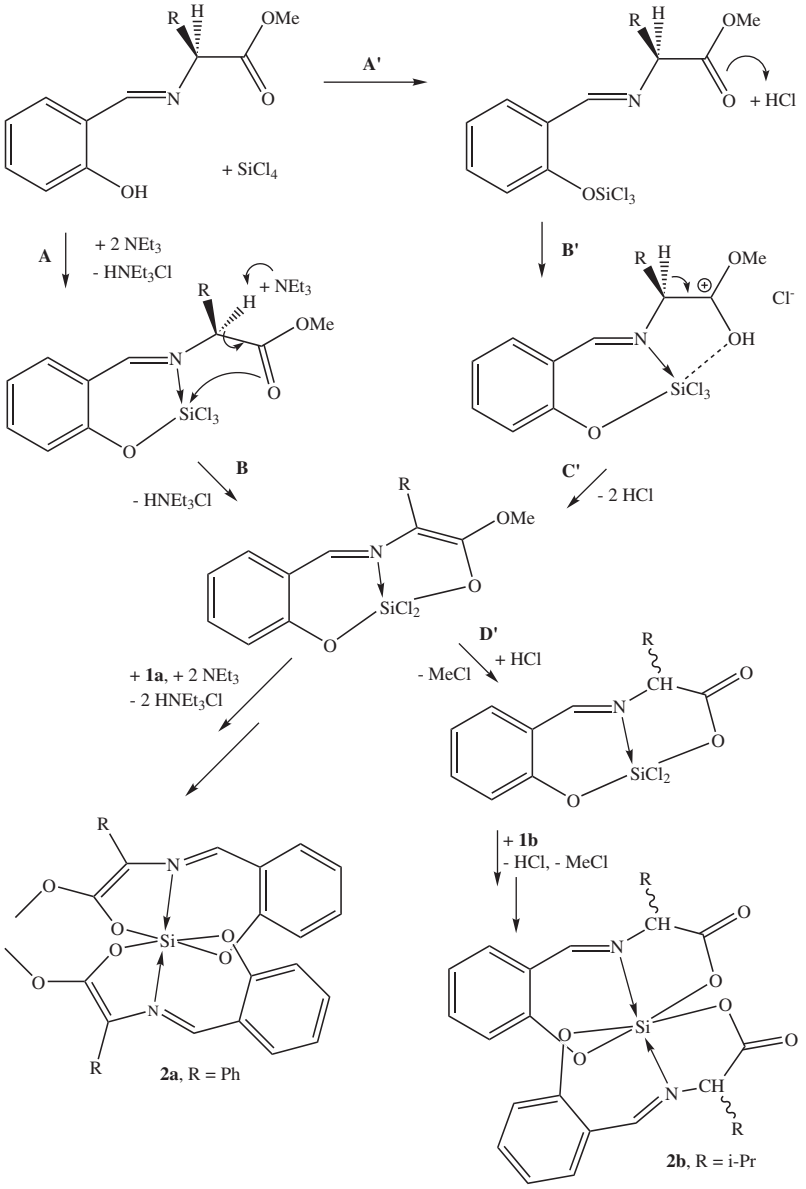
O3–Sn1–C16	94.67(7)	O3–Sn1–O1	157.31(5)
O3–Sn1–C17	98.05(7)	C16–Sn1–O1	89.79(8)
C16–Sn1–C17	142.76(8)	C17–Sn1–O1	91.63(7)
O3–Sn1–N1	83.41(5)	C16–Sn1–N1	112.15(7)
N1–Sn1–O1	74.33(5)	C17–Sn1–N1	104.01(6)

reaction of **1b** with dimethyltindichloride. Single crystals of **3a** were obtained from THF. The molecular structure is shown in Fig. 3, selected bond lengths and angles in Tables 6 and 7. The compound crystallizes as orthorhombic crystals in the space group $P2_12_12_1$ with four molecules in the unit cell. Only one enantiomer is present in this chiral space group. Inspection of the chirality at C2 shows, that the R-configuration of the ligand system has been retained during the synthesis. The pentacoordinated compound is a 1:1 complex where the dimethyl tin unit is coordinated to one tridentate Schiff base ligand. The coordination geometry around the tin atom can be analyzed with the Addison parameter τ [27]. The value of τ is 0.24, which corresponds to a distorted square pyramid with the atoms O1, O3, C16 and C17 forming the base and N1 the top of the pyramid. For crystallographic data see experimental section. The phenylic amino acid group has a nearly perpendicular orientation to the plane formed by the atoms C10 to C15 and O3, C9, N1, C2, C1, O1 and O2. The two tin bound methyl groups at 88.9° have a nearly perpendicular orientation to the ligand plane. The tin atom is in the same plane with the atoms N1, C16 and C17, which is proved by the angular sum of 358.9°.

3.3. Discussion of reaction mechanisms

Scheme 1 shows the general outcome of the performed reactions. Three different reaction pathways have been observed. The reaction of **1a** with silicon tetrachloride in presence of triethylamine gives an octahedral complex **2a** with a planarized ligand system. The reaction of the ligand molecule **1b** with silicon tetrachloride leads to an octahedral complex **2b** with a racemized ligand system. The reaction of **1a** with dimethyltindichloride yields a pentacoordinate complex **3a** showing retention of the chiral information.

A possible mechanism for the formation of **2a** is shown in Scheme 2 (left column). In a first step (**A**) the silicontetrachloride reacts with the phenolic hydroxide group eliminating a molecule of hydrogen chloride. This is bound by triethylamine as its hydrochloride which forms a precipitate. The second eq. triethylamine abstracts the α-proton of the amino acid moiety (**B**) resulting in a planar ketene acetal structure. The second ligand molecule can react in equal manner leading to the hexacoordinated silicon complex **2a**.



Scheme 2.

As the reaction of **1b** with silicon tetrachloride was carried out without triethylamine, racemization has taken place under acidic conditions. During the racemization process there has to be an intermediate step which includes a planar coordination, i.e. a sp^2-hybrid geometry around the α carbon atom of the amino acid moiety. A possible mechanism is shown in Scheme 2 (right column). Again silicon tetrachloride reacts with the phenolic hydroxyl function and a molecule hydrogen chloride is released (**A′**). In this case, it is not neutralized by an equivalent of triethylamine but can protonate the amino acid carbonyl oxygen (**B′**). The carbocation neutralizes its positive charge through the formation of a double bond with the α carbon atom (**C′**) under cleavage of the C–H-bond at the chiral carbon atom. This results in an enlargement of the conjugated system and a ketene acetal structure, which is the same intermediate as in the mechanism discussed for the formation of **2a**. In contrast to the formation of **2a** the reaction proceeds with the protonation of the α carbon atom by hydrogen chloride present in the reaction mixture (**D′**). This can happen from both sides of the prochiral molecule, yielding to racemization of the ligand molecule. At the end, the carbonyl function is reformed resulting in an ester cleavage while an equivalent of methylchloride is formed. The reaction with the second molecule **1b** proceeds in the same way, leading to the hexacoordinated silicon complex **2b**.

Another point, which can be seen as a reason for the different outcome of reactions with **1a** and **1b** respectively is the nature of the amino acid. Ligand **1a** has a phenyl group which increases in complex **2a** the system of delocalized π electrons containing the aromatic ring of the salicylaldehyde moiety, the built up ketene acetal structure, and the aromatic amino acid group. In contrast to this, ligand **1b** includes the valine alkyl group which does not give any stabilization effect to the planar ketene acetal structure in the silicon complex. Quite contrary to this the alkyl group destabilizes the double bond because of its +I effect.

4. Conclusion

Enantiomerically pure tridentate O,N,O′ ligands prepared from amino acid esters and salicylaldehyde react with silicon tetrachloride to hexacoordinated 1:2 silicon–Schiff base-complexes. Depending on the reaction conditions and the nature of the amino acid group the Schiff-base ligand yields a ketene acetal structure or a racemized ligand system. In both cases the stereochemical information is lost. It needs a careful choice of reagents and reaction conditions in order to retain the chirality. We were able to demonstrate the possibility to prepare a chiral complex in case of **3a**. The reduced Lewis acidity of the tin compound allowed the preservation of chirality in this reaction. The two silicon complexes **2a** and **2b** with their surprising structural features allowed us to develop a uniform concept explaining the racemization of the ligand system during complex formation.

Appendix A. Supplementary data

CCDC 876252, 876259, and 876286 contain the supplementary crystallographic data for **2a**, **2b**, and **3a**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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