Conformational Analysis of Nonbridged Bent Metallocene Ziegler-Catalyst Precursors−Detection of the Third Torsional Isomer

Markus Knickmeier, Gerhard Erker,* and Thomas Fox

Contribution from the Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität, Corrensstrasse 40, D-48149 Münster, Germany

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Abstract: The series of (1-terpenylindenyl)$_2$ZrCl$_2$ bent metallocene complexes (with terpenyl substituents neomenthyl, neoisomenthyl, menthyl, and isomenthyl) were obtained from the reaction of the respective 1-terpenylindenyl lithium reagents with ZrCl$_4$. In each case a single racem-like diastereoisomer was isolated pure by crystallization. The conformational analysis of the bent metallocene systems was carried out by variable temperature ^{1}H NMR spectroscopy. It has revealed the existence and equilibration of three different bent metallocene torsional isomers. Two of these are C_2-symmetric and carry their bulky terpenyl substituents either in the lateral or the front sector of the bent metallocene wedge (descriptors *bis-lateral:anti* (conformer **A**) and *bis-central:syn* (conformer **B**)), whereas the rotational isomer **C** (*central,lateral:gauche*) is of lower symmetry. The (1-terpenylindenyl)$_2$ZrCl$_2$/methylalumoxane systems are active propene polymerization catalysts. The equilibrium amount of the "stereochemically productive" C_2-symmetric *bis-lateral:anti* bent metallocene conformer **A** correlates qualitatively with the observed isotacticity of the propene polymerization process at the respective group 4 bent metallocene catalyst system.

Introduction

The group 4 metallocene derived homogeneous Ziegler catalysts have gone through a remarkable development in recent years. Structural variation and amendment of the bent metallocene complex precursors has led to catalyst systems that produce α-olefin polymers, copolymers, and oligomers with an amazing selectivity and selection.[1] Mostly ansa-metallocenes exhibiting small groups bridging between the modified cyclopentadienyl, indenyl, or fluorenyl ligands have been used for this very successful experimental development.[2] We had proposed that there may also be applications where the use of open nonbridged bent metallocene derived catalyst systems is advised.[3] In these cases, the torsional isomerism of the group 4 metallocene units should be known and made use of.[4] In an early paper we have presented some first evidence that the equilibrium situation of the rotational isomerism of substituted bis(indenyl)zirconocene derived systems might be reflected by the stereocontrol of the (low temperature) propene polymerization process at the metallocene/methylalumoxane Ziegler catalysts derived from these very systems.[5] Since then a few other examples have been described where a similar stereocontrol by means of torsional metallocene isomerism may take place.[6] An example of this type, that has received considerable public attention, is the formation of polypropylene elastomers by bis(2-arylindenyl)zirconocene/methylalumoxane (MAO) systems where two interconverting rotational isomers of different

symmetry properties are thought to give rise to the formation of the stereochemically differentiated block structures along the polymer chain.[7]

Most of these systems have in common that two torsional isomers are thought to be involved in a "non-Curtin−Hammett" situation[8] at the active catalyst stage, giving rise to a switching on/switching off alternative between suited or nonsuited symmetry properties for stereoselective α-olefin polymerization at the bent metallocene backbone.

For a small group of bis(1-terpenyltetrahydroindenyl)ZrCl$_2$ complexes a combined dynamic NMR/X-ray diffraction study
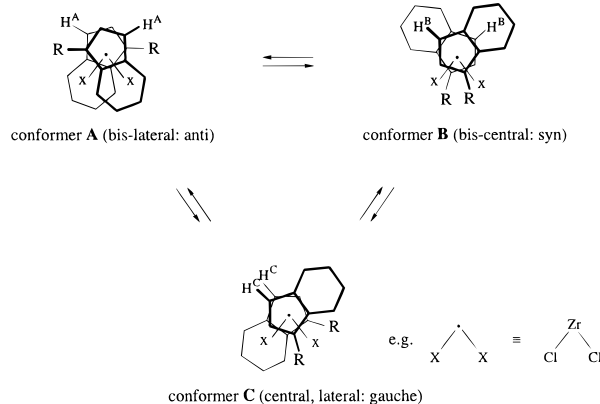

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Scheme 1. Schematic Representation of the Three Possible Group 4 Bent Metallocene Torsional Isomers of Racem-like (rl) Bis(1-hydrocarbylindenyl)MX$_2$ Type Complexes

conformer **A** (bis-lateral: anti)   conformer **B** (bis-central: syn)

conformer **C** (central, lateral: gauche)

has revealed the structures of the interconverting metallocene rotamers and their activation barriers of rearrangement.[5] For the bis(1-neomenthyltetrahydroindenyl)ZrCl$_2$ system two rotational isomers of types **A** and **C** were identified (see Scheme 1). These are distinguished by their relative orientations of the bulky terpenyl substituents at the framework of the bent metallocene. The **A**-type conformer exhibits both annulated six-membered rings in a central position oriented to the open front side of the bent metallocene wedge and consequently exhibits the bulky terpenyl groups arranged anti to each other, i.e., pointing to the opposite bent metallocene lateral sectors. This torsional bent metallocene isomer is characterized by the conformational descriptor *bis-lateral:anti*. In contrast the **C**-type rotational isomer (descriptor *central,lateral:gauche*) exhibits one 1-hydrocarbyl substituent up front and the other in the adjacent lateral sector (see Scheme 1).

From this description it is rather obvious that the equilibrating situation of only two rotameric types of different symmetry properties is probably the exception rather than the rule. It is more likely that at least one additional bent metallocene conformer is principally participating, namely the *bis-central: syn* isomer **B**. This rotamer is also of C_2-symmetry but will certainly exhibit properties of catalytic stereocontrol rather different from the C_2-symmetric *bis-lateral:anti* bent metallocene conformer type **A**.

We have now for the first time detected the "third bent metallocene rotational isomer" (**B**: *bis-central:syn*) by studying the dynamic NMR spectra of bis(1-terpenylindenyl)ZrCl$_2$ complexes using the complete series of the menthone-derived substituents. This has revealed an interesting dependence of the rotational isomer distribution of the bent metallocene systems from the specific terpenyl substitution pattern and in coincidence with this the qualitative degree of stereoselective polypropylene formation at the homogeneous Ziegler-catalysts derived from these metallocene systems.

Results and Discussion

Metallocene Preparation. The syntheses of the metallocene dihalides **4**−**7** were carried out similarly as recently described, starting from commercially available (+)-menthol (i.e., 1S,3S,4R-4-isopropyl-1-methylcyclohexan-3-ol) and (+)-isomenthol (i.e., 1R,3S,4R-4-isopropyl-1-methylcyclohexan-3-ol), respectively. The tosylates (or mesylates) of all four diastereomeric alcohols (menthol, isomenthol, neomenthol, and neoisomenthol) where prepared according to literature procedures.[9] Treatment of these sulfonates with indenyllithium gave the corresponding terpenyl substituted indenes. Subsequent deprotonation employing *n*-

butyllithium in ether furnished the corresponding 1-terpenyl-substituted indenyllithium compounds. Since the solvent was changed to toluene for the metallocene preparation, all substituted indenyllithium compounds were isolated as solids.

Indenyl anions containing chiral substituents attached to the 1-positions possess diastereotopic faces. Therefore, the coordination of a pair of homochiral 1-terpenyl-indenyls to zirconium can result in the formation of three diastereomeric bent metallocene complexes that are characterized by the combinations of planar chirality descriptors (pR, pR), (pS, pS), and (pR, pS), respectively.[10] The former two exhibit racem-like ("rl") bent metallocene configurations, the latter is meso-like ("ml"). All three are, of course, chiral and obtained optically active when the enantiomerically enriched (or pure) terpenol precursors have been used.

For this study we have reacted the substituted indenyllithium reagents with zirconium tetrachloride both suspended as solids in toluene at −78 °C. The respective mixtures were allowed to warm to room temperature and kept there for several hours before workup. This procedure gave the bis(1-terpenyl-indenyl)ZrCl$_2$ complexes **4**−**7** as nonstatistical mixtures of diastereomers. In case of the neomenthyl-, neoisomenthyl-, and isomenthyl-substituted complexes[11] one of the racem-like diastereomer was formed predominately, whereas the meso-like isomer was the major product obtained in case of the menthyl-substituted metallocene complex (see Table 1). It was easy to distinguish the racem-like from the meso-like isomers due to their different overall symmetry properties (C_2 vs C_1) by NMR spectroscopy at high temperature: each of the racem-like isomers gives rise to a single pair of ^{1}H NMR resonances of the methine hydrogens at the five-membered ring moieties, whereas the meso-like diastereomer exhibits four such signals.

Washing with pentane and fractionating crystallization produced one racem-like diastereomer spectroscopically pure in each of the four different terpenylindenyl complex series (**rl-4**, **rl-5**, **rl-6**, **rl-7**). In addition, diastereomerically pure samples of the meso-like isomers **6** and **7** were obtained (**ml-6**, **ml-7**).

In a similar way the analogous (1-neomenthyl-4,7-dimethyl-indenyl)$_2$ZrCl$_2$ system (**8**) was synthesized (as previously described);[5] recrystallization furnished a pure racem-like diastereomer (**rl-8**).

Metallocene Conformational Analysis. In this study the conformational analysis of the 1-substituted bis(indenyl)zirconocene dichloride complexes was carried out by dynamic ^{1}H NMR spectroscopy. We had previously observed that the rapid rotation about the zirconium-Cp vector in bis(tetrahydroindenyl)-zirconocene dichloride complexes exhibiting bulky secondary alkyl substituents at their indenyl 1-positions could be "frozen" on the ^{1}H NMR time scale using a sufficiently high field NMR

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Table 1. Characterization of the Mixtures of Diastereomeric Bis(1-terpenylindenyl)ZrCl$_2$ Complexes Obtained from the Reaction of the Corresponding (1-Terpenylindenyl)lithium Reagents with Zirconium Tetrachloride
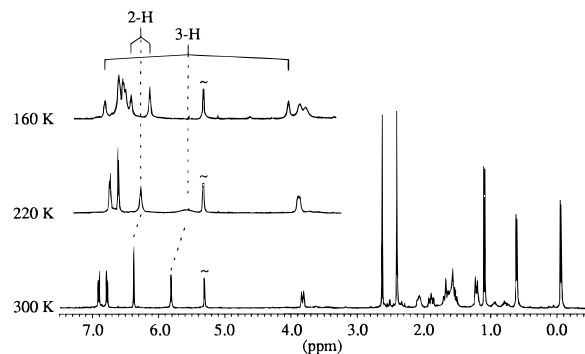
(terpenyl-)	rl-I:rl-II:ml[a]	rl-I[b]		rl-II[b]		ml[b]			
4 neomenthyl-	70:6:24	6.59	5.53	6.58	5.75	6.65	6.48	5.38	5.05
5 neoisomenthyl-	62:11:26	6.23	5.72	6.35	5.88	6.19	6.05	5.95	5.78
6 menthyl-	28:6:66	6.68	6.20	6.61	6.07	6.33	6.07	5.92	5.74
7 isomenthyl-	53:11:31	6.21	6.00	6.28	6.11	6.29	6.24	5.65	5.63
8 neomenthyl-4,7-dimethyl	98:1:1	6.39	5.82						

[a] Ratio of diastereomeric isomers (in %). [b] ^{1}H NMR chemical shifts (ppm δ-scale) of the indenyl 2-H and 3-H resonances (in CD$_2$Cl$_2$, 300 K, 200 or 600 MHz).

Scheme 2
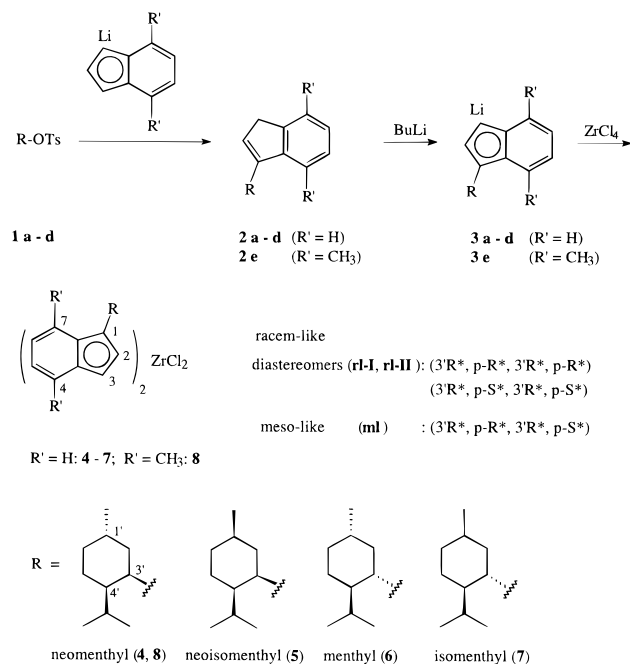
spectrometer.[5,6,12] Typically, the corresponding (1-neomenthyl-4,5,6,7-tetrahydroindenyl)zirconium rotational activation barrier was determined at $\Delta G^{\ddagger}$ (200 K) $\approx$ 11 $\pm$ 0.5 kcal mol^{-1}. The here presented series of investigation has now revealed that the analogous bis(1-terpenylindenyl)ZrCl$_2$ systems exhibit similar barriers of η^5-indenyl-zirconium rotation; their conformational analysis can thus be carried out by simply "freezing" the ligand-metal rotation at low temperature on the NMR time scale. The symmetry properties of the participating rotational isomers can then easily be determined from the obtained ^{1}H NMR spectra under static limiting low temperature conditions and their relative contribution estimated by integrating corresponding pairs of resonances.
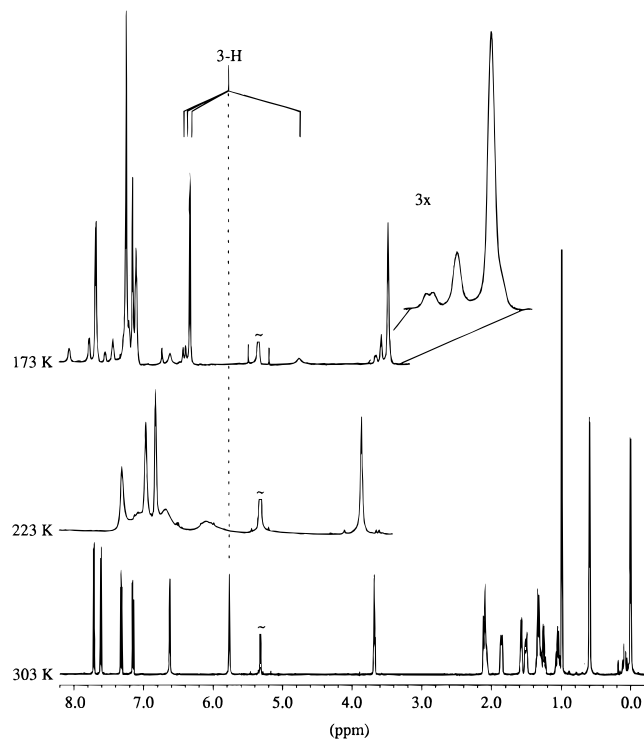
We first investigated the bis(1-neomenthyl-4,7-dimethylin-denyl)zirconium dichloride system **rl-8** (racem-like diastere-omer). At ambient temperature complex **rl-8** exhibits a ^{1}H NMR spectrum (at 600 MHz, bottom of Figure 1) that would be compatible with an apparent C_2-symmetric structure of this metallocene dihalide complex in solution. It shows three neomenthyl-methyl resonances (doublets at δ -0.10, 0.60 and 1.10) and two singlets (δ 2.41, 2.64) corresponding to the 4- and 7-methyl substituents at the indenyl rings. The indenyl 5-H and 6-H signals are at δ 6.79, 6.91 (^3J = 7.2 Hz). The indenyl

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Figure 1. Dynamic ^{1}H NMR spectra (600 MHz) of bis(1-neomenthyl-4,7-dimethylindenyl)zirconium dichloride **rl-8** in CD$_2$Cl$_2$.

2-H and 3-H resonances are observed at δ 5.82 and 6.39 (^3J = 3.2 Hz). These signals of the pair of hydrogens at the indenyl five-membered ring (in addition to the neomenthyl 3′-H resonance at δ 3.83) will be most diagnostic for the metallocene conformational analysis.

Lowering the temperature makes most of the signals broad and eventually leads to splitting of most resonances. A rather complicated set of spectra ensues, but a clear analysis is possible by looking at selected resonances. Below 220 K the 3′-H neomenthyl resonance splits into two signals in ca. 60:40 ratio indicating that there are two rotational isomers of **rl-8** in an equilibrium. The symmetry properties and probable structures of these two bent metallocene rotamers become clear upon looking at the temperature dependent behavior of the indenyl 2-H and 3-H resonances. Upon lowering the temperature the 2-H signal at δ 6.39 broadens and separates into two lines of 40:60 intensity ratio at δ 6.56 and 6.24 (see Figure 1). More dramatically, the 3-H resonance at δ 5.82 rapidly gets broad and eventually splits into two resonances that are extremely far apart: below coalescence one of the resulting signals is found at δ 7.00, whereas the other has moved up considerably to high field and is then found at δ 3.85 (see Figure 1, top).

It is the number of resulting resonances below the coalescence point and the very characteristic chemical shifts of some of these signals that allows for an unambiguous assignment of the rotameric isomers making up the bis(1-neomenthyl-4,7-di-methylindenyl)zirconium dichloride system **rl-8**. The low temperature (160 K) ^{1}H NMR spectrum clearly shows the presence of two C_2-symmetric metallocene rotamers in solution. The slightly favored (60%) component exhibits the 2-H and 3-H indenyl resonances in the typical range (δ 7.00, 6.24) and is very likely to be assigned the structure of the *bis-lateral:anti* conformer **rl-8A**. In contrast, the other C_2-symmetric torsional isomer (40%) only exhibits the 2-H indenyl resonance in the usual rage (δ 6.56), whereas the 3-H signal is shifted so far upfield (δ 3.85) that a special shielding effect must be assumed,

Figure 2. Dynamic ¹H NMR spectra of **rl-4** (in CD_2Cl_2, 600 MHz).

Figure 3. Temperature dependent dynamic ¹H NMR spectra of (1-isomenthylindenyl)₂ZrCl₂ (**rl-7**) in CD_2Cl_2 (600 MHz).

that is very likely due to entering of the 3-H proton of one indenyl ring system into the deshielding anisotropy area of the annulated arene ring system of the other indenyl ligand system at the zirconium enter. This strongly indicates that this newly observed metallocene conformer is the "third" rotamer, here **rl-8B**, that has for the first time been observed for this very metallocene system. This rotational isomer, the *bis-central: syn*-conformer, is C_2-symmetric and has the neomenthyl substituents oriented in the front of the bent metallocene wedge in a close projection to each other; the annulated arene rings are placed in the lateral ("northwest" and "northeast") positions at the bent metallocene framework. We thus conclude that the bis(1-neomenthyl-4,7-indenyl)zirconium dichloride is unique among the bis(indenyl)MX₂ type systems as it represents a situation where two different C_2-symmetric metallocene rotamers of close to equal population (60:40) are rapidly equilibrating, one being characterized as the often observed *bis-lateral: anti* bent metallocene conformational type (here **rl-8A**), whereas the other to our knowledge represents the first example of the *bis-central:syn* bis(indenyl)MX₂ conformer (**rl-8B**) (see Scheme 1).

We next investigated the corresponding bis(1-neomenthyl-indenyl)zirconium dichloride system (**rl-4**) and found a related, but not identical, conformational behavior. At ambient temperature a 600 MHz ¹H NMR spectrum as expected for a single C_2-symmetric species is observed (see Figure 2, bottom), but this spectral appearance is just due to a rapid conformational equilibration. Cooling the sample inside the probe of the NMR spectrometer rapidly led to a broadening of the signals and then splitting. The low temperature situation is more complicated than in the related 4,7-dimethylindenyl system: in the (1-neomenthylindenyl)ZrCl₂ case three bent metallocene conformers can be distinguished. There are two proton resonances that can best serve to illustrate this conformational behavior. The neomenthyl 3′-H signal at δ 3.68 (see Figure 2, bottom) splits into resonances belonging to the three different rotational isomers. At 173 K (Figure 2, top) there are two broad singlets, belonging to two C_2-symmetric metallocene conformers, and two additional features, in a 1:1 ratio, indicating the presence
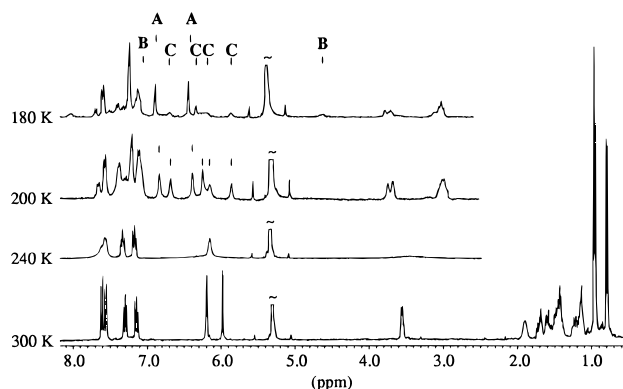
of a third conformer of lower overall symmetry, whose 1-neo-menthylindenyl ligands are not symmetry equivalent. This behavior also becomes clearly evident from the changing appearance of the indenyl 3-H resonance with decreasing temperature. The 3-H signal (δ 5.77 at 303 K, see Figure 2) rapidly broadens upon cooling (see Figure 2) and eventually separates into a dominating resonance at δ 6.29 (70%), a 15% high field resonance (δ 4.71), and a 1:1 pair of resonances (δ 6.39, 6.36) of ca. 15% combined intensity. We assume that the major signal indicates the presence of the dominating C_2-symmetric *bis-lateral:anti* metallocene conformer **rl-4A**, whereas the low temperature high field 3-H signal is very characteristic of the related C_2-symmetric *bis-central:syn* rotameric isomer **rl-4B**. The additional pairs of 3′-H and 3-H resonances indicate the presence of an additional conformer to which we ascribe the structure of the system with *central,lateral:gauche* ligand group orientation (**rl-4C**) (see Scheme 1). Many of the remaining low temperature ¹H NMR signals were assigned using ROESY and TOCSY experiments (see Experimental Section) and support these structural assignments.

Bis(1-isomenthylindenyl)zirconium dichloride (**rl-7**) exhibits a very similar dynamic behavior. The high temperature limiting ¹H NMR spectrum at 300 K pretends the presence of a singular species of apparent C_2-symmetry, but lowering the monitoring temperature rapidly reveals the dynamic situation of three equilibrating conformeric species, two, **rl-7A** and **rl-7B**, of C_2-symmetry, each exhibiting pairs of symmetry equivalent (1-terpenylindenyl)ligand systems and one, **rl-7C**, of lower symmetry, showing a pair of nonsymmetry equivalent (1-iso-menthylindenyl) moieties. The bent metallocene rotational isomers **rl-7A**, **rl-7B**, and **rl-7C** are present in a ratio of ca. 40:30:30 at 200 K, although the exact determination of this equilibrium ratio was hampered by their apparently different solubilities in dichloromethane at low temperature (see Figure 3).

The remaining two racem-like metallocene complexes in this series behave quite differently. For both, the bis(1-neoisomen-thylindenyl)ZrCl₂ (**rl-5**) and the bis(1-menthylindenyl)ZrCl₂ (**rl-6**) systems, there is evidence that the C_2-symmetric *bis-lateral: anti* conformers (**rl-5A** and **rl-6A**, respectively) are by far dominating the bent metallocene conformational equilibrium situation. The ¹H NMR spectrum (600 MHz) of complex **rl-5** shows the typical appearance of an apparent C_2-symmetric species, exhibiting four resonances of the aromatic methine hydrogens 4-H to 7-H at δ 7.13, 7.32, 7.55, and 7.62, the neoisomenthyl 3′-H signal at δ 3.54 and the typical pair of indenyl 2-H and 3-H resonances at δ 6.23 and 5.72. The spectrum changes only slightly upon decreasing the temperature from 300 to 160 K. Apart from some slightly temperature
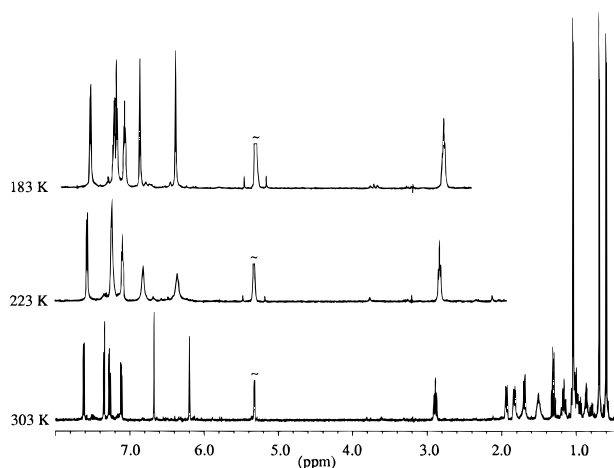
Figure 4. Dynamic ^{1}H NMR behavior (600 MHz) of bis(1-menthyl-indenyl)ZrCl$_2$ (**rl-6**) in CD$_2$Cl$_2$

dependent shifting of a few resonances only the indenyl 3-H signal starts to get broad at about 200 K and eventually has disappeared into the base line at the lowest temperature reached in this experiment (160 K). At that temperature also the low field aromatic signal has started to broaden. All other signals have remained sharp. In view of the very different behavior of the other examples of this metallocene complex family this probably indicates that the C_2-symmetric *bis-central:anti* form represents the by far dominating bent metallocene conformer in the bis(1-neoisomenthylindenyl)ZrCl$_2$ system.

The dominance of the *bis-lateral:anti* conformation is probably even more pronounced for the bis(1-menthylindenyl)-zirconium dichloride complex system. It exhibits the typical "C_2-symmetric ^{1}H NMR appearance" at high temperature (indenyl 4-H to 7-H: δ 7.62, 7.35, 7.27, 7.11; 2-H, 3-H: δ 6.68, 6.20; menthyl 3′-H: δ 2.89). Upon lowering the temperature to 223 K only the 2-H, 3-H resonances get broad but become sharp again on lowering the temperature further to 183 K (see Figure 4), without any new signals becoming visible within the detection limits of the dynamic ^{1}H NMR method. All other resonances remain unaffected by the temperature change. Thus it appears that in this case the dominating C_2-symmetric *bis-lateral:anti* conformer **rl-6A** is in an equilibrium with a very small amount of another rotameric form whose equilibrium contribution is rapidly getting smaller with decreasing temperature to eventually fall below the detection limit of the NMR method.

The meso-like bis(1-menthylindenyl)ZrCl$_2$ complex **ml-6** also exhibits dynamic ^{1}H NMR spectra. Due to the high complexity of these spectra sound assignments of the conformers involved could, however, not be made so far.

Polymerization Behavior. Most of the **rl-4-7** metallocenes give reasonably active homogeneous Ziegler catalyst systems for propene polymerization upon activation by a large excess of methylalumoxane.[13] The catalyst activities are temperature dependent, as is usually observed with such systems. It appears that most of these systems exhibit rather pronounced activity maxima in the temperature range looked at in this study. This is evident from the data shown in Table 3 for the bis-(menthylindenyl)ZrCl$_2$ (**rl-6**)/MAO system but also is observed for most of the other catalyst systems **4−7**/MAO as well [very pronounced for **ml-6** (activity at 0 °C: 33 g polypropylene/g Zr·h·bar; −25 °C: 945; −50 °C: 93) and **rl-7**/MAO (act. at −3 °C: 58, −30 °C: 2300, −50 °C: 430), less for **ml-7** (act. at −3 °C: 22, −33 °C: 65, −45 °C: 18)].

These isomeric bis(terpenylindenyl)ZrCl$_2$/MAO Ziegler catalysts show extremely different stereoselectivities in the propene

Table 2. Distribution of the Three Different Bent Metallocene Conformers *Bis-Lateral:Anti* (**A**, C_2-symmetry), *Bis-Central:Syn* (**B**, C_2) and *Central,Lateral:Gauche* (**C**, C_1) of the Complexes **rl4−8** as Determined by Temperature Dependent ^{1}H NMR Spectroscopy

complex	terpenyl substituent	(**A**,C_2):(**B**,C_2):(**C**,C_1)^a
rl-4	neomenthyl-	70:15:15
rl-5	neoisomenthyl-	≥95:≤5
rl-6	menthyl-	≥95:≤5
rl-7	isomenthyl-	30:10:60
rl-8	neomenthyl-4,7-dimethyl-	60:40

^{a} Relative ratio in %.

Table 3. Selected Data Concerning the Propene Polymerization at the Homogeneous **4-8**/MAO Ziegler Catalysts

compd	T (°C)	Al/Zr	act^a	M$_\eta$^{b}	mmmm	ω	α	ee*^{c}	ref
rl-4	−5	560	300	26	0.33	0.65	0.72	0.29	5
	−30	910	2200	134	0.24	0.94	0.75	0.46	
rl-5	−5	560	240	100	0.77	0.80	0.95	0.72	5
	−30	700	350	260	0.76	0.89	0.97	0.84	
rl-6	+4	1150	150	25	0.40	0.69	0.81	0.43	d
	−25	1200	2800	81	0.71	0.99	0.93	0.85	
	−50	1360	1300	173	0.71	0.99	0.93	0.85	
rl-7	−3	1670	60	42	0.08	0.03	0.99	0.03	d
	−30	1400	2300	60	0.12	0.12	0.91	0.10	
ml-6	−25	1150	950	43	0.19	0.75	0.76	0.39	d
	−50	1210	90	62	0.20	0.80	0.76	0.42	
ml-7	−3	1050	22	25	0.05	0.02	0.99	0.02	d
rl-8	−30	630	60	32	0.13	0.91	0.71	0.38	5
	−50	950	20	110	0.18	0.98	0.74	0.47	

^{a} g polypropylene/g [Zr]·h·bar. ^{b} k Dalton. ^{c} ee* = $(2\alpha-1)\omega$. ^{d} This work.

polymerization reaction.[14] The lowest stereoselectivity is observed with the meso-like bis(isomenthylindenyl)ZrCl$_2$ (**ml-7**)/MAO catalyst. Only atactic polypropylene is obtained with this catalyst system. This is not necessarily only due to the meso-like character of this diastereomer since the pure racem-like diastereomer (**rl-7**) also gives a nonstereoselective catalyst system upon activation with methylalumoxane (MAO) (see Table 3). The conformational analysis of the **rl-7** catalyst precursor has revealed, that this very metallocene framework favours a C_1-symmetric *central,lateral:gauche* type metallocene conformer to the extent of ca. 60%. Assuming the usual mechanism of stereocontrol at the active bent metallocene catalyst system, such a conformation should not be suited for transferring the intrinsic bent metallocene chirality information onto the growing carbon chain (only one out of the four quadrants in front of the active bent metallocene site is effectively shielded by the annulated ring system of the indene ligand).

In contrast to the stereochemically very unfavorable **ml-7** derived catalyst system, the catalyst formed by reacting the meso-like bis(menthylindenyl)ZrCl$_2$ complex with excess methylalumoxane shows some stereoselectivity.[15] At −25 °C a polypropylene is obtained with a reasonable catalyst activity, whose ^{13}C NMR methyl pentade analysis shows a ca. 20% intensity of the mmmm methyl resonance. The pentade analysis further reveals that ca. 75% ($= \omega$) of enantiomorphic site control contributes to the stereochemistry of the formed polypropylene in this situation of double stereodifferentiation[14] (the rest is formally due to chain end control). The probability α that the controlling metal center at the catalyst produces a lk configuration at the polymer chain is 76% under these conditions. This amounts to a diastereoselectivity of ee* = $(2\alpha - 1)\,\omega \approx 39\%$ for this specific example. Further lowering the temperature did not change this value (see Table 3). So probably the **ml-6** derived catalyst finds a metallocene conformation under the

(13) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

conditions of the active catalysis process that allows for some transfer of its chirality information.

This is much more pronounced at the respective racem-like bis(menthylindenyl)ZrCl$_2$/MAO catalyst. At low temperature a regime is reached where ca. 70% mmmm intensity is found by ^{13}C NMR methyl pentade analysis. Only enantiomorphic site control is observed. This pronounced selectivity of isotactic polypropylene formation parallels the observation that only the C_2-symmetric *bis-lateral:anti* bent metallocene conformation was detected in the dynamic NMR conformational analysis of the respective **rl-6** catalyst precursor.

An analogous conformational situation was found for the bis-(neoisomenthylindenyl)ZrCl$_2$ catalyst precursor. One might, therefore, expect that the **rl-5**/MAO catalyst should also exhibit a reasonably high enantiomorphic site control giving rise to the formation of isotactic polypropylene. That is indeed observed, as can be seen in Table 3. Qualitatively, the stereocontrol exhibited by the metallocenes **rl-5** and **rl-6** in their respective methylalumoxane activated homogeneous Ziegler catalyst systems is quite similar, as are the conformational properties of these bent metallocene dihalides.

Remains the case of the racem-like bis(neomenthylindenyl)-zirconocene dichloride system (**rl-4**). Here the conformational situation is such that ca. 85% of the rotamers are C_2-symmetric, but this is separated into the *bis-lateral:anti* and *bis-central: syn* isomers in a 70:15 ratio. The diminished amount of the stereochemically "productive" *bis-lateral:anti* isomer is clearly visible in a reduced isotacticity of the obtained polypropylene. At −30 °C a high percentage (94%) of enantiomorphic site control is observed, but this leads only to a moderate isotacticity (α = 75%). Overall, the diastereoselectivity of the propene CC-coupling process at the **rl-4**/MAO catalyst is much smaller (ee* = 0.46 at -30°C; 0.29 at −5 °C) than it is observed at the **rl-5**/MAO and **rl-6**/MAO catalyst systems.

The metallocene **rl-8** also exhibits a reduced amount of the *bis-lateral:anti* conformer in solution. Consequently, the polypropylene formed at the **rl-8**/MAO catalyst system exhibits a reduced degree of isotacticity (ee* = 0.38 at −30 °C).[16]

Thus we conclude that there is good evidence that the distribution of equilibrating rotational bent metallocene isomers determines the stereocontrol at these catalyst systems[17] in the limiting low temperature regime. Therefore, controlling the conformational behavior of the bent metallocene system seems to provide an effective means of stereoselectivity control at such catalyst systems. In the series of examples looked at, this control is exerted by the relative stereochemistry of the attached terpene derived substituents. Developing other ways of determining the polymer stereochemistry via control of dynamic features of the bent metallocene catalyst backbone is actively pursued in our laboratory.

(14) Determined by ^{13}C NMR methyl pentade analysis: Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173. Sheldon, R. A.; Fueno, T.; Tsuntsuga, R.; Kurukawa, J. *J. Polym. Sci., Part B* **1965**, *3*, 23. Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 1565. Farina, M.; *Top. Stereochem.* **1987**, *17*, 1. For the statistical treatment of the obtained NMR data see: Inoue, J.; Itabashi, Y.; Chujo, R.; Doi, Y. *Polymer* **1984**, *25*, 1640. Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1989**, *101*, 642, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 628.

(15) For a similar example, see: Thiele, S.; Erker, G.; Fritze, C.; Psiorz, C.; Fröhlich, R. *Z. Naturforsch.* **1995**, *50b*, 982.

(16) Some of the polypropylenes obtained at these catalyst systems exhibit elastomeric properties. Whether this is actually due to an isotactic/ atactic block structure, whose formation is controlled by an interconversion of the bent metallocene torsional isomers, is currently being investigated in our laboratory.

(17) Which is a hydrocarbyl metallocene cation species: Jordan, R. *Adv. Organomet. Chem.* **1991**, *32*, 325, and references cited therein.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. Compounds **1a−d** were prepared as described in literature.[9] Preparation of compounds **2c** and **2d** followed a literature procedure.[5,9] The following instruments were used for physical characterization: Varian Unity plus 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{19}F: 564 MHz) and Bruker AM 360 NMR spectrometer (^{1}H: 360 MHz, ^{13}C: 90 MHz); Nicolet 5 DXC FT-IR spectrometer. Du Pont 2910 DSC, STA Instruments. Propene polymerization reactions and the polymer analysis were carried out as previously described by us.[5]

(+)-3-[(1′S,3′S,4′R)-4′-Isopropyl-1′-methylcyclohexyl]indene (3-Menthylindene) (2c). (+)-Neomenthyl mesylate (**1c**) (1.41 g, 6.03 mmol) was treated with 1.40 g (11.5 mmol) of indenyllithium to give 0.76 g (50%) of a pale yellow oil: **2c**: $[\alpha]^{25}_D = +62°$ (*c* 86 in ethanol); ^{1}H NMR (200 MHz, CDCl$_3$, 300 K) δ 7.45−7.42 (m, 2H, 4-H, 7-H), 7.26−7.15 (m, 2H, 5-H, 6-H), 6.15 (bs, 1H, 2-H), 3.30 (bs, 2H, 1-H), 2.61 (pdt, ^3J(H,H) = 11.5 Hz, ^3J(H,H) = 3.3 Hz, 1H, 3′-H), 1.85−1.03 (m, 9H, 1′-H, 2′-H, 4′-H−6′-H, 8′-H), 0.86 (d, ^3J(H,H) = 7.0 Hz, 3H, CH$_3$), 0.81 (d, ^3J(H,H) = 6.9 Hz, 3H, CH$_3$), 0.67 (d, ^3J(H,H) = 6.4 Hz, 3H, CH$_3$); ^{13}C NMR (50 MHz, [D$_8$]toluene, 350 K) δ 149.5, 145.7, 145.3 (C3, C8, C9), 127.2 (C2), 126.0, 124.6, 124.0, 119.6 (C4−C7), 46.8 (C3′), 43.5 (C1), 41.3 (C4′), 37.7, 35.7, 25.4 (C2′, C5′, C6′), 33.4, 28.0 (C1′, C8′), 22.4, 21.4, 15.9 (C7′, C9′, C10′); IR (NaCl) $\tilde{\nu}$ (cm^{-1}) 3068, 3039, 3017, 2952, 2918, 2867, 1605, 1456, 1395, 1383, 1367, 970, 766, 719. Anal. Calcd for C$_{19}$H$_{26}$ (254.4): C, 89.70; H, 10.30. Found: C, 89.53; H, 10.32.

(+)-3-[(1′R,3′S,4′R)-4′-Isopropyl-1′-methylcyclohexyl]indene (3-Isomenthylindene) (2d). (+)-Neoisomenthyl tosylate (**1d**) (22.2 g, 71.8 mmol) was treated with 10.0 g (82.2 mmol) of indenyllithium analogously to yield 6.34 g (35%) of (+)-3-isomenthylindene (**2d**): $[\alpha]^{25}_D = +21°$ (*c* 85 in ether); ^{1}H NMR (200 MHz, CDCl$_3$, 300 K) δ 7.35−7.05 (m, 4H, 4-H - 7-H), 6.10 (bs, 1H, 2-H), 3.20 (m, 2H, 1-H), 2.75 (pdt, ^3J(H,H) = 9.4 Hz, ^3J(H,H) = 4.3 Hz, 1H, 3′-H), 1.90−1.20 (m, 9H, 1′-H, 2′-H, 4′-H−6′-H, 8′-H), 0.95 (d, ^3J(H,H) = 7.1 Hz, 3H, CH$_3$), 0.75 (d, ^3J(H,H) = 6.9 Hz, 3H, CH$_3$), 0.65 (d, ^3J(H,H) = 6.8 Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, 300 K) δ 148.5, 145.0, 142.5 (C3, C8, C9), 126.0, 124.5, 124.0, 119.6 (C4−C7), 127.9 (C2), 38.0 (C1), 46.5, 39.4, 34.6, 21.8 (C1′, C3′, C4′, C8′), 31.9, 28.1, 27.9 (C2′, C5′, C6′), 19.5, 18.7, 16.8 (C7′, C9′, C10′); IR (NaCl) $\tilde{\nu}$ (cm^{-1}) 3072, 3016, 2959, 2900, 1462, 965, 765, 720. Anal. Calcd for C$_{19}$H$_{26}$ (254.4): C, 89.70; H, 10.30. Found: C, 89.73; H, 10.33.

(1-Menthylindenyl)lithium (3c). To a solution of 2.26 g (8.90 mmol) of (+)-3-menthylindene (**2c**) in 50 mL of ether was added dropwise 5.56 mL (8.90 mmol) of a *n*-butyllithium solution in *n*-hexane. The solution was stirred for 2 h at room temperature. Solvent was removed in vacuo, and the residue was washed twice with pentane (50 mL each) to yield 2.04 g (88%) of the lithium compound.

(1-Isomenthylindenyl)lithium (3d). Analogously as described above (+)-3-isomenthylindene (**2d**) (6.30 g, 24.8 mmol) dissolved in 100 mL of ether was treated with 15.5 mL (24.8 mmol) of a solution of *n*-butyllithium in *n*-hexane to yield 5.10 g (74%) of (1-isomenthylindenyl)lithium (**3d**).

(+)-Bis(1-neomenthylindenyl)zirconium Dichloride (rl-4). To a suspension of 4.90 g (18.8 mmol) of (1-neomenthylindenyl)lithium in 200 mL of toluene 2.22 g (9.53 mmol) of zirconium tetrachloride was added at −78 °C. The mixture was allowed to warm up to room temperature within 16 h while stirring continued. ^{1}H NMR spectroscopy of a sample of the mixture revealed that the diastereomeric complexes **rl-4-I**, **rl 4-II**, and **ml-4** were formed in a ratio of 70:6:24.[5]

The remaining solution was filtered off from the precipitated lithium chloride. From the clear filtrate solvent was removed in vacuo. The obtained yellow solid was washed three times with pentane (50 mL each) and treated with 100 mL of dichloromethane. The clear solution was concentrated in vacuo and allowed to crystallize at −30 °C. Repeated recrystallization of the obtained material from dichloromethane gave complex **rl-4** diastereomerically pure: yield 3.72 g (60%); mp 145 °C; $[\alpha]^{25}_D = +68°$ (*c* 0.5 in toluene); ^{1}H NMR (200 MHz, 300 K, CDCl$_3$) δ 7.74 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 0.9 Hz, 1H, 7-H), 7.66 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.0 Hz, 1H,

4-H), 7.31 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 0.9 Hz, 1H, 5-H), 7.14 (ddd, ^3J(H,H) = 8.7 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.0 Hz, 1H, 6-H), 6.59 (d, ^3J(H,H) = 3.2 Hz, 1H, 2-H), 5.53 (d, ^3J(H,H) = 3.2 Hz, 1H, 3-H), 3.68 (m, 1H, 3′-H), 2.21−1.00 (m, 9H, 1′-H, 2′-H, 4′-H−6′-H, 8′-H), 0.95 (d, ^3J(H,H) = 6.4 Hz, 3H, CH$_3$), 0.60 (d, ^3J(H,H) = 6.7 Hz, 3H, CH$_3$), −0.04 (d, ^3J(H,H) = 6.7 Hz, 3H, CH$_3$).

^{1}H NMR (600 MHz, [D$_2$]dichloromethane, 173 K): conformer **A** δ 7.65, 7.21 double intensity, 7.07 (each m, 4-H−7-H), 7.13, 6.30 (each bs, 2-H, 3-H), 3.45 (bs, 3′-H); conformer **B** δ 8.03, 7.75, 7.40, 7.14 (each m, 4-H−7-H), 6.59, 4.73 (each bs, 2-H, 3-H), 3.55 (bs, 3′-H); conformer **C** δ 7.04, 6.70, 6.40, 6.36 (each bs, 2-H, 3-H), 3.64, 3.62 (each bs, 3′-H).

(+)-Bis(1-neoisomenthylindenyl)zirconium Dichloride (rl-5). Analogously as described above 6.19 g (23.8 mmol) of (1-neoisomenthylindenyl)lithium (**3b**) was treated with 2.81 g (21.1 mmol) of zirconium tetrachloride in 200 mL of toluene. From a sample of the reaction mixture solvent was removed in vacuo and the **rl-5-I:rl-5-II:ml-5** diastereomeric ratio was determined by ^{1}H NMR spectroscopy as 62:11:26.[5]

The solution was filtered from the precipitated lithium chloride, and from the clear filtrate solvent was removed in vacuo. Threefold washing with pentane (50 mL each) and crystallization from dichloromethane gave the pure diastereomer **rl-5** (1.64 g, 21%): mp 120 °C; [α]$^{25}_D$ = + 71° (*c* 0.3 in toluene); ^{1}H NMR (200 MHz, 300 K, CDCl$_3$) δ 7.62 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.0 Hz, 1H, 7-H), 7.55 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 0.9 Hz, 1H, 4-H), 7.32 (m, 1H, 5-H), 7.13 (m, 1H, 6-H), 6.23 (d, ^3J(H,H) = 3.1 Hz, 1H, 2-H), 5.72 (d, ^3J(H,H) = 3.1 Hz, 1H, 3-H), 3.54 (m, 1H, 3′-H), 2.00−0.95 (m, 9H, 1′-H, 2′-H, 4′-H−6′-H, 8′-H), 0.90 (d, ^3J(H,H) = 6.5 Hz, 3H, CH$_3$), 0.71 (d, ^3J(H,H) = 6.7 Hz, 3H, CH$_3$), −0.17 (d, ^3J(H,H) = 6.7 Hz, 3H, CH$_3$).

Bis(1-menthylindenyl)zirconium Dichloride (rl-6 and ml-6). (1-Menthylindenyl)lithium (**3c**) (2.00 g, 7.68 mmol) was treated with 0.90 g (3.48 mmol) of zirconium tetrachloride analogously as described above. ^{1}H NMR spectroscopy of a sample of the reaction mixture revealed that the diastereomeric complexes **rl-6-I**, **rl-6-II**, and **ml-6** were formed in a ratio of 28:6:66.

The solution was filtered from the precipitated lithium chloride, the clear filtrate was concentrated, and the solid residue was washed three times with pentane (50 mL portions). The obtained yellow solid was dissolved in dichloromethane, the clear solution concentrated in vacuo and allowed to crystallize at −30 °C to give diastereomerically pure **rl-6-I** (0.30 g, 13%): mp 186 °C; [α]$^{25}_D$ = −87° (*c* 0.5 in dichloromethane); ^{1}H NMR (600 MHz, 300 K, [D$_2$]dichloromethane) δ 7.62 (dd, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 1.1 Hz, 1H, 7-H), 7.35 (pd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) ≤ 0.6 Hz, 1H, 4-H), 7.27 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.2 Hz, 1H, 5-H), 7.11 (ddd, ^3J(H,H) = 9.0 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.2 Hz, 1H, 6-H), 6.68 (d, ^3J(H,H) = 3.0 Hz, 1H, 2-H), 6.20 (d, ^3J(H,H) = 3.0 Hz, 1H, 3-H), 2.89 (pdt, ^3J(H,H) = 11.4 Hz, ^3J = 3.0 Hz, 1H, 3′-H), 1.96−0.79 (m, 9H, 1′-H, 2′-H, 4′-H - 6′-H, 8′-H), 1.05 (d, ^3J(H,H) = 7.2 Hz, 3H, CH$_3$), 0.70 (d, ^3J(H,H) = 6.6 Hz, 3H, CH$_3$), 0.60 (d, ^3J(H,H) = 6.6 Hz, 3H, CH$_3$); ^{13}C NMR (150 MHz, 300 K, [D$_2$]dichloromethane) δ 130.8, 129.7, 126.2 (C1, C8, C9), 127.1, 126.8, 125.0, 124.9 (C4 - C7), 116.1 (C2), 97.7 (C3), 48.9 (C3′), 39.3 (C2′), 35.5 (C4′), 33.4, 27.3, 25.6 (C1′, C5′, C6′, C8′), 23.0, 22.1, 16.8 (C7′, C9′, C10′), one resonance not detected; IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3088, 2960, 2950, 2943, 2921, 2889, 2867, 1459, 1451, 1261, 1136, 1017, 812, 745. Anal. Calcd for C$_{38}$H$_{50}$Cl$_2$Zr (668.9): C, 68.23; H, 7.53. Found: C, 67.08; H, 7.51.

The combined pentane phases were concentrated in vacuo to 20 mL and allowed to crystallize at −30 °C to give diastereomerically pure **ml-6** (0.16 g, 7%): mp 148 °C; [α]$^{25}_D$ = + 205° (*c* = 0.5 in dichloromethane); ^{1}H NMR (600 MHz, 300 K, [D$_2$]dichloromethane) δ 7.81 (ddd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 1.0 Hz, ^5J(H,H) = 0.9 Hz, 1H, 7A-H), 7.67 (ddd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.1 Hz, ^5J(H,H) = 0.9 Hz, 1H, 7B-H), 7.51 (pdt, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, 4A-H), 7.31 (pdt, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, 4B-H), 7.29 (ddd, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.1 Hz, 1H, 6A-H), 7.24 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, 5B-H), 7.17 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.0 Hz, 1H, 5A-H), 7.07 (ddd, ^3J(H,H) = 8.7 Hz, ^3J(H,H) =

6.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, 6B-H), 6.33 (d, ^3J(H,H) = 3.3 Hz, 1H, 2A-H), 6.07 (bs, 1H, 3A-H), 5.92 (pd, ^3J(H,H) = 3.2 Hz, 1H, 3B-H), 5.74 (d, ^3J(H,H) = 3.3 Hz, 1H, 2B-H), 2.91 (pdt, ^3J(H,H) = 11.5 Hz, ^3J(H,H) = 3.1 Hz, 1H, 3′B-H), 2.76 (ddd, ^3J(H,H) = 12.1 Hz, ^3J(H,H) = 11.4 Hz, ^3J(H,H) = 3.4 Hz, 1H, 3′A-H), 2.10 (ddd, ^2J(H,H) = 12.8 Hz, ^3J(H,H) = 3.4 Hz, ^3J(H,H) = 2.2 Hz, 1H, 2′$_{eq}$A-H), 1.88 (ddd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 3.1 Hz, ^3J(H,H) = 2.3 Hz, 1H, 2′$_{eq}$B-H), 1.83−1.78 (m, 2H, 5′-H, 6′-H), 1.72 (m, 1H, 2′$_{ax}$A-H), 1.67−1.63 (m, 1H, 6′-H), 1.56 (ptt, ^3J(H,H) = 11.5 Hz, ^3J(H,H) = 2.8 Hz, 1H, 4′A-H), 1.52−1.44 (m, 2H, 1′A-H, 1′B-H), 1.18−0.61 (m, 9H, 2′$_{ax}$B-H, 4′B-H, 5′-H, 6′-H, 8′-H), 0.97 (d, ^3J(H,H) = 6.6 Hz, 3H, 7′B-H), 0.96 (d, ^3J(H,H) = 6.0 Hz, 3H, 7′A-H), 0.65, 0.63 (each d, each ^3J(H,H) = 7.2 Hz, each 3H, 9′B-H, 10′B-H), 0.64, 0.54 (each d, each ^3J(H,H) = 6.6 Hz, each 3H, 9′A-H, 10′A-H); ^{13}C NMR (150 MHz, 300 K, [D$_2$]dichloromethane) δ 131.8, 128.5, 128.4, 126.9, 125.8, 123.7 (C1A, C1B, C8A, C8B, C9A, C9B), 126.5^2 (C4A), 126.5^0 (C5B), 125.7, 125.5 (C6A, C4B), 124.9 (C7A), 124.8 (C6B), 124.6 (C7B), 124.3 (C5A), 124.2 (C2A), 117.1 (C3A), 112.8 (C2B), 100.4 (C3B), 53.2 (C4′B), 47.2 (C4′A), 43.7 (C3′A), 42.7 (C2′B), 42.4 (C2′A), 39.0 (C3′B), 35.3 (C1′A), 35.2 (C1′B), 33.8, 32.9 (C8′A, C8′B), 27.5, 26.8, 25.3, 24.9 (C5′A, C5′B, C6′A, C6′B), 22.7^4, 22.7^2 (C7′A, C7′B), 22.0, 21.6, 16.6, 15.3 (C9′A, C9′B, C10′A, C10′B); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3085, 2955, 2926, 2864, 2841, 1454, 1368, 1345, 1098, 1085, 818, 809, 750, 741, 455. Anal. Calcd for C$_{38}$H$_{50}$Cl$_2$Zr (668.9): C, 68.23; H, 7.53. Found: C, 66.94; H, 7.59.

Bis(1-isomenthylindenyl)zirconium Dichloride (rl-7 and ml-7). Analogously as described above 1.50 g (5.76 mmol) of (1-isomenthylindenyl)lithium (**3d**) was treated with 0.68 g (2.28 mmol) of zirconium tetrachloride in 100 mL of toluene. From a sample of the reaction mixture solvent was removed in vacuo and the **rl-7-I, rl-7-II,** and **ml-7** diastereomeric ratio was determined by ^{1}H NMR spectroscopy as 53:11:31.

The solution was filtered from the lithium chloride, and from the clear filtrate solvent was removed in vacuo. Threefold washing with pentane (50 mL each) and crystallization from dichloromethane gave the pure diastereomer **rl-7-I** (0.32 g, 17%): mp 200 °C; [α]$^{25}_D$ = −6° (*c* 0.2 in dichloromethane); ^{1}H NMR (600 MHz, 300 K, [D$_2$]-dichloromethane) δ 7.62 (ddd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.2 Hz, ^5J(H,H) = 0.6 Hz, 1H, 7-H), 7.57 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 0.6 Hz, 1H, 4-H), 7.31 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.2 Hz, 1H, 5-H), 7.16 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 0.6 Hz, 1H, 6-H), 6.21 (d, ^3J(H,H) = 3.0 Hz, 1H, 2-H), 6.00 (dd, ^3J(H,H) = 3.0 Hz, ^5J(H,H) = 0.6 Hz, 1H, 3-H), 3.57 (m, 1H, 3′-H), 1.94−1.12 (m, 9H, 1′-H, 2′-H, 4′-H−6′-H, 8′-H), 0.98, 0.97, 0.81 (broadened) (each d, each ^3J(H,H) = 6.6 Hz, each 3H, 7′-H, 9′-H, 10′-H); ^{13}C NMR (150 MHz, 300 K, [D$_2$]dichloromethane) δ 131.5, 127.7, 125.3 (C1, C8, C9), 126.8, 126.4, 125.0 double intensity (C4−C7), 120.9 (C2), 97.7 (C3), 48.9 (broadened, C3′), 35.0 (broadened, C2′), 34.2 (C4′), 30.4, 22.2 (C5′, C6′), 28.8, 27.6 (C1′, C8′), 22.2, 21.1, 19.5 (C7′, C9′, C10′); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3103, 3092, 2955, 2928, 2885, 2863, 1460, 1385, 1378, 1100, 1066, 1056, 806, 750, 740, 454. Anal. Calcd for C$_{38}$H$_{50}$Cl$_2$Zr (668.9): C, 68.23; H, 7.53. Found: C, 66.64; H, 7.62.

^{1}H NMR (600 MHz, 180 K, [D$_2$]dichloromethane) conformer **A** δ 6.85, 6.34 (each bs, 2-H, 3-H); conformer **B** δ 7.00, 4.54 (each bs, 2-H, 3-H); conformer **C** δ 6.68, 6.24, 6.14, 5.87 (each bs, 2-H, 3-H).

The combined pentane phases were concentrated in vacuo to a volume of 10 mL and allowed to crystallize at −30 °C to give diastereomerically pure **ml-7** (0.27 g, 14%): mp 55 °C; [α]$^{25}_D$ = + 73° (*c* 0.3 in dichloromethane); ^{1}H NMR (600 MHz, 300 K, [D$_2$]-dichloromethane) δ 7.66 (pt, ^3J(H,H) = 8.4 Hz, 2H, 7A-H, 7B-H), 7.46 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.2 Hz, 1H, 4A-H or 4B-H), 7.38 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.0 Hz, 4A-H or 4B-H), 7.32−7.18 (m, 4H, 5A-H, 5B-H, 6A-H, 6B-H), 6.29, 6.24, 5.65, 5.63 (each bs, each 1H, 2A-H, 2B-H, 3A-H, 3B-H), 3.61, 3.56 (each m, each 1H, 3′A-H, 3′B-H), 2.04−1.12 (m, 18H, 1′A-H, 2′A-H, 4′A-H - 6′A-H, 8′A-H, 1′B-H, 2′B-H, 4′B-H−6′B-H, 8′B-H), 1.04, 0.95, 0.92, 0.90, 0.78, 0.77 (each d, 2x ^3J(H,H) = 6.8 Hz, ^3J(H,H) = 6.7 Hz, ^3J(H,H) = 6.6 Hz, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 6.3 Hz, each 3H, 7′A-H, 7′B-H, 9′A-H, 9′B-H, 10′A-H, 10′B-H); ^{13}C NMR (150 MHz, 300 K, CDCl$_3$): δ = 130.4 (broadened), 128.9 (broadened), 127.5 (broadened), 127.2 (broadened), 125.8, 125.3 (C1A, C1B, C8A, C8B, C9A, C9B),

126.3, 126.0, 125.9, 125.8, 125.1, 124.9, 124.8, 124.5 (C4A - C7A, C4B - C7B), 120.8, 120.7, 99.5, 99.4 (C2A, C2B, C3A, C3B), 49.4, 43.2 (C3′A, C3′B), 35.8, 33.8, 28.4, 27.9, 27.7, 21.2 (C4′A, C4′B, C7′A, C7′B, C8′A, C8′B), 36.8, 30.7 double intensity, 30.3, 23.2, 21.4 (C2′A, C2′B, C5′A, C5′B, C6′A, C6′B), 22.1, 21.8, 21.2 (broadened), 20.5 (broadened), 20.0 (broadened), 19.0 (broadened) (C7′A, C7′B, C9′A, C9′B, C10′A, C10′B); IR (KBr) $\bar{\nu}$ (cm^{-1})= 3085, 2942, 2923, 2863, 2847, 1454, 1439, 1384, 763, 748, 466. Anal. Calcd for C$_{38}$H$_{50}$Cl$_2$Zr (668.9): C, 68.23; H, 7.53. Found: C, 66.87; H, 7.60.

Bis(1-neomenthyl-4,7-dimethylindenyl)zirconium Dichloride (rl-8). To a suspension of 2.33 g (6.20 mmol) of ZrCl$_4$(THF)$_2$ in 80 mL of toluene was added at a temperature of −50 °C a solution of 3.61 g (12.5 mmol) of (1-neomenthyl-4,7-dimethylindenyl)lithium (**3e**) in 100 mL of tetrahydrofuran. After warm up to room temperature the solvent was removed in vacuo. ^{1}H NMR spectroscopy of a sample of the residue revealed that the diastereomeric complexes **rl-8-I**, **rl-8-II**, and **ml-8** were formed in a ratio of 98:1:1. The obtained yellow solid was washed three times with pentane (50 mL each) and treated with dichloromethane, and the solution was filtered from the precipitated lithium chloride. The clear filtrate was concentrated in vacuo and allowed to crystallize at −30 °C to yield 1.22 g (28%) of diastereo-merically pure **rl-8**: mp 132 °C, $[\alpha]^{25}_D$ = −180° (*c* 0.2 in toluene); ^{1}H NMR (200 MHz, 300 K, [D$_2$]dichloromethane) δ 6.91, 6.79 (each

d, each ^3J(H,H) = 7.2 Hz, each 1H, 5-H, 6-H), 6.39 (d, ^3J(H,H) = 3.2 Hz, 1H, 2-H), 5.82 (d, ^3J(H,H) = 3.2 Hz, 1H, 3-H), 3.83 (m, 1H, 3′-H), 2.64, 2.41 (each s, each 3H, 4″-H, 7″-H), 2.20 - 1.18 (m, 9H, 1′-H, 2′-H, 4′-H - 6′-H, 8′-H), 1.10 (d, ^3J(H,H) = 7.0 Hz, 3H, 7′-H), 0.62, −0.05 (each d, each ^3J(H,H) = 6.0 Hz, each 3H, 9′-H, 10′-H); ^{1}H NMR (600 MHz, 160 K, [D$_2$]dichloromethane) conformer **A** δ 7.00, 6.24 (each bs, 2-H, 3-H), 3.66 (bs, 3′-H); conformer **B** δ 6.56, 3.85 (each bs, 2-H, 3-H), 3.55 (bs, 3′-H); ^{13}C NMR (50 MHz, 300 K, [D$_2$]-dichloromethane) δ 135.3 (C8), 134.1, 132.4 (C7, C4), 133.2 (C9), 127.7, 126.6 (C5, C6), 118.3 (C2), 93.6 (C3), 46.7 (C3′), 35.5, 28.1, 25.6 (C1′, C4′, C8′), 32.7, 29.0, 23.7 (C2′, C5′, C6′), 24.4, 21.1, 20.8 (C7′, C9′, C10′), 19.2, 19.0 (C4″, C7″); IR (KBr) $\bar{\nu}$ (cm^{-1}) 3112, 2956, 2928, 2868, 1464, 1387, 1383, 817, 801, 793, 773. Anal. Calcd for C$_{42}$H$_{58}$Cl$_2$Zr (725.1): C, 69.57; H, 8.06. Found: C, 69.33; H, 8.68.