Bis("ferrocene-saliminato") group 4 metal complexes: synthesis, structural features and use in homogenous Ziegler-Natta polymerization catalysis

Jochen Niemeyer,[a] Gerald Kehr,[a] Roland Fröhlich[a] and Gerhard Erker*[a]

Supporting information:

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 commercially available starting materials were used without further purification. The hydroxyferrocenes (*p*-*S*)-**3a**, (*p*-*S*)-**3b** and (*p*-*S*)-**3c** were prepared according to the synthetic route described in a previous paper.

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: 151 MHz); Varian INOVA 500 (^{1}H: 500 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 [$\mathrm{deg \cdot ml \cdot g^{-1} \cdot dm^{-1}}$], the respective concentration is given in a unit of [$\mathrm{10\ mg \cdot ml^{-1}}$])

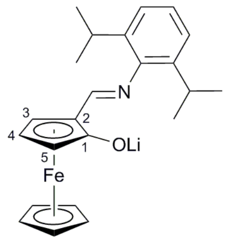
X-ray crystal structure determinations: Data sets were collected with Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, **276**, 307-326), 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, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997)).

CCDC 714224 – 714227 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:

Synthesis of the lithium salts:

(*p-S*)-(−)-N-2,6-Diisopropylphenyl-2-iminomethylferrocen-1-olato lithium ((p-S)-4a)



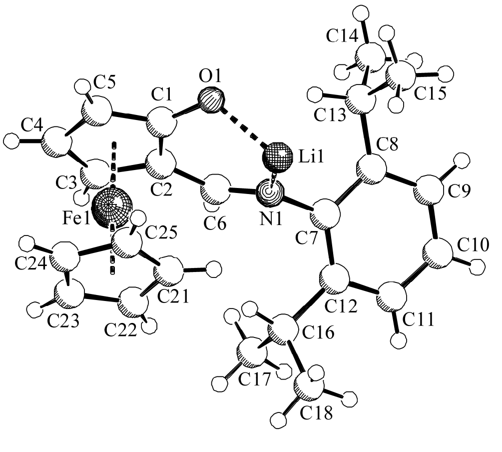
(*p-S*)-**4a**

The alcohol (*p-S*)-**3a** (1.70 g, 4.37 mmol) and lithium diisopropylamide (468 mg, 4.37 mmol) were suspended in toluene (20 ml). The mixture was stirred for three hours and the solvent was removed, giving an oily residue. Addition of pentane (20 ml) and removal of the solvent gave product (*p-S*)-**4a** as a deep red powder (1.62 g, 93.8 %).

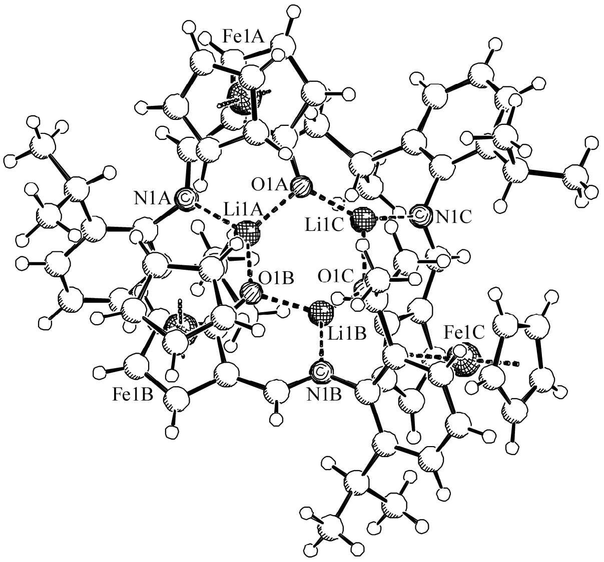
Crystals suitable for X-ray crystal structure diffraction were obtained from a solution of (*p-S*)-**4a** in pentane at room temperature.

Crystal data for $(C_{23}H_{26}FeLiNO)_3$, M = 1185.71, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 14.828(1), b = 17.780(1), c = 23.866(1) Å, V = 6292.1(6) Å^3, D_c = 1.252 g cm^{-3}, μ = 0.730 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 198(2) K, 37121 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å^{-1}, 12696 independent (R_{int} = 0.073), and 9287 observed reflections [$I \geq 2\sigma(I)$], 742 refined parameters, R = 0.046, wR^2 = 0.084, Flack -0.02(1).

Mp 274 °C (DSC); $[\alpha]_D^{20}$ -533 (*c* 0.100 in CH_2Cl_2); (Found: C, 69.89; H, 6.90; N, 3.33. $C_{23}H_{26}FeLiNO$ requires C, 69.89; H, 6.63%; N, 3.54); ν_{max}(KBr)/cm^{-1} 3066, 2960, 2867, 1612, 1587, 1473, 1361, 1104, 782, 728 and 700; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$, 228K) 7.97 (1 H, s, C*H*N), 7.26 (1 H, m, *p*-aryl), 7.16 (2 H, m, *m*-aryl^B), 3.94 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 3-H), 3.75 (5 H, s, Cp), 3.67 (1 H, t, ^3J = 2.8 Hz, 4-H), 3.45 (1 H, bs, 5-H), 3.36 (1 H, sept, ^3J = 6.9 Hz, CH^A), 2.91 (1 H, sept, ^3J = 6.9 Hz, CH^B), 1.40 (3 H, d, ^3J = 6.9 Hz, CH_3^A), 1.34 (3 H, d, ^3J = 6.9 Hz, $CH_3^{A'}$), 1.06 (3 H, d, ^3J = 6.9 Hz, CH_3^B) and 1.03 (3 H, d, ^3J = 6.9 Hz, $CH_3^{B'}$); δ_C (151 MHz; CD_2Cl_2; CD_2Cl_2, 228K) 170.5 (*C*HN), 148.7 (*i*-aryl), 139.5 (*o*-aryl^A), 139.0 (*o*-aryl^B), 135.6 (C-1), 124.8 (*m*-aryl^B), 123.5 (*m*-aryl^A), 122.9 (*p*-aryl), 68.2 (Cp), 63.5 (C-2), 63.3, 63.2 (C-3, C-4), 58.9 (C-5), 27.6 (*C*H^B), 27.2 (*C*H^A), 25.5 (*C*H$_3^{B'}$), 24.2 (*C*H$_3^A$), 23.1 (*C*H$_3^{A'}$) and 22.1 (*C*H$_3^B$); H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$, 228K): δ_H / δ_H = 7.26 / 7.16 (*p*-aryl / *m*-aryl), 7.16 / 7.26 (*m*-aryl / *p*-aryl), 3.94 / 3.67 (3-H / 4-H), 3.67 / 3.94, 3.45 (4-H / 3-H, 5-H), 3.45 / 3.67 (5-H / 4-H), 3.36 / 1.40, 1.34 (C*H*^{A} / C*H*$_3^A$, C*H*$_3^{A'}$), 2.91 / 1.06, 1.03 (C*H*^{B} / C*H*$_3^B$, C*H*$_3^{B'}$), 1.40 / 3.36 (C*H*$_3^A$ / C*H*^{A}), 1.34 / 3.36 (C*H*$_3^{A'}$ / C*H*^{A}), 1.06 / 2.91 (C*H*$_3^B$ / C*H*^{B}) and 1.03 / 2.91 (C*H*$_3^{B'}$ / C*H*^{B}); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$, 228K): δ_H / δ_C = 7.97 / 170.5 (C*H*N), 7.26 /122.9 (*p*-aryl), 7.16 / 124.8, 123.5 (*m*-aryl), 3.94, 3.67 / 63.3, 63.2 (3, 4), 3.75 / 68.2 (Cp), 3.45 / 58.9 (5), 3.36 / 27.2 (C*H*^{A}), 2.91 / 27.6 (C*H*^{B}), 1.40 / 24.2 (C*H*$_3^A$), 1.34 / 23.1 C*H*$_3^{A'}$), 1.06 / 22.1 (C*H*$_3^B$) and 1.03 / 25.5 (C*H*$_3^{B'}$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$, 228K): δ_H / δ_C = 7.97 / 148.7, 135.6, 63.5 (C*H*N / *i*-aryl, C-1, C-2), 7.26 / 148.7, 139.5, 123.5 (*p*-aryl / *i*-aryl, *o*-aryl^A, *m*-aryl^A), 7.16 / 148.7, 139.5, 139.0, 122.9 (*m*-aryl / *i*-aryl, *o*-aryl^A, *o*-aryl^B, *p*-aryl), 3.94 / 135.6, 63.3, 63.2 (5-H / C-1, C-3, C-4), 3.94 / 135.6, 63.3, 63.2, 58.9 (3-H / C-1, C-4, C-5), 3.67 / 135.6, 63.3, 63.2, 58.9 (4-H / C-1, C-3, C-5), 3.45 / 135.6, 63.3, 63.2 (5-H / C-1, C-3, C-4), 3.36 / 148.7, 139.5, 122.9, 24.2, 23.1 (C*H*^{A} / *i*-aryl, *o*-aryl^A, *p*-aryl, *C*H$_3^A$, *C*H$_3^{A'}$), 2.91 / 148.7, 139.0, 123.5, 25.5, 22.1 (C*H*^{B} / *i*-aryl, *o*-aryl^B, *m*-aryl^A, *C*H$_3^{B'}$, *C*H$_3^B$), 1.40 / 139.5, 27.2, 23.1 (C*H*$_3^A$ / *o*-aryl^A, *C*H^A, *C*H$_3^{A'}$), 1.34 / 139.5, 27.2, 24.2 (C*H*$_3^{A'}$ / *o*-aryl^A, *C*H^A, *C*H$_3^A$), 1.06 / 139.0, 27.6, 25.5 (C*H*$_3^B$ / *o*-aryl^B, *C*H^B, *C*H$_3^{B'}$) and 1.03 / 139.0, 27.6, 22.1 (C*H*$_3^{B'}$ / *o*-aryl^B, *C*H^B, *C*H$_3^B$).

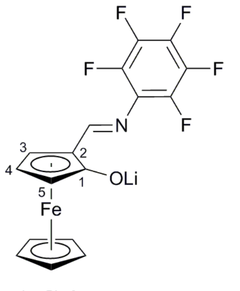


A view of the monomeric subunit of the cyclic trimer [(*p-S*)-**4a**]$_3$



A projection of the cyclotrimeric associated structure of complex [(*p*-*S*)-**4a**]$_3$ in the crystal.

(*p-S*)-(−)-N-Pentafluorophenyl-2-iminomethylferrocen-1-olato lithium ((p-S)-4c)



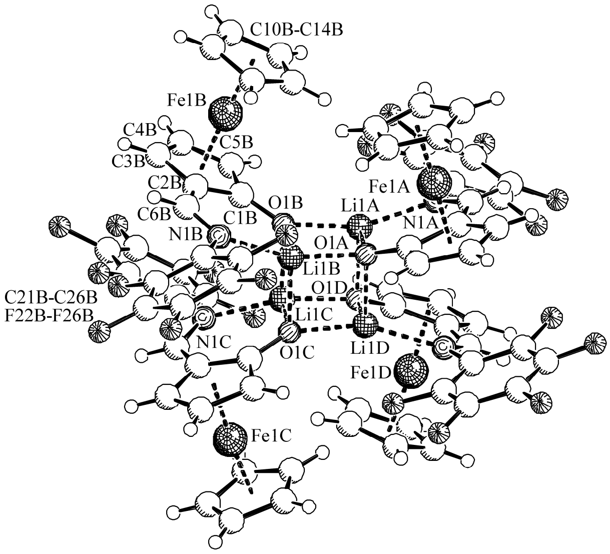
(*p*-*S*)-**4c**

The alcohol (*p*-*S*)-**3c** (1.12 g, 2.84 mmol) and lithium diisopropylamide (304 mg, 2.84 mmol) were suspended in toluene (20 ml). The mixture was stirred for three hours and the solvent was removed, giving an oily residue. Addition of pentane (20 ml) and removal of the solvent gave product (*p*-*S*)-**4c** as a deep purple powder (1.05 g, 92.2 %).

Crystals suitable for X-ray crystal structure diffraction were obtained from a solution of (*p*-*S*)-**4c** in toluene at –30°C. Alternatively, crystals could be obtained by diffusion of pentane into a solution of (*p*-*S*)-**4c** in dichloromethane at –30°C.

Crystal data for $(C_{17}H_9F_5FeLiNO)_4$, M = 1604.16, monoclinic, space group $P2_1$ (No. 4), a = 12.0617(3), b = 21.5748(6), c = 12.9461(3) Å, β = 100.689(1)°, V = 3310.5(2) $Å^3$, D_c = 1.609 g cm^{-3}, μ = 0.967 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 223(2) K, 20161 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 $Å^{-1}$, 13091 independent (R_{int} = 0.034), and 10449 observed reflections [$I \geq 2\sigma(I)$], 937 refined parameters, R = 0.052, wR^2 = 0.138, Flack 0.03(2).

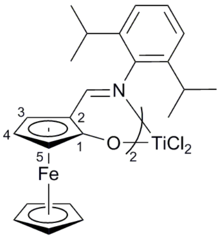
Mp 256 °C (DSC); $[\alpha]^{20}$ -1155 (436 nm, *c* 0.020 in CH_2Cl_2); (Found: C, 50.68; H, 2.39; N, 3.48. $C_{17}H_9F_5FeLiNO$ requires C, 50.91; H, 2.26; N, 3.49%); ν_{max}(KBr)/cm^{-1} 3093, 2921, 1654, 1594, 1515, 1473, 1460, 1365, 1105, 1002, 975, 811, 730, 678, 627 and 540; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$) 8.50 (1 H, bs, C*H*N), 4.17 (1 H, bs, 3-H), 3.93 (5 H, s, Cp), 3.91 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 5-H) and 3.83 (1 H, t, ^3J = 2.8 Hz, 4-H); δ_F (564.1 MHz; CD_2Cl_2; CCl_3F) −154.9 (2 F, m, *o*-C_6F_5), −162.9 (1 F, t, $^3J_{FF}$ = 21.4 Hz, *p*-C_6F_5) and −164.6 (2 F, m, *m*-C_6F_5); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$) 176.1 (t, $^4J_{FC}$ = 5.2 Hz, *C*HN), 141.5 (dm, $^1J_{FC}$ ≈ 247 Hz) and 138.5 (dm, $^1J_{FC}$ ≈ 249 Hz) (*o*-C_6F_5 and *m*-C_6F_5), 137.8 (dm, $^1J_{FC}$ ≈ 250 Hz, *p*-C_6F_5), 136.1 (C-1), 126.4 (b, *i*-C_6F_5) 70.0 (Cp), 65.7 (C-4), 64.7 (C-5), 64.3 (C-2) and 61.5 (C-3); ^1H / ^1H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 8.50 / 4.17, 3.91 (C*H*N / 3-H, 5-H), 4.17 / 8.50, 3.91, 3.83 (3-H / C*H*N, 5-H, 4-H), 3.91 / 8.50, 4.17, 3.83 (5-H / C*H*N, 3-H, 4-H) and 3.83 / 4.17, 3.91 (4-H / 3-H, 5-H); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.50 / 176.1 (*C*HN), 4.17 / 61.5 (3), 3.93 / 70.0 (Cp), 3.91 / 64.7 (5) and 3.83 / 65.7 (4); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.50 / 136.1, 126.3, 64.3, 61.5 (C*H*N / C-1, *i*-C_6F_5, C-2, C-3), 4.17 / 136.1, 65.7, 64.7, 64.3 (3-H / C-1, C-4, C-5, C-2), 3.75 / 136.1, 65.7, 64.3, 61.5 (5-H / C-1, C-4, C-2, C-3) and 3.83 / 136.1, 64.7, 64.3, 61.5 (4-H / C-1, C-5, C-2, C-3).



Molecular structure of the tetrameric aggregate [(*p*-*S*)-**4c**]$_4$ in the crystal.

Synthesis of the chelate complexes:

(+)-Dichlorobis[(κN,κO-(p-S)-N-2,6-diisopropylphenyl-2-iminomethyl-ferrocen-1-olato]titanium (5a)



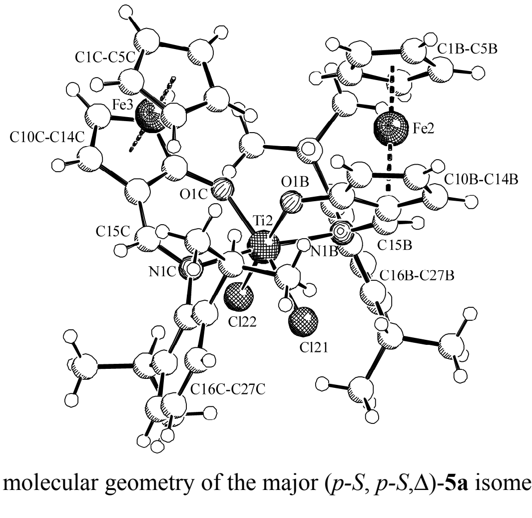
5a

The lithium salt (*p-S*)-**4a** (91.0 mg, 0.230 mmol) and titanium tetrachloride-bis-thf-adduct (38.4 mg, 0.115 mmol) were dissolved in toluene (4 ml) and the resulting deep blue reaction mixture was stirred overnight. After filtration the resulting solution was diluted with pentane (4 ml) and stored at –30°C for one week. The resulting black crystals were isolated by removal of the mother liquor and dried in vacuo to give 64.2 mg (60.3 %) of complex **5a**. The crystals were suitable for X-ray crystal structure analysis.

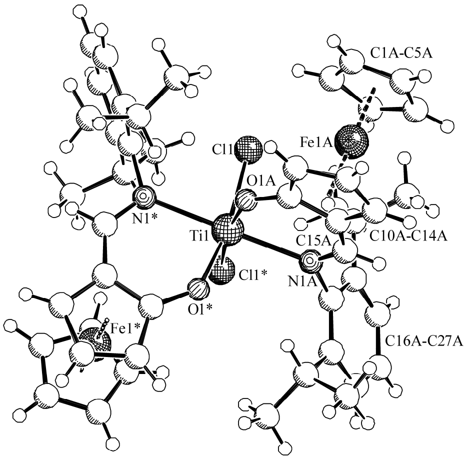
Crystal data for $C_{46}H_{52}Cl_2Fe_2N_2O_2Ti * 1/3\ C_7H_8$, $M = 926.11$, orthorhombic, space group $P2_12_12$ (No. 18), $a = 15.3532(2)$, $b = 31.8628(6)$, $c = 14.3849(2)$ Å, $V = 7037.0(2)$ Å^3, $D_c = 1.311$ g cm^{-3}, $\mu = 0.929$ mm^{-1}, $Z = 4$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 31187 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 12364 independent ($R_{int} = 0.056$), and 8419 observed reflections $[I \geq 2\sigma(I)]$, 766 refined parameters, $R = 0.057$, w$R^2 = 0.153$, Flack -0.03(2).

Mp 123 °C (DSC); $[\alpha]^{20}$ +1804 (436 nm, *c* 0.021 in CH_2Cl_2); (Found: C, 62.48; H, 5.99; N, 3.01. $C_{46}H_{52}Cl_2Fe_2N_2O_2Ti \cdot 1/3\ C_7H_8$ [a] requires C, 62.88; H, 5.95; N, 3.02%); ν_{max}(KBr)/cm^{-1} 3082, 2962, 2867, 1622, 1584, 1566, 1466, 1449, 1346, 1212, 1107, 1023, 822, 789, 762, 735 and 650; *Λ*-isomer: δ_H (600 MHz; CD_2Cl_2; $SiMe_4$; 238 K) 8.40 (2 H, s, C*H*N), 7.16 (2 H, m, *p*-aryl), 7.09, 7.09 (each 2 H, each m, 2 x *m*-aryl), 4.73 (2 H, bs, 5-H), 4.63 (2 H, dd, $^3J = 2.8$ Hz, $^4J = 1.2$ Hz, 3-H), 4.52 (10 H, s, Cp), 4.50 (2 H, t, $^3J = 2.8$ Hz, 4-H), 3.39 (2 H, sept, $^3J = 6.6$ Hz, CH^A), 3.17 (2 H, sept, $^3J = 6.6$ Hz, CH^B), 1.312, 1.310 (each 6 H, each d, $^3J = 6.6$ Hz, 2 x CH_3^A), 1.04 and 0.97 (each 6 H, each d, $^3J = 6.6$ Hz, 2 x CH_3^B); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$; 238 K) 171.5 (*C*HN), 153.0 (*i*-aryl), 141.1, 141.0 (2 x *o*-aryl), 127.2 (C-1), 126.4 (*p*-aryl), 124.0, 122.7 (*m*-aryl), 70.5 (Cp), 68.5 (C-4), 67.2 (C-2), 66.5 (C-3), 59.7 (C-5), 27.4 (CH^A), 27.3 (CH^B), 25.7, 24.1 (2 x CH_3^A), 25.1 and 23.9 (2 x CH_3^B); ^1H / ^1H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$; 238 K): $\delta_H / \delta_H = 7.16 / 7.09$ (*p*-aryl / *m*-aryl), 7.09 / 7.16 (*m*-aryl / *p*-aryl), 4.73 / 4.63, 4.50 (5-H / 3-H, 4-H), 4.63 / 4.73, 4.50 (3-H / 5-H, 4-H), 4.50 / 4.73, 4.63 (4-H / 5-H, 3-H), 3.39 / 1.312, 1.310 (CH^A / CH_3^A), 3.17 / 1.04, 0.97 (CH^B / CH_3^B), 1.312, 1.310 / 3.39 (CH_3^A / CH^A) and 1.04, 0.97 / 3.17 (CH_3^B / CH^B); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$; 238 K): $\delta_H / \delta_C = 8.40 / 171.5$ (*CH*N), 7.16 / 126.4 (*p*-aryl), 7.09 / 122.7, 124.0 (*m*-aryl), 4.73 / 59.7 (5), 4.63 / 66.5 (3), 4.52 / 70.5 (Cp), 4.50 / 68.5 (4), 3.39 / 27.4 (CH^A), 3.17 / 27.3 (CH^B), 1.312, 1.310 / 24.1, 25.7 (CH_3^A) and 1.04, 0.97 / 25.1, 23.9 (CH_3^B); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$; 238 K): $\delta_H / \delta_C = 8.40 / 153.0$, 127.2, 67.2 (C*H*N / *i*-aryl, C-1, C-2), 7.16 / 141.1, 141.0 (*p*-aryl / *o*-aryl), 7.09 / 153.0, 124.0, 122.7, 27.4, 27.3 (*m*-aryl / *i*-aryl, *m*-aryl, CH^A, CH^B), 4.73 / 127.2, 68.5, 67.2, 66.5 (5-H / C-1, C-4, C-2, C-3), 4.63 / 127.2, 68.5, 67.2, 59.7 (3-H / C-1, C-4, C-2, C-5), 4.50 / 127.2, 67.2, 66.5, 59.7 (4-H / C-1, C-2, C-3, C-5), 3.39 / 153.0, 141.1, 141.0, 122.7, 25.7, 24.1 (CH^A / *i*-aryl, *o*-aryl, *m*-aryl, CH_3^A), 3.17 / 153.0, 141.1, 141.0, 124.0, 25.1, 23.9 (CH^B / *i*-aryl, *o*-aryl, *m*-aryl, CH_3^B), 1.312 / 141.1, 141.0, 27.4, 25.7 (CH_3^A / *o*-aryl, CH^A, CH_3^A), 1.310 / 141.1, 141.0, 27.4, 24.1 (CH_3^A / *o*-aryl, CH^A, CH_3^A), 1.04 / 141.1, 141.0, 27.3, 25.1 (CH_3^B / *o*-aryl, CH^B, CH_3^B) and 0.97 / 141.1, 141.0, 27.3, 23.9 (CH_3^B / *o*-aryl, CH^B, CH_3^B).

[a] 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, one third of an equivalent of toluene was cocrystallized per formula unit of **5a**.

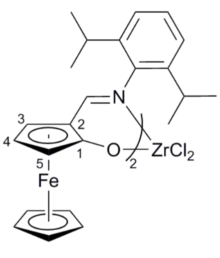


A view of the molecular geometry of the major (*p-S*, *p-S*,Δ)-**5a** isomer in the crystal



Molecular structure of the minor (*p*-*S*,*p*-*S*,Λ)-**5a** diastereoisomer in the crystal.

(+)-Dichlorobis[(κN,κO-(p-S)-N-2,6-diisopropylphenyl-2-iminomethyl-ferrocen-1-olato]zirconium (6a)



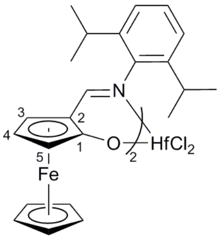
6a

The lithium salt (*p*-*S*)-**4a** (160 mg, 0.405 mmol) and zirconium tetrachloride (47.2 mg, 0.203 mmol) were suspended in toluene (4 ml) and the obtained reaction mixture was stirred overnight. After filtration on 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 complex **6a** (175 mg, 76.8 %). The obtained crystals were suitable for X-ray crystal structure analysis.

Mp 113 °C (DSC); $[\alpha]^{20}$ +138 (436 nm, *c* 0.020 in $\mathrm{CH_2Cl_2}$); (Found: C, 63.32; H, 6.03; N, 2.65. $\mathrm{C_{46}H_{52}Cl_2Fe_2N_2O_2Zr \cdot 2\,C_7H_8}$ [a] requires C, 64.17; H, 6.10; N, 2.49%); ν_{max}(KBr)/cm^{-1} 3086, 3059, 3022, 2963, 2865, 1622, 1593, 1565, 1471, 1439, 1364, 1353, 1328, 1213, 1106, 1023, 881, 829, 789, 743, 733 and 656; *Λ*-isomer: δ_{H} (600 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$) 8.29 (1 H, d, ^4J = 0.7 Hz, C*H*N), 7.27 (1 H, m, *p*-aryl), 7.22 (2 H, m, *m*-aryl$^{\mathrm{A,B}}$), 4.48 (1 H, m, 3-H), 4.43 (5 H, s, Cp), 4.34 (1 H, t, ^3J = 2.8 Hz, 4-H), 4.30 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.3 Hz, 5-H), 3.53 (1 H, sept, ^3J = 6.8 Hz, $\mathrm{C}H^{\mathrm{A}}$), 3.40 (1 H, sept, ^3J = 6.8 Hz, $\mathrm{C}H^{\mathrm{B}}$), 1.60 (3 H, d, ^3J = 6.8 Hz, $\mathrm{C}H_3^{\mathrm{B}}$), 1.34 (3 H, d, ^3J = 6.8 Hz, $\mathrm{C}H_3^{\mathrm{A}}$), 1.27 (3 H, d, ^3J = 6.8 Hz, $\mathrm{C}H_3^{\mathrm{A}\prime}$) and 1.11 (3 H, d, ^3J = 6.8 Hz, $\mathrm{C}H_3^{\mathrm{B}\prime}$); δ_{C} (151 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$) 176.5 (*C*HN), 151.7 (*i*-aryl), 142.1 (*o*-aryl$^{\mathrm{A}}$), 141.9 (*o*-aryl$^{\mathrm{B}}$), 127.1 (*p*-aryl), 126.5 (C-1), 124.2 (*m*-aryl$^{\mathrm{A}}$), 123.8 (*m*-aryl$^{\mathrm{B}}$), 70.4 (Cp), 67.6 (C-4), 65.7 (C-2), 65.2 (C-5), 60.8 (C-3), 28.0 ($C\mathrm{H}^{\mathrm{A}}$ + $C\mathrm{H}^{\mathrm{B}}$), 25.8 ($C\mathrm{H}_3^{\mathrm{A}\prime}$), 25.6 ($C\mathrm{H}_3^{\mathrm{B}\prime}$), 24.0 ($C\mathrm{H}_3^{\mathrm{B}}$) and 23.6 ($C\mathrm{H}_3^{\mathrm{A}}$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{H} = 8.29 / 4.49 – 4.48 (C*H*N / 3-H), 7.27 / 7.22 (*p*-aryl / *m*-aryl$^{\mathrm{A,B}}$), 7.22 / 7.27 (*m*-aryl$^{\mathrm{A,B}}$ / *p*-aryl), 4.48 / 8.29, 4.34 (3-H / C*H*N, 4-H), 4.34 / 4.48, 4.30 (4-H / 3-H, 5-H), 4.30 / 4.34 (5-H / 4-H), 3.53 / 1.34, 1.27 ($\mathrm{C}H^{\mathrm{A}}$ / $\mathrm{C}H_3^{\mathrm{A}}$, $\mathrm{C}H_3^{\mathrm{A}\prime}$), 3.40 / 1.60, 1.11 ($\mathrm{C}H^{\mathrm{B}}$ / $\mathrm{C}H_3^{\mathrm{B}}$, $\mathrm{C}H_3^{\mathrm{B}\prime}$), 1.60 / 3.40 ($\mathrm{C}H_3^{\mathrm{B}}$ / $\mathrm{C}H^{\mathrm{B}}$), 1.34 / 3.53 ($\mathrm{C}H_3^{\mathrm{A}}$ / $\mathrm{C}H^{\mathrm{A}}$), 1.27 / 3.53 ($\mathrm{C}H_3^{\mathrm{A}\prime}$ / $\mathrm{C}H^{\mathrm{A}}$) and 1.11 / 3.40 ($\mathrm{C}H_3^{\mathrm{B}\prime}$ / $\mathrm{C}H^{\mathrm{B}}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{C} = 8.29 / 176.5 (*CH*N), 7.27 / 127.1 (*p*-aryl), 7.22 / 124.2, 123.8 (*m*-aryl$^{\mathrm{A,B}}$), 4.49 – 4.48 / 60.8 (3), 4.43 / 70.4 (Cp), 4.34 / 67.6 (4), 4.30 / 65.2 (5), 3.53 / 28.0 (CH^{A}), 3.40 / 28.0 (CH^{B}), 1.60 / 24.0 (CH_3^{B}), 1.34 / 23.6 (CH_3^{A}), 1.27 / 25.8 ($CH_3^{\mathrm{A}\prime}$) and 1.11 / 25.6 ($CH_3^{\mathrm{B}\prime}$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{C} = 8.29 / 151.7, 126.5, 65.7 (C*H*N / *i*-aryl, C-1, C-2), 7.27 / 142.1 (*p*-aryl / *o*-aryl$^{\mathrm{A}}$), 7.22 / 151.7, 141.9, 124.2, 28.0 (*m*-aryl$^{\mathrm{A,B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{B}}$), 4.49 – 4.48 / 67.6, 65.2 (3-H / C-4, C-5), 4.34 / 65.2, 60.8 (4-H / C-5, C-3), 4.30 / 60.8 (5-H / C-3), 3.53 / 151.7, 142.1, 124.2, 25.8, 23.6 ($\mathrm{C}H^{\mathrm{A}}$ / *i*-aryl, *o*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{A}}$, $C\mathrm{H}_3^{\mathrm{A}\prime}$, $C\mathrm{H}_3^{\mathrm{A}}$), 3.40 / 151.7, 141.9, 123.8, 25.6, 24.0 ($\mathrm{C}H^{\mathrm{B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{B}}$, $C\mathrm{H}_3^{\mathrm{B}\prime}$, $C\mathrm{H}_3^{\mathrm{B}}$), 1.60 / 141.9, 28.0, 25.6 ($\mathrm{C}H_3^{\mathrm{B}}$ / *o*-aryl$^{\mathrm{B}}$, $C\mathrm{H}^{\mathrm{B}}$, $C\mathrm{H}_3^{\mathrm{B}\prime}$), 1.34 / 142.1, 28.0, 25.8 ($\mathrm{C}H_3^{\mathrm{A}}$ / *o*-aryl$^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{A}}$, $C\mathrm{H}_3^{\mathrm{A}\prime}$), 1.27 / 142.1, 28.0, 23.6 ($\mathrm{C}H_3^{\mathrm{A}\prime}$ / *o*-aryl$^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{A}}$, $C\mathrm{H}_3^{\mathrm{A}}$) and 1.11 / 141.9, 28.0, 24.0 ($\mathrm{C}H_3^{\mathrm{B}\prime}$ / *o*-aryl$^{\mathrm{B}}$, $C\mathrm{H}^{\mathrm{B}}$, $C\mathrm{H}_3^{\mathrm{B}}$); *Δ*-isomer: δ_{H} (600 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$) 8.35 (1 H, d, ^4J = 0.7 Hz, C*H*N), 7.22 (1 H, m, *p*-aryl), 7.18 (1 H, dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, *m*-aryl$^{\mathrm{A}}$), 7.14 (1 H, dd, ^3J = 7.5 Hz, ^4J = 1.6 Hz, *m*-aryl$^{\mathrm{B}}$), 4.74 (1 H, ddd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, ^4J = 0.7 Hz, 3-H), 4.52 (5 H, s, Cp), 4.41 (1 H, t, ^3J = 2.8 Hz, 4-H), 4.40 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 5-H), 3.52 (1 H, sept, ^3J = 6.7 Hz, $\mathrm{C}H^{\mathrm{A}}$), 3.16 (1 H, sept, ^3J = 6.7 Hz, $\mathrm{C}H^{\mathrm{B}}$), 1.46 (3 H, d, ^3J = 6.7 Hz, $\mathrm{C}H_3^{\mathrm{A}}$), 1.42 (3 H, d, ^3J = 6.7 Hz, $\mathrm{C}H_3^{\mathrm{A}\prime}$), 1.12 (3 H, d, ^3J = 6.7 Hz, $\mathrm{C}H_3^{\mathrm{B}}$) and 1.02 (3 H, d, ^3J = 6.7 Hz, $\mathrm{C}H_3^{\mathrm{B}\prime}$); δ_{C} (151 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$) 175.6 (*C*HN), 150.8 (*i*-aryl), 142.3 (*o*-aryl$^{\mathrm{B}}$), 141.8 (*o*-aryl$^{\mathrm{A}}$), 127.1 (*p*-aryl), 126.4 (C-1), 124.6 (*m*-aryl$^{\mathrm{B}}$), 123.5 (*m*-aryl$^{\mathrm{A}}$), 70.6 (Cp), 68.3 (C-4), 66.4 (C-2), 66.0 (C-5), 61.1 (C-3), 28.3 ($C\mathrm{H}^{\mathrm{A}}$), 27.9 ($C\mathrm{H}^{\mathrm{B}}$), 26.1 ($C\mathrm{H}_3^{\mathrm{A}\prime}$), 25.5 ($C\mathrm{H}_3^{\mathrm{B}\prime}$) and 24.4 ($C\mathrm{H}_3^{\mathrm{A}}$), 23.9 ($C\mathrm{H}_3^{\mathrm{B}}$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{H} = 8.35 / 4.74 (C*H*N / 3-H), 7.22 / 7.18, 7.14 (*p*-aryl / *m*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{B}}$), 7.18 / 7.22 (*m*-aryl$^{\mathrm{A}}$ / *p*-aryl), 7.14 / 7.22 (*m*-aryl$^{\mathrm{B}}$ / *p*-aryl), 4.74 / 8.35, 4.41 (3-H / C*H*N, 4-H), 4.41 / 4.74, 4.40 (4-H / 3-H, 5-H), 4.40 / 4.41 (5-H / 4-H), 3.52 / 1.46, 1.42 ($\mathrm{C}H^{\mathrm{A}}$ / $\mathrm{C}H_3^{\mathrm{A}}$, $\mathrm{C}H_3^{\mathrm{A}\prime}$), 3.16 / 1.12, 1.02 ($\mathrm{C}H^{\mathrm{B}}$ / $\mathrm{C}H_3^{\mathrm{B}}$, $\mathrm{C}H_3^{\mathrm{B}\prime}$), 1.46 / 3.52 ($\mathrm{C}H_3^{\mathrm{A}}$ / $\mathrm{C}H^{\mathrm{A}}$), 1.42 / 3.52 ($\mathrm{C}H_3^{\mathrm{A}\prime}$ / $\mathrm{C}H^{\mathrm{A}}$), 1.12 / 3.16 ($\mathrm{C}H_3^{\mathrm{B}}$ / $\mathrm{C}H^{\mathrm{B}}$) and 1.02 / 3.16 ($\mathrm{C}H_3^{\mathrm{B}\prime}$ / $\mathrm{C}H^{\mathrm{B}}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{C} = 8.35 / 175.6 (*CH*N), 7.22 / 127.1 (*p*-aryl), 7.18 / 123.5 (*m*-aryl$^{\mathrm{A}}$), 7.14 / 124.6 (*m*-aryl$^{\mathrm{B}}$), 4.74 / 61.1 (3), 4.52 / 70.6 (Cp), 4.41 / 68.3 (4), 4.40 / 66.0 (5), 3.52 / 28.3 (CH^{A}), 3.16 / 27.9 (CH^{B}), 1.46 / 24.4 (CH_3^{A}), 1.42 / 26.1 ($CH_3^{\mathrm{A}\prime}$), 1.12 / 23.9 (CH_3^{B}) and 1.02 / 25.5 ($CH_3^{\mathrm{B}\prime}$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; $\mathrm{CD_2Cl_2}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{C} = 8.35 / 150.8, 126.4, 66.4 (C*H*N / *i*-aryl, C-1, C-2), 7.18 / 150.8, 141.8, 28.3 (*m*-aryl$^{\mathrm{A}}$ / *i*-aryl, *o*-aryl$^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{A}}$), 7.14 / 150.8, 142.3, 27.9 (*m*-aryl$^{\mathrm{B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{B}}$, $C\mathrm{H}^{\mathrm{B}}$), 4.74 / 126.4, 68.3 (3-H / C-1, C-4), 4.41 / 66.0, 61.1 (4-H / C-5, C-3), 4.40 / 68.3, 61.1 (5-H / C-4, C-3), 3.52 / 150.8, 141.8, 123.5, 26.1, 24.4 ($\mathrm{C}H^{\mathrm{A}}$ / *i*-aryl, *o*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{A}}$, $C\mathrm{H}_3^{\mathrm{A}\prime}$, $C\mathrm{H}_3^{\mathrm{A}}$), 3.16 / 150.8, 142.3, 124.6, 25.5, 23.9 ($\mathrm{C}H^{\mathrm{B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{B}}$, $C\mathrm{H}_3^{\mathrm{B}\prime}$, $C\mathrm{H}_3^{\mathrm{B}}$), 1.46 / 141.8, 28.3, 26.1 ($\mathrm{C}H_3^{\mathrm{A}}$ / *o*-aryl$^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{A}}$, $C\mathrm{H}_3^{\mathrm{A}\prime}$), 1.42 / 141.8, 28.3, 24.4 ($\mathrm{C}H_3^{\mathrm{A}\prime}$ / *o*-aryl$^{\mathrm{A}}$, $C\mathrm{H}^{\mathrm{A}}$, $C\mathrm{H}_3^{\mathrm{A}}$), 1.12 / 142.3, 27.9, 25.5 ($\mathrm{C}H_3^{\mathrm{B}}$ / *o*-aryl$^{\mathrm{B}}$, $C\mathrm{H}^{\mathrm{B}}$, $C\mathrm{H}_3^{\mathrm{B}\prime}$) and 1.02 / 142.3, 27.9, 23.9 ($\mathrm{C}H_3^{\mathrm{B}\prime}$ / *o*-aryl$^{\mathrm{B}}$, $C\mathrm{H}^{\mathrm{B}}$, $C\mathrm{H}_3^{\mathrm{B}}$); [*Δ*-isomer / *Λ*-isomer at 298K ≈ 1 : 0.9].

[a] 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 **6a**.

(+)-Dichlorobis[(κN,κO-(p-S)-N-2,6-diisopropylphenyl-2-iminomethyl-ferrocen-1-olato]hafnium (7a)

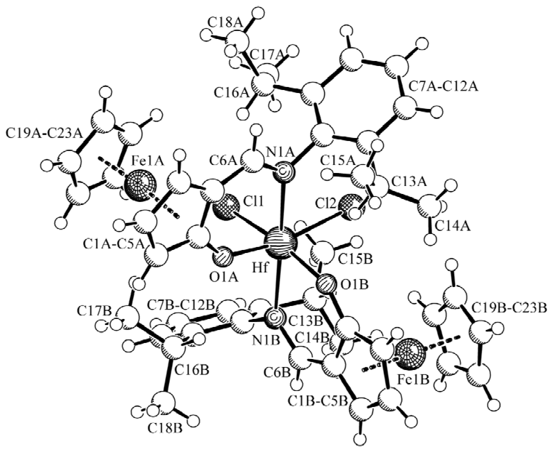


7a

The lithium salt (*p-S*)-**4c** (106 mg, 0.268 mmol) and hafnium tetrachloride (42.9 mg, 0.134 mmol) were suspended in toluene (3 ml) and the mixture was stirred overnight. After filtration on a glass frit, the resulting solution was diluted with toluene (5 ml) and stored at –30°C for one week. A first fraction of pink crystals (65.6 mg) was isolated by removal of the mother liquor, which was stored at –30°C for another week to give again 35.6 mg of the complex **7a** (total yield: 101 mg, 62.3 %). The obtained crystals were suitable for X-ray crystal structure analysis.
Alternatively, crystals for X-ray crystal structure analysis were obtained by diffusion of pentane into a solution of **6a** in dichloromethane at –30°C.
Crystal data for $C_{46}H_{52}Cl_2Fe_2HfN_2O_2$ * 2 C_7H_8, *M* = 1210.25, monoclinic, space group $P2_1$ (No. 4), *a* = 11.4955(1), *b* = 19.5379(2), *c* = 12.5595(1) Å, *β* = 105.900(1)°, *V* = 2712.92(4) Å^3, D_c = 1.482 g cm^{-3}, μ = 2.578 mm^{-1}, *Z* = 2, λ = 0.71073 Å, *T* = 223(2) K, 18591 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å^{-1}, 11270 independent (R_{int} = 0.032), and 10874 observed reflections [I ≥ 2σ(*I*)], 632 refined parameters, *R* = 0.024, wR^2 = 0.060, Flack -0.014(4).

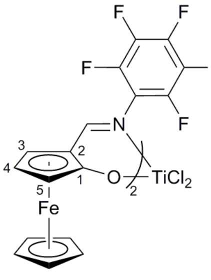
Mp 109 °C (DSC); $[\alpha]^{20}$ +753 (436 nm, *c* 0.020 in CH_2Cl_2); (Found: C, 58.62; H, 5.65; N, 2.30. $C_{46}H_{52}Cl_2Fe_2N_2O_2Hf \cdot 2\ C_7H_8$ [a] requires C, 59.54; H, 5.66; N, 2.31%); $\nu_{\max}$(KBr)/cm^{-1} 3023, 2966, 2924, 2865, 1623, 1593, 1566, 1474, 1440, 1364, 1353, 1215, 1171, 1106, 1023, 1001, 889, 854, 829, 789, 744, 733 and 658; *Λ*-isomer: δ_{H} (600 MHz; CD_2Cl_2; $SiMe_4$) 8.29 (1 H, d, ^{4}*J* = 0.7 Hz, C*H*N), 7.30 – 7.13 (3 H, m, *m*-aryl, *p*-aryl), 4.50 (1 H, ddd, ^{3}*J* = 2.6 Hz, ^{3}*J* = 1.3 Hz, ^{3}*J* = 0.7 Hz, 3-H), 4.41 (5 H, s, Cp), 4.35 (1 H, t, ^{3}*J* = 2.8 Hz, 4-H), 4.29 (1 H, dd, ^{3}*J* = 2.8 Hz, ^{4}*J* = 1.3 Hz, 5-H), 3.57 (1 H, sept, ^{3}*J* = 6.8 Hz, C*H*$^{\mathrm{A}}$), 3.48 (1 H, sept, ^{3}*J* = 6.8 Hz, C*H*$^{\mathrm{B}}$), 1.59 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{B}}$), 1.34 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{A}}$), 1.27 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{A}'}$) and 1.12 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{B}'}$); δ_{C} (151 MHz; CD_2Cl_2; $SiMe_4$) 177.5 (*C*HN), 151.3 (*i*-aryl), 142.4 (*o*-aryl$^{\mathrm{A}}$), 142.3 (*o*-aryl$^{\mathrm{B}}$), 127.3 (*p*-aryl), 127.1 (C-1), 124.2 (*m*-aryl$^{\mathrm{A}}$), 124.0 (*m*-aryl$^{\mathrm{B}}$), 70.4 (Cp), 67.9 (C-4), 65.5 (C-2), 65.0 (C-5), 61.3 (C-3), 28.0 (*C*H$^{\mathrm{A}}$), 27.9 (*C*H$^{\mathrm{B}}$), 25.9 (*C*H$_3^{\mathrm{A}'}$), 25.7 (*C*H$_3^{\mathrm{B}'}$), 24.1 (*C*H$_3^{\mathrm{B}}$) and 23.7 (*C*H$_3^{\mathrm{A}}$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_{H} / δ_{H} = 8.29 / 4.50 (C*H*N / 3-H), 4.50 / 8.29, 4.35, 4.29 (3-H / C*H*N, 4-H, 5-H), 4.35 / 4.50, 4.29 (4-H / 3-H, 5-H), 4.29 / 4.50, 4.35 (5-H / 3-H, 4-H), 3.57 / 1.34, 1.27 (C*H*$^{\mathrm{A}}$ / C*H*$_3^{\mathrm{A}}$, C*H*$_3^{\mathrm{A}'}$), 3.48 / 1.59, 1.12 (C*H*$^{\mathrm{B}}$ / C*H*$_3^{\mathrm{B}}$, C*H*$_3^{\mathrm{B}'}$), 1.59 / 3.48 (C*H*$_3^{\mathrm{B}}$ / C*H*$^{\mathrm{B}}$), 1.34 / 3.57 (C*H*$_3^{\mathrm{A}}$ / C*H*$^{\mathrm{A}}$), 1.27 / 3.57 (C*H*$_3^{\mathrm{A}'}$ / C*H*$^{\mathrm{A}}$) and 1.12 / 3.48 (C*H*$_3^{\mathrm{B}'}$ / C*H*$^{\mathrm{B}}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_{H} / δ_{C} = 8.29 / 177.5 (*CH*N), 7.30-7-13 / 127.3, 124.2, 124.0 (*m*-aryl, *p*-aryl), 4.50 / 61.3 (3-H), 4.41 / 70.4 (Cp), 4.35 / 67.9 (4), 4.29 / 65.0 (5), 3.57 / 28.0 (*CH*$^{\mathrm{A}}$), 3.48 / 27.9 (*CH*$^{\mathrm{B}}$), 1.59 / 24.1 (*CH*$_3^{\mathrm{B}}$), 1.34 / 23.7 (*CH*$_3^{\mathrm{A}}$) and 1.27 / 25.9 (*CH*$_3^{\mathrm{A}'}$), 1.12 / 25.7 (*CH*$_3^{\mathrm{B}'}$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_{H} / δ_{C} = 8.29 / 151.3, 127.1, 65.5 (C*H*N / *i*-aryl, C-1, C-2), 7.30-7.13 / 151.3, 142.4, 142.3, 124.2, 124.0, 28.0, 27.9 (*m*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{A}}$, *o*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{B}}$, *C*H$^{\mathrm{A}}$, *C*H$^{\mathrm{B}}$), 4.50 / 67.9, 65.5 (3-H / C-4, C-2), 4.35 / 61.3 (4-H / C-3), 3.57 / 151.3, 142.3, 124.2, 25.9, 23.7 (C*H*$^{\mathrm{A}}$ / *i*-aryl, *o*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{A}}$, *C*H$_3^{\mathrm{A}'}$, *C*H$_3^{\mathrm{A}}$), 3.48 / 151.3, 142.3, 124.0, 25.7, 24.1 (C*H*$^{\mathrm{B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{B}}$, *C*H$_3^{\mathrm{B}'}$, *C*H$_3^{\mathrm{B}}$), 1.59 / 142.3, 27.9, 25.7 (C*H*$_3^{\mathrm{B}}$ / *o*-aryl$^{\mathrm{B}}$, *C*H$^{\mathrm{B}}$, *C*H$_3^{\mathrm{B}'}$), 1.34 / 142.4, 28.0, 25.9 (C*H*$_3^{\mathrm{A}}$ / *o*-aryl$^{\mathrm{A}}$, *C*H$^{\mathrm{A}}$, *C*H$_3^{\mathrm{A}'}$), 1.27 / 142.4, 28.0, 23.7 (C*H*$_3^{\mathrm{A}'}$ / *o*-aryl$^{\mathrm{A}}$, *C*H$^{\mathrm{A}}$, *C*H$_3^{\mathrm{A}}$) and 1.12 / 142.3, 27.9, 24.1 (C*H*$_3^{\mathrm{B}'}$ / *o*-aryl$^{\mathrm{B}}$, *C*H$^{\mathrm{B}}$, *C*H$_3^{\mathrm{B}}$); *Δ*-isomer: δ_{H} (600 MHz; CD_2Cl_2; $SiMe_4$) 8.36 (1 H, d, ^{4}*J* = 0.7 Hz, C*H*N), 7.30-7.13 (3 H, m, *m*-aryl, *p*-aryl), 4.77 (1 H, ddd, ^{3}*J* = 2.8 Hz, ^{4}*J* = 1.3 Hz, ^{4}*J* = 0.7 Hz, 3-H), 4.52 (5 H, s, Cp), 4.42 (1 H, t, ^{3}*J* = 2.8 Hz, 4-H), 4.38 (1 H, dd, ^{3}*J* = 2.8 Hz, ^{4}*J* = 1.3 Hz, 5-H), 3.59 (1 H, sept, ^{3}*J* = 6.8 Hz, C*H*$^{\mathrm{A}}$), 3.18 (1 H, sept, ^{3}*J* = 6.8 Hz, C*H*$^{\mathrm{B}}$), 1.46 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{A}}$), 1.42 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{A}'}$), 1.11 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{B}}$) and 1.02 (3 H, d, ^{3}*J* = 6.8 Hz, C*H*$_3^{\mathrm{B}'}$); δ_{C} (151 MHz; CD_2Cl_2; $SiMe_4$) 176.6 (*C*HN), 150.6 (*i*-aryl), 142.6 (*o*-aryl$^{\mathrm{B}}$), 142.1 (*o*-aryl$^{\mathrm{A}}$), 127.3 (C-1), 127.2 (*p*-aryl), 124.7 (*m*-aryl$^{\mathrm{B}}$), 123.6 (*m*-aryl$^{\mathrm{A}}$), 70.7 (Cp), 68.5 (C-4), 66.2 (C-2), 65.7 (C-5), 61.6 (C-3), 28.2 (*C*H$^{\mathrm{A}}$), 27.9 (*C*H$^{\mathrm{B}}$), 26.2 (*C*H$_3^{\mathrm{A}'}$), 25.5 (*C*H$_3^{\mathrm{B}'}$), 24.5 (*C*H$_3^{\mathrm{A}}$) and 24.0 (*C*H$_3^{\mathrm{B}}$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_{H} / δ_{H} = 8.36 / 4.77 (C*H*N / 3-H), 4.77 / 8.36, 4.42, 4.38 (3-H / C*H*N, 4-H, 5-H), 4.42 / 4.77, 4.38 (4-H / 3-H, 5-H), 4.38 / 4.77, 4.42 (5-H / 3-H, 4-H), 3.59 / 1.46, 1.42 (C*H*$^{\mathrm{A}}$ / C*H*$_3^{\mathrm{A}}$, C*H*$_3^{\mathrm{A}'}$), 3.18 / 1.11, 1.02 (C*H*$^{\mathrm{B}}$ / C*H*$_3^{\mathrm{B}}$, C*H*$_3^{\mathrm{B}'}$), 1.46 / 3.59 (C*H*$_3^{\mathrm{A}}$ / C*H*$^{\mathrm{A}}$), 1.42 / 3.59 (C*H*$_3^{\mathrm{A}'}$ / C*H*$^{\mathrm{A}}$), 1.11 / 3.18 (C*H*$_3^{\mathrm{B}}$ / C*H*$^{\mathrm{B}}$) and 1.02 / 3.18 (C*H*$_3^{\mathrm{B}'}$ / C*H*$^{\mathrm{B}}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_{H} / δ_{C} = 8.36 / 176.6 (*CH*N), 7.30-7.13 / 127.2, 124.7, 123.6 (*m*-aryl, *p*-aryl), 4.77 / 61.6 (3), 4.52 / 70.7 (Cp), 4.42 / 68.5 (4), 4.38 / 65.7 (5), 3.59 / 28.2 (*CH*$^{\mathrm{A}}$), 3.18 / 27.9 (*CH*$^{\mathrm{B}}$), 1.46 / 24.5 (*CH*$_3^{\mathrm{A}}$), 1.42 / 26.2 (*CH*$_3^{\mathrm{A}'}$), 1.11 / 24.0 (*CH*$_3^{\mathrm{B}}$) and 1.02 / 25.5 (*CH*$_3^{\mathrm{B}'}$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_{H} / δ_{C} = 8.36 / 150.6, 127.3, 66.2 (C*H*N / *i*-aryl, C-1, C-2), 7.30-7.13 / 150.6, 124.7, 123.6, 28.2, 27.9 (*m*-aryl / *i*-aryl, *m*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{A}}$, *C*H$^{\mathrm{A}}$, *C*H$^{\mathrm{B}}$), 4.77 / 66.2 (3-H / C-2), 4.38 / 61.6 (5-H / C-3), 3.59 / 150.6, 142.1, 123.6, 26.2, 24.5 (C*H*$^{\mathrm{A}}$ / *i*-aryl, *o*-aryl$^{\mathrm{A}}$, *m*-aryl$^{\mathrm{A}}$, *C*H$_3^{\mathrm{A}'}$, *C*H$_3^{\mathrm{A}}$), 3.18 / 150.6, 142.6, 124.7, 25.5, 24.0 (C*H*$^{\mathrm{B}}$ / *i*-aryl, *o*-aryl$^{\mathrm{B}}$, *m*-aryl$^{\mathrm{B}}$, *C*H$_3^{\mathrm{B}'}$, *C*H$_3^{\mathrm{B}}$), 1.46 / 142.1, 28.2, 26.2 (C*H*$_3^{\mathrm{A}}$ / *o*-aryl$^{\mathrm{A}}$, *C*H$^{\mathrm{A}}$, *C*H$_3^{\mathrm{A}'}$), 1.42 / 142.1, 28.2, 24.5 (C*H*$_3^{\mathrm{A}'}$ / *o*-aryl$^{\mathrm{A}}$, *C*H$^{\mathrm{A}}$, *C*H$_3^{\mathrm{A}}$), 1.11 / 142.6, 27.9, 25.5 (C*H*$_3^{\mathrm{B}}$ / *o*-aryl$^{\mathrm{B}}$, *C*H$^{\mathrm{B}}$, *C*H$_3^{\mathrm{B}'}$) and 1.02 / 142.6, 27.9, 24.0 (C*H*$_3^{\mathrm{B}'}$ / *o*-aryl$^{\mathrm{B}}$, *C*H$^{\mathrm{B}}$, *C*H$_3^{\mathrm{B}}$[*Δ*-isomer / *Λ*-isomer at 298K ≈ 1 : 0.9].

[a] 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 **7a**.



A projection of the molecular structure of the hafnium complex (*p*-*S*,*p*-*S*,Λ)-**7a**

(+)-Dichlorobis[(κN,κO-(p-S)-N-pentafluorophenyl-2-iminomethylferrocen-1-olato]titanium ((*p-S*,*p-S*)-5c)

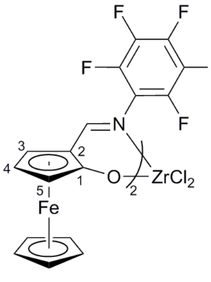


(*p-S*,*p-S*)-**5c**

The lithium salt (*p-S*)-**4c** (100 mg, 0.250 mmol) and titanium tetrachloride-bis-thf-adduct (41.7 mg, 0.125 mmol) were suspended in toluene (4 ml) and the mixture was stirred for two days. After filtration, pentane (20 ml) was added to the solution. The resulting precipitate was collected on a glass frit, washed with pentane (3 × 2 ml) and dried in vacuo. Complex (*p-S*,*p-S*)-**5c** was obtained as a deep blue powder (78.5 mg, 69.2 %).

Mp 208 °C (DSC); $[\alpha]^{20}$ -1653 (436 nm, *c* 0.020 in CH_2Cl_2); (Found: C, 45.32; H, 2.32; N, 2.83. $C_{34}H_{18}Cl_2F_{10}Fe_2N_2O_2Ti$ requires C, 45.03; H, 2.00; N, 3.09%); ν_{max}(KBr)/cm^{-1} 3095, 1576, 1519, 1453, 1453, 1351, 1214, 1157, 1107, 1005, 985, 861, 837, 773 and 633; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$) 8.32 (1 H, s, C*H*N), 4.60 (5 H, s, Cp), 4.513, 4.509 (each 1 H, each m, C_5H_3) and 4.36 (1 H, br, C_5H_3); δ_F (564 MHz; CD_2Cl_2; CCl_3F) −143.2, −146.9 (each 1 F, each br, *o*-C_6F_5), −158.7 (1 F, t, $^3J_{FF}$ = 21.4 Hz, *p*-C_6F_5), −162.9 and −164.2 (each 1 F, each br, *m*-C_6F_5); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$) 177.3 (*C*HN), 126.8 (C-1), 71.5 (Cp), 69.8 (C_5H_3), 68.4 (C-2), 67.0 (C_5H_3) and 60.5 (C_5H_3), signals for C_6F_5 were not observed; ^1H / ^1H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 8.32 / 4.36 (C*H*N / C_5H_3), 4.513, 4.509 / 4.36 (C_5H_3 / C_5H_3) and 4.36 / 8.32, 4.513, 4.509 (3-H / C*H*N, C_5H_3); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.32 / 177.3 (*CH*N), 4.60 / 71.5 (Cp), 4.513, 4.509 / 69.8, 67.0 (C_5H_3) and 4.36 / 60.5 (C_5H_3); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.32 / 126.8, 68.4, 67.0 (C*H*N / C-1, C-2, C_5H_3), 4.513, 4.509 / 126.8, 69.8, 68.4, 60.5 (C_5H_3 / C-1, C_5H_3, C-2, C_5H_3) and 4.36 / 69.8, 68.4, 67.0 (C_5H_3 / C_5H_3, C-2, C_5H_3).

(+)-Dichlorobis[(κN,κO-(p-S)-N-pentafluorophenyl-2-iminomethylferrocen-1-olato]zirconium ((*p-S*,*p-S*)-6c)



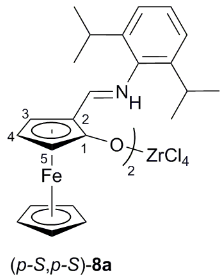
(*p-S*,*p-S*)-**6c**

The lithium salt (*p-S*)-**4c** (114 mg, 0.285 mmol) and zirconium tetrachloride (33.2 mg, 0.142 mmol) were suspended in toluene (12 ml) and the reaction mixture was stirred for 28 hours. After filtration on a glass frit, pentane (20 ml) was added to the solution. The resulting precipitate was collected on a glass frit, washed with pentane (3 ml) and dried in vacuo. Complex (*p-S*,*p-S*)-**6c** was obtained as a purple powder (102 mg, 75.6 %).

Mp 247 °C (DSC); $[\alpha]^{20}$ +660 (436 nm, *c* 0.021 in CH_2Cl_2); (Found: C, 43.21; H, 2.07; N, 2.97. $C_{34}H_{18}Cl_2F_{10}Fe_2N_2O_2Zr$ requires C, 42.97; H, 1.91; N, 2.95%); ν_{max}(KBr)/cm^{-1} 3092, 2922, 1580, 1509, 1472, 1460, 1355, 1215, 1159, 1107, 1107, 985, 860, 838, 760, 668, 631 and 555; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$) 8.38 (1 H, s, C*H*N), 4.50 (1 H, m, 3-H), 4.50 (5 H, s, Cp), 4.45 (1 H, t, ^3J = 2.9 Hz, 4-H) and 4.32 (1 H, dd, ^3J = 2.9 Hz, ^4J = 1.4 Hz, 5-H); δ_F (564.1 MHz; CD_2Cl_2; CCl_3F) −144.4, −147.8 (each 1 F, each br, *o*-C_6F_5), −158.4 (1 F, t, $^3J_{FF}$ = 21.4 Hz, *p*-C_6F_5), −162.7 and −163.8 (each 1 F, each br, *m*-C_6F_5); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$) 180.5 (*C*HN), 125.3 (C-1), 71.4 (Cp), 69.8 (C-4), 66.2 (C-2), 66.0 (C-5) and 62.2 (C-3), signals for C_6F_5 were not observed; ^1H / ^1H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 8.38 / 4.50 (C*H*N / 3-H), 4.50 / 8.38, 4.45, 4.32 (3-H / C*H*N, 4-H, 5-H), 4.45 / 4.50, 4.32 (4-H / 3-H, 5-H) and 4.32 / 4.50, 4.45 (5-H / 3-H, 4-H); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.38 / 180.5 (*CH*N), 4.50 / 62.2 (3), 4.50 / 71.4 (Cp), 4.45 / 69.8 (4) and 4.32 / 66.0 (5); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.38 / 125.3, 69.8, 66.2 (C*H*N / C-1, C-4, C-2), 4.50 / 66.2 (3-H / C-2), 4.45 / 125.3, 66.2 (4-H / C-1, C-2) and 4.32 / 125.3, 66.2 (4-H / C-1, C-2).

Synthesis of the zwiterionic complexes:

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



(*p-S*,*p-S*)-**8a**

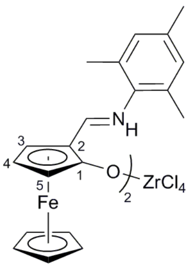
The alcohol (*p-S*)-**3a** (156 mg, 0.401 mmol) and zirconium tetrachloride (46.7 mg, 0.201 mmol) were dissolved in dichloromethane (5 ml), instantly giving a deep blue solution. The reaction mixture was stirred overnight and the solvent was removed, giving complex (*p-S*,*p-S*)-**8a** (187 mg, 92.0 %) as a deep blue solid.

Mp >300 °C (DSC); $[\alpha]^{20}$ +665 (436 nm, *c* 0.020 in CH_2Cl_2); (Found: C, 54.36; H, 5.31; N, 2.87. $C_{46}H_{54}Cl_4Fe_2N_2O_2Zr$ requires C, 54.61; H, 5.38; N, 2.77%); ν_{max}(KBr)/cm^{-1} 3144, 2962, 2924, 1621, 1478, 1340, 790, 757 and 733; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$; 218 K) 12.05 (1 H, d, ^3J = 15.8 Hz, N*H*), 8.30 (1 H, d, ^3J = 15.8 Hz, C*H*N), 7.44 (1 H, t, ^3J = 7.8 Hz, *p*-aryl), 7.28 (1 H, d, ^3J = 7.8 Hz, *m*-aryl^B), 7.22 (1 H, d, ^3J = 7.8 Hz, *m*-aryl^A), 5.67 (1 H, br d, ^3J = 2.8 Hz, 5-H), 4.77 (1 H, t, ^3J = 2.8 Hz, 4-H), 4.58 (5 H, s, Cp), 4.33 (1 H, br, 3-H), 3.36 (1 H, sept, ^3J = 6.8 Hz, C*H*^{A}), 3.00 (1 H, sept, ^3J = 6.8 Hz, C*H*^{B}), 1.34, 1.19 (each 3 H, each d, ^3J = 6.8 Hz, 2 x CH_3^{A}), 1.10 and 1.07 (each 3 H, each d, ^3J = 6.8 Hz, 2 x CH_3^{B}); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$; 218 K) 173.4 (*C*HN), 144.3 (*o*-aryl^A), 143.9 (*o*-aryl^B), 133.5 (*i*-aryl), 130.3 (C-1), 130.0 (*p*-aryl), 124.1 (*m*-aryl^A), 124.0 (*m*-aryl^B), 72.7 (C-4), 71.5 (Cp), 67.7 (C-5), 65.7 (C-3), 58.7 (C-2), 28.1 (*C*H^B), 28.0 (*C*H^A), 23.9 (*C*H$_3^{A}$), 23.4 (*C*H$_3^{B\prime}$), 23.3 (*C*H$_3^{A\prime}$) and 22.8 (*C*H$_3^{B}$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$; 218 K): δ_H / δ_H = 12.05 / 8.30 (N*H* / C*H*N), 8.30 / 12.05 (C*H*N / N*H*), 7.44 / 7.28, 7.22 (*p*-aryl / *m*-aryl^B, *m*-aryl^A), 7.28 / 7.44 (*m*-aryl^B / *p*-aryl), 7.22 / 7.44 (*m*-aryl^A / *p*-aryl), 5.67 / 4.77, 4.33 (5-H / 4-H, 3-H), 4.77 / 5.67, 4.33 (4-H / 5-H, 3-H), 4.33 / 5.67, 4.77 (3-H / 5-H, 4-H), 3.36 / 1.34, 1.19 (C*H*^{A} / CH_3^{A}), 3.00 / 1.10, 1.07 (C*H*^{B} / CH_3^{B}), 1.34, 1.19 / 3.36 (CH_3^{A} / C*H*^{A}) and 1.10, 1.07 / 3.00 (CH_3^{B} / C*H*^{B}); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$; 218 K): δ_H / δ_C = 8.30 / 173.4 (*CH*N), 7.44 / 130.0 (*p*-aryl), 7.28 / 124.0 (*m*-aryl^B), 7.22 / 124.1 (*m*-aryl^A), 5.67 / 67.7 (5), 4.77 / 72.7 (4), 4.58 / 71.5 (Cp), 4.33 /65.7 (3), 3.36 / 28.0 (*CH*^{A}), 3.00 / 28.1 (*CH*^{B}), 1.34, 1.19 / 23.9, 23.3 (CH_3^{A}) and 1.10, 1.07 / 23.4, 22.8 (CH_3^{B}); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$; 218 K): δ_H / δ_C = 8.30 / 133.5, 130.3, 65.7, 58.7 (C*H*N / *i*-aryl, C-1, C-3, C-2), 7.44 / 144.3, 143.9, 133.5, 124.1, 124.0 (*p*-aryl / *o*-aryl^A, *o*-aryl^B, *i*-aryl, *m*-aryl^A, *m*-aryl^B), 7.28 / 143.9, 133.5, 124.1 (*m*-aryl^B / *o*-aryl^B, *i*-aryl, *m*-aryl^A), 7.22 / 144.3, 133.5, 124.0 (*m*-aryl^A / *o*-aryl^A, *i*-aryl, *m*-aryl^B), 5.67 / 130.3, 72.7, 65.7, 58.7 (5-H / C-1, C-4, C-3, C-2), 4.77 / 130.3, 67.7, 65.7, 58.7 (4-H / C-1, C-5, C-3, C-2), 4.33 / 130.3, 72.7, 67.7, 58.7 (3-H / C-1, C-4, C-5, C-2), 3.36 / 144.3, 133.5, 124.1, 23.3 (C*H*^{A} / *o*-aryl^A, *i*-aryl, *m*-aryl^A, *C*H$_3^{A\prime}$), 3.00 / 143.9, 133.5, 124.0, 22.8 (C*H*^{B} / *o*-aryl^B, *i*-aryl, *m*-aryl^B, *C*H$_3^{B}$), 1.34 / 144.3, 28.0, 23.3 (CH_3^{A} / *o*-aryl^A, *C*H^A, *C*H$_3^{A\prime}$), 1.19 / 144.3, 28.0, 23.9 (CH_3^{A} / *o*-aryl^A, *C*H^A, *C*H$_3^{A}$), 1.10 / 143.9, 28.1, 23.4 (CH_3^{B} / *o*-aryl^B, *C*H^B, *C*H$_3^{B\prime}$) and 1.07 / 143.9, 28.1, 22.8 (CH_3^{B} / *o*-aryl^B, *C*H^B, *C*H$_3^{B}$).

Conversion of 8a to 6a by bis(dehydrochlorination):

Complex **8a** (40.0 mg, 0.0395 mmol) and lithium diisopropyl amide (8.46 mg, 0.0790 mmol) were dissolved in 0.7 ml of CD_2Cl_2. NMR-analysis of the mixture showed an immediate and complete conversion to complex **6a** with liberation of two equivalents of diisopropylamine. The isolation of complex **6a** via this route was not attempted.

(+)-Tetrachlorobis[(κO-(p-S)-N-2,4,6-trimethylphenyllferrocen-2-iminium-methylferrocen-1-olato zirconium ((*p-S*,*p-S*)-8b)

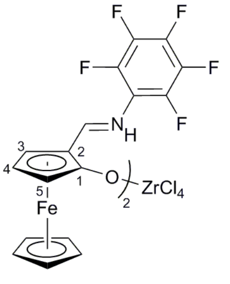


(*p-S*,*p-S*)-**8b**

A solution of alcohol (*p-S*)-**3b** (95.6 mg, 0.275 mmol) in dichloromethane (8 ml) was slowly added to a suspension of zirconium tetrachloride (32.1 mg, 0.138 mmol) in dichloromethane (10 ml), instantly giving a deep blue solution. The reaction mixture was stirred for three days and the solvent was evaporated to a volume of 5 ml. Addition of pentane (20 ml) yielded a blue precipitate, which was collected by filtration and dried in vacuo. Complex (*p-S*,*p-S*)-**8b** was obtained as a blue solid (95.0 mg, 74.2 %).

Mp (decomp.) 229 °C (DSC); $[\alpha]^{20}$ +661 (436 nm, *c* 0.021 in CH_2Cl_2); (Found: C, 51.55; H, 4.66; N, 3.15. $C_{40}H_{42}Cl_4Fe_2N_2O_2Zr$ requires C, 51.80; H, 4.56; N, 3.02%); ν_{max}(KBr)/cm^{-1} 3147, 3099, 2920, 1635, 1482, 1456, 1385, 1338, 1218, 1153, 1135, 1107, 1022, 862, 831, 776, 727, 654, 581 and 528; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$) 11.91 (1 H, d, ^3J = 15.4 Hz, N*H*), 8.29 (1 H, d, ^3J = 15.4 Hz, C*H*N), 7.00 (2 H, s, *m*-mes), 5.73, 4.30 (each 1 H, each br, 3-H, 5-H), 4.79 (1 H, t, ^3J = 2.8 Hz, 4-H), 4.61 (5 H, s, Cp), 2.40 (6 H, s, *o*-CH_3) and 2.33 (3 H, s, *p*-CH_3); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$) 173.3 (*C*HN), 140.0 (*p*-mes), 134.9 (*i*-mes), 133.5 (*o*-mes), 131.7 (C-1), 130.0 (*m*-mes), 73.2 (C-4), 72.2 (Cp), 68.5 (br),, 65.9 (C-3, C-5), 59.5 (C-2), 21.1 (*p*-*C*H$_3$) and 18.9 (*o*-*C*H$_3$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 11.91 / 8.29 (N*H* / C*H*N), 8.29 / 11.91 (C*H*N / N*H*), 7.00 / 2.40, 2.33 (*m*-mes / *o*-CH$_3$, *p*-CH$_3$), 5.73, 4.30 / 4.79 (3-H, 5-H / 4-H), 4.79 / 5.73, 4.30 (4-H / 3-H, 5-H), 2.40 / 7.00, 2.33 (*o*-CH_3 / *m*-mes, *p*-CH_3) and 2.33 / 7.00, 2.40 (*p*-CH_3 / *m*-mes, *o*-CH_3); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.29 / 173.3 (*CH*N), 7.00 / 130.0 (*m*-mes), 5.73, 4.30 / 68.5, 65.9 (3, 5), 4.79 / 73.2 (4), 4.61 / 72.2 (Cp), 2.40 / 18.9 (*o*-CH_3) and 2.33 / 21.1 (*p*-CH_3); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.29 / 134.9, 131.7, 59.5 (C*H*N / *i*-mes, C-1, C-2), 7.00 / 134.9, 130.0, 21.1, 18.9 (*m*-mes / *i*-mes, *m*-mes, *p*-*C*H$_3$, *o*-*C*H$_3$), 4.79 / 131.7, 59.5 (4-H / C-1, C-2), 4.30 / 131.7, 59.5 (3-H, 5-H / C-1, C-2), 2.40 / 134.9, 133.5, 130.0 (*o*-CH_3 / *i*-mes, *o*-mes, *m*-mes) and 2.33 / 140.0, 130.0 (*p*-CH_3 / *p*-mes, *m*-mes).

(+)-Tetrachlorobis[(κO-(p-S)-N-pentafluorophenylferrocen-2-iminium-methylferrocen-1-olato] irconium ((*p-S*,*p-S*)-8c)

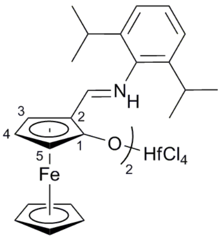


(*p-S*,*p-S*)-**8c**

A solution of alcohol (*p-S*)-**3c** (318 mg, 0.804 mmol) in dichloromethane (30 ml) was slowly added to a suspension of zirconium tetrachloride (93.7 mg, 0.402 mmol) in dichloromethane (30 ml), instantly giving a deep blue reaction mixture. The suspension was stirred for three days and the product was isolated by filtration, followed by drying in vacuo. Complex (*p-S*,*p-S*)-**8c** as obtained as a blue solid (279 mg, 67.8 %).

Mp 173 °C (DSC); $[\alpha]^{20}$ +1941 (436 nm, *c* 0.020 in CH_2Cl_2); (Found: C, 39.93; H, 2.05; N, 2.80. $C_{34}H_{20}Cl_4F_{10}Fe_2N_2O_2Zr$ requires C, 39.91; H, 1.97; N, 2.74%); ν_{max}(KBr)/cm^{-1} 3157, 3114, 1611, 1525, 1483, 1347, 1319, 1220, 1009, 984, 782 and 752; δ_H (500 MHz; CD_2Cl_2 / C_7D_8; $SiMe_4$) 11.32 (1 H, d, ^3J = 14.3 Hz, N*H*), 8.52 (1 H, d, ^3J = 14.3 Hz, C*H*N), 6.12, 4.21 (each 1 H, each br, 3-H, 5-H), 5.17 (1 H, t, ^3J = 2.9 Hz, 4-H) and 4.76 (5 H, s, Cp); δ_F (470 MHz; CD_2Cl_2 / C_7D_8; CCl_3F) −147.2 (2 F, br, *o*-C_6F_5), −153.4 (1 F, br, *p*-C_6F_5) and −160.3 (2 F, br, *m*-C_6F_5); 1D-tocsy (500 MHz; CD_2Cl_2 / C_7D_8; $SiMe_4$): δ_{irr} / δ_{res} = 8.52 / 11.32 (C*H*N / N*H*), 6.12 / 5.17, 4.21 (3-H, 5-H / 4-H, 3-H, 5-H), 5.17 / 6.12, 4.21 (4-H / 3-H, 5-H) and 4.21 / 6.12, 5.17 (3-H, 5-H / 3-H, 5-H, 4-H); due to the low solubility of complex (*p-S*,*p-S*)-**8c** no further NMR characterization was possible.

(+)-Tetrachlorobis[(κO-(p-S)-N-2,6-diisopropylphenylferrocen-2-iminium-methylferrocen-1-olato] hafnium ((*p-S*,*p-S*)-9a)



(*p-S*,*p-S*)-**9a**

The alcohol (*p-S*)-**3a** (200 mg, 0.514 mmol) and hafnium tetrachloride (82.3 mg, 0.257 mmol) were dissolved in dichloromethane (5 ml), instantly giving a deep blue solution. The reaction mixture was stirred for two days and the solvent was removed, giving 250 mg (88.5 %) of complex (*p-S*,*p-S*)-**9a** as a deep blue solid.

Mp >300 °C (DSC); $[\alpha]^{20}$ +659 (436 nm, *c* 0.020 in CH_2Cl_2); (Found: C, 49.53; H, 5.00; N, 2.47. $C_{46}H_{54}Cl_4Fe_2N_2O_2Hf$ requires C, 50.28; H, 4.95; N, 2.55%); ν_{max}(KBr)/cm^{-1} 3135, 3102, 2963, 2928, 2868, 1621, 1586, 1485, 1340, 1216, 1022, 832, 790, 757, 733 and 654; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$; 228 K) 12.07 (1 H, d, ^3J = 15.3 Hz, N*H*), 8.30 (1 H, d, ^3J = 15.3 Hz, C*H*N), 7.44 (1 H, t, ^3J = 7.8 Hz, *p*-aryl), 7.29 (1 H, d, ^3J = 7.8 Hz, *m*-aryl^A), 7.23 (1 H, d, ^3J = 7.8 Hz, *m*-aryl^B), 5.63 (1 H, bs, 5-H), 4.77 (1 H, br, 4-H), 4.57 (5 H, s, Cp), 4.31 (1 H, bs, 3-H), 3.37 (1 H, sept, ^3J = 6.5 Hz, C*H*^{A}), 3.01 (1 H, sept, ^3J = 6.5 Hz, C*H*^{B}), 1.36, 1.22 (each 3 H, each d, ^3J = 6.5 Hz, C*H*$_3^A$), 1.11 and 1.09 (each 3 H, each d, ^3J = 6.5 Hz, C*H*$_3^B$); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$; 228 K) 173.6 (*C*HN), 144.4 (*o*-aryl^A), 143.9 (*o*-aryl^B), 133.6 (*i*-aryl), 131.2 (C-1), 130.0 (*p*-aryl), 124.1, 124.0 (*m*-aryl^{A,B}), 72.6 (C-4), 71.5 (Cp), 67.3 (C-5), 65.4 (C-3), 58.9 (C-2), 28.2 (*C*H^B), 28.1 (*C*H^A), 24.0 (*C*H$_3^A$), 23.44 (*C*H$_3^{B\prime}$), 23.37 (*C*H$_3^{A\prime}$) and 22.9 (*C*H$_3^B$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$; 228 K): δ_H / δ_H = 12.07 / 8.30 (N*H* / C*H*N), 8.30 / 12.07 (C*H*N / N*H*), 7.44 / 7.29, 7.23 (*p*-aryl / *m*-aryl^A, *m*-aryl^B), 7.29 / 7.44 (*m*-aryl^A / *p*-aryl), 7.23 / 7.44 (*m*-aryl^B / *p*-aryl), 5.63 / 4.77 (5-H / 4-H), 4.77 / 5.63, 4.31 (4-H / 5-H, 3-H), 4.31 / 4.77 (3-H / 4-H), 3.37 / 1.36, 1.22 (C*H*^{A} / C*H*$_3^A$), 3.01 / 1.11, 1.09 (C*H*^{B} / C*H*$_3^B$), 1.36, 1.22 / 3.37 (C*H*$_3^A$ / C*H*^{A}) and 1.11, 1.09 / 3.01 (C*H*$_3^B$ / C*H*^{B}); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$; 228 K): δ_H / δ_C = 8.30 / 173.6 (*CH*N), 7.44 / 130.0 (*p*-aryl), 7.29, 7.23 / 124.1, 124.0 (*m*-aryl^A, *m*-aryl^B), 5.63 / 67.3 (5), 4.77 / 72.6 (4), 4.57 / 71.5 (Cp), 4.31 /65.4 (3), 3.37 / 28.1 (*CH*^{A}), 3.01 / 28.2 (*CH*^{B}), 1.36 / 24.0 (*CH*$_3^A$), 1.22 / 23.37 (*CH*$_3^{A\prime}$), 1.11 / 22.9 (*CH*$_3^B$) and 1.09 / 23.44 (*CH*$_3^{B\prime}$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$; 228 K): δ_H / δ_C = 7.44 / 144.4, 143.9, 133.6, 124.1, 124.0 (*p*-aryl / *o*-aryl^A, *o*-aryl^B, *i*-aryl, *m*-aryl^A, *m*-aryl^B), 7.29 / 133.6, 124.1, 124.0, 28.1 (*m*-aryl^A / *i*-aryl, *m*-aryl^B, *C*H^A), 7.23 / 133.6, 124.1, 124.0, 28.2 (*m*-aryl^B / *i*-aryl, *m*-aryl^A, *C*H^B), 5.63 / 131.2, 72.6, 65.4, 58.9 (5-H / C-1, C-4, C-3, C-2), 4.77 / 131.2, 67.3, 65.4, 58.9 (4-H / C-1, C-5, C-3, C-2), 4.31 / 131.2, 72.6, 67.3, 58.9 (3-H / C-1, C-4, C-5, C-2), 3.37 / 144.4, 133.6, 124.1, 124.0, 23.37 (C*H*^{A} / *o*-aryl^A, *i*-aryl, *m*-aryl^A, *C*H$_3^{A\prime}$), 3.01 / 143.9, 133.6, 124.1, 124.0, 22.9 (C*H*^{B} / *o*-aryl^B, *i*-aryl, *m*-aryl^B, *C*H$_3^B$), 1.36 / 144.4, 28.1, 23.37 (C*H*$_3^A$ / *o*-aryl^A, *C*H^A, *C*H$_3^{A\prime}$), 1.22 / 144.4, 28.1, 24.0 (C*H*$_3^{A\prime}$ / *o*-aryl^A, *C*H^A, *C*H$_3^A$), 1.11 / 143.9, 28.2, 23.44 (C*H*$_3^B$ / *o*-aryl^B, *C*H^B, *C*H$_3^{B\prime}$) and 1.09 / 143.9, 28.2, 22.9 (C*H*$_3^{B\prime}$ / *o*-aryl^B, *C*H^B, *C*H$_3^B$).

Conversion of 9a to 7a by bis(dehydrochlorination):

Complex **9a** (30.0 mg, 0.0273 mmol) and lithium diisopropyl amide (5.85 mg, 0.0546 mmol) were dissolved in 0.7 ml of CD_2Cl_2. NMR-analysis of the mixture showed an immediate and complete conversion to complex **7a** with liberation of two equivalents of diisopropylamine. The isolation of complex **7a** via this route was not attempted.

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 the respective complex was cooled to –78°C and 0.7 ml of CD_2Cl_2 were slowly added from a syringe. In case of the Ti-complex **22**, the solvent was precooled to –78 °C in a schlenk flask and quickly transferred to the NMR-tube using a teflon tube. The NMR-tube was immersed into the spectrometer, which was precooled to –80°C and then adjusted to the temperature used for the kinetic measurement. All measurements were repeated to proof reproducibility (series 1 and 2).

Calculation of the activation barrier:

The mean values were calculated as the average of the highest and lowest numbers obtained, with the deviation being the difference of the average value and either one of the extremes.

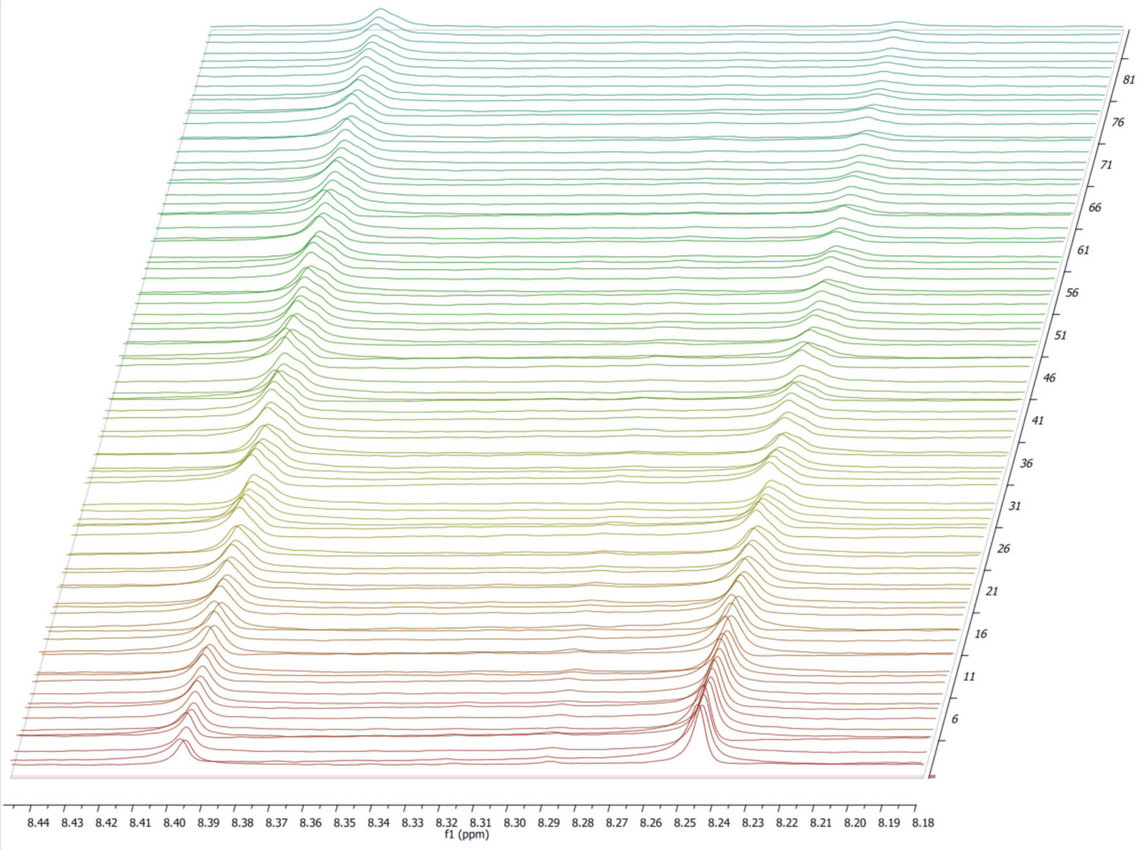
Dichlorobis[(κN,κO-(p-S)-N-2,6-diisopropylphenylferrocen-2-iminomethyl-ferrocen-1-olato]titanium (5a)

The kinetics were measured at –60°C.

Observation of decreasing of δ^1H (starting material) = 8.25 (1 H, CHN).
Observation of increasing of δ^1H (product) = 8.40 (1 H, CHN).

	Signal observed	tau	$\Delta G^\ddagger$ (kJ / mol)	$\Delta G^\ddagger$ (kcal / mol)
Series 1	$\delta = 8.25$	2561	65.49	15.64
	$\delta = 8.40$	1246	64.21	15.33
Series 2	$\delta = 8.25$	5584	66.87	15.96
	$\delta = 8.40$	5276	66.77	15.94

Time-dependant ^{1}H-NMR spectra (CHN-region, CD_2Cl_2, 213 K) from the kinetic experiments:



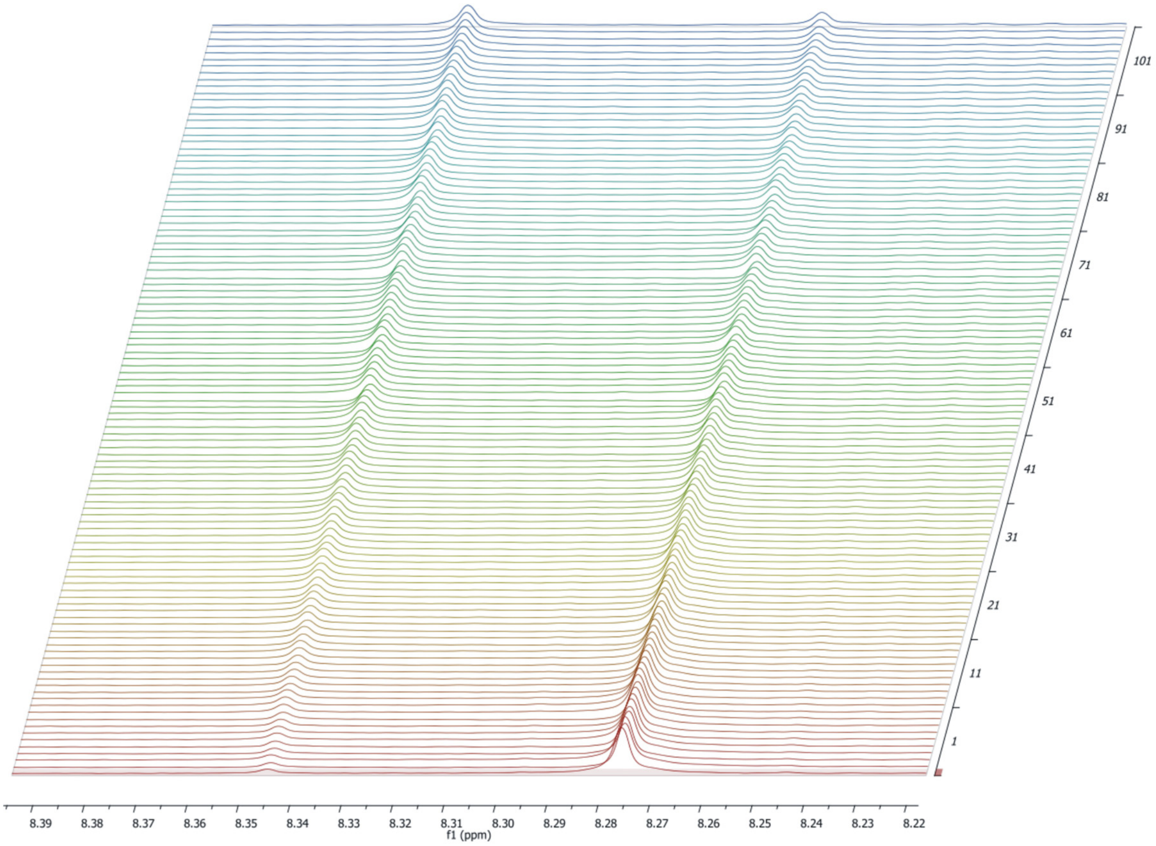
Dichlorobis[(κN,κO-(p-S)-N-2,6-diisopropylphenylferrocen-2-iminomethyl-ferrocen-1-olato]zirconium (6a)

The kinetics were measured at –25°C.

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	ΔG‡ (kJ / mol)	ΔG‡ (kcal / mol)
Series 1	δ = 8.28	2787	76.65	18.32
	δ = 8.35	2067	76.03	18.17
Series 2	δ = 8.28	3868	77.32	18.48
	δ = 8.35	3490	77.10	18.43

Time-dependant ^{1}H-NMR spectra (CHN-region, CD_2Cl_2, 248 K) from the kinetic experiments:



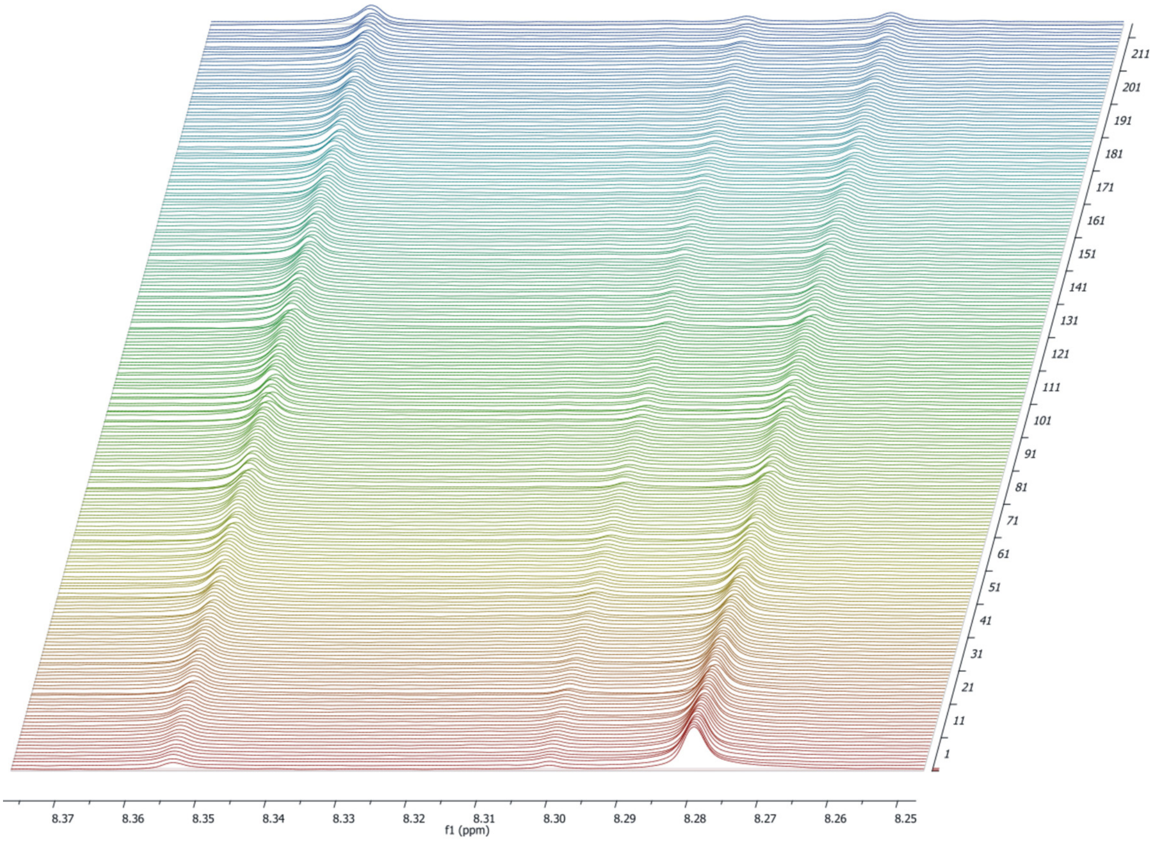
Dichlorobis[(κN,κO-(p-S)-N-2,6-diisopropylphenylferrocen-2-iminomethyl-ferrocen-1-olato]hafnium (7a)

The kinetics were measured at –5°C.

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	δ = 8.28	1695	81.96	19.57
	δ = 8.35	1128	81.05	19.35
Series 2	δ = 8.28	3802	83.76	20.00
	δ = 8.35	1108	81.01	19.35

Time-dependant ^{1}H-NMR spectra (CHN-region, CD_2Cl_2, 268 K) from the kinetic experiments:



Ethylene Polymerizations:

All polymerizations were performed in a thermostated Büchi glass autoclave system. The autoclave was evacuated and purged with argon for 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

Complex 5a:

Catalyst	µmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
5a	5	2000	20	1	0.109	10.9	134.3
5a	5	2000	20	1	0.086	8.60	
5a	5	2000	80	1	0.128	12.8	136.3
5a	5	2000	80	1	0.0960	9.60	

Complex 6a

Catalyst	µmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
6a	5	2000	20	2	0.221	11.1	138.3
6a	5	2000	20	2	0.160	8.00	
6a	5	2000	80	2	0.775	38.9	141.9
6a	5	2000	80	2	0.742	37.1	
6a	5	2000	100	2	1.36	68.0	
6a	5	2000	100	2	1.69	84.5	136.5
6a	5	2000	100	2	1.52	76.0	
6a	5	2000	125	2	2.12	106	134.3
6a	5	2000	125	2	2.46	123	

Complex 7a:

Catalyst	μmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
7a	5	2000	125	2	0.0951	4.76	132.8
7a	5	2000	125	2	0.116	5.82	

Complex 5c:

Catalyst	μmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
5c	5	2000	20	2	0.171	8.55	135.3
5c	5	2000	20	2	0.162	8.10	
5c	5	2000	80	2	0.182	9.10	132.1
5c	5	2000	80	2	0.266	13.3	

5 **Complex 6c:**

Catalyst	μmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
6c	5	2000	20	1	0.145	14.5	133.9
6c	5	2000	20	1	0.127	12.7	
6c	5	2000	80	1	0.571	57.1	132.6
6c	5	2000	80	1	0.596	59.6	

Complex 8a:

Catalyst	µmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
8a	5	2000	20	2	0.175	8.75	134.4
8a	5	2000	20	2	0.140	7.00	
8a	5	2000	80	2	1.02	51.0	138.3
8a	5	2000	80	2	0.739	37.0	
8a	5	2000	100	2	1.63	81.4	135.5
8a	5	2000	100	2	1.41	70.7	
8a	5	2000	125	2	1.99	99.5	130.7
8a	5	2000	125	2	2.17	109	

Complex 8b:

Catalyst	µmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
8b	5	2000	20	2	0.112	5.60	134.5
8b	5	2000	20	2	0.148	7.40	

Complex 8c:

Catalyst	µmol	MAO (eq)	*T*(°C)	Time (h)	Yield PE (g)	Activity[a]	Mp (DSC)
8c	5	2000	20	1	0.255	25.5	133.8
8c	5	2000	20	1	0.169	16.9	
8c	5	2000	80	1	0.417	41.7	131.8
8c	5	2000	80	1	0.627	62.7	

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

Comments on CHECKCIF:

4a: All alerts (PLAT220, 222, 241, 234, 242) are connected with the relative high thermal parameters of the iso-propyl-groups connected to the phenyl rings. Attempts to get a better model using split positions (using PART) didn't improve the results.

4c: All alerts (PLAT 220, 230, 234, 241) are coming from the "free" Cp-rings showing the typical "banana"-shaped form of the thermal ellipsoids. Also here a refinement with split positions didn't improve the model. Concerning the PLAT 601 allert, the low remaining electron density in the void couldn't be assign chemically meaningful to a solvent molecule.

5a: The disordered solvent molecule (refined with geometrical and thermal restraints) lead to the PLAT 411 alert. Alternatively we refined the structure without the solvent, that increase the size of the solvent accessible voids (PLAT 601). Therefor we decided to keep the solvent molecule. Also in this case the low remaining electron density in the void couldn't be assign chemically meaningful to futher solvent molecules. All other alerts are related to thermal motions of "free" Cp-rings and/or disordered iso-propyl-groups, also here refinements with split positions didn't improve the model.

7a: All alerts are related to thermal motions of "free" Cp-rings and/or disordered iso-propyl-groups, also here refinements with split positions didn't improve the model.