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Articles

High Comonomer Selectivity in Ethylene/Hexene Copolymerization by Unbridged Indenyl Metallocenes

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ABSTRACT: Catalysts derived from unbridged 2-arylindene metallocenes of Hf and Zr are active for ethylene/hexene copolymerization and show a much higher selectivity toward hexene than unsubstituted bis(indenyl) metallocenes. The ligand substitution pattern and the nature of the metal ion have a strong influence on the ability of unbridged 2-arylindenyl metallocenes to incorporate 1-hexene comonomer in ethylene/hexene copolymerizations. Our data support the hypothesis that arene substituents near the active site promote the α-olefin coordination and insertion, thereby providing comonomer-rich polyethylenes. Hafnium-based metallocenes incorporate α-olefins better than their zirconium congeners. The sterically encumbered bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)hafnium dichloride incorporates α-olefins with an ability comparable to the cyclopentadienylamido metallocene $\{\eta^1:\eta^5$-[(*tert*-butylamido)dimethylsilyl]-(2,3,4,5-tetramethyl-1-cyclopentadienyl)$\}$titanium dichloride ($Me_2Si(Me_4Cp)^tBuNTiCl_2$).

Introduction

Polyethylene is one of the world's largest volume thermoplastics.[1,2] The density of polyethylene, one of the critical parameters influencing its properties, is controlled by the level and distribution of branching. The catalytic copolymerization of ethylene with α-olefins is a typical way of introducing short-chain branching. New generations of catalysts are leading to new families of polyethylenes due to the ability of these catalyst systems to introduce controlled amounts of α-olefins into polyethylene with uniform and homogeneous sequence and composition distributions. Differences in comonomer content and distribution can cause significant changes in the polymer properties, such as differences in melting and glass transition temperatures, melt viscosity, and mechanical and optical properties, all of which define the type and useful range of application of these materials.[3−11] One of the basic parameters governing the synthesis of well-defined ethylene copolymers is the kinetic selectivity of the catalyst for ethylene and the α-olefin. Despite the importance of this parameter, our understanding of the relationship between the catalyst structure and its ability to incorporate both monomers is incomplete. While important advances are being made both experimentally[12−24] and computationally,[25,26] it is still impossible to predict a priori the kinetic selectivity between ethylene and an α-olefin for a given catalyst structure or given catalyst/cocatalyst combination. Most of our understanding is based on empirical correlations and are largely based on steric concepts, which have nevertheless proven a useful and powerful guide for catalyst design.

As part of our investigations on the polymerization behavior of unbridged metallocene catalysts, we observed that bis(2-arylindenyl) metallocene catalysts are surprisingly effective at incorporating α-olefins and far superior to unsubstituted bis(indenyl) metallocenes.[22,27−29] In this paper, we report the synthesis and copolymerization behavior of a series of 2-arylindene metallocenes with diverse ligand substitution patterns to study the influence of the type and the position of the substituents on the catalysts' reactivity toward ethylene and 1-hexene. Reactivity ratios are used as a measure of the catalysts' ability to incorporate comonomer[2,30] and are defined as the ratio of the rate constants of the homopropagation to the cross-propagation rates ($r_e = k_{ee}/k_{eh}$, $r_h = k_{hh}/k_{he}$). The copolymerization behavior of closely isostructural zirconium and hafnium analogues was investigated to probe the role of the transition metal on monomer selectivity.

Results

Five metallocene catalysts were investigated for their ethylene/1-hexene copolymerization characteristics: (1-methyl-2-phenylindenyl)(2-phenylindenyl)zirconium dichloride (**1**), bis(4,7-dimethyl-2-phenylindenyl)zirconium dichloride (**2**), bis(4,7-dimethyl-2-phenylindenyl)hafnium dichloride (**3**), bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)zirconium dichloride (**4**), bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)hafnium dichloride (**5**), and the known[15,31,32] (cyclopentadienyldimethylsilyl-*tert*-butylamido)titanium dichloride (**6**) (Figure 1). All compounds were prepared according to modified literature procedures.[31,33−35] The 3′,5′-di-*tert*-butyl-2-phenylindene ligand was synthesized by a slight modification of the procedure reported by Witte et al.[34] Metalation conditions with hafnium were similar to the conditions published and used to prepare zirconocene catalysts.[28,33,36]

Ethylene/1-hexene copolymerizations were carried out in a 300 mL stainless steel reactor in neat 1-hexene with

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Table 1. Ethylene/1-Hexene Copolymerizations at 20 °C in Neat 1-Hexene

metallocene	[M] (μmol)	E pressure (psig)	% E in polymer[a]	M_n (g/mol)[b]	M_w/M_n[b]	polymer yield (g)	productivity[c]
1	2.4	60	51	66 300	5.6	1.26	15 934
2	2.0	45	55	45 600	3.1	0.75	11 333
3	6.0	120	51	15 100	3.4	0.35	1 170
4	0.4	150	53	140 000	4.2	0.43	21 350
5	4.0	191	52	22 000	2.7	0.30	1 505
6	10.0	211	52	7 700	2.8	0.41	211

[a] Determined by ^{13}C NMR. [b] Determine by high-temperature gel permeation chromatography using polyethylene standards. [c] Calculated as kg of polymer/(mol of Zr h).

Table 2. Reactivity Rations for Ethylene/1-hexene Copolymerizations

metallocene	N_{exp}[a]	X_e/X_h[b]	% E (polymer)[c]	r_e[d,e]	r_h[d,e]	$r_e r_h$[f]	r_h/r_e ($\times 10^5$)
1	7	0.04−0.19	24−75	13 ± 3	0.091 ± 0.008	1.2 ± 0.3	700
2	5	0.05−0.16	44−76	19 ± 3	0.064 ± 0.006	1.2 ± 0.2	337
3	5	0.09−0.28	31−59	4.5 ± 0.9	0.16 ± 0.01	0.7 ± 0.1	3555
4	5	0.09−0.31	29−66	7 ± 3	0.18 ± 0.04	1.2 ± 0.5	2571
5	6	0.26−0.47	45−62	3.2 ± 0.5	0.25 ± 0.03	0.8 ± 0.2	7812
6	3	0.30−0.32	42−56	4 ± 1	0.4 ± 0.1	1.5 ± 0.6	10000

[a] Number of experiments used to determine the average reactivity ratios. [b] Range of the ratios of mole fractions of ethylene and 1-hexene in the monomer feed. [c] Range of the mol % E in the copolymers as determined by ^{13}C NMR. [d] Calculated by optimization of reaction probabilities from the triads over all N runs simultaneously. [e] Standard deviation calculated as $[(1/(N-1))\Sigma(r_{e,h(exp)} - r_{e,h(opt)})^2]^{1/2}$. [f] Standard deviation calculated as $[(\sigma_{re} r_h)^2 + (\sigma_{rh} r_e)^2]^{1/2}$.

Table 3. Selected Structural Parameters for Comparison between Zirconocene and Hafnocene Catalysts[a]

catalyst	Cen−M (av), Å	Cen−M−Cen[b] (av), deg	M−Cl (av), Å	Cl−M−Cl[c] (av), deg	reference
Cp_2ZrCl_2	2.198	129.38	2.448	96.97	52, 53
Cp_2HfCl_2	2.182	129.14	2.424	96.18	53
Ind_2ZrCl_2	2.230	128.27	2.440	94.74	52
$(2PhInd)_2ZrCl_2$ syn (meso)	2.237	131.19	2.427	94.39	41
$(2PhInd)_2HfCl_2$ syn (meso)	2.222	131.41	2.405	94.02	54
$(2PhInd)_2ZrCl_2$ anti (rac)	2.242	131.54	2.424	95.44	41
$(2PhInd)_2HfCl_2$ anti (rac)	2.225	131.89	2.403	95.07	54
2	2.248	132.15	2.431	96.12	35
3	2.227	132.53	2.402	96.12	35

[a] Literature data obtained as .cif file from Cambridge Structural Database. All bond lengths and angles calculated using crystallographic tool Platon (shareware available online). [b] Cp centroid−metal−Cp centroid angle. [c] Chloride−metal−chloride angle.

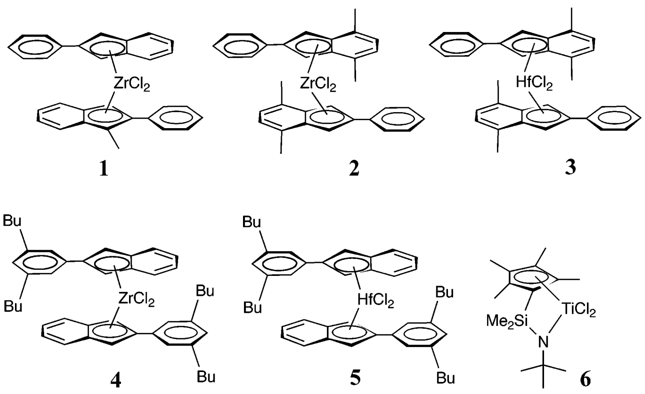

Figure 1. Structures of catalyst precursors studied.

an overpressure of ethylene. Conversion of 1-hexene was kept below 5% to ensure a constant comonomer feed throughout the polymerization; polymer yields were kept below 3 g to avoid mass transfer limitations.[37] Copolymerizations were carried out over a variety of comonomer feed ratios to obtain copolymers with a wide range of ethylene incorporation.[38]

The productivities of copolymerizations are reported in Tables 1 and 4. All metallocene catalysts are active ethylene/1-hexene copolymerization catalysts with similar productivities, suggesting that at no point do the substituents interfere with the ability to coordinate and insert monomer. The 4,7-dimethyl- and 1-methyl-substituted metallocenes show higher productivities at similar monomer feeds (e.g., $X_e/X_h = 0.092$; 0.148−0.163, see Table 4) than 3′,5′-di-*tert*-butylphenyl-substituted catalysts. The zirconocenes are more productive than the hafnocenes and yield higher molecular weights at 20 °C.[17,39] The low productivity of **6** is due to the low polymerization temperatures of 20 °C employed—this catalyst is typically utilized at higher temperatures (160 °C)[1,3] but was run under similar conditions for comparison.

The reactivity ratios reported in Table 2 provide an indication of the kinetic selectivities of these catalysts. All of the metallocenes incorporate hexene reasonably well with r_e's ranging from 3.2 to 19 and r_h's from 0.064 to 0.25. These values were determined using the first-order Markov model and are optimized over the full range of feed ratios using Microsoft Excel Solver optimization.[27] The ratio r_h/r_e provides a crude measure of the selectivity of the various catalysts to incorporate hexene (Table 2). These ratios show that both the ligand substitution pattern and the nature of the metal ion influence the selectivity toward 1-hexene. The 3′,5′-di-*tert*-butylphenyl-substituted catalyst **4** incorporates hexene more readily than the 4,7-dimethyl-substituted complex **2** or the 1-methyl-substituted complex **1**. For comparable ligand environments, the hafnocene catalysts **3** and **5** show a significantly higher selectivity for hexene than the zirconocenes **2** and **4**, and the unbridged metallocene **5** is comparable to **6** in its ability to incorporate hexene.

Table 4. Ethylene/1-Hexene Copolymerizations with the Metallocene/MAO System

entry	metallocene	E^a (psig)	T^b (°C)	$[M]^c$ ($\times 10^{-6}$)	polymer yield (g)	$X_e/X_h{}^d$	% E in polymer^e	productivity^f ($\times 10^3$)
1	(1-Me,2-PhInd)(2PhInd)$ZrCl_2$ (**1**)	15	20	9	0.37	0.035	23.8	3.1
2		31	20	9	0.79	0.054	35.3	6.6
3		45	20	9	1.25	0.072	42.6	10.5
4		60	20	6	1.26	0.092	50.9	15.9
5		80	20	9	1.93	0.119	61.0	16.2
6		100	20	6	2.02	0.148	64.0	25.5
7[g,h]		130	20	5	1.36	0.195	74.8	13.6
8	bis(4,7- Me_2-PhInd)$ZrCl_2$ (**2**)	30	20	5	0.43	0.053	43.8	6.5
9		45	20	5	0.75	0.072	55.0	11.3
10		60	20	5	1.01	0.092	60.0	15.3
11		75	20	5	1.90	0.112	67.7	28.8
12		110	20	1	0.49	0.163	75.7	36.8
13	bis(4,7- Me_2-PhInd)$HfCl_2$ (**3**)	61	20	20	0.39	0.093	30.7	1.0
14		91	20	20	0.40	0.135	40.4	1.0
15		120	20	15	0.35	0.179	51.3	1.2
16		150	20	15	0.76	0.228	54.7	2.5
17		180	20	15	0.75	0.281	59.0	2.5
18	bis(2-(3′,5′-ditBuPhInd))$ZrCl_2$ (**4**)	61	20	2.5	0.23	0.093	29.0	7.0
19		100	20	1	0.18	0.148	39.5	13.6
20[g]		150	20	1	0.43	0.228	53.3	21.4
21[h]		170	20	5	0.73	0.262	66.2	15.3
22[h]		200	20	5	1.56	0.315	71	23.7
23	bis(2-(3′,5′-ditBuPhInd))$HfCl_2$ (**5**)	170	20	25	1.41	0.262	44.5	2.8
24		191	20	10	0.30	0.301	52.2	1.5
25		211	20	25	0.85	0.341	57.3	1.7
26		170	0	25	0.27	0.353	52.2	0.5
27		191	0	25	0.61	0.410	57.2	1.2
28		211	0	25	0.51	0.469	61.9	1.0
29	**6**	191	20	25	0.51	0.301	42.1	1.6
30		211	20	25	0.41	0.341	51.9	1.2
31[h]		200	20	12.5	0.70	0.323	56.3	4.2

[a] Pressure of ethylene during the polymerization. [b] Temperature during polymerization. [c] Catalyst's concentration in the polymerization media. [d] Monomer feed ratio (mole fraction of E/mole fraction of H). [e] Determined by ^{13}C NMR. [f] Productivity = kg of polymer/(mol of catalyst h). [g] Polymerizations run for 30 min. [h] MMAO of a different batch was used.

Discussion

In an effort to develop understanding of copolymerization characteristics of homogeneous metallocene catalysts and of the factors influencing the polymer microstructure in metallocene-catalyzed copolymerization, it is critical to address the relationship between metallocene structure with its ability to incorporate monomers. Such fundamental structure–function relationship studies are focused toward better understanding of the combination of the parameters contributing to the polymerization and copolymerization behavior of these homogeneous systems.[16,18,20,21,38,40,41] We aimed our current efforts at understanding the monomer kinetic selectivities of a series of unbridged arylindenyl-based metallocene systems as we see these catalysts being excellent candidates for production of new generation of polyethylene copolymers with novel properties.[27,28]

Early encouraging results from our group suggested that not only are arylindenyl metallocenes active catalysts for copolymerization of ethylene with higher α-olefins, they also show a unexpected tendency to incorporate high amounts of comonomer when compared to known cyclopentadienyl or indenyl systems.[27,28,33] Most of the correlations from the literature reports imply that high comonomer incorporation relies on an open coordination geometry where bulkier comonomer can easily coordinate and subsequently insert. As such, bridged metallocenes when compared to unbridged analogues typically show a significantly lower r_e, which corresponds to higher comonomer incorporation under identical conditions.[1] However, recent evidence[12,27,28,35,42] reveals that steric effects are insufficient to predict copolymerization behavior.

Among the zirconocene catalysts studied, all show productivities between 3000 to 37 000 kg of polymer/(mol of Zr h). While metallocenes **1**, **2**, and **4** are less productive than catalysts derived from bis(2-phenylindenyl)zirconocene dichloride (12 000–93 000 kg of polymer/(mol of Zr h)),[27,43] it is clear that their bulky alkyl substituents do not inhibit α-olefin insertion. The ligand environment can be used to tune the catalysts' activities as evidenced by the fact that 4,7-dimethyl substituents increase the productivities while 3′,5′-di-*tert*-butyl substituents cause a drop in activity.[16,44]

The hafnocene analogues **3** and **5** are significantly less productive and yield lower molecular weights at 20 °C than the zirconocenes.[17,23,39,45] The lower productivities[43] might be rationalized by the higher hafnium–carbon (Hf–C) bond strengths. Despite the hafnocene's low productivity, they exhibit a higher selectivity for incorporation of α-olefins (Table 2). The lower molecular weights of the hafnium congeners may be related to this behavior if chain transfer to hexene is more facile for hafnium; further studies would be required to test this hypothesis. The reactivity ratio r_h more than doubles going from **2** to **3** (0.064 vs 0.16); for **3** r_e drops to a quarter of the value obtained with **2** (4.5 vs 19). Less drastic changes are noticed when comparing metallocenes **4** and **5**: the already low r_e of **4** drops by ~50% (7 (**4**) vs 3.2 (**5**)) (Table 2). Kaminsky and Koivumaki[17,39] have also observed that hafnocenes show higher comonomer incorporation relative to zirconocenes. Given the fact that hafnium and zirconium catalysts of known structure are practically identical structurally (see Table 3), it is difficult to invoke steric arguments to interpret these differences. The higher selectivity of the hafnocenes toward 1-hexene insertion may be due to either some subtle electronic influence of the metal or the metal's interaction with the cocatalyst counterion.[40,44]

The open coordination gap of constrained geometry catalyst **6** has been proposed as the origin of these catalysts' ability to incorporate a high amount of comonomer.[19,31] For this reason, the selection of *ansa*-metallocenes with large coordination gap apertures has proven a useful guiding principle for incorporating high amounts of α-olefin comonomer.[22,29] However, as our results distinctly show, appropriately substituted unbridged metallocenes can exhibit comonomer selectivities competitive with some of the best *ansa*-metallocenes (Table 2). The origin of these high comonomer selectivities remains obscure, but it appears that highly conjugated metallocenes, such as those containing fluorenyl ligands,[46,47] or those substituted with aryl substituents near the coordination gap are particularly adept at comonomer incorporation.[27] The conjugation with the ligand framework may not necessarily be responsible for the observed "arene effect" as in most cases the phenyl substituents are tilted away from the plane of the indenyl portion of the ligand, evidenced by the X-ray structure of catalysts **1**,[33] **2**, and **3**.[35]

For the unbridged 2-arylindenyl metallocenes, both the nature and the position of substituents influence the ability to incorporate hexene. Introduction of methyl substituents at one of the 1-indenyl positions or at both 4,7-positions results in a modest drop in the hexene selectivity relative to bis(2-phenylindenyl)$ZrCl_2$ (**7**) (r_e = 8, r_h = 0.09,), but **1** and **2** are still comparable or slightly better than the prototypical *ansa*-metallocene ethylenebis(indenyl)$ZrCl_2$ (r_e = 14, r_h = 0.03).[27] Introduction of sterically demanding *tert*-butyl substituents at the 3′,5′-positions of the 2-aryl results in an approximately 2-fold increase in the selectivity toward 1-hexene **4** (r_h/r_e ($\times 10^5$) = 2571) relative to bis(2-phenylindenyl)$ZrCl_2$ (r_h/r_e ($\times 10^5$) = 1100).[27] Because of this effect and the greater incorporating abilities of the hafnium congeners, the unbridged hafnocene **5** exhibits outstanding selectivity for incorporating 1-hexene, comparable to that of **6**.

As we have previously discussed, the conformational dynamics of unbridged metallocenes[27] and the possible role of counterions[48] add additional levels of complexity to the interpretation of the very high comonomer selectivities of metallocenes **1**−**5**. One very important and fairly unexplored factor is the anion interaction with the cationic metal center.[49] From a purely structural standpoint, it would appear that the slightly larger Cen−M−Cen angles of the unbridged 2-arylindene ligands would if anything suggest that these metallocenes should be less able to incorporate α-olefins than the unsubstituted bis(cyclopentadienyl) and bis(indenyl) metallocenes (Table 3). A sterically crowded metal center that is shielded by virtue of its substituents from close contact with the bulky and ill-defined MAO counterion might allow for an easier approach of the α-olefin. In addition, it is possible that for unbridged metallocenes the role of substituents is to influence the conformational dynamics to yield higher populations of conformational states that are better able to incorporate α-olefins. At this time, it is impossible to assess the relative importance of these factors in the absence of independent data on the copolymerization behavior of well-defined conformationally locked metallocenes as well as a better understanding on the influence of counterions on copolymerization behavior. Studies along these lines are ongoing in our laboratories.

Conclusion

Unbridged 2-arylindene metallocenes can exhibit very high incorporations of 1-hexene into ethylene/hexene copolymers. Hafnocenes incorporate 1-hexene better than zirconocenes, and metallocenes derived from the bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)$HfCl_2$ metallocene incorporate 1-hexene as well as the CpA *ansa*-metallocenes **6**, which are utilized commercially. While the precise origin of these high α-olefin selectivities is unknown, it is clear that simple structural arguments are insufficient to predict high comonomer selectivity in ethylene/α-olefin copolymerization reactions.

Experimental Section

General Consideration. All organometallic reactions were conducted using standard Schlenk and drybox techniques. Elemental analyses were performed by E&R Microanalytical Laboratory. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. 1-Hexene, methylene chloride, and pentane were distilled from calcium hydride prior to use. Toluene was passed through two purification columns packed with activated alumina and supported copper catalyst and collected under argon. Chloroform-*d* was vacuum-transferred from calcium hydride. Benzene-d_6 was vacuum-transferred from sodium benzophenone. Magnesium powder, α,α′-dichloro-*o*-xylene, and 3,5-di-*tert*-butylbenzoic acid were purchased from Aldrich. Zirconium tetrachloride ($ZrCl_4$) was purchased from Fluka, and hafnium tetrachloride was purchased from Cerac Inc. Modified methylaluminoxane type 4 (MMAO-4)) was purchased from AkzoNobel as a solution in toluene. It was dried under vacuum and used in its powder form in polymerizations. NMR spectra were recorded on a Varian Gemini 400 MHz and a Varian UI 300 MHz. 3-Methyl-2-phenylindene, (1-methyl-2-phenylindenyl)(2-phenylindenyl)-zirconium dichloride (**1**),[50] and {η^1:η^5-[(*tert*-butylamido)dimethylsilyl](2,3,4,5-tetramethyl-1-cyclopentadienyl)}titanium dichloride (**6**) were prepared according to literature procedures.

Preparation of 3,5-Di-*tert*-butylmethylbenzoate. 3,5-Di-*tert*-butylbenzoic acid (10.7 mmol) was dissolved in 25 mL of methanol. The reaction flask was cooled in an ice bath under nitrogen and thionyl chloride (16.05 mmol) was added. The reaction was stirred at room temperature under a nitrogen atmosphere overnight. All solvent was removed by vacuum to yield a white solid, pure by ^{1}H NMR. Yield: 98%.

Synthesis of 3′,5′-Di-*tert*-butyl-2-phenylindene. A slightly modified literature procedure was followed.[34] Magnesium powder (50 mesh, 1.167 g, 48.00 mmol) was dried in a 500 mL three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel by heating to 120 °C under vacuum (10−20 mTorr) overnight. After the mixture was cooled to room temperature, the apparatus was repressurized with argon. THF (10 mL) and 0.25 mL (3.00 mmol) of 1,2-dibromoethane were added, and the mixture was heated with a heat gun. The heating was stopped 1 min after gas evolution occurred. All volatiles were removed in vacuo. After the apparatus was purged with argon, 10 mL of THF was added, and 2.3 g (12.00 mmol) of α,α′-dichloro-*o*-xylene (purified by Kugelrohr distillation prior to use) was dissolved in 125 mL of THF in the addition funnel while the apparatus was purged with argon. The solution in the addition funnel was added dropwise over a period of 3−4 h, and the reaction mixture was stirred vigorously for 15 h at room temperature. The magnesium was filtered off using a Schlenk frit under argon to yield a pale green solution. The receiving flask was equipped with a pressure-equalizing addition funnel, and the apparatus was purged with a vigorous argon flow for 15 min. The 3,5-di-*tert*-

butylmethylbenzoate (1.99 g, 8 mmol) was dissolved in 65 mL of THF in the addition funnel and added to the di-Grignard solution at −78 °C over approximately 60 min, with the temperature consistently maintained below −70 °C during the addition. The reaction mixture was warmed to room temperature over 3−4 h, cooled again to 0 °C, and quenched by slow addition of 15−20 mL of distilled water. After the reaction mixture was warmed to room temperature, the THF was removed, and the remaining suspension was acidified to pH 1 and extracted with diethyl ether. The combined organic layers were dried over magnesium sulfate, and all solvent was removed by a rotavap. 0.300 g (1.57 mmol) of *p*-toluenesulfonic acid hydrate and 100 mL of toluene were added, and the mixture was refluxed for 2 h. The toluene was washed with water, and subsequently, the water layer was extracted with diethyl ether. All organic layers were combined and dried with magnesium sulfate, and solvents were removed by a rotavap. The crude product—dark brown/orange oil—was transferred to silica gel and purified by flash chromatography with pentane to give an off-white solid in 47% yield. The ^{1}H and ^{13}C NMR were identical to that previously reported.[51]

Synthesis of Bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)zirconium (Hafnium) Dichloride. The ligand (2.3 mmol) was dissolved in 80−100 mL of diethyl ether. The solution was cooled to −78 °C, and 0.95 mL (2.38 mmol) of *n*-butyllithium (2.5 M in hexanes) was added via a syringe dropwise. The cooling bath was removed, and the mixture was stirred at ambient temperature for 2 h. Zirconium (hafnium) tetrachloride (1.16 mmol) was weighed into another Schlenk flask and suspended in 80 mL of pentane. Both the ligand solution and the metal slurry were cooled to −78 °C, and the ligand solution was added via a cannula to the metal salt suspension. The solution was allowed to stirr overnight at room temperature to form a dark yellow suspension. All volatiles were then removed in vacuo, and 50 mL of methylene chloride was added. The suspension was filtered over Celite through a Schlenk frit under argon to obtain a light yellow clear solution. The Celite was washed with methylene chloride until the filtered liquid remained colorless. All solvent was removed *in vacuo*, and the remaining solid was washed twice with diethyl ether to afford bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)zirconium dichloride as a yellow solid in 10% yield. Elemental analysis: % C 71.84 calcd, 71.79 found; % H 7.08 calcd, 7.10 found. The ^{1}H NMR and ^{13}C NMR spectra were as previously reported.[51] Bis(3′,5′-di-*tert*-butyl-2-phenylindenyl)hafnium dichloride: Yield: yellow solid, 30%. Elemental analysis: % C 59.35 calcd, 59.08 found. % H 4.40 calcd, 4.54 found. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.58 ppm (2H, d), 7.55 ppm (1H, t), 6.98 (2H, dd), 6.70 ppm (2H, dd), 6.67 (2H, s), 1.48 ppm (18H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 31.78, 35.34, 103.46, 121.65, 122.98, 124.59, 125.38, 127.10, 128.61, 131.64, 151.83.

Synthesis of Bis(4,7-dimethyl-2-phenylndenyl)zirconium (Hafnium) Dichloride. Full synthesis, characterization, and X-ray structure details will be reported in an upcoming publication.[35]

Ethylene/1-Hexene Copolymerization. The reactor was flushed 3−4 times with ethylene. In a nitrogen drybox, 130 mg of MAO was suspended and stirred in 35 mL of 1-hexene. An injector was charged with the 1-hexene/MAO mixture, and the solution was injected into the reactor under ethylene pressure. The reaction mixture was cooled to the reaction temperature and overpressurized with ethylene to a certain total pressure. This monomer mixture (1-hexene, MAO, ethylene) was equilibrated at the reaction temperature under constant ethylene pressure for at least 20 min. Catalyst stock solution in toluene was prepared in a drybox. The appropriate volume of catalyst solution (less than 1 mL) was diluted with 1-hexene to a total volume of 5 mL, added into a 10 mL injector, and injected into the reactor under ethylene pressure. Please note that, immediately prior to catalyst injection, the ethylene line was disconnected and the reactor was vented by 5 psi to provide the pressure differential and allow catalyst solution to flow into the reactor. The ethylene hose was reconnected directly after the catalysts injection. The reaction was run for 20 min at constant pressure and temperature; it was then quenched by injection of MeOH (20 mL), and the reactor was slowly vented and opened. The polymer was precipitated in acidified MeOH (5% HCl), filtered, washed with MeOH, and dried in a vacuum oven at 40 °C to a constant weight.

Polymer Characterization. Polymer molecular weights and molecular weight distributions were determined by high-temperature gel permeation chromatography using polyethylene for GPC calibration. A Varian UI 300 spectrometer was used to perform ^{13}C NMR measurements. Copolymer samples were prepared by dissolving 100−200 mg of each copolymer in 3 mL of *o*-dichlorobenzene/10 vol % benzene-d_6 with addition of paramagnetic "relaxation agent" chromium acetylacetonate, Cr(acac)$_3$, into a 10 mm tube. The spectra were measured at 100 °C using acquisition times = 1 s, additional delays = 5 s, and gated proton decoupling.

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