Influence of Alkyl Substituents on the Polymerization Behavior of Asymmetric Ethylene-Bridged Zirconocene Catalysts[†]

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A series of substituted indenyl−fluorenyl asymmetric ethylene-bridged ligands have been prepared from the reaction of 1-(9-fluorenyl)-2-bromoethane and the lithium salt of the desired indenyl moiety. The ligands have been converted to the corresponding substituted asymmetric ethylene-bridged metallocenes (M = Zr, Hf). These metallocenes have been evaluated as catalyst precursors for the polymerization of ethylene and propylene. The influence of substitution on the selectivity of the propylene polymerization has been studied. The metallocene [1-(9-fluorenyl)-2-(2,4,7-trimethyl-1-indenyl)ethane]zirconium dichloride was found to produce highly isotactic polypropylene with an [*mmmm*] value of 86%.

Introduction

Following the discoveries that group 4 metallocenes when activated by a cocatalyst were useful systems for the polymerization of α-olefins,[1] much work has been done in the field of Ziegler−Natta type catalysts. One area of special interest is that of stereochemical control in the polymerization of propylene, which can be polymerized to give polypropylene (PP) with different types of stereoregularity (tacticity): atactic, syndiotactic, and isotactic PP. In the early 1980s Ewen et al.[2] and Kaminsky et al.[3] independently discovered that the bridged C_2-symmetric *rac*-ethylenebis(tetrahydroindenyl) dichloro complexes of titanium and zirconium, respectively, produced isotactic polypropylene when activated with MAO. Spaleck et al. subsequently studied the effects of placing substituents at key positions on the indenyl fragments of C_2-symmetric complexes in order to produce more highly isotactic polypropylene.[4] They found that substitution at the 2- and 4-positions of the indenyl rings could greatly bias the degree of isotacticity obtained.

Asymmetric C_1-symmetric catalysts have been synthesized and found to produce polypropylene with microstructures varying from stereoblock[5−7] to hemiso-

Scheme 1

3a
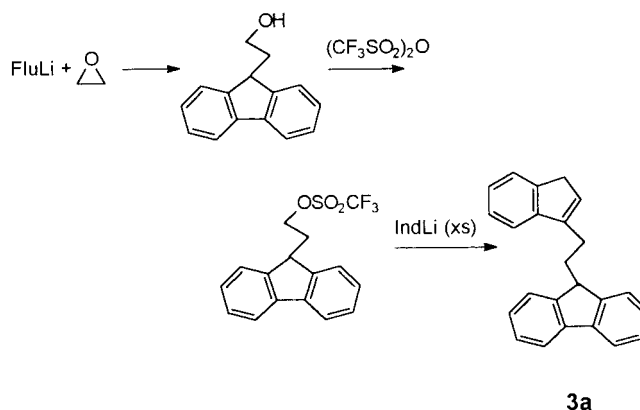
tactic,[8,9] syndiotactic,[9,10] atactic,[9,11] or isotactic.[9,12,13] Most of these compounds involved single-atom carbon or silicon bridges. In 1994 Rieger et al.[13] published a route to asymmetric ethylene-bridged zirconocenes containing indenyl and fluorenyl fragments (Scheme 1). They also varied substitution on the ethylene bridge. The unsubstituted system [1-(η^5-9-fluorenyl)-2-(η^5-1-

† Presented at the XVIII International Conference of Organometallic Chemistry in Munich, Germany, on Aug 16-21, 1998. See Book of Abstracts A175.

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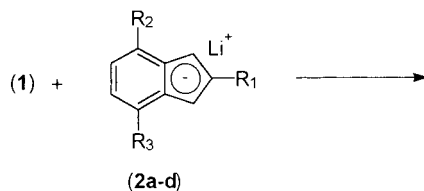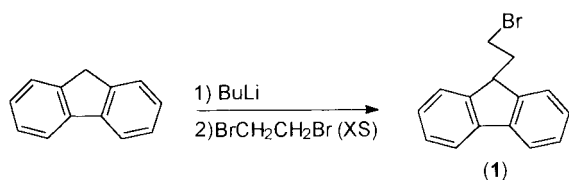
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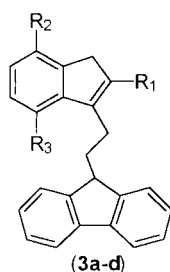
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Scheme 2

(2a-d)

2a = $R_{1,2,3}$, = H
2b = R_1 = Me; $R_{2,3}$ = H
2c = R_1 = H; $R_{2,3}$ = Me
2d = $R_{1,2,3}$ = Me

(3a-d)

3a = $R_{1,2,3,4}$ = H
3b = R_1 = Me; $R_{2,3}$ = H
3c = R_1 = H; $R_{2,3}$ = Me
3d = $R_{1,2,3}$ = Me

Scheme 3

(3a,b,c,d)

3a = $R_{1,2,3}$ = H
3b = R_1 = Me; $R_{2,3}$ = H
3c = R_1 = H; $R_{2,3}$ =Me
3d = $R_{1,2,3}$ = Me

(4a,b,c,d)

4a = $R_{1,2,3}$ = H
4b = R_1 = Me; $R_{2,3}$ = H
4c = R_1 = H; $R_{2,3}$ = Me
4d = $R_{1,2,3}$ = Me

**Table 1. Polymerization of Ethylene with
Asymmetric Zirconocenes Activated with MAO[a]**

cat. precursor	yield (g)	$10^{-7}A^b$
4b	0.665	9.7
4c	0.430	6.3
4d	0.661	9.6
4a	0.100	1.5

[a] Polymerization conditions: [Zr] = 5 μM; Al/Zr = 4000/1; time of polymerization 6 min; temperature 50 °C; pressure 15 psi. [b] A (activity) = g of polymer/((mol of Zr)([C$_2$])h).

indenyl)ethane]zirconium dichloride (**4a**) was shown to be moderately isospecific. The goal of the present research was to develop a more general synthetic route to this type of *ansa*-metallocene and to place substituents at key positions in order to study the stereochemical directing effects of such substitution, with the aim of producing isotactic polypropylene.
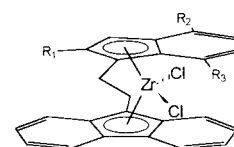
Results and Discussion

Synthesis of Catalyst Precursors. We have developed an alternative route to asymmetric ethylene-bridged ligands compared to that published by Rieger et al. The ligands were prepared according to Scheme 2. 1-(9-Fluorenyl)-2-bromoethane (**1**) was prepared by modification of a literature procedure.[14] The lithium salts of the appropriately substituted indene moieties were then reacted with **1**. This synthesis offers several advantages over that used by Rieger et al. in that the synthesis is shorter, it does not require an excess of the indene, it avoids the use of ethylene oxide, and the fluorenyl intermediate (bromide vs triflate) is stable and isolable. The indene moieties were prepared by literature procedures. It was of particular interest to determine the effect of the different methyl group substitutions in the ligands **3b–d** on propylene polymerization. The new ligands were converted to their corresponding metallocenes **4b–d** (Scheme 3). The ligands were deprotonated with 2 equiv of *n*-butyllithium in diethyl ether

followed by reaction with $^1/_2$ equiv of zirconium or hafnium tetrachloride. The complexes were recrystallized from toluene or dichloromethane.

Ethylene Polymerizations. The present zirconocene precursors when activated with MAO are very effective ethylene polymerization catalysts, and activities of 10^7g/ ((mol of Zr)([C$_2$])h) were obtained (Table 1). The lowest value was found for the unsubstituted precursor **4a**, suggesting no steric hindrance for complexation and for migratory insertion of the ethylene monomer in the case of **4b–d**. A single methyl substituent in **4b** raised the activity versus that of **4a** 6-fold. Similar increases have been reported for methyl-substituted zirconocenes/MAO for ethylene polymerization by Ewen et al.[9a] and for methyl-substituted indenyl titanium precursors for syndiospecific polymerization of styrene by Ready et al.[15]

Propylene Polymerizations. A range of temperatures and pressures were used to study their effect on the propylene polymerization behavior of **4b–d**. As expected, the polymerization activity of each precursor increases with increase in T_p (temperature of polymerization) when activated by MAO (Table 2). All of the activities obtained in Table 2 are very high ((0.6–4.8)

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Table 2. Polymerization of Propylene with Asymmetric Zirconocenes Activated with MAO[a]

cat. precursor	temp (°C)	yield (g)	$10^{-7}A$[b]	T_m (°C)	mol wt	[*mmmm*][c]
4b	20	7.9	0.63			7
4b	70	5.3	3.02	ca. 80		48
4c	20	8.0	0.63			5
4c	70	2.0	1.10			14
4d	20	17	1.40	132	9000	86
4d	70	8.5	4.80	124	4500	80

[a] Polymerization conditions: [Zr] = 25 μM; Al/Zr = 4000/1; time of polymerization 1 h; pressure 30 psi. [b] A (activity) = g of polymer/((mol of Zr)([C$_3$])h). [c] Equal to [*mmmm*] (%) determined by ^{13}C NMR at 80 °C in C$_6$D$_5$Cl.

$\times\ 10^7$ g PP/((mol of Zr)([C$_3$])h)) and are comparable to those of previously reported high-performance catalysts.[4]

It is very interesting that polypropylenes having different steric microstructures were produced by the present three asymmetric *ansa*-zirconocenes **4b**−**d**. The precursor **4b** has methyl substitution at the 2-position of indene. When activated with MAO at T_p = 50 °C, it gave PP with [*mmmm*] = 44% and $T_m \approx$ 80 °C.[16] At a higher T_p of 70 °C, a comparable homosteric meso pentad of 48% was obtained and no noticeable effect on T_m was observed. However, polymerization at 20 °C afforded less stereoregular PP without any hint of crystallinity. In other words, the polymerization was less stereospecific at lower T_p. This is in contrast to the polymerization of propylene catalyzed by C_2-symmetric catalysts which generally exhibit increased stereospecificity with a decrease of T_p.[17] Studies in our laboratories with **4a**/MAO have shown that at room temperature the PP obtained is also of lower isotacticity.[16]

For complex **4c** the PP formed was a viscous gumlike material that had no melting point and exhibited very low isotacticity under all polymerization conditions.

In the case of **4d**/MAO, where methyl groups have been placed at the 2-, 4-, and 7-positions of indene, the PP obtained at T_p = 20 °C was highly isotactic with [*mmmm*] = 86% and T_m = 132 °C. The material formed at 70 °C was almost as isotactic with [*mmmm*] = 80% and T_m = 124 °C.

The hafnium catalyst precursor **5** produced only trace amounts of polypropylene as well as polyethylene and appeared to have a lifetime of only a few minutes in solution under polymerization conditions, as indicated by the rapid loss of the pink color of the solution of the catalytic species. A similar observation concerning hafnocenes has been made by Razavi et al.[9b]

Polymerizations were also carried out at 20 and 70 °C at 5 psi of propylene pressure to study the effect of monomer concentration on tacticity using catalyst pre-

cursors **4b**−**d**, but the results showed little or no effect on either activity or stereoregularity.[18]

Discussion. As can be seen from the results discussed above, the microstructures of the polypropylenes we have obtained vary considerably depending on the catalyst system employed. Our overall goal of this work was the production of isotactic polypropylene (*i*-PP) using novel asymmetric C_1 catalysts. While this is by no means a new phenomenon, the majority of metallocene catalysts used for *i*-PP production are C_2-symmetric catalysts. Many studies have been published concerning the stereospecific behavior of propylene polymerization by homogeneous group IV metallocenes, and the mechanism by which isotactic polypropylene is produced using C_2-symmetric systems is widely accepted and understood, i.e., enantiomorphic site control.[2,3]

The mechanism for C_1-symmetric catalysts is less clearly defined.[6,7,9,12,13] C_1-symmetric metallocenes have two different coordination sites diastereotopically related to each other. Monomer insertion can occur at either of these two sites, and generally it can be said that one site leads to isospecific propagation while the other leads to aspecific propagation. Furthermore, the polymer chain can favor one of these environments over the other (chain end control), and site switching occurs to allow the polymer to lie in the less hindered position. Depending on the structure of the catalysts, the energetic difference between the two sites varies. Therefore, a variety of stereochemical polymer structures results.

For example, in the case of elastomeric polypropylene, this two-state, site-switching model for polymerization has been proposed to account for the stereoblock nature of the polymer.[5−7] Both crystallizable and amorphous segments of polymer arise from consecutive monomer insertions at the isospecific site and the aspecific site, respectively. Interconversion between these two states results in a polymer consisting of both types of segments. A very different example was reported by Razavi et al.[9b,12b] In that study, *i*-PP was produced using the asymmetric catalyst (η^5-C$_5$H$_3$-*t*-C$_4$H$_9$-CMe$_2$-η^5-C$_{13}$H$_8$)-ZrCl$_2$. In this case, it was found that the *t*-Bu group on the cyclopentadienyl moiety resided above one of the coordination sites and sterically interacted with the growing polymer chain. Therefore, monomer coordination occurred selectively at that site in a stereospecific manner, leading to highly isotactic PP.

From our studies, we have found that placing methyl groups at various positions on the indene ring greatly affects the resulting polypropylene microstructure. It seems apparent that substitution at both the 2- and the 4-positions of the indenyl ligand is required in order to obtain isospecific propagation; i.e., a synergistic effect could be occurring. This observation was previously demonstrated by Spaleck et al.[4] for C_2-symmetric catalysts, and while the synergistic effect was most relevant to molecular weight, it was also shown to have some importance for stereochemical control. Further studies of related asymmetric metallocenes are underway, as

(16) A reviewer has recommended that we include polymerization data of **4a** compared with **4b**−**d** carried out in our own laboratories. Limited studies had been performed due to the extensive polymerization data already reported by Rieger et al.[13] Polymerization of propylene with MAO/**4a** was compared with MAO/**4b** under the following conditions: monomer pressure 15 psi; time of polymerization 20 min; [Zr] = 50 μM; Al/Zr = 4000/1. The activity for MAO/**4a** at 20 °C was 3.96 × 10^5 vs 5.5 × 10^5 for MAO/**4b**. At 50 °C the activities were 2.86 × 10^6 and 7.3 × 10^6, respectively. Units of activity are expressed as g of polymer/((mol of Zr)([C$_3$])h). No melting points were observed with the polymers obtained with either catalyst at 20 °C. At 50 °C, ^{13}C analysis showed [*mmmm*] = 53% for the polymer obtained from **4a**, and [*mmmm*] = 44% using **4b**.
(17) Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **1990**, *23*, 3559.

(18) Additional polymerization studies of **4b**−**d** performed under the following conditions: MAO/Zr = 15 000 mol/mol, 70 °C in liquid propylene for 1 h resulted in polypropylene with [*mm*] triads of 57, 25, and 91%, respectively. The respective GPC molecular weights were 40 000, 22 000, and 27 000 g/mol. Melting points of 114 and 151 °C were observed for the PP obtained using **4b** and **4d**, respectively. No melting point was observed for PP obtained using **4c**.

well as molecular modeling studies of these systems, in order to try to fully elucidate the polymerization mechanisms of this class of asymmetric catalysts.

Experimental Section

General Procedures. Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo Nobel and used as received. All other reagents were purchased from Aldrich and used without further purification. Toluene, diethyl ether, THF, and pentane were distilled from Na/K alloy under argon. Dichloromethane was distilled from CaH_2 under argon. The indene ligands **2b**,[19a] **2c**,[19b] and **2d**[19c] were prepared by literature procedures. ^{1}H NMR spectra were recorded on a AC-200 spectrometer. ^{13}C NMR spectra were recorded on DPX 300/AMX500 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

1-(9-Fluorenyl)-2-bromoethane (1). A modification of the patent procedure of Alt et al. was used.[14] To a solution of 10.38 g (62.5 mmol) of fluorene in 250 mL of THF at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (39.05 mL, 62.5 mmol). The solution was stirred for 3 h at room temperature and then added dropwise over a period of 2 h via cannula to 125 mL (1.45 mol) of 1,2-dibromoethane. The solution was stirred overnight at room temperature. After hydrolysis with 125 mL of aqueous NH_4Cl the organic layer was separated. The aqueous layer was extracted twice with ether. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were removed. The excess 1,2-dibromoethane was recovered by trap-to-trap distillation at 0.5 mmHg with gentle heating by a warm water bath. A chilled receiving flask was used. The resulting yellow residue was dissolved in pentane, and this solution was filtered, concentrated, and cooled to −20 °C to give **1** (10.25 g, 60%) as a yellow solid; mp 48−49 °C (lit.[20] mp 49 °C). ^{1}H NMR data were consistent with those reported in the literature.[20]

1-(9-Fluorenyl)-2-(3-indenyl)ethane (3a) was prepared by a route different from that reported by Rieger et al.[13] To a solution of 0.85 mL (7.32 mmol) of indene **2a** in 50 mL of THF at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (4.6 mL, 7.32 mmol). The solution was stirred for 6 h at room temperature and then added via cannula to a solution of **1** (2.00 g, 7.32 mmol) in 30 mL of THF cooled to −10 °C. The mixture was stirred overnight at room temperature and then hydrolyzed with 50 mL of aqueous NH_4Cl. The organic phase was separated, and the aqueous layer was extracted with ether. The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was removed. The residue was recrystallized from hot 100% ethanol to give 1.7 g of **3a** (74%); mp 93−95 °C (lit.[13] mp 99−100 °C). ^{1}H NMR data were consistent with those reported in the literature.[13]

1-(9-Fluorenyl)-2-(2-methyl-3-indenyl)ethane (3b). Following the procedure described for **3a**, the 2-methylindene **2b** (1.5 g, 11 mmol), 1.6 M butyllithium (6.9 mL, 11 mmol), and **1** (3.0 g, 11 mmol) gave **3b** (2.0 g, 57%) as a white solid; mp 162−164 °C. ^{1}H NMR ($CDCl_3$): δ 7.80−7.05 (m, 12 H, arom), 4.13−4.09 (t, 1 H, Flu-C_5 H), 3.16 (s, 2 H, Ind C-1 H), 2.39−2.09 (m, 4 H, bridge), 1.85 (s, 3 H, CH_3). Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.90; H, 6.79.

1-(9-Fluorenyl)-2-(4,7-dimethyl-1-indenyl)ethane (3c). Following the procedure described for **3a**, the 4,7-dimethylindene **2c** (2.00 g, 13.9 mmol), 1.6 M butyllithium (8.67 mL, 13.9 mmol), and **1** (3.79 g, 13.9 mmol) gave **3c** (1.77 g, 38%)

as a white solid; mp 149−151 °C. ^{1}H NMR ($CDCl_3$): δ 7.76−6.79 (m, 10 H, arom and Ind vinylic H), 6.41−6.37 (d, 1 H, Ind vinylic H), 3.95−3.90 (t, 1 H, Flu-C_5 H), 3.40−3.36 (d, 1 H, Ind C-1 H), 2.37 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 1.99−1.26 (m, 4 H, bridge). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.53; H, 7.13.

1-(9-Fluorenyl)-2-(2,4,7-trimethyl-1-indenyl)ethane (3d). Following the procedure described for **3a**, the 2,4,7-trimethylindene **2d** (2.90 g, 18.3 mmol), 1.6 M butyllithium (11.45 mL, 18.3 mmol), and **1** (5.00 g, 18.3 mmol) gave **3d** (1.86 g, 29%) as a white solid; mp 178−179 °C. ^{1}H NMR ($CDCl_3$): δ 7.77−7.28 (m, 8 H, Flu arom H), 6.96−6.74 (dd, 2 H, Ind arom H), 6.55 (s, 1 H, Ind C_5 vinylic H), 3.86−3.83 (t, 1 H, Flu-C_5 H), 3.15 (s, 1 H, Ind-C-1 H), 2.36 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 1.88 (s 3 H, CH_3) 1.66−1.23 (m, 4 H, bridge). MS: m/z 350 (M[+]). Anal. Calcd for $C_{27}H_{26}$: C, 92.52; H, 7.48. Found: C, 92.03; H, 7.32.

[1-(9-Fluorenyl)-2-(1-indenyl)ethane]zirconium dichloride (4a) was prepared under conditions different from those described by Rieger et al.[13] To a solution of **3a** (1.00 g, 3.25 mmol) in 50 mL of diethyl ether at 0 °C was added 2 equiv of 1.6 M butyllithium (4.06 mL, 6.5 mmol). The resulting suspension was stirred for 6 h at room temperature. The solvent was removed, and the solid was washed with 2 × 20 mL portions of pentane. The solid was suspended in 60 mL of diethyl ether and cooled to 0 °C. $ZrCl_4$ (0.757 g, 3.25 mmol) was added as a solid. The mixture was stirred overnight at room temperature, and the solvent was removed by filtration. The orange solid was extracted with CH_2Cl_2, concentrated, and stored at −20 °C to give **4a** (0.70 g, 47%) as an orange solid. ^{1}H NMR data were consistent with those reported by Rieger et al.[13]

[1-(9-Fluorenyl)-2-(2-methyl-1-indenyl)ethane]zirconium Dichloride (4b). Following the procedure described for **4a**, **3b** (1.6 g, 5.0 mmol), 1.6 M butyllithium (6.2 mL, 10 mmol), and $ZrCl_4$ (1.15 g, 5.0 mmol) gave **4b** (0.9 g, 38%) as an orange solid. ^{1}H NMR ($CDCl_3$): δ 7.90−6.97 (m, 12 H, arom), 6.22 (s, 1 H, Ind-C_5 H), 4.72−3.75 (m, 4 H, bridge), 2.20 (s, 3 H, CH_3). Anal. Calcd for $C_{25}H_{20}Cl_2Zr$: C, 62.23; H, 4.18. Found: C, 62.09; H, 4.15.

[1-(9-Fluorenyl)-2-(4,7-dimethyl-1-indenyl)ethane]zirconium Dichloride (4c). Following the procedure described for **4a**, **3c** (1.50 g, 4.46 mmol), 1.6 M butyllithium (5.58 mL, 8.92 mmol), and $ZrCl_4$ (1.04 g, 4.46 mmol) gave **4c** (0.5 g, 23%) as a yellow-orange solid. ^{1}H NMR ($CDCl_3$): δ 7.99−7.36 (m, 8 H, Flu arom H), 6.73−6.64 (m, 2 H, Ind arom H), 6.42−6.41 (d, 2 H, Ind-C_5 H), 5.32 (s, 0.2 H, CH_2Cl_2), 4.52−3.71 (m, 4 H, bridge), 2.60 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3). Anal. Calcd for $C_{26}H_{22}Cl_2Zr\cdot0.1CH_2Cl_2$: C, 62.07; H, 4.43. Found: C, 61.71; H, 4.34.

[1-(9-Fluorenyl)-2-(2,4,7-trimethyl-1-indenyl)ethane]zirconium Dichloride (4d). Following the procedure described for **4a**, **3d** (1.35 g, 3.85 mmol), 1.6 M butyllithium (4.81 mL, 7.7 mmol), and $ZrCl_4$ (1.90 g, 3.85 mmol) gave **4d** (0.40 g, 20%) as an orange solid. ^{1}H NMR ($CDCl_3$): δ 7.93−7.10 (m, 8 H, Flu arom H), 6.74−6.68 (m, 2 H, Ind arom H), 6.25 (s, 1 H, Ind-C_5 H), 4.54−3.94 (m, 4 H, bridge), 3.06 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3). MS: m/z 508 (M[+]). Anal. Calcd for $C_{27}H_{22}Cl_2Zr$: C, 63.51; H, 4.74. Found: C, 61.76; H, 4.61.

[1-(9-Fluorenyl)-2-(2-methyl-1-indenyl)ethane]hafnium Dichloride (5). Following the procedure described for **4a**, **3b** (0.83 g, 2.57 mmol), 1.6 M butyllithium (3.21 mL, 5.14 mmol), and $HfCl_4$ (0.82 g, 2.57 mmol) gave **5** (0.6 g, 41%) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.90−6.93 (m, 12 H, arom), 6.11 (s, 1 H, Ind-C_5 H), 5.32 (s, 0.1 H, CH_2Cl_2), 4.68−3.91 (m, 4 H, bridge), 2.27 (s, 3 H, CH_3). Anal. Calcd for $C_{27}H_{22}Cl_2Hf\cdot0.05CH_2Cl_2$: C, 52.41; H, 3.53. Found: C, 51.97; H, 3.45.

Polymerizations. A 250 mL crown-capped glass pressure reactor containing 50 mL of toluene was equilibrated with the appropriate monomer and pressure at the desired temperature. The desired amount of methylaluminoxane (MAO) was added as a solution in toluene via syringe, and the solution

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was stirred for 5 min. One milliliter of the appropriate catalyst solution in toluene was added, and the mixture was stirred until the desired reaction time was reached. The mixture was quenched with 2% HCl in methanol and filtered, and the residue was dried in a vacuum oven at an appropriate temperature for the polymer sample.

Polymer Analyses. Melting points were determined by DSC with a Perkin-Elmer DSC-4 system. ^{13}C NMR spectra were determined on a DPX300 spectrometer in CDCl$_3$ at room temperature and at 80 °C in C$_6$D$_5$Cl on an AMX 500 spectrometer.