

Mastering the Third Dimension of Salicylaldimine-Type Ligand Systems: Development of a Convenient Route to Bis(“ferrocene–saliminato”)-zirconium Chemistry

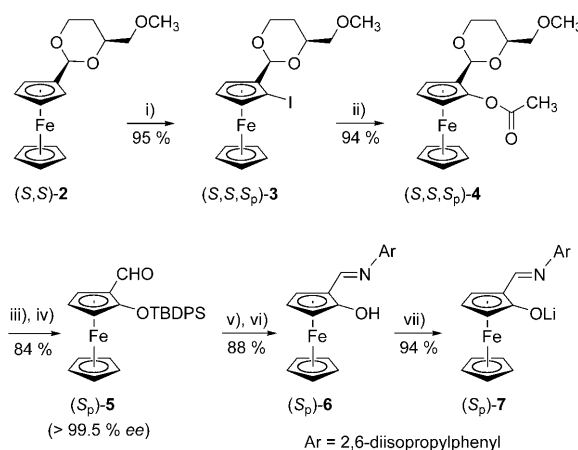
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The Group 4 metallocenes have made a considerable impact on Ziegler–Natta olefin polymerization chemistry.^[1] These systems were subsequently complemented by the chelate ligand late transition metal alkene polymerization catalysts that have been developed to a state where they may match the Group 4 bent metallocenes and related systems in catalyst performance.^[2] The overall development of new homogeneous Ziegler–Natta catalysts formally turned full circle with the usage of various chelate ligand early metal systems.^[3–6] Among these, the salicylaldimine-derived titanium, zirconium and hafnium systems play an important role.^[4–6] A characteristic of the isolated, for example, Zr(salicylaldiminato) subunit is its planar geometry, that is, its absence of chirality. It might be interesting to start to explore an expansion of this catalytically important structural moiety into the third dimension. This can in principle be done by formally replacing the planar arene framework by the 3D extension of the ferrocene unit.^[7–10]

We would thus replace the two-dimensional carbocyclic arene by an electronically related three-dimensional linear metallocene system. Of course, care has to be taken to account for the resulting consequences originating from the necessary introduction of an element of planar chirality into the system; this could result in a complicated formation of diastereomers upon the combination of more than one such a substructural unit in a molecular Group 4 metal-based complex system. Therefore, the use of enantiomerically pure building blocks seems to be advisable for this chemistry. We have now prepared the first examples of such “ferrocene–saliminato”-type related compounds of the ubiquitous salicylaldiminato ligands and used them for the construction of

first zirconium(IV) complexes of this kind. The remarkable structural chemistry and some preliminary catalytic experiments of a first representative example are reported in this brief account.

Different routes to optically active 2-hydroxyferrocene-carbaldehyde (**1**) have been described by Kagan^[7] and Ito et al.^[8] Due to the generally high sensitivity of hydroxyferrocenes and especially of **1** we developed a synthesis to our target ligand (**6**) that avoided these very sensitive compounds as intermediates as much as possible. Our synthesis (see Scheme 1) utilized previous work carried out by Kagan et al.^[7,11] and started with the precursor **2**, featuring the same acetal as a chiral auxiliary.



Scheme 1. i) *t*BuLi, -78°C , then I_2 followed by $\text{Na}_2\text{S}_2\text{O}_3$; ii) AcOH, Cu_2O , CH_3CN ; iii) NaOCH_3 , DMF, then *t*BuPh₂SiCl; iv) *p*-TsOH, $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$; v) 2,6-diisopropylaniline, *p*-TsOH, 80°C , toluene; vi) $[\text{Bu}_4\text{N}]\text{F}$, THF, single crystals from pentane at -30°C ; vii) LDA, toluene.

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(*S,S*)-**2** was subjected to a directed lithiation. Treatment with *tert*-butyllithium followed by quenching of the resulting substituted ferrocenyllithium product with iodine stereoselectively gave the protected 2-iodoferrocene carbaldehyde

derivative (S,S,S_p)-**3** with 93% *de*. The oxygen functionality was then introduced by subsequent treatment with copper(I) oxide/acetic acid^[12] to yield the corresponding acetoxyferrocene carbaldehyde derivative (S,S,S_p)-**4**. Saponification generated the free ferrocene alcoholate in situ, which was immediately trapped by *t*BuPh₂SiCl. The O-protected hydroxyferrocene carbaldehyde derivative (S_p)-**5** was obtained by subsequent acid-catalyzed liberation of the free aldehyde from the cyclic acetal. It was then converted to the corresponding aldimine by treatment with 2,6-diisopropylaniline. The silyl protective group was subsequently removed by treatment with tetra-*n*-butylammonium fluoride to yield the free “ferrocene–salimine” (S_p)-**6**^[13] as a dark red crystalline material in a total yield of 62% over six steps starting from (S,S)-**2**. The enantiomeric purity of the material was determined at the stage of the O-silyl protected hydroxyferrocene carbaldehyde intermediate (S_p)-**5** by HPLC (relative to the independently synthesized racemic reference material) as >99.5% *ee* after two-fold recrystallization from pentane.

Compound (S_p)-**6** was characterized by C,H,N elemental analysis, spectroscopic and X-ray crystal structure analysis. The compound features a ¹H NMR Cp singlet (5H) at δ 4.24 (in CDCl₃) and an ABC pattern of signals of the protons of the 1,2-disubstituted ferrocene Cp ring [δ 4.54, 4.14, 4.03]. The OH proton NMR signal was observed at δ 9.02, the aldimine CH=N signal at δ 8.30 (corresponding ¹³C NMR resonance at δ 168.1). The attached 2,6-diisopropylphenyl substituent features a pair of diastereotopic -CHMe₂ methyl group signals [δ 1.22, 1.18 each 6H, 3.07 (CH-septet, 2H)].

The structure and absolute configuration of (S_p)-**6** were confirmed by the X-ray crystal structure analysis (see Figure 1). The crystal features independent molecules of (S_p)-**6**. As expected, the ferrocene core is made up of a η^5 -C₅H₅ ring bonded to iron [with Fe–C21 to C25 distances being in a uniform range of 2.030(2) to 2.048(2) Å] and the *ortho*-disubstituted hydroxy-C₅H₃-imino ligand. Again, the Fe to C(Cp) bonds on this side of the ferrocene core are in a very narrow range (2.031(2) to 2.079(2) Å). The “upper” Cp ring bears the OH group (O1–C2 1.348(2) Å) and the carbaldimino substituent (C1–C6 1.444(3), C6–N1 1.275(3) Å). The imino group features the usual *E* configuration (dihedral angle C1–C6–N1–C7 –178.0(2)°). The imino nitrogen is oriented toward the adjacent OH group (θ C2–C1–C6–N1 –2.1(3)°) with which it seems to form a weak hydrogen bond. The plane of the bulky 2,6-diisopropylphenyl substituent is oriented close to perpendicular to the mean hydroxy-Cp-carbaldimino plane [angle between the mean O1–C2–C1–C6–N1 vs. C7 to C12 planes: 103.8°].

Treatment of the neutral “ferrocene–salimine” system [(S_p)-**6**] with 0.5 molar equiv of zirconium tetrachloride in dichloromethane (RT, overnight) gave a deep blue solution from which the 2:1 complex (S_p,S_p)-**8** was isolated as a deep blue solid material in >90% yield. Complex **8** shows a C₂-symmetric structure in solution, as indicated by the observed single set of resonances for the pairs of unsubstituted Cp rings [δ 4.58, 10H] and disubstituted C₃H₅ units [δ 5.67,

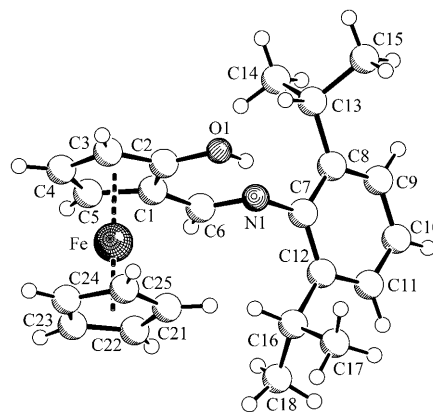


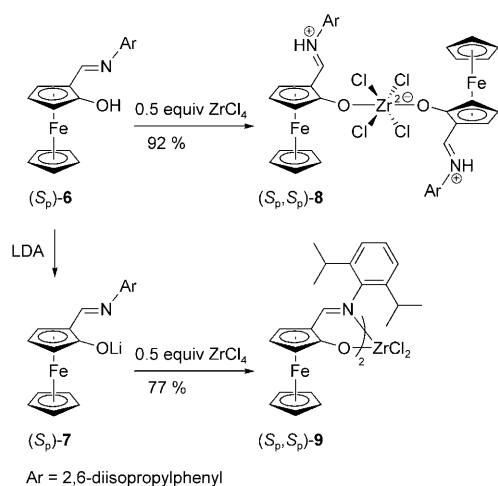
Figure 1. Projection of the molecular structure of the parent (S_p)-**6** “ferrocene–salimine” ligand system.

4.77, 4.33, each 2H]. Upon lowering the temperature to 218 K, the rotation of the 2,6-diisopropylphenyl substituent around the N–C bond is hindered, so that we monitor two CHMe₂ ¹H NMR septets and a total of four methyl ¹H NMR doublets of the two corresponding pairs of isopropyl methyl groups. Yet, the overall C₂ symmetry is retained, so that we assume formation of a pseudo-octahedral structure with a *trans*-arrangement of the NH tautomers of a pair of “ferrocene–salimine” ligands, which was previously observed for a related bis(salicylaldimine)TiCl₄ complex.^[4] The NH resonance is observed at δ 12.1 ppm and is strongly coupled to the carbaldimine hydrogen (³J_{HH} = 15.8 Hz).

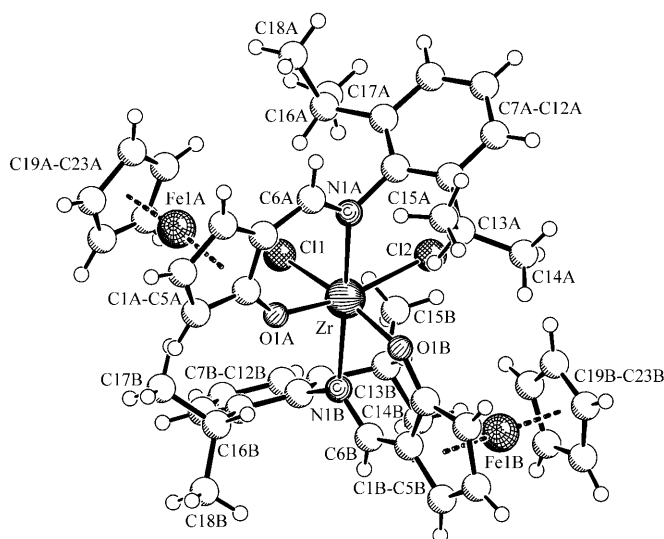
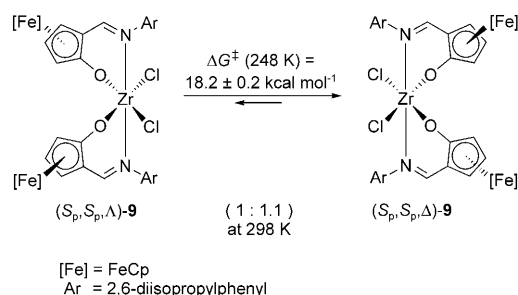
The free hydroxyferrocene (S_p)-**6** was deprotonated by treatment with LDA to yield the corresponding lithium salt (S_p)-**7** (Scheme 2). The reaction of this lithiated reagent with 0.5 molar equiv of ZrCl₄ (RT, toluene, overnight) proceeded with precipitation of lithium chloride to yield the pseudo-octahedral (bis-chelate-ligand)ZrCl₂ complex (S_p,S_p)-**9**. Treatment of the zwitterionic species **8** with two equivalents of LDA also led to a clean formation of chelate complex **9** with liberation of diisopropylamine in solution, although we did not isolate complex **9** in pure form via this route.

Pink-coloured single crystals of complex **9** were obtained by slow (one week) recrystallization from toluene at –30°C. The structure is characterized by a *cis*-ZrCl₂ unit (Zr–Cl1 2.447(2), Zr–Cl2 2.454(2) Å, angle Cl1–Zr–Cl2: 88.80(5)°). The imino nitrogens are oriented *trans* to each other in the pseudo-octahedral geometry (Zr–N1A 2.384(3), Zr–N1B 2.381(3) Å, angle N1A–Zr–N1B 174.33(12)°) and their remaining chelate oxygen atoms are consequently bonded *cis* to each other at the central zirconium atom (Zr–O1A 1.994(3), Zr–O1B 1.992(3) Å, angle O1A–Zr–O1B 93.14(14)°). The resulting six-membered chelate rings are planar (deviation of Zr from for example, the O1A–C1A–C2A–C6A–N1A plane: –0.044 Å).

The combination of a pair of chiral (S_p)-configured chelate ligands at the ZrCl₂ unit in the observed *cis*-O,*trans*-N-fashion can give rise to two optically active diastereoisomers. In this case we have found only the (S_p,S_p,Λ)-**9** isomer in the crystal (see Figure 2 and Scheme 3).



Scheme 2.

Figure 2. A view of the molecular structure of the bis(“ferrocene–saliminato”)ZrCl₂ complex (*S_p,S_p,Δ*)-**9** in the crystal.

Scheme 3.

We dissolved this crystalline material at low temperature (< 233 K) in CD₂Cl₂ and monitored the NMR spectra of the pure (*S_p,S_p,Δ*)-**9** isomer in solution. The system is C₂-symmetric and gives rise to a single set of NMR signals for its pair of symmetry-equivalent chelate ligands [e.g., ¹H: δ 8.29

(-CH=N-Ar), 4.43 (Cp), 4.48/4.34/4.30 (η⁵-C₅H₃)]. When the solution was warmed to temperatures > 243 K, rapid rearrangement and equilibration with a second C₂-symmetric isomer was observed. We tentatively assigned the structure to the corresponding *trans*-N,*cis*-O-(*S_p,S_p,Δ*)-**9** diastereoisomer. It is characterized again by a single set of NMR signals of the pair of symmetry-equivalent “ferrocene–salimine” chelate ligands, but distinctly different from the other isomer [for example, ¹H: δ 8.35 (-CH=N-Ar), 4.52 (Cp), 4.74/4.41/4.40 (η⁵-C₅H₃)]. The activation energy of the (*S_p,S_p,Δ*)-**9** to (*S_p,S_p,Λ*)-**9** rearrangement was determined as Δ*G*[‡] (248 K) = 18.2 ± 0.2 kcal mol⁻¹.^[14] The equilibrium ratio is 1:1.1 in CD₂Cl₂ at 298 K.

We also tested compounds **8** and **9** as precursors for the generation of homogeneous Ziegler–Natta olefin polymerization catalysts. For this purpose the mixture of the (*S_p,S_p,Λ*)- and (*S_p,S_p,Δ*)-**9** isomers was activated by treatment with a large excess of methylalumoxane (MAO) in toluene. The ethylene polymerization activity of the generated catalysts was rather low at room temperature (see Table 1), but it increased markedly with polymerization temperature. At the highest temperature employed here (125 °C) the catalyst seems to be stable and moderately active.

Table 1. Selected ethylene polymerization results using the **8**/MAO and **9**/MAO catalyst systems.^[a]

Compound	<i>T</i> [°C]	PE [g]	Activity ^[b]	M.p. [°C]
8	20	0.2	9	134
8	80	0.7	37	138
8	100	1.6	81	136
8	125	2.2	109	131
9	20	0.2	11	138
9	80	0.8	39	141
9	100	1.5	76	137
9	125	2.1	106	134

[a] 5 μmol of [Zr], Al:Zr=2000, 5 min catalyst preactivation, 2 bar ethene, 2 h reaction time. [b] g PE·mmol [Zr]⁻¹·bar (ethene)⁻¹·h⁻¹.

We note that the catalyst systems that we alternatively generated from the zwitterionic precursor (*S_p,S_p*)-**8** featured an almost identical ethylene polymerization behaviour which indicates that in both cases similar active catalysts were generated from these different precursors.

We conclude that “ferrocene–salimines”, the planarly chiral three-dimensional relatives of the ubiquitous salicylaldehyde-type ligands can be readily obtained in high yield and highly enantiomerically enriched [that is, (*S_p*)-**6** or (*S_p*)-**7**] by means of the short synthesis described in this article. They can be used for the preparation of octahedrally chiral bis(“ferrocene–salimine”)ZrCl₂ complexes that undergo a well defined Λ/Δ isomerization reaction at temperatures a little below RT, and these systems give thermally robust ethylene polymerization catalysts upon treatment with MAO. These first results in this series may open promising new catalytic applications in the future using variations of this not frequently employed ligand family^[15] derived from an organometallic backbone.

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Keywords: ferrocene • planar chirality • polymerization • Schiff-base ligands • zirconium

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- [13] Analytical data for (*S_p*)-**6**: M.p. 161 °C; [α]_D²⁰ = –1657 (c = 0.208 in dichloromethane); ¹H NMR (499.8 MHz, CDCl₃, 298 K): δ = 9.02 (br, OH), 8.30 (d, ⁴J(H,H) = 0.6 Hz, 1H, CHN), 7.16–7.11 (m, 3H, *m*-Ph, *p*-Ph), 4.54 (ddd, ³J(H,H) = 2.7, ⁴J(H,H) = 1.4, ⁴J(H,H) = 0.6 Hz, 1H, H-3), 4.24 (s, 5H, Cp), 4.14 (dd, ³J(H,H) = 2.7, ⁴J(H,H) = 1.4 Hz, 1H, H-5), 4.03 (t, ³J(H,H) = ³J(H,H) = 2.7 Hz, 1H, H-4), 3.07 (sept, ³J(H,H) = 7.0 Hz, 2H, CH), 1.22 (d, ³J(H,H) = 7.0 Hz, 6H, CH₃), 1.18 ppm (d, ³J(H,H) = 7.0 Hz, 6H, CH₃); ¹³C{¹H} NMR (125.7 MHz, [D₂]chloroform, 298 K): δ = 168.1 (CHN), 147.4 (*ipso*-Ph), 138.5 (*o*-Ph), 134.8 (C-1), 124.8 (*p*-Ph), 123.1 (*m*-Ph), 69.6 (Cp), 63.8 (C-2), 63.1 (C-4), 62.6 (C-5), 58.2 (C-3), 27.9 (CH), 23.7 (CH₃), 23.4 ppm (CH₃); IR (KBr): $\tilde{\nu}$ = 1615 cm⁻¹ (C=N); elemental analysis calcd (%) for C₂₃H₂₇FeNO: C 70.96, H 6.99, N 3.60; found: C 70.82, H 6.95, N 3.64.
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