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The Role of Torsional Isomers of Planarly Chiral Nonbridged Bis(indenyl)metal Type Complexes in Stereoselective Propene Polymerization

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Abstract: Reaction of enantiomerically pure (1-neomenthylindenyl)lithium with ZrCl$_4$(THF)$_2$ gave the three diastereomeric bis(1-neomenthylindenyl)zirconium dichloride complexes **4a-A**, **-B**, and **-C**, in a 93:2:5 ratio. Similarly, a 82:7:11 mixture of the three bis(1-neoisomenthylindenyl)zirconium dichloride diastereoisomers (**4b-A,B,C**) was obtained from (1-neoisomenthylindenyl)lithium and the zirconium tetrachloride–bis(tetrahydrofuran) adduct. Recrystallization from methylene chloride furnished the (optically active) pure diastereomers **4a-A** and **4b-A**, respectively. Catalytic hydrogenation (PtO$_2$, 50–60 bar of H$_2$, CH$_2$Cl$_2$) converted them into the pure (p-*S*, p-*S*)-bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (**5a-A**) and (p-*R*,p-*R*)-bis(1-neoisomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (**5b-A**) complexes. All four metallocenes were characterized by X-ray crystal structure analyses. Complex **4a-A** crystallizes in space group $P2$ with cell parameters a = 10.510(1) Å, b = 6.975(1) Å, c = 12.421(1) Å, β = 108.18(1)°, Z = 1, R = 0.037, R_w = 0.041; **4b-A** $P2_1$, a = 7.559(2) Å, b = 9.046(2) Å, c = 25.015(3) Å, β = 96.72(1)°, Z = 2, R = 0.037, R_w = 0.040; **5a-A** $P2_12_12$, a = 15.422(1) Å, b = 18.716(1) Å, c = 7.118(1) Å, Z = 2, R = 0.062, R_w = 0.074; **5b-A** $P2_12_12$, a = 10.103(1) Å, b = 26.626(5) Å, c = 6.762(1) Å, Z = 2, R = 0.030, R_w = 0.037. Complexes **4a-A**, **5a-A**, and **5b-A** exhibit C_2-symmetric bent metallocene conformations in the crystal which are characterized as having the bulky terpenyl substituents oriented antiperiplanarly toward the lateral sectors of the bent metallocene wedge ("bis-lateral:anti" conformation). In contrast, the bis(neoisomenthylindenyl)zirconium dichloride complex **4b-A** has only one hydrocarbyl substituent arranged laterally whereas the other is oriented to the open front side of the metallocene backbone (C_1-symmetric "central,lateral:gauche" conformation). In solution the conformational behavior of these complexes is different. By dynamic temperature-dependent ^{1}H and ^{13}C NMR spectroscopy both neoisomenthyl-substituted complexes **4b-A** and **5b-A** appear as single C_2-symmetric species in solution. In contrast, the neomenthyl-substituted complexes **4a-A** and **5a-A** exhibit equilibrating conformational mixtures. In the case of the (p-*S*,p-*S*)-bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride system (**5a-A**) it was shown that two conformational isomers are present in a ca. 80:20 ratio. These are C_2- (major isomer) and C_1-symmetric (minor isomer) and probably correspond to the "bis-lateral:anti" and "central,lateral:gauche" conformational types, respectively, that were identified by X-ray diffraction in the crystal. These conformational properties seem to determine the outcome of the stereoselective propene polymerization to a considerable extent, which was carried out at homogeneous bent metallocene/methylalumoxane Ziegler-type catalysts derived from the complexes **4** and **5**. Both neoisomenthyl-substituted systems produce isotactic high molecular weight polypropylene with purely enantiomorphic site control at low temperature. The isomeric neomenthyl-substituted systems are much less stereoselective. It is assumed that the bis(1-neomenthyltetrahydroindenyl)zirconium catalyst switches back and forth between the C_2- and C_1-symmetric conformations of the bent metallocene backbone during the catalytic process, thereby probably giving rise to the formation of alternating isotactic and near to atactic sequences along the growing polymer chain.

The serendipitous discovery of the extremely active group 4 bent metallocene/alumoxane catalysts has led to remarkable world-wide research activities in homogeneous catalytic α-olefin polymerization. The majority of this work has been carried out with the *ansa*-metallocene-derived catalyst systems, since Brintzinger, Kaminsky, Ewen, and others have demonstrated that such bridged metallocene/alumoxane catalysts produce highly isotactic or syndiotactic polypropylene at very high reaction rates.[1-3]

In an "enantiomorphic site controlled" process the chirality information of the racemic *ansa*-metallocene backbone is being transferred onto the growing polymer chain repeatedly and uniformly in each single carbon–carbon bond forming step. The intrinsic chirality information of each catalytically active transition metal center originates from the specific mode of attachment of the group 4 metal atom to the enantiotopic *re* or *si* faces of the planarly prochiral 1-substituted indenyl ligand moieties. A *re*,*re* or *si*,*si* combination then produces the racemic *ansa*-metallocene complex whereas the respective *re*,*si* attachment leads to the formation of its achiral meso diastereoisomer. Thus the intrinsic chirality properties of the group 4 *ansa*-bent metallocene complexes frequently used as components of stereoselective homogeneous α-olefin polymerization catalysts are not originating

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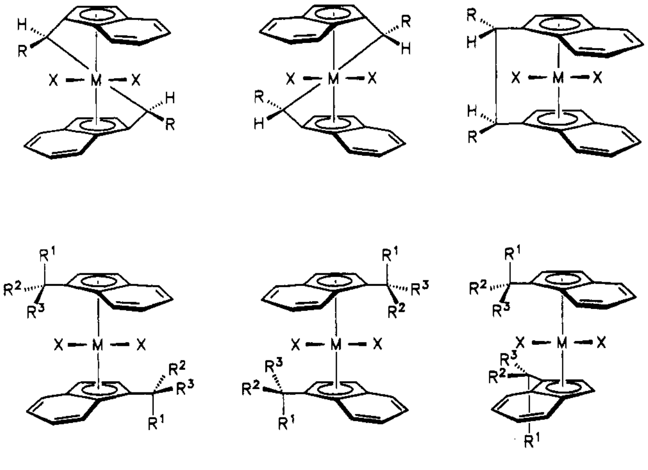
Scheme I



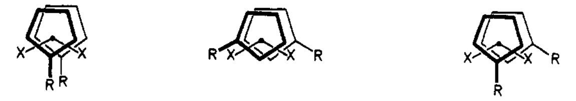
R*,p-R*,p-R*,R* ("racem-like-**A**") R*,p-S*,p-S*,R* ("racem-like-**B**") R*,p-R*,p-S*,R* ("meso-like-**C**")

from and are not even directly related to the rigid hydrocarbyl (or silyl) bridge between the indenyl ligands. Therefore, a completely analogous stereochemical configurational situation is obtained when two 1-hydrocarbyl-substituted indenyl or 4,5,6,7-tetrahydroindenyl ligands are attached, e.g. to a $\mathrm{ZrX_2}$ unit, similarly yielding a set of meso and racemic diastereoisomers.

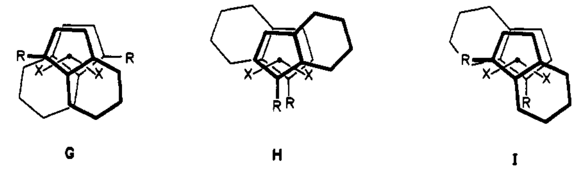
Further stereochemical labeling necessarily has equivalent consequences in both series of metallocene complexes, i.e. is independent whether they belong to the open nonbridged or the ligand-bridged *ansa*-metallocene series. To illustrate this point let us assume that two alkyl substituents become attached to the α-positions of the ethylene bridge in the [(ethylene)(1-indenyl)$_2$]-$\mathrm{MX_2}$ system in such a way that two new homochiral centers are created. Inspection of the overall stereochemical situation then reveals the possible formation of three diastereomeric metallocene complexes, all being chiral. The same situation ensues when homochiral substituents are attached at the 1-positions of each indenyl ligand in an open nonbridged metallocene. As in the *ansa*-metallocene series this leads to the occurrence of three chiral nonbridged metallocene diastereomers characterized by a combination of relative configurational descriptors *R**,p-*R**,p-*R**,*R** ("racemic-like A"), *R**,p-*S**,p-*S**,*R** ("racemic-like B"), and *R**,p-*R**,p-*S**,*R** ("meso-like C") (see Scheme I). We have recently described such a chiral nonbridged bent metallocene system, namely bis[(3-cholestanyl)indenyl]zirconium dichloride, and shown the ability of the major "racemic-like" isomer to serve as a component in an active homogeneous metallocene/alumoxane catalyst system for the production of highly isotactic polypropylene.[4]

However, there remains a fundamental difference between the bridged and nonbridged metallocene systems. The ansa-metallocenes typically used for stereoselective olefin polymerization are very rigid molecules.[5] Torsional deformation of the bent metallocene backbone is severely limited. They are characterized by very steep torsional potentials which effectively restrict even small rotations about the metal–Cp vector. In contrast, the open, nonbridged bent metallocenes possess extremely low torsional energy barriers. Rotation about the metal–η^5-indenyl vector is almost unhindered. To our knowledge "freezing" of the metal–indenyl rotation of a bis(indenyl)$\mathrm{MX_2}$-type bent metallocene complex in solution had not been achieved prior to this study (see below).[6]

Scheme II



D ("bis-central: syn") **E** ("bis-lateral: anti") **F** ("cental, lateral: gauche")



G **H** **I**

Thus the interconversion of torsional isomers of substituted bent metallocene complexes $(\mathrm{RCp})_2\mathrm{MX}_2$ and (R-indenyl)$_2\mathrm{MX}_2$ can take place freely. There is substantial evidence for the occurrence of three basic types of $(\mathrm{RCp})_2\mathrm{MX}_2$ rotamers, which can be characterized according to their relative substituent positions by the descriptors "bis-central:syn" (**D**), "bis-lateral: anti" (**E**), and "central,lateral:gauche" (**F**). It is known that small primary alkyl substituents (methyl, benzyl) at the Cp rings favor population of the "bis-central:syn" conformer whereas bulky *tert*-alkyl groups R are found to occupy the substituent positions of the "bis-lateral:anti" torsional isomer. There is evidence that the three conformational $(\mathrm{RCp})_2\mathrm{MX}_2$ isomers are close in energy when R is secondary alkyl and hence all three bent metallocene rotational conformations tend to be populated.[7] The same trends seem to apply for each of the respective *rac*-(R-indenyl)$_2\mathrm{MX}_2$ systems.[8] The idealized geometries of the three respective torsional isomers are depicted in Scheme II. Two of these (**G**, **H**) are of C_2 symmetry and have their annulated six-membered rings oriented both toward the front or the lateral sides of the bent metallocene wedge, respectively, whereas the third conformer (**I**) has one six-membered ring up front and the other oriented laterally and therefore is of lower overall symmetry (C_1).

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Table I. Selected ^{13}C NMR Data of the Indenyl-Derived Frameworks of the Complexes **4** and **5**[a]

complex	C(1)	C(2)	C(3)	C(4),C(7)	C(5),C(6)	C(8),C(9)
4a-A	126.2	122.5	98.0	126.1,125.8	125.1,124.5	128.5,126.7
4b-A	123.7	118.9	95.7	127.0,125.7	125.0,124.6	132.4,128.5
5a-A	130.1	108.9	102.0	24.4,[b]22.5,22.1[c]		137.3,135.3
5b-A	127.7	105.8	102.6	24.5,23.5,22.6,21.8[c]		138.6,135.8

[a] In CDCl$_3$, chemical shifts relative to TMS, δ-scale. [b] Double intensity. [c] C(4)–C(7) sequence not assigned.

Since the chirality information of the bent metallocene backbone is thought to be an important factor in determining the degree of stereoselectivity achieved at the homogeneous ((*R*)-indenyl)$_2$MX$_2$/alumoxane catalyst, it is essential to know and influence the population of the symmetrically different conformational types of the respective planarly chiral bis(indenyl)metal complex systems. We have prepared and characterized a series of bis(indenyl)- and bis(tetrahydroindenyl)zirconium complexes bearing neomenthyl or neoisomenthyl substituents at the 1-positions of the respective π-ligands. For some of these complexes information about the torsional isomers present in solution was obtained which can potentially be related to the effectiveness of transferring these bent metallocenes' stereochemical information onto the growing polypropylene chain during CC coupling in the catalytic process.

Results and Discussion

Synthesis of the Chirally Substituted Metallocene Complexes. We have attached chiral substituents derived from the terpene chiral pool at the 1-positions of the η^5-indenyl and η^5-tetrahydroindenyl ligands. A synthetic route was employed that closely followed the methods used by Kagan et al. for the preparation of terpenylcyclopentadienyl metal complexes.[9]

(–)-Menthol (i.e. 1*R*,2*S*,5*R* configurated 2-isopropyl-5-methylcyclohexanol) was converted to (–)-menthyl tosylate (**1a**). This was subjected to S_N2 substitution with indenyllithium to give 3-neomenthylindene (**2a**, 1′*S*,2′*S*,5′*R* configuration at the chiral substituent) in 37% yield. The hydrocarbon **2a** was treated with methyllithium (equimolar) in ether to afford (1-neomenthylindenyl)lithium (**3a**) in 82% yield. The lithium reagent **3a** was characterized by NMR spectroscopy in a benzene-d_6/tetrahydrofuran-d_8 (10:1) solvent mixture. At these conditions the 2-H and 3-H protons at the five-membered ring appear at δ 6.83 and 6.23, respectively, with a vicinal coupling constant of $^3J = 3.3$ Hz. The 4-H, 7-H and 5-H, 6-H protons at the aromatic six-membered ring give rise to two separate sets of multiplets centered at δ 7.72 and 6.92, respectively. The 1′-H hydrogen at the tertiary substituent position adjacent to the cyclopentadienyl moiety has a ^{1}H NMR resonance at δ 3.97. The ^{13}C NMR spectrum of **3a** (benzene-d_6/tetrahydrofuran-d_8, 10:1) exhibits nine separate resonances of the carbon atoms of the indenyl framework in addition to the neomenthyl substituent signals. The indenyl C1 resonance is at δ 109.2 whereas the C2 and C3 signals appear at δ 116.7 and 88.9, respectively, with a characteristic pattern of ^1J (155 and 162 Hz) and ^2J (6 and 3 Hz) C,H coupling constants. The C4, C7 and C5, C6 resonance pairs are at δ 120.2 ($^1J = 153$, $^2J = 5$ Hz), 114.8 ($^1J = 154$, $^2J = 8$ Hz) and δ 118.4 ($^1J = 153$, $^2J = 5$ Hz), 115.6 ($^1J = 154$, $^2J = 8$ Hz), respectively. The C8 and C9 resonances appear at δ 126.8 and 126.7.

The reaction of (1-neomenthylindenyl)lithium (**3a**) with 0.5 molar equiv of ZrCl$_4$(thf)$_2$ produced bis(1-neomenthylindenyl)zirconium dichloride (**4a**). It is expected (see above) that three diastereomers of this bent metallocene containing two chirally substituted planarly chiral ligand systems can be formed. These correspond to the "racemic-like **A**", "racemic-like **B**", and "meso-like **C**" isomers (see Scheme I) and may be described by the minimum combination of absolute configurations of basic chiral units necessary to distinguish them. For this we have used the configurations at the substituent carbon atoms C1′ (the absolute configurations at C2′ and C5′ are then determined by the specific terpene diastereomer employed) and the descriptors of each of the planarly chiral 1-substituted indenyl ligand–metal attachments (their absolute configurational assignment is made according to the specific rules for such metallocene complex types as proposed by Schlögl and Brintzinger[10]). The three **4a** diastereomers are characterized accordingly by the stereochemical descriptors 1′*S*,p-*S*,p-*S*,1′*S* (**4a-A**), 1′*S*,p-*R*,p-*R*,1′*S* (**4a-B**), and 1′*S*,p-*R*,p-*S*,1′*S* (**4a-C**). Under the reaction conditions applied, a mixture of all three diastereomers was formed. However, their ratio deviated much from the statistical (**A**:**B**:**C** = 1:1:2) distribution. The reaction of the chiral lithium reagent **3a** with ZrCl$_4$(thf)$_2$ is highly diastereoselective. Formation of the "racemic-like" 1′*S*,p-*S*,p-*S*,1′*S* stereoisomer **4a-A** is by far predominating. The reaction produces a 93:2:5 mixture of **4a-A**:**4a-B**:**4a-C**. Crystallization from methylene chloride furnished the diastereomerically and consequently enantiomerically pure metallocene **4a-A** in >60% yield. The "racemic-like" (**A**, **B**) and "meso-like" (**C**) diastereoisomers of these 1-substituted bis(indenyl)metal complexes can readily be distinguished by their NMR spectra due to their different symmetry. Thus, the neomenthylindenyl ligands of the "meso-like" (**C**) series are diastereotopic and hence give rise to four distinct ^{1}H NMR signals of the indenyl 2-H, 3-H hydrogens (observed at δ 6.61, 6.52, 5.88, and 5.38 in CDCl$_3$). In contrast each of the "racemic-like" (**A**, **B**) type isomers is C_2-symmetric and thus shows only one set of symmetry equivalent 2-H, 3-H resonances each (δ 6.59, 5.53 and δ 6.84, 5.86, respectively). Their absolute stereochemical assignment had to rely on X-ray crystallography. The major diastereoisomer formed here (**4a-A**) was thus assigned the 1′*S*,p-*S*,p-*S*,1′*S* configuration (see below).

The pure **4a-A** isomer was subsequently subjected to catalytic hydrogenation (PtO$_2$, 50 bar of H$_2$) to give the corresponding bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride complex **5a-A** in 91% yield. Complex **5a-A** was characterized spectroscopically (see e.g. Table I) and by X-ray diffraction (see below). As expected, it belongs to the "racemic-like" series and is also to be described by the 1′*S*,p-*S*,p-*S*,1′*S* stereochemical descriptor.

We have prepared the corresponding bis(1-neoisomenthylindenyl)zirconium dichloride complexes analogously starting from (+)-(1*S*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexanol [(+)isomenthol]. Reaction of the corresponding tosylate (**1b**) with indenyllithium gave 3-neoisomenthylindene (**2b**, 1′*R*,2′*R*,5′*R* configurated at the substituent). Deprotonation furnished the 1-neoisomenthylindenyl reagent **3b** in >90% yield (for its spectroscopic characterization, see the Experimental Section). Subsequent treatment of ZrCl$_4$(thf)$_2$ with 2 molar equiv of **3b** produced a 82:7:11 mixture of the respective **4b-A,B,C** diastereoisomers. Crystallization furnished the pure major isomer (**4b-A**) in 25% yield. Its absolute configuration was assigned as 1′*R*,p-*R*,p-*R*,1′*R*. The products **4b-A** and **4a-A** thus both belong to the same diastereomeric series, namely "racemic-like **A**" as described

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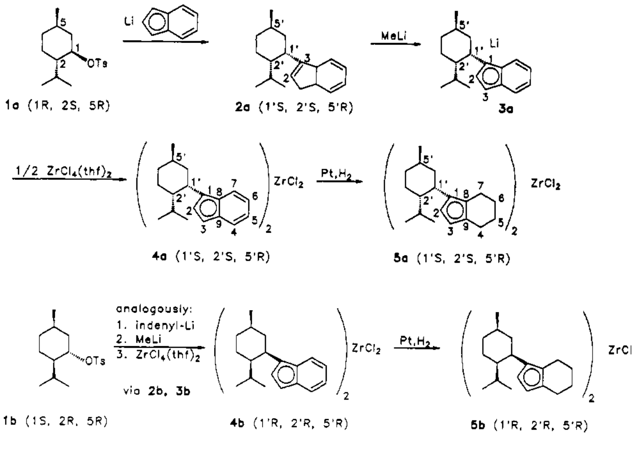
Scheme III



in Scheme I. Catalytic hydrogenation of **4a-A** gave (1′*R*,p-*R*,p-*R*,1′*R*)-bis(1-neoisomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (**5b-A**) in 95% yield.

X-ray Crystal Structure Analyses

The bis(1-hydrocarbylindenyl)- and -(tetrahydroindenyl)ZrCl$_2$ complexes **4a,b** and **5a,b** were characterized by X-ray diffraction. In bis(1-neomenthylindenyl)zirconium dichloride (**4a-A**) the metal atom is pseudotetrahedrally coordinated by two Cl ligands (d(Zr–Cl) = 2.424(1) Å) and two η^5-bound 1-substituted indenyl ligands. The Cl–Zr–Cl* angle is 91.6°. The D–Zr–D* angle is 129.6° (D and D* denote the centroids of the η^5-(cyclo-C$_5$) systems bonded to zirconium). The Zr atom is situated at a 2-fold rotation axis. Therefore, the two Cl ligands and the η^5-indenyl structural subunits are equivalent by crystallographic symmetry. The five metal–(sp^2 carbon) bond lengths are not completely equidistant. There is a small systematic trend observable. First we notice that the metal–(bridgehead carbon) separations at 2.589(4) [Zr–C(4)] and 2.570(3) Å [Zr–C(9)] are larger than the Zr–C(1) [2.552(3)], Zr–C(2) [2.507(3)], and Zr–C(3) [2.486(3) Å] bonds. Among the latter the M–C distance to the carbon atom [C(1)] bearing the bulky neomenthyl substituent is markedly increased. This is probably indicating that attaching the large terpenoid group at the C(1) indenyl positions has resulted in some steric constraints, although the observed distorsions within the Zr–η^5-(cyclo-C$_5$) subunits are far from being severe. This also becomes apparent from the carbon–carbon bond lengths distribution within the η^5-(cyclo-C$_5$) unit at 1.443(5) [C(1)–C(9)], 1.409(4) [C(1)–C(2)], 1.402(4) [C(2)–C(3)], 1.421(5) [C(3)–C(4)], and 1.409(5) Å [C(4)–C(9)]. The C(4)–C(9) bond is part of the annulated six-membered ring completing the indenyl framework. Its remaining carbon–carbon bond lengths are 1.419(6) [C(4)–C(5)], 1.385(9) [C(5)–C(6)], 1.36(1) [C(6)–C(7)], 1.334(9) [C(7)–C(8)], and 1.441(6) Å [C(8)–C(9)]. The observed systematic bond length distortion within the six-membered ring is clearly not toward a nonaromatic bond alternation. The noncoordinated C(5) to C(8) section is uniformly within the range of aromatic C(sp^2)–C(sp^2) bond distances.[11] Coordination of the bulky metal center to the annulated five-membered ring [C(1)–C(4), C(9)] has just led to some lengthening of the adjacent bonds [C(4)–C(5); C(8)–C(9)] inside the attached six-membered ring system.

The neomenthyl substituent is attached to carbon atom C(1) of the indene framework. The C(1)–C(10) distance (1.518(5) Å) is as expected for a C(sp^2)–C(sp^3) single bond. The bulky indenyl ligand moiety is oriented axially at the cyclohexane chair of the neomenthyl substituent. This allows the isopropyl group and the methyl substituent of this specific terpenyl diastereomer both to be placed in equatorial positions. The bulk of the neomenthyl substituent is arranged toward the outside of the bent metallocene core. The C(2)–C(1)–C(10)–C(11) torsional angle is 78.8°. The C(14)–C(19) vector is arranged close to parallel with the mean plane of the indenyl framework. Only a single carbon atom [C(15)] has become oriented toward the crowded inner part of the bent metallocene framework in the conformational substituent arrangement observed here.

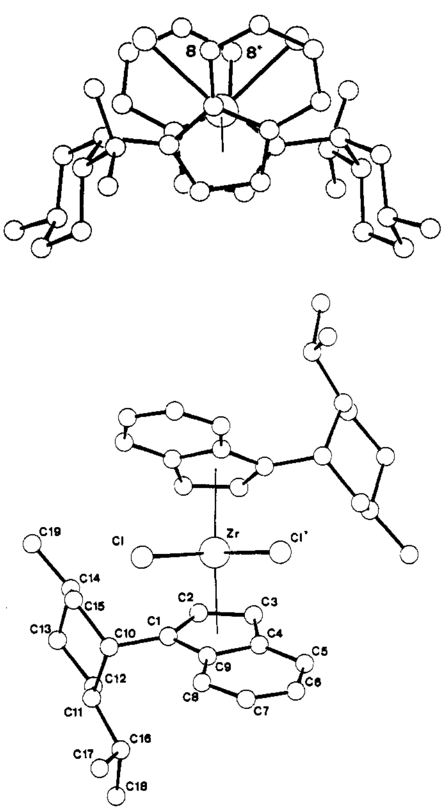


Figure 1. Two views of the molecular geometry of bis(1-neomenthylindenyl)zirconium dichloride (**4a-A**) (with unsystematic numbering scheme).

As the absolute configurations of the three stereogenic centers at the neomenthyl substituent are known from the stereochemically strictly defined synthetic path (see above), the X-ray structure analysis has revealed the absolute configurational assignment of the planarly chiral metallocene unit. Using the Schlögl/Brintzinger definition,[10] complex **4a–A** has been identified as the p-*S*,p-*S* metallocene diastereoisomer ($\kappa = 0$[12]) ("racemic-like **A**", see Scheme I).

In the crystal complex **4a-A** adopts a C_2-symmetric bent metallocene conformation. The π-ligands are rotated such that the neomenthyl substituents become oriented toward the lateral sectors of the bent metallocene unit. Their arrangement is almost ideally antiperiplanar (as becomes visualized by the positioning of the C(1)–C(10) and C(1*)–C(10*) vectors in the projection shown in Figure 1). Consequently the annulated aromatic six-membered rings must then be oriented toward the open front side of the bent metallocene wedge in the *S*,p-*S*,p-*S*,*S* diastereomer **4a-A**. Their respective C(6)–C(7) and C(6*)–C(7*) vectors become oriented almost perfectly above the area occupied by the Cl and Cl* ligands. In the projection (see Figure 1) the planes of the annulated benzenoid aromatic rings overlap slightly. For visualization of this effect and for the purpose of comparison, we

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Table II. A Comparison of Selected Bond Lengths and Angles of the Complexes **4a-A** and **4b-A**

	4a-A	**4b-A**	
Zr–Cl	2.424(1)	2.409(5)	2.442(1)
Zr–C(1)	2.552(3)	2.608(4)	2.573(3)
Zr–C(2)	2.507(3)	2.481(5)	2.502(3)
Zr–C(3)	2.486(3)	2.445(4)	2.473(3)
Zr–C(4)	2.589(4)	2.604(3)	2.594(4)
Zr–C(9)	2.570(3)	2.636(3)	2.584(4)
C(1)–C(10)	1.518(5)	1.509(5)	1.496(4)
C(1)–C(9)	1.443(5)	1.442(7)	1.455(9)
C(1)–C(2)	1.409(4)	1.402(4)	1.405(5)
C(2)–C(3)	1.402(4)	1.433(5)	1.407(5)
C(3)–C(4)	1.421(5)	1.401(6)	1.431(9)
C(4)–C(5)	1.419(6)	1.452(8)	1.421(8)
C(5)–C(6)	1.385(9)	1.344(8)	1.328(9)
C(6)–C(7)	1.36(1)	1.403(8)	1.431(7)
C(7)–C(8)	1.334(9)	1.346(9)	1.355(9)
C(8)–C(9)	1.441(6)	1.419(6)	1.427(8)
C(10)–C(15)	1.546(5)	1.530(7)	1.53(1)
C(10)–C(11)	1.554(5)	1.562(5)	1.560(5)
Cl*–Zr–Cl	91.6(1)	96.7(1)	
C(10)–C(1)–C(9)	124.5(3)	124.2(3)	124.1(4)
C(10)–C(1)–C(2)	130.2(3)	128.1(5)	129.4(5)
C(9)–C(1)–C(2)	104.7(3)	107.4(3)	106.1(3)
C(3)–C(2)–C(1)	111.0(3)	109.2(4)	111.2(5)
C(4)–C(3)–C(2)	107.1(3)	107.4(3)	107.4(3)
C(9)–C(4)–C(3)	107.4(3)	108.6(4)	107.3(4)
C(6)–C(5)–C(4)	117.3(5)	118.7(4)	119.3(4)
C(9)–C(8)–C(7)	118.8(4)	118.7(4)	118.7(4)
C(8)–C(9)–C(4)	118.7(4)	120.6(4)	119.4(5)
C(8)–C(9)–C(1)	131.8(3)	132.2(3)	132.8(3)
C(4)–C(9)–C(1)	109.5(3)	107.1(3)	107.7(4)
C(15)–C(10)–C(11)	108.6(3)	111.3(4)	111.6(3)
C(15)–C(10)–C(1)	115.1(3)	112.7(3)	111.6(4)
C(11)–C(10)–C(1)	113.1(3)	113.9(3)	114.8(3)

have defined a "dihedral overlap angle" θ [C(8)–D–D*–C(8*)]. In complex **4a**–A this amounts to 12.9°.

Thus we conclude that complex **4a**–A in the crystal adopts a specific chiral C_2-symmetric bent metallocene conformation. The metallocene rotamer observed by X-ray crystallography comes very close to the idealized geometry **G** as depicted in Scheme II with the C(8)–C(9) and C(8*)–C(9*) vectors of the annulated six-membered ring systems both being found in the "bis-central: syn" orientation and the secondary cycloalkyl substituents at the five-membered rings of the π-ligand systems arranged antiperiplanarly in the lateral sectors of the bent metallocene unit.

The bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dihalide complex **5a-A** has very similar structural features in the solid state. The structure is C_2-symmetric, and the 1-hydrocarbyl-substituted η^5-tetrahydroindenyl ligands are equivalent by crystallographic symmetry, again. The Cl–Zr–Cl* angle [91.4(1)°] is almost identical as found in **4a-A**. The D–Zr–D* angle in **5a-A** is 128.8°. As expected, the Zr–C(Cp) distances fall into two series: the metal–C(sp^2) bonds to the substituted carbon atoms are slightly longer [2.587(6) Å, Zr–C(1); 2.578(7) Å, Zr–C(4); 2.574(7) Å, Zr–C(9)] than the Zr–(CH) distances [2.489(6) Å, Zr–C(2); 2.486(7) Å, Zr–C(3)]. The annulated six-membered ring system adopts a twist-chair conformation. This introduces an additional conformational chirality element into the **5a-A** complex. However, it appears that for each ring system the resulting diastereotopomers are near to equally populated. In the X-ray crystal stucture analysis of **5a-A**, which has a disordered additional pentane molecule in the asymmetric unit, this shows up as a 50:50 disorder of the respective carbon atoms C(6) and C(7).

The conformational arrangement of groups at the cyclohexyl substituent chair in **5a-A** is almost identical as observed in **4a-A**. The metallocene configuration is p-*S*,p-*S*. The rotational arrangement of the bis(1-neomenthyltetrahydroindenyl)metal unit is again closely related to the "bis-central:syn" bis(indenyl) type

Table III. A Comparison of Selected Bond Lengths and Angles of the Complexes **5a-A** and **5b-A**

	5a-A	**5b-A**
Zr–Cl	2.444(2)	2.448(1)
Zr–C(1)	2.587(6)	2.556(2)
Zr–C(2)	2.489(6)	2.463(2)
Zr–C(3)	2.486(7)	2.467(2)
Zr–C(4)	2.578(7)	2.576(2)
Zr–C(9)	2.574(7)	2.589(2)
C(1)–C(10)	1.51(1)	1.507(3)
C(1)–C(9)	1.43(1)	1.431(3)
C(2)–C(3)	1.41(1)	1.415(3)
C(3)–C(4)	1.39(1)	1.412(3)
C(4)–C(9)	1.40(3)	1.407(3)
C(4)–C(5)	1.50(1)	1.514(3)
C(10)–C(15)	1.55(1)	1.527(3)
C(10)–C(11)	1.54(1)	1.555(3)
Cl*–Zr–Cl	91.4(1)	94.9(1)
C(10)–C(1)–C(9)	124.5(7)	126.5(2)
C(10)–C(1)–C(2)	130.5(7)	126.6(2)
C(9)–C(1)–C(2)	104.8(6)	106.8(2)
C(3)–C(2)–C(1)	109.7(6)	108.6(2)
C(4)–C(3)–C(2)	108.6(6)	108.0(2)
C(9)–C(4)–C(3)	106.9(6)	108.1(2)
C(6)–C(5)–C(4)	110.6(9)	112.7(2)
C(7)–C(8)–C(9)	115.5(9)	109.8(2)
C(8)–C(9)–C(4)	119.8(7)	122.0(2)
C(8)–C(9)–C(1)	130.2(6)	129.3(2)
C(4)–C(9)–C(1)	109.9(7)	108.4(2)
C(15)–C(10)–C(11)	107.9(6)	111.2(2)
C(15)–C(10)–C(1)	115.6(6)	112.1(2)
C(11)–C(10)–C(1)	113.0(6)	114.1(2)

bent metallocene conformation **G** (see Scheme II) with the annulated six-membered ring systems both oriented toward the front section of the bent metallocene wedge and again slightly overlapping in the projection onto the central molecular plane. The dihedral overlap angle θ [C(8)–D–D*–C(8*)] in **5a**–A is 17.7°.

According to its X-ray crystal structure the bis(1-neoisomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride complex **5b-A** also belongs to the "bis-central:syn" (**G**) bent metallocene conformational type. Here the overlap angle θ [C(8)–D–D*–C(8*)] is −14.3°. The metal–carbon dissymmetry of the Zr–(η^5-cyclo-C_5) unit is similar as is observed in **5a–A** [**5b-A**: 2.556(2) Å, Zr–C(1); 2.576(2) Å, Zr–C(4); 2.589(2), Zr–C(9); vs 2.463(2) Å, Zr–C(2) and 2.467(2) Å, Zr–C(3)]. The annulated six-membered rings adopt a twist-chair conformation and also show a diastereotopomeric disorder (60:40) of the carbon atoms C(6) and C(7).

The neoisomenthyl substituents are arranged antiperiplanarly at the bent metallocene backbone. The overall arrangement of the groups at the cyclohexyl substituent chair is necessarily different from the **4a,b** series. In **5b**–A the indenyl framework is attached in an equatorial position. This leaves the adjacent isopropyl group of the neoisomenthyl system bonded axially and the distant methyl group equatorially. Again a conformational orientation at the C(1)–C(10) vector is found that orientates the bulky isopropyl group away from the center of the bent metallocene [C(2)–C(1)–C(10)–C(11) = −103°]. However, it appears that the C(15), C(14), C(19) part of the substituent is penetrating the inner section of the bent metallocene more than this was the case in the respective neomenthyl series (**4a-A**, **5a-A**).

The X-ray crystal structure analysis reveals that complex **5b-A** belongs to the p-*R*,p-*R* configurational bent metallocene series,[10] i.e. has the opposite absolute configuration [$\kappa = 0$[12]] as compared to the complexes **4a-A** and **5a**–A whose structures are described above. This formal configurational inversion of **5b-A** is due to the fact that a substituent with inverted configuration at the connecting chiral center was used for determining the configurational features of **5b-A**. Thus, complex **5b-A** has the config-

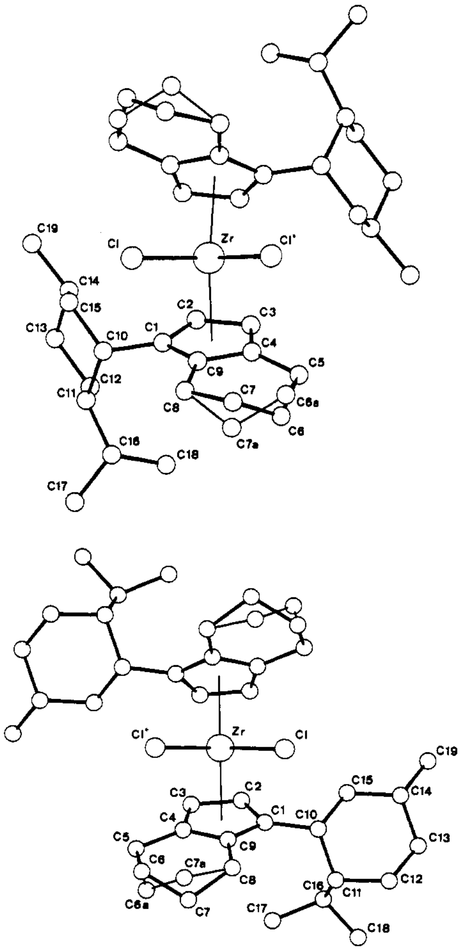

Figure 2. Views of the molecular geometries of the substituted bis(tetrahydroindenyl)zirconium dichloride complexes **5a-A** (top) and **5b-A** (bottom, with unsystematical numbering scheme).

urational descriptor of *R*,p-*R*,p-*R*,*R*. It thus belongs to the same diastereomeric type as do complexes **4a-A** and **5a-A**, but represents an example of the opposite enantiomeric series.

In the crystal several structural featurs of bis(1-neoisomenthylindenyl)zirconium dichloride (**4b-A**) are similar to those of the three related metallocene complexes described above. The configurational properties of complex **4b-A** are as expected: the chiral metallocene dihalide belongs to the *R*,p-*R*,p-*R*,*R* series and behaves in this respect in principle analogously to the other three examples, as described above. In addition complex **4b-A** shows conformational features that makes its molecular structure in the crystal distinctly different from the otherwise related examples **4a-A**, **5a-A**, and **5b-A**.

In contrast to these C_2-symmetric systems complex **4b-A** exhibits a reduced molecular symmetry. Its 1-substituted indenyl ligands differ in their rotational positions, and the attached hydrocarbyl substituents thus occupy nonsymmetry-related sectors at the bent metallocene backbone. In the C_1-symmetric complex **4b-A** the 1-neoisomenthylindenyl ligand containing the C(1)–C(9) indene framework is oriented similarly as observed in their C_2-symmetric relatives (see above), i.e. the annulated six-membered ring system is oriented toward the open front of the bent metallocene wedge and is, therefore, eclipsed with the Zr–Cl(1) vector. The Zr–[C(1)–C(4),C(9)] distances are spanning a rather large range [maximal Δd(Zr–C(Cp)) = 0.19 Å]. Even though the typical overall bond distance pattern is followed [Zr–C(1), 2.608(4) Å; Zr–C(4), 2.604(3) Å; Zr–C(9), 2.636(3) Å; vs Zr–C(2), 2.481(5) Å; Zr–C(3), 2.445(4) Å], the observed distortion seems to indicate considerable steric strain. The attached neoisomenthyl substituent is positioned in the lateral sector of the bent metallocene. Its conformational properties

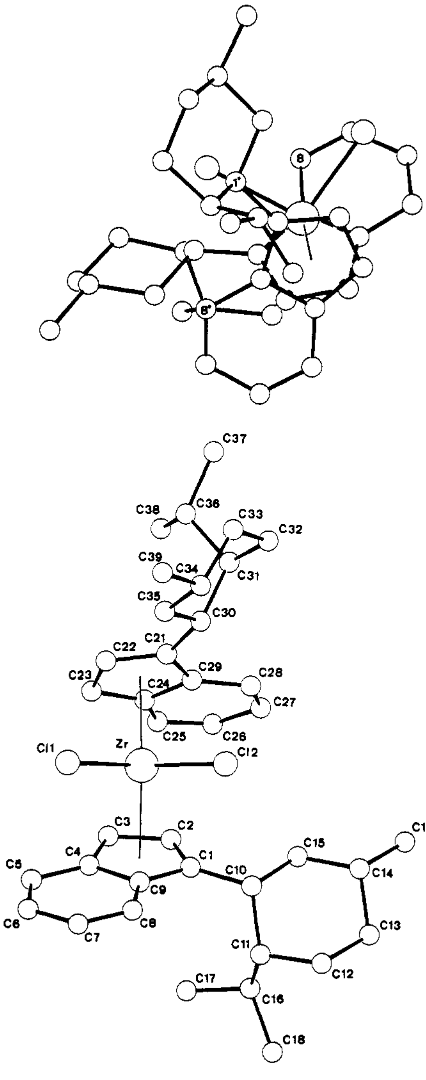

Figure 3. Two projections of the molecular geometry of bis(1-neoisomenthylindenyl)zirconium dichloride (**4b-A**; with unsystematical numbering scheme).

Table IV. A Comparison of Characteristic Structural Parameters of the Complexes **4** and **5**

complex	bite angle[a] (Φ)	C(8)–D–D*–C(8*) (θ)	D–Zr–D*	Cl–Zr–Cl*
4a-A	55.4	12.9	129.5	91.6
4b-A	54.8	109.9[b]	130.3	96.7
5a-A	57.1	17.7	128.8	91.4
5b-A	58.0	14.3	130.1	94.9
6a[c]	62		119.0	98.7
6b[d]	55	67.5	125.2	98.6

[a] Angle between the mean planes of the η^5-cyclo-C_5 ligands. [b] C(8)–D(1)–D(2)–C(28). [c] *rac*-$Me_2Si(indenyl)_2ZrCl_2$, see ref 13. [d] Ethylenebis(4,5,6,7-tetrahydroindenyl)$ZrCl_2$, see ref 14.

and its relative orientation at the bent metallocene backbone are similar as found for complex **5b-A**.

The second 1-neoisomenthylindenyl ligand in **4b-A** is oriented differently. It has the annulated six-membered ring oriented laterally and the terpenyl substituent placed up front (see Figure 3). In contrast to the other three examples of this study, the C(8)–D(1)–D(2)–C(28) torsional angle in **4b-A** is +109.9°; the dihedral overlap angle θ is defined by the C(8)–D(1)–D(2)–C(30) torsional angle at +38.3°. At this ligand the neoisomenthyl substituent is oriented markedly toward the outer side of the metallocene [torsional angle C(22)–C(21)–C(30)–C(35), 20.4° vs C(2)–C(1)–C(10)–C(15), 15.8°]. This conformational arrangement of the second neoisomenthylindenyl ligand seems to

Table V. Details of the X-ray Crystal Structure Analyses of the Bent Metallocene Complexes **4a,b-A** and **5a,b-A**[a]

	4a	**4b**	**5a**	**5b**
formula	$C_{38}H_{50}Cl_2Zr$	$C_{38}H_{50}Cl_2Zr$	$C_{38}H_{58}Cl_2Zr{\cdot}C_5H_{12}$	$C_{38}H_{58}Cl_2Zr$
mol wt	668.9	668.9	749.2	677.0
crystal color	yellow	yellow	white	colorless
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
space group [no.]	$P2$[3]	$P2_1$[4]	$P2_12_12$[18]	$P2_12_12$[18]
a, Å	10.510(1)	7.559(2)	15.422(1)	10.103(1)
b, Å	6.975(1)	9.046(2)	18.716(1)	26.626(5)
c, Å	12.421(1)	25.015(3)	7.118(3)	6.762(1)
β, deg	108.18(1)	96.72(1)	90.0	90.0
V, Å^3	865.0	1698.8	2054.6	1818.9
Z	1	2	2	2
D_{calcd}, g cm^{-3}	1.28	1.31	1.21	1.24
μ, cm^{-1}	4.91	5.00	4.20	4.67
Mo Kα radiation, λ, Å	0.71069	0.71069	0.71069	0.71069
$F(000)$, e	352	1160	804	720
diffractometer	Enraf-Nonius CAD4			
scan mode	ω–2θ	ω–2θ	ω–2θ	ω–2θ
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.65	0.75	0.70	0.70
T, °C	20	20	20	20
abs correction (min–max)	analytical 1.069–1.359	none	none	none
no. of measd reflcns ($\pm h,+k,+l$)	4450	5809	3418	6134
no. of indep reflcns	3917	5642	3394	5306
no. of obsd reflcns ($I > 2\sigma(I)$)	3573	5110	2495	4905
no. of refined params	186	371	205	185
R	0.037	0.037	0.062	0.030
R_w ($w = 1/\sigma^2(F_o)$)	0.041	0.040	0.074	0.037
enantiopol parameter	–0.01(5)	–0.015(3)	–0.17(15)	0.01(4)
resid electron dens, e Å^{-3}	1.21	0.60	0.79	0.55
			C(6), C(7) and pentane 50:50 disordered	C(6), C(7) 60:40 disordered

[a] All structures were solved with heavy-atom method, H atom positions were calculated and kept fixed in the final refinement stage.

be sterically unproblematic in the solid state as judged from the comparatively narrow range of the respective [C(21)–C(24),C-(29)] carbon metal distances [Zr–C(21), 2.573(3) Å; Zr–C(24), 2.594(4) Å; Zr–C(29), 2.584(4) Å and Zr–C(22), 2.502(3) Å; Zr–C(23), 2.473(3) Å].

Thus we conclude that the bis(1-hydrocarbylindenyl)zirconium dichloride complexes in the solid state may exhibit different conformational preferences. Of the four examples looked at by X-ray diffraction three (**4a-A**, **5a-A**, **5b-A**) belong to the C_2-symmetric "bis-central:syn" (**G**) conformational type (see Scheme II) whereas the fourth complex in this series (**4b-A**) represents an example where the less symmetric "central,lateral:gauche" (**I**) type conformation appears to be favored in the crystal.

Propene Polymerization Reactions

The four complexes **4a,b** and **5a,b** described above were used for generating homogeneous Ziegler-type α-olefin polymerization catalysts. The chiral bent metallocene complexes were dissolved in toluene solution and activated in the presence of excess olefin by treatment with a large excess of oligomeric methylalumoxane. Typically, Al/Zr ratios of ca. 750 ± 200 were employed.[15] In this orientating series of experiments we only looked at the polymerization of propene at two temperatures (–30 and –5 °C). A few selected experiments were done in a similar way at other temperatures.

In a typical experiment, the bis(neoisomenthylindenyl)zirconium complex **4b-A** was activated with $(AlMeO)_x$ at –30 °C (Al:Zr = 700). Propene was polymerized during 3 h. The reaction mixture was then quenched (HCl in methanol) and the polymer isolated (3.3 g). The obtained polypropylene (PP1) had a molecular weight of $\bar{M}_\eta$ = 260 000. Its stereochemical composition was determined by means of a ^{13}C NMR methyl pentade analysis combined with a statistical evaluation. Detailed descriptions of these analytical procedures and the computational methods employed have been published previously.[15,16] The ^{13}C NMR methyl resonance originating from the mmmm pentade of polypropylene PP1 amounts to 76% relative to the total CH_3 signal intensities. In addition there are the methyl resonances corresponding to the mmmr, mmrr, and mrrm sequences clearly visible in a 2:2:1 ratio. The remaining methyl pentades are only marginally populated (see Table VI). This observed pattern qualitatively indicates a dominating stereocontrol of the propene carbon carbon coupling by the enantiomorphic site in the course of the polymerization reaction at low temperature (this is nicely visualized in Figure 4 by the appearance of the ^{13}C NMR methyl signals of a polypropylene sample obtained at –50 °C with the **4b-A** derived catalyst system).

A quantitative assessment of the effectiveness of the chirality transfer from the chiral metal catalyst (here introduced via the chiral bent metallocene backbone) was carried out by fitting the observed ^{13}C NMR methyl resonance intensities (monitored at the pentade resolution level) with a simple mathematical model using the statistical descriptors ω, α, and σ. The numerical values of the latter two serve as formal isotacticity measures for enantiomorphic site control (α) and chain end control contributions (σ) (with both being applied to the typical statistics of these two regimes of stereocontrol[1,15,16]) under this overall double stereodifferentiation situation.[17] The magnitude of ω in this three-parameter model denotes the fraction of the polymer whose stereochemistry is calculated to be due to enantiomorphic site control. We have found it practical and illustrative to combine α and ω by the equation $(2\omega - 1)\alpha = ee^*$. The ee* value so defined could be termed a "relative enantioselectivity"[15] and constitutes a useful numerical value for describing the effective transfer of chirality from the chiral active catalytic site.

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[15] For experimental details of the propene polymerization reactions and the polymer analysis, see e.g.: Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Krüger, C.; Noe, R. *J. Am. Chem. Soc.* **1991**, *113*, 7594.

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Table VI. A Compilation of Selected Data Concerning Propene Polymerization Reactions at Metallocene/Methylalumoxane Catalysts Generated from Complexes **4** and **5**

	substituent/ligand type, complex							
	neoisomenthyl-/-indenyl, **4b**-A		-tetrahydroindenyl, **5b**-A		neomenthyl-/-indenyl, **4a**-A		-tetrahydroindenyl, **5a**-A	
polymerization temp (°C)	−30	−5	−30	−5	−30	−5	−30	−5
polymer	PP1	PP2	PP3	PP4	PP5	PP6	PP7	PP8
Al/Zr ratio	700	560	730	600	910	560	640	570
g of PP isolated	3.3	2.0	6.0	25.0	19.0	1.8	6.6	5.6
activity[a]	350	240	360	3800	2200	300	630	900
$\bar{M}_\eta$	260000	100000	183000	60000	134000	26000	12000	21000
mmmm[b]	0.76 (0.77)	0.77 (0.77)	0.56 (0.56)	0.45 (0.45)	0.24 (0.25)	0.33 (0.33)	0.37 (0.37)	0.16 (0.16)
mmmr	0.05 (0.06)	0.10 (0.09)	0.15 (0.14)	0.16 (0.16)	0.18 (0.17)	0.17 (0.16)	0.20 (0.19)	0.13 (0.13)
rmmr	0.00 (0.01)	0.00 (0.00)	0.02 (0.01)	0.02 (0.02)	0.05 (0.04)	0.04 (0.03)	0.04 (0.03)	0.07 (0.06)
mmrr	0.05 (0.06)	0.07 (0.07)	0.13 (0.12)	0.14 (0.13)	0.15 (0.16)	0.13 (0.11)	0.08 (0.08)	0.10 (0.11)
mmrm + rmrr	0.00 (0.03)	0.03 (0.03)	0.06 (0.06)	0.10 (0.10)	0.14 (0.15)	0.17 (0.17)	0.18 (0.19)	0.22 (0.23)
rmrm	0.04 (0.01)	0.00 (0.01)	0.02 (0.02)	0.03 (0.04)	0.06 (0.07)	0.06 (0.06)	0.07 (0.06)	0.14 (0.11)
rrrr	0.02 (0.02)	0.00 (0.00)	0.01 (0.01)	0.01 (0.02)	0.04 (0.03)	0.01 (0.03)	0.01 (0.01)	0.06 (0.04)
mrrr	0.02 (0.02)	0.00 (0.00)	0.01 (0.02)	0.04 (0.03)	0.08 (0.07)	0.07 (0.05)	0.03 (0.03)	0.07 (0.10)
mrrm	0.06 (0.03)	0.02 (0.03)	0.06 (0.06)	0.06 (0.07)	0.07 (0.08)	0.03 (0.06)	0.03 (0.04)	0.05 (0.06)
ω	0.84	0.80	0.86	0.78	0.94	0.65	0.020	0.09
α	0.97	0.95	0.90	0.83	0.75	0.72	0.93	0.99
σ	0.62	0.93	0.79	0.90	0.79	0.87	0.73	0.54
ee*[c]	0.84	0.72	0.69	0.51	0.46	0.29	0.17	0.09

[a] Grams of polymer/grams of [Zr]·h. [b] Relative ^{13}C NMR methyl pentade intensity observed (calculated[15]). [c] For definitions of ω, α, σ, and ee* see text and ref 15.

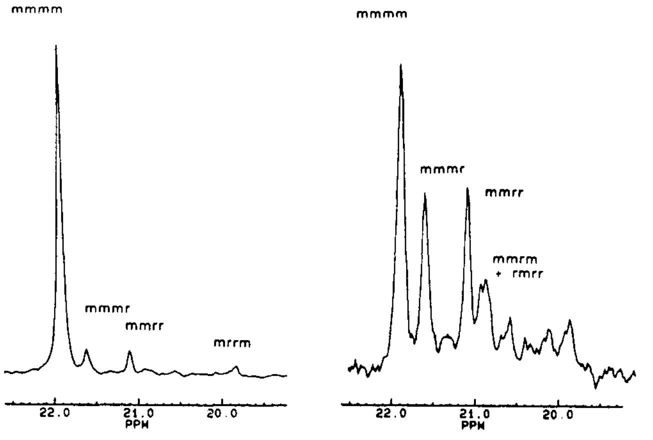


Figure 4. ^{13}C NMR methyl resonances of polypropylenes formed at the bis(neoisomenthylindenyl)zirconium dichloride/$(AlMeO)_x$ (left) and bis(neomenthylindenyl)zirconium dichloride/$(AlMeO)_x$ (right) catalyst systems at −50 °C.

For PP1 84% of the stereocontrol is due to the enantiomorphic site. The overall effective transfer of chirality from the chiral bis(neoisomenthylindenyl)zirconium backbone also amounts to ee* = 84%. We thus conclude that the catalyst derived from this readily available chiral, optically active open nonbridged metallocene complex (**4b**-A) is able to produce an isotactic polypropylene, the major portion of which contains only singular stereochemical mistakes as the detectable defect structures. Apparently this nonbridged zirconocene complex is able to control the stereochemistry of the CC coupling of propene monomeric units in a similar way as it is usually assumed for many *ansa*-metallocene-derived catalyst systems.[1-3] This similarity between planarly chiral nonbridged bis(indenyl)MX_2 and the respective *ansa*-metallocene systems with regard to their general ability for stereocontrol was expected from the overall stereochemical analysis of these related complex systems as outlined in the introductory paragraph.[4]

Increasing the temperature of the **4b**-A/$(AlMeO)_x$ propene polymerization system from −30 to −5 °C under otherwise analogous conditions (see Table VI) resulted in a slight *decrease* in polymerization activity [a = 240 g of polypropylene/g of Zr·h at −5 °C vs a = 350 at −30 °C]. Not unexpectedly, the molecular weight of the polypropylene (PP2) is lower ($\bar{M}_\eta$ = 100 000) and the stereoselectivity is slightly reduced to an ee* value of 72%. The overall fraction of enantiomorphic site control is still high at ω = 80%.

At −30 °C, the bis(neoisomenthyltetrahydroindenyl)zirconium dichloride (**5b**-A)/methylalumoxane catalyst behaves similar to the **4b**-A/$(AlMeO)_x$ system with regard to activity (a = 360) and molecular weight of the polymer formed (PP3: $\bar{M}_\eta$ = 183 000). However, the chirality transfer is somewhat lower (ee* = 69%). At −5 °C the usual reduction of $\bar{M}_\eta$ and ee* is observed (see Table VI), but the polymerization activity is drastically increased by almost a factor of 10. For this specific catalyst system additional polymerization reactions were carried out at higher temperatures. This has revealed an interesting temperature dependency of the polymerization activities going through a maximum and then decreasing again with increasing reaction temperatures. $\bar{M}_\eta$ and ee* both get smaller when the polymerization temperature is raised [+10 °C (PP9): a = 2100, $\bar{M}_\eta$ = 17 000, ω = 0.93, α = 0.80, ee* = 0.56; +25 °C (PP10): a = 1300, $\bar{M}_\eta$ = 5000, ω = 0.92, α = 0.72, ee* = 0.40].

Similar relative trends are observed when the propene polymerization reaction is carried out with the homogeneous Ziegler catalyst systems derived from the neomenthyl-substituted metallocene complexes. However, it was noticed that the ability for chirality transfer from these metallocene complexes is significantly reduced as compared to their neoisomenthyl-substituted isomers. Thus the **4a**-A/$(AlMeO)_x$ catalyst system is rather active at −30 °C (a = 2200) and produces high molecular weight polypropylene (PP5: $\bar{M}_\eta$ = 134 000). Enantiomorphic site control is still dominating at ω = 0.94, but there are many "mistakes" along the polymer chain (α = 0.75). The overall effective chirality transfer is as low as ee* = 46% (see also Figure 4 for a visualization of this effect). Raising the temperature decreases the ee* even further (Table VI). At higher temperature there is also a marked decrease of the ω value. This becomes even more pronounced when the neomenthyl-substituted tetrahydroindenyl systems are employed: the overall chirality transfer has dropped to a mere ee* = 17% (PP7, −30 °C) and ee* = 9% (PP8, −5 °C), respectively.

Conformational Behavior in Solution

The neomenthyl- and neoisomenthyl-substituted metallocene derived catalyst systems behave quite differently with regard to the transferring of their inherent chirality information onto the growing polymer chain. From our experiments it appears that the neoisomenthyl systems are far superior in this respect as

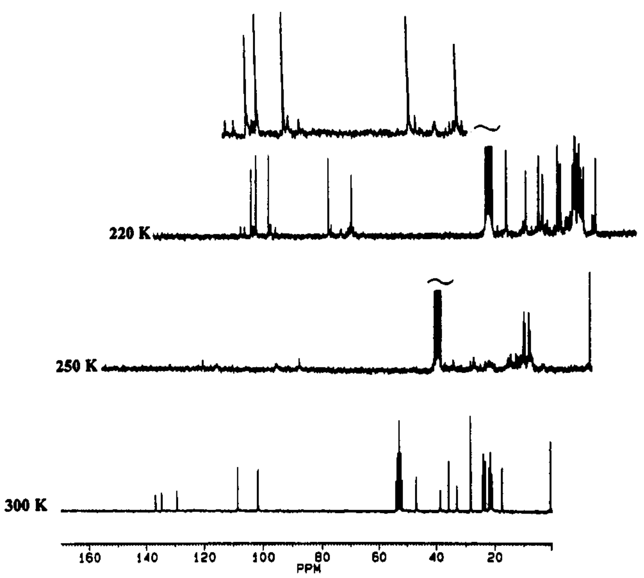


Figure 5. Temperature-dependent ^{13}C NMR spectra of complex **5b-A** in methylene-d_2 chloride.

compared to their neomenthyl-substituted isomers. According to the X-ray structural analyses of the respective substituted metallocene dichloride catalyst precursors in the solid state (see above) one might have forseen the opposite behavior: in the crystal the neomenthylindenyl-derived system is nicely C_2-symmetric whereas its neoisomenthyl counterpart (**4b-A**) exhibits a reduced (C_1) symmetry which, if conveyed to the stage of the active catalyst, is expected to constitute a less favorable environment for a highly stereoselective carbon–carbon coupling in the vicinity of the bent metallocene backbone. Therefore, it seems likely that in this case the structural characterization of these substituted bent metallocene systems by X-ray diffraction in the solid state is not completely representative of the detailed conformational features of the terpenylindenyl and -tetrahydroindenyl zirconium complexes in solution. We have thus tried to get some independent information about the stereochemical (i.e. especially the conformational) properties of the catalyst precursors **4a,b** and **5a,b** by dynamic NMR spectroscopy in solution. At ambient temperature all these compounds exhibit ^1H and ^{13}C NMR spectra that are as expected for the presence of a singular C_2-symmetric species each (see above and the Experimental Section). Both the bis(neoisomenthylindenyl)- and the bis(neoisomenthyltetrahydroindenyl)zirconium dichloride systems did not show any appreciable change from this NMR behavior when their solutions in toluene-d_8 were measured at variable temperature down to −60 °C. In contrast, both neomenthyl-substituted systems (**4a-A** and **5a-A**) have exhibited dynamic NMR spectra in the 300–190 K temperature range. Of these two systems, the bis(neomenthylindenyl)zirconium dichloride complex showed a rather complicated temperature-dependent variation of its NMR spectra indicating the presence of at least three different rotameric forms. Because of too many overlapping signals this does not allow for a clear description and interpretation at present. At this time we will therefore limit ourselves to presenting the much simpler case of the $^1H/^{13}C$ NMR conformational analysis of the bis(1-neomenthyltetrahydroindenyl)zirconium dichloride catalyst precursor **5a-A**.

(p-*S*,p-*S*)-Bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (**5a-A**) exhibits a ^{13}C NMR spectrum in methylene-d_2 chloride at 300 K that is compatible with an apparent C_2 molecular symmetry (see above and Figure 5). The symmetry-equivalent substituted η^5-cyclopentadienyl subunits thus give rise to a single set of five separate resonances at δ 137.8, 135.6, 130.3 (quaternary carbons), 109.4, and 102.6 (methine carbon atoms). On lowering the monitoring temperature all these signals become very broad. At 250 K they have almost completely disappeared in the noise level of the base line, only to reappear at even lower temperature. At 220 K we register the five Cp resonances of the C_2-symmetric metallocene species at slightly different δ values (135.9, 134.2, 130.0, 109.8, 101.8). In addition one observes six newly appeared lines in the quaternary carbon range at δ 139.0, 137.8, 135.2, 134.8, 129.5, and 127.3. Similarly, several lines of equal intensity become observable in the Cp-*C*H resonance region, out of which four may tentatively be assigned to the newly appeared set of signals (δ 108.7, 102.9, 102.2, 100.8). Thus, complex **5a-A** has turned out to show dynamic behavior on the ^{13}C NMR time scale. We conclude that in solution complex **5a-A** actually exists as a mixture of two rapidly interconverting isomers of different symmetry. At low temperature their mutual rearrangement can be "frozen" on the ^{13}C NMR time scale which reveals their actual symmetry properties and ratio (ca. 80:20 mixture of a C_2- and a C_1-symmetric species).

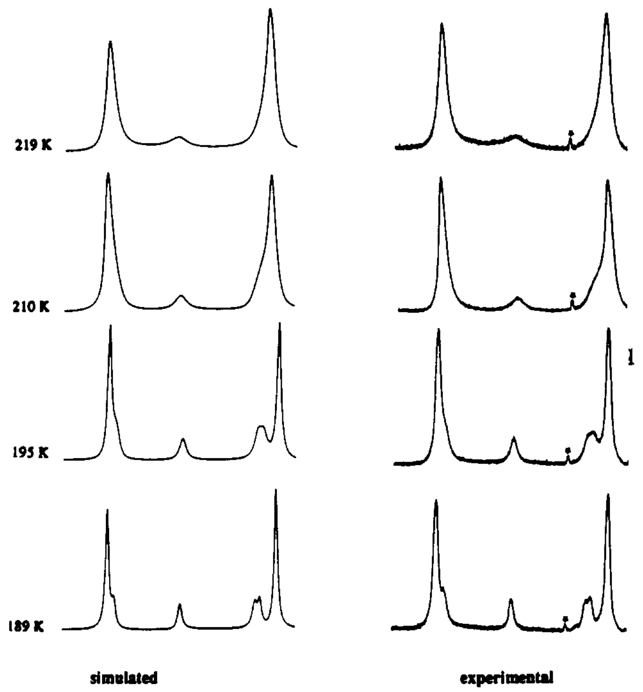


Figure 6. Observed and calculated temperature-dependent ^1H NMR spectra of **5b-A** (in methylene-d_2 chloride; only the η^5-Cp-methine C(2)-*H* and C(3)-*H* resonances are shown).

Complex **5a-A** shows a similar dynamic behavior in the temperature-dependent ^1H NMR spectra in various solvents. In methylene-d_2 chloride the relevant Cp-C*H* signals become all sufficiently resolved. At 300 K the 1-neomenthyltetrahydroindenyl ligands of the equilibrating metallocene system **5a-A** are symmetry equivalent and exhibit an AX type pattern of the η^5-cyclopentadienyl methine hydrogens at δ 6.40 and 5.62 ($^3J = 2.8$ Hz). With decreasing temperature these two resonances get broad and then sharp again (see Figure 6). Below 220 K a second set of C*H* resonances appears. At 189 K one observes the cyclopentadienyl-CHCH signals of the C_2-symmetric isomer at δ 6.53 and 5.52 in addition to the four respective resonances of the minor C_1-symmetric component (δ 6.49, 6.08, 5.64, 5.62) whose 1-substituted tetrahydroindenyl ligand systems are not-symmetry related. The two isomers of **5a-A** are present in a ca. 80:20 ratio as judged from the static ^1H NMR spectrum at 189 K (4.7 T). Similarly dynamic ^1H NMR behavior of **5a-A** was observed in tetrahydrofuran-d_8 or toluene-d_8 although in both cases the four cyclopentadienyl methine hydrogen resonances were only partly resolved [THF-d_8, 207 K: δ 6.88, 5.55 (C_2-symmetric isomer), δ 6.84, 6.30, 5.77 (double intensity) (C_1-symmetric isomer); toluene-d_8, 189 K: δ 5.69, 5.25 (major isomer, C_2), δ 5.89, 5.36

(two lines hidden under signals of the other isomer) (minor component)].

The temperature-dependent ^{1}H NMR spectra measured in methylene-d_2 chloride were simulated using the DNMR 5 program package (Figure 6).[18] From the obtained temperature-dependent exchange rate constants ($k_{\mathrm{exchange}} = 2k_{\mathrm{isom}}$[19]) we have calculated the activation barriers of the isomerization between the major and minor component present in solution as $\Delta G^{\ddagger}(200\ \mathrm{K}) \approx 11.3 \pm 0.5$ kcal mol^{-1}. Formal Eyring treatment by plotting $\ln k_{\mathrm{isom}}/T$ vs T^{-1} gave the activation enthalpy as $\Delta H^{\ddagger} = 11.1 \pm 0.5$ kcal mol^{-1} and the activation entropy as $\Delta S^{\ddagger} = -1.0 \pm 2.3$ cal K^{-1} mol^{-1}. At 189 K the energy difference of the major and minor isomer of **5a-A** is approximately 0.6 kcal mol^{-1}.

Conclusions

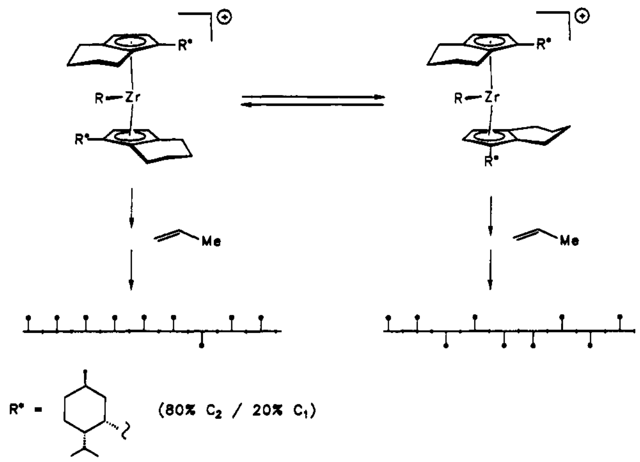
The X-ray crystal structure analyses of the series of complexes investigated in this study have revealed the occurrence of two different conformational types of 1-substituted bis(indenyl)- and -(tetrahydroindenyl)zirconium dichloride complexes. These correspond to the idealized geometries **G** and **I** as depicted in Scheme II. The two types of observed rotational isomers differ in their molecular symmetry. The **G**-type isomer (as found for the complexes **4a-A**, **5a-A**, and **5b-A**) is C_2-symmetric and has the bulky terpenyl substituents oriented antiperiplanarly in the lateral sectors of the bent metallocene wedge. In contrast, the **I**-type conformer (in the solid state observed for complex **4b-A**) has only one substituent oriented laterally whereas the other is directed toward the open front side of the bent metallocene. Consequently, this conformational isomer is of lower molecular symmetry (C_1).

Our study further shows that the fixed conformations of the bis(1-hydrocarbylindenyl)- and -(tetrahydroindenyl)zirconium dichloride complexes found in the solid state do not necessarily correspond to the equilibrium situation of conformational isomers in solution. Thus, bis(1-neoisomenthylindenyl)zirconium dichloride (**4b-A**), which exhibits a C_1-symmetric structure in the crystal, appears as a C_2-symmetric species in solution according to its NMR spectra at low temperature ($\geq$-60 °C at 4.7 T). Similarly, we have not obtained any evidence that bis(1-neoisomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (**5b-A**) in solution exhibits a conformation other than C_2-symmetric.

In view of the conformational features of a closely related system (see below), it is likely that the observed static variable-temperature NMR behavior of **4b-A** and **5b-A** may indeed indicate the presence of only a single dominanting (C_2-symmetric) metallocene rotameric type in solution. Of course, it cannot principally be ruled out that this NMR appearance might be caused by the presence of a set of extremely rapidly interconverting bent metallocene conformers, including such of lower molecular symmetry.

The situation seems to be quite different for the neomenthyl-substituted complexes **4a-A** and **5a-A**. In solution, bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride exhibits two conformational isomers in a 80:20 ratio which are rapidly interconverted on the NMR time scale. The major rotational isomer is C_2-symmetric whereas the minor isomer possesses C_1-molecular symmetry. We conclude that it is very likely that these two rotational isomers correspond to the conformational types **G** and **I** (see Scheme II). Complex **4a-A** shows similar dynamic behavior but may even represent a more complicated case of equilibration between bent metallocene conformers.

Scheme IV



There is reason to believe that similar conformational equilibria are present at the stage of the bent metallocene derived active propene polymerization catalyst described above. Although we cannot observe the rotational isomers directly, they may transfer their different symmetry features onto the growing polymer chain and thereby reflect their presence. This seems to serve as an ample explanation for the unexpected trends in product stereoselectivities observed in the series of catalysts derived from the complexes **4a-A**, **4b-A**, **5a-A**, and **5b-A**. Both neoisomenthyl-substituted systems have produced polypropylenes of higher isotacticities as compared to their neomenthyl counterparts. In view of the pronounced conformational differences of these systems at the metallocene dihalide state, this probably reflects similar differences in the conformational behavior and population of different rotational isomers at the actual active catalyst. We assume that the neoisomenthyl-substituted systems are largely C_2-symmetric and hence produce isotactic polypropylene with occasional singular stereochemical mistakes by overall enantiomorphic site control. At the neomenthyl-substituted catalysts we may have encountered a situation where equilibration between markedly populated rotational isomers of different symmetry of the metallocene backbone may become of importance. As long as the system "rests" on the C_2-symmetric side, it is able to produce an isotactic type I polymer section[1] under enantiomorphic site control with a small number of singular "mistakes". Crossing the barrier to the other rotational isomer (C_1 metallocene backbone symmetry) will then lead to a situation where we expect a reduced degree of stereocontrol. Lacking the presence of C_2 symmetry related pairs of uncongested sectors for propene coordination, the C_1-symmetric metallocene catalyst backbone is expected to allow for a much higher number of singular mistakes in polypropylene formation under enantiomorphic site control. At the extreme this may even lead to a situation where atactic or isotactic block (polypropylene "type II", formed by chain end control) polymer formation takes place. Switching between two (or more) conformational types of the bent metallocene backbone at the stage of the active catalyst may actually result in the formation of various types of block polymer structures, of which the production of alternating sequences of different isotacticities represents a simple case which is likely to have occurred with some of the above described systems. Investigations aimed at systematically using this conformational effect for preparing novel types of block polymer structures are currently being carried out in our laboratory.

Experimental Section

All reactions with organometallic reagents were carried out in an inert atmosphere (argon) using Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. NMR spectra were measured on a Bruker AC 200 P (200 MHz ^{1}H; 50 MHz ^{13}C), WM 300 (300 MHz

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[18] Stephenson, D. S.; Binsch, G. DNMR 5: A Computer Program for Iterative Analysis of Exchange-Broadened NMR Spectra. Quantum Chemistry Program Exchange **1978**, *10*, 365. Binsch, G. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 45. Binsch, G.; Kessler, H. *Angew. Chem.* **1980**, *92*, 445; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411.

[19] Green, M. L. H.; Wong, L.-L.; Selia, A. *Organometallics* **1992**, *11*, 2660.

^{1}H), or WM 400 (400 MHz, ^{1}H) NMR spectrometer. IR spectra were recorded on a Nicolet 5 DXC FT IR spectrometer. Optical rotation: Perkin-Elmer polarimeter Model 241 MC, sodium vapor lamp ($\lambda = 589$ nm), ambient temperature, concentration *c* in g/100 mL. Melting points: Büchi SMP 20 or DuPont DSC 910, melting points are uncorrected. Elemental analyses: Perkin-Elmer Model 240. Methylalumoxane was prepared according to a literature procedure.[20] The propene polymerization reactions were carried out as was previously described in detail[15] [in toluene/propene solution ($\approx$3:1) with no external propene pressure applied; the Zr catalyst concentration employed was ca. 0.1 mM; polymerization reactions were usually carried out at −30 and −5 °C with a few additional experiments done at other temperatures (see, e.g., Figure 4); further details of these standard polymerization experiments are listed in Table VI. The ^{13}C NMR methyl pentade analysis of polypropylene and the statistical analysis were performed analogously as described previously.[15,16] $ZrCl_4(THF)_2$ was synthesized as described in the literature.[21]

(−)-(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl *p*-Toluenesulfonate ("Menthyl Tosylate", 1a).[22] To a mixture of 235 g (1.5 mol) of (−)-menthol and 480 g (6.0 mol) of pyridine was added 315 g (1.65 mol) of *p*-toluenesulfonyl chloride in several portions at 10–15 °C. The reaction mixture was stirred for 3 h at room temperature and then added to a mixture of 2000 g of ice/750 mL of concentrated HCl. The product was collected by filtration, washed with water, and dried to give 401 g (86%) of **1a**: $[\alpha]_D = -74°$ ($c = 0.16$, ethanol); ^{1}H NMR ($CDCl_3$) δ 7.79, 7.35 (AA′XX′, 2 H each, C_6H_4), 4.42 [m, $^3J = 11$ Hz (1-H, 2-H), 11 Hz (1-H, 6-H$_{ax}$), 5 Hz (1-H, 6-H$_{eq}$)], 2.46 (s, 3 H, $C_6H_4CH_3$), 2.1–0.9 (m, 9 H, 2-H–6-H, 8-H), 0.83 and 0.79 (each d, $^3J = 9$ Hz, 6 H, isopropyl-CH_3), 0.42 (d, $^3J = 7$ Hz, 3 H, CH_3).

(+)-(1*S*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl *p*-Toluenesulfonate ("Isomenthyl Tosylate", 1b). Analogously 156 g (1.0 mol) of (+)-isomenthol was reacted with 210 g (1.1 mol) of *p*-toluenesulfonyl chloride to yield 231 g (70%) of (+)-isomenthyl tosylate: $[\alpha]_D = +6°$ ($c = 0.15$, ethanol); ^{1}H NMR ($CDCl_3$) δ 7.75, 7.29 (AA′XX′, 2 H each, C_6H_4), 4.68 (m, 1 H, 1-H), 2.40 (s, 3 H, $C_6H_4CH_3$), 1.9–0.9 (m, 9 H, 2-H–6-H, 8-H), 0.81, 0.75, 0.71 (each d, each 3 H, CH_3).

(+)-3-[(1′*S*,2′*S*,5′*R*)-2′-Isopropyl-5′-methylcyclohexyl]indene ("3-Neomenthylindene", 2a). A solution containing 9.2 g (76.0 mmol) indenyllithium in 75 mL of tetrahydrofuran/55 mL of *n*-hexane was prepared according to a literature procedure[23] from indene and *n*-butyllithium. To this solution was added dropwise at 0 °C a solution of 20.6 g (67.0 mmol) of (−)-menthyl tosylate (**1a**) in 100 mL of tetrahydrofuran. The mixture was stirred for 1 h at room temperature and then refluxed for 72 h. The mixture was hydrolyzed with water (75 mL). Ether (100 mL) was added. The organic phase was separated and washed three times with water (30-mL portions). The aqueous phase was extracted twice with ether (30-mL portions). The combined organic layers were dried over sodium sulfate. Solvent was removed in vacuo and the remaining residue distilled (98 °C, 0.1 Torr) to give 6.4 g (37%) of 3-neomenthylindene (**2a**): mp 46 °C; $[\alpha]_D = +79°$ ($c = 0.43$, methylene chloride); ^{1}H NMR ($CDCl_3$) δ 7.50–7.12 (m, 4 H, 4-H–7-H), 6.37 (m, 1 H, 2-H), 3.36 (m, 2 H, 1-H), 3.34 (m, 1 H, 1′-H), 1.98–0.84 (m, 9 H, 2′-H–6′-H, 8′-H), 0.93 (d, $^3J = 6.6$ Hz, 3 H, CH_3), 0.79 (d, $^3J = 6.4$ Hz, 3 H, CH_3), 0.73 (d, $^3J = 6.5$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 146.6, 144.6, 143.8 (C-3, C-8, C-9), 125.9 ($^1J_{CH} = 159$ Hz, $^2J_{CH} = 7$ Hz), 124.3 (160, 7), 123.6 (159, 8), 118.8 (158, 7, C-4–C-7), 129.4 (165, 6, C-2), 38.3 (129, C-1), 47.6 (115), 34.1 (127), 30.0 (126), 26.7 (125, C-1′, C-2′, C-5′, C-8′), 39.5 (129), 35.6 (126), 27.2 (119, C-3′, C-4′, C-6′), 22.4 (125), 21.5 (124), 21.4 (124, C-7′, C-9′, C-10′); IR ν (cm^{-1}) 3069, 3018, 2945, 2925, 2868, 2841, 1457, 973, 769, 720. Anal. Calcd for $C_{19}H_{26}$ (254.2): C, 89.70; H, 10.30. Found: C, 89.93; H, 10.52.

(+)-3-[(1′*R*,2′*R*,5′*R*)-2′-Isopropyl-5′-methylcyclohexyl]indene ("3-Neoisomenthylindene" 2b). (+)-Isomenthyl tosylate (**1b**) (93.1 g, 300 mmol) was reacted with 49.0 g (400 mmol) of indenyllithium analogously as described above to yield 30.2 g (40%) of (+)-3-neoisomenthylindene (**2b**): bp 126 °C (0.1 Torr); $[\alpha]_D = +79°$ ($c = 0.46$, toluene); ^{1}H NMR ($CDCl_3$) δ 7.56–7.15 (m, 4 H, 4-H–7-H), 6.32 (m, 1 H, 2-H), 3.43 (m, 2 H, 1-H), 3.03 (m, 1 H, 1′-H), 2.25–1.40 (m, 9 H, 2′-H–6′-H), 1.20 (d, $^3J = 7.1$ Hz, 3 H, CH_3), 1.02 (d, $^3J = 6.9$ Hz, 3 H, CH_3), 0.89 (d, $^3J = 6.8$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 149.5, 145.7, 144.3 (C-3, C-8, C-9), 125.8 ($^1J_{CH} = 159$ Hz, $^2J_{CH} = 7$ Hz), 124.3 (159, 7), 123.7 (158, 8), 119.5 (158, 8, C-4–C-7), 126.6 (165, 5, C-2), 37.6 (120, C-1), 41.3 (124), 40.9 (121), 33.2 (121), 26.0 (123, C-1′, C-2′, C-5′, C-8′), 35.3 (117), 31.2 (124), 29.3 (125, C-3′, C-4′, C-6′), 24.1 (124), 22.9 (124), 21.7 (124, C-7′, C-9′, C-10′); IR ν (cm^{-1}) 3068, 3018, 2956, 2922, 2868, 1458, 965, 768, 754, 720. Anal. Calcd for $C_{19}H_{26}$ (254.2): C, 89.70; H, 10.30. Found: C, 89.72; H, 10.32.

(1-Neomenthylindenyl)lithium (3a). To a solution of 6.4 g (25.2 mmol) of (+)-3-neomenthylindene (**2a**) in 100 mL of ether was added dropwise 11.5 mL (25.2 mmol) of a 2.2 M ethereal methyllithium solution. The mixture was stirred for 2 h at room temperature. Solvent was removed in vacuo and the residue washed twice with pentane (30 mL each) to yield 5.4 g (82%) of **3a**. The lithium compound was characterized spectroscopically: ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8, 10:1) δ 7.72 (m, 2 H, 4-H, 7-H), 6.92, 6.91 (m, 2 H, 5-H, 7-H), 6.83, 6.23 (AX, $^3J = 3.3$ Hz, 2-H, 3-H), 3.97 (m, 1 H, 1′-H), 2.10–1.01 (m, 9 H, 2′-H–6′-H, 8′-H), 0.92 (d, $^3J = 6.5$ Hz, CH_3), 0.89 (d, $^3J = 6.9$ Hz, CH_3), 0.87 (d, $^3J = 6.2$ Hz, CH_3); ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8, 10:1) δ 126.8, 126.7 (C-8, C-9), 120.2 ($^1J_{CH} = 153$ Hz, $^2J_{CH} = 5$ Hz), 118.4 (153, 5), 115.6 (154, 8), 114.8 (154, 8, C-4–C-7), 116.7 (155, 6, C-2), 109.2 (C-1), 88.9 (162, 3, C-3), 49.4 (122), 34.8 (123), 31.0 (125), 27.6 (121, C-1′, C-2′, C-5′, C-8′), 45.5 (126), 36.7 (123), 27.4 (121, C-3′, C-4′, C-6′), 23.5 (124), 22.4 (126), 21.5 (124, C-7′, C-9′, C-10′).

(1-Neoisomenthylindenyl)lithium (3b). Analogously as described above (+)-3-neoisomenthylindene (**2b**) (26.0 g, 102 mmol) dissolved in 300 mL of ether was reacted with 46.5 mL (102 mmol) of a 2.2 M solution of methyllithium in ether to yield 24.2 g (91%) of **3b**: ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8, 10:1) δ 7.84, 7.82 (m, 1 H, each, 4-H, 7-H), 7.04, 7.01 (m, 1 H each, 5-H, 6-H), 6.77, 6.32 (AX, $^3J = 3.3$ Hz, 2 H, 2-H, 3-H), 3.71 [m, $^3J = 12.4$ Hz (1′-H, 6′-H$_{ax}$), 3.2 (1′-H, 6′-H$_{eq}$), 3.2 (1′-H, 2′-H)], 2.35–1.22 (m, 9 H, 2′-H–6′-H, 8′-H), 1.18 (d, $^3J = 6.3$ Hz, CH_3), 1.04 (d, $^3J = 6.8$ Hz, CH_3), 0.35 (d, $^3J = 6.5$ Hz, CH_3); ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8, 10:1) δ 127.7, 125.3 (C-8, C-9), 120.5 ($^1J_{CH} = 153$ Hz, $^2J_{CH} = 5$ Hz), 118.9 (153, 5), 115.6 (154, 8), 114.6 (154, 8, C-4–C-7), 113.0 (155, 5, C-2), 112.3 (C-1), 88.7 (162, C-3), 44.0 (121), 41.7 (119), 34.7 (124), 26.3 (125, C-1′, C-2′, C-5′, C-8′), 38.7 (123), 32.2 (122), 29.9 (122, C-3′, C-4′, C-6′), 24.4 (124), 23.7 (124), 22.3 (125, C-7′, C-9′, C-10′).

Bis(1-neomenthylindenyl)zirconium Dichloride (4a). To a suspension of 2.9 g (7.7 mmol) of $ZrCl_4(THF)_2$ in 50 mL of toluene was added at −78 °C a cold solution of 4.0 g (15.4 mmol) of (1-neomenthylindenyl)lithium (**3a**) in 200 mL of tetrahydrofuran. The mixture was allowed to warm to ambient temperature during 6 h with stirring and then kept at room temperature for 12 h. Solvent was removed in vacuo. ^{1}H NMR spectroscopy of a sample of the residue revealed that the diastereomeric complexes **4a-A,B,C** were formed in a ratio of 93:2:5. The obtained yellow solid was washed twice with pentane (50 mL each) and treated with 100 mL of methylene chloride, and the solution was filtered from the precipitated lithium chloride. The clear filtrate was concentrated in vacuo and allowed to crystallize at −28 °C. The crystals obtained were suited for the X-ray crystal structure analysis (for details see Table V). The mother liquor was further concentrated and cooled to −28 °C for crystallization. Repeated recrystallization of the obtained material from methylene chloride furnished complex **4a-A** diastereomerically pure: yield 3.15 g (61%); mp 146 °C; $[\alpha]_D = -77°$ ($c = 0.23$, toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (m, 1 H, 7-H), 7.65 (m, 1 H, 4-H), 7.32 (m, 1 H, 5-H), 7.14 (m, 1 H, 6-H), 6.59, 5.53 (AX, $^3J = 3.1$ Hz, 1 H each, 2-H, 3-H), 3.68 (m, 1 H, 1′-H), 2.14 (m, 1 H, 2′-H), 2.04 (m, 1 H, 5′-H), 1.92 (m, 2 H, 4′-H), 1.37–0.96 (m, 5 H, 3′-H, 6′-H, 8′-H), 0.94 (d, $^3J = 6.4$ Hz, 3 H, CH_3), 0.60 (d, $^3J = 6.7$ Hz, 3 H, CH_3), −0.05 (d, $^3J = 6.7$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 128.5, 126.7, 126.2 (C-1, C-8, C-9), 126.1 ($^1J_{CH} = 162$ Hz, $^2J_{CH} = 8$ Hz), 125.8 (164, 8), 125.1 (163, 7), 124.5 (161, 8, C-4–C-7), 122.5 (169, C-2), 98.0 (175, 5, C-3), 48.1 (119, C-1′), 39.0 (134, C-6′), 36.1 (125, C-2′), 34.2 (124, C-4′), 28.9 (125, double intensity, C-2′, C-5′), 23.6 (124, C-7′), 22.3 (124, C-3′), 22.3 (126), 18.3 (129, C-9′, C-10′); IR (KBr) ν (cm^{-1}) 3103, 2954, 2925, 1634, 1457, 1448, 1390, 1369, 806, 743. Anal. Calcd for $C_{38}H_{50}Cl_2Zr$ (668.9): C, 68.22; H, 7.53. Found: C, 67.90; H, 7.67.

Bis(1-neoisomenthylindenyl)zirconium Dichloride (4b). Analogously as described above 3.6 g (13.7 mmol) of (1-neoisomenthylindenyl)lithium (**3b**) was reacted with 2.5 g (8.5 mmol) of $ZrCl_4(THF)_2$. The reaction mixture was stirred for 24 h at room temperature. Solvent was removed from the yellow suspension in vacuo and the **4b-A**:**B**:**C** diastereomer ratio determined by ^{1}H NMR spectroscopy of a sample as 82:7:11. The residue was extracted with 150 mL of methylene chloride. Twofold crystallization from methylene chloride gave the pure diastereomer **4b-A** (1.1 g, 25%):

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mp 123 °C; $[\alpha]_D = +71°$ ($c = 0.28$, toluene); ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 1 H, 7-H), 7.45 (m, 1 H, 4-H), 7.29 (m, 1 H, 5-H), 7.12 (m, 1 H, 6-H), 6.19, 5.61 (AX, $^3J = 2.9$ Hz, 2 H, 2-H, 3-H), 3.54 (m, 1 H, 1′-H), 1.98–0.75 (m, 9 H, 2′-H–6′-H, 8′-H), 0.90 (d, $^3J = 6.2$ Hz, 3 H, CH_3), 0.71 (d, $^3J = 6.8$ Hz, 3 H, CH_3), –0.17 (d, $^3J = 6.5$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 132.4, 128.5, 123.7 (C-1, C-8, C-9), 127.0, 125.7, 125.0, 124.6, 118.0 (C-2, C-4–C-7), 95.7 (C-3), 43.0, 40.6, 32.7, 25.7 (C-1′, C-2′, C-5′, C-8′), 34.0, 30.7, 29.6 (C-3′, C-4′, C-6′), 23.5, 22.9, 21.7 (C-7′, C-9′, C-10′) [for details concerning the X-ray crystal structure analysis of **4b-A**, see Table V]; IR (KBr) ν (cm^{-1}) 3087, 2947, 2925, 2866, 1457, 1441, 1387, 1347, 1221, 1157, 807, 745. Anal. Calcd for $C_{38}H_{50}Cl_2Zr$ (668.9): C, 68.22; H, 7.53. Found: C, 67.83; H, 7.88.

(p-*S*,p-*S*)-Bis(1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium Dichloride (5a-A). A suspension of 1.20 g (1.79 mmol) of (p-*S*,p-*S*)-bis(1-neomenthylindenyl)zirconium dichloride (**4a-A**) and 80 mg of PtO_2 in 60 mL of methylene chloride was hydrogenated in a 100-mL laboratory autoclave for 3.5 h at 50 bar of H_2 with stirring at room temperature. The catalyst was then removed by filtration. Solvent was then removed in vacuo to give 1.09 g (91%) of **5a-A**. Recrystallization from methylene chloride gave crystals suitable for X-ray diffraction (see Table V): mp 312 °C; $[\alpha]_D = +3°$ ($c = 0.20$, toluene); ^{1}H NMR ($CDCl_3$) δ 6.36, 5.56 (AX, $^3J = 2.8$ Hz, 1 H each, 2-H, 3-H), 3.05–2.80 (m, 3 H), 2.62–2.34 (m, 2 H), 2.10–1.22 (m, 11 H), 1.18–0.93 (m, 2 H), 0.89 (d, $^3J = 6.3$ Hz, 3 H, CH_3), 0.83 (d, $^3J = 6.6$ Hz, 3 H, CH_3), 0.31 (d, $^3J = 6.6$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 137.3, 135.3, 130.1 (C-1, C-8, C-9), 108.9 ($^1J_{CH} = 170$ Hz), 102.0 (170, C-2, C-3), 47.6 (124), 36.3 (127), 28.9 (124), 28.8 ($^1J_{CH}$ not determined, C-1′, C-2′, C-5′, C-8′), 24.5 (129), 24.4 ($^1J_{CH}$ not determined), 22.5 (124), 22.1 ($^1J_{CH}$ not determined, C-4–C-7), 39.5 (127), 33.7 (127), 21.9 (124, C-3′, C-4′, C-6′), 24.0 (130), 21.8 (122), 18.2 (125, C-7′, C-9′, C-10′); IR (KBr) ν (cm^{-1}) 3111, 2941, 2865, 1465, 818, 808, 797. Anal. Calcd for $C_{38}H_{58}Cl_2Zr$ (677.0): C, 67.42; H, 8.64. Found: C, 67.32; H, 8.84. The dynamic ^{1}H NMR spectra of **5a-A** were recorded at six temperatures between 215.0 ± 0.5 and 189.0 ± 0.5 K at 4.7 T in methylene chloride. The exchange rate constants at these temperatures were determined by a complete line shape analysis of the 2-H, 3-H resonances using the DNMR 5 computer program package. The following k_{exchange} values were thus obtained from which the Gibbs activation energies of the conformational isomerization of the major C_2- to the minor C_1-symmetric rotamer of **5a-A** was calculated (averaged esd's of k_{exchange} are ca. ± 0.1 s^{-1}, of $\Delta G^{\ddagger}$ ca. 0.2 kcal mol^{-1}): $k_{\text{exchange}} = 14.4$ s^{-1}, $\Delta G^{\ddagger}$ 11.3 kcal mol^{-1} (215 K); 11.8, 11.3 (213 K); 7.2, 11.4 (210 K); 1.8, 11.4 (201 K); 1.0, 11.3 (195 K); 0.3, 11.3 (189 K).

(p-*R*,p-*R*)-Bis(1-neoisomenthyl-4,5,6,7-tetrahydroindenyl)zirconium Dichloride (5b-A). Hydrogenation of 1.00 g (1.49 mmol) of complex **4b-A** carried out analogously as described above (50 mL of methylene chloride, 50 mg of PtO_2, 50 bar of H_2, 2.5-h reaction time) gave 0.95 g (95%) of **5b-A**. Recrystallization from methylene chloride produced crystals for the X-ray diffraction study (see Table V): mp 280 °C; $[\alpha]_D = +4°$ ($c = 0.25$, toluene); ^{1}H NMR ($CDCl_3$) δ 6.03, 5.67 (AX, $^3J = 2.7$ Hz, 1 H each, 2-H, 3-H), 3.02–2.70 (m, 3 H), 2.55–2.34 (m, 2 H), 2.10–1.78 (m, 3 H), 1.68–1.10 (m, 8 H), 1.08–0.85 (m, 2 H), 0.86 (d, $^3J = 5.1$ Hz, 3 H, CH_3), 0.83 (d, $^2J = 5.1$ Hz, 3 H, CH_3), 0.31 (d, $^3J = 6.4$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 138.6, 135.8, 127.7 (C-1, C-8, C-9), 105.8 ($^1J_{CH} = 170$ Hz), 102.6 (168, C-2, C-3), 41.6 (121), 40.3 (127), 32.6 (124), 25.5 (128, C-1′, C-2′, C-5′, C-8′), 35.5 (131), 30.7 (126), 29.3 (125, C-3′, C-4′, C-6′), 24.5 (123), 23.5 ($^1J_{CH}$ not determined), 22.6 (120), 21.8 (125, C-4–C-7), 24.4 ($^1J_{CH}$ not determined), 22.9 ($^1J_{CH}$ not determined), 21.5 (128, C-7′, C-9′, C-10′); IR (KBr) ν (cm^{-1}) 3103, 2940, 2855, 1456, 838, 828, 811. Anal. Calcd for $C_{38}H_{58}Cl_2Zr$ (677.0): C, 67.42; H, 8.64. Found: C, 67.26; H, 8.89.

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Supplementary Material Available: Details of the X-ray crystal structure analyses of complexes **4a-A**, **4b-A**, **5a-A**, and **5b-A** including complete listings of bond lengths and angles, atomic fractional coordinates, and thermal parameters (28 pages); observed and calculated structure factors (59 pages). Ordering information is given on any current masthead page.