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Chelate-Controlled Synthesis of *rac*- and *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$

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The reaction of the chelated bis-amide complex $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ (**2**) with $Li_2[Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2]$ yields *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-**3**) in >98% yield. In contrast, the reaction of $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)_2$ (**4**) or the related mono-THF adduct $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)$ (**5**) with $Li_2[Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2]$ yields *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-**6**) in quantitative NMR yield and 89% isolated yield. X-ray crystallographic analyses show that the $Zr\{RN(CH_2)_3NR\}$ chelate ring in *rac*-**6** has a pronounced twist conformation, while that in *meso*-**3** has a flatter, envelope conformation. It is proposed that the conformations of the $Zr\{RN(CH_2)_3NR\}$ chelate rings in the stereodetermining transition states for addition of the second Cp^- ring in these reactions are similar to those in the metallocene products and control the diastereoselectivity. *meso*-**3** and *rac*-**6** are converted to *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*meso*-**1**) and *rac*-**1**, respectively, by reaction with HCl in Et_2O.

Introduction

The application of structurally complex *ansa*-zirconocenes, particularly bis-indenyl systems, as stereoselective catalysts has been studied extensively.[1] This field would be advanced significantly by the development of efficient syntheses of *rac*-metallocenes derived from simple, easily accessible, bis-Cp^- ligands. In this regard, the synthesis of *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*rac*-**1**) has attracted considerable interest.[2] This metallocene has been prepared by salt elimination and amine elimination reactions, which produce *rac*/*meso* mixtures,[3,4] and by photochemical isomerization of *rac*-**1**/*meso*-**1** mixtures.[5] To date, the most efficient route to **1**, developed by Brintzinger and co-workers, comprises reaction of $Sn(NMe_2)_4$ with $Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2$ to yield a silastannaindacene, followed by transmetalation with $ZrCl_4$ to produce *rac*-**1** (>98% de, 60% overall isolated yield).[6] Here we describe highly stereoselective syntheses of *rac*-**1** and *meso*-**1**.

We recently reported a highly selective, "chelate controlled" synthesis of *rac*-*ansa*-bis(indenyl) zirconocenes, which is based on the reaction of lithium *ansa*-bis(indenyl) salts with the chelated bis-amide compound $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ (**2**) and is shown in Scheme 1.[7] This procedure works well for *rac*-(SBI)$Zr\{PhN(CH_2)_3NPh\}$ and 2-Me-substituted and 2-Me-4-aryl-substituted derivatives thereof, as well as for *rac*-(EBI)$Zr\{PhN(CH_2)_3NPh\}$.[7]

The key to Scheme 1 is the use of the $[PhN(CH_2)_3NPh]^{2-}$ ligand to control diastereoselectivity. The $Zr\{PhN(CH_2)_3NPh\}$ chelate rings in **2** and several $(C_5R_5)_2Zr\{PhN(CH_2)_3NPh\}$ metallocenes adopt twist conformations which place the N−Ph groups on opposite sides of the N−Zr−N plane, as shown in Scheme 1.[7] This arrangement complements the *rac*-metallocene structure but strongly disfavors the *meso* isomer. The mechanism of $[X(indenyl)_2]^{2-}$ substitution of the chloride and THF ligands of **2** is unknown and may be complicated by ion-pairing, solvation, and other factors.[3] However, the simple model in Scheme 1 provides useful insights. We postulate that, while rotation around the Zr−(indenyl centroid) in the mono-indenyl intermediate **A** can occur, the bridge (X) must be close to the "back" position in the transition state for the second indenyl

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* Corresponding author.

[1] (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (c) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262. (d) Halterman, R. L. In *Synthesis of Chiral Titanocene and Zirconocene Dichlorides*; Togni, A., Halterman, R. L., Eds.; Metallocenes: Synthesis, Reactivity, Applications: Wiley-VCH: Weinheim, 1998; Vol. 1, Chapter 8.

[2] For polymerization studies using **1** see: (a) Suzuki, N.; Yamaguchi, Y.; Fries, A.; Mise, T. *Macromolecules* **2000**, *33*, 4602. (b) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853. (c) Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. For other examples of metallocenes based on *ansa*-bis-$(3\text{-}R\text{-}C_5H_3)$ ligands see: (d) Sutton, S. C.; Nantz, M. H.; Parkin, S. R. *Organometallics* **1993**, *12*, 2248. (e) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695. (f) Chen, Z.; Halterman, R. L. *Organometallics* **1994**, *13*, 3932. (g) Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 777. (h) Kuntz B. J.; Ramachandran, R.; Taylor N. J.; Guan, J.; Collins, S. *J. Organomet. Chem.* **1995**, *497*, 133.

[3] Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359.

[4] Diamond, G. M.; Jordan, R. F.; Petersen, J. F. *Organometallics* **1996**, *15*, 4045.

[5] Schmidt, K.; Reinmuth, A.; Rief, U.; Diebold, J.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 1724.

[6] (a) Hüttenhofer, M.; Weeber, A.; Brintzinger, H. H. *J. Organomet. Chem.* **2002**, *663*, 58. (b) Hüttenhofer, M.; Schaper, F.; Brintzinger, H. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2268.

[7] (a) Zhang, X.; Zhu, Q.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 8093. (b) LoCoco, M. D.; Jordan, R. F. *Abstracts of Papers*, 225th ACS National Meeting, New Orleans, LA, March 23−27, 2003, INOR-723. (c) SBI = $Me_2Si(indenyl)_2$, EBI = 1,2-bis(indenyl)ethane. (d) X-ray crystallographic analyses show that the $Zr\{PhN(CH_2)_3NPh\}$ chelate rings in $Cp_2Zr\{PhN(CH_2)_3NPh\}$, *rac*-(SBI)$Zr\{PhN(CH_2)_3NPh\}$, and *rac*-$\{Me_2Si(2\text{-}Me\text{-}4,5\text{-}benz\text{-}1\text{-}indenyl)_2\}Zr\{PhN(CH_2)_3NPh\}$ adopt twist conformations.[7a,b]

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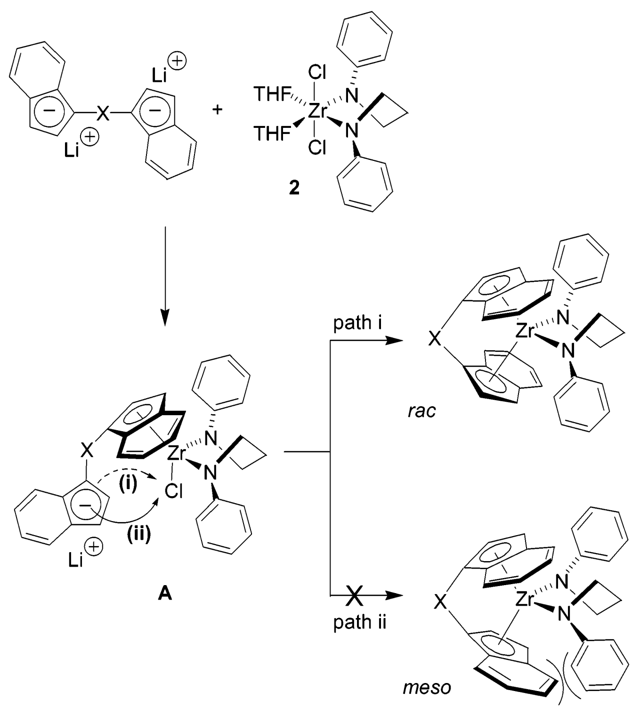
Scheme 1[a]

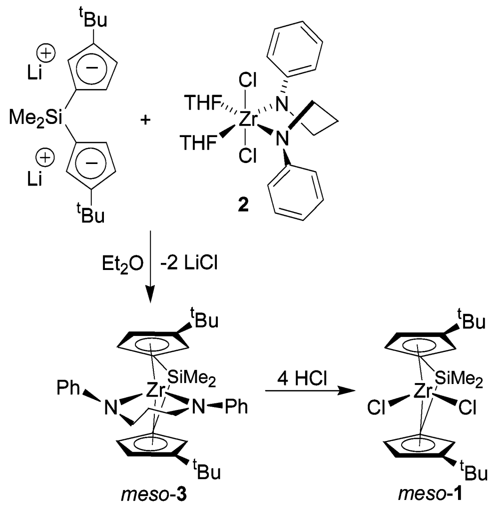


addition, as required in the *ansa*-metallocene product. As the second indenyl adds, N−Ph/indenyl steric interactions block formation of the *meso* product by path (ii), and the *rac* product forms by path (i). Significant N−Ph/indenyl steric interactions would arise on the crowded side of the *meso* isomer (and transition state leading thereto) unless the Zr{PhN(CH_2)$_3$NPh} chelate ring adopted a different conformation, which is unfavorable.[7,8]

Application of this strategy to the synthesis of **1** led to a surprising result. The reaction of $Li_2[Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2]$ with **2** in Et_2O yields pure *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-**3**) quantitatively (Scheme 2)! The ^1H NMR spectrum of *meso*-**3** contains two sets of phenyl resonances and two Si−Me resonances, which establishes the *meso* stereochemistry. Reaction of *meso*-**3** with HCl (1 M Et_2O solution) in benzene yields *meso*-**1** in >95% NMR yield. The use of 4 equiv of HCl in Scheme 2 facilitates the identification of *meso*-**1** by precipitation of the $HNPh(CH_2)_3NPhH$ coproduct as $[H_2NPh(CH_2)_3NPhH_2]Cl_2$.

To probe the stereocontrol mechanism in Scheme 2, the molecular structure of *meso*-**3** was determined by X-ray diffraction (Figure 1). Surprisingly, the Zr{PhN(CH_2)$_3$NPh} ring adopts an envelope conformation in which C(10), C(9), and C(8) are close to the N(1)−Zr(1)−N(2) plane (respective deviations: −0.056, 0.083, 0.148 Å), while C(7) lies 0.63 Å below and C(1) lies 0.56 Å above this plane. This unusual conformation is enforced by the bulky ^{t}Bu groups, which make close contact with and thus flatten the C(10)−C(8) segment of the chelate.[9] Puckering of the C(8)−C(7)−N(1) segment is required to maintain a normal N(1)−Zr(1)−N(2) angle of 95.3(1)°. The C(10) phenyl group on the crowded side of the molecule lies in the N−Zr−N plane. The steric crowding associated with the ^{t}Bu groups is manifested in several other ways. The ^{t}Bu groups are bent 9.5° out of their respective Cp planes, and the Zr−C(^{t}Bu) distances (Zr−C(28) 2.693(3) Å; Zr−C(17) 2.782(3) Å) are longer than the other Zr−Cp distances (range 2.49−2.65 Å). Additionally, the two Cp rings are canted such that the angle between the C(27)−C(28) and C(18)−C(17) bond vectors is 24.9°. The Cp rings are rotated around the Zr−centroid axes such that the $SiMe_2$ bridge is displaced by 16.3° from the back position of the metallocene, and the ^{t}Bu groups are displaced toward the front of the metallocene by a corresponding amount. This "lateral distortion"[10] is smaller than those in *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr(1,1'\text{-binaphth-}2'\text{-ol-}2\text{-olato})Cl$ (27.1°)[5] and *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrMe_2$ (24.6°)[11] and appears to be limited by steric crowding between the C(10) phenyl group and the Cp and C(34) methyl groups.[12]

Scheme 2



These structural data provide clues to the origin of the surprising selectivity for the *meso* product in Scheme 2. As for Scheme 1, we postulate that steric interactions in the mono-Cp intermediate and the transition state for addition of the second Cp^- ring are similar to those in the metallocene product. That is, as illustrated in Scheme 3, we postulate that steric interactions force the Zr{PhN(CH_2)$_3$NPh} chelate ring of mono-Cp intermediate **B** into an envelope conformation. Steric interactions between the ^{t}Bu group of the incoming Cp^- ligand and the puckered segment of the chelate ring block formation of *rac*-**3** via path (i), so that *meso*-**3** forms via path (ii).

To favor the formation of a *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{RN(CH_2)_3NR\}$ metallocene, we sought to modify the controlling $[RN(CH_2)_3NR]^{2-}$ ligand to increase the steric

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[8] In contrast, metallocene syntheses using Ti binaphtholate or Zr biphenolate compounds that adopt twist conformations gave low yields[a] or *rac*/*meso* mixtures that were isomerized to *rac* products using TEMPO.[b] (a) Erikson, M. S.; Fronczek, F. R.; McLaughlin, M. L. *J. Organomet. Chem.* **1991**, *415,* 75. (b) Damrau, H.-R.; Royo, E.; Obert, S.; Schaper, F.; Weeber, A.; Brintzinger, H.-H. *Organometallics* **2001**, *20,* 5258.

[9] Close contacts (Å): H(24C)- -H(9B) 2.30, H(9A)- -H(31A) 2.43, H(32C)- -H(8A) 2.20, H(23A)- -H(7A) 2.13, C(10)- -H(24C) 2.75.

[10] (a) Burger, P.; Diebold, J.; Gutman, S.; Hund, H. U.; Brintzinger, H. H. *Organometallics* **1992**, *11,* 1319. (b) Burger, P.; Hortman, K.; Brintzinger, H. H. *Makromol. Chem., Macromol. Symp.* **1993**, *66,* 127.

[11] Chirik, P. J.; Henling, L. M.; Bercaw, J. E. *Organometallics* **2001**, *20,* 534.

[12] Close H−H contacts (Å): H(15)- -H(29) 2.26, H(15)- -H(16) 2.47, H(15)- -H(34A) 2.40.

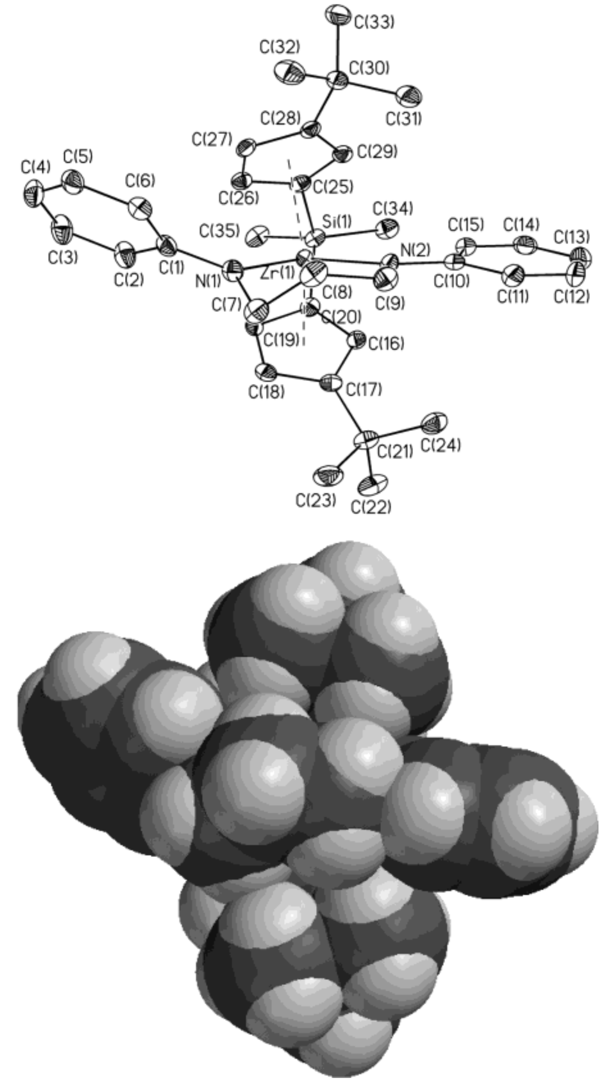
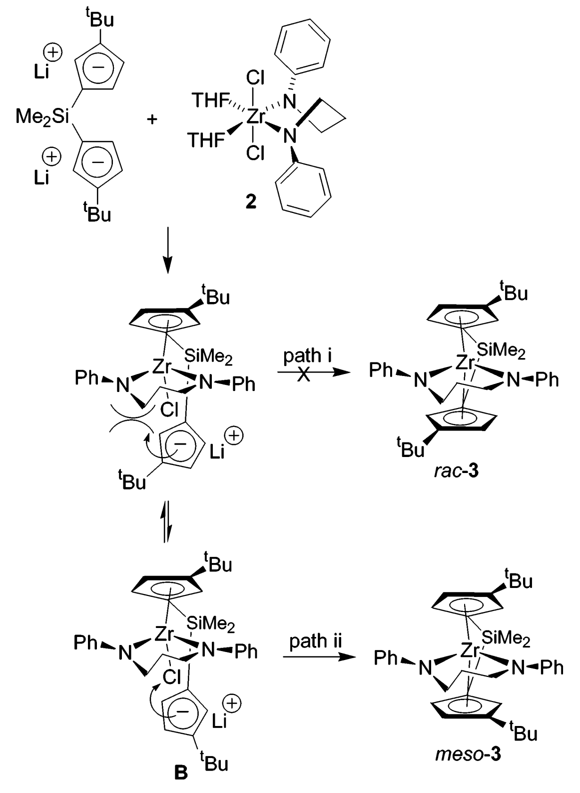
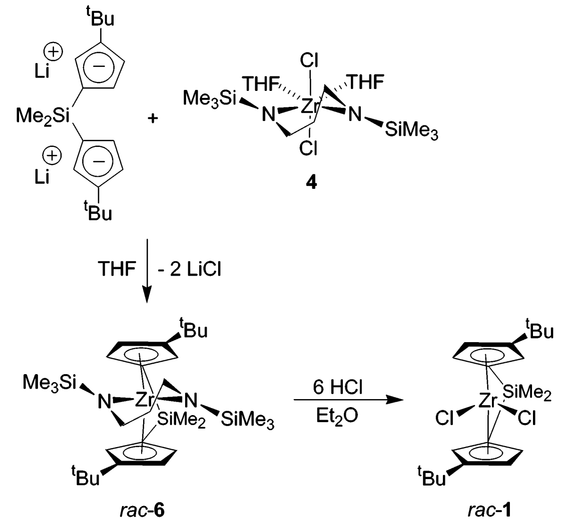


Figure 1. Molecular structure and corresponding space-filling diagram of *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-**3**). H atoms are omitted in the ORTEP view. Bond distances (Å): Zr−N(1) 2.076(3), Zr−N(2) 2.176(3), Zr−{C(16)−C(20) centroid} 2.328(3), Zr−{C(25)−C(29) centroid} 2.308(3). Bond angles (deg): centroid−Zr−centroid 124.2(9).

Scheme 3



Scheme 4



crowding between the Cp−^{t}Bu and N−R groups, to provide a stronger preference for the chelate twist conformation in the metallocene product (and presumably the transition state for the second Cp^- addition). This can be achieved by replacing the N−Ph groups with N−$SiMe_3$ groups, which feature greater three-dimensional steric bulk. The reaction of $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)_2$ (**4**)[13] or the related mono-THF adduct $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)$ (**5**) with $Li_2[Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2]$ in THF yields pure *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-**6**) in quantitative NMR yield and 89% isolated yield (Scheme 4). The ^1H NMR spectrum of *rac*-**6** contains singlets for the ^{t}Bu, $SiMe_2$, and $SiMe_3$ groups, which confirms the *rac* stereochemistry. *rac*-**6** is cleanly converted to *rac*-**1** by reaction with 6 equiv of HCl in Et_2O. The 3-fold excess of HCl is necessary because the $Me_3SiNH(CH_2)_3NHSiMe_3$ coproduct reacts with HCl to yield $[H_3N(CH_2)_3NH_3]Cl_2$ and $ClSiMe_3$.

The molecular structure of *rac*-**6** is shown in Figure 2. *rac*-**6** has approximate C_2 symmetry with the C_2 axis lying along the Zr- - -C(12) vector. In contrast to *meso*-**3**, the $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ chelate ring has the familiar twist conformation,[7] which places the N−$SiMe_3$ groups in the sterically open quadrants of the *rac*-metallocene and minimizes $SiMe_3$/^{t}Bu steric interactions.[14,15] We propose that the twist conformation

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[13] (a) Freidrich, S.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *Organometallics* **1995**, *14*, 5344. (b) Freidrich, S.; Gade, L. H.; Trosch, D. J. M.; Scowen, I. J.; McPartlin, M. *Inorg. Chem.* **1999**, *38*, 5295.

[14] (a) Deviations (Å) of C and Si atoms from the N(1)−Zr−N(2) plane: Si(2) 0.88, C(11) −0.87, C(12) 0.10, C(13) 0.71, Si(1) −0.61. (b) The conformation of the $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ chelate ring in *rac*-**6** is similar to that in **4**; see ref 13b.

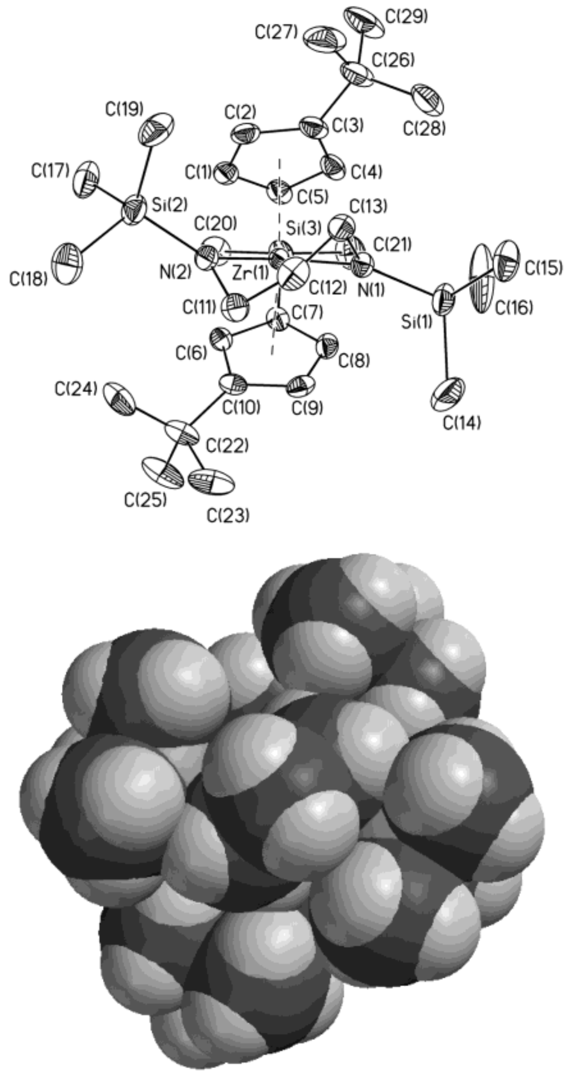

Figure 2. Molecular structure and corresponding space-filling diagram of *rac*-$Me_2Si(3-{}^tBu-C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-**6**). H atoms are omitted from the ORTEP view. Bond distances (Å): Zr−N(1) 2.114(2), Zr−N(2) 2.103(2), N(1)−Si(1) 1.725(2), N(2)−Si(2) 1.737(2), Zr−{C(1)−C(5) centroid} 2.328(3), Zr−{C(6)−C(10) centroid} 2.340(3). Bond angles (deg): N(1)−Zr−N(2) 92.63(8), centroid−Zr−centroid 122.5(9).

dictates the formation of *rac*-**6** in a manner analogous to Scheme 1.

Conclusions

This work expands the scope of the "chelate-controlled" approach to metallocene synthesis to include simple *ansa*-bis-Cp systems. The present results suggest that suitable modification of the controlling bis-amide ligand may enable the synthesis of a wide range of *rac*-metallocenes by this method. These studies also provide new insights into the factors that control diastereoselectivity in *ansa*-metallocene formation.

Experimental Section

General Procedures. All reactions were performed under nitrogen or vacuum using standard Schlenk techniques or in a nitrogen-filled drybox. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Pentane, hexanes, toluene, and benzene were distilled from sodium/benzophenone or purified by passage through columns of activated alumina and BASF R3-11 oxygen removal catalyst. Benzene-d_6 was distilled from sodium/benzophenone. The compounds $Me_2Si(3-{}^tBu-C_5H_3)_2$,[3] $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$,[7a,b] $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}_2$,[13a] and $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)_2$[13a] were prepared by literature procedures.

Elemental analyses were performed by Midwest Microlabs. ESI-mass spectra were obtained with an Agilent 1100 instrument using direct injection via a syringe pump (ca. 10^{-6} M solutions). Good agreement between observed and calculated isotope patterns was observed in all cases. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-500 or AC-400 spectrometer in flame-sealed or Teflon-valved tubes at ambient probe temperatures. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. Coupling constants are given in Hz.

$Li_2[Me_2Si(3-{}^tBu-C_5H_3)_2]$.[3] A Schlenk flask was charged with a solution of $Me_2Si(3-{}^tBu-C_5H_3)_2$ (2.75 g, 9.03 mmol) in Et_2O (50 mL). The solution was cooled to −78 °C, and a solution of n-BuLi in hexanes (2.5 M, 7.22 mL, 18 mmol) was added by syringe. The mixture was stirred for 4 h at −78 °C, warmed to 0 °C in an ice bath, and then stirred overnight while being allowed to warm gradually to room temperature. The volatiles were removed under vacuum to yield a white solid. Toluene (50 mL) was added by cannula transfer. The slurry was stirred for 30 min and filtered through a medium-porosity glass frit (10−20 μm pore size) to yield a white solid. The solid was dried under vacuum overnight (2.55 g, 89%). ^1H NMR (THF-d_8): δ 5.86 (m, 4H, Cp), 5.74 (t, $J = 3$, 2H, Cp), 1.21 (s, 18H, ^{t}Bu), 0.26 (s, 6H, $SiMe_2$).

***meso*-$Me_2Si(3-{}^tBu-C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (*meso*-3).** A flask was charged with $Li_2[Me_2Si(3-{}^tBu-C_5H_3)_2]$ (0.705 g, 2.22 mmol) and $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ (1.18 g, 2.22 mmol). Diethyl ether (100 mL) was added by vacuum transfer at −196 °C. The mixture was warmed to 0 °C and stirred for 6 h and then warmed to room temperature and stirred overnight. The volatiles were removed under vacuum at 25 °C to yield a red solid. Toluene (100 mL) was added by vacuum transfer at −196 °C, and the mixture was warmed to room temperature and stirred for 30 min. The mixture was filtered through a Celite column, and the volatiles were removed from the filtrate under vacuum at 25 °C. The remaining red solid was dried under vacuum (1.36 g, 99%). This material, which was spectroscopically pure, was recrystallized from pentane/hexamethyldisiloxane.[16] ^1H NMR (C_6D_6): δ 7.28 (t, $J = 8$, 2H, *m*-Ph), 7.22 (t, $J = 8$, 2H, *m*-Ph), 6.96 (t, $J = 8$, 1H, *p*-Ph), 6.79 (m, 3H, *o*-Ph and *p*-Ph), 6.47 (d, $J = 8.0$ 2H, *o*-Ph), 6.22 (m, 4H, Cp), 6.00 (t, $J = 3.0$, 2H, Cp), 3.57 (t, $J = 6$, 2H, NCH_2), 3.26 (t, $J = 6$, 2H, NCH_2), 1.67 (p, $J = 6$, 2H, CH_2), 0.92 (s, 18H, ^{t}Bu), 0.60 (s, 3H, SiMe), 0.55 (s, 3H, SiMe). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 162.9, 160.0, 148.4, 129.2, 128.5, 122.6, 120.8, 120.4, 118.3, 117.4, 111.8, 109.7, 106.0, 53.6, 52.9, 33.7, 31.5, 29.7, −2.6, −5.4; the signal at δ 118.3 is broadened by restricted rotation around an N−Ph bond at room temperature but is sharp at 60 °C. Anal. Calcd for $C_{35}H_{46}N_2SiZr$: C, 68.45; H, 7.54; N, 4.56. Found: C, 68.30; H, 7.52; N, 4.61.

***meso*-$Me_2Si(3-{}^tBu-C_5H_3)_2ZrCl_2$ (*meso*-1).** An NMR tube was charged with *meso*-$Me_2Si(3-{}^tBu-C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (0.023 g, 0.037 mmol), and C_6D_6 (1.0 mL) was added by syringe. A solution of HCl in Et_2O (1.0 M, 77.5 μL, 0.077 mmol) was added by syringe. The volatiles were removed under vacuum

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(15) In contrast to *meso*-**3**, *rac*-**6** does not display a significant lateral distortion. However, the Zr−N bond distances, N−Zr−N bond angle, displacement of the ^{t}Bu groups from the Cp planes, and the trend in Zr−C(Cp) distances in *rac*-**6** are similar to the data for *meso*-**3**. The angle between the C(2)−C(3) and C(10)−C(9) bond vectors is 9.9°.

(16) For other examples of the use of hexamethyldisiloxane as a recrystallization solvent see: (a) Kloppenburg, L.; Petersen, J. L. *Polyhedron* **1995**, *14*, 69. (b) Strauch, J. W.; Petersen, J. L. *Organometallics* **2001**, *20*, 2623.

immediately, and fresh C_6D_6 was added by vacuum transfer at −196 °C. The tube was warmed to room temperature, and a ^1H NMR spectrum was obtained, which showed that complete conversion to $Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*meso*/*rac* 30:1)[3] and $HNPh(CH_2)_3NHPh$ had occurred. ^1H NMR (C_6D_6) for *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$: δ 6.84 (t, $J = 2$, 2H, Cp), 5.87 (t, $J = 2$, 2H, Cp), 5.54 (t, $J = 2$, 2H, Cp), 1.45 (s, 18H, ^tBu), 0.29 (s, 3H, SiMe), 0.08 (s, 3H, SiMe). ^1H NMR (C_6D_6) for $HNPh(CH_2)_3NPhH$: δ 7.17 (t, $J = 7$, 4H, Ph), 6.76 (t, $J = 7$, 2H, Ph), 6.46 (d, $J = 7$, 4H, Ph), 3.50 (br s, 2H, NH), 2.73 (t, $J = 7$, 4H, NCH_2), 1.32 (p, $J = 7$, CH_2).

Generation of *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*meso*-1) from *meso*-3 and 4 Equiv of HCl. An NMR tube was charged with *meso*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{PhN(CH_2)_3NPh\}$ (0.028 g, 0.045 mmol), and C_6D_6 (1.0 mL) was added by syringe. A solution of HCl in Et_2O (1.0 M, 181.0 μL, 0.181 mmol) was added by syringe. The volatiles were removed under vacuum immediately, and fresh C_6D_6 was added by vacuum transfer at −196 °C. The tube was warmed to room temperature to yield a slurry of a white precipitate in a yellow supernatant. The supernatant was decanted from the precipitate to yield a clear yellow solution. ^1H NMR analysis of the solution established that complete conversion to $Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*meso*/*rac* 20:1) had occurred. The white solid was isolated and identified as $[H_2NPh(CH_2)_3NH_2Ph]Cl_2$ by NMR and ESI-MS.

$[H_2NPh(CH_2)_3NH_2Ph]Cl_2$. A flask was charged with a solution of $HNPh(CH_2)_3NHPh$ (1.12 g, 4.94 mmol) in benzene (25 mL). A solution of HCl in Et_2O (1.0 M, 9.89 mL, 9.89 mmol) was added over a 10 min period by syringe. The mixture was stirred for 1 h at room temperature and filtered to afford a white solid. The solid was washed with hexanes (2 × 20 mL) and benzene (20 mL). The solid was then taken up as a slurry in hexanes (20 mL), and the volatiles were removed under vacuum to yield a white solid. ^1H NMR (D_2O): δ 7.46 (br m, 6H, Ph), 7.32 (br d, $J = 7$, 4H, Ph), 3.43 (t, $J = 8$, 4H, NCH_2), 2.03 (p, $J = 8$, 2H, CH_2). $^{13}C\{^1H\}$ NMR (D_2O): δ 134.0, 130.3, 129.7, 122.0, 47.6, 21.4. ESI-MS: $[HNPh(CH_2)_3NH_2Ph]^+$ calcd *m*/*z* 227.1, found 227.1.

$Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)$ (5). A flask was charged with $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}_2$ (3.04 g, 5.79 mmol) and $ZrCl_4$ (1.35 g, 5.79 mmol). Toluene (100 mL) was added, and the mixture was heated to 60 °C for 3 days. The volatiles were removed under vacuum, and the resulting white solid was washed with pentane (75 mL) and dried under vacuum (4.20 g, 95%). The solid was dissolved in THF (40 mL). The bis-THF adduct $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)_2$ (**4**) can be isolated from this solution by crystallization at −35 °C as described by Gade[13a,b] or by removal of the volatiles under vacuum and vacuum-drying the sample for a few minutes. Drying under vacuum overnight yielded $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)$ as a white solid (5.01 g, 95%). ^1H NMR (C_6D_6): δ 3.72 (m, 4H, OCH_2), 3.23 (t, $J = 5$, 4H, NCH_2CH_2), 1.74 (p, $J = 5$, 2H, NCH_2CH_2), 1.25 (m, 4H, OCH_2CH_2), 0.31 (s, 18H, $SiMe_3$).

***rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (*rac*-6).** A flask was charged with $Li_2[Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2]$ (0.853 g, 2.69 mmol) and $Zr\{Me_3SiN(CH_2)_3NSiMe_3\}Cl_2(THF)$ (1.21 g, 2.69 mmol), and THF (100 mL) was added by vacuum transfer at −196 °C. The mixture was warmed to 0 °C in an ice bath and then stirred for 20 h while the bath was allowed to warm to room temperature. The volatiles were removed under vacuum at 25 °C to yield a yellow solid. Benzene (100 mL) was added by vacuum transfer at −196 °C, and the mixture was warmed to room temperature and stirred for 3 h. The mixture was filtered through a medium-porosity glass frit, and the volatiles were removed from the filtrate under vacuum at 25 °C. The resulting yellow solid was dried under vacuum (1.46 g, 89%). This material, which was spectroscopically pure, was recrystallized from pentane. ^1H NMR (C_6D_6): δ 6.85 (t, $J = 2$, 2H, Cp), 5.91 (t, $J = 2$, 2H, Cp), 5.84 (t, $J = 2$, 2H, Cp), 3.32 (dt, $J = 16, 4$; 2H, NCH_2), 3.04 (m, 2H, NCH_2), 1.23 (s, 18H, ^tBu), 1.00 (br m, 2H, CH_2), 0.47 (s, 6H, $SiMe_2$), 0.27 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 148.8, 116.1, 111.3, 107.9, 106.5, 46.2, 33.7, 31.3, 28.5, 3.6, −4.3. Anal. Calcd for $C_{29}H_{54}N_2Si_3Zr$: C, 57.45; H, 8.98; N, 4.57. Found: C, 57.19; H, 8.97; N, 4.57.

Table 1. Summary of Crystal Data for *meso*-3 and *rac*-6

	meso-**3**	*rac*-**6**
formula	$C_{35}H_{46}N_2SiZr$	$C_{29}H_{54}N_2Si_3Zr$
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	10.324(2)	14.712(7)
b (Å)	18.201(3)	11.872(6)
c (Å)	16.753(3)	19.306(9)
β (deg)	100.203(2)	104.373(8)
V (Å^3)	3094.8(8)	3266(3)
Z	4	4
μ (mm^{-1})	0.420	0.466
cryst dimens (mm)	0.2 × 0.2 × 0.2	0.40 × 0.25 × 0.25
cryst color, habit	red, fragment	yellow, fragment
T (K)	100	135
diffractometer	Bruker Smart Apex	Bruker Smart Apex
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
θ range (deg)	2.24−25.03	2.03−25.02
data collected: $h;k;l$	±12; −21,19; −18,19	±17; ±14; ±22
no. of reflns	19 612	23 087
no. of indep reflns (R_{int})[a]	5476 (0.0322)	5755 (0.0252)
abs corr	SADABS	SADABS
max., min. transmn	1.00, 0.854	1.00, 0.852
no. of data/restraints/params	5467/0/360	5755/0/330
R indices ($I > 2\sigma(I)$)[b]	R1 = 0.0456 wR2 = 0.0899	R1 = 0.0331 wR2 = 0.0817
R indices (all data)[b]	R1 = 0.0465 wR2 = 0.0904	R1 = 0.0347 wR2 = 0.0826

[a] $R_{int} = \sum|F_o^2 - \langle F_o^2\rangle|/\sum|F_o^2|$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

***rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*rac*-1). NMR Scale.** An NMR tube was charged with *rac*-$Me_2Si(1\text{-}C_5H_3\text{-}3\text{-}^tBu)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (0.0274 g, 0.0451 mmol) and C_6D_6 (1 mL). A solution of HCl in Et_2O (1.0 M, 271 μL, 0.271 mmol) was added by syringe. The volatiles were removed under vacuum to yield a yellow solid. THF-d_8 (1 mL) was added by vacuum transfer at −196 °C, and the tube was warmed to room temperature to yield a slurry of a white solid in a yellow supernatant. The supernatant was decanted off and transferred to a new NMR tube. NMR analysis confirmed that quantitative conversion to *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ had occurred. ^1H NMR of *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (THF-d_8): δ 6.74 (t, $J = 3$, 2H), 6.06 (t, $J = 3$, 2H, Cp), 5.92 (t, $J = 3$, 2H, Cp), 1.32 (s, 18H, ^tBu), 0.68 (s, 6H, $SiMe_2$). The white solid was washed with benzene (2 mL) and hexanes (2 mL) and dried under vacuum. NMR and ESI-MS analysis established that the white solid was $[H_3N(CH_2)_3NH_3]Cl_2$. Data for $[H_3N(CH_2)_3NH_3]Cl_2$: ^1H NMR (D_2O): δ 3.14 (t, $J = 8$, 4H, NCH_2), 2.10 (p, $J = 8$, 2H, CH_2). $^{13}C\{^1H\}$ NMR (D_2O): δ 36.59, 25.41. ESI-MS (DMSO): $[H_3N(CH_2)_3NH_2]^+$ calcd *m*/*z* 75.1, found 75.2.

***rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2ZrCl_2$ (*rac*-1). Preparative Scale.** A flask was charged with *rac*-$Me_2Si(3\text{-}^tBu\text{-}C_5H_3)_2Zr\{Me_3SiN(CH_2)_3NSiMe_3\}$ (1.554 g, 2.563 mmol) and benzene (80 mL). A solution of HCl in Et_2O (1.0 M, 15.38 mL, 15.38 mmol) was added by syringe over a 10 min period. The volatiles were removed under vacuum to yield a yellow solid. Benzene (50 mL) was added by vacuum transfer at −196 °C, and the mixture was warmed to room temperature and stirred for 45 min. The mixture was filtered through a medium-porosity glass frit. The volatiles were removed from the filtrate under vacuum. The remaining yellow solid was dried under vacuum (1.00 g, 84%). ^1H NMR (C_6D_6): δ 6.72 (t, $J = 3$, 2H), 5.69 (t, $J = 3$, 2H, Cp), 5.65 (t, $J = 3$, 2H, Cp), 1.40 (s, 18H, ^tBu), 0.18

(s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR: δ 152.9, 125.8, 116.2, 110.2, 105.4, 33.6, 30.3, −5.8.

Reaction of $Me_3SiNH(CH_2)_3NHSiMe_3$ with 4 Equiv of HCl. An NMR tube was charged with a solution of $Me_3SiNH(CH_2)_3NHSiMe_3$ (0.049 g, 0.23 mmol) in C_6D_6 (2 mL). A solution of HCl in Et_2O (1.0 M, 0.9 mL, 0.9 mmol) was added by syringe, and a white precipitate formed. The volatiles were vacuum transferred to a new NMR tube. The white solid was identified as $[H_3N(CH_2)_3NH_3]Cl_2$ by NMR and ESI-MS. The presence of $ClSiMe_3$ in the volatiles was established by ^1H NMR and confirmed by spiking with additional $ClSiMe_3$.

X-ray Structure Determinations. Crystal data, data collection details, and solution and refinement procedures are summarized in Table 1, and full details are provided in the Supporting Information. Crystals of *meso*-**3** were obtained from a 5:1 pentane/hexamethyldisiloxane solution which was heated to 80 °C and then allowed to cool to room temperature over a 24 h period. Crystals of *rac*-**6** were obtained from a saturated pentane solution cooled to −35 °C.

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Supporting Information Available: Additional experimental details and tables of crystallographic data for *meso*-**3** and *rac*-**6**; data are also available for these compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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