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Cp-Substituent Additivity Effects Controlling the Stereochemistry of the Propene Polymerization Reaction at Conformationally Unrestricted $(Cp\text{-}CHR^1R^2)_2ZrCl_2$/Methylalumoxane Catalysts

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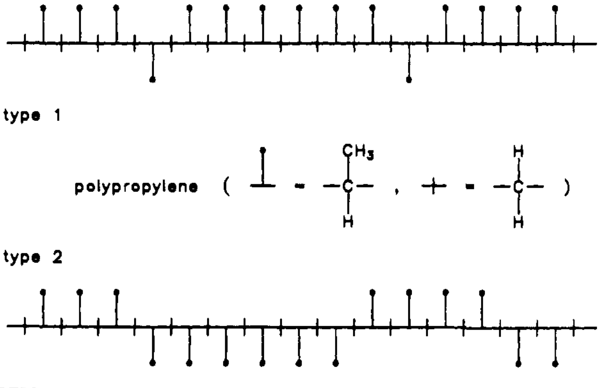
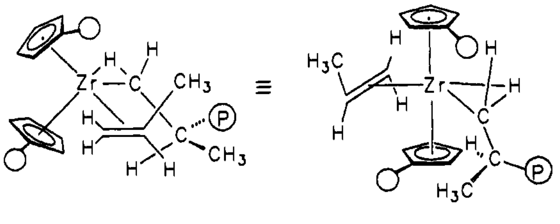
Abstract: Four chiral bent metallocene complexes $(Cp\text{-}CHR^1R^2)_2ZrCl_2$ (**1–4**, Cp = C_5H_4) were prepared and used to generate homogeneous Ziegler catalyst systems for the stereoselective polymerization of propene. 6-Cyclohexyl-6-methylfulvene was reduced by intermolecular β-hydride transfer from primary alkyllithium reagents $LiCH_2CHRR'$ (**6**; R, R′ = H, alkyl, aryl) to give $[Cp\text{-}CH(CH_3)Cy]Li$ (**7a**). Subsequent reaction with zirconium tetrachloride resulted in a 1:1 mixture of the $[Cp\text{-}CH(CH_3)Cy]_2ZrCl_2$ diastereomers (**1**), from which the chiral complex *rac*-**1** was obtained >98% isomerically pure by fractional crystallization. *rac*-$[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$ (*rac*-**2**) was obtained analogously from 6-methyl-6-phenylfulvene. Regioselective α-deprotonation of 6-cyclohexyl-6-methylfulvene with lithium diisopropylamide followed by treatment with $ZrCl_4$ gave $[Cp\text{-}C(Cy){=}CH_2]_2ZrCl_2$ (**9a**), which was characterized by X-ray diffraction. Complex **9a** crystallizes in space group $C2/c$ with cell constants a = 28.044 (6) Å, b = 6.627 (1) Å, c = 13.150 (2) Å, β = 108.59 (1)°, Z = 4, R = 0.024, and R_w = 0.031. Hydroboration of **9a** gave a 1:1 mixture of the $[Cp\text{-}CH(Cy)CH_2(9\text{-}BBN)]_2ZrCl_2$ diasteromers (**3**). Isomerically pure *rac*-**3** was recovered by fractional crystallization. The chiral metallocene complex *rac*-$[Cp\text{-}CH(Ph)CH_2(9\text{-}BBN)]_2ZrCl_2$ (*rac*-**4**) was similarly prepared by means of a regioselective 9-BBN addition to the C=C double bonds of $[Cp\text{-}C(Ph){=}CH_2]_2ZrCl_2$ (**9b**). The activation of the metallocene dihalide *rac*-**1** with excess oligomeric methylalumoxane (Al:Zr ≈ 900) produced a propene polymerization catalyst that gave isotactic polypropylene at −50 °C. ^{13}C NMR pentad analysis in combination with a statistical treatment using a two-parameter model revealed a combined influence of "enantiomorphic-site control" (statistical descriptor α, statistical weight fraction ω) and "chain-end control" (σ, $1 - \omega$) similar to what is observed as double stereodifferentiation in conventional organic synthesis. The effectiveness of chirality transfer from the chiral metallocene backbone of this catalyst system was expressed by a "relative enantioselectivity" [$ee^* = (2\alpha - 1)\omega$] of 13%. Systematic variation of the metallocene Cp substituents revealed a remarkable additivity effect. Exchange of the cyclohexyl groups in **1** for phenyl doubled the asymmetric induction of the C–C coupling process (the ee* of the *rac*-**2**-derived catalyst at −50 °C was 25%) as did the formal exchange of the substituent methyl group for the bulkier $-CH_2(9\text{-}BBN)$ moiety (*rac*-**3**: ee* = 30% at −50 °C). Both amendments combined in a single catalyst system quadrupled the efficiency of the metallocene chirality transfer (*rac*-**4**: ee* = 60% at −50 °C). This observation should be helpful in the continuing efforts toward a rational design of catalyst systems combining high stereoselectivity with high reaction rates.

In 1980 Sinn, Kaminsky, et al. described a novel Ziegler type catalyst for olefin polymerization. The homogeneous system was derived from activating a group 4 bent metallocene complex (e.g. zirconocene dichloride) with a large excess of an oligomeric alumoxane [e.g. $(MeAlO)_x$]. The $Cp_2ZrX_2/(MeAlO)_x$ catalyst system exhibited very high activities but lacked selectivity.[1] Brintzinger et al. substituted the achiral Cp_2MX_2 component for rigid chiral ansa metallocenes [e.g. the CH_2CH_2-bridged *rac*-$(-CH_2\text{–}indenyl)_2ZrCl_2$] and obtained very reactive catalysts for the production of highly isotactic polypropylene. The isotactic polymer formed with the ansa metallocene/methylalumoxane catalysts contained mainly singular stereochemical "mistakes" (type 1 isotactic polypropylene) which indicated a reaction mechanism where the chirality information of the chiral metallocene backbone had effectively controlled the stereochemistry of each olefin-insertion step ("enantiomorphic-site control").[2]



Scheme I



From the work of Eisch, Gassman, Jordan, Bochmann, Turner, and others came convincing evidence that cationic metallocenyl complexes (e.g. $Cp_2M\text{–}R^+$) constituted the active principle of these

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reactive catalysts.[3] With studies related to the catalytic polymerization reaction, Pino, Waymouth, Brintzinger, and others[4] obtained some information about the actual mechanism by which a chirality transfer from the metallocene species to the growing carbon chain could be taking place. The essentials of this process are depicted in Scheme I, showing a drawing of the molecular geometry of a possible alkyl(olefin)metallocenyl cation intermediate leading to the observed stereospecific carbon–carbon coupling reaction.

There is a major and principal complication that has to be taken into account in attempts to describe the actual pathway of chirality transfer of the metallocenyl cation catalyst. Ewen has shown that the catalysts derived from achiral metallocene precursors, such as diphenyltitanocene, can give rise to the formation of isotactic polypropylene as well. In this case, type 2 polypropylene is formed, consisting of a sequence of isotactic blocks, which is indicative of chirality transfer from the newly formed stereogenic carbon center at the end of the growing polymer chain in the position β to the active metal atom ("chain-end control").[5]

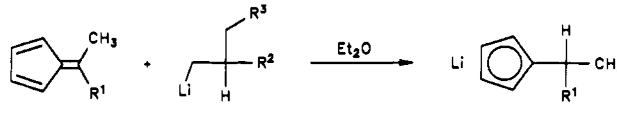
What makes an a priori rational design of new catalyst systems of this type for stereoselective α-olefin polymerization so complicated is that these two major controlling stereochemical factors are not independent of each other. The influences of the chiral metallocene unit and the carbon chirality center within the growing product chain exert an interrelated influence on the incoming prochiral olefin similar to what is known as double stereodifferentiation in conventional organic synthesis.[6] We have recently described a typical example where the combined effects of enantiomorphic-site control and chain-end control for determining the stereochemistry of the polypropylene formed could be demonstrated experimentally.[7]

The difficult situation one is faced with is illustrated in Scheme I. The stereochemistry of the catalytic carbon–carbon coupling reaction at the cationic metal catalyst is determined by two factors of which we can only control and synthetically vary one in a direct and active way, namely the chiral bent metallocene, whereas controlling the stereochemical participation of the chiral chain end as a part of the newly formed product cannot be done directly. In this difficult situation, the discovery of an additivity effect of stereochemically controlling substituents attached to the Cp rings of the zirconocene catalyst precursors may be helpful. A set of four $(\text{Cp-CHR}^1\text{R}^2)_2\text{ZrCl}_2$ examples revealing additivity of their R^1/R^2 substituent influence on the stereochemical outcome of the polypropylene formation is described in this paper. Knowledge of a linear substituent influence such as found for this specific series of examples should be useful for the ongoing development of stereoselective bent metallocene/alumoxane-based catalyst systems.

Results and Discussion

Preparation of the $(\text{Cp-CHR}^1\text{R}^2)_2\text{ZrCl}_2$ Complexes. The first pair of zirconium complexes synthesized for this study were made by the metallocene halides $[\text{Cp-CH(CH}_3)\text{Cy}]_2\text{ZrCl}_2$ (**1**, Cy = cyclohexyl) and $[\text{Cp-CH(CH}_3)\text{Ph}]_2\text{ZrCl}_2$ (**2**), exhibiting a chirality center at each Cp substituent adjacent to the η-C_5H_4 ring system. Complexes **1** and **2** were both prepared from the corresponding 6,6-disubstituted pentafulvene systems. From Ziegler's early work, it is well-known that fulvenes can behave as the all-carbon analogues of organic carbonyl compounds: nucleophiles may add to the C(6) atom, and treatment with nonnucleophilic bases may result in α-deprotonation.[8]

The $\text{Cp-CH(CH}_3)\text{Ph}$ ligand system could thus easily be prepared by means of a hydride addition to the C(6) atom of 6-methyl-6-phenylfulvene. This can be achieved by treatment of the fulvene system with a variety of primary alkyllithium reagents. We observed that n-butyllithium in diethyl ether solution does not add as such to the fulvene but rather transfers a hydride from the carbon center β to the lithium to give $[\text{Cp-CH(CH}_3)\text{Ph}]\text{Li}$ (**7b**) in moderate yield. A deuterium-labeling experiment employing 2,2-dideuterio-1-lithiobutane (**6g**) confirmed the β-hydride transfer reaction which appears to proceed similarly to the mechanistically related Meerwein–Pondorf–Verley reaction or some Grignard reductions of organic carbonyl functional groups.[8c]



5a (R^1 = Cy)
5b (R^1 = Ph)

6a (R^2 = H, R^3 = CH_3)
6b (R^2 = H, R^3 = H)
6c (R^2 = CH_3, R^3 = H)
6d (R^2 = Ph, R^3 = H)
6e (R^2 = Cy, R^3 = H)
6f (R^2 = Ph, R^3 = CH_3)
6g (R^2 = D, R^3 = CH_3)

7a (R^1 = Cy)
7b (R^1 = Ph)

As expected, the hydride-donating ability of suitably branched primary alkyllithium reagents can be superior to that of ethyl-, n-propyl-, or n-butyllithium. Whereas the reaction of 6-methyl-6-phenylfulvene with the n-alkyllithium reagents produced **7b** in only moderate yield (20–30% isolated), the reaction with isobutyllithium (**6c**) gave a 60% yield of $[\text{Cp-CH(CH}_3)\text{Ph}]\text{Li}$ as a white solid which precipitated from the reaction mixture.

We briefly checked whether the use of an optically active alkyllithium reagent might lead to asymmetric induction in the β-hydride transfer step from a secondary alkyl chirality center. For this purpose, we synthesized the optically active lithium reagents (S)-1-lithio-2-phenylpropane (S-**6d**), (S)-1-lithio-2-cyclohexylpropane (S-**6e**), and (R)-1-lithio-2-phenylbutane (S-**6f**).[9] Their reaction with 6-methyl-6-phenylfulvene (**5b**) or 6-methyl-6-cyclohexylfulvene (**5a**) in an ethereal solution gave the

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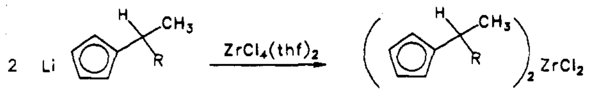
corresponding lithiocyclopentadienyls $[Cp\text{-}CH(CH_3)Ph]Li$ (**7b**) and $[Cp\text{-}CH(CH_3)Cy]Li$ (**7a**) in acceptable yields (ca. 45% and 75%, respectively). However, we have not found any indication of a measurable degree of asymmetric induction in these reactions. This we deduced from the observation that almost identical *meso-*:*rac*-metallocene product ratios were obtained in the subsequent reaction with $ZrCl_4$ (see below), regardless of whether optically active, racemic, or achiral alkyllithium reagents were used as starting materials for the intermolecular β-hydride transfer reaction.

The reaction of $[Cp\text{-}CH(CH_3)Ph]Li$ (**7b**) with zirconium tetrachloride in a 2:1 molar ratio in toluene/tetrahydrofuran (1:10) gave $[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$ (**2**) in ca. 40% yield.[10] Attaching to the transition-metal center two Cp entities possessing one chiral substituent each should give rise to the formation of two diastereoisomeric zirconocene complexes, a meso and a racemic form. The two Cp ligands in each separate diastereomer are symmetry-equivalent and exhibit identical NMR resonances. The Cp ligand NMR signals of the meso and racemic series should, however, be differentiated from one another. Due to the adjacent substituent chirality center, the four methine units of the $\eta\text{-}C_5H_4R^*$ group must be inequivalent, giving four different sets of CH signals in the NMR spectra of each $[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$ diastereoisomer.



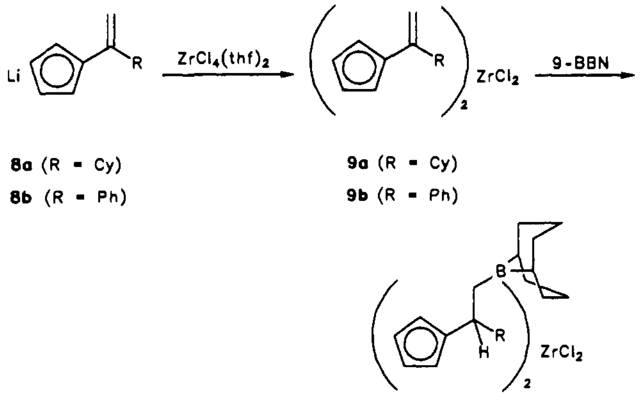
7a (R = Cy)
7b (R = Ph)

1 (R = Cy; meso/rac ≈ 1:1)
2 (R = Ph; meso/rac ≈ 1:1)

This was experimentally observed. The ^1H NMR spectrum of the unseparated product mixture obtained from the **7b** + $ZrCl_4$ reaction contained two series of cyclopentadienyl C*H* resonances ($CDCl_3$, 200 MHz; δ 6.51, 6.23, 6.13, 5.86 and 6.51, 6.18, 6.09, 5.86) in a 1:1 ratio. There was no clear a priori assignment indicating which set of the observed resonances belonged to the racemic or meso diastereoisomer of **7b**. However, the stereospecific propene polymerization achieved with one of the (separated) isomers in connection with the result of an X-ray crystal structure analysis[7] allowed for an unambiguous stereochemical assignment, the reaction product showing the former set of C*H* NMR resonances as being due to the *rac*-$[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$ complex (*rac*-**2**).

The reaction between $ZrCl_4$ and $[Cp\text{-}CH(CH_3)Cy]Li$ proceeded similarly; again, we obtained a nearly equimolar mixture of the respective diastereoisomers *meso*-**1** and *rac*-**1**. Their relative assignment was again based on the stereochemical outcome of a propene polymerization reaction employing catalysts derived from the separated (i.e. >95:5% diastereomerically enriched) *rac*-**1** isomer. The diastereomers could then easily be characterized by their $^1H/^{13}C$ NMR spectra [$^1H/^{13}C$ cyclopentadienyl methine resonances in $CDCl_3$ solution: *rac*-**1** δ 6.45, 6.28, 6.10, 6.05/116.8, 115.7, 114.8, 107.1; *meso*-**1** δ 6.39, 6.31, 6.11, 6.05/116.6, 115.9, 114.6 (double intensity)].

The $[Cp\text{-}CH(CH_3)R]_2ZrCl_2$ complexes **1** and **2** were also obtained via an alternative route involving hydrogenation reactions. We had observed that the outcome of the reaction of 6-methyl-6-phenylfulvene (**5b**) with the primary alkyllithium reagents **6** was quite solvent dependent. In contrast to the above described hydride transfer, taking place in diethyl ether solution, only α-deprotonation was observed upon treatment of **5b** with $n\text{-}C_4H_9Li$ (**6a**) in tetrahydrofuran to give [(1-phenylethenyl)cyclopentadienyl]lithium (**8b**). On a preparative scale, it was more convenient to carry out this reaction with lithium diisopropylamide (LDA) in thf. This gave the $[Cp\text{-}C(Ph){=}CH_2]Li$ reagent (**8b**) in ca. 80% yield. The corresponding $[Cp\text{-}C(Cy){=}CH_2]Li$ anion equivalent (**8a**) was formed similarly upon treatment of 6-cyclohexyl-6-methylfulvene with LDA in tetrahydrofuran. [(1-Phenylethenyl)cyclopentadienyl]lithium (**8b**) was reacted with $^1/_2$ molar equiv of $ZrCl_4(thf)_2$ in toluene/thf solution at 0 °C to yield the doubly alkenyl-substituted-Cp metallocene complex $[Cp\text{-}C(Ph){=}CH_2]_2ZrCl_2$ (**9b**). Similarly, $[Cp\text{-}C(Cy){=}CH_2]_2ZrCl_2$ (**9a**) was obtained in >70% yield by reacting **8a** with the zirconium tetrachloride bis(tetrahydrofuran) adduct.



8a (R = Cy)
8b (R = Ph)

9a (R = Cy)
9b (R = Ph)

3 (R = Cy; meso/rac ≈ 1:1)
4 (R = Ph; meso/rac ≈ 1:1)

The catalytic hydrogenation of metallocene dihalide **9b** bearing phenylalkenyl substituents at the Cp rings took place smoothly on a heterogeneous platinum catalyst at elevated pressure (PtO_2, 50 bar of H_2) in dichloromethane solution at ambient temperature. Under these conditions, both phenyl ring systems were hydrogenated in addition to the C=C double bonds to give the cyclohexyl-substituted $[Cp\text{-}CH(CH_3)Cy]_2ZrCl_2$ diastereoisomers *meso*-**1** and *rac*-**1** in a nearly 1:1 ratio (isolated in almost quantitative yield).

The catalytic hydrogenation with use of Rh(I)-based homogeneous hydrogenation catalysts proceeded more selectively, leading only to H_2 addition to the 1,1-disubstituted carbon–carbon double bonds of **9b**. Unfortunately, no asymmetric induction was observed upon employing two frequently used optically active catalyst systems. The hydrogenation (50 bar of H_2) of **9b** with $[RhCl(cod)]_2$/(+)-DIOP in toluene at room temperature gave the $[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$ *meso*-**2** and *rac*-**2** diastereoisomers in a nearly 1:1 ratio. Using the $[RhCl(cod)]_2$/(−)-BINAP-derived catalyst system resulted in a 45:55 mixture of the respective products.

The alkenyl-substituted metallocene halides $[Cp\text{-}C(Ph){=}CH_2]_2ZrCl_2$ (**9b**) and $[Cp\text{-}C(Cy){=}CH_2]_2ZrCl_2$ (**9a**) were used as starting materials for the preparation of the other pair of $[Cp\text{-}CHR^1R^2]_2ZrCl_2$ complexes, completing the series of four catalyst precursors used in this study. They were obtained by 9-borabicyclo[3.3.1]nonane addition to the C=C double bonds of the Cp substituents. In each case, a completely regioselective hydroboration reaction of the organometallic substrate was achieved with the bulky 9-BBN group ending up in the β-position of the Cp substituent.[11] The reaction of $[Cp\text{-}C(Ph){=}CH_2]_2ZrCl_2$ (**9b**) with 9-BBN yielded a 1:1 mixture of the respective diastereomers (*meso*-**4** and *rac*-**4**) of the $[Cp\text{-}CH(Ph)CH_2(9\text{-}BBN)]_2ZrCl_2$ system (90% combined yield). The isomers could be distinguished by their slightly different $^1H/^{13}C$ CH resonances of the substituted Cp units. The absolute assignment (C_6D_6; *rac*-**4** δ 5.41, 5.63, 5.80, 6.42/110.8, 113.8, 114.3, 116.8; *meso*-**4** δ 5.49, 5.67, 5.80, 6.42/111.4, 112.8, 115.1, 116.3) was again based on the stereochemical outcome of the propene polymerization reaction (see below). The hydroboration of $[Cp\text{-}C(Cy){=}CH_2]_2ZrCl_2$ (**9a**) produced a nearly 1:1 mixture of *meso*- and *rac*-[Cp-CH(Cy)-

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(10) Complex **1** had previously been described in the literature: Leblanc, J. C.; Moise, C. *J. Organomet. Chem.* **1976**, *120*, 65. Couturier, S.; Gautheron, B. *Ibid.* **1978**, *157*, C 61. Cesarotti, E.; Ugo, R.; Kagan, H. B. *Angew. Chem.* **1979**, *91*, 842; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 779.

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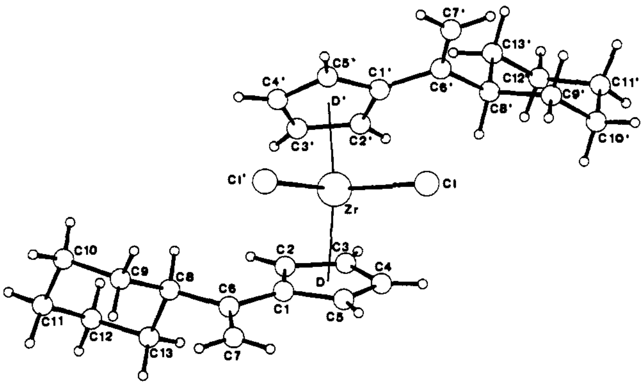


Figure 1. Molecular geometry of crystalline **9a**.

Table I. Selected Bond Distances (Å) and Angles (deg) for **9a**

Zr–Cl	2.437 (1)	Zr–C(1)	2.590 (1)
Zr–C(2)	2.508 (1)	Zr–C(3)	2.485 (1)
Zr–C(4)	2.499 (1)	Zr–C(5)	2.529 (1)
Zr–D	2.215 (1)	C(1)–C(2)	1.423 (2)
C(1)–C(5)	1.423 (2)	C(1)–C(6)	1.476 (2)
C(2)–C(3)	1.423 (2)	C(3)–C(4)	1.405 (2)
C(4)–C(5)	1.416 (2)	C(6)–C(7)	1.330 (2)
C(6)–C(8)	1.515 (2)	C(8)–C(9)	1.533 (2)
C(8)–C(13)	1.540 (2)	C(9)–C(10)	1.529 (2)
C(10)–C(11)	1.524 (2)	C(11)–C(12)	1.528 (2)
C(12)–C(13)	1.533 (2)		
Cl*–Zr–D	106.1 (1)	Cl*–Zr–Cl	98.0 (1)
D–Zr–Cl	106.0 (1)	D*–Zr–D	130.1 (1)
C(6)–C(1)–C(5)	127.0 (1)	C(6)–C(1)–C(2)	126.1 (1)
C(5)–C(1)–C(2)	106.9 (1)	C(3)–C(2)–C(1)	108.4 (1)
C(4)–C(3)–C(2)	107.8 (1)	C(5)–C(4)–C(3)	108.3 (1)
C(4)–C(5)–C(1)	108.4 (1)	C(8)–C(6)–C(7)	123.1 (1)
C(8)–C(6)–C(1)	117.1 (1)	C(7)–C(6)–C(1)	119.8 (1)
C(13)–C(8)–C(9)	109.4 (1)	C(13)–C(8)–C(6)	110.5 (1)
C(9)–C(8)–C(6)	114.2 (1)	C(10)–C(9)–C(8)	110.6 (1)
C(11)–C(10)–C(9)	111.5 (1)	C(12)–C(11)–C(10)	111.4 (1)
C(13)–C(12)–C(11)	111.8 (1)	C(12)–C(13)–C(8)	111.6 (1)

CH_2(9-BBN)$]_2ZrCl_2$ (**3**), which were analogously characterized by their distinctive $^1H/^{13}C$ NMR spectra in connection with their catalytic properties (cyclopentadienyl methine resonances in C_6D_6: *rac*-**3** δ 5.59, 5.82, 6.02, 6.31/106.2, 114.0, 115.2, 117.9; *meso*-**3** δ 5.68, 5.82, 6.01, 6.33/107.1, 114.0, 114.6, 118.7).

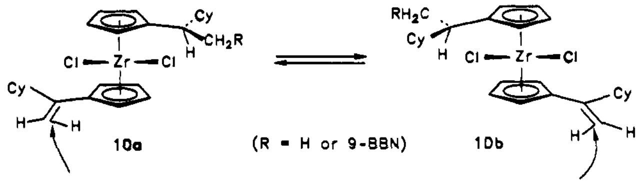
Molecular Structure of [Cp-C(Cy)=$CH_2]_2ZrCl_2$ (9a). The molecular structure of **9a** in the solid state was determined by X-ray diffraction. The [Cp-C(Cy)=$CH_2]_2ZrCl_2$ structure is C_2-symmetric. The zirconium center in this bent metallocene complex is pseudotetrahedrally coordinated by two [η^5-Cp-C(Cy)=CH_2] and two chloride ligands. The Cl–Zr–Cl angle in **9a** is 98.0 (1)°, which is about 4° smaller than found in many $(RCp)_2ZrCl_2$ complexes bearing e.g. bulky *tert*-alkyl substituents at the Cp rings.[12] The Zr–Cl distance is 2.437 (1) Å. The substituted Cp ring systems are oriented almost eclipsed. The C(Cy)=CH_2 side chains are pointed away from each other. They are positioned in a trans arrangement and directed toward the lateral sectors of the bent metallocene unit. This conformational arrangement is similar to what is found in many (*tert*-alkyl-Cp)$_2ZrCl_2$ complexes such as (*tert*-butyl-Cp)$_2ZrCl_2$ or bis(1-methylcyclohexyl)zirconocene dichloride,[12] although the antiperiplanar substituent positioning is not so pronounced in **9a**. The substituent dihedral angle in [Cp-C(Cy)=$CH_2]_2ZrCl_2$, defined as θ_s (C(6)–D–D′–C(6′)) (with D and D′ being the symmetry-related Cp centroids), is 134° whereas it is close to 180° for the above mentioned (*tert*-alkyl-Cp)$_2ZrCl_2$ complexes.

Table II. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) with Standard Deviations in Parentheses for **9a**[a]

atom	x	y	z	U_{eq}
Zr	0.0000	0.2538 (1)	0.2500	0.011 (1)
Cl	−0.0381 (1)	0.4950 (1)	0.1073 (1)	0.021 (1)
C(1)	0.0948 (1)	0.1834 (2)	0.2866 (1)	0.013 (1)
C(2)	0.0690 (1)	−0.0028 (2)	0.2822 (1)	0.014 (1)
C(3)	0.0361 (1)	−0.0310 (2)	0.1757 (1)	0.017 (1)
C(4)	0.0402 (1)	0.1394 (2)	0.1155 (1)	0.018 (1)
C(5)	0.0751 (1)	0.2742 (2)	0.1836 (1)	0.016 (1)
C(6)	0.1352 (1)	0.2628 (2)	0.3798 (1)	0.014 (1)
C(7)	0.1611 (1)	0.4248 (2)	0.3685 (1)	0.022 (1)
C(8)	0.1470 (1)	0.1455 (2)	0.4837 (1)	0.013 (1)
C(9)	0.1689 (1)	0.2737 (2)	0.5849 (1)	0.016 (1)
C(10)	0.1772 (1)	0.1453 (2)	0.6856 (1)	0.017 (1)
C(11)	0.2123 (1)	−0.0317 (2)	0.6879 (1)	0.019 (1)
C(12)	0.1932 (1)	−0.1592 (2)	0.5862 (1)	0.021 (1)
C(13)	0.1830 (1)	−0.0304 (2)	0.4847 (1)	0.017 (1)
H(2)	0.0749 (6)	−0.095 (3)	0.341 (1)	0.017 (4)
H(3)	0.0171 (7)	−0.141 (3)	0.152 (1)	0.023 (5)
H(4)	0.0219 (7)	0.166 (3)	0.044 (1)	0.020 (4)
H(5)	0.0827 (6)	0.405 (3)	0.161 (1)	0.018 (4)
H(7a)	0.1872 (7)	0.476 (3)	0.428 (1)	0.026 (5)
H(7b)	0.1542 (7)	0.490 (3)	0.304 (2)	0.026 (5)
H(8)	0.1147 (6)	0.086 (3)	0.489 (1)	0.015 (4)
H(9a)	0.2009 (7)	0.331 (3)	0.584 (1)	0.015 (4)
H(9e)	0.1470 (6)	0.393 (3)	0.582 (1)	0.020 (4)
H(10a)	0.1455 (8)	0.095 (3)	0.687 (2)	0.033 (5)
H(10e)	0.1919 (8)	0.229 (3)	0.748 (2)	0.021 (5)
H(11a)	0.2471 (7)	0.022 (3)	0.696 (1)	0.026 (5)
H(11e)	0.2155 (7)	−0.122 (3)	0.747 (2)	0.029 (5)
H(12a)	0.161 (1)	−0.227 (3)	0.584 (2)	0.041 (7)
H(12e)	0.2174 (8)	−0.266 (3)	0.585 (2)	0.023 (5)
H(13a)	0.2155 (7)	0.035 (3)	0.481 (1)	0.021 (4)
H(13e)	0.1683 (7)	−0.116 (3)	0.422 (1)	0.025 (5)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{\bar{a}}_i\cdot\mathbf{\bar{a}}_j$.

Scheme II



The 1,1-disubstituted C=CH_2 double bond of the substituent is almost coplanar with the adjacent Cp ring (dihedral angle C(5)–C(1)–C(6)–C(7) = 7.8°). The C(1)–C(6) bond length is 1.476 (2) Å, and the C(6)–C(7) distance is 1.330 (2) Å, as is expected for an ordinary carbon–carbon double bond.[13]

The cyclohexyl substituents bonded to C(6) and C(6′) are arranged toward the lateral sectors of the bent metallocene. The C(6)–C(7) vector points to the "open" side of the bent metallocene wedge, the C=CH_2 methylene group being placed almost exactly above the zirconium-bound chloride ligand. This results in an effective shielding of one face of the C=CH_2 moiety. Chemical attack on the trigonally planar carbon center of this double bond is therefore expected to predominantly take place by reagents approaching from the outside of the [Cp-CH(Cy)=$CH_2]_2ZrCl_2$ molecular unit.

Despite the intramolecular diastereotopic C=CH_2 shielding, the addition reactions carried out at the 1,1-disubstituted alkene moiety of **9a** (and **9b**, as well) turned out to be nonselective (see above). If the Cp substituents in the respective intermediates (**10**) were also essentially trans-positioned, as are the C(Cy)=CH_2 groups in the starting material **9a**, nondiastereoselectivity in the second addition could simply be due to insufficient energy sepa-

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Table III. Stereochemical Polypropylene ^{13}C NMR Methyl Pentad Assignment and the Standard Algorithms Used for the Statistical Analysis

pentad	$^{13}CH_3$ chemical shift[a]	enantiomorphic-site control[b] (ω)	chain-end control ($1 - \omega$)
mmmm	21.9	$1 - 5\beta + 5\beta^2$	σ^4
mmmr	21.6	$2\beta - 6\beta^2$	$2\sigma^3(1 - \sigma)$
rmmr	21.4	β^2	$\sigma^2(1 - \sigma)^2$
mmrr	21.1	$2\beta - 6\beta^2$	$2\sigma^2(1 - \sigma)^2$
mmrm	20.9	$2\beta^2$	$2\sigma^3(1 - \sigma)$
rmrr	20.9	$2\beta^2$	$2\sigma(1 - \sigma)^3$
rmrm	20.7	$2\beta^2$	$2\sigma^2(1 - \sigma)^2$
rrrr	20.4	β^2	$(1 - \sigma)^4$
mrrr	20.2	$2\beta^2$	$2\sigma(1 - \sigma)^3$
mrrm	20.0	$\beta - 3\beta^2$	$\sigma^2(1 - \sigma)^2$

[a] In 1,2,4-trichlorobenzene, 90 °C, 50 MHz, δ scale. [b] $\beta = \alpha(1 - \alpha)$.

ration of the two possible diastereomeric rotamers (**10a**,**b**). Attack from the *re* or *si* face would than be expected to take place with similar probabilities as indicated in Scheme II.

Propene Polymerization Reactions. Complexes **1**–**4** were obtained as meso/racemic mixtures of variable compositions in the preparations as described above. To use them as homogeneous Ziegler catalyst precursors for the objectives outlined in the introduction, it was necessary to separate the chiral racemic diastereomers, which we intended to use for our stereochemical propene polymerization study, from their respective achiral meso congeners. For this series of substituted-Cp zirconocene complexes, this could satisfactorily be achieved by fractional crystallization.

Crystallization of an equimolar mixture of the $[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$ diastereoisomers from dichloromethane produced a 90:10 mixture of *rac*-**2** and *meso*-**2**. The chiral *rac*-**2** isomer was then obtained with >98% diastereomeric purity upon one additional subsequent recrystallization from CH_2Cl_2. The stereochemical assignment of *rac*-**2** was based upon the result of an X-ray crystal structure analysis of a representative sample.[7] In addition, this diastereomerically pure material was used for a propene polymerization experiment. The *rac*-$[Cp\text{-}CH(CH_3)Ph]_2ZrCl_2$/methylalumoxane catalyst produced isotactic polypropylene with a considerable degree of enantiomorphic-site control (see below). The result of these two experimental observations allowed us to rely on the outcome of the stereospecific propene polymerization reaction to make a positive distinction between the achiral (meso) and chiral (racemic) diastereoisomers for each $[Cp\text{-}CHR^1R^2]_2ZrCl_2$ complex prepared and used in this study.

The complex *rac*-$[Cp\text{-}CH(CH_3)Cy]_2ZrCl_2$ was analogously separated from its *meso*-**1** diastereomer by repeated fractional crystallization from CH_2Cl_2 and eventually obtained >95% diastereoisomerically pure. From the boron-containing complexes **3** and **4**, the racemic forms were obtained sufficiently pure by 2-fold recrystallization from methylene chloride (**3**) and toluene (**4**) (see Figure 2). In each case, we also recovered a fraction that was substantially enriched in the respective meso isomers (containing ca. 80% enriched *meso*-**3** or 90% enriched *meso*-**4**, respectively).

Propene polymerization reactions were carried out with catalysts derived from the diastereomerically enriched complexes *meso*-**3** and *meso*-**4** as well as the pure *rac*-**1**–**4** isomers. For this purpose, the $[Cp\text{-}CHR^1R^2]_2ZrCl_2$ complexes were activated by their reaction with excess methylalumoxane[1] in a toluene/propene (8:1) solution at −50 °C. The $(MeAlO)_x$ activator was used in large excess (Al:Zr ≈ 500–2000). The propene polymerization reactions of this study were all carried out at −50 °C. Depending on the activity of the respective catalyst system, the reaction mixtures were quenched (HCl in methanol) after proceeding for an appropriate period of time to allow for the isolation of sufficient quantities of polymer for the stereochemical characterization. The polypropylenes (PP1–PP6; see Table IV) were stereochemically analyzed by observing their ^{13}C NMR methyl resonances at the pentad level resolution,[14] followed by statistical analysis using a combination of standard procedures (see Table III). In Table III, the statistical factor α denotes the probability that an *R* controlling center produces an *R*-configured product under enantiomorphic-site control ($\alpha = 0$ or 1 describes an isotactic type 1 polyolefin, $\alpha = 0.5$ atactic); σ gives the probability of finding an m diad under chain-end control (Bernoullian site) ($\sigma = 1$ describes an isotactic type 2 polyolefin, $\sigma = 0.5$ atactic, $\sigma = 0$ syndiotactic).[5,15]

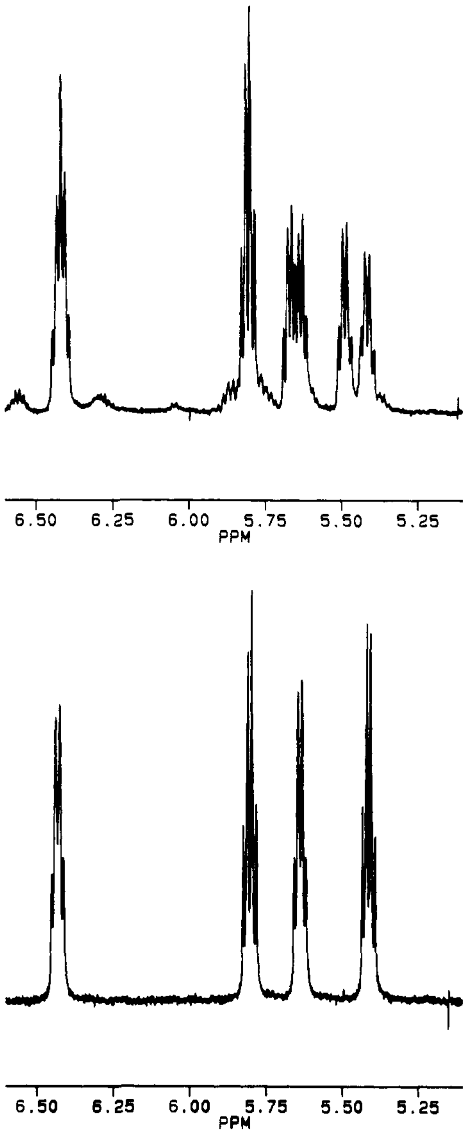

Figure 2. ^{1}H NMR spectra of $[Cp\text{-}CH(Ph)CH_2(9\text{-}BBN)]_2ZrCl_2$ (**4**) (in C_6D_6; only the Cp methine resonances are shown): *rac*-**4**/*meso*-**4** mixture as obtained from the reaction (top); *rac*-**4** after two crystallizations from toluene (bottom).

The $[Cp\text{-}CH(Cy)CH_2(9\text{-}BBN)]_2ZrCl_2$ (8:2 *meso*-**3**/*rac*-**3**)/$(MeAlO)_x$ catalyst (Al:Zr ≈ 780) produced polypropylene at −50 °C with an activity of 137 g of PP (g of Zr complex)$^{-1}$ h^{-1}. The obtained polymer had an averaged molecular weight of $\bar{M}_\eta \approx$

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Table IV. ^{13}C NMR Pentad Analysis of the Polypropylene Obtained with the $[Cp\text{-}CHR^1R^2]_2ZrCl_2$ (*rac*-**1**–**4**)/$(MeAlO)_x$ Catalysts at −50 °C

cat.	PP	ω	α	ee*[a]	σ	mmmm[b]	mmmr	rmmr	mmrr	mmrm + rmrr	rmrm	rrrr	mrrr	mrrm
1	PP3	0.15	0.94	13	0.78	0.43	0.20	0.03	0.07	0.19	0.07	0.00	0.00	0.02
						0.43	0.20	0.03	0.06	0.19	0.05	0.00	0.02	0.03
2	PP4	0.27	0.96	25	0.79	0.51	0.17	0.03	0.06	0.16	0.05	0.00	0.00	0.02
						0.50	0.17	0.02	0.06	0.16	0.04	0.00	0.01	0.03
3	PP5	0.33	0.96	30	0.80	0.54	0.16	0.02	0.06	0.15	0.04	0.00	0.01	0.03
						0.55	0.16	0.02	0.06	0.15	0.04	0.00	0.00	0.02
4	PP6	0.67	0.95	60	0.92	0.75	0.10	0.00	0.06	0.05	0.01	0.00	0.00	0.03
						0.76	0.11	0.00	0.07	0.05	0.00	0.00	0.00	0.02

[a] In %. [b] Observed (upper line) and calculated values.

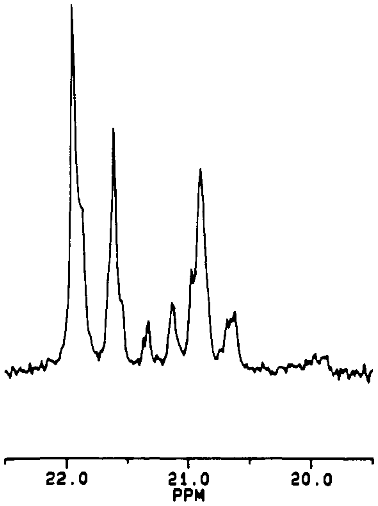

Figure 3. ^{13}C NMR methyl resonances of the polypropylene (PP1) obtained with the meso-enriched $[Cp\text{-}CH(Cy)CH_2(9\text{-}BBN)]_2ZrCl_2/(MeAlO)_x$ catalyst at −50 °C.

Table V. Selected Experimental Details of the Propene Polymerization Reactions Using the Chiral $[Cp\text{-}CHR^1R^2]_2ZrCl_2$ (*rac*-**1**–**4**)/Methylalumoxane Catalyst Systems

	PP3	PP4	PP5	PP6
cat.	*rac*-**1**	*rac*-**2**	*rac*-**3**	*rac*-**4**
mg of cat.	13.1	24.9	15.8	14.8
mmol of cat.	0.026	0.050	0.021	0.020
g of cocat.	1.44	1.55	1.20	1.18
mmol of cocat.	24.0	26.7	20.7	20.3
Al:Zr[a]	930	530	970	1015
T, °C	−50	−50	−50	−50
reacn time, h	18	15.5	7	7
g of PP	12.1	2.0	1.8	0.8
a[b]	287	28	135	60
$\bar{M}_\eta$	310 000	86 000	11 000	10 000

[a] Al:Zr = mmol of $(MeAlO)_x$:mmol of $[(R^*\text{-}Cp)_2ZrCl_2]$. [b] g of PP (g of Zr complex)$^{-1}$ h^{-1}.

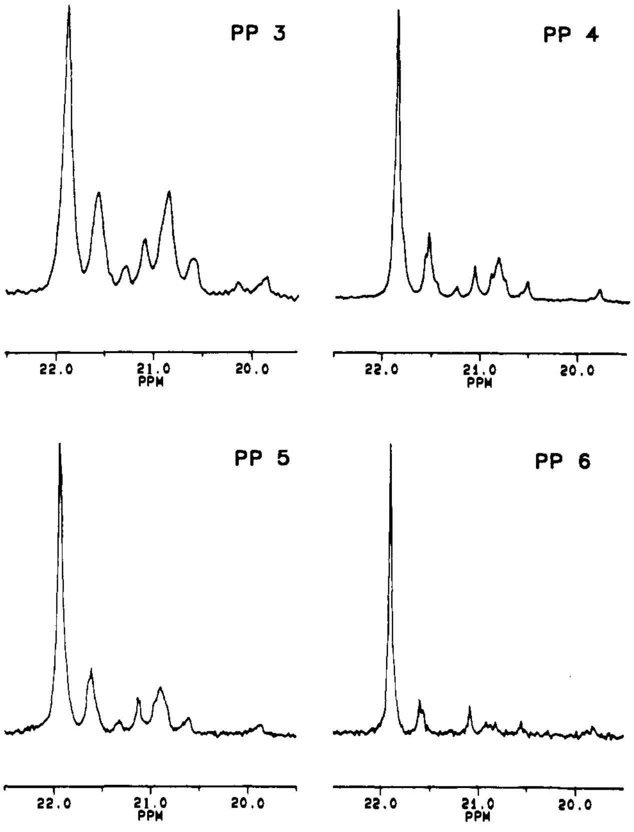

Figure 4. ^{13}C NMR methyl pentad signals of polypropylenes obtained with the methylalumoxane activated catalysts derived from *rac*-**1** (PP3), *rac*-**2** (PP4), *rac*-**3** (PP5), and *rac*-**4** (PP6) at −50 °C.

10 000 and was isotactic. The ^{13}C NMR pentad analysis [the ^{13}C NMR methyl resonance region of this polymer (PP1) is shown in Figure 3] revealed that an isotactic block polymer was formed, characterized by averaged lengths of the isotactic blocks of $\langle m\rangle_n\sigma \approx 4$. Thus we conclude that the rather small degree of isotacticity found in the propene polymerisate obtained with the *meso*-**3**/methylalumoxane catalyst originated from transferring the chirality information from the chiral β-carbon center in the growing hydrocarbyl chain (stereochemical chain-end control). A very similar result was obtained when the meso-enriched $[Cp\text{-}CH(Ph)CH_2(9\text{-}BBN)]_2ZrCl_2$ (9:1 *meso*-**4**/*rac*-**4**)/methylalumoxane catalyst was employed. An isotactic block polymer was obtained at −50 °C containing short alternating m-diad-containing blocks (PP2; $\langle m\rangle_n\sigma \approx 5$).

A different result was obtained when catalysts derived from the chiral metallocene dihalides *rac*-**1**–**4** were used for the propene polymerization reaction. The reaction of *rac*-$[Cp\text{-}CH(CH_3)\text{-}Cy]_2ZrCl_2$ (*rac*-**1**, >95% diastereomerically enriched) with methylalumoxane produced an active propene polymerization catalyst ($a \approx 300$ g of polymer (g of Zr complex)$^{-1}$ h^{-1} at −50 °C; Al:Zr = 635). The polymer (PP3) showed a ^{13}C NMR set of methyl pentad signals of which the mmmm resonance amounted to ca. 43% relative intensity. The intensity relation of the remaining set of eight CH_3 resonances (the mmrm and rmrr signals were not resolved under the experimental conditions applied) could not be described with acceptable accuracy by using a simple one-parameter statistical model. Neither the standard statistical treatment for enantiomorphic-site control nor chain-end control alone as usually applied[5,15] for the a posteriori stereochemical analysis and interpretation of the dominating modes of stereocontrol at the active catalytic site resulted in an acceptable reproduction of the observed spectral features. However, the experimentally observed methyl pentad distribution could be fitted satisfactorily with a model using a combination of the statistical parameters α (describing the probability of finding an R-configured stereogenic center at an R controlling site under enantiomorphic-site control), σ (giving the probability of observing the formation of an m diad at the active site under chain-end control), and ω (giving the relative amount of the pentads represented by the α-descriptor; $\omega - 1$ gives the analogous number for the σ-described portion at the same polymer chain). For the specific polypropylene (PP3) examined, this treatment led to an assignment of 18% ($\omega = 0.18$) stereocontrol being due to enantiomorphic-site control ($\alpha = 0.93$, $\langle m\rangle_n\alpha \approx 16$), the nature of the remaining 82% of the stereogenic centers being formally controlled by the chain-end interaction ($\sigma = 0.78$, $\langle \mathrm{m}\rangle_n\sigma \approx 4.5$).

It should be emphasized that these two ways of influencing and determining the stereochemistry of the catalytic C–C coupling process of two prostereogenic sp^2-carbon centers were here arbitrarily separated by means of a mathematical calculation. In reality, their combined action determines the stereochemical outcome of this polymerization reaction. These two influences are acting in combination similar to what is found in double stereodifferentiation in some stereoselective C–C coupling processes in stoichiometric organic synthesis.[5,7,16]

The m diad diastereomeric excess (de) obtained by a purely enantiomorphic-site-controlled process is expressed by the numerical value of $(2\alpha - 1)$. Hence, in the double-stereodifferentiating situation encountered here, the m diad de is $\omega(2\alpha - 1)$. This combination of the factors ω and α serves to express the (averaged) transfer of chirality from each stereogenic catalytically active zirconium center in the carbon–carbon coupling step. If we had used an optically active catalyst producing a (e.g. low molecular weight) chiral product, the achieved enantiomeric excess would have been equal to the $\omega(2\alpha - 1)$ value. Therefore, we might term this specific diastereoselectivity descriptor $\omega(2\alpha - 1)$ as a "relative enantioselectivity" ee*, in the same useful sense as relative configurations (e.g. *R**) are assigned as diastereomeric descriptors to racemic chiral compounds. For the polypropylene (PP3) formed on the [Cp-CH(CH$_3$)Cy]$_2$ZrCl$_2$ catalyst *rac*-**1**, the "relative enantioselectivity" under the reaction conditions specified above was ee* = 13%.

Systematic variation of the substituents at the carbon center α to the Cp ring system of the [Cp-CHR^{1}R^2]$_2$ZrCl$_2$ catalyst precursors had a profound influence on the stereochemical outcome of the propene carbon–carbon coupling process at the homogeneous bent metallocene/methylalumoxane catalyst system. We first changed the cyclohexyl moiety for phenyl and employed the *rac*-[Cp-CH(CH$_3$)Ph]$_2$ZrCl$_2$ (*rac*-**2**)/(MeAlO)$_x$ catalyst. At −50 °C with Al:Zr ≈ 530, polypropylene (PP4) was formed with moderate activity. The polymer partition reflecting the chirality features of the Zr center was pronouncedly increased ($\omega = 0.27$, $\alpha = 0.96$) as compared to that of the *rac*-[Cp-CH(CH$_3$)-Cy]$_2$ZrCl$_2$-derived catalyst system. This amounts to an almost doubled ee* of ≈ 25% for the *rac*-[Cp-CH(CH$_3$)Ph]$_2$ZrCl$_2$ catalyst.

We then turned back to the starting point and modified the methyl group of the (1-cyclohexylethyl)cyclopentadienyl ligand. The active catalyst derived from *rac*-[Cp-CH(Cy)CH$_2$(9-BBN)]$_2$ZrCl$_2$ produced polypropylene (PP5) at −50 °C ($a = 135$; Al:Zr = 970), which was stereochemically very similar to the polymer (PP4) formed on the *rac*-**2**/(MeAlO)$_x$ catalyst. The polypropylene (PP5) obtained from the *rac*-**3**-derived system ($\omega = 0.33$, $\alpha = 0.96$) was formed with an ee* of approximately 30%.

The next experiment in the course of this study was carried out to learn how the two systematic changes of the catalyst structure, whose separate influences were determined as described above, would behave when combined in one single system. Would one of the substituent effects dominate and leave no room for the other to exert its influence on stereocontrol? Would they cancel out and lead to a less stereoselective catalyst, or could the factors responsible for controlling the stereochemistry of the sp^2-C–sp^2-C coupling eventually be additive? We used the *rac*-[Cp-CH(Ph)CH$_2$(9-BBN)]$_2$ZrCl$_2$ (*rac*-**4**)/methylalumoxane catalyst system for polymerizing propene (−50 °C, Al:Zr ≈ 1000, $a \approx 60$) and found indeed that the latter was true. The *rac*-**4**/(MeAlO)$_x$ catalyst system produced polypropylene (PP6) with a much better stereoselectivity than observed for each of the three previously described examples (*rac*-**1**–**3**). The enantiomorphic-site-controlled partition amounted to $\omega = 0.67$ with $\alpha = 0.95$. From these values, a relative enantioselectivity (ee*) of ca. 60% was calculated, which was about twice as much as found for the singular *rac*-**2**/(MeAlO)$_x$ and *rac*-**3**/(MeAlO)$_x$ catalysts, respectively, and four times better than that of the *rac*-**1**/methylalumoxane catalyst, resulting in a transfer of the metal chirality information to the organic product chain in the course of the stereoselective catalytic carbon–carbon coupling step.

Conclusions

Methylalumoxane/zirconocene catalysts derived from a small number of specific ansa metallocene dihalides have been known to produce highly isotactic polypropylene with almost exclusive control of the stereochemistry being due to enantiomorphic-site control. Stereocontrol and catalyst activities of a limited number of "Brintzinger type" catalysts may even be sufficiently good to make them the basis of competitive industrial processes in the future.[2,17] Our results show that the unexpected single-parameter stereocontrol of the ansa metallocene catalysts could just be serendipitous. We have demonstrated with the selected examples presented and discussed in this article that simple unbridged zirconocenes, suitably substituted to give them a persistent metallocene chirality while probably maintaining their typical very low metal–Cp rotational barriers, produce active polymerization catalysts for the stereoselective α-olefin polymerization, as well. However, the active stereocontrol here is taking place, quite as expected, by means of a combined influence of enantiomorphic-site control and chain-end control. Substituent additivity effects such as those described in this paper should be helpful in the continuing search for ways to overcome this a priori unfavorable situation of controlling the product stereochemistry by a rational design of stereoselective catalyst systems. We have shown that rather small structural alterations may bring about very pronounced effects resulting in the enhancement of the stereocontrol exerted by the chiral metallocene backbone and make the stereochemical contribution of the chiral chain end less important. A reduced number of screening experiments should now allow us to gain a fundamental knowledge about which substituent combination to select for achieving an almost complete enantiomorphic-site control. From the respective resolved optically active metallocene complexes, it may then be possible to obtain conformationally unrestricted artificial catalysts for carrying out enantioselective transformations of organic substrates at high reaction rates.

Experimental Section

General Procedures and Materials. All reactions with organometallic compounds were carried out under an inert atmosphere (argon) with use of Schlenk type glassware. Solvents were dried and distilled under argon prior to use. The following spectrometers were used: A Bruker WP 200 SY NMR spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^1J(C,H) coupling constants (Hz) are given in parentheses) and a Nicolet 5 DXC FT IR spectrometer. Melting points were determined in sealed glass capillaries and are uncorrected. The following materials and reagents were prepared according to literature procedures: 6-cyclohexyl-6-methylfulvene (**5a**), 6-methyl-6-phenylfulvene (**5b**), (*S*)-1-chloro-2-phenylpropane, (*S*)-1-chloro-2-cyclohexylpropane, (*R*)-1-chloro-2-phenylbutane.[9,18]

Reaction of 6-Methyl-6-phenylfulvene (5b) with Primary Alkyllithium Reagents. A sample of 10.0 g (59 mmol) of **5b** was dissolved in 60 mL of diethyl ether. To this solution was added dropwise at 0 °C a total of 40 mL (65 mmol) of an ethereal *n*-propyllithium solution. The resulting yellowish suspension was stirred for 2 h at ambient temperature. The precipitated cyclopentadienyllithium compound **7b** was collected by filtration, washed with ether and petroleum ether, and dried in vacuo; yield 3.8 g (29%). ^{1}H NMR (thf-d_8): δ 7.25 (m, 2 H, Ph), 7.15 (m, 2 H, Ph), 7.01 (m, 1 H, Ph), 5.49 (m, 4 H, Cp), 3.98 (q, 1 H, CH), 1.52 (d, 3 H, CH$_3$). ^{13}C NMR (benzene-d_6/thf-d_8, 2:1): δ 151.8 (ipso C, Ph), 128.1, 127.8, 125.0 (Ph), 125.5 (ipso C, Cp), 103.0, 102.9 (Cp), 41.6 (CH), 24.2 (CH$_3$). Analogously carried out reactions of **5b** with the following primary alkyllithium reagents in parentheses (some of which were prepared in situ by reacting the corresponding alkyl chlorides with lithium powder) gave **7b** in yields of 60% (isobutyllithium), 43% (1-lithio-2-phenyl-

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propane), 62% (1-lithio-2-cyclohexylpropane), and 28% (1-lithio-2-phenylbutane).

Reaction of 6-Cyclohexyl-6-phenylfulvene (5a) with Primary Alkyllithium Reagents. The preparation of **7a** was carried out as described for **7b**. Treatment of e.g. 2.55 g (13.6 mmol) of **5a** with 1-lithio-2-cyclohexylpropane (in situ generated from 23.5 mmol of 1-chloro-2-cyclohexylpropane and lithium) in 20 mL of ether at 0 °C and subsequent stirring of the mixture for 5 h at room temperature gave 1.86 g (76%) of **7b**, which was collected by filtration. ^{1}H NMR (benzene-d_6/thf-d_8, 2:1): δ 5.95, 5.83 (m, 2 H, each, Cp), 2.65 (m, 1 H, CH), 1.50 (m, 11 H, Cy), 1.32 (d, ^3J = 7.1 Hz, 3 H, CH_3). ^{13}C NMR (benzene-d_6/thf-d_8, 2:1): δ 125.0 (ipso C, Cp), 102.3, 101.7 (Cp), 46.4 (Cp–*C*H), 41.0 (cyclohexyl *C*H), 31.9, 31.2, 27.6, 27.4 (CH_2), 20.3 (CH_3).

Bis[(1-cyclohexylethyl)cyclopentadienyl]zirconium Dichloride (1). To a suspension of 1.89 g (5.0 mmol) of $ZrCl_4(thf)_2$ in 40 mL of toluene was added dropwise a solution of 1.82 g (10.0 mmol) of the cyclopentadienyllithium reagent **7a** in 40 mL of tetrahydrofuran. The reaction mixture was held for 24 h at 50 °C. During this time, a white precipitate formed. The resulting mixture was then stripped in vacuo and extracted with 15 mL of methylene chloride to remove the precipitated lithium chloride. The clear yellow filtrate was cooled to −30 °C. Complex **1** crystallized as a 1:1 mixture of the *meso*- and *rac* diastereoisomer with a combined yield of 2.2 g (86%). Fractionating crystallization from methylene chloride gave >95% isomerically pure *rac*-**1**, mp 207–208 °C dec. Anal. Calcd for $C_{26}H_{38}Cl_2Zr$ (M_r = 510.7): C, 61.15; H, 7.10. Found: C, 60.75; H, 7.16. ^{1}H NMR ($CDCl_3$): *rac*-**1** δ 6.45, 6.28, 6.10, 6.05 (m, 2 H each, Cp), 2.93 (m, 2 H, Cp–C*H*), 1.80–0.80 (m, 22 H, Cy), 1.13 (d, ^3J = 7.1 Hz, 6 H, CH_3); *meso*-**1** δ 6.39, 6.31, 6.12, 6.05 (m, 2 H each, Cp), 2.93 (m, 2 H, Cp–C*H*), 1.80–0.80 (m, 22 H, Cy), 1.14 (d, 6 H, CH_3). ^{13}C NMR ($CDCl_3$): *rac*-**1** δ 140.1 (ipso C, Cp), 116.8, 115.7, 114.8, 107.1 (Cp), 45.1 (122, *C*HCH_3), 39.3 (127, cyclohexyl *C*H), 30.6, 29.0, 26.74, 26.71, 26.6 (*C*H_2), 14.8 (*C*H_3); *meso*-**1** δ 139.6 (ipso C, Cp), 116.6, 115.9, 114.6, 108.0 (Cp), 45.2 (*C*HCH_3), 39.3 (cyclohexyl *C*H), 30.6, 28.9, 26.7, 26.6 (*C*H_2), 14.7 (*C*H_3).

Bis[(1-phenylethyl)cyclopentadienyl]zirconium Dichloride (2). The lithium reagent **7b** (3.8 g, 17.0 mmol) was dissolved in 100 mL of tetrahydrofuran, and the resulting mixture was then added dropwise to a suspension of zirconium tetrachloride (2.0 g, 8.5 mmol) in 10 mL of toluene at 0 °C. The mixture was then stirred for 3 h at 60 °C. Solvent was removed in vacuo, the residue was taken up in 20 mL of dichloromethane, and the resulting solution was filtered. From the clear yellow solution, a light yellowish solid precipitated at −20 °C, which consisted of a 90:10 mixture of *rac*-**2** and *meso*-**2** (2.0 g, 42% combined yield). Subsequent recrystallization from methylene chloride gave the >98% pure *rac*-**2** diastereoisomer, mp 199–200 °C. Anal. Calcd for $C_{26}H_{26}Cl_2Zr$ (M_r = 500.6): C, 62.38; H, 5.24. Found: C, 62.06; H, 5.18. ^{1}H NMR ($CDCl_3$): *rac*-**2** δ 7.33–7.14 (m, 10 H, Ph), 6.51, 6.18, 6.09, 5.86 (m, 2 H each, Cp), 4.31 (q, 2 H, CH), 1.57 (d, 6 H, CH_3); *meso*-**2** δ 6.51, 6.23, 6.13, 5.86 (m, 2 H, each, Cp), remaining signals identical with those of *rac*-**2**. ^{13}C NMR ($CDCl_3$): *rac*-**2** δ 146.1 (ipso C, Ph), 139.1 (ipso C, Cp), 128.6, 127.7, 126.5 (Ph), 116.9, 115.0, 112.5, 112.2 (Cp), 40.2 (CH), 22.0 (CH_3).

(1-Cyclohexylethen-1-yl)cyclopentadienyllithium (8a). At −78 °C, 4.30 g (40.1 mmol) of LDA was dissolved in 400 mL of tetrahydrofuran. A solution of 6.40 g (40.2 mmol) of 6-cyclohexyl-6-methylfulvene in 30 mL of diethyl ether was added dropwise during 30 min. The mixture was stirred for 20 h at ambient temperature Solvent was removed in vacuo. The viscous yellow residue was suspended in 50 mL of ether, and the suspension was vigorously stirred for about 2 h. The resulting fine white solid **8a** was recovered by filtration. Yield 5.0 g (75%). ^{1}H NMR (benzene-d_6/thf-d_8, 4:1): δ 1.20–1.87 (2 m, 8 H, $-CH_2-$), 2.14 (m, 2 H, methylene H), 2.68 (m, 1 H, CH), 4.65 and 5.28 (AX, ^2J = 2.1 Hz, 2 H, $=CH_2$), 6.09 and 6.32 (m, 2 H each, Cp). ^{13}C NMR (benzene-d_6/thf-d_8, 4:1): δ 27.4 (123, $-CH_2-$), 27.9 (128, 2 × $-CH_2-$), 34.6 (126, 2 × $-CH_2-$), 43.4 (121, CH), 97.3 (159, $=CH_2$), 102.3 (159) and 104.5 (160, Cp), 121.6 (ipso C, Cp), 152.7 (*C*$=CH_2$).

(1-Phenylethen-1-yl)cyclopentadienyllithium (8b). (a) A solution of 5.11 g (30.4 mmol) of 6-methyl-6-phenylfulvene (**5b**) in 80 mL of ether was cooled to 0 °C. Then 45.6 mL of an 0.8 M ethereal phenyllithium solution (36.5 mmol) was added dropwise, and the mixture was stirred for 3 h at ambient temperature. The resulting precipitate was collected by filtration and dried in vacuo to yield 2.5 g (47%) of **8b**.

(b) A solution of 7.39 g (69.0 mmol) of lithium diisopropylamide in 450 mL of tetrahydrofuran was cooled to −78 °C. A solution of 16.1 g (95.9 mmol) of **5b** in diethyl ether was added dropwise during 30 min. The mixture was allowed to warm to room temperature and then stirred for 22 h. Solvent was removed in vacuo, the residue suspended in 100 mL of ether, and the majority of the ether again removed by vacuum distillation. The viscous residue was vigorously stirred with another 100-mL portion of ether for 3 h until it had solidified. The resulting pale yellow precipitate was filtered out and dried in vacuo to give 9.6 g (≈ 80%) of **8b**. ^{1}H NMR (benzene-d_6/thf-d_8, 4:1): δ 4.71 and 5.30 (AX, ^2J = 2.7 Hz, 1 H, each, $=CH_2$), 5.94 and 6.07 (m, 2 H each, Cp), 7.10–7.30, 7.65 (2 m, 5 H, Ph). ^{13}C NMR (benzene-d_6/thf-d_8, 4:1): δ 101.9 (155, $=CH_2$), 105.0 (160) and 105.1 (160, Cp), 120.5 (ipso C, Cp), 126.6 (158), 127.6 (157), 129.2 (160, Ph), 146.1 (ipso C, Ph), 149.5 (*C*$=CH_2$).

Bis[η-(1-cyclohexylethen-1-yl)cyclopentadienyl]zirconium Dichloride (9a). $ZrCl_4(thf)_2$ (3.16 g, 9.16 mmol) was suspended in 25 mL of toluene at 0 °C. To this suspension was added dropwise a solution of 3.30 g (18.3 mmol) of (1-cyclohexylethen-1-yl)cyclopentadienyllithium (**8a**) in 60 mL of tetrahydrofuran. The mixture was then stirred for 15 h at room temperature. Solvent was removed in vacuo, the residue taken up in 150 mL of CH_2Cl_2, and the solution filtered. The filtrate was concentrated to a volume of ca. 20 mL and cooled to 5 °C. During 24 h, fine needles of the organometallic product formed, which were recovered by filtration to yield 3.3 g (73%) of **9a**, mp 137 °C dec. Anal. Calcd for $C_{26}H_{34}Cl_2Zr$ (M_r = 508.7): C, 61.39; H, 6.73. Found: C, 61.34; H, 6.83. ^{1}H NMR ($CDCl_3$): δ 1.05–1.35, 1.50–1.72 and 1.89–1.96 (3 m, 20 H, 10 × $-CH_2-$), 2.43 (m, 2 H, C*H*), 5.06 and 5.37 (AX, ^2J = 0.6 Hz, $=CH_2$), 5.89 and 6.26 (m, 4 H each, Cp). ^{13}C NMR ($CDCl_3$): δ 26.4 (126, $-CH_2-$), 26.8 (127, 2 × $-CH_2-$), 33.2 (127, 2 × $-CH_2-$), 42.0 (119, CH), 110.8 (154, $=CH_2$), 130.6 (ipso C, Cp), 114.6 (172) and 114.8 (172, Cp), 146.7 (*C*$=CH_2$). IR (KBr): ν (cm^{-1}) 3109, 3077, 1637 (C=C), 900.

X-ray Crystal Structure Determination of 9a. A suitable crystal (dimensions 0.36 × 0.40 × 0.47 mm) was mounted under argon in a glass capillary. Data ($\pm h,\pm k,+l$) were collected at 100 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants, obtained from a least-squares refinement with the setting angles of 25 centered reflections, correspond to a monoclinic cell with cell dimensions a = 28.044 (6) Å, b = 6.627 (1) Å, c = 13.150 (2) Å, β = 108.59 (1)°, V = 2316.4 Å^3; Z = 4, calculated density = 1.46 g cm^{-3}, $F(000)$ = 1056 e, and μ = 7.09 cm^{-1} (no absorption correction applied). On the basis of the systematic absences of hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$), the space group was assigned to $C2/c$ (No. 15). A total of 6636 reflections [ω–2θ scan technique, $((\sin\theta)/\lambda)_{max}$ = 0.70 Å^{-1}] were collected, of which 3363 were unique (R_{av} = 0.05); 3075 observed reflections [$I > 2\sigma(I)$] were used for the structure solution (Patterson method, SHELX86) and subsequent full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically, and all H atoms were located and included in the final refinement with isotropic displacement parameters; R = 0.024, R_w = 0.031 [$w = 1/\sigma^2(F_o)$]; GOF = 1.83; final residual electron density = 0.49 e Å^{-3}.

Bis[η-(1-phenylethen-1-yl)cyclopentadienyl]zirconium Dichloride (9b). A suspension of $ZrCl_4(thf)_2$ (4.50 g, 13.1 mmol) in 30 mL of toluene was cooled to 0 °C. To this was added dropwise a solution of the lithium reagent **8b** (4.54 g, 26.1 mmol) in 200 mL of tetrahydrofuran. The mixture was stirred for 12 h at room temperature, and the solvent was removed in vacuo. The yellow residue was then treated with 100 mL of methylene chloride, and the resulting solution was filtered from the precipitated lithium chloride. The filtrate was concentrated to about one-fifth of its original volume and kept at −30 °C for several hours. The resulting fine crystalline precipitate of the zirconium compound was recovered by filtration and dried in vacuo to give 5.0 g (78%) of **9b**, mp 173 °C dec. Anal. Calcd for $C_{26}H_{22}Cl_2Zr$ (M_r = 496.7): C, 62.88; H, 4.46. Found: C, 62.03; H, 4.68. ^{1}H NMR ($CDCl_3$): δ 5.26 and 5.54 (AX, ^2J = 0.8 Hz, 2 H each, $=CH_2$), 6.17 and 6.35 (2m, 4 H each, Cp), 7.17–7.25 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$): δ 114.9 (175) and 116.7 (175, Cp), 116.6 (159, $=CH_2$), 127.9 (ipso C, Cp), 128.0 (159), 128.3 (161, double intensity, Ph), 140.6 (ipso C, Ph), 142.0 (*C*$=CH_2$). IR (KBr): ν (cm^{-1}) 3111, 3101, 3058, 1612 (C=C), 900.

Bis[η-(1-cyclohexyl-2-(9-borabicyclo[3.3.1]nonyl-*B*)ethyl)cyclopentadienyl]zirconium Dichloride (3). A mixture of 2.09 g (4.11 mmol) of **9a** and 1.00 g (8.22 mmol) of 9-BBN in 50 mL of toluene was kept for 2 days at 55 °C in a sealed Schlenk tube with stirring. Then an additional portion of 0.50 g (4.11 mmol) of 9-BBN was added to the clear solution and heating at 55 °C continued for another 2 days. The reaction mixture was then cooled to 5 °C and maintained at that temperature for 12 h. Fine needlelike crystals appeared. The supernatant solution was decanted and residual solvent removed from the crystals in vacuo to give 0.6 g of a 90:10 mixture of *rac*-**3** and *meso*-**3**. Subsequent recrystallization gave >99% pure *rac*-**3** (0.45 g), mp 208–211 °C. From the combined mother liquors of the two crystallizations, an additional crystal fraction (1.5 g) of a 1:1 mixture of *meso*- and *rac*-**3** could be obtained, making the combined yield of **3** 65%. Repeated crystallization of this 1:1 mixture of diastereoisomers eventually resulted in a filtrate in which the achiral isomer was enriched (*rac*-**3**:*meso*-**3** ≈ 20:80). Data for *rac*-**3** are as follows. Anal. Calcd for $C_{42}H_{64}B_2Cl_2Zr$ (M_r = 752.7): C, 67.02; H, 8.57. Found: C, 66.69; H, 8.77. ^{1}H NMR (benzene-d_6): δ 0.56 (m, 2 H, B–C*H*), 0.85–1.15 (m, 8 H), 1.30–1.65 (m, 16 H), 1.90–2.05 (m, 28 H), 3.58 (m, 2 H, Cp–C*H*), 5.59, 5.82, 6.02, 6.31 (m, 2 H each, Cp). ^{13}C NMR (benzene-d_6): δ 23.8 (126, $-CH_2-$), 26.9 (128, 2 × $-CH_2-$), 27.2 (128, 2 × $-CH_2-$), 27.3 (128, 2 × $-CH_2-$), 30.7 (123, 4 × $-CH_2-$, and CH_2–B, signal broadened by adjacent boron nucleus), 31.9 (124, 2 × $-CH_2-$), 31.9 (signal broadened by adjacent boron nucleus, 4 × B–*C*H), 34.1 (126, 4 × $-CH_2-$), 34.4 (126, 4 × $-CH_2-$), 42.6 (129, 2 × –CH–), 46.0 (121, 2 × –CH–), 106.2 (173), 114.0 (174), 115.2 (173), 117.9 (172), 141.4 (Cp). IR (KBr): ν (cm^{-1}) 3098, 2923, 2849, 825. Data for *meso*-**3** are as follows. ^{1}H NMR (benzene-d_6): δ 5.68, 5.82, 6.01 and 6.33 (m, 2 H each, Cp). The remaining substituent signals were not distinguished from those of *rac*-**3**. ^{13}C NMR (benzene-d_6): δ 107.1, 114.0, 114.6, 118.7, 140.6 (Cp). The remaining ^{13}C NMR resonances were very similar to those of *rac*-**3**.

Bis[η-(1-phenyl-2-(9-borabicyclo[3.3.1]nonyl-*B*)ethyl)cyclopentadienyl]zirconium Dichloride (4). In a 200-mL Schlenk flask, 2.73 g (5.50 mmol) of the zirconium complex **9b** and 1.34 g (11.0 mmol) of 9-BBN were suspended in 50 mL of toluene. The mixture was then stirred at 55 °C for 20 h. The resulting clear yellow solution was kept for 2 days at −15 °C. The resulting white solid was recovered by filtration and dried in vacuo to yield 3.7 g (90%) of a 1:1 mixture of *rac*-**4** and *meso*-**4**, mp 150 °C dec. Subsequent 2-fold crystallization of this sample from 5 mL of dichloromethane gave the chiral *rac*-**4** diastereoisomer >99% pure. The achiral isomer (*meso*-**4**) could be enriched in the mother liquor by several crystallization steps to about 90:10 *meso*-**4**:*rac*-**4**. Data for *rac*-**4** are as follows. Anal. Calcd for $C_{42}H_{52}B_2Cl_2Zr$ (M_r = 740.6): C, 68.11; H, 7.07. Found: C, 68.44; H, 7.28. ^{1}H NMR (benzene-d_6): δ 1.03 (m, 4 H, B(–CH–)$_2$), 1.41–1.82 (2m, 24 H, 12 × 9-BBN–CH_2), 2.34 (m, 4 H, B–CH_2), 4.89 (m, 2 H, C*H*–Ph), 6.93–7.25 (m, 10 H, Ph), 5.41, 5.63, 5.80 and 6.42 (m, 2 H each, Cp). ^{13}C NMR (benzene-d_6): δ 23.4 (123, 4 × $-CH_2-$), 32.0 (129, 4 × B–*C*H, broadened signal), 33.3 (128, 4 × $-CH_2-$), 33.4 (128, 4 × $-CH_2-$), 35.4 (115, 2 × *C*H_2–B, broadened signal), 42.5 (127, *C*H–Ph), 128.7 (159, double intensity), 126.6 (160, Ph), 146.8 (ipso C, Ph), 110.8 (172), 113.8 (171), 114.3 (172), 116.8 (173), 141.2 (Ph). IR (KBr): ν (cm^{-1}) 3084, 3047, 2920, 2837, 815, 801, 699. MS (EI, 70 eV): *m/z* 738 (6%, M$^+$), 91 (100). Data for *meso*-**4** are as follows. ^{1}H NMR (benzene-d_6): δ 5.49, 5.67, 5.80, 6.42 (m, each 2 H, Cp). The remaining substituent signals are almost identical to those of *rac*-**4**. ^{13}C NMR (benzene-d_6): δ 111.4, 112.8, 115.1, 116.3, 141.2 (Cp). The other ^{13}C NMR resonances were not distinguished from those of *rac*-**4**.

Catalytic Hydrogenation of Bis[η-(1-phenylethen-1-yl)cyclopentadienyl]zirconium Dichloride (9b). (a) A glass tube was charged with a solution of 0.40 g (0.81 mmol) of **9b** in 20 mL of dichloromethane and 0.04 g (0.17 mmol) of PtO_2. The reaction vessel was then transferred to an autoclave and treated with hydrogen at a pressure of 50 bar for 5 h. The reaction mixture was filtered under ambient conditions and the filtrate stripped in vacuo to give a 1:1 mixture of *rac*-**1** and *meso*-**1** in nearly quantitative yield.

(b) From 10 mg (20 μmol) of bis(μ-chloro)bis[(cycloocta-1,5-diene)rhodium(I)] and 23 mg (46 μmol) of (+)-DIOP in 5 mL of toluene, the active hydrogenation catalyst was prepared during 30 min of stirring at room temperature. To this was added a solution of 0.12 g (0.24 mmol) of **9b** in 15 mL of toluene. Hydrogenation was carried out in an autoclave fitted with a glass inlet at 50 bar of H_2 at room temperature for 20 h. The ^{1}H NMR spectrum of an aliquot revealed a nearly quantitative formation of *rac*-**2** and *meso*-**2** in a 1:1 ratio.

(c) Stirring 10 mg (20 μmol) of bis(μ-chloro)bis[(cycloocta-1,5-diene)rhodium(I)] and 26 mg (42 μmol) of (−)-BINAP in 5 mL of toluene at room temperature for 30 min gave the catalyst solution to which was added a solution of 0.12 g (0.24 mmol) of **9b** in 15 mL of toluene. Complete hydrogenation of the C=CH_2 units of **9b** was achieved during 4 days at a H_2 pressure of 60 bar. The ^{1}H NMR spectrum of a representative sample revealed that the products *rac*-**2** and *meso*-**2** were formed in a 55:45 ratio.

Propene Polymerization Reactions (General Procedure). A 500-mL two-necked Schlenk flask was charged with the methylalumoxane cocatalyst dissolved in 250 mL of toluene and then cooled to −50 °C. Propene (ca. 30–35 mL) was then condensed into the solution, and the metallocene catalyst component dissolved in toluene was added. The propene polymerization reaction was then allowed to take place for a given period of time, and then the reaction mixture was quenched by pouring it into 500 mL of HCl containing methanol. The unreacted propene was evaporated. The organic phase was separated from the mixtures and the aqueous phase extracted with ether. The polymer was recovered from the combined organic phases by removing the solvent in vacuo. The ^{13}C NMR spectroscopic characterization (see Tables III and IV) was carried out by using polymer solutions in 1,2,4-trichlorobenzene at 92 °C (50 MHz). The molecular weight ($\bar{M}_\eta$) determination was carried out in Decalin at 135 °C with an Ubbelohde viscometer. $\bar{M}_\eta$ was calculated by the Mark–Houwink equation with constants $K = 1.1 \times 10^{-4}$ and $a = 0.8$ for the conditions specified. Further details of the polymerization experiments are given in Tables III–V. The polymers PP5 and PP6 were fractionated to verify that the stereochemical analysis was representative of a uniform material and not due to a mixture of stereochemically different types of polymers. A sample of 3.10 g of PP5 [$\omega = 0.31$, $\alpha = 0.95$, $\sigma = 0.80$, $\langle m \rangle_n\alpha = 19.1$, $\langle m \rangle_n\sigma = 5.0$] contained a fraction of 2.25 g soluble in cold pentane [$\omega = 0.32$, $\alpha = 0.96$, $\sigma = 0.80$, $\langle m \rangle_n\alpha = 24.0$, $\langle m \rangle_n\sigma = 5.0$] and a fraction of 0.52 g soluble in cold hexane [$\omega = 0.34$, $\alpha = 0.95$, $\sigma = 0.82$, $\langle m \rangle_n\alpha = 19.1$, $\langle m \rangle_n\sigma = 5.6$]. Only 0.29 g (i.e. less than 10%) was soluble in boiling hexane [$\omega = 0.26$, $\alpha = 0.94$, $\sigma = 0.87$, $\langle m \rangle_n\alpha = 15.7$, $\langle m \rangle_n\sigma = 7.7$]. The almost twice as isotactic PP6 showed an even higher degree of uniformity in the extraction experiment. A sample of 0.50 g of PP6 [$\omega = 0.68$, $\alpha = 0.96$, $\sigma = 0.85$, $\langle m \rangle_n\alpha = 24.0$, $\langle m \rangle_n\sigma = 6.70$] gave only 0.03 g of some unidentified sticky material soluble in cold hexane, whereas 0.45 g (i.e. 90%) was recovered from the boiling hexane fraction [$\omega = 0.67$, $\alpha = 0.96$, $\sigma = 0.84$, $\langle m \rangle_n\alpha = 24.0$, $\langle m \rangle_n\sigma = 6.20$].

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Registry No. 1, 135366-76-6; *rac*-**2**, 66349-68-6; *rac*-**3**, 135366-78-8; *rac*-**4**, 135366-79-9; **5a**, 131733-17-0; **5b**, 2320-32-3; **7a**, 135366-72-2; **7b**, 78759-82-7; **8a**, 135366-73-3; **8b**, 135366-74-4; **9a**, 135366-77-7; **9b**, 63461-57-4; LDA, 4111-54-0; 9-BBN, 280-64-8; PrLi, 2417-93-8; *i*-BuLi, 920-36-5; $LiCH_2CH(Ph)CH_3$, 64740-49-4; $ZrCl_4(thf)_2$, 21959-01-3; $ZrCl_4$, 10026-11-6; LiPh, 591-51-5; $LiCH_2CH(Ph)(CH_2)_2H$, 135366-71-1; 1-lithio-2-cyclohexylpropane, 135366-70-0; polypropene (homopolymer), 9003-07-0.

Supplementary Material Available: For **9a**, tables giving crystal data and details of the data collection, final positional and thermal parameters, and distances and angles and a computer program for the stereochemical polymer analysis (10 pages); a listing of final observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.