1-Olefin Polymerization at Bis(pentamethylcyclopentadienyl)zirconium and -hafnium Centers: Enantioface Selectivity†

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ABSTRACT: $Cp^*_2MCl_2$/MAO catalysts (Cp^* = pentamethylcyclopentadienyl; M = Zr, Hf; MAO = methylaluminoxane) polymerize 1-butene to a low molecular weight, predominantly syndiotactic poly(1-butene) with 68% (Zr) and 77% (Hf) rr triads at −20 °C. The mechanism of stereocontrol is shown to be syndiospecific chain end control in primary (head-to-tail) polyinsertion. The temperature dependence of the r/m ratio shows an approximate $E_s - E_i$ of −2 kcal/mol for syndiotactic versus isotactic dyad formation in both systems and a remarkably high (for homogeneous, achiral systems) stereospecificity even above ambient temperature, which surpasses that of all known stereoregular 1-olefin polymerizations operating with chain-end control. Stereoregulation is lost with 1-olefins bearing larger substituents, as observed in the case of 4-methyl-1-pentene.

Introduction

The difference between the cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp^*) ligands in bent metallocene organometallic chemistry is well established. An even more striking difference has been emerging between Cp_2M(IV) and Cp^*_2M(IV) catalyst precursors (M = Zr, Hf) in homogeneous olefin polymerization, seemingly due to the drastic variation in steric bulk around the metal atom on going from the cyclopentadienyl to the pentamethylcyclopentadienyl ligand. For example, 1,5-hexadiene undergoes cyclopolymerization to *trans*-polymethylenecyclopentane with Cp_2M-type catalysts, while *cis*-polymethylenecyclopentane is obtained with Cp^*_2M-type catalysts;[1] atactic propylene oligomers are obtained with both metallocenes but with different chain-transfer mechanisms: β-H elimination at Cp_2M- and β-CH_3 elimination at Cp^*_2M- centers.[2]

Here we report on the stereospecificity of propene and 1-butene insertion with $Cp^*_2MCl_2$/MAO (M = Zr, Hf; MAO = methylaluminoxane) in comparison with other achiral, C_{2v} symmetric metallocene/MAO catalysts. These data provide a further example of the uniqueness of the Cp^* ligand.

Results and Discussion

We recently reported on the different chain-transfer mechanisms operating in propene oligomerization with Cp_2MCl_2/MAO and $Cp^*_2MCl_2$/MAO catalysts.[2c,d] The methyl triad distribution analysis on these oligopropenes showed an expected, slight preference for m dyad formation (higher at lower polymerization temperature and higher with Hf than Zr) with Cp_2MCl_2/MAO and an unexpected, slight preference for r dyad formation with $Cp^*_2MCl_2$/MAO.[2d]

Methyl triad and dyad distributions and Bernoulli trial values B for oligo/polypropenes obtained from $Cp^*_2MCl_2$ in comparison with those from Cp_2MCl_2, Ind_2ZrCl_2, and $Me_2Si(Me_4Cp)_2ZrCl_2$ are reported in Table I, together with the corresponding racemic dyad excess. This value, reminescent of the diastereomeric excess, is defined as

$$\%\,\mathrm{rde} = 100([\mathrm{r}] - [\mathrm{m}])/([\mathrm{r}] + [\mathrm{m}]) = \%\,\mathrm{r} - \%\,\mathrm{m}$$

and is particularly useful because it gives at the same time both the dyad and the rr−mm triad excess. A positive value indicates syndiospecificity, and a negative one isospecificity. (Similarly, the meso dyad excess can be defined as %mde = %m − %r. In this case, the meaning of the signs is reversed.)

All samples are highly regioregular (1-2 polyinsertion as shown by end-group analysis[2c,d]), with the notable exception of that obtained from Ind_2ZrCl_2 (which shows the presence of 1.0% 1-3 enchainments[3]) and follow the simple Bernoullian statistic for dyad formation. While polypropene obtained from Ind_2ZrCl_2 is nearly statistically atactic, $Cp^*_2ZrCl_2$ and $Cp^*_2HfCl_2$ produce propene oligomers with %rde at 0 °C of 16.8 and 22.2, respectively. Of course, such small deviations from pure aspecificity ($P_m = P_r = 0.5$, or %de = 0) are too small to be of any mechanistic relevance. The polymer microstructure, however, changes drastically on going from propene to 1-butene polymers.

Polymerization results of 1-butene are reported in Table II. Samples 1-11 are viscous oils of low molecular weight, while 12 is a crystalline, low-melting-point polymer. As already observed for propene, also in the case of 1-butene $Cp^*_2ZrCl_2$/MAO is less active than $Cp^*_2HfCl_2$/MAO. ^{13}C NMR analysis of the pendant methylene carbon (the most sensitive one to the stereochemical environment[4]) allows the evaluation of the traid distribution in polybutene.

Triad and dyad compositions together with their statistical analysis and %rde values are reported in Table III. As readily seen, all polybutenes obtained from $Cp^*_2ZrCl_2$ and $Cp^*_2HfCl_2$ catalyst precursors (samples 1-8) are predominantly syndiotactic, with syndiospecificity increasing by lowering the polymerization temperature T_p and on going from Zr to Hf, from a minimum of ≈70% r dyads with $Cp^*_2ZrCl_2$ at 50 °C to a maximum of ≈88% r dyads with $Cp^*_2HfCl_2$ at −20 °C. All samples 1-12 are highly regioregular, as no head-to-head or tail-to-tail linkages[5] could be observed in any of their ^{13}C NMR spectra. Triad distributions for samples 1-11 fit reasonably well the Bernoullian statistical model for chain-end control (enantioface selection due to the configuration of

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Table I
Triad Distribution and Statistical Analysis for Polypropylenes from Different Metallocene/MAO Catalysts[a]

metallocene	T_p, °C	% triads mm	% triads mr	% triads rr	% dyads m	% dyads r	B[b]	%rde[c]
$Cp^*_2ZrCl_2$[d]	0	17.4	48.3	34.3	41.6	58.4	1.0	16.8
$Cp^*_2HfCl_2$[d]	0	15.3	47.2	37.5	38.9	61.1	1.0	22.2
Cp_2ZrCl_2[d]	0	31.1	51.6	17.3	56.9	43.1	0.8	-13.8
	-50	42.0	49.0	9.0	66.5	33.5	0.6	-33.0
Cp_2HfCl_2[d]	50	36.1	50.0	13.9	61.1	38.9	0.8	-22.2
	0	44.1	47.0	8.9	67.6	32.4	0.7	-35.2
Ind_2ZrCl_2[e]	50	30.5	47.4	22.1	54.2	45.8	1.2	-8.4
$Me_2Si(Me_4Cp)_2ZrCl_2$	50	18.7	50.3	31.0	43.8	56.2	0.9	12.4

[a] For polymerization conditions see ref 2d. [b] Bernoullian triad test, 4[mm][rr]/[mr]^2. B = 1 for perfect Bernoullian distribution. [c] %rde = % racemic dyad excess = %r − %m. Positive numbers indicate syndiospecificity, negative ones isospecificity. [d] From ref 2d. [e] Contains 1.0% 1-3 units; see text.

Table II
1-Butene Polymerization[a]

sample	metallocene	amt of metallocene, μmol	MAO,[b] mmol Al	T_p,[c] °C	t_p, h	amt of 1-butene, mL	activity, $g_{PB}/(mmol_M\ h)$
1	$Cp^*_2ZrCl_2$	4.3	4.4	50	2	20	165
2		2.3	2.5	20	1	50	365
3		4.2	4.4	0	4	20	80
4		11.6	11.6	-19	2	50	150
5	$Cp^*_2HfCl_2$	1.9	1.9	50	1	50	1235
6		1.9	2.6	22	1	50	1240
7		4.2	4.4	0	4	20	445
8		9.6	9.5	-19	2	50	240
9	Cp_2ZrCl_2	4.3	4.3	0	4	20	600
10	Ind_2ZrCl_2	2.5	2.8	20	1	50	312
11	$Me_2Si(Me_4Cp)_2ZrCl_2$	21.7	2.4	0	4	50	210
12	$Me_2C(Cp)(Flu)ZrCl_2$[d]	4.6	8.5	40	1	437	19800

[a] Conditions: 100-mL glass autoclave, 50 mL of toluene, metallocene/MAO aged 5–10 min at room temperature in 10 mL of toluene prior to addition to the monomer. [b] MAO Schering, isolated powder. [c] External bath, typically ±1 °C. [d] Büchi 1-L steel autoclave.

Table III
Poly(1-butene): Triad Distribution[a] and Statistical Analysis

sample	metallocene	T_p, °C	% triads mm	% triads mr	% triads rr	% dyads m	% dyads r	B[b]	E[c]	rmrr/mrrr	%rde
1	$Cp^*_2ZrCl_2$	50	8.3	43.9	47.8	30.2	69.8	0.8	0.4	nm[d]	39.6
2		20	7.8	38.4	53.8	27.0	73.0	1.1	0.4	0.9_4	46.0
3		0	5.6	32.7	61.7	22.0	78.0	1.3	0.3	0.9_1	56.0
4		-19	3.8	27.9	68.3	17.8	82.2	1.3	0.3	0.8_7	64.4
5	$Cp^*_2HfCl_2$	50	5.6	37.9	56.5	24.6	75.4	0.9	0.3	nm[d]	50.8
6		22	3.8	30.3	65.9	18.3	81.7	1.1	0.2	0.9_3	63.4
7		0	2.8	24.9	72.3	15.2	84.8	1.3	0.2	0.9_3	69.6
8		-19	1.5	21.4	77.1	12.2	87.8	1.0	0.1	0.7_6	75.6
9	Cp_2ZrCl_2	0	36.0	48.2	15.8	60.1	39.9	1.0			-20.2
10	Ind_2ZrCl_2	20	25.1	46.4	28.5	48.3	51.7	1.3			3.4
11	$Me_2Si(Me_4Cp)_2ZrCl_2$	0	17.6	45.1	37.3	40.2	59.8	1.3			19.6
12	$Me_2C(Cp)(Flu)ZrCl_2$	40	2.1	6.1	91.8	5.2	94.8	20.7	0.7		89.6

[a] From ^{13}C NMR analysis of the pendant methylene carbon. [b] Bernoullian triad test, 4[mm][rr]/[mr]^2. B = 1 for perfect Bernoullian distribution. [c] Enantiomorphic site triad test, 2[mm]/[mr]. E = 1 for perfect site control. [d] nm = not measurable because of mmrm, rmrr pentad overlapping.

the methine of the last inserted monomer; Bernoullian value B = 4[mm][rr]/[mr]^2 = 1 for perfect chain-end control), with deviations likely due to small errors in triad evaluation arising from partial overlapping of rmmr and mmrr pentads. This triad distribution, together with the rmrr/mrrr ratio being always ≈1 (uncertainty due to rrrr/mrrr partial overlapping), the virtual absence of mmmm, and the very low levels of rmmr pentads, shows that the mechanism of chain propagation in 1-butene polymerization with $Cp^*_2MCl_2$/MAO catalysts is syndiospecific chain-end control. From end-group analysis we already observed that 1-butene insertion is primary (1–2 or head-to-tail).[2d] Thus, this is the first clearcut example of *syndiospecific chain-end control in primary 1-olefin polyinsertion* for metallocene catalysts, the last of the four possible stereoregular propagation mechanisms for 1–2 polymerization (Scheme I).[6-12] A highly syndiotactic polybutene[13] (sample 12) was prepared with Ewen's propene syndiospecific catalyst[11] as a reference sample. Its pentad distribution (rrrr = 84%, rmmr:mmrr:mrrr = 1.2:1.8:2) confirms the mechanism of syndiospecific site control[11] also in the case of 1-butene.

The ^{13}C NMR spectra (pendant methylene region, 24.2–25.6 ppm, HMDS scale) for polybutene samples 10 (Ind_2ZrCl_2/MAO, atactic), 12 ($Me_2C(Cp)(Flu)ZrCl_2$/MAO, highly syndiotactic from site control), and 8 ($Cp^*_2HfCl_2$/MAO, predominantly syndiotactic from chain-end control) are shown in Figure 1 together with pentad assignments.[14]

There seems to be a direct relationship between the steric bulk around the ligand and the degree of syndiospecificity: while Cp_2ZrCl_2/MAO produces a polybutene with a slight prevalence of m dyads (in analogy to what is observed in propene oligomerization) and Ind_2ZrCl_2/MAO an almost perfectly atactic polymer, Me_2Si-

Scheme I
Four Possible Mechanisms for Stereospecific Primary 1-Olefin Polyinsertion

polymerization mechanism	polym microstructure with isolated stereoinversion	main pentad	triad/triad and pentad/pentad relationships for isolated stereoinversion	ref
Primary insertion → site control → error correction → iso specific	m m m m m r r m m m m m	mmmm	mr = 2rr mmmr = mmrr = 2mrrm	10
Primary insertion → site control → error correction → syndio specific	r r r r r m m r r r r r	rrrr	mr = 2mm rrrm = mmrr = 2rmmr	11
Primary insertion → chain-end control → error propagation → iso specific	m m m m m r m m m m m m	mmmm	mr only mmmr = mmrm	10b
Primary insertion → chain-end control → error propagation → syndio specific	r r r r r m r r r r r r	rrrr	mr only rrrm = rrmr	this work

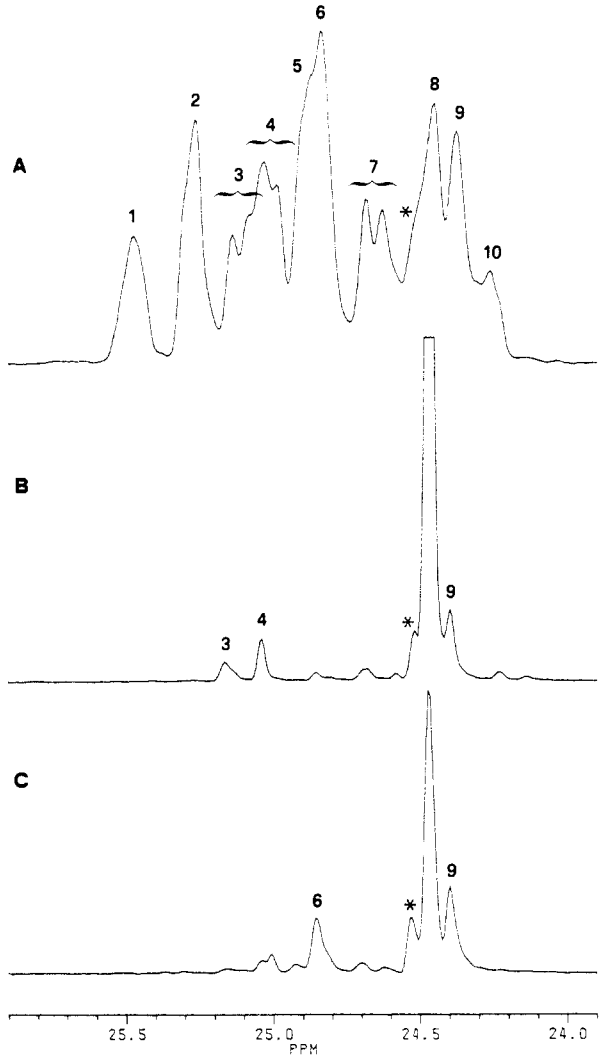

Figure 1. ^{13}C NMR ($C_2D_2Cl_4$, 373 K, HMDS = 0) of the pendant methylene carbon region of atactic polybutene sample 10 (A), syndiotactic polybutene sample 12 (B), and syndiotactic polybutene sample 8 (C). Pentad assignment: 1 = mmmm; 2 = mmmr; 3 = rmmr; 4 = mmrr; 5 = mmrm; 6 = rmrr; 7 = mrmr; 8 = rrrr; 9 = mrrr; 10 = mrrm. *: attributed to mrrrrr heptad. Note the sensitivity at the heptad level also for rmmr, mmrr and mrmr pentads.

$(Me_4Cp)_2ZrCl_2$/MAO already shows a prevalence of r dyads. Thus, the r dyad content grows according to

$$Cp_2ZrCl_2 < Ind_2ZrCl_2 < Me_2Si(Me_4Cp)_2ZrCl_2 < Cp^*_2ZrCl_2 < Cp^*_2HfCl_2$$

This increase in syndiospecificity can be easily accounted for by the increase of steric encumbrance around the metal atom, at least for the zirconocenes. The higher selectivity found for Hf with respect to Zr is similar to that observed for β-CH_3/β-H selectivity in propene oligomerization[2] and could be related as well to steric factors, although too few crystallographic studies on hafnocene alkyl cations[2b] are available to allow one to draw any conclusions.

It is worth noting that while with the known catalysts operating with chain-end control the stereoregulating effect is washed out as the olefin side group becomes larger[9d,15] and the polymerization temperature approaches ambient temperature,[10b,12,16] with $Cp^*_2MCl_2$/MAO catalysts we observe an *increase* in stereoregulation on passing from propene to 1-butene and a remarkable syndiospecificity even at temperatures *above* ambient. From the experimental temperature dependence of the r/m ratio and the relationships[16]

$$k_i = A_i \exp(-E_i/RT), \quad k_s = A_s \exp(-E_s/RT), \quad k_i/k_s = P_m/P_r = [m]/[r] \quad (1)$$

$$\ln([r]/[m]) = \ln(A_s/A_i) + (E_i - E_s)/RT \quad (2)$$

where i and s stand for isotactic and syndiotactic placements respectively, and E is the empirical activation energy for the process, we find an $E_i - E_s$ value for the two competing events, formation of m vs r dyads, of about 2 kcal/mol for both catalysts (Figure 2).

From comparison with known systems[10b,12,16] we observe that $E_i - E_s$ is in the normal range for chain-end controlled stereospecific polymerizations. Thus, the difference in stereospecificity at a given polymerization temperature among the different catalysts (and monomers) must reside in the preexponential terms A_i, A_s. These terms can be in first approximation written as $A_j = p_j Z_j$, where p is the frequency factor or number of collisions and Z the steric factor which reflects the probability of the reaction j.[17] Substituting into eqs 1 and 2 (being $p_s \equiv p_i$) we have

$$\ln([r]/[m]) = \ln(Z_s/Z_i) + (E_i - E_s)/RT \quad (3)$$

From eq 3 and the similarity in $E_i - E_s$ values for the different stereospecific catalysts, we can conclude that the Cp^*_2M moiety is *sterically* more effective—at a given polymerization temperature—than the VCl_4 or Cp_2M-based catalysts in increasing the population of conformations at the active site (the ligands–metal–growing chain framework) which are favorable to stereoregular propagation or, in other words, the two bulky Cp* ligands are more effective than Cp or Cl in orienting the last unit of the growing chain in a conformation able to select the

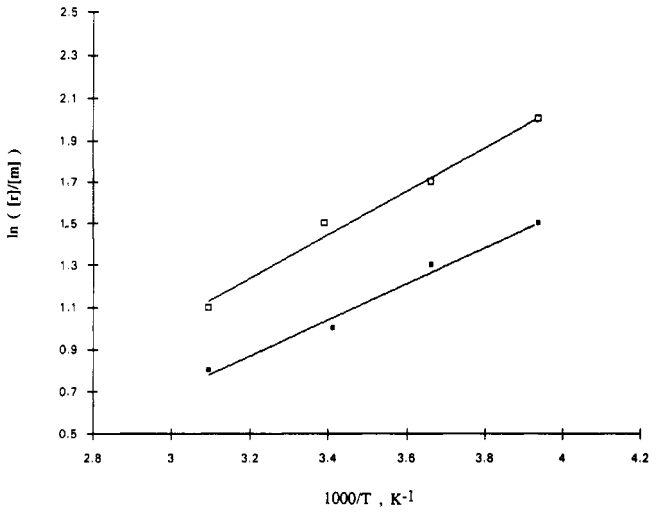

Figure 2. Arrhenius plots of ln ([r]/[m]) vs $1/T$ for polybutene samples 1–4 ($Cp^*_2ZrCl_2$/MAO, correlation parameter 0.983, $E_i - E_s = 1.73 \pm 0.16$), lower; and polybutene samples 5–8 ($Cp^*_2HfCl_2$/MAO, correlation parameter 0.990, $E_i - E_s = 2.09 \pm 0.15$), upper. For triad and dyad values see Table III.

incoming olefin enantioface, such as Z_s/Z_i is larger for Cp^*_2M than for VCl_4 and larger than Z_i/Z_s for Cp_2M.[18]

By further enlarging the olefin substituent, we observe the loss of stereospecificity: in fact, poly(4-methyl-1-pentene) obtained from $Cp^*_2HfCl_2$/MAO at 0 °C is largely atactic, as it is that obtained from Cp_2ZrCl_2/MAO at the same temperature.[19] Apparently, the bulky i-Bu substituent at C2 of the last inserted 4-methyl-1-pentene unit, being sterically very similar to the rest of the growing chain (i.e., making C2 achiral as far as the approaching monomer can see), renders all possible chain conformations at the active site aspecific in nature.

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(3) The 4-methylene sequence typical of 1–3 insertion,[3a–d] in this case in an atactic environment, is clearly detectable at 35–36.5 ppm ($S_{\alpha\delta}$), 28.5–28.8 ppm ($T_{\beta\gamma^+}$) and 25.4–25.8 ppm ($S_{\beta\gamma}$) with the $P_{\beta\gamma^+}$ being hidden under the methyl pentad resonances. 2–1 regioinversions are barely detectable in this sample. (a) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 305–310. (b) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617–622. (c) Cheng, H.; Ewen, J. *Makromol. Chem.* **1989**, *190*, 1931–1943. (d) Rieger, B.; Mu, X.; Mallin, D.; Rausch, M.; Chien, J. *Macromolecules* **1990**, *23*, 3559–3568.

(4) Pentad analysis of polybutene has been reported by Asakura et al.[4a–b] for mainly isotactic homopolymers, while no studies were found with regard to syndiotactic and atactic ones. In our spectra we observe more signals than reported, arising from partial sensitivity at the heptad level. By comparison with the chemical shifts calculated by Asakura on the basis of the γ-effect and taking into consideration the relative intensities of the signals, we were able to assign with good confidence the ^{13}C peaks to the respective stereosequences. (a) Asakura, T.; Omaki, K.; Zhu, S.; Chujo, R. *Polym. J.* **1984**, *16*, 717–726. (b) Asakura, T.; Demura, M.; Yamamoto, K.; Chujo, R. *Polymer* **1987**, *28*, 1037–1040.

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(6) Syndiospecific, chain end controlled propene polymerization with V-based homogeneous catalysts occurs through *secondary* monomer insertion.[7] The same is the case for syndiospecific polymerization of styrene.[8] Fractions of syndiotactic-rich polypropene can be isolated from isotactic polypropene obtained with heterogeneous, Ti-based catalysts. These fractions seem to be made of iso–syndio stereoblocks and the mechanism of stereocontrol has been shown to arise from *primary* propene insertion, possibly chain-end controlled.[9a–c] The same mechanism has been proposed in the case of the formation of partially syndiotactic polybutene fractions with the $MgCl_2/TiCl_4$–PhSi-$(OEt)_3/AlEt_3$ catalyst.[9d] Recently, the onset of a slight syndiospecificity arising from chain end control in propene polymerization with $(i\text{-PrCp})_2TiPh_2$/MAO at 10 °C has been observed.[12] These polypropenes show a % de quite similar to those reported by us for propene polymerizations with $Cp^*_2MCl_2$/MAO at 0 °C.[2d]

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(14) Pendant methylene pentads ^{13}C NMR chemical shifts for polybutene samples reported in Figure 1. Sample 10 (A): mmmm, 25.47 ppm; mmmr, 25.26 ppm; rmmr, 25.14, 25.09 ppm; mmrr, 25.03, 24.98 ppm; mmrm, 24.87 ppm; rmrr, 24.84 ppm; mrmr, 24.68, 24.63 ppm; rrrr, 24.52, 24.45 ppm; mrrr, 24.38 ppm; mrrm, 24.26 ppm. Sample 12 (B): rmmr, 25.17 ppm; mmrr, 25.04 ppm; rrrr, 24.52, 24.48 ppm; mrrr, 24.40 ppm. Sample 8 (C): rmrr, 24.85 ppm; rrrr, 24.52, 24.47 ppm; mrrr, 24.40 ppm.

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(18) This does not necessarily mean that this conformation is more stable than other aspecific conformations, as the observed $E_i - E_s$ reflects both the differences in transition energies for the two different reaction paths and the difference in energy of the starting active site conformations.

(19) In the ^{13}C NMR spectra of both poly(4-methyl-1-pentene) samples all resonances are broad and unresolved, especially the backbone methyne resonance at 28.5–30 ppm which appears to be the most sensitive to the polymer microstructure (i.e., the broader). NMR analysis of 4-methyl-1-pentene polymers of different tacticities is in progress in our laboratories.

Registry No. PP, 9003-07-0; bis(pentamethylcyclopentadienyl)zirconium chloride, 54039-38-2; bis(pentamethylcyclopentadienyl)hafnium chloride, 85959-83-7; polybutene, 9003-28-5; poly(4-methyl-1-pentene), 25068-26-2.