Efficient Synthesis of Chiral *ansa*-Metallocenes by Amine Elimination. Synthesis, Structure, and Reactivity of *rac*-(EBI)Zr(NMe_2)$_2$

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Abstract: The amine elimination reaction of Zr(NMe_2)$_4$ (**2**) and (EBI)H_2 (1,2-bis(3-indenyl)ethane, **3**) in toluene at 100 °C affords pure *rac*-(EBI)Zr(NMe_2)$_2$ (*rac*-**4**, EBI = ethylene-1,2-bis(1-indenyl)) in 68% isolated yield. This reaction proceeds via the rapidly formed mono-indenyl intermediate (η^5-$C_9H_6CH_2CH_2C_9H_7$)Zr(NMe_2)$_3$ (**6**) which undergoes reversible intermolecular amine elimination with a second equivalent of **2** to give the binuclear species (μ-η^5,η^5-EBI){Zr(NMe_2)$_3$}$_2$ (**5**, *rac* and *meso* isomers) or reversible intramolecular amine elimination to give either *rac*-**4** or *meso*-**4**. The kinetic metallocene product is a 1/1 mixture of *rac*-**4** and *meso*-**4**, the thermodynamic product is *rac*-**4**, and the *meso*-**4** to *rac*-**4** isomerization is catalyzed by the NMe_2H co-product. The *rac*-**4**/*meso*-**4** product ratio can be controlled by adjusting the rate of NMe_2H removal from the reaction vessel and the steady state concentration of amine in the reaction mixture. The molecular structure of *rac*-**4** has been determined by X-ray crystallography. *rac*-**4** is converted to *rac*-(EBI)$ZrCl_2$ (*rac*-**1**) in high yield by reaction with NMe_2H·HCl (92% isolated) or Me_3SiCl (quantitative). The syntheses of **2**, *rac*-**4**, and *rac*-**1** can be combined in a "one pot" synthesis of *rac*-**1** from $ZrCl_4$ in 68% overall yield. Alkylation of *rac*-**4** with $AlMe_3$ affords *rac*-(EBI)$ZrMe_2$ (*rac*-**7**) in 90% isolated yield. *rac*-**4** can be used directly as a catalyst precursor for the isospecific polymerization of propylene.

Introduction

Chiral group 4 *ansa*-metallocenes are the basis of a new class of stereoselective olefin polymerization catalysts,[1] and have been employed as stereoselective catalysts or reagents for a wide variety of other reactions,[2] including olefin hydrogenation,[3a,b] epoxidation,[3c,d,e] isomerization,[3f] hydrooligomerization,[3g,h] and cyclopolymerization reactions,[3i,j] olefin−pyridine coupling,[3k] imine hydrogenation,[3l,m,n] enamine hydrogenation,[3o] Diels−Alder reactions,[3p,q] allylic amine synthesis,[3r] allylic alcohol synthesis,[3s,t] carbomagnesation reactions,[3u] kinetic resolution of pyrans,[3v] hydrosilylation of ketones,[3w,x] and dehydrogenative phenylsilane oligomerization.[3y] However, practical application of *ansa*-metallocene catalysts and reagents is hindered by the fact that current *ansa*-metallocene syntheses, which are based on salt elimination reactions between MCl_x compounds and bis-cyclopentadienyl dianion reagents, are inefficient. Here we describe in detail a new approach to *ansa*-metallocene synthesis based on amine elimination chemistry.

Among the first chiral *ansa*-metallocenes to be prepared were the ethylene-bridged, bis-indenyl complexes (EBI)MCl_2 (M = Ti, Zr, Hf; EBI = ethylene-1,2-bis(1-indenyl)) and their hydrogenated derivatives (EBTHI)MCl_2 (EBTHI = ethylene-1,2-bis(1-tetrahydroindenyl)).[4−7] These prototypical *ansa*-met-

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allocenes were the first to be used for olefin polymerization catalysis,[8] and are still widely used for comparison purposes in olefin polymerization studies,[1f,9] as models in mechanistic and theoretical studies,[10] and as stereoselective catalysts in synthetic organic reactions.[3]

rac-(EBI)ZrCl$_2$ (*rac*-**1**) was first prepared by Brintzinger from ZrCl$_4$(THF)$_2$ and (EBI)Li$_2$, in 35% yield.[4b] Collins proposed that the low yield of this reaction was due mainly to the formation of polymeric byproducts which had to be removed in subsequent washing steps, and improved the yield of *rac*-**1** to 52% by using high dilution and slow mixing of THF solutions of ZrCl$_4$(THF)$_2$ and (EBI)Li$_2$.[6] Buchwald employed (EBI)K$_2$ and obtained **1** in 70% yield but as a 2/1 mixture of *rac* and *meso* diastereomers.[7] However, the Collins and Buchwald syntheses both require a washing step with aqueous HCl, which, if not performed rapidly and on a completely dried reaction mixture, can result in partial hydrolysis of (EBI)ZrCl$_2$ and varying purity of the final product. Piemontesi recently reported an alternative workup which avoids the acid wash, employs a CH$_2$Cl$_2$ Soxhlet extraction step, and affords pure *rac*-**1** in 40% yield.[11] Van Beek has reported that the reaction of (EBI)Li$_2$ with ZrCl$_4$ in dimethoxyethane affords *rac*-**1** in 65% yield.[12] These syntheses of *rac*-**1** are among the most refined and efficient *ansa*-metallocene preparations yet developed. In general, current syntheses of chiral C_2-symmetric *ansa*-metallocenes by salt elimination reactions produce the desired *rac* isomer in 10−30% yield,[1e,f,k,13] and separation of the chiral *rac* isomer from the undesired, achiral *meso* isomer is not always possible.[9,14]

Amine elimination reactions of group 4 metal dialkylamide compounds with protic reagents have been used to prepare a wide variety of organometallic and inorganic complexes.[15] In 1968, Lappert showed that the reaction of Zr(NMe$_2$)$_4$ (**2**) with excess cyclopentadiene (CpH) in refluxing benzene affords Cp$_2$Zr(NMe$_2$)$_2$ and 2 equiv of NMe$_2$H.[16] The analogous reaction with indene (IndH) gave only the mono-indenyl compound (Ind)Zr(NMe$_2$)$_3$. Lappert attributed this difference in reactivity to the greater steric bulk of IndH compared with CpH; however, the lower acidity of IndH versus CpH may also play a role (pK_a in Me$_2$SO: IndH = 20.1, CpH = 18.0).[17] Lappert also found that the reaction of Ti(NMe$_2$)$_4$ with excess CpH gave only CpTi(NMe$_2$)$_3$, and ascribed the lack of formation of Cp$_2$Ti(NMe$_2$)$_2$ to the greater steric crowding around Ti versus Zr (effective ionic radii in 8-coordinate environment: Ti^{4+} 0.74 Å, Zr^{4+} 0.84 Å;[18] M−NMe$_2$ bond lengths: Ti 1.91−1.92 Å[19] and Zr 2.03−2.11 Å).[15,20]

Amine elimination reactions of cyclopentadiene reagents and actinide metal M(NR$_2$)$_4$ compounds have been described by several authors.[21] Takats reported that Cp$_2$U(NR$_2$)$_2$ (R = Et, Ph) could be prepared in high yield via amine elimination, though for R = Et, the product contained about 3% Cp$_3$U(NEt$_2$), and attempts to prepare Cp$_2$U(NMe$_2$)$_2$ invariably gave mixtures of Cp$_2$U(NMe$_2$)$_2$ and Cp$_3$U(NMe$_2$).[21a] Subsequently, Zanella reported that CpH reacts with M(NEt$_2$)$_4$ (M = U, Th) to yield mixtures of CpM(NEt$_2$)$_3$, Cp$_2$M(NEt$_2$)$_2$, Cp$_3$M(NEt$_2$), and Cp$_4$M, depending on the reaction conditions and stoichiometry.[21b] The tendency to form Cp$_3$M(NR$_2$) and Cp$_4$M complexes reflects in part the larger size and decreased steric crowding of actinide versus group 4 metal M(NR$_2$)$_4$ complexes (effective ionic radii in 8-coordinate environment: Th^{4+} 1.05 Å and U^{4+} 1.00 Å;[18] M−NR$_2$ (M = Th, U) bond lengths 2.25−2.35 Å).[22]

Recently, Herrmann reported the synthesis of the achiral Me$_2$Si-bridged metallocene Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(NEt$_2$)$_2$ via the reaction of Me$_2$Si(C$_5$H$_5$)$_2$ and Zr(NEt$_2$)$_4$.[23] Also, Collins has reported that the *ansa*-metallocene Me$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_9$H$_6$)ZrCl$_2$ may be prepared by the reaction of Me$_2$Si(C$_5$H$_5$)(C$_9$H$_7$) and Zr(NMe$_2$)$_4$, followed by protonolysis of the bis-amide intermediate using anhydrous HCl.[24] Bridged cyclopentadienylamide derivatives of the type {η^5,η^1-C$_5$H$_4$(CH$_2$)$_3$NMe}M(NMe$_2$)$_2$ (M = Zr, Hf)[25] and {η^5,η^1-Cp′SiMe$_2$NR′}M(NR$_2$)$_2$ (Cp′ = C$_5$H$_4$, C$_9$H$_6$; R′ = Ph, ^{t}Bu; M = Ti, Zr, Hf; R = Me, Et)[26] have also been prepared via amine elimination reactions.

Group 4 metal amide complexes are useful precursors to a wide range of derivatives.[15] For example, reactions of M(NR$_2$)$_4$

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complexes with other amines (NR'_2H) provide routes to either $M(NR'_2)_4$ or mixed-amide $M(NR_2)_{4-x}(NR'_2)_x$ complexes, and amine elimination reactions with alcohols, thiols, and acidic hydrocarbons provide routes to alkoxide, sulfide, and organometallic derivatives.[15,16a,27] Group 4 metal amides may be converted to halide derivatives via protonolysis (anhydrous HX or $NR_2H{\cdot}HX$)[24,25] or amide−halide exchange reactions (e.g. reaction with $M'Cl_4$, M′ = Ti, Zr, Hf, Si, Ge, Sn)[28,29] and may be converted to alkyl derivatives using AlR_3 reagents.[30]

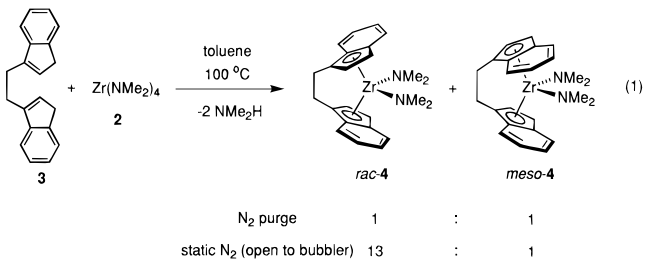
Since the most widely used and highly developed chiral *ansa*-metallocenes contain bridged bis-indenyl ligands, we decided to study the reactions of bridged bis-indenes and group 4 metal dialkylamides as a possible route to chiral *ansa*-metallocenes. Our working hypothesis was that if the indenes were linked, the chelate effect should favor the formation of *ansa*-metallocene bis-amide complexes over mono-indenyl products.[23−26] Additionally, it was felt that control of the reaction conditions and/or manipulation of the amide steric properties might provide a means of controlling the stereochemistry. Finally, it was anticipated that the *ansa*-metallocene bis-amide products could be converted to dihalide and other derivatives for catalytic applications. Here we describe in detail the synthesis of *rac*-(EBI)ZrX_2 (X = NMe_2, Cl, Me) complexes by amine elimination reactions.[31] Subsequent papers in this series will discuss the extension of this approach to different metals, amides,[32] bridging groups,[33] and Cp substituents.[34]

Results and Discussion

Improved Synthesis of $Zr(NMe_2)_4$ (2). $Zr(NMe_2)_4$ was first prepared by Bradley in 1959, via the reaction of $ZrCl_4$ and $LiNMe_2$ in Et_2O. Extraction of the crude product into benzene followed by sublimation gave pure $Zr(NMe_2)_4$ in 59% yield.[27] Chisholm showed that $Zr(NMe_2)_4$ and $LiNMe_2$ react irreversibly in THF to give $Li_2(THF)_2Zr(NMe_2)_6$, which is non-volatile and does not release $Zr(NMe_2)_4$ upon heating under vacuum, and proposed that the formation of $Li_2(ether)_2Zr(NMe_2)_6$ species might account for the modest yield of $Zr(NMe_2)_4$.[20b]

The use of toluene rather than THF or Et_2O as the solvent for the synthesis of $Zr(NMe_2)_4$ avoids the formation of $Li_2(ether)_2Zr(NMe_2)_6$ and results in an improved yield. Thus, addition of solid $ZrCl_4$ to a suspension of $LiNMe_2$ in toluene at room temperature, followed by stirring at room temperature (18 h), removal of solvent under reduced pressure, and sublimation, reproducibly yields pure $Zr(NMe_2)_4$ (83% isolated). $Zr(NMe_2)_4$ is monomeric in the gas phase,[20c] adopts an amide-bridged dimeric structure $(Me_2N)_3Zr(\mu\text{-}NMe_2)_2Zr(NMe_2)_3$ in the solid state, and exists in a monomer/dimer equilibrium in solution.[20b,35]

Synthesis of *rac*-(EBI)$Zr(NMe_2)_2$ (*rac*-4). The reaction of $Zr(NMe_2)_4$ (**2**) and $(EBI)H_2$ (1,2-bis(3-indenyl)ethane, **3**)[6] in toluene at 100 °C with N_2 bubbling through the reaction solution to sweep away the volatile NMe_2H co-product (bp 7 °C) affords (EBI)$Zr(NMe_2)_2$ (**4**) in 90% NMR yield (eq 1). Thus the chelate effect does indeed favor the formation of *ansa* bis-indenyl complexes. However, under these conditions **4** is obtained as a 1/1 mixture of *rac* and *meso* diastereomers. Crystallization from toluene affords pure *rac*-**4** as orange/red crystals in 25% yield.



The poor stereoselectivity of the N_2-purged reaction of **2** and **3** was disappointing, but it was soon found that if the N_2 purge is replaced by a static N_2 atmosphere, and the evolved NMe_2H simply allowed to escape from the reaction vessel via an oil bubbler, the stereoselectivity increases dramatically. Under these "open conditions", **4** is obtained in 90% NMR yield in a *rac*/*meso* ratio of 13/1 (eq 1). Pure *rac*-**4** is isolated in 68% yield by a single crystallization. The use of chlorobenzene or nonane as reaction solvents and crystallization from hexane or nonane gives similar results (90% crude **4**, *rac*/*meso* ratio of >9/1; pure *rac*-**4** in 55−70% isolated yield after recrystallization).[36]

Stereocontrol Mechanism in the Synthesis of *rac*-(EBI)$Zr(NMe_2)_2$. Several observations provide insight to the mechanism and stereoselectivity of the reaction of **2** and **3**.

(i) Exclusion of light from the reaction vessel had no effect upon the *rac*/*meso* ratio or yield, indicating that the high *rac*/*meso* ratio is not due to photoisomerization.[4,14b,d,37]

(ii) Monitoring the reaction of **2** and **3** at 100 °C in toluene (open conditions), by ^1H NMR analysis of aliquots taken from the reaction solution, showed that a binuclear species (μ-η^5,η^5-EBI){$Zr(NMe_2)_3$}$_2$ (**5**, *rac* and *meso* isomers) and a mono-indenyl species (η^5-$C_9H_6CH_2CH_2C_9H_7$)$Zr(NMe_2)_3$ (**6**) were present at early stages of the reaction (each *ca.* 10 mol % after 2 h). The structures of these species are shown in Scheme 1. Complexes **5** and **6** disappeared completely after *ca.* 15−20 h if NMe_2H was allowed to escape from the system.

Compound **5** was prepared independently by the reaction of 2 equiv of **2** with **3** in toluene at room temperature. ^1H NMR analysis of the crude product showed that **5** was present in 75% yield in a 1/1 isomer ratio. Recrystallization from hexane afforded pure **5** in 19% yield as a yellow crystalline solid in an isomer ratio of 2/1. The ^1H NMR spectrum of **5** contains a singlet in the NMe_2 region and a pair of doublets in the indenyl C_5 region for each isomer, but it is not possible to identify which isomer is *rac* and which is *meso*.

Complex **6** was characterized by ^1H NMR spectroscopy. The reaction of **2** and **3** in C_6D_6 at room temperature for 10 min yields 33% **6**, 2% **5**, NMe_2H, and unreacted **2** and **3**. The ^1H NMR spectrum of **6** contains η^5-indenyl and NMe_2 resonances, which are very similar to those of **5**, and free C_9H_7 resonances, which are similar to those of **3**.

(iii) The reaction of **2** and **3** in C_6D_6 at room temperature for 30 min (closed system) resulted in complete consumption of **2**

(27) (a) Bradley, D. C.; Thomas, I. M. *Proc. Chem. Soc*. **1959**, 225. (b) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc*. **1960**, 3857.

(28) Benzing, E.; Kornicker, W. *Chem. Ber*. **1961**, *94*, 2263.

(29) Wade, S. R.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1981**, 1264.

(30) Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489.

(31) Preliminary communication: Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5.

(32) (a) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics*, in press. (b) Ross, K. J.; Jordan, R. F.; Swenson, D. C.; Rogers, R. D. Manuscript in preparation.

(33) Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics*, in press.

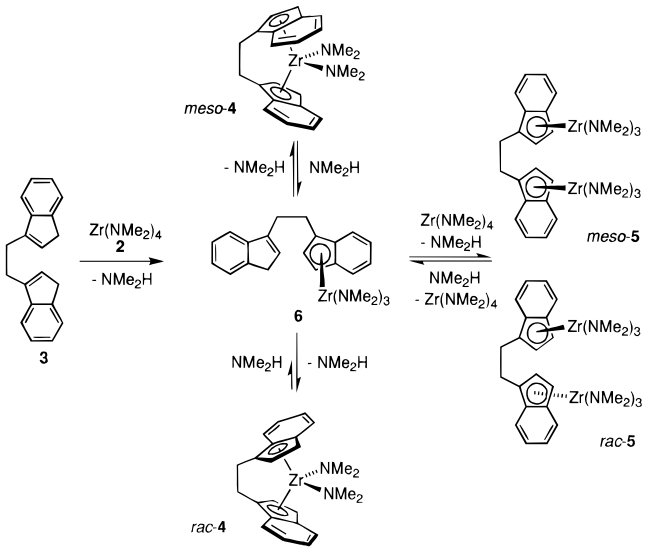
(34) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics*, in press.

(35) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. A* **1969**, 980.

(36) The reaction of **2** and **3** in chlorobenzene (125 °C, 17 h, NMe_2H allowed to escape via oil bubbler), followed by solvent removal and recrystallization from hexane, yielded *rac*-**4** as red/orange crystals (70%). The reaction of **2** and **3** in nonane (150 °C, 13 h, NMe_2H allowed to escape via oil bubbler), followed by concentration, filtration, and cooling of the reaction solution to −20 °C, afforded *rac*-**4** in 55% isolated yield.

(37) Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 1869.

Scheme 1



and formation of a 2/1/1 mixture of **6**, **5**, and unreacted **3**, along with NMe_2H. After 70 min the **6**/**5**/**3** ratio was unchanged. When a further 2 equiv of **3** was added to this mixture, the ratio of **6**/**5** increased to >4/1 over 3 h. These results indicate that the reaction of **2** and **3** to give **5** and **6** is rapid even at room temperature and that a dynamic equilibrium exists between **3**, **5**, and **6** at room temperature in the presence of NMe_2H. The 2/1/1 equilibrium ratio of **6**/**5**/**3** is the statistical ratio, and under normal reaction conditions **5** is always observed in a 1/1 *rac*/*meso* ratio. These observations suggest that for **3**, **6**, and **5**, the indenyl groups of the EBI ligand, though joined by a CH_2CH_2 bridge, react independently with $Zr(NMe_2)_4$ and NMe_2H; *i.e.* metalation at one indenyl group has little effect upon the reactivity of the other, in terms of both metalation and stereochemistry.

(iv) The reaction of **2** and **3** in toluene at 100 °C for 18 h in a closed vessel, from which the Me_2NH cannot escape, yielded a mixture of **3**, **4**, **5** and **6**. This observation is consistent with the reversibility of the amine elimination reactions noted above, and indicates that for the reaction to go to completion the NMe_2H co-product must be allowed to escape from the system.

(v) Monitoring the reaction of **2** and **3** at 100 °C in toluene (open system) showed that the *rac*/*meso* ratio of **4** is initially low (2/1 after 2 h) but increases with reaction time (>50/1 after 5 days), indicating that *rac*-**4** is the thermodynamic product. A reaction time of 15 to 20 h is optimum for the preparation of *rac*-**4**, since prolonged heating (>1 day) is accompanied by formation of insoluble products.[38]

(vi) When N_2 was bubbled through the reaction solution to sweep out the NMe_2H rapidly as it was formed, the reaction of **2** and **3** went to completion, but the final *rac*-**4**/*meso*-**4** ratio was 1/1.

These observations may be rationalized by the mechanism in Scheme 1. In Scheme 1, **2** reacts rapidly with **3** to form the key intermediate **6**. Intermediate **6** may undergo reversible *intermolecular* amine elimination with a second equivalent of **2** to give binuclear species **5** or reversible *intramolecular* amine elimination to give either *meso*-**4** or *rac*-**4**. Removal of NMe_2H from the system drives these equilibria to **4**. Under fast N_2 purge conditions, the steady state concentration of NMe_2H is low and the aminolysis of **4** back to **6** is slow. The 1/1 *rac*-**4**/*meso*-**4** product ratio obtained under these conditions indicates that the intramolecular amine eliminations of **6** to *rac*-**4** or *meso*-**4** occur at comparable rates, i.e. a 1/1 *rac*-**4**/*meso*-**4** mixture is the kinetic product. Thus the formation of *rac*-**4** and *meso*-**4** from intermediate **6** is not stereoselective. However, when the NMe_2H is allowed to escape slowly via an oil bubbler and is thus present in a higher steady state concentration, *meso*-**4** is isomerized to the thermodynamic product *rac*-**4**. Thus the stereoselectivity derives from the amine-catalyzed *meso*-**4** to *rac*-**4** isomerization, and the *rac*-**4**/*meso*-**4** ratio is sensitive to the rate of NMe_2H removal. The similarity of the rates of conversion of **6** to *rac*-**4** and *meso*-**4** and the fact that *rac*-**4** is thermodynamically favored over *meso*-**4** together imply that the rate of aminolysis of *rac*-**4** to **6** is slower than that of *meso*-**4** to **6**.

The key aspects of Scheme 1 were confirmed by studies of the reactions of *rac*-**4** and *meso*-**4** with NMe_2H. Figure 1 shows the results of an experiment in which 2 equiv of NMe_2H were added to a 1/1 mixture of *rac*-**4** and *meso*-**4** in C_6D_6 in a Teflon-valved NMR tube. This figure illustrates the time dependence of the concentrations of *rac*-**4**, *meso*-**4**, and intermediate species (**6** + **5**), as determined by NMR integration versus an internal standard. Immediately after the addition of NMe_2H, the Zr distribution was 50% *rac*-**4** and 50% *meso*-**4**. After 110 h at 20 °C with the NMR tube closed, the Zr distribution was 50% *rac*-**4**, 3% *meso*-**4**, and 47% intermediates (**6** + **5**). Thus NMe_2H reacts selectively with *meso*-**4** to form **6** and **5**. The NMe_2H and C_6D_6 were then removed under vacuum and fresh C_6D_6 was added. The NMR tube was heated to 60 °C and opened under a stream of N_2 to allow evolved NMe_2H to escape. After 4 h the Zr distribution was 59% *rac*-**4**, 11% *meso*-**4**, and 30% intermediates (**6** + **5**). Thus the intermediates (**6** + **5**) are initially converted to *rac*-**4** and *meso*-**4** at similar rates, supporting the proposal that the conversion of **6** to *rac*-**4** and *meso*-**4** is not stereoselective, and a 1/1 *rac*/*meso* mixture is the kinetic product. On continued heating, the increase of *rac*-**4** exceeded that of *meso*-**4**, and after 88 h the Zr distribution was 78% *rac*-**4**, 18% *meso*-**4**, and 4% intermediates (**6** + **5**). Thus the *rac*-**4**/*meso*-**4** ratio increased from 1/1 to approximately 4/1. The total Zr concentration (as measured versus the internal standard) decreased by only 5% over the entire length of the experiment.

In a control experiment, NMe_2H (2 equiv) was added to a solution of pure *rac*-**4** in C_6D_6. After 24 h at room temperature (with the NMR tube closed), the Zr distribution was 98% *rac*-**4**, 2% intermediates (**6** + **5**). On heating the closed NMR tube at 100 °C, an equilibrium mixture of 72% *rac*-**4**, 7% *meso*-**4**, and 21% intermediates (**6** + **5**) was established in less than 13 h and remained constant for the next 45 h at 100 °C. These results indicate that the reaction of *rac*-**4** and NMe_2H to form **6** is very slow at room temperature, but does occur at elevated temperatures. In a second control experiment, a mixture of *rac*-**4** and *meso*-**4** in C_6D_6 was heated in the absence of NMe_2H. No change in the *rac*-**4**/*meso*-**4** ratio was observed, even on heating to 100 °C for 2 days. Therefore, the amine is required for the interconversion of *rac*-**4** and *meso*-**4**.[39]

(38) One possible mechanism for thermal decomposition of Zr amide complexes is cyclometallation. Labeling studies provide evidence for facile metallation of NMe_2 ligands of $Zr(NMe_2)_4$ at elevated temperatures. Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161.

(39) At low NMe_2H concentrations, the rate of conversion of **5** to **6** is slow relative to the rate of conversion of **6** to **4**. For example, in the experiment in Figure 1, the **6**/**5** ratio was 5/1 after 110 h at 20 °C with the NMR tube closed, but was reduced to 2/1 after removal of the NMe_2H and heating at 60 °C for 4 h (open system). Similarly, when the synthesis of **4** (eq 1) was performed using an N_2 purge (*m*-xylene, 100 °C), only **3**, **5**, and **4** (1/1 *rac*/*meso* ratio) were present after 7 h. The absence of **6** is consistent with the proposal that at low NMe_2H concentrations the conversion of **5** to **6** is significantly slower than conversion of **6** to **4**.

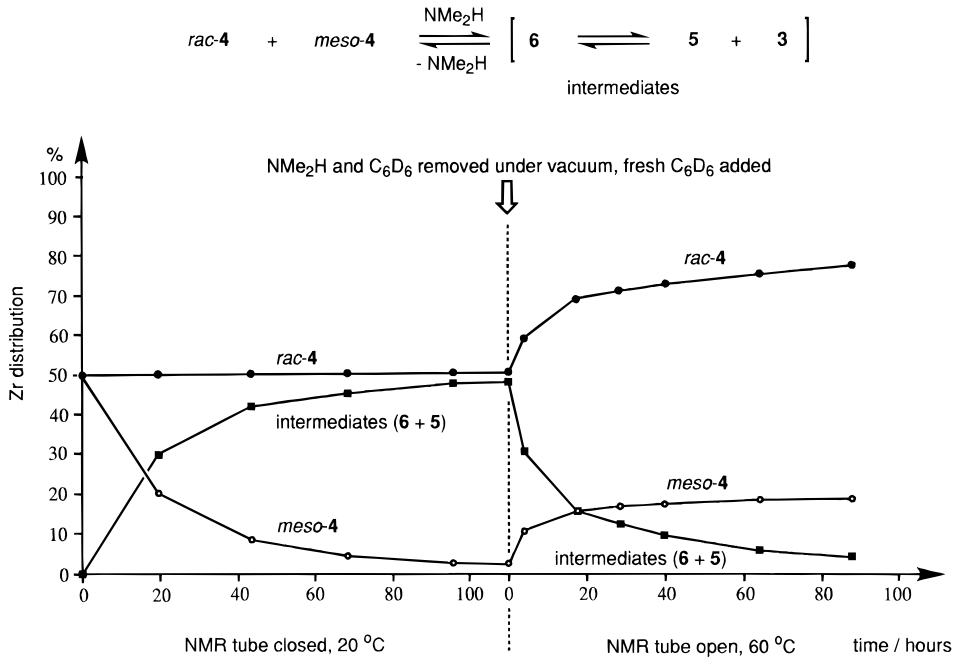


Figure 1. Time dependence of the concentrations of *rac*-**4**, *meso*-**4**, and intermediate species (**6** + **5**) after addition of 2 equiv of NMe_2H to a 1/1 mixture of *rac*-**4** and *meso*-**4** (20 °C, C_6D_6, sealed tube). After 110 h, the volatiles (C_6D_6 and NMe_2H) were removed, fresh C_6D_6 was added, and the tube was opened to allow evolved NMe_2 to escape. The mass balance of total Zr species was >95% over the course of the experiment as assessed by NMR integration versus an internal standard.

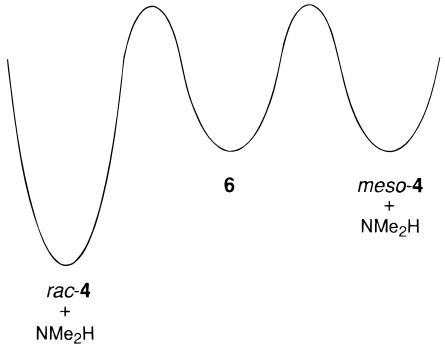


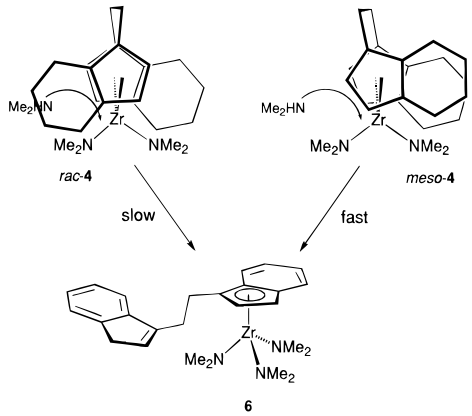
Figure 2. Qualitative energy diagram describing the equilibrium between *rac*-**4**, *meso*-**4**, **6**, and NMe_2H.

A qualitative energy diagram describing the equilibrium between *rac*-**4**, *meso*-**4**, **6**, and NMe_2H is given in Figure 2. This figure illustrates the conclusions discussed above that (i) the conversion of **6** to *rac*-**4** and *meso*-**4** occurs at similar rates, (ii) *rac*-**4** is the thermodynamic product, and (iii) *meso*-**4** is converted to **6** via reaction with NMe_2H more rapidly than is *rac*-**4**.

The relative stabilities of *rac*-**4** and *meso*-**4** likely reflect steric factors. As illustrated in Scheme 2, *meso*-**4** is destabilized by severe steric crowding which results from the proximity of one of the amide groups to the two 6-membered rings of the EBI ligand. On the other hand, one lateral coordination site of *meso*-**4** is relatively open, so that nucleophilic attack of NMe_2H and subsequent proton transfer leading to **6** are facile. In contrast, due to the presence of one 6-membered EBI ring on each side of the molecule, *rac*-**4** does not suffer from severe steric interactions, but also does not have a sterically open site for NMe_2H attack.

A critical aspect of Scheme 1 is the amine-catalyzed isomerization of *meso*-**4** to *rac*-**4**. Marks has recently reported that the C_1 symmetric complexes $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R^*)$-$LnCH(SiMe_3)_2$ and $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R^*)LnN(SiMe_3)_2$ (Ln = Y, La, Sm, Lu; R* = (+)-neomenthyl or (−)-menthyl) are configurationally stable in toluene at 60 °C, but undergo facile epimerization in the presence of *n*-propylamine.[40] Marks

Scheme 2



proposed that epimerization proceeds via reversible aminolysis of the Ln−(C_5H_3-3-R*) bond, similar to the mechanism we have proposed for the amine-catalyzed epimerization of **4**.

Structure and Bonding of *rac*-(EBI)Zr(NMe_2)$_2$ (*rac*-4). The molecular structure of *rac*-**4** was determined by single crystal X-ray diffraction (Figure 3, Tables 1−3). *rac*-**4** adopts the expected monomeric, *ansa*-bridged, bent metallocene structure, with approximate C_2 symmetry. The centroid−Zr−centroid (122.2°) and N−Zr−N (99.4°) angles of *rac*-**4** are similar to the centroid−Zr−centroid (125.3°) and Cl−Zr−Cl (99.1°) angles of *rac*-(EBI)$ZrCl_2$ (*rac*-**1**).[11] However, the average Zr−C bond lengths for the indenyl C_5 rings of *rac*-**4** (2.601 and 2.609 Å) are about 0.1 Å longer than for *rac*-**1** (2.514 Å). The large thermal parameters for the bridge carbons C(19) and C(20) suggest that *rac*-**4** may be disordered between the indenyl-forward and indenyl-backward conformations described by Brintzinger.[41] However, attempts to refine the structure of *rac*-**4** using a disordered model were unsuccessful. Note that

(40) (a) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212. (b) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

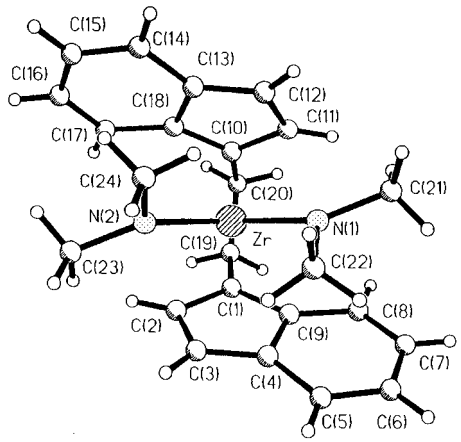


Figure 3. Molecular structure of *rac*-(EBI)Zr(NMe$_2$)$_2$ (*rac*-**4**).

Table 1. Summary of Crystallographic Data for *rac*-(EBI)Zr(NMe$_2$)$_2$ (*rac*-**4**)

compd	*rac*-(EBI)Zr(NMe$_2$)$_2$·$^1/_2$(C$_7$H$_8$)
empirical formula	$C_{27.5}H_{32}N_2Zr$
formula wt	481.77
temperature	293(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	$P2_1/n$
unit cell dimensions	$a = 23.799(7)$ Å; $\alpha = 90°$ $b = 8.191(1)$ Å; $\beta = 96.42(4)°$ $c = 12.367(5)$ Å; $\gamma = 90°$
volume	2395.7(12) Å^3
Z	4
density (calcd)	1.336 g/cm^3
abs coeff	4.75 cm^{-1}
F(000)	1004
crystal size	0.40 × 0.40 × 0.20 mm
θ range for data collection	1.78 to 25.00°
index ranges	$-1 \le h \le 28$, $-1 \le k \le 9$, $-14 \le l \le 14$
reflcns collected	5161
independent reflcns	4179 ($R_{int} = 0.0376$)
abs correction	empirical (PSI scans)
range of transmission coeff	0.746−0.813
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3656/4/300
goodness-of-fit on F^2	1.067
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0892$, $wR2 = 0.2091$
R indices (all data)	$R1 = 0.1509$, $wR2 = 0.3538$
largest diff peak and hole	1.740 and −0.617 eÅ^{-3}

rac-**1** adopts the indenyl-forward conformation in the solid state but undergoes rapid interconversion between the two conformations in solution.[11]

As *rac*-**4** is a 16-electron complex, N to Zr π-donation is expected.[15a,42] As illustrated in Figure 4, the LUMO of a d^0 Cp_2MX_2 complex is metal-based and localized in the equatorial plane between the Cp ligands.[43] For d^0 $Cp_2M(NR_2)X$ complexes, N to Zr π-donation is maximized with a perpendicular orientation of the NR_2 ligand (i.e. 90° dihedral angle between N−Zr−X and C−N−C planes) and minimized with a parallel orientation (i.e. 0° N−Zr−X/C−N−C dihedral angle).

(41) Brintzinger, H. H. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 249.

(42) (a) Andersen, R. A.; Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 2741. (b) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.*, **1976**, *9*, 273. (c) Giolando, D. M.; Kirschbaum, K.; Graves, L. J.; Bolle, U. *Inorg. Chem.* **1992**, *31*, 3887.

(43) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. (c) Green, J. C.; Green, M. L. H.; Prout, C. K.; *J. Chem. Soc., Chem. Commun.* **1972**, 421.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for *rac*-(EBI)Zr(NMe$_2$)$_2$ (*rac*-**4**)

	x	y	z	U(eq)[a]
Zr	6462(1)	2211(1)	9814(1)	44(1)
N(1)	5949(4)	1041(11)	8602(7)	60(2)
N(2)	5853(4)	3277(12)	10632(8)	72(3)
C(1)	7380(5)	3691(15)	9506(12)	78(4)
C(2)	7029(7)	4841(15)	9933(10)	83(4)
C(3)	6567(5)	5183(12)	9168(9)	65(3)
C(4)	6623(4)	4318(12)	8217(8)	51(2)
C(5)	6311(5)	4269(17)	7165(9)	75(3)
C(6)	6495(7)	3250(17)	6386(10)	88(5)
C(7)	6974(7)	2298(17)	6621(13)	90(4)
C(8)	7288(6)	2318(15)	7582(14)	89(4)
C(9)	7134(4)	3333(12)	8427(10)	57(3)
C(10)	7350(5)	884(16)	10777(11)	74(4)
C(11)	7073(7)	−353(16)	10125(11)	87(4)
C(12)	6578(6)	−712(12)	10567(10)	69(3)
C(13)	6553(4)	161(12)	11528(9)	53(3)
C(14)	6189(5)	153(17)	12355(11)	80(4)
C(15)	6298(7)	1181(24)	13226(12)	99(5)
C(16)	6734(9)	2163(22)	13305(12)	109(6)
C(17)	7133(6)	2230(15)	12596(11)	85(4)
C(18)	7042(5)	1200(13)	11665(9)	61(3)
C(19)	7922(6)	3089(20)	10028(17)	150(9)
C(20)	7920(6)	1485(21)	10614(16)	135(8)
C(21)	6037(7)	−435(17)	7996(10)	101(5)
C(22)	5427(5)	1896(20)	8144(12)	101(5)
C(23)	5869(8)	4777(18)	11290(12)	118(6)
C(24)	5339(5)	2387(21)	10776(11)	102(5)
C(25)	5079(12)	5878(55)	5006(23)	119(15)
C(26)	5199(12)	4836(55)	4202(21)	145(46)
C(27)	4987(16)	3287(52)	4164(28)	196(37)
C(28)	4655(17)	2779(54)	4930(37)	194(51)
C(29)	4535(15)	3821(61)	5734(31)	155(25)
C(30)	4747(13)	5371(60)	5772(23)	141(36)
C(31)	5338(29)	7622(52)	5075(43)	175(38)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *rac*-(EBI)Zr(NMe$_2$)$_2$ (*rac*-**4**)[a]

Zr−N(1)	2.061(8)	Zr−N(2)	2.053(9)
Zr−In(1)	2.307	Zr−In(2)	2.319
Zr−C(1)	2.565(11)	Zr−C(10)	2.550(11)
Zr−C(2)	2.537(11)	Zr−C(11)	2.559(11)
Zr−C(3)	2.583(10)	Zr−C(12)	2.573(11)
Zr−C(4)	2.682(10)	Zr−C(13)	2.694(10)
Zr−C(9)	2.639(10)	Zr−C(18)	2.669(10)
N(1)−C(21)	1.45(2)	N(2)−C(23)	1.47(2)
N(1)−C(22)	1.48(2)	N(2)−C(24)	1.45(2)
N(2)−Zr−N(1)	99.4(4)	In(1)−Zr−In(2)	122.2
C(21)−N(1)−C(22)	111.1(10)	C(23)−N(2)−C(24)	108.8(11)
C(21)−N(1)−Zr	131.0(8)	C(23)−N(2)−Zr	130.6(10)
C(22)−N(1)−Zr	117.5(8)	C(24)−N(2)−Zr	119.9(9)

[a] In(1) and In(2) are the centroids of the five-membered indenyl rings.

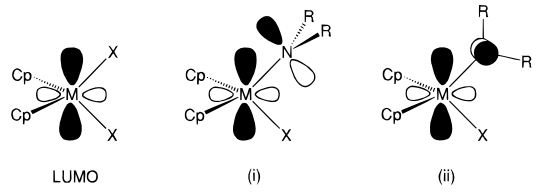


Figure 4. LUMO for d^0 group 4 metal Cp_2MX_2 complexes and limiting geometries for $Cp_2M(NR_2)X$ complexes, with the planar NR_2 ligand (i) perpendicular or (ii) parallel to the metallocene equatorial plane.

The amide groups of *rac*-**4** are flat (sum of angles around N(1) is 359.6°, and N(2) is 359.3°), and the Zr−N distances (2.06 Å average) are in the range observed for other unsaturated

Zr(IV) amide complexes (2.00−2.17 Å).[15,20] The dihedral angles between the N−Zr−N plane and the amide C−N−C planes of *rac*-**4** are 34.6° for N(1) and 35.4° for N(2); i.e. the NMe_2 ligands are twisted about 35° from the equatorial plane of the metallocene or about 55° from the optimum orientation for Zr−N π-bonding (see Figure 4). These data indicate that some N to Zr π-donation is present in *rac*-**4**, although the strength of the interaction is difficult to quantify.

It is likely that steric crowding between the EBI ligand framework and the NMe_2 ligands in *rac*-**4** prevents the amides from adopting more perpendicular orientations. Close nonbonded H···H contacts are present between H atoms on C(21) and C(11) (2.30 Å) and between H atoms on C(23) and C(2) (2.18 Å). Additionally, the Zr−N(1)−C(21) and Zr−N(2)−C(23) angles are widened from the idealized sp^2 value (120°) to 131.0° and 130.6°, respectively, and the C(21)−N(1)−C(22) and C(23)−N(2)−C(24) angles are narrowed to 111.1° and 108.8°, respectively.

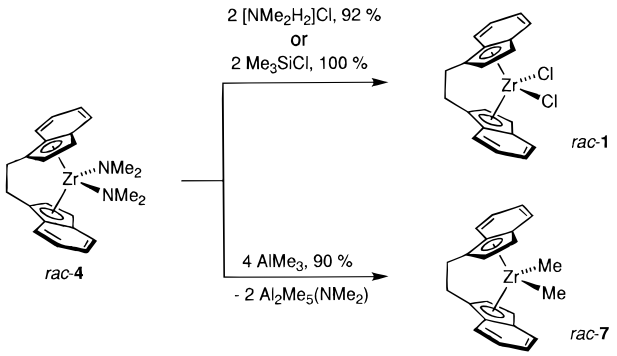
Previously, Bercaw reported that the H−Hf−N/Me−N−H dihedral angle in $Cp^*_2Hf(H)(NHMe)$ is 63°, i.e., the amide ligand is rotated only 27° from the orientation for optimum π-bonding.[44] Variable-temperature NMR studies establish an upper limit of ca. 10 kcal mol^{-1} for the strength of the M−N π-interaction in this case.[45] However, NMR results establish that the amide groups in more crowded $Cp^*_2Hf(H)(NRR')$ complexes (NRR′ = NHPh, NHTol, NMe_2) adopt more parallel orientations and that Hf−N π-bonding is much weaker in these cases.[44,46]

It should be noted that both NMe_2 p orbitals in *rac*-**4** compete for the same Zr π-acceptor orbital. Hence, at most only partial double bond character is expected for each Zr−N bond. The similarities of the N geometries (both amides are flat), Zr−N bond lengths and N−Zr−N/C−N−C dihedral angles, indicate that the Zr−N π-interaction in *rac*-**4** is distributed over both Zr−N bonds. Other d^0 group 4 metallocene bis-amide complexes (e.g. $Cp_2Zr(NC_4H_4)_2$)[20e] and some bis-phosphide complexes (e.g. $(C_5H_4Me)_2Zr\{P(SiMe_3)_2\}_2$) exhibit similar structures.[47,48] However, $Cp_2Hf(PR_2)_2$ (R = Et, $SiMe_3$) and $Cp_2Zr\{As(SiMe_3)_2\}_2$ adopt structures with one short (double) M−E bond to a planar, sp^2-hybridized ER_2 group and one long (single) M−E bond to a pyramidal, sp^3-hybridized ER_2 group.[49,50]

Reactivity of *rac*-(EBI)Zr(NMe$_2$)$_2$ (*rac*-4). To fully exploit the amine elimination based metallocene synthesis, we have investigated the synthesis of commonly used *rac*-(EBI)$ZrCl_2$ (*rac*-**1**) and *rac*-(EBI)$ZrMe_2$ (*rac*-**7**) complexes (Scheme 3) and the direct generation of olefin polymerization catalysts from *rac*-**4**.

(i) Conversion of *rac*-4 to *rac*-(EBI)ZrCl$_2$ (*rac*-1). *rac*-**4** is cleanly converted to *rac*-**1** in high yield (92% isolated) by reaction with 2 equiv of NMe_2H·HCl in CH_2Cl_2 or chlorobenzene (Scheme 3).[25] However, this reaction does not work well in hydrocarbon solvents (e.g. toluene) due to the poor solubility of NMe_2H·HCl and the difficulty of separating the product *rac*-**1** from unreacted NMe_2H·HCl. It would thus be desirable to find a reagent for the chlorination of *rac*-(EBI)$Zr(NMe_2)_2$ that (i) is soluble in toluene, (ii) reacts more rapidly than NMe_2H·HCl, (iii) selectively cleaves Zr−N rather than Zr−C bonds, and (iv) can be used in excess so that strict stoichiometry control is not required.

Scheme 3



Amide−halide exchange reactions of group 4 metal amide complexes have been known for some time.[28] In 1981, Willey described a variety of amide−chloride exchange reactions of $CpTi(NMe_2)_3$ and $Cp_2Zr(NMe_2)_2$, including the reaction of $Cp_2Zr(NMe_2)_2$ with $M'Cl_4$ (M = Si or Ge) to give Cp_2ZrCl_2 and $M'Cl_2(NMe_2)_2$.[29] These precedents prompted us to investigate the use of Me_3SiCl as a chlorinating reagent. The addition of 2 equiv of Me_3SiCl to a red/orange solution of *rac*-**4** in CD_2Cl_2 resulted in an immediate color change to bright yellow and complete conversion to *rac*-**1** and 2 equiv of Me_3SiNMe_2 (Scheme 3). Subsequent addition of excess Me_3SiCl had no effect, even after 3 days at room temperature. This reaction also proceeds quantitatively in benzene (1 h, room temperature); in this case *rac*-**1** precipitates slowly from solution and again the addition of excess Me_3SiCl has no further effect. Thus Me_3SiCl is an excellent reagent for the conversion of *rac*-**4** to *rac*-**1** in both chlorinated and non-chlorinated solvents.

(ii) "One-Pot" Synthesis of *rac*-1 from ZrCl$_4$. The reactions described above for the syntheses of $Zr(NMe_2)_4$ (**2**), *rac*-**4**, and *rac*-**1** can be combined in a "one-pot" synthesis of *rac*-**1**, using toluene as a reaction solvent throughout. The course of the reaction was followed quantitatively by ^1H NMR, using C_6Me_6 as an internal standard. The reaction of $ZrCl_4$ with 4 equiv of $LiNMe_2$ in toluene at room temperature gave **2** in 85% yield (based on $ZrCl_4$). Addition of a toluene solution of $(EBI)H_2$ (**3**) and heating to 100 °C for 17 h (open system) gave **4** in 80% yield (based on $ZrCl_4$) with a *rac*/*meso* ratio of 11/1. The reaction mixture was filtered to remove LiCl, and a toluene solution of excess Me_3SiCl was added to the clear red filtrate. A yellow solid precipitated immediately. The mixture was stirred at room temperature for 1 h, and pure *rac*-**1** was isolated by filtration in 68% overall yield based on $ZrCl_4$.

(iii) Conversion of *rac*-4 to *rac*-(EBI)ZrMe$_2$ (*rac*-7). We previously reported the synthesis of *rac*-**7** via methylation of *rac*-(EBI)$ZrCl_2$ (*rac*-**1**).[3k] When the methylation was performed using MeLi at room temperature, a 1/1 mixture of *rac*- and *meso*-**7** was obtained. Lowering the reaction temperature to −40 °C gave a higher *rac*/*meso* ratio of 19/1, but the isomerization could never be entirely suppressed, so other methylation reagents were investigated. The reaction of *rac*-**1** with $AlMe_3$ gave the mono-methyl derivative *rac*-(EBI)ZrMeCl in 57% yield. Methylation of *rac*-**1** using MeMgBr or MeMgCl gave exclusively *rac*-**7** but complete separation of the magnesium

(44) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309.

(45) Fehlner[45a] noted that the Hf−N bond length of 2.027 Å in $Cp^*_2Hf(H)(NHMe)$ is very close to the Ta−C bond length of 2.026 Å for the Ta=CH2 group of the isoelectronic complex Cp2Ta(=CH2)(CH3),[45b] consistent with significant double bond character for the Hf−NHMe bond. (a) Aradi, A. A.; Fehlner, T. P. *Adv. Organomet. Chem.* **1990**, *30*, 189. (b) Schrock, R. R.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 6578.

(46) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

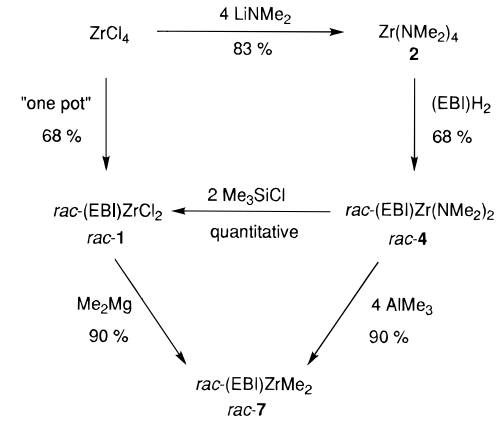
(47) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661.

(48) Lindenberg, F.; Hey-Hawkins, E. *J. Organomet. Chem.* **1992**, *435*, 291.

(49) (a) Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049. (b) Weber, L.; Meine, G.; Boese, R.; Augart, N. *Organometallics* **1987**, *6*, 2484.

(50) Hey-Hawkins, E.; Lindenberg, F. *Organometallics* **1994**, *13*, 4643.

Scheme 4



salts from the product was not achieved.[51] However, the reaction of *rac*-**1** with Me_2Mg in Et_2O, followed by treatment with dioxane to form insoluble Mg salts, gave pure *rac*-**7** in 90% yield.[3k]

The reaction of *rac*-**4** with 5 equiv of $AlMe_3$ in toluene results in clean alkylation of the metallocene to give *rac*-**7** and $Al_2Me_5(NMe_2)$ as the main aluminum product (Scheme 3). The aluminum co-products are easily removed by washing the crude product with pentane, and pure *rac*-**7** is obtained in 90% yield. This efficient alkylation reaction, coupled with the efficient synthesis developed for *rac*-**4**, provides a very attractive route to *rac*-**7**.

(iv) Use of *rac*-4 as an Olefin Polymerization Catalyst Precursor. As described in detail elsewhere, *rac*-**4** is activated for propylene polymerization by treatment with MAO (Al/Zr $\approx$ 1000/1).[30] The resulting catalyst displays similar isoselectivity but lower activity versus the standard *rac*-**1**/MAO catalyst. However, initial alkylation of *rac*-**4** with AlR_3 reagents followed by activation with MAO or cationic activators ($[Ph_3C][B(C_6F_5)_4]$ or $[R_3NH][B(C_6F_5)_4]$) yields catalysts with performance competitive with that of *rac*-**1**/MAO.

Advantages of Amine Elimination. Compared with the current syntheses of *rac*-(EBI)$ZrCl_2$ via salt elimination reactions, the amine elimination route described here has several advantages: (i) generation of $(EBI)^{2-}$ reagent is not required, (ii) high dilution and simultaneous addition procedures are not required, (iii) no acid wash steps, Soxhlet extractions, or recrystallizations are needed, and (iv) pure *rac*-(EBI)$ZrCl_2$ is obtained in good yield from $ZrCl_4$ in a one-pot procedure.

Conclusion

Amine elimination offers an efficient approach to the synthesis of *rac*-(EBI)ZrX_2 complexes (Scheme 4). The amide starting material $Zr(NMe_2)_4$ (**2**) is obtained in high yield from the reaction of $ZrCl_4$ and $LiNMe_2$ in toluene and is efficiently converted to *rac*-(EBI)$Zr(NMe_2)_2$ (*rac*-**4**) by the amine elimination reaction with $(EBI)H_2$ (**3**). The *rac*-**4**/*meso*-**4** product ratio can be controlled by adjusting the reaction conditions; a 1/1 *rac*-**4**/*meso*-**4** ratio is the kinetic product, *rac*-**4** is the thermodynamic product, and the *meso*-**4** to *rac*-**4** isomerization is catalyzed by the NMe_2H co-product. The reversibility of the amine elimination is the key to the stereoselectivity of the reaction. *rac*-**4** can be converted to *rac*-(EBI)$ZrCl_2$ (*rac*-**1**) by protonolysis or amide−halide exchange reactions, and the syntheses of **2**, *rac*-**4**, and *rac*-**1** can be combined in a simple and reproducible one-pot synthesis of *rac*-**1**. Alkylation of *rac*-**4** using $AlMe_3$ provides an efficient route to *rac*-(EBI)$ZrMe_2$ (*rac*-**7**). This work establishes that amine elimination offers an attractive route to chiral *ansa*-zirconocenes. This approach is quite versatile, as will be described in subsequent contributions.[32−34]

(51) Rodewald, S. Ph.D. Thesis, University of Iowa, 1994.

Experimental Section

General Procedures. All reactions were performed under a purified N_2 atmosphere using standard glovebox and Schlenk techniques. Solvents were distilled from Na/benzophenone, except for toluene (Na) and chlorinated solvents (CaH_2), and stored under N_2. $ZrCl_4$ was purchased from Aldrich, CERAC Inc. or GFS Chemicals and sublimed under vacuum before use. $LiNMe_2$ was obtained from Aldrich and washed with Et_2O and dried under vacuum before use. $(EBI)H_2$ (1,2-bis(3-indenyl)ethane, **3**) was prepared by the literature procedure[6] or purchased from Aldrich. NMR spectra were recorded on a Bruker AMX-360 spectrometer, in Teflon-valved or flame-sealed tubes, at ambient probe temperature (298 K) unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Elemental analyses were performed by E + R Microanalytical Laboratory (Corona, NY) or Desert Analytics Laboratory (Tucson, AZ).

Improved Synthesis of Zr(NMe$_2$)$_4$ (2). Solid $ZrCl_4$ (12 g, 52 mmol) was added in several portions over 2 h to a suspension of $LiNMe_2$ (11 g, 220 mmol) in toluene (150 mL) at 23 °C. The reaction mixture was stirred for 18 h at 23 °C. The solvent was removed under reduced pressure leaving an off-white solid, from which pure $Zr(NMe_2)_4$ (**2**) was obtained by sublimation at 80 °C/0.05 mmHg, in 83% yield (12 g). The yield of this reaction is very dependent on the purity of the starting materials. For optimum yield the $ZrCl_4$ should be freshly sublimed and the $LiNMe_2$ should be washed with Et_2O and dried under vacuum before use. ^1H NMR (C_6D_6): δ 2.96 (s, 24 H, NMe_2).

***rac*-(EBI)Zr(NMe$_2$)$_2$ (*rac*-4).** A Schlenk vessel was charged with $Zr(NMe_2)_4$ (1.0 g, 3.7 mmol), $(EBI)H_2$ (1,2-bis(3-indenyl)ethane, 0.96 g, 3.7 mmol), and toluene (20 mL). The reaction mixture was stirred and heated to 100 °C for 17 h, and NMe_2H was allowed to escape via an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed that **4** was present in 90% yield in a *rac*/*meso* ratio of 13/1. The reaction mixture was filtered, concentrated under reduced pressure, and cooled to −20 °C. Filtration afforded pure *rac*-**4** as orange/red crystals in 68% yield (1.1 g). Anal. Calcd for $C_{24}H_{28}N_2Zr$: C, 66.16; H, 6.48; N, 6.43. Found: C, 66.42; H, 6.40; N, 6.24. ^1H NMR (C_6D_6): δ 7.42 (d, J = 9 Hz, 2 H, indenyl), 7.40 (d, J = 9 Hz, 2 H, indenyl), 6.93 (dd, J = 7 Hz, J = 9 Hz, 2 H, indenyl), 6.71 (dd, J = 7 Hz, J = 9 Hz, 2 H, indenyl), 6.35 (d, J = 3 Hz, 2 H, C_5 indenyl), 5.88 (d, J = 3 Hz, 2 H, C_5 indenyl), 3.31 (m, 2 H, CH_2), 3.10 (m, 2 H, CH_2), 2.53 (s, 12 H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 130.0 (C), 125.8 (CH), 123.3 (CH), 123.2 (CH), 121.3 (C) 120.7 (CH), 117.3 (C), 113.9 (CH), 100.6 (CH), 47.7 (NMe_2), 28.9 (CH_2CH_2).

***meso*-(EBI)Zr(NMe$_2$)$_2$ (*meso*-4).** This species was characterized by ^1H NMR spectroscopy only. ^1H NMR (C_6D_6): δ 7.56 (d, J = 8 Hz, 2 H, indenyl), 7.39 (d, J = 9 Hz, 2 H, indenyl), 6.88 (m, 2 H, indenyl), 6.70 (m, 2 H, indenyl), 6.41 (d, J = 3 Hz, 2 H, C_5 indenyl), 5.86 (d, J = 3 Hz, 2 H, C_5 indenyl), 3.50 (m, 2 H, CH_2), 2.99 (s, 6 H, NMe_2), 2.94 (m, 2 H, CH_2), 1.82 (s, 6 H, NMe_2).

(μ-η^5,η^5-EBI){Zr(NMe$_2$)$_3$}$_2$ (5). A solution of $(EBI)H_2$ (0.24 g, 0.93 mmol) in toluene (20 mL) was added dropwise at 23 °C to a solution of $Zr(NMe_2)_4$ (0.50 g, 1.9 mmol) in toluene (20 mL). The reaction mixture was stirred for 17 h at room temperature. The solvent was removed under reduced pressure affording an orange oil. The ^1H NMR spectrum of the oil showed that **5** was present in 75% yield in a *rac*/*meso* ratio of 1/1. Recrystallization from hexane afforded pure **5** in 19% yield (0.12 g) as a yellow crystalline solid in an isomeric ratio of 2/1. Anal. Calcd for $C_{32}H_{52}N_6Zr_2$: C, 54.65; H, 7.45; N, 11.95. Found: C, 54.86; H, 7.26; N, 11.76. Major isomer: ^1H NMR (C_6D_6): δ 7.59−7.45 (m, 4 H, indenyl), 6.96−6.88 (m, 4 H, indenyl), 6.36 (d, J = 3 Hz, 2 H, C_5 indenyl), 6.20 (d, J = 3 Hz, 2 H, C_5 indenyl), 3.39−3.21 (m, 4 H, CH_2CH_2), 2.80 (s, 36 H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 126.3 (C), 125.2 (C), 123.1 (CH), 122.6 (CH), 122.1 (CH), 121.7 (CH), 116.4 (CH), 114.3 (C), 96.0 (CH), 44.1 (NMe_2), 29.4 (CH_2CH_2). Minor isomer: ^1H NMR (C_6D_6): δ 7.59−7.45 (m, 4 H, indenyl), 6.96−6.88 (m, 4 H, indenyl), 6.26 (d, J = 3 Hz, 2 H, C_5 indenyl), 6.20

(d, $J = 3$ Hz, 2 H, C_5 indenyl), 3.43 (m, 2 H, CH_2), 3.17 (m, 2 H, CH_2), 2.79 (s, 36 H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 126.5 (C), 125.0 (C), 123.1 (CH), 122.6 (CH), 122.2 (CH), 121.7 (CH), 116.9 (CH), 114.1 (C), 95.7 (CH), 44.1 (NMe_2), 29.2 (CH_2CH_2).

Characterization of (η^5-$C_9H_6CH_2CH_2C_9H_7$)Zr(NMe_2)$_3$ (6). A Teflon-valved NMR tube was charged with $Zr(NMe_2)_4$ (0.027 g, 0.10 mmol), $(EBI)H_2$ (**3**) (0.026 g, 0.10 mmol), and C_6D_6 (0.6 mL), maintained at 23 °C and monitored periodically by ^1H NMR. After 10 min, (η^5-$C_9H_6CH_2CH_2C_9H_7$)Zr(NMe_2)$_3$ (**6**, 33%) and (μ-η^5,η^5-EBI)-{$Zr(NMe_2)_3$}$_2$ (**5**, 2%) were formed. After 30 min all $Zr(NMe_2)_4$ was consumed and a mixture of **6**, **5**, and **3** was obtained, in a 2/1/1 ratio, along with NMe_2H. After 70 min the **6**/**5**/**3** ratio had not changed. Intermediate **6** was characterized by ^1H NMR spectroscopy. ^1H NMR (C_6D_6): δ 7.53 (d, $J = 7$ Hz, 1 H, η^5-C_9H_6), 7.47 (d, $J = 8$ Hz, 1 H, η^5-C_9H_6), 7.34 (d, $J = 7$ Hz, 1 H, C_9H_7), 7.32 (d, $J = 7$ Hz, 1 H, C_9H_7), 7.25 (pseudo t, $J = 7$ Hz, 1 H, C_9H_7), 7.15 (pseudo t, $J = 7$ Hz, 1 H, C_9H_7), 6.93 (m, 1 H, η^5-C_9H_6), 6.89 (m, 1 H, η^5-C_9H_6), 6.36 (d, $J = 3$ Hz, 1 H, η^5-C_9H_6), 6.21 (d, $J = 3$ Hz, 1 H, η^5-C_9H_6), 6.03 (br. t, $J = 2$ Hz, 1 H, C_9H_7), 3.4−3.1 (m, 4 H, CH_2CH_2), 3.07 (br. s, 2 H, C_9H_7), 2.78 (s, 18 H, NMe_2).

***rac*-(EBI)ZrCl_2 (*rac*-1) from *rac*-(EBI)Zr(NMe_2)$_2$.** A solution of NMe_2H·HCl (0.093 g, 1.1 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of *rac*-**4** (0.25 g, 0.57 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The clear, yellow solution was stirred at 23 °C for 30 min. The solvent was removed under reduced pressure and the residue was washed with hexane and extracted with toluene. The solvent was removed under reduced pressure yielding pure *rac*-**1** (92% isolated, 0.22 g) as a yellow solid. ^1H NMR (CD_2Cl_2): δ 7.68 (d, $J =$ 9 Hz, 2 H, indenyl), 7.45 (d, $J = 9$ Hz, 2 H, indenyl), 7.31 (m, 2 H, indenyl), 7.20 (m, 2 H, indenyl), 6.54 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 6.24 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 3.74 (m, 4 H, CH_2CH_2).

"One-Pot" Synthesis of *rac*-(EBI)ZrCl_2 (*rac*-1) from $ZrCl_4$ Using NMe_2H·HCl as a Chlorinating Agent. Solid $ZrCl_4$ (0.93 g, 4.0 mmol) was added to a suspension of $LiNMe_2$ (0.82 g, 16 mmol) in toluene (40 mL) at room temperature. C_6Me_6 (0.16 g, 1.0 mmol) was added as an internal standard, to allow the reaction to be followed quantitatively by ^1H NMR. The reaction mixture was stirred for 20 h at 23 °C. An aliquot was removed and analyzed by ^1H NMR. The ^1H NMR spectrum showed that $Zr(NMe_2)_4$ was present in 80% yield (based on $ZrCl_4$). A toluene (20 mL) solution of $(EBI)H_2$ (0.98 g, 3.8 mmol) was added. The reaction mixture was stirred and heated to 100 °C for 22 h, and NMe_2H was allowed to escape from the reaction vessel via an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed that (EBI)Zr(NMe_2)$_2$ (**4**) was present in a *rac*/*meso* ratio of 12/1 in 80% yield (based on $ZrCl_4$). The reaction solution was filtered at 23 °C to remove LiCl, and the clear red filtrate was added to solid NMe_2H·HCl (0.55 g, 6.8 mmol). The reaction mixture was stirred at 23 °C. After 15 h, ^1H NMR analysis of an aliquot showed that the 90% of **4** had been consumed. After 40 h the reaction was complete, and the yellow solid that had slowly precipitated from the reaction solution was collected by filtration, washed with pentane (25 mL), and dried under vacuum. The yellow solid (1.04 g) was *rac*-(EBI)$ZrCl_2$ (*rac*-**1**) contaminated with 5 mol % NMe_2H·HCl, corresponding to an overall yield of *rac*-(EBI)$ZrCl_2$ of 59% based on $ZrCl_4$.

Reaction of *rac*-(EBI)Zr(NMe_2)$_2$ with Me_3SiCl in CD_2Cl_2. Using a microsyringe, Me_3SiCl (15 μL, 0.11 mmol) was added to a solution of *rac*-**4** (0.025 g, 0.057 mmol) in CD_2Cl_2 in a Teflon-valved NMR tube. The tube was agitated to mix the contents, and the clear red/orange solution turned bright yellow in seconds. The ^1H NMR spectrum showed complete conversion to *rac*-**1** and Me_3SiNMe_2. The addition of excess Me_3SiCl (30 μL, 0.22 mmol) had no effect, even after 3 days at room temperature. Me_3SiNMe_2: ^1H NMR (CD_2Cl_2): δ 2.42 (s, 6 H, NMe_2), 0.02 (s, 9 H, $SiMe_3$).

Reaction of *rac*-(EBI)Zr(NMe_2)$_2$ with Me_3SiCl in C_6D_6. Using a microsyringe, Me_3SiCl (15 μL, 0.11 mmol) was added to a solution of *rac*-**4** (0.025 g, 0.057 mmol) in C_6D_6 in a Teflon-valved NMR tube. When the tube was agitated to mix the contents, no color change was observed. Over 1 h at 23 °C, the color slowly changed from red/orange to bright yellow and a yellow solid began to precipitate from solution. The ^1H NMR spectrum after 1 h showed complete consumption of *rac*-**4**. The addition of excess Me_3SiCl (30 μL, 0.22 mmol) had no effect. *rac*-**1:** ^1H NMR (C_6D_6): δ 7.27 (d, $J = 9$ Hz, 2 H, indenyl), 7.15 (d, $J = 8$ Hz, 2 H, indenyl), 7.09 (m, 2 H, indenyl), 6.91 (m, 2 H, indenyl), 6.46 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 5.75 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 2.96 (m, 4 H, CH_2CH_2). Me_3SiNMe_2: ^1H NMR (C_6D_6): δ 2.38 (s, 6 H, NMe_2), 0.05 (s, 9 H, $SiMe_3$).

"One-Pot" Synthesis of *rac*-(EBI)ZrCl_2 (*rac*-1) from $ZrCl_4$ Using Me_3SiCl as the Chlorinating Reagent. Solid $ZrCl_4$ (0.93 g, 4.0 mmol) was added to a suspension of $LiNMe_2$ (0.82 g, 16 mmol) in toluene (40 mL) at 23 °C. C_6Me_6 (0.16 g, 1.0 mmol) was added as an internal standard. The reaction mixture was stirred for 16 h at 23 °C. An aliquot was removed and analyzed by ^1H NMR which showed that $Zr(NMe_2)_4$ was present in 85% yield (based on $ZrCl_4$). A toluene (20 mL) solution of $(EBI)H_2$ (0.98 g, 3.8 mmol) was added. The reaction mixture was stirred and heated to 100 °C for 17 h, and NMe_2H was allowed to escape via an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed that (EBI)Zr(NMe_2)$_2$ (**4**) was present in a *rac*/*meso* ratio of 11/1 in 80% yield (based on $ZrCl_4$). The reaction mixture was filtered at 23 °C to remove LiCl. A toluene (5 mL) solution of Me_3SiCl (2.17 g, 20 mmol) was added to the clear red filtrate at 23 °C. A yellow solid precipitated immediately. The mixture was stirred at 23 °C for 1 h and filtered. The yellow solid was washed with hexane (30 mL) and dried under vacuum. Yield = 1.1 g, 68% based on $ZrCl_4$, pure *rac*-**1**. When this procedure was repeated on a 25-mmol scale, pure *rac*-**1** was isolated in 79% yield (8.3 g).

***rac*-(EBI)ZrMe_2 (*rac*-7) from *rac*-(EBI)Zr(NMe_2)$_2$.** A toluene (40 mL) solution of *rac*-**4** (0.71 g, 1.6 mmol) was cooled to −10 °C, and a hexane (10 mL) solution of $AlMe_3$ (0.58 g, 8.0 mmol, 5 equiv) was added over 15 min. During the addition the color of the reaction solution changed from red/orange to yellow. The solution was stirred at 23 °C for 2 h, the solvent was removed under reduced pressure, and the solid was dried under vacuum. The solid was washed with pentane and dried under vacuum. Yield 0.56 g, 90%, pure *rac*-**7**. ^1H NMR (C_6D_6): δ 7.31 (d, $J = 8$ Hz, 2 H, indenyl), 7.08 (d, $J = 9$ Hz, 2 H, indenyl), 7.06 (m, 2 H, indenyl), 6.89 (m, 2 H, indenyl), 6.42 (d, $J =$ 3 Hz, 2 H, C_5 indenyl), 5.65 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 2.81 (m, 2 H, CH_2), 2.67 (m, 2 H, CH_2), −0.97 (s, 6 H, $ZrMe_2$).

X-ray Diffraction Study of *rac*-(EBI)Zr(NMe_2)$_2$ (*rac*-4). The structure of *rac*-**4** was determined by J.L.P. at WVU. Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda =$ 0.71073 Å) and fixed ω scans of 4 deg/min (scan width ±0.60°). During data collection it was evident that the line widths of many of the diffraction peaks were broad, thereby indicating that the crystal was of marginal quality. Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured periodically during data collection. The data were corrected for Lorentz−polarization effects and an empirical absorption correction based upon the PSI scans ($\chi \approx \pm 90°$) was applied. The structure solution was provided by the first E-map calculated with the phase assignments determined by the direct methods structure solution program available in SHELXTL-IRIS operating on a Silicon Graphics Iris Indigo workstation. The coordinates for all the remaining non-hydrogen atoms of the zirconium complex were located by Fourier methods. The hydrogen atom positions were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. As the structural refinement progressed, it became apparent that the crystal lattice contained a molecule of toluene disordered around a crystallographic center of inversion. In order to model this disorder it was necessary to refine the six carbons (C(25) through C(30)) of the phenyl ring as a rigid group and restrain the C(25)−C(31) distance to 1.54 ± 0.01 Å and the two nonbonded C(26)−C(31) and C(30)−C(31) distances to 2.54 ± 0.01 Å. In addition, due to the large thermal displacements associated with C(19) and C(20) of the ethylene bridge, the C(19)−C(20) bond length of the ethylene bridge was restrained to 1.54 ± 0.01 Å. Full-matrix least-squares refinement with SHELXL-93,[52] based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = [\sigma^2(F_o^2) + (0.0809P)^2 + 19.47P]$ where $P = (\text{Max-}$

(52) SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut fur Anorganische Chemie, University of Gottingen, D-37077, Gottingen, Germany) for single-crystal X-ray structural analyses.

(F_o^2,0) + 2F_c^2)/3, converged to give final discrepancy indices[53] of $R1 = 0.0892$, $wR2 = 0.2091$, and GOF = 1.067 for 2699 reflections with $I > 2\ \sigma(I)$.

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(53) The discrepancy indices were calculated from the expressions $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum(w_i(F_o^2 - F_c^2)^2)/\sum(w_i(F_o^2)^2)]^{1/2}$ and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.

Supporting Information Available: X-ray structural analysis of *rac*-[$C_2H_4(C_9H_6)_2$]Zr(NMe_2)$_2$·$^1/_2C_7H_8$, tables of summary of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, interatomic distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for *rac*-**4**, and alternate views of *rac*-**4** (10 pages). See any current masthead page for ordering and Internet access instructions.

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