CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Mastering the Third Dimension of Salicylaldimine-type Ligand Systems: Development of a Convenient Route to Bis("ferrocene-saliminato")zirconium Chemistry

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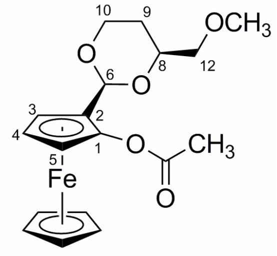
General remarks:

Materials: All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Ferrocenes (*S*,*S*)-**2** and (*S*,*S*,*S*$_p$)-**3** were prepared according to literature procedures.[1]
Techniques: The following instruments were used for physical characterization of the compounds: melting points: TA-instruments DSC Q-20; elemental analyses: Foss–Heraeus CHNO-Rapid; HPLC: Chiralcel OD-H column, hexanes : isopropanol = 95 : 5 at 1 ml/min; IR: Varian 1300 FT-IR; NMR: Varian UNITY plus NMR spectrometer (^{1}H: 599.9 MHz; ^{13}C: 150.8 MHz); Varian INOVA 500 (^{1}H: 499.8 MHz, ^{13}C: 125.7 MHz) (numbering schemes used for the NMR listings are unsystematic); Polarimetric measurements: Perkin-Elmer Polarimeter 341 (unit used for all values of optical rotations is [deg · ml · g^{-1} · dm^{-1}], the respective concentration is given in a unit of [10 mg · ml^{-1}])
X-ray crystal structure determinations: Data sets were collected with Nonius KappaCCD diffractometer, equipped wit a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics SCHAKAL (E. Keller, 1997).
CCDC 690703 and 690704 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Syntheses of new compounds:

*1) (2S,4S,S$_p$)-(–)-1-Acetoxy-2-(4-methoxymethyl-1,3-dioxan-2-yl)ferrocene ((S,S,S$_p$)-**4**)*



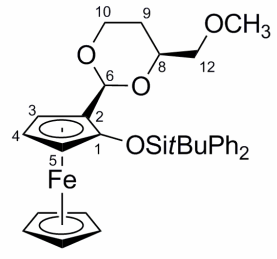
(*S*,*S*,*S*$_p$)-**4**

The iodoferrocene **3** (17.2 g, 38.9 mmol, 1 eq) and copper(I)oxide (5.57 g, 38.9 mmol, 1 eq) were suspended in 500 ml of acetonitrile. After addition of acetic acid (11.2 ml, 195 mmol, 5 eq), the mixture was heated to 80 °C for three hours under an argon atmosphere. The solvent was removed and the crude product was purified by column chromatography (cyclohexane : ethyl acetate = 2 : 1) to yield the product (*S*,*S*,*S*$_p$)-**4** as an orange oil (13.7 g, 36.6 mmol, 94.1 %).

$[\alpha]_D^{20}$ = -111.2 (c = 1.02 in dichloromethane); **^{1}H NMR** (499.8 MHz, [D$_6$]benzene, 298 K): δ = 5.55 (s, 1 H; H-6), 4.47 (dd, ^{3}J(H,H) = 2.7 Hz, ^{4}J(H,H) = 1.6 Hz, 1 H, H-3), 4.35 (dd, ^{3}J(H,H) = 2.7 Hz, ^{4}J(H,H) = 1.6 Hz, 1 H, H-5), 4.27 (s, 5 H, Cp), 3.92 (ddd, ^{2}J(H,H) = 11.4 Hz, ^{3}J(H,H) = 5.1 Hz, ^{3}J(H,H) = 1.4 Hz, 1 H, H-10$_{eq}$), 3.75 (dddd, ^{3}J(H,H) = 11.4 Hz, ^{3}J(H,H) = 5.7 Hz, ^{3}J(H,H) = 4.7 Hz, ^{3}J(H,H) = 2.5 Hz, 1 H, H-8), 3.70 (t, ^{3}J(H,H) = 2.7 Hz, 1 H, H-4), 3.51 (ddd, ^{3}J(H,H) = 12.5 Hz, ^{2}J(H,H) = 11.4 Hz, ^{3}J(H,H) = 2.6 Hz, 1 H, H-10$_{ax}$), 3.29 (dd, ^{2}J(H,H) = 10.2 Hz, ^{3}J(H,H) = 5.7 Hz, 1 H, H-12), 3.14 (dd, ^{2}J(H,H) = 10.2 Hz, ^{3}J(H,H) = 4.7

Hz, 1 H, H-12´), 3.11 (s, 3 H, OMe), 1.82 (s, 3 H, CO<u>Me</u>), 1.62 (dddd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 12.5 Hz, ^3J(H,H) = 11.4 Hz, ^3J(H,H) = 5.1 Hz, 1 H, H-9_{ax}), 1.01 (dtd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 2.5 Hz, ^3J(H,H) = 1.4 Hz, 1 H, H-9_{eq}); **^{13}C NMR** (125.7 MHz, [D_6]benzene, 298 K): δ = 168.4 (<u>C</u>OMe), 114.3 (C-1), 99.0 (C-6), 78.3 (C-2), 76.3 (C-8), 75.8 (C-12), 70.6 (Cp), 66.6 (C-10), 62.8 (C-5), 62.4 (C-4), 62.0 (C-3), 59.1 (OMe), 28.5 (C-9), 20.7 (CO<u>Me</u>); **IR** (ATR): ν bar= 1757 cm^{-1} (C=O); **elemental analysis** calcd (%) for $C_{18}H_{22}FeO_5$: C 57.77, H 5.93; found: C 57.51, H 5.96.

*2) (2S,4S,S$_p$)-(–)-1-(tert-Butyldiphenylsiloxy)-2-(4-methoxy-methyl-1,3-dioxan- 2-yl)-ferrocene ((S,S,S$_p$)-**5a**)*

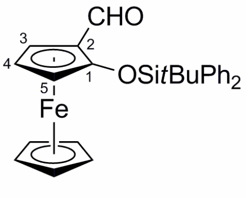


(S,S,S_p)-**5a**

The acetate **4** (7.50 g, 20.0 mmol, 1 eq) was dissolved in 60 ml of *N*,*N*-dimethylformamide and sodium methoxide (1.19 g, 22.0 mmol, 1.1 eq) was added in one portion, yielding a dark red solution. After 90 minutes, *tert*-butylchlorodiphenylsilane (5.73 ml, 22.0 mmol, 1.1 eq) was added and the bright yellow mixture was stirred overnight. The solvent was removed and the residue was purified by column chromatography (cyclohexane : ethyl acetate = 6 : 1) to yield (S,S,S_p)-**5a** (10.8 g, 18.9 mmol, 94.6 %) as a yellow oil.

[α]$_D^{20}$ = -139.9 (c = 1.01 in dichloromethane); **^{1}H NMR** (599.6 MHz, [D_1]chloroform, 298 K): δ =7.90 (ps d, 2 H, *o*-Ph), 7.66 (ps d, 2 H, *o*-Ph´), 7.50-7.44 (m, 3 H, *m*-Ph, *p*-Ph), 7.37 (m, 1 H, *p*-Ph´), 7.30 (ps t, 2 H, *m*-Ph´), 5.78 (s, 1 H, H-6), 4.34 (dd, ^2J(H,H) = 11.4 Hz, ^3J(H,H) = 4.8 Hz, 1 H, H-10_{eq}), 4.10 (s, 5 H, Cp), 4.06-3.96 (m, 3 H, H-3, H-8, H-10_{ax}), 3.50 (t, ^3J(H,H) = 2.5 Hz, 1 H, H-4), 3.45 (m, 1 H, H-5), 3.43 (dd, ^2J(H,H) = 10.0 Hz, ^3J(H,H) = 5.0 Hz, 1 H, H-12), 3.35 (dd, ^2J(H,H) = 10.0 Hz, ^3J(H,H) = 5.6 Hz, 1 H, H-12´), 3.30 (s, 3 H, OMe), 1.85 (dtd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 12.5 Hz, ^3J(H,H) = 5.0 Hz, 1 H, H-9_{ax}), 1.56 (bd, ^2J(H,H) = 13.2 Hz, 1 H, H-9_{eq}), 1.06 (s, 9 H, C(CH_3)$_3$); **^{13}C NMR** (150.8 MHz, [D_6]benzene, 298 K): δ = 135.7, 135.6 (*o*-Ph, o-Ph´), 133.8 (*ipso*-Ph), 132.1 (*ipso*-Ph´), 130.0 (*p*-Ph), 129.7 (*p*-Ph´), 127.7 (*m*-Ph), 127.5 (*m*-Ph´), 120.3 (C-1), 99.5 (C-6), 76.0 (C-8), 75.4 (C-12), 74.7 (C-2), 69.7 (Cp), 67.2 (C-10), 60.3 (C-4), 60.0 (C-3), 59.8 (C-5), 59.3 (OMe), 28.5 (C-9), 26.5 (C($\underline{CH_3}$)$_3$), 19.4 (<u>C</u>(CH_3)$_3$); **IR** (ATR): ν bar = 1198 cm^{-1} (C-OSi); **elemental analysis** calcd (%) for $C_{32}H_{38}FeO_4Si$: C 67.36, H 6.71; found: C 67.18, H 6.84.

*3) (S$_p$)-(+)-1-(tert-Butyldiphenylsiloxy)-2-formylferrocene ((S$_p$)-**5**)*



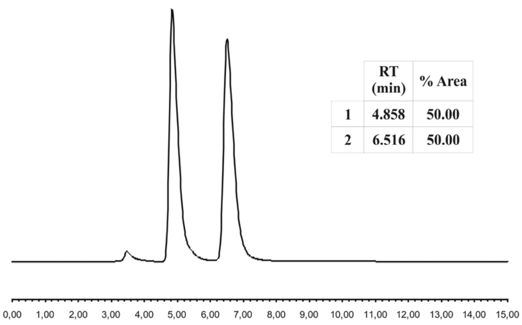
(S_p)-**5**

The acetal **5a** (16.7 g, 29.3 mmol, 1 eq) and *p*-toluene sulfonic acid (11.1 g, 58.5 mmol, 2 eq) were dissolved in a two-phase mixture of 300 ml of dichloromethane and 100 ml of water. The mixture was heated to reflux for three hours under vigorous stirring, the phases were separated and the organic phase was dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by filtration on silica (cyclohexane : ethyl acetate = 4 : 1). The resulting deep red oil was dissolved in 150 ml of pentane and the solution was stored at 4 °C overnight. Removal of the supernatant liquid gave a red solid, which was recrystallized twice from pentane at – 30 °C. This gave 12.2 g of the product (S_p)-**5** (26.0 mmol, 88.7 %, *ee* > 99.5 %).

M.p. 117°C; **[α]$_D^{20}$** = +465 (c = 0.53 in dichloromethane)); **^{1}H NMR** (599.7 MHz, [D$_6$]benzene, 298 K): δ = 10.8 (s, 1 H, CHO), 7.85 (m, 2 H, *o*-Ph), 7.62 (m, 2 H, *o*-Ph´), 7.24-7.19 (m, 3 H, *m*-Ph, *p*-Ph), 7.14-7.07 (m, 3 H, *m*-Ph´, *p*-Ph´), 4.48 (dd, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.5 Hz, 1 H, H-3), 3.93 (s, 5 H, Cp), 3.74 (dd, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.5 Hz, 1 H, H-5), 3.55 (t, ^3J(H,H) = 2.8 Hz, 1 H, H-4), 1.08 (s, 9 H, $C(\underline{CH_3})_3$); **^{13}C NMR** 125.7 MHz, [D$_6$]benzene, 298 K): δ = 190.9 (CHO), 136.0 (*o*-Ph), 135.8 (*o*-Ph´), 133.4 (*ipso*-Ph), 132.1 (*ipso*-Ph´), 130.6 (*m*-Ph), 130.4 (*m*-Ph´), 128.2 (*p*-Ph, *p*-Ph´), 125.0 (C-1), 70.6 (Cp), 69.7 (C-2), 65.5 (C-4), 63.4 (C-5), 61.5 (C-3), 26.7 ($C(\underline{CH_3})_3$), 19.6 ($\underline{C}(CH_3)_3$); **IR** (KBr): $\bar{\nu}$ bar = 1674 cm^{-1} (C=O); **elemental analysis** calcd (%) for $C_{27}H_{28}FeO_2Si$: C 69.23; H 6.02, found: C 69.24, H 6.01.

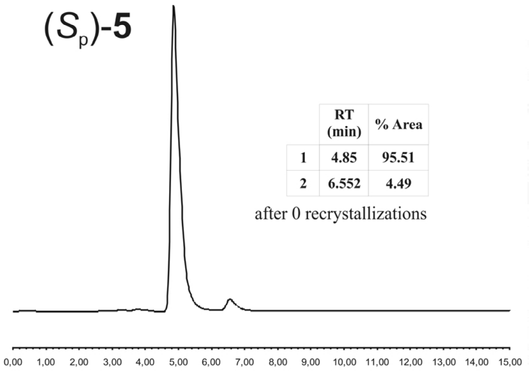
HPLC-analysis:

(*rac*)-**5**



	RT (min)	% Area
1	4.858	50.00
2	6.516	50.00

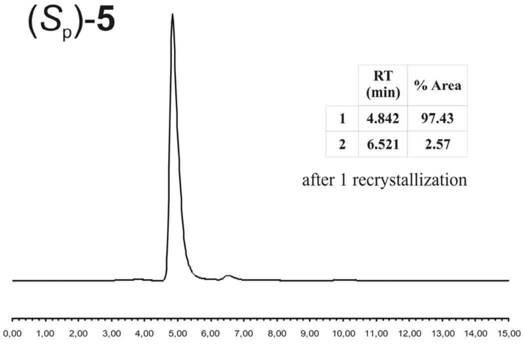
(S_p)-**5**



	RT (min)	% Area
1	4.85	95.51
2	6.552	4.49

after 0 recrystallizations

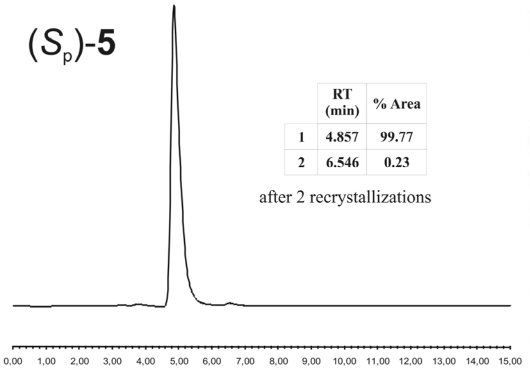
(S_p)-**5**



	RT (min)	% Area
1	4.842	97.43
2	6.521	2.57

after 1 recrystallization

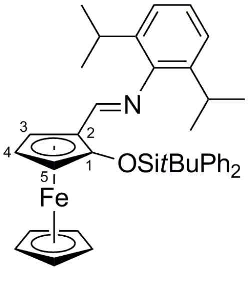
(S_p)-**5**



	RT (min)	% Area
1	4.857	99.77
2	6.546	0.23

after 2 recrystallizations

*4) (S_p)-(+)-N-2,6-Diisopropylphenyl-1-tert-butyldiphenylsiloxy-2-iminomethylferrocene ((**S_p)-6a**)*

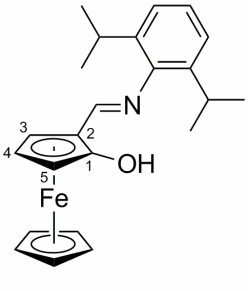


(S_p)-**6a**

The aldehyde **5** (5.00 g, 10.7 mmol, 1 eq), 2,6-diisopropylaniline (10.1 ml, 53.4 mmol, 5 eq) and *p*-toluene sulfonic acid (203 mg, 1.07 mmol, 0.1 eq) were dissolved in 40 ml of toluene and heated to 80°C overnight. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane : triethylamine = 9 : 1) to give the imine (S_p)-**6a** as an orange solid (6.27 g, 9.99 mmol, 93.3 %).

M.p. 116°C; **$[\alpha]_D^{20}$** = +505 (c = 1.03 in dichloromethane); **^{1}H NMR** (499.8 MHz, [D$_1$]chloroform, 298 K): δ = 8.51 (t, ^4J(H,H) = 0.6 Hz, ^5J(H,H) = 0.6 Hz, 1 H, CHN), 7.85 (m, 2 H, *o*-Ph$^{\text{Si}}$), 7.60 (m, 2 H, *o*-Ph$^{\prime\text{Si}}$), 7.50 (m, 1H, *p*-Ph$^{\text{Si}}$), 7.46 (m, 2 H, *m*-Ph$^{\text{Si}}$), 7.42 (m, 1 H, *p*-Ph$^{\prime\text{Si}}$), 7.34 (m, 2 H, *m*-Ph$^{\prime\text{Si}}$), 7.16 (m, 2 H, *m*-Ph), 7.10 (m, 1 H, *p*-Ph), 4.66 (ddd, ^3J(H,H) = 2.7 Hz, ^4J(H,H) = 1.5 Hz, ^4J(H,H) = 0.6 Hz, 1 H, H-3), 4.15 (s, 5 H, Cp), 3.91 (td, ^3J(H,H) = 2.7 Hz, ^5J(H,H) = 0.6 Hz, 1 H, H-4), 3.72 (dd, ^3J(H,H) = 2.7 Hz, ^4J(H,H) = 1.5 Hz, 1 H, H-5), 3.16 (sept, ^3J(H,H) = 7.0 Hz, 2 H, CH), 1.27 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH$_3$), 1.20 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH$_3$´), 1.02 (s, 9 H, C(CH$_3$)$_3$); **^{13}C NMR** (125.7 MHz, [D$_1$]chloroform, 298 K): δ = 160.8 (CHN), 149.8 (*ipso*-Ph), 138.0 (*o*-Ph), 135.7 (*o*-Ph$^{\text{Si}}$), 135.5 (*o*-Ph$^{\prime\text{Si}}$), 133.3 (*ipso*-Ph$^{\text{Si}}$), 132.0 (*ipso*-Ph$^{\prime\text{Si}}$), 130.3 (*p*-Ph$^{\text{Si}}$), 130.1 (*p*-Ph$^{\prime\text{Si}}$), 127.9 (*m*-Ph$^{\text{Si}}$), 127.8 (*m*-Ph$^{\prime\text{Si}}$), 123.7 (*p*-Ph), 123.3 (C-1), 122.9 (*m*-Ph), 70.4 (C-2), 69.9 (Cp), 63.6 (C-4), 61.5 (C-5), 60.0 (C-3), 27.7 (CH), 26.7 (C($\underline{\text{CH}_3}$)$_3$), 23.8 (CH$_3$´), 23.6 (CH$_3$), 19.4 ($\underline{\text{C}}$(CH$_3$)$_3$); **IR** (KBr): $\bar{\nu}$ = 1629 cm^{-1} (C=N); **elemental analysis** calcd (%) for C$_{39}$H$_{45}$FeNOSi: C 74.62, H 7.23, 2.23; found: C 75.09, H 7.34, N 2.29.

*5) (S$_p$)-(–)-N-2,6-Diisopropylphenyl-2-iminomethylferrocen-1-ol ((S$_p$)-**6**)*



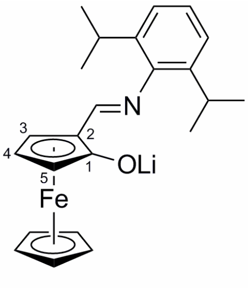
(S_p)-**6**

The imine **6a** (5.19 g, 8.27 mmol, 1 eq) and tetra-*n*-butyl ammonium fluoride (5.22 g, 16.5 mmol, 2 eq) were dissolved in 200 ml of tetrahydrofurane and the solution was stirred for two hours. The solvent was removed and the crude product was purified by column chromatography under argon (cyclohexane : ethyl acetate : triethylamine = 8 : 1 : 1, solvents were degassed before use). Two fractions were collected and the solvent was removed. The oily residues were dissolved in 100 ml of pentane each and the solutions were kept at –30°C for two days. The deep red crystals of (S_p)-**6** were isolated by removal of the mother liquors, to give a combined yield of 3.03 g (7.78 mmol, 94.1 %).

The crystals were suitable for X-ray analysis. X-ray crystal structure analysis for **6a**: formula C$_{23}$H$_{27}$FeNO, M = 389.31, red crystal 0.50 x 0.40 x 0.10 mm, a = 6.046(1), b = 16.281(1), c = 20.324(1) Å, V = 2000.6(4) Å^3, ρ_calc = 1.293 g cm^{-3}, μ= 0.764 mm^{-1}, empirical absorption correction (0.701 ≤ T ≤ 0.928), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ= 0.71073 Å, T = 198(2) K, ω and φ scans, 13921 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 4547 independent (R_int = 0.031) and 4110 observed reflections [$I \geq 2\ \sigma(I)$], 240 refined parameters, R = 0.032, wR^2 = 0.076, max. (min.) residual electron density 0.16 (-0.25) e Å^{-3}, Flack parameter 0.00(2), hydrogen atoms calculated and refined as riding atoms.

M.p. 161°C; **$[\alpha]_D^{20}$** = -1657 (c = 0.208 in dichloromethane); **^{1}H NMR** (499.8 MHz, [D$_1$]chloroform, 298 K): δ = 9.02 (bs, OH), 8.30 (d, ^4J(H,H) = 0.6 Hz, 1 H, CHN), 7.16-7.11 (m, 3 H, *m*-Ph, *p*-Ph), 4.54 (ddd, ^3J(H,H) = 2.7 Hz, ^4J(H,H) = 1.4 Hz, ^4J(H,H) = 0.6 Hz, 1 H, H-3), 4.24 (s, 5 H, Cp), 4.14 (dd, ^3J(H,H) = 2.7 Hz, ^4J(H,H) = 1.4 Hz, 1 H, H-5), 4.03 (t, ^3J(H,H) = 2.7 Hz, 1 H, H-4), 3.07 (sept, ^3J(H,H) = 7.0 Hz, 2 H, CH), 1.22 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH$_3$), 1.18 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH$_3$´); **^{13}C NMR** (125.7 MHz, [D$_1$]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 (CH$_3$´), 23.4 (CH$_3$); **IR** (KBr): $\bar{\nu}$ = 1615 cm^{-1} (C=N); **elemental Analysis** calcd (%) for C$_{23}$H$_{27}$FeNO: C 70.96, H 6.99, N, 3.60; found: C 70.82, H, 6.95, N 3.64.

*6) (S_p)-(–)-N-2,6-Diisopropylphenyl-2-iminomethylferrocen-1-olato lithium ((S_p)-**7**)*

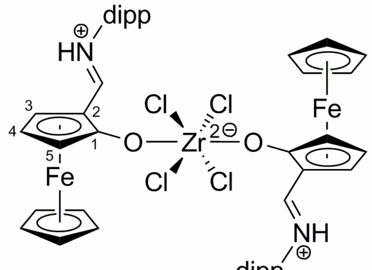


(S_p)-**7**

The alcohol **6** (1.70 g, 4.37 mmol, 1 eq) and lithium diisopropyl amide (468 mg, 4.37 mmol, 1 eq) were suspended in 20 ml of toluene. The mixture was stirred for three hours and the solvent was removed, giving an oily residue. Addition of 20 ml of pentane and removal of the solvent gave the product (S_p)-**7** as a deep red powder (1.62 g, 4.10 mmol, 93.8 %).

M.p. 274°C; $\mathbf{[\alpha]_D^{20}}$ = -533 (c = 0.100 in dichloromethane)); ^{1}**H NMR** (599.6 MHz, [D$_2$]dichloromethane, 228 K): δ = 7.97 (s, 1 H, CHN), 7.26 (dd, ^3J(H,H) = 5.4 Hz, ^4J(H,H) = 3.8 Hz, 1 H, *p*-Ph), 7.16 (d, ^3J(H,H) = 5.4 Hz, 1 H, *m*-Ph^A), 7.16 (d, ^3J(H,H) = 3.8 Hz, 1 H, *m*-Ph^B), 3.94 (dd, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.5 Hz, 1 H, H-3), 3.75 (s, 5 H, Cp), 3.67 (t, ^3J(H,H) = 2.8 Hz, 1 H, H-4), 3.45 (bs, 1 H, H-5), 3.36 (sept, ^3J(H,H) = 6.9 Hz, 1 H, CH^B), 2.91 (sept, ^3J(H,H) = 6.9 Hz, 1 H, CH^A), 1.40 (d, ^3J(H,H) = 6.9 Hz, 3 H, CH$_3^B$), 1.34 (d, ^3J(H,H) = 6.9 Hz, 3 H, CH$_3^{B'}$), 1.06 (d, ^3J(H,H) = 6.9 Hz, 3 H, CH$_3^A$), 1.03 (d, ^3J(H,H) = 6.9 Hz, 3 H, CH$_3^{A'}$); ^{13}**C NMR** (150.8 MHz, [D$_2$]dichloromethane, 228 K): δ = 170.5 (CHN), 148.7 (*ipso*-Ph), 139.5 (*o*-Ph^B), 139.0 (*o*-Ph^A), 135.6 (C-1), 124.8 (*m*-Ph^A), 123.5 (*m*-Ph^B), 122.9 (*p*-Ph), 68.2 (Cp), 63.5, 63.3, 63.2 (C-2,3,4), 58.9 (C-5), 27.6 (CH^A), 27.2 (CH^B), 25.5 (CH$_3^{A'}$), 24.2 (CH$_3^B$), 23.1 (CH$_3^{B'}$), 22.1 (CH$_3^A$); **IR** (KBr): ν bar = 1612 cm^{-1} (C=N); **elemental analysis** calcd (%) for $C_{23}H_{26}FeLiNO$: C 69.89, H 6.63, N 3.54; found: C 69.89, H 6.90, N 3.33.

*7) (+)-Tetrachlorobis[(κO-(S_p)-N-2,6-diisopropylphenylferrocen-2-iminium-methylferrocen-1-olato]zirconium ((S_p,S_p)-**8**)*

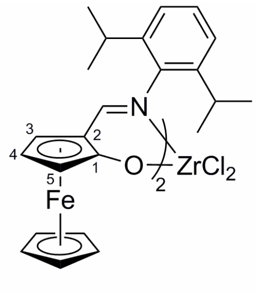


(S_p,S_p)-**8**

The alcohol **6** (156 mg, 0.401 mmol, 2 eq) and zirconium tetrachloride (46.7 mg, 0.201 mmol, 1 eq) were dissolved in 5 ml of dichloromethane, instantly giving a deep blue solution. The mixture was stirred overnight and the solvent was removed, giving 187 mg (0.185 mmol, 92.0 %) of the complex (S_p,S_p)-**8** as a deep blue solid.

M.p. >300°C; $\mathbf{[\alpha]^{20}}$ = +665 (436 nm, c = 0.021 in dichloromethane); ^{1}**H NMR** (599.6 MHz, [D$_2$]dichloromethane, 218 K): δ = 12.1 (d, ^3J = 15.8 Hz, 2 H, NH), 8.30 (d, ^3J = 15.8 Hz, 2 H, CHN), 7.44 (t, ^3J = 7.8 Hz, 2 H, *p*-Ph), 7.28 (d, ^3J = 7.8 Hz, 2 H, *m*-Ph^A), 7.22 (d, ^3J = 7.8 Hz, 2 H, *m*-Ph^B), 5.67 (bd, ^3J = 2.8 Hz, 2 H, H-5), 4.77 (t, ^3J = 2.8 Hz, 2 H, H-4), 4.58 (s, 10 H, Cp), 4.33 (bs, 2 H, H-3), 3.36 (sept, ^3J = 6.8 Hz, 2 H, CH^A), 3.00 (sept, ^3J = 6.8 Hz, 2 H, CH^B), 1.34 (d, ^3J = 6.8 Hz, 6 H, CH$_3^A$), 1.19 (d, ^3J = 6.8 Hz, 6 H, CH$_3^{A'}$), 1.10 (d, ^3J = 6.8 Hz, 6 H, CH$_3^B$), 1.07 (d, ^3J = 6.8 Hz, 6 H, CH$_3^{B'}$); ^{13}**C NMR** (150.8 MHz, [D$_2$]dichloromethane, 218 K): δ = 173.4 (CHN), 144.3 (*o*-Ph^A), 143.9 (*o*-Ph^B), 133.5 (*ipso*-Ph), 130.3 (C-1), 130.0 (*p*-Ph), 124.1 (*m*-Ph^A), 124.0 (*m*-Ph^B), 72.7 (C-4), 71.5 (Cp), 67.7 (C-5), 65.7 (C-3), 58.7 (C-2), 28.1 (CH^B), 28.0 (CH^A), 23.9 (CH$_3^A$), 23.4 (CH$_3^{B'}$), 23.3 (CH$_3^{A'}$), 22.9 (CH$_3^B$); **IR** (KBr): ν bar = 1621 cm^{-1} (C=N); **elemental analysis** calcd (%) for $C_{46}H_{54}Cl_4Fe_2N_2O_2Zr$: C 54.61, H 5.38, N 2.77; found: C 54.36, H 5.31, N 2.87.

*8) (+)-Dichlorobis[(κN,κO-(S_p)-N-2,6-diisopropylphenyl-2-iminomethyl-ferrocen-1-olato]zirconium ((S_p,S_p)-**9**)*



(S_p,S_p)-**9**

The lithium salt **7** (160 mg, 0.405 mmol, 2 eq) and zirconium tetrachloride (47.2 mg, 0.203 mmol, 1 eq) were suspended in 8 ml of toluene and the mixture was stirred overnight. After filtration through a glass frit, the resulting solution was stored at –30°C for one week. The resulting pink crystals were isolated by removal of the mother liquor and dried in vacuo to give 175 mg (0.156 mmol, 76.8 %) of the complex (S_p,S_p)-**9**.

The crystals were suitable for X-ray analysis. Alternatively, X-ray quality single crystals could be obtained by diffusion of pentane into a solution of **9** in dichloromethane at –30°C.

X-ray crystal structure analysis for **9**: formula $C_{46}H_{52}Cl_2Fe_2N_{22}O_2Zr$ * 0.25 CH_2Cl_2 * 0.75 C_5H_{12}, M = 1014.06, black crystal 0.40 x 0.20 x 0.15 mm, a = 20.4726(2), b = 23.3256(3), c = 10.5489(1) Å, V = 5037.48(9) Å^3, ρ_{calc} = 1.337 g cm^{-3}, μ= 0.942 mm^{-1}, empirical absorption correction ($0.704 \leq T \leq 0.872$), Z = 4, orthorhombic, space group $P2_12_12$ (No. 18), λ= 0.71073 Å, T = 223 K, ω and φ scans, 34232 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 11676 independent (R_{int} = 0.058) and 8397 observed reflections [$I \geq 2\ \sigma(I)$], 573 refined parameters, R = 0.052, wR^2 = 0.151, max. (min.) residual electron density 0.87 (-0.49) e Å^{-3}, Flack parameter –0.02(2), hydrogen atoms calculated and refined as riding atoms, the mixture of solvents was refined with PART -1 using geometrical restraints (SADI for CH_2Cl_2 and DFIX for C_5H_{12}).

M.p. 113°C; **[*α*]^{20}** = +138 (436 nm, c = 0.020 in dichloromethane); **^{1}H NMR** (599.6 MHz, [D_2]dichloromethane, 298 K)[a]: Λ-isomer: δ = 8.29 (d, ^4J(H,H) = 0.7 Hz, 1 H, CHN), 7.27 (1 H), 7.22 (2 H) (each m, *m*-Ph^A, *m*-Ph^B, *p*-Ph), 4.48 (m, 1 H, H-3), 4.43 (s, 5 H, Cp), 4.34 (t, ^3J(H,H) = 2.8 Hz, 1 H, H-4), 4.30 (dd, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.3 Hz, 1 H, H-5), 3.53 (sept, ^3J(H,H) = 6.8 Hz, 1 H, CH^A), 3.40 (sept, ^3J(H,H) = 6.8 Hz, 1 H, CH^B), 1.60 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3^B), 1.34 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3^A), 1.27 (d, ^3J(H,H) = 6.8 Hz, 3 H, $CH_3^{A'}$), 1.11 (d, ^3J(H,H) = 6.8 Hz, 3 H, $CH_3^{B'}$); Δ-isomer: δ = 8.35 (d, ^4J = 0.7 Hz, 1 H, CHN), 7.22 (m, 1 H, *p*-Ph), 7.18 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.6 Hz, 1 H, *m*-Ph^A), 7.14 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.6 Hz, 1 H, *m*-Ph^B), 4.74 (ddd, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.4 Hz, ^4J(H,H) = 0.7 Hz, 1 H, H-3), 4.52 (s, 5 H, Cp), 4.41 (t, ^3J(H,H) = 2.8 Hz, 1 H, H-4), 4.40 (dd, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.4 Hz, 1 H, H-5), 3.52 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CH^A), 3.16 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CH^B), 1.46 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3^A), 1.42 (d, ^3J(H,H) = 6.7 Hz, 3 H, $CH_3^{A'}$), 1.12 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3^B), 1.02 (d, ^3J(H,H) = 6.7 Hz, 3 H, $CH_3^{B'}$); **^{13}C NMR** (125.7 MHz, [D_6]benzene, 298 K): Λ-isomer: δ = 176.5 (CHN), 151.7 (*ipso*-Ph), 142.1 (*o*-Ph^A), 141.9 (*o*-Ph^B), 127.1 (*p*-Ph), 126.5 (C-1), 124.2 (*m*-Ph^A), 123.8 (*m*-Ph^B), 70.4 (Cp), 67.6 (C-4), 65.7 (C-2), 65.2 (C-5), 60.8 (C-3), 28.0 (2 C, CH^A, CH^B), 25.8 ($CH_3^{A'}$), 25.6 ($CH_3^{B'}$), 24.0 (CH_3^B), 23.6 (CH_3^A); Δ-isomer: δ = 175.6 (CHN), 150.8 (*ipso*-Ph), 142.3 (*o*-Ph^B), 141.8 (*o*-Ph^A), 127.1 (*p*-Ph), 126.4 (C-1), 124.6 (*m*-Ph^B), 123.5 (*m*-Ph^A), 70.6 (Cp), 68.3 (C-4), 66.4 (C-2), 66.0 (C-5), 61.1 (C-3), 28.3 (CH^A), 27.9 (CH^B), 26.2 ($CH_3^{A'}$), 25.5 ($CH_3^{B'}$), 24.4 (CH_3^A), 23.9 (CH_3^B); **IR (KBr):** ν bar = 1622 (s), 1565 (s) cm^{-1} (C=N); **elemental analysis** calcd (%) for $C_{46}H_{52}Cl_2Fe_2N_2O_2Zr \cdot 2 \times C_7H_8$[b]: C 64.17, H 6.10, N 2.49 found: C 63.32, H 6.03, N 2.65.

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[a]: Dissolution of the crystalline material of (S_p,S_p,Λ)-**9** at a temperature of < 233 K resulted in observance of a single set of resonances which were assigned to the isomer observed by X-ray analysis (Λ). Warming to

temperatures > 243K resulted in isomerization to a second isomer, assigned to be the Δ-isomer. The equilibrium ratio at 298 K was measured to be Λ : Δ = 1 : 1.1 by integration in the ^{1}H-NMR spectrum.

[b] A sample of crystalline material obtained from crystallization from toluene was used for the elemental analysis. According to X-ray and NMR analyses of this material, two equivalents of toluene were cocrystallized per formula unit of **9**.

Kinetic measurements

Basic equations:

Formation of the product:

$I = A_1 \exp(-t/tau) + A_3$

$[P]_t = [P]_0 \exp(-k_{obs}\ t)$

$-t/tau = -k_{obs}\ t$

$k_{obs} = 1/tau$

$\Delta G^{\ddagger} = -R\ T \ln((k_{obs}\ h)/(k_b\ T))$

$R = 8.31451\ (m^2 \cdot kg)/(s^2 \cdot K \cdot mol)$

$k_b = 1.380658\ 10^{-23}\ J/K$

$h = 6.6260755\ 10^{-34}\ J\ s$

Consumption of the starting material: $I = -A_1 \exp(-t/tau) + A_3 - A_1$

Kinetic experiments:

An NMR-tube containing the crystalline material of complex (*p*-*S*,*p*-*S*)-**9** was cooled to –78°C and 0.7 ml of dichloromethane-[d_2] were slowly added from a syringe. The NMR-tube was immersed into the spectrometer, which was precooled to –80°C and then adjusted to -25 °C. The measurement was repeated to proof reproducibility (series 1 and 2).

Observation of decreasing of δ^1H (starting material) = 8.28 (1 H, CHN).
Observation of increasing of δ^1H (product) = 8.35 (1 H, CHN).

	Signal observed	tau	$\Delta G^{\ddagger}$ (kJ / mol)	$\Delta G^{\ddagger}$ (kcal / mol)
Series 1	$\delta = 8.28$	2787	76.65	18.30
	$\delta = 8.35$	2067	76.03	18.16
Series 2	$\delta = 8.28$	3868	77.32	18.46
	$\delta = 8.35$	3490	77.10	18.41

Ethylene Polymerization:

All polymerizations were performed in a thermostated Büchi glass autoclave system. The autoclave was evacuated and purged with argon three times. 200 ml of toluene (polymerization temperatures up to 100°C) or *m*-xylene (polymerization temperatures > 100°C) were added into the autoclave, followed by 5 ml of a methylalumoxane solution (1.6 M in toluene). The respective catalyst was dissolved in 5 ml of toluene and preactivated by addition of 1.25 ml of a methylalumoxane solution (1.6 M in toluene). After five minutes, the catalyst was transferred to the addition funnel, the autoclave system was briefly evacuated and then pressurized with ethylene (2 bar). After addition of the catalyst, the polymerization was performed for the indicated time and then terminated by venting of the ethylene monomer, followed by addition of 10 ml of a mixture of methanol and 4 N aqueous HCl (1 : 1). 500 ml of methanol were added and the precipitate was isolated by filtration. After washing with methanol (2 x 100 ml), water (2 x 100 ml) and acetone (100 ml), the polyethylene was dried at 100°C overnight.

Polymerisation results:

Catalyst	μmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
8	5	2000	20	2	0.221	11.1	138
8	5	2000	20	2	0.160	8.00	
8	5	2000	80	2	0.775	38.9	141
8	5	2000	80	2	0.742	37.1	
8	5	2000	100	2	1.69	84.5	137
8	5	2000	100	2	1.52	76.0	
8	5	2000	125	2	2.12	106	134
8	5	2000	125	2	2.46	123	
9	5	2000	20	2	0.175	8.75	134
9	5	2000	20	2	0.140	7.00	
9	5	2000	80	2	1.02	51.0	138
9	5	2000	80	2	0.739	37.0	
9	5	2000	100	2	1.63	81.4	136
9	5	2000	100	2	1.41	70.7	
9	5	2000	125	2	1.99	99.5	131
9	5	2000	125	2	2.17	109	

[a] g PE $\cdot$ mmol $[Zr]^{-1} \cdot$ bar (ethene) $^{-1} \cdot h^{-1}$

References:

[1] Riant, O. Samuel, T. Flessner, S. Taudien, H. B. Kagan, *J. Org. Chem.* **1997**, *62*, 6733-6745.