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Synthesis, Characterization, and Polymerization Properties of Bis(2-menthylindenyl)zirconium Dichloride and Bis(2-menthyl-4,7-dimethylindenyl)zirconium Dichloride

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The tetrakis(triphenylphosphine)palladium-catalyzed cross coupling of 2-bromoindene or 2-bromo-4,7-dimethylindene with menthylmagnesium chloride gave the novel ligands 2-menthylindene (**10**) and 2-menthyl-4,7-dimethylindene (**11**) in 66 and 57% yields. These indenes were deprotonated with n-BuLi to give isolated indenyllithium complexes which were metalated with zirconium tetrachloride to give bis(2-menthylindenyl)zirconium dichloride (**14**) and bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride (**15**) in 40 and 66% yields. Both complexes formed as their single possible stereoisomer and were characterized by X-ray crystallography and MS, NMR, and IR spectroscopy. The variable-temperature ^{1}H NMR spectrum of bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride (**15**) showed that it interconverts with a rotational activation barrier of about 12.5 ± 0.5 kcal/mol, and that a 60:40 mixture of C_2-symmetric diastereomeric conformations was present at −50 °C. The ^{1}H NMR spectrum of bis(2-menthylindenyl)zirconium dichloride (**14**) was invariant between −50 and +50 °C. Complexes **14** and **15** polymerized propene in the presence of methylaluminumoxane (MAO) and hydrogen (10 960 and 33 750 g PP/g Zr h, respectively). The molecular weights and stereoregularity of the polymers produced were low.

Introduction

Chiral metallocenes are now being widely employed as reagents or catalysts for stereoselective polymerization of alkenes[1] and enantioselective carbon−carbon,[2] carbon−hydrogen,[3] and carbon−oxygen[4] bond formations. Some of our ongoing work in this research area has focused on the use of ligand symmetry to facilitate the preparation of new chiral metallocenes.[5] The most widely applied chiral metallocenes are conformationally constrained *ansa*-metallocenes such as *ansa*-bis(tetrahydroindenyl)zirconium dichloride, **1** (Figure 1).[6] Drawbacks in its use are that metalation of the enantiotopic faces of the ligand results in mixtures of diastereomers and that the enantiomers of the DL-diastereomer must be resolved through diastereomeric derivatives. Once resolved, zirconocene **1** is a single helical enantiomer that is configurationally stable under most conditions; it can be used as a single enantiomer for enantioselective reactions.[7] Until now, metalation of indenes pos-

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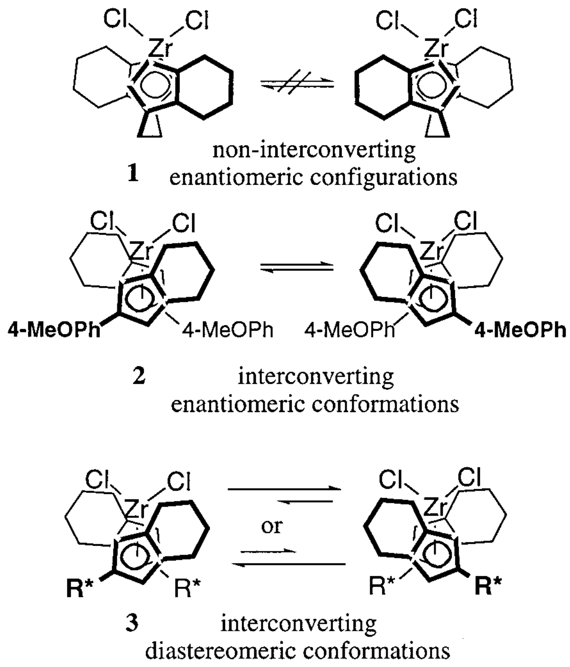


1 non-interconverting enantiomeric configurations

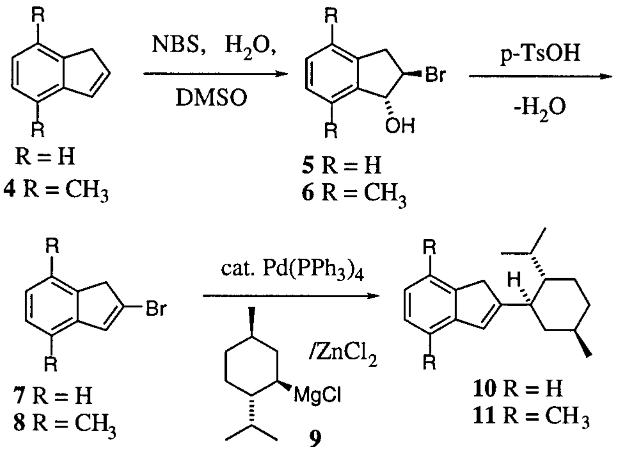
2 interconverting enantiomeric conformations

3 interconverting diastereomeric conformations

Figure 1. Conformations of bis(indenyl)zirconium dichlorides.

sessing homotopic ligand faces has resulted in achiral metallocenes such as zirconocene **2**. An advantage of metalating ligands with homotopic faces is seen in that only one stereoisomeric metallocene can form. While zirconocene **2** can adopt chiral helical conformations, the complex is conformationally labile and each such helical conformation will freely interconvert with its enantiomer to form a racemic mixture of the conformational isomers. While this facile isomerization prevents the utilization of this complex for enantioselective reactions, this achiral metallocene has been used in the surprisingly highly isotactic polymerization of propene.[8] In an effort to retain the benefit of metalating homotopic indenyl-type ligands while at the same time preventing the formation of equal amounts of enantiomeric chiral conformations, we have prepared bis(indenyl)metal complexes bearing a chiral substituent on the 2-indenyl position such as shown for zirconocene **3**. The corresponding helical conformations that were enantiotopic in complex **2** are now diastereotopic in **3**. Even if the complexes are still conformationally mobile, one helical diastereomeric conformation of **3** could be favored as illustrated in Figure 1; such complexes could be meaningfully applied as enantioselective catalysts. We report here that bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride provides the first demonstration of conformational diastereoselectivity in bis(indenyl)metal complexes of homotopic indenyl ligands.[9] Given our facile synthesis of ligands of this type, the concept of using a chiral 2-indenyl substituent to favor one conformation can now be more widely explored.[10]

Scheme 1



Results and Discussion

The introduction of substituents, especially secondary alkyl groups such as the chiral menthyl group, at the 2-position of indene has previously been difficult to achieve in good yield. The direct alkylation of indenyl anions is electronically favored at the 1-position and cannot be used to prepare 2-substituted indenes. Alkylation of the 1-indanone enolate with primary alkyl halides was known to proceed in moderate yields,[11] but our attempts to extend this alkylation to menthyl or neomenthyl tosylates or mesylates failed to give isolable amounts of the desired 2-substituted 1-indanone. The addition of menthylmagnesium chloride to 2-indanone also failed to give any isolable amounts of 2-menthylindanol or 2-menthylindene.

We have now developed a facile, successful approach to 2-menthylindenes based on the known nickel- or palladium-catalyzed coupling of 2-bromoindene with alkyl Grignard reagents to give 2-alkylindenes.[11,12] We have extended this method to now include the coupling of 2-bromoindene or 2-bromo-4,7-dimethylindene with menthylmagnesium chloride as outlined in Scheme 1. 2-Bromoindene (**7**) was readily prepared according to the literature method from indene through a bromohydration, dehydration sequence.[13] We applied this same sequence to 4,7-dimethylindene[14] to give 2-bromo-4,7-dimethylindene (**8**) in good overall yield (Scheme 1). Menthylmagnesium chloride (**9**) is known to be readily prepared in two steps from menthol (ZnCl$_2$/HCl generation of menthyl chloride followed by Grignard formation) and that it could add to electrophiles with preservation of the menthyl stereochemistry.[15] We investigated the

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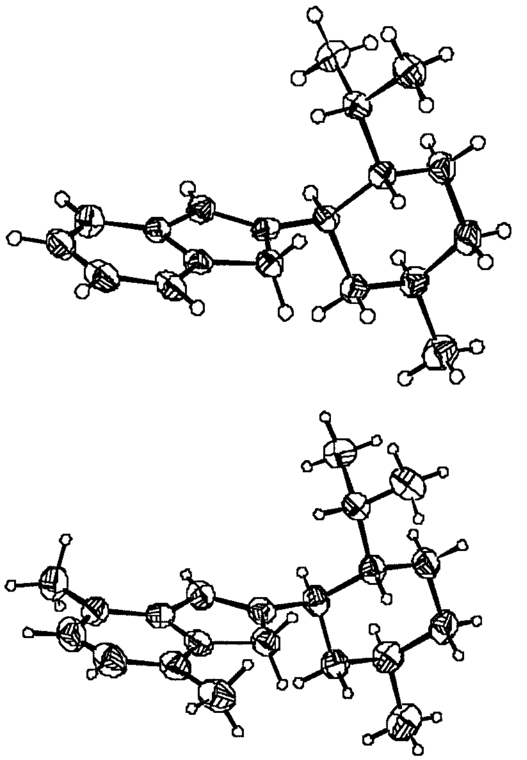


Figure 2. ORTEPs of 2-menthylindene 10 and 2-menthyl-4,7-dimethylindene 11.

coupling of menthylmagnesium chloride and 2-bromoindene or 2-bromo-4,7-dimethylindene in the presence of $ZnCl_2$ with a variety of catalysts. Both nickel and palladium catalysts[5e] provided the desired 2-menthylindene along with varying amounts of the diastereomeric 2-neomenthylindenes. The use of tetrakis(triphenylphosphine)palladium in conjunction with premixed menthylmagnesium chloride and $ZnCl_2$ was found to give the highest reproducible yields of desired menthylindenes **10** and **11** (66 and 57%, respectively).

The menthyl stereochemistry of the coupled indene products **10** and **11** could be surmised from the diagnostic axial 3-menthyl hydrogen that appeared at 2.74 or 2.60 ppm in the ^1H NMR spectrum. In each case, the line width of the multiplet was most consistent with two large axial–axial $J_{1,3}$-couplings and one small axial–equatorial $J_{1,3}$-coupling. The solid-state structure of 2-menthylindene (**10**) was determined by X-ray diffraction methods, which confirmed this stereochemical assignment (Figure 2). Complete crystallographic details and tables for 2-menthylindene **(10)** are given in the Supporting Information.

Scheme 2

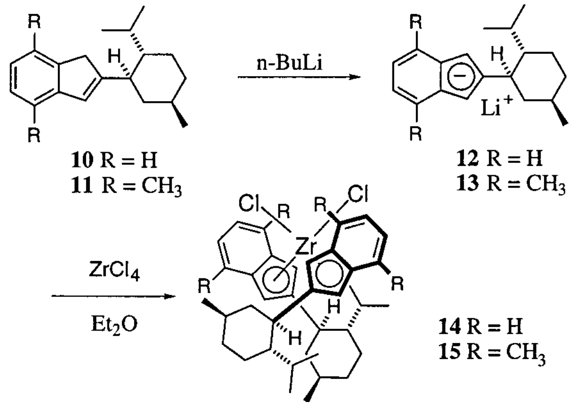


Table 1. Crystallograhic Data for 14 and 15

	14	**15**
identification code	rh845a	r*h*10b
empirical formula	C45 H58 Cl2 Zr	C42 H58 Cl2 Zr
fw	761.03	725.00
temperature	173(2) K	295(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	orthorhombic
space group	*P*2(1)	*P*2(1)2(1)2(1)
unit cell dimens	$a = 15.326(2)$ Å $b = 17.054(3)$ Å $c = 15.553(2)$ Å $\alpha = 90°$ $\beta = 94.935(10)°$ $\gamma = 90°$	$a = 15.515(3)$ Å $b = 15.671(3)$ Å $c = 16.397(5)$ Å $\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
volume, *Z*	4050.1(10) $Å^3$, 4	3987(2) $Å^3$, 4
density (calcd)	1.248 Mg/m^3	1.208 Mg/m^3
abs coeff	0.433 mm^{-1}	0.436 mm^{-1}
F(000)	1608	1536
cryst size	0.46 × 0.42 × 0.38 mm	0.24 × 0.18 × 0.08 mm
θ range for data	1.78 to 25.03°	1.80 to 22.50°
limiting indices	$-18 \leq h \leq 18$, $-13 \leq k \leq 20$, $-18 \leq l \leq 18$	$0 \leq h \leq 16$ $0 \leq k \leq 16$ $0 \leq l \leq 17$
no. of reflns collected	10 748	2938
no. of ind reflns	10023 [*R*(int) = 0.0391]	2938
abs corr	semiempirical from ψ-scans	semiempirical from ψ-scans
max and min transmn	0.3467 and 0.3178	0.4785 and 0.4137
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	10019/1/874	2937/101/196
goodness-of-fit on F^2	1.027	1.053
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0324 wR2 = 0.0847	R1 = 0.1193 wR2 = 0.2627
R indices (all data)	R1 = 0.0355 wR2 = 0.0957	R1 = 0.2246 wR2 = 0.3440
abs struct param	−0.01(3)	−0.1(3)
largest diff peak and hole	0.546 and −0.611 e $Å^{-3}$	1.137 and −0.988 e $Å^{-3}$

Both 2-menthylindenes **10** and **11** could be deprotonated by n-BuLi in diethyl ether to give isolable indenyllithium salts **12** and **13** (Scheme 2). These lithium salts were quite air and moisture sensitive but could be fully characterized. In the solution NMR spectra of these salts, the ligands exhibited C_2-symmetry. This is consistent with either no tight coordination of the lithium to the ligand faces or rapid (on the NMR time scale) exchange of lithium between the faces of the ligand. If the lithium were tightly bound to the ligand under slow exchange conditions, diastereotopic signals on the 1 and 3, 4 and 5, 6 and 7 positions should have been—but were not—evident. The two indenyllithium complexes **12** and **13** were converted under standard conditions ($ZrCl_4$, Et_2O) to the corresponding zirconocene dichloride complexes **14** and **15**. Since the faces of the indenyl ligands are symmetry equivalent, only the one possible stereoisomeric product was observed in each case.

Solid-State Structures of 14 and 15. The solid-state structures of both **14** and **15** were determined by X-ray diffraction methods. The resulting crystallographic data are summarized in Tables 1 and 2, and the structures are depicted in Figure 3. For the 2-menthylindenyl complex **14**, two independent molecules corresponding to two slightly different conformations are

Table 2. Selected Bond Lengths and Angles for 14 and 15

compound	bond length (Å)	bond angle (deg)
14	Cp(1)−Zr(1) 2.314(3)	Cp−Zr(1)−Cp 134.7
	Cp(2)−Zr(1) 2.234(4)	Cp−Zr(2)−Cp 131.2
	Cp(1)−Zr(2) 2.232(4)	Cl−Zr(1)−Cl 93.98(3)
	Cp(2)−Zr(2) 2.240(4)	Cl−Zr(2)−Cl 91.91(3)
15	Cp(1)−Zr 2.26(2)	Cp−Zr−Cp 135.4(3)
	Cp(2)−Zr 2.25(2)	Cl−Zr−Cl 96.6(4))

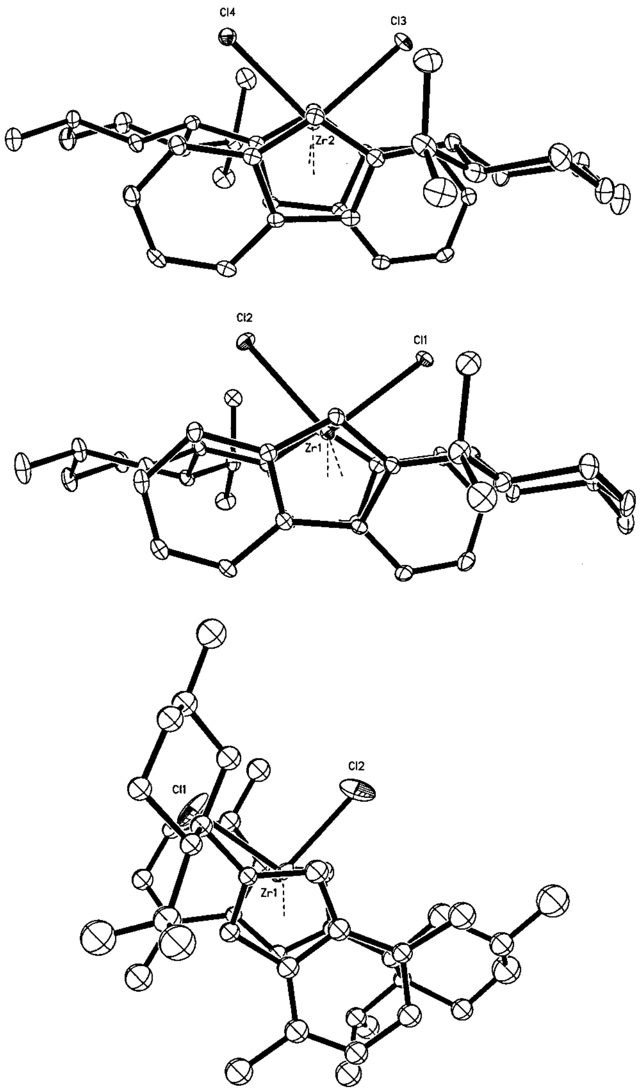
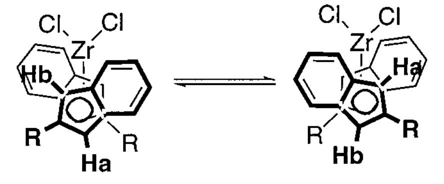
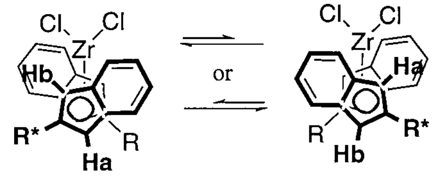


Figure 3. ORTEP drawings for **14** and **15** (30% probability elipsoids).



2 R = Aryl, Enantiomeric Conformations, δa = δb



3 R* =Menthyl, Diastereomeric Conformations, δa ≠ δb

Figure 4. Helical conformations of 2-R* indenyl complexes.

found in the unit cell. In each conformation, the indenyl ligands are oriented in an approximately C_2-symmetrical conformation about the zirconium dichloride moiety. It is particularly noteworthy that only one diastereomeric orientation of the indenyl ligands is observed in each conformation. Referring back to Figure 1, we see that chiral 2-substituted indenyl complexes **3** can adopt two interconvertible diastereomeric helical conformations corresponding to enantiomeric helical conformations in achiral complexes **2**. In the bis(2-menthylindenyl)zirconium complex **14**, the menthyl groups apparently favor the exclusive formation of one helical orientation of the indenyl groups in the solid state. In the 2-menthyl-4,7-dimethylindenyl complex **15**, the indenyl ligands are in a C_1-symmetrical conformation that places the arene ring of one indenyl ligand and the menthyl group of the other indenyl ligand over one of the chlorine atoms. Only one helical orientation of the ligands is found in the solid state of **15**, again demonstrating the ability of the 2-menthyl group to select for one indenyl orientation. Other than these unique conformational details, the structures of **14** and **15** are similar to other unbridged bis(indenyl)zirconium complexes. The Cp−Zr−Cp "bite" angle is 134.7° and 131.2° for the two molecules of **14** and 135.4° for **15**.

Solution-State Conformations. As illustrated in Figure 4 for a generalized C_2-symmetrical conformation, the 1- and 3-indenyl hydrogen atoms in 2-arylindenyl complexes **2** will exchange positions between being in a shielded position over an indenyl ring and being in open space away from the indenyl ring. Since these two interconverting helical orientations of the indenyl rings are energetically equivalent, Ha and Hb will spend the same amount of time in each environment and will give one averaged signal in the rapid exchange NMR spectrum. The corresponding hydrogen atoms in 2-menthylindenyl complex **14** can also be in a shielded or nonshielded position, but since one diastereomeric conformation can now be energetically favored, each pair of diastereotopic hydrogens can spend a different amount of time in each position, and they should give averaged signals of equal intensity at two different frequencies in the rapid exchange spectrum. At the low-temperature limit, two pairs of signals having different relative integrations should be observed for each diastereotopic pair of signals. In 2-menthylindenyl complex **14**, these 1- and 3-indenyl hydrogens are found as sharp signals at 6.17 and 5.64 ppm in the ^{1}H NMR spectrum. In 2-menthyl-4,7-dimethyindenyl complex **15**, they appear at 20 °C as broadened signals at 6.30 and 5.96 ppm. 2-Menthylindenyl complex **14** exhibited C_2-symmetry in its ^{1}H NMR spectrum and showed no broadening of any signals in the temperature range studied from +50 to −60 °C. The dimethylindenyl derivative **15** also exhibited C_2-symmetry in its ^{1}H NMR spectrum but gave sharp signals above 40 °C, some broadened signals around room temperature, coalescence of several signals between 0 and −10 °C, and two sets of signals below −40 °C (see Supporting Information). In the spectrum shown at −50 °C (Figure 5), the signal intensities indicate that an approximately 60:40 mixture of two C_2-symmetrical diastereomeric conformations have been

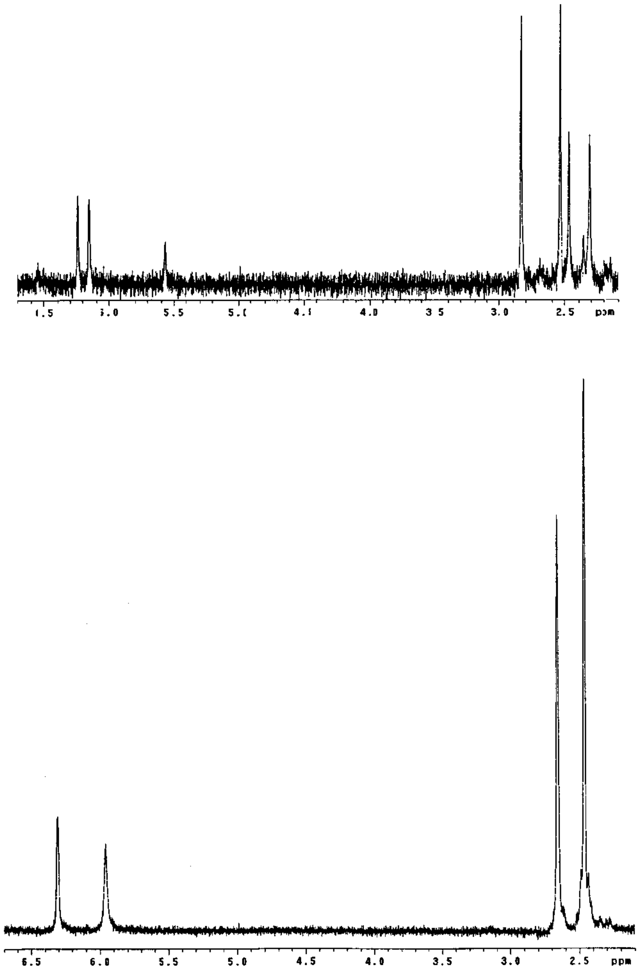


Figure 5. Partial ^{1}H NMR spectra of **15** at +50 and −50 °C.

frozen out. The energy of activation for converting these stereoisomers was determined from the coalescence temperature to be about 12 ± 0.5 kcal/mol. While we cannot from the information at hand state which conformations are present or preferred, we can surmise that one helical orientation is favored over the diastereomeric conformation in each complex.

Polymerization Behavior. Neither complex **14** nor **15** exhibited significant activity for the polymerization of propene at 70 °C in the presence of methylaluminoxane (MAO). These two metallocenes showed negligible polymerization activity in the absence of hydrogen, although enough polymer was obtained in each case to enable GPC and NMR analysis. In the presence of hydrogen at an initial reactor concentration of 8 mmol/L, measurable levels of polymerization activity were seen for **14** and **15**. Of the two complexes, bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride (**15**) appears to form the more active catalyst with MAO. The polymerization results are summarized in Table 3, and polymer analysis is summarized in Table 4. In the presence of added hydrogen, the polymerization activities of **14** and **15** are very high in comparison with Erker's polymerization results using bis(1-neomenthylindenyl)zirconium dichloride and related complexes.[9c] GPC analysis of the polymer produced by **15** shows that the molecular weight distribution has two maxima. The first, centered at 51 kg/mol, is the primary peak and appears to shift to 12 kg/mol when the polymerization was carried out in the presence of hydrogen. The second peak centered at 1.5 kg/mol appears to be unaffected by the addition of hydrogen. The metallocene **14**, in the absence of hydrogen, also produced polymer with a broad distribution of molecular weights, consisting of a peak at 1.7 kg/mol with a substantial high molecular weight shoulder. In the presence of hydrogen a narrower distribution of molecular weights was obtained, centered at 1.2 kg/mol, but still having a detectable high molecular weight tail. According to analysis by ^{13}C NMR spectroscopy, both catalysts exhibited much lower isotactic stereoregularity than Erker's compounds,[9c] and no meaningful correlation between any conformational preferences of **14** and **15** with stereoregularity could be drawn.

Table 3. Propene Polymerization Results and Conditions

	polymerization conditions[a]			productivity
catalyst	temp		[Zr] M	(g PP/g Zr h)
15	70 °C	0	5.82×10^{-7}	~0
15	70 °C	8 mmol/L H_2	5.82×10^{-7}	33 750
14	70 °C	0	1.75×10^{-6}	~0
14	70 °C	8 mmol/L H_2	1.92×10^{-6}	10 960

[a] Polymerizations run in liquid propylene in the presence of MAO, 10 000:1 Al:Zr.

Table 4. Analysis of Polypropylene Polymers Produced from 14 and 15/MAO

		GPC kg/mol			NMR		
catalyst	*T* (°C)	M_n	M_w	M_w/M_n	%[mm]	%[mr]	%[rr]
15	70 °C	11.5	138.0	12.0	17.5	11.1	71.4
15/H_2	70 °C	5.9	27.9	4.7	36.0	17.0	47.0
14	70 °C	4.1	6.3	6.3	34.5	25.1	40.4
14/H_2	70 °C	1.7	2.3	2.3	33.5	26.8	39.7

Summary. A facile synthesis of bis(2-menthylindenyl)zirconium dichlorides was developed. These complexes bear a chiral substituent at the 2-indenyl position, but have homotopic faces. It was demonstrated for the bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride complex **15** that one C_2-symmetric diastereomeric conformation is slightly favored (60:40) and that it interconverts with a rotational activation barrier of about 12.5 ± 0.5 kcal/mol. These complexes were not very active for the polymerization of propene and gave low stereoregularity.

Experimental Section

General Comments. All reactions involving air or moisture sensitive reagents or intermediates were performed under nitrogen or argon using drybox and Schlenk line techniques. Ethereal and aromatic solvents were distilled under nitrogen from sodium benzophenone ketyl, and methanol was distilled from magnesium turnings. NMR solvents (Aldrich or Merck Isotopes) were stored over 4 Å molecular sieves for routine samples. NMR solvents for air or moisture sensitive samples were vacuum distilled (pyridine from 4 Å molelcular sieves, chloroform from P_2O_5, benzene from sodium benzophenone ketyl) and stored under nitrogen. Additional details about experimental procedures and equipment can be found in refs 16 and 17.

4,7-Dimethylindene (4).[14] Sodium (45.0 g, 1.96 mol) was added over 10 h at 0 °C to methanol (400 mL) [gas evolution!]

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followed by addition of freshly distilled cyclopentadiene (65.00 g, 0.98 mol). The resulting pale pink, cloudy mixture was stirred 1 h at room temperature then cooled to 0 °C. 2,5-Hexanedione (80.00 mL, 0.680 mol) was added to give a solution that turned brown during 1 h at 0 °C followed by 10 h at room temperature. The mixture was carefully hydrolyzed with water (200 mL), acidified with 1 M HCl, and extracted with diethyl ether (3 × 150 mL). The combined brown organic portion was dried ($MgSO_4$), filtered, concentrated by rotary evaporation, and fractionally distilled to give **4** as a yellow oil (61.96 g, 63% yield), bp 42 °C (10^{-5} bar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, $^{3}J = 7.6$ Hz, 1 H, H^{6}), 7.04 (dt, $^{3}J = 5.6$ Hz, $^{4}J = 2.0$ Hz, 1 H, H^{3}), 6.98 (d, $^{3}J = 7.6$ Hz, 1 H, H^{5}), 6.62 (dt, $^{3}J = 5.6$ Hz, $^{3}J = 2.0$ Hz, 1 H, H^{2}), 3.35 (dd, $^{3}J = 2.0$ Hz,$^{4}J = 5.6$ Hz, 2 H, H^{1}), 2.49 (s, 3 H, H^{10}), 2.40 (s, 3 H, H^{11}). ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ 143.19, 142.13 (C^{8,9}), 133.24, 130.50, 127.55, 125.79 (C^{2,3,5,6}), 130.14, 127.69 (C^{4,7}), 38.25 (C^{1}), 18.42, 18.26 (C$^{10/11}$). IR (KBr, film): $\bar{\nu} = 3067$, 3033, 3013, 2919, 1700, 1553, 1492, 1379, 1251, 1034, 1018, 949, 910, 826, 803 cm^{-1}. MS (EI, 70 eV, rel intensity): *m*/*z* 144 (52%) $[M]^+$, 129 (100) $[C_{10}H_9]^+$, 115 (7) $[C_9H_7]^+$. Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.12; H, 7.96.

2-Bromoindan-1-ol (5).[13] To indene (81.79 g, 704.1 mmol) and water (25 mL) in dimethyl sulfoxide (210 mL) was added at 0 °C freshly recrystallized *N*-bromosuccinimide (128.3 g, 720.8 mmol). The resulting orange solution was allowed to warm to room temperature and was stirred 10 h. The reaction mixture was hydrolyzed with water (250 mL) at 0 °C and extracted with diethyl ether (3 × 200 mL). The combined orange organic portion was dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to give **5** (147.3 g, 98% yield) as yellow crystals, mp 131 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41−7.21 (m, 4 H, H^{4,5,6,7}), 5.30 (d, $^{3}J = 5.8$ Hz, 1 H, H^{1}), 4.27 (m, 1 H, H^{2}), 3.58 (dd, $^{2}J = 16.3$ Hz,$^{3}J = 7.2$ Hz, 1 H, H^{3}), 3.21 (dd, $^{2}J = 16.3$ Hz,$^{3}J = 7.4$ Hz, 1 H, H$^{3'}$), 2.85 (s, 1 H, OH). MS (EI, 70 eV, rel intensity): *m*/*z* (%) 212 (12) $[M]^+$, 133 (100) $[C_9H_9O]^+$, 116 (7) $[C_9H_8]^+$, 105 (13) $[C_8H_9]^+$. Anal. Calcd for C_9H_9BrO: C, 50.73; H, 4.26. Found: C, 50.42; H 3.91.

2-Bromo-4,7-dimethylindan-1-ol (6). The procedure for the synthesis of **5** was followed using 4,7-dimethylindene (**4**) (61.01 g, 423.0 mmol), water (15 mL), dimethyl sulfoxide (320 mL), and *N*-bromosuccinimide (76.81 g, 431.5 mmol) to give **6** (95.73 g, 94%) as a beige solid, mp 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, $^{3}J = 7.7$ Hz, 1 H, H^{5}), 7.00 (d, $^{3}J = 7.7$ Hz, 1 H, H^{6}), 5.36 (d, $^{3}J = 2.6$ Hz, 1 H, H^{1}), 4.36 (m, 1 H, H^{2}), 3.63 (dd, $^{2}J = 17.3$ Hz,$^{3}J = 6.5$ Hz, 1 H, H^{3}), 3.14 (dd, $^{2}J = 17.3$ Hz,$^{3}J = 3.5$ Hz, 1 H, H$^{3'}$), 2.66 (s, 1 H, OH), 2.38 (s, 3 H, H^{11}), 2.00 (s, 3 H, H^{10}). ^{13}C{^{1}H} NMR (100.64 MHz, $CDCl_3$): δ 139.30 (C^{9}), 139.00 (C^{8}), 132.77 (C^{7}), 131.48 (C^{4}), 130.32 (C^{5}), 129.10 (C^{6}), 83.23 (C^{1}), 54.13 (C^{2}), 39.83 (C^{3}), 18.38 (C^{10}), 17.79 (C^{11}). IR (CsI): $\bar{\nu} = 3260$, 3206, 3168, 2953, 2919, 1712, 1501, 1448, 1170, 1095, 1038, 814, 803. MS (EI, 70 eV, rel intensity): *m*/*z* 240 (25) $[M]^+$, 161 (100) $[C_{11}H_{13}O]^+$, 144 (30) $[C_{11}H_{12}]^+$, 129 (12) $[C_{10}H_9]^+$, 115 (13) $[C_9H_7]^+$. Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.55; H, 5.23.

2-Bromoindene (7).[13] To 2-bromoindan-1-ol (**5**) (143.0 g, 671 mmol) suspended in toluene (600 mL) was added *p*-toluenesulfonic acid monohydrate (5.00 g, 26.3 mmol) under nitrogen. The mixture was heated under reflux for 30 h, and water was removed by a Dean-Stark apparatus. The resulting dark brown suspension was filtered in air, and the volatiles were removed by rotary evaporation. The residue was passed through silica gel with hexanes to give after concentration a yellow crude product that was fractionally distilled under vacuum to give **7** (78.09 g, 60% yield) as colorless crystals, bp 52 °C (10^{-5} bar). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.52−7.27 (m, 4 H, H^{4,5,6,7}), 7.05 (m, 1 H, H^{3}), 3.70 (m, 2 H, H^{1}). ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ 143.95, 142.54, 124.83 (C^{2,8,9}), 132.92, 126.63, 124.73, 123.10, 120.10 (C^{3,4,5,6,7}), 45.31 (C^{1}). IR (CsI): $\bar{\nu} = 3069$, 3052, 3028, 3017, 2897, 1557, 1455, 1391, 1013, 851, 749. MS (EI, 70 eV, rel intensity): *m*/*z* 194 (13) $[M]^+$, 115 (100) $[C_9H_7]^+$, 97 (2) $[M]^{2+}$, 89 (5) $[C_7H_5]^+$. Anal. Calcd for C_9H_7Br: C, 55.42; H, 3.62. Found: C, 55.16; H, 3.54.

2-Bromo-4,7-dimethylindene (8). The procedure for the synthesis of **7** was followed using 2-bromo-4,7-dimethylindan-1-ol (**6**) (95.00 g, 394.0 mmol), toluene (540 mL), and *p*-toluenesulfonic acid monohydrate (4.00 g, 21.03 mmol) to give **8** (79.56 g, 91%) as colorless crystals, mp 90 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.05 (t, $^{4}J = 1.6$ Hz, 1 H, H^{3}), 6.99 (d, $^{3}J = 7.7$ Hz, 1 H, H$^{5/6}$), 6.90 (d, $^{3}J = 7.7$ Hz, 1 H, H$^{5/6}$), 3.50 (d, $^{4}J = 1.6$ Hz, 2 H, H^{1}), 2.36 (s, 3 H, H$^{10/11}$), 2.30 (s, 3 H, H$^{10/11}$). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 142.50, 141.16, 129.74, 126.95, 124.01 (C^{2,4,7,8,9}), 131.66, 128.02, 126.17 (C^{3,5,6}), 44.70 (C^{1}), 18.21, 18.07 (C$^{10/11}$). IR (CsI): $\bar{\nu} = 3052$, 3018, 2977, 2970, 2963, 2946, 2921, 2895, 2886, 1594, 1379, 1273, 838, 803 cm^{-1}. Anal. Calcd for $C_{11}H_{11}Br$: C, 59.22; H, 4.97. Found: C, 58.88; H, 4.61.

(−)-2-Menthylindene (10). To a suspension of anhydrous $ZnCl_2$ (38.53 g, 282.7 mmol) in THF (50 mL) at 0 °C was added (+)-menthylmagnesium chloride (**9**)[15] (0.71 M in THF, 342 mL, 243 mmol). After this gray cloudy mixture was stirred 1 h at 0 °C, an orange suspension of tetrakis(triphenylphosphine)palladium(0) (8.05 g, 6.97 mmol) and 2-bromoindene (**7**) (38.70 g, 198.4 mmol) in THF (100 mL) was added. The resulting yellow suspension was warmed to room temperature and stirred 3 days. The reaction mixture was carefully hydrolyzed with saturated aqueous ammonium chloride (100 mL) and extracted with diethyl ether (3 × 80 mL). The combined organic portion was washed with saturated aqueous sodium chloride (40 mL), dried ($MgSO_4$), and condensed by rotary evaporation. The resulting brown residue was first purified by column chromatography (SiO_2, hexane) to give a light yellow oil, which was further purified by vacuum distillation to remove the final traces of residual 2-bromoindene to give **10** as a colorless, analytically pure oil (33.41 g, 66%), bp 95 °C (2×10^{-5} bar). Upon standing at room temperature, this compound slowly crystallized; mp 63 °C. $[\alpha]^{25}_{D}$ −19.3° (neat). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, $J = 7.3$ Hz, 1 H), 7.51 (m, 1 H), 7.47 (m, 1 H), 7.35 (m, 1 H), 6.77 (m, 1 H), 3.55 (m, 1 H), 3.47 (m, 1 H), 2.74 (m, 1 H), 2.03 (m, 1 H), 1.99 (m, 1 H), 1.95 (m, 1 H), 1.91 (m, 1 H), 1.70 (m, 1 H), 1.56 (m, 1 H), 1.38 (m, 1 H), 1.35 (m, 1 H), 1.24 (m, 1 H), 1.17 (d, $J = 6.4$ Hz, 3 H), 1.10 (d, $J = 7.0$ Hz, 3 H), 0.99 (d, $J = 6.8$ Hz, 3 H). ^{13}C{^{1}H} NMR (100.64 MHz, $CDCl_3$): δ 154.53, 145.40, 142.97, 126.53, 126.23, 123.48, 123.47, 119.90, 47.02, 43.70, 43.67, 37.58, 35.20, 32.87, 27.83, 24.28, 22.57, 21.53, 15.23. IR (CsI): $\bar{\nu} =$ 3052, 3018, 2954, 2917, 2869, 2845, 1461, 750, 717 cm^{-1}. MS (EI, 70 eV, rel intensity): *m*/*z* 254 (100) $[M]^+$, 239 (1) $[C_{18}H_{23}]^+$, 211 (21) $[C_{16}H_{19}]^+$, 130 (13) $[C_{10}H_{10}]^+$, 115 (11) $[C_9H_7]^+$. Anal. Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 87.37; H, 10.11.

(−)-2-Menthyl-4,7-dimethylindene (11). Following the procedure for the preparation of **10**, but using $ZnCl_2$ (9.60 g, 70.43 mmol) in THF (45 mL), (+)-menthylmagnesium chloride (**9**) (0.71 M in THF, 95.2 mL, 67.6 mmol), tetrakis(triphenylphosphine)palladium(0) (3.57 g, 3.09 mmol), and 2-bromo-4,7-dimethylindene (**8**) (13.46 g, 60.33 mmol) in THF (40 mL) gave a dark red suspension, which was worked up as above and purified by chromatography (SiO_2, 10:1 hexane/ethyl acetate) and distillation to give **11** (9.71 g, 57%) as a light yellow analytically pure oil that slowly crystallized at room temperature, bp 124 °C (3×10^{-5} bar), mp 89 °C. $[\alpha]^{25}_{D}$ −47.0° (*c* 21.9, diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, $J = 7.6$ Hz, 1 H), 6.92 (d, $J = 7.6$ Hz, 1 H), 6.70 (m, 1 H), 3.28 (m, 1 H), 3.20 (m, 1 H), 2.60 (m, 1 H), 2.47 (s, 3 H), 2.39 (s, 3 H), 1.90 (m, 1 H), 1.86 (m, 1 H), 1.82 (m, 1 H), 1.79 (m, 1 H), 1.54 (m, 1 H), 1.41 (m, 1 H), 1.25 (m, 1 H), 1.21 (m, 1 H), 1.05 (m, 1 H), 0.99 (d, $J = 6.4$ Hz, 3 H), 0.93 (d, $J = 6.8$ Hz, 3 H), 0.82 (d, $J = 6.8$ Hz, 3 H). ^{13}C{^{1}H} NMR (100.64 MHz, $CDCl_3$): δ 153.82, 143.72, 141.36, 129.95, 127.63, 126.18, 124.96, 124.85, 47.11, 43.90, 43.86, 36.75, 35.15, 32.94, 27.80, 24.30, 22.80, 21.55, 18.33, 18.22, 15.22. IR (CsI): $\bar{\nu} = 3041$, 3013, 2957, 2944, 2925, 2869, 2846, 1616, 1453, 857, 845, 802 cm^{-1}. MS (EI, 70 eV, rel intensity): *m*/*z* 282 (100) $[M]^+$, 267 (1) $[C_{20}H_{27}]^+$, 239 (10) $[C_{18}H_{23}]^+$, 197 (50) $[C_{15}H_{17}]^+$, 158 (13) $[C_{12}H_{14}]^+$, 143 (8) $[C_{11}H_{11}]^+$, 128 (4) $[C_{10}H_8]^+$. Anal. Calcd for $C_{21}H_{30}$: C, 89.29; H, 10.70. Found: C, 88.88; H, 10.42.

(−)-(2-Menthylindenyl)lithium (**12**). To (−)-2-menthylindene (**10**) (33.00 g, 129.7 mmol) in diethyl ether (100 mL) at 0 °C was added n-BuLi (1.6 M in *n*-hexane, 90 mL, 19.2 mmol). The yellow solution was stirred 1 h at 0 °C followed by 10 h at room temperature. The solvent was removed under vacuum, and *n*-hexane (10 mL) was added to the resulting yellowish residue. The suspension was stirred 10 h at room temperature, filtered, and washed with *n*-hexane (2 × 5 mL). After drying under vacuum, (−)-2-menthylindenyllithium (**12**) was isolated as a white powder (28.79 g, 85%), mp 168 °C (dec). $[\alpha]^{25}_{D}$ −63.5° (*c* 0.2, diethyl ether). ^{1}H NMR (400 MHz, [D$_5$]-pyridine): δ 7.83 (m, 2 H), 6.84 (m, 2 H), 6.58 (m, 2 H), 3.02 (m, 1 H), 2.57 (m, 1 H), 2.37 (m, 1 H), 1.90 (m, 1 H), 1.85 (m, 1 H), 1.83 (m, 1 H), 1.78 (m, 1 H), 1.57 (m, 1 H), 1.28 (m, 1 H), 1.13 (m, 1 H), 0.96 (d, J = 7.0 Hz, 3 H), 0.92 (d, J = 6.4 Hz, 3 H), 0.84 (d, J = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, [D$_5$]-pyridine): δ 140.0, 131.3, 117.5, 110.6, 92.4, 49.5, 48.3, 44.6, 36.0, 33.8, 27.2, 25.2, 23.1, 22.1, 16.0. MS (EI, 70 eV, rel intensity): *m/z* 260 (1) [M]$^+$, 254 (100) [$C_{19}H_{26}$]$^+$, 169 (66) [$C_{13}H_{13}$]$^+$, 121 (1) [(C_9H_6)Li]$^+$, 116 (83) [C_9H_8]$^+$. Anal. Calcd for $C_{19}H_{25}Li$: C, 87.65; H, 9.68. Found: C, 87.79; H, 9.84.

(−)-(2-Menthyl-4,7-dimethylindenyl)lithium (**13**). As in the preparation of **12**, (−)-2-menthyl-4,7-dimethylindene (**11**) (4.30 g, 15.22 mmol), diethyl ether (50 mL), and n-BuLi (1.6 M in *n*-hexane, 12 mL, 19.2 mmol) gave **13** as a white powder (3.0 g, 68%), mp 138 °C (dec). $[\alpha]^{25}_{D}$ −20.1° (*c* 19.1, diethyl ether). ^{1}H NMR (400 MHz, [D$_5$]-pyridine): δ 6.68 (m, 2 H), 6.56 (m, 2 H), 3.07 (m, 1 H), 2.76 (s, 6 H), 2.63 (m, 1 H), 2.42 (m, 1 H), 1.89 (m, 1 H), 1.88 (m, 1 H), 1.84 (m, 1 H), 1.83 (m, 1 H), 1.58 (m, 1 H), 1.31 (m, 1 H), 1.16 (m, 1 H), 1.00 (d, J = 6.9 Hz, 3 H), 0.94 (d, J = 6.3 Hz, 3 H), 0.85 (d, J = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (100.64 MHz, [D$_5$]-pyridine): δ 138.3, 130.7, 122.7, 111.8, 91.7, 49.8, 48.6, 44.9, 36.3, 33.0, 27.3, 25.3, 23.3, 22.3, 20.6, 16.2. MS (EI, 70 eV, rel intensity) *m/z* 288 (2) [M]$^+$, 282 (100) [$C_{21}H_{30}$]$^+$, 158 (15) [$C_{12}H_{14}$]$^+$, 143 (10) [$C_{11}H_{12}$]$^+$. Anal. Calcd for $C_{21}H_{29}Li$: C, 87.46; H, 10.13. Found: C, 87.03; H, 9.71.

Bis(2-menthylindenyl)zirconium Dichloride (**14**). To a solid mixture of lithium salt **12** (0.50 g, 1.92 mmol) and $ZrCl_4$ (0.22 g, 0.94 mmol) at −78 °C under argon was added diethyl ether (20 mL). After stirring the mixture at room temperature overnight, the solvent was removed under vacuum. The resulting solid was stirred with methylene chloride (20 mL) for 30 min and filtered through a Schlenk frit. The solvent was removed under vacuum, and hexane (20 mL) was added to the resulting solid to give a yellow slurry. After stirring the slurry for 30 min, the suspension was filtered and the filtrate concentrated under vacuum to give **14** as a yellow solid (0.25 g, 40%). A portion of this compound was recrystallized from hexane to give crystals suitable for X-ray diffraction, mp >230 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, J = 6.0 Hz, 2 H), 7.69 (d, J = 6.0 Hz, 2 H), 7.20 (m, 4 H), 6.17 (br s, 2 H), 5.64 (br s, 2 H), 2.20 (ddd, J = 11.0, 11.0, 4.5 Hz, 2H), 0.86 (d, J = 6.5 Hz, 6 H), 0.77 (d, J = 6.5 Hz, 6 H), 0.60 (d, J = 7.0 Hz, 6 H), 0.60−1.80 (m, 18 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.4, 128.7, 125.9, 125.1, 124.8, 124.4, 122.6, 106.4, 100.9, 49.9, 41.6, 40.5, 35.0, 32.1, 26.8, 24.3, 22.5, 21.3, 15.3. MS (EI 12 eV, rel intensity): *m/z* 668 (M$^+$ + 2, 4%), 666 (M$^+$, 4), 416 (65), 415 (58), 414 (50), 413 (100), 254 (3). Anal. Calcd for $C_{38}H_{50}ZrCl_2$ H, 7.53; C, 68.23. Found: H, 8.08; C, 67.94.

Bis(2-menthyl-4,7-dimethylindenyl)zirconium Dichloride (**15**). Following the procedure for the synthesis of **14** but using (2-menthyl-4,7-dimethylindenyl)lithium (**13**) (0.55 g, 1.91 mmol), $ZrCl_4$ (0.22 g, 0.94 mmol) gave **15** as a yellow solid (0.45 g, 66%). A portion of this compound was recrystallized from hexane to give crystals suitable for X-ray diffraction, mp >230 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$, 50 °C): δ 6.90 (d, J = 6.5 Hz, 2 H), 6.84 (d, J = 6.5 Hz, 2 H), 6.30 (br s 2 H), 5.96 (br s, 2 H), 2.68 (s, 6 H), 2.45 (s, 6 H), 2.44 (m, 2 H), 1.72 (br d, J = 11.0 Hz, 2 H), 1.61 (br d, J = 10.0 Hz, 2 H), 0.7−1.1 (m, 10 H), 0.92 (d, J = 7.0 Hz, 6 H), 0.79 (d, J = 7.0 Hz, 6 H), 0.63 (d, J = 7.0 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 132.2, 126.1, 125.4, 124.8, 51.0, 42.3, 40.0, 35.2, 32.7, 32.6, 27.0, 24.6, 22.6, 21.6, 20.0, 15.5 (several aromatic C's not observed). IR (KBr): ν = 2958, 2923, 2870, 1458, 1383, 1346, 831 cm^{-1}. MS (EI, 12 eV, rel intensity): *m/z* 449 (5%), 447 (22), 445 (64), 444 (32), 442 (100), 440 (96). Anal. Calcd for $C_{42}H_{58}ZrCl_2$: H, 8.06; C: 69.58. Found: H, 8.18; C, 69.64.

X-ray Structure Determination of 14 and 15. The data were collected on a Siemens P4 diffractometer,[18] using Mo Kα (ν = 0.71073 Å) radiation. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans[19] was applied. The structures were solved by the heavy atom method using the SHELXTL system[20] and refined by full-matrix least-squares on F using all reflections. All the non-hydrogen atom were refined anisotropically for **14**, and for **15** only the Zr and Cl atoms were refined unisotropically. Hydrogen atoms were included in the refinement with idealized parameters for both structures. **14** contains two independent molecule in the asymmetric unit along with two molecules of toulene solvent. For **14** final R1 = 0.032 is based on 9616 observed reflections, and final wR = 0.096 is based on all reflections (10 019 unique data). Crystals for **15** were thin plates, and a crystal with a width of only 0.08 mm was used for data collection. As a result, the data were generally very weak. Data collection was terminated at 45° since there were only 10−15% observed reflections beyond that point. Overall quality of data is poor, which resulted in a high value of R1 and wR. Despite the high R-factors, the final geometry of the molecule is quite reasonable. Limitation of the data also prevented the unisotropic refinement of all non-hydrogen atoms; only the Zr and Cl atoms were refined unisotropically and all the carbon atoms were refined isotropically. Final R1 = 0.1193 is based on 1377 observed" reflections, and the final wR = 0.3440 is based on all reflections (2938 unique data).

Polymerization Conditions. Polymerization experiments were carried out in a 1-gallon stainless steel autoclave reactor. The catalyst solution was prepared by the addition of enough 10% MAO in toluene (Albemarle) to the metallocene to give a 10 000:1 molar excess of aluminum. The catalyst solution was charged to the reactor followed by 2.5 L of propylene monomer and any desired hydrogen. This mixture was then quickly brought to 70 °C, and this temperature was then maintained for 1 h. Stirring with a three-blade propeller stirrer was maintained at 1200 rpm. The reaction was stopped by venting the volatiles. The resulting solids were washed with acidic methanol and dried under vacuum to give the isolated polymer. The polymer was characterized by GPC and ^{13}C NMR spectroscopic methods.

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Supporting Information Available: Crystallographic tables for (−)-2-menthylindene (**10**), (−)-2-menthyl-4,7-dimethylindene (**11**), bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride (**14**), and bis(2-menthyl-4,7-dimethylindenyl)zirconium dichloride (**15**). Variable-temperature NMR spectra of **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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