Supporting information for:

Control of *Ansa*-Zirconocene Stereochemistry by Reversible Exchange of Cyclopentadienyl and Chloride Ligands

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Contents

I. Synthesis and Characterization of New Compounds

A. General procedures.

All manipulations were performed under purified nitrogen in a drybox or on a high-vacuum line using Schlenk or high vacuum techniques unless otherwise noted. Nitrogen was purified by passage through columns of activated molecular sieves and Q-5 oxygen scavenger. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl. Pentane, hexanes, toluene and benzene were purified by passage through columns of activated alumina and BASF R3-11 oxygen-removal catalyst. C_6D_6, THF-d_8, Et_2O-d_{10} were purchased from Cambridge Isotope, degassed, dried over sodium/benzophenone ketyl and stored under vacuum. MeLi (Aldrich), ^{n}BuLi (Aldrich), PhLi (Acros), LiN^iPr$_2$ (Aldrich) and HCl (Et_2O solution, Aldrich) were titrated prior to use. Cyclododecanone (Acros), pyrrolidine (Acros), MeOH (Fisher), $Li[B(C_6F_5)_4](Et_2O)_{2.8}$ (Boulder Scientific), LiCl (Aldrich, anhydrous, <100 ppm), Cp_2ZrCl_2 (Boulder Scientific), Cp'_2ZrCl_2 (Boulder Scientific) and TEMPO (Aldrich) were used as received. Cyclopentadiene was thermally cracked from dicyclopentadiene (Fluka) and stored at –80 ^oC prior to use. Me_2SiCl_2 (Acros) was degassed and vacuum distilled from CaH_2 prior to use. Me_3SiCp was prepared by a literature method[1] or provided by Boulder Scientific. Cyclopenta-2,4-dienylidenecyclohexane and 6,6-dimethylfulvene were prepared by literature methods[2] and purified by vacuum distillation. In the case of 6,6-dimethylfulvene, GC-MS analysis showed the final product used for further reaction comprised 9/1 w/w dimethylfulvene/dicyclopentadiene. $Li_2[Me_2Si(3\text{-}^t\text{Bu-}C_5H_3)_2]$ (**1a**) was prepared by the reaction of $Me_2Si(3\text{-}^t\text{Bu-}C_5H_4)_2$ with 2

equiv ^{n}BuLi in Et_2O at –78 ^{o}C.[3] [$^{n}Bu_4N$]Cl (Fluka) was dried under vacuum at 130 ^{o}C for 16 h and recrystallized from dry THF prior to use. Complexes $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)_2$ (**2**),[4] $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ (**3**)[5] and *meso*-$Me_2Si(3\text{-}^{t}Bu\text{-}C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-**5a**)[6] were prepared as described previously.

NMR spectra were recorded on Bruker DRX-400 or DRX-500 spectrometers in J. Young NMR tubes at ambient probe temperature unless otherwise specified. ^{1}H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Coupling constants are reported in Hz. Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN). GC-MS analyses were performed using a Hewlett Packard/Agilent Technologies 6890 Series Gas Chromatograph and 5973 Network Mass Selective Detector. Melting points are uncorrected.

B. Synthesis of $Li_2[Me_2Si(3\text{-}R\text{-}C_5H_3)_2]$ (1b-g).

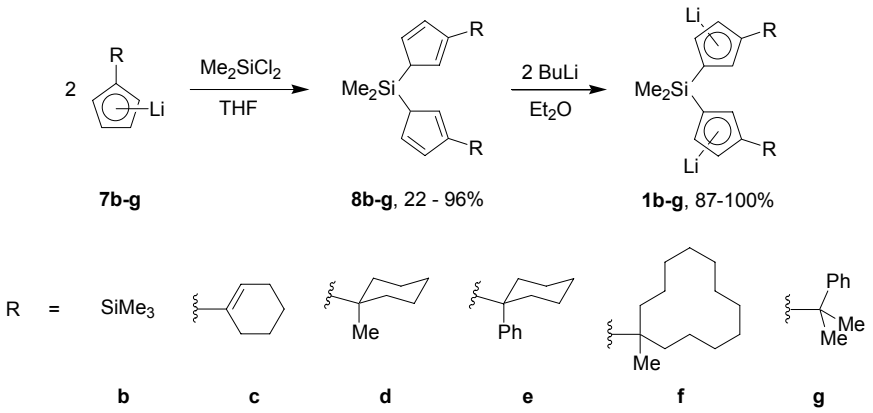
The general route used to prepare **1b-g** is shown in Scheme S1. General features of this route are noted in this section, and specific procedures for each case are discussed below.

$Li[RC_5H_4]$ salts **7b-e,g** (Scheme S1) were generated from $CpSiMe_3$[7] or simple fulvenes[8] using known procedures or modifications thereof.[9] Fulvene **9** (Scheme S2) was prepared from cyclododecanone[8b] and treated with MeLi to afford **7f** in 93% yield. Salts **7b-g** were treated with Me_2SiCl_2 to afford **8b-g**.[10] Aliquots of these reaction mixtures were quenched with water and analyzed by GC-MS. In the cases of **8b,c,e-g**, GC-MS

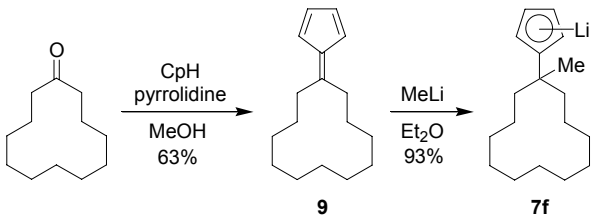
analysis showed the presence of **8** and RC_5H_5 (formed by protonation of **7**) in a ratio of *ca*. 4/1 after 3-12 h. GC-MS analysis of the reaction between **7d** and Me_2SiCl_2 showed **8d** as the only product. **8c,e** could only be purified with difficulty from contaminating RC_5H_5 by chromatography, which resulted in reduced yields (**8c**, 30%; **8e**, 22%).

8b-e,g were isolated in pure form as viscous oils and **8f** was isolated as a white solid. ^{1}H NMR and GC-MS analysis showed that these compounds exist as mixtures of isomers. Treatment of **8b-g** with 2 equiv ^{n}BuLi in Et_2O afforded $Li_2[Me_2Si(3\text{-}R\text{-}C_5H_3)_2]$ (**1b-g**) in 87-100% isolated yield. ^{1}H NMR analysis of **1b-g** in THF-d_8 showed the presence of only one isomer in each case.

Scheme S1



Scheme S2



$Me_2Si(3\text{-}SiMe_3\text{-}C_5H_4)_2$ (8b). A modification of a literature procedure was used.[10] A solution of Me_3SiCp (25.4 g, 179 mmol) in THF (150 mL) was prepared and cooled to –78 °C. A solution of ^{n}BuLi in hexanes (72 mL, 2.5 M, 180 mmol) was added and the resulting yellow solution was warmed to room temperature over 1 h. The mixture was added dropwise to Me_2SiCl_2 (10.9 mL, 89.5 mmol) over 90 min to afford an orange suspension. The mixture was stirred overnight, quenched with brine solution (200 mL), and diluted with Et_2O (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and evaporated under vacuum to afford an orange liquid. The liquid was vacuum distilled (bp 115 °C, 0.01 mmHg) to afford **8b** as a clear, colorless liquid (mixture of isomers, 20.3 g, 68%). The ^{1}H NMR spectrum was complex due to the presence of several isomers. ^{1}H NMR (C_6D_6): δ 6.88-6.47 (br m, vinylic C*H*), 3.72-2.86 (br m, allylic C*H*), 0.51-–0.12 (m, $SiMe_2$ and $SiMe_3$). GC-MS *m*/*z*: 332 (M^+).

$Li_2[Me_2Si(3\text{-}SiMe_3\text{-}C_5H_3)_2]$ (1b). A solution of **8b** (5.225 g, 15.70 mmol) in Et_2O (100 mL) was cooled to –78 °C. A solution of ^{n}BuLi in hexanes (12.0 mL, 2.61 M, 31.4 mmol) was added and the mixture was stirred and warmed to room temperature over 12 h. A white suspension formed. The solvent was removed under vacuum and pentane (50 mL) was added. The resulting suspension was filtered and the solid was washed with pentane (2 x 10 mL) and dried under vacuum to afford **1b** as a white solid (5.38 g, 100%). ^{1}H NMR (THF-d_8): δ 6.21 (s, 2H, Cp), 6.17 (s, 2H, Cp), 6.05 (s, 2H, Cp), 0.33 (s, 6H, $SiMe_2$), 0.10 (s, 18H, $SiMe_3$).

Li[(cyclohexen-1-yl)-C_5H_4] (7c). A solution of cyclopenta-2,4-dienylidene-cyclohexane (20.0 mL, 131 mmol) in THF (250 mL) was cooled to –78 °C and a solution of $LiN(i\text{-}Pr)_2$ (heptane/THF/ethylbenzene, 59.8 mL, 2.09 M, 125 mmol) was added. The

mixture was stirred for 2 h at –78 °C and warmed to room temperature overnight. The solvent was removed under vacuum and pentane (100 mL) was added. The suspension was filtered through a glass frit and the solid was washed with pentane (2 x 75 mL). The solid was dried under vacuum overnight affording **7c** as a cream-colored solid (18.46 g, 97%). ^{1}H NMR (THF-d_8): δ 5.78 (t, *J*=3, 2H, Cp), 5.63 (m, 1H, C*H*), 5.56 (t, *J*=3, 2H, Cp), 2.36 (m, 2H, CH_2), 2.11 (m, 2H, CH_2), 1.69 (m, 2H, CH_2), 1.60 (m, 2H, CH_2).

$Me_2Si\{3\text{-(cyclohexen-1-yl)-}C_5H_4\}_2$ (8c). A solution of **7c** (9.196 g, 60.44 mmol) in THF (30 mL) was added dropwise over 80 min to neat Me_2SiCl_2 (3.68 mL, 30.2 mmol) at room temperature. The mixture was stirred for 17 h at room temperature. An aliquot of the reaction mixture was quenched with water and analyzed by GC-MS, which showed that **8c** and cyclopenta-2,4-dienylidene-cyclohexane were present in a 85/15 ratio. The mixture was diluted with water (100 mL) and extracted with Et_2O (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$, filtered through Celite, and evaporated under vacuum to afford an orange oil. The oil was purified by column chromatography (silica; petroleum ether then 9/1 v/v petroleum ether/Et_2O) to afford **8c** as a viscous yellow oil (3.18 g, 30%). The purity of this material was *ca*. 97 mol% by GC-MS and was sufficient for further reaction. The ^{1}H NMR spectrum was complex due to the presence of several isomers. ^{1}H NMR (C_6D_6): δ 6.99-6.80 (br m), 6.63-6.30 (br m), 6.11 (br m), 5.88-5.81 (br m), 5.46-5.00 (br m), 3.49-2.97 (br m), 2.50-1.90 (br m), 1.70-1.40 (br m), 0.70-–0.30 (br m). GC-MS *m*/*z*: 348 (M^+).

$Li_2[Me_2Si\{3\text{-(cyclohexen-1-yl)-}C_5H_3\}_2]$ (1c). A solution of **8c** (3.176 g, 9.111 mmol) in Et_2O (50 mL) was cooled to –78 °C and a solution of ^{n}BuLi in hexanes (7.33 mL, 19.1 mmol) was added. The mixture was stirred and warmed to room temperature

over 19 h. A white suspension formed. The solvent was removed under vacuum and pentane (35 mL) was added. The suspension was stirred briefly and filtered. The solid was washed with pentane (35 mL) and dried under vacuum to afford **1c** as a white solid (3.269 g, 100%). ^{1}H NMR (THF-d_8): δ 6.10 (t, *J*=2, 2H, Cp), 5.93 (t, *J*=2, 2H, Cp), 5.89 (t, *J*=2, 2H, Cp), 5.66 (m, 2H, C*H*), 2.37 (m, 4H, CH_2), 2.09 (m, 4H, CH_2), 1.67 (m, 4H, CH_2), 1.57 (m, 4H, CH_2), 0.28 (s, 6H, $SiMe_2$).

Li[(1-Me-Cy)-C_5H_4] (7d). A modification of a literature procedure was used.[11] A solution of MeLi in Et_2O (80.0 mL, 1.47 M, 118 mmol) was diluted with Et_2O (500 mL) and cooled to –78 °C. Cyclopenta-2,4-dienylidene-cyclohexane (18.8 mL, 123 mmol) was added and the mixture was vigorously stirred and warmed to room temperature over 2 h, resulting in a thick, white suspension. The mixture was filtered. The solid was washed with Et_2O and dried under vacuum overnight to afford **7d** as a white solid (19.2 g, 97%). ^{1}H NMR (THF-d_8): δ 5.54 (m, 2H, Cp), 5.50 (m, 2H, Cp), 1.83 (m, 2H, Cy), 1.54 (m, 2H, Cy), 1.47-1.44 (m, 5H, Cy), 1.34 (m, 1H, Cy), 1.14 (s, 3H, Me). ^{13}C{^{1}H} NMR (THF-d_8): δ 130.6, 101.6, 100.4, 41.2, 35.6, 31.8, 27.9, 24.1.

Me_2Si{3-(1-Me-Cy)-C_5H_4}$_2$ (8d). A solution of **7d** (18.39 g, 109.3 mmol) in THF (45 mL) was added dropwise over 4 h to neat Me_2SiCl_2 (6.65 mL, 54.7 mmol) at room temperature, and the mixture was stirred for 3.5 h. The resulting suspension was poured into saturated aqueous NH_4Cl (100 mL). The mixture was extracted with Et_2O (50 mL). The organic layer was separated, dried over $MgSO_4$, filtered through a pad of Celite and evaporated under vacuum to afford an amber oil (20.0 g, 96%). GC-MS analysis showed that this material was pure **8d**. NMR analysis showed that this material comprised 76 mol % of *rac*- and *meso*-Me_2Si{2-(1-Me-Cy)-cyclopenta-1,3-dien-5-yl}$_2$

(*rac*/*meso* = 1.2/1 based on the intensity of $SiMe_2$ resonances) and other minor isomers. Anal. Calcd for $C_{26}H_{40}Si$: C, 82.03; H, 10.59. Found: C, 81.87; H, 10.39. ^{1}H NMR for *rac*/*meso*-Me_2Si\{2-(1-Me-Cy)-cyclopenta-1,3-dien-5-yl\}$_2$ (C_6D_6): δ 6.68 (s, vinylic C_5H_4) and 6.67 (s, vinylic C_5H_4), 2H total; 6.50 (s, 2H, vinylic C_5H_4), 6.19 (s, 2H, vinylic C_5H_4), 3.27 (s, 2H, allylic C_5H_4), 1.87 (br m, 4H total, Cy), 1.56-1.32 (br m, 16H, Cy), 1.17 (s, 6H, Me), –0.16 (s, *rac*-$SiMe_2$ and *meso*-$SiMe_2$) and –0.22 (s, *meso*-$SiMe_2$), 6H total. GC-MS *m*/*z*: 380 (M^+).

Li_2[Me_2Si\{3-(1-Me-Cy)-C_5H_3\}$_2$] (1d). A solution of **8d** (7.77 g, 20.4 mmol) in Et_2O (100 mL) was cooled to –78 °C. A solution of ^{n}BuLi in hexanes (17.2 mL, 2.61 M, 44.9 mmol) was added and the mixture was stirred and warmed to room temperature over 16 h. A white precipitate formed. The solvent was removed under vacuum and pentane (250 mL) was added. The resulting white suspension was filtered to afford a solid, which was washed with pentane and dried under vacuum to afford **1d** as a white solid (6.94 g, 87%). ^{1}H NMR (THF-d_8): δ 5.88 (m, 4H, Cp), 5.74 (t, *J*=2, 2H, Cp), 1.82 (m, 4H, Cy), 1.50 (br m, 14H, Cy), 1.30 (br m, 2H, Cy), 1.15 (s, 6H, Me), 0.26 (s, 6H, $SiMe_2$). ^{13}C\{^{1}H\} NMR (THF-d_8): δ 133.4, 111.3, 110.5, 107.4, 103.4, 41.4, 35.5, 30.9, 27.9, 24.1, 2.4.

Li[(1-Ph-Cy)-C_5H_4] (7e). A modification of a literature procedure was used.[12] A solution of cyclopenta-2,4-dienylidene-cyclohexane (16.0 mL, 105 mmol) in Et_2O (500 mL) was cooled to –78 °C. A solution of PhLi in *n*-Bu_2O (60.0 mL, 1.88 M, 113 mmol) was added and the mixture was vigorously stirred and warmed to room temperature over 16 h, resulting in a thick, white suspension. The mixture was filtered. The solid was washed with Et_2O and dried under vacuum overnight to afford **7e** as a white solid (21.5 g,

89%). ^{1}H NMR (THF-d_8): δ 7.39 (d, *J*=7, 2H, *o*-Ph), 7.15 (t, *J*=7, 2H, *m*-Ph), 6.96 (t, *J*=7, 1H, *p*-Ph), 5.53 (m, 4H, Cp), 2.20 (br m, 4H, Cy), 1.67 (br m, 2H, Cy), 1.43 (br m, 4H, Cy).

$Me_2Si\{3\text{-}(1\text{-}Ph\text{-}Cy)\text{-}C_5H_4\}_2$ (8e). A solution of **7e** (13.84 g, 60.09 mmol) in THF (40 mL) was added dropwise over 3 h to neat Me_2SiCl_2 (3.66 mL, 30.0 mmol) at room temperature. The mixture was stirred for 12 h and an orange suspension formed. An aliquot of the reaction mixture was quenched with water and analyzed by GC-MS, which showed that **8e** and C_5H_5-(1-Ph-Cy) were present in a 4/1 ratio. The mixture was poured into water (100 mL) to afford a yellow suspension. The suspension was extracted with Et_2O (50 mL). The organic layer was separated, dried over $MgSO_4$, filtered through Celite, and evaporated under vacuum to afford an amber oil. The oil was purified by column chromatography (silica; pentane then 95/5 v/v pentane/Et_2O) to afford **8e** as an amber oil (3.28 g, 22%). The purity of this material was *ca*. 97 mol% by GC-MS and was sufficient for further reaction. NMR analysis showed that this material comprised 74 mol % of *rac*- and *meso*-$Me_2Si\{2\text{-}(1\text{-}Ph\text{-}Cy)\text{-}cyclopenta\text{-}1,3\text{-}dien\text{-}5\text{-}yl\}_2$ (*rac*/*meso* = 1/1 based on the intensity of $SiMe_2$ resonances) and other minor isomers. ^{1}H NMR for *rac*/*meso*-$Me_2Si\{2\text{-}(1\text{-}Ph\text{-}Cy)\text{-}cyclopenta\text{-}1,3\text{-}dien\text{-}5\text{-}yl\}_2$ (C_6D_6): δ 7.36 (d, *J*=8, 4H, *o*-Ph), 7.21 (t, *J*=8, 4H, *m*-Ph), 7.06 (t, *J*=8, 2H, *p*-Ph), 6.49 (s, 2H, vinylic C_5H_4), 6.36 (s, 2H, vinylic C_5H_4), 6.14 (s, vinylic C_5H_4) and 6.11 (s, vinylic C_5H_4), 2H total; 3.17 (s, 2H, allylic C_5H_4), 2.11 (br m, 8H, Cy), 1.65-1.30 (br m, 12H, Cy), –0.24 (s, *meso*-$SiMe_2$), –0.27 (s, *rac*-$SiMe_2$), –0.32 (s, *meso*-$SiMe_2$). GC-MS *m*/*z*: 504 (M^+).

$Li_2[Me_2Si\{3\text{-}(1\text{-}Ph\text{-}Cy)\text{-}C_5H_4\}_2]$ (1e). A solution of **8e** (3.275 g, 6.487 mmol) in Et_2O (30 mL) was cooled to –78 °C. A solution of ^{n}BuLi in hexanes (5.0 mL, 2.6 M, 13

mmol) was added and the mixture was stirred and warmed to room temperature over 16 h. A white suspension formed. The solvent was removed under vacuum and pentane (20 mL) was added. The resulting suspension was filtered and the solid was washed with pentane (20 mL) and dried under vacuum to afford **1e** as a white solid (3.03 g, 90%). ^{1}H NMR (THF-d_8): δ 7.40 (d, *J*=8, 4H, *o*-Ph), 7.15 (t, *J*=8, 4H, *m*-Ph), 6.95 (t, *J*=8, 2H, *p*-Ph), 5.83 (s, 4H, Cp), 5.61 (s, 2H, Cp), 2.29 (br s, 4H, Cy), 2.13 (br m, 4H, Cy), 1.62 (br s, 4H, Cy), 1.41 (br m, 8H, Cy), 0.19 (s, 6H, $SiMe_2$).

Cyclopenta-2,4-dienylidene-cyclododecane (9). A solution of cyclododecanone (40.00 g, 219.4 mmol) and pyrrolidine (27.5 mL, 329 mmol) in MeOH (150 mL) was prepared in air. Cyclopentadiene (44.8 mL, 549 mmol) was added and the yellow mixture was vigorously stirred for 20 h at room temperature. A yellow crystalline precipitate formed. The mixture was filtered, and the precipitate was washed with cold MeOH (2 x 20 mL) and dried under vacuum to afford **9** as a yellow crystalline solid (31.63 g, 63%). Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.67; H, 11.32. ^{1}H NMR (C_6D_6): δ 6.59 (m, 4H, C_5H_4), 2.37 (m, 4H, C=CCH_2), 1.44 (m, 4H, C=C$CH_2C$$H_2$), 1.23 (m, 14H, $C_{12}H_{22}$). ^{13}C{^{1}H} NMR (C_6D_6): δ 156.9, 144.8, 131.4, 121.4, 31.7, 26.2, 26.1, 25.6, 23.7, 22.8. GC-MS *m*/*z*: 230 (M^+). Mp 55 ^{o}C.

Li[(1-Me-*cyclo*-$C_{12}H_{22}$)-C_5H_4] (7f). A solution of **9** (12.22 g, 53.05 mmol) in Et_2O (500 mL) was cooled to 0 ^{o}C. A solution of MeLi in Et_2O (35.9 mL, 1.55 M, 55.7 mmol) was added and the mixture was vigorously stirred and warmed to room temperature over 4 h. A white precipitate formed. The mixture was filtered and the solid was washed with Et_2O and dried under vacuum for 24 h to afford **7f** as a white solid (12.38 g, 93%). ^{1}H NMR (THF-d_8): δ 5.57 (s, 2H, Cp), 5.53 (s, 2H, Cp), 1.64-1.10 (m,

25H, Me and $C_{12}H_{22}$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 129.0, 100.5, 99.8, 36.7, 36.2, 30.6, 27.1, 26.2, 22.7, 22.5, 20.0.

***rac*/*meso*-Me$_2$Si{2-(1-Me-*cyclo*-C$_{12}$H$_{22}$)-cyclopenta-1,3-dien-5-yl}$_2$ (8f).** A solution of **7f** (12.51 g, 49.56 mmol) in THF (60 mL) was added dropwise over 2 h to neat Me_2SiCl_2 (3.0 mL, 25 mmol) at room temperature. The mixture was stirred for 5 h. An aliquot of the reaction mixture was quenched with water and analyzed by GC-MS which showed **8f** and C_5H_5-(1-Me-*cyclo*-$C_{12}H_{22}$) in a 9:1 ratio. The mixture was poured into saturated aqueous NH_4Cl (80 mL). The mixture was diluted with water (50 mL) and extracted with Et_2O (70 mL). The organic layer was separated, dried over $MgSO_4$, filtered through Celite, and evaporated under vacuum to afford an amber oil. Pentane (100 mL) was added and the resulting solution was cooled to –80 °C for 16 h. A white precipitate formed and was isolated by filtration and dried under vacuum (7.428 g, 97% pure **8f** by GC-MS). The solid was redissolved in pentane (100 mL) and cooled to –80 °C for 16 h. A precipitate formed and was isolated by filtration and dried under vacuum to afford pure **8f** as a white solid (4.68 g, 34%, *rac*/*meso* = 1.2/1). Anal. Calcd for $C_{38}H_{64}Si$: C, 83.13; H, 11.75. Found: C, 82.78; H, 11.82. ^1H NMR (C_6D_6): δ 6.71 (m, 2H, vinylic C_5H_4), 6.50 (m, 2H, vinylic C_5H_4), 6.20 (s, 2H, vinylic C_5H_4), 3.26 (s, allylic C_5H_4) and 3.22 (s, allylic C_5H_4), 2H, total; 1.73 (br m, 2H, $C_{12}H_{22}$), 1.60 (br m, 6H, $C_{12}H_{22}$), 1.37 (br m, 36H, $C_{12}H_{22}$), 1.17 (s, 6H, Me), –0.13 (s, *rac*-$SiMe_2$ and *meso*-$SiMe_2$) and –0.21 (s, *meso*-$SiMe_2$), 6H total. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 155.5, 133.7, 131.6, 125.1, 125.0, 49.9, 49.6, 38.2, 34.5, 34.2, 28.6, 28.5, 27.5, 26.8, 23.2, 23.1, 22.8, 20.5, 20.3, –4.3, –4.4, –5.2. GC-MS *m*/*z*: 548 (M^+ – H). Mp 82-84 °C.

$Li_2[Me_2Si\{3\text{-}(1\text{-}Me\text{-}cyclo\text{-}C_{12}H_{22})\text{-}C_5H_3\}_2]$ (1f). A solution of **8f** (4.048 g, 7.373 mmol) in Et_2O (200 mL) was cooled to 0 °C and a solution of ^{n}BuLi in hexanes (6.21 mL, 2.61 M, 16.2 mmol) was added. The mixture was stirred and warmed to room temperature over 16 h. A white precipitate formed. The solvent was removed under vacuum and pentane (100 mL) was added. The resulting suspension was filtered and the solid was washed with pentane and dried under vacuum to afford **1f** as a white solid (3.617 g, 87%). ^{1}H NMR (THF-d_8): δ 5.89 (m, 4H, Cp), 5.75 (t, *J*=3, 2H, Cp), 1.64 (br m, 4H, $C_{12}H_{22}$), 1.56 (br m, 4H, $C_{12}H_{22}$), 1.39 (br s, 20H, $C_{12}H_{22}$), 1.30 (br m, 16H, $C_{12}H_{22}$), 1.11 (s, 6H, Me), 0.25 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 132.2, 111.0, 110.6, 107.9, 103.9, 37.8, 37.2, 31.8, 28.2, 27.2, 23.8, 23.5, 21.1, 2.5.

$Li[CMe_2Ph\text{-}C_5H_4]$ (7g). A solution of PhLi in *n*-Bu_2O (39.9 mL, 1.88 M, 75.0 mmol) was diluted with pentane (200 mL). 6,6-Dimethylfulvene (11.7 mL, 89 wt% pure, 86.3 mmol) was added and the mixture was stirred at room temperature for 1 h. The resulting pink suspension was filtered through a medium glass frit. The solid was washed with Et_2O and dried under vacuum to afford **7g** as a cream-colored solid (12.3 g, 86%). ^{1}H NMR (THF-d_8): δ 7.30 (d, *J*=8, 2H, *o*-Ph), 7.08 (t, *J*=7, 2H, *m*-Ph), 6.94 (t, *J*=7, 1H, *p*-Ph), 5.56 (s, 4H, Cp), 1.61 (s, 6H, Me).

$Me_2Si(3\text{-}CMe_2Ph\text{-}C_5H_4)_2$ (8g). A solution of **7g** (2.485 g, 13.06 mmol) in THF (30 mL) was prepared. Me_2SiCl_2 (0.795 mL, 6.530 mmol) was added at room temperature and the mixture was stirred for 3.5 h. The mixture was diluted with water (40 mL) and extracted with Et_2O (30 mL). The organic layer was separated, washed with water (2 x 40 mL), dried over $MgSO_4$, filtered, evaporated under vacuum, and finally heated at 80 °C under vacuum (10^{-3} mmHg) to afford an amber oil (mixtue of isomers,

2.60 g, 95%). GC-MS analysis showed that this material was pure **8g**. NMR analysis showed that this material comprised 62 mol % of *rac*- and *meso*-$Me_2Si\{2\text{-}CMe_2Ph\text{-}cyclopenta\text{-}1,3\text{-}dien\text{-}5\text{-}yl\}_2$ (*rac*/*meso* = 1.1/1 based on the intensity of $SiMe_2$ resonances) and other isomers. Anal. Calcd for $C_{30}H_{36}Si$: C, 84.84, H, 8.54. Found: C, 84.98, H, 8.63. ^{1}H NMR for $Me_2Si\{2\text{-}(CMe_2Ph)\text{-}cyclopenta\text{-}1,3\text{-}dien\text{-}5\text{-}yl\}_2$ (toluene-d_8): δ 7.38 (d, *J*=8, 4H, *o*-Ph), 7.20 (t, *J*=8, 4H, *m*-Ph), 7.08 (t, *J*=8, 2H, *p*-Ph), 6.41 (s, 2H, vinylic C_5H_4), 6.38 (s, 2H, vinylic C_5H_4), 6.20 (s, 2H, vinylic C_5H_4), 3.21 (s, 2H, allylic C_5H_4), 1.57 (s, 12H, Me), –0.19 (s, *rac*-$SiMe_2$ and *meso*-$SiMe_2$), –0.24 (s, *meso*-$SiMe_2$), 6H total. GC-MS *m*/*z*: 424 (M^+).

Li_2[$Me_2Si(3\text{-}CMe_2Ph\text{-}C_5H_4)_2$] (1g). A solution of **8g** (2.53 g, 5.95 mmol) in Et_2O (40 mL) was cooled to –78 °C and a solution of ^{n}BuLi in hexanes (4.47 mL, 2.66 M, 11.9 mmol) was added. The mixture was stirred for 4 h at –78 °C and then warmed to 0 °C. The resulting pale orange suspension was stirred and warmed to room temperature overnight. The solvent was removed under vacuum and pentane (40 mL) was added. The resulting suspension was stirred for 90 min and filtered. The solid was washed with pentane and dried under vacuum to afford **1g** as a cream-colored solid (2.35 g, 91%). ^{1}H NMR (THF-d_8): δ 7.35 (d, *J*=8, 4H, *o*-Ph), 7.09 (t, *J*=7, 4H, *m*-Ph), 6.95 (t, *J*=7, 2H, *p*-Ph), 5.92 (t, *J*=2, 2H, Cp), 5.90 (t, *J*=2, 2H, Cp), 5.67 (t, *J*=3, 2H, Cp), 1.61 (s, 12H, Me), 0.25 (s, 6H, $SiMe_2$).

C. Synthesis of *ansa*-Zirconocenes.

***rac*-$Me_2Si(\eta^5\text{-}3\text{-}SiMe_3\text{-}C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-4b).** A flask was charged with **1b** (1.004 g, 2.914 mmol) and **2** (1.523 g, 2.914 mmol) and cooled to –196

^{o}C. THF (125 mL) was added by vacuum transfer and the mixture was warmed to room temperature over 15 min to afford a yellow solution. The solution was stirred for 24 h at room temperature. The solvent was removed under vacuum and pentane (10 mL) was added. The resulting suspension was filtered and the solid was washed with pentane (2 x 10 mL). The combined filtrate and wash was evaporated under vacuum to afford *rac*-**4b** as a yellow solid (1.85 g, 100%), which was pure by NMR. Analytical samples were prepared by recrystallization from pentane at –35 ^{o}C over 1 d. Several elemental analyses of several different spectroscopically pure, recrystallized samples were erroneous. Anal. Calcd for $C_{27}H_{54}N_2Si_5Zr + 0.42C_5H_{12}$ (pentane content established by NMR): C, 52.26; H, 8.90; N, 4.19. Found: C, 51.38; H, 8.40; N, 4.05. ^{1}H NMR (C_6D_6): δ 7.18 (t, *J*=2, 2H, Cp), 6.08 (s, 2H, Cp), 6.07 (s, 2H, Cp), 3.37 (dt, *J*=16, 2; 2H, NCH_2), 3.00 (dt, *J*=16, 8; 2H, NCH_2), 1.01 (m, 2H, NCH_2CH_2), 0.48 (s, 6H, $SiMe_2$), 0.29 (s, 18H, $SiMe_3$), 0.24 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 131.9, 125.1, 118.8, 113.3, 110.7, 46.7, 28.3, 4.0, 0.2, –4.5.

***rac*/*meso*-$Me_2Si(\eta^5$-3-$SiMe_3$-$C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*/*meso*-4b, *rac*/*meso* = 1.5/1).** A flask was charged with **1b** (345 mg, 1.00 mmol) and **2** (523 mg, 1.00 mmol), and THF (25 mL) was added by vacuum transfer at –196 ^{o}C. The mixture was warmed to room temperature over 5 min to afford a pale-yellow solution. The mixture was stirred for 2 h at room temperature and the solvent was removed under vacuum. Pentane (15 mL) was added and the mixture was stirred to afford a suspension of a white precipitate in a yellow supernatant. The mixture was filtered through Celite. The Celite was washed with pentane (2 x 5 mL), and the washes were combined with the filtrate. The combined filtrate and washes were again filtered through Celite, and the

Celite was washed with pentane (2 x 5 mL). The clear combined filtrate and washes were evaporated under vacuum to afford *rac/meso*-**4b** (*rac*/*meso* = 1.5/1) as a yellow solid (582 mg, 91%). Characterization data for *rac*-**4b** in C_6D_6 are reported above. ^{1}H NMR for *rac*-**4b** in THF-d_8: δ 7.04 (t, *J*=2, 2H, Cp), 6.03 (t, *J*=2, 2H, Cp), 5.99 (t, *J*=2, 2H, Cp), 3.30 (dt, *J*=16, 1; 2H, NCH_2), 3.26 (dt, *J*=16, 8; 2H, NCH_2), 1.00 (m, 2H, NCH_2CH_2), 0.67 (s, 6H, $SiMe_2$), 0.17 (s, 18H, $SiMe_3$), 0.15 (s, 18H, $SiMe_3$). ^{1}H NMR for *meso*-**4b** in THF-d_8: δ 6.70 (t, *J*=2, 2H, Cp), 6.25 (m, 4H, Cp), 3.13 (t, *J*=6, 2H, NCH_2), 2.88 (t, *J*=6, 2H, NCH_2), 1.11 (m, 2H, NCH_2CH_2), 0.74 (s, 3H, $SiMe_2$), 0.57 (s, 3H, $SiMe_2$), 0.20 (s, 18H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 0.07 (s, 9H, $SiMe_3$).

***rac*-$Me_2Si(\eta^5$-3-$SiMe_3$-$C_5H_3)_2ZrCl_2$ (*rac*-6b).** A flask was charged with *rac*-**4b** (497 mg, 779 μmol) and pentane (15 mL). A solution of HCl in Et_2O (4.7 mL, 1.0 M, 4.7 mmol) was added and the mixture was stirred at room temperature for 5 min. A white suspension formed immediately. The volatiles were removed under vacuum and pentane (10 mL) was added. The mixture was filtered and the solid was washed with pentane (10 mL). The combined filtrate and wash was evaporated under vacuum to afford *rac*-**6b** as a white solid (375 mg, 98%). NMR data for this material matched literature data.[10]

***rac*-$Me_2Si\{\eta^5$-3-(cyclohexen-1-yl)-$C_5H_3\}_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-4c).** A flask was charged with **1c** (1.014 g, 2.814 mmol) and **2** (1.471 g, 2.814 mmol), and THF (125 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to room temperature over 10 min to afford a yellow solution. The solution was heated to 60 °C for 20 h, and then cooled to room temperature. The solvent was removed under vacuum. Pentane (40 mL) was added and the resulting suspension was filtered. The filtrate was evaporated under vacuum to afford *rac*-**4c** as a fluffy yellow solid (1.84 g,

100%), which was pure by NMR. An analytical sample was prepared by recrystallization from hexanes at –35 °C over 1 d. Anal. Calcd for $C_{33}H_{54}N_2Si_3Zr$: C, 60.58; H, 8.32; N, 4.28. Found: C, 60.54; H, 8.68; N, 4.52. ^{1}H NMR (C_6D_6): δ 7.08 (t, *J*=3, 2H, Cp), 6.02 (m, 2H, C*H*), 5.90 (t, *J*=3, 2H, Cp), 5.88 (t, *J*=3, 2H, Cp), 3.35 (dt, *J*=16, 2; 2H, NCH_2), 3.02 (dt, *J*=16, 8; 2H, NCH_2), 2.33 (m, 4H, CH_2), 2.08 (m, 4H, CH_2), 1.61 (m, 4H, CH_2), 1.51 (m, 4H, CH_2), 0.98 (m, 2H, NCH_2CH_2), 0.50 (s, 6H, $SiMe_2$), 0.27 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (THF-d_8): δ 137.1, 131.5, 123.5, 114.9, 109.3, 109.0, 108.6, 45.6, 28.7, 27.7, 26.4, 23.8, 23.1, 3.8, –4.7.

***rac*/*meso*-Me$_2$Si{η^5-3-(cyclohexen-1-yl)-C$_5$H$_3$}$_2$Zr{Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$}**

(*rac*/*meso*-4c, *rac*/*meso* = 2/1). A flask was charged with **1c** (252 mg, 699 μmol) and **2** (365 mg, 699 μmol), and THF (15 mL) was added by vacuum transfer at –196 °C. The mixture was quickly warmed to room temperature to afford a clear, yellow-orange solution. The mixture was stirred for 5 min at room temperature and the solvent was removed under vacuum. Pentane (15 mL) was added and the mixture was stirred to afford a suspension of a white precipitate in a yellow supernatant. The mixture was filtered through Celite. The Celite was washed with pentane (2 x 5 mL), and the washes were combined with the filtrate. The combined filtrate and washes were again filtered through Celite, and the Celite was washed with pentane (2 x 5 mL). The clear combined filtrate and washes were evaporated under vacuum to afford *rac/meso*-**4c** (*rac*/*meso* = 2/1) as a fluffy yellow solid (430 mg, 94%). Characterization data for *rac*-**4c** in C_6D_6 are reported above. Key ^{1}H NMR resonances for *rac*-**4c** in THF-d_8: δ 6.91 (m, 2H, Cp), 5.99 (m, 2H, C*H*), 5.85 (m, 2H, Cp), 5.77 (t, *J*=3, 2H, Cp), 3.23 (dt, *J*=16, 1; 2H, NCH_2), 2.90 (dt, *J*=16, 8; 2H, NCH_2), 0.89 (m, 2H, NCH_2CH_2), 0.62 (s, 6H, $SiMe_2$). Key ^{1}H NMR

resonances for *meso*-**4c** in THF-d_8: δ 6.54 (m, 2H, Cp), 6.07 (m, 4H, Cp & C*H*), 5.82 (t, *J*=3, 2H, Cp), 3.14 (t, *J*=6, 2H, NCH_2), 2.96 (t, *J*=6, 2H, NCH_2), 1.00 (m, 2H, NCH_2CH_2), 0.66 (s, 3H, $SiMe_2$), 0.59 (s, 3H, $SiMe_2$). The broad multiplets for the cyclohexen-1-yl CH_2 groups of *rac*- and *meso*-**4c** overlap significantly.

***rac*-$Me_2Si\{\eta^5$-3-(cyclohexen-1-yl)-$C_5H_3\}_2ZrCl_2$ (*rac*-6c).** A flask was charged with *rac*-**4c** (576 mg, 880 μmol) and pentane (15 mL). A solution of HCl in Et_2O (5.3 mL, 1.0 M, 5.3 mmol) was added and the mixture was stirred for 5 min. A white solid precipitated. The volatiles were removed under vacuum and pentane (15 mL) was added. The mixture was filtered and the solid was washed with pentane (15 mL). The combined filtrate and wash was evaporated under vacuum to afford *rac*-**6c** as a fluffy yellow solid (309 mg, 69%), which was pure by NMR. An analytical sample was prepared by recrystallization from pentane at –35 °C. Anal. Calcd for $C_{24}H_{30}Cl_2SiZr + 0.05C_5H_{12}$ (pentane content established by NMR): C, 56.84; H, 6.01. Found: C, 56.74; H, 6.10. ^{1}H NMR (C_6D_6): δ 6.88 (t, *J*=2, 2H, Cp), 6.10 (m, 2H, C*H*), 5.65 (t, *J*=2, 2H, Cp), 5.53 (t, *J*=2, 2H, Cp), 2.43 (m, 2H, CH_2), 2.31 (m, 2H, CH_2), 2.25-2.00 (m, 4H, CH_2), 1.75-1.45 (m, 8H, CH_2), 0.21 (s, 6H, $SiMe_2$). ^{13}C NMR (C_6D_6): δ 143.3, 131.1, 127.6, 122.7, 114.0, 108.2, 106.0, 27.4, 26.0, 22.9, 22.5, –5.7.

***rac*-$Me_2Si\{\eta^5$-3-(1-Me-Cy)-$C_5H_3\}_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-4d).** A flask was charged with **1d** (2.484 g, 6.328 mmol) and **2** (3.308 g, 6.328 mmol), and THF (200 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to 0 °C over 15 min to afford a yellow solution. The solution was stirred and warmed to room temperature over 2 h. The solvent was removed under vacuum and pentane (100 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to room temperature

to afford a yellow suspension. The mixture was filtered and the filtrate was evaporated under vacuum to afford *rac*-**4d** as a fluffy yellow solid (4.32 g, 100%), which was pure by NMR. An analytical sample was prepared by recrystallization from hexanes at –35 ^{o}C. Anal. Calcd for $C_{35}H_{62}N_2Si_3Zr$: C, 61.25; H, 9.10; N, 4.08. Found: C, 61.21; H, 9.14; N, 4.19. ^{1}H NMR (C_6D_6, assignments based on NOESY data): δ 6.93 (s, 2H, Cp-H^4), 5.96 (s, 2H, Cp-H^2), 5.87 (s, 2H, Cp-H^5), 3.32 (dm, *J*=16, 2H, equatorial NCH_2), 3.09 (dt, *J*=16, 8; 2H, axial NCH_2), 1.74-1.46 (m, 18H, Cy), 1.27 (s, 6H, Me), 1.15 (m, 2H, Cy), 1.03 (m, 2H, NCH_2CH_2), 0.51 (s, 6H, $SiMe_2$), 0.29 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 150.5, 115.8, 110.9, 107.4, 106.0, 46.2, 39.7, 37.4, 36.5, 28.2, 26.2, 22.3, 3.3, –4.5.

***rac*-$Me_2Si\{\eta^5$-3-(1-Me-Cy)-$C_5H_3\}_2ZrCl_2$ (*rac*-6d).** A flask was charged with *rac*-**4d** (3.393 g, 4.943 mmol) and pentane (100 mL). A solution of HCl in Et_2O (30 mL, 1.0 M, 30 mmol) was added and the mixture was stirred for 30 min at room temperature. A white solid precipitated. The volatiles were removed under vacuum and pentane (100 mL) was added. The mixture was filtered and the solid was washed with pentane. The combined filtrate and wash was evaporated under vacuum to afford *rac*-**6d** as a pale-yellow solid (2.41 g, 90%), which was pure by NMR. An analytical sample was prepared by recrystallization from hexanes at –35 ^{o}C. Anal. Calcd for $C_{26}H_{38}Cl_2SiZr$: C, 57.75; H, 7.08. Found: C, 57.80; H, 6.85. ^{1}H NMR (C_6D_6): δ 6.78 (t, *J*=2, 2H, Cp), 5.78 (t, *J*=2, 2H, Cp), 5.74 (t, *J*=2, 2H, Cp), 1.90-1.80 (m, 8H, Cy), 1.55-1.44 (m, 12H, Cy), 1.50 (s, 6H, Me), 0.24 (s, 6H, $SiMe_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.3, 125.7, 116.1, 110.1, 105.1, 37.9, 37.6, 36.7, 26.1, 22.8, 22.2, 22.1, –5.7.

***meso*-$Me_2Si\{\eta^5$-3-(1-Me-Cy)-$C_5H_3\}_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-5d).** A flask was charged with **1d** (1.005 g, 2.560 mmol) and **3** (1.359 g, 2.560 mmol), and Et_2O (100 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to 0 °C over 15 min to afford an orange suspension. The mixture was stirred and warmed to room temperature over 2 h. The solvent was removed under vacuum and pentane (100 mL) was added. The resulting suspension was filtered and the filtrate was evaporated under vacuum to afford *meso*-**5d** as a fluffy orange solid (1.66 g, 91%), which was pure by NMR. An analytical sample was prepared by recrystallization from toluene/hexanes (1:1 v/v) at –35 °C over 1 week. Anal. Calcd for $C_{41}H_{54}N_2SiZr$: C, 70.94; H, 7.84; N, 4.04. Found: C, 70.85; H, 7.90; N, 4.00. ^{1}H NMR (C_6D_6, assignments based on NOESY data): δ 7.30 (t, *J*=8, 2H, *m*-Ph *endo*[13]), 7.22 (t, *J*=8, 2H, *m*-Ph *exo*), 6.96 (t, *J*=8, 1H, *p*-Ph *exo*), 6.83 (d, *J*=8, 2H, *o*-Ph *exo*), 6.80 (t, *J*=8, 1H, *p*-Ph *endo*), 6.44 (d, *J*=8, *o*-Ph *endo*), 6.28 (s, 4H, Cp-H^2 & Cp-H^4), 6.05 (s, 2H, Cp-H^5), 3.62 (t, *J*=6, 2H, NCH_2 *exo*), 3.27 (t, *J*=6, 2H, NCH_2 *endo*), 1.73 (t, *J*=6, 2H, NCH_2CH_2), 1.44-1.21 (m, 20H, Cy), 0.94 (s, 6H, Me), 0.62 (s, 3H, $SiMe_2$ *endo*), 0.56 (s, 3H, $SiMe_2$ *exo*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.4, 159.3, 150.4, 122.5, 121.1, 120.7, 120.6, 120.5, 117.9, 117.3, 111.7, 108.9, 105.1, 54.1, 52.5, 39.1, 38.5, 36.4, 29.7, 26.4, 25.9, 23.7, 22.6, –2.5, –5.5. An analogous reaction to the above was conducted on an NMR scale, which afforded *meso*-**5d** in >95% NMR yield.

***rac*/*meso*-$Me_2Si\{\eta^5$-3-(1-Me-Cy)-$C_5H_3\}_2ZrCl_2$ (6d, *rac*/*meso* = 1/16).** A flask was charged with *meso*-**5d** (915 mg, 1.32 mmol) and pentane (50 mL). A solution of HCl in Et_2O (5.3 mL, 1.0 M, 5.3 mmol) was added and the mixture was stirred for 10 min at 22 °C. A white solid precipitated. The volatiles were removed under vacuum and

pentane (25 mL) was added. The mixture was filtered and the solid was washed with pentane (25 mL). The combined filtrate and wash was evaporated under vacuum to afford **6d** as a pale-yellow solid in a 1/16 *rac*/*meso* isomer ratio (502 mg, 71%). ^{1}H NMR for *meso*-**6d** in C_6D_6: δ 6.91 (m, 2H, Cp), 6.00 (m, 2H, Cp), 5.59 (m, 2H, Cp), 1.94 (m, 6H, Cy), 1.82 (m, 2H, Cy), 1.56 (s, 6H, Me), 1.54-1.43 (br m, 12H, Cy), 0.32 (s, 3H, $SiMe_2$), 0.13 (s, 3H, $SiMe_2$). $^{13}C\{^{1}H\}$ NMR for *meso*-**6d** (C_6D_6): δ 148.1, 131.4, 118.5, 110.9, 103.4, 39.1, 38.6, 36.6, 26.4, 24.5, 22.6, 22.5, –3.2, –7.1.

***rac*-$Me_2Si\{\eta^5$-3-(1-Ph-Cy)-$C_5H_3\}_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-4e).** A flask was charged with **1e** (1.008 g, 1.951 mmol) and **2** (1.020 g, 1.951 mmol), and THF (125 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to room temperature over 5 min. A yellow solution formed and was stirred overnight. The solvent was removed under vacuum and pentane (40 mL) was added. The resulting suspension was filtered and the filtrate was evaporated under vacuum to afford *rac*-**4e** as a fluffy yellow solid (1.58 g, 100%), which was pure by NMR. An analytical sample was prepared by recrystallization from toluene/hexanes (1:1 v/v) at –35 °C. Anal. Calcd for $C_{45}H_{66}N_2Si_3Zr$: C, 66.69; H, 8.21; N, 3.46. Found: C, 66.34; H, 8.12; N, 3.50. ^{1}H NMR (THF-d_8): δ 7.32 (d, *J*=8, 4H, *o*-Ph), 7.19 (t, *J*=8, 4H, *m*-Ph), 7.02 (t, *J*=7, 2H, *p*-Ph), 6.72 (s, 2H, Cp), 5.87 (s, 2H, Cp), 5.56 (s, 2H, Cp), 3.34 (dt, *J*=15, 1; 2H, NCH_2), 3.03 (dt, *J*=15, 7; 2H, NCH_2), 2.77 (d, *J*=13, 2H, Cy), 2.55 (d, *J*=13, 2H, Cy), 2.11 (t, *J*=13, 2H, Cy), 1.95 (t, *J*=13, 2H, Cy), 1.54 (br m, 6H, Cy), 1.30 (br m, 6H, Cy), 1.00 (br m, 2H, NCH_2CH_2), 0.46 (s, 6H, $SiMe_2$), 0.08 (s, 18H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (THF-d_8): δ 149.7, 146.0, 128.9, 128.5, 126.0, 118.1, 112.8, 108.2, 106.2, 47.4, 45.3, 36.0, 34.7, 28.6, 27.1, 23.3, 23.1, 3.4, –4.4.

***rac*-$Me_2Si\{\eta^5$-3-(1-Ph-Cy)-$C_5H_3\}_2ZrCl_2$ (*rac*-6e).** A flask was charged with *rac*-**4e** (539 mg, 665 μmol) and pentane (10 mL). A solution of HCl in Et_2O (4.0 mL, 1.0 M, 4.0 mmol) was added and the mixture was stirred for 5 min at room temperature. A white solid precipitated. The volatiles were removed under vacuum, and pentane (10 mL) and toluene (10 mL) were added. The mixture was stirred for 5 min and filtered through a glass frit. The filtrate was evaporated under vacuum to afford *rac*-**6e** as a yellow solid (378 mg, 86%). NMR data for this material matched literature data.[10]

***meso*-$Me_2Si\{\eta^5$-3-(1-Ph-Cy)-$C_5H_3\}_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-5e).** A flask was charged with **1e** (1.025 g, 1.984 mmol) and **3** (1.053 g, 1.984 mmol), and Et_2O (125 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to 0 °C over 15 min and an orange suspension formed. The mixture was stirred and warmed to room temperature over 2 h. The solvent was removed under vacuum and pentane (40 mL) was added. The resulting suspension was filtered and the filtrate was evaporated under vacuum to afford *meso*-**5e** as an orange solid (1.16 g, 71%), which was pure by NMR. An analytical sample was prepared by recrystallization from toluene/hexanes (1:1 v/v) at –30 °C. Anal. Calcd for $C_{51}H_{58}N_2SiZr$: C, 74.85; H, 7.14; N, 3.42. Found: C, 74.48; H, 7.15; N, 3.58. ^{1}H NMR (C_6D_6): δ 7.34 (t, *J*=8, 2H, *m*-*N*-Ph), 7.23 (t, *J*=8, 2H, *m*-*N*-Ph), 7.07 (d, *J*=8, 4H, *o*-Ph), 7.00 (t, *J*=8, 4H, *m*-Ph), 6.93 (t, *J*=8, 1H, *p*-*N*-Ph), 6.88 (m, 3H, *p*-Ph, *p*-*N*-Ph), 6.73 (d, *J*=8, 2H, *o*-*N*-Ph), 6.55 (d, *J*=8, 2H, *o*-*N*-Ph), 6.31 (s, 2H, Cp), 6.16 (s, 2H, Cp), 5.88 (s, 2H, Cp), 3.38 (m, 2H, NCH_2), 3.32 (m, 2H, NCH_2), 2.36 (d, *J*=13, 2H, Cy), 2.21 (d, *J*=13, 2H, Cy), 1.91 (br m, 2H, NCH_2CH_2), 1.74 (t, *J*=13, 2H, Cy), 1.40 (br m, 7H, Cy), 1.25 (br m, 7H, Cy), 0.50 (s, 3H, $SiMe_2$), 0.31 (s, 3H, $SiMe_2$). ^{13}C NMR (THF-d_8): δ 162.3, 158.9, 149.2, 145.7, 129.7, 128.9, 128.8, 128.4, 125.9,

123.6, 120.9, 120.7, 117.5 (br), 116.9, 112.2, 109.5, 105.5, 53.5, 52.4, 44.7, 36.7, 34.7, 32.1, 27.1, 23.3, 23.2, –2.6, –5.6. An analogous reaction to the above was conducted on an NMR scale, which afforded *meso*-**5e** in >95% NMR yield.

***rac*-$Me_2Si\{\eta^5$-3-(1-Me-*cyclo*-$C_{12}H_{22})$-$C_5H_3\}_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-4f).** A flask was charged with **1f** (2.236 g, 3.987 mmol) and **2** (2.084 g, 3.987 mmol), and THF (150 mL) was added by vacuum transfer at –196 °C. The mixture was warmed to 0 °C over 15 min to afford a yellow solution. The solution was stirred and warmed to room temperature over 2 h. The volatiles were removed under vacuum and hexanes (100 mL) was added. The resulting suspension was stirred for 5 min and filtered through a glass frit. The solid was washed with hexanes (2 x 25 mL) and toluene (25 mL). The combined filtrate and washes were evaporated under vacuum to afford *rac*-**4f** as a yellow solid (3.394 g, 100%), which was pure by NMR. An analytical sample was prepared by recrystallization from toluene/hexanes (1:1 v/v) at –30 °C. Anal. Calcd for $C_{47}H_{86}N_2Si_3Zr$: C, 66.05; H, 10.14; N, 3.28. Found: C, 65.72; H, 9.85; N, 3.30. ^{1}H NMR (C_6D_6): δ 6.96 (s, 2H, Cp), 6.04 (s, 2H, Cp), 5.95 (s, 2H, Cp), 3.39 (dt, *J*=16, 1; 2H, NCH_2), 3.17 (dt, *J*=16, 8; 2H, NCH_2), 1.69 (br m, 4H, $C_{12}H_{22}$), 1.55 (br m, 4H, $C_{12}H_{22}$), 1.39 (s, 6H, Me), 1.31 (br m, 32H, $C_{12}H_{22}$), 1.09 (br m, 2H, NCH_2CH_2), 0.98 (br m, 4H, $C_{12}H_{22}$), 0.51 (s, 6H, $SiMe_2$), 0.34 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.1, 116.9, 111.9, 106.9, 106.4, 46.4, 39.0, 36.4, 35.5, 28.6, 27.1, 27.0, 26.9, 26.5, 24.8, 22.8, 22.4, 22.3, 20.0, 19.8, 3.6, –4.2.

***rac*-$Me_2Si\{\eta^5$-3-(1-Me-*cyclo*-$C_{12}H_{22})$-$C_5H_3\}_2ZrCl_2$ (*rac*-6f).** A flask was charged with *rac*-**4f** (2.266 g, 2.651 mmol) and pentane (100 mL) was added. A solution of HCl in Et_2O (16.0 mL, 1.00 M, 16.0 mmol) was added and the mixture was stirred for

90 min. A white solid precipitated. The volatiles were removed under vacuum, and hexanes (25 mL) and toluene (75 mL) were added. The mixture was stirred for 5 min and filtered through a glass frit. The filtrate was evaporated under vacuum affording *rac*-**6f** as a cream-colored solid, which was dried under vacuum overnight (1.616 g, 86%), which was pure by NMR. An analytical sample was prepared by recrystallization from pentane at –35 °C. Anal. Calcd for $C_{38}H_{62}Cl_2SiZr$: C, 64.36; H, 8.81. Found: C, 64.05; H, 8.58. ^{1}H NMR (C_6D_6): δ 6.82 (s, 2H, Cp), 5.86 (s, 2H, Cp), 5.79 (s, 2H, Cp), 2.20 (br m, 2H, $C_{12}H_{22}$), 1.90 (br t, *J*=11, 2H, $C_{12}H_{22}$), 1.66 (m, 6H, $C_{12}H_{22}$), 1.50-1.13 (br m, 40H, $C_{12}H_{22}$ and Me), 0.22 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.5, 126.8, 116.2, 111.1, 105.4, 39.5, 36.7, 33.5, 27.2, 27.0, 26.7, 26.6, 24.9, 22.8, 22.4, 22.3, 20.1, 19.6, –5.4.

***rac*-$Me_2Si(\eta^5$-3-CMe_2Ph-$C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-4g).** A flask was charged with **1g** (686 mg, 1.57 mmol) and **2** (821 mg, 1.57 mmol). The flask was cooled to –196 °C and THF (55 mL) was added by vacuum transfer. The mixture was quickly warmed to 0 °C and then stirred and gradually warmed to room temperature over 23 h. The solvent was removed under vacuum to afford a yellow solid. The solid was extracted with benzene (4 x 20 mL) and the combined extracts were filtered through a glass frit. The filtrate was evaporated under vacuum at 45 °C to afford *rac*-**4g** as a yellow solid (1.14 g, 99%), which was pure by NMR. An analytical sample was prepared by recrystallization from pentane at –35 °C. Anal. Calcd for $C_{39}H_{58}N_2Si_3Zr$: C, 64.13; H, 8.00; N, 3.84. Found: C, 64.18; H, 7.98; N, 3.94. ^{1}H NMR (C_6D_6): δ 7.07 (t, *J*=8, 4H, *m*-Ph), 7.04 (s, 2H, Cp), 6.99 (d, *J*=8, 4H, *o*-Ph), 6.94 (t, *J*=7, 2H, *p*-Ph), 5.96 (s, 2H, Cp), 5.90 (s, 2H, Cp), 3.41 (d, *J*=15, 2H, NCH_2), 3.14 (dt, *J*=16, 8; 2H, NCH_2), 1.72 (s, 6H,

Me), 1.70 (s, 6H, Me), 1.05 (br s, 2H, NCH_2CH_2), 0.32 (s, 6H, $SiMe_2$), 0.27 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 153.2, 147.0, 128.5, 126.4, 126.0, 118.9, 114.6, 108.8, 107.0, 47.0, 41.4, 29.6, 28.8, 28.0, 3.5, –4.2.

***rac*-$Me_2Si\{\eta^5$-3-CMe_2Ph-$C_5H_3\}_2ZrCl_2$ (*rac*-6g).** A solution of *rac*-**4g** (980 mg, 1.34 mmol) in benzene (50 mL) was prepared. A solution of HCl in Et_2O (7.78 mL, 1.00 M, 7.78 mmol) was added over 15 min and the mixture was stirred for 90 min. The volatiles were removed under vacuum to afford a yellow solid. The solid was extracted with benzene (2 x 45 mL) and the combined extracts were filtered through a glass frit. The filtrate was evaporated under vacuum at 45 ^oC to afford *rac*-**6g** as a yellow solid (758 mg, 97%). A fraction of this material (100 mg) was recrystallized from hexanes/toluene (8:1 v/v) at –35 ^oC to afford a spectroscopically pure sample of *rac*-**6g** (67 mg). NMR data for this material matched literature data.[10]

II. NMR Monitoring and Kinetics of Epimerization Reactions.

Epimerization of *rac*/*meso*-4b starting with 1b and 2. The epimerization reactions of *in situ* generated **4b** summarized in Figure S1 were performed by the following general procedure. An NMR tube was charged with **1b** (19.1 mg, 55.5 μmol), **2** (29.0 mg, 55.5 μmol) and Cp_2Fe (10.0 mg, 53.8 μmol, internal standard). THF-d_8 (1.00 mL) was added by vacuum transfer at –196 ^{o}C. The tube was thawed and warmed to 22 ^{o}C over 30 sec. For run *i*, the tube was exposed to ambient fluorescent light, whereas for run *ii*, the tube was wrapped in foil. The tube was then maintained at 22 ^{o}C and ^{1}H NMR spectra were recorded periodically. After 1 h, a 1.5/1 *rac*-**4b**/*meso*-**4b** mixture had formed quantitatively. The *rac*-**4b**/*meso*-**4b** ratio increased over time while the total concentration of **4b** remained constant (Figure S1).

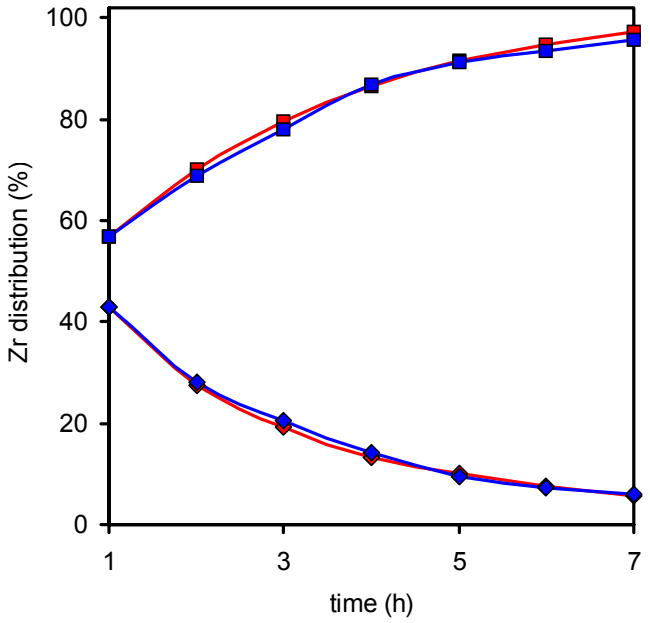


Figure S1. Time dependence of the concentrations of *rac*-**4b** and *meso*-**4b** (% total Zr; measured relative to an internal standard) during the epimerization reaction of a 1.5/1 *rac*-**4b**/*meso*-**4b** mixture (generated *in situ*) in the presence of 2 equiv LiCl, in the presence or absence of ambient fluorescent light, in THF-d_8 at 22 °C; *rac*-**4b** (squares, upper curves), *meso*-**4b** (diamonds, lower curves). Run *i*, 2 equiv LiCl and light present (red); run *ii*, 2 equiv LiCl and no light present (blue).

The concentration data for conversion of *meso*-**4b** to *rac*-**4b** (eq 1) for run *i* were analyzed using first-order kinetics (eq 2):[14]

$$\textit{meso}\text{-}\mathbf{4b} \xrightarrow{k_1} \textit{rac}\text{-}\mathbf{4b} \qquad (1)$$

$$\ln\left(\frac{[\textit{meso}\text{-}\mathbf{4b}]}{[\textit{meso}\text{-}\mathbf{4b}]_0}\right) = -k_1 t \qquad (2)$$

where [*meso*-**4b**]$_0$ is the concentration of *meso*-**4b** after 2 h of reaction time (complete consumption of starting materials occurred after *ca*. 1 h, *vide supra*), k_1 is the forward first-order rate constant and t is time measured relative to the observation at 2 h. Eq 2 assumes (*i*) $k_1 >> k_{-1}$ which is reasonable given that K_{eq} = [*rac*-**4b**]$_\infty$/[*meso*-**4b**]$_\infty$ = k_1/k_{-1} > 30/1 and (*ii*) no competing reactions occurred during epimerization. For each ^{1}H NMR spectrum recorded, the integrated area of the internal standard resonance (Cp_2Fe, δ 4.11, s) was set to 10.000 and the quantity ln([*meso*-**4b**]/[*meso*-**4b**]$_0$) was computed using the integrated area of the *meso*-**4b** resonance at δ 6.25 (m, 4H, Cp). The linear least-squares fit (Microsoft® Excel 2000) and k_1 obtained are shown in Figure S2. These results show the epimerization of *meso*-**4b** to *rac*-**4b** is first-order in [*meso*-**4b**] and not influenced by ambient light.

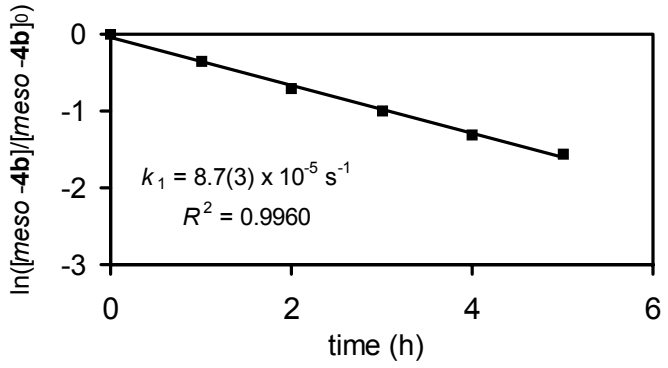


Figure S2. Plot of ln([*meso*-**4b**]/[*meso*-**4b**]$_0$) vs time (h); THF-d_8, 22 ^{o}C, [LiCl] = 111 mM.

Epimerization of *rac*/*meso*-4b starting with preformed *rac*/*meso*-4b. The epimerization reactions of preformed **4b** summarized in Figure S3 were performed by the

following general procedure. An NMR tube was charged with *rac*/*meso*-**4b** (*rac*/*meso* = 1.5/1, 35.4 mg, 55.5 μmol). The appropriate additive ($Li[B(C_6F_5)_4](Et_2O)_{2.8}$ or [^{n}Bu$_4$N]Cl), and Cp_2Fe (10.0 mg, 53.8 μmol, internal standard) were added. THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The tube was thawed and warmed to 22 °C over 30 sec. At this point, the reaction was considered initiated (t = 0). The tube was then maintained at 22 °C and ^{1}H NMR spectra were recorded periodically. These results show that *meso*-**4b** is catalytically epimerized to *rac*-**4b** by soluble Cl^- and not by Li^+ or THF.

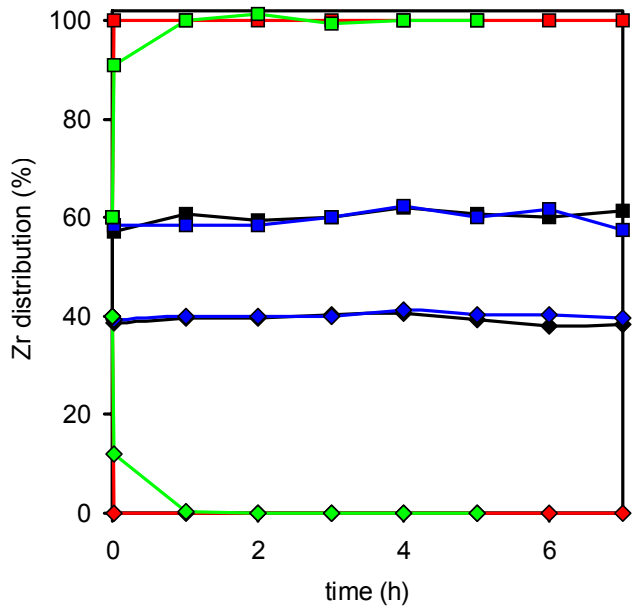


Figure S3. Time dependence of the concentrations of *rac*-**4b** and *meso*-**4b** (% total Zr; measured relative to an internal standard) during the epimerization reaction of a 1.5/1 *rac*-**4b**/*meso*-**4b** mixture in the presence or absence of additives in THF-d_8 at 22 °C; *rac*-**4b** (squares, upper curves), *meso*-**4b** (diamonds, lower curves). Additives: run *i*, no

additives (black); run *ii*, 2 equiv $Li[B(C_6F_5)_4]$ (blue); run *iii*, 2 equiv $[^nBu_4N]Cl$ (red); run *iv*, 0.15 equiv $[^nBu_4N]Cl$ (green).

Epimerization of *rac*/*meso*-4c starting with 1c and 2. The epimerization reactions of **4c** summarized in Figure S4 were performed by the following general procedure. An NMR tube was charged with **1c** (20.0 mg, 55.5 μmol), **2** (29.0 mg, 55.5 μmol) and Cp_2Fe (10.0 mg, 53.8 μmol, internal standard). THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The tube was thawed, warmed to 22 °C over 30 sec and immersed in a 60.0 °C constant temperature bath. At this point, the reaction was considered initiated. For run *i*, the tube was exposed to ambient fluorescent light, whereas for run *ii*, the tube was wrapped in foil. The tube was maintained at 60.0 °C for 5 h and ^{1}H NMR spectra were recorded periodically at 22 °C. The quantitative formation of a 2/1 *rac*-**4c**/*meso*-**4c** mixture was observed after 5 min. Conversion of this mixture toward pure *rac*-**4c** was subsequently observed (Figure S4).

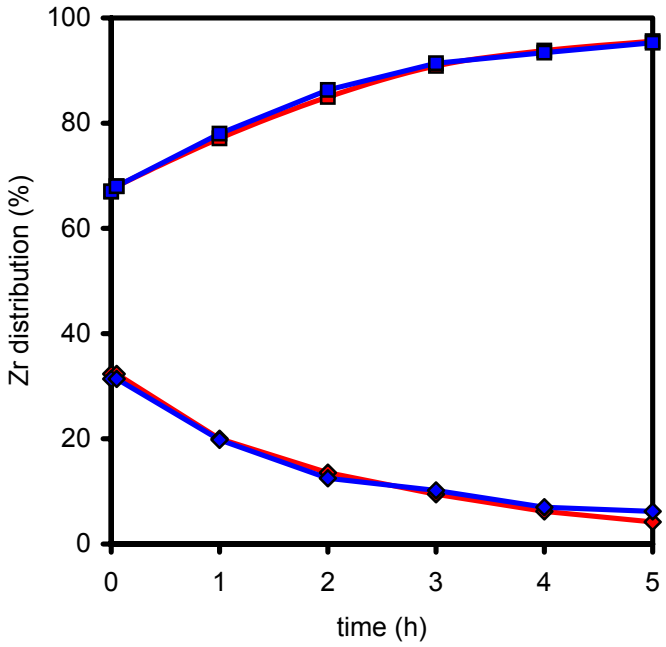


Figure S4. Time dependence of the concentrations of *rac*-**4c** and *meso*-**4c** (% total Zr; measured relative to an internal standard) during the epimerization reaction of a 2/1 *rac*-**4c**/*meso*-**4c** mixture (generated *in situ*) in the presence of 2 equiv LiCl, and in the presence or absence of ambient fluorescent light, in THF-d_8 at 60 ^{o}C; *rac*-**4c** (squares, upper curves), *meso*-**4c** (diamonds, lower curves). Run *i*, 2 equiv LiCl and light present (red); run *ii*, 2 equiv LiCl and no light present (blue).

The concentration data for conversion of *meso*-**4c** to *rac*-**4c** (eq 3) for run *i* were analyzed using first-order kinetics, eq 4:[14]

$$\textit{meso}\text{-}\mathbf{4c} \xrightarrow{k_1} \textit{rac}\text{-}\mathbf{4c} \quad (3)$$

$$\ln\left(\frac{[\textit{meso}\text{-}\mathbf{4c}]}{[\textit{meso}\text{-}\mathbf{4c}]_0}\right) = -k_1 t \quad (4)$$

where [*meso*-**4c**]$_0$ is the concentration of *meso*-**4c** after 5 min of reaction time (complete consumption of starting materials occurred in < 5 min, *vide supra*), k_1 is the forward first-order rate constant and t is time measured relative to the observation at 5 min. Eq 4 assumes (*i*) $k_1 >> k_{-1}$ which is reasonable given that K_{eq} = [*rac*-**4c**]$_\infty$/[*meso*-**4c**]$_\infty$ = k_1/k_{-1} > 30/1 and (*ii*) no competing reactions occurred during epimerization. For each of the ^{1}H NMR spectra recorded, the integrated area of the internal standard resonance (Cp_2Fe, δ 4.11, s) was set to 10.000 and the quantity ln([*meso*-**4c**]/[*meso*-**4c**]$_0$) was computed using the integrated area of the *meso*-**4c** resonances at δ 6.07 (m, 4H, overlapping Cp & C*H*). The linear least-squares fit (Microsoft® Excel 2000) and k_1 obtained are shown in Figure S5. These results show the epimerization of *meso*-**4c** to *rac*-**4c** is first-order in [*meso*-**4c**] and not influenced by ambient light.

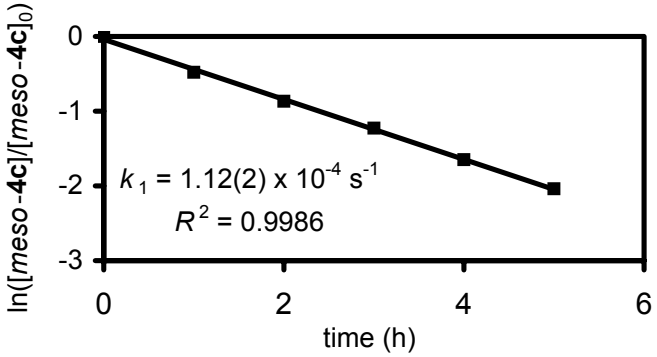


Figure S5. Plot of ln([*meso*-**4c**]/[*meso*-**4c**]$_0$) vs time (h), THF-d_8, 60 ^{o}C, [LiCl] = 111 mM.

Epimerization of *rac*/*meso*-4c starting with preformed *rac*/*meso*-4c. The epimerization reactions of **4c** summarized in Figure S6 were performed by the following

general procedure. An NMR tube was charged with *rac*/*meso*-**4c** (*rac*/*meso* = 2/1, 36.3 mg, 55.5 μmol). The appropriate additive ($Li[B(C_6F_5)_4](Et_2O)_{2.8}$ or $[^nBu_4N]Cl$, 111 μmol), and Cp_2Fe (10.0 mg, 53.8 μmol, internal standard) were added. THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The tube was thawed, warmed to 22 °C over 30 sec and immersed in a 60.0 °C constant temperature bath. At this point, the reaction was considered initiated (t = 0). The tube was then maintained at 60.0 °C and ^1H NMR spectra were recorded periodically over 5 h at 22 °C (Figure S6). These results show that *meso*-**4c** is epimerized to *rac*-**4c** by soluble Cl^- and not by Li^+ or THF.

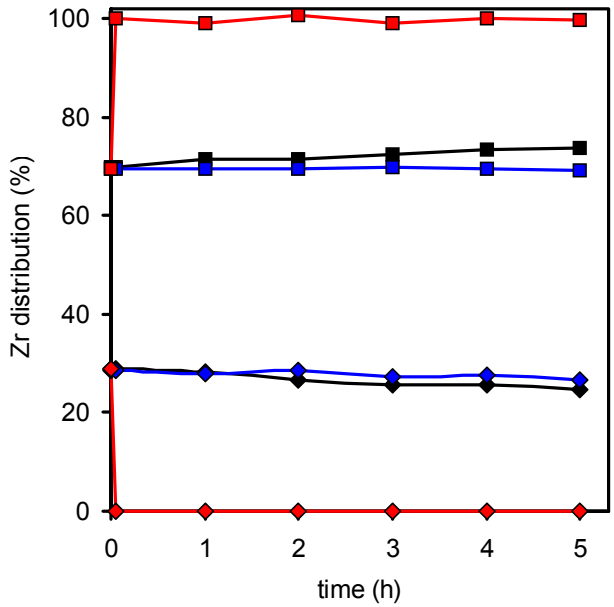


Figure S6. Time dependence of the concentrations of *rac*-**4c** and *meso*-**4c** (% total Zr; measured relative to an internal standard) during the epimerization reaction of a 2/1 *rac*-**4c**/*meso*-**4c** mixture in the presence or absence of additives in THF-d_8 at 60 °C; *rac*-**4c** (squares, upper curves), *meso*-**4c** (diamonds, lower curves). Additives: run *i*, no additives (black); run *ii*, 2 equiv $Li[B(C_6F_5)_4]$ (blue); run *iii*, 2 equiv $[^nBu_4N]Cl$ (red).

NMR monitoring of the reaction of 1a and 3 in Et_2O-d_{10}. An NMR tube was charged with **1a** (17.3 mg, 55.5 μmol), **3** (29.5 mg, 55.5 μmol), and Cp_2Fe (10.0 mg, 53.8 μmol, internal standard). Et_2O-d_{10} (1.00 mL) was added by vacuum transfer at –196 °C. The mixture was thawed, warmed to 22 °C over 30 sec, and monitored by ^{1}H NMR over 2 h. Within 4-7 min, the formation of *meso*-**5a** and free THF was observed. Quantitative formation of *meso*-**5a** was observed after 2 h; no *rac*-**5a** was observed. These results show that *meso*-**5a** is the kinetic product of the reaction between **1a** and **3** in Et_2O. ^{1}H NMR for *meso*-**5a** in Et_2O-d_{10}: δ 7.16 (t, J = 8, 2H, *m*-Ph), 7.04 (t, J = 8, 2H, *m*-Ph), 6.80 (t, J = 8, 1H, *p*-Ph), 6.71 (d, J = 8, 2H, *o*-Ph), 6.56 (t, J = 8, 1H, *p*-Ph), 6.34 (d, J = 8, 2H, *o*-Ph), 6.12 (t, J = 2, 2H, Cp), 6.06 (t, J = 2, 2H, Cp), 6.02 (t, J = 2, 2H, Cp), 3.65-3.60 (signal obscured by THF, 2H, NCH_2), 3.30 (t, J = 6, 2H, NCH_2), 1.85 (t, J = 6, 2H, NCH_2CH_2), 0.85 (s, 18H, ^{t}Bu), 0.77 (s, 3H, $SiMe_2$), 0.76 (s, 3H, $SiMe_2$).

NMR monitoring of the reaction of 1a and 3 in THF-d_8. An NMR tube was charged with **1a** (17.3 mg, 55.5 μmol), **3** (29.5 mg, 55.5 μmol), and Cp_2Fe (14.2 mg, 76.3 μmol, internal standard). THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The tube was thawed, warmed to 0 °C over 30 sec, and inserted into the probe of an NMR spectrometer maintained at 0 °C. At this point, the reaction was considered initiated (t = 0). ^{1}H NMR spectra were recorded periodically over 4 h and showed that **1a** and **3** reacted smoothly to form a mixture of *rac*-**5a** and *meso*-**5a** (Figure S7). The *rac*/*meso* ratio for **5a** during the first 4 h of reaction was constant (Figure S8), indicating formation of *rac*/*meso*-**5a** from **1a** and **3** is fast relative to epimerization of *rac*/*meso*-**5a** under these conditions. After 4 h, the *rac*/*meso* ratio was 1/3. The tube was then transferred to a 0.0

^{o}C constant temperature bath. Periodically over an additional 13 days, the tube was removed from the bath, ^{1}H NMR spectra were recorded at 22 ^{o}C, and the tube was returned to the bath. These spectra showed that the *rac*/*meso* ratio changed to 1.6/1. The tube was then transferred to a 22.0 ^{o}C constant temperature bath and ^{1}H NMR spectra were recorded periodically at 22 ^{o}C over 3 days. These spectra showed that the *rac*/*meso* ratio changed to an equilibrium value of 3.0(4). Overall, these results show that for the reaction of **1a** and **3** in THF, *meso*-**5a** is the kinetically-preferred product, *rac*-**5a** is the thermodynamically-preferred product and that differences in solvation (Et_2O vs THF) influence kinetic *rac*/*meso* selectivity. ^{1}H NMR for *meso*-**5a** in THF-d_8: δ 7.15 (t, J = 8, 2H, *m*-Ph), 7.04 (t, J = 8, 2H, *m*-Ph), 6.76 (t, J = 8, 1H, *p*-Ph), 6.75 (d, J = 8, 2H, *o*-Ph), 6.54 (t, J = 8, 1H, *p*-Ph), 6.36 (d, J = 8, 2H, *o*-Ph), 6.15 (m, 4H, Cp), 6.10 (t, J = 2, 2H, Cp), 3.63 (t, J = 6, 2H, NCH_2), 3.28 (t, J = 6, 2H, NCH_2), 1.85 (t, J = 6, 2H, NCH_2CH_2), 0.86 (s, 18H, ^{t}Bu), 0.79 (s, 3H, $SiMe_2$), 0.78 (s, 3H, $SiMe_2$). Key ^{1}H NMR resonances for *rac*-**5a** in THF-d_8: δ 7.10 (t, J = 8, 4H, *m*-Ph), 6.70 (t, J = 8, 2H, *p*-Ph), 6.65 (d, J = 8, 4H, *o*-Ph), 6.13 (t, J = 2, 2H, Cp), 6.04 (t, J = 2, 2H, Cp), 5.89 (t, J = 2, 2H, Cp), 3.40 (dt, J = 15, 4; 2H, NCH_2), 1.03 (s, 18H, ^{t}Bu), 0.73 (s, 6H, $SiMe_2$).

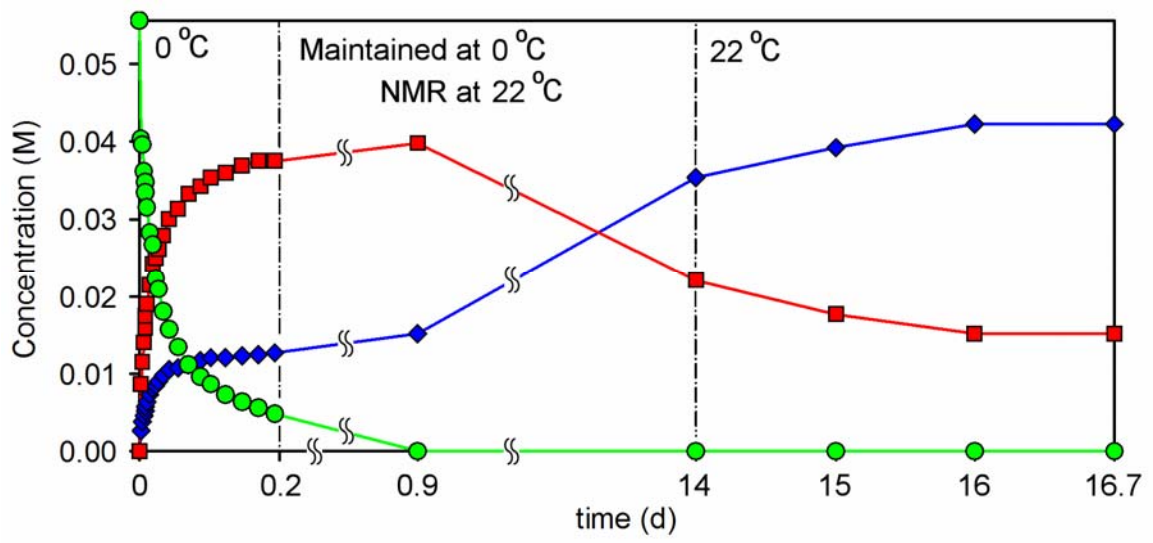


Figure S7. Time course of the reaction of **1a** and **3** to produce *rac*/*meso*-**5a**. Concentrations (M) of **1a** (circles), *meso*-**5a** (squares) and *rac*-**5a** (diamonds) measured relative to an internal standard versus time. The temperatures (0 °C, 22 °C) at which the reaction mixture was maintained during the experiment are indicated. The *rac*/*meso* ratio at equilibrium was 3.0(4)/1.

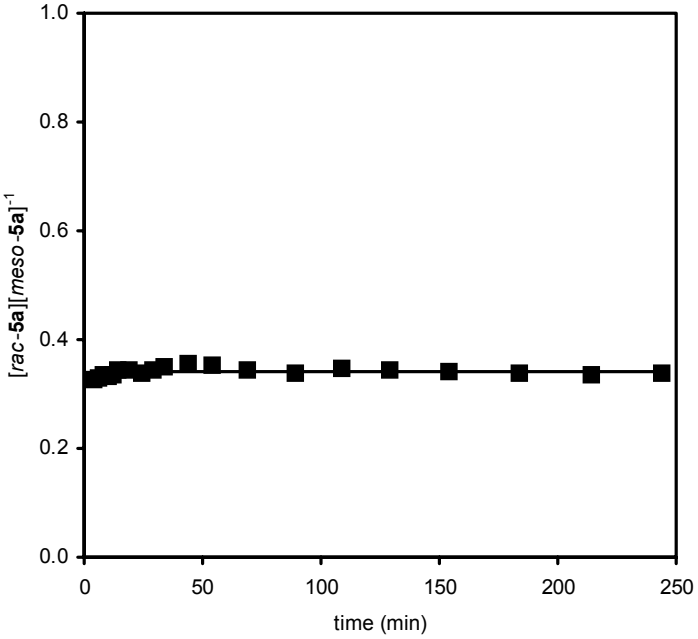


Figure S8. Plot of [*rac*-**5a**][*meso*-**5a**]$^{-1}$ versus time (min) for the formation of 1/3 *rac*/*meso*-**5a** during the first 4 h of reaction, THF-d_8, 0 ^{o}C.

Epimerization of *meso*-5a with [^{n}Bu$_4$N]Cl: Determination of Reaction Order in [5a]. An NMR tube was charged with *meso*-**5a** (34.1 mg, 55.5 μmol), [^{n}Bu$_4$N]Cl (30.8 mg, 111 μmol), and Cp_2Fe (10.6 mg, 57.0 μmol, internal standard). THF-d_8 (1.00 mL) was added by vacuum transfer at –196 ^{o}C. The mixture was thawed, warmed to 0 ^{o}C over 30 s, and inserted into the probe of an NMR spectrometer maintained at 0 ^{o}C. At this point, the reaction was considered initiated (t = 0). ^{1}H NMR spectra were recorded periodically over 1.5 h and showed that *meso*-**5a** had converted to a 2.45/1 mixture of *rac*/*meso*-**5a** (Figure S9). The tube was transferred at 0 ^{o}C to a 0.0 ^{o}C constant temperature bath and additional ^{1}H NMR spectra were recorded (at room temperature) after 16.5 h and 2 weeks. The *rac*/*meso* ratio in both spectra was 3.0(4)/1, indicating that

equilibrium had been reached. The tube was then warmed to 22 °C and two additional ^{1}H NMR spectra were recorded over 2 h which showed no further change.

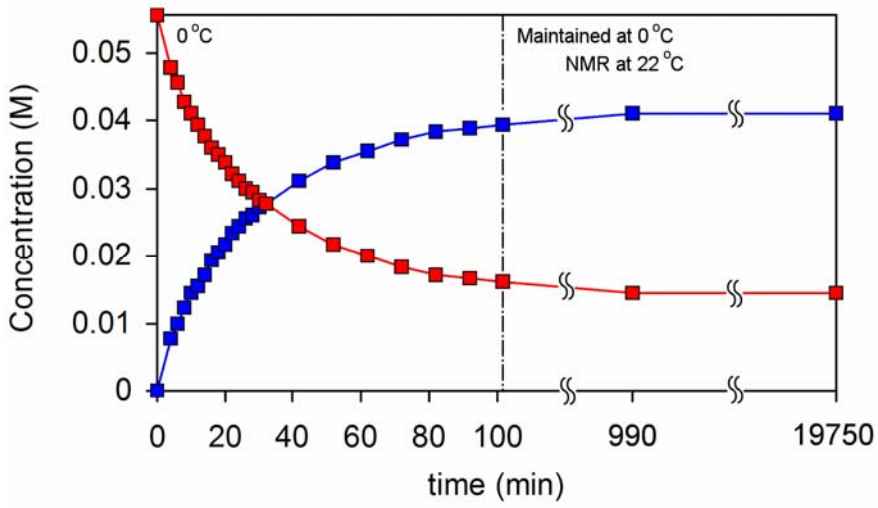


Figure S9. Concentrations (M) of *meso*-**5a** (red) and *rac*-**5a** (blue) measured relative to an internal standard vs time (min) at 0 °C. The solution was saturated in [^{n}Bu$_4$N]Cl. The temperatures (0 °C, 22 °C) at which the reaction mixture was maintained during the experiment are indicated.

The concentration data for the equilibration of *meso*-**5a** and *rac*-**5a** (eq 5) during the 0 °C reaction period were treated using first-order approach-to-equilibrium kinetics (eq 6-9):[14]

$$\textit{meso}\text{-}\mathbf{5a} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{rac}\text{-}\mathbf{5a} \qquad (5)$$

$$\ln\left(\frac{[\textit{meso}\text{-}\mathbf{5a}] - [\textit{meso}\text{-}\mathbf{5a}]_\infty}{[\textit{meso}\text{-}\mathbf{5a}]_0 - [\textit{meso}\text{-}\mathbf{5a}]_\infty}\right) = -k_{obs}t \qquad (6)$$

$$\ln\left(1-\frac{[rac\text{-}\mathbf{5a}]}{[rac\text{-}\mathbf{5a}]_\infty}\right)=-k_{obs}t \quad (7)$$

$$k_{obs}=k_1+k_{-1} \quad (8)$$

$$K_{eq}=[rac\text{-}\mathbf{5a}]_\infty / [meso\text{-}\mathbf{5a}]_\infty = k_1 / k_{-1} = 3.0(4) \quad (9)$$

where $[meso\text{-}\mathbf{5a}]_0$ is the starting concentration of *meso*-**5a** at $t = 0$, $[meso\text{-}\mathbf{5a}]_\infty$ and $[rac\text{-}\mathbf{5a}]_\infty$ are the equilibrium concentrations of *meso*-**5a** and *rac*-**5a** respectively, and k_{obs} is the observed first-order rate constant for approach to equilibrium, which is equal to the sum of the forward (k_1) and reverse (k_{-1}) first-order rate constants (eq 8). For each ^{1}H NMR spectrum recorded, the integrated area of the internal standard resonance (Cp_2Fe, δ 4.11, s) was set to 10.000. The concentration of *meso*-**5a** measured from each ^{1}H NMR spectrum was determined as follows: the integrated area of the *meso*-**5a** resonance at δ 6.36 (d, J = 8, 2H, *o*-Ph) was divided by 2 (normalization) and then multiplied by the concentration of internal standard. The concentration of *rac*-**5a** measured from each ^{1}H NMR spectrum was determined as follows: the integrated area of the *rac*-**5a** resonance at δ 5.89 (t, J = 2, 2H, Cp) was divided by 2 (normalization) and then multiplied by the concentration of internal standard. The linear least-squares fits (Microsoft® Excel 2000) and rate constants obtained, based on data for *meso*-**5a** (Figure S10) and *rac*-**5a** (Figure S11), are shown below.

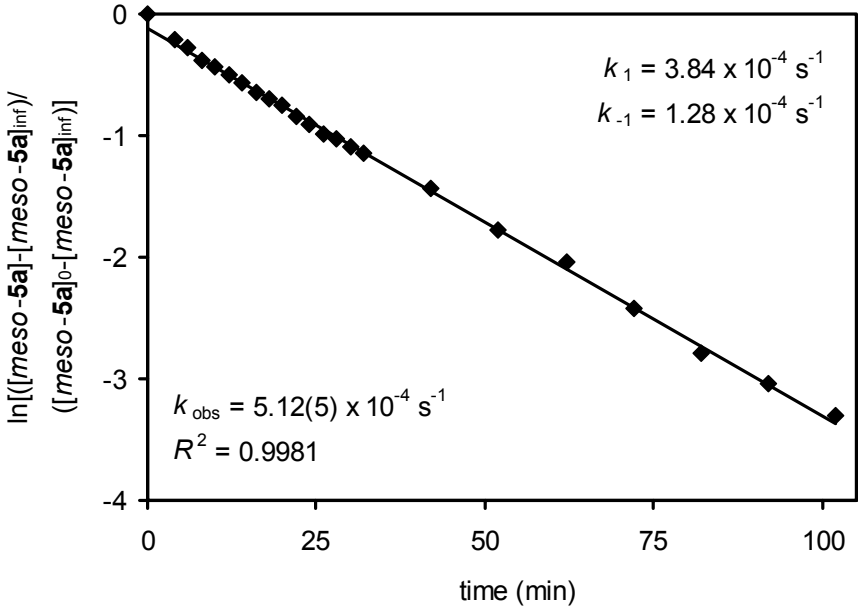


Figure S10. Plot of ln{([*meso*-**5a**]-[*meso*-**5a**]$_\infty$)/([*meso*-**5a**]$_0$-[*meso*-**5a**]$_\infty$)} vs time (min).

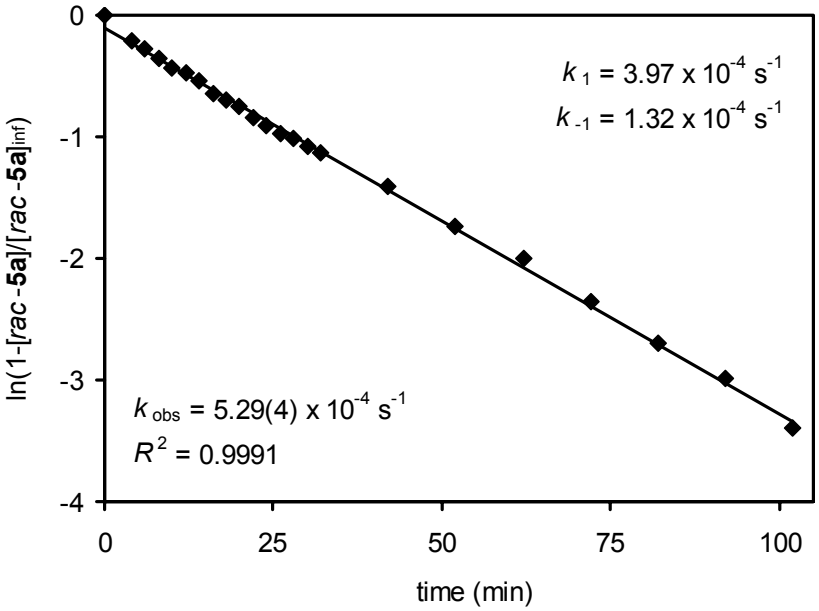


Figure S11. Plot of ln(1-[*rac*-**5a**]/[*rac*-**5a**]$_\infty$) vs time (min).

The values of k_{obs} obtained from analysis of the data for *meso*-**5a** and *rac*-**5a** are in close agreement (k_{obs}(average) = 5.21(6) x 10^{-4} s^{-1}). Assuming that K_{eq} is the same at 0 ^{o}C as at 22 ^{o}C, k_1 and k_{-1} for each case were calculated using eqs 8, 9 and are shown in Figures S10, S11 (k_1(average) = 3.91 x 10^{-4} s^{-1}, k_{-1}(average) = 1.30 x 10^{-4} s^{-1}). These results show that *meso*-**5a** smoothly undergoes epimerization to an equilibrium 3.0(4)/1 *rac*/*meso*-**5a** mixture by soluble Cl^{-}; this reaction follows approach to equilibrium kinetics and is first-order in [*meso*-**5a**].

Epimerization of *meso*-5a with varying [LiCl]: Determination of Reaction Order in [Cl^{-}]. Epimerization reactions of **5a** in the presence of different concentrations of LiCl were performed by the following procedure. A stock solution of LiCl in THF (182.(5) mM) was prepared. A measured quantity of the stock solution was added to an NMR tube (0–900 mg solution). The solvent was removed under vacuum and the tube was charged with *meso*-**5a** (50.0 mg, 81.0 μmol) and Cp_2Fe (internal standard). THF-d_8 (1.00 mL) was added by vacuum transfer at –78 ^{o}C. The mixture was rapidly warmed to 60.0 ^{o}C in a constant temperature bath. At this point, the reaction was considered initiated (t = 0). Periodic reaction monitoring was performed by rapidly cooling the tube to 22 ^{o}C and recording ^{1}H NMR spectra at 22 ^{o}C. No significant epimerization was observed at 22 ^{o}C.

The [Cl^{-}] was varied over the range 0-180 mM. Plots of [*meso*-**5a**] and [*rac*-**5a**] versus time exhibited approach-to-equilibrium kinetics and are shown for a representative example (run 2, [Cl^{-}] = 170 mM) in Figure S12.

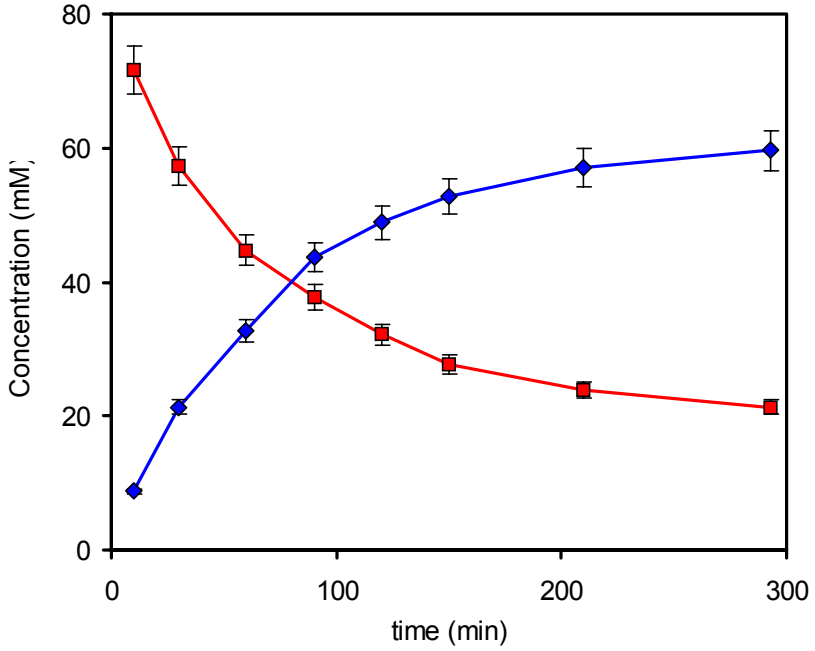


Figure S12. Time dependence of [*meso*-**5a**] (squares) and [*rac*-**5a**] (diamonds) versus time (min) for run 2. Conditions: THF-d_8, 60.0 °C, [Cl^-] = 170 mM.

For runs 1–11, the [*meso*-**5a**] and [*rac*-**5a**] data obtained were analyzed using first-order approach-to-equilibrium kinetics (eqs 6-9) as described above. A plot of $\ln\{([meso\text{-}\mathbf{5a}]-[meso\text{-}\mathbf{5a}]_\infty)/([meso\text{-}\mathbf{5a}]_0-[meso\text{-}\mathbf{5a}]_\infty)\}$ versus time for a representative example (run 2) is shown in Figure S13.

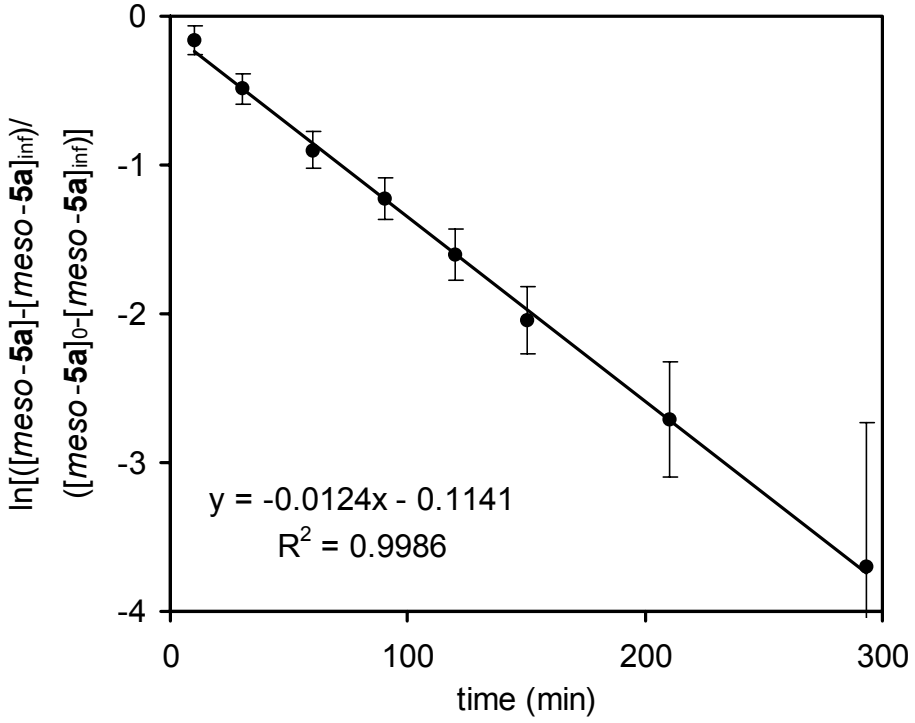


Figure S13. Plot of ln{([*meso*-**5a**]-[*meso*-**5a**]$_\infty$)/([*meso*-**5a**]$_0$-[*meso*-**5a**]$_\infty$)} vs time (min) for run 2.

Several runs were taken to completion (*i.e.* until no further change in [*meso*-**5a**], [*rac*-**5a**] occurred) and K_{eq} = [*rac*-**5a**][*meso*-**5a**]$^{-1}$ = 3.0(4) was determined (eq 9). The values of k_{obs} were determined by linear least-squares regression (Microsoft® Excel 2000) and are shown in Table S1. The values of k_1 (s^{-1}) and k_{-1} (s^{-1}) for each run were determined from k_{obs} and K_{eq} (eqs 8, 9), and are listed in Table S1.

Table S1. Summary of Kinetic Data for Epimerization of *meso*-5a (LiCl, 60.0 °C).[a]

Entry	[Cl^-] (mM)	10^4 k_{obs}	10^4 k_1	10^4 k_{-1}
1	180	1.79	1.34	0.45
2	170	2.06	1.55	0.52
3	150	1.68	1.26	0.42
4	130	1.49	1.11	0.37
5	130	1.54	1.16	0.39
6	110	1.20	0.90	0.30
7	87	1.22	0.91	0.30
8	70	0.87	0.65	0.22
9	49	0.77	0.58	0.19
10	30	0.67	0.50	0.17
11	10	0.44	0.33	0.11
12	138	1.99	1.49	0.50
13	0	0.00	0.00	0.00
14	135	1.89	1.42	0.47
15	26	0.61	0.46	0.15
16	0	0.09	0.07	0.02

[a]Rate constants are reported in units of s^{-1}.

The plot of k_{obs} versus [Cl^-] (Figure S14) is linear, indicating epimerization of *meso*-**5a** has a linear dependence on [Cl^-].

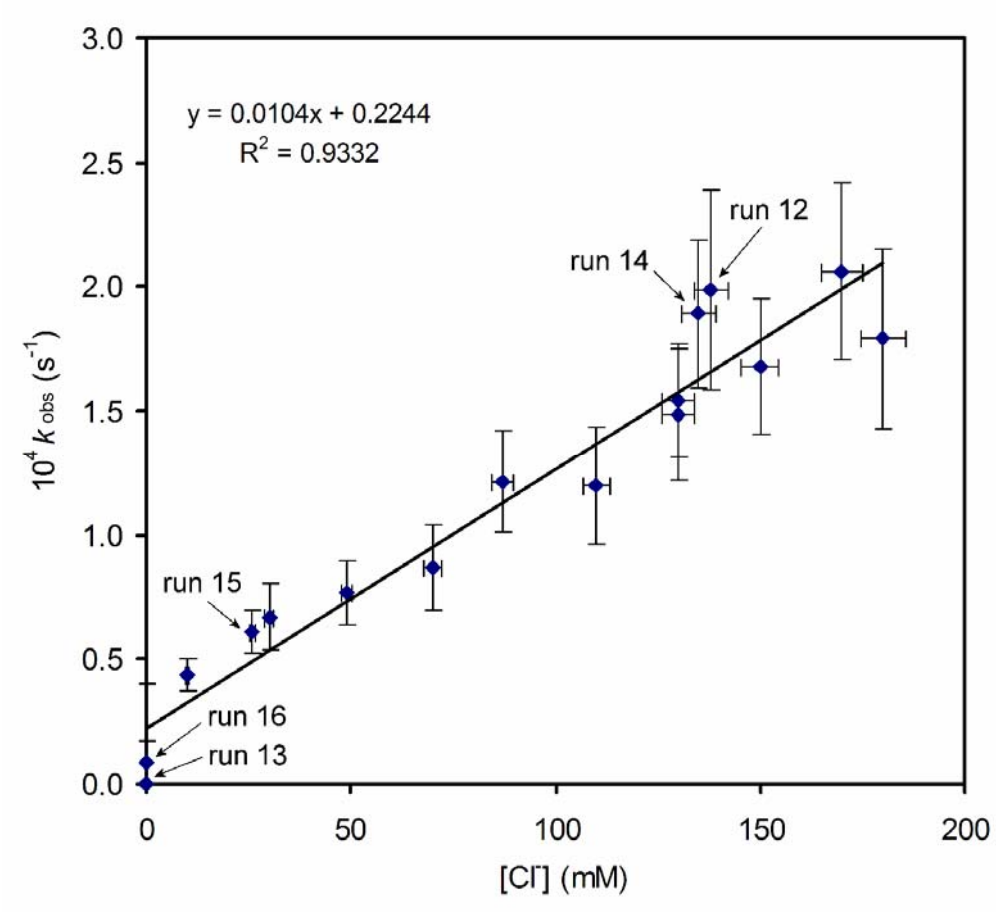


Figure S14. Plot of 10^4 x k_{obs} (s^{-1}) versus [Cl^-] (mM) for runs 1-16.

The intercept of the plot of k_{obs} vs [Cl^-] in Figure S14 appears to be slightly greater than zero (0.22 ± 0.05). This suggests that a slow background non-LiCl-catalyzed epimerization may be operative. To probe this issue, several experiments were performed (runs 12–16) and the resulting concentration data were analyzed as performed for runs 1-11. Run 12 was conducted in the dark using [Cl^-] = 138 mM. The k_{obs} value obtained for run 12 does not differ significantly from that predicted by the regression analysis. Run 13 was conducted with omission of LiCl and showed no epimerization over 3 d at 60 °C. It was noted that for all runs, trace amounts of *N*,*N*'-diphenyl-1,3-diaminopropane were present (2-8% relative to Zr) and most likely due to adventitious

hydrolysis of *meso*-**5a**. Efforts to completely eliminate this material through careful purification of starting materials and rigorous exclusion of air and moisture proved unsuccessful. Run 14 ([Cl^-] = 135 mM) and run 15 ([Cl^-] = 26 mM) were conducted with added *N*,*N*'-diphenyl-1,3-diaminopropane ([*N*,*N*'-diphenyl-1,3-diaminopropane]/[Zr] = 0.2–0.5 equiv). The k_{obs} values obtained for runs 14 and 15 did not differ significantly from that predicted by the regression analysis. Run 16 was conducted with added deionized water (10% relative to Zr); in this case partial hydrolysis of *meso*-**5a** and slow epimerization over 2 d was observed. Therefore, the background epimerization observed in these experiments is attributed to trace hydrolysis of *meso*-**5a**.

Epimerization of 6d with [^{n}Bu$_4$N]Cl. Epimerization reactions of $Me_2Si\{3\text{-}(1\text{-}Me\text{-}Cy)\text{-}C_5H_3\}_2ZrCl_2$ (**6d**) by [^{n}Bu$_4$N]Cl, were performed using the following general procedure. An NMR tube was charged with either *rac*-**6d** (run *i*, 30.0 mg, 55.5 μmol) or *rac*/*meso*-**6d** (run *ii*, *rac*/*meso* = 1/16, 30.0 mg, 55.5 mmol). [^{n}Bu$_4$N]Cl (15.4 mg, 55.5 μmol) and Cp_2Fe (internal standard) were added. Control reactions were also prepared, wherein the [^{n}Bu$_4$N]Cl was omitted. THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The mixture was thawed and the tube was immersed in a 60.0 °C constant temperature bath. At this point, the reaction was considered initiated (t = 0). The mixture was monitored periodically by ^{1}H NMR at 22 °C over *ca*. 3 d. In cases where [^{n}Bu$_4$N]Cl was present, the reactants were converted to a 1/2 equilibrium mixture of *rac*/*meso*-**6d**. No reaction was observed in the absence of chloride. Key ^{1}H NMR resonances for *rac*-**6d** in THF-d_8: δ 6.72 (m, 2H, Cp), 6.13 (m, 2H, Cp), 6.03 (m, 2H, Cp), 0.69 (s, 6H, $SiMe_2$). Key ^{1}H NMR resonances for *meso*-**6d** in THF-d_8: δ 6.85 (m,

2H, Cp), 6.45 (m, 2H, Cp), 5.99 (m, 2H, Cp), 0.79 (s, 3H, $SiMe_2$), 0.55 (s, 3H, $SiMe_2$). The broad multiplets for the 1-Me-cyclohexyl groups of *rac*/*meso*-**6d** overlap significantly.

The concentration data for both *rac*-**6d** and *meso*-**6d** in runs *i* and *ii* are plotted in Figure S15. The kinetic profiles shown in these plots exhibit approach-to-equilibrium kinetics; the total metallocene concentration remained constant throughout the runs.

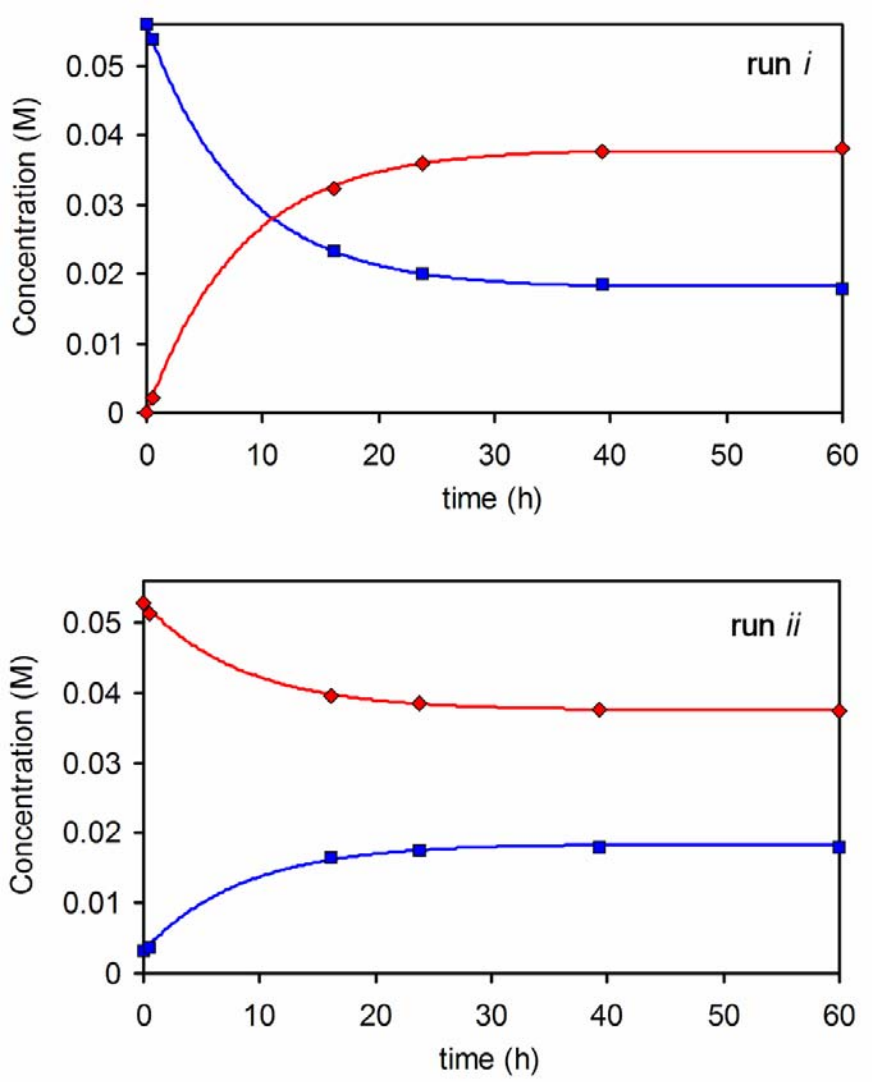


Figure S15. Time dependence of concentrations of *meso*-**6d** (diamonds) and *rac*-**6d** (squares) versus time (h). Conditions: THF-d_8, 60 °C, [Cl^-] = 55.5 mM. Run *i*: starting with *rac*-**6d**. Run *ii*: starting with *rac*/*meso*-**6d** (*rac*/*meso* = 1/16).

The concentration data for the equilibration of *meso*-**6d** and *rac*-**6d** (eq 10) in runs *i* and *ii* were treated using first-order approach-to-equilibrium kinetics (eqs 11, 12):[14]

$$\textit{meso}\text{-}\mathbf{6d} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{rac}\text{-}\mathbf{6d} \qquad (10)$$

$$\ln\left(\frac{[\textit{meso}\text{-}\mathbf{6d}] - [\textit{meso}\text{-}\mathbf{6d}]_\infty}{[\textit{meso}\text{-}\mathbf{6d}]_0 - [\textit{meso}\text{-}\mathbf{6d}]_\infty}\right) = -k_{obs}t \qquad (11)$$

$$K_{eq} = [\textit{rac}\text{-}\mathbf{6d}]_\infty / [\textit{meso}\text{-}\mathbf{6d}]_\infty = k_1 / k_{-1} = 0.50 \qquad (12)$$

where k_{obs} is the observed first-order rate constant for approach to equilibrium, which is equal to the sum of the forward (k_1) and reverse (k_{-1}) first-order rate constants (eq 8). For each ^{1}H NMR spectrum recorded, the integrated area of the internal standard resonance (Cp_2Fe, δ 4.11, s) was set to 10.000. The concentration of *meso*-**6d** measured from each ^{1}H NMR spectrum was determined as follows: the integrated area of the *meso*-**6d** resonance at δ 5.99 (m, 2H, Cp) was divided by 2 (normalization) and then multiplied by the concentration of internal standard. The linear least-squares fits (Microsoft® Excel 2000) and rate constants obtained, based on data for *meso*-**6d** from run *i* (Figure S16) and run *ii* (Figure S17) are shown below.

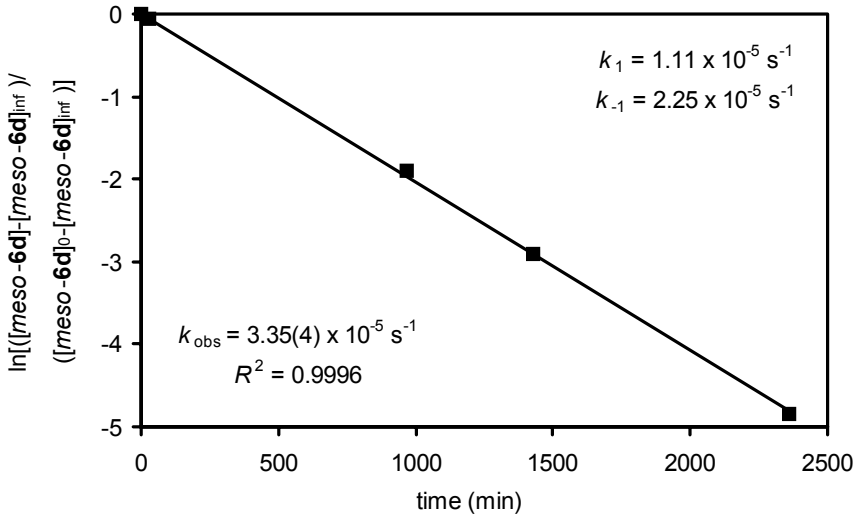


Figure S16. Plot of ln{([*meso*-**6d**]-[*meso*-**6d**]$_\infty$)/([*meso*-**6d**]$_0$-[*meso*-**6d**]$_\infty$)} vs time (min) for run *i*.

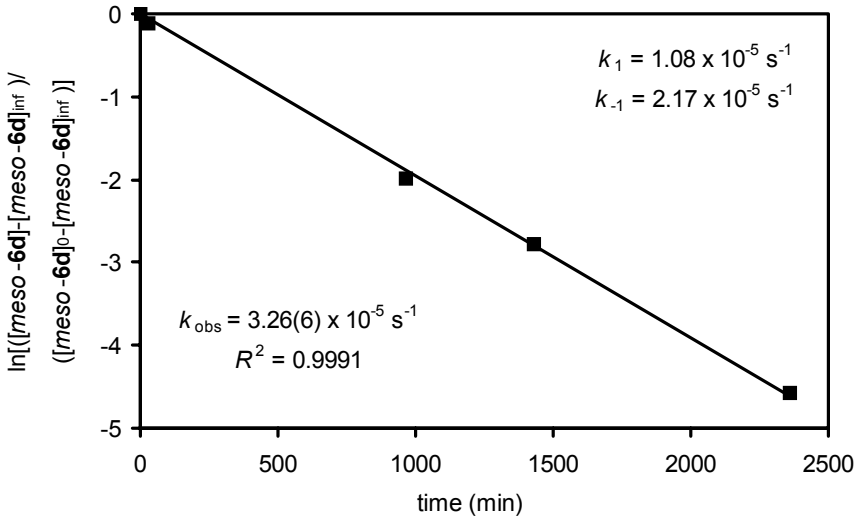


Figure S17. Plot of ln{([*meso*-**6d**]-[*meso*-**6d**]$_\infty$)/([*meso*-**6d**]$_0$-[*meso*-**6d**]$_\infty$)} vs time (min) for run *ii*.

The values of k_{obs} obtained from analysis of the data for runs *i* and *ii* are in close agreement (k_{obs}(average) = 3.31(7) x 10^{-5} s^{-1}). The values of k_1 and k_{-1} for each case were calculated using eqs 8, 12 and are shown in Figures S16, S17 (k_1(average) = 1.10 x 10^{-5} s^{-1}, k_{-1}(average) = 2.21 x 10^{-5} s^{-1}). These results show that both *rac*-**6d** and *meso*-**6d** smoothly undergo epimerization to an equilibrium 1/2 *rac*/*meso*-**6d** mixture by soluble Cl^-; these reactions follow approach-to-equilibrium kinetics and are first-order in [*meso*-**6d**].

Epimerization of *rac*-6b with 2 equiv [^{n}Bu$_4$N]Cl. The epimerization reactions of *rac*-**6b** were performed using the following general procedure. An NMR tube was charged with *rac*-**6b** (27.4 mg, 55.5 μmol), [^{n}Bu$_4$N]Cl (30.8 mg, 111 μmol) and Cp_2Fe (internal standard). A control reaction was also prepared, wherein the [^{n}Bu$_4$N]Cl was omitted. THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The mixture was thawed and the tube was immersed in a 22.0 °C constant temperature bath. At this point, the reaction was considered initiated (t = 0). The mixture was monitored periodically by ^{1}H NMR at 22 °C. In the case where [^{n}Bu$_4$N]Cl was present, a 7/1 *rac*/*meso*-**6b** mixture was observed after 2.5 h and an equilibrium 0.5/1 *rac*/*meso*-**6b** was observed after 2 d. No reaction was observed in the absence of chloride. These results show that the epimerization of *rac*/*meso*-**6b**, a zirconocene dichloride complex, is significantly slower than that for the analogous *rac*/*meso*-**4b** (Figure S3, run *iii*), a zirconocene bis-amide complex, under identical conditions. ^{1}H NMR for *rac*-**6b** in THF-d_8: δ 6.94 (t, J = 3, 2H, Cp), 6.30 (t, J = 3, 2H, Cp), 6.12 (t, J = 3, 2H, Cp), 0.74 (s, 6H, $SiMe_2$), 0.25 (s, 18H, $SiMe_3$). ^{1}H NMR for *meso*-**6b** in THF-d_8: δ 7.07 (t, J = 3, 2H, Cp), 6.49 (t, J = 3, 2H,

Cp), 6.13 (t, J = 3, 2H, Cp), 0.82 (s, 3H, $SiMe_2$), 0.64 (s, 3H, $SiMe_2$), 0.28 (s, 18H, $SiMe_3$).

Epimerization of *rac*-6c with 2 equiv [^{n}Bu$_4$N]Cl. The epimerization reactions of *rac*-**6c** were performed using the following general procedure. An NMR tube was charged with *rac*-**6c** (28.2 mg, 55.5 μmol), [^{n}Bu$_4$N]Cl (30.8 mg, 111 μmol) and Cp_2Fe (internal standard). A control reaction was also prepared, wherein the [^{n}Bu$_4$N]Cl was omitted. THF-d_8 (1.00 mL) was added by vacuum transfer at –196 ^{o}C. The mixture was thawed and the tube was immersed in a 60.0 ^{o}C constant temperature bath. At this point, the reaction was considered initiated (t = 0). The mixture was monitored periodically by ^{1}H NMR at 22 ^{o}C. In the case where [^{n}Bu$_4$N]Cl was present, the reactants were converted to an equilibrium 0.9/1 *rac*/*meso*-**6c** mixture after 82 min. No reaction was observed in the absence of chloride. The total metallocene concentration remained constant throughout the experiment in both cases. Key ^{1}H NMR resonances for *rac*-**6c** in THF-d_8: δ 6.77 (t, J = 3, 2H, Cp), 5.92 (m, 4H, Cp), 0.70 (s, 6H, $SiMe_2$). Key ^{1}H NMR resonances for *meso*-**6c** in THF-d_8: δ 6.71 (t, J = 3, 2H, Cp), 5.91 (t, J = 3, 2H, Cp), 5.80 (t, J = 3, 2H, Cp), 0.75 (s, 3H, $SiMe_2$), 0.66 (s, 3H, $SiMe_2$). The broad multiplets for the cyclohexen-1-yl groups of *rac*/*meso*-**6c** overlap significantly.

The concentration data for *rac*-**6c** and *meso*-**6c** are plotted in Figure S18. The kinetic profiles shown exhibit approach-to-equilibrium kinetics.

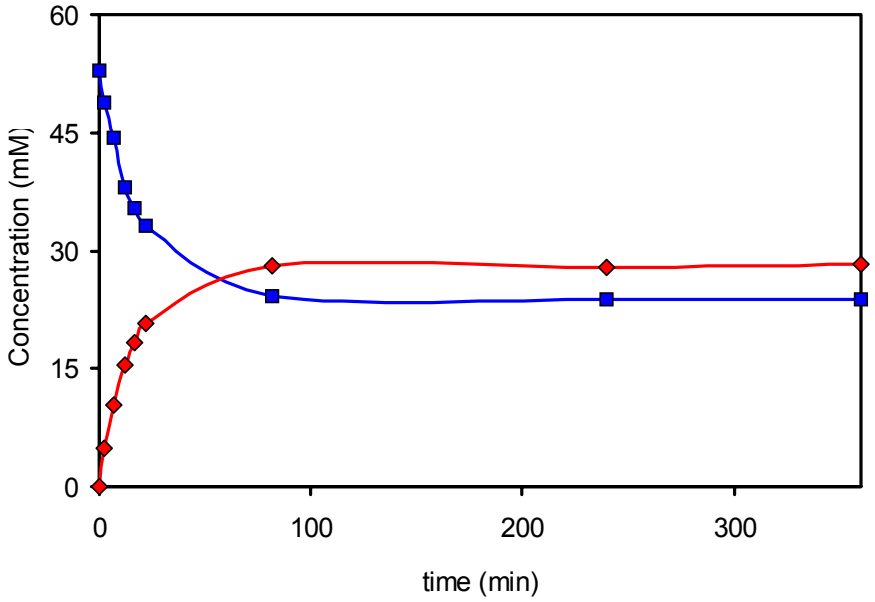


Figure S18. Time dependence of the concentrations (mM) of *meso*-**6c** (diamonds) and *rac*-**6c** (squares) versus time (min). Conditions: THF-d_8, 60 °C, [Cl^-] = 111 mM.

The concentration data for the equilibration of *meso*-**6c** and *rac*-**6c** (eq 13) were treated using first-order approach-to-equilibrium kinetics (eqs 14, 15):[14]

$$\textit{meso}\text{-}\mathbf{6c} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{rac}\text{-}\mathbf{6c} \qquad (13)$$

$$\ln\left(\frac{[\textit{meso}\text{-}\mathbf{6c}] - [\textit{meso}\text{-}\mathbf{6c}]_\infty}{[\textit{meso}\text{-}\mathbf{6c}]_0 - [\textit{meso}\text{-}\mathbf{6c}]_\infty}\right) = -k_{obs}t \qquad (14)$$

$$K_{eq} = [\textit{rac}\text{-}\mathbf{6c}]_\infty / [\textit{meso}\text{-}\mathbf{6c}]_\infty = k_1 / k_{-1} = 0.9 \qquad (15)$$

where k_{obs} is the observed first-order rate constant for approach to equilibrium, which is equal to the sum of the forward (k_1) and reverse (k_{-1}) first-order rate constants

(eq 8). For each ^{1}H NMR spectrum recorded, the integrated area of the internal standard resonance (Cp_2Fe, δ 4.11, s) was set to 10.000. The concentration of *meso*-**6c** measured from each ^{1}H NMR spectrum was determined as follows: the integrated area of the *meso*-**6c** resonance at δ 0.75 (s, 3H, $SiMe_2$) was divided by 3 (normalization) and then multiplied by the concentration of internal standard. The linear least-squares fit (Microsoft® Excel 2000) and rate constant obtained, based on data for *meso*-**6c** are shown in Figure 19.

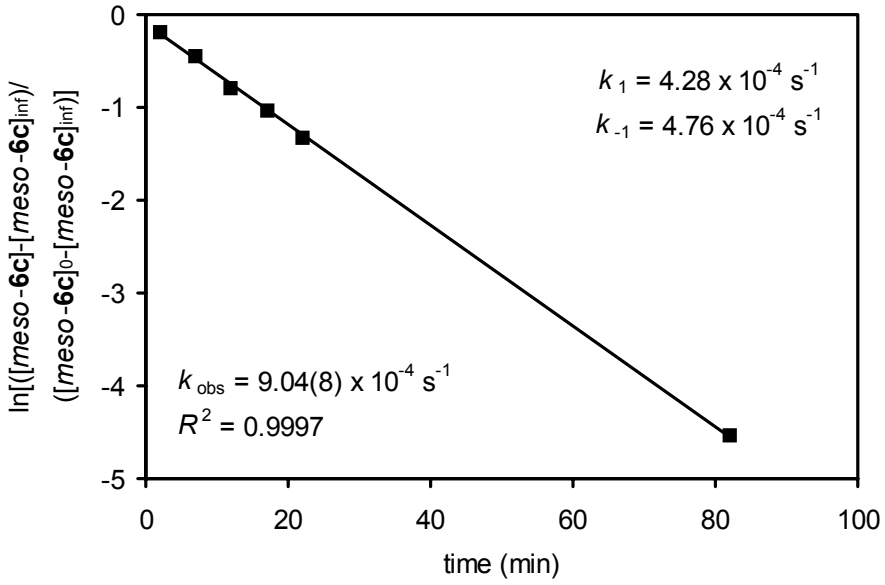


Figure S19. Plot of ln{([*meso*-**6c**]-[*meso*-**6c**]$_\infty$)/([*meso*-**6c**]$_0$-[*meso*-**6c**]$_\infty$)} vs time (min).

The values of k_1 and k_{-1} for each case were calculated using eqs 8, 15 and are shown in Figures S19. These results show that *rac*-**6c** smoothly undergoes epimerization to an equilibrium 0.9/1 *rac*/*meso*-**6c** mixture by soluble Cl^-. This reaction follows approach-to-equilibrium kinetics, is first-order in [*meso*-**6c**] and is significantly slower

than the analogous reaction for *rac*/*meso*-**4c** (Figure S6, run *iii*), a zirconocene bis-amide complex, under identical conditions.

Cp/Cp' Exchange in Zirconocene Dichlorides (Cp = C_5H_5; Cp' = C_5H_4Me). An NMR tube was charged with Cp_2ZrCl_2 (16.1 mg, 55.0 μmol), Cp'_2ZrCl_2 (17.6 mg, 55.0 μmol), [^{n}Bu$_4$N]Cl (7.7 mg, 28.0 μmol) and Cp_2Fe (2.7 mg, 15.0 μmol, internal standard). THF-d_8 (1.00 mL) was added by vacuum transfer at –196 °C. The tube was warmed to 22 °C and a ^{1}H NMR spectrum was recorded within 10 min which showed that no reaction had occurred. The tube was immersed in a 60.0 °C constant temperature bath for 1 h, cooled to 22 °C over 30 s, and a ^{1}H NMR spectrum was recorded, which showed that a 1/2/1 mixture of Cp_2ZrCl_2, $Cp(Cp')ZrCl_2$ and Cp'_2ZrCl_2 was present. No further change in the ^{1}H NMR spectrum of this mixture was observed upon heating at 60.0 °C for an additional 2 h. The solvent was removed under vacuum and $CDCl_3$ was added by vacuum transfer at –196 °C. The mixture was warmed to 22 °C and a ^{1}H NMR spectrum was recorded which confirmed the presence of $Cp(Cp')ZrCl_2$.[15] An identical reaction conducted in the dark yielded the same equilibrium mixture. No reaction was observed in the absence of chloride. Overall, these results show that Cp exchange between zirconocenes is catalyzed by soluble Cl^-. ^{1}H NMR for Cp_2ZrCl_2 (THF-d_8): δ 6.51 (s, Cp). ^{1}H NMR for Cp'_2ZrCl_2 (THF-d_8): δ 6.40 (t, J = 2, 4H, Cp'), 6.19 (t, J = 2, 4H, Cp'), 2.22 (s, 6H, Me). ^{1}H NMR for $Cp(Cp')ZrCl_2$ (THF-d_8): δ 6.53 (s, 5H, Cp), 6.44 (t, J = 2, 2H, Cp'), 6.20 (t, J = 2, 2H, Cp'), 2.22 (s, 3H, Me).

III. References.

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