Effect of Metal on the Stereospecificity of 2-Arylindene Catalysts for Elastomeric Polypropylene

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Abstract: Polymerization of propylene with bis(2-phenylindenyl)zirconium dichloride and bis(2-[3,5-bistrifluoro-methyl)indenyl]zirconium dichloride produces elastomeric polypropylene. The elastomeric properties of these polymers have been interpreted in terms of a stereoblock microstructure. Analysis of the microstructure by ^{13}C NMR reveals isotactic pentad contents [*mmmm*] ranging from 6 to 74%. The hafnium derivatives were investigated to probe the influence of the transition metal on the polymerization behavior. The hafnium-based catalysts yield polypropylenes that are significantly less isotactic than the corresponding zirconium compounds, although molecular weights and productivities were similar for hafnium and zirconium derivatives. The X-ray crystal studies of these catalysts show nearly identical structures for corresponding zirconium and hafnium compounds. Variable temperature NMR of the metallocene dibenzyl analogues showed behavior consistent with rotation of indenyl ligands, where rotation of the indenyl ligand of bis(2-phenylindenyl)zirconium dibenzyl was 6800 Hz and that of hafnium was 6700 Hz at 20 °C. Based on our proposed mechanism of polymerization, the origin of the different microstructures can be ascribed to a faster propagation of the isospecific zirconium site relative to that of the isospecific hafnium site.

Introduction

Soluble metallocene complexes provide well-defined homogeneous Ziegler−Natta catalysts for olefin polymerization.[1] Correlation of the catalyst structure with the catalyst productivity, polymer molecular weight, molecular weight distribution, and polymer microstructure can reveal important insights into the mechanism of polymerization. The ligand environment has an important influence on microstructures of polymers produced by these catalysts: stereorigid chiral racemic *ansa*-metallocenes have been used to produce isotactic polypropylenes,[2,3] while achiral catalysts have been employed to produce syndiotactic and atactic polypropylenes.[1]

We have recently reported that the unbridged indenyl metallocene bis(2-phenylindenyl)zirconium dichloride (**1**), when combined with methylaluminoxane under a propylene atmosphere generates rubbery, elastomeric polypropylenes.[4,5] The elastomeric properties of these polymers have been interpreted in terms of a stereoblock atactic/isotactic microstructure. This structure was, in turn, proposed to arise through a mechanism involving fluctuation in the catalyst geometry from achiral to chiral during the course of the polymerization reaction (Figure 1).[4]

The microstructures of polymers produced by **1** are intermediate between atactic and isotactic. Analysis of the polymers by ^{13}C NMR reveals that the stereospecificity of the catalyst as measured by the isotacticity index, [*mmmm*], is in the range of 6−40%. The ligand environment has a profound effect on the

stereospecificity of the catalyst; substitutions on the phenyl ring yield polypropylenes that span the range from [*mmmm*] = 6% to [*mmmm*] = 75%.[4]

We now report the influence of the transition metal center on the polymerization behavior of these catalysts. Substitution of zirconium with hafnium yields complexes that are isostructural with the original zirconium catalysts but which produce polypropylenes of lower isotacticities than those from parent zirconium compounds.

Results

(PhInd)$_2$ZrCl$_2$ (**1**, (PhInd = 2-phenylindenyl), ((CF$_3$)$_2$-PhInd)$_2$ZrCl$_2$ (**3**, (CF$_3$)$_2$PhInd = 2-[3,5-bis(trifluoromethyl)-phenyl]) and ((CF$_3$)$_2$PhInd)$_2$HfCl$_2$ (**4**) were prepared as previously described.[4] The hafnium derivative of **1**, (2-PhInd)$_2$HfCl$_2$ (**2**), was prepared analogously by reaction of lithium 2-phenylindene with hafnium tetrachloride in toluene at room temperature.

Crystallization of the PhInd hafnium complex **2** from toluene at −18 °C gave crystals suitable for X-ray crystal analysis. The crystal structure of **2** (Figure 2) is nearly identical to that of the PhInd zirconium compound **1** (Figure 3). Both structures show *syn* and *anti* isomers in the unit cell. The bond lengths of the corresponding metal−cyclopentadienyl bonds are nearly identical (Table 1); the hafnium complex displays average metal−carbon bond lengths that are 0.005−0.016 Å shorter than those for the zirconium complex.

Similarly, the X-ray crystal structures of (trifluoromethyl)-phenyl-substituted complexes of zirconium (**3**,[4b] Figure 4) and hafnium (**4**, Figure 5) are nearly identical (Table 2). Corresponding metal−carbon bond lengths are within 0.020 Å, where

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(4) (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219. (b) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586−11587.
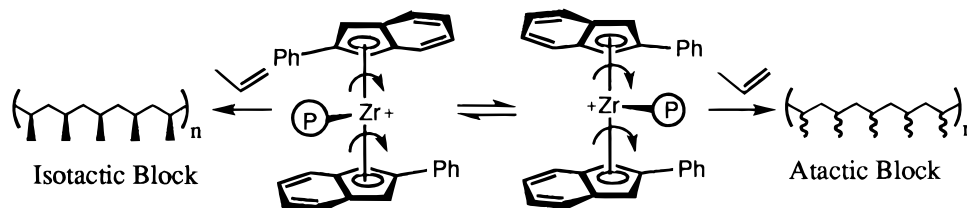
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Figure 1. Production of stereoblock polypropylenes with (2-PhInd)$_2$ZrCl$_2$.

Figure 2. ORTEPs of *anti*- and *syn*-bis(2-phenylindenyl)hafnium dichloride (**2**).
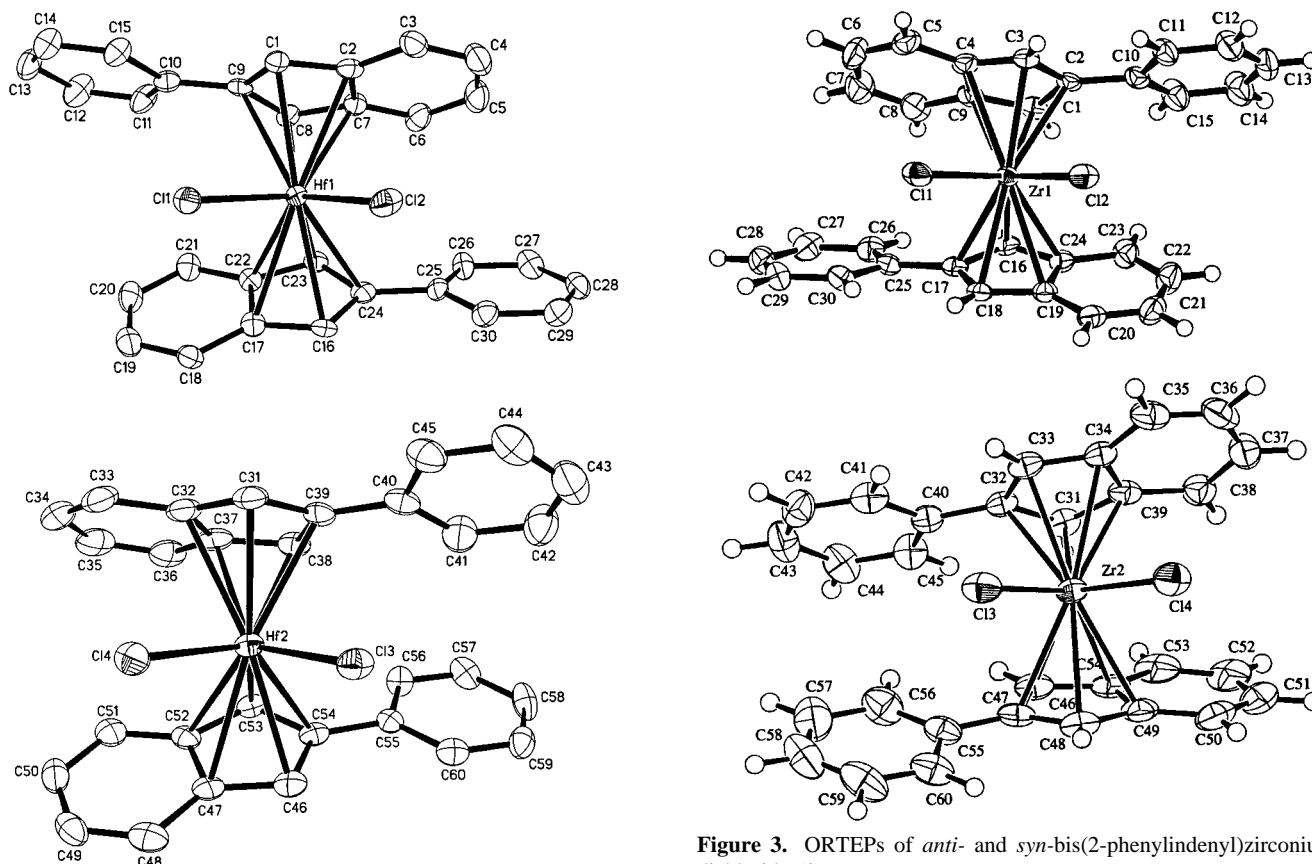

Figure 3. ORTEPs of *anti*- and *syn*-bis(2-phenylindenyl)zirconium dichloride (**1**).

the hafnium−carbon bond lengths are shorter than those of the zirconium derivative. The ligand environment has only a small effect on the bond lengths; the (CF$_3$)$_2$PhInd-substituted complexes have average metal−carbon bond lengths that are approximately 0.005 Å shorter than those of the corresponding 2-PhInd complexes.

The solution structure of these metallocenes was investigated by variable temperature NMR spectroscopy.[6,7] At room temperature, the ^{1}H NMR spectra at 400 MHz of the zirconocene dichloride **1** and the hafnocene dichloride **2** exhibit time-averaged C_2 symmetry consistent with rapid rotation of the indenyl ligands.[8,9] Coalescence was not observed at any temperature down to −100 °C. The same was observed for the dimethyl derivative of **1**, bis(2-phenylindenyl)zirconium dimethyl (**5**). For this reason, the dibenzyl derivatives of **1** and **2**, bis(2-phenylindenyl)zirconium dibenzyl (**6**) and bis(2-phenylindenyl)hafnium dibenzyl (**7**) were synthesized by reaction of **1** and **2** with benzylmagnesium chloride.

At room temperature, the benzylic protons H$_a$ and H$_b$ (Figure 6) are equivalent and appear as sharp singlets at 0.11 (**6**) and −0.19 ppm (**7**). The cyclopentadienyl protons H$_c$ and H$_d$ appear as broad singlets at 5.92 (**6**) and 5.87 ppm (**7**). At −70 °C, the benzylic protons become diastereotopic and appear as a doublet of doublets (**6**, $\Delta\nu$, = 123 Hz, J = 11.16 Hz, Figure 7; **7**, $\Delta\nu$ = 238 Hz, J = 10.94 Hz, Figure 8), while the cyclopentadienyl protons split into two singlets (**6**, $\Delta\nu$ = 502 Hz; **7**, $\Delta\nu$ = 472 Hz). As the temperature is varied, the signals for the benzylic protons exhibit behavior consistent with coupled two-site exchange (H$_a$↔H$_b$), while those for the cyclopentadienyl protons exhibit behavior consistent with uncoupled two-site exchange (H$_c$↔H$_d$).[6]

The dynamics were investigated by comparing the experimental spectrum with a calculated spectrum at each temperature.[9,10] For the cyclopentadienyl protons, simulated spectra were calculated from the modified Bloch equations for uncoupled two-site exchange,[11,12] while simulations corresponding to the benzylic protons were calculated from Alexander's and Johnson's equations for coupled two-site exchange.[7,13] Simula-

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Table 1.   Representative M−C Bond Lengths (Å) for
(2-PhInd)$_2$MCl$_2$

Anti Isomer			
Zr(1)−C(1)	2.482(5)	Hf(1)−C(1)	2.538(6)
Zr(1)−C(2)	2.561(3)	Hf(1)−C(7)	2.517(10)
Zr(1)−C(3)	2.558(3)	Hf(1)−C(9)	2.542(6)
Zr(1)−C(4)	2.612(4)	Hf(1)−C(17)	2.618(6)
Zr(1)−C(9)	2.531(5)	Hf(1)−C(23)	2.454(6)
average	2.548	average	2.533
Zr(1)−C(16)	2.465(3)	Hf(1)−C(2)	2.591(7)
Zr(1)−C(17)	2.551(3)	Hf(1)−C(8)	2.461(8)
Zr(1)−C(18)	2.564(3)	Hf(1)−C(16)	2.547(5)
Zr(1)−C(19)	2.622(3)	Hf(1)−C(22)	2.516(5)
Zr(1)−C(24)	2.527(3)	Hf(1)−C(24)	2.542(6)
average	2.545	average	2.531
Syn Isomer			
Zr(2)−C(31)	2.476(4)	Hf(2)−C(32)	2.582(6)
Zr(2)−C(32)	2.504(4)	Hf(2)−C(38)	2.459(9)
Zr(2)−C(33)	2.523(3)	Hf(2)−C(46)	2.528(6)
Zr(2)−C(34)	2.624(3)	Hf(2)−C(52)	2.563(6)
Zr(2)−C(39)	2.570(3)	Hf(2)−C(54)	2.485(7)
average	2.539	average	2.523
Zr(2)−C(46)	2.485(5)	Hf(2)−C(31)	2.511(2)
Zr(2)−C(47)	2.553(4)	Hf(2)−C(37)	2.551(7)
Zr(2)−C(48)	2.529(3)	Hf(2)−C(39)	2.543(7)
Zr(2)−C(49)	2.591(3)	Hf(2)−C(47)	2.614(6)
Zr(2)−C(54)	2.559(4)	Hf(2)−C(53)	2.471(7)
average	2.543	average	2.538
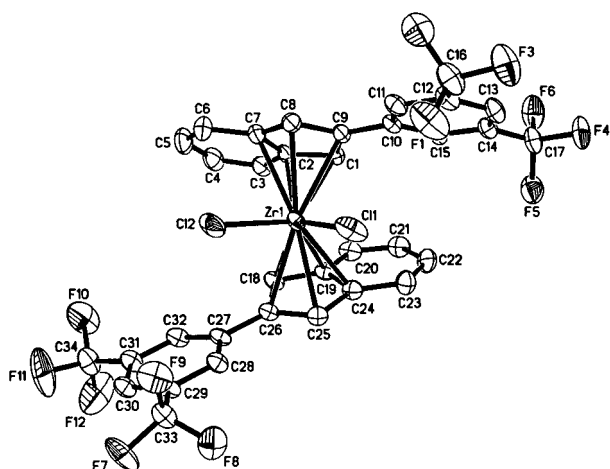
Figure 4.   ORTEPs of bis(2-[3,5-bistrifluoromethyl)phenyl]indenyl)-
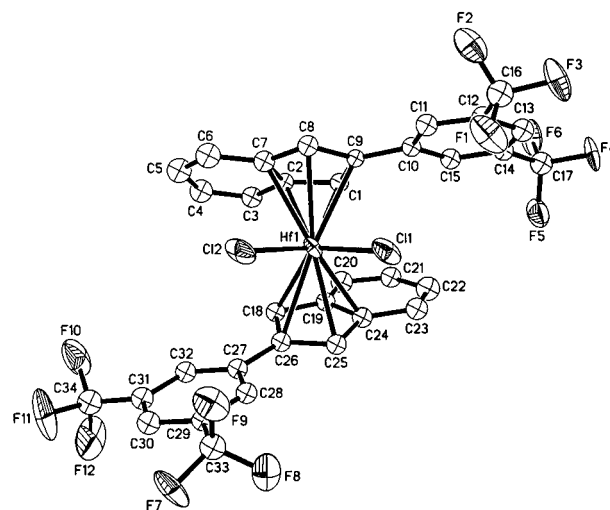zirconium dichloride (**3**).

tions were carried out on a locally written routine. These studies revealed that the rate of exchange of the cyclopentadienyl protons was equal to that of the benzylic protons, strongly implicating indenyl rotation as the dynamic process resulting in the observed exchanges.

The exchange rates are presented in Table 3. The values of $\Delta G^{\ddagger}$ were calculated at each temperature using the Eyring equation (eq 1). A plot of $\Delta G^{\ddagger}$ versus temperature[14] yielded

$$k = \kappa(k_B T/h) \exp(-\Delta G^{\ddagger}/RT) \qquad (1)$$

the following activation parameters: **6**, $\Delta H^{\ddagger}$ = 7.8(±2.3) kcal/mol, $\Delta S^{\ddagger}$ = −15.4(±10.1) cal/mol; **7**, $\Delta H^{\ddagger}$ = 7.1(±3.0) kcal/mol, $\Delta S^{\ddagger}$ = −17.3(±11.0) cal/mol.[9]

Comparison of the rates and activation parameters for the zirconium derivative **6** and the hafnium derivative **7** indicate that the exchange rates for the two different metals were the same within experimental error.

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Figure 5.   ORTEPs of bis(2-[3,5-bis(trifluoromethyl)phenyl]indenyl)-hafnium dichloride (**2**).

Table 2.   Representative M−C Bond Lengths for
(2-[3,5-Bis(trifluoromethyl)phenyl]indenyl)$_2$MCl$_2$

Zr(1)−C(1)	2.486(3)	Hf(1)−C(1)	2.474(12)
Zr(1)−C(7)	2.587(4)	Hf(1)−C(7)	2.561(14)
Zr(1)−C(9)	2.551(3)	Hf(1)−C(9)	2.541(11)
Zr(1)−C(2)	2.562(4)	Hf(1)−C(2)	2.543(12)
Zr(1)−C(8)	2.538(4)	Hf(1)−C(8)	2.550(13)
average	2.545(4)	average	2.534(13)
Zr(1)−C(18)	2.517(3)	Hf(1)−C(18)	2.503(12)
Zr(1)−C(24)	2.524(4)	Hf(1)−C(24)	2.487(14)
Zr(1)−C(26)	2.565(3)	Hf(1)−C(26)	2.558(12)
Zr(1)−C(19)	2.588(4)	Hf(1)−C(19)	2.552(13)
Zr(1)−C(25)	2.508(4)	Hf(1)−C(25)	2.502(13)
average	2.540(4)	average	2.520(13)
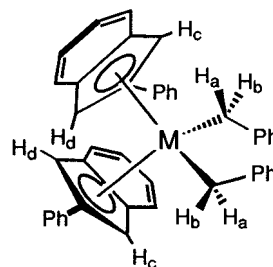
Figure 6.   Bis-(2-phenylindenyl)$_2$M(CH$_2$Ph)$_2$.

The metallocene dichlorides **1**−**4** are active propylene polymerization catalysts when combined with methylaluminoxane (MAO) in toluene (Table 4).[4,5] Polymerizations were carried out under a variety of pressure/temperature combinations, using two methods of addition of the catalyst to the polymerization reactor. In method A, 200 psig argon gas was used to inject 20 mL of aged catalyst/cocatalyst toluene solution from a 50 mL single-ended injection tube into a 300 mL stirred Parr reactor. Method B employed propylene pressure and a double-ended injection tube to inject the catalyst solution.

The productivities of these catalysts range from 200 to 3000 kg of PP/(mol of M·h), depending on the reaction conditions. The productivities of the hafnium complexes are approximately equal to those the zirconium complexes. The trends for the different ligands are less clear, but the zirconium bis(triflouromethyl) derivative **3** appears to be slightly less productive than the 2-phenylindene derivative **1**. As previously observed, there is generally an increase in productivity with increasing propylene pressures for each catalyst system.[4]

Molecular weights produced by all complexes in solution are in the range of 200 000 < M_w < 1 000 000. Molecular weights
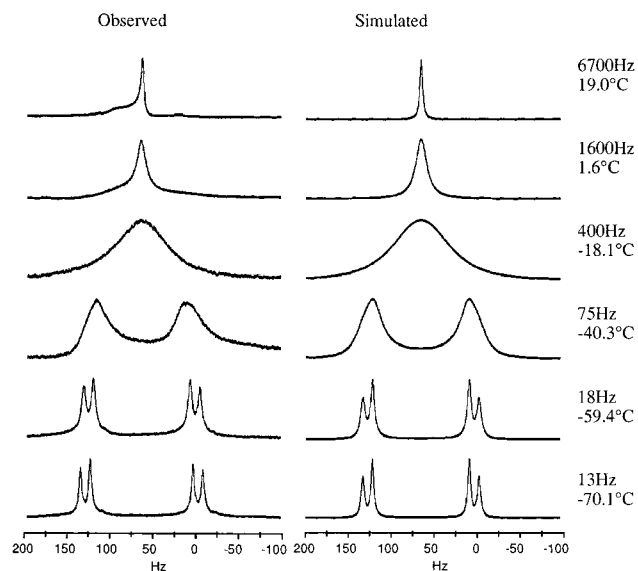
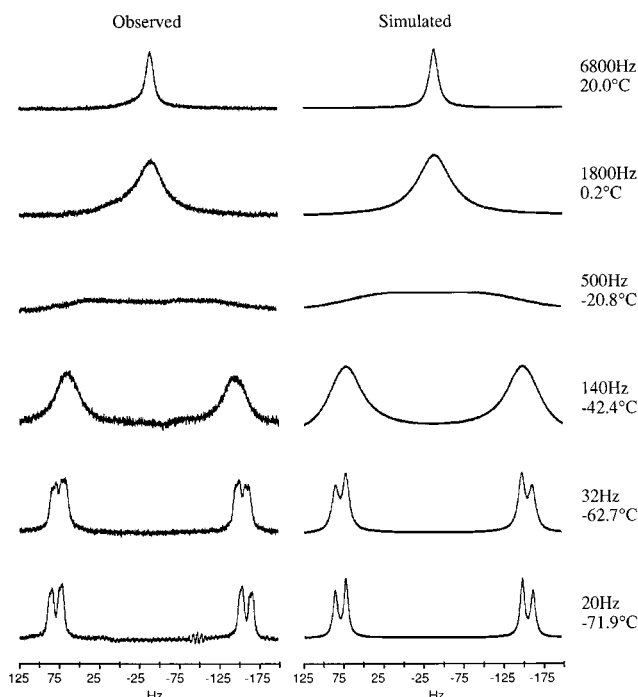**Figure 7.** Variable temperature spectra and simulations of **6**.

Figure 8. Variable temperature spectra and simulations of **7**.

increase with increasing propylene pressure of polymerization as well as with decreasing temperature. The M_w of polymers produced by hafnium catalysts are approximately the same as those produced by the zirconium catalysts. The polydispersities (M_w/M_n) of polymers produced with (2-PhInd)$_2$HfCl$_2$ (**2**) are close to $M_w/M_n = 2$; polydispersities for polymers obtained from zirconium **3** are as high as $M_w/M_n = 4$. There appears to be a correlation between isotacticity ([*mmmm*]) and the polydispersity. Polydispersities appear to be higher for catalysts that produce more highly isotactic polymer: **2** < **4** < **1** < **3**.

The microstructure of polypropylene is measured by examining the methyl region of the polymer ^{13}C NMR spectrum, which gives the relative stereochemistry to the pentad level of stereosequences.[15] Two measures of isotacticity are the percentage of *meso* dyads ([*m*]) and the percentage of isotactic pentads ([*mmmm*]). Polymerization of propylene with the zirconocene

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1 yields elastomeric polypropylenes with isotactic pentad contents in the range of [*mmmm*] = 28−36%. The value of [*mmmm*] increases with increasing propylene pressure. For solution polymerizations, a decrease in isotacticity is observed with increasing temperature.

Polymers produced with the PhInd hafnium catalyst **2** are tacky atactic materials that exhibit no melting transition. The microstructure of polymer varies only slightly with propylene pressure; the isotacticity index ranges from [*mmmm*] = 6% to 10% upon increasing propylene pressure from 25 to 100 psig. Molecular weights exhibit the same trends as those for **1**. Productivity of **2** is approximately the same as that of **1** and similarly increases slightly with increasing pressure and temperature.

The influence of the ligand on the stereospecificity, as previously described,[4b] can be significant: the (CF$_3$)$_2$PhInd zirconium derivative **3** yields polypropylenes with higher isotacticities than those of the unsubstituted 2-PhInd catalyst **1**. A similar trend is observed for the hafnium derivatives **4** and **2**, although the differences in these two cases are small. The nature of the metal also has a large effect on the stereospecificity: for both ligands, the zirconium derivatives **1** and **3** produce more isotactic polymers than their hafnium congeners **2** and **4**. Productivities of **3** and **4** are about half those of the corresponding 2-PhInd derivatives **1** and **2**, and again the hafnium catalyst exhibits productivity similar to that of the zirconium catalyst. Molecular weights and polydispersities are comparable.

Discussion

Unbridged 2-arylindene catalysts produce elastomeric polypropylenes with a wide range of isotacticities.[4] The nature of the ligand has a dramatic effect on the stereospecificity of the catalyst.[4] In this paper, we report that the stereospecificity of this class of catalysts is also quite sensitive to the nature of the metal atom (Zr vs Hf).

Zirconium and hafnium are similar group 4 metals separated by only one row on the periodic table of the elements. Complexes of zirconium and hafnium with the same ligand environments are closely isostructural and possess similar chemical properties.[16] In fact, the solid-state structures of zirconium and hafnium metallocenes derived from 2-arylindene ligands are nearly identical. Comparison of the crystal structures of the (PhInd) zirconium and hafnium complexes **1** and **2** as well as the ((CF$_3$)$_2$PhInd) complexes **3** and **4** reveals close structural similarity. For each hafnium−zirconium pair, corresponding metal−cyclopentadienyl bond lengths are nearly identical, with the hafnium−cyclopentadienyl bonds approximately 0.01 Å shorter, consistent with the lanthanide contraction.

The solution structure and dynamics of hafnium and zirconium complexes also appear very similar. Solution NMR studies of the zirconium dichloride **1** and the corresponding dimethyl derivative (2-PhInd)$_2$ZrMe$_2$ (**5**) from −80 to 25 °C reveal time-averaged C_2 symmetry consistent with rapid rotation of the indenyl ligands in solution. Substitution of the choride ligands of **1** and **2** for benzyl ligands yields the dibenzyl derivatives **6** and **7**. The low-temperature (−70 °C) ^{1}H NMR spectra of (2-PhInd)$_2$Zr(CH$_2$Ph)$_2$ (**6**) and (2-PhInd)$_2$Zr(CH$_2$Ph)$_2$ (**7**) show two cyclopentadienyl resonances and two doublets corresponding to diastereotopic benzylic protons. These spectra imply that the observed exchange at −70 °C is between the

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Table 3. Dynamic NMR Data for (2-PhInd)$_2$M(CH$_2$Ph)$_2$ Complexes **6** and **7**

	M = zirconium (**6**)			M = hafnium (**7**)	
T/°C	k/Hz	$\Delta G^{\ddagger}$/kcal	T/°C	k/Hz	$\Delta G^{\ddagger}$/kcal
19.0 ± 0.2	6700 ± 300	12.0 ± 0.1	20.0 ± 0.2	6800 ± 300	12.0 ± 0.1
12.5	3300 ± 200	12.0	10.0	3500 ± 200	11.9
1.6	1600 ± 100	12.0	0.2	1800 ± 100	11.9
−8.2	775 ± 50	11.9	−9.8	850 ± 50	11.8
−18.1	400 ± 25	11.8	−20.8	500 ± 25	11.6
−29.7	150 ± 20	11.7	−30.7	290 ± 20	11.4
−40.3	75 ± 12	11.5	−42.7	140 ± 12	11.1
−50.8	32 ± 5	11.3	−52.7	60 ± 5	11.0
−59.4	18 ± 3	11.1	−62.7	32 ± 3	10.7
−70.1	13 ± 2	10.7	−71.9	20 ± 2	10.4

Table 4. Polypropylenes Produced with Catalysts **1**−**4**

expt	cat.	method	conditions[d]	prodvty[a]	M_w[b]	M_w/M_n[b]	m[c] (%)	$mmmm$[c] (%)
1	**1**	B[d]	35 psig, 20 °C	952	232 000	3.8	63	23
2	**1**	B	50 psig, 20 °C	832	250 000	3.3	66	27
3	**1**	B	75 psig, 20 °C	1480	399 000	3.8	68	29
4	**1**	B	100 psig, 20 °C	960	435 000	3.0	70	31
5	**1**	B	75 psig, 0 °C	1544	973 000	3.2	73	35
6	**2**	B	35 psig, 20 °C	1080	345 000	2.3	55	8
7	**2**	B	50 psig, 20 °C	1460	198 000	2.0	57	9
8	**2**	B	75 psig, 20 °C	1440	375 000	2.2	58	9
9	**2**	B	100 psig, 20 °C	1180	486 000	2.1	57	9
10	**2**	B	50 psig, 0 °C	1160	812 000	2.1	56	10
11	**3**	A	25 psig, 25 °C	250			75	45
12	**3**	A	35 psig, 25 °C	500	243 000	3.2	78	51
13	**3**	A	50 psig, 25 °C	730	296 000	3.4	80	58
14	**3**	A	75 psig, 25 °C	1370	332 000	3.7	86	73
15	**3**	B	35 psig, 20 °C	206	454 000	4.0	85	56
16	**3**	B	50 psig, 20 °C	582	470 000	3.9	85	59
17	**3**	B	75 psig, 20 °C	624	631 000	4.3	88	64
18	**3**	B	100 psig, 20 °C	638	608 000	5.6	87	67
19	**4**	A	35 psig, 25 °C	1130	285 000	2.9	55	12
20	**4**	A	50 psig, 25 °C	1350	330 000	2.4	64	18
21	**4**	A	75 psig, 25 °C	2190	415 000	2.4	58	15
22	**4**	A	90 psig, 25 °C	3050	483 000	2.5	57	21
23	**4**	B	35 psig, 20 °C	506	292 000	2.4	54	10
24	**4**	B	50 psig, 20 °C	360	376 000	2.2	56	11
25	**4**	B	75 psig, 20 °C	660	474 000	2.4	56	11
26	**4**	B	100 psig, 20 °C	700	531 000	2.3	57	12

[a] In kg of PP/(mol of Zr·h). [b] Determined by GPC vs polypropylene. [c] Determined by ^{13}C NMR spectroscopy. [d] [M] = 5.0×10^{-5} M, [Al]/[Zr] = 1000, t = 1 h. Method A, [M]/MAO in 20 mL of toluene injected under 200 psig Ar; method B, [M]/MAO in 20 mL of toluene injected under P + 5 psig propylene.

two enantiomers of the chiral *anti* conformation. The *syn* (or *meso*) conformer is not observed as an energetic minimum, although it cannot be ruled out as an intermediate in the exchange process.

Line shape analysis was used to determine the rates of exchange. The benzylic protons were modeled as a coupled two-site exchange, and the cyclopentadienyl protons were modeled as an uncoupled two-site exchange.[6] These model spectra were compared to the observed spectra to determine the rate of exchange at each temperature. At any given temperature, the cyclopentadienyl protons exhibit the same rate of exchange as the benzylic protons, strongly implicating indenyl rotation as the mechanism for the observed exchange.

Comparison of the data obtained from line shape analysis of the VT spectra of zirconium dibenzyl **6** and hafnium dibenzyl **7** leads to the conclusion that exchange rates of **6** and **7** are the same within experimental error at each temperature. The Eyring equation yields $\Delta G^{\ddagger}$ values that are nearly the same for hafnium as zirconium. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from a plot of $\Delta G^{\ddagger}$ vs temperature. The values differ slightly from zirconium to hafnium but are within the wider experimental error for this method. These data indicate that hafnium and zirconium exhibit nearly identical solution behavior, consistent with the nearly identical X-ray crystal structures.

All catalysts **1**−**4** produce polypropylene when combined with MAO under a propylene atmosphere. In each case, the productivities of the hafnium and zirconium catalysts are approximately the same. The similar productivities of the Hf and Zr catalysts could be a consequence of similar rate constants; however, hafnium complexes are typically less reactive than the zirconium congeners.[17] The other possibility is that, for hafnium, the average number of active sites over the course of the polymerization is greater than that for zirconium, but the number of active centers is balanced by a lower reactivity of hafnium.

Zirconium and hafnium catalysts with identical ligand environments produce polymers with approximately the same weight-average molecular weights, 200 000 < M_w < 1 000 000. As the hafnium catalysts produce more monodisperse polymer than zirconium, the number-average molecular weights are larger for Hf than for Zr, although this difference is small for the triflouromethyl-substituted ligands. The values of M_w/M_n for atactic polymers produced by the hafnium catalysts are approximately 2.1, consistent with the value of 2 observed for homogeneous Ziegler−Natta systems. The higher M_w/M_n for

(17) Ewen, J. A.; Haspeslach, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544−6545.

Scheme 1. Proposed Mechanism of Polymerization

rac- (**A**)   meso- (**B**)
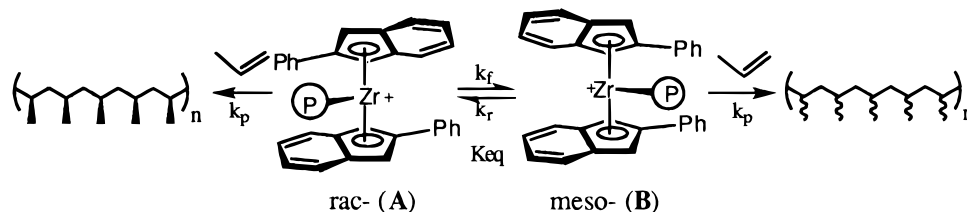
the more isotactic polymers might be a consequence of a two-site switching process, where each site is predisposed to give different molecular weight polymers.[18]

In spite of the close structural similarities and similar rotational rate for the indenyl ligands, the zirconium and hafnium complexes produce quite different polypropylene microstructures. For both 2-PhInd and $(CF_3)_2$PhInd systems, the zirconium derivatives yield much higher isotacticities ([*mmmm*] by ^{13}C NMR) than the corresponding hafnium complexes. These differences are difficult to rationalize on purely structural grounds. However, we have previously proposed a mechanism that might account for the large differences in stereospecificity for these 2-arylindene zirconium and hafnium metallocenes. The mechanistic model invokes the interconversion of different catalyst states during the polymerization:[4] a chiral *rac*-like state (**A**) and an achiral *meso*-like state (**B**) (Scheme 1). State **A** is predicted to produce isotactic polypropylene, while state **B** should yield atactic polypropylene. The exchange of sites is postulated to occur by rotation of the unbridged indenyl ligands. As long as the rate of site switching is slower than the rate of polymerization, the catalyst will produce blocks of isotactic stereosequences and blocks of atactic stereosequences; if the rate of rotation is faster than the rate of propagation, block lengths will become negligible, and polymer stereochemistry will be random (atactic).

According to this mechanism, the rate of conversion of state **A** to state **B** is given by $R_A = k_f[A]$, and that of state **B** to site **A** is given by $R_B = k_r[B]$. There is also an equilibrium constant for this exchange, given by $K_{eq} = k_r/k_f$. The rate of polymerization is assumed to be second order: $R_{pA} = k_{pA}[C_3H_6][A]$ for the isospecific site and $R_{pB} = k_{pB}[C_3H_6][B]$ for the aspecific site. According to these definitions, the block lengths of the polymers are defined as the ratio of propagation to rotation: $BL_A = R_{pA}/R_A$ and $BL_B = R_{pB}/R_B$. Therefore, only when $R_A < R_{pA}$ will blocks of isotactic polymer will be produced. As R_A approaches R_{pA}, the blocks will grow progressively shorter. As the length of an isotactic stereosequence approaches unity, placement of stereocenters becomes random, and atactic polymer is produced.

As the polymers made from the hafnium catalysts have the lowest isotacticities ([*mmmm*] and [*m*]), it follows that hafnium-produced polymers have shorter average isotactic sequence lengths than polymers made from the zirconium catalysts. In the context of this mechanism, there are three possible explanations for the differences between hafnium and zirconium catalysts: a difference in the steady-state concentration of isospecific and aspecific states (K_{eq}), a difference in the rate of interconversion of the two states, and/or a different rate of propagation for the isospecific site. The structural similarities of the zirconium and hafnium complexes and the similar rates of rotation for the dibenzyl derivatives of the metallocenes argue

against either the equilibrium constant or the rate of interconversion as the origin of the lower stereoselectivity for hafnium relative to zirconium. Thus, we believe the most reasonable explanation is that hafnium has a slower rate of propagation at the isospecific site than zirconium ($k_{p[Hf]} < k_{p[Zr]}$). If the rate of propagation for hafnium is slower, such that it is similar to the rate of inconversion of the two sites, then the polymer produced would have very short isotactic block lengths and have a lower [*mmmm*].

The conclusion that rate of propagation at the isospecific site is lower for hafnium is what might be expected, given that organohafnium compounds are typically less reactive than organozirconium compounds.[16] However, this conclusion is seemingly inconsistent with similar productivities of zirconium and hafnium catalysts. However, as stated previously, productivities are not necessarily indicative of the rate constants of propagation.[19] Similar productivities for hafnium could be a consequence of a higher number of active centers for hafnium relative to those for zirconium but a lower rate of propagation at hafnium centers than at zirconium centers.[20] Assuming that the two effects balance each other, it may be concluded that hafnium produces atactic polymer by slow propagation at many sites, and zirconium produces stereoblock polymer by fast propagation at a few sites.

A further point with regard to the proposed mechanism is the rate of rotation of the dibenzyl compounds relative to the rate of polymerization. The measured rates of rotation for the dibenzyl derivatives are faster than reasonable estimates for the propagation rates. A turnover frequency for propylene insertion of 10 s^{-1} can be estimated for catalyst **1**/MAO at 75 psig and 20 °C.[21] This is several orders of magnitude slower than the rate of rotation of 6700 Hz observed for the dibenzyl complexes. (This is true even if less than 100% active centers is assumed.)[19] These rates are seemingly inconsistent with the proposed mechanism, since, for a block structure to be produced, the rate of polymerization should be faster than the rate of interconversion of the two sites. However, the rate of interconversion for the active catalyst is not known, and the rates measured for the dibenzyls may be poorly representative of the rate for the actual catalyst. The fact that the rate of ligand rotation for the dibenzyl derivatives **6** and **7** is slower than that for either the dichlorides **1** and **2** or the dimethyl **5** demonstrates that the rate of ligand rotation is quite sensitive to the nature of the ligands bound to the transition metal center. Given that the active catalysts contain a growing polymer chain and are likely cationic with some associated anion of ill-defined structure, it is likely that the rate of ligand rotation will be different from that of the dibenzyl derivatives. Current efforts are underway to devise more realistic models for the active catalyst to investigate the ligand dynamics.

(18) For example, if the isospecific site is predisposed to give $M_w = 500\,000$ with PDI = 2.0, and the aspecific site gives $M_w = 100\,000$ with PDI = 2.0, a switching site catalyst would give an intermediate M_w with a much broader PDI in order to encompass both the isotactic and atactic only distributions. See: Coleman, B. D.; Fox, T. G. *J. Am. Chem. Soc.*, **1963**, *85*, 1241−1244.

(19) Chien, J. C. W. *J. Polym. Sci. A.: Polym. Chem.* **1991**, *29*, 459−470.

(20) A higher average active site concentration for hafnium might result from a slower rate of inactivation of hafnium catalysts sites over the course of the polymerization reaction.

(21) At 75 psig, 20 °C, the productivity of 1 is 1480 kg of PP/mol of Zr. This corresponds to 9.78 insertions/s.

In summary, we have provided an unusual example of isostructural metallocene catalysts which have quite different stereospecificities in propylene polymerization. This is remarkable in that, in stereospecific catalysis, it is generally held that the coordination geometry of the catalyst site is a key element in stereodifferentiation. The large differences between the isostructural hafnium and zirconium catalysts are most readily rationalized in terms of the different dynamics of propagation relative to isomerization in these dynamic catalyst systems.

Experimental Section

General Comments. All organometallic reactions were performed under an inert argon or nitrogen atmosphere using standard Schlenk or drybox techniques. 2-Phenylindene, 2-[3,5-bis(trifluoromethyl)phenyl]-indene, bis(2-phenylindenyl)zirconium dichloride, and bis(2-[3,5-bis-(trifluoromethyl)phenyl]indenyl)zirconium dichloride were prepared as previously described.[4] Benzylmagnesium chloride (1.0 M in THF), phenylmagnesium bromide (3.0 M in diethyl ether), and *n*-butyllithium (2.5 M in hexanes) were purchased from Aldrich and used without further purification. Zirconium tetrachloride was purchased from Fluka and used without further purification. Hafnium tetrachloride (99.9%, 0.14% Zr) was purchased from Cerac and used without further purification. MAO (type IV, 7.4% in toluene) was purchased from Akzo and dried *in vacuo* prior to use.

THF, diethyl ether, and benzene were each distilled from sodium-benzophenone ketyls prior to use. Propylene and toluene were passed through two columns: one containing alumina (Kaiser, dried by passing N_2 through the column at 350 °C for 5 h) and one containing Q-5 reactant (Englehard, prepared by passing N_2 through the column at 300 °C for 3 h, followed by 5% H_2 for 3 h, followed by N_2 for 3 h).[22]

^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 400 MHz for protons and 100 MHz for ^{13}C. All polymer ^{13}C spectra were deconvoluted on an Silicon Graphics Indigo workstation using Felix. GPC data were recorded in trichlorobenzene on a GPC operating at 135 °C and referenced to a polypropylene standard. Productivities of the catalysts were calculated from the weight of polymer produced.

Dynamic NMR simulations were performed on a Macintosh computer, using locally written software, DYNMR (see Supporting Information for full details of dynamic NMR simulations).

Metallocene Synthesis. Bis(2-phenylindenyl)hafnium Dichloride (2). To a stirred solution of 1.89 g (9.83 mmol) of 2-phenylindene and 40 mL of THF was added dropwise 3.93 mL (9.83 mmol) of *n*-butyllithium (2.5 M in hexanes) at −78 °C under Ar. After the solution was warmed to room temperature, the THF was removed *in vacuo* and replaced with toluene. Next, 1.57 g (4.90 mmol) of hafnium tetrachloride was added via cannula as a slurry in 20 mL of toluene at room temperature. After 24 h, the yellow solution was filtered over Celite. The compound was isolated by recrystallization from toluene to give 0.62 g (20%) of yellow crystals.

^{1}H NMR (400 MHz, 20 °C, CDCl$_3$): δ 7.36 (d, 4H, J = 7.2 Hz), 7.18 (m, 4H), 7.12 (m, 2H), 7.07 (dd, 4H, J = 6.6, 3.1 Hz) 6.88 (dd, 4H, J = 6.6, 3.1 Hz), 6.29 (s, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 20 °C, C$_6$D$_6$): δ 133.7, 132.1, 128.9, 128.5, 127.3, 126.5, 126.1, 125.2, 101.4 ppm. Anal. Calcd for C$_{30}$H$_{22}$HfCl$_2$: C, 57.02; H, 3.51; Cl, 11.22. Found: C, 56.64; H, 3.65; Cl, 10.91.

Bis(2-[3,5-bis(trifluoromethyl)phenyl]hafnium Dichloride (4). *n*-Butyllithium (1.6 M in hexanes, 2 mL, 3.20 mmol) was added dropwise at ambient temperature to a solution of 2-[3,5-bis(trifluoromethyl)-phenyl]indene (1.03 g, 3.14 mmol) in 10 mL of diethyl ether. After the solution was stirred for 30 min, the solvent was removed *in vacuo*, leaving a green-yellow solid. In an N$_2$ drybox, HfCl$_4$ (510 mg, 1.59 mmol) was added to the lithium salt. The solids were then cooled to −78 °C, at which temperature 45 mL of toluene was slowly added. The flask was allowed to reach ambient temperature, and the suspension was stirred at room temperature for 24 h. The solvent was removed *in vacuo*, and the residual solid was extracted with CH$_2$Cl$_2$. The solution was filtered and purified by precipitation by hexanes from CH$_2$Cl$_2$.

^{1}H NMR (400 MHz, 20 °C, CDCl$_3$): δ 7.65 (s, 2H), 7.51 (s, 4H), 6.7−7.3 (m, 8H), 5.63 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, 20 °C, C$_6$D$_6$): δ 135.8, 132.9, 131.6, 127.2, 126.3, 126.0, 125.6, 123.8, 121.7, 100.1. Anal. Calcd for C$_{34}$H$_{18}$F$_2$HfCl$_2$: C, 45.10; H, 1.87. Found: C, 45.18; H, 2.01.

Bis(2-phenylindenyl)zirconium Dibenzyl (6). To a solution of 205 mg (0.376 mmol) of bis(2-phenylindenyl)zirconium dichloride in 20 mL of THF was added 0.451 mL (0.903 mmol) of benzylmagnesium chloride (1.0 M in THF) at room temperature under Ar. After 24 h, the THF was removed *in vacuo* and replaced with toluene. The orange solution was filtered and dried *in vacuo*. The compound was isolated by recrystallization from toluene to give 102 mg (41%) of orange crystals.

^{1}H NMR (400 MHz, −60 °C, CD$_2$Cl$_2$): δ 7.57 (t, 4H, J = 7 Hz), 7.43 (m, 6H), 7.21 (t, 4H, J = 7 Hz), 7.02 (t, 4H, J = 8 Hz), 6.86 (t, 2H, J = 7 Hz), 6.78 (d, 4H, J = 8 Hz), 6.51 (dd, 4H, J = 62, 7 Hz), 5.78 (d, 4H, J = 502 Hz), 0.15 (dd, 4H, J = 123, 11 Hz) ppm. ^{1}H NMR (400 MHz, 17 °C, CD$_2$Cl$_2$): δ 7.57 (t, 4H, J = 7 Hz), 7.43 (m, 6H), 7.21 (t, 4H, J = 7 Hz), 7.02 (t, 4H, J = 8 Hz), 6.86 (t, 2H, J = 7 Hz), 6.78 (d, 4H, J = 8 Hz), 6.51 (s, 4H), 5.78 (s, 4H), 0.15 (s, 4H) ppm. Anal. Calcd for C$_{44}$H$_{36}$Zr: C, 80.56; H, 5.53. Found: C, 80.53; H, 5.40.

Bis(2-phenylindenyl)hafnium Dibenzyl (7). To a solution of 98 mg (0.155 mmol) of bis(2-phenylindenyl)hafnium dichloride in 20 mL of THF was added 0.170 mL (0.341 mmol) of benzylmagnesium chloride (1.0 M in THF) at room temperature under Ar. After 24 h, the THF was removed *in vacuo* and replaced with toluene. The orange solution was filtered and dried *in vacuo*. The product was isolated by recrystallization from toluene to give 52 mg (42%) of yellow crystals.

^{1}H NMR (400 MHz, −70 °C, CD$_2$Cl$_2$): δ 7.60 (t, 4H, J = 7 Hz), 7.44 (m, 6H), 7.22 (t, 4H, J = 7 Hz), 7.12 (t, 4H, J = 8 Hz), 6.84 (t, 2H, J = 7 Hz), 6.76 (d, 4H, J = 8 Hz), 6.47 (dd, 4H, J = 38, 9 Hz), 5.82 (d, 4H, J = 445 Hz), −0.09 (dd, 4H, J = 237, 12 Hz) ppm. ^{1}H NMR (400 MHz, 17 °C, CD$_2$Cl$_2$): δ 7.60 (t, 4H, J = 7 Hz), 7.44 (m, 6H), 7.22 (t, 4H, J = 7 Hz), 7.12 (t, 4H, J = 8 Hz), 6.84 (t, 2H, J = 7 Hz), 6.76 (d, 4H, J = 8 Hz), 6.47 (s, 4H), 5.82 (s, 4H), −0.09 (s, 4H) ppm. Anal. Calcd for C$_{44}$H$_{36}$Hf: C, 71.10; H, 4.88. Found: C, 71.27; H, 5.10.

Crystallography. Single crystals suitable for X-ray analysis were prepared by recrystallization from toluene (**1** and **2**) or toluene/hexane (**4**) at −25 °C.

Data Collection and Reduction of Bis(2-phenylindenyl)zirconium Dichloride (1). A yellow plate crystal of **1**, C$_{30}$H$_{22}$Cl$_2$Zr, with approximate dimensions of 0.600 mm × 0.400 mm × 0.150 mm, was mounted in paratone oil on a glass fiber. The specimen was placed in a cold stream of nitrogen on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 8658 reflections were collected, of which 8274 were unique (R_{int} = 0.026). Crystallographic details are summarized in Table 5.

The structure was solved by direct methods[23] and expanded using Fourier techniques.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier maps but included at idealized position 0.95 Å from their parent atoms. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 6362 observed reflections (I > $3\sigma(I)$) and 613 variable parameters and converged (largest parameter shift was 0.20 times its estimated standard deviation) with unweighted and weighted agreement factors of R = 0.032 and R_w = 0.032.

Two rotational isomers of the complex were observed in the refined structure. The complex displaying eclipsed ligands (*syn*) was determined to be slightly disordered and was refined at 96% occupancy. Only the heavy atoms (Zr(3), Cl(5), and Cl(6)) of the disordered molecule were observed and were modeled at 4%. All calculations were performed using the teXsan software package (Molecular Structure Corp.).

(22) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(23) SAPI91: Fan, H.-F. Structure Analysis Programs with Intelligent Control; Rigaku Corp. Tokyo, Japan, 1991.

(24) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system; Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

Table 5. Crystallographic Details of **1**, **2**, and **4**

	1	**2**	**4**
empirical formula	$C_{30}H_{22}Cl_2Zr$	$C_{30}H_{22}Cl_2Hf$	$C_{34}H_{18}Cl_2F_{12}Hf$
formula weight	544.63	631.9	903.9
color; habit	yellow plate	yellow plate	yellow prism
crystal size (mm)	$0.60 \times 0.40 \times 0.15$	$0.04 \times 0.20 \times 0.23$	$0.23 \times 0.24 \times 0.36$
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$
unit cell dimensions			
a (Å)	13.538(2)	13.4826(16)	16.983(2)
b (Å)	14.553(2)	14.5600(11)	8.3677(11)
c (Å)	15.365(1)	15.3248(12)	22.495(3)
α (deg)	65.780(1)	65.740(7)	
β (deg)	64.950(1)	64.631(9)	105.862(5)
γ (deg)	63.160(6)	63.116(9)	
volume (Å³)	2355.4(6)	2334.8(4)	3079.0(7)
Z	4	4	4
density (calcd)	1.563 g/cm³	1.798 mg/m³	1.950 mg/m³
absorption coeff	7.1	4.714 mm⁻¹	3.660 mm⁻¹
$F(000)$	1104.00	1232	1744
diffactometer used	Enraf-Nonius CAD-4	Siemens P4RA	Siemens P4
radiation	Mo Kα(λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
temperature (K)	203	158	163
monochromator	highly-oriented graphite	highly oriented graphite crystal	highly oriented graphite crystal
2θ range	$40° < 2\theta < 42°$	4.0–50.0°	4.0–50.0°
scan type	ω	θ–2θ	θ–2θ
scan speed	5.5 deg/min (θ)	const. (ω, 4.00 deg/min)	const. (ω, 3.00 deg/min)
reflections collected	8658	8513	6029
ind reflns	8274(R_{int} = 2.60%)	8138 (R_{int} = 1.12%)	5131 (R_{int} = 7.3%)
obsd reflns	6362	7050 ($F > 3.0\sigma(F)$)	4834 ($F > 2.0\sigma(F)$)
no. params refined	613	595	272
R indicies (obsd data)	R_F = 3.2%, R_{wF} = 3.2%	R_F = 3.6%, R_{wF} = 4.1%	R_F = 7.5%, R_{wF} = 8.9%
data-to-param ratio	10.4	11.8:1	17.8:1
largest diff peak (e Å⁻³)	0.62	5.08	6.17
largest diff hole (e Å⁻³)	−0.88	−1.25	−4.20

Data Collection and Reduction of Bis(2-phenylindenyl)hafnium Dichloride (2). A yellow crystal of approximate dimensions 0.04 mm × 0.20 mm × 0.23 mm was oil-mounted on a glass fiber and transferred to the Siemens P4 rotating-anode diffractometer. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard techniques.[25] Low temperature (158 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation. Crystallographic details are given in Table 5.

All 8513 data were corrected for absorption[26] and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value |F₀| = 0. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. All crystallographic calculations were carried out using the UCI-modified version of the UCLA Crystallographic Computing Package[27] and the SHELXTL PLUS program set.[26] The quantity minimized during least-squares analysis was $\sum w(|F_0| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_0|) + 0.0002(|F_0|)^2$.

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques. There are two independent molecules of the formula unit present. Hydrogen atoms were included using a riding model with d(C−H) = 0.96 Å and U(iso) = 0.06 Å². Refinement of the model led to convergence with R_F = 3.6%, R_{wF} = 4.1%, and GOF = 1.78 for 595 variables refined against those 7050 data with |F₀| > 3.0σ(|F₀|). A final difference Fourier map yielded ρ(max) = 5.08 e Å⁻³ at a distance of 1.873 from Hf(2) and 1.805 from Cl(3).

Data Collection and Reduction of Bis(2-[3,5-bis(trifluoromethyl)-phenyl]indenyl)hafnium Dichloride(4). A yellow crystal of approximate dimensions 0.23 mm × 0.24 mm × 0.36 mm was oil-mounted on a glass fiber and transferred to the Siemens P4 rotating-anode diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard techniques.[25] Low-temperature (163 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation. Crystallographic details are given in Table 5.

All 6029 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. An absorption correction was not done because the orientation of the crystal was inadvertently changed prior to collection of ψ-scans. All crystallographic calculations were carried out using the UCI-modified version of the UCLA Crystallographic Computing Package[27] and the SHELXTL PLUS program set.[26] The quantity minimized during least-squares analysis was $\sum w(|F_0| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_0|) + 0.0002(|F_0|)^2$.

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques. There are two independent molecules of the formula unit present. Hydrogen atoms were included using a riding model with d(C−H) = 0.96 Å and U(iso) = 0.06 Å². Refinement of the model led to convergence with R_F = 7.5%, R_{wF} = 8.9%, and GOF = 3.46 for 272 variables refined against those 4834 data with |F₀| > 2.0σ(|F₀|)). A final difference Fourier map yielded ρ(max) = 6.2 e Å⁻³ at distances of 0.93 and 1.05 Å from Hf(1). The high difference peaks, the necessity for isotropic refinement of carbon atoms, and the higher than expected residuals are most likely due to the absence of an absorption correction.

Polymerization of Propylene. Method A. In a N₂-filled glovebox, a 100 mL two-ended SS (Wiley) injection tube was loaded with 80 mL of toluene. Then, 2.5 mL (5 × 10⁻⁶ mol from stock solution of 20 × 10⁻⁶ mol of toluene) of metallocene dichloride was mixed with 17.5 mL of toluene and 289 mg (5 × 10⁻³mol) of MAO. The solution was aged for 10 min and loaded into a 50 mL single-ended SS (Wiley) injection tube.

After a 300 mL SS Parr reactor was cleaned and evacuated to 30 mTorr, it was pressurized to 150 psig Ar and vented three times. Toluene was injected into the reactor under 100 psig Ar from the 100 mL injection tube. The reactor was vented and refilled twice with propylene of the appropriate pressure. The reactor was allowed to equilibrate for 10 min. The equilibrated catalyst solution in the 50 mL injection tube was injected into the reactor with 200 psig Ar.

(25) *XSCANS Software Users Guide*, Version 2.1; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

(26) SHELXTL.

(27) UCLA Crystallographic Computing Package.

The reactor pressure and temperature were maintained for 60 min. The reaction was quenched by injecting 10 mL of methanol into the reactor. The reactor was vented, and the polymer/toluene slurry was stirred in 300 mL of methanol for 6 h. The solvent was decanted, and the polymer was dried overnight in a vaccuum oven at 40 °C.

Method B. In a N_2-filled glovebox, a 100 mL two-ended SS (Wiley) injection tube was loaded with 80 mL of toluene. Then, 2.5 mL (5×10^{-6} mol from stock solution of 20×10^{-6} mol in 10.0 mL of toluene) of metallocene dichloride was mixed with 17.5 mL of toluene and 289 mg (5×10^{-3} mol) of MAO. The solution was aged for 10 min and loaded into a 50 mL single-ended SS (Wiley) injection tube.

After a 300 mL SS Parr reactor was cleaned and evacuated to 30 mTorr, it was pressurized to 150 psig Ar and vented three times. Toluene was injected into the reactor under 100 psig Ar from the 100 mL injection tube. The reactor was vented and refilled twice with propylene of the appropriate pressure. The reactor was allowed to equilibrate for 10 min, at which time the reactor was vented to 10 psig below reaction pressure. The equilibrated catalyst solution in the 50 mL injection tube was injected into the reactor with propylene of reaction pressure.

Supporting Information Available: Crystal structure parameters and coordinates for **1**, **2**, and **4**, and dynamic NMR spectra and simulations for **6** and **7** (43 pages). See any current masthead page for ordering and Internet access instructions.

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