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A new type of chiral pentacoordinated silicon compounds with azomethine ligands made from acetylacetone and amino acids

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ABSTRACT

Azomethines of acetylacetone with amino acids have been utilized to prepare chiral pentacoordinated silicon compounds. The sodium salt of the ligand **6** has been synthesized from acetylacetone and L-phenylalanine in presence of sodium hydroxide. Reaction of **6** with equimolar amounts of dichlorodiorganosilanes in presence of triethylamine gave the chiral silicon complexes **7a–c**. These contain a R_2SiONO' skeleton, wherein the pentacoordination is reached by coordination of the acetylacetonate oxygen, the imine nitrogen, and one carboxylate oxygen atom of the azomethine ligand to the SiR_2 unit. **7a–c** were characterized by elemental analyses, single crystal X-ray diffraction, UV–Vis–spectroscopy, value of optical rotation, and NMR-spectroscopy.

1. Introduction

Established methods for the preparation of chiral silicon compounds use for instance the resolution of diasteromers formed with (−)-menthol, the kinetic resolution of racemic mixtures with chiral reagents, and asymmetric synthesis starting from prochiral compounds $R_1R_2SiX_2$ [1]. During our work with pentacoordinate silicon complexes we developed new methods to obtain chiral products utilizing amino acids from the chiral pool in the ligand backbone. Thereby different types of chiral silicon complexes have been prepared. Schiff bases of chiral amino alcohols (**1**) giving chiral silicon complexes (**2**) under retention of the chiral information (see Scheme 1) [2]. The synthesis of the amino alcohols containing the "magic" diphenyl hydroxmethyl group [3] is laborious and needs several preparative steps.

The reaction of salicylideneimines of amino acids (**3**) seems to be an alternative to access chiral silicon complexes. But it has been shown recently that the reaction of these ligands with silicon tetrachloride yields to planarization (**4**) or racemization (**5**) of the chiral amino acid group in dependence on the reaction conditions (see Scheme 2) [4]. In each case the chiral information is lost.

Herein we present an alternative synthesis of chiral pentacoordinated silicon complexes with another ligand system.

2. Experimental

2.1. General considerations

The necessary chemicals were used as commercially available. The preparation of the protonated ligand **6** and the complexes **7a**, **7b**, and **7c** were performed in Schlenk tubes under dry argon with dry and air-free solvents. Organic solvents were dried and purified according to standard procedures. Melting points were determined with a Polytherm A from Wagner & Munz apparatus by using samples in sealed capillaries. NMR spectra were recorded with a BRUKER DPX 400 spectrometer operating at 400.13 MHz (^{1}H) with TMS as internal standard. Elemental analyses were performed with a Foss Heraeus CHN-O-Rapid instrument. A Perkin Elmer Polarimeter 241 was used for the determination of the value of optical rotation.

2.2. Synthesis of ligands and complexes

2.2.1. Preparation of 6

Sodium hydroxide (0.80 g, 20 mmol) was dissolved in absolute MeOH. L-phenylalanine (3.30 g, 20 mmol) was added. The reaction mixture was stirred and the amino acid was dissolved. Afterwards acetylacetone (2.10 g, 21 mmol) in 20 ml abs. MeOH was added. The solution became light yellow and after a few minutes a white fluffy precipitation appeared. This suspension was stirred 15 min at room temperature and then refluxed for 5 h. During this time the precipitation disappeared. After cooling to room temperature the resulting solution was stirred several days. Then the volatiles

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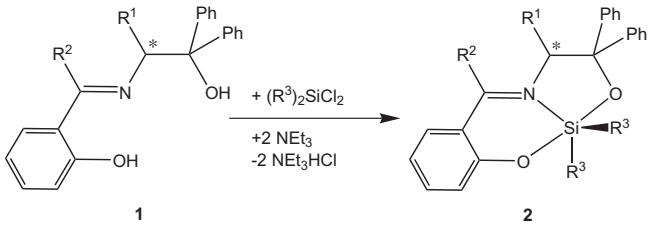


Scheme 1. Synthesis of **2** (R^1, R^3 = alkyl, aryl; R^2 = H, Me).

were removed under reduced pressure and the light yellow residue was dried in a vacuum at about 373 K.

Light yellow solid (4.86 g, 90.2%, m.p. 412–414 K). *Anal.* Calc. for $C_{14}H_{16}NO_3Na$ (269.276 g/mol): C, 62.45; H, 5.99; N, 5.20. Found: C, 60.85; H, 6.19; N, 5.07%.

^{1}H NMR (DMSO-d_6): δ 1.44 (s, 3 H, CH_3), 1.80 (s, 3 H, CH_3), 2.73 (dd, 1 H, CH_2, $^3J_{HH}$ = 9.1 Hz, $^2J_{HH}$ = 13.5 Hz), 3.19 (dd, 1 H, CH_2, $^3J_{HH}$ = 4.0 Hz, $^2J_{HH}$ = 13.5 Hz), 3.97 (dt, 1 H, CH–COO, $^3J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 9.1 Hz), 4.70 (s, 1 H, CH = C–N), 7.15–7.25 (mm, 5 H, CH_{ar}), 10.88 (d, 1 H, N–H, $^3J_{HH}$ = 9.1 Hz).

^{13}C NMR (DMSO-d_6): δ 18.5 ($\underline{C}H_3$–C=N), 28.6 ($\underline{C}H_3$–C=O), 40.7 (CH_2), 60.4 (N–$\underline{C}$H–CH_2), 94.1 (C=$\underline{C}$H–C=O), 126.0 (HC_{ar}), 128.1 (2 HC_{ar}), 129.4 (2 HC_{ar}), 139.2 (*i*-$\underline{C}_{ar}$), 161.8 (CH_3–$\underline{C}$–N), 174.0 (COO), 191.6 (CH_3–$\underline{C}$ = O).

$[\alpha]^{20}_D = -326.7°$ (c = 1 g/100 ml DMSO). UV–Vis ($c = 4.085 \times 10^{-4}$ mol/l, in DMSO) λ_{max} (ε, l mol^{-1} cm^{-1}) = 301 (11 475), 256 (2653) nm.

2.2.2. General procedure for the synthesis of *7a*, *7b*, and *7c*

The protonated ligand **6** (5 mmol) and triethylamine (5.5 mmol, 10% excess) were stirred in tetrahydrofuran (25 ml) at 273 K. A solution of dichlorodiorganylsilane (5.25 mmol, 5% excess) in tetrahydrofuran (15 ml) was added dropwise. A white precipitation was formed and the resulting suspension was stirred 30 min at 0 °C and then several days at room temperature. The triethylamine hydrochloride and sodium chloride were filtered off and washed with tetrahydrofuran (2× 10 ml). The volatiles were removed completely from the filtrate under reduced pressure. Then the residue was dissolved in deuterated chloroform (3 ml). After the solution NMR spectra were recorded this solution was concentrated to 1–2 ml in vacuum whereby the formation of colorless crystals occurred.

7a: 1.33 g **6** (4.94 mmol), 0.67 g dichlorodimethylsilane (5.19 mmol, 5% excess), and 0.55 g triethylamine (5.43 mmol, 10% excess) giving colorless crystals, 0.83 g, 46.3% (calculated with $CHCl_3$) respectively 55.4% (calculated without $CHCl_3$), m.p. 348–353 K partial decomposition, 393–395 K remaining crystals melted. Single crystals for the X-ray structure analysis were grown from $CHCl_3$ solution. These contain 1 mol $CHCl_3$ per 2 mol silicon complex. The remaining bulk product was dried in a vacuum. Thereby the $CHCl_3$ is removed. This can be seen in the results of the elemental *Anal.* Calc. without $CHCl_3$: $C_{16}H_{21}NO_3Si$ (303.434 g/mol) C, 63.33; H, 6.98; N, 4.62. Found: C, 62.87; H, 6.91 N, 4.66%.

^{29}Si NMR ($CDCl_3$): δ −64.9.

^{1}H NMR ($CDCl_3$): δ 0.12 (s, 3 H, Si–CH_3), 0.28 (s, 3 H, Si–CH_3), 1.55 (s, 3 H, CH_3–C–O), 2.05 (s, 3 H, CH_3–C–N), 3.32 (dd, 1 H, CH_2, $^3J_{HH}$ = 9.1 Hz, $^2J_{HH}$ = 13.7 Hz), 3.35 (dd, 1 H, CH_2, $^3J_{HH}$ = 3.8 Hz, $^2J_{HH}$ = 13.7 Hz), 4.40 (dd, 1 H, CH–COO, $^3J_{HH}$ = 3.8 Hz, $^3J_{HH}$ = 9.1 Hz), 5.29 (s, 1 H, CH–C=N), 7.11–7.28 (mm, 5, H_{ar}).

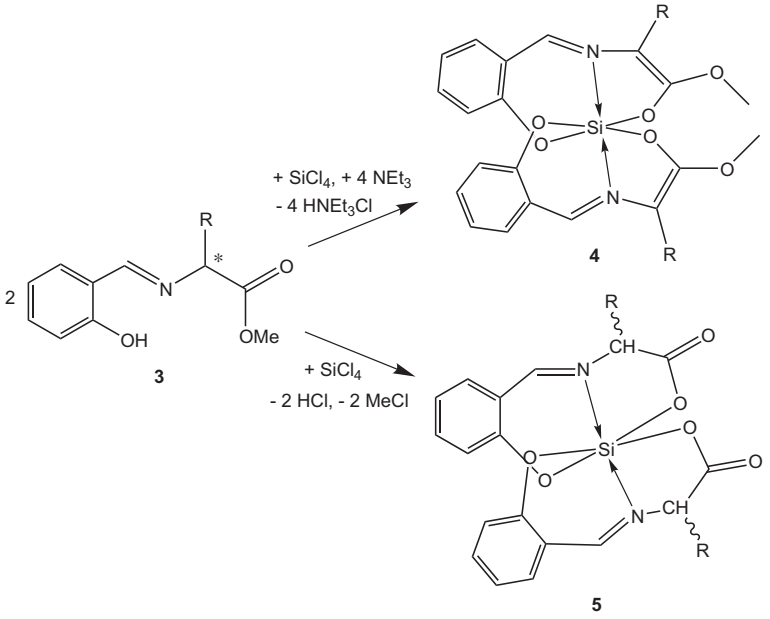
^{13}C NMR ($CDCl_3$): δ 0.5, 5.0 (Si–CH_3), 22.7 ($\underline{C}H_3$–C=N), 24.8 ($\underline{C}H_3$–C–O), 40.4 (CH_2), 62.6 ($\underline{C}$H–COO), 101.2 ($\underline{C}$H=C–O), 127.4 (C_{ar}), 128.9 (2 C_{ar}), 129.9 (2 C_{ar}), 136.2 (C_{ar}), 172.0 (CH_3–$\underline{C}$–N), 174.7 (COO), 184.9 (CH_3–$\underline{C}$–O).

$[\alpha]^{20}_D = -872.9°$ (c = 0.68 g/ 100 ml $CHCl_3$). UV–Vis ($c = 3.855 \times 10^{-4}$ mol/l, in $CHCl_3$) λ_{max} (ε, l mol^{-1} cm^{-1}) = 329 (9246), 321 (9341).

7b: 1.43 g **6** (5.31 mmol), 1.38 g $SiCl_2Ph_2$(3% excess, 5.47 mmol), and 0.59 g NEt_3 (10% excess, 5.83 mmol) giving colorless crystals of **7b** (2.13 g, 93.8%, m.p. 456–460 K). *Anal.* Calc. for $C_{26}H_{25}NO_3Si$ (427.576 g/mol): C, 73.04; H, 5.89; N, 3.28. Found: C, 72.43; H, 5.85; N, 3.27%.

^{29}Si NMR ($CDCl_3$): δ −97.0.

^{1}H NMR ($CDCl_3$): δ 1.56 (s, 3 H, CH_3–C–O), 2.36 (s, 3 H, CH_3–C–N), 2.82 (dd, 1 H, CH_2, $^3J_{HH}$ = 10.9 Hz, $^2J_{HH}$ = 13.7 Hz), 3.43 (dd, 1 H, CH_2, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 13.7 Hz), 4.70 (dd, 1 H, CH–COO, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 10.9 Hz), 5.50 (s, 1 H, CH–C=N), 7.26–8.22 (mm, 15 H, H_{ar}).



Scheme 2. Synthesis of **4** and **5** (R = alkyl, aryl).