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Synthesis of Group 4 Metal *rac*-(EBI)M(NR_2)$_2$ Complexes by Amine Elimination. Scope and Limitations

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The synthesis of (EBI)M(NR_2)$_2$ (M = Ti, Zr, Hf; EBI = ethylene-1,2-bis(1-indenyl)) complexes by amine elimination reactions of (EBI)H_2 (1,2-bis(3-indenyl)ethane) and M(NR_2)$_4$ complexes has been investigated. The reaction of (EBI)H_2 and Zr(NEt_2)$_4$ in toluene at 100 °C (15 h) yields the mono(indenyl) complex (η^5-$C_9H_6CH_2CH_2C_9H_7$)Zr(NEt_2)$_3$ via a single amine elimination. Under more forcing conditions (1,2-dichlorobenzene, 180 °C, 21 h) this reaction yields the metallocene dichloride derivative (EBI)$ZrCl_2$ (80% NMR, *rac*/*meso* ratio = 1.7/1). The reaction of (EBI)H_2 with Zr(NMe_2)$_2$(N^iPr_2)$_2$ in *m*-xylene at 140 °C (16 h) affords the sterically least hindered *ansa*-metallocene product, (EBI)Zr(NMe_2)$_2$ (70% NMR, *rac*/*meso* ratio = 2/1), via N^iPr_2H elimination. The reaction of (EBI)H_2 with the pyrrolidide complex Zr(NC_4H_8)$_4$ in *m*-xylene at 140 °C (7 h) yields (EBI)Zr(NC_4H_8)$_2$ (95%, *rac*/*meso* ratio = 6/1) and pure *rac*-(EBI)Zr(NC_4H_8)$_2$ in 42% isolated yield. (EBI)H_2 reacts with the sterically open titanium azetidide complex Ti(NC_3H_6)$_4$ to yield the mono(indenyl) species (η^5-$C_9H_6CH_2$-$CH_2C_9H_7$)Ti(NC_3H_6)$_3$ but does not react with Ti(NMe_2)$_4$ (toluene, 100 °C, 17 h). The reaction of (EBI)H_2 and Hf(NMe_2)$_4$ in *m*-xylene at 140 °C (21 h) provides (EBI)Hf(NMe_2)$_2$ in 85% NMR yield (*rac*/*meso* ratio = 6/1) and *rac*-(EBI)Hf(NMe_2)$_2$ in 47% isolated yield.

Introduction

Chiral *ansa*-zirconocenes have been developed as stereoselective olefin polymerization catalysts[1] and as catalysts or reagents for an increasingly wide range of synthetic organic reactions.[2] However, practical application of these catalysts is hindered by the fact that current *ansa*-zirconocene syntheses, which are based on salt elimination reactions of $ZrCl_4$ and bis(cyclopentadienyl) dianion reagents, are inefficient. In general, current syntheses of C_2-symmetric chiral *ansa*-zirconocenes produce the desired *rac* isomer in 10−30% yield, and separation from the undesired, achiral *meso* isomer is not always possible.[3,4]

Chiral *ansa*-titanocene complexes have also attracted attention as stereoselective catalysts or reagents for asymmetric organic reactions,[2] including olefin hydrogenation,[5a] epoxidation,[5b−d] and isomerization,[5e] imine and enamine hydrogenation,[5f−h] Diels−Alder reactions,[5i,j] allylic alcohol synthesis,[5k] and hydrosilylation of ketones.[5l,m] However, current syntheses of chiral *ansa*-titanocenes via salt elimination suffer from the same problems as *ansa*-zirconocene syntheses. For example, (EBI)$TiCl_2$ (EBI = ethylene-1,2-bis(1-indenyl)) was first prepared by Brintzinger from $TiCl_4$ and (EBI)Li_2 in THF, as a mixture of *rac* and *meso* diastereomers, in 22% yield.[6] Collins improved the yield of (EBI)$TiCl_2$ to 60% by using high dilution and slow mixing of THF solutions of $TiCl_4$ and (EBI)Li_2 to minimize the formation of oligomeric/polymeric byproducts, but a mixture

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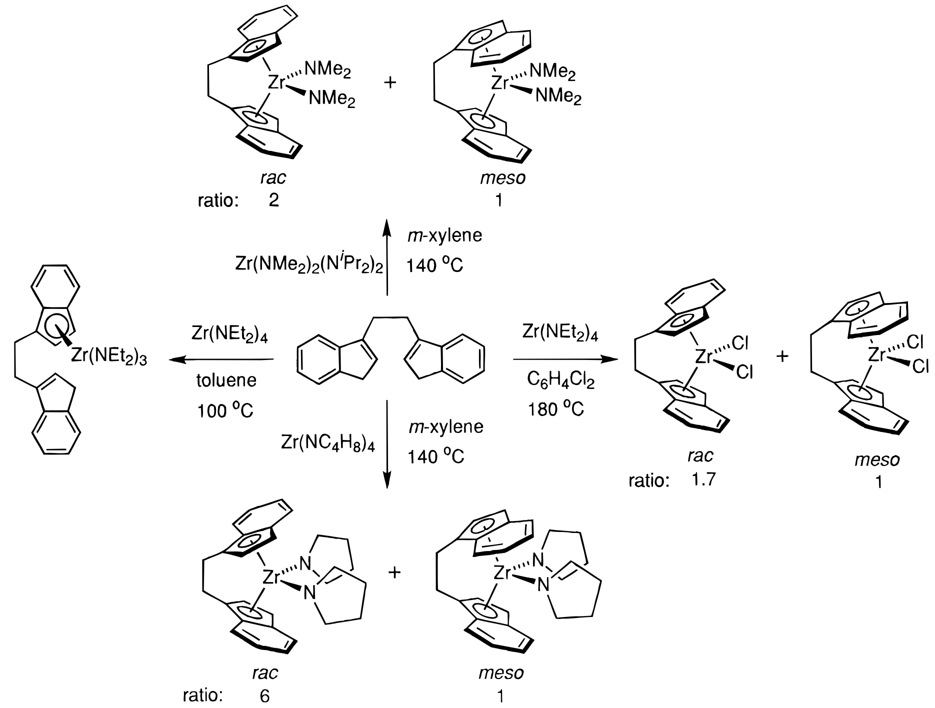
Scheme 1



of *rac* and *meso* diastereomers was still obtained.[7] Collins later noted that this reaction is rather capricious, often giving (EBI)TiCl$_2$ in much lower yield.[8]

Chiral *ansa*-hafnocene complexes are of interest primarily as precursors for stereoselective olefin polymerization catalysts. At conventional propylene polymerization temperatures (50−80 °C), catalysts derived from *rac*-(EBI)HfCl$_2$ and methylalumoxane (MAO) produce polypropylene with molecular weight 1 order of magnitude higher than that obtained with the Zr analog.[9,10] However, current salt elimination syntheses of chiral *ansa*-hafnocenes are even less efficient than analogous syntheses of *ansa*-zirconocenes. For example, the reaction of HfCl$_4$ and (EBI)Li$_2$ in THF affords *rac*-(EBI)HfCl$_2$ in 11% yield,[9] and the use of high dilution and slow mixing of THF solutions of HfCl$_4$ and (EBI)K$_2$ increases the yield to only 37%.[11]

We recently reported that the amine elimination reaction of (EBI)H$_2$ (1,2-bis(3-indenyl)ethane) and Zr(NMe$_2$)$_4$ in toluene at 100 °C affords (EBI)Zr(NMe$_2$)$_2$ in 90% NMR yield in a *rac*/*meso* ratio of 13/1 and pure *rac*-(EBI)Zr(NMe$_2$)$_2$ in 68% isolated yield.[12] A key feature of this synthesis is that the NMe$_2$H byproduct catalyzes the *rac*/*meso* isomerization via reversible formation of the mono(indenyl) intermediate (η^5-$C_9H_6CH_2CH_2C_9H_7$)-Zr(NMe$_2$)$_3$. *rac*-(EBI)Zr(NMe$_2$)$_2$ is a versatile synthetic intermediate which can be cleanly converted to *rac*-(EBI)ZrCl$_2$ (NMe$_2$H·HCl or Me$_3$SiCl) or *rac*-(EBI)ZrMe$_2$ (AlMe$_3$)[12] or activated for propylene polymerization via in situ alkylation (AlR$_3$) followed by treatment with MAO or cationic activators ([Ph$_3$C][B(C$_6$F$_5$)$_4$] or [R$_3$NH][B(C$_6$F$_5$)$_4$]).[13]

In this paper we describe initial studies of the scope and limitations of this new approach to *ansa*-metallocenes. The specific goals of the present work were (i) to probe the influence of the steric and basicity properties of the amide ligands in the amine elimination syntheses of (EBI)Zr(NR$_2$)$_2$ complexes and (ii) to determine if titanium and hafnium *rac*-(EBI)M(NR$_2$)$_2$ complexes could be prepared via amine elimination. Extension of the amine elimination approach to chiral group 4 *ansa*-metallocenes containing substituted Me$_2$Si-bridged bis(cyclopentadienyl) and bis(indenyl) ligands[14,15] and group 3 *ansa*-metallocenes[16] will be described in later papers in this series.

Results and Discussion

Influence of Amide Ligand Structure on Synthesis of *rac*-(EBI)Zr(NR$_2$)$_2$ Complexes. In an effort to optimize the synthesis of *rac*-(EBI)Zr(NR$_2$)$_2$ complexes, we investigated the effect of amide steric bulk on the reaction of (EBI)H$_2$ and Zr(NR$_2$)$_4$ complexes (Scheme 1).[17−19] Our working hypothesis was that increasing the size of the amide ligands would selec-

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tively destabilize the *meso*-(EBI)Zr$(NR_2)_2$ structure, due to steric crowding resulting from the proximity of one of the amide ligands to both indenyl 6-membered rings,[12,20] and thus increase the *rac*/*meso* ratio.

Most of the reactions discussed in this paper were initially performed under conditions similar to those employed for the synthesis of *rac*-(EBI)Zr$(NMe_2)_2$ (i.e., toluene solvent, 100 °C, 15−20 h, reaction vessel open to an oil bubbler to allow escape of volatile amine coproduct).[12] These reaction conditions will be referred to as "standard open conditions".

(i) Reaction of (EBI)H_2 and Zr$(NEt_2)_4$. Under "standard open conditions", the reaction of (EBI)H_2 and Zr$(NEt_2)_4$ did not produce the desired (EBI)Zr$(NEt_2)_2$ metallocene; rather, the product mixture contained 50% starting materials and 50% mono(indenyl) species (η^5-$C_9H_6CH_2CH_2C_9H_7$)Zr$(NEt_2)_3$ (Scheme 1),[21] the analog of the key intermediate in the synthesis of (EBI)Zr$(NMe_2)_2$. The use of longer reaction times lead to the formation of insoluble decomposition products,[22] and bubbling N_2 through the reaction mixture to help sweep away the NEt_2H byproduct (bp 55 °C) had no effect. It is likely that the lack of formation of (EBI)Zr$(NEt_2)_2$ is due to the greater steric bulk of NEt_2 versus NMe_2. However, the reaction of (EBI)H_2 and Zr$(NEt_2)_4$ in 1,2-dichlorobenzene at 180 °C (21 h) gave (EBI)ZrCl_2 in 80% NMR yield with a *rac*/*meso* ratio of 1.7/1 (Scheme 1). Thus, under these rather forcing conditions, metallocene formation occurs and the solvent acts as a chlorinating agent. We previously found that the reaction of Zr$(NMe_2)_4$ with the N_4-macrocycle $(Me_4taen)H_2$ yields $(Me_4taen)Zr(NMe_2)_2$ in pentane and $(Me_4taen)ZrCl_2(NMe_2H)$ in CH_2Cl_2.[23]

(ii) Reaction of (EBI)H_2 and Zr$(NMe_2)_2(N^iPr_2)_2$. In a second approach, we investigated the reaction of (EBI)H_2 with the mixed-amide complex Zr$(NMe_2)_2(N^iPr_2)_2$. It was postulated that the small NMe_2 ligands would provide sterically accessible sites for amine elimination, while the sterically demanding N^iPr_2 ligands would disfavor the formation of the *meso* product. The reaction of (EBI)H_2 and Zr$(NMe_2)_2(N^iPr_2)_2$ under standard open conditions yielded a mixture of (EBI)Zr$(NMe_2)_2$ (30% NMR, *rac*/*meso* ratio = 1/1), starting materials (50%), and other products (20%). When the toluene solvent was replaced with *m*-xylene and the reaction mixture heated to 140 °C for 16 h, (EBI)Zr$(NMe_2)_2$ was obtained in 70% NMR yield in a *rac*/*meso* ratio of 2/1 (Scheme 1). Thus, despite the fact that NMe_2H is more volatile and is a slightly weaker acid than N^iPr_2H,[24,25] N^iPr_2H elimination occurs and (EBI)Zr$(NMe_2)_2$ is formed in preference to (EBI)Zr$(N^iPr_2)_2$. The X-ray crystal structure of *rac*-(EBI)Zr$(NMe_2)_2$ shows evidence of steric crowding between the NMe_2 ligands and the EBI framework;[12] evidently, the increased crowding which would be present in *rac*-(EBI)Zr$(N^iPr_2)_2$ disfavors the formation of this compound.

(iii) Synthesis of *rac*-(EBI)Zr$(NC_4H_8)_2$. To further probe steric effects, we investigated the reaction of (EBI)H_2 and the pyrrolidide complex Zr$(NC_4H_8)_4$. The slightly smaller cone angle of the cyclic NC_4H_8 ligand versus NMe_2 was expected to enhance the rate of amine elimination.[26] However, it was anticipated that removal of the pyrrolidine coproduct (bp 87 °C) from the system might be difficult and that this might influence the extent and stereoselectivity of the reaction. The new compound Zr$(NC_4H_8)_4$ was prepared via reaction of Zr$(NMe_2)_4$ and excess pyrrolidine (reflux, 15 h, open to oil bubbler). Removal of amine under reduced pressure followed by drying of the resulting solid under vacuum provided pure Zr$(NC_4H_8)_4$ in 85% isolated yield.

The reaction of (EBI)H_2 and Zr$(NC_4H_8)_4$ was first studied under the standard open conditions. After 15 h at 100 °C, ^1H NMR analysis of an aliquot showed that the desired *ansa*-metallocene (EBI)Zr$(NC_4H_8)_2$ was present in 65% NMR yield in a *rac*/*meso* ratio of 7/1. However, when N_2 was bubbled through the reaction mixture to help drive off the pyrrolidine coproduct, (EBI)Zr$(NC_4H_8)_2$ was formed in the same yield and *rac*/*meso* ratio in 2 h.

Higher yields of (EBI)Zr$(NC_4H_8)_2$ were obtained at higher temperatures. Thus, the reaction of (EBI)H_2 and Zr$(NC_4H_8)_4$ in *m*-xylene at 140 °C for 7 h, with a slow N_2 flow through the reaction vessel, produced (EBI)Zr$(NC_4H_8)_2$ in 95% NMR yield in a *rac*/*meso* ratio of 6/1 (Scheme 1). Recrystallization from Et_2O afforded pure *rac*-(EBI)Zr$(NC_4H_8)_2$ in 42% isolated yield.[27]

These results indicate that (i) the rate of formation of (EBI)Zr$(NR_2)_2$ from (EBI)H_2 and Zr$(NR_2)_4$ is similar for NC_4H_8 and NMe_2 and (ii) the rate of removal of pyrrolidine influences the yield of (EBI)Zr$(NC_4H_8)_2$ but not the *rac*/*meso* ratio. It is likely that even when an N_2 purge is used, the steady-state concentration of pyrrolidine in solution is sufficient to efficiently catalyze the *rac*/*meso* isomerization.[12] The fact that a *rac*/*meso* ratio of 7/1 is obtained (at 100 °C) under conditions where the extent of reaction is limited by its reversibility indicates that this is the thermodynamic product ratio.

Attempted Synthesis of (EBI)Ti$(NR_2)_2$ Complexes via Amine Elimination. (EBI)H_2 does not react with Ti$(NMe_2)_4$ in toluene (100 °C, 17 h, standard open conditions, Scheme 2). This contrasts with the reaction of (EBI)H_2 and Zr$(NMe_2)_4$ which gives (EBI)Zr$(NMe_2)_2$ in 90% NMR yield (*rac*/*meso* ratio = 13/1) under the same conditions.[12] Earlier, Lappert showed that the reaction of Ti$(NMe_2)_4$ with excess cyclopentadiene (CpH) in refluxing benzene yields the mono-Cp compound CpTi$(NMe_2)_3$, while the corresponding reaction with Zr$(NMe_2)_4$ yields $Cp_2Zr(NMe_2)_2$.[18] Similarly,

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(21) (η^5-$C_9H_6CH_2CH_2C_9H_7$)Zr$(NEt_2)_3$ ^1H NMR (C_6D_6): δ 7.6−6.9 (m, 8 H, η^5-C_9H_6 and C_9H_7), 6.47 (d, J = 3 Hz, 1 H, η^5-C_9H_6), 6.23 (d, J = 3 Hz, 1 H, η^5-C_9H_6), 6.03 (br s, 1 H, C_9H_7), 3.5−3.2 (m, 4 H, CH_2CH_2), 3.05 (br s, 2 H, C_9H_7), 3.22 (m, 12 H, NCH_2), 0.96 (t, J = 7 Hz, 18 H, CH_3).

(22) One possible mechanism for thermal decomposition of Zr amide complexes is metalation of the NR_2 ligands. See: Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161.

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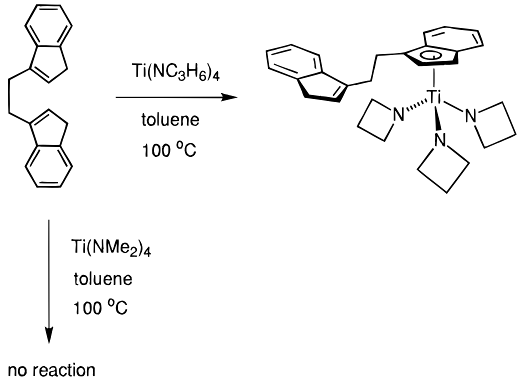
(24) Boiling points (1 atm): NMe_2H, 7 °C; $N\textit{i}Pr_2H$, 84 °C.

(25) Gas-phase acidity (NR_2H/NR_2^-): ΔG_{acid} = 389 kcal mol^{-1} for NMe_2H, 383 kcal mol^{-1} for $N\textit{i}Pr_2H$. Grimm, D. T.; Bartmess, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 1227.

(26) The C−N−C angles for the amide ligands in *rac*-$Me_2Si(1\text{-}C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}\textit{t}Bu)_2Zr(NC_4H_8)_2$ are 98.1° and 103.4°,[14] compared with 108.8 and 111.1° for *rac*-(EBI)Zr$(NMe_2)_2$;[12] the N−C bond lengths are very similar in both complexes (1.45−1.48 Å).

(27) Similar results are obtained without the N_2 purge, but longer reaction times are required. The reaction of (EBI)H_2 and Zr$(NC_4H_8)_4$ in *m*-xylene at 140 °C for 18 h, under a static N_2 atmosphere (open to an oil bubbler), affords (EBI)Zr$(NC_4H_8)_2$ in 90% NMR yield in a *rac*/*meso* ratio of 6/1 (Scheme 1). Recrystallization from hexane afforded pure *rac*-(EBI)Zr$(NC_4H_8)_2$ as an orange crystalline solid in 43% isloated yield.

Scheme 2

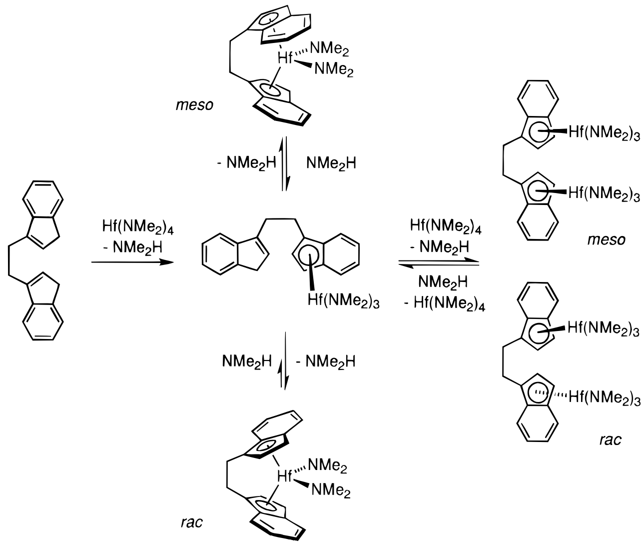


the reactions of M(NMe$_2$)$_4$ (M = Ti, Zr) with excess NR$_2$H (R = SiMe$_3$, ^{i}Pr) yield M(NMe$_2$)$_3$(NR$_2$) for M = Ti but M(NMe$_2$)$_2$(NR$_2$)$_2$ for M = Zr.[18,19] Lappert ascribed these reactivity differences to the fact that Ti amides are more crowded than the analogous Zr species due to the smaller metal radius and shorter M−NR$_2$ bonds: (effective ionic radii in an 8-coordinate environment, Ti^{4+} = 0.74 Å, Zr^{4+} = 0.84 Å;[28] M−NMe$_2$ bond lengths, Ti = 1.91−1.92 Å,[29] Zr = 2.03−2.11 Å).[23,30] It is likely that the lack of reaction of (EBI)H$_2$ and Ti(NMe$_2$)$_4$ is also due to steric crowding.

In an effort to circumvent the steric problems associated with amine elimination reactions of titanium amide complexes, we briefly investigated the titanium azetidide complex Ti(NC$_3$H$_6$)$_4$. In monomeric form, this species is less crowded than Ti(NMe$_2$)$_4$ because the α-CH$_2$ groups are tied back in a four-membered ring.[31] Ti(NC$_3$H$_6$)$_4$ was prepared by the reaction of Ti(NMe$_2$)$_4$ and excess azetidine (C$_3$H$_6$NH) in hexane at room temperature in 70% isolated yield and ca. 90% purity. This material was used without further purification. The reaction of (EBI)H$_2$ with Ti(NC$_3$H$_6$)$_4$ in toluene at 100 °C for 17 h (standard open conditions) gave the mono(indenyl) complex (η^5-C$_9$H$_6$CH$_2$CH$_2$C$_9$H$_7$)Ti(NC$_3$H$_6$)$_3$ as the only titanium species in solution (ca. 30% NMR yield), along with (EBI)H$_2$ (70%) and insoluble decomposition products (Scheme 2). Thus, reducing the steric bulk of the amide ligand does increase the reactivity of Ti(NR$_2$)$_4$ complexes toward amine elimination but does not lead to the desired *ansa*-titanocene.

It is unlikely that ring strain in the (EBI)Ti unit is responsible for the lack of formation of *ansa*-titanocenes in these reactions. The molecular structures of *rac*-(EBTHI)TiCl$_2$,[6,7] (η^5,η^5-(C$_5$H$_4$CH$_2$CH$_2$C$_5$H$_4$))TiCl$_2$,[32] and other C$_2$-bridged *ansa*-titanocenes[33] show little deviation in the titanocene framework compared with Cp$_2$TiCl$_2$.[34]

Scheme 3



Synthesis of *rac*-(EBI)Hf(NMe$_2$)$_2$. The reaction of (EBI)H$_2$ and Hf(NMe$_2$)$_4$ was studied under a variety of conditions (Scheme 3). After 1 h at 23 °C in C$_6$D$_6$, no reaction was observed; however, at 100 °C in toluene (standard open conditions, 18 h) a mixture of the mono(indenyl) species (η^5-C$_9$H$_6$CH$_2$CH$_2$C$_9$H$_7$)Hf(NMe$_2$)$_3$ (50%, based on Hf), the binuclear species (μ-η^5,η^5-EBI){Hf(NMe$_2$)$_3$}$_2$ (40%, two isomers), and *rac*-(EBI)Hf(NMe$_2$)$_2$ (10%) was formed. In contrast, the reaction of (EBI)H$_2$ and Zr(NMe$_2$)$_4$ at 23 °C (30 min) yields a mixture of (η^5-C$_9$H$_6$CH$_2$CH$_2$C$_9$H$_7$)Zr(NMe$_2$)$_3$ and (μ-η^5,η^5-EBI){Zr(NMe$_2$)$_3$}$_2$.[12]

The mono(indenyl) species (η^5-C$_9$H$_6$CH$_2$CH$_2$C$_9$H$_7$)Hf(NMe$_2$)$_3$ was characterized by ^{1}H NMR only; key spectral features include resonances for the (η^5-C$_9$H$_6$CH$_2$CH$_2$)Hf(NMe$_2$)$_3$ fragment which are very similar to those of (μ-η^5,η^5-EBI){Hf(NMe$_2$)$_3$}$_2$ and resonances for the pendant indene which are similar to those of (EBI)H$_2$.[35] The binuclear species (μ-η^5,η^5-EBI){Hf(NMe$_2$)$_3$}$_2$ was isolated in crude form in 80% yield from the reaction of 2 equiv of (EBI)H$_2$ with Hf(NMe$_2$)$_4$ (*m*-xylene, 140 °C, 18 h) as a 1/1 mixture of *rac* and *meso* diastereomers (Scheme 3). However, attempts to recrystallize this compound failed to give pure (μ-η^5,η^5-EBI){Hf(NMe$_2$)$_3$}$_2$. The ^{1}H NMR spectrum includes 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*.[36]

When the reaction of (EBI)H$_2$ with Hf(NMe$_2$)$_4$ was performed at higher temperatures, the NMR yield of (EBI)Hf(NMe$_2$)$_2$ increased.[37] Under the optimum conditions found in these studies (*m*-xylene solvent, 140 °C, 21 h , reaction vessel open to bubbler to allow escape of

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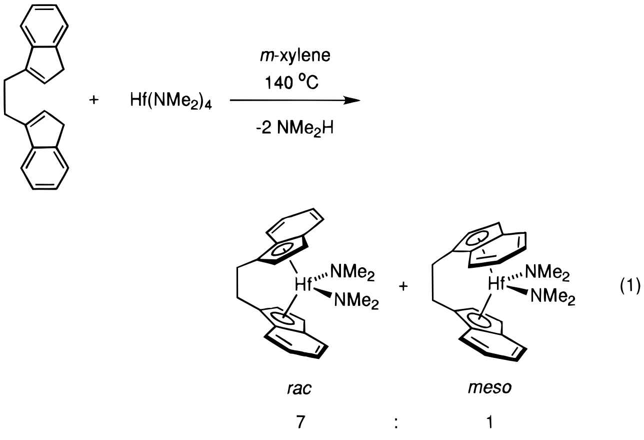
(35) (η^5-C$_9$H$_6$CH$_2$CH$_2$C$_9$H$_7$)Hf(NMe$_2$)$_3$: ^{1}H NMR (C$_6$D$_6$): δ 7.6−6.9 (m, 8 H, η^5-C$_9$H$_6$ and C$_9$H$_7$), 6.33 (d, J = 3 Hz, 1 H, η^5-C$_9$H$_6$), 6.18 (d, J = 3 Hz, 1 H, η^5-C$_9$H$_6$), 6.02 (br s, 1 H, C$_9$H$_7$), 3.4−3.1 (m, 4 H, CH$_2$-CH$_2$), 3.07 (br s, 2 H, C$_9$H$_7$), 2.83 (s, 18 H, NMe$_2$).

(36) (μ-η^5,η^5-EBI){Hf(NMe$_2$)$_3$}$_2$: ^{1}H NMR (C$_6$D$_6$): isomer a, δ 7.6−7.4 (m, 4 H, indenyl), 7.0−6.9 (m, 4 H, indenyl), 6.31 (d, J = 3 Hz, 2 H, C$_5$ indenyl), 6.16 (d, J = 3 Hz, 2 H, C$_5$ indenyl), 3.4−3.1 (m, 4 H, CH$_2$CH$_2$), 2.84 (s, 36 H, NMe$_2$); isomer b, δ 7.6−7.4 (m, 4 H, indenyl), 7.0−6.9 (m, 4 H, indenyl), 6.22 (d, J = 3 Hz, 2 H, C$_5$ indenyl), 6.16 (d, J = 3 Hz, 2 H, C$_5$ indenyl), 3.4−3.1 (m, 4 H, CH$_2$CH$_2$), 2.83 (s, 36 H, NMe$_2$).

(37) The use of chlorobenzene as a reaction solvent (125 °C, 21 h, open system) gave (EBI)Hf(NMe$_2$)$_2$ in 30% NMR yield (along with (μ-η^5,η^5-EBI){Hf(NMe$_2$)$_3$}$_2$ and (η^5-C$_9$H$_6$CH$_2$CH$_2$C$_9$H$_7$)Hf(NMe$_2$)$_3$).

NMe$_2$H), (EBI)Hf(NMe$_2$)$_2$ was obtained in 85% NMR yield in a *rac*/*meso* ratio of 7/1 (eq 1). Recrystallization from Et$_2$O afforded pure *rac*-(EBI)Hf(NMe$_2$)$_2$ as a yellow crystalline solid in 47% yield. Heating the reaction mixture for 60 h (140 °C) resulted in an increase in the *rac*/*meso* ratio to 16/1, indicating that *rac*-(EBI)Hf(NMe$_2$)$_2$ is the thermodynamic product.



The observations described above are consistent with the reaction pathway shown in Scheme 3, which is directly analogous to that for the reaction of (EBI)H$_2$ and Zr(NMe$_2$)$_4$.[12] The amine elimination reactions are significantly slower for Hf compared with Zr under the same conditions, most likely as a result of the higher bond strengths of Hf−NR$_2$ versus Zr−NR$_2$ bonds.[38] As Zr and Hf are very similar in size (effective ionic radii in 8-coordinate environment: $Zr^{4+} = 0.84$ Å, $Hf^{4+} = 0.83$ Å),[28] steric crowding in Zr and Hf M(NR$_2$)$_4$ and (EBI)M(NR$_2$)$_2$ complexes should be nearly identical.

Structure and Bonding of *rac*-(EBI)Hf(NMe$_2$)$_2$. The molecular structure of *rac*-(EBI)Hf(NMe$_2$)$_2$ was determined by single-crystal X-ray diffraction (Figure 1, Tables 1 and 2). *rac*-(EBI)Hf(NMe$_2$)$_2$ adopts the expected monomeric *ansa*-bridged bent metallocene structure. The Hf atom lies on a crystallographic 2-fold rotation axis that bisects the N−Hf−N plane, and the structure suffers from a 2-fold (50:50) disorder of the two mirror image forms. Although the Hf atoms are located in the same position in both disordered sites, the N−Hf−N planes are rotated by 60° with respect to each other. Efforts were made to refine the structure either as a racemic twin or as two independent half-weighted molecules. Of these two approaches, the latter gave somewhat better agreement and therefore was used to complete the structural refinement. Both structures are shown in Figure 1.

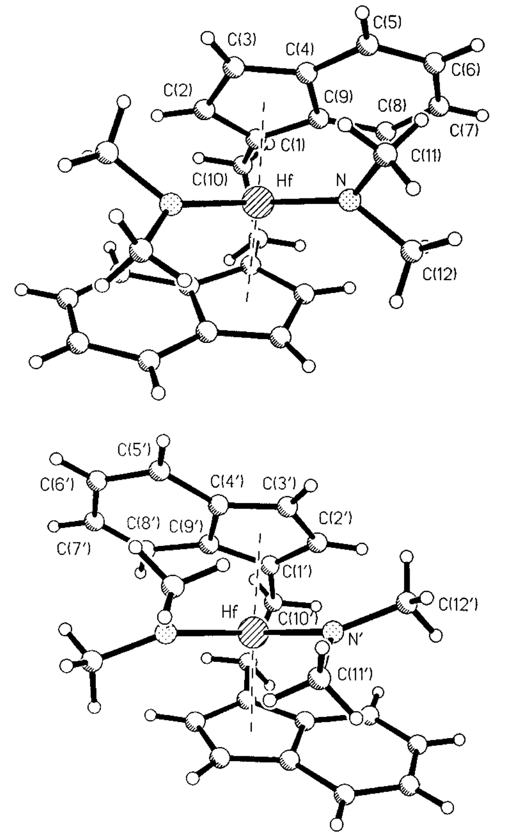


Figure 1. Molecular structures of the two disordered sites of *rac*-(EBI)Hf(NMe$_2$)$_2$.

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

empirical formula	$C_{24}H_{28}HfN_2$
fw	522.97
temp	293(2) K
wavelength	0.710 73 Å
cryst system	orthorhombic
space group	*Ibca*
unit cell dimens	$a = 13.269(1)$ Å, $\alpha = 90°$; $b = 15.715(1)$ Å, $\beta = 90°$; $c = 20.197(1)$ Å, $\gamma = 90°$
V	4211.5(5) Å^3
Z	8
D(calcd)	1.650 g/cm^3
abs coeff	49.64 cm^{-1}
F(000)	2064
cryst size	0.07 × 0.34 × 0.46 mm
θ range for data collcn	2.02−27.50°
index ranges	$-1 \le h \le 17$, $-1 \le k \le 20$, $0 \le l \le 26$
reflcns collcd	2808
indepdt reflcns	2328 ($R_{int} = 0.0292$)
refinement method	full-matrix least squares on F^2
data/restraints/params	1930/4/102
goodness-of-fit on F^2	1.194
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0570$, w$R2 = 0.1584$
R indices (all data)	$R1 = 0.1068$, w$R2 = 0.1821$
extinction coeff	0.000 29(4)
largest diff peak and hole	1.758 and −0.719 e Å^{-3}

The overall molecular structure of *rac*-(EBI)Hf(NMe$_2$)$_2$ is similar to those of *rac*-(EBI)Zr(NMe$_2$)$_2$[12] and *rac*-(EBI)HfCl$_2$.[9] However, the (EBI)Hf fragment of *rac*-(EBI)Hf(NMe$_2$)$_2$ adopts the unusual indenyl-backward conformation first described by Brintzinger;[39] in contrast *rac*-(EBI)MCl$_2$ (M = Zr, Hf) adopt the more common indenyl-forward conformation,[9,20] while the structure of *rac*-(EBI)Zr(NMe$_2$)$_2$ is disordered between the indenyl-forward and indenyl-backward conformations.[12b]

The Hf−N and Hf−N′ bond lengths (2.06, 2.08 Å) are similar to the Zr−N bond lengths in *rac*-(EBI)Zr(NMe$_2$)$_2$ (2.06 Å average) and are in the range observed for other Hf(IV) amide complexes (2.03−2.12 Å).[40] The amide groups of *rac*-(EBI)Hf(NMe$_2$)$_2$ are flat (sum of angles

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for *rac*-(EBI)Hf$(NMe_2)_2$[a,b]

Hf−N	2.064(5)	Hf−N′	2.081(5)
Hf−C(1)	2.532	Hf−C(1′)	2.561
Hf−C(2)	2.506	Hf−C(2′)	2.538
Hf−C(3)	2.618	Hf−C(3′)	2.554
Hf−C(4)	2.658	Hf−C(4′)	2.631
Hf−C(9)	2.618	Hf−C(9′)	2.602
Hf−Cp(c)	2.290	Hf−Cp′(c)	2.279
N−C(11)	1.432(12)	N′−C(11′)	1.441(11)
N−C(12)	1.462(11)	N′−C(12′)	1.460(11)
N−Hf−N*	99.9(3)	N′−Hf−N′*	96.3(3)
Cp(c)−Hf−Cp(c)*	118.1	Cp′(c)−Hf−Cp′(c)*	123.7
C(11)−N−C(12)	105.2(11)	C(11′)−N′−C(12′)	112.2(11)
C(11)−N−Hf	130.6(9)	C(12′)−N′−Hf	114.4(6)
C(11)−N−Hf	124.2(8)	C(12′)−N′−Hf	132.2(9)

[a] Symmetry transformation used to generate equivalent atoms: (*) $-x + 1 - 1$, $-y + 1/2$, $z + 1 - 1$. [b] Cp(c) designates the centroid of the cyclopentadienyl ring of the indenyl ligand.

around N = 360°, N′ = 359°) and are twisted 48° (N) and 33° (N′) from the equatorial plane of the metallocene, or about 42 and 57°, respectively, from the optimum orientation for Hf−N π-bonding.[41] These data are consistent with sp^2 hybridization at N and partial N to Hf π-donation. The molecular structure of *rac*-(EBI)Zr$(NMe_2)_2$ showed similar evidence for partial M−N π-bonding.[12]

Summary

This investigation of the influence of amide ligand structure on the synthesis of *rac*-(EBI)Zr$(NR_2)_2$ complexes via amine elimination shows that the optimum starting material is Zr$(NMe_2)_4$. As noted earlier, the reaction of (EBI)H_2 with Zr$(NMe_2)_4$ under the standard open conditions (toluene, 100 °C, 17 h, system open to bubbler) affords (EBI)Zr$(NMe_2)_2$ in 90% NMR yield in a *rac*/*meso* ratio of 13/1 and pure *rac*-(EBI)Zr$(NMe_2)_2$ in 68% isolated yield.[12] In contrast, the reaction of (EBI)H_2 with Zr$(NEt_2)_4$ under the same conditions yields only the mono(indenyl) complex $(\eta^5\text{-}C_9H_6CH_2CH_2C_9H_7)Zr(NEt_2)_3$. It is likely that the greater steric bulk of NEt_2 versus NMe_2 disfavors the formation of (EBI)Zr$(NEt_2)_2$. The reaction of (EBI)H_2 with Zr$(NEt_2)_4$ in 1,2-dichlorobenzene at 180 °C does result in metallocene formation, but under these forcing conditions the solvent acts as a chlorinating agent and the dichloride derivative (EBI)ZrCl_2 is obtained (*rac*/*meso* = 1.7/1).

The reaction of (EBI)H_2 with the mixed-amide complex Zr$(NMe_2)_2(N^iPr_2)_2$ yields the sterically least hindered *ansa*-metallocene product, (EBI)Zr$(NMe_2)_2$ (*rac*/*meso*) = 2/1). In this case the overall reaction rate and stereoselectivity are reduced compared with the corresponding Zr$(NMe_2)_4$ reaction. The increased steric crowding due to the bulky N^iPr_2 groups inhibits the amine elimination and disfavors the formation of *rac*-(EBI)Zr$(N^iPr_2)_2$.

The reaction of (EBI)H_2 with Zr$(NC_4H_8)_4$ illustrates the importance of the reversibility of the amine elimination reactions and the volatility of the amine byproduct. Under the standard open conditions, the formation of (EBI)Zr$(NC_4H_8)_2$ is rapid, but the yield is limited by the presence of the pyrrolidine byproduct in the reaction mixture. (EBI)Zr$(NC_4H_8)_2$ is obtained in high yield only when the reaction is performed at higher temperatures or when an N_2 purge is used to help remove the pyrrolidine from the reaction vessel. Even under N_2 purge conditions the steady-state concentration of pyrrolidine is sufficient to catalyze the *meso*/*rac* isomerization and the thermodynamic *rac*/*meso* product ratio (7/1) is obtained.

The reactions of (EBI)H_2 and titanium amide complexes did not give *ansa*-titanocene products. Even with the azetidide complex Ti$(NC_3H_6)_4$, only a single amine elimination occurs, giving $(\eta^5\text{-}C_9H_6CH_2CH_2C_9H_7)Ti(NC_3H_6)_3$. It likely that increased steric crowding around the smaller Ti (versus Zr) disfavors *ansa*-metallocene formation. However amine elimination does offer an attractive route to *rac*-(EBI)HfX_2 complexes. The reaction of (EBI)H_2 with Hf$(NMe_2)_4$ in *m*-xylene at 140 °C provides (EBI)Hf$(NMe_2)_2$ in 85% NMR yield (6/1 *rac*/*meso* ratio) and pure *rac*-(EBI)Hf$(NMe_2)_2$ in 47% isolated yield.

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 or vacuum. $ZrCl_4$, $TiCl_4$, and $HfCl_4$ were purchased from Aldrich, CERAC Inc., or GFS Chemicals. $LiNMe_2$, $LiNEt_2$, N^iPr_2H, and pyrrolidine were obtained from Aldrich. Azetidine was obtained from Eastman. Amines were dried over Na, distilled under vacuum before use, and stored under N_2. (EBI)H_2 (1,2-bis(3-indenyl)ethane) was prepared by the literature procedure[7] 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 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. NMR yields were determined by reference to an internal standard. Elemental analyses were performed by E + R Microanalytical Laboratory (Corona, NY).

Zr$(NEt_2)_4$. In a modification of Bradley's original procedure,[19] solid $ZrCl_4$ (6.1 g, 26 mmol) was added, in several portions over 1 h, to a suspension of $LiNEt_2$ (8.7 g, 110 mmol) in toluene (80 mL) at room temperature. The reaction mixture was stirred for an additional 20 h at room temperature. The solvent was removed under reduced pressure leaving a brown oily residue, from which pure Zr$(NEt_2)_4$ was obtained, as a yellow liquid, by distillation at 120 °C/0.05 mmHg, in 65% yield (6.5 g). ^1H NMR (C_6D_6): δ 3.33 (q, J = 7 Hz, 16 H, NCH_2), 1.14 (t, J = 7 Hz, 24 H, CH_3).

Reaction of (EBI)H_2 and Zr$(NEt_2)_4$ in 1,2-Dichlorobenzene. A mixture of Zr$(NEt_2)_4$ (0.38 g, 1.0 mmol) and (EBI)H_2 (1,2-bis(3-indenyl)ethane) (0.26 g, 1.0 mmol) in 1,2-dichlorobenzene (10 mL) was stirred and heated to 180 °C for 21 h, with the reaction vessel open to an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed the product mixture contained 80% (EBI)ZrCl_2 (*rac*/*meso* ratio = 1.7/1) and 20% (EBI)H_2. ^1H NMR (C_6D_6): *rac*-(EBI)ZrCl_2, 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); *meso*-(EBI)ZrCl_2, δ 7.35−6.75 (m, 8 H, indenyl), 6.60 (d, J = 3 Hz, 2 H, C_5 indenyl), 5.89 (d, J = 3 Hz, 2 H, C_5 indenyl), 3.24 (m, 2 H, CH_2), 2.78 (m, 2 H, CH_2).

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(40) (a) Cp^*_2Hf(H)(NHMe), 2.03 Å: Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309. (b) (Me_4taen)Hf$(NMe_2)_2$, 2.09 Å: Black, D. G.; Jordan, R. F.; Rogers, R. D. Manuscript in preparation. (c) Hf{NH(2,6-$^iPr_2$-C_6H_3)}$_2${=N(2,6-$^iPr_2$-C_6H_3)}(4-pyrrolidinopyridine)$_2$, 2.12 Å average: Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689.

(41) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

$Zr(NMe_2)_2(N^iPr_2)_2$. In a modification of Bradley's original procedure,[19] N^iPr_2H (12 g, 120 mmol) was added to a Schlenk vessel containing $Zr(NMe_2)_4$ (2.7 g, 10 mmol). The Schlenk vessel was fitted with a condenser, the reaction mixture was stirred and refluxed for 39 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 complete conversion to $Zr(NMe_2)_2(N^iPr_2)_2$. The volatiles were removed under reduced pressure and the residue was sublimed at 80 °C/0.05 mmHg, to yield pure $Zr(NMe_2)_2(N^iPr_2)_2$ as a pale green solid (2.7 g, 70%). ^1H NMR (C_6D_6): δ 3.50 (sept, $J = 6$ Hz, 4 H, NC*H*Me$_2$), 3.04 (s, 12 H, NMe_2), 1.22 (d, $J = 6$ Hz, 24 H, NCH*Me$_2$*).

Reaction of $(EBI)H_2$ and $Zr(NMe_2)_2(N^iPr_2)_2$. A toluene (30 mL) solution of $Zr(NMe_2)_2(N^iPr_2)_2$ (0.50 g, 1.3 mmol) and $(EBI)H_2$ (0.34 g, 1.3 mmol) was stirred and heated to 100 °C for 18 h, with the reaction vessel open to an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed the presence of approximately 50% starting materials, 30% $(EBI)Zr(NMe_2)_2$ (*rac*/*meso* ratio = 1/1), and 20% other products. The toluene was removed under reduced pressure, and *m*-xylene (10 mL) was added. The reaction mixture was stirred and heated to 140 °C for 16 h. The volatiles were removed under reduced pressure yielding a red/orange oil, which was shown by ^1H NMR to be a mixture of $(EBI)Zr(NMe_2)_2$ (70%, *rac*/*meso* ratio = 2/1),[12] $(EBI)H_2$ (30%), and insoluble decomposition products.

$Zr(NC_4H_8)_4$. Pyrrolidine (C_4H_8NH, 13 g, 180 mmol) was added to a Schlenk vessel containing $Zr(NMe_2)_4$ (2.0 g, 7.5 mmol). The vessel was fitted with a condenser, and the reaction mixture was stirred and refluxed for 15 h, open to an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed complete conversion to $Zr(NC_4H_8)_4$. The volatiles were removed under reduced pressure yielding a pale yellow solid which was dried under vacuum overnight (2.4 g, 85%). Anal. Calcd for $C_{16}H_{32}N_4Zr$: C, 51.70; H, 8.68; N, 15.08. Found: C, 51.48; H, 8.80; N, 15.11. ^1H NMR (C_6D_6): δ 3.45 (m, 16 H, NCH_2), 1.62 (m, 16 H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 52.6 (NCH_2), 27.2 (CH_2).

***rac*-$(EBI)Zr(NC_4H_8)_2$.** A solution of $Zr(NC_4H_8)_4$ (0.37 g, 1.0 mmol) and $(EBI)H_2$ (0.26 g, 1.0 mmol) in *m*-xylene (20 mL) was stirred and heated to 140 °C for 18 h, with the reaction vessel open to an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed that $(EBI)Zr(NC_4H_8)_2$ was present in 90% yield in a *rac*/*meso* ratio of 6/1. The volatiles were removed under reduced pressure and the crude product was recrystallized from hexane, yielding pure *rac*-$(EBI)Zr(NC_4H_8)_2$ as an orange crystalline solid (0.21 g, 43%). When the experiment was repeated with a slow N_2 flow through the reaction vessel and a reduced reaction time (7 h), $(EBI)Zr(NC_4H_8)_2$ was obtained in 95% NMR yield in a *rac*/*meso* ratio of 6/1, and recrystallization from Et_2O afforded pure *rac*-$(EBI)Zr(NC_4H_8)_2$ in 42% yield. ^1H NMR (C_6D_6): δ 7.44 (d, $J = 9$ Hz, 2 H, indenyl), 7.31 (d, $J = 8$ Hz, 2 H, indenyl), 6.90 (m, 2 H, indenyl), 6.75 (m, 2 H, indenyl), 6.33 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 5.95 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 3.36 (m, 2 H, CH_2), 3.14 (m, 2 H, CH_2), 3.14 (m, 4 H, NCH_2), 2.85 (m, 4 H, NCH_2), 1.43 (m, 4 H, NCH$_2$*CH$_2$*), 1.27 (m, 4 H, NCH$_2$*CH$_2$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 129.3 (C), 125.2 (CH), 122.9 (CH), 122.6 (CH), 122.0 (C), 120.7 (CH), 116.9 (C), 113.1 (CH), 100.8 (CH), 56.1 (NCH_2), 29.1 (CH_2CH_2), 27.7 (NCH$_2$*CH$_2$*).

$Ti(NMe_2)_4$. In a modification of Bradley's original procedure,[19] a toluene (25 mL) solution of $TiCl_4$ (5.3 g, 28 mmol) was added dropwise over 1 h to a toluene (75 mL) solution of $LiNMe_2$ (5.9 g, 120 mmol) at 0 °C. The reaction mixture was stirred for 17 h at 23 °C. The solvent was removed under reduced pressure leaving a green oily residue, from which pure $Ti(NMe_2)_4$ was obtained, as a yellow liquid, by distillation at 100 °C/0.1 mmHg (5.1 g, 81%). ^1H NMR (C_6D_6): δ 3.08 (s, 24 H, NMe_2).

Generation of $Ti(NC_3H_6)_4$ and Reaction with $(EBI)H_2$. A solution of azetidine (C_3H_6NH, 0.68 g, 12 mmol) in hexane (15 mL) was added dropwise over 15 min to a solution of $Ti(NMe_2)_4$ (0.53 g, 2.4 mmol) in hexane (10 mL). The reaction mixture was stirred for 19 h at 23 °C. An aliquot was removed and analyzed by ^1H NMR which showed conversion to $Ti(NC_3H_6)_4$ (ca. 90% purity). The reaction mixture was filtered, the solvent was removed from the filtrate under reduced pressure, and the resulting orange solid was dried under vacuum overnight, yielding $Ti(NC_3H_6)_4$ (0.45 g, 70%, 90% pure by ^1H NMR). ^1H NMR (C_6D_6): δ 4.51 (t, $J = 7$ Hz, 16 H, NCH_2), 2.32 (pentet, $J = 7$ Hz, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 58.1 (NCH_2), 23.2 (CH_2).

Reaction with $(EBI)H_2$. A solution of $Ti(NC_3H_6)_4$ (0.170 g, 0.624 mmol) and $(EBI)H_2$ (0.161 g, 0.624 mmol) in toluene (25 mL) was stirred and heated to 100 °C for 17 h with the reaction vessel open to an oil bubbler. An aliquot was removed and analyzed by ^1H NMR which showed that $(\eta^5\text{-}C_9H_6CH_2CH_2C_9H_7)Ti(NC_3H_6)_3$ (30% NMR) and unreacted $(EBI)H_2$ (70% NMR) were present. Resonances for $Ti(NC_3H_6)_4$ or *ansa*-metallocene species were not were not observed. ^1H NMR (C_6D_6) for $(\eta^5\text{-}C_9H_6CH_2CH_2C_9H_7)Ti(NC_3H_6)_3$: δ 7.6−6.9 (m, 8 H, $\eta^5\text{-}C_9H_6$ and C_9H_7), 6.12 (d, $J = 3$ Hz, 1 H, $\eta^5\text{-}C_9H_6$), 6.09 (br t, $J = 2$ Hz, 1 H, C_9H_7), 6.06 (d, $J = 3$ Hz, 1 H, $\eta^5\text{-}C_9H_6$), 4.33 (m, 12 H, NCH_2), 3.4−3.2 (m, 4 H, CH_2CH_2), 3.09 (br s, 2 H, C_9H_7), 2.06 (m, 6 H, CH_2).

$Hf(NMe_2)_4$. In a modification of Lappert's original procedure,[18] solid $HfCl_4$ (16 g, 0.050 mol) was added, in several portions over 3 h, to a suspension of $LiNMe_2$ (11 g, 0.20 mol) in toluene (150 mL) at room temperature. The reaction mixture was stirred for an additional 14 h at room temperature. The solvent was removed under reduced pressure leaving an off-white solid, from which pure $Hf(NMe_2)_4$ was obtained by sublimation at 80 °C/0.05 mmHg (10 g, 59%). ^1H NMR (C_6D_6): δ 2.98 (s, 24 H, NMe_2).

***rac*-$(EBI)Hf(NMe_2)_2$.** A solution of $Hf(NMe_2)_4$ (0.53 g, 1.5 mmol) and $(EBI)H_2$ (0.39 g, 1.5 mmol) in *m*-xylene (15 mL) was stirred and heated to 140 °C for 21 h. The evolved 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 85% conversion (based on Hf) to $(EBI)Hf(NMe_2)_2$ with a *rac*/*meso* ratio of 7/1. The volatiles were removed under reduced pressure and the crude product was recrystallized from Et_2O, yielding pure *rac*-$(EBI)Hf(NMe_2)_2$ as a yellow crystalline solid (0.37 g, 47%). Anal. Calcd for $C_{24}H_{28}N_2Hf$: C, 55.12; H, 5.40; N, 5.36. Found: C, 54.99; H, 5.51; N, 5.28. ^1H NMR (C_6D_6): δ 7.43 (d, $J = 8$ Hz, 2 H, indenyl), 7.40 (d, $J = 8$ Hz, 2 H, indenyl), 6.93 (m, 2 H, indenyl), 6.74 (m, 2 H, indenyl), 6.26 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 5.80 (d, $J = 3$ Hz, 2 H, C_5 indenyl), 3.27 (m, 4 H, CH_2CH_2), 2.56 (s, 12 H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 130.2 (C), 125.5 (CH), 123.5 (CH), 123.3 (CH), 121.0 (C), 120.6 (CH), 115.8 (C), 113.1 (CH), 98.6 (CH), 47.2 (NMe_2), 28.4 (CH_2CH_2).

X-ray Diffraction Study of *rac*-$(EBI)Hf(NMe_2)_2$. The structure of *rac*-$(EBI)Hf(NMe_2)_2$ was determined by J.L.P. at WVU. A crystal was sealed under nitrogen in a glass capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The unit cell dimensions were initially determined by indexing 16 reflections randomly selected from a preliminary rotation photograph. The final lattice parameters and orientation matrix for the orthorhombic unit cell were calculated from a least-squares fit of the orientation angles for 30 reflections (range: $18° < 2\theta < 29°$) at 22 °C. The observed systematic absences are $\{0kl\}$, $k = 2n + 1$; $\{h0l\}$, $l = 2n + 1$; $\{hk0\}$, $h = 2n + 1$; and $\{hkl\}$, $h + k + l = 2n + 1$, with the additional condition that all data with l = odd number are noticeably weaker in intensity. For the centrosymmetric *Ibca* space group, this latter restriction constrains the Hf atom to lie on a crystallographic 2-fold axis. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 1.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and variable ω scans (2−10°/min). 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 and did not show any indication of sample decomposition. The raw data were corrected for Lorentz−polarization effects. ψ scans were measured for 9 reflections ($\chi \approx \pm 90°$; $5° < 2\theta < 35°$) and showed substantial dependence of the measured intensities on the ψ angle. Because of the small value of one of the crystal dimensions, an empirical lamina absorption correction with the minimum glancing angle set at 5.0° was applied. The resultant transmission coefficients based on the ψ scan data ranged from $T_{\min} = 0.229$ to $T_{\max} = 0.738$.

The slow scan rate used to measure the weak reflections helped verify the observed systematic absences for the $\{0kl\}$ and $\{h0l\}$ data. For the $\{hk0\}$ reflections, the intensities of 15 reflections with h or k odd were not rigorously zero, but their mean intensity was 100 times less than the mean intensity for all of the observed reflections. The presence of these weak reflections, however, led us to consider *Ibam* as an alternative space group to *Ibca* for this system.

Initial coordinates for the Hf atom were determined by interpretation of the Patterson peaks using the Harker vectors associated with the *Ibca* and *Ibam* space groups. Of the two space group choices, only the *Ibca* setting placed the Hf atom on the crystallographic 2-fold rotation axis (with $x = 0.0000$ and $y = 0.2500$) bisecting the N−Hf−N bond angle. In the process of locating the remaining non-hydrogen atoms, it became readily apparent that the rest of the structure suffers from a 50:50 disorder of the two mirror image forms of *rac*-(EBI)Hf(NMe_2)$_2$. Although the Hf atom is located in the same position in both disordered sites, the corresponding N−Hf−N planes are rotated by ca. 60° with respect to each other. Each independent indenyl fragment was refined as a rigid group. The atomic coordinates used for the nine carbon and six hydrogen atoms of the indenyl fragment were taken from the structural analysis of the corresponding Zr analog.[12b] The remaining non-hydrogen atoms were refined anisotropically. 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. The two N−C distances for each independent dimethylamido ligand were restrained to 1.43 ± 0.02 Å. Full-matrix least-squares refinement with SHELXL-93,[42] based upon the minimization of $\Sigma w_i|F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = [\sigma^2(F_o^2) + (0.0428P)^2 + 138.11P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$, converged to give final discrepancy indices[43] of $R1 = 0.0570$ and $wR2 = 0.1584$ for the 1318 reflections with $I > 2\sigma(I)$ and overall GOF value = 1.194. The final difference Fourier map revealed one large positive residual peak of electron density (1.76 e Å^{-3}) near the Hf.

Although the quality of this structural analysis is clearly marginal, it is sufficient to establish the atom connectivity in *rac*-(EBI)Hf(NMe_2)$_2$. The observed variations between chemically equivalent bond distances and angles for the two disordered sites are probably due to the limitations associated with our refinement of this complex disorder and may reflect some systematic error introduced by the empirical absorption correction.

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Supporting Information Available: Text describing X-ray procedures and tables of X-ray parameters, atom positional and thermal parameters, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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[42] 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.

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