General Synthesis of Racemic Me_2Si-Bridged Bis(indenyl) Zirconocene Complexes

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Chiral racemic *ansa*-zirconocene complexes can be activated by MAO or other cocatalysts to generate excellent catalysts for isotactic α-olefin polymerization and other stereoselective reactions.[1] Racemic $SiMe_2$-bridged bis(indenyl) zirconocenes that contain methyl and aryl substituents at the indenyl 2 and 4 positions, respectively, are among the best metallocene catalysts for the production of high molecular weight, isotactic poly(α-olefins).[2] *ansa*-Zirconocenes are normally synthesized by salt-elimination reactions between *ansa*-bis(indenyl) dianion reagents and ZrX_4 or ZrX_4L_2 compounds. However, the factors that control chemoselectivity (i.e. metallocene vs dinuclear products) and diastereoselectivity (i.e. *rac*/*meso* selectivity) in these reactions are not well understood, and extensive screening studies of reagents, counterions, solvents, use of added ligands, and reaction conditions are required for each case to optimize yields.[3] Amine elimination reactions of *ansa*-bis(indenes) and $Zr(NR_2)_4$ compounds provide efficient routes to simple *ansa*-zirconocenes, but this approach is not successful for sterically crowded cases.[4] Here we report a general, high-yield synthesis of *rac*-$SiMe_2$-bridged bis(indenyl) zirconocenes that exploits the conformational properties of a simple chelating diamide ligand to control diastereoselectivity.

The chelated propylene−diamide complex $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ (**1**) can be prepared by two methods as shown in Scheme 1. The reaction of $ZrCl_4$ and 2 equiv of $Li_2[PhN(CH_2)_3NPh]$ in toluene affords $Zr\{PhN(CH_2)_3NPh\}_2$ as a yellow solid in 73% isolated yield. The reaction of $ZrCl_4$ and $Zr\{PhN(CH_2)_3NPh\}_2$ in THF/Et_2O (1:1 by volume) yields **1** as a yellow solid quantitatively.[5] Alternatively, **1** can be prepared directly by the reaction of $ZrCl_4$ with 1 equiv of $Li_2[PhN(CH_2)_3NPh]$ in THF/Et_2O in 81% isolated yield.

A view of the molecular structure of **1** which highlights the conformation of the chelate ring is shown Figure 1.[6] Compound **1** is monomeric and has approximate C_2 symmetry with the C_2 axis lying along the Zr- - -C(2) vector and bisecting the O(1)−Zr−O(2) angle. The geometry at Zr is distorted octahedral and the weak donor THF ligands are trans to the strong donor amide groups. The Zr−N bond distances (2.082(2), 2.080(2) Å) are normal and the N(1)−Zr−N(2) angle (91.63(6)°) is close to the ideal octahedral value. The six-membered C(1)−N(1)−Zr−N(2)−C(3)−C(2) chelate ring adopts a twist conformation.[7] The N(1), Zr, N(2), and C(2) atoms are coplanar to within 0.02 Å, and C(1) and C(3) lie 0.79 Å above and below the N(1)−Zr−N(2)−C(2) plane, respectively. This conformation places the two phenyl rings on opposite sides of the N(1)−Zr−N(2)−C(2) plane; the C(4)−N(1)- -N(2)−C(10) torsion angle is 145.2°.[8] However, the ^1H NMR spectrum of **1** contains two methylene resonances for the diamide ligand in a 2:1 intensity ratio down to −105 °C (THF-d_8), which implies that ring inversion is fast on the NMR scale in solution.

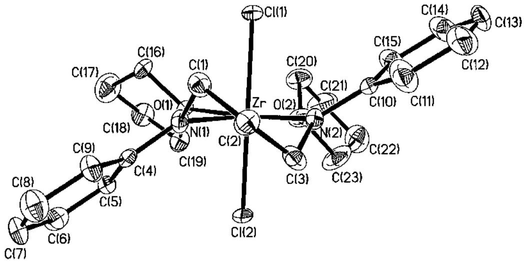
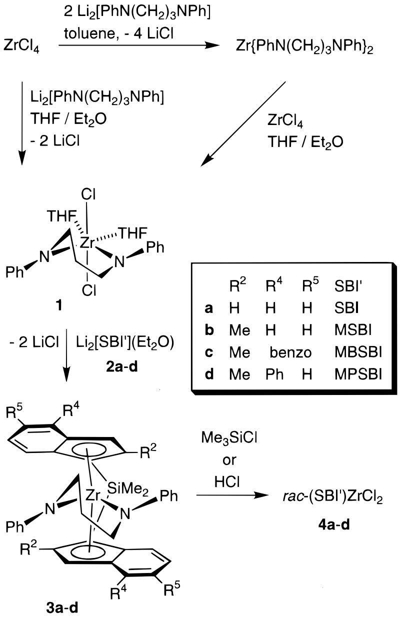


Figure 1. Molecular structure of $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ (**1**). Bond distances (Å): Zr−Cl(1) 2.4785(5), Zr−Cl(2) 2.4565(5), Zr−O(1) 2.321(1), Zr−O(2) 2.302(2). Bond angles (deg): Cl(1)−Zr−Cl(2) 164.00(2), O(1)−Zr−O(2) 79.32(5). Torsion angles (deg): N(1)−Zr−N(2)−C(10) −133.8(2), N(2)−Zr−N(1)−C(4) −127.8(2).

Scheme 1



	R^2	R^4	R^5	SBI'
a	H	H	H	SBI
b	Me	H	H	MSBI
c	Me	benzo		MBSBI
d	Me	Ph	H	MPSBI

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(5) This procedure is based on the reported synthesis of $Zr(NMe_2)_2Cl_2(THF)_2$. Brenner, S.; Kempe, R.; Arndt, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2021.

(6) X-ray data for **1**: tetragonal, $P4_2/n$, $a = b = 24.977(1)$ Å, $c = 7.8479(4)$ Å, $V = 4895.8(4)$ Å^3, $Z = 8$, $T = 173(2)$ K, $D_{calc} = 1.440$ g/cm^3; $R1 = 0.0248$, $wR2 = 0.0708$ for 5002 independent reflections with $I > 2\sigma(I)$; GOF on $F^2 = 0.997$.

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(8) In contrast, the chelate rings in 4- and 5-coordinate Zr(IV) and Ti(IV) propylene−diamide complexes containing bulky aryl or silyl N-substituents adopt boat conformations. (a) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478. (b) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (c) Lee, C. H.; La, Y.; Park, J. W. *Organometallics* **2000**, *19*, 344.

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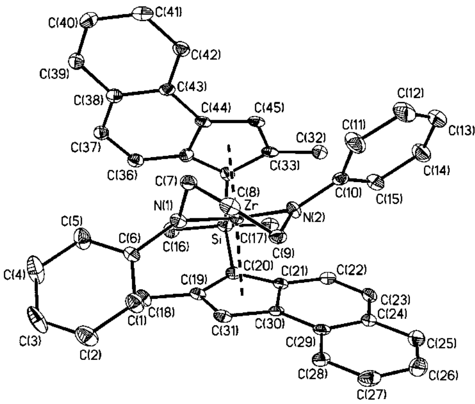

Figure 2. Molecular structure of *rac*-(MBSBI)Zr{PhN(CH$_2$)$_3$NPh} (**3c**). Bond distances (Å): Zr−N(1) 2.073(2), Zr−N(2) 2.122(2). Torsion angles (deg): N(1)−Zr−N(2)−C(10) −141.9(3), N(2)−Zr−N(1)−C(6) −131.2(3).

The reaction of **1** with 1 equiv of the lithium *ansa*-bis(indenyl) reagents Li$_2$[SBI′](Et$_2$O) **2a−d** (**2a**, SBI′ = (1-indenyl)$_2$SiMe$_2$ (SBI); **2b**, SBI′ = (2-methyl-1-indenyl)$_2$SiMe$_2$ (MSBI); **2c**, SBI′ = (2-methyl-4,5-benz-1-indenyl)$_2$SiMe$_2$ (MBSBI); **2d**, SBI′ = (2-methyl-4-phenyl-1-indenyl)$_2$SiMe$_2$, (MPSBI)) in Et$_2$O affords the corresponding *rac*-(SBI′)Zr{PhN(CH$_2$)$_3$NPh} zirconocenes **3a−d** in >90% NMR yield (Scheme 1). The ^{1}H NMR spectra of **3a−d** each contain one SiMe$_2$ resonance, one 2-H (for **3a**) or 2-Me (for **3b−d**) resonance, three NCH$_2$CH$_2$CH$_2$N methylene resonances, and appropriate indenyl resonances consistent with C_2 symmetry. The *meso* isomers of **3a−d** were not detected. Compounds **3c** and **3d** were isolated in pure form as red solids in 90% and 87% yield, respectively.

The molecular structure of **3c** was determined by X-ray crystallography (Figure 2).[9] The Zr−diamide unit in **3c** is structurally similar to that in **1**. The twist conformation of the chelate ring, the large C(6)−N(1)- -N(2)−C(10) torsion angle (142.8°), and the N(1)−Zr−N(2) angle (86.77(9)°) are very similar to the corresponding features in **1**. The Zr−centroid distances (2.342, 2.291 Å) and centroid−Zr−centroid angle (123.1°) are comparable to those in *rac*-(MBSBI)ZrCl$_2$ (2.247 Å, 127.9°).[2b]

A reasonable explanation for the high selectivity for *rac*-metallocene products in Scheme 1 is that the twist conformation of the Zr propylene−bisamide chelate ring constrains the two N−Ph groups to lie above and below the N−Zr−N plane, which accommodates the *rac*-metallocene structure but sterically disfavors the *meso* structure (and the transition state and η^5,η^1-bis(indenyl) intermediate leading thereto).[10] For comparison, the reaction of **2c** with Zr(NMePh)$_2$Cl$_2$(THF)$_2$, the *nonchelated* analogue of **1**, yields a 1/1 mixture of *rac*- and *meso*-(MBSBI)Zr(NMePh)$_2$ along with 20% of the dinuclear species (MBSBI){Zr(NMePh)$_2$Cl}$_2$.[11] X-ray crystallographic analyses show that the Zr(NMePh)$_2$ units in Zr(NMePh)$_2$Cl$_2$(THF)$_2$ and *rac*-(MBSBI)Zr(NMePh)$_2$ (Figure 3a) are structurally similar to the Zr{PhN(CH$_2$)$_3$NPh} units in **1** and **3c**, with approximate C_2 symmetry, large C(Ph)−N- -N−C(Ph) torsion angles (155.5° and 152.8°, respectively), and placement of the two N-phenyl groups on opposite sides of the N−Zr−N plane. However, *meso*-(MBSBI)Zr(NMePh)$_2$ can form because the nonchelated Zr−NMePh ligands can rotate to relieve steric crowding between the *N*-phenyl and indenyl groups on the crowded side of the metallocene, as illustrated in Figure 3b. Similarly, the reaction of **2c** with the 0.5 equiv of the *ethylene*−diamide complex {Zr(PhNCH$_2$CH$_2$NPh)Cl(THF)}$_2$(μ-Cl)$_2$ yields a 2/1 mixture of *rac*- and *meso*-(MBSBI)Zr(PhNCH$_2$CH$_2$NPh).[11] X-ray crystallographic studies show that the ZrNCH$_2$CH$_2$N chelate rings in *rac*- and *meso*-(MBSBI)Zr(PhNCH$_2$CH$_2$NPh) (Figure 3c,d) adopt envelope conformations in which one N−Ph group lies in the N−Zr−N plane, which allows the *meso* isomer to form.

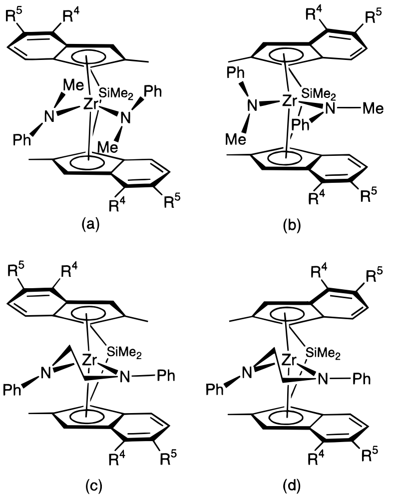

Figure 3. Schematic drawings of the molecular structures of *rac*- and *meso*-(MBSBI)Zr(NMePh)$_2$ (a, b) and *rac*- and *meso*-(MBSBI)Zr(PhCH$_2$CH$_2$NPh) (c, d) based on X-ray crystallographic analyses (R^4 and R^5 = benzo).

We previously reported that *rac*-(SBI)Zr(NMe$_2$)$_2$ and *rac*-(EBI)Zr(NMe$_2$)$_2$ (EBI = 1,2-ethylenebis(indenyl)) are quantitatively converted to *rac*-(SBI)ZrCl$_2$ (**4a**) and *rac*-(EBI)ZrCl$_2$ by reaction with Me$_3$SiCl.[4] Similarly, **3a** is cleanly converted to **4a** (100% NMR) by reaction with Me$_3$SiCl in CD$_2$Cl$_2$ at 60 °C (sealed tube, Scheme 1). In contrast, no reaction is observed between **3d** and Me$_3$SiCl in CD$_2$Cl$_2$ (100 °C, 30 h, sealed tube). However, **3b−d** react cleanly with HCl in Et$_2$O or toluene at −78 °C to afford the corresponding *rac* zirconocene dichlorides **4b−d** in high yield (Scheme 1). *rac*-(MBSBI)ZrCl$_2$ (**4c**) was isolated in 70% yield (vs **1**) by initial generation of **3c** from **1** and **2c**, filtration to remove the LiCl coproduct, treatment with HCl at −78 °C, removal of the solvent, and washing with benzene to remove the PhNH(CH$_2$)$_3$NHPh coproduct. Dichlorides **4b** and **4d** were isolated in 76% and 51% yield, respectively (vs ZrCl$_4$), by in situ generation of **1** from ZrCl$_4$ and Li$_2$[PhN(CH$_2$)$_3$NPh], treatment with the appropriate Li$_2$[SBI′](Et$_2$O) reagent, filtration to remove the LiCl coproduct, treatment with HCl at −78 °C, and filtration. The lower isolated yield for **4d** is due to its high solubility.

These results show that reaction of the easily accessible propylene−diamide complex Zr{PhN(CH$_2$)$_3$NPh}Cl$_2$(THF)$_2$ (**1**) with Li$_2$[SBI′](Et$_2$O) reagents provides a general, high-yield, stereoselective route to *rac*-(SBI′)Zr{PhN(CH$_2$)$_3$NPh} complexes, including those with 2-Me substituents. These zirconocene−diamide complexes, which can be isolated or used in situ, can be converted to the corresponding *rac*-(SBI′)ZrCl$_2$ complexes by reaction with Me$_3$SiCl (for **3a**) or HCl (for **3b−d**). The conformational properties of the PhN(CH$_2$)$_3$NPh^{2-} ligand are the key to the stereoselectivity in these reactions and this method should be applicable to a wide variety of *ansa*-metallocenes. Work is in progress to extend this approach to the enantioselective synthesis of *ansa*-metallocenes using chiral diamide ligands.

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Supporting Information Available: Synthetic procedures, characterization data for new compounds, and details of the X-ray structure determinations of **1** and **3c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) X-ray data for **3c**: triclinic, $P\bar{1}$, a = 10.3355(6) Å, b = 12.1037(7) Å, c = 14.8777(8) Å, α = 93.503(1)°, β = 97.219(1)°, γ = 107.125(1)°, V = 1755.1(2) Å^3, Z = 2, T = 173(2) K, D_{calc} = 1.382 g/cm^3; $R1$ = 0.0453, $wR2$ = 0.0751 for 7121 independent reflections with $I > 2\sigma(I)$; GOF on F^2 = 1.010.

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(11) (a) Zhang, X. W.; Jordan, R. F. Manuscript in preparation. (b) X-ray crystallographic analyses of Zr(NMePh)$_2$Cl$_2$(THF)$_2$, *rac*- and *meso*-(MBSBI)Zr(NMePh)$_2$, {Zr(PhNCH$_2$CH$_2$NPh)Cl(THF)}$_2$(μ-Cl)$_2$, and *rac*- and *meso*-(MBSBI)Zr(PhNCH$_2$CH$_2$NPh) will be included in a full report.