Articles

Racemo-Selective Synthesis of *ansa*-Zirconocene Derivates from Zirconium Biphenolate Complexes

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Stereoselective reactions of zirconium biphenolate complexes of the general formula (BIP)-$ZrCl_2(THF)_2$ (**1a**−**c**), where BIP = 3,3′-$^iPr_2$-6,6′-Me_2-1,1′-bi-2-phenolate (**a**), 3,3′-$^tBu_2$-5,5′-Me_2-1,1′-bi-2-phenolate (**b**), or 3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenolate (**c**), with 1 equiv of the lithium or magnesium salts of various *ansa*-bis(indenyl) ligands give the *ansa*-zirconocenes *rac*-$C_2H_4(Ind)_2Zr(BIP)$ (**2b**), *rac*-$Me_2Si(Ind)_2Zr(BIP)$ (**3c**), *rac*-Me_2Si(2-Me-Ind)$_2$Zr(BIP) (**4c**), *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2$Zr(BIP) (**5c**), and *rac*-Me_2Si(2-Me-Benz[*e*]Ind)$_2$Zr(BIP) (**6c**) in isolated yields of 60−75%. Reactions of $C_2H_4(Ind)_2Mg(THF)_2$ with **1a** and **1b** and of $Me_2Si(Ind)_2Li_2$ with **1c** give directly the pure diastereomers *rac*-**2a**, *rac*-**2b**, and *rac*-**3c**, respectively. More highly substituted indenyl ligands, on the other hand, give initially kinetically controlled mixtures of the *rac*- and *meso*-zirconocene BIP derivatives **4c**, **5c**, and **6c**, from which the pure *rac*-derivatives are obtained as thermodynamically favored products by heating the reaction mixtures to 75 °C for 5−7 h. The *meso*-to-*rac* isomerization of **6c** is catalyzed by addition of TEMPO and is thus likely to occur by way of radical intermediates. Crystal and molecular structures of **1b** and **2b** and of **1c** and **6c** indicate that formation of the racemo diastereomers is favored by repulsive interactions between biphenolate and *ansa*-bis(indenyl) ligands.

Introduction

Practical application of chiral *ansa*-metallocene catalysts for the polymerization of α-olefins[1] demands their preparation on a scale where nonselective formation of racemic and meso isomers and their subsequent separation is no longer tolerable. In recent years, substantial efforts have thus been aimed at the development of *ansa*-metallocene syntheses which yield the racemic isomer selectively.[2−7] While considerable degrees of stereocontrol can be achieved for complex formations with particularly designed *ansa*-ligands or ligand transfer reagents,[2,3] more generally useful stereocontrol strategies can result only from *ansa*-metallocene syntheses with appropriately designed metal precursor complexes.[4−7]

Noteworthy in this regard is the stereoselective reaction of zirconium diamide chelates $Cl_2Zr(PhN(CH_2)_3$-NPh)$(THF)_2$ with lithium salts of Me_2Si-bridged bis(indenyl) ligands, which gives the pure racemic *ansa*-zirconocene-diamides in high yields.[6] Another *rac*-selective reaction of C_2Me_4(1-Cp-3-$^tBu)_2Li_2$ with a titanium binaphtholate complex of composition Cl_2Ti-(BIN) (BIN = binaphtholate) to C_2Me_4(1-Cp-3-$^tBu)_2Ti$-(BIN) was described by McLaughlin and co-workers some time ago.[7] This reaction proceeds with a yield of only 15%. In the meantime, it has become apparent that related complexes of the type Cl_2Ti(BIN) have oligomeric, polynuclear structures,[8] which might interfere

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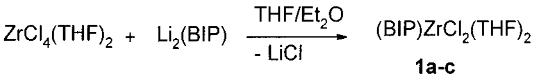
Scheme 1



$$ZrCl_4(THF)_2 + Li_2(BIP) \xrightarrow[-\ LiCl]{THF/Et_2O} \underset{\mathbf{1a\text{-}c}}{(BIP)ZrCl_2(THF)_2}$$

1a, BIP = 3,3′-^{i}Pr$_2$-6,6′-Me$_2$-biphenolate
1b, BIP = 3,3′-^{t}Bu$_2$-5,5′-Me$_2$-biphenolate
1c, BIP = 3,3′,5,5′-^{t}Bu$_4$-biphenolate

with their efficient conversion to a monomeric *ansa*-metallocene complex. Recently, several titanium and zirconium biphenolate complexes with substituents in their 3 and 3′ positions, designed for use as dissymmetric Lewis acid catalysts,[9] have been reported to be monomeric in the solid state and in solution by the groups of Heppert and of Schaverien.[8,10] Since substituted biphenol derivatives are rather easily accessible,[11] we have investigated the use of 3,3′-substituted zirconium biphenolate complexes as synthons for the racemoselective synthesis of *ansa*-zirconocene derivatives.

Results and Discussion

1. Zirconium Biphenolate Complexes. The zirconium biphenolate complexes (BIP)ZrCl$_2$(THF)$_2$ (**1a**−**c**),[10] where BIP = 3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate (**1a**), 3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate (**1b**), or 3,3′-5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate (**1c**), were prepared by deprotonation of the appropriate biphenols with NaH or BuLi[12] and subsequent reaction with ZrCl$_4$(THF)$_2$ in yields of 70−85% (Scheme 1).

While **1a** was obtained as a microcrystalline powder, **1b** and **1c** gave crystals suitable for diffractometric structure determination (Table 1, Figure 1). Both complexes are monomeric in the crystalline state. Complex **1b** has a distorted octahedral geometry of almost perfect C_2-symmetry, with the Cl ligands mutually trans and the THF ligands cis to each other. Complex **1c** also shows a slightly distorted octahedral geometry. Here, however, both the Cl and THF ligands are mutually cis-coordinated to the Zr center. In both complexes, the seven-membered Zr-biphenolate chelate rings adopt a twisted conformation with C1−O1···O2−C2 dihedral angles of 53 ± 2° between the two phenoxy units. The ^{1}H NMR signals of **1a** in C_6D_6 solution (Table 2) indicate the presence of two C_2-symmetric complexes, a minor species and a major one. These we assign to (3,3′-^{i}Pr$_2$-6,6′-Me$_2$- biphenolate)ZrCl$_2$ complexes with one and two THF ligands, respectively, based on the observation that the minor species is converted to the major one upon addition of THF to these solutions. For each of the complexes **1b** and **1c** only one species, presumably the bis-THF adduct, was apparent in their room-temperature ^{1}H NMR spectra (Table 2).

Table 1. Selected Distances (Å) and Angles (deg) for Complexes 1b, 1c, 2b, and 6c

	1b	1c	2b	6c
Zr−O(1)	1.927(6)	1.931(3)	1.978(2)	2.023(4)
Zr−O(2)	1.954(6)	1.986(3)	2.028(2)	2.040(4)
Zr−O(3)	2.284(7)	2.264(3)		
Zr−O(4)	2.270(7)	2.269(3)		
Zr−Cl(1)	2.461(3)	2.4056(11)		
Zr−Cl(2)	2.433(3)	2.4705(13)		
Zr−Z(1)[a]			2.269	2.289
Zr−Z(2)[a]			2.251	2.292
O(1)−C	1.376(1)	1.361(4)	1.349(3)	1.369(8)
O(2)−C	1.365(1)	1.361(4)	1.361(3)	1.370(7)
O(1)−Zr−O(2)	91.5(2)	89.1(1)	93.4(8)	95.3(2)
Cl(1)−Zr−Cl(2)	166.0(1)	91.3(1)		
Z(1)−Zr−Z(2)[a]			123.3	125.5
Zr−O(1)−C	134.0(5)	138.1(2)	136.9(2)	126.3(4)
Zr−O(2)−C	135.7(6)	136.6(2)	117.1(2)	126.1(4)
C−O(1)- -O(2)−C	54.5	51.2	59.9	65.6

[a] Z(1) and Z(2) are the centroids of the indenyl C_5-rings.

2. Reactions with *ansa*-Bis(indenyl) Magnesocenes. To study transformations of the biphenolate complexes **1a**, **1b**, and **1c** to chiral *ansa*-zirconocenes, we have initially chosen as reaction partners the conveniently available and well-characterized *ansa*-magnesocenes *rac*-C_2H_4(Ind)$_2$Mg(THF)$_2$ and *rac*-Me$_2$Si-(Ind)$_2$Mg(THF)$_2$.[13] When complex **1a** was reacted with *rac*-C_2H_4(Ind)$_2$Mg(THF)$_2$ for 2 days in toluene solution at room temperature, ^{1}H NMR spectra of the reaction mixture showed that the reactants were completely consumed under formation of a single, apparently C_2-symmetric reaction product. Due to its high solubility even in nonpolar solvents, this reaction product proved difficult to isolate by crystallization. Partial evaporation of the solvent finally gave a crop of yellow-green crystals, the elemental analysis and ^{1}H NMR spectrum of which document the presence of the pure *rac*-isomer of C_2H_4(Ind)$_2$Zr(3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate) (**2a**). While **2a** was thus isolated in only 19% yield, NMR data of the crude mixture indicate that **1a** is completely transformed to **2a** according to the reaction represented in Scheme 2.

Reaction of complex **1b** with *rac*-C_2H_4(Ind)$_2$Mg(THF)$_2$ for 2 days at room temperature in toluene similarly gave complete conversion of the reactants to the racemic *ansa*-zirconocene complex C_2H_4(Ind)$_2$Zr(3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate) (**2b**) as indicated by the ^{1}H NMR spectrum of the sole product. Even though **2b** is likewise highly soluble in hydrocarbon solvents, crystallization from hexane at −30 °C allowed isolation of the product in 62% yield in the form of a yellow powder. Platelet-shaped crystals were obtained by recrystallization from a concentrated toluene solution.

A diffractometric structure determination of complex **2b** (Table 1, Figure 2) revealed a geometry which deviates slightly from C_2-symmetry, in that the lines

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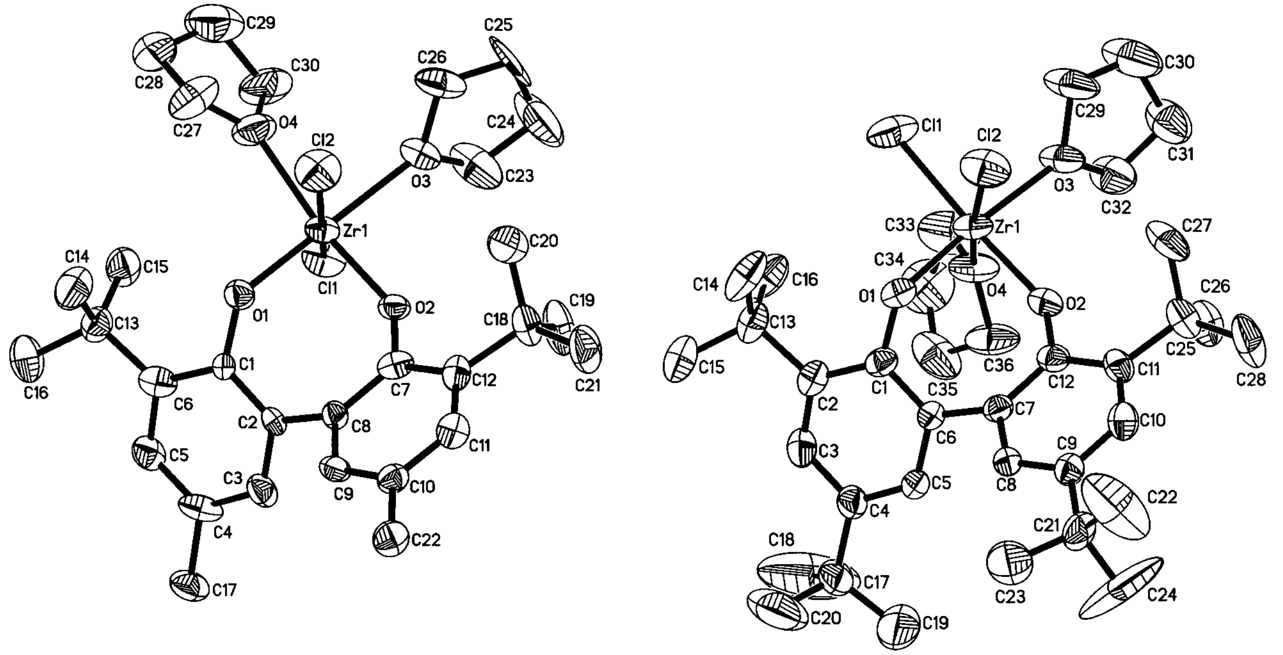
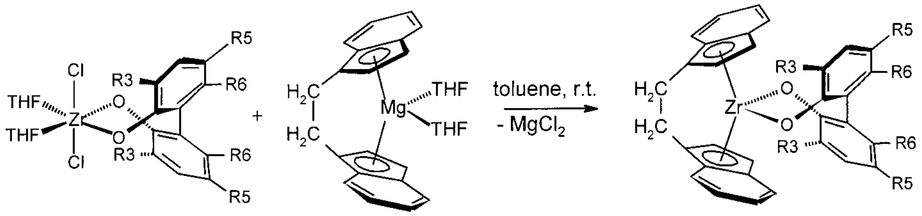


Figure 1. Molecular structure of **1b** (left) and of **1c** (right). Thermal ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity.

Table 2. ^1H NMR Shifts for Complexes 1a, 1b, and 1c (C_6D_6, 250 MHz, 298 K)

1a-maj	**1a**-min	**1b**	**1c**	assignment
7.08 (d, 2H)	7.24 (d, 2H)	7.26 (d, 2H); ^4J(2.17 Hz)	7.57 (d, 2H); ^4J(2.5 Hz)	C_6H_2
6.82 (d, 2H)	6.74 (d, 2H)	7.04 (d, 2H); ^4J(2.02 Hz)	7.32 (d, 2H); ^4J(2.5 Hz)	C_6H_2
4.35 (b)		4.06 (b, 8H)	4.10 (b, 8H)	THF
3.40 (m, 2H)				$(CH_3)_2CH$
1.95 (s, 6H)	1.87 (s, 6H)	2.21 (s, 6H)		CH_3
		1.75 (s, 18H)	1.78, 1.32 (s, 18H)	$C(CH_3)_3$
1.14 (b)		1.07 (b, 8H)	1.31 (b, 8H)	THF
1.14, 1.29 (d, 6H)	1.24 (d, 6H)			$(CH_3)_2CH$

Scheme 2



1a,b **2a,b**

a: R3 = ^{i}Pr; R5 = H; R6 = Me
b: R3 = ^{t}Bu; R5 = Me; R6 = H

connecting the Zr center with the midpoints of the C_2H_4 bridge and the biphenolate unit are not quite collinear. The seven-membered Zr-biphenolate chelate ring has a twisted geometry similar to that in **1b**. The C21−O1- - O2−C32 dihedral angle (59.9°) is widened, however, from the value found in **1b** (54.5°), presumably due to steric repulsion between the $C_2H_4(Ind)_2$ framework and the *tert*-butyl groups at the biphenolate ligand. The Zr−Cp centroid distances (2.269, 2.251 Å) and the centroid−Zr−centroid angle (123.3°) are comparable to those in *rac*-$C_2H_4(Ind)_2ZrCl_2$,[14] and the O1−Zr−O2 angle (93.4°) is similar to that found in previously studied *ansa*-bis(indenyl) zirconium binaphtholate derivatives.[7,15] The five-membered chelate ring including the ethano bridge assumes the λ-1R,1′R conformation in complex **2b**, which places the indenyl rings in a "backward" orientation. This rather unusual conformation[14,16] is apparently caused by repulsive contacts between the indenyl C(16)H and C(7)H groups and the *tert*-butyl methyl groups which would arise in the normally preferred "forward" configuration. Similar interligand repulsions, to be expected in a stereoisomer

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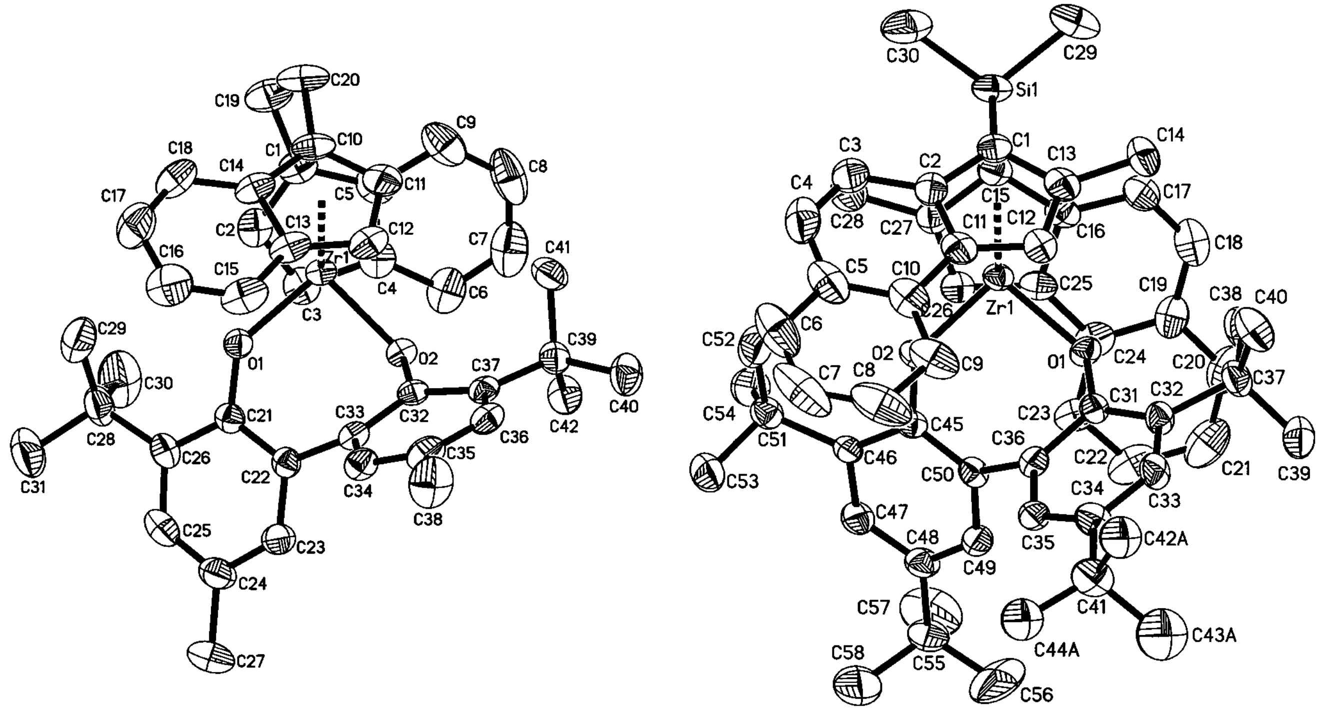

Figure 2. Molecular structure of *rac*-**2b** (left) and of *rac*-**6c** (right). Thermal ellipsoids drawn at the 50% probability level, hydrogen atoms and disordered *tert*-butyl C atoms C42B, C43B, and C44B of *rac*-**6c** omitted for clarity.

of **2b** with *meso*-oriented indenyl rings,[16,17] are likely to cause the exclusive formation of the axially symmetric isomer of complex **2b**.

When $Me_2Si(Ind)_2Mg(THF)_2$[18] was reacted with (3,3′-$^tBu_2$-5,5′-Me_2-1,1′-bi-2-phenolate)$ZrCl_2(THF)_2$ (**1b**), substantial fractions of the reactants were still detected by ^1H NMR even after 4 days at room temperature, with only minor signals assignable to the expected product *rac*-$Me_2Si(Ind)_2Zr$(3,3′-$^tBu_2$-5,5′-Me_2-1,1′-bi-2-phenolate) (**3b**). Longer reaction times lead to the appearance of signals of the protonated ligand. Analogous reactions of $Me_2Si(2\text{-}Me\text{-}Ind)_2Mg(THF)_2$[18] with **1b** in toluene did not go to completion either, even after 8 days at room temperature. The reaction mixtures gave rise to minor ^1H NMR signals assignable to the product *rac*-$Me_2Si(2\text{-}Me\text{-}Ind)_2Zr$(3,3′-$^tBu_2$-5,5′-$Me_2$-1,1′-bi-2-phenolate) (**4b**) but predominantly again to those of the hydrolyzed ligand. Apparently, the driving force for the formation of the rather severely strained Me_2Si-bridged zirconocene complexes from their structurally more flexible magnesocene precursors is not sufficient for an efficient conversion, such that side reactions, e.g., proton abstraction from Zr-coordinated THF,[19] become prevalent.

3. Reactions of 1c with Me_2Si-Bridged Bis(indenyl) Dilithium Salts. To exploit the more polar nature and higher reactivity of indenyl-lithium compounds for the synthesis of Me_2Si-bridged zirconocene complexes, we prepared the dilithium salts $Me_2Si(Ind)_2Li_2$, $Me_2Si(2\text{-}Me\text{-}Ind)_2Li_2$, $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2Li_2$, and Me_2Si(2-Me-benz[*e*]Ind)$_2Li_2$ by reaction of the neutral ligands with 2 equiv of BuLi.[20,21] Reaction of complex **1c** with $Me_2Si(Ind)_2Li_2$ for 3 h at room temperature in a toluene/THF mixture gave complete conversion of the reactants to the racemic *ansa*-zirconocene complex $Me_2Si(Ind)_2Zr$(3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenolate) (**3c**, Scheme 3), as indicated by the ^1H NMR spectrum of the reaction mixture. After separating the orange solution from the LiCl precipitate by filtration and evaporating the solvent under reduced pressure, the pure racemic isomer **3c** was isolated as a yellow powder in 65% yield.

When $Me_2Si(2\text{-}Me\text{-}Ind)_2Li_2$ was reacted at room temperature with (3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenolate)$ZrCl_2(THF)_2$ (**1c**) in C_6D_6/THF or C_6D_6/DME in a NMR tube, the ^1H NMR spectra showed that $Me_2Si(2\text{-}Me\text{-}Ind)_2Zr$(3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenolate) (**4c**) is cleanly formed after 30 min. Surprisingly, the C_2-symmetric isomer was not the only product of this reaction. Instead, both diastereomers of complex **4c** were formed in a *rac:meso* ratio of 3:7, as indicated by three singlets in the Me_2Si region at 0.79, 0.89, and 1.12 ppm with an 1:0.9:1 integral ratio. Upon heating the reaction mixture to 80 °C, the *rac:meso* ratio changed after 1.5 h toward a *rac: meso* ratio of ca. 3:1 without indication of decomposition (1,1,2,2-tetrachloroethane used as internal reference). After another 1 h, a *rac:meso* ratio of ca. 16:1 was reached, which then remained constant. When the scale of the reaction was increased, the time for the *rac*−*meso* isomerization at 80 °C was increased to ca. 5 h but

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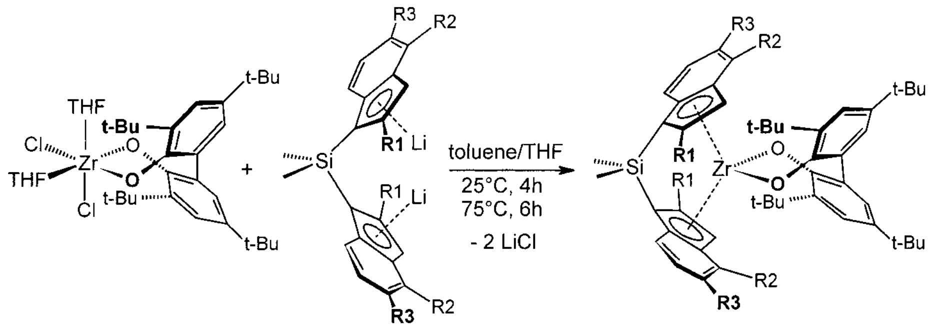
Scheme 3



1c

3c, R1=R2=R3=H
4c, R1=Me; R2=R3=H
5c, R1=Me, R2=Ph, R3=H
6c, R1=Me; R2, R3=Benz[e]

yielded complex **4c** in the same final isomer ratio as before. Filtration of the bright yellow solution from the LiCl precipitate, evaporation of the solvent under reduced pressure, extraction from the solid residue with pentane, and evaporation to dryness of the filtrate produced a yellow powder in 74% yield which was identified by ^{1}H NMR as pure *rac*-**4c**.

Analogous results were obtained when **1c** was reacted with $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2Li_2$. The reaction yielded, after 5 h at room temperature in toluene/THF solution, $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2Zr(3,3',5,5'\text{-}^tBu_4\text{-}1,1'\text{-}bi\text{-}2\text{-}phenolate)$ (**5c**) as a mixture of both diastereomers in a *rac:meso* ratio of 1:2. Upon heating to 80 °C, the isomer ratio changed continuously toward the racemic isomer. After ca. 7 h, a *rac:meso* ratio of ca. 16:1 was reached, which then remained constant.

Reaction of $Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2Li_2$ with **1c** in toluene/THF (or DME) gave, after 6 h at room temperature in toluene/THF solution, both diastereomers of $Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2Zr(3,3',5,5'\text{-}^tBu_4\text{-}1,1'\text{-}bi\text{-}2\text{-}phenolate)$ (**6c**) in a *rac:meso* ratio of 2:3. When a solution of complex **6c** in C_6D_6/THF (ca. 10:1) was heated in an NMR tube to 70 °C (internal reference: 1,1,2,2-tetrachloroethane), the isomer ratio changed very slowly toward the racemic isomer. The isomerization process was accelerated, however, when 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) was added to this mixture in a ratio of $[TEMPO]/[Zr] = 0.8$. After heating such a solution to 70−80 °C for only 1 h, it contained almost exclusively the *rac*-**6c** isomer, as indicated by its ^{1}H NMR spectrum (see Experimental Section).

Acceleration of related isomerization processes by TEMPO has been observed before.[22] It is indicative of a radical reaction mechanism in which TEMPO facilitates the release of a cylopentadienyl or indenyl ligand from the Zr center. Rotation and recoordination of this aromatic radical would then result in the observed *meso*-to-*rac* conversion.[23] From an analogous reaction on a preparative scale, pure *rac*-**6c** was isolated in 66% yield by crystallization from toluene. Crystals suitable for X-ray diffraction analysis were obtained when a toluene/THF (1:1) solution of complex *rac*-**6c** was kept at −15 °C for 1 day.

A diffractometric crystal structure determination of complex *rac*-**6c** (Table 1, Figure 2) revealed a geometry with approximate C_2-symmetry. The Zr−Cp centroid distances (2.289, 2.292 Å) are slightly larger and the centroid−Zr−centroid angle (125.5°) is slightly smaller than the respective values for *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]\text{-}Ind)_2ZrCl_2$ (average Zr−centroid = 2.247 Å, centroid−Zr−centroid = 127.9°). These deviations are indicative, again, of a mutual repulsion between the substituted bis(indenyl) and biphenolate ligands. An increased biphenolate dihedral C31−O1- -O2−C45 angle of 65.6°, compared to 51.2° found in **1c**, likewise indicates significant repulsion between the Me_2Si-bridged annulated indenyl ligands and the *tert*-butyl groups of the biphenolate unit in complex *rac*-**6c**. The twisted conformation of the seven-membered Zr-biphenolate chelate ring disfavors again a *meso*-configurated *ansa*-zirconocene structure and appears to cause the *rac* isomer to be the thermodynamically favored reaction product.

By reaction with methylaluminoxane (MAO), the zirconocene biphenolate complexes described above are directly converted to catalysts for the isospecific polymerization of propene which yield, under identical reaction conditions, activities and polymer properties equal to those obtained with customary catalyst systems, derived by activation with MAO from the respective zirconocene dichloride complexes.

Experimental Section

General Information. All manipulations were performed at an argon/vaccum manifold or in a glovebox under nitrogen atmosphere. Solvents were dried over sodium-benzophenone, degassed under reduced pressure, and stored under argon. 1,1,2,2-Tetrachloroethane used as internal reference in the NMR experiments was dried over CaH_2 and distilled before use. $C_2H_4(IndH)_2$,[24] $Me_2Si(IndH)_2$,[20] $Me_2Si(2\text{-}Me\text{-}indH)_2$,[20] $Me_2Si(2\text{-}Me\text{-}[benz]\text{-}IndH)_2$,[21] $Me_2Si(Ind)_2Li_2$,[20] $Me_2Si(2\text{-}Me\text{-}Ind)_2Li_2$,[20] $Me_2Si(2\text{-}Me\text{-}benz[e]\text{-}Ind)_2Li_2$,[21] $3,3'\text{-}^tBu_2\text{-}5,5'\text{-}Me_2\text{-}1,1'\text{-}bi\text{-}2\text{-}phenol$,[11] $3,3'\text{-}^iPr_2\text{-}6,6'\text{-}Me_2\text{-}1,1'\text{-}bi\text{-}2\text{-}phenol$,[11] and $3,3',5,5'\text{-}^tBu_4\text{-}1,1'\text{-}bi\text{-}2\text{-}phenol$[11] were prepared according to previous reports. Dibutylmagnesium for the preparation of *ansa*-magnesocene derivatives was purchased from Aldrich. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 250 or DRX 600 spectrometers. Proton and carbon resonances were assigned by ^{1}H NMR ROESY and HMQC techniques, respectively.

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(23) (a) Schmidt, K.; Reinmuth, A.; Rief, U.; Diebold, J.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 1724. (b) Miyake, S.; Henling, L. M.; Bercaw, J. E. *Organometallics* **1998**, *17*, 5528.

(24) Maréchal, E.; Chaintron, G. *Bull. Soc. Chim. Fr.* **1967**, 2954.

(3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (1a). To a solution of 2.75 g (9.23 mmol) of 3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenol in ca. 150 mL of THF was slowly added 0.443 g (18.46 mmol) of NaH. Excess H$_2$ gas pressure was allowed to escape via a bubbler. The slightly yellow suspension was heated for 24 h under reflux. After allowing the solution to come to room temperature, 3.8 g (10 mmol) of ZrCl$_4$(THF)$_2$ was added, and the reaction mixture was further heated for 12 h under reflux. The suspension was filtered from the white precipitate, presumably NaCl, and washed with THF, and the solvent was removed ander reduced pressure to yield a white foam. Addition of ca. 40 mL of Et$_2$O initially gave a nearly clear solution, from which a white precipitate was formed after several minutes. The precipitate was isolated by filtration, washed with small amounts of Et$_2$O, and dried in vacuo to yield 2.67 g (47%) of (3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate)-ZrCl$_2$(THF)$_2$ (**1a**). Concentration of the mother liquor and cooling to −30 °C for several days yielded an additional crop of 1.17 g (23%). ^{1}H NMR spectra: see Table 2. Anal. Calcd for C$_{28}$H$_{40}$Cl$_2$O$_4$Zr (602.74): C, 55.79; H, 6.69. Found: C, 55.69; H, 6.98.

3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (1b). Treatment of 3.27 g (10 mmol) of 3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate with 0.483 g (20 mmol) of NaH and then with 3.8 g (10 mmol) of ZrCl$_4$(THF)$_2$, under a protocol analogous to that described for **1a**, gave 5.05 g (80%) of (3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (**1b**). Single crystals suitable for an X-ray analysis were obtained from a THF solution covered by a hexane layer. ^{1}H NMR: see Table 2. Anal. Calcd for C$_{30}$H$_{44}$Cl$_2$O$_4$Zr (630.80): C, 57.12; H, 7.03. Found: C, 56.96; H, 7.04.

(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (1c). To a solution of 1.48 g (3.60 mmol) of 3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenol in 75 mL of Et$_2$O, precooled to 0 °C, was slowly added 4.6 mL (8.0 mmol) of a 1.6 M solution of n-BuLi in hexane. Excess gas pressure was allowed to escape via a bubbler. The yellow suspension was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the foamy yellow solid washed with cold hexane and dried under vacuum. To the resulting white powder, a solution of 1.39 g (3.7 mmol) of ZrCl$_4$(THF)$_2$ in 75 mL of THF was added. The reaction mixture was stirred for 12 h at room temperature and heated for a further 2 h under reflux. After allowing the resulting suspension to cool to room temperature, THF was removed under reduced pressure to yield a white foam. Addition of ca. 50 mL of Et$_2$O and filtration resulted in a clear solution, from which a white crystalline solid was isolated by filtration. This was then dried at 20 °C in vacuo to yield 4.47 g (84%) of (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (**1c**). ^{1}H NMR spectra: see Table 2.

C$_2$H$_4$(Ind)$_2$Zr(3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate) (2a). To a dry mixture of 0.459 g (1.08 mmol) of C$_2$H$_4$(Ind)$_2$Mg(THF)$_2$ and 0.65 g (1.08 mmol) of (3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate)-ZrCl$_2$(THF)$_2$ (**1a**) was added 30 mL of toluene. Stirring the mixture for 2 days at room temperature gave a yellow solution and a white precipitate, presumably MgCl$_2$(THF)$_2$. The solvent was removed under vacuum and hexane added to the residue. The resulting suspension was filtered, the MgCl$_2$(THF)$_2$ precipitate washed with hexane, and the combined filtrate concentrated under reduced pressure. Cooling this solution to −30 °C for several days yielded a yellow powderlike precipitate, which was isolated by decantation, washed with small amounts of cold hexane, and dried in vacuo to give 0.13 g (19%) of C$_2$H$_4$(Ind)$_2$Zr(3,3′-^{i}Pr$_2$-6,6′-Me$_2$-1,1′-bi-2-phenolate) (**2a**). Further concentration and cooling to −30 °C of the combined mother liquor and washing solution did not yield additional isolable complex. ^{1}H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 7.36, 6.71 (d, each 2H, $^3J_{\mathrm{HH}}$ 8.5 Hz; Ind-*H*7/7′, *H*4/4′); 7.15 (obscured by C$_6$D$_6$ signal), 6.80, (d, 2H, $^3J_{\mathrm{HH}}$ 7.6 Hz; biphenolate-*H*5/5′); 6.94, 6.87 (m, each 2H; Ind-*H*6/6′, *H*5/5′); 5.93, 5.53 (d, each 2H, $^3J_{\mathrm{HH}}$ 3.0 Hz; Ind-*H*2/2′, H3/3′); 3.23 (s, 4H, C$_2$*H*$_4$); 2.82 (sp, 2H $^3J_{\mathrm{HH}}$ 6.8 Hz biphenolate-C*H*Me$_2$); 1.91 (s, 6H; biphenolate-*Me*); 1.40, 1.16 (d, each 6H; $^3J_{\mathrm{HH}}$ 6.6 Hz, $^3J_{\mathrm{HH}}$ 7.1 Hz; biphenolate-CH*Me$_2$*). ^{13}C NMR (C$_6$D$_6$, 150 MHz, 298 K): δ 158.1 (biphenolate-*C*2/2′); 135.9, 132.8, 132.7 (biphenolate-*C*1/1′, -*C*3/3′, -*C*6/6′); 125.4, 125.4, 125.0, 120.4, 113.4, 103.5 (Ind-*C*5/5′, -*C*4/4′, -*C*6/6′, -*C*7/7′, -*C*2/2′, -*C*3/3′); 124.0, 121.5 (biphenolate-*C*4/4′, -*C*5/5′); 28.7 (*C*$_2$H$_4$); 26.8 (biphenolate-*C*HMe$_2$); 25.0, 21.2 (biphenolate-CH*Me$_2$*); 20.3 (biphenolate-*Me*). Anal. Calcd for C$_{40}$H$_{40}$O$_2$Zr (643.97): C, 75.06; H, 6.59. Found: C, 75.31; H, 7.48.

C$_2$H$_4$(Ind)$_2$Zr(3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate) (2b). Reaction of C$_2$H$_4$(Ind)$_2$Mg(THF)$_2$ (0.49 g, 1.15 mmol) with (3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (0.73 g, 1.15 mmol) as described above for **2a** (except with heptane instead of hexane used for recrystallization) gave 0.48 g (63%) of C$_2$H$_4$(Ind)$_2$Zr(3,3′-^{t}Bu$_2$-5,5′-Me$_2$-1,1′-bi-2-phenolate) (**2b**). ^{1}H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 7.41, 7.00 (d, each 2H, $^3J_{\mathrm{HH}}$ 8.3 Hz; Ind-*H*7/7′, *H4*/*4*′); 7.21, 6.80, (d, each 2H, $^4J_{\mathrm{HH}}$ 1.8 Hz; biphenolate-*H*4/4′ H6/6′); 6.97, 6.88 (m, each 2H; Ind-*H*6/6′, H5/5′); 6.0, 5.76 (d, each 2H, $^3J_{\mathrm{HH}}$ 3.0 Hz; Ind-*H*2/2′, H3/3′); 3.23 (m, 4H, C$_2$H$_4$); 2.18 (s, 6H; biphenolate-*Me*); 1.36 (s, 18H; biphenolate-^{t}*Bu*).^{13}C NMR (C$_6$D$_6$, 150 MHz, 298 K): δ 158.6, 134.6, 132.9, 130.2, 127.8, 127.5 (biphenolate-*C*2/2′, -*C*3/3′, -*C*6/6′, -*C*1/1′, *C*5/5′, *C*4/4′); 132.5, 126.1, 125.7, 125.3, 124.6, 121.0, 120.5, 115.6, 103.0 (Ind-*C*3a, -*C*5/5′, -*C*6/6′, -*C*4/4′, -*C*7a, -*C*1/1′, *C*7/7′, *C*2/2′, *C*3/3′); 35.4 (biphenolate-^{t}*Bu*); 31.9 (biphenolate-^{t}*Bu*); 29.1 (*C*$_2$H$_4$); 20.8 (biphenolate-*Me*). Anal. Calcd for C$_{42}$H$_{44}$O$_2$Zr (672.02): C, 75.06; H, 6.59. Found: C, 74.84; H, 7.02.

Me$_2$Si(Ind)$_2$Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (3c). Reaction of Me$_2$Si(Ind)$_2$Li$_2$ (0.43 g, 1.43 mmol) with (3,3′,5,5′-^{t}-Bu$_4$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (**1c**) (1.02 g, 1.43 mmol) as described above for **2a**, except that a 10:1 toluene/THF mixture was used as solvent for the reaction and a 10:3 toluene/hexane mixture for the recrystallization, gave 0.73 g (65%) of pure *rac*-Me$_2$Si(Ind)$_2$Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (*rac*-**3c**) as a yellow powder. ^{1}H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 7.56, 6.99, (d, each 2H, $^3J_{\mathrm{HH}}$ 8.4 Hz; Ind-*H*7/7′, *H*4/4′); 7.54, 7.10 (d, 2H, $^4J_{\mathrm{HH}}$ 2.4 Hz; biphenolate-*H*4/4′, *H*6/6′); 6.93, 6.87, (dd, each 2H, $^3J_{\mathrm{HH}}$ 8.4 Hz, $^3J_{\mathrm{HH}}$ 8.4 Hz; Ind-*H*6/6′; *H*5/5′); 6.25, 6.24 (d, each 2H, $^3J_{\mathrm{HH}}$ 9.0 Hz; Ind-*H*2/2′, *H*3′/3′); 1.38, 1.29 (s, each 18H; biphenolate-^{t}*Bu*); 0.81 (s, 6H; *Me$_2$*Si−). ^{13}C NMR (C$_6$D$_6$, 150 MHz, 298 K): δ158.9, 141.1, 135.6, 133.8, 130.5, 129.9, 129.4, 126.5, 126.4, 125.4, 123.6, 123.3, 119.1, 110.2, 94.8, (benz[*e*]Ind + *C$_{arom}$*-biphenolate); 35.7, 34.3, 31.9, 31.8, (biphenolate-^{t}*Bu*); −1.52, (*Me$_2$*Si−). EI-MS (70 eV): parent ion at *m*/*e* 782−791 with appropriate isotope ratios, and two main fragment ions corresponding to protonated biphenol (410) and *ansa*-bis(indene) ligands (288). Anal. Calcd for C$_{48}$H$_{58}$SiO$_2$Zr (786.30): C, 73.32; H, 7.43; Zr, 11.60. Found: C, 71.65; H, 7.71; Zr, 11.41.

Me$_2$Si(2-Me-Ind)$_2$Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (4c). A suspension of (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (**1c**) in ca. 20 mL of a 10:1 toluene/THF mixture, prepared in situ by reacting 1.50 g (4.0 mmol) of ZrCl$_4$(THF)$_2$ and 1.6 g (3.9 mmol) of (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)Li$_2$, is transferred via cannula to a suspension of Me$_2$Si(2-Me-Ind)$_2$Li$_2$ in ca. 20 mL of a 10:1 toluene/THF mixture, prepared in situ by mixing 1.23 g (3.9 mmol) of Me$_2$Si(2-Me-IndH)$_2$ and 3.2 mL (5.07 mmol) of a solution 1.6 M BuLi in toluene. Stirring the reaction mixture for 5 h at room temperature gave an orange solution and a white precipitate (LiCl). The mixture was then heated for 5 h to 70−80 °C. After cooling to room temperature, LiCl was removed by filtration. Evaporation of the filtrate to dryness in vacuo gave 2.38 g (74%) of pure *rac*-Me$_2$Si(2-Me-Ind)$_2$Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (**4c**). ^{1}H NMR (C$_6$D$_6$, 600 MHz, 298 K): *rac*-**4c**: δ 7.60, 7.26, (d, each 2H, $^3J_{\mathrm{HH}}$ 8.4 Hz; Ind-*H*7/7′, *H*4/4′); 7.49, 7.18, (d, each 2H, $^4J_{\mathrm{HH}}$ 2.4 Hz; biphenolate-*H*4/4′, *H*6/6′); 6.85, 6.77, (dd, each 2H, $^3J_{\mathrm{HH}}$ 8.4 Hz, $^3J_{\mathrm{HH}}$ 7.2 Hz; Ind-*H*6/6′, *H*5/5′); 5.83, (s, 2H; Ind-*H*3/3′); 2.21 (s, 6H; Ind-*Me*); 1.36, 1.33, (s, each 18H; biphenolate-^{t}*Bu*); 0.89

Table 3. Crystallographic Data for Complexes 1b, 1c, 2b, and 6c

	1b	**1c**	**2b**	**6c**
formula	$C_{30}H_{44}Cl_2O_4Zr$	$C_{36}H_{56}Cl_2O_4Zr$	$C_{42}H_{44}O_2Zr$	$C_{66}H_{82}O_4SiZr$
cryst color and form	colorless needles	colorless needles	yellow plates	yellow plates
cryst syst	tetragonal	monoclinic	triclinic	triclinic
space group	$P\bar{4}2_1c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	22.882(11)	13.504(3)	10.235(4)	12.765(4)
b [Å]	22.882(11)	15.494(3)	13.165(8)	15.036(5)
c [Å]	12.761(7)	18.227(2)	13.911(6)	15.733(5)
α [deg]	90	90	69.82(5)	95.162(17)
β [deg]	90	98.034(11)	78.45(3)	92.496(16)
γ [deg]	90	90	87.35(3)	104.998(13)
Z, V [Å^3]	8, 6681.5(58)	4, 3776.0(12)	2, 1723.2(14)	2, 2898.1(16)
cryst size [mm]	0.05 × 0.05 × 0.2	0.3 × 0.3 × 0.3	0.2 × 0.3 × 0.4	0.2 × 0.3 × 0.4
T [K], d_{calcd}, [g/cm^3]	235, 1.254	243, 1.342	252, 1.295	233, 1.213
μ [mm^{-1}], F(000)	0.518, 2640	0.471, 1608	0.353, 704	0.257, 1128
scan mode; θ range [deg]	$\omega/2\theta$, 1.8−22.5	ω, 2.0−26.0	ω, 1.6−27.0	ω, 1.3−25.0
reflns collected	9444	8536	9873	8767
ind reflns (R_{int})	4300 (7.90%)	7429 (2.77%)	7269 (3.49%)	8385 (4.91%)
no. of params; GOF(F^2)	334, 1.054	388, 1.009	406, 1.113	631, 1.029
$R(F)$,[a] $R_w(F^2)$[b]	5.91%, 17.47%	5.36%, 13.66%	4.10%, 11.13%	7.86%, 19.64%
weighting scheme:[a,b]	0.0778, 0	0.0517, 3.63	0.0315, 2.54	0.0724, 7.06
largest diff peak [e$^-$/Å^3]	0.755	0.603	0.966	0.659
abs corr	Ψ-scan	none	none	Ψ-scan
Flack x-param	0.00(10)			

[a] Observed data ($I > 2\sigma(I)$). [b] All data, weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (F_o^2 + 2F_c^2)/3$.

(s, 6H; *Me*$_2$Si−). *meso*-**4c**: 7.56, 7.41, 6.97 (d, 1H, biphenolate), 7.8, 7.56, 7.23, 7.60, (Ind) 2.34, (s, 6H, 2-*Me*-Ind); 1.70, 1.53, 1.28, 0.80 (s, 9H, biphenolate-^{t}*Bu*), 1.12, 0.79, (s, 3H, *Me*$_2$Si−). ^{13}C NMR (C_6D_6, 150 MHz, 298 K): δ 161.1, 141.2, 135.3, 134.8, 134.3, 131.8, 130.9, 129.7, 126.0, 126.8, 124.9, 123.3, 121.8, 111.6, 92.4 (Ind; C_{arom}-biphenolate); 34.3, 32.5, 32.1, 31.8 (biphenolate-^{t}*Bu*); 18.8 (Ind-*Me*); 2.55 (*Me*$_2$Si−).

Recrystallization of this foamy orange solid from hexane or pentane gave 0.70 g (22%) of complex *rac*-**4c** as a yellow microcrystalline powder. EI-MS (70 eV): parent ion at *m*/*e* 812−821 with appropriate isotope ratios and two fragment ions corresponding to protonated biphenol (*m*/*e* 410) and *ansa*-bis(indene) ligands (*m*/*e* 316). Anal. Calcd for $C_{50}H_{62}SiO_2Zr$ (814.35): C, 73.74; H, 7.67; Zr, 11.20. Found: C, 73.64; H, 7.73; Zr, 11.06.

Me$_2$Si(2-Me-4-Ph-Ind)$_2$Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (5c). In a procedure similar to that described for complex **4c**, a suspension of (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (**1c**) in ca. 100 mL of a 10:1 toluene/THF mixture, prepared in situ by reacting 4.0 g (10.70 mmol) of ZrCl$_4$THF$_2$ and 4.39 g (10.69 mmol) of Li$_2$(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-biphenolate)), is transferred via cannula to a suspension of Me$_2$Si(2-Me-4-Ph-Ind)$_2$Li$_2$, prepared in situ by mixing 4.9 g (10.49 mmol) of Me$_2$Si(2-Me-4-Ph-IndH)$_2$ in ca. 70 mL of a 10:1 toluene/THF mixture with 13.7 mL (21.9 mmol) of a 1.6 M solution of n-BuLi. The resulting orange suspension was stirred for 5 h at room temperature and heated to 95 °C for another 7 h. After removal of the LiCl by filtration, the product was isolated by crystallization from a toluene solution at room temperature to give, after several days, 6.7 g (60%) of pure *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$Zr (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (*rac*-**5c**). ^{1}H NMR (C_6D_6, 25 °C, 600 MHz): δ 7.75 (d, 2H, $^3J_{HH}$ 8.5 Hz; Ind-*H*7/7′); 7.42 (d, 2H, $^4J_{HH}$ 3.0 Hz, biphenolate-*H*4/4′); 7.31, (d, 4H, $^3J_{HH}$ 7.2 Hz; Ind-C$_6$*H*$_5$ (*H*$_o$/*H*$_o$′)); 7.07 (dd, 4H, $^3J_{HH}$ 7.2 Hz, $^3J_{HH}$ 7.2 Hz; Ind-C$_6$*H*$_5$ (H$_m$/H$_m$′)); 7.01, (m, 4H, Ind-*H*6/6′ and Ind-C$_6$*H*$_5$ *H*$_p$/*H*$_p$′); 6.97 (d, 2H, $^3J_{HH}$ 6.6 Hz; Ind-*H*5/5′); 6.49 (d, 2H, $^4J_{HH}$ 3.0 Hz, biphenolate-*H*6/6′); 6,34 (s, 2H; Ind-H3/3′); 2.26 (s, 6H; 2-*Me*-Ind); 1.31, 1.26 (s, each 18H; biphenolate-^{t}*Bu*); 0.99 (s, 6H; *Me*$_2$Si−). ^{13}C NMR (C_6D_6, 25 °C, 150 MHz): δ 111.4, 127.3, 125.6, 122.9 (Ind-C3, -C5, -C6, -C7;); 123.41, 130.9 (biphenolate-C4, -C6); 128.6, 127.5, 128.9 (C$_o$, C$_m$, C$_p$, Ind-Ph); 93.4, 130.3, 131.5, 134.2, 135.1, 135.5, 137.2, 140.6, 141.2, 160 (Ind; biphenolate); 35.9, 34.3, 33.1, 31.9 (biphenolate-^{t}*Bu*); 19.1 (2-*Me*-Ind); 2.5 (*Me*$_2$Si−). EI-MS (70 eV): parent ion at *m*/*e* 964−974 with appropriate isotope ratios. Anal. Calcd for $C_{58}H_{66}SiO_2Zr$ (1058.66): C, 78.65; H, 7.59. Found: C, 78.28; H, 7.42.

Me$_2$Si(2-Me-benz[*e*]ind)$_2$Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (6c). In a procedure analogous to that described for complexes **4c** or **5c**, a suspension of (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)ZrCl$_2$(THF)$_2$ (**1c**) in toluene/THF, prepared in situ by reacting 1.62 g (4.30 mmol) of ZrCl$_4$THF$_2$ and 1.77 g (4.20 mmol) of (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)Li$_2$, is added via a cannula to a suspension of Me$_2$Si(2-Me-benz[*e*]ind)$_2$Li$_2$, prepared in situ by slow addition of 3.15 mL (5.04 mmol) of a toluene solution in 1.6 M BuLi to a stirred solution of 1.75 g (4.20 mmol) of Me$_2$Si(2-Me-benz[*e*]IndH)$_2$ in a 10:1 toluene/THF mixture. Stirring for 5 h at room temperature gave an orange solution and a white precipitate (LiCl). After removal of the LiCl by filtration, the mixture was heated to 70−80 °C in the presence of TEMPO (0.52 g, 3.36 mmol; [TEMPO]/[Zr] = 0.8) for 1 h. After allowing the mixture to cool to room temperature, the product was isolated by crystallization from toluene solution at room temperature to give, after several days, 2.55 g (66%) of pure *rac*-Me$_2$Si(2-Me-benz[*e*]ind)$_2$Zr-(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (*rac*-**6c**). ^{1}H NMR (chloroform-d_1, 600 MHz, 298 K): *rac*-**5c**: δ 7.62, 7.19, (d, each 2H, $^3J_{HH}$ 8.5 Hz; benz[*e*]Ind-*H*8/8′, *H*9/9′); 7.47 (d, 2H, $^3J_{HH}$ 7.8 Hz, benz[*e*]Ind-*H*7/7′); 7.11, 6.24, (d, each 2H, $^4J_{HH}$ 2.5 Hz; biphenolate-*H*4/4′, *H*6/6′); 7.10 (dd, 2H, $^3J_{HH}$ 7.8 Hz, $^3J_{HH}$ 7.3 Hz; benz[*e*]Ind-*H*6/6′); 6.95, (dd, 2H, $^3J_{HH}$ 7.9 Hz, $^3J_{HH}$ 7.3 Hz; benz[*e*]Ind-*H*5/5′); 6.65 (d, 2H, $^3J_{HH}$ 7.9 Hz; benz[*e*]Ind-*H*4/4′); 6.34 (s, 2H; benz[*e*]Ind-*H*3/3′); 2.63 (s, 6H; 2-*Me*-benz[*e*]Ind); 1.38 (s, 6H; *Me*$_2$Si-); 1.28, 1.02 (s, each 18H; biphenolate-^{t}*Bu*).^{1}H NMR (chloroform-d_1, 600 MHz, 298 K) *meso*-**6c**: δ 7.79, 7.52, 7.25, (d, each 2H, benz[*e*]Ind), 7.40, 6.52, 6.48, 6.21, (d, each 1H, biphenolate); 7.25, 6.61, (dd, each 2H, benz[*e*]Ind); 6.65 (s, 2H, benz[*e*]Ind); 2.68, (s, 6H, 2-*Me*-benz[*e*]Ind); 1.70, 1.38, 1.22, 0.10 (s, each 9H, biphenolate-*t*-Bu), 1.54, 1.24, (s, each 3H, *Me*$_2$Si). ^{13}C NMR (chloroform-d_1, 150 MHz, 298 K) rac-**6c**: δ 158.1, 139.1, 133.3, 133.1, 131.8, 131.6, 130.1, 128.9, 128.2, 127.6, 127.2, 126.4, 125.6, 124.1, 124.0, 121.2, 110.8, 97.3 (benz[*e*]Ind; C_{arom}-biphenolate); 35.3, 34.0, 33.1, 31.8 (biphenolate-^{t}*Bu*); 19.1 (2-*Me*-benzInd); 2.9 (*Me*$_2$Si−). EI-MS (70 eV): parent ion at *m*/*e* 906−915 with appropriate isotope ratios. Anal. Calcd for $C_{58}H_{66}SiO_2Zr$ (914.47): C, 76.18; H, 7.27; Zr, 9.97. Found: C, 75.99; H, 7.09; Zr, 9.83.

Crystal Structures. X-ray diffraction analysis was carried out on a Siemens P4 four-circle diffractometer using Mo Kα radiation (71.073 pm) and a graphite monochromator. Crystal decay was monitored by measuring three standard reflections every 100 reflections. Structures were solved using direct methods (Sheldrick, G. M. *SHELXS-86*; University of Göttingen: Göttingen, Germany, 1986). All non-hydrogen atoms were refined anisotropically by least-squares procedures based on F^2 with exception of the disordered atoms in **6c** (one *tert*-butyl group, one noncoordinating THF molecule), which were refined isotropically. Hydrogens were refined on calculated positions with fixed isotropic *U*, using riding model techniques (Sheldrick, G. M. *SHELXL-93* (**1b**, **1c**, **2b**), *SHELXL-97* (**6c**), Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1993 and 1997). Details of the X-ray diffraction analysis are given in Table 3. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 164857-164860. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Polymerization Studies. In a Schlenk vessel, 1.5 μmol (1.22 mg) of complex **4c** was incubated with 1.2 mL of a 10 wt % solution of MAO in toluene for 5 min. This solution was then transferred to a 1 L autoclave containing another 3.8 mL of the MAO solution and 400 mL toluene at 50 °C ([Al]:[Zr] = 5000:1). Exposure to propene at 2 bar for 45 min, subsequent quenching with MeOH/HCl, and drying gave 22.1 g of polypropene with an isotacticity of 84% [mmmm]. Identical experiments with 1.5 μmol of $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ instead of complex **4c** gave 18.6 g of polypropene with an isotacticity of 82% [mmmm]. Extension of the incubation times to 45 min left the product yields (20.8 and 18.7 g, respectively) practically unchanged.

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Supporting Information Available: Details of crystal structure determinations, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles of complexes **1b**, **1c**, **2b**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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