Highly Isospecific Polymerization of Propylene with Unsymmetrical Metallocene Catalysts

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ABSTRACT: Novel unsymmetrical *ansa*-metallocenes $Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}R\text{-}C_9H_5)MCl_2$ (R = *t*-Bu; M = Ti (**1a**), M = Zr (**1b**), M = Hf (**1c**)), $Me_2Si(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (**2**), and $Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}Me\text{-}C_9H_5)ZrCl_2$ (**3**) were synthesized and separated into *threo* and *erythro* isomers by repeated recrystallization. The molecular structure of $Me_2C(3\text{-}t\text{-}BuC_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (*threo*-**1b**) was determined by X-ray crystallography. Polymerization of propylene with one of these metallocene complexes (*threo*-**1b**) coupled with MAO (methylaluminoxane) in toluene was found to afford a highly isotactic polymer of M_w 105 000 with % *mm* > 99.6 which shows an extremely high melting point of 161 °C.

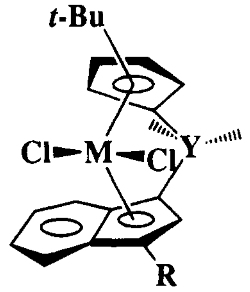
Introduction

A series of group 4 metallocene/methylaluminoxane (MAO) systems constitutes a class of homogeneous catalysts for stereospecific polymerization of propylene.[1−3] *ansa*-Metallocene complexes have been discovered that polymerize propylene with either isotactic or syndiotactic polymers, respectively. Ewen obtained C_s-symmetric iPr(Cp)(Flu)$ZrCl_2$ for syndiospecific propylene polymerization.[2] In contrast, a variety of metallocene complexes, which possess C_2 symmetry, produce IPP (isotactic polypropylene).[1a−q] Ewen and Kaminsky reported that *rac*-Et(Ind)$_2$MCl$_2$ (M = Ti, Zr, Hf) produce the IPP, but the resulting polymer exhibited a low isotacticity (% *mmmm* = 84.5) and melting point (134 °C).[1a−d] More recently, Spaleck has reported the preparation of polymers with high isotacticities (% *mm* = 96) and a high melting point (161 °C) using *rac*-Me$_2$Si(2-Me-4-naphthylindenyl)$_2$ZrCl$_2$ of C_2 symmetry at 70 °C.[1n] However, metallocenes with C_1 symmetry generally produce hemiisotactic polypropylene or polyolefins with elastomeric properties. More recently a few metallocenes with C_1 symmetry were reported to catalyze the isospecific polymerization of propylene.[1r−t] Here we describe a highly isospecific (% *mm* > 96) polymerization of propylene using novel *ansa*-metallocene complexes with C_1 symmetry (Chart 1).

Results and Discussion

Synthesis and Structure. A series of novel ligands (**e** and **h**) was prepared by the coupling reaction of a substituted indenyllithium with a substituted fulvene in tetrahydrofuran, as depicted in Scheme 1. After quenching the reaction mixture with water, **e** and **h** were isolated in 40% and 46% yield, respectively, by vacuum distillation. Dimethylsilylene-bridged ligand **i** was synthesized by the coupling reaction of dimethyldichlorosilane with lithium salts of **a** and **c** in a stepwise manner.

Chart 1



1a: M=Ti, Y=C, R=*t*-Bu
1b: M=Zr, Y=C, R=*t*-Bu
1c: M=Hf, Y=C, R=*t*-Bu
2: M=Zr, Y=Si, R=*t*-Bu
3: M=Zr, Y=C, R=Me

The reaction of the dilithium salts of **e**, **h**, or **i** with $ZrCl_4$ in CH_2Cl_2 solution at −78 °C provided *ansa*-zirconocene dichlorides **1b**, **2**, or **3** in ca. ~65% isolated yield. At this stage, each of the complexes **1b**, **2**, and **3** was present as a diastereomeric mixture. The expected *threo* and *erythro* isomers are shown in Scheme 2. In the case of the *threo* form, the two bulky alkyl groups attached to the cyclopentadienyl (Cp) ring are located on the opposite side regarding the central metal, and the *erythro* form has two alkyl groups on the same side of the central metal. The *threo*-formed metallocene could be separated from the *erythro*-formed metallocene by repeated crystallization from toluene. Thus, the *threo*-**1b** complex was obtained as orange crystals and the *erythro*-**1b** complex as a yellow powder from a hexane−toluene solution. In a similar manner, the pure *threo* complexes (**1a**, **1c**, **2**, **3**) could be separated by fractional crystallization from toluene.

The solid-state structure of *threo*-**1b** was determined by single X-ray crystallography. The ORTEP diagram illustrated in Figure 1 clearly confirms the stereochemical relationship between the two *t*-Bu groups. Crystal data are shown in Table 1 and selected bond distances and angles in Table 2. The Zr−Cl bond distances (2.411 (2) and 2.435 (2) Å) and Cl−Zr−Cl angles (98.5 (0)°) (see Table 2) of the present *ansa*-zirconocene dichloride agree well with those for reported metallocenes of C_s symmetry; e.g., for iPr(Cp)(Flu)$ZrCl_2$, Zr−Cl, 2.422 Å; Cl−Zr−Cl, 98.2°; Cp(Cen)−Zr−Flu(Cen), 118.6°.[4a] Because the cyclopentadienyl ring and the indenyl ring are bridged by one carbon atom, the angle of Cp(Cen)−Zr−Ind(Cen) becomes smaller (117.5°C) compared with those of ethylene- or silylene-bridged zirconocene complexes; i.e., for Et(Ind)$_2$ZrCl$_2$, Ind(Cen)−Zr−Ind(Cen), 125.2°; for Me$_2$SiCp$_2$ZrCl$_2$, Cp(Cen)−Zr−Cp(Cen), 125.4°; for Cp$_2$ZrCl$_2$, Cp(Cen)−Zr−Cp(Cen), 126°.[4]

We also synthesized the related titanocene complex **1a** and hafnocene complex **1c**. **1a** was prepared by the reaction of TiCl$_4$(THF)$_2$ with the dilithium salt of **e** in THF at −78 °C. This procedure gave **1a** as dark green crystals. The hafnocene complex **1c** was prepared from $HfCl_4$ and the dilithium salt of **e** under the same conditions as described for **1b**.

Propylene Polymerization. Polymerization or propylene with these unsymmetrical metallocenes in the

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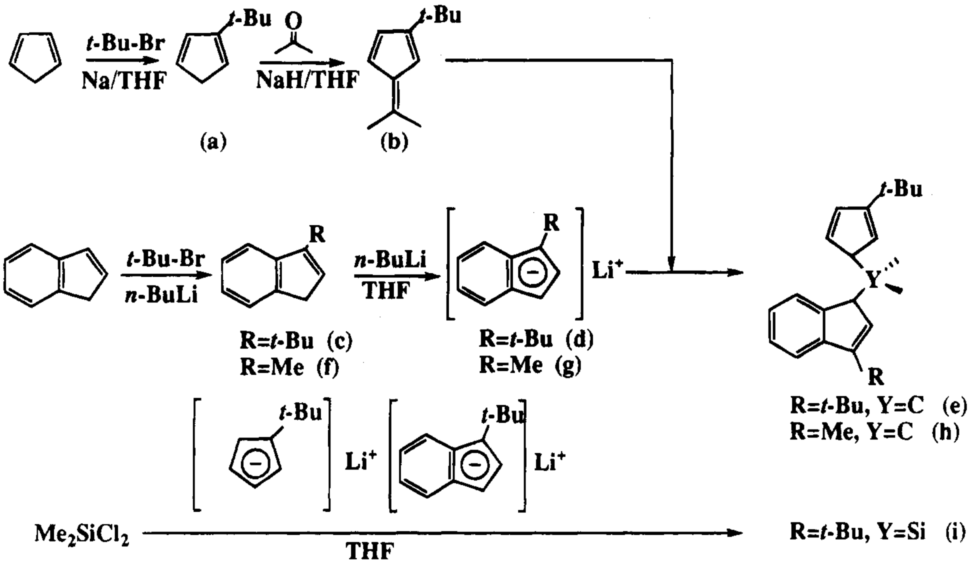
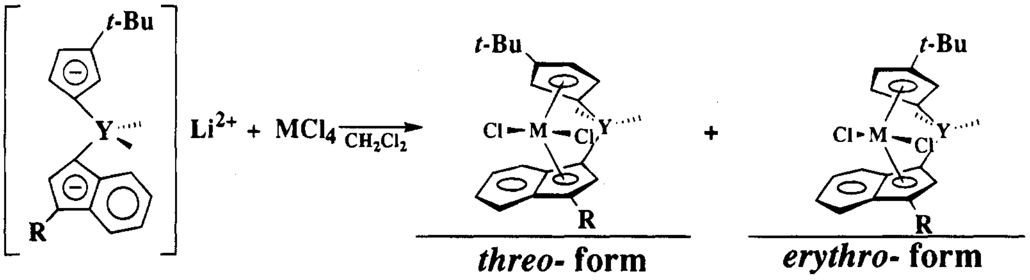
Scheme 1. Syntheses of the Ligands Used for Metallocenes 1–3



Scheme 2



1a: M=Ti, Y=C, R=t-Bu; 1b: M=Zr, Y=C, R=t-Bu; 1c: M=Hf, Y=C, R=t-Bu
2: M=Zr, Y=Si, R=t-Bu; 3: M=Zr, Y=C, R=Me

presence of methylaluminoxane (Al/Zr = 2000) was investigated in toluene at various temperatures, and the results are summarized in Table 3. Diastereomeric *threo* forms of metallocenes (**1a–c**, **2**, and **3**), especially in the case of **1a–c**, were found to produce highly isotactic polypropylene (% *mm* = 99.5–99.6). In addition, a tertiary butyl (*t*-Bu) substituent on the indene ring (*threo*-**1b**) is suited for highly isotactic polymerization compared with Me-substituted *threo*-**3**. Although iPr(Cp)(Ind)$ZrCl_2$ provided low molecular weight atactic polypropylene, introduction of bulky *tert*-butyl groups to both the cyclopentadienyl and indenyl rings led to very active and isospecific catalysts.

Chien reported that *rac*-[ethylidene(tetramethylcyclopentadienyl)(indenyl)]dichlorotitanium/MAO produces stereoblock homopolypropylene having the attributes of a thermoplastic elastomeric (TPE) material; he proposed that the catalytic species can exist in two interconverting states, polymerizing propylene stereoseletively by one state but nonstereoselectively by the other state.[3] From this viewpoint, one may say that the catalytic species of *threo*-**1b** can be fixed in a single state, polymerizing propylene stereoselectively through the effect of the bulky *tert*-butyl groups and the indenyl ring. For comparison, we also prepared C_2-symmetric *rac*-$Me_2Si(3\text{-}t\text{-}BuInd)_2ZrCl_2$ (**4**).[5] However, polymerization of propylene with **4** yielded low isotactic polypropylene (% *mm* = 75.5). As far as *t*-Bu-substituted metallocenes are concerned, it is obvious that the C_2 symmetry of metallocene is not essential to achieve highly isospecific polymerization of propylene.

It is important to note here that polymerization temperature dependence of isotacticity (% *mm*) was not observed for the *threo*-type metallocenes, although a significant decrease in isotacticity was reported in the case of a C_2-symmetric metallocene catalyst, e.g., $Et(Ind)_2ZrCl_2$/MAO, % *mm* at −10 °C polymerization = 97.0 and % *mm* at 30 °C polymerization = 91.6.[9b]

Interestingly, the *threo*-formed metallocene **1b** generates highly isotactic polypropylene with 10 times greater activity compared to the *erythro* isomer. From this viewpoint, one may estimate that highly isotactic polymers bearing a low content of atactic polypropylene (<8%) could be obtained even when using a diastereomer mixture. A similar result has been reported for the polymerization catalyzed by the C_2-symmetric zirconocene; i.e., *meso* isomers are less active than the racemic counterparts.[1q]

The catalytic activity of the present unsymmetrical metallocenes is somewhat lower than that of the C_2-symmetric metallocene, *rac*-$Et(Ind)_2ZrCl_2$. In the case of *threo*-**1a–c**, the observed activity decreases in the order Ti > Zr > Hf, in line with the order of the atomic number. This effect can be explained by considering that the M–P (metal–polymer) bond becomes stronger in the order Ti < Zr < Hf, and the high activity of **1a** is also explained by the geometrically constrained structure due to the small ionic radius of Ti. As the polymerization temperature rises, the catalytic activity increases but the molecular weight of the resulting polymer decreases. This is ascribable to the enhancement of β-hydrogen elimination at higher temperature.

The polypropylene synthesized with the Hf complex *threo*-**1c** has a lower molecular weight than that with the Zr complex *threo*-**1b**, while $Et(Ind)_2HfCl_2$ provides higher molecular weight polypropylene than $Et(Ind)_2$-

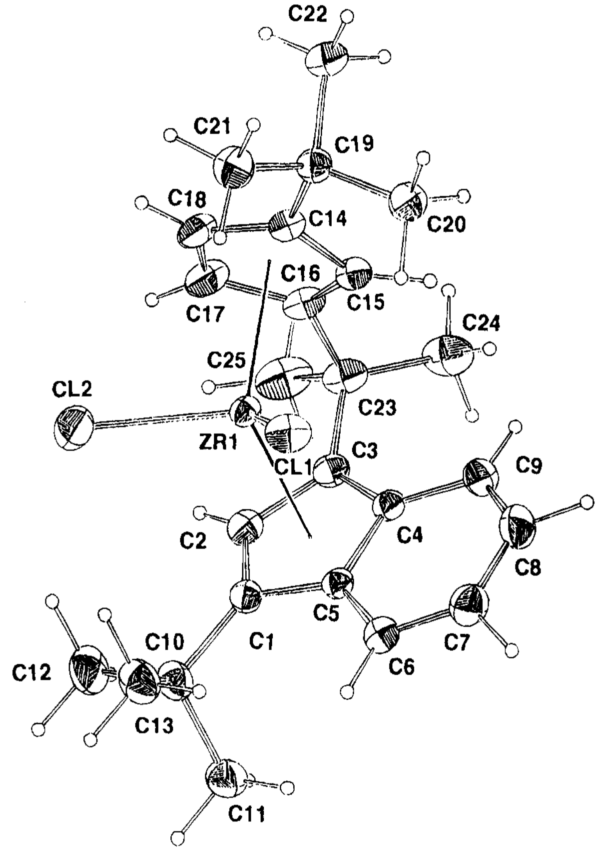
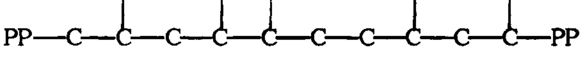


Figure 1. X-ray structure of *threo*-**1b**.

$ZrCl_2$.[1d] For *threo*-**1b** and *threo*-**1c**, the activity differs by a factor of 20, whereas the M_n differs by only a factor of 4. Thus, if anything, the rate of chain transfer is slower for the Hf complex compared with the Zr complex. It would be better to say that the slower propagation rate of the Hf complex would cause reduction of the M_n.

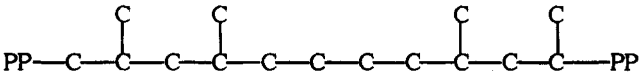
Although the M_w/M_n values of the polymers synthesized by **1a**, **1b**, **3**, and **4** at 1, 30, and 40 °C were relatively narrow, a broad molecular weight distribution (MWD) was observed for the polymers synthesized by **1c** and **2** at 1 °C. We speculate that the reason for the broadening of MWD for **1c** and **2** is that slow and complicated termination occurs at low polymerization temperature. In the higher range of reaction temperature (30−40 °C), the MWD becomes narrower even when the same complex was used.

Properties of Polypropylene. As reported in the literature,[9] isotactic polypropylene obtained by *rac*-Et(Ind)$_2$ZrCl$_2$ and *rac*-Et(THIN)$_2$ZrCl$_2$ coupled with methylaluminoxane includes a small amount of regioirregular structural units formed by 2,1-insertion and 1,3-insertion of propylene monomer in addition to the ordinary 1,2-inserted monomer units.



$$\mathrm{PP{-}C{-}\overset{C}{C}{-}C{-}\overset{C}{C}{-}\overset{C}{C}{-}C{-}C{-}\overset{C}{C}{-}C{-}\overset{C}{C}{-}PP}$$

2,1-insertion



$$\mathrm{PP{-}C{-}\overset{C}{C}{-}C{-}\overset{C}{C}{-}C{-}C{-}C{-}C{-}\overset{C}{C}{-}C{-}\overset{C}{C}{-}PP}$$

1,3-insertion

In order to compare the nature of isotactic polypropylenes obtained with *threo*-**1b** and with Et(THIN)$_2$ZrCl$_2$, the melting temperatures and microstructure of the polymer are summarized in Table 4. The percentage of irregularly inserted monomer was determined by ^{13}C-NMR spectroscopy and evaluated according to the literature.[9] As can be seen from the table, the melting temperature of the polymer obtained by *threo*-**1b** was higher than that obtained by Et(THIN)$_2$ZrCl$_2$. The % *mmmm* value reached 98.8%, and this value did not change over a wide range of polymerization temperature. This high melting temperature is derived from not only higher isotacticity but also a smaller amount of misinsertion.

Table 1. Crystal Data and Experimental Parameters for X-ray Structure Determination of *threo*-1b[a]

mol formula	$C_{25}H_{32}Cl_2Zr$
mol wt	494.66
cryst syst	orthorhombic
space group	$P2_12_12_1$
cell constants	$a = 14.174$ (3), $b = 16.670$ (4), $c = 9.963$ (2) Å $V = 2355.7$ (10) Å^3
Z value	4
D_{calcd}	1.395 g/cm^3
μ(Mo Kα)	3.332 cm^{-1}
cryst size	0.3 × 0.3 × 0.3 mm
diffractometer	Rigaku AFC-5R
radiation	Mo (λ = 0.710 690 Å) graphite-monochromated rotating anode (45 kV, 200 mA)
temp	13 °C
2θ angle	3−62°
scan mode	$2\theta/\theta$
scan speed	8°/min (2θ)
no. of unique reflctns	2982
no. of obsd reflctns	2759 ($>3\sigma(F_o)$)
no. of param	254
data solution	direct methods
structure	block diagonal least-squares methods
refinement	anisotropic (C, Cl, and Zr)
temp factors	isotropic (H, observed by difference Fourier syntheses)
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.0354
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0441
weighting scheme	$w = 1/\sigma^2(F_o)$

[a] Atomic scattering factors were applied from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 72. All calculations were performed by the ACOS2000 computer at Tohoku University using the applied liberty program UNICS III system (Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem.*) and the RANTAN 81 direct method program (Jia-xing, Y. *Acta Crystallogr.* **1981**, *A37*, 642; **1983**, *A39*, 35[8]) with some modification.

Polymerization Mechanism. In the field of isotactic polymerization of olefins with C_2-symmetrical metallocene catalysts, many theoretical studies and important experimental evidence for understanding the stereospecific polymerization mechanism have been reported.[6,7] It is known that (i) isotactic propylene polymerization with zirconocene catalysts takes place

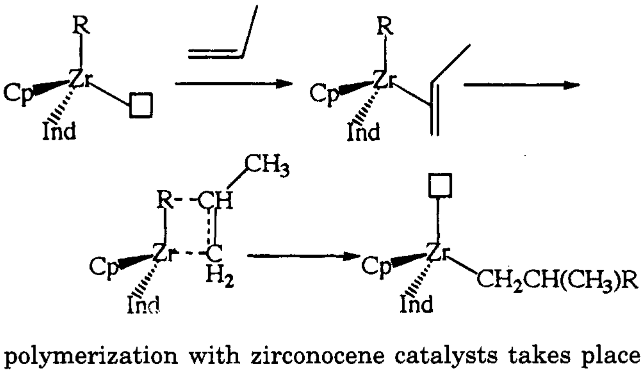
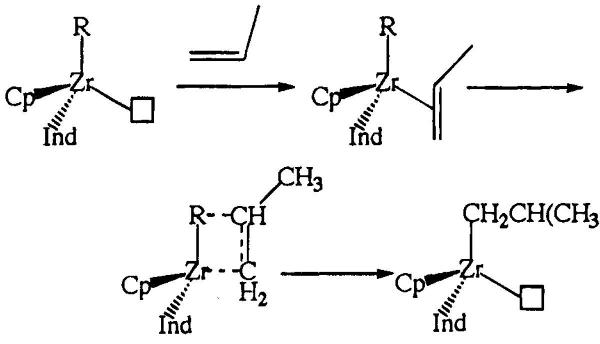


Table 2. Selected Bond Distances (Å) and Angles (deg) in *threo*-1b with Estimated Standard Deviations in Parentheses

Zr−Cl1	2.411 (2)	Zr−C15	2.488 (7)
Zr−Cl2	2.435 (2)	Zr−C16	2.439 (7)
Zr−C1	2.667 (6)	Zr−C17	2.449 (7)
Zr−C2	2.489 (6)	Zr−C18	2.570 (6)
Zr−C3	2.430 (7)	C3−C23	1.546 (9)
Zr−C4	2.521 (6)	C16−C23	1.530 (9)
Zr−C5	2.666 (6)	Zr−Ind(Cen)	2.247[a]
Zr−C14	2.632 (7)	Zr−Cp(Cen)	2.210
Cl1−Zr−Cl2	98.5 (0)	C3−C23−C16	99.2 (5)
Cp(Cen)−Zr−Ind(Cen)	117.5		

[a] Ind(Cen) and Cp(Cen) are the centroids of C1−C5 of the indene ligand of and C14−C18 of the Cp ligand, respectively.

by a regioselective 1,2-insertion of the propylene monomer into the metal−polymer bond; it is accepted that (ii) monomer insertion takes place at two active sites on the metal center in an alternating manner, and the stereochemistry on one site must be the same as that on the other site and (iii) the substituents on the Cp rings determine the conformation of the polymer chain end, and the fixed polymer chain end conformation in turn determines the stereochemistry of olefin insertion in the transition state (indirect steric control).[7c] By contrast, in the case of C_1-symmetrical metallocene catalysts, because the stereochemistry on the two sites is different, it seems reasonable that monomer insertion takes palce at the same active site on the metal center according to Cossee's mechanism. Although this mechanism is known as unfavorable "migration" in the iso- and syndiospecific polymerization of propylene with C_2- and C_s-symmetrical metallocenes, respectively,[2b] high isotacticity should be achieved by unidirectional migration in this C_1-symmetric metallocene.



Experimental Section

General Considerations. All operations were performed under argon using standard Schlenk techniques. Hexane, tetrahydrofuran, toluene, and diethyl ether used in the organometallic reactions were all dried over a sodium−potassium alloy and degassed before use. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. Mass spectra were run on a JEOL JMS-AX500.

Preparation of Ligands. *tert*-Butylcyclopentadiene and *tert*-butylidene were synthesized according to the literature.[10]

3-*tert*-Butyl-6,6-dimethylfulvene (b). To a suspension of NaH (10.8 g, 450 mmol) in 500 mL of THF was slowly added with vigorous magnetic stirring at 50 °C *tert*-butylcyclopentadiene (53.8 g, 440 mmol). The reaction mixture was refluxed for 2 h, and then excess NaH was removed by centrifuging. To the reaction mixture was added with vigorous stirring at room temperature acetone (30.7 g, 530 mmol), and the stirring was continued overnight. The resultant mixture was then quenched with 200 mL of water. The organic layer phases were dried over magnesium sulfate and evaporated to dryness. 3-*tert*-Butyl-6,6-dimethylfulvene was obtained as a bright yellow oil by vacuum distillation (bp 59 °C at 3 mmHg) (62%). ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 9H, $-C(CH_3)_3$), 2.11 (s, 6H, CH_3), 6.03 (m, 1H, Cp−H), 6.42 (m, 2H, Cp−H_2).

2-(3-*tert*-Butylcyclopentadienyl)-2-(3-*tert*-butylindenyl)propane (e). To a solution of 22.5 mL of TMEDA (tetramethylethylenediamine) in 600 mL of dry hexane under an argon atmosphere was added with vigorous magnetic stirring at 0 °C a hexane solution of butyllithium (93.8 mL, 150 mmol). After stirring at 0 °C for 30 min, the reaction mixture was warmed to room temperature, and 25.6 g (149 mmol) of *tert*-butylindene was slowly added with a dropping funnel. The solution was stirred at room temperature for 2 h to yield a white precipitate. The white precipitate was washed with dry hexane (2×) and was dissolved in 500 mL of THF. To the resultant red solution was added dropwise at room temperature 24.3 g (150 mmol) of 3-*tert*-butyl-6,6-dimethylfulvene. The mixture was stirred for 12 h and then treated with 200 mL of water. The organic layer was extracted with three 100-mL portions of diethyl ether. The combined organic phases were dried over magnesium sulfate, and a yellow oil was obtained through evaporation. Vacuum distillation (bp 146 °C at 0.3 mmHg) gave 30 g of **e** as a mixture of the 1,2- and 1,3-isomers as a pale yellow oil. Anal. Calcd for $C_{25}H_{34}$: C, 89.8; H, 10.24. Found: C, 89.6; H, 10.26. MS: *m/e* 334.

2-(3-*tert*-Butylcyclopentadienyl)-2-(3-methylindenyl)propane (h). The synthesis of **h** was carried out according to the route used for the preparation of **e**. By the reaction of lithium salts of 1-methylindene (13.6 g, 105 mmol) and 3-*tert*-butyl-6,6-dimethylfulvene (17.9 g, 110 mmol), a yellow oil **h** was obtained. Vacuum distillation (bp 125 °C at 0.3 mmHg) gave 18.8 g (58.4%) of **h**. MS: *m/e* 292.

3-*tert*-Butylcyclopentadienyl-(3-*tert*-butylindenyl)dimethylsilane (i). To a solution of dimethyldichlorosilane (7.5 g, 58 mmol) in 300 mL of dry THF was added at 0 °C a THF solution of *tert*-butylcyclopentadienyllithium (100 mL, 58 mmol). After 4 h of stirring at 40 °C, a THF solution of *tert*-butylindenyllithium (100 mL, 58 mmol) was added at room temperature. The resultant solution was stirred for 12 h and then treated with 200 mL of water. The organic layer was then extracted several times with 100 mL of hexane. The combined organic phases were dried over magnesium sulfate and the solvents removed, yielding a brown oil. Vacuum distillation (bp 140 °C at 0.3 mmHg) gave 43 g (31%) of **i** as a pale yellow oil. MS: m/e 345.

Synthesis of $Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (1b). 2-(3-*tert*-Butylcyclopentadienyl)-2-(3-*tert*-butylindenyl)propane (**e**, 14.8 g, 44 mmol) was dissolved in 300 mL of dry THF, and the solution was cooled to −78 °C. *n*-Butyllithium (55.6 mL of a 1.6 M solution in hexane) was added dropwise over 15 min. The resulting red solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed, and the residue was dissolved in 200 mL of CH_2Cl_2 at −78 °C.

The ligand solution was added to a suspension of $ZrCl_4$ (10.3 g, 44 mmol) in CH_2Cl_2 at −78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was removed, and the residue was extracted several times with 200-mL portions of dry hexane; the lithium salts were separated from the extracts by filtration. Concentration of the extract followed by cooling to −20 °C gave a mixture of *threo*-**1b** and *erythro*-**1b** (1:1) in 40% yield. Repeated recrystallization from toluene gave *threo*-**1b**. Anal. Calcd for $C_{25}H_{32}Cl_2Zr$: C, 60.7; H, 6.52. Found: C, 60.3; H, 6.82. ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 9H, $-C(CH_3)_3$), 1.50 (s, 9H, $-C(CH_3)_3$), 1.86 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 5.57 (t, 1H, Cp−H), 5.69 (dd, 1H, Cp−H), 5.83 (s, 1H, Ind−H), 6.26 (dd, 1H, Cp−H), 6.97 (t, 1H, Ind−H), 7.28 (t, 1H, Ind−H), 7.64 (d, 1H, Ind−H), 7.85 (d, 1H, Ind−H). IR (KBr): 2950 (s), 2810 (s), 1510 (w), 1421 (m), 1332 (m), 1203 (m), 1030 (w), 1002 (w), 956 (w), 821 (s), 803 (m), 722 (s), 508 (w), 430 (m) cm^{-1}.

erythro-**1b** was obtained from the mother liquor and recrystallized from toluene/hexane. Anal. Calcd for $C_{25}H_{32}Cl_2Zr$: C, 60.7; H, 6.52. Found: C, 60.4; H, 6.79. ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 9H, $-C(CH_3)_3$), 1.51 (s, 9H, $-C(CH_3)_3$), 1.84 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 5.51 (dd, 1H, Cp−H), 5.85 (s, 1H, Ind−H), 5.93 (t, 1H, Cp−H), 6.23 (dd, 1H, Cp−H), 7.25 (t, 1H, Ind−H), 7.28 (t, 1H, Ind−H), 7.72 (d, 1H, Ind−H), 7.85 (d, 1H, Ind−H).

Table 3. Polymerization of Propylene with Unsymmetrical Metallocenes/Methylaluminoxane Catalysts[a]

metallocene	polym temp (°C)	activity (g of PP/mmol of Zr·h)	$10^{-3}M_w$	M_w/M_n	% *mm*
$Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)TiCl_2$ (*threo*) (**1a**)	1	1950	34.1	2.6	99.6
$Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (*threo*) (**1b**)	1	620	105.0	2.3	99.6
	30	2000	38.0	2.4	99.2
	60	42000	9.0	2.7	99.2
$Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (*erythro*) (**1b**)	1	60	9.0	2.0	51.8
$Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)HfCl_2$ (*threo*) (**1c**)	1	30	39.0	3.3	99.5
	40	1400	11.9	2.7	n.d.
$Me_2Si(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (*threo*) (**2**)	1	110	28.0	3.5	98.6
	30	1900	10.2	2.3	n.d.
$Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}Me\text{-}C_9H_5)ZrCl_2$ (*threo*) (**3**)	1	1300	79.0	2.5	95.1
	40	92700	19.6	2.8	95.1
$Me_2Si(3\text{-}t\text{-}Bu\text{-}C_9H_5)_2ZrCl_2$[b] (*rac*) (**4**)	1	2600	5.0	2.0	75.5
$Me_2C(Cp)(Ind)ZrCl_2$[c]	1	730	1.1	1.7	35.2
$Et(THIN)_2ZrCl_2$ (*rac*)[d]	1	1100	73.0	2.6	96.2
$Et(Ind)_2ZrCl_2$ (*rac*)[e]	1	8000	63.0	2.5	95.6

[a] Al/Zr (Ti, Hf) = 2000; [metallocene] = $2-4 \times 10^{-3}$ mmol/300 mL of toluene; [propylene] = 2 mol. [b] $Me_2Si(3\text{-}t\text{-}Bu\text{-}C_9H_5)_2ZrCl_2$ = diemthylsilenebis(3-*tert*-butylindenyl)zirconium dichloride. [c] $Me_2C(Cp)(Ind)ZrCl_2$ = isopropylidene(cyclopentadienyl)(indenyl)zirconium dichloride. [d] $Et(THIN)_2ZrCl_2$ (*rac*) = ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (*rac*). [e] $Et(Ind)_2ZrCl_2$ (*rac*) = ethylenebis(indenyl)zirconium dichloride (*rac*).

Synthesis of $Me_2Si(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)ZrCl_2$ (2). The procedure described for the zirconium analogue **1b** was applied; 3.0 g (8.6 mmol) of **i**, 2.31 g (9.9 mmol) of $ZrCl_4$, and 10.7 mL of *n*-butyllithium (1.6 M in hexane) were used to provide 3 g of the title compound as a yellow powder. *threo*-**2** was isolated by recrystallization from toluene. ^1H NMR ($CDCl_3$): δ 0.73 (s, 3H, $SiCH_3$), 1.03 (s, 3H, $SiCH_3$), 1.08 (s, 9H, $-C(CH_3)_3$), 1.54 (s, 9H, $-C(CH_3)_3$), 5.81 (t, 1H, Cp−H), 5.94 (dd, 1H, Cp−H), 6.02 (s, 1H, Ind−H), 6.42 (dd, 1H, Cp−H), 7.16 (t, 1H, Ind−H), 7.34 (t, 1H, Ind−H), 7.57 (d, 1H, Ind−H), 7.97 (d, 1H, Ind−H).

Synthesis of $Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)TiCl_2$ (1a). The synthesis of **1a** was carried out according to the route for the preparation of **1b**. Starting with $TiCl_4 \cdot 2THF$, the complex **1a** was obtained as a green powder. *threo*-**1a** was isolated by recrystallization from toluene. Anal. Calcd for $C_{25}H_{32}Cl_2Ti$: C, 66.5; H, 7.15. Found: C, 66.8; H, 7.18. ^1H NMR ($CDCl_3$): δ 1.13 (s, 9H, $-C(CH_3)_3$), 1.54 (s, 9H, $-C(CH_3)_3$), 1.83 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 5.48 (m, 2H, Cp−H), 5.47 (s, 1H, Ind−H), 6.42 (dd, 1H, Cp−H), 6.92 (t, 1H, Ind−H), 7.38 (t, 1H, Ind−H), 7.54 (d, 1H, Ind−H), 7.85 (d, 1H, Ind−H).

Synthesis of $Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}t\text{-}Bu\text{-}C_9H_5)HFCl_2$ (1c). The synthesis of **1c** was carried out according to the procedure for preparation of **1b**. Starting with $HfCl_4$ (Rare Metallic Co., Ltd., 99.99%), we obtained **1c** as a yellow powder. *threo*-**1c** was isolated by recrystallization from toluene. ^1H NMR ($CDCl_3$): δ 1.14 (s, 9H, $-C(CH_3)_3$), 1.50 (s, 9H, $-C(CH_3)_3$), 1.88 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 5.50 (t, 1H, Cp−H), 5.61 (dd, 1H, Cp−H), 5.80 (s, 1H, Ind−H), 6.21 (dd, 1H, Cp−H), 6.94 (t, 1H, Ind−H), 7.23 (t, 1H, Ind−H), 7.66 (d, 1H, Ind−H), 7.82 (d, 1H, Ind−H). MS: *m/e* 581.

Synthesis of $Me_2C(3\text{-}t\text{-}Bu\text{-}C_5H_3)(3\text{-}Me\text{-}C_9H_5)ZrCl_2$ (3). The synthesis of **3** was carried out according to the procedure for the preparation of **1b**. Starting with **h**, we obtained **3** as an orange powder. *threo*-**1c** was isolated by recrystallization from toluene. Anal. Calcd for $C_{22}H_{26}Cl_2Zr$: C, 58.4; H, 5.79. Found: C, 58.7; H, 6.02. ^1H NMR ($CDCl_3$): δ 1.18 (s, 9H, $-C(CH_3)_3$), 1.87 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 5.46 (t, 1H, Cp−H), 5.64 (dd, 1H, Cp−H), 5.68 (s, 1H, Ind−H), 6.39 (dd, 1H, Cp−H), 6.97 (t, 1H, Ind−H), 7.24 (t, 1H, Ind−H), 7.47 (d, 1H, Ind−H), 7.54 (d, 1H, Ind−H).

X-ray Structure Analysis of 1b. Single crystals of **1b** were obtained by crystallization from toluene. The structure was solved by the RANTAN 81 direct method program, and the program system UNICS III was used for calculations utilizing a total of 2759 reflections ($|F_0| > 3\sigma|F_o|$). The hydrogen atoms were located in the difference Fourier maps. Refinement was made by block diagonal least-squares methods, $R = 0.035$ ($R_w = 0.044$): The positional and temperature factors of the hydrogen atoms were also refined. The structural parameters for **1b** thus obtained are listed in Table 5, and selected bond distances and angles are shown in Table 2.

Polymerization and Polymer Analysis. Into a 1.5-L thermostable steel autoclave were added in the following order, under N_2 atmosphere, 300 mL of dry toluene, a solution of 0.46 g of methylaluminoxane (Toso Akzo) in 35 mL of toluene, and a solution of metallocene complex (2 μmol) in 2 mL of toluene (Al/Zr ≈ 2000). The reaction mixture was stirred for 15 min at 20 °C, and then the temperature was adjusted to the desired value. Propylene (2 mol) was added to the autoclave, and the polymerization temperature was controlled over the entire reaction period. Finally, the autoclave was vented, and the reaction mixture was poured into 2 L of methanol acidified with 10 mL of concentrated aqueous HCl. The precipitated polymer was collected by filtration, washed with methanol, and dried at 50 °C to a constant weight.

Table 4. Characterization of IPP Obtained by *threo*-1b and *rac*-$Et(THIN)_2ZrCl_2$ with Methylaluminoxane

metallocene	polym temp (°C)	T_m (°C)	*mmmm* %	% insertion	
				2,1	1,3
threo-**1b**	1	161.7	98.4	0.19	<0.01
	30	159.0	98.8	0.07	0.03
	60	159.1	98.6	0.10	0.03
rac-$Et(THIN)_2ZrCl_2$	1	147.2	93.4	0.72	0.11

Table 5. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms in *threo*-1b[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Zr	8224 (0)	3039 (0)	3033 (0)	3.0
Cl1	7916 (1)	4155 (1)	1559 (2)	4.2
Cl2	8936 (1)	2135 (1)	1403 (2)	5.5
C1	6657 (4)	2173 (3)	2725 (6)	2.6
C2	7191 (4)	1935 (4)	3847 (6)	3.1
C3	7243 (4)	2534 (4)	4845 (7)	2.9
C4	6713 (4)	3197 (3)	4339 (5)	2.5
C5	6344 (3)	2978 (3)	3046 (6)	2.5
C6	5751 (4)	3523 (4)	2332 (7)	3.2
C7	5581 (5)	4258 (4)	2872 (9)	4.3
C8	5961 (5)	4485 (4)	4114 (8)	4.3
C9	6506 (5)	3984 (4)	4839 (7)	3.4
C10	6336 (5)	1672 (4)	1546 (7)	3.6
C11	5255 (5)	1550 (4)	1692 (8)	4.2
C12	6808 (6)	837 (4)	1595 (9)	5.0
C13	6549 (5)	2068 (5)	184 (7)	4.5
C14	9583 (4)	3914 (4)	4078 (7)	2.9
C15	8831 (4)	3781 (4)	5019 (6)	2.9
C16	8786 (4)	2942 (4)	5340 (6)	3.5
C17	9465 (5)	2566 (4)	4548 (8)	4.1
C18	9954 (4)	3161 (4)	3780 (7)	3.5
C19	9984 (4)	4727 (4)	3688 (6)	3.0
C20	9249 (5)	5388 (4)	3797 (8)	3.7
C21	10395 (5)	4711 (4)	2275 (7)	4.1
C22	10784 (5)	4889 (4)	4683 (8)	4.0
C23	7943 (5)	2546 (4)	6035 (7)	3.8
C24	7598 (5)	3006 (6)	7245 (6)	5.1
C25	8170 (6)	1686 (5)	6477 (9)	5.6

[a] Positional parameters are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors.

The molecular weights of the polymers were determined by gel permeation chromatography on a Waters 150C instrument (Shodex-AT80M/S; eluent 1,2,4-trichlorobenzene at 135 °C). Melting temperatures were determined with a Perkin-Elmer DSC-7 system at a heating rate of 20 °C/min. The results of the second scan are reported. ^{13}C-NMR measurements were performed on a JEOL EX-400 instrument at 120 °C (solvent: 1,2,4-trichlorobenzene/benzene-d_6; volume ratio, 3/1); stereo- and regioregularities of the polypropylene were calculated from the integration of the spectra according to the literature.[9]

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Supplementary Material Available: Tables of bond distances, bond angles, and anisotropic displacement parameters for *threo*-**1b** (10 pages); tables of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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