Syndiospecific Propylene Polymerization with C_1 Symmetric Group 4 *ansa*-Metallocene Catalysts†

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ABSTRACT: C_1 symmetric group 4 *ansa*-metallocenes [Me_2C(Cp)(3-CH_2X-2-R-Ind)MCl_2 (M = Zr, R = H, X = Me (**3**); M = Zr, R = H, X = $SiMe_3$ (**4**); M = Zr, R = Me, X = $SiMe_3$ (**5**); M = Hf, R = H, X = $SiMe_3$ (**6**); M = Hf, R = Me, X = $SiMe_3$ (**7**); Cp = cyclopentadienyl, Ind = indenyl), upon activation with methylaluminoxane (MAO), catalyze the polymerization of propylene to predominantly syndiotactic polypropylene. The preparations of complexes **3**−**7** and the molecular structures of **3** and **4** are reported. The polypropylenes produced have [*rrrr*] pentad contents ranging from 43 to 75% depending on the employed transition metal, ligand substitution pattern, and polymerization conditions. The 2-Me-substituted catalysts **5**/MAO and **7**/MAO exhibit higher activities and higher stereospecificities than their unsubstituted analogues **4**/MAO and **6**/MAO. Stereoselectivities of the zirconium catalysts **3**−**5**/MAO are sensitive to the monomer concentration, showing decreasing syndiotacticities with decreasing propylene pressure due to increasing amount of skipped insertions. The dependence of the stereospecificity and polymerization activity on the ligand structure suggests that the conformation of the 3-(trimethylsilyl)-methyl substituent can be perturbed by introduction of a 2-substituent, thus providing a tool to control the stereoerror formation.

Introduction

Fifteen years after the initial discoveries,[1,2] the stereoselective polymerization of α-olefins with metallocene-based catalyst systems has expanded to a field of enormous academic and industrial significance.[3−5] Isotactic,[6,7] hemiisotactic,[8−12] syndiotactic,[8,9,13−19] and isotactic−atactic stereoblock[20−27] polypropylenes have been obtained by employing appropriately substituted bis(cyclopentadienyl) group 4 metallocene catalysts. C_2 symmetric metallocenes were among the first to produce highly isotactic polypropylene.[1,2,6,7] C_1 symmetric metallocene catalysts have been shown to exhibit a range of stereospecificities from isotactic to hemiisotactic[8,9] and atactic, depending on the nature of the substituents.[4]

The development of syndiospecific metallocene catalysts represents a milestone in stereospecific polymerization reactions. This pioneering development by Ewen and Razavi was one of the first examples where metallocene catalysts could provide well-defined microstructures that are not readily obtained with hetereogeneous catalysts.[8,9,13−17] Mechanistic insights provided from many careful studies of metallocene catalysts have illuminated many of the details of olefin enchainment and stereospecificity.[4]

The syndiospecific polymerization of propylene to syndiotactic polypropylene (sPP) by enantiomorphic site control mechanism has been mainly restricted to two general classes of C_s symmetric *ansa*-metallocene catalysts or their closely C_s symmetric variants. The first class are the now-prototypical C_s symmetric *ansa*-cyclopentadienyl/fluorenyl metallocenes **1** of Ewen and Razavi[13,16,17,28] and variants thereof,[4,9,29−31] and the second class are represented by recently developed C_s and C_1 symmetric metallocenes **2** devised by Bercaw (Figure 1).[18,19]

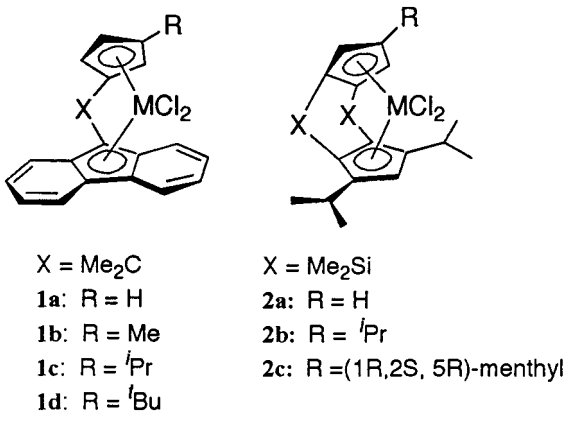

Figure 1. Structures of metallocenes **1** and **2**.

Recent attention in stereospecific propylene polymerization has focused on exploiting the tunability of metallocene catalysts to generate microstructures which cannot be readily accessed by the now highly optimized heterogeneous catalysts for isotactic polypropylene.[4] For isotactic polypropylene, these efforts have resulted in lower tacticity polypropylenes, some of which have interesting elastomeric properties.[20−27,32−42] This interest in the synthesis and properties of these lower tacticity polypropylenes, coupled with recent results suggesting the low miscibility of sPP with atactic polypropylene,[43,44] motivated us to investigate metallocenes for the synthesis of syndiotactic polypropylene with controlled amounts of atactic stereosequences.[31,45,46] We describe here the preparation of C_1 symmetric group 4 *ansa*-metallocenes [Me_2C(Cp)(2-R-3-XCH_2-Ind)]MCl_2 (**3**−**7,** X = CH_3, Me_3Si; R = H, Me; M = Zr, Hf; Cp = cyclopentadienyl, Ind = indenyl)[12,47] and their application for the *syndiospecific* polymerization of propylene (Figure 2). Catalyst precursors were

† This paper is dedicated to the memory of Professor Jan Näsman.

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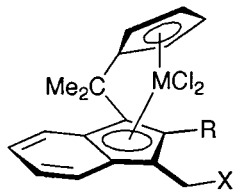
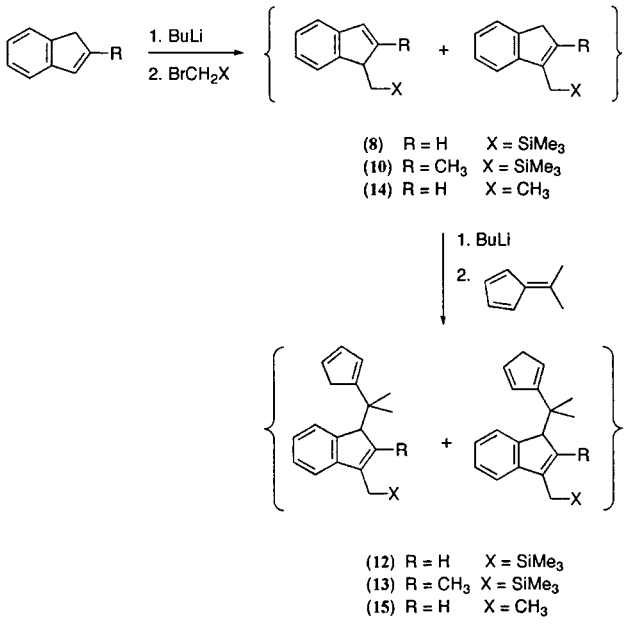


3 M = Zr, R = H, X = Me
4 M = Zr, R = H, X = $SiMe_3$
5 M = Zr, R = Me, X = $SiMe_3$
6 M = Hf, R = H, X = $SiMe_3$
7 M = Hf, R = Me, X = $SiMe_3$

Figure 2. Structure of C_1 symmetric metallocenes **3**−**7**.

Scheme 1



chosen to exploit the conformational flexibility of the 3-indenyl substituent to control the stereoerror formation in syndiospecific propylene polymerization.[31]

Results

Ligand precursors **12**, **13**, and **15** were prepared by alkylation of indenyllithium/2-methylindenyllithium with ethyl/(trimethylsilyl)methyl bromide to afford the substituted indene systems **8, 10**, and **14**. Deprotonation and subsequent reaction with 6,6-dimethylfulvene yields **12**, **13**, and **15** in moderate to good yields (Scheme 1).

Metallocene dichlorides **3**−**7** were prepared in 30−40% isolated yields by reacting the dilithiated ligand precursors with MCl_4 (M = Zr, Hf) in Et_2O, followed by subsequent workup and crystallization steps. The molecular structures of **3** and **4** are shown in Figures 3 and 4. The contracted Cen(Cp)−Zr−Cen(Ind) angles (ca. 118°) and the small angle at the bridging carbon atoms C(13)−C(10)−C(3) [ca. 100°] are typical for C_1-bridged group 4 *ansa*-metallocenes.[48−50] Likewise, the metal−ligand bond distances ranging from 2.420 to 2.641 Å and the Cl−Zr−Cl angles [100°−101°] are similar to those reported previously for related C_1-bridged mixed ligand cyclopentadienyl−indenyl and cyclopentadienyl−fluorenyl zirconium dichlorides.[15,16,24,25,47,51−53]

The diastereotopic CH_2 protons of the trimethylsilylmethyl groups in **4** and **6** are indistinguishable by ^{1}H NMR in $CDCl_3$, showing sharp singlets at 2.27 (**4**) and 2.25 ppm (**6**), respectively. For complexes **5** and **7** an AB spin system with ^2J = 15.0 Hz is observed for these protons at 2.36/2.25 ppm (**5**) and 2.34/2.23 ppm (**7**).[54] In C_6D_6 both complexes **4** and **5** show the characteristic AB doublets in their ^{1}H NMR spectra at 2.45/2.27 ppm (**4**, ^2J = 14.5 Hz) and 2.47/2.20 ppm (**5**, ^2J = 15.0 Hz).

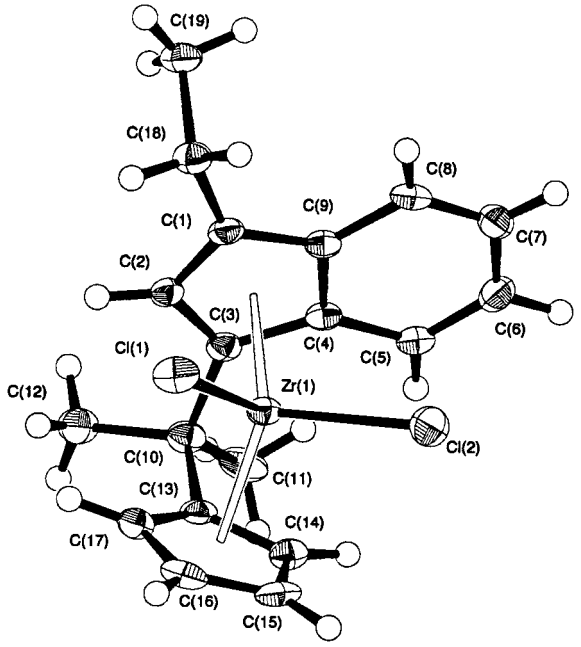


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level.

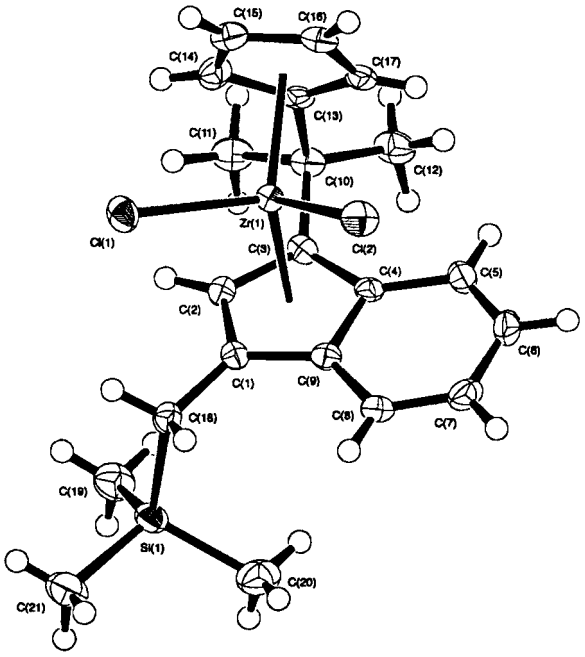


Figure 4. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level.

Representative results for the polymerization of propylene using catalyst precursors **3**−**7** activated with methylaluminoxane (MAO) are presented in Table 1. Catalysts derived from metallocenes **3**−**7** yielded predominantly syndiotactic polypropylenes with [*rrrr*] pentad contents ranging from 43 to 75%; isotactic [*mmmm*] pentads are absent in polymers derived from **3**−**7**. Polymers derived from metallocene **3** are tacky, low molecular weight amorphous solids, while those derived from metallocenes **4**−**7** were isolated as semicrystalline powdery solids. Among the studied systems, complex **5** exhibits the highest polymerization activity corresponding to 9900 kg of PP/(mol of Zr h) in liquid propylene at T_p = 20 °C. Catalysts from zirconocenes **4** and **5** are considerably more productive and more syndiospecific

Table 1. Propylene Polymerization Data with 3−7/MAO[a]

catalyst	T_p (°C)	P (bar)	A (kg of PP/(mol of M h))	[*rrrr*][d] (%)	[*r*][d,e] (%)	M_w[f] (g/mol)	M_w/M_n[f]	T_m[g] (°C)	ΔH[h] (J/g)
3	20	8.8[b]	1200	49	84	4 200[i]	N/A	N/A	N/A
4	0	5.8[b]	700	65	91	11 700	1.8	35−115	45
4	20	8.8[b]	4300	66	89	12 000	1.3	30−110	40
4	20	6.2	1900	53	84	12 700	2.0	30−100	30
4	20	3.6[c]	1300	49	83	11 900	2.0	30−90	20
5	0	5.8[b]	2600	75	94	35 800	2.1	40−135	65
5	20	8.8[b]	9900	74	90	30 900	2.1	35−125	45
5	20	6.2	3100	69	90	24 400	2.1	30−120	40
5	20	3.6	2100	66	87	22 500	2.0	30−110	45
6	20	8.8[b]	300	43	82	114 500	1.9	35−70	15
7	20	8.8[b]	1100	58	87	326 000	2.6	30−110	30

[a] MAO as cocatalyst, [Al]:[M] = 1000:1; [M] = 2.5×10^{-5}; t = 20 min. [b] Liquid propylene. [c] t = 60 min. [d] By ^{13}C NMR. [e] [*r*] = [*rr*] + 0.5[*mr*]. [f] By GPC. [g] Melting range from DSC curves. [h] By DSC. [i] M_n, determined by end group analysis from ^{1}H NMR data.

Table 2. Experimental Pentad Distribution for Propylene Polymerization with 3−5/MAO[a]

			pentads								
catalyst	P (bar)	A[b]	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*rmrm*	*rrrr*	*rrrm*	*mrrm*
3	8.8[c]	1200	0	1.8	2.8	3.9	17.9	2.9	48.9	20.7	1.1
4	8.8[c]	4300	0	0.5	2.0	3.6	12.9	0	65.6	15.4	0
4	6.2	1900	0	1.0	2.5	5.2	15.2	4.3	52.9	19.1	0
4	3.6[d]	1300	0	0.9	2.5	4.8	18.3	3.0	49.2	21.4	0
5	8.8[c]	9900	0	0.7	2.4	5.1	6.6	1.3	73.8	10.1	0
5	6.2	3100	0	0.2	2.2	6.0	9.6	0	68.5	13.6	0
5	3.6	2100	0	0.3	2.2	6.1	12.3	0	65.8	13.2	0

[a] MAO as cocatalyst, [Al]:[M] = 1000:1; [M] = 2.5×10^{-5}; t = 20 min. [b] A expressed in kg of PP/(mol of M h). [c] Liquid propylene. [d] t = 60 min.

than their hafnium congeners but produce polypropylenes with significantly lower molecular weights. Activities of the zirconium complexes increase with increasing polymerization temperature (0−20 °C) and increasing monomer concentration [$P(C_3H_6)$ = 3.6−8.8 bar, T_p = 20 °C]. The introduction of a CH_3 substituent in position 2 results in a 2-fold increase in the activity, along with a 2−3-fold increase in the molecular weights of the produced polymers (compare **4** vs **5** and **6** vs **7**). The 2-CH_3 substituted catalysts **5**/MAO and **7**/MAO exhibit higher stereospecificities than their unsubstituted analogues **4**/MAO and **6**/MAO, producing polypropylenes with 10−17% higher [*rrrr*] pentad contents under otherwise identical polymerization conditions (Table 1).

The polymerization behavior of the zirconium catalysts **4** and **5** was studied at a variety of monomer concentrations to investigate the influence of monomer concentration on the stereoselectivity; results are shown in Tables 1 and 2. The stereospecificities of catalysts derived from metallocenes **4** and **5** are sensitive to the monomer concentration and polymerization temperature. Their syndiospecificities, as measured by the [*rrrr*] pentad contents of the produced polypropylenes, increase with increasing monomer concentration from 49 to 66% for metallocene **4** and from 66 to 74% for metallocene **5** ($P(C_3H_6)$ = 3.6−8.8 bar). This increase in syndiospecificity is manifested in a decrease in certain types of stereoerrors. For example, the percentage of [*xmrx*] pentads decreases from 18 to 13% with increasing monomer concentration for **4** and decreases from 12 to 7% for **5**. In contrast, stereoerrors of the [*rmmr*] type are insensitive to the propylene concentration (Table 2).[19,28,31]

DSC analysis of polymer samples derived from metallocenes **4**−**7** showed broad bimodal or trimodal melting transitions with ΔH values ranging from 15 to 50 J/g. The 2-CH_3 substituted zirconium catalyst **5**/MAO produced the polymers with highest peak melting points at 127 and 115 °C for samples prepared in liquid monomer at 0 and 20 °C, respectively. A low-syndiotacticity sample obtained with the hafnium catalyst **6**/MAO at T_p = 20 °C gave a bimodal melting curve with high- and low-temperature endotherms of 62 and 47 °C.

Discussion

While Natta was the first to prepare and structurally characterize syndiotactic polypropylene,[55] it was not until the advent of metallocene catalysts that samples of sufficient purity and stereoregularity were available for detailed studies of the physical properties.[56−59] Investigations of soluble metallocene catalysts not only have provided access to new types of polypropylenes but also have revealed important insights into the mechanism and origin of stereospecificity in olefin insertion reactions.[4] The commonly accepted mechanism for the syndiospecific polymerization of propylene by an enantiomorphic site control mechanism involves the alternating enchainment of the propylene monomer at two different heterotopic sites which are selective for opposite enantiofaces of the α-olefin.[4,13,60] The first catalysts to achieve this with a high degree of stereospecificity were the C_s symmetric complexes derived from bridged cyclopentadienyl fluorenylmetallocene **1a** of Figure 1.[13,15] The enantiotopic sites of this catalyst are provided by a mirror plane of symmetry bisecting the two coordination sites for olefin insertion; introduction of alkyl substituents on the 3-position of the cyclopentadienyl ring (complexes **1b**−**d**) breaks up the symmetry of the catalysts and leads to either hemiisotactic or isotactic polypropylene depending on the nature of the substituent.[4] The steric and geometric requirements for syndiospecificity were further illuminated by Bercaw,[18,19] who prepared a series of doubly bridged syndiospecific metallocenes (**2a**−**c**); disruption of the C_s symmetry of these catalysts similarly compromises the syndiospecificity of these catalysts. For example, metallocene **2c** (R = (1*R*,2*S*,5*R*)-menthyl) yields polypro-

pylenes that range from isotactic to hemiisotactic with syndiospecificities no higher than [*rrrr*] = 0.38, depending on monomer concentration.

While Ewen's symmetry rules[4,29] have proven powerful for correlating catalyst symmetry with stereospecificity, it should be noted that strict C_s symmetry is neither sufficient nor necessary for enantiomorphic-site syndiospecificity. Necessary and sufficient conditions for a syndiospecific enantiomorphic site control mechanism are a predominantly alternating insertion at metal coordination sites exhibiting selectivity for opposite olefin enantiofaces. These requirements are apparently met by metallocenes **3**−**7** which have heterotopic coordination sites by virtue of a 3-ethyl or 3-trimethylsilylmethyl substituent on the indene.

The synthesis of metallocenes **3**−**7** was carried out by metalation of the dilithiated ligands in yields of 30−40%.[12] Single-crystal X-ray analysis of zirconocenes **3** and **4** (Figures 3 and 4) reveals a distorted tetrahedral geometry about the zirconium atoms typical of carbon-bridged *ansa*-metallocenes[15,16,24,25,47,51−53] where the 3-alkyl substituent in both metallocenes **3** and **4** adopts a conformation such that the β-carbon (or β-silicon) of the substituent is directed away from the equatorial wedge of the metallocene.[47]

Activation of metallocenes **3**−**7** with MAO yields active catalysts for the polymerization of propylene. The productivities of metallocenes **3**−**7** are low at 300−9900 kg of PP/(mol of M h) (M = Zr, Hf), and the molecular weights of polymers derived from the zirconocenes are modest, at 11 000−35 000 g/mol. (For comparison, activities of some of the most active metallocenes can approach 1 300 000 kg of PP/(mol of Zr h).[4]) These productivities and molecular weights are comparable to those reported for related carbon- and silicon-bridged cyclopentadienyl−indenylmetallocenes.[6]

The stereospecificities of metallocenes **3**−**7** and the molecular weights of the derived polymers depend on the nature of the metal ion (Zr vs Hf), the nature of the substituents in the 2- and 3-positions of the indene, the monomer concentration, and the temperature. Polymers obtained from metallocene **3**, containing a 3-ethyl substituent, are amorphous while those derived from metallocenes **4**−**7** are semicrystalline powdery solids. Analysis of the ^{13}C NMR spectra reveals similar microstructures for polymers obtained from **3** and **4**; the difference in physical properties of the two polymers is likely a consequence of the lower molecular weight of the polymers derived from **3**.

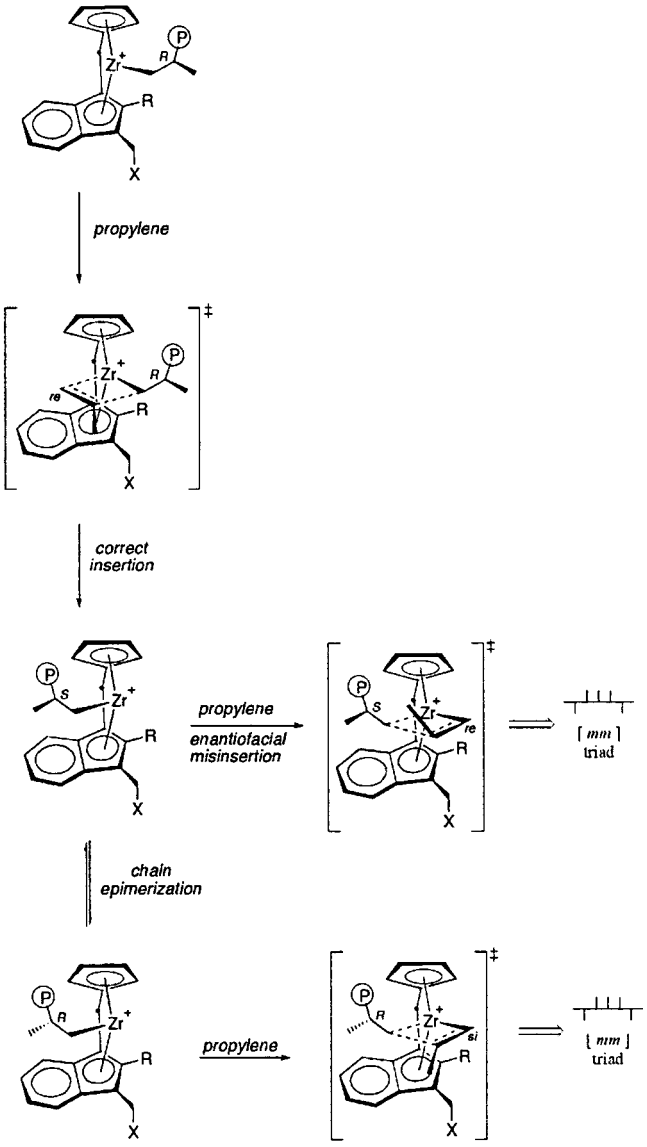
Catalysts derived from the zirconocenes are more productive but produce lower molecular weight polymers than the hafnium congeners under similar conditions (Table 1). The zirconocenes are also more highly syndiospecific than the hafnocenes, exhibiting approximately 30% higher values of the [*rrrr*] pentads. This is similar to observations by Ewen[61] and Razavi[30] for metallocenes **1a,b** and has been attributed by Razavi to the more diffuse orbitals and higher effective nuclear charge of the Hf derivatives related to the lanthanide contraction.[30]

The nature of the 3-indenyl substituent appears to be a critical factor of the stereospecificity exhibited by catalysts derived from metallocenes **3**−**7**. Chien reported that the 3-methyl-substituted analogue Me_2C(Cp)(3-MeInd)$ZrCl_2$ (**17**) yields hemiisotactic polypropylene;[12] the unsubstituted derivatives Me_2C(Cp)(Ind)MCl_2 (**16**) are known to give atactic, hemiisotactic, or isotactic/atactic stereoblock polypropylenes depending on the polymerization conditions.[12,23−25,33,62,63] These results have been rationalized by positing that C_1 symmetric metallocenes typified by **16** and **17** possess one isospecific and one aspecific site; strictly alternating insertion at each site produces hemiisotactic polypropylene, and multiple insertions at a given site yield either atactic or stereoblock polypropylenes depending on the relative rate of insertion vs site isomerization.[12,25,33]

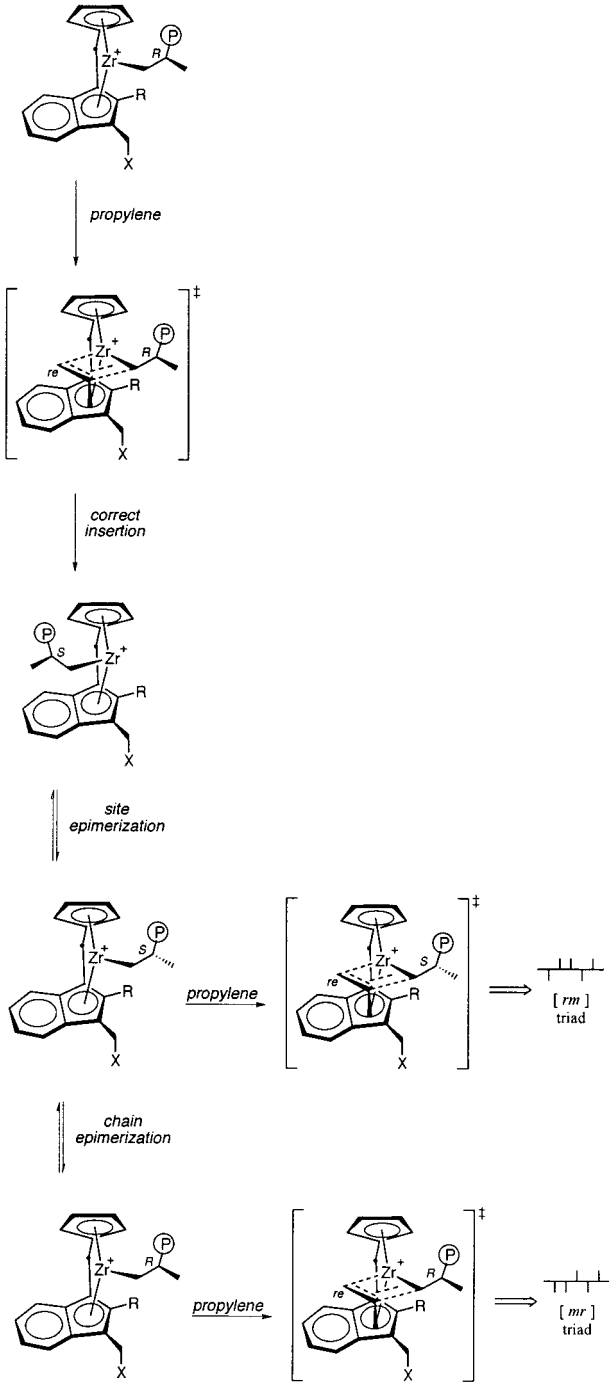
Our experiments demonstrate that bridged cyclopentadienyl-3-R-indenylmetallocenes substituted by an ethyl (**3**) or a trimethylsilylmethyl (**4**) group generate syndiospecific polypropylene. The modest but clear syndiospecificity of **3** suggests that introduction of an ethyl substituent at the 3-indenyl position renders both coordination sites stereospecific and selective for opposite enantiofaces. Furthermore, analogous complexes possessing either fused carbocyclic rings[4] or two methyl substituents[64] on positions 2 and 3 of the indenyl ligand were also reported to yield syndiotactic polypropylenes. These results are in concert with other systems in which methyl groups are sufficient to alter the stereoselectivity and specificity, especially in bridged bis(3-R-cp) metallocenes.[65,66]

The nature of the substituent in the 2-position also influences both the molecular weight and the stereospecificity of metallocenes **4**−**7**; introduction of a methyl group in the 2-position of the indenyl ligand adjacent to the trimethylsilylmethyl substituent results in higher molecular weight polymers and a higher degree of syndiotacticity in the resulting polymers than those obtained from the unsubstituted analogues. We had envisioned that conformationally flexible 3-(trimethylsilylmethyl) or 3-ethyl substituents on the indenyl ligand might have an influence on the number of stereoerrors produced by these catalysts. Introduction of a methyl group at the 2-position was expected to limit the conformational degrees of freedom of the trimethylsilylmethyl substituent and thus indirectly influence the stereospecificity. For C_2 symmetric isospecific bis(indenyl)-type catalysts introduction of a 2-CH_3 substituent was shown to result in a 1−9% increase in the isospecificity and regiospecificity, a large increase in the molecular weight, and, in the absence of additional 4-aryl substituents, a moderate decrease in the polymerization activity.[6,7] The significantly higher stereospecificities and higher activities observed here for the 2-CH_3 substituted catalysts suggest that the conformation of the 3-(trimethylsilyl)methyl substituent can be perturbed by introduction of a 2-substituent, thereby indirectly influencing the stereospecificity and polymerization activity of the complex. There are two possible origins of this effect: (1) that the 2-methyl substituent increases the stereospecificity at one or both of the coordination sites, leading to higher syndiotacticities,[4] or (2) that the presence or absence of this substituent influences the frequency of site epimerization (chain migration without insertion or *backskip*)[19,67,68] or chain epimerization.[4,69] As both site and chain epimerization involve unimolecular processes that compete with the stereodifferentiating monomer insertion event, the relative contributions of (1) and (2) were studied by investigating the influence of monomer concentration on the types and frequencies of stereoerrors produced by these metallocenes.

Scheme 2



Scheme 3



Two predominant types of stereoerrors are observed in highly regioregular syndiotactic polypropylenes. These errors have been classified by Ewen as *type I* errors, related to two consecutive isotactic placements (an [*mm*] stereodefect), and *type II* errors, arising from an isolated isotactic placement (an [*m*] stereodefect).[28] The [*mm*] stereoerrors are characteristic of either enantiofacial misinsertions or epimerization of the last inserted stereogenic center and are signatures of an enantiomorphic site control mechanism (Scheme 2). Isolated [*m*] stereoerrors can arise from either a chain end control mechanism or an enantiomorphic site control mechanism where site epimerization (i.e., chain migration without insertion)[70] or two sequential insertion errors such as site epimerization followed by chain epimerization lead to an isolated [*m*] stereoerror (Scheme 3). The relative percentage of the two types of errors (*I* and *II*) can be estimated from the percentages of [*mrrm*] and [*xmrx*] pentads with the *mm* = [*mrrm*] and the *m* defects = $^1/_2$[*xmrx*].

The influence of monomer concentration on the stereospecificity was investigated for catalysts derived from metallocenes **4** and **5**. As shown in Tables 1 and 2, the syndiospecificity of catalysts derived from metallocenes **4** and **5** increases with increasing monomer concentration.[19,28,31] For both catalysts this increase in the syndiotactic [*rrrr*] pentad with concentration is a consequence primarily of a strong decrease in the [*xrmx*] pentad. These observations are most consistent with an enantiomorphic site control mechanism, since one would not expect a concentration dependence on the stereospecificity for a chain-end control mechanism. The fact that the [*xrmx*] pentad decreases with increasing monomer concentration while the [*rmmr*] pentad is unchanged also suggests that epimerization of the growing chain is not a significant source of stereoerrors, in which case a stronger concentration dependence on the *rmmr* pentad would be expected.[71] Similar conclusions were reached by Bercaw for metallocenes **2a**.[19]

That the primary source of stereoerrors is due to isomerization of the site prior to monomer insertion is

Table 3. Calculated Probability Parameters Using Zr Systems 3−5/MAO[a]

catalyst	*P* (bar)	*a*	*c*	Af × 100
3	8.8[b]	0.984_7	0.148_8	4.43
4	8.8[b]	0.984_0	0.083_7	2.99
4	6.2	0.971_5	0.118_9	4.76
4	3.6[c]	0.985_6	0.149_7	5.59
5	8.8[b]	0.969_4	0.036_8	1.23
5	6.2	0.968_6	0.055_9	2.60
5	3.6	0.972_9	0.070_0	3.60

[a] [Al]:[M] = 1000:1; [M] = 2.5×10^{-5}; t = 20 min; T = 20 °C. [b] Liquid propylene. [c] t = 60 min.

further supported by statistical modeling of the pentad distributions using the model developed by Farina and Di Silvestro.[72,73] This analysis can be used to test various models for stereocontrol and to estimate the relative contributions of various sources of stereoerrors. In Farina's model, all possible pentads are described in terms of four probability parameters (*a*, *b*, *c*, *d*) which represent the events involved in the propagation steps. In the most general case, parameter *a* represents the probability that *at a given site* the stereogenic carbon of the entering monomeric unit assumes *a certain configuration*; parameter *b* is the probability that at the complementary site the stereogenic carbon of the entering monomeric unit assumes *the same configuration*. These two parameters represent the site stereospecificity. Parameters *c* and *d* are defined as the probabilities of successive monomer insertions at the catalyst sites related to parameters *a* and *b*, respectively. Consideration of the geometric properties of syndiospecific, C_s symmetric systems (e.g., **1a**, **2a**−**c**) allows a simplification of the model. In this case, it is assumed that the stereospecificities of the two enantiotopic sites are equal in magnitude ($a = 1 - b$) and that the probabilities of multiple insertions at each site are also equal ($c = d$). While this simplification is clearly reasonable for C_s symmetric systems, it is arguably less valid for catalysts **3**−**5** in which the two coordination sites are not enantiotopic. Nevertheless, to keep the number of adjustable parameters to a minimum and to evaluate the relative contributions of enantioface stereoerrors to those caused by backskip, we have assumed identical stereospecificities of the two sites in our statistical analysis. Thus, the pentad distribution was simulated using a series of expressions that are a function of two parameters, *a* and *c*.[74]

Values of *a* and *c* for metallocenes **3**−**5** were derived from simulations of the observed pentad distributions for each set of polymerization conditions (Table 3). An optimized set of simulated line intensities, as well as the corresponding parameters *a* and *c* for each case, were found through minimization of Hamilton's agreement factor

$$\mathrm{Af} = \sqrt{\frac{\sum (I_{\mathrm{obs}} - I_{\mathrm{calc}})^2}{\sum (I_{\mathrm{obs}})^2}} \qquad (1)$$

in which I_{obs} and I_{calc} are the observed and calculated intensities, respectively. The combined results are shown in Table 3. A table containing the experimental and simulated line intensities is included in the Supporting Information.

The magnitudes of the agreement factors obtained ($(1.23-5.59) \times 10^{-2}$) compared to those reported by Farina and Di Silvestro[72,73] imply that the experimental data are adequately modeled by this simplified Farina model where the two sites have similar stereospecificities ($a = 1 - b$) and probabilities of backskip ($c = d$). The simulations suggest that the stereospecificities for both sites are high ($a \geq 0.97$ in all cases) and point to multiple insertions at a given site as the major source of stereoerrors, as evidenced by the values of *c* which range from 4 to 16%. The observation that the calculated values of *c* increase with decreasing monomer concentration further supports that backskip is the major source of stereoerrors.

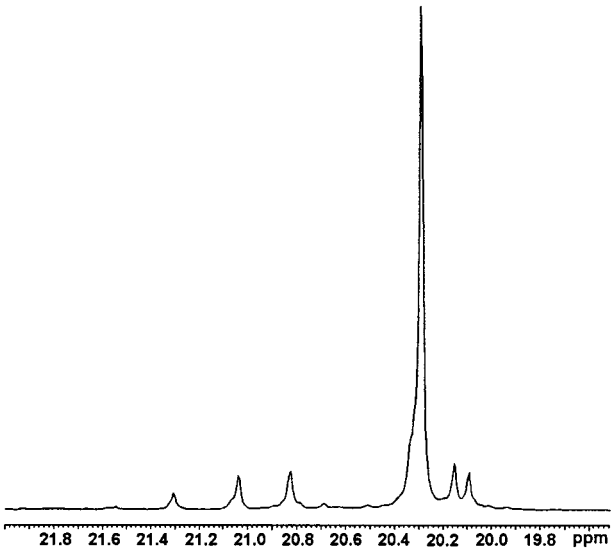


Figure 5. ^{13}C NMR (methyl region) of syndiotactic polypropylene synthesized using **5**/MAO.

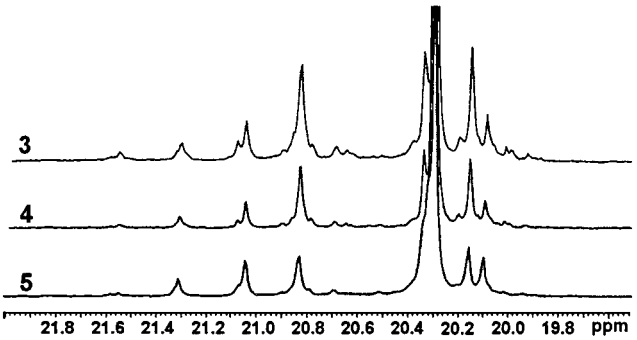


Figure 6. ^{13}C NMR (methyl region) of polypropylene samples synthesized using complexes **3**−**5**, activated by MAO at 20 °C in liquid propylene. Signals at 20.15 and 20.08 ppm correspond to *(r)rrrm(m)* and *(r)rrrm(r)* heptads, respectively.

Furthermore, the higher calculated values of *c* for **4** (0.084−0.160) relative to those for **5** (0.037−0.070) would suggest that the higher stereospecificity of catalysts derived from **5** is a consequence of less frequent backskip for this catalytic system. This conclusion is also supported by an inspection of the relative intensities of the resonances at 20.15 and 20.08 ppm, which have been assigned to the *(r)rrrm(r)* and *(r)rrrm(m)* heptads, respectively.[4] The fact that the *(r)rrrm(r)*/*(r)rrrm(m)* ratio is higher for polymers derived from **4** than those from **5** is also consistent with a higher degree of backskip for **4** (Figure 6).

The implication that the less highly substituted metallocene **4** is more prone to backskip than the 2-methyl substituted **5** might be explained by the higher productivities of **5** relative to **4**: if the olefin insertion rate for **5** were higher than **4** and the rates of backskip

roughly comparable, then a higher percentage of backskip errors would be expected for **4**. While the origin of this difference is not yet clear, it is clear that the presence of a methyl substituent in the 2-position results in an increase in syndiospecificity. Furthermore, the implication that this difference is a consequence of differing probabilities for multiple insertions at a given site provides an opportunity to modulate the nature and number of stereoerrors in syndiotactic polypropylenes by varying substituents in positions 3 and 2 of the indenyl ligand. Further studies along this line are in progress.

The variation in tacticities in these polymers is also manifested in differing in thermal properties: the degree of crystallinity, as indicated by the observed heats of fusion (ΔH_f), increases with increasing syndiotacticity (Table 1). The multiple melting peaks observed for these polymers are common to low-tacticity syndiotactic polypropylenes[59,75,76] and may at least partially result from the melting−recrystallization−remelting mechanism.[51,59,77]

In summary, we have shown that C_1 symmetric bridged cyclopentadienyl−indenylmetallocenes catalyze the syndiospecific polymerization of propylene. The introduction of a conformationally flexible substituent provides the ability to control the stereospecificity to give polymers with a range of tacticities. The syndiospecificities of these catalyst systems are sensitive to the choice of transition metal (Zr vs Hf), ligand substitution pattern, and the monomer concentration.

Experimental Section

General Considerations. All operations involving air-sensitive reagents and materials were carried out under nitrogen or argon atmosphere using standard Schlenk, vacuum, or drybox techniques. Solvents were dried and distilled under nitrogen prior to use or purified by passing through towers containing Q5 and alumina. Indene (Aldrich, tech.) was distilled in vacuo prior to use. Bromomethyltrimethylsilane (Gelest); *n*-BuLi, 6,6-dimethylfulvene, 2-methylindene, $ZrCl_4$ (99.9+%) (Aldrich); and $HfCl_4$ (99%) (Cerac) were used as received. NMR spectra were recorded using a Varian GX-400 NMR spectrometer and referenced against TMS or the residual protons of the deuterated solvents (^{1}H NMR: δ $CDCl_3$ = 7.26 ppm, CD_2Cl_2 = 5.36 ppm, C_6D_6 = 7.16 ppm; ^{13}C NMR: δ $CDCl_3$ = 77.0 ppm). Elemental analyses were obtained from E+R Microanalytical Laboratory, Inc., Parsippany, NJ.

3-(Trimethylsilylmethyl)indene (8). To a solution of indene (7.76 g, 66.8 mmol) in THF (50 mL) at 0 °C was added dropwise *n*-BuLi (27.0 mL of a 2.5 M solution in hexanes, 67.5 mmol), and the reaction mixture was stirred overnight at room temperature. The indenyllithium solution was added dropwise at −78 °C to a solution of bromomethyltrimethylsilane (11.2 g, 66.8 mmol) in THF (40 mL). After completed addition, the reaction mixture was gradually warmed to room temperature and stirred overnight. GC/MS analysis indicated the presence of an approximately 9:1 ratio of **8** as a 7:2 mixture of the 1- and 3-indenyl double bond isomers and the byproduct 1,3-bis(trimethylsilylmethyl)indene (**9**). The red solution was evaporated to dryness to give an off-red oil that was extracted with CH_2Cl_2 (100 mL) and filtered through Celite to remove LiBr. The solvent was evaporated, and the crude product was fractionally distilled in vacuo to give 6.82 g (50.5%) of **8** as a light yellow oil (bp 71−72 °C/35 mTorr) and 0.66 g (3.4%) of **9** as a dark yellow oil (bp 95 °C/35 mTorr). Compound **8** isomerizes during the workup and distillation to the single 3-indenyl isomer. **8**: ^{1}H NMR ($CDCl_3$, δ): 7.50−7.48 (m, 1H), 7.35−7.34 (m, 1H), 7.28−7.22 (m, 2H) (arom C*H*); 6.07 (s, br, 1H, α-C*H*); 3.38 (s, br, 2H, CH_2); 2.08 (s, 2H, Si−CH_2); 0.08 (s, 9H, Si−CH_3). ^{13}C NMR ($CDCl_3$, δ): 146.17, 144.38, 141.50 ($C_{quat.}$); 125.83, 125.70, 124.11, 123.41, 119.19 (*C*H); 37.63 (*C*H_2); 17.50 (Si−*C*H_2); −1.26 (3C, Si−*C*H_3). **9**: ^{1}H NMR ($CDCl_3$, δ): 7.38−7.36 (m, 1H), 7.30−7.17 (m, 3H) (arom C*H*); 5.99 (s, 1H, C*H*); 3.48−3.45 (m, 1H, C*H*); 1.99 (d, ^4J = 1.2 Hz, 2H, C−Si−CH_2); 1.30 (dd, ^2J = 14.6 Hz, ^3J = 4.2 Hz, 1H, CH−Si−CH_2); 0.62 (dd, ^2J = 14.6 Hz, ^3J = 11.0 Hz, 1H, CH−Si−CH_2); 0.05 (s, 9H, Si−CH_3); 0.04 (s, 9H, Si−CH_3). ^{13}C NMR ($CDCl_3$, δ): 151.26, 144.78, 139.53 ($C_{quat.}$); 132.75, 125.72, 124.38, 122.28, 119.19 (*C*H); 45.09 (*C*H); 19.36 (Si−*C*H_2); 17.26 (Si−*C*H_2); −0.53 (3C, Si−*C*H_3); −1.20 (3C, Si−*C*H_3).

1- and 3-(Trimethylsilylmethyl)-2-methylindene (10). To a solution of 2-methylindene (9.72 g, 74.7 mmol) in THF (80 mL) at 0 °C was added dropwise *n*-BuLi (30.2 mL of a 2.5 M solution in hexanes, 75.5 mmol), and the reaction mixture was stirred for 3 h at room temperature. The 2-methylindenyllithium solution was added dropwise at −78 °C to a solution of bromomethyltrimethylsilane (12.5 g, 74.7 mmol) in THF (50 mL). After completed addition, the reaction mixture was gradually warmed to room temperature and stirred overnight. GC/MS analysis indicated the presence of an approximately 8:1:1 ratio of **10** as a 1:1 mixture of the 1- and 3-indenyl double bond isomers, unreacted 2-methylindene, and the byproduct 1,3-bis(trimethylsilylmethyl)-2-methylindene (**11**). The red solution was evaporated to dryness to give an off-red oil that was extracted with CH_2Cl_2 (80 mL) and filtered through Celite to remove LiBr. The solvent was evaporated, and the crude product was fractionally distilled in vacuo to give 11.7 g (72.7%) of **10** as a light yellow oil (bp 77−78 °C/60 mTorr) and an approximately 1:1 mixture of the 1- and 3-indenyl isomers as shown by ^{1}H NMR. The distillation was continued and a second fraction (0.73 g) consisting of a mixture of **10** and **11** was obtained. No further attempts were made to obtain the byproduct **11** in pure form. ^{1}H NMR ($CDCl_3$, δ): 7.39−7.01 (m, 4 + 4H, arom C*H*, both isom); 6.47 (br s, 1H, *β*-C*H*, 1-Ind); 3.48−3.45 (m, 1H, C*H*, 1-Ind); 3.30 (s, 2H, CH_2, 3-Ind); 2.10 (s), 2.05 (s), 1.99 (s) (3 + 3 + 2H, C−CH_3, both isom; Si−CH_2, 3-Ind); 1.37 (dd, ^2J = 15.0 Hz, ^3J = 5.5 Hz, 1H, Si−CH_2, 1-Ind); 1.22 (dd, ^2J = 15.0 Hz, ^3J = 5.8 Hz, 1H, Si−CH_2, 1-Ind); 0.06 (s, 9H), −0.22 (s, 9H) (Si−CH_3, both isom). ^{13}C NMR ($CDCl_3$, δ): 151.01, 148.86, 147.44, 144.53, 142.63, 134.80, 134.56 (C_{quat}, both isom); 126.29, 126.08, 125.74, 123.42, 123.39, 123.11, 122.82, 119.67, 118.55 (*C*H, both isom); 48.95 (*C*H, 1-Ind); 42.37 (*C*H_2, 3-Ind); 16.89, 15.55, 15.33, 14.58 (Si-*C*H_2, *C*H_3, both isom); −0.20 (3C), −0.66 (3C) (Si−*C*H_3, both isom).

2-(Cyclopentadienyl)-2-(3-(trimethylsilylmethyl)indenyl)propane (12). To a solution of **8** (6.68 g, 33.0 mmol) in THF (50 mL) at 0 °C was added dropwise *n*-BuLi (13.3 mL of a 2.5 M solution in hexanes, 33.3 mmol), and the reaction mixture was stirred overnight at room temperature. The resulting solution was added dropwise at −78 °C to a solution of 6,6-dimethylfulvene (3.50 g, 33.0 mmol) in THF (60 mL). After completed addition, the reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was hydrolyzed with saturated ammonium chloride solution (150 mL) and diluted with Et_2O (100 mL). The aqueous layer was extracted with additional portions of Et_2O (2 × 50 mL), and the combined organic extracts were washed with water (2 × 100 mL) and dried over sodium sulfate. Evaporation of the solvents left an orange oil that solidified from a concentrated pentane solution to give 7.55 g (74.2%) of **12** as a partially oily orange solid. The product consists of an approximately 6:4 mixture of two cyclopentadienyl double bond isomers (1,3- and 1,4-Cp) as shown by ^{1}H NMR analysis. The remaining mother liquor was dried in vacuo to give an additional 1.45 g (14.2%) of **12** as a fairly pure orange oil; total yield 88.4%. ^{1}H NMR ($CDCl_3$, δ): 7.23−7.16 (m, 2 + 2H, Ind-C*H*, major + minor isomer); 7.04−6.99 (m, 1 + 1H, arom Ind-C*H*, maj + min); 6.95−6.93 (m, 1H, arom Ind-C*H*, maj); 6.84−6.82 (m, 1H, arom Ind-C*H*, min); 6.79−6.76 (m, 1H, Cp-C*H*, maj); 6.53−6.51 (m, 1H, Cp−C*H*, maj); 6.50−6.48 (m, 1H, Cp-C*H*, min); 6.37−6.36 (m, 1H, Cp-C*H*, min); 6.19−6.18 (m, 1H, Cp-C*H*, min); 5.99−5.98 (m, 1H, Cp-C*H*, maj); 5.94 (m, 1 + 1H, Ind−α-C*H*, maj + min); 3.61 (br s, 1H, Ind−C*H*, maj); 3.57 (br s, 1H, Ind−C*H*, min); 3.08 (d, ^3J = 1.2 Hz, Cp−CH_2, min); 3.04 (d, ^3J = 1.5 Hz, Cp−CH_2, maj); 1.97 (br s, 2 + 2H, Si−CH_2, maj + min); 1.29 (s, 3H, C−CH_3, min); 1.25 (s, 3H,

C−CH_3, maj); 0.98 (s, 3H, C−CH_3, maj); 0.96 (s, 3H, C−CH_3, min); 0.02 (s, 9 + 9H, Si−CH_3, maj + min). ^{13}C NMR ($CDCl_3$, δ): 158.15, 155.70 (2C), 146.62, 146.56, 145.87, 141.22, 141.14 ($C_{quat.}$, both isom); 133.86, 132.98, 132.08, 130.72, 129.09 (2C) (Cp−*C*H, both isom); 126.02, 125.95, 125.65, 124.26, 124.11, 123.97, 123.84, 123.82, 119.01, 118.92 (Ind−*C*H, both isom); 59.22, 57.36 (Ind−*C*H, both isom); 40.88, 40.50, 39.31, 38.20 (Cp−CH_2 + *C*−CH_3, both isom); 28.99, 27.25, 23.40, 22.84 (C−*C*H_3, both isom); 17.37 (1 + 1C, Si−*C*H_2, both isom); −1.24 (3 + 3C, Si−*C*H_3, both isom).

2-(Cyclopentadienyl)-2-(2-methyl-3-(trimethylsilylmethyl)indenyl)propane (13). To a solution of **10** (10.6 g, 48.8 mmol) in THF (50 mL) at 0 °C was added dropwise *n*-BuLi (19.7 mL of a 2.5 M solution in hexanes, 49.3 mmol), and the reaction mixture was stirred for 4 h at room temperature. The resulting red solution was added dropwise at −78 °C to a solution of 6,6-dimethylfulvene (5.18 g, 48.8 mmol) in THF (60 mL). After completed addition, the reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was hydrolyzed with saturated ammonium chloride solution (200 mL) and diluted with Et_2O (100 mL). The aqueous layer was extracted with additional portions of Et_2O (2 × 60 mL) and the combined organic extracts were washed with water (3 × 100 mL) and dried over sodium sulfate. Evaporation of the solvents and drying in vacuo gave 15.3 g (97.3%) of fairly pure **13** as an approximately 6:4 mixture of two cyclopentadienyl double bond isomers (1,3- and 1,4-Cp) as shown by ^{1}H NMR analysis. The product was used in the subsequent steps without further purification. ^{1}H NMR ($CDCl_3$, δ): 7.24−7.20 (m, 2H), 7.10−7.08 (m, 3H), 7.00−6.97 (m, 2H), 6.92−6.90 (m, 1H) (arom Ind−C*H*, both isomers); 6.82−6.80 (m, 1H), 6.55−6.54 (m, 1H) (Cp−C*H*, maj isom); 6.51−6.49 (m, 1H), 6.39−6.38 (m, 1H), 6.17 (br s, 1H) (Cp−C*H*, min isom); 5.95 (t, ^3J = 1.6 Hz, 1H, Cp−C*H*, maj isom); 3.50 (s, 1H, Ind−C*H*, maj isom); 3.48 (s, 1H, Ind−C*H*, min isom); 3.09 (s, 2H, Cp−CH_2, min isom); 3.02 (s, 2H, Cp−CH_2, maj isom); 1.98−1.96 (m, 2 + 2H, Si−CH_2, both isom); 1.83 (s, 3H, α-CH_3, min isom); 1.80 (s, 3H, α-CH_3, maj isom); 1.22 (s, 3H, C−CH_3, maj isom); 1.17 (s, 6H, CH_3−C−CH_3, min isom); 1.12 (s, 3H, C−CH_3, maj isom); 0.05 (s, 9 + 9H, Si−CH_3, both isom). ^{13}C NMR ($CDCl_3$, δ): 158.90, 156.30, 147.31, 147.15, 144.99, 137.67, 137.41, 136.43, 136.17, 135.12 ($C_{quat.}$, both isom); 133.77, 133.29, 132.13, 130.53, 126.04, 125.98, 125.35, 124.38, 124.14, 123.68, 122.85, 122.69, 118.09, 118.04 (Ind−*C*H, Cp−*C*H, both isom); 62.10 (Ind−*C*H, min isom); 60.23 (Ind−*C*H, maj isom); 40.73 (Cp−*C*H_2, maj isom); 40.55 (Cp−*C*H_2, min isom); 39.73 (C_{quat}, maj isom); 38.58 (C_{quat}, min isom); 26.81, 26.40 (*C*H_3−C−*C*H_3, min isom); 26.28, 24.62 (*C*H_3−C−*C*H_3, maj isom); 16.02 (α-*C*H_3, min isom); 15.98 (α-*C*H_3, maj isom); 15.53 (1 + 1C, Si−*C*H_2, both isom); −0.60 (3 + 3C, Si−*C*H_3, both isom).

3-Ethylindene (14). The synthesis of **14** was performed following the procedure previously described for **8**. Distillation under reduced pressure gave an 88:12 mixture of the target compound contaminated with unreacted indene. Approximately 6.5% of indene remained in the redistilled product that was used as such in the subsequent steps. The ^{1}H NMR spectrum of **14** is consistent with that reported in the literature.[78]

2-(Cyclopentadienyl)-2-(3-ethylindenyl)propane (15). To a solution of **14** (3.45 g, 23.9 mmol, containing approximately 6% of indene) in THF (30 mL) at 0 °C was added dropwise *n*-BuLi (9.7 mL of a 2.5 M solution in hexanes, 24.3 mmol), and the reaction mixture was stirred for 7 h at room temperature. The resulting solution was added dropwise at −78 °C to a solution of 6,6-dimethylfulvene (2.54 g, 23.9 mmol) in THF (30 mL). After completed addition, the reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was hydrolyzed with saturated ammonium chloride solution (150 mL) and diluted with Et_2O (150 mL). The organic extract was washed with water (2 × 150 mL) and dried over sodium sulfate. Evaporation of the solvents left 5.84 g of a yellow oil consisting of fairly pure **15** as a 6:4 mixture of two cyclopentadienyl double bond isomers (1,3- and 1,4-Cp) as shown by ^{1}H NMR analysis. Crystallization from pentane at −45 °C gave 3.53 g (59.0%) of pure **15** as an off-yellow oily solid and a 1:1 mixture of the Cp isomers. ^{1}H NMR ($CDCl_3$, δ): 7.28−7.22 (m, 2 + 2H, Ind−C*H*, maj + min isomer); 7.07−7.02 (m, 1 + 1H, arom Ind−C*H*, maj + min); 6.97−6.96 (m, 1H, arom Ind−C*H*, maj); 6.87−6.85 (m, 1H, arom Ind−C*H*, min); 6.82−6.80 (m, 1H, Cp−C*H*, maj); 6.56−6.55 (m, 1H, Cp−C*H*, maj); 6.51−6.50 (m, 1H, Cp−C*H*, min); 6.39−6.37 (m, 1H, Cp−C*H*, min); 6.20 (m, 1H, Cp−C*H*, min); 6.14 (s, 1 + 1H, Ind−α-C*H*, maj + min); 6.01−6.00 (m, 1H, Cp−C*H*, maj); 3.61 (s, 1H, Ind−C*H*, maj); 3.58 (s, 1H, Ind−C*H*, min); 3.10 (s, 2H, Cp−CH_2, min); 3.06 (s, 2H, Cp−CH_2, maj); 2.57−2.50 (m, 2 + 2H, CH_3−CH_2, maj + min); 1.31−1.25 (overlapping signals, 3 + 3 + 3 + 3H, CH_3−CH_2, maj + min, C−CH_3, maj + min); 0.98 (s, 3H, C−CH_3, maj); 0.97 (s, 3H, C−CH_3, min). ^{13}C NMR ($CDCl_3$, δ): 158.30, 155.62, 146.06, 146.01, 145.91, 145.86, 145.80 (2C) (C_{quat}, both isom); 133.90, 132.91, 132.07, 130.73, 129.97 (2C) (Cp−*C*H, both isom.); 126.16, 126.10, 125.70, 124.38, 124.31, 124.20, 124.12, 124.06, 118.59, 118.48 (Ind−*C*H, both isom); 59.10, 57.24 (Ind−*C*H, both isom); 40.89, 40.49 (Cp−*C*H_2 both isom); 39.14, 38.04 (*C*−CH_3, both isom); 28.83, 27.06, 23.32, 22.64 (C−*C*H_3, both isom); 20.66 (1 + 1C, CH_3−*C*H_2, both isom); 12.50 (1 + 1C, *C*H_3−CH_2, both isom).

[Isopropylidene(cyclopentadienyl)(3-ethylindenyl)]-zirconium Dichloride (3). To a solution of **15** (1.15 g, 4.59 mmol) in Et_2O (100 mL) at 0 °C was added dropwise *n*-BuLi (3.7 mL of a 2.5 M solution in hexanes, 9.25 mmol). The resulting dark orange solution was stirred for 5 h at room temperature and cooled to 0 °C. $ZrCl_4$ (1.07 g, 4.59 mmol) was added portionwise during a period of 3 min. The reaction mixture was stirred overnight at room temperature, giving a bright orange suspension. The solvents were removed in vacuo, and the remaining solid was extracted with CH_2Cl_2 (80 mL) and filtered through Celite to remove LiCl. The solvent was evaporated, and the remaining orange/red powder was suspended in Et_2O (80 mL) and cooled to −45 °C. The precipitate was isolated after cannula transfer of the mother liquor and recrystallized from CH_2Cl_2 (80 mL) layered with pentane (20 mL) at −45 °C to give 0.94 g (49.9%) of **14** as a bright orange crystalline solid. A second crop of 0.06 g of suitable for X-ray structure analysis was obtained by slow cooling of the concentrated mother liquor (pentane removed) to −45 °C. Anal. Calcd for $C_{19}H_{20}ZrCl_2$: C, 55.60; H, 4.91. Found: C, 55.46; H, 4.89. ^{1}H NMR (CD_2Cl_2, δ): 7.64−7.62 (m, 1H), 7.52−7.50 (m, 1H), 7.30−7.27 (m, 1H), 7.00−6.96 (m, 1H) (arom Ind−C*H*); 6.53−6.51 (m, 1H), 6.46−6.44 (m, 1H), 5.83−5.81 (m, 1H) (Cp−C*H*); 5.81 (s, AB*M*X_3, 1H, Ind−α-C*H*); 5.56−5.54 (m, 1H, Cp−C*H*); 2.91−2.74 (m, *AB*MX_3, 2H, CH_3−CH_2); 2.17 (s, 3H), 1.91 (s, 3H) (CH_3−C−CH_3); 1.23−1.19 (m, ABMX_3, 3H, CH_3−CH_2). ^{13}C NMR ($CDCl_3$, δ): 127.95 (C_{quat}); 126.70; 125.82; 124.27 (arom Ind−*C*H); 123.91 (arom Ind−*C*H); 121.20 (arom Ind−*C*H); 120.47 (arom Ind−*C*H); 120.20; 119.44 (C_{quat}); 113.21; 105.87; 104.48 (*C*H); 99.73 (C_{quat}); 39.44 (CH_3−*C*−CH_3); 26.55, 25.71 (CH_3−C−CH_3); 21.01 (CH_2−CH_3); 14.47 (3C, CH_2−CH_3).

[Isopropylidene(cyclopentadienyl)(3-(trimethylsilylmethyl)indenyl)]zirconium Dichloride (4). To a solution of **12** (1.52 g, 4.93 mmol) in Et_2O (60 mL) at 0 °C was added dropwise *n*-BuLi (4.0 mL of a 2.5 M solution in hexanes, 9.90 mmol). The resulting dark orange solution was stirred for 4 h at room temperature and cooled to 0 °C. $ZrCl_4$ (1.15 g, 4.93 mmol) was added portionwise during a period of 3 min. The reaction mixture was stirred overnight at room temperature, giving a deep red suspension. The solvents were removed in vacuo to give an orange/red solid that was extracted with CH_2Cl_2 (70 mL) and filtered through Celite to remove LiCl. The solvent was evaporated, and the remaining dark orange/red solid was extracted with Et_2O (60 mL). The deep red solution was concentrated and cooled to −15 °C to provide 0.67 g (29.0%) of **4** as a bright orange crystalline solid that was recrystallized from the same solvent for analysis and polymerization runs. Anal. Calcd for $C_{21}H_{26}SiZrCl_2$: C, 53.81; H, 5.59. Found: C, 53.68; H, 5.57. ^{1}H NMR (CDCl3, δ): 7.59−7.57 (m, 1H), 7.44−7.42 (m, 1H), 7.28−7.25 (m, 1H), 6.97 (ddd, ^3J = 8.9 Hz, 6.6 Hz, ^4J = 1.0 Hz, 1H) (arom Ind−C*H*); 6.57−6.54 (m, 1H), 6.52−6.49 (m, 1H), 5.83−5.81 (m, 1H) (Cp−C*H*);

5.49 (s, 1H, Ind−α-C*H*); 5.47−5.45 (m, 1H, Cp−C*H*); 2.27 (s, 2H, Si−CH_2); 2.20 (s, 3H), 1.89 (s, 3H) (CH_3−C−CH_3); −0.04 (s, 9H, Si−CH_3). ^{13}C NMR ($CDCl_3$, δ): 128.23 (C_{quat}); 126.41 (arom Ind−*C*H); 125.80 (C_{quat}); 125.03, 124.43, 123.11 (arom Ind−*C*H); 120.14 (2C, Cp−*C*H); 119.75, 118.10 (C_{quat}); 111.84, 105.29, 103.44 (*C*H); 97.79 (C_{quat}); 38.85 (CH_3−*C*−CH_3); 26.38, 25.61 (*C*H_3−C−*C*H_3); 17.82 (Si−*C*H_2); −1.42 (3C, Si−*C*H_3). ^{1}H NMR (C_6D_6, δ): 7.28−7.26 (m, 1H), 7.22−7.19 (m, 1H), 7.14−7.10 (m, 1H), 6.79−6.75 (m, 1H) (arom Ind−C*H*); 6.40−6.38 (m, 1H), 6.31−6.29 (m, 1H), 5.38−5.36 (m, 1H) (Cp−C*H*); 5.29 (s, 1H, Ind−α-C*H*); 5.08−5.06 (m, 1H, Cp−C*H*); 2.45 (AB, 1H, ^2J = 14.5 Hz, Si−CH_2); 2.27 (AB, 1H, ^2J = 14.5 Hz, Si−CH_2); 1.57 (s, 3H), 1.32 (s, 3H) (CH_3−C−CH_3); −0.12 (s, 9H, Si−CH_3).

[Isopropylidene(cyclopentadienyl)(3-(trimethylsilylmethyl)indenyl)]hafnium Dichloride (6). To a solution of **12** (1.70 g, 5.51 mmol) in Et_2O (100 mL) at 0 °C was added dropwise *n*-BuLi (4.4 mL of a 2.5 M solution in hexanes, 11.1 mmol). The resulting dark orange solution was stirred for 4 h at room temperature and cooled to 0 °C. $HfCl_4$ (1.76 g, 5.51 mmol) was added portionwise during a period of 3 min. The reaction mixture was stirred overnight at room temperature, giving a dark yellow suspension. The solvents were removed in vacuo to give an orange solid that was extracted with CH_2Cl_2 (80 mL) and filtered through Celite to remove LiCl. The solvent was evaporated, and the remaining bright orange solid was extracted with Et_2O (50 mL). The deep orange solution was concentrated and cooled to −15 °C to provide 1.19 g (38.8%) of **6** as an orange crystalline solid. Anal. Calcd for $C_{21}H_{26}SiHfCl_2$: C, 45.37; H, 4.71. Found: C, 45.15; H, 4.82. ^{1}H NMR ($CDCl_3$, δ): 7.61−7.58 (m, 1H), 7.39−7.37 (m, 1H), 7.24−7.20 (m, 1H), 6.94−6.91 (m, 1H) (arom Ind−C*H*); 6.51−6.48 (m, 1H), 6.44−6.42 (m, 1H), 5.75−5.73 (m, 1H) (Cp-C*H*); 5.45 (s, 1H, Ind−α-C*H*); 5.43−5.41 (m, 1H, Cp−C*H*); 2.25 (s, 2H, Si−CH_2); 2.19 (s, 3H), 1.90 (s, 3H) (CH_3−C−CH_3); −0.05 (s, 9H, Si−CH_3). ^{13}C NMR ($CDCl_3$, δ): 127.16 (C_{quat}); 126.10, 124.85, 124.31, 123.07 (arom Ind−*C*H); 122.76, 120.16 ($C_{quat.}$); 119.08, 119.01 (Cp−*C*H); 117.92 (C_{quat}); 110.08, 103.00, 100.96 (*C*H); 98.69 (C_{quat}); 39.10 (CH_3−*C*−CH_3); 26.59, 25.78 (*C*H_3−C−*C*H_3); 17.64 (Si−*C*H_2); −1.41 (3C, Si−*C*H_3).

[Isopropylidene(cyclopentadienyl)(3-(trimethylsilylmethyl)-2-methylindenyl)]zirconium Dichloride (5). To a solution of **13** (3.05 g, 9.46 mmol) in Et_2O (120 mL) at 0 °C was added dropwise *n*-BuLi (7.6 mL of a 2.5 M solution in hexanes, 19.0 mmol). The resulting orange solution was stirred for 4 h at room temperature and cooled to 0 °C. $ZrCl_4$ (2.20 g, 9.44 mmol) was added portionwise during a period of 3 min. The reaction mixture was stirred overnight at room temperature, giving a dark red suspension. The solvents were removed in vacuo to give a red solid that was extracted with CH_2Cl_2 (80 mL) and filtered through Celite to remove LiCl. The solvent was evaporated, and the remaining orange solid was suspended in Et_2O (80 mL) and cooled to −78 °C. The orange precipitate was isolated after cannula transfer of the mother liquor, which was concentrated and cooled to −45 °C to provide a second crop. The combined precipitates were dissolved in hot toluene (50 mL). Concentration and cooling to −45 °C gave 1.44 g (31.5%) of **5** as a bright orange powder. Anal. Calcd for $C_{22}H_{28}SiZrCl_2$: C, 54.74; H, 5.85. Found: C, 54.57; H, 6.10. ^{1}H NMR ($CDCl_3$, δ): 7.72−7.70 (m, 1H), 7.44−7.42 (m, 1H), 7.28−7.24 (m, 1H), 6.95−6.91 (m, 1H) (arom Ind−C*H*); 6.57−6.55 (m, 1H), 6.47−6.45 (m, 1H), 5.81−5.79 (m, 1H), 5.59−5.57 (m, 1H) (Cp−C*H*); 2.36 (AB, 1H, ^2J = 15.0 Hz, Si−CH_2); 2.30 (s, 3H, Ind−α-CH_3); 2.25 (AB, 1H, ^2J = 15.0 Hz, Si−CH_2); 2.12 (s, 3H), 2.09 (s, 3H) (CH_3−C−CH_3); −0.02 (s, 9H, Si−CH_3). ^{13}C NMR ($CDCl_3$, δ): 127.60, 126.03 (C_{quat}); 125.82 (arom Ind−*C*H); 124.78 (C_{quat}); 124.50, 123.35, 120.81 (arom Ind−*C*H); 119.59 (2C, Cp−*C*H); 119.30, 117.55 ($C_{quat.}$); 105.84, 101.74 (Cp−*C*H); 93.38 ($C_{quat.}$); 40.93 (CH_3−*C*−CH_3); 28.83, 28.14 (*C*H_3−C−*C*H_3); 17.24 (Si−*C*H_2); 15.96 (Ind−α-*C*H_3) −0.51 (3C, Si−*C*H_3). ^{1}H NMR (C_6D_6, δ): 7.36−7.31 (m, 2H), 7.17−7.13 (m, 1H), 6.77−6.73 (m, 1H) (arom Ind−C*H*); 6.39−6.36 (m, 1H), 6.30−6.28 (m, 1H), 5.40−5.38 (m, 1H), 5.19−5.17 (m, 1H) (Cp-C*H*); 2.47 (AB, 1H, ^2J = 15.0 Hz, Si−CH_2); 2.20 (AB, 1H, ^2J = 15.0 Hz, Si−CH_2); 1.89 (s, 3H, Ind−α-CH_3); 1.69 (s, 3H), 1.57 (s, 3H) (CH_3−C−CH_3); −0.15 (s, 9H, Si−CH_3).

[Isopropylidene(cyclopentadienyl)(3-trimethylsilylmethyl-2-methylindenyl)]hafnium Dichloride (7). To a solution of **13** (2.09 g, 6.48 mmol) in Et_2O (120 mL) at 0 °C was added dropwise *n*-BuLi (5.2 mL of a 2.5 M solution in hexanes, 13.0 mmol). The resulting orange solution was stirred for 3 h at room temperature and cooled to 0 °C. $HfCl_4$ (2.08 g, 6.48 mmol) was added portionwise during a period of 2 min. The reaction mixture was stirred overnight at room temperature, giving a yellow suspension. The solvents were removed in vacuo to give a yellow/orange solid that was extracted with CH_2Cl_2 (80 mL) and filtered through Celite to remove LiCl. The solvent was evaporated, and the remaining off-yellow solid was suspended in Et_2O (40 mL) and cooled to −45 °C. The bright yellow precipitate was isolated after cannula transfer of the mother liquor and crystallized from a 1:1 mixture of toluene/pentane (60 mL) to give 1.04 g (28.2%) of **7** as yellow/orange crystals. Anal. Calcd for $C_{22}H_{28}SiHfCl_2$: C, 46.36; H, 4.95. Found: C, 46.26; H, 4.78. ^{1}H NMR ($CDCl_3$, δ): 7.75−7.72 (m, 1H), 7.40−7.38 (m, 1H), 7.23−7.19 (m, 1H), 6.91−6.88 (m, 1H) (arom Ind−C*H*); 6.51−6.49 (m, 1H), 6.41−6.39 (m, 1H), 5.74−5.72 (m, 1H), 5.57−5.55 (m, 1H) (Cp−C*H*); 2.34 (AB, 1H, ^2J = 15.0 Hz, Si−CH_2); 2.28 (s, 3H, Ind−α-CH_3); 2.23 (AB, 1H, ^2J = 15.0 Hz, Si−CH_2); 2.16 (s, 3H), 2.11 (s, 3H) (CH_3−C−CH_3); −0.03 (s, 9H, Si−CH_3). ^{13}C NMR ($CDCl_3$, δ): 126.57 (C_{quat}); 125.50, 124.42, 124.30, 123.35 (arom Ind−*C*H); 123.00, 122.32 (C_{quat}); 119.93 (Cp−*C*H); 119.77 (C_{quat}); 118.50 (Cp−*C*H); 117.46 (C_{quat}); 103.16, 99.24 (Cp−*C*H); 94.48 ($C_{quat.}$); 40.95 (CH_3−*C*−CH_3); 29.03, 28.27 (*C*H_3−C−*C*H_3); 17.00 (Si−*C*H_2); 15.78 (Ind−α-*C*H_3) −0.51 (3C, Si−*C*H_3).

Polymerization Procedures and Polymer Fractionation. Toluene, gaseous propylene (Matheson, 99.5%), and liquid propylene (Amoco, 99.5% or Scott Specialty Gases, 99.5%) were purified by passing through towers containing Q5 and alumina prior to use. Methylaluminoxane (Akzo Nobel, MMAO type 4, solution in toluene) was dried in vacuo before use. Polymerizations were carried out in a 300 mL Parr reactor equipped with a mechanical stirrer. Polymerization temperature was controlled via an ethylene glycol/water cooling loop. Catalyst solutions were prepared in a drybox by dissolving the metallocenes in toluene to give stock solutions of c = (0.9−2.6) × 10^{-3} M. The desired amount of dry MAO was dissolved in toluene followed by addition of an appropriate aliquot of the metallocene solution to give a total volume of 20 mL (polymerizations in liquid propylene) or 5 mL (polymerizations in gaseous propylene). The catalyst solutions were stirred for at least 3 min at room temperature prior to injection. The evacuated reactor was backfilled with N_2 and flushed three times with gaseous propylene before introducing the monomer. For bulk polymerizations the reactor was filled with 100 mL of liquid propylene and brought to the desired polymerization temperature. The polymerization was started by injecting the catalyst solution under argon pressure and stirred at 1000 rpm for 20 min. For solution polymerizations the reactor was filled with 95 mL of toluene and equilibrated with gaseous propylene for at least 1 h. The polymerization was started by injecting the catalyst solution under propylene pressure and stirred at 1450 rpm for 20−60 min. All polymerizations were quenched by injection of 20 mL of MeOH under argon pressure. The polymers were stirred overnight in 5% HCl/MeOH, filtered, washed 3 × 50 mL each with MeOH, saturated $NaHCO_3$ solution, water, and MeOH, and dried in a vacuum oven at 50 °C to constant weight. Fractionations of the polymer samples were carried out in a Kumigawa extraction apparatus. Approximately 2.0 g of polymer was extracted into 150 mL of refluxing Et_2O for 24 h. The Et_2O-soluble polymer was precipitated into MeOH, and both fractions were dried in a vacuum oven. The insoluble polymer was further extracted with refluxing heptane and treated accordingly.

Polymer Analysis. ^{13}C NMR spectra of the polypropylene samples were obtained from solutions of 80−100 mg of polymer either in $C_2D_2Cl_4$ or in a 1:3 mixture of $C_2D_2Cl_4$ (lock solvent) and $C_2H_2Cl_4$ at 100 °C using a Varian VXR-300 NMR spectrometer and 5 mm NMR tubes. The [*rrrr*] methyl signal of

polypropylene ($\delta = 20.29$ ppm) was used as internal reference. The spectra were recorded using a calibrated 90° pulse, and at least 3000 scans were obtained. The normalized signal integral data were extracted from deconvolution experiments. The melting temperatures and enthalpies were determined using a Perkin-Elmer DSC 7 differential scanning calorimeter. The samples were annealed by cooling from 200 to 25 °C at 10 °C/min and analyzed with a heating rate of 10 °C/min. Molecular weights and molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C ALC/GPC instrument equipped with two Polymer Laboratories PLGEL 10 μm mixed-B columns and differential refractive index detector in 1,2,4-trichlorobenzene at 139 °C (sample concentration 0.067% w/v, flow rate 1.0 mL/min). The calibration was made by using polypropylene broad standards. Alternatively, a Polymer Laboratories PL-GPC210 equipped with PLGEL 20 μm mixed-A columns and PD2040 precision detectors was used for the analysis.

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Supporting Information Available: Tables containing calculated and observed pentad distributions, details of crystal structure determination, and tables of bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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