Synthesis, Structure, Dynamic Properties, and Indenyl Transfer Reactions of {AlMe$_2$(THF)(indenyl)}$_2$SiMe$_2$

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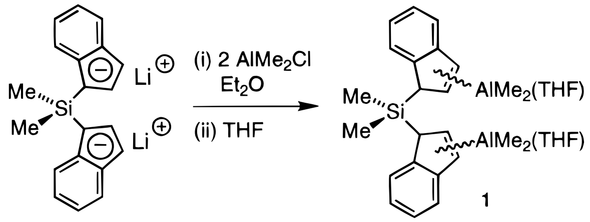
*Summary: The reaction of Li_2SBI (SBI = $Me_2Si(1$-indenyl$)_2$) with 2 equiv of $AlMe_2Cl$ in Et_2O, followed by treatment with THF, affords {$AlMe_2$(THF)(indenyl)}$_2$-$SiMe_2$ (**1**), which is isolated as a ca. 1/1 mixture of rac and meso isomers, from which rac-**1** is obtained by crystallization from toluene. An X-ray crystallographic analysis establishes that rac-**1** exists as the 1,3 isomer, i.e., (1-{$AlMe_2$(THF)-1-indenyl})(3-{$AlMe_2$(THF)}-1-indenyl)$SiMe_2$, in the solid state. NMR studies establish that in toluene-d_8, rac-**1** exists as a 2/1 mixture of 1,3 and 1,1 Al−indenyl isomers which interconvert rapidly on the NMR time scale at room temperature. Rac-**1** undergoes slow isomerization to a 1/1 rac/meso mixture (3 days, 23 °C, benzene) and also undergoes slow partial disproportionation by ligand redistribution (28% conversion, 2 days, 23 °C, benzene). Compound **1** (1/1 to 1.4/1 rac/meso mixture) reacts with $Zr(NMe_2)_4$ and $Hf(NMe_2)_4$ under mild conditions to yield (SBI)$Zr(NMe_2)_2$ in >90% NMR yield (rac/meso = 4.5/1) and rac-(SBI)$Hf(NMe_2)_2$ in 61% isolated yield, respectively.*

Chiral group 4 *ansa*-metallocenes play an important role in stereoselective catalysis, and the development of efficient synthetic methods for these compounds is an important challenge.[1,2] We recently described the synthesis of *rac*-(EBI)Zr(NMe$_2$)$_2$ (EBI = ethylenebis(indenyl)), *rac*-(SBI)Zr(NMe$_2$)$_2$ (SBI = Me$_2$Si(1-indenyl)$_2$), and other *ansa*-metallocenes by amine elimination reactions of M(NMe$_2$)$_4$ compounds and *ansa*-cyclopentadienes.[3,4] However, the amine-elimination approach is less useful for the synthesis of Ti or Hf *ansa*-metallocenes (order of reactivity: Zr > Hf > Ti) and does not work well with crowded metal amides or crowded or weakly acidic cyclopentadienes. For example, the reaction of Hf(NMe$_2$)$_4$ with (SBI)H$_2$ requires vigorous conditions (neat, 32 h, 120 °C) and affords *rac*-(SBI)Hf(NMe$_2$)$_2$ in only 20% isolated yield, and the rearrangement product Me$_2$Si(η^5-1-indenyl)(η^3-2-indenyl)Hf(NMe$_2$)$_2$ is observed as a side product.[5]

Ansa-metallocene bis(amides) react quantitatively with AlMe$_3$ to yield the corresponding *ansa*-metallocene dialkyl derivatives along with Al$_2$Me$_4$(μ-NMe$_2$)$_2$ (major) and Al$_2$Me$_5$(μ-NMe$_2$) (minor).[6] These results suggested that aluminum *ansa*-cyclopentadienyl compounds might be useful reagents for the synthesis of *ansa*-metallocenes.[7] The use of aluminum cyclopentadienyl compounds for cyclopentadienyl transfer is very limited, one example being the synthesis of Cp$_2$TiCl$_2$ by the reaction of {(η^1-C$_5$H$_5$)$_2$Al(μ-O^{i}Pr}$_2$ with TiCl$_4$.[7g] Here, we describe the synthesis, structure, and dynamic properties of {AlMe$_2$(THF)(indenyl)}$_2$SiMe$_2$ (**1**) and its use in the stereoselective synthesis of group 4 *ansa*-metallocenes.

The reaction of Li$_2$SBI with 2 equiv of AlMe$_2$Cl in Et$_2$O, followed by treatment with THF, affords **1** as a colorless solid (eq 1). Compound **1** is highly soluble in benzene, toluene, methylene chloride, and THF and is



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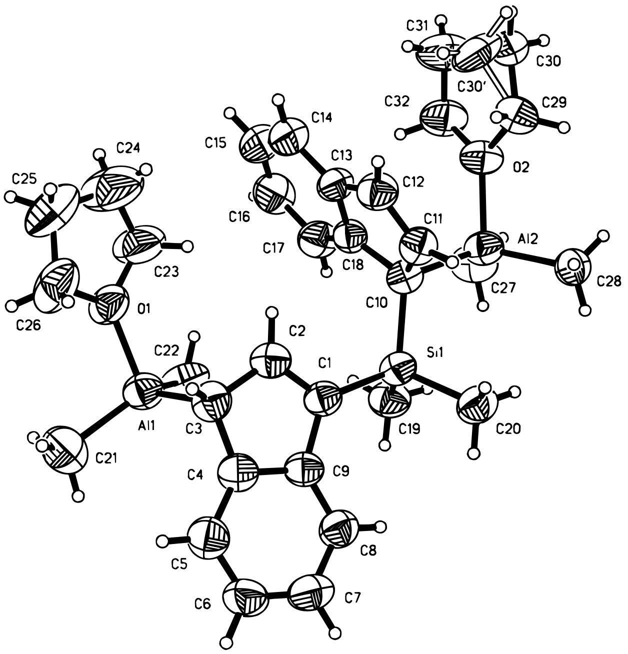


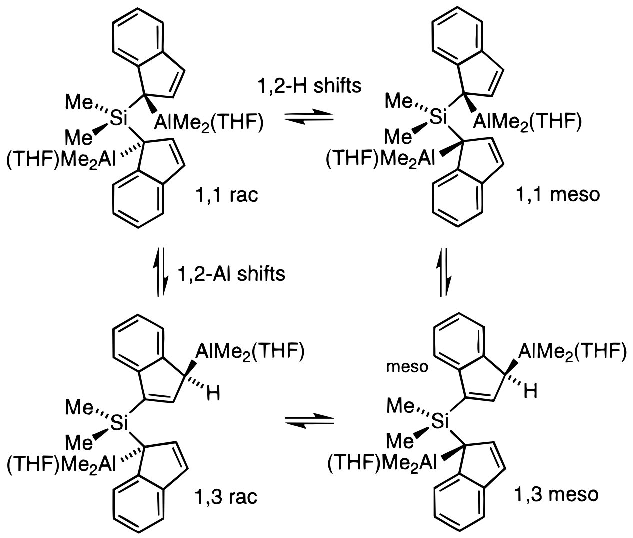
Figure 1. Molecular structure of *rac*-1.

air and moisture sensitive. Exposure of a C_6D_6 solution of **1** to air results in formation of the hydrolysis products $(SBI)H_2$ and CH_4 and an insoluble residue (presumably Al_2O_3). The ^1H NMR spectrum of isolated solid **1** in C_6D_6 (23 °C, freshly dissolved, vide infra) establishes that this material is a mixture of *rac* and *meso* isomers. The spectrum of *rac*-**1** contains one $SiMe_2$ resonance and one $AlMe_2$ resonance, whereas that of *meso*-**1** contains two $SiMe_2$ resonances of equal intensity and one $AlMe_2$ resonance. The *rac/meso* ratio for isolated **1** varies from 1/1 to 1.4/1.

Recrystallization of the *rac*-**1**/*meso*-**1** mixture from toluene yields pure *rac*-**1**. The molecular structure of *rac*-**1** in the solid state was established by X-ray crystallography (Figure 1).[8] The two $-AlMe_2(THF)$ groups bond to the five-membered rings of the $Me_2Si(indenyl)_2$ ligand in an η^1-fashion at the 1 and 3 positions, respectively. The Al atoms exhibit normal tetrahedral geometry. The $Al-CH_3$ distances range from 1.945(4) to 1.986(4) Å and are similar to the Al−C(terminal) distance in Al_2Me_6 (average 1.97 Å).[9] The Al−C(indenyl) bond distances (2.043(4), 2.067(4) Å) are similar to those found for $(\eta^1\text{-Cp})_3Al(CN^tBu)$ (2.067(6) Å) and $\{(\eta^1\text{-Cp})_2AlO^iPr\}_2$ (2.003(2) Å).[7f,g]

The low-temperature (−60 °C) ^1H NMR spectrum of *rac*-**1** in toluene-d_8 establishes that this compound is present as a 2/1 mixture of the 1,3-*rac* and 1,1-*rac* isomers (Scheme 1). This spectrum contains the following key features: (i) three $SiMe_2$ resonances of equal intensity, corresponding to the two equivalent Si−Me groups of 1,1-*rac*-**1** and the two inequivalent Si−Me groups of 1,3-*rac*-**1**, (ii) five Al−Me resonances in a 1:1:1:1:2 intensity ratio (−90 °C) corresponding to the six inequivalent Al−Me groups in this isomer mixture, (iii) five vinyl resonances (δ 7.5−6.5) and an allylic resonance (δ 4.1) all of equal intensity, for the H2 and H3 indenyl hydrogens of the two isomers, and (iv) six resonances of equal intensity for the H4 and H7 hydrogens of the two isomers. The 3,3-*rac* isomer was not detected. The 23 °C ^1H NMR spectrum of *rac*-**1** (C_6D_6) is much simpler and contains a singlet for the $SiMe_2$ groups, two singlets (δ = 7.08, 5.67 br) for the indenyl H2 and H3 hydrogens, and one set of indenyl H4 and H7 resonances. These observations establish that exchange of the 1,1 and 1,3 isomers is slow on the NMR time scale at −60 °C but is rapid at 23 °C. The (1,1)/(1,3) exchange presumably occurs by sequential 1,2-Al shifts (and isoindene intermediates).[10] It should be noted that under conditions of fast (1,1)/1,3) exchange, the $-AlMe_2(THF)$ groups remain bonded to the same indenyl face and, therefore, two Al−Me resonances and two α-THF resonances are expected for *rac*-**1**. However, the 23 °C NMR spectrum of *rac*-**1** contains one broad Al−Me resonance and two broad, nearly coalesced α-THF resonances (coalescence temperature ca. 40 °C), which suggests that THF dissociation accompanies and may be required for the (1,1)/1,3) exchange. This proposal is consistent with Jutzi's observation that the barrier for 1,2-B shifts in $(C_5Me_5)BCl_2(pyridine)$ (>25 kcal/mol) is much greater than that in the base-free analogue $(C_5Me_5)BCl_2$ (<5 kcal/mol).[11] Exchange of the coordinated THF of *rac*-**1** with free THF is rapid on the NMR time scale.

Scheme 1



Rac-**1** isomerizes slowly (3 days) at 23 °C and rapidly (min) at 70 °C to a 1/1 equilibrium mixture of *rac*-**1**/*meso*-**1** in C_6D_6 (Scheme 1). The interconversion of *rac*-**1** and *meso*-**1** proceeds by 1,2-H shifts and isoindene intermediates and is analogous to *rac*/*meso* isomerization of $(SBI)H_2$.[12] The low-temperature NMR spectra of *rac*-**1**/*meso*-**1** mixtures are complex, and it was not possible to determine the solution structure of *meso*-**1**; however, 1,1 and 1,3 isomers (Scheme 1) as well as a 3,3 isomer are possible for this species.

NMR monitoring of benzene-d_6 solutions of *rac*-**1**/*meso*-**1** reveals that **1** is ca. 28% converted to new Al−

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[8] Crystal data: colorless block, monoclinic, a = 11.6395(5) Å, b = 15.8068(7) Å, c = 17.8951(8) Å, β = 102.241(1)°, V = 3217.5(2) Å^3, space group $P2_1/c$, Z = 4, fw = 544.74, calcd density 1.125 Mg/m^3, goodness of fit on F^2 = 1.060, R1 = 0.0719; wR2 = 0.1418 for 3192 reflections with $I > 2\sigma(I)$.

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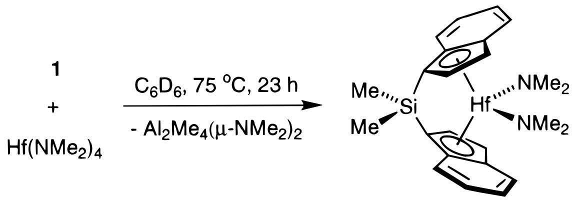
Me species after 2 days at 23 °C. A similar but faster reaction is observed for **1** in THF-d_8 (36% conversion, 12 h, 23 °C); in this case, one of the major products is $AlMe_3(THF)$ (δ −0.99). These results suggest that **1** undergoes partial disproportionation by ligand redistribution in solution. Similar behavior has been reported for other cyclopentadienylaluminum compounds; e.g., $CpAlMe_2(THF)$ undergoes ca. 25% disproportionation to $AlMe_3(THF)$ and $Cp_2AlMe(THF)$ in benzene-d_6 at 23 °C.[13] However, other than $AlMe_3(THF)$, the disproportionation products of **1** have not yet been identified.

To test the hypothesis that **1** can function as an indenyl-transfer agent, we first investigated its reaction with $Zr(NMe_2)_4$ on an NMR scale. The reaction of $Zr(NMe_2)_4$ with 1.3 equiv of **1** (*rac*/*meso* = 1/1) in C_6D_6 (50 h, 23 °C) affords $(SBI)Zr(NMe_2)_2$ (*rac*/*meso* = 4.5/1) in >90% NMR yield (based on $Zr(NMe_2)_4$), with simultaneous formation of $Al_2Me_4(\mu\text{-}NMe_2)_2$.[14] An excess of **1** must be employed due to the disproportionation noted above. Similarly, the reaction of $Hf(NMe_2)_4$ with 1.3 equiv of **1** (*rac*/*meso* = 1.3/1) in benzene (70 °C, 21 h) affords $(SBI)Hf(NMe_2)_2$ in 70% NMR yield (based on $Hf(NMe_2)_4$) in a 10/1 *rac*/*meso* ratio (eq 2). *Rac*-$(SBI)Hf(NMe_2)_2$ was isolated as pale orange needles in 61% yield after crystallization from toluene/hexanes. These conditions are much milder than those required for the synthesis of $(SBI)Zr(NMe_2)_2$ and *rac*-$(SBI)Hf(NMe_2)_2$ by amine elimination.[3b,5] Complete removal of residual chloride (LiCl or AlCl species) from **1** is important for selective indenyl transfer. The reaction of $Zr(NMe_2)_4$ with samples of **1** containing residual chloride yielded $(SBI)Zr(NMe_2)_2$ in lower yield with variable *rac*/*meso* ratios, along with significant amounts of *rac*-$(SBI)Zr(NMe_2)Cl$ and *rac*- and *meso*-$(SBI)ZrCl_2$.



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These results show that *ansa*-indenyl aluminum compounds are easily accessible and function as effective indenyl-transfer reagents. Work is in progress to extend this approach to the synthesis of *ansa*-metallocenes which are not easily accessible by other methods.[15]

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Supporting Information Available: Text giving the experimental details and characterization data for new compounds, tables of X-ray structural data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, torsion angles, and hydrogen atom coordinates, and an ORTEP diagram for *rac*-**1** (12 pages). Ordering information is given on any current masthead page.

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[14] The 4.5/1 *rac*/*meso* ratio is the thermodynamic ratio for $(SBI)Zr(NMe_2)_2$; see ref 3b.

(15) Synthesis of *rac and meso*-$\{AlMe_2(THF)(indenyl)\}_2SiMe_2$ (**1**): A solution of $AlMe_2Cl$ (2.13 g, 23.0 mmol) in hexanes (10 mL) was diluted with Et_2O (50 mL). The colorless solution was slowly added (10 min) to solid Li_2SBI (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 (C_6D_6) established that this product was a 1.2/1 mixture of *rac*- and *meso*-$\{AlMe_2(THF)(indenyl)\}_2SiMe_2$. Anal. Calcd for $C_{32}H_{46}Al_2O_2Si$: 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. The low C and Si values are likely due to SiC formation. ^1H NMR (C_6D_6): δ 7.87 (d, J = 7.2 Hz, 4H, indenyl), 7.60 (d, J = 7.2 Hz, 4H, indenyl), 7.29 (d, J = 3.6 Hz, 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, $SiMe_2$ meso), 0.88 (s, 6H, $SiMe_2$ rac), 0.64 (s, 16H, THF), 0.53 (s, 3H, $SiMe_2$ meso), −0.44 (s, 12H, $AlMe_2$ meso), −0.47 (s, 12H, $AlMe_2$ rac). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 147.1, 146.9, 146.6, 145.3, 144.3 (br), 123.3, 123.1, 122.9, 121.6, 121.4, 121.2, 121.1, 120.8, 71.8 (THF), 24.6 (THF), 1.1 ($SiMe_2$), −0.39 ($SiMe_2$), −7.9 (br, $AlMe_2$). Additional NMR data for *rac*- and *meso*-**1** are provided in the Supporting Information. Compound **1** undergoes ligand redistribution reactions in benzene and THF, as described in the text. Isolation of *rac*-**1**: Recrystallization of the *rac*-**1**/*meso*-**1** mixture from above from toluene at −20 °C afforded pure *rac*-**1** as colorless cubes. ^1H NMR (C_6D_6) rapid exchange of 1,3 and 1,1 isomers: δ 7.89 (d, J = 7.2 Hz, 2H, H4 or H7), 7.62 (d, J = 7.2 Hz, 2H, H4 or H7), 7.15 (H5 and H6), 7.08 (br, 2H, H2), 5.71 (br, 2H, H3), 2.64 (br, 4H, THF), 2.43 (br, 4H, THF), 0.88 (s, 6H, $SiMe_2$), 0.54 (br, 8H, THF), −0.47 (s, 12H, $AlMe_2$). ^1H NMR (toluene-d_8, 213 K, 2/1 mixture of slowly exchanging 1,3 and 1,1 isomers): δ 8.04 (br, 2H, H4 or H7), 7.88 (br, 2H, H4 or H7), 7.82 (br, 2H, H4 or H7), 7.73 (br, 2H, H4 or H7), 7.69 (br, 2H, H4 or H7), 7.59 (br, 2H, H4 or H7), 7.46 (br, 2H, vinylic H), 7.27 (br, 12H, H5 and H6), 6.97 (br, 2H, vinylic H), 6.78 (br, 2H, vinylic H), 6.57 (br, 2H, vinylic H), 6.52 (br, 2H, vinylic H), 4.09 (br, 2H, allylic H), 2.65, 2.51, 2.18, and 1.89 (br, 24H, THF), 1.06 (s, 6H, $SiMe_2$), 1.02 (s, 6H, $SiMe_2$), 0.93 (s, 6H, $SiMe_2$), 0.70, 0.55, and 0.40 (br, 24H, THF), −0.21 (s, 12H, $AlMe_2$), −0.28 (s, 6H, $AlMe_2$), −0.43 (s, 6H, $AlMe_2$), −0.62 (s, 12H, $AlMe_2$).