

Aluminum *ansa*-Indenyl Compounds. Synthesis, Structures, Dynamic Properties, and Application in the Synthesis of Group 4 *ansa*-Metallocenes

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The synthesis, structures, dynamic properties, and indenyl transfer reactions of aluminum *ansa*-bis(indenyl) compounds are described. The reaction of 2 equiv of AlMe_2Cl with 1 equiv of $\text{Li}_2[(1\text{-indenyl})_2\text{SiMe}_2]$, $\text{Li}_2[(2\text{-Me-1-indenyl})_2\text{SiMe}_2]$, $\text{Li}_2[(2\text{-Me-4,5-benz-1-indenyl})_2\text{SiMe}_2] \cdot \text{Et}_2\text{O}$, $\text{Li}_2[(2\text{-Me-4-Ph-1-indenyl})_2\text{SiMe}_2] \cdot \text{Et}_2\text{O}$, or $\text{Li}_2[1,2\text{-(3-indenyl)}_2\text{-C}_2\text{H}_4]$ in Et_2O followed by treatment with the appropriate Lewis base (L) affords $\{\text{AlMe}_2(\text{THF})(\text{indenyl})\}_2\text{SiMe}_2$ (**1**), $\{[1\text{-AlMe}_2(1,4\text{-dioxane})_{0.5}\text{-2-Me-1-indenyl}]_2\text{SiMe}_2\}_n$ (**2a**), $\{1\text{-AlMe}_2(\text{Et}_2\text{O})\text{-2-Me-4,5-benz-1-indenyl}\}_2\text{SiMe}_2$ (**3**), $\{1\text{-AlMe}_2(\text{Et}_2\text{O})\text{-2-Me-4-Ph-1-indenyl}\}_2\text{SiMe}_2$ (**4a**), $\{1\text{-AlMe}_2(\text{THF})\text{-2-Me-4-Ph-1-indenyl}\}_2\text{SiMe}_2$ (**4b**), or $1,2\text{-}\{3\text{-AlMe}_2(\text{THF})\text{-1-indenyl}\}_2\text{-C}_2\text{H}_4$ (**5**), respectively, as colorless to pale yellow solids in 41–70% isolated yields. Compounds **2a** and **4b** are isolated as the *rac* isomers, whereas **1** and **3** are isolated as *rac/meso* mixtures from which the *rac* isomer can be separated by recrystallization. Compound **5** was isolated as a single diastereomer of $1,2\text{-}\{3\text{-AlMe}_2(\text{THF})\text{-1-indenyl}\}_2\text{-C}_2\text{H}_4$. The molecular structures of *rac*-**2a** and *rac*-**3** have been determined by X-ray crystallography. Low-temperature NMR studies establish that, in toluene- d_8 , *rac*-**1** exists as a 2/1 mixture of two isomers, $\{[1\text{-AlMe}_2(\text{THF})\text{-1-indenyl}]\{1\text{-AlMe}_2(\text{THF})\text{-3-indenyl}\}\text{SiMe}_2$ (*rac*-**1a**) and $\{1\text{-AlMe}_2(\text{THF})\text{-1-indenyl}\}_2\text{SiMe}_2$ (*rac*-**1b**), which interconvert rapidly on the NMR time scale at room temperature. In contrast, similar studies establish that *rac*-**2b** (in THF- d_8) and *rac*-**3** and *rac*-**4b** (in toluene- d_8) exist as the *rac*- $\{1\text{-AlMe}_2\text{L-1-indenyl}\}_2\text{SiMe}_2$ isomers; in these cases no other isomers are detected. *rac*-**1**, *rac*-**3**, and *rac*-**4b** isomerize to *rac/meso* mixtures slowly (days) at ambient temperature and more rapidly (minutes) at 70 °C. Compounds **1** and **5** undergo slow partial disproportionation by ligand redistribution (e.g. **1**: 28% conversion, 2 days, 23 °C, benzene); the more highly substituted indenyl compounds **3** and **4b** are more resistant to this process. Compounds **1**, **2**, **3**, **4a**, and **5** react with $\text{Zr}(\text{NMe}_2)_4$ and $\text{Hf}(\text{NMe}_2)_4$ in benzene or toluene under mild conditions to yield the corresponding *ansa*-metallocenes $\{(1\text{-indenyl})_2\text{SiMe}_2\}\text{-M}(\text{NMe}_2)_2$ (**6**, M = Zr, *rac/meso* = 4/1; **7**, M = Hf, *rac/meso* = 10/1), $\{(2\text{-Me-1-indenyl})_2\text{SiMe}_2\}\text{-Zr}(\text{NMe}_2)_2$ (**8**, *rac/meso* = 3/4), $\{(2\text{-Me-4,5-benz-1-indenyl})_2\text{SiMe}_2\}\text{Zr}(\text{NMe}_2)_2$ (**9**, *rac/meso* = 9/10), $\{(2\text{-Me-4-Ph-1-indenyl})_2\text{SiMe}_2\}\text{Zr}(\text{NMe}_2)_2$ (**10**, *rac/meso* = 2/3) and $\{1,2\text{-(3-indenyl)}_2\text{-C}_2\text{H}_4\}\text{M}(\text{NMe}_2)_2$ (**11**, M = Zr, *rac/meso* = 7.3/1; **12**, M = Hf, *rac/meso* = 7/1) in 70–90% NMR yields.

Introduction

Chiral group 4 *ansa*-metallocenes are important because of their utility as stereoselective olefin polymerization catalysts and selective reagents or catalysts for other reactions.¹ *ansa*-Metallocenes are normally prepared by the reaction of metal halides with alkali-metal or alkaline-earth-metal *ansa*-cyclopentadienyl reagents, but this method is often inefficient and control

of stereoselectivity is difficult.² We have described the synthesis of *rac*- $\{(1\text{-indenyl})_2\text{SiMe}_2\}\text{Zr}(\text{NMe}_2)_2$, *rac*- $\{1,2\text{-(1-indenyl)}_2\text{-C}_2\text{H}_4\}\text{Zr}(\text{NMe}_2)_2$, and other *ansa*-metallocenes by amine elimination reactions of $\text{M}(\text{NMe}_2)_4$ compounds and *ansa*-bis(indenes) or cyclopentadienes.^{3,4} However, this approach is less useful for the synthesis of Ti or Hf *ansa*-metallocenes (order of reactivity: Zr > Hf > Ti) and does not work well for crowded metal amides or crowded or weakly acidic *ansa*-bis(indenes).⁵

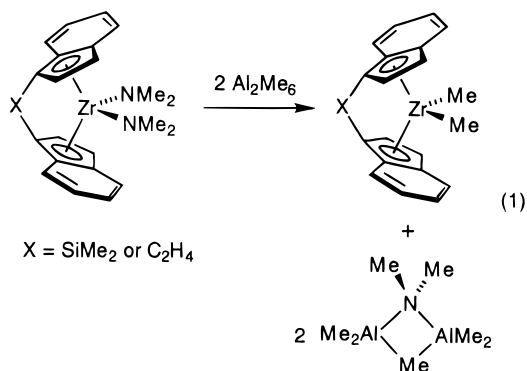
Several groups have shown that silicon and tin cyclopentadienyl derivatives can be used to synthesize group 4 *ansa*-metallocene dichlorides.⁶ Nifant'ev synthesized several *ansa*-metallocenes by the reaction of MCl_4 (M = Zr, Hf) with distannylated bis(cyclopentadienyl) or bis(indenyl) reagents; in particular, it was

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shown that *rac*-1,2-(3-SiMe₃-1-indenyl)₂-ethane reacts stereoselectively with ZrCl₄ to yield *rac*-{1,2-(1-indenyl)₂-C₂H₄}ZrCl₂.⁷ Brintzinger reported the synthesis of the *meso*-Me₂Si(3-^tBu-C₅H₃)₂ZrCl₂ and *meso*-Me₂Si(2,4-Me₂-C₅H₂)₂ZrCl₂ by the reaction of ZrCl₄ with the corresponding *meso* silastannatetrahydro-*s*-indacenes.⁸ Additionally, Resconi reported the diastereoselective synthesis of *rac*- and *meso*-{1,2-(4,7-Me₂-1-indenyl)₂-C₂H₄}ZrCl₂ by the reaction of ZrCl₄ with *rac*- and *meso*-1,2-(4,7-Me₂-1-SiMe₃-3-indenyl)₂-ethane, respectively.⁹ In these cases indenyl transfer is presumed to occur with inversion of configuration via backside attack of Zr at the Si-C_{indenyl} or Sn-C_{indenyl} center.¹⁰

rac-{1,2-(1-indenyl)₂-C₂H₄}Zr(NMe₂)₂, *rac*-{(1-indenyl)₂SiMe₂}Zr(NMe₂)₂, and other *ansa*-zirconocene bis(amides) react quantitatively with AlMe₃ to yield the corresponding metallocene dialkyl derivatives and Al₂Me₅(μ -NMe₂) as the major Al product (eq 1).¹¹ These



facile alkyl/amide exchange reactions suggested that aluminum *ansa*-bis(indenyl) compounds might undergo analogous *ansa*-bis(indenyl)/NMe₂ exchange reactions with M(NMe₂)₄ compounds, which could be exploited in the synthesis of group 4 *ansa*-metallocenes.

Cyclopentadienyl aluminum compounds are accessible by halide displacement reactions of alkali-metal or alkaline-earth-metal cyclopentadienyl reagents and aluminum halides or, less commonly, by alkane elimination reactions of cyclopentadiene and aluminum alkyls.^{12,13} Electron-precise cyclopentadienyl aluminum compounds (e.g. eight-electron CpAlX₂L species) normally exhibit η^1 Cp-Al coordination. In contrast, electron-deficient species (e.g. CpAlX₂) often exhibit multihapto Cp-Al bonding and η^1 , η^2 , η^3 , and η^5 Cp-Al bonding modes have all been observed in the solid state.¹²⁻¹⁴ Aluminum cyclopentadienyl species are normally fluxional in solution and, like other Al compounds, may undergo ligand redistribution and disproportionation reactions.^{15,16} The use of cyclopentadienylaluminum compounds as cyclopentadienyl transfer agents is very limited, one notable example being the synthesis of Cp₂TiCl₂ by the reaction of {(η^1 -C₅H₅)₂Al(μ -OⁱPr)}₂ with TiCl₄.¹⁷

The objectives of the present work were to synthesize aluminum *ansa*-bis(indenyl) compounds and to explore their utility in the synthesis of group 4 *ansa*-metallocenes by transmetalation. This paper describes studies

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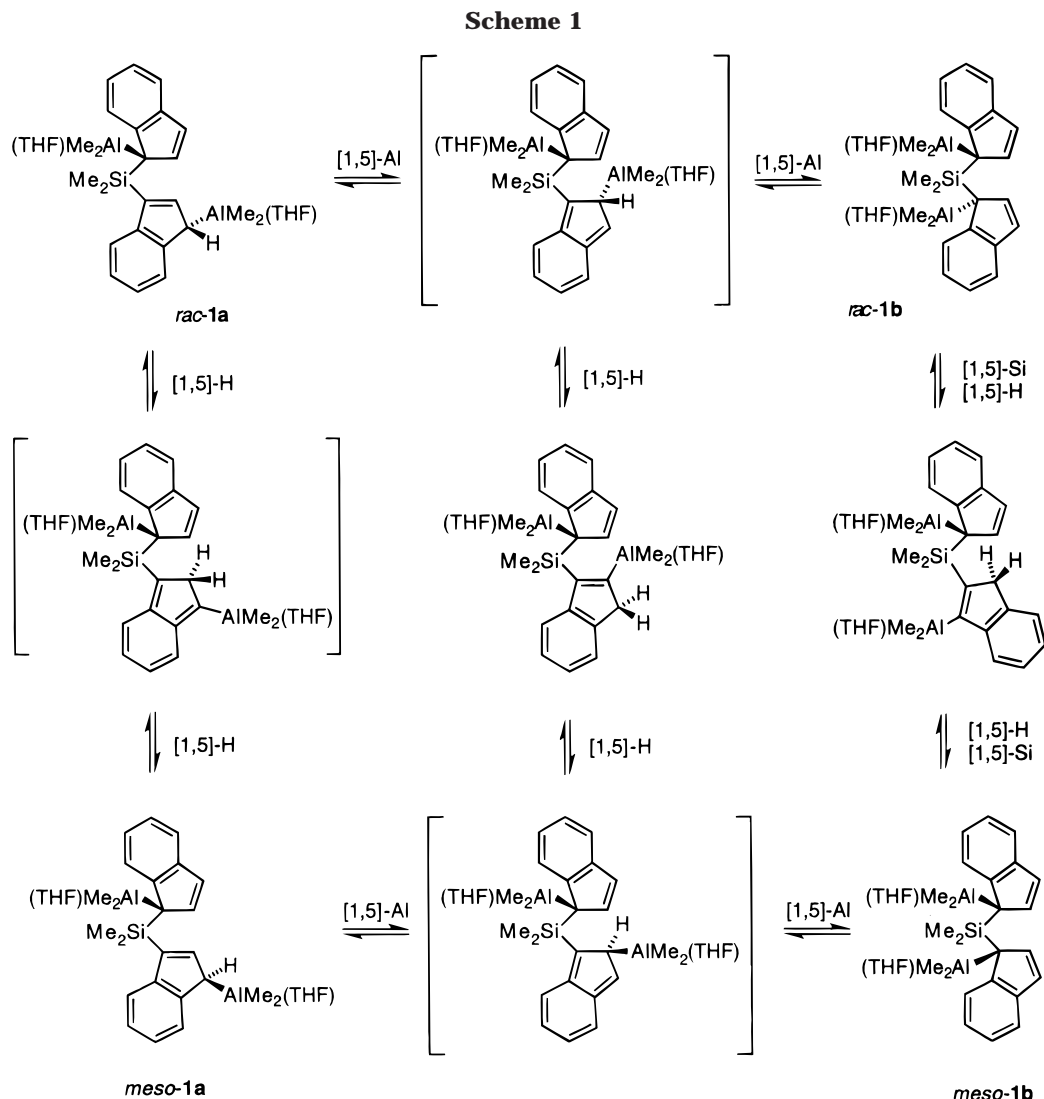
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^a Stereochemistry not established.

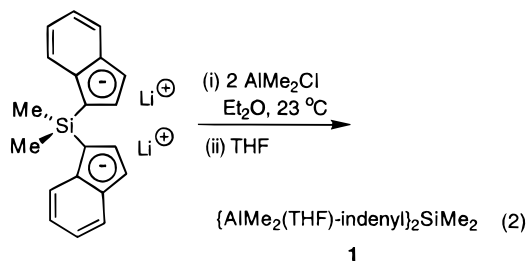
of {(AlMe₂L)-indenyl}₂SiMe₂ compounds that contain indenyl or substituted-indenyl rings and are stabilized by Lewis bases (L). In particular, Al derivatives of (2-Me-4-Ph-1-indenyl)₂SiMe₂ and (2-Me-4,5-benz-1-indenyl)₂SiMe₂ have been investigated as possible reagents for the synthesis of {(2-Me-4-Ph-indenyl)₂SiMe₂}MX₂ and {(2-Me-4,5-benz-1-indenyl)₂SiMe₂}MX₂ metallocenes, which are precursors to high-performance olefin polymerization catalysts.^{2m,o,p} Additionally, 1,2-{(AlMe₂L)-indenyl}₂-ethane compounds have been investigated for comparison to the SiMe₂-bridged compounds. The incorporation of Lewis bases (L = THF, dioxane, Et₂O) facilitates the isolation of these Al indenyl compounds in solid form free of residual chloride and enforces η¹-indenyl-Al bonding, which simplifies the structural chemistry.

Results

Aluminum *ansa*-Bis(indenyl) Compounds. We first discuss the synthesis, structures, and dynamic properties of aluminum *ansa*-bis(indenyl) compounds. The synthetic results are summarized in Table 1, and specific details of each system are described in the following sections.

***rac*- and *meso*-{(AlMe₂(THF)-indenyl)₂SiMe₂ (**1**).** The synthesis and reactivity of {(AlMe₂(THF)-indenyl)₂SiMe₂ (**1**) have been described in a recent communication.¹⁸ The key properties of this system are summarized here to provide a basis for the subsequent discussion of more elaborate SiMe₂-bridged and ethylene-bridged aluminum *ansa*-bis(indenyl) compounds. The reaction of Li₂[(1-indenyl)₂SiMe₂] and 2 equiv of AlMe₂Cl in Et₂O, followed by treatment with THF, yields {(AlMe₂(THF)-

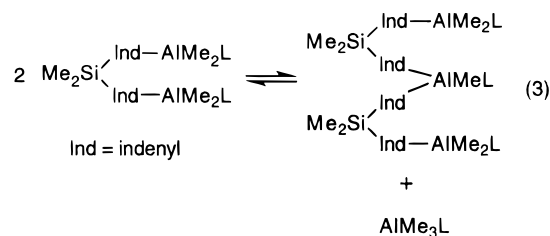
indenyl₂SiMe₂ (**1**) as a ca. 1/1 mixture of *rac* and *meso* isomers (eq 2 and Table 1), which differ in the relative configurations of the Al–indenyl units.



Recrystallization of the *rac*-**1**/*meso*-**1** mixture from toluene at –20 °C affords small quantities of pure *rac*-**1** as colorless cubes. An X-ray crystallographic analysis established that *rac*-**1** crystallizes as a single isomer, i.e., *rac*-{1-AlMe₂(THF)-1-indenyl}{1-AlMe₂(THF)-3-indenyl}SiMe₂ (*rac*-**1a**; Scheme 1). However, low-temperature ¹H NMR studies (≤ –60 °C) show that *rac*-**1** exists as a 2/1 mixture of *rac*-**1a** and *rac*-{1-AlMe₂(THF)-1-indenyl}₂SiMe₂ (*rac*-**1b**, Scheme 1) in toluene-*d*₈. In the –80 °C spectrum, the vinyl H2 and H3 resonances of the 1-Al-1-Si-substituted indenyl rings of *rac*-**1a** and *rac*-**1b** appear as doublets in the range δ 6.5–7.5 (*J* = 4 Hz), and the vinyl H2 and allylic H3 resonances of the 1-Al-3-Si-substituted indenyl ring of *rac*-**1a** appear as singlets at δ 6.49 and 4.10, respectively. Interconversion of these positional isomers is slow on the NMR time scale at –60 °C but rapid at 23 °C in toluene-*d*₈. The *rac*-**1a**/*rac*-**1b** exchange likely occurs by sequential suprafacial [1,5]-Al shifts via isoindene intermediates, as illustrated in the horizontal processes in Scheme 1. THF dissociation, which is not shown in Scheme 1, accompanies and may be required for this process.¹⁵ The *rac*-**1a**/*rac*-**1b** exchange could also occur by a combination of [1,5]-Si and [1,5]-H shifts (not shown), but these processes are expected to be much slower than the observed isomerization. For comparison, [1,5]-Si shifts are slow on the NMR time scale and [1,5]-H shifts are slow on the laboratory time scale below ca. 150 °C for 1-SiMe₃-indene and related compounds.¹⁹

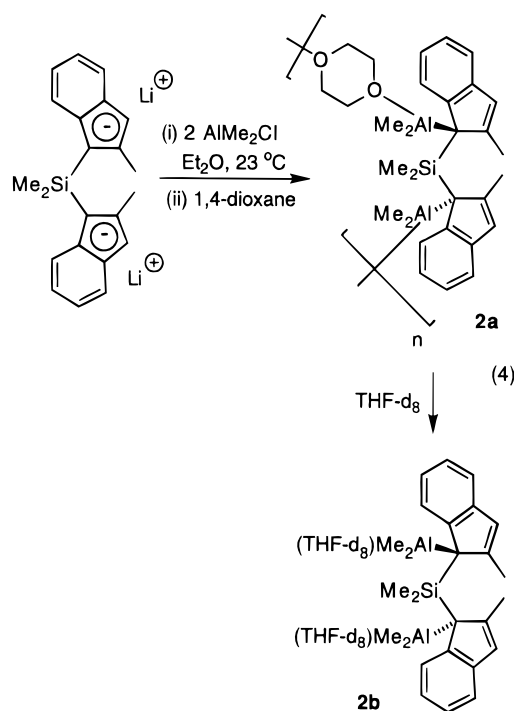
rac-**1** isomerizes slowly (3 days) at 23 °C and rapidly (minutes) at 70 °C to a 1/1 *rac*-**1**/*meso*-**1** mixture in benzene-*d*₆. The interconversion of *rac*-**1** and *meso*-**1** requires inversion of configuration of one of the sp³ carbon centers of the indenyl rings. This process may occur by combinations of [1,5]-Al or [1,5]-Si shifts and [1,5]-H shifts, as illustrated in the vertical processes in Scheme 1. However, it should be noted that the *rac*/*meso* isomerization of **1** is accompanied by significant decom-

position; e.g., ¹H NMR monitoring of benzene-*d*₆ solutions of *rac*-**1**/*meso*-**1** reveals that **1** is ca. 28% converted to new Al–Me species after 2 days at 23 °C. A similar but faster reaction is observed for **1** in THF-*d*₈ (36% conversion, 12 h, 23 °C); in this case one of the major products is AlMe₃(THF) (δ –0.99). These results suggest that **1** undergoes partial disproportionation by ligand redistribution in solution.²⁰ Therefore, the *rac*-**1**/*meso*-**1** isomerization may be more complicated than implied by Scheme 1 and may involve intermolecular exchange of –AlMe₂L units between indenyl rings, as illustrated schematically in eq 3. It was not possible to identify the



positional isomer(s) of *meso*-**1** but is reasonable to presume that, as for *rac*-**1**, both 1-Al-1-Si- and 1-Al-3-Si-substituted isomers are possible.

[*rac*-{1-AlMe₂(1,4-dioxane)_{0.5}-2-Me-1-indenyl}₂-SiMe₂]_n (*rac*-**2a**). The reaction of Li₂[(2-Me-1-indenyl)₂-SiMe₂] with 2 equiv of AlMe₂Cl in Et₂O at 23 °C, followed by removal of the volatiles, extraction of the product into hexanes to remove LiCl, and treatment with 1,4-dioxane at 23 °C, affords the polymeric 1,4-dioxane adduct [*rac*-{1-AlMe₂(1,4-dioxane)_{0.5}-2-Me-1-indenyl}₂SiMe₂]_n (**2a**, 41% isolated) as a colorless solid (eq 4). Compound **2a** is insoluble in benzene, toluene,



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and methylene chloride and dissolves in THF and dioxane with decomposition. However, low-temperature NMR spectra of freshly dissolved **2a** in THF-*d*₈ establish that **2a** undergoes ligand substitution by the solvent to yield free 1,4-dioxane and *rac*-{1-AlMe₂(THF-*d*₈)-2-Me-

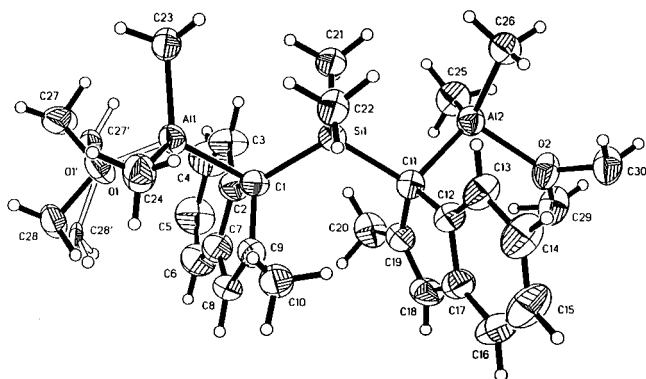


Figure 1. Molecular structure of the monomeric unit of $[rac\{-1-AlMe_2(1,4-dioxane)_{0.5}-2-Me-1-indenyl\}_2SiMe_2]_n$ (*rac-2a*).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[rac\{-1-AlMe_2(1,4-dioxane)_{0.5}-2-Me-1-indenyl\}_2SiMe_2]_n$ (*rac-2a*)

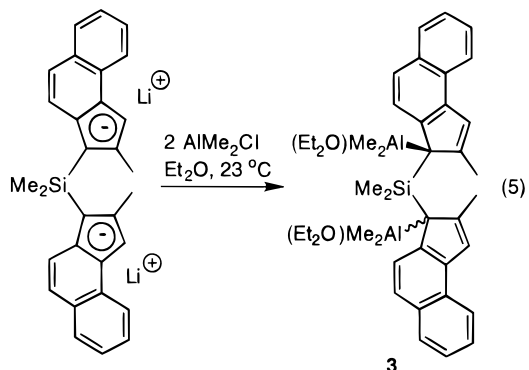
Si(1)–C(1)	1.889(3)	Al(1)–C(23)	1.963(4)
Si(1)–C(11)	1.929(3)	Al(1)–C(24)	1.960(4)
Si(1)–C(21)	1.880(4)	Al(2)–C(25)	1.980(4)
Si(1)–C(22)	1.868(3)	Al(2)–C(26)	1.970(4)
Al(1)–O(1)	1.973(3)	Al(2)–O(2)	1.939(3)
Al(2)–C(11)	2.047(4)		
C(1)–Si(1)–C(11)	113.8(1)	C(23)–Al(1)–C(24)	116.3(2)
C(21)–Si(1)–C(22)	104.8(2)	C(25)–Al(2)–C(26)	113.8(2)
C(23)–Al(1)–C(1)	116.1(2)	C(25)–Al(2)–C(11)	119.9(2)
C(23)–Al(1)–C(24)	116.3(2)	C(25)–Al(2)–C(26)	113.8(2)
C(23)–Al(1)–C(1)	116.1(2)	C(25)–Al(2)–C(11)	119.9(2)
C(24)–Al(1)–C(1)	115.8(2)	C(26)–Al(2)–C(11)	115.8(2)
O(1)–Al(1)–C(23)	99.6(1)	O(2)–Al(2)–C(25)	99.3(1)
O(1)–Al(1)–C(24)	100.0(2)	O(2)–Al(2)–C(26)	102.3(1)
O(1)–Al(1)–C(1)	105.3(1)	O(2)–Al(2)–C(11)	101.0(1)
Si(1)–C(11)–Al(2)	105.8(2)	Si(1)–C(1)–Al(1)	110.1(2)

1-indenyl) $_2$ SiMe $_2$ (**2b**), along with a small amount (ca. 10% at -90 °C) of other species. The 1H NMR spectrum of *rac-2b* (generated in situ) in THF- d_6 at -90 °C contains two singlets (δ -0.72 , -0.95 ; 6H each) for the diastereotopic Al–Me groups, a singlet (δ 0.93, 6H) for the two equivalent Si–Me groups, a singlet (δ 1.08, 6H) for the two equivalent 2-Me groups, and a singlet at δ 6.09 ppm (2H) for the vinylic hydrogens (H3). As **2b** is derived from **2a** by ligand substitution at Al, it is likely that isolated **2a** is structurally analogous to **2b**. Attempts to isolate other $\{1-AlMe_2(L)-2-Me-1-indenyl\}_2-SiMe_2$ compounds (L = THF, Et $_2$ O) yielded oily products which could not be purified or characterized. **2b** decomposes (ca. 24 h at 23 °C) in THF- d_6 , and consequently possible isomerization processes could not be investigated.

Crystallization of isolated **2a** from 3/1 toluene/dioxane at 23 °C by slow evaporation yields *rac-2a* as colorless blocks. The solid-state structure of *rac-2a* was established by X-ray crystallography (Figures 1 and 2; Table 2). *rac-2a* adopts a polymeric structure in which the $-AlMe_2$ (dioxane) groups are bonded to the indenyl groups in an η^1 -fashion at the 1-position, and the 1,4-dioxane ligands bridge the monomer units. The aluminum atoms exhibit distorted-tetrahedral geometry. The O–Al–C angles (average 101.3°) are ca. 15° smaller than the C–Al–C angles (average 116.3°), as expected

on the basis of electronegativity values.²¹ The Al–CH $_3$ distances range from 1.960(4) to 1.980(4) Å and are similar to the Al–CH $_3$ distances in *rac-1a* (1.945(4)–1.986(4) Å) and Al $_2$ Me $_6$ (average Al–C(terminal) 1.97 Å).²² The Al–C(indenyl) bond distances in **2a** (2.055(3), 2.047(4) Å) are similar to those in *rac-1a* (2.043(4), 2.067(4) Å) and the Al–Cp distances in $(\eta^1-Cp)_3Al(NC^t-Bu)$ (2.067(6) Å) and $\{(\eta^1-Cp)_2AlO^iPr\}_2$ (2.003(2) Å).^{12,17a}

rac- and meso- $\{1-AlMe_2(Et_2O)-2-Me-4,5-benz-1-indenyl\}_2SiMe_2$ (3**).** The reaction of $Li_2[(2-Me-4,5-benz-1-indenyl)_2SiMe_2] \cdot Et_2O$ with 2 equiv of AlMe $_2$ Cl in Et $_2$ O, followed by removal of volatiles, extraction of the residue with toluene, solvent removal, and hexane washing, yields $\{1-AlMe_2(Et_2O)-2-Me-4,5-benz-1-indenyl\}_2SiMe_2$ (**3**) as a colorless solid (70% isolated, eq 5). The 1H NMR



spectrum of isolated **3** in benzene- d_6 (23 °C) establishes that this material is a 2/1 mixture of *rac* and *meso* isomers. The spectrum of *rac-3* contains one SiMe $_2$ resonance and one broad AlMe $_2$ resonance, whereas that of *meso-3* contains two SiMe $_2$ resonances of equal intensity and one broad AlMe $_2$ resonance. The vinylic hydrogen (H3) resonances for *rac* and *meso-3* appear at δ 6.46 and 6.15, respectively.

Recrystallization of the *rac-3*/*meso-3* mixture from toluene/hexanes (3:2) at 23 °C by slow evaporation yields pure *rac-3* as colorless blocks. An X-ray crystallographic analysis of *rac-3* (Figure 3, Table 3) confirms that the $-AlMe_2(Et_2O)$ units bind to the indenyl groups in an η^1 fashion at the 1-position. The Al atoms exhibit distorted-tetrahedral geometry and the Al–CH $_3$ distances (1.991(8), 1.988(3) Å) and Al–C $_{indenyl}$ distance (2.039(3) Å) are in the expected range.

The low-temperature (-20 °C) 1H NMR spectrum of *rac-3* in toluene- d_8 is consistent with the solid-state structure. There is no indication of the presence of other isomers. This spectrum contains one Si–Me resonance, two Al–Me resonances of equal intensity, one 2-Me resonance, and a singlet at δ 6.46 (2H) for the H3 vinylic hydrogens. The observation of two Al–Me resonances indicates that Et $_2$ O exchange is slow on the NMR time scale under those conditions; however, this exchange is rapid at 23 °C. *rac-3* isomerizes rapidly (<5 min) to a 1.2/1 equilibrium mixture of *rac-3*/*meso-3* at 80 °C in

(20) (a) Similar disproportionation processes have been reported for other cyclopentadienylaluminum compounds; e.g., CpAlMe $_2$ (THF) undergoes ca. 25% conversion to AlMe $_3$ (THF) and Cp $_2$ AlMe(THF) in benzene- d_6 at 23 °C.¹⁶ (b) However, other than AlMe $_3$ (THF), the disproportionation products of **1** have not yet been identified.

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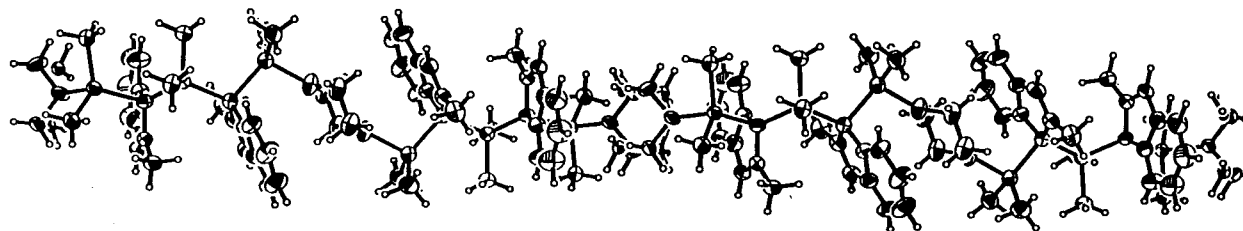


Figure 2. Polymeric structure of *rac-2a*.

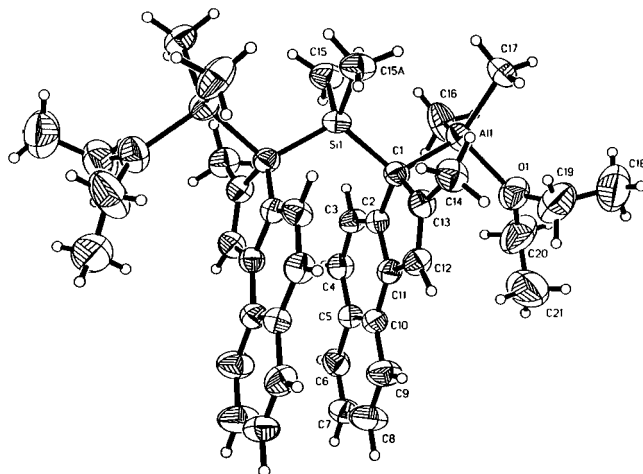


Figure 3. Molecular structure of *rac*-{1- $\text{AlMe}_2(\text{Et}_2\text{O})$ -2-Me-4,5-benz-1-indenyl} $_2\text{SiMe}_2$ (*rac-3*).

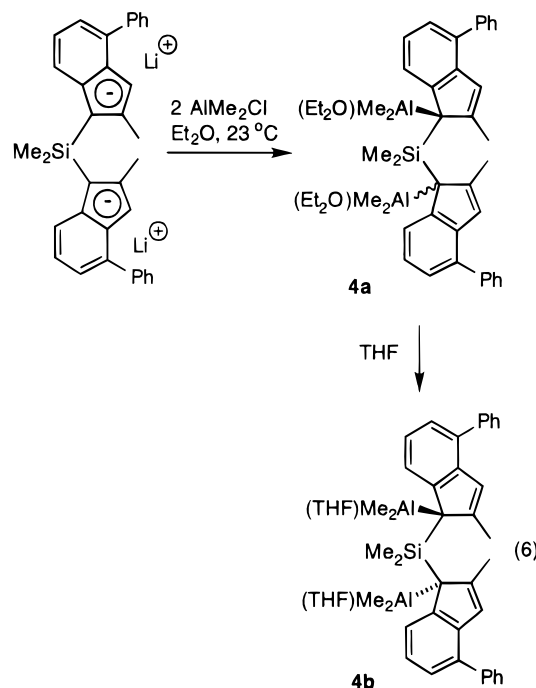
Table 3. Selected Bond Lengths (Å) and Angles (deg) for *rac*-{1- $\text{AlMe}_2(\text{Et}_2\text{O})$ -2-Me-4,5-benz-1-indenyl} $_2\text{SiMe}_2$ (*rac-3*)

Si(1)–C(1)	1.899(3)	Si(1)–C(15)	1.879(3)
Al(1)–C(17)	1.988(3)	Al(1)–C(16)	1.991(4)
Al(1)–O(1)	1.922(3)	Al(1)–C(1)	2.039(3)
C1–Si(1)–C1A	111.0(2)	C(15)–Si(1)–C(15A)	102.8(2)
Si(1)–C(1)–Al(1)	111.7(2)	C(16)–Al(1)–C(17)	110.9(2)
O(1)–Al(1)–C(17)	103.6(2)	O(1)–Al(1)–C(16)	103.7(2)
C(16)–Al(1)–C(1)	116.4(2)	C(17)–Al(1)–C(1)	117.2(2)
O(1)–Al(1)–C(1)	102.8(1)		

benzene- d_6 ; however, this isomerization also occurs slowly at 23 °C (2.5/1 *rac-3*/*meso-3* mixture produced after 27 h). In contrast to the case of **1**, the *rac-3*/*meso-3* isomerization is not accompanied by significant disproportionation.

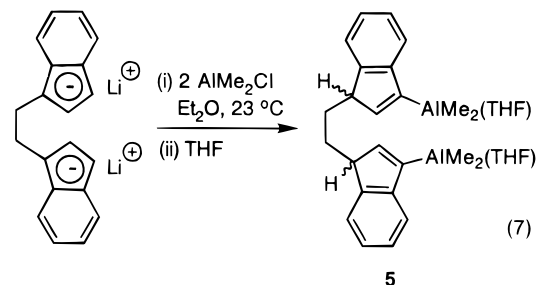
***rac*- and *meso*-{1- $\text{AlMe}_2(\text{Et}_2\text{O})$ -2-Me-4-Ph-1-indenyl} $_2\text{SiMe}_2$ (**4a**) and *rac*-{1- $\text{AlMe}_2(\text{THF})$ -2-Me-4-Ph-1-indenyl} $_2\text{SiMe}_2$ (**4b**).** The reaction of $\text{Li}_2[2\text{-Me-4-Ph-1-indenyl}]_2\text{SiMe}_2 \cdot \text{Et}_2\text{O}$ with 2 equiv of AlMe_2Cl in Et_2O , followed by removal of volatiles, extraction of the residue with toluene, solvent removal, and hexane washing yields {1- $\text{AlMe}_2(\text{Et}_2\text{O})$ -2-Me-4-Ph-1-indenyl} $_2\text{SiMe}_2$ (**4a**) as a colorless solid. Compound **4a** is isolated in very low yield (6%, 2/3 mixture of *rac* and *meso* isomers) by this method due to its high solubility in hexanes. However, addition of THF to the hexane wash obtained from the separation of **4a** results in the precipitation of *rac*-{1- $\text{AlMe}_2(\text{THF})$ -2-Me-4-Ph-1-indenyl} $_2\text{SiMe}_2$ (**4b**) as a colorless solid (62% isolated, eq 6).

The low-temperature (–30 °C) ^1H NMR spectrum of *rac-4b* in toluene- d_8 contains two singlets of equal intensity (δ –0.44, –0.17; 6H each) for the diastereotopic Al–Me groups, one singlet (δ 1.38, 6H) for the two equivalent Si–Me groups, and a singlet (δ 6.58, 2H)



for the H3 vinylic hydrogens. The observation of two sharp Al–Me resonances indicates that THF exchange is slow on the NMR time scale under these conditions; however, the Al–Me resonances are significantly broadened at 23 °C due to THF exchange. There is no indication of the presence of other isomers even at –90 °C. *rac-4b* slowly isomerizes to a *rac*/*meso* mixture (3.5/1 *rac*/*meso*, 17 h, 23 °C; 1.7/1 *rac*/*meso*, 8 h, 75 °C). As for **3**, no significant disproportionation of *rac-4b* is observed during the isomerization under these conditions.

1,2-{3- $\text{AlMe}_2(\text{THF})$ -1-indenyl} $_2\text{-C}_2\text{H}_4$ (5**).** The reaction of $\text{Li}_2[1,2\text{-}(1\text{-indenyl})_2\text{-ethane}]$ with 2 equiv of AlMe_2Cl at 23 °C in Et_2O , followed by treatment with THF, affords 1,2-{3- $\text{AlMe}_2(\text{THF})$ -1-indenyl} $_2\text{-C}_2\text{H}_4$ (**5**) as a colorless to pale yellow solid (54% isolated, eq 7). The



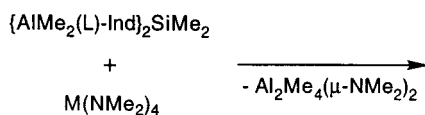
low-temperature (–90 °C) ^1H NMR spectrum of **5** in toluene- d_8 establishes that only one isomer is present; key resonances include a broad AlMe_2 resonance (δ –0.21, 6H), singlets for the H1 (δ 4.14, 2H) and H2 (δ

7.08, 2H) hydrogens of the indenyl C₅ ring, and resonances for the α - (δ 2.57, 1.92; each 4 H) and β -hydrogens (δ 0.44, 8H) of the coordinated THF. This isomer is assigned as 1,2-{3-AlMe₂(THF)-1-indenyl}₂-C₂H₄ on the basis of the chemical shifts of and lack of coupling between the H1 and H2 resonances and the observation of a 2D-COSY correlation between H1 and the ethylene bridge hydrogens; however, the *rac/meso* stereochemistry could not be established. The 1,2-{1-AlMe₂(THF)-3-indenyl}₂-C₂H₄ and 1,2-{1-AlMe₂(THF)-1-indenyl}₂-C₂H₄ isomers were not detected. The ¹H NMR spectrum of **5** in C₆D₆ at 23 °C (freshly dissolved, vide infra) is similar to the low-temperature spectrum, except that the AlMe₂ resonance is sharper and the α -THF resonances are collapsed to a broad singlet (δ 2.78). These observations indicate that THF exchange is rapid on the NMR time scale at ambient temperature. Compound **5** undergoes ca. 50% isomerization/disproportionation after 2 days at 23 °C in benzene-*d*₆.

Synthesis of *ansa*-Metalloenes. The aluminum *ansa*-indenyl compounds **1–5** react with Zr(NMe₂)₄ and Hf(NMe₂)₄ to yield the corresponding group 4 *ansa*-metallocene bis-amide complexes and Al₂Me₄(μ -NMe₂)₂ as illustrated in eqs 8 and 9. The NMR yields and stereoselectivities of these reactions are summarized in eqs 8 and 9, and specific details of each case are discussed in the following sections. In general, an excess of **1–5** is required in these reactions because the disproportionation/decomposition reactions of the Al compounds discussed above are competitive with metallocene formation.

Reaction of M(NMe₂)₄ (M = Zr, Hf) with **1.** The reaction of Zr(NMe₂)₄ with 1.3 equiv of **1** (*rac/meso* = 1/1) in benzene-*d*₆ (50 h, 23 °C) affords {(1-indenyl)₂SiMe₂}Zr(NMe₂)₂ (**6**, *rac/meso* = 4/1) in 90% NMR yield (vs Zr(NMe₂)₄), along with Al₂Me₄(μ -NMe₂)₂ (eq 8). Complete removal of residual chloride (LiCl or AlCl species) from **1** is important for selective indenyl transfer. The reaction of Zr(NMe₂)₄ with samples of **1** containing residual chloride gave **6** in lower yield with variable *rac/meso* ratios, along with significant amounts of *rac*-{(1-indenyl)₂SiMe₂}Zr(NMe₂)Cl and *rac*- and *meso*-{(1-indenyl)₂SiMe₂}ZrCl₂. Similarly, the reaction of Hf(NMe₂)₄ with 1.3 equiv of **1** (*rac/meso* = 1.3/1) in benzene-*d*₆ (70 °C, 21 h) affords {(1-indenyl)₂SiMe₂}Hf(NMe₂)₂ (**7**, *rac/meso* = 10/1) in 70% NMR yield (vs Hf(NMe₂)₄) and Al₂Me₄(μ -NMe₂)₂. *rac*-**7** was isolated as pale orange needles in 61% yield by crystallization from toluene/hexanes. Monitoring the reaction of Hf(NMe₂)₄ and **1** at 23 °C in benzene-*d*₆ by ¹H NMR revealed that after 20 min the starting materials are completely consumed and intermediate species with NMe₂ resonances in the range δ 2.7–2.9 (presumably mixed Hf/Al indenyl compounds) are formed. After 24 h at 23 °C, *rac*-**7** is formed in 10% yield; after 24 h at 75 °C the intermediates are converted to products.

Reaction of Zr(NMe₂)₄ with **2a.** The reaction of Zr(NMe₂)₄ with 1.3 equiv of **2a** (*rac*) in benzene-*d*₆ or toluene (75 °C, 24 h) affords {(2-Me-1-indenyl)₂SiMe₂}Zr(NMe₂)₂ (**8**; 90% vs Zr(NMe₂)₄, *rac/meso* = 3/4, eq 8). Polymeric **2a** is insoluble in benzene-*d*₆ but dissolves after a few minutes at 75 °C due to the reaction with Zr(NMe₂)₄. Compound **8** was isolated by crystallization from toluene at –20 °C as mixture of red (*rac*) and



Al reagent

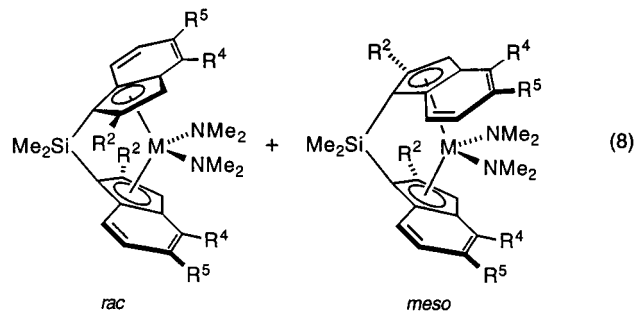
1

1

2a

3

4a



Metallocene	NMR yield (%)	<i>rac/meso</i>
6 M = Zr, R ² = R ⁴ = R ⁵ = H	90	4/1
7 M = Hf, R ² = R ⁴ = R ⁵ = H	70	10/1
8 M = Zr, R ² = Me, R ⁴ = R ⁵ = H	90	3/4
9 M = Zr, R ² = Me, R ⁴ & R ⁵ = benzo	75	9/10
10 M = Zr, R ² = Me, R ⁴ = Ph, R ⁵ = H	75	3/4

yellow (*meso*) crystals in 61% total yield. The crystals were manually separated and characterized by ¹H and ¹³C NMR and an X-ray crystal structure determination, which confirmed the stereochemistry.²³

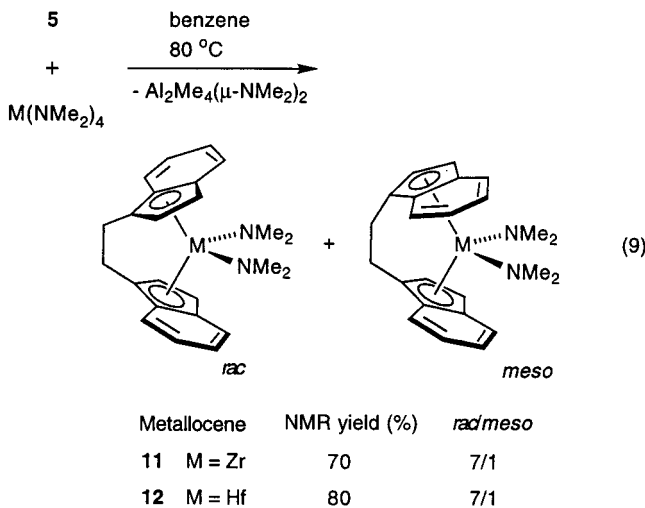
Reaction of Zr(NMe₂)₄ with **3.** The reaction of Zr(NMe₂)₄ with 1.3 equiv of **3** (*rac/meso* = 2.5/1) in benzene-*d*₆ (70 °C, 24 h) affords {(2-Me-4,5-benz-1-indenyl)₂SiMe₂}Zr(NMe₂)₂ (**9**; 75% vs Zr(NMe₂)₄, *rac/meso* = 9/10, eq 8). Crystallization of the crude product from toluene affords **9** (57%) as a 3/5 mixture of pale orange (*rac*) and red (*meso*) crystals. The ¹H NMR spectrum of *C*₂-symmetric *rac*-**9** contains one SiMe₂, one NMe₂, and one 2-Me resonance, while the spectrum of *C*_s-symmetric *meso*-**9** contains two SiMe₂ and two NMe₂ resonances and one 2-Me resonance. One of the NMe₂ resonances for *meso*-**9** is broad and appears at high field (δ 0.93 at 23 °C). This feature is attributed to anisotropic shielding and restricted rotation around the Zr–N bond of the amide group that lies between the two benz-indenyl groups on the crowded side of the *meso* structure. The high-field amide resonance splits into two singlets of equal intensity at –53 °C (δ 1.72, 0.14; 3H each) and collapses to a sharp singlet at 70 °C (δ 0.89).

Reaction of Zr(NMe₂)₄ with **4a and **4b**.** The reaction of Zr(NMe₂)₄ with 1.2 equiv of the Et₂O adduct **4a** (2/3 *rac/meso*) in benzene-*d*₆ (70 °C, 17 h) yields {(2-Me-4-Ph-1-indenyl)₂SiMe₂}Zr(NMe₂)₂ (**10**; 75% vs Zr-

(23) Structural studies of *rac*-**8** and *meso*-**8** will be published separately.

(NMe₂)₄, *rac/meso* = 3/4, eq 8). In contrast, the reaction of Zr(NMe₂)₄ with an excess of the THF adduct **rac-4b** under similar conditions affords only a low yield (5%) of **10** even after prolonged heating (>5 days, 75 °C).

Reaction of M(NMe₂)₄ (M = Zr, Hf) with 5. The reaction of Zr(NMe₂)₄ with 1.2 equiv of **5a** in benzene-*d*₆ (80 °C, 19 h) affords {1,2-(indenyl)₂-C₂H₄}Zr(NMe₂)₂ (**11**; *rac/meso* = 7/1) in 70% yield (vs Zr(NMe₂)₄) and Al₂Me₄(μ-NMe₂)₂ (eq 9). Similarly, the reaction of Hf-



(NMe₂)₄ with 1.3 equiv of **5** in benzene-*d*₆ (80 °C, 27 h) yields {1,2-(indenyl)₂-C₂H₄}Hf(NMe₂)₂ (**12**; 80% vs Hf(NMe₂)₄, *rac/meso* = 7/1).

Reaction of Al *ansa*-Bis(indenyl) Reagents with Zirconium Chlorides. The reactions of several *rac*-Al-*ansa*-bis(indenyl) reagents with simple Zr chlorides were investigated briefly to determine whether stereoselective indenyl/chloride exchange occurs. The reaction **1** enriched in the *rac* isomer (*rac/meso* = 4/1) with ZrCl₄ in benzene-*d*₆ proceeds readily (30 min) at 23 °C to yield a 1/1 *rac/meso* mixture of {(1-indenyl)₂SiMe₂}ZrCl₂ (74% NMR).²⁴ Similarly, **rac-4b** reacts with ZrCl₄ in CD₂Cl₂ rapidly (<1 h) at 23 °C to yield a 1/1 *rac/meso* mixture of {(2-Me-4-Ph-1-indenyl)SiMe₂}ZrCl₂ (84% isolated). Additionally, **rac-3** reacts with ZrCl₄(SMe₂)₂ in benzene (23 °C, 1 h) to yield a 1.2/1 *rac/meso* mixture of {(2-Me-4,5-benz-1-indenyl)₂SiMe₂}ZrCl₂ (73% isolated). In all three cases, little *rac/meso* isomerization of the *rac*-Al-indenyl reagent is expected under the reaction conditions in the absence of the Zr chloride compound, on the basis of the control experiments discussed above. Therefore, while Al-indenyl reagents react readily with simple Zr chlorides under mild conditions, these reactions are not stereoselective.

Discussion

Aluminum *ansa*-bis(indenyl) compounds, {(AlMe₂L)-indenyl}₂SiMe₂ and 1,2-{(AlMe₂L)-indenyl}₂-C₂H₄, which contain unsubstituted or substituted indenyl rings, are accessible by salt elimination reactions of the appropriate Li *ansa*-bis(indenyl) reagents and AlMe₂Cl. A key feature of this synthesis is the use of Lewis bases (L = THF, 1,4-dioxane, Et₂O) to stabilize the Al-indenyl

species and modify the solubility properties to facilitate isolation in solid form.²⁵ As summarized in Table 1, **2a** and **4b** are isolated as pure *rac* isomers, while **1** and **3** are isolated as *rac/meso* mixtures; in the latter cases the *rac* isomers may be obtained by selective crystallization. The factors which control the *rac/meso* product ratios in these reactions are not known.

Detailed structural assignments for the *rac* isomers of **1**, **2a,b**, **3**, and **4b** are available from NMR and X-ray crystallographic studies. η¹-Indenyl-Al bonding is observed in all cases, as expected for 4-coordinate Al-indenyl species. For the unsubstituted *ansa*-bis(indenyl) compound **rac-1**, a 2/1 mixture of regioisomers is observed in solution: the major isomer **rac-1a** contains *one* 1-Al-3-Si-substituted and *one* 1-Al-1-Si-substituted indenyl ring, while the minor isomer **rac-1b** contains *two* 1-Al-1-Si-substituted indenyl rings (Scheme 1). The **rac-1a/rac-1b** isomer ratio likely reflects a balance of electronic and steric effects. The 1-Al-1-Si-substituted indenyl structure allows electronic stabilization of the Al-indenyl bond by the adjacent Si center²⁶ but is destabilized by steric interactions between the Al and Si substituents. In contrast, the *rac* isomers of the 2-Me-indenyl compounds **2a,b**, **3**, and **4b** all contain *two* 1-Al-1-Si-substituted indenyl rings. In these cases the 1-Al-3-Si-substituted indenyl unit would be destabilized by steric interactions between the neighboring (and coplanar) 2-Me and 3-SiMe₂(indenyl) groups.

rac-1a and **rac-1b** interconvert rapidly on the NMR time scale at 23 °C. The most reasonable mechanism for this exchange involves [1,5]-Al shifts, as illustrated in Scheme 1. Similar [1,5]-Al shifts in the 2-Me-indenyl compounds **2a,b**, **3**, and **4b**, would be undetectable in the present experiments because the concentration of 1-Al-3-Si-substituted isomers is below the NMR detection limit.

Compounds **1**, **3**, and **4b** undergo *rac/meso* isomerization at 23 °C (days) and ca. 75 °C (minutes to hours). For **1**, this isomerization may occur by combinations of [1,5]-Al or [1,5]-Si shifts and [1,5]-H shifts as illustrated in Scheme 1. However, **3** and **4** cannot undergo *rac/meso* isomerization by this mechanism, due to the presence of the 2-Me-indenyl substituent, which precludes the formation of indenyl or isoindenyl intermediates with local C_s symmetry at a given indenyl ring. In these cases, and probably in **1** as well, *rac/meso* isomerization likely results from intermolecular exchange of -AlMe₂L units between indenyl rings, as illustrated in eq 3. Intermolecular exchange also probably leads to the decomposition/disproportionation observed for the two least-crowded compounds **1** and **5**.

The aluminum *ansa*-indenyl complexes react with M(NMe₂)₄ (M = Zr, Hf) under mild conditions (23–80 °C in aromatic solvents) to yield the corresponding *ansa*-metallocene bis(amide) compounds in 70–90% NMR yield along with Al₂Me₄(μ-NMe₂)₂ as the main Al

(25) Attempts to prepare {(AlMe₂-indenyl)₂SiMe₂ or {(AlMe₂L)-indenyl}₂SiMe₂ compounds by alkane elimination reactions were unsuccessful; e.g., no reaction was observed between AlMe₃ and (1-indenyl)₂SiMe₂ at 80 °C (neat, 12 h). Attempts to prepare AlR-{(indenyl)₂SiMe₂} and AlR(L){(indenyl)₂SiMe₂} compounds by salt elimination reactions were also unsuccessful.

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(24) The principal coproducts are tentatively identified as *rac* and *meso* zirconocene methyl chloride compounds.

product. These reaction conditions are much milder than those required to synthesize these metallocenes by amine elimination. For example, the synthesis of **6** from (1-indenyl)₂SiMe₂ and Zr(NMe₂)₄ requires efficient removal of NMe₂H, and the synthesis of **7**, **11**, and **12** from the appropriate *ansa*-bis(indenes) and M(NMe₂)₄ compounds requires elevated temperatures.^{3–5} The 2-Me-substituted *ansa*-metallocenes **8–10** are not accessible by amine elimination reactions.²⁷ The high stability of Al₂Me₄(μ -NMe₂)₂ and the strong three-center–four-electron μ -NMe₂ bridges in this species probably contribute to the driving force for the facile indenyl/amide exchange reactions observed here.

The *rac*/*meso* ratios for the metallocene products in eqs **8** and **9** appear to be close to the thermodynamic *rac*/*meso* ratios. The *rac*/*meso* ratio of 4/1 observed for metallocene **6** is identical with the thermodynamic *rac*/*meso* ratio established for **6** in amine elimination studies.^{3b} The *rac*/*meso* ratio of 7/1 for **11** is somewhat lower than the thermodynamic ratio (ca. >20/1) determined by studies of amine elimination reactions.^{3a} The 2-Me-substituted metallocenes **8** and **9** are produced with essentially no diastereoselectivity, even though the starting Al *ansa*-bis(indenyl) reagents **2a** (pure *rac*) and **3** (*rac*/*meso* = 2.5/1) are enriched in the *rac* isomers. The thermodynamic *rac*/*meso* ratios for **8** and **9** have not been established but probably are close to 1/1. At present, the factors that govern the stereoselectivity of these indenyl/amide exchange reactions are unknown. This issue is complicated by the fact that the Al indenyl reagents undergo regioisomerization (e.g. *rac*-**1a**/*rac*-**1b** exchange), *rac*/*meso* isomerization, and (for **1** and **5**) disproportionation/decomposition processes under the reaction conditions.

The results described here show that aluminum *ansa*-bis(indenyl) compounds react readily with M(NMe₂)₄ (M = Zr, Hf) and ZrCl₄ compounds to afford *ansa*-metallocenes in high yield. However, the practical utility of this approach to metallocene synthesis is limited by the necessity of synthesizing the Al indenyl reagents (yields 40–70%), by the requirement of using excess Al indenyl reagent to compensate for the disproportionation/decomposition reactions, and in some cases by low *rac*/*meso* ratios in the product metallocene. Conventional salt elimination or amine elimination methods provide more efficient routes to the specific metallocenes studied here.²⁸

Experimental Section

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere. Solids were handled in a Vacuum Atmospheres glovebox filled with purified nitrogen. Tetrahydrofuran, toluene, benzene, dioxane, and ether were distilled under nitrogen from sodium/benzophenone ketyl, and solutions were prepared and manipulated using standard Schlenk techniques. ZrCl₄ and HfCl₄ were purchased from CERAC Inc. and sublimed before use. LiNMe₂ and AlMe₂-Cl were purchased from Aldrich and used without further

purification. (1-indenyl)₂SiMe₂^{3b,29} {1,2-(3-indenyl)₂-C₂H₄}^{2c,1} and (2-Me-1-indenyl)₂SiMe₂^{2p} were prepared by literature methods and converted to the corresponding dilithio salts by reaction with ⁿBuLi (2 equiv, 23 °C, overnight in hexanes, followed by filtration, hexane washing, and vacuum drying). (2-Me-4,5-benz-1-indenyl)₂SiMe₂^{2o} and (2-Me-4-Ph-1-indenyl)₂SiMe₂^{2p} were prepared by literature methods and converted to the corresponding dilithio salts (mono-Et₂O adducts) by reaction with ⁿBuLi (2 equiv, 23 °C, overnight in Et₂O, followed by filtration, hexane washing, and vacuum drying). Zr(NMe₂)₄,^{3a,30} Hf(NMe₂)₄,^{3c,31} and ZrCl₄(SiMe₂)₂³² were prepared by literature procedures. NMR spectra were recorded on a Bruker AMX-360 spectrometer in Teflon-valved tubes at ambient probe temperature (23 °C) unless indicated otherwise. ¹H and ¹³C NMR chemical shifts are reported versus SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent peaks. Coupling constants are reported in Hz. COSY spectra were recorded in C₆D₆ with a 5 s delay, TD(F2) = 2048, TD(F1) = 512, NS = 16, and SW = 9 ppm. Elemental analyses were performed by Desert Analytics Laboratory (Tucson, AZ). Low % C and % Si values (multiple analyses) were obtained for the aluminum *ansa*-indenyl complexes, even for recrystallized samples that were spectroscopically pure. However, % H and % Al values were satisfactory. The origin of the low % C and % Si values is not known.

***rac*- and *meso*-{AlMe₂(THF)-indenyl}₂SiMe₂ (**1**).** A solution of AlMe₂Cl (2.13 g, 23.0 mmol) in hexanes (10 mL) was diluted with Et₂O (50 mL). The colorless solution was slowly added (10 min) to solid Li₂[(1-indenyl)₂SiMe₂] (3.48 g, 11.5 mmol) via cannula. The yellow slurry was stirred overnight at 23 °C. The volatiles were removed under vacuum, affording a yellow-orange residue. The residue was taken up in hexanes (50 mL), and the mixture was filtered to afford a pale yellow filtrate and a white solid (LiCl, 0.95 g; 0.97 g expected). The filtrate volume was reduced to ca. 10 mL under vacuum, THF (10 mL) was added, and the solution was stirred for 5 min. The volatiles were removed under vacuum. The red-orange residue was taken up in hexanes (50 mL) and stirred for 3 h at 23 °C, which resulted in the precipitation of an off-white solid. The mixture was filtered, yielding a cream-colored solid which was dried under vacuum (3.12 g). The filtrate was concentrated to ca. 15 mL, cooled to –78 °C for 30 min, and filtered cold to yield a second crop of white solid (0.28 g), which was combined with the first crop. Total yield: 3.40 g (54%). The ¹H NMR spectrum (C₆D₆) established that this product was a 1.2/1 mixture of *rac*- and *meso*-{AlMe₂(THF)-indenyl}₂-SiMe₂. Anal. Calcd for C₃₂H₄₆Al₂O₂Si: C, 70.55; H, 8.51; Al, 9.90, Si, 5.15. Found: C, 69.65; H, 8.26; Al, 9.76, Si, 4.20. ¹H NMR (C₆D₆): δ 7.87 (d, *J* = 6.3, 4H, indenyl), 7.60 (d, *J* = 6.3, 4H, indenyl), 7.29 (d, 2H, H2 *meso*), 7.15 (overlapped with solvent signal), 7.08 (br, 2H, H2 *rac*), 5.69 (br, 4H, H3 *rac* and *meso*), 2.59 (br, 16H, THF), 0.96 (s, 3H, SiMe₂ *meso*), 0.88 (s, 6H, SiMe₂ *rac*), 0.64 (s, 16H, THF), 0.53 (s, 3H, SiMe₂ *meso*), –0.44 (s, 12H, AlMe₂ *meso*), –0.47 (s, 12H, AlMe₂ *rac*). ¹H NMR (THF-*d*₆, fast solvent exchange): δ 7.52 (m, 4H, indenyl), 7.37 (m, 4H, indenyl), 6.90 (m, 10H, indenyl), 6.78 (br, 2H, H2 *rac*), 5.36 (br, 4H, H3 *rac* and *meso*). 0.59 (s, 3H, SiMe₂ *meso*), 0.51 (s, 6H, SiMe₂ *rac*), 0.22 (s, 3H, SiMe₂ *meso*), –0.91 (s, 12H, AlMe₂ *rac*), –0.94 (s, 12H, AlMe₂ *meso*).

***rac*-**1**.** Recrystallization of a *rac*-**1**/*meso*-**1** mixture from above in toluene at –20 °C afforded pure *rac*-**1** as colorless cubes. ¹H NMR (C₆D₆; rapid exchange of 1,3- and 1,1-isomers): δ 7.89 (d, *J* = 6.3, 2H, H4 or H7), 7.62 (d, *J* = 6.3, 2H, H4 or H7), 7.15 (H5 and H6, partially obscured by solvent

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signal), 7.08 (br, 2H, H₂), 5.71 (br, 2H, H₃), 2.64 (br, 4H, THF), 2.43 (br, 4H, THF), 0.88 (s, 6H, SiMe₂), 0.54 (br, 8H, THF), -0.47 (s, 12H, AlMe₂). ¹H NMR (toluene-*d*₈, 193 K, 2/1 mixture of slowly exchanging isomers): δ 8.11 (br, 2H, H₄ or H₇), 7.91 (d, *J* = 7, 2H, H₄ or H₇), 7.85 (d, *J* = 7, 2H, H₄ or H₇), 7.81 (d, *J* = 7, 2H, H₄ or H₇), 7.75 (d, *J* = 7, 2H, H₄ or H₇), 7.65 (d, *J* = 7, 2H, H₄ or H₇), 7.51 (br d, 2H, vinylic H), 7.34 (br, 12H, H₅ and H₆), 7.0 (br, 2H, vinylic H, obscured by solvent), 6.82 (d, *J* = 4, 2H, vinylic H), 6.61 (d, *J* = 4, 2H, vinylic H), 6.49 (s, 2H, vinylic H), 4.10 (s, 2H, allylic H), 2.67 & 2.54 & 2.12 & 1.88 (br, 24H, THF), 1.20 (s, 6H, SiMe₂), 1.08 (s, 6H, SiMe₂), 1.04 (s, 6H, SiMe₂), 0.75 & 0.58 & 0.38 (br, 24H, THF), -0.08 (s, 12H, AlMe₂), -0.20 (s, 6H, AlMe₂), -0.38 (s, 6H, AlMe₂), -0.54 (s, 12H, AlMe₂).

[*rac*-{1-AlMe₂(dioxane)_{0.5}-2-Me-1-indenyl}₂SiMe₂]_{*n*} (2a**).**

A solution of AlMe₂Cl (1.66 g, 17.9 mmol) in hexanes (7.5 mL) was diluted with Et₂O (30 mL). The colorless solution was slowly added to solid Li₂[(2-Me-1-indenyl)₂SiMe₂] (2.97 g, 9.07 mmol) via cannula. The resulting red-brown slurry was stirred at 23 °C for 1 h. The volatiles were removed under vacuum, affording a red oily residue. The residue was taken up in hexanes (40 mL), and the mixture was filtered to afford a red-brown filtrate and a white solid (LiCl). The volatiles were removed from the filtrate under vacuum, and the red oily residue was dissolved in dioxane (10 mL) and stirred for 10 min. The volatiles were removed from the clear red solution under vacuum, and the red-orange residue was dried overnight under vacuum. The residue was taken up in hexanes (30 mL) and stirred overnight at 23 °C, which resulted in the formation of a solid. Additional hexanes (20 mL) were added, and the mixture was stirred for 1 h and filtered, yielding a yellowish white solid. The solid was washed thoroughly with hexanes (30 mL) and dried under vacuum, yielding a cream-colored solid (2.23 g, 41%). Anal. Calcd for C₃₀H₄₂Al₂O₂Si: C, 69.72; H, 8.20; Al, 10.44; Si, 5.43. Found: C, 66.52; H, 7.79; Al, 10.32; Si, 3.93. A sample of **2a** in THF-*d*₈ (which forms THF-*d*₈ adduct **2b**) was prepared at -196 °C and kept cold prior to NMR analysis at -90 °C. ¹H NMR (THF-*d*₈, -90 °C): δ 7.64 (d, *J* = 7.2, 2H, H₄ or H₇), 7.23 (d, *J* = 7.2, 2H, H₄ or H₇), 6.93 (m, 4H, H₅ and H₆), 6.09 (s, 2H, H₃), 3.53 (m, dioxane, partially obscured by solvent), 1.08 (s, 6H, 2-Me), 0.93 (s, 6H, SiMe₂), -0.67 (s, 6H, AlMe), -0.90 (s, 6H, AlMe). ¹³C{¹H} NMR (THF-*d*₈, -50 °C): δ 151.5 (C), 148.0 (C), 144.0 (C), 123.7 (CH), 121.2 (CH), 119.8 (CH), 119.6 (CH), 119.3 (CH), 67.7 (dioxane, partially obscured by solvent), 17.5 (2-Me), 6.1 (SiMe₂), -6.5 (Al Me), -7.4 (Al Me). The C1 resonance was not observed due to quadrupolar broadening by ²⁷Al.

***rac*- and *meso*-{1-AlMe₂(Et₂O)-2-Me-4,5-benz-1-indenyl}₂SiMe₂ (**3**).** A solution of AlMe₂Cl (1.46 g, 15.8 mmol) in hexanes (4 mL) was diluted with Et₂O (100 mL). The colorless solution was slowly added to yellow solid Li₂[(2-Me-4,5-benz-1-indenyl)₂SiMe₂]·Et₂O (4.00 g, 7.83 mmol) via cannula. The colorless slurry was stirred at 23 °C for 2 h. The volatiles were removed under vacuum, affording a colorless solid which was dried overnight. Toluene (90 mL) was added, and the colorless slurry was stirred for 10 min and filtered to afford a pale yellow filtrate and a colorless solid (LiCl). The LiCl was washed with toluene (40 mL), and the wash was combined with the filtrate. The volatiles were removed from the filtrate under vacuum, affording a colorless solid. Hexanes (75 mL) were added to the solid, and the resulting colorless slurry was stirred for 30 min, cooled to 0 °C for 1 h, and filtered to yield a colorless solid and a yellow filtrate. The solid was dried under vacuum (3.76 g, 70%). The ¹H NMR spectrum in C₆D₆ at 23 °C established that the solid was a 2/1 mixture of *rac*- and *meso*-{1-AlMe₂(Et₂O)-2-Me-4,5-benz-1-indenyl}₂SiMe₂ (**3**). This material was recrystallized from toluene/hexanes (3/2 by volume) at 23 °C by slow evaporation, yielding pure *rac*-**3** as colorless blocks. Data for *rac*-**3**: Anal. Calcd for C₄₂H₅₈Al₂O₂Si: C, 74.66; H, 8.63; Al, 7.96; Si, 4.14. Found: C, 72.21; H, 8.38; Al, 7.96; Si, 3.54. ¹H NMR (C₆D₆): δ 8.15 (d, *J* = 7.2, 2H), 8.11 (d, *J* = 7.2,

2H), 7.91 (d, *J* = 7.2, 2H), 7.54 (d, *J* = 7.2, 2H), 7.40 (t, *J* = 7.2, 2H), 7.34 (t, *J* = 7.2, 2H), 6.46 (s, 2H, H₃ on indenyl C₅ ring), 2.47 (br, 8H, Et₂O), 1.83 (s, 6H, 2-Me), 1.30 (s, 6H, SiMe₂), 0.40 (br, 12H, Et₂O), -0.28 & -0.40 (two br s, 12H, AlMe₂). ¹H NMR (toluene-*d*₈, -20 °C): δ 8.17 (d, *J* = 3.6, 2H), 8.15 (d, *J* = 3.6, 2H), 7.91 (d, *J* = 7.2, 2H), 7.54 (d, *J* = 7.2, 2H), 7.45 (m, 2H), 7.37 (m, 2H), 6.64 (s, 2H, H₃ on indenyl C₅ ring), 2.36 (q, *J* = 7.2, 4H, Et₂O), 2.20 (q, *J* = 7.2, 4H, Et₂O), 1.66 (s, 6H, 2-Me), 1.39 (s, 6H, SiMe₂), -0.08 (t, *J* = 7.2, 12H, Et₂O), -0.24 (s, 6H, AlMe₂), -0.44 (s, 6H, AlMe₂). ¹³C{¹H} NMR (C₆D₆): δ 151.0 (C), 144.1 (C), 139.2 (C), 130.7 (C), 128.6 (2 CH), 128.4 (C), 124.6 (CH), 124.5 (CH), 124.1 (CH), 124.0 (CH), 119.9 (CH), 109.9 (br, indenyl C1), 67.2 (Et₂O), 18.3 (2-Me), 12.8 (Et₂O), 5.1 (SiMe₂), -6.5 (br, AlMe₂). Data for *meso*-**3** (from *rac/meso* mixture) are as follows. ¹H NMR (C₆D₆, 60 °C): δ 7.98 (d, *J* = 7.2, 2H), 7.72 (d, *J* = 7.2, 2H), 7.64 (d, *J* = 7.2, 2H), 7.30 (m, overlapped with *rac* resonance), 6.15 (s, 2H, H₃ on indenyl C₅ ring), 2.56 (q, *J* = 7.2, Et₂O, overlapped with *rac* resonance), 2.49 (s, 6H, 2-Me), 1.08 (s, 3H, SiMe₂), 0.97 (s, 3H, SiMe₂), 0.15 (t, *J* = 7.2, Et₂O, overlapped with *rac* resonance), -0.47 (s, 12H, AlMe). ¹³C{¹H} NMR (C₆D₆, 60 °C): δ 151.8 (C), 144.2 (C), 139.6 (C), 130.7 (C), 128.6 (C), 124.5 (CH), 124.1 (CH), 122.9 (CH), 124.5 (CH), 124.1 (CH), 120.1 (CH), 100.4 (indenyl C1), 67.5 (Et₂O, overlapped with *rac* resonance), 19.5 (2-Me), 12.9 (Et₂O, overlapped with *rac* resonance), 4.4 (SiMe₂), 4.1 (SiMe₂), -7.0 (br, Al-Me). One aromatic resonance is obscured.

***rac*- and *meso*-{1-AlMe₂(Et₂O)-2-Me-4-Ph-1-indenyl}₂SiMe₂ (**4a**) and *rac*-{1-AlMe₂(THF)-2-Me-4-Ph-1-indenyl}₂SiMe₂ (**4b**).** A solution of AlMe₂Cl (0.68 g, 7.3 mmol) in hexanes (4.0 mL) was diluted with Et₂O (60 mL). The colorless solution was slowly added to yellow solid Li₂[(2-Me-4-Ph-1-indenyl)₂SiMe₂]·Et₂O (2.00 g, 3.65 mmol) via cannula. The pale yellow slurry was stirred at 23 °C for 2 h. The volatiles were removed under vacuum, affording a pale brown foamy solid, which was dried overnight. Toluene (40 mL) was added, and the resulting slurry was filtered to afford a pale yellow filtrate and a colorless solid (LiCl). The volatiles were removed from the filtrate under vacuum, affording a pale brown foamy solid. Hexanes (50 mL) were added to the solid, and the resulting slurry was stirred for 30 min, concentrated to 10 mL, and filtered to yield a colorless solid and a yellow filtrate. The solid was dried under vacuum (0.16 g, 6.0%). ¹H NMR analysis (C₆D₆, 23 °C) established that the solid was a 2/3 mixture of *rac*- and *meso*-{1-AlMe₂(Et₂O)-2-Me-4-Ph-1-indenyl}₂SiMe₂ (**4a**). Data for **4a** are as follows. ¹H NMR (C₆D₆, 70 °C): δ 7.85 (d, *J* = 7.2, 2H, indenyl *rac*), 7.72 (d, *J* = 7.2, 2H, indenyl *rac*), 7.66 (d, *J* = 7.2, 2H, indenyl *meso*), 7.42 (m, indenyl *rac* and *meso*), 7.31 (m, indenyl *rac* and *meso*), 7.05 (d, *J* = 7.2, 2H, indenyl *meso*), 6.86 (t, *J* = 7.2, 2H, indenyl *meso*), 6.34 (s, 2H, H₃ of C₅ indenyl ring, *rac*), 6.30 (s, 2H, H₃ of C₅ indenyl ring, *meso*), 2.57 (br, 16H, Et₂O *rac* and *meso*), 2.44 (s, 6H, 2-Me *meso*), 1.76 (s, 6H, 2-Me *rac*), 1.22 (s, 3H, SiMe₂ *meso*), 1.18 (s, 6H, SiMe₂ *rac*), 1.04 (s, 3H, SiMe₂ *meso*), 0.31 (br, 24H, Et₂O *rac* and *meso*), -0.43 (s, 24H, AlMe *rac*), -0.47 (s, 24H, AlMe *meso*). ¹³C{¹H} NMR (C₆D₆): δ 151.1 (C), 150.0 (C), 148.5 (C), 147.7 (C), 143.9 (C), 143.8 (C), 142.1 (C), 141.4 (C), 133.0 (C), 132.2 (C), 129.5 (CH), 129.4 (2 CH), 128.6 (2 CH), 128.4 (CH), 126.5 (CH), 126.2 (CH), 123.1 (CH), 123.0 (CH), 121.9 (CH), 121.8 (CH), 120.3 (CH), 119.7 (CH), 118.7 (br, indenyl C1 *rac* or *meso*), 115.5 (br, indenyl C1 *rac* or *meso*), 66.7 (Et₂O), 19.4 (2-Me *rac*), 18.0 (2-Me *meso*), 12.8 (br, Et₂O), 6.0 (SiMe₂ *meso*), 5.4 (SiMe₂ *rac*), 5.1 (SiMe₂ *meso*), -6.1 (br, AlMe). THF (10 mL) was added to the yellow filtrate, and the mixture was stirred for 5 min. The volatiles were removed under vacuum to give a colorless solid. Hexanes (70 mL) were added, and the mixture was stirred overnight and filtered, yielding a colorless solid which was washed with hexanes and dried under vacuum (1.63 g, 61.7%). ¹H NMR analysis (C₆D₆, 23 °C) established that the solid was pure *rac*-{1-AlMe₂(THF)-2-Me-4-Ph-1-indenyl}₂SiMe₂ (*rac*-**4b**). Anal. Calcd for C₄₆H₅₈Al₂O₂Si: C,

76.19; H, 8.07, Al, 7.44; Si, 4.14. Found: C, 75.21; H, 8.19; Al, 7.41; Si, 4.53. Data for *rac*-**4b** are as follows. $^1\text{H NMR}$ (C_6D_6): δ 7.97 (d, $J = 7.2$, 2H), 7.75 (d, $J = 7.2$, 4H), 7.42 (t, $J = 7.2$, 4H), 7.24 (m, 6H), 6.50 (s, 2H, H3 of C_5 indenyl ring), 2.65 (br, 4H, THF), 2.26 (br, 4H, THF), 1.72 (s, 6H, 2-Me), 1.35 (s, 6H, SiMe_2), 0.54 (br, 8H, THF), -0.26 & -0.40 (two br s, 12H, AlMe_2). $^1\text{H NMR}$ (toluene- d_8 , -30°C): δ 8.01 (d, $J = 7.2$, 2H), 7.80 (d, $J = 7.2$, 4H), 7.46 (t, $J = 7.2$, 4H), 7.27 (m, 6H), 6.58 (s, 2H, H3 of C_5 indenyl ring), 2.57 (br, 4H, THF), 2.06 (br, THF, partially obscured by solvent), 1.67 (s, 6H, 2-Me), 1.38 (s, 6H, SiMe_2), 0.45 (br, 8H, THF), -0.17 (s, 6H, AlMe_2), -0.44 (s, 6H, AlMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 152.2 (C), 148.9 (C), 144.3 (C), 142.1 (C), 133.1 (C), 129.6 (2 CH), 129.0 (CH), 126.6 (CH), 123.6 (CH), 121.9 (CH), 120.5 (CH), 119.2 (br, indenyl C1), 71.9 (THF), 24.4 (THF), 18.1 (2-Me), 5.6 (SiMe_2), -6.8 (br, AlMe_2). Data for *meso*-**4b** (from a *rac/meso* mixture generated by thermolysis of *rac*-**4b** (toluene- d_8 , 75°C , 8 h) are as follows. $^1\text{H NMR}$ (toluene- d_8): δ 7.56 (d, $J = 7.2$, 4H), 7.41 (d, $J = 7.2$, 2H, partially overlapped with *rac* resonance), 7.24 (m, overlapped with *rac* resonance), 6.96 (t, $J = 7.2$, 2H), 6.76 (t, $J = 7.2$, 2H), 6.43 (s, H3 of C_5 indenyl ring, overlapped with *rac* resonance), 2.68 (br, THF, overlapped with *rac* resonance), 2.48 (s, 6H, 2-Me), 2.29 (br, THF, overlapped with *rac* resonance), 1.33 (s, 3H, SiMe_2), 1.12 (s, 3H, SiMe_2), 0.64 (br, THF, overlapped with *rac* resonance), -0.42 (br, AlMe_2 , overlapped with *rac* resonance). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8): δ 150.2 (C), 147.7 (C), 143.8 (C), 141.0 (C), 132.0 (C), 129.3 (2 CH), 128.3 (CH), 126.1 (CH), 122.3 (CH), 120.0 (CH), 119.0 (CH), 117.4 (br, indenyl C1), 71.8 (THF, overlapped with *rac* resonance), 24.5 (THF, overlapped with *rac* resonance), 19.5 (2-Me), 6.3 (SiMe_2), 5.2 (SiMe_2), -6.8 (br, AlMe_2 , overlapped with *rac* resonance).

1,2-{3- $\text{AlMe}_2(\text{THF})$ -1-indenyl} $_2$ -ethane (5). A solution of AlMe_2Cl (3.86 g, 41.7 mmol) in hexanes (4 mL) was diluted with Et_2O (60 mL) at 10°C . The colorless solution was slowly added to pale yellow solid $\text{Li}_2[1,2\text{-}(\text{indenyl})_2\text{-ethane}]$ (5.39 g, 19.8 mmol) via cannula at 0°C . The yellow slurry was stirred at 23°C for 2 h. The reaction mixture was filtered to afford a pale orange filtrate and a white solid (LiCl). The filtrate was concentrated to ca. 15 mL under vacuum. THF (8 mL) was added at 0°C , and the solution was stirred for 5 min at 0°C . The volatiles were removed under vacuum, affording an orange oily residue. The residue was taken up in hexanes (40 mL) and stirred overnight. Toluene (20 mL) was added, and the mixture was stirred for 3 h. The resulting slurry was filtered, yielding a cream-colored solid and a pale yellow filtrate. Hexanes (40 mL) were added to the solid, and the mixture was stirred for 2 h and filtered to yield an off-white solid and a pale yellow filtrate. The solid was dried under vacuum (5.62 g). The filtrates were combined, and the volatiles were removed under vacuum. The residue was taken up in hexanes (20 mL), stirred for 10 h, and filtered to yield a white crystalline powder (0.12 g), which was combined with the first crop. Total yield: 5.74 g (53.6%). The $^1\text{H NMR}$ spectrum (C_6D_6) established that this product is a single isomer of 1,2-{3- $\text{AlMe}_2(\text{THF})$ -1-indenyl} $_2$ - C_2H_4 (**5**). The solid was recrystallized from toluene at -20°C , affording a white crystalline solid. Anal. Calcd for $\text{C}_{32}\text{H}_{44}\text{Al}_2\text{O}_2$: C, 74.66; H, 8.63; Al, 10.48. Found: C, 73.65; H, 8.28; Al, 10.63. $^1\text{H NMR}$ (C_6D_6): δ 7.73 (d, $J = 7.2$, 2H, H4 or H7), 7.70 (d, $J = 7.2$, 2H, H4 or H7), 7.29 (m, 4H, H5 and H6), 7.00 (s, 2H, H2), 3.99 (s, 2H, H1), 3.29 (m, 4H, C_2H_4), 2.78 (br s, 8H, THF), 0.70 (br s, 8H, THF), -0.46 (br, 12H, AlMe). $^1\text{H NMR}$ (toluene- d_8 , -90°C): δ 7.83 (br s, 2H), 7.66 (br s, 2H), 7.35 (br s, 4H), 7.08 (br s, 2H, H2), 4.14 (s, 2H, H1), 3.28 (m, 4H, C_2H_4), 2.57 (br s, 4H, THF), 1.92 (br s, 4H, THF), 0.44 (br s, 8 H, THF), -0.21 (br, 12H, AlMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 147.9 (C), 141.9 (C), 132.5 (CH), 129.0 (br, C3), 122.1 (CH), 121.8 (CH), 121.5 (CH), 118.6 (CH), 71.3 (THF), 52.4 (C1), 28.4 (C_2H_4), 24.7 (THF), -9.5 (br AlMe).

{(1-indenyl) $_2$ SiMe $_2$ }Zr(NMe $_2$) $_2$ (6). NMR Scale. An NMR tube was charged with { $\text{AlMe}_2(\text{THF})$ -indenyl} $_2$ SiMe $_2$ (**1**; *rac*/

meso = 1/1, 0.16 g, 0.29 mmol), $\text{Zr}(\text{NMe}_2)_4$ (0.060 g, 0.22 mmol), and C_6D_6 (0.5 mL). The tube was maintained at 23°C and monitored periodically by $^1\text{H NMR}$. The pale yellow solution became dark orange. After 50 h at 23°C , the $^1\text{H NMR}$ spectrum established that the starting materials were completely consumed and (SBI)Zr(NMe $_2$) $_2$ (90% vs $\text{Zr}(\text{NMe}_2)_4$ based on total NMe $_2$, *rac/meso* = 4/1) and $\text{Al}_2\text{Me}_4(\mu\text{-NMe}_2)_2$ were present. The THF resonances had shifted to positions characteristic of free THF (δ 3.60, 1.42). The $^1\text{H NMR}$ data for the products are consistent with literature data.

***rac*-{(1-indenyl) $_2$ SiMe $_2$ }Hf(NMe $_2$) $_2$ (7).** (a) NMR Scale. An NMR tube was charged with { $\text{AlMe}_2(\text{THF})$ -indenyl} $_2$ SiMe $_2$ (*rac/meso* = 1.3/1, 0.10 g, 0.18 mmol), Hf(NMe $_2$) $_4$ (0.048 g, 0.13 mmol), and C_6D_6 (0.5 mL). The tube was maintained at 70°C and monitored periodically by $^1\text{H NMR}$. The pale yellow solution became orange. After 21 h at 70°C , the $^1\text{H NMR}$ spectrum established that the starting materials were consumed and {(1-indenyl) $_2$ SiMe $_2$ }Hf(NMe $_2$) $_2$ (70% vs Hf(NMe $_2$) $_4$ based on total NMe $_2$, *rac/meso* = 10/1), $\text{Al}_2\text{Me}_4(\mu\text{-NMe}_2)_2$, and unidentified intermediates (δ NMe $_2$ 2.7–2.9) were present. The $^1\text{H NMR}$ data for the reaction products are consistent with literature data.

(b) Preparative Scale. A solution of Hf(NMe $_2$) $_4$ (1.24 g, 3.49 mmol) in benzene (35 mL) was added to solid { $\text{AlMe}_2(\text{THF})$ -indenyl} $_2$ SiMe $_2$ (**1**; 2.50 g, 4.59 mmol). The pale yellow solution was heated to 76°C and stirred for 24 h. The volatiles were removed under vacuum, affording an orange solid. The solid was extracted with a mixture of toluene (15 mL) and hexanes (110 mL). The extract was filtered, concentrated to ca. 30 mL, and cooled to -38°C . After 2 h, pale orange needles were collected by filtration and dried under vacuum (1.19 g, 61% based on Hf(NMe $_2$) $_4$). The $^1\text{H NMR}$ spectrum established that this product is pure *rac*-(SBI)Hf(NMe $_2$) $_2$.

{(2-Me-1-indenyl) $_2$ SiMe $_2$ }Zr(NMe $_2$) $_2$ (8). (a) NMR Scale. An NMR tube was charged with {1- $\text{AlMe}_2(\text{dioxane})_{0.5}$ -2-Me-1-indenyl} $_2$ SiMe $_2$ (0.038 g, 0.063 mmol), $\text{Zr}(\text{NMe}_2)_4$ (0.013 g, 0.048 mmol), and C_6D_6 (1 mL). The reaction mixture was a pale yellow slurry, as {1- $\text{AlMe}_2(\text{dioxane})_{0.5}$ -2-Me-1-indenyl} $_2$ SiMe $_2$ is insoluble in C_6D_6 . The tube was heated to 75°C . A clear yellow solution formed within a few minutes and turned orange after several hours. After 24 h at 75°C , the $^1\text{H NMR}$ spectrum established that the starting materials were completely consumed and {(2-Me-1-indenyl)SiMe $_2$ }Zr(NMe $_2$) $_2$ (>90% vs $\text{Zr}(\text{NMe}_2)_4$ based on total NMe $_2$, *rac/meso* = 3/4) and $\text{Al}_2\text{Me}_4(\mu\text{-NMe}_2)_2$ were present. The dioxane resonance had shifted to δ 3.53, the position characteristic of free dioxane.

(b) Preparative Scale. Toluene (25 mL) was added to a mixture of $\text{Zr}(\text{NMe}_2)_4$ (0.30 g, 1.1 mmol) and [{1- $\text{AlMe}_2(\text{dioxane})_{0.5}$ -2-Me-1-indenyl] $_2$ SiMe $_2$] $_n$ (0.84 g, 1.4 mmol) at 23°C . The mixture was heated to 77°C for 21 h. The volatiles were removed under vacuum, and the resulting red solid was dried overnight, taken up in toluene (20 mL), and filtered. The filtrate was concentrated to 15 mL and cooled to -20°C to afford a mixture of red and yellow crystals. The red and yellow crystals were collected by filtration, dried under vacuum (0.21 g, 38%), manually separated, and identified as *rac*-{(2-Me-1-indenyl) $_2$ SiMe $_2$ }Zr(NMe $_2$) $_2$ (*rac*-**8**) and *meso*-{(2-Me-1-indenyl) $_2$ SiMe $_2$ }Zr(NMe $_2$) $_2$ (*meso*-**8**), respectively, by X-ray crystallography and $^1\text{H NMR}$. The *rac*-**8**/*meso*-**8** ratio in the bulk sample was determined to be ca. 1/2 by $^1\text{H NMR}$. The mother liquor was concentrated to 10 mL, pentane (5 mL) was added, and the solution was cooled to -20°C for 3 days. The yellow precipitate was collected by filtration and dried under vacuum (0.13 g, 23.5%). The $^1\text{H NMR}$ spectrum established that the yellow solid is enriched in the *meso* isomer (*rac/meso* = 1/7.5). Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{SiZr}$ (1/2 *rac/meso* mixture): C, 63.22; H, 6.95; N, 5.67. Found: C, 63.05; H, 7.09; N, 5.48. Data for *rac*-{(2-Me-1-indenyl) $_2$ SiMe $_2$ }Zr(NMe $_2$) $_2$ are as follows. $^1\text{H NMR}$ (C_6D_6): δ 7.78 (d, $J = 7.2$, 2H, H4 or H7), 7.50 (d, $J = 7.2$, 2H, H4 or H7), 6.92 (m, 2H, H5 or H6), 6.72 (m, 2H, H5 or H6), 6.56 (s, 2H, H3), 2.57 (s, 12H, NMe $_2$), 2.40 (s, 6H, 2-Me),

0.92 (s, 6H, SiMe₂). ¹³C{¹H} NMR (C₆D₆): δ 131.4 (C), 127.9 (C), 127.6 (C), 125.2 (CH), 123.6 (CH), 123.3 (CH), 123.1 (CH), 111.3 (CH), 96.5 (C1), 49.1 (NMe₂), 18.4 (2-Me), 2.2 (SiMe₂). Data for *meso*-(2-Me-1-indenyl)₂SiMe₂Zr(NMe₂)₂ are as follows. ¹H NMR (C₆D₆): δ 8.08 (d, *J* = 7.2, 2H, H4 or H7), 7.40 (d, *J* = 7.2, 2H, H4 or H7), 6.89 (m, 2H, H5 or H6), 6.72 (m, 2H, H5 or H6), 6.47 (s, 2H, H3), 3.08 (s, 6H, NMe₂), 2.16 (s, 6H, 2-Me), 1.76 (s, 6H, NMe₂), 1.13 (s, 3H, SiMe), 0.72 (s, 3H, SiMe). ¹³C{¹H} NMR (C₆D₆): δ 134.7 (C), 132.1 (C), 129.6 (C), 125.5 (CH), 123.9 (CH), 123.0 (CH), 122.5 (CH), 107.7 (CH), 94.6 (C1), 49.1 (NMe₂), 44.7 (NMe₂), 17.6 (2-Me), 2.5 (SiMe), 2.4 (SiMe).

{(2-Me-4,5-benz-1-indenyl)₂SiMe₂Zr(NMe₂)₂ (9). (a) NMR Scale. A solution of {1-AlMe₂(Et₂O)-2-Me-4,5-benz-1-indenyl)₂SiMe₂ (*rac/meso* = 2/1, 0.16 g, 0.25 mmol) and Zr(NMe₂)₄ (0.051 g, 0.19 mmol) in C₆D₆ (1 mL) was heated to 70 °C and monitored periodically by ¹H NMR. The pale yellow solution became dark orange. After 2.5 days at 70 °C, the ¹H NMR spectrum established that the starting materials were completely consumed and {(2-Me-4,5-benz-1-indenyl)₂SiMe₂Zr(NMe₂)₂ (>75% vs Zr(NMe₂)₄ based on total NMe₂, *rac/meso* = 0.90) and Al₂Me₄(*μ*-NMe₂)₂ were present. The Et₂O resonances had shifted to δ 1.10 and 3.25, which are characteristic of free Et₂O.

(b) Preparative Scale. Toluene (25 mL) was added to a solid mixture of Zr(NMe₂)₄ (0.58 g, 2.2 mmol) and {1-AlMe₂(Et₂O)-2-Me-4,5-benz-1-indenyl)₂SiMe₂ (*rac/meso* = 2/1, 1.85 g, 2.70 mmol) at 23 °C. The resulting clear solution was heated for 24 h at 75 °C. The volatiles were removed under vacuum, and the red-orange residue was taken up in pentane (120 mL) and filtered to give an orange filtrate and a yellow solid. The volatiles were removed from the filtrate under vacuum, and the residue was heated to 62 °C for 3 h. The residue was dissolved in toluene (10 mL) and filtered. The filtrate was cooled to 0 °C for 3 h, affording yellow-orange crystals, which were isolated by filtration and dried under vacuum (0.54 g). The filtrate was concentrated to ca. 5 mL, cooled to 0 °C for 6 days, and filtered to yield a yellow-orange solid (0.19 g), which was combined with the first fraction. Total yield: 0.73 g (57%). The ¹H NMR spectrum established that the product consists of a 3/5 mixture of *rac* (pale orange) and *meso* (red) {(2-Me-4,5-benz-1-indenyl)₂SiMe₂Zr(NMe₂)₂. Recrystallization of this material from hexanes at -20 °C gave a mixture of pale orange and red crystals which were manually separated in some trials. Data for *rac*-(2-Me-4,5-benz-1-indenyl)₂SiMe₂Zr(NMe₂)₂ are as follows. Anal. Calcd for C₃₄H₃₈N₂SiZr: C, 68.74; H, 6.46; N, 4.71. Found: C, 68.39; H, 6.60; N, 4.43. ¹H NMR (C₆D₆): δ 7.96 (d, *J* = 7.2, 2H), 7.73 (d, *J* = 10.8, 2H), 7.58 (d, *J* = 7.2, 2H), 7.30 (m, 6H), 6.99 (s, 2H, H3), 2.42 (s, 6H, 2-Me), 2.00 (s, 12H, NMe₂), 0.93 (s, 6H, SiMe₂). ¹³C{¹H} NMR (C₆D₆): δ 132.0 (C), 130.6 (C), 128.5 (CH), 127.6 (C), 127.3 (C), 126.3 (CH), 125.4 (CH), 124.6 (CH), 124.5 (CH), 123.0 (CH), 110.8 (CH), 101.7 (C1), 48.0 (NMe₂), 18.0 (2-CH₃), 2.03 (SiMe). One aromatic resonance is obscured. Data for *meso*-(2-Me-4,5-benz-1-indenyl)₂SiMe₂Zr(NMe₂)₂ are as follows. ¹H NMR (C₆D₆): δ 7.92 (d, *J* = 7.2, 4H), 7.42 (m, 2H), 7.2 (m, 6H), 6.98 (s, 2H, H3), 3.13 (s, 6H, NMe₂), 2.27 (s, 6H, 2-Me), 1.10 (s, 3H, SiMe₂), 0.93 (br, 6H, NMe₂), 0.77 (s, 3H, SiMe₂). ¹³C{¹H} NMR (C₆D₆): δ 132.0 (C), 130.1 (C), 129.7 (C), 128.8 (C), 128.7 (C), 126.0 (CH), 125.4 (CH), 123.9 (CH), 123.8 (CH), 107.6 (CH), 100.8 (C), 51.3 (NMe₂), 44.8 (NMe₂), 17.4 (2-Me), 2.1 (SiMe₂), 2.5 (SiMe₂). Two aromatic resonances are obscured.

{(2-Me-4-Ph-1-indenyl)₂SiMe₂Zr(NMe₂)₂ (10). A solution of {1-AlMe₂(Et₂O)-2-Me-4-Ph-1-indenyl)₂SiMe₂ (*rac/meso* = 3/2, 0.12 g, 0.16 mmol) and Zr(NMe₂)₄ (0.035 g, 0.13 mmol) in C₆D₆ (0.6 mL) in an NMR tube was heated to 75 °C and monitored periodically by ¹H NMR. The pale yellow solution became red. After 17 h at 75 °C, the ¹H NMR spectrum established that the starting materials were completely consumed and {(2-Me-4-Ph-1-indenyl)₂SiMe₂Zr(NMe₂)₂ (>75% vs Zr(NMe₂)₄ based on total NMe₂, *rac/meso* = 3/4) and Al₂Me₄(*μ*-NMe₂)₂ were present. ¹H NMR (C₆D₆): *rac*-**10**, δ 6.70 (s, 2H, C5 indenyl), 2.24 (s, 12H, NMe₂), 2.20 (s, 6H, 2-Me), 0.98 (s, 6H, SiMe₂); *meso*-**10**, δ 6.81 (s, 2H, C5 indenyl), 3.12 (s, 6H, NMe₂), 2.12 (s, 6H, 2-Me), 1.81 (s, 6H, NMe₂), 1.21 (s, 3H, SiMe₂), 0.74 (s, 3H, SiMe₂). The aromatic resonances of the *rac* and *meso* isomers are extensively overlapped and could not be assigned.

Table 4. Summary of Crystal Data for *rac*-2a** and *rac*-**3****

	<i>rac</i> - 2a	<i>rac</i> - 3
formula	C ₃₀ H ₄₂ Al ₂ O ₂ Si	C ₂₁ H ₂₉ AlO ₅ Si
fw	516.69	338.47
cryst size, mm	0.20 × 0.20 × 0.12	0.40 × 0.35 × 0.15
color/shape	colorless/block	colorless/block
<i>d</i> (calcd), Mg/m ³	1.192	1.150
cryst syst	monoclinic	orthorhombic
space group	<i>C2/c</i>	<i>Pbcn</i>
<i>a</i> , Å	32.701(2)	14.4047(3)
<i>b</i> , Å	10.7556(6)	11.9718(2)
<i>c</i> , Å	16.3851(8)	22.6699(5)
β, deg	91.937(1)	
<i>V</i> , Å ³	5759.6(5)	3909.43(14)
<i>Z</i>	8	8
temp, K	173(2)	173(2)
diffractometer	Siemens SMART	Siemens SMART
	CCD	CCD
radiation (λ), Å	0.710 73	0.710 73
θ range, deg	1.25–25.02	1.80–25.04
data collected: <i>h</i> ; <i>k</i> ; <i>l</i>	±38; 0–12; 0–19	0–17; 0–14; 0–26
no. of rflns	13 811	18 905
no. of unique rflns	4993	3442
<i>R</i> _{int}	0.0358	0.0306
no. of obsd rflns	<i>I</i> > 2σ(<i>I</i>), 3562	<i>I</i> > 2σ(<i>I</i>), 2894
μ, mm ⁻¹	0.167	0.138
transmission range, %	82–100	85 to 100
no. of data/restraints/params	4992/18/343	3421/21/232
structure soln	direct methods	direct methods
GOF on <i>F</i> ²	1.040	1.121
<i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0642, w <i>R</i> 2 = 0.1262	<i>R</i> 1 = 0.0709, w <i>R</i> 2 = 0.1789
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0996, w <i>R</i> 2 = 0.1404	<i>R</i> 1 = 0.0839, w <i>R</i> 2 = 0.1889
max resid density, e/Å ³	0.694	0.568

(*μ*-NMe₂)₂ were present. ¹H NMR (C₆D₆): *rac*-**10**, δ 6.70 (s, 2H, C5 indenyl), 2.24 (s, 12H, NMe₂), 2.20 (s, 6H, 2-Me), 0.98 (s, 6H, SiMe₂); *meso*-**10**, δ 6.81 (s, 2H, C5 indenyl), 3.12 (s, 6H, NMe₂), 2.12 (s, 6H, 2-Me), 1.81 (s, 6H, NMe₂), 1.21 (s, 3H, SiMe₂), 0.74 (s, 3H, SiMe₂). The aromatic resonances of the *rac* and *meso* isomers are extensively overlapped and could not be assigned.

{1,2-(indenyl)₂C₂H₄}Zr(NMe₂)₂ (11). An NMR tube was charged with 1,2-{3-AlMe₂(THF)-1-indenyl)₂C₂H₄ (0.086 g, 0.16 mmol), Zr(NMe₂)₄ (0.034 g, 0.13 mmol), and C₆D₆ (~0.5 mL). The tube was heated to 80 °C and monitored by ¹H NMR. The pale yellow solution became dark orange. After 19 h at 80 °C, the ¹H NMR spectrum established that the starting materials were completely consumed and {1,2-(indenyl)₂C₂H₄}Zr(NMe₂)₂ (70% vs Zr(NMe₂)₄ based on total NMe₂, *rac/meso* = 7.3/1) and Al₂Me₄(*μ*-NMe₂)₂ were present. The THF resonances had shifted to positions characteristic of free THF. The ¹H NMR data for the reaction products are consistent with literature data.^{3e}

{1,2-(indenyl)₂C₂H₄}Hf(NMe₂)₂ (12). An NMR tube was charged with {1,2-{3-AlMe₂(THF)-1-indenyl)₂C₂H₄ (0.12 g, 0.24 mmol), Hf(NMe₂)₄ (0.064 g, 0.18 mmol), and C₆D₆ (0.5 mL). The tube was heated to 80 °C and monitored by ¹H NMR. The pale yellow solution became dark orange. After 27 h at 80 °C, the ¹H NMR spectrum established that the starting materials were completely consumed and {1,2-(indenyl)₂C₂H₄}Hf(NMe₂)₂ (80% vs Hf(NMe₂)₄ based on total NMe₂, *rac/meso* = 7/1) and Al₂Me₄(*μ*-NMe₂)₂ were present. The THF resonances had shifted to positions characteristic of free THF. ¹H NMR data for the reaction products are consistent with literature data.^{3c}

X-ray Crystallographic Analysis of *rac*-2**.** Crystallographic details are summarized in Table 4. A crystal of the compound was attached to a glass fiber and mounted on the Siemens SMART system for data collection at 173(2) K. The space group *C2/c* was determined on the basis of systematic

absences and intensity statistics.³³ All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Individual monomers are linked in infinite chains through dioxane bridges. Both dioxanes are centered over inversion centers; therefore, only half of each is found in the asymmetric unit. One dioxane is disordered in a 0.56:0.44 ratio in two chair conformations, where the oxygen is mutual in both fragments.

X-ray Crystallographic Analysis of *rac*-3. Crystallographic details are summarized in Table 4. The space group *Pbcn* was determined on the basis of systematic absences and intensity statistics.²⁵ Halves of the molecule are related to each

(33) SHELXTL-Plus V5.0; Siemens Industrial Automation, Inc., Madison, WI.

other by a crystallographic 2-fold axis. The diethyl ether ligand is disordered.

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Supporting Information Available: For *rac*-2a and *rac*-3, tables giving crystal data, data collection, and solution and refinement details, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and torsion angles and figures giving additional views and the structure and atom-numbering scheme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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